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Mechanistic Studies of the Deslongchamps Annulation

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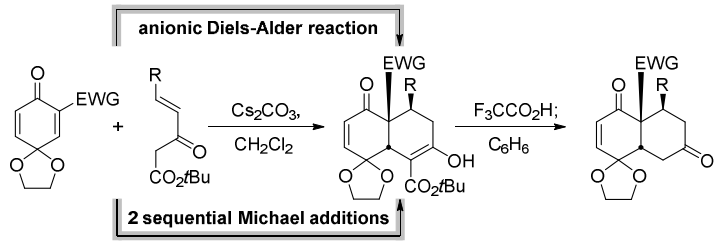
Supporting Information

ABSTRACT: The Cs_2CO_3-mediated annulations ("Deslongchamps annulations") of three spirocyclic benzoquinone monoketals **5b-d** with an ester or acyl substituent at C-2 to two *tert*-butyl esters of γ,δ-unsaturated β-ketocarboxyl acids ("Nazarov reagents"; **2a**,**b**) were monitored ^{1}H-NMR spectroscopically. This revealed that a primary product, by all likelihood the Michael adduct, forms fast and prior to the appearance of the Deslongchamps adduct. These primary products form reversibly. This was proved by two cross-over and four scavenging experiments. Therein, components already incorporated in one of the mentioned primary products ended up in Deslongchamps adducts different from the one, which would have resulted if the respective primary product had reacted alone. However, these experiments leave open whether our primary products are intermediates en route to Deslongchamps products or whether they represent dead ends.



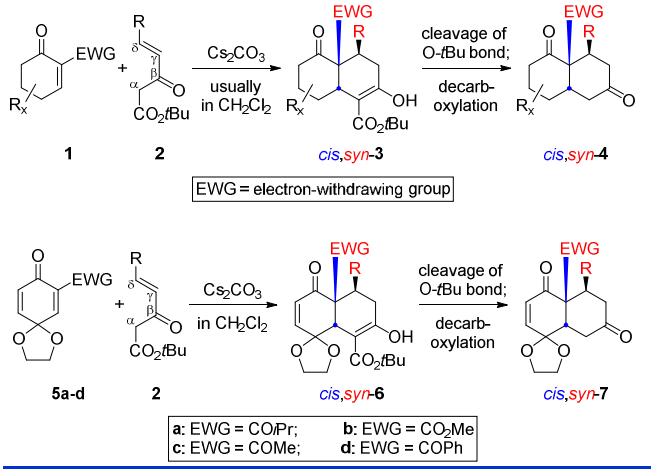
INTRODUCTION

The term "Deslongchamps annulation" acknowledges the eponymous investigator´s merits for a [2+4] annulation approach to functionalized decalin frameworks.[1] It entails different reactants than the [2+4] Robinson annulation: In Deslongchamps´ approach the two carbon atoms contributor is an acceptor-substituted cyclohexenone **1** while the four carbon atoms contributor is a γ,δ-unsaturated active methylene compound ("Nazarov reagent[2]"; Scheme 1). In most instances, the latter is a γ,δ-unsaturated β-ketoester **2**. Archetypical Deslongchamps annulations provide *cis*-fused decalindiones at the initial stage (→**3**; 1 carbonyl group fully enolized) and after de(alkoxycarbonylation) (→**4**). Deslongchamps annulations have been used since 25 years for accessing *cis*-decalins.[3-21] The latter comprise a variety of steroids[4,5,8-13,15] including the cardenolides oubagenin[16,18] and ouabain[18] and a related tricyclic triterpenoid named cassaine.[20] Over the years the substrate scope of this reaction has grown steadily.[6,7,13,14,17,19,21]

A while ago we disclosed modified Deslongchamps annulations.[21] They employ benzoquinone monoketals **5** as the two carbon atoms contributor (Scheme 1, bottom) and deliver *cis*-fused octalindiones both initially (→ *cis*,*syn*-**6**; 1 carbonyl group fully enolized) and after removing the CO_2tBu group (→ *cis*,*syn*-**7**). The newly accessible products *cis*,*syn*-**6** and *cis*,*syn*-**7** are valuable[22] because they possess an extra C=C bond compared to *cis*,*syn*-**3** and *cis*,*syn*-**4**. It allows to perform follow-up transformations.[23]

Two mechanisms of Deslongchamps annulations are discussed – or at least held possible – in the literature: a Diels-Alder reaction or two sequential Michael additions[24,25] (Scheme 2). However, most references left this issue open, simply referring to the process as an "anionic cycloaddition".[26] As described in the pioneering study,[3] the simple diastereoselectivity of the Cs_2CO_3-mediated Deslongchamps annulation of the Nazarov reagent **2** (R = Me) with methyl cyclohex-2-en-1-one-2-carboxylate (**1**, EWG = CO_2Me, R_x = H) is solvent-dependent: It furnished *cis,syn*-**4** (EWG = CO_2Me, R = Me, R_x = H) with 95:5 to 99.5:0.5 preferences over *cis,anti*-**4** (EWG = CO_2Me, R = Me, R_x = H) in what were called "less polar solvents" (benzene, THF, AcOEt, $CHCl_3$, and CH_2Cl_2).[3] In DMF and MeCN, which were referred to as "very polar solvents", the *cis,syn*-**4**:*cis,anti*-**4** ratios were only 54:46 and 75:25, respectively.[3] Deslongchamps and Lavallée interpreted these results as "strong evidence for the existence of a Diels-Alder mechanism in less polar solvents"[3] and that "it is likely that the reaction takes place via a sequential double Michael addition in the more polar solvent"[3,27].

Scheme 1. Deslongchamps annulations of CO_2tBu-containing Nazarov reagents 2 with acceptor-substituted cyclohexenones 1 (examples: ref.[1]) or with acceptor-substituted benzoquinone monoketals 5a-d (examples: ref.[21]). Deslongchamps annulations with compound 5b were studied in the present investigation again and Deslongchamps annulations with compounds 5c,d for the first time.

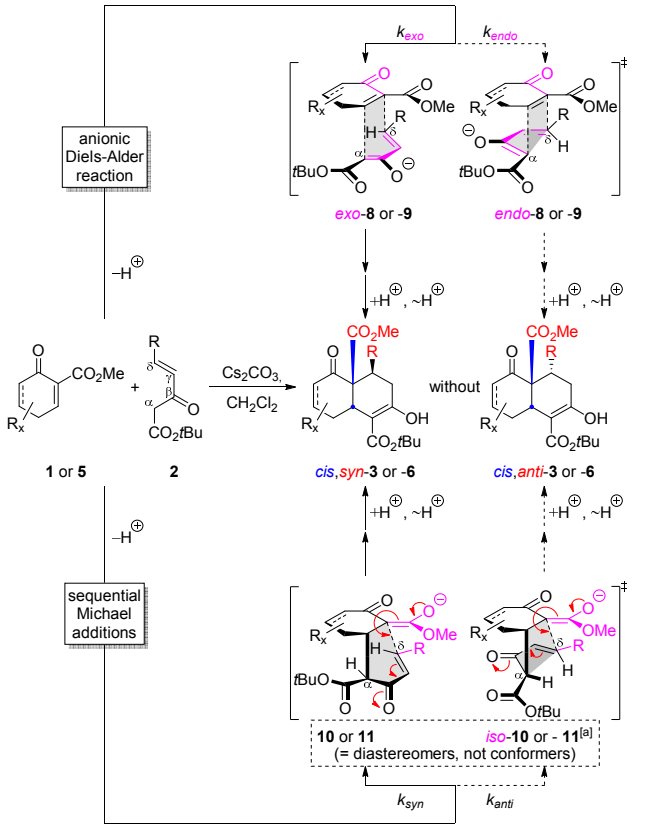


We disagree with the preceding analysis with respect to the concertedness of the annulation in "less polar solvents". If one accepts the Dimroth-Reichardt parameter $E_T(30)$ as a measure for solvent polarity,[28] the order of increasing polarity of the mentioned solvents is the following: benzene (E_T = 34.3), THF (E_T = 37.4), AcOEt (E_T = 38.1), $CHCl_3$ (E_T = 39.1), CH_2Cl_2 (E_T = 40.7), DMF (E_T = 43.2), and MeCN (E_T = 45.6). Firstly, this ordering does not parallel the variation of the *syn*:*anti*-ratios. The latter rather increase from 95:5 in the least polar solvent, namely benzene ($\Rightarrow \Delta E_{a,\text{formation of } anti\text{- vs. } syn\text{-adduct}}$ = 1.65 kcal/mol), to 99.5:0.5 in $CHCl_3$, i. e., at medium polarity ($\Rightarrow \Delta E_{a,\text{formation of } anti\text{- vs. } syn\text{-adduct}}$ = 3.13 kcal/mol), to decrease sharply in the most polar solvents DMF (54:46) and MeCN (75:25) ($\Rightarrow \Delta E_{a,\text{formation of } anti\text{- vs. } syn\text{-adduct}}$ = 0.09 and 0.65 kcal/mol, respectively). Secondly, the assumption that an increase of polarity would benefit the Diels-Alder mechanism to a lesser extent than the sequential Michael additions appears questionable. After deprotonating the Nazarov reagent to an acceptor-substituted enolate, the latter proceeds to react to an acceptor-free enolate. The Diels-Alder mechanism realizes this in a single step while the sequential Michael addition mechanism requires two steps because of the intermediacy of another acceptor-substituted enolate (**10**/**11**;

Scheme 2). Thus, neither mechanism changes the overall charge nor does it create an additional charge. As a consequence we see no compelling reason why there should be a sizable solvent effect at all, let alone a differential solvent effect. Thirdly, it should be remembered that there is no a-priori-reason why a Diels-Alder reaction would be more subject to simple diastereocontrol than a Michael addition.[29] On top, it seems unclear why simple diastereocontrol in a Diels-Alder mechanism of the Deslongchamps annulation would favor the *syn*- vs. the *anti*-diastereomer of the annulation products (*cis*-**3**,

Scheme 2): A survey of the stereochemistry of the [4+2]-annulation products, which were obtained from *uncharged* 1,3-dienes and alkyl cyclohex-2-en-1-one-2-carboxylates (**1**, EWG = CO_2R; Scheme 1) – often in the presence of a Lewis acid – reveals that the CO_2R group ended up in a *syn*-orientation[30] (as defined in Scheme 1) in a number of cases but in an *anti*-orientation[31] more frequently.

Scheme 2. The Deslongchamps annulations of Scheme 1 as an overall transformation (middle; the de-*tert*-butoxy-carbonylation step is not comprised) and with regard to the originally discussed mechanisms: concerted bond formations at C-α and at C-δ ("anionic Diels-Alder reaction"; top) vs. sequential bond formations at C-α first and at C-δ subsequently ("sequential Michael additions"; bottom).[a]

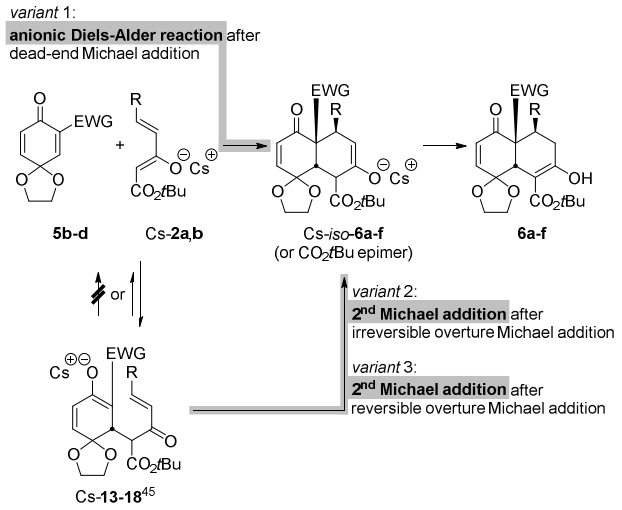


[a] For orbital overlap and ring-strain constraints, respectively, the newly forming ring must adopt a boat (grey shades) rather than chair conformation (not shown). The transition structures for the second Michael additions, i.e. **10**/**11** and *iso*-**10**/*iso*-**11**, are depicted with the highest possible similarity to the Diels-Alder transition states *exo*-**8**/*exo*-**9** and *endo*-**8**/*endo*-**9** respectively. This shall not express any energetical preference for these geometries, though.– In this Scheme, each compound except the Nazarov reagent has a pair of formula numbers. The first number in each such pair refers to a cyclohexadienone, a cyclohexadienone-based transition state, a cyclohexadienone-based intermediate or a cyclohexadienone-based product. The second number in each formula number pair refers to the analogous cyclohexenone(-based species).

According to Deslongchamps et al.[3] the acceptor-substituted cyclohexenone **1** (EWG = CO_2Me, R_x = H; Scheme 1), a particular Nazarov reagent **2** (R = Me, Scheme 1), and Cs_2CO_3 gave the annulation product *cis*,*syn*-**3** (EWG = CO_2Me, R_x = H, R = Me) via a *sequential Michael addition pathway in acetonitrile*. This statement was based on the following observations: After 30 min[7] at –15°C, the reactants delivered essentially what was called a "single Michael adduct"[3] (53% yield[7]).

When the latter was re-dissolved in acetonitrile at room temperature, re-treated with Cs_2CO_3 for 3.5 h,[7] and freed from the CO_2tBu group by TsOH in refluxing benzene the follow-up product *cis*,*syn*-**4** of the annulation product *cis*,*syn*-**3** (EWG = CO_2Me, R_x = H, R = Me) resulted as a 68:32[3] or 70:30[7] *cis,syn*:*cis,anti* mixture (55% yield[7]). When the original reactants were combined in acetonitrile *at room temperature right from the beginning and reacted without an interruption* and then freed from the CO_2tBu group they gave the same follow-up product *cis*,*syn*-**4** as a 75:25 *cis,syn*:*cis,anti* mixture.[3,7] The near-identity of these selectivities led the cited study[3] to suggest that the Michael addition occurred *on* the annulation route – as an "overture reaction" of sorts. A subsequent cyclization would render the Deslongchamps adduct.[3] However, this interpretation fails to recognize an alternative analysis: the Michael adduct in question forms *off* the annulation route in what would be a "dead-end *equilibrium*".[32] When re-exposed to Cs_2CO_3 in acetonitrile this Michael adduct might revert to the reactants, which, thereupon, give the annulation product by an anionic Diels-Alder reaction. The possibility that such Michael adducts form reversibly was neither considered in the suggested scenario of being formed *on* the annulation route.[3]

Scheme 3. Conceivable roles of Michael adducts during the Deslongchamps annulations investigated in the present study.



The incertitude about the mechanism of the Deslongchamps annulation hampers designing novel cycloalkenonecarboxylate / Nazarov reagent pairs in order to expand the product portfolio. Having touched the field twice,[17,21] we looked at the role of Michael adducts in Deslongchamps annulations anew. Scheme 3 specifies these entities as cesium enolates Cs-**13-18**. It places them in the context of the three mechanistic variants in line with the analyses of the preceding paragraphs. However, the Michael adducts Cs-**13-18** in Scheme 3 are different than Deslongchamps': because their two carbon atoms contributors are acceptor-substituted benzoquinone monoketals **5b-d** rather than cyclohexenones **1**. The mechanistic tool-kit for our investigations comprised (1) monitoring the progress of the respective Deslongchamps annulations by discontinuous probing, (2) performing cross-over experiments, and (3) executing scavenging experiments. Calculations were undertaken, too, but did not help.[33]

RESULTS AND DISCUSSION

Synthesizing Deslongchamps Adducts From Benzoquinone Monoketals

The substrate portfolio of Scheme 3 allowed for six Deslongchamps annulations engaging the acceptor-substituted benzoquinone monoketals **5b-d** and the Nazarov reagents **2a**[34] and **b**.[35] We realized them as already reported[21] (**5b** + **2a**; **5d** + **2a**) or for the first time (**5b** + **2b**; **5c** + **2a**; **5c** + **2b**; **5d** + **2b**). After purification by flash-chromatography on silica gel,[36] this provided the Deslongchamps adducts *cis*,*syn*-**6a-f** in 71-95% yield[22] exclusively as enols (δ_{OH} = 12.49−12.62 ppm in $CDCl_3$ solution) rather than β-ketoesters (Scheme 4).

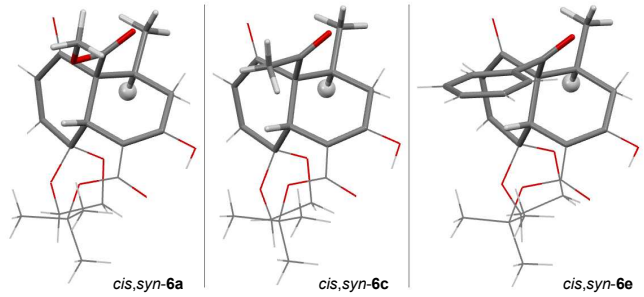
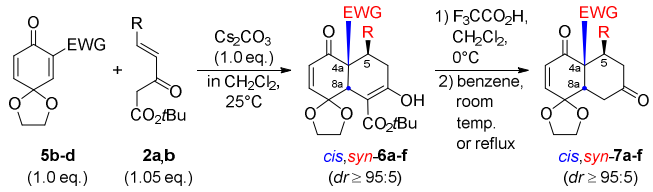


Figure 1. Single crystal structures of *cis*,*syn*-6a[37] (left), *cis*,*syn*-6c[38] (middle), and *cis*,*syn*-6e[39] (right) specifying the relative configurations of the three newly generated stereogenic centers.[a]

[a] The decalin scaffolds are oriented like in the drawing of Scheme 3. Four of the decalin substituents are depicted with bold bonds. The remainder of this illustration uses thin bonds – for not obscuring the focus on the new stereocenters.

The *cis*,*syn*-configuration of H at C-8a, EWG at C-4a, and R at C-5 was proved for compounds **6a**, **c**, and **e** by single crystal structure analyses (c.f. Figure 1[37,38,39]) and assumed by analogy for compounds **6b**, **d**, and **f**.

Scheme 4. The Deslongchamps annulations, whose mechanism was studied in the present investigation (details: see text). The conceivable constitutional and configurational isomers of the protonated forms of the Michael adducts derived from the shown reactants are depicted in footnote 44.[a]



Annulation	5	EWG	2	R	>80% conversion of 5 after ...	>70% formation of 6 after ...	6	Yield	7	R	Yield
1	**b**	CO_2Me	**a**	Me	1 min	7 min	**a**	94%[a]	**a**	Me	75%
2	**b**	CO_2Me	**b**	*i*Bu	1 min	10 min	**b**	75%[a]	**b**	*i*Bu	75%
3	**c**	COMe	**a**	Me	1 min	37 min	**c**	95%	**c**	Me	90%
4	**c**	COMe	**b**	*i*Bu	2 min	23 min	**d**	71%	**d**	*i*Bu	53%
5	**d**	COPh	**a**	Me	1 min	35 min	**e**	84%	**e**	Me	76%
6	**d**	COPh	**b**	*i*Bu	2 min	295 min	**f**	71%	**f**	*i*Bu	34%

[a] Our studies for ref.21 had provided compound *cis*,*syn*-6a in 89% yield and compound *cis*,*syn*-6b in 99% yield.

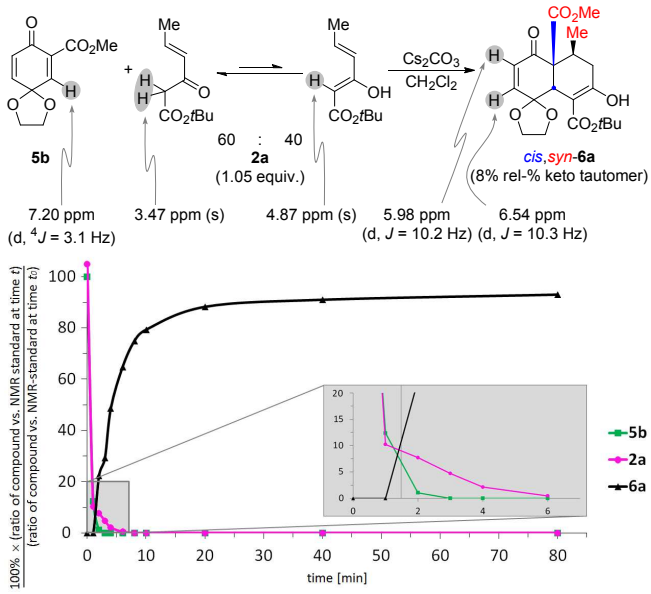


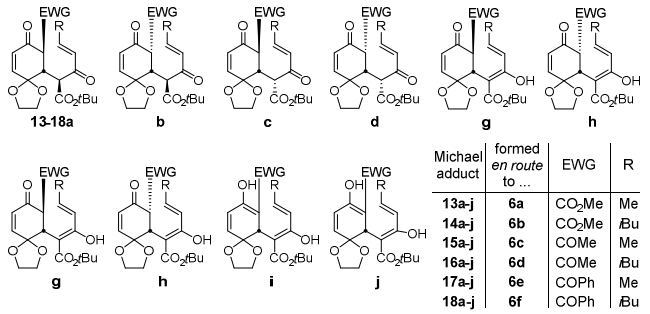
Figure 2. Progress with time (*t*) of the Deslongchamps annulation numbered "1" in Scheme 4; after 80 min the adduct *cis*,*syn*-6a[21] had formed in 93% yield [yield quantifications: 300 MHz ^{1}H-NMR integrals of characteristic resonances (indicated under the formulas) relative to the low-field singlet (δ_{Ar-H} = 7.66 ppm) of 2,4,6-tribromotoluene, which was present as a ^{1}H-NMR standard]. Overview plot of concentration/time pairs on white background and, in grey boxes, analogous close-up plots for the early stages of this reaction. In the close-up at right, the vertical grey line shows that after 1.5 min ≥90% 5b and >90% 2a were consumed and ≤10% *cis*,*syn*-6a had formed.41

The Deslongchamps adducts *cis*,*syn*-**6a-f** were de-*tert*-butoxycarbonylated in two steps (Scheme 4): 1) ester cleavage by trifluoroacetic acid (0°C, 2 h); 2) decarboxylation of the crude β-ketocarboxylic acid (benzene; either room temperature / 8 days or reflux / 2 h. After purification by flash-chromatography on silica gel,[36] this furnished the decalindiones *cis*,*syn*-**7a-f** in up to 90% yield.[22] An X-ray structural analysis proved the (stereo)structure of compound *cis*,*syn*-**7a** (as published earlier[21]).

Monitoring Deslongchamps Annulations

We probed the Deslongchamps annulations of Scheme 4 at room temperature for the intermediacy of Michael adducts. To this end we monitored their progress ^{1}H-NMR spectroscopically. This was done discontinuously, namely by sampling and examining 10-12 aliquots from the respective reaction mixture.[40] Each such mixture was heterogeneous because Cs_2CO_3 or the cesium enolates Cs-**2**, to which they should give rise, is incompletely soluble[41] in the solvent (in CH_2Cl_2). As a consequence we could not help changing the Cs_2CO_3/solute ratio by our sampling. Therefore we could not aspire for concentration/time profiles at an exactitude level, which would allowing to calculate rate constants. Because of this limitation we did not steady the progress of our annulations by a thermostat.

Technically, the Deslongchamps annulations of Scheme 4 were monitored as follows. The benzoquinone monoketal **5b-d** [1 equiv.; 0.25 mmol except for preparing *cis*,*syn*-**6c** (0.50 mmol) and *cis*,*syn*-**6f** (2.5 mmol)], the Nazarov reagent **2a**,**b** (1.05 equiv.), and 2,4,6-tribromotoluene (for calibrating the ^{1}H-NMR integrals; 0.50 equiv.) were dissolved in CH_2Cl_2 (4–40 mL; $c_{\mathbf{5b-d}}$ = 0.06 mol/L). Each annulation was started by adding solid Cs_2CO_3 (1.00 equiv.) while stirring magnetically from then onward. Aliquots of 0.4 mL were sampled from the resulting suspension by a plastic syringe starting after 1 min. We sampled again after 2, 3, 4, 6, 8, 10, 20, 40, and 80 min (and also after 160 and 320 min when monitoring the formation of *cis*,*syn*-**6f**). Each sample was applied without delay to a short chromatography column filled with silica gel. Elution with AcOEt (3 mL) and evaporation of the eluent provided 10-12 Cs_2CO_3-free mixtures per annulation. Their contents of unconsumed starting materials **5** and **2** and already formed annulates *cis*,*syn*-**6a-f** were quantified ^{1}H-NMR spectroscopically (300 MHz, $CDCl_3$) relative to a fixed amount of 2,4,6-tribromotoluene added as a standard.[42]



Michael adduct	formed *en route* to ...	EWG	R
13a-j	6a	CO_2Me	Me
14a-j	6b	CO_2Me	*i*Bu
15a-j	6c	COMe	Me
16a-j	6d	COMe	*i*Bu
17a-j	6e	COPh	Me
18a-j	6f	COPh	*i*Bu

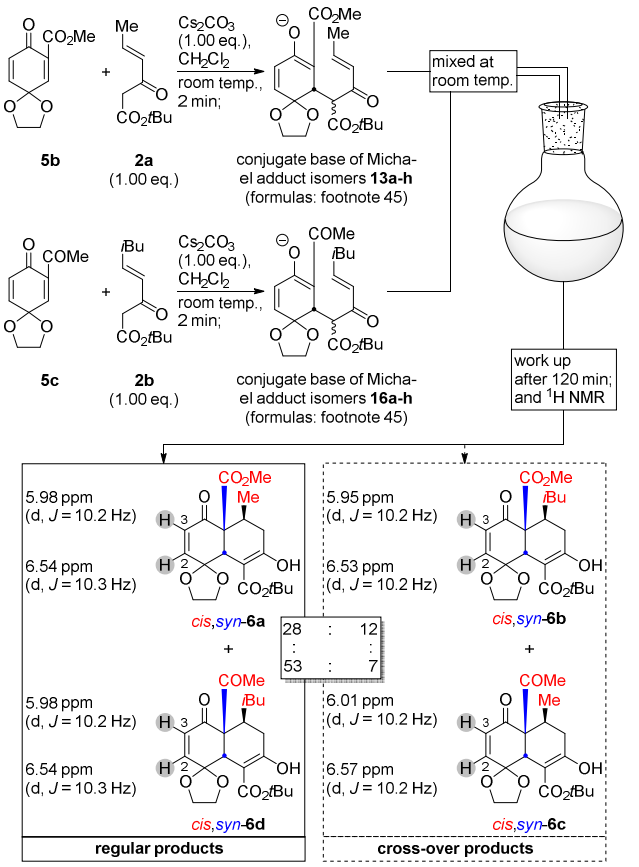
Figure 3. Conceivable structures of the Michael adducts 13-18 intervening in the formation of the Deslongchamps adducts 6a-d.

The resulting concentration/time diagrams (Figure 2 and in Section **SI-4** of the Supporting Information) show that reactants **2** and **5** are already gone after a minute or a few minutes (vs. *cis*,*syn*-**6f**: after 4 min). Concomitantly, less than 10% of whatever Deslongchamps adduct had formed, often *considerably* less. The yields of the latter surpassed the 70% threshold no earlier than 7-37 min later(vs. *cis*,*syn*-**6f**: 5 h later). It required an hour or so until the reactions giving *cis*,*syn*-**6a-e** were mostly over. Undisputably, our Deslongchamps substrates did not react to give Deslongchamps products directly.[43] We stopped monitoring when yields of 93% *cis*,*syn*-**6a** (Figure 2), 98% *cis*,*syn*-**6b** (2nd concentration/time diagram in Section **SI-4** of the Supporting Information), 89% *cis*,*syn*-**6c** (3rd concentration/time diagram *loc. cit.*), 97% *cis*,*syn*-**6d** (4th concentration/time diagram *loc. cit.*), 83% *cis*,*syn*-**6e** (5th concentration/time diagram *loc. cit.*), and 82% *cis*,*syn*-**6f** (6th concentration/time diagram *loc. cit.*) were attained. I. e., each primary product – or Michael adduct[44] (formula: Figure 3; corroborated by isolating the latter starting from reactants **5b** and **2a**43) – had continued to react giving a Deslongchamps adduct eventually.

Performing Deslongchamps Annulations as Cross-Over Experiments

We wondered whether our (surmised) Michael adducts[44] precede Deslongchamps products by forming irreversibly *on* the respective reaction coordinate. Dubbed "variant 2" in Scheme 3 this mechanism would entail Michael adducts as genuine intermediates. Alternatively, our (surmised) Michael adducts[44] might form reversibly. This is conceivable *off* or *on* the pathway giving Deslongchamps adducts. It would correspond to what Scheme 3 designates as the variants "1" and "3" of the plausible Deslongchamps annulation mechanisms, respectively. In the "variant 1" mechanism the Michael adduct arises *off* the formation route of the Deslongchamps adduct. Representing a dead end, this Michael adduct must revert to the substrates before the latter have a chance to form the Deslongchamps adduct by an anionic Diels-Alder reaction. We discarded the variant 2 mechanism – including an irreversible Michael adduct fomation – and gained support for the variants 1 or 3 – having a reversible Michael adduct fomation in common – by the cross-over experiments shown in Scheme 5 and Scheme 6.

Scheme 5. Cross-over experiment I.[a] Dieses Schema verweist 2 × auf Lit.-stelle[44].

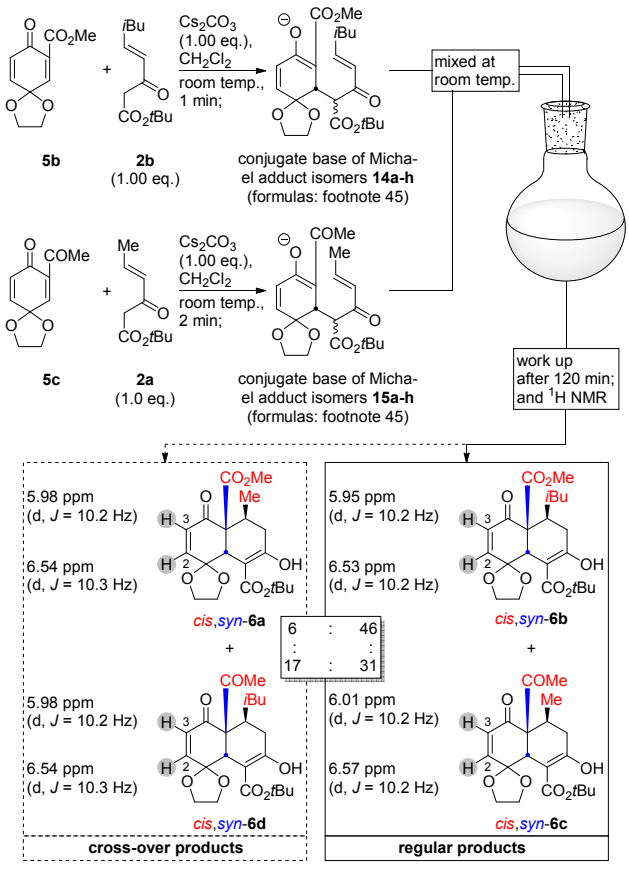


[a] We started the Deslongchamps annulations **5b** + **2a** → **13** → *cis*,*syn*-**6a** (numbered "1" in Scheme 4) and **5c** + **2b** → **16** → *cis*,*syn*-**6d** (numbered "4" in Scheme 4) separately but concomitantly. After 2 min we combined the two mixtures. After 2 h the nature and relative amounts of the resulting Deslongchamps adducts were assessed ^{1}H-NMR spectroscopically (500 MHz, $CDCl_3$). In addition to the "regular products" *cis*,*syn*-**6a** (resulting from **13**) and *cis*,*syn*-**6d** (resulting from **16**) we found the "cross-over products" *cis*,*syn*-**6b** (resulting from **5b** + **2b**) and *cis*,*syn*-**6c** (resulting from **5c** + **2a**). The latter pairings would have been impossible if the Michael adducts **13** and **16** had not reformed their respective precursors **5b**/**2a** and **5c**/**2b** over the course of the reaction time; that is, these Michael adducts form reversibly.

According to Scheme 5 two Deslongchamps annulations were started as parallel reactions. In the first flask the benzoquinone monoketal **5b** and the Nazarov reagent **2a** were poised for the Deslongchamps annulation numbered "1" in Scheme 4. However, we let the reaction undisturbed for only 2 minutes. At this duration the monitoring experiment of Figure 2 predicted a ~90% yield of the Michael adducts[44] **13** and a ~10% yield of the ensuing Deslongchamps adduct *cis*,*syn*-**6a**. In the second flask we let the benzoquinone monoketal **5c** and the Nazarov reagent **2b** initiate the Deslongchamps annulation numbered "4" in Scheme 4, and again for only 2 minutes. For this moment in time the monitoring experiment of the 4th concentration/time diagram in Section **SI-4** of the Supporting Information let us expect the Michael adducts[44] **16** to have been

formed in about 90% yield and the ensuing Deslongchamps adduct *cis*,*syn*-**6d** in less than 10% yield. We then pooled the two surmised 90:10 mixtures in a single flask. After another 118 min the Deslongchamps adducts, which had resulted by then were worked up by filtering the reaction mixture through a pad of silica, eluting with AcOEt, and evaporating the solvent. A 500 MHz ^{1}H-NMR spectrum of a $CDCl_3$ solution of the residue revealed the presence of not just two entities [*cis*,*syn*-**6a** (28 rel-%) + *cis*,*syn*-**6d** (53 rel-%)] but four [+ *cis*,*syn*-**6b** (12 rel-%) + *cis*,*syn*-**6c** (7 rel-%)]. This observation establishes that the Michael adducts **13** and **16** must have undergone >19% reversal to their precursors **5b**/**2a** and **5c**/**2b**, respectively. Otherwise **5b** could not have combined with **2b** giving the cross-over product *cis*,*syn*-**6b** and, likewise, **5c** could not have combined with **2a** giving the cross-over product *cis*,*syn*-**6c**. Differently expressed, the occurrence of these cross-over products proves that the Michael adducts **13** and **16** form reversibly.

Scheme 6. Cross-over experiment II.[a] Dieses Schema verweist 2 × auf Lit.-stelle[44].



[a] We started the Deslongchamps annulations **5b** + **2b** → **14** → *cis*,*syn*-**6b** (numbered "2" in Scheme 4) and **5c** + **2a** → **15** → *cis*,*syn*-**6c** (numbered "3" in Scheme 4) separately and a delay of 1 min. 1 and 2 min, respectively, after launching these reactions, we combined the two mixtures. After 2 h the nature and relative amounts of the resulting Deslongchamps adducts were assessed ^{1}H-NMR spectroscopically (500 MHz, $CDCl_3$). In addition to the "regular products" *cis*,*syn*-**6b** (resulting from **14**) and *cis*,*syn*-**6c** (resulting from **15**) we found the "cross-over products" *cis*,*syn*-**6a** (resulting from **5b** + **2a**) and *cis*,*syn*-**6d** (resulting from **5c** + **2b**). The latter pairings would have been impossible unless the Michael adducts **14** and **15** had re-formed their respective precursors **5b**/**2b** and **5c**/**2a** under the reaction conditions; i. e., these Michael adducts form reversibly.

We started another pair of Deslongchamps annulations separately and in parallel – from the same substrates as before (Scheme 5) but swapping their pairings (Scheme 6). In flask 1 the benzoquinone monoketal **5b** and the Nazarov reagent **2b** were combined for undergoing the Deslongchamps annulation numbered "2" in Scheme 4. In flask 2 the benzoquinone monoketal **5c** and the Nazarov reagent **2a** were combined for undergoing the Deslongchamps annulation "3". We left the first mixture undisturbed for 1 min and the second for 2 min. These time laps should have sufficed for ca. 90% Michael adducts[44] **14** and **15**, respectively, to form plus ca. 10% of the Deslongchamps adducts *cis*,*syn*-**6b** and **c**, respectively. This expectation followed from the close-ups in the earlier monitorings (2nd and 3rd concentration/time diagram in Section **SI-4** of the Supporting Information, respectively). Combining the two reaction mixtures then, allowing them to react for another 118 min, working them up, and analyzing them NMR-spectroscopically like in Scheme 5 revealed the presence of the regular Deslongchamps products *cis*,*syn*-**6b** (46 rel-%) and *cis*,*syn*-**6c** (31 rel-%) and of the cross-over products *cis*,*syn*-**6a** (6 rel-%) and *cis*,*syn*-**6d** (17 rel-%). Thus the constituents **5b** and **2b** of the Michael adduct **14** ended up not only in the "regular" Deslongchamps adduct *cis*,*syn*-**6b** but also in the "crossed" Deslongchamps adducts *cis*,*syn*-**6a** and *cis*,*syn*-**6d**, respectively. Similarly, the constituents **5c** and **2a** of the Michael adduct **15** ended up not only in the "regular" Deslongchamps adduct *cis*,*syn*-**6c** but in the "crossed" Deslongchamps adducts *cis*,*syn*-**6d** and *cis*,*syn*-**6a**, respectively, as well. This outcome would be inexplicable unless the Michael adducts **14** and **15** had formed reversibly, i. e., re-formed their precursors **5b**/**2b** and **5c**/**2a**, respectively, under the reaction conditions.

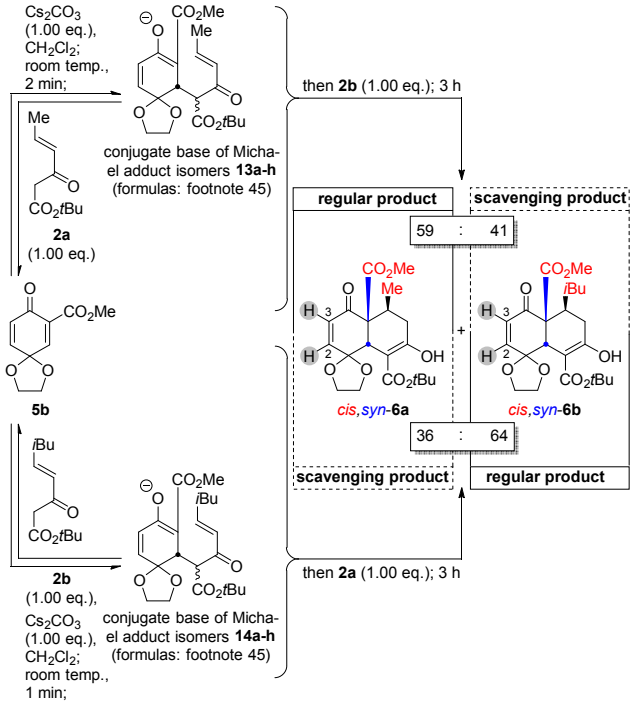
We ascertained that the cross-over products *cis*,*syn*-**6b**/**6c** of the cross-over experiment of Scheme 5 arose under kinetic, not thermodynamic control. This was done by exposing a mixture of the Deslongchamps adducts *cis*,*syn*-**6b** and **c** to the conditions of the cross-over experiment (CH_2Cl_2 solution, 2 equiv. of solid Cs_2CO_3, room temp.) but 3 times longer. After 1, 2, 3, and 6 h, ^{1}H-NMR spectroscopic (500 MHz, $CDCl_3$) examinations revealed identity with the original mixture of *cis*,*syn*-**6b** and **c**. If these Michael adducts had reverted to their precursors with similar rates, the latter would have recombined to a total of 4 Michael adducts *cis*,*syn*-**6a**-**d**. Accordingly, the Deslongchamps annulations of Scheme 5 proceeded irreversibly. An analogous exposure of the cross-over products *cis*,*syn*-**6a**/**6d** of the cross-over experiment of Scheme 6 to a suspension of solid Cs_2CO_3 in CH_2Cl_2 revealed that those compounds formed irreversibly, too.

Scavenging Experiments

Cross-over experiments are elaborated variants of scavenging experiments. For instance, the cross-over experiment of Scheme 5 engaged (1) the benzoquinone monoketal **5b** in a pre-reaction with the Nazarov reagent **2a** and (2) the benzo-

quinone monoketal **5c** in a pre-reaction with the Nazarov reagent **2b**. Whenever the first pre-reaction proceeded backwards, regenerating some benzoquinone monoketal **5b** and an identical amount of the Nazarov reagent **2a**, chances were a scavenging reagent for *either* of the latter was present due to the concomitant partial reversal of the second pre-reaction: the latter would provide the benzoquinone monoketal **5c**, a scavenger for the mentioned Nazarov reagent **2a**, along with the Nazarov reagent **2b**, a scavenger for the mentioned benzoquinone monoketal **5b**. In the experiments described in the following, we did not regenerate a pair of scavengers from a pertinent pre-reaction. We rather added a single scavenger as a pure compound.

Scheme 7. Scavenging experiments I, using the benzoquinone monoketal 5b.[a]

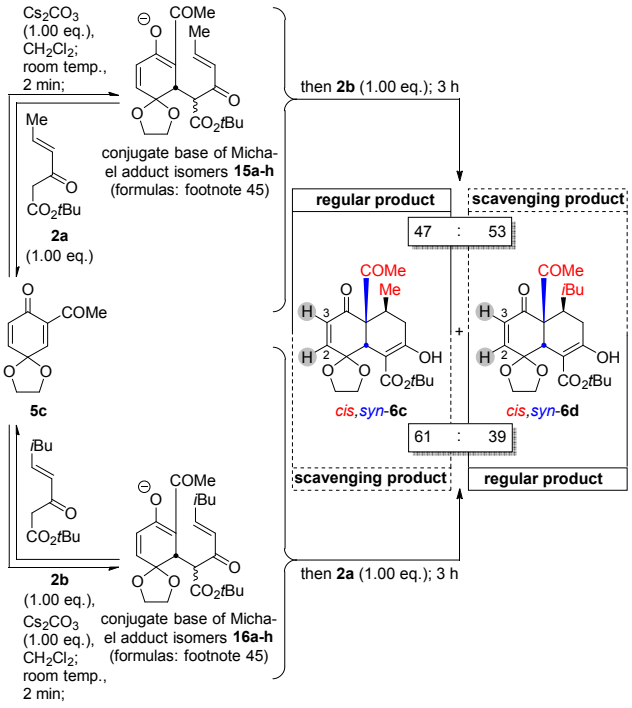


[a] Top: interfering in the formation of the Deslongchamps adduct *cis,syn*-6a from the Nazarov reagent **2a** via the Michael adduct **13** by adding, 2 min after launching the respective reaction, the Nazarov reagent **2b** as a scavenger (+ **5b** → *cis,syn*-**6b**). Bottom: interfering in the formation of the Deslongchamps adduct *cis,syn*-**6b** from the Nazarov reagent **2b** via the Michael adduct **14** and by adding, 1 min after launching the respective reaction, the Nazarov reagent **2a** as a scavenger (+ **5b** → *cis,syn*-**6a**). In both experiments, the nature and relative amounts of the resulting Deslongchamps adducts were assessed after 3 h ^{1}H-NMR spectroscopically (500 MHz, $CDCl_3$).

Scheme 7 shows two scavenging experiments starting from the benzoquinone monoketal **5b**. The experiment reproduced in the top half affected first just the Nazarov reagent **2a**. After 2 min, the Michael adduct **13** should have resulted in ca. 90% yield (cf. the respective monitoring experiment: Figure 2). We added the Nazarov reagent **2b** as a scavenger. From then onward, the original Michael adduct **13** and/or the original reactants **5b** and **2a** could still afford the Deslongchamps adduct *cis,syn*-**6a**. Alternatively, the same Michael adduct **13** regenerated the benzoquinone monoketal **5b** (along with **2a**) such that it could combine with the scavenger giving the Michael adduct **14** fast and the respective Deslongchamps adduct *cis,syn*-**6b** slowly. In the event, a ^{1}H-NMR analysis of the crude products present after 3 h characterized them as a 59:41 mixture of the Deslongchamps adduct *cis,syn*-**6a** of the original reactants and the Deslongchamps adduct *cis,syn*-**6b** incorporating the scavenger.[45] The experiment shown in the bottom part of Scheme 7 began with the benzoquinone monoketal **5b** and at first nothing but the Nazarov reagent **2b** and from 1 min (2nd concentration/time diagram in Section **SI-4** of the Supporting Information) onward one equivalent of the Nazarov reagent **2a**, added as a scavenger. After 3 h, we had obtained a 64:36 mixture of the Deslongchamps adduct *cis,syn*-**6b** of the original reactant pairing and the Deslongchamps adduct *cis,syn*-**6a** of the scavenger.

It is noteworthy that we obtained oppositely composed mixtures of the Deslongchamps adducts *cis,syn*-**6a** and *cis,syn*-**6b** in the scavenging experiments for Scheme 7. No matter which was the original and which scavenging Nazarov reagent, there was a slight preference for delivering the Deslongchamps adduct of the original reagent pairing. The respective yield differences are 59%−41% = 18% and 64%−36% = 28%, respectively. If kinetic rather than thermodynamic control of the portfolio of Deslongchamps adduct formation prevailed here as in our cross-over experiments (Scheme 5, Scheme 6) these yield differences would be due to the 2 minutes and 1 minute advances, which the original reactant combinations had under the conditions of Scheme 7. Unfortunately, the respective monitorings (**5b** + **2a** → *cis,syn*-**6a**: see Figure 2 for t = 2 min; **5b** + **2b** → *cis,syn*-**6b**: see 2nd concentration/time diagram in Section **SI-4** of the Supporting Information for t = 1 min) are not sufficiently precise to bear on the suspicion that, in addition, part of these yield biases stem from the Michael adducts **13** and **14** rather being on than off the Deslongchamps-delivering reaction coordinate.

Scheme 8. Scavenging experiments II, using the benzoquinone monoketal 5c.[a]



[a] Top: interfering in the formation of Deslongchamps adduct *cis,syn*-**6c** from the Nazarov reagent **2a** via the Michael adduct **15** by adding, 2 min after launching the respective reaction, the Nazarov reagent **2b** as a scavenger (+ **5c** → *cis,syn*-**6d**). Bottom: interfering in the formation of the Deslongchamps adduct *cis,syn*-**6d** from the Nazarov reagent **2b** via the Michael adduct **16** by adding, 2 min after launching the respective reaction, the Nazarov reagent **2a** as a scavenger (+ **5c** → *cis,syn*-**6c**). In both experiments, the nature and relative amounts of the resulting Deslongchamps adducts were assessed after 3 h ^{1}H-NMR spectroscopically (500 MHz, $CDCl_3$).

Scheme 8 is an analogous documentation of two scavenging experiments starting from the benzoquinone monoketal **5c**. They concern successive additions of the Nazarov reagents **2a** and **2b** (at top) and vice versa (at bottom). Proceeding as described for the scavenging experiments of Scheme 7, we found that in either case we obtained a mixture of two Deslongchamps adducts (Scheme 8).45 Surprisingly, in either case the *major* adduct stemmed from the Nazarov reagent, which was added as the scavenger. This observation shows that the Michael adducts **15** and **16**, which must have formed first (according to the monitorings of the 3rd and 4th concentration/time diagram in Section **SI-4** of the Supporting Information, respectively) underwent extensive reversal to their precursors **5c**/**2a** and **5c**/**2b**, respectively, on the time-scale of Deslongchamps adduct formation. However, the two-fold predominance of the scavenging product must have another reason: a preferred loss and/or decomposition of the *originally* added Nazarov reagent. In that context we note that the relative amount of Cs_2CO_3 automatically dropped to 0.5 equiv. when we added the second, that is scavenging Nazarov reagent.

CONCLUSION

In the course of Deslongchamps annulations of acceptor-substituted benzoquinone monoketals (and, by extrapolation, possibly also of acceptor-substituted cyclohexenones in general) Michael adducts form within minutes, in about 90% yield, and reversibly. None of this was known before. In contrast, the Deslongchamps adducts formed irreversibly (and, by extrapolation, related Deslongchamps adducts might do so as well). This was neither demonstrated before.

Viewed differently, our reactants underwent Michael additions for starters and not Diels-Alder reactions. By this preference they seized the only opportunity to form a C–C bond *without turning an acceptor-substituted into an acceptor-free enolate*. Proceding to a Deslongchamps adduct from there – either by an intramolecular Michael addition of the initial Michael adduct or after dissociation into the reactants via an anionic Diels-Alder reaction – requires going from *an acceptor-substituted to an acceptor-free enolate*. Overcoming the corresponding energy barrier seems to cost time – so much, in fact, that the original Michael adducts formed reversibly rather than irreversibly.

That property, however, prevented us from determining whether these Michael adducts arose *off* the route to the Deslongchamps adducts (mechanism "1" of Scheme 3) or *on* it (mechanism "3" of Scheme 3). Accordingly, it remains unknown whether the product-forming step of Deslongchamps annulations like ours is the second Michael addition or an anionic Diels-Alder reaction.[46]

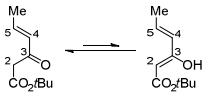
EXPERIMENTAL SECTION

General Working Technique: All reactions were carried out under an N_2-atmosphere. Reaction flasks were dried in vacuo with a heat gun prior to use. Liquids were added with a syringe through a septum. Solids were added in an N_2-counterflow. THF was distilled over potassium, Et_2O over sodium/potassium alloy, and CH_2Cl_2 was distilled over CaH_2 under an N_2-atmosphere prior to use. Other solvents and reagents were purchased and used without further purification. **Flash chromatography:**[36] Macherey-Nagel silica gel 60® (230-400 mesh). All eluents were distilled prior to use. Chromatography conditions are documented as in, for example, "[*a* cm × *b* cm, *c*C_6H_{12}:EtOAc = *c*:*d* (v:v), *e* mL] ... F10-20", which means: a column with a diameter of *a* cm was packed with *b* cm of silica, it was eluted with *c*C_6H_{12} and EtOAc in a *c*:*d* ratio (v:v), fractions of the size of *e* mL were taken, and the product was isolated from fractions 10-20. **Nuclear magnetic resonance spectra:** Bruker Avance 500 (500 MHz and 125 MHz for ^{1}H and ^{13}C respectively), Bruker Avance 400 spectrometer (400 MHz and 100 MHz for ^{1}H and ^{13}C respectively) and Avance 300 spectrometer (300 MHz for ^{1}H respectively) referenced internally by the ^{1}H- and ^{13}C NMR signals of the solvent [$CDCl_3$: 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C); $(CD_3)_2CO$: 2.05 ppm (^{1}H) and 29.84 ppm (^{13}C); $(CH_3)_4Si$: 0.00 ppm (^{1}H) and 0.00 ppm (^{13}C)]. ^{1}H NMR data are reported as follows: chemical shift (δ in ppm), multiplicity (s for singlet; d for doublet; t for triplet; sept for septet, m for multiplet; m_c for symmetrical multiplet; br for broad signal), number of protons (concluded from the integrals), coupling constant(s) (Hz), specific assignment or integral. ^{13}C NMR data are reported in terms of chemical shift and assignment. For AB signals the high-field part was named A and the low-field part

B. The atom numbering used for NMR assignments follows the IUPAC nomenclature unless noted otherwise. **High-resolution mass spectra** were obtained on a Finnigan MAT 8200 instrument (EI: 70 eV; CI/NH_3: 110 eV) using an orbitrap analyzer. **Elemental analyses** were obtained on a CHNS analysator Elementar Vario EL. **Melting points** were determined in a Büchi melting point apparatus using open glass capillaries and are uncorrected. **IR spectra** were obtained on an FT-IR Perkin Elmer Paragon 1000 spectrometer as a film of the substance on a polyethylene-foil (Spectra-Tech Inc.; self-absorption may compete in the regions 2920-2850, 1480-1430, and 740-700 cm^{-1}.

Synthesizing Nazarov Reagents and Benzoquinone Monoketals:

***tert*-Butyl (*E*)-3-Oxohex-4-enoate (2a)**

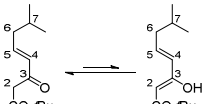


keto-**2a** enol-**2a**

60:40 mixture in $CDCl_3$ (concluded from the integral heights of the resonances of **5**-H_{keto} vs. **5**-H_{enol})

The title compound was prepared from crotonic acid and mono-*tert*-butylmalonate:[47] Oxalyl chloride (4.4 mL, 52 mmol, 1.1 equiv.) was added dropwise to a solution of DMF (4.0 mL, 51 mmol, 1.1 equiv.) in CH_2Cl_2 (45 mL) at –10°C within 5 min. Crotonic acid (4.0 g, 47 mmol, 1.0 equiv.) was added in one portion. The mixture was stirred for 45 min. In another flask *i*PrMgCl (1.9 M, in THF, 0.1 L, 4.1 equiv.) was added dropwise to a solution of mono-*tert*-butylmalonate (15 mL, 98 mmol, 2.1 equiv.) in THF (70 mL) at 0°C. Stirring was continued for 10 min. At 0°C the solution obtained from crotonic acid was added dropwise within 30 min via cannula to the solution of the magnesium enolate. The resulting mixture was stirred at room temp. for another 30 min. The reaction was quenched by adding HCl (conc., 15 mL) and water (20 mL). The layers were separated. The aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3 × 80 mL) until the aqueous layer was no longer acidic. The combined aqueous layers were re-extracted with EtOAc (2 × 80 mL). The combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [7.5 cm × 15 cm, *c*C_6H_{12}:EtOAc 10:1 (v:v) to 2:1, 100 mL] to render the title compound (F9-12; 3.95 g, 46%) as a pale orange oil. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 1.46 (s, 9H, *t*$Bu_{of\ keto}$), 1.49 (s, 9H, *t*$Bu_{of\ enol}$), 1.85 (dd, 2H, $J_{6,5}$ = 6.9 Hz, $^4J_{6,4}$ = 1.6 Hz, 6-$H_{3\ of\ enol}$), 1.93 (dd, 3H, $J_{6,5}$ = 6.8 Hz, $^4J_{6,4}$ = 1.7 Hz, 6-$H_{3\ of\ keto}$), 3.47 (s, 2H, 2-$H_{2\ of\ keto}$), 4.87 (s, 1H, 2-$H_{of\ enol}$), 5.77 (dqd, 1H, $J_{4,3}$ = 15.4 Hz, $^4J_{4,6}$ = 1.7 Hz, $^4J_{4,3\text{-}OH}$ = 1.6 Hz, 4-$H_{of\ enol}$), 6.18 (qd, 1H, $J_{4,5}$ = 15.8 Hz, $^4J_{4,6}$ = 1.7 Hz, 4-$H_{of\ keto}$), 6.62 (qd, 1H, $J_{5,4}$ = 15.4 Hz, $J_{5,6}$ = 6.9 Hz, 5-$H_{of\ enol}$), 6.89 (qd, 1H, $J_{5,4}$ = 15.8 Hz, $J_{5,6}$ = 6.8 Hz, 5-$H_{of\ keto}$), 12.01 (d, 1H, $^4J_{3\text{-}OH,4}$ = 1.3 Hz, 3-$OH_{of\ enol}$). These NMR signals agree with the literature.7

***tert*-Butyl (*E*)-7-Methyl-3-oxooct-4-enoate (2b)**

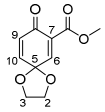


keto-**2b** enol-**2b**

82:18 mixture in $CDCl_3$ (concluded from the integral heights of the resonances of **5**-H_{keto} vs. **5**-H_{enol})

The title compound was prepared from (*E*)-5-methylhex-2-enoic acid and mono-*tert*-butylmalonate. Oxalyl chloride (3.0 mL, 35 mmol, 1.1 equiv.) was added dropwise to a solution of DMF (2.7 mL, 34 mmol, 1.1 equiv.) in CH_2Cl_2 (31 mL) at –10°C within 5 min. (*E*)-5-Methylhex-2-enoic acid (4.0 g, 31 mmol, 1.0 equiv.) was added in one portion. The mixture was stirred for 35 min. In another flask *i*PrMgCl (2.8 M, 45 mL, 4.1 equiv.) was added at 0°C dropwise to a solution of mono-*tert*-butylmalonate (10 mL, 66 mmol, 2.1 equiv.) in THF (47 mL). The mixture was stirred for 10 min. At 0°C the solution of the acid chloride was added dropwise within 30 min via cannula to the solution of the magnesium enolate. The resulting mixture was stirred for 30 min at room temp. The reaction was quenched at 0°C by the addition of HCl (conc., 20 mL) and water (20 mL). The layers were separated. The aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with a saturated aqueous solution of NH_4CO_3 (3 × 80 mL) until the aqueous layer was no longer acidic. The combined aqueous layers were re-extracted with EtOAc (2 × 80 mL). The combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [7.5 cm × 16.5 cm, *c*C_6H_{12}:EtOAc 100:1 (v:v) to 2:1, 100 mL] to render the title compound (F21-33; 3.89 g, 55%) as a pale yellow oil. **^{1}H NMR** (300.13 MHz, $CDCl_3$): δ = 0.91 (d, $J_{8,7}$ = 6.2 Hz, 6H, 2 × $CH_{3\ of\ enol}$), 0.93 (d, $J_{8,7}$ = 6.2 Hz, 6H, 2 × $CH_{3\ of\ keto}$), 1.46 (s, 9H, *t*$Bu_{of\ keto}$), 1.49 (s, 9H, *t*$Bu_{of\ enol}$), 1.73 (m_c, 1H, 7-$H_{of\ enol}$), 1.78 (m_c, 1H, 7-$H_{of\ keto}$), 2.06 (ddd, $J_{6,5}$ = 7.6 Hz, $J_{6,7}$ = 6.7 Hz, $^4J_{6,4}$ = 1.3 Hz, 2H, 6-$H_{2\ of\ enol}$), 2.13 (ddd, $J_{6,5}$ = 7.3 Hz, $J_{6,7}$ = 6.8 Hz, $^4J_{6,4}$ = 1.4 Hz, 2H, 6-$H_{2\ of\ keto}$), 3.48 (s, 2H, 2-$H_{2\ of\ keto}$), 4.90 (s, 1H, 2-$H_{of\ enol}$), 5.74 (dqd, $J_{4,5}$ = 15.5 Hz, $^4J_{4,6}$ = 1.4 Hz, $^4J_{4,\ 3\text{-}OH}$ = 1.4 Hz, 1H, 4-$H_{of\ enol}$), 6.14 (dt, $J_{4,5}$ = 15.8 Hz, $^4J_{4,6}$ = 1.4 Hz, 1H, 4-$H_{of\ keto}$), 6.59 (dt, $J_{5,4}$ = 15.3 Hz, $J_{5,6}$ = 7.6 Hz, 1H, 5-$H_{of\ enol}$), 6.85 (dt, $J_{5,4}$ = 15.8 Hz, $J_{5,6}$ = 7.4 Hz, 1H, 5-$H_{of\ keto}$), 12.03 (d, $^4J_{3\text{-}OH,4}$ = 1.1 Hz, 1H, 3-$OH_{of\ enol}$). The preceding NMR signals agree with the literature.21

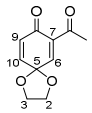
Methyl 8-Oxo-1,4-dioxaspiro[4.5]deca-6,9-diene-7-carboxylate (5b)



A solution of methyl 2-hydroxy-5-(2-hydroxyethoxy)benzoate[47] (1.18 g, 5.55 mmol, 1.0 equiv.) and $NaHCO_3$ (1.59 g, 18.9 mmol, 3.4 equiv.) in CH_2Cl_2 (110 mL) was stirred at room temp. for 20 min under exclusion of light. $PhI(O_2CCF_3)$ (2.87 g, 6.66 mmol, 1.2 equiv.) was added in one portion and stirring was continued for 30 min. The reaction mixture was cooled to 0°C, washed with ice cold water (110 mL), and the layers were separated immediately. The organic layer was recooled in an ice bath for 3 min and washed with ice-cold water once more (110 mL). The layers were separated immediately. The organic layer was dried over $MgSO_4$. The solvent was evaporated at a maximum of 30°C (water bath) and the residue was immediately (previously prepared) purified by flash chromatography on silica gel36 [3.5 cm × 10 cm, *c*C_6H_{12}:EtOAc:CH_2Cl_2 3:1:1 (v:v:v), 20 mL] to render the title compound (F7-9; 330 mg, 93%) as a yellow solid. **Melting point:** 40-43°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OMe), 4.17 (s, 4H, 2-H_2 and 3-H_2), 6.20 (d, $J_{9,10}$ = 10.2 Hz, 1H, 9-H), 6.60 (dd, $J_{10,9}$ = 10.2 Hz, $^4J_{10,6}$ = 3.1 Hz, 1H, 10-H), 7.20 (d, $^4J_{6,10}$ = 3.1 Hz, 1H, 6-H). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 52. 7 (OMe)^A, 66.2 (C-2 and C-3)^A, 98.3 (C-5)^B, 129.9 (C-9)^A, 130.9 (C-7)^B, 142.3 (C-10)^A, 146.9 (C-6)^A, 164.1 [(*C*=O)OMe]^B, 181.1 (C-8)^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nu-

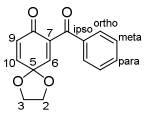
clei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 52.7 (OMe) ↔ δ_H = 3.84 (OMe); δ_C = 66.2 (C-2 and C-3) ↔ δ_H = 4.17 (2-H_2 and 3-H_2); δ_C = 129.9 (C-9) ↔ δ_H = 6.20 (9-H); δ_C = 142.3 (C-10) ↔ δ_H = 6.60 (10-H); δ_C = 146.9 (C-6) ↔ δ_H = 7.20 (6-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 98.3 (C-5) ↔ δ_H = 4.17 (2-H_2 and 3-H_2), δ_H = 6.20 (9-H), δ_H = 6.60 (10-H), and δ_H = 7.20 (6-H); δ_C = 130.9 (C-7) ↔ δ_H = 3.84 (OMe), δ_H = 6.20 (9-H), δ_H = 6.60 (10-H), and δ_H = 7.20 (6-H); δ_C = 164.1 [(*C*=O)OMe] ↔ δ_H = 3.84 (OMe), δ_H = 6.20 (9-H), and δ_H = 7.20 (6-H); δ_C = 181.1 (C-8) ↔ δ_H = 6.20 (9-H), δ_H = 6.60 (10-H), and δ_H = 7.20 (6-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^1H) \leftrightarrow \delta_H(^1H)$]: δ_H = 6.60 (10-H) ↔ δ_H = 6.20 (9-H); δ_H = 7.20 (6-H) ↔ δ_H = 6.60 (10-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 3055, 2990, 2955, 2900, 2850, 1745, 1685, 1650, 1275, 1220, 1140, 1045, 980, 945, 915 cm^{-1}. **HRMS** (pos. APCI) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}O_5$, 211.0601; found, 211.0601.

7-Acetyl-1,4-dioxaspiro[4.5]deca-6,9-dien-8-one (5c)



1-(2-Hydroxy-5-(2-hydroxyethoxy)phenyl)ethan-1-one[47] (201 mg, 1.02 mmol, 1.0 equiv.) and $NaHCO_3$ (297 mg, 3.06 mmol, 3.0 equiv.) were suspended in CH_2Cl_2 (20 mL) and the suspension was stirred at room temp. for 20 min under exclusion of light. $PhI(O_2CCF_3)_2$ (482 mg, 1.12 mmol, 1.1 equiv.) was added in one portion and stirring was continued for 30 min. The reaction mixture was cooled in an ice bath for 5 min and washed with ice cold water (35 mL). The layers were separated immediately and the organic layer was cooled in an ice bath for 3 min and washed again with ice cold water (35 mL). The layers were separated immediately. The organic layer was dried over $MgSO_4$. The solvent was evaporated at a maximum of 30°C (water bath) and the residue was immediately purified by flash chromatography on silica gel36 [2 cm × 10 cm, *c*C_6H_{12}:EtOAc:CH_2Cl_2 7:3:1 (v:v:v), 9 mL]. This rendered the title compound (F3-9; 170 mg, 86%) as a pale orange oil. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 2.51 (s, 3H, CO*Me*), 4.17 (s, 4H, 2-H_2, 3-H_2), 6.19 (d, $J_{9,10}$ = 10.1 Hz, 1H, 9-H), 6.62 (dd, $J_{10,9}$ = 10.1 Hz, $^4J_{10,6}$ = 3.2 Hz, 1H, 10-H), 7.13 (d, $J_{6,10}$ = 3.2 Hz, 1H, 6-H). **^{13}C NMR** (500.3 MHz, $CDCl_3$): δ = 30.9 (CO*Me*)^A, 66.2 (C-2, C-3)^A, 98.5 (C-5)^B, 130.0 (C-9)^A, 137.0 (C-7)^B, 142.8 (C-10)^A, 146.0 (C-6)^A, 183.5 (C-8)^B, 197.4 (*C*OMe)^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 30.9 (CO*Me*) ↔ δ_H = 2.51 (CO*Me*); δ_C = 66.3 (C-2, C-3) ↔ δ_H = 4.17 (2-H_2, 3-H_2); δ_C = 130.0 (C-9) ↔ δ_H = 6.19 (9-H); δ_C = 142.8 (C-10) ↔ δ_H = 6.62 (10-H); δ_C = 146.0 (C-6) ↔ δ_H = 7.13 (6-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 98.5 (C-5) ↔ δ_H = 4.17 (2-H_2, 3-H_2), δ_H = 6.19 (9-H), δ_H = 6.62 (10-H), and δ_H = 7.13 (6-H); δ_C = 137.0 (C-7) ↔ δ_H = 2.51 ([CO]Me), δ_H = 6.19 (9-H), and δ_H = 7.13 (6-H); δ_C = 142.8 (C-10) ↔ δ_H = 6.19 (9-H), and δ_H = 7.13 (6-H); δ_C = 146.0 (C-6) ↔ δ_H = 6.19 (9-H), and δ_H = 6.62 (10-H); δ_C = 183.5 (C-8) ↔ δ_H = 6.19 (9-H), δ_H = 6.62 (10-H), and δ_H = 7.13 (6-H); δ_C = 197.4 (*C*OMe) ↔ δ_H = 2.51 (CO*Me*), δ_H = 6.19 (9-H), and δ_H = 7.13 (6-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2895, 1700, 1675, 1640, 1385, 1360, 1285, 1250, 1145, 1030, 975, 945, 830, 745 cm^{-1}. **Elemental analysis:** $C_{10}H_{10}O_4$ (194.2); Calcd: C: 61.85%, H: 5.19%; found: C: 61.96%, H: 5.32%. **HRMS** (pos. APCI) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}O_4$, 195.0652; found, 195.0653.

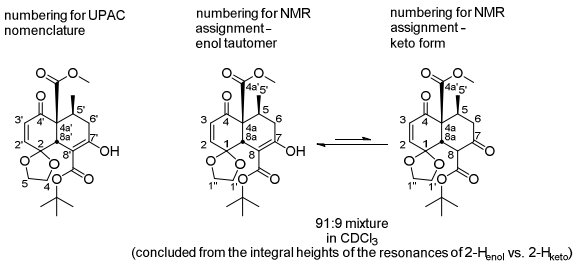
7-Benzoyl-1,4-dioxaspiro[4.5]deca-6,9-dien-8-one (5d)



[2-Hydroxy-5-(2-hydroxyethoxy)phenyl]phenyl-methanone[47] (501 mg, 1.49 mmol, 1.0 equiv.) and $NaHCO_3$ (490 mg, 5.83 mmol, 3.0 equiv.) were suspended in CH_2Cl_2 (39 mL) and the suspension was stirred at room temp. for 20 min under exclusion of light. $PhI(O_2CCF_3)_2$ (919 mg, 2.14 mmol, 1.1 equiv.) was added in one portion and stirring was continued for 30 min. The reaction mixture was cooled in an ice bath for 5 min and washed with ice cold water (70 mL). The layers were separated immediately and the organic layer was cooled in an ice bath for 3 min and again washed with ice cold water (60 mL). The layers were separated immediately and the organic layer was dried over $MgSO_4$. The solvent was evaporated at a maximum of 30°C (water bath) and the residue was immediately (previously prepared) purified by flash chromatograpy on silica gel36 [3 cm × 10 cm, *c*C_6H_{12}:EtOAc:CH_2Cl_2 3:1:1 (v:v:v), 20 mL] to render the title compound (F6-14; 437 mg, 88%) as a yellow solid. **Melting point:** 83-85°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 4.17 (m_c, 4H, 2-H_2, 3-H_2), 6.25 (d, $J_{9,10}$ = 10.1 Hz, 1H, 9-H), 6.70 (dd, $J_{10,9}$ = 10.1 Hz, $^4J_{10,6}$ = 3.1 Hz, 1H, 10-H), 6.77 (d, $J_{6,10}$ = 3.1 Hz, 1H, 6-H), 7.43-7.48 (m, 2H, meta-H_2), 7.56-7.61 (m, 1H, para-H), 7.82-7.84 (m, 2H, ortho-H_2). **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 66.2 (C-2 and C-3)^A, 98.3 (C-5)^B, 128.7 (C-meta)^A, 129.3 (C-9)^A, 129.7 (C-ortho)^A, 134.0 (C-para)^A, 136.3 (C-ipso)^B, 138.8 (C-7)^B, 142.6 (C-6)^A, 143.5 (C-10)^A, 182.9 (C-8)^B, 192.7 [(*C*=O)Ph]^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 66.2 (C-2 and C-3) ↔ δ_H = 4.17 (2-H_2, 3-H_2); δ_C = 128.7 (C-meta) ↔ δ_H = 7.46 (meta-H); δ_C = 123.0 (C-9) ↔ δ_H = 6.25 (9-H); δ_C = 129.7 (C-ortho) ↔ δ_H = 7.83 (ortho-H); δ_C = 134.0 (C-para) ↔ δ_H = 7.61 (para-H); δ_C = 142.6 (C-6) ↔ δ_H = 6.77 (6-H); δ_C = 143.5 (C-10) ↔ δ_H = 6.70 10-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 98.3 (C-5) ↔ δ_H = 4.17 (2-H_2, 3-H_2), δ_H = 6.25 (9-H), and δ_H = 6.77 (6-H); δ_C = 136.3 (C-ipso) ↔ δ_H = 7.46 (meta-H); δ_C = 138.8 (C-7) ↔ δ_H = 6.25 (9-H) and δ_H = 6.77 (6-H); δ_C = 182.9 (C-8) ↔ δ_H = 6.25 (9-H), δ_H = 6.70 (10-H), and δ_H = 6.77 (6-H); δ_C = 192.7 [(*C*=O)Ph] ↔ δ_H = 6.25 (9-H), δ_H = 6.77 (6-H), and δ_H = 7.83 (ortho-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz),] [$\delta_H(^1H) \leftrightarrow \delta_H(^1H)$]: δ_H = 6.70 10-H ↔ δ_H = 6.25 (9-H); δ_H = 6.77 (6-H) ↔ δ_H = 6.70 10-H; δ_H = 7.58 (para-H) ↔ δ_H = 7.46 (meta-H); δ_H = 7.83 (ortho-H) ↔ δ_H = 7.46 (meta-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 3060, 2960, 2895, 1680, 1645, 1600, 1580, 1270, 1220, 1145, 1115, 1065, 980, 945, 915 cm^{-1}. **Elemental analysis:** $C_{15}H_{12}O_4$ (256.3); Calcd: C: 70.31%, H: 4.72%; found: C: 70.09%, H: 4.65%. **HRMS** (pos. APCI) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}O_4$, 257.0808; found, 257.0809.

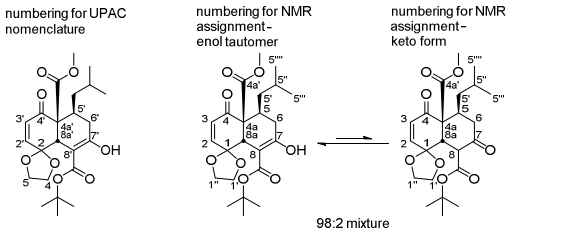
Synthesizing Deslongchamps Adducts:

8'-(*tert*-Butyl) 4a'-Methyl (4a'*S*,5'*S*,8a'*S*)-7'-Hydroxy-5'-methyl-4'-oxo-6',8a'-dihydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4a',8'(5'*H*)-dicarboxylate (*cis,syn*-6a)



Cs_2CO_3 (553 mg, 1.70 mmol, 1.05 equiv.) was added to a solution of benzoquinone monoketal **5b** (340 mg, 1.62 mmol, 1.0 equiv.) and β-ketoester **2a** (356 mg, 1.94 mmol, 1.2 equiv.) in CH_2Cl_2 (54 mL) at 25°C in one portion. The reaction mixture was stirred at 25°C for 3.5 h and filtered through a pad of celite® (2 cm × 1 cm). The pad was rinsed with EtOAC (75 mL). The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [3 cm × 15 cm, *c*C_6H_{12}:EtOAC 4:1 to 1:1 (v:v), 20 mL] to render the title compound (F5-24; 593 mg, 93%) as a colorless solid. **Melting point:** 49-51°C. **^{1}H NMR** (500.32 MHz, TMS as internal standard, $CDCl_3$): δ = 1.07 (d, $J_{5',5}$ = 6.9 Hz, 3H, 5'-$H_{3\ of\ keto}$), 1.10 (d, $J_{5',5}$ = 6.9 Hz, 3H, 5'-$H_{3\ of\ enol}$), 1.46 (s, 9H, 3 × 8"-$Me_{of\ keto}$), 1.48 (s, 9H, 3 × 8"-$Me_{of\ enol}$), 2.51 (m, 2H, 6-$H_{2\ of\ enol}$), 2.77 (m, 1H, 5-$H_{of\ enol}$), 3.65 (s, 3H, $CO_2Me_{of\ enol}$), 3.70 (s, 3H, $CO_2Me_{of\ keto}$), 3.71-3.75 (m, 1H, 1'-$H^1_{of\ enol}$)*, 3.85-3.93 (m, 2H, 1"-$H_{2\ of\ enol}$)*, 4.01-4.05 (m, 1H, 1'-$H^2_{of\ enol}$)*, 4.19 (s, 1H, 8a-$H_{of\ enol}$), 5.98 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ enol}$), 6.12 (d, $J_{3,2}$ = 10.4 Hz, 1H, 3-$H_{of\ keto}$), 6.54 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ enol}$), 6.57 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ keto}$), 12.62 (7-O*H*); *: assignment interchangeable. **^{13}C NMR** (125.8 MHz, TMS as internal standard, $CDCl_3$): δ = 15.9 (C-5')^A, 28.2 (3 × 8"-*Me*)^A, 29.9 (C-5)^A, 35.2 (C-6)^A, 44.2 (C-8a)^A, 51.8 (CO_2Me)^A, 61.7 (C-4a)^B, 64.5 (C-1")*,^{A}, 66.4 (C-1')*,^{A}, 81.2 (C-8")^B, 94.9 (C-8)^B, 104.7 (C-1)^B, 127.2 (C-3)^A, 146.1 (C-2)^A, 169.6 (C-4a')^B, 171.6 (C-8')^B, 175.5 (C-7)^B, 197.4 (C-4)^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons; * assignment interchangeable. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 15.9 (C-5') ↔ δ_H = 1.07 (5'-H_3); δ_C = 28.2 (3 × 8"-*Me*) ↔ δ_H = 2.77 (3 × 8"-*Me*); δ_C = 29.9 (C-5) ↔ δ_H = 2.77 (5-H); δ_C = 35.2 (C-6) ↔ δ_H = 2.51 (6-H_2); δ_C = 44.2 (C-8a) ↔ δ_H = 4.19 (8a-H); δ_C = 51.8 (CO_2Me) ↔ δ_H = 3.65 (CO_2Me); δ_C = 64.5 (C-1") ↔ δ_H = 3.89 (1"-H_2); δ_C = 66.4 (C-1') ↔ δ_H = 3.73 (1'-H^1); δ_C = 66.4 (C-1') ↔ δ_H = 4.03 (1'-H^2); δ_C = 127.2 (C-3) ↔ δ_H = 5.98 (3-H); δ_C = 146.1 (C-2) ↔ δ_H = 6.54 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 61.7 (C-4a) ↔ δ_H = 1.07 (5'-H_3), δ_H = 2.51 (6-H_2), δ_H = 2.77 (5-H), δ_H = 4.19 (8a-H), and δ_H = 5.98 (3-H); δ_C = 81.2 (C-8") ↔ δ_H = 2.77 (3 × 8"-*Me*); δ_C = 94.9 (C-8) ↔ δ_H = 4.19 (8a-H), δ_H = 6.54 (2-H), and δ_H = 12.62 (7-O*H*); δ_C = 104.7 (C-1) ↔ δ_H = 3.73 (1'-H^1), δ_H = 3.89 (1"-H_2), δ_H = 4.03 (1'-H^2), δ_H = 4.19 (8a-H), δ_H = 5.98 (3-H), and δ_H = 6.54 (2-H); δ_C = 169.6 (C-4a') ↔ δ_H = 2.77 (5-H), δ_H = 3.65 (CO_2Me), δ_H = 4.19 (8a-H), and δ_H = 5.98 (3-H); δ_C = 171.6 (C-8') ↔ δ_H = 4.19 (8a-H); δ_C = 175.5 (C-7) ↔ δ_H = 1.07 (5'-H_3), δ_H = 2.51 (6-H_2), δ_H = 4.19 (8a-H), and δ_H = 12.62 (7-O*H*); δ_C = 197.4 (C-4) ↔ δ_H = 4.19 (8a-H) and δ_H = 6.54 (2-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [δ_H(^{1}H) ↔ δ_H(^{1}H)]: δ_H = 1.07 (5'-H_3) ↔ δ_H = 2.77 (5-H); δ_H = 2.51 (6-H_2) ↔ δ_H = 2.77 (5-H); δ_H = 3.73 (1'-H^1) ↔ δ_H = 3.89 (1"-H_2); δ_H = 3.73 (1'-H^1) ↔ δ_H = 4.03 (1'-H^2); δ_H = 3.89 (1"-H_2) ↔ δ_H = 4.03 (1'-H^2); δ_H = 5.98 (3-H) ↔ δ_H = 6.54 (2-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2980, 2890, 1745, 1680, 1640, 1400, 1370, 1295, 1235, 1155, 1090, 1075, 1050, 1015, 950 cm^{-1}. **Elemental analysis:** $C_{20}H_{26}O_8$ (394.4); Calcd: C: 60.90%, H: 6.64%; found: C: 60.55%, H: 6.59%. **HRMS** (neg. APCI) m/z: $[M + NH_4]^+$ calcd for $C_{20}H_{30}O_8N$, 412.1966; found, 412.1967.

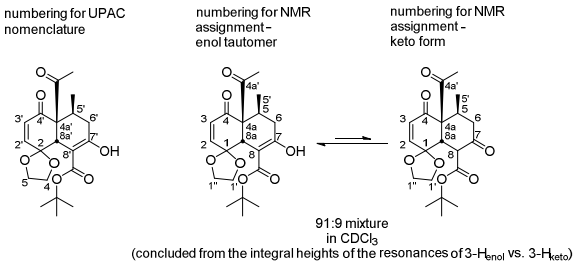
8'-(*tert*-Butyl) 4a'-Methyl (4a'S,5'S,8a'S)-7'-Hydroxy-5'-isobutyl-4'-oxo-6',8a'-dihydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4a',8'(5'*H*)-dicarboxylate (*cis,syn*-6b)



Cs_2CO_3 (309 mg, 947 μmol, 1.1 equiv.) was added to a solution of benzoquinone monoketal **5b** (181 mg, 861 μmol, 1.0 equiv.) and Nazarov reagent **2b** (253 mg, 1.12 mmol, 1.3 equiv.) in CH_2Cl_2 (21 mL) at 25°C in one portion. The mixture was stirred at 25°C for 3.5 h and filtered through a pad of silica gel (2 cm × 1 cm). The pad was rinsed with EtOAc (40 mL) and the solvent was evaporated. The residue was purified by flash chromatography on silica gel36 [2.5 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 4:1 (v:v), 20 mL] to render the title compound (F7-27; 269 mg, 72%) as colorless needles. **Melting point:** 103-105°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 0.72 (d, $J_{5'''-H,5''-H}$ = 6.4 Hz, 3H, 5'''-$H_{3\ of\ keto}$), 0.74 (d, $J_{5'''-H,5''-H}$ = 6.5 Hz, 3H, 5'''-$H_{3\ of\ enol}$), 0.86 (d, $J_{5''''-H,5''-H}$ = 6.3 Hz, 3H, 5''''-$H_{3\ of\ keto}$),0.87 (d, $J_{5''''-H,5''-H}$ = 6.6 Hz, 3H, 5''''-$H_{3\ of\ enol}$), 1.09 (ddd, J_{gem} = 13.9 Hz, $J_{5'-H(1),5}$ = 10.0 Hz, $J_{5'-H(1),5''-H}$ = 3.8 Hz, 1H, 5'-$H^1_{of\ enol}$), 1.40-1.58 (m, 1H, 5-$H_{of\ enol}$), 1.45 (s, 9-H, 3 × $CH_{3\ of\ keto}$), 1.48 (s, 9-H, 3 × $CH_{3\ of\ enol}$), 1.78 (ddd, J_{gem} = 14.1 Hz, $J_{5'-H(2),5}$ = 10.0 Hz, $J_{5'-H(2),5''-H}$ = 4.2 Hz, 1H, 5'-$H^1_{of\ enol}$), AB-signal (δ_A = 2.41, δ_B = 2.60, J_{AB} = 18.7, , additionally split by $J_{A,5}$ = 9.8 Hz, and $J_{B,5}$ = 7.8 Hz, 6-$H_{2\ of\ enol}$), 2.71 (dddd, $J_{5-H,5'-H(1)}$ = $J_{5-H,5'-H(2)}$ = 9.9 Hz, $J_{5-H,6-H(B)}$ = 7.7 Hz, $J_{5-H,5'-H(1)}$ = 2.9 Hz, 1H, 5-$H_{of\ enol}$), 3.72 (ddd, $J_{1'-H(1),1''-H(A)}$ = 8.1 Hz, J_{gem} = 7.4 Hz, $J_{1'-H(1),1''-H(B)}$ = 6.2 Hz, 1H, 1'-$H^1_{of\ enol}$)*, AB-signal (δ_A = 3.86, δ_B = 3.91, J_{AB} = 8.1 Hz, additionally split by $J_{A,1'-H(1)}$ = 8.1 Hz, $J_{A,1'H(2)}$ = 6.1 Hz, $J_{B,1'-H(1)}$ = 6.2 Hz, and $J_{B,1'-H(2)}$ = 3.5 Hz, 1"-$H_{2\ of\ enol}$)**, 4.04 (ddd, J_{gem} = 7.4 Hz, $J_{1'-H(2),1''-H(A)}$ = 6.1 Hz, $J_{1'-H(2),1''-H(B)}$ = 3.5 Hz, 1H, 1'-$H^2_{of\ enol}$)*, 4.17 (s, 1H, 8a-H), 5.96 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ enol}$), 6.07 (d, $J_{3,2}$ = 10.3 Hz, 1H, 3-$H_{of\ keto}$), 6.53 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ enol}$), 6.56 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ keto}$), 12.60 (s, 1H, 7-$OH_{of\ enol}$);*** assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 21.3 (C-5''')^A, 243.0 (C-5'''')^A, 25.8 (C-5'')^A, 28.3 (3 × *C*H_3)^A, 32.9 (C-5)^A, 34.0 (C-6)^A, 40.1 (C-5')^A, 44.4 (C-8a)^A, 52.0 (CO_2Me)^A, 62.6 (C-4a)^B, 64.7 (C-1")^{A,*}, 66.6 (C-1')^{A,*}, 81.3 (*C*$(CH_3)_3$)^B, 95.1 (C-8)^B, 104.9 (C-1)^B, 127.2 (C-3)^A, 146.1 (C-2)^A, 169.9 (C-4a')^B, 171.7 (C-8')^B, 175.8 (C-7)^B, 197.9 (C-4)^B; * assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distin-

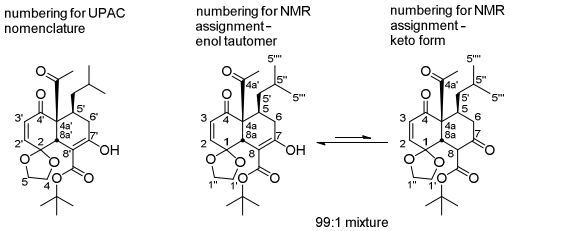
guished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 21.3 (C-5''') $\leftrightarrow$ δ_H = 0.74 (5'''-H_3); δ_C = 24.0 (C-5'''') $\leftrightarrow$ δ_H = 0.87 (5''''-H_3); δ_C = 25.8 (C-5'') $\leftrightarrow$ δ_H = 1.49 (5''-H); δ_C = 28.3 (3 × CH_3) $\leftrightarrow$ δ_H = 1.48 (3 × CH_3); δ_C = 32.9 (C-5) $\leftrightarrow$ δ_H = 2.71 (5-H); δ_C = 34.0 (C-6) $\leftrightarrow$ δ_H = 2.41 (6-H^A); δ_C = 34.0 (C-6) $\leftrightarrow$ δ_H = 2.60 (6-H^B); δ_C = 40.1 (C-5') $\leftrightarrow$ δ_H = 1.09 (5'-H^1); δ_C = 40.1 (C-5') $\leftrightarrow$ δ_H = 1.78 (5'-H^2); δ_C = 44.4 (C-8a) $\leftrightarrow$ δ_H = 4.17 (8a-H); δ_C = 52.0 (CO_2*Me*) $\leftrightarrow$ δ_H = 3.64 (CO_2*Me*); δ_C = 64.7 (C-1'') $\leftrightarrow$ δ_H = 3.86 (1''-H^A); δ_C = 64.7 (C-1'') $\leftrightarrow$ δ_H = 3.91 (1''-H^B); δ_C = 66.6 (C-1') $\leftrightarrow$ δ_H = 3.72 (1'-H^1); δ_C = 66.6 (C-1') $\leftrightarrow$ δ_H = 4.04 (1'-H^2); δ_C = 127.2 (C-3) $\leftrightarrow$ δ_H = 5.96 (3-H); δ_C = 146.1 (C-2) $\leftrightarrow$ δ_H = 6.53 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 62.6 (C-4a) $\leftrightarrow$ δ_H = 1.09 (5'-H^1), δ_H = 2.60 (6-H^B), δ_H = 4.17 (8a-H), δ_H = and 5.96 (3-H); δ_C = 81.3 ($C(CH_3)_3$) $\leftrightarrow$ δ_H = 1.48 (3 × CH_3); δ_C = 95.2 (C-8) $\leftrightarrow$ δ_H = 2.41 (6-H^A), δ_H = 2.60 (6-H^B), δ_H = 4.17 (8a-H), δ_H = 6.53 (2-H), and δ_H = 12.60 (7-OH); δ_C = 104.9 (C-1) $\leftrightarrow$ δ_H = 2.41 (6-H^A), δ_H = 3.72 (1'-H^1), δ_H = 3.86 (1''-H^A), δ_H = 3.91 (1''-H^B), δ_H = 4.04 (1'-H^2), δ_H = 4.17 (8a-H), δ_H = 5.96 (3-H), and δ_H = 6.53 (2-H); δ_C = 169.9 (C-4a') $\leftrightarrow$ δ_H = 2.71 (5-H), δ_H = 3.64 (CO_2*Me*), δ_H = 4.17 (8a-H), and δ_H = 5.96 (3-H); δ_C = 171.7 (C-8') $\leftrightarrow$ δ_H = 4.17 (8a-H); δ_C = 175.8 (C-7) $\leftrightarrow$ δ_H = 1.09 (5'-H^1), δ_H = 2.41 (6-H^A), δ_H = 2.60 (6-H^B), δ_H = 4.17 (8a-H), and δ_H = 12.60 (7-OH); δ_C = 197.9 (C-4) $\leftrightarrow$ δ_H = 2.71 (5-H), δ_H = 4.17 (8a-H), and δ_H = 6.53 (2-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^1H) \leftrightarrow \delta_H(^1H)$]: δ_H = 1.49 (5''-H) $\leftrightarrow$ δ_H = 0.74 (5'''-H_3), δ_H = 0.87 (5''''-H_3), and δ_H = 1.09 (5'-H^1); δ_H = 1.78 (5'-H^2) $\leftrightarrow$ δ_H = 1.09 (5'-H^1) and δ_H = 1.49 (5''-H); δ_H = 2.60 (6-H^B) $\leftrightarrow$ δ_H = 2.41 (6-H^A); δ_H = 2.71 (5-H) $\leftrightarrow$ δ_H = 1.09 (5'-H^1), δ_H = 1.78 (5'-H^2), δ_H = 2.41 (6-H^A), and δ_H = 2.60 (6-H^B); δ_H = 3.86 (1''-H^A) $\leftrightarrow$ δ_H = 3.72 (1'-H^1); δ_H = 3.91 (1''-H^B) $\leftrightarrow$ δ_H = 3.72 (1'-H^1); δ_H = 4.04 (1'-H^2) $\leftrightarrow$ δ_H = 3.72 (1'-H^1), δ_H = 3.86 (1''-H^A), and δ_H = 3.91 (1''-H^B); δ_H = 6.53 (2-H) $\leftrightarrow$ δ_H = 5.96 (3-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2950, 1745, 1680, 1640, 1400, 1370, 1300, 1230, 1160, 1100, 1065, 1020, 995, 975, 950 cm^{-1}. **Elemental analysis:** $C_{23}H_{32}O_8$ (436.50); Calcd: C 63.29%, H 7.39%; Found: C 63.15%, H 7.35%.

8'-(*tert*-Butyl) (4a'*R*,5'*S*,8a'*R*)-4a'-Acetyl-7'-hydroxy-5'-methyl-4'-oxo-4a',5',6',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-8'-carboxylate (*cis,syn*-6c)



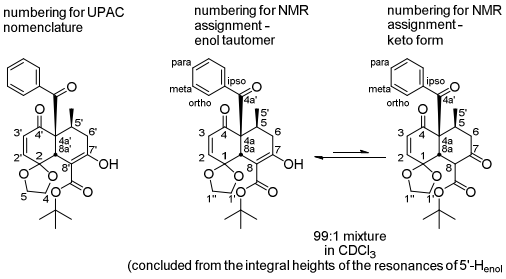
Cs_2CO_3 (85.9 mg, 264 µmol, 1.05 equiv.) was added to the solution of benzoquinone monoketal **5c** (48.4 mg, 249 µmol, 1.0 equiv.) and β-ketoester **2a** (48.4 mg, 263 µmol, 1.05 equiv.) in CH_2Cl_2 (4 mL) at 25°C in one portion. The reaction mixture was stirred at 25°C for 3.5 h and filtered through a pad of silica gel (2 cm × 1 cm). The pad was rinsed with EtOAc (20 mL). The solvent was evaporated and the redisu was purified by flash chromatography an silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 9:1 (v:v), 20 mL] to render the title compound (F5-22; 90.2 mg, 95%) as pale orange crystals. **Melting point:** 121-125°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 0.91 (d, $J_{5',5}$ = 6.8, 3H, 5'-$H_{3\ of\ keto}$), 1.04 (d, $J_{5',5}$ = 6.9 Hz, 3H, 5'-$H_{3\ of\ enol}$), 1.46 (s, 9H, 3 × 8''-$Me_{\ of\ keto}$), 1.49 (s, 9H, 3 × 8''-$Me_{\ of\ enol}$), 2.01 [s, 3H, C(=O)$Me_{of\ enol}$], 2.51 (m_c, 2H, 6-$H_{2\ of\ enol}$), 2.65-2.71 (m, 1H, 5-$H_{\ of\ enol}$), 3.74 (ddd, $J_{1'\text{-}H(1),1''\text{-}H(A)}$ = 8.1 Hz, J_{gem} = 7.4 Hz, $J_{1'\text{-}H(1),1''\text{-}H(B)}$ = 6.1 Hz, 1H, 1'-$H^1_{\ of\ enol}$)*, AB signal (δ_A = 3.89, δ_B = 3.93, J_{AB} = 8.1 Hz, A part additionally split by $J_{1''\text{-}H(A),1'\text{-}H(1)}$ = 8.1 Hz, $J_{1''\text{-}H(A),1'\text{-}H(2)}$ = 6.1 Hz, B part additionally split by $J_{1''\text{-}H(B),1'\text{-}H(1)}$ = 6.1 Hz, $J_{1''\text{-}H(B),1'\text{-}H(2)}$ = 3.5 Hz, 1''-$H_{2\ of\ enol}$)*, 4.03 (s, 1H, 8a-$H_{of\ enol}$) superimposed by 4.05 (ddd, J_{gem}= 7.4 Hz, $J_{1'\text{-}H(2),1''\text{-}H(A)}$ = 6.1 Hz, $J_{1'\text{-}H(1),1''\text{-}H(B)}$ = 3.4 Hz, 1H, 1'-$H^2_{of\ enol}$)*, 4.24 (m_c, 1H, 1'-$H_{2\ of\ keto}$)**, 4.37 (m_c, 1H, 1''-$H_{2\ of\ keto}$)**, 6.01 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ enol}$), 6.17 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ keto}$), 6.57 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ enol}$), 6.64 (d, $J_{2,3}$ = 10.1 Hz, 1H, 2-$H_{of\ keto}$), 12.49 (s, 1H, 7-$OH_{of\ enol}$); *·** assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 16.0 (C-5')^A, 27.3 [C(=O)*Me*]^A, 28.4 (3 × C-8''Me)^A, 30.5 (C-5)^A, 35.4 (C-6)^A, 43.5 (C-8a)^A, 64.7 (C-1'')*, ^{A}, 65.5 (C-4a)^B, 66.6 (C-1')*, ^{A}, 81.6 (C-8'')^B, 93.9 (C-8)^B, 104.8 (C-1)^B, 127.8 (C-3)^A, 146.3 (C-2)^A, 171.4 (C-7)^B, 176.9 (C-8')^B, 199.5 (C-4a')^B, 203.3 (C-4)^B; *assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 16.0 (C-5') $\leftrightarrow$ δ_H = 1.04 (5'-H_3); δ_C = 27.3 [C(=O)*Me*] $\leftrightarrow$ δ_H = 2.01 [C(=O)*Me*]; δ_C = 28.4 (3 × C-8''-Me) $\leftrightarrow$ δ_H = 1.49 (3 × 8''-Me); δ_C = 30.5 (C-5) $\leftrightarrow$ δ_H = 2.68 (5-H); δ_C = 35.4 (C-6) $\leftrightarrow$ δ_H = 2.51 (6-H_2); δ_C = 43.5 (C-8a) $\leftrightarrow$ δ_H = 4.03 (8a-H); δ_C = 64.7 (C-1'') $\leftrightarrow$ δ_H = 3.91 (1''-H_2); δ_C = 66.6 (C-1') $\leftrightarrow$ δ_H = 3.74 (1'-H^1); δ_C = 66.6 (C-1') $\leftrightarrow$ δ_H = 4.04 (1'-H^2); δ_C = 127.8 (C-3) $\leftrightarrow$ δ_H = 6.01 (3-H); δ_C = 146.3 (C-2) $\leftrightarrow$ δ_H = 6.57 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 65.5 (C-4a) $\leftrightarrow$ δ_H = 1.04 (5'-H_3), δ_H = 2.01 [C(=O)*Me*], δ_H = 4.03 (8a-H), and δ_H = 6.01 (3-H); δ_C = 81.6 (C-8'') $\leftrightarrow$ δ_H = 1.49 (8'''-H_9); δ_C = 93.9 (C-8) $\leftrightarrow$ δ_H = 2.51 (6-H_2) and δ_H = 4.03 (8a-H); δ_C = 104.8 (C-1) $\leftrightarrow$ δ_H = 4.03 (8a-H) and δ_H = 6.01 (3-H); δ_C = 171.4 (C-7) $\leftrightarrow$ δ_H = 4.03 (8a-H); δ_C = 176.9 (C-8') $\leftrightarrow$ δ_H = 2.51 (6-H_2) and δ_H = 4.03 (8a-H); δ_C = 199.5 (C-4a') $\leftrightarrow$ δ_H = 6.57 (2-H); δ_C = 203.3 (C-4) $\leftrightarrow$ δ_H = 2.01 [C(=O)*Me*], δ_H = 1.04 (5'-H_3), and δ_H = 4.03 (8a-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2920, 2850, 1720, 1675, 1640, 1460, 1365, 1295, 1230, 1145, 1090, 1035, 1005, cm^{-1}. **Elemental analysis:** $C_{20}H_{26}O_7$ (378.4); Calcd: C: 63.48%, H: 6.93%; Found: C: 63.10%, H: 7.13%. **HRMS** (pos. APCI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{26}O_7Na$, 401.1576; found, 401.1577.

8'-(*tert*-Butyl) (4a'*R*,5'*S*,8a'*R*)-4a'-Acetyl-7'-hydroxy-5'-isobutyl-4'-oxo-4a',5',6',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-8'-carboxylate (*cis,syn*-6d)



Cs_2CO_3 (282 mg, 0.87 mmol, 1.05 equiv.) was added to a solution of benzoquinone monoketal **5c** (160 mg, 0.82 mmol, 1.0 equiv.) and β-ketoester **2b** (242 mg, 1.07 mmol, 1.3 equiv.) in CH_2Cl_2 (16 mL) in one portion at 25°C. The reaction mixture was stirred at 25°C for 2 h and filtered through a pad of celite® (2 cm × 1 cm). The pad was rinsed with EtOAC (40 mL). The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm x 15 cm, *c*C_6H_{12}:EtOAC 10:1 to 1:1 (v:v), 20 mL] to render the title compound (F7-21; 260 mg, 75%) as colorless solid. **Melting point**: 134-136°C. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 0.72 (d, $J_{5'''',5''}$ = 6.5 Hz, 3H, 5''''-$H_{3\ of\ enol}$), 0.85 (d, $J_{5'''',5''}$ = 6.5 Hz, 3H, 5''''-$H_{3\ of\ enol}$), 0.94-1.00 (m, 1H, 5'-$H^1_{of\ enol}$), 1.40-1.52 (m, 1H, 5''-$H_{of\ enol}$), 1.49 (s, 9H, 3 x 8''-*Me* $_{of\ enol}$), 1.73-1.79 (m, 1H, 5'-$H^2_{of\ enol}$), 2.01 (s, 3H, 4a'-*Me* $_{of\ enol}$), 2.04 (s, 3H, 4a'-*Me* $_{of\ keto}$), 2.39-2.46 (m, 6-$H^1_{of\ enol}$), 2.54-2.64 (m, 3H, 5-H and 6-$H^2_{of\ enol}$), 3.70-3.74 (m, 1'-$H^1_{of\ enol}$)*, 3.85-3.94 (m, 2H, 1''-$H_{2\ of\ enol}$)*, 4.02 (s, 1H, 8a'-$H_{of\ enol}$), 4.04-4.08 (m, 1H, 1'-$H^2_{of\ enol}$)*, 5.99 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-H $_{of\ enol}$), 6.12 (d, $J_{3,2}$ = 10.3 Hz, 1H, 3-H $_{of\ keto}$), 6.56 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-H $_{of\ enol}$), 6.63 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-H $_{of\ keto}$), 12.49 (s, 1H, OH $_{of\ enol}$); *: assignment interchangeable. **^{13}C NMR** (125.8 MHz, $CDCl_3$): δ = 21.2 (C-5''')^A, 23.9 (C-5'''')^A, 25.9 (C-5'')^A, 27.2 (C-4a'-*Me*)^A, 28.4 (C-8''-*Me*)^A, 33.3 (C-5)^A, 34.0 (C-6)^A, 39.9 (C-5')^A, 43.6 (C-8a)^A, 64.7 (C-1')^{A,*}, 66.2 (C-4a)^B, 66.7 (C-1'')^{A,*}, 81.6 (C-8'')^B, 93.9 (C-8)^B, 104.8 (C-1)^B, 127.7 (C-3)^A, 146.2 (C-2)^A, 171.4 (C-8')^B, 177.1 (C-7)^B, 199.9 (C-4)^B, 203.7 (C-4a')^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons; * assignment interchangeable. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 21.2 (C-5''') ↔ δ_H = 0.72 (5'''-H_3); δ_C = 23.9 (C-5'''') ↔ δ_H = 0.85 (5''''-H_3); δ_C = 25.9 (C-5'') ↔ δ_H = 1.45 (5''-H); δ_C = 27.2 (C-4a'-*Me*) ↔ δ_H = 2.01 (4a'-*Me*); δ_C = 28.4 (C-8''-*Me*) ↔ δ_H = 1.49 (3 x 8''-*Me*); δ_C = 33.3 (C-5) ↔ δ_H = 2.61 (5-H); δ_C = 34.0 (C-6) ↔ δ_H = 2.43 (6-H^1); δ_C = 34.0 (C-6) ↔ δ_H = 2.57 (6-H^2); δ_C = 39.9 (C-5') ↔ δ_H = 0.95 (5'-H^1); δ_C = 39.9 (C-5') ↔ δ_H = 1.76 (5'-H^2); δ_C = 43.6 (C-8a) ↔ δ_H = 4.02 (8a-H); δ_C = 64.6 (C-1') ↔ δ_H = 3.72 (1'-H^1); δ_C = 64.6 (C-1') ↔ δ_H = 4.06 (1'-H^2); δ_C = 66.7 (C-1'') ↔ δ_H = 3.90 (1''-H_2); δ_C = 127.7 (C-3) ↔ δ_H = 5.99 (3-H); δ_C = 146.2 (C-2) ↔ δ_H = 6.56 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 66.2 (C-4a) ↔ δ_H = 0.95 (5'-H^1), δ_H = 1.76 (5'-H^2), δ_H = 1.76 (5'-H^2), δ_H = 2.01 (4a'-*Me*), δ_H = 2.43 (6-H^1), δ_H = 2.57 (6-H^2), δ_H = 2.61 (5-H), δ_H = 4.02 (8a-H), δ_H = 5.99 (3-H), and δ_H = 6.56 (2-H); δ_C = 81.6 (C-8'') ↔ δ_H = 1.49 (3 x 8''-*Me*); δ_C = 93.9 (C-8) ↔ δ_H = 2.43 (6-H^1), δ_H = 2.57 (6-H^2), δ_H = 4.02 (8a-H), δ_H = 6.56 (2-H), and δ_H = 12.49 (OH); δ_C = 104.8 (C-1) ↔ δ_H = 2.43 (6-H^1), δ_H = 2.57 (6-H^2), δ_H = 3.72 (1'-H^1), δ_H = 3.90 (1''-H_2), δ_H = 4.06 (1'-H^2), δ_H = 4.02 (8a-H), δ_H = 5.99 (3-H), and δ_H = 6.56 (2-H); δ_C = 171.4 (C-8') ↔ δ_H = 2.57 (6-H^2) and δ_H = 4.02 (8a-H); δ_C = 177.1 (C-7) ↔ δ_H = 0.95 (5'-H^1), δ_H = 2.43 (6-H^1), δ_H = 2.57 (6-H^2), δ_H = 2.61 (5-H), δ_H = 4.02 (8a-H), and δ_H = 12.49 (OH); δ_C = 199.9 (C-4) ↔ δ_H = 2.61 (5-H), δ_H = 4.02 (8a-H), δ_H = 5.99 (3-H), and δ_H = 6.56 (2-H); δ_C = 203.7 (C-4a') ↔ δ_H = 2.43 (6-H^1), δ_H = 2.57 (6-H^2), δ_H = 2.61 (5-H), δ_H = 4.02 (8a-H), and δ_H = 5.99 (3-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [$\delta_H(^1H) \leftrightarrow \delta_H(^1H)$]: δ_H = 1.45 (5''-H) ↔ δ_H = 0.72 (5'''-H_3); δ_H = 1.45 (5''-H) ↔ δ_H = 0.85 (5''''-H_3); δ_H = 1.45 (5''-H) ↔ δ_H = 1.76 (5'-H^2); δ_H = 1.76 (5'-H^2) ↔ δ_H = 0.95 (5'-H^1); δ_H = 1.76 (5'-H^2) ↔ δ_H = 1.45 (5''-H); δ_H = 2.57 (6-H^2) ↔ δ_H = 2.43 (6-H^1); δ_H = 2.61 (5-H) ↔ δ_H = 0.95 (5'-H^1); δ_H = 2.61 (5-H) ↔ δ_H = 1.76 (5'-H^2); δ_H = 2.61 (5-H) ↔ δ_H = 2.43 (6-H^1); δ_H = 3.90 (1''-H_2) ↔ δ_H = 3.72 (1'-H^1); δ_H = 4.06 (1'-H^2) ↔ δ_H = 3.72 (1'-H^1); δ_H = 4.06 (1'-H^2) ↔ δ_H = 3.90 (1''-H_2); δ_H = 6.56 (2-H) ↔ δ_H = 5.99 (3-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2955, 1720, 1675, 1645, 1300, 1220, 1155, 1100, 1030, 975, 950 cm^{-1}. **Elemental analysis:** $C_{23}H_{32}O_7$ (420.50); Calcd: C 65.70%, H 7.67%; Found: C 65.60%, H 7.51%. **HRMS** (neg. APCI) m/z: $[M - H]^-$ calcd for $C_{23}H_{31}O_7$, 419.2075, found, 419.2077.

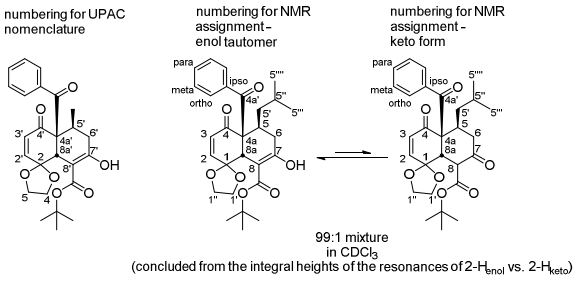
8'-(*tert*-Butyl) (4a'*S*,5'*S*,8a'*R*)-4a'-Benzoyl-7'-hydroxy-5'-methyl-4'-oxo-4a',5',6',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-8'-carboxylate (*cis,syn*-6e)



Cs_2CO_3 (85.6 mg, 263 μmol, 1.05 equiv.) was added to a solution of benzoquinone monoketal **5d** (64.1 mg, 250 μmol, 1.0 equiv.) and β-ketoester **2a** (48.4 mg, 263 μmol, 1.05 equiv.) in CH_2Cl_2 (4 mL) at 25°C in one portion. The reaction mixture was stirred at 25°C for 3.5 h and filtered through a pad of celite® (2 cm × 1 cm). The pad was rinsed with EtOAc (20 mL). The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAC 8:1 to 4:1 (v:v), 20 mL] to render the title compound (F9-20; 78.1 mg, 71%) as colorless needles. **Melting point:** 130-134°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 1.10 (s, 9H, 3 × 8''-$Me_{\ of\ enol}$), 1.20 (d, $J_{5',5}$ = 6.7, 3H, 5'-$H_{3\ of\ enol}$), 1.67 (s, 9H, 3 × 8''-$Me_{\ of\ keto}$), 1.80 (d, $J_{5',5}$ = 7.3 Hz, 3H, 5'-$H_{3\ of\ keto}$), AB signal (δ_A = 2.58, δ_B = 2.63, J_{AB} = 18.8 Hz, A part additionally split by $J_{6\text{-}H(A),5}$ = 8.1 Hz, B part additionally split by $J_{6\text{-}H(B),5}$ = 9.1 Hz, 6-$H_{2\ of\ enol}$), 2.82 (ddq, $J_{5,6\text{-}H(B)}$ = 9.2 Hz, $J_{5,6\text{-}H(A)}$ = 8.3 Hz, $J_{5,5'}$ = 7.0, 1H, 5-$H_{of\ enol}$), 3.72 (ddd, $J_{1'\text{-}H(1),1''\text{-}H(B)}$ = 8.1 Hz, J_{gem} = 7.4 Hz, $J_{1'\text{-}H(1),1''\text{-}H(A)}$ = 5.9 Hz, 1H, 1'-$H^1_{of\ enol}$)*, AB-Signal (δ_A = 3.85, δ_B = 3.87, A part additionally split by $J_{1''\text{-}H(A),1'\text{-}H(1)}$ = 5.8 Hz, $J_{1''\text{-}H(A),1'\text{-}H(2)}$ = 4.0 Hz, B part additionally split by $J_{1''\text{-}H(B),1'\text{-}H(1)}$ = 8.1 Hz, $J_{1''\text{-}H(B),1'\text{-}H(2)}$ = 5.5 Hz, 2H, 1'-$H_{2\ of\ enol}$)*, 4.04 (ddd, J_{gem} = 7.4 Hz, $J_{1'\text{-}H(2),1''\text{-}H(B)}$ = 5.7 Hz, $J_{1'\text{-}H(2),1''\text{-}H(A)}$ = 4.2 Hz, 1H, 1'-$H^2_{\ of\ enol}$)*, 4.23 (s, 1H, 4a-$H_{of\ enol}$), 6.18 (d, $J_{3,2}$ = 10.3 Hz, 1H, 3-$H_{of\ enol}$), 6.66 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ enol}$), 6.72 (d, $J_{2,3}$ = 10.5 Hz, 1H, 2-$H_{of\ keto}$), 7.32 (m, 2H, 2 × meta-$H_{of\ enol}$), 7.46 (m, 1H, para-$H_{of\ enol}$), 7.50-7.53 (m, 2H, 2 × ortho-$H_{of\ enol}$), 12.60 (s, 1H, 7-$OH_{of\ enol}$); *assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 16.3 (C-5')^A, 27.9 (3 × C-8''-Me)^A, 31.8 (C-5)^A, 35.5 (C-6)^A, 44.8

(C-8a)[A], 63.9 (C-4a)[B], 64.7 (C-1')*, [A], 66.6 (C-1")*, [A], 80.9 (C-8")[B], 93.9 (C-8)[B], 104.8 (C-1)[B], 127.9 (C-3)[A], 128.3 (2 × C-meta)[A], 128.9 (2 × C-ortho)[A], 131.8 (C-para)[A], 136.4 (C-ipso)[B], 147.0 (C-2)[A], 171.3 (C-7)[B], 176.8 (C-8')[B], 197.6 (C-4a')[B], 199.4 (C-4)[B]; *assignment interchangeable; [A] the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; [B] the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^{2}J, ^{3}J and/or ^{4}J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^{1}H)$]: δ_C = 16.3 (C-5') ↔ δ_H = 1.2 (5'-H_3); δ_C = 27.9 (3 × C-8"-Me) ↔ δ_H = 1.10 (3 × 8"-Me); δ_C = 31.8 (C-5) ↔ δ_H = 2.86 (5-H); δ_C = 35.5 (C-6) ↔ δ_H = 2.60 (6-H_2); δ_C = 44.8 (C-8a) ↔ δ_H = 4.23 (8a-H); δ_C = 64.7 (C-1") ↔ δ_H = 3.86 (1"-H_2); δ_C = 66.6 (C-1') ↔ δ_H = 3.73 (1'-H^A); δ_C = 66.6 (C-1') ↔ δ_H = 4.04 (1'-H^B); δ_C = 127.9 (C-3) ↔ δ_H = 6.18 (3-H); δ_C = 128.3 (2 × C-meta) ↔ δ_H = 7.34 (2 × meta-H); δ_C = 128.9 (2 × C-ortho) ↔ δ_H = 7.52 (2 × ortho-H); δ_C = 131.8 (C-para) ↔ δ_H = 7.46 (para-H); δ_C = 147.0 (C-2) ↔ δ_H = 6.66 (2-H); *assignment interchangeable. **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^{1}H)$]: δ_C = 63.9 (C-4a) ↔ δ_H = 1.20 (5'-H_3), δ_H = 2.60 (6-H_2), δ_H = 4.23 (8a-H), and δ_H = 6.18 (3-H); δ_C = 80.9 (C-8") ↔ δ_H = 1.10 (3 × 8"-Me); δ_C = 93.9 (C-8) ↔ δ_H = 1.10 (3 × 8"-Me), δ_H = 2.60 (6-H_2), δ_H = 4.23 (8a-H), δ_H = 12.60 (7-OH), and δ_H = 1.10 (3 × 8"-Me); δ_C = 104.8 (C-1) ↔ δ_H = 4.23 (8a-H) and δ_H = 6.18 (3-H); δ_C = 136.4 (C-ipso) ↔ δ_H = 7.34 (2 × meta-H); δ_C = 171.3 (C-7) ↔ δ_H = 4.23 (8a-H); δ_C = 176.8 (C-8') ↔ δ_H = 2.60 (6-H_2), δ_H = 4.23 (8a-H), and δ_H = 12.60 (7-OH); δ_C = 197.6 (C-4a') ↔ δ_H = 7.52 (2 × ortho-H) and δ_H = 4.23 (8a-H); δ_C = 199.4 (C-4) ↔ δ_H = 4.23 (8a-H) and δ_H = 6.66 (2-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^{1}H) \leftrightarrow \delta_H(^{1}H)$]: δ_H = 2.86 (5-H) ↔ δ_H = 2.60 (6-H_2) and δ_H = 1.20 (5'-H_3); δ_H =3.90 (1"-H_2) ↔ δ_H = 3.73 (1'-H^A); δ_H =4.04 (1'-H^B) ↔ δ_H = 3.73 (1'-H^A), δ_H = 3.90 (1"-H_2); δ_H =6.66 (2-H) ↔ δ_H = 6.18 (3-H); δ_H =7.46 (para-H) ↔ δ_H = 7.34 (meta-H); δ_H =7.52 (ortho-H) ↔ δ_H =7.34 (meta-H). **IR** ($CDCl_3$): $\tilde{\nu}$ = 2980, 1690, 1670, 1640, 1300, 1230, 1160, 1090, 1050, 990, 950 cm^{-1}. **HRMS** (pos. APCI) m/z: [M + Na]$^+$ calcd for $C_{25}H_{28}O_7Na$, 463.1733; found, 463.1734.

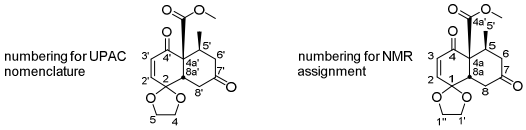
8'-(*tert*-Butyl) (4a'*S*,5'*S*,8a'*R*)-4a'-Benzoyl-7'-hydroxy-5'-isobutyl-4'-oxo-4a',5',6',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-8'-carboxylate (*cis,syn*-6f)



Cs_2CO_3 (56.5 mg, 173 μmol, 1.05 equiv.) was added to a solution of benzoquinone monoketal **5d** (42.3 mg, 165 μmol, 1 equiv.) and β-ketoester **2b** (36.8 mg, 173 μmol, 1.05 equiv.) in CH_2Cl_2 (6 mL) at 25°C in one portion. The reaction mixture was stirred at 25°C for 22 h and filtered through a pad of celite® (2 cm × 1 cm). The pad was rinsed with EtOAC (15 mL). The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 16 cm, *c*C_6H_{12}:EtOAC 3:1 (v:v), 9 mL] to render the title compound (F5-22; 55.1 mg, 71%) as colorless solid. **Melting Point**: 115-118°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 0.77 (d, $J_{5''',5''}$ = 6.5 Hz, 3H, 5'''-$H_{3\ of\ enol}$)*, 0.90 (d, $J_{5'''',5''}$ = 6.6 Hz, 3H, 5''''-$H_{3\ of\ enol}$)*, 1.10 (s, 9H, *t*Bu-$H_{9\ of\ enol}$), 1.19 (ddd, $J_{5'\text{-}H',5'\text{-}H(2)}$ = 14.2 Hz, $J_{5'\text{-}H(1),5''\text{-}H}$ = 9.8 Hz, $J_{5'\text{-}H(1),5\text{-}H}$ = 2.9 Hz, 1H, 5'-$H^1_{of\ enol}$), 1.50-1.58 (m, 1H, 5"-$H_{of\ enol}$), 1.67 (s, 9H, *t*Bu-$H_{9\ of\ keto}$), 1.95 (ddd, $J_{5'\text{-}H(2),5'\text{-}H(1)}$ = 14.2 Hz, $J_{5'\text{-}H(2),5''\text{-}H}$ = 9.8 Hz, $J_{5'\text{-}H(2),5\text{-}H}$ = 4.4 Hz, 1H, 5'-$H^2_{of\ enol}$), AB-Signal (δ_A = 2.53 Hz, δ_B = 2.65 Hz, J_{AB} = 18.7 Hz additionally split by $J_{6\text{-}H(A),5\text{-}H}$ = 9.6 Hz, $J_{6\text{-}H(B),5\text{-}H}$ = 7.7 Hz, 2H, 6-$H_{2\ of\ enol}$), 2.74 (ddd, $J_{5\text{-}H,6\text{-}H(A)}$ = 9.7 Hz, $J_{5,6\text{-}H(B)}$ = 7.6 Hz, $^4J_{5,5'\text{-}H(1)}$ = 2.8 Hz, 1H, 5-$H_{of\ enol}$), 3.68-3.74 (m, 1H, 1'-$H^1_{of\ enol}$)**, 3.82-3.89 (m, 2H, 1"-$H_{2\ of\ enol}$)**, 4.03-4.07 (m, 1H, 1'-$H^2_{of\ enol}$)*, 4.22 (s, 1H, 8a-$H_{of\ enol}$), 6.10 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ keto}$), 6.15 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-$H_{of\ enol}$), 6.57 (d, $J_{2,3}$ = 9.0 Hz, 1H, 2-$H_{of\ keto}$), 6.66 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-$H_{of\ enol}$), 7.32-7.36 (m, 2H, meta-$H_{2\ of\ enol}$), 7.43-7.47 (m, 1H, para-H), 7.50-7.52 (m, 2H, ortho-$H_{2\ of\ enol}$), 12.60 (s, 1H, 7-OH); *, **, assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 21.4 (C-5''')[A,*], 23.9 (C-5'''')[A,*], 26.2 (C-5")[A], 27.8 (3 × C-8"-Me)[A], 34.2 (C-6)[A], 34.7 (C-5)[A], 40.2 (C-5')[A], 44.9 (C-8a)[A], 64.7 (C-1")[A,**], 64.8 (C-4a)[B], 66.7 (C-1')[A,**], 80.9 (C-8")[B], 93.9 (C-8)[B], 104.9 (C-1)[B], 127.8 (C-3)[A], 128.3 (C-meta)[A], 128.9 (C-ortho)[A], 131.8 (C-para)[A], 136.5 (C-ipso)[B], 147.0 (C-2)[A], 171.2 (C-7)[B], 177.0 (C-8')[B], 197.9 (C-4a')[B], 199.9 (C-4)[B]; [A] the indicated ^{13}C nuclei – they are non-quaternary – were indicated in an edHSQC spectrum by their crosspeaks with directly bonded protons; [B] the indicated ^{13}C nuclei are quaternary and were distinguished in a HMBC spectrum by their crosspeaks due to ^{2}J, ^{3}J and/or ^{4}J couplings to "remote" protons;*, ** assignment interchangeable. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^{1}H)$]: δ_C = 21.4 (C-5''') ↔ δ_H = 0.77 (5'''-H_3); δ_C = 23.9 (C-5'''') ↔ δ_H = 0.90 (5''''-H_3); δ_C = 26.2 (C-5") ↔ δ_H = 1.54 (5"-H); δ_C = 27.8 (3 × C-8"-Me) ↔ δ_H = 1.10 (3 × 8"-Me); δ_C = 34.2 (C-6) ↔ δ_H = 2.53 (6-H^A); δ_C = 34.2 (C-6) ↔ δ_H = 2.65 (6-H^B); δ_C = 34.7 (C-5) ↔ δ_H = 2.74 (5-H); δ_C = 40.2 (C-5') ↔ δ_H = 1.19(5'-H^1); δ_C = 40.2 (C-5') ↔ δ_H = 1.95 (5'-H^2); δ_C = 44.9 (C-8a) ↔ δ_H = 4.22 (8a-H); δ_C = 64.7 (C-1") ↔ δ_H = 3.85 (1"-H_2); δ_C = 66.7 (C-1') ↔ δ_H = 3.71 1'-H^1); δ_C = 66.7 (C-1') ↔ δ_H = 4.05 (1'-H^2); δ_C = 127.8 (C-3) ↔ δ_H = 6.15 (3-H); δ_C = 128.3 (C-meta) ↔ δ_H = 7.34 (meta-H); δ_C = 128.9 (C-ortho) ↔ δ_H = 7.51 (ortho-H); δ_C = 131.8 (C-para) ↔ δ_H = 7.45 (para-H); δ_C = 147.0 (C-2) ↔ δ_H = 6.66 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^{1}H)$]: δ_C = 64.8 (C-4a) ↔ δ_H = 1.95 (5'-H^2), δ_H = 2.65 (6-H^B), δ_H = 4.22 (8a-H), and δ_H = 6.15 (3-H); δ_C = 80.9 (C-8") ↔ δ_H = 1.10 (3 × 8"-Me); δ_C = 93.9 (C-8) ↔ δ_H = 2.53 (6-H^A), δ_H = 2.65 (6-H^B), δ_H = 4.22 (8a-H), δ_H = 6.66 (2-H), and δ_H = 12.60 (7-OH); δ_C = 104.9 (C-1) ↔ δ_H = 2.53 (6-H^A), δ_H = 3.71 (1'-H^1), δ_H = 4.05 (1'-H^2), δ_H = 4.22 (8a-H), δ_H = 6.15 (3-H), and δ_H = 6.66 (2-H); δ_C = 136.5 (C-ipso) ↔ δ_H = 7.34 (meta-H); δ_C = 171.2 (C-7) ↔ δ_H = 4.22 (8a-H); δ_C = 177.0 (C-8') ↔ δ_H = 2.53 (6-H^A), δ_H = 2.65 (6-H^B), δ_H = 4.22 (8a-H), and δ_H = 12.60 (7-OH); δ_C = 197.9 (C-4a') ↔ δ_H = 4.22 (8a-H) and δ_H = 7.51 (ortho-H); δ_C = 199.9 (C-4) ↔ δ_H = 4.22 (8a-H) and δ_H = 6.66 (2-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^{1}H) \leftrightarrow \delta_H(^{1}H)$]: δ_H = 0.77 (5'''-H_3) ↔ δ_H = 1.54 (5"-H); δ_H = 0.90 (5''''-H_3) ↔ δ_H = 1.54 (5"-H); δ_H = 1.19 (5'-H^1) ↔ δ_H = 1.54 (5"-H) and δ_H = 1.95 (5'-H^2); δ_H = 1.95 (5'-H^2) ↔ δ_H = 2.74 (5-H); δ_H = 2.53 (6-H^A) ↔ δ_H = 2.65 (6-H^B) and δ_H = 2.74 (5-H); δ_H = 2.65 (6-H^B) ↔ δ_H = 2.74 (5-H); δ_H = 6.15 (3-H) ↔ δ_H = 6.66 (2-H); δ_H = 7.34 (meta-H) ↔ δ_H = 7.45 (para-H) and δ_H = 7.51 (ortho-H). **IR**: (CH_2Cl_2)**:** $\tilde{\nu}$ = 2445, 1690,

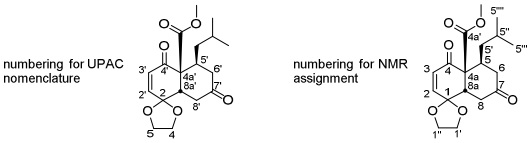
1670, 1640, 1300, 1250, 1230, 1155, 1090, 1025, 985, 950 cm^{-1}. **HRMS** (pos. APCI) m/z: $[M + Na]^+$ calcd for $C_{28}H_{34}O_7Na$, 505.2202; found, 505.2205.

Methyl (4a'*S*,5'*S*,8a'*S*)-5'-Methyl-4',7'-dioxo-6',7',8',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4a'(5'*H*)-carboxylate (*cis,syn*-7a)



At 0°C F_3CCO_2H (1 mL) was added dropwise to the solution of Deslongchamps adduct *cis,syn*-**6a** (40.6 mg, 103 µmol, 1 equiv.) in CH_2Cl_2 (4 mL) within 5 min and stirring was continued at 0°C for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 4 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (4 mL) and stirred at room temp. for 8 d. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 1:1 (v:v), 20 mL] to render the title compound (F36-50; 22.8 mg, 75%) as colorless solid. **Melting point:** 87-94°C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 1.12 (d, $J_{5',5}$ = 6.6 Hz, 3H, 5'-H_3), 2.04 (dd, $J_{8\text{-}H(1),8\text{-}H(2)}$ = 16.4 Hz, $J_{8\text{-}H(1),8a}$ = 5.9 Hz, 1H, 8-H^1), 2.44 (ddd, $J_{6\text{-}H(1),6\text{-}H(2)}$ = 15.2 Hz, $J_{6\text{-}H(1),5}$ = 4.1 Hz, $J_{6\text{-}H(1),8\text{-}H(2)}$ = 1.9 Hz, 1H, 6-H^1), 2.53 (ddd, $J_{8\text{-}H(2),8\text{-}H(1)}$ = 16.4 Hz, $J_{8\text{-}H(2),6\text{-}H(1)}$ = $J_{8\text{-}H(2),\ 8a}$ = 2.3 Hz, 1H, 8-H^2), 2.71-2.78 (m, 1H, 6-H^2), 2.77-2.85 (m, 1H, 5-H), 3.41 (dd, $J_{8a,8\text{-}H(1)}$ = 5.8 Hz, $J_{8a,8\text{-}H(2)}$ = 2.6 Hz, 1H, 8a-H), 3.77 (s, 3H, CO_2*Me*), 3.82-3.89 (m, 1H, 1'-H^1)*, 3.95-4.03 (m, 2H, 1'-H^2 and 1"-H^1)*, 4.15-4.20 (m, 1H, 1"-H^2)*, 6.01 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-H), 6.54 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-H);* assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 16.4 (C-5')^A, 33.6 (C-5)^A, 37.5 (C-8)^A, 45.5 (C-6)^A, 46.5 (C-8a)^A, 52.5 (CO_2*Me*)^A, 61.6 (C-4a)^B, 64.8 (C-1")^{A,}*, 65.9 (C-1')^{A,}*, 104.3 (C-1)^B, 127.5 (C-3)^A, 143.7 (C-2)^A, 170.1 (*C*O_2Me)^B, 196.1 (C-4)^B, 207.2 (C-7)^B; * assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 16.4 (C-5') ↔ δ_H = 1.12 (5'-H_3); δ_C = 33.6 (C-5) ↔ δ_H = 2.81 (5-H); δ_C = 37.5 (C-8) ↔ δ_H = 2.04 (8-H^1); δ_C = 37.5 (C-8) ↔ δ_H = 2.53 (8-H^2); δ_C = 45.5 (C-6) ↔ δ_H = 2.44 (6-H^1); δ_C = 45.5 (C-6) ↔ δ_H = 2.74 (6-H^2); δ_C = 46.5 (C-8a) ↔ δ_H = 3.41 (8a-H); δ_C = 52.5 (CO_2*Me*) ↔ δ_H = 3.77 (CO_2*Me*), δ_C = 64.8 (C-1") ↔ δ_H = 3.99 (1"-H^1); δ_C = 64.8 (C-1") ↔ δ_H = 4.19 (1"-H^2); δ_C = 65.9 (C-1') ↔ δ_H = 2.85 (1'-H^1); δ_C = 65.9 (C-1') ↔ δ_H = 3.99 (1'-H^2); δ_C = 127.5 (C-3) ↔ δ_H = 6.01 (3-H); δ_C = 143.7 (C-2) ↔ δ_H = 6.54 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 104.3 (C-1) ↔ δ_H = 2.04 (8-H^1), δ_H = 3.41 (8a-H), δ_H = 3.99 (1"-H^1), δ_H = 3.99 (1'-H^2), δ_H = 4.19 (1"-H^2), and δ_H = 6.01 (3-H); δ_C = 170.1 (*C*O_2Me) ↔ δ_H = 2.81 (5-H), δ_H = 3.41 (8a-H), and δ_H = 3.77 (CO_2*Me*); δ_C = 196.1 (C-4) ↔ δ_H = 2.53 (8-H^2) and δ_H = 6.54 (2-H); δ_C = 207.2 (C-7) ↔ δ_H = 2.04 (8-H^1), δ_H = 2.53 (8-H^2), δ_H = 2.81 (5-H), δ_H = 3.41 (8a-H), and δ_H = 3.77 (CO_2*Me*). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^1H) \leftrightarrow \delta_H(^1H)$]: δ_H = 2.53 (8-H^2) ↔ δ_H = 2.04 (8-H^1); δ_H = 2.74 (6-H^2) ↔ δ_H = 2.44 (6-H^1); δ_H = 2.81 (5-H) ↔ δ_H = 1.12 (5'-H_3), δ_H = 2.44 (6-H^1), and δ_H = 2.74 (6-H^2); δ_H = 3.41 (8a-H) ↔ δ_H = 2.04 (8-H^1) and δ_H = 2.53 (8-H^2); δ_H = 4.19 (1"-H^2) ↔ δ_H = 2.85 (1'-H^1); δ_H = 6.54 (2-H) ↔ δ_H = 6.01 (3-H). **IR** (Film): υ = 2935, 1730, 1695, 1680, 1520, 1245, 1185, 1120, 1055, 1020, 940, 915 cm^{-1}. **HRMS** (pos. APCI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{18}O_6Na$, 317.0996; found, 317.0997.

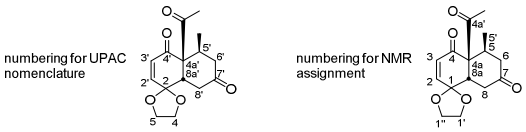
Methyl (4a'S,5'S,8a'S)-5'-isobutyl-4',7'-dioxo-6',7',8',8a'-tetrahydro-4'H-spiro(naphthalene-2,1'-[1,3]dioxolane)-4a'(5'H)-carboxylate (*cis,syn*-7b)



At 0°C F_3CCO_2H (1 mL) was added dropwise to a solution of the Deslongchamps adduct *cis,syn*-**6b** (45.0 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) within 5 min. The mixture was stirred at 0°C for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 4 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (4 mL) and stirred at room temp. for 8 d. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 1:1 (v:v), 20 mL] to render the title compound (F30-38; 25.9 mg, 75%) as colorles oil. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 0.70 (d, $J_{5''',5''}$ = 6.4 Hz, 3H, 5'''-H_3), 0.85 (d, $J_{5'''',5''}$ = 6.6 Hz, 3H, 5''''-H_3), 1.22 (ddd, $J_{5'\text{-}H(1),5'\text{-}H(2)}$ = 14.2 Hz, $J_{5'\text{-}(1),6}$ = 9.9 Hz, $J_{5'\text{-}H(1),5}$ = 2.3 Hz, 1H, 5'-H^1), 1.39-1.50 (m, 1H, 5"-H), 1.67 (ddd, $J_{5'\text{-}H(2),5'\text{-}H(1)}$ = 14.2 Hz, $J_{5'\text{-}H(2),5}$ = 9.0 Hz, $J_{5'\text{-}H(2),5'}$ = 4.3 Hz, 1H, 5'-H^2), 2.01 (dd, $J_{8\text{-}H(1),8\text{-}H(2)}$ = 16.4 Hz, $J_{8\text{-}H(1),8a}$ = 5.8 Hz, 1H, 8-H^1), 2.54 [ddd, $J_{8\text{-}H(2),8\text{-}H(1)}$ = 16.6 Hz, $J_{8\text{-}H(2),8a}$ = 2.4 Hz, $^4J_{8\text{-}H(2),6}$ = 1.4 Hz (the existence of this 4-bond W-coupling indicates an equatorial position of this 8-H), 1H, 8-H^2], 2.58 (m, 2H, 6-H_2), 2.67 (dddd, $J_{5,6}$ = 18.6 Hz, $J_{5,5'\text{-}H(2)}$ = 9.6 Hz, $J_{5,6}$ = 7.3 Hz, $J_{5,5'\text{-}H(1)}$ = 2.2 Hz, 1H, 5-H), 3.42 (dd, $J_{8a,8\text{-}H(1)}$ = 5.8 Hz, $J_{8a,8\text{-}H(2)}$ = 2.3 Hz, 1H, 8a-H), 3.77 (s, 3H, CO_2*Me*), 3.82-3.56 (m, 1H, 1'-H^1)*, 3.95-4.00 (m, 1H, 1"-H^1)**, 4.00-4.04 (m, 1H, 1'-H^2)*, 4.17-4.22 (m, 1H, 1"-H2)**, 5.98 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-H), 6.54 (d, $J_{2,3}$ = 10.3 Hz, 1H, 2-H); *** assignment interchangeable. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 21.3 (C-5''')^A, 23.8 (C-5'''')^A, 25.9 (C-5")^A, 36.6 (C-5)^A, 37.5 (C-8)^A, 39.8 (C-5')^A, 43.7 (C-6)^A, 46.6 (C-8a)^A, 52.6 (CO_2*Me*)^A, 62.5 (C-4a)^B, 64.8 (C-1")^{A,}*, 66.0 (C-1')^{A,}*, 104.4 (C-1)^B, 127.3 (C-3)^A, 143.6 (C-2)^A, 170.3 (*C*O_2Me)^B, 196.5 (C-4)^B, 207.3 (C-7)^B; *assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow \delta_H(^1H)$]: δ_C = 21.3 (C-5''') ↔ δ_H = 0.70 (5'''-H_3); δ_C = 23.8 (C-5'''') ↔ δ_H = 0.85 (5''''-H_3); δ_C = 25.9 (C-5") ↔ δ_H = 1.44 (5"-H); δ_C = 36.6 (C-5) ↔ δ_H = 2.68 (5-H); δ_C = 37.5 (C-8) ↔ δ_H = 2.01 (8-H^1); δ_C = 37.5 (C-8) ↔ δ_H = 2.54 (8-H^2); δ_C = 39.8 (C-5') ↔ δ_H = 1.22 (5'-H^1); δ_C = 39.8 (C-5') ↔ δ_H = 1.67 (5'-H^2); δ_C = 43.7 (C-6) ↔ δ_H = 2.58 (6-H_2); δ_C = 46.6 (C-8a) ↔ δ_H = 3.42 (8a-H); δ_C = 52.6 (CO_2*Me*) ↔ δ_H = 3.77 (CO_2*Me*); δ_C = 64.8 (C-1") ↔ δ_H = 3.98 (1"-H^1); δ_C = 64.8 (C-1") ↔ δ_H = 4.19 (1"-H^2); δ_C = 66.0 (C-1') ↔ δ_H = 3.84 (1'-H^1); δ_C = 66.0 (C-1') ↔ δ_H = 4.02 (1'-H^2); δ_C = 127.3 (C-3) ↔ δ_H = 5.98 (3-H); δ_C = 143.6 (C-2) ↔ δ_H = 6.54 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (100.6/400.13 MHz), $CDCl_3$] [$\delta_C(^{13}C) \leftrightarrow$

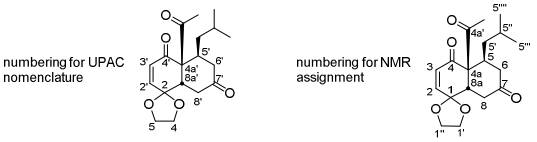
$\delta_H(^1H)$]: δ_C = 62.5 (C-4a) ↔ δ_H = 1.22 (5'-H^1), δ_H = 2.54 (8-H^2), δ_H = 2.58 (6-H_2), δ_H = 3.42 (8a-H), and δ_H = 5.98 (3-H); δ_C = 104.4 (C-1) ↔ δ_H = 2.01 (8-H^1), δ_H = 3.42 (8a-H), δ_H = 3.84 (1'-H^1), δ_H = 3.98 (1"-H^1), δ_H = 4.02 (1'-H^2), δ_H = 4.19 (1"-H^2), δ_H = 5.98 (3-H), and δ_H = 6.54 (2-H); δ_C = 170.3 (*C*O_2Me) ↔ δ_H = 3.42 (8a-H); δ_C = 196.5 (C-4) ↔ δ_H = 6.54 (2-H); δ_C = 207.3 (C-7) ↔ δ_H = 2.01 (8-H^1), δ_H = 2.54 (8-H^2), δ_H = 2.58 (6-H_2), and δ_H = 3.42 (8a-H). **DQF-COSY** ["H,H-COSY spectrum" (400.13 MHz), $CDCl_3$] [$\delta_H(^1H)$ ↔ $\delta_H(^1H)$]: δ_H = 0.85 (5'"-H_3) ↔ δ_H = 0.70 (5'"-H_3); δ_H = 1.44 (5"-H) ↔ δ_H = 0.70 (5'"-H_3), δ_H = 0.85 (5""-H_3), and δ_H = 1.22 (5'-H^1); δ_H = 1.67 (5'-H^2) ↔ δ_H = 1.22 (5'-H^1) and δ_H = 1.44 (5"-H); δ_H = 2.54 (8-H^2) ↔ δ_H = 2.01 (8-H^1); δ_H = 2.68 (5-H) ↔ δ_H = 1.22 (5'-H^1), δ_H = 1.67 (5'-H^2), and δ_H = 2.58 (6-H_2); δ_H = 3.42 (8a-H) ↔ δ_H = 2.01 (8-H^1) and δ_H = 2.54 (8-H^2); δ_H = 4.19 (1"-H^2) ↔ δ_H = 3.84 (1'-H^1); δ_H = 6.54 (2-H) ↔ δ_H = 5.98 (3-H). **IR** (Film): υ = 2955, 1745, 1715, 1680, 1240, 1150, 1120, 1110, 1065, 1020, 980, 970, 915, 930, 915 cm^{-1}. **HRMS** (pos. ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{24}O_6Na$, 359.1465; found, 359.1467.

(4a'*R*,5'*S*,8a'*S*)-4a'-Acetyl-5'-methyl-5',6',8',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4',7'(4a'*H*)-dione (*cis*,*syn*-7c)



At 0°C F_3CCO_2H (1 mL) was added dropwise to a solution of the Deslongchamps adduct *cis*,*syn*-**6c** (39.0 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) within 5 min. The mixture was stirred at 0°C for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 4 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (4 mL) and stirred at room temp. for 8 d. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 1:1 (v:v), 20 mL] to render the title compound (F40-50; 25.7 mg, 90%) as colorless solid. **Melting point:** 132-136°C. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 1.00 (d, $J_{5',5}$ = 6.8 Hz, 3H, 5'-H_3), 1.98 (dd, J_{gem} = 16.3 Hz, $J_{8-H(1),8a}$ = 5.7 Hz, 1H, 8-H^1), 2.13 (s, 3H, CO*Me*), 2.40 (ddd, J_{gem} = 16.2 Hz, $J_{6-H(1),5}$ = 5.4 Hz, $^4J_{6-H(1),8-H(2)}$ = 1.9 Hz, 1H, 6-H^1), 2.49 (ddd, J_{gem} = 16.3 Hz, $J_{8-H(2),8a}$ = 2.9 Hz, $^4J_{8-H(2),6-H(1)}$ = 2.0 Hz, 1H, 8-H^2), 2.61-2.70 (m, 1H, 5-H), 2.86 (dd, J_{gem} = 16.3 Hz, $J_{6-H(2),5}$ = 11.6 Hz, 1H, 6-H^2), 3.20 (dd, $J_{8a,8-H(1)}$ = 5.7 Hz, $J_{8a,8--H(2)}$ = 3.0 Hz, 1H, 8a-H), 3.84-3.89 (m, 1H, 1'-H^A)*, 3.98-4.04 (m, 2H, 1'-H^B, 1"-H^A)*,**, 4.16-4.20 (m, 1H, 1"-H^B)**, 6.05 (d, $J_{3,2}$ = 10.2 Hz, 1H, 3-H), 6.59 (d, $J_{2,3}$ = 10.3 Hz, 1H, 2-H);*,**, assignment interchangeable. **^{13}C NMR** (125.8 MHz, $CDCl_3$): δ = 16.1 (C-5')^A, 28.2 (CO*Me*)^A, 33.9 (C-5)^A, 36.8 (C-8)^A, 44.9 (C-8a)^A, 45.5 (C-6)^A, 64.9 (C-1")$^{*,\ A}$, 65.2 (C-4a)^B, 65.9 (C-1')$^{**,\ A}$, 104.2 (C-1)^B, 128.1 (C-3)^A, 144.2 (C-2)^A, 198.3 (C-4)^B, 204.7 (*C*OMe)^B, 207.3 (C-7)^B; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons; *, ** assignment interchangeable. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C)$ ↔ $\delta_H(^1H)$]: δ_C = 16.1 (C-5') ↔ 1.00 (5'-H_3); δ_C = 28.2 (CO*Me*) ↔ δ_H = 2.13 (CO*Me*); δ_C = 33.9 (C-5) ↔ δ_H = 2.66 (5-H); δ_C = 36.8 (C-8) ↔ δ_H = 1.98 (8-H^1); δ_C = 36.8 (C-8) ↔ δ_H = 2.49 (8-H^2); δ_C = 44.9 (C-8a) ↔ δ_H = 3.20 (8a-H); δ_C = 45.5 (C-6) ↔ δ_H = 2.40 (6-H^1); δ_C = 45.5 (C-6) ↔ δ_H = 2.86 (6-H^2); δ_C = 64.9 (C-1") ↔ δ_H = 4.01 (1"-H^A); δ_C = 64.9 (C-1") ↔ δ_H = 4.18 (1"-H^B); δ_C = 65.9 (C-1') ↔ δ_H = 3.86 (1'-H^A); δ_C = 65.9 (C-1') ↔ δ_H = 4.01 (1'-H^B); δ_C = 128.1 (C-3) ↔ δ_H = 6.05 (3-H); δ_C = 144.2 (C-2) ↔ δ_H = 6.59 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [$\delta_C(^{13}C)$ ↔ $\delta_H(^1H)$]: δ_C = 65.2 (C-4a) ↔ δ_H = 1.00 (5-H), δ_H = 1.98 (8-H^1), δ_H = 2.13 (CO*Me*), δ_H = 2.40 (6-H^1), δ_H = 2.49 (8-H^2), δ_H = 2.66 (5'-H_3), δ_H = 2.86 (6-H^2), δ_H = 3.20 (8a-H), and δ_H = 6.05 (3-H), δ_C = 104.2 (C-1) ↔ δ_H = 1.98 (8-H^1), δ_H = 3.20 (8a-H), δ_H = 3.86 (1'-H^A), δ_H = 4.01 (1"-H^A, 1'-H^B), δ_H = 4.18 (1"-H^B), and δ_H = 6.05 (3-H), δ_C = 198.3 (C-4) ↔ δ_H = 2.66 (5'-H_3), δ_H = 3.20 (8a-H), and δ_H = 6.59 (2-H), δ_C = 204.7 (*C*OMe) ↔ δ_H = 2.66 (5'-H_3) and δ_H = 3.20 (8a-H), δ_C = 207.3 (C-7) ↔ δ_H = 1.00 (5-H), δ_H = 1.98 (8-H^1), δ_H = 2.40 (6-H^1), δ_H = 2.49 (8-H^2), δ_H = 2.86 (6-H^2), and δ_H = 3.20 (8a-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [$\delta_H(^1H)$ ↔ $\delta_H(^1H)$]: δ_H = 2.49 (8-H^2) ↔ δ_H = 1.98 (8-H^1); δ_H = 2.66 (5-H) ↔ δ_H = 1.00 (5'-H_3) and δ_H = 2.40 (6-H^1); δ_H = 2.86 (6-H^2) ↔ δ_H = 2.40 (6-H^1) and δ_H = 2.66 (5-H); δ_H = 3.20 (8a-H) ↔ δ_H = 1.98 (8-H^1) and δ_H = 2.49 (8-H^2); δ_H = 4.01 (1"-H^A, 1'-H^B) ↔ δ_H = 3.86 (1'-H^A); δ_H = 4.18 (1"-H^B) ↔ δ_H = 3.86 (1'-H^A) and δ_H = 4.01 (1"-H^A, 1'-H^B); δ_H = 6.59 (2-H) ↔ δ_H = 6.05 (3-H). **IR** (Film): υ = 2940, 1715, 1670, 1265, 1210, 1145, 1120, 1100, 1020, 990, 985, 975, 950, 910 cm^{-1}. **HRMS** (pos. APCI) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}O_5$, 279.1227; found, 279.1229.

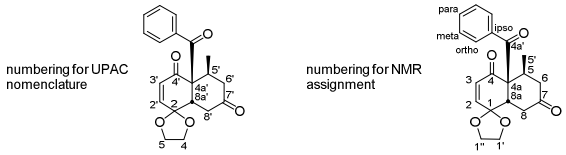
(4a'*R*,5'*S*,8a'*S*)-4a'-Acetyl-5'-isobutyl-5',6',8',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4',7'(4a'*H*)-dione (*cis*,*syn*-7d)



At room temp. F_3CCO_2H (0.8 mL) was added dropwise to a solution of the Deslongchamps adduct *cis*,*syn*-**6d** (65.6 mg, 0.16 mmol, 1.0 equiv.) in CH_2Cl_2 (3.1 mL) within 5 min and the mixture was stirred at room temp. for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 1.5 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (1.6 mL) and heated under reflux for 4 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 20 cm, *c*C_6H_{12}:EtOAc 4:1 to 2:1 (v:v), 20 mL] to render the title compound (F22-43; 26.5 mg, 53%) as colorless solid. **Melting point:** 168-170°C. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 0.68 (d, $J_{5''',5''}$ = 6.6 Hz, 3H, 5'"-H_3), 0.83 (d, $J_{5'''',5''}$ = 6.6 Hz, 3H, 5""-H_3), 1.10 (ddd, J_{gem} = 14.1 Hz, $J_{5'-H(1),5''}$ = 9.9 Hz, $J_{5'-H(1),5}$ = 2.3 Hz, 1H, 5'-H^1), 1.37-1.42 (m, 1H, 5-H), 1.56 (ddd, J_{gem} = 14.0 Hz, $J_{5'-H(2),5}$ = 9.4 Hz, $J_{5'-H(1),5''}$ = 4.4 Hz, 1H, 5'-H^2), 1.94 (dd, J_{gem} = 16.3 Hz, $J_{8-H(1),8a}$ = 5.6 Hz, 1H, 8-H^1), 2.13 (s, 3H, CO*Me*), 2.48-2.58 (m, 3H, 8-H^2, 6-H^A, 5-H), 2.74 (dd, J_{gem} = 17.8 Hz, $J_{6-H(B),5}$ = 13.0 Hz, 1H, 6-H^2), 3.22 (dd, $J_{8a,8-H(1)}$ = 5.7 Hz, $J_{8a,8-H(2)}$ = 2.7 Hz, 1H, 8a-H), 3.82-3.88 (m, 1H, 1'-H^A)*, 3.99-4.04 (m, 2H, 1'-H^B, 1"-H^A)*,**, 4.16-4.22 (m, 1H, 1"-H^B)**, 6.02 (d, $J_{3,2}$ = 10.3 Hz, 1H, 3-H), 6.59 (d, $J_{2,3}$ = 10.2 Hz, 1H, 2-H); *,** assignment interchangeable. **^{13}C NMR** (125.8 MHz, $CDCl_3$): δ = 21.2 (C-5'")^A, 23.8 (C-5"")^A, 25.8 (C-5")^A, 28.1 (CO*Me*)^A, 36.8 (C-5)^A, 36.8 (C-8)^A, 39.5 (C-5')^A, 43.6 (C-6)^A, 45.2 (C-8a)^A, 64.9 (C-1")^{A,*}, 66.0 (C-4a)^B, 66.1 (C-1')^{A,**}, 104.3 (C-1)^B, 127.9 (C-3)^A, 144.0 (C-2)^A, 198.7 (C-4)^B, 205.0 (*C*OMe)^B,

207.3 (C-7)^{B}; *,** assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^{2}J, ^{3}J and/or ^{4}J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 21.2 (C-5''') ↔ δ_H = 21.20 (5'''-H$_3$); δ_C = 23.8 (C-5'''') ↔ δ_H = 0.83 (5''''-H$_3$); δ_C = 25.8 (C-5'') ↔ δ_H = 1.43 (5''-H); δ_C = 28.1 (CO*Me*) ↔ δ_H = 2.13 (CO*Me*); δ_C = 36.8 (C-5) ↔ δ_H = 2.53 (5-H); δ_C = 36.8 (C-8) ↔ δ_H = 1.94 (8-H^1); δ_C = 36.8 (C-8) ↔ δ_H = 2.53 (8-H^2); δ_C = 39.5 (C-5') ↔ δ_H = 1.10 (5'-H^1); δ_C = 39.5 (C-5') ↔ δ_H = 1.56 (5'-H^2); δ_C = 43.6 (C-6) ↔ δ_H = 2.53 (6-H^A); δ_C = 43.6 (C-6) ↔ δ_H = 2.74 (6-H^B); δ_C = 45.2 (C-8a) ↔ δ_H = 3.22 (8a-H); δ_C = 64.9 (C-1'') ↔ δ_H = 4.01 (1''-H^A); δ_C = 64.9 (C-1'') ↔ δ_H = 4.19 (1''-H^B); δ_C = 66.1 (C-1') ↔ δ_H = 3.85 (1'-H^A); δ_C = 66.1 (C-1') ↔ δ_H = 4.01 (1'-H^B); δ_C = 127.9 (C-3) ↔ δ_H = 6.02 (3-H); δ_C = 144.0 (C-2) ↔ δ_H = 6.59 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 66.0 (C-4a) ↔ δ_H = 1.10 (5'-H^1), δ_H = 1.56 (5'-H^2), δ_H = 1.94 (8-H^1), δ_H = 2.13 (CO*Me*), δ_H = 2.53 (8-H^2, 6-H^A, 5-H), δ_H = 2.74 (6-H^B), δ_H = 3.22 (8a-H), and δ_H = 6.02 (3-H); δ_C = 104.3 (C-1) ↔ δ_H = 1.94 (8-H^1), δ_H = 2.53 (8-H^2, 5-H), δ_H = 3.22 (8a-H), δ_H = 3.85 (1'-H^A), δ_H = 4.01 (1'-H^B, 1''-H^A), δ_H = 4.19 (1''-H^B), and δ_H = 6.02 (3-H); δ_C = 198.7 (C-4) ↔ δ_H = 2.53 (8-H^2, 6-H^A, 5-H), δ_H = 3.22 (8a-H), and δ_H = 6.59 (2-H); δ_C = 205.0 (*C*OMe) ↔ δ_H = 2.13 (CO*Me*), δ_H = 2.53 (8-H^2, 6-H^A, 5-H), and δ_H = 3.22 (8a-H); δ_C = 207.3 (C-7) ↔ δ_H = 1.10 (5'-H^1), δ_H = 1.94 (8-H^1), δ_H = 2.53 (8-H^2, 6-H^A, 5-H), δ_H = 2.74 (6-H^B), and δ_H = 3.22 (8a-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [δ_H(^{1}H) ↔ δ_H(^{1}H)]: δ_H = 0.83 (5''''-H$_3$) ↔ δ_H = 21.20 (5'''-H$_3$); δ_H = 1.43 (5''-H) ↔ δ_H = 21.20 (5'''-H$_3$), 0.83 (5''''-H$_3$), and 1.10 (5'-H^1); δ_H = 1.56 (5'-H^2) ↔ δ_H = 1.10 (5'-H^1); δ_H = 2.53 (8-H^2) ↔ δ_H = 1.94 (8-H^1); δ_H = 2.53 (5-H) ↔ δ_H = 1.56 (5'-H^2); δ_H = 2.74 (6-H^B) ↔ δ_H = 2.53 (5-H); δ_H = 3.22 (8a-H) ↔ δ_H = 1.94 (8-H^1) and 2.53 (8-H^2); δ_H = 4.01 (1'-H^B, 1''-H^A) ↔ δ_H = 3.85 (1'-H^A); δ_H = 4.19 (1''-H^B) ↔ δ_H = 3.85 (1'-H^A) and 4.01 (1'-H^B, 1''-H^A); δ_H = 6.59 (2-H) ↔ δ_H = 6.02 (3-H). **IR** (Film): υ = 2960, 2920, 2870, 1715, 1670, 1205, 1135, 1015, 975, 915 cm^{-1}. **HRMS** (pos. APCI) m/z: [M + H]$^+$ calcd for $C_{18}H_{25}O_5$, 321.1697; found, 321.1695.

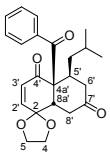
(4a'*S*,5'*S*,8a'*S*)-4a'-Benzoyl-5'-methyl-5',6',8',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4',7'(4a'*H*)-dione (*cis*,*syn*-7e)



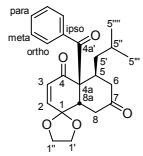
At 0°C F_3CCO_2H (1 mL) was added dropwise to a solution of the Deslongchamps adduct *cis*,*syn*-**6e** (45.4 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) within 5 min. The mixture was stirred at 0°C for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 4 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (4 mL) and stirred at room temp. for 8 d. The solvent was evaporated and the residue was purified by flash chromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 1:1 (v:v), 20 mL] to render the title compound (F34-45; 26.1 mg, 76%) as colorless solid. **Melting point:** 115-120°C. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 1.45 (d, $J_{5',5}$ = 6.9 Hz, 3H, 5'-H$_3$), 1.88 (dd, J_{gem} = 16.4 Hz, $J_{8-H(1),8a}$ = 5.8 Hz, 1H, 8-H^1), 2.40 (ddd, J_{gem} = 16.4 Hz, $J_{8-H(2),8a}$ = 2.2 Hz, $^4J_{8-H(2),6-H(1)}$ = 2.2 Hz, 1H, 8-H^2), 2.50 (ddd, J_{gem} = 16.5 Hz, $J_{6-H(1),5}$ = 5.4 Hz, $^4J_{6-H(1),8-H(2)}$ = 2.0 Hz, 1H, 6-H^1), 2.79 (m$_c$, 1H, 5-H), 3.07 (dd, J_{gem} = 16.4 Hz, $J_{6-H(2),5}$ = 12.0 Hz, 1H, 6-H^2), 3.52 (dd, $J_{8a,8-H(1)}$ = 5.7 Hz, $J_{8a,8-H(2)}$ = 2.3 Hz, 1H, 8a-H), 3.82-3.87 (m, 1H, 1'-H^A)*, 4.00-4.05 (m, 2H, 1'-H^B, 1''-H^A)*,**, 4.16-4.20 (m, 1H, 1''-H^B)**, 6.21 (d, $J_{3,2}$ = 10.6 Hz, 1H, 3-H), 6.71 (d, $J_{2,3}$ = 10.6 Hz, 1H, 2-H), 7.38-7.42 (m, 2H, 2 × meta-H), 7.49-7.52 (m, 1H, para-H), 7.66-7.68 (m, 2H, 2 × ortho-H); *,** assignment interchangeable. **^{13}C NMR** (125.8 MHz, $CDCl_3$): δ = 16.2 (C-5')^A, 35.1 (C-5)^A, 36.5 (C-8)^A, 45.7 (C-6)^A, 46.9 (C-8a)^A, 63.0 (C-4a)^B, 64.9 (C-1'')^{*,A}, 66.0 (C-1')^{*,A}, 104.2 (C-1)^B, 127.9 (C-3)^A, 128.7 (2 × C-meta)^A, 129.5 (2 × C-ortho)^A, 133.0 (C-para)^A, 134.5 (C-ipso)^B, 144.6 (C-2)^A, 197.3 (*C*OPh)^B, 198.0 (C-4)^B, 207.6 (C-7)^B; * assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^{2}J, ^{3}J and/or ^{4}J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 16.2 (C-5') ↔ δ_H = 1.15 (5'-H$_3$); δ_C = 35.1 (C-5) ↔ δ_H = 2.79 (5-H); δ_C = 36.5 (C-8) ↔ δ_H = 1.88 (8-H^1); δ_C = 36.5 (C-8) ↔ δ_H = 2.40 (8-H^2); δ_C = 45.7 (C-6) ↔ δ_H = 2.50 (6-H^1); δ_C = 45.7 (C-6) ↔ δ_H = 3.07 (6-H^2); δ_C = 46.9 (C-8a) ↔ δ_H = 3.52 (8a-H); δ_C = 64.9 (C-1'') ↔ δ_H = 4.03 (1''-H^A); δ_C = 64.9 (C-1'') ↔ δ_H = 4.18 (1''-H^B); δ_C = 66.0 (C-1') ↔ δ_H = 3.84 (1'-H^A); δ_C = 66.0 (C-1') ↔ δ_H = 4.03 (1'-H^B); δ_C = 127.9 (C-3) ↔ δ_H = 6.21 (3-H); δ_C = 128.7 (C-meta) ↔ δ_H = 7.40 (meta-H); δ_C = 129.5 (C-ortho) ↔ δ_H = 7.67 (ortho-H); δ_C = 133.0 (C-para) ↔ δ_H = 7.51 (para-H); δ_C = 144.6 (C-2) ↔ δ_H = 6.71 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 63.0 (C-4a) ↔ δ_H = 1.15 (5'-H$_3$), δ_H = 1.88 (8-H^1), δ_H = 2.40 (8-H^2), δ_H = 2.50 (6-H^1), δ_H = 2.79 (5-H), δ_H = 3.07 (6-H^2), δ_H = 3.52 (8a-H), and δ_H = 6.21 (3-H); δ_C = 104.2 (C-1) ↔ δ_H = 1.88 (8-H^1), δ_H = 2.40 (8-H^2), δ_H = 3.52 (8a-H), δ_H = 3.84 (1'-H^A), δ_H = 4.03 (1'-H^B, 1''-H^A), δ_H = 4.18 (1''-H^B), δ_H = 6.21 (3-H), and δ_H = 6.71 (2-H); δ_C = 134.5 (C-ipso) ↔ δ_H = 7.40 (meta-H); δ_C = 197.4 (*C*OPh) ↔ δ_H = 2.79 (5-H), δ_H = 3.52 (8a-H), δ_H = 7.40 (meta-H), and δ_H = 7.67 (ortho-H); δ_C = 198.0 (C-4) ↔ δ_H = 6.21 (3-H) and δ_H = 6.71 (2-H); δ_C = 207.6 (C-7) ↔ δ_H = 1.15 (5'-H$_3$), δ_H = 1.88 (8-H^1), δ_H = 2.40 (8-H^2), δ_H = 2.50 (6-H^1), δ_H = 3.07 (6-H^2), and δ_H = 3.52 (8a-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [δ_H(^{1}H) ↔ δ_H(^{1}H)]: δ_H = 2.40 (8-H^2) ↔ δ_H = 1.88 (8-H^1); δ_H = 2.79 (5-H) ↔ δ_H = 1.15 (5'-H$_3$) and δ_H = 2.50 (6-H^1); δ_H = 3.07 (6-H^2) ↔ δ_H = 2.50 (6-H^1) and δ_H = 1.15 (5'-H$_3$); δ_H = 3.52 (8a-H) ↔ δ_H = 1.88 (8-H^1) and δ_H = 2.40 (8-H^2); δ_H = 4.03 (1'-H^B, 1''-H^A) ↔ δ_H = 3.84 (1'-H^A); δ_H = 4.18 (1''-H^B) ↔ δ_H = 3.84 (1'-H^A) and δ_H = 4.03 (1'-H^B, 1''-H^A); δ_H = 6.71 (2-H) ↔ δ_H = 6.21 (3-H); δ_H = 7.51 (para-H) ↔ δ_H = 7.40 (meta-H); δ_H = 7.67 (ortho-H) ↔ δ_H = 7.40 (meta-H). **IR** (Film): υ = 2985, 2920, 2870, 1715, 1675, 1265, 230, 1020, 970, 915 cm^{-1}. **HRMS** (pos. APCI) m/z: [M + H]$^+$ calcd for $C_{20}H_{21}O_5$, 341.1384; found, 341.1383.

(4a'*S*,5'*S*,8a'*S*)-4a'-benzoyl-5'-isobutyl-5',6',8',8a'-tetrahydro-4'*H*-spiro(naphthalene-2,1'-[1,3]dioxolane)-4',7'(4a'*H*)-dione (*cis*,*syn*-7f)

numbering for UPAC nomenclature



numbering for NMR assignment



At 0°C F_3CCO_2H (1 mL) was added dropwise to a solution of the Deslongchamps adduct *cis*,*syn*-**6f** (49.7 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) within 5 min. The mixture was stirred at 0°C for 2 h. The solvent was removed and F_3CCO_2H was removed azeotropically with C_6H_6 (3 × 4 mL) under reduced pressure. The remaining solid was dissolved in C_6H_6 (4 mL) and stirred at room temp. for 8 d. The solvent was evaporated and the residue was purified by flash chlromatography on silica gel36 [2 cm × 15 cm, *c*C_6H_{12}:EtOAc 8:1 to 1:1 (v:v), 20 mL] to render the title compound (F26-38; 11.4 mg, 29%) as pale orange oil. **^{1}H NMR** (500.32 MHz, $CDCl_3$): δ = 0.71 (d, $J_{5''',5''}$ = 6.5 Hz, 3H, 5'''-H_3), 0.87 (d, $J_{5'''',5''}$ = 6.6 Hz, 3H, 5''''-H_3), 1.33 (ddd, J_{gem} = 14.3 Hz, $J_{5'\text{-}H(1),5}$ = 9.8 Hz, $J_{5'\text{-}H(1),5''}$ = 2.2 Hz, 1H, 5'-H^1), 1.43-1.50 (m, 1H, 5''-H), 1.70-1.77 (m, 1H, 5'-H^2), 1.84 (dd, J_{gem} = 16.4 Hz, $J_{8\text{-}H(1),8a}$ = 5.7 Hz, 1H, 8-H^1), 2.38 (ddd, J_{gem} = 16.4 Hz, $J_{8\text{-}H(2),8a}$ = 2.2 Hz, $^4J_{8\text{-}H(2),6\text{-}H(A)}$ = 2.2 Hz, 1H, 8-H^2), 2.62-2.69 (m, 2H, 5-H, 6-H^A), 2.87-2.94 (m, 1H, 6-H^B), 3.53 (dd, $J_{8a,8\text{-}H(1)}$ = 5.6 Hz, $J_{8a,8\text{-}H(2)}$ = 2.3 Hz, 1H, 8a-H), 3.81-3.87 (m, 1H, 1'-H^A)*, 4.00-4.06 (m, 2H, 1'-H^B, 1''-H^A)*,**, 4.16-4.20 (m, 1H, 1''-H^B)**, 6.19 (d, $J_{3,2}$ = 10.3 Hz, 1H, 3-H), 6.71 (d, $J_{2,3}$ = 10.3 Hz, 1H, 2-H), 7.38-7.42 (m, 2H, meta-H), 7.94-7.53 (m, 1-H, para-H), 7.65-7.68 (m, 2H, ortho-H); *,** assignment interchangeable. **^{13}C NMR** (125.8 MHz, $CDCl_3$): δ = 21.4 (C-5''')^A, 23.7 (C-5'''')^A, 26.3 (C-5'')^A, 36.5 (C-8)^A, 38.2 (C-5)^A, 39.7 (C-5')^A, 44.0 (C-6)^A, 47.1 (C-8a)^A, 64.0 (C-4a)^B, 64.9 (C-1'')^{*,A}, 66.0 (C-1')^{*,A}, 104.2 (C-1)^B, 127.9 (C-3)^A, 128.7 (2 × C-mata)^A, 129.6 (2 × C-ortho)^A, 133.0 (C-para)^A, 134.5 (C-ipso)^B, 144.5 (C-2)^A, 197.7 (*C*OPh)^B, 198.3 (C-4)^B, 207.5 (C-7)^{B,*} assignment interchangeable; ^{A} the indicated ^{13}C nuclei – they are non-quaternary – were identified in an edHSQC spectrum by their crosspeaks with directly bonded protons; ^{B} the indicated ^{13}C nuclei are quaternary and were distinguished in an HMBC spectrum by their crosspeaks due to ^2J, ^3J and/or ^4J couplings to "remote" protons. **edHSQC** ["short-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 21.4 (C-5''') ↔ δ_H = 0.71 (5'''-H_3); δ_C = 23.7 (C-5'''') ↔ δ_H = 0.87 (5''''-H_3); δ_C = 26.3 (C-5'') ↔ δ_H = 1.47 (5''-H); δ_C = 36.5 (C-8) ↔ δ_H = 1.84 (8-H^1); δ_C = 36.5 (C-8) ↔ δ_H = 2.38 (8-H^2); δ_C = 38.2 (C-5) ↔ δ_H = 2.66 (5-H); δ_C = 39.7 (C-5') ↔ δ_H = 1.33 (5'-H^1); δ_C = 39.7 (C-5') ↔ δ_H = 1.74 (5'-H^2); δ_C = 44.0 (C-6) ↔ δ_H = 2.66 (6-H^A); δ_C = 44.0 (C-6) ↔ δ_H = 2.91 (6-H^B); δ_C = 47.1 (C-8a) ↔ δ_H = 3.53 (8a-H); δ_C = 64.9 (C-1'') ↔ δ_H = 4.03 (1''-H^A); δ_C = 64.9 (C-1'') ↔ δ_H = 4.18 (1''-H^B); δ_C = 66.0 (C-1') ↔ δ_H = 3.84 (1'-H^A); δ_C = 66.0 (C-1') ↔ δ_H = 4.03 (1'-H^B); δ_C = 127.9 (C-3) ↔ δ_H = 6.19 (3-H); δ_C = 128.7 (C-mata) ↔ δ_H = 7.40 (meta-H); δ_C = 129.6 (C-ortho) ↔ δ_H = 7.66 (ortho-H); δ_C = 133.0 (C-para) ↔ δ_H = 7.51 (para-H); δ_C = 144.5 (C-2) ↔ δ_H = 7.51 (2-H). **HMBC** ["long-range C,H-COSY spectrum" (125.8/500.32 MHz), $CDCl_3$] [δ_C(^{13}C) ↔ δ_H(^{1}H)]: δ_C = 64.0 (C-4a) ↔ δ_H = 1.33 (5'-H^1), δ_H = 2.38 (8-H^2), δ_H = 2.66 (5-H, 6-H^A), δ_H = 3.53 (8a-H), and δ_H = 6.19 (3-H); δ_C = 104.2 (C-1) ↔ δ_H = 1.84 (8-H^1), δ_H = 3.53 (8a-H), δ_H = 4.03 (1'-H^B, 1''-H^A), δ_H = 4.18 (1''-H^B), and δ_H = 6.19 (3-H); δ_C = 134.5 (C-ipso) ↔ δ_H = 7.40 (meta-H); δ_C = 197.7 (*C*OPh) ↔ δ_H = 7.66 (ortho-H); δ_C = 198.3 (C-4) ↔ δ_H = 2.66 (5-H, 6-H^A), δ_H = 2.91 (6-H^B), δ_H = 3.53 (8a-H), and δ_H = 7.51 (2-H); δ_C = 207.5 (C-7) ↔ δ_H = 1.84 (8-H^1), δ_H = 2.38 (8-H^2), δ_H = 2.66 (5-H, 6-H^A), δ_H = 2.91 (6-H^B), and δ_H = 3.53 (8a-H). **DQF-COSY** ["H,H-COSY spectrum" (500.32 MHz), $CDCl_3$] [δ_H(^{1}H) ↔ δ_H(^{1}H)]: δ_H = 1.47 (5''-H) ↔ δ_H = 0.71 (5'''-H_3), δ_H = 0.87 (5''''-H_3), and δ_H = 1.33 (5'-H^1); δ_H = 1.74 (5'-H^2) ↔ δ_H = 1.33 (5'-H^1); δ_H = 2.38 (8-H^2) ↔ δ_H = 1.84 (8-H^1); δ_H = 2.66 (5-H, 6-H^A) ↔ δ_H = 1.74 (5'-H^2); δ_H = 2.91 (6-H^B) ↔ δ_H = 2.66 (5-H, 6-H^A); δ_H = 3.53 (8a-H) ↔ δ_H = 1.84 (8-H^1) and δ_H = 2.38 (8-H^2); δ_H = 4.03 (1'-H^B, 1''-H^A) ↔ δ_H = 3.84 (1'-H^A); δ_H = 4.18 (1''-H^B) ↔ δ_H = 3.84 (1'-H^A) and δ_H = 4.03 (1'-H^B, 1''-H^A); δ_H = 7.51 (2-H) ↔ δ_H = 6.19 (3-H); δ_H = 7.51 (para-H) ↔ δ_H = 7.40 (meta-H); δ_H = 7.66 (ortho-H) ↔ δ_H = 7.40 (meta-H). **IR** (Film): υ = 3180, 2990, 2930, 2870, 1715, 1700, 1675, 1235, 1140, 1100, 985, 975, 935, 915, cm^{-1}. **HRMS** (pos. ESI) m/z: [M + Na]$^+$ calcd for $C_{23}H_{26}O_5Na$, 405.1673; found, 405.1672.

Monitoring Deslongchamps Annulations:

The indicated quinone monoketal **5b**, **c** or **d** (1.0 equiv.), a Nazarov reagent **2a** or **b** (1.05 equiv.), and the internal standard 2,4,6-tribromotoluene (0.5 equiv.) were dissolved in CH_2Cl_2 (c = 0.06 mol/L) at room temperature (scale of these experiments: Section **SI-4** of the Supporting Information). The reaction was started (t = 0) by the addition of Cs_2CO_3 (1.0 equiv.) in one portion. Aliquots of the reaction mixture (0.4 mL) were sampled after 1, 2, 3, 4, 6, 8, 10, 20, 40, and 80 min (when monitoring the formation of *cis*,*syn*-**6f**, we also sampled after 160 and 320 min). Each sample was loaded onto a small glass column filled with silica gel (∅ = 5 mm, h = 2 cm) and eluted with AcOEt (3 mL). The eluate was collected, the solvent evaporated, and the residue analyzed ^{1}H-NMR spectroscopically at 300 MHz. The respective results for each monitoring reaction are detailed in Section **SI-4** of the Supporting Information).

Performing Deslongchamps Annulations as Cross-over Experiments:

The quinone monoketal/ Nazarov reagent pairs **5b**/**2a** and **5c**/**2b** (0.42 mmol of each of the reactants) were dissolved in CH_2Cl_2 (*c* = 0.05 mol/L each) at room temperature in two separate flasks. The reactions were started simultaneously by addition of Cs_2CO_3 (0.42 mmol, 1.0 equiv. each). After two minutes the contents of the two flasks were mixed. Stirring was continued for another 2 h. The reaction was stopped by filtration over silica gel (∅ = 2 cm, h = 1 cm) and eluted with EtOAc (50 mL). The solvent was evaporated. The ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude product mixture was compared to the spectra of the individual products prepared independently (cf. Scheme 5). More details: see Supporting Information **SI-5**.

Cross-over Experiment of Scheme 6. The setup for this experiment was like in the cross-over experiment described above (Scheme 5). The Enone/Nazarov reagent pairs **5b**/**2b** and **5c**/**2a** (0.42 mmol, 1.0 equiv. for both pairs of enone and Nazarov reagent) were dissolved in CH_2Cl_2 (c = 0.05 mol/L each) at room temperature in two separate flasks. The reactions were started with a delay of 1 min by addition of Cs_2CO_3 (0.42 mmol, 1.0 equiv. each). After 2 min (1 min for **5b** + **2b**) the contents of the two flasks were mixed together in one flask and the resulting mixture was stirred for another 2 h. The reaction was stopped by filtration over silica gel (∅ = 2 cm, h = 1 cm) and eluted with EtOAc (50 mL). The solvent was evaporated. The ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude product mixture was compared to the spectra of the individual products prepared independently (cf. Scheme 6).

Reversibility Experiments:

The Deslongchamps adduct pair *cis*,*syn*-**6a**/**6d** (211 µmol per component) was dissolved in CH_2Cl_2 (8.4 mL) at room temperature. The reaction was started by adding solid Cs_2CO_3 (138 mg, 422 µmol, 2.0 equiv.). The mixture was stirred for 6 h. After 1, 2, 3, and 6 h aliquots of 0.4 mL were sampled, Each specimen was filtered through a syringe filter (0.2 µm pore) and eluted with EtOAc (3 mL). The filtrate was evaporated. The ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of the respective residue was identical with the spectrum of the unaltered adduct pair *cis*,*syn*-**6a**/**6d**, that is, no reaction had occurred.

An analogous experiment was performed starting with another pair of Deslongchamps adducts: *cis*,*syn*-**6b** and *cis*,*syn*-**6c**. The execution and the result of this experiment were identical to the one described above

Performing Deslongchamps Annulations as Scavenging Experiments:

Each of the enone / "first Nazarov reagent" pairs **5b**/**2a**, **5b**/**2b**, **5c**/**2a**, and **5c**/**2b** (228 µmol per compound) and 2,4,6-tribromotoluene (37.5 mg, 114 µmol, 0.5 equiv.) was dissolved in CH_2Cl_2 (4.2 mL) separately at room temperature. The respective reactions were started by addition of Cs_2CO_3 (74.3 mg, 288 µmol, 1.0 equiv.). After 2 min (1 min for **5b**/**2b**; more details: see main body of the text), the "second Nazarov reagent" (228 µmol, 1.0 equiv.) was added (**2b** for reactions begun with **2a** as the "first Nazarov reagent"; **2a** for reactions begun with **2b** as the "first Nazarov reagent").

The resulting mixtures were stirred for 6 h. After 1, 2, 3, and 6 h aliquots of 0.4 mL were sampled, filtered through a syringe filter (0.2 µm pore width), and eluted with EtOAc (3 mL). The solvent was evaporated. The ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of the respective residue was compared to the spectra of the independently prepared reference products (see Scheme 7, Scheme 8). More details: Supporting Information **SI-6**.

ASSOCIATED CONTENT

Supporting Information: Detailed procedures for the synthesis of Nazarov reagents **2a-b** and quinone monoketals **5b-d**, concentration/time diagrams for the discontinuous NMR monitorings of the formation of Deslongchamps adducts *cis*,*syn*-**6b-f**, details of the cross-over and scavenging experiments, copies of NMR spectra, and X-ray details of Deslongchamps adducts **6a**, **6c**, and **6e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Interestingly, the substitution patterns of annulates **6** and **7** are inaccessible by "genuine" Diels-Alder reactions of benzoquinone monoketals. Examples are listed in Section **SI-9** of the Supporting Informations.

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(24) (a) What we call "sequential Michael additions" would be "domino Michael additions" according to the nomenclature suggested by Tietze:[25a] "A domino reaction is a process involving two or more bond-forming transformations (usually C-C bonds) which take place under the same reaction conditions without adding additional reagents and catalysts, and in which the subsequent reactions result as a consequence of the functionality formed in the previous step." (b) "Cascade Michael additions", "tandem Michael additions", or "consecutive Michael additions" might be terms preferred by others when referring to the identical course of events.[25]

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(27) Occam's razor prefers a simple explanation (e. g., one mechanism) over a complicated one (e. g., two mechanisms) – unless there is a necessity for the contrary.

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(30) *Syn*-selective Diels-Alder reactions of 1,3-dienes and alkyl cycloalk-2-en-1-one-2-carboxylates are exemplified in Section **SI-9** of the Supporting Informations.

(31) Examples for *anti*-selective Diels-Alder reactions of 1,3-dienes and alkyl cyclohex-2-en-1-one-2-carboxylates are exemplified in Section **SI-9** of the Supporting Informations.

(32) The same acceptor-substituted cyclohexenone **1** (EWG = CO_2Me, R_x = H; Scheme 1) and another and sterically more hindered Nazarov reagent than the one mentioned so far combined to form a Michael adduct at −15°C in acetonitrile as well.[6,7] However, it gave no Deslongchamps annulation product under any circumstances, which was described as if it corroborated sequential Michael additions occurring in the course of Deslongchamps annulations, which, in contrast, work.[16] However, the non-feasibility of a Deslongchamps annulation with the "sterically more hindered Nazarov reagent" mentioned above implies nothing *certain* about the mechanism of a Deslongchamps annulation, which is actually feasible.

(33) DFT calculations regarding the alternative mechanisms were undertaken in our laboratory, too, employing various functionals (Weber, F. *Dissertation*, Universität Freiburg **2015**). They revealed that an "anionic" Diels-Alder reaction is impossible and that the first Michael addition is irreversible. The first result may be true or not, whereas the second result disagrees with the experiments reported in this manuscript.

(34) (a) First mentioning in the literature: ref.[3]. (b) First description of a respective synthesis: ref.[7]. (c) New synthesis of Nazarov reagent **2a**: Experimental section and Section **SI-1** of the Supporting Informations.

(35) (a) First mentioning in the literature: ref.[21]. (b) New synthesis of Nazarov reagent **2b**: Experimental section.

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(37) The crystallographic data of Deslongchamps adduct **6a** are contained in CCDC 1557446. They can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via the link www.ccdc.cam.ac.uk/data_request/cif.

(38) The crystallographic data of Deslongchamps adduct **6c** are contained in CCDC 1557445. They can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via the link www.ccdc.cam.ac.uk/data_request/cif.

(39) The crystallographic data of Deslongchamps adduct **6e** are contained in CCDC 1557447. They can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via the link www.ccdc.cam.ac.uk/data_request/cif.

(40) We could not monitor these reactions in the spectrometer – in CD_2Cl_2 *solutions* – because Cs_2CO_3 is insoluble therein, forming *suspensions*.

(41) The close-ups of Figure 2, the 2nd, and the 4th-6th concentration/time diagram in Section **SI-4** of the Supporting Information illustrate that at times our reaction mixture contained less Nazarov reagent **2** than benzoquinonemonoketal **5**. This was in spite of using 5 mol-% more **2** than **5**. A depletion of **2** relative to **5** nonetheless might be due to **2** dimerizing or to **2** escaping our sampling procedure by precipitating as the cesium salt Cs-**2** (formula: Scheme 3).

(42) It was not self-evident that we would be able to monitor Deslongchamps adducts in the presence of the suspected Michael adduct intermediates (plural voice; cf. footnote[44]) by the ^{1}H-NMR resonances of the sp^2-bound protons in their cyclohexenone moiety. Chances were that signal overlap interfered. The factual evidence to the contrary means that the Michael adduct intermediates contained no cyclohexenones because tautomerism gave cyclohexadienols (cf. **e**, **f**, **i**, and **j** in Figure 3).

(43) The significant delay between reactant consumption and Deslongchamps adduct formation means that a fast initial reaction preceded product formation. Unfortunately, ^{1}H NMR signal overlap made a direct determination of the concentration of the intermediate(s) and/or side-product(s) impossible. To which extent intermediates and/or side-products accumulated in the course of our annulations, was an estimate, accordingly. We equalled their total amount to the difference between the initial amount of the starting material and the sum of the amounts of residual starting material and already formed Deslongchamps product.

(44) The singular form "the Michael adduct" for the intermediates **13**-**18** (Figure 3) should not be understood literally. This is because the tri-keto tautomer of each such compound contains three stereocenters and might therefore comprise four diastereomers **a**-**d**. Moreover, the acyclic β-ketoester moiety of the Michael adduct may be enolized (⥱**e**, **f**). The same is conceivable for the cyclohexenone moiety (⥱**g**, **h**) and, in addition, concomitantly in the acyclic in β-ketoester and in the cyclohexenone moiety (⥱**i**, **j**; see also footnote 42). Two enols of a given constitution – i. e., the kinds of isomers mentioned last – may arise as pairs of (*E*)- and (*Z*)-isomers. Furthermore, each component therein might represent a diastereomeric mixture because it contains two stereocenters.

(45) We used a total excess of 1.00 equiv. of Nazarov reagent in each of the four scavenging experiments of Scheme 7 and Scheme 8. After the respective mixture had reacted fore 3 h, we found no Nazarov reagent in any reaction mixture (500 MHz ^{1}H NMR). A "sink" for excess Nazarov reagents might precipitating as the cesium salt Cs-**2** (formula: Scheme 3). Since we filtered the crude product without exposing it to water, such a precipate might have evaded our analyses.

(46) An intramolecular 6-ring formation between a dienolate and an enoate – preceding a follow-up reaction leading to an 6-ring free isomer – was calculated to proceed via a Michael/Michael tandem addition rather than by an anionic Diels-Alder reaction by Kiss, E.; Campbell, C. D.; Driver, R. W.; Jolliffe, J. D.; Lang, R.; Sergeieva,

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(47) The latter compound was obtained as described in the Supporting Information.