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Stereocontrolled Synthesis of 1,3,5-Triols by an Iteration of Asymmetric Dihydroxylation and Deoxygenation

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Dedicated to Professor Bernd Giese on the occasion of his 70th birthday

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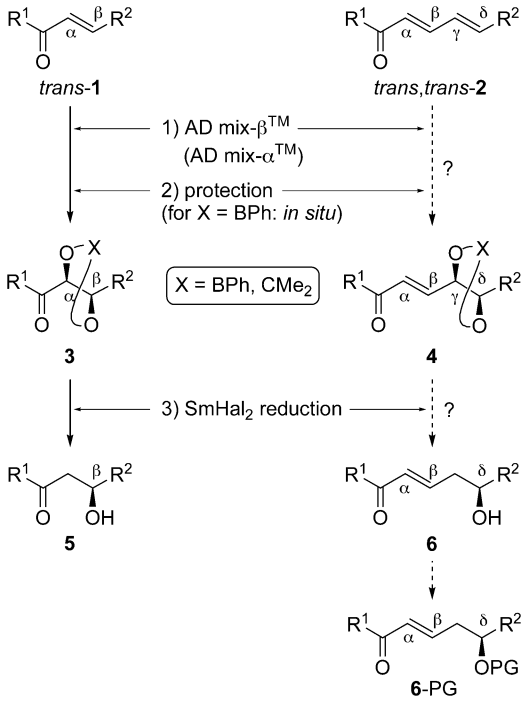
Asymmetric dihydroxylation of the C^{γ}=C^{δ} bonds in *trans*-configured α,β,γ,δ-unsaturated esters, carbonate formation, and Pd^0-catalyzed deoxygenation of C^{γ} provided α,β-unsaturated δ-hydroxy esters. Protection and chain-extension provided the corresponding α,β-unsaturated ketones. Their asymmetric dihydroxylation in the presence of phenylboronic acid delivered dioxaborolanes. $SmBr_2$-mediated deoxygenation of C^{α}, followed by Narasaka–Prasad and Claisen–Tishchenko reductions, respectively, selectively provided monoprotected ^{1,3}*syn*,^{3,5}*syn*-, ^{1,3}*syn*,^{3,5}*anti*-, ^{1,3}*anti*,^{3,5}*syn*-, and ^{1,3}*anti*,^{3,5}*anti*-configured 1,3,5-triols. Enones with a bulky $OSiR_3$ group at C^{δ} were dihydroxylated with significantly poorer *syn* (vs. *anti*) selectivities. Dominating reagent control modulated by opposing ("*mismatched case*") or enhancing ("*matched case*") substrate control, respectively, might be responsible.

Introduction

1,3,5-Polyols without substituents at their C^2, C^4, C^6, etc. centers represent the core structure of the polyol/polyene macrolide antibiotics.[1] Although the OH groups are interspersed regularly, they are configured irregularly, forming random sequences of *syn*- and *anti*-configured 1,3-diol units.[2] Synthesizing larger arrays of such polyols in a stereocontrolled manner is a challenge – particularly when striving for convergency. In our laboratory, Körber and Risch approached this problem in an unprecedented manner[3,4] (Scheme 1, left-hand column),[5] starting by subjecting the α,β-unsaturated ketones *trans*-**1** to an asymmetric dihydroxylation ("AD"), which delivered α,β-dihydroxy ketones with almost 100% *ee*. Samarium(II) iodide was added, with or without prior protection of the OH group, to cleave the C^{α}–O bond while leaving the C^{β}–O bond intact. The β-hydroxy ketones **5** resulted, which upon further reduction gave *syn*- or *anti*-configured 1,3-diols.

The current study was undertaken in order to extend the described strategy – which has recently been embellished[6] – to the vinylogous case (Scheme 1, right-hand column): the α,β,γ,δ-unsaturated ketones ("dienones") *trans,trans*-**2** should be convertible by γ,δ-selective AD, protection



Scheme 1. Left: Körber/Risch strategy for the synthesis of the enantiomerically pure β-hydroxy ketones **5** from the enones *trans*-**1**. Right: extendability to the vinylogous case: that is, the synthesis of enantiomerically pure δ-hydroxy enones (unprotected: **6**; protected: **6**-PG) from the *trans,trans*-dienones **2**.

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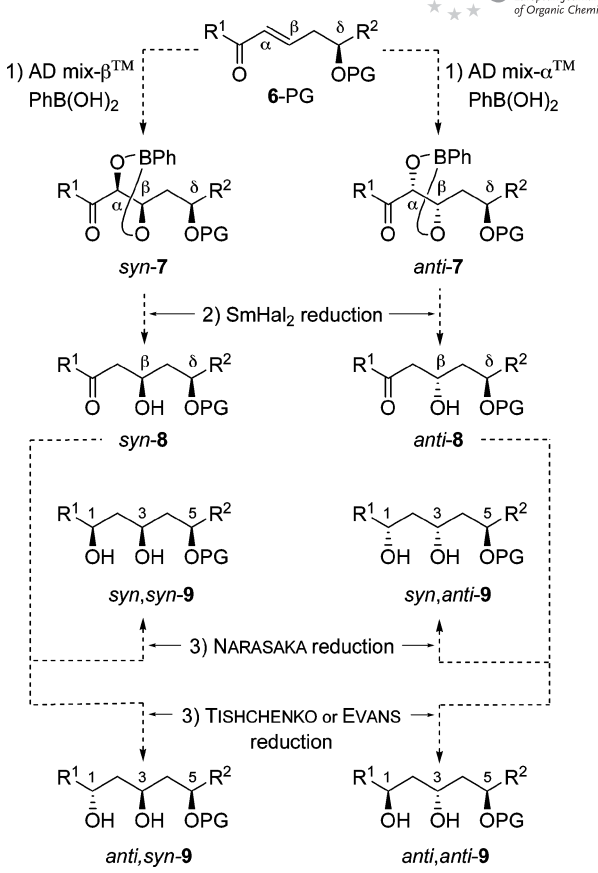
(optional), and γ-selective C–O bond rupture into the α,β-unsaturated δ-hydroxy ketones ("δ-hydroxy enones") **6**. Protection of the OH group should furnish the functionalized enones **6**-PG. These would be a subset of substrates of type **1** and so should be amenable to the reaction sequence previously discussed for the simple enones **1**.

This plan warrants a few comments. One prerequisite for achieving it was fulfilled, because the all-*trans*-configured α,β,γ,δ-unsaturated ketones undergo ADs with the required regioselectivity.[7] The same is true from analogous starting esters and Weinreb amides.[7b,7i] These findings were reassuring in view of the possibility that we might be forced – as eventually we were – to modify the original idea. The second prerequisite for tackling the dienones *trans*,*trans*-**2** as envisaged was that their AD products – whether protected (**4**) or unprotected (not shown) – should lose their C^{γ}–O bonds when combined with a reductant. No such reaction based on Sm^{II} reagents had been described, although Pd^0-catalyzed hydrogenolysis was an established means for breaking C^{γ}–O bonds in cyclic carbonates derived from γ,δ-dihydroxylation products of α,β,γ,δ-unsaturated esters ("dienoates"). The same kind of carbonates, as well as the analogous sulfites or acetonides, also undergo SmI_2-induced C^{γ}–O bond cleavage but their C^{α}=C^{β} bonds migrate to become C^{γ}=C^{δ} bonds.[8]

Depending on whether the dihydroxylation of the protected δ-hydroxy enones **6**-PG were to be performed with AD mix-β™ or AD mix-α™, the resulting C^{α}–O/C^{β}–O bond pair would be *syn*- or *anti*-oriented, respectively, relative to the C^{δ}–O bond (Scheme 2). If our AD reaction could be executed under Muñiz's and Hövelmann's conditions[9] it would yield the boronates *syn*- and *anti*-**7** rather than the parent glycols. The Muñiz–Hövelmann procedure extends Narasaka's *vic*-*cis*-dihydroxylation/diol phenylboronylation protocol from racemic products[10] to materials of ≥98% *ee*. In our laboratory it was applied to α,β-unsaturated ketones for the first time.[6] The attractiveness of the Muñiz–Hövelmann 1-pot transformation in this context is due to the susceptibility of the resulting ketoboronate to reduction by Sm^{II} reagents: a SmI_2-mediated C^{α}–O rather than C^{β}–O cleavage in the boronates *syn*- and *anti*-**7** would lead to the hemiprotected β,δ-dihydroxy ketones *syn*- and *anti*-**8**, respectively. Their free OH groups should control inter- or intramolecular hydride deliveries such that the ^{1,3}*syn*- and ^{1,3}*anti*-configured monoprotected 1,3,5-triols **9**, respectively, would be produced. Specifically, Narasaka–Prasad reductions were expected to deliver the triols ^{1,3}*syn*,^{3,5}*syn*- and ^{1,3}*syn*,^{3,5}*anti*-**9**[11,12] and Claisen–Tishchenko[13,14] or Evans[15] reductions the ^{1,3}*anti*,^{3,5}*syn*- and ^{1,3}*anti*,^{3,5}*anti*-**9** epimers.

Contemplating how well the transformations shown in Scheme 1–Scheme 2 might be turned into practice, we realized that the AD step **6**-PG→**7** was critical: 100% reagent control of diastereoselectivity was desired – but might the OPG group at the C^{δ} stereocenter interfere by contributing some substrate control of diastereoselectivity? We are aware of the stereochemical outcomes of very few ADs of δ-oxygenated enones **6** or **6**-PG.[3,16] C^{δ}-OPG effects variously



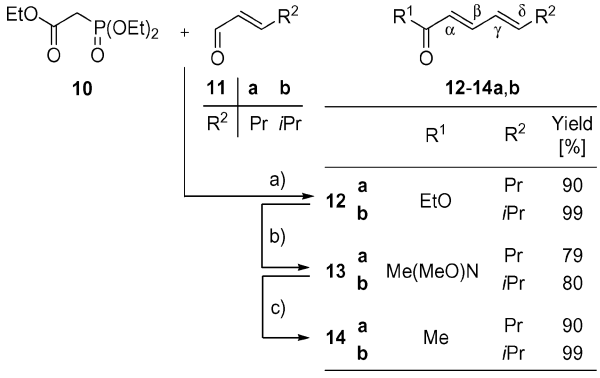
Scheme 2. Elaboration of protected (**6**-PG) δ-hydroxy enones into the *syn*,*syn*-, *syn*,*anti*-, *anti*,*syn*-, and *anti*,*anti*-1,3,5-triols **9**.

showed up[3] or did not[3,16b,16c] or were obscured by the competing effect of another remote stereocenter.[16a] ADs of free or *O*-protected δ-hydroxy enoates have been studied more frequently[17] but with no emphasis on investigation of C^{δ}-OPG or C^{δ}-OH effects.

Results and Discussion

The generic *trans*,*trans*-**2** structure of the dienone substrates for this study was accessed with the substitution patterns *trans*,*trans*-**14a** and *trans*,*trans*-**14b** (Table 1). These are methyl ketones with either a propyl (**a**) or an isopropyl substituent (**b**) at C^{δ}. A Wittig reaction between hex-2-enal (**11a**) and the corresponding ylide gave the desired dienone **14a** as a 97:3 mixture of the $^{\alpha,\beta}$*trans*,$^{\gamma,\delta}$*trans* and the $^{\alpha,\beta}$*trans*,$^{\gamma,\delta}$*cis* isomers. The corresponding Horner–Wadsworth–Emmons reaction produced these isomers in a 93:7 ratio. None of the mixtures was separable by flash chromatography on silica gel.[18] Surprisingly, Horner–Wadsworth–Emmons reactions[19] performed in otherwise analogous manner furnished the elusive dienone **14a**'s dienoate counterparts **12a** and **12b** as pure $^{\alpha,\beta}$*trans*,$^{\gamma,\delta}$*trans* isomers (Table 1). From the esters **12a** and **12b** we proceeded to the ketones **14a** and **14b** – which were isomerically pure when prepared in this manner – in two steps and 71% and 79% yields, respectively. The intermediates en route were the Weinreb amides ("dieneamides") **13a** and **13b**[20] and the source of the methyl group was MeLi.[21]

Table 1. Synthesis of the *trans,trans*-configured α,β,γ,δ-unsaturated esters **12**, Weinreb amides **13**, and ketones **14**.[a]



		R^1	R^2	Yield [%]
12	**a**	EtO	Pr	90
	b		*i*Pr	99
13	**a**	Me(MeO)N	Pr	79
	b		*i*Pr	80
14	**a**	Me	Pr	90
	b		*i*Pr	99

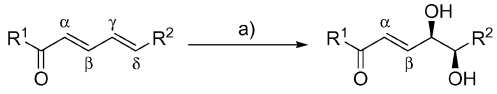
[a] *Reagents and conditions*: a) NaH (60% dispersion in mineral oil, 1.8 equiv.), THF, –10 °C, addition of **10** (1.7 equiv.), 1 h; addition of **11**, 1 h. b) **12**, Me(MeO)NH·HCl (3.0 equiv.), THF, –30 °C, addition of *i*PrMgCl·LiCl (6.0 equiv.), 30 min. c) THF, –20 °C, addition of MeLi (2.2 equiv.), 1 h; → 0 °C, 2 h.

The dienoates *trans,trans*-**12a** and *trans,trans*-**12b** and the dieneamides *trans,trans*-**13a** and *trans,trans*-**13b** being as handy as the dienones *trans,trans*-**14a** and *trans,trans*-**14b**, we decided to subject each compound to as many as possible of the seven or so key transformations shown in Schemes 1 and 2 (round #1 transformations: γ,δ-AD, in situ or explicit diol protection, γ-defunctionalization, alcohol protection; round #2 transformations: α,β-AD, in situ or explicit diol protection, α-defunctionalization; terminating step: ketone reduction, i.e., triol production). This broad approach should allow identification of the best suited substrate for our endeavor in terms of chemical yield, regioselectivity, and enantioselectivity.

The AD reactions summarized in Table 2 were effected under Sharpless' "improved" conditions[22] [i.e., with employment of 1 mol-% rather than 0.2 mol-% of $K_2OsO_2(OH)_4$ as an Os^{VIII} progenitor and 5 mol-% rather than 1 mol-% of $(DHQD)_2PHAL$ as a chiral auxiliary[23]]. This saved costs relative to the conditions of O'Doherty and Zhang; their ADs of conjugated dienoates used 10 mol-% OsO_4 and 11 mol-% $(DHQD)_2PHAL$ or $(DHQ)_2PHAL$.[7i] The γ,δ-dihydroxy enoates **15a**(**b**) were obtained from the dienoates **12a**(**b**) in 66% (78%) yield and with 98% (98.5%) *ee* after separation from their initial 98:2 (96:4) mixtures with the α,β-dihydroxy enoates. Perfect regiocontrol was observed in the ADs of the dieneamides **16a** and **16b** (58–84%, 96.6–98.9% *ee*) and of the dienones **17a** and **17b** (52–55%, 97.2–98.2% *ee* values). The absolute configuration of each product is assumed to comply with "Sharpless' mnemonic".[24]

Earlier experiences had taught that α,β-dihydroxy ketones can be, but do not need to be, derivatized before SmI_2 cleaves their C^α–O bond efficiently.[5] Nevertheless, the unprotected γ,δ-dihydroxy enone **21** decomposed when it was exposed to SmI_2.[25] Accordingly we derived the acetonide **20** from *this* diol, and both the phenylboronate **18** and the carbonate **25a** from the γ,δ-dihydroxy enone **17a**

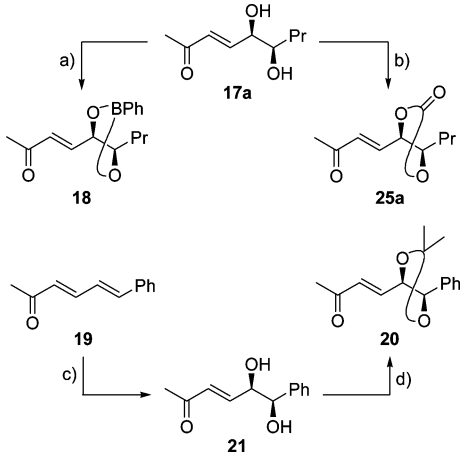
Table 2. AD of the *trans,trans*-configured α,β,γ,δ-unsaturated esters **12**, Weinreb amides **13**, and ketones **14** under Sharpless' conditions.[a]



		R^1	R^2		Yield [%]	*ee* [%]
12	**a**	EtO	Pr	**15** **a**	78[b]	98.5
	b		*i*Pr	**b**	66[c]	98.0
13	**a**	Me(MeO)N	Pr	**16** **a**	58	96.6
	b		*i*Pr	**b**	84	98.9
14	**a**	Me	Pr	**17** **a**	52	97.2
	b		*i*Pr	**b**	55	98.2

[a] *Reagents and conditions*: a) "Improved"[22] AD mix-β™ [i.e., $K_2OsO_2(OH)_4$ (1 mol-%), $(DHQD)_2PHAL$ (5 mol-%), $K_3Fe(CN)_6$ (3.0 equiv.), K_2CO_3 (3.0 equiv.)], $NaHCO_3$ (3.0 equiv.), $MeSO_2NH_2$ (1.0 equiv.), *t*BuOH/H_2O (1:1, v/v), 0 °C, 4 d. [b] Separated from initial 98:2 mixture with the C^α=C^β-dihydroxylation product. [c] Separated from initial 96:4 mixture with the C^α=C^β-dihydroxylation product.

(Scheme 3). Coincidentally, the last transformation was also a plausible prerequisite for a C^γ–O bond scission by Pd^0-catalyzed hydrogenolysis as described by O'Doherty et al.[26] These workers obtained the highest yields with the cyclic carbonates rather than with open-chain mixed carbonates or dibenzoates of γ,δ-dihydroxy enoates.

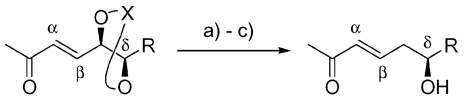


Scheme 3. Synthesis of the γ,δ-dihydroxy enones **20**, **18**, and **25a**. *Reagents and conditions*: a) $PhB(OH)_2$ (1.2 equiv.), CH_2Cl_2, room temp., 24 h; 85%. b) Triphosgene (1.1 equiv.), pyridine (5.0 equiv.), CH_2Cl_2, 0 °C, 1.5 h; 95%. c) "Improved"[22] AD mix-β™ [i.e., $K_2OsO_2(OH)_4$ (1.0 mol-%), $(DHQD)_2PHAL$ (5 mol-%), $K_3Fe(CN)_6$ (3.0 equiv.), K_2CO_3 (3.0 equiv.)], $NaHCO_3$ (3.0 equiv.), $MeSO_2NH_2$ (1.0 equiv.), *t*BuOH/H_2O (1:1, v/v), 0 °C, 20 h; 70%. d) Camphorsulfonic acid (5 mol-%), 2,2-dimethoxypropane (36 equiv.), no additional solvent, room temp., 3 h; 66%.

In exploratory experiments (Table 3), γ-defunctionalization of the dihydroxy enone derivatives **20** (acetonide), **18** (phenylboronate), or **25a** (carbonate) discussed above failed in two cases [**20** + SmI_2; **18** + HCO_2^- $HNEt_3^+$ + cat. $Pd(PPh_3)_4$] but worked in the third case: when **25a** and HCO_2^- $HNEt_3^+$ were allowed to react in the presence of

cat. $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ the desired hydroxy enone **28a** resulted. It was the major constituent of a 89:11 mixture (72% yield) with the isomer with a $C^\beta{=}C^\gamma$ rather a $C^\alpha{=}C^\beta$ bond (*iso*-**28a**; formula in Table 5) and could not be separated therefrom. In O'Doherty's γ-defunctionalization of the carbonates of dihydroxy enoates the C=C bond stayed fixed.[26] That carbonate **25a** was attacked by Pd^0 but the corresponding phenylboronate **18a** was not was no real surprise: enoate-containing phenylboronates are *obtained in the presence of* $Pd(PPh_3)_4$ from γ,δ-epoxy enoates and phenylboronic acid.[27]

Table 3. Attempted γ-deoxygenation of the γ,δ-dihydroxy enones **18**, **20**, and **25a**.[a]



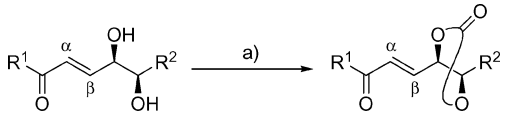
20, **18**, **25a** → **22**, **28a**

	X	R	Reagent(s)		Yield [%]	$C^\alpha{=}C^\beta$: $C^\beta{=}C^\gamma$
20	CMe_2	Ph	SmI_2	**22**	–[b]	
18	BPh	Pr	$Pd(PPh_3)_4$	**28a**	–[c]	
25a	C=O		$Pd_2(dba)_3{\cdot}CHCl_3$, PPh_3		72	89:11

[a] *Reagents and conditions*: a) SmI_2 (2.2 equiv.), THF, –78 °C, addition of substrate in THF/MeOH/HMPA (10:1:5, v/v/v); → room temp., 30 min. b) $Pd(PPh_3)_4$ (2.5 mol-%), NEt_3 (3.1 equiv.), HCO_2H (3.1 equiv.), THF, reflux, 2 h. c) $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol-%), PPh_3 (6.3 mol-%), NEt_3 (3.1 equiv.), HCO_2H (3.1 equiv.), THF, reflux, 2 h. [b] Decomposition, no **20** reisolated. [c] Partial decomposition, 51% **18** reisolated.

The screening results shown in Table 3 allowed us to convert not only the γ,δ-dihydroxy enone **17b** but also the γ,δ-dihydroxy enoates **15a** and **15b** and their Weinreb amides **16a** and **16b** into cyclic carbonates (Table 4). This occurred in 72–95% yields under O'Doherty's conditions for carbonate formation from γ,δ-dihydroxy enoates[26a] (i.e., by exposure to triphosgene and pyridine in CH_2Cl_2).

Table 4. Carbonate formation from the α,β-unsaturated γ,δ-dihydroxy esters **15**, the Weinreb amides **16**, and the ketones **17**.[a]



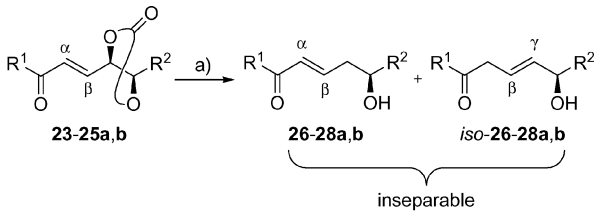
15-17a,b → **23-25a,b**

		R^1	R^2			Yield [%]
15	**a**	EtO	Pr	**23**	**a**	88
	b		*i*Pr		**b**	78
16	**a**	Me(MeO)N	Pr	**24**	**a**	72
	b		*i*Pr		**b**	78
17	**a**	Me	Pr	**25**	**a**	95
	b		*i*Pr		**b**	83

[a] *Reagents and conditions:* a) Triphosgene (1.1 equiv.), pyridine (5.0 equiv.), CH_2Cl_2, 0 °C, 1.5 h.

Table 5 lists the ensuing $Pd_2(dba)_3{\cdot}CHCl_3$-catalyzed C^γ–O bond scissions in the γ,δ-carbonatoesters **23a** and **23b**, the γ,δ-carbonatoenamides **24a** and **24b**, and the γ,δ-carbonatoenones **25a** and **25b**. Yields were highest for the esters (→ 71–73%), somewhat lower for the ketones (→ 55–72%), and smallest for the amides (→ 30–65%). The interference of $C^\alpha{=}C^\beta \rightarrow C^\beta{=}C^\gamma$ shifts was almost negligible for the esters (→ 3–4% bond-shift) but sizable for the Weinreb amides (→ 10–11% bond-shift) and still greater for the ketones (→ 11–18% bond-shift). Purification by flash chromatography on silica gel[18] allowed us to isolate the corresponding mixtures of $C^\alpha{=}C^\beta$ (**26a/b**[28]–**28a/b**) and $C^\beta{=}C^\gamma$ (*iso*-**26a/b**–*iso*-**28a/b**) isomers but turned out to be insufficient for obtaining the desired major components isomerically pure. As a consequence we considered the "genuine" mixtures of the Weinreb δ-hydroxy enamides **27a/27b**/*iso*-**27a**/*iso*-**27b** or of the δ-hydroxy enones **28a/28b**/*iso*-**28a**/*iso*-**28b** to be less well suited than the δ-hydroxy enoates **26a/26b** with their "tiny" isomer contents for perusal in our proceedings. Accordingly, we disregarded processing of **27a/27b**/*iso*-**27a**/*iso*-**27b** or **28a/28b**/*iso*-**28a**/*iso*-**28b** any further and focused on **26a** (as a 97:3 mixture with *iso*-**26a**) and **26b** (as a 96:4 mixture with *iso*-**26b**) as the sources of our 1,3,5-triols.

Table 5. Palladium catalyzed γ-deoxygenation of carbonates **23**–**25**.[a]



23-25a,b → **26-28a,b** + *iso*-**26-28a,b**

		R^1	R^2			Yield [%]	$C^\alpha{=}C^\beta : C^\beta{=}C^\gamma$
23	**a**	EtO	Pr	**26**	**a**	71	97 : 3
	b		*i*Pr		**b**	73	96 : 4
24	**a**	Me(MeO)N	Pr	**27**	**a**	30	90 : 10
	b		*i*Pr		**b**	65	89 : 11
25	**a**	Me	Pr	**28**	**a**	72	89 : 11
	b		*i*Pr		**b**	55	82 : 18

[a] *Reagents and conditions*: a) HCO_2H (3.1 equiv.), NEt_3 (3.1 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol-%), PPh_3 (6.3 mol-%), THF, reflux, 2 h.

It was gratifying to find that protection of the OH groups of the δ-hydroxy enoates **26a/26b**/*iso*-**26a**/*iso*-**26b** delivered the mixed acetals **29a** and **29b** ("BOM ethers"), the *para*-methoxybenzyl ethers **30a** and **30b** ("PMB ethers"), and the *tert*-butyldiphenylsilyl ethers **31a** and **31b** ("TBDPS ethers") in 70–98% yields *and that flash chromatography on silica gel*[18] *removed the* $C^\beta{=}C^\gamma$*-containing contaminant in each instance* (Table 6). Benzylation was successful only with PMB-OC(=NH)CCl_3, but the reaction, lasting 11 days, was still tedious. The *O*-protected δ-hydroxy enoates **29a/b**–**31a/b** were carried on via the Weinreb amides[20] **32a/b**–**34a/b** to the corresponding methyl ketones[21] **35a/b**–**37a/b** in good to excellent overall yields.

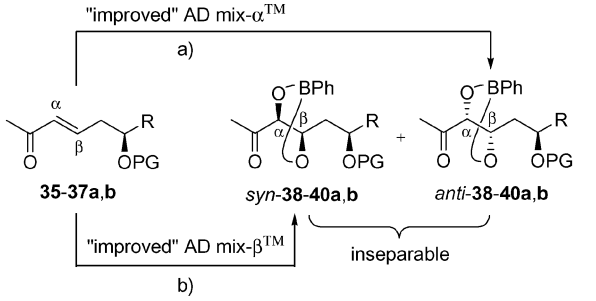
Table 6. Protection of the δ-oxygenated α,β-unsaturated esters **26a** and **26b** and their subsequent conversion into isomer-free protected α,β-unsaturated Weinreb amides and ketones.[a]

a) or b) or c) → d) → e)

		PG = BOM		PG = PMB		PG = TBDPS	
R^1	R^2		Yield [%]		Yield [%]		Yield [%]
EtO	Pr	**29a**	83	**30a**	77[b]	**31a**	98
	*i*Pr	**29b**	78	**30b**	70[c]	**31b**	79
Me(MeO)N	Pr	**32a**	79	**33a**	65	**34a**	87
	*i*Pr	**32b**	80	**33b**	99	**34b**	75
Me	Pr	**35a**	90	**36a**	88	**37a**	83
	*i*Pr	**35b**	99	**36b**	87	**37b**	78

[a] *Reagents and conditions*: a) BOM-Cl (4.0 equiv.), NEt_3 (4.0 equiv.), 1,2-dichlorethane, reflux, 4 h. b) PMB-OC(=NH)CCl_3 (2.3 equiv.), pyridinium *p*-toluenesulfonate (0.6 equiv.), CH_2Cl_2, room temp., 11 d. c) TBDPS-Cl (2.0 equiv.), imidazole (4.0 equiv.), DMF, 65 °C, 2 d. d) Me(MeO)NH·HCl (3.0 equiv.), THF, –30 °C, addition of *i*PrMgCl·LiCl (6.0 equiv.), 30 min. e) **32**–**34**, THF, –20 °C, addition of MeLi (2.2 equiv.), 1 h; → 0 °C, 2 h. [b] Incomplete conversion, 15% **26a** reisolated. [c] Incomplete conversion, 21% **26b** reisolated.

Table 7. AD of the protected δ-hydroxy enones **35**–**37** under Muñiz's conditions.[a]



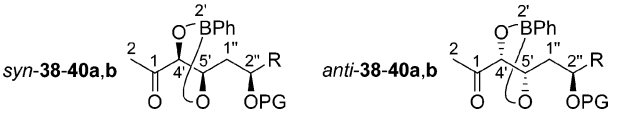
		PG	R	AD mix-β™ Yield [%]	AD mix-β™ *syn* [%]	AD mix-α™ Yield [%]	AD mix-α™ *anti* [%]
35, **38**	**a**	BOM	Pr	68	90	73	92
	b		*i*Pr	76	91	65	92
36, **39**	**a**	PMB	Pr	77	92	82	92
	b		*i*Pr	66	93	59	92
37, **40**	**a**	TBDPS	Pr	82	76	61	89
	b		*i*Pr	51	71	40	94

[a] *Reagents and conditions*: a) "Improved"[22] AD mix-α™ [i.e., $K_2OsO_2(OH)_4$ (1 mol-%), $(DHQ)_2PHAL$ (5 mol-%), $K_3Fe(CN)_6$ (3.0 equiv.), K_2CO_3 (3.0 equiv.)], $NaHCO_3$ (3.0 equiv.), $PhB(OH)_2$ (1.2 equiv.), *t*BuOH/H_2O (1:1, v/v), 0 °C, 2 d. b) Same as (a), but with $(DHQD)_2PHAL$ instead of $(DHQ)_2PHAL$.

The enone BOM ethers **35a** and **35b**, PMB ethers **36a** and **36b**, and *tert*-butyldiphenylsilyl ethers **37a** and **37b** were subjected to the AD reactions summarized in Table 7. With $(DHQD)_2PHAL$ on the one hand and with $(DHQ)_2PHAL$ on the other for controlling the facial selectivity of C=C attack, we expected[24] the newly formed C^{α}–O and C^{β}–O bonds to be *syn*- and *anti*-oriented, respectively, relative to the previously introduced C^{δ}–O bond. The inherently low reactivities of the electron-deficient C=C bonds in our substrates were overcome by use of the "improved" conditions[22] that we had already used for the ADs shown in Table 2. Moreover, we added phenylboronic acid to our AD mixtures[9] so that we obtained the phenylboronates **38a/b**–**40a/b** rather than the parent diols. Except in the case of the sterically most hindered substrate (**37b**), yields were between 59 and 82%.

The *syn*- and *anti*-configured boronates **38a/b**–**40a/b** were isolated as mixtures. Depending on whether they had been formed by the action of "improved" AD mix-α™ or AD mix-β™ the major products prevailed to a significant extent (71–94%). This allowed us to extract unequivocally the ^1H and ^{13}C NMR shifts of all nuclei in the stereochemically differentiating string $C^{5'}$(-H)–$C^{1''}$(-H_A)(-H_B)–$C^{2''}$(-H). The bottom rows of Table 8 and Table 9 list the average chemical shift difference for each nucleus of this string in the *syn* and the *anti* diastereomer. No single one of these average values correctly describes the corresponding shift order in *all* the compounds. In other words, there is no NMR shift criterion for assigning *syn* or *anti* configurations in this group of compounds. Accordingly the stereochemical identities of compounds *syn*- and *anti*-**38**–**40** are based solely on the validity of Sharpless' mnemonic.[24]

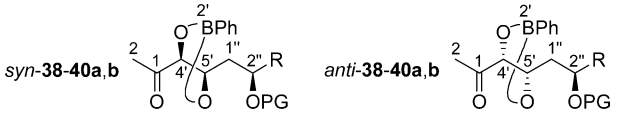
Table 8. Characteristic ^1H NMR shifts for the *syn*- and *anti*-configured dioxaborolanes **38a/b**–**40a/b** in $CDCl_3$ solutions (400 MHz).



		PG	R	$\delta_{5'-H}$ [ppm]	$\delta_{1''-H_A}$ [ppm]	$\delta_{1''-H_B}$ [ppm]	$\delta_{2''-H}$ [ppm]
syn-	**38a**	BOM	Pr	4.65	1.69	2.06	3.92
anti-				4.71	1.86	1.95	4.03
syn-	**38b**		*i*Pr	4.68	1.93	2.05	3.67
anti-				4.71	1.79	1.89	3.89
syn-	**39a**	PMB	Pr	4.67	1.94	2.07	3.68
anti-				4.71	1.87	1.94	3.77
syn-	**39b**		*i*Pr	4.70	1.90	2.03	3.45
anti-				4.70	1.81	1.86	3.62
syn-	**40a**	TBDPS	Pr	4.61	1.87	1.91	4.07
anti-				4.60	1.79	1.88	4.10
syn-	**40b**		*i*Pr	4.42	1.79	1.91	3.94
anti-				4.48	1.68	1.82	3.99
Average value δ_{syn}-δ_{anti}				–0.03	+0.12	–0.12	–1.16

The diastereoselectivities of the AD reactions listed in Table 7 are 90–92% for the BOM ethers **35a** and **35b** and 92–93% for the PMB ethers **36a** and **36b**. In the *syn* series this statement is as valid as in the *anti* series. The *anti*-dihy-

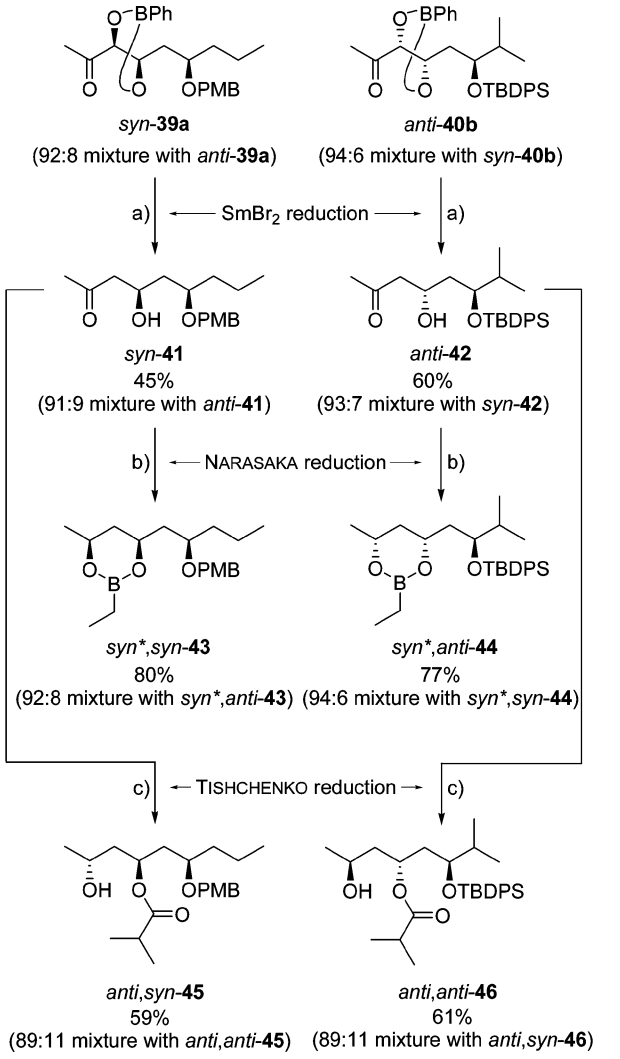
Table 9. Characteristic ^{13}C NMR shifts for the *syn*- and *anti*-configured dioxaborolanes **38a/b**–**40a/b** in $CDCl_3$ solutions (100 MHz).



		PG	R	$\delta_{C-5'}$ [ppm]	$\delta_{C-1''}$ [ppm]	$\delta_{C-2''}$ [ppm]
syn-	**38a**	BOM	Pr	77.39	41.25	74.62
anti-				77.19	42.41	74.08
syn-	**38b**		*i*Pr	79.96	37.83	77.82
anti-				79.91	38.05	77.37
syn-	**39a**	PMB	Pr	77.47	40.61	75.07
anti-				77.47	42.10	75.26
syn-	**39b**		*i*Pr	79.99	36.74	77.94
anti-				80.10	37.88	77.34
syn-	**40a**	TBDPS	Pr	70.14	43.20	77.04
anti-				69.73	44.13	77.02
syn-	**40b**		*i*Pr	74.38	41.33	77.00
anti-				73.99	39.61	77.00
Average value δ_{syn}-δ_{anti}				+0.19	–1.16	+0.30

droxylations of the TBDPS ethers **37a** and **37b** exhibit virtually identical diastereoselectivities: *ds* = 89 and 94%, respectively. In marked contrast, the *syn*-dihydroxylations of the TBDPS ethers **37a** and **37b** revealed no more than 76 and 71% *ds*.[29] In principle each substrate of Table 7 allows stereocontrol through double stereodifferentiation,[30] so it appears plausible to invoke matched (→ *anti*-**40a/b**) vs. mismatched (→ *syn*-**40a/b**) substrate/reagent pairs to explain the diastereoselectivities of the ADs of the TBDPS ethers **37a** and **37b**. Quite differently, there is no such effect in the ADs of the BOM (**35a**, **35b**) and PMB ethers (**36a**, **36b**), in which the *ds* values are invariant to swapping of the additive. It is tempting to suggest that our combined observations mean that AD diastereocontrol is *completely* due to reagent control with respect to the BOM and PMB ethers but only *partly* with respect to the TBDPS ethers. However, such an interpretation neglects the fact that the diastereoselectivities of Table 7 distinctly lag behind typical enantioselectivities of ADs of "simple" – and achiral – enones:[6] these deliver at least 97% of the preferred enantiomer and not infrequently >99%. Accordingly, an attenuation of stereocontrol in AD reactions of enones with increased steric demand must be diagnosed.

With the finish line approaching, the phenylboronates *syn*-**39a** (92:8 mixture with *anti*-**39a**) and *anti*-**40b** (94:6 mixture with *syn*-**40b**) – those obtained with the highest diastereoselectivities – were deoxygenated at C^{α} (Scheme 4). With use of $SmBr_2$ as established by Zörb[6] this furnished the δ-protected β,δ-dihydroxy ketones *syn*-**41** and *anti*-**42** in 45% and 60% yields, respectively. These species were chromatographically inseparable 91:9 and 93:7 mixtures with their corresponding diastereomers. Compound *syn*-**41** was then subjected to a pair of highly diastereoselective carbonyl reductions, and *anti*-**42** was treated likewise. As a result we completed the diprotected 1,3,5-triols ^{1,3}*syn*,^{3,5}*syn*-**43** and ^{1,3}*syn*,^{3,5}*anti*-**44** when *syn*-**41** was reduced and the triprotected 1,3,5-triols ^{1,3}*anti*,^{3,5}*syn*-**45** and ^{1,3}*anti*,^{3,5}*anti*-**46** when *anti*-**42** was reduced.



* Here this term is used exclusively for the sake of compatibility and easier comparability with the stereodescriptors of the acyclic 1,3,5-triol derivatives. The IUPAC nomenclature would call for the term *cis* or (*R*)/(*S*) designations.

Scheme 4. $SmBr_2$-mediated α-reductions of the dioxaborolanes *syn*-**39a** and *anti*-**40b** to the corresponding monoprotected β,δ-dihydroxy ketones *syn*-**41** and *anti*-**42** and subsequent *syn*- and *anti*-selective reductions. *Reagents and conditions:* a) $SmBr_2$ [0.1 M in THF, 3.2 equiv.; prepared overnight from Sm powder (2.05 equiv.) and 1,1,2,2-tetrabromoethane (0.5 equiv.)], THF, –78 °C, addition of substrate in THF/MeOH (2:1, v/v), 90 min. b) BEt_3 (1.1 equiv.), THF/MeOH (4:1, v/v), room temp., 1 h, then –78 °C, addition of dioxaborolane in THF, 2 h, addition of $NaBH_4$ (1.2-fold molar quantity), 16 h. c) Isobutyraldehyde (4.0 equiv.), THF, –10 °C, addition of SmI_2 [0.1 M in THF, 10 mol-%; prepared overnight from Sm powder (1.05 equiv.) and 1,2-diiodoethane (1.0 equiv.)], 1 h.

In detail, reductions by the Narasaka procedure[11,12] did not provide the expected *syn*-1,3-diol moiety but the derived *cis*-*B*-ethyldioxaborinanes ^{1,3}*syn*,^{3,5}*syn*-**43** (80% from *syn*-**41**; inseparable 92:8 mixture with ^{1,3}*syn*,^{3,5}*anti*-**43**) and ^{1,3}*syn*,^{3,5}*anti*-**44** (77% from *anti*-**42**; inseparable 94:6 mix-

ture with ^{1,3}*syn*,^{3,5}*syn*-**44**). We are aware of a single literature report on the formation *at all* of a 1,3,2-dioxaborinane under the conditions of a Narasaka–Prasad reduction: the *cis*-substituted *B*-ethylated heterocycle and the *syn*-configured 1,3-diol arose in a 1:1 ratio.[12i] At room temp. the former product gave the latter after 3 h of a K_2CO_3-mediated methanolysis in methanol/ether 3:1.[31] *anti*-Selective Claisen–Tishchenko reductions in the presence of isobutyraldehyde and SmI_2[13,14] converted *syn*-**41** into ^{1,3}*anti*,^{3,5}*syn*-**45** (59%) and *anti*-**42** into ^{1,3}*anti*,^{3,5}*anti*-**46** (61%); both products were 89:11 mixtures with an inseparable diastereomer. In this step the already present protecting group on O^5 is preserved and an isobutyrate moiety is introduced on O^3.

Conclusions

The Körber/Risch strategy for synthesizing sterically homogeneous 1,3-diols (including monoprotected variants) from conjugated enones was elaborated into a vinylogous strategy of sorts. It leads from conjugated dienoates to sterically homogeneous di- or triprotected 1,3,5-triols. A centerpiece of our approach is the iteration of Sharpless' enantioselective AD reaction – which establishes two C–O bonds – and a regioselective reduction – which removes one C–O bond. The last step is a Narasaka–Prasad or Claisen–Tishchenko reduction.

In the resulting 1,3,5-triols (or rather their derivatives) the configurations of two C–O bonds are imposed by the choice of the ligand (AD mix-α™ or AD mix-β™). The configuration of the third C–O bond is determined by substrate control. Importantly, each of the stereochemical controls operates such that it is left entirely to the experimenter's judgement to decide which stereoisomer to go for. This was illustrated by making a complete set ("library") of differently protected 1,3,5-triols **43**–**46** with the four possible accessible combinations of the next-to-vicinal *syn* or *anti* relationships.

Experimental Section

General Information: Reactions were performed in oven-dried (110 °C) glassware under N_2. THF was freshly distilled from K; CH_2Cl_2 was distilled from CaH_2. Products were purified by flash chromatography[18] (column diameter, filling height, fraction volume, and eluents are given in parentheses; fractions containing the isolated product are indicated in each description as "fractions *xx*–*yy*") on Acros silica gel 60 (0.035–0.060 mm). Yields refer to analytically pure samples. ^{1}H NMR [$CHCl_3$ (δ = 7.26 ppm) as internal standard in $CDCl_3$ or C_6D_5H (δ = 7.16 ppm) as internal standard in C_6D_6]: Varian Mercury VX 300, Bruker AM 400, and Bruker DRX 500. Integrals agree with the given assignments. Coupling constants are given in Hz. ^{13}C NMR [$CDCl_3$ (δ = 77.10 ppm) as internal standard in $CDCl_3$ or C_6D_6 (δ = 128.06 ppm) as internal standard in C_6D_6]: Bruker AM 400 and Bruker DRX 500. Assignments of ^{1}H and ^{13}C NMR resonances refer to the IUPAC nomenclature except for substituents (where primed position numbers are used). Combustion analyses: E. Hickl and F. Tönnies. Chiral HPLC: G. Fehrenbach. MS: Dr. J. Wörth and C. Warth, all at the Institut für Organische Chemie und Biochemie, Universität Freiburg. IR spectra: Perkin–Elmer FT-IR Paragon 1000. Optical rotations (α_{exp}) were measured with a Perkin–Elmer 341 MC polarimeter at 589 nm, 578 nm, 546 nm, 436 nm, and 365 nm/20 °C and calculated according to the Drude equation $\{[a]_D = (\alpha_{exp} \times 100)/(c \times d)\}$; rotational values are the averages of five measurements of α_{exp} in a given solution of the sample.

Ethyl (2*E*,4*E*)-Octa-2,4-dienoate (12a): NaH [60% dispersion in mineral oil (3.10 g, 77.6 mmol, 1.8 equiv.)] was suspended in THF (72 mL) and cooled to –20 °C. Triethyl phosphonoacetate (**10**, 16.4 g, 73.3 mmol, 1.7 equiv.) was added over a period of 30 min. After the mixture had been stirred for 30 min at this temperature, *trans*-hex-2-enal (5.00 mL, 4.23 g, 43.1 mmol) was added slowly and the mixture was kept for 20 min at –20 °C. The reaction mixture was then quenched cautiously with satd. aq. NH_4Cl (35 mL). The phases were separated and the aq. phase was extracted with MTBE (*tert*-butyl methyl ether, 3 × 40 mL). The combined organic phases were washed with brine (10 mL) and dried with $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography (4 × 20 cm, 20 mL, cyclohexane/EtOAc 100:1) provided the title compound (fractions 8–29, 6.53 g, 90%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.71 (t, $J_{8,7}$ = 7.4 Hz, 8-H_3), 1.00 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 1.13 (qt, $J_{7,8}$ = 7.4, $J_{7,6}$ = 7.4 Hz, 7-H_2), 1.75 (m_c, approximately interpretable as tdd, $J_{6,7} = J_{6,5}$ = 7.3, $^4J_{6,4}$ = 1.3 Hz, 6-H_2), 4.01 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_3), 5.64 (dt, $J_{5,4}$ = 15.2, $J_{5,6}$ = 7.2 Hz, 5-H), 5.86 (m, 5-H), 5.87 (d, $J_{4,5}$ = 15.4 Hz, 4-H), 7.45 ppm (dd, $J_{3,2}$ = 15.3 Hz, $J_{3,4}$ = 11.2 Hz, 3-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 13.64 (C-8), 14.35 (C-2′), 22.06 (C-7), 35.01 (C-6), 60.02 (C-1′), 120.00 (C-2), 128.91 (C-4), 143.83 (C-5), 145.07 (C-3), 166.76 ppm (C-1). IR (film): $\tilde{\nu}$ = 3415, 2960, 2935, 2875, 1715, 1645, 1620, 1510, 1465, 1370, 1330, 1305, 1265, 1220, 1180, 1140, 1100, 1040, 1000, 865, 805, 770, 715 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{10}H_{16}O_2$ 168.11503 $[M]^+$; found 168.11510 (+0.4 ppm).

Ethyl (2*E*,4*E*)-6-Methylhepta-2,4-dienoate (12b): This compound was prepared from (*E*)-4-methylpent-2-enal (0.90 mL, 0.76 g, 7.74 mmol) as described for **12b**. Flash chromatography (2.5 × 19 cm, 20 mL, cyclohexane/EtOAc 100:1) provided the title compound (fractions 5–26, 1.29 g, 99%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.76 [d, $J_{7,6}$ and alternatively $J_{6\text{-Me},6}$ = 6.7 Hz, 6-$(CH_3)_2$], 1.00 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 2.02 (qqdd, $J_{6,5} = J_{6,6\text{-Me}} = J_{6.7}$ = 6.8, $^4J_{6.4}$ = 1.2 Hz, 6-H), 4.07 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_2), 5.63 (br. dd, $J_{5,4}$ = 15.1, $J_{5,6}$ = 6.9 Hz, 5-H), 5.86 (dddd, $J_{4,5}$ = 15.4, $J_{4,3}$ = 10.8, $^4J_{4.6}$ = 1.3, $^4J_{4.2}$ = 0.6 Hz, 4-H), 5.88 (dd, $J_{2,3}$ = 15.3, $^4J_{2,4}$ = 1.2 Hz, 2-H), 7.44 ppm (ddd, $J_{3,2}$ = 15.2 Hz, $J_{3,4}$ = 11.0 Hz, $^4J_{3,5}$ = 0.6 Hz, 3-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 14.35 (C-2′), 21.70 [6-$(CH_3)_2$], 31.56 (C-6), 60.02 (C-1′), 120.18 (C-2), 125.89 (C-4), 145.30 (C-5), 150.51 (C-3), 166.71 ppm (C-1). IR (film): $\tilde{\nu}$ = 3410, 2965, 2870, 1715, 1645, 1620, 1465, 1365, 1300, 1280, 1260, 1240, 1190, 1145, 1110, 1045, 1000, 875, 830 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{10}H_{16}O_2$ 168.11503 $[M]^+$; found 168.11480 (–1.4 ppm).

(2*E*,4*E*)-*N*-Methoxy-*N*-methylocta-2,4-dienamide (13a): Compound **12a** (2.50 g, 14.9 mmol) and Me(MeO)NH·HCl (4.35 g, 23.5 mL, 44.6 mmol, 3.0 equiv.) were dissolved in THF (270 mL) and cooled to –30 °C. *i*PrMgCl·LiCl (1.9 M in THF, 47.0 mL, 9.2 mmol, 6.0 equiv.) was then added over a period of 1 h. After 30 min at –30 °C the reaction mixture was quenched cautiously with satd. aq. NH_4Cl (120 mL), the phases were separated, and the aq. phase was extracted with MTBE (3 × 150 mL). The combined organic phases were washed with brine (120 mL) and dried with $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography (3.5 × 18 cm, 10 mL, cyclohexane/EtOAc 6:1) provided the

title compound (fractions 14–39, 2.16 g, 79%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.73 (t, $J_{8,7}$ = 7.4 Hz, 8-H_3), 1.18 (qt, $J_{7,8}$ = $J_{7,6}$ = 7.4 Hz, 7-H_2), 1.82 (tdd, $J_{6,7}$ = $J_{6.5}$ = 7.2, $^4J_{6.4}$ = 1.4 Hz, 6-H_2), 2.97 (s, NCH_3), 3.08 (s, OCH_3), 5.72 (dt, $J_{5,4}$ = 15.1, $J_{5,6}$ = 7.1 Hz, 5-H), 6.07 (ddtd, $J_{4,5}$ = 15.1, $J_{4.3}$ = 11.1, $^4J_{4.6}$ = 1.5, $^4J_{4.2}$ = 0.7 Hz, 4-H), 6.50 (d, $J_{2,3}$ = 15.2 Hz, 2-H), 7.71 ppm (ddd, $J_{3,2}$ = 15.2 Hz, $J_{3,4}$ = 11.2 Hz, $^4J_{3.5}$ = 0.8 Hz, 3-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 13.67 (C-8), 22.14 (C-7), 32.25 [N(CH)$_3$(OCH_3)], 35.11 (C-6), 61.02 [N(CH_3)$_3$(OCH_3)], 118.11 (C-2), 129.51 (C-4), 143.00 (C-5), 143.88 (C-3), 167.46 ppm (C-1). IR (film): $\tilde{\nu}$ = 3405, 2960, 2935, 2875, 1665, 1635, 1465, 1415, 1385, 1180, 1120, 1000 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{10}H_{17}NO_2$ 183.1259 [M]$^+$; found 183.1258 (–0.7 ppm).

(2*E*,4*E*)-*N*-Methoxy-*N*,6-dimethylhepta-2,4-dienamide (13b): This compound was prepared from **12b** (670 mg, 3.98 mmol) as described for **13a**. Flash chromatography (2 × 18.5 cm, 10 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 13–33, 584 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.80 (d, $J_{7,6}$ and alternatively $J_{6\text{-Me},6}$ = 6.7 Hz, 7-H_6), 2.08 (qqdd, $J_{6,5}$ = $J_{6,6\text{-Me}}$ = $J_{6,7}$ = 6.8, $^4J_{6.4}$ = 1.3 Hz, 6-H), 2.97 (s, NCH_3), 3.11 (s, OCH_3), 5.72 (br. dd, $J_{5,4}$ = 15.2, $J_{5,6}$ = 6.8 Hz, 5-H), 6.06 (dddd, $J_{4,5}$ = 15.3, $J_{4,3}$ = 11.1, $^4J_{4.6}$ = 1.4, $^4J_{4.2}$ = 0.7 Hz, 4-H), 6.51 (d, $J_{2,3}$ = 15.2 Hz, 2-H), 7.67 ppm (ddd, $J_{3,2}$ = 15.2 Hz, $J_{3,4}$ = 10.9 Hz, $^4J_{3,5}$ = 0.8 Hz, 3-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 21.81 [6-(CH_3)$_2$], 31.58 (C-6), 32.24 [N(CH)$_3$(OCH_3)], 61.02 [N(CH_3)$_3$(OCH_3)], 118.31 (C-2), 126.45 (C-4), 14.05 (C-5), 149.71 (C-3), 167.41 ppm (C-1). IR (film): $\tilde{\nu}$ = 3480, 2960, 2870, 1660, 1630, 1610, 1465, 1415, 1380, 1340, 1215, 1180, 1115, 1090, 1005, 875, 820, 775, 700 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{10}H_{17}NO_2$ 183.1259 [M]$^+$; found 183.1261 (+0.9 ppm).

(3*E*,5*E*)-Nona-3,5-dien-2-one (14a): Compound **13a** (1.80 g, 9.82 mmol) was dissolved in THF (18 mL) and cooled to –20 °C. MeLi (1.6 M in Et_2O, 13.5 mL, 21.6 mmol, 2.2 equiv.) was then added over 10 min. After 1 h at this temperature the reaction mixture was warmed to 0 °C and stirred for an additional 2 h. The reaction mixture was then quenched cautiously with satd. aq. NH_4Cl (10 mL) and the phases were separated. The aq. phase was extracted with MTBE (3 × 10 mL) and the combined organic phases were washed with brine (10 mL) and dried with $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography (3 × 17 cm, 20 mL, cyclohexane/EtOAc 40:1) provided the title compound (fractions 33–57, 1.22 g, 90%) as a slightly yellow oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.74 (t, $J_{9,8}$ = 7.3 Hz, 9-H_3), 1.19 (qt, $J_{8,9}$ = $J_{8,7}$ = 7.4 Hz, 8-H_2), 1.80 (tdd, $J_{7,8}$ = $J_{7.6}$ = 7.2, $^4J_{7.5}$ = 1.4 Hz, 7-H_2), 1.89 (s, 1-H_3), 5.67 (dt, $J_{6,5}$ = 15.0, $J_{6,7}$ = 7.1 Hz, 6-H), 5.84 (ddtd, $J_{5,6}$ = 15.2, $J_{5,4}$ = 10.7, $^4J_{5.7}$ = 1.4, $^4J_{5.3}$ = 0.7 Hz, 5-H), 5.93 (d, $J_{3,4}$ = 15.7 Hz, 3-H), 6.91 ppm (ddd, $J_{4,3}$ = 15.7 Hz, $J_{4,5}$ = 10.7 Hz, $^4J_{4.6}$ = 0.5 Hz, 4-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 13.66 (C-9), 22.13 (C-8), 27.06 (C-1), 35.14 (C-7), 129.31 (C-3), 129.44 (C-5), 142.82 (C-6), 144.17 (C-4), 196.50 ppm (C-2). IR (film): $\tilde{\nu}$ = 3325, 2960, 2930, 2875, 1690, 1635, 1595, 1460, 1435, 1360, 1330, 1310, 1295, 1255, 1185, 1150, 1110, 1045, 1000, 960, 895, 855, 740 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_9H_{14}O$ 138.1045 [M]$^+$; found 138.1045 (+0.2 ppm).

(3*E*,5*E*)-7-Methylocta-3,5-dien-2-one (14b): This compound was prepared from **13b** (1.45 g, 7.89 mmol) as described for **14a**. Flash chromatography (3 × 15 cm, 20 mL, cyclohexane/EtOAc 60:1) provided the title compound (fractions 34–62, 1.08 g, 99%) as a slightly yellow oil. ^{1}H NMR (400 MHz, C_6D_6/C_6D_5H): δ = 0.81 (d, $J_{8,7}$ and alternatively $J_{7\text{-Me},7}$ = 6.7 Hz, 8-H_6), 1.90 (s, 1-H_3), 2.06 (qqdd, $J_{7,6}$ = $J_{7.7\text{-Me}}$ = $J_{7.8}$ = 6.8, $^4J_{7.5}$ = 0.6 Hz, 7-H), 5.65 (br. dd, $J_{6,5}$ = 15.3, $J_{6,7}$ = 6.8 Hz, 6-H), 5.83 (dddd, $J_{5,6}$ = 15.2, $J_{5,4}$ = 10.6, $^4J_{5.7}$ = 1.2, $^4J_{5.3}$ = 0.6 Hz, 5-H), 5.94 (d, $J_{3,4}$ = 15.7 Hz, 3-H), 6.90 ppm (dd, $J_{4,3}$ = 15.6 Hz, $J_{4,5}$ = 10.4 Hz, 4-H). ^{13}C NMR (100 MHz, C_6D_6): δ = 21.76 [7-(CH_3)$_2$], 27.04 (C-1), 31.69 (C-7), 126.40 (C-3), 129.51 (C-5), 143.07 (C-6), 150.86 (C-4), 196.46 ppm (C-2). IR (film): $\tilde{\nu}$ = 3320, 2960, 2930, 2870, 1670, 1635, 1595, 1465, 1425, 1360, 1275, 1255, 1235, 1155, 1110, 995 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_9H_{14}O$ 138.1045 [M]$^+$; found 138.1045 (+0.2 ppm).

Ethyl (4*R*,5*R*,*E*)-4,5-Dihydroxyoct-2-enoate (15a): Compound **12a** (1.54 g, 9.13 mmol) was added at 0 °C to a stirred mixture of $K_2OsO_2(OH)_4$ (33.7 mg, 1 mol-%), $(DHQD)_2PHAL$ (357 mg, 5 mol-%), $K_3Fe(CN)_6$ (9.02 g, 27.4 mmol, 3.0 equiv.), K_2CO_3 (3.78 g, 27.4 mmol, 3.0 equiv.), $NaHCO_3$ (2.30 g, 27.4 mmol, 3.0 equiv.), and $MeSO_2NH_2$ (0.87 mg, 9.13 mmol, 1.0 equiv.) in a mixture of *t*BuOH and H_2O (1:1, 90 mL). After the system had been kept for 4 d at this temperature, EtOAc (40 mL) was added and the phases were separated. The aq. phase was extracted with EtOAc (3 × 30 mL). The combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (3 × 14 cm, 20 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 20–38, 1.44 g, 78%) as a colorless oil. $[\alpha]_{589}^{20}$ = +29.3, $[\alpha]_{578}^{20}$ = +30.8, $[\alpha]_{546}^{20}$ = +35.2, $[\alpha]_{436}^{20}$ = +63.2, $[\alpha]_{365}^{20}$ = +108.2 (*c* = 0.60, $CHCl_3$). The *ee* (98.5%) was determined by chiral HPLC [Chiralpak AD-H, *n*-heptane/EtOH (70:30), 0.8 mL min^{-1}, 215 nm]: $t_{r(4R,5R)}$ = 10.7 min, $t_{r(4S,5S)}$ = 7.1 min (determined with racemic material). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 (dd, $J_{8,7\text{-H(A)}}$ = $J_{8,7\text{-H(B)}}$ = 7.0 Hz, 8-H_3), 1.28 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 1.31–1.58 (m, 6-H_2, 7-H_2), 2.28 (d, $J_{5\text{-OH},5}$ = 4.7 Hz, 5-OH), 2.64 (d, $J_{4\text{-OH},4}$ = 5.3 Hz, 4-OH), 3.56 (m_c, 5-H), 4.11 (dddd, $J_{4,3}$ = $J_{4,4\text{-OH}}$ = $J_{4,5}$ = 5.2, $^4J_{4,2}$ = 1.7 Hz, 4-H), 4.19 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H), 6.12 (dd, $J_{2,3}$ = 15.7, $^4J_{2,4}$ = 1.7 Hz, 2-H), 6.92 ppm (dd, $J_{3,2}$ = 15.7 Hz, $J_{3,4}$ = 5.1 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.02 (C-2′), 14.29 (C-8), 18.87 (C-7), 35.26 (C-6), 60.69 (C-1′), 73.85 (C-5), 74.26 (C-4), 122.59 (C-2), 146.89 (C-3), 166.41 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2960, 2935, 2875, 1705, 1660, 1465, 1395, 1370, 1305, 1275, 1220, 1180, 1130, 1080, 1035, 985, 870, 770 cm^{-1}. $C_{10}H_{18}O_4$ (202.25): calcd. C 59.39, H 8.97; found C 59.09, H 8.98.

Ethyl (4*R*,5*R*,*E*)-4,5-Dihydroxy-6-methylhept-2-enoate (15b): This compound was prepared from **12b** (2.0 g, 12 mmol) as described for **15a**. Flash chromatography (3 × 16 cm, 20 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 25–44, 1.59 g, 66%) as a colorless oil. $[\alpha]_{589}^{20}$ = +15.5, $[\alpha]_{578}^{20}$ = +16.8, $[\alpha]_{546}^{20}$ = +19.0, $[\alpha]_{436}^{20}$ = +35.2, $[\alpha]_{365}^{20}$ = +61.1 (*c* = 0.61, $CHCl_3$). The *ee* (98.0%) was determined by chiral HPLC [Chiralpak AD-H, *n*-heptane/EtOH (80:20), 0.8 mL min^{-1}, 215 nm]: $t_{r(4R,5R)}$ = 16.4 min, $t_{r(4S,5S)}$ = 10.3 min (determined with racemic material). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 and 0.93 [2 × d, $J_{6\text{-Me},6}$ = 6.8 Hz, 6-(CH_3)$_2$], 1.28 (t, $J_{2',1'}$ = 7.2 Hz, 2′-H_3), 1.79 (qqd, $J_{6,7}$ = $J_{6,6\text{-Me}}$ = 6.7, $J_{6,5}$ = 5.8 Hz, 6-H), 2.00, (d, $J_{4\text{-OH},4}$ = 4.9 Hz, 4-OH), 2.37 (d, $J_{5\text{-OH},5}$ = 5.7 Hz, 5-OH), 3.24 (m_c, approximately interpretable as ddd, $J_{5,5\text{-OH}}$ = 5.2, $J_{5,4}$ = $J_{5,6}$ = 4.9 Hz, 5-H), 4.14 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H), 4.25 (dddd, $J_{4,3}$ = $J_{4,4\text{-OH}}$ = $J_{4,5}$ = 4.9, $^4J_{4,2}$ = 1.7 Hz, 4-H), 6.07 (dd, $J_{2,3}$ = 15.7, $^4J_{2,4}$ = 1.7 Hz, 2-H), 6.87 ppm (dd, $J_{3,2}$ = 16.0 Hz, $J_{3,4}$ = 4.9 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.30 (C-2′), 17.10 and 19.72 [6-(CH_3)$_2$], 30.10 (C-6), 60.66 (C-2′), 71.90 (C-4), 78.75 (C-5), 122.41 (C-2), 147.39 (C-3), 166.39 ppm (C-1). IR (film): $\tilde{\nu}$ = 3420, 2960, 2875, 1715, 1655, 1465, 1370, 1305, 1275, 1175, 1115, 1090, 1040, 980, 940, 875, 820, 770 cm^{-1}. $C_{10}H_{18}O_4$ (202.25): calcd. C 59.39, H 8.97; found C 59.16, H 8.99.

(4*R*,5*R*,*E*)-4,5-Dihydroxy-*N*-methoxy-*N*-methyloct-2-enamide (16a): This compound was prepared from **13a** (120 mg, 0.65 mmol) as

described for **15a**. Flash chromatography (1 × 10 cm, 4.5 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 32–55, 82.5 mg, 58%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = –33.8, $[\alpha]_{578}^{20}$ = –35.5, $[\alpha]_{546}^{20}$ = –40.7, $[\alpha]_{436}^{20}$ = –73.3, $[\alpha]_{365}^{20}$ = –128.5 (*c* = 0.87, $CHCl_3$). The *ee* (96.6%) was determined by chiral HPLC [Chiralpak OD-H, *n*-heptane/EtOH (100:3), 1.0 mL min^{-1}, 40 °C isotherm, 215 nm]: $t_{r(4R,5R)}$ = 24.7 min, $t_{r(4S,5S)}$ = 29.1 min (determined with racemic material). ^{1}H NMR (500 MHz, $CDCl_3$/$CHCl_3$): δ = 0.91 (dd, $J_{8,7\text{-H(A)}} = J_{8,7\text{-H(B)}}$ = 6.9 Hz, 8-H_3), 1.30–1.56 (m, 7-H_2, 6-H_2), 3.11 (br. s, 5-OH), 3.23 (s, NCH_3), 3.37 (br. s, 4-OH), 3.55 (ddd, $J_{5,6\text{-H(A)}}$ = 8.0, $J_{5,6\text{-H(B)}} = J_{5,4}$ = 4.6 Hz, 5-H), 3.67 (s, OCH_3), 4.12 (m_c, 4-H), 6.68 (d, $J_{2,3}$ = 15.4 Hz, 2-H), 6.92 ppm (dd, $J_{3,2}$ = 15.4 Hz, $J_{3,4}$ = 5.0 Hz, 3-H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.04 (C-8), 18.91 (C-7), 32.44 [N(*C*H)$_3$(OCH_3)], 35.18 (C-6), 61.90 [N(CH_3)$_3$(O*C*H$_3$)], 73.92 (C-4), 74.62 (C-5), 119.61 (C-2), 146.20 (C-3), 166.59 ppm (C-1). IR (film): $\tilde{\nu}$ = 3400, 2960, 2935, 2875, 1660, 1620, 1425, 1385, 1180, 1080, 1000, 850 cm^{-1}. $C_{10}H_{19}NO_4$ (217.26): calcd. C 55.28, H 8.81, N 6.45; found C 55.13, H 9.01, N 6.25.

(4*R*,5*R*,*E*)-4,5-Dihydroxy-*N*-methoxy-*N*,6-dimethylhept-2-enamide (16b): This compound was prepared from **13b** (100 mg, 0.55 mmol) as described for **15a**. Flash chromatography (1 × 11 cm, 4.5 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 20–42, 100 mg, 84%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +17.9, $[\alpha]_{578}^{20}$ = +18.7, $[\alpha]_{546}^{20}$ = +21.6, $[\alpha]_{536}^{20}$ = +39.6, $[\alpha]_{365}^{20}$ = +69.8 (*c* = 0.94, $CHCl_3$). The *ee* (98.9%) was determined by chiral HPLC [Chiralpak AD-H, *n*-heptane/EtOH (90:10), 0.8 mL min^{-1}, 215 nm]: $t_{r(4R,5R)}$ = 34.7 min, $t_{r(4S,5S)}$ = 25.5 min (determined with racemic material). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.97 and 0.97 [2 × d, $J_{6\text{-Me},6}$ = 6.8 Hz, 6-(CH_3)$_2$], 1.85 (qqd, $J_{6,7} = J_{6,6\text{-Me}}$ = 6.8, $J_{6,5}$ = 5.8 Hz, 6-H), 2.88 (d, $J_{5\text{-OH},5}$ = 4.8 Hz, 5-OH), 3.13 (d, $J_{4\text{-OH},4}$ = 6.3 Hz, 4-OH), 3.70 (s, NCH_3), 3.29 (ddd, $J_{5,6}$ = 5.5, $J_{5,4} = J_{5,5\text{-OH}}$ = 5.0 Hz, 5-H), 3.70 (s, OCH_3), 4.32 (dddd, $J_{4,4\text{-OH}}$ = 6.3, $J_{4,5} = J_{4,3}$ = 4.8, $^4J_{4,2}$ = 1.6 Hz, 4-H), 6.69 (dd, $J_{2,3}$ = 15.6, $^4J_{2,4}$ = 1.2 Hz, 2-H), 6.93 ppm (dd, $J_{3,2}$ = 15.3 Hz, $J_{3,4'}$ = 4.9 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.25 and 19.74 [6-(CH_3)$_2$], 30.03 (C-6), 32.45 [N(*C*H$_3$)(OCH_3)], 61.90 [N(CH_3)(O*C*H$_3$)], 72.27 (C-4), 78.82 (C-5), 119.46 (C-2), 146.68 (C-3), 166.62 ppm (C-1). IR (film): $\tilde{\nu}$ = 3385, 2960, 1735, 1720, 1685, 1660, 1615, 1425, 1385, 1245, 1180, 1145, 1125, 1085, 995 cm^{-1}. $C_{10}H_{19}NO_4$ (217.26): calcd. C 55.28, H 8.81, N 6.45; found C 55.19, H 9.09, N 6.23.

(5*R*,6*R*,*E*)-5,6-Dihydroxynon-3-en-2-one (17a): This compound was prepared from **14a** (800 mg, 5.79 mmol) as described for **15a**. Flash chromatography (2 × 14 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound [fractions 28–52, 518 mg, 52% (in a 78:22 mixture (w/w) with $MeSO_2NH_2$, which co-chromatographed with **17a**. An analytically pure sample of **17a** was obtained by following the same procedure but in the absence of $MeSO_2NH_2$; the yield then, however, was only 44%)] as a yellow oil. $[\alpha]_{589}^{20}$ = +35.4, $[\alpha]_{578}^{20}$ = +37.1, $[\alpha]_{546}^{20}$ = +42.6, $[\alpha]_{436}^{20}$ = +73.0 (*c* = 0.96, $CHCl_3$). The *ee* (97.2%) was determined by chiral HPLC [Chiralpak AD-H, *n*-heptane/EtOH (80:20), 0.8 mL min^{-1}, 215 nm]: $t_{r(5R,6R)}$ = 12.4 min, $t_{r(5S,6S)}$ = 9.7 min (determined with racemic material). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.94 (dd, $J_{9,8\text{-H(A)}} = J_{9,8\text{-H(B)}}$ = 6.8 Hz, 9-H_3), 1.33–1.57 (m, 7-H_2, 8-H_2), 2.28 (s, 1-H_3), 2.78 (d, $J_{6\text{-OH},6}$ = 4.9 Hz, 6-OH), 3.22 (d, $J_{5\text{-OH},5}$ = 5.3 Hz, 5-OH), 3.58 (m_c, 6-H), 4.14 (dddd, $J_{5,4} = J_{5,6} = J_{5,5\text{-OH}}$ = 5.2, $^4J_{5,3}$ = 1.6 Hz, 5-H), 6.35 (dd, $J_{3,4}$ = 15.9, $^4J_{3,5}$ = 1.6 Hz, 3-H), 6.78 ppm (dd, $J_{4,3}$ = 15.9 Hz, $J_{4,5}$ = 5.1 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.01 (C-9), 18.88 (C-8), 27.62 (C-1), 35.33 (C-7), 73.84 (C-5), 74.25 (C-6), 130.90 (C-3), 146.13 (C-4), 198.87 ppm (C-2). IR (film): $\tilde{\nu}$ = 3395, 2960, 2870, 1675, 1635, 1505, 1465, 1425, 1365, 1260, 1120, 1075, 1025, 980 cm^{-1}. HRMS (Cl, NH_3): calcd. for $C_9H_{20}NO_3$ 190.1443 [M – NH_4]$^+$; found 190.1447 (+2.0 ppm). $C_9H_{16}O_3$ (172.22): calcd. C 62.77, H 9.36; found C 62.90, H 9.38.

(5*R*,6*R*,*E*)-5,6-Dihydroxy-7-methyloct-3-en-2-one (17b): This compound was prepared from **14b** (738 mg, 5.34 mmol) as described for **15a**. Flash chromatography (2 × 12 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound [fractions 24–42, 506 mg, 55% (in a 80:20 mixture (w/w) with $MeSO_2NH_2$, which co-chromatographed with **17b**; an analytically pure sample of **17b** was obtained by following the same procedure but in the absence of $MeSO_2NH_2$; the yield then, however, was only 35%)] as a yellow oil. $[\alpha]_{589}^{20}$ = +12.9, $[\alpha]_{578}^{20}$ = +13.3, $[\alpha]_{546}^{20}$ = +15.3, $[\alpha]_{436}^{20}$ = +21.8, $[\alpha]_{365}^{20}$ = +54.5 (*c* = 0.48, $CHCl_3$). The *ee* (98.2%) was determined by chiral HPLC [Chiralpak AD-H, *n*-heptane/EtOH (70:30), 0.8 mL min^{-1}, isotherm 10 °C, 215 nm]: $t_{r(5R,6R)}$ = 11.3 min, $t_{r(5S,6S)}$ = 8.8 min (determined with racemic material). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 and 0.93 [2 × d, $J_{7\text{-Me},7}$ = 6.8 Hz, 7-(CH_3)$_2$], 1.78 (qqd, $J_{7,8} = J_{7,7\text{-Me}}$ = 6.8, $J_{7,6}$ = 5.9 Hz, 7-H), 2.40, (br. s, 6-OH), 2.81 (br. s, 5-OH), 3.24 (m_c, 6-H), 4.27 (m_c, 5-H), 6.30 (dd, $J_{3,4}$ = 16.0, $^4J_{3,5}$ = 1.6 Hz, 3-H), 6.71 ppm (dd, $J_{4,3}$ = 16.0, $J_{4,5}$ = 5.1 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.24 and 19.69 [7-(CH_3)$_2$], 27.67 (C-7), 30.23 (C-1), 71.90 (C-5), 78.81 (C-6), 130.75 (C-3), 146.48 (C-4), 198.66 ppm (C-2). IR (film): $\tilde{\nu}$ = 3395, 2960, 2930, 2875, 1675, 1635, 1505, 1465, 1425, 1360, 1260, 1175, 1140, 1120, 1090, 1045, 1010, 980, 945, 805, 725 cm^{-1}. HRMS (Cl, NH_3): calcd. for $C_9H_{20}NO_3$ 190.1443 [M – NH_4]$^+$; found 190.1445 (+1.0 ppm). $C_9H_{16}O_3$ (172.22): calcd. C 62.77, H 9.36; found C 62.61, H 9.55.

(*E*)-4-[(4*R*,5*R*)-2-Phenyl-5-propyl-1,3,2-dioxaborolan-4-yl]-but-3-en-2-one (18): Compound **17a** (205 mg, 1.19 mmol) and phenylboronic acid (176 mg, 1.43 mmol, 1.2 equiv.) were dissolved in CH_2Cl_2 (7 mL) and stirred at room temp. for 24 h. The solvent was removed under reduced pressure and flash chromatography (1.5 × 18 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 12–30, 316 mg, 85%) as a colorless oil. $[\alpha]_{589}^{20}$ = –47.9, $[\alpha]_{578}^{20}$ = –50.5, $[\alpha]_{546}^{20}$ = –58.7, $[\alpha]_{436}^{20}$ = –113.3, $[\alpha]_{365}^{20}$ = –192.1 (*c* = 0.70, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 1.10 (dd, $J_{3'',2''\text{-H(A)}} = J_{3'',2''\text{-H(B)}}$ = 7.3 Hz, 3''-H_3), 1.51–1.73 (m, 2''-H_2), AB signal (δ_A = 1.78, δ_B = 1.86, J_{AB} = 13.4, A part additionally split by $J_{A,2''\text{-H(A)}}$ = 9.8, $J_{A,2''\text{-H(B)}}$ = 5.9, $J_{A,5}$ = 5.3 Hz, B part additionally split by $J_{B,2''\text{-H(B)}}$ = 10.1 Hz, $J_{B,5}$ = 7.4 Hz, $J_{B,2''\text{-H(A)}}$ = 5.5 Hz, 1''-H_2), 2.39 (d, $^4J_{1,3}$ = 0.4 Hz, 1-H_3), 4.36 (ddd, $J_{5',4'} = J_{5',1''\text{-H(B)}}$ = 7.1, $J_{5',1''\text{-H(A)}}$ = 5.3 Hz, 5'-H), 4.82 (m_c, approximately interpretable as ddd, $J_{4',5'}$ = 6.9, $J_{4',4}$ = 5.3, $^4J_{4',3}$ = 1.6 Hz, 4'-H), 6.48 (dd, $J_{3,4}$ = 15.9, $^4J_{3,4'}$ = 1.5 Hz, 3-H), 6.88 (ddd, $J_{4,3}$ = 15.9, $J_{4,4'}$ = 5.2, $^4J_{4,1}$ = 0.5 Hz, 4-H), 7.49 (m_c, 2× *meta*-H), 7.59 (m_c, *para*-H), 7.94 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.99 (C-3''), 18.43 (C-2''), 27.86 (C-1), 38.00 (C-1''), 81.66 (C-5'), 82.41 (C-4'), 127.98 (2× *meta*-C, *para*-C), 130.13 (C-3), 131.83 (*ipso*-C), 135.01 (2× *ortho*-C), 143.89 (C-4), 197.88 ppm (C-2). IR (film): $\tilde{\nu}$ = 3395, 3080, 3055, 3025, 2960, 2935, 2875, 1700, 1680, 1635, 1605, 1500, 1440, 1405, 1360, 1320, 1255, 1235, 1210, 1175, 1115, 1095, 1070, 1030, 985, 945, 890, 850, 800, 770 cm^{-1}. $C_{15}H_{19}BO_3$ (258.12): calcd. C 69.8, H 7.42; found C 69.59, H 7.31.

Ethyl (*E*)-3-[(4*R*,5*R*)-2-Oxo-5-propyl-1,3-dioxolan-4-yl]acrylate (23a): Compound **17a** (366 mg, 1.81 mmol) and pyridine (0.73 mL, 0.72 g, 9.10 mmol, 5.0 equiv.) were dissolved in CH_2Cl_2 (5 mL) and the mixture was cooled to 0 °C. A solution of triphosgene (590 mg, 1.99 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL) was then slowly added. The reaction was stirred for 1.5 h and quenched cautiously with satd. aq. NH_4Cl (10 mL). The phases were separated and the aq. phase was extracted with MTBE (3 × 10 mL). The combined or-

ganic phases were washed with satd. aq. $NaHCO_3$ (10 mL) and brine (10 mL) and dried with $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography (2 × 18 cm, 10 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 8–19, 356 mg, 88%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +42.4, $[\alpha]_{578}^{20}$ = +44.0, $[\alpha]_{546}^{20}$ = +50.0, $[\alpha]_{436}^{20}$ = +83.2, $[\alpha]_{365}^{20}$ = +127.4 (*c* = 0.51, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.97 (dd, $J_{3''',2'''\text{-H(A)}}$ = $J_{3''',2'''\text{-H(B)}}$ = 7.4 Hz, 3′′′-H_3), 1.29 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), AB signal (δ_A = 1.44, δ_B = 1.53, J_{AB} = 13.3 Hz, A part additionally split by $J_{A,1'''\text{-H(A)}}$ = 9.7 Hz, $J_{A,3'''}$ = 7.2 Hz, $J_{A,1'''\text{-H(B)}}$ = 6.2 Hz, B part additionally split by $J_{B,1'''\text{-H(B)}}$ = 9.4 Hz, $J_{B,3'''}$ = 7.5 Hz, $J_{B,1'''\text{-H(A)}}$ = 5.6 Hz, 2′′′-H_2), AB signal (δ_A = 1.70, δ_B = 1.80, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,2'''\text{-H(A)}}$ = 9.5 Hz, $J_{A,5''}$ = 8.1 Hz, $J_{A,2'''\text{-H(B)}}$ = 5.7 Hz, B part additionally split by $J_{B,2'''\text{-H(B)}}$ = 9.5 Hz, $J_{B,2'''\text{-H(A)}}$ = 6.1 Hz, $J_{B,5''}$ = 4.8 Hz, 1′′′-H_2), 4.21 (q, $J_{1',2'}$ = 7.2 Hz, 2′-H_3), 4.35 (ddd, $J_{5'',1'''\text{-H(A)}}$ = 7.8, $J_{5'',4''}$ = 7.2, $J_{5'',1'''\text{-H(B)}}$ = 5.0 Hz, 5′′-H), 4.80 (ddd, $J_{4'',5''}$ = 7.2, $J_{4'',3}$ = 5.7, $^4J_{4'',2}$ = 1.5 Hz, 4′′-H), 6.16 (dd, $J_{2,3}$ = 15.7, $^4J_{2,4''}$ = 1.5 Hz, 2-H), 6.82 ppm (dd, $J_{3,2}$ = 15.7 Hz, $J_{3,4''}$ = 5.7 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.62 (C-3′′′), 14.18 (C-2′), 18.08 (C-2′′′), 35.28 (C-1′′′), 61.18 (C-1′), 79.92 (C-5′′), 81.26 (C-4′′), 125.00 (C-3), 139.35 (C-2), 153.68 (C-2′′), 164.97 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2965, 2940, 2875, 1810, 1725, 1665, 1510, 1465, 1370, 1305, 1275, 1180, 1090, 1035, 980, 870, 770 cm^{-1}. $C_{11}H_{16}O_5$ (228.24): calcd. C 57.88, H 7.07; found C 57.77, H 7.21.

Ethyl (*E*)-3-[(4*R*,5*R*)-5-Isopropyl-2-oxo-1,3-dioxolan-4-yl]acrylate (23b): This compound was prepared from **15b** (934 mg, 4.62 mmol) as described for **23a**. Flash chromatography (1.5 × 15 cm, 5 mL, cyclohexane/EtOAc 6:1) provided the title compound (fractions 10–18, 822 mg, 78%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +33.0, $[\alpha]_{578}^{20}$ = +34.7, $[\alpha]_{546}^{20}$ = +39.3, $[\alpha]_{436}^{20}$ = +64.8, $[\alpha]_{365}^{20}$ = +98.4 (*c* = 0.45, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 1.01 and 1.05 [2 × d, $J_{1'''\text{-Me},1'''}$ = 6.8 Hz, 1′′′-$(CH_3)_2$], 1.30 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 2.01 (qqd, $J_{1''',2'''}$ = $J_{1''',1'''\text{-Me}}$ = $J_{1''',5''}$ = 6.8 Hz, 1′′′-H), 4.13 (dd, $J_{5'',4''}$ = $J_{5'',1''}$ = 6.6 Hz, 5′′-H), 4.22 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_2), 4.91 (ddd, $J_{4'',5''}$ = 6.6, $J_{4'',3}$ = 5.4, $^4J_{4'',2}$ = 1.3 Hz, 4′′-H), 6.18 (dd, $J_{2,3}$ = 15.7, $^4J_{2,4''}$ = 1.5 Hz, 2-H), 6.82 ppm (dd, $J_{3,2}$ = 15.7 Hz, $J_{3,4''}$ = 5.4 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.21 (C-1′), 17.13 and 17.22 [1′′′-$(CH_3)_2$], 31.74 (C-1′′′), 61.20 (C-1′), 77.63 (C-4′′), 85.74 (C-5′′), 124.61 (C-3), 140.35 (C-2), 153.92 (C-2′′), 165.08 ppm (C-1). IR (film): $\tilde{\nu}$ = 3425, 2970, 2935, 2880, 1810, 1720, 1665, 1465, 1395, 1365, 1310, 1280, 1250, 1185, 1095, 1055, 980 cm^{-1}. $C_{11}H_{16}O_5$ (228.24): calcd. C 57.88, H 7.07; found C 57.73, H 7.06.

(*E*)-3-[(4*R*,5*R*)-2-Oxo-5-propyl-1,3-dioxolan-4-yl]-*N*-methoxy-*N*-methylacrylamide (24a): This compound was prepared from **16a** (534 mg, 2.46 mmol) as described for **23a**. Flash chromatography (2 × 14 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 17–38, 430 mg, 72%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +56.5, $[\alpha]_{578}^{20}$ = +58.9, $[\alpha]_{546}^{20}$ = +67.1, $[\alpha]_{436}^{20}$ = +115.4, $[\alpha]_{365}^{20}$ = +186.4 (*c* = 0.68, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.99 (dd, $J_{3'',2''\text{-H(A)}}$ = $J_{3'',2''\text{-H(B)}}$ = 7.4 Hz, 3′′-H_3), AB signal (δ_A = 1.45, δ_B = 1.56, J_{AB} = 13.3 Hz, A part additionally split by $J_{A,1''\text{-H(A)}}$ = 9.8 Hz, $J_{A,3''}$ = 7.2 Hz, $J_{A,1''\text{-H(B)}}$ = 6.3 Hz, B part additionally split by $J_{B,1''\text{-H(B)}}$ = 9.5 Hz, $J_{B,3''}$ = 7.6 Hz, $J_{B,1''\text{-H(A)}}$ = 5.7 Hz, 2′′-H_2), AB signal (δ_A = 1.73, δ_B = 1.82, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,2''\text{-H(A)}}$ = 9.8 Hz, $J_{A,5'}$ = 8.0 Hz, $J_{A,2''\text{-H(B)}}$ = 5.5 Hz, B part additionally split by $J_{B,2''\text{-H(B)}}$ = 9.5 Hz, $J_{B,2''\text{-H(A)}}$ = 6.1 Hz, $J_{B,5'}$ = 4.8 Hz, 1′′-H_2), 3.26 (s, NCH_3), 3.72 (s, OCH_3), 4.37 (ddd, $J_{5',1''\text{-H(A)}}$ = $J_{5',4'}$ = 7.6, $J_{5',1''\text{-H(B)}}$ = 5.0 Hz, 5′-H), 4.86 (ddd, $J_{4',5'}$ = 7.4, $J_{4',3}$ = 4.7, $^4J_{4,2'}$ = 1.1 Hz, 4′-H), 6.78 (d, $J_{2,3}$ = 15.8 Hz, 2-H), 6.85 ppm (dd, $J_{3,2}$ = 15.4 Hz, $J_{3,4'}$ = 4.7 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.68 (C-3′′), 18.15 (C-2′′), 32.45 [N(CH_3)(OCH_3)], 35.33 (C-1′′), 62.14 [N(CH_3)(OCH_3)], 80.43 (C-5′), 81.60 (C-4′), 122.09 (C-2), 137.91 (C-3), 153.94 (C-2′), 164.87 ppm (C-1). IR (film): $\tilde{\nu}$ = 3445, 2960, 2940, 2875, 1805, 1670, 1635, 1460, 1420, 1380, 1310, 1220, 1180, 1120, 1085, 1060, 1035, 995, 770 cm^{-1}. $C_{11}H_{17}NO_5$ (243.26): calcd. C 54.31, H 7.04; found C 54.10, H 7.03.

(*E*)-3-[(4*R*,5*R*)-5-Isopropyl-2-oxo-1,3-dioxolan-4-yl]-*N*-methoxy-*N*-methylacrylamide (24b): This compound was prepared from **16b** (2.66 g, 12.2 mmol) as described for **23a**. Flash chromatography (3 × 15 cm, 20 mL, cyclohexane/EtOAc 3:1) provided the title compound (fractions 32–55, 2.32 mg, 78%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +51.6, $[\alpha]_{578}^{20}$ = +54.0, $[\alpha]_{546}^{20}$ = +61.5, $[\alpha]_{436}^{20}$ = +106.7, $[\alpha]_{365}^{20}$ = +175.2 (*c* = 0.93, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 1.01 and 1.05 [2 × d, $J_{1''\text{-Me},1''}$ = 6.7 Hz, 1′′-$(CH_3)_2$], 2.01 (qqd, $J_{1'',2''}$ = $J_{1'',1''\text{-Me}}$ = $J_{1'',5'}$ = 6.6 Hz, 1′′-H), 3.26 (s, NCH_3), 3.71 (s, OCH_3), 4.13 (dd, $J_{5',1'}$ = $J_{5',4'}$ = 6.6 Hz, 5′-H), 4.96 (ddd, $J_{4',5'}$ = 6.7, $J_{4',3}$ = 4.5, $^4J_{4',2}$ = 1.1 Hz, 4′-H), 6.76 (d, $J_{2,3}$ = 15.8 Hz, 2-H), 6.84 ppm (dd, $J_{3,2}$ = 15.4 Hz, $J_{3,4'}$ = 4.5 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.12 and 17.27 [$(CH_3)_2$–1′′], 31.72 (C-1′′), 32.42 [N(CH_3)(OCH_3)], 62.11 [N(CH_3)(OCH_3)], 78.11 (C-5′), 85.97 (C-4′), 121.64 (C-2), 138.97 (C-3), 153.92 (C-2′), 164.90 ppm (C-1). IR (film): $\tilde{\nu}$ = 2965, 2940, 2880, 1810, 1670, 1640, 1465, 1425, 1385, 1275, 1170, 1125, 1050, 995, 770 cm^{-1}. $C_{11}H_{17}NO_5$ (243.26): calcd. C 54.31, H 7.04; found C 54.10, H 7.14.

(4*R*,5*R*)-4-[(*E*)-3-Oxobut-1-enyl]-5-propyl-1,3-dioxolan-2-one (25a): This compound was prepared from **17a** (4.04 g, 23.5 mmol) as described for **23a**. Flash chromatography (4.5 × 18 cm, 50 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 8–25, 4.43 g, 95%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +44.7, $[\alpha]_{578}^{20}$ = +46.7, $[\alpha]_{546}^{20}$ = +53.1, $[\alpha]_{436}^{20}$ = +92.7, $[\alpha]_{365}^{20}$ = +181.8 (*c* = 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.98 (dd, $J_{3',2'\text{-H(A)}}$ = $J_{3',2'\text{-H(B)}}$ = 7.3 Hz, 3′-H_3), AB signal (δ_A = 1.45, δ_B = 1.54, J_{AB} = 13.3 Hz, A part additionally split by $J_{A,1'\text{-H(A)}}$ = 9.8 Hz, $J_{A,3'}$ = 7.2 Hz, $J_{A,1'\text{-H(B)}}$ = 6.2 Hz, B part additionally split by $J_{B,1'\text{-H(B)}}$ = 9.5 Hz, $J_{B,3'}$ = 7.5 Hz, $J_{B,1'\text{-H(A)}}$ = 5.6 Hz, 2′-H_2), AB signal (δ_A = 1.72, δ_B = 1.82, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,2'\text{-H(A)}}$ = 9.8 Hz, $J_{A,5}$ = 8.0 Hz, $J_{A,2'\text{-H(B)}}$ = 5.5 Hz, B part additionally split by $J_{B,2'\text{-H(B)}}$ = 9.6 Hz, $J_{B,2'\text{-H(B)}}$ = 6.1 Hz, $J_{B,5}$ = 4.8 Hz, 1′-H_2), 2.31 (s, 4′′-H_3), 4.37 (ddd, $J_{5,1'\text{-H(A)}}$ = 7.9, $J_{5,4}$ = 7.1, $J_{5,1'\text{-H(B)}}$ = 4.9 Hz, 5-H), 4.82 (ddd, $J_{4,5}$ = 7.1, $J_{4,1''}$ = 5.6, $^4J_{4,2''}$ = 1.4 Hz, 4-H), 6.41 (dd, $J_{2'',1''}$ = 15.9, $^4J_{2'',4}$ = 1.4 Hz, 2′′-H), 6.65 ppm (dd, $J_{1'',2''}$ = 15.9 Hz, $J_{1'',4}$ = 5.6 Hz, 1′′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.64 (C-3′), 18.10 (C-2′), 28.37 (C-4′′), 35.35 (C-1′), 80.09 (C-5), 81.35 (C-4), 132.15 (C-2′′), 137.53 (C-1′′), 153.68 (C-2), 196.65 ppm (C-3′′). IR (film): $\tilde{\nu}$ = 3580, 2965, 2940, 2875, 1810, 1705, 1680, 1640, 1545, 1465, 1430, 1365, 1305, 1255, 1225, 1180, 1120, 1085, 1055, 1035, 980, 895, 775, 750, 720 cm^{-1}. $C_{10}H_{14}O_4$ (198.22): calcd. C 60.59, H 7.12; found C 60.49, H 7.08.

(4*R*,5*R*)-4-Isopropyl-5-[(*E*)-3-oxobut-1-enyl]-1,3-dioxolan-2-one (25b): This compound was prepared from **17b** (192 mg, 11.1 mmol) as described for **23a**. Flash chromatography (1.5 × 16 cm, 5 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 20–38, 183 mg, 83%) as a slightly yellow oil. $[\alpha]_{589}^{20}$ = +11.2, $[\alpha]_{578}^{20}$ = +11.3, $[\alpha]_{546}^{20}$ = +12.6, $[\alpha]_{436}^{20}$ = +16.3, $[\alpha]_{365}^{20}$ = +24.2 (*c* = 0.97, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 1.01 and 1.05 [2 × d, $J_{1'\text{-Me},1'}$ = 6.8 Hz, 1′-$(CH_3)_2$], 2.01 (qqd, $J_{1',2'}$ = $J_{1',1'\text{-Me}}$ = $J_{1',5}$ = 6.7 Hz, 1′-H), 2.30 (s, 4′′-H_3), 4.14 (dd, $J_{5,4}$ = $J_{5,1'}$ = 6.5 Hz, 5-H), 4.92 (ddd, $J_{4,5}$ = 6.5, $J_{4,1''}$ = 5.2, $^4J_{4,2''}$ = 1.3 Hz, 4-H), 6.42 (dd, $J_{2'',1''}$ = 15.9, $^4J_{2'',4}$ = 1.5 Hz, 2′′-H), 6.65 ppm (dd, $J_{1'',2''}$ =

15.9 Hz, $J_{1'',4}$ = 5.4 Hz, 1''-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.13 and 17.18 [1'-$(CH_3)_2$], 28.48 (C-4''), 31.75 (C-1'), 77.78 (C-4), 85.80 (C-5), 131.67 (C-2''), 38.50 (C-1''), 153.70 (C-2), 198.69 ppm (C-2''). IR (film): $\tilde{\nu}$ = 3390, 2970, 2880, 1800, 1685, 1640, 1470, 1425, 1365, 1310, 1255, 1170, 1055, 980, 770 cm^{-1}. $C_{10}H_{14}O_4$ (198.22): calcd. C 60.59, H 7.12; found C 60.30, H 7.23.

Ethyl (*R*,*E*)-5-Hydroxyoct-2-enoate [26a; as a mixture (97:3) with ethyl (*R*,*E*)-5-hydroxyoct-3-enoate (*iso*-26a)]: $Pd_2(dba)_3{\cdot}CHCl_3$ (0.11 g, 0.11 mmol, 2.5 mol-%) and PPh_3 (73 mg, 0.28 mmol, 6.3 mol-%) were dissolved in THF (25 mL) and stirred at room temp. for 30 min. Compound **23a** (998 mg, 4.37 mmol) in THF (5 mL), triethylamine (1.85 mL, 1.33 g, 13.1 mmol, 3.0 equiv.) and formic acid (0.50 mL, 0.60 g, 13 mmol, 3.0 equiv.) were then successively added and the system was heated at reflux for 2 h. The reaction mixture was allowed to cool to room temp. and quenched with satd. aq. $NaHCO_3$ (20 mL). The phases were separated. The aq. phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. After removal of the solvent under reduced pressure, flash chromatography (3.5 × 18 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 46–75, 578 mg, 71%) as a yellow oil. Compound **26a** (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.93 (dd, $J_{8,7\text{-H(A)}} = J_{8,7\text{-H(B)}}$ = 6.9 Hz, 8-H_3), 1.28 (t, $J_{2',1'}$ = 7.1 Hz, 2'-H_2), 1.30–1.52 (m, 6-H_2, 7-H_2), 1.61 (br. s, 5-OH), AB signal (δ_A = 2.32, δ_B = 2.40, J_{AB} = 14.4 Hz, A part additionally split by $J_{A,3}$ = 7.7 Hz, $J_{A,5}$ = 7.2 Hz, $^4J_{A,2}$ = 1.3 Hz, B part additionally split by $J_{B,3}$ = 7.3 Hz, $J_{B,5}$ = 4.6 Hz, $^4J_{B,2}$ = 1.6 Hz, 4-H_2), 3.77 (m_c, 5-H), 4.18 (q, $J_{1',2'}$ = 7.1 Hz, 1'-H), 5.90 (ddd, $J_{2,3}$ = 15.6 Hz, $^4J_{2,4\text{-H(A)}} = {}^4J_{2,4\text{-H(B)}}$ = 1.5 Hz, 2-H), 6.97 ppm (ddd, $J_{3,2}$ = 15.6 Hz, $J_{3,4\text{–H(A)}} = J_{3,4\text{–H(B)}}$ = 7.4 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.03 (C-2'), 14.33 (C-8), 18.85 (C-7), 39.35 (C-6), 40.28 (C-4), 60.37 (C-1'), 70.37 (C-5), 123.96 (C-2), 145.26 (C-3), 166.42 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2960, 2935, 2875, 1720, 1655, 1465, 1395, 1370, 1320, 1270, 1210, 1170, 1125, 1095, 1045, 985, 850, 750 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_8H_{13}O_2$ 141.0916 [M – OCH_2CH_3]$^+$; found 141.0912 (–2.5 ppm).

Ethyl (*S*,*E*)-5-Hydroxy-6-methylhept-2-enoate [26b; as a mixture (96:4) with ethyl (*R*,*E*)-5-hydroxy-6-methylhept-2-enoate (*iso*-26b)]: This compound was prepared from **23b** (513 mg, 2.23 mmol) as described for **26a**. Flash chromatography (3 × 16 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 44–65, 306 mg, 73%) as a yellow oil. Compound **26b** (major isomer): $[\alpha]_{589}^{20}$ = –17.2, $[\alpha]_{578}^{20}$ = –18.4, $[\alpha]_{546}^{20}$ = –20.9, $[\alpha]_{436}^{20}$ = –37.8 (c = 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.93 and 0.94 [2 × d, $J_{6,6\text{-Me}}$ = 9.4 Hz, 6-$(CH_3)_2$], 1.28 (t, $J_{2',1'}$ = 7.1 Hz, 2'-H_2), 1.60 (br. d, 5-OH), 1.70 (qqd, $J_{6,7} = J_{6,6\text{-Me}}$ = 6.8, $J_{6,5}$ = 5.8 Hz, 6-H), AB signal (δ_A = 2.30, δ_B = 2.41, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,5}$ = 8.2 Hz, $J_{A,3}$ = 7.9 Hz, $^4J_{A,2}$ = 1.4 Hz, B part additionally split by $J_{B,3}$ = 7.0 Hz, $J_{B,5}$ = 3.9 Hz, $^4J_{B,2}$ = 1.6 Hz, 4-H_2), 3.52 (m_c, 5-H), 4.18 (q, $J_{1',2'}$ = 7.1 Hz, 1'-H), 5.91 (ddd, $J_{2,3}$ = 15.7, $^4J_{2,4\text{-H(A)}} = {}^4J_{2,4\text{-H(B)}}$ = 1.5 Hz, 2-H), 7.00 ppm (ddd, $J_{3,2}$ = 15.7 Hz, $J_{3,4\text{–H(A)}}$ = 7.8 Hz, $J_{3,4\text{–H(B)}}$ = 6.9 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.34 (C-2'), 17.31 and 18.78 [6-$(CH_3)_2$], 33.47 (C-6), 37.25 (C-4), 60.36 (C-1'), 75.42 (C-5), 123.80 (C-2), 145.88 (C-3), 166.44 ppm (C-1). IR (film): $\tilde{\nu}$ = 3450, 2960, 2900, 2875, 1715, 1650, 1465, 1385, 1365, 1310, 1270, 1215, 1165, 1095, 1045, 980 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{10}H_{19}O_3$ 187.1334 [M + H]$^+$; found 187.1335 (–0.4 ppm).

(*R*,*E*)-5-Hydroxy-*N*-methoxy-*N*-methyloct-2-enamide [27a; as a mixture (90:10) with (*R*,*E*)-5-hydroxy-*N*-methoxy-*N*-methyloct-3-enamide (*iso*-27a)]: This compound was prepared from **24a** (80 mg, 0.33 mmol) as described for **26a**. Flash chromatography (1 × 14 cm, 5 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 22–36, 20 mg, 30%) as a slightly yellow oil. Compound **27a** (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 (dd, $J_{8,7\text{-H(A)}} = J_{8,7\text{-H(B)}}$ = 6.9 Hz, 8-H_3), 1.30–1.53 (m, 6-H_2, 7-H_2), 1.64 (br. s, 5-OH), AB signal (δ_A = 2.36, δ_B = 2.44, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,3} = J_{A,5}$ = 7.7 Hz, $^4J_{A,2}$ = 1.3 Hz, B part additionally split by $J_{B,3}$ = 7.2 Hz, $J_{B,5}$ = 4.7 Hz, $^4J_{B,2}$ = 1.6 Hz, 4-H_2), 3.24 (s, NCH_3), 3.70 (s, OCH_3), 3.78 (m_c, 5-H), 6.49 (ddd, $J_{2,3}$ = 15.4, $^4J_{2,4\text{-H(A)}} = {}^4J_{2,4\text{-H(B)}}$ = 1.3 Hz, 2-H), 6.98 ppm (ddd, $J_{3,2}$ = 15.3 Hz, $J_{3,4\text{–H(A)}}$ = 8.0 Hz, $J_{3,4\text{–H(B)}}$ = 7.2 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.08 (C-8), 18.90 (C-7), 32.44 [N(CH_3)(OCH_3)], 39.27 (C-6), 40.69 (C-4), 61.81 [N(CH_3)(OCH_3)], 70.44 (C-5), 121.60 (C-2), 143.62 (C-3), 166.66 ppm (C-1). IR (film): $\tilde{\nu}$ = 3410, 2960, 2935, 2875, 1660, 1625, 1460, 1420, 1385, 1180, 1120, 1000 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{10}H_{20}NO_3$ 202.1442 [M + H]$^+$; found 202.1443 (+0.1 ppm).

(*S*,*E*)-5-Hydroxy-*N*-methoxy-*N*,6-dimethylhept-2-enamide [27b; as a mixture (89:11) with (*R*,*E*)-5-hydroxy-*N*-methoxy-*N*,6-dimethylhept-3-enamide (*iso*-27b)]: This compound was prepared from **24b** (78 mg, 0.32 mmol) as described for **26a**. Flash chromatography (1 × 11 cm, 5 mL, cyclohexane/EtOAc 1:1) provided the title compound (fractions 14–36, 42 mg, 65%) as a slightly yellow oil. Compound **27b** (major isomer): $[\alpha]_{578}^{20}$ = –11.3, $[\alpha]_{546}^{20}$ = –13.1, $[\alpha]_{436}^{20}$ = –22.7, $[\alpha]_{365}^{20}$ = –31.4 (c = 0.60, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 (d, $J_{7,6}$ and alternatively $J_{6\text{-Me},6}$ = 6.7 Hz, 7-H_6), 1.69 (m_c, 6-H), 2.12 (br. s, 5-OH), AB signal (δ_A = 2.32, δ_B = 2.42, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,5} = J_{A,3}$ = 8.1 Hz, $^4J_{A,2}$ = 1.1 Hz, B part additionally split by $J_{B,3}$ = 8.1 Hz, $J_{B,5}$ = 4.1 Hz, $^4J_{B,2}$ = 1.5 Hz, 4-H_2), 3.19 (s, NCH_3), 3.49 (m_c, 5-H), 3.67 (s, OCH_3), 6.46 (br. d, $J_{2,3}$ = 15.4 Hz, 2-H), 6.97 ppm (ddd, $J_{3,2}$ = 15.2 Hz, $J_{3,4\text{–H(A)}} = J_{3,4\text{–H(B)}}$ = 7.9 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.34 and 18.86 [6-$(CH_3)_2$], 32.45 [N(CH_3)(OCH_3)], 33.40 (C-6), 37.65 (C-4), 61.81 [N(CH_3)(OCH_3)], 75.38 (C-5), 121.42 (C-2), 144.25 (C-3), 166.68 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2960, 2895, 2875, 1660, 1625, 1465, 1420, 1385, 1295, 1180, 1150, 1120, 1045, 995 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{10}H_{20}NO_3$ 202.1443 [M + H]$^+$; found 202.1439 (+2.1 ppm).

(*R*,*E*)-6-Hydroxynon-3-en-2-one [28a; as a mixture (89:11) with (*R*,*E*)-6-hydroxynon-4-en-2-one (*iso*-28a)]: This compound was prepared from **25a** (82 mg, 0.41 mmol) as described for **26a**. Flash chromatography (1 × 16 cm, 5 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 34–45, 47 mg, 72%) as a yellow oil. Compound **28a** (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 (dd, $J_{9,8\text{-H(A)}} = J_{9,8\text{-H(B)}}$ = 7.1 Hz, 9-H_3), 1.28–1.56 (m, 7-H_2, 8-H_2), 1.73 (br. s, 6-OH), 2.25 (s, 1-H_3), AB signal (δ_A = 2.33, δ_B = 2.42, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,4} = J_{A,6}$ = 7.4 Hz, $^4J_{A,3}$ = 1.4 Hz, B part additionally split by $J_{B,4}$ = 7.2 Hz, $J_{B,6}$ = 4.4 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.79 (m_c, 6-H), 6.13 (ddd, $J_{3,4}$ = 16.0, $^4J_{3,5\text{-H(A)}} = {}^4J_{3,5\text{-H(B)}}$ = 1.4 Hz, 3-H), 6.84 ppm (ddd, $J_{4,3}$ = 16.0 Hz, $J_{4,5\text{–H(A)}} = J_{4,5\text{–H(B)}}$ = 7.3 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.03 (C-9), 18.84 (C-8), 27.02 (C-1), 39.52 (C-7), 40.46 (C-5), 70.46 (C-6), 133.49 (C-3), 144.52 (C-4), 198.55 ppm (C-2). IR (film): $\tilde{\nu}$ = 3425, 2960, 2935, 2875, 1675, 1625, 1425, 1365, 1320, 1260, 1170, 1125, 1060, 1020, 985, 850, 750 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_9H_{20}NO_2$ 174.1494 [M + NH_4]$^+$; found 174.1496 (+1.1 ppm).

(*S*,*E*)-6-Hydroxy-7-methyloct-3-en-2-one [28b; as a mixture (82:18) with (*R*,*E*)-6-hydroxy-7-methyloct-4-en-2-one (*iso*-28b)]: This compound was prepared from **25b** (69 mg, 0.35 mmol) as described for **26a**. Flash chromatography (1 × 12 cm, 5 mL, cyclohexane/EtOAc 7:1) provided the title compound (fractions 44–62, 30 mg, 55%) as a yellow oil. Compound **28a** (major isomer): $[\alpha]_{589}^{20}$ = –6.7, $[\alpha]_{578}^{20}$ =

–7.6, $[\alpha]_{546}^{20}$ = –8.1, $[\alpha]_{436}^{20}$ = –14.6, $[\alpha]_{365}^{20}$ = –19.7 (*c* = 0.64, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 and 0.94 [2 × d, $J_{7,7\text{-Me}}$ = 6.7 Hz, 7-$(CH_3)_2$], 1.70 (m_c, 7-H), 1.76 (br. s, 6-OH), 2.24 (s, 1-H_3), AB signal (δ_A = 2.32, δ_B = 2.42, J_{AB} = 14.7 Hz, A part additionally split by $J_{A,6}$ = 8.2 Hz, $J_{A,4}$ = 7.6 Hz, $^4J_{A,3}$ = 0.8 Hz, B part additionally split by $J_{B,4}$ = 6.9 Hz, $J_{B,6}$ = 3.9 Hz, $^4J_{B,3}$ = 1.3 Hz, 5-H_2), 3.52 (m_c, 6-H), 6.14 (br. d, $J_{3,4}$ = 16.0 Hz, 3-H), 6.86 ppm (ddd, $J_{4,3}$ = 16.0 Hz, $J_{4,5\text{–H(A)}}$ = $J_{4,5\text{–H(B)}}$ = 7.2 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.36 and 18.84 [7-$(CH_3)_2$], 27.02 (C-1), 33.68 (C-7), 37.46 (C-5), 75.60 (C-6), 133.38 (C-3), 145.13 (C-4), 198.50 ppm (C-2). IR (film): $\tilde{\nu}$ = 3425, 2960, 2930, 2875, 1675, 1625, 1510, 1455, 1425, 1360, 1320, 1260, 1170, 1125, 1080, 1060, 1020, 980, 850 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_9H_{17}O_2$ 157.1229 $[M + H]^+$; found 157.1225 (+2.3 ppm).

Ethyl (*R*,*E*)-5-(Benzyloxymethoxy)oct-2-enoate (29a): Compound **26** (604 mg, 3.24 mmol) was dissolved in 1,2-dichlorethane (32 mL) and benzyl chloromethyl ether (1.80 mL, 1.67 g, 13.0 mmol, 4.0 equiv.) and *i*Pr_2NEt (2.15 mL, 2.03 g, 13.0 mmol, 4.0 equiv.) were added. The reaction mixture was stirred under reflux for 4 h. After the addition of H_2O (15 mL), the phases were separated and the aq. phase was extracted with MTBE (3 × 15 mL). The combined organic phases were washed with brine (15 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure and flash chromatography (3.5 × 19.5 cm, 50 mL, cyclohexane/EtOAc 50:1) provided the title compound (fractions 37–52, 824 mg, 83%) as a colorless oil. $[\alpha]_{589}^{20}$ = +27.3, $[\alpha]_{578}^{20}$ = +28.4, $[\alpha]_{546}^{20}$ = +32.5, $[\alpha]_{436}^{20}$ = +58.8 (*c* = 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 (dd, $J_{8,7\text{-H(A)}}$ = $J_{8,7\text{-H(B)}}$ = 7.5 Hz, 8-H_3), 1.27 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 1.33–1.63 (m, 6-H_2, 7-H_2), AB signal (δ_A = 2.43, δ_B = 2.47, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,3}$ = 7.5 Hz, $J_{A,5}$ = 5.9 Hz, $^4J_{A,2}$ = 1.5 Hz, B part additionally split by $J_{B,3}$ = 7.3 Hz, $J_{B,5}$ = 5.7 Hz, $^4J_{B,2}$ = 1.5 Hz, 4-H_2), 3.79 (m_c, approximately interpretable as dddd, $J_{5,6\text{-H(A)}}$ = 6.4, $J_{5,6\text{-H(B)}}$ = 5.8, $J_{5,4\text{-H(A)}}$ = $J_{5,4\text{-H(B)}}$ = 5.7 Hz, 5-H), 4.18 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_2), 4.62 (s, OCH_2OCH_2Ar), 4.79 (s, OCH_2OCH_2Ar), 5.88 (ddd, $J_{2,3}$ = 15.6, $^4J_{2,4\text{-H(A)}}$ = $^4J_{2,4\text{-H(B)}}$ = 1.5 Hz, 2-H), 6.99 (ddd, $J_{3,2}$ = 15.6, $J_{3,4\text{-H(A)}}$ = $J_{3,4\text{-H(B)}}$ = 7.5 Hz, 3-H), 7.26–7.37 ppm (m, 2 × *ortho*-H, 2 × *meta*-H, *para*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 (C-2′), 14.33 (C-8), 18.67 (C-7), 36.56 (C-6), 37.32 (C-4), 60.28 (C-1′), 69.77 (OCH_2OCH_2Ar), 75.98 (C-5), 93.47 (OCH_2OCH_2Ar), 123.73 (C-2), 127.77 (*para*-C), 127.92 (2 × *ortho*-C) 128.50 (2 × *meta*-C), 137.89 (*ipso*-C), 145.23 (C-3), 166.38 ppm (C-1). IR (film): $\tilde{\nu}$ = 3420, 3065, 3030, 2960, 2935, 2875, 1720, 1655, 1490, 1455, 1360, 1320, 1260, 1210, 1180, 1100, 1040, 985 cm^{-1}. $C_{18}H_{26}O_4$ (306.40): calcd. C 70.56, H 8.55; found C 70.19, H 8.41.

Ethyl (*S*,*E*)-5-(Benzyloxymethoxy)-6-methylhept-2-enoate (29b): This compound was prepared from **26b** (1.01 g, 5.42 mmol) as described for **26a**. Flash chromatography (4 × 18 cm, 50 mL, cyclohexane/EtOAc 30:1) provided the title compound (fractions 12–33, 1.30 g, 78%) as a colorless oil. $[\alpha]_{589}^{20}$ = +21.9, $[\alpha]_{578}^{20}$ = +23.0, $[\alpha]_{546}^{20}$ = +26.4, $[\alpha]_{436}^{20}$ = +48.2 (*c* = 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.94 and 0.95 [2 × d, $J_{6\text{-Me},6}$ = 6.8 Hz, 6-$(CH_3)_2$], 1.27 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_2), 1.88 (qqd, $J_{6,7}$ = $J_{6,6\text{-Me}}$ = 6.8, $J_{6,5}$ = 3.8 Hz, 6-H), 2.44 (ddd, $J_{4,3}$ = 7.4, $J_{4,5}$ = 5.9, $^4J_{4,2}$ = 1.5 Hz, 4-H_2), 3.56 (dt, $J_{5,4}$ = $J_{5,6}$ = 5.6 Hz, 5-H), 4.17 (q, $J_{1',2'}$ = 7.2 Hz, 1′-H), 4.63 (s, OCH_2OCH_2Ar), 4.78 (s, OCH_2OCH_2Ar), 5.90 (dt, $J_{2,3}$ = 15.7, $^4J_{2,4}$ = 1.5 Hz, 2-H), 7.02 (dt, $J_{3,2}$ = 15.7, $J_{3,4}$ = 7.5 Hz, 3-H), 7.26–7.36 ppm (m, 2 × *ortho*-H, 2 × *meta*-H, *para*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.33 (C-2′′),18.08 and 18.16 (Me_2-6), 31.22 (C-6), 34.09 (C-4), 60.26 (C-1′′), 69.86 (OCH_2OCH_2Ar), 81.37 (C-5), 94.05 (OCH_2OCH_2Ar), 123.49 (C-2), 127.75 (2 × *para*-C), 127.90 (2 × *ortho*-C), 128.49 (2 × *meta*-C), 137.91 (*ipso*-C), 145.86 (C-3), 166.39 ppm (C-1). IR (film): $\tilde{\nu}$ = 3420, 3090, 3065, 3030, 2960, 2890, 2360, 1955, 1870, 1720, 1655, 1605, 1540, 1495, 1465, 1455, 1385, 1365, 1315, 1265, 1210, 1175, 1135, 1100, 1040, 975, 905, 860 cm^{-1}. $C_{18}H_{26}O_4$ (306.40): calcd. C 70.56, H 8.55; found C 70.51, H 8.84.

Ethyl (*R*,*E*)-5-(4-Methoxybenzyloxy)oct-2-enoate (30a): Compound **26** (853 mg, 4.48 mmol) was dissolved in CH_2Cl_2 (40 mL) and 4-methoxybenzyl trichloroacetimidate (2.91 g, 10.3 mmol, 2.3 equiv.) was added. A solution of pyridinium *p*-toluenesulfonate (676 mg, 2.69 mmol, 0.6 equiv.) in CH_2Cl_2 (5 mL) was added over 10 min and the resulting mixture was stirred for 11 d. After addition of satd. aq. $NaHCO_3$ (25 mL), the phases were separated and the aq. phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine (25 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure, and flash chromatography (4.5 × 21.5 cm, 50 mL, cyclohexane/EtOAc 40:1) provided the title compound (fractions 26–41, 1.06 g, 77%) as a colorless oil, together with reisolated starting material (15%). $[\alpha]_{589}^{20}$ = +14.4, $[\alpha]_{578}^{20}$ = +14.6, $[\alpha]_{546}^{20}$ = +16.8, $[\alpha]_{436}^{20}$ = +28.9, $[\alpha]_{365}^{20}$ = +44.5 (*c* = 0.69, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.90 (dd, $J_{8,7\text{-H(A)}}$ = $J_{8,7\text{-H(B)}}$ = 7.2 Hz, 8-H_3), 1.25–1.60 (m, 6-H_2, 7-H_2), 1.29 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), AB signal (δ_A = 2.41, δ_B = 2.45, J_{AB} = 14.7 Hz, A part additionally split by $J_{A,3}$ = 7.4 Hz, $J_{A,5}$ = 5.8 Hz, $^4J_{A,2}$ = 1.5 Hz, B part additionally split by $J_{B,3}$ = 7.4 Hz, $J_{B,5}$ = 5.8 Hz, $^4J_{B,2}$ = 1.5 Hz, 4-H_2), 3.50 (m_c, approximately interpretable as dddd, $J_{5,6\text{-H(A)}}$ = 6.9, $J_{5,4\text{-H(A)}}$ = $J_{5,4\text{-H(B)}}$ = 5.7, $J_{5,6\text{-H(B)}}$ = 4.8 Hz, 5-H), 3.81 (s, OCH_3), 4.19 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_2), AB signal (δ_A = 4.43, δ_B = 4.48, J_{AB} = 11.1 Hz, OCH_2Ar), 5.87 (ddd, $J_{2,3}$ = 15.7, $^4J_{2,4\text{-H(A)}}$ = $^4J_{2,4\text{-H(B)}}$ = 1.5 Hz, 2-H), AA′BB′ signal (peaks centered at δ_A = 6.87, δ_B = 7.25, 2 × *ortho*-H, 2 × *meta*-H), 6.98 ppm (ddd, $J_{3,2}$ = 15.6, $J_{3,4\text{–H(A)}}$ = $J_{3,4\text{–H(B)}}$ = 7.4 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 (C-2′), 14.35 (C-8), 18.68 (C-7), 36.46 (C-6), 36.95 (C-4), 55.35 (OCH_3), 60.25 (C-1′), 70.88 (OCH_2Ar), 77.31 (C-5), 113.846 (2 × *ortho*-C), 123.43 (C-2), 129.40 (2 × *meta*-C), 130.72 (*ipso*-C), 145.61 (C-3), 159.26 (C-4′′), 166.47 ppm (C-1). IR (film): $\tilde{\nu}$ = 3370, 2980, 2935, 2870, 2840, 2365, 2065, 1890, 1715, 1655, 1615, 1585, 1560, 1540, 1515, 1465, 1365, 1320, 1300, 1250, 1210, 1175, 1940, 980, 820 cm^{-1}. $C_{18}H_{26}O_4$ (306.40): calcd. C 70.56, H 8.55; found C 70.35, H 8.68.

Ethyl (*S*,*E*)-5-(4-Methoxybenzyloxy)-6-methylhept-2-enoate (30b): This compound was prepared from **26b** (708 mg, 3.80 mmol) as described for **30a**. Flash chromatography (3.5 × 19 cm, 50 mL, cyclohexane/EtOAc 40:1) provided the title compound (fractions 27–38, 815 mg, 70%) as a colorless oil, together with reisolated starting material (21%). $[\alpha]_{365}^{20}$ = +8.8 (*c* = 0.79, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 and 0.95 [2 × d, $J_{6\text{-Me},6}$ = 6.8 Hz, 6-$(CH_3)_2$], 1.30 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_2), 1.88 (qqd, $J_{6,7}$ = $J_{6,6\text{-Me}}$ = 6.8, $J_{6,5}$ = 3.8 Hz, 6-H), AB signal (δ_A = 2.40, δ_B = 2.44, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,3}$ = 7.6 Hz, $J_{A,5}$ = 6.2 Hz, $^4J_{A,2}$ = 1.3 Hz, B part additionally split by $J_{B,3}$ = 7.2 Hz, $J_{B,5}$ = 5.5 Hz, $^4J_{B,2}$ = 1.6 Hz, 4-H_2), 3.26 (ddd, $J_{5,4\text{–H(A)}}$ = $J_{5,4\text{–H(B)}}$ = $J_{5,6}$ = 5.7 Hz, 5-H), 3.81 (s, OCH_3), 4.20 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H), AB signal (δ_A = 4.44, δ_B = 4.49, J_{AB} = 11.0 Hz, OCH_2Ar), 5.89 (ddd, $J_{2,3}$ = 15.7, $^4J_{2,4\text{–H(AHz)}}$ = $^4J_{2,4\text{–H(B)}}$ = 1.5 Hz, 2-H), AA′BB′ signal (peaks centered at δ_A = 6.88, δ_B = 7.27, 2 × *ortho*-H, 2 × *meta*-H), 7.02 ppm (ddd, $J_{3,2}$ = 15.6 Hz, $J_{3,4\text{–H(A)}}$ = $J_{3,4\text{–H(B)}}$ = 7.4 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.37 (C-2′′), 18.27 and 18.31 [6-$(CH_3)_2$], 31.24 (C-6), 33.86 (C-4), 55.35 (OCH_3), 60.22 (C-1′′), 71.74 (OCH_2Ar), 82.78 (C-5), 113.84 (2 × *ortho*-C), 123.19 (C-2), 129.44 (2 × *meta*-C), 130.80 (*ipso*-C), 146.29 (C-3), 159.24 (C-4′′), 166.51 ppm (C-1). IR (film): $\tilde{\nu}$ = 3420, 2960, 2905, 2875, 2840, 2065, 1720, 1655, 1615, 1585, 1515, 1465, 1385, 1365, 1345, 1300, 1250, 1170, 1110, 1070, 1035, 975, 820 cm^{-1}. $C_{18}H_{26}O_4$ (306.40): calcd. C 70.56, H 8.55; found C 70.56, H 8.72.

Ethyl (*R*,*E*)-5-(*tert*-Butyldiphenylsilyloxy)oct-2-enoate (31a): Compound **26** (265 mg, 1.42 mmol) was dissolved in DMF (7 mL) and imidazole (387 mg, 5.68 mmol, 4.0 equiv.) was added. *tert*-Butyldiphenylsilyl chloride (0.740 mL, 781 mg, 2.84 mmol, 2.0 equiv.) was added over 5 min and the mixture was stirred at 65 °C for 2 d. After the addition of H_2O (35 mL), the phases were separated and the aq. phase was extracted with MTBE (3 × 4 mL). The combined organic phases were washed with H_2O (3 mL) and brine (3 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure, and flash chromatography (3 × 21 cm, 20 mL, cyclohexane/EtOAc 50:1) provided the title compound (fractions 17–27, 592 mg, 98%) as a colorless oil. $[\alpha]_{589}^{20}$ = +33.8, $[\alpha]_{578}^{20}$ = +35.2, $[\alpha]_{546}^{20}$ = +40.8, $[\alpha]_{436}^{20}$ = +75.3, $[\alpha]_{365}^{20}$ = +134.1 (*c* = 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.75 (dd, $J_{8,7-H(A)} = J_{8,7-H(B)}$ = 7.3 Hz, 8-H_3), 1.05 (s, 2′′-H_9), 1.20–1.30 (m, 7-H_2), 1.28 (t, $J_{2',1'}$ = 7.1 Hz, 2′-H_3), 1.38–1.45 (m, 6-H_2), AB signal (δ_A = 2.27, δ_B = 2.32, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,3}$ = 7.7 Hz, $J_{A,5}$ = 5.4 Hz, $^4J_{A,2}$ = 1.3 Hz, B part additionally split by $J_{B,3}$ = 7.4 Hz, $J_{B,5}$ = 5.9 Hz, $^4J_{B,2}$ = 1.3 Hz, 4-H_2), 3.84 (dddd, $J_{5,6-H(A)} = J_{5,6-H(B)} = J_{5,4-H(A)} = J_{5,4-H(B)}$ = 5.7 Hz, 5-H), 4.17 (q, $J_{1',2'}$ = 7.1 Hz, 1′-H_2), 5.72 (ddd, $J_{2,3}$ = 15.7 Hz, $^4J_{2,4-H(A)} = {}^4J_{2,4-H(B)}$ = 1.5 Hz, 2-H), 6.90 (ddd, $J_{3,2}$ = 15.7 Hz, $J_{3,4-H(A)} = J_{3,4-H(B)}$ = 7.5 Hz, 3-H), 7.34–7.45 (m, 4× *ortho*-H, 2× *para*-H), 7.65–7.69 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.09 (C-2′), 14.36 (C-8), 18.20 (C-7), 19.45 (C-1′′), 27.13 (C_3-2′′), 38.81 (C-6), 39.43 (C-4), 60.19 (C-1′), 72.10 (C-5), 123.43 (C-2), 127.60 and 127.62 (4× *meta*-C), 129.69 and 129.70 (2× *para*-C), 134.26 and 134.31 (2× *ipso*-C), 135.99 and 136.02 (4× *ortho*-C), 145.71 (C-3), 166.67 ppm (C-1). IR (film): $\tilde{\nu}$ = 3420, 3070, 2960, 2930, 2860, 1720, 1655, 1465, 1465, 1425, 1390, 1365, 1320, 1265, 1205, 1170, 1110, 1040, 985, 820 cm^{-1}. $C_{26}H_{28}O_3Si$ (424.65): calcd. C 73.54, H 8.54; found C 73.28, H 8.47.

Ethyl (*R*,*E*)-5-(*tert*-Butyldiphenylsilyloxy)-6-methylhept-2-enoate (31b): This compound was prepared from **26b** (241 mg, 1.29 mmol) as described for **31a**. Flash chromatography (2 × 20.5 cm, 20 mL, cyclohexane/EtOAc 40:1) provided the title compound (fractions 24–33, 434 mg, 79%) as a colorless oil. $[\alpha]_{589}^{20}$ = +46.3, $[\alpha]_{578}^{20}$ = +49.0, $[\alpha]_{546}^{20}$ = +55.9, $[\alpha]_{436}^{20}$ = +102.1, $[\alpha]_{365}^{20}$ = +178.2 (*c* = 0.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.84 and 0.91 [2 × d, $J_{6-Me,6}$ = 6.8 Hz, 6-$(CH_3)_2$], 1.07 (s, 2′′′-H_9), 1.26 (t, $J_{2'',1''}$ = 7.1 Hz, 2′′-H_3), 1.71 (qqd, $J_{6,7} = J_{6,6-Me}$ = 6.8 Hz, $J_{6,5}$ = 3.8 Hz, 6-H), AB signal (δ_A = 2.25, δ_B = 2.29, J_{AB} = 15.6 Hz, A part additionally split by $J_{A,3}$ = 7.8 Hz, $J_{A,5}$ = 6.3 Hz, $^4J_{A,2}$ = 1.5 Hz, B part additionally split by $J_{B,3}$ = 7.6 Hz, $J_{B,5}$ = 6.3 Hz, $^4J_{B,2}$ = 1.4 Hz, 4-H_2), 3.66 (ddd, $J_{5,4-H(B)} = J_{5,4-H(B)}$ = 6.1 Hz, $J_{5,6}$ = 3.8 Hz, 5-H), 4.14 (q, $J_{1'',2''}$ = 7.2 Hz, 1′′-H), 5.65 (ddd, $J_{2,3}$ = 15.6 Hz, $^4J_{2,4-H(A)} = {}^4J_{2,4-H(B)}$ = 1.5 Hz, 2-H), 6.78 (ddd, $J_{3,2}$ = 15.5 Hz, $J_{3,4-H(A)} = J_{3,4-H(B)}$ = 7.6 Hz, 3-H), 7.34–7.46 (m, 4× *ortho*-H, 2× *para*-H), 7.65–7.71 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.34 (C-2′′), 17.15 and 18.38 [6-$(CH_3)_2$], 19.62 (C-1′′′), 27.18 (C_3-2′′′), 32.80 (C-6), 36.58 (C-4), 60.15 (C-1′′), 76.96 (C-5), 123.10 (C-2), 127.55 and 127.60 (4× *meta*-C), 129.65 and 129.71 (2× *para*-C), 134.07 and 134.39 (2× *ipso*-C), 136.10 and 136.11 (4× *ortho*-C), 146.16 (C-3), 166.39 ppm (C-1). IR (film): $\tilde{\nu}$ = 3395, 3070, 3050, 2960, 2935, 2895, 2860, 1665, 1635, 1470, 1425, 1385, 1305, 1260, 1180, 1110, 1055, 1005, 940, 820 cm^{-1}. $C_{26}H_{28}O_3Si$ (424.65): calcd. C 73.54, H 8.54; found C 73.37, H 8.47.

(*R*,*E*)-5-(Benzyloxymethoxy)-*N*-methoxy-*N*-methyloct-2-enamide (32a): This compound was prepared from **29b** (1.41 g, 4.60 mmol) as described for **13a**. Flash chromatography (3 × 18.5 cm, 20 mL, cyclohexane/EtOAc 5:1) provided the title compound (fractions 35–58, 555 mg, 70%) as a colorless oil. $[\alpha]_{589}^{20}$ = +33.8, $[\alpha]_{578}^{20}$ = +35.2, $[\alpha]_{546}^{20}$ = +40.8, $[\alpha]_{436}^{20}$ = +75.3, $[\alpha]_{365}^{20}$ = +134.1 (*c* = 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 (dd, $J_{8,7-H(A)} = J_{8,7-H(B)}$ = 7.2 Hz, 8-H_3), 1.32–1.60 (m, 6-H_2, 7-H_2), AB signal (δ_A = 2.47, δ_B = 2.51, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,3}$ = 7.4 Hz, $J_{A,5}$ = 5.9 Hz, $^4J_{A,2}$ = 1.4 Hz, B part additionally split by $J_{B,3}$ = 7.5 Hz, $J_{B,5}$ = 5.8 Hz, $^4J_{B,2}$ = 1.5 Hz, 4-H_2), 3.23 (s, NCH_3), 3.68 (s, OCH_3), 3.79 (m_c, approximately interpretable as dddd, $J_{5,6-H(A)}$ = 6.4 Hz, $J_{5,4-H(A)} = J_{5,4-H(B)} = J_{5,6-H(B)}$ = 5.9 Hz, 5-H), 4.63 (s, OCH_2OCH_2Ar), AB signal (δ_A = 4.78, δ_B = 4.81, J_{AB} = 7.1 Hz, OCH_2OCH_2Ar), 6.46 (ddd, $J_{2,3}$ = 15.3 Hz, $^4J_{2,4-H(A)} = {}^4J_{2,4-H(B)}$ = 1.3 Hz, 2-H), 7.00 (ddd, $J_{3,2}$ = 15.0 Hz, $J_{3,4-H(A)} = J_{3,4-H(B)}$ = 7.4 Hz, 3-H), 7.26–7.37 ppm (m, 2× *ortho*-H, *para*-H, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.20 (C-8), 18.67 (C-7), 32.42 [N(CH_3)(OCH_3)], 37.72 (C-6), 37.72 (C-4), 61.76 [N(CH_3)(OCH_3)], 69.72 (OCH_2OCH_2Ar), 76.34 (C-5), 93.59 (OCH_2OCH_2Ar), 121.13 (C-2), 127.82 (*para*-C), 127.97 (2× *ortho*-C) 128.50 (2× *meta*-C), 137.97 (*ipso*-C), 143.68 (C-3), 166.70 ppm (C-1). IR (film): $\tilde{\nu}$ = 3470, 3065, 3030, 2960, 2935, 2875, 1735, 1665, 1635, 1490, 1455, 1415, 1380, 1295, 1170, 1100, 1040, 1000 cm^{-1}. $C_{18}H_{27}NO_4$ (306.40): calcd. C 67.26, H 8.47, N 4.36; found C 67.96, H 8.74, N 4.08.

(*S*,*E*)-5-(Benzyloxymethoxy)-*N*-methoxy-*N*,6-dimethylhept-2-enamide (32b): This compound was prepared from **29b** (1.41 g, 4.60 mmol) as described for **13a**. Flash chromatography (3 × 18.5 cm, 20 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 28–48, 1.08 g, 73%) as a colorless oil. $[\alpha]_{589}^{20}$ = +32.6, $[\alpha]_{578}^{20}$ = +33.8, $[\alpha]_{546}^{20}$ = +39.0, $[\alpha]_{436}^{20}$ = +70.5, $[\alpha]_{365}^{20}$ = +122.3 (*c* = 0.89, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.95 and 0.95 [2 × d, $J_{6-Me,6}$ = 6.8 Hz, 6-$(CH_3)_2$], 1.89 (qqd, $J_{6,7} = J_{6,6-Me}$ = 6.8 Hz, $J_{6,5}$ = 3.8 Hz, 6-H), AB signal (δ_A = 2.46, δ_B = 2.50, J_{AB} = 14.5 Hz, A part additionally split by $J_{A,3}$ = 7.4 Hz, $J_{A,5}$ = 5.8 Hz, $^4J_{A,2}$ = 1.5 Hz, B part additionally split by $J_{B,3}$ = 7.8 Hz, $J_{B,5}$ = 6.5 Hz, $^4J_{B,2}$ = 1.4 Hz, 4-H_2), 3.23 (s, NCH_3), 3.57 (ddd, $J_{5,4-H(A)} = J_{5,4-H(B)} = J_{5,6}$ = 5.6 Hz, 5-H), 3.67 (s, OCH_3), 4.63 (s, OCH_2OCH_2Ar), AB signal (δ_A = 4.78, δ_B = 4.80, J_{AB} = 7.1, OCH_2OCH_2Ar), 6.48 (ddd, $J_{2,3}$ = 15.3 Hz, $^4J_{2,4-H(A)} = {}^4J_{2,4-H(B)}$ = 1.4 Hz, 2-H), 7.02 (ddd, $J_{3,2}$ = 15.3 Hz, $J_{3,4-H(A)} = J_{3,4-H(B)}$ = 7.6 Hz, 3-H), 7.26–7.36 ppm (m, 2× *ortho*-H, 2× *meta*-H, *para*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.88 and 18.32 [6-$(CH_3)_2$], 31.27 (C-6), 32.41 [N(CH_3)(OCH_3)], 34.52 (C-4), 61.74 [N(CH_3)(OCH_3)], 69.80 (OCH_2OCH_2Ar), 81.65 (C-5), 94.19 (OCH_2OCH_2Ar), 120.09 (C-2), 127.70 (*para*-C), 127.94 (2× *ortho*-C) 128.48 (2× *meta*-C), 137.98 (*ipso*-C), 144.26 (C-3), 166.72 ppm (C-1). IR (film): $\tilde{\nu}$ = 3275, 3065, 3030, 2960, 2895, 1720, 1665, 1635, 1500, 1455, 1415, 1380, 1295, 1165, 1100, 1040, 1005, 840, 820 cm^{-1}. $C_{18}H_{27}NO_4$ (321.41): calcd. C 67.26, H 8.47, N 4.36; found C 66.97, H 8.31, N 4.35.

(*R*,*E*)-*N*-Methoxy-5-(4-methoxybenzyloxy)-*N*-methyloct-2-enamide (33a): This compound was prepared from **30a** (522 mg, 1.70 mmol) as described for **13a**. Flash chromatography (2 × 13.5 cm, 20 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 30–54, 356 mg, 65%) as a colorless oil. $[\alpha]_{436}^{20}$ = +33.9, $[\alpha]_{365}^{20}$ = +53.9, (*c* = 0.27 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.90 (dd, $J_{8,7-H(A)} = J_{8,7-H(B)}$ = 7.2 Hz, 8-H_3), 1.28–1.60 (m, 6-H_2, 7-H_2), AB signal (δ_A = 2.44, δ_B = 2.51, J_{AB} = 14.5 Hz, A part additionally split by $J_{A,3}$ = 7.5 Hz, $J_{A,5}$ = 6.0 Hz, $^4J_{A,2}$ = 1.5 Hz, B part additionally split by $J_{B,3}$ = 7.4 Hz, $J_{B,5}$ = 5.9 Hz, $^4J_{B,2}$ = 1.4 Hz, 4-H_2), 3.24 (s, NCH_3), 3.52 (m_c, approximately interpretable as dddd, $J_{5,6-H(A)}$ = 6.7 Hz, $J_{5,4-H(A)} = J_{5,6-H(B)}$ = 6.1 Hz, $J_{5,6-H(B)}$ = 4.5 Hz, 5-H), 3.68 (s, OCH_3), 3.81 (s, 4′-OCH_3), AB signal (δ_A = 4.43, δ_B = 4.50, J_{AB} = 11.1 Hz, OCH_2Ar), 6.46 (ddd, $J_{2,3}$ = 15.4 Hz, $^4J_{2,4-H(A)} = {}^4J_{2,4-H(B)}$ = 1.3 Hz, 2-H), AA′BB′ signal (peaks centered at δ_A = 6.86, δ_B = 7.26, 2× *ortho*-H, 2× *meta*-H),

7.00 ppm (ddd, $J_{3,2}$ = 15.3 Hz, $J_{3,4–H(A)} = J_{3,4–H(B)}$ = 7.6 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16 (C-8), 18.63 (C-7), 32.38 [N(CH_3)(OCH_3)], 36.50 (C-6), 37.38 (C-4), 55.30 (H_3CO-4′), 61.70 [N(CH_3)(OCH_3)], 70.92 (OCH_2Ar), 77.61 (C-5), 113.79 (2× *ortho*-C), 120.84 (C-2), 129.33 (2× *meta*-C), 130.82 (*ipso*-C), 144.05 (C-3), 159.17 (*para*-C), 166.76 ppm (C-1). IR (film): $\tilde{\nu}$ = 3395, 2960, 2935, 2870, 2365, 1665, 1635, 1615, 1515, 1460, 1420, 1380, 1300, 1250, 1175, 1070, 1035, 995, 820 cm^{-1}. $C_{18}H_{27}NO_4$ (321.41): calcd. C 67.26, H 8.47, N 4.36; found C 67.02, H 8.77, N 4.18.

(*R*,*E*)-*N*-Methoxy-5-(4-methoxybenzyloxy)-*N*,6-dimethylhept-2-enamide (33b): This compound was prepared from **30b** (926 mg, 3.02 mmol) as described for **13a**. Flash chromatography (3.5×14 cm, 50 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 9–18, 962 mg, 99%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 and 0.94 [2×d, $J_{6\text{-Me},6}$ = 6.7 Hz, 6-(CH_3)$_2$], 1.87 (qqd, $J_{6,7} = J_{6,6–Me}$ = 6.8 Hz, $J_{6,5}$ = 5.3 Hz, 6-H), 2.45 (ddd, $J_{4,3}$ = 7.4 Hz, $J_{4,5}$ = 6.0 Hz, $^4J_{4,2}$ = 1.4 Hz, 4-H_2), 3.24 (s, NCH_3), 3.28 (dt, $J_{5,4} = J_{5,6}$ = 5.6 Hz, 5-H), 3.66 (s, OCH_3), 3.79 (s, 4′-OCH_3), AB signal (δ_A = 4.43, δ_B = 4.48, J_{AB} = 11.1 Hz, OCH_2Ar), 6.46 (dt, $J_{2,3}$ = 15.4 Hz, $^4J_{2,4}$ = 1.4 Hz, 2-H), AA′BB′ signal (peaks centered at δ_A = 6.86, δ_B = 7.26, 2× *ortho*-H, 2× *meta*-H), 7.03 ppm (dt, $J_{3,2}$ = 15.2 Hz, $J_{3,4}$ = 7.6 Hz, 3-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.10 and 18.41 [6-(CH_3)$_2$], 31.36 (C-6), 32.42 [N(CH_3)(OCH_3)], 34.40 (C-4), 55.34 (H_3CO-4′), 61.72 [N(CH_3)(OCH_3)], 71.85 (OCH_2Ar), 83.00 (C-5), 113.78 (2× *ortho*-C), 120.64 (C-2), 129.40 (2× *meta*-C), 130.96 (*ipso*-C), 144.77 (C-3), 159.16 (*para*-C), 166.86 ppm (C-1). IR (film): $\tilde{\nu}$ = 3470, 3065, 2960, 2935, 2905, 2870, 2835, 2065, 1665, 1635, 1615, 1585, 1515, 1465, 1440, 1415, 1380, 1300, 1250, 1175, 1150, 1110, 1070, 1035, 1000, 975, 820 cm^{-1}. $C_{18}H_{27}NO_4$ (321.41): calcd. C 67.26, H 8.47, N 4.36; found C 67.05, H 8.69, N 4.16.

(*R*,*E*)-5-(*tert*-Butyldiphenylsilyloxy)-*N*-methoxy-*N*-methyloct-2-enamide (34a): This compound was prepared from **31a** (1.02 g, 2.40 mmol) as described for **13a**. Flash chromatography (3×16.5 cm, 20 mL, cyclohexane/EtOAc 7:1) provided the title compound (fractions 16–38, 919 mg, 87%) as a colorless oil. $[\alpha]_{589}^{20}$ = +30.5, $[\alpha]_{578}^{20}$ = +32.5, $[\alpha]_{546}^{20}$ = +37.4, $[\alpha]_{436}^{20}$ = +69.4, $[\alpha]_{365}^{20}$ = +126.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.76 (dd, $J_{8,7–H(A)} = J_{8,7–H(B)}$ = 7.3 Hz, 8-H_3), 1.06 (s, 2′-H_9), 1.20–1.35 (m, 7-H_2), 1.40–1.47 (m, 6-H_2), AB signal (δ_A = 2.31, δ_B = 2.38, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,3}$ = 7.6 Hz, $J_{A,5}$ = 4.8 Hz, $^4J_{A,2}$ = 1.6 Hz, B part additionally split by $J_{B,3}$ = 7.5 Hz, $J_{B,5}$ = 6.5 Hz, $^4J_{B,2}$ = 1.3 Hz, 4-H_2), 3.22 (s, NCH_3), 3.64 (s, OCH_3), 3.85 (dddd, $J_{5,6–H(A)} = J_{5,6–H(B)} = J_{5,4–H(B)}$ = 6.1 Hz, $J_{5,4–H(A)}$ = 4.9 Hz, 5-H), 6.30 (ddd, $J_{2,3}$ = 15.4 Hz, $^4J_{2,4–H(A)} = {}^4J_{2,4–H(B)}$ = 1.5 Hz, 2-H), 6.89 (ddd, $J_{3,2}$ = 15.3 Hz, $J_{3,4–H(A)} = J_{3,4–H(B)}$ = 7.6 Hz, 3-H), 7.34–7.45 (m, 4× *ortho*-H, 2× *para*-H), 7.66–7.71 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.09 (C-8), 18.03 (C-7), 19.44 (C-1′), 27.12 (C_3-2′), 32.40 [N(CH_3)(OCH_3)], 38.59 (C-6), 39.79 (C-4), 61.70 [N(CH_3)(OCH_3)], 72.26 (C-5), 120.88 (C-2), 127.58 and 127.59 (4× *meta*-C), 129.64 and 129.68 (2× *para*-C), 134.34 and 134.38 (2× *ipso*-C), 135.97 and 136.02 (4× *ortho*-C), 143.91 (C-3), 166.78 ppm (C-1). IR (film): $\tilde{\nu}$ = 3395, 3070, 3050, 2960, 2930, 2860, 1665, 1690, 1590, 1465, 1425, 1380, 1260, 1175, 1110, 1040, 1005, 940, 895, 865, 820 cm^{-1}. $C_{26}H_{37}NO_3Si$ (439.66): calcd. C 71.03, H 8.48, N 3.19; found C 70.86, H 8.47, N 3.01.

(*S*,*E*)-5-(*tert*-Butyldiphenylsilyloxy)-*N*-methoxy-*N*,6-dimethylhept-2-enamide (34b): This compound was prepared from **31b** (1.47 g, 3.46 mmol) as described for **13a**. Flash chromatography (3.5×15.5 cm, 20 mL, cyclohexane/EtOAc 7:1) provided the title compound (fractions 19–38, 1.14 mg, 75%) as a colorless oil. $[\alpha]_{589}^{20}$ = +48.8, $[\alpha]_{578}^{20}$ = +51.0, $[\alpha]_{546}^{20}$ = +58.8, $[\alpha]_{436}^{20}$ = +109.0, $[\alpha]_{365}^{20}$ = +194.8 (c = 1.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.86 and 0.91 [2×d, $J_{6\text{-Me},6}$ = 6.8 Hz, 6-(CH_3)$_2$], 1.07 (s, 2′-H_9), 1.71 (qqd, $J_{6,6–Me}$ = $J_{6,7}$ = 6.8 Hz, $J_{6,5}$ = 3.7 Hz, 6-H), AB signal (δ_A = 2.28, δ_B = 2.36, J_{AB} = 14.3 Hz, A part additionally split by $J_{A,3}$ = 7.2 Hz, $J_{A,5}$ = 5.6 Hz, $^4J_{A,2}$ = 1.3 Hz, B part additionally split by $J_{B,3}$ = 7.3 Hz, $J_{B,5}$ = 7.2 Hz, $^4J_{B,2}$ = 1.3 Hz, 4-H_2), 3.20 (s, NCH_3), 3.62 (s, OCH_3), 3.68 (m_c, approximately interpretable as ddd, $J_{5,4–H(B)}$ = 7.2 Hz, $J_{5,4–H(A)}$ = 5.2 Hz, $J_{5,6}$ = 3.7 Hz, 5-H), 6.22 [br. d, $J_{2,3}$ = 15.5 Hz, 2-H], 6.78 (ddd, $J_{3,2}$ = 15.3 Hz, $J_{3,4–H(A)} = J_{3,4–H(B)}$ = 7.5 Hz, 3-H), 7.34–7.45 (m, 4× *ortho*-H, 2× *para*-H), 7.66–7.71 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.75 and 18.93 [6-(CH_3)$_2$], 19.65 (C-1′), 27.19 (C_3-2′), 32.43 [N(CH_3)(OCH_3)], 37.31 (C-6), 37.82 (C-4), 61.70 [N(CH_3)(OCH_3)], 77.30 (C-5), 120.48 (C-2), 127.53 and 127.59 (4× *meta*-C), 129.59 and 129.67 (2× *para*-C), 134.10 and 134.54 (2× *ipso*-C), 136.09 and 136.12 (4× *ortho*-C), 144.33 (C-3), 166.73 ppm (C-1). IR (film): $\tilde{\nu}$ = 3395, 3070, 3050, 2960, 2935, 2895, 2860, 1665, 1635, 1470, 1425, 1385, 1305, 1260, 1180, 1110, 1055, 1005, 940, 820 cm^{-1}. $C_{26}H_{37}NO_3Si$ (439.66): calcd. C 71.03, H 8.48, N 3.19; found C 70.74, H 8.49, N 3.15.

(*R*,*E*)-6-(Benzyloxymethoxy)non-3-en-2-one (35a): This compound was prepared from **32a** (326 mg, 1.01 mmol) as described for **14a**. Flash chromatography (3×16.5 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 25–35, 205 mg, 73%) as a colorless oil. $[\alpha]_{589}^{20}$ = +30.9, $[\alpha]_{578}^{20}$ = +32.4, $[\alpha]_{546}^{20}$ = +37.4, $[\alpha]_{436}^{20}$ = +69.9, $[\alpha]_{365}^{20}$ = +125.1 (c = 0.89, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.93 (dd, $J_{9,8–H(A)} = J_{9,8–H(B)}$ = 7.3 Hz, 9-H_3), 1.30–1.61 (m, 7-H_2, 8-H_2), 2.21 (s, 1-H_3), AB signal (δ_A = 2.44, δ_B = 2.50, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,4}$ = 7.4 Hz, $J_{A,6}$ = 5.8 Hz, $^4J_{A,3}$ = 1.5 Hz, B part additionally split by $J_{B,4}$ = 7.0 Hz, $J_{B,6}$ = 5.4 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.80 (dddd, $J_{6,7–H(A)}$ = 6.8 Hz, $J_{6,7–H(B)} = J_{6,5–H(B)} = J_{6,5–H(A)}$ = 5.5 Hz, 5-H), 4.62 (s, OCH_2OCH_2Ar), AB signal (δ_A = 4.79, δ_B = 4.81, J_{AB} = 7.2 Hz, OCH_2OCH_2Ar), 6.12 (ddd, $J_{3,4}$ = 16.0 Hz, $^4J_{3,5–H(A)} = {}^4J_{3,5–H(B)}$ = 1.5 Hz, 3-H), 6.83 (ddd, $J_{4,3}$ = 16.0 Hz, $J_{4,5–H(A)} = J_{4,5–H(B)}$ = 7.3 Hz, 4-H), 7.26–7.37 ppm (m, 2× *ortho*-H, 2× *meta*-H, *para*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 (C-9), 18.70 (C-8), 26.89 (C-1), 36.75 (C-7), 37.59 (C-5), 69.79 (OCH_2OCH_2Ar), 76.10 (C-6), 93.56 (OCH_2OCH_2Ar), 127.82 (2× *ortho*-C, *para*-C), 128.55 (2× *meta*-C), 133.52 (C-3), 137.82 (*ipso*-C), 144.38 (C-4), 198.43 ppm (C-2). IR (film): $\tilde{\nu}$ = 3500, 3065, 3030, 2960, 2935, 2875, 1700, 1675, 1630, 1495, 1455, 1430, 1360, 1320, 1255, 1205, 1165, 1100, 1080, 1040, 985, 910, 815, 740 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{17}H_{28}NO_3$ 294.2069 [M + NH_4]$^+$; found 294.2068 (–0.4 ppm). $C_{17}H_{24}O_3$ (276.37): calcd. C 73.88, H 8.75; found C 73.72, H 8.75.

(*S*,*E*)-6-(Benzyloxymethoxy)-7-methyloct-3-en-2-one (35b): This compound was prepared from **32b** (580 mg, 1.80 mmol) as described for **14a**. Flash chromatography (3×17 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 27–44, 419 mg, 84%) as a colorless oil. $[\alpha]_{589}^{20}$ = +21.7, $[\alpha]_{578}^{20}$ = +22.9, $[\alpha]_{546}^{20}$ = +26.6, $[\alpha]_{436}^{20}$ = +49.9, $[\alpha]_{365}^{20}$ = +90.2 (c = 0.79, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.94 and 0.96 [2×d, $J_{7\text{-Me},7}$ = 6.8 Hz, 7-(CH_3)$_2$], 1.87 (qqd, $J_{7,8}$ = $J_{7,7–Me}$ = 6.9 Hz, $J_{7,6}$ = 3.7 Hz, 7-H), 2.18 (s, 1-H_3), AB signal (δ_A = 2.45, δ_B = 2.48, J_{AB} = 15.5 Hz, A part additionally split by $J_{A,4}$ = 7.7 Hz, $J_{A,6}$ = 5.9 Hz, $^4J_{A,3}$ = 1.3 Hz, B part additionally split by $J_{B,4}$ = 7.6 Hz, $J_{B,6}$ = 5.7 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.56 (ddd, $J_{6,5–H(A)} = J_{6,5–H(B)} = J_{6,7}$ = 5.6 Hz, 6-H), 4.63 (s, OCH_2OCH_2Ar), AB signal (δ_A = 4.79, δ_B = 4.81, J_{AB} = 7.1 Hz, OCH_2OCH_2Ar), 6.13 (ddd, $J_{3,4}$ = 16.0, $^4J_{3,5–H(A)} = {}^4J_{3,5–H(B)}$ = 1.4, 3-H), 6.85 (ddd, $J_{4,3}$ = 15.9 Hz, $J_{4,5–H(A)} = J_{4,5–H(B)}$ = 7.3 Hz, 4-H), 7.26–7.37 ppm (m, 2× *ortho*-

H, 2× *meta*-H, *para*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.13 and 18.18 [7-(CH_3)$_2$], 26.81 (C-1), 31.43 (C-7), 34.43 (C-5), 69.86 (OCH_2OCH_2Ar), 81.66 (C-6), 94.19 (C-OCH_2OCH_2Ar), 127.76 (2× *ortho*-C), 127.81 (*para*-C), 128.54 (2× *meta*-C), 133.28 (C-3), 137.82 (*ipso*-C), 145.10 (C-4), 198.43 ppm (C-2). IR (film): $\tilde{\nu}$ = 3310, 3065, 3030, 2960, 2885, 2365, 1955, 1870, 1695, 1675, 1630, 1500, 1465, 1455, 1425, 1385, 1360, 1290, 1255, 1210, 1165, 1135, 1100, 1040, 970, 905, 855 cm^{-1}. $C_{17}H_{24}O_3$ (276.37): calcd. C 73.88, H 8.75; found C 73.95, H 8.48.

(*R*,*E*)-6-(4-Methoxybenzyloxy)non-3-en-2-one (36a): This compound was prepared from **33a** (275 mg, 0.86 mmol) as described for **14a**. Flash chromatography (2.5×15.5 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 21–32, 208 mg, 88%) as a colorless oil. $[\alpha]_{365}^{20}$ = +16.0 (*c* = 0.49, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): 0.92 (dd, $J_{9,8-H(A)} = J_{9,8-H(B)}$ = 7.2 Hz, 9-H_3), 1.29–1.63 (m, 7-H_2, 8-H_2), 2.24 (s, 1-H_3), AB signal (δ_A = 2.43, δ_B = 2.48, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,4}$ = 7.3 Hz, $J_{A,6}$ = 6.0 Hz, $^4J_{A,3}$ = 1.3 Hz, B part additionally split by $J_{B,4}$ = 7.1 Hz, $J_{B,6}$ = 5.4 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.52 (m_c, approximately interpretable as dddd, $J_{6,7-H(A)}$ = 6.5, $J_{6,5-H(A)} = J_{6,5-H(B)}$ = 5.7 Hz, $J_{6,7-H(B)}$ = 5.0 Hz, 6-H), 3.81 (s, OCH_3), 4.47 (s, OCH_2Ar), 6.11 (ddd, $J_{3,4}$ = 16.0 Hz, $^4J_{3,5-H(A)} = {}^4J_{3,5-H(B)}$ = 1.4 Hz, 3-H), 6.81 ppm (ddd, $J_{4,3}$ = 16.0 Hz, $J_{4,5-H(A)} = J_{4,5-H(B)}$ = 7.3 Hz, 4-H), AA′BB′ signal (peaks centered at δ_A = 6.89 and δ_B = 7.26, 2× *ortho*-H, 2× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.18 (C-9), 18.67 (C-8), 26.82 (C-1), 36.44 (C-5) 37.13 (C-7), 55.35 (OCH_3), 70.84 (OCH_2Ar), 77.23 (C-6), 113.90 (2× *meta*-C), 129.43 (2× *ortho*-C), 130.64 (*ipso*-C), 133.32 (C-3), 144.86 (C-4), 159.31 (*para*-C), 198.54 ppm (C-2). IR (film): $\tilde{\nu}$ = 3420, 2960, 2905, 2870, 2345, 2065, 1890, 1720, 1655, 1615, 1585, 1560, 1540, 1515, 1465, 1385, 1365, 1345, 1315, 1300, 1250, 1220, 1170, 1140, 1110, 1070, 1040, 970, 840, 820 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{17}H_{28}NO_3$ 294.2069 $[M + NH_4]^+$; found 294.2065 (–1.4 ppm).

(*S*,*E*)-6-(4-Methoxybenzyloxy)-7-methyloct-3-en-2-one (36b): This compound was prepared from **33b** (317 mg, 0.99 mmol) as described for **14a**. Flash chromatography (2.5×14 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 15–29, 237 mg, 87%) as a colorless oil. $[\alpha]_{436}^{20}$ = +19.8, $[\alpha]_{365}^{20}$ = +27.7 (*c* = 0.59, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.92 and 0.95 [2× d, $J_{7\text{-Me},7}$ = 6.8 Hz, 7-(CH_3)$_2$], 1.89 (qqd, $J_{7,8} = J_{7,7-Me}$ = 6.8 Hz, $J_{7,6}$ = 3.7 Hz, 7-H), 2.21 (s, 1-H_3), AB signal (δ_A = 2.39, δ_B = 2.44, J_{AB} = 14.8 Hz, A part additionally split by $J_{A,4}$ = 7.5 Hz, $J_{A,6}$ = 5.1 Hz, $^4J_{A,3}$ = 1.4 Hz, B part additionally split by $J_{B,4}$ = 7.2 Hz, $J_{B,6}$ = 5.0 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.27 (m_c, 6-H), 3.80 (s, OCH_3), AB signal (δ_A = 4.43, δ_B = 4.47, J_{AB} = 11.1 Hz, OCH_2Ar), 6.10 (ddd, $J_{3,4}$ = 16.0, $^4J_{3,5-H(A)} = {}^4J_{3,5-H(B)}$ = 1.4 Hz, 3-H), 6.81 ppm (ddd, $J_{4,3}$ = 16.0 Hz, $J_{4,5-H(A)} = J_{4,5-H(B)}$ = 7.3 Hz, 4-H), AA′BB′ signal (peaks centered at δ_A = 6.87, δ_B = 7.25, 2× *ortho*-H, 2× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.06 and 18.46 [7-(CH_3)$_2$], 26.78 (C-1), 31.18 (C-7), 33.92 (C-5), 55.35 (OCH_3), 71.65 (OCH_2Ar), 82.72 (C-6), 113.88 (2× *meta*-C), 129.48 (2× *ortho*-C), 130.70 (*ipso*-C), 133.09 (C-3), 145.81 (C-4), 159.30 (*para*-C), 198.57 ppm (C-2). IR (film): $\tilde{\nu}$ = 3310, 2960, 2870, 2840, 2060, 1695, 1675, 1625, 1615, 1585, 1515, 1465, 1440, 1360, 1300, 1250, 1210, 1175, 1110, 1070, 1035, 980, 845, 820 cm^{-1}. $C_{17}H_{24}O_3$ (276.37): calcd. C 73.88, H 8.75; found C 73.95, H 9.04.

(*R*,*E*)-6-(*tert*-Butyldiphenylsilyloxy)non-3-en-2-one (37a): This compound was prepared from **34a** (916 mg, 2.08 mmol) as described for **14a**. Flash chromatography (3×16.5 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 8–15, 682 mg, 83%) as a colorless oil. $[\alpha]_{589}^{20}$ = +38.8, $[\alpha]_{578}^{20}$ = +40.7, $[\alpha]_{546}^{20}$ = +47.2, $[\alpha]_{436}^{20}$ = +90.0, $[\alpha]_{365}^{20}$ = +169.1 (*c* = 1.29, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.77 (dd, $J_{8,7-H(A)} = J_{8,7-H(B)}$ = 7.3 Hz, 9-H_3), 1.06 (s, 2′-H_9), 1.19–1.33 (m, 8-H_2), 1.40–1.48 (m, 7-H_2), 2.15 (s, 1-H_3), AB signal (δ_A = 2.30, δ_B = 2.35, J_{AB} = 14.4 Hz, A part additionally split by $J_{A,4}$ = 7.4 Hz, $J_{A,6}$ = 5.5 Hz, $^4J_{A,3}$ = 1.5 Hz, B part additionally split by $J_{B,4}$ = 7.2 Hz, $J_{B,6}$ = 5.6 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.87 (dddd, $J_{6,7-H(A)} = J_{6,7-H(B)} = J_{6,5-H(B)} = J_{6,5-H(A)}$ = 5.7 Hz, 5-H), 5.96 (ddd, $J_{3,4}$ = 15.8 Hz, $^4J_{3,5-H(A)} = {}^4J_{3,5-H(B)}$ = 1.4 Hz, 2-H), 6.73 (ddd, $J_{4,3}$ = 15.5 Hz, $J_{4,5-H(A)} = J_{4,5-H(B)}$ = 7.7 Hz, 3-H), 7.35–7.46 (m, 4× *ortho*-H, 2× *para*-H), 7.65–7.69 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.08 (C-9), 18.24 (C-8), 19.46 (C-1′), 26.66 (C-1), 27.10 (C_3-2′), 39.06 (C-7), 39.63 (C-5), 72.18 (C-6), 127.66 and 127.68 (4× *meta*-C), 129.77 and 129.80 (2× *para*-C), 133.40 (C-3), 134.15 and 134.25 (2× *ipso*-C), 135.97 and 136.01 (4× *ortho*-C), 145.09 (C-4), 198.56 ppm (C-2). IR (film): $\tilde{\nu}$ = 3395, 3070, 3050, 3000, 2960, 2930, 2860, 1700, 1675, 1630, 1590, 1470, 1465, 1425, 1390, 1360, 1250, 1175, 1110, 1070, 1040, 985, 940, 895, 820 cm^{-1}. $C_{25}H_{34}O_2Si$ (394.62): calcd. C 76.09, H 8.68; found C 75.85, H 8.71.

(*R*,*E*)-6-(*tert*-Butyldiphenylsilyloxy)-7-methyloct-3-en-2-one (37b): This compound was prepared from **34b** (584 mg, 1.32 mmol) as described for **14a**. Flash chromatography (3×19.5 cm, 20 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 7–11, 409 mg, 78%) as a colorless oil. $[\alpha]_{589}^{20}$ = +48.1, $[\alpha]_{578}^{20}$ = +50.4, $[\alpha]_{546}^{20}$ = +58.2, $[\alpha]_{436}^{20}$ = +110.3, $[\alpha]_{365}^{20}$ = +217.4 (*c* = 1.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CHCl_3$): δ = 0.85 and 0.93 [2× d, $J_{7\text{-Me},7}$ = 6.8 Hz, 7-(CH_3)$_2$], 1.07 (s, 2′′-H_9), 1.74 (qqd, $J_{7,8} = J_{7,7-Me}$ = 6.8 Hz, $J_{7,6}$ = 3.9 Hz, 7-H), 2.05 (s, 1-H_3), AB signal (δ_A = 2.27, δ_B = 2.31, J_{AB} = 14.6 Hz, A part additionally split by $J_{A,4}$ = 7.3 Hz, $J_{A,6}$ = 5.8 Hz, $^4J_{A,3}$ = 1.5 Hz, B part additionally split by $J_{B,4}$ = 7.3 Hz, $J_{B,6}$ = 5.8 Hz, $^4J_{B,3}$ = 1.5 Hz, 5-H_2), 3.69 (ddd, $J_{6,5-H(A)} = J_{6,5-H(B)}$ = 5.9 Hz, $J_{6,7}$ = 3.9 Hz, 6-H), 5.88 (ddd, $J_{3,4}$ = 15.9 Hz, $^4J_{3,5-H(A)} = {}^4J_{3,5-H(B)}$ = 1.4 Hz, 2-H), 6.59 (ddd, $J_{4,3}$ = 15.8 Hz, $J_{4,5-H(A)} = J_{4,5-H(B)}$ = 7.3 Hz, 3-H), 7.35–7.46 (m, 4× *ortho*-H, 2× *para*-H), 7.65–7.70 ppm (m, 4× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.56 and 17.99 [7-(CH_3)$_2$], 19.64 (C-1′), 26.35 (C-1), 27.15 (C_3-2′), 33.26 (C-6), 36.55 (C-4), 127.61 and 127.67 (4× *meta*-C), 129.74 and 129.81 (2× *para*-C), 133.05 (C-3), 133.90 and 134.41 (2× *ipso*-C), 136.07 (4× *ortho*-C), 145.73 (C-4), 198.51 ppm (C-2). IR (film): $\tilde{\nu}$ = 3345, 3070, 3050, 2960, 2930, 2895, 2860, 1700 1675, 1630, 1590, 1470, 1425, 1390, 1360, 1315, 1255, 1175, 1110, 1045, 985, 940, 820 cm^{-1}. $C_{25}H_{34}O_2Si$ (394.62): calcd. C 76.09, H 8.68; found C 76.01, H 8.70.

1-{(4*S*,5*R*)-5-[(*R*)-2-(Benzyloxymethoxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-38a; as a mixture (90:10) with 1-{(4*R*,5*S*)-5-[(*R*)-2-(benzyloxymethoxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*anti*-38a)]: Compound **35a** (102 mg, 0.37 mmol) was added at 0 °C to a stirred mixture of $K_2OsO_2(OH)_4$ (1.4 mg, 1 mol-%), $(DHQD)_2PHAL$ (14 mg, 5 mol-%), $K_3Fe(CN)_6$ (365 mg, 1.11 mmol, 3.0 equiv.) K_2CO_3 (153 mg, 1.11 mmol, 3.0 equiv.), $NaHCO_3$ (93 mg, 1.1 mmol, 3.0 equiv.) and phenylboronic acid (54 mg, 0.44 mmol, 1.2 equiv.) in a 1:1 mixture (3 mL) of *t*BuOH and H_2O. After the system had been kept for 2 d at 0 °C, EtOAc (1 mL) was added and the phases were separated. The aq. phase was extracted with EtOAc (3×1 mL) and the combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (2.5×15.5 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 15–38, 99 mg, 68%) as a slightly yellow oil. Compound *syn*-**38a** (major diastereomer): $[\alpha]_{436}^{20}$ = –24.1, $[\alpha]_{365}^{20}$ = –50.3 (*c* = 0.41, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.96 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5′′-H_3), 1.36–1.52 (m, 4′′-H_2), 1.64–1.71 (m, 3′′-H_2), AB signal (δ_A = 1.96, δ_B = 2.06, J_{AB} = 14.4 Hz, A part additionally split by $J_{A,2''}$ = 5.8 Hz, $J_{A,5'}$ =

5.0 Hz, B part additionally split by $J_{B,5'}$ = 7.6 Hz, $J_{B,2''}$ = 5.7 Hz, 1′′-H_2), 2.31 (s, 2-H_3), 3.92 (dddd, $J_{2'',1'''-H(A)} = J_{2'',1'''-H(A)} = J_{2'',3''-H(B)}$ = 5.9 Hz, $J_{2'',3''-H(B)}$ = 5.9 Hz, 2′′-H), 4.50 (d, $J_{4',5'}$ = 6.4 Hz, 4′-H), AB signal (δ_A = 4.61, δ_B = 4.67, J_{AB} = 11.9 Hz, OCH_2OCH_2Ar), 4.65 (ddd, $J_{5',1''-H(B)}$ = 7.5 Hz, $J_{5',4'}$ = 6.5 Hz, $J_{5',1''-H(A)}$ = 4.9 Hz, 5′-H), AB signal (δ_A = 4.80, δ_B = 4.83, J_{AB} = 7.0 Hz, OCH_2OCH_2Ar), 7.26–7.35 (m, 2× *ortho*′-H, 2× *meta*′-H, *para*′-H), 7.41 (m_c, 2× *meta*-H), 7.52 ppm (m_c, *para*-H), 7.86 (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.29 (C-5′′), 18.50 (C-4′′), 26.28 (C-2), 36.68 (C-3′′), 41.25 (C-1′′), 69.78 (OCH_2OCH_2Ar), 74.62 (C-2′′), 77.39 (C-5′), 86.73 (C-4′), 93.94 (OCH_2OCH_2Ar), 127.71 (*para*′-C), 127.88 (2× *ortho*′-C), 128.03 (2× *meta*-C, *para*-C), 128.48 (2× *meta*′-C), 132.01 (*ipso*-C), 135.07 (2× *ortho*-C), 138.03 (*ipso*′-C), 208.46 ppm (C-1). IR (film): $\tilde{\nu}$ = 3455, 3030, 2960, 2935, 2875, 1720, 1605, 1500, 1440, 1405, 1360, 1315, 1255, 1210, 1170, 1100, 1040, 765, 750 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{16}H_{23}O_4B$ 290.1689 [M – OCH_2Ar]$^+$; found 290.1683 (–2.2 ppm). $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.68, H 7.55.

1-{(4*R*,5*S*)-5-[(*R*)-2-(Benzyloxymethoxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-38a; as an inseparable mixture (92:8) with 1-{(4*S*,5*R*)-5-[(*R*)-2-(benzyloxymethoxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-38a)]: Compound **35a** (104 mg, 0.38 mmol) was added at 0 °C to a stirred mixture of $K_2OsO_2(OH)_4$ (1.4 mg, 1 mol-%), $(DHQ)_2PHAL$ (15 mg, 5 mol-%), $K_3Fe(CN)_6$ (372 mg, 1.13 mmol, 3.0 equiv.) K_2CO_3 (156 mg, 1.13 mmol, 3.0 equiv.), $NaHCO_3$ (95 mg, 1.1 mmol, 3.0 equiv.), and $PhB(OH)_2$ (55 mg, 0.45 mmol, 1.2 equiv.) in a 1:1 mixture (3 mL) of *t*BuOH and H_2O. After the system had been kept for 2 d at 0 °C, EtOAc (1 mL) was added and the phases were separated. The aq. phase was extracted with EtOAc (3 × 1 mL). The combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (2.5 × 17 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 19–44, 109 mg, 73%) as a slightly yellow oil. Compound *anti*-**38a** (major diastereomer): $[\alpha]_{436}^{20}$ = –22.9 (*c* = 0.34, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.94 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5′′-H_3), 1.41 (m_c, 4′′-H_2), AB signal (δ_A = 1.59, δ_B = 1.66, J_{AB} = 13.7 Hz, A part additionally split by $J_{A,\ 4''-H(A)}$ = 8.6 Hz, $J_{A,2''} = J_{A,\ 4''-H(B)}$ = 6.5 Hz, B part additionally split by $J_{B,\ 4''-H(B)}$ = 8.4 Hz, $J_{B,\ 4''-H(A)}$ = 7.9 Hz, $J_{B,\ 2''}$ = 5.4 Hz, 3′′-H_2), AB signal (δ_A = 1.87, δ_B = 1.95, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,5'}$ = 9.5 Hz, $J_{A,2''}$ = 3.7 Hz, B part additionally split by $J_{B,2''}$ = 9.0 Hz, $J_{B,5'}$ = 3.9 Hz, 1′′-H_2), 2.29 (s, 2-H_3), 4.03 (dddd, $J_{2'',1'''-H(B)}$ = 9.1 Hz, $J_{2'',3''-H(A)}$ = 6.1 Hz, $J_{2'',3''-H(B)}$ = 5.6 Hz, $J_{2'',1'''-H(A)}$ = 3.5 Hz, 2′′-H), 4.44 (d, $J_{4',5'}$ = 6.7 Hz, 4′-H), AB signal (δ_A = 4.65, δ_B = 4.69, J_{AB} = 11.7 Hz, OCH_2OCH,Ar), 4.71 (ddd, $J_{5',1''-H(A)}$ = 9.4 Hz, $J_{5',4'}$ = 6.7, $J_{5',1''-H(B)}$ = 3.8 Hz, 5′-H), AB signal (δ_A = 4.86, δ_B = 4.89 Hz, J_{AB} = 7.0, OCH_2OCH_2Ar), 7.26–7.43 (m, 2× *ortho*-H, 2× *ortho*′-H, 2× *meta*′-H, *para*′-H), 7.52 (m_c, *para*-H), 7.85 ppm (m_c, 2× *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.33 (C-5′′), 18.18 (C-4′′), 26.18 (C-2), 37.11 (C-3′′), 42.41 (C-1′′), 69.76 (OCH_2OCH_2Ar), 74.08 (C-2′′), 77.19 (C-5′), 86.77 (C-4′), 93.91 (OCH_2OCH_2Ar), 127.72 (*para*′-C), 127.93 (2× *ortho*′-C), 128.00 (2× *meta*-C, *para*-C), 128.49 (2× *meta*′-C), 131.99 (*ipso*-C), 135.09 (2× *ortho*-C), 138.03 (*ipso*′-C), 208.06 ppm (C-1). IR (film): $\tilde{\nu}$ = 3425, 3060, 3030, 2960, 2935, 2875, 1720, 1605, 1500, 1455, 1440, 1405, 1360, 1305, 1210, 1170, 1100, 1040, 910, 765, 750 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{16}H_{23}O_4B$ 290.1689 [M – OCH_2Ar]$^+$; found 290.1685 (–1.5 ppm). $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.57, H 7.45.

1-{(4*S*,5*R*)-5-[(*S*)-2-(Benzyloxymethoxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-38b; as a mixture (91:9) with 1-{(4*R*,5*S*)-5-[(*S*)-2-(benzyloxymethoxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*anti*-38b)]: This compound was prepared from **35b** (130 mg, 0.47 mmol) as described for *syn*-**38a**. Flash chromatography (2 × 14.5 cm, 10 mL, cyclohexane/EtOAc 8:1) provided the title compound (fractions 8–28, 142 mg, 76%) as a slightly yellow oil. Compound *syn*-**38b** (major diastereomer): $[\alpha]_{589}^{20}$ = –19.9, $[\alpha]_{578}^{20}$ = –21.1, $[\alpha]_{546}^{20}$ = –24.3, $[\alpha]_{436}^{20}$ = –46.5, $[\alpha]_{365}^{20}$ = –83.9 (*c* = 0.93, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.96 and 1.00 [2× d, $J_{3''\text{-Me},3''}$ = 6.8 Hz, 3′′-$(CH_3)_2$], AB signal (δ_A = 1.93, δ_B = 2.05, J_{AB} = 14.3 Hz, A part additionally split by $J_{A,5'}$ = 5.8 Hz, $J_{A,2''}$ = 4.6 Hz, B part additionally split by $J_{B,5'}$ = $J_{B,2''}$ = 6.9 Hz, 1′′-H_2), 2.05–2.14 (m, 3′′-H), 2.30 (s, 2-H_3), 3.67 (ddd, $J_{2'',1'''-H(B)}$ = 6.8 Hz, $J_{2'',3''} = J_{2'',1'''-H(A)}$ = 4.7 Hz, 2′′-H), 4.50 (d, $J_{4',5'}$ = 6.4 Hz, 4′-H), AB signal (δ_A = 4.63, δ_B = 4.69, J_{AB} = 11.9 Hz, OCH_2OCH_2Ar), 4.68 (m_c, 5′-H), AB signal (δ_A = 4.81, δ_B = 4.86, J_{AB} = 6.9 Hz, OCH_2OCH_2Ar), 7.27–7.37 (m, 2× *ortho*′-H, 2× *meta*′-H, *para*′-H), 7.42 (m_c, 2× *meta*-H), 7.52 (m_c, *para*-H), 7.86 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.84 and 18.09 [$(CH_3)_{2-}$3′′], 26.18 (C-2), 31.29 (C-3′′), 37.83 (C-1′′), 69.89 (OCH_2OCH_2Ar), 77.82 (C-2′′), 79.96 (C-5′), 86.75 (C-4′), 94.75 (OCH_2OCH_2Ar), 127.68 (*para*′-C), 127.84 (2× *ortho*′-C), 128.02 (2× *meta*-C), 128.48 (2× *meta*′-C), 131.99 (*para*-C), 135.07 (2× *ortho*-C), 138.04 (*ipso*′-C), 208.60 ppm (C-1). IR (film): $\tilde{\nu}$ = 3425, 3080, 3060, 3030, 3005, 2955, 2935, 2875, 1720, 1605, 1500, 1455, 1440, 1405, 1380, 1360, 1305, 1250, 1205, 1165, 1100, 1030 cm^{-1}. $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.58, H 7.55.

1-{(4*R*,5*S*)-5-[(*S*)-2-(Benzyloxymethoxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-38b; as a mixture (92:8) with 1-{(4*S*,5*R*)-5-[(*S*)-2-(benzyloxymethoxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-38b)]: This compound was prepared from **35b** (126 mg, 0.46 mmol) as described for *anti*-**38a**. Flash chromatography (2 × 15 cm, 10 mL, cyclohexane/EtOAc 8:1) provided the title compound (fractions 10–28, 117 mg, 65%) as a slightly yellow oil. Compound *anti*-**38b** (major diastereomer): $[\alpha]_{589}^{20}$ = –23.1, $[\alpha]_{578}^{20}$ = –24.0, $[\alpha]_{546}^{20}$ = –26.9, $[\alpha]_{436}^{20}$ = –39.0, $[\alpha]_{365}^{20}$ = –38.9 (*c* = 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.93 and 0.97 [2× d, $J_{3''\text{-Me},3''}$ = 6.9 Hz, 3′′-$(CH_3)_2$], AB signal (δ_A = 1.79, δ_B = 1.89, J_{AB} = 14.3 Hz, A part additionally split by $J_{A,5'}$ = 9.7 Hz, $J_{A,2''}$ = 2.8 Hz, B part additionally split by $J_{B,2''}$ = 9.7 Hz, $J_{B,5'}$ = 3.5 Hz, 1′′-H_2), 2.01–2.13 (m, 3-H), 2.28 (s, 2-H_3), 3.89 (ddd, $J_{2'',1'''-H(B)}$ = 9.7 Hz, $J_{2'',3''}$ = 4.1 Hz, $J_{2'',1'''-H(A)}$ = 2.9 Hz, 2′′-H), 4.46 (d, $J_{4',5'}$ = 6.7 Hz, 4′-H), 4.68 (s, OCH_2OCH_2Ar), 4.71 (ddd, $J_{5',1''-H(A)}$ = 9.9 Hz, $J_{5',4'}$ = 6.5 Hz, $J_{5',1''-H(B)}$ = 3.4 Hz, 5′-H), 4.89 (s, OCH_2OCH_2Ar), 7.25–7.44 (m, 2× *ortho*′-H, 2× *meta*′-H, *para*′-H), 7.42 (m_c, 2× *meta*-H), 7.52 (m_c, *para*-H), 7.86 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.91 and 18.26 [$(CH_3)_{2-}$3′′], 26.11 (C-2), 31.18 (C-3′′), 38.05 (C-1′′), 69.84 (OCH_2OCH_2Ar), 77.37 (C-2′′), 79.91 (C-5′), 86.82 (C-4′), 94.62 (OCH_2OCH_2Ar), 127.69 (*para*′-C_r), 127.84 (2× *ortho*′-C), 127.99 and 128.02 (2× *meta*-C), 128.48 (2× *meta*′-C), 131.97 (*ipso*-C), 135.07 (*para*-C), 135.09 (2× *ortho*-C), 138.02 (*ipso*′-C), 208.12 ppm (C-1). IR (film): $\tilde{\nu}$ = 3455, 3060, 3030, 2960, 2935, 2875, 1720, 1605, 1500, 1455, 1440, 1405, 1360, 1315, 1305, 1255, 1210, 1170, 1100, 1040, 1030, 975 cm^{-1}. $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.49, H 7.63.

1-{(4*S*,5*R*)-5-[(*R*)-2-(4-Methoxybenzyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-39a; as a mixture (92:8) with 1-{(4*R*,5*S*)-5-[(*R*)-2-(4-methoxybenzyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*anti*-39a)]: This compound was prepared from **36a** (85 mg, 0.31 mmol) as described for *syn*-**38a**. Flash chromatography (2.5 × 16 cm, 10 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 13–36, 94 mg, 77%) as a

slightly yellow oil. Compound *syn*-**39a** (major diastereomer): $[\alpha]_{589}^{20}$ = –30.8, $[\alpha]_{578}^{20}$ = –32.8, $[\alpha]_{546}^{20}$ = –38.0, $[\alpha]_{436}^{20}$ = –72.2, $[\alpha]_{365}^{20}$ = –133.3 (*c* = 0.48, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.95 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5''-H_3), 1.34–1.50 (m, 4''-H_2), 1.54–1.71 (m, 3''-H_2), AB signal (δ_A = 1.94, δ_B = 2.07, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,2''} = J_{A,5'}$ = 5.5 Hz, B part additionally split by $J_{B,5'} = J_{B,2''}$ = 6.6 Hz, 1''-H_2), 2.30 (s, 2-H_3), 3.68 (m_c, 2''-H), 3.79 (s, OCH_3), AB signal (δ_A = 4.42, δ_B = 4.46, J_{AB} = 10.9 Hz, OCH_2Ar), 4.57 (d, $J_{4',5'}$ = 6.4 Hz, 4'-H), 4.67 (m_c, approximately interpretable as ddd, $J_{5',1''-H(B)} = J_{5',4'}$ = 6.2 Hz, $J_{5',1''-H(A)}$ = 6.0 Hz, 5'-H), AA'BB' signal (peaks centered at δ_A = 6.86 and δ_B = 7.27, 2× *ortho'*-H, 2× *meta'*-H), 7.42 (m_c, 2× *meta*-H), 7.53 (m_c, *para*-H), 7.86 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.32 (C-5''), 18.48 (C-4''), 26.24 (C-2), 36.12 (C-3''), 40.61 (C-1''), 55.35 (OCH_3), 70.65 (OCH_2Ar), 75.07 (C-2''), 77.47 (C-5'), 86.60 (C-4'), 113.85 (2× *meta'*-C), 128.02 (2× *meta*-C), 129.53 (*ipso'*-C, 2× *ortho'*-C), 130.88 (*ipso*-C), 131.97 (*para*-C), 135.07 (2× *ortho*-C), 159.22 (*para'*-C), 208.45 ppm (C-1). IR (film): $\tilde{\nu}$ = 3425, 2955, 2935, 2870, 1720, 1605, 1585, 1515, 1465, 1440, 1405, 1360, 1300, 1250, 1210, 1175, 1100, 1035, 825, 760 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{15}H_{21}O_3B$ 260.1584 $[M - CH_2C_6H_4OCH_3]^+$; found 260.1580 (–1.5 ppm). $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.73, H 7.56.

1-{(4*R*,5*S*)-5-[(*R*)-2-(4-Methoxybenzyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-39a; as a mixture (92:8) with 1-{(4*S*,5*R*)-5-[(*R*)-2-(4-methoxybenzyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-39a)]: This compound was prepared from **36a** (81 mg, 0.29 mmol) as described for *anti*-**38a**. Flash chromatography (2.5 × 15 cm, 10 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 11–37, 95 mg, 82%) as a slightly yellow oil. Compound *anti*-**39a** (major diastereomer): $[\alpha]_{589}^{20}$ = –28.8, $[\alpha]_{578}^{20}$ = –30.3, $[\alpha]_{546}^{20}$ = –34.4, $[\alpha]_{436}^{20}$ = –57.2, $[\alpha]_{365}^{20}$ = –82.3 (*c* = 0.71, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.95 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5''-H_3), 1.41 (m_c, 4''-H_2), AB signal (δ_A = 1.56, δ_B = 1.65, J_{AB} = 13.8 Hz, A part additionally split by $J_{A,4''-H(A)}$ = 8.7 Hz, $J_{A,2''} = J_{A,4''-H(B)}$ = 6.4 Hz, B part additionally split by $J_{B,4''-H(B)}$ = 8.1 Hz, $J_{B,4''-H(A)}$ = 7.9 Hz, $J_{B,2''}$ = 5.6 Hz, 3''-H_2), AB signal (δ_A = 1.87, δ_B = 1.94, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,5'}$ = 8.6 Hz, $J_{A,2''}$ = 3.7 Hz, B part additionally split by $J_{B,2''}$ = 9.1 Hz, $J_{B,5'}$ = 4.9 Hz, 1''-H_2), 2.26 (s, 2-H_3), 3.77 (dddd, $J_{2'',1''-H(B)}$ = 9.1 Hz, $J_{2'',3''-H(A)} = J_{2'',3''-H(B)}$ = 5.7 Hz, $J_{2'',1''-H(A)}$ = 3.4 Hz, 2''-H), 3.80 (s, OCH_3), AB signal (δ_A = 4.45, δ_B = 4.56, J_{AB} = 10.9 Hz, OCH_2Ar), 4.49 (d, $J_{4',5'}$ = 6.6 Hz, 4'-H), 4.71 (ddd, $J_{5',1''-H(A)}$ = 8.5 Hz, $J_{5',4'}$ = 6.5 Hz, $J_{5',1''-H(B)}$ = 4.8 Hz, 5'-H), AA'BB' signal (peaks centered at δ_A = 6.88 and δ_B = 7.28, 2× *ortho'*-H, 2× *meta'*-H), 7.42 (m_c, 2× *meta*-H), 7.52 (m_c, *para*-H), 7.85 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.38 (C-5''), 18.27 (C-4''), 26.25 (C-2), 36.50 (C-3''), 42.10 (C-1''), 55.36 (OCH_3), 70.99 (OCH_2Ar), 75.26 (C-2''), 77.47 (C-5'), 86.72 (C-4'), 113.84 (2× *meta'*-C), 127.99 (2× *meta*-C), 129.44 (*ipso'*-C, 2× *ortho'*-C), 130.99 (*ipso*-C), 131.93 (*para*-C), 135.06 (2× *ortho*-C), 159.22 (*para'*-C), 207.71 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 3000, 2955, 2930, 2870, 2835, 1720, 1605, 1585, 1515, 1465, 1440, 1360, 1300, 1250, 1210, 1175, 1095, 1035, 825, 760 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{15}H_{21}O_3B$ 260.1584 $[M - CH_2C_6H_4OCH_3]^+$; found 260.1577 (–2.6 ppm). $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.73, H 7.66.

1-{(4*S*,5*R*)-5-[(*S*)-2-(4-Methoxybenzyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-39b; as a mixture (93:7) with 1-{(4*R*,5*S*)-5-[(*S*)-2-(4-methoxybenzyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*anti*-39b)]: This compound was prepared from **36b** (84 mg, 0.30 mmol) as described for *syn*-**38a**. Flash chromatography (2.5 × 16 cm, 10 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 14–39, 80 mg, 66%) as a slightly yellow oil. Compound *syn*-**39b** (major diastereomer): $[\alpha]_{589}^{20}$ = –52.2, $[\alpha]_{578}^{20}$ = –55.1, $[\alpha]_{546}^{20}$ = –63.1, $[\alpha]_{436}^{20}$ = –115.2, $[\alpha]_{365}^{20}$ = –203.7 (*c* = 0.77, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.95 and 0.96 [2 × d, $J_{3''\text{-Me},3''}$ = 6.8 Hz, 3''-$(CH_3)_2$], AB signal (δ_A = 1.90, δ_B = 2.03, J_{AB} = 14.4 Hz, A part additionally split by $J_{A,5'}$ = 6.5 Hz, $J_{A,2''}$ = 3.8 Hz, B part additionally split by $J_{B,2''}$ = 7.7 Hz, $J_{B,5'}$ = 5.9 Hz, 1''-H_2), 2.04–2.14 (m, 3''-H), 2.30 (s, 2-H_3), 3.45 (ddd, $J_{2'',1''-H(B)}$ = 7.7 Hz, $J_{2'',3''}$ = 4.7 Hz, $J_{2'',1''-H(A)}$ = 3.8 Hz, 2''-H), 3.80 (s, OCH_3), AB signal (δ_A = 4.42, δ_B = 4.48, J_{AB} = 10.7 Hz, OCH_2Ar), 4.58 (d, $J_{4',5'}$ = 6.3 Hz, 4'-H), 4.70 (ddd, $J_{5',1''-H(A)} = J_{5',1''-H(B)} = J_{5',4'}$ = 6.2 Hz, 5'-H), AA'BB' signal (peaks centered at δ_A = 6.87 and δ_B = 7.29, 2× *ortho'*-H, 2× *meta'*-H), 7.42 (m_c, 2× *meta*-H), 7.53 (m_c, *para*-H), 7.87 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.38 and 18.46 [$(CH_3)_2$–3''], 26.16 (C-2), 30.27 (C-3''), 36.74 (C-1''), 55.33 (OCH_3), 71.19 (OCH_2Ar), 77.94 (C-2''), 79.99 (C-5'), 86.60 (C-4'), 113.81 (2× *meta'*-C), 128.02 (2× *meta*-C), 129.50 (*ipso'*-C, 2× *ortho'*-C), 131.02 (*ipso*-C), 131.96 (*para*-C), 135.07 (2× *ortho*-C), 159.18 (*para'*-C), 208.67 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2960, 2930, 2870, 1720, 1610, 1605, 1585, 1515, 1500, 1465, 1440, 1405, 1360, 1300, 1250, 1210, 1175, 1145, 1095, 1035, 820 cm^{-1}. $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.60, H 7.58.

1-{(4*R*,5*S*)-5-[(*S*)-2-(4-Methoxybenzyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-39b; as a mixture (92:8) with 1-{(4*S*,5*R*)-5-[(*S*)-2-(4-methoxybenzyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-39b)]: This compound was prepared from **36b** (86 mg, 0.31 mmol) as described for *anti*-**38a**. Flash chromatography (2.5 × 15 cm, 10 mL, cyclohexane/EtOAc 9:1) provided the title compound (fractions 18–40, 73 mg, 59%) as a slightly yellow oil. Compound *anti*-**39b** (major diastereomer): $[\alpha]_{589}^{20}$ = –40.0, $[\alpha]_{578}^{20}$ = –41.5, $[\alpha]_{546}^{20}$ = –47.1, $[\alpha]_{436}^{20}$ = –78.0, $[\alpha]_{365}^{20}$ = –112.0 (*c* = 1.32, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.95 and 0.96 [2 × d, $J_{3''\text{-Me},3''}$ = 6.8 Hz, 3''-$(CH_3)_2$], AB signal (δ_A = 1.81, δ_B = 1.86, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,5'}$ = 8.1 Hz, $J_{A,2''}$ = 4.0 Hz, B part additionally split by $J_{B,2''}$ = 8.1 Hz, $J_{B,5'}$ = 5.2 Hz, 1''-H_2), 2.00–2.10 (m, 3''-H), 2.25 (s, 2-H_3), 3.62 (ddd, $J_{2'',1''-H(B)}$ = 8.6 Hz, $J_{2'',3''}$ = 4.4 Hz, $J_{2'',1''-H(A)}$ = 4.0 Hz, 2''-H), 3.79 (s, OCH_3), AB signal (δ_A = 4.46, δ_B = 4.59, J_{AB} = 10.9 Hz, OCH_2Ar), 4.52 (d, $J_{4',5'}$ = 6.4 Hz, 4'-H), 4.70 (ddd, $J_{5',1''-H(A)}$ = 8.2 Hz, $J_{5',4'}$ = 6.4 Hz, $J_{5',1''-H(B)}$ = 5.3 Hz, 5'-H), AA'BB' signal (peaks centered at δ_A = 6.88 and δ_B = 7.28, 2× *ortho'*-H, 2× *meta'*-H), 7.42 (m_c, 2× *meta*-H), 7.53 (m_c, *para*-H), 7.86 ppm (m_c, 2× *ortho*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.02 and 18.49 [$(CH_3)_2$–3''], 26.20 (C-2), 30.47 (C-3''), 37.88 (C-1''), 55.34 (OCH_3), 71.76 (OCH_2Ar), 77.34 (C-2''), 80.10 (C-5'), 86.75 (C-4'), 113.82 (2× *meta'*-C), 127.98 (2× *meta*-C), 129.37 (*ipso'*-C, 2× *ortho'*-C), 131.13 (*ipso*-C), 131.92 (*para*-C), 135.05 (2× *ortho*-C), 159.17 (*para'*-C), 208.65 ppm (C-1). IR (film): $\tilde{\nu}$ = 3430, 2960, 2930, 2870, 2875, 1720, 1610, 1605, 1585, 1515, 1500, 1465, 1440, 1405, 1380, 1360, 1318, 1300, 1250, 1205, 1175, 1095, 1035, 985, 820 cm^{-1}. $C_{23}H_{29}BO_5$ (396.28): calcd. C 69.71, H 7.38; found C 69.59, H 7.62.

1-{(4*S*,5*R*)-5-[(*R*)-2-(*tert*-Butyldiphenylsilyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-40a; as a mixture (76:24) with 1-{(4*R*,5*S*)-5-[(*R*)-2-(*tert*-butyldiphenylsilyloxy)-pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*anti*-40a)]: This compound was prepared from **37a** (150 mg, 0.38 mmol) as described for *syn*-**38a**. Flash chromatography (2.5 × 17 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 8–26, 160 mg, 82%) as a slightly yellow oil. Compound *syn*-**40a** (major diastereomer):

$[\alpha]_{589}^{20}$ = –10.9, $[\alpha]_{578}^{20}$ = –11.3, $[\alpha]_{546}^{20}$ = –13.0, $[\alpha]_{436}^{20}$ = –26.2, $[\alpha]_{365}^{20}$ = –47.6 (*c* = 0.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.79 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5′′-H_3), 1.06 (s, 2′′′-H_9), 1.11–1.60 (m, 3′′-H_2, 4′′-H_2), AB signal (δ_A = 1.87, δ_B = 1.91, J_{AB} = 14.1 Hz, A part additionally split by $J_{A,5'} = J_{A,2''}$ = 4.7 Hz, B part additionally split by $J_{B,2''}$ = 6.3 Hz, $J_{B,5'}$ = 5.0 Hz, 1′′-H_2), 2.27 (s, 2-H_3), 4.07 (dddd, $J_{2'',1''-H(B)} = J_{2'',3''-H(A)}$ = 6.0 Hz, $J_{2'',3''-H(B)}$ = 5.7 Hz, $J_{2'',1''-H(A)}$ = 5.1 Hz, 2′′-H), 4.33 (d, $J_{4',5'}$ = 6.4 Hz, 4′-H), 4.61 (ddd, $J_{5',1''-H(A)}$ = 7.9 Hz, $J_{5',4'}$ = 6.2 Hz, $J_{5',1''-H(B)}$ = 5.1 Hz, 5′-H), 7.30–7.47 (m, 2× *meta*-H, 4× *ortho*′-H, 2× *para*′-H), 7.52 (m_c, *para*-H), 7.66–7.80 ppm (m_c, 2× *ortho*-H, 4× *meta*′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.19 (C-5′′), 18.13 (C-4′′), 19.41 (C-2), 26.16 (C-3′′), 27.13 (C_3-2′′′), 38.19 (C-1′′′), 43.20 (C-1′′), 70.14 (C-5′), 77.04 (C-2′′), 86.80 (C-4′), 127.58 and 127.61 (4× *meta*′-C), 127.94 (2× *para*′-C), 129.64 (2× *meta*-C), 131.92 (*para*-C), 134.32 (*ipso*-C), 134.56 (2× *ipso*′-C), 135.07 (4× *ortho*′-C), 135.97 (2× *ortho*-C), 208.09 ppm (C-1). IR (film): $\tilde{\nu}$ = 3460, 3070, 3050, 2960, 2930, 2860, 1965, 1900, 1825, 1720, 1605, 1590, 1500, 1470, 1460, 1440, 1425, 1375, 1360, 1315, 1255, 1205, 1155, 1110, 1070, 1040, 1005, 895, 820, 805, 765, 740, 700 cm^{-1}. $C_{31}H_{39}BO_4Si$ (514.54): calcd. C 72.36, H 7.64; found C 72.09, H 7.79.

1-{(4*R*,5*S*)-5-[(*R*)-2-(*tert*-Butyldiphenylsilyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-40a; as a mixture (89:11) with 1-{(4*S*,5*R*)-5-[(*R*)-2-(*tert*-butyldiphenylsilyloxy)pentyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-40a)]: This compound was prepared from **37a** (150 mg, 0.38 mmol) as described for *anti*-**38a**. Flash chromatography (2.5 × 17 cm, 10 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 9–29, 119 mg, 61%) as a slightly yellow oil. Compound *anti*-**40a** (major diastereomer): $[\alpha]_{589}^{20}$ = –17.3, $[\alpha]_{578}^{20}$ = –18.0, $[\alpha]_{546}^{20}$ = –20.4, $[\alpha]_{436}^{20}$ = –32.5, $[\alpha]_{365}^{20}$ = –51.0 (*c* = 0.85, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.71 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5′′-H_3), 1.06 (s, 2′′′-H_9), 1.08–1.67 (m, 3′′-H_2, 4′′-H_2), AB signal (δ_A = 1.79, δ_B = 1.88, J_{AB} = 13.9 Hz, A part additionally split by $J_{A,5'}$ = 9.7 Hz, $J_{A,2''}$ = 4.0 Hz, B part additionally split by $J_{B,2''}$ = 8.3 Hz, $J_{B,5'}$ = 3.7 Hz, 1′′-H_2), 2.21 (s, 2-H_3), 4.10 (dddd, $J_{2'',1''-H(B)}$ = 8.5 Hz, $J_{2'',3''-H(A)} = J_{2'',3''-H(B)}$ = 5.2 Hz, $J_{2'',1''-H(A)}$ = 4.0 Hz, 2′′-H), 4.19 (d, $J_{4',5'}$ = 7.0 Hz, 4′-H), 4.60 (ddd, $J_{5',1''-H(A)}$ = 9.7 Hz, $J_{5',4'}$ = 7.0 Hz, $J_{5',1''-H(B)}$ = 3.7 Hz, 5′-H), 7.29–7.47 (m, 2× *meta*-H 4× *ortho*′-H, 2× *para*′-H), 7.51 (m_c, *para*-H), 7.65–7.79 ppm (m_c, 2× *ortho*-H, 4× *meta*′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.06 (C-5′′), 17.70 (C-4′′), 19.57 (C-2), 25.88 (C-3′′), 27.16 (C_3-2′′′), 39.61 (C-1′′′), 44.13 (C-1′′), 69.73 (C-5′), 77.02 (C-2′′), 86.83 (C-4′), 127.57 and 127.61 (4× *meta*′-C), 127.95 (2× *para*′-C), 129.63 (2× *meta*-C), 131.92 (*para*-C), 134.27 (*ipso*-C), 134.46 (2× *ipso*′-C), 135.09 (4× *ortho*′-C), 136.09 and 136.13 (2× *ortho*-C), 207.89 ppm (C-1). IR (film): $\tilde{\nu}$ = 3465, 3070, 3050, 2960, 2930, 2855, 1965, 1900, 1825, 1720, 1605, 1590, 1500, 1470, 1460, 1440, 1425, 1380, 1360, 1315, 1240, 1205, 1155, 1110, 1040, 1005, 1000, 940, 910, 820, 805, 760, 740, 700 cm^{-1}. $C_{31}H_{39}BO_4Si$ (514.54): calcd. C 72.36, H 7.64; found C 72.07, H 7.88.

1-{(4*S*,5*R*)-5-[(*S*)-2-(*tert*-Butyldiphenylsilyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*syn*-40b; as a mixture (71:29) with 1-{(4*R*,5*S*)-5-[(*R*)-2-(*tert*-butyldiphenylsilyloxy)3-methylbutyl]-2-phenyl-1,3,2-dioxa-borolan-4-yl}ethanone (*anti*-40b)]: This compound was prepared from **37b** (135 mg, 0.34 mmol) as described for *syn*-**38b**. Flash chromatography (2.5 × 17 cm, 10 mL, cyclohexane/EtOAc 20:1) provided the title compound (fractions 12–29, 90 mg, 51%) as a slightly yellow oil. Compound *syn*-**40b** (major diastereomer): $[\alpha]_{589}^{20}$ = –10.1, $[\alpha]_{578}^{20}$ = –10.7, $[\alpha]_{546}^{20}$ = –12.4, $[\alpha]_{436}^{20}$ = –23.5, $[\alpha]_{365}^{20}$ = –45.4 (*c* = 2.03, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.90 and 0.98 [2× d, $J_{3''-Me,3''}$ = 6.8 Hz, 3′′-$(CH_3)_2$], 1.07 (s, 2′′′-H_9), 1.64–1.75 (m, 3′′-H), AB signal (δ_A = 1.79, δ_B = 1.91, J_{AB} = 14.1 Hz, A part additionally split $J_{A,5'}$ = 9.3 Hz, $J_{A,2''}$ = 4.7 Hz, B part additionally split $J_{B,2''}$ = 7.8 Hz, $J_{B,5'}$ = 4.0 Hz, 1′′-H_2), 2.20 (s, 2-H_3), 3.94 (ddd, $J_{2'',1''-H(B)}$ = 7.8 Hz, $J_{2'',1''-H(A)}$ = 4.6 Hz, $J_{2'',3''}$ = 3.2 Hz, 2′′-H), 4.17 (d, $J_{4',5'}$ = 6.3 Hz, 4′-H), 4.42 (ddd, $J_{5',1''-H(A)}$ = 9.2 Hz, $J_{5',4'}$ = 6.3, $J_{5',1''-H(B)}$ = 4.0 Hz, 5′-H), 7.27–7.47 (m, 2× *meta*-H, 4× *ortho*′-H, 2× *para*′-H), 7.48–7.54 (m, *para*-H), 7.65–7.77 ppm (m, 2× *ortho*-H, 4× *meta*′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.36 and 19.23 [$(CH_3)_2$-3′′], 19.67 (C-2), 26.10 (C-3′′), 27.20 (C_3-2′′′), 31.76 (C-1′′′), 41.33 (C-1′′), 74.38 (C-5′), 77.00 (C-2′′), 86.75 (C-4′), 127.51 and 127.56 (4× *meta*′-C), 127.89 (2× *para*′-C), 129.55 and 129.64 (2× *meta*-C), 131.90 (*para*-C), 135.08 (4× *ortho*′-C), 136.08 (*ipso*-C), 136.11 (2× *ipso*′-C), 136.24 (2× *ortho*-C), 208.15 ppm (C-1). IR (film): $\tilde{\nu}$ = 3455, 3070, 3050, 2960, 2930, 2860, 1965, 1900, 1825, 1720, 1660, 1605, 1590, 1500, 1470, 1460, 1440, 1425, 1375, 1360, 1315, 1205, 1155, 1110, 1070, 1040, 1005, 935, 895, 820, 805, 765, 740, 700 cm^{-1}. $C_{31}H_{39}BO_4Si$ (514.54): calcd. C 72.36, H 7.64; found C 72.20, H 7.70.

1-{(4*R*,5*S*)-5-[(*S*)-2-(*tert*-Butyldiphenylsilyloxy)-3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone [*anti*-40b; as a mixture (94:6) with 1-{(4*S*,5*R*)-5-[(*R*)-2-(*tert*-butyldiphenylsilyloxy)3-methylbutyl]-2-phenyl-1,3,2-dioxaborolan-4-yl}ethanone (*syn*-40b)]: This compound was prepared from **37b** (134 mg, 0.34 mmol) as described for *anti*-**38b**. Flash chromatography (2 × 15 cm, 10 mL, cyclohexane/EtOAc 20:1) provided the title compound (fractions 15–29, 70 mg, 40%) as a slightly yellow oil. Compound *anti*-**40a** (major diastereomer): $[\alpha]_{365}^{20}$ = –16.0 (*c* = 1.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3/CDCl_3$): δ = 0.76 and 0.94 [2× d, $J_{3''-Me,3''}$ = 6.9 Hz, 3′′-$(CH_3)_2$], 1.09 (s, 2′′′-H_9), AB signal (δ_A = 1.68, δ_B = 1.82, J_{AB} = 14.0 Hz, A part additionally split by $J_{A,5'}$ = 10.3 Hz, $J_{A,2''}$ = 3.5 Hz, B part additionally split by $J_{B,2''}$ = 8.8 Hz, $J_{B,5'}$ = 3.3 Hz, 1′′-H_2), 1.80–1.93 (m, 3′′-H), 2.16 (s, 2-H_3), 3.99 (ddd, $J_{2'',1''-H(B)}$ = 8.8 Hz, $J_{2'',1''-H(A)} = J_{2'',3''}$ = 3.2 Hz, 2′′-H), 4.17 (d, $J_{4',5'}$ = 7.1 Hz, 4′-H), 4.48 (ddd, $J_{5',1''-H(A)}$ = 10.2 Hz, $J_{5',4'}$ = 7.0 Hz, $J_{5',1''-H(B)}$ = 3.3 Hz, 5′-H), 7.34–7.48 (m, 2× *meta*-H, 4× *ortho*′-H, 2× *para*′-H), 7.50 (m_c, *para*-H), 7.66–7.77 ppm (m, 2× *ortho*-H, 4× *meta*′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.68 and 17.83 [$(CH_3)_2$-3′′], 19.66 (C-2), 25.74 (C-3′′), 27.22 (C_3-2′′′), 33.30 (C-1′′′), 39.61 (C-1′′), 73.99 (C-5′), 77.00 (C-2′′), 86.93 (C-4′), 127.57 (4× *meta*′-C), 127.90 (2× *para*′-C), 129.55 and 129.69 (2× *meta*-C), 131.89 (C-4′′), 134.12 (*ipso*-C), 134.56 (2× *ipso*′-C), 135.08 (4× *ortho*′-C), 136.25 (2× *ortho*-C), 207.82 ppm (C-1). IR (film): $\tilde{\nu}$ = 3445, 3070, 3050, 2960, 2930, 2860, 1965, 1900, 1825, 1720, 1600, 1590, 1500, 1470, 1460, 1440, 1425, 1380, 1360, 1315, 1240, 1205, 1155, 1110, 1040, 1005, 940, 910, 820, 760, 740, 700 cm^{-1}. $C_{31}H_{39}BO_4Si$ (514.54): calcd. C 72.36, H 7.64; found C 71.12, H 7.94.

Preparation of $SmBr_2$ in THF: 1,1,2,2-Tetrabromoethane (354 mg, 1.02 mmol, 0.5 equiv.) was dissolved in THF (21 mL) and degassed at –78 °C. It was cannulated onto Sm powder (40 mesh, 308 mg, 2.05 mmol). After stirring at room temp. for 16 h, we obtained a black suspension. Its concentration in $SmBr_2$ was assumed to be 0.1 M. Because of the low stability of this solution it was prepared immediately before use.

(4*R*,6*R*)-4-Hydroxy-6-(4-methoxybenzyloxy)nonan-2-one [*syn*-41; as a mixture (91:9) with (4*S*,6*R*)-4-hydroxy-6-(4-methoxybenzyloxy)-nonan-2-one (*anti*-41)]: A degassed solution of *syn*-**39a** (254 mg, 0.64 mmol) in THF (6.5 mL) and MeOH (3 mL) was slowly added at –78 °C to a freshly prepared $SmBr_2$ suspension (0.1 M in THF, 21 mL, 2.04 mmol, 3.2 equiv.). After 90 min at this temperature the mixture was added into satd. aq. $NaHCO_3$ (20 mL). After addition of HCl (1 N, 50 mL) the phases were separated and the aq. phase

was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (2 × 15 cm, 10 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 24–38, 85 mg, 45%) as a slightly yellow oil. Compound *syn*-**41** (major diastereomer): $[\alpha]_{589}^{20}$ = –53.7, $[\alpha]_{578}^{20}$ = –56.6, $[\alpha]_{546}^{20}$ = –66.1, $[\alpha]_{436}^{20}$ = –114.0, $[\alpha]_{365}^{20}$ = –181.8; (*c* = 0.45, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): 0.93 (dd, $J_{9,8-H(A)} = J_{9,8-H(B)}$ = 7.3 Hz, 9-H_3), 1.31–1.44 (m, 8-H_2), 1.48–1.65 (m, 7-H_2), AB signal (δ_A = 1.59, δ_B = 1.70, J_{AB} = 14.3 Hz, A part additionally split by $J_{A,6}$ = 4.1 Hz, $J_{A,4}$ = 3.6 Hz, B part additionally split by $J_{B,4} = J_{B,6}$ = 8.8 Hz, 5-H_2), 2.15 (s, 1-H_3), AB signal (δ_A = 2.47, δ_B = 2.59, J_{AB} = 16.6 Hz, A part additionally split by $J_{A,4}$ = 4.5 Hz, B part additionally split by $J_{B,4}$ = 7.8 Hz, 3-H_2), 3.66 (dddd, $J_{6,5-H(B)}$ = 9.0 Hz, $J_{6,7-H(A)} = J_{6,5-H(A)} = J_{6,7-H(B)}$ = 4.4 Hz, 6-H), 3.73 (d, $J_{4,4-OH}$ = 1.9 Hz, 4-OH), 3.87 (s, OCH_3), 4.20 (m_c, 4-H), AB signal (δ_A = 4.37, δ_B = 4.54, J_{AB} = 10.6 Hz, OCH_2Ar), AA′BB′ signal (peaks centered at δ_A = 6.86, δ_B = 7.24, 2 × *ortho*-H, 2 × *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.37 (C-9), 18.13 (C-8), 30.98 (C-1), 35.76 (C-7), 40.45 (C-5), 50.70 (C-3), 55.37 (OCH_3), 67.29 (C-4), 70.29 (OCH_2Ar), 78.28 (C-6), 114.00 (2 × *meta*-C), 129.61 (2 × *ortho*-C), 130.37 (*ipso*-C), 159.38 (*para*-C), 208.83 ppm (C-2). IR (film): $\tilde{\nu}$ = 3460, 3000, 2955, 2935, 2870, 1710, 1615, 1585, 1515, 1465, 1425, 1360, 1300, 1250, 1175, 1035, 820, 740, 705 cm^{-1}.

(4*S*,6*S*)-6-(*tert*-Butyldiphenylsilyloxy)-4-hydroxy-7-methyloctan-2-one [*anti*-42; as a mixture (93:7) with (4*R*,6*S*)-6-(*tert*-butyldiphenylsilyloxy)-4-hydroxy-7-methyloctan-2-one (*syn*-42)]: This compound was prepared from *anti*-**40b** (329 mg, 0.64 mmol) as described for *syn*-**41**. Flash chromatography (2.5 × 18 cm, 20 mL, cyclohexane/EtOAc 6:1) provided the title compound (fractions 11–18, 158 mg, 60%) as a slightly yellow oil. Compound *anti*-**42** (major diastereomer): $[\alpha]_{589}^{20}$ = +2.5, $[\alpha]_{578}^{20}$ = +2.9, $[\alpha]_{546}^{20}$ = +6.8, $[\alpha]_{436}^{20}$ = +10.8, $[\alpha]_{365}^{20}$ = +12.1 (*c* = 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.77 and 0.92 [2 × d, $J_{7\text{-}Me,7}$ = 6.8 Hz, 7-$(CH_3)_2$], 1.07 (s, 2′-H_9), AB signal (δ_A = 1.41, δ_B = 1.45, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,4}$ = 7.1 Hz, $J_{A,6}$ = 3.7 Hz, B part additionally split by $J_{B,4}$ = 8.4 Hz, $J_{B,6}$ = 3.9 Hz, 5-H_2), 1.83 (qqd, $J_{7,8} = J_{7,7-Me}$ = 6.9 Hz, $J_{7,6}$ = 3.9 Hz, 7-H), 2.03 (s, 1-H_3), AB signal (δ_A = 2.27, δ_B = 2.36, J_{AB} = 17.0 Hz, A part additionally split by $J_{A,4}$ = 3.5 Hz, B part additionally split by $J_{B,4}$ = 8.6 Hz, 3-H_2), 2.36 (br. d, $J_{4\text{-}OH,\ 4}$ = 3.5 Hz, 4-OH), 3.82 (m_c, approximately interpretable as ddd, $J_{6,5-H(A)}$ = 7.5 Hz, $J_{6,5-H(B)} = J_{6,7}$ = 3.8 Hz, 6-H), 4.01 (m_c, approximately interpretable as dddd, $J_{4,3-H(B)} = J_{4,5-H(B)}$ = 8.5 Hz, $J_{4,5-H(A)}$ = 7.5 Hz, $J_{4,3-H(A)}$ = 3.8 Hz, 4-H), 7.35–7.47 (m, 4 × *ortho*-H, 2 × *para*-H), 7.66–7.77 ppm (m, 4 × *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.27 and 18.07 [7-$(CH_3)_2$], 19.68 (C-1), 27.20 (C_3-2′), 30.54 (C-1′), 33.51 (C-7), 39.00 (C-5), 50.70 (C-3), 64.51 (C-4), 74.91 (C-5), 127.61 and 127.63 (4 × *meta*-C), 129.69 and 129.72 (4 × *ortho*-C), 134.30 and 134.47 (2 × *para*-C), 136.14 and 136.15 (2 × *ipso*-C), 208.96 ppm (C-2). IR (film): $\tilde{\nu}$ = 3435, 3050, 3070, 2960, 2930, 2895, 2860, 1715, 1470, 1430, 1390, 1360, 1310, 1250, 1160, 1110, 1075, 1050, 1005, 940, 940, 880, 820, 740, 705, 690, 610 cm^{-1}. $C_{25}H_{36}O_3Si$ (412.64): calcd. C 72.77, H 7.79; found C 72.65, H 7.92.

(4*S*,6*S*)-2-Ethyl-4-[(*R*)-2-(4-methoxybenzyloxy)pentyl]-6-methyl-1,3,2-dioxaborinane {*syn*,*syn*-43; as a mixture (92:8) with (4*R*,6*R*)-2-ethyl-4-[(*R*)-2-(4-methoxybenzyloxy)pentyl]-6-methyl-1,3,2-dioxaborinane (*syn*,*anti*-43)}: BEt_3 (1.0 M in THF, 0.13 mL, 0.13 mmol, 1.2 equiv.) was dissolved in a 4:1 mixture of THF (0.6 mL) and MeOH (0.15 mL) and stirred at room temp. for 1 h. The mixture was then cooled to –78 °C and a solution of *syn*-**41** (32 mg, 0.11 mmol) in THF (0.5 mL) was added. After the system had been kept for 2 h at this temperature $NaBH_4$ (5.0 mg, 0.13 mmol, 1.2 equiv.) was added and the mixture was stirred overnight at –78 °C. After addition of satd. aq. NH_4Cl (1 mL) the phases were separated and the aq. phase was extracted with MTBE (3 × 1 mL). The combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (1 × 18.5 cm, 5 mL, cyclohexane/EtOAc 10:1) provided the title compound (fractions 18–21, 29 mg, 80%) as a slightly yellow oil. Compound *syn*,*syn*-**43** (major diastereomer): $[\alpha]_{589}^{20}$ = –10.3, $[\alpha]_{578}^{20}$ = –12.0, $[\alpha]_{546}^{20}$ = –14.8, $[\alpha]_{436}^{20}$ = –26.1, $[\alpha]_{365}^{20}$ = –45.2; (*c* = 0.13, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$/$CDCl_3$): δ = 0.65 (q, $J_{1'',2''}$ = 7.9 Hz, 1″-H_2), 0.87 (t, $J_{2'',1''}$ = 7.9 Hz, 1″-H_3), 0.92 (dd, $J_{5'',4''-H(A)} = J_{5'',4''-H(B)}$ = 7.3 Hz, 5″-H_3), 1.19 (d, $J_{6\text{-}Me,6}$ = 6.3 Hz, 6-CH_3), 1.32–1.48 (m, 4″-H_2), 1.49–1.61 (m, 1″-H_2, 3″-H_2), AB signal (δ_A = 1.70, δ_B = 1.88, J_{AB} = 13.8 Hz, A part additionally split by $J_{A,2''} = J_{A,4'''}$ = 2.7 Hz, B part additionally split by $J_{B,2''} = J_{B,4'''}$ = 6.9 Hz, 5-H_2), 3.56 (m_c, 2″-H), 3.80 (s, OCH_3), 3.93–4.08 (m, 4-H, 6-H), AB signal (δ_A = 4.39, δ_B = 4.46, J_{AB} = 11.3 Hz, OCH_2Ar), AA′BB′ signal (peaks centered at δ_A = 6.87, δ_B = 7.25, 2 × *ortho*-H, 2 × *meta*-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.95 (C-2′), 14.31 (C-5″), 18.83 (C-4″), 23.23 (CH_3-6), 36.27 (C-3″), 40.74 (C-1″), 41.62 (C-5), 55.36 (OCH_3), 67.73 (C-4), 68.73 (C-6), 70.10 (OCH_2Ar), 74.64 (C-2″), 113.81 (2 × *meta*-C), 129.64 (2 × *ortho*-C), 131.10 (*ipso*-C), 159.23 ppm (*para*-C). IR (film): $\tilde{\nu}$ = 2960, 2930, 2875, 2350, 2285, 1615, 1515, 1460, 1425, 1400, 1380, 1330, 1300, 1275, 1250, 1210, 1175, 1110, 1090, 1040, 820, 755 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{19}H_{31}BO_4$ 334.2315 $[M]^+$; found 334.2308 (δ =2.2 ppm).

***tert*-Butyl{(*S*)-1-[(4*R*,6*R*)-2-ethyl-6-methyl-1,3,2-dioxaborinan-4-yl]-3-methylbutan-2-yloxy}diphenylsilane [*syn*,*anti*-44; as a mixture (94:6) with *tert*-butyl{(*S*)-1-[(4*S*,6*S*)-2-ethyl-6-methyl-1,3,2-dioxaborinan-4-yl]-3-methylbutan-2-yloxy}diphenylsilane (*syn*,*syn*-44)]:** This compound was prepared from *anti*-**42** (42 mg, 0.10 mmol) as described for *syn*,*syn*-**43**. Flash chromatography (1 × 16 cm, 5 mL, cyclohexane/EtOAc 50:1) provided the title compound (fractions 8–10, 35 mg, 77%) as a slightly yellow oil. Compound *syn*,*anti*-**44** (major diastereomer): $[\alpha]_{589}^{20}$ = –20.0, $[\alpha]_{578}^{20}$ = –21.0, $[\alpha]_{546}^{20}$ = –23.4, $[\alpha]_{436}^{20}$ = –36.9, $[\alpha]_{365}^{20}$ = –52.5 (*c* = 0.57, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$/$CDCl_3$): δ = 0.54 (q, $J_{1''',2'''}$ = 7.9 Hz, 1‴-H_2), 0.76 and 0.90 [2 × d, $J_{3'\text{-}Me,3'}$ = 6.9 Hz, 3′-$(CH_3)_2$], 0.76 (t, $J_{2''',1'''}$ = 7.9 Hz, 1‴-H_3), 1.06 (s, 2-H_9), 1.14 (d, $J_{6''\text{-}Me,6''}$ = 6.0 Hz, 6″-CH_3), AB signal (δ_A = 1.46, δ_B = 1.38, J_{AB} = 13.8 Hz, A part additionally split by $J_{A,2'}$ = 8.4 Hz, $J_{A,4''}$ = 3.1 Hz, $J_{B,2'}$ = 9.6 Hz, $J_{B,4''}$ = 3.3 Hz, 1′-H_2), 1.56 (m_c, 5″-H_2), 1.76 (qqd, $J_{3',4'} = J_{3',3'-Me}$ = 6.9 Hz, $J_{3',2'}$ = 3.1 Hz, 3′-H), 3.74–3.82 (m, 4″-H, 6″-H), 4.03 (ddd, $J_{2',1'-H(A)}$ = 8.2 Hz, $J_{2',3'} = J_{2',1'-H(B)}$ = 3.2 Hz, 2′-H), 7.35–7.43 (m, 4 × *ortho*-H, 2 × *para*-H), 7.67–7.71 ppm (m, 4 × *meta*-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.08 (C-2‴), 16.92 and 17.77 [$(CH_3)_2$–3′], 19.75 (CH_3-6″), 23.23 (C-1), 27.25 (C_3-2), 33.52 (C-3′), 40.20 (C-1′), 41.21 (C-5″), 67.71 (C-4″), 67.97 (C-6″), 74.21 (C-2′), 127.40 and 127.46 (4 × *meta*-C), 129.46 and 129.54 (4 × *ortho*-C), 134.62 and 134.99 (2 × *para*-C), 136.05 and 136.13 ppm (2 × *ipso*-C). IR (film): $\tilde{\nu}$ = 3070, 2960, 2930, 2860, 2355, 1640, 1460, 1430, 1400, 1330, 1300, 1275, 1215, 1150, 1110, 1080, 1050, 905, 820, 790, 735, 700, 685, 615 cm^{-1}. $C_{27}H_{41}BO_3Si$ (452.51): calcd. C 71.76, H 9.42; found C 71.67, H 9.13.

Preparation of SmI_2 in THF: 1,2-Diiodoethane (1.0 g) was dissolved in MTBE (30 mL), washed with satd. aq. Na_2SO_3 (2 × 30 mL), and dried with $MgSO_4$. After evaporation of the solvent the obtained residue (500 mg, 1.77 mmol) was dissolved in THF (17 mL) and degassed at –78 °C. The resulting solution was cannulated onto Sm powder (40 mesh, 279 mg, 1.86 mmol, 1.05 equiv.). After stirring at room temp. for 16 h, we obtained a dark blue solution. Its concentration in SmI_2 was assumed to be

0.1 M. Because of its low stability this solution was made directly before it was used.

(2*R*,4*S*,6*R*)-2-Hydroxy-6-(4-methoxybenzyloxy)nonan-4-yl Isobutyrate [*anti*,*syn*-45; as a mixture (89:11) with (2*R*,4*S*,6*R*)-2-hydroxy-6-(4-methoxybenzyloxy)nonan-4-yl isobutyrate (*anti*,*anti*-45)]: A freshly prepared SmI_2 suspension (0.1 M in THF, 0.15 mL, 15 mol-%) was slowly added at –10 °C to a degassed solution of *syn*-**41** (30 mg, 0.10 mmol) and isobutyraldehyde (0.06 mL, 44.1 mg, 0.61 mmol, 6.0 equiv.) in THF (1 mL). After the system had been kept for 60 min at this temperature, satd. aq. $NaHCO_3$ (1 mL) was added, and the phases were separated. The aq. phase was extracted with EtOAc (3 × 1 mL) and the combined organic phases were dried with $MgSO_4$. Removal of the solvent under reduced pressure and flash chromatography (1 × 15 cm, 5 mL, cyclohexane/EtOAc 4:1) provided the title compound (fractions 10–12, 22 mg, 59%) as a slightly yellow oil. Compound *anti*,*syn*-**45** (major diastereomer): $[\alpha]_{589}^{20}$ = –9.7, $[\alpha]_{578}^{20}$ = –11.0, $[\alpha]_{546}^{20}$ = –12.5, $[\alpha]_{436}^{20}$ = –21.9, $[\alpha]_{365}^{20}$ = –33.6 (*c* = 0.43, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.89 (dd, $J_{9',8'-H(A)} = J_{9',8'-H(B)}$ = 7.3 Hz, 9′-H_3), 1.14 und 1.16 [2 × d, $J_{2\text{-Me},2}$ = 6.9 Hz, 3-$(CH_3)_2$], 1.16 (d, $J_{1',2'}$ = 6.2 Hz, 1′-H_3), 1.28–1.54 (m, 7′-H_2, 8′-H_2), 1.55–1.62 (m, 5′-H_2), AB signal (δ_A = 1.66, δ_B = 1.98, J_{AB} = 14.2 Hz, A part additionally split by $J_{A,2'}$ = 6.6 Hz, $J_{A,4'}$ = 4.9 Hz, B part additionally split by $J_{B,2'}$ = 8.0 Hz, $J_{B,4'}$ = 6.1 Hz, 3′-H_2), 2.53 (qq, $J_{2,3} = J_{2,2\text{-Me}}$ = 7.0 Hz, 2-H), 3.10 (d, $J_{2'\text{-OH},2'}$ = 3.8 Hz, 2′-OH), 3.41 (dddd, $J_{6',5'-H(A)}$ = 6.2, $J_{6',5'-H(B)} = J_{6',7'-H(A)}$ = 6.1 Hz, $J_{6',7'-H(B)}$ = 5.8 Hz), 3.62 (m_c, 4′-H), 3.80 (s, OCH_3), 4.42 (s, OCH_2Ar), 5.18 ppm (m_c, 2′-H), AA′BB′ signal (peaks centered at δ_A = 6.87, δ_B = 7.26, 2 × *ortho*-H, 2 × *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.23 (C-9′), 18.41 (C-8′), 19.11 and 19.20 [$(CH_3)_2$_3], 22.95 (C-1′), 34.34 (C-2), 36.00 (C-7′), 39.25 (C-3′), 45.02 (C-5′), 55.39 (OCH_3), 63.29 (C-4′), 69.16 (C-2′), 70.43 (OCH_2Ar), 75.18 (C-6′), 113.89 (2 × *meta*-C), 129.51 (2 × *ortho*-C), 130.79 (*ipso*-C), 159.23 (*para*-C), 178.35 ppm (C-1). IR (film): $\tilde{\nu}$ = 3425, 2960, 2930, 2875, 2285, 1730, 1615, 1515, 1465, 1385, 1300, 1250, 1200, 1160, 1070, 1035, 820, 755 cm^{-1}. HRMS (CI, NH_3): calcd. for $C_{21}H_{35}O_5$ 367.2485 [M + H]$^+$; found 367.2478 (+1.8 ppm).

(2*S*,4*R*,6*S*)-6-(*tert*-Butyldiphenylsilyloxy)-2-hydroxy-7-methyloctan-4-yl Isobutyrate [*anti*,*anti*-46; as a mixture (89:11) with (2*R*,4*S*,6*S*)-6-(*tert*-butyldiphenylsilyloxy)-2-hydroxy-7-methyloctan-4-yl isobutyrate (*anti*,*syn*-46)]: This compound was prepared from *anti*-**42** (32 mg, 0.08 mmol) as described for *anti,syn*-**45**. Flash chromatography (1 × 14 cm, 5 mL, cyclohexane/EtOAc 6:1) provided the title compound (fractions 13–15, 23 mg, 61%) as a slightly yellow oil. Compound *anti*,*anti*-**46** (major diastereomer): $[\alpha]_{589}^{20}$ = +4.6, $[\alpha]_{578}^{20}$ = +5.4, $[\alpha]_{546}^{20}$ = +6.5, $[\alpha]_{436}^{20}$ = +10.5, $[\alpha]_{365}^{20}$ = +13.5 (*c* = 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$/$CDCl_3$): δ = 0.72 and 0.91 [2 × d, $J_{7'\text{-Me},7'}$ = 6.8 Hz, 7′-$(CH_3)_2$], 0.98 and 0.99 [2 × d, $J_{7'\text{-Me},7'}$ = 6.9 Hz, 7′-$(CH_3)_2$], 1.05 (s, 2′′-H_9), 1.10 (br. d, $J_{1',2'}$ = 5.8 Hz, 1′-H_3), 1.34–1.46 (m, 5′-H_2), AB signal (δ_A = 1.55, δ_B = 1.69, J_{AB} = 14.5 Hz, A part additionally split by $J_{A,2'}$ = 7.8 Hz, $J_{A,4'}$ = 3.2 Hz, $J_{B,2'}$ = 9.2 Hz, $J_{B,4'}$ = 3.5 Hz, 3′-H_2), 1.65–1.78 (m, 7′-H), 2.33 (qq, $J_{2,1} = J_{2,2\text{-Me}}$ = 7.0 Hz, 2-H), 3.12 (d, $J_{2'\text{-OH},2'}$ = 2.9 Hz, 2′-OH), 3.42–3.50 (m, 4′-H, 6′-H), 5.02 (m_c, 2′-H), 7.32–7.46 (m, 4 × *ortho*-H, 2 × *para*-H), 7.62–7.73 ppm (m, 4 × *meta*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.87 and 17.60 [$(CH_3)_2$_7′], 18.82 and 19.06 [$(CH_3)_2$_2], 19.52 (C-1′), 22.69 (C-1′′), 27.21 (C_3-2′′), 33.22 (C-2), 34.16 (C-7′), 38.20 (C-5′), 45.71 (C-3′), 63.08 (C-4′), 69.29 (C-2′), 74.87 (C-6′), 127.46 and 127.63 (4 × *meta*-C), 129.61 and 129.64 (4 × *ortho*-C), 133.92 and 134.62 (2 × *para*-C), 136.05 and 136.15 (2 × *ipso*-C), 178.09 ppm (C-1). IR (film): $\tilde{\nu}$ = 3070, 2960, 2930, 2860, 2355, 1640, 1460, 1430, 1400, 1330, 1300, 1275, 1215, 1150, 1110, 1080, 1050, 905, 820, 790, 735, 700, 685, 615 cm^{-1}. HRMS (EI, 70 eV): calcd. for $C_{25}H_{35}O_4Si$ 427.2305 [M – C_4H_9]$^+$; found 427.2301 (δ = 0.9 ppm).

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[1] a) J.-M. Beau, in: G. Lukacs, M. Ohno (Ed.) *Recent Progress in the Chemical Syntheses of Antibiotics*, Springer Verlag, Berlin, **1990**, 137–179; b) S. Omura, H. Tanaka, S. Omura (Eds.), *Macrolide Antibiotics*, Academic Press Inc., New York, **1994**, pp. 351–404; c) S. D. Rychnovsky, *Chem. Rev.* **1995**, *95*, 2021–2040; d) C. J. Sinz, S. D. Rychnovsky, *Top. Curr. Chem.* **2001**, *216*, 52–92.

[2] a) T. Oishi, T. Nakata, *Synthesis* **1990**, 635–645; b) C. Schneider, *Angew. Chem.* **1998**, *110*, 1445–1448; c) C. Schneider, *Angew. Chem. Int. Ed.* **1998**, *37*, 1375–1378; d) J. Dougherty, M. Zhou, G. A. O'Doherty, *Chemtracts: Org. Chem.* **2005**, *18*, 349–363; e) S. E. Bode, M. Wolberg, M. Müller, *Synthesis* **2006**, *4*, 557–588.

[3] K. Körber, Dissertation, University of Freiburg, **2004**.

[4] P. Risch, *Rapport de Stage*, University of Freiburg, **2005**.

[5] K. Körber, P. Risch, R. Brückner, *Synlett* **2005**, *19*, 2905–2910.

[6] A. Zörb, R. Brückner, *Eur. J. Org. Chem.* **2010**, 000–000, preceding contribution in this issue.

[7] a) D. Xu, G. A. Crispino, K. B. Sharpless, *J. Am. Chem. Soc.* **1992**, *114*, 7570–7571; b) H. Becker, M. A. Soler, K. B. Sharpless, *Tetrahedron* **1995**, *51*, 1345–1376; c) P. Allevi, G. Tarocco, A. Longo, M. Anastasia, F. Cajone, *Tetrahedron: Asymmetry* **1997**, *8*, 1315–1316; d) Z. Xu, C. W. Johannes, D. S. La, G. E. Hofilena, A. H. Hoveyda, *Tetrahedron* **1997**, *53*, 16377–16390; e) T. Sunazuka, T. Hirose, Y. Harigaya, S. Takamatsu, M. Hayashi, K. Komiyama, S. Omura, *J. Am. Chem. Soc.* **1997**, *119*, 10247–10248; f) T. Ueki, Y. Morimoto, T. Kinoshita, *Chem. Com.* **2001**, *18*, 1820–1821; g) J. A. Bodkin, E. J. Humphries, M. D. McLeod, *Aust. J. Chem.* **2003**, *56*, 795–804; h) M. Ahmed, G. O'Doherty, *Tetrahedron Lett.* **2005**, *46*, 3015–3020; i) Y. Zhang, G. A. O'Doherty, *Tetrahedron* **2005**, *61*, 6337–6351; j) M. Ahmed, G. O'Doherty, *Carbohydr. Res.* **2006**, *341*, 1505–1521; k) J. Schmidt-Leithoff, R. Brückner, *Synlett* **2006**, 2641–2645; l) J. Han, Y. Su, T. Jiang, Y. Xu, X. Huo, X. She, X. Pan, *J. Org. Chem.* **2009**, *74*, 3930–3932; m) See ref.[26a–26j].

[8] S.-K. Kang, S.-G. Kim, D.-C. Park, J.-S. Lee, W.-J. Yoo, C. S. Pak, *J. Chem. Soc. Perkin Trans. 1* **1993**, 9–10.

[9] C. H. Hövelmann, K. Muñiz, *Chem. Eur. J.* **2005**, *11*, 3951–3958.

[10] N. Iwasama, T. Kato, K. Narasaka, *Chem. Lett.* **1988**, 1721–1724.

[11] Method: a) K. Narasaka, F.-C. Pai, *Chem. Lett.* **1980**, 1415–1418; b) K. Narasaka, F.-C. Pai, *Tetrahedron* **1984**, *40*, 2233–2238; c) K.-M. Chen, G. E. Hardtmann, K. Prasad, O. Repic, M. J. Shapiro, *Tetrahedron Lett.* **1987**, *28*, 155–158; d) K.-M. Chen, K. G. Gunderson, G. E. Hardtmann, K. Prasad, O. Repic, M. J. Shapiro, *Chem. Lett.* **1987**, 1923–1926.

[12] For Narasaka–Prasad reductions of δ-chiral β-hydroxy ketones, see: a) Y. Mori, Y. Kohchi, T. Ota, M. Suzuki, *Tetrahedron Lett.* **1990**, *31*, 2915–2916; b) Y. Mori, Y. Kohchi, M. Suzuki, S. Carmeli, R. E. Moore, G. M. L. Patterson, *J. Org. Chem.* **1991**, *56*, 631–637; c) Y. Mori, Y. Kohchi, H. Noguchi, M. Suzuki, S. Carmeli, R. E. Moore, G. M. L. Patterson, *Tetrahedron* **1991**, *47*, 4889–4904; d) Z. Wang, D. Deschênes, *J. Am. Chem. Soc.* **1992**, *114*, 1090–1091; e) Y. Mori, N. Kawajiri, H. Furukawa, R. E. Moore, *Tetrahedron* **1994**, *50*, 11133–11142; f) D. Muñoz-Torrero, R. Brückner, *Eur. J. Org. Chem.* **1998**, 1031–1043; g) F. Yokokawa, T. Asano, T. Shioiri, *Org.*

Lett. **2000**, *2*, 4169–4172; h) F. Yokokawa, T. Asano, T. Shioiri, *Tetrahedron* **2001**, *57*, 6311–6327; i) S. A. Burova, F. E. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 8188–8189; j) S. A. Burova, F. E. McDonald, *J. Am. Chem. Soc.* **2004**, *126*, 2495–2500; k) D. A. Evans, W. C. Trenkle, J. Zhang, J. D. Burch, *Org. Lett.* **2005**, *7*, 3335–3338; l) G. Coste, S. Gerber-Lemaire, *Synlett* **2006**, *5*, 685–688; m) M. J. Mitton-Fry, A. J. Cullen, T. Sammakia, *Angew. Chem. Int. Ed.* **2007**, *46*, 1066–1070; n) J. D. Waetzig, P. R. Hanson, *Org. Lett.* **2008**, *10*, 109–112.

[13] a) For the method with SmI_2, see: D. A. Evans, A. H. Hoveyda, *J. Am. Chem. Soc.* **1990**, *112*, 6447–6449. For the method with $Zr(OtBu)_4$, see: b) C. Schneider, M. Hansch, *Chem. Commun.* **2001**, *13*, 1218–1219; c) C. Schneider, K. Klapa, M. Hansch, *Synlett* **2005**, 91–94; d) C. Schneider, K. Klapa, M. Hansch, *Chem. Eur. J.* **2005**, *11*, 3010–3021.

[14] For the Claisen–Tishchenko reduction of δ-chiral β-hydroxy ketones (with SmI_2), see: a) D. A. Evans, B. D. Allison, M. G. Yang, C. E. Masse, *J. Am. Chem. Soc.* **2001**, *123*, 10840–10852 (Supporting Information); b) C. J. Sinz, S. D. Rychnovsky, *Angew. Chem. Int. Ed.* **2001**, *40*, 3224–3227; c) C. J. Sinz, S. D. Rychnovsky, *Tetrahedron* **2002**, *58*, 6561–6576; d) A. B. Smith III, J. M. Cox, N. Furuichi, C. S. Kenesky, J. Zheng, O. Atasoylu, W. M. Wuest, *Org. Lett.* **2008**, *10*, 5501–5504.

[15] For the method with tetramethylammonium triacetoxyborohydride, see: a) D. A. Evans, K. T. Chapman, *Tetrahedron Lett.* **1986**, *27*, 5939–5942; b) D. A. Evans, K. T. Chapman, E. M. Carreira, *J. Am. Chem. Soc.* **1988**, *110*, 3560–3578. For the method with sodium triacetoxyborohydride, see: c) Y. Roeyeke, M. Keller, H. Kluge, S. Grabley, P. Hammann, *Tetrahedron* **1991**, *47*, 3335–3346.

[16] For the diastereoselective AD of δ-chiral enones, see: a) K. C. Nicolaou, Y. Li, K. Sugita, H. Monenschein, P. Guntupalli, H. J. Mitchell, K. C. Fylaktakidou, D. Vourloulis, P. Giannakakou, A. O'Brate, *J. Am. Chem. Soc.* **2003**, *125*, 15443–15454; b) See ref.[5] c) J. S. Yadav, C. Venugopal, *Synlett* **2007**, *14*, 2262–2266.

[17] For the diastereoselective AD of protected δ-hydroxy enoates, see: a) K. J. Hale, J. A. Lennon, S. Manaviazar, M. H. Javaid, *Tetrahedron Lett.* **1995**, *36*, 1359–1362; b) J. N. Shepherd, J. Na, D. C. Myles, *J. Org. Chem.* **1997**, *62*, 4558–4559; c) H. Toshima, A. Watanabe, H. Sato, A. Ichihara, *Tetrahedron Lett.* **1998**, *39*, 9223–9226; d) T. Matsushima, M. Mori, N. Nakajima, H. Maeda, J. Uenishi, O. Yonemitsu, *Chem. Pharm. Bull.* **1998**, *46*, 1335–1336; e) H. Toshima, H. Sato, A. Ichihara, *Tetrahedron* **1999**, *55*, 2581–2590; f) T. Matsushima, M. Mori, B.-Z. Zheng, H. Maeda, N. Nakajima, J. Uenishi, O. Yonemitsu, *Chem. Pharm. Bull.* **1999**, *47*, 308–321; g) F. Song, S. Fidanze, A. B. Benowitz, Y. Kishi, *Org. Lett.* **2002**, *4*, 647–650; h) J. S. Yadav, P. N. Lakshmi, S. J. Harshavardhan, B. V. S. Reddy, *Synlett* **2007**, 1945–1947; i) P. Gupta, P. Kumar, *Tetrahedron: Asymmetry* **2007**, *18*, 1688–1692; j) P. Gupta, P. Kumar, *Eur. J. Org. Chem.* **2008**, 1195–1202. Diastereoselective AD of unprotected δ-hydroxy enoates: k) A. K. Ghosh, J.-H. Kim, *Tetrahedron Lett.* **2003**, *44*, 3967–3970; l) M. M. Ahmed, G. A. O'Doherty, *Carbohydr. Res.* **2006**, *341*, 1505–1521; m) See ref.[26f]

[18] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

[19] For a procedure adopted from an analogous synthesis of ethyl (*E*,*E*)-hepta-2,4-dienoate, see: S. Mann, S. Carillon, O. Breyne, C. Duhayon, L. Hamon, A. Marquet, *Eur. J. Org. Chem.* **2002**, 736–744.

[20] For conditions adopted from transformation of conjugated dienoates into Weinreb amides, see: A. Wada, N. Fujioka, M. Ito, *Chem. Pharm. Bull.* **1999**, *47*, 171–176.

[21] For conditions from transformation of sorbic acid Weinreb amide into ketones, see: S. V. Ley, G. Meek, K.-H. Metten, C. Pique, *J. Chem. Soc., Chem. Commun.* **1994**, 1931–1932.

[22] a) Y. L. Bennani, K. B. Sharpless, *Tetrahedron Lett.* **1993**, *34*, 2079–2082; b) P. Blundell, A. K. Ganguly, V. M. Girijavallabhan, *Synlett* **1994**, 263–265. The authors of ref.[22a] increased the normal amounts of $K_2OsO_2(OH)_4$ and $(DHQ)_2PHAL$ by a factor of 5 (as we did) while the authors of ref.[22b] increased them by a factor of 10.

[23] We chose $(DHQD)_2PHAL$ instead of $(DHQ)_2PHAL$ because in general the former is a slightly more potent inducer of asymmetry than the latter: see ref. 3 in ref.[6]

[24] a) K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu, X.-L. Zhang, *J. Org. Chem.* **1992**, *57*, 2768–2771 (empirically and in line with the rule for monoesters as ligands by E. N. Jacobsen, I. Markó, W. S. Mungall, G. Schröder, K. B. Sharpless, *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970); b) H. C. Kolb, P. G. Andersson, K. B. Sharpless, *J. Am. Chem. Soc.* **1994**, *116*, 1278–1291 (empirically, refined); c) N. Moitessier, C. Henry, C. Len, Y. Chapleur, *J. Org. Chem.* **2002**, *67*, 7275–7282 (calculationally); d) P. Fristrup, D. Tanner, P.-O. Norby, *Chirality* **2003**, *15*, 360–368 (calculationally).

[25] K. Körber, postdoctoral work with R. Brückner, **2005**.

[26] For Pd^0-catalyzed C^{γ}-O clevages in γ,δ-dihydroxy enoate-based carbonates, see: a) T. J. Hunter, G. A. O'Doherty, *Org. Lett.* **2001**, *3*, 1049–1052; b) T. J. Hunter, G. A. O'Doherty, *Org. Lett.* **2001**, *3*, 2777–2780; c) S. D. Garaas, T. J. Hunter, G. A. O'Doherty, *J. Org. Chem.* **2002**, *67*, 2682–2685; d) T. J. Hunter, G. A. O'Doherty, *Org. Lett.* **2002**, *4*, 4447–4450; e) C. M. Smith, G. A. O'Doherty, *Org. Lett.* **2003**, *5*, 1959–1962; f) M. M. Ahmed, B. P. Berry, T. J. Hunter, D. J. Tomcik, G. A. O'Doherty, *Org. Lett.* **2005**, *7*, 745–748; g) M. Li, G. A. O'Doherty, *Org. Lett.* **2006**, *8*, 3987–3990; h) M. M. Ahmed, M. S. Mortensen, G. A. O'Doherty, *J. Org. Chem.* **2006**, *71*, 7741–7746; i) M. Li, G. A. O'Doherty, *Org. Lett.* **2006**, *8*, 6087–6090; j) H. Guo, M. S. Mortensen, G. O'Doherty, *Org. Lett.* **2008**, *10*, 3149–3152. Pd^0-catalyzed C^{γ}-OMs cleavages in γ-oxygenated enoates: H. Nakamura, M. Ono, Y. Shida, H. Akita, *Tetrahedron: Asymmetry* **2002**, *13*, 705–713.

[27] X.-Q. Yu, A. Hirai, M. Miyashita, *Chem. Lett.* **2004**, *33*, 764–765.

[28] Established pathways to nonracemic δ-hydroxy enoates akin to **26** are described in ref.[26] and in: a) J. Sakaki, Y. Sugita, M. Sato, C. Kaneko, *Tetrahedron* **1991**, *47*, 6197–6414; b) I. Shimizu, T. Omura, *Chem. Lett.* **1993**, 1759–1760; c) C. M. Smith, G. O'Doherty, *Org. Lett.* **2003**, *5*, 1959–1962; d) C. Ensch, M. Hesse, *Helv. Chim. Acta* **2003**, *86*, 233–246; e) B. Bazán-Tejeda, G. Bluet, G. Broustal, J.-M. Campagne, *Chem. Eur. J.* **2006**, *12*, 8358–8366; f) S. Simsek, M. Horzella, M. Kalesse, *Org. Lett.* **2007**, *9*, 5637–5639.

[29] It is difficult to tell how common such "remote effects" on the stereoselectivity of AD reactions are (i.e., how often substrate control interferes). Substrate control of 100% was exerted by a γ-chiral α,β-unsaturated δ-hydroxy ketone, which delivered an *identically* composed 63:37 mixture of diastereomeric α,β,δ-trihydroxy ketones no matter whether dihydroxylated by AD mix-α™ or by mix-β™.

[30] a) For the general concept, see: S. Masamune, W. Choy, J. S. Peterson, L. R. Rita, *Angew. Chem.* **1985**, *97*, 1–31; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1–30. For AD reactions of chiral olefins, see: b) J. K. Cha, N.-S. Kim, *Chem. Rev.* **1995**, *95*, 1761–1795; c) O. I. Kolodiazhnyi, *Tetrahedron* **2003**, *59*, 5953–6018

[31] The usual workup of Narasaka–Prasad reductions entails dissolving the crude product in MeOH, evaporating the resulting solution to dryness, and repeating this procedure several times. We failed to expel the boron in this manner because we skipped the treatment with MeOH for fear of a concomitant evaporative loss of the desired compound.

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