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SYNTHESIS OF ANNULATED 1,4-DIOXANES AND PERHYDRO-1,4-OXAZINES BY DOMINO-WACKER-CARBONYLATION AND DOMINO-WACKER-MIZOROKI-HECK REACTIONS

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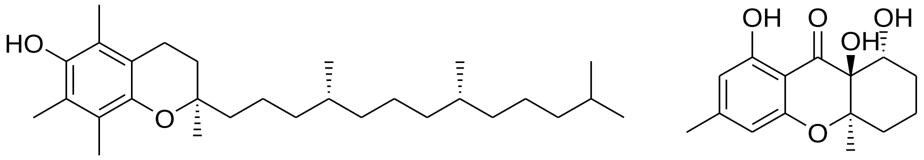
Dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday

Abstract – Palladium(II)-catalyzed domino reactions for the formation of 1,4-dioxanes and perhydro-1,4-oxazines starting from hydroxy alkenes are described. The domino-Wacker-carbonylation comprises a Wacker oxidation, subsequent CO-insertion and a nucleophilic substitution of the intermediately formed Pd-species. The domino-Wacker-Mizoroki-Heck reaction proceeds via a Wacker oxidation, subsequent insertion into the olefinic π-bond of α,β-unsaturated carbonyl compounds and β-hydride elimination.

INTRODUCTION

The domino-Wacker-carbonylation and the domino-Wacker-Mizoroki-Heck reaction are versatile methods for the synthesis of chromanes.[1] The procedure has been used by us not only for the preparation of natural products and analogues as vitamin E (**1**)[2] and 4-dehydroxydiversonol (**3**),[3] but also for the production of different heterocycles.[4]

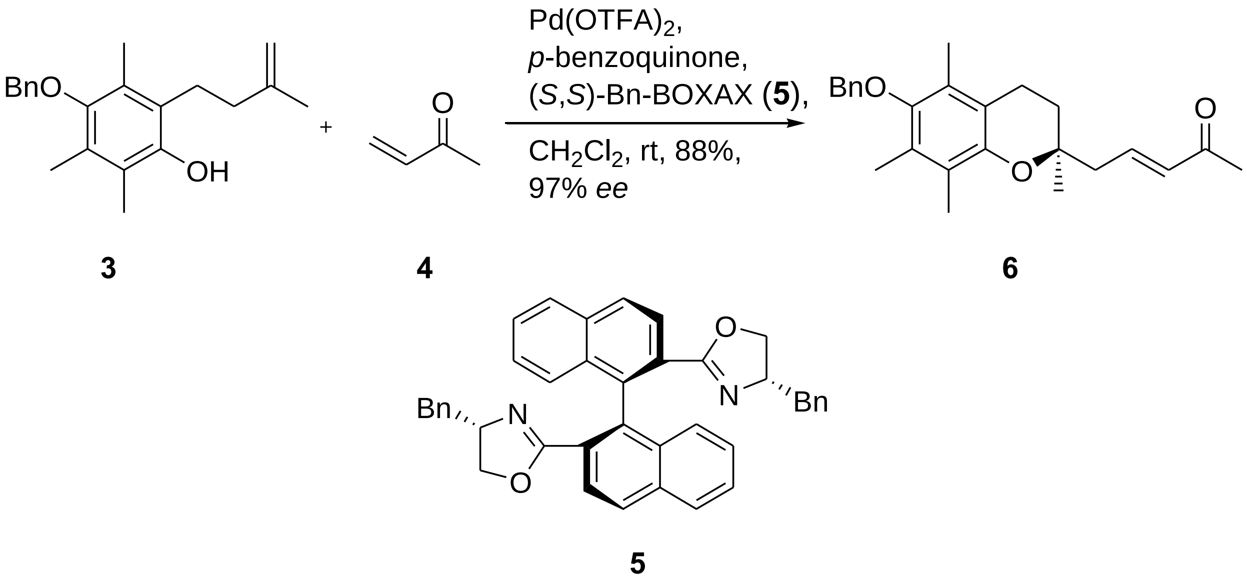


vitamin E (**1**)

4-dehydroxydiversonol (**2**)

Scheme 1. Structures of compounds synthesized using a Pd-catalyzed domino-reaction

In these transformations a phenol as **3** containing an unsaturated side chain is treated with Pd(OTFA)$_2$ and an α,β-unsaturated carbonyl compound or an alcohol under a CO-atmosphere. Thus, reaction of **3** with methyl vinyl ketone (**4**) in the presence of a catalytic amount of the (*S*,*S*)-Bn-BOXAX ligand (**5**)[5] led to chroman **6** in up to 86% yield with 97% *ee*, which was transformed in a few steps into **1**.

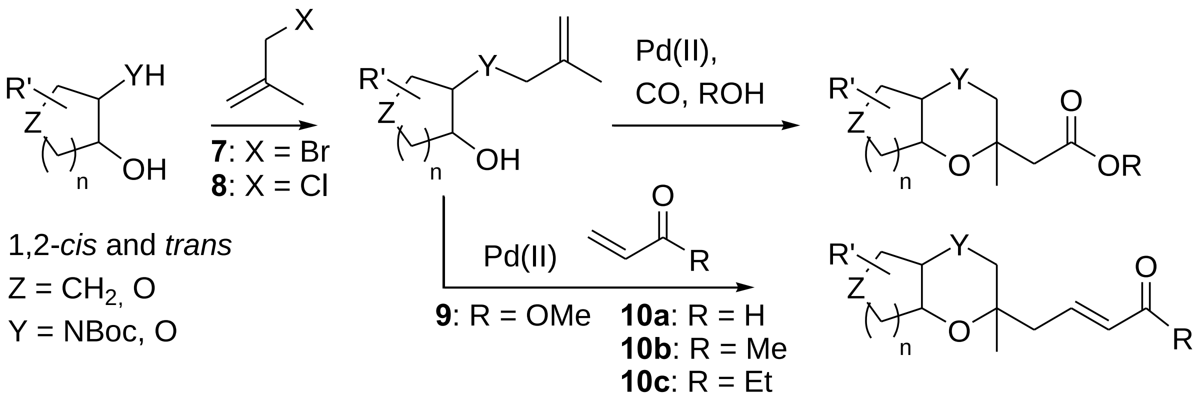


Scheme 2. Enantioselective formation of the precursor **6** for the synthesis of vitamin E (**1**)

However, as described in this article, these domino reactions can not only be performed using phenols but also alicyclic alcohols as substrates to give 1,4-dioxanes. Moreover, it also allows the synthesis of perhydro-1,4-oxazines.

RESULTS AND DISCUSSION

The synthesis of 1,4-dioxanes and perhydro-1,4-oxazines using a Pd-catalyzed domino-Wacker-carbonylation and a domino-Wacker-Mizoroki-Heck reaction, respectively, requires the use of mono-*O*-allylated aliphatic 1,2-diols or *N*-allylated 2-aminoalcohols as substrates. The synthesis of these compounds can efficiently be accomplished by a selective allylation of one of the two hydroxy groups of the 1,2-diols or the nitrogen of *N*-Boc protected 2-aminoalcohols by a nucleophilic substitution with allyl halides **7** or **8**. The further transformation of these compounds to give the desired products is accomplished using a catalytic amount of Pd(OTFA)$_2$ or PdCl$_2$, equimolar amounts of *p*-benzoquinone for reoxidizing the in situ formed Pd^0 species and either CO and an alcohol usually MeOH or a α,β-unsaturated carbonyl compound **9** or **10** (Scheme 3).



Scheme 3. General scheme for the synthesis of 1,4-dioxanes and perhydro-1,4-oxazines using Pd-catalyzed domino-reactions

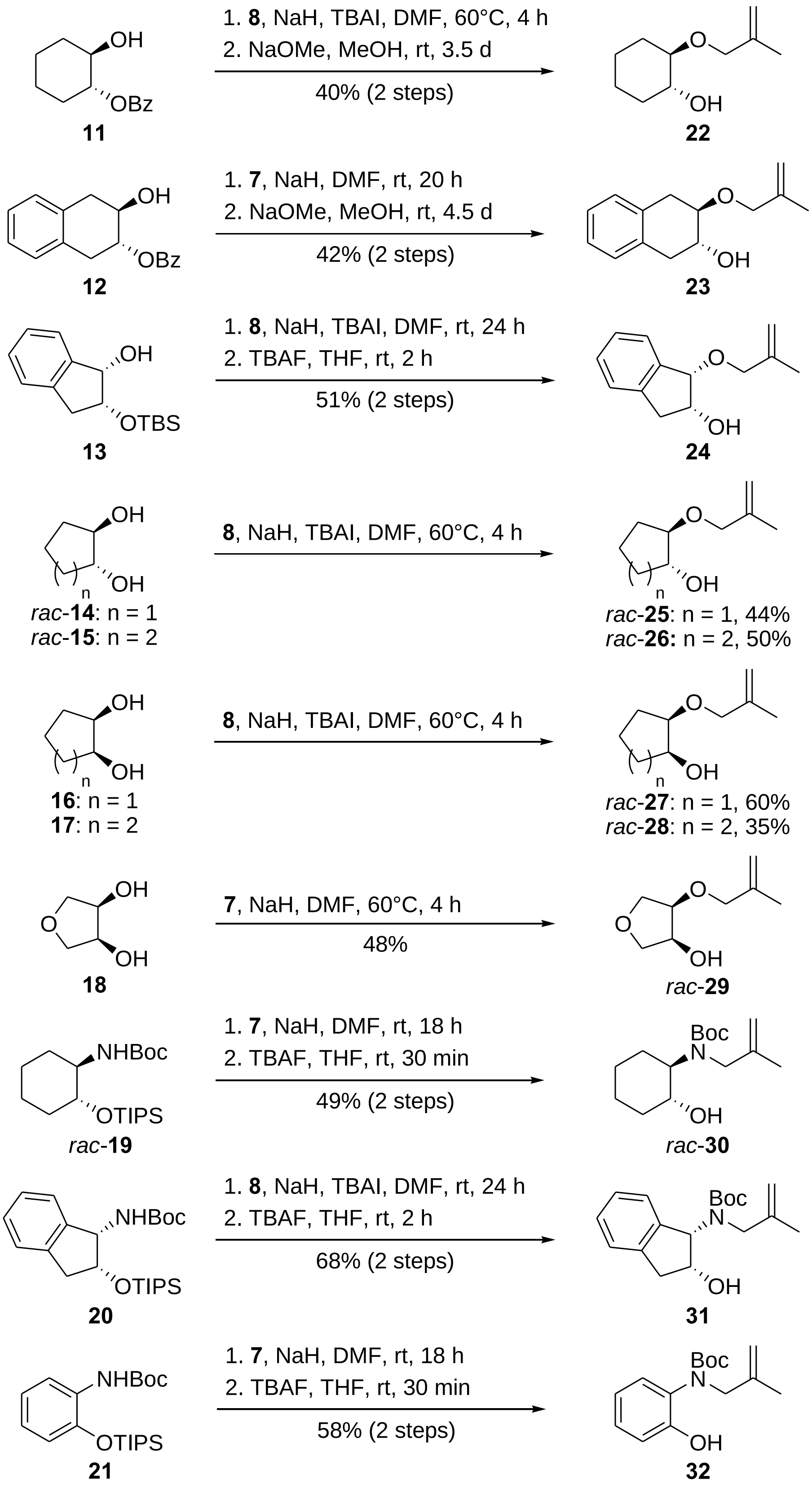
SYNTHESIS OF THE SUBSTRATES FOR DOMINO-REACTIONS

The substrates **22–29** for the domino-Wacker-carbonylation reactions and the domino-Wacker-Mizoroki-Heck reactions were prepared by allylation of either mono- or unprotected 1,2-diols **11–18** with β-methallyl bromide (**7**) or chloride (**8**) and sodium hydride as base (Scheme 4). Using β-methally chloride (**8**) as reagent TBAI had to be added to allow a reasonable transformation.

The enantiomerically pure dihydroxy-compounds **11** and **12** were obtained via an epoxidation of cyclohexene and 1,4-dihydronaphthalene, respectively followed by an enantioselective opening of the *meso*-compounds using an enantiopure Co-salene complex and benzoate.[6] Enantiopure compound **13** was synthesized using a Sharpless-dihydroxylation of indene and selective TBS protection.[7] Allylation of these compounds with **7** or **8** followed by removal of the protecting groups led to **22**, **23** and **24** in 40–50% yield over two steps.

The substrates *rac*-**25**–*rac*-**29** were prepared directly from the corresponding 1,2-diols *rac*-**14**–*rac*-**15** and the *meso* compounds **16**–**18** by monoallylation in 35–60% yield together with the bisallylated compounds and starting material.

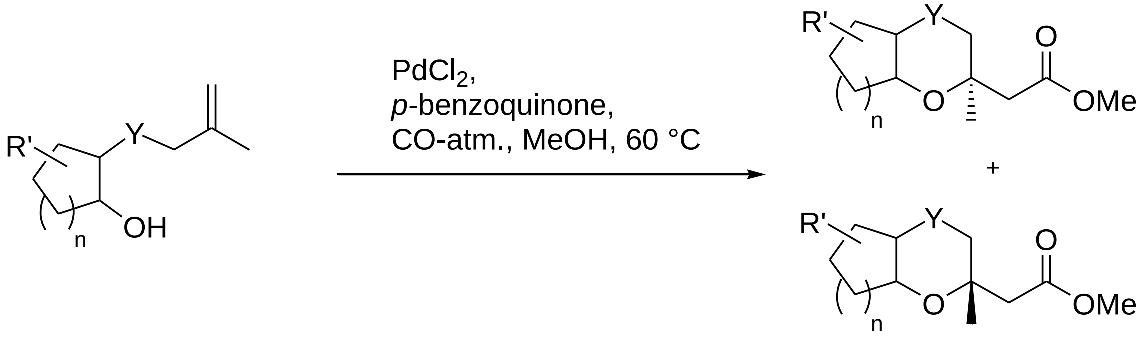
As the domino-transformations did not tolerate basic amino functionalities, *N*-Boc protected substrates *rac*-**30**, **31** and **32** were prepared from *rac*-**19**, enantiopure **20** and **21**. To assure a selective *N*-allylation, the employed corresponding 2-aminoalcohols were transformed into the *N*-Boc amides, then the hydroxy group was protected as silyl ether. The allylation with **7** or **8** and the following silyl ether cleavage led to *rac*-**30** as well as enantiopure **31**[8] and **32** in 49–68% yield over two steps.



Scheme 4. Synthesis of the substrates for the Pd-catalyzed domino reactions

DOMINO-WACKER-CARBONYLATION REACTION

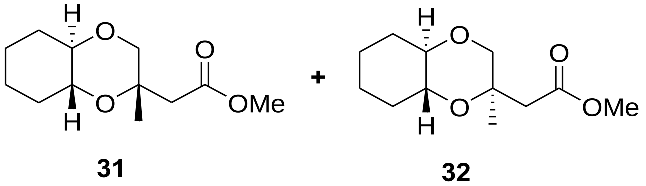
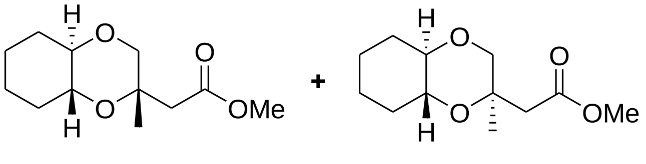
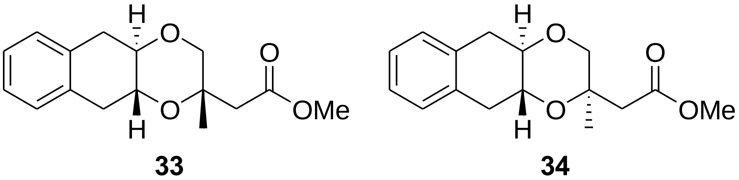
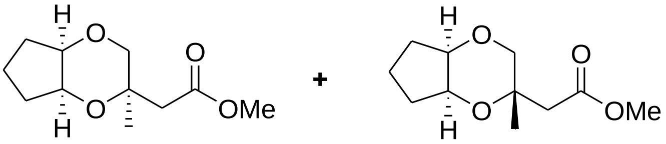
The domino-Wacker-carbonylation reaction of enantiopure **22** and **23** as well as of *rac*-**22**, *rac*-**27** and *rac*-**30** using palladium(II)chloride in methanol under an atmosphere of CO for 1.5–4 h at 60 °C led to the desired compounds **31–38** in 72–90% yield. As expected two diastereomers were obtained in a 19:81 to 34:66 ratio (Table 1).

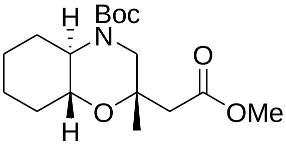
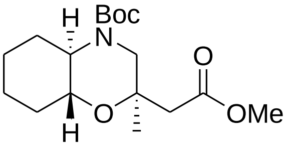
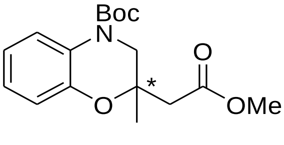


Scheme 5. Domino-Wacker-carbonylation reactions

Interestingly, the *cis*-1,2-disubstituted cyclohexane derivative *rac*-**28** and the *trans*-1,2-disubstituted cyclopentane derivative *rac*-**25** did not react under these conditions. The reaction of the *N*-Boc protected compound *rac*-**30** gave a mixture of *rac*-**37** and *rac*-**38** in 79% yield in a ratio of 22:78 after a reaction time of 4 h, which is probably due to a strong steric hindrance caused by the BOC-group.

Table 1. Domino-Wacker-carbonylation reactions

substrate	condictions	product	yield [%]	ratio
22	2 h[a]	 **31** + **32**	90	19:81
rac-**22**	2 h[a]	 *rac*-**31** + *rac*-**32**	88	19:81
23	1.5 h[a]	 **33** **34**	72	34:66
rac-**27**	2 h[a]	 *rac*-**35** + *rac*-**36**	86	29:71

rac-**30**	4 h[a]	 *rac*-**37** +  *rac*-**38**	79	22:78
32	6 h[b]	 **30**	70	87 % ee

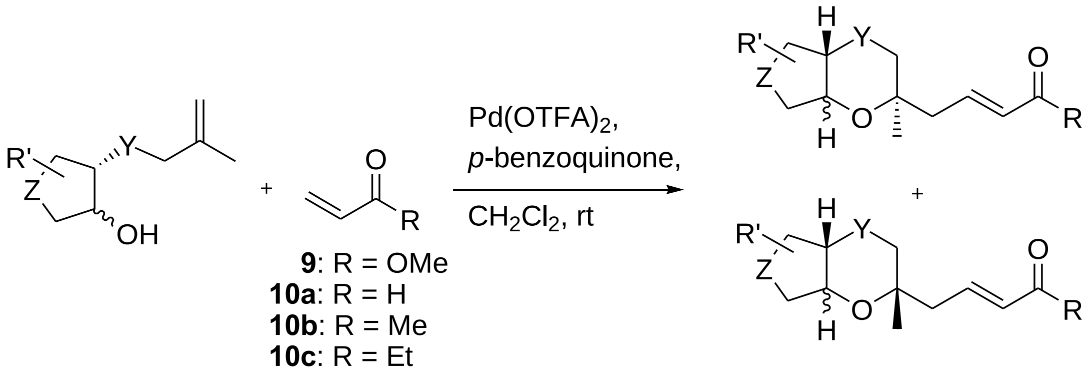
[a] 0.10 eq. $PdCl_2$, 4.00 eq. *p*-benzoquinone, CO-atmosphere, MeOH, 60 °C.
[b] 0.05 eq. $Pd(TFA)_2$, 0.15 eq. (*S*,*S*)-Bn-BOXAX, 4.00 eq. *p*-benzoquinone, CO-atm., MeOH, 60 °C.

For comparison we also used achiral **32** which could be transformed in an asymmetric reaction in the presence of the BOXAX ligand **5** to give **39** in 70% yield and 87% *ee*. We have also tried to perform a kinetic resolution using *rac*-**22** and *rac*-**27** in the presence of BOXAX ligand **5**. However, under these conditions the reaction slowed down considerably, that even after 10 days less than 10% of the desired product was formed.

DOMINO-WACKER-MIZOROKI-HECK REACTION

For the domino-Wacker-Mizoroki-Heck reactions of the alkenyl phenols we used $Pd(OTFA)_2$ and equimolar amounts of *p*-benzoquinone in the presence of methyl acrylate (**9**), acrolein (**10a**), methyl vinly ketone (**10b**) and ethyl vinyl ketone (**10c**) in CH_2Cl_2 as solvent at rt. These conditions had also been used in the already described transformations using phenols.[2,4a] Thus, reaction of the *trans*- and *cis*-cyclopentanediol and *cis*-tetrahydrofuran-3,4-diol derivatives *rac*-**25**, *rac*-**27** and *rac*-**29** led to the 1,4-dioxanes *rac*-**40**–*rac*-**54** in yields of 33 to 77%. The lowest yield was obtained using acrolein (**10a**), whereas the highest yield was observed using methyl acrylate (**9**). However, methyl and ethyl vinyl ketone (**10b** and **10c**) gave comparable yields. Interestingly, using the domino-Wacker-Mizoroki-Heck reaction also the trans-disubstituted cyclopentane derivative *rac*-**25** reacted though in only 39% yield, whereas in the domino-Wacker-carbonylation reaction a transformation could not be achieved with this substrate. On the other hand, the usage of methyl crotylate as a more hindered α,β-unsaturated carbonyl compound failed since only traces of the desired product were formed within five days. Also, a kinetic resolution starting with racemic substrates in the presence of the (*S*,*S*)-Bn-BOXAX (**5**) ligand was not possible due to a strong reduction of the reaction rate. However, enantiopure 1-(methallyloxy)indane-2-ol (**24**) and *N*-Boc-protected 1-(methallylamino)indane-2-ol **31** provided the annulated tricyclic 1,4-dioxans **54** and **55** and the perhydro-1,4-oxazines **56** and **57** in 56 and 91% yield, respectively. In all transformations, diastereomers were formed as expected ranging from 50:50 to 70:30.

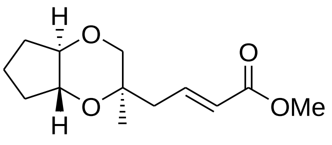
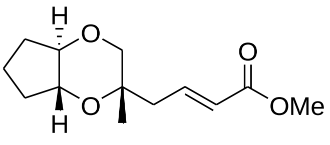
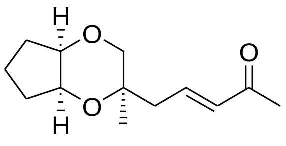
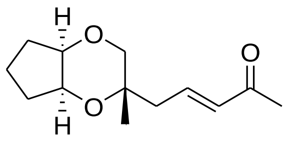
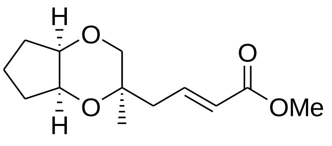
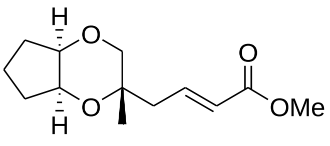
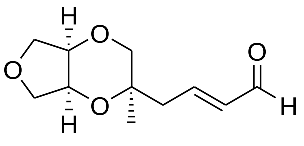
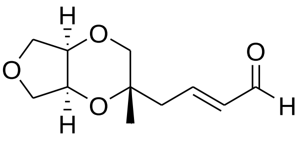
It should be noted that there is a main difference between the domino-Wacker-carbonylation reaction and the domino-Wacker-Heck-Mizoroki reaction, which concerns the reaction rate. Whereas using the first procedure a full transformation is accomplished within a few hours, the second procedure usually needs a few days.

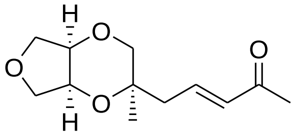
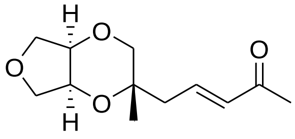
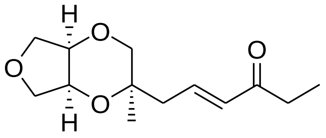
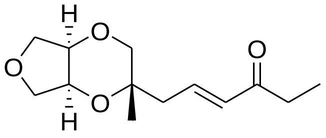
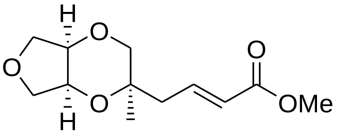
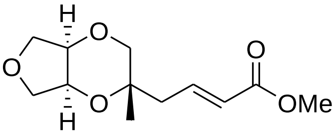
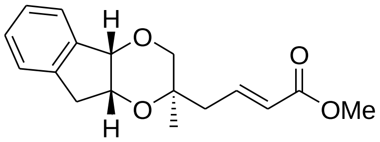
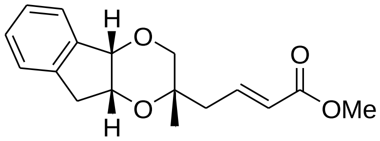
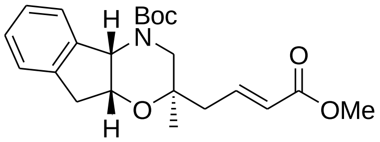
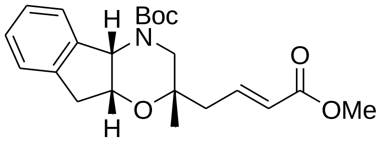


9: R = OMe
10a: R = H
10b: R = Me
10c: R = Et

Scheme 6. Domino-Wacker-Mizoroki-Heck reaction of hydroxy alkenes

Table 2. Domino-Wacker-Mizoroki-Heck reaction according to scheme 6

substrate	conditions[a]	product		yield [%]	ratio
rac-**25**	3 d	 *rac*-**40**	 *rac*-**41**	39	50:50
rac-**27**	3 d	 *rac*-**42**	 *rac*-**43**	70	50:50
rac-**27**	3 d	 *rac*-**44**	 *rac*-**45**	61	50:50
rac-**29**	2 d	 *rac*-**46**	 *rac*-**47**	33	65:55

rac-**29**	2 d	 *rac*-**48**  *rac*-**49**	68	55:45
rac-**29**	3 d	 *rac*-**50**  *rac*-**51**	62	70:30
rac-**29**	3 d	 *rac*-**52**  *rac*-**53**	77	60:40
24	4 d	 **54**  **55**	56	60:40
31	2 d	 **56**  **57**	91	60:40

[a] Pd(OTFA)$_2$ (0.10 eq.), *p*-benzoquinone (4.0 eq), α,β-unsaturated carbonyl compound (3.0 eq.), rt

STRUCTURE DETERMINATION

The relative configuration of the obtained diastereomers could be determined for **31**, **32**, **37** and **38** using NOESY experiments. In all other cases a differentiation employing NMR spectroscopy was not possible.

CONCLUSION

We have reported on a new and operationally simple methods for the preparation of 1,4-dioxanes and perhydro-1,4-oxazines starting from rapidly available precursors. The methodology is based on an efficient palladium-catalyzed domino-reaction, initiated by a Wacker oxidation and subsequent insertion of the Pd-species formed into the π-bonds of CO or α,β-unsaturated carbonyl compounds.

EXPERIMENTAL

General Procedure A: Allylation using NaH: The substrate, dissolved in dry DMF (3 mL/mmol), was carefully treated with NaH (1.00 eq.) at 0 °C. After warming up to rt and the end of gas release, the allyl hallide **7** or **8** as well as TBAI (cat.) in the case of using **8** were added and the reaction mixture stirred for 2–24 h at 60 °C (TLC-Control). Then H_2O (5 mL/mmol) was added, the solution neutralized with 1 N HCl and the aqueous phase extracted with Et_2O (3 × 5 mL/mmol). The combined organic layers were washed with H_2O (15 mL/mmol) and brine, dried over $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by column chromatography on silica gel.

General Procedure B*:* Domino-Wacker-carbonylation reaction: A mixture of palladium(II)chloride (0.10 eq.), *p*-benzoquinone (4.00 eq.) and the substrate in MeOH (2 mL) was stirred at 60 °C for 1–4 h under a CO-atmosphere using a balloon filled with carbon monoxide. Then the reaction mixture was treated with 1 N HCl (50 mL) and the aqueous phase extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with 1 N NaOH (3 × 10 mL), brine and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product purified by column chromatography on silica gel.

General Procedure C: Domino-Wacker-Mizoroki-Heck reaction: A mixture of palladium trifluoroacetate (0.032 mmol) and *p*-benzoquinone (1.29 mmol) in CH_2Cl_2 (0.5 mL) was stirred at rt for 30 min. Afterwards the substrate (0.320 mmol) and the α,β-unsaturated carbonyl compound **9** or **10** (0.96 mmol) were added as solution in CH_2Cl_2 (0.5 mL) and the mixture was stirred at rt. After complete conversion (TLC-control, typically several days) the mixture was treated with 1N HCl (5 mL) and the aqueous phase extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with 1N NaOH solution (3 × 5 mL) and brine and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product purified by column chromatography on silica gel.

(1*R*,2*R*)-2-Hydroxycyclohexyl benzoate (11): A solution of (*S*,*S*)-(+)-*N*,*N*-bis (3,5-di-*tert*-butylsalicyliden)-1,2-cyclohexanediaminocobalt (31.0 mg, 51.0 μmol) and benzoic acid (680 mg, 5.60 mmol) in TBME (2 mL) was stirred under O_2 for 30 min. Volatile materials were removed in vacuo. The flask was recharged with nitrogen, *i*-Pr_2NEt (724 mg, 976 μL, 5.60 mmol) was added, and the stirred mixture was cooled to 4 °C. Cyclohexene oxide (500 mg, 5.09 mmol) was added and the resulting dark brown solution was stirred at 4 °C for 5 d. The product mixture was diluted with Et_2O (10 mL), washed with 1 N aq. HCl (5 × 2 mL) and saturated aq. $NaHCO_3$ (2 × 2 mL), dried over $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and the resulting solid was recrystallized four times from CH_2Cl_2/heptane to afford the product **11** (567 mg, 2.62 mmol, 51%) as colorless crystals. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.21–2.20 (m, 8 H, 3-H_2, 4-H_2, 5-H_2, 6-H_2), 2.39 (d, J = 3.7 Hz, 1 H, OH), 3.65–3.75 (m, 1 H, 2-H), 4.79 (m_c, 1 H, 1-H), 7.38–7.45 (m, 2 H, Ph-H_m), 7.54 (tt, J = 7.4, 2.2 Hz, 1 H, Ph-H_p), 8.00–8.07 (m, 2 H, Ph-H_o). **^{13}C-NMR** (50.3 MHz, C_6D_6): δ = 23.67 (C-4), 23.83 (C-5), 29.94

(C-6), 32.94 (C-3), 72.70 (C-2), 77.21 (C-1), 128.31 (Ph-C̲H$_m$), 129.61 (Ph-C̲H$_o$), 130.28 (Ph-C̲$_i$), 132.98 (Ph-C̲H$_p$), 166.38 (Ph-C̲O$_2$). **IR** (KBr): ν(cm^{-1}) = 3533, 2936, 2860, 1692, 1454, 1323, 1279, 1133, 1071, 995, 917, 850, 711. **UV** (CH_3CN): λ_{max} (lg ε) = 192.5 nm (4.5717), 197.5 (4.5997), 227.5 (4.1039), 272 (2.9441), 279.5 (2.8488). **MS** (DCI, 200 eV): *m*/*z* (%) = 458 (15) [2M+NH$_4$]$^+$, 255 (10) [M+NH$_3$+NH$_4$]$^+$, 238 (100) [M+NH$_4$]$^+$.

(2*R*,3*R*)-(3-Hydroxy-1,2,3,4-tetrahydronaphthalene-2-yl)(phenyl)methanone 12: A solution of 1,4-dihydronaphthalene (779 mg, 5.98 mmol) in CH_2Cl_2 (11 mL) was cooled to 0 °C and *m*CPBA (2.21 g, 8.97 mmol) was added. The mixture was stirred at rt for 16 h, then aq. $NaHCO_3$ (10 mL) was added and stirring was continued for another 30 min. The organic layer was washed with aq. $NaHCO_3$ (2 ×10 mL), dried over $MgSO_4$ and the solvent removed in vacuo to provide *meso*-1a,2,7,7a-tetrahydronaphtho[2,3-*b*]oxirene (873 mg, 5.97 mmol, quant.) after column chromatography on silica gel (P/Et_2O = 8:1) as a colourless solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 3.18 (d, *J* = 17.6 Hz, 2 H, 2-H$_a$, 7-H$_a$), 3.31 (d, *J* = 17.6 Hz, 2 H, 2-H$_b$, 7-H$_b$), 3.47 (dd, *J* = 2.4, 1.3 Hz, 2 H, 1a-H, 7a-H), 7.04 (dd, *J* = 5.6, 3.5 Hz, 2 H, 4-H, 5-H), 7.14 (dd, *J* = 5.6, 3.5 Hz, 2 H, 3-H, 6-H). **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ = 29.66 (C-2, C-7), 51.69 (C-1a, C-7a), 126.48 (C-4, C-5), 129.20 (C-5, C-8), 131,42 (C-2a, C-6a). **IR** (film): ν(cm^{-1}) = 3343, 3004, 2909, 2247, 1498, 1456, 1422, 1062, 1043, 818, 746. **UV** (CH_3CN): λ_{max} (lg ε) = 194.5 nm (4.5457), 264 (2.4285), 271 (2.4009). **MS** (DCI, 200 eV): *m*/*z* (%) = 181 (12) [M+NH$_3$+NH$_4$]$^+$, 164 (100) [M+NH$_4$]$^+$. A solution of (*S*,*S*)-(+)-*N*,*N*-bis-(3,5-di-*tert*-butylsalicyliden)-1,2-cyclohexanediaminocobalt (62.0 mg, 103 µmol,) and benzoic acid (276 mg, 2.26 mmol) in TBME (2 mL) was stirred under O_2 for 30 min. Volatile materials were removed in vacuo. The flask was recharged with nitrogen, *i*-Pr$_2$NEt (292 mg, 393 µL, 2.26 mmol) and *meso*-1a,2,7,7a-tetrahydronaphtho[2,3-*b*]oxirene (300 mg, 2.05 mmol) was added (300 mg, 2.05 mmol) and the resulting dark brown solution stirred at rt for 3 d. The product mixture was diluted with Et_2O (10 mL), washed with 1 N aq. HCl (5 ×2 mL) and saturated aq. $NaHCO_3$ (2 × 2 mL), dried over $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and the resulting solid was recrystallized 4 times from CH_2Cl_2/heptane to afford the product **12** (386 mg, 1.43 mmol, 70%) as a colourless solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 2.93 (dd, *J* = 16.1, 8.8 Hz, 1 H, 4-H$_a$), 2.99 (dd, *J* = 16.1, 8.6 Hz, 1 H, 1-H$_a$), 3.28 (dd, *J* = 16.5, 5.7 Hz, 1 H, 4-H$_b$), 3.41 (dd, *J* = 16.5, 5.8 Hz, 1-H, 4-H$_b$), 4.24 (ddd, *J* = 8.8, 8.4, 5.7 Hz, 1 H, 3-H), 5.29 (ddd, *J* = 8.6, 8.4, 5.8 Hz, 1 H, 2-H), 7.13 (m$_c$, 4 H, 5-H, 6-H, 7-H, 8-H), 7.44 (m$_c$, 2 H, Ph-H$_m$), 7.57 (m$_c$, 1 H, Ph-H$_p$), 8.05 (m$_c$, 2 H, Ph-H$_o$). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 33.31, 36.08 (C-1, C-4), 69.59 (C-3), 75.25 (C-2), 126.48, 126.53 (C-6, C-7), 128.44 (Ph-C̲H$_m$), 128.67, 128.87 (C-5, C-8), 129.69 (Ph-C̲H$_o$), 129.95 (Ph-C̲$_i$), 132.99, 133.34 (C-4a, C-8a), 133.24 (Ph-C̲H$_p$), 166.65 (C̲O$_2$Ph). **IR** (pellet): ν(cm^{-1}) = 3517, 2933, 2901, 2851, 1692, 1452, 1278, 1124, 1028, 991, 713, 438. **UV**

(CH_3CN): λ_{max} (lg ε) = 192.5 nm (4.9177), 194.5 (4.9452), 216.5 (4.1612), 228 (4.1613), 265 (3.1388), 272 (3.1773), 279.5 (2.9243). **MS** (DCI, 200 eV): *m*/*z* (%) = 554 (15) $[2M+NH_4]^+$, 286 (100) $[M+NH_4]^+$, 269 (10) $[M+H]^+$.

***tert*-Butyl *rac-trans*-2-(triisopropylsilyloxy)cyclohexylcarbamate *rac*-19:** A suspension of 2-aminocyclohexanol hydrochloride (1.00 g, 6.60 mmol) in THF (30 mL) was treated with NaH (60% in mineral oil, 264 mg, 6.60 mmol) and stirred at rt for 1.5 h. Afterwards di-*tert*-butyl dicarbonate (1.51 g, 6.93 mmol) was added, and the mixture was stirred at rt for 4 h. The solvent was removed in vacuo, H_2O (10 mL) was added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The solvent was removed under reduced to provide *rac-tans-tert*-butyl 2-hydroxycyclohexylcarbamate (940 mg, 4.37 mmol, 66%) as a colourless solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, $C(C\underline{H}_3)_3$), 1.67 (s, 1 H, OH), 1.06–1.37 (m, 4 H, 4-H_2, 5-H_2), 1.64–1.76 (m, 2 H, 3-H_a, 6-H_a), 1.91–2.09 (m, 2 H, 3-H_b, 6-H_b), 3.21–3.39 (m, 2 H, 1-H, 2-H), 4.54 (s_{br}, 1 H, NH). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 24.00, 24.68 (C-4, C-5), 28.32 ($C(\underline{C}H_3)_3$), 31.74, 34.13 (C-3, C-6), 56.35 (C-1), 75.35 (C-2), 79.93 ($\underline{C}(CH_3)_3$), 157.20 ($\underline{C}O_2C(CH_3)_3$). **IR** (pellet): ν (cm^{-1}) = 3329, 2932, 1681, 1535, 1449, 1363, 1240, 1176, 1125, 1068, 1016, 854, 645. **MS** (ESI): *m*/*z* (%) = 238 (100) $[M+Na]^+$, 453 (8) $[2M+Na]^+$. To a solution of *rac-tans-tert*-butyl 2-hydroxycyclohexylcarbamate (940 mg, 4.37 mmol) and imidazole (446 mg, 6.55 mmol) in CH_2Cl_2 (20 mL) was added Chlorotriisopropylsilane (1.26 g, 1.40 mL, 6.55 mmol). The mixture was stirred at rt for 3 d, H_2O (10 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (P/Et_2O = 20:1) to provide *rac*-**19** (1.16 g, 3.14 mmol, 72 %) as a colourless solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.07 (s, 18 H, 3 × $CH(C\underline{H}_3)_2$), 1.43 (s, 9 H, $C(C\underline{H}_3)_3$), 0.84–1.57 (m, 7 H, 3 × $C\underline{H}(CH_3)_2$, 4-H_2, 5-H_2), 1.63–1.90 (m, 3 H, 3-H_2, 6-H_a), 2.02–2.14 (m, 1 H, 6-H_b), 3.34–3.64 (m, 2 H, 1-H, 2-H), 4.55 (m_c, 1 H, NH). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 12.55 ($\underline{C}H(CH_3)_2$), 18.16 ($CH(\underline{C}H_3)_2$), 23.13, 23.45 (C-4, C-5), 28.40 ($C(\underline{C}H_3)_3$), 30.45, 33.69 (C-3, C-6), 55.23 (C-1), 72.80 (C-2), 82.18 ($\underline{C}(CH_3)_3$), 155.51 ($\underline{C}O_2(C(CH_3)_3$). **IR** (pellet): ν (cm^{-1}) = 3368, 2943, 2866, 1686, 1532, 1462, 1366, 1321, 1179, 1107, 1045, 1023, 883, 779, 678. **MS** (ESI): *m*/*z* (%) = 372 (100) $[M+H]^+$. HRMS (ESI): calcd for $[C_{20}H_{41}NO_3Si + Na]^+$: 371.286; confirmed.

***tert*-Butyl 2-(triisopropylsilyloxy)phenylcarbamate 21:** 2-Aminophenol (2.00 g, 18.3 mmol) in THF (20 mL) was treated with di-*tert*-butyl dicarbonate (4.20 g, 19.2 mmol) and stirred at rt for 13 h. Afterwards the solvent was removed unter reduced pressure, H_2O (50 mL) was added and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, the solvent was removed in vacuo and the resulting solid washed with CCl_4 (4 × 50 mL) to give *tert*-butyl 2-hydroxyphenylcarbamate (2.98 g, 14.2 mmol, 78%) as a colourless solid. **^{1}H-NMR** (300 MHz,

CD_3OD): δ =1.53 (s, 9 H, C(C$\underline{H}_3$)$_3$), 6.52–6.90 (m, 4 H, 3-H, 4-H, 5-H, 6-H), 7.62 (d, J = 7.9 Hz, 1 H, NH). **^{13}C-NMR** (125 MHz, CD_3OD): δ=28.64 (C($\underline{C}H_3$)$_3$), 81.27 ($\underline{C}(CH_3)_3$), 116.12, 120.67, 121.03, 124.69, 127.69 (C-1, C-3, C-4, C-5, C-6), 148.19 (C-2), 155.48 ($\underline{C}O_2C(CH_3)_3$). **IR** (pellet): ν(cm^{-1}) = 3427, 3292, 2986, 1691, 1614, 1522, 1456, 1326, 1227, 1151, 1054, 927, 842, 777, 750, 735, 611. **UV** (CH_3CN): λ_{max} (lg ε) = 204.5 nm (4.6047), 235.0 (4.0397), 281.5 (3.5691). **MS** (ESI): *m*/*z* (%) = 232 (100) [M+Na]$^+$. To a solution of *tert*-butyl 2-hydroxyphenylcarbamate (2.00 g, 9.56 mmol) and imidazole (977 mg, 14.3 mmol) in CH_2Cl_2 (30 mL) was added Chlorotriisopropylsilane (2.76 g, 14.3 mmol). The mixture was stirred at rt for 20 h, H_2O (15 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL), dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (P/Et_2O = 100:1) to provide **21** (2.86 g, 7.82 mmol, 82%) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.12 (d, J = 7.3 Hz, 18 H, 3 × CH(C$\underline{H}_3$)$_2$), 1.24–1.41 (m, 3 H, 3 × C$\underline{H}$(CH$_3$)$_2$), 1.51 (s, 9 H, C(C$\underline{H}_3$)$_3$), 6.78–6.89 (m, 2 H, 3-H, 5-H), 6.93 (dt, J = 6.9, 2.2 Hz, 1 H, 4-H), 7.11 (s$_{br}$, 1 H, NH), 7.99 (d, J = 8.0 Hz, 1 H, 6-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 12.71 (3 × $\underline{C}$H(CH$_3$)$_2$), 17.89 (3 × CH($\underline{C}$H$_3$)$_2$), 28.30 (C($\underline{C}$H$_3$)$_3$), 80.00 ($\underline{C}$(CH$_3$)$_3$), 117.31, 118.54, 121.53, 122.18 (C-3, C-4, C-5, C-6), 129.83 (C-1), 143.92 (C-2), 152.75 ($\underline{C}O_2C(CH_3)_3$). **IR** (film): ν(cm^{-1}) = 3438, 2946, 2869, 1735, 1598, 1520, 1450, 1392, 1367, 1328, 1265, 1234, 1158, 1113, 1049, 998, 916, 883, 828, 749, 707, 683. **UV** (CH_3CN): λ_{max} (lg ε) = 206.5 nm (4.6141), 237 (4.155), 280 (3.493). **MS** (DCI, 200 eV): *m*/*z* (%) = 749 (53) [2M+NH$_4$]$^+$, 383 (100) [M+NH$_4$]$^+$, 367 (35) [M+H]$^+$.

SYNTHESIS OF MONOALLYL ETHERS

(1*R*,2*R*)-*trans*-2-(2-Methallyloxy)cyclohexanol (22): According to general procedure A, **11** (551 mg, 2.50 mmol) was reacted with β-methallyl chloride (**8**) (451 mg, 488 μL, 5.00 mmol) within 24 h at 60 °C to provide (1*R*,2*R*)-2-(2-methallyloxy)cyclohexyl benzoate (612 mg, 2.23 mmol, 89%) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 20:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, 2'-CH$_3$), 1.16–2.12 (m, 8 H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 6-H$_2$), 3.44–3.53 (m, 1 H, 1-H), 3.94 (d, J = 12.4 Hz, 1 H, 1'-H$_a$), 4.02 (d, J = 12.4 Hz, 1 H, 1'-H$_b$), 4.78 (m$_c$, 1 H, 3'-H$_a$), 4.96 (m$_c$, 1 H, 3'-H$_b$), 5.01– 5.11 (m, 1 H, 2-H), 7.33–7.49 (m, 2 H, Ph-H$_m$), 7.51–7.60 (m, 1 H, Ph-H$_p$), 8.02–8.10 (m, 2 H, Ph-H$_o$). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 13.41 (2'-CH$_3$), 23.03, 23.11 (C-4, C-5), 29.58, 29.62 (C-3, C-6), 68.10 (C-1'), 73.47 (C-1), 78.02 (C-2), 111.92 (C-3'), 128.25 (Ph-C$_m$), 129.54 (Ph-C$_o$), 129.60 (Ph-C$_i$), 132.70 (Ph-C$_p$), 142.63 (C-2'), 166.22 ($\underline{C}$O2Ph). **UV** (CH_3CN): λ_{max} (lg ε) = 192.5 nm (4.6262), 194.5 (4.6446), 228.0 (4.1016), 272 (2.9359), 279.5 (2.8395). **MS** (ESI): *m*/*z* (%) = 297 (100) [M+Na]$^+$, 275 (5) [M+H]$^+$. A solution of (1*R*,2*R*)-2-(2-methallyloxy)cyclohexyl benzoate (612 mg, 2.23 mmol) in MeOH (36 mL) was cooled to 0 °C, and a 0.5 M NaOMe-solution was added dropwise. The mixture was stirred at rt for 3.5 d, aq. saturated NH_4Cl (10 mL) was added and the aqueous phase was extracted with

Et_2O (3 × 30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (P/Et_2O = 5 : 1) to provide **22** (169 mg, 995 μmol, 45%) as a colorless liquid. **^{1}H-NMR** (300 MHz, C_6D_6): δ = 1.73 (s, 3 H, 2'-CH_3), 1.04–2.09 (m, 8 H, 3-H_2, 4-H_2, 5-H_2, 6-H_2), 2.69 (s, 1 H, OH), 3.05 (ddd, J = 10.5, 8.7, 4.4 Hz, 1 H, 2-H), 3.44 (m_c, 1 H, 1-H), 3.85 (d, J = 12.3 Hz, 1 H, 1'-H_a), 4.02 (d, J = 12.3 Hz, 1 H, 1'-H_b), 4.86 (m_c, 1 H, 3'-H_a), 4.95 (m_c, 1 H, 3'-H_b). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 19.61 (2'-CH_3), 23.93, 24.19 (C-4, C-5), 29.04 (C-6), 31.98 (C-3), 72.64 (C-1'), 73.84 (C-2), 83.21 (C-1), 112.07 (C-3'), 142.55 (C-2'). **IR** (film): ν (cm^{-1}) = 3442, 3075, 2934, 2861, 1656, 1373, 1233, 1082, 997, 898, 848. **MS** (DCI, 200 eV): m/z (%) = 188 (100) $[M+NH_4]^+$. **GC**: temperature: 90 °C, pressure: 65 kPa, column: heptakis(6-*O*-TBDMS-2,3-di-*O*-methyl)-β-cyclodextrin (50% in OV 1701), t_R = 19.865 min (E1), 20.687 (E2); *ee* = 86%.

***rac-trans*-2-(2-Methallyloxy)cyclohexanol (*rac*-22):** According to general procedure A, *rac-trans*-cyclohexane-1,2-diol (**15**, 2.00 g, 17.2 mmol) was reacted with β-methallyl chloride (**8**) (1.87 g, 2.02 mL, 20.7 mmol) within 12 h at 60 °C to provide *rac*-**22** (1.45 g, 8.55 mmol, 50%) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 4 : 1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, 2'-CH_3), 1.04-2.14 (m, 8 H, 3-H_2, 4-H_2, 5-H_2, 6-H_2), 2.73 (s, 1 H, OH), 3.08 (m_c, 1 H, 2-H), 3.45 (m_c, 1 H, 1-H), 3.87 (d, J = 12.3 Hz, 1 H, 1'-H_a), 4.05 (d, J = 12.3 Hz, 1 H, 1'-H_b), 4.88 (m_c, 1 H, 3'-H_a), 4.94 (m_c, 1 H, 3'-H_b). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 19.61 (2'-CH_3), 23.93, 24.19 (C-4, C-5), 29.04 (C-6), 31.98 (C-3), 72.64 (C-1'), 73.84 (C-2), 83.21 (C-1), 112.07 (C-3'), 142.55 (C-2'). **IR** (film): ν (cm^{-1}) = 3418, 3076, 2934, 2861, 1725, 1656, 1451, 1373, 1234, 1082, 997, 899, 849. **MS** (DCI, 200 eV): m/z (%) = 188 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $[C_{10}H_{18}O_2 + Na]^+$: 193.1204; confirmed.

(2*R*,3*R*)-3-(2-Methallyloxy)-1,2,3,4-tetrahydronaphthalen-2-ol 23: According to general procedure A, **12** (234 mg, 870 μmol) was reacted with β-methallyl bromide (**7**) (235 mg, 175 μL, 1.74 mmol) within 20 h at rt to provide (2*R*,3*R*)-3-(2-methallyloxy)-1,2,3,4-tetrahydronaphthalen-2-yl benzoate (127 mg, 395 μmol, 45%) as a colourless solid after column chromatography on silica gel (P/Et_2O = 10 : 1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.69 (s, 3 H, 2'-CH_3), 2.94 (t, J = 6.1 Hz, 1 H, 4-H_a), 2.99 (t, J = 6.2 Hz, 1 H, 1-H_a), 3.22 (dd, J = 16.8, 5.0 Hz, 1 H, 1-H_b), 3.39 (dd, J = 17.0, 5.0 Hz, 1 H, 4-H_b), 3.96 (ddd, J = 6.6, 6.5, 5.1 Hz, 1 H, 3-H), 4.06 (s, 1 H, 1'-H_2), 4.85 (m_c, 1 H, 3'-H_a), 4.95 (m_c, 1 H, 3'-H_b), 5.51 (dd, J = 12.0, 6.0 Hz, 1 H, 2-H). 7.13 (m_c, 4 H, 5-H, 6-H, 7-H, 8-H), 7.40 (m_c, 2 H, Ph-H_m), 7.53 (m_c, 1 H, Ph-H_p), 7.98 (m_c, 2 H, Ph-H_o). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 19.52 (2'-CH_3), 32.45, 32.71 (C-1, C-4), 71.67 (C-2), 73.64 (C-1'), 74.31 (C-3), 112.50 (C-3'), 126.27, 126.30 (C-6, C-7), 128.39 (Ph-$\underline{C}H_m$), 128.84, 128.97 (C-5, C-8), 129.68 (Ph-$\underline{C}H_o$), 130.39 (Ph-$\underline{C}_i$), 133.03 (Ph-$\underline{C}H_p$), 133.14, 133.41 (C-4a, C-8a), 142.31 (C-2'), 166.04 ($\underline{C}O_2Ph$). **IR** (film): ν(cm^{-1}) = 3414, 3065, 3023, 2929, 1719, 1602, 1584, 1494, 1451, 1350, 1272, 1176, 1110, 1026, 904, 743, 711. **UV** (CH_3CN): λ_{max} (lg ε) = 192.5 nm (4.7873), 195.5 (4.8457), 216.5 (4.1586), 228 (4.1696), 265 (3.1466), 272 (3.1821), 280 (2.9322). **MS** (DCI, 200 eV): *m*/*z* (%) = 357 (54) $[M+NH_3+NH_4]^+$, 340 (100) $[M+NH_4]^+$, 323 (10) $[M+H]^+$. A solution of (2*R*,3*R*)-3-(2-methallyloxy)-1,2,3,4-tetrahydronaphthalen-2-yl benzoate (120 mg, 372 μmo) in MeOH (6 mL) was cooled to 0 °C, and a 5.4 M NaOMe-solution (7.50 μL, 37.2 μmol) was added dropwise. The mixture was stirred at rt for 3.5 d, saturated aq. NH_4Cl (5 mL) was added and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (P/Et_2O = 5 : 1) to provide **23** (169 mg, 995 μmol, 45%) as a colorless liquid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.79 (s, 3 H, 2'-CH_3), 2.73 (dd, *J* = 16.2, 10.0 Hz, 1 H, 4-H_a), 2.82 (dd, *J* = 16.4, 10.1 Hz, 1 H, 1-H_a), 2.87 (s, 1 H, OH), 3.20 (dd, *J* = 10.8, 5.6 Hz, 1 H, 1-H_b), 3.25 (dd, *J* = 10.5, 5.6 Hz, 1 H, 4-H_b), 3.57 (ddd, *J* = 9.8, 9.1, 5.5 Hz, 1 H, 3-H), 3.96 (m_c, 1 H, 2-H), 3.99 (d, *J* = 12.3 Hz, 1 H, 1'-H_a), 4.14 (d, *J* = 12.3 Hz, 1-H, 1'-H_b), 4.92 (m_c, 1 H, 3'-H_a), 5.01 (m_c, 1 H, 3'-H_b), 7.11 (m_c, 4 H, 5-H, 6-H, 7-H, 8-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 19.63 (2'-CH_3), 33.74 (C-4), 36.03 (C-1), 70.54 (C-2), 73.27 (C-1'), 79.19 (C-3), 112.62 (C-3'), 126.16, 126.27 (C-6, C-7), 128.89, 128.92 (C-5, C-8), 133.63, 133.85 (C-4a, C-8a), 142.21 (C-2'). **IR** (film): ν(cm^{-1}) = 3440, 3065, 3021, 2907, 1655, 1494, 1454, 1373, 1216, 1112, 902, 744. **UV** (CH_3CN): λ_{max} (lg ε) = 265 nm (2.7335), 272 (2.7432). **MS** (DCI, 200 eV): *m*/*z* (%) = 253 (12) $[M+NH_3+NH_4]^+$, 236 (100) $[M+NH_4]^+$. **HPLC** (Chiralcel OD): Wavelength: 211 nm, Eluent: *n*-hexane / *iso*-propanol = 98:1, Flow: 0.8 mL/min, t_R = 9.64 min , *ee* > 99.99 %.

***rac*-*trans*-2-(2-Methallyloxy)cyclopentanol (*rac*-25):** According to general procedure A, *rac*-*trans*-cyclopentane-1,2-diol (**14**, 1.00 g, 9.79 mmol) was reacted with β-methallyl chloride (**8**) (974 mg, 1.05 mL, 10.8 mmol) within 3 h at 60 °C to provide *rac*-**25** (666 mg, 4.27 mmol, 44%) as a pale yellow oil after column chromatography on silica gel (P/Et_2O = 3 : 1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, 2'-CH_3), 1.80 (d, *J* = 2.9 Hz, 1 H, OH), 1.50–2.16 (m, 6 H, 3-CH_2, 4-H_2, 5-H_2), 3.66–3.72 (m, 1 H, 2-H), 3.89 (d, *J* = 12.6 Hz, 1 H, 1'-H_a), 3.94 (d, *J* = 12.6 Hz, 1 H, 1'-H_b), 4.14 (m_c, 1 H, 1-H), 4.88 (m_c, 1 H, 3'-H_a), 4.97 (m_c, 1 H, 3'-H_b). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 19.54 (2'-CH_3), 20.43, 29.22, 32.05 (C-3, C-4, C-5), 73.23 (C-1'), 76.79 (C-1), 86.23 (C-2), 111.93 (C-3'), 142.54 (C-2'). **IR** (film): ν(cm^{-1}) = 3383, 3076, 2966, 1657, 1453, 1348, 1099, 898. **MS** (DCI, 200 eV): *m*/*z* (%) = 191 (60) $[M+NH_3+NH_4]^+$, 174 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $[C_9H_{16}O_2 + Na]^+$: 179.1043; confirmed.

***rac-cis*-2-(2-Methallyloxy)cyclopentanol (*rac*-27):** According to general procedure A, *meso*-cyclopentane-1,2-diol (**16**, 1.10 g, 10.8 mmol) was reacted with β-methallyl chloride (**8**) (1.07 g, 1.16 mL, 11.9 mmol) within 2 h at 60 °C to provide *rac*-**27** (1.01 g, 6.49 mmol, 60%) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 3 : 1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.42–1.91 (m, 6 H, 3-H_2, 4-H_2, 5-H_2), 1.76 (s, 3 H, 2'-CH_3), 2.50 (d, J = 4.0 Hz, 1 H, OH), 3.69–3.77 (m, 1 H, 2-H), 3.94 (m_c, 2 H, 1'-H_2), 4.06–4.12 (m, 1 H, 1-H), 4.89 (m_c, 1 H, 3'-H_a), 4.98 (m_c, 1 H, 3'-H_b). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 19.50 (2'-CH_3), 19.65, 27.81, 31.14 (C-3, C-4, C-5), 72.16 (C-1), 73.29 (C-1'), 80.95 (C-2), 112.11 (C-3'), 142.12 (C-2'). **IR** (film): ν (cm^{-1}) = 3461, 3076, 2968, 1656, 1450, 1335, 1098, 899. **MS** (DCI, 200 eV): *m/z* (%) = 174 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $[C_9H_{16}O_2 + Na]^+$: 179.1043; confirmed.

***rac-cis*-2-(2-Methallyloxy)cyclohexanol (*rac*-28):** According to general procedure **A**, *meso*-cyclohexane-1,2-diol (**17**, 1.00 g, 8.61 mmol) was reacted with β-methallyl chloride (**8**) (857 mg, 926 μL, 9.47 mmol) within 4 h at 60 °C to provide *rac*-**28** (519 mg, 3.03 mmol, 35%) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 5 : 1). **^{1}H–NMR** (300 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, 2'-CH_3), 1.20–1.88 (m, 8 H, 3-H_2, 4-H_2, 5-H_2, 6-H_2), 2.28 (s, 1 H, OH), 3.42 (m_c, 1 H, 1-H), 3.83 (m_c, 1 H, 2-H), 3.88 (d, J = 12.5 Hz, 1 H, 1'-H_a), 3.97 (d, J = 12.5 Hz, 1 H, 1'-H_b), 4.88 (m_c, 1 H, 3'-H_a), 4.96 (m_c, 1 H, 3'-H_b); **^{13}C–NMR** (125 MHz, $CDCl_3$): δ = 19.52 (2'-CH_3), 21.18, 22.12 (C-4, C-5), 26.49 (C-6), 30.42 (C-3), 68.69 (C-1'), 72.04 (C-1), 77.81 (C-2), 111.84 (C-3'), 142.50 (C-2'); **IR** (film): ν (cm^{-1}) = 3410, 3076, 2936, 2861, 1726, 1449, 1368, 1249, 1080, 985, 910, 848; **MS** (DCI, 200 eV): *m/z* (%) = 188 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $[C_{10}H_{18}O_2 + Na]^+$: 193.1204; confirmed.

(*rac*)-*cis*-4-(2-Methallyloxy)tetrahydrofuran-3-ol (*rac*-29): According to general procedure A *cis*-tetrahydrofuran-3,4-diol (**18**, 2.08 g, 20.0 mmol)) was reacted in dry DMF (60 mL) with β-methallyl chloride (**7**,1.99 g, 22.0 mmol) for 6.5 h at rt. After work-up and column chromatography (silica gel, *n*-pentane/Et_2O = 1 / 1) *rac*-**29** (1.54 g, 9.6 mmol, 48%) was provided as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 1.76 (s_{br}, 3 H, 3'-CH_3), 2.86 (d, J = 5.7 Hz, 1 H, OH), 3.73–3.80 (m, 2 H, 5-H_a, 5-H_b), 3.88–3.93 (m, 2 H, 2-H_a, 2-H_b), 3.99–4.03 (m, 3 H, 4 –H, 1'-H_a, 1'-H_b), 4.28 (ddd, J = 10.5, 5.30, 5.30 Hz, 1 H, 3-H), 4.95 (s_{br}, 1 H, 3'-H_a), 5.00 (s_{br}, 1 H, 3'-H_b) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 19.37 (2'-CH_3), 69.93 (C-5), 70.23 (C-3), 73.33, 74.21 (C-2, C-1'), 77.79 (C-4), 113.01 (C-3'), 141.23 (C-2') ppm; **IR** (Film): $\tilde{\nu}$ = 2941 cm^{-1}, 2870, 1656, 1455, 1409, 1375, 1334, 1261, 1215, 1193, 1132, 1071, 1008, 905.6, 824.1, 731.4; **MS** (70 eV, EI): *m/z* (%) = 158.2 (12) $[M]^+$, 103.1 (8) $[M - C_4H_7]^+$, 87.1 (16) $[M - OC_4H_7]^+$, 72.1 (48) $[C_4H_7O]^+$, 55.1 (100) $[C_4H_7]^+$; HRMS (ESI): calcd for $[C_8H_{14}O_3 + Na]^+$: 181.0841; confirmed.

***tert*-Butyl *rac-trans*-2-hydroxycyclohexyl(2-methallyl)carbamate *rac*-30:** According to general procedure A, *rac*-**19** (1.15 g, 3.11 mmol) was reacted with β-methallyl bromide (**7**) (1.26 g, 940 µL, 9.33 mmol) within 24 h at 60 °C to provide *rac-trans-tert*-butyl 2-methallyl-(2-(triisopropylsilyloxy)cyclohexyl)carbamate (1.02 g, 2.41 mmol, 77%) as a colorless liquid after column chromatography on silica gel ($P/Et_2O = 100:1$). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.03 (s, 18 H, $3 \times CH(C\underline{H}_3)_2$), 1.39 (s, 9 H, $3 \times C(C\underline{H}_3)_2$), 1.68 (s, 3 H, 2'-$CH_3$), 1.10–2.06 (m, 11 H, $C\underline{H}(CH_3)_3$, 3-H_2, 4-H_2, 5-H_2, 6-H_2), 3.47–4.23 (m, 4 H, 1-H, 2-H, 1'-H_2), 4.78 (m_c, 2 H, 3'-H_2). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 12.89 ($3 \times \underline{C}H(CH_3)_2$), 18.29 ($3 \times CH(\underline{C}H_3)_2$), 20.19 (2'-$CH_3$), 24.48, 24.64 (C-4, C-5), 28.38 ($C(\underline{C}H_3)_3$), 25.60, 36.47 (C-3, C-6), 64.64 (C-1'), 71.43 (C-1), 78.81 (C-2), 79.24 ($\underline{C}(CH_3)_3$), 110.86 (C-3'), 143.15 (C-2'), 155.57 ($\underline{C}O_2C(CH_3)_3$). **IR** (film): $\nu(cm^{-1})$ = 2941, 2866, 1693, 1365, 1325, 1172, 1110, 989, 883, 775, 678. **MS** (ESI): *m/z* (%) = 448 (100) $[M+Na]^+$. To a solution of *rac-trans-tert*-butyl 2-methallyl(2-(triisopropylsilyloxy)cyclohexyl)carbamate (1.02 g, 2.41 mmol) in THF (25 mL) was added TBAF · 3 H_2O (1.14 g, 3.61 mmol). The mixture was stirred at rt for 1 h, the solvent removed in vacuo to provide *rac*-**30** (405 mg, 1.50 mmol, 63 %) as a colorless liquid after column chromatography on silica gel ($P/Et_2O = 1:1$). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, $C(CH_3)_3$), 1.71 (s, 3 H, 2'-CH_3), 1.10–1.33 (m, 4 H, 4-H_2, 5-H_2), 1.61–2.08 (m, 4 H, 3-H_2, 6-H_2), 2.40 (s_{br}, 1 H, OH), 3.70 (s_{br}, 2 H, 1'-H_2), 3.43–3.78 (m, 2 H, 1-H, 2-H), 4.82 (m_c, 2 H, 3'-H_2). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 20.26 (2'-CH_3), 24.35, 25.35 (C-4, C-5), 29.30, 35.07 (C-3, C-6), 28.31 ($C(\underline{C}H_3)_3$), 49.13 (C-1'), 61.82, 71.43 (C-1, C-2), 79.96 ($\underline{C}(CH_3)_3$), 110.57 (C-3'), 143.34 (C-2'), 157.03 ($\underline{C}O_2C(CH_3)_3$). **IR** (film): $\nu(cm^{-1})$ = 3438, 2934, 2860, 1692, 1454, 1365, 1246, 1170, 977, 882, 768. **MS** (ESI): *m/z* (%) = 561 (11) $[2M+Na]^+$, 292 (100) $[M+Na]^+$. HRMS (ESI): calcd for $[C_{15}H_{27}NO_3 + Na]^+$: 292.1883; confirmed.

***tert*-Butyl 2-hydroxyphenyl(2-methallyl)carbamate 32:** According to general procedure A, **21** (2.84 g, 7.77 mmol) was reacted with *β*-methallyl bromide (**7**) (3.15 g, 2.35 mL, 23.3 mmol) within 18 h at rt to provide *tert*-butyl 2-methallyl (2-(triisopropylsilyloxy)phenyl)carbamate (2.53 g, 6.02 mmol, 77 %) as a colorless solid after column chromatography on silica gel ($P/Et_2O = 50:1$). **^{1}H-NMR** (300 MHz, DMSO-d_6): δ = 1.15 (d, J = 7.1 Hz, 18 H, $3 \times CH(C\underline{H}_3)_2$), 1.27–1.42 (m, 3 H, $3 \times C\underline{H}(CH_3)_2$), 1.33 (s, 9 H, $C(C\underline{H}_3)_3$), 1.71 (s, 3 H, 2'-CH_3), 2.99 (s, 2 H, 1'-H_2), 4.68 (m_c, 1 H, 3'-H_a), 4.75 (m_c, 1 H, 3'-H_b), 6.82–6.92 (m, 2 H, 3-H, 5-H), 7.08 (dd, J = 8.2, 1.8 Hz, 1 H, 6-H), 7.14 (ddd, J = 8.3, 7.3, 1.8 Hz, 1 H, 4-H). **^{13}C-NMR** (75.5 MHz, DMSO-d_6): δ = 11.88 ($3 \times \underline{C}H(CH_3)_2$), 17.21 ($3 \times CH(\underline{C}H_3)_2$), 19.38 (2'-$CH_3$), 27.39 ($C(\underline{C}H_3)_3$), 78.29 ($\underline{C}(CH_3)_3$), 111.52 (C-3'), 118.27, 119.85, 127.28, 130.21 (C-3, C-4, C-5, C-6), 130.21 (C-1), 141.17 (C-2'). **IR** (pellet): $\nu(cm^{-1})$ = 2967, 2946, 2867, 1693, 1599, 1581, 1499, 1381, 1365, 1346, 1300, 1284, 1254, 1206, 1173, 1142, 1116, 1057, 1040, 999, 939, 908, 881, 868, 801, 756, 719, 683, 669, 620, 582, 517, 441. **UV** (CH_3CN): λ_{max} (lg ε) = 272.5 nm (3.2899), 278 (3.2546). **MS** (EI, 70 eV): *m*/*z* (%) = 419 (47) $[M]^+$, 346 (100) $[M-C_4H_9O]^+$. To a solution of *tert*-butyl 2-methallyl-(2-(tri-isopropylsilyloxy)phenyl)carbamate (2.53 g, 6.02 mmol) in THF (50 mL) was added TBAF · 3 H_2O (2.85 g, 9.02 mmol). The mixture was stirred at rt for 1 h, the solvent was removed in vacuo to provide **32** (1.19 g, 4.52 mmol, 75%) as a colourless solid after column chromatography on silica gel (P/Et_2O = 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.49 (s, 9 H, $C(C\underline{H}_3)_3$), 1.72 (s, 3 H, 2'-CH_3), 4.16 (s, 2 H, 1'-H_2), 4.87 (m_c, 2 H, 3'-H_2), 6.90 (dt, *J* = 7.4, 1.5 Hz, 1 H, 5-H), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1 H, 3-H), 7.10–7.19 (m, 2 H, 4-H, 6-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.12 (2'-CH_3), 28.17 ($C(\underline{C}H_3)_3$), 56.79 (C-1'), 82.06 ($\underline{C}(CH_3)_3$), 111.54 (C-3'), 119.5 (C-3), 121.06 (C-5), 127.69 (C-4, C-6), 130.90 (C-1), 141.25 (C-2'), 150.99 (C-2), 155.53 ($\underline{C}O_2C(CH_3)_3$). **IR** (pellet): ν (cm^{-1}) = 3247, 2972, 1650, 1596, 1513, 1403, 1366, 1321, 1293, 1241, 1158, 1109, 1056, 902, 861, 759. **UV** (CH_3CN): λ_{max} (lg ε) = 194 nm (4.6041), 274.5 (3.4139). **MS** (EI, 70 eV): *m*/*z* (%) = 263 (6) $[M]^+$, 207 (66) $[M-C_4H_7]^+$, 57 (100) $[^tBu]^+$.

DOMINO-WACKER-CARBONYLATION REACTION

Methyl *rac*-2-(2-methyloctahydrobenzo[*b*][1,4]dioxin-2-yl)acetate (*rac*-31) and (*rac*-32): According to general procedure B, *rac*-**22** (50.7 mg, 298 μmol) was reacted with *p*-benzoquinone (129 mg, 1.19 mmol) and $PdCl_2$ (5.28 mg, 29.8 μmol) within 2 h to provide a mixture of *rac*-**31** and *rac*-**32** (59.7 mg, 262 μmol, 88%, 19:81) as a pale yellow liquid after column chromatography on silica gel (P/Et_2O = 5:1). **^{1}H-NMR** (300 MHz, C_6D_6): δ = 1.21 (s, 2.4 H, 2'-CH_3), 1.49 (s, 0.6 H, 2'-CH_3), 0.92–1.86 (m, 8 H, 5'-H_2, 6'-H_2, 7'-H_2, 8'-H_2), 2.32 (d, *J* = 14.4 Hz, 0.2 H, 2-H_a), 2.40 (d, *J* = 14.4 Hz, 0.2 H, 2-H_b), 2.51 (d, *J* = 13.5 Hz, 0.8 H, 2-H_a), 2.89 (ddd, *J* = 11.2, 9.2, 4.3 Hz, 1 H, 4a'-H), 3.04 (d, *J* = 13.5 Hz, 0.8 H, 2-H_b), 3.26 (s, 0.6 H, OCH_3), 3.27 (dd, *J* = 11.5, 0.7 Hz, 0.8 H, 3'-H_a), 3.32 (s, 2.4 H, OCH_3), 3.87 (ddd, *J* = 11.1, 9.0, 4.2 Hz, 0.2 H, 8a'-H), 3.54 (ddd, *J* = 11.0, 9.1, 4.6 Hz, 0.8 H, 8a'-H), 3.64 (dd, *J* = 11.3, 0.9 Hz, 0.2 H, 3'-H_a), 3.69 (dd, *J* = 11.5 Hz, 0.8 H, 3'-H_b), 3.83 (d, *J* = 11.3 Hz, 0.2 H, 3'-H_b). **^{13}C-NMR** (150 MHz, C_6D_6): δ = 19.80, 23.66 (2'-CH_3), 24.42, 24.43, 24.52, 24.53 (C-6', C-7'), 30.36, 30.38, 30.97 (C-5', C-8'), 38.86, 44.76 (C-2), 50.96, 51.00 ($O\underline{C}H_3$), 71.90, 72.03 (C-2'), 73.62, 73.75 (C-8a'), 74.24, 74.37 (C-3'), 80.61, 80.77 (C-4a'), 170.17, 170.91 ($\underline{C}O_2CH_3$). **IR** (film): ν (cm^{-1}) = 2939, 2864, 1738, 1513, 1322, 1227, 1095, 1020, 853. **UV** (CH_3CN): λ_{max} (lg ε) = 286 nm (2.2717). **MS** (DCI, 200 eV): *m*/*z* (%) = 246 (100) $[M+NH_4]^+$, 229 (45) $[M+H]^+$. HRMS (ESI): calcd for $[C_{12}H_{20}O_4 + Na]^+$: 251.2746; confirmed.

Methyl 2-((4a*R*,10a*R*)-2-methyl-2,3,4a,5,10,10a-hexahydronaphtho[2,3-*b*][1,4]dioxin-2-yl)acetate (33) and (34): According to general procedure B, **23** (45.0 mg, 206 μmol) was reacted with *p*-benzoquinone (89.1 mg, 825 μmol) and $PdCl_2$ (3.62 mg, 22.9 μmol) within 90 min to provide a mixture of **37** and **38** (41.0 mg, 148 μmol, 72%, 34:64) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 5:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.28 (s, 2 H, 2'-CH_3), 1.50 (s, 1 H, 2'-CH_3), 2.51 (s, 0.7 H, 2-H_2), 2.68 (d, J = 13.7 Hz, 0.7 H, 2-H$_a$), 2.81 (m$_c$, 2 H, 10'-H$_a$, 5'-H$_a$), 2.96 (dd, J = 16.0, 5.9 Hz, 1 H, 5'-H$_b$), 3.07 (d, J = 13.7 Hz, 0.7 H, 2-H$_b$), 3.06, 3.12 (2 x dd, J = 6.0, 2.5 Hz, 1 H, 10'-H$_b$), 3.49 (d, J = 11.8 Hz, 1 H, 3'-H$_a$), 3.50 (m$_c$, 1 H, 4a' H), 3.68 (s, 3 H, OCH_3), 3.82 (d, J = 11.8 Hz, 1 H, 3'-H$_b$), 3.92 (ddd, J = 10.8, 9.8, 5.8 Hz, 0.66 H, 10a'-H), 4.00 (ddd, J = 10.8, 9.9, 5.9 Hz, 0.34 H, 10a'-H), 7.10 (m$_c$, 4 H, 6'-H, 7'-H, 8'-H, 9'-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 19.54, 23.33 (2'-CH_3), 34.33, 34.34 (C-5'), 35.01, 35.03 (C-10'), 38.54, 44.54 (C-2), 51.60 (OCH_3), 69.95, 70.12 (C-10a'), 73.48, 73.72 (C-3'), 76.43, 76.60 (C-4a'), 126.22, 126.24, 126.26, 128.96, 128.99 (C-6', C-7', C-8', C-9'), 133.48, 133.56 (C-5a'), 133.76, 133.80 (C-9a'), 170.47, 171.16 ($\underline{C}O_2CH_3$). **MS** (DCI, 200 eV): *m*/*z* (%) = 574 (10) [2M+Na]$^+$, 299 (100) [M+Na]$^+$. HRMS: calcd for [$C_{16}H_{20}O_4$ + Na]$^+$: 299.1259; confirmed.

Methyl *rac*-2-(2-methyl-hexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-2-yl)acetate (*rac*-35) and (*rac*-36): According to general procedure B, *rac*-**27** (49.7 mg, 318 μmol) was reacted with *p*-benzoquinone (127 mg, 1.27 mmol) and $PdCl_2$ (5.65 mg, 31.8 μmol) within 75 min to provide a mixture of *rac*-**35** and *rac*-**36** (58.7 mg, 274 μmol, 86%, 29:71) as a pale yellow liquid after column chromatography on silica gel (P/Et_2O = 8:1). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 1.21 (s, 2.1 H, 2'-CH_3), 1.35 (s, 0.9 H, 2'-CH_3), 1.41–2.03 (m, 6 H, 5'-H_2, 6'-H_2, 7'-H_2), 2.46 (d, J = 14.1 Hz, 0.3 H, 2-H$_a$), 2.52 (d, J = 14.1 Hz, 0.3 H, 2-H$_b$), 2.66 (d, J = 13.8 Hz, 0.7 H, 2-H$_a$), 2.85 (d, J = 13.8 Hz, 0.7 H, 2-H$_b$), 3.29 (d, J = 11.7 Hz, 0.3 H, 3'-H$_a$), 3.41 (d, J = 11.8 Hz, 0.7 H, 3'-H$_a$), 3.53 (d, J = 11.8 Hz, 0.7 H, 3'-H$_b$), 3.65 (s, 0.9 H, OCH_3), 3.66 (s, 2.1 H, OCH_3), 3.81 (d, J = 11.7 Hz, 0.3 H, 3'-H$_b$), 3.96 (dt, J = 7.8, 4.5 Hz, 0.3 H, 4a'-H), 4.01 (dt, J = 8.4, 4.5 Hz, 0.7 H, 4a'-H), 4.04 (dd, J = 4.7, 2.3 Hz, 0.3 H, 7a'-H), 4.12 (dt, J = 4.8, 1.7 Hz, 0.7 H, 7a'-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.12, 23.70 (2'-CH_3), 20.39, 20.51, 24.49, 25.75, 30.76, 30.93 (C-5', C-6', C-7'), 38.93, 44.18 (C-2), 51.46, 51.52 (OCH_3), 66.19, 66.59 (C-3'), 69.94, 70.21 (C-7a'), 70.59, 70.69 (C-2'), 76.29, 76.91 (C-4a'), 170.77, 171.28 ($\underline{C}O_2CH_3$). **IR** (film): ν (cm^{-1}) = 2953, 1737, 1437, 1316, 1223, 1131, 1024, 969, 914. **UV** (CH_3CN): λ_{max} (lg ε) = 288 nm (1.6481). **MS** (DCI, 200 eV): *m*/*z* (%) = 249 (5) [M+NH_3+NH_4]$^+$, 232 (100) [M+NH_4]$^+$, 215 (75) [M+H]$^+$. HRMS (ESI): calcd for [$C_{11}H_{18}O_4$ + Na]$^+$: 237.1103; confirmed.

***tert*-Butyl *rac*-2-(2-methoxy-2-oxoethyl)-2-methyloctahydrobenzo[*b*][1,4]oxazine-4-carboxylate (*rac*-37) and (*rac*-38):** According to general procedure B, *rac*-**30** (49.0 mg, 181 μmol) was reacted with *p*-benzoquinone (78.6 mg, 728 μmol) and $PdCl_2$ (3.23 mg, 18.1 μmol) within 4 h to provide a mixture of *rac*-**37** and *rac*-**38** (47.3 mg, 144 μmol, 79%, 22:78) as a colorless liquid after column chromatography on silica gel (P/Et_2O = 5:1). **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 1.12 (ddd, J = 23.5, 12.0, 3.4 Hz, 1 H, 5a-H$_a$), 1.21 (s, 2.3 H, 2-CH$_3$)’ 1.27 (s, 0.7 H, 2-CH$_3$), 1.24–1.32 (m, 3 H, 6-H$_a$, 7-H$_a$, 8-H$_a$), 1.42 (s, 2 H, $C(C\underline{H}_3)_3$), 1.43 (s, 7 H, $C(C\underline{H}_3)_3$), 1.64 (m$_c$, 1 H, 7-H$_b$), 1.72 (m$_c$, 1 H, 6-H$_b$), 1.86 (m$_c$, 1 H, 8-H$_b$), 2.18 (dd, J = 10.3, 2.3 Hz, 1 H, 5-H$_b$), 2.42 (d, J = 15.9 Hz, 0.2 H, 1'-H$_a$), 2.46 (d, J = 14.1 Hz, 0.8 H, 1'-H$_a$), 2.53 (d, J = 14.1 Hz, 0.8 H, 1'-H$_b$), 3.09 (d, J = 14.6 Hz, 0.2 H, 3-H$_a$), 3.26 (ddd, J = 10.8, 10.7, 3.4 Hz, 1 H, 4a-H), 3.43 (d, J = 14.3 Hz, 0.8 H, 3-H$_a$), 3.48 (ddd, J = 10.7, 8.4, 4.0 Hz, 1 H, 8a-H), 3.63 (s, 0.7 H, OCH$_3$), 3.65 (s, 2.3 H, OCH$_3$), 3.78 (d, J = 14.3 Hz, 0.8 H, 3-H$_b$), 4.06 (d, J = 14.6 Hz, 0.2 H, 3-H$_b$). **^{13}C-NMR** (125 MHz, CDCl$_3$): δ = 23.37, 25.67 (2-CH$_3$), 24.40, 24.57, 24.62 (C-6, C-7), 28.30, 28.38 ($C(\underline{C}H_3)_3$), 29.31, 29.56 (C-5), 31.98, 32.03 (C-8), 43.09, 44.00 (C-1), 45.77, 45.89 (C-3), 51.34, 51.58 (OCH$_3$), 60.21, 60.28 (C-4a), 71.78, 72.68 (C-8a), 75.47, 75.73 (C-2), 79.69 ($\underline{C}(CH_3)_3$), 155.36, 155.72 ($\underline{C}O_2C(CH_3)_3$), 170.65, 170.78 ($\underline{C}O_2OCH_3$). **IR** (Film): ν(cm^{-1}) = 2935, 1740, 1695, 1407, 1366, 1157, 1016, 862. HRMS (ESI): calcd for [$C_{17}H_{29}NO_5$ + Na]$^+$: 350.1943; confirmed.

***tert*-Butyl 2-(2-methoxy-2-oxoethyl)-2-methyl-2,3-dihydrobenzo[*b*][1,4]oxazine-4-carboxylate 39:** A mixture of Pd(OTFA)$_2$ (3.21 mg, 9.65 µmol) and (*S*,*S*)-Bn-BOXAX (16.6 mg, 28.9 µmol) in MeOH (2 mL) was stirred at rt for 10 min. Afterwards *p*-benzochinone (83.3 mg, 772 µmol) and **32** (50.8 mg, 193 µmol) were added and the mixture stirred under CO-atmosphere at 60 °C for 6 h. After workup according to general procedure B and column chromatography on silica gel (P/Et$_2$O = 5 : 1) **30** was obtained as a yellow liquid (43.1 mg, 134 µmol, 70%). **^{1}H-NMR** (300 MHz, C$_6$D$_6$): δ = 1.30 (s, 3 H, 2-CH$_3$), 1.41 (s, 9 H, C(CH$_3$)$_3$), 2.38 (d, J = 15.4 Hz, 1 H, 1'-H$_a$), 2.44 (d, J = 15.4 Hz, 1 H, 1'-H$_b$), 3.23 (s, 3 H, OCH$_3$), 3.52 (d, J = 13.5 Hz, 1 H, 3-H$_a$), 3.94 (d, J = 13.5 Hz, 1 H, 3-H$_b$), 6.84 (m$_c$, 2 H, 6-H, 7-H), 6.95 (m$_c$, 8 H), 8.07 (m$_c$, 1 H, 5-H). **^{13}C-NMR** (125 MHz, C$_6$D$_6$): δ = 22.40 (2-CH$_3$), 28.11 ($C(\underline{C}H_3)_3$), 41.26 (C-1'), 48.93 (C-3), 51.10 (OCH$_3$), 74.67 (C-2), 80.94 ($\underline{C}(CH_3)_3$), 117.68 (C-8), 124.87, 127.92 (C-6, C-7), 128.29 (C-5), 145.49 ($\underline{C}O_2C(CH_3)_3$), 169.77 ($\underline{C}O_2OCH_3$). **IR** (film): ν(cm^{-1}) = 2978, 1784, 1704, 1586, 1495, 1372, 1151, 1020, 927, 861. **UV** (CH$_3$CN): λ_{max} (lg ε) = 211 nm (4.5992), 239.5 (3.9811), 281.5 (3.5323). **MS** (EI, 70 eV): m/z (%) = 344 (100) [M+Na]$^+$, 665 (11) [2M+Na]$^+$. HRMS (ESI): calcd for [$C_{17}H_{23}NO_5$ + Na]$^+$: 344.3580; confirmed.

DOMINO-WACKER-MIZOROKI-HECK REACTION

***rac*-*trans*-(*E*)-Methyl 4-(2-methylhexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-2-yl)but-2-enoate (*rac*-40) and (*rac*-41):** According to general procedure C *rac*-**25** (50.0 mg, 0.330 mmol) was reacted with methyl acrylate (**9**, 78.0 mg, 0.96 mmol) for 3 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 4 / 1) *rac*-**40** and *rac*-**41** (30.0 mg, 0.125 mmol, 39%, 50:50 mixture) were provided as yellow oil. **^{1}H-NMR** (300 MHz, CDCl$_3$, * indicates the minor epimer): δ = 1.12*, 1.39 (s, 1.8 H, 2'-CH$_3$), 1.39–1.92 (m, 6 H, 5'-H$_2$, 6-H$_2$, 7'-H$_2$), 2.35 (m, 2 H, 4-H$_2$), 3.05–3.30 (m, 1 H, 4'a-H), 3.22–3.72

(m, 3 H, 3-H_2, 7'a-H), 3.74 (s, 3 H, OCH_3), 5.90 (m, 1 H, 2-H), 7.00 (m, 1 H, 3-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.25, 20.43 (2-CH_3), 23.14, 23.85, 23.88, 24.46, 24.48(C-5', C-6', C-7'), 36.22, 42.35 (C-4), 51.42, 51.44 (OCH_3), 73.00, 73.17 (C-3'), 74.21, 74.42 (C-7a'), 74.54, 74.72 (C-2'), 81.39, 81.68(C-4a'), 123.93, 123.97 (C-2), 143.61, 144.15 (C-3), 166.55 ($\underline{C}O_2CH_3$). **IR** (film): ν (cm^{-1}) = 2973, 2881, 1724, 1657, 1436, 1384, 1274, 1127, 1022, 984, 895. **UV** (CH_3CN): λ_{max} (lg ε) = 206 nm (4.0901). **MS** (DCI, 200 eV): *m*/*z* (%) = 258 (100) $[M+NH_4]^+$.

***rac-cis*-(*E*)-5-(2-Methylhexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-2-yl)pent-3-en-2-one (*rac*-42) and (*rac*-43):** According to general procedure C *rac*-**27** (50.0 mg, 0.330 mmol) was reacted with methyl vinyl ketone (**10b**, 67.3 mg, 0.96 mmol) for 2 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 4 / 1) *rac*-**42** and *rac*-**43** (51.0 mg, 0.228 mmol, 70%, 50:50 mixture) were provided as yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$, * indicates the minor epimer): δ = 1.09, 1.24 (s, 3 H, 2'-CH_3), 1.44–2.12 (m, 6 H, 5'-H_2, 6'-H_2, 7'-H_2), 2.25–2.50 (m, 2 H, 4-H_2), 2.25 (s, 3 H, 1-CH_3), 3.19, 3.26 (d, J = 11.7 Hz, 1 H, 3'-H_a), 3.57 (d, J = 11.7 Hz, 1 H, 3'-H_b), 4.03 (m, 2 H, 4'a-H, 7'a-H), 6.13 (m, 1 H, 2-H), 6.85 (m, 1 H, 3-H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 20.24, 23.57 (2'-CH_3), 20.27, 20.57, 24.34, 25.84, 30.65, 30.98 (C-5', C-6', C-7'), 26.70, 26.88 (1-CH_3), 36.61, 42.80 (C-4), 66.55, 67.29 (C-3'), 69.79, 70.17 (C-7a'), 71.34, 71.40 (C-2'), 76.21, 76.96 (C-4a'), 133.71, 133.90 (C-2) 143.25, 143.38 (C-3), 198.39 ($\underline{C}OCH_3$). **IR** (film): ν (cm^{-1}) = 2968, 1697, 1673, 1628, 1435, 1361, 1254, 1130, 1057, 981. **UV** (CH_3CN): λ_{max} (lg ε) = 221 nm (1.1073). HRMS (ESI): calcd for $[C_{13}H_{20}O_3 + Na]^+$: 247.13047; confirmed.

Methyl *rac-cis*-(*E*)-4-(2-methyl-hexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-2-yl)but-2-enoate *rac*-44 and *rac*-45: According to general procedure C *rac*-**27** (50.0 mg, 0.330 mmol) was reacted with methyl acrylate (**57**, 78.0 mg, 0.96 mmol) for 3 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 4 / 1) *rac*-**44** and *rac*-**45** (47.0 mg, 0.196 mmol, 61%, 50:50 mixture) were provided as yellow oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.09 (s, 1.5 H, 2'-CH_3), 1.24 (s, 1.5 H, 2'-CH_3), 1.41–2.12 (m, 6 H, 5'-H_2, 6'-H_2, 7'-H_2), 2.25–2.45 (m, 2 H, 4-H_2), 3.18 (d, J = 11.6 Hz, 0.5 H, 3'-H_a), 3.25 (d, J = 11.7 Hz, 0.5 H, 3'-H_a), 3.55 (d, J = 11.7 Hz, 0.5 H, 3'-H_b), 3.57 (d, J = 11.6 Hz, 0.5 H, 3'-H_b), 3.74 (s, 3 H, OCH_3), 4.03 (m, 2 H, 4'a-H, 7'a-H), 5.90 (m, 1 H, 2-H), 7.00 (m, 1 H, 3-H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.09, 23.64 (2'-CH_3), 20.37, 20.59, 24.53, 25.73, 30.78, 30.99 (C-5', C-6', C-7'), 36.51, 42.55 (C-4), 51.45 (OCH_3), 66.58, 67.27 (C-3'), 69.85, 70.24 (C-7a'), 71.39, 71.42 (C-2'), 76.87(C-4a'), 123.71, 123.90 (C-2) 144.36, 144.59 (C-3), 166.66 ($\underline{C}O_2CH_3$). **IR** (film): ν (cm^{-1}) = 2953, 1724, 1657, 1436, 1274, 1198, 1131, 1091, 1057. **UV** (CH_3CN): λ_{max} (lg ε) = 206 nm (4.0711). **MS** (EI): *m*/*z* (%) = 141 (100) $[M–C_4H_7O_2]^+$. HRMS (ESI): calcd for $[C_{13}H_{20}O_4 + Na]^+$: 263.12538; confirmed.

(*rac*)-4-(2-Methylhexahydro-(*cis*-furo[3,4-*b*][1,4]dioxin)-2-yl)but-2-enal (*rac*-46) and (*rac*-47): According to general procedure C *rac*-**29** (51.0 mg, 0.320 mmol) was reacted with acrolein (**10a**, 54.0 mg, 0.960 mmol) for 2 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 2 / 1) *rac*-**46** and *rac*-**47** (22.6 mg, 0.106 mmol, 33%, 65:35 mixture) were provided as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$, * indicates the minor epimer): δ = 1.23*, 1.26 (s, 3 H, 2'-CH_3), 2.38–2.63, 2.98–3.06* (m, 2 H, 4-H$_a$, 4-H$_b$), 3.23, 3.30* (d, *J* = 11.9 Hz, 1 H, 3'-H$_a$), 3.59, 3.60* (d, *J* = 11.9 Hz, 1 H, 3'-H$_b$), 3.79–4.04 (m, 4 H, 5'-H$_a$, 5'-H$_b$, 7'-H$_a$, 7'-H$_b$), 4.14–4.35 (m, 2 H, 4a'-H, 7a'-H), 6.14, 6.21* (dddd, *J* = 15.7, 7.8, 1.3, 1.3 Hz, 1 H, 2-H), 6.85*, 6.94 (ddd, *J* = 15.7, 7.7, 6.9 Hz, 1 H, 4-H), 9.53, 954* (d, *J* 7.8 Hz, 1 H, 1-H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, * indicates the minor epimer): δ = 20.25, 23.55* (2'-CH_3), 37.18*, 42.84 (C-4), 66.25*, 67.55*, 67.71, 68.26, 68.57*, 68.93, 73.02*, 73.13, 73.47*, 74.62 (C-3', C-4a', C-5', C-7', C-7a'), 71.36*, 71.53 (C-2'), 135.6, 135.8* (C-2), 152.5*, 152.9 (C-3), 193.5*, 193.7 (C-1) ppm; **MS** (ESI): *m/z* (%) = 251.1 (50) $[M + K]^+$, 235.1 (100) $[M + Na]^+$; HRMS (ESI): calcd for $[C_{11}H_{16}O_4 + Na]^+$: 235.0946; confirmed.

(*rac*)-5-(2-Methylhexahydro(*cis*-furo[3,4-*b*][1,4]dioxin)-2-yl)pent-3-en-2-one (*rac*-48) and (*rac*-49): According to general procedure C *rac*-**29** (51.0 mg, 0.320 mmol) was reacted with methyl vinyl ketone (**10b**, 78.0 mg, 0.960 mmol) for 2 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 2 / 1) *rac*-**48** and *rac*-**49** (49.0 mg, 0.220 mmol, 68%, 55:45 mixture) were provided as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$, * indicates the minor epimer): δ = 1.17*, 1.27 (s, 3 H, 2'-CH_3), 2.27*, 2.28 (s, 3 H, 1-H$_3$), 2.31–2.54, 2.85–2.96* (m, 1 H, 5-H$_a$), 3.21–3.33, 3.58–3.62* (m, 1 H, 3'-H$_b$), 3.81–4.06 (m, 4 H, 5'-H$_a$, 5'-H$_b$, 7'-H$_a$, 7'-H$_b$), 4.18–4.35 (m, 2 H, 4a'-H, 7a'-H), 6.12*, 6.20 (ddd, *J* = 15.9, 1.2, 1.2 Hz, 1 H, 3-H), 6.79, 6.87* (ddd, *J* = 15.9, 8.0, 6.9 Hz, 1 H, 4-H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, * indicates the minor epimer): δ = 20.12, 23.56* (2'-CH_3), 26.86, 27.10* (C-1), 37.01, 42.68 (C-5), 66.27*, 68.19 (C-3'), 67.49*, 67.59, 73.04*, 73.13 (C-5', C-7'), 68.49*, 68.81 (C-4a'), 71.40, 71.56 (C-2'), 73.48*, 74.56 (C-7a'), 134.1, 134.2* (C-3), 142.3, 142.7* (C-4), 198.1*, 198.4 (C-2) ppm; **IR** (Film): $\tilde{\nu}$ = 2955 cm^{-1}, 2926, 2872, 1697, 1673, 1628, 1461, 1428, 1363, 1256, 1186, 1132, 1079, 984.5, 951.0, 897.3, 870.1, 831.3, 789.6, 716.6; **UV** (CH_3CN): λ_{max} (lg ε) = 222.0 (4.058) nm; MS (ESI): *m/z* (%) = 265.1 (15) $[M + K]^+$, 249.1 (100) $[M + Na]^+$, 244.2 (60) $[M + NH_4]^+$, 227.1 (50) $[M + H]^+$; HRMS (ESI): calcd for $[C_{12}H_{18}O_4 + Na]^+$: 249.1103; confirmed.

(*rac*)-6-(2-Methylhexahydro(*cis*-furo[3,4-*b*][1,4]dioxin)-2-yl)hex-4-en-3-one (*rac*-50) and (*rac*-51): According to general procedure C *rac*-**29** (51.0 mg, 0.320 mmol) was reacted with ethyl vinyl ketone (**10c**, 80.1 mg, 0.960 mmol) for 3 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 2 / 1) *rac*-**50** and *rac*-**51** (52.0 mg, 0.220 mmol, 62%, 70:30 mixture) were provided as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$, * indicates the minor epimer) δ = 1.02*, 1.02 (t, *J* = 7.3 Hz, 3

H, 1-H$_3$), 1.08, 1.17* (s, 3 H, 2'-CH$_3$), 2.22–2.43, 2.74–2.80* (m, 2 H, 6-H$_a$, 6-H$_b$), 2.25 (q, J = 7.30 Hz, 2-H$_2$), 3.13–3.25 (m, 1 H, 3'-H$_a$), 3.48–3.54 (m, 1 H, 3'-H$_b$), 3.71–3.96 (m, 4 H, 5'-H$_a$, 5'-H$_b$, 7'-H$_a$, 7'-H$_b$), 4.10–4.25 (m, 2 H, 4a'-H, 7a'-H), 6.05*, 6.13 (ddd, J = 15.9, 1.4, 1.4 Hz, 1 H, 4-H), 6.74, 6.80* (ddd, J = 15.9, 8.1, 6.9 Hz, 1 H, 5-H) ppm; **^{13}C NMR** (75 MHz, CDCl$_3$, * indicates the minor epimer): δ = 7.86, 7.92* (C-1), 19.94*, 23.43 (2'-CH$_3$), 32.96*, 33.28 (C-2), 36.87, 42.51* (C-6), 66.12, 67.31, 67.34*, 67.98*, 68.35, 68.67* 69.98*, 71.45, 72.91, 72.98*, 73.35, 74.36* (C-2', C-3', C-4a', C-5', C-7', C-7a'), 132.9*, 132.9 (C-4), 140.9*, 141.1 (C-5), 200.4, 200.7* (C-3) ppm; **MS** (ESI): *m/z* (%) = 481.28 [2M + H]$^+$, 265.1 (100) [M + Na]$^+$, 241.1 (6) [M + H]$^+$; HRMS (ESI): calcd for [C$_{13}$H$_{20}$O$_4$ + Na]$^+$: 263.1259; confirmed.

(*rac*)-4-(2-Methylhexahydro(*cis*-furo[3,4-b][1,4]dioxin)-2-yl)but-2-enoic acid methyl ester (*rac*-52) and (*rac*-53): According to general procedure C *rac*-**29** (51.0 mg, 0.320 mmol) was reacted with methyl acrylate (**9**, 78.0 mg, 0.960 mmol) for 2 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 7 / 1 → 4 / 1) *rac*-**52** and *rac*-**53** (60.0 mg, 0.230 mmol, 77%, 60:40 mixture) were provided as yellow oil. **^{1}H NMR** (300 MHz, CDCl$_3$, * indicates the minor epimer) δ = 1.12, 1.22* (s, 3 H, 2'-CH$_3$), 2.25–2.47, 2.74–2.84* (m, 2 H, 4-H$_a$, 4-H$_b$), 3.17–3.28 (m, 1 H, 3'-H$_a$), 3.51–3.57 (m, 1 H, 3'-H$_b$), 3.70*, 3.70 (s, 3 H, OCH$_3$), 3.75–4.01 (m, 4 H, 5'-H$_a$, 5'-H$_b$, 7'-H$_a$, 7'-H$_b$), 4.13–4.29 (m, 2 H, 4a'-H, 7a'-H), 5.85*, 5.91 (ddd, J = 15.7, 1.4, 1.4 Hz, 1 H, 2-H), 6.87–6.96 (m, 1 H, 3-H) ppm; **^{13}C NMR** (75 MHz, CDCl$_3$, * indicates the minor epimer): δ = 19.80*, 23.47 (2'-CH$_3$), 36.68, 42.18* (C-4), 51.46*, 51.50 (OCH$_3$), 66.10, 67.14*, 67.29, 67.98*, 68.39, 68.72*, 69.98*,71.33*, 71.47, 73.02, 73.39, 74.25* (C-2', C-3', C-4a', C-5', C-7', C-7a'), 125.1*, 124.2 (C-2), 143.6*, 143.7 (C-3), 166.5, 166.5* (C-1) ppm; **IR** (Film): $\tilde{\nu}$ = 2952 cm^{-1}, 2874, 1723, 1657, 1460, 1437, 1276, 1201, 1133, 1079, 987.2, 950.6, 906.7, 853.0, 791.1, 731.8; **UV** (CH$_3$CN): λ_{max} (lg ε) = 207.0 (4.058) nm; **MS** (ESI): *m/z* (%) = 506.9 (12) [2M + Na]$^+$, 265.1 (100) [M + Na]$^+$, 243.1 (6) [M + H]$^+$; HRMS (ESI): calcd for [C$_{11}$H$_{18}$O$_5$ + Na]$^+$: 265.1052; confirmed.

4-(2-Methyl-2,3,9,9a-tetrahydro-4a*H*-1,4-dioxafluoren-2-yl)but-2-enoic acid methyl ester (54) and (55): According to general procedure C **24** (68.4 mg, 0.320 mmol) was reacted with methyl acrylate (**9**, 78.0 mg, 0.960 mmol) for 2 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 7 / 1) **54** and **55** (51.8 mg, 0.180 mmol, 56%, 60:40 mixture) were provided as pale yellow oil. **^{1}H NMR** (300 MHz, CDCl$_3$, * indicates the minor epimer): δ = 1.38, 1.81* (s, 3 H, 2'-CH$_3$), 2.05 (ddd, J = 14.1, 8.4, 1.3 Hz, 1 H, 4-H$_a$), 2.17 (ddd, J = 14.1, 7.0, 1.4 Hz, 1 H, 4-H$_b$), 2.48* (ddd, J = 14.1, 8.4, 1.3 Hz, 1 H, 4-H$_a$), 2.72* ddd, J = 14.1, 7.0, 1.4 Hz, 1 H, 4-H$_b$), 2.95–3.11 (m, 2 H, 9-H$_a$, 9-H$_b$), 3.24–3.47 (m, 2 H, 3'-H$_a$, 3'-H$_b$), 3.69*, 3.75 (s, 3 H, OCH$_3$), 4.56 (m$_c$, 1 H, 9a'-H), 5.04–5.08 (m, 1 H, 4a'-H), 5.76*, 5.98 (ddd, J = 15.6, 1.4, 1.4 Hz, 1 H, 2-H), 6.84*, 7.01 (ddd, J = 15.6, 8.4, 7.0 Hz, 1 H, 3-H), 7.23–7.39 (m, 4 H, 5-H, 6-H, 7-H, 8-H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, * indicates the minor epimer): δ = 18.73, 19.57* (2’-CH_3), 35.76, 37.67*, 37-73, 41.84* (C-4, C9’), 51.37*, 51, 45 (OCH_3),66.74, 67.35* (C-3’), 70.53, 70.75* (C9a’), 71.17*, 71.30 (C-2’), 77.95, 78.31* (C-4a’), 123.8*, 124.1 (C-2), 125.5*, 125.5, 125.5*, 125.6, 126.6, 128.1*, 128.1, 128.9* (C-5’, C-6’, C-7’, C-8’), 138.9, 139.0* (C-4b’), 140.8, 140.9* (C-8a’), 143.5*, 144.5 (C-3), 166.5*, 166.6 (C-1) ppm; **MS** (ESI): *m/z* (%) = 311.1 (100) $[M + Na]^+$, 289.1 (25) $[M + H]^+$; HRMS (ESI): calcd for $[C_{17}H_{20}O_4 + Na]^+$: 311.1259; confirmed.

2-(3-Methoxycarbonylallyl)-2-methyl-2,3,9,9a-tetrahydro-4aH-1-oxa-4-azafluorene-4-carboxylic acid *tert*-butyl ester (56) and (57): According to general procedure C **21** (106.0 mg, 0.320 mmol) was reacted with methyl acrylate (**9**, 78.0 mg, 0.960 mmol) for 4 d at rt. After work-up and column chromatography (silica gel, *n*-pentane/EtOAc = 7 / 1) **56** and **57** (117 mg, 0.300 mmol, 91%, 60:40 mixture) were provided as pale yellow oil. **^{1}H NMR** (300 MHz, DMSO, 100°C, * indicates the minor epimer): δ = 0.92, 1.21* (s, 3 H, 2’-CH_3), 1.51, 1.52* (s, 9 H, $OC(CH_3)_3$), 2.24–2.16 (m, 1 H, 1’-H_a), 2.49 (m_c, 1 H, 1-’H_b), 2.46–2.71 (m, 2 H, 3-H_a, 3-H_b), 2.76 (d, *J* = 15.6 Hz, 1 H, 9-H_a), 3.09 (dd, *J* = 15.6, 4.3 Hz, 9-H_b), 3.63, 3.69* (s, 3 H, OCH_3), 4.53–4.58 (m, 1 H, 9a-H), 5.32 (s_{br}, 1 H, 4a-H), 5.83, 6.00* (ddd, *J* = 15.6, 1.3, 1.3 Hz, 1 H, 3’-H), 6.74, 6.88* (ddd, *J* = 15.6, 7.6, 7.6 Hz, 1 H, 2’-H), 7.04–7.07 (m, 1 H), 7.19–7.28 (m, 4 H, 5-H, 6-H, 7-H, 8-H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, * indicates the minor epimer): δ = 17.88, 23.49* (2-CH_3), 27.51*, 27.55 ($C(\underline{C}H_3)_3$), 34.62, 37.35, 37.42*, 41.57 (C-3, C-9, C-1’), 50.31, 50.40* (OCH_3), 70.91*, 71.04 (C-9a), 71.34*, 71.56 (C-2), 79.06, 79.19* ($O\underline{C}(CH_3)_3$), 122.4, 124.6, 124.6*, 125.9, 125.9*, 126.9, 126.9* (C-5, C-6, C-7, C-8), 123.1, 123.3* (C-3’), 138.7*, 138.7, 140.5, 140.5* (C-4b, C-8a), 142.8, 143.4* (C-2’), 154.1, 154.3 (C=O), 165.1, 165.2* (C-1’) ppm; **IR** (Film): $\tilde{\nu}$ = 2977 cm^{-1}, 2931, 1724, 1694, 1417, 1393, 1366, 1320, 1276, 1219, 1198, 1169, 1131, 1100, 1084, 1065, 1019, 991.1, 957.4, 927.2, 910.0, 880.6, 862.8, 851.0, 823.7, 746.2; **UV** (CH_3CN): λ_{max} (lg ε) = 264.5 (3.014), 271.0 (3.017), 257.5 (2.92,) nm; **MS** (ESI): *m/z* (%) = 426.2 (25) $[M + K]^+$, 410.2 (100) $[M + Na]^+$, 405.2 (90) $[M + NH_4]^+$, 388.2 (20) $[M + H]^+$; HRMS (ESI): calcd for $[C_{22}H_{29}NO_5 + Na]^+$: 410.1943; confirmed.

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