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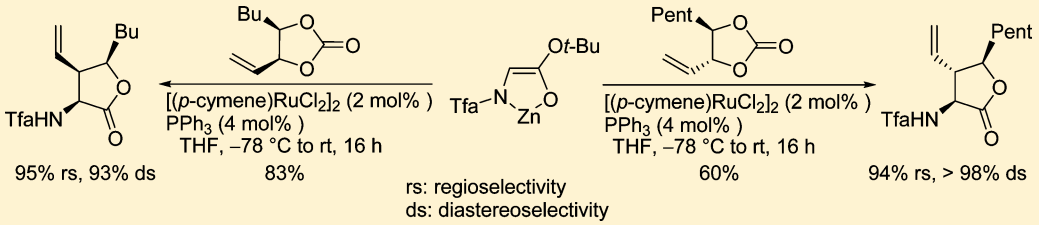
Ruthenium-Catalyzed Allylic Alkylations of Chelated Enolates Using Vinyl Dioxolanon-2-ones

Anton Bayer and Uli Kazmaier*

Institut für Organische Chemie, Universität des Saarlandes, Campus, Geb. C4.2, D-66123 Saarbruecken, Germany

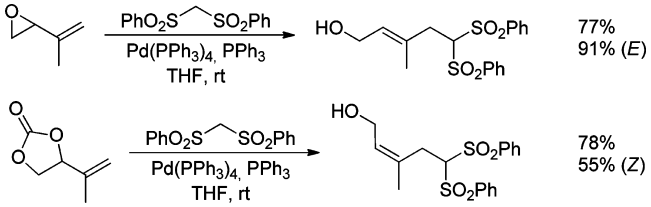
Supporting Information



ABSTRACT: 4-Vinyl-substituted 1,3-dioxolan-2-ones are found to be good substrates for Ru-catalyzed allylic alkylations of chelated amino acid ester enolates. *cis*-1,3-Dioxolan-2-ones are more reactive than the corresponding *trans*-isomers. The attack occurs preferentially with regioretention at the position of the leaving group with perfect chirality transfer. Therefore, this protocol is a good complement to the Pd-catalyzed processes, which give only linear products with this type of substrate.

Transition metal-catalyzed allylic alkylations play a dominant role in organometallic chemistry, and besides Pd, which is by far the most applied metal,[1] a wide range of other transition metal complexes can be used as catalysts.[2] Besides Rh[3] and Ir,[4] especially Ru became more and more interesting during the past few years.[5] In general, allyl acetates, carbonates or phosphates are used as substrates,[1,2] but for the introduction of functionalized allylic side chains also vinyl epoxides[6] or 4-vinyl 1,3-dioxolan-2-ones[7] are suitable candidates, at least for Pd-catalyzed reactions. Both classes of substrates have been investigated in detail by Trost et al., using soft nucleophiles such as disulfones.[8] One might expect the same product (ratio) from equivalent substrates, but significant differences have been observed (Scheme 1). Although in both cases the nucleophile attacked at the sterically least hindered position, distal to the remaining OH-functionality, the *E*/*Z*-ratio depended on the substrate used. In the presence of suitable chiral ligands symmetric 4,5-divinyl-dioxolan-2-one (*D*/*L* or *meso*) react with several nucleophiles providing the expected substitution products with excellent ee's.[9]

Scheme 1. Allylic Alkylations Using Vinyl Epoxides and Vinyl 1,3-Dioxolan-2-ones



Kang et al. investigated not only reactions of 4,5-disubstituted dioxolan-2-ones in the presence of $Pd(PPh_3)_4$ but also the Ru-complex $CpRuCl(PPh_3)_2$ with a wide range of nucleophiles.[10] The results described previously by Trost could be confirmed also for this class of substrates. In the presence of the Pd-catalyst attack occurred exclusively at the distal position giving rise to the (*E*)-configured products. In contrast, the Ru-catalyst gave rise to a mixture of the two regioisomers as an almost 1:1 mixture (Scheme 2).

Ru-catalysts in general show a high flexibility with respect to the nucleophile used. Besides stabilized carbanions, a wide range of heteronucleophiles such as thiols,[11] amines[12] or alcohols,[13] can be applied. In general, Pd- and Ru-catalysts give access to different regioisomeric substitution products, as illustrated in Scheme 2, but in case of Ru the regioselectivity strongly depends on the catalyst used. $[Cp^*Ru(NCCH_3)_3]PF_6$, a catalyst intensively used by Trost[14] and Bruneau[15] et al. generates a π-allyl-Ru-complex,[16] such as the Pd-catalysts do, resulting in a mixture of regioisomers. In contrast, $[(p\text{-cymene})RuCl_2]_2$ gives rise to products with excellent regioretention and perfect chirality transfer.[17]

Our group is also investigating transition metal-catalyzed allylic alkylations using chelated amino acid esters as nucleophiles.[18] This approach gives direct access to γ,δ-unsaturated amino acids and peptides.[19] Although the same structural motif can also be obtained *via* Claisen rearrangement,[20] the transition metal-catalyzed approach gives rise to the opposite diastereomer.[21] By far the most investigations have been carried out with Pd-catalysts,[22] but several other transition metals such as Rh[23] and Ir got into our focus during the past years. Recently, we reported on Ru-catalyzed allylic alkylations (Scheme 3) proceeding with excellent regioselectivity (rs) and

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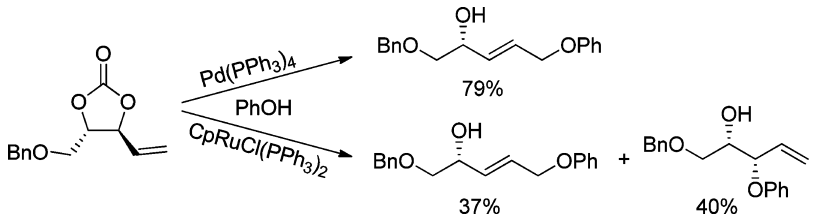
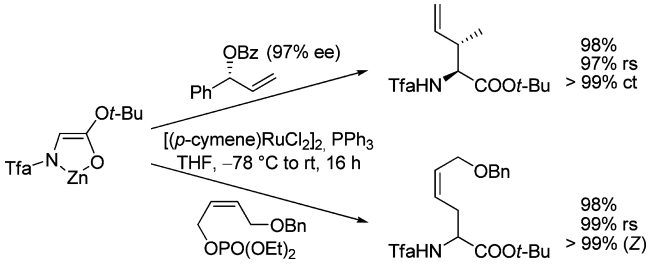
Scheme 2. Transition Metal-Catalyzed Allylations Using Vinyl 1,3-Dioxolan-2-ones



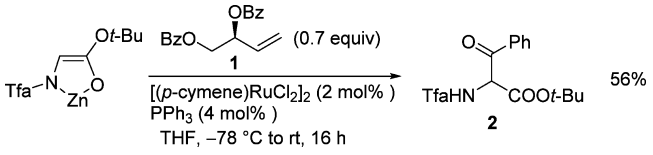
Scheme 3. Ru-Catalyzed Allylic Alkylations of Chelated Enolates



chirality transfer (ct).[24] The reactions perform smoothly isomerization-free probably *via* an $\sigma-\pi$-allyl intermediates. This would explain the perfect selectivities obtained. This protocol also allows us to convert (*Z*)-allylic substrates to (*Z*)-substitution products selectively

The last example clearly indicates that also functionalized allylic substrates can be used, and one might expect the corresponding branched products starting from an analogous functionalized allylic substrate such as **1**. But surprisingly, not the desired allylated product was formed, but the acylated product **2**,[25] resulting from a nucleophilic attack of the enolate on one of the benzoates (Scheme 4). The situation was similar with the corresponding diacetate, although the yield in this case was lower (45%).

Scheme 4. Reaction of Chelated Enolates with Dibenzoate 1



It should be mentioned that such side reactions have never been observed under Pd-catalyzed reactions, which provide selectively the linear, (*E*)-configured substitution product as expected.[18] Obviously, the direct nucleophilic attack of the enolate on the allylbenzoate is faster than the attack on the allyl-Ru-complex, if this complex is formed at all. This result was completely unexpected, since terminal allyl benzoates in general react fast and under mild conditions (see also Scheme 3). We assumed that the problems might be caused by the second benzoate group, which might be able to coordinate to the allyl-Ru-intermediate formed, generating a stable, inactive bidentate Ru-complex.

To tackle this issue, we decided to switch to the corresponding cyclic carbonate **3**, which should not be able to form such a bidentate complex. The influence of several transition metal catalysts on the outcome of the reaction has been investigated (Table 1). In principle, three different products (**4**–**6**) can be expected: the linear product **4** from an attack of the nucleophile at the sterically least hindered position of the allyl intermediate, the branched product **5**, and if the alcoholate intermediate formed attacks the ester functionality, also the five-membered lactone **6** (Table 1).

First experiments were carried out with the catalyst used by Trost[14] and Bruneau.[15] Indeed, with **3** a reaction could be observed. Under standard conditions a mixture of the linear product **4**[18b] and the lactone **6** was formed, while **6** was the major product (entry 1), although the yield of the combined products was moderate. The *anti*-product was formed preferentially, and the linear product was (*E*)-configured. The reaction started at a temperature of −60 °C, and therefore we run the reaction also at −50 °C to suppress the lactonization and to obtain the branched product **5** (entry 2). The selectivities observed under these mild conditions were similar to the first experiment, but the yield was even worse. Therefore, we switched to $[(p\text{-cymene})RuCl_2]_2$, the catalyst we used successfully in our previous work (entries 3 and 4).[24] The regioselectivities were comparable, but the yield, especially under standard conditions (entry 3) was excellent. Also here, the cyclization could be suppressed almost completely if the reaction was carried out at low temperature (entry 4). For comparison, we also investigated the Pd-catalyzed allylation (entries 5 and 6). As expected, here the linear product was formed almost exclusively as a ∼ 4:1 (*E*)/(*Z*)-mixture, independent of the reaction conditions used. In contrast, with Wilkinson's catalyst no allylation product could be obtained, although the starting material was consumed (entry 7). A complex mixture of side products was formed, which was not further analyzed.

These first experiments clearly indicate that especially the cymene-Ru-complex is a good catalyst for these types of allylic substrates, providing products that are not available by other transition metal catalysts. Therefore, we next investigated 4,5-disubstituted divinyldioxolan-2-ones (**7**). The introduction of a second substituent on the heterocyclic ring should influence the coordination properties of the catalyst, and therefore, one might expect a different reaction behavior of the *cis* and *trans* isomers.

The required substrates were obtained according to a protocol described by Trombini et al. using a Zn-mediated Barbier reaction (Scheme 5).[26] The required disubstituted dioxolan-2-ones were obtained in acceptable yield as *cis/trans* mixtures. While the *cis* products were formed preferentially for R = alkyl, the *trans* product was preferred in case of the aryl-substituted carbonates. While the arylated substrates could easily be separated by flash chromatography, this was not always the case for the alkylated ones. In some cases a fraction of a *cis/trans* mixture was obtained. To make this portion also utilizable, we subjected it to a Pd-catalyzed isomerization toward the thermodynamically more stable *trans* isomer, as

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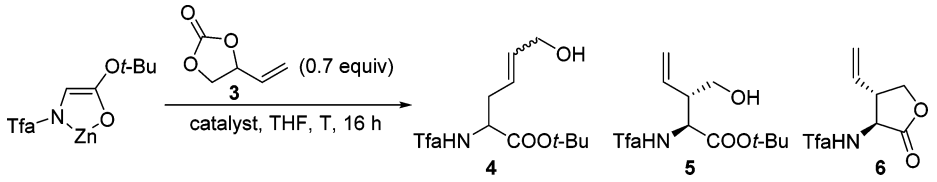
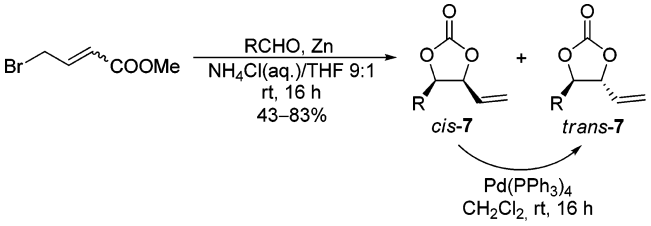
Table 1. Transition Metal-Catalyzed Allylic Alkylations Using Carbonate 3



			ratio[a]	ratio (5,6)[a]	yield (%)[b]	
entry	catalyst (mol %)	T (°C)	4:5:6	*anti*:*syn*	4	5/6
1	$[Cp^*Ru(MeCN)_3]PF_6$ (2)	−78 to rt	37:0:63	82:18	19	33 (**6**)
2	$[Cp^*Ru(MeCN)_3]PF_6$ (2)	−50	31.65:4	81:19	11	25 (**5**)
3	$[(p\text{-cymene})RuCl_2]_2$ (2) PPh_3 (4)	−78 to rt	35:0:65	65:35	12	65 (**6**)
4	$[(p\text{-cymene})RuCl_2]_2$ (2) PPh_3 (4)	−50	41:54:5	68:32	25	52 (**5**)
5	$[allylPdCl]_2$ (2) PPh_3 (9)	−78 to rt	96:4:0	−−	62 (*E*) 13 (*Z*)	−−
6	$[allylPdCl]_2$ (2) PPh_3 (9)	−50	96:4:0	n.d.	59 (*E*) 18 (*Z*)	−−
7	$RhCl(PPh_3)_3$ (2.5) $P(OEt)_3$ (10)	−78 to rt	−−	−−	−−	−−

[a]Determined by GC (*L*-Chirasil-Val). [b]Isolated yields

Scheme 5. Synthesis of 4,5-Disubstituted 1,3-Dioxolan-2-ones 7



described by Garcia et al.[27] According to these procedures, both required isomers could be obtained in sufficient amounts.

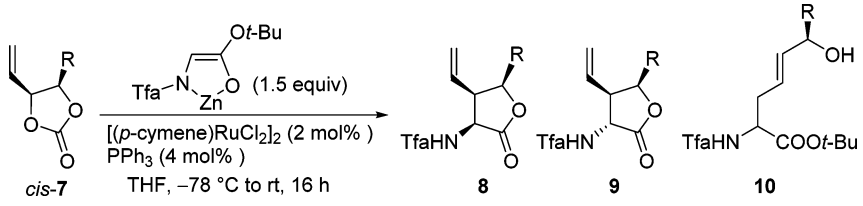
The alkyl-substituted *cis*-dioxolan-2-ones were found to be suitable substrates for the investigated Ru-catalyzed alkylations (Table 2, entries 1−4). With the $[(p\text{-cymene})RuCl_2]_2$ complex the lactones were formed preferentially under standard conditions (warm-up to room temperature overnight) in good yields and high diastereoselectivity for the all-*cis*-product. If enantioenriched carbonates such as (4*S*,5*R*)-**7e** were used, a perfect chirality transfer into the product was observed (entry 5). This is a clear indication that also with these substrates no isomerization occurs on the Ru-allyl intermediates.

The aryl-substituted derivatives **7f** and **7g** were found to be significantly less suitable (entries 6 and 7). They showed also a preference for the all-*cis*-lactone, but the regioselectivities and also the yields were worse compared to the alkyl derivatives **7a−e**. In addition, a range of not identified side reactions occurred with **7g**, which makes it impossible to determine the product ratio by GC. Therefore, in Table 2 only the isolated yield is shown.

Quite different was the situation with the corresponding *trans*-configured carbonates. These derivatives are significantly less reactive. With the linear alkyl-substituted carbonates *trans*-**7a** and **7b** also a good regioselectivity toward the lactone and an excellent diastereoselectivity for the all-*trans*-product was obtained (Scheme 6). No allylation product could be isolated from reactions of the sterically more demanding derivatives *trans*-**7c** and **7d** and the aryl-substituted carbonates **7f** and **7g**. The configuration of the allylation products could be confirmed by H,H-NOESY spectra of the different isomers.

The differences in the reaction behavior of the *cis* and *trans* dioxolanones can be explained by different steric interactions in the ionization step (Figure 1). The attack of the sterically

Table 2. Allylic Alkylations Using *syn*-4,5-Disubstituted Carbonates 7



			ratio[a]		yield (%)[b]		
entry	7	R	8+9:10	8:9	8	9	10
1	(±)-**7a**	Et	89:11	>98:<2	70		
2	(±)-**7b**	*n*-Pent	90:10	86:14	60	8	10
3	(±)-**7c**	*i*-Pr	82:18	96:4	69		
4	(±)-**7d**	*c*-Hex	86:14	>98:<2	62		
5	(4*S*,5*R*)-**7e** (92% ee)	*n*-Bu	95:5	93:7	76	7	
6	(±)-**7f**	Ph	93:7	96:4	47		
7	(±)-**7g**	*p*-BrPh	n.d.	n.d.	34		

[a]Determined by GC (*L*-Chirasil-Val). [b]Isolated yields

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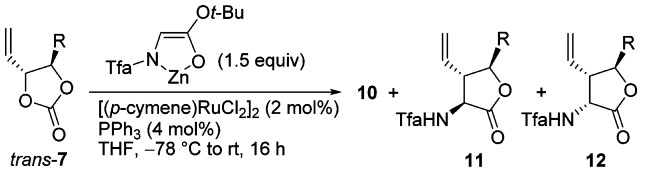
Scheme 6. Allylic Alkylations Using *anti*-4,5-Disubstituted Carbonates 7



	R	Yield (**11**)	ratio **10**:(**11**+**12**)	ratio **11**:**12**
(2 mol%)	Et	50%	20:80	> 98:< 2
	n-Pent	60%	6:94	> 98:< 2

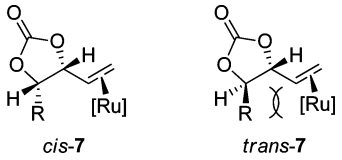


Figure 1. Formation of alkene-Ru-complexes as initial ionization step

demanding Ru-complex on the vinylcarbonate occurs from the face opposite to the leaving group (stereoretention *via* double inversion). In case of *cis*-**7** this face is open, while severe interactions occur for *trans*-**7**. Obviously, a linear alkyl chain is accepted, but a sterically more demanding branched or aromatic substituent blocks this face, and the coordination/ionization is suppressed.

In conclusion, we could show that *cis*-4-vinyl-substituted 1,3-dioxolan-2-ones are good substrates for Ru-catalyzed allylic alkylations of chelated amino acid ester enolates. The attack occurs preferentially with regioretention at the position of the leaving group with perfect chirality transfer. Therefore this protocol is a good complement to the Pd-catalyzed processes, which give only linear products. In contrast, the corresponding *trans* isomers are significantly less reactive.

EXPERIMENTAL SECTION

General Remarks. All air- or moisture-sensitive reactions were carried out in dried glassware (>100 °C) under an atmosphere of nitrogen. THF was distilled from Na/benzophenone. The products were purified by flash chromatography on silica gel columns (0.063–0.2 mm). Mixtures of ethyl acetate and hexanes were generally used as eluents. Analytical TLC was performed on precoated silica gel plates. Visualization was accomplished with UV-light and $KMnO_4$ solution. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz (^1H) and 100 MHz (^{13}C) spectrometer in $CDCl_3$. Chemical shifts are reported in ppm relative to TMS, and $CHCl_3$ was used as the internal standard. The correct assignment of signals was verified by *H,H*-COSY and *C,H*-COSY spectral data. Selected signals for the minor regio- and diastereomers are extracted from the spectra of the isomeric mixture. Regioisomeric and diastereomeric ratios were determined by GC equipped with a *L*-ChiraSilVal capillary column (25 m × 0.25 mm). Nitrogen was used as carrier gas. Mass spectra were recorded with a high resolution quadrupole spectrometer (CI) and with an ion trap spectrometer (ESI). 3-Buten-1,2-diol and 4-vinyl-1,3-dioxolanone (**2**) were purchased from commercial suppliers. ***cis*-7c**, ***cis*-7d** and ***cis*/*trans*-7f** were prepared as described by Lombardo.[26] (4*S*)-3,4-Dihydroxy-1-octene was obtained by deprotection of (4*S*)-3-hydroxy-4-*tert*-butyldimethylsilyloxy-1-octene[28] with TBAF.

General Procedure 1 (GP1): Ru-Catalyzed Allylic Alkylations of Chelated Enolates. A solution of hexamethyldisilazane (335 mg, 2.07 mmol) in THF (2.0 mL) was prepared in a Schlenk flask under nitrogen. After the solution was cooled to −20 °C, a solution of *n*-butyl-lithium in hexanes (1.6M, 1.17 mL, 1.88 mmol) was added slowly. The cooling bath was removed, and stirring was continued for further 10 min. The solution was cooled to −78 °C, and the TFA-protected *tert*-butyl glycinate (171 mg, 0.75 mmol) dissolved in THF (1 mL) was added to the freshly prepared LHMDS solution. After 10 min a solution of dried $ZnCl_2$ (123 mg, 0.90 mmol) in THF (1.0 mL) was added, and stirring was continued for 30 min at −78 °C. A second solution was prepared from $[(p\text{-cymene})RuCl_2]_2$ (6.4 mg, 0.01 mmol) and triphenylphosphine (5.2 mg, 0.02 mmol) in THF (1 mL). The solution was stirred for 5 min at room temperature while turning red. The allylic substrate (0.50 mmol) was added, and the resulting solution was slowly transferred to the chelated enolate at −78 °C. The mixture was allowed to warm to room temperature overnight. The solution was diluted with diethyl ether before 1 M $KHSO_4$ was added. After separation of the layers, the aqueous layer was extracted twice with diethyl ether, and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated in vacuo, and the crude product was purified by flash chromatography (SiO_2).

***tert*-Butyl 3-hydroxymethyl-2-trifluoroacetylamino-4-pentenoate (5).** Following a slightly modified GP1 (reaction temperature: −50 °C, 16 h) the reaction of **3** (114 mg, 1.00 mmol) with *tert*-butyl *N*-trifluoroactyl-glycinate (342 mg 1.50 mmol) gave rise to a separable mixture of the branched alcohol **5** (155 mg, 0.52 mmol, 52%) (ratio *anti*:*syn* 68:32) and the linear (*E*)-configured alcohol (*E*)-**4**[18b] (83 mg, 0.25 mmol, 25%) as colorless oils. *anti*-**5** (68%): ^1H NMR (400 MHz, $CDCl_3$) δ = 1.47 (s, 9 H), 2.96 (tdd, *J* = 9.5, 5.4, 3.1 Hz, 1 H), 3.11 (s_{br}, 1 H), 3.41 (dd, *J* = 12.1, 9.4 Hz, 1 H), 3.59 (dd, *J* = 12.1, 5.5 Hz, 1 H), 4.80 (dd, *J* = 7.9, 3.0 Hz, 1 H), 5.19 (d, *J* = 17.1 Hz, 1 H), 5.23 (d, *J* = 10.4 Hz, 1 H), 5.48 (ddd, *J* = 17.1, 10.5, 8.8 Hz, 1 H), 7.23 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.0, 49.1, 52.9, 61.9, 83.9, 115.6 (*J* = 287 Hz), 120.5, 131.2, 158.3 (*J* = 38.0 Hz), 169.0. *syn*-**5** (32%): ^1H NMR (400 MHz, $CDCl_3$) δ = 1.48 (s, 9 H), 2.27 (s_{br}, 1 H), 2.76 (dq, *J* = 9.0, 5.1 Hz, 1 H), 3.79 (d, *J* = 5.1 Hz, 2 H), 4.65 (dd, *J* = 8.1, 5.2 Hz, 1 H), 5.23 (d, *J* = 17.1 Hz, 1 H), 5.26 (d, *J* = 10.3 Hz, 1 H), 5.74 (ddd, *J* = 17.1, 10.5, 8.4 Hz, 1 H), 7.49 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.9, 47.3, 54.5, 63.1, 83.7, 115.7 (*J* = 287 Hz), 119.6, 133.6, 157.1 (*J* = 37.4 Hz), 168.7; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*R*)-**5** (*anti*) = 50.76′, t_R(2*S*,3*S*)-**5** (*anti*) = 54.68′, t_R(2*R*,3*S*)-**5** (*syn*) = 65.98′, t_R(2*S*,3*R*)-**5** (*syn*) = 68.89′, t_R(*E*,2*R*)-**4** = 72.85′, t_R(*E*,2*S*)-**4** = 75.88′; HRMS (CI) for $C_{12}H_{19}F_3NO_4$ $[M + H]^+$ calcd 298.1261, found 298.1273.

***trans*-2-Trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (*trans*-6).** Following GP1 the reaction of 4-vinyl-1,3-dioxolan-2-one **3** (570 mg, 5.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (1.70 g, 7.50 mmol) provided a mixture of the linear product (*E*)-**4** and the lactone **6** as a diastereomeric mixture (*cis*/*trans* 35:65). Flash chromatography gave rise to *cis*-**6** (204 mg, 0.91 mmol, 18%), *trans*-**6** (525 mg, 2.35 mmol, 47%) and (*E*)-**4** (178 mg 0.60 mmol, 12%) as colorless oils. The lactones **6** crystallized slowly on standing. *trans*-**6**: mp 82–85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.27 (tt, *J* = 11.0, 8.1 Hz, 1 H), 4.08 (dd, *J* = 10.7, 9.4 Hz, 1 H), 4.51 (dd, *J* = 9.2, 8.2 Hz, 1 H), 4.66 (dd, *J* = 11.7, 8.4 Hz, 1 H), 5.28 (d, *J* = 10.3 Hz, 1 H), 5.30 (d, *J* = 17.1 Hz, 1 H), 5.80 (ddd, *J* = 17.1, 10.2, 8.0 Hz, 1 H), 7.22 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 47.0, 53.9, 69.2, 115.5 (*J* = 287 Hz), 120.7, 131.8, 157.8 (*J* = 38.4 Hz), 172.8. *cis*-**6**: mp 84–89 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.62 (ddd, *J* = 8.9, 8.4, 5.4 Hz, 1 H), 4.38 (d, *J* = 9.6 Hz, 1 H), 4.55 (dd, *J* = 9.6, 5.1 Hz, 1 H), 4.77 (t, *J* = 8.9 Hz, 1 H), 5.28 (d, *J* = 17.0 Hz, 1 H), 5.34 (d, *J* = 10.3 Hz, 1 H), 5.65 (ddd, *J* = 17.0, 10.3, 8.9 Hz, 1 H), 6.90 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, selected signals) δ = 43.2, 52.5, 70.9, 121.5, 130.3, 172.8; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min, 20 min) t_R(2*R*,3*S*)-**6** (*cis*) = 51.66′, t_R(2*S*,3*R*)-**6** (*cis*) = 51.88′, t_R(*E*,2*R*)-**4** = 72.85′, t_R(*E*,2*S*)-**4** = 75.88′, t_R(2*R*,3*R*)-**6** (*trans*) = 83.94′, t_R(2*S*,3*S*)-**6** (*trans*) = 84.55′; HRMS (CI) for $C_8H_9F_3NO_3$ $[M + H]^+$ calcd 224.0529, found 224.0522.

General Procedure 2 (GP2): Synthesis of 5-Substituted 4-Vinyl-1,3-dioxolan-2-ones.[26] (a) Activiation of zinc powder: Zinc powder was treated with 10% HCl for 2 min. Afterward it was washed with water, then acetone and dried in a high vacuum overnight. (b) Triethylamine on silica gel: 25 g of silica gel and 5 mL of triethylamine

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were stirred in diethylether for 1 h, before the solvent was removed in vacuo.

3-Bromopropenyl methyl carbonate[26] (1.2 mmol) and activated zinc powder (1.5 mmol) were added to a solution of the corresponding aldehyde (1 mmol) in sat. NH_4Cl solution/THF (9:1; 5 mL). The heterogenic mixture was stirred at room temperature for 2−4 h. The aqueous phase was extracted twice with diethyl ether, and the unreacted aldehyde was removed by stirring for 2 h with 1 M $NaHSO_3/Na_2S_2O_5$ solution. The organic phase was dried over Na_2SO_4, and the solvent was removed in vacuo. The crude product was dissolved in diethyl ether (10 mL) and stirred with Et_3N/SiO_2 (1.5 g) at room temperature for 16 h. The solvent was removed in vacuo, and the product was purified by flash chromatography (hexanes/ethyl acetate 9:1).

General Procedure 3 (GP3): *cis-trans*-Isomerization of 5-Substituted 4-Vinyl-1,3-dioxolan-2-ones.[27] A *cis*-configured or a *cis*/*trans* mixture of 5-substituted 4-vinyl-1,3-dioxolan-2-one (5 mmol) was dissolved in a 25 mL flask in CH_2Cl_2 (15 mL). $Pd(PPh_3)_4$ (280 mg, 5 mol%, 0.25 mmol) was added, and the flask was filled up with CH_2Cl_2 and sealed to minimize the loss of CO_2. The solution was stirred at room temperature for 16−32 h. Then the reaction mixture was quickly filtered through a short pad of silica to remove the catalyst. After concentration of the filtrate in vacuo, the crude product was purified by flash chromatography (hexanes/ether or hexanes/ ethyl acetate).

***cis*-4-Ethyl-5-vinyl-1,3-dioxolan-2-one (*cis*-7a).** Following GP2 *cis*-**7a** (536 mg, 3.77 mmol, 37%) and *trans*-**7a** (211 mg, 1.48 mmol, 15%) were obtained as clear colorless oils from 3-bromo-propenyl methyl carbonate (2.34 g, 12.0 mmol, 64% *cis*) and propanal (581 mg, 10.0 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.03 (t, J = 7.4 Hz, 3 H), 1.55 −1.75 (m, 2 H), 4.63 (ddd, J = 9.3, 7.6, 4.6 Hz, 1 H), 5.09 (tt, J = 7.3, 1.0 Hz, 1 H), 5.45 (dt, J = 10.5, 1.0 Hz, 1 H), 5.50 (dt, J = 17.2, 1.0 Hz, 1 H), 5.84 (ddd, J = 17.2, 10.4, 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 9.8, 23.3, 80.0, 81.3, 121.5, 129.3, 154.4; GC (CP-Chirasil-Dex-CB, 110 °C, 10 min, 110 to 180 °C, 5 °C/min) t_R(4*S*,5*R*)-**7a** = 15.51′, t_R(4*R*,5*S*)-**7a** = 15.72′; HRMS (CI) for $C_7H_{11}O_3$ $[M + H]^+$ calcd 143.0703, found 143.0724.

***trans*-4-Ethyl-5-vinyl-1,3-dioxolan-2-one (*trans*-7a).** *trans*-**7a** was obtained after chromatography as minor stereoisomer using GP2 or according to GP3 via *cis-trans* isomerization of the crude product (711 mg, 3.85 mmol, 67% *cis*) as clear colorless oil (410 mg, 2.22 mmol, 58%, >99% *trans*): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.05 (t, J = 7.4 Hz, 3 H), 1.74−1.83 (m, 2 H), 4.26 (ddd, J = 7.1, 7.0, 5.9 Hz, 1 H), 4.65 (tt, J = 7.1, 0.9 Hz, 1 H), 5.42 (ddd, J = 10.5, 1.0, 1.0 Hz, 1 H), 5.48 (ddd, J = 17.4, 0.9, 0.9 Hz, 1 H), 5.87 (ddd, J = 17.3, 10.4, 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.9, 26.0, 82.2, 82.9, 121.1, 132.2, 154.3; GC (CP-Chirasil-Dex-CB, 110 °C, 10 min, 110 to 180 °C, 5 °C/min) t_R(4*R*,5*R*)-**7a** = 11.72′, t_R(4*S*,5*S*)-**7a** = 12.31′; HRMS (CI) for $C_7H_{11}O_3$ $[M + H]^+$ calcd 143.0703, found 143.0708.

***cis*-4-Pentyl-5-vinyl-1,3-dioxolan-2-one (*cis*-7b).** Following GP2 *cis*-**7b** (1.13, 6.12 mmol, 61%) and *trans*-**7b** (413 mg, 2.24 mmol, 22%) were obtained as clear colorless oils from 3-bromo-propenyl methyl carbonate (2.34 g, 12.0 mmol, 64% *cis*) and hexanal (1.00 g, 10.0 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, J = 7.1 Hz, 3 H), 1.25−1.44 (m, 5 H), 1.45−1.58 (m, 2 H), 1.58−1.73 (m, 1 H), 4.69 (ddd, J = 9.7, 7.6, 3.8 Hz, 1 H), 5.08 (tt, J = 7.5, 1.1 Hz, 1 H), 5.45 (ddd, J = 10.4, 0.9, 0.9 Hz, 1 H), 5.48 (ddd, J = 17.1, 0.9, 0.9 Hz, 1 H), 5.84 (ddd, J = 17.0, 10.5, 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.3, 25.1, 29.9, 31.3, 80.0, 80.1, 121.5, 129.4, 154.4; GC (CP-Chirasil-Dex-CB, 110 °C, 10 min, 110 to 180 °C, 5 °C/min) t_R(4*S*,5*R*)-**7b** = 22.15′, t_R(4*R*,5*S*)-**7b** = 22.36′; HRMS (CI) for $C_{10}H_{17}O_3$ $[M + H]^+$ calcd 185.1172, found 185.1180.

***trans*-4-Pentyl-5-vinyl-1,3-dioxolan-2-one (*trans*-7b).** Following GP3 *trans*-**7b** (602 mg, 3.27 mmol, 79%, > 99% *trans*) was obtained as clear colorless oil from *cis*-**7b** (770 mg, 4.15 mmol, 85% *cis*): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, J = 7.1 Hz, 3 H), 1.28−1.35 (m, 4 H), 1.40 (m, 1 H), 1.48 (m, 1 H), 1.63−1.80 (m, 2 H), 4.30 (td, J = 7.6, 5.0 Hz, 1 H), 4.63 (tt, J = 7.3, 0.9 Hz, 1 H), 5.42 (ddd, J = 10.4, 0.8, 0.8 Hz, 1 H), 5.48 (ddd, J = 17.3, 0.9, 0.9 Hz, 1 H), 5.86 (ddd, J = 17.3, 10.4, 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.3, 24.3, 31.2, 32.9, 81.9, 82.7, 121.2, 132.1, 154.3; GC (CP-Chirasil-Dex-CB, 110 °C, 10 min, 110 to 180 °C, 5 °C/min) t_R(4*R*,5*R*)-**7b** = 20.25′, t_R(4*S*,5*S*)-**7b** = 20.49′; HRMS (CI) for $C_{10}H_{17}O_3$ $[M + H]^+$ calcd 185.1172, found 185.1171.

(4*S*,5*R*)-4-Butyl-5-vinyl-1,3-dioxolan-2-one [(4*S*,5*R*)-7e]. To a 0 °C cold solution of (4*S*,5*R*)-3,4-dihydroxy-1-octene[29] (720 mg, 4.15 mmol) in THF (10 mL), triethylamine (809 mg, 8.0 mmol) and ethyl chloroformate (651 mg, 6.0 mmol) were added. The reaction mixture was allowed to warm up to room temperature and was stirred for 16 h. The solution was washed with 1 M HCl, sat. $NaHCO_3$ solution and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was taken up in diethyl ether and was stirred for 4 h with NEt_3/SiO_2 (see GP2b). After filtration the solvent was removed in vacuo, and the residue was purified by column chromatography (hexanes/ethyl acetate = 75:25) giving rise to cyclic carbonate (4*S*)-**7e** (666 mg, 3.92 mmol, 92%, *cis*:*trans* = 63:37) as colorless oil. The diastereomeric mixture was further purified by column chromatography (hexanes/ethyl acetate = 85:15) providing pure (4*S*,5*R*)-**7e** (300 mg, 1.76 mmol, >99% *cis*, 92% *ee*). The minor *trans*-configured diastereomer ((4*S*,5*S*)-**7e**) could not be obtained in diastereomeric pure form: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (t, J = 7.2 Hz, 3 H), 1.28−1.40 (m, 3 H), 1.40−1.58 (m, 2 H), 1.65 (m, 1 H), 4.69 (ddd, J = 9.8, 7.6, 3.8 Hz, 1 H), 5.07 (tt, J = 7.5, 1.0 Hz, 1 H), 5.45 (ddd, J = 10.6, 0.8, 0.8 Hz, 1 H), 5.49 (dt, J = 17.0, 1.0, 1.0 Hz, 1 H), 5.84 (ddd, J = 17.2, 10.4, 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.2, 27.5, 29.6, 80.0, 80.1, 121.5, 129.4, 154.4; GC (CP-Chirasil-Dex-CB, 110 °C, 10 min, 110 to 180 °C, 5 °C/min) t_R(4*R*,5*R*)-**7e** = 53.31′, t_R(4*S*,5*S*)-**7e** = 53.66′, t_R(4*S*,5*R*)-**7e** = 65.22′, t_R(4*R*,5*S*)-**7e** = 65.99′; HRMS (CI) for $C_9H_{15}O_3$ $[M + H]^+$ calcd 171.1015, found 171.1000.

***trans*-4-(4-Bromophenyl)-5-vinyl-1,3-dioxolan-2-one (*trans*-7g).** According to GP2 *trans*-**7g** (1.13 g, 4.19 mmol, 42%) and *cis*-**7g** (622 mg 2.31 mmol, 23%) were obtained as clear colorless oils from 3-bromo-propenylmethylcarbonat (2.34 g, 12.0 mmol, 64% *cis*) and 4-bromobenzaldehyde (1.84 g, 10.0 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.80 (ddt, J = 8.2, 7.1, 0.9 Hz, 1 H), 5.23 (d, J = 8.2 Hz, 1 H), 5.45 (d, J = 17.1 Hz, 1 H), 5.49 (d, J = 10.5 Hz, 1 H), 5.97 (ddd, J = 17.4, 10.5, 7.2 Hz, 1 H), 7.23 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 82.3, 84.6, 122.6, 123.8, 127.4, 130.9, 132.4, 133.6, 153.6; HRMS (CI) for $C_{11}H_{10}{}^{79}BrO_3$ $[M + H]^+$ calcd 268.9807, found 268.9806.

***cis*-4-(4-Bromophenyl)-5-vinyl-1,3-dioxolan-2-one (*cis*-7g).** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.15−5.30 (m, 2 H), 5.34 (dd, J = 7.9, 6.1 Hz, 1 H), 5.42 (ddd, J = 17.1, 9.9, 6.2 Hz, 1 H), 5.75 (d, J = 7.9 Hz, 1 H), 7.10 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 79.9, 80.8, 121.6, 123.4, 127.8, 129.8, 132.0, 132.1, 154.1; HRMS (CI) for $C_{11}H_{10}{}^{79}BrO_3$ $[M + H]^+$ calcd 268.9807, found 268.9819.

all-*cis*-4-Ethyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8a). According to GP1 the all-*cis*-lactone **8a** (84 mg, 0.35 mmol, 70%) was obtained as colorless solid from *cis*-**7a** (71 mg, 0.50 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (170 mg, 0.75 mmol): mp 117−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.01 (t, J = 7.4 Hz, 3 H), 1.58 (m, 1 H), 1.82 (m, 1 H), 3.56 (ddd, J = 10.4, 7.0, 4.3 Hz, 1 H), 4.48 (ddd, J = 7.7, 6.7, 4.3 Hz, 1 H), 4.78 (t, J = 6.5 Hz, 1 H), 5.29 (dd, J = 16.4, 1.9 Hz, 1 H), 5.38 (dd, J = 10.2, 1.7 Hz, 1 H), 5.48 (ddd, J = 16.2, 10.2, 10.2 Hz, 1 H), 6.90 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 23.8, 48.4, 54.0, 82.9, 115.5 (J = 287 Hz), 123.5, 127.1, 157.2 (J = 38.6 Hz), 172.6; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,5*S*)-**8a** = 61.41′, t_R(2*S*,3*R*,5*R*)-**8a** = 62.40′, t_R(*E*,2*R*,6*R*)-**10a** = t_R(*E*,2*R*,6*S*)-**10a** = 79.33′, t_R(*E*,2*S*,6*S*)-**10a** = t_R(*E*,2*S*,6*R*)-**10a** = 82.09′; HRMS (CI) for $C_{10}H_{13}F_3NO_3$ $[M + H]^+$ calcd 252.0842, found 252.0849.

all-*cis*-4-Pentyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8b). Following GP1 all-*cis*-lactone **8b** (176 mg, 0.60 mmol, 60%), *trans*,*cis*-lactone **9b** (31 mg, 0.08 mmol, 8%) and the linear, (*E*)-configured allylation product **10b** (54 mg, 0.10 mmol, 10%) were obtained as colorless solid, respectively, as colorless oils from *cis*-**7b** (184 mg, 1.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (341 mg, 1.50 mmol): mp 72−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.82 (t, J = 7.0 Hz, 3 H), 1.18−1.28 (m, 4 H), 1.28−1.52 (m, 3 H),

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1.70 (m, 1 H), 3.48 (ddd, J = 10.4, 7.0, 4.3 Hz, 1 H), 4.49 (ddd, J = 8.2, 5.8, 4.3 Hz, 1 H), 4.70 (t, J = 6.4 Hz, 1 H), 5.21 (dd, J = 16.6, 1.7 Hz, 1 H), 5.31 (dd, J = 10.2, 1.8 Hz, 1 H), 5.41 (ddd, J = 16.4, 10.2, 10.2 Hz, 1 H), 6.72 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.4, 24.8, 30.5, 31.4, 48.7, 54.0, 81.7, 115.4 (J = 287 Hz), 123.4, 127.3, 157.2 (J = 38.3 Hz), 172.7; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8b** = 85.91′, t_R(2*S*,3*R*,4*R*)-**8b** = 86.72′, t_R(*E*)-**10b** = 103.23′, t_R(*E*)-**10b** = 104.91′, t_R(2*R*,3*R*,4*R*)-**9b** = 117.48′, t_R(2*S*,3*S*,4*S*)-**9b** = 117.85′; HRMS (CI) for $C_{13}H_{19}F_3NO_3$ $[M + H]^+$ calcd 294. 1312, found 294.1320.

***trans*,*cis*-4-Pentyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (9b).** *trans*,*cis*-Lactone **9b** was the minor diastereomer obtained in the preparation of **8b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, J = 6.0 Hz, 3 H), 1.22−1.40 (m, 4 H), 1.42−1.70 (m, 4 H), 3.31 (ddd, J = 12.0, 8.4, 8.4 Hz, 1 H), 4.61 (ddd, J = 10.6, 8.5, 3.4 Hz, 1 H), 4.81 (dd, J = 12.1, 8.7 Hz, 1 H), 5.28 (d, J = 16.4 Hz, 1 H), 5.29 (d, J = 10.7 Hz, 1 H), 5.80 (ddd, J = 17.2, 9.8, 8.4 Hz, 1 H), 7.16 (d, J = 8.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.4, 25.3, 30.8, 31.3, 49.5, 52.0, 81.3, 115.5 (J = 287 Hz), 121.0, 131.0, 157.8 (s, J = 38.1 Hz), 173.0; HRMS (C) for $C_{13}H_{19}F_3NO_3$ $[M + H]^+$ calcd 294. 1312, found 294.1340.

(*E*)-*tert*-Butyl 6-hydroxy-2-(2,2,2-trifluoroacetamido)undec-4-enoate [(*E*)-10b]. Linear allylation product (*E*)-**10b** was the minor regioisomer obtained in the preparation of **8b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (t, J = 6.7 Hz, 3 H), 1.21−1.35 (m, 4 H), 1.40−1.55 (m, 4 H), 1.48 (s, 9 H), 1.69 (s_{br}, 1 H) 2.51 (m, 1 H), 2.67 (m, 1 H), 4.04 (td, J = 6.3, 6.3 Hz, 1 H), 4.52 (dt, J = 7.3, 5.5 Hz, 1 H), 5.47 (dt, J = 15.4, 6.8 Hz, 1 H), 5.58 (dd, J = 15.3, 6.3 Hz, 1 H), 7.01 (d, J = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.5, 25.0, 27.8, 31.6, 34.4, 37.0, 52.6, 72.3, 83.6, 115.6 (J = 288 Hz), 123.2, 138.7, 156.6 (J = 37.3 Hz), 169.3; HRMS (CI) for $C_{17}H_{29}F_3NO_4$ $[M + H]^+$ calcd 368.2042, found 368.2032.

all-*cis*-4-Isopropyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8c). Following GP1 the all-*cis*-lactone **8c** (176 mg, 0.69 mmol, 69%) was obtained as colorless solid from *cis*-**7c** (156 mg, 1.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (341 mg, 1.50 mmol): mp 118−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (d, J = 6.7 Hz, 3 H), 1.11 (d, J = 6.5 Hz, 3 H), 1.88 (dqq, J = 10.7, 6.6, 6.5 Hz, 1 H), 3.58 (ddd, J = 10.6, 6.9, 4.0 Hz, 1 H), 4.08 (dd, J = 10.7, 4.0 Hz, 1 H), 4.77 (t, J = 6.4 Hz, 1 H), 5.29 (dd, J = 16.7, 1.6 Hz, 1 H), 5.39 (dd, J = 10.2, 1.7 Hz, 1 H), 5.49 (ddd, J = 16.5, 10.6, 10.3 Hz, 1 H), 6.87 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 16.6, 19.8, 28.9, 47.9, 54.3, 86.9, 115.3 (J = 287 Hz), 123.5, 127.1, 157.2 (J = 38.6 Hz), 172.7; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8c** = 64.50′, t_R(2*S*,3*R*,4*R*)-**8c** = 65.56′, t_R(*E*)-**10c** = 83.77′, t_R(*E*)-**10c** = 84.13′, t_R(*E*)-**10c** = 86.21′, t_R(*E*)-**10c** = 86.66′, t_R(2*R*,3*R*,4*R*)-**9c** = 99.87′, t_R(2*S*,3*S*,4*S*)-**9c** = 99.94′. Analysis calcd for $C_{11}H_{14}F_3NO_3$ (265.23): C 49.81, H 5.32, N 5.28, found C 49.61, H 5.09, N 5.52.

all-*cis*-4-Cyclohexyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8d). Following GP1 all-*cis*-lactone **8d** (189 mg, 0.62 mmol, 62%) was obtained as colorless solid from from *cis*-**7d** (196 mg, 1.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (341 mg, 1.50 mmol): mp 118−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.70−1.09 (m, 2 H), 1.12−1.33 (m, 4 H), 1.53−1.81 (m, 4 H), 2.05−2.13 (m, 1 H), 3.59 (ddd, J = 10.5, 6.9, 4.0 Hz, 1 H), 4.16 (dd, J = 10.5, 4.0 Hz, 1 H), 4.72 (dd, J = 6.4, 6.4 Hz, 1 H), 5.29 (dd, J = 16.7, 1.6 Hz, 1 H), 5.40 (dd, J = 10.2, 1.7 Hz, 1 H), 5.49 (ddd, J = 16.5, 10.2, 10.2 Hz, 1 H), 6.71 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.0, 25.1, 26.1, 26.6, 30.0, 37.8, 47.6, 54.1, 85.5, 115.3 (J = 287 Hz), 123.4, 127.1, 157.2 (J = 38.1 Hz), 172.6; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8d** = 101.36′, t_R(2*S*,3*R*,4*R*)-**8d** = 102.30′, t_R(*E*)-**10d** = 121,90′, t_R(*E*)-**10d** = 124.18′; HRMS (CI) for $C_{14}H_{19}F_3NO_3$ $[M + H]^+$ calcd 306.1312, found 306.1328.

(2*R*,3*S*,4*S*)-4-Butyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8e). Following GP1 all-*cis*-lactone (2*R*,3*S*,4*S*)-**8e** (212 mg, 0.76 mmol, 76%) was obtained as colorless solid from (4*S*,5*R*)-**7e** (170 mg, 1.00 mmol, 92% *ee*) and *tert*-butyl *N*-trifluoroactyl-glycinate (342 mg, 1.50 mmol): mp 112−114 °C; $[\alpha]_D^{20}$ = −145.9 ° (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (t, J = 7.1 Hz, 3 H), 1.30−1.60 (m, 5 H), 1.76 (m, 1 H), 3.54 (ddd, J = 10.6, 7.0, 4.3 Hz, 1 H), 4.55 (ddd, J = 8.2, 5.9, 4.3 Hz, 1 H), 4.78 (t, J = 6.5 Hz, 1 H), 5.28 (dd, J = 16.6, 1.6 Hz, 1 H), 5.38 (dd, J = 10.2, 1.7 Hz, 1 H), 5.48 (ddd, J = 16.4, 10.3, 10.3 Hz, 1 H), 6.91 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.3, 27.2, 30.2, 48.7, 54.0, 81.7, 115.3 (J = 287 Hz), 123.4, 127.2, 157.2 (J = 38.3 Hz), 172.7; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8e** = 77.05′, t_R(2*S*,3*R*,4*R*)-**8e** = 77.72′, t_R(2*R*,6*S*)-**10e** = 94.62′, t_R(2*S*,6*S*)-**10e** = 96.24′, t_R(2*R*,3*R*,4*R*)-**9e** = 107.98′, t_R(2*S*,3*S*,4*S*)-**9e** = 108.42′. Analysis calcd for $C_{12}H_{16}F_3NO_3$ (279.26): C 51.61, H 5.78, N 5.02. Found: C 51.38, H 5.54, N 5.21.

(2*S*,3*S*,4*S*)-4-Butyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (9e). *trans*,*cis*-Lactone (2*S*,3*S*,4*S*)-**9e** (21 mg, 0.07 mmol, 7%) was obtained as minor stereoisomer from (4*S*,5*R*)-**7e** (170 mg, 1.00 mmol, 92% *ee*) and *tert*-butyl *N*-trifluoroactyl-glycinate (342 mg, 1.50 mmol) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (t, J = 7.0 Hz, 3 H), 1.30−1.80 (m, 6 H), 3.31 (ddd, J = 12.1, 8.4, 3.4 Hz, 1 H), 4.61 (ddd, J = 10.7, 8.2, 3.5 Hz, 1 H), 4.82 (dd, J = 12.2, 8.6 Hz, 1 H), 5.29 (d, J = 17.0 Hz, 1 H), 5.29 (d, J = 10.3 Hz, 1 H), 5.81 (ddd, J = 17.3, 9.9, 8.6 Hz, 1 H), 7.26 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.2, 27.7, 30.5, 49.7, 52.1, 81.3, 115.5 (J = 288 Hz), 121.1, 131.0, 157.2 (J = 38.3 Hz), 172.9; HRMS (CI) for $C_{12}H_{17}F_3NO_3$ $[M + H]^+$ calcd 280.1154, found 280.1129.

all-*cis*-4-Phenyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (8f). Following GP1 all-*cis*-lactone **8f** (135 mg, 0.47 mmol, 47%) was obtained from *cis*-**7f** (190 mg, 1.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (342 mg, 1.50 mmol) as colorless solid: mp 168−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.88 (ddd, J = 10.5, 7.1, 4.6 Hz, 1 H), 5.03 (t, J = 6.6 Hz, 1 H), 5.05 (dd, J = 17.0, 1.4 Hz, 1 H), 5.12 (dd, J = 10.3, 1.4 Hz, 1 H), 5.27 (ddd, J = 16.7, 10.4, 10.4 Hz, 1 H), 5.78 (d, J = 4.7 Hz, 1 H), 6.88 (s_{br}, 1 H), 7.20−7.44 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.5, 54.2, 81.4, 115.3 (J = 287 Hz), 123.3, 125.2, 127.3, 128.4, 128.6, 134.2, 157.2 (J = 38.5 Hz), 172.3; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8f** = 107.24′, t_R(2*S*,3*R*,4*R*)-**8f** = 108.28′, t_R(*E*)-**10f** = 134.09′, t_R(*E*)-**10f** = 137,43′, t_R(2*R*,3*R*,4*R*)-**9f** = 155.77′, t_R(2*S*,3*S*,4*S*)-**9f** = 157.07′; HRMS (CI) for $C_{14}H_{13}F_3NO_3$ $[M + H]^+$ calcd 300.0842, found 300.0841. Analysis calcd for $C_{14}H_{12}F_3NO_3$ (299.25): C 56.19, H 4.04, N, 4.68. Found: C 56.00, H 4.01, N, 4.56.

all-*cis*-4-(4-Bromphenyl)-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lacton (8g). Following GP1 the all-*cis*-lactone **8g** (65 mg, 0.17 mmol, 34%) was obtained from *cis*-**7g** (135 mg, 0.50 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (170 mg, 0.75 mmol) as colorless solid: mp 152−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.87 (ddd, J = 9.9, 7.0, 4.7 Hz, 1 H), 5.01 (t, J = 6.6 Hz, 1 H), 5.07 (dd, J = 16.1, 2.0 Hz, 1 H), 5.15 (dd, J = 10.1, 1.9 Hz, 1 H), 5.22 (ddd, J = 16.2, 10.2, 10.2 Hz, 1 H), 5.72 (d, J = 4.6 Hz, 1 H), 6.85 (s_{br}, 1 H) 7.14 (d, J = 8.5 Hz, 2 H), 7.52 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.3, 54.2, 80.7, 115.3 (J = 288 Hz), 122.5,123.8, 26.9, 127.0, 131.9, 133.3, 157.2 (J = 38.3 Hz) 172.0; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(2*R*,3*S*,4*S*)-**8g** = 96.98′, t_R(2*S*,3*R*,4*R*)-**8g** = 97.35′. Analysis calcd for $C_{14}H_{11}BrF_3NO_3$ (378.14): C 44.47, H 2.93, N 3.70. Found: C 44.68, H 3.15, N 3.76.

all-*trans*-4-Ethyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (11a). Following GP1 the all-*trans*-lactone **11a** (121 mg 0.48 mmol, 50%) was obtained as colorless oil from *trans*-**7a** (136 mg, 0.95 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (343 mg, 1.50 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.49 (m, 3 H), 1.67 (ddq, J = 14.8, 7.8, 7.4 Hz, 1 H), 1.86 (dqd, J = 15.0, 7.5, 3.6 Hz, 1 H), 2.85 (dt, J = 11.5, 9.4 Hz, 1 H), 4.19 (ddd, J = 9.9, 8.0, 3.6 Hz, 1 H), 4.75 (dd, J = 11.8, 8.6 Hz, 1 H), 5.27 (d, J = 17.0 Hz, 1 H), 5.27 (d, J = 10.6 Hz, 1 H), 5.76 (ddd, J = 17.2, 10.0, 8.5 Hz, 1 H), 7.29 (s_{br}, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 9.6, 25.8, 52.7, 54.9, 83.0, 115.5 (J = 288 Hz), 121.1, 132.2, 157.7 (J = 38.3 Hz), 172.5; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(*E*,2*R*,6*R*)-**10a** = t_R(*E*,2*R*,6*R*)-**10a** = 75.91′, t_R(*E*,2*S*,6*S*)-**10a** = t_R(*E*,2*S*,6*R*)-**10a** = 78.36′, t_R(2*R*,3*S*,5*S*)-**11a** = 94.99′, t_R(2*S*,3*R*,5*R*)-**11a** = 96.23′; HRMS (CI) for $C_{10}H_{13}F_3NO_3$ $[M + H]^+$ calcd 252.0842, found 252.0856.

all-*trans*-4-Pentyl-2-trifluoroacetylamino-3-vinyl-butyro-1,4-lactone (11b). Following GP3 the all-*trans*-lactone **11b** (176 mg, 0.60

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mmol, 60%) was obtained as colorless oil from *trans*-**7b** (184 mg, 1.00 mmol) and *tert*-butyl *N*-trifluoroactyl-glycinate (343 mg, 1.50 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, J = 7.0 Hz, 3 H), 1.28−1.35 (m, 4 H), 1.35−1.60 (m, 2 H), 1.65 (m, 1 H), 1.78 (m, 1 H), 2.80 (dt, J = 11.6, 8.6 Hz, 1 H), 4.23 (ddd, J = 9.9, 8.5, 3.3 Hz, 1 H), 4.73 (dd, J = 11.8, 8.5 Hz, 1 H), 5.28 (d, J = 17.0 Hz, 1 H), 5.28 (d, J = 10.8 Hz, 1 H), 5.77 (ddd, J = 17.3, 10.0, 8.5 Hz, 1 H), 7.07 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 22.4, 25.1, 31.4, 32.8, 53.4, 54.9, 81.8, 115.5 (J = 288 Hz), 121.1, 132.2, 157.6 (J = 38.5 Hz), 172.3; GC (*L*-ChiraSilVal, 80 °C, 10 min, 80 to 180 °C, 1 °C/min) t_R(*E*,2*R*,6*R*)-**10b** = t_R(*E*,2*R*,6*S*)-**10b** = 103.38′, t_R(*E*,2*S*,6*S*)-**10b** = t_R(*E*,2*S*,6*R*)-**10b** = 105.01′, t_R(2*R*,3*R*,4*S*)-**11b** = 116.45′, t_R(2*S*,3*S*,4*R*)-**11b** = 118.18′; HRMS (CI) for $C_{13}H_{19}F_3NO_3$ $[M + H]^+$ calcd 294.1312, found 294.1318. Analysis calcd for $C_{13}H_{18}F_3NO_3$ (293.28): C 53.24, H 6.19, N 4.78. Found: C 53.22, H 6.27, N 4.75.

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra and chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: u.kazmaier@mx.uni-saarland.de.

Notes

The authors declare no competing financial interest.

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