Tandem Benzylic Oxidation/Dihydroxylation of α-Vinyl- and α-Alkenylbenzyl Alcohols

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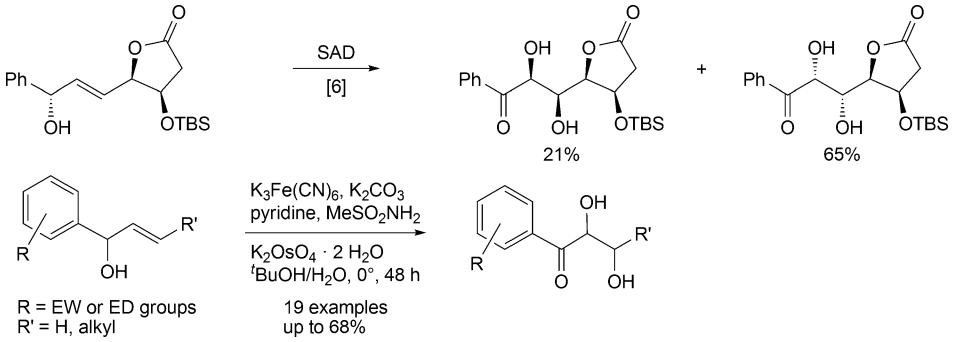
A *de novo* tandem benzylic oxidative dihydroxylation of α-vinyl- and α-alkenylbenzyl alcohols has been developed to give α,β-dihydroxypropiophenones (=2,3-dihydroxy-1-phenylpropan-1-ones) and α,β-dihydroxyalkyl phenones. This method was shown to be substrate-selective and specific for the oxidation of benzylic alcohols.

Introduction. – The catalytic oxidative functionalization of alkenes is an important process in synthetic organic chemistry. The OsO_4-catalyzed dihydroxylation of alkenes is one of the easiest and reliable processes for the preparation of vicinal diols [1]. Sometimes, the formation of overoxidation products has been observed in Os^{VI}-catalyzed dihydroxylations [2]. Apart from *syn*-dihydroxylation and aminohydroxylation [3], Os^{VI} has been explored for oxidation reactions in combination with Cu salts or DABCO (=1,4-diazabicyclo[2.2.2]octane) [4]. Recently, *Devari et al.* reported the oxidation of allylic and benzylic alcohols by using Os^{VI} and chloramine-T [5]. During the protecting-group-free synthesis of (+)-cardiobutanolide [6], we observed a *de novo* tandem oxidation/dihydroxylation under the *Sharpless* asymmetric dihydroxylation (SAD) conditions (*Scheme 1*). Prior to our findings, there was no such report of *in situ* oxidation of benzylic alcohol followed by dihydroxylation of adjacent C=C bond known in the literature. We studied the oxidative dihydroxylation of α-vinyl- and

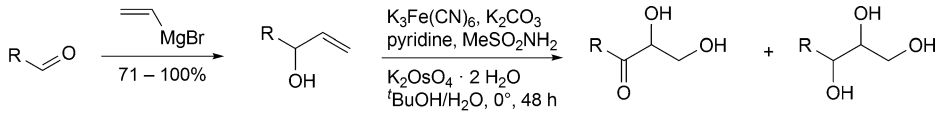
Scheme 1. De novo *Tandem Benzylic Oxidation/Dihydroxylation*. TBS, ^{t}BuMe$_2$Si; EW, electron withdrawing; ED, electron donating.



α-alkenylbenzyl alcohols to obtain various α,β-dihydroxypropiophenones and α,β-dihydroxyalkyl phenones. The known general and straightforward method for synthesis of α,β-dihydroxy ketones [7][8] involves the preparation of α,β-unsaturated ketones, followed by dihydroxylation, requiring additional steps [9]. Herein, we report a one-pot tandem oxidation/dihydroxylation of diverse α-vinyl- and α-alkenylbenzyl alcohols.

Results and Discussion. – Various α-vinylbenzyl alcohols **2a**–**2g** were prepared easily from the corresponding aldehydes, **1a**–**1g** by (vinyl)MgBr addition [10]. 4-Methoxy-α-vinylbenzyl alcohol **2a**, upon catalytic dihydroxylation by using the standard *Sharpless* protocol [1], led to benzylic oxidation product **3a** in lower yield in comparison to triol product **4a**. It was observed during the synthesis of cardiobutanolide that the oxidation of the benzylic OH group occurred prior to dihydroxylation [6]. To ensure maximum benzylic oxidation, we doubled the amount of reagents and catalyst compared to the case of the SAD reaction (here pyridine replaced the chiral ligands). The results obtained are compiled in *Table 1* (*Entries 1–7*). The *para*-substituted α-vinylbenzyl alcohols **2a** and **2b**, under dihydroxylation reaction conditions, gave the α,β-dihydroxypropiophenones (=2,3-dihydroxy-1-phenylpropan-1-ones) **3a** [11a] and **3b** in 58 and 61% yields, respectively (*Entries 1 and 2*). The corresponding 1,2,3-triols **4a** [11b] and **4b** [12] were also isolated in 21 and 25% yields, respectively, as mixture of diastereoisomers. Similarly, (ethenyl)(naphthalen-1-yl)methanol (**2c**) furnished α,β-dihydroxy ketone **3c** in 43% and 1,2,3-triol **4c** [12] in 45% yields (*Entry 3*). α-Vinylbenzyl alcohol (**2d**) led to α,β-dihydroxypropiophenone **3d** [13a] in 45% yield along with 1,2,3-triol **4d** [13b] in 30% yield (*Table 1*, *Entry 4*). (Benzodioxol-5-yl)(vinyl)carbinol (**2e**) afforded the α,β-dihydroxy ketone **3e** under similar conditions in 56% yield and 1,2,3-triol **4e** [14] in 24% yield (*Entry 5*). Surprisingly, 2-chloro- and 4-nitro-substituted α-vinylbenzyl alcohols **2f** and **2g** gave exclusively 1,2,3-triols **4f** and **4g** [15] in 67 and 73% yields, respectively (*Entries 6* and *7*). No benzylic oxidative products were observed in these two cases.

Table 1. *Synthesis of α,β-Dihydroxypropiophenones through Tandem Benzylic Oxidation/Dihydroxylation*



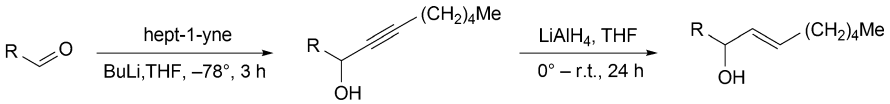
1a – 1g **2a – 2g** **3a – 3e** **4a – 4g**

Entry	Substrate	R	Product **3**	Yield [%]	Product **4**	Yield[a]) [%]
1	**2a**	4-MeO–C_6H_4	**3a**	58	**4a**	21
2	**2b**	4-Cl–C_6H_4	**3b**	61	**4b**	25
3	**2c**	Naphthalen-1-yl	**3c**	43	**4c**	45
4	**2d**	Ph	**3d**	45	**4d**	30
5	**2e**	1,3-Benzodioxol-5-yl	**3e**	56	**4e**	24
6	**2f**	2-Cl–C_6H_4	–		**4f**	67
7	**2g**	4-NO_2–C_6H_4	–		**4g**	73

[a]) Mixture of diastereoisomers (*ca.* 2:1 to 1:1, determined by ^{1}H-NMR).

We next turned our attention to extend the oxidation of α-alkenylbenzyl alcohols with an internal C=C bond. For the preparation of α-alkenylbenzyl alcohols, we applied different approaches. In one case, lithiumheptylide was added to aromatic aldehydes **1a** – **1d** to give the alkynols **5a** – **5d**, respectively, in good-to-excellent yields (82 – 100%; *Table 2*) [16]. The alkynols **5a** – **5d**, on treatment with $LiAlH_4$ in THF, furnished (*E*)-α-heptenylbenzyl alcohols **6a** – **6d**, respectively, in excellent yields (*Table 2*). In another approach, the α-hexenylbenzyl alcohol **6e** was obtained from **2d** by cross-metathesis with hex-1-ene (*Scheme 2*). The α-heptenylbenzyl alcohol **6f** was prepared from the α,β-unsaturated ester **7** [17c] by DIBAL-H (= diisobutylaluminium hydride) reduction to aldehyde and 2-MeO–C_6H_4MgBr addition (*Scheme 2*).

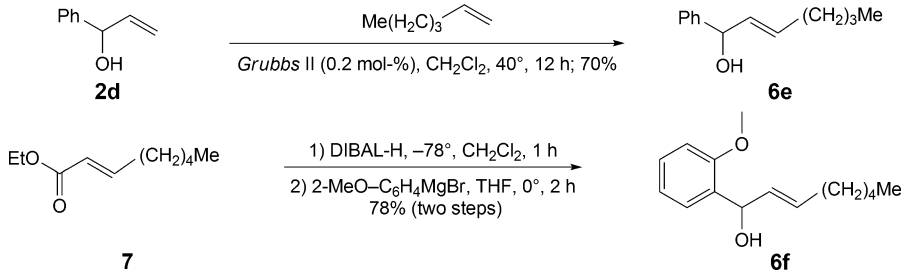
Table 2. *Synthesis of α-Hept-1-enylbenzyl Alcohols from Aldehydes* **1**



1a – 1d **5a – 5d** **6a – 6d**

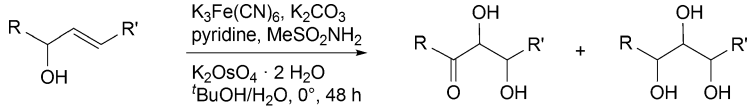
Entry	Aldehyde	R	Alkynol	Yield [%]	Benzyl alcohol	Yield [%]
1	**1a**	4-MeO–C_6H_4	**5a**	100	**6a**	86
2	**1b**	4-Cl–C_6H_4	**5b**	94	**6b**	92
3	**1c**	Naphthalen-1-yl	**5c**	91	**6c**	87
4	**1d**	Ph	**5d**	82	**6d**	94

Scheme 2. *Synthesis of* **6e** *and* **6f**



The α-alkenylbenzyl alcohols were then examined for catalytic oxidative dihydroxylation reaction. The 4-substituted α-heptenylbenzyl alcohols **6a** and **6b** gave the α,β-dihydroxyalkyl phenones **8a** and **8b**, respectively, in 43 and 40% yields, along with 1,2,3-triols **9a** and **9b**, as diastereoisomeric mixtures in 21 and 35% yields, respectively, (*Table 3*; *Entries 1* and *2*). The (heptenyl)(naphthalen-1-yl)methanol **6c**, under similar conditions, afforded α,β-dihydroxyalkyl ketone **8c** in 36% and 1,2,3-triol **9c** in 28% yield, respectively (*Entry 3*). The α-heptenylbenzyl alcohol **6d** gave the corresponding α,β-dihydroxyalkyl phenone **8d** [8b] in 45% and the corresponding 1,2,3-triol **9d** in 31% yield, respectively (*Table 3*, *Entry 4*). The α-hexenylbenzyl alcohol **6e**, on catalytic dihydroxylation, afforded α,β-dihydroxyalkyl phenone **8e** [7] in 42% and 1,2,3-triol **9e**

Table 3. *Synthesis of α,β-Dihydroxyalkyl Phenones through Oxidative Dihydroxylation*



6a – 6f **8a – 8f** **9a – 9f**

Entry	Substrate	R	R′	Product	Yield [%]	Product	Yield [%]
1	**6a**	4-MeO–C_6H_4	C_5H_{11}	**8a**	43	**9a**	21
2	**6b**	4-Cl–C_6H_4	C_5H_{11}	**8b**	40	**9b**	35
3	**6c**	Naphthalen-1-yl	C_5H_{11}	**8c**	36	**9c**	28
4	**6d**	Ph	C_5H_{11}	**8d**	45	**9d**	31
5	**6e**	Ph	C_4H_9	**8e**	42	**9e**	32
6	**6f**	2-MeO–C_6H_4	C_5H_{11}	**8f**	38	**9f**	33
7	**6d**	Ph	C_5H_{11}	(2*S*,3*R*)-**8d**	46 (92% ee)[b])	**9d**	33
8	**6e**	Ph	C_4H_9	(2*S*,3*R*)-**8e**	43% (96% ee)[b])	**9e**	36
9	**6f**	2-MeO–C_6H_4	C_5H_{11}	(2*S*,3*R*)-**8f**	41% (94% ee)[b])	**9f**	35

[a]) Mixture of diastereoisomers (*ca.* 2:1 to 1:1, determined by ^{1}H-NMR). [b]) $(DHQD)_2PHAL$ (= hydroquinidine phthalizine-1,4-diyl ether) ligand was used instead of pyridine.

[18] in 32% yield, respectively (*Entry 5*). Similarly, α-heptenyl-2-methoxybenzyl alcohol (**6f**) formed α,β-dihydroxyalkyl phenone **8f** [8c] in 38% and 1,2,3-triol **9f** in 33% yield, respectively (*Entry 6*). The oxidation method was extended to the synthesis of chiral α,β-dihydroxyalkyl phenones using *Sharpless* asymmetric dihydroxylation version by using cinchona alkaloid ligands instead of pyridine. To this end, the α-alkenylbenzyl alcohols **6d** and **6e** were subjected separately to oxidative dihydroxylation using $(DHQD)_2PHAL$ (= hydroquinidine phthalizine-1,4-diyl ether) ligand to give (2*S*,3*R*)-α,β-dihydroxyalkyl phenones (2*S*,3*R*)-**8d** and (2*S*,3*R*)-**8e** in 46 and 43% yield, respectively, and the corresponding 1,2,3-triols **9d** and **9e** were also isolated from the reaction in 33 and 36% yield, respectively (*Table 3*, *Entries 7* and *8*). The α,β-dihydroxyalkyl phenones (2*S*,3*R*)-**8d** and (2*S*,3*R*)-**8e** prepared by this method had good ee values of 92 and 96%, respectively. Similarly, α-heptenyl-2-methoxybenzyl alcohol **6f** gave (2*S*,3*R*)-**8f** in 41% yield with 94% ee (*Entry 9*). The configurations are based on the pneumonic device proposed by *Sharpless* [1a].

We further explored the substrate scope of this oxidation method and designed three substrates as shown in the *Figure*. Compound **10** has an allylic rather than a benzylic OH group, and compound **11** has an OH group in allylic and homobenzylic position. Substrate **12** was designed with two OH groups, one in benzylic/allylic and the other in homoallylic position. The synthesis of these substrates is outlined in *Scheme 3*. The nucleophilic addition of hexylmagnesium bromide to cinnamaldehyde (**13**) gave compound **10** [19] in 85% yield. Compound **11** was prepared from α,β-unsaturated ester **14** [20] by DIBAL-H reduction to the corressponding aldehyde, followed by addition of BnMgBr (69% overall yield). The compound **12** was obtained from ester **15** [21][1]). DIBAL-H reduction of the ester group to the corresponding aldehyde

[1]) Prepared by a similar approach as its enantiomer, see: [21].

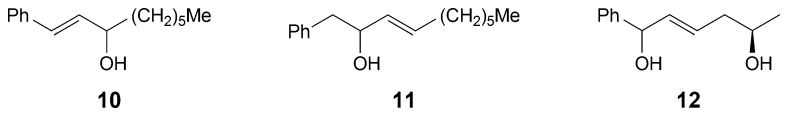
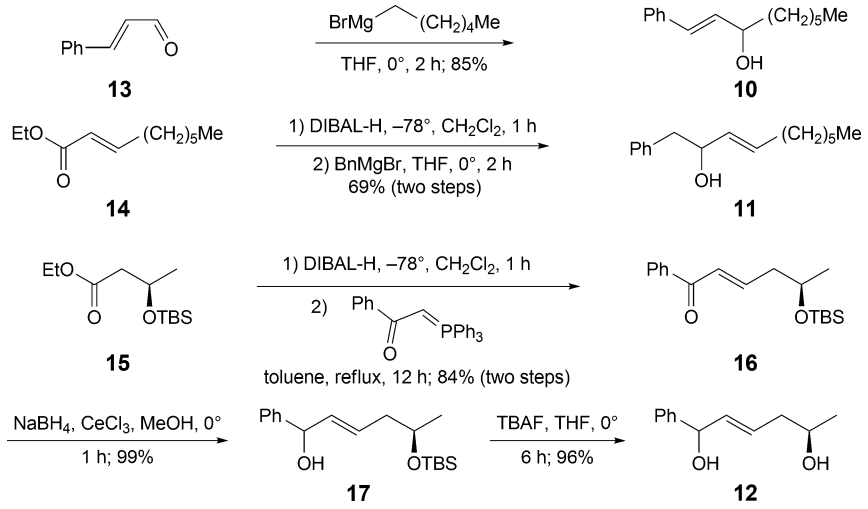


Figure. *Substrates for selective oxidative dihydroxylation*

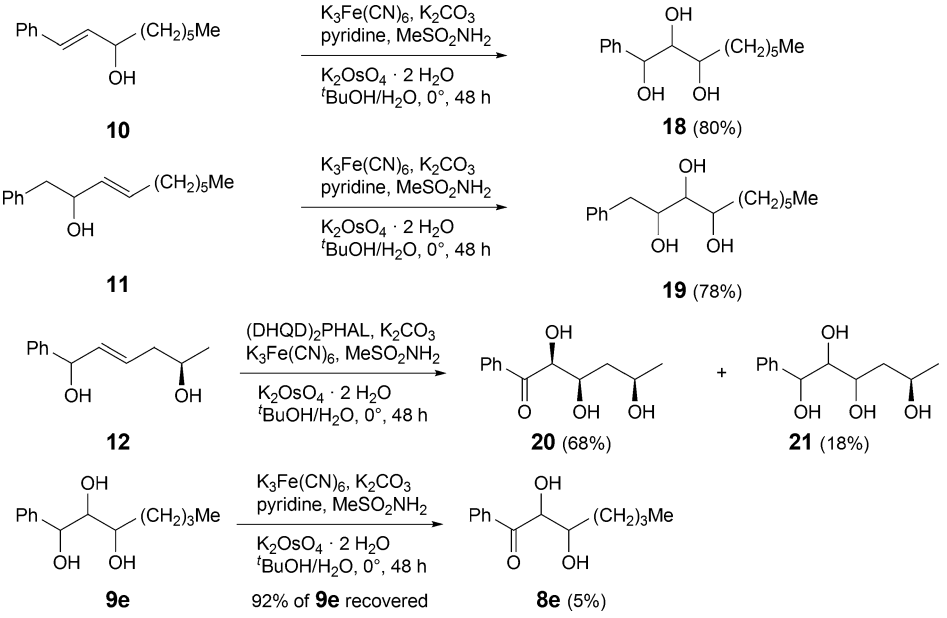
Scheme 3. *Syntheses of Substrates* **10**–**12**. TBAF, Bu_4NF.



was followed by *Wittig* reaction to give the enone **16** in 84% yield over both steps. The $NaBH_4$ reduction of the oxo group gave the benzyl alcohol **17** and further TBDMS (^{t}BuMe$_2$Si) deprotection gave the desired compound **12** in excellent yield (96%).

The compounds **10**–**12** were examined for selective oxidative dihydroxylation (*Scheme 4*). Compound **10** gave only the 1,2,3-triol **18** in 80% yield with dr of *ca.* 1:1. Oxidation of the OH group in allylic position was not observed. Under similar conditions, compound **11** also afforded the triol **19** in 78% yield with dr of *ca.* 1:1. These reactions indicated substrate selectivity requiring benzylic alcohols. The oxidative dihydroxylation of **12** was more interesting by using the $(DHQD)_2PHAL$ ligand. Trihydroxy phenone **20** was obtained in 68% yield with dr > 9:1 and accompanied by tetrol **21**, isolated in 18% yield as a mixture of diastereoisomers. Thus, the reaction showed the selective tandem oxidation of the benzylic OH group and dihydroxylation of the olefin. The systematic study revealed that the method is specific for oxidation of benzylic OH groups by also tolerating non-benzylic OH groups. To confirm that the 2,3-dihydroxy ketones were not obtained from benzylic oxidation of 1,2,3-triol formed, triol **9e** was exposed to standardized dihydroxylation reaction conditions, but only 5% of the dihydroxy ketone **8e** was isolated, and 92% of triol **9e** was recovered (*Scheme 4*). This further confirmed that the 2,3-dihydroxy ketones result from first benzylic oxidation, followed by dihydroxylation of the adjacent C=C bond.

Scheme 4. *Substrate Scope for Oxidative Dihydroxylation.* $(DHQD)_2PHAL$, Hydroquinidinephthalizine-1,4-diyl ether.



Conclusions. – We have developed an efficient tandem benzylic oxidation/dihydroxylation for the synthesis of α,β-dihydroxypropiophenones and α,β-dihydroxyalkyl phenones from the corresponding benzyl alcohols. The method is easy to perform and has substrate selectivity, specifically for the oxidation of an OH group which is flanked by an aryl, vinyl, or alkenyl group. The (2*S*,3*R*)-α,β-dihydroxyalkyl phenones prepared by this method had high ee values up to 96%. The *syn*-α,β-dihydroxyalkyl phenones are important synthons in organic synthesis due to their highly reactive keto functional group for further synthetic modifications. Further synthetic applications of this method are in progress in our laboratory.

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Experimental Part

General. Flasks were oven- or flame-dried and cooled in a desiccator. Anh. reactions were carried out under Ar or N_2. Solvents and reagents were purified by standard methods. TLC: *EM 250 Kieselgel 60 F254* silica-gel plates; visualization by staining with $KMnO_4$ or by UV lamp. HPLC: *JASCO-(PU-2089PLUS)* quaternary gradient pump equipped with a *MD-2010PLUS* multiwavelength detector. Optical rotations: *Jasco P-2000* polarimeter. IR Spectra: *Perkin–Elmer Spectrum One* FT-IR spectrometer; and samples prepared by evaporation from $CHCl_3$ on CsBr plates or as KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance III* spectrometer, at 400 and 100 MHz; chemical shifts (δ [ppm]) based on the Me_4Si (δ(H) 0.00 for ^1H) and the $CDCl_3$ signal (δ(C) 77.00 (*t*) or the(D_6)acetone

signal at δ(C) 29.80 (*sept.*) for ^{13}C); *J* in Hz. HR-MS: *Bruker Maxis Impact* spectrometer; in positive-ion electrospray-ionization (ESI) mode; in *m*/*z*.

General Procedure for the Preparation of α-Vinylbenzyl Alcohols **2a**–**2g** (*GP 1*). To a stirred soln. of arenecarbaldehyde **1a**–**1g** (1.0 equiv.) in dry THF was added vinylmagnesium bromide (1.6M in hexanes; 1.2 equiv.) dropwise at 0°. The mixture was stirred for 2 h, and then the reaction was quenched with sat. aq. NH_4Cl. The soln. was extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; petroleum ether (PE)/AcOEt 9:1) to give α-vinylbenzyl alcohols **2a**–**2g**, respectively, as colorless oils.

1-(4-Methoxyphenyl)prop-2-en-1-ol (**2a**) [10a]. From **1a** (0.2 g, 1.47 mmol) by *GP 1*. Yield: 0.241 g (quant.). IR ($CHCl_3$): 3418, 3011, 2838, 1612, 1514, 1464, 1249, 1175, 1035, 927, 832, 667. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.27 (*d*, *J* = 8.6, 2 H); 6.87 (*d*, *J* = 8.7, 2 H); 6.02 (*ddd*, *J* = 16.9, 10.5, 6.1, 1 H); 5.31 (*d*, *J* = 17.2, 1 H); 5.16 (*d*, *J* = 10.3, 1 H); 5.13 (*d*, *J* = 5.6, 1 H); 3.78 (*s*, 3 H); 2.23 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.1; 140.3; 134.8; 127.6; 114.7; 113.8; 74.8; 55.2. HR-ESI-MS: 187.0730 ($C_{10}H_{12}NaO_2^+$; calc. 187.0730).

1-(4-Chlorophenyl)prop-2-en-1-ol (**2b**) [10a]. From **1b** (0.2 g, 1.42 mmol) by *GP 1*. Yield: 0.187 g (78%). IR ($CHCl_3$): 3400, 3017, 2928, 1635, 1597, 1492, 1408, 1093, 1015, 930, 669. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.29 (*m*, 4 H); 6.00 (*ddd*, *J* = 17.0, 10.3, 6.2, 1 H); 5.34 (*dt*, *J* = 17.1, 1.3, 1 H); 5.22 (*dd*, *J* = 10.3, 1.2, 1 H); 5.18 (*d*, *J* = 6.7, 1 H); 2.01 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.9; 139.9; 133.4; 128.7; 127.7; 115.6; 74.7. HR-ESI-MS: 191.0238 ($C_9H_9ClNaO^+$; calc. 191.0234).

1-(Naphthalen-1-yl)prop-2-en-1-ol (**2c**) [10b]. From **1c** (0.3 g, 1.92 mmol) by *GP 1*. Yield: 0.286 g (81%). IR ($CHCl_3$): 3370, 3050, 3011, 2982, 1641, 1597, 1510, 1395, 1355, 1259, 1227, 1166, 1117, 1049, 989, 926, 865, 848, 802, 781, 669. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.18 (*d*, *J* = 9.0, 1 H); 7.88 (*dd*, *J* = 6.9, 2.5, 1 H); 7.81 (*d*, *J* = 8.2, 1 H); 7.62 (*d*, *J* = 7.0, 1 H); 7.55–7.45 (*m*, 3 H); 6.24 (*ddd*, *J* = 17.1, 10.5, 5.5, 1 H); 5.91 (*d*, *J* = 5.0, 1 H); 5.44 (*d*, *J* = 17.2, 1 H); 5.28 (*dt*, *J* = 10.4, 1.2, 1 H); 2.37 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.5; 138.0; 133.9; 130.6; 128.7; 128.4; 126.0; 125.6; 125.4; 123.9; 123.7; 115.6; 72.2. HR-ESI-MS: 207.0785 ($C_{13}H_{12}NaO^+$; calc. 270.0780).

1-Phenylprop-2-en-1-ol (**2d**) [10a]. From **1d** (0.5 g, 4.71 mmol) by *GP 1*. Yield: 0.6 g (95%). IR ($CHCl_3$): 3393, 3063, 3030, 2868, 1599, 1492, 1453, 1279, 1245, 1194, 1118, 1074, 1026, 989, 928, 836, 701. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.27 (*m*, 5 H); 6.05 (*ddd*, *J* = 16.9, 10.5, 6.1, 1 H); 5.35 (*dt*, *J* = 17.5, 3.5, 1 H); 5.22–5.18 (*m*, 2 H); 2.01 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.5; 140.1; 128.4; 127.6; 126.3; 115.0; 75.2.

1-(1,3-Benzodioxol-5-yl)prop-2-en-1-ol (**2e**) [10a]. From **1e** (0.3 g, 2.0 mmol) by *GP 1*. Yield: 0.3 g (84%). IR ($CHCl_3$): 3392, 3079, 3013, 2983, 2893, 1643, 1610, 1505, 1488, 1445, 1248, 1094, 1040, 991, 934, 866, 812, 794. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.87–6.76 (*m*, 3 H); 6.01 (*ddd*, *J* = 17.1, 10.3, 5.9, 1 H); 5.94 (*s*, 2 H); 5.33 (*dt*, *J* = 17.1, 1.4, 1 H); 5.18 (*dt*, *J* = 10.3, 1.3, 1 H); 5.12 (*d*, *J* = 3.8, 1 H); 2.00 (*d*, *J* = 3.5, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 147.8; 147.1; 140.1; 136.6; 119.8; 114.9; 108.1; 106.9; 101.0; 75.0. HR-ESI-MS: 201.0525 ($C_{10}H_{10}NaO_3^+$; calc. 201.0522).

1-(2-Chlorophenyl)prop-2-en-1-ol (**2f**) [10a]. From **1f** (0.4 g, 2.84 mmol) by *GP 1*. Yield: 0.34 g (71%). IR ($CHCl_3$): 3369, 3069, 3016, 2926, 1575, 1472, 1444, 1197, 1113, 1028, 990, 929, 833, 712. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*dd*, *J* = 7.7, 1.7, 1 H); 7.35 (*dd*, *J* = 7.9, 1.3, 1 H); 7.32–7.20 (*m*, 2 H); 6.04 (*ddd*, *J* = 17.1, 10.4, 5.5, 1 H); 5.64 (*d*, *J* = 5.1, 1 H); 5.38 (*dt*, *J* = 17.2, 1.3, 1 H); 5.22 (*dt*, *J* = 10.4, 1.3, 1 H); 2.21 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.8; 138.3; 132.4; 129.5; 128.8; 127.6; 127.2; 115.6; 71.4. HR-ESI-MS: 191.0230 ($C_9H_9ClNaO^+$; calc. 191.0234).

1-(4-Nitrophenyl)prop-2-en-1-ol (**2g**) [10a]. From **1g** (0.2 g, 1.32 mmol) by *GP 1*. Yield: 0.175 g (74%). IR ($CHCl_3$): 3410, 3016, 2926, 1607, 1520, 1348, 1109, 1046, 933, 855, 822, 711. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.21 (*d*, *J* = 8.8, 2 H); 7.56 (*d*, *J* = 8.7, 2 H); 6.00 (*ddd*, *J* = 17.0, 10.3, 6.6, 1 H); 5.40 (*dt*, *J* = 17.1, 1.1, 1 H); 5.32 (*d*, *J* = 5.6, 1 H); 5.28 (*dt*, *J* = 10.2, 1.0, 1 H); 2.22 (*d*, *J* = 3.2, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 149.5; 147.4; 139.2; 126.9; 123.7; 116.8; 74.6. HR-ESI-MS: 202.0473 ($C_9H_9NaNO_3^+$; calc. 202.0475).

General Procedure for Oxidative Dihydroxylation of α-Vinylbenzyl Alcohols **2a**–**2g** (*GP 2*). To a mixture of $K_3Fe(CN)_6$ (6.0 equiv.), K_2CO_3 (6.0 equiv.), and pyridine (2.0 mol-%) in ^{t}BuOH/H_2O 1:1 at 0° was added $K_2OsO_4 \cdot 2\,H_2O$ (0.8 mol%), followed by $MeSO_2NH_2$ (2.0 equiv.) After stirring for 5 min at 0°, the alkene, **2a**–**2g**/**6a**–**6f** (1.0 equiv.), was added in one portion. The mixture was stirred at 0° for 48 h,

and then the reaction was quenched with solid Na_2SO_3 (0.4 g/mmol). The stirring was continued for additional 45 min, and the soln. was extracted with AcOEt (5 × 10 ml). The combined org. phases were washed with 2N KOH, H_2O, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 1:1) to give **3a**–**3e**/**8a**–**8f**, and further elution with PE/AcOEt 2:3 provided triol **4a**–**4g**/**9a**–**9f**, resp.

2,3-Dihydroxy-1-(4-methoxyphenyl)propan-1-one (**3a**) *and 1-(4-Methoxyphenyl)propane-1,2,3-triol* (**4a**). From **2a** (50 mg, 0.304 mmol) by *GP 2*. Yield: 34.6 mg (58%) of **3a** as colorless solid and 12.6 mg (21%) of **4a** as colorless oil.

Data of **3a**. M.p. 110–112°. IR ($CHCl_3$): 3348, 3019, 2930, 2846, 1675, 1606, 1575, 1464, 1408, 1316, 1255, 1180, 1124, 1056, 1028, 998, 860, 822. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.94 (*dd*, *J* = 6.9, 2.0, 2 H); 6.98 (*dd*, *J* = 6.9, 2.0, 2 H); 5.14–5.10 (*m*, 1 H); 4.05 (*d*, *J* = 6.0, OH); 4.04–3.98 (*m*, 1 H); 3.93 (*s*, 3 H); 3.89–3.69 (*m*, 1 H); 2.26–2.22 (*m*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 197.5; 164.4; 131.0; 126.2; 114.2; 74.2; 65.6; 55.6. HR-ESI-MS: 219.0630 ($C_{10}H_{12}NaO_4^+$; calc. 219.0628).

Data of **4a**. IR ($CHCl_3$): 3413, 2926, 2855, 1614, 1515, 1464, 1304, 1250, 1178, 1102, 1033, 880, 834, 773. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 7.27–7.24 (*m*, 4 H); 6.88–6.84 (*m*, 4 H); 4.76 (*d*, *J* = 4.9, 1 H); 4.60 (*d*, *J* = 6.6, 1 H); 3.77 (*s*, 6 H); 3.73–3.66 (*m*, 2 H); 3.55–3.51 (*m*, 2 H); 3.44–3.42 (*m*, 2 H); 2.11 (br. *s*, 6 OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.4; 159.3; 132.5; 132.4; 127.9; 127.6; 114.0; 75.9; 75.3; 74.7; 74.5; 63.2; 62.9; 55.2. HR-ESI-MS: 221.0783 ($C_{10}H_{14}NaO_4^+$; calc. 221.0784).

1-(4-Chlorophenyl)-2,3-dihydroxypropan-1-one (**3b**) *and 1-(4-Chlorophenyl)propane-1,2,3-triol* (**4b**). From **2b** (60 mg, 0.356 mmol) by *GP 2*. Yield: 43.6 mg (61%) of **3a** as colorless solid and 18.0 mg (25%) of **4b** as colorless oil.

Data of **3b**. M.p. 135–137°. IR ($CHCl_3$): 3391, 2926, 2854, 1679, 1592, 1488, 1402, 1317, 1284, 1265, 1230, 1094, 1055, 912, 864, 820. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88 (*d*, *J* = 8.5, 2 H); 7.49 (*d*, *J* = 8.5, 2 H); 5.12 (*t*, *J* = 3.9, 1 H); 4.01 (*dd*, *J* = 11.8, 3.2, 1 H); 3.88 (*dd*, *J* = 11.8, 4.7, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 198.3; 140.9; 131.7; 130.0; 129.4; 74.5; 65.2. HR-ESI-MS: 223.0132 ($C_9H_9ClNaO_3^+$; calc. 223.0132).

Data of **4b** [12]. IR ($CHCl_3$): 3372, 3018, 2928, 2884, 1656, 1596, 1491, 1459, 1411, 1090, 1039, 1015, 881, 829, 669. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 7.35–7.29 (*m*, 8 H); 4.83 (*d*, *J* = 5.0, 1 H); 4.70 (*d*, *J* = 6.5, 1 H); 3.80–3.78 (*m*, 1 H); 3.73–3.60 (*m*, 4 H); 3.52–3.48 (*m*, 1 H); 3.22 (br. *s*, 3 OH); 1.82–1.73 (br. *s*, 3 OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.9; 138.8; 133.9; 133.7; 128.8; 128.7; 128.0; 127.6; 75.7; 75.1; 74.5; 74.2; 63.3; 62.7. HR-ESI-MS: 225.0289 ($C_9H_{11}ClNaO_3^+$; calc. 225.0289).

2,3-Dihydroxy-1-(naphthalen-1-yl)propan-1-one (**3c**) *and 1-(Naphthalen-1-yl)propane-1,2,3-triol* (**4c**). From **2c** (90 mg, 0.488 mmol) by *GP 2*. Yield: 45.4 mg (43%) of **3c** as colorless oil and 47.9 mg (45%) of **4c** as colorless solid.

Data of **3c**. IR ($CHCl_3$): 3434, 3047, 2925, 1675, 1593, 1509, 1415, 1283, 1243, 1124, 1070, 891, 773, 647. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.48 (*d*, *J* = 8.45, 1 H); 8.06 (*d*, *J* = 8.4, 1 H); 7.91–7.89 (*m*, 1 H); 7.80 (*d*, *J* = 7.1, 1 H); 7.67–7.49 (*m*, 3 H); 5.23 (*t*, *J* = 3.6, 1 H); 3.95 (*dd*, *J* = 11.8, 3.2, 1 H); 3.72 (*dd*, *J* = 11.8, 4.2, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 203.0; 134.0; 133.7; 131.6; 130.3; 128.5; 128.4; 127.7; 126.9; 125.4; 124.2; 76.1; 64.8. HR-ESI-MS: 239.0676 ($C_{13}H_{12}NaO_3^+$; calc. 239.0679).

Data of **4c** [12]. M.p. 76–78°. IR ($CHCl_3$): 3389, 3019, 2927, 2890, 1598, 1420, 1511, 1330, 1157, 1028, 929, 876, 669. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 8.11 (*d*, *J* = 7.8, 1 H); 8.04 (*d*, *J* = 7.6, 1 H); 7.88 (*d*, *J* = 7.8, 2 H); 7.82 (*d*, *J* = 8.2, 2 H); 7.74 (*d*, *J* = 7.2, 1 H); 7.67 (*d*, *J* = 7.1, 1 H); 7.54–7.47 (*m*, 6 H); 5.74 (*d*, *J* = 4.4, 1 H); 5.55 (*d*, *J* = 5.6, 1 H); 4.84–4.81 (br. *s*, 4 OH); 4.12–4.04 (*m*, 2 H); 3.82–3.78 (*m*, 1 H); 3.70–3.68 (*m*, 1 H); 3.62–3.57 (*m*, 2 H); 1.72–1.65 (br. *s*, 2 OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.2; 133.7; 130.5; 128.9; 128.5; 128.3; 126.2; 125.6; 125.4; 125.3; 124.5; 123.5; 123.0; 122.7; 75.0; 73.4; 71.2; 63.6; 62.6. HR-ESI-MS: 241.0835 ($C_{13}H_{14}NaO_3^+$; calc. 241.0835).

2,3-Dihydroxy-1-phenylpropan-1-one (**3d**) *and 1-Phenylpropane-1,2,3-triol* (**4d**). From **2d** (100 mg, 0.745 mmol) by *GP 2*. Yield: 55.7 mg (45%) of **3d** as colorless solid and 37.6 mg (30%) of **4d** as colorless oil.

Data of **3d** [13a]. M.p. 80–82°. IR ($CHCl_3$): 3447, 3066, 2928, 2884, 1686, 1597, 1580, 1450, 1401, 1319, 1264, 1229, 1182, 1118, 1603, 1002, 978, 962, 885, 847, 691. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.95 (*d*, *J* = 7.3,

2 H); 7.64 (*t*, *J* = 7.4, 1 H); 7.54 (*t*, *J* = 7.7, 2 H); 5.21 – 5.15 (*m*, 1 H); 4.04 (*s*, OH); 4.02 (*d*, *J* = 10.2, 1 H); 3.77 (*dd*, *J* = 11.6, 4.2, 1 H); 2.22 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 199.4; 134.3; 133.4; 129.0; 128.5; 74.6; 65.3. HR-ESI-MS: 189.0523 ($C_9H_{10}NaO_3^+$; calc. 189.0522).

Data of **4d** [13b]: IR ($CHCl_3$): 3401, 1647, 1456, 1316, 1154, 1106, 1031. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 7.30 – 7.25 (*m*, 10 H); 4.78 (*d*, *J* = 4.1, 1 H); 4.58 (*d*, *J* = 6.9, 1 H); 4.18 (br. *s*, OH); 3.95 (br. *s*, 2 OH); 3.74 – 3.36 (*m*, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.5; 140.4; 128.4; 128.3; 128.0; 127.6; 126.7; 126.3; 76.0; 75.2; 74.9; 74.6; 63.0; 62.5. HR-ESI-MS: 191.0682 ($C_9H_{12}NaO_3^+$; calc. 191.0679).

1-(1,3-Benzodioxol-5-yl)-2,3-dihydroxypropan-1-one (**3e**) *and 1-(1,3-Benzodioxol-5-yl)propane-1,2,3-triol* (**4e**). From **2e** (50 mg, 0.281 mmol) by *GP 2*. Yield: 33.0 mg (56%) of **3e** as colorless solid and 14.3 mg (24%) of **45e** as colorless oil.

Data of **3e**. M.p. 115 – 117°. IR ($CHCl_3$): 3428, 3019, 2891, 1669, 1446, 1261, 1089, 1041, 924, 894, 669. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*dd*, *J* = 8.2, 1.8, 1 H); 7.42 (*d*, *J* = 1.7, 1 H); 6.90 (*d*, *J* = 8.2, 1 H); 6.09 (*s*, 2 H); 5.09 – 5.06 (*m*, 1 H); 4.03 – 3.97 (*m*, 2 H); 3.76 – 3.70 (*m*, OH); 2.24 – 2.01 (*m*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 197.2; 152.9; 148.5; 127.9; 125.2; 108.3; 108.2; 102.2; 74.2; 65.7. HR-ESI-MS: 233.0415 ($C_{10}H_{10}NaO_5^+$; calc. 233.0420).

Data of **4e** [14]. IR ($CHCl_3$): 3431, 3018, 2926, 2855, 1646, 1505, 1489, 1446, 1377, 1249, 1095, 1039, 930, 669. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 6.86 (*d*, *J* = 5.0, 2 H); 6.77 (*d*, *J* = 5.3, 4 H); 5.93 (*s*, 4 H); 4.71 (*d*, *J* = 5.2, 1 H); 4.56 (*d*, *J* = 6.9, 1 H); 3.77 – 3.41 (*m*, 6 H); 2.81 – 2.74 (br. *s*, 6 OH). ^{13}C-NMR (100 MHz, $CDCl_3$): 148.0; 147.9; 147.5; 147.4; 134.4; 134.3; 120.2; 119.8; 108.3; 107.0; 106.7; 101.12; 101.11; 75.8; 75.5; 74.8; 74.6; 63.3; 63.0. HR-ESI-MS: 235.0574 ($C_{10}H_{12}NaO_5^+$; calc. 235.0577).

1-(2-Chlorophenyl)propane-1,2,3-triol (**4f**). From **2e** (100 mg, 0.593 mmol) by *GP 2*. Yield: 80.5 mg (67%). Colorless oil. IR ($CHCl_3$): 3396, 2932, 1644, 1467, 1441, 1318, 1153, 1083, 1034, 990, 880, 707. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers *ca.* 2:1): 7.61 – 7.53 (*m*, 2 H); 7.34 – 7.21 (*m*, 6 H); 5.33 – 5.31 (*m*, 1 H); 5.14 – 5.12 (*m*, 1 H); 4.02 – 3.52 (*m*, 12 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.6; 132.1; 129.53; 129.48; 129.02; 129.0; 128.2; 127.7; 127.2; 74.2; 73.1; 72.4; 71.1; 64.2; 62.5. HR-ESI-MS: 225.0285 ($C_9H_{11}ClNaO_3^+$; calc. 225.0289).

1-(4-Nitrophenyl)propane-1,2,3-triol (**4g**) [15]. From **2g** (60 mg, 0.335 mmol) by *GP 2*. Yield: 52 mg (73%). Colorless oil. IR ($CHCl_3$): 3398, 2929, 2890, 1692, 1605, 1519, 1411, 1350, 1259, 1196, 1107, 1043, 929, 855, 832, 755, 702. ^{1}H-NMR (400 MHz, (D_6)acetone; mixture of diastereoisomers, *ca.* 1:1): 8.20 – 8.12 (*m*, 4 H); 7.71 – 7.68 (*m*, 4 H); 4.91 (*d*, *J* = 4.2, 1 H); 4.81 (*d*, *J* = 6.4, 1 H); 3.75 – 3.71 (*m*, 2 H); 3.68 – 3.61 (*m*, 4 H); 3.49 – 3.45 (*m*, 2 H); 3.10 (br. *s*, 4 OH). ^{13}C-NMR (100 MHz, (D_6)acetone): 152.2; 148.2; 129.3; 128.9; 124.0; 123.8; 76.7; 76.2; 75.2; 74.0; 64.5; 64.1. HR-ESI-MS: 236.0529 ($C_9H_{11}NaNO_5^+$; calc. 236.0529).

General Procedure for Preparation of Alkynols **5a** – **5d** (*GP 3*). To a stirred soln. of hept-1-yne (1.5 equiv.) in THF was added BuLi (1.6M in hexanes; 1.8 equiv.) dropwise at − 78°, and the mixture was stirred for 15 min. Then, a soln. of aldehyde **1a** – **1d** (1.0 equiv.) in THF, was added and the mixture was stirred at − 78° for 1 h and slowly warmed to r.t. over 2 h. The reaction was then quenched with sat. aq. NH_4Cl, and the soln. was extracted with AcOEt (3 × 20 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 17:3) to give the alkynols **5a** – **5d**, resp. as colorless oils.

1-(4-Methoxyphenyl)oct-2-yn-1-ol (**5a**) [16a]. From **1a** (0.4 g, 2.94 mmol) by *GP 3*. Yield: 0.683 g (quant.). IR ($CHCl_3$): 3421, 3003, 2956, 2934, 2860, 2279, 2223, 1611, 1587, 1512, 1465, 1378, 1332, 1304, 1248, 1173, 1133, 1108, 1035, 996, 934, 835, 803, 694. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.46 (*d*, *J* = 8.6, 2 H); 6.89 (*d*, *J* = 8.6, 2 H); 5.40 (*d*, *J* = 5.0, 1 H); 3.80 (*s*, 3 H); 2.26 (*td*, *J* = 7.2, 2.0, 2 H); 1.58 – 1.51 (*m*, 2 H); 1.42 – 1.29 (*m*, 4 H); 0.90 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.5; 133.6; 128.0; 113.8; 87.5; 80.0; 64.4; 55.3; 31.0; 28.3; 22.1; 18.7; 13.9. HR-ESI-MS: 255.1352 ($C_{15}H_{20}NaO_2^+$; calc. 255.1356).

1-(4-Chlorophenyl)oct-2-yn-1-ol (**5b**) [16c]. From **1b** (0.5 g, 3.56 mmol) by *GP 3*. Yield: 0.792 g (94%). IR ($CHCl_3$): 3360, 2956, 2932, 2860, 2280, 2225, 1646, 1596, 1489, 1466, 1429, 1409, 1379, 1327, 1266, 1191, 1173, 1135, 1091, 1014, 943, 849, 826, 790, 670. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.47 (*d*, *J* = 8.5, 2 H); 7.33 (*d*, *J* = 8.5, 2 H); 5.41 – 5.39 (*m*, 1 H); 2.31 (br. *s*, OH); 2.26 (*td*, *J* = 7.2, 2.0, 2 H); 1.57 – 1.50 (*m*,

2 H); 1.40–1.25 (*m*, 4 H); 0.89 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.7; 133.9; 128.6; 128.0; 88.1; 79.5; 64.1; 31.0; 28.2; 22.1; 18.7; 13.9. HR-ESI-MS: 259.0863 ($C_{14}H_{17}ClNaO^+$; calc. 259.0860).

1-(Naphthalen-1-yl)oct-2-yn-1-ol (**5c**). From **1c** (0.2 g, 1.28 mmol) by *GP 3*. Yield: 0.294 g (91%). IR ($CHCl_3$): 3391, 3051, 2956, 2931, 2860, 2279, 2228, 1599, 1511, 1466, 1395, 1379, 1328, 1305, 1261, 1233, 1164, 1136, 1077, 1061, 1015, 986, 913, 864, 780, 629. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.33 (*d*, *J* = 8.4, 1 H); 7.89–7.83 (*m*, 3 H); 7.58–7.46 (*m*, 3 H); 6.13–6.12 (*m*, 1 H); 2.31–2.27 (*m*, 3 H); 1.60–1.53 (*m*, 2 H); 1.42–1.29 (*m*, 4 H); 0.90 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.3; 134.0; 130.6; 129.1; 128.6; 126.3; 125.8; 125.2; 124.4; 124.0; 88.4; 79.7; 63.0; 31.1; 28.2; 22.2; 18.8; 14.0. HR-ESI-MS: 275.1408 ($C_{18}H_{20}NaO^+$; calc. 275.1406).

1-Phenyloct-2-yn-1-ol (**5d**) [16b]. From **1d** (0.2 g, 1.88 mmol) by *GP 3*. Yield: 0.312 g (82%). IR ($CHCl_3$): 3391, 3065, 3032, 3012, 2958, 2932, 2861, 2279, 2227, 1603, 1494, 1455, 1379, 1330, 1274, 1191, 1135, 1106, 1076, 995, 917, 842, 698, 635. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*d*, *J* = 1.5, 2 H); 7.38–7.28 (*m*, 3 H); 5.43–5.41 (*m*, 1 H); 2.25 (*td*, *J* = 7.2, 2.0, 2 H); 2.22 (br. *s*, OH); 1.57–1.51 (*m*, 2 H); 1.50–1.26 (*m*, 4 H); 0.88 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.2; 128.5; 128.2; 126.6; 87.7; 79.9; 64.8; 31.0; 28.2; 22.1; 18.8; 13.9. HR-ESI-MS: 225.1246 ($C_{14}H_{18}NaO^+$; calc. 225.1250).

General Procedure for Synthesis of α-Heptenylbenzyl Alcohols **6a**–**6d** (*GP 4*). To a stirred suspension of $LiAlH_4$ (2.0 equiv.) in THF was added a soln. of alkynol **5a**–**5d** (1.0 equiv.) in THF at 0°, and the mixture was warmed to r.t. and stirred for 24 h. The reaction was then quenched with AcOEt, MeOH, and 3N NaOH at 0°. The white solid suspension was filtered through a small pad of SiO_2/*Celite* and washed with AcOEt (4 × 20 ml). The filtrate was concentrated under reduced pressure, and the residue was purified by CC (SiO_2; PE/AcOEt 17:3) to give α-alkenylbenzyl alcohols, **6a**–**6d**, respectively, as colorless oils.

*(2*E*)-1-(4-Methoxyphenyl)oct-2-en-1-ol* (**6a**). From **5a** (100 mg, 0.430 mmol) by *GP 4*. Yield: 86.7 mg (86%). IR ($CHCl_3$): 3462, 3000, 2931, 2858, 1679, 1608, 1512, 1465, 1377, 1302, 1249, 1174, 1107, 1036, 968, 831. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.29 (*d*, *J* = 8.6, 2 H); 6.88 (*d*, *J* = 8.6, 2 H); 5.76–5.70 (*m*, 1 H); 5.68–5.62 (*m*, 1 H); 5.11 (*d*, *J* = 6.4, 1 H); 3.80 (*s*, 3 H); 2.04 (*q*, *J* = 7.0, 2 H); 1.88 (br. *s*, OH); 1.40–1.24 (*m*, 6 H); 0.88 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.0; 135.7; 132.5; 132.3; 127.4; 113.8; 74.8; 55.3; 32.1; 31.4; 28.7; 22.5; 14.0. HR-ESI-MS: 257.1512 ($C_{15}H_{22}NaO_2^+$; calc. 257.1512).

*(2*E*)-1-(4-Chlorophenyl)oct-2-en-1-ol* (**6b**). From **5b** (0.25 g, 1.06 mmol) by *GP 4*. Yield: 0.232 g (92%). IR ($CHCl_3$): 3382, 2957, 2928, 2857, 1668, 1620, 1490, 1467, 1403, 1269, 1175, 1091, 1014, 971, 826, 669. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.28 (*m*, 4 H); 5.79–5.73 (*m*, 1 H); 5.71–5.57 (*m*, 1 H); 5.14 (*d*, *J* = 7.0, 1 H); 2.07–2.02 (*m*, 2 H); 1.96 (br. *s*, OH); 1.42–1.24 (*m*, 6 H); 0.88 (*t*, *J* = 6.8, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.8; 133.4; 131.9; 128.5; 127.5; 126.1; 74.6; 32.1; 31.4; 28.7; 22.5; 14.0. HR-ESI-MS: 261.1019 ($C_{14}H_{19}ClNaO^+$; calc. 261.1017).

*(2*E*)-1-(Naphthalen-1-yl)oct-2-en-1-ol* (**6c**). From **5c** (100 mg, 0.396 mmol) by *GP 4*. Yield: 87.7 mg (87%). IR ($CHCl_3$): 3366, 3051, 2956, 2927, 2856, 1666, 1597, 1510, 1466, 1378, 1260, 1165, 1049, 972, 798, 778, 671. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.18 (*d*, *J* = 6.9, 1 H); 7.88 (*d*, *J* = 7.8, 1 H); 7.79 (*d*, *J* = 8.2, 1 H); 7.66 (*d*, *J* = 7.1, 1 H); 7.54–7.46 (*m*, 3 H); 5.91–5.89 (*m*, 1 H); 5.86–5.84 (*m*, 2 H); 2.08–2.04 (*m*, 2 H); 1.42–1.23 (*m*, 6 H); 0.87 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.8; 133.8; 133.4; 131.5; 130.6; 128.7; 128.2; 125.9; 125.5; 125.4; 123.9; 123.4; 72.2; 32.2; 31.4; 28.7; 22.5; 14.0. HR-ESI-MS: 277.1563 ($C_{18}H_{22}NaO^+$; calc. 277.1563).

*(2*E*)-1-Phenyloct-2-en-1-ol* (**6d**) [17a]. From **5d** (100 mg, 0.494 mmol) by *GP 4*. Yield: 95 mg (94%). IR ($CHCl_3$): 3378, 3062, 3028, 2957, 2927, 2857, 1666, 1619, 1602, 1492, 1452, 1378, 1194, 1089, 1069, 1004, 972, 914, 838, 699, 634. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.27 (*m*, 4 H); 7.29–7.27 (*m*, 1 H); 5.81–5.73 (*m*, 1 H); 5.69–5.63 (*m*, 1 H); 5.17 (*d*, *J* = 6.4, 1 H); 2.08 (*q*, *J* = 7.0, 2 H); 1.95 (br. *s*, OH); 1.43–1.25 (*m*, 6 H); 0.88 (*t*, *J* = 6.8, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.4; 132.9; 132.1; 128.4; 127.4; 126.1; 75.2; 32.1; 31.4; 28.7; 22.5; 14.0. HR-ESI-MS: 227.1405 ($C_{14}H_{20}NaO^+$; calc. 227.1406).

*(2*E*)-1-Phenylhept-2-en-1-ol* (**6e**) [17b]. To a stirred and degassed soln. of **2d** (0.2 g, 1.49 mmol) and hex-1-ene (0.251 g, 2.98 mmol, 2.0 equiv.) in dry CH_2Cl_2 (10 ml) was added the *Grubbs* second-generation (G-II) catalyst (2.5 mg, 0.00298 mmol, 0.2 mol%) at r.t., and the mixture was heated at 40° for 12 h. After cooling to r.t., it was filtered through a small pad of SiO_2, and the filtrate was concentrated. The residue was purified by CC (SiO_2; AcOEt 17:3) to give **6e** (0.198 g, 70%). Colorless oil. IR ($CHCl_3$): 3410, 3013, 2958, 2930, 2859, 1666, 1494, 1455, 1380, 1091, 970, 840, 700, 670. ^{1}H-NMR (400 MHz, $CDCl_3$):

7.40–7.32 (*m*, 4 H); 7.29–7.24 (*m*, 1 H); 5.79–5.72 (*m*, 1 H); 5.68–5.62 (*m*, 1 H); 5.15 (*d*, *J* = 6.6, 1 H); 2.08–2.02 (*m*, 2 H); 1.93 (br. *s*, OH); 1.39–1.28 (*m*, 4 H); 0.88 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.3; 132.7; 132.1; 128.4; 127.4; 126.1; 75.1; 31.8; 31.2; 22.2; 13.9. HR-ESI-MS: 213.1249 ($C_{13}H_{18}NaO^+$; calc. 213.1250).

*(2*E*)-1-(2-Methoxyphenyl)oct-2-en-1-ol* (**6f**). To a soln. of **7** (0.5 g, 2.94 mmol) in dry CH_2Cl_2 (20 ml) was added DIBAL-H (1.75M soln. in hexane; 2.0 ml, 3.53 mmol, 1.2 equiv.) dropwise over 10 min at −78°. The mixture was stirred for 1 h, and the reaction was quenched with sat. aq. sodium potassium tartrate soln. (8 ml), and the mixture was stirred for 1 h at r.t. The aq. layer was extracted with CH_2Cl_2 (3 × 15 ml), and the combined org. layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated to give the corresponding aldehyde (0.5 g), which was used directly in the next reaction.

To a stirred soln. of the above aldehyde (0.5 g) in dry THF (20 ml) was added freshly prepared 2-MeO–C_6H_4MgBr (0.5M in THF; 8.8 ml; 4.41 mmol, 1.5 equiv.) at 0°, and the mixture was stirred for 2 h. The reaction was then quenched with sat. aq. NH_4Cl. The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 9:1) to give **6f** (0.537 g, 78%). Colorless oil. IR ($CHCl_3$): 3411, 2957, 2927, 2857, 1668, 1601, 1491, 1465, 1439, 1287, 1242, 1187, 1088, 1051, 1031, 972, 671. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.23 (*m*, 2 H); 6.97–6.94 (*m*, 1 H); 6.89 (*d*, *J* = 8.2, 1 H); 5.80–5.68 (*m*, 2 H); 5.35 (*t*, *J* = 5.4, 1 H); 3.86 (*s*, 3 H); 2.78 (*d*, *J* = 5.7, OH); 2.07–2.02 (*m*, 2 H); 1.42–1.25 (*m*, 6 H); 0.88 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 156.7; 132.2; 131.5; 130.9; 128.5; 127.3; 120.8; 110.7; 71.7; 55.3; 32.2; 31.4; 28.8; 22.5; 14.0. HR-ESI-MS: 257.1516 ($C_{15}H_{22}NaO_2^+$; calc. 257.1512).

2,3-Dihydroxy-1-(4-methoxyphenyl)octan-1-one (**8a**) *and 1-(4-Methoxyphenyl)octane-1,2,3-triol* (**9a**). From **6a** (120 mg, 0.512 mmol) by *GP 2*. Yield: 58.6 mg (43%) of **8a** as colorless solid and 28.6 mg (21%) of **9a** as colorless oil.

Data of **8a**. M.p. 88–90°. IR ($CHCl_3$): 3412, 2930, 2857, 1674, 1602, 1575, 1514, 1464, 1313, 1260, 1175, 1134, 1097, 1029, 981, 829, 609. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88 (*d*, *J* = 8.9, 2 H); 6.97 (*d*, *J* = 8.9, 2 H); 4.95 (*d*, *J* = 3.9, 1 H); 3.99–3.98 (*m*, 1 H); 3.88 (*s*, 3 H); 1.85 (br. *s*, OH); 1.72–1.65 (*m*, 2 H); 1.62 (br. *s*, OH); 1.55–1.23 (*m*, 6 H); 0.89–0.83 (*t*, *J* = 6.8, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 198.4; 164.2; 130.9; 126.4; 114.2; 74.9; 73.3; 55.6; 34.8; 31.7; 25.6; 22.6; 14.0. HR-ESI-MS: 289.1403 ($C_{15}H_{22}NaO_4^+$, calc. 289.1410).

Data of **9a**. IR ($CHCl_3$): 3409, 2954, 2932, 2859, 1613, 1515, 1464, 1304, 1250, 1177, 1133, 1036, 832, 774. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 2:1): 7.30 (*dd*, *J* = 8.6, 4.4, 4 H); 6.88 (*dd*, *J* = 8.7, 2.6, 4 H); 4.89 (*d*, *J* = 3.5, 1 H); 4.75 (*d*, *J* = 6.04, 1 H); 3.80 (*s*, 6 H); 3.62 (br. *s*, 2 OH); 3.51–3.45 (*m*, 4 H); 1.56–1.33 (*m*, 4 H); 1.29–1.18 (*m*, 12 H); 0.90–0.79 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.4; 132.8; 127.9; 127.6; 113.95; 113.92; 76.8; 75.3; 73.7; 72.9; 71.5; 55.3; 34.4; 32.5; 31.7; 31.68; 25.5; 25.3; 22.5; 14.0. HR-ESI-MS: 291.1565 ($C_{15}H_{24}NaO_4^+$; calc. 291.1567).

1-(4-Chlorophenyl)-2,3-dihydroxyoctan-1-one (**8b**) *and 1-(4-Chlorophenyl)octane-1,2,3-triol* (**9b**). From **6b** (50 mg, 0.209 mmol) by *GP 2*. Yield: 22.7 mg (40%) of **8b** and 20.0 mg (35%) of **9b**. Colorless oils.

Data of **8b**. IR ($CHCl_3$): 3446, 2929, 2858, 1683, 1592, 1490, 1402, 1264, 1093, 1015, 982, 911, 852. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.88 (*d*, *J* = 8.6, 2 H); 7.48 (*d*, *J* = 8.6, 2 H); 4.94 (*d*, *J* = 4.1, 1 H); 3.89–3.87 (*m*, 2 H); 1.84 (br. *s*, OH); 1.74–1.72 (*m*, 2 H); 1.68–1.27 (*m*, 6 H); 0.90 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 199.2; 140.5; 132.1; 129.9; 129.3; 75.5; 72.9; 34.6; 31.7; 25.5; 22.6; 14.0. HR-ESI-MS: 293.0912 ($C_{14}H_{19}ClNaO_3^+$; calc. 293.0915).

Data of **9b**. IR ($CHCl_3$): 3391, 2925, 289, 1649, 1598, 1490, 1467, 1197, 1129, 1089, 825, 701, 623. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 7.38–7.30 (*m*, 8 H); 4.94–4.91 (*m*, 1 H); 4.81–4.77 (*m*, 1 H); 3.88–3.85 (*m*, OH); 3.72–3.42 (*m*, 4 H); 3.11–3.08 (*m*, 2 OH); 2.94–2.92 (*m*, OH); 2.51–2.49 (*m*, OH); 1.89–1.86 (*m*, OH); 1.56–1.19 (*m*, 16 H); 0.89–0.82 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.28; 139.26; 133.7; 133.4; 128.63; 128.6; 128.1; 127.4; 76.1; 75.7; 75.3; 75.0; 71.7; 70.2; 34.2; 33.6; 31.7; 31.6; 25.3; 25.2; 22.5; 14.0. HR-ESI-MS: 295.1073 ($C_{14}H_{21}ClNaO_3^+$; calc. 295.1071).

2,3-Dihydroxy-1-(naphthalen-1-yl)octan-1-one (**8c**) *and 1-(Naphthalen-1-yl)octane-1,2,3-triol* (**9c**). From **6c** (52 mg, 0.204 mmol) by *GP 2* 21.1 mg (36%) of **8c** and 16.5 mg (28%) of **9c**. Colorless oils.

Data of **8c**. IR ($CHCl_3$): 3439, 3010, 2928, 2856, 1689, 1593, 1509, 1464, 1410, 1382, 1281, 1246, 1135, 1065, 945, 775, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.39 (*d*, *J* = 8.3, 1 H); 8.04 (*d*, *J* = 8.3, 1 H); 7.89 (*d*,

$J = 8.5$, 1 H); 7.71 (*dd*, $J = 7.2$, 1.1, 1 H); 7.63–7.51 (*m*, 3 H); 5.04 (*d*, $J = 2.8$, 1 H); 4.13–4.09 (*m*, 1 H); 3.77 (br. *s*, OH); 1.80 (br. *s*, OH); 1.65–1.61 (*m*, 2 H); 1.42–1.21 (*m*, 6 H); 0.85 (*t*, $J = 6.8$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 204.1; 134.0; 133.2; 132.9; 130.3; 128.4; 128.2; 126.92; 126.87; 125.5; 124.2; 77.3; 72.8; 34.7; 31.6; 25.4; 22.5; 14.0. HR-ESI-MS: 309.1464 ($C_{18}H_{22}NaO_3^+$; calc. 309.1461).

Data of **9c**. IR ($CHCl_3$): 3429, 3013, 2930, 2858, 1598, 1513, 1456, 1261, 1124, 1058, 872, 669. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 2:1): 8.08 (*d*, $J = 7.9$, 1 H); 7.99–7.95 (*m*, 1 H); 7.89–7.86 (*m*, 2 H); 7.84 (*d*, $J = 7.1$, 2 H); 7.74 (*d*, $J = 7.2$, 1 H); 7.68 (*d*, $J = 7.0$, 2 H); 7.54–7.46 (*m*, 5 H); 5.80–5.78 (*m*, 1 H); 5.61 (*d*, $J = 4.6$, 1 H); 3.82–3.75 (*m*, 3 H); 3.59–3.57 (*m*, 1 H); 1.59–1.50 (*m*, 4 H); 1.33–1.03 (*m*, 12 H); 0.88 (*t*, $J = 6.7$, 3 H); 0.83 (*t*, $J = 6.9$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.3; 136.1; 133.8; 133.6; 130.65; 130.1; 129.0; 128.5; 128.3; 126.4; 126.3; 125.7; 125.6; 125.43; 125.4; 124.6; 123.5; 122.9; 122.7; 75.6; 74.9; 74.0; 72.4; 72.2; 70.2; 34.3; 33.8; 31.6; 31.5; 25.3; 25.1; 22.5; 22.4; 14.0; 13.9. HR-ESI-MS: 311.1618 ($C_{18}H_{24}NaO_3^+$; 311.1618).

2,3-Dihydroxy-1-phenyloctan-1-one (**8d**) *and 1-Phenyloctane-1,2,3-triol* (**9d**). From **6d** (50 mg, 0.245 mmol) by *GP 2*. Yield: 26 mg (45%) of **8d** and 18.1 mg (31%) of **9d**. Colorless oils.

Data of **8d** [8b]. IR ($CHCl_3$): 3432, 3020, 2927, 2856, 1695, 1451, 1416, 1318, 1267, 1177, 1071, 981, 911, 713, 668. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.89 (*dd*, $J = 8.5, 1.3$, 2 H); 7.63–7.61 (*m*, 1 H); 7.53–7.50 (*m*, 2 H); 5.01–4.98 (*m*, 1 H); 3.94–3.92 (*m*, 2 H); 1.73 (br. *s*, OH); 1.72–1.66 (*m*, 2 H); 1.52–1.24 (*m*, 6 H); 0.90 (*t*, $J = 6.9$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 200.3; 134.0; 133.7; 128.9; 128.5; 75.4; 72.9; 34.7; 31.7; 25.5; 22.6; 14.0. HR-ESI-MS: 259.1307 ($C_{14}H_{20}NaO_3^+$; calc. 259.1305).

Data of **9d**. IR ($CHCl_3$): 3412, 3032, 2955, 2931, 2860, 1653, 1495, 1455, 1134, 1061, 917, 841, 702, 670. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1): 7.41–7.28 (*m*, 10 H); 4.95 (*d*, $J = 4.5$, 1 H); 4.81 (*d*, $J = 5.6$, 1 H); 3.77–3.52 (*m*, 4 H); 1.61–1.15 (*m*, 22 H); 0.90–0.84 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.7; 140.6; 128.6; 128.56; 128.1; 127.8; 126.7; 126.0; 77.2; 76.9; 75.7; 75.4; 71.8; 70.2; 34.3; 33.8; 31.7; 31.6; 25.24; 25.2; 22.5; 14.0. HR-ESI-MS: 261.1461 ($C_{14}H_{22}NaO_3^+$; calc. 261.1461).

2,3-Dihydroxy-1-phenylheptan-1-one (**8e**) *and 1-Phenylheptane-1,2,3-triol* (**9e**). From **6e** (100 mg, 0.525 mmol) by *GP 2*. Yield: 49.0 mg (42%) of **8e** and 37.7 mg (32%) of **9e**. Colorless oils.

Data of **8e** [7]. IR ($CHCl_3$): 3451, 3064, 3014, 2957, 2932, 2861, 1683, 1599, 1580, 1450, 1404, 1305, 1269, 1240, 1133, 1089, 1002, 978, 854, 691. ^{1}H-NMR (400 MHz, $CDCl_3$/TMS): 7.89 (*dd*, $J = 8.5, 1.3$, 2 H); 7.65–7.61 (*m*, 1 H); 7.53–7.50 (*m*, 2 H); 5.01 (*dd*, $J = 5.5, 1.4$, 1 H); 3.97–3.93 (*m*, 2 H); 1.85–1.82 (*m*, OH); 1.77–1.72 (*m*, 2 H); 1.54–1.32 (*m*, 4 H); 0.93 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 200.3; 133.9; 133.7; 128.9; 128.4; 75.4; 72.9; 34.3; 27.9; 22.6; 14.0. HR-ESI-MS: 245.1153 ($C_{13}H_{18}NaO_3^+$; calc. 245.1148).

Data of **9e** [18]. IR ($CHCl_3$): 3392, 3062, 3031, 2955, 2931, 2871, 2857, 1636, 1493, 1466, 1454, 1324, 1270, 1198, 1130, 1052, 1021, 913, 849, 869, 794, 702. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 2:1): 7.38–7.27 (*m*, 10 H); 4.92 (*d*, $J = 4.1$, 1 H); 4.77 (*d*, $J = 5.9$, 1 H); 4.00–3.98 (br. *s*, OH); 3.70–3.62 (*m*, 2 H); 3.55–3.46 (*m*, 3 H); 3.28–3.13 (*m*, 2 H); 2.70–2.68 (*m*, OH); 2.07–2.04 (*m*, OH); 1.58–1.39 (*m*, 4 H); 1.38–1.19 (*m*, 8 H); 0.92–0.81 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.8; 140.7; 128.4; 127.9; 127.6; 126.7; 126.0; 76.9; 76.6; 75.5; 71.5; 70.2; 33.9; 33.3; 27.7; 27.6; 22.53; 22.5; 13.9. HR-ESI-MS: 247.1304 ($C_{13}H_{20}NaO_3^+$; calc. 247.1305).

2,3-Dihydroxy-1-(2-methoxyphenyl)octan-1-one (**8f**) *and 1-(2-Methoxyphenyl)octane-1,2,3-triol* (**9f**). From **6f** (50 mg, 0.213 mmol) by *GP 2*. Yield: 21.6 mg (38%) of **8f** and 18.9 mg (33%) of **9f**. Colorless oils.

Data of **8f** [8c]. IR ($CHCl_3$): 3445, 2930, 2858, 1668, 1560, 1487, 1469, 1293, 1247, 1165, 1135, 1090, 1021, 985, 646. ^{1}H-NMR (400 MHz, $CDCl_3$/TMS): 7.86 (*dd*, $J = 7.8, 1.8$, 1 H); 7.54 (*td*, $J = 7.8, 1.8$, 1 H); 7.09–7.05 (*m*, 1 H); 6.99 (*d*, $J = 8.4$, 1 H); 5.06 (*d*, $J = 0.8$, 1 H); 4.12 (br. *s*, OH); 3.91 (*s*, 3 H); 3.88–3.83 (*m*, 1 H); 1.79 (br. *s*, OH); 1.73–1.64 (*m*, 2 H); 1.52–1.25 (*m*, 6 H); 0.90 (*t*, $J = 6.9$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 201.6; 158.5; 134.9; 131.6; 123.9; 121.4; 111.4; 78.7; 71.8; 55.4; 35.2; 31.7; 25.5; 22.6; 14.0. HR-ESI-MS: 289.1417 ($C_{15}H_{22}NaO_4^+$; calc. 289.1410).

Data of **9f**. IR ($CHCl_3$): 3410, 2932, 2859, 1677, 1603, 1589, 1492, 1465, 1439, 1289, 1241, 1136, 1051, 1029, 938, 838. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 2:1): 7.47–7.42 (*m*, 2 H); 7.31–7.26 (*m*, 2 H); 7.03–6.99 (*m*, 2 H); 6.92–6.87 (*m*, 2 H); 5.20 (*d*, $J = 4.5$, 1 H); 5.00 (*d*, $J = 6.0$, 1 H); 3.86 (*s*, 3 H); 3.83 (*s*, 3 H); 3.76–3.73 (*m*, 2 H); 3.57 (*dd*, $J = 6.1, 2.0$, 2 H), 3.50–3.46 (*m*, 2 H); 2.62 (br. *s*, 4 OH); 1.61–1.16 (*m*, 16 H); 0.90–0.82 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 156.3; 156.0; 128.9;

128.0; 121.3; 120.9; 110.6; 110.3; 76.0; 73.4; 71.7; 70.5; 55.5; 55.3; 33.8; 33.7; 31.8; 31.7; 25.4; 25.3; 22.6; 22.5; 14.0. HR-ESI-MS: 291.1573 ($C_{15}H_{24}NaO_4^+$; calc. 291.1567).

*(2*S*,3*R*)-2,3-Dihydroxy-1-phenyloctan-1-one* ((−)-(2*S*,3*R*)-**8d**) *and 1-Phenyloctane-1,2,3-triol* (**9d**). To a mixture of $K_3Fe(CN)_6$ (484 mg, 1.47 mmol, 6.0 equiv.), K_2CO_3 (203 mg, 1.47 mmol, 6.0 equiv.), and $(DHQD)_2PHAL$ (3.8 mg, 0.0049 mmol, 2.0 mol%) in ^{t}BuOH/H_2O 1:1 (4.0 ml), cooled at 0°, was added $K_2OsO_4 \cdot 2\,H_2O$ (0.72 mg, 0.00196 mmol, 0.8 mol%), followed by $MeSO_2NH_2$ (46.6 mg, 0.490 mmol, 2.0 equiv.). After stirring for 5 min at 0°, **6d** (50 mg, 0.245 mmol) was added in one portion. The mixture was stirred at 0° for 48 h, and then the reaction was quenched with solid Na_2SO_3 (900 mg). The stirring was continued for additional 45 min, and the soln. was extracted with AcOEt (5 × 10 ml). The combined org. phases were washed with 2N KOH, H_2O, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 7:3) to give (2*S*,3*R*-**8d**, 26.6 mg, 46%), and further elution gave the triol **9d** (19.2 mg, 33%), both as colorless oil.

(2*S*,3*R*)-**8d**. $[\alpha]_D^{25} = -1.2$ ($c = 0.6$, $CHCl_3$). Other spectroscopic and analytical data were the same as those racemic **8d**. The ee (92%) was determined by converting to the acetonide and HPLC analysis (column, *CHIRALCEL OD-H*; eluent, hexane/^{i}PrOH 99:1; flow rate, 0.5 ml/min; UV detector, 254 nm; t_R (minor) 8.68 and (major) 9.88 min.

*(2*S*,3*R*)-2,3-Dihydroxy-1-phenylheptan-1-one* ((−)-(2*S*,3*R*)-**8e**) *and 1-Phenylheptane-1,2,3-triol* (**9e**). From **6e** (50 g, 0.263 mmol) by a similar procedure as described for (2*S*,3*R*)-**8d**. Yield: (25.1 mg (43%) of (2*S*,3*R*)-**8e** and 21.2 mg (36%) of **9e**. Colorless oil.

(2*S*,3*R*)-**8e**. $[\alpha]_D^{25} = -7.1$ ($c = 1.2$, $CHCl_3$). Other spectroscopic and anal. data were the same as those of racemic **8e**. The ee (96%) was determined by HPLC analysis (column, *CHIRALCEL OD-H*; eluent, hexane/^{i}PrOH 4:1; flow rate, 0.8 ml/min; UV detector, 254 nm; t_R (major) 6.55 and (minor) 8.02 min.

*(2*S*,3*R*)-2,3-Dihydroxy-1-(2-methoxyphenyl)octan-1-one* ((−)-(2*S*,3*R*)-**8f**) *and 1-(2-Methoxyphenyl)octane-1,2,3-triol* (**9f**). From **6f** (50 mg, 0.213 mmol) by a similar procedure as described for (2*S*,3*R*-**8d**). Yield: 23.3 mg (41%) of (2*S*,3*R*)-**8f** and 20.0 mg (35%) of **9f**. Colorless oils.

(2*S*,3*R*)-**8f**. $[\alpha]_D^{25} = -38.6$ ($c = 0.75$, $CHCl_3$). Other spectroscopic and anal. data were the same as those of racemic **8f**. The ee (94%) was determined by HPLC analysis (column, *CHIRALCEL OD-H*; eluent, hexane/^{i}PrOH 7:3; flow rate, 0.8 ml/min; UV detector, 254 nm; t_R (major) 6.29 and (minor) 8.48 min.

*(1*E*)-1-Phenylnon-1-en-3-ol* (**10**) [19]. To a stirred soln. of *cinnamaldehyde* (**13**; 0.5 g, 3.78 mmol) in dry THF (10 ml) was added freshly prepared (hexyl)MgBr (0.5M in THF; 11.4 ml, 5.68 mmol, 1.5 equiv.) at 0°, and the mixture was stirred for 2 h. The reaction was then quenched with sat. aq. NH_4Cl soln., and the mixture was extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 9:1) to give **10** (0.702 g, 85%). Colorless oil. IR ($CHCl_3$): 3428, 3062, 3027, 2955, 2930, 2858, 1607, 1495, 1464, 1455, 1379, 1277, 1178, 1070, 967, 891, 695, 668. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.37 (*m*, 2 H); 7.33–7.29 (*m*, 2 H); 7.25–7.21 (*m*, 1 H); 6.56 (*d*, $J = 15.9$, 1 H); 6.21 (*dd*, $J = 15.9$, 6.8, 1 H); 4.27 (*q*, $J = 6.5$, 1 H); 1.71–1.55 (*m*, 3 H); 1.45–1.19 (*m*, 8 H); 0.88 (*t*, $J = 6.9$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.7; 132.6; 130.2; 128.5; 127.6; 126.4; 73.1; 37.4; 31.8; 29.2; 25.4; 22.6; 14.1. HR-ESI-MS: 257.1300 ($C_{15}H_{22}KO^+$; calc. 257.1302).

*(3*E*)-1-Phenyldec-3-en-2-ol* (**11**). To a soln. of *ethyl (2*E*)-non-2-enoate* **14** (0.45 g, 2.44 mmol) in dry CH_2Cl_2 (20 ml) was added DIBAL-H (1.75M soln., in hexane, 1.7 ml, 2.94 mmol, 1.2 equiv.) dropwise over 10 min at −78°. The mixture was stirred for 1 h, and the reaction was quenched with sat. aq. sodium potassium tartrate soln. (8 ml), and the mixture was stirred for 1 h at r.t. The aq. layer was extracted with CH_2Cl_2 (3 × 15 ml), and the combined org. layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated to give the corresponding aldehyde (0.45 g), which was used directly in the next reaction.

To a stirred soln. of above aldehyde (0.45 g) in dry THF (20 ml) was added freshly prepared BnMgBr (0.5M in THF; 7.4 ml, 3.67 mmol, 1.5 equiv.) at 0°, and the mixture was stirred for 2 h. The reaction was then quenched with sat. aq. NH_4Cl soln., and the aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 9:1) to give **11** (0.391 g, 69%). Colorless oil. IR ($CHCl_3$): 3391, 3063, 3028, 2955, 2926, 2856, 1670, 1603, 1495, 1455, 1379, 1341, 1307, 1094, 1077, 1030, 967, 857, 828,

700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 – 7.29 (*m*, 2 H); 7.26 – 7.21 (*m*, 3 H); 5.68 – 5.61 (*m*, 1 H); 5.56 – 5.50 (*m*, 1 H); 4.27 (*q*, *J* = 6.5, 1 H); 2.81 (*qt*, *J* = 13.5, 6.5, 2 H); 2.02 (*q*, *J* = 7.0, 2 H); 1.37 – 1.25 (*m*, 8 H); 0.89 (*t*, *J* = 6.9, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.0; 132.5; 131.8; 129.6; 128.4; 126.4; 73.6; 44.2; 32.2; 31.7; 29.1; 28.8; 22.6; 14.1. HR-ESI-MS: 255.1723 ($C_{16}H_{24}NaO^+$; calc. 255.1719).

*(2*E,5R*)-5-{[(*tert*-Butyl)(dimethyl)silyl]oxy}-1-phenylhex-2-en-1-one* (**16**). To a soln. of *ethyl 3-{[(*tert*-butyl)dimethylsilyl]oxy}butanoate* (**15**; 0.5 g, 2.029 mmol) in dry CH_2Cl_2 (20 ml) at $-78°$ was added DIBAL-H (1.75M soln. in hexane, 1.3 ml, 2.27 mmol, 1.1 equiv.) dropwise over 10 min and stirred for 1 h. The reaction was then quenched with sat. aq. sodium potassium tartrate soln. (10 ml), and the mixture was stirred at r.t. for 1 h. The aq. layer was extracted with CH_2Cl_2 (3 × 20 ml), and the combined org. layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated to give the corresponding aldehyde (0.5 g), which was used directly in the next reaction.

To a stirred soln. of above aldehyde (0.5 g,) in dry toluene (25 ml) was added freshly prepared *Wittig* ylide $PhCOCH{=}PPh_3$ (1.93 g, 5.072 mmol, 2.5 equiv.) at r.t., and the mixture was heated to reflux for 12 h. H_2O (10 ml) was then added, and the soln. was extracted with AcOEt (3 × 20 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 19 : 1) to give **16** (0.519 g, 84%). Colorless oil. $[\alpha]_D^{25} = -3.2$ (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): 3059, 2956, 2929, 2894, 2857, 1672, 1655, 1625, 1599, 1578, 1472, 1463, 1448, 1376, 1361, 1333, 1310, 1234, 1199, 1132, 1089, 1004, 939, 901, 837, 806, 776, 695. ^{1}H-NMR (400 MHz, $CDCl_3$/TMS): 7.95 – 7.91 (*m*, 2 H); 7.57 – 7.53 (*m*, 1 H); 7.48 – 7.44 (*m*, 2 H); 7.08 – 7.00 (*m*, 1 H); 6.89 (*dt*, *J* = 15.4, 1.2, 1 H); 3.99 (*q*, *J* = 6.0, 1 H); 2.48 – 2.42 (*m*, 2 H); 1.19 (*d*, *J* = 6.1, 3 H); 0.86 (*s*, 9 H); 0.05 (*s*, 3 H); 0.03 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 190.7; 146.6; 137.9; 132.6; 128.50; 128.47; 127.8; 67.7; 43.1; 25.8; 23.9; 18.0; −4.6; −4.8. HR-ESI-MS: 327.1748 ($C_{18}H_{28}NaO_2Si^+$; calc. 327.1751).

*(2*E,5R*)-5-{[(*tert*-Butyl)(dimethyl)silyl]oxy}-1-phenylhex-2-en-1-ol* (**17**). To a stirred soln. of **16** (100 mg, 0.328 mmol) in MeOH (10 ml) was added $CeCl_3 \cdot 7\,H_2O$ (183 mg, 0.492 mmol, 1.5 equiv.), followed by $NaBH_4$ (14.9 mg, 0.393 mmol, 1.2 equiv.) at 0° and stirred for 1 h. H_2O (5 ml) was then added to the mixture, and the soln. was extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 9 : 1) to give **17** (99.7 mg, 99%). Colorless oil. $[\alpha]_D^{25} = -7.5$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3392, 3063, 3029, 2956, 2928, 2892, 2857, 1667, 1602, 1493, 1471, 1462, 1407, 1376, 1217, 1132, 1089, 1003, 939, 893, 875, 835, 809, 774, 699, 666. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39 – 7.33 (*m*, 4 H); 7.29 – 7.27 (*m*, 1 H); 5.78 – 5.71 (*m*, 2 H); 5.17 (*d*, *J* = 5.6, 1 H); 3.87 – 3.81 (*m*, 1 H); 2.24 – 2.13 (*m*, 2 H); 1.96 (br. *s*, OH); 1.12 (*dd*, *J* = 6.1, 1.1, 3 H); 0.88 (*s*, 9 H); 0.04 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.2; 134.4; 134.35; 129.3; 129.1; 128.44; 128.4; 127.5; 127.48; 126.2; 126.1; 75.2; 75.1; 68.4; 68.3; 42.5; 25.9; 23.5; 18.1; −4.5; −4.7. HR-ESI-MS: 329.1910 ($C_{18}H_{30}NaO_2Si^+$; calc. 329.1907).

*(2*E,5R*)-1-Phenylhex-2-ene-1,5-diol* (**12**). To a stirred soln. of **17** (100 mg, 0.326 mmol) in THF (10 ml) was added Bu_4NF (1M in THF; 0.49 ml, 0.489 mmol, 1.5 equiv.) at 0° and stirred for 6 h. H_2O (5 ml) was then added to the mixture, and the soln. was extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by CC (SiO_2; PE/AcOEt 1 : 1) to give **12** (60.2 mg, 96%). Colorless oil. $[\alpha]_D^{25} = -20.5$ (*c* = 1.45, $CHCl_3$). IR ($CHCl_3$): 3398, 2969, 2927, 1667, 1493, 1454, 1426, 1374, 1314, 1127, 1071, 1016, 971, 937, 834, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35 – 7.29 (*m*, 4 H); 7.26 – 7.22 (*m*, 1 H); 5.75 – 5.70 (*m*, 2 H); 5.12 (*dd*, *J* = 6.4, 4.8, 1 H); 3.84 – 3.77 (*m*, 1 H); 2.22 – 2.02 (*m*, 2 H); 1.15 (*d*, *J* = 6.2, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.0; 135.7; 135.6; 128.4; 127.7; 127.4; 127.35; 126.2; 126.1; 74.8; 74.6; 67.1; 67.06; 41.9; 41.5; 22.9; 22.6. HR-ESI-MS: 215.1044 ($C_{12}H_{16}NaO_2^+$; calc. 215.1043).

1-Phenylnonane-1,2,3-triol (**18**). From **10** (50 mg, 0.229 mmol) by *GP 2*. Yield: 46.2 mg (80%). Colorless solid. M.p. 58 – 60°. IR ($CHCl_3$): 3429, 3064, 3015, 2930, 2858, 1650, 1494, 1455, 1066, 917, 845, 702, 669. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1 : 1): 7.37 – 7.27 (*m*, 10 H); 4.89 (*t*, *J* = 3.1, 1 H); 4.76 – 4.74 (*m*, 1 H); 3.75 – 3.45 (*m*, 5 H); 3.23 (*d*, *J* = 5.5, 1 H); 3.06 (*d*, *J* = 5.6, 1 H); 2.98 (*d*, *J* = 5.4, 1 H); 2.62 (*d*, *J* = 6.6, 1 H); 2.01 (br. *s*, 1 H); 1.56 – 1.45 (*m*, 6 H); 1.28 – 1.22 (*m*, 14 H); 0.90 – 0.84 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.9; 140.8; 128.5; 128.0; 127.8; 126.7; 126.3; 76.8; 75.6; 73.6; 73.2; 71.6; 34.3; 32.6; 31.73; 31.7; 29.2; 29.1; 25.8; 25.5; 22.6; 22.5; 14.1; 14.0. HR-ESI-MS: 275.1619 ($C_{15}H_{24}NaO_3^+$; calc. 275.1618).

1-Phenyldecane-2,3,4-triol (**19**). From **11** (50 mg, 0.215 mmol) by *GP 2*. Yield: 44.7 mg (78%). Colorless solid. M.p. 83–85°. IR ($CHCl_3$): 3412, 3065, 3018, 2929, 2858, 1603, 1523, 1496, 1455, 1379, 1127, 1049, 929, 853, 701, 669. ^{1}H-NMR (400 MHz, $CDCl_3$/TMS; mixture of diastereoisomers, *ca.* 1:1): 7.35–7.23 (*m*, 10 H); 4.00–3.96 (*m*, 4 H); 3.69–3.72 (*m*, 1 H); 3.36–3.30 (*m*, 2 H); 2.97–2.72 (*m*, 8 H); 2.04–2.01 (*m*, 1 H); 1.63–1.27 (*m*, 20 H); 0.91–0.86 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.0; 137.8; 129.4; 129.3; 128.7; 128.6; 126.6; 126.58; 75.3; 75.1; 74.3; 74.1; 73.2; 70.7; 40.3; 39.8; 33.8; 33.6; 31.8; 31.7; 29.3; 29.2; 25.6; 25.5; 22.6; 22.56; 14.1; 14.0. HR-ESI-MS: 289.1772 ($C_{16}H_{26}NaO_3^+$; calc. 289.1774).

*(2*S*,3*R*,5*R*)-2,3,5-Trihydroxy-1-phenylhexan-1-one* (**20**) *and (5*R*)-1-Phenylhexane-1,2,3,5-tetrol* (**21**). From **12** (60 mg, 0.312 mmol) by a similar procedure as described for (2*S*,3*R*)-**8d**. Yield: 47.6 mg (68%) of **20** and 12.7 mg (18%) of **21**. Colorless oils.

Data of **20**. $[\alpha]_D^{25} = -7.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3338, 3252, 3020, 2928, 1714, 1688, 1577, 1451, 1412, 1331, 1141, 1075, 979, 668. ^{1}H-NMR (400 MHz, $CDCl_3$/TMS; mixture of diastereoisomers, > 9:1): 7.93 (*d*, *J* = 9.8, 2 H); 7.65–7.58 (*m*, 1 H); 7.52–7.48 (*m*, 2 H); 5.01 (br. *s*, 1 H); 4.28–4.23 (*m*, 1 H); 4.15–4.03 (*m*, 1 H); 3.96–3.91 (*m*, 1 H); 2.86 (br. *s*, OH); 2.40 (br. *s*, OH); 1.89–1.72 (*m*, 2 H); 1.24 (*d*, *J* = 6.2, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 200.0; 134.1; 133.8; 128.9; 128.6; 75.7; 72.9; 67.8; 41.9; 24.2. HR-ESI-MS: 247.0942 ($C_{12}H_{16}NaO_4^+$; calc. 247.0941).

Data of **21**. IR ($CHCl_3$): 3399, 3033, 2968, 2925, 1645, 1494, 1453, 1427, 1378, 1321, 1199, 1140, 1062, 910, 840, 734, 702, 649. ^{1}H-NMR (400 MHz, $CDCl_3$; mixture of diastereoisomers, *ca.* 1:1.5): 7.36–7.28 (*m*, 10 H); 4.90–4.87 (*m*, 1 H); 4.79–4.76 (*m*, 1 H); 4.03–3.95 (*m*, 4 H); 3.72–3.75 (*m*, 2 H); 3.52–3.45 (*m*, 4 H); 1.80–1.76 (*m*, 4 H); 1.48–1.41 (*m*, 4 H); 1.14–1.11 (*m*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.9; 140.6; 128.53; 128.5; 128.0; 127.7; 126.8; 126.1; 77.8; 76.1; 75.2; 71.8; 71.0; 68.1; 41.8; 41.2; 24.2; 24.0. HR-ESI-MS: 249.1098 ($C_{12}H_{18}NaO_4^+$; calc. 249.1097).

REFERENCES

[1] a) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483; b) A. B. Zaitsev, H. Adolfsson, *Synthesis* **2006**, 1725; c) H. C. Kolb, K. B. Sharpless, in 'Transition Metals for Organic Synthesis', Vol. 2, Eds. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 2004, p. 275.

[2] B. B. Lohray, V. Bhushan, R. K. Kumar, *J. Org. Chem.* **1994**, *59*, 1375; X. Lu, Z. Xu, G. Yang, *Org. Proc. Res. Dev.* **2000**, *4*, 575; T. Watanabe, Y. Ohashi, R. Yoshino, N. Komano, M. Eguchi, S. Maruyama, T. Ishikawa, *Org. Biomol. Chem.* **2003**, *1*, 3024; J. Collins, M. Drouin, X. Sun, U. Rinner, T. Hudlicky, *Org. Lett.* **2008**, *10*, 361; W. Gong, T. V. Rajan Babu, *Chem. Sci.* **2013**, *4*, 3979.

[3] K. B. Sharpless, A. O. Chong, K. Oshima, *J. Org. Chem.* **1976**, *41*, 177; G. Li, H.-T. Chang, K. B. Sharpless, *Angew. Chem., Int. Ed.* **1996**, *35*, 451; J. Rudolph, P. C. Sennhenn, C. P. Vlaar, K. B. Sharpless, *Angew. Chem., Int. Ed.* **1996**, *35*, 2810; L. Harris, S. P. H. Mee, R. H. Furneaux, G. J. Gainsford, A. Luxenburger, *J. Org. Chem.* **2011**, *76*, 358.

[4] C. Döbler, G. M. Mehltretter, U. Sundermeier, M. Eckert, H.-C. Militzer, M. Beller, *Tetrahedron Lett.* **2001**, *42*, 8447; J. Muldoon, S. N. Brown, *Org. Lett.* **2002**, *4*, 1043.

[5] S. Devari, R. Deshidi, M. Kumar, A. Kumar, S. Sharma, M. Rizvi, M. Kushwaha, A. P. Gupta, B. A. Shah, *Tetrahedron Lett.* **2013**, *54*, 6407.

[6] R. A. Fernandes, P. Kattanguru, *Asian J. Org. Chem.* **2013**, *2*, 74.

[7] R. A. Bhunnoo, Y. Hu, D. I. Lainé, R. C. D. Brown, *Angew. Chem., Int. Ed.* **2002**, *41*, 3479.

[8] a) N. Yoshikawa, N. Kumagai, S. Matsunaga, G. Moll, T. Ohshima, T. Suzuki, M. Shibasaki, *J. Am. Chem. Soc.* **2001**, *123*, 2466; b) N. Kumagai, S. Matsunaga, N. Yoshikawa, T. Ohshima, M. Shibasaki, *Org. Lett.* **2001**, *3*, 1539; c) N. Kumagai, S. Matsunaga, T. Kinoshita, S. Harada, S. Okada, S. Sakamoto, K. Yamaguchi, M. Shibasaki, *J. Am. Chem. Soc.* **2003**, *125*, 2169.

[9] T. Mugishima, M. Tsuda, Y. Kasai, H. Ishiyama, E. Fukushi, J. Kawabata, M. Watanabe, K. Akao, J. Kobayashi, *J. Org. Chem.* **2005**, *70*, 9430.

[10] a) J. Yin, C. E. Gallis, J. D. Chisholm, *J. Org. Chem.* **2007**, *72*, 7054; b) A. Bouziane, B. Carboni, C. Bruneau, F. Carreaux, J.-L. Renaud, *Tetrahedron* **2008**, *64*, 11745.

[11] a) A. P. Beracierta, D. A. Whiting, *J. Chem. Soc., Perkin Trans 1* **1978**, 1257; b) S.-W. Lee, G. Li, K.-S. Lee, D.-K. Song, J.-K. Son, *Arch. Pharm. Res.* **2003**, *26*, 591.

[12] G.-L. Zhao, P. Dziedzic, I. Ibrahem, A. Córdova, *Synlett* **2006**, 3521.
[13] a) M. H. Delton, G. U. Yuen, *J. Org. Chem*. **1968**, *33*, 2473; b) Z. Wang, Y.-T. Cui, Z.-B. Xu, J. Qu, *J. Org. Chem*. **2008**, *73*, 2270.
[14] M. A. A. Rahman, S.-S. Moon, *Arch. Pharm. Res.* **2007**, *30*, 1374.
[15] X. Hao, T. Nguyen, D. B. Kearns, C. C. Arpin, R. Fall, T. Sammakia, *Bioorg. Med. Chem. Lett*. **2011**, *21*, 5583.
[16] a) J.-R. Labrosse, P. Lhoste, D. Sinou, *J. Org. Chem*. **2001**, *66*, 6634; b) Y. Zhou, T. Lecourt, L. Micouin, *Adv. Synth. Catal*. **2009**, *351*, 2595; c) M. Bhanuchandra, M. R. Kuram, A. K. Sahoo, *Org. Biomol. Chem*. **2012**, *10*, 3538.
[17] a) Y. Kobayashi, R. Mizojiri, E. Ikeda, *J. Org. Chem*. **1996**, *61*, 5391; b) A. E. Lurain, P. J. Carroll, P. J. Walsh, *J. Org. Chem*. **2005**, *70*, 1262; c) B. C. Raju, P. Suman, *Chem. – Eur. J.* **2010**, *16*, 11840.
[18] G. Fouche, R. M. Horak, O. Meth-Cohn, *J. Chem. Soc., Chem. Commun.* **1993**, 119.
[19] C. Morrill, R. H. Grubbs, *J. Am. Chem. Soc.* **2005**, *127*, 2842.
[20] A. Fernández-Mateos, S. E. Madrazo, P. H. Teijón, R. R. González, *Eur. J. Org. Chem*. **2010**, 856.
[21] R. A. Fernandes, S. V. Mulay, *J. Org. Chem.* **2010**, *75*, 7029.

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