

100. Synthesis of Chiral 12-Phenyl(²H)dodecanoic Acids: Useful Metabolic Probes for the Biosynthesis of 1-Alkenes from Fatty Acids

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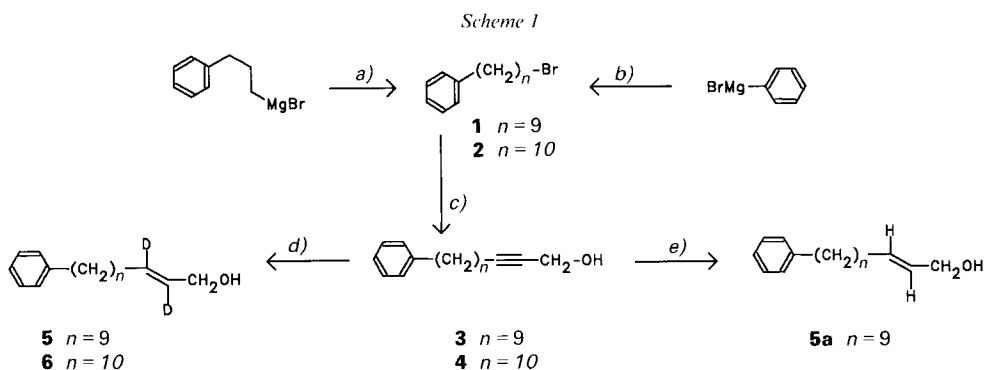
The synthesis of chiral 12-phenyl(²H)dodecanoic acids as metabolic probes for the evaluation of the stereochemical course of the biosynthesis of 1-alkenes from fatty acids in plants and insects is described. The diastereoisomeric (2*R*,3*R*)- or (2*S*,3*S*)-12-phenyl(2,3-²H₂)dodecanoic acids **11** are obtained in high chemical and optical yield (> 97% e.e.) from the readily available (*E*)-12-phenyl(2,3-²H₂)dodec-2-enoic acid (**10**) or (*E*)-12-phenyldodec-2-enoic acid (**10a**) by microbial reduction with wet packed cells of *Clostridium tyrobutyricum* in either ²H₂O or H₂O buffer. (2*R*)- and (2*S*)-12-phenyl(2-²H)dodecanoic acids **9** (> 97% e.e.) are accessible from the allylic alcohol **6** via Sharpless epoxidation with (+)-L- or (–)-D-diethyl tartrate. Synthetic routes to the (*E*)- and (*Z*)-11-phenyl(1-²H) undec-1-enes **16** and **16a** as reference compounds are also included.

Introduction. – The vinyl group is a widespread structural element of numerous natural products like, e.g., porphyrins, terpenoids, simple olefins, pheromones, or polyacetylenes. Notwithstanding its nearly ubiquitous presence in all kinds of natural products, surprisingly little is known about its biosynthesis. In spite of detailed studies in the field of porphyrins [1] and experimental evidence for carboxylic acids being precursors in the case of the polyacetylenes [2] and olefins, there exists no profound mechanistic study on the stereochemical course of the biosynthesis of 1-alkenes from fatty-acid precursors.

Recently, we have shown, that all previous biosynthetic hypotheses proposing paths *via* intermediates of the β -oxidation cycle are incorrect; instead of the postulated 3-hydroxy-, 3-oxo- or 2-alkenoic acids, the biosynthesis of 1-alkenes requires the nonfunctionalized free fatty acids as precursors [3]. These results were obtained with germinating seeds of *Carthamus tinctorius* (dyers thistle) which produce high amounts of vinylic C₁₅- and C₁₇ polyolefins. As precursors, we used either ²H-labelled linolenic acids or, with benefit, 12-phenyl(²H)dodecanoic acids as artificial substitutes for the natural substrates. Such aromatic acids are rapidly incorporated and smoothly converted into the corresponding 11-phenyl(²H)undec-1-enes which provide excellent mass-spectroscopic properties for their unambiguous identification among other hydrocarbons. Since 12-phenyldodecanoic acids are resistant towards autooxidation, readily available by synthesis, and effective substitutes for linolenic – or linoleic acid, they were further used as metabolic probes to unravel the stereochemical course of the biosynthesis of 1-alkenes from fatty acids in the plant and animal kingdom.

We now report an efficient and highly enantioselective synthesis of chiral 12-phenyl- (^3H)dodecanoic acids which may serve as convenient metabolic probes of broad applicability to follow the stereochemical course of enzymatic activities at the polar head of poly-unsaturated C_{18} fatty acids.

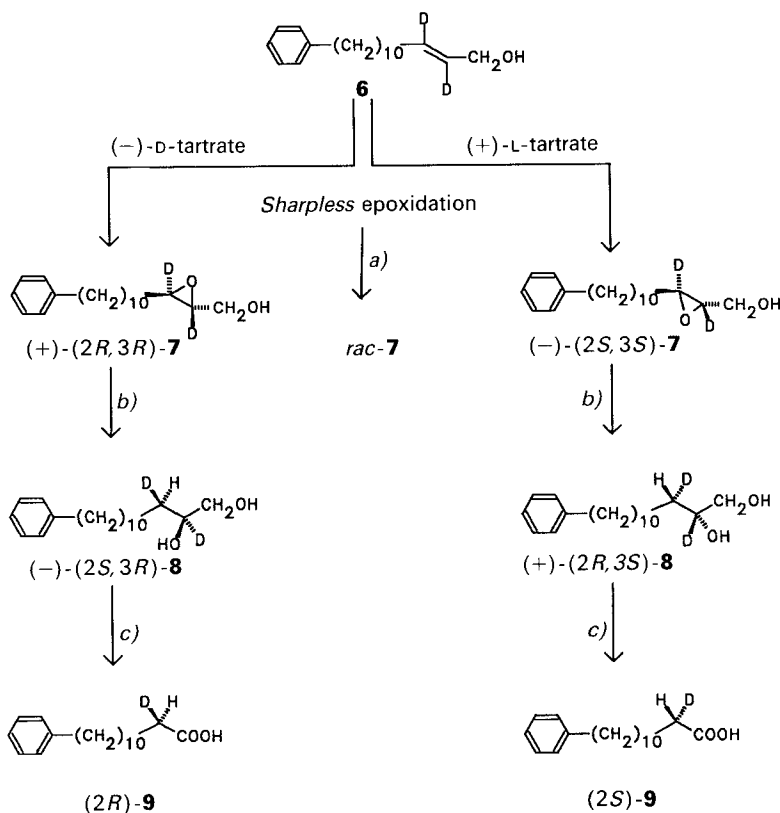
^3H -Substituted 12-Phenyldodecanoic Acids. – The preparation of the required 12-phenyl- or 13-phenyl-alk-2-en-1-ols **5**, **5a**, and **6** is accomplished through the sequence of reactions outlined in *Scheme 1*. Coupling of (3-phenylpropyl)magnesium bromide or phenylmagnesium bromide with either 1,6-dibromohexane or 1,10-dibromodecane according to [4] gives the terminal (bromoalkyl)benzenes **1** and **2** along with some 1,12-dipenyldodecane or 1,10-diphenyldecane, respectively. The alkynols **3** and **4** are then obtained in high yields on treatment of **1** or **2** with {3-[(tetrahydropyran-2-yl)oxy]prop-1-ynyl}lithium and subsequent deblocking of the alcohol moiety.



a) $\text{Br(CH}_2\text{)}_6\text{Br}$, Li_2CuCl_4 . *b)* $\text{Br(CH}_2\text{)}_{10}\text{Br}$, Li_2CuCl_4 . *c)* 1. $\text{Li-C}\equiv\text{C-CH}_2\text{O-THP}$, 2. $\text{MeOH/Py}\cdot\text{TsOH}$. *d)* 1. LiAlH_4 , 2. $^2\text{H}_2\text{O}$. *e)* 1. LiAlH_4 , 2. H_2O .

Due to lacking regioselectivity, the conventional introduction of a ^3H -label *via* LiAlH_4 reduction of the alkynols **3** and **4** followed by hydrolysis with $^2\text{H}_2\text{O}$ is not satisfactory (75% of ^3H at C(3) and 25% of ^3H at C(2)). However, simultaneous labelling of C(2) and C(3) of the alkynols **3** and **4** using LiAl^3H_4 for reduction and $^2\text{H}_2\text{O}$ for hydrolysis is readily achieved ($\geq 99\%$ ^3H at both C-atoms of **5** and **6**) and circumvents the necessity of regiospecific labelling. Then, the resulting (*E*)-alkenol **6** is subjected to a catalytical *Sharpless* epoxidation [5] with either (+)-L or (–)-D-diethyl tartrate as chiral ligands yielding the two diastereoisomeric epoxyalcohols (2*R*,3*R*)- and (2*S*,3*S*)-**7** (*Scheme 2*) in $\geq 97\%$ enantiomeric excess (determined by $^1\text{H-NMR}$ analysis of the corresponding *Mosher* esters [6]). After addition of $\text{Ti}(\text{i-PrO})_4$ to (2*R*,3*R*)- or (2*S*,3*S*)-**7**, the resulting alkoxytitanates are reduced with LiBH_4 [7] to the 1,2-diols (2*S*,3*R*)- and (2*R*,3*S*)-**8** which can be oxidatively cleaved to the epimeric ^3H -substituted acids (2*R*)- and (2*S*)-**9**, respectively. Final $^1\text{H-NMR}$ analysis of their mandelate diesters indicate both acids to be at least $\geq 97\%$ enantiomerically pure (*vide infra*). Thus, both steps (reduction and oxidation) proceed virtually without racemization.

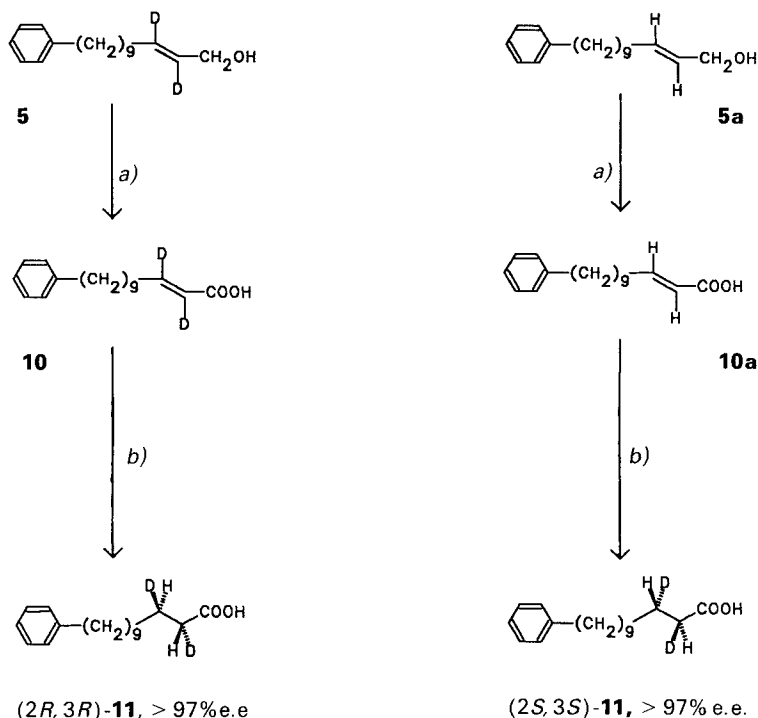
Scheme 2



a) 3-ClC₆H₄CO₃H. b) 1. Ti(i-PrO)₄, 2. LiBH₄. c) RuCl₃·3H₂O/NaIO₄.

For the enantioselective synthesis of chiral 12-phenyl(2,3-²H₂)dodecanoic acids, microbial reduction of 2-alkenoates like **10** or **10a** is a direct and attractive approach [8]. For this purpose, the (*E*)-alcohols **5** or **5a** are first oxidized to an aldehyde (MnO₂) and then to the required acids **10** and **10a** by NaClO₂/α-amylenes (= 2-methylbut-2-ene) under neutral conditions [9]. This two-step sequence is superior to the usual oxidation procedures (Cr(VI)/H⁺; Ag(I)/OH⁻ etc.), since the latter give less pure products, mainly contaminated by the nonseparable 10-phenyldecanoic acid (10–25%) as a result of an oxidative attack on the double bond. Although the acids **10** and **10a** are largely insoluble in H₂O or aq. buffer systems, suspensions of substrate **10** in a 0.1M phosphate buffer, pH 7.0, are rapidly reduced by thawed wet packed cells of *Clostridium tyrobutyricum* (strain C. La 1, DSM-No. 1460, Scheme 3). The reduction cleanly ceases after the uptake of 1 equiv. of ¹H₂ gas. Extractive workup of the heterogeneous mixture (Et₂O) gives the (2*R*,3*R*)-acid **11** in 61% yield, along with ca. 2–3% of the starting material. If the (¹H)acid **10a** is reduced by the same method in a ²H₂O buffer and with ¹H₂ gas, the required enantiomer (2*S*,3*S*)-**11** is obtained in 67% overall yield.

Scheme 3



a) 1. MnO_2 , 2. NaClO_2/α -amylene, NaH_2PO_4 buffer, pH 7. b) H_2O , *Clostridium tyrobutyricum* (C. La 1).

Product Chirality by the Mandelate-Diester Approach. – To determine the enantiomeric excess (e.e.) of the above 12-phenyl(^2H)dodecanoic acids **9** and **11**, they are converted into their mandelate diesters and analyzed by ^1H -NMR (Fig.). To provide highest accuracy for the integration of the relative peak areas of the diastereotopic proton(s) at C(2), the vicinal coupling with $\text{H}-\text{C}(3)$ is eliminated by irradiation at 1.60 ppm ($\text{H}-\text{C}(3)$). The mandelates of the racemic acids *rac*-**9** and *rac*-**11** display two *s* of equal intensity at 2.40 and 2.455 ppm, while the mandelates of chiral acids comprise only one signal, located at 2.455 ppm (*2S*) or 2.40 ppm (*2R*), respectively. The spectra provide no evidence for the presence of the opposite enantiomer. Thus, within the limits of error of the ^1H -NMR method, the enantiomeric excess of all chiral (^2H)acids is $\geq 97\%$. The downfield appearance of the proton at C(2) of the mandelates of (*2S*)-($2\text{-}^2\text{H}$)acids is in agreement with the examples reported by Parker [10]. It is also in agreement with the known site specificity of the enoate reductase of *Clostridium tyrobutyricum* [11] or the stereochemical course of the Sharpless epoxidation.

To visualize the enantiospecificity of the microbial reduction with respect to the proton at C(3), the acid (*2R,3R*)-**11** is esterified (CH_2N_3) and treated with PhLi , and the resulting tertiary alcohol eliminated under acidic conditions to yield the 1,1,12-triphenyl-dodec-1-ene **12** (Scheme 4). After oxidative cleavage of the double bond with Ru(VIII) [12], the resulting (*2R*)-11-phenyl(^2H)undecanoic acid ((*2R*)-**13**) is converted into the

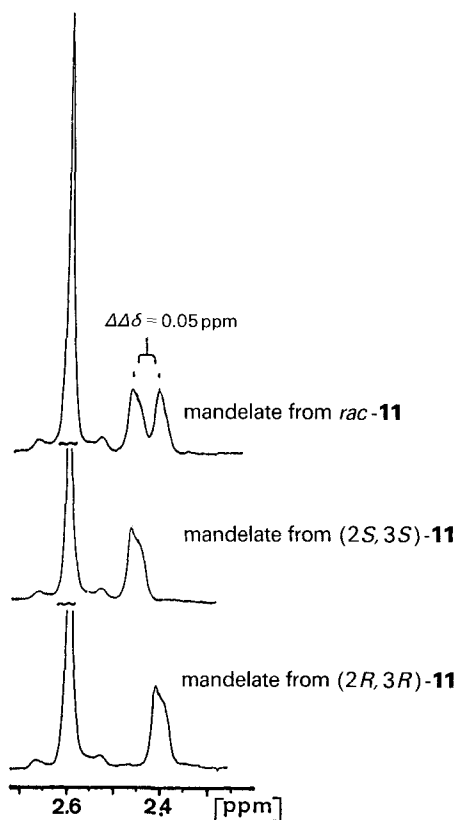
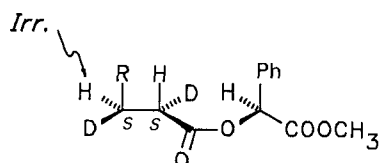
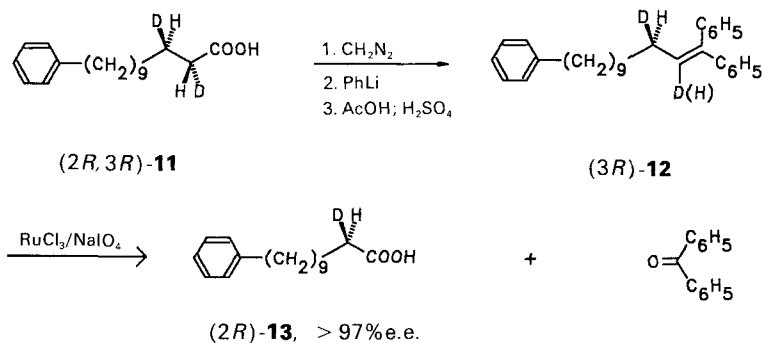


Figure. 250-MHz ^1H -NMR spectra of mandelate diesters from *rac*-**11** (2*S*,3*S*)-**11**, and (2*R*,3*R*)-**11**. Spectra were recorded in CDCl_3 with irradiation at 1.60 ppm of the adjacent $\text{H}-\text{C}(3)$. The mandelates from (2*S*)-**9** and (2*R*)-**9** gave the same signals, respectively.



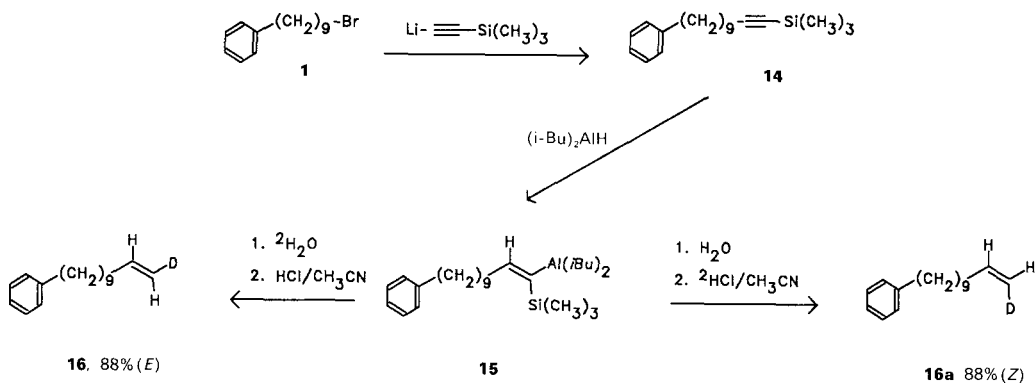
mandelate diester and analyzed as before. Again, no indication for the presence of a second enantiomer is found. Thus, the reduction of **10** and **10a** by *Clostridium tyrobutyricum* had occurred with $\geq 97\%$ e.e. with respect to both centers, as has been previously shown with other substrates [11].

Scheme 4

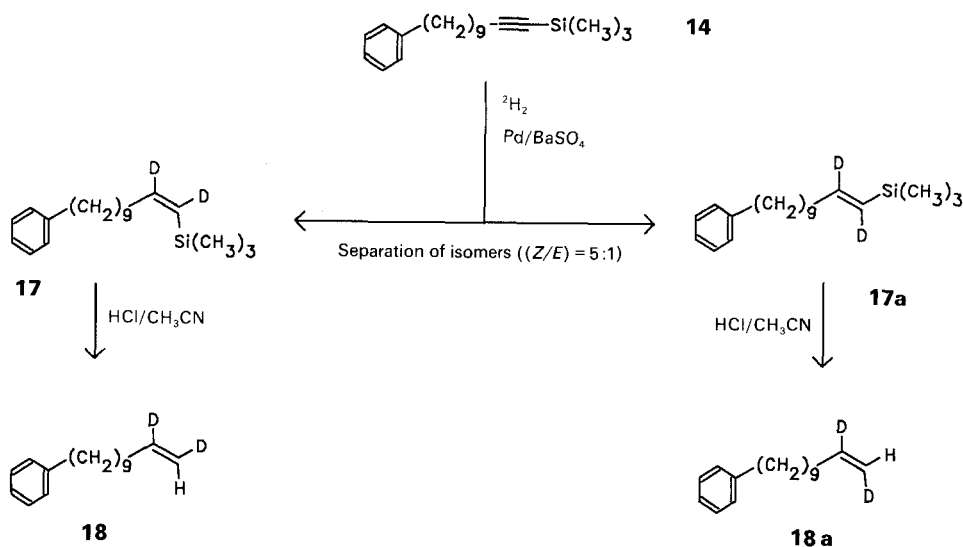


(*E*)- and (*Z*)-11-Phenyl(²H)undec-1-enes. – To study the stereochemical course of the biosynthesis of 1-alkenes in plants with the 12-phenyl(²H)dodecanoic acids as metabolic probes, the corresponding (*E*)- or (*Z*)-11-phenyl(1-²H)undec-1-enes are required as configurationally pure references. These compounds are readily available from **1** by substitution of the bromide by 1-lithio-2-(trimethylsilyl)acetylene. Next, the (trimethylsilyl)-alkyne **14** is reacted with *DIBAL-H* (diisobutylaluminium hydride) [13]. If the resulting organoaluminium intermediate **15** is first hydrolyzed with ²H₂O, followed by removal of the silyl group with H⁺/CH₃CN, the (*E*)-11-phenyl(1-²H)undec-1-ene (**16**; 88% (*E*)) is obtained. Reversal of the sequence (1. H₂O, 2. ²HCl) leads to the (*Z*)-isomer **16a** (88% (*Z*)), *Scheme 5*.

Scheme 5



Scheme 6



The two isomeric 11-phenyl(1,2- $^2\text{H}_2$)undec-1-enes **18** and **18a** are synthesized from **14** via hydrogenation with $^2\text{H}_2$ gas and Lindlar's catalyst (*Scheme 6*). Although this reduction is expected to give a high amount of the (*Z*)-(trimethylsilyl)alkene **17**, we have observed rapid isomerization of the original compound after *ca.* 50% conversion of the starting material. Obviously, the unfavorable steric interaction between the bulky trimethylsilyl group and the aliphatic side chain leads to rotation around the terminal C–C σ -bond after labilization of the C=C bond at the noble metal catalyst. After complete conversion of **14**, the product consists of 85% (*Z*)- and 15% (*E*)-(trimethylsilyl)alkenes **17** and **17a**. Both are readily separated by medium-pressure liquid chromatography (MPLC) on silver-impregnated silica gel (10% AgNO_3). Hydrolysis with $\text{HCl}/\text{CH}_3\text{CN}$ provides the configurationally pure (*Z*)- and (*E*)-11-phenyl(1,2- $^2\text{H}_2$)undec-1-enes (**18** and **18a**, respectively). In contrast to the (*E*)- and (*Z*)-(1- ^2H)olefines **16** and **16a**, **18** or **18a** display virtually identical IR- and ^1H -NMR spectra and can not be used to follow the stereochemical course of the biosynthesis of 1-alkenes from fatty acids.

Administration experiments with the 12-phenyl(^2H)dodecanoic acids **9** and **11** and germinating seeds of *Carthamus tinctorius* were already successful. The experiments establish a high preference of the plant's enzyme(s) for the *pro-S* H-atom at C(3) of the precursor acid. The overall stereochemical course is consistent with an *anti*-elimination of the H-atom and the carboxyl group. The detailed study will be published elsewhere [15].

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Experimental Part

General. Reactions were performed under Ar. Solvents and reagents were purified and dried prior to use. Anhydrous MgSO_4 was used for drying operations. Solns. were usually concentrated by flash evaporation under reduced pressure. Anal. TLC: 20 $\times$ 20 cm TLC plates, SiO_2 60 F_{254} , layer thickness 0.2 mm (*E. Merck & Co.*, Darmstadt, FRG). Anal. GLC: Carlo-Erba gas chromatograph, HRGC 5300, Mega series, equipped with fused silica capillaries, SE 30 (10 m $\times$ 0.31 mm); carrier gas, H_2 at 30 cm/s. Polarimetry: Perkin-Elmer 141, optical rotations at 21°. IR (cm^{-1}): Perkin Elmer 882 IR spectrophotometer. ^1H -NMR (250 or 400 MHz, CDCl_3 , TMS as internal standard): Bruker Cryospec WM 250 and Bruker WM 400. MS (m/z): Finnigan 4510 GLC/MS system and Finnigan ITD 800 combined with a Carlo Erba gas chromatograph, model Vega; carrier gas, He at 30 cm/s.

(9-Bromononyl)benzene (**1**). At 0°, (3-phenylpropyl)magnesium bromide (0.45 ml) in THF (250 ml) was slowly added to a well stirred soln. of 1,6-dibromohexane (0.40 mol) and Li_2CuCl_4 (4.0 mmol) in THF (200 ml). During addition, the temp. was kept below 10° to avoid the formation of larger amounts of 1,12-diphenyldodecane. Stirring was continued over night at r.t., and 300 ml of sat. NH_4Cl soln. were added. Following extraction (3 $\times$ 100 ml Et_2O), washing (sat. NaCl soln., 2N HCl , 10% Na_2CO_3 soln., and H_2O), drying, and evaporation the crude product was purified by distillation: 49.8 g (44%). B.p. 115°/0.2 Torr. IR: 3090w, 3070w, 3030m, 3000w, 2930s, 2860s, 1605m, 1500s, 1470s, 1455s, 1030w, 740s, 700s. ^1H -NMR: 7.21 (m, C_6H_5); 3.38 (t, CH_2Br); 2.60 (t, $\text{C}_6\text{H}_5\text{CH}_2$); 1.82 (quint., $\text{CH}_2\text{CH}_2\text{Br}$); 1.61 (br. m, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$); 1.43–1.23 (m, 5 CH_2). MS: 284, 282 (8, 8, M^+), 238 (2), 147 (3), 133 (8), 117 (4), 104 (10), 92 (82), 91 (100), 78 (4), 65 (16), 55 (10), 41 (25). HR-MS: 282.0994, 284.0925 ($\text{C}_{15}\text{H}_{23}\text{Br}$, M^+ , calc. 282.0972, 284.0954).

(10-Bromodecyl)benzene (**2**). Prepared from phenylmagnesium bromide (0.45 mol) and 1,10-dibromodecane (0.40 mol) as described for **1**: 48.0 g (44%). B.p. 119°/0.07 Torr. IR: identical with that of **1**. ^1H -NMR: identical with that of **1**, except: 1.43–1.23 (br. s, 6 CH_2). MS: 298, 296 (12, 12, M^+), 254 (0.5), 161 (1), 147 (2), 133 (10), 119 (3), 104 (8), 92 (92), 91 (100), 77 (5), 65 (14), 55 (14), 41 (28). HR-MS: 296.1160, 298.1136 ($\text{C}_{16}\text{H}_{25}\text{Br}$, M^+ , calc. 296.1130, 298.1110).

12-Phenyldodec-2-yn-1-ol (3). A soln. of 3-[(tetrahydropyran-2-yl)oxy]prop-1-yne (27.4 g, 0.196 mol) in dry THF (220 ml) at r.t. was treated dropwise with BuLi (0.21 mol; 86.2 ml of 2.5M soln. in hexane). After stirring for 15 min, hexamethylphosphoric triamide (HMPA) (15 ml) was added. Then, a soln. of **1** (0.151 mol) in HMPA (10 ml) was added in 3 portions at which the temp. raised to ca. 40°. Stirring was continued over night, followed by addition of H₂O (100 ml). The mixture was extracted with Et₂O (3 × 150 ml), and the org. layers were washed with H₂O, dried, and evaporated. The crude product was then dissolved in MeOH (500 ml) containing pyridinium *p*-toluenesulfonate (0.5 g) and refluxed for 30 min to remove the protecting group. After addition of pyridine (7 ml) and cooling, the solvent was removed *i.v.* at 35°. The dark residue was dissolved in Et₂O (200 ml) and washed with 2N HCl (2 × 100 ml). After drying and evaporation of the solvent, the product was purified by CC on silica gel using hexane/Et₂O 8:2 (*v/v*): 26.7 g (68%). IR: 3360s (br.), 3090w, 3070w, 3030m, 3000w, 2935s, 2860s, 2300w, 2290w, 2230w, 1605m, 1495s, 1465s, 1455s, 1140s, 1020s, 750s, 700s. ¹H-NMR: 7.21 (*m*, C₆H₅); 4.25 (*t*, CH₂OH); 2.60 (*t*, C₆H₅CH₂); 2.20 (*t*, CH₂C≡C); 1.63 (br. *m*, C₆H₅CH₂CH₂, OH); 1.51 (*m*, CH₂CH₂C≡C); 1.40–1.25 (br. *m*, 5 CH₂). MS: 258 (2, *M*⁺), 157 (2), 143 (7), 130 (11), 117 (12), 104 (23), 91 (100), 79 (21), 70 (31), 65 (23), 55 (21), 41 (31), 39 (34). HR-MS: 258.1988 (C₁₈H₂₆O, *M*⁺, calc. 258.1977).

13-Phenyltridec-2-yn-1-ol (4). Prepared from **2** (0.151 mol) as described for **3**: 28.5 g (72%). IR: identical with that of **3**. ¹H-NMR: identical with that of **3**, except: 1.40–1.25 (*m*, 6 CH₂). MS: 272 (0.5, *M*⁺), 254 (0.4), 197 (0.4), 183 (1.3), 169 (2), 155 (3), 143 (7), 131 (14), 117 (14), 104 (13), 91 (100), 79 (18), 70 (63), 55 (20), 41 (29), 39 (21). HR-MS: 272.2168 (C₁₉H₂₈O, *M*⁺, calc. 272.2133).

Phenylalk-2-en-1-ols: General Procedure. A soln. of *ω*-phenylalkynol **3** or **4** (147.0 mmol) in dry THF (150 ml) was added slowly with stirring at r.t. to a suspension of LiAlH₄ or LiAlH₂H₄ (147.0 mmol) in THF (250 ml). After brief reflux for 30 min, the mixture was chilled and hydrolyzed by slow addition of sufficient H₂O or ²H₂O (99.7% ²H). In the case of ²H-labelling, stirring was continued for 30 min prior to addition of ²HCl. Further 150 ml of H₂O were added, and the products were extracted with Et₂O (3 × 100 ml). After drying and evaporation, the residue was chromatographed on silica gel with hexane/Et₂O 8:2.

(*E*)-12-Phenyl(2,3-²H₂)dodec-2-en-1-ol (**5**). From **3** and LiAl²H₄ and ²H₂O in 87% yield (> 99% ²H). IR: 3335 (br.), 3090w, 3070w, 3030m, 2930s, 2860s, 2220w, 1640w, 1605w, 1495m, 1455m, 1080m, 910 (br.), 745m, 720m, 700s. ¹H-NMR: 7.21 (*m*, C₆H₅); 4.08 (*d*, CH₂OH); 2.60 (*t*, C₆H₅CH₂); 2.03 (*t*, CH₂CD=CD); 1.52–1.61 (br. *m*, OH, C₆H₅CH₂CH₂); 1.42–1.22 (br. *m*, 6 CH₂). MS: 244 (4, *M*⁺ – H₂O), 144 (5), 131 (20), 117 (16), 104 (55), 91 (100), 75 (12), 70 (19), 59 (21), 41 (28). HR-MS: 244.2152 (C₁₈H₂₆²H₂O, *M*⁺ – H₂O, calc. 244.2158).

(*E*)-12-Phenyldodec-2-en-1-ol (**5a**). From **3** LiAlH₄ in 83% yield. IR: 3350m (br.), 3090w, 3065w, 3030m, 3000w, 2930s, 2860s, 1605w, 1500m, 1460m, 1465m, 1090m, 1005m, 970s, 745m, 700s. ¹H-NMR: 7.21 (*m*, C₆H₅); 5.66 (*m*, CH=CHCH₂OH); 4.08 (*t*, CH₂OH); 2.60 (*t*, C₆H₅CH₂); 2.03 (*quint.*, CH₂CH=CH); 1.61 (*m*, C₆H₅CH₂CH₂, OH); 1.41–1.25 (br. *m*, 6 CH₂). MS: 242 (4, *M*⁺ – H₂O), 199 (3), 143 (4), 129 (20), 117 (18), 104 (62), 91 (100), 81 (15), 70 (12), 67 (23), 55 (31), 41 (48). HR-MS: 242.2018 (C₁₈H₂₆O, *M*⁺ – H₂O, calc. 242.2035).

(*E*)-13-Phenyl(2,3-²H₂)tridec-2-en-1-ol (**6**). From **4** and LiAl²H₄ and ²H₂O in 91% yield (> 99% ²H). *M.p.* 29°. IR: identical with that of **5**. ¹H-NMR: identical with that of **5**, except: 1.42–1.22 (br. *m*, 7 CH₂). MS: 258 (8, *M*⁺ – H₂O), 199 (1), 186 (1), 157 (2), 144 (4), 131 (18), 117 (17), 104 (71), 91 (100), 83 (7), 65 (13), 59 (25), 55 (17), 41 (24). HR-MS: 258.2327 (C₁₉H₂₈²H₂O, *M*⁺ – H₂O, calc. 258.2308).

(+)-(2*R*,3*R*)-trans-2,3-Epoxy-13-phenyl(2,3-²H₂)tridecan-1-ol ((2*R*,3*R*)-**7**). To a suspension of molecular sieves (4 Å 1.5 g) and (–)-D-diethyl tartrate (0.62 g, 2.5 mmol) in dry CH₂Cl₂ (175 ml), Ti(*i*-PrO)₄ (0.75 ml, 2.5 mmol) was added with stirring at –22°. After 5 min *t*-BuOOH (33.3 ml, 0.1 mol; 3M in 2,2,4-trimethylpentane) was added within 5 min, and the catalyst was 'aged' for 30 min. Then, a soln. of **6** (13.8 g, 50.0 mmol) in dry CH₂Cl₂ (25 ml) was added within 20 min, while the temp. was kept at –22°. After 150 min, the mixture was allowed to come to 0° and poured into a chilled soln. of FeSO₄·7H₂O (16.5 g, 60.0 mmol) and tartaric acid (5.0 g; 30 mmol) in H₂O (100 ml). Stirring was continued for 5 min, and the two phases were allowed to separate. The aq. phase was extracted with Et₂O (2 × 30 ml), and the combined org. layers were treated with 5.0 mol of a soln. of NaOH (30%) in sat. NaCl (1:1, *v/v*) with stirring for 30 min at 0°. H₂O (50 ml) was added and the product extracted with CH₂Cl₂ (2 × 50 ml). After drying and evaporation, the residue was purified by CC on silica gel (hexane/Et₂O 6:4) and crystallization from 60 ml of pentane/Et₂O 1:1 at –20°: 8.7 g (60%) of colorless crystals. *M.p.* 39°. [*α*]_D²⁰ = 19.3 (CH₂Cl₂, *c* = 5.00). IR: 3350 (br.), 3090w, 3070w, 3030w, 2920s, 2850s, 2200w, 1500m, 1465m, 1450m, 1080m, 1060m, 1050m, 955m, 905m, 815m, 700m. ¹H-NMR: 7.21 (*m*, C₆H₅); 3.91 (*d*, 1H, CH₂OH); 3.62 (*d*, 1H, CH₂OH); 2.60 (*t*, C₆H₅CH₂); 2.05 (br. *s*, OH); 1.68–1.50 (*m*, C₆H₅CH₂CH₂, CH₂CDO); 1.45–1.20 (br. *m*, 7CH₂). MS: 274 (2, *M*⁺ – H₂O), 253 (3), 229 (2), 207 (8), 193 (2), 171 (2), 147 (3), 131 (8), 117 (10), 104 (40), 92 (43), 91 (100), 75 (7), 65 (18), 55 (17), 41 (36). Anal. calc. for C₁₉H₂₉²H₂O₂ (293.44): calc. C 78.03, H 11.02; found: C 78.00, H 10.92.

(-)-(2*S*,3*S*)-trans-2,3-Epoxy-13-phenyl(2,3-²H₂)tridecan-1-ol ((2*S*,3*S*)-7). Prepared from **6** (50.0 mmol) and (+)-L-diethyl tartrate as described for (2*R*,3*R*)-7. Yield: 9.5 g (65%). M.p. 39°. [α]_D = -19.15 (CH₂Cl₂, *c* = 4.99). Spectroscopic data: identical with that of (2*R*,3*R*)-7.

rac-trans-2,3-Epoxy-13-phenyl(2,3-²H₂)tridecan-1-ol (*rac*-7). Prepared from **6** (6.15 g, 22.3 mmol) and 3-chloroperoxybenzoic acid (5.0 g, 29.0 mmol) in CH₂Cl₂ (150 ml) at 0°. After 60 min, the soln. was washed with sat. NaHCO₃ soln. (2 × 100 ml) and H₂O (2 × 100 ml), dried, and evaporated. Purification over silica gel with hexane/Et₂O 6:4 afforded 5.54 g (85%) of *rac*-7. Spectroscopic data: identical with (2*R*,3*R*)-7.

Mosher Esters of the 2,3-Epoxyalcohols: General Procedure [6]. A soln. of epoxyalcohol (73.0 mg, 0.25 mmol) and (+)-(S)-2-methoxy-2-phenyl-2-(trifluoromethyl)acetyl chloride (87.5 mg, 0.35 mmol) in dry pyridine (750 μ l) and CCl₄ (750 μ l) was stirred for 60 min at r.t. Then, 3-(dimethylamino)propylamine (50.0 mg, 0.5 mmol) was added and stirring continued for 5 min. Then, Et₂O (20 ml) was added and the org. layer washed with 2*N* HCl (10 ml), sat. Na₂CO₃ soln. (10 ml), and brine (10 ml). After drying and evaporation, the product was purified by CC on silica gel using hexane/Et₂O 8:2 (TLC control (same solvent)): 93.0 mg (73%). IR (identical for all Mosher esters): 3070w, 3030w, 2930s, 2860s, 2250w, 1750s, 1600w, 1500m, 1450m, 1275s, 1250s, 1185s, 1120m, 1080m, 1020w, 910m, 760m, 735s, 720s, 700m. ¹H-NMR (*Mosher* ester of *rac*-7): 7.47 (*m*, C₆H₅CCF₃); 7.21 (*m*, C₆H₅CH₂); 4.57, 4.52 (2*d*, *J* = 11.5, 1 H, CH₂O); 4.23, 4.18 (2*d*, *J* = 11.5, 1 H, CH₂O); 3.56 (*s*, CH₃O); 2.60 (*t*, C₆H₅CH₂); 1.65–1.50 (*m*, C₆H₅CH₂CH₂, CH₂CHOC); 1.42–1.22 (*br. s*, 7 CH₂). *Mosher* ester of (2*S*,3*S*)-7: 4.53 (*d*, 1 H); 4.23 (*d*, 1 H); no evidence for (2*R*,3*R*)-7. *Mosher* ester of (2*R*,3*R*)-7: 4.57 (*d*, 1 H); 4.21 (*d*, 1 H), no evidence for (2*S*,3*S*)-7. MS (identical for all Mosher esters): 508 (1, *M*⁺), 256 (1.5), 246 (1.2), 189 (81), 165 (1), 152 (1), 139 (3), 131 (18), 117 (13), 105 (21), 104 (22), 96 (5), 92 (20), 91 (100), 77 (4), 69 (11), 55 (15), 41 (15).

(-)-(2*S*,3*R*)-13-Phenyl(2,3-²H₂)tridecan-1,2-diol ((2*S*,3*R*)-8). A soln. of (2*R*,3*R*)-7 (6.0 g, 20.5 mmol) in dry benzene (200 ml) was treated at r.t. with Ti(*i*-PrO)₄ (11.1 g, 39.0 mmol). Stirring was continued for 5 min at r.t., followed by cooling to 10° and addition of LiBH₄ (1.7 g, 78.0 mmol) in three portions. The soln. was allowed to come to r.t., and after 5 h the mixture was quenched by addition of cold 5% H₂SO₄ soln. (250 ml). When 2 clear phases had formed, the aq. layer was extracted with Et₂O, and the combined org. extracts were washed with H₂O, dried, and evaporated. The product was purified by recrystallization from Et₂O (150 ml) at -20°: 3.3 g (55%) of colorless crystals. M.p. 52°. [α]_D = -0.31 (CH₂Cl₂, *c* = 5.13). IR: 3400s (*br.*), 3090w, 3070w, 3035w, 2920s, 2850s, 2150w, 2080w, 1605w, 1500m, 1470s, 1450m, 1155m, 950m, 845m, 740m, 720m, 695m. ¹H-NMR: 7.21 (*m*, C₆H₅); 3.65 (*d*, 1 H, CH₂OH); 3.42 (*d*, 1 H, CH₂OH); 2.60 (*t*, C₆H₅CH₂); 2.33 (*br. s*, 2 OH); 1.61 (*quint.*, C₆H₅CH₂CH₂); 1.48–1.20 (*br. m*, H–C(3), 8 CH₂). MS: 294 (27, *M*⁺), 148 (2), 147 (2), 133 (6), 117 (3), 104 (8), 92 (62), 91 (100), 77 (3), 65 (12), 55 (3), 41 (8). Anal. calc. for C₁₉H₃₀²H₂O₂ (294.45): C 77.55, H 11.63; found: C 77.70, H 11.43.

(+)-(2*R*,3*S*)-13-Phenyl(2,3-²H₂)tridecan-1,2-diol ((2*R*,3*S*)-8). From (2*S*,3*S*)-7 (20.5 mmol) as described for (2*S*,3*R*)-8: 4.0 g (66%). [α]_D = 0.31 (CH₂Cl₂, *c* = 5.13). Spectroscopic data: identical with that of (2*S*,3*R*)-8.

rac-13-Phenyl(2,3-²H₂)tridecan-1,2-diol (*rac*-8). From *rac*-7 (3.0 g, 10.3 mmol) as described for (2*S*,3*R*)-8: 1.8g (59%). Spectroscopic data: identical with that of (2*S*,3*R*)-8.

(2*R*)-12-Phenyl(2-²H)dodecanoic Acid ((2*R*)-9). To a soln. of 2.2 g (7.48 mmol) of (2*S*,3*R*)-8 in CCl₄ (15 ml), CH₃CN (15 ml), and H₂O (22.4 ml), NaIO₄ (6.65 g, 31.4 mmol) and RuCl₃ · 3 H₂O (43.0 mg, 0.16 mmol) are added with stirring at r.t. After 60 min H₂O (50 ml) and CH₂Cl₂ (50 ml) were added, and the aq. layer was extracted with additional portions of CH₂Cl₂ (3 × 20 ml). Drying and evaporation afforded crude (2*R*)-9. Chromatography on silica gel with hexane/Et₂O 7:3 removed admixtures of the catalyst and yielded, after recrystallization from heptane at -20°, 1.2 g (58%) of colorless crystals. M.p. 59°. IR: 3340m (*br.*), 3090w, 3070w, 3030m, 2920s, 2850s, 1700s, 1470m, 1460m, 1450m, 1420m, 1315m, 1290m, 950m-w, 940m, 745s, 700s. ¹H-NMR: 7.22 (*m*, C₆H₅); 2.60 (*t*, C₆H₅CH₂); 3.32 (*t*, 1 H, CHD); 1.61 (*br. quint.*, C₆H₅CH₂CH₂CH₂CDH); 1.40–1.20 (*br. s*, 7 CH₂). MS (methyl ester): 291 (5, *M*⁺), 259 (32), 241 (2), 200 (3), 185 (1), 168 (11), 150 (7), 131 (7), 117 (9), 104 (26), 92 (36), 91 (100), 75 (18), 65 (16), 55 (15), 41 (24). Anal. calc. for C₁₈H₂₇²H₁O₂ (278.65): C 77.94, H 10.53; found: C 78.05, H 10.43.

(2*S*)-12-Phenyl(2-²H)dodecanoic Acid ((2*S*)-9). Prepared from (2*R*,3*S*)-8 as described for (2*R*)-9 in 53% yield. Spectroscopic data: identical with that of (2*R*)-9.

rac-12-Phenyl(2-²H)dodecanoic Acid (*rac*-9). Prepared from *rac*-8 as described for (2*R*)-9 in 48% yield. Spectroscopic data: identical with that of (2*R*)-9.

(E)-12-Phenyldodec-2-enoic Acid (10a). MnO₂ (34.8 g, 0.40 mol) was added with stirring to soln. of **5a** (3.48 g, 13.4 mmol) in CH₂Cl₂ (100 ml). Complete oxidation was achieved within 1 h and the MnO₂ removed by suction. Evaporation of the solvent *i.v.* afforded the crude aldehyde (80% yield). A soln. of this compound (1.1 g, 4.23 mmol) in *t*-BuOH (88 ml) and 2-methylbut-2-ene (21.0 ml) was successively treated with stirring at r.t. with a soln. of NaClO₂ (3.5 g, 29.2 mmol) and NaH₂PO₄ (3.5 g, 28 mmol) in H₂O (35 ml). The yellow soln. turned colorless

within 2 h. Solvents were removed *i.v.*, and the residue was taken up in H₂O (90 ml). Unpolar by-products were removed by extraction with hexane (2 × 50 ml), and the aq. layer was acidified with 2N HCl to pH 3.0. Extraction with Et₂O (3 × 50 ml), washing with H₂O, drying, and evaporation gave crude **10a**. Recrystallization from heptane at –20° afforded 0.8 g (68%) of pure **10a**. M.p. 40°. IR: 3430m (br.), 3090w, 3030w, 2925s, 2855s, 1695s, 1650s, 1605w, 1500m, 1470m, 1450m, 1420m, 1370m, 1340m, 1320m, 1135w, 1030w, 990w, 975m, 930m, 850m, 810m, 695m. ¹H-NMR: 7.21 (m, C₆H₅); 7.09 (dt, CH₂CH=CH); 5.82 (d, CH₂CH=CH); 2.60 (t, C₆H₅CH₂); 2.21 (dt, CH₂CH=CH); 1.61 (quint., C₆H₅CH₂CH₂); 1.45 (quint., CH₂CH₂CH=CH); 1.40–1.23 (br. s, 5 CH₂). MS (Me₃Si ester): 347 (5, M⁺ – CH₃), 331 (18), 257 (15), 255 (15), 165 (3), 155 (33), 143 (13), 129 (33), 117 (100), 104 (30), 91 (53), 81 (24), 75 (18), 65 (19). Anal. calc. for C₁₈H₂₆O₂ (274.40): C 78.80, H 9.54; found: C 78.88, H 9.53.

(*E*)-12-Phenyl(2,3-²H₂)dodec-2-enoic Acid (**10**). Prepared from **5** (4.23 mmol) as described for **10a**: 60%. IR: 3430m (br.), 3090w, 3070w, 3030w, 2920s, 2855s, 1690s, 1620s, 1500m, 1470m, 1455m, 1415m, 1290s, 1095w, 1030w, 940m, 850w, 745w, 730w, 720w, 700w. ¹H-NMR: 7.21 (m, C₆H₅); 2.60 (t, C₆H₅CH₂); 2.21 (t, CH₂CD=CD); 1.61 (quint., C₆H₅CH₂CH₂); 1.45 (quint., CH₂CH₂CD=CD); 1.40–1.23 (br. s, 5 CH₂). MS (Me₃Si ester) 349 (17, M⁺ – CH₃), 33 (61), 257 (27), 157 (52), 144 (40), 131 (53), 118 (72), 117 (75), 104 (39), 91 (100), 83 (18), 73 (33), 65 (33). Anal. calc. for C₁₈H₂₄²H₂O₂ (276.39): C 78.21, H 10.11; found: C 78.50, H 9.92.

12-Phenyl(2,3-²H₂)dodecanoic Acids by Microbial Reduction: General Procedure. *Clostridium tyrobutyricum* (DSM-No. 1460) was grown, stored, and manipulated as described in [8] [14]. For the experiment in deuterium buffer (see **10a**), wet packed cells were freeze-dried for removal of H₂O (under exclusion of O₂) and resuspended in ²H₂O. For the preparation of (2*R*,3*R*)-**11**, a total volume of 10 ml containing 0.6 mmol of sodium salt of **10**, 1.3 g of wet packed cells, 1.0 mg of tetracycline, 1.0 mM methylviologen, and 0.1M potassium phosphate buffer at pH 7.0 was shaken at 35° under an atmosphere of 1 bar ¹H₂ gas (vessel equipped with a mercury-filled Warburg manometer). After 1.5 h, the H₂ uptake ceased, and the substrate was converted. The suspension was acidified to pH 1.5 with dil. H₂SO₄ soln. and extracted with Et₂O. For the preparation of (2*S*,3*S*)-**11**, in a total volume of 14 ml 0.1M potassium phosphate ²H₂O-buffer, p²H 7.0, 1 mmol of the undeuterated sodium salt of **10a** was converted under ¹H₂ (not ²H₂) in the presence of 1 mM methylviologen, 1.4 mg of tetracycline, and 550 mg of freeze-dried cells of *C. tyrobutyricum* within ca. 40 h as described above. After extraction, drying, and evaporation, the crude acid was purified by CC on silica gel using hexane/Et₂O 6:4. Recrystallization from heptane at –20° afforded the pure acids.

(2*S*,3*S*)-12-Phenyl(2,3-²H₂)dodecanoic Acid ((2*S*,3*S*)-**11**). Prepared from **10** in H₂O buffer in 63% yield as described. M.p. 59°. IR: 3420w (br.), 3090w, 3070w, 3030w, 2920s, 2850s, 2680w, 2165w, 1700s, 1600w, 1500w, 1470m, 1465m, 1450m, 1420m, 1310m, 1290m, 1260m, 1250m, 1240m, 1030w, 960m, 935m, 745s, 700s. ¹H-NMR: 7.21 (m, C₆H₅); 2.61 (t, C₆H₅CH₂); 232 (d, CHD²COOH); 1.61 (br. m, CHDCHD²COOH, C₆H₅CH₂CH₂); 1.40–1.22 (br. s, 7 CH₂). MS (methyl ester): 292 (3, M⁺), 260 (21), 242 (5), 169 (7), 151 (7), 144 (8), 131 (7), 117 (10), 104 (27), 92 (45), 91 (100), 75 (21), 65 (16), 55 (11), 41 (21). Anal. calc. for C₁₈H₂₆²H₂O₂ (278.40): C 77.58, H 10.91; found: C 77.58, H 10.91.

(2*S*,3*S*)-12-Phenyl(2,3-²H₂)dodecanoic Acid ((2*S*,3*S*)-**11**). Prepared from **10a** and ²H₂O buffer in 69% yield as described. M.p. 59°. Spectroscopic data: identical with that of (2*R*,3*R*)-**11**.

rac-12-Phenyl(2,3-²H₂)dodecanoic Acid (rac-**11**). A suspension of 10% Pt/C (250 mg) in THF (60 ml) containing 1.5 g (5.4 mmol) of the (²H₂)acid **10** was stirred under H₂ until the uptake of H₂ ceased. Workup and recrystallization from heptane at –20° yielded 1.1 g (73%) of rac-**11**. Spectroscopic data: identical with that of (2*R*,3*R*)-**11**.

Mandelate Diesters: General Procedure. To a soln. of 0.36 mmol of the corresponding ω-phenyl(²H)-dodecanoic acid and 4-(dimethylamino)pyridine (1 mg) CH₂Cl₂ (3 ml), methyl (+)-(*S*)-mandelate (60.0 mg, 0.36 mmol) and dicyclohexylcarbodiimide (74.6 mg, 0.36 mmol) were added with stirring at –10°. Stirring was continued for 4 h at –10°, followed by removal of solids by suction and evaporation. Addition of CH₂Cl₂ (3.0 ml) precipitated the last amounts of dicyclohexylurea, and after removal of the solids by filtration and evaporation, the mandelate diesters were purified by CC on silica gel with hexane/Et₂O 9:1 (TLC control (hexane/Et₂O 8:2)): 100 mg (64%). IR (diesters of (2*R*,3*R*)-**11** and (2*S*,3*S*)-**11**): 3090w, 3070w, 3030w, 3000w, 2930s, 2855s, 2170w, 1760s, 1745s, 1605w, 1500m, 1455m, 1435m, 1350m, 1270m, 1215s, 1170s, 1080w, 1050m, 1030m, 750m, 740m, 700s. IR (diesters of (2*S*)-**9**, (2*R*)-**9**, and (2*R*)-**13**): 3090w, 3070w, 3030w, 2930s, 2860s, 2215w, 1755s, 1730m, 1600w, 1500m, 1470m, 1450m, 1375w, 1370w, 1270s, 1240s, 1185s, 1170s, 1125s, 1080m, 1020m, 1000m, 765m, 740m, 720m, 700m. ¹H-NMR (diesters of (2*S*,3*S*)-**11** and (2*R*,3*R*)-**11**): 7.42 (m, C₆H₅CHCOOMe); 7.21 (m, C₆H₅CH₂); 5.92 (s, C₆H₅CHCOOMe); 3.72 (s, CH₃O); 2.60 (t, C₆H₅CH₂); 2.455 (d, CDHCDHCOO, for (2*S*,3*S*)-**11**); 2.40 (d, CDHCDHCOO, for (2*R*,3*R*)-**11**); 1.81–1.65 (m, C₆H₅CH₂CH₂, CDHCDHCOO); 1.40–1.22 (m, 7 CH₂). ¹H-

NMR (diesters of (2*S*)-**9**, (2*R*)-**9**, and (2*R*)-**13**): 7.42 (*m*, C₆H₅CHCOOMe); 7.21 (*m*, C₆H₅CH₂); 5.92 (*s*, C₆H₅CHCOOMe); 3.71 (*s*, CH₃O); 2.60 (*t*, C₆H₅CH₂); 2.41 (*t*, CDHCOO, for (2*R*)-**9** and (2*R*)-**13**); 2.465 (*t*, CDHCOO, for (2*S*)-**9**); 1.81–1.65 (*m*, C₆H₅CH₂CH₂, CH₂CDHCOO); 1.40–1.22 (*m*, 7 CH₂, 6 CH₂ for (2*R*)-**13**). MS (diesters of (2*S*,3*S*)-**11** and (2*R*,3*R*)-**11**): 427, 426 (0.03, *M*⁺ and *M*⁺ + 1), 381 (0.18), 277 (2), 259 (42), 150 (49), 131 (25), 117 (21), 105 (28), 92 (23), 91 (100), 77 (9), 65 (4), 55 (11), 41 (11). MS (diesters of (2*S*)-**9** and (2*R*)-**9**): 426, 425 (0.02, *M*⁺ and *M*⁺ + 1), 380 (0.2), 258 (43), 150 (49), 131 (21), 117 (20), 105 (25), 92 (20), 91 (100), 77 (8), 65 (5), 55 (15), 41 (14). MS (diester of (2*R*)-**13**): 352 (0.04, *M*⁺ – COOCH₃), 244 (32), 150 (29), 131 (15), 117 (12), 105 (20), 92 (13), 91 (100), 77 (6), 65 (4), 55 (8), 41 (9).

1-(Trimethylsilyl)-11-phenylundec-1-yne (**14**). A soln. of bis(trimethylsilyl)acetylene (3.0 g, 18.2 mmol) in dry THF (60 ml) was gradually treated with stirring at r.t. with 13.4 ml (20.1 mmol) of a 1.5*M* soln. of CH₃Li/LiBr. After 30 min, the soln. was cooled to –78° and a soln. of **1** (4.0 g) in dry HMPA (10 ml) added. The mixture was allowed to come to r.t. and stirring continued for 60 min. The soln. was poured into 10% Na₂CO₃ soln. (30 ml) and the aq. layer extracted with Et₂O (2 × 20 ml). After washings (H₂O, brine), drying, and evaporation, the product was chromatographed with hexane on silica gel: 3.1 g (73%) of a colorless liquid. IR: 3090*w*, 3070*w*, 3030*m*, 3000*w*, 2930*s*, 2860*s*, 2190*s*, 1620*w*, 1515*m*, 1470*m*, 1465*m*, 1250*s*, 1030*m*, 840*s*, 765*s*, 730*m*, 700*s*. ¹H-NMR: 7.21 (*m*, C₆H₅); 2.61 (*t*, C₆H₅CH₂); 2.21 (*t*, CH₂C≡C); 1.61 (*quint.*, C₆H₅CH₂CH₂); 1.52 (*quint.*, CH₂CH₂C≡C); 1.40–1.22 (*br. s.*, 5 CH₂); 0.16 (*s*, (CH₃)₃Si). MS: 300 (2, *M*⁺), 285 (52), 269 (1), 226 (8), 204 (12), 183 (2), 168 (6), 155 (3), 143 (10), 135 (19), 109 (11), 91 (37), 80 (8), 73 (100), 59 (18), 39 (11). HR-MS: 300.2303 (C₂₀H₃₂Si, *M*⁺, calc. 300.2274).

(*E*)-11-Phenyl(1-²H)undec-1-ene (**16**). A soln. of **14** (0.52 g, 1.73 mmol) in dry Et₂O (10 ml) was treated with stirring at 0° with neat DIBAL-H (387 μl, 2.1 mmol). The mixture was kept at 0° for 60 min and then at r.t. for 5 h. Hydrolysis with ²H₂O (> 99% ²H) at 0°, extraction with Et₂O, drying, and evaporation afforded a crude (*Z*)-vinylsilane which was purified by CC on silica gel coated with AgNO₃ (10%) using hexane for elution: 270 mg (52%) of a colorless liquid. A soln. of this vinylsilane (199.3 mg, 0.66 mmol) and conc. HCl (100 μl) in CH₃CN (4 ml) was refluxed for 15 min. After cooling, ice/H₂O (4 ml) was added and the product extracted with pentane (2 × 15 ml). The combined org. layers were washed with H₂O (2 × 5 ml), dried, and evaporated. CC on silica gel, coated with AgNO₃ (10%), using pentane gave 84 mg (55%) of a colorless liquid. ¹H-NMR: 88% of (*E*)- and 12% of (*Z*)-isomer. IR: 3090*w*, 3070*w*, 3030*m*, 3000*w*, 2930*s*, 2860*s*, 2250*w*, 1730*w*, 1620*w*, 1600*w*, 1500*m*, 1465*m*, 1460*m*, 800*m*, 740*m*, 725*m*, 700*s*. ¹H-NMR: 7.21 (*m*, C₆H₅); 5.82 (*m*, CH₂CH=C); 4.99 (*d*, *J* = 14.8, CH=CHD); 2.61 (*t*, C₆H₅CH₂); 2.05 (*dt*, CH₂CH=C); 1.62 (*quint.*, C₆H₅CH₂CH₂); 1.40–1.22 (*br. s.*, 6 CH₂). MS: 231 (12, *M*⁺), 188 (0.5), 174 (0.5), 159 (0.5), 145 (1), 131 (6), 117 (14), 104 (100), 98 (1), 91 (80), 79 (2), 65 (3), 55 (11), 41 (11). HR-MS: 231.2092 (C₁₇H₂₅²H, *M*⁺, calc. 231.2090).

(*Z*)-11-Phenyl(1-²H)undec-1-ene (**16a**). Prepared from **14** via reversal of hydrolytic steps (1. H₂O, 2. ²HCl) in 43% overall yield. ¹H-NMR: 88% of (*Z*)- and 12% of (*E*)-isomer. IR: 3090*w*, 3070*w*, 3030*m*, 3000*w*, 2930*s*, 2860*s*, 2240*w*, 1620*w*, 1600*w*, 1485*m*, 1465*m*, 1460*m*, 980*m*, 920*w*, 750*m*, 740*m*, 700*s*. ¹H-NMR: 7.21 (*m*, C₆H₅); 5.82 (*m*, CH₂CH=C); 4.92 (*d*, *J* = 11.4, CH=CHD); 2.61 (*t*, C₆H₅CH₂); 2.05 (*dt*, CH₂CH=C); 1.62 (*quint.*, C₆H₅CH₂CH₂); 1.40–1.22 (*br. s.*, 6 CH₂). MS: identical with that of **16**.

(*Z*)-11-Phenyl(1,2-²H₂)undec-1-ene (**18**) and (*E*)-11-Phenyl(1,2-²H₂)undec-1-ene (**18a**). To a soln. of **14** (1.3 g, 4.0 mmol) and quinoline (100 μl) in dry hexane (130 ml), Lindlar's catalyst (*Fluka*; 300 mg) was added. After the uptake of 1 equiv. of ²H₂ gas, the catalyst was filtered off and the soln. extracted with 2*N* HCl (2 × 60 ml) and H₂O (2 × 60 ml). Evaporation of the solvent yielded a 5:1 mixture of (*Z*)- and (*E*)-vinylsilanes **17** and **17a**, resp., which was separated by MPLC on silica gel, coated with 10% AgNO₃, using hexane/CHCl₃ 9:1. The pure compounds were desilylated as described for **16**. Overall yield: 390 mg (33%) of **18** and 80 mg (8%) of **18a**, with identical spectra. IR: 3090*w*, 3070*w*, 3030*m*, 3000*w*, 2930*s*, 2860*s*, 2280*w*, 2210*w*, 1600*m*, 1495*m*, 1470*m*, 1460*m*, 1030*w*, 885*m*, 770*m*, 720*m*, 700*s*. ¹H-NMR: 7.21 (*m*, C₆H₅); 4.99 (*s*, CH=CHD); 2.61 (*t*, C₆H₅CH₂); 2.03 (*t*, CH₂CD=C); 1.62 (*quint.*, C₆H₅CH₂CH₂); 1.40–1.22 (*br. s.*, 6 CH₂). MS: 232 (9, *M*⁺), 145 (2), 131 (10), 117 (17), 104 (100), 91 (54), 85 (2), 65 (11), 57 (3). HR-MS: 232.2157 (C₁₇H₂₄²H₂, *M*⁺, calc. 232.2152).

(3*R*)-1,1,12-Triphenyl(2,3-²H₂)dodec-1-ene (**12**). In the usual manner, 198 mg (0.72 mmol) of (2*R*,3*R*)-**11** were esterified with CH₂N₂. After evaporation, the ester was redissolved in dry Et₂O (3.0 ml) and PhLi (0.90 ml, 1.8 mmol; 2*M* in cyclohexane/Et₂O 7:3) added with stirring at 0°. Stirring was continued at 0° for 10 min and then the soln. hydrolyzed by addition of ice/H₂O (10 ml). The crude alcohol was extracted with Et₂O (2 × 10 ml) and the extract dried and evaporated. Brief treatment with 20% H₂SO₄ in AcOH at 60° for 0.5 min yielded **12** which was purified by CC on silica gel (hexane; TLC control (hexane)): 100 mg (35%). IR: 3085*m*, 3065*m*, 3030*m*, 2930*s*, 2860*s*, 1945*w*, 1600*w*, 1495*m*, 1465*m*, 1450*m*, 1440*m*, 1260*m*, 1095*m*, 1070*m*, 1030*m*, 910*m*, 720*m*, 700*s*. ¹H-NMR: 7.40–7.18 (*br. m.*, 3 C₆H₅); 6.08 (*d*, 0.2 H, CD(H)=C); 2.60 (*t*, C₆H₅CH₂); 2.08 (*t*, 1 H; CDHCD=C); 1.61 (*quint.*,

$C_6H_5CH_2CH_2$); 1.42 (quint., CH_2CHD); 1.36–1.18 (br. m, 6 CH_2). MS: 398 (12, M^+), 397 (3), 256 (2), 207 (2), 195 (65), 194 (48), 181 (55), 180 (48), 167 (30), 131 (10), 117 (45), 116 (46), 104 (9), 92 (50), 91 (100), 77 (6), 69 (2), 65 (10), 55 (9), 48 (3), 41 (20).

(2*R*)-11-Phenyl(2-²H)undecanoic Acid ((2*R*)-13). Prepared from (3*R*)-12 (90.0 mg, 0.22 mmol) as described for (2*R*)-9: 30.0 mg (51%). IR: identical with that of (2*R*)-9. ¹H-NMR: identical with that of (2*R*)-9, except: 1.40–1.25 (br. m, 6 CH_2). MS (methyl ester): 277 (1, M^+), 245 (22), 227 (6), 154 (8), 131 (11), 117 (9), 104 (25), 92 (38), 91 (100), 75 (17), 65 (16), 55 (13), 41 (28). Anal. calc. for $C_{17}H_{25}^2HO_2$ (263.39): C 77.59, H 10.32; found: C 77.47, H 10.26.

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