SUPPLEMENTARY MATERIAL

Synthesis of Long-Chain Polyketide Fragments by Reaction of
1,3-Dioxy-1,3-dienes with Allylsilanes : Umpolung with Sulfur
Dioxide

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General remarks

Commercial reagents (Fluka, Aldrich) were used without purification. Solvents were distilled prior to use : THF from Na and benzophenone; MeOH from Mg and I_2 ; DMF and CH_2Cl_2 from CaH_2 . Light petroleum ether used refers to the fraction boiling at 40-60°C. Solutions after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC) : columns of silica gel (0.040-0.63 mm, Merck No.9385 silica gel 60, 240-400 mesh). TLC for reaction monitoring : Merck silica gel 60F₂₅₄ plates; detection by UV light; Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4 , H_2O] or $KMnO_4$. IR spectra : Perkin-Elmer-1420 spectrometer. 1H NMR spectra : Bruker-ARX-400 spectrometer (400 MHz); $\delta(H)$ in ppm relative to the solvent's residual 1H signal [$CHCl_3$, $\delta(H)$ 7.27; CH_3OD , $\delta(H)$ 3.31; C_6H_6 , $\delta(H)$ 7.3] as internal reference; all 1H assignments were confirmed by 2D-COSY-45 spectra. ^{13}C NMR spectra : same instrument as above (100.6 MHz); $\delta(C)$ in ppm relative to solvent's C-signal [$CDCl_3$, $\delta(C)$ 77.0; CD_3OD , $\delta(C)$ 49.2; C_6D_6 , $\delta(C)$ 128.5] as internal reference; coupling constants J in Hz. MS : Nermag R-10-10C, chemical ionization (NH_3) mode m/z (amu) [% relative base peak (100%)], HRMS : Jeol AX-505. Elemental analyses : Ilse Beetz, D-96301 Kronach, Germany.

(1E,3Z) 1-Benzyloxy-2-methyl-penta-1,3-dien-3-yl acetate (8)

General procedure: To the solution of keto derivative **C** (4.09 g, 20.0 mmol, 1 eq.) in Et₂O (120 mL), cooled to -20°C, was added triethylamine (6.4 mL, 46.0 mmol, 2.3 eq.) followed by trimethyl silyltriflate (3.98 mL, 22.0 mmol, 1.1 eq.). The reaction mixture was stirred for 3 h at -20°C and then 1 h at 0°C. Cold pentane (-30°C) (500 mL) was added and the resulting suspension was quickly filtered through a small silica gel pad (suspended in pentane containing 2% NEt₃). The organic layer obtained was washed with ice cold aqueous solution of NaHCO₃ (70 mL), ice cold aqueous solution of citric acid solution (2 times 50 mL), again ice cold aqueous solution of NaHCO₃ (2 times 50 mL), brine (2 times 50 mL), dried (Na₂SO₄) and evaporated. Crude product **D** 5.37 g (97%) is sufficiently pure for the next step.

To the solution of the silyl derivative **D** (5.37 g, 19.4 mmol) in THF (160 mL) was added acetyl fluoride (1.22 mL, 19.6 mmol, 1.01 eq.) at -15°C, followed by 1M THF solution of TBAF (0.4 mL, 0.4 mmol, 0.02 eq.). The mixture was stirred at this temperature for 30 min. (¹H NMR control). The solvent was

evaporated and the residue purified by flash chromatography on silica gel (CH₂Cl₂), yielding 4.30 g (90%) of **8**, colorless oil.

IR (film): 2984, 2940, 1742, 1498, 1455, 1372, 1243, 1210, 1122, 1047, 1016. ¹H NMR (400 MHz, CDCl₃): 7.40-7.31 (m, 5H, H(Ar)), 6.34 (s, 1H, H1), 5.24 (q, ³J(H4-H5)=6.99, 1H, H4), 4.87 (s, 2H, H1'), 2.20 (s, 3H, CH₃CO), 1.81 (d, ⁴J(H1-H(2-CH₃))=1.61, H(2-CH₃)), 1.57 (d, ³J(H5-H5)=6.99, 3H, H5). ¹³C NMR (100.6 MHz, CDCl₃): 168.2 (s, CO), 146.9 (s, C3), 143.0 (d, ¹J(C,H) =179, C1), 137.1 (s, (C1Ph)), 128.5 (d, ¹J(C,H) = 160, (C3,C5Ph)), 128.0 (d, ¹J(C,H) = 160, (C4Ph)), 127.3 (d, ¹J(C,H) = 158, (C2,C6Ph)), 110.2 (s, C2), 108.7 (d, ¹J(C,H) =157, C4), 72.3 (t, ¹J(C,H) =145, 1''), 20.4 (q, ¹J(C,H) =129, CH₃CO), 11.2 (q, ¹J(C,H) =128, 2-CH₃), 10.3 (q, ¹J(C,H) =129, C5). MS- CI (NH₃): 246 (M⁺, 3), 186(7), 144(3), 108(11), 105(9), 102(12), 92(23), 91(100). Calc for (C₁₅H₁₈O₃ + Na) 269.1154, found 269.1193.

(2Z,4SR,5SR)-5-Benzyloxy-5-methyl-octa-2,7-dien-3-yl acetate (13a)

Allyltrimethylsilane (0.20 ml, 1.26 mmol, 0.3 eq.) and bistrifluoromethanesulfonimide (0.5 M in CH₂Cl₂) (0.25 ml, 1.26 mmol, 0.30 eq) were mixed in dichloromethane (7 ml) and

stirred for 10 min at 20°C. Then SO₂ (~7 ml, ~157 mmol, ~37 eq) dried over a column of P₂O₅ and alumina was transferred through the vacuum line to the frozen solution (-196 °C). The mixture was allowed to melt and to warm at -78 °C. After 30 minutes at this temperature a mixture of **8** (1.03 g, 4.20 mmol, 1 eq.) and allyltrimethylsilane **9** (1.34 ml, 8.40 mmol, 1.1 eq.) in anhydrous CH₂Cl₂ (0.7 ml) was added dropwise. The reaction mixture was stirred at -78°C for 24 hours. SO₂ was evaporated at -78°C under vacuum for 2 h. Then a solution of triethylamine (0.76 ml, 5.45 mmol, 1.3 eq), trimethylsilyl trifluoromethanesulfonate (0.76 ml, 4.20 mmol, 1 eq) in 2 ml anhydrous MeOH was added at -78°C. The temperature was allowed to rise until -50°C over 3 h. Reaction mixture was poured in cold saturated aqueous solution of NaHCO₃ (50 ml) and extracted by dichloromethane (3x30 ml). The combined organic phase was washed successively with saturated aqueous solution of NaHCO₃, brine, dried (Na₂SO₄) and evaporated. The crude was purified by column chromatography on silica gel (Petrol ether 96/ Ethyl acetate 4) to give 0.82 g (68%) of **13a**, colorless oil.

IR(film): 2977, 2920, 2865, 1756, 1693, 1640, 1497, 1455, 1369, 1215, 1186, 1169, 1072, 1028. ¹H NMR (400 MHz, CDCl₃): 7.35-7.26 (m, 5H, Ph), 5.88 (dddd, ³J_{trans}(H7-H8)=17.3, ³J_{cis}(H7-H8)=9.9, ³J(H7-H6)=7.4, ³J(H7-H6')=6.8 1H, H7), 5.19 (q, ³J(H2-H1)=7.40, 1H, H2), 5.11 (ddd, ³J_{trans}(H7-H8)=17.3, ²J(H8-H8')=1.8, ⁴J(H8-H6)=1.2, 1H, H8), 5.06 (dt, ³J_{cis}(H7-H8)=9.9,

$^2J(H8-H8')=^4J(H8-H6)=1.3$, 1H, H8'), 4.55 (d, $^2J(H(\underline{CH}_2Ph)-H'(\underline{CH}_2Ph))=11.7$, H($\underline{CH}_2Ph$)), 4.52 (d, $^2J(H(\underline{CH}_2Ph)-H'(\underline{CH}_2Ph))=11.7$, H'($\underline{CH}_2Ph$)), 3.47 (ddd, $^3J(H5-H4)=6.7$, $^3J(H4-H6)=5.5$, $^3J(H4-H6')=4.3$, 1H, H5), 2.67 (quintet, $^3J(H4-4-(\underline{CH}_3))=6.8$, $^3J(H4-H5)=6.2$, 1H, H4), 2.36-2.28 (m, 1H, H6'), 2.24 (tdd, $^2J(H6-H6')=14.8$, $^3J(H6-H7)=7.4$, $^4J(H6-H8)=1.0$, 1H, H6), 2.11 (s, 3H, $\underline{CH}_3CO$), 1.50 (d, 3H, $^3J(H1-H2)=6.8$, 3H, H1), 1.07 (d, $^3J(H4-4-(\underline{CH}_3))=7.4$, 3H, H(4- $\underline{CH}_3$)). ^{13}C NMR (100.6 MHz, $CDCl_3$): 168.5 (s, C=O), 149.9 (s, C3), 138.7 (s, (PhC1)), 135.7, (d, $^1J(C,H)=154$, C7)), 128.3 (d, $^1J(C,H)=160$, (PhC3,C5)), 127.9 (d, $^1J(C,H)=157$, (PhC2,C6)), 127.6 (s, $^1J(C,H)=157$, (PhC4)), 116.7 (t, $^1J(C,H)=156$, C8), 112.4 (d, $^1J(C,H)=154$, C2), 79.9 (d, $^1J(C,H)=141$, C5), 71.8 (t, $^1J(C,H)=145$, ($\underline{CH}_2Ph$)), 40.8 (d, $^1J(C,H)=129$, C4), 34.9 (t, $^1J(C,H)=125$, C6), 20.7 (q, $^1J(C,H)=129$, $\underline{CH}_3CO$), 12.6 (q, $^1J(C,H)=131$, 4- $\underline{CH}_3$), 11.1 (q, $^1J(C,H)=128$, C1). MS-CI (NH_3): 306($[M+18]^+$, 84), 289($[M+1]^+$, 89), 247(9), 229(34), 176(15), 161(28), 139(10), 127(14), 108(33), 91(100). El. anal. calc. $C_{18}H_{24}O_3$ (288.38): C 74.97, H 8.39. Found: C 74.88, H 8.38.

(2Z,4SR,5SR) 5-Benzyloxy-7-chloromethyl-4-methyl-octa-2,7-dien-3-yl acetate (13b)

Same procedure as that described for the preparation of **13a** starting from diene **8** and using **10** instead of **9**. Yield 34%, colorless oil.

IR(film): 2876, 2923, 2880, 1755, 1694, 1645, 1498, 1455, 1370, 1218, 1166, 1070, 1028. ^1H NMR (400 MHz, CDCl_3): 7.36-7.29 (m, 5H, Ph), 5.21 (s+q, 2H, $^3\text{J}(\text{H1-H2})=6.8$, H2, H8), 5.06 (s, 1H, H8'), 4.55 (d, 1H, $^2\text{J}(\text{H}(\text{CH}_2\text{Ph})-\text{H}'(\text{CH}_2\text{Ph}))=11.7$, H(CH_2Ph)), 4.43 (d, 1H, $^2\text{J}(\text{H}(\text{CH}_2\text{Ph})-\text{H}'(\text{CH}_2\text{Ph}))=11.7$, H(CH_2Ph)), 4.08 (s, 2H, CH_2Cl), 3.62 (ddd, 1H, $^3\text{J}(\text{H5-H6})=9.0$, $^3\text{J}(\text{H5-H6}')=3.2$, $^3\text{J}(\text{H4-H5})=4.6$, 1H, H5), 2.76 (dq, $^3\text{J}(\text{H4-4-(CH}_3\text{)})=7.0$, $^3\text{J}(\text{H4-H5})=4.6$, 1H, H4), 2.44 (ddd, $^2\text{J}(\text{H6-H6}')=14.6$, $^3\text{J}(\text{H5-H6}')=3.2$, $^4\text{J}(\text{H6}'-\text{H8})=0.9$, 1H, H6'), 2.29 (ddd, $^2\text{J}(\text{H6-H6}')=14.6$, $^3\text{J}(\text{H5-H6})=8.9$, $^4\text{J}(\text{H6-H8})=0.7$, 1H, H6), 2.14 (s, 3H, CH_3CO), 1.51 (dd, 3H, $^3\text{J}(\text{H1-H2})=6.8$, $^5\text{J}(\text{H1-H4})=1.2$, 3H, H1), 1.10 (d, $^3\text{J}(\text{H4-4-(CH}_3\text{)})=7.0$, 3H, H(4- CH_3)). ^{13}C NMR (100.6 MHz, CDCl_3): 168.1 (C=O), 149.6 (C3), 142.9 (C7), 138.2 (PhC1), 128.3 (PhC3,C5), 127.9 (PhC2,C6), 127.6 (PhC4), 116.8 (C8), 112.0 (C2), 78.6 (CH_2Ph), 71.5 (C5), 48.6 (CH_2Cl), 40.1 (C4), 33.8 (C6), 20.7 (CH_3CO), 11.8 (4- CH_3), 11.0 (C1). MS-CI (NH_3): 354 ($[\text{M}+18]^+$, 70), 340(16), 339(45), 338(44), 337($[\text{M}+1]^+$, 91), 336(M^+ , 12), 295(10), 277(45), 241(12), 209(17), 176(25), 157(10), 127(15), 108(26), 91(95).

$\text{C}_{19}\text{H}_{25}\text{ClO}_3$ (336.15). El. anal. calc. $\text{C}_{19}\text{H}_{25}\text{ClO}_3$ (336.85): C 67.75, H 7.48, Cl 10.52. Found: C 67.88, H 7.39, Cl 10.58.

**(±)-(1*E*,3*Z*)-2-Methyl-1-(1'-phenylethoxy)penta-1,3-dien-3-yl
isobutyrate (14a)**

Same procedure as that described for the preparation of **8** using isobutyryl fluoride instead of acetyl fluoride and (±)-(*E*) 2-methyl-1-(1-phenylethoxy)-pent-1-en-one (**E**) instead of **A**. Yield 80%, colorless oil.

IR (film): 3062, 2929, 1760, 1665, 1640, 1453, 1375, 1216, 1192. ^1H NMR (400 MHz, CDCl_3): 7.37–7.26 (m, 5H, Ph), 6.20 (s, 1H, H1), 5.18 (q, 1H, $^3\text{J}(\text{H1}'-\text{H2}')=7.4$ Hz, H1'), 4.78 (q, 1H, $^3\text{J}(\text{H4}-\text{H5})=6.8$ Hz, H4), 2.60 (sept, 1H, $^3\text{J}=7.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.80 (s, 3H, 2-Me), 1.54 (d, 3H, $^3\text{J}(\text{H4}-\text{H5})=6.2$ Hz, H5), 1.51 (d, 3H, $^3\text{J}(\text{H1}'-\text{H2}')=6.8$ Hz, H2'), 1.16, 1.13 (2d, 6H, $^3\text{J}=6.8$ Hz, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (100.6 MHz, CDCl_3): 173.5 (s, CO), 146.9 (s, C3), 142.7 (s, Ph), 142.1 (d, $^1\text{J}_{\text{C}-\text{H}}=180$ Hz, H1), 128.5, 127.7, 126.0 (3d, $^1\text{J}_{\text{C}-\text{H}}=160$ Hz, $^1\text{J}_{\text{C}-\text{H}}=160$ Hz, $^1\text{J}_{\text{C}-\text{H}}=154$ Hz, Ph), 110.0 (s, C2), 108.1 (d, $^1\text{J}_{\text{C}-\text{H}}=148$ Hz, C4), 80.0 (d, $^1\text{J}_{\text{C}-\text{H}}=148$ Hz, C1'), 34.0 (d, $^1\text{J}_{\text{C}-\text{H}}=135$ Hz, $\text{CH}(\text{CH}_3)_2$), 23.6 (q, $^1\text{J}_{\text{C}-\text{H}}=128$ Hz, C2'), 19.0 (q, $^1\text{J}_{\text{C}-\text{H}}=122$ Hz, $\text{CH}(\text{CH}_3)_2$), 11.0, 10.3 (2q, $^1\text{J}_{\text{C}-\text{H}}=125$ Hz, $^1\text{J}_{\text{C}-\text{H}}=128$ Hz, C5, C(2Me)). MS-CI (NH_3): 306 ($[\text{M}+18]^+$, 5), 185(10), 105(89), 85(22), 71(100). HRMS (MALDI): calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}^+$ 311.1623 $[\text{M}+\text{Na}^+]$, found 311.1684.

(-)-(1Z,3Z,1'S)-2-Methyl-1-(1'-phenylethoxy)penta-1,3-dien-3-yl benzoate (14b)

Same procedure as that described for the preparation of **8** using (-)-(1*E*,1'*S*) 2-methyl-1-(1-phenylethoxy)-pent-1-en-one (**G**) instead of **C**, and benzoyl fluoride instead of acetyl fluoride. Yield 90%, colorless oil.

$\alpha]_{\text{D}}^{25} = -22$; $\alpha]_{577}^{25} = -24$; $\alpha]_{546}^{25} = -27$; $\alpha]_{435}^{25} = -47$; $\alpha]_{405}^{25} = -56$ ($c=1.01$, CHCl_3).

IR (film): 3356, 3062, 2977, 1732, 1660, 1634, 1493, 1451, 1246, 1176, 1088. ^1H NMR (400 MHz, CDCl_3): 8.09 (d, $^3J=7.36$, 2H, Bz), 7.63 (t, $^3J=7.34$, 1H, Bz), 7.49 (t, $^3J=7.68$, 2H, Bz), 7.32-7.21 (m, 5H, Ph), 6.30 (s, 1H, H1), 5.31 (q, $^3J=7.04$, 1H, H1'), 4.74 (q, $^3J=6.40$, 1H, H4), 1.88 (s, 3H, 2Me), 1.59 (d, $^3J=7.04$, 3H, H2'), 1.51 (d, $^3J=6.40$, 3H, H5). ^{13}C NMR (100.6 MHz, CDCl_3): 164.0 (s, CO), 147.4 (s, C3), 142.7 (s, Ar), 142.6 (d, $^1J(\text{C},\text{H}) = 178$, C3), 133.3 (d, $^1J(\text{C},\text{H}) = 161$, Ar), 130.1 (d, $^1J(\text{C},\text{H}) = 160$, Ar), 129.5 (s, Ar), 128.6 (d, $^1J(\text{C},\text{H}) = 163$, Ar), 128.5 (d, $^1J(\text{C},\text{H}) = 160$, Ar), 127.7 (d, $^1J(\text{C},\text{H}) = 161$, Ar), 125.9 (d, $^1J(\text{C},\text{H}) = 161$, Ar), 110.0 (s, C2), 108.6 (d, $^1J(\text{C},\text{H}) = 156$, C1), 80.2 (d, $^1J(\text{C},\text{H}) = 144$, C1'), 23.5 (q, $^1J(\text{C},\text{H}) = 129$, C2'),

11.3 (q, $^1J(\text{C},\text{H}) = 128$, 2Me), 10.5 (q, $^1J(\text{C},\text{H}) = 127$, C5). HRMS (MALDI): calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{Na}^+$ 345.1467 $[\text{M}+\text{Na}^+]$, found 345.1434.

(*E*, *Z*, 1'*R*)-1-(1-phenylethoxy)penta-1,4-dien-3-yl benzoate
(ent-14 c)

Same procedure as that described for the preparation of **8** using (*E*, 1*R*)-1-(1-phenylethoxy)penta-1-ene-3-one (**I**) instead of **C** and benzoyl fluoride instead of acetyl fluoride. The product is obtained as a mixture 68:25:7 of (*E*,*Z*), (*E*,*E*), (*Z*,*Z*) isomers. Yield: 72 %, colorless oil.

$R_f = 0.35$ (Petrol ether 80/ Ether 20). UV (CH_3CN) : 260 (6392), 255 (7600), 227 (4839), 191 (880), 237 (592). IR (KBr) : 3062, 2978, 2930, 1736, 1673, 1626, 1601, 1451, 1374, 1316, 1248, 1210, 1167, 1091, 1068, 1026, 915, 762, 701. ^1H NMR (400 MHz, CDCl_3 , only main isomer is described) : 8.12 (d, $J=8.4$, 2 arom. CH), 7.62 (d, $J=7.4$, 1 arom. CH), 7.49 (d, $J=8.0$, 2 arom. CH), 7.33-7.25 (m, 5 arom. CH), 6.43 (d, $^3J(\text{H}-\text{C}(1), \text{H}-\text{C}(2))=12.4$, 1H, H-C(1)), 5.60 (d, $^3J(\text{H}-\text{C}(2), \text{H}-\text{C}(1))=12.4$, 1H, H-C(2)), 5.18 (q, $^3J(\text{H}-\text{C}(4), \text{Me}-\text{C}(4))=7.0$, 1H, H-C(4)), 4.83 (q, $^3J(\text{H}-\text{C}(1'), \text{H}-\text{C}(2'))=6.5$, H-C(1')), 1.56 (d, $^3J(\text{Me}-\text{C}(4), \text{H}-\text{C}(4))=7.0$, Me-C(4)), 1.51 (d, $^3J(\text{H}-\text{C}(2'), \text{H}-\text{C}(1'))=6.5$, H-C(2')). ^{13}C NMR (100.6 MHz, CDCl_3) (only main isomer is described): 163.7 (s, CO), 147.4 (d, $J^1(\text{C},\text{H}) = 161$, arom. C),

145.9 (d, $J^1(\text{C},\text{H}) = 180$, C(2)), 144.6-142.2 (2s, arom. C + C(3)), 133.4-130.0-128.5-127.7-125.7 (d, $J^1(\text{C},\text{H}) = 161$, arom. C), 111.2 (d, $J^1(\text{C},\text{H}) = 157$, C(4)), 103.8 (d, $J^1(\text{C},\text{H}) = 154$, C(1)), 78.9 (d, $J^1(\text{C},\text{H}) = 143$, C(1')), 23.3 (q, $J^1(\text{C},\text{H}) = 128$, C(2')), 11.1 (q, $J^1(\text{C},\text{H}) = 128$, Me-C(4)). MS (EI) : 246 (2, M), 205 (5), 142 (41), 122 (10), 105 (100), 100 (50), 77 (23). HRMS (MALDI): calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{Na}^+$ 331.1310 $[\text{M}+\text{Na}^+]$, found 331.1298.

(±)-(2Z, 1'RS,4RS,5RS)-4-Methyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl isobutyrate (17a)

Same procedure as that described for the preparation of **13a** using diene (±)-**14a** instead of diene **8**. Yield: 68%, colorless oil.

IR (film) : 3029, 2975, 2933, 2878, 1750, 1690, 1644, 1454, 1368, 1238, 1138, 1090. ^1H NMR (400 MHz, CDCl_3): 7.35-7.25 (m, 5H, Ph), 5.67 (dddd, 1H, $^3J(\text{H7}-\text{H8a})=16.6$ Hz, $^3J(\text{H7}-\text{H8b})=10.0$ Hz, $^3J(\text{H7}-\text{H6a})=6.4$ Hz, $^3J(\text{H7}-\text{H6b})=7.0$ Hz, H7), 5.17 (dq, 1H, $^3J(\text{H1}-\text{H2})=6.4$ Hz, $^4J(\text{H2}-\text{H4})=1.3$ Hz H2), 4.98 (dm, 1H, $^3J(\text{H7}-\text{H8a})=16.6$ Hz, H8a), 4.94 (dm, 1H, $^3J(\text{H7}-\text{H8b})=10.0$ Hz, H8b), 4.49 (q, 1H, $^3J(\text{H1}'-\text{H2}')=6.4$ Hz, H1'), 3.36 (dt, 1H, $^3J(\text{H5}-\text{H4})=5.1$ Hz, $^3J(\text{H5}-\text{H6})=7.0$ Hz, H5), 2.80 (m, 2H, H4), 2.60

(sept, 1H, $^3J=7.0$ Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 2.13-2.09 (m, 2H, H6), 1.48 (dd, 3H, $^3J(\text{H1-H2})=7.4$ Hz, $^5J(\text{H1-H4})=1.3$ Hz, H1), 1.41 (d, 3H, $^3J=6.4$ Hz, H2'), 1.16, 1.15 (2d, 6H, $^3J=7.0$ Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 1.08 (d, 3H, $^3J=7.0$ Hz, H(4-Me)). ^{13}C NMR (100.6 MHz, CDCl_3): 174.4 (s, CO), 150.2 (s, C3), 143.9 (s, Ph), 136.1 (d, $^1J_{\text{C-H}}=153$ Hz, C7), 128.2, 127.4, 126.8 (3d, $^1J_{\text{C-H}}=154$ Hz, $^1J_{\text{C-H}}=157$ Hz, $^1J_{\text{C-H}}=160$ Hz, Ph), 116.1 (t, $^1J_{\text{C-H}}=157$ Hz, C8), 111.4 (d, $^1J_{\text{C-H}}=155$ Hz, C2), 76.6 (d, $^1J_{\text{C-H}}=141$ Hz, C1'), 75.5 (d, $^1J_{\text{C-H}}=143$ Hz, C5), 39.3 (d, $^1J_{\text{C-H}}=125$ Hz, C4), 34.7 (t, $^1J_{\text{C-H}}=125$ Hz, C6), 34.1 (d, $^1J_{\text{C-H}}=130$ Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 24.1 (q, $^1J_{\text{C-H}}=126$ Hz, C2'), 19.0, 19.1 (2q, $^1J_{\text{C-H}}=127$ Hz, $\underline{\text{CH}}(\text{CH}_3)_2$), 11.3, 10.8 (2q, $^1J_{\text{C-H}}=127$ Hz, $^1J_{\text{C-H}}=125$ Hz, C1, 4-Me). MS-CI (NH_3): 331 ($[\text{M}+1]^+$, 5), 227(60), 105(100). El. anal. calc. $\text{C}_{21}\text{H}_{30}\text{O}_3$ (330.46): C 76.33, H 9.15. Found: C 76.22, H 9.10.

(-)-(2Z,1'S, 4S,5S)-4-Methyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl benzoate (17b)

Same procedure as that described for the preparation of **13a** using diene **14b** instead of diene **8**. Yield 70%, colorless oil.

$[\alpha]_{\text{D}}^{25} = -34$; $[\alpha]_{577}^{25} = -41$; $[\alpha]_{546}^{25} = -36$; $[\alpha]_{435}^{25} = -54$; $[\alpha]_{405}^{25} = -63$ ($c=1.04$, CHCl_3).

IR (film): 3063, 2975, 2926, 1732, 1694, 1601, 1452, 1260, 1174, 1090. ^1H NMR (400 MHz, CDCl_3): 8.08 (d, $^3J=7.36$, 2H, Bz),

7.65 (t, $^3J=7.68$, 1H, Bz), 7.50 (t, $^3J=7.68$, 2H, Bz), 7.23-7.20 (m, 2H, Ph), 7.17-7.14 (m, 3H, Ph), 5.69 (ddt, $^3J=17.27$, $^3J=10.24$, $^3J=7.04$, 1H, H7), 5.33 (q, $^3J=7.04$, 1H, H2), 5.06-4.96 (m, 2H, H8), 4.50 (q, $^3J=6.40$, 1H, H1'), 3.50 (dt, $^3J=7.68$, $^3J=4.16$, 1H, H5), 2.97 (m, 1H, H4), 2.28-2.15 (m, 2H, H6), 1.58 (d, $^3J=6.78$, 3H, H1), 1.44 (d, $^3J=6.40$, 3H, H2'), 1.20 (d, $^3J=7.04$, 3H, 4Me). ^{13}C NMR (100.6 MHz, CDCl_3): 164.1 (s, CO), 150.3 (s, C3), 143.6 (s, Ar), 136.0 (d, $^1J(\text{C,H}) = 153$, Ar), 133.2 (d, $^1J(\text{C,H}) = 160$, Ar), 129.9 (d, $^1J(\text{C,H}) = 165$, Ar), 128.4 (d, $^1J(\text{C,H}) = 163$, Ar), 128.0 (d, $^1J(\text{C,H}) = 162$, Ar), 127 (d, $^1J(\text{C,H}) = 160$, Ar), 126.8 (d, $^1J(\text{C,H}) = 160$, Ar), 116.1 (t, $^1J(\text{C,H}) = 153$, C8), 112.0 (d, $^1J(\text{C,H}) = 158$, C2), 76.8 (d, $^1J(\text{C,H}) = 145$, C1'), 75.7 (d, $^1J(\text{C,H}) = 143$, C5), 39.6 (d, $^1J(\text{C,H}) = 128$, C4), 34.8 (t, $^1J(\text{C,H}) = 121$, C6), 23.9 (q, $^1J(\text{C,H}) = 129$, C2'), 11.6 (q, $^1J(\text{C,H}) = 128$, 4Me), 11.0 (q, $^1J(\text{C,H}) = 128$, C1). HRMS (MALDI): calcd for $\text{C}_{24}\text{H}_{28}\text{O}_3\text{Na}^+$ 387.1936 $[\text{M}+\text{Na}^+]$, found 387.1935. El. anal. calc. $\text{C}_{24}\text{H}_{28}\text{O}_3$ (364.48): C 79.09, H 7.74. Found: C 79.12, H 7.72.

(1Z,1'R,3R)-7-methyl-5-(1-phenylethoxy)octa-2,7-dien-3-yl benzoate (18a)

Same procedure as that described for the preparation of **13a** using diene **ent-14c** and (2-methylenepropa-1,3-

diyl)bis(trimethylsilane) **15** instead of **8** and **9**, respectively.
Yield : 69%, colorless oil.

IR(film): 3070, 2974, 2928, 2864, 1732, 1698, 1602, 1452, 1262, 1174, 1088, 1068, 1026, 890, 760, 709, 702. UV (CH₃CN): 273 (2025), 263 (2179), 261 (2215), 238 (8577), 226 (6321), 203 (891), 189 (1061). ¹H NMR (400 MHz, CDCl₃): 8.09 (d, ³J=7.4, 2H, Bz), 7.63 (d, ³J=7.4, 1H, Bz), 7.49 (d, ³J=7.4, 2H, Bz), 7.27-7.20 (m, 5H, Ph), 5.29 (q, ³J(H-C(2), H-C(1))=6.8, 1H, H-C(2)), 4.68-4.64 (2s, 2H, H-C(8)), 4.54 (q, ³J(H-C(1'), H-C(2'))=6.2, 1H, H-C(1')), 3.57 (quint., 1H, ³J(H-C(3), H-C(4))=6.2, 1H, H-C(5)), 2.57 (dd, ²J(H-C(4), H-C(4))=14.8, ³J(H-C(4), H-C(5))=5.5, 1H, H-C(4)), 2.54 (dd, ²J(H-C(4), H-C(4))=14.8, ³J(H-C(4), H-C(5))=5.5, 1H, H-C(4)), 2.17 (2 dd, ²J(H-C(6), H-C(6))=14.2, ³J(H-C(6), H-C(5))=7.4, 2H, H-C(6)), 1.58 (d, ³J(H-C(1), H-C(2))=6.8, 3H, H-C(1)), 1.41 (s, 3H, Me-C(7)), 1.37 (d, ³J(H-C(2'), H-C(1'))=6.2, 3H, H-C(2')). ¹³C NMR (100.6 MHz, CDCl₃): 164.2 (s, CO), 146.5-143.9-142.4 (3s, arom. C + C(3) + C(7)), 133.3-129.9-128.5-128.1-128.0-127.3-126.7 (1s + 6d, ¹J(C,H) =163, arom. C), 113.9 (d, ¹J(C,H) =160, C(2)), 113.0 (t, ¹J(C,H) =160, C(8)), 76.0 (d, ¹J(C,H) =141, C(1')), 72.2 (d, ¹J(C,H) =141, C(5)), 43.7 (t, ¹J(C,H) =126, C(6)), 38.6 (t, ¹J(C,H) =128, C(4)), 23.9 (q, ¹J(C,H) =130, C(2')), 22.4 (q, ¹J(C,H) =130, Me-C(7)), 10.9 (q, ¹J(C,H) =124, C(1)). El. anal. calc. C₂₄H₂₈O₃ (364.48): C 79.09, H 7.74. Found: C 79.09, H 7.74.

(-)-(2Z,4S,5S,1'S)-4,7-Dimethyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl benzoate (18b)

Same procedure as that described for the preparation of **13a** using diene **14b** and **15** instead of diene **8** and **9**, respectively. Yield: 74%, colorless oil.

$[\alpha]_D^{25} = -10$; $[\alpha]_{577}^{25} = -11$; $[\alpha]_{546}^{25} = -11$; $[\alpha]_{435}^{25} = -12$; $[\alpha]_{405}^{25} = -10$ ($c=1.28$, CHCl_3).
 IR(film): 3065, 2974, 2925, 1732, 1694, 1601, 1452, 1260, 1165, 1090. ^1H NMR (400 MHz, CDCl_3): 7.74 (d, $^3J=7.36$, 2H, Bz), 7.36 (d, $^3J=7.36$, 1H, Bz), 7.20 (d, $^3J=7.68$, 2H, Bz), 6.86-6.74 (m, 5H, Ph), 5.00 (dq, $^3J=6.72$, $^4J=1.00$, 1H, H2), 4.40 (s, 2H, H8), 4.14 (q, $^3J=6.72$, 1H, H1'), 3.29 (dt, $^3J=7.36$, $^3J=4.16$, 1H, H5), 2.75-2.69 (m, 1H, H4), 1.84-1.82 (n, 2H, H6), 1.27 (dd, $^3J=6.72$, $^4J=1.30$, 3H, H1), 1.11 (d, $^3J=6.72$, 3H, H2'), 1.10 (s, 3H, 7Me), 0.94 (d, $^3J=6.72$, 3H, 4Me). ^{13}C NMR (100.6 MHz, CDCl_3): 164.1 (s, CO), 150.5 (s, C3), 143.3 (s, C7), 143.1 (s, Ar), 133.3 (d, $^1J(\text{C,H}) = 163$, Ar), 130.0 (d, $^1J(\text{C,H}) = 163$, Ar), 129.7 (s, Ar), 128.5 (d, $^1J(\text{C,H}) = 165$, Ar), 128.0 (d, $^1J(\text{C,H}) = 156$, Ar), 127.3 (d, $^1J(\text{C,H}) = 159$, Ar), 127.0 (d, $^1J(\text{C,H}) = 161$, Ar), 112.6 (t, $^1J(\text{C,H}) = 152$, C8), 112.0 (d, $^1J(\text{C,H}) = 160$, C2), 75.1 (d, $^1J(\text{C,H}) = 141$, C1'), 74.3 (d, $^1J(\text{C,H}) = 141$, C5), 39.0 (d, $^1J(\text{C,H}) = 129$, C4), 38.6 (d, $^1J(\text{C,H}) = 125$, C6), 23.9 (q, $^1J(\text{C,H}) = 129$, C2'), 22.2 (q, $^1J(\text{C,H}) = 130$,

7Me), 11.1 (q, $^1J(\text{C},\text{H}) = 127$, 4Me), 11.0 (q, $^1J(\text{C},\text{H}) = 128$, Cl).
 HRMS (MALDI): calcd for $\text{C}_{25}\text{H}_{30}\text{O}_3\text{Na}^+$ 401.2093 $[\text{M}+\text{Na}^+]$, found 401.2091. El. anal. calc. $\text{C}_{25}\text{H}_{30}\text{O}_3$ (378.5): C 79.33, H 7.99.
 Found: C 79.29, H 8.10.

(±)-(2Z, 1'RS, 4RS, 5RS)-7-(Acetyloxy)methyl-4-methyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl isobutyrate (19a).

Same procedure as that described for the preparation of **13a** using diene **14a** and **16** instead of diene **8** and **9**, respectively. 1:1 mixture of toluene/ CH_2Cl_2 was used as solvent. Yield: 69%, colorless oil.

IR(film): 3067, 2974, 1747, 1730, 1653, 1455, 1428, 1371, 1248, 1119, 1089. ^1H NMR (400 MHz, CDCl_3): 7.33–7.24 (m, 5H, Ph), 5.17 (dq, $^3J=7.04$, $^4J=1.28$, 1H, H2), 5.00 (bd, $^4J=1.28$, 1H, H8a), 4.91 (bs, 1H, H8b), 4.46 (q, $^3J=6.40$, 1H, H1'), 4.26 (AB syst. $^2J=14.7$, 2H, 7- CH_2OAc), 3.45 (ddd, $^3J=8.96$, $^3J=4.48$, $^3J=3.20$, 1H, H5), 2.88 (m, 1H, H4), 2.54 (sept, $^3J=7.04$, 1H, Me_2CHCOO), 2.16 (dd, $^2J=14.08$, $^3J=2.56$, 1H, H6a), 2.10 (dd, $^2J=14.08$, $^3J=5.11$, 1H, H6b), 2.05 (s, 3H, OAc), 1.48 (dd, $^3J=7.04$, $^4J=1.21$, 3H, H1), 1.41 (d, $^3J=6.40$, 3H, H2'), 1.15, 1.13 (2d, $^3J=7.40$, 6H, Me_2CHCOO), 1.10 (d, $^3J=7.40$, 4Me). ^{13}C NMR (100.6 MHz, CDCl_3): 174.4 (s, CO), 170.5 (s, CO), 150.1 (s,

C3), 143.4 (s, C7), 141.4 (s, Ar), 128.2 (d, $^1J(\text{C,H}) = 160$, Ar), 127.6 (d, $^1J(\text{C,H}) = 157$, Ar), 126.9 (d, $^1J(\text{C,H}) = 154$, Ar), 114.4 (t, $^1J(\text{C,H}) = 157$, C8), 111.5 (d, $^1J(\text{C,H}) = 154$, C2), 75.0 (d, $^1J(\text{C,H}) = 141$, C5), 74.8 (d, $^1J(\text{C,H}) = 145$, C1'), 66.7 (t, $^1J(\text{C,H}) = 157$, 7-CH₂OAc), 38.8 (d, $^1J(\text{C,H}) = 128$, C4), 34.1 (d, $^1J(\text{C,H}) = 125$, Me₂CHCOO), 33.9 (t, $^1J(\text{C,H}) = 125$, C6), 24.2 (q, $^1J(\text{C,H}) = 125$, Me₂CHCOO), 20.9 (q, $^1J(\text{C,H}) = 128$, C2'), 19.0 (q, $^1J(\text{C,H}) = 128$, OAc), 10.8, 10.7 (2q $^1J(\text{C,H}) = 128$, C1, 4Me). MS- CI (NH₃): 420 ([M+18]⁺, 41), 403 ([M+1]⁺, 2), 300 (29), 155 (36), 105 (100), 71 (25). El. anal. calc. C₂₄H₃₄O₅ (402.52): C 71.61, H 8.51. Found: C 71.70, H 8.58.

(-)-(2Z,4S,5S,1'S)-7-(Acetyloxy)methyl-4-methyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl benzoate (19b)

Same procedure as that described for the preparation of **13a** using diene **14b** and **16** instead of diene **8** and **9**, respectively. 1:1 mixture of toluene/CH₂Cl₂ was used as solvent. Yield: 71%, colorless oil.

$\alpha]_{\text{D}}^{25} = -8$; $\alpha]_{577}^{25} = -8$; $\alpha]_{546}^{25} = -10$; $\alpha]_{435}^{25} = -11$; $\alpha]_{405}^{25} = -10$ (c=1.03, CHCl₃).

IR(film) : 3063, 2975, 1737, 1653, 1601, 1452, 1372, 1260, 1165, 1098. ¹H NMR (400 MHz, CDCl₃): 8.00 (d, $^3J = 7.36$, 2H, Bz),

7.63 (d, $^3J=7.68$, 1H, Bz), 7.48 (d, $^3J=7.68$, 2H, Bz), 7.09–7.00 (m, 5H, Ph), 5.28 (q, $^3J=6.72$, 1H, H2), 4.97 (s, 1H, H8), 4.90 (s, 1H, H8), 4.39 (q, $^3J=6.40$, 1H, H1'), 4.18 (AB system, $^2J=14.7$, 2H, 7-CH₂OAc), 3.52 (dt, $^3J=9.28$, $^3J=3.2$, 1H, H5), 3.01–2.95 (m, 1H, H4), 2.21 (dd, $^2J=14.40$, $^3J=3.2$, 1H, H6), 2.10 (dd, $^2J=14.4$, $^3J=9.28$, 1H, H6), 2.02 (s, 3H, Ac), 1.53 (d, $^3J=6.72$, 3H, H1), 1.37 (d, $^3J=6.40$, 3H, H2'), 1.16 (d, $^3J=7.36$, 3H, 4Me). ^{13}C NMR (100.6 MHz, CDCl₃): 170.6 (s, CO(Ac)), 164.1 (s, CO(Bz)), 150.3 (s, C3), 142.9 (s, C7), 141.2 (s, Ar), 133.4 (d, $^1J(\text{C,H})=161$, Ar), 130.1 (d, $^1J(\text{C,H})=164$, Ar), 129.6 (s, Ar), 128.6 (d, $^1J(\text{C,H})=166$, Ar), 128.1 (d, $^1J(\text{C,H})=161$, Ar), 127.5 (d, $^1J(\text{C,H})=160$, Ar), 127.0 (d, $^1J(\text{C,H})=162$, Ar), 114.7 (t, $^1J(\text{C,H})=156$, C8), 112.2 (d, $^1J(\text{C,H})=160$, C2), 75.2 (d, $^1J(\text{C,H})=143$, C1'), 74.6 (d, $^1J(\text{C,H})=144$, C5), 66.7 (t, $^1J(\text{C,H})=148$, 7-CH₂OAc), 39.0 (d, $^1J(\text{C,H})=130$, C4), 34.0 (t, $^1J(\text{C,H})=120$, C6), 23.7 (q, $^1J(\text{C,H})=128$, C2'), 20.9 (q, $^1J(\text{C,H})=130$, OAc), 11.0 (q, $^1J(\text{C,H})=128$, C1), 10.9 (q, $^1J(\text{C,H})=128$, 4Me). HRMS (MALDI): calcd for C₂₇H₃₂O₅Na⁺ 459.2147 [M+Na⁺], found 459.2148. El. anal. calc. C₂₇H₃₂O₅ (436.54): C 74.29, H 7.39. Found: C 74.10, H 7.32.

(+)-(2Z,1'R,5R)-7-(Acetyloxy)methyl-5-(1'-phenylethoxy)octa-2,7-dien-3-yl benzoate (ent-19c)

Same procedure as that described for **13a** using diene **ent-14c** and **16** instead of **9** and toluene as solvent instead of CH₂Cl₂. Yield: 62%, colorless oil.

$\alpha]_{\text{D}}^{25} = +53$; $\alpha]_{577}^{25} = +49$; $\alpha]_{546}^{25} = +64$; $\alpha]_{435}^{25} = +109$; $\alpha]_{405}^{25} = +131$ ($c=0.88$, CHCl₃).

R_f = 0.24 (Petrol ether 70/ Ether 30). UV (CH₃CN) : 273 (2683), 263 (2843), 260 (2920), 237 (10867), 205 (6312), 188 (1377). IR (neat) : 3061, 3030, 2975, 2926, 1739, 1734, 1699, 1652, 1602, 1493, 1452, 1371, 1262, 1174, 1087, 1068, 1026, 965, 912, 761, 702. ¹H NMR (400 MHz, CDCl₃) : 8.08 (d, J=8.4, arom. CH), 7.63 (t, J=7.4, 1 arom. CH), 7.50 (t, J=7.9, 2 arom. CH), 7.20 (m, 5 arom. CH), 5.28 (q, 1H, ³J(H-C(1'), H-C(2'))= 6.6, H-C(1')), 5.00-4.88 (2s, 2H, C(8)), 4.50 (q, 1H, ³J(H-C(2), H-C(1))= 6.6, H-C(2)), 4.27 (2d, 2H, ²J= 1.7, CH₂-C(7)), 3.54 (quint, 1H, ³J(H-C(5), H-C(4, 6))= 6.9, H-C(5)), 2.61 (dd, 2H, ²J(H-C(4), H-C(4))=14.8, ³J(H-C(4), H-C(5))=5.2, H-C(4)), 2.22 (dd, 2H, ²J(H-C(6), H-C(6))=14.8, ³J(H-C(6), H-C(5))=6.6, H-C(6)), 1.97 (s, 3H, Me-CO), 1.57 (d, 3H, ³J(H-C(2'), H-C(1'))= 6.6, H-C(2')), 1.37 (d, 3H, ³J(H-C(1), H-C(2))= 6.6, H-C(1)).

^{13}C NMR (100.6 MHz, CDCl_3): 170.5-164.3 (2s, CO + CO), 146.2-143.5-140.6 (3s, C(3), C(7), arom. C), 133.4-130.0-129.6-128.5-127.5-126.7 (m, arom. C), 115.1 (t, $^1\text{J}(\text{C-H})=157$, C(8)), 114.1 (d, $^1\text{J}(\text{C-H})=128$, C(1')), 75.9 (d, $^1\text{J}(\text{C-H})$ = not measurable, C(5)), 72.3 (d, $^1\text{J}(\text{C-H})=144$, C(5)), 66.8 (d, $^1\text{J}(\text{C-H})=147$, $\text{CH}_2\text{-C}(7)$), 39.0 (t, $^1\text{J}(\text{C-H})=132$, C(6)), 38.2 (t, $^1\text{J}(\text{C-H})=128$, C(4)), 23.8 (q, $^1\text{J}(\text{C-H})=127$, C(1)), 20.8 (q, $^1\text{J}(\text{C-H})=130$, MeCO), 10.9 (q, $^1\text{J}(\text{C-H})=127$, C(2')). MS ($\text{M}^+ \text{Na}$): 445 (60, $[\text{M}+\text{Na}]$), 234 (51), 137 (100), 105 (88). HRMS (MALDI): calcd for $\text{C}_{26}\text{H}_{30}\text{O}_5\text{Na}^+$ 445.1991 $[\text{M}+\text{Na}^+]$, found 445.1996.

(1'R,2S,3R)-2-Methyl-3-(1'-phenylethoxy)penta-1,5 diyl di(4-nitro)benzoate (20)

Ozone was bubbled through the solution of **ent-17b** (1.00 g, 2.74 mmol, 1 eq) in Et_2O (30 mL) at -78°C until saturation (20 min.). Excess of ozone was removed by passing dry nitrogen gas through the reaction mixture. $\text{BH}_3\cdot\text{Me}_2\text{S}$ (2.3 mL, 21.9 mmol, 8 eq) was added at -78°C . The reaction mixture was stirred for

24 h at -78°C and then was let to reach $+20^{\circ}\text{C}$. Additional 30 mL of Et_2O was added and the solution was washed with brine (3 times 15 mL), dried (Na_2SO_4) and concentrated at room temperature. The residue was redissolved in Et_2O (30 mL), LiAlH_4 (0.52 g, 13.5 mmol, 5 eq) was added and the mixture was refluxed for 1h. Water (1 mL) was added slowly at -20°C followed by 10% aqueous solution of NaOH (0.9 mL). The resulted mixture was stirred at RT until complete precipitation, filtered and evaporated. Purification of the residue by chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) gave **K** 0.46 g (70%) as colorless oil.

To the solution of diol **K** (100 mg, 0.42 mmol, 1 eq) and DMAP (210 mg, 1.72 mmol, 4 eq) in CH_2Cl_2 (6 mL) was added *p*-nitrobenzoyl chloride (242 mg, 1.3 mmol, 3 eq) at -10°C . The reaction mixture was let to reach RT and stirred for 4 h (TLC control). Ethyl acetate (20 mL) was added and the resulted solution was successively washed with aq. sat. CuSO_4 solution (3 times 7 mL), brine (2 times 5 mL), dried over Na_2SO_4 and evaporated. Solid crude product was purified by chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$). Yield 0.18 g (81%), white solid. Analytical sample for X-ray analysis was obtained by recrystallization from pentane/ CH_2Cl_2 mixture (mp. $103\text{--}104^{\circ}\text{C}$). X-Ray crystallographic data have been submitted to CCDC.

IR(KBr): 2986, 1725, 1608, 1530, 1422, 1351, 1118, 1104, 1015.

^1H NMR (400 MHz, CDCl_3) : 8.22 (d, $^3J=9.25$, 2H, *p* $\text{NO}_2\text{-Bz}$), 8.08

(d, $^3J=9.25$, 2H, $p\text{NO}_2\text{-Bz}$), 8.03 (d, $^3J=9.25$, 2H, $p\text{NO}_2\text{-Bz}$), 7.85 (d, $^3J=9.25$, 2H, $p\text{NO}_2\text{-Bz}$), 7.29 (d, $^3J=7.40$, 2H, Ph), 7.21 (t, $^3J=7.40$, 2H, Ph), 7.13 (t, $^3J=6.80$, 1H, Ph), 4.56 (q, $^3J=6.20$, 1H, 1'), 4.43 (ddd, $^2J=10.78$, $^3J=5.30$, $^3J=4.90$, 1H, H5a), 4.28 (m, 3H, H5b, H1), 3.61 (dt, $^3J=8.31$, $^3J=4.10$, 1H, H3), 2.59 (dq, $^3J=6.69$, $^3J=4.10$, 1H, H2), 1.84 (m, 2H, H4), 1.48 (d, $^3J=6.20$, 3H, H2'), 1.12 (d, $^3J=7.40$, 3H, 2-Me). ^{13}C NMR (100.6 MHz, CDCl_3) : 164.4, 164.3 (2s, CO), 150.5, 150.3 (2s, $p\text{NO}_2\text{-Bz}$), 143.1 (s, Ph), 135.5, 135.3 (2s, $p\text{NO}_2\text{-Bz}$), 130.6, 130.4 (2d, $^1J(\text{C,H})=170$, $p\text{NO}_2\text{-Bz}$), 128.5 (d, $^1J(\text{C,H})=160$, Ph), 127.7 (d, $^1J(\text{C,H})=160$, Ph), 126.8 (d, $^1J(\text{C,H})=152$, Ph), 123.5 (d, $^1J(\text{C,H})=167$, $p\text{NO}_2\text{-Bz}$), 123.2 (d, $^1J(\text{C,H})=173$, $p\text{NO}_2\text{-Bz}$), 75.3 (d, $^1J(\text{C,H})=141$, C1'), 72.0 (d, $^1J(\text{C,H})=141$, C3), 67.6 (t, $^1J(\text{C,H})=148$, C1), 62.5 (t, $^1J(\text{C,H})=145$, C5), 33.8 (d, $^1J(\text{C,H})=129$, C2), 28.7 (t, $^1J(\text{C,H})=125$, C4), 23.9 (q, $^1J(\text{C,H})=125$, C2'), 11.2 (q, $^1J(\text{C,H})=128$, 2Me). HRMS (MALDI) : calcd for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_9\text{Na}^+$ 559.1693 $[\text{M}+\text{Na}]^+$, found 559.1682.

(+)-(2Z,1'S,4S,5S)-4-Methyl-7-((dimethyl(phenyl)silyl)methyl)-5-(1'-phenylethoxy)octa-2,7-dien-3-yl benzoate (21)

Same procedure as that described for the preparation of **22** using diene **19b** instead **ent-19c**. Yield: quant, colorless oil.

$\alpha]_{\text{D}}^{25} = +0.3$; $\alpha]_{577}^{25} = +0.5$; $\alpha]_{546}^{25} = +0.7$; $\alpha]_{435}^{25} = +8.5$; $\alpha]_{405}^{25} = +15$ ($c=1.05$, CHCl_3).

IR(film): 3068, 2974, 1731, 1693, 1634, 1601, 1492, 1452, 1258, 1164, 1089, 1026. ^1H NMR (400 MHz, CDCl_3): 8.98 (d, $^3J=7.71$, 2H, Bz), 7.62 (t, $^3J=7.40$, 1H, Bz), 7.49-7.47 (m, 2H, Ph), 7.41 (t, $^3J=7.40$, 2H, Bz), 7.36 (m, 3H, Ph), 7.14-7.11 (m, 2H, Ph), 7.08-6.99 (m, 2H, Ph), 5.25 (q, $^3J=6.78$, 1H, H2), 4.64 (s, 1H, H8), 4.52 (s, 1H, H8), 4.42 (q, $^3J=6.50$, 1H, H2'), 3.64-3.59 (m, 1H, H5), 3.05-2.99 (m, 1H, H4), 2.03-2.01 (m, 2H, H6), 1.55 (d, $^3J=6.78$, 3H, H1), 1.53 (d, $^3J=14.0$, 1H, 7- CH_2Si), 1.39 (d, $^3J=6.47$, 3H, H2'), 1.36 (d, $^3J=14.0$, 1H, 7- CH_2Si), 1.15 (d, $^3J=7.09$, 3H, 4Me), 0.27, 0.26 (2s, 6H, SiMe_2). ^{13}C NMR (100.6 MHz, CDCl_3): 164.1 (s, CO), 150.5 (s, C3), 143.7 (s, C7), 143.3 (s, Ar), 139.3 (s, Ar), 133.6 (d, $^1J(\text{C,H}) = 158$, Ar), 133.2 (d, $^1J(\text{C,H}) = 162$, Ar), 130.0 (d, $^1J(\text{C,H}) = 164$, Ar), 129.6 (s, Ar), 128.9 (d, $^1J(\text{C,H}) = 158$, Ar), 128.5 (d, $^1J(\text{C,H}) = 153$, Ar), 127.9 (d, $^1J(\text{C,H}) = 160$, Ar), 127.7 (d, $^1J(\text{C,H}) = 160$, Ar), 127.2 (d, $^1J(\text{C,H}) = 166$, Ar), 127.0 (d, $^1J(\text{C,H}) = 153$, Ar), 112.0 (d, $^1J(\text{C,H}) = 156$, C2), 110.8 (t, $^1J(\text{C,H}) = 156$, C8), 75.0 (d, $^1J(\text{C,H}) = 141$, C5), 74.3 (d, $^1J(\text{C,H}) = 146$, C1'), 38.8 (d, $^1J(\text{C,H}) = 130$, C4 and t, $^1J(\text{C,H}) = 128$, C6), 25.0 (t, $^1J(\text{C,H}) = 120$, 7- CH_2Si), 23.8 (q, $^1J(\text{C,H}) = 129$, C2'), 11.0 (q, $^1J(\text{C,H}) = 130$, 4Me), 10.9 (q, $^1J(\text{C,H}) = 130$, C1), -2.7, -3.1 (2q, $^1J(\text{C,H})$

=120, SiMe_2). HRMS (MALDI): calcd for $\text{C}_{33}\text{H}_{40}\text{O}_5\text{SiNa}^+$ 535.2644 $[\text{M}+\text{Na}^+]$, found 535.2646. El. anal. calc. $\text{C}_{33}\text{H}_{40}\text{O}_5\text{Si}$ (512.75): C 77.30, H 7.86, Si 5.48. Found: C 77.27, H 7.74, Si 5.59.

(+)-(1Z, 1'R 3R)-7-{[dimethyl(phenyl)silyl]methyl}-5-(1-phenylethyloxy)octa-2,7-dien-3-yl benzoate (22)

To a suspension of lithium shots (0.888 g, 0.128 mol, 4.52 eq) in 25 ml THF at 0°C dimethyl(phenyl)chlorosilane (5 ml, 28.30 mmol) was added dropwise. The mixture was stirred vigorously for 18 h at 0°C. The dark red solution was transferred via a syringe to a solution of CuCN (1.30 g, 14.37 mmol, 0.5 eq) in anhydrous THF (16.5 ml). After 20 min at 0°C, temperature was lowered to -78°C. A solution of **ent-19c** (5.3g, 12.54 mmol) in THF (14 ml) was then added dropwise. After stirring for 2 h the reaction mixture was poured into an ice-cold saturated aqueous solution of NH_4Cl . The organic phase was separated and washed with saturated aqueous NaHCO_3 (30 ml) then with water (30 ml) and brine (30 ml). After drying (Na_2SO_4) organic phase was filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel (9:1 petroleum

ether/ Et₂O) giving 6.25 g (12.54 mmol, 100 %) of **21** as colorless oil.

$\alpha]_{\text{D}}^{25} = +41$; $\alpha]_{577}^{25} = +39$; $\alpha]_{546}^{25} = +50$; $\alpha]_{435}^{25} = +84$; $\alpha]_{405}^{25} = +99$ (c=0.78, CHCl₃).

R_f = 0.47 (Petrol ether 90/ Ether 10). UV (CH₃CN) : 263 (2065), 260 (2124), 235 (10469), 224 (8323), 205 (1089), 198 (878). IR (neat) : 3069, 3027, 2974, 2954, 2923, 1732, 1698, 1633, 1602, 1586, 1493, 1452, 1427, 1261, 1174, 1110, 1086, 1068, 1026, 876, 836, 760, 729, 700. ¹H NMR (400 MHz, CDCl₃): 8.07 (d, J=8.4, arom. CH), 7.63 (t, J=7.4, 1 arom. CH), 7.48 (t, J=8.0, 2 arom. CH), 7.40-7.19 (m, 11 arom. CH), 5.25 (q, 1H, ³J(H-C(2), H-C(1))= 6.8, H-C(2)), 4.55-4.45 (m, 5H, H-C(4) + H-C(8)), 3.51 (quint, 1H, ³J(H-C(5), H-C(4, 6))= 6.0, H-C(5)), 2.49 (d, 2H, ³J(H-C(4), H-C(5))=5.7, H-C(4)), 2.04 (m, 2H, H-C(6)), 1.55 (d, 3H, ³J(H-C(2'), H-C(1'))= 6.8, H-C(2')), 1.43 (d, 2H, ³J(CH₂-C(7), H-C(8))= 3.9, CH₂-C(7)), 1.34 (d, 3H, ³J(H-C(1), H-C(2))= 6.5, H-C(1)), 0.19-0.18 (2s, 3H, SiMe). ¹³C NMR (100.6 MHz, CDCl₃) : 164.2 (CO), 164.2 (s, CO), 146.5-143.9-143.3-139.0 (4s, C(3), C(7), 2 arom. C), 133.5-133.3-129.9-129.7-128.9-128.5-128.2-128.1-127.3-126.7 (m, arom. C), 113.8 (d, ¹J(C-H)=156, C(2)), 111.0 (t, ¹J(C-H)=155, C(8)), 75.9 (d, ¹J(C-H)= not measurable, C(1')), 72.4 (d, ¹J(C-H)=141, C(5)), 43.9 (t, ¹J(C-H)=122, C(4)), 38.3 (t, ¹J(C-H)=128, C(6)), 25.3 (t, ¹J(C-H)=119, CH₂-C(7)), 23.8 (q, ¹J(C-H)=127, C(2')), 10.9 (q, ¹J(C-H)=127, C(1)), -3.1 (2q, ¹J(C-H)=119, SiMe₂). MS (M+

Na) FAB : 521 (36, [M+Na]), 273 (26), 137 (94), 105 (100). HRMS (MALDI): calcd for $C_{32}H_{38}O_3SiNa^+$ 521.2488 [M+Na⁺], found 521.2497. El. anal. calc. $C_{32}H_{38}O_3Si$ (498.74): C : 77.07, H : 9.68, O : 5.63 ; Found: C : 77.03, H : 7.67.

(-)-(2Z,11Z,1'S,1''S,4S,5S,9S,10S)-4,10-Dimethyl-7-methylidene-5,9-bis(1'-phenylethoxy)trideca-2,11-diene-3,11-diyl-dibenzoate (23)

Same procedure as that described for the preparation of **13a** using diene **14b** and **22** and toluene as solvent instead of CH_2Cl_2 . Yield: 62%, colorless oil.

$[\alpha]_D^{25} = -24$; $[\alpha]_{577}^{25} = -24$; $[\alpha]_{546}^{25} = -26$; $[\alpha]_{435}^{25} = -37$; $[\alpha]_{405}^{25} = -43$ ($c=0.55$, $CHCl_3$).

IR(film): 3063, 2975, 2926, 1731, 1644, 1602, 1452, 1260, 1165, 1090, 1068. 1H NMR (400 MHz, $CDCl_3$): 7.97 (d, $^3J=8.32$, 4H, Bz), 7.59 (t, $^3J=7.40$, 2H, Bz), 7.41 (t, $^3J=7.71$, 4H, Bz), 7.12-7.03 (m, 10H, Ph), 5.16 (dq, $^3J=6.78$, $^4J=1.00$, 2H, H2, H12), 4.65 (s, 2H, 7=CH₂), 4.38 (q, $^3J=6.47$, 2H, H1', H1''), 3.39 (dt, $^3J=8.94$, $^3J=3.70$, 2H, H5, H9), 2.82-2.75 (m, 2H, H4, H10), 1.86 (dd, $^2J=14.18$, $^3J=8.94$, 2H, H6, H8), 1.76 (dd,

$^2J=14.20$, $^3J=3.40$, 2H, H6, H8, 1.46 (dd, $^3J=6,78$, $^4J=1.00$, 6H, H1, H13), 1.33 (d, $^3J=6.47$, 6H, H2', H2''), 1.05 (d, $^3J=7.09$, 6H, 4Me, 10Me). ^{13}C NMR (100.6 MHz, CDCl_3): 164.2 (s, CO), 150.4 (s, C3, C11), 143.6 (s, C7), 143.4 (s, Ar), 133.3 (d, $^1J(\text{C,H})=161$, Ar), 130.0 (d, $^1J(\text{C,H})=157$, Ar), 129.7 (s, Ar), 128.5 (d, $^1J(\text{C,H})=160$, Ar), 127.9 (d, $^1J(\text{C,H})=161$, Ar), 127.3 (d, $^1J(\text{C,H})=162$, Ar), 127.0 (d, $^1J(\text{C,H})=159$, Ar), 114.8 (t, $^1J(\text{C,H})=161$, $7=\underline{\text{CH}_2}$), 112.2 (d, $^1J(\text{C,H})=153$, C2, C11), 75.3 (2d, $^1J(\text{C,H})=144$, C5, C9, C1', C1''), 40.0 (d, $^1J(\text{C,H})=129$, C4, C10), 37.3 (t, $^1J(\text{C,H})=126$, C6, C8), 23.9 (q, $^1J(\text{C,H})=135$, C2', C2''), 12.0 (q, $^1J(\text{C,H})=129$, C1, C13), 11.1 (q, $^1J(\text{C,H})=132$, 4Me, 10Me). HRMS (MALDI), Calc for $\text{C}_{46}\text{H}_{52}\text{O}_6\text{Na}^+$ 723.3662 $[\text{M}+\text{Na}^+]$, found 723.3668. El. anal. calc. $\text{C}_{46}\text{H}_{52}\text{O}_6\cdot\text{H}_2\text{O}$ (718.92): C 76.85, H 7.57. Found: C 76.71, H 7.24.

(2Z,11Z,1'R,1''S 5R,9S)-7-Methylidene-5,9-(1'-phenylethoxy)trideca-2,11-dien-3,11-diyl dibenzoate (24)

Same procedure as that described for the preparation of **13a** using **14c** and **21** instead of **9** and toluene as solvent instead of CH_2Cl_2 . Yield: 81%, colorless oil.

$$\alpha]_{\text{D}}^{25}=0; \alpha]_{577}^{25}=0; \alpha]_{546}^{25}=0; \alpha]_{435}^{25}=0; \alpha]_{405}^{25}=0 (c=0.46, \text{CHCl}_3).$$

R_f = 0.13 (Petrol ether 70/ Ether 30). UV (CH₃CN) : 272 (3180), 261 (3358), 260 (3443), 235 (10400), 212 (8120), 194 (2630), 191 (1695). IR (neat) : 3064, 3029, 2970, 2926, 2865, 1732, 1601, 1490, 1452, 1263, 1174, 1088, 1068, 1026, 761, 710, 702. ¹H NMR (400 MHz, CDCl₃) : 8.05 (d, J=7.0, 1 arom. CH), 7.59 (t, J=7.7, 1 arom. CH), 7.48 (t, J=7.7, 2 arom. CH), 7.17-7.13 (m, 6 arom. CH), 5.15 (q, 1H, ³J(H-C(2), H-C(1))= 7.0, H-C(2)), 4.62 (s, 2H, CH₂-C(7)), 4.44 (q, 1H, ³J(H-C(1'), H-C(2'))= 6.4, H-C(1')), 3.42 (quint, 1H, ³J(H-C(5), H-C(4, 6))= 5.8, H-C(5)), 2.41 (bs, 2H, H-C(4)), 1.93 (d, 2H, ³J(H-C(6), H-C(5))= 7.0, H-C(6)), 1.53 (d, 3H, ³J(H-C(1), H-C(2))= 7.0, H-C(1)), 1.28 (d, 3H, ³J(H-C(2'), H-C(1'))= 6.4, H-C(2')). ¹³C NMR (100.6 MHz, CDCl₃) : 164.2 (CO), 146.5-143.8-142.7 (C(3), C(7), 1 arom. C), 133.3-129.2-129.7-128.4-128.0-127.2-126.6 (arom C.), 115.2 (CH₂-C(7)), 113.8 (C(2)), 75.6 (C(1')), 72.4 (C(5)), 41.6 (C(4)), 38.2 (C(6)), 23.7 (C(1)), 10.9 (C(2')); 164.2 (s, CO), 146.5-143.8-142.7 (3s, C(3), C(7), 1 arom. C), 133.3-129.2-129.7-128.4-128.0-127.2-26.6 (7d, ¹J(C-H)=162, 7 arom. C), 115.2 (t, ¹J(C-H)=155, CH₂-C(7)), 113.8 (d, ¹J(C-H)=156, C(2)), 75.6 (d, ¹J(C-H)= 142, C(1')), 72.4 (d, ¹J(C-H)=144, C(5)), 41.6 (t, ¹J(C-H)=128, C(4)), 38.2 (t, ¹J(C-H)=129, C(6)), 23.7 (q, ¹J(C-H)=127, C(1)), 10.8 (q, ¹J(C-H)=127, C(2')). MS (M+ Na) FAB : 695 (50, [M+Na]), 365 (30), 177 (78), 155 (94), 137 (100). HRMS (MALDI): calcd for C₄₄H₄₈O₆Na⁺ 695.3348 [M+Na⁺], found 695.3344.

(+)-(2Z,11Z,4S,5S,9S,10S)-5,9-Dihydroxy-4,10-dimethyl-7-methylidene-trideca-2,11-diene-3,11-diyl dibenzoate (25)

Product **24** (0.28 g, 0.40 mmol) was dissolved in CH₂Cl₂ (4 ml) and EtSH (4 ml). The solution was cooled to 0°C and BF₃·OEt₂ (1.01 ml, 8.0 mmol, 20 eq.) was added. The mixture was stirred at 0°C for 2 h. Then NEt₃ (6 ml) was added and the solvent was evaporated. The residue was purified by column chromatography on silica gel (Petrol ether / Ethyl acetate). Yield : 128 mg, (65%) of **25**, colorless oil.

$\alpha]_D^{25} = +18$; $\alpha]_{577}^{25} = +16$; $\alpha]_{546}^{25} = +21$; $\alpha]_{435}^{25} = +33$; $\alpha]_{405}^{25} = +38$ (c=0.62, CHCl₃).

IR (film): 3492, 3070, 2922, 1722, 1643, 1601, 1452, 1261, 1176, 1093, 1068, 1026. ¹H NMR (400 MHz, CDCl₃): 8.01 (d, ³J=8.00, 4H, Bz), 7.62 (t, ³J=7.36, 2H, Bz), 7.48 (t, ³J=7.68, 4H, Bz), 5.35 (q, ³J=7.04, 2H, H2, H12), 4.98 (s, 2H, 7=CH₂), 3.59 (dt, ³J=8.64, ³J=2.24, 2H, H5, H9), 3.42 (bs, 2H, 5-OH, 9-OH), 2.50-2.43 (m, 4H, H4, H10, H6, H10), 2.13 (dd, ²J=14.40, ³J=9.92, 2H, H6, H10), 1.50 (d, ³J=6.72, 6H, H1, H13), 1.09 (d, ³J=7.04, 6H, 4Me, 10Me). ¹³C NMR (100.6 MHz, CDCl₃): 165.2 (s, CO), 149.5 (s, C3, C11), 144.3 (s, C7), 133.6 (d, ¹J(C,H) =164, Ar), 130.2 (d, ¹J(C,H) =167, Ar), 129.2 (s, Ar), 128 (d,

$^1J(\text{C},\text{H}) = 162$, Ar), 115.1 (t, $^1J(\text{C},\text{H}) = 153$, $7=\text{CH}_2$), 114.2 (d, $^1J(\text{C},\text{H}) = 156$, C2, C12), 70.6 (d, $^1J(\text{C},\text{H}) = 143$, C5, C9), 45.8 (d, $^1J(\text{C},\text{H}) = 133$, C4, C10), 39.9 (t, $^1J(\text{C},\text{H}) = 129$, C6, C8), 14.2 (q, $^1J(\text{C},\text{H}) = 129$, C1, C13), 11.1 (q, $^1J(\text{C},\text{H}) = 128$, 4Me, 10Me). HRMS (MALDI), Calc for $\text{C}_{30}\text{H}_{36}\text{O}_6\text{Na}^+$ 515.2410 $[\text{M}+\text{Na}^+]$, found 515.2404. El. anal. calc. $\text{C}_{30}\text{H}_{36}\text{O}_6 \cdot \text{H}_2\text{O}$ (510.62): C 70.57, H 7.50. Found: C 70.47, H 7.41.

Stereochemical Determinations.

The samples of diastereomerically pure major products **13a**, **17a**, **17b** (Table 1) were subjected to a series of transformations as shown in Scheme 1. Acyl-silyl exchange and subsequent ozonolysis provided products **26**, which after reduction, cyclization and removing of the corresponding O-protection led to known product **30**.¹ The coupling $^3J(\text{H}2-\text{H}3) = 3.5$ Hz confirmed the C(4)-C(5) anti-relationship.

Scheme 1.

References

1. Kiyooka, S.-i.; Shahid, K. A. *Bull. Chem. Soc. Jpn.* **2001**, 74, 1485.