Total Synthesis of (+)-Cryptocaryalactone and of a Diastereoisomer of (+)-Strictifolione *via* Ring-Closing Metathesis (RCM) and Olefin Cross-Metathesis (CM)

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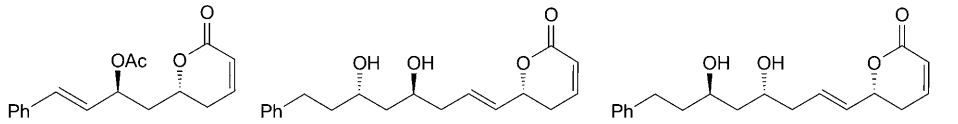
Ring-closing metathesis (RCM) and olefin cross-metathesis (CM) reactions were used as the key steps for the synthesis of (+)-cryptocaryalactone (**1**) and the first synthesis of the diastereoisomer **3** of (+)-strictifolione, starting from the commercially available L-malic acid (=(2*S*)-2-hydroxybutanedioic acid).

Introduction. – The α,β-unsaturated δ-lactone moiety is a ubiquitous motif present in a large number of natural products displaying a broad range of potent biological activities [1]. Moreover, it has been shown that the unsaturated moiety plays an essential role in the biological activity, due to its potential to act as a *Michael* acceptor in the presence of protein functional groups [2]. Cryptocaryalactone (=(6*R*)-6-[(2*S*,3*E*)-2-(acetyloxy)-4-phenylbut-3-en-1-yl]-5,6-dihydro-2*H*-pyran-2-one; **1**) [3] and (+)-strictifolione (=(6*R*)-6-[(1*E*,4*S*,6*S*)-4,6-dihydroxy-8-phenyloct-1-en-1-yl]-5,6-dihydro-2*H*-pyran-2-one; **2**) [4] are such natural products showing a wide variety of activities.



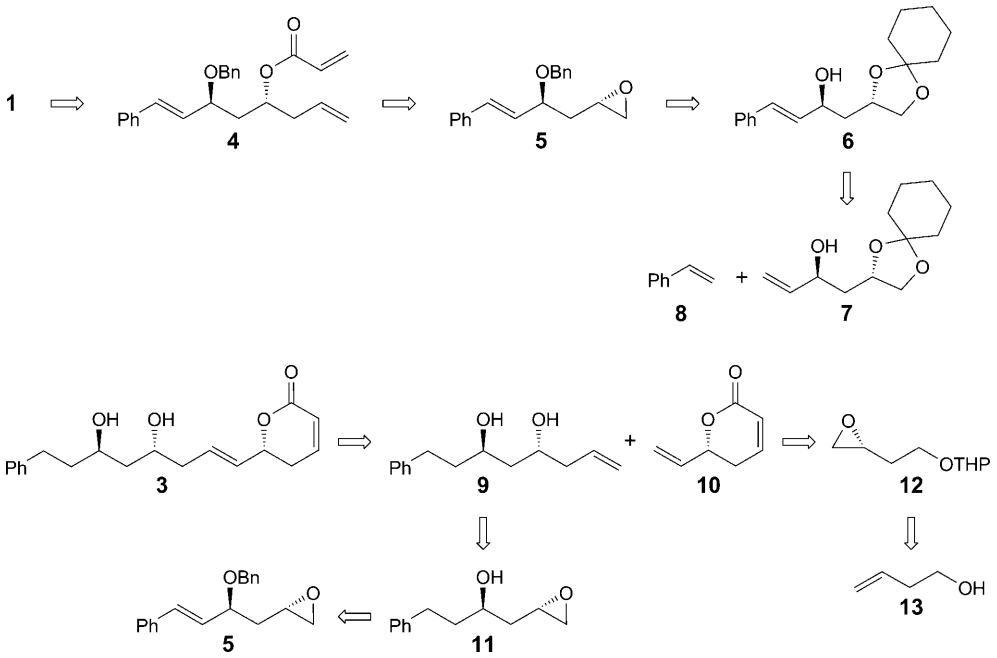
(+)-Cryptocaryalactone (**1**) (+)-Strictifolione (**2**) Diastereoisomer **3** of (+)-strictifolione

In continuation of our studies on the synthesis of biologically active lactones [5], we planned to synthesize (+)-cryptocaryalactone (**1**) and a diastereoisomer **3** of strictifolione by means of ring-closing metathesis (RCM) and olefin cross-metathesis (CM) protocols as key steps. Eventhough, three reports on the synthesis of (+)-cryptocaryalactone (**1**) [3][5g] have appeared. To the best of our knowledge, the synthesis of **3** has not been reported.

Results and Discussion. – The retrosynthetic plan for **1** is depicted in *Scheme 1*. The target compound **1** could be obtained from **4** by RCM in the presence of *Grubbs*' catalyst, followed by debenzylation and acetylation. Oxirane **5** in turn could be prepared from **6**. Whereas **6** can be prepared from coupling of **7** with **8** by an olefin cross-metathesis (CM) protocol. Chiral allylic alcohol **7** can be obtained from L-malic

acid (=(2*S*)-2-hydroxybutanedioic acid) by simple chemical transformations. On the other hand, retrosynthesis for the target molecule **3** shows that it could be obtained by an olefin cross-metathesis reaction of **9** and **10**. *anti*-Diol **9** in turn could be prepared from **11**. Similarly, **11** could be obtained from intermediate **5**. Vinyl lactone **10** could be synthesized from oxirane **12**, easily accessible by the *Jacobsen* hydrolytic kinetic resolution (*Jacobsen*'s HKR) protocol. The racemic oxirane was obtained from but-3-en-1-ol (**13**).

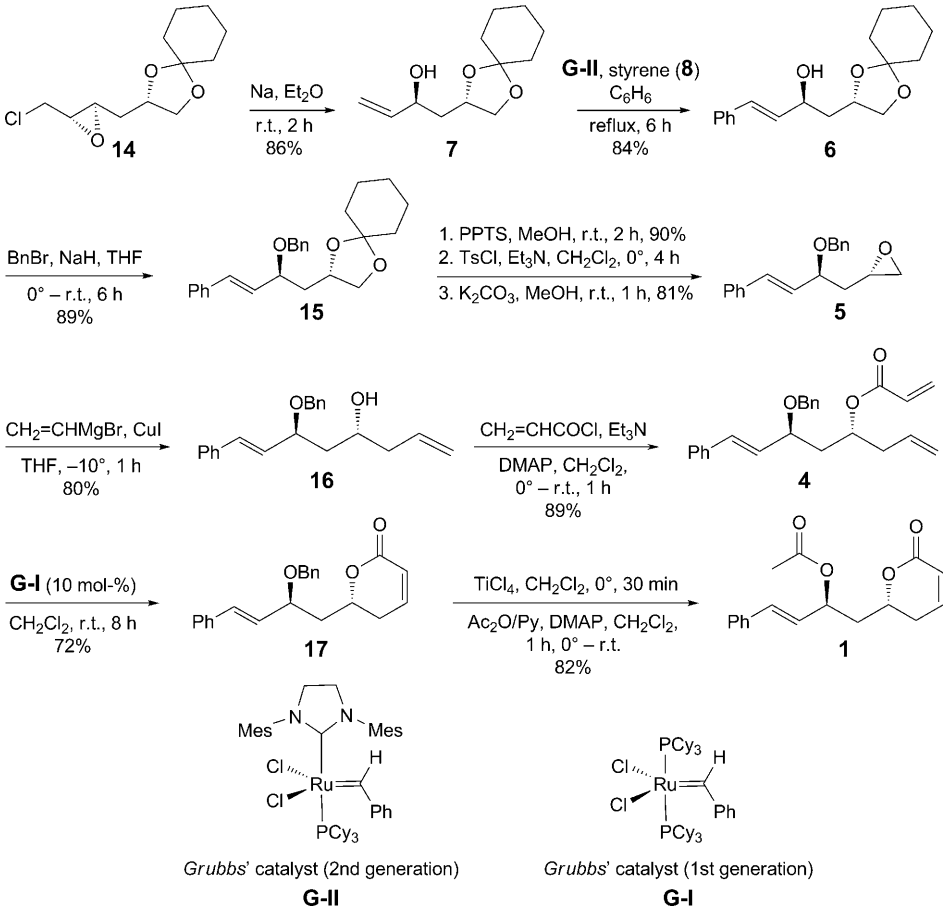
Scheme 1. *Retrosynthetic Analysis for* **1** *and* **3**



The synthesis of (+)-cryptocaryalactone (**1**) began with the (chloromethyl)oxirane **14**, prepared conveniently on a multi-gram scale following a known procedure [6]. The oxirane **14** was converted into a chiral allyl alcohol **7** in 86% yield. Next, olefin cross-metathesis reaction of allyl alcohol **7** with styrene (**8**) in the presence of *Grubbs*' second-generation catalyst **G-II** (10 mol-%) in benzene at reflux temperature afforded a cross-coupling product **6** in 84% yield and with excellent stereoselectivity ((*E*)/(*Z*) ratio 20:1) as observed by ^{1}H-NMR spectroscopy. The secondary OH group in **6** was protected as its benzyl ether (BnBr, NaH/room temp.) to afford **15** in 89% yield. Removal of the cyclohexylidene group in compound **15** proceeded smoothly with pyridinium toluene-4-sulfonate (PPTS) in MeOH at room temperature to afford the corresponding diol with excellent yield. The latter, on selective monotosylation (TsCl, Et_3N, CH_2Cl_2) of the primary OH group, followed by base treatment (K_2CO_3, MeOH at r.t.) furnished oxirane **5** in 81% yield (*Scheme 2*).

Regioselective opening of oxirane **5** with CH_2=CHMgBr in the presence of catalytic CuI in anhydrous THF at $-10°$ for 1 h afforded homoallyl alcohol **16** in 80%

Scheme 2

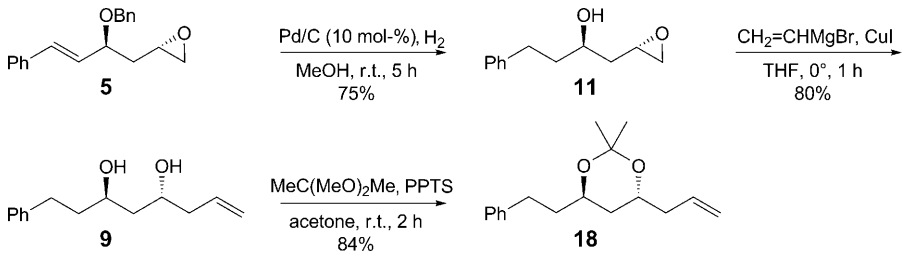


yield. There was no trace of the formation of the primary alcohol due to the ring opening at the secondary C(2) of the oxirane. Acylation of the secondary OH group with acryloyl chloride and anhydrous Et_3N in CH_2Cl_2 at 0° afforded the acrylate **4** in 89% yield. The crucial ring-closing olefin metathesis of **4** in the presence of *Grubbs*' first-generation catalyst **G-I** [7] furnished pyranone **17** as a single product. The pyranone **17**, on debenzylation with $TiCl_4$ in CH_2Cl_2 for 30 min, afforded the lactone in good yield, which was subjected to acetylation by Ac_2O/pyridine in the presence of *N*,*N*-dimethylpyridin-4-amine (DMAP; cat.) in CH_2Cl_2 at room temperature for 1 h to give the natural crystalline (+)-cryptocaryalactone (**1**) as crystals.

The synthesis of **3** also involved intermediate **5**. Accordingly, compound **5**, on exposure to Pd/C (10 mol-%) under H_2 at room temperature for 5 h, gave key oxirane **11** in 75% yield. Opening of oxirane **11** with CH_2=CHMgBr in the presence of catalytic CuI in anhydrous THF at 0° for 1 h afforded homoallyl alcohol **9** in 80% yield with the required *anti*-1,3-diol configuration (*Scheme 3*). The relative *anti*-configuration of the 1,3-diol was established by its conversion to the corresponding acetonide **18** (PPTS, 2,2-

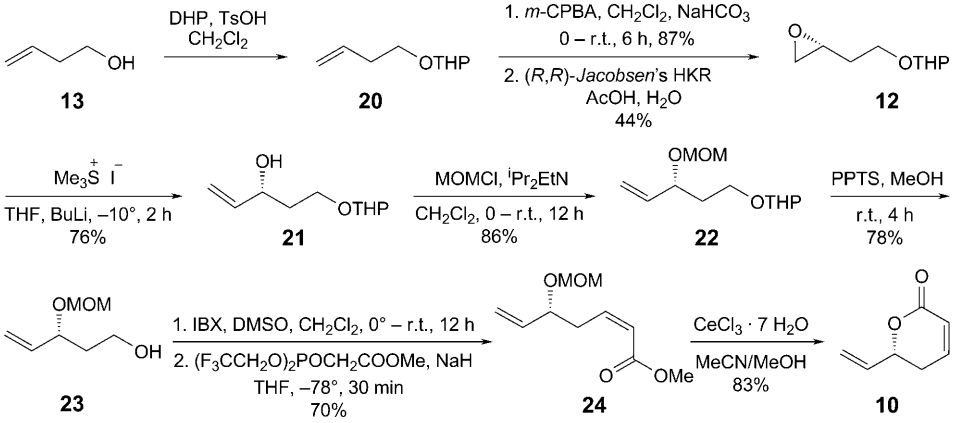
dimethoxypropane, dry acetone, room temperature, 2 h, 84% yield), followed by the analysis of the ^{13}C-NMR spectrum (δ 24.8 (2 Me) and 100.3 ((MeO)$_2$*C*)) [8].

Scheme 3



The other key intermediate lactone **10** (*Scheme 4*) was synthesized from but-3-en-1-ol (**13**). Accordingly, the alcohol **13** was protected as its tetrahydropyranyl (THP) derivative **20**, and the epoxidation of compound **20** with 3-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 at 0° afforded a racemic oxirane, which on hydrolytic kinetic resolution with (*R*,*R*)-*Jacobsen*'s HKR provided the chiral oxirane **12** in 44% yield. Opening of oxirane **12** with trimethylsulfonium iodide [9] and BuLi in dry THF at −10° provided the secondary allyl alcohol **21** in 76% yield, which was converted to the (*Z*)-configurated olefinic ester **24** in three steps by protection of alcohol **21** as a methoxymethyl (MOM) ether (→**22**), followed by deprotection of the THP group with PPTS in MeOH resulting in the primary alcohol **23** in good yield. The latter was oxidized to the aldehyde which, without isolation, was subjected to a *Still*–*Gennari* reaction (→**24**). Finally, smooth deprotection of the MOM group and concomitant cyclization under neutral conditions in the presence of $CeCl_3 \cdot 7\ H_2O$ in MeOH/MeCN 1:1 gave the required vinyl lactone **10** in very good yield.

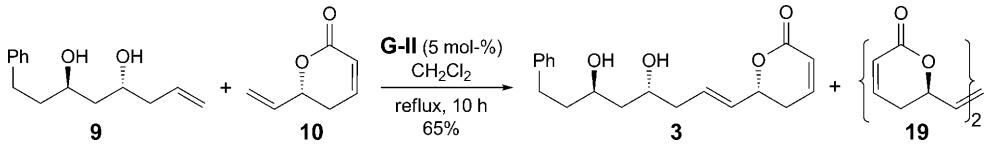
Scheme 4



Next, olefin cross-metathesis reaction (for a recent review, see [10]) of **9** with the vinyl lactone **10** (*Scheme 5*) in the presence of *Grubbs*' second-generation catalyst **G-II** (5 mol-%) in CH_2Cl_2 under reflux afforded the diastereoisomer **3** of (+)-strictifolione

(**2**) in 65% yield as a white solid. The structure of lactone **3** was confirmed by spectral analysis. A dimer **19** of the vinyl lactone was isolated in 8% yield along with **3**.

Scheme 5



In conclusion, we have disclosed the synthesis of (+)-cryptocaryalactone (**1**) and of a diastereoisomer **3** of (+)-strictifolione (**2**). The highlights of the synthesis are the successful utilization of RCM and olefin cross-metathesis (CM) protocols.

B. V. thanks *UGC*, and *S. S. S. R.* thanks *CSIR*, New Delhi, for the award of fellowships.

Experimental Part

General. Reactions were conducted under N_2 in anh. solvents such as CH_2Cl_2, THF, and Et_2O. All reactions were monitored by TLC (silica gel-coated (SiO_2) plates and visualizing under UV light). Hexanes (b.p. 60–80°) were used. Yields refer to chromatographically and spectroscopically (^{1}H- and ^{13}C-NMR) homogeneous material. Air-sensitive reagents were transferred by syringe or double-ended needle. Evaporation of solvents was performed under reduced pressure. TLC: *Merck 60 F_{254}* SiO_2 plates. Column chromatography (CC): SiO_2 (60–120 mesh; *Acme Chemical Co.*, India). Optical rotations: *Jasco-DIP-370* polarimeter at 20°. IR Spectra: *Thermo-Nicolet Nexus 670 FT-IR*; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Varian-FT-200* (*Gemini*) and *Bruker-UXNMR-FT-300* (*Avance*) spectrometers; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, J in Hz. MS: *LC-MSD* (*Agilent Technologies*) spectrometers under EI conditions at 70 eV; m/z (rel. %). HR-MS: *QSTAR-XL* hybrid MS/MS system (*Applied Biosystems*/*MDS Sciex*, Foster City, USA), equipped with an ESI source (*IICT*, Hyderabad).

(αS,2S)-α-Ethenyl-1,4-dioxaspiro[4.5]decane-2-ethanol (**7**). To a suspension of Na (0.93 g, 40.65 mmol) in dry Et_2O (20 ml), a soln. of **14** (5 g, 20.32 mmol) in dry Et_2O (10 ml) was added at 0° and stirred at r.t. for 2 h. The mixture was quenched with MeOH (8 ml) and concentrated and the residue purified by CC (SiO_2, AcOEt/hexane 2:8): **7** (3.68 g, 86%). Clear liquid. $[\alpha]_D = +6.52$ ($c = 0.41$, $CHCl_3$). IR (neat): 700, 1150, 1200, 1750, 2900, 3150. ^{1}H-NMR (200 MHz): 1.34–1.48 (*m*, 4 H); 1.5–1.74 (*m*, 8 H); 2.12–2.34 (*m*, 2 H); 3.49–3.58 (*m*, 1 H); 3.80–3.94 (*m*, 1 H); 4.0–4.09 (*m*, 1 H); 4.22–4.36 (*m*, 1 H); 5.02–5.19 (*m*, 2 H); 5.71–5.92 (*m*, 1 H). ESI-MS: 235 ($[M+Na]^+$).

(αS,2S)-α-[(1Z)-2-Phenylethenyl]-1,4-dioxaspiro[4.5]decane-2-ethanlol (**6**). *Grubbs*' second-generation catalyst **G-II** (0.145 g, 0.17 mmol, 5 mol-%) was dissolved in C_6H_6 (10 ml), and the soln. was added dropwise to a soln. of **7** (3.0 g, 14.15 mmol) and styrene (**8**; 2.20 g, 21.22 mmol) in C_6H_6 (200 ml) at 0°. After the addition, the mixture was stirred under reflux for 6 h. The solvent was evaporated and the crude product purified by CC (SiO_2, AcOEt/hexane 2:8): pure **6** (3.22 g, 84%). Clear liquid. R_f 0.42 (AcOEt/hexane 2:8). $[\alpha]_D^{25} = -40.0$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.35–1.62 (*m*, 10 H); 1.79 (*dd*, J = 13.5, 7.5, 1 H); 1.90 (*dd*, J = 7.5, 13.5, 1 H); 2.60 (br. *s*, OH); 3.56 (*dd*, J = 7.5, 8.0, 1 H); 4.05 (*dd*, J = 6.0, 8.0, 1 H); 4.23–4.39 (*m*, 1 H); 4.46–4.57 (*m*, 1 H); 6.21 (*dd*, J = 5.3, 15.8, 1 H); 6.60 (*d*, J = 15.8, 1 H); 7.15–7.41 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 23.7; 23.9; 25; 35.0; 36.5; 40.3; 69.0; 69.7; 72.9; 109.4; 126.3; 127.4; 128.4; 129.6; 131.9; 136.6. ESI-MS: 311 ($[M+Na]^+$). HR-ESI-MS: 311.1615 ($[M+Na]^+$, $C_{18}H_{24}NaO_3^+$; calc. 311.1623).

(2S)-2-[(2S,3E)-2-(Benzyloxy)-4-phenylbut-3-en-1-yl]-1,4-dioxaspiro[4.5]decane (**15**). To a stirred suspension of freshly activated NaH (NaH was washed with dry hexane thoroughly; 0.66 g, 27.77 mmol) in THF (30 ml) under N_2, **6** (3.2 g, 11.11 mmol) in dry THF (10 ml) was added dropwise at 0°. After stirring for 45 min at 0°, benzyl bromide (2.84 g, 16.66 mmol) was added dropwise within 10 min. The mixture was stirred for 6 h at r.t. Then, cold H_2O (15 ml) was added cautiously. The aq. layer was

extracted with AcOEt (3 × 50 ml), the combined org. layer washed with H_2O (2 × 30 ml) and brine (2 × 20 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2): **15** (3.75 g, 89%). Clear liquid. R_f 0.72 (AcOEt/hexane 3:7). $[\alpha]_D^{25} = -41.3$ ($c = 0.25$, $CHCl_3$). IR (neat): 3028, 2936, 2859, 1600, 1495, 1448, 1364, 1279, 1163, 1101, 1067, 969, 931, 745, 695. ^{1}H-NMR (200 MHz): 1.35–1.60 (*m*, 10 H); 1.85 (*t*, *J* = 7.0, 2 H); 3.50 (*t*, *J* = 7.8, 1 H); 4.03 (*dd*, *J* = 6.2, 7.8, 1 H), 4.08–4.20 (*m*, 1 H); 4.23–4.33 (*m*, 1 H); 4.39 (*d*, *J* = 11.7, 1 H); 4.62 (*d*, *J* = 11.3, 1 H); 6.09 (*dd*, *J* = 7.8, 16.4, 1 H); 6.55 (*d*, *J* = 16.4, 1 H); 7.18–7.42 (*m*, 10 arom.). ESI-MS: 401 ($[M+Na]^+$). HR-ESI-MS: 401.2110 ($[M+Na]^+$, $C_{25}H_{30}NaO_3^+$; calc. 401.2092).

*(2*S*)-2-[(2*S*,3*E*)-2-(Benzyloxy)-4-phenylbut-3-en-1-yl]oxirane* (**5**). To a stirred a soln. of **15** (3.6 g, 9.52 mmol) in MeOH (20 ml) was added a cat. amount of PPTS, and the mixture was stirred at r.t. for *ca.* 2 h. After evaporation, the crude residue was purified by CC (SiO_2): *(2*S*,4*S*,5*E*)-4-(benzyloxy)-6-phenylhex-5-ene-1,2-diol* (2.56 g, 90%). Viscous liquid. R_f 0.20 (AcOEt/hexanes 5:5). $[\alpha]_D^{25} = -42.84$ ($c = 0.5$, $CHCl_3$). IR (neat): 3302 (br. *s*, 2 OH), 3027, 2935, 1650, 1599, 1494, 1452, 1385, 1065, 1005, 912, 877, 745, 695. ^{1}H-NMR (200 MHz): 1.64–1.97 (*m*, 2 H); 2.36 (br. *s*, OH); 3.03 (br. *s*, OH); 3.40 (*dd*, *J* = 11.0, 6.6, 1 H); 3.48–3.62 (*m*, 1 H); 3.84–4.06 (*m*, 1 H); 4.17–4.30 (*m*, 1 H); 4.39 (*d*, *J* = 11.7, 1 H); 4.64 (*d*, *J* = 11.7, 1 H); 6.15 (*dd*, *J* = 16.1, 8.0, 1 H); 6.56 (*d*, *J* = 16.1, 1 H); 7.06–7.41 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 38.7; 66.7; 69.0; 70.4; 77.2; 125.8; 126.5; 127.6; 127.8; 128.4; 128.5; 129.2; 132.5; 132.4; 136.2; 138.1.

To a stirred mixture of the above diol (2.2 g, 7.38 mmol), Et_3N (0.74 g, 7.38 mmol) and DMAP (0.01 g, 10 mol-%) in dry CH_2Cl_2 (30 ml) at 0°, TsCl (1.40 g, 7.38 mmol) in dry CH_2Cl_2 (8 ml) was added over 15 min. The mixture was allowed to warm to r.t. and stirred for 4 h. After completion of the reaction (TLC monitoring), the mixture was quenched with sat. aq. $NaHCO_3$ soln., the org. layer extracted with CH_2Cl_2 (3 × 40 ml), and the combined org. layer washed with H_2O (2 × 30 ml) and brine (2 × 30 ml), dried (anh. Na_2SO_4), and concentrated. The crude residue was directly used in the next reaction without purification. The residue was dissolved in MeOH (20 ml), K_2CO_3 (2.04 g, 14.76 mmol) added, and the mixture stirred for 1 h. The MeOH was evaporated, the residue diluted with AcOEt, the AcOEt phase washed with H_2O (2 × 30 ml) and brine (2 × 30 ml), dried (anh. Na_2SO_4), and concentrated, and the yellow oily product purified by CC (SiO_2): **5** (1.66 g, 81%). Colorless liquid. R_f 0.85 (AcOEt/hexane 2:8). $[\alpha]_D^{25} = -72.03$ ($c = 0.25$, $CHCl_3$). IR (neat): 3028, 2923, 2854, 1631, 1494, 1453, 1382, 1067, 1027, 968, 919, 842, 745, 695. ^{1}H-NMR (300 MHz): 1.55–1.66 (*m*, 1 H); 1.93–2.05 (*m*, 1 H); 2.39–2.50 (*m*, 1 H); 2.72–2.79 (*m*, 1 H); 3.07–3.16 (*m*, 1 H); 4.17 (*td*, *J* = 8.3, 3.8, 1 H); 4.43 (*d*, *J* = 11.3, 1 H); 4.65 (*d*, *J* = 11.3, 1 H); 6.11 (*dd*, *J* = 7.5, 15.8, 1 H); 6.57 (*d*, *J* = 15.8, 1 H); 7.09–7.38 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 39.5; 47.5; 49.5; 70.4; 77.5; 127.5; 127.7; 125.8; 126.5; 128.4; 128.6; 129.6; 132.6; 136.3; 138.4. ESI-MS: 307.7 ($[M+Na]^+$). HR-ESI-MS: 303.1349 ($[M+Na]^+$, $C_{19}H_{20}NaO_2^+$; calc. 303.1360).

*(4*R*,6*S*,7*E*)-6-(Benzyloxy)-8-phenylocta-1,7-dien-4-ol* (**16**). To a stirred soln. of **5** (0.75 g, 2.67 mmol) and CuI (cat.) in THF (30 ml) was added freshly prepared CH_2=CHMgBr (0.72 ml, 5.35 mmol) at −10°, and the mixture was stirred at −10° for *ca.* 1 h, quenched with sat. NH_4Cl soln. (5 ml), and extracted with AcOEt (3 × 30 ml). The combined org. layer was washed with brine (2 × 20 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC: **16** (1.66 g, 80%). Thick syrup. R_f 0.65 (AcOEt/hexane 2:8). $[\alpha]_D^{25} = -34.81$ ($c = 1.5$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.62–1.89 (*m*, 2 H); 2.10–2.25 (*m*, 2 H); 3.86–4.02 (*m*, 1 H); 4.20–4.29 (*m*, 1 H); 4.40 (*d*, *J* = 12.0, 1 H); 4.65 (*d*, *J* = 12.0, 1 H); 5.07 (*dd*, *J* = 1.5, 12.0, 2 H); 5.71–5.88 (*m*, 1 H); 6.16 (*dd*, *J* = 7.5, 15.8, 1 H); 6.57 (*dd*, *J* = 8.3, 15.8, 1 H); 7.07–7.42 (*m*, 10 H). ^{13}C-NMR (75 MHz): 39.2; 42.0; 67.6; 70.5; 77.5; 117.5; 126.4; 127.6; 127.7; 128.2; 128.3; 128.5; 129.4; 132.3; 134.7; 136.2; 138.0. HR-ESI-MS: 331.1660 ($[M+Na]^+$, $C_{21}H_{24}NaO_2^+$; calc. 331.1673; −4.2273 ppm error).

*(1*R*,3*S*,4*E*)-3-(Benzyloxy)-5-phenyl-1-(prop-2-en-1-yl)pent-4-en-1-yl Prop-2-enoate* (**4**). Acryloyl chloride (= prop-2-enoyl chloride; 0.25 g, 2.8 mmol) was added dropwise under N_2 to a a soln. of **16** (0.6 g, 1.94 mmol), Et_3N (0.55 ml, 3.9 mmol), and DMAP (10 mol-%) in dry CH_2Cl_2 (20 ml). The mixture was stirred at r.t. for 1 h. After completion, the mixture was poured into brine (10 ml) and extracted with CH_2Cl_2 (2 × 20 ml). The org. phase was washed with 1M aq. HCl and brine (1 × 20 ml), dried (Na_2SO_4), and concentrated, and the crude product purified by CC (SiO_2): **4** (0.63 g, 89%). Colorless oil. R_f 0.55 (AcOEt/hexane 2:8). $[\alpha]_D^{25} = -26.99$ ($c = 1.25$, $CHCl_3$). IR (neat): 3027, 2924, 2856, 1722, 1638, 1494, 1452, 1404, 1269, 1192, 1050, 982, 917, 749, 696. ^{1}H-NMR (300 MHz): 1.74–1.99 (*m*,

2 H); 2.24–2.42 (*m*, 2 H); 3.92 (*td*, *J* = 8.3, 3.7, 1 H); 4.31 (*d*, *J* = 11.3, 1 H); 4.55 (*d*, *J* = 11.3, 1 H); 5.01–5.09 (*m*, 2 H); 5.27–5.36 (*m*, 1 H); 5.67–5.81 (*m*, 2 H); 5.96–6.11 (*m*, 2 H); 6.34 (*dd*, *J* = 15.8, 7.0, 1 H); 6.51 (*d*, *J* = 15.8, 1 H); 7.08–7.37 (*m*, 10 H). ^{13}C-NMR (75 MHz): 39.2; 42.3; 70.3; 70.5; 117.9; 126.4; 127.4; 127.7; 128.0; 128.2; 128.5; 128.6; 129.7; 130.2; 132.3; 133.2; 136.3; 138.1; 165.4. ESI-MS: 385.7 ($[M+Na]^+$). HR-ESI-MS: 385.1784 ($[M+Na]^+$, $C_{24}H_{26}NaO_3^+$; calc. 385.1779; +1.1302 ppm error).

*(6*R*)-6-[(2*S*,3*E*)-2-(Benzyloxy)-4-phenylbut-3-en-1-yl]-5,6-dihydro-2*H*-pyran-2-one* (**17**). A soln. of *Grubbs*' first-generation catalyst **G-I** (0.056 g, 0.069 mmol, 10 mol-%) in CH_2Cl_2 (5 ml) was added dropwise to a a soln. of **4** (0.5 g, 1.38 mmol) in CH_2Cl_2 (500 ml) at r.t., and stirring was continued for 8 h. The solvent was evaporated and the crude product purified by CC (SiO_2): **17** (0.33 g, 72%). Colorless oil. R_f 0.3 (AcOEt/hexane 3:7). $[\alpha]_D^{25} = -25.0$ ($c = 0.2$, $CHCl_3$). IR (neat): 2924, 2854, 1718, 1452, 1247, 1065, 746, 695. ^{1}H-NMR (300 MHz): 1.83–2.05 (*m*, 2 H); 2.23–2.38 (*m*, 2 H); 4.18–4.29 (*m*, 1 H); 4.40 (*d*, *J* = 11.3, 1 H); 4.62 (*d*, *J* = 11.3, 1 H); 4.68–4.78 (*m*, 1 H); 6.00 (*dt*, *J* = 9.8, 2.2, 1 H); 6.08 (*dd*, *J* = 15.8, 8.3, 1 H); 6.63 (*dd*, *J* = 15.8, 2.2, 1 H); 6.77–6.87 (*m*, 1 H); 7.21–7.41 (*m*, 10 H). ^{13}C-NMR (75 MHz): 29.8; 41.7; 70.7; 74.4; 75.6; 121.4; 126.5; 127.7; 127.9; 128.4; 128.6; 129.3; 132.8; 133.9; 136.2; 138.2; 145.1; 164.2. ESI-MS: 357.0 ($[M+Na]^+$). HR-ESI-MS: 357.1482 ($[M+Na]^+$, $C_{22}H_{22}NaO_3^+$; calc. 357.1466; +4.2993 ppm error).

(+)-Cryptocaryalactone (**1**). To a stirred soln. of **17** (0.2 g, 0.598 mmol) in anh. CH_2Cl_2 (3 ml) under N_2 at 0°, $TiCl_4$ (0.065 g, 0.598 mmol) was added, and the mixture was stirred at 0° for 30 min. Then the reaction was quenched with sat. $NaHCO_3$ soln. (3 ml), the mixture extracted with CH_2Cl_2 (4 × 30 ml), and the combined org. layer washed with H_2O (2 × 10 ml) and brine (2 × 15 ml), dried (Na_2SO_4), and evaporated. To the crude, CH_2Cl_2 (25 ml), pyridine (0.06 ml, 0.718 mmol), and DMAP (cat.) were added, followed by Ac_2O (0.085 ml, 0.718 mmol) at 0°. The mixture was stirred for 1 h and then diluted with CH_2Cl_2 (10 ml), the org. layer washed with 5% $NaHCO_3$ soln. (2 × 15 ml) and brine (2 × 15 ml), dried (anh. Na_2SO_4), and concentrated, and the residue subjected to CC (petroleum ether/AcOEt 1:1): 0.11 g (82% yield over two steps) of **1**. Crystals. R_f 0.64 (AcOEt/hexane 1:1). M.p. 125–126°. $[\alpha]_D^{25} = +17.9$ ($c = 0.25$, $CHCl_3$). IR (neat): 3040, 2925, 1730, 1492, 1425, 1375, 1240, 1075, 1034, 966. ^{1}H-NMR (300 MHz): 2.08 (*s*, 3 H); 2.04–2.10 (*m*, 1 H); 2.20 (*ddd*, *J* = 14.5, 8.1, 4.5, 1 H); 2.34–2.42 (*m*, 2 H); 4.50–4.55 (*m*, 1 H); 5.61–5.67 (*m*, 1 H); 6.03 (*dt*, *J* = 10.2, 2.0, 1 H); 6.11 (*dd*, *J* = 15.9, 7.4, 1 H); 6.66 (*d*, *J* = 15.9, 1 H); 6.85 (*dt*, *J* = 10.0, 4.5, 1 H); 7.20–7.40 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 21.29 (*Me*C=O); 29.5; 39.9; 70.7; 74.2; 121.5; 126.5; 126.6; 128.1; 128.6; 135.9; 133.3; 144.5; 163.9 (C=O); 169.9 (Me*C*=O). ESI-MS: 309 ($[M+Na]^+$). HR-ESI-MS: 309.1115 ($[M+Na]^+$, $C_{17}H_{18}NaO_4^+$; calc. 309.1102).

*(3*R*,5*R*)-1-Phenyloct-7-ene-3,5-diol* (**9**). To **5** (0.6 g, 2.42 mmol) in MeOH (30 ml) was added a cat. amount of 10% Pd/C (20 mol-%), and the mixture was stirred at r.t. under H_2 for 5 h. Then, the catalyst was filtered off and washed with AcOEt (2 × 20 ml), the filtrate concentrated, and the residue purified by CC: *(α*R*,2*S*)-α-(2-phenylethyl)oxirane-2-ethanol* (**11**; 0.31 g, 75%). Colorless liquid. ^{1}H-NMR (200 MHz): 1.42–1.63 (*m*, 2 H); 1.72–1.92 (*m*, 2 H); 2.05 (br. *s*, OH); 2.42–2.59 (*m*, 2 H); 2.63–2.82 (*m*, 2 H); 2.99–3.10 (*m*, 1 H); 3.73–3.90 (*m*, 1 H); 7.11–7.28 (*m*, 5 H). LC-MS: 215.0 ($[M+Na]^+$).

To a stirred soln. of **11** (0.15 g, 0.781 mmol) and CuI (cat.) in THF (30 ml) was added freshly prepared CH_2=CHMgBr (0.21 ml, 1.56 mmol) at 0°, and the mixture was stirred at 0° for *ca.* 1 h. After quenching with sat. NH_4Cl soln. (4 ml), the mixture was extracted with AcOEt (3 × 30 ml), the combined org. layer washed with brine (2 × 20 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC: **9** (0.136 g, 80%). Light yellow liquid. $[\alpha]_D^{25} = -32.0$ ($c = 0.25$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.62 (*t*, *J* = 5.3, 2 H); 1.67–1.91 (*m*, 2 H); 2.07–2.50 (br. *s*, 1 H); 2.23 (*t*, *J* = 7.5, 2 H); 2.59–2.71 (*m*, 1 H); 2.72–2.84 (*m*, 1 H); 3.87–4.01 (*m*, 2 H); 5.07–5.16 (*m*, 2 H); 5.70–5.85 (*m*, 1 H); 7.09–7.27 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 29.6; 32.2; 39.0; 42.0; 68.2; 68.7; 118.3; 125.8; 128.4; 134.5; 142.0. HR-ESI-MS: 243.1371 ($[M+Na]^+$, $C_{14}H_{20}NaO_2^+$; calc. 243.1360).

*(4*R*,6*R*)-2,2-Dimethyl-4-(2-phenylethyl)-6-(prop-2-en-1-yl)-1,3-dioxane* (**18**). To a soln. of **9** (0.05 g, 0.227 mmol) in dry acetone (5 ml), 2,2-dimethoxypropane (0.055 ml, 0.4545 mmol) and PPTS (10 mol-%) were added. The mixture was stirred at r.t. for 2 h. $NaHCO_3$ was added to neutralize PPTS and the mixture filtered. Removal of solvent and purification by CC (SiO_2) afforded **18** (51 mg, 84%). Clear liquid. $[\alpha]_D^{25} = -24.7$ ($c = 0.5$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.30 (*s*, 3 H); 1.33 (*s*, 3 H); 1.48–1.60 (*m*, 2 H); 1.64–1.87 (*m*, 2 H); 2.08–2.30 (*m*, 2 H); 2.52–2.80 (*m*, 2 H); 3.65–3.86 (*m*, 2 H); 4.98–5.08 (*m*,

2 H); 5.67–5.83 (*m*, 1 H); 7.10–7.26 (*m*, 5 H). ^{13}C-NMR (75 MHz): 24.85 (2 C); 31.6; 37.5; 38.1; 40.1; 65.7; 66.2; 100.3; 116.8; 125.7; 128.3; 128.4; 134.4; 142.0. LC-MS: 283.0 ($[M+Na]^+$).

*Tetrahydro-2-{2-[(2*R*)-oxiran-2-yl]ethoxy}-2*H*-pyran* (**12**). To a stirred soln. of **20** (5.0 g, 3.20 mmol) in CH_2Cl_2 (15 ml) at 0°, *m*-CPBA (50% dispersion in H_2O, 6.6 g, 3.84 mmol) in CH_2Cl_2 (60 ml) was added, and the mixture was stirred for 6 h. The mixture was filtered, the filtrate washed with sat. $NaHCO_3$ soln. (3×40 ml), dried (Na_2SO_4), and concentrated, and the crude product purified by CC (SiO_2, AcOEt/hexane 1:9): racemic oxirane (4.8 g, 87%). Colorless liquid which was used as such in the next step.

A mixture of {(1*R*,2*R*)-*N*,*N*′-bis[3,5-di(*tert*-butyl)salicylidene]cyclohexane-1,2-diaminato(2−)}cobalt(II) (0.07 g, 0.12 mmol), toluene (1 ml), and AcOH (0.014 g, 0.25 mmol) was stirred in open air for 1 h at r.t. The solvent was evaporated and the brown residue, {(1*R*,2*R*)-*N*,*N*′-bis[3,5-di(*tert*-butyl)salicylidene]cyclohexane-1,2-diaminato(2−)}cobalt(III) acetate, was dried under vacuum. To the brown residue, racemic oxirane (0.48 g, 2.79 mmol) was added, and the mixture was then cooled under stirring in an ice-water bath. H_2O (0.24 ml, 13.61 mmol) was slowly added keeping the bath temp. at 15°. After 20 min, the addition was completed, the ice-water bath removed, and the mixture stirred at r.t. for 16 h. The crude mixture was purified by CC (SiO_2, AcOEt/hexane 1:9): **12** (2.06 g, 44%). $[\alpha]_D^{25}=+3.5$ ($c=1.0$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.44–1.92 (*m*, 8 H); 2.44–2.51 (*m*, 1 H); 2.70–2.76 (*m*, 1 H); 3.05 (*m*, 1 H); 3.55 (*m*, 2 H); 3.91 (*m*, 2 H); 4.59 (br. *s*, 1 H). ^{13}C-NMR (75 MHz): 19.3; 25.2; 30.4; 32.7; 46.8; 49.9; 61.9; 64.1; 98.4. ESI-MS: 195.0 ($[M+Na]^+$).

*(3*R*)-5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]pent-1-en-3-ol* (**21**). To a suspension of trimethylsulfonium iodide (10.13 g, 46.51 mmol) in dry THF (50 ml) at −10° under N_2 was added 2.5M BuLi in hexane (18.60 ml, 46.51 mmol). After 40 min, **12** (2.0 g, 11.627 mmol) in THF (15 ml) was introduced, producing a milky suspension. The mixture was allowed to warm to 0° over *ca.* 30 min and then to r.t. and stirred for 2 h. The reaction was quenched with H_2O at 0°, the mixture extracted with AcOEt (2×50 ml), the combined org. layer dried (Na_2SO_4) and concentrated, and the crude mixture purified by CC (SiO_2, AcOEt/hexane 2:8): **21** (1.64 g, 76%). Yellow liquid. $[\alpha]_D^{25}=-9.6$ ($c=3.75$, $CHCl_3$). ^{1}H-NMR (300 MHz): 5.92–5.80 (*m*, 1 H); 5.31–5.06 (*m*, 2 H); 4.60–4.55 (*m*, 1 H); 4.36–4.26 (*m*, 1 H); 4.00–4.34 (*m*, 4 H); 2.74 (*s*, OH); 1.91–1.47 (*m*, 8 H). ^{13}C-NMR (50 MHz): 140.4; 114.2; 98.8; 71.9; 65.6; 62.1; 36.2; 30.4; 25.2; 19.3. ESI-MS: 209 ($[M+Na]$)$^+$.

*Tetrahydro-2-{[(3*R*)-3-(methoxymethoxy)pent-4-en-1-yl]oxy}-2*H*-pyran* (**22**). MOMCl (2.43 ml, 32.25 mmol) and ^{i}Pr$_2$EtN (10.5 ml, 64.51 mmol) were added to a stirred soln. of **21** (1.5 g, 8.06 mmol) in CH_2Cl_2 (20 ml) at 0°. The mixture was stirred at r.t. for 12 h and then quenched by adding H_2O (8 ml). The mixture was extracted with CH_2Cl_2 (3×25 ml), the org. extract washed with brine (2×20 ml), dried (Na_2SO_4), and evaporated, and the crude product purified by CC: pure **22** (1.59 g, 86%). Pale yellow liquid. R_f 0.78 (AcOEt/hexane 3:7). $[\alpha]_D^{25}=+35.8$ ($c=1.4$, $CHCl_3$). IR (neat): 3078, 2939, 2881, 1636, 1441, 1353, 1030, 987, 920, 869. ^{1}H-NMR (300 MHz): 1.47–1.69 (*m*, 6 H); 1.70–1.90 (*m*, 2 H); 3.34 (*s*, 3 H); 3.37–3.52 (*m*, 2 H); 3.72–3.88 (*m*, 2 H); 4.14 ('*quint*', $J=6.8$, 1 H); 4.49 (*d*, $J=6.8$, 1 H); 4.55 (*q*, $J=4.5$, 1 H); 4.66 (*d*, $J=6.0$, 1 H); 5.15–5.27 (*m*, 2 H); 5.61–5.75 (*m*, 1 H). ^{13}C-NMR (75 MHz): 19.5; 25.4; 30.7; 35.5; 62.2; 63.8; 74.3; 74.7; 93.8; 98.9; 117.1; 138.1. ESI-MS: 253.0 ($[M+Na]^+$). HR-ESI-MS: 253.1426 ($[M+Na]^+$, $C_{12}H_{22}NaO_4^+$; calc. 253.1415; +4.0327 ppm error).

*(3*R*)-3-(Methoxymethoxy)pent-4-en-1-ol* (**23**). To a stirred soln. of **22** (1.0 g, 4.34 mmol) in MeOH (20 ml) was added cat. PPTS (10 mol-%), and the mixture was stirred at r.t. for 4 h. The MeOH was evaporated and the crude product purified by CC (SiO_2): **23** (0.49 g, 78%). Colorless liquid. R_f 0.68 (AcOEt/hexane 3:7). $[\alpha]_D^{25}=+100.6$ ($c=0.9$, $CHCl_3$). IR (neat): 3424, 2945, 1643, 1423, 1151, 1096, 1030, 922. ^{1}H-NMR (300 MHz): 1.77 (*t*, $J=6.0$, 2 H); 2.40 (br. *s*, 1 H); 3.36 (*s*, 3 H); 3.63–3.80 (*m*, 2 H); 4.21 (*q*, $J=7.5$, 1 H); 4.49 (*d*, $J=6.8$, 1 H); 4.65 (*d*, $J=6.8$, 1 H); 5.15–5.26 (*m*, 2 H); 5.62–5.75 (*m*, 1 H). ^{13}C-NMR (75 MHz): 37.7; 55.5; 59.6; 75.9; 93.8; 117.3; 137.6. ESI-MS: 169.0 ($[M+Na]^+$). HR-ESI-MS: 169.0846 ($[M+Na]^+$, $C_7H_{14}NaO_3^+$; calc. 169.0840).

*Methyl (2*Z*,5*R*)-5-(Methoxymethoxy)hepta-2,6-dienoate* (**24**). A soln. of **23** (0.45 g, 3.08 mmol) in CH_2Cl_2 (10 ml, plus 2×4 ml of rinse) was added to an ice-cooled soln. of 2-iodoxybenzoic acid (IBX; 2.15 g, 7.67 mmol) in DMSO (1.5 ml). The mixture was stirred at r.t. for 12 h and then filtered through a *Celite* pad and washed with CH_2Cl_2 (4×20 ml). The combined org. filtrate was washed with H_2O ($2\times$ 10 ml) and brine (10 ml), dried (Na_2SO_4), and concentrated to obtain a crude aldehyde which was

used for the next stage without further purification. A soln. of methyl 2-[*P,P*-bis(2,2,2-trifluoroethoxy)-phosphinyl]acetate (1.17 g, 3.69 mmol) in THF (10 ml) was slowly added to a stirred soln. of NaH (0.15 g, 6.16 mmol) in THF (35 ml) at 0° under N_2. The mixture was stirred at 0° for 30 min. Then, the mixture was cooled to −78°, and the above crude aldehyde in THF (5 ml, plus 2 × 2 ml of rinse) was added dropwise over 10 min. The resulting mixture was stirred at −78° for 30 min. Then, the mixture was quenched with sat. NH_4Cl soln. (4 ml) and extracted with AcOEt (3 × 20 ml), the extract dried (Na_2SO_4) and evaporated (water-bath temp. should not exceed 30°), and the crude product purified by CC (SiO_2): **24** (0.43 g, 70%). Colorless liquid. R_f 0.75 (AcOEt/hexane 3:7). $[\alpha]_D^{25} = +55.3$ ($c = 0.9$, $CHCl_3$). IR (neat): 2928, 1723, 1646, 1439, 1407, 1178, 1152, 1032, 921, 820. ^{1}H-NMR (300 MHz): 2.93 (*td*, $J = 7.5$, 2.2, 2 H); 3.34 (*s*, 3 H); 4.13 (*q*, $J = 6.0$, 1 H); 4.51 (*d*, $J = 6.8$, 1 H); 4.65 (*d*, $J = 6.8$, 1 H); 5.17–5.30 (*m*, 2 H); 5.64–5.77 (*m*, 1 H); 5.84 (*dt*, $J = 11.3$, 2.2, 1 H); 6.30 (*dt*, $J = 11.3$, 2.2, 1 H). ^{13}C-NMR (75 MHz): 34.6; 51.1; 55.5; 76.3; 93.8; 117.5; 120.8; 137.4; 145.7; 166.6. ESI-MS: 223.2 ($[M + Na]^+$). HR-ESI-MS: 223.0957 ($[M + Na]^+$, $C_{10}H_{16}NaO_4^+$; calc. 223.0946).

Data of corresponding (2*E*)-compound: ^{1}H-NMR (200 MHz): 2.45 (*dt*, $J = 7.3$, 2.2, 2 H); 3.33 (*s*, 3 H); 3.71 (*s*, 3 H); 4.12 (*q*, $J = 6.6$, 1 H); 4.48 (*d*, $J = 6.6$, 1 H); 4.65 (*d*, $J = 7.3$, 1 H); 5.18–5.31 (*m*, 2 H); 5.58–5.77 (*m*, 1 H); 5.86 (*dt*, $J = 15.4$, 1.5, 1 H); 6.84–7.01 (*m*, 1 H).

*(6*R*)-6-Ethenyl-5,6-dihydro-2*H*-pyran-2-one* (**10**). $CeCl_3 \cdot 7\,H_2O$ (10 mol-%) was added to a stirred soln. of **24** (0.2 g, 1.0 mmol) in MeOH/MeCN 1:1 (16 ml) and the mixture kept at reflux temp. for 8 h. Then, the mixture was quenched with solid $NaHCO_3$, stirred at r.t. for 10 min, and filtered. The solvent was evaporated and the crude product purified by CC (SiO_2): **10** (100 mg, 83%). R_f 0.55 (AcOEt/hexane 3:7). $[\alpha]_D^{25} = +97.3$ ($c = 0.75$, $CHCl_3$). ^{1}H-NMR (300 MHz): 2.41–2.47 (*m*, 2 H); 4.92 (*qt*, $J = 5.6$, 1.3, 1 H); 5.29 (*t*, $J = 10.7$, 1 H); 5.41 (*dt*, $J = 17.3$, 1.1, 1 H); 5.87–6.00 (*m*, 1 H); 6.03 (*dt*, $J = 9.8$, 2.0, 1 H); 6.81–6.87 (*m*, 1 H). ^{13}C-NMR (75 MHz): 29.3; 77.7; 117.8; 121.6; 134.8; 144.3; 163.75. ESI-MS: 147.1 ($[M + Na]^+$). HR-ESI-MS: 147.0428 ($[M + Na]^+$, $C_7H_8NaO_2^+$; calc. 147.0421; +4.0852 ppm error).

*(6*R*)-6-[(1*E*,4*R*,6*R*)-4,5-Dihydroxy-8-phenyloct-1-en-1-yl]-5,6-dihydro-2*H*-pyran-2-one* (**3**; *Diastereoisomer of (+)-Strictifolione* (**2**)). A soln. of *Grubbs*' second-generation catalyst **G-II** (0.015 g, 0.018 mmol, 10 mol-%) in CH_2Cl_2 (5 ml) was added dropwise to a soln. of **10** (0.068 g, 0.5454 mmol) and **9** (0.080 g, 0.3636 mmol) in CH_2Cl_2 (90 ml) at 0°. After the addition, the mixture was stirred under reflux for 10 h. The solvent was evaporated, and the crude product purified by CC (SiO_2): pure **3** (7.4 mg, 65%). White solid. M.p. 113–115°. R_f 0.6 (AcOEt/hexane 8:2). $[\alpha]_D^{25} = +34.34$ ($c = 0.7$, $CHCl_3$). IR (neat): 3303, 2930, 1721, 1492, 1445, 1385, 1344, 1242, 1151, 1109, 1030, 971, 823, 756, 703. ^{1}H-NMR (200 MHz): 1.58 (*t*, $J = 5.1$, 2 H); 1.65–1.85 (*m*, 2 H); 2.21 (*t*, $J = 5.8$, 2 H); 2.31–2.47 (br. *s*, 4 H); 2.52–2.83 (*m*, 2 H); 3.81–4.04 (*m*, 2 H); 4.83 (*q*, $J = 7.3$, 1 H); 5.61 (*dd*, $J = 5.1$, 15.4, 1 H); 5.81 (*dt*, $J = 5.1$, 15.4, 1 H); 5.98 (*d*, $J = 9.5$, 1 H); 6.82 (*ddd*, $J = 3.6$, 4.4, 9.5, 1 H); 7.07–7.24 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 29.69; 32.16; 38.98; 40.33; 42.14; 68.15; 68.64; 77.88; 121.47; 125.85; 128.38; 128.40; 129.94; 131.29; 141.87; 144.81; 164.05. HR-ESI-MS: 339.1556 ($[M + Na]^+$, $C_{19}H_{24}NaO_4^+$; calc. 339.1572; −4.8037 ppm error).

*Data of (6*R*,6′*R*)-6,6′-(ethene-1,2-diyl)bis[5,6-dihydro-2*H*-pyran-2-one]* (**19**): Light yellow liquid. R_f 0.4 (AcOEt/hexane 8:2). ^{1}H-NMR (200 MHz): 2.32–2.55 (*m*, 2 H); 4.86–4.99 (*m*, 1 H); 6.0 (*dt*, $J = 9.5$, 1.5, 1 H); 6.02–5.91 (*m*, 1 H); 6.79–6.90 (*m*, 1 H). ^{13}C-NMR (75 MHz): 29.4; 76.2; 121.4; 129.5; 144.5; 163.4. LC-MS: 243 ($[M + Na]^+$).

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