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Radical mediated stereoselective synthesis of (4*R*,8*R*)-4,8-dimethyldecanal, an aggregation pheromone of *Tribolium* flour beetles

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Abstract—(4*R*,8*R*)-4,8-Dimethyldecanal, a common aggregation pheromone of *Tribolium* flour beetles, has been synthesized from (*R*)-2,3-*O*-isopropylideneglyceraldehyde in 11 steps and 7% overall yield. The key step in the synthesis is the highly diastereoselective chelation-controlled radical reaction of ethyl (4*S*,5*R*)-4-benzyloxy-5,6-(isopropylidenedioxy)-2-methylenehexanoate with ethyl (*R*)-5-iodo-3-methylpentanoate performed in the presence of 7 equiv of $MgBr_2 \cdot OEt_2$.

1. Introduction

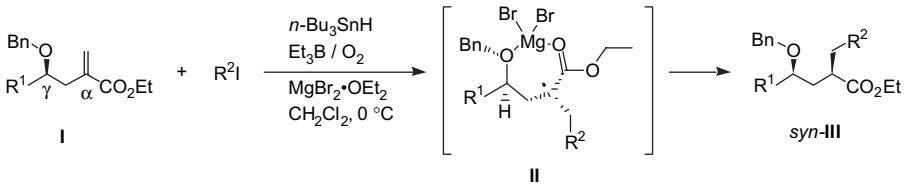
The 1,5-*syn*-dimethylalkyl motif is ubiquitous in many natural products such as tocopherols, several insect pheromones, and membrane lipids of archaebacteria. The stereoselective construction of the structural motif is therefore of particular interest[1–3] and we intend to apply the chelation-controlled radical reaction of γ-benzyloxy-α-methylenecarboxylic acid ester **I** yielding *syn*-adduct **III**, recently developed in our laboratory,[4] to the synthesis of these natural products (Scheme 1). The highly *syn*-selective addition of alkyl iodide R^2I to **I** is referred to the H-atom transfer to the outside face of radical center in the sharply folded seven-membered chelate intermediate **II**.[4c–e]

We now report the radical mediated stereoselective synthesis of (4*R*,8*R*)-4,8-dimethyldecanal (**1**), a common aggregation pheromone produced by the male flour beetles of *Tribolium castaneum*, *Tribolium confusum*, *Tribolium freemani*, and *Tribolium madens* (Coleoptera: Tenebrionidae).[5,6] The pheromone possessing a 1,5-dimethylalkyl motif would be synthesized by using the radical addition of alkyl iodide **IV** to optically active γ-benzyloxy-α-methylenecarboxylic acid ester **I** followed by the reduction of the ethoxycarbonyl group to a methyl group (Scheme 2).

The first synthesis of (4*R*,8*R*)-4,8-dimethyldecanal (**1**) and three other stereoisomers from (*R*)-citronellol and (*R*)-citronellic acid has established that the absolute configuration of the pheromone is (4*R*,8*R*).[7,8] Since the identification of the structure, several stereoselective syntheses of the pheromone **1** have been reported.[9]

2. Results and discussion

Scheme 3 shows the synthetic route of (4*R*,8*R*)-4,8-dimethyldecanal (**1**) starting from (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**2**), which is prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol.[10] The Reformatsky reaction of aldehyde **2** with ethyl 2-(bromomethyl)propeonate (**3**) gave an inseparable diastereomeric mixture of γ-hydroxy



Scheme 1. Chelation-controlled diastereoselective radical reactions of α-methylene-γ-oxycarboxylic acid esters **I** with alkyl iodides R^2I yielding *syn*-adducts **III**.

Keywords: *Tribolium* flour beetle; Pheromone; (4*R*,8*R*)-4,8-Dimethyldecanal; Radical reaction; 1,3-Asymmetric induction.
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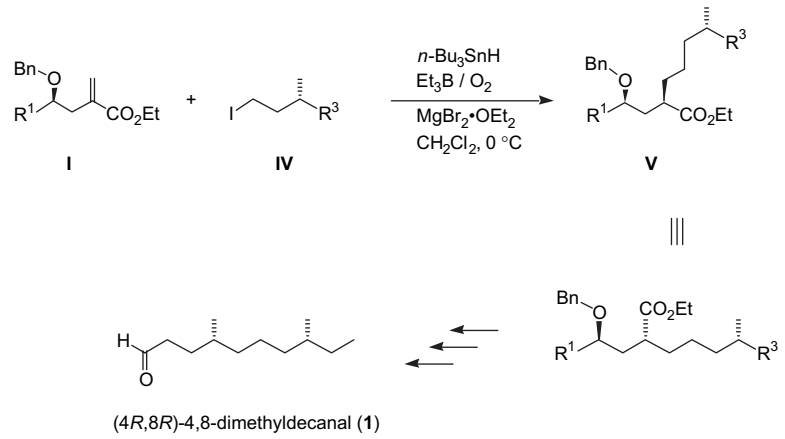
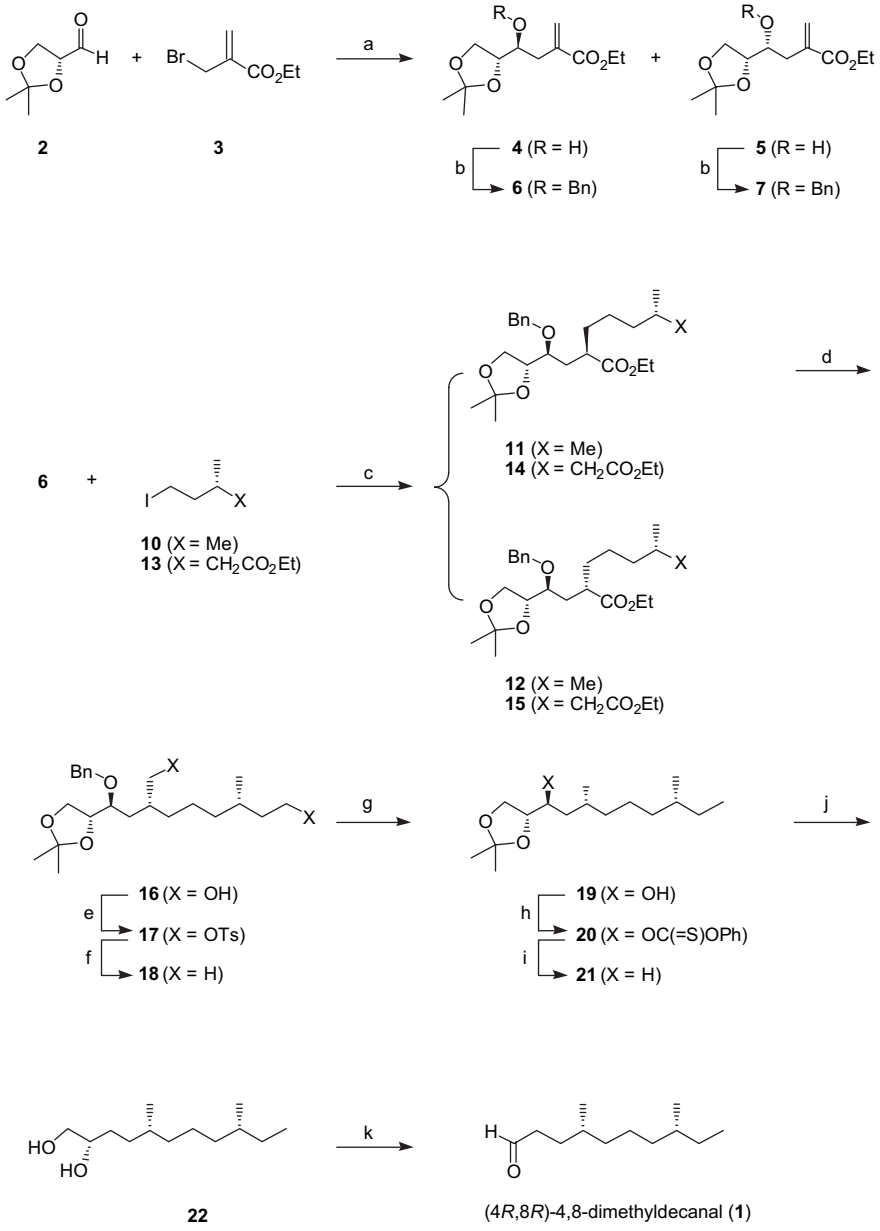
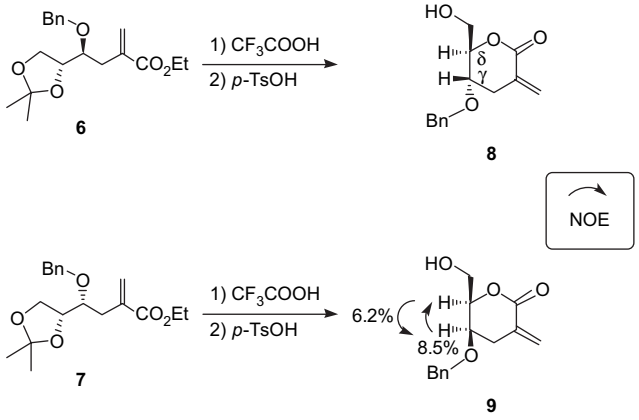


Scheme 2. Synthetic plan of (4*R*,8*R*)-4,8-dimethyldecanal (**1**).



Scheme 3. Synthetic route of (4*R*,8*R*)-4,8-dimethyldecanal (**1**). Reagents: (a) Zn, THF, aq NH_4Cl; (b) $PhCH_2Br$, Ag_2O, toluene; (c) *n*-Bu_3SnH, Et_3B, $MgBr_2 \cdot OEt_2$, CH_2Cl_2; (d) $LiAlH_4$, diethyl ether; (e) *p*-TsCl, pyridine, CH_2Cl_2; (f) $LiAlH_4$, diethyl ether; (g) H_2, Pd–C, ethanol; (h) $PhOC(=S)Cl$, pyridine, CH_2Cl_2; (i) *n*-Bu_3SnH, AIBN, toluene, 85 °C; (j) 1 mol dm^{-3} HCl, THF–H_2O (1:1); (k) $NaIO_4$, aq CH_3CN.

esters **4** and **5** in a ratio of 2.8:1.[11] Treatment of the mixture with benzyl bromide and silver oxide gave a mixture of benzyl ethers **6** and **7**, which was easily separated by silica gel column chromatography to give **6** in 26% yield from 1,2:5,6-di-*O*-isopropylidene-D-mannitol. To assign unambiguously the stereochemistry of the newly formed chiral center in the Reformatsky reaction,[11] the benzyl ethers **6** and **7** were transformed into δ-lactones **8** and **9**, respectively, and their NOE experiments were performed (Scheme 4). For the lactone **9**, NOE enhancements of γ-H (6.2%) and δ-H (8.5%) were observed by irradiating δ-H and γ-H, respectively, while for the lactone **8**, irradiation of γ-H and δ-H did not enhance the signals of their vicinal methine protons. The NOE difference spectra of the δ-lactones **8** and **9** thus established the stereochemistry of **6** and **7** as 4,5-*anti* and 4,5-*syn*, respectively.



Scheme 4. Determination of the configurations of **6** and **7**.

The radical reaction of the major diastereomer **6** with 1-iodo-3-methylbutane (**10**) was at first performed under the reaction conditions used in our previous work[4] [iodide **10** (3 equiv), *n*-Bu_3SnH (2 equiv), Et_3B (1 equiv), $MgBr_2\cdot OEt_2$ (3 equiv) in CH_2Cl_2 at 0 °C] to give the 2,4-*syn*-adduct **11** and 2,4-*anti*-adduct **12** in 63% yield and 14:1 diastereomer ratio. In order to ameliorate the stereoselectivity, the radical reaction was then performed using 7 equiv of $MgBr_2\cdot OEt_2$. The diastereoselectivity and yield were improved to **11**/**12**>50:1 and 73%, respectively.

In our previous work,[4c] we confirmed the seven-membered chelate ring formation of the starting material **I** (R^1=Ph) by the complexation experiment with 3 equiv of $MgBr_2\cdot OEt_2$ in $CDCl_3$. The large difference in chemical shift increments $\Delta\delta=[\delta_H$ (substrate+$MgBr_2\cdot OEt_2)-\delta_H$ (substrate)] by adding the Lewis acid between the diastereotopic β-methylene protons suggests the formation of bidentate complexation. However, in the complexation experiment of **6** with 3 equiv of $MgBr_2\cdot OEt_2$, only slight chemical shift increments were observed. The results of the complexation experiment of **6** with 7 equiv of $MgBr_2\cdot OEt_2$ are shown in Figure 1. The large $\Delta\delta$ values suggest that the addition of 7 equiv of the Lewis acid is required to achieve the chelate ring formation and the highly diastereoselective radical addition reaction.[12]

The radical addition of ethyl (*R*)-5-iodo-3-methylpentanoate (**13**)[13] to **6**, i.e., the key step in the synthesis of (4*R*,8*R*)-4,8-

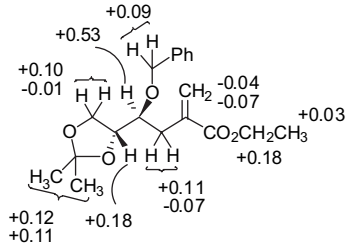
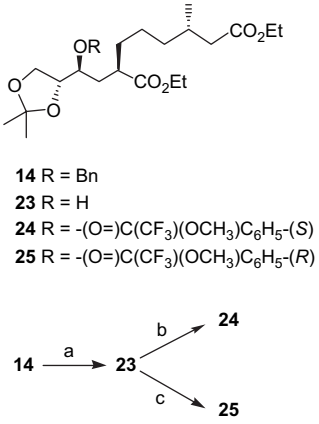


Figure 1. $\Delta\delta$ values (ppm) for the substrate **6**. $\Delta\delta_H=\delta_H$ (substrate **6**+$MgBr_2\cdot OEt_2)-\delta_H$ (substrate **6**). The δ_H (substrate **6**+$MgBr_2\cdot OEt_2$) value was obtained after sonication of **6** with 7 equiv of $MgBr_2\cdot OEt_2$ in $CDCl_3$.

dimethyldecanal (**1**), was carried out using 7 equiv of $MgBr_2\cdot OEt_2$. The desired 2,4-*syn*-adduct **14** was obtained in 71% yield and >96% de. The ^1H NMR and ^{13}C NMR spectra of α-methoxy-α-(trifluoromethyl)phenylacetates **24** and **25**, which were transformed from **14** via the corresponding alcohol **23**, did not show the epimerization of aldehyde **2** during the Reformatsky reaction of **2** with **3** (Scheme 5).



Scheme 5. Reagents: (a) H_2, Pd–C, ethanol; (b) (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 4-dimethylaminopyridine, pyridine; (c) (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 4-dimethylaminopyridine, pyridine.

The diester **14** was then reduced with lithium aluminium hydride to give the corresponding diol **16** in 89% yield. The tosylation of the diol with *p*-toluenesulfonyl chloride followed by the reduction with lithium aluminium hydride gave compound **18** in 76% yield. The hydrogenolysis of **18** over Pd–C gave alcohol **19** quantitatively. The alcohol was then treated with phenyl chlorothionoformate to give phenoxythiocarbonyl ester **20**, which was then reduced under radical conditions using AIBN and *n*-Bu_3SnH to give compound **21** in 71% two-step yield. The acid catalyzed hydrolysis of **21** followed by the oxidative cleavage of the resulting diol **22** with sodium periodate gave (4*R*,8*R*)-4,8-dimethyldecanal (**1**), as an oil, $[\alpha]_D^{23}$ −5.7 (*c* 1.0, $CHCl_3$) (lit.[7b] $[\alpha]_D^{22.5}$ −7.3 (*c* 2.04, $CHCl_3$)), in 85% two-step yield. The IR, ^1H NMR, ^{13}C NMR, and MS spectral data of the synthetic aldehyde **1** were identical with those of (4*R*,8*R*)- and (4*S*,8*S*)-4,8-dimethyldecanals reported in the literatures.[7,9,14]

We have thus synthesized (4*R*,8*R*)-4,8-dimethyldecanal (**1**) from (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**2**) in 11 steps and 7% overall yield.

3. Conclusion

We have synthesized (4*R*,8*R*)-4,8-dimethyldecanal (**1**) from (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**2**), easily prepared from D-mannitol, in 11 steps and 7% overall yield. The key step in the synthesis is the highly diastereoselective chelation-controlled radical reaction of γ-benzyloxy-α-methylenecarboxylic acid ester **6** and ethyl (*R*)-5-iodo-3-methylpentanoate (**13**) performed in the presence of 7 equiv of $MgBr_2 \cdot OEt_2$.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on a JEOL GSX-400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on the instrument operating at 100.5 MHz with $CDCl_3$ as the solvent and internal standard (*δ* 77.0). IR spectra were taken on a SIMADZU FTIR-8700 spectrometer. Mass spectra (EI^+) were obtained on a JEOL JMS-700 mass spectrometer. Precoated Merck Kieselgel 60 F_{254} and Kanto silica gel 60 (spherical neutral) were used for thin layer chromatography and column chromatography, respectively.

4.1.1. Ethyl (4*S*,5*R*)- and (4*R*,5*R*)-4-hydroxy-5,6-(isopropylidenedioxy)-2-methylenehexanoates (4) and (5). (*R*)-2,3-*O*-Isopropylideneglyceraldehyde (**2**) was prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol (2.87 g, 10.9 mmol) following the reported procedures.[10] To a solution of the aldehyde **2** in THF (36 cm^3) were added ethyl 2-(bromomethyl)propeonate (**3**) (5.95 g, 30.8 mmol), saturated aqueous NH_4Cl (57 cm^3), and activated zinc powder (3.34 g, 51.3 mmol) and the mixture was stirred at 0 °C for 3 h. The product was extracted with ethyl acetate and the extract was washed with saturated brine and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (8:1)] to give an inseparable mixture of **4** and **5** (3.38 g, 63% yield from 1,2:5,6-di-*O*-isopropylidene-D-mannitol; **4**/**5**=2.8:1) as an oil. MS *m*/*z* 229 (M^+−Me, 68%), 143 (94), 123 (71), 101 (100); HRMS calcd for $C_{11}H_{17}O_5$ [M^+−Me] 229.1076, found 229.1082. *Major diastereomer* **4**. ^{1}H NMR *δ* 1.32 (3H, t, *J*=7.2 Hz, CH_3), 1.36 (3H, s, CH_3), 1.43 (3H, s, CH_3), 2.37 (1H, ddd, *J*=14.2, 8.4, 0.8 Hz, C*H*HC=CH_2), 2.70 (1H, ddd, *J*=14.2, 3.6, 0.8 Hz, CH*H*C=CH2), 2.86 (1H, d, *J*=3.6 Hz, OH), 3.75–4.10 (4H, m, C*H*(–O)C*H*OH, $CO_2CH_2CH_3$), 4.21 (1H, dd, *J*=14.2, 7.0 Hz, C*H*HO), 4.25 (1H, dd, *J*=14.2, 7.0 Hz, CH*H*O), 5.74 (1H, d, *J*=1.6 Hz, C=C*H*H), 6.29 (1H, d, *J*=1.2 Hz, C=CH*H*); ^{13}C NMR *δ* 14.20, 25.30, 26.67, 36.15, 61.19, 65.94, 71.28, 78.10, 109.12, 128.00, 136.92, 167.89. *Minor diastereomer* **5**. ^{1}H NMR *δ* 1.31 (3H, t, *J*=7.2 Hz, CH_3), 1.37 (3H, s, CH_3), 1.44 (3H, s, CH_3), 2.41–2.49 (2H, m, CH_2C=CH_2), 2.86 (1H, d, *J*=3.6 Hz, OH), 3.75–4.10 (4H, m, C*H*(–O)C*H*OH, $CO_2CH_2CH_3$), 4.20 (1H, dd, *J*=14.2, 6.8 Hz, C*H*HO), 4.23 (1H, dd, *J*=14.2, 6.8 Hz, CH*H*O), 5.72 (1H, d, *J*=1.6 Hz, C=C*H*H), 6.28 (1H, d, *J*=1.2 Hz, C=CH*H*); ^{13}C NMR *δ* 14.22, 25.30, 26.58, 36.77, 60.93, 66.00, 70.62, 78.40, 109.36, 127.69, 136.64, 167.08.

4.1.2. Ethyl (4*S*,5*R*)- and (4*R*,5*R*)-4-benzyloxy-5,6-(isopropylidenedioxy)-2-methylenehexanoates (6) and (7). To a solution of alcohols **4** and **5** (29.2 mg, 0.12 mmol) in toluene (2 cm^3) were added benzyl bromide (0.05 cm^3, 0.36 mmol) and freshly prepared silver oxide (84.5 mg, 0.36 mmol). The mixture was stirred at room temperature for 48 h and then filtered through a pad of Celite. The filtrate was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (20:1)] to give **6** (14 mg) and **7** (8.3 mg), and **6** (12.3 mg). *Major diastereomer* **6**. $[\alpha]_D^{23}$ +22.0 (*c* 1.95, $CHCl_3$); ^{1}H NMR *δ* 1.28 (3H, t, *J*=7.0 Hz, CH_3), 1.35 (3H, s, CH_3), 1.43 (3H, s, CH_3), 2.46 (1H, dd, *J*=14.2, 7.8 Hz, C*H*HC=CH_2), 2.72 (1H, ddd, *J*=14.2, 4.4, 0.8 Hz, CH*H*C=CH_2), 3.73 (1H, m, CH–O), 3.90 (1H, dd, *J*=7.8, 6.0 Hz, C*H*H–O), 4.03 (1H, d, *J*=7.8, 6.4 Hz, CH*H*–O), 4.12 (1H, dd, *J*=10.5, 6.0 Hz, CH–O), 4.16 (2H, q, *J*=7.0 Hz, CH_2–O), 4.59 (2H, s, PhCH_2O), 5.68 (1H, d, *J*=1.2 Hz, C=C*H*H), 6.23 (1H, d, *J*=1.2 Hz, C=CH*H*), 7.28–7.32 (5H, m, Ph); ^{13}C NMR *δ* 14.24, 25.36, 26.56, 34.25, 60.72, 66.00, 72.98, 77.42, 77.82, 109.12, 127.50, 127.63, 127.78, 128.17, 136.91, 138.16, 166.91; MS *m*/*z* 319 (M^+−Me, 26%), 233 (95), 101 (58), 91 (100); HRMS calcd for $C_{18}H_{23}O_5$ [M^+−Me] 319.1545, found 319.1552. *Minor diastereomer* **7**. ^{1}H NMR *δ* 1.28 (3H, t, *J*=7.2 Hz, CH_3), 1.37 (3H, s, CH_3), 1.45 (3H, s, CH_3), 2.42–2.52 (2H, m, CH_2C=CH_2), 3.63 (1H, m, CH–O), 3.79 (1H, dd, *J*=8.0, 7.3 Hz, C*H*H–O), 3.99 (1H, d, *J*=8.0, 6.5 Hz, CH*H*–O), 4.13–4.23 (3H, m, CH–O, CH_2–O), 4.59 (1H, d, *J*=11.7 Hz, PhC*H*H–O), 4.70 (1H, d, *J*=11.7 Hz, PhCH*H*–O), 5.69 (1H, d, *J*=1.2 Hz, C=C*H*H), 6.23 (1H, d, *J*=1.6 Hz, C=CH*H*), 7.26–7.36 (5H, m, Ph); ^{13}C NMR *δ* 14.24, 25.47, 26.53, 34.09, 60.72, 65.88, 72.93, 77.95, 78.05, 109.30, 127.41, 127.83, 127.88, 128.11, 136.64, 138.38, 166.80. MS *m*/*z* 319 (M^+−Me, 25%), 233 (94), 101 (54), 91 (100); HRMS calcd for $C_{18}H_{23}O_5$ [M^+−Me] 319.1545, found 319.1597.

4.1.3. (5*S*,6*R*)-5-Benzyloxy-6-hydroxymethyl-3-methylenetetrahydropyran-2-one (8). To a solution of **6** (18.2 mg, 0.054 mmol) in THF–H_2O (4:1, 1 cm^3) was added trifluoroacetic acid at 0 °C. The solution was stirred at room temperature overnight and then the product was extracted with ethyl acetate and the extract was washed with saturated brine and dried over anhydrous sodium sulfate. Concentration of the solution gave a crude product, which was used without further purification. To a solution of the crude product in benzene (1 cm^3) was added catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (2:1)] to give **8** (6.9 mg, 51%) as an oil. ^{1}H NMR *δ* 2.66 (1H, m, C*H*HCHOBn), 3.03 (1H, m, CH*H*CHOBn), 3.85 (1H, m, C*H*OBn), 3.86 (1H, dd, *J*=12.3, 3.4 Hz, C*H*HOH), 3.93 (1H, dd, *J*=12.3, 3.4 Hz, CH*H*OH), 4.34 (1H, dt, *J*=7.8, 3.4 Hz, C*H*CH_2OH), 4.60 (1H, d, *J*=11.5 Hz, PhC*H*H), 4.68 (1H, d, *J*=11.5 Hz, PhCH*H*), 5.65 (1H, m, C=C*H*H), 6.46 (1H, m, C=CH*H*), 7.30–7.39 (5H, m, Ph); ^{13}C NMR *δ* 33.16, 61.74, 70.14, 71.50, 82.14, 127.72, 128.06,

128.52, 130.18, 131.19, 137.20, 164.53; MS *m/z* 248 (M^+, 14%), 124 (15), 97 (41), 91 (100); HRMS calcd for $C_{14}H_{16}O_4$ [M^+] 248.1049, found 248.1055.

4.1.4. (5*R*,6*R*)-5-Benzyloxy-6-hydroxymethyl-3-methylenetetrahydropyran-2-one (9). To a solution of **7** (12.9 mg, 0.039 mmol) in THF–H_2O (4:1, 1 cm^3) was added trifluoroacetic acid at 0 °C. The solution was stirred at room temperature overnight and then the product was extracted with ethyl acetate and the extract was washed with saturated brine and dried over anhydrous sodium sulfate. Evaporation of the solvent in vacuo gave the product, which was used without further purification. To a solution of the product in benzene (1 cm^3) was added catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (2:1)] to give **9** (3.5 mg, 37%) as an oil. ^{1}H NMR δ 2.65 (1H, m, C*H*HCHOBn), 3.07 (1H, dd, *J*=16.4, 3.9 Hz, CH*H*CHOBn), 3.78 (1H, dd, *J*=11.9, 5.1 Hz, C*H*HOH), 3.93 (1H, m, C*H*OBn), 3.99 (1H, dd, *J*=11.9, 6.6 Hz, CH*H*OH), 4.42 (1H, d, *J*=12.1 Hz, PhC*H*H), 4.45 (1H, m, C*H*CH_2OH), 4.66 (1H, d, *J*=12.1 Hz, PhCH*H*), 5.63 (1H, m, C=C*H*H), 6.52 (1H, m, C=CH*H*), 7.28–7.38 (5H, m, Ph); ^{13}C NMR δ 31.88, 62.42, 69.33, 70.22, 82.00, 127.69, 128.09, 128.53, 130.31, 130.57, 137.03, 164.16; MS *m/z* 248 (M^+, 7%), 124 (18), 97 (27), 91 (100); HRMS calcd for $C_{14}H_{16}O_4$ [M^+] 248.1049, found 248.1058.

4.1.5. Ethyl (2*R*)-2-[(2*S*,3*R*)-2-benzyloxy-3,4-(isopropylidenedioxy)butyl]-6-methyl-heptanoate (11). To a solution of α-methylene ester **6** (21.5 mg, 0.064 mmol) in dry CH_2Cl_2 (1.3 cm^3) was added $MgBr_2\cdot OEt_2$ (117 mg, 0.45 mmol) under N_2 and the mixture was stirred at room temperature for 15 min. To the suspension cooled to 0 °C were added 1-iodo-3-methylbutane (**10**) (0.026 cm^3, 0.19 mmol), *n*-Bu_3SnH (0.036 cm^3, 0.13 mmol), and Et_3B (0.064 cm^3, 1.0 mol dm^{-3} in hexane). The mixture was stirred at 0 °C for 6 h. KF and water were added and the mixture was stirred at room temperature overnight. After filtration through a pad of Florisil, the filtrate was evaporated in vacuo and the residue was purified by column chromatography on silica gel [2 g; eluent: hexane then hexane–ethyl acetate (30:1)] to give a mixture of **11** and **12** (19 mg, 73% yield; **11/12**>50:1) as an oil. ^{1}H NMR δ 0.85 (6H, d, *J*=6.3 Hz, 2×CH_3), 1.22 (3H, t, *J*=7.0 Hz, CH_3), 1.13–1.65 (8H, m, C*H*HCH(CH_2)$_3$C*H*(CH_3)$_2$), 1.35 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.95 (1H, ddd, *J*=14.2, 11.3, 3.0 Hz, C*H*H), 2.68 (1H, m, CHC=O), 3.52 (1H, m, CH–O), 3.88 (1H, dd, *J*=8.0, 7.6 Hz, C*H*H–O), 4.00–4.14 (4H, m, CH*H*–O, CH–O, CH_2–O), 4.55 (1H, d, *J*=11.0 Hz, PhC*H*H), 4.65 (1H, d, *J*=11.0 Hz, PhCH*H*), 7.26–7.34 (5H, m, Ph); ^{13}C NMR δ 14.39, 22.57, 22.66, 25.02, 25.33, 26.59, 27.84, 33.72, 33.98, 38.77, 41.54, 60.13, 66.06, 73.36, 77.62, 77.73, 109.04, 127.54, 127.85, 128.23, 138.34, 176.09; MS *m/z* 391 (M^+−Me, 13%), 305 (76), 101 (32), 91 (100); HRMS calcd for $C_{23}H_{35}O_5$ [M^+−Me] 391.2485, found 391.2504.

4.1.6. Diethyl (2*R*,6*S*)-2-[(2*S*,3*R*)-2-benzyloxy-3,4-(isopropylidenedioxy)butyl]-6-methyl-1,8-octanedioate (14). The radical reaction of **6** (83 mg, 0.25 mmol) with iodide **13** (210 mg, 0.78 mmol) in the presence of $MgBr_2\cdot OEt_2$ (453 mg, 1.75 mmol) as described above gave **14** (85 mg, 71% yield; 96% de) as an oil. $[\alpha]_D^{23}$ −3.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR δ 0.91 (3H, d, *J*=6.3 Hz, CH_3), 1.22 (3H, t, *J*=7.3 Hz, CH_3), 1.25 (3H, t, *J*=7.3 Hz, CH_3), 1.35 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.13–1.62 (7H, m), 1.92–1.99 (2H, m, CH_2C=O), 2.07 (1H, dd, *J*=14.7, 7.8 Hz, C*H*H), 2.26 (1H, dd, *J*=14.7, 5.8 Hz, CH*H*), 2.65 (1H, m, CHC=O), 3.52 (1H, m, C*H*OBn), 3.86 (1H, dd, *J*=8.0, 6.5 Hz, C*H*H–O), 4.00–4.16 (6H, m, CH–O, CH*H*–O, 2×CH_2–O), 4.55 (1H, d, *J*=11.0 Hz, PhC*H*H), 4.64 (1H, d, *J*=11.0 Hz, PhCH*H*), 7.27–7.34 (5H, m, Ph); ^{13}C NMR δ 14.41, 19.75, 24.64, 25.36, 26.65, 30.30, 33.59, 33.95, 36.57, 41.49, 41.87, 60.13, 60.20, 66.08, 73.34, 77.59, 77.68, 109.02, 127.51, 127.80, 128.19, 138.25, 172.94, 175.85; MS *m/z* 463 (M^+−Me, 22%), 377 (95), 285 (46), 101 (45), 91 (100); HRMS calcd for $C_{26}H_{39}O_7$ [M^+−Me] 463.2695, found 463.2740.

4.1.7. (2*R*,6*S*)-2-[(2*S*,3*R*)-2-Benzyloxy-3,4-(isopropylidenedioxy)butyl]-6-methyloctane-1,8-diol (16). To a solution of diester **14** (248 mg, 0.52 mmol) in dry diethyl ether (13 cm^3) was added lithium aluminium hydride (3.3 equiv) at 0 °C and the mixture was stirred at room temperature for 12 h. To the mixture cooled to 0 °C were added dropwise water, then 15% aqueous sodium hydroxide. After filtration through a pad of Celite, the filtrate was dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (2:1)] to give diol **16** (181 mg, 89%) as an oil. $[\alpha]_D^{23}$ −0.52 (*c* 2.2, $CHCl_3$); ^{1}H NMR δ 0.88 (3H, d, *J*=6.3 Hz, CH_3), 1.36 (3H, s, CH_3), 1.11–1.40 (7H, m, (CH_2)$_3$CH), 1.43 (3H, s, CH_3), 1.44–1.64 (4H, m, 2×CH_2), 1.73 (1H, m, CH), 3.42 (1H, dd, *J*=11.2, 6.4 Hz, CH–O), 3.51 (1H, dd, *J*=11.2, 4.4 Hz, CH–O), 3.63–3.72 (3H, m, CH–O, CH_2–O), 3.86–4.18 (3H, m, CH–O, CH_2–O), 4.61 (1H, d, *J*=11.3 Hz, PhC*H*H), 4.71 (1H, d, *J*=11.3 Hz, PhCH*H*), 7.26–7.37 (5H, m, Ph); ^{13}C NMR δ 19.71, 24.26, 25.28, 26.55, 29.36, 32.26, 33.54, 37.18, 39.91, 61.10, 65.63, 66.31, 72.80, 78.05, 109.02, 127.79, 127.96, 128.38, 137.87; MS *m/z* 379 (M^+−Me, 4%), 185 (91), 101 (24), 91 (100); HRMS calcd for $C_{22}H_{35}O_5$ [M^+−Me] 379.2485, found 379.2516.

4.1.8. (2*R*,3*S*,5*R*,9*S*)-3-Benzyloxy-1,2-(isopropylidenedioxy)-9-methyl-11-(*p*-toluenesulfonyloxy)-5-(*p*-toluenesulfonyloxymethyl)undecane (17). To a solution of diol **16** (181 mg, 0.46 mmol) in dry CH_2Cl_2 (7 cm^3) were added pyridine (0.3 cm^3) and *p*-toluenesulfonyl chloride (879 mg, 4.6 mmol) at 0 °C. The solution was stirred at room temperature overnight. After dilution with water, the product was extracted with chloroform. The extract was washed with water, saturated sodium hydrogencarbonate solution, and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (6:1)] to give tosylate **17** (294 mg, 91%) as an oil. $[\alpha]_D^{23}$ −7.5 (*c* 2.1, $CHCl_3$); ^{1}H NMR δ 0.74 (3H, d, *J*=6.1 Hz, CH_3), 0.97–1.48 (10H, m), 1.34 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.60 (1H, m, CH), 1.80 (1H, m, CH), 2.44 (3H, s, CH_3), 2.45 (3H, s, CH_3), 3.49 (1H, m, CH–O), 3.77 (1H, dd, *J*=9.8, 4.9 Hz, CH–O), 3.83 (2H, m, CH–O), 3.97–4.11 (4H, m, CH–O), 4.45 (1H,

d, J=11.7 Hz, PhC*H*H), 4.67 (1H, d, J=11.7 Hz, PhCH*H*), 7.25–7.38 (9H, m, Ar), 7.73 (2H, d, J=8.3 Hz, Ar), 7.78 (2H, d, J=8.3 Hz, Ar); ^{13}C NMR δ 19.01, 21.69, 23.74, 25.23, 26.45, 29.10, 31.78, 32.44, 33.91, 35.67, 36.61, 65.70, 68.88, 71.92, 72.88, 76.06, 78.11, 108.98, 127.66, 127.77, 127.78, 127.84, 128.29, 129.75, 132.75, 133.01, 138.13, 144.58, 144.66.

4.1.9. (2*R*,3*S*,5*R*,9*R*)-3-Benzyloxy-1,2-(isopropylidenedioxy)-5,9-dimethylundecane (18). To a solution of tosylate **17** (134.3 mg, 0.19 mmol) in dry diethyl ether (10 cm^3) was added lithium aluminium hydride (3.3 equiv) at 0 °C. The mixture was stirred at room temperature for 12 h. To the mixture cooled to 0 °C were added dropwise water and then 15% aqueous sodium hydroxide. After filtration through a pad of Celite, the filtrate was dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (40:1)] to give **18** (57.3 mg, 83%) as an oil. $[\alpha]_D^{23}$ −6.6 (c 1.8, $CHCl_3$); ^{1}H NMR δ 0.83 (6H, d, J=6.4 Hz, 2×CH_3), 0.85 (3H, t, J=7.3 Hz, CH_3), 1.03–1.66 (12H, m, 5×CH_2, 2×CH), 1.37 (3H, s, CH_3), 1.43 (3H, s, CH_3), 3.70 (1H, dt, J=10.0, 3.4 Hz, C*H*OBn), 3.94 (1H, dd, J=7.8, 7.3 Hz, C*H*H–O), 4.02 (1H, dd, J=7.8, 6.3 Hz, CH*H*–O), 4.10 (1H, m, CH–O), 4.59 (1H, d, J=11.2 Hz, PhC*H*H), 4.77 (1H, d, J=11.2 Hz, PhCH*H*), 7.27–7.34 (5H, m, Ph); ^{13}C NMR δ 11.47, 19.31, 19.41, 24.42, 25.43, 26.53, 29.12, 29.49, 34.42, 36.87, 38.25, 39.43, 65.59, 73.41, 76.62, 79.08, 108.84, 127.47, 127.74, 128.23, 138.66; MS m/z 347 (M^+−Me, 16%), 261 (23), 101 (73), 91 (100); HRMS calcd for $C_{22}H_{35}O_3$ [M^+−Me] 347.2587, found 347.2578.

4.1.10. (2*R*,3*S*,5*R*,9*R*)-1,2-(Isopropylidenedioxy)-5,9-dimethylundecan-3-ol (19). A solution of **18** (47.2 mg, 0.13 mmol) in dry ethanol (5 cm^3) was stirred with Pd–C (35.5 mg, 0.032 mmol) under hydrogen atmosphere at room temperature for 12 h. The mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo to give **19** in quantitative yield. $[\alpha]_D^{23}$ −0.73 (c 1.86, $CHCl_3$); ^{1}H NMR δ 0.84 (3H, d, J=6.4 Hz, CH_3), 0.85 (3H, t, J=7.3 Hz, CH_3), 0.90 (3H, d, J=6.8 Hz, CH_3), 1.05–1.69 (12H, m, 5×CH_2, 2×CH), 1.37 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.92 (1H, br s, OH), 3.87–4.02 (4H, m, CH_2–O, CH–O, C*H*OH); ^{13}C NMR δ 11.47, 19.09, 19.30, 24.43, 25.37, 26.52, 29.18, 29.48, 34.42, 36.88, 38.24, 39.70, 64.44, 68.29, 79.15, 108.83; MS m/z 257 (M^+−Me, 100%), 229 (18), 101 (13); HRMS calcd for $C_{15}H_{29}O_3$ [M^+−Me] 257.2117, found 257.2121.

4.1.11. (2*R*,3*S*,5*R*,9*R*)-3-Phenoxythiocarbonyloxy-1,2-(isopropylidenedioxy)-5,9-dimethylundecane (20). To a solution of alcohol **19** (55.5 mg, 0.20 mmol) in dry CH_2Cl_2 (3 cm^3) were added dry pyridine (0.050 cm^3, 0.60 mmol) and *O*-phenyl chlorothionoformate (0.032 cm^3, 0.23 mmol) at 0 °C. The solution was stirred at room temperature for 3 h. The reaction mixture was then washed with water, saturated sodium hydrogencarbonate solution, and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (60:1)] to give phenoxythiocarbonyl ester **20** (62.1 mg, 75%) as an oil. $[\alpha]_D^{23}$ −18.7 (c 1.74, $CHCl_3$); ^{1}H NMR δ 0.85 (3H, d, J=6.4 Hz, CH_3), 0.86 (3H, d, J=6.4 Hz, CH_3), 0.98 (3H, d, J=6.8 Hz, CH_3), 1.22–1.43 (10H, m, 4×CH_2, 2×CH), 1.39 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.62 (1H, m, CH), 1.84 (1H, ddd, J=14.1, 10.0, 3.9 Hz, CH), 3.94 (1H, dd, J=8.3, 6.4 Hz, CH–O), 4.12 (1H, m, CH–O), 4.33 (1H, m, CH–O), 5.69 (1H, m, PhOC(=S)OC*H*), 7.09–7.44 (5H, m, Ph); ^{13}C NMR δ 11.49, 19.32, 19.78, 24.37, 25.32, 26.32, 29.03, 29.51, 34.42, 36.83, 37.36, 37.86, 65.55, 76.91, 82.48, 109.86, 121.87, 126.47, 129.41, 153.28, 195.09; MS m/z 393 (M^+−Me, 10%), 254 (54), 239 (56), 197 (32), 179 (47), 149 (48), 127 (100), 123 (45), 101 (55), 97 (47), 69 (95); HRMS calcd for $C_{22}H_{33}O_4S$ [M^+−Me] 393.2099, found 393.2053.

4.1.12. (2*S*,5*R*,9*R*)-1,2-(Isopropylidenedioxy)-5,9-dimethylundecane (21). To a solution of **20** (23.8 mg, 0.059 mmol) in dry toluene (2 cm^3) were added n-Bu_3SnH (0.027 cm^3, 0.12 mmol) and AIBN (12.8 mg, 0.064 mmol). The mixture was stirred at 85 °C for 3 h. KF and water were then added and the reaction mixture was stirred at room temperature overnight. After filtration though a pad of Florisil, the filtrate was evaporated in vacuo and the residue was purified by column chromatography on silica gel to give **21** (14.1 mg, 95%) as an oil. $[\alpha]_D^{23}$ +10.8 (c 1.95, $CHCl_3$); ^{1}H NMR δ 0.84 (3H, d, J=6.9 Hz, CH_3), 0.85 (3H, t, J=7.6 Hz, CH_3), 0.87 (3H, d, J=6.3 Hz, CH_3), 1.08–1.45 (13H, m, 5×CH_2, 3×CH), 1.36 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.68 (1H, m, CH), 3.52 (1H, m, CH–O), 4.02–4.07 (2H, m, CH_2–O); ^{13}C NMR δ 11.48, 19.32, 19.67, 24.47, 25.81, 27.02, 29.50, 31.17, 32.82, 32.90, 34.44, 36.95, 37.19, 69.58, 76.49, 108.52; MS m/z 241 (M^+−Me, 100%), 101 (9); HRMS calcd for $C_{15}H_{29}O_2$ [M^+−Me] 241.2246, found 241.2218.

4.1.13. (2*S*,5*R*,9*R*)-5,9-Dimethyl-1,2-undecanediol (22). To a solution of **21** (32.1 mg, 0.12 mmol) in THF–H_2O (1:1, 2 cm^3) was added 1 mol dm^{-3} HCl at 0 °C. The solution was stirred at room temperature overnight. The reaction mixture was then extracted with ethyl acetate. The extract was washed with saturated brine, and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel [eluent: hexane–ethyl acetate (3:1)] to give **22** (24.0 mg, 89%) as an oil. $[\alpha]_D^{23}$ −3.4 (c 1.0, $CHCl_3$); ^{1}H NMR δ 0.84 (3H, d, J=5.9 Hz, CH_3), 0.85 (3H, t, J=7 Hz, CH_3), 0.87 (3H, d, J=6.8 Hz, CH_3), 1.06–1.45 (14H, m, 6×CH_2, 2×CH), 2.02 (1H, br s, OH), 2.13 (1H, br s, OH), 3.45 (1H, m, C*H*OH), 3.66–3.68 (2H, m, CH_2OH); ^{13}C NMR δ 11.48, 19.32, 19.63, 24.51, 29.50, 30.75, 32.73, 32.87, 34.44, 36.96, 37.34, 66.89, 72.66; MS m/z 185 (M^+−CH_2OH, 100%), 111 (43), 97 (64), 83 (56), 69 (50); HRMS calcd for $C_{12}H_{25}O$ [M^+−CH_2OH] 185.1905, found 185.1854.

4.1.14. (4*R*,8*R*)-4,8-Dimethyldecanal (1). To a solution of **22** (24.0 mg, 0.11 mmol) in aqueous acetonitrile (60%, 2 cm^3) was added $NaIO_4$ (18.4 mg, 0.079 mmol) at 0 °C and the mixture was stirred at 0 °C for 1 h. The reaction mixture was then filtered through a pad of Celite and extracted with chloroform. The extract was washed with water and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel

[eluent: hexane–ethyl acetate (60:1)] to give (4*R*,8*R*)-4,8-dimethyldecanal (**1**) (18.5 mg, 91%) as an oil. $[\alpha]_D^{23}$ −5.6 (*c* 1.1, $CHCl_3$); IR (neat) 2961, 2929, 2714, 1712, 1463, 1379 cm^{-1}; ^1H NMR δ 0.84 (3H, d, *J*=6.3 Hz, CH_3), 0.85 (3H, d, *J*=7.2 Hz, CH_3), 0.88 (3H, d, *J*=5.6 Hz, CH_3), 1.04–1.14 (12H, m, 5×CH_2, 2×CH), 2.40–2.46 (2H, m, C*H*$_2$CH═O), 9.78 (1H, t, *J*=1.2 Hz, CH═O); ^{13}C NMR δ 11.47, 19.30, 19.45, 24.43, 28.92, 29.48, 32.46, 34.43, 36.88, 37.07, 41.77, 202.95; MS *m*/*z* 184 (M^+, 1%), 140 (67), 111 (42), 85 (54), 81 (57), 70 (90), 57 (100); HRMS calcd for $C_{12}H_{24}O$ [M^+] 184.1827, found 184.1802.

4.1.15. α-Methoxy-α-(trifluoromethyl)phenylacetate 24. ^1H NMR δ 0.88 (3H, d, *J*=6.3 Hz, CH_3), 1.00–1.40 (4H, m), 1.25 (3H, t, *J*=7.3 Hz, CH_3), 1.29 (3H, t, *J*=7.0 Hz, CH_3), 1.33 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.46–1.60 (1H, m), 1.65 (1H, ddd, *J*=14.1, 10.7, 3.4 Hz), 1.89 (1H, m), 1.99 (1H, ddd, *J*=14.1, 11.9, 2.4 Hz), 2.05 (1H, dd, *J*=15.1, 7.8 Hz), 2.15–2.25 (1H, m), 2.23 (1H, dd, *J*=14.6, 5.9 Hz), 3.59 (3H, s, OCH_3), 3.76 (1H, dd, *J*=8.3, 6.4 Hz, C*H*H–O), 3.99 (1H, dd, *J*=8.3, 6.4 Hz, CH*H*–O), 4.12 (2H, q, *J*=7.3 Hz, CH_2–O), 4.17 (2H, q, *J*=7.0 Hz, CH_2–O), 4.22 (1H, m, CH–O), 5.13 (1H, m, CH–O), 7.39–7.43 (3H, m, Ph), 7.57–7.60 (2H, m, Ph); ^{13}C NMR δ 14.30, 14.34, 19.61, 24.34, 24.94, 26.21, 30.14, 32.28, 33.18, 36.26, 41.02, 41.78, 55.54, 60.15, 60.59, 65.58, 74.30, 76.23, 77.20, 109.75, 127.36, 128.31, 129.58, 132.03, 165.90, 173.01, 175.06.

4.1.16. α-Methoxy-α-(trifluoromethyl)phenylacetate 25. ^1H NMR δ 0.91 (3H, d, *J*=6.4 Hz, CH_3), 1.13 (1H, m), 1.25 (3H, t, *J*=7.0 Hz, CH_3), 1.20–1.35 (3H, m), 1.27 (3H, t, *J*=67.0 Hz, CH_3), 1.30 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.43 (1H, m), 1.56–1.64 (1H, m), 1.69 (1H, ddd, *J*=14.1, 10.2, 39 Hz), 1.92 (1H, m), 2.03–2.13 (2H, m), 2.25 (1H, dd, *J*=15.0, 6.0 Hz), 2.39 (1H, m), 3.69 (1H, dd, *J*=8.5, 6.9 Hz, C*H*H–O), 3.52 (3H, s, OCH_3), 3.91 (1H, dd, *J*=8.5, 6.4 Hz, CH*H*–O), 4.10 (1H, m, CH–O), 4.12 (2H, q, *J*=6.4 Hz, CH_2–O), 4.16 (2H, q, *J*=7.0 Hz, CH_2–O), 5.14 (1H, m, CH–O), 7.39–7.43 (3H, m, Ph), 7.57–7.60 (2H, m, Ph); ^{13}C NMR δ 14.29, 14.35, 19.67, 24.43, 25.17, 26.26, 30.18, 33.08, 33.27, 36.37, 41.26, 41.81, 55.36, 60.16, 60.63, 65.93, 74.34, 76.35, 109.69, 127.55, 128.26, 128.38, 129.66, 131.62, 165.90, 173.01, 174.96.

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