One-Pot Synthesis of Trisubstituted Conjugated Dienes via Sequential Suzuki-Miyaura Cross- Coupling with Alkenyl- and Alkyltrifluoroborates

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Supporting Information

General: Melting points were uncorrected. ^1H -, ^{13}C - and ^{19}F -NMR spectra were measured on spectrometers at 500.39 or 360.13, 125.83, and 470.79 MHz, respectively. ^{19}F -NMR chemical shifts were referenced to external CFCl_3 (0.0 ppm). Chemical shifts are given in ppm relative to SiMe_4 (^1H NMR and ^{13}C NMR) or CFCl_3 (^{19}F NMR). ^{11}B NMR spectra at 128.38 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Coupling constants J are given in Hz. High-resolution mass spectra of potassium trifluoroborate derivatives were obtained in the negative ion mode. Toluene was distilled from sodium benzophenone ketyl before use. H_2O used for cross-coupling reactions was distilled under N_2 and degassed using nitrogen. All reactions were carried out under a N_2 atmosphere. Reaction temperatures were bath temperatures. 1,1-Dibromo-2-cyclohexylethene (**1**),¹ 1,1-dibromonon-1-ene (**34**),² and 1,1-dibromo-4-phenylbut-1-ene (**36**)³ were synthesized according to literature procedures. Potassium (*E*)-1-hex-5-enoic acid trifluoroborate, methyl ester (**2**),⁴ potassium (*E*)-5-chloro-1-pent-1-enyl trifluoroborate (**24**),⁴ potassium (*E*)-4-phenyl-1-but-1-enyl trifluoroborate (**27**),⁵ and potassium (*E*)-1-dec-1-enyl trifluoroborate (**30**),⁴ were synthesized according to literature procedures. Potassium 4-benzoyloxybutyl trifluoroborate (**7**),⁶ potassium 5-oxohexyl trifluoroborate (**11**),⁷ potassium 3-phenylthiopropyl trifluoroborate (**13**),⁸ potassium 2-phenylethyl trifluoroborate (**3**),⁷ and potassium methyl trifluoroborate (**15**)⁸ were also synthesized according to literature procedures.

(S)-(+)-1,1-Dibromo-4,8-dimethyl-1,7-nonadiene (38).¹ CBr₄ (11.8 g, 35.6 mmol) was dissolved in CH₂Cl₂ (90 mL) and cooled to 0 °C. PPh₃ (17.7 g, 67.5 mmol) was added and the mixture was stirred for 0.25 h. Et₃N (2.02 g, 20 mmol) was added and the mixture was cooled to –78 °C. (S)-(-)-Citronellal (3.08 g, 20 mmol) dissolved in CH₂Cl₂ (15 mL) was added and the mixture was stirred at –78 °C for 2 h and at rt for 5 h. A saturated aqueous solution of Na₂CO₃ was added and the two phases were separated. The aq phase was extracted twice with CH₂Cl₂ and the organic fractions were combined, washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The crude residue was triturated three times with hexane and distilled to give 5.4 g (87%) of the dibromide (colorless oil, bp 80 °C/3 mm Hg). ¹H NMR (500 MHz, CDCl₃) δ 6.40 (t, *J* = 7.38 Hz, 1H), 5.10-5.07 (m, 1H), 2.13-2.08 (m, 1H), 2.02-1.94 (m, 3H), 1.69 (s, 3H), 1.64-1.54 (m, 1H), 1.61 (s, 3H), 1.38-1.31 (m, 1H), 1.24-1.18 (m, 1H), 0.92 (d, *J* = 7.38 Hz, 3H); ¹³C NMR (125.8 MHz, CDCl₃) δ 137.8, 131.5, 124.4, 88.9, 40.1, 36.6, 32.1, 25.7, 25.5, 19.5, 17.7. HRMS (ESI): *m/z* calcd. for C₁₁H₁₈Br₂ [M]⁺ 307.9775, found 307.9783; IR (neat): 2913, 1620, 1455, 1378, 1118, 828, 780 cm⁻¹; [α]_D²⁰ = +67.1 (c=0.5 CHCl₃).

(S)-(+)-1-(2,2-Dibromoethenyl)-4-isopropenylcyclohex-1-ene (40).¹ CBr₄ (11.8 g, 35.6 mmol) was dissolved in CH₂Cl₂ (90 mL) and cooled to 0 °C. Ph₃P (17.7 g, 67.5 mmol) was added and the mixture was stirred for 0.25 h. Et₃N (2.02 g, 20 mmol) was added and the mixture was cooled to –78 °C. (S)-(-)-Perillaldehyde (3.0 g, 20 mmol) dissolved in CH₂Cl₂ (15 mL) was added and the mixture was stirred at –78 °C for 2 h and at rt for 5 h. A saturated aqueous solution of Na₂CO₃ was added and the two phases were separated.

The aqueous phase was extracted twice with CH₂Cl₂ and the organic fractions were combined, washed with brine, dried (MgSO₄) and concentrated under reduced pressure. The crude residue was triturated three times with hexane and purified by column chromatography (SiO₂, hexane) to give 4.8 g (78%) of the dibromide (colorless oil). ¹H NMR (500 MHz, CDCl₃) δ 6.91 (s, 1H), 5.96 (brs, 1H), 4.73 (d, *J* = 13.5 Hz, 2H), 2.41-2.38 (m, 2H), 2.24-2.16 (m, 2H), 2.02-1.99 (m, 1H), 1.88-1.85 (m, 1H), 1.74 (s, 3H), 1.55-1.43 (m, 1H); ¹³C NMR (125.8 MHz, CDCl₃) δ 149.2, 139.4 (2C), 132.0, 109.0, 85.2, 40.2, 31.2, 27.7, 27.4, 20.8; HRMS (ESI): *m/z* calcd. for C₁₁H₁₄Br₂ [M]⁺ 303.9462, found 307.9476; IR (neat): 2935, 1789, 1720, 1644, 1606, 1434, 1375, 890, 872, 820, 660 cm⁻¹; [α]_D²⁰ = +70.0 (c = 0.5, CHCl₃).

Potassium (*E*)-5-Cyano-1-pent-1-enyl Trifluoroborate (21). To 5-cyanopent-1-yne (2.44 g, 26.2 mmol) in CH₂Cl₂ (12 mL) in a 100-mL flask fitted with a reflux condenser was slowly added a soln of Br₂BH·SMe₂ (26.2 mL, 1 M in CH₂Cl₂, 26.2 mmol). The reaction was exothermic. After the addition, the mixture was stirred for 4 h under N₂. This reaction mixture, cooled to 0 °C and was added to a stirred mixture of H₂O (4.8 mL, 266 mmol) and Et₂O (13 mL) at 0 °C (ice bath) through a double-ended needle. The mixture was stirred for 0.5 h after the addition and the aqueous (lower) layer was separated. The organic layer was washed with cold H₂O (15 mL) twice, and dried (MgSO₄). On evaporation of the solvent under reduced pressure, the boronic acid was obtained in reasonably pure form.⁹ To a soln of the crude boronic acid in Et₂O (27 mL) was added KHF₂ (6.0 g, 76.8 mmol), followed by H₂O (24 mL) over a period of 0.5 h. After stirring at rt for 3 h, the soln was concentrated and the crude compound was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by

dissolving in hot acetone and precipitating with Et₂O, resulting in a white solid (3.3 g, 14.0 mmol, 51%),⁴ mp 168 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.49 (dt, *J* = 17.2, 6.5 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.04-2.00 (m, 2H), 1.60 (dt, *J* = 14.8, 7.0 Hz, 2H); ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 140.7 (brs), 132.7, 121.8, 35.1, 25.8, 16.7; ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -138.0; ¹¹B NMR (128.4 MHz, acetone-*d*₆) δ 2.99 (q, *J* = 50.1 Hz); HRMS (negative ion mode): *m/z* calcd. for C₆H₈BF₃N [M-K]⁻ 162.0702, found 162.0700. IR (KBr): 2942, 2867, 2257, 1643, 1442, 1418, 1269, 1225, 1096, 957 cm⁻¹.

Potassium 4-Trimethylacetoxylbutyl Trifluoroborate (5). To 4-trimethylacetoxylbut-1-ene (6.24 g, 40 mmol) in CH₂Cl₂ (18 mL) in a 100-mL flask fitted with a reflux condenser was slowly added a soln of Br₂BH·SMe₂ (40 mL, 1 M in CH₂Cl₂, 40 mmol). The reaction was exothermic. After the addition, the mixture was stirred for 17 h under N₂. This reaction mixture, cooled to 0 °C, was added to a stirred mixture of H₂O (7.4 mL, 411 mmol) and Et₂O (20.4 mL) at 0 °C (ice bath) through a double-ended needle. The mixture was stirred for 0.5 h after the addition, and the aqueous (lower) layer was separated. The organic layer was washed with cold H₂O (30 mL) twice, and dried (MgSO₄). On evaporation of the solvent under reduced pressure, the boronic acid was obtained in reasonably pure form.⁹ To a soln of the crude boronic acid in Et₂O (67 mL) was added KHF₂ (8.7 g, 111 mmol), followed by H₂O (35 mL) over a period of 0.5 h. After stirring at rt for 3 h, the soln was concentrated and the crude compound was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by

dissolving in hot acetone and precipitating with Et₂O, resulting in a white solid (5.0 g, 18.9 mmol, 47%),⁴ mp 134 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.97 (t, *J* = 6.8 Hz, 2H), 1.51 (dt, *J* = 14.3, 7.0 Hz, 2H), 1.24-1.19 (m, 2H), 1.16 (s, 9H), 0.05 to -0.05 (m, 2H); ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 178.4, 65.5, 39.1, 32.7, 27.8 (3C), 22.7, 20.3 (brs); ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -137.5; ¹¹B NMR (128.4 MHz, acetone-*d*₆) δ 5.56 (q, *J* = 54.6 Hz); HRMS (negative ion mode): *m/z* calcd. for C₉H₁₇BF₃O₂ [M-K]⁻ 225.1274, found 225.1281; IR (KBr): 2931, 1728, 1700, 1480, 1284, 1179, 1063, 946, 878, 756 cm⁻¹.

Potassium 4-Cyanobutyl Trifluoroborate (9). To 4-pentenitrile (143 mg, 1.76 mmol) in CH₂Cl₂ (0.8 mL) in a 25-mL flask fitted with a reflux condenser was slowly added a soln of Br₂BH·SMe₂ (1.76 mL, 1 M in CH₂Cl₂, 1.76 mmol). The reaction was exothermic. After the addition, the mixture was stirred for 17 h under N₂. This reaction mixture, cooled to 0 °C, was added to a stirred mixture of H₂O (0.33 mL, 18.3 mmol) and Et₂O (0.9 mL) at 0 °C (ice bath) through a double-ended needle. The mixture was stirred for 0.5 h after the addition and the aqueous (lower) layer was separated. The organic layer was washed with cold H₂O (10 mL) twice, and dried (MgSO₄). On evaporation of the solvent under reduced pressure, the boronic acid was obtained in reasonably pure form.⁹ To a soln of the crude boronic acid in Et₂O (3.0 mL) was added KHF₂ (383 mg, 4.9 mmol), followed by H₂O (0.5 mL) over a period of 0.5 h. After stirring at rt for 3 h, the soln was concentrated and the crude compound was dissolved in acetone, filtered and concentrated. The resulting white solid was purified by dissolving in hot acetone and precipitating with Et₂O, resulting in an orange solid (200 mg, 1.06 mmol, 60%),⁴ mp 133

°C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 2.40 (t, $J = 7.3$ Hz, 2H), 1.49 (dt, $J = 14.7, 7.2$ Hz, 2H), 1.31-1.25 (m, 2H), 0.05 to -0.05 (m, 2H); ^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) δ 122.1, 29.1, 25.7, 20.3 (brs), 17.1; ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -137.4; ^{11}B NMR (128.4 MHz, $\text{acetone-}d_6$) δ 4.31 (q, $J = 56.7$ Hz). HRMS (negative ion mode): m/z calcd. for $\text{C}_5\text{H}_8\text{BF}_3\text{N} [\text{M-K}]^-$ 150.0702, found 150.0708; IR (KBr): 2933, 2250, 1464, 1285, 1212, 1057, 938, 837, 745, 723 cm^{-1} .

Potassium Ethyl Trifluoroborate (17). To a soln of B(OMe)_3 (4.63 g, 44.6 mmol) in Et_2O (20 mL) was added dropwise EtMgBr (3.0 M in Et_2O , 12 mL, 36 mmol) at -80 °C. The resulting suspension was stirred for 20 min at -80 °C and then allowed to warm to rt for 1 h. The mixture was then cooled to 0 °C and KHF_2 (14 g, 179 mmol) was added followed by H_2O (24 mL) over a period of 0.5 h. After stirring at rt for 3 h, the soln was concentrated, and the crude material was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by dissolving in hot acetone and precipitating with Et_2O to obtain a white solid (2.9 g, 21.3 mmol, 59%),⁴ mp >260 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 0.70 (t, $J = 7.5$ Hz, 3H), 0.00--0.1 (m, 2H); ^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) δ 12.5 (brs), 10.6; ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -139.4 (q, $J = 59.3$ Hz); ^{11}B NMR (128.4 MHz, $\text{acetone-}d_6$) δ 5.90 (q, $J = 64.1$ Hz); Anal. calcd for $\text{C}_2\text{H}_5\text{BF}_3\text{K}$: C, 17.67; H, 3.71. Found: C, 17.74; H, 3.72; IR (KBr): 2956, 1303, 1035, 914, 879, 718 cm^{-1} .

Potassium 4-Pentenyl Trifluoroborate (19). To a soln of B(OMe)₃ (3.98 g, 38.3 mmol) in Et₂O (17 mL) was added dropwise pentenylmagnesium bromide (1.12 M in Et₂O, 30 mL, 33.6 mmol) at -80 °C. The resulting suspension was stirred for 0.5 h at -80 °C and then allowed to warm to rt for 1 h. The mixture was then cooled to 0 °C and KHF₂ (13 g, 166 mmol) was added followed by H₂O (22.3 mL) over a period of 0.5 h. After stirring at rt for 2 h, the soln was concentrated and the crude material was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by dissolving in hot acetone and precipitating with Et₂O to obtain a white solid (3.9 g, 22.1 mmol, 66%),⁴ mp >260 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.86-5.78 (m, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H), 1.96 (dt, *J* = 14.5, 7.2 Hz, 2H), 1.26 (dt, *J* = 12.4, 7.5 Hz, 2H), 0.04-0.00 (m, 2H); ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ 141.1, 113.7, 37.8, 25.7 20.0 (brs); ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -137.4; ¹¹B NMR (128.4 MHz, acetone-*d*₆) δ 5.65 (q, *J* = 50.7 Hz); HRMS (negative ion mode): *m/z* calcd. for C₅H₉BF₃ [M-K]⁻ 137.0749, found 137.0747; IR (KBr): 3077, 2915, 1641, 1440, 1084, 990, 895, 824, 784 cm⁻¹.

Representative Procedure for the Cross-coupling Reaction of Alkenyl Dibromides with Potassium Alkenyltrifluoroborates and Alkytrifluoroborates. (*E,E*)-8-Cyclohexyl-7-(4-trimethylacetoxymethyl)-octa-5,7-dienoic Acid, Methyl Ester (6).

1,1'-Dibromo-2-cyclohexylethene (268 mg, 1.0 mmol) was added slowly to a toluene-H₂O soln (3.0 mL+1.0 mL) of Cs₂CO₃ (977 mg, 3 mmol), **2** (245 mg, 1.05 mmol), and Pd(PPh₃)₄ (80 mg, 0.07 mmol) at 60 °C under N₂. After stirring for 2.0 h, **5** (291 mg, 1.1

mmol) and an aqueous soln of Cs₂CO₃ (3.0 M, 1.0 mL) were added to the reaction mixture. After stirring for 2 h at 80 °C, a mixture of silica gel and Na₂SO₄ (1/1, 13 g) was added to the mother liquor and this mixture was passed through a short column of silica gel (7.0 g, hexane) and eluted with Et₂O (120 mL). Concentration of this eluent followed by column chromatographic purification (SiO₂, hexane/Et₂O, 20/1) afforded the title compound (348 mg, 89%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 5.91 (d, *J* = 15.9 Hz, 1H), 5.49 (dt, *J* = 15.9, 6.6 Hz, 1H), 5.19 (d, *J* = 9.8 Hz, 1H), 4.08 (t, *J* = 6.3 Hz, 2H), 3.66 (s, 3H), 2.31 (t, *J* = 8.0 Hz, 2H), 2.23-2.20 (m, 3H), 2.11 (q, *J* = 7.6 Hz, 2H), 1.74-1.58 (m, 10H), 1.47-1.43 (m, 2H), 1.29-1.26 (m, 2H), 1.19 (s, 9H), 1.18-1.05 (m, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 178.6, 174.0, 137.5, 135.5, 134.7, 125.8, 64.2, 51.4, 38.7, 37.2, 33.5, 33.3 (2C), 32.3, 28.9, 27.2 (3C), 26.7, 26.0, 25.9 (2C), 25.8, 24.8; HRMS (ESI): *m/z* calcd. for C₂₄H₄₀NaO₄ [M+Na]⁺ 415.2824, found 415.2823; IR (neat): 2926, 2851, 1732, 1448, 1284, 1155, 966, 771 cm⁻¹.

(*E,E*)-8-Cyclohexyl-7-(4-benzoyloxybutyl)-octa-5,7-dienoic Acid, Methyl Ester (8).

This product was obtained in 90% as a colorless oil by the general method from the reaction of **7**, **2**, and **1**. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 6.9 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 5.93 (d, *J* = 15.5 Hz, 1H), 5.52 (dt, *J* = 15.5, 7.1 Hz, 1H), 5.21 (d, *J* = 9.7 Hz, 1H), 4.35 (t, *J* = 6.2 Hz, 2H), 3.67 (s, 3H), 2.32-2.26 (m, 5H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.82 (dt, *J* = 14.9, 7.1 Hz, 2H), 1.74-1.44 (m, 8H), 1.28-1.06 (m, 6H); ¹³C NMR (125.8 MHz, CDCl₃) δ 183.0, 176.0, 137.5, 135.5, 134.7, 132.8, 130.5, 129.5, 129.4, 128.3 (2C), 125.8, 64.7, 51.4, 37.2, 33.5, 33.3 (2C), 32.3, 28.9, 26.6,

26.0, 25.9 (2C), 25.8, 24.8; HRMS (ESI): m/z calcd. for $C_{26}H_{36}NaO_4$ $[M+Na]^+$ 435.2511, found 415.2508; IR (neat): 2925, 2850, 1721, 1450, 1274, 1175, 1156, 967, 712 cm^{-1} .

(*E,E*)-8-Cyclohexyl-7-(4-cyanobutyl)-octa-5,7-dienoic Acid, Methyl Ester (10). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **9**, **2**, and **1**. 1H NMR (360 MHz, $CDCl_3$) δ 5.91(d, J = 15.3 Hz, 1H), 5.49 (dt, J = 15.3, 6.7 Hz, 1H), 5.22 (d, J = 9.8 Hz, 1H), 3.66 (s, 3H), 2.34 (dt, J = 14.7, 6.8 Hz, 2H), 2.26-2.09 (m, 8H), 1.75-1.51(m, 9H), 1.31-1.05 (m, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.1, 137.8, 134.7, 134.5, 127.2, 126.0, 119.6, 51.5, 37.2, 33.4, 33.3 (2C), 32.3, 28.3, 26.1, 26.0, 25.9, 25.4, 24.8, 17.1. HRMS (CI): m/z calcd. for $C_{20}H_{31}NO_2$ $[M]^+$ 317.2355, found 317.2342; IR (neat): 2924, 2850, 2246, 1738, 1447, 1158, 967, 802 cm^{-1} .

(*E,E*)-8-Cyclohexyl-7-(5-oxohexyl)-octa-5,7-dienoic Acid, Methyl Ester (12). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **11**, **2**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 5.90 (d, J = 16.0 Hz, 1H), 5.48 (dt, J = 16.0, 6.7 Hz, 1H), 5.18 (d, J = 9.6 Hz, 1H), 3.66 (s, 3H), 2.44 (t, J = 7.3 Hz, 2H), 2.31 (t, J = 7.3 Hz, 2H), 2.20-2.10 (m, 5H), 2.14 (s, 3H), 1.71-1.69 (m, 4H), 1.62-1.57 (m, 4H), 1.42-1.31 (m, 2H), 1.30-1.24 (m, 2H), 1.20-1.14 (m, 2H), 1.09-1.01 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.0, 174.1, 137.4, 135.5, 134.7, 125.8, 51.5, 43.7, 37.1, 33.5, 33.3 (2C), 32.3, 29.8, 29.1, 26.9, 26.0, 25.9 (2C), 24.8, 24.2; HRMS (ESI): m/z calcd. for $C_{21}H_{34}NaO_3$ $[M+Na]^+$ 357.2406, found 357.2391; IR (neat): 2925, 2852, 1739, 1717, 1448, 1360, 1156, 966 cm^{-1} .

(*E,E*)-8-Cyclohexyl-7-(3-phenylthiopropyl)-octa-5,7-dienoic Acid, Methyl Ester

(14). This product was obtained in 90% yield as a colorless oil by the general method from the reaction of **13**, **2**, and **1**. ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.25 (m, 4H), 7.16-7.13 (m, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.58 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.11 (d, *J* = 9.1 Hz, 1H), 3.67 (s, 3H), 2.89 (t, *J* = 7.5 Hz, 2H) 2.39-2.33 (m, 1H), 2.30 (t, *J* = 7.7 Hz, 2H), 2.27 (t, *J* = 7.3 Hz, 2H), 2.14 (dt, *J* = 14.4, 7.4 Hz, 1H), 1.80-1.60 (m, 9H), 1.33-1.28 (m, 3H), 1.26-1.14 (m, 1H), 1.08-1.00 (m, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 174.0, 137.0, 135.8 (3C), 132.8, 128.8, 128.7, 127.0, 125.6 (2C), 51.5, 36.2, 33.5, 33.4 (2C), 33.1, 33.0, 32.7, 28.1, 26.0, 25.9 (2C), 24.8; HRMS (CI): *m/z* calcd. for C₂₄H₃₄SO₂ [M]⁺ 386.2280, found 386.2266; IR (neat): 2922, 2849, 1736, 1584, 1437, 1260, 1091, 1024, 800, 737 cm⁻¹.

(*E,E*)-8-Cyclohexyl-7-(2-phenylethyl)-octa-5,7-dienoic Acid, Methyl Ester (4). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **3**, **2**, and **1**. ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.23 (m, 2H), 7.21-7.16 (m, 3H), 5.96 (d, *J* = 15.7 Hz, 1H), 5.59 (dt, *J* = 15.7, 7.1 Hz, 1H), 5.21 (d, *J* = 9.8 Hz, 1H), 3.68 (s, 3H), 2.70 (dd, *J* = 10.5, 7.4 Hz, 2H), 2.51 (dd, *J* = 8.5, 5.8 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 3H), 2.21-2.05 (m, 4H), 1.79-1.61 (m, 3H), 1.45-1.43 (m, 2H), 1.26-1.15 (m, 3H), 1.01-0.99 (m, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 174.1, 142.4, 138.0, 134.8, 134.5, 128.4 (2C), 128.3 (2C), 125.9, 125.8, 51.5, 37.2, 35.6, 33.5, 33.4, 33.1, 32.3, 30.3, 29.2, 26.0, 25.9, 24.8; HRMS (CI): *m/z* calcd. for C₂₃H₃₂O₂ [M]⁺ 340.2402, found 340.2417; IR (neat): 2924, 2851, 1740, 1603, 1449, 1163, 966, 746, 699 cm⁻¹.

(*E,E*)-8-Cyclohexyl-7-methylocta-5,7-dienoic Acid, Methyl Ester (16). This product was obtained in 84% yield as a colorless oil by the general method from the reaction of MeBF₃K (1.5 equiv), **2**, and **1**. In this case, the second coupling reaction was carried out at 90 °C with addition of PdCl₂(dppf)•CH₂Cl₂. Solid Cs₂CO₃ was used instead of an aqueous soln of Cs₂CO₃ during the second coupling reaction. ¹H NMR (360 MHz, CDCl₃) δ 6.03 (d, *J* = 15.6 Hz, 1H), 5.49 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.21 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 2.32 (t, *J* = 7.3 Hz, 2H), 2.30-2.25 (m, 1H), 2.12 (dt, *J* = 14.0, 7.3 Hz, 2H), 1.77-1.60 (m, 7H), 1.72 (s, 3H), 1.31-1.15 (m, 3H), 1.10-1.03 (m, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 174.2, 137.3, 136.1, 131.5, 126.0, 51.5, 37.1, 33.5, 33.1 (2C), 32.2, 26.1, 26.0 (2C), 24.8, 12.6; HRMS (ESI): *m/z* calcd. for C₁₆H₂₆O₂ [M]⁺ 250.1933, found 250.1936; IR (neat): 2925, 2851, 1741, 1447, 1208, 1153, 964, 894 cm⁻¹.

(*E,E*)-8-Cyclohexyl-7-ethylocta-5,7-dienoic Acid, Methyl Ester (18). This product was obtained in 82% yield as a colorless oil by the general method from the reaction of EtBF₃K (1.5 equiv), **2**, and **1**. In this case, the second coupling reaction was carried out at 90 °C with addition of PdCl₂(dppf)•CH₂Cl₂. Solid Cs₂CO₃ was used instead of the aq soln of Cs₂CO₃ during the second coupling reaction. ¹H NMR (360 MHz, CDCl₃) δ 5.91 (d, *J* = 16.3 Hz, 1H), 5.53 (dt, *J* = 16.3, 6.7 Hz, 1H), 5.15 (d, *J* = 9.5 Hz, 1H), 3.66 (s, 3H), 2.32 (t, *J* = 7.4 Hz, 2H), 2.21 (dt, *J* = 15.3, 7.7 Hz, 3H), 2.12 (dt, *J* = 13.9, 7.0 Hz, 2H), 1.76-1.63 (m, 8H), 1.28-1.25 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125.8 MHz, CDCl₃) δ 174.1, 137.8, 136.6, 134.4, 125.7, 51.5, 37.0, 33.5, 33.4 (2C), 32.3, 29.7, 26.1,

26.0, 24.8, 20.2, 14.4; HRMS (ESI): m/z calcd. for $C_{17}H_{28}O_2$ $[M]^+$ 264.2089, found 264.2091; IR (neat): 2925, 2850, 1741, 1448, 1210, 1153, 965, 895 cm^{-1} .

(*E,E*)-8-Cyclohexyl-7-(4-pentenyl)-octa-5,7-dienoic Acid, Methyl Ester (20). This product was obtained in 83% yield as a colorless oil by the general method from the reaction of **19** (1.5 equiv), **2**, and **1**. In this case, the second coupling reaction was carried out at 90 °C with addition of $PdCl_2(dppf) \cdot CH_2Cl_2$. Solid Cs_2CO_3 was used instead of the aqueous soln of Cs_2CO_3 during the second coupling reaction. 1H NMR (360 MHz, $CDCl_3$) δ 5.91 (d, J = 15.3 Hz, 1H), 5.87-5.78 (m, 1H), 5.50 (dt, J = 15.3, 6.8 Hz, 1H), 5.18 (d, J = 9.4 Hz, 1H), 5.06-4.97 (m, 2H), 3.66 (s, 3H), 2.31 (t, J = 7.4 Hz, 2H), 2.21-2.05 (m, 7H), 1.77-1.57 (m, 6H), 1.49-1.43 (m, 2H), 1.31-1.03 (m, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.1, 138.8, 137.3, 135.8, 134.7, 125.8, 114.6, 51.4, 37.1, 33.9, 33.5, 33.3 (2C), 32.3, 28.7, 26.5, 26.0, 25.9 (2C), 24.8; HRMS (CI): m/z calcd. for $C_{20}H_{32}O_2$ $[M]^+$ 304.2402, found 304.2410; IR (neat): 2925, 2851, 1741, 1448, 1208, 1169, 966, 910 cm^{-1} .

(*E,E*)-7-Cyano-1-cyclohexyl-2-(4-trimethylacetoxymethyl)-hepta-1,3-diene (22). This product was obtained in 91% yield as a colorless oil by the general method from the reaction of **5**, **21**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 6.00 (d, J = 15.8 Hz, 1H), 5.47 (dt, J = 15.8, 6.9 Hz, 1H), 5.26 (d, J = 9.9 Hz, 1H), 4.11 (t, J = 6.2 Hz, 2H), 2.37 (t, J = 7.1 Hz, 2H), 2.29-2.24 (m, 5H), 1.82-1.61 (m, 8H), 1.58-1.45 (m, 2H), 1.35-1.24 (m, 4H), 1.23 (s, 9H), 1.21-1.07 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 178.5, 138.3, 136.0,

135.2, 123.8, 119.6, 64.1, 37.2, 33.3 (2C), 31.6, 29.0, 27.2 (3C), 26.7, 26.0, 25.9 (2C), 25.8 (2C), 25.3, 16.5; HRMS (ESI): m/z calcd. for $C_{23}H_{37}NaNO_2$ $[M+Na]^+$ 382.2722, found 382.2712; IR (neat): 2926, 2851, 2246, 1727, 1480, 1449, 1285, 1157, 968, 896 cm^{-1} .

(*E,E*)-7-Cyano-1-cyclohexyl-2-(5-oxohexyl)-hepta-1,3-diene (23). This product was obtained in 87% yield as a colorless oil by the general method from the reaction of **11**, **21**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 5.95 (d, J = 15.7 Hz, 1H), 5.44 (dt, J = 15.7, 7.0 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H), 2.44 (t, J = 7.3 Hz, 2H), 2.33 (t, J = 7.3 Hz, 2H), 2.27-2.15 (m, 4H), 2.13 (s, 3H), 1.79-1.56 (m, 8H), 1.40-1.15 (m, 7H), 1.10-1.03 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 208.8, 138.2, 136.0, 135.3, 123.9, 119.7, 43.6, 37.2, 33.3 (2C), 31.6, 29.8, 29.0, 26.9, 26.0, 25.9 (2C), 25.3, 24.1, 16.4; HRMS (ESI): m/z calcd. for $C_{20}H_{31}NaNO$ $[M+Na]^+$ 324.2303, found 324.2298; IR (neat): 2925, 2851, 2246, 1715, 1448, 1358, 1163, 968, 896 cm^{-1} .

(*E,E*)-7-Chloro-1-cyclohexyl-2-(4-trimethylacetoxymethyl)-hepta-1,3-diene (25). This product was obtained in 91% yield as a colorless oil by the general method from the reaction of **5**, **24**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 5.95 (d, J = 15.7 Hz, 1H), 5.49 (dt, J = 15.7, 6.7 Hz, 1H), 5.21 (d, J = 9.8 Hz, 1H), 4.08 (t, J = 6.3 Hz, 2H), 3.53 (t, J = 6.9 Hz, 2H), 2.26-2.16 (m, 5H), 1.86 (dt, J = 14.2, 6.4 Hz, 2H), 1.74-1.55 (m, 8H), 1.49-1.41 (m, 2H), 1.33-1.21 (m, 2H), 1.19 (s, 9H), 1.15-1.01 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 178.6, 137.7, 135.4, 135.1, 124.9, 64.1, 44.4, 38.8, 37.2, 33.3 (2C), 32.4, 30.0,

29.0, 27.2 (3C), 26.7, 26.0, 25.9 (2C), 25.8; HRMS (ESI): m/z calcd. for $C_{22}H_{37}ClO_2$ $[M]^+$ 368.2482, found 386.2476; IR (neat): 2926, 2851, 1729, 1480, 1448, 1284, 1155, 966 cm^{-1} .

(*E,E*)-7-Chloro-1-cyclohexyl-2-(5-oxohexyl)-hepta-1,3-diene (26). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **11**, **24**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 5.94 (d, J = 15.9 Hz, 1H), 5.48 (dt, J = 15.9, 7.0 Hz, 1H), 5.20 (d, J = 9.4 Hz, 1H), 3.54 (t, J = 6.6 Hz, 2H), 2.44 (t, J = 7.4 Hz, 2H), 2.26-2.16 (m, 5H), 2.14 (s, 3H), 1.87 (dt, J = 14.5, 6.4 Hz, 2H), 1.73-1.56 (m, 7H), 1.43-1.25 (m, 4H), 1.21-1.16 (m, 1H), 1.10-1.03 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 208.9, 137.6, 135.5, 135.1, 125.0, 44.5, 43.7, 37.2, 33.3 (2C), 32.4, 30.0 (2C), 29.1, 27.0, 26.0, 25.9 (2C), 24.1; HRMS (CI): m/z calcd. for $C_{19}H_{31}ClO$ $[M]^+$ 310.2063, found 310.2055; IR (neat): 2925, 2851, 1716, 1448, 1358, 1261, 1162, 966, 896 cm^{-1} .

(*E,E*)-1-Cyclohexyl-6-phenyl-2-(4-trimethylacetoxymethyl)-hexa-1,3-diene (28). This product was obtained in 90% yield as a colorless oil by the general method from the reaction of **5**, **21**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.20-7.17 (m, 3H), 5.95 (d, J = 15.9 Hz, 1H), 5.58 (dt, J = 15.9, 6.8 Hz, 1H), 5.20 (d, J = 9.8 Hz, 1H), 4.07 (t, J = 6.6 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 2.39 (dt, J = 15.3, 7.3 Hz, 2H), 2.22 (t, J = 7.7 Hz, 3H), 1.72-1.56 (m, 6H), 1.48-1.43 (m, 2H), 1.32-1.15 (m, 4H), 1.20 (s, 9H), 1.10-1.05 (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 178.6, 142.0, 137.4, 135.6, 134.1, 128.4 (2C), 128.3 (2C), 126.4, 125.8, 64.2, 37.2, 36.2 (2C), 34.9, 33.3 (2C), 28.9, 27.2

(3C), 26.7, 26.0, 25.9 (2C), 25.8; HRMS (ESI): m/z calcd. for $C_{27}H_{40}NaO_2$ $[M+Na]^+$ 419.2926, found 419.2933; IR (neat): 3026, 2926, 2851, 1729, 1604, 1496, 1480, 1450, 1284, 1155, 966, 699 cm^{-1} .

(*E,E*)-1-Cyclohexyl-6-phenyl-2-(5-oxohexyl)-hexa-1,3-diene (29). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **11**, **21**, and **1**. 1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.20-7.18 (m, 3H), 5.95 (d, J = 15.7 Hz, 1H), 5.58 (dt, J = 15.7, 6.7 Hz, 1H), 5.19 (d, J = 9.5 Hz, 1H), 2.71 (t, J = 7.7 Hz, 2H), 2.44-2.38 (m, 4H), 2.23-3.18 (m, 3H), 2.14 (s, 3H), 1.74-1.55 (m, 6H), 1.41-1.22 (m, 5H), 1.19-1.03 (m, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.0, 142.0, 137.3, 135.7, 134.1, 128.4 (2C), 128.3 (2C), 126.4, 125.7, 43.7, 37.2, 36.2, 34.9, 33.3 (2C), 29.8, 29.0, 26.9, 26.0, 25.9 (2C), 24.2; HRMS (CI): m/z calcd. for $C_{24}H_{34}O$ $[M]^+$ 338.2610, found 338.2618; IR (neat): 3026, 2925, 2851, 1717, 1604, 1496, 1448, 1357, 1161, 966, 699 cm^{-1} .

(*E,E*)-1-Cyclohexyl-2-(4-trimethylacetoxymethyl)-dodeca-1,3-diene (31). This product was obtained in 87% yield as a colorless oil by the general method from the reaction of **5**, **30**, and **1**. In this case, the first coupling reaction was carried out at 80 °C. 1H NMR (500 MHz, $CDCl_3$) δ 5.90 (d, J = 15.8 Hz, 1H), 5.54 (dt, J = 15.9, 6.9 Hz, 1H), 5.18 (d, J = 9.7 Hz, 1H), 4.08 (t, J = 6.3 Hz, 2H), 2.24-2.20 (m, 3H), 2.08-2.04 (m, 2H), 1.72-1.58 (m, 8H), 1.49-1.45 (m, 2H), 1.38-1.20 (m, 14H), 1.19 (s, 9H), 1.19-1.02 (m, 2H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 179.2, 136.8, 135.8, 133.5, 127.6, 64.2,

37.1, 33.4 (2C), 33.0, 31.9, 29.7 (2C), 29.5, 29.3, 29.2, 29.0, 27.2 (3C), 26.8, 26.0, 25.9 (2C), 25.8, 22.7, 14.1; HRMS (ESI): m/z calcd. for $C_{27}H_{48}NaO_2$ $[M+Na]^+$ 427.3552, found 427.3540; IR (neat): 2925, 2853, 1731, 1604, 1480, 1450, 1284, 1154, 965 cm^{-1} .

(*E,E*)-1-Cyclohexyl-2-(5-oxohexyl)-dodeca-1,3-diene (32). This product was obtained in 89% yield as a colorless oil by the general method from the reaction of **11**, **30**, and **1**. In this case, the first coupling reaction was carried out at 80 °C. 1H NMR (500 MHz, $CDCl_3$) δ 5.89 (d, J = 15.9 Hz, 1H), 5.53 (dt, J = 15.9, 7.2 Hz, 1H), 5.16 (d, J = 9.5 Hz, 1H), 2.43 (t, J = 7.8 Hz, 2H), 2.22-2.16 (m, 3H), 2.13 (s, 3H), 2.06 (dt, J = 14.3, 7.6 Hz, 2H), 1.72-1.58 (m, 6H), 1.42-1.09 (m, 18H), 1.07-1.04 (m, 2H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.0, 136.7, 135.8, 133.5, 127.6, 43.7, 37.2, 33.4 (2C), 33.0, 31.9, 29.8, 29.7, 29.5, 29.3, 29.2, 29.1, 27.0, 26.1, 26.0 (2C), 24.2, 22.7, 14.1; HRMS (CI): m/z calcd. for $C_{24}H_{42}O$ $[M]^+$ 346.3236, found 346.3223; IR (neat): 2924, 2853, 1720, 1448, 1357, 1161, 964 cm^{-1} .

(*E,E*)-1-Cyclohexyl-2-(2-phenylethyl)-dodeca-1,3-diene (33). This product was obtained in 85% yield as a colorless oil by the general method from the reaction of **3** (1.1 equiv), **30**, and **1**. In this case, the first coupling reaction was carried out at 80 °C. 1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 5.94 (d, J = 15.7 Hz, 1H), 5.65 (dt, J = 15.7, 7.2 Hz, 1H), 5.18 (d, J = 9.5 Hz, 1H), 2.70 (dt, J = 10.3, 7.4 Hz, 2H), 2.51 (dt, J = 8.6, 5.8 Hz, 2H), 2.12-2.08 (m, 3H), 1.77-1.60 (m, 5H), 1.43-1.11 (m, 15H), 1.03-0.95 (m, 2H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 142.5, 137.3, 135.1, 133.3, 128.4 (2C), 128.3 (2C), 127.7, 125.8, 37.2, 35.6, 33.2, 33.0,

31.9, 29.7, 29.5, 29.3 (2C), 29.2, 26.0 (2C), 25.9 (2C), 22.7, 14.1; HRMS (ESI): m/z calcd. for $C_{26}H_{40} [M]^+$ 352.3130, found 352.3118; IR (neat): 3025, 2924, 2852, 1604, 1495, 1449, 964, 896, 744, 698 cm^{-1} .

(*E,E*)-7-(4-Trimethylacetoxymethyl)-pentadeca-5,7-dienoic Acid, Methyl Ester (35).

This product was obtained in 85% yield (*E,E/E,Z* = 92/8) as a colorless oil by the general method from the reaction of **5**, **2**, and **34**. 1H NMR (500 MHz, $CDCl_3$) δ 5.94 (d, J = 15.2 Hz, 1H), 5.49 (dt, J = 15.2, 7.2 Hz, 1H), 5.36 (t, J = 7.4 Hz, 1H), 4.07 (t, J = 6.8 Hz, 2H), 3.66 (s, 3H), 2.31 (t, J = 7.2 Hz, 2H), 2.21 (t, J = 7.6 Hz, 2H), 2.11 (q, J = 7.1 Hz, 2H), 2.07 (q, J = 7.4 Hz, 2H), 1.73 (dt, J = 15.0, 7.4 Hz, 2H), 1.64 (dt, J = 22.1, 7.1 Hz, 2H), 1.48-1.41 (m, 2H), 1.36-1.22 (m, 10H), 1.19 (s, 9H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 178.6, 174.1, 137.4, 134.5, 131.6, 125.5, 64.2, 51.5, 38.7, 33.5, 32.3, 31.8, 29.8, 29.4, 29.2, 28.9, 28.1, 27.2 (3C), 26.5, 25.3, 24.8, 22.7, 14.1; HRMS (CI): m/z calcd. for $C_{25}H_{44}NaO_4 [M+Na]^+$ 431.3137, found 431.3155; IR (neat): 2926, 2856, 1731, 1480, 1461, 1284, 1154, 966 cm^{-1} .

(*E,E*)-10-Phenyl-7-(4-trimethylacetoxymethyl)-deca-5,7-dienoic Acid, Methyl Ester

(37). This product was obtained in 87% yield (*E,E/E,Z* = 94/6) as a colorless oil by the general method from the reaction of **5**, **2**, and **36**. 1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.20-7.18 (m, 3H), 5.94 (d, J = 15.7 Hz, 1H), 5.50 (dt, J = 15.7, 6.9 Hz, 1H), 5.40 (t, J = 7.2 Hz, 1H), 4.04 (t, J = 6.4 Hz, 2H), 3.66 (s, 3H), 2.68 (t, J = 7.4 Hz, 2H), 2.41 (dt, J = 15.3, 7.8 Hz, 2H), 2.31 (t, J = 7.3 Hz, 2H), 2.19 (t, J = 7.6 Hz, 2H),

2.11 (dt, $J = 14.1$, 6.8 Hz, 2H), 1.73 (dt, $J = 14.9$, 7.4 Hz, 2H), 1.61 (dt, $J = 14.9$, 6.6 Hz, 2H), 1.43-1.36 (m, 2H), 1.18 (s, 9H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 178.6, 174.0, 141.9, 138.0, 134.3, 130.1, 128.4, 128.3 (2C), 128.2, 126.1, 125.9, 64.1, 51.5, 36.0, 33.4 (2C), 32.2, 30.2, 28.8, 27.2 (3C), 26.5, 25.2, 24.8; HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{38}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 437.2668, found 437.2667; IR (neat): 3025, 2930, 2869, 1728, 1480, 1453, 1284, 1155, 966, 699 cm^{-1} .

(*S*)-(+)-(*E,E*)-10,14-Dimethyl-7-(4-trimethylacetoxymethyl)-pentadeca-5,7,13-trienoic Acid, Methyl Ester (39). This product was obtained in 86% yield ($E,E/E,Z = 92/8$) as a colorless oil by the general method from the reaction of **5**, **2**, and **38**. ^1H NMR (500 MHz, CDCl_3) δ 5.96 (d, $J = 15.9$ Hz, 1H), 5.49 (dt, $J = 15.9$, 6.8 Hz, 1H), 5.37 (t, $J = 7.4$ Hz, 1H), 5.11-5.08 (m, 1H), 4.07 (t, $J = 6.9$ Hz, 2H), 3.67 (s, 3H), 2.32 (t, $J = 7.4$ Hz, 2H), 2.21 (t, $J = 7.9$ Hz, 2H), 2.12-1.89 (m, 6H), 1.75 (dt, $J = 14.6$, 7.4 Hz, 2H), 1.68 (s, 3H), 1.67-1.62 (m, 2H), 1.60 (s, 3H), 1.53-1.30 (m, 4H), 1.19 (s, 9H), 1.19-1.10 (m, 1H), 0.88 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 178.6, 174.1, 138.1, 134.6, 131.1, 130.2, 125.5, 124.8, 64.1, 51.4, 36.9, 35.4, 33.5, 33.3, 32.3 (2C), 28.9, 27.2 (3C), 26.6, 25.7 (2C), 25.2, 24.8, 19.6, 17.6; HRMS (ESI): m/z calcd. for $\text{C}_{27}\text{H}_{46}\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 457.3294, found 457.3273; IR (neat): 2955, 2927, 2870, 1731, 1480, 1460, 1376, 1284, 1155, 966 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = +136.4$ ($c=0.5$ CHCl_3).

(*S*)-(+)-(*E,E*)-8-(4-isopropenylcyclohex-1-enyl)-7-(4-trimethylacetoxymethyl)-octa-5,7-dienoic Acid, Methyl Ester (41). This product was obtained in 90% yield as a colorless oil by the general method from the reaction of **5**, **2**, and **40**. ^1H NMR (500 MHz,

CDCl₃) δ 5.96 (d, J = 15.6 Hz, 1H), 5.75 (s, 1H), 5.64 (brs, 1H), 5.58 (dt, J = 15.6, 7.0 Hz, 1H), 4.73 (d, J = 6.1 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 3.67 (s, 3H), 2.38 (dd, J = 8.5, 6.7 Hz, 2H), 2.32 (t, J = 7.9 Hz, 2H), 2.20-2.14 (m, 6H), 2.10-2.02 (m, 1H), 1.88-1.81 (m, 1H), 1.76-1.71 (m, 5H), 1.66 (dt, J = 15.0, 7.0 Hz, 2H), 1.55-1.48 (m, 3H), 1.19 (s, 9H); ¹³C NMR (125.8 MHz, CDCl₃) δ 178.5, 174.0, 149.7, 137.2, 135.4, 135.0, 132.4, 127.1, 126.5, 108.6, 64.1, 51.4, 40.7, 38.7, 33.4, 32.3, 31.3, 29.5, 29.0, 27.8, 27.4, 27.2 (3C), 26.2, 24.8, 20.8; HRMS (ESI): m/z calcd. for C₂₇H₄₂NaO₄ [M+Na]⁺ 453.2981, found 453.2962; IR (neat): 2928, 1730, 1643, 1480, 1435, 1284, 1155, 966, 887 cm⁻¹; $[\alpha]_D^{20}$ = 253.9 (c=0.5 CHCl₃).

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