

(1R,4R,4aR,5R,6R,12R,12aS)-1-[(*tert*-Butyldiphenylsiloxy)methyl]-1,2,3,4,4a,5,6,7,8,11,12,12a-dodecahydro-4-isopropyl-6,10-dimethyl-5,12-epoxybenzocyclodecen-6-ol (20): colorless oil; IR (neat, cm^{-1}) 3518, 1452, 1427, 1374; ^1H NMR (300 MHz, CDCl_3) δ 7.69-7.33 (m, 10H), 5.66 (m, 1H), 4.09 (m, 1H), 3.80 (d, $J = 2.8$ Hz, 1H), 3.63 (dd, $J = 8.5, 10.0$ Hz, 1H), 3.51 (dd, $J = 5.4, 10.2$ Hz, 1H), 3.02 (br s, 1H), 2.84 (br d, $J = 14.0$ Hz, 1H), 1.97 (m, 2H), 1.91-1.69 (m, 9H), 1.40-1.21 (m, 6H), 1.25 (s, 3), 1.05 (s, 9H), 0.92 (d, $J = 6.8$ Hz, 3H), 0.72 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.7, 135.6, 135.6, 135.5, 133.6, 129.7, 129.6, 128.2, 128.1, 127.9, 127.7, 127.6, 127.6, 125.5, 90.2, 80.5, 75.2, 66.2, 41.6, 40.2, 38.4, 36.0, 30.3, 29.7, 29.6, 29.4, 29.0, 28.9, 28.7, 26.9, 22.3, 21.8, 19.2, 18.9, 16.7, 14.1; FAB MS m/z ($\text{M}^+ + \text{H}$) calcd for $\text{C}_{36}\text{H}_{53}\text{O}_3\text{Si}$ 561.38, obsd 561.28; $[\alpha]_{\text{D}}^{20} +42.6$ (c 0.32, CHCl_3).

(1R,4R,4aR,5R,6R,10R,12R,12aS)-1-[(*tert*-Butyldiphenylsiloxy)methyl]tetradecahydro-4-isopropyl-6,10-dimethyl-5,12:6,10-diepoxycyclodecen-9-ol (21): IR (film, cm^{-1}) 3450, 1462, 1428, 1112; ^1H NMR (300 MHz, CDCl_3) δ 7.70-7.26 (series of m, 10H), 3.99-3.95 (m, 1H), 3.63 (s, 1H), 3.54 (d, $J = 6.4$ Hz, 2H), 3.40-3.20 (m, 1H), 2.75-2.40 (m, 2H), 2.25-1.80 (m, 3H), 1.85-1.60 (m, 4H), 1.55-1.15 (series of m, 7H), 1.43 (s, 3H), 1.22 (s, 3H), 1.06 (s, 9H), 0.90 (m, 3H), 0.71 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.8, 135.6, 135.6, 135.5, 133.8, 133.7, 129.7, 129.6, 127.9, 127.8, 127.6, 125.5, 93.0, 82.9, 77.2, 76.8, 71.8, 67.3, 45.2, 44.3, 40.4, 38.5, 32.2, 30.3, 29.7, 27.8, 27.2, 27.0, 24.7, 23.0, 22.5, 21.6, 19.2, 17.9, 17.3, 15.4; FAB MS m/z ($\text{M}^+ + \text{H}$) calcd for $\text{C}_{36}\text{H}_{53}\text{O}_4\text{Si}$ 577.37, obsd 577.35; $[\alpha]_{\text{D}}^{20} +7.8$ (c 0.36, CHCl_3).

(1R,4R,4aR,5R,6R,9R,12R,12aS)-1-[(*tert*-Butyldiphenylsiloxy)methyl]tetradecahydro-4-isopropyl-6,10-dimethyl-5,12:6,10-diepoxycyclodecen-9-ol Acetate (22a) and (1R,4R,4aR,5R,6R,10R,12R,12aS)-1-[(*tert*-Butyldiphenylsiloxy)methyl]tetradecahydro-4-isopropyl-6,10-dimethyl-5,12:6,10-diepoxycyclodecen-9-ol Acetate (22b).

For **22a**: IR (film, cm^{-1}) 1737, 1462, 1428, 1244, 1104; ^1H NMR (300 MHz, CDCl_3) δ 7.70-7.26 (series of m, 10H), 4.60 (br s, 1H), 3.97 (t, $J = 4.9$ Hz, 1H), 3.65 (s, 1H), 3.54 (d, $J = 6.6$ Hz, 1H), 2.88-2.66 (m, 1H), 2.50 (q, $J = 4.5$ Hz, 1H), 2.27-2.02 (m, 2H), 2.08 (s, 3H), 1.85-1.60 (m, 6H), 1.57-1.40 (m, 3H), 1.39-1.15 (m, 3H), 1.26 (s, 3H), 1.13 (s, 3H), 1.06 (s, 9H), 0.90 (d, $J = 6.9$ Hz, 3H), 0.70 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 135.7, 135.6, 135.5, 129.6, 127.6, 93.1, 82.7, 75.7, 75.2, 73.7, 67.4, 45.5, 44.9, 44.5, 40.8, 40.7, 38.5, 30.1, 29.7, 29.2, 27.4, 27.0, 26.8, 22.6, 21.6, 21.3, 21.2, 19.3, 17.5, 15.6; FAB MS m/z (M^++H) calcd for $\text{C}_{38}\text{H}_{55}\text{O}_5\text{Si}$ 619.38, obsd 619.37; $[\alpha]_{\text{D}}^{20} +11.8$ (c 0.51, CHCl_3).

For **22b**: IR (film, cm^{-1}) 1739, 1463, 1428, 1370, 1238; ^1H NMR (300 MHz, CDCl_3) δ 7.68-7.35 (m, 10H), 4.54 (dd, $J = 3.9, 11.9$ Hz, 1H), 3.95 (t, $J = 5.0$ Hz, 1H), 3.64 (s, 1H), 3.60-3.53 (m, 2H), 2.53-2.46 (m, 2H), 2.43-2.27 (m, 1H), 2.10-2.06 (m, 1H), 2.04 (s, 3H), 1.75-1.45 (series of m, 8H), 1.41-1.20 (m, 3H), 1.26 (s, 3H), 1.17 (s, 3H), 1.07 (s, 9H), 0.88 (d, $J = 6.8$ Hz, 3H), 0.68 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.4, 135.7, 135.6, 134.2, 134.1, 129.6, 129.5, 127.6, 92.9, 82.3, 77.2, 76.8, 76.0, 67.2, 44.7, 41.1, 40.9, 40.7, 38.4, 36.3, 32.3, 29.7, 29.2, 27.2, 27.0, 24.4, 22.5, 21.6, 21.4, 19.3, 17.3, 15.5; FAB MS m/z (M^++H) calcd for $\text{C}_{38}\text{H}_{55}\text{O}_5\text{Si}$ 619.38, obsd 619.34; $[\alpha]_{\text{D}}^{20} +6.3$ (c 0.23, CHCl_3).

(4*R*,4*aR*,5*R*,6*R*,9*S*,10*R*,12*R*,12*aR*)-Tetradecahydro-4-isopropyl-6,10-dimethyl-1-methylene-5,12:6,10-diepoxybenzocyclodecen-9-ol (2).

For the primary carbinol: IR (film, cm^{-1}) 3440, 1735, 1448, 1371, 1073; ^1H NMR (300 MHz, CDCl_3) δ 4.63 (d $J = 3.6$ Hz, 1H), 4.03 (dd, $J = 5.0, 4.0$ Hz, 2H), 3.69 (s, 1H), 3.62-3.50 (m, 2H), 2.79-2.66 (m, 1H), 2.58 (q, $J = 4.6$ Hz, 1H), 2.35-2.00 (m, 2H), 2.09 (s, 3H), 1.87 (dd, $J = 1.0, 14.7$ Hz, 1H), 1.82-1.57 (m, 4H), 1.55-1.41 (m, 2H), 1.43 (s, 3H), 1.35-1.18 (m, 2H), 1.21 (s, 3H), 1.11 (s, 3H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.78 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.8, 92.9, 82.7, 75.9, 75.2, 73.6, 66.4, 45.4, 44.2,

40.7, 40.6, 38.6, 30.2, 30.0, 29.2, 27.4, 22.6, 22.5, 21.6, 21.2, 17.5, 15.6; HRMS (EI) m/z (M^+) calcd for $C_{22}H_{36}O_5$ 380.2563, obsd 380.2551; $[\alpha]_D^{20} +26.7$ (c 0.22, $CHCl_3$).

For **23**: IR (film, cm^{-1}) 3355, 1449, 1108, 1073; 1H NMR (600 MHz, $CDCl_3$) δ 4.66 (br d, $J = 2.8$ Hz, 1H), 4.65 (br d, $J = 2.8$ Hz, 1H), 3.95 (ddd, $J = 5.1, 5.1, 1.4$ Hz, 1H), 3.63 (s, 1H), 3.48 (dd, $J = 6.8, 6.8$ Hz, 1H), 3.29 (dd, $J = 2.5, 3.4$ Hz, 1H), 2.71 (dddd, $J = 3.2, 5.7, 13.6, 13.6$ Hz, 1H), 2.27 (d, $J = 8.0, 11.0$ Hz, 1H), 2.25 (ddd, $J = 2.9, 2.9, 13.7$ Hz, 1H), 2.05 (dd, $J = 4.7, 14.6$ Hz, 1H), 1.97 (br dd, $J = 13.4, 13.4$ Hz, 1H), 1.93 (dd, $J = 14.6, 1.3$ Hz, 1H), 1.79 (ddd, $J = 5.6, 14.5, 14.5$ Hz, 1H), 1.70 (m, 2H), 1.68 (m, 1H), 1.66 (dq, $J = 1.9, 7.0, 7.0$ Hz, 1H), 1.35 (s, 3H), 1.23 (br dd, $J = 9.0, 9.0$ Hz, 1H), 1.12 (s, 3H), 0.97 (dddd, $J = 12.9, 12.9, 12.9, 2.8$ Hz, 1H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.78 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3, 108.7, 93.9, 82.2, 76.8, 76.0, 71.8, 49.6, 44.9, 44.3, 43.8, 31.3, 30.9, 29.5, 29.1, 27.6, 24.6, 24.5, 21.9, 15.8; HRMS (EI) m/z (M^+) calcd for $C_{20}H_{32}O_3$ 320.2351, obsd 320.2353; $[\alpha]_D^{20} -5.3$ (c 0.26, $CHCl_3$).

(4R,4aR,5R,6R,10R,12R,12aR)-Dodecahydro-4-isopropyl-6,10-dimethyl-1-methylene-5,12:6,10-diepoxybenzocyclodecen-9(1H)-one (24). IR (film, cm^{-1}) 1730, 1709, 1447, 1365, 1093; 1H NMR (300 MHz, $CDCl_3$) δ 4.70 (s, 1H), 4.68 (d, $J = 1.8$ Hz, 1H), 3.94 (dd, $J = 6.6, 6.6$ Hz, 1H), 3.86 (s, 1H), 3.25 (dd, $J = 6.8, 6.8$ Hz, 1H), 2.91 (dd, $J = 13.9, 7.0$ Hz, 1H), 2.63-2.57 (m, 2H), 2.32-2.17 (m, 3H), 2.13-1.94 (m, 2H), 1.78 (d, $J = 14.0$ Hz, 1H), 1.73-1.66 (m, 2H), 1.30 (s, 3H), 1.27-1.22 (m, 1H), 1.20 (s, 3H), 1.17-0.98 (m, 1H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.79 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.6, 147.6, 109.2, 91.8, 83.0, 79.3, 74.3, 52.7, 47.0, 44.7, 42.4, 35.1, 32.1, 31.0, 29.2, 28.1, 25.4, 24.6, 21.8, 16.0; HRMS (EI) m/z (M^+) calcd for $C_{20}H_{30}O_3$ 318.2195, obsd 318.2219; $[\alpha]_D^{20} -59.3$ (c 0.14, $CHCl_3$).

(4R,4aR,5R,6R,9R,10R,12R,12aR)-Tetradeca-hydro-4-isopropyl-6,10-dimethyl-1-methylene-5,12:6,10-diepoxybenzocyclodecen-9-ol (23). IR (film, cm^{-1}) 3424, 1448, 1370, 1329, 1085, 1065; 1H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 1H), 4.66 (s, 1H), 3.94 (dd, $J = 5.2, 5.2$ Hz, 1H), 3.65 (s, 1H), 3.44 (dd, $J = 6.8, 6.8$ Hz, 1H), 3.37 (dd, J

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= 10.8, 3.6 Hz, 1H), 2.54 (dd, $J = 14.8, 5.3$ Hz, 1H), 2.32-2.18 (m, 3H), 2.03-1.85 (m, 2H), 1.74-1.54 (m, 4H), 1.37 (s, 3H), 1.36-1.24 (m, 2H), 1.07 (s, 3H), 1.05-0.80 (m, 2H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.76 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.1, 108.7, 93.7, 81.4, 77.7, 75.6, 74.7, 50.9, 45.1, 43.6, 39.4, 35.6, 32.5, 31.3, 29.5, 27.1, 27.0, 24.6, 21.9, 15.8; HRMS (EI) m/z (M^+) calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3$ 320.2351, obsd 320.2373; $[\alpha]_{\text{D}}^{20}$ -14.7 (c 0.095, CHCl_3).