Unusual Effects in the Pd-Catalyzed Asymmetric Allylic Alkylation (AAA) Synthesis of Chiral Chromans

Barry M. Trost, Hong C. Shen, Li Dong and Jean-Philippe Surivet

Department of Chemistry, Stanford University, Stanford, CA 94305-5080

Supporting Information

Experimental Section

General procedure:

To a degassed mixture of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2 mol%) and (*R,R*) chiral ligand **3a** (6 mol%) was added dichloromethane. The solution was stirred for 10 min under argon to yield a yellow solution. To this solution was added acetic acid (1-1.2 eq.). After 5 min., a solution of carbonate in dichloromethane was added. The reaction mixture was stirred at rt for 1-10h. The volatiles were removed under reduced pressure and the residue was purified directly over silica gel eluting with 1:11 of diethyl ether in petroleum ether to afford the chiral chroman.

2b

5b

(*R*)-5-Methoxy-2,7-dimethyl-2-vinylchroman (**2b**): a colorless oil. $[\alpha]_D^{25} = +47.2^\circ$ (c 2.35, CHCl_3 , 84% ee); IR (neat): 2936, 1618, 1586, 1139 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 6.40 (s, 1H), 6.25 (s, 1H), 5.85 (dd, $J=10.7, 17.3$ Hz, 1H), 5.20 (dd, $J=1.2, 17.3$ Hz, 1H), 5.07 (dd, $J=1.2, 10.7$ Hz, 1H), 3.81 (s, 3H), 2.68 (td, $J=5.6, 16.8$ Hz, 1H), 2.47 (ddd, $J=6.1, 9.8, 16.8$ Hz, 1H), 2.31 (s, 3H), 1.93 (ddd, $J=4.8, 5.8, 13.4$ Hz, 1H), 1.79 (ddd, $J=5.6, 9.8, 13.4$ Hz, 1H), 1.43 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 157.4, 154.3, 141.3, 136.9, 113.6, 110.0, 107.2, 102.6, 76.1, 55.2, 31.0, 26.7, 21.6, 16.7; HRMS m/z Calc'd for $\text{C}_{14}\text{H}_{18}\text{O}_2$ [M^+]: 218.1307; Found: 218.1303; Chromatographic separation (GC, Cyclosil B): T oven = 160°C , t_R (*S*, minor) = 18.5 min, t_R (*R*, major) = 18.9 min.

(*S*)-5-Methoxy-2,7-dimethyl-2-vinylchroman (**5b**): $[\alpha]_D^{25} = -54.0^\circ$ (*c* 2.18, CHCl₃, 97% ee)
 Chromatographic separation (GC, Cyclosil B): T oven=160°C, *t_R* (*S*, major)=18.5 min, *t_R* (*R*, minor)=18.9 min.

(*R*)-5,8-Dimethoxy-2,6,7-trimethyl-2-vinylchroman (**2c**): a colorless oil. IR (neat): 2935, 1463, 1414, 1329, 1259, 1132, 1088, 1027, 970, 920 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 5.89 (dd, *J*=11, 17 Hz, 1H), 5.21 (d, *J*=17 Hz, 1H), 5.07 (d, *J*=11 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.79-2.52 (m, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 1.96-1.72 (m, 2H), 1.46 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃): δ 151.5, 145.2, 142.7, 141.4, 128.5, 120.1, 113.5, 113.3, 76.3, 60.1, 31.2, 26.8, 17.4, 12.2, 12.0; HRMS *m/z* Calc'd for C₁₆H₂₂O₃ [*M*⁺]: 262.1569; Found: 262.1562; Chromatographic separation (GC, Cyclosil B): T oven=170°C, *t_R* (*S*, minor)=32.4 min, *t_R* (*R*, major)=31.6 min.

(*R*)-2-Methyl-2-vinylchroman (**2d**): (*S*)-2-Methyl-2-vinylchroman (**5a**): a colorless oil.
 $[\alpha]_D^{25} = -48.1^\circ$ (*c* 0.55, CDCl₃, 95% ee, **5a**); IR (neat): 2932w, 2850m, 1649w, 1494s, 1434m, 1259m, 1218s, 1198m, 1139m, 1045m, 999m, 930m, 872w, 847w, 810m, 792w cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): δ 7.10 (t, *J*=7.5 Hz, 1H), 7.02 (d, *J*=7.5 Hz, 1H), 6.86 (d, *J*=7.5 Hz, 1H), 6.82 (td, *J*=1.0, 7.5 Hz, 1H), 5.85 (dd, *J*=10.5, 17.0 Hz, 1H), 5.18 (dd, *J*=1.0, 17.5 Hz, 1H), 5.06 (dd, *J*=1.0, 11.0 Hz, 1H), 2.71 (m, 2H), 1.93 (m, 1H), 1.83 (m, 1H), 1.39 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 154.0, 141.2, 129.3, 127.3, 121.3, 119.7, 116.8, 113.9, 76.6, 31.7, 29.1, 27.1; HRMS *m/z* Calc'd for C₁₀H₉O: submitted
 Found: submitted; Chromatographic separation (GC, Cyclosil B): T oven=120°C, *t_R*(*S*)=21.6 min, *t_R*(*R*)=22.7 min.

2e

5e

(*R*)-6-Fluoro-2-vinylchroman (**2e**): (*S*)-6-Fluoro-2-vinylchroman (**5e**): $[\alpha]_D = -62.4^\circ$ (*c* 0.35, Et₂O, 80% ee, **2e**); IR (neat): 2926s, 2853m, 1493s, 1434w, 1258m, 1217s, 1138w, 1044w, 997w, 929m, 871w, 809m cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 6.78 (m, 3H), 5.96 (ddd, *J*=5.6, 10.4, 17.2 Hz, 1H), 5.36 (dt, *J*=1.2, 17.2 Hz, 1H), 5.23 (dt, *J*=1.2, 10.4 Hz, 1H), 4.51 (m, 1H), 2.84 (ddd, *J*=6.4, 10.0, 16.8 Hz, 1H), 2.73 (dt, *J*=4.8, 16.4 Hz, 1H), 2.05 (m, 1H), 1.84 (m, 1H); ¹³C-NMR (125 MHz, CDCl₃): δ 157.9, 150.7, 137.6, 123.0 (d, *J*=7.6 Hz), 117.8 (d, *J*=8.1 Hz), 116.7, 115.5 (d, *J*=9.9 Hz), 114.2 (d, *J*=22.9 Hz), 76.3, 27.4, 24.6; HRMS *m/z* Calc'd for C₁₁H₁₁OF: 178.0794; Found: 178.0791; AD column (Flow rate: 0.4 mL/min, *S* isomer : 15.80 min, *R* isomer: 16.68 min).

2f

5d

(*R*)-2-Vinylchromane (**2f**), (*S*)-2-Vinylchromane (**5d**): a colorless oil. $[\alpha]_D = -80.3^\circ$ (*c* 0.27, CH₂Cl₂, **2f**), 84% ee (HPLC: Chiralpak[®] OJ, 100% heptane); IR (neat) 1581, 1488, 1458, 1233 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.86 (m, 1 H), 2.08 (m, 1 H), 2.86-2.73 (m, 2 H), 4.55 (m, 1 H), 5.24 (ddd, *J* = 10.5, 1.2, 1.2 Hz, 1 H), 5.39 (ddd, *J* = 17.4, 1.5, 1.5 Hz, 1 H), 6.00 (ddd, *J* = 17.4, 10.5, 5.4 Hz, 1 H), 6.84 (m, 2 H), 7.09 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 152.1, 137.5, 129.5, 127.3, 121.7, 120.1, 116.8, 116.2, 76.1, 27.4, 24.1, 20.4; HRMS *m/z* calcd for C₁₁H₁₂O[M]⁺: 160.0888; Found: 160.0888.

2g

5c

(*R*)-6-Methyl-2-vinylchromane (**2g**): A clear oil (96%). $[\alpha]_D = -76.8^\circ$ (*c* 0.69, CHCl₃, **2g**), 87% ee (HPLC: Chiralpak[®] OJ, 99.7% heptane/0.3% *i*-PrOH). IR (neat) 1498, 1243,

1227 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.84 (m, 1 H), 2.03 (m, 1 H), 2.24 (s, 3 H), 2.82-2.69 (m, 2 H), 4.51 (m, 1 H), 5.22 (ddd, $J = 10.5, 1.5, 1.5$ Hz, 1 H), 5.39 (ddd, $J = 17.4, 1.5, 1.5$ Hz, 1 H), 5.97 (ddd, $J = 17.4, 10.5, 5.4$ Hz, 1 H), 6.74 (m, 2 H), 6.87 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.2, 137.6, 129.8, 127.9, 127.3, 121.4, 116.5, 116.1, 76.0, 27.5, 24.1, 20.4; HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}[\text{M}]^+$: 174.1044; Found: 174.1047.

2h

(*R*)-6-Methoxy-2-vinylchromane (**2h**): a colorless oil. $[\alpha]_{\text{D}} = -74.6^\circ$ (c 2.19, CHCl_3); 89% ee (HPLC: Chiralpak[®] OJ, 99.7% heptane/0.3% *i*-PrOH); IR (neat): 1496, 1425, 1269, 1269, 1221, 1051 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.82 (m, 1 H), 2.03 (m, 1 H), 2.72 (m, 1 H), 2.81 (m, 2 H), 3.74 (s, 3 H), 4.49 (m, 1 H), 5.22 (ddd, $J = 10.5, 1.5, 1.5$ Hz, 1 H), 5.36 (ddd, $J = 17.4, 1.5, 1.5$ Hz, 1 H), 5.98 (ddd, $J = 17.4, 10.5, 5.4$ Hz, 1 H), 6.58 (d, $J = 3.0$ Hz, 1 H), 6.67 (m, 1 H), 6.78 (d, $J = 9.0$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.2, 148.5, 137.6, 122.3, 117.3, 116.2, 113.9, 113.3, 76.0, 55.7, 27.5, 24.5; HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}[\text{M}]^+$: 174.1045; Found: 174.1040.

2i

(*R*)-8-Methoxy-6-methyl-2-vinylchromane (**2i**): A white solid (82%); mp. 35-36 $^\circ\text{C}$; $[\alpha]_{\text{D}} = -62.3^\circ$ (c 0.21, CHCl_3), 82% ee (HPLC: Chiralpak[®] OJ, 99.7% heptane/0.3% *i*-PrOH). IR (neat) 1592, 1554, 1493, 1275, 1228 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 1.86 (m, 1 H), 2.05 (m, 1 H), 2.26 (s, 3 H), 2.79-2.70 (m, 2 H), 3.84 (s, 3 H), 4.62 (m, 1 H), 5.21 (ddd, $J = 13.0, 2.0, 2.0$ Hz, 1 H), 5.35 (ddd, $J = 21.5, 1.5, 1.5$ Hz, 1 H), 6.01 (m, 1 H), 6.74 (m, 2 H), 6.47 (s, 1 H), 6.53 (s, 1 H); ^{13}C NMR (125 MHz, CDCl_3): δ 148.0, 141.4, 137.3, 128.9, 122.0, 121.4, 116.4, 110.1, 76.2, 55.8, 27.0, 23.6, 20.0; HRMS m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2[\text{M}]^+$: 204.1150; Found: 204.1045.

6

(*R*)-5-Methoxy-2,7-dimethyl-chroman-2-carboxyaldehyde (**6**): To a solution of (*R*)-5-methoxy-2,7-dimethyl-2-vinylchroman **2b** (0.20 g, 0.92 mmol, ee=97%, prepared from **4b** and (*S,S*)-ligand **ent-3a**) in 3.5 mL of dichloromethane was added *N*-methylmorpholine-*N*-oxide (0.3 g, 2.56 mmol) and aqueous osmium tetroxide (0.27 mL, 4% in water, 0.043 mmol). The solution was stirred for 5 h. at rt and diluted with water (10 mL) and dichloromethane (20 mL). The organic layer was dried over magnesium sulfate and evaporated to dryness. The residue was chromatographed with 1:1 to 1:5 of petroleum ether in diethyl ether. The resulting brown oil (contaminated with osmium residue) was resuspended in acetone (4 mL) and a solution of sodium periodate (0.4 g, 1.87 mmol) in water (1 mL) was added. After a white precipitate was formed the reaction mixture was stirred at rt for an additional 20 min. It was filtered through a pad of celite and the filtrate was partitioned between water (5 mL) and dichloromethane (10 mL). The aqueous layer was extracted with dichloromethane (10 mLx2). The combined organic layers were washed with brine (20 mL) and dried over magnesium sulfate. The residue was separated by flash chromatography eluting with 5% to 25% diethyl ether in petroleum ether to afford the aldehyde **6** as a colorless oil (0.19 g, 0.86 mmol, 94%).

$[\alpha]_D^{25} +16.3^\circ$ (*c* 0.47, Et₂O); IR (film): 2935, 1738, 1619, 1587, 1463, 1146, 1113 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 9.65 (s, 1H), 6.44 (s, 1H), 6.27 (s, 1H), 3.78 (s, 3H), 2.64 (td, *J*=6.4, 17.3 Hz, 1H), 2.47 (ddd, *J*=6.6, 9.2, 16.1 Hz, 1H), 2.30 (s, 3H), 2.22 (m, 1H), 1.77 (ddd, *J*=6.6, 9.5, 15.8 Hz, 1H), 1.40 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃): δ 203.5, 157.5, 153.5, 137.4, 110.0, 107.1, 103.4, 80.0, 55.3, 27.2, 21.5, 21.2, 16.1; HRMS Calc'd for C₁₃H₁₆O₃: 220.1099; Found: 220.1093.

7

(*R*)-5-Methoxy-2,7-dimethyl-2-(4-methyl-penta-1,3-dienyl)-chroman (**7**): To lithium bis(trimethylsilyl)amide (22 mg, 0.13 mmol) were added prenylphenyltetrazole (30 mg, 0.11 mmol) in 0.5 mL of a mixture of DMF and HMPA (4:1) at -78°C to result a yellow solution. Immediately after this to this mixture was added a solution of aldehyde **6** (10 mg, 0.045 mmol) in 0.5 mL of a mixture of DMF and HMPA (4:1). The resultant solution was slowly warmed to rt over 2h. This mixture was directly chromatographed eluting with 2-5 % diethyl ether in petroleum ether to afford desired 5-methoxy-2,7-dimethyl-2-(4-methyl-penta-1,3-dienyl)-chroman **7** (12 mg, 0.044 mmol, 98%, *E/Z* =20:1).

$[\alpha]_D^{25} = -5.0^\circ$ (*c* 1.27, CHCl₃); IR (film): 2929, 1618, 1585, 1352, 1115 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃): δ 6.42 (dd, *J*=10.8, 15.1 Hz, 1H), 6.39 (s, 1H), 6.24 (s, 1H), 5.79 (d, *J*=10.8 Hz, 1H), 5.62 (d, *J*=15.1 Hz, 1H), 3.81 (s, 3H), 2.65 (td, *J*=5.8, 16.8 Hz, 1H), 2.51 (ddd, *J*=6.1, 9.3, 15.6 Hz, 1H), 2.30 (s, 3H), 1.93 (td, *J*=5.8, 13.4 Hz, 1H), 1.82 (m, 1H), 1.76 (s, 3H), 1.71 (s, 3H), 1.44 (s, 3H); ¹³C-NMR (125 MHz, CDCl₃): δ 157.4, 154.3, 136.8, 135.3, 134.0, 125.2, 124.5, 110.1, 107.3, 102.5, 75.9, 55.2, 31.8, 26.7, 25.9, 21.6, 18.2, 16.8. HRMS Calc'd for C₁₈H₂₄O₂: 272.1776; Found: 272.1776.

(*R*)-2,7-Dimethyl-2-(4-methylpenta-1,3-dienyl)-chroman-5-ol (**8**) XXIII-29, XXIII-42: To 3 mL of anhydrous DMF (from a newly-opened bottle, quality is important) at 0 °C was added sodium hydride (153 mg, 60%) followed by the addition of ethanethiol (0.26 mL). The solution was warmed to rt and stirred for 30 min before the addition of diene **7** (119 mg, 0.44 mmol) in 4 mL of anhydrous DMF. The solution was heated at 120 °C for 18 h. To the mixture was added 20 mL of water and extracted with diethyl ether (50 mL x 3). The combined organic fractions were dried with magnesium sulfate and concentrated. The residue was chromatographed eluting with 5% to 20% diethyl ether to afford phenol **8** (110 mg, 0.43 mmol, 97%) as a pale yellow oil.

$[\alpha]_D^{25} = -10.1^\circ$ (*c* 1.2, CHCl₃); IR (film): 3419b, 2925s, 2857m, 1627m, 1586s, 1516w, 1436s, 1415s, 1352m, 1312m, 1274s, 1254s, 1130m, 1088s, 1051m, 996m, 872w, 822w,

739 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 6.29 (dd, $J=10.8, 15.3$ Hz, 1H), 6.24 (s, 1H), 5.67 (d, $J=10.8$ Hz, 1H), 5.50 (d, $J=15.6$ Hz, 1H), 4.48 (s, 1H), 2.46 (m, 1H), 2.13 (s, 3H), 1.80 (m, 2H), 1.65 (s, 3H), 1.59 (s, 3H), 1.33 (s, 3H); ^{13}C -NMR (100 MHz, CDCl_3): δ 154.8, 153.4, 137.3, 135.6, 133.7, 125.5, 124.4, 110.1, 107.2, 105.7, 76.0, 31.7, 29.7, 26.9, 25.9, 21.2, 18.3, 16.7; HRMS calc'd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.1620; Found: 258.1618.

(*R*)-2,7-Dimethyl-5-(3-methyl-but-2-enyloxy)-2-(4-methylpenta-1,3-dienyl)-chroman: To a solution of phenol **8** (4.0 mg, 0.016 mmol) in acetone (0.5 mL) were added potassium carbonate (8.6 mg, 0.062 mmol) and 4-bromo-2-methyl-2-butene (5.2 mg, 4 μL , 0.034 mmol). The reaction mixture was under reflux for 2h and chromatographed eluting with 5% to 10% diethyl ether in petroleum ether to afford ether (5.0 mg, 0.015 mmol, 99%).

$[\alpha]_D = -15.7$ (c 1.1, CDCl_3 , 29.4 $^\circ\text{C}$) IR (film): 2964s, 2926s, 2857s, 1617m, 1585s, 1434s, 1414s, 1381s, 1352m, 1259s, 1235m, 1097s, 1013m, 959w, 810m cm^{-1} ; ^1H -NMR (500 MHz, CDCl_3): δ 6.38 (dd, $J=11.0, 15.0$ Hz, 1H), 6.35 (s, 1H), 6.23 (s, 1H), 5.76 (dd, $J=1.0, 11.0$ Hz, 1H), 5.60 (d, $J=16.0$ Hz, 1H), 5.48 (m, 1H), 4.47 (d, $J=6.5$ Hz, 2H), 2.63 (dt, $J=5.5, 11.0$ Hz, 1H), 2.52 (ddd, $J=6.0, 9.0, 11.0$ Hz, 1H), 2.27 (s, 3H), 1.89 (m, 1H), 1.79 (m, 1H), 1.78 (s, 3H), 1.73 (s, 3H), 1.72 (s, 3H), 1.69 (s, 3H), 1.41 (s, 3H); ^{13}C -NMR (125 MHz, CDCl_3): δ 156.9, 154.4, 137.0, 136.7, 135.3, 134.2, 125.2, 124.6, 123.9, 120.3, 110.0, 103.8, 75.9, 64.9, 31.9, 26.8, 25.9, 25.8, 21.6, 18.3, 18.2, 17.0. HRMS calc'd for $\text{C}_{22}\text{H}_{30}\text{O}_2$: 326.2246; Found: 326.2247.

Clusifoliol (**9**): To (*R*)-2,7-Dimethyl-5-(3-methyl-but-2-enyloxy)-2-(4-methylpenta-1,3-dienyl)-chroman (12 mg, 0.037 mmol) in 1.5 mL of distilled benzene was added montmorillonite KFC (24 mg, in two portions, Aldrich) at rt. It was stirred at rt for 2 d

before it was chromatographed eluting with 5% diethyl ether in petroleum ether to afford the desired natural product clusifoliol (3,4-dihydro-2,7-dimethyl-6-(3-methyl-2-butenyl)-2-(4-methyl-1,3-pentadienyl)-2*H*-1-benzo-pyran-5-ol) **9** (7 mg, 0.021 mmol, 58%).

$[\alpha]_D^{25} = +0.68^\circ$ (*c* 0.9, EtOH); $[\alpha]_D^{25} = +0.62^\circ$ (*c* 0.7, EtOH, authentic sample); IR (film): 3420, 2925, 2855, 1660, 1619, 1592, 1446, 1417, 1259, 1101, 1071, 985, 961 cm^{-1} ; ^1H -NMR (500 MHz, CDCl_3): δ (Experimental value) 6.33 (dd, $J=15.0, 11.0$ Hz, 1H), 6.17 (s, 1H), 5.76 (d, $J=11.0$ Hz, 1H), 5.55 (d, $J=15.5$ Hz, 1H), 5.14 (tm, $J=7.0$ Hz, 1H), 4.46 (bs, 1H), 3.36 (dd, $J=7.0, 14.0$ Hz, 1H), 3.25 (dd, $J=7.0, 14.5$ Hz, 1H), 2.62 (ddd, $J=5.5, 5.5, 16.5$ Hz, 1H), 2.49 (ddd, $J=6.0, 9.5, 16.5$ Hz, 1H), 2.21 (s, 3H), 1.91 (ddd, $J=6.0, 6.0, 12.5$ Hz, 1H), 1.77 (s, 3H), 1.73 (m, 1H), 1.73 (s, 3H), 1.66 (s, 3H), 1.66 (s, 3H), 1.41 (s, 3H); (Literature value) 6.36 (dd, $J=10.6, 15.4$ Hz, 1H), 6.14 (s, 1H), 5.76 (d, $J=10.6$ Hz, 1H), 5.55 (d, $J=15.5$ Hz, 1H), 5.14 (t, $J=7.1$ Hz, 1H), 3.36 (dd, $J=7.1, 14.9$ Hz, 1H), 3.25 (dd, $J=7.1, 14.9$ Hz, 1H), 2.62 (ddd, $J=5.6, 5.6, 16.3$ Hz, 1H), 2.49 (ddd, $J=6.2, 9.7, 16.3$ Hz, 1H), 2.20 (s, 3H), 1.91 (ddd, $J=5.9, 5.9, 13.3$ Hz, 1H), 1.77 (s, 3H), 1.73 (m, 1H), 1.73 (s, 1H), 1.64 (s, 3H), 1.64 (s, 3H), 1.40 (s, 3H); ^{13}C -NMR (100 MHz, CDCl_3): δ Experimental (Literature value) 152.1 (152.2), 151.1 (151.2), 135.2 (135.1), 135.0 (135.0), 134.1 (134.2), 130.3 (130.3), 125.0 (125.1), 124.5 (124.5), 123.2 (123.3), 120.0 (120.0), 107.7 (107.7), 105.9 (105.9), 76.0 (75.9), 31.5 (31.4), 27.4 (27.5), 26.0 (26.0), 25.9 (25.9), 24.9 (25.0), 19.5 (19.3), 18.3 (18.2), 18.0 (17.9), 17.0 (17.2); Chiral HPLC separation (AD column): flow rate 1 mL/min, t_R (*S*, minor) = 3.52 min, t_R (*R*, major) = 4.79 min, e.e = 98%. HRMS: Calc'd for $\text{C}_{22}\text{H}_{30}\text{O}_2$: 326.2246; Found: 326.2245.