Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

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Supporting Information

General. All experiments were conducted under argon atmosphere. THF, ether, CH₂Cl₂, and benzene were dried and distilled by the standard methods. ZnCl₂ and ZnBr₂ were flame-dried under vacuum prior to use. ⁿBuLi, ^sBuLi, ^tBuLi, TBSCl, TBDPSCl, CF₃CO₂H, propanal, cyclohexylamine, MeI, ⁿBuNC, (*S*)-2-amino-1-propanol (97% ee), CBr₄, DIBAL-H (1.0 M in hexanes), (COCl)₂, DMAP, anhydrous ⁱPr₂NH, ⁱPr₂NEt, LiOH, TBAF (1.0 M in THF), NCP(O)(OEt)₂, (*R*)- and (*S*)-1-(1-naphthyl)ethylamine (98% ee), *trans*-2-butene, ^tBuOK (1.0 M in THF), (+)-Ipc₂BOMe, imidazole, AD-mix-α, NaIO₄, Zn dust, anhydrous DMF, Me₂Zn (2.0 M in toluene), TFP, and Cl₂Pd(dppf) were purchased from Aldrich and used as received. HZrCp₂Cl, Me₃Al, ⁱBu₃Al, PPh₃, and Pd₂(dba)₃ were purchased from Strem and used as received. TESCl and trimethylsilylacetylene were purchased from GFS chemicals and used as received. PyBroP was purchased from Fluka and used as received. Pd(PPh₃)₄,^a Cl₂Pd(DPEphos),^b Cl₂Pd(PPh₃)₂,^b Pd(^tBu₃P)₂,^c and (+)-(NMI)₂ZrCl₂^d were prepared according to the literature procedure.

Flash chromatographic separations were carried out on 230 – 400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatography using a HP-5 capillary column (30 m X 0.32 mm, 0.5 μ m film) with appropriate hydrocarbons as internal standards. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Varian Inova-300 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL 95 mass spectrometers, respectively. Microanalyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Optical rotations were measured on an Autopol III automatic polarimeter.

(S)-2-Methyl-4-phenyl-1-butanol (6). To prepare the promoter isobutylaluminumoxane (IBAO), triisobutylaluminum (neat, 7.6 mL, 30 mmol) was dissolved in CH_2Cl_2 (30 mL) in a flame-dried 50 mL round bottom flask at 23 $^\circ\text{C}$. To this was added dropwise water (0.54 mL, 30 mmol) at -45 $^\circ\text{C}$, and the resultant mixture was warmed to 23 $^\circ\text{C}$ over 1 h with stirring.

To a solution of (+)-(NMI) $_2\text{ZrCl}_2^{\text{d}}$ (1.003 g, 1.5 mmol) in CH_2Cl_2 (80 mL) was added trimethylaluminum (neat, 5.75 mL, 60 mmol) at 23 $^\circ\text{C}$ and the promoter IBAO prepared as above. The resulting yellow solution was cooled to 0 $^\circ\text{C}$ and 4-phenyl-1-butene (4.51 mL, 3.97 g, 30 mmol) was added. The resulting red orange solution was stirred at 0 $^\circ\text{C}$ for 4 h, and warmed to 23 $^\circ\text{C}$ over 3 h. O_2 was allowed to bubble through the reaction mixture at 0 $^\circ\text{C}$ for 1 h. To the resulting slurry cooled to 0 $^\circ\text{C}$ was added 10 % NaOH (40 mL) carefully. The mixture was filtered through Celite, washed and extracted with CH_2Cl_2 . The combined organic layers were washed with 2 N NaOH (50 mL), H_2O

(50 mL), and brine (50 mL) successively, dried over MgSO_4 , and concentrated. Flash chromatography (Silica gel, ethyl acetate/hexanes = 1/9) afforded the title compound (4.19 g, 85%) as a slightly yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 1.11 (d, J = 6.9 Hz, 3 H), 1.5-1.6 (m, 1 H), 1.7-1.95 (m, 2 H), 2.65-2.9 (m, 2 H), 2.98 (s, 1 H), 3.45-3.65 (m, 2 H), 7.25-7.45 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.71, 33.47, 35.18, 35.45, 68.00, 125.85, 128.48 (2 C), 128.52 (2 C), 142.83.

Determination of ee value: to a stirred solution of oxalyl chloride (2.4 mL, 27.4 mmol) in CH_2Cl_2 (125 mL) cooled to $-78\text{ }^\circ\text{C}$ was added a solution of DMSO (3.9 mL, 54.8 mmol) in CH_2Cl_2 (10 mL) in 2 min. After the mixture was stirred at $-78\text{ }^\circ\text{C}$ for 15 min., a solution of (*S*)-2-methyl-4-phenyl-1-butanol (**6**) (3.75 g, 22.8 mmol) in CH_2Cl_2 (25 mL) was added. The reaction mixture was stirred for 50 min. Triethylamine (9.53 mL, 68.4 mmol) was added at $-78\text{ }^\circ\text{C}$. The reaction mixture was warmed to $23\text{ }^\circ\text{C}$ over 1.5 h, and quenched with water (70 mL). The separated aq. layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with 1 % HCl (100 mL), satd. NaHCO_3 (100 mL), and brine (100 mL) successively, dried over MgSO_4 , and concentrated. Vacuum drying afforded a crude aldehyde (*S*)-2-methyl-4-phenyl-1-butyraldehyde (3.96 g) as orange oil which was used directly in the next reaction without further purification. A solution of this crude aldehyde (0.52 g, 3.2 mmol) in $t\text{BuOH}$ (19.2 mL) and a PH 4.4 buffer solution of $\text{KMnO}_4/\text{KH}_2\text{PO}_4$ (35 mL) prepared from KH_2PO_4 (0.7 g) and KMnO_4 (3.04 g) in H_2O (33 mL)^e was stirred at $23\text{ }^\circ\text{C}$ for 3 min., quenched with aq. Na_2SO_3 , and acidified to PH 2 using 37% aq. HCl. The resultant mixture was extracted with CH_2Cl_2 , dried over MeSO_4 , and concentrated. Flash Chromatography (Silica gel, ethyl acetate/hexanes = 1/4) gave (*S*)-2-methyl-4-phenyl-1-butyric acid as an

oil (0.4 g, 70%): ^1H NMR (300 MHz, CDCl_3) δ 1.31 (d, $J = 6.9$ Hz, 3 H), 1.75-1.9 (m, 1 H), 2.05-2.2 (m, 1 H), 2.55-2.65 (m, 1 H), 2.75 (t, $J = 8.1$ Hz, 2 H), 7.25-7.4 (m, 5 H), 11.6 (bs, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.89, 33.33, 35.09, 38.83, 125.94, 128.37 (2 C), 128.39 (2 C), 141.44, 183.32. To a stirred solution of this acid (30 mg, 0.17 mmol) in DMF (1 mL) were added successively NCP(O)(OEt)_2 (50 μL , 48 mg, 0.30 mmol), (*S*)-1-(1-naphthyl)ethylamine (40 μL , 42 mg, 0.25 mmol), and Et_3N (0.1 mL, 73 mg, 0.72 mmol). The resultant mixture was stirred at 23 $^\circ\text{C}$ for 20 h, quenched with water, extracted with ether, and dried over MgSO_4 . A sample of this crude amide as a diastereomeric mixture of *SS*- and *RS*-diastereomers were analyzed by GC. GC analysis disclosed a pair of two peaks at the retention time of 14.49 min. (*SS*-diastereomer) and 14.86 min. (*RS*-diastereomer) in an area ratio of 89:11, corresponding to 78% ee. The process described above was repeated by replacing (*S*)-1-(1-naphthyl)ethylamine with (*R*)-1-(1-naphthyl)ethylamine under otherwise identical condition. And the GC analysis of the crude amide disclosed a pair of two peaks at the retention time of 14.40 min. (*RR*-diastereomer) and 14.93 min. (*SR*-diastereomer) in an area ratio of 11:89, corresponding to 78% ee. The crude amide was purified (51.2 mg, 92% yield) by column chromatography (Silica gel, ethyl acetate/hexanes = 1/4) and its structure was confirmed by ^1H and ^{13}C NMR.

(2*E*,4*S*)-2,4-Dimethyl-6-phenyl-2-hexen-1-al (7) (3-step procedure). To a mixture of Ph_3P (35.9 g, 0.137 mol) and K_2CO_3 (3.15 g, 0.0228 mol) in CH_2Cl_2 (400 mL) was added CBr_4 (22.7 g, 0.0684 mol) at 0 $^\circ\text{C}$. The red orange reaction mixture was stirred for 30 min. at 0 $^\circ\text{C}$ followed by the addition of the crude (*S*)-2-methyl-4-phenyl-1-butyraldehyde (3.96 g, ~0.0228 mol) as a solution in CH_2Cl_2 (100 mL) via cannula. The

red orange mixture was then stirred at 0 °C for 1 h. Pentane (300 mL) was added and the precipitates formed were filtered off through Celite. The solid residue was dissolved in CH₂Cl₂ (50 mL), reprecipitated with pentane (100 mL), and filtered again. This process was repeated a total of three times. The combined pentane filtrates were concentrated and the resulting liquid was purified on silica gel (pentane) to give (*S*)-1,1-dibromo-3-methyl-5-phenyl-1-pentene (6.96 g, 96 % over 2 steps) as a clear slightly yellow liquid: ¹H NMR (300 MHz, CDCl₃) δ 1.15 (d, *J* = 6.6 Hz, 3 H), 1.75-1.8 (m, 2 H), 2.55-2.7 (m, 1 H), 2.72 (t, *J* = 7.8 Hz, 2 H), 6.34 (d, *J* = 9.6 Hz, 1 H), 7.25-7.4 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 19.38, 33.71, 38.01, 38.21, 88.07, 125.99, 128.50 (4 C), 141.98, 144.05.

To a solution of (*S*)-1,1-dibromo-3-methyl-5-phenyl-1-pentene (6.96 g, 21.9 mmol) in THF (100 mL) cooled to -78 °C was added ⁿBuLi (19.3 mL, 2.5 M in hexanes, 48.1 mmol). The resulting yellow solution was stirred at -78 °C for 15 min., then warmed to 0 °C and stirred at 0 °C for 30 min. The reaction mixture was cooled back to -78 °C and MeI (6.8 mL, 109 mmol) was added. The reaction mixture was slowly warmed to 23 °C over 12 h. Aqueous NH₄Cl (30 mL) was added. The precipitates thus formed were filtered off through Celite and the separated aq. layer was extracted with ethyl ether (50 mL). The combined org. layers were dried over MgSO₄ and concentrated. Flash chromatography (silica gel, pentane) gave (*S*)-4-methyl-6-phenyl-2-hexyne [3.62 g, 92%, 3 steps from (*S*)-2-methyl-4-phenyl-1-butanol (**6**)] as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 1.27 (d, *J* = 6.9 Hz, 3 H), 1.75-1.85 (m, 2 H), 1.94 (d, *J* = 2.4 Hz, 3 H), 2.45-2.55 (m, 1 H), 2.75-3.0 (m, 2 H), 7.25-7.4 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 3.61, 21.54, 25.64, 33.87, 39.13, 76.21, 83.57, 125.82, 128.40 (2 C), 128.59 (2 C), 142.40; IR (neat) 1717, 1604, 1496, 1454, 1374, 1031 cm⁻¹; MS (EI, 70 eV) *m/z* (%) 172 (25) [M⁺].

A suspension of $\text{Cp}_2\text{Zr(H)Cl}$ (10.6 g, 39.2 mmol) and (*S*)-4-methyl-6-phenyl-2-hexyne (5.07 g, 29.4 mmol) in THF (90 mL) was stirred at 60 °C for 2 h in the dark. GC analysis of an aliquot of the reaction mixture indicated that the hydrozirconation was completed. To the resulting orange solution was added $n\text{BuNC}$ (3.2 mL, 29.4 mmol) at 0 °C. The mixture was stirred at 45 °C for 3 h, cooled to -78 °C and 50 % HOAc aq. solution (90 mL, V/V) was added. After being warmed to 23 °C, the red orange mixture was filtered through Celite and washed with ethyl ether. The filtrate was transferred to a large beaker and carefully neutralized with aq. NaHCO_3 . The separated organic layer was washed with brine (100 mL), dried over MgSO_4 , and concentrated. Flash chromatography afforded the title compound (**7**) (5.19 g, 87 %) as a clear liquid: ^1H NMR (300 MHz, CDCl_3) δ 1.15 (d, J = 6.6 Hz, 3 H), 1.76 (d, J = 1.2 Hz, 3 H), 1.7-1.95 (m, 2 H), 2.64 (t, J = 7.8 Hz, 2 H), 2.7-2.85 (m, 1 H), 6.30 (dg, J = 10.2 and 1.2 Hz, 1 H), 7.15-7.35 (m, 5 H), 9.46 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 9.30, 19.72, 32.98, 33.60, 38.20, 125.86, 128.21 (2 C), 128.29 (2 C), 138.22, 141.58, 159.74, 195.37. 1 D ^1H NOE study of the title compound (**7**) disclosed a 2.6% NOE between the alkenyl hydrogen (6.30 ppm on ^1H NMR) and the aldehyde hydrogen (9.46 ppm on ^1H NMR), indicating a desired *E*-trisubstituted alkene geometry.

(2*E*,4*S*)-2,4-Dimethyl-6-phenyl-2-hexen-1-al (7) (Corey-Peterson olefination procedure). To a stirring -78 °C solution of *N*-cyclohexyl-(2-triethylsilylpropylidene)amine^{f-h} (5.13 g, 20.2 mmol) in THF (29 mL) was added $^s\text{BuLi}$ (13.3 mL, 1.4 M in cyclohexane, 18.7 mmol). The resulting red-orange mixture was stirred at -78 °C for 30 min., and treated with the crude (*S*)-2-methyl-4-phenyl-1-butyraldehyde (2.52 g, ~15.6 mmol) in THF (14 mL). The resultant red-orange mixture

was immediately warmed to -20 °C and stirred for 1 h, quenched with H₂O (28 mL), extracted with ether, washed with brine, and dried over MgSO₄. The organic layers thus obtained were concentrated and dried under vacuum to give an orange oil (~7.35 g), which was dissolved in THF (70 mL), cooled to 0 °C, and treated with CF₃CO₂H (1.44 mL, 2.13 g, 18.7 mmol). The resulting mixture was stirred for 1 h at 0 °C and H₂O (28 mL) was added. The reaction mixture was stirred for 12 h at 0 °C, quenched carefully with satd. NaHCO₃, extracted with ether, washed with brine, dried over MgSO₄, and concentrated. Distillation under reduced pressure gave the title compound (**7**) (2.55 g, 81%, b.p. 116-118 °C/1.5 mmHg) as a clear oil.

(3R,4R,5E,7S)-3,5,7-Trimethyl-9-phenyl-1,5-nonadien-4-ol (5). To a stirring -78 °C solution of ^tBuOK in THF (15.3 mL, 1.0 M in THF, 15.3 mmol) was added via cannula *trans*-2-butene (3.45 mL, 30.6 mmol) followed by the addition of ⁿBuLi (6.13 mL, 2.5 M in hexanes, 15.3 mmol). The resulting orange solution was stirred for 25 min. at -45 °C then cooled back to -78 °C and (+)-Ipc₂BOMe (5.82 g, 18.4 mmol) in ether (18.4 mL) was added. The resulting colorless solution was stirred for 30 min. and BF₃·Et₂O (2.64 mL, 20.8 mmol) was added. The mixture was stirred for 5 min. followed by the addition of (2*E*,4*S*)-2,4-dimethyl-6-phenyl-2-hexen-1-al (**7**) (2.48 g, 12.3 mmol) in ether (18.3 mL) via cannula. The mixture was stirred for 15 h at -78 °C, and satd. NaOAc (8.2 mL) and 30 % H₂O₂ (8.2 mL) were added. After being stirred for 15 h at 23 °C, the mixture was diluted with ether and washed with brine. The separated aq. layer was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄ and concentrated. Flash chromatography (silica gel, ethyl acetate/ hexanes = 1/25) gave the title compound (**5**) (2.53 g, 80 %) as a clear oil (≥99% diastereomerically pure): ¹H NMR

(300 MHz, CDCl₃) δ 0.95 (d, J = 6.9 Hz, 3 H), 1.02 (d, J = 6.6 Hz, 3 H), 1.55-1.8 (m, 2 H), 1.64 (d, J = 1.2 Hz, 3 H), 1.78 (s, 1 H), 2.3-2.45 (m, 1 H), 2.4-2.55 (m, 1 H), 2.6-2.75 (m, 2 H), 3.70 (d, J = 8.7 Hz, 1 H), 5.15-5.3 (m, 3 H), 5.75-5.9 (m, 1 H), 7.2-7.35 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 11.28, 16.76, 20.90, 31.69, 33.79, 39.08, 42.03, 81.15, 116.15, 125.46, 128.12 (2 C), 128.28 (2 C), 133.81, 134.66, 141.15, 142.61.

(3*E*,5*R*,6*R*,7*E*,9*S*)-3,5,7,9-Tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (11). To a stirred solution of (3*R*,4*R*,5*E*,7*S*)-3,5,7-trimethyl-9-phenyl-1,5-nonadien-4-ol (**5**) (2.53 g, 9.8 mmol), imidazole (1.33 g, 19.6 mmol), and DMAP (60 mg, 0.49 mmol) in DMF (20 mL) was added TBSCl (1.77 g, 11.8 mmol). The mixture was stirred for 12 h at 23 °C. Water (10 mL) was added and the mixture was extracted with ether, washed with brine, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, hexanes) afforded (3*R*,4*R*,5*E*,7*S*)-3,5,7-trimethyl-4-(*t*-butyldimethylsilyloxy)-9-phenyl-1,5-nonadiene (3.47 g, 95 %) as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 0.08 (s, 3 H), 0.10 (s, 3 H), 0.93 (d, J = 6.9 Hz, 3 H), 0.96 (s, 9 H), 1.02 (d, J = 6.9 Hz, 3 H), 1.55-1.8 (m, 2 H), 1.63 (d, J = 1.5 Hz, 3 H), 2.3-2.75 (m, 4 H), 3.74 (d, J = 7.5 Hz, 1 H), 5.0-5.05 (m, 1 H), 5.07 (ddd, J = 9.0, 2.1 and 0.9 Hz, 1 H), 5.19 (dt, J = 9.6 and 0.9 Hz, 1 H), 5.93 (ddd, J = 17.1, 10.5 and 7.5 Hz, 1 H), 7.20-7.35 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.85, -4.31, 11.79, 16.79, 18.26, 21.13, 25.89 (3 C), 31.80, 33.96, 39.48, 42.23, 82.82, 113.70, 125.55, 128.25 (2 C), 128.33 (2 C), 133.15, 135.38, 142.21, 142.95.

To a stirring solution of (3*R*,4*R*,5*E*,7*S*)-3,5,7-trimethyl-4-(*t*-butyldimethylsilyloxy)-9-phenyl-1,5-nonadiene (3.48 g, 9.30 mmol) in a mixture of ^tBuOH (46.5 mL) and water (46.5 mL) was added AD-mix- α (14.0 g, 1.5 g/mmol). The

mixture was stirred vigorously at 23 °C for 48 h, filtered through Celite, washed with and extracted with ether, dried over MgSO₄ and concentrated to give a crude diol (4.18 g) as a slightly yellow viscous oil which was used directly in the next reaction without further purification.

To the above crude diol in THF (30 mL) and water (30 mL) was added NaIO₄ (3.58 g, 16.7 mmol) and the mixture was stirred for 30 min. at 23 °C. The mixture was filtered through Celite, washed with ether, dried over MgSO₄ and concentrated to give the crude (2*S*,3*S*,4*E*,6*S*)-2,4,6-trimethyl-3-(*t*-butyldimethylsilyloxy)-8-phenyl-4-octen-1-al (**9**) (3.75 g) as clear viscous oil which was used directly in the next reaction without further purification.

To a stirred -78 °C solution of *N*-cyclohexyl-(2-triethylsilylpropylidene)amine^{f-h} (1.15 g, 4.53 mmol) in THF (6.3 mL) was added ^sBuLi (3.0 mL, 1.4 M in cyclohexane, 4.18 mmol). The resulting red-orange mixture was stirred at -78 °C for 30 min., and treated with the crude (2*S*,3*R*,4*E*,6*S*)-2,4,6-trimethyl-3-(*t*-butyldimethylsilyloxy)-8-phenyl-4-octen-1-al (**9**) (1.305 g, 3.48 mmol) in THF (3.2 mL). The resultant red-orange mixture was immediately warmed to -20 °C and stirred for 1 h, quenched with H₂O (6.3 mL), extracted with ether, washed with brine, and dried over MgSO₄. The organic layers thus obtained were concentrated and dried under vacuum to give an orange oil (~ 2.38 g), which was dissolved in THF (15.7 mL), cooled to 0 °C, and treated with CF₃CO₂H (0.32 mL, 476 mg, 4.18 mmol). The resulting mixture was stirred for 1 h at 0 °C and H₂O (6.3 mL) was added. The reaction mixture was stirred for 12 h at 0 °C, quenched carefully with satd. NaHCO₃, extracted with ether, washed with brine, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, ethyl acetate/hexanes = 1/25) gave

(*2E,4R,5R,6E,8S*)-2,4,6,8-tetramethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-2,6-decadien-1-al (**10**) (1.15 g, 80%) as a clear oil.

To a mixture of Ph₃P (1.45 g, 5.51 mmol) and Zn dust (0.36 g, 5.51 mmol) in CH₂Cl₂ (20 mL) was added CBr₄ (1.83 g, 5.51 mmol) at 0 °C. The resultant yellow slurry was stirred at 0 °C for 15 min. and 23 °C for 15 min. (*2E,4R,5R,6E,8S*)-2,4,6,8-tetramethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-2,6-decadien-1-al (**10**) (1.14 g, 2.755 mmol) in CH₂Cl₂ (8 mL) was added via cannula. The reaction mixture was stirred at 23 °C for 6 h. Pentane (100 mL) was added and the precipitates formed were filtered off through Celite. The solid residue was dissolved in CH₂Cl₂ (10 mL), reprecipitated with pentane (30 mL), and filtered again. This process was repeated a total of three times. The combined pentane filtrates were concentrated and the resulting liquid was purified on silica gel (1% ethyl acetate/hexanes) to give (*3E,5R,6R,7E,9S*)-1,1-dibromo-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyl oxy)-11-phenyl-1,3,7-undecatriene (1.54 g, 98 %) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 0.11 (s, 3 H), 0.12 (s, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.99 (s, 9 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 1.6-1.8 (m, 2 H), 1.67 (s, 3 H), 2.00 (s, 3 H), 2.45-2.8 (m, 4 H), 3.83 (d, *J* = 6.9 Hz, 1 H), 5.26 (d, *J* = 9.3 Hz, 1 H), 5.64 (d, *J* = 9.6 Hz, 1 H), 7.04 (s, 1 H), 7.2-7.45 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.87, -4.40, 11.96, 15.57, 17.37, 18.13, 21.12, 25.82 (3 C), 31.81, 33.93, 37.51, 39.42, 82.40, 84.98, 125.55, 128.26 (2 C), 128.30 (2 C), 131.02, 133.23, 135.14, 139.95, 141.09, 142.79.

To a stirring solution of (*3E,5R,6R,7E,9S*)-1,1-dibromo-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-1,3,7-undecatriene (1.52 g, 2.66 mmol) in THF (14 mL) cooled to -78 °C was added ⁿBuLi (2.23 mL, 2.5 M in hexanes, 5.59 mmol). The resulting yellow solution was stirred for 15 min. at -78 °C then warmed to 0 °C and

stirred 30 min. at 0 °C. Satd. NH_4Cl was added. The mixture was diluted with ether, washed with brine until PH 7. The combined organic layers were dried over MgSO_4 and concentrated. Flash chromatography (silica gel, 1% ethyl acetate/hexanes) gave the title compound (**11**) (1.01 g, 92%) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 0.16 (s, 3 H), 0.19 (s, 3 H), 0.96 (d, $J = 6.6$ Hz, 3 H), 1.03 (s, 9 H), 1.09 (d, $J = 6.9$ Hz, 3 H), 1.6-1.85 (m, 2 H), 1.70 (s, 3 H), 1.94 (d, $J = 0.9$ Hz, 3 H), 2.5-2.8 (m, 4 H), 2.85 (s, 1 H), 3.84 (d, $J = 7.2$ Hz, 1 H), 5.28 (d, $J = 9.6$ Hz, 1 H), 5.94 (d, $J = 9.6$ Hz, 1 H), 7.2-7.4 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.89, -4.49, 11.62, 17.12, 17.36, 18.10, 21.14, 25.80 (3 C), 31.77, 33.92, 37.81, 39.42, 73.40, 82.64, 87.14, 116.51, 125.55, 128.21 (2 C), 128.34 (2 C), 133.53, 135.08, 142.82, 143.41.

(1E,3E,5R,6R,7E,9S)-1-Iodo-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-1,3,7-undecatriene (8). A mixture of (3E,5R,6R,7E,9S)-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (**11**) (375 mg, 0.91 mmol) and HfCp_2Cl (495 mg, 1.83 mmol) in THF (3.6 mL) was stirred at 23 °C in the dark for 4 h, and I_2 (370 mg, 1.46 mmol) was added. The resultant mixture was stirred at 0 °C for 1 h and 23 °C for 1 h, quenched with satd. $\text{Na}_2\text{S}_2\text{O}_3$, filtered through Celite, washed and extracted with ether, dried over MgSO_4 , and concentrated. Flash chromatography (silica gel, hexanes) gave the title compound (**8**) (423 mg, 86%) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 0.10 (s, 6 H), 0.94 (d, $J = 7.2$ Hz, 3 H), 0.97 (s, 9 H), 1.06 (d, $J = 6.6$ Hz, 3 H), 1.6-1.8 (m, 2 H), 1.66 (s, 3 H), 1.81 (s, 3 H), 2.45-2.85 (m, 4 H), 3.83 (d, $J = 6.6$ Hz, 1 H), 5.25 (d, $J = 9.6$ Hz, 1 H), 5.47 (d, $J = 9.6$ Hz, 1 H), 6.19 (d, $J = 14.4$ Hz, 1 H), 7.16 (d, $J = 14.7$ Hz, 1 H), 7.2-7.45 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.87, -4.44,

11.93, 12.32, 17.65, 18.10, 21.14, 25.80 (3 C), 31.81, 33.92, 37.42, 39.43, 72.66, 82.52, 125.54, 128.26 (2 C), 128.32 (2 C), 133.21, 133.90, 135.19, 138.41, 142.80, 150.00.

(3*E*,5*R*,6*R*,7*E*,9*S*)-3,5,7,9-Tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (11) (The procedure involved in the **1,1-dibromo-1-alkene chemistry**). To a mixture of Ph₃P (4.88 g, 18.6 mmol) and Zn dust (1.22 g, 18.6 mmol) in CH₂Cl₂ (150 mL) was added CBr₄ (6.17 g, 18.6 mmol) at 0 °C. The resultant yellow slurry was stirred at 0 °C for 15 min. and 23 °C for 15 min. The crude aldehyde (**9**) (3.75 g) (For its preparation, see the preparation of the compound **11** for details) in CH₂Cl₂ (50 mL) was added via cannula. The reaction mixture was stirred at 23 °C for 6 h. Pentane (200 mL) was added and the precipitates formed were filtered off through Celite. The solid residue was dissolved in CH₂Cl₂ (20 mL), reprecipitated with pentane (100 mL), and filtered again. This process was repeated a total of three times. The combined pentane filtrates were concentrated and the resulting liquid was purified on silica gel (hexanes) to give (3*R*,4*R*,5*E*,7*S*)-1,1-dibromo-3,5,7-trimethyl-4-(*t*-butyldimethylsilyloxy)-9-phenyl-1,5-nonadiene (4.54 g, 92 % over 3 steps from **5**) as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 0.07 (s, 3 H), 0.12 (s, 3 H), 0.97 (s, 9 H), 0.98 (d, *J* = 7.2 Hz, 3 H), 1.00 (d, *J* = 6.9 Hz, 3 H), 1.55-1.8 (m, 2 H), 1.62 (d, *J* = 1.2 Hz, 3 H), 2.4-2.8 (m, 4 H), 3.84 (d, *J* = 6.0 Hz, 1 H), 5.23 (dt, *J* = 9.6 and 1.2 Hz, 1 H), 6.34 (d, *J* = 9.6 Hz, 1 H), 7.2-7.35 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ -5.01, -4.41, 12.24, 16.31, 18.11, 21.11, 25.81 (3 C), 31.70, 33.86, 39.32, 43.17, 80.97, 88.03, 125.55, 128.22 (2 C), 128.39 (2 C), 133.31, 134.62, 141.75, 142.80.

To trimethylsilylacetylene (0.21 mL, 147 mg, 1.5 mmol) in THF (2 mL) cooled to -78 °C was added ⁿBuLi (0.6 mL, 2.5 M in hexanes, 1.5 mmol). The resultant mixture

was stirred at $-78\text{ }^{\circ}\text{C}$ for 25 min. and to this was added via cannula a solution of dry ZnBr_2 (338 mg, 1.5 mmol) in THF (2 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 5 min. and warmed to $23\text{ }^{\circ}\text{C}$ over 25 min. In another flask, to $\text{Cl}_2\text{Pd}(\text{DPEPhos})$ (36 mg, 0.05 mmol) in THF (1 mL) was added DIBAH (0.1 mL, 1.0 M in hexanes, 0.1 mmol). The red-brown mixture was stirred at $23\text{ }^{\circ}\text{C}$ for 5 min. then added via cannula to a solution of (3*R*,4*R*,5*E*,7*S*)-1,1-dibromo-3,5,7-trimethyl-4-(*t*-butyldimethylsilyloxy)-9-phenyl-1,5-nonadiene (530 mg, 1 mmol) in THF (1 mL). The resultant brown mixture was stirred at $23\text{ }^{\circ}\text{C}$ for 10 min. and to this was added via cannula the zinc reagent generated as above. The mixture thus obtained was stirred at $23\text{ }^{\circ}\text{C}$ for 12 h, quenched with H_2O , filtered through Celite, washed and extracted with ether, dried over MgSO_4 , and concentrated. Flash chromatography (silica gel, 1% ethyl acetate/hexanes) gave (3*Z*,5*R*,6*R*,7*E*,9*S*)-1-trimethylsilyl-3-bromo-5,7,9-trimethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (411 mg, 75%) as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 0.13 (s, 3 H), 0.18 (s, 3 H), 0.27 (s, 9 H), 1.04 (s, 12 H), 1.06 (d, $J = 7.2\text{ Hz}$, 3 H), 1.6-1.8 (m, 2 H), 1.68 (s, 3 H), 2.45-2.6 (m, 1 H), 2.6-2.8 (m, 2 H), 2.9-3.05 (m, 1 H), 3.93 (d, $J = 5.7\text{ Hz}$, 1 H), 5.30 (d, $J = 9.3\text{ Hz}$, 1 H), 6.34 (d, $J = 9.3\text{ Hz}$, 1 H), 7.2-7.4 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -5.07, -4.35, -0.34 (3 C), 12.40, 16.31, 18.18, 21.18, 25.84 (3 C), 31.65, 33.86, 39.40, 41.89, 81.18, 94.47, 102.07, 102.60, 125.52, 128.22 (2 C), 128.41 (2 C), 133.11, 134.83, 142.83, 144.04.

To a stirred solution of (3*Z*,5*R*,6*R*,7*E*,9*S*)-1-trimethylsilyl-3-bromo-5,7,9-trimethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (148 mg, 0.27 mmol) and $\text{Pd}(\text{t}\text{-Bu}_3\text{P})_2$ (2.8 mg, 0.0054 mmol) in THF (1.4 mL) at $0\text{ }^{\circ}\text{C}$ was added Me_2Zn (0.13 mL, 2.0 M in toluene, 0.26 mmol). The resultant mixture was stirred at $23\text{ }^{\circ}\text{C}$ for 1

h, quenched with H₂O, filtered through Celite, washed and extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, 1% ethyl acetate/hexanes) gave (3*E*,5*R*,6*R*,7*E*,9*S*)-1-trimethylsilyl-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (130 mg, 100%) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 0.11 (s, 3 H), 0.15 (s, 3 H), 0.26 (s, 9 H), 0.90 (d, *J* = 6.9 Hz, 3 H), 0.99 (s, 9 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 1.6-1.8 (m, 2 H), 1.66 (s, 3 H), 1.88 (d, *J* = 1.2 Hz, 3 H), 2.4-2.8 (m, 4 H), 3.79 (d, *J* = 7.5 Hz, 1 H), 5.23 (d, *J* = 9.6 Hz, 1 H), 5.85 (dd, *J* = 10.2 and 1.2 Hz, 1 H), 7.2-7.4 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.96, -4.48, 0.11 (3 C), 11.57, 16.99, 17.38, 18.13, 21.13, 25.82 (3 C), 31.75, 33.91, 37.88, 39.42, 82.86, 89.62, 109.08, 117.54, 125.55, 128.23 (2 C), 128.34 (2 C), 133.58, 135.13, 142.84, 143.21.

A mixture of (3*E*,5*R*,6*R*,7*E*,9*S*)-1-trimethylsilyl-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (130 mg, 0.27 mmol) and K₂CO₃ in MeOH (2.7 mL) was stirred at 23 °C for 3 h, quenched with satd. NH₄Cl, washed and extracted with ether, dried over MgSO₄, and concentrated to give (3*E*,5*R*,6*R*,7*E*,9*S*)-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl-3,7-undecadien-1-yne (**11**) (109 mg, 98%) as a colorless oil.

Ethyl (2*E*,4*E*,8*E*,10*E*,12*R*,13*R*,14*E*,16*S*)-2,10,12,14,16-pentamethyl-13-(*t*-butyldimethylsilyloxy)-18-phenyl-2,4,8,10,14-octadecapentaen-6-ynoate (14). To ^{*i*}Pr₂NH (68 μL, 49 mg, 0.485 mmol) in THF (2 mL) cooled to -78 °C was added ^{*n*}BuLi (0.19 mL, 2.5 M in hexanes, 0.485 mmol). The resultant mixture was stirred at -78 °C for 30 min., and added dropwise via cannula to a solution of ethyl (2*E*,4*E*)-2-methyl-2,4-heptadien-6-ynoate (**12**)^{*i*} (80 mg, 0.485 mmol) in THF (1 mL). The resultant brown

mixture was stirred at -78 °C for 20 min., and a solution of dry ZnBr₂ (109 mg, 0.485 mmol) in THF (1 mL) was added. The red-brown mixture thus obtained was stirred at -78 °C for 5 min. and warmed to 0 °C over 10 min. In another flask, to Cl₂Pd(PPh₃)₂ (11 mg, 0.016 mmol) in THF (1 mL) was added DIBAL-H (0.032 mL, 1.0 M in hexanes, 0.032 mmol). The resultant mixture was stirred at 23 °C for 5 min., and to this was added via cannula a solution of (1*E*,3*E*,5*R*,6*R*,7*E*,9*S*)-1-iodo-3,5,7,9-tetramethyl-6-(*t*-butyldimethylsilyloxy)-11-phenyl -1,3,7-undecatriene (**8**) (174 mg, 0.32 mmol) in THF (1 mL). The resultant mixture was stirred at 23 °C for 5 min., and to this was added via cannula the red-brown dienyne zinc reagent generated as above. The mixture thus obtained was stirred at 23 °C for 3 h, quenched with H₂O, filtered through Celite, washed and extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, ethyl acetate/hexanes = 1/50) gave the title compound (175 mg, 94%) as a viscous oil: $[\alpha]_D^{23} +98.3^\circ$ (c 1.4, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 0.07 (s, 6 H), 0.93 (s, 12 H), 1.03 (d, *J* = 6.3 Hz, 3 H), 1.39 (t, *J* = 6.9 Hz, 3 H), 1.6-1.9 (m, 2 H), 1.64 (s, 3 H), 1.82 (s, 3 H), 2.05 (s, 3 H), 2.4-2.8 (m, 4 H), 3.81 (d, *J* = 6.9 Hz, 1 H), 4.30 (q, *J* = 6.9 Hz, 2 H), 5.22 (d, *J* = 9.3 Hz, 1 H), 5.59 (d, *J* = 9.6 Hz, 1 H), 5.71 (d, *J* = 15.6 Hz, 1 H), 6.14 (d, *J* = 15.0 Hz, 1 H), 6.77 (d, *J* = 15.9 Hz, 1 H), 6.91 (dd, *J* = 15.0 and 12.0 Hz, 1 H), 7.15-7.4 (m, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.88, -4.48, 11.81, 12.24, 12.86, 14.26, 17.61, 18.06, 21.10, 25.75 (3 C), 31.78, 33.88, 37.85, 39.38, 60.66, 82.65, 90.27, 96.37, 104.56, 118.24, 125.51, 128.20 (2 C), 128.29 (2 C), 128.70, 133.15, 133.27, 135.17, 135.44, 137.03, 141.10, 142.75, 147.85, 167.98.

6,7-Dehydrostipiamide (1). A solution of ethyl (2*E*,4*E*,8*E*,10*E*,12*R*,13*R*,14*E*,16*S*)-2,10,12,14,16-pentamethyl-13-(*t*-butyldimethylsilyl

oxy)-18-phenyl-2,4,8,10,14-pentaen-6-ynoate (**14**) (328 mg, 0.57 mmol) and TBAF (2.85 mL, 1.0 M in THF, 2.85 mmol) was stirred at 23 °C for 24 h, quenched with water, filtered through Celite, extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, 20% ethyl acetate/hexanes) gave ethyl (2*E*,4*E*,8*E*,10*E*,12*R*,13*R*,14*E*,16*S*)-2,10,12,14,16-pentamethyl-13-hydroxy-18-phenyl-2,4,8,10,14-octadecapentaen-6-ynoate (223 mg, 85%) as a clear viscous oil: ¹H NMR (300 MHz, CDCl₃) δ 0.92 (d, *J* = 6.6 Hz, 3 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.5-1.75 (m, 2 H), 1.64 (s, 3 H), 1.86 (s, 3 H), 2.02 (s, 3 H), 2.4-2.55 (m, 1 H), 2.55-2.7 (m, 2 H), 2.7-2.85 (m, 1 H), 3.76 (d, *J* = 8.1 Hz, 1 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 5.26 (d, *J* = 9.3 Hz, 1 H), 5.58 (d, *J* = 9.9 Hz, 1 H), 5.74 (dd, *J* = 15.9 and 2.1 Hz, 1 H), 6.11 (dd, *J* = 15.0 and 1.5 Hz, 1 H), 6.75 (d, *J* = 15.6 Hz, 1 H), 6.88 (dd, *J* = 15.3 and 11.7 Hz, 1 H), 7.15-7.35 (m, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 11.46, 12.32, 12.90, 14.26, 17.34, 20.97, 31.80, 33.83, 37.07, 39.06, 60.72, 82.20, 90.73, 95.83, 105.66, 118.08, 125.53, 128.19 (2 C), 128.35 (2 C), 128.92, 133.96, 134.90, 134.97, 135.72, 136.96, 139.14, 142.62, 147.09, 168.01; HRMS calcd for C₃₁H₄₀O₃ [M+H]⁺ 461.3056, found 461.3053.

To a solution of ethyl (2*E*,4*E*,8*E*,10*E*,12*R*,13*R*,14*E*,16*S*)-2,10,12,14,16-pentamethyl-13-hydroxy-18-phenyl-2,4,8,10,14-octadecapentaen-6-ynoate (52 mg, 0.11 mmol) in THF/MeOH (0.6 mL/0.3 mL) was added a LiOH aq. solution (0.6 mL, 2.0 M, 1.2 mmol). The resultant blood-red mixture was stirred at 23 °C for 6 h, diluted with H₂O/EtOAc, extracted with EtOAc, dried over MgSO₄, filtered, and concentrated to give a crude carboxylic acid (47 mg, 96%) as a clear viscous oil. To a solution of this crude carboxylic acid (47 mg, 0.109 mmol) in CH₂Cl₂ (2.2 mL) was added ⁱPr₂NEt (57 μL, 42

mg, 0.33 mmol), (*S*)-2-amino-1-propanol (17 μ L, 16 mg, 0.22 mmol), and bromotripyrrolidinophosphonium hexafluorophosphate (PyBroP) (61 mg, 0.13 mmol) successively. The resultant mixture was stirred at 23 °C in the dark for 12 h, quenched with H₂O (2 mL), extracted with EtOAc, dried over MgSO₄, filtered, and concentrated. Flash chromatography (silica gel, ethyl acetate) gave the final target **6,7-dehydrostipiamide (1)** (50 mg, 95%) as a clear viscous oil: ¹H NMR (300 MHz, CDCl₃) δ 0.88 (d, *J* = 6.9 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 1.23 (t, *J* = 6.9 Hz, 3 H), 1.5-1.7 (m, 2 H), 1.60 (s, 3 H), 1.81 (s, 3 H), 1.99 (s, 3 H), 2.35-2.5 (m, 1 H), 2.5-2.65 (m, 2 H), 2.65-2.8 (m, 1 H), 3.5-3.6 (m, 1 H), 3.72 (d, *J* = 8.4 Hz, 2 H), 4.1-4.2 (m, 1 H), 5.22 (d, *J* = 9.3 Hz, 1 H), 5.53 (d, *J* = 9.6 Hz, 1 H), 5.69 (dd, *J* = 15.9 and 2.1 Hz, 1 H), 5.97 (d, *J* = 7.5 Hz, 1 H), 6.02 (dd, *J* = 15.0 and 2.1 Hz, 1 H), 6.70 (d, *J* = 15.9 Hz, 1 H), 6.80 (dd, *J* = 15.0 and 11.7 Hz, 1 H), 6.95 (d, *J* = 11.7 Hz, 1 H), 7.1-7.3 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ 11.44, 12.30, 13.15, 17.01, 17.33, 20.94, 31.77, 33.81, 37.06, 39.05, 47.96, 66.88, 82.19, 90.68, 95.32, 105.65, 117.14, 125.51, 128.17 (2 C), 128.33 (2 C), 131.33, 133.10, 133.96, 134.91 (2 C), 135.47, 139.03, 142.62, 146.91, 169.14.

(4*R*,5*R*,6*E*,8*S*)-4,6,8-Trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-6-decen-2-yne (16). To a solution of (3*R*,4*R*,5*E*,7*S*)-1,1-dibromo-3,5,7-trimethyl-4-(*t*-butyldimethylsilyloxy)-9-phenyl-1,5-nonadiene [For its preparation, refer to the preparation of the compound (**11**) by the procedure involved in the 1,1-dibromo-1-alkene chemistry] (6.90 g, 13.0 mmol) in THF (65 mL) cooled to -78 °C was added ^{*n*}BuLi (17.2 mL, 2.5 M in hexanes, 42.9 mmol) in 5 min. The resulting yellow solution was stirred for 15 min. at -78 °C then warmed to 0 °C and stirred for 30 min. at 0 °C. The reaction mixture was then cooled back to -78 °C and MeI (4.0 mL, 65 mmol) was added. The

reaction mixture was gradually warmed to 23 °C over 12 h, quenched with satd. NH₄Cl, filtered through Celite, extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, 1% ethyl acetate/hexanes) gave the title compound (5.00 g, 100%) as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 0.10 (s, 3 H), 0.15 (s, 3 H), 0.96 (s, 9 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 1.00 (d, *J* = 7.2 Hz, 3 H), 1.55-1.8 (m, 2 H), 1.59 (d, *J* = 1.5 Hz, 3 H), 1.82 (d, *J* = 2.4 Hz, 3 H), 2.4-2.75 (m, 4 H), 3.85 (d, *J* = 8.4 Hz, 1 H), 5.19 (d, *J* = 9.6 Hz, 1 H), 7.2-7.25 (m, 3 H), 7.3-7.35 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.84, -4.55, 3.61, 11.20, 17.80, 18.27, 21.05, 25.79 (3 C), 31.74 (2 C), 33.90, 39.36, 75.97, 82.77, 82.92, 125.57, 128.25 (2 C), 128.31 (2 C), 134.21, 134.62, 142.83.

Ethyl (2*E*,4*E*,8*E*,10*E*,12*R*,13*R*,14*E*,16*S*)-2,10,12,14,16-pentamethyl-13-(*t*-butyldimethylsilyloxy)-18-phenyl-2,4,8,10,14-octadecapentaen-6-ynoate (14) [The procedure involved in the cross-coupling between (*E,E,E*)-BrCH=CHC≡CCH=CHCH=C(Me)COOEt (15) and the alkyne 16]. A mixture of (4*R*,5*R*,6*E*,8*S*)-4,6,8-trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-6-decen-2-yne (16) (387 mg, 1 mmol) and HZrCp₂Cl (546 mg, 2 mmol) in THF (4 mL) was stirred at 23 °C in the dark for 10 min. and 60 °C for 2.5 h, and cooled down to 23 °C. To this was added via cannula a solution of dry ZnCl₂ (274 mg, 2 mmol) in THF (3 mL). In another flask, to Cl₂Pd(PPh₃)₂ (35 mg, 0.05 mmol) and tri-(2-furyl)phosphine (TFP) (23 mg, 0.1 mmol) in THF (2 mL) was added DIBAH (0.1 mL, 1.0 M in hexanes, 0.1 mmol) at 23 °C and the resultant mixture was stirred at 23 °C for 10 min. To this was added via cannula a solution of ethyl (2*E*,4*E*,8*E*)-2-methyl-9-bromo-2,4,8-nonatrien-6-ynoateⁱ (15) (323 mg, 1.2 mmol) in THF (2 mL). The resultant red-orange mixture was stirred at 23 °C for 15 min., and added to the previous reaction mixture. The reaction mixture thus obtained was

stirred at 23 °C in the dark for 20 h, quenched with water, filtered through Celite, extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, ethyl acetate/hexanes = 1/25) gave the title compound (328 mg, 57%) as a clear oil.

(2*E*,4*R*,5*R*,6*E*,8*S*)-2-Iodo-4,6,8-trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-2,6-decadiene (17). A mixture of (4*R*,5*R*,6*E*,8*S*)-4,6,8-trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-6-decen-2-yne (**16**) (785 mg, 2.04 mmol) and HZrCp₂Cl (1.107 g, 4.08 mmol) in THF (8.2 mL) was stirred at 60 °C in the dark for 2.5 h, cooled down to 0 °C and I₂ (828 mg, 3.26 mmol) was added. The resultant mixture was stirred at 0 °C for 1 h and 23 °C for 1 h, quenched with satd. Na₂S₂O₃, filtered through Celite, washed and extracted with ether, dried over MgSO₄, and concentrated. Flash chromatography (silica gel, hexanes) gave the title compound (**17**) (774 mg, 74%) and its 3-iodo regioisomer (2*E*,4*R*,5*R*,6*E*,8*S*)-3-iodo-4,6,8-trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-2,6-decadiene (188 mg, 18%) as colorless oils. Identification data for the iodide **17**: ¹H NMR (300 MHz, CDCl₃) δ 0.12 (s, 3 H), 0.17 (s, 3 H), 0.90 (d, *J* = 7.2 Hz, 3 H), 1.00 (s, 9 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 1.6-1.85 (m, 2 H), 1.65 (s, 3 H), 2.45-2.8 (m, 4 H), 2.48 (s, 3 H), 3.75 (d, *J* = 7.5 Hz, 1 H), 5.23 (d, *J* = 9.3 Hz, 1 H), 6.07 (d, *J* = 10.8 Hz, 1 H), 7.2-7.4 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.69, -4.49, 11.43, 17.03, 18.06, 21.06, 25.84 (3 C), 27.96, 31.75, 33.92, 39.33, 40.30, 82.42, 93.85, 125.57, 128.24 (2 C), 128.34 (2 C), 133.84, 134.86, 142.78, 144.96. Identification data for the 3-iodo regioisomer of iodide **17**: ¹H NMR (300 MHz, CDCl₃) δ 0.14 (s, 3 H), 0.24 (s, 3 H), 0.83 (d, *J* = 6.3 Hz, 3 H), 0.97 (s, 9 H), 1.07 (d, *J* = 6.6 Hz, 3 H), 1.6-1.8 (m, 2 H), 1.72 (s, 3 H), 1.84 (d, *J* = 6.9 Hz, 3 H), 2.25-2.35 (m, 1 H), 2.45-2.6 (m, 1 H), 2.6-2.8 (m, 2 H), 3.87 (d, *J* = 9.3 Hz, 1 H), 5.31 (d, *J* = 9.3 Hz, 1 H), 6.42 (q, *J* = 7.2 Hz, 1 H), 7.25-7.4 (m,

5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.62, -4.30, 11.34, 17.09, 18.08, 18.57, 20.86, 25.80 (3 C), 31.90, 34.01, 39.26, 40.97, 82.44, 114.21, 125.61, 128.27 (4 C), 134.19, 135.09, 136.13, 142.74.

(3*E*,5*E*,7*R*,8*R*,9*E*,11*S*)-1-Trimethylsilyl-5,7,9,11-tetramethyl-8-(*t*-butyldimethylsilyloxy)-13-phenyl-3,5,9-tridecatrien-1-yne. To (*E*)-1-bromo-4-trimethylsilyl-1-buten-3-yne^k (61 mg, 0.3 mmol) in ether (1 mL) cooled to -78 °C was added ^tBuLi (0.35 mL, 1.7 M in pentane, 0.6 mmol). The resulting colorless solution was stirred at -78 °C for 30 min. A solution of dry ZnBr_2 (68 mg, 0.3 mmol) in THF (0.5 mL) was added via cannula. The resultant mixture was stirred at -78 °C for 5 min and warmed to 0 °C over 20 min. Solvents were removed under vacuum at 23 °C until a yellow-green viscous oil left. In another flask, a solution of $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 0.005 mmol) and TFP (4.6 mg, 0.02 mmol) in THF (0.5 mL) was stirred at 23 °C for 10 min., then treated with (2*E*,4*R*,5*R*,6*E*,8*S*)-2-iodo-4,6,8-trimethyl-5-(*t*-butyldimethylsilyloxy)-10-phenyl-2,6-decadiene (**17**) (103 mg, 0.2 mmol) in dry DMF (1 mL). The resultant mixture was stirred at 23 °C for 5 min., and added via cannula to the previously generated organozinc reagent. The resultant deep orange mixture was stirred at 23 °C for 20 h, quenched with water, filtered through Celite, extracted with ether, dried over MgSO_4 , and concentrated. Flash chromatography (silica gel, ethyl acetate/hexanes = 1/99) gave the title compound (87 mg, 85%) as an oil: $[\alpha]_D^{23} +25.4^\circ$ (c 0.69, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 0.07 (s, 6 H), 0.28 (s, 9 H), 0.91 (d, $J = 7.2$ Hz, 3 H), 0.94 (s, 9 H), 1.03 (d, $J = 6.6$ Hz, 3 H), 1.6-1.75 (m, 2 H), 1.64 (s, 3 H), 1.79 (s, 3 H), 2.4-2.8 (m, 4 H), 3.81 (d, $J = 6.9$ Hz, 1 H), 5.22 (d, $J = 9.3$ Hz, 1 H), 5.5-5.6 (m, 2 H), 6.77 (d, $J = 16.5$ Hz, 1 H), 7.2-7.4 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.84, -4.46, 0.05 (3 C), 11.84, 12.24, 17.71, 18.08,

21.12, 25.80 (3 C), 31.80, 33.91, 37.88, 39.43, 82.70, 94.98, 104.74, 105.43, 125.53, 128.24 (2 C), 128.32 (2 C), 132.91, 133.24, 135.30, 140.36, 142.81, 147.82.

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zeng-1-006-1, 08/13/01
Pulse Sequence: szpul

Efficient and Selective Synthesis of 6,7-Dihydrostipiamide via Zr-Catalyzed
Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-006-1

INDEX	FREQUENCY	PPM	HEIGHT
1	10773.127	142.832	12.1
2	9693.396	128.517	85.0
3	9690.375	128.477	83.1
4	9491.954	125.846	49.9
5	5129.217	68.004	45.6
6	2674.139	35.454	48.4
7	2653.491	35.181	47.2
8	2524.065	33.465	47.0
9	1260.518	16.712	40.0

Efficient and Selective Synthesis of 6,7-Dehydrosipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

zeng-1-022-1, 09/15/01
Pulse Sequence: zgpg30

**Efficient and Selective Synthesis of 6,7-Dehydrosipamide via Zr-Catalyzed
Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs**

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-022-1

INDEX	FREQUENCY	PPM	HEIGHT
1	14735.647	139.368	35.1
2	12048.406	139.740	26.3
3	10678.599	141.579	12.9
4	10425.285	138.221	10.3
5	9676.423	128.292	77.6
6	9669.876	128.205	86.2
7	9492.607	129.855	47.9
8	5839.451	77.421	8.5
9	5807.724	77.000	8.7
10	5775.493	76.573	8.9
11	2881.271	38.200	46.0
12	2534.266	33.600	42.7
13	2487.451	32.979	39.5
14	1487.290	19.719	40.3
15	701.161	9.296	20.0

Efficient and Selective Synthesis of 6,7-Dehydrosipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-022-1

INDEX	FREQUENCY	PPM	HEIGHT
1	14735.647	195.368	25.9
2	12048.406	159.740	19.3
3	10678.599	141.579	9.5
4	10425.285	138.221	7.6
5	9676.423	128.292	57.2
6	9669.876	128.205	63.6
7	9492.607	125.855	35.3
8	5839.451	77.421	6.3
9	5807.724	77.000	6.4
10	5775.493	76.573	6.5
11	2881.271	38.200	33.9
12	2534.286	33.600	31.5
13	2487.451	32.979	29.1
14	1487.290	19.719	29.7
15	701.161	9.296	14.8

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carbolumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

zeng-1-016-5, 09/03/01
Pulse Sequence: zgpg30

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

Efficient and Selective Synthesis of 6,7-Dehydrostipnamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs
 Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-o16-1

INDEX	FREQUENCY	PPM	HEIGHT
1	10756.658	142.614	9.3
2	10645.865	141.145	18.0
3	10156.360	134.655	21.7
4	10092.905	133.814	11.3
5	9675.416	128.279	56.7
6	9663.330	128.118	51.8
7	9462.895	125.461	29.1
8	8760.868	116.153	18.0
9	6120.463	81.146	23.9
10	5839.451	77.421	5.1
11	5807.724	77.000	5.2
12	5775.493	76.573	5.3
13	3169.837	42.026	27.8
14	2947.243	39.075	27.9
15	2548.891	33.794	26.0
16	2390.255	31.690	26.1
17	1576.428	20.901	27.1
18	1264.193	16.761	27.1
19	850.732	11.279	18.1

xz-430-3, 12/16/03
Data collected on: novas300-1-nova300
Archive directory: /nfs/nova300-1/d2/negishi/xzeng/vnmr/sys/data
Sample directory: /nfs/nova300-1/d2/negishi/xzeng/vnmr/sys/data
File: PROTON
Pulse Sequence: szpul

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-430-3

INDEX	FREQUENCY	PM	HEIGHT
1	10816.548	143.408	25.0
2	10771.955	142.817	34.6
3	10188.503	135.081	37.9
4	10071.122	133.525	21.7
5	9680.140	126.341	98.3
6	9670.358	126.212	96.6
7	9469.545	125.549	45.5
8	8787.908	116.513	33.1
9	6572.137	87.135	23.9
10	6232.941	82.638	31.5
11	5839.656	77.423	37.8
12	5807.723	77.000	39.6
13	5775.789	76.577	40.3
14	5535.849	73.395	32.9
15	2973.322	39.421	30.8
16	2851.625	37.807	42.0
17	2556.173	33.917	40.5
18	2396.199	31.769	44.4
19	1946.239	25.804	79.0
20	1594.097	21.135	26.0
21	1364.801	18.095	36.9
22	1308.276	17.359	23.6
23	1290.863	17.115	27.2
24	876.578	11.622	22.2
25	-338.659	-4.490	31.5
26	-368.580	-4.887	30.8

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-430-3

INDEX	FREQUENCY	PPM	HEIGHT
1	10816.548	143.408	16.9
2	10771.955	142.817	23.3
3	10168.503	135.081	25.6
4	10071.122	133.525	14.6
5	9680.140	128.341	66.3
6	9670.358	128.212	65.2
7	9469.545	125.549	30.7
8	8787.988	116.513	22.3
9	6572.137	87.135	16.2
10	6232.941	82.638	21.3
11	5839.658	77.423	25.5
12	5807.723	77.000	26.8
13	5775.789	76.577	27.2
14	5535.849	73.395	22.2
15	2973.322	39.421	20.8
16	2851.625	37.807	28.4
17	2558.173	33.917	27.3
18	1916.239	25.804	53.3
19	1594.097	21.135	17.6
20	1364.801	18.085	24.9
21	1309.276	17.359	15.9
22	1290.863	17.115	18.4
23	876.578	11.622	15.0
24	-338.659	-4.490	21.3
25	-368.580	-4.887	20.8

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs
Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

xz-431-1, 12/18/03
Data Collected on: inova300-2-inova300
Archive directory: /nfs/inova300-2/d2/negishi/xzeng/vnmr sys/data
Sample name: 8
Sample category:
File: PROTON
Pulse Sequence: szpu1

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

xz-432-1, 12/20/03
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Archive directory: /nts/inova300-2/dz/nejishi/xzeng/vnmr-sys/data
Sample description:
File: PROTON
Pulse Sequence: szpul

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carbolumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-432-1

INDEX	FREQUENCY	PPM	HEIGHT
1	12669.899	167.980	20.0
2	11151.428	147.848	26.0
3	10767.064	142.752	26.6
4	10642.203	141.097	15.1
5	10335.804	137.034	31.3
6	10215.546	135.440	31.8
7	10194.832	135.165	29.9
8	10051.558	133.266	17.0
9	10042.927	133.151	30.2
10	9707.471	128.704	24.5
11	9676.112	128.288	82.6
12	9669.783	128.204	87.7
13	9466.668	125.511	34.7
14	8918.028	118.237	22.5
15	7886.630	104.563	18.1
16	7268.654	96.389	20.4
17	6808.337	90.286	17.1
18	6233.804	82.649	22.8
19	5839.658	77.423	75.4
20	5807.723	77.000	79.9
21	5775.789	76.577	79.9
22	4575.225	60.659	20.7
23	2969.869	39.375	21.9
24	2854.502	37.846	26.7
25	2555.008	33.875	28.2
26	2397.062	31.781	29.9
27	1942.211	25.750	65.5
28	1591.220	21.097	21.6
29	1361.924	18.057	34.4
30	1328.264	17.610	21.0
31	1075.665	14.261	24.1
32	970.079	12.862	19.1
33	923.185	12.240	18.6
34	890.387	11.805	19.0
35	-337.796	-4.479	26.1
36	-368.292	-4.883	26.8

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carbosulmination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-432-1

INDEX	FREQUENCY	PPM	HEIGHT
1	12689.899	167.980	13.9
2	11151.428	147.846	18.1
3	10767.064	142.752	19.9
4	10642.203	141.097	10.5
5	10335.804	137.034	22.2
6	10215.546	135.440	22.2
7	10194.832	135.165	20.8
8	10051.556	133.266	11.8
9	10042.927	133.151	21.0
10	9707.471	128.704	17.1
11	9676.112	128.288	57.6
12	9669.783	128.204	61.2
13	9466.668	125.511	24.2
14	8918.028	118.237	15.7
15	7886.630	104.563	12.6
16	7268.654	96.389	14.3
17	6808.337	90.286	11.9
18	6233.804	82.649	15.9
19	5839.658	77.423	52.6
20	5807.723	77.000	55.7
21	5775.789	76.577	55.7
22	4379.623	60.950	15.3
23	2969.669	39.375	18.6
24	2854.502	37.846	19.6
25	2555.008	33.875	20.8
26	2397.062	31.781	45.7
27	1942.211	25.750	15.0
28	1591.220	21.097	24.0
29	1361.924	18.057	14.6
30	1328.264	17.610	16.8
31	1075.665	14.261	13.3
32	970.079	12.862	13.0
33	923.185	12.240	13.2
34	830.387	11.805	18.2
35	-337.796	-4.479	18.7
36	-366.292	-4.883	18.7

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carbosulmination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-436-1, 12/29/03

Data Collected on: inova300
Archive directory: /nfs/inova300-1/42/negishi/xzeng/vnmr/sy/data

XZ-438-1, 12/29/03
Data Collected on: Inova300-1-Inova300
Archive directory: /nfs/inova300-1/d2/negishi/xzeng/vnmr/sys/fat
Sample directory:
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Pulse Sequence: szpu1

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed
Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs
Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

zeng-1-031-3, 10/03/01
Pulse Sequence: zgpg30

**Efficient and Selective Synthesis of 6,7-Dihydrostipiamide via Zr-Catalyzed
Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs**

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

X Zeng - 1 - 031 - 36

INDEX	FREQUENCY	PPM	HEIGHT
1	10772.772	142.828	12.7
2	10153.337	134.615	14.1
3	10123.121	134.214	21.1
4	9677.934	128.312	63.6
5	9672.897	128.245	59.5
6	9476.952	125.568	31.7
7	6253.318	82.916	12.3
8	6242.839	82.769	24.9
9	5839.954	77.427	13.9
10	5807.723	77.000	20.3
11	5775.996	76.579	20.4
12	5730.168	75.972	11.5
13	2968.897	39.362	27.5
14	2556.948	33.901	25.9
15	2394.283	31.744	54.2
16	1945.067	25.788	102.5
17	1586.010	21.054	26.6
18	1376.007	18.270	10.7
19	1342.754	17.803	26.4
20	844.686	11.199	19.1
21	272.089	3.607	20.9
22	-343.318	-4.552	19.9
23	-364.973	-4.839	18.7

Efficient and Selective Synthesis of 6,7-Dehydrostipiamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-1-031-36

INDEX	FREQUENCY	PPM	HEIGHT
1	10153.841	134.622	8.9
2	10123.121	134.214	13.1
3	9677.934	128.312	39.8
4	9672.897	128.245	37.3
5	9470.952	125.566	19.9
6	8242.839	82.769	15.6
7	8039.954	77.487	12.4
8	8007.723	77.000	12.7
9	5775.996	76.579	12.6
10	2966.897	39.362	17.2
11	2556.948	33.901	16.3
12	2394.283	31.744	34.0
13	1945.067	25.788	64.2
14	1588.010	21.054	16.7
15	1342.754	17.803	16.4
16	844.688	11.199	12.0
17	272.089	3.607	13.1
18	-343.318	-4.552	12.5
19	-364.973	-4.839	11.6

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

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xz-167-2, 04/11/04
Data Collected on: novas300-1-nova300
Archive directory: /nfs/nova300-1/d2/negishi/xzeng/vnmr sys/data
Sample directory:
File: PROTON
Pulse Sequence: szpu1

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

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XZ-467-2

INDEX	FREQUENCY	PPM	HEIGHT
1	10933.928	144.964	24.5
2	10769.077	142.779	23.7
3	10171.816	134.860	26.2
4	10094.713	133.898	24.5
5	9679.852	128.357	64.5
6	9672.064	128.235	66.1
7	9471.271	125.572	31.2
8	7078.466	93.848	20.2
9	6216.542	82.420	24.4
10	5839.658	77.423	93.7
11	5807.723	77.000	95.8
12	5775.789	76.577	94.5
13	3039.760	40.302	25.9
14	2966.704	39.333	26.0
15	2558.748	33.924	28.3
16	2395.068	31.754	28.1
17	2108.501	27.955	25.9
18	1949.116	25.842	90.6
19	1588.630	21.062	24.1
20	1382.500	18.064	27.7
21	1284.246	17.027	24.4
22	862.193	11.431	29.2
23	-338.659	-4.490	27.4
24	-353.620	-4.688	27.5

Efficient and Selective Synthesis of 6,7-Dehydrostipnamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

xz-478-2, 05/18/04
Data Collected on: inovas300-1-inovas300
Archive directory: /nfs/inovas300-1/42/negishi/xzeng/ymr/sys/data
Sample directory:
File: PROTON
Pulse Sequence: szpu1

Efficient and Selective Synthesis of 6,7-Dehydrostipianide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*

XZ-484-1

INDEX	FREQUENCY	PPM	HEIGHT
1	11149.414	147.821	17.5
2	10771.091	142.805	23.7
3	10586.677	140.360	20.1
4	10205.189	135.303	24.9
5	10049.832	133.243	19.7
6	10024.515	132.907	24.0
7	9878.701	128.382	64.1
8	9672.660	128.242	70.1
9	9466.106	125.530	27.5
10	7952.225	105.432	13.5
11	7899.864	104.798	18.0
12	7163.644	94.977	12.1
13	6237.832	82.702	19.6
14	5839.658	77.423	105.0
15	5807.723	77.000	107.1
16	5775.789	76.577	104.7
17	2973.609	39.425	24.1
18	2857.091	37.880	20.6
19	2557.598	33.909	24.0
20	2398.788	31.804	23.5
21	1952.281	25.884	13.7
22	1945.951	25.800	82.2
23	1592.946	21.120	22.4
24	1363.358	18.083	28.0
25	1336.031	17.713	20.7
26	923.185	12.240	22.3
27	893.284	11.843	25.6
28	3.701	0.049	72.7
29	-336.646	-4.463	25.9
30	-365.128	-4.841	26.4

Efficient and Selective Synthesis of 6,7-Dehydrostipamide via Zr-Catalyzed Asymmetric Carboalumination and Pd-Catalyzed Cross-Coupling of Organozincs

Xingzhong Zeng, Fanxing Zeng, and Ei-ichi Negishi*