Supporting Information
for DOI: 10.1055/s-0037-1609343
© Georg Thieme Verlag KG Stuttgart · New York 2018
Supporting Information

Stereoselective Allylation of Linear and Chiral β-Amino-α-Hydroxy Aldehydes: Total Syntheses of tetraacetyl α-lyxo-, α-ribo-, and α-arabino-Phytosphingosines

In-Soo Myeong, Jin-Seok Kim, Muyng-Gyu Park, Hwan-Hee Jeon, Changyoung Jung, Yong-Taek Lee, and Won-Hun Ham

whham@skku.edu

School of Pharmacy, Sungkyunkwan University, Seobu-ro 2066, Suwon-si, Gyeonggi-do 16419, Republic of Korea

Scheme 1. Preparation of desired aldehydes

(S)-tert-butyl 1-(tert-butylimidemethylsilyloxy)-3-oxopent-4-en-2-ylcarbamate (SI-1)
affording SI-1 as a crude oil; [α]D25 +2.1 (c 1.0, CHCl3); IR (neat) νmax 3020, 1718, 1500, 1217, 838, 769 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 6.56 (dd, J = 17.4, 10.6 Hz, 1H), 6.35 (d, J = 17.5 Hz, 1H), 5.83 (d, J = 10.6 Hz, 1H), 5.35 (d, J = 7 Hz, 1H), 4.60 (dt, J = 7.4, 3.6 Hz, 1H), 4.01 (dd, J = 10.2, 1.3 Hz, 1H), 3.86 (dd, J = 10.2, 4.3 Hz, 1H), 1.45 (s, 9H), 0.84 (s, 9H), −0.03−0.03 (m, 6H); 13C NMR (101 MHz, CDCl3) δ 196.9, 155.3, 133.2, 129.4, 79.8, 63.4, 59.5, 28.3, 32.5, 18.2, −5.6; HRMS (EI+) [(M+)+] m/z calcd for C₁₉H₃₁NO₄Si 329.2022; found 329.2019.

tert-butyl (2S,3R)-1-(tert-butylimidemethylsilyloxy)-3-hydroxypent-4-en-2-ylcarbamate (SI-2)
affording SI-2 as a crude oil; [α]D25 +2.4 (c 0.4, CHCl3); IR (neat) νmax 3020, 2360, 1716, 1500, 1217, 838, 769 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 6.58 (ddd, J = 17.1, 10.6, 4.9 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 5.13−5.24 (m, 2H), 4.15−4.24 (m, 1H), 3.86 (dd, J = 10.4, 2.9 Hz, 1H), 3.69 (dd, J = 10.4, 2.2 Hz, 1H), 3.53−3.58 (m, 1H), 3.40 (d, J = 8.4 Hz, 1H), 1.38 (s, 9H), 0.83 (s, 9H), −0.03−0.03 (m, 6H); 13C NMR (101 MHz, CDCl3) δ 155.8, 137.9, 115.9, 79.6, 74.9, 54.1, 28.4, ...

S1
(S)-benzyl 1-(tert-butyldimethylsilyloxy)-3-oxopent-4-en-2-ylcarbamate (SI-3)

affording SI-3 as a crude oil; \([\alpha]_D^{25} +1.8\) (c 1.0, CHCl_3); IR (neat) \(\nu_{\text{max}}\) 3020, 1715, 1500, 1254, 1217, 1110, 837, 769 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 7.24–7.33 (m, 5H), 6.58 (dd, \(J = 17.4, 10.5\) Hz, 1H), 6.37 (d, \(J = 17.4\) Hz, 1H), 5.86 (d, \(J = 10.6\) Hz, 1H), 5.81 (d, \(J = 7.1\) Hz, 1H), 5.13 (s, 2H), 4.67 (dt, \(J = 7.4, 3.7\) Hz, 1H), 4.05 (dd, \(J = 10.3, 3.1\) Hz, 1H), 3.89 (dd, \(J = 10.3, 4.4\) Hz, 1H), 0.84 (s, 9H), -0.02–0.02 (m, 6H); \(^13\)C NMR (101 MHz, CDCl_3) \(\delta\) 196.3, 155.8, 136.3, 133.0, 129.7, 128.5, 128.2, 128.1, 67.0, 63.3, 60.0, 25.8, 25.7, 18.2, -5.6; HRMS (EI+)) [M\(^+\)]\(^+\) m/z calcd for C\(_{16}\)H\(_{33}\)NO\(_3\)Si 331.2179; found 331.2182.

**b**enzyl (25,3R)-1-(tert-butyldimethylsilyloxy)-3-hydroxypent-4-en-2-ylcarbamate (SI-4)

affording SI-4 as a crude oil; [\(\alpha]_D^{25} +16.3\) (c 1.0, CHCl_3); IR (neat) \(\nu_{\text{max}}\) 3020, 2954, 2928, 2884, 2856, 2360, 1706, 1507, 1470, 1255, 1217, 1085, 1028, 835, 772, 697 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 7.30–7.41 (m, 5H), 5.88 (dd, \(J = 17.4, 10.5, 4.8\) Hz, 1H), 5.48 (d, \(J = 8.1\) Hz, 1H), 5.34 (d, \(J = 17.2\) Hz, 1H), 5.20 (d, \(J = 10.5\) Hz, 1H), 5.07 (s, 2H), 4.24 (br s, 1H), 3.91 (dd, \(J = 10.4, 1.8\) Hz, 1H), 3.62–3.74 (m, 2H), 3.29 (br s, 1H), 0.84 (s, 9H), 0.00 (m, 6H); \(^13\)C NMR (101 MHz, CDCl_3) \(\delta\) 156.2, 137.7, 136.4, 128.5, 128.1, 116.2, 66.8, 63.4, 54.5, 25.8, 18.1, -5.7; HRMS (EI+)) [(M\(^+\)+H\(^+\))]\(^+\) m/z calcd for C\(_{19}\)H\(_{29}\)NO\(_5\)Si 363.1866; found 363.1864.

(3S,4S)-4-(benzylloxycarboxylamino)-5-(tert-butyldimethylsilyloxy)pent-1-en-3-yl benzoate (SI-5)

affording SI-5 as a crude oil; [\(\alpha]_D^{25} +8.6\) (c 1.0, CHCl_3); IR (neat) \(\nu_{\text{max}}\) 3020, 2954, 2929, 2885, 2857, 1715, 1506, 1254, 1218, 1109, 1069, 837, 771, 712 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 8.03 (d, \(J = 7.7\) Hz, 2H), 7.56 (t, \(J = 7.6\) Hz, 1H), 7.43 (t, \(J = 7.6\) Hz, 2H), 7.21–7.28 (m, 5H), 5.91 (ddd, \(J = 17.1, 10.4, 6.6\) Hz, 1H), 5.72 (t, \(J = 6.4\) Hz, 2H), 5.41 (d, \(J = 17.2\) Hz, 1H), 5.31 (d, \(J = 10.5\) Hz, 1H), 5.09–5.18 (m, 1H), 5.03 (s, 2H), 4.06 (td, \(J = 9.3, 5.3\) Hz, 1H), 3.79 (dd, \(J = 10.1, 3.1\) Hz, 1H), 3.66 (dd, \(J = 10.1, 5.3\) Hz, 1H), 0.87 (s, 9H), -0.02–0.03 (m, 6H); \(^13\)C NMR (101 MHz, CDCl_3) \(\delta\) 165.6, 156.2, 136.3, 133.4, 133.1, 130.0, 129.7, 128.4, 128.3, 128.1, 119.3, 74.1, 68.9, 62.1, 55.0, 25.8, 18.2, -5.6; HRMS (EI+)) [(M\(^+\)+H\(^+\))]\(^+\) m/z calcd for C\(_{26}\)H\(_{35}\)NO\(_5\)Si 469.2284; found 469.2285.

benzyl (25,3S)-1-(tert-butyldimethylsilyloxy)-3-hydroxypent-4-en-2-ylcarbamate (SI-6)

affording SI-6 as a crude oil; [\(\alpha]_D^{25} +3.8\) (c 1.0, CHCl_3); IR (neat) \(\nu_{\text{max}}\) 3020, 2954, 2928, 2884, 2857, 2359, 1705, 1507, 1253, 1217, 1109, 1055, 1028, 835, 772 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl_3) \(\delta\) 7.22–7.31 (m, 5H), 5.79 (ddd, \(J = 17.0, 10.7, 5.3\) Hz, 1H), 5.24–5.34 (m, 2H), 5.13 (dt, \(J = 10.5, 1.3\) Hz, 1H) 4.99–5.08 (m, 2H), 4.42 (br s, 1H), 3.75–3.81 (m, 1H), 3.64 (dd, \(J = 7.5, 3.4\) Hz, 1H), 3.25 (br s, 1H), 0.83 (s, 9H), -0.01–0.02 (m, 6H); \(^13\)C NMR (101 MHz, CDCl_3) \(\delta\) 156.6, 137.3, 136.5, 128.5, 128.1, 128.0, 127.6, 127.0, 116.3, 73.1, 66.6, 65.3, 64.9, 54.9, 25.8, 18.1, -5.6; HRMS (EI+)) [(M\(^+\)+H\(^+\))]\(^+\) m/z calcd for C\(_{19}\)H\(_{31}\)NO\(_4\)Si 365.2022; found 365.2026.
OBn
NHCbz
TBSO
3
tetraacetyl D-lyxo-
Phosphingosine (13)
tetraacetyl D-lyxo-
Phosphingosine (13)
tetraacetyl o-ribo-Phtosphingosine (16)
tetraacetyl D-ribo-Phtosphingosine (16)
Tetraacetyl α-arabinobin-Phosphingosine (19)
tetracetyl-D-arabinophosphingosine (19)