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Stereoselective total synthesis of penaresidin A starting from D-galactal

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ABSTRACT

A stereoselective total synthesis of penaresidin A has been accomplished involving Sharpless asymmetric epoxidation, regioselective ring-opening of epoxide, azetidine formation via S_N2 reaction, Jung's protocol, and Julia–Kocienski olefination. This approach has successfully demonstrated the synthetic utility of D-galactal in the construction of azetidine core of the natural product.

Marine sponge is a rich source of various sphingosine derivatives. In particular, penaresidin A (**1**) and B (**2**) were isolated from Okinawan marine sponge *Penares* sp.[1] in 1991 as a mixture of the corresponding tetraacetyl derivatives (Fig. 1). They are known to behave as potent actomyosin ATPase activators. Penaresidin A constitutes an azetidine core which is separated from a hydroxy isobutyl subunit by a long alkyl chain. The absolute configuration of the five stereogenic centers was established as 2*S*,3*R*,4*S*,15*S* and 16*S* by spectroscopic methods[1,2] and subsequent synthetic studies.[3]

Following our interest on the total synthesis of natural products,[4] we herein report a concise approach for the total synthesis of penaresidin A (**1**) starting from 3,4,6-tri-*O*-benzyl-D-galactal. Our retrosynthetic analysis is shown in Scheme 1.

According to our approach, we envisaged that the target molecule could be accomplished from the intermediate **3** through a Julia–Kocienski olefination of aldehyde **4** with sulfoxide **5**. The azetidine core **4** was assumed to be accessed from amino alcohol **6** which could in turn be prepared from allyl alcohol **7,** derived from 3,4,6-tri-*O*-benzyl-D-galactal. The sulfoxide moiety **5** could be prepared from epoxy alcohol **8**, derived from nonanediol.

The synthesis of the key fragment **4** began with D-galactal. Accordingly, treatment of 3,4,6-tri-*O*-benzyl-D-galactal with $HgSO_4$ in the presence of aq H_2SO_4 in dioxane[5] at room temperature afforded the hydroxy-*trans*-enal exclusively which was then subjected to chemoselective reduction with $CeCl_3{\cdot}7H_2O/NaBH_4$ under Luche conditions[6] to furnish the allyl alcohol **7**. Asymmetric epoxidation of allyl alcohol **7** under Sharpless conditions[7] followed by ring opening of the epoxide with Red-Al gave triol **9** in 57% yield**.** Protection of triol **9** with 2,2-DMP in the presence of cat. *p*-TSA gave 1,3-acetonide **10**. The secondary hydroxyl group of **10** was protected as its mesylate and then converted into azide **11** using NaN_3 in DMF under reflux conditions. Reduction of azide with LAH followed by tosylation with tosyl chloride and triethylamine provided the tosyl derivative **12** in 90% yield. Removal of acetonide **12** using *p*-TSA in methanol followed by selective protection of the primary hydroxyl group with *tert*-butyldiphenylsilyl chloride afforded the TBDPS ether **6** in good yields. Conversion of free hydroxyl group of **6** as its mesylate using methanesulfonyl chloride in pyridine followed by cyclization with NaH gave azetidine **13** in 51% yield over two steps. Desilylation of **13** using TBAF followed by oxidation of the hydroxyl group with IBX in DMSO gave the key

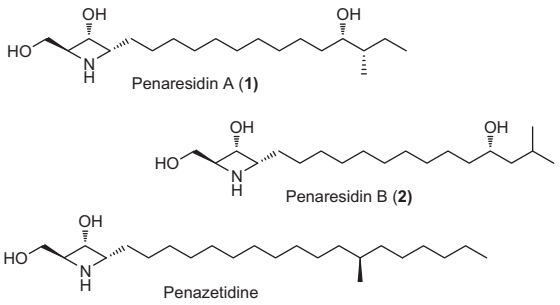

Figure 1. Representative examples of azetidine natural products.

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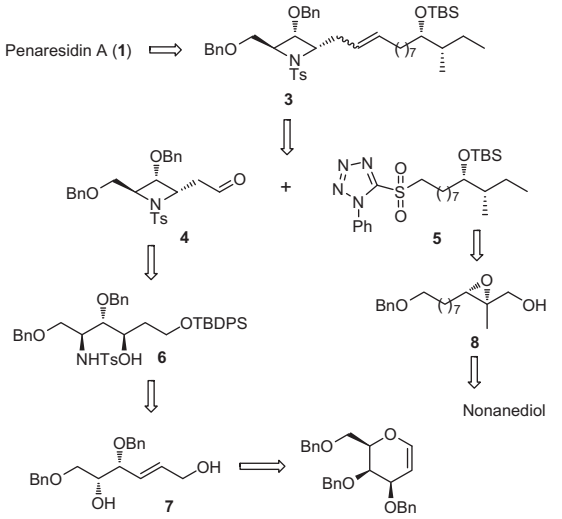
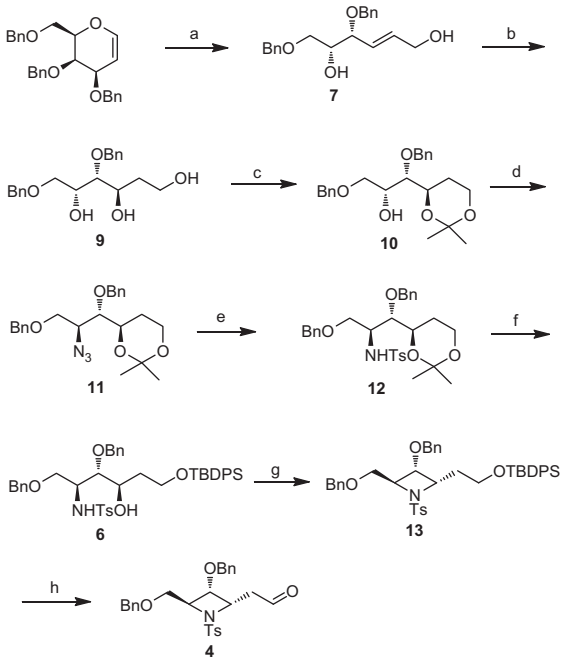


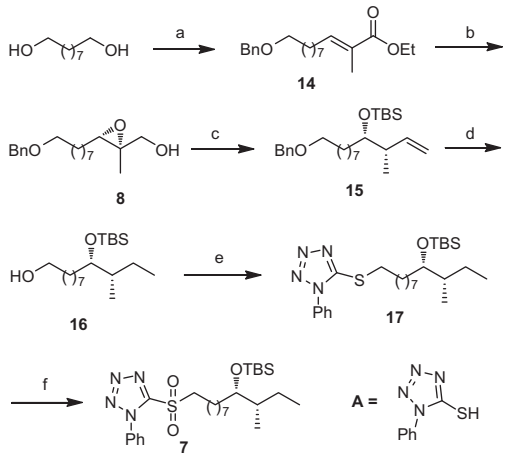
Scheme 1. Retrosynthetic analysis of penaresidin A.



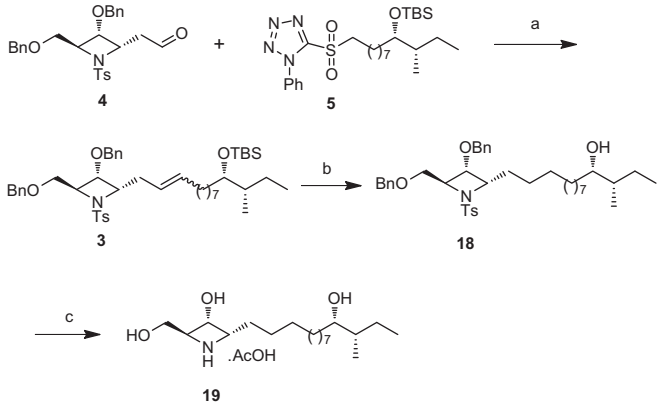
Scheme 2. Reagents and conditions: (a) (i) $HgSO_4$/aq H_2SO_4, dioxane, rt, 12 h, (ii) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, CH_3OH, 0 °C, 1 h, 65% two steps; (b) (i) (+)-DIPT, $Ti(O^iPr)_4$, TBHP, CH_2Cl_2, 4 Å MS, −20 °C, 6 h, (ii) Red-Al, THF, 0 °C, 8 h, 57% two steps; (c) 2,2-DMP, *p*-TSA, CH_2Cl_2, 4 h, 85%; (d) (i) MsCl, Et_3N, CH_2Cl_2, 0 °C, 4 h, (ii) NaN_3, DMF, 90 °C, 6 h, 75%; (e) (i) $LiAlH_4$, THF, 0 °C, (ii) TsCl, Et_3N, CH_2Cl_2, 0 °C, 3 h, 90%; (f) (i) *p*-TSA, CH_3OH, 0 °C, 1 h, (ii) TBDPSCl, imidazole, CH_2Cl_2, rt, 72%; (g) (i) MsCl, pyridine, 0 °C, (ii) NaH, THF, 0 °C, 51%; (h) (i) TBAF, THF, rt, 3 h, (ii) IBX, DMSO, CH_2Cl_2, 0 °C, 2 h, 56% two steps.

aldehyde **4**, which was used directly in Julia–Kocienski olefination (Scheme 2).

Another key fragment **5** was prepared from 1,9-nonanediol. Mono-protection of nonanediol as its benzyl ether followed by oxidation and a subsequent Wittig reaction with a stable ylide gave the 2,3-unsaturated ester **14** in 73% yield with *E*-stereoselectivity. The stereochemistry of olefin was confirmed by comparing the chemical shift value of methyl protons attached to olefinic carbon with previous reports.[8] Further treatment of ester **14** with DIBAL-H in CH_2Cl_2 gave the methyl substituted allylic alcohol, which was



Scheme 3. Reagents and conditions: (a) (i) NaH, BnBr, DMF, 0 °C–rt, 5 h, (ii) $(COCl)_2$, DMSO, Et_3N, −78 °C, (iii) $Ph_3P{=}C(CH_3)CO_2Et$, benzene, reflux, 6 h, 73%; (b) (i) DIBAL-H, CH_2Cl_2, 0 °C, (ii) (+)-DIPT, $Ti(O^iPr)_4$, TBHP, CH_2Cl_2, 4 Å MS, −20 °C, 4 h; (c) TBSOTf, DIPEA, MS 4 Å, −78 °C, 3 h, (ii) *n*-BuLi, Ph_3PCH_3Br, THF, −78 °C, 56%; (d) $Pd(OH)_2$, MeOH, H_2, 5 h, 90%; (e) A, Ph_3P, DIAD, THF, 0–rt, 3 h, 80%; (f) ammonium molybdate, H_2O_2, EtOH, 6 h, 85%.



Scheme 4. Reagents and conditions: (a) KHMDS, THF, −78 °C, 70%; (b) P-TSA, MeOH, rt; (c) (i) Pd/C, H_2, EtOH, 4 h, 85%, (ii) Na, naphthalene, DME, 0 °C.

then subjected to Sharpless asymmetric epoxidation[9] to afford the epoxy alcohol **8**. Protection of **8** with TBSOTf and DIPEA in DCM at −20 °C under Jung's conditions[10] afforded the aldehyde, which was further treated with a C1 ylide to give the terminal olefin **15**. Reduction of **15** with $Pd(OH)_2$/C afforded the alcohol **16** in 90% yield, which was then converted into thioester **17** using 1-phenyl-1*H*-tetrazole-5-thiol in the presence of TPP/DIAD. Oxidation of thioester with molybdenum salt and hydrogen peroxide gave sulfone **5** in 85% yield (Scheme 3).

Having both aldehyde and sulfone fragments in hand, we next attempted the Julia–Kocienski olefination using KHMDS as a base at −78 °C to give the olefin **3** in 70% yield. Desilylation of **3** with *p*-TSA in methanol gave alcohol **18** in 80% yield (Scheme 4). Treatment of **18** with 10% Pd/C under hydrogen atmosphere followed by treatment with Na/naphthalene and a subsequent salt formation with acetic acid gave the acetic acid salt of the target molecule **19** in 60% yield (Scheme 4). The spectral data of penaresidin A (**1**) were in good agreement with the data reported in the literature.[3e,11]

In conclusion, we have developed an efficient synthetic approach for the synthesis of penaresidin A starting from 3,4,6-tri-*O*-benzyl-D-galactal and 1,9-nonanediol. The key steps involved in this synthesis are Sharpless asymmetric epoxidation,

regioselective ring-opening of epoxide, S_N2 reaction for azetidine formation, Jung's protocol, and Julia–Kocienski olefination. The azedine core was constructed from the allyl alcohol **7**, which was in turn derived from D-galactal in two steps with 65% yield. The reactions involved in the azetidine formation, are highly stereoselective with no possibility of formation of other stereoisomers. The present synthetic approach involves 19 steps from D-galactal with 2.1% overall yield.

Acknowledgements

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11. *(R)-4-((1S,2S)-2-Azido-1,3-bis(benzyloxy)propyl)-2,2-dimethyl-1,3-dioxane (**11**):* $[\alpha]_D^{25}$ −1.0 (*c* 5.5, $CHCl_3$). IR (neat): *ν* 3063, 2989, 2868, 2097, 1455, 1375, 1270, 1104, 741, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.29 (m, 10H), 4.64 (s, 2H), 4.53 (d, *J* = 4.5 Hz, 2H), 3.98–3.43 (m, 7H), 1.67 (m, 1H), 1.46 (m, 1H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 137.8, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 98.3, 81.0, 74.2, 73.3, 69.5, 68.9, 61.5, 59.7, 29.7, 27.1, 18.8; ESI-MS [M+Na] 434; HRMS [M+Na] calcd for $C_{23}H_{29}O_4N_3Na$ 434.2050, found: 434.2043.
*(2S,3R,4S)-3-(Benzyloxy)-2-((benzyloxy)methyl)-4-(2-((tert-butyldiphenylsilyl)oxy) ethyl)-1-tosylazetidine (**13**):* $[\alpha]_D^{25}$ +16.9 (*c* 7.3, $CHCl_3$). IR (neat): *ν* 3282, 3066, 3031, 2927, 2857, 2097, 1596, 1455, 1331, 1160, 1107,740, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.67 (m, 5H), 7.42 (m, 5H), 5.12 (d, *J* = 7.7 Hz, 1H), 4.63 (m, 2H), 4.30 (d, *J* = 2.4 Hz, 2H), 3.81 (m, 2H), 3.69 (t, *J* = 5.2 Hz, 1H), 3.57 (m, 1H), 3.31 (m, 1H), 2.34 (s, 3H), 1.76 (m, 2H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 138.8, 129.5, 128.3, 127.8, 127.5, 113.8, 75.9, 74.9, 70.9, 70.7, 60.1, 55.2, 39.5, 36.0, 33.8, 32.0, 24.5, 22.6, 14.0. ESI-MS [M+H] 720; HRMS [M+H] calcd for $C_{43}H_{50}O_5NSSi$ 720.3173, found: 720.3172.
*(E)-Ethyl 11-(benzyloxy)-2-methylundec-2-enoate (**14**):* IR (neat): *ν* 2930, 2860, 1710, 1648, 1448, 1366, 1266, 1096, 1028, 742, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.31 (m, 5H), 6.76 (m,1H), 4.50 (s, 2H, 4.19) (q, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.19–2.12 (m, 2H), 1.82 (s, 3H), 1.60 (m, 2H), 1.43–1.28 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 169.0, 138.6, 133.2, 129.5, 128.2, 127.5, 127.4, 72.7, 70.3, 60.1, 34.3, 29.6, 29.2, 29.1, 28.9, 17.2, 14.2; ESI-MS [M+Na] 341.
*((2S,3S)-3-(8-(Benzyloxy)octyl)-2-methyloxiran-2-yl)methanol (**8**):* $[\alpha]_D^{25}$ −50 (*c* 0.3, $CHCl_3$); IR (neat): *ν* 3428, 2929, 2858, 1602, 1455, 1384, 1276, 1114, 1070, 713 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.33 (m, 5H), 4.51 (s, 2H), 3.63 (m, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.03 (t, *J* = 6.8 Hz, 1H), 1.60 (m, 4H), 1.34 (m, 10H, 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 132.7, 129.9, 128.2, 73.9, 67.3, 65.0, 62.6, 29.3, 29.1, 28.5, 26.7, 25.8. ESI-MS [M+Na] 329; HRMS [M+Na] calcd for $C_{19}H_{30}O_3Na$ 329.2087, found: 329.2084.
*(((3S,4S)-12-(Benzyloxy)-3-methyldodec-1-en-4-yl)oxy)(tert-butyl)dimethylsilane (**15**):* $[\alpha]_D^{25}$ −7 (*c* 1.7, $CHCl_3$). IR (neat): *ν* 3067, 2930, 2855, 1638, 1431, 1253, 1102, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.30 (m, 5H), 5.85 (m, 1H), 4.98 (m, 2H), 4.50 (s, 2H), 3.52 (m, 1H), 3.46 (t, *J* = 6.0 Hz, 2H), 1.61 (m, 2H), 1.32 (m, 12H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 141.7, '138.7, 128.3, 127.4, 113.6, 75.9, 72.8, 70.5, 42.7, 33.8, 29.7, 29.5, 29.4, 26.2, 25.9, 25.2, 18.2, 14.8, −4.3, −4.4; ESI-MS [M+Na] 441.
*(9S,10S)-9-((tert-Butyldimethylsilyl)oxy)-10-methyldodecan-1-ol (**16**):* $[\alpha]_D^{25}$ −2 (*c* 3.0, $CHCl_3$); IR (neat): *ν* 3339, 2930, 2857, 1464, 1381, 1252, 1056, 835, 773, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 3.64 (*J* = 6.6 Hz), 3.51 (m, 1H), 1.57 (m, 2H), 1.28 (m, 14H), 0.88 (s, 9H), 0.83 (m, 16H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 75.6, 63.1, 39.6, 36.6, 33.5, 32.8, 29.8, 29.6, 29.4, 27.1, 25.9, 25.2, 19.2, 18.2, 14.1, 13.8, 12.2, −4.2, −4.4. ESI-MS [M+H] 331.
5-(((9S,10S)-9-((tert-Butyldimethylsilyl)oxy)-10-methyldodecyl)thio)-2-phenyl-2H-tetrazole (17): $[\alpha]_D^{25}$ −3.5 (*c* 3.0, $CHCl_3$); IR (neat): *ν* 3090, 2929, 2855, 1597, 1500, 1463, 1385, 1250, 1053, 835, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.56 (m, 5H), 3.51 (m, 1H), 3.40 (t, *J* = 7.5 Hz, 2H), 1.82 (q, *J* = 5.5 Hz, 2H), 1.44 (m, 2H), 1.27 (m, 10H), 0.88 (s, *J* = 5.0 Hz, 9H), 0.83 (m, 6H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 154.4, 133.7, 129.9, 129.7, 123.8, 75.6, 39.6, 33.3, 33.5, 29.7, 29.4, 29.0, 28.6, 25.9, 25.8, 25.1, 18.1, 13.8, 12.2, −4.2, −4.5; ESI-MS [M+H] 491; HRMS [M+H] calcd for $C_{26}H_{47}ON_4SSi$ 491.3234, found: 491.3222.
*(2S,3R,4S)-3-(Benzyloxy)-2-((benzyloxy)methyl)-4-((11S,12S)-11-((tert-Butyldimethylsilyl)oxy)-12-methyltetradec-2-en-1-yl)-1-tosylazetidine (**3**):* $[\alpha]_D^{25}$ −15.0 (*c* 0.1, $CHCl_3$). IR (neat): *ν* 3448, 2925, 2854, 1461, 1259, 1159, 1093, 800, 772 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.68 (m, 2H), 7.24 (m, 12H), 6.16–5.64 (m, 1H), 5.52–4.86 (m, 1H), 4.49–4.35 (m, 4H), 4.19 (m, 1H), 3.67 (m, 1H), 3.45 (m, 2H), 2.55 (t, *J* = 6.6 Hz, 1H), 2.38 (s, 3H), 2.13–1.90 (m, 1H), 1.29 (s, 16H), 0.88 (s, 9H), 0.82 (m, 6H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.0, 136.5, 135.4, 133.8, 129.4, 129.0, 128.3, 127.7, 127.5, 127.4, 127.3, 127.2, 126.8, 125.1, 78.0, 75.6, 73.1, 72.2, 71.5, 70.5, 56.6, 39.6, 33.5, 32.7, 30.6, 29.8, 29.6, 29.5, 29.3, 29.1, 25.9, 25.2, 22.7, 21.5, 13.9, 12.3, −4.2, −4.4. ESI-MS [M+Na] 798.
*(3S,4S)-14-((2S,3R,4S)-3-(Benzyloxy)-4-((benzyloxy)methyl)-1-tosylazetidin-2-yl) -3-methyltetradec-12-en-4-ol (**18**):* $[\alpha]_D^{25}$ −13.3 (*c* 0.3, $CHCl_3$). IR (neat): *ν* 3486, 3030, 2927, 2866, 1598, 1495, 1453, 1337, 1155, 1093, 1047, 700, 676 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.67 (m, 2H), 7.24 (m, 12H), 6.12 (m, 1H), 5.96–5.66 (m, 1H), 5.49–5.19 (m, 1H), 4.41 (m, 4H), 4.18 (m, 1H), 3.93 (m, 1H), 3.71–3.36 (m, 3H), 2.39 (s, 2H), 2.11–1.93 (m, 2H), 1.33 (m, 16H), 0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.1, 138.0, 137.7, 137.9, 136.4, 135.4, 133.7, 129.4, 129.1, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.8, 121.6, 78.9, 74.9, 73.1, 72.2, 71.5, 70.5, 69.8, 68.6, 68.4, 68.2, 56.6, 39.9, 34.5, 32.6, 31.9, 29.6, 29.5, 29.3, 26.2, 22.6, 21.5, 14.1, 13.1, 11.8. ESI-MS [M+Na] 684; HRMS [M+Na] calcd for $C_{40}H_{55}NO_5SNa$ 684.3699, found: 684.3696.
*Penaresidine A acetic acid salt (**19**):* $[\alpha]_D^{25}$ −15.0 (*c* 0.25, $CHCl_3$); IR (neat): *ν* 3427, 2924, 2854, 1565, 1410, 1123, 654 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): *δ* 4.53–4.49 (m, 1H), 4.21–4.15 (m, 1H), 4.07–4.02 (m, 1H), 3.85–3.80 (m, 2H), 3.45–3.41 (m, 1H), 1.96–1.79 (m, 2H), 1.90 (s, 3H), 1.53–1.44 (m, 1H), 1.43–1.22 (m, 19H), 1.20–1.14 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD): *δ* 178.3, 75.5, 69.8, 66.6, 65.1, 60.0, 41.5, 35.4, 30.9, 30.8, 30.75, 30.7, 30.6, 30.5, 27.9, 27.5, 27.1, 26.2, 13.9, 12.3. ESI-MS: 330 [M+H]. HRMS (ESI): *m/z* [M+H] calcd for $C_{19}H_{40}NO_3$ 330.3008, found: 330.2994.