Bornanesultam-Directed Asymmetric Synthesis of Crystalline, Enantiomerically Pure Syn Aldols

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Supplement: Characterization Data for "BORNANESULTAM-DIRECTED ASYMMETRIC SYNTHESIS OF CRYSTALLINE, ENANTIOMERICALLY PURE 'SYN'-ALDOLS.

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N-Propionylbornane-10,2-sultam (2a).

$[\alpha]_{578}$ = -113.17°, $[\alpha]_{546}$ = -128.79°, $[\alpha]_{436}$ = -222.15°, $[\alpha]_{365}$ = -361.5° (c = 2.65). IR(CCl_4): 2960, 2950, 2880, 1710, 1340, 1260, 1220, 1140, 1050. ^{1}H-NMR: 0.95(*s*, 3H); 1.15(*s*, 3H); 1.15(*t*, *J* = 7.5, 3H); 1.30-1.45(2H); 1.80-1.95(3H); 2.05-2.15(2H); 2.66-2.78(2H); 3.41(*d*, *J* = 13.5, 1H); 3.47(*d*, *J* = 13.5, 1H); 3.84(*dd*, *J* = 5.0, 6.7, 1H). ^{13}C-NMR: 172.60(*s*), 65.20(*d*), 52.88(*t*), 48.43(*s*), 47.72(*s*), 44.61(*d*), 38.47(*t*), 32.78(*t*), 28.68(*t*), 26.42(*t*), 20.80(*q*), 19.85(*q*), 8.37(*q*); MS: 271(5, $C_{13}H_{21}NO_3S^{+\cdot}$), 216(10), 207(40), 192(40), 178(25), 164(45), 57(100). HR-MS: 271.1241 ($C_{13}H_{21}NO_3S^{+\cdot}$, calc. 271.1242).

N-Butanoylbornane-10,2-sultam (2g).

$[\alpha]_{578}$ = -99.9°, $[\alpha]_{546}$ = -113.8°, $[\alpha]_{436}$ = -195.7°, $[\alpha]_{365}$ = -316.7°. (*c* = 0.84). IR(CCl_4): 2980, 1710, 1340, 1220, 1140. ^{1}H-NMR: 0.93(*s*, 3H); 0.94(*t*, *J* = 7.5, 3H); 1.13(*s*, 3H); 1.30-1.42(2H); 1.63-1.75(2H); 1.82-1.96(3H); 2.02-2.16(2H); 2.60-2.76(2H); 3.41(*d*, *J* = 13.5, 1H); 3.52(*d*, *J* = 13.5, 1H); 3.87(*dd*, *J* = 5.5, 7.5, 1H). ^{13}C-NMR: 171.87(*s*), 65.16(*d*), 52.93(*t*), 48.31(*s*), 47.70(*s*), 44.61(*d*), 38.51(*t*), 37.27(*t*), 32.81(*t*), 26.41(*t*), 20.78(*q*), 19.85(*q*), 17.89(*t*), 13.49(*q*); MS: 285(5, $C_{14}H_{23}NO_3S^{+\cdot}$), 257(10), 206(20), 193(25), 178(25), 134(25), 108(28), 93(25), 71(100), 67(15), 55(32); HR-MS: 285.1385 ($C_{14}H_{23}NO_3S^{+\cdot}$, calc. 285.1399).

N-Hexanoylbornane-10,2-sultam (2j).

$[\alpha]_{578}$ = -88.57°, $[\alpha]_{546}$ = -100.67°, $[\alpha]_{436}$ = -172.55°, $[\alpha]_{365}$ = -278.64°; (c = 1.33). IR(CCl_4): 2960, 2930, 2880, 1700, 1340, 1260, 1210, 1140. ^{1}H-NMR: 0.85(*t*, 3H); 0.93(*s*, 3H); 1.14(*s*, 3H); 1.26-1.42(5H); 1.56-1.72(3H); 1.80-1.94(3H); 2.02-2.16(2H); 2.62-2.78(2H); 3.41(*d*, *J* = 13.5, 1H); 3.52(*d*, *J* = 13.5, 1H); 3.87(*dd*, *J* = 5.5, 7.5, 1H). ^{13}C-NMR: 172.10(*s*), 65.22(*d*), 52.95(*t*), 48.34(*s*), 47.73 (*s*), 44.64(*d*), 38.52(*t*), 35.46(*t*), 32.83(*t*), 31.10(*t*), 26.43(*t*), 24.13(*t*), 22.33(*t*), 20.816(*q*), 19.89(*q*), 13.89(*q*). MS: 314 (1, [$C_{16}H_{27}NSO_3^{+\cdot}$+1]), 313(1), 312(0.5), 257(40), 135(50), 99(100), 71(55); HR-MS. 313.1691 ($C_{16}H_{27}SO_3N^+$, calc. 313.1712).

N-*[(2R,3R)-2-Methyl-3-hydroxy-3-phenyl-propanoyl]bornane-10,2-sultam* (3a).

$[\alpha]_{578}$ = -101.5°, $[\alpha]_{546}$ = -115.9°, $[\alpha]_{436}$ = -205.1°, $[\alpha]_{365}$ = -344.3° (*c* = 0.65). IR(CCl_4): 3550, 2970, 1680, 1340, 1230, 1130. ^{1}H-NMR: 0.97(*s*, 3H); 1.14(*d*, *J* = 7, 3H); 1.15(*s*, 3H); 1.30-1.48(2H); 1.88-1.95(3H); 2.05-2.16(2H); 3.38(*dq*, *J* = 2.5, 7.5, 1H); 3.47(*d*, *J* = 14.0, 1H); 3.52(*d*, *J* = 14.0, 1H); 3.63(*d*, *J* = 1.7, 1H, D_2O exchangeable); 3.92 (*t*, *J* = 6.5, 1H); 5.2(*d*, *J* = 2.5, 1H); 7.23-7.45(5H). ^{13}C-NMR: 177.08(*s*), 140.93(*s*), 128.16(2C,*d*), 127.25(*d*), 126.09(2C,*d*), 72.06(*d*), 64.96(*d*), 53.03(*t*), 48.45(*s*), 47.77(*s*), 45.93(*d*), 44.64(*d*), 38.30(*t*), 32.83(*t*), 26.41(*t*), 20.84(*q*), 19.85(*q*), 10.84(*q*). MS: 271(5, $C_{20}H_{27}NSO_4$-$C_7H_7O^{+\cdot}$), 135(25), 105(40), 93(20), 77(50), 67(15), 57(100). *O*-TBDMS-derivative 7a: HR-MS: 434.1825 ($C_{26}H_{41}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 434.1829).

N-*[(2R-3S)-3-Hydroxy-2-methylbutanoyl]bornane-10,2-sultam* (3b).

$[\alpha]_{578}$ = -88.5°, $[\alpha]_{546}$ = -100.7°, $[\alpha]_{436}$ = -171.7°, $[\alpha]_{365}$ = -273.5° (*c* = 0.67). IR(CCl_4): 3550, 2970, 1680, 1340, 1230, 1130. ^{1}H-NMR: 0.94(*s*,3H); 1.12(*s*,3H); 1.16(*d*,*J* = 7.5,3H); 1.25(*d*,*J* = 7.5,3H); 1.30-1.44(2H); 1.85-1.96(3H); 2.02-2.06(2H); 3.01(*dq*, *J* = 3.0, 7.5, 1H);

3.08(*d*, br, 1H); 3.46(*d*, *J* = 14.0, 1H); 3.52(*d*, *J* = 14.0, 1H); 3.90(*t*, *J* = 6.5, 1H,); 4.18(*m*, 1H). ^{13}C-NMR: 177.15(*s*), 66.66(*d*), 64.93(*d*), 53.03(*t*), 48.36(*s*), 47.76(*s*), 45.03(*d*), 44.57(*d*), 38.29(*t*), 32.80(*t*) 26.41(*t*), 20.78(*q*), 19.84(*q*), 19.74(*q*), 11.23(*q*). MS: 271(5, $C_{15}H_{25}NSO_4$-$C_2H_6O^{+\cdot}$), 135(25), 105(40), 93(20), 77(50), 67(15), 57(100). *O*-TBDMS-derivative 7b: HR-MS: 372.1663 ($C_{21}H_{39}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 372.1666).

N-*[(2R,3S)-3-Hydroxy-2-methylpentanoyl]bornane-10,2-sultam* (3c). $[\alpha]_{578}$ = -103.6°, $[\alpha]_{546}$ = -117.8°, $[\alpha]_{436}$ = -200.3°, $[\alpha]_{365}$ = -318.6°; (c=1.06). IR: 3635, 3620-3300, 3000, 2965, 2940, 2885, 1675, 1455, 1413, 1335, 1265, 1165, 1133, 1110, 1060. ^{1}H-NMR: 0.94(*t*, *J* = 7.5, 3 H); 0.96(*s*, 3H); 1.14(*s*, *3H); 1.23(d*, *J* = 7.5, 3 H); 1.3-1.46(3H); 1.54(*m*, 1H); 1.8-1.97(3H); 2.0-2.06(2H); 3.06(*dq*, *J* = 3, 7.5, 1H, irradiation at 1.23 → *d*, *J* = 3); 3.12(*s*, 1H, disappears with D_2O); 3.42(*d*, *J* = 13.5, 1 H); 3.50 (*d*, *J* = 13.5, 1 H); 3.84(*m*, 1H); 3.86(*t*, *J* = 6.5). ^{13}C-NMR: 177.26(*s*), 72.03(*d*), 64.86(*d*), 53.03(*t*), 48.31(*s*), 47.70(*s*), 44.54(*d*), 43.41(*d*), 38.24(*t*), 32.76(*t*), 26.63(*t*), 26.37(*t*), 20.76(*q*), 19.81(*q*), 11.21(*q*), 10.27(*q*). MS: 271(11, $C_{16}H_{27}NO_4S^{+\cdot}$ - C_2H_5CHO), 216(12), 151(41), 135(80), 108(34), 107(33), 93(46), 91(25), 79(32), 77(18), 69(46), 59(55), 57(100), 55(46), 45(43).

N-*[(2R,3S)-3-Hydroxy-2,4-dimethylpentanoyl]bornane-10,2-sultam* (3d). $[\alpha]_{578}$ = -87.2°, $[\alpha]_{546}$ = -99.2°, $[\alpha]_{436}$ = -169.2°, $[\alpha]_{365}$ = -268.6° (*c* = 0.77). IR(CCl_4): 3550, 2970, 1680, 1340, 1230, 1130. ^{1}H-NMR(200MHz): 0.87(*d*, *J* = 7.5, 3H); 0.97(*s*, 3H); 1.01(*d*, *J* = 7.5, 3H); 1.14(*s*, 3H); 1.22(*d*,*J* = 7.5, 3H); 1.28-1.46(2H); 1.70(*m*, 1H); 1.86-2.06(5H); 3.25(*d*, *J* = 2.5, 1H); 3.27(*dq*, *J* = 2.4, 7.5, 1H); 3.50(d, *J* = 14.0, 1H); 3.44(d, *J* = 14.0, 1H); 3.53(*m*, 1H); 3.88(*t*, *J* = 6.5, 1H). ^{13}C-NMR: 177.55(*s*), 75.80(*d*), 64.89(*d*), 53.05(*t*), 48.38(*s*), 47.76(*s*), 44.58(*d*), 41.07(*d*), 38.31(*t*), 32.83(*t*), 30.35(*d*), 26.42(*t*), 20.80(*q*), 19.85(*q*), 19.06(*q*),

18.90(*q*), 11.16(*q*); MS: 300(3, $C_{17}H_{29}NSO_4^{+\cdot}$-*i*Pr), 271(5), 216(15), 135(40), 108(20), 93(30), 83(25), 67(25), 57(100). *O*-TBDMS-derivative 7d: HR-MS: 400.1990 ($C_{23}H_{43}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 400.1980).

N-[(E)-(2R,3S)-2-Methyl-3-hydroxy-4-hexenoyl]bornane-10,2-sultam (3e).

$[\alpha]_{578}$ = -97.5°, $[\alpha]_{546}$ = -111.7°, $[\alpha]_{436}$ = -190.9°, $[\alpha]_{365}$ = -307.1° IR(CCl_4) 3550, 3025-2890, 1675, 1340, 1230, 1130. ^{1}H-NMR: 0.97(*s*, 3H); 1.15(*s*, 3H); 1.25(*d*, *J* = 7.5, 3H); 1.30-1.48(2H); 1.72(*dt*, *J* = 7.0, 1.5, 3H); 1.85-2.0(3H); 2.05-2.10(2H); 3.12(*s*, br, 1H, D_2O exchangeable); 3.15(*dq*, *J* = 3.0, 7.5, 1H); 3.53(*d*, *J* = 13.5, 1H); 3.49(*d*, *J* = 13.5, 1H); 3.92(*t*, *J* = 6.5, 1H); 4.49(*m*, 1H); 5.51(*m*, 1H); 5.80(*m*, 1H). ^{13}C-NMR: 176.56(*s*), 129.97(*d*), 128.06(*d*), 71.44(*d*), 64.90(*d*), 53.03(*t*), 48.31(*s*), 47.7(*s*), 44.66(*d*), 44.53(*d*), 38.24(*t*), 32.75(*t*), 26.37(*t*), 20.75(*q*), 19.80(*q*), 17.72(*q*), 11.83(*q*); MS: 271(5, $C_{17}H_{27}NO_4S$-$C_4H_6O^{+\cdot}$), 135(25), 105(40), 93(20), 77(50), 67(15), 57(100). *O*-TBDMS-derivative 7e: HR-MS: 398.1829 ($C_{23}H_{41}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 398.1823).

N-[(2R,3R)-2-Methyl-3-hydroxy-3-(4-methoxyphenyl)-propanoyl]bornane-10,2-sultam (3f).

$[\alpha]_{578}$ = -97.4°, $[\alpha]_{546}$ = -111.6°, $[\alpha]_{436}$ = -198.7°, $[\alpha]_{365}$ = 337.2° (c = 0.86). IR 3500(br), 3010, 2950, 1670, 1515, 1335. ^{1}H-NMR: 0.96(*s*, 3H); 1.12(*s*, 3H); 1.13(*d*, *J* = 7.5, 3H); 1.30-1.46(2H); 1.86-1.98(3H); 2.05-2.10(2H); 3.35(*dq*, *J* = 2.5, 7.5, 1H); 3.48(*d*, *J* = 13.5, 1H); 3.52(*s*, 1H); 3.55(*d*, *J* = 13.5, 1H); 3.80(*s*, 3H); 3.94(*t*, *J* = 6.5, 1H); 5.15(*s*, *br*, 1H); 6.88-6.92(2H); 7.32-7.38(2H). ^{13}C-NMR: 177.0(*s*), 158.8(*s*), 133.15(*s*), 127.3(*d*,2C), 113.55(*d*,2C), 71.85(*d*), 64.95(*d*), 55.24(*q*), 53.03(*t*), 48.4(*s*), 47.8(*s*), 46.07(*d*), 44.61(*d*), 38.3(*t*), *32.81*(*t*), 26.41(*t*), 20.83(*q*), 19.84(*q*), 11.04(*q*). MS: 271(10, $C_{21}H_{29}SO_5N$-$C_8H_8O^{+\cdot}$), 207(20), 135(55), 77(59), 57(100). *O*-TBDMS-derivative 7f: HR-MS: 464.1946 ($C_{21}H_{43}NO_5SiS$-$C_4H_9^{+\cdot}$, calc. 464.1937).

N-[(2R,3S)-2-Hydroxybenzyl-butanoyl]bornane-10,2-sultam (3g).

$[\alpha]_{578}$ = -90.78°, $[\alpha]_{546}$ = -104.78°, $[\alpha]_{436}$ = -187.15°, $[\alpha]_{365}$ = -321.23°, IR: 3530, 2980, 1675, 1340, 1230,1130. ^{1}H-NMR: 0.82(*t*, *J* = 7.5, 3H); 0.99(*s*, 3H); 1.18(*s*, 3H); 1.32-1.52(3H); 1.84-2.00(4H); 2.14-2.18(2H); 3.38(*m*, 1H); 3.55(*d*, *J* = 13.5, 1H); 3.61(*d*, *J* = 13.5, 1H); 3.58(*d*, *J* = 2.0, 1H); 4.02(*t*, *J* = 6.0, 1H); 5.22(*s*, br, 1H); 7.27-7.48(5H). ^{13}C-NMR: 176.60(*s*), 140.97(*s*), 128.04(2C,*d*), 127.09(*d*), 125.98(2C,*d*), 71.69(*d*), 65.30(*d*), 53.18(*t*), 52.68(*d*), 48.23(*s*), 47.72(*s*), 44.70(*d*), 38.52(*t*), 32.96(*t*), 26.36(*t*), 20.79(*q*), 19.87(*q*), 19.10(*t*), 11.42(*q*); MS: 285(3, $C_{21}H_{29}NSO_4$-$C_7H_6O^{+\cdot}$), 257(2), 149(11), 135(25), 105(47), 77(88), 71(100), 55(39). *O*-TBDMS-derivative 7g: HR-MS: 448.1967 ($C_{27}H_{43}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 448.1979).

N-[(2R,3S)-2-Ethyl-3-hydroxylbutanoyl]bornane-10,2-sultam (3h).

$[\alpha]_{578}$ = -127.34°, $[\alpha]_{546}$ = -141.66°, $[\alpha]_{436}$ = -240.88°, $[\alpha]_{365}$ = -388.02°, (*c* = 0.384). IR: 3520, 2980, 2880, 1670, 1340. ^{1}H-NMR: 0.90(*t*, *J* = 7.5, 3H); 0.92(*s*, 3H); 1.12(*s*, 3H); 1.19(*d*, *J* = 6.5, 3H); 1.28-1.31(2H); 1.70-1.94(5H); 2.06-2.08(2H); 2.80(*d*, *J* = 2.0, 1H, D_2O exchangeable); 3.03(*m*, 1H); 3.45(*d*, *J* = 14.0, 1H); 3.51(*d*, *J* = 14.0, 1H); 3.92(*t*, *J* = 6.0, 1H); 4.11(*m*, 1H). ^{13}C-NMR: 175.87(*s*), 67.14(*d*), 65.35(*d*), 53.22(*t*), 52.04(*d*), 48.02(*s*), 47.68(*s*), 44.63(*d*), 38.56(*t*), 32.92(*t*), 26.35(*t*),20.76(*q*), 20.65(*t*), 19.84(2C,*q*), 11.57(*q*). MS: 329 ($C_{16}H_{27}NSO_4^{+\cdot}$ not observed), 285(4), 216(4), 151(48), 135(73), 108(47), 93(53), 76(36), 71(100), 69(79), 55(92). *O*-TBDMS-derivative 7h: HR-MS: 386.1819 ($C_{22}H_{41}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 386.1823).

N-[(2R,3S)-2-Ethyl-3-hydroxy-4-methylpentanoyl]bornane-10,2-sultam (3i).

$[\alpha]_{578}$ = -149.3°, $[\alpha]_{546}$ = -173.15°, $[\alpha]_{436}$ = -299.1°, $[\alpha]_{365}$ = -487.6°,(*c* = 0.32). IR: 3530, 2980-2880, 1680, 1340. ^{1}H-NMR: 0.86(*d*, *J* =

7.0, 3H); 0.90(*t*, *J* = 7.5, 3H); 0.94(*s*, 3H); 0.98(*d*, *J* = 6.5, 3H); 1.14(*s*, 3H); 1.30-1.44(2H); 1.62-1.78(2H); 1.82-1.98(4H); 2.06-2.10(2H); 3.12(*d*, *J* = 2.0, 1H, D_2O exchangeable); 3.28(*m*, 1H); 3.47(*d*, *J* = 13.5, 1H); 3.51(*d*, *J* = 13.5, 1H); 3.50(*m*, 1H); 3.92(*t*, *J* = 6.0,1H). ^{13}C-NMR: 107.02(*s*), 75.64(*d*), 65.22(*d*), 53.17(*t*), 48.14(*s*), 47.74(*s*), 47.70(*d*), 44.60(*d*), 38.50(*t*), 32.93(*t*), 30.69(*d*), 26.37(*t*), 20.71(*q*), 19.85(*q*), 19.45(*t*),19.35(*q*), 18.86(*q*), 11.54(*q*); MS: 356($C_{18}H_{31}NSO_4^{+\cdot}$ not observed), 314(2), 285(50), 216(24), 151(20), 135(78), 107(32), 93(34), 71(100), 55(87). *O*-TBDMS-derivative 7i: HR-MS: 414.2113 ($C_{24}H_{45}NO_4SiS$-$C_4H_9^{+\cdot}$, calc. 414.2136).

N-*[(2R,3R)-2-Hydroxybenzyl-hexanoyl]bornane-10,2-sultam* (3j).

$[\alpha]_{578}$ = -92.9°, $[\alpha]_{546}$ = -107.0°, $[\alpha]_{436}$ = -194.3°, $[\alpha]_{365}$ = -339.4°; (*c* = 0.62). IR($CHCl_3$): 3550, 2970, 1680, 1340, 1230, 1130. ^{1}H-NMR: 0.76(*t*, *J* = 7.0, 3H); 1.05-1.50(8H); 1.00(*s*, 3H); 1.19(*s*, 3H); 1.85-2.00(4H); 2.12-2.20(2H); 3.46(*m*, 1H); 3.52(*d*, *J* = 14.0, 1H); 3.47(*d*, *J* = 14.0, 1H); 4.02(*t*, *J* = 6.5, 1H); 5.24(*s*, br, 1H); 7.35-7.50(5H). ^{13}C-NMR: 176.8(*s*), 140.98(*s*), 128.09(*d*), 127.09(*d*), 125.97(*d*), 71.74(*d*), 65.32(*d*), 53.23(*t*), 51.34(*d*), 48.32(*s*), 47.76(*s*), 44.73(*d*), 38.51(*t*), 32.99(*t*), 29.20(*t*), 26.41(*t*), 25.52(*t*), 22.57(*t*), 20.72(*q*), 19.89(*q*), 13.76(*q*); MS: 419(0.5, $C_{23}H_{33}NSO_4^{+\cdot}$), 355(0.6), 313(8), 257(35), 135(60), 99(100), 77(70).

N-*[(2S,3R)-2-Methyl-3-hydroxy-3-phenylpropanoyl]bornane-10,2-sultam* (5a).

$[\alpha]_{578}$ = -24.4°, $[\alpha]_{546}$ = 26.9°, $[\alpha]_{436}$ = -36.1°, $[\alpha]_{365}$ = -40.1°; (c = 1.04). IR: 3000-2800, 1690, 1220, 780. ^{1}H-NMR: 0.78(*s*, 3H); 0.9(*s*, 3H); 1.25 (*d*, *J* = 7, 3H); 1.2-1.4(2H); 1.7 - 2.0(5H); 2.45(*d*, *J* = 3, 1H); 3.39(*d*, *J* = 14, 1H); 3.43(*d*, *J* = 14, 1H); 3.5(*quintet*, *J* = 6, 1H); 4.96(*dd*, *J* = 5.5, 3, 1H); 7.25-7.43(5H). ^{13}C-NMR: 174.46(*s*), 141.23(*s*), 128.23(*d*,2C), 127.79(*d*), 126.68(*d*,2C), 75.41(*d*), 65.12(*d*), 53.08(*t*),

48.19(*s*), 47.57(*s*), 47.20(*d*), 38.24(*t*), 32.89(*t*), 26.39(*t*) 20.68(*q*), 19.78(*q*) 11.85(*q*). MS: (0.5, $C_{20}H_{27}NO_4S^{+\cdot}$), 271 (38), 135 (100), 107(40), 79(35).

N-*[(2S,3R)-3-hydroxy-2,4-dimethylpentanoyl]bornane-10,2-sultam* (5d).

$[\alpha]_{578}$= -61°, $[\alpha]_{546}$= -67.8°, $[\alpha]_{436}$= -111°, $[\alpha]_{365}$= -170°; (*c* = 0.09, T = 22.5°C). IR: 3000-2800, 1700, 1460, 1220, 750. ^{1}H-NMR: 0.85(*d*, *J*= 7, 3H); 0.9(*s*, 3H); 0.93(*d*, *J* = 7, 3H); 1.03 (*s*, 3H); 1.1(*d*, *J* = 7, 3H); 1.23-1.4(2H); 1.61(*sextet*, *J* = 7, 1H); 1.8-1.9((2H); 1.99-2.02(2H); 2.26(*d*, *J* = 4.0, 1H); 3.3(*dq*, *J* = 4.0, 7.0, 1H); 3.48(*d*, *J* = 14.0, 1H); 3.43(*d*, *J* = 14.0, 1H); 3.48(*m*, 1H); 3.87(*t*, *J* = 6.0, 1H). ^{13}C-NMR: 176.12(*s*), 77.55(*d*), 65.11(*d*), 53.12(*t*), 48.34(*s*), 47.77(*s*), 44.61(*d*), 42.20(*d*), 38.50(*t*), 32.85(*t*), 31.10(*d*), 26.43(*t*), 20.82(*q*), 19.86(*q*), 19.12(*q*), 18.27(*q*), 10.05(*q*). MS: 300(20, $C_{17}H_{29}NO_4S$ - $C_3H_7+\cdot$), 271(30), 216(60), 135(100), 108(25), 93(30), 73(20), 57(40). HR-MS: 300.1270 ($C_{17}H_{29}NO_4S$ - $C_3H_7^{+\cdot}$, calc. 300.1269).

[(2S,3R)-3-hydroxy-2-methylhexanoyl]bornane-10,2-sultam (5k).

$[\alpha]_{578}$ = -50.6°, $[\alpha]_{546}$ = -56.5°, $[\alpha]_{436}$ = -94°, $[\alpha]_{365}$ = -145°; (c = 1.52). IR: 3000-2880, 1685, 1455, 1335, 1265. ^{1}H-NMR: 0.90(*t*, *J* = 7, 3H); 0.96(*s*, 3H); 1.15(*s*, 3H); 1.17(*d*, *J* = 7, 3H); 1.27-1.58(6H); 1.82-1.96(3H); 2.03-2.08(2H); 2.32(*d*, *J* = 4, 1H); 3.15(*dq*, *J* = 4, 7, 1H); 3.4(*d*, *J* = 14, 1H); 3.53(*d*, *J* = 14, 1H); 3.84(*m*, 1 H); 3.88(*t*, *J* = 6.5, 1H). ^{13}C-NMR: 175.48(*s*), 72.45(*d*), 65.14(*d*), 53.08(*t*), 48.26(*s*), 47.68(*s*), 44.65(*d*), 44.57(*d*), 38.46(*t*), 36.19(*t*), 32.84(*t*), 26.37(*t*), 20.78(*q*), 19.82(*q*), 19.82(*q*), 18.96(*t*), 13.90(*q*), 10.35(*q*). MS: 328(4, $C_{17}H_{30}NO_4S$ - $CH_3^{+\cdot}$), 310(1), 300(5), 271(40), 216(25), 151(70), 135(100), 108(42), 93(50), 57(98). HR-MS: 344.1954 ($C_{17}H_{30}NSO_4+\cdot$, calc. 344.1895).

N-*[(2S,3R-)2-methyl-3-hydroxy-(E)-4-hexenoyl]bornane-10,2-sultam* (5e).

IR: 3000-2860, 1680, 1455, 1330, 1265. ^{1}H-NMR: 0.98(*s*, 3H); 1.18(*s*, 3H); 1.22(*d*, *J* = 7, 3H); 1.3-1.46(2H); 1.68(*dd*, *J* = 6.5, 1.5, 1H); 1.84-2.0(3H); 2.0-2.13(2H); 2.18(*d*, *J* = 3.5, 1H); 3.25(*quintet*, *J* = 6.5, 1H); 3.44(*d*, *J* = 14, 1H); 3.53(*d*, *J* = 14, 1H); 3.9(*m*, 1H); 4.25(*m*, 1H); 5.53(*m*, 1H); 5.73(*m*, 1H). ^{13}C-NMR: 174.16(*s*), 130.36(*d*), 129.13(*d*), 74.88(*d*), 65.17(*d*), 53.14(*t*), 48.19(*s*), 47.64(*s*), 45.75(*d*), 44.62(*d*), 38.27(*t*), 32.82(*t*), 26.39(*t*), 20.68(*q*), 19.85(*q*), 17.71(*q*), 11.98(*q*). MS: 341(20, $C_{17}H_{27}NO_4S^{+\cdot}$), 323(50), 284(30), 271(25), 207(10), 151(20), 135(50), 108(35, 93(25), 57(100). HR-MS: 341.1701 ($C_{17}H_{27}NO_4S^{+\cdot}$, calc. 341.1661).

N-*[(2S,3R)-2-hydroxybenzyl-butanoyl]bornane-10,2-sultam* (5g)

$[\alpha]_{578}$ = -33.5°, $[\alpha]_{546}$ = -37.2°, $[\alpha]_{436}$ = -45.5°, $[\alpha]_{365}$ = -55.1°; (c = 0.96). IR: 3620, 3540, 2970, 2890, 1693, 1680, 1350, 1220, 1140. ^{1}H-NMR: 0.80(*t*, *J* = 7.5, 3H); 0.87(*s*,6H); 1.16-1.50(4H); 1.72-1.94(4H); 1.98(*m*, 1H); 2.42(*d*, *J* = 2.5, 1 H); 3.4(*d*, *J* = 14, 1 H); 3.42(*m*, 1 H)); 3.47(*d*, *J* = 14, 1 H); 3.85(*m*, 1H); 5.06 (*dd*, *J* = 2.5, 4.5, 1H); 7.25-7.43(5H). ^{13}C-NMR: 173.54(*s*), 141.12(*s*), 128.16(*d*,2C), 127.62(*d*), 126.43(*d*,2C), 74.46(*d*), 65.14(*d*), 54.09(*d*), 53.24(*t*), 48.20(*s*), 47.66(*s*), 44.55(*d*), 38.42(*t*), 32.83(*t*), 26.44(*t*), 20.73(*q*), 19.82(*q*), 18.92(*t*), 11.64(*q*). MS: 392(1, $C_{21}H_{29}NSO_4^{+\cdot}$), 374(3), 285(23), 270(5), 135(100), 107(60), 79(55), 71(35), 55(40). HR-MS: 373.1682 ($C_{21}H_{29}NSO_4$ - $H_2O^{+\cdot}$, calc. 373.1711).

N-*[(2S,3R)-2-Ethyl-3-hydroxy-4-methylpentanoyl]bornane-10,2-sultam* (5i).

$[\alpha]_{578}$ = -64.1°, $[\alpha]_{546}$ = -72.5°, $[\alpha]_{436}$ = -118.3°, $[\alpha]_{365}$ = -175.5° (c = 1.31). IR: 2880-3000, 1675, 1470, 1335, 1275. ^{1}H-NMR: 0.93(*d*, *J* = 6.5, 3H); 0.95(*t*, *J* = 7.5, 3H); 0.98(*s*, 3H); 1.02(*d*, *J* = 6.5, 3H); 1.16(*s*, 3H); 1.31-1.48(2H); 1.57(*m*, 1H); 1.73(*m*, 1H); 1.8-1.98(4H); 2.05-2.11(2H); 2.20(*d*, *J* = 3.5, 1H); 3.30(*m*, 1H); 3.44(*m*, 1H); 3.45(*d*, *J* = 14, 1H); 3.53(*d*, *J* = 14, 1H); 3.94(*t*, *J* = 6.5, 1H). ^{13}C-NMR: 175.15(*s*), 77.51(*d*),

65.05(*d*), 53.17(*t*), 49.73(*d*), 48.19(*s*), 47.70(*s*), 44.50(*d*), 38.45(*t*), 32.77(*t*), 31.49(*d*), 26.38(*t*), 20.78(*q*), 19.81(*q*), 19.08(*q*), 18.94(*q*), 17.43(*t*), 11.94(*q*). MS: 358(0.5, $C_{18}H_{32}NO_4S^{+\cdot}$), 314(4), 285(12), 270(4), 216(43), 151(59), 135(10), 107(29), 93(40), 79(26), 71(65), 55(89). HR-MS: 314.1416 ($C_{18}H_{32}NO_4S$ - $C_3H_8^{+\cdot}$ calc. 314.1425).

N-*[(2S,3R)-2-ethyl-3-hydroxy-(E)-4-hexenoyl]bornane-10,2-sultam* (51). IR: 3540, 3010-2860, 1780, 1455, 1330, 1270. ^{1}H-NMR: 0.93(*t*, *J* = 7.5, 3H); 0.98(*s*, 3H); 1.19(*s*, 3H); 1.30-1.46(2H); 1.60(*m*, 1H); 1.7(*dd*, *J* = 6.5, 1.5, 3H); 1.70-1.90(4H); 2.05-2.10((2H); 2.20(*d*, *J* = 3, 1H); 3.23(*m*, 1H); 3.45(*d*, *J* = 14, 1H); 3.54(*d*, *J* = 14, 1H); 3.94(*t*, *J* = 6.5, 1H); 4.26(*m*, 1H); 5.55(*m*, 1H); 5.71(*m*, 1H). ^{13}C-NMR: 172.80(*s*), 130.00(*d*), 129.22(*d*), 74.88(*d*), 65.32(*d*), 53.31(*t*), 53.10(*d*), 48.00(*s*), 47.64(*s*), 44.56(*d*), 38.41(*t*), 32.83(*t*), 26.49(*t*), 20.93(*t*), 20.66(*q*), 19.85(*q*), 17.76(*q*), 11.69(*q*). MS: 355(10, $C_{18}H_{29}NO_4S^{+\cdot}$), 337(30), 285(20), 151(20), 135(40), 108(25), 93(25), 71(100). HR-MS: 340.1586 ($C_{18}H_{29}NO_4S^{+\cdot}$, calc. 340.1663).

(2R,3S)-Methyl-2-methyl-3-hydroxy-3-phenylpropanoate (12a).- $[\alpha]_{578}$ = +24.4°, $[\alpha]_{546}$ = +27.26°, $[\alpha]_{436}$ = +43.16°, $[\alpha]_{365}$ = +58.54°,(c = 3.23); lit.: [4b] $[a]_D$ = +23.2°, c = 3.2, $CHCl_3$). IR: 3600, 3520(br), 3040, 3000, 2950, 2900, 1725, 1450, 1430, 1200, 1175. ^{1}H-NMR(200 MHz): 1.12(*d*, *J* = 7.1, 3H); 2.77(*dq*, *J* = 4.1, 7.1, 1H); 2.94(*d*, *J* = 3.2, 1H); 3.67(*s*, 3H); 5.10(*dd*, *J* = 4.1, 3.2, 1H); 7.25-7.35(5H). ^{13}C-NMR: 176.22(*s*), 141.36(*s*), 128.25(2C,*d*), 127.51(*d*), 125.93(2C,*d*), 73.58(*d*), 51.87(q), 46.33(*d*), 10.68(*q*); MS: 194(7, $C_{11}H_{14}O_3^{+\cdot}$), 163(2), 117(4), 107(75), 88(100), 79(40), 57(25).

(2R,3S)-Methyl-2-methyl-3-hydroxybutyrate (12b).- $[\alpha]_{578}$ = -14.08°, $[\alpha]_{546}$ = +15.90°, $[\alpha]_{436}$ = -28.96°, $[\alpha]_{365}$ = -47.88°,(c = 0.867, MeOH); lit.(antipode): [21a] $[\alpha]_D$ = +14.3°, c = 5.0,

MeOH, T = 20°C). IR: 3600, 3520(br), 3040, 3000, 2950, 2900, 1725, 1450, 1430, 1200, 1175. ^{1}H-NMR(200 MHz): 1.16(*d*, *J* = 6.3, 3H); 1.17(*d*, *J* = 7.4, 3H); 2.51(*dq*, *J* = 4.1, 7.2, 1H); 2.57(*d*, *br*, *J* = 4.7, 1H); 3.70(*s*, 3H); 4.07(*m*, 1H). ^{13}C-NMR: 176.35(*s*), 67.96(*q*), 51.75(*d*), 45.40(*d*), 19.75(*q*), 10.99(*q*); MS: 132(40, $C_6H_{12}O_3^{+\cdot}$), 119(60), 108(65), 93(55), 83(60), 74(100), 67(30), 56(60).

(2R,3S)-Methyl-2,4-dimethyl-3-hydroxypentanoate (12d).-

$[\alpha]_{578}$ = +7.77°, $[\alpha]_{546}$ = +8.73°, $[\alpha]_{436}$ = +13.71°, $[\alpha]_{365}$ = +19.02°; (c = 2.51); lit.: [4b] $[\alpha]_D$ = +7.7°, (c = 5.4, $CHCl_3$, T = 25°C). IR: 3600, 3540, 2980, 2890, 1725, 1460, 1440, 1200, 1175, 980. ^{1}H-NMR(200MHz): 0.85(*d*, *J* = 6.8, 3H); 0.98(*d*, *J*= 6.5, 3H); 1.16(*d*, *J* = 7.4, 3H); 1.67(*m*, 1H); 2.49(*d*, *J* = 3.5, 1H, D_2O exchangeable); 2.65(*dq*, *J* = 3.6, 7.4, 1H); 3.54(*m*, 1H); 3.68(*s*, 3H). ^{13}C-NMR: 176.97(*s*), 76.79(*q*), 51.80(d), 41.71(*d*), 30.57(*d*), 19.02(*q*), 18.60(*q*), 10.14(*q*); MS: 145(3, $C_8H_{16}O_3$ -$CH_3^{+\cdot}$), 129(10), 117(45), 88(100), 73(20), 57(65).

(2R,3S)-Methyl-2-ethyl-3-hydroxy-3-phenylpropanoate (12g).-

$[\alpha]_{546}$ = +15.74°, $[\alpha]_{436}$ = +22.00°, $[\alpha]_{365}$ = +22.60°; (c = 1.55); lit.: [6c] $[\alpha]_D$ = +12.0°, (c = 1.58, $CHCl_3$, 96% e.e.). IR: 3600, 3520(br), 3040, 3000, 2950, 2900, 1730, 1450, 1200, 1175. ^{1}H-NMR(200MHz): 0.86(*t*, *J*=7.5, 3H); 1.60-1.77(2H); 2.65(*ddd*, *J* = 10.08, 5.55, 4.2, 1H); 2.81(*d*, *J* = 3.2, 1H); 3.60(*s*, 3H); 4.94(*dd*, *J* = 5.55, 3.2, 1H); 7.26-7.35(5H). ^{13}C-NMR: 175.4(*s*), 141.64(*s*), 128.29(2C,*d*), 127.68(*d*), 126.09(2C,*d*), 74.06(*d*), 54.52(*q*), 51.58(*d*), 20.20(*t*), 12.03(*q*); MS: 208($C_{12}H_{16}O_3^+$, 20), 179(20), 161(10), 149(10), 131(15), 107(60), 102(100), 87(85), 79(45), 55(20).

(2S,3R)-Methyl-2-methyl-3-hydroxyhexanoate (13k).-

$[\alpha]_{578}$ = +12.52°, $[\alpha]_{546}$ = +14.09°, $[\alpha]_{436}$ = +24.27°, $[\alpha]_{365}$ = +38.46°; (c = 1.92, T = 25.5°C). IR: 3560, 3000-2880, 1740. ^{1}H-NMR: 0.92(*t*, *J* = 7, 3H); 1.17(*d*, *J* = 7.5, 3H); 1.27-1.40(2H); 1.47(*m*, 1H);

2.43(*m*, 1H); 2.52(*dq J* = 3.5, 7.5, 1H); 3.70(*s*, 3H); 3.90(*m*, 1H). MS: 161(1, $C_8H_{16}O_3$ + $1^{+\cdot}$), 143(2), 129(2), 117(14), 88(100), 85(24), 83(7), 73(6), 71(6), 57(62).

(2S,3R)-Methyl-2-methyl-3-hydroxy-(E)-4-hexenoate (13e).-

$[\alpha]_{578}$ = +12.25°, $[\alpha]_{546}$ = +14.09°, $[\alpha]_{436}$ = +25.73°, $[\alpha]_{365}$ = +44.12°; (c = 0.82, T = 25.5°C). IR: 3610, 3530, 3010, 2995, 2960, 2920, 2885, 2860, 1730, 1455, 1435, 1365. ^{1}H-NMR: 1.17(*d*, *J* = 7, 3H); 1.70(*d*, *J* = 7, 3H); 2.50(*d*, *J* = 4.5, 1H); 2.61(*dq*, *J* = 4.5, 7, 1H); 3.7(*s*, 3H); 4.3(*m*, 1H); 5.48(*m*, 1H); 5.73(*m*, 1H). MS: 158(5, $C_8H_{14}O_3^{+\cdot}$), 143(4), 127(8), 111(2), 88(98), 71(100), 57(40).

(2S,3R)-Methyl-2-ethyl-4-methyl-3-hydroxypentanoate (13i).-

$[\alpha]_{578}$ = -7.83°, $[\alpha]_{546}$ = -8.55°, $[\alpha]_{436}$ = -13.09°, $[\alpha]_{365}$ = -17.11°; (c = 0.97); lit. (antipode): [6c] $[\alpha]_D$ = +7.6°. IR: 3700 - 3400, 3000-2880, 1760. ^{1}H-NMR: 0.9(*d*, *J* = 6.5, 3H); 0.91(*t*, *J* = 8, 3H); 0.98(*d*, *J* = 6.5, 3H); 1.63-1.78(3H); 2.30(*d*, *J* = 4.2, 1H); 2.49(*dt*, *J* = 9.5, 5.5, 1H); 3.53(*m*, 1H); 3.7(*s*, 3H). ^{13}C-NMR: 176.24(*s*), 76.86(*d*), 51.56(*d*), 50.26(*d*), 30.98(*q*), 20.10(*t*), 19.49(*q*), 17.33(*q*), 12.15(*q*). MS: 174(0, $C_9H_{13}O_3^{+\cdot}$), 145(10), 131(40), 99(90), 87(100), 55(25)

(2S,3R)-2-ethyl-3-hydroxyhexenoate (13l).-

$[\alpha]_{578}$ = -7.39° $[\alpha]_{546}$ = -8.37° $[\alpha]_{436}$ = -13.45° $[\alpha]_{365}$ = -19.56° (c = 0.92). IR: 3700 -3400, 3000-2860, 1730. ^{1}H-NMR: 0.91(*t*, *J* = 7, 3H); 1.58-1.70(4H); 2.27(*d*, *J* = 4, 1H); 2.45(*dt*, *J* = 9, 5.5, 1H); 3.68(*s*, 3H); 4.22(*m*, 1H); 5.49(*m*, 1H); 5.7(*m*, 1H). MS: 172(1, $C_9H_{16}O_3^{+\cdot}$), 155(43), 102(67), 87(100), 71(99), 55(45), 53(16).

(1R,2S)-1-Phenyl-2-methylpropane-1,3-diol (11a).-

$[\alpha]_{578}$ = +59.3°, $[\alpha]_{546}$ = +68.2°, $[\alpha]_{436}$ = +117.56°, $[\alpha]_{365}$ = +186.67°; (c = 0.45). IR: 3600, 3490(br), 3000, 2970, 2890, 1450, 1040. ^{1}H-NMR(200 MHz,$CDCl_3/D_2O$): 0.81(*d*, *J* = 7.2, 3H); 2.08(*m*, 1H); 3.63(*d*, *J* =

5.9, 2H); 4.91(*d*, *J* = 3.5, 1H); 7.28-7.34(5H). ^{13}C-NMR: 142.61(*s*), 128.15(2C,*d*), 127.26(*d*), 126.12(2C,*d*), 76.71(*d*), 66.44(*t*), 41.37(*d*), 10.76(*q*); MS: 166(35, $C_{10}H_{14}O_2^{+\cdot}$), 148(20), 117(10), 107(100), 79(45).

(2S,3S)-2-Methylbutane-1,3-diol (11b).-

$[\alpha]_{578}$ = +5.97°, $[\alpha]_{546}$ = +6.91°, $[\alpha]_{436}$ = +9.74°, $[\alpha]_{365}$ = +14.45°; (c = 0.32). IR: 3620, 3500(br), 3010, 2970, 2910, 1470, 1100, 1020. ^{1}H-NMR(200 MHz,$CDCl_3$): 0.89(*d*, *J* = 6.9, 3H); 1.18(*d*, *J* = 6.5, 3H); 1.81(*m*, 1H); 2.61(*d*, *J* = 6.9, 2H); 3.68(*d*, br, *J* = 4.7, 2H); 4.04(*m*, 1H). ^{13}C-NMR: 70.73(*d*), 66.53(*t*), 40.05(*d*), 19.46(*q*), 10.67(*q*).

(2S,3S)-2,4-Dimethylpentane-1,3-diol (11d).-

$[\alpha]_{578}$ = +9.3°, $[\alpha]_{546}$ = +10.16°, $[\alpha]_{436}$ = +16.94°, $[\alpha]_{365}$ = +26.96°, (c = 0.71); lit.: [21b] $[\alpha]_D$ = +11.3°, c = 0.6, $CHCl_3$, T = 20°C). IR: 3620, 3450(br), 3000, 2970, 2890, 1475, 1470, 1075, 975. ^{1}H-NMR(200 MHz,$CDCl_3/D_2O$): 0.82(*d*, *J* = 6.7, 3H); 0.91(*d*, *J* = 7.1, 3H); 0.98(*d*, *J*=6.5, 3H); 1.66(*m*, 1H); 1.82(*m*, 1H); 3.37(*dd*, *J* = 9.0, 2.4, 1H); 3.67(*m*, 2H). ^{13}C-NMR: 79.67(*d*), 67.68(*t*), 36.03(*d*), 31.30(*d*), 19.42(*q*), 18.95(*q*), 8.86(*q*).

(2S,3S)-3-t-Butyldimethylsilyloxy-2-methylpentan-1-ol (14).-

$[\alpha]_{578}$ = -5.1°, $[\alpha]_{546}$ = -6.1°, $[\alpha]_{436}$ = -9.5°, $[\alpha]_{365}$ = -15.9°; (c = 0.883, T = 25°C); Lit.: [14b] $[\alpha]_D$ = -3.5° (c = 1.98). IR: 3630, 3600 - 3300, 2960, 2940, 2880, 2860, 1464, 1253, 1050, 1000, 840. ^{1}H-NMR: 0.09(*s*, 3H); 0.11(*s*, 3H); 0.84(*d*, *J* = 7, 3 H); 0.9(*t*, *J* = 7, 3 H); 0.9(*s*, 9H); 1.48 - 1.58 (2H); 1.98 (*m*, 1H); 2.6(*s.br*, 1H); 3.54(*m*, 1H); 3.67 - 3.75 (2H); (CCl_4): 0.07(*m*, 6H); 0.73 (*m*, 3H); 0.8 - 0.9 (12H); 1.4 - 1.5 (2H); 1.63(*s,br.* 1H); 1.76(*s.br* 1H); 3.34 (*m*, 1H); 3.48(*m*, 1 H); 3.61(*m*, 1H). ^{13}C-NMR: 77.28(*d*), 66.09(*t*), 39.21(*d*), 25.84(*q*), 25.09(*t*), 18.01(*s*), 11.87(*q*), 10.78(*q*), -4.39(*q*), -4.51(*q*).