S2 File. NMR analyses of biotin esters

(C-11)-biotin ester (**4a**) = Methyl (3*S*,4*R*,5*S*,8*S*,10*S*,11*S*)-11-hydroxy-5-methoxy-4,6,6,8,10-pentamethyl-11-{(2*R*,3*R*)-2-methyl-3-[(*S*)-4-methylpent-3-en-2-yl]oxiran-2-yl}-7-oxo-11-{5-{(3a*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl}pentanoyloxy}un-decanoate

R_f = 0.35 (ethyl acetate/MeOH 10 : 1). ^{1}H-NMR (800 MHz, $CDCl_3$) δ = 0.90 (d, *J* = 6.3 Hz, 3H, 23-H), 0.92 (d, *J* = 7.0 Hz, 3H, 18-H), 1.00 (d, *J* = 6.3 Hz, 3H, 22-H), 1.06-1.16 (m, 1H, 9-H_b), 1.095 (d, *J* = 6.0 Hz, 3H, 25-H), 1.101 (s, 3H, 21-H), 1.21 (s, 3H, 20-H), 1.28-1.37 (m, 1H, 9-H_a), 1.39 (s, 3H, 24-H), 1.47-1.50 (m, 1H, 4'-H_b), 1.50-1.57 (m, 1H, 4'-H_a), 1.60-1.69 (m, 3H, 4-H, 5'-H_b, 3'-H_b), 1.69 (s, 3H, 26-H), 1.71 (s, 3H, 17-H), 1.73-1.80 (m, 3H, 10-H, 5'-H_a, 3'-H_a), 2.35-2.40 (m, 1H, 2'-H_b), 2.44-2.47 (m, 1H, 2'-H_a), 2.47-2.50 (m, 1H, 2-H_b), 2.52-2.60 (m, 2H, 2-H_a, 14-H), 2.71-2.75 (m, 2H, 9'-H_b, 13-H), 2.92-2.97 (m, 1H, 9'-H_a), 3.05-3.10 (m, 1H, 8-H), 3.16-3.21(m, 1H, 6'-H), 3.36 (2, 3H, 19-H), 3.52-3.54 (m, 1H, 5-H), 3.73 (s, 3H, COO*Me*), 3.94-3.99 (m, 1H, 3-H), 4.25-4.29 (m, 1H, 11-H), 4.35-4.40 (m, 1H, 7'-H), 4.51-4.55 (m, 1H, 8'-H), 4.72 (brs, 1H, N*H*), 4.94-4.99 (m, 1H, 15-H), 5.66 (brs, 1H, N*H*) ppm. ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 8.8 (C-18), 12.2 (C-24), 15.1 (C-23), 15.9 (C-22), 18.3 (C-26), 19.1 (C-21), 20.5 (C-20), 21.2 (C-25), 25.1 (C-3'), 25.8 (C-17), 28.2 (C-5'), 28.4 (C-4'), 32.2 (C-14), 32.4 (C-10), 34.3 (C-2'), 36.6 (C-9), 37.7 (C-8), 39.3 (C-2), 39.7 (C-4), 40.6 (C-9'), 51.9 (COOMe), 52.0 (C-6), 55.6 (C-6'), 60.1 (C-8'), 60.3 (C-19), 61.6 (C-7'), 62.7 (C-12), 68.6 (C-13), 70.8 (C-3), 82.7 (C-11), 86.3 (C-5),124.8 (C-15), 132.5 (C-16), 163.0 (C-10'), 172.9 (C-1'), 173.4 (C-1) ppm. MS (ESI) *m/z* = 733 $[M+Na]^+$, 693, 449. HRMS (ESI) *m/z*: calcd. for $C_{37}H_{62}N_2O_9SNa^+$ = 733.4068, found: 733.4076 $[M+Na]^+$. FT-IR (ATR) $\tilde{\nu}$ = 3283 (m), 2924 (vs), 2854 (s), 2671 (w), 2483 (w), 2359 (w), 1735 (s), 1697 (s), 1558 (w), 1460 (s), 1378 (m), 1256 (m), 1164 (m), 1099 (m), 989 (m) cm^{-1}. $[\alpha]_D^{20}$ = + 2.6 (c = 1.00, CH_2Cl_2)

(C-3)-biotin ester (**4b**) = Methyl (3*S*,4*R*,5*S*,8*S*,10*S*,11*S*)-11-hydroxy-5-methoxy-4,6,6,8,10-pentamethyl-11-{(2*R*,3*R*)-2-methyl-3-[(*S*)-4-methylpent-3-en-2-yl]oxiran-2-yl}-7-oxo-3-{5-{(3a*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl}pentanoyloxy}un-decanoate

R_f = 0.30 (ethyl acetate/MeOH 10 : 1). ^{1}H-NMR (800 MHz, $CDCl_3$) δ = 0.81 (d, *J* = 6.7 Hz, 3H, 23-H), 0.96 (d, *J* = 7.0 Hz, 3H, 18-H), 1.02 (d, *J* = 6.5 Hz, 3H, 22-H), 1.10 (s, 3H, 21-H), 1.11 (d, J = 6.7 Hz, 3H, 25-H), 1.19-1.24 (m, 1H, 9-H_b), 1.23 (s, 3H, 20-H), 1.27 (s, 3H, 24-H), 1.43-1.56 (m, 3H, 4'-H_b, 4'-H_a, 10-H), 1.61-1.71 (m, 2H, 5'-H_b, 3'-H_b), 1.64 (s, 3H, 26-H), 1.70 (s, 3H, 17-H), 1.72-1.80 (m, 2H, 5'-H_a, 3'-H_a), 1.95-2.00 (m, 1H, 4-H), 2.31-2.35 (m, 1H, 14-H), 2.35-2.38 (m, 1H, 2'-H_b), 2.43-2.48 (m, 1H, 2'-H_a), 2.60-2.66 (m, 3H, 13-H, 2-H_b, 2-H_a), 2.71-2.78 (m, 2H, 11-H, 9'-H_b), 2.92-2.97 (m, 1H, 9'-H_a), 3.13-3.22 (m, 2H, 8-H, 6'-H), 3.31 (2, 3H, 19-H), 3.46-3.48 (m, 1H, 5-H), 3.70 (s, 3H, COO*Me*), 4.34-4.38 (m, 1H, 7'-H), 4.52-4.56 (m, 1H, 8'-H), 4.95-4.99 (m, 1H, 15-H), 5.17-5.21 (m, 1H, 3-H), 5.27 (brs, 1H, N*H*), 5.57 (brs, 1H, N*H*) ppm. ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 9.9 (C-18), 11.4 (C-24), 15.7 (C-23), 16.4 (C-22), 18.4 (C-26), 21.7 (C-21), 19.0 (C-25), 19.8 (C-20), 24.8 (C-3'), 25.9 (C-17), 28.19 (C-5'), 28.21 (C-4'), 32.5 (C-14), 33.4 (C-10), 34.1 (C-2'), 36.9 (C-2), 37.5 (C-9), 37.6 (C-4), 38.3 (C-8), 40.6 (C-9'), 51.9 (COOMe), 54.0 (C-6), 55.2 (C-6'), 60.2 (C-8'), 60.4 (C-19), 61.9 (C-7'), 64.4 (C-12), 68.4 (C-13), 73.6 (C-3), 82.7 (C-11), 84.9 (C-5),125.0 (C-15), 132.1 (C-16), 163.5 (C-10'), 171.0 (C-1), 172.9 (C-1') ppm. MS (ESI) *m/z* = 733 $[M+Na]^+$, 711, 693, 599. HRMS (ESI) *m/z*: calcd. for $C_{37}H_{62}N_2O_9SNa^+$ = 733.4068, found: 733.4067 $[M+Na]^+$. FT-IR (ATR) $\tilde{\nu}$ = 3260 (m), 2924 (vs), 2854 (s), 2558 (w), 2365 (w), 2183 (w), 1967 (w), 1736 (s), 1698 (s), 1456 (s), 1377 (m), 1260 (s), 1160 (m), 1099 (s), 989 (m), 801 (m) cm^{-1}. $[\alpha]_D^{20}$ = + 2.0 (c = 1.00, CH_2Cl_2)

^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of (C-11)-biotin ester 4a

1D spectrum of the C-11 compound

```
NAME        C11-Prod_110123
EXPNO                    1
PROCNO                   1
Date_             20110123
Time                 2.19
INSTRUM             spect
PROBHD   5 mm CPTXI 1H-
PULPROG                 zg
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8417.509 Hz
FIDRES            0.128441 Hz
AQ                3.8928883 sec
RG                     45.2
DW                   59.400 usec
DE                   10.00 usec
TE                   298.0 K
D1                0.50000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.75 usec
PL1                  5.00 dB
PL1W          6.51349163 W
SFO1         599.8835993 MHz
SI                   32768
SF           599.8800000 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                   1.00
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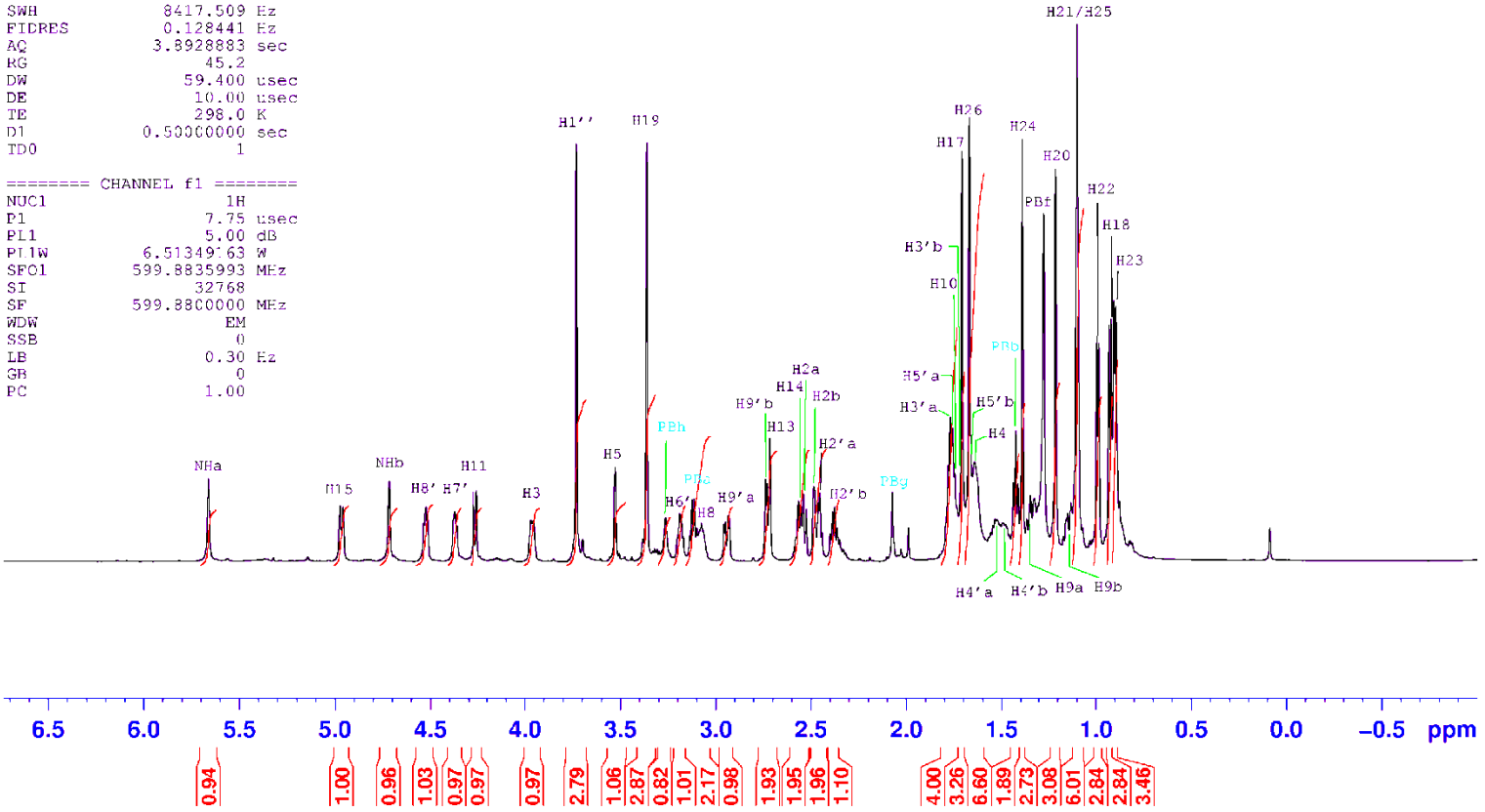

^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of (C-3)-biotin ester 4b

1D spectrum of C-3 sample

NAME	C3-Prod_110124	
EXPNO	1	
PROCNO	1	
Date_	20110124	
Time	2.44	
INSTRUM	spect	
PROBHD	5 mm CPTXI 1H-	
PULPROG	zg	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	8417.509	Hz
FIDRES	0.128441	Hz
AQ	3.8928883	sec
RG	45.2	
DW	59.400	usec
DE	10.00	usec
TE	298.0	K
D1	0.50000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	7.63	usec
PL1	5.00	dB
PL1W	6.51349163	W
SFO1	599.8835993	MHz
SI	32768	
SF	599.8800000	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00