Supporting Information

Diversity-Oriented Synthesis of a Molecular Library of Immunomodulatory α-Galactosylceramides with Fluorous-Tag-Assisted Purification and Evaluation of Their Bioactivities

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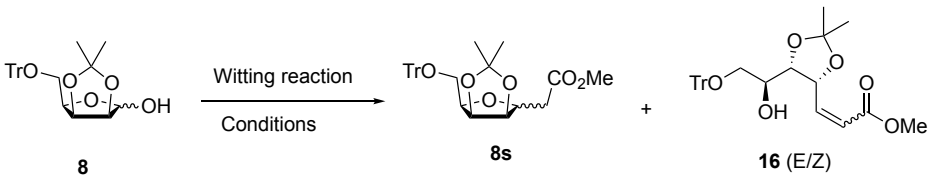
Materials. All reactions were performed in oven-dried glassware (120 °C) under a nitrogen atmosphere unless indicated otherwise. All chemicals were purchased as reagent grade and used without further purification. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride. Tetrahydrofuran (THF) and ether were distilled over sodium metal/benzophenone ketyl. Anhydrous N,N-dimethylformamide (DMF) was purchased from Merck. Molecular sieves (MS) for glycosylation were MS 4Å (Aldrich) and activated by flame. ^1H and ^{13}C NMR spectra were recorded on either a Bruker AV-400 or AV-600 spectrometer operating at 400 or 600 MHz for ^1H and 100 or 150 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm and referenced to the solvent used ($CDCl_3$, δ 7.24 and 77.0; CD_3OD, δ 3.31 and 49.0; D_2O, δ 4.67), with coupling constants (*J*) reported in Hz. Two-dimensional (COSY) experiments were used to assist in assignment of the products. High-resolution mass spectra were recorded under ESI-TOF mass spectroscopy conditions. Analytical thin-layer chromatography (TLC) was performed on pre-coated plates (silica gel 60). Silica gel 60 (E. Merck) was employed for all flash-chromatography experiments. All fluorus-assisted purification was performed using FluoroFlash® SPE cartridge (Fluorous Tech. Inc., USA). The reactions were monitored by examination under UV light (254 nm) and by staining with *p*-anisaldehyde, ninhydrin, cerium molybdate, or potassium permanganate solutions.

Known compounds. Compounds **5**,[1] **8**,[2] **17**,[2] **18**,[2] **20**,[2] **24**,[3] **27**,[4] **1a**,[5] **1b**,[6] and **1db**[7] have been previously synthesized and reported in the cited papers and their NMR spectra are in good agreement with the literature data.

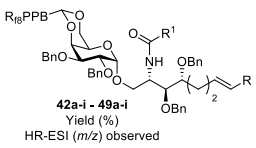
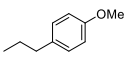
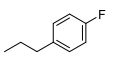
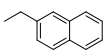
Table S1. Optimization of the Witting reaction



8 **8s** **16** (E/Z)

Entry	Condition	Solvent	Temperature (°C)	Product	Yield (%)
1	$(EtO)_2P(O)CH_2CO_2Et$, LiCl, DBU	CH_3CN	rt	No reaction	—
2	$(EtO)_2P(O)CH_2CO_2Et$, LiHMDS	THF	0 °C to rt	No reaction	—
3	$(EtO)_2P(O)CH_2CO_2Et$, NaH	DMSO	0 °C to rt	No reaction	—
4	$Ph_3P{=}CHCO_2Me$, Benzoic acid	Toluene	90	No reaction	—
5	$Ph_3P{=}CHCO_2Me$, Benzoic acid	CH_2Cl_2	40	No reaction	—
6	$Ph_3P{=}CHCO_2Me$, Benzoic acid	CH_3CN	40	No reaction	—
7	$Ph_3P{=}CHCO_2Me$	Toluene	90	**8s**	50
8	$Ph_3P{=}CHCO_2Me$	CH_3CN	40	**8s**	70
9	$Ph_3P{=}CHCO_2Me$	CH_3CN	80	**8s**	50
10	$Ph_3P{=}CHCO_2Me$	CH_2Cl_2	rt	*Z*-**16**	20
11	$Ph_3P{=}CHCO_2Me$	1,4-dioxane	rt	**16** (*E*/*Z*)	30
12	$Ph_3P{=}CHCO_2Me$	DMF	rt	**16** (*E*/*Z*)	30
13	$Ph_3P{=}CHCO_2Me$	DMF	80	**8s**	75
14	$Ph_3P{=}CHCO_2Me$	$CHCl_3$	rt	**16** (*E*/*Z*)	50
15	$Ph_3P{=}CHCO_2Me$	$CHCl_3$	50	**16** (*E*/*Z*)	85

Table S2. Details of the structures, yields, and the HRMS (ESI-TOF) data of **42-49**.

 42a-i - 49a-i Yield (%) HR-ESI (*m/z*) observed	R = CH_2CH_3	$(CH_2)_9CH_3$	$(CH_2)_{16}CH_3$	4-ClPh	$(CH_2)_2Ph$	$(CH_2)_5Ph$	$CHCH_3(CH_2)_2CH(CH_3)_2$	$(CH_2)_24$-CF_3Ph
R^1 = C_7H_{15}	**42a** (91) (1438.5248)	—	**44a** (85) (1625.7705)	**45a** (87) (1520.4857)	**46a** (88) (1514.5560)	**47a** (85) (1556.6033)	**48a** (91) (1520.6031)	**49a** (85) (1582.5430)
$C_{25}H_{51}$	**42b** (92) (1690.8063)	**43a** (97) (1802.9323)	**44b** (93) (1091.0418)	**45b** (84) (1772.7678)	**46b** (95) (1766.8377)	**47b** (88) (1808.8849)	**48b** (90) (1565.8351)	**49b** (84) (1834.8234)
	**42c** (92) (1450.4077)	—	**44c** (93) (1660.6427)	**45c** (86) (1532.3692)	**46c** (91) (1526.4390)	**47c** (89) (1568.4862)	**48c** (85) (1532.4855)	**49c** (86) (1594.4275)
	**42d** (91) (1450.4341)	—	**44d** (85) (1660.6691)	**45d** (88) (1532.3951)	**46d** (88) (1526.4652)	**47d** (92) (1568.5129)	**48d** (82) (1532.5131)	**49d** (85) (1571.4644)
	**42e** (95) (1474.4892)	—	**44e** (83) (1684.7235)	**45e** (87) (1556.4498)	**46e** (93) (1550.5197)	**47e** (91) (1592.5667)	**48e** (89) (1556.5668)	**49e** (92) (1618.5081)
	**42f** (92) (1462.4685)	—	**44f** (88) (1672.7032)	**45f** (86) (1544.4295)	**46f** (91) (1538.4998)	**47f** (85) (1580.5462)	**48f** (88) (1544.5467)	**49f** (90) (1606.4883)
	**42g** (88) (1480.4785)	—	**44g** (91) (1690.7124)	**45g** (85) (1562.4396)	**46g** (90) (1556.5097)	**47g** (83) (1598.5560)	**48g** (93) (1562.5563)	**49g** (90) (1624.4973)
	**42h** (92) (1482.5250)	—	**44h** (92) (1696.7590)	**45h** (92) (1568.4857)	**46h** (93) (1562.5559)	**47h** (87) (1604.6030)	**48h** (90) (1568.6029)	**49h** (93) (1630.5427)
	**42i** (90) (1514.5554)	**43b** (88) (1626.6811)	**44i** (93) (1724.7911)	**45i** (92) (1596.5177)	**46i** (92) (1590.5875)	**47i** (89) (1632.6340)	**48i** (89) (1996.6345)	**49i** (88) (1658.5746)

Synthesis of compounds

General procedure for the final deprotection of compounds 42-49. The fully unprotected glycolipid library was constructed by two deprotection steps: the hydrolysis of ^{F}benzylidene acetal was performed using CSA following a similar method as described in the synthesis of compound **30**, and subjected to reductive hydrogenolysis to remove benzyl ethers and reduce unsaturation in the phytosphingosine chain. In a typical experiment, CSA (1.0 eq.) was added to a solution of corresponding 4,6-*O*-^{F}benzylidene derivative (1 eq.) in MeOH/$CHCl_3$ (1/1, 2 mL) at rt with vigorous stirring. After being stirred for 8 h, the reaction mixture was quenched with Et_3N, concentrated under reduced pressure, and used without further purification. To a solution of above crude product in MeOH/CH_2Cl_2 (1/1, 2 mL), 10% $Pd(OH)_2$ (10 w/w %) was added. The resultant mixture was degassed and saturated with balloon filled with H_2 gas and left stirring at rt for 8 h under a positive pressure of H_2. The catalyst was removed by filtration through celite, rinsed with MeOH. The combined filtrates were evaporated *in vacuo*, and

subjected to flash column chromatography on silica to afford pure α-GalCer glycolipids.

Compound 1bb. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +24.77 (c = 2.82, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 3H), 1.22-1.66 (m, 56H), 2.22 (t, *J* = 7.5 Hz, 2H, H-1"), 3.55 (m, 1H), 3.60 (t, *J* = 6.2 Hz, 1H). 3.67-3.71 (m, 3H), 3.74 (dd, *J* = 3.2, 10.1 Hz, 1H), 3.78 (dd, *J* = 3.7, 10.1 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.87-3.90 (m, 2H), 4.21 (dd, *J* = 4.6, 10.4 Hz, 1H), 4.87 (1H merged with water); ^{13}C NMR (150 MHz, MeOD): δ 14.55, 23.85, 23.87, 27.12, 27.22, 30.56, 30.57, 30.67, 30.80 (2C), 30.85 (18C), 33.18, 33.24, 37.42, 52.03, 62.93, 68.49, 70.42, 71.23, 71.71, 72.77, 73.15, 75.74, 101.35, 176.07; HRMS (ESI-TOF) *m/z* calcd for $C_{42}H_{83}NO_9Na$ $[M+Na]^+$ 768.5960, found 768.5952.

Compound 1bc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +38.62 (c = 2.28, MeOH/DCM = 1/1); 1H NMR (600 MHz, MeOD): δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.25-1.44 (m, 10H), 3.62 (ddd, *J* = 2.5, 6.7, 9.2 Hz, 1H), 3.67 (dd, *J* = 5.1, 11.4, 1H), 3.70 (dd, *J* = 5.4, 11.4 Hz, 1H), 3.73-3.85 (m, 5H), 3.87 (d, *J* = 2.9 Hz, 1H), 4.03 (dd, *J* = 4.6, 10.1 Hz, 1H), 4.47 (td, *J* = 5.1, 5.4 Hz, 1H), 4.93 (d, *J* = 3.8 Hz, 1H), 7.45-7.85 (m, 4H); ^{13}C NMR (150 MHz, MeOD): δ 14.52, 23.82, 26.97, 30.54, 33.14, 33.49, 52.87, 62.97, 68.29, 70.39, 71.27, 71.72, 72.78, 73.19, 75.82, 101.37, 128.57 (2C), 129.69 (2C), 132.83, 135.99, 170.12; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{36}ClNO_9Na$ $[M+Na]^+$ 528.1971, found 528.1964.

Compound 1bd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +33.16 (c = 5.03, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.26-1.67 (m, 10H), 2.57, (t, *J* = 7.1 Hz, 2H), 3.13, (t, *J* = 7.1 Hz, 2H), 3.46-3.79 (m, 8H), 3.85 (dd, *J* = 4.6, 10.8 Hz, 1H), 3.89 (d, *J* = 2.7 Hz, 1H), 4.21 (td, *J* = 4.7, 9.7 Hz, 1H), 4.86 (d, *J* = 3.7 Hz, 1H), 6.82-7.14 (m, 3H); ^{13}C NMR (100 MHz, MeOD): δ 14.51, 23.52, 26.07, 26.64, 30.32, 32.83, 33.31, 38.88, 51.56, 62.63, 67.99, 69.90, 70.79, 71.21, 72.04, 72.74, 75.53, 100.81, 124.23, 125.52, 127.63, 144.21, 173.90; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{36}ClNO_9Na$ $[M+Na]^+$ 528..2238, found 528.2240.

Compound 1be. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +33.16 (c = 5.03, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.26-1.67 (m, 10H), 2.57, (t, *J* = 7.1 Hz, 2H), 3.13, (t, *J* = 7.1 Hz, 2H), 3.46-3.79 (m, 8H), 3.85 (dd, *J* = 4.6, 10.8 Hz, 1H), 3.89 (d, *J* = 2.7 Hz, 1H), 4.21 (td, *J* = 4.7, 9.7 Hz, 1H), 4.86 (d, *J* = 3.7 Hz, 1H), 6.82-7.14 (m, 3H); ^{13}C NMR (100 MHz, MeOD): δ 14.51, 23.52, 26.07, 26.64, 30.32, 32.83, 33.31, 38.88, 51.56, 62.63, 67.99, 69.90, 70.79, 71.21, 72.04, 72.74, 75.53, 100.81, 124.23, 125.52, 127.63, 144.21, 173.90; HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{36}ClNO_9Na$ $[M+Na]^+$ 528..2238, found 528.2240.

Compound 1bf . R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +39.21 (c = 2.21, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.26-1.64 (m, 10H), 2.49 (t, *J* = 7.7 Hz, 2H, H-1"), 2.88 (t, *J* = 7.7 Hz, 2H, H-2"), 3.46 (m, 1H), 3.50 (t, *J* = 6.0 Hz, 1H), 3.61 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.66-3.79 (m, 5H), 3.81 (dd, *J* = 4,6, 10.8 Hz, 1H), 3.85 (d, *J* = 2.5 Hz, 1H), 4.18 (td, *J* = 4.8, 10.1 Hz, 1H), 4.82 (d, *J* = 3.7 Hz, 1H), 6.95-6.99 (m, 2H), 7.19-7.22 (m, 2H); ^{13}C NMR (100 MHz, MeOD): δ 14.59, 23.86, 26.99, 30.66, 32.10, 33.19, 33.41, 39.04, 51.98, 62.91, 68.26, 70.33, 71.18, 71.64, 72.74, 73.02, 75.82, 101.25, 116.07, 131.16, 131.24, 138.28, 161.80, 164.21, 174.84; HRMS (ESI-TOF) *m/z* calcd for $C_{25}H_{40}FNO_9Na$ $[M+Na]^+$ 540.2579, found 540.2573.

Compound 1bh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{27}$ = +38.48 (c = 2.19, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90 (t, *J* = 5.9 Hz, 3H), 1.18-1.73 (m, 16H), 2.22 (t, *J* = 7.4 Hz, 2H, H-1"), 2.61 (t, *J* = 7.7 Hz, 2H, H-5"), 3.53-3.74 (m, 6H), 3.79 (dd, *J* = 3.5, 10.1, 1H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.88 (d, *J* = 3.6 Hz, 1H), 3.89 (dd, *J* = 4.1, 10.5 Hz, 1H), 4.22 (td, *J* = 4,9, 10.1 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 7.12-7.25 (m, 5H); ^{13}C NMR (150 MHz, MeOD): δ 14.57, 23.86, 27.03, 27.09, 30.09, 30.66, 32.57, 33.22, 33.40, 36.86, 37.33, 52.02, 62.93, 68.45, 70.40, 71.23, 71.71, 72.76, 73.15, 75.87, 101.33, 126.81, 129.42 (2C), 129.54 (2C), 143.94, 175.96; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{47}NO_9Na$ $[M+Na]^+$ 564.3143, found 564.3138.

Compound 1bi. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{27}$ = +33.84 (c = 2.21, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.16-1.72 (m, 20H), 2.22 (t, *J* = 7.5 Hz, 2H, H-1"), 2.60 (t, *J* = 7.7 Hz, 2H, H-7"), 3.53-3.75 (m, 6H), 3.79 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.83 (t, *J* = 5.9 Hz, 1H), 3.89 (m, 2H, H), 4.21 (td, *J* = 4,7, 10.7 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 7.11-7.25 (m, 5H); ^{13}C NMR (150 MHz, MeOD): δ 14.58, 23.86, 27.10, 27.68, 30.47, 30.66, 31.10 32.85, 33.22, 34.77, 37.04, 37.38, 38.84, 39.15, 52.02, 62.93, 68.47, 70.40, 71.23, 71.71, 72.75, 73.14, 75.82, 101.32, 126.76, 129.39 (2C), 129.52 (2C), 144.10, 176.03; HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{51}NO_9Na$ $[M+Na]^+$ 592.3456, found 592.3453.

Compound 1ca. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +16.31 (c = 2.23, MeOH/DCM = 1/1); ^{1}H NMR (800 MHz, MeOD/DCM = 1/1): δ 0.85 (t, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 6.2 Hz, 3H), 1.24-1.64 (m, 50H), 2.19 (t, *J* = 7.6 Hz, 2H, H-1"), 3.52-3.74 (m, 6H, H-3, H-6a, H-1', H-3', H-4',), 3.77 (dd, *J* = 3.8, 10.1 Hz, 1H), 3.79 (d, *J* = 6.0 Hz, 1H), 3.86 (dd, *J* = 4.6, 10.8 Hz, 1H), 3.90 (d, *J* = 2.6 Hz, 1H), 4.18 (td, *J* = 4.7, 9.8 Hz, 1H), 4.87 (d, *J* = 3.8 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (200 MHz, MeOD / DCM = 1 / 1): δ 14.43, 14.46, 23.31, 23.35, 26.58, 26.63, 29.78, 29.99, 30.05, 30.34, 30.37 (7C), 30.40 (4C), 30.42, 30.46, 30.49, 32.44, 32.63, 33.06, 37.09, 51.25, 62.47, 67.95, 69.1, 70.54, 71.03, 71.73, 72.64, 75.29, 100.55, 175.38; HRMS (ESI-TOF) *m/z* calcd for $C_{39}H_{77}NO_9Na$ $[M+Na]^+$ 703.5598, found 703.5592.

Compound 1cb. R_f 0.5 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +7.53 (c = 1.91, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/DCM = 1/1): δ 0.85 (t, *J* = 6.8 Hz, 6H), 1.16-1.66 (m, 82H), 2.18 (t, *J* = 7.3 Hz, 2H, H-1"), 3.51-3.74 (m, 6H, H-3, H-6a, H-1', H-3', H-4',), 3.77 (dd, *J* = 3.7, 9.9 Hz, 1H), 3.78 (t, *J* = 5.7 Hz, 1H), 3.85 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.90 (d, *J* = 3.0 Hz, 1H), 4.16 (td, *J* = 4.6, 9.5 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (200 MHz, MeOD/DCM = 1/1): δ 13.31, 13.34, 22.19, 22.23, 25.46, 25.51, 28.66, 28.88, 28.93, 29.21, 29.25 (18C), 29.30 (12C), 29.34, 29.37, 31.32, 31.51, 31.94, 35.97, 50.13, 61.35, 66.83, 68.59, 69.42, 69.91, 70.61, 71.52, 74.17, 99.43, 174.26; HRMS (ESI-TOF) *m/z* calcd for

$C_{57}H_{113}NO_9Na$ $[M+Na]^+$ 955.8415, found 955.8421.

Compound 1cc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +19.69 (c = 1.89, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.25-1.69 (m, 40H), 3.60 (m, 1H), 3.64-3.83 (m, 7H), 3.86 (d, *J* = 3.4 Hz, 1H), 4.0 (dd, *J* = 4.4, 10.9 Hz, 1H), 4.44 (dd, *J* = 4.9, 10.8 Hz, 1H), 4.89 (1H merge with water), 7.46-7.86 (m, 4H); ^{13}C NMR (100 MHz, MeOD): δ 14.46, 23.32, 26.39, 26.45, 30.02, 30.35 (14C), 32.60, 33.22, 51.93, 62.47, 67.74, 69.65, 70.53, 71.0, 71.67, 72.65, 75.28, 100.52, 127.89 (2C), 129.19 (2C), 132.41, 134.95, 169.31; HRMS (ESI-TOF) *m/z* calcd for $C_{38}H_{66}ClNO_9Na$ $[M+Na]^+$ 738.4318, found 738.4312.

Compound 1cd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +22.31 (c = 1.76, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.90 (d, *J* = 6.8 Hz, 3H), 1.29-1.67 (m, 40H), 2.37 (dt, *J* = 2.4, 7.4 Hz, 2H, H-1"), 3.14 (t, *J* = 7.4 Hz, 2H, H-2"), 3.50 (m, 1H), 3.56 (t, *J* = 6.1 Hz, 1H), 3.64-3.82 (m, 6H), 3.86 (dd, *J* = 4.2, 10.5 Hz, 1H), 3.87 (d, *J* = 4.1 Hz, 1H), 4.20 (dd, *J* = 4.7, 10.4 Hz, 1H), 4.85 (d, *J* = 3.7 Hz, 1H), 6.84-7.18 (m, 3H); ^{13}C NMR (200 MHz, MeOD): δ 14.60, 23.89, 26.41, 26.93, 27.07, 30.63, 30.92 (8C), 30.98 (6C), 33.23, 33.30, 39.17, 52.04, 62.92, 68.29, 70.35, 71.20, 71.63, 72.74, 73.00, 75.74, 101.30, 124.54, 125.86, 127.95, 144.73, 175.26; HRMS (ESI-TOF) *m/z* calcd for $C_{38}H_{69}NO_9SNa$ $[M+Na]^+$ 738.4585, found 738.4577.

Compound 1ce. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +25.38 (c = 2.15, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.84 (d, *J* = 6.1 Hz, 3H), 1.23-1.61 (m, 40H), 2.49 (t, *J* = 7.7 Hz, 2H, H-1"), 2.86 (t, *J* = 7.7 Hz, 2H, H-2"), 3.47-3.79 (m, 11H, H-2, H-3, H-5, H-6a, H-1', H-3', H-4', OMe), 3.83 (dd, *J* = 4.6, 10.8 Hz, 1H), 3.87 (d, *J* = 2.6 Hz, 1H), 4.20 (td, *J* = 4.7, 10.1 Hz, 1H), 4.85 (1H merge with water), 6.82-7.14 (m, 4H); ^{13}C NMR (100 MHz, MeOD): δ 14.52, 23.50, 26.76, 29.60, 29.86, 30.21, 30.53 (12C), 32.47, 32.79, 33.06, 37.18, 41.28, 51.47, 55.94, 62.57, 68.05, 69.87, 70.70, 71.19, 72.02, 72.75, 75.35, 100.75, 114.71, 129.35 (2C), 130.09 (2C), 158.50, 175.58; HRMS (ESI-TOF) *m/z* calcd for $C_{41}H_{73}NO_{10}Na$ $[M+Na]^+$ 762.5127, found 762.5123.

Compound 1cf. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +24.44 (c = 2.01, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.87 (d, *J* = 6.7 Hz, 3H), 1.25-1.63 (m, 40H), 2.49 (t, *J* = 7.7 Hz, 2H, H-1"), 2.89 (t, *J* = 7.7 Hz, 2H, H-2"), 3.47-3.79 (m, 8H), 3.81 (dd, *J* = 4.6, 10.8 Hz, 1H), 3.88 (d, *J* = 3.0 Hz, 1H), 4.18 (td, *J* = 5.0, 9.6 Hz, 1H), 4.85 (d, *J* = 3.6 Hz, 1H), 6.93-7.20 (m, 4H); ^{13}C NMR (200 MHz, MeOD): δ 14.48, 23.41, 26.57, 30.12, 30.40, 30.44 (9C), 30.48 (4C), 30.57, 31.67, 32.70, 33.22, 38.72, 51.38, 62.53 67.91, 69.76, 70.60, 71.09, 71.88, 72.62, 75.40, 100.64, 115.78, 115.88, 130.57, 130.61, 137.39, 61.77, 162.98, 174.11; HRMS (ESI-TOF) *m/z* calcd for $C_{40}H_{70}FNO_9Na$ $[M+Na]^+$ 750.4927, found 750.4924.

Compound 1cg. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +26.93 (c = 1.85, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.90 (d, *J* = 6.8 Hz, 3H), 1.16-1.57 (m, 40H), 3.49 (m, 1H)3.55-3.72 (m, 10H), 3.72 (s, 2H, H-1"), 3.75 (dd, *J* = 3.9, 10.1Hz, 1H), 3.87 (dd, *J* = 4.2, 10.6 Hz, 1H), 4.19 (dd, *J* = 4.4, 10.6 Hz, 1H), 4.84 (d, *J* = 3.9 Hz, 1H), 7.43-7.84 (m, 7H); ^{13}C NMR (100 MHz, MeOD): δ 14.22, 22.88, 26.03, 29.56, 29.86 (2C), 29.91 (7C), 29.94 (6C), 32.14, 32.96, 43.26, 50.68, 62.22, 69.14, 70.04, 70.47, 70.81, 70.93, 72.41, 74.93, 99.84, 125.94, 126.35, 129.75 (2C), 129.94, 130.01, 130.10, 131.99, 136.64, 137.86, 172.64; HRMS (ESI-TOF) *m/z* calcd for $C_{43}H_{71}NO_9Na$ $[M+Na]^+$ 768.5021, found 768.5017.

Compound 1ch. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +23.51 (c = 2.12, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.86 (d, *J* = 6.7 Hz, 3H), 1.16-1.69 (m, 46H), 2.20 (t, *J* = 7.5 Hz, 2H, H-1"), 2.59 (t, *J* = 7.6 Hz, 2H, H-5"), 3.47-3.82 (m, 8H), 3.86 (dd, *J* = 4.3, 10.6 Hz, 1H), 3.90 (d, *J* = 3.3 Hz, 1H), 4.17 (dd, *J* = 5.2, 9.6 Hz, 1H), 4.87 (d, *J* = 3.4 Hz, 1H), 6.95-7.24 (m, 5H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.39, 23.16, 26.38, 26.92, 29.85 (2C), 30.20 (14C), 32.43, 32.97, 33.06, 33.94, 37.90, 38.23, 51.01, 62.34, 67.86, 69.47, 70.33, 70.80, 71.38, 72.53, 75.15, 100.27, 126.16, 128.75 (2C), 128.84 (2C), 143.02,

Compound 1ci. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +18.37 (c = 1.71, MeOH/DCM = 1/1);

^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.82 (d, *J* = 6.8 Hz, 3H), 1.25-1.69 (m, 50H), 2.19 (t, *J* = 7.5 Hz, 2H, H-1"), 2.49 (t, *J* = 7.6 Hz, 2H, H-7"), 3.48-3.82 (m, 8H), 3.86 (dd, *J* = 4.9, 10.8 Hz, 1H, H,H-6b), 3.90 (d, *J* = 3.3 Hz, 1H), 4.17 (td, *J* = 5.2, 9.6 Hz, 1H), 4.87 (d, *J* = 3.4 Hz, 1H), 6.92-7.24 (m, 5H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.55, 23.61, 26.76, 26.88, 27.40, 27.70, 30.28, 30.33, 30.64 (14C), 32.30, 32.59, 32.92, 34.46, 38.44, 38.81, 51.63, 62.67, 69.15, 70.04, 70.86, 71.34, 72.24, 72.84, 73.56, 75.30, 100.91, 127.16, 129.14 (2C), 129.17 (2C), 143.80, 175.71; HRMS (ESI-TOF) *m/z* calcd for $C_{45}H_{81}NO_9Na$ $[M+Na]^+$ 802.5804, found 802.5800.

Compound 1da. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +46.69 (c = 2.09, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.19-1.74 (m, 16H), 2.21 (t, *J* = 7.7 Hz, 2H, H-1"), 2.62 (t, *J* = 7.5 Hz, 2H), 3.53-3.75 (m, 7H), 3.78 (dd, *J* = 3.8, 10.0 Hz, 1H). 3.82 (t, *J* = 5.9 Hz, 1H), 3.87 (d, *J* = 4.4 Hz, 1H), 3.88 (dd, *J* = 4.4, 10.6 Hz, 1H), 4.21 (td, *J* = 4.8, 10.7 Hz, 1H), 4.87 (d, *J* = 3.8 Hz, 1H), 7.11-7.24 (m, 5H); ^{13}C NMR (150 MHz, MeOD): δ 14.54, 23.83, 26.76, 27.20, 27.69, 30.30, 30.51, 32.96, 33.05, 37.11, 37.41, 52.02, 62.94, 68.49, 70.41, 71.24, 71.71, 72.78, 73.01, 75.81, 101.35, 126.75, 129.39 (2C), 129.55 (2C), 144.13, 176.04; HRMS (ESI-TOF) *m/z* calcd for $C_{28}H_{47}NO_9Na$ $[M+Na]^+$ 564.3143, found 564.3135.

Compound 1db. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +29.95 (c = 2.35, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90 (t, *J* = 6.6 Hz, 3H), 1.25-1.77 (m, 52H), 2.20 (t, *J* = 7.6 Hz, 2H, H-1"), 2.59 (t, *J* = 7.4 Hz, 2H), 3.61-3.85 (m, 8H), 3.87 (d, *J* = 2.6 Hz, 1H), 4.02 (dd, *J* = 4.5, 10.9 Hz, 1H), 4.46 (td, *J* = 4.9, 10.8 Hz, 1H), 4.93 (d, *J* = 3.8 Hz, 1H), 7.10-7.24 (m, 5H); ^{13}C NMR (150 MHz, MeOD): δ 14.55, 23.85, 26.48 26.62, 27.68, 30.29, 30.58 (2C), 30.86 (17C), 32.84, 33.16, 33.19, 37.01, 52.89, 62.98, 68.35, 70.40, 71.26, 71.72, 72.81, 73.06, 75.78, 101.40, 126.70, 129.36 (2C), 129.54 (2C), 144.11, 170.15; HRMS (ESI-TOF) *m/z* calcd for $C_{46}H_{83}NO_9Na$ $[M+Na]^+$ 816.5960, found 816.5954.

Compound 1dc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +52.20 (c = 2.0, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 1.43-1.78 (m, 6H), 2.59 (t, *J* = 7.4 Hz, 2H), 3.61-3.85 (m, 8H), 3.86 (d, *J* = 2.9 Hz, 1H). 4.02 (dd, *J* = 4.5, 10.8 Hz, 1H), 4.46 (td, *J* = 4.9, 10.6 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 7.11-7.85 (m, 9H); ^{13}C NMR (150 MHz, MeOD): δ 26.63, 30.87, 32.85, 37.02, 52.89, 62.98, 68.34, 70.41, 71.26, 71.73, 72.82, 73.06, 75.78, 101.40 126.71, 128.58 (2C), 129.36 (2C), 129.54 (2C), 129.71 (2C), 132.83, 136.00, 144.11, 170.15; HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{36}ClNO_9Na$ $[M+Na]^+$ 576.1971, found 576.1970.

Compound 1dd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +48.79 (c = 2.28, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 1.55-1.71 (m, 6H), 2.50 (dt, *J* = 3.4, 7.7 Hz, 2H, 1”), 2.61 (t, *J* = 7.9 Hz, 2H), 2.88 (t, *J* = 7.7 Hz, 2H, H-2”), 3.48-3.80 (m, 8H), 3.85 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.88 (d, *J* = 5.0 Hz, 1H), 4.20 (td, *J* = 4.8, 10.3 Hz, 1H), 4.84 (d, *J* = 3.8 Hz, 1H), 6.96-7.24 (m, 8H); ^{13}C NMR (150 MHz, MeOD): δ 26.66, 32.10, 32.97, 33.20, 37.09, 39.05, 52.04, 62.96, 68.39, 70.38, 71.23, 71.68, 72.77, 72.93, 75.86, 101.32, 126.75, 129.39 (2C), 129.55 (2C), 131.15, 131.21, 134.14, 138.30, 144.14, 174.76; HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{39}NO_9SNa$ $[M+Na]^+$ 576.2238, found 576.2229.

Compound 1de. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +48.38 (c = 2.0, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 1.55-1.71 (m, 6H), 2.48 (t, *J* = 7.7 Hz, 2H, H-1”), 2.61 (t, *J* = 7.7 Hz, 2H), 2.84 (t, *J* = 7.7 Hz, 2H, H-2”), 3.48-3.80 (m, 11H, , H-2, H-3, H-5, H-6a, H-1’, H-3’, H-4’, OMe), 3.83 (dd, *J* = 4.8, 10.7 Hz, 1H), 3.86 (d, *J* = 3.2 Hz, 1H), 4.19 (td, *J* = 5.0, 10.1 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 6.81-7.24 (m, 9H); ^{13}C NMR (150 MHz, MeOD): δ 26.68, 32.14, 32.98, 33.20, 37.09, 39.33, 52.03, 55.85, 62.98, 68.39, 70.40, 71.24, 71.68, 72.77, 72.94, 75.88, 101.34, 115.08 (2C), 126.75, 129.40 (2C), 129.56 (2C), 130.47 (2C), 134.33, 144.16, 159.75, 175.09; HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{43}NO_{10}Na$ $[M+Na]^+$ 600.2779, found 600.2777.

Compound 1df. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +46.90 (c = 2.15, MeOH/DCM = 1/1);

^{1}H NMR (600 MHz, MeOD): δ 1.56-1.73 (m, 6H), 2.21 (t, *J* = 7.6 Hz, 2H, H-1"), 2.61 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H, H-2"), 3.51-3.88 (m, 8H), 3.88 (d, *J* = 3.9 Hz, 1H), 3.89 (dd, *J* = 4.2, 10.7 Hz, 1H), 4.21 (td, *J* = 4.9, 10.6 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 6.81-7.24 (m, 9H); ^{13}C NMR (150 MHz, MeOD): δ 26.75, 30.21, 32.84, 32.96, 37.11, 39.32, 52.01, 62.94, 68.48, 70.40, 71.2, 71.70, 72.75, 72.99, 75.81, 101.33, 115.08 (2C), 126.74, 129.38 (2C), 129.55 (2C), 130.46 (2C), 134.32, 144.13, 159.74, 176.04; HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{40}FNO_9Na$ $[M+Na]^+$ 588.2579, found 588.2584.

Compound 1dh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +44.79 (c = 2.10, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.15-1.70 (m, 12H), 2.21 (t, *J* = 7.3 Hz, 2H, H-1"), 2.59 (t, *J* = 7.56 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H, H-2"), 3.53-3.84 (m, 8H), 3.87 (d, *J* = 3.7 Hz, 1H), 3.88 (dd, *J* = 4.2, 9.9 Hz, 1H), 4.21 (dd, *J* = 5.0, 9.6 Hz, 1H), 4.85 (1H merged with water), 7.11-7.26 (m, 10H); ^{13}C NMR (100 MHz, MeOD): δ 27.68, 30.09, 30.88, 32.98, 34.74 36.87, 37.12, 37.30, 39.14, 51.97, 62.91, 68.41, 70.37, 71.20, 71.66, 72.76, 72.93, 75.69, 101.30, 126.75, 126.81, 129.39 (2C), 129.42 (2C), 129.55 (4C), 143.93, 144.10, 175.95; ; HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{40}FNO_9Na$ $[M+Na]^+$ 588.2579, found 588.2584.

Compound 1ea. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +46.70 (c = 1.94, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.13-1.67 (m, 20H), 2.18 (t, *J* = 7.6 Hz, 2H, H-1"), 2.57 (t, *J* = 7.7 Hz, 2H, H-10'), 3.52-3.80 (m, 8H), 3.86 (dd, *J* = 4.6, 10.7 Hz, 1H). 3.90 (d, *J* = 2.0 Hz, 1H), 4.19 (td, *J* = 3.9, 9.2 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.12-7.23 (m, 5H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.41, 23.28, 26.60, 27.12, 29.74, 29.97, 30.29, 32.26, 32.41, 33.08, 34.17, 36.61, 37.08, 51.22, 62.46 67.92, 69.68, 70.52, 71.02, 71.70, 72.59, 75.33, 100.53, 126.20, 128.84 (2C), 129.01 (2C), 143.52, 175.36; HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{51}NO_9Na$ $[M+Na]^+$ 592.3456, found 592.3450.

Compound 1eb. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +24.48 (c = 2.85, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.25-1.69 (m, 56H),

2.20 (t, *J* = 7.6 Hz, 2H, H-1"), 2.58 (t, *J* = 7.7 Hz, 2H, H-10'), 3.53-3.82 (m, 8H), 3.86 (dd, *J* = 4.3, 10.6 Hz, 1H). 3.89 (d, *J* = 3.16 Hz, 1H), 4.18 (td, *J* = 3.8, 10.0 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.11-7.24 (m, 5H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.53, 23.53, 26.70, 26.86, 30.24 (2C), 30.33, 30.53 (18C), 32.51, 32.83, 33.02, 34.40, 36.81, 37.22, 51.51, 62.60, 68.08, 69.94, 70.74, 71.24, 72.09, 72.74, 75.38, 100.79, 126.39, 129.03 (2C), 129.19 (2C), 143.71, 175.62; HRMS (ESI-TOF) *m/z* calcd for $C_{48}H_{87}NO_9Na$ $[M+Na]^+$ 844.6273, found 844.6277.

Compound 1ec. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +43.87 (c = 1.89, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.11-1.71 (m, 10H), 2.54 (t, *J* = 7.7 Hz, 2H, H-10'), 3.58-3.82 (m, 8H), 3.88 (d, *J* = 3.0 Hz, 1H), 3.99 (dd, *J* = 4.7, 10.8 Hz, 1H), 4.43 (td, *J* = 4.8, 9.7 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 7.11-7.24 (m, 5H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.41, 29.99, 30.24, 32.28, 34.20, 36.60, 52.03, 62.53, 67.78, 69.74, 70.59, 71.09, 71.83, 72.64, 75.35, 100.63 126.22, 127.95 (2C), 128.87 (2C), 129.05 (2C), 129.25 (2C), 132.45, 135.06, 143.58, 169.38; HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{40}ClNO_9Na$ $[M+Na]^+$ 604.2284, found 604.2277.

Compound 1ee. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +39.34 (c = 2.01, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.17-1.63 (m, 10H), 2.47 (t, *J* = 7.8 Hz, 2H, H-1"), 2.57 (t, *J* = 7.7 Hz, 2H, H-10'), 2.84 (t, *J* = 7.7 Hz, 2H, H-2"), 3.47-3.76 (m, 11H, H-2, H-3, H-5, H-6a, H-1', H-3', H-4', OMe), 3.80 (dd, *J* = 4.8, 10.9 Hz, 1H), 3.88 (d, *J* = 2.8 Hz, 1H), 4.16 (m, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 6.78-7.23 (m, 9H); ^{13}C NMR (200 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.39, 29.98, 30.29, 31.60, 32.29, 33.07, 36.59, 38.87, 51.30, 55.59, 62.43, 67.76, 69.69, 70.52, 71.00, 71.83, 72.46, 75.31, 100.56, 114.54 (2C), 126.18, 128.83 (2C), 128.99 (2C), 129.92 (2C), 133.60, 143.52, 158.88, 174.38; HRMS (ESI-TOF) *m/z* calcd for $C_{32}H_{47}NO_{10}Na$ $[M+Na]^+$ 628.3092, found 628.3088.

Compound 1ef. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +44.59 (c = 2.06, MeOH/DCM = 1/1);

^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.25-1.59 (m, 10H), 2.20 (t, *J* = 7.6 Hz, 2H, H-1”), 2.57 (t, *J* = 7.7 Hz, 2H, H-10’), 2.79 (t, *J* = 7.6 Hz, 2H, H-2”), 3.52-3.82 (m, 8H), 3.87 (dd, *J* = 4.7, 10.9 Hz, 1H), 3.89 (d, *J* = 3.0 Hz, 1H), 4.19 (td, *J* = 4.7, 9.7 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 6.92-7.42 (m, 9H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.74, 30.29, 30.61, 31.92, 32.66, 33.27, 36.90, 38.87, 51.68, 62.73, 68.07, 70.06, 70.90, 71.37, 72.35, 72.77, 75.58, 100.96, 115.90, 116.11, 126.51, 129.15 (2C), 129.31 (2C), 130.86, 130.93, 137.84, 143.86, 161.49, 163.91, 174.45; HRMS (ESI-TOF) *m/z* calcd for $C_{31}H_{44}FNO_9$ Na $[M+Na]^+$ 616.2892, found 616.2883.

Compound 1eg. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +26.91 (c = 2.15, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.20-1.63 (m, 10H), 2.55 (t, *J* = 7.7 Hz, 2H), 3.43 (s, 2H), 3.44-3.89 (m, 8H, H-2, H-3, H-5, H-6a, H-1’, H-3’, H-4’, H-1”), 3.82 (d, *J* = 2.4 Hz, 1H), 3.88 (m, 1H), 4.14 (td, *J* = 4.4, 9.0 Hz, 1H), 4.83 (d, *J* = 3.8 Hz, 1H), 6.93-7.23 (m, 12H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.24, 29.52, 29.84, 30.10, 32.06, 36.46, 43.47, 51.05, 62.37, 67.73, 69.44, 70.33, 70.77, 71.28, 72.53, 75.06, 100.23, 126.04, 126.11, 126.63, 128.70 (2C), 128.86 (2C), 129.33, 129.55, 130.01, 130.35, 132.43, 136.25, 136.55, 136.71, 143.37, 173.07; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{45}NO_9$ Na $[M+Na]^+$ 634.2987, found 634.2984.

Compound 1eh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +34.93 (c = 1.73, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.25-1.67 (m, 16H), 2.19 (t, *J* = 7.5 Hz, 2H, H-1”), 2.56 (t, *J* = 7.5 Hz, 2H, H-10’), 2.58 (t, *J* = 7.5 Hz, 2H, H-5”), 3.50-3.80 (m, 8H), 3.86 (dd, *J* = 4.8, 10.9 Hz, 1H), 3.88 (d, *J* = 3.0 Hz, 1H), 4.19 (td, *J* = 4.7, 9.7 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.59, 26.63, 29.71, 30.15, 30.43, 32.10, 32.44, 33.14, 36.51, 36.74, 37.07, 51.43, 62.56, 68.02, 69.86, 70.67, 71.19, 72.00, 72.70, 75.43, 100.74, 126.33, 126.44, 128.98 (2C), 129.03 (2C), 129.14 (4C), 143.37, 143.66, 175.42; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{51}NO_9$ Na $[M+Na]^+$ 640.3456,

found 640.3452.

Compound 1ei. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +31.69 (c = 1.94, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.25-1.60 (m, 20H), 2.19 (t, *J* = 7.5 Hz, 2H, H-1"), 2.57 (t, *J* = 7.5 Hz, 4H, H-10', H-7"), 3.52-3.81 (m, 8H), 3.86 (dd, *J* = 4.6,10.7 Hz, 1H), 3.89 (d, *J* = 2.2 Hz, 1H), 4.18 (td, *J* = 4.4, 9.2 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.09-7.24 (m, 10H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.61, 26.72, 29.93, 30.07, 30.13, 30.41, 32.36, 32.41, 33.07, 34.30, 36.69, 36.72, 37.13, 51.39, 62.55, 68.01, 69.84, 70.65, 71.17, 71.95, 72.68, 75.39, 100.70, 126.32, 126.35, 128.96 (2C), 128.98 (2C), 129.12 (4C), 143.57, 143.64, 175.47; HRMS (ESI-TOF) *m/z* calcd for $C_{36}H_{55}NO_9$ Na $[M+Na]^+$ 668.3769, found 668.3766.

Compound 1fa. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +33.70 (c = 2.04, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.11-1.69 (m, 26H), 2.19 (t, *J* = 7.6 Hz, 2H, H-1"), 2.57 (t, *J* = 7.7 Hz, 2H, H-13'), 3.52-3.82 (m, 8H), 3.86 (dd, *J* = 4.7, 10.9 Hz, 1H), 3.89 (d, *J* = 2.6 Hz, 1H), 4.18 (td, *J* = 4.6, 9.6 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.11-7.24 (m, 5H); ^{13}C NMR (100 MHz, MeOD): δ 14.42, 23.30, 26.56, 26.61, 29.76, 29.98, 30.22, 30.31, 30.40, 30.45, 32.29, 32.42, 33.06, 34.18, 36.63, 37.08, 51.23, 62.46, 67.93, 69.69, 70.52, 71.02, 71.71, 72.62, 75.29 100.53, 126.19, 128.85 (2C), 129.02 (2C), 143.58, 175.37; HRMS (ESI-TOF) *m/z* calcd for $C_{33}H_{57}NO_9Na$ $[M+Na]^+$ 634.3926, found 634.3925.

Compound 1fb. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +22.53 (c = 1.88, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.35-1.69 (m, 62H), 2.19 (t, *J* = 7.5 Hz, 2H, H-1"), 2.56 (t, *J* = 7.8 Hz, 2H, H-10'), 3.53-3.79 (m, 8H), 3.86 (dd, *J* = 4.4, 10.5 Hz, 1H), 3.89 (m, 1H), 4.17 (m, 1H), 4.87 (d, *J* = 3.3 Hz, 1H), 7.12-7.24 (m, 5H); ^{13}C NMR (200 MHz, MeOD): δ 14.40, 23.20, 26.41, 26.46, 29.89 (2C), 29.99, 30.11, 30.18 (2C), 30.21 (12C), 30.24 (4C), 30.30, 30.34, 32.06, 32.47, 32.97, 34.03, 36.47, 37.00, 51.06, 62.37, 67.90, 69.53, 70.36, 70.86, 71.44, 72.54, 75.28, 100.33, 126.07, 128.72 (2C), 128.89 (2C), 143.39, 175.22; HRMS (ESI-TOF) *m/z* calcd for $C_{51}H_{93}NO_9Na$ $[M+Na]^+$ 886.6743, found 886.6741.

Compound 1fc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +29.24 (c = 2.05, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.26-1.72 (m, 16H), 2.57 (t, *J* = 7.7 Hz, 2H, H-10'), 3.60 (m, 1H), 3.65-3.84 (m, 7H), 3.89 (d, *J* = 2.8 Hz, 1H), 4.0 (dd, *J* = 4.5, 10.9 Hz, 1H), 4.43 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.92 (d, *J* = 3.8 Hz, 1H), 7.10-7.24 (m, 5H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 16.96, 17.66, 26.77, 30.34, 30.55, 30.68, 32.74, 33.17, 36.96, 52.72, 62.80, 68.04, 70.15, 71.00, 71.45, 72.53, 72.88, 75.41, 101.13, 126.57, 129.21, 129.36 (2C), 129.46 (2C), 129.69 (2C), 130.11 (2C), 132.20, 143.94, 168.66; HRMS (FAB) *m/z* calcd for $C_{32}H_{46}ClNO_9Na$ $[M+Na]^+$ 646.2753, found 646.2755.

Compound 1fd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +27.88 (c = 1.50, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.26-1.63 (m, 16H), 2.57 (t, *J* = 7.5 Hz, 4H, H-1", H-13'), 3.13 (t, *J* = 7.5 Hz, 2H, H-2"), 3.46-3.80 (m, 8H), 3.84 (dd, *J* = 4.5,10.8 Hz, 1H), 3.88 (d, *J* = 2.8 Hz, 1H), 4.17 (m, 1H), 4.85 (d, *J* = 3.7 Hz, 1H), 6.82-7.24 (m, 8H); ^{13}C NMR (100 MHz, MeOD): δ 16.97, 17.66, 26.34, 26.83, 26.92, 30.39, 30.65, 30.76, 32.79, 36.99, 39.08, 51.87, 62.82, 68.20, 70.20, 71.03, 71.48, 72.48, 72.90, 75.67, 101.13, 124.43, 125.74, 126.62, 127.84, 129.26 (2C), 129.42 (2C), 143.99, 144.53, 174.15; HRMS (ESI-TOF) *m/z* calcd for $C_{32}H_{49}NO_9SNa$ $[M+Na]^+$ 646.3020, found 646.3023.

Compound 1fe. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +35.87 (c = 1.67, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.11-1.66 (m, 16H), 2.45 (t, *J* = 7.7 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 3.46-3.84 (m, 12H, H-2, H-3, H-5, H-6, H-1', H-3', H-4', OMe), 3.87 (d, *J* = 2.2 Hz, 1H), 4.15 (m, 1H), 4.82 (d, *J* = 3.7 Hz, 1H), 6.77-7.21 (m, 9H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 27.24, 27.55, 30.10, 30.46, 30.55, 31.76, 32.42, 34.30, 36.73, 38.59, 39.01, 51.42, 55.73, 62.58, 67.92, 69.81, 70.66, 71.13, 71.92, 72.64, 75.43, 100.68, 114.67 (2C), 126.30, 128.95 (2C), 129.12 (2C), 130.04 (2C), 133.74, 143.68, 159.00, 174.50; HRMS (ESI-TOF) *m/z* calcd for $C_{35}H_{53}NO_{10}Na$ $[M+Na]^+$ 670.3562, found 670.3557.

Compound 1ff. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +34.23 (c = 2.11, MeOH/DCM = 1/1);

^{1}H NMR (400 MHz, MeOD): δ 1.29-1.66 (m, 16H), 2.51 (t, *J* = 7.5 Hz, 2H, H-13'), 2.58 (t, *J* = 7.7 Hz, 2H, H-1"), 2.90 (t, *J* = 7.7 Hz, 2H, H-2"), 3.47-3.80 (m, 8H), 3.84 (dd, *J* = 4.6, 11.0 Hz, 1H), 3.87 (d, *J* = 2.4 Hz, 1H),4.20 (td, *J* = 4.7, 9.7 Hz, 1H), 4.85 (d, *J* = 3.7 Hz, 1H), 6.96-7.25 (m, 9H); ^{13}C NMR (100 MHz, MeOD): δ 27.03, 30.49, 30.75, 30.87, 30.90, 30.95, 32.13, 32.93, 33.32, 37.07, 39.05, 51.96, 62.91, 68.24, 70.32, 71.19, 71.62, 72.76, 72.96, 75.75, 101.26, 116.07, 116.29, 126.73, 129.37 (2C), 129.51 (2C), 131.144, 131.22, 138.29, 144.13, 161.80, 164.21, 174.74; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{50}FNO_9Na$ $[M+Na]^+$ 658.3362, found 658.3357.

Compound 1fg. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +23.21 (c = 2.13, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.19-1.63 (m, 16H), 2.54 (t, *J* = 7.7 Hz, 2H, H-13'), 3.42-3.89 (m, 10H, H-2, H-3, H-5, H-6a, H-1', H-3', H-4', H-1"), 3.82 (d, *J* = 2.4 Hz, 1H), 3.86 (m, 1H), 4.14 (td, *J* = 4.4, 9.0 Hz, 1H), 4.83 (d, *J* = 3.8 Hz, 1H), 6.91-7.24 (m, 12H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.22, 27.80, 29.52, 29.80, 29.84, 30.10, 30.18, 32.06, 36.46, 43.47, 51.05, 62.37, 67.73, 69.44, 70.33, 70.77, 71.28, 72.53, 75.06, 99.73, 125.74, 126.01, 126.53, 128.64 (2C), 128.78 (2C), 129.33, 129.55, 130.01, 130.35, 132.43, 136.25, 136.55, 136.71, 143.37, 174.17; HRMS (ESI-TOF) *m/z* calcd for $C_{37}H_{51}NO_9$ Na $[M+Na]^+$ 676.3456, found 676.3455.

Compound 1fh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +27.92 (c = 2.03, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.14-1.69 (m, 22H), 2.20 (t, *J* = 7.5 Hz, 2H, H-13'), 2.56 (t, *J* = 7.7 Hz, 2H, H-1"), 2.59 (t, *J* = 7.7 Hz, 2H, H-2"), 3.52-3.82 (m, 8H), 3.86 (dd, *J* = 4.9, 11.1 Hz, 1H), 3.89 (d, *J* = 2.3 Hz, 1H), 4.19 (m, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (200 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.47, 27.16, 29.62, 30.01, 30.34, 30.43, 30.49, 31.99, 32.32, 33.11, 34.21, 36.42, 36.65, 36.99 51.28, 62.48, 67.96, 69.72, 70.56, 71.05, 71.77, 72.65, 75.33, 100.57, 126.22, 126.35, 128.88 (2C), 128.94 (2C), 129.04 (2C), 129.05 (2C), 143.24, 143.61, 175.28; HRMS (ESI-TOF) *m/z* calcd for $C_{37}H_{57}NO_9Na$

$[M+Na]^+$ 682.3926, found 682.3923.

Compound 1fi. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +25.77 (c = 2.0, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.14-1.69 (m, 26H), 2.20 (t, *J* = 7.4 Hz, 2H, H-1"), 2.56 (t, *J* = 7.1 Hz, 2H, H-13'), 2.59 (t, *J* = 7.4 Hz, 2H, H-7"), 3.53-3.82 (m, 8H), 3.86 (dd, *J* = 4.6, 10.9 Hz, 1H), 3.89 (m, 1H), 4.19 (m, 1H), 4.87 (d, *J* = 3.2 Hz, 1H), 7.11-7.24 (m, 10H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 26.69, 26.81, 29.81, 30.05 30.20, 30.46, 30.55, 30.66, 30.80, 32.22, 32.56, 34.42, 36.60, 36.83, 37.23, 51.55, 62.63 68.14, 69.98, 70.79, 71.29, 72.15, 72.80, 75.37, 100.84, 126.41, 126.53, 129.06, 129.11, 129.22, 143.47, 143.77, 175.64; HRMS (ESI-TOF) *m/z* calcd for $C_{39}H_{61}NO_9Na$ $[M+Na]^+$ 710.4239, found 710.4231.

Compound 1ga. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +17.52 (c = 1.64, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.26-1.35 (m, 14H), 1.56-1.67 (m, 6H), 2.20 (t, *J* = 7.6 Hz, 2H, H-1"), 2.67 (t, *J* = 7.8 Hz, 2H, H-10'), 3.52-3.83 (m, 8H), 3.87 (dd, *J* = 4.0, 10.3 Hz, 1H), 3.89 (d, *J* =2.7 Hz, 1H), 4.19 (td, *J* =4.7, 10.0 Hz, 1H), 4.88 (d, *J* = 3.7 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1) δ 14.66, 23.71, 26.87, 27.10, 30.20, 30.32, 30.40, 30.61, 32.36, 32.87, 33.15, 36.77, 37.39, 51.72, 62.81, 68.25, 70.17, 70.79, 71.49, 72.41, 72.89, 75.60, 101.06, 126.14, 129.93 (4C), 130.94, 148.47, 175.81; HRMS (FAB) *m/z* calcd for $C_{31}H_{50}NO_9F_3Na$ [M + Na]$^+$ 660.3335, found 660.3339.

Compound 1gb. R_f 0.5 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +8.33 (c = 0.88, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.84 (t, *J* = 6.7, 3H), 1.18-1.31 (m, 50H), 1.53-1.62 (m, 6H), 2.17 (t, *J* = 7.6 Hz, 2H, H-1"), 2.63 (t, *J* = 7.7 Hz, 2H, H-10'), 3.52 (m, 2H), 3.64 (dd, *J* = 2.8, 11.1 Hz, 1H), 3.67-3.77 (m, 5H), 3.84 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.89 (d, *J* = 2.8 Hz, 1H), 4.16 (td, *J* = 4.4, 8.8 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H, merge with $CDCl_3$); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.28, 23.06, 26.14, 26.32, 29.64, 29.76, 29.84, 29.97, 30.08 (18C), 31.61, 32.33, 32.77, 36.14, 36.85,

50.90, 62.18, 67.66, 69.37, 70.16, 70.70 71.33, 72.29, 75.05, 100.19, 125.48, 129.14 (4C), 132.62, 147.52, 175.04; HRMS (FAB) *m/z* calcd for $C_{48}H_{86}NO_9F_3Na$ $[M + Na]^+$ 912.6147, found 912.6149.

Compound 1gc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +23.36 (c = 2.05, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD): δ 1.29-1.47 (m, 4H), 1.56-1.62 (m, 3H), 1.68-1.70 (m, 1H), 2.64 (d, *J* = 7.8 Hz, 2H, H-10'), 3.59-3.63 (m, 1H), 3.66-3.84 (m, 7H), 3.86 (d, *J* = 3.3 Hz, 1H), 4.01 (dd, *J* = 4.4, 10.8 Hz, 1H), 4.44 (dd, *J* = 5.0, 10.7 Hz, 1H), 4.92 (d, *J* = 3.8 Hz, 1H, H-1, merge with water), 7.32 (d, *J* = 8.0 Hz, 2H), 7.45-7.48 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.82-7.85 (m, 2H); ^{13}C NMR (100 MHz, MeOD); δ 26.67, 30.19, 30.37, 32.33, 32.96, 36.60, 52.84, 62.79, 68.04, 70.21, 71.06, 71.50, 72.70, 72.81, 75.39, 101.23, 126.11, 129.71 (2C), 130.00 (2C), 130.21 (4C), 134.46, 138.76, 148.74, 168.73. HRMS (FAB) *m/z* calcd for $C_{30}H_{39}NO_9F_3ClNa$ $[M + Na]^+$ 672.2163, found 672.2166.

Compound 1gd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +25.11 (c = 2.32, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.35-1.67 (m, 10H), 2.59 (dt, *J* = 2.7, 7.3 Hz, 2H, H-1"), 2.70 (t, *J* = 7.7 Hz, 2H, H-10'), 3.14 (d, *J* = 7.3 Hz, 2H, H-2"), 3.50 (m, 1H), 3.54-3.73 (m, 5H), 3.78 (d, *J* = 3.6, 10.1 Hz, 1H). 3.80 (m, 1H), 3.86 (dd, *J* = 4.6, 11.0 Hz, 1H), 3.87 (d, *J* = 4.0 Hz, 1H), 4.21 (td, *J* = 4.7, 10.3 Hz, 1H), 4.85 (d, *J* = 3.6 Hz, 1H), 6.83-6.84 (m, 1H), 6.88-6.90 (m, 1H), 7.16 (d, *J* = 5.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, MeOD) δ 26.81 (2C), 30.30, 30.60, 32.41, 33.13, 36.69, 39.03, 51.90, 62.79, 68.18, 70.23, 71.08, 71.50, 72.61, 72.84, 75.63, 101.18, 124.41, 125.73, 126.13, 127.82, 130.06 (4C), 133.08, 144.59, 148.77, 174.19. HRMS (FAB) *m/z* calcd for $C_{30}H_{42}NO_9F_4SNa$ $[M + Na]^+$ 672.2430, found 672.2435.

Compound 1ge. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +22.71 (c = 1.54, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1) δ 1.27-1.35 (m, 6H), 1.52-1.53 (m, 1H), 1.64-1.66 (m, 3H), 2.48 (t, *J* = 7.7 Hz, 2H, H-1"), 2.68 (t, *J* = 7.7 Hz, 2H, H-2"), 2.85 (t, *J* = 7.7 Hz, 2H,

H-10'), 3.47-3.53 (m, 2H), 3.63 (dd, *J* = 4.7, 10.7 Hz, 1H), 3.68-3.79 (m, 5H), 3.76 (s, 3H, OMe), 3.82 (dd, *J* = 4.7, 10.1 Hz, 1H), 3.87 (d, *J* = 2.9 Hz, 1H), 4.19 (dd, *J* = 4.8, 9.9 Hz, 1H), 4.83 (1H merged with water peak), 6.80 (d, *J* = 8.53 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1) δ 26.59, 30.11, 30.41, 31.86, 32.18, 33.01, 36.54, 39.06, 51.59, 55.61, 62.63, 67.96, 69.98, 70.82 71.27, 72.28, 72.60, 75.44, 100.89, 114.74 (2C), 125.95, 129.78 (2C), 130.14 (4C), 133.88, 148.39, 159.28, 174.69; HRMS (FAB) *m/z* calcd for $C_{79}H_{77}NO_{11}F_{20}Na$ $[M+Na]^+$ 1618.5075, found 1618.5081.

Compound 1gf. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +23.62 (c = 1.05, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1): δ 1.25-1.65 (m, 10H), 2.49 (t, *J* = 7.7, 2H, H-1"), 2.66 (t, *J* = 7.7 Hz, 2H, H-2"), 2.88 (t, *J* = 7.7 Hz, 2H, H-10'), 3.47-3.52 (m, 2H), 3.63 (dd, *J* = 4.5, 10.9 Hz, 1H), 3.67-3.83 (m. 6H, H-2, H-3, H5), 3.88 (d, *J* = 2.7 Hz, 1H), 4.18 (m, 1H), 4.84 (d, *J* = 3.7 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.18 (d, *J* = 5.5 Hz, 1H), 7.30 (d, *J* = 8. Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1) δ 26.78, 30.29, 30.62, 32.01, 32.45, 33.30, 36.75, 38.99, 51.75, 62.82, 68.15, 70.13, 70.98, 71.45, 72.40, 72.83, 75.66, 101.03, 116.00, 116.22, 124.44, 126.30, 128.86, 129.18, 129.94, 130.93, 131.01, 137.85, 137.88, 148.48, 161.55, 163.97, 174.53. HRMS (FAB) calcd for $C_{32}H_{43}NO_9F_4Na$ $[M + Na]^+$ 684.2772, found 684.2770.

Compound 1gg. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +20.52 (c = 3.61, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1) δ 1.16-1.57 (m, 10H), 2.61 (t, *J* = 7.6 Hz, 2H, H-10'), 3.49 (ddd, *J* = 2.3, 5.9, 9.5 Hz, 1H), 3.56-3.70 (m, 7H), 3.71 (brs, 2H, H-1"), 3.73 (d, *J* = 4.8 Hz, 1H), 3.76 (dd, *J* = 3.8, 10.0 Hz, 1H), 3.87 (dd, *J* = 4.1, 10.6 Hz, 1H), 4.19 (td, *J* = 4.3, 6.5 Hz, 1H), 4.85 (d, *J* = 3.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.43-7.48 (m, 3H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.79-7.82 (m, 4H). ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1) δ 26.76, 30.20, 30.45, 32.26, 32.74, 36.63, 44.23, 52.65, 62.83, 68.31, 70.18, 71.01, 71.44, 72.55, 72.89, 75.28,

101.12, 126.07, 126.81, 127.24, 128.31, 128.68, 128.71, 128.85, 129.31, 130.02 (4C), 133.90, 134.44, 135.01, 148.80, 173.44. HRMS (FAB) calcd for $C_{35}H_{44}NO_9F_3Na$ $[M+Na]^+$ 702.2866, found 702.2862.

Compound 1gh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +20.83 (c = 3.31, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD/$CDCl_3$ = 1/1) δ 1.31-1.66 (m, 16H), 2.21 (t, *J* = 7.6 Hz, 2H, H-1"), 2.59 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H, H-10"), 3.51-3.83 (m, 8H), 3.87 (dd, *J* = 4.6, 10.6 Hz, 1H), 3.88 (d, *J* = 2.2 Hz, 1H), 4.20 (td, *J* = 4.5, 5.8 Hz, 1H), 4.88 (1H merged with water peak), 7.12-7.15 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.4, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1) δ 26.68, 27.71, 29.78, 30.13, 30.40, 32.16, 32.25, 32.91, 36.54, 36.56, 37.05, 51.56, 58.68, 68.03, 69.98, 70.78, 71.29, 72.29, 72.68, 75.39, 100.88, 125.94, 126.50, 129.09 (2C), 129.20 (4C), 129.76 (2C), 143.48, 148.34, 175.53. HRMS (FAB) *m/z* calcd for $C_{35}H_{50}NO_9F_3Na$ $[M+Na]^+$ 708.3335, found 708.3340.

Compound 1gi. R_f 0.5 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +19.12 (c = 5.25, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 1.30 (brs, 10H), 1.53-1.60 (m, 8H), 2.17 (t, *J* = 7.7 Hz, 2H, H-1"), 2.56 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H, H-10"), 3.50-3.78 (m, 8H), 3.84 (dd, *J* = 4.7, 10.7 Hz, 1H), 3.88 (d, *J* = 3.0 Hz, 1H), 4.15 (m, 1H), 4.86 (d, *J* = 3.8 Hz, 1H), 7.12-7.14 (m, 3H), 7.20-7.22 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, MeOD): δ 26.89, 27.06, 30.20, 30.34 (3C), 30.56, 32.37, 32.74, 32.89, 36.67, 36.90, 37.21, 51.80, 62.75, 68.23, 70.22, 71.04, 71.51, 72.62, 72.85, 75.50, 101.14, 126.10, 126.13, 126.62, 129.24 (2C), 129.3 (4C), 130.02 (2C), 143.92, 148.73, 175.82; HRMS (FAB) m/z calcd for $C_{37}H_{54}NO_9F_3Na$ $[M+Na]^+$ 736.3648, found 736.3648.

Compound 1ha. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +40.55 (c = 2.2, MeOH/DCM = 1/1); ^{1}H NMR (600 MHz, MeOD): δ 0.90-1.69 (m, 38H), 2.26 (t, *J* = 7.4 Hz, 2H, H-1"), 3.58-3.86 (m, 8H), 3.92 (m, 2H), 4.24 (td, *J* = 5.1, 9.2 Hz, 1H), 4.87 (1H merge with water); ^{13}C NMR

(150 MHz, MeOD): δ 14.55, 23.14, 23.23, 23.83, 27.22, 27.50, 28.45, 29.28, 30.34, 30.52, 30.85, 33.03, 33.20, 34.14, 37.41, 38.46, 38.60, 38.64, 40.70, 55.99, 62.94, 68.50, 70.38, 71.27, 71.68, 72.66, 73.14, 75.66, 101.28, 176.01; HRMS (ESI-TOF) m/z calcd for $C_{30}H_{59}NO_9Na$ $[M+Na]^+$ 600.4082, found 600.4078.

Compound 1hb. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +4.21 (c = 2.6, MeOH/DCM = 1/1); ^1H NMR (600 MHz, MeOD/$CDCl_3$ = 1/1): δ 0.83-1.60 (m, 74H), 2.20 (t, *J* = 7.5 Hz, 2H, H-1"), 3.53-3.82 (m, 8H), 3.86 (dd, *J* = 4.5, 10.6 Hz, 1H), 3.89 (d, *J* = 3.0 Hz, 1H), 4.18 (td, *J* = 4.8, 10.0 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, MeOD/$CDCl_3$ = 1/1): δ 14.55, 20.21, 23.12, 23.21, 23.56, 25.76, 26.89, 27.20, 28.18, 28.93, 30.27 (2C), 30.38, 30.49, 30.57 (16C), 32.86, 33.05, 33.79, 37.23, 38.16, 38.29, 40.35, 51.54, 62.62, 68.12, 69.96, 70.77, 71.26, 72.12, 72.84, 75.30, 100.81, 175.62; HRMS (ESI-TOF) m/z calcd for $C_{48}H_{95}NO_9Na$ $[M+Na]^+$ 852.6899, found 852.6893.

Compound 1hc. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +10.94 (c = 1.6, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD): δ 0.82 (d, *J* = 6.60 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 6H), 1.00-1.72 (m, 16H), 3.61 (ddd, *J* = 2.5, 4.6, 9.1 Hz, 1H), 3.65-3.86 (m, 7H), 3.87 (dd, *J* = 0.7, 3.3 Hz, 1H), 4.01 (dd, *J* = 4.4, 10.8 Hz, 1H), 4.44 (td, *J* = 5.0, 10.8 Hz, 1H), 4.92 (d, *J* = 3.7 Hz, 1H), 7.47-7.84 (m, 4H); ^{13}C NMR (100 MHz, MeOD): δ 20.23, 23.16, 23.25, 26.06, 27.35, 28.28, 29.30, 33.30, 34.12, 38.43, 38.57, 40.68, 52.98, 62.94, 68.20, 70.35, 71.21, 71.64, 72.81, 73.00, 75.52, 101.36, 129.85 (2C), 130.36 (2C), 134.59, 138.88, 168.85; HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{48}ClNO_9Na$ $[M+Na]^+$ 612.2910, found 612.2906.

Compound 1hd. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +38.44 (c = 1.5, MeOH/DCM = 1/1); ^1H NMR (400 MHz, MeOD): δ 0.85 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H), 1.05-1.63 (m, 16H), 2.57 (dt, *J* = 2.4, 7.4 Hz, 2H, H-1"), 3.12 (t, *J* = 7.4 Hz, 2H, H-2"), 3.46-3.80 (m, 8H), 3.83 (dd, *J* = 4.2, 10.5 Hz, 1H), 3.85 (d, *J* = 4.1 Hz, 1H), 4.19 (td, *J* = 4.7, 10.5 Hz, 1H), 4.83 (d, *J* = 3.7 Hz, 1H), 6.82-7.60 (m, 3H); ^{13}C NMR (100 MHz, MeOD): δ 20.30, 23.25,

26.09, 26.40, 26.93, 27.45, 28.48, 29.31, 33.40, 34.15, 38.49, 38.65, 39.17, 40.71, 52.03, 62.91, 68.30, 70.35, 71.19, 71.62, 72.73, 73.01, 75.74, 101.30, 124.54, 125.86, 127.95, 144.72, 174.31; HRMS (ESI-TOF) *m/z* calcd for $C_{29}H_{51}NO_9SNa$ $[M+Na]^+$ 612.3177, found 612.3174.

Compound 1he. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +11.73 (c = 1.53, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.87 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H), 1.10-1.64 (m, 19H), 2.50 (t, *J* = 7.6 Hz, 2H, H-1"), 2.86 (t, *J* = 7.6 Hz, 2H, H-2"), 3.52 (m, 2H), 3.64 (dd, *J* = 4.7, 10.7 Hz, 1H), 3.67-3.79 (m, 5H), 3.76 (s, 3H, OMe), 3.83 (dd, *J* = 4.6, 10.7 Hz, 1H), 3.87 (d, *J* = 2.5 Hz, 1H), 4.20 (td, *J* = 4.7, 11.0 Hz, 1H), 4.85 (d, *J* = 3.8 Hz, 1H), 6.83-7.13 (m, 4H); ^{13}C NMR (100 MHz, MeOD): δ 20.29, 23.16, 23.25, 26.08, 27.41, 28.45, 29.30, 32.19, 33.40, 34.16, 38.45, 38.61, 39.37, 40.71, 51.99, 55.82, 62.94, 68.30, 70.36, 71.21, 71.64, 72.75, 73.03, 75.78, 101.29, 115.05 (2C), 130.47 (2C), 134.30, 159.73, 175.08; HRMS (ESI-TOF) *m/z* calcd for $C_{32}H_{55}NO_{10}Na$ $[M+Na]^+$ 636.3718, found 636.3720.

Compound 1hf. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{30}$ = +32.29 (c = 1.77, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.87 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H), 1.12-1.64 (m, 16H), 2.52 (t, *J* = 7.7 Hz, 2H, H-1"), 2.91 (t, *J* = 7.7 Hz, 2H, H-2"), 3.47-3.80 (m, 8H), 3.84 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.88 (d, *J* = 2.5 Hz, 1H), 4.2 (td, *J* = 4.8, 10.2 Hz, 1H), 4.91 (merged with water peak, 1H), 6.99-7.23 (m, 4H); ^{13}C NMR (100 MHz, MeOD): δ 20.28, 23.15, 23.24, 26.07, 27.41, 28.45, 29.30, 32.14, 33.45, 34.15, 38.47, 38.61, 39.07, 40.70, 51.99, 62.93, 68.30, 70.34, 71.21, 71.64, 72.76, 73.04, 75.78, 101.28, 116.08, 116.29, 131.23 138.31, 161.81, 164.22, 174.76; HRMS (ESI-TOF) *m/z* calcd for $C_{31}H_{52}FNO_9Na$ $[M+Na]^+$ 624.3518, found 624.3514.

Compound 1hg. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{31}$ = +1.85 (c = 1.37, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.82 (d, *J* = 6.5 Hz, 3H), 0.88 (s, *J* = 6.6 Hz, 6H), 0.99-1.59 (m, 16H), 3.49 (m, 1H), 3.56 (dd, *J* = 2.5, 8.5 Hz, 1H, H-1'-a), 3.59-3.77 (m, 7H), 3.72 (s, 2H), 3.87 (dd, *J* = 4.1, 10.6 Hz, 1H), 4.2 (td, *J* = 4.4, 10.6 Hz, 1H), 4.84 (d, *J* = 3.9 Hz, 1H), 7.44-

7.84 (m, 7H); ^{13}C NMR (100 MHz, MeOD): δ 20.23, 23.16, 23.26, 26.10, 27.44, 28.44, 29.31, 33.17, 34.08, 38.39, 38.64, 40.72, 44.39, 52.21, 62.99, 68.44, 70.34, 71.17, 71.60, 72.70, 73.20, 75.51, 101.36, 126.98, 127.42, 128.45, 128.85, 128.89, 129.03, 129.49, 134.08, 134.59, 135.19, 173.60; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{53}NO_9Na$ $[M+Na]^+$ 642.3613, found 642.3607.

Compound 1hh. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{28}$ = +6.25 (c = 1.43, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.86 (d, *J* = 6.0 Hz, 3H), 0.87 (s, *J* = 6.6 Hz, 6H), 1.10-1.69 (m, 22H), 2.22 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 3.55-3.72 (m, 5H), 3.74 (dd, *J* = 3.0, 7.1 Hz, 1H), 3.79 (dd, *J* = 3.6, 10.1 Hz, 1H), 3.83 (t, *J* = 6.1 Hz, 1H), 3.88 (m, 2H), 4.21 (td, *J* = 4.7, 10.3 Hz, 1H), 4.90 (1H merged with water), 7.11-7.26 (m, 5H); ^{13}C NMR (100 MHz, MeOD): δ 18.72, 21.60, 21.69, 24.51, 25.50, 25.99, 26.90, 27.73, 28.55, 29.33, 31.07, 32.59, 35.33, 35.76, 36.94, 37.09, 39.14, 50.43, 61.34, 66.86, 68.82, 69.64, 70.11, 71.18, 71.55, 74.11, 99.73, 125.26, 127.86 (2C), 127.98 (2C), 142.35, 174.37; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{59}NO_9Na$ $[M+Na]^+$ 648.4082, found 648.4085.

Compound 1hi. R_f 0.4 (DCM/MeOH = 6/1); $[\alpha]_D^{29}$ = +35.99 (c = 1.57, MeOH/DCM = 1/1); ^{1}H NMR (400 MHz, MeOD): δ 0.86 (d, *J* = 6.5 Hz, 3H), 0.87 (s, *J* = 6.6 Hz, 6H), 1.07-1.63 (m, 26H), 2.22 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 3.55 (m, 1H), 3.61 (t, *J* = 6.0 Hz, 1H), 3.65-3.80 (m, 5H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.88 (m, 2H), 4.20 (td, *J* = 4.5, 10.4 Hz, 1H), 4.90 (1H merged with water), 7.11-7.25 (m, 5H); ^{13}C NMR (100 MHz, MeOD): δ 20.29, 23.16, 23.25, 26.09, 27.21, 27.55, 28.45, 29.30, 30.37, 30.51, 30.89, 32.91, 33.17, 34.16, 37.07, 37.38, 38.50, 38.63, 40.71, 51.99, 62.91, 68.44, 70.38, 71.21, 71.66, 72.75, 73.10, 75.61 101.29, 126.77, 129.39 (2C), 129.52 (2C), 144.07, 175.98; HRMS (ESI-TOF) *m/z* calcd for $C_{36}H_{63}NO_9Na$ $[M+Na]^+$ 676.4395, found 676.4388.

Compound 6a. To a solution of **11** (1.5 g, 3.26 mmol) and triphenyl phosphine (1.0 g, 3.92 mmol) in THF (30.0 mL) was added diisopropyl azodicaboxylate (0.8 mL, 3.92 mmol) at 0 °C. Subsequently, 2-mercaptobenzothiazole (655.6 mg, 3.92 mmol) was added and the resulting

solution was stirred under N_2 while gradually warmed to rt. After 5 h, TLC showed complete conversion and the reaction was quenched with brine. The aqueous layer was extracted with EtOAc (x2) and the combined organic layers were dried ($MgSO_4$) and concentrated. Purification by column chromatography gave **6a** (1.7 g, 84%) as a yellow oil, R_f 0.55 (n-hexanes/EtOAc = 3/1); $[\alpha]_D^{31}$ = +2.63 (c = 3.3, CH_2Cl_2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (s, 3H), 1.12 (s, 3H), 3.29 (ddd, *J* = 2.7, 6.4, 9.5 Hz, 1H), 3.41 (dd, *J* = 6.4, 10.0 Hz, 1H), 3.51 (dd, *J* = 2.7, 10.0 Hz, 1H), 3.73 (dd, *J* = 2.4, 14.4 Hz, 1H),3.82 (dt, *J* = 10.3, 14.4 Hz, 1H), 4.12 (dd, *J* = 5.7, 9.5 Hz, 1H), 4.75 (dt, *J* = 2.4, 5.7, 10.3 Hz, 1H), 7.15-8.10 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.47, 27.87, 33.88, 60.67, 63.64, 66.60, 76.06, 81.99, 109.52, 120.97, 121.52, 124.30, 126.03, 127.12 (3C), 127.83 (6C), 128.56 (6C), 135.27, 143.79 (3C), 152.95, 166.10; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{32}N_4O_3S_2Na$ $[M+Na]^+$ 631.1808, found 631.1809.

Compound 9. To a stirred solution of **8**[2] (10 g, 23.1 mmol) in MeOH (200 mL) at 0 °C was added sodium borohydride (1.3 g, 34.7 mmol) dropwise. After being stirred at 0 °C for 3 h, the reaction mixture was quenched by adding AcOH and the resulting solution was concentrated. The residue was diluted with EtOAc and the resulting organic layer was washed by H_2O and brine. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated. The crude product was purified by flash chromatography to obtain a colorless oil **9** (9.5 g, 94%), R_f 0.2 (n-hexanes/EtOAc = 2/1); $[\alpha]_D^{28}$ = +9.58 (c = 8, CH_2Cl_2); ^{1}H NMR (400 MHz, MeOD): δ 1.33 (s, 3H), 1.45 (s, 3H), 3.25 (ddd, *J* = 6.2, 9.1, 13.0 Hz, 2H), 3.72 (d, *J* = 5.2 Hz, 2H), 3.87 (dt, *J* = 2.6, 6.2 Hz, 1H), 4.19 (dt, *J* = 5.2, 6.8 Hz, 1H), 4.37 (dd, *J* = 2.6, 6.8 Hz, 1H), 7.17-7.27 (m, 9H), 7.45-7.48 (m, 6H). ^{13}C NMR (100 MHz, MeOD): δ 25.39, 27.27, 62.01, 66.42, 69.32, 77.62, 78.93, 87.94, 109.14, 128.04 (3C), 128.72 (6C), 129.77 (6C), 145.24 (3C). HRMS (ESI) *m/z* calcd for $C_{27}H_{30}O_5Na$ $[M+Na]^+$ 457.1944, found: 457.1991.

Compound 10. To a solution of **9** (2 g, 4.6 mmol) in 50 mL of pyridine in an ice bath was

added dropwise benzoyl chloride (0.6 mL, 5.06 mmol). The mixture was stirred at 0 °C for 3 h, and then the reaction was quenched with MeOH. After the mixture was concentrated, the residue was diluted with EtOAc and then washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated. The crude product was purified by flash chromatography to obtain a colorless oil **10** (2.2 g, 89%), R_f 0.45 (n-hexanes/EtOAc = 3/1); $[\alpha]_D^{30}$ = +6.78 (c = 11, CH_2Cl_2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.48 (s, 3H), 3.23 (dd, *J* = 5.8, 9.4 Hz, 1H), 3.28 (dd, *J* = 5.8, 9.4 Hz, 1H), 3.87 (dt, *J* = 2.8, 5.8 Hz, 1H), 4.39 (dt, *J* = 2.8, 7.2 Hz, 1H), 4.46 (dd, *J* = 6.6, 13.1 Hz, 2H), 4.53 (dt, *J* = 7.2, 13.1 Hz, 1H), 7.20-8.04 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.16, 27.30, 64.45, 65.34, 68.49, 75.27, 76.37, 87.09, 108.96, 125.70, 127.27 (3C), 128.02 (6C), 128.51 (2C), 128.78 (6C), 129.87 (2C), 133.21, 143.88 (3C), 166.41; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{34}O_6Na^+$ $[M+Na]^+$ 561.2248, found 561.2249.

Compound 11. To a solution **10** (2.5 g, 4.6 mmol) and PPh_3 (1.5 g, 5.6 mmol) in THF (50 mL) was added diisopropyl azodicaboxylate (1.1 mL, 5.6 mmol) at 0 °C. Subsequently, diphenylphosphoryl azide (1.2 mL, 5.6 mmol) was added to the mixture. After the reaction was stirred for overnight, the mixture was poured into H_2O and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated to afford a crude residue. The residue was purified by flash column chromatography on silica gel eluting with *n*-hexanes/EtOAc (3/1) to get yellow oil (2.2 g, 90%; R_f 0.25 in n-hexanes/EtOAc = 3/1). The intermediate was treated with NaOMe (65 mg, 1.2 mmol) in MeOH (40 mL). The reaction mixture was stirred at rt for 1 h and then neutralized with Amberlite IR-120 (H^+) resin. The mixture was filtrated and the MeOH was evaporated. The residue was purified by flash chromatography to afford a colorless syrup **11** (1.6 g, 87%). R_f 0.25 (n-hexanes/EtOAc = 3/1); $[\alpha]_D^{30}$ = +4.33 (c = 11, CH_2Cl_2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 3H), 1.30 (s, 3H), 2.05 (s, 1H), 3.36 (dd, *J* = 7.3, 10.1 Hz, 1H), 3.55 (dd, *J* = 2.6, 10.1 Hz, 1H), 3.61 (ddd, *J* = 2.6, 7.3, 9.9 Hz, 1H), 3.72 (dd, *J* = 6.0, 11.7 Hz, 1H), 3.79 (dd, *J* = 4.8, 11.7 Hz, 1H), 3.99 (dd, *J* = 5.9,

9.9 Hz, 1H), 4.22 (dt, *J* = 4.8, 5.9 Hz, 1H), 7.20-7.47 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.49, 27.96, 60.35, 61.12, 64.53, 75.06, 77.77, 87.60, 109.01, 127.34 (3C), 128.08 (6C), 143.84 (3C); HRMS (ESI-TOF) *m/z* calcd for $C_{27}H_{29}N_3O_4Na^+$ $[M+Na]^+$ 482.2050, found 482.2055.

Compound 12. Tosyl chloride (3.15 g, 16.54 mmol) was added to a solution of **11** (2.5 g, 5.51 mmol) in pyridine (55 mL) at ice bath temeprature. After 2 h, the reaction was quenched with methanol and the reaction mixture was concentrated to afford crude residues. Then, it was extracted with EtOAc (x2) and the combined organic layers were dried ($MgSO_4$) and concentrated. Purification by column chromatography gave **12** (2.95 g, 87%) as a yellow oil. R_f 0.50 (Hexanes/EtOAc = 4/1); ^{1}H NMR (400 MHz, CDCl3): δ 1.23 (s, 6H), 2.42 (s, 3H), 3.34 (dd, *J* = 6.0, 12.3 Hz, 1H, H-5), 3.36 (dd, *J* = 6.0, 12.3 Hz, 1H, H-5'), 3.46 (m, 1H, H-2), 4.0 (m, 2H, H-1), 4.21 (dd, *J* = 3.9, 10.3 Hz, 1H, H-3), 4.25 (dt, *J* = 3.9, 6.0 Hz, 1H, H-4), 7.15-8.10 (m, 19H); ^{13}C NMR (100 MHz, CDCl3): δ 21.87, 25.60, 27.71, 59.77, 64.28, 68.21, 74.82, 75.10, 87.63, 109.83, 127.39 (3C), 128.10 (6C), 128.28 (2C), 128.87 (6C), 130.10 (2C), 133.00, 143.72 (3C), 145.26; HRMS (ESI-TOF) calcd for $C_{34}H_{35}N_3O_6SNa^+$ $[M+Na]^+$: 636.2139, found :636.2140.

Compound 13. $P(OEt)_3$ (5 mL) and **12** (165 mg, 0.27 mmol) was combined and the solution was refluxed at 150 ^{o}C for 16 h. The reaction mixture was concentrated and extracted with EtOAc (x2). Then, the combined organic layers were dried ($MgSO_4$) and concentrated. Purification by column chromatography obtained **13** (114 mg, 73%) as a yellow oil. R_f 0.15 (Hexanes/EtOAc = 4/1); ^{1}H NMR (400 MHz, d-Acetone): δ 1.21 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.25 (s, 3H), 1.41 (s, 3H), 3.20 (dd, *J* = 4.3, 9.6 Hz, 1H, H-1), 3.26 (dd, *J* = 5.1, 9.6 Hz, 1H, H-1'), 3.41 (dd, *J* = 4.5, 11.6 Hz, 1H, H-5), 3.50 (ddd, *J* = 3.1, 4.5, 11.6 Hz, 1H, H-5'), 3.85 (dt, *J* = 4.3, 9.1 Hz, 1H, H-2), 3.90-4.0 (m, 4H, H-1), 4.59 (dd, *J* = 3.1, 5.8 Hz, 1H, H-4), 4.82 (m, 1H, H-3), 7.25-7.48 (m, 15H); ^{13}C NMR (100 MHz, d-Acetone): δ 16.64, 24.44, 26.61, 54.12, 62.51, 65.64, 65.83, 81.79, 81.86, 84.26, 84.34, 88.18, 111.84, 128.06 (3C),

128.80 (6C), 129.68 (6C), 144.91 (3C); HRMS (ESI-TOF) calcd for $C_{31}H_{38}N_3O_6PNa^+$ $[M+Na]^+$: 602.2390, found : 602.2395.

Compound 14. To a solution of **6a** (1.35 g, 2.22 mmol) in CH_2Cl_2 (30 mL) at 0 ℃ was added solid $NaHCO_3$ (932 mg, 11.10 mmol) and followed by addition of *m*-CPBA (1.15 g, 6.66 mmol). The resulting suspension was warmed to rt and stirred for overnight. The reaction was quenched with aq. $Na_2S_2O_3$ (sat.) and diluted with CH_2Cl_2. The organic layer was washed with aq. $Na_2S_2O_3$ solution (sat. 3x) and the combined aqueous layers were subsequently extracted with CH_2Cl_2 (3x). The combined organic layers were washed with aq. $NaHCO_3$ (sat. 3x) and brine. The organic layer was dried ($MgSO_4$) and concentrated. The product was purified by column chromatography to give **14** (1.2 g, 85%) as a colorless oil. R_f 0.3 (Hexanes/EtOAc = 3/1); $[\alpha]_D^{29}$ = +12.52 (c = 5, CH_2Cl_2): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (s, 3H), 1.12 (s, 3H), 3.29 (ddd, *J* = 2.7, 6.5, 9.6 Hz, 1H), 3.41 (dd, *J* = 6.5, 10.3 Hz, 1H), 3.51 (dd, *J* = 2.7, 10.3 Hz, 1H), 3.73 (dd, *J* = 2.4, 14.4 Hz, 1H), 3.82 (dd, *J* = 10.4, 14.4 Hz, 1H), 4.12 (dd, *J* = 5.6, 9.6 Hz, 1H), 4.75 (ddd, *J* = 2.4, 5.6, 10.4 Hz, 1H), 7.22-7.63 (m, 17H), 7.98-8.02 (m, 1H), 8.18-8.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.77, 28.21, 57.50, 59.36, 59.87, 64.28, 71.25, 75.54, 87.70, 110.46, 122.59, 124.21, 126.50, 127.25, 127.40 (3C), 128.11 (6C), 136.21, 143.67 (3C), 154.11, 178.12; HRMS (ESI-TOF) *m/z* calcd for $C_{34}H_{32}N_4O_5S_2Na$ $[M+Na]^+$ 663.1706, found 663.1710.

Compound 26. TMSI (0.4 mL, 2.96 mmol) was added to a solution of the **24**[3] (1.44 g, 2.69 mmol) in CH_2Cl_2 (27 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then 10 mL of anhydrous toluene were added. After azeotroping three times with toluene, the crude product **25** was dissolved in toluene (10 mL) and kept under N_2. In a separate flask, 4Å MS (2.0 g), TBAI (1.42 g, 3.84 mmol), **6c** (1.2 g, 2.24 mmol), and diisopropylethylamine (0.56 mL, 3.36 mmol) were mixed in toluene (20 mL). The mixture was stirred under N_2 at 90 °C for 20 min, and then **25** was cannulated into the reaction mixture. After the reaction mixture was stirred at 90 °C for 2 h, the solution was filtered and extracted with EtOAc and $Na_2S_2O_{3(aq.)}$.

The organic layer was dried with $MgSO_4$ and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (n-hexanes : EtOAc 4:1) to give product **26** (0.8 g, 45%) as a colorless oil. R_f 0.4 (Hexanes/EtOAc = 4:1); $[\alpha]_D^{30}$ = +20.54 (c = 2.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-2.0 (m, 7H), 3.26 (t, *J* = 6.8 Hz, 2H, H-1), 3.52-3.75 (m, 7H, H-4, H-6, H-2', H-3', H-4', H-6'), 3.87 (m, 1H, H-5'), 3.96 (m, 2H, H-7), 4.07 (dd, *J* = 3.3, 10.0 Hz, 1H, H-5), 4.48 (d, *J* = 11.5 Hz, 1H), 4.56-4.71 (m, 5H), 4.75 (dd, *J* = 11.8 Hz, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.90 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 (dd, *J* = 11.6 Hz, 1H), 7.22-7.84 (m, 29H); ^{13}C NMR (100 MHz, CDCl3): δ 25.22, 28.98, 31.50, 33.70, 62.12, 62.58, 68.57, 71.13, 72.20, 73.49, 73.56, 73.95, 74.69, 75.32, 76.59, 78.75, 78.87, 79.00, 98.84, 121.14, 121.66, 124.37, 126.23, 127.78 (2C), 127.93 (2C), 128.03, 128.12 (4C), 128.26, 128.29, 128.37, 128.40, 128.49 (2C), 128.61 (6C), 128.66 (2C), 128.75 (2C), 135.36, 138.06, 138.18, 138.80, 138.87, 153.48, 167.23, 170.76; HRMS (ESI-TOF) calcd for $C_{57}H_{60}N_4O_9S_2Na^+$ $[M+Na]^+$: 1031.3694; Found: 1031.3698.

Compound 34. Yield (210mg, 90%). R_f 0.5 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{28}$ = +24.55 (c = 2.53, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.27-2.28 (m, 26H), 3.58 (m, 1H), 3.67-3.77 (m, 4H), 3.88 (dt, *J* = 1.8, 12.6 Hz, 1H), 4.01 (dd, *J* = 3.1, 6.2 Hz, 1H), 4.05 (t, *J* = 5.8 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.08-4.18 (m, 2H), 4.09 (dd, *J* = 3.3, 10.0 Hz, 1H), 4.16 (d, *J* = 3.0 Hz, 1H), 4.50 (dd, *J* = 2.9, 11.5 Hz, 1H), 4.58-4.70 (m, 4H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.98 (d, *J* = 3.3 Hz, 1H), 5.38 (m, 2H), 5.42 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.23-7.34 (m, 18H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.29, 20.84, 22.89, 27.60, 28.24, 28.74, 29.56, 29.61, 29.87 (3C), 30.32, 32.14, 32.84, 62.05, 63.26, 66.66, 68.75, 69.53, 72.28, 72.35, 73.74, 74.02, 74.91, 75.75, 76.11, 79.16, 79.30, 99.43, 101.15, 114.34 (2C), 127.69, 127.74, 127.85, 127.92 (4C), 127.97 (4C), 128.04 (2C), 128.46 (2C), 128.49 (2C), 128.60 (3C), 129.18, 129.65, 130.99, 131.23, 131.52, 138.31, 138.63, 139.03 (2C), 159.27; HRMS (ESI-

TOF) *m/z* calcd for $C_{70}H_{78}F_{17}N_3O_9Na$ $[M+Na]^+$ 1450.5359, found 1450.5345.

Compound 35. Yield (666 mg, 78%). R_f 0.5 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{28}$ = +11.28(c = 3.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.28 (m, 31H), 1.75 (m, 1H), 1.92-2.16 (m, 6H), 2.30 (m, 2H), 3.55 (m, 1H), 3.63-3.74 (m, 4H), 3.86 (dt, *J* = 1.9, 12.5 Hz, 1H), 3.98 (dd, *J* = 3.2, 6.1 Hz, 1H), 4.03 (t, *J* = 6.0 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.03 (m, 1H), 4.07 (dd, *J* = 3.2, 10.0 Hz, 1H), 4.13 (d, *J* = 3.0 Hz, 1H), 4.47 (dd, *J* = 2.8, 11.5 Hz, 1H), 4.56-4.60 (m, 2H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.2 Hz,1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.79 (d, *J* = 12.3 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.95 (d, *J* = 3.2 Hz, 1H), 5.35 (m, 2H, H-7. H-8), 5.39 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.21-7.33 (m, 18H), 7.38 (d, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.15, 20.59, 22.76, 23.26, 27.45, 28.00, 28.56, 29.33, 29.45, 29.79 (8C), 30.06, 30.22, 32.01, 32.71, 61.75, 63.07, 66.37, 68.52, 69.34, 72.09, 72.19, 73.60, 73.86, 74.70, 75.53, 75.88, 78.87, 79.14, 99.23, 100.99, 114.10 (2C), 127.54, 127.60, 127.70, 127.78 (4C), 127.8 (4C), 127.92 (2C), 128.31 (2C), 128.34 (4C), 132.08, 129.01. 129.48, 130.81, 130.97, 131.37, 138.12, 138.43, 138.83 (2C), 159.10; HRMS (ESI-TOF) *m/z* calcd for $C_{77}H_{92}F_{17}N_3O_9Na$ $[M+Na]^+$ 1548.6460, found 1548.6462.

Compound 36. Yield (530 mg, 67%). R_f 0.3 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{31}$ = +21.33 (c = 5.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67-2.37 (m, 8H), 3.57(m, 1H), 3.63-3.75 (m, 3H), 3.80 (dd, *J* = 3.5, 6.8 Hz, 1H), 3.89 (dd, *J* = 1.5, 12.6 Hz, 1H), 4.00-4.11 (m, 4H), 4.04 (t, *J* = 5.8 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.15 (d, *J* = 2.8 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.98 (d, *J* = 3.3 Hz, 1H), 5.41 (s, 1H), 6.11 (dt, *J* = 6.8, 15.7 Hz, 1H), 6.25 (d, *J* = 15.7 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.19-7.34 (m, 22H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.69, 28.09, 28.32, 29.11, 61.78, 63.19, 66.49, 68.54, 69.44, 72.15, 72.18, 73.76, 74.06, 74.74, 75.60, 75.99, 78.58, 78.93, 99.35, 101.10, 114.22 (2C), 127.31,

127.68, 127.72, 127.91 (8C), 128.06 (2C), 128.10 (2C), 128.42 (2C), 128.46 (2C), 128.59 (4C), 128.76 (2C), 129.27, 130.23, 131.03, 131.17, 132.61, 136.33, 138.16, 138.37, 138.89 (2C), 159.20; HRMS (ESI-TOF) *m/z* calcd for $C_{66}H_{61}F_{17}N_3O_9Na$ $[M+Na]^+$ 1420.3723, found1420.3729.

Compound 37. Yield (600 mg, 93%). R_f 0.6 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{28}$ = +23.31 (c = 2.51, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (m, 1H), 1.70 (m, 1H), 1.97-2.36 (m, 6H), 2.63 (d, *J* = 7.8 Hz, 2H, H-10), 3.54 (m, 1H), 3.61-3.70 (m, 4H), 3.85 (dd, *J* = 6.0, 11.1 Hz, 1H), 3.96-4.08 (m, 4H), 4.02 (t, *J* = 6.0 Hz, $F_{tag}CH_2CH_2CH_2O$), 4.12 (d, *J* = 3.0 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.56 (*J* = 11.6 Hz, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 7.2 Hz, 1H), 4.71 (d, *J* = 12.3 Hz, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 4.83 (d, *J* = 11.9 Hz, 1H), 4.95 (d, *J* = 2.9 Hz), 5.31-5.44 (m, 2H), 5.39 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.12-7.31 (m, 23H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.59, 23.31, 27.99, 28.50, 29.26, 36.09, 61.78, 63.06, 66.39, 68.53, 69.32, 72.07, 72.19, 73.58, 73.85, 74.68, 75.53, 75.88, 78.85, 79.15, 99.23. 100.97, 114.11 (2C), 125.84, 127.53, 127.58, 127.70, 127.75 (4C), 127.80 (4C), 127.89, 127.91, 128.29, 128.31, 128.33 (2C), 128.44 (4C), 128.48, 128.50, 129.45, 129.91, 130.21, 130.33, 130.98, 138.10, 138.37, 138.39, 138.82 (2C), 142.09, 159.09; HRMS (ESI-TOF) *m/z* calcd for $C_{68}H_{66}F_{17}N_3O_9Na$ $[M+Na]^+$ 1414.4425, found 1414.4435.

Compound 38. Yield (670 mg, 88%). R_f 0.6 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{28}$ = +28.41 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24-2.20 (m, 16H), 2.29 (dd, *J* = 8.28, 18.04 Hz, 1H), 2.36 (dd, *J* = 7.64, 18.04 Hz, 1H), 2.57 (dt, *J* = 6.28, 15.16 Hz, 2H, H-13), 3.54 (m, 1H), 3.61-3.70 (m, 3H), 3.73 (dd, *J* = 3.48, 6.48 Hz, 1H), 3.86 (m, 1H), 3.95-4.06 (m, 3H), 4.02 (t, *J* = 5.94 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.06 (dd, *J* = 3.28, 13.52 Hz, 1H), 4.12 (d, *J* = 3.00 Hz, 1H), 4.46 (d, *J* = 11.52 Hz, 1H), 4.55-4.60 (m, 1H), 4.58 (d, *J* = 11.52 Hz, 1H), 4.63-4.67 (m, 2H), 4.71 (d, *J* = 12.32 Hz, 1H), 4.78 (d, *J* = 12.32 Hz, 1H), 4.83 (d, *J* = 11.88 Hz, 1H), 4.95

(d, *J* = 3.28 Hz, 1H), 5.26-5.38 (m, 2H), 5.39 (s, 1H), 6.85 (d, *J* = 8.80 Hz, 2H), 7.13-7.31 (m, 23H), 7.36-7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.78, 23.45,28.19, 29.05, 29.23, 29.64, 29.78, 31.56, 31.61, 32.70, 36.13, 61.96, 63.22, 66.59, 68.71, 69.49, 72.25, 72.35, 73.73, 74.01, 74.85, 75.70, 76.06, 79.10, 79.33, 99.40, 101.13, 114.29 (2C), 125.79, 127.68, 127.73, 127.84 (2C), 127.91 (4C), 127.95 (4C), 128.03 (2C), 128.07 (2C), 128.44 (2C), 128.48 (2C), 128.58 (4C), 129.30, 129.79, 130.75, 131.16, 131.29, 138.28, 138.58, 138.99 (2C), 143.03, 159.24; HRMS (ESI-TOF) *m/z* calcd for $C_{71}H_{72}F_{17}N_3O_9Na$ $[M+Na]^+$ 1456.4889, found 1456.4894.

Compound 39. Yield (550 mg, 74%). R_f 0.6 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{28}$ = +14.57 (c = 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (ddd, *J* = 1.0, 6.7, 10.4 Hz, 3H), 1.10-1.26 (m, 3H), 1.50 (d, *J* = 7.7 Hz, 3H), 1.59 (d, *J* = 8.2 Hz, 3H), 1.69-2.25 (m, 9H), 3.49 (m, 1H), 3.55-3.68 (m, 4H), 3.79 (dd, *J* = 4.3, 12.1 Hz, 1H), 3.90-3.97 (m, 3H), 3.95 (t, *J* = 5.8 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.01 (dd, *J* = 3.3, 10.0 Hz, 1H), 4.07 (d, *J* = 2.9 Hz, 1H), 4.42 (dd, *J* = 7.3, 11.6 Hz, 1H), 4.52 (m, 2H), 4.57-4.61 (m, 2H), 4.66 (d, *J* = 12.3, 1H), 4.73 (d, *J* = 12.3, 1H), 4.78 (d, *J* = 11.9), 4.89 (d, *J* = 3.2 Hz, 1H), 5.01 (m, 1H), 5.05-5.27 (m, 2H), 5.33 (s, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.13-7.25 (m, 18H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.92, 20.80, 25.92, 26.29, 28.02, 28.20, 28.38, 29.91, 31.80, 36.51, 37.42, 37.90, 51.55, 63.31, 66.61, 68.04, 69.54, 71.92, 72.50, 73.57, 73.74, 74.25, 74.54, 76.29, 79.15, 80.31, 99.70, 101.10, 114.29 (2C), 127.75 (2C), 127.82, 127.87, 127.94 (2C), 127.98 (2C), 128.0 (2C), 128.16 (2C), 128.52 (2C), 128.63 (4C), 128.69 (2C), 128.87 (2C), 131.10, 131.36, 132.96, 137.10, 137.33, 137.76, 138.49, 138.58, 138.76, 159.23; HRMS (ESI-TOF) *m/z* calcd for $C_{68}H_{72}F_{17}N_3O_9Na$ $[M+Na]^+$ 1420.4895, found 1420.4906.

Compound 40. Yield (1.0 g, 75%). R_f 0.6 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{30}$ = +23.57 (c = 5.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54-2.36 (m, 10H), 2.64-2.70 (m, 2H, H-10), 3.55 (brs, 1H), 3.60-3.73 (m, 4H), 3.86 (d, *J* = 12.0 Hz, 1H), 3.95-4.05 (m, 3H), 4.02 (t, *J* = 6.0 Hz,

2H, $F_{tag}CH_2CH_2CH_2O$) 4.05-4.07 (m, 1H), 4.13 (brs, 1H), 4.43 (dd, *J* = 3.4, 11.4 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.71 (d, *J* = 12.4 Hz, 1H), 4.78 (d, *J* = 12.1 Hz, 1H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.94 (d, *J* = 3.3, 1H), 5.35-5.36 (m, 2H), 5.39 (s, 1H), 6.85 (m, 2H), 7.20-7.50 (m, 26H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.57, 23.26, 27.97, 28.48, 28.81, 29.85, 34.01, 35.75, 61.72, 63.04, 66.37, 68.49, 69.31, 72.06, 73.58, 73.87, 74.64, 75.46, 75.86, 78.60, 78.86, 79.10, 99.02, 100.96, 114.08 (2C), 125.19, 127.51, 127.56, 127.71 (2C), 127.73 (4C), 127.78 (2C), 127.80 (2C), 127.83 (2C), 127.87 (2C), 128.30 (2C), 128.31 (2C), 128.42 (4C), 128.77, 129.44, 130.39, 130.90, 138.05, 138.30, 138.78 (2C), 146.19, 159.06. HRMS (FAB) *m/z* calcd for $C_{69}H_{65}N_3O_9F_{20}Na$ $[M+Na]^+$ 1482.4299, found 1482.4297.

Compound 41. Yield (132.4 mg, 38%). R_f 0.4 (n-hexanes/EtOAc = 4/1); $[\alpha]_D^{31}$ = +19.13 (c = 2.11, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58-2.39 (m, 8H), 3.52 (dd, *J* = 6.5, 13.7 Hz, 2H), 3.57(m, 1H), 3.64-3.80 (m, 4H), 3.88 (m, 1H), 4.0-4.11 (m, 4H), 4.04 (t, *J* = 5.9 Hz, 2H, $F_{tag}CH_2CH_2CH_2O$), 4.15 (d, *J* = 2.5 Hz, 1H), 4.49 (t, *J* = 10.5 Hz, 1H), 4.58-4.69 (m, 4H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 12.4 Hz, 1H), 4.86 (d, *J* = 11.8 Hz, 1H), 4.98 (d, *J* = 3.0 Hz, 1H), 5.42 (s, 1H), 5.46-5.67 (m, 2H), 6.76-7.34 (m, 23H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.72, 24.20, 25.87 27.90, 28.12, 28.34, 29.88, 61.81, 63.17, 66.52, 68.65, 69.46, 72.24, 73.73, 73.95, 74.79, 75.63, 75.97, 78.83, 79.16, 79.27, 99.33, 101.11, 114.23 (2C), 123.63, 124.22, 127.01, 127.73, 127.90 (8C), 127.93 (6C), 128.43 (2C), 128.47 (2C), 128.57 (4C), 129.05, 131.06, 138.16, 138.26, 138.55 138.92 (2C), 159.20; HRMS (ESI-TOF) *m/z* calcd for $C_{65}H_{62}F_{17}N_3O_9SNa$ $[M+Na]^+$ 1406.3833, found1406.3831.

General procedure for the synthesis of compounds 42-49. These compounds were prepared from corresponding azides (**33-41**) in a two-step sequence as describe below. The azides were converted to amines by Staudinger reduction, and the resultant amines were subsequently reacted with 9-different fatty acids, respectively. In a typical procedure, an azide (1.0 eq.) was dissolved in THF/H_2O (1 mL, 1:1 v/v) to which a 1M solution of PMe_3 in THF was added (2.5

eq.). After being stirred at rt for 12 h or until the azide was completely consumed, the solution was evaporated under reduced pressure. The residue was subjected to a FSPE cartridge to get the desired amine. A solution of amine (1 eq.) in anhydrous DMF (3 mL) was treated with acid (1.5 eq.), HBTU (1.2 eq.), and *N,N*-diisopropylethylamine (1.5 eq.) at 0 ºC. The reaction mixture was stirred at rt for 16 h or until TLC indicated the disappearance of amine, then concentrated under reduced pressure and extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The residue was purified by a FSPE cartridge (70% aqueous MeOH to 100% MeOH elution) to afford pure amides (**42-49)** (82-97% yield for 2-steps). The homogeneity of the compounds was verified by HR-ESI MS analysis. Isolated yields and observed m/z values are shown in parentheses (Table S2).

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