Supporting Information for:

Synthetic Glycoimmunochemistry. Effect of Phenolic Glycolipids From *Mycobacterium kansasii* on Proinflammatory Cytokine Release

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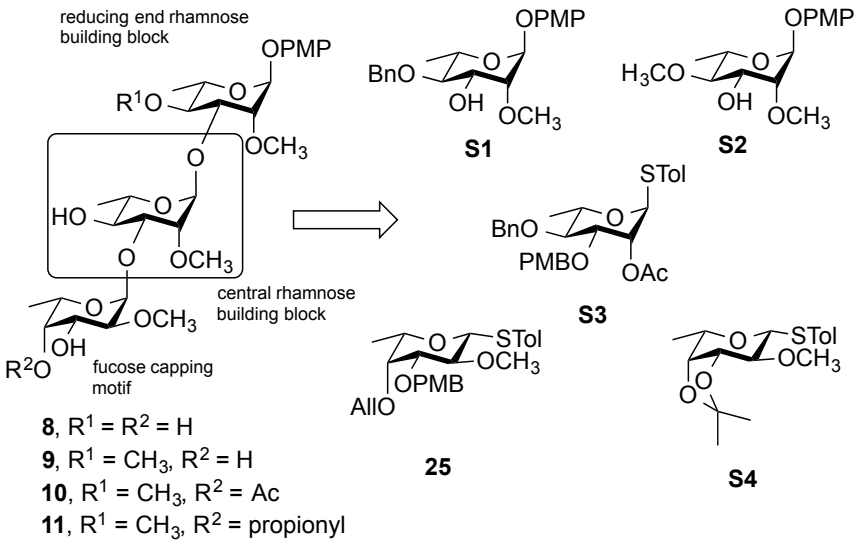
List of Abbreviations

Abbreviation	Meaning
[α]	specific rotation
μM	micromolar
Ac	acetyl
AcOH	acetic acid
All	allyl
AllBr	allyl bromide
appt	apparent triplet (NMR spectra)
Ac_2O	acetic anhydride
aq.	aqueous
Bn	benzyl
BnBr	benzyl bromide
br	broad
Bu	butyl
Bz	benzoyl
BzCl	benzoyl chloride
n-Bu_4NI	tetra-*n*-butylammonium iodide

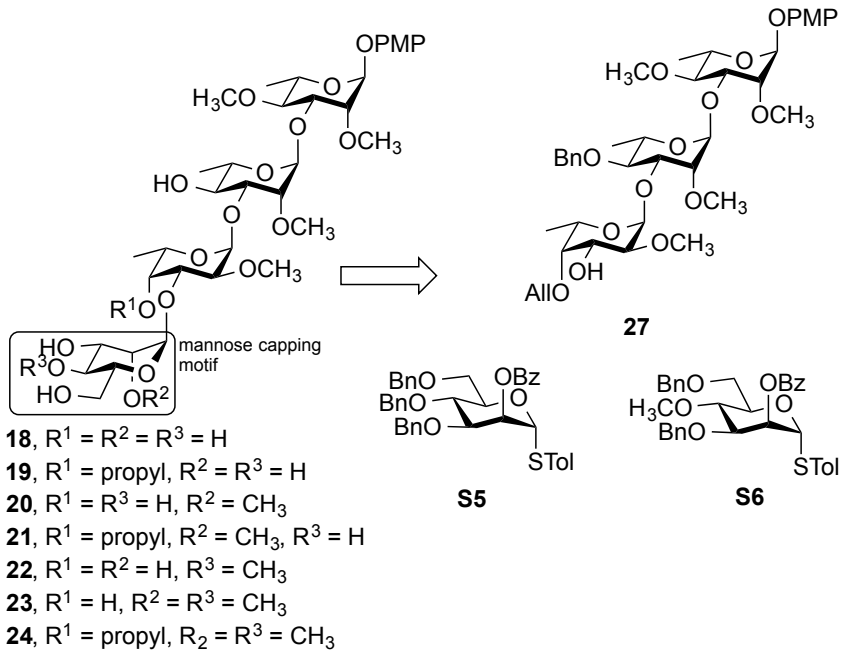
calcd	calculated
COSY	correlation spectroscopy
°C	degree Celsius
CSA	(±)-camphor-10-sulfonic acid
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	*N*,*N*'-dicyclohexylcarbodiimide
d	doublet (NMR spectra)
dd	doublet of doublet (NMR spectra)
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*'-dimethylformamide
DMSO	dimethylsulfoxide
DMP	2,3-dimethoxypropane
equiv.	equivalent
Et	ethyl
Et_3N	triethylamine
h	hour(s)
HOAc	acetic acid
Hz	hertz
J	coupling constant
LA	levulinic acid
m	multiplet (NMR spectra)
M	molar
Me	methyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	millilitre(s)

mM	millimole(s)
Milli-Q	(deionized) distilled water
NIS	*N*-iodosuccinimide
NTM	non-tuberculosis mycobacteria
NMR	nuclear magnetic resonance
Ph	phenyl
PMA	phorbol 12-myristate 13-acetate
ppm	parts per million (NMR spectra)
p-TsOH	*p*-toluenesulfonic acid
Py	pyridine
PMPOH	*p*-methoxyphenol
*p*HBA	*p*-hydroxybenzoic acid
p-MBCl	*p*-methoxybenzyl chloride
PGL(s)	phenolic glycolipid(s)
q	quartet (NMR spectra)
R_f	retention factor
PIMs	phosphatidyl-*myo*-inositol mannosides
PDIMs	phthiocerol dimycocerosates
PMP	*p*-methoxyphenyl
rt	room temperature
s	singlet (NMR spectra)
satd.	saturated
TB	tuberculosis
TMSOTf	trimethylsilyltrifluoromethanesulfonate
Tol	tolyl
t	triplet (in NMR)
TBAF	tetra-*n*-butylammonium fluoride

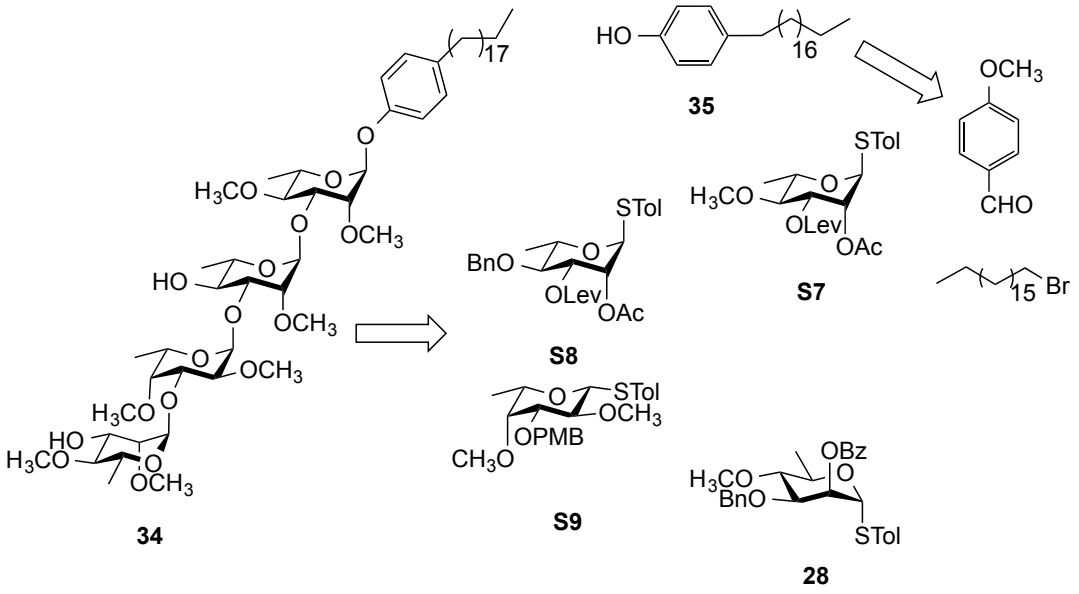
TEA	triethylamine
$(CH_3)_3SiH$	trimethylsilane
TFA	trifluoroacetic acid
OTf	trifluoromethanesulfonyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Ts	tosyl, *p*-toluenesulfonyl
TsCl	tosyl chloride, *p*-toluenesulfonyl chloride
TBDPS	*tert*-butyldiphenylsilyl
TBDPSCl	*tert*-butyldiphenylsilyl chloride
TolSH	*p*-toluenethiol
TEOA	triethyl orthoacetate



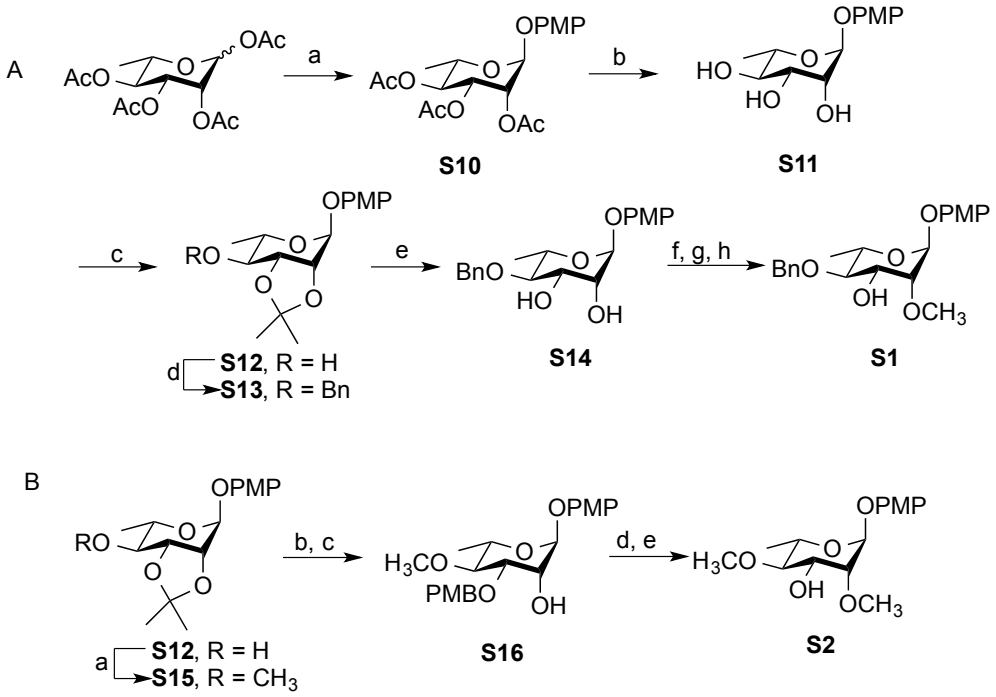
Scheme S1. Retrosynthetic analysis of analogs **8** and **9**.



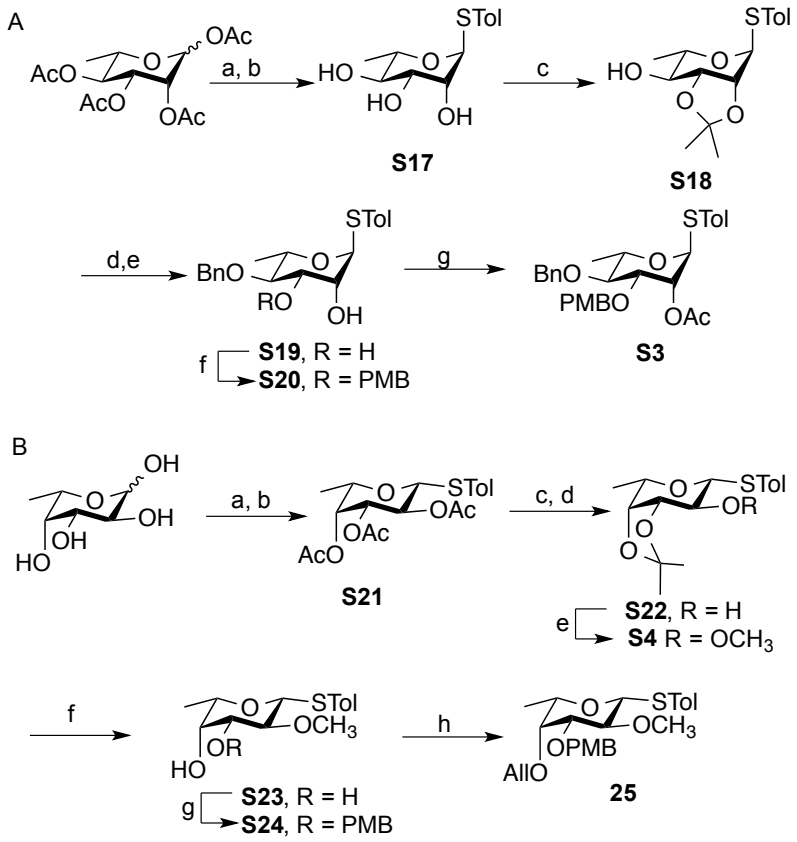
Scheme S2. Retrosynthetic analysis of analogs **18–24**.



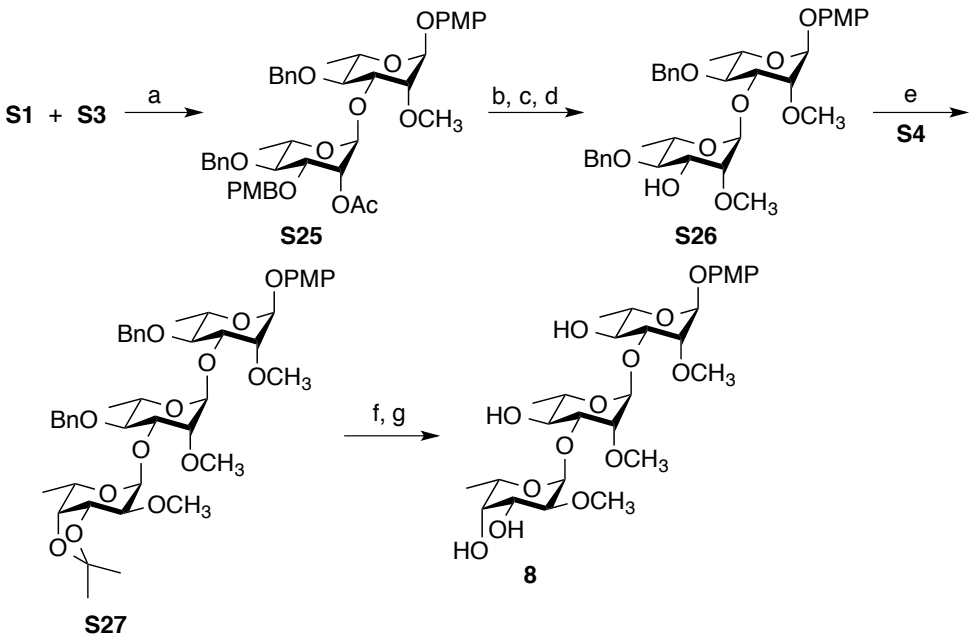
Scheme S3. Retrosynthetic analysis of glycolipid **34**



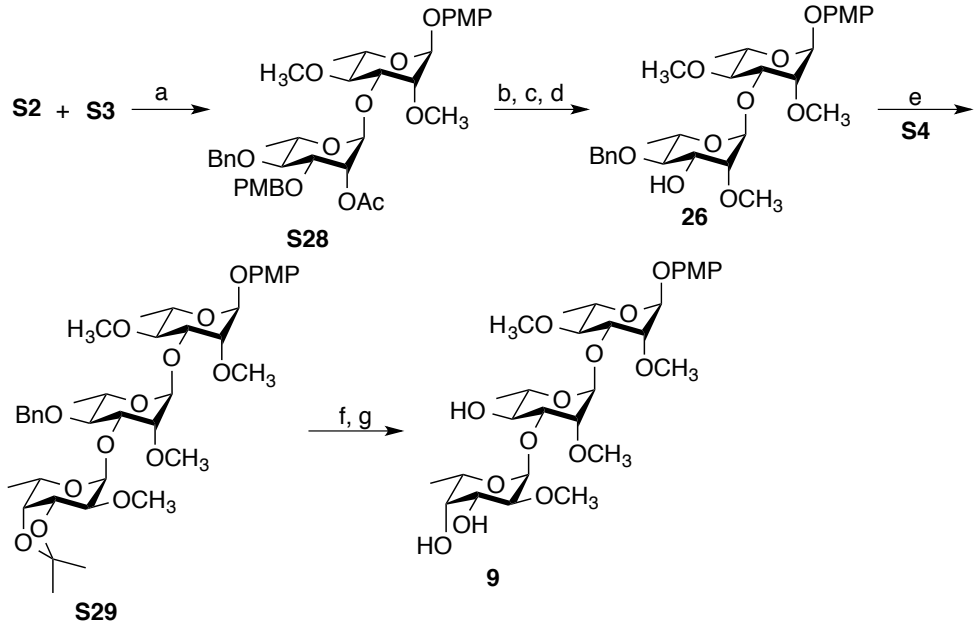
Scheme S4. Synthesis of building blocks **S1** and **S2**. Reagents and conditions: A) a) $BF_3 \cdot Et_2O$, PMPOH, CH_2Cl_2, overnight, 88%; b) $NaOCH_3$, CH_3OH/CH_2Cl_2, 2 h, 96%; c) DMP, Acetone, *p*-TSA, 40 min, 91%; d) BnBr, NaH, DMF, 4 h, 95%; e) *p*-TSA, CH_3OH, 3 h, 82%; f) *n*-Bu_2SnO, toluene, 120 ºC, 1 h; *p*-MBCl, *n*-Bu_4NI, 62 ºC, 7 h; g) CH_3I, NaH, DMF, 1 h; h) 5% TFA, CH_2Cl_2, 0 ºC, 30 min, 81 % over three steps. B) a) CH_3I, NaH, DMF, 1 h, 96%; b) 1. *p*-TSA, CH_3OH/CH_2Cl_2, 1 h; c) *n*-Bu_2SnO, toluene, 120 ºC, 1 h; *p*-MBCl, *n*-Bu_4NI, 62 ºC, 7 h, 78% over two steps; d) CH_3I, NaH, DMF, 1 h; e) 5% TFA, CH_2Cl_2, 30 min, 81% over two steps.



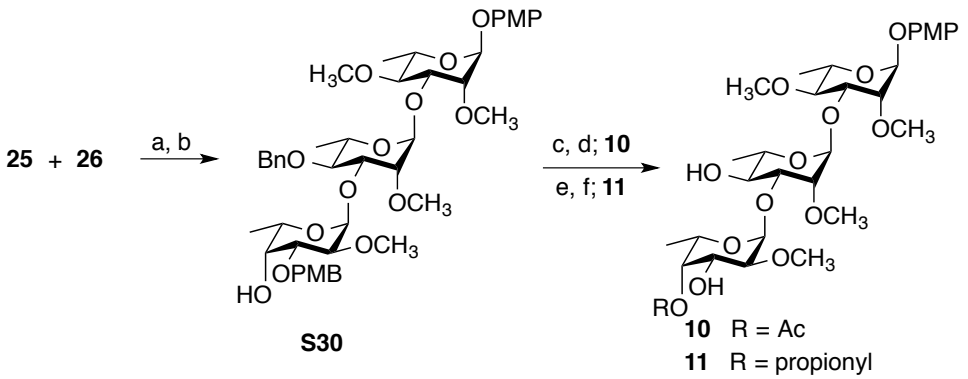
Scheme S5. Synthesis of building blocks **S3**, **S4** and **25**. Reagents and conditions: A) a) $BF_3{\cdot}Et_2O$, TolSH, CH_2Cl_2, 7 h; b) $NaOCH_3$, CH_3OH/CH_2Cl_2, 78% over two steps; c) DMP, acetone, *p*-TSA, 30 min, 96%; d) BnBr, NaH, DMF, 1 h; e) *p*-TSA, CH_3OH/CH_2Cl_2, 3 h, 81%, over two steps; f) *n*-Bu_2SnO, toluene, 120 ºC, 1 h; *p*-MBCl, *n*-Bu_4NI, 62 ºC 6 h, 86%; g) Ac_2O, pyridine, 3 h, 95%. B) a) Ac_2O, pyridine, 7 h; b) $BF_3.Et_2O$, TolSH, CH_2Cl_2, overnight, 91% over two steps; c) $NaOCH_3$, CH_3OH/CH_2Cl_2, 2 h; d) DMP, *p*-TSA, acetone, 45 min, 90% over two steps; e) CH_3I, NaH, DMF, 1 h, 94 %; f) *p*-TSA, CH_3OH/CH_2Cl_2, 4 h, 80%; g) *n*-Bu_2SnO, toluene, 120 ºC, 1h; *p*-MBCl, *n*-Bu_4NI, 63 ºC, 5h, 83%; h) AllBr, NaH, DMF, 2 h, 86%.



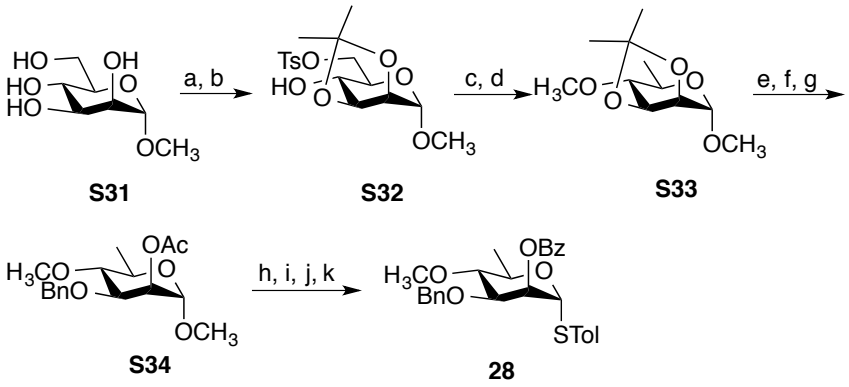
Scheme S6. Synthesis of trisaccharide **8**. Reagents and conditions: a) NIS, AgOTf, –20 ºC, 30 min, 81%; b) $NaOCH_3$, CH_3OH/CH_2Cl_2, 1 h; c) CH_3I, NaH, DMF, 1 h; d) 5% TFA, CH_2Cl_2, 0 ºC, 30 min, 87% over three steps; e) NIS, AgOTf, CH_2Cl_2, –40 ºC, 30 min, 80%; f) *p*-TSA, CH_3OH/CH_2Cl_2, 2 h; g) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 87% over two steps.



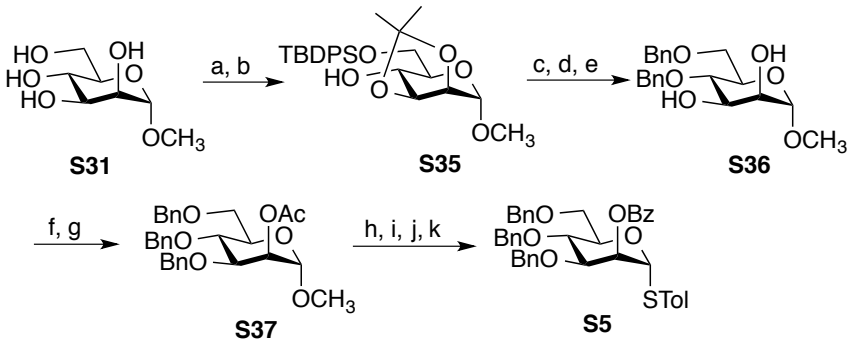
Scheme S7. Synthesis of trisaccharide **9**. Reagents and conditions: a) NIS, AgOTf, –20 ºC, 30 min, 85%; b) $NaOCH_3$, CH_3OH/CH_2Cl_2, 1 h; c) CH_3I, NaH, DMF, 1 h; d) 5% TFA, CH_2Cl_2, 0 ºC, 30 min, 80% over three steps; e) NIS, AgOTf, CH_2Cl_2, –40 ºC, 30 min, 83%; f) *p*-TSA, CH_3OH/CH_2Cl_2, 3 h; g) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 79% over two steps.



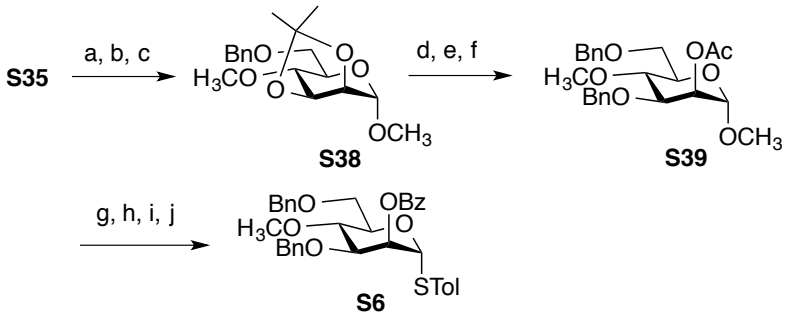
Scheme S8. Synthesis of trisaccharide **10** and **11**. Reagents and conditions: a) NIS, AgOTf, –40 ºC, 30 min; b) $(Ph_3P)_4Pd$, HOAc, overnight, 71% over twp steps; c) Ac_2O, pyridine, 2 h; d) Pd/C, H_2, CH_3OH/CH_2Cl_2 overnight, 81% over two steps; e) 1. $(C_2H_7CO)_2O$, pyridine, 2 h; f) Pd/C, H_2, CH_3OH/ CH_2Cl_2, overnight, 76% over two steps.



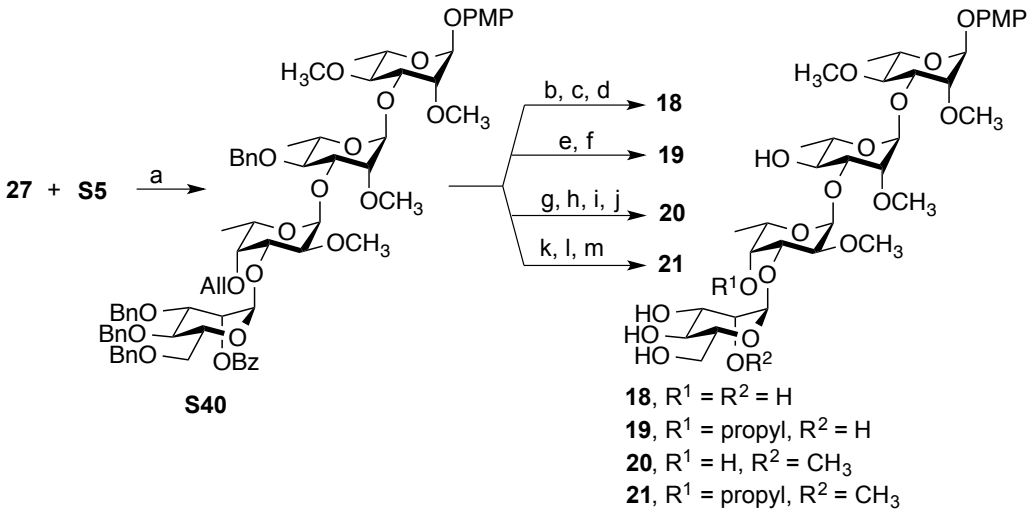
Scheme S9. Synthesis of building block **28**. Reagents and conditions: a) TsCl, pyridine, DMAP, overnight; b) 2,2-Dimethoxypropane, acetone, 2 h, 78% over two steps; c) $NaBH_4$, DMSO, 80 ºC, 8h; d) CH_3I, NaH, DMF, 1 h, 69 % over two steps; e) *p*-TSA, CH_2Cl_2/CH_3OH, 3h; f) Bu_2SnO, toluene, 130 ºC, 1h; BnBr, *n*-Bu_4NBr, 63 ºC, overnight; g) Ac_2O, pyridine, 1 h, 79% over three steps, h) Ac_2O, H_2SO_4, 0 ºC, 2h; i) TolSH, $BF_3 \cdot Et_2O$, CH_2Cl_2, -20 ºC, 5h; j) $NaOCH_3$, CH_2Cl_2/CH_3OH, 2 h; k) BzCl, pyridine, 2h, 53% over four steps.



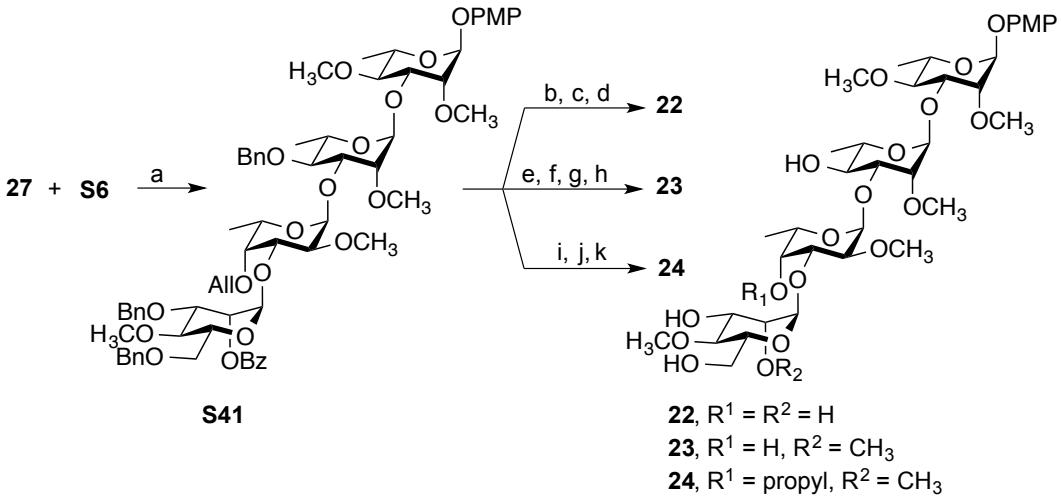
Scheme S10. Synthesis of building block **S5**. Reagents and conditions: a) TBDPSCl, Et_3N, pyridine, 60 ºC, 3 h; b) DMP, *p*-TSA, acetone, 3 h, 88%, over two steps; c) TBAF, THF, 2 h; d) BnBr, NaH, DMF, 2 h; e) *p*-TSA, CH_3OH, overnight, 74% over three steps; f) *n*-Bu_2SnO, toluene, 120 ºC, 1 h; BnBr, *n*-Bu_4NI, 62 ºC, overnight; g) Ac_2O, pyridine, 1 h, 84% over two steps; h) Ac_2O, H_2SO_4, 0 ºC, 1 h; i) TolSH, $BF_3.Et_2O$, CH_2Cl_2, 0 ºC, overnight; j) $NaOCH_3$, CH_3OH/CH_2Cl_2, 2 h; k) BzCl, pyridine, 0 ºC to r.t., 3 h, 59 % over four steps.



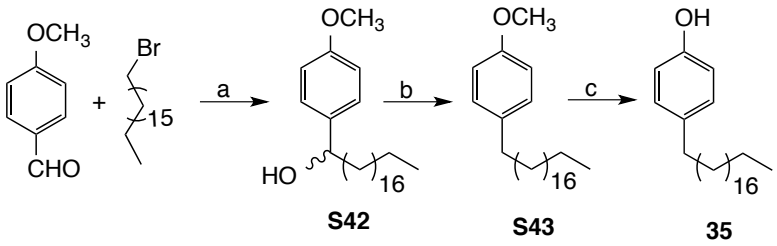
Scheme S11. Synthesis of building block **S6**. Reagents and conditions: a) CH_3I, NaH, DMF, 1 h; b) TBAF, THF, 2 h; c) BnBr, NaH, DMF, 3 h, 78% over three steps; d) *p*-TSA, CH_3OH/CH_2Cl_2, 4 h; e) *n*-Bu_2SnO, toluene, 120 ºC, 1 h; BnBr, *n*-Bu_4NI, 62 ºC, 7 h; f) Ac_2O, pyridine, 1 h, 73%, over three steps; g) Ac_2O, H_2SO_4, 0 ºC, 1 h; h) TolSH, $BF_3.Et_2O$, CH_2Cl_2, 0 ºC, overnight; i) $NaOCH_3$, CH_3OH/CH_2Cl_2, 2 h; j) BzCl, pyridine, 0 ºC to r.t., 2 h, 61 % over four steps.



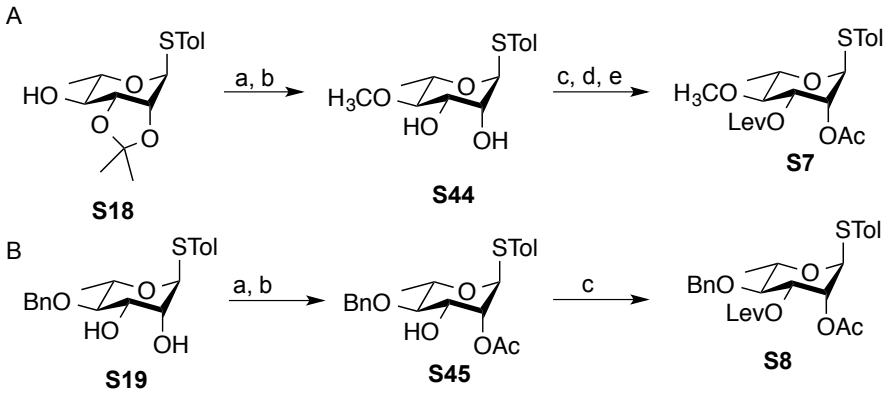
Scheme S12. Synthesis of tetrasaccharides **18–21**. Reagents and conditions: a) NIS, AgOTf, CH_2Cl_2, –20 ºC, 3 min, 68%; b) $NaOCH_3$, CH_3OH /CH_2Cl_2, 3 h; c) $(Ph_3P)_4Pd$, HOAc, overnight; d) Pd/C, H_2, CH_3OH/CH_2Cl_2, three days, 69% over three steps, e) $NaOCH_3$, CH_3OH/CH_2Cl_2, 3 h; f) Pd/C, CH_3OH/CH_2Cl_2, overnight, 73% over two steps; g) $NaOCH_3$, CH_3OH/CH_2Cl_2, 3 h; h) CH_3I, NaH, DMF, 1 h; i) $(Ph_3P)_4Pd$, HOAc, overnight; j) Pd/C, H_2, two days, 60 % over four steps; k) $NaOCH_3$, CH_3OH/CH_2Cl_2, 3 h; l) CH_3I, NaH, DMF, 1 h; m) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 71% over three steps.



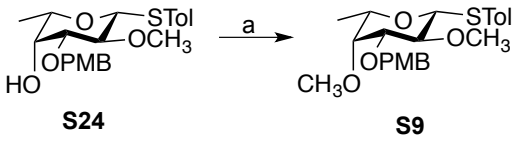
Scheme S13. Synthesis of tetrasaccharides **22–24**. Reagents and conditions: a) NIS, AgOTf, CH_2Cl_2, –20 ºC, 3 min, 63%; b) $NaOCH_3$, CH_3OH/CH_2Cl_2, 4 h; c) $(Ph_3P)_4Pd$, HOAc, overnight; d) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 81% over three steps; e) $NaOCH_3$, CH_3OH/CH_2Cl_2, 4 h; h) CH_3I, NaH, DMF, 1 h; g) $(Ph_3P)_4Pd$, HOAc, overnight; h) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 71% over four steps; i) $NaOCH_3$, CH_3OH/CH_2Cl_2, 4 h; j) CH_3I, NaH, DMF, 1 h; k) Pd/C, H_2, CH_3OH/CH_2Cl_2, overnight, 74% over three steps.



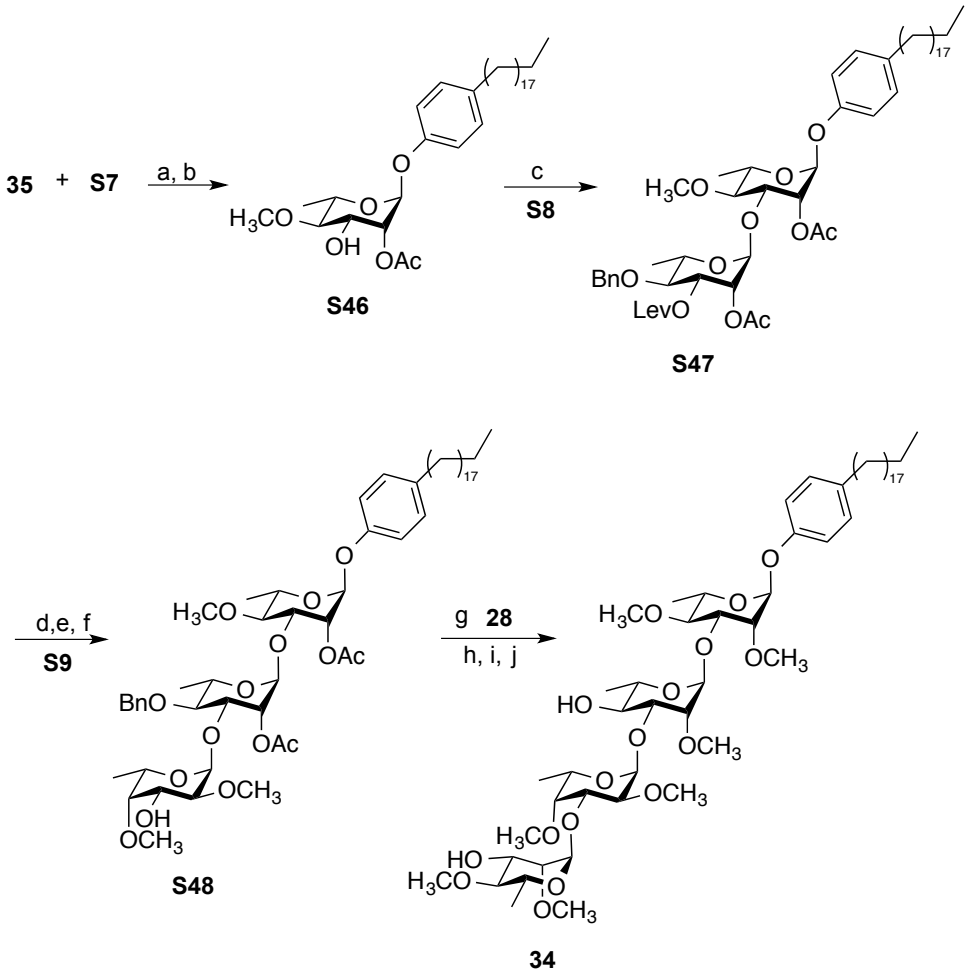
Scheme S14. Synthesis of building block **35**. Reagents and conditions: a) Mg, THF, r.t. to 50 ºC for 3 h, 75%; b) Me_3SiH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 1h, 94%; c) BCl_3, *n*-Bu_4NI, CH_2Cl_2, –78 ºC to rt, 1 h, 96%.



Scheme S15. Synthesis of building blocks **S7** and **S8**. Reagents and conditions: (A) a) CH_3I, NaH, DMF, 1h; b) *p*-TSA, CH_3OH/CH_2Cl_2, 3h, 84% over two steps; c) TEOA, CH_2Cl_2, CSA, 2 h; d) 70% AcOH, 30 min; e) LA, DCC, DMAP, 3 h, 82% over three steps. (B) a) TEOA, CH_2Cl_2, CSA, 2 h; b) 70% AcOH, 30 min; c) LA, DCC, DMAP, CH_2Cl_2, 3 h, 79% over three steps.



Scheme S16. Synthesis of building block **S9**. Reagents and conditions: a) CH_3I, NaH, DMF, 1 h, 89%.

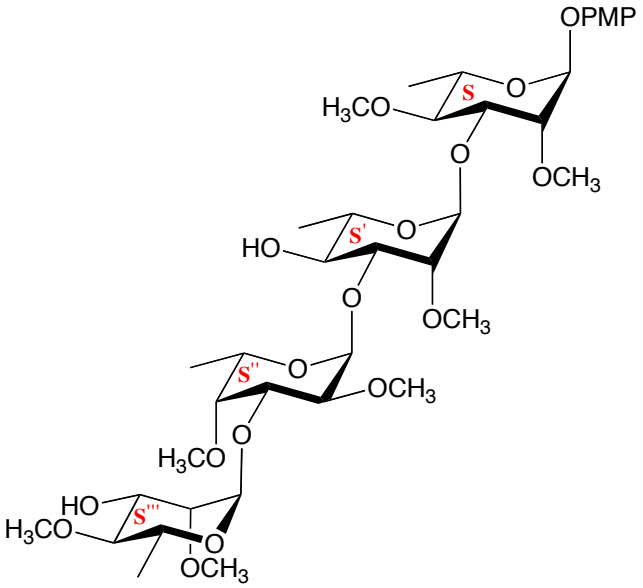


Scheme S17. Synthesis of glycolipid **34**. Reagents and conditions: a) NIS, AgOTf, CH_2Cl_2, –20 ºC, 30 min; b) NH_2NH_2·HAc, CH_2Cl_2, 5 h, 66 % over two steps; c) NIS, AgOTf, CH_2Cl_2, –20 ºC, 30 min, 79%; d) NH_2NH_2·HAc, CH_2Cl_2, 5 h; e) NIS, AgOTf, CH_2Cl_2, –20 ºC, 30 min; f) 5% TFA, CH_2Cl_2, 0 ºC, 45 min, 39 % over three steps; g) NIS, AgOTf, CH_2Cl_2, –20 ºC, 30 min; h) $NaOCH_3$, CH_2Cl_2/CH_3OH_3, 4 h; i) CH_3I, NaH, DMF, 1 h; j) Pd/C, H_2, CH_2Cl_2 /CH_3OH, overnight, 54% over four steps.

Experimental

General Methods

Solvents used in reactions were purified by successive passage through columns of alumina and copper under an argon atmosphere before use. All reagents used in reactions were purchased from commercial sources and were used without further purification unless noted otherwise. All reactions were carried out under a positive pressure of argon atmosphere and monitored by TLC on Silica Gel G-25 UV_{254} (0.25 mm) unless stated otherwise. Spots were detected under UV light and/or by charring with a solution of anisaldehyde in ethanol, acetic acid, and H_2SO_4. Column chromatography was performed on Silica Gel 60 (40–60 μm). The ratio between silica gel and residue ranged from 100:1 to 20:1 (w/w). Organic solutions were concentrated under vacuum at < 50 °C. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 or 500 MHz. ^{1}H NMR chemical shifts are referenced to TMS (0.0, $CDCl_3$) or CD_3OD (4.78, CD_3OD). ^{13}C NMR chemical shifts are referenced to $CDCl_3$ (77.23, $CDCl_3$). ^{1}H NMR data are reported as though they are first order and the peak assignments were made on the basis of 2D-NMR (^{1}H–^{1}H COSY and HMQC) experiments. The monosaccharide residues in the disaccharide and trisaccharides are labelled by no prime, prime, double, and tri–prime as shown in Figure 1 and these labels are maintained in the assignment of NMR spectra of all compounds. Optical rotations were measured at 21 ± 2 °C at the sodium D line (589 nm) and are in units of deg•mL(dm•g)$^{-1}$. ESI-MS spectra were carried out on samples suspended in DCM or CH_3OH and added NaCl.



Numbering system for labelling data.

***p*-Methoxyphenyl 2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranoside (8)**

To a solution of **S27** (16.5 mg, 0.02 mmol) in 1:1 CH_3OH–CH_3Cl_2 (10 mL), *p*-TSA (3 mg) was added and the solution was stirred for 3 h at rt. The reaction mixture was neutralized with Et_3N (50 μL), concentrated and the resulting residue was purified by chromatography (1:2 hexane–EtOAc) to give a syrup. The syrup was dissolved in 1:1 CH_3OH–CH_3Cl_2 (15 mL), Pd–C (3 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere at rt. The reaction mixture was then filtered, concentrated and the resulting residue was purified by chromatography (15:1 CH_2Cl_2–CH_3OH) to give **8** (10.5 mg, 87 %) as a colorless thick syrup: R_f 0.45 (15:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +67.8 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.02–6.99 (m, 2H, Ar-2,6), 6.85–6.82 (m, 2H, Ar-3,5), 5.44 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.20 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.4 Hz, H-1″), 4.25–4.21 (m, 1H, H-5″), 4.07–4.03 (m, 2H, H-3, H-3′), 3.89 (dq, 1H, $J_{4',5'}$ = 9.4 Hz, $J_{5',6'}$ = 6.3 Hz, H-5′), 3.84–3.83 (m, 1H, H-5), 3.80–3.74 (m, 3H, H-4, H-4′, H-4″), 3.78 (s, 3H, OCH_3), 3.72–3.68 (m, 1H, H-3″), 3.66 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 3.64–3.61 (m, 1H, H-2′) 3.54 (s, 3H, OCH_3), 3.52–3.51 (m, 1H, H-2″), 3.50 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 2.52

(br s, 1H, OH), 2.31 (br s, 2H, OH x 2), 1.35 (d, 3H, $J_{5'',6''}$ = 6.4 Hz, H-6″), 1.31 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6), 1.29 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 155.0 (Ar), 150.5 (Ar), 117.5 (Ar x 2), 114.7 (Ar x 2), 99.8, 99.2, 95.5, 83.0, 80.2, 80.1(4), 80.1, 79.5, 71.9 , 71.7, 71.5, 69.9, 69.0, 68.9, 66.5, 59.3 (O*C*H$_3$), 58.7 (O*C*H$_3$), 58.6 (O*C*H$_3$), 55.7 (O*C*H$_3$), 18.0, 17.8, 16.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{28}H_{44}NaO_{14}$: 627.2623. Found 627.2621.

***p*-Methoxyphenyl 2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (9)**

To a solution of **S29** (10 mg, 0.013 mmol) in 1:1 CH_3OH–CH_3Cl_2 (10 mL), *p*-TSA (2 mg) was added. The reaction mixture was stirred for 3 h at rt before the addition of Et_3N (50 μL) and concentration. The resulting residue was purified by chromatography (1:2 hexane–EtOAc) to give a colorless oil (8 mg). The oil was dissolved in 1:1 CH_3OH–CH_3Cl_2 (20 mL), Pd–C (2 mg, 20% w/w) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere at rt. The reaction mixture was filtered, concentrated and the resulting crude product was purified by chromatography (15:1 CH_2Cl_2–CH_3OH) to give **9** (7.5 mg, 90%) as a thick syrup: R_f 0.55 (15:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –19.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.02–6.99 (m, 2H, Ar-2,6), 6.85–6.82 (m, 2H, Ar-3,5), 5.44 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.20 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.4 Hz, H-1″), 4.24 (dq, 1H, $J_{4'',5''}$ = 2.7 Hz, $J_{5'',6''}$ = 6.5 Hz, H-5″), 4.10 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 4.05 (dd, 1H, $J_{2',3'}$ = 3.0 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 3.87 (dq, 1H, $J_{4',5'}$ = 9.5 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.84–3.83 (m, 1H, H-3″), 3.77–3.74 (m, 1H, H-5), 3.78 (s, 3H, OC*H*$_3$), 3.71–3.68 (m, 2H, H-2″, H-4″), 3.67 (dd, 1H, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.0 Hz, H-2′), 3.60 (app t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.5 Hz, H-4′), 3.55 (s, 3H, OC*H*$_3$), 3.53 (s, 3H, OC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 3.51–3.49 (m, 1H, H-2), 3.46 (s, 3H, OC*H*$_3$), 3.22 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 2.80 (br s, 1H, OH), 2.43 (br s, 1H, OH), 1.68 (br s, 1H, OH), 1.35 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 1.31 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.29 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 155.0 (Ar), 150.5 (Ar), 117.5 (Ar x 2), 114.7 (Ar x 2), 99.8, 99.2, 95.5,

83.0, 80.2(0), 80.1(7), 80.1, 79.5, 71.9, 71.7, 71.5, 69.9, 68.9, 68.8, 66.5, 61.1 (O*C*H$_3$), 59.3 (O*C*H$_3$), 58.7 (O*C*H$_3$), 58.6 (O*C*H$_3$), 55.7 (O*C*H$_3$), 18.0, 17.8, 16.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{29}H_{46}NaO_{14}$: 641.2780. Found 641.2775.

***p*-Methoxyphenyl 4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (10)**

To a solution of **S30** (20 mg, 0.024 mmol) in pyridine (2 mL), Ac_2O (1 mL) was added and the reaction mixture was stirred for 2 h at rt. Water (5 mL) was then added and the solution was diluted with CH_2Cl_2 (10 mL), washed with water (2 x 8 mL), 1M HCl soln (2 x 8 mL) and brine. The organic layer was dried ($NaSO_4$), concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in the 1:1 CH_2Cl_2–CH_3OH (20 mL), Pd–C (4 mg) was added and the reaction mixture was stirred under a hydrogen atmosphere overnight. The reaction mixture was then filtered, concentrated and the resulting syrup was purified by chromatography (10:0.25 CH_2Cl_2–CH_3OH) to give **10** (12.9 mg, 81%) as a thick syrup: R_f 0.45 (10:0.25 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –32.5 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 6.99–6.97 (m, 2H, Ar-2,6), 6.82–6.81 (m, 2H, Ar-3,5), 5.39 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.23–5.22 (m, 1H, H-4″), 5.17 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.4 Hz, H-1″), 4.30 (dq, 1H, $J_{4'',5''}$ = 2.1 Hz, $J_{5'',6''}$ = 6.4 Hz, H-5″), 4.23 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, $J_{3',4'}$ = 9.8 Hz, H-3′), 4.09 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.86 (dq, 1H, $J_{4',5'}$ = 9.8 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.76 (s, 3H, OC*H*$_3$), 3.71–3.68 (m, 2H, H-3″, H-5), 3.65–3.63 (m, 2H, H-2, H-2′), 3.55 (s, 3H, OC*H*$_3$), 3.54 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 3.49–3.47 (m, 2H, H-2″, H-4′), 3.45 (s, 3H, OC*H*$_3$), 3.22 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4), 2.18 (s, 3H, C*H*$_3$CO), 1.36 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.28 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.12 (d, 3H, $J_{5'',6''}$ = 6.4 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 171.3 (*C*=O), 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.0, 99.2, 95.6, 83.0, 82.3, 80.5, 80.3, 79.4, 79.0, 73.4, 71.5, 68.9, 68.7, 68.6, 65.5, 61.0 (O*C*H$_3$), 59.4

(O*C*H$_3$), 59.0 (O*C*H$_3$), 58.5 (O*C*H$_3$), 55.7 (O*C*H$_3$), 20.8 (*C*H$_3$CO), 17.8(8), 17.8(4), 16.3. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{31}H_{48}NaO_{15}$: 683.2885. Found 683.2880.

***p*-Methoxyphenyl 2-*O*-methyl-4-*O*-propionyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L- rhamnopyranoside (11)**

To a solution of **S30** (10 mg, 0.012 mmol) in pyridine (2 mL), propanoic anhydride (1 mL) was added and the reaction mixture was stirred for 2 h at rt. After 2 h, water (5 mL) was added and the solution was diluted with CH_2Cl_2 (10 mL), washed with water (2 x 8 mL), 1M HCl soln (2 x 8 mL) and brine (8 mL). The organic layer was separated, concentrated and the resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in the 1:1 CH_2Cl_2–CH_3OH (20 mL), Pd–C (2 mg) was added and the reaction mixture was stirred overnight under hydrogen. The reaction mixture was then filtered, concentrated and the resulting residue was purified by chromatography (10:0.25 CH_2Cl_2–CH_3OH) to give **11** (7.4 mg, 88%) as a thick syrup: R_f 0.60 (20:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ –21.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.00–6.97 (m, 2H, Ar-2,6), 6.83–6.80 (m, 2H, Ar-3,5), 5.39 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.23 (m, 1H, H-4″), 5.17 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 4.31 (dq, 1H, $J_{4'',5''}$ = 2.1 Hz, $J_{5'',6''}$ = 6.5 Hz, H-5″), 4.23 (dd, 1H, $J_{2',3'}$ = 3.5 Hz, $J_{3',4'}$ = 9.7 Hz, H-3′), 4.10 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.86 (dq, 1H, $J_{4',5'}$ = 9.7 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.78–3.76 (m, 1H, H-5), 3.75 (s, 3H, OC*H*$_3$), 3.71–3.68 (m, 2H, H-2′, H-3″), 3.65–3.63 (m, 2H, H-2, H-4′), 3.55 (s, 3H, OC*H*$_3$), 3.54 (s, 3H, OC*H*$_3$), 3,52 (s, 3H, OC*H*$_3$), 3.48 (dd, 1H, $J_{1'',2''}$ = 3.3 Hz, $J_{2'',3''}$ = 9.8 Hz, H-2″), 3.46 (s, 3H, OC*H*$_3$), 3.22 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 2.47 (q, 2H, *J* = 7.6 Hz, C*H*$_2$CH$_3$), 1.35 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.26 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.19 (t, 3H, *J* = 7.6 Hz, C*H*$_3$CH$_2$), 1.12 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 174.8 (*C*=O), 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.0, 99.2, 95.6, 83.0, 82.3, 80.5, 80.3, 79.4, 79.0, 73.2, 71.5, 69.0, 68.7, 68.7, 65.6, 61.0 (OC*H*$_3$), 59.3 (OC*H*$_3$),

59.0 (OC*H*$_3$), 58.5 (OC*H*$_3$), 55.7 (OC*H*$_3$), 27.5 (*C*H$_2$CH$_3$), 17.8(9), 17.8(4), 16.3, 9.3 (*C*H$_3$CH$_2$). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{32}H_{50}NaO_{15}$: 697.3042. Found 697.3037.

_p_-Methoxyphenyl α-D-mannopyranosyl-(1→3)-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl -α-L-rhamnopyranoside (18)

To a solution of **S40** (15 mg, 0.012 mmol) in 1:1 CH_3OH–CH_2Cl_2 (10 mL), 1M $NaOCH_3$ (0.5 mL) was added. The reaction mixture was stirred for 3 h at rt before it was neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in AcOH (5 mL), $(Ph_3P)_4Pd$ (4 mg, 10% w/w) was added and the reaction mixture was stirred overnight at rt and then it was filtered. The filtrate was dilited with water (10 mL) and CH_2Cl_2 (20 mL), being being washed with water (2 x 10 mL), and brine (10 mL). The organic layer was dried ($NaSO_4$), concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a colorless oil. To the solution of the oil in 1:1 CH_3OH–CH_2Cl_2 (15 mL), Pd–C (3 mg) was added and the reaction mixture was stirred overnight under hydrogen. The reaction mixture was then filtered, concentrated and the resulting residue was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **18** (7.6 mg, 81%) as an amorphous solid: R_f 0.4 (10:0.75 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –45.3 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.01–6.98 (m, 2H, Ar-2,6), 6.68–6.82 (m, 2H, Ar-3,5), 5.42 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.20 (d, 1H, $J_{1'',2''}$ = 3.2 Hz, H-1″), 5.13 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.04 (d, 1H, $J_{1''',2'''}$ = 1.6 Hz, H-1‴), 4.12–4.04 (m, 2H, H-3′, H-5), 4.00 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.90–3.88 (m, 2H, H-3″, H-5′), 3.86–3.81 (m, 4H, H-5″, H-5‴, H-6‴ x 2), 3.78 (dd, 1H, $J_{1''',2'''}$ = 1.6 Hz, $J_{2''',3'''}$ = 3.1 Hz, H-2‴), 3.74 (s, 3H, OC*H*$_3$), 3.72–3.72 (m, 1H, H-2), 3.68–3.62 (m, 4H, H-2′, H-2″, H-3‴, H-4′), 3.58–3.56 (m, 2H, H-4″, H-4‴), 3.54 (s, 3H, OC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 3.50 (s, 3H, OC*H*$_3$), 3.47 (s, 3H, OC*H*$_3$), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 1.29 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 1.22 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.20 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 101.8, 100.1, 98.9, 95.56, 82.4(9), 82.4(8), 82.2, 80.7, 80.3, 79.2, 78.4, 78.3,

73.8, 71.3, 71.3, 71.0, 69.0, 68.7, 66.9, 66.5, 61.3, 61.1 (O*C*H$_3$), 59.2 (O*C*H$_3$), 59.0 (O*C*H$_3$), 58.3 (O*C*H$_3$), 55.6 (O*C*H$_3$), 18.0, 17.8, 16.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{35}H_{56}NaO_{19}$: 803.3308. Found 803.3303.

_p_-Methoxyphenyl α-D-mannopyranosyl-(1→3)-2-_O_-methyl-4-_O_-propyl-α-L-fucopyranosyl-(1→3)-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (19)

To a solution of **S40** (15 mg, 0.012 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.15 mL) was added and the reaction mixture was stirred for 4 h at rt. It was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. To the solution of this syrup in 1:1 CH_3OH–CH_2Cl_2 (20 mL), Pd–C (4 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere. The reaction mixture was then filtered, concentrated and the resulting residue was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **19** (8.6 mg, 87%) as an amorphous solid: R_f 0.55 (20:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –33.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.01–6.98 (m, 2H, Ar), 6.84–6.82 (m, 2H, Ar), 5.40 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.21 (br s, 1H, H-1′), 5.16 (br s, 1H, H-1‴), 5.12 (d, 1H, $J_{1'',2''}$ = 3.1 Hz, H-1″), 4.16–4.09 (m, 2H, H-5″, H-3′), 4.06 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.99–3.80 (m, 5H, H-3″, H-5′, H-5‴, H-6‴ x 2), 3.79 (s, 3H, OC*H*$_3$), 3.75–3.68 (m, 5H, H-2, H-2‴, H-5, C*H*$_2$O x 2), 3.64–3.59 (m, 4H, H-2′, H-2″, H-3‴, H-4′), 3.56–3.54 (m, 1H, H-4‴), 3.54 (s, 3H, OC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 3.45 (s, 3H, OC*H*$_3$) 3.44–3.42 (m, 1H, H-4), 3.24–3.20 (m, 1H, H-4″), 1.66–1.59 (m, 2H, C*H*$_2$CH$_3$), 1.33 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 1.26 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.25 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 0.95 (t, 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 101.6, 100.1, 98.9, 95.6, 82.4, 82.1, 80.7, 80.5, 80.3, 79.8, 79.6, 75.8 (*C*H$_2$O), 73.2, 71.4, 71.1, 70.9, 69.1, 68.7, 67.4, 66.5, 61.2, 61.0, 59.0 (O*C*H$_3$), 58.9 (O*C*H$_3$), 58.2 (O*C*H$_3$), 55.7 (O*C*H$_3$), 55.7 (O*C*H$_3$), 23.5 (*C*H$_2$CH$_3$), 18.0, 17.8, 16.6, 10.8 (CH$_2$*C*H$_3$). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{38}H_{62}NaO_{19}$: 845.3778. Found 845.3776.

***p*-Methoxyphenyl 2-*O*-methyl-α-D-mannopyranosyl-(1→3)-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (20)**

To a solution of **S40** (20 mg, 0.016 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.15 mL) was added and the reaction mixture was stirred for 3 h at rt. It was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (2 mL), CH_3I (0.1 mL) and NaH (60% in mineral oil, 0.7 mg, 0.027 mmol) were added at 0 ºC. The reaction mixture was stirred for 1 h at rt the addition of chilled water (5 mL) and CH_2Cl_2 (10 mL). The organic layer was washed with water (2 x 10 mL), and brine (10 mL) and then separated and concentrated. The resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give syrup. To the solution of the syrup in AcOH (5 mL), $(Ph_3P)_4Pd$ (2 mg, 10% w/w) was added and the reaction mixture was stirred overnight at rt before it was filtered. The filtrate was diluted with water (10 mL) and CH_2Cl_2 (20 mL), and then the organic layer was washed with water (2 x 10 mL) and brine (10 mL) before it was dried ($NaSO_4$) and concentrated. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give a colorless oil. To the solution of the oil in 1:1 CH_3OH–CH_2Cl_2 (15 mL), Pd–C (2 mg) was added and the reaction mixture was stirred for two days under a hydrogen atmosphere. It was then filtered, concentrated and the resulting residue was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **20** (9 mg, 71%) as an amorphous solid: R_f 0.50 (10:0.75 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –19.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.02–6.98 (m, 2H, Ar-2,6), 6.85–6.82 (m, 2H, Ar-3,5), 5.40 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.21 (br s, 1H, H-1′), 5.15 (br s, 1H, H-1‴), 5.10 (d, 1H, $J_{1″,2″}$ = 3.2 Hz, H-1″), 4.17 (dq, 1H, $J_{4″,5″}$ = 2.6 Hz, $J_{5″,6″}$ = 6.5 H, H-5″), 4.12–4.08 (m, 2H, H-3, H-3′), 3.97–3.80 (m, 7H, H-2, H-3″, H-5, H-5′, H-5‴, H-6‴ x 2), 3.79 (s, 3H, OCH_3), 3.72–3.70 (m, 3H, H-2′, H-2″, H-2‴), 3.69–3.65 (m, 2H, H-3‴, H-4″), 3.64–3.59 (m, 2H, H-4′, H-4‴), 3.56 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.24 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 1.36 (d, 3H, $J_{5″,6″}$ = 6.5 Hz, H-6″), 1.29–1.26 (m, 6H, H-6, H-6′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.7, 99.3, 97.8, 95.6, 83.1, 82.3, 80.6, 80.4, 80.2,

78.9, 78.5(3), 78.4(4), 72.5, 71.7, 71.6, 71.5, 69.2, 69.0, 68.7, 66.5, 62.6, 61.1 (O*C*H$_3$), 59.9 (O*C*H$_3$), 59.0 (O*C*H$_3$), 58.8 (O*C*H$_3$), 58.6 (O*C*H$_3$), 55.7 (O*C*H$_3$), 17.8(6), 17.8(5), 16.3. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{36}H_{58}NaO_{19}$: 817.3465. Found 817.3462.

_p_-Methoxyphenyl 2-_O_-methyl-α-D-mannopyranosyl-(1→3)-2-_O_-methyl-4-_O_-propyl-α-L-fucopyranosyl-(1→3)-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (21)

To a solution of **S40** (15 mg, 0.012 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.15 mL) was added and the reaction mixture was stirred for 3 h at rt. It was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (1 mL), CH_3I (0.1 mL) and NaH (60% in mineral oil, 0.5 mg, 0.022 mmol) were added at 0 ºC. The reaction mixture was stirred for 1 h at rt before the addition of chilled water (5 mL), and CH_2Cl_2 (10 mL). The organic layer was washed with water (2 x 10 mL) and brine (10 mL) and then separated, concentrated and the resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. To the solution of the syrup in 1:1 CH_3OH–CH_2Cl_2 (10 mL), Pd–C (4 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere. The solution was then filtered, concentrated and the resulting residue was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **21** (7.6 mg, 76%) as a thick syrup: R_f 0.45 (20:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –38.1 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 6.99–6.96 (m, 2H, Ar-2,6), 6.83–6.80 (m, 2H, Ar-3,5), 5.39 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.28 (br s, 1H, H-1′), 5.16 (br s, 1H, H-1‴), 5.09 (d, 1H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 4.16–4.17 (m, 2H, H-3′, H-5″), 4.08 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.89–3.85 (m, 3H, H-3″, H-6‴ x 2), 3.82–3.77 (m, 2H, H-5′, H-5‴), 3.76 (s, 3H, OC*H*$_3$), 3.74–3.67 (m, 5H, C*H*$_2$O x 2, H-2, H-2′, H-5), 3.65–3.62 (m, 2H, H-2″, H-2‴), 3.56–3.55 (m, 1H, H-3‴), 3.53 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 3.50 (s, 3H, OC*H*$_3$), 3.49–3.47 (m, 2H, H-4′, H-4‴), 3.46 (s, 3H, OC*H*$_3$), 3.43–3.42 (m, 1H, H-4″), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 1.65–1.58 (m, 2H, C*H*$_2$CH$_3$), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6),

1.26 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.21 (d, 1H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 0.94 (t, 3H, J = 7.7 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.3, 99.3, 97.8, 95.6, 82.9, 82.2, 80.6, 80.5, 80.3, 80.2, 79.3, 75.9 (CH_2O), 75.8, 72.6, 71.5, 71.4, 69.0, 68.8, 68.7, 67.6, 62.5, 61.1, 59.1 (OCH_3), 58.9 (OCH_3), 58.7 (OCH_3), 58.5 (OCH_3), 55.7 (OCH_3 x 2), 23.5 (CH_2CH_3), 17.9, 17.8, 16.5, 10.8 (CH_2CH_3). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{39}H_{64}NaO_{19}$: 859.3934. Found 859.3925.

***p*-Methoxyphenyl 4-*O*-methyl-α-D-mannopyranosyl-(1→3)-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (22)**

To a solution of **S41** (20 mg, 0.02 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.15 mL) was added and the reaction mixture was stirred for 4 h at rt. The reaction mixture was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting crude product was purified by chromatography (1:1 hexane–EtOAc) to give a syrup. To the solution of this syrup in AcOH (3 mL), $(Ph_3P)_4Pd$ (4 mg, 20 % w/w) was added and the reaction mixture was stirred overnight and then filtered. The filtrate was diluted with water (10 mL), and CH_2Cl_2 (20 mL) and then washed with water (2 x 10 mL) and brine (10 mL). The organic layer was separated, dried ($NaSO_4$), concentrated and the resulting oil was dissolved in 1:1 CH_3OH–CH_2Cl_2 (20 mL). To this solution, Pd–C (4 mg, 20% w/w) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere before it was filtered and concentrated. The resulting crude product was purified by chromatography (10:0.75, CH_2Cl_2–CH_3OH) to give **22** (11.3 mg, 71%) as a thick syrup: R_f 0.50 (10:0.75, CH_2Cl_2–CH_3OH); $[\alpha]_D$ –41.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.01–6.98 (m, 2H, Ar-2,6), 6.85–6.81 (m, 2H, Ar-3,5), 5.40 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.19–5.18 (m, 2H, H-1′, H-1‴), 5.11 (d, 1H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 4.20–4.16 (m, 1H, H-5″), 4.11–4.08 (m, 2H, H-3′, H-3), 4.02–4.01 (m, 1H, H-3″), 3.95–3.85 (m, 4H, H-5, H-5′, H-6‴ x 2), 3.81–3.79 (m, 3H, H-2, H-2‴, H-5‴), 3.78 (s, 3H, OCH_3), 3.72–3.68 (m, 2H, H-2′, H-2″), 3.67–3.62 (m, 3H, H-3‴, H-4′, H-4″), 3.59 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.52 (s, 6H, OCH_3 x 2), 3.47 (s, 3H, OCH_3), 3.46–3.43 (m, 1H, H-4‴), 3.23 (app

t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 1.37 (d, 3H, $J_{5'',6''}$ = 6.4 Hz, H-6″), 1.28–1.26 (m, 6H, H-6, H-6′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 101.0, 100.1, 98.9, 95.6, 82.8, 82.2, 80.5, 80.3, 79.2, 78.8, 78.7, 78.4, 78.2, 71.3, 71.1, 69.0, 68.7, 68.6, 66.5, 66.3, 62.0, 61.1 (OCH_3), 60.8 (OCH_3), 59.5 (OCH_3), 59.0 (OCH_3), 58.2 (OCH_3), 55.7 (OCH_3), 18.0, 17.8, 16.3. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{36}H_{58}NaO_{19}$: 817.3465. Found 817.3459.

***p*-Methoxyphenyl 2,4-di-*O*-methyl-α-D-mannopyranosyl-(1→3)-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (23)**

To a solution of **S41** (15 mg, 0.012 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL) was added 1M $NaOCH_3$ (0.15 mL) and the reaction mixture was stirred for 4 h at rt. The reaction mixture was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting crude product was dissolved in DMF (4 mL), CH_3I (0.1 mL) and NaH (60% in mineral oil, 6 mg) were added at 0 ºC. The reaction mixture was stirred for 1 h at rt before the addition of water (8 mL), and CH_2Cl_2 (10 mL). The organic layer was washed with water (2 x 10 mL) and brine (10 mL) before being concentrated. The resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in AcOH (3 mL), $(Ph_3P)_4Pd$ (3 mg, 20% w/w) was added and the reaction mixture was stirred overnight. The reaction mixture was then filtered, and the filtrate was dilted with water (10 mL), and CH_2Cl_2 (20 mL). The organic layer was washed with water (2 x 10 mL) and brine (10 mL), and then separated, dried ($NaSO_4$), and concentrated to give an oil that was dissolved in 1:1 CH_3OH–CH_2Cl_2 (20 mL). To this solution, Pd–C (4 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere. The reaction mixture was then filtered, concentrated and the resulting crude product was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **23** (7.2 mg, 74%) as a thick syrup: R_f 0.39 (20:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –39.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 6.99–6.96 (m, 2H, Ar-2,6), 6.83–6.80 (m, 2H, Ar-3,5), 5.40 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.21 (br s, 1H, H-1′), 5.18 (br s, 1H, H-1‴), 5.09 (d, 1H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 4.15–4.07 (dq, 1H, $J_{4'',5''}$ = 2.8

Hz, $J_{5'',6''}$ = 6.4 H, H-5″), 4.11 (dd, 1H, $J_{2',3'}$ = 3.0 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 4.07 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.91–3.86 (m, 4H, H-3″, H-5′, H-6‴ x 2), 3.80–3.76 (m, 3H, H-2, H-5, H-5‴), 3.78 (s, 3H, OC*H*$_3$), 3.74–3.69 (m, 3H, H-2′, H-2″, H-2‴), 3.66–3.62 (m, 3H, H-3‴, H-4′, H-4″), 3.58 (s, 3H, OC*H*$_3$), 3.56 (s, 3H, OC*H*$_3$), 3.53 (s, 3H, OC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$), 3.48 (s, 3H, OC*H*$_3$), 3.30–3.23 (m, 2H, H-4, H-4‴), 2.70 (br s, 1H, OH), 2.51 (d, 1H, *J* = 8.5 Hz, OH), 1.72 (br s, 2H, OH x 2), 1.36 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.28 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.26 (d, 3H, $J_{5'',6''}$ = 6.4 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.7, 99.3, 97.7, 95.6, 83.2, 82.3, 80.6(2), 80.6(0), 80.3, 78.9, 78.5, 78.4, 78.3, 72.3, 71.7, 71.6, 71.4, 69.0, 68.7, 66.4, 62.4, 61.1 (O*C*H$_3$), 60.8 (O*C*H$_3$), 60.0 (O*C*H$_3$), 59.0 (O*C*H$_3$), 58.8 (O*C*H$_3$), 58.6 (O*C*H$_3$), 55.7 (O*C*H$_3$), 17.8(6), 17.8(4), 16.3. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{37}H_{60}NaO_{19}$: 831.3621. Found 831.3613.

***p*-Methoxyphenyl 2,4-di-*O*-methyl-α-D-mannopyranosyl-(1→3)-2-*O*-methyl-4-*O*-isopropyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (24)**

To a solution of **S41** (15 mg, 0.012 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.15 mL) was added and the reaction mixture was stirred for 4 h at rt. The reaction mixture was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting crude product was dissolved in DMF (4 mL), CH_3I (0.1 mL) and NaH (60% in mineral oil, 4 mg) were added at 0 ºC. The reaction mixture was stirred for 1 h at rt before the addition of water (8 mL). The mixture was diluted with CH_2Cl_2 (15 mL), washed with water (2 x 10 mL) and brine (20 mL). The organic layer was separated, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. To the solution of this syrup in 1:1 CH_3OH–CH_2Cl_2 (20 mL), Pd–C (4 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere. The reaction mixture was then filtered, concentrated and the resulting crude product was purified by chromatography (10:0.75, CH_2Cl_2–CH_3OH) to give **24** (7.3 mg,

71%) as a thick syrup: R_f 0.44 (10:0.75, CH_2Cl_2–CH_3OH); $[\alpha]_D$ –27.6 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.01–6.98 (m, 2H, Ar-2,6), 6.85–6.81 (m, 2H, Ar-3,5), 5.40 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.20 (br s, 1H, H-1′), 5.18 (br s, 1H, H-1‴), 5.08 (d, 1H, $J_{1'',2''}$ = 3.2 Hz, H-1″), 4.21–4.06 (m, 3H, H-3, H-3′, H-5″), 3.91–3.86 (m, 3H, H-3″, H-5′, H-6‴ x 2), 3.80–3.76 (m, 3H, H-2, H-5, H-5‴), 3.78 (s, 3H, OCH_3), 3.74–3.71 (m, 4H, H-2′, H-2″, CH_2O), 3.70–3.62 (m, 3H, H-2‴, H-3‴, H-4′), 3.57 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.40–3.38 (m, 1H, H-4″), 3.30 (app t, 1H, $J_{3''',4'''} = J_{4''',5'''}$ = 9.8 Hz, H-4‴), 3.21 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 1.61 (q, 1H, *J* = 7.5 Hz, C$H_2$$CH_2$O), 1.35 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.26 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.20 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 0.94 (t, 1H, *J* = 7.5 Hz, C$H_3$$CH_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 100.4, 99.4, 97.5, 95.6, 83.1, 82.2, 80.6(0), 80.5(6), 80.5, 80.4, 80.3, 79.3, 78.3, 75.8 (*C*H_2O), 72.7, 72.1, 71.6, 69.4, 69.0, 68.7, 67.7, 62.5, 61.1 (O*C*H_3), 60.9 (O*C*H_3), 59.3 (O*C*H_3), 58.9 (O*C*H_3), 58.6(1) (O*C*H_3), 58.5(8) (O*C*H_3), 55.7 (O*C*H_3), 23.52 (*C*$H_2$$CH_3$), 17.8(6), 17.8(4), 16.3, 10.8 (*C*$H_3$$CH_2$). HRMS (ESI) Calcd. for (M + Na) $C_{40}H_{66}NaO_{19}$: 873.4091. Found 873.4083.

_p_-Tolyl 4-_O_-allyl-3-_O_-_p_-methoxybenzyl-2-_O_-methyl-1-thio-β-L-fucopyranoside (25)

To a solution of compound **S24** (1 g, 2.47 mmol) and AllBr (0.2 mL, 2.29 mmol) in DMF (10 mL) at 0 °C was added NaH (60% in mineral oil, 95 mg, 3.95 mmol). The reaction mixture was stirred for 2 h at rt before the addition of chilled water (30 mL). The solution was concentrated, diluted with CH_2Cl_2 (50 mL) and washed with water (2 × 50 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (5:1 hexane–EtOAc) to give **25** (0.94 g, 86%) as a colorless oil: R_f 0.61 (5:1 hexane–EtOAc); $[\alpha]_D$ –14.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.49–7.46 (m, 2H, Ar), 7.31–7.27 (m, 2H, Ar), 7.09–7.07 (m, 2H, Ar), 6.90–6.87 (m, 2H, Ar), 5.98–5.88 (m, 1H, CH_2=C*H*), 5.28–5.27 (m, 1H, *C*H_2=CH), 5.17–5.14 (m, 1H, *C*H_2=CH), 4.66, 4.62 (ABq, 2H, *J* = 11.5 Hz, ArCH_2), 4.43–4.37 (m, 2H, *C*H_2O, H-1), 4.13–4.08 (m, 1H, *C*H_2O), 3.81 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3),

3.52–3.45 (m, 3H, H-2, H-4, H-5), 3.41 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 3.1 Hz, H-3), 2.32 (s, 3H, ArCH_3), 1.28 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.2 (=*C*H), 137.1 (Ar), 135.6 (*C*H_2=), 132.2 (Ar x 2), 130.5 (Ar), 129.4 (Ar x 2), 129.2 (Ar x 2), 116.2 (Ar x 2), 113.8 (Ar x 2), 87.9, 83.8, 79.0, 76.4 (Ar*C*H_2), 74.5 (*C*H_2O), 73.9, 72.4, 61.1 (O*C*H_3), 55.3 (O*C*H_3), 21.1 (Ar*C*H_3), 17.2 (C-6). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{25}H_{32}NaO_5S$: 467.1863. Found 467.1855.

***p*-Methoxyphenyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (26)**

To a solution of **S28** (0.5 g, 0.72 mmol) in 1:1 CH_3OH–CH_2Cl_2 (30 mL), 1M $NaOCH_3$ (0.5 mL) was added. The reaction mixture was stirred for 1 h at rt and then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (5 mL) and CH_3I (0.1 mL, 0.86 mmol) was added. To this solution, cooled to 0 °C, NaH (60% in mineral oil, 27.50 mg, 1.16 mmol) was added and then the reaction mixture was stirred for additional 1 h at rt. After 1 h, chilled water (10 mL) was added and the solution was diluted with CH_2Cl_2 (30 mL), washed with water (2 x 20 mL), 1M HCl soln (2 x 20 mL) and brine (20 mL). The organic layer was separated, dried (Na_2SO_4), filtered, concentrated and the resulting purified by chromatography (4:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in CH_2Cl_2 (20 mL) and TFA (1 mL, 5% v/v) was added dropwise over 2 min at 0 ºC. The reaction mixture was stirred for additional 30 min at 0 ºC before the addition of Et_3N (3 mL) and concentration. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give **26** (0.32 g, 80%) as a colorless oil: R_f 0.40 (2:1 hexane–EtOAc); $[\alpha]_D$ –46.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.34 (m, 5H, Ar), 7.01–6.97 (m, 2H, Ar-2,6), 6.84–6.81 (m, 2H, Ar-3,5), 5.38 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.22 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 4.92, 4.70 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.13 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.02 (dd, 1H, $J_{2',3'}$ = 3.3 Hz, $J_{3',4'}$ = 9.6 Hz, H-3′), 3.87 (dq, 1H, $J_{4',5'}$ = 9.6 Hz, $J_{5',6'}$ = 6.5 Hz, H-5′), 3.77 (s, 3H, OCH_3), 3.70 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.5 Hz, H-5), 3.67 (dd, 1H, $J_{1',2'}$ = 1.7 Hz, $J_{2',3'}$ = 3.3 Hz, H-2′), 3.62 (dd,

1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 3.55 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 3.31 (app t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz, H-4′), 3.25 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 1.35 (d, 1H, $J_{5',6'}$ = 6.5 Hz, H-6′), 1.27 (d, 1H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 138.5 (Ar), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.8 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 98.3, 95.9, 82.6, 82.1, 81.2, 80.3, 78.3, 75.1 (ArCH_2), 71.5, 68.8, 67.8, 61.0 (OCH_3), 59.2 (OCH_3), 58.7 (OCH_3), 55.7 (OCH_3), 18.1, 17.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{29}H_{40}NaO_{10}$: 571.2514. Found 571.2509.

***p*-Methoxyphenyl 4-*O*-allyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (27)**

Two solutions were prepared. Solution A was prepared by dissolving donor **25** (0.29 g, 0.65 mmol) in CH_2Cl_2 (15 mL); containing crushed 4 Å molecular sieves (50 mg). Solution B was prepared by dissolving acceptor **26** (300 mg, 0.55 mmol) in CH_2Cl_2 (15 mL); containing crushed 4 Å molecular sieves (100 mg). Both solutions were then stirred for 30 min at rt before solution B solution was cooled to –40 ºC, NIS (144 mg, 0.64 mmol) and AgOTf (39 mg, 0.15 mmol) were added. Solution A was then added to solution B dropwise over 5 min while stirring. Then, the reaction mixture was stirred for additional 30 min at –40 ºC before it was neutralized by the addition of Et_3N (1 mL). The solution was filtered, concentrated and the resulting residue was dissolved in CH_2Cl_2 (15 mL). To this solution, TFA (0.75 mL, 5% v/v) was added dropwise over 1 min at 0 ºC and reaction mixture was then stirred for additional 30 min at 0 ºC before it was neutralized by the addition of Et_3N (2 mL). The solution was concentrated and the resulting crude product was purified by chromatography (1:1 hexanes–EtOAc) to give **27** (312 mg, 76%) as a colorless oil: R_f 0.54 (1:1 hexanes–EtOAc); $[\alpha]_D$ +25.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.23 (m, 5H, Ar), 7.00–6.96 (m, 2H, Ar-2,6), 6.83–6.80 (m, 2H, Ar-3,5), 6.01–5.93 (m, 1H, CH_2=CH), 5.39 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.31–5.27 (m, 1H, CH_2=CH), 5.23 (d, 1H, $J_{1'',2''}$ = 3.4 Hz, H-1″), 5.20–5.18 (m, 1H, CH_2=CH), 5.16 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′) 5.13, 4.58 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.35–4.31 (m, 1H, CH_2O), 4.22–

4.17 (m, 2H, C*H*$_2$O, H-5″), 4.14–4.08 (m, 2H, H-4″, H-3″), 4.06 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 4.02 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′) 3.95 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.76 (s, 3H, OC*H*$_3$), 3.74–3.72 (m, 2H, H-2, H-2′), 3.68 (dq, 1H, $J_{4',5'}$ = 9.5 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.59–3.58 (m, 1H, H-2″), 3.54 (s, 3H, OC*H*$_3$), 3.50 (s, 3H, OC*H*$_3$), 3.48 (s, 3H, OC*H*$_3$), 3.49–3.46 (m, 1H, H-4′), 3.29 (s, 3H, OC*H*$_3$), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 2.34 (d, 1H, $J_{3'',OH\text{-}3''}$ = 2.5 Hz, OH-3″), 1.30 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 1.27 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.25 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.5 (Ar), 139.1 (Ar), 135.0 (=*C*H), 128.2 (Ar x 2), 127.4 (Ar x 2), 127.3 (Ar), 117.5 (Ar x 2), 117.4 (*C*H$_2$=CH), 114.6 (Ar x 2), 99.1, 98.6, 95.5, 81.9, 80.7, 80.2, 80.1, 79.5, 79.4, 78.8, 74.9, 74.8, 70.2, 68.7(0), 68.6(8), 66.4, 61.2, 58.8 (O*C*H$_3$), 58.1 (O*C*H$_3$), 57.7(1) (O*C*H$_3$), 55.6(5) (O*C*H$_3$ x 2), 18.3, 17.9, 16.9. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{39}H_{56}NaO_{14}$: 771.3562. Found 771.3560.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-4-*O*-methyl-1-thio-α-D-mannopyranoside (28)**

To a solution of compound **S34** (0.5 g, 1.54 mmol) in Ac_2O (10 mL) was added H_2SO_4 (0.1 mL) after the solution was cooled to 0 ºC. The reaction mixture was stirred for additional 2 h at 0 ºC before the addition of satd. aq. $NaHCO_3$ soln (10 mL), water (10 mL) and dilution with CH_2Cl_2 (40 mL). The organic layer was separated, washed with satd. aq. $NaHCO_3$ soln (2 x 30 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in CH_2Cl_2 (25 mL) and *p*-thiocresol (0.25 g, 2 mmol) was added. To this solution, $BF_3.Et_2O$ (0.25 mL, 2 mmol) was added at 0 ºC and the reaction mixture was stirred overnight at rt. Then, satd. aq. $NaHCO_3$ soln (25 mL) was added and the mixture was diluted with CH_2Cl_2 (30 mL). The organic layer was separated, washed with water (2 x 50 mL), brine (50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in 1:1 CH_3OH–CH_2Cl_2 (20 mL), 1M $NaOCH_3$ (0.25 mL) was added and the reaction mixture was stirred for 2 h at rt. The solution was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolve in pyridine (5 mL) and BzCl, benzoyl chloride (0.21 mL, 2 mmol) was added at 0 ºC. The reaction mixture was stirred for

additional 2 h at rt before the addition of water (20 mL) and dilution with CH_2Cl_2 (40 mL). The organic layer washed with satd. aq. $NaHCO_3$ soln (2 x 30 mL), brine (30 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (7:1 hexane–EtOAc) to give **28** (0.39 g, 53%) as a colorless oil: R_f 0.70 (7:1 hexane–EtOAc); $[\alpha]_D$ +91.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.70–7.67 (m, 1H, Ar), 7.59–7.53 (m, 3H, Ar), 7.47–7.44 (m, 2H, Ar), 7.38–7.26 (m, 6H, Ar), 7.11 (d, 2H, J = 8.0 Hz, Ar), 5.80 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.46 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.78, 4.61 (ABq, 2H, J = 11.5 Hz, ArC*H*$_2$), 4.21 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.91 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.61 (s, 3H, OC*H*$_3$), 3.33 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.32 (s, 3H, ArC*H*$_3$), 1.40 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.7 (*C*=O), 137.9 (Ar x 2), 134.5 (Ar), 133.2 (Ar), 132.3 (Ar), 130.6 (Ar), 130.1 (Ar), 129.9(3) (Ar), 129.8(7) (Ar x 2), 128.8(8) (Ar), 128.8(7) (Ar), 128.39 (Ar x 2), 128.33 (Ar x 2), 127.92 (Ar), 127.67 (Ar), 86.5, 82.4, 78.1, 71.7 (Ar*C*H$_2$), 71.1, 69.1, 61.2 (O*C*H$_3$), 21.1 (Ar*C*H$_3$), 17.9 (C-6). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{28}H_{30}NaO_5S$: 501.1712. Found 501.1710.

***p*-Methoxyphenyl 2-*O*-benzoyl-3-benzyl-6-deoxy-4-*O*-methyl-α-D-mannopyranosyl-(1→3)-4-*O*-allyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (29)**

To a solution of donor **28** (131 mg, 0.27 mmol) and acceptor **27** (120 mg, 0.16 mmol) in CH_2Cl_2 (20 mL), crushed 4 Å molecular sieves (200 mg) were added. After the mixture was stirred at rt for 30 min, it was cooled to –20 ºC, NIS (67.4 mg, 0.3 mmol) and AgOTf (15.4 mg, 0.06 mmol) were added and the reaction mixture was stirred for additional 30 min at –20 ºC before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was purified by chromatography (2:1 hexane–EtOAc) to give **29** (122 mg, 69%) as an amorphous solid: R_f 0.38 (2:1 hexane–EtOAc); $[\alpha]_D$ +28.5 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09–8.07 (m, 2H, Ar), 7.58–7.55 (m, 1H, Ar), 7.47–7.44 (m, 2H, Ar), 7.30–7.09 (m, 10H, Ar), 7.01–6.95 (m, 2H, Ar), 6.85–6.80 (m, 2H, Ar), 5.94–5.86 (m, 1H, CH_2=C*H*), 5.67 (dd, 1H, $J_{1''',2'''}$ = 1.8

Hz, $J_{2''',3'''}$ = 3.1 Hz, H-2‴), 5.39 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.28–5.27 (m, 1H, CH_2=CH), 5.25–5.24 (m, 1H, CH_2=CH), 5.17–5.14 (m, 3H, H-1′, H-1″, H-1‴), 5.13, 4.52 (ABq, 2H, J = 11.3 Hz, ArCH_2), 4.78.459 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.34–4.30 (m, 1H, –CH_2O), 4.23–4.20 (m, 2H, H-3″, H-5″), 4.10–4.06 (m, 2H, H-3′, CH_2O), 4.00 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.94 (dq, 1H, $J_{4',5'}$ = 9.5 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.90 (dd, 1H, $J_{2''',3'''}$ = 3.1 Hz, $J_{3''',4'''}$ = 9.6 Hz, H-3‴), 3.84–3.78 (m, 1H, H-2), 3.76 (s, 3H, OCH_3), 3.75–3.68 (m, 4H, H-2′, H-2″, H-5, H-5‴), 3.59 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.53–3.46 (m, 2H, H-4′, H-4″), 3.50 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.26 (app t, 1H, $J_{3''',4'''}$ = $J_{4''',5'''}$ = 9.6 Hz, H-4‴), 3.22 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 1.38 (d, 3H, $J_{5''',6'''}$ = 6.3 Hz, H-6‴), 1.33 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 1.27 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.24 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.6 (*C*=O), 154.9 (Ar), 150.5 (Ar), 139.1 (Ar), 138.1 (Ar), 135.1 (=*C*H), 133.1 (Ar), 130.1 (Ar x 2), 129.9 (Ar x 2), 128.4 (Ar x 2), 128.3 (Ar x 2), 128.1 (Ar x 2), 127.9 (Ar x 2), 127.6 (Ar), 127.5 (Ar), 127.1 (Ar), 117.5 (Ar x 2), 117.3 (*C*H_2=), 114.6 (Ar x 2), 99.7, 99.1, 98.5, 95.6, 82.4, 82.0, 81.5, 80.7, 80.2, 80.0, 79.5, 79.4, 79.0, 75.5, 75.1, 74.4, 71.3, 69.3, 68.7, 68.6(5), 68.5, 66.9, 61.3, 61.2 (O*C*H_3), 58.9 (O*C*H_3), 58.6 (O*C*H_3), 57.8 (O*C*H_3), 55.7 (O*C*H_3), 55.6 (O*C*H_3), 18.2, 18.2, 17.9, 16.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{60}H_{78}NaO_{19}$: 1125.5030. Found 1125.5020.

_p_-Methoxyphenyl 3-benzyl-6-deoxy-2,4-di-_O_-methyl-α-D-mannopyranosyl-(1→3)-4-_O_-allyl-2-_O_-methyl-α-L-fucopyranosyl-(1→3)-4-_O_-benzyl-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (30)

To a solution of **29** (100 mg, 0.09 mmol) in 1:1 CH_3OH–CH_2Cl_2 (20 mL), 1M $NaOCH_3$ (0.2 mL) was added and the reaction mixture was stirred for 5 h at rt. The reaction mixture was then neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (3 mL), and then CH_3I (0.1 mL) and NaH (60% in mineral oil, 10 mg) were added. The reaction mixture was stirred for 1 h at rt before chilled water (8 mL) was added. The solution was diluted with CH_2Cl_2 (15 mL), washed

with water (2 x 10 mL) and finally brine (10 mL). The organic layer was separated, concentrated and the resulting residue was purified by chromatography (3:1 hexane–EtOAc) to give **30** (83 mg, 91%) as a colorless oil: R_f 0.45 (3:1 hexane–EtOAc); $[\alpha]_D$ –28.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.22 (m, 10H, Ar), 7.00–6.96 (m, 2H, Ar), 6.83–6.81 (m, 2H, Ar), 5.92–5.84 (m, 1H, =C*H*), 5.39 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.26–5.22 (m, 1H, CH_2=CH), 5.17–5.14 (m, 5H, H-1′, H-1″, H-1‴, CH_2=CH, ArCH_2), 4.72, 4.68 (ABq, 2H, *J* = 12.5 Hz, ArCH_2), 4.56 (d, 1H, *J* = 11.5 Hz, ArCH_2), 4.31–4.27 (m, 1H, CH_2O), 4.21–4.14 (m, 2H, H-3″, H-5″), 4.07–4.02 (m, 2H, H-3′, CH_2O), 3.99 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.94 (dq, 1H, $J_{4',5'}$ = 9.5 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.76 (s, 3H, OCH_3), 3.75–3.72 (m, 2H, H-3‴, H-2), 3.70–3.67 (m, 2H, H-2′, H-2″), 3.66–3.60 (m, 2H, H-5, H-5‴), 3.58 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.48–3.46 (m, 3H, H-2‴, H-4′, H-4″), 3.47 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.22–3.18 (m, 2H, H-4, H-4‴), 3.17 (s, 3H, OCH_3), 1.33–1.31 (m, 6H, H-6, H-6′), 1.26 (d, 3H, $J_{5''',6'''}$ = 6.2 Hz, H-6‴), 1.21 (d, 3H, $J_{5'',6''}$ = 6.7 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.5 (Ar), 139.3 (Ar), 138.5 (Ar), 135.1 (=*C*H), 128.3 (Ar x 2), 128.1 (Ar x 2), 127.9 (Ar x 2), 127.6 (Ar), 127.3 (Ar x 2), 127.2 (Ar), 117.5 (Ar x 2), 117.3 (*C*H_2=), 114.6 (Ar x 2), 99.6, 98.5, 98.4, 95.5, 82.2, 82.0, 80.7, 80.2, 80.1, 79.6, 79.2, 79.0, 78.9, 78.4, 75.9, 75.0, 74.3, 72.2, 68.7(0), 68.6(5), 66.9, 61.2, 61.1, 58.8 (O*C*H_3), 58.7 (O*C*H_3), 58.1 (O*C*H_3), 57.6 (O*C*H_3), 57.6 (O*C*H_3), 55.7 (O*C*H_3), 55.6 (O*C*H_3), 18.2, 17.9, 17.8, 16.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{54}H_{76}NaO_{18}$: 1035.4924. Found 1035.4920.

_p_-Nonadecylphenyl 6-deoxy-2,4-di-_O_-methyl-α-D-mannopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-fucopyranosyl-(1→3)-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (34)

To a solution of **S48** (20 mg, 0.02 mmol) and **28** (13.4 mg, 0.03 mmol) in CH_2Cl_2 (10 mL) was added crushed 4 Å molecular sieves (50 mg). After stirring for 30 min at rt, the reaction mixture cooled to –20 ºC, and then NIS (4.5 mg, 0.02 mmol) and AgOTf (1.6 mg, 0.006 mmol) were added. The reaction was stirred

for additional 30 min before the addition of Et_3N (0.25 mL) concentration. The resulting crude residue was dissolved in 1:1 CH_3OH–CH_2Cl_2 (10 mL), and then 1M $NaOCH_3$ (0.1 mL) was added and the reaction mixture was stirred for 4 h at rt before being neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (2 mL), CH_3I (0.2 mL) and NaH (60% in mineral oil, 5 mg) were added and the reaction mixture was stirred for 1 h at rt before the addition of chilled water (5 mL) and CH_2Cl_2 (10 mL). The organic layer was washed with water (2 x 8 mL) and brine (8 mL), and then separated, dried ($NaSO_4$), filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. To the solution of the syrup in CH_2Cl_2 (10 mL), Pd–C (4 mg) was added and the reaction mixture was stirred overnight under a hydrogen atmosphere before it was filtered and concentrated. The resulting residue was purified by chromatography (20:1 CH_2Cl_2–CH_3OH) to give **34** (12 mg, 59%) as a thick syrup: R_f 0.55 (20:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ –48.8 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.11–7.09 (m, 2H, Ar-2,6), 7.00–6.97 (m, 2H, Ar-3,5), 5.47 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.24 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.20 (d, 1H, $J_{1'',2''}$ = 3.8 Hz, H-1″), 5.15 (d, 1H, $J_{1''',2'''}$ = 1.7 Hz, H-1‴), 4.17–4 .14 (m, 2H, H-2‴, H-3′), 4.04–3.97 (m, 2H, H-3, H-5‴), 3.87–3.81 (m, 2H, H-3″, H-5), 3.73–3.69 (m, 3H, H-2′, H-5′, H-5″), 3.66–3.62 (m, 2H, H-2, H-2″), 3.60 (s, 3H, OC*H*$_3$), 3.59 (s, 3H, OC*H*$_3$), 3.58–3.57 (m, 1H, H-3‴), 3.56 (s, 3H, OC*H*$_3$), 3.55 (s, 3H, OC*H*$_3$), 3.53–3.51 (m, 1H, H-4′), 3.50 (s, 3H, OC*H*$_3$), 3.47 (s, 3H, OC*H*$_3$), 3.46 (s, 3H, OC*H*$_3$), 3.29–3.28 (m, 1H, H-4‴), 3.26 (app t, 1H, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.6 Hz, H-4″), 3.00 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.56 (t, 1H, $J_{1,2}$ = 7.8 Hz, C*H*$_2$-1$_{agly}$), 2.42 (br s, 1H, OH), 1.80 (br s, 1H, OH), 1.62–1.56 (m, 2H, C*H*$_2$-2$_{agly}$), 1.40 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 1.34 (d, 3H, $J_{5''',6'''}$ = 6.5 Hz, H-6‴), 1.31–1.27 (m, 35H, H-6″, C*H*$_2$ x 16), 1.24 (d, 3H, $J_{5',6'}$ = 6.5 Hz, H-6′), 0.89 (t, 3H, $J_{18,19}$ = 7.0 Hz, C*H*$_3$-19$_{agly}$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.5 (Ar), 136.8 (Ar), 129.3 (Ar x 2), 116.1 (Ar x 2), 101.4, 97.7, 97.6, 95.4, 84.0, 82.7, 82.2, 81.3, 80.7, 80.5, 78.8, 77.5, 75.7, 72.6, 71.6, 71.3, 69.1, 68.8, 67.1, 66.8, 62.0 (O*C*H$_3$), 61.0 (O*C*H$_3$), 61.1 (O*C*H$_3$), 59.3 (O*C*H$_3$), 58.6 (O*C*H$_3$), 57.3 (O*C*H$_3$), 57.1 (O*C*H$_3$), 35.1 (*C*H$_2$), 32.0 (*C*H$_2$), 31.7 (*C*H$_2$), 29.7 (*C*H$_2$ x 10), 29.6 (*C*H$_2$), 29.6 (*C*H$_2$), 29.4 (*C*H$_2$), 29.3 (*C*H$_2$), 22.7 (*C*H$_2$), 18.1,

17.8(7), 17.8(4), 16.2, 14.1 (C-19_{agly}). HRMS (ESI) Calcd for $(M + Na)^+$ $C_{56}H_{98}O_{17}Na$: 1065.6696. Found 1065.6691.

4-Nonadecylphenol (35)

To a solution of **S43** (0.5 g, 1.33 mmol) and *n*-Bu_4NI (1.23 g, 3.33 mmol) in CH_2Cl_2 (20 mL) at –78 ºC, BCl_3 (3.3 mL of 1M soln in heptanol, 3.33 mmol) was added dropwise over 5 min and then the reaction mixture was stirred for 30 min. After warming to rt, water (30 mL) was added and the solution was diluted with CH_2Cl_2 (50 mL), and then washed with water (2 x 30 mL) and brine (30 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (7:1 hexane–EtOAc) to afford **35** (460 mg, 96%) as an amorphous solid: R_f 0.46 (7:1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.06–7.02 (m, 2H, Ar-2,6), 6.76–6.73 (m, 2H, Ar-3,5), 2.53 (t, 2H, $J_{1',2'}$ = 7.6 Hz, CH_2-1′), 1.61–1.55 (m, 2H, CH_2-2′), 1.32–1.26 (m, 32 H, CH_2 x 16), 0.89 (t, 3H, $J_{18',19'}$ = 7.4 Hz, CH_3-19′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 153.5 (Ar), 135.4 (Ar), 129.6 (Ar x 2), 115.2 (Ar x 2), 35.2 (*C*H_2), 32.3 (*C*H_2), 31.9 (*C*H_2), 29.9 (*C*H_2 x 11), 29.8 (*C*H_2), 29.7 (*C*H_2), 29.5 (*C*H_2), 29.4 (*C*H_2), 14.3 (*C*H_3-19′). HRMS (ESI) Calcd for $(M)^+$ $C_{25}H_{44}O$: 360.3392. Found 360.3390.

***p*-Methoxyphenyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (S1)**

Diol **S14** (1 g, 2.77 mmol) was dissolved in toluene (40 mL) and *n*-Bu_2SnO (0.7 g, 2.77 mmol) was added. The reaction mixture was stirred at 120 °C for 1 h and then it was cooled to 62 ºC before PMBCl (0.5 g, 3.05 mmol) and *n*-Bu_4NI (1.02 g, 2.77 mmol) were added. The reaction mixture was stirred at 62 ºC for additional 7 h and then concentrated. The resulting crude product was purified by chromatography (1:1 hexane–EtOAc) to give colorless syrup. This syrup (1.05 g) was dissolved in DMF (10 mL) and CH_3I (0.2 mL, 3.32 mmol) was added. The reaction mixture was cooled to 0 ºC before NaH (60% in mineral oil, 106 mg, 4.43 mmol) was added and then the solution was stirred for additional 1 h at rt. Chilled water (20 mL) was added and the

solution was diluted with CH_2Cl_2 (50 mL). The organic layer was separated, washed with water (2 x 40 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and TFA (1.5 mL) was added dropwise over 2 min at 0 ºC. The reaction mixture was stirred for additional 30 min at 0 ºC before Et_3N (3 mL) was added. The mixture was concentrated and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to give **S1** (0.84 g, 81%) as an amorphous solid: R_f 0.55 (1:1 hexane–EtOAc); $[\alpha]_D$ –29.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.39–7.27 (m, 5H, Ar), 7.01–6.98 (m, 2H, Ar-2,6), 6.85–6.81 (m, 2H, Ar-3,5), 5.46 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.93, 4.70 (ABq, 2H, J = 11.3 Hz, ArCH_2), 4.15–4.13 (m, 1H, H-3), 3.81 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.78 (s, 3H, OCH_3), 3.68 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 3.55 (s, 3H, OCH_3), 3.34 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.44 (br s, 1H, OH-3), 1.29 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 138.4 (Ar), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.8 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 95.2, 82.1, 80.6, 75.1 (ArCH_2), 71.5, 67.8, 59.1 (OCH_3), 55.7 (OCH_3), 18.0 (C-6). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{21}H_{26}NaO_6$: 397.1622. Found 397.1629.

***p*-Methoxyphenyl 2,4-di-*O*-methyl-α-L-rhamnopyranoside (S2)**

To a solution of **S16** (1.3 g, 3.22 mmol) and CH_3I (0.25 mL, 3.86 mmol) in DMF (10 mL), NaH (60% in mineral oil, 0.13 g, 5.15 mmol) was added at 0 °C. The reaction mixture was stirred for 4 h at rt before chilled water (30 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (100 mL) and washed with water (2 × 100 mL). The organic layer was separated, dried (Na_2SO_4), filtered, concentrated. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and TFA (1.5 mL, 5% v/v) was added at 0 ºC. The solution was stirred for additional 30 min and then Et_3N (3 mL) was added. After concentration of the solution, the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give **S2** (0.78 g, 81%) as a colorless oil: R_f 0.36 (2:1 hexane–EtOAc); $[\alpha]_D$ –57.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.03–6.99 (m, 2H, Ar-2,6), 6.87–6.81 (m, 2H, Ar-3,5), 5.45 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.05 (ddd, 1H, $J_{2,3}$ =

3.3 Hz, $J_{3,4}$ = 9.3 Hz, $J_{3,OH\text{-}3}$ = 8.9 Hz, H-3), 3.80 (s, 3H, OC*H*$_3$), 3.74 (dq, 1H, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.68 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 3.62 (s, 3H, OC*H*$_3$), 3.56 (s, 3H, OC*H*$_3$), 3.07 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, H-4), 2.45 (d, 1H, $J_{3,OH\text{-}3}$ = 8.9 Hz, OH-3), 1.30 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 155.2 (Ar), 150.7 (Ar), 117.8 (Ar x 2), 114.9 (Ar x 2), 95.5, 84.0, 80.8, 71.4, 68.2, 61.2 (O*C*H$_3$), 59.3 (O*C*H$_3$), 55.9 (O*C*H$_3$), 18.2 (C-6). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{15}H_{22}NaO_6$: 321.1314. Found 321.1313.

***p*-Tolyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-1-thio-α-L-rhamnopyranoside (S3)**

To a solution of **S20** (2.2 g, 4.58 mmol) in pyridine (5 mL) at 0 °C, Ac_2O (3 mL) was added. The reaction mixture was stirred for 3 h at rt before water (10 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (30 mL) and washed with water (2 × 30 mL). The organic layer was separated, dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (5:1 hexane–EtOAc) to give **S3** (2.27 g, 95%) as an amorphous solid: R_f 0.52 (5:1 hexane–EtOAc); $[\alpha]_D$ –73.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40–7.27 (m, 9H, Ar-H), 7.14 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.90–6.86 (m, 2H, Ar-H), 5.61 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.35 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.95, 4.64 (ABq, 2H, *J* = 10.7 Hz, ArC*H*$_2$), 4.67, 4.51 (ABq, 2H, *J* = 11.0 Hz, ArC*H*$_2$), 4.25 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.92 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.82 (s, 3H, OC*H*$_3$), 3.50 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.35 (s, 3H, C*H*$_3$CO), 2.16 (s, 3H, ArC*H*$_3$), 1.36 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.5 (*C*=O), 159.6 (Ar), 138.7 (Ar), 138.1 (Ar), 132.6 (Ar x 2), 130.4 (Ar x 2), 130.1 (Ar x 4), 128.6 (Ar x 2), 128.2 (Ar x 2), 128.0 (Ar), 114.1 (Ar x 2), 86.8, 80.4, 78.1, 75.7 (Ar*C*H$_2$), 71.7 (Ar*C*H$_2$), 70.9, 69.3, 55.5 (O*C*H$_3$), 21.4 (Ar*C*H$_3$), 18.1 (C-6). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{30}H_{34}NaO_6S$: 545.1968. Found 545.1967.

***p*-Tolyl 3,4-*O*-isopropylidene-2-*O*-methyl-1-thio-β-L-fucopyranoside (S4)**

To a solution of **S22** (2 g, 6.45 mmol) and CH_3I (0.5 mL, 7.73 mmol) in DMF (15 mL), at 0 °C, NaH (60% in mineral oil, 0.25 g, 10.3 mmol) was added portion-wise over 10 min. The reaction mixture was stirred for 4 h at rt before it water (30 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (100 mL), and washed with water (2 × 100 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting residue was purified by chromatography (3:1 hexane–EtOAc) to give **S4** (1.96 g, 94%) as a colorless oil: R_f 0.42 (3:1 hexane–EtOAc); $[\alpha]_D$ –41.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.45–7.43 (m, 2H, Ar-2,6), 7.10–7.08 (m, 2H, Ar-3,5), 4.41 (d, 1H, J = 9.7 Hz, H-1), 4.09 (app t, 1H, $J_{1,2} = J_{2,3}$ = 9.7 Hz, H-2), 4.00 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{4.5}$ = 2.1 Hz, H-4), 3.76 (dq, 1H, $J_{4,5}$ = 2.1 Hz, $J_{5,6}$ = 6.5 Hz, H-5), 3.52 (s, 3H, ArOCH_3), 3.20 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 2.9 Hz, H-3), 2.31 (s, 3H, ArCH_3), 1.46 (s, 3H, (CH_3)$_2$C), 1.37 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 1.33 (s, 3H, (CH_3)$_2$C); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 137.6 (Ar), 132.9 (Ar x 2), 129.6 (Ar), 129.5 (Ar x 2), 109.6 ((CH$_3$)$_2$*C*), 86.3, 80.4, 79.7, 76.4, 72.4, 59.6 (ArO*C*H$_3$), 28.0 ((*C*H$_3$)$_2$C), 26.4 ((*C*H$_3$)$_2$C), 21.1 (Ar*C*H$_3$), 21.08 (C-6). (ESI) Calcd. for $(M + Na)^+$ $C_{17}H_{24}O_4SNa$: 347.1293. Found 347.1289.

***p*-Tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (S5)**

To a solution of compound **S37** (1.22 g, 2.41 mmol) in Ac_2O (20 mL), H_2SO_4 (0.2 mL) was added at 0 ºC. The reaction mixture was stirred for additional 1 h at 0 ºC before the addition of satd. aq. $NaHCO_3$ soln (15 mL), water (15 mL) and CH_2Cl_2 (50 mL). The organic layer was separated, washed with satd. aq. $NaHCO_3$ soln (2 x 40 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in CH_2Cl_2 (20 mL) and *p*-thiocresol (0.38 g, 3.13 mmol) was added. To this solution, $BF_3{\cdot}Et_2O$ (0.4 mL, 3.13 mmol) was added at 0 ºC and the mixture was stirred overnight at rt. Then, satd. aq. $NaHCO_3$ soln (20 mL) and CH_2Cl_2 (20 mL) were added. The organic layer was separated, washed with water (2 x 30 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by

chromatography (6:1 hexane–EtOAc) to give an oil. To the soultion of this oil in 1:1 CH_3OH–CH_2Cl_2 (20 mL), 1M $NaOCH_3$ (0.2 mL) was added and the reaction mixture was stirred for 2 h at rt. The solution was then neutralized by the addition of Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolve in pyridine (8 mL) and BzCl (0.3 mL, 3.13 mmol) was added at 0 ºC. The reaction mixture was stirred for additional 2 h at rt before the addition of water (30 mL). The solution was diluted with CH_2Cl_2 (50 mL), washed with satd. aq. $NaHCO_3$ soln (2 x 40 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (6:1 hexane–EtOAc) to give **S5** (0.94 g, 59%) as a colorless oil: R_f 0.65 (6:1 hexane–EtOAc); $[\alpha]_D$ +36.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.19–8.17 (m, 3H, Ar), 8.08–8.06 (m, 1H, Ar), 7.70–7.67 (m, 2H, Ar), 7.57–7.52 (m, 4H, Ar), 7.47–724 (m, 13H, Ar), 7.08–7.06 (m, 1H, Ar), 5.88 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.0 Hz, H-2), 5.59 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.92, 4.59 (ABq, 2H, J = 10.8 Hz, ArCH_2), 4.82, 4.62 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.71, 4.52 (ABq, 2H, J = 11.8 Hz, ArCH_2), 4.43 (ddd, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 4.1 Hz, H-5), 4.18 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 4.09 (dd, 1H, $J_{5,6a}$ = 4.1 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.96 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.7 Hz, H-3), , 3.81 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6b), 2.31 (s, 3H, ArCH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.6 (*C*=O), 138.4 (Ar), 138.3 (Ar), 137.9(6) (Ar), 137.9(3) (Ar), 134.5 (Ar), 133.2 (Ar), 133.0 (Ar), 132.4 (Ar), 130.6 (Ar x 3), 129.9(5) (Ar), 129.9(0) (Ar), 129.9 (Ar), 129.7 (Ar x 2), 128.8(9) (Ar x 3), 128.8(8) (Ar), 128.4(1) (Ar), 128.3(9) (Ar), 128.3(5) (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5(3) (Ar), 127.4(6) (Ar), 99.0, 78.4, 75.4, 74.6, 73.7, 72.0, 71.5, 69.2, 68.9, 21.1 (Ar*C*H_3). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{41}H_{40}NaO_6S$: 683.2443. Found 683.2444.

***p*-Tolyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (S6)**

To a solution of compound **S39** (1.04 g, 2.42 mmol) in Ac_2O (15 mL), H_2SO_4 (0.15 mL) was added at 0 ºC and the reaction mixture was stirred for additional 1 h at 0 ºC. A solution of satd. aq. $NaHCO_3$ soln (25 mL)

was added followed by water (25 mL) and CH_2Cl_2 (60 mL). The organic layer was separated, washed with satd. aq. $NaHCO_3$ soln (2 x 50 mL), brine (50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and *p*-thiocresol (0.4 g, 3.13 mmol) was added. To this solution, $BF_3{\cdot}Et_2O$ (0.4 mL, 3.13 mmol) was added at 0 ºC and the mixture was stirred overnight at rt. The reaction A solution of satd. aq. $NaHCO_3$ (50 mL) was added and then resulting mixture was diluted with CH_2Cl_2 (30 mL). The organic layer was separated, washed with water (2 x 50 mL), brine (50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by chromatography (6:1 hexane–EtOAc) to give a thick syrup. This syrup was dissolved in 1:1 CH_3OH–CH_2Cl_2 (20 mL) and catalytic amount of 1M $NaOCH_3$ (0.2 mL) was added. The reaction mixture was stirred for 2 h at rt and then it was neutralized by Amberlite IR-120 H^+ resin, filtered and concentrated. To the resulting residue in pyridine (10 mL), BzCl (0.3 mL, 3.13 mmol) was added at 0 ºC. The reaction mixture was stirred for additional 2 h at rt before the addition of water (30 mL). The mixture was diluted with CH_2Cl_2 (50 mL), washed with satd. aq. $NaHCO_3$ soln (2 x 40 mL), brine (40 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (6:1 hexane–EtOAc) to give **S6** (0.96 g, 68%) as a colorless oil: R_f 0.61 (6:1 hexane–EtOAc); $[\alpha]_D$ +41.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.06–8.04 (m, 2H, Ar), 7.55–7.52 (m, 1H, Ar), 7.41–7.26 (m, 14H, Ar), 7.08–7.06 (d, 2H, J = 8.0 Hz, Ar), 5.83 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.0 Hz, H-2), 5.57 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.81, 4.63 (ABq, 2H, J = 12.0 Hz, ArCH_2), 4.74, 4.56 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.32 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 1.8 Hz, H-5), 3.98–3.93 (m, 2H, H-3, H-6a), 3.87 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.81 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6b), 3.57 (s, 3H, OCH_3), 2.31 (s, 3H, ArCH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.6 (*C*=O), 138.5 (Ar), 137.9 (Ar x 2), 137.8 (Ar), 133.2 (Ar), 132.4 (Ar), 130.6 (Ar), 130.0 (Ar x 2), 129.9 (Ar x 2), 128.9 (Ar), 128.3(8) (Ar x 2), 128.3(6) (Ar x 2), 128.3 (Ar x 2), 128.0 (Ar x 2), 127.7 (Ar), 127.4(7) (Ar x 2), 127.4(4) (Ar), 86.9, 78.4, 76.3, 73.4, 72.6, 70.7, 69.2, 61.1 (O*C*H_3), 21.1 (Ar*C*H_3). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{35}H_{36}NaO_6S$: 607.2130. Found 607.2131.

***p*-Tolyl 2-*O*-acetyl-3-*O*-levulinoyl-4-*O*-methyl-1-thio-α-L-rhamnopyranoside (S7)**

To a solution of **S44** (0.78 g, 2.77 mmol) and triethyl orthoacetate (1.0 mL, 5.55 mmol) in CH_2Cl_2 (20 mL) was added CSA (128 mg, 0.55 mmol). The reaction mixture was stirred for 2 h at rt before it was concentrated and dissolved in 80% aqueous HOAc. After stirring for additional 30 min at rt. water (10 mL) was added to the solution and it was concentrated. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with water (2 × 20 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting syrup was carried to the next step without further purification. To a solution of the syrup in CH_2Cl_2 (20 mL) were added levulinic acid (0.4 mL, 3.60 mmol), DCC (0.74g, 3.60 mmol) and DMAP (67 mg, 0.55 mmol) and the reaction mixture was stirred for 3 h at rt. The solution was filtered, concentrated, and the resulting residue was purified by chromatography (4:1 hexane–EtOAc) to give **S7** (0.96 g, 8 %) as a colorless oil: R_f 0.46 (4:1 hexane–EtOAc); $[\alpha]_D$ –76.4 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δH) 7.35–7.32 (m, 2H, Ar-2,6), 7.12–7.08 (m, 2H, Ar-3,5), 5.46 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.29 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.27 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.22 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.53 (s, 3H, OC*H*$_3$), 3.29 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.89–2.49 (m, 4H, C*H*$_2$CO, C*H*$_2$COO), 2.33 (s, 3H, ArC*H*$_3$), 2.21 (s, 3H, C*H*$_3$CO), 2.13 (s, 3H, C*H*$_3$CO), 1.36 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 206.7 (*C*=O), 172.0 (*C*=O), 170.2 (*C*=O), 138.2 (Ar), 132.7 (Ar), 132.7 (Ar x 2), 130.1 (Ar x 2), 86.2, 80.6, 72.3, 71.9, 69.2, 60.9 (O*C*H$_3$), 38.1, 30.1, 28.2, 21.4, 21.2 (Ar*C*H$_3$), 17.9. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{21}H_{28}O_7NaS$: 447.1448. Found 447.1446.

***p*-Tolyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-levulinoyl-1-thio-α-L-rhamnopyranoside (S8)**

To a solution of compound **S45** (0.9 g, 2.23 mmol) in CH_2Cl_2 (20 mL), levulinic acid (0.4 mL, 3.60 mmol), DCC (0.74 g, 3.60 mmol) and DMAP (67 mg, 0.55 mmol) were added and the reaction mixture was stirred for 3 h at rt. The solution was filtered, concentrated, and the resulting residue was purified by

chromatography (4:1 hexane–EtOAc) to give **S8** (1.03 g, 92%) as a colorless oil: R_f 0.42 (4:1 hexane–EtOAc); $[\alpha]_D$ –96.6 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.39–7.28 (m, 7H, Ar), 7.12 (d, 2H, J = 8.4 Hz, Ar-2,6), 5.51 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.34–5.31 (m, 2H, H-1, H-3), 4.79, 4.68 (ABq, J = 11.2 Hz, ArCH_2), 4.38 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.60 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.80–2.66 (m, 2H, COCH_2), 2.55–2.49 (m, 2H, CH_2CO), 2.34 (s, 3H, ArCH_3), 2.19 (s, 3H, CH_3COCH$_2$), 2.15 (s, 3H, CH_3CO), 1.37 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 206.4 (*C*=O), 172.0 (*C*=O), 170.2 (*C*=O), 138.3 (Ar), 138.2 (Ar), 132.7 (Ar x 2), 130.1 (Ar x 2), 130.0 (Ar), 128.7 (Ar x 2), 128.1 (Ar), 128.0 (Ar x 2), 86.3, 79.1, 77.0, 72.6, 72.0, 69.2, 38.1, 30.1, 28.2, 21.4, 21.2 (Ar*C*H$_3$), 18.1. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{27}H_{32}O_7NaS$: 523.1761. Found 523.1755.

***p*-Tolyl 2,4-di-*O*-methyl-3-*O*-*p*-methoxybenzyl-1-thio-β-L-fucopyranoside (S9)**

To a solution of **S27** (0.89 g, 2.21 mmol) and CH_3I (0.21 mL, 3.32 mmol) in DMF (10 mL) at 0 °C, NaH (60% in mineral oil, 110 mg, 4.43 mmol) was added after. The reaction mixture was stirred for 1 h at rt and then diluted with chilled water (30 mL), and CH_2Cl_2 (30 mL). The organic layer was washed with water (2 x 20 mL), brine (20 mL) and then dried ($NaSO_4$), filtered, concentrated and the resulting oil was purified by chromatography (4:1 hexanes–EtOAc) to yield **S9** (0.82 g, 89%) as a colorless oil: R_f 0.49 (4:1 hexane–EtOAc); $[\alpha]_D$ –36.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.46–7.44 (m, 2H, Ar), 7.31–7.25 (m, 2H, Ar), 7.10–7.05 (m, 2H, Ar), 6.90–6.86 (m, 2H, Ar), 4.68, 4.64 (ABq, 2H, J = 12.6 Hz, ArCH_2), 4.41 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 3.8 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3) , 3.58 (s, 3H, OCH_3), 3.49–3.39 (m, 3H, H-2, H-3, H-5), 3.27–3.26 (m, 1H, H-4), 2.39 (s, 3H, ArCH_3) 1.27 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 137.4 (Ar), 132.2 (Ar), 130.7 (Ar x 2), 130.3 (Ar), 129. (Ar), 129.4 (Ar x 2), 129.3 (Ar x 2), 113.8 (Ar x 2), 88.1, 83.6, 79.7, 79.3, 74.5, 72.4, 61.8 (O*C*H$_3$), 61.2 (O*C*H$_3$), 55.3 (O*C*H$_3$), 21.1 (Ar*C*H$_3$), 16.9. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{23}H_{30}NaO_5S$: 441.1712. Found 441.1701.

***p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (S10)**

To a solution of 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose (5 g, 15.05 mmol) and *p*-methoxyphenol (2.4 g, 18.05 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added $BF_3.OEt_2$ (2.3 mL, 18.05 mmol) dropwise over 10 min. The reaction mixture was stirred for 6 h at 0 °C, diluted with CH_2Cl_2 (100 mL) and washed with satd aq $NaHCO_3$ soln (100 mL) and brine (100 mL). The organic layer was separated, dried with Na_2SO_4, filtered and the resulting oil was purified by chromatography (3:1 hexane–EtOAc) to afford **S10** (5.24 g, 88%) as a colorless oil: R_f 0.30 (3:1 hexane–EtOAc); $[\alpha]_D$ +112.4 (*c*, 0.3 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.00 (d, 2H, J = 9.1 Hz, Ar-2,6), 6.83 (d, 2H, J = 9.1 Hz, Ar-3,5), 5.52–5.49 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.0 Hz, H-3), 5.43–5.42 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 5.34 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.15 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 4.07–4.00 (dq, 1H, $J_{4,5}$ = 10 Hz, $J_{5,6}$ = 6.0 Hz, H-5), 3.77 (s, 3H, ArOCH_3), 2.18 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 1.22 (d, 3H, $J_{6,5}$ = 6.0 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.1 (*C*=O), 170.0 (*C*=O), 169.98 (*C*=O), 117.6 (Ar x 2), 115.8 (Ar), 114.6 (Ar), 114.5 (Ar x 2), 96.4, 70.9, 69.7, 68.9, 66.9, 55.5, 20.7, 20.6(3), 20.5(8), 17.3. HRMS (ESI) calcd $(M + Na)^+$ $C_{19}H_{24}O_9Na$: 419.1318. Found: 419.1317.

***p*-Methoxyphenyl α-L-rhamnopyranoside (S11)**

To a solution of **S10** (5 g, 12.6 mmol) in 1:1 CH_2Cl_2–CH_3OH (100 mL) and 1M $NaOCH_3$ in CH_3OH (1 mL) was added. After stirring for 2 h at rt, the reaction mixture was neutralized with Amberlite IR-120 H^+ resin, filtered, and concentrated. The resulting oil was purified by chromatography (10:1 CH_2Cl_2–CH_3OH) to afford **S11** (3.27 g, 96%) as a white amorphous solid: R_f 0.32 (10:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +67.5 (*c*, 0.1 CH_3OH); ^{1}H NMR (400 MHz, CD_3OD, δ_H) 6.99–6.95 (m, 2H, Ar-2,6), 6.85–6.82 (m, 2H, Ar-3,5), 5.26 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 3.98–3.97 (m, 1H, H-3), 3.83 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.6 Hz, H-2), 3.74 (s, 3H, ArOCH_3), 3.48–3.40 (m, 1H, H-5), 3.29–3.28 (m, 1H, H-4), 1.23 (d, 3H, $J_{6,5}$ = 6.0 Hz, H-6); ^{13}C NMR (125 MHz,

$CDCl_3$, δ_C) 156.3 (Ar), 151.7 (Ar), 118.7 (Ar x 2), 115.5 (Ar x 2), 100.6, 73.8, 72.1, 72.0, 70.3, 55.9, 17.8. HRMS (ESI) calcd $(M + Na)^+$ $C_{13}H_{18}O_6Na$: 293.1001. Found: 293.1001.

_p_-Methoxyphenyl 2,3-_O_-isopropylidene-α-L-rhamnopyranoside (S12)

To a solution of **S11** (3 g, 11.11 mmol) and 2,2-dimethoxypropane (2.72 mL, 22.22 mmol) in acetone (40 mL) was added *p*-TSA (0.07 g, 0.52 mmol). The reaction mixture was stirred for 40 min at rt, diluted with CH_2Cl_2 (80 mL) and washed with satd aq $NaHCO_3$ soln (60 mL) and brine (60 mL). The organic layer was dried with Na_2SO_4, filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to afford **S12** (3.13 g, 91%) as a white amorphous solid: R_f 0.58 (2:1 hexane–EtOAc); $[\alpha]_D$ +127.0 (*c*, 0.3 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 6.98 (d, 2H, J = 9.1 Hz, Ar-2,6), 6.84 (d, 2H, J = 9.1 Hz, Ar-3,5), 5.26 (br s, 1H, H-1), 4.27 (d, 1H, $J_{2,3}$ = 5.9 Hz, H-2), 4.02–3.99 (dd, 1H, $J_{2,3}$ = 5.9 Hz, $J_{3,4}$ = 7.2 Hz, H-3), 3.68 (s, 3H, ArOCH_3), 3.62–3.53 (dd, 1H, $J_{4,5}$ = 9.1 Hz, $J_{5.6}$ = 6.0 Hz, H-5), 3.15–3.09 (dt, 1H, $J_{3,4}$ = 7.2 Hz, $J_{4,5}$ = 9.1 Hz, H-4), 1.41 (s, 3H, (CH_3)$_2$C), 1.29 (s, 3H, (CH_3)$_2$C), 1.04 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.3 (Ar), 149.3 (Ar), 118.1 (Ar x 2), 114.3 (Ar x 2), 108.2, 95.7, 77.8, 75.0, 73.0, 66.4, 55.1, 27.7, 26.1, 17.1. HRMS (ESI) calcd $(M + Na)^+$ $C_{16}H_{22}O_6Na$: 333.1314. Found: 333.1313.

_p_-Methoxyphenyl 4-_O_-benzyl-2,3-_O_-isopropylidene-α-L-rhamnopyranoside (S13)

To a solution of **S12** (2 g, 6.45 mmol) and BnBr (0.92 mL, 7.73 mmol) in DMF (15 mL) at 0 °C was added NaH (60% in mineral oil, 0.25 g, 10.3 mmol) portion-wise over 10 min. The reaction mixture was stirred for 4 h at rt before water (30 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (100 mL), and washed with water (2 × 100 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting crude product was purified by chromatography (5:1 hexane–EtOAc) to give **S13** (2.45 g, 95%) as a colorless oil: R_f 0.50 (3:1 hexane–EtOAc); $[\alpha]_D$ –43.6 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40–

7.27 (m, 5H, Ar), 7.02–6.97 (m, 2H, Ar-2,6), 6.86–6.82 (m, 2H, Ar-3,5), 5.60 (d, 1H, $J_{1,2}$ = 0.6 Hz, H-1), 4.94, 4.66 (ABq, 2H, J = 12.0 Hz, ArCH_2), 4.45–4.42 (m, 1H, H-3), 4.37–4.36 (dd, 1H, $J_{1,2}$ = 0.6 Hz, $J_{2,3}$ = 5.8 Hz, H-2), 3.90–3.83 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.0 Hz, H-5), 3.78 (s, 3H, ArOCH_3), 3.31–3.27 (dd, 1H, $J_{3,4}$ = 7.0 Hz, $J_{4,5}$ = 9.4 Hz H-4), 1.55 (s, 3H, (CH_3)$_2$C), 1.43 (s, 3H, (CH_3)$_2$C), 1.25 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.8 (Ar), 150.7 (Ar), 138.4 (Ar), 128.9 (Ar), 128.7 (Ar), 128.3 (Ar), 128.2 (Ar x 2), 127.9 (Ar x 2), 127.6 (Ar x 2), 109.4, 96.1, 81.0, 78.5, 76.0, 72.9, 65.3, 55.5, 27.9, 26.3, 17.7. HRMS (ESI) calcd (M + Na)$^+$ $C_{23}H_{28}O_6Na$: 423.1784. Found: 423.1784.

_p_-Methoxyphenyl 4-_O_-benzyl-α-L-rhamnopyranoside (S14)

To a solution of **S13** (2 g, 5 mmol) in CH_3OH (40 mL) was added _p_-TSA (76 mg, 0.49 mmol). The reaction mixture was stirred for 3 h at rt before it was neutralized with Et_3N (1 mL) and concentrated. The crude product was purified by chromatography (2:1 EtOAc–hexane) to afford **S14** (1.26 g, 82%) as an amorphous solid: R_f 0.55 (2:1 EtOAc–hexane); $[\alpha]_D$ –50.4 (_c_ 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.38–7.27 (m, 5H, Ar), 6.99–6.97 (m, 2H, Ar-2,6), 6.85–6.82 (m, 2H, Ar-3,5), 5.40 (s, 1H, H-1), 4.79, 4.74 (ABq, 2H, J = 12.0 Hz, ArCH_2), 4.14–4.10 (m, 2H, H-2, H-3), 3.90–3.86 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-5), 3.78 (s, 3H, ArOCH_3), 3.43 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.50 (br s, 1H, OH-2), 2.38 (br s, 1H, OH-3), 1.33 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 154.8 (Ar), 150.1 (Ar), 138.1 (Ar), 128.6 (Ar x 2), 128.0 (Ar), 127.8 (Ar x 2), 117.5 (Ar x 2), 114.5 (Ar x 2), 98.0, 81.5, 71.2, 71.0, 67.8, 55.6, 18.0. HRMS (ESI) calcd (M + Na)$^+$ $C_{20}H_{24}O_6Na$: 383.1471. Found: 383.1470.

_p_-Methoxyphenyl 2,3-_O_-isopropylidene-4-_O_-methyl-α-L-rhamnopyranoside (S15)

To a solution of compound **S12** (2 g, 6.45 mmol) and CH_3I (0.49 mL, 7.73 mmol) in DMF (15 mL) was added NaH (60% in mineral oil, 0.25 g, 10.3 mmol) at 0 °C. The reaction mixture was then stirred for 4 h at rt before chilled water (30 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (100 mL) and

washed with water (2 × 100 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (5:1 hexane–EtOAc) to give **S15** (2.01 g, 96%) as a colorless oil: R_f 0.56 (5:1 hexane–EtOAc); $[\alpha]_D$ –77.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.02–6.98 (m, 2H, Ar-2,6), 6.87–6.82 (m, 2H, Ar-3,5), 5.60 (br s, 1H, H-1), 4.35–4.29 (m, 2H, H-2, H-3), 3.81–3.74 (m, 1H, H-5), 3.79 (s, 3H, OC*H*$_3$), 3.57 (s, 3H, OC*H*$_3$), 3.07 (dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 1.60 (s, 3H, (C*H*$_3$)$_2$C), 1.42 (s, 3H, (C*H*$_3$)$_2$C), 1.25 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 155.2 (Ar), 150.5 (Ar), 118.0 (Ar x 2), 114.9 (Ar x 2), 109.6, 96.5, 83.8, 78.5, 76.3, 65.7, 59.7 (O*C*H$_3$), 55.9 (O*C*H$_3$), 28.3, 26.6, 18.0. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{17}H_{24}NaO_6$: 347.1465. Found 347.1468.

_p_-Methoxyphenyl 3-_O_-_p_-methoxybenzyl-4-_O_-methyl-α-L-rhamnopyranoside (S16)

To a solution of **S15** (2.4 g, 7.40 mmol) in 1:1 CH_3OH–CH_2Cl_2 (30 mL), *p*-TSA (100 mg) was added and the reaction mixture was stirred for 1 h at rt. The solution was then neutralized with Et_3N (2 mL) and concentrated. The resulting diol (2 g, 7.01 mmol) was dissolved in toluene (60 mL) and *n*-Bu_2SnO (1.75 g, 7.03 mmol) was added. The reaction mixture was stirred for 1 h at 120 °C, then cooled to 62 ºC before PMBCl (1.20 g, 7.73 mmol) and *n*-Bu_4NI (3.04 g, 8.28 mmol) were added. The reaction mixture was then stirred for additional 6 h at 62 ºC and then concentrated. The resulting crude product was purified by chromatography (1:1 hexane–EtOAc) to give **S16** (2.33 g, 78%) as a colorless oil: R_f 0.46 (1:1 hexane–EtOAc); $[\alpha]_D$ –97.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.28 (m, 2H, Ar), 7.01–7.97 (m, 2H, Ar), 6.95–6.90 (m, 2H, Ar), 6.86–6.82 (m, 2H, Ar), 5.42 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.73, 4.69 (ABq, 2H, *J* = 11.1 Hz, ArC*H*$_2$), 4.16 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 3.91 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 3.84 (s, 3H, OC*H*$_3$), 3.79 (s, 3H, OC*H*$_3$), 3.78–3.74 (m, 1H, H-5), 3.60 (s, 3H, OC*H*$_3$), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, H-4), 2.60 (br s, 1H, OH-2), 1.28 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.7 (Ar), 155.1 (Ar), 150.5 (Ar), 130.4 (Ar), 129.7 (Ar x 2), 117.9 (Ar x 2), 114.9 (Ar x

2), 114.2 (Ar x 2), 98.2, 82.1, 79.5, 72.3, 68.9, 68.2, 61.3 (OC*H*$_3$), 55.6 (OC*H*$_3$), 55.5 (OC*H*$_3$), 18.0. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{22}H_{28}NaO_7$: 427.1727. Found 427.1726.

***p*-Tolyl 1-thio-α-L-rhamnopyranoside (S17)**

To a solution of 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose (5 g, 15.05 mmol) and thiocresol (2.24 g, 18.05 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added BF_3•OEt_2 (2.3 mL, 18.05 mmol) dropwise over 10 min. The reaction mixture was stirred for 7 h at 0 °C, diluted with CH_2Cl_2 (50 mL) and washed with satd aq $NaHCO_3$ soln (100 mL) and brine (100 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated. The resulting residue was dissolved in 1:1 CH_2Cl_2–CH_3OH (100 mL) and 1M $NaOCH_3$ in CH_3OH (5 mL) was added. After stirring for 2 h at rt, the reaction mixture was neutralized with Amberlite IR-120 H^+ resin, filtered, and concentrated. The resulting oil was purified by chromatography (10:1 CH_2Cl_2–CH_3OH) to afford **S17** (3.2 g, 78%) as a white amorphous solid: R_f 0.45 (10:1 CH_2Cl_2–CH_3OH); $[\alpha]_D$ +41.3 (*c*, 0.2 CH_3OH); ^{1}H NMR (400 MHz, CD_3OD, δ_H) 7.35–7.31 (m, 2H, Ar-2,6), 7.13–7.09 (m, 2H, Ar-3,5), 5.28 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 4.05–4.01 (m, 2H, H-2, H-5), 3.63 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.43 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 2.30 (s, 3H, ArC*H*$_3$), 1.25 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 138.5 (Ar), 133.1 (Ar x 2), 132.1 (Ar), 130.6 (Ar x 2), 90.4, 74.0, 73.6, 72.8, 70.7, 20.9, 17.7. HRMS (ESI) calcd $(M + Na)^+$ $C_{13}H_{18}O_4SNa$: 293.0818. Found: 293.0818.

***p*-Tolyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S18)**

To a solution of **S17** (2.5 g, 9.25 mmol) and 2,2-dimethoxypropane (2.09 mL, 17.05 mmol) in acetone (30 mL) was added *p*-TSA (0.13 g, 0.9 mmol). The reaction mixture was stirred for 30 min at rt, diluted with CH_2Cl_2 (100 mL) and washed with satd aq $NaHCO_3$ soln (60 mL) and brine (60 mL). The organic layer was separated, dried with Na_2SO_4, filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to afford **S18** (2.75 g, 96%) as a white amorphous solid: R_f 0.41 (2:1

hexane–EtOAc); $[\alpha]_D$ +74 (*c*, 1.8 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.38–7.35 (m, 2H, Ar-2,6), 7.14–7.12 (d, 2H, *J* = 7.9 Hz, Ar-3,5), 5.67 (d, 1H, $J_{1,2}$ = 0.4 Hz, H-1), 4.35–4.34 (dd, 1H, $J_{1,2}$ = 0.4 Hz, $J_{2,3}$ = 5.6 Hz, H-2), 4.12–4.06 (m, 2H, H-3, H-4), 3.45 (dq, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 2.34 (s, 3H, Ar*CH*$_3$), 1.53 (s, 3H, (C*H*$_3$)$_2$C), 1.37 (s, 3H, (C*H*$_3$)$_2$C), 1.25 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 137.8 (Ar), 132.4 (Ar x 2), 129.7 (Ar x 2), 129.4 (Ar), 109.6, 84.0, 78.3, 76.4, 75.1, 66.8, 28.1, 26.3, 21.0, 17.0. HRMS (ESI) calcd $(M + Na)^+$ $C_{16}H_{22}O_4SNa$: 333.1137. Found: 333.1136.

***p*-Tolyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (S19)**

To a solution of **S18** (2 g, 6.45 mmol) and BnBr (0.92 mL, 7.73 mmol) in DMF (15 mL), NaH (60% in mineral oil, 0.25 g, 10.3 mmol) was added portion-wise at 0 °C over 2 min. The reaction mixture was stirred for 1 h at rt before water (30 mL) was added. The solution was concentrated, diluted with CH_2Cl_2 (60 mL) and washed with water (2 × 50 mL). The organic layer was separated, dried (Na_2SO_4), filtered, concentrated and the resulting residue was carried to the next step without further purification. To a solution of the residue in 3:1 CH_3OH–CH_2Cl_2 (20 mL) was added *p*-TSA (40 mg, 20% w/w) and the reaction mixture was stirred for an additional 3 h. The reaction mixture was then neutralized with Et_3N (1 mL). The solution was concentrated, and the resulting residue was purified by chromatography (2:1 EtOAc–hexane) to give **S19** (1.88 g, 81%) as an amorphous solid: R_f 0.36 (2:1 EtOAc–hexane); $[\alpha]_D$ –152.7 (*c*, 1.3 CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.41–7.30 (m, 7H, Ar), 7.12 (d, 2H, *J* = 7.9 Hz, Ar), 5.40 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 4.78, 4.75 (ABq, 2H, *J* = 11.0 Hz, ArC*H*$_2$), 4.25 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 4.18 (ddd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.4 Hz, $J_{2,OH\text{-}2}$ = 3.9 Hz, H-2), 3.96 (ddd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.4 Hz, $J_{3,OH\text{-}3}$ = 5.3 Hz, H-3), 3.44 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.87 (d, 1H, $J_{2,OH\text{-}2}$ = 3.9 Hz, OH-2), 2.63 (d, 1H, $J_{3,OH\text{-}3}$ = 5.3 Hz, OH-3), 2.33 (s, 3H, ArC*H*$_3$), 1.36 (d, 1H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.1 (Ar), 137.6 (Ar), 132.0 (Ar x 2), 130.1 (Ar), 129.8 (Ar), 128.6 (Ar x 2), 128.0 (Ar x 2), 127.9 (Ar x 2), 87.7,

81.8, 75.0, 72.5, 71.8, 68.5, 21.0, 17.8. HRMS (ESI) calcd $(M + Na)^+$ $C_{20}H_{24}O_4SNa$: 383.1288. Found: 383.1291.

_p_-Tolyl 4-_O_-benzyl-3-_O_-_p_-methoxybenzyl-1-thio-α-L-rhamnopyranoside (S20)

Diol **S19** (1 g, 2.77 mmol) was dissolved in toluene (60 mL) and *n*-Bu_2SnO (0.7 g, 2.76 mmol) was added. The reaction mixture was stirred at 120 °C for 1 h and then it was cooled to 62 ºC before PMBCl (0.49 g, 3.05 mmol) and *n*-Bu_4NI (2.40 g, 6.52 mmol) were added. The reaction mixture was stirred at 62 ºC for additional 6 h and then concentrated. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give **S20** (1.14 g, 86%) as an amorphous solid: R_f 0.42 (2:1 hexane–EtOAc); $[\alpha]_D$ –173.1 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.28 (m, 9H, Ar), 7.12–7.01 (m, 2H, Ar-2,6), 6.90–6.87 (m, 2H, Ar-3,5), 5.45 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.89, 4.64 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.65, 4.63 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.23–4.17 (m, 2H, H-2, H-5), 3.85 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.82 (s, 3H, OCH_3), 3.50 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 2.67 (br s, 1H, OH-2), 2.33 (s, 3H, ArCH_3), 1.30 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.5 (Ar), 138.4 (Ar), 137.6 (Ar), 132.1 (Ar x 2), 130.3 (Ar), 129.8 (Ar x 2), 129.8 (Ar), 129.7 (Ar x 2), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.8 (Ar), 114.0 (Ar x 2), 87.3, 80.1, 79.8, 75.4, 71.9, 70.1, 68.7, 55.3 (O*C*H_3), 21.1, 17.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{28}H_{32}NaO_5S$: 503.1863. Found 503.1865.

_p_-Tolyl 2,3,4-tri-_O_-acetyl-1-thio-β-L-fucopyranoside (S21)

To a solution of L-fucose (5 g, 30.48 mmol) in pyridine (25 mL) at 0 °C was added Ac_2O (20 mL). The reaction mixture was stirred for 7 h at rt before water (100 mL) was added. The solution was diluted with CH_2Cl_2 (150 mL) and washed with 1M HCl soln (100 mL x 2), satd aq $NaHCO_3$ soln (100 mL), water (100 mL x 2), and brine (100 mL). The organic layer was dried with Na_2SO_4, filtered and the resulting oil was purified by chromatography (3:1 hexane–EtOAc) to afford **S21** (10.98 g, 91%) as colorless oil: R_f 0.55 (3:1

hexane–EtOAc); $[\alpha]_D$ –113.7 (*c* 0.6, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40 (d, 2H, *J* = 8.2 Hz, Ar-2,6), 7.11 (d, 2H, *J* = 8.2 Hz, Ar-3,5), 5.23 (dd, 1H, $J_{3,4}$ = 3.1 Hz, $J_{4,5}$ = 2.8 Hz, H-4), 5.19 (app t, 1H, $J_{1,2}$ = $J_{2,3}$ = 9.9 Hz, H-2), 5.02 (dd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.1 Hz, H-3), 4.63 (d, 1H, $J_{1,2}$ = 9.9 Hz, H-1), 3.79 (dq, 1H, $J_{4,5}$ = 2.8 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 2.33 (s, 3H, ArC*H*$_3$), 2.13 (s, 3H, C*H*$_3$CO), 2.08 (s, 3H, C*H*$_3$CO), 1.96 (s, 3H, C*H*$_3$CO), 1.22 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.6 (*C*=O), 170.1 (*C*=O), 169.5 (*C*=O), 138.2 (Ar), 132.9 (Ar x 2), 129.6 (Ar x 2), 129.1 (Ar), 86.9, 73.1, 72.5, 70.4, 67.4, 21.2, 20.9, 20.7, 20.6, 16.5. HRMS (ESI) calcd $(M + Na)^+$ $C_{19}H_{24}O_7SNa$: 419.1141. Found: 419.1139.

***p*-Tolyl 3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (S22)**

To a solution of **S21** (5 g, 12.62 mmol) in 1:1 CH_2Cl_2–CH_3OH (50 mL), 1M $NaOCH_3$ in CH_3OH (5 mL) was added. After stirring for 2 h at rt, the reaction mixture was neutralized with Amberlite IR-120 H^+ resin and filtered. The filtrate was concentrated, and the resulting oil and was dissolved in acetone (50 mL) to which 2,2-dimethoxypropane (4.52 mL, 36.92 mmol) and *p*-TSA (200 mg) were added. The reaction mixture was stirred for 40 min at rt, neutralized with Et_3N (3 mL), diluted with CH_2Cl_2 (100 mL) and washed with satd. aq. $NaHCO_3$ soln. (100 mL) and brine (100 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to afford **S22** (3.5 g, 90%) as an amorphous solid: R_f 0.32 (1:1 hexane–EtOAc); $[\alpha]_D$ –81.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.46–7.44 (m, 2H, Ar-2,6), 7.14–7.12 (m, 2H, Ar-3,5), 4.36 (d, 1H, $J_{1,2}$ = 10.2 Hz, H-1), 4.06–4.02 (m, 2H, H-3, H-4), 3.85 (dq, 1H, $J_{4,5}$ = 2.3 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.51 (ddd, 1H, $J_{1,2}$ = 10.2 Hz, $J_{2,3}$ = 8.4 Hz, $J_{2,OH\text{-}2}$ = 2.2 Hz, H-2), 2.45 (d, 1H, $J_{OH\text{-}2,2}$ = 2.2 Hz, OH-2), 2.32 (s, 3H, ArC*H*$_3$), 1.44 (s, 3H, (C*H*$_3$)$_2$C), 1.42 (s, 3H, (C*H*$_3$)$_2$C), 1.35 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 138.3 (Ar), 133.2 (Ar x 2), 129.7 (Ar x 2), 128.3 (Ar), 109.8, 88.2, 79.1, 76.4, 72.8, 71.3, 28.1, 26.4, 21.1, 17.0. HRMS (ESI) Calcd. for (M + Na) $C_{16}H_{22}O_4NaS$: 333.1131. Found 333.1135.

***p*-Tolyl 2-*O*-methyl-1-thio-β-L-fucopyranoside (S23)**

To a solution of **S4** (1.5 g, 4.62 mmol) in 3:1 CH_3OH–CH_2Cl_2 (20 mL) was added *p*-TSA (300 mg, 20% w/w) and the reaction mixture was stirred for 4 h, and then neutralized with Et_3N (2 mL). The solution was concentrated and the resulting residue was purified by chromatography (1:2 hexane–EtOAc) to give **S23** (1.1 g, 80%) as an amorphous solid: R_f 0.3 (1:2 hexane–EtOAc); $[\alpha]_D$ –25.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.44 (d, 2H, J = 8.1 Hz, Ar-2,6), 7.10 (d, 2H, J = 8.1 Hz, Ar-3,5), 4.43 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 3.74–3.73 (m, 1H, H-4), 3.64 (s, 3H, OC*H*$_3$), 3.61–3.57 (m, 2H, H-3, H-5), 3.22 (app t, 1H, $J_{1,2}$ = $J_{2,3}$ = 9.6 Hz, H-2), 2.78 (br s, 1H, OH), 2.31 (s, 3H, Ar*C*H$_3$), 2.20 (br s, 1H, OH), 1.32 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 137.8 (Ar), 132.5 (Ar x 2), 129.8 (Ar), 129.6 (Ar x 2), 87.5, 80.0, 75.5, 74.4, 71.9, 61.2 (O*C*H$_3$), 21.1, 16.6. (ESI) Calcd. for $(M + Na)^+$ $C_{14}H_{20}O_4SNa$: 307.0980. Found 307.0980.

***p*-Tolyl 3-*O*-*p*-methoxybenzyl-2-*O*-methyl-1-thio-β-L-fucopyranoside (S24)**

Diol **S23** (1 g, 3.50 mmol) was dissolved in toluene (30 mL) and *n*-Bu_2SnO (0.87 g, 3.51 mmol) was added. The reaction mixture was stirred for 1 h at 120 ºC and then it was cooled to 62 ºC before PMBCl (0.60 g, 3.86 mmol) and *n*-Bu_4NI (1.43 g, 3.86 mmol) were added. The reaction mixture was stirred at 62 ºC for additional 5 h and then concentrated. The resulting was purified by chromatography (2:1 hexane–EtOAc) to give **S24** (1.17 g, 83%) as an amorphous solid: R_f 0.35 (2:1 hexane–EtOAc); $[\alpha]_D$ +1.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.48–7.45 (m, 2H, Ar), 7.30–7.27 (m, 2H, Ar), 7.11–7.09 (m, 2H, Ar), 6.90–6.86 (m, 2H, Ar), 4.64 (br s, 2H, ArC*H*$_2$), 4.41 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 3.80 (s, 3H, OC*H*$_3$), 3.75–3.74 (m, 1H, H-4), 3.60 (s, 3H, OC*H*$_3$), 3.51 (dq, 1H, $J_{4,5}$ = 2.7 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.44 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 2.7 Hz, H-3), 3.32 (dd, 1H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 2.32 (s, 3H, ArC*H*$_3$), 2.23 (s, 1H, OH-4), 1.34 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.4 (Ar), 137.6 (Ar), 132.7 (Ar x 2), 129.9 (Ar), 129.8 (Ar), 129.4(7) (Ar x 2), 129.4(5) (Ar x 2), 113.9 (Ar x 2), 87.5, 82.5, 78.4, 74.1, 71.8, 69.5, 61.2

(O*C*H$_3$), 55.3 (O*C*H$_3$), 21.1, 16.7. HRMS (ESI) Calcd. for (M + Na)$^+$ $C_{22}H_{28}NaO_5S$: 427.1555. Found 427.1549.

***p*-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (S25)**

To a solution of donor **S3** (0.95 g, 1.82 mmol) and acceptor **S2** (0.82 g, 2.2 mmol) in CH_2Cl_2 (30 mL) was added crushed 4 Å molecular sieves (300 mg). After the mixture was stirred at rt for 30 min, it was cooled to –20 ºC, and then NIS (416 mg, 1.85 mmol) and AgOTf (123 mg, 0.48 mmol) were added. The reaction mixture was stirred for an additional 30 min at –20 ºC before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was purified by chromatography (3:1 hexane–EtOAc) to give **S25** (1.13 g, 81%) as an amorphous solid: R_f 0.50 (2:1 hexane–EtOAc); $[\alpha]_D$ –25.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.36–7.27 (m, 10 H, Ar), 7.21–7.19 (m, 2H, Ar), 6.97–6.96 (m, 2H, Ar), 6.83–6.78 (m, 4H, Ar), 5.52 (dd, 1H, $J_{1',2'}$ = 1.8 Hz, $J_{2',3'}$ = 3.3 Hz, H-2′), 5.40 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.09 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 4.92, 4.40 (ABq, 2H, *J* = 11.0 Hz, ArC*H*$_2$), 4.80, 4.61 (ABq, 2H, *J* = 11.0 Hz, ArC*H*$_2$), 4.59 (ABq, 2H, *J* = 10.5 Hz, ArC*H*$_2$), 4.22 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.00–3.95 (m, 2H, H-3′, H-5′), 3.81–3.78 (m, 1H, H-5), 3.76 (s, 3H, OC*H*$_3$), 3.74 (s, 3H, OC*H*$_3$), 3.71 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 3.52 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.49 (s, 3H, OC*H*$_3$), 3.44 (app t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.4 Hz, H-4′), 2.11 (s, 3H, C*H*$_3$CO), 1.35 (d, 3H, $J_{5',6'}$ = 6.0 Hz, H-6′), 1.24 (d, 1H, $J_{5,6}$ = 6.0 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.1 (*C*=O), 159.3 (Ar), 154.9 (Ar x 2), 150.4 (Ar x 2), 138.6 (Ar), 138.1 (Ar), 130.1 (Ar), 129.7 (Ar x 2), 128.5 (Ar x 2), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.8 (Ar), 127.7 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 113.8 (Ar x 2), 99.8, 95.6, 80.3, 80.1, 80.0, 78.8, 77.6, 75.4, 75.4, 71.4, 69.2, 68.7, 68.5, 58.9 (O*C*H$_3$), 55.7 (O*C*H$_3$), 55.2 (O*C*H$_3$), 21.1, 18.2, 18.0. HRMS (ESI) Calcd. for (M + Na)$^+$ $C_{44}H_{52}NaO_{12}$: 795.3351. Found 795.3343.

***p*-Methoxyphenyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (S26)**

To a solution of **S25** (0.5 g, 0.65 mmol) in 1:1 CH_3OH–CH_2Cl_2 (15 mL), 1M $NaOCH_3$ (0.5 mL) was added and the reaction mixture was stirred for 1 h at rt. The solution was then neutralized with Amberlite IR-120 H^+ resin, filtered and concentrated. The resulting residue was dissolved in DMF (5 mL) and CH_3I (0.1 mL, 0.9 mmol) was added and the solution was cooled to 0 °C. To this solution, NaH (60% in mineral oil, 30 mg, 1.18 mmol) was added and then the reaction mixture was stirred for 1 h at rt. Chilled water (20 mL) was then added and the mixture was diluted with CH_2Cl_2 (40 mL), washed with water (2 x 30 mL), 1M HCl soln (2 x 30 mL) and brine (30 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (4:1 hexane–EtOAc) to give a syrup. The syrup was dissolved in CH_2Cl_2 (20 mL) and TFA (1 mL, 5% v/v) was added dropwise over 2 min after the solution was cooled to 0 ºC. The reaction mixture was stirred for additional 30 min at 0 ºC, before the addition of Et_3N (3 mL) and concentration. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give **S26** (0.35 g, 87%) as a colorless oil: R_f 0.35 (3:1 hexane–EtOAc); $[\alpha]_D$ –6.9 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.41–7.26 (m, 10H, Ar), 7.03–7.00 (m, 2H, Ar-2,6), 6.86–6.83 (m, 2H, Ar-3,5), 5.43 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.18 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 4.93, 4.82 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.71, 4.71 (ABq, 2H, J = 11.2 Hz, ArCH_2), 4.26 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 4.03 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 3.91–3.84 (m, 2H, H-5, H-5′), 3.78 (s, 3H, OCH_3), 3.73 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 3.58 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.54 (s, 3H, OCH_3), 3.49 (dd, 1H, $J_{1',2'}$ = 1.5 Hz, $J_{2',3'}$ = 3.7 Hz, H-2′), 3.31 (app t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.5 Hz, H-4′), 3.23 (s, 3H, OCH_3), 1.37 (d, 3H, $J_{5',6'}$ = 6.4 Hz, H-6′), 1.29 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.4 (Ar), 138.6 (Ar), 138.4 (Ar), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.8 (Ar x 2), 127.7 (Ar x 2), 127.1 (Ar x 2), 117.6 (Ar x 2), 114.7 (Ar x 2), 98.7, 95.8, 82.1, 81.0, 80.6, 80.4, 78.7, 75.1, 71.6, 68.8, 67.9, 59.1 (OCH_3), 58.6 (OCH_3), 55.7 (OCH_3), 18.2, 18.0. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{35}H_{44}NaO_{10}$: 647.2827. Found 647.2823.

***p*-Methoxyphenyl 3,4-*O*-isopropylidene-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside (S27)**

Two solutions were prepared. Solution A was prepared by dissolving donor **S4** (50 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) containing crushed 4 Å molecular sieves (50 mg). Solution B was prepared by dissolving acceptor **S26** (80 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) and crushed 4 Å molecular sieves (100 mg) was added. Both solutions A and B were stirred for 30 min at rt and then solution B was cooled to –40 ºC before NIS (36 mg, 0.16 mmol) and AgOTf (10.3 mg, 0.04 mmol) were added. Solution A was then added dropwise over 5 min to solution B while stirring. The reaction mixture was stirred for additional 30 min at –40 ºC before Et_3N (1 mL) was added. The solution was filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give **S27** (86 mg, 80%) as a colorless oil: R_f 0.40 (2:1 hexane–EtOAc); $[\alpha]_D$ +0.8 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.55 (m, 10H, Ar), 7.00–6.89 (m, 2H, Ar-2,6), 6.83–6.81 (m, 2H, Ar-3,5), 5.42 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.17 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.2 Hz, H-1″), 5.15, 4.53 (ABq, 2H, J = 10.75 Hz, ArCH_2), 4.84, 4.64 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.39 (dq, 1H, $J_{4'',5''}$ = 2.7 Hz, $J_{5'',6''}$ = 6.3 Hz, H-5″), 4.32 (dd, 1H, $J_{2'',3''}$ = 8.9 Hz, $J_{3'',4''}$ = 2.8 Hz, H-3″), 4.21 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 4.06 (dd, 1H, $J_{3'',4''}$ = 2.8 Hz, $J_{4'',5''}$ = 2.7 Hz, H-4″), 4.02 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, $J_{3',4'}$ = 9.6 Hz, H-3′), 3.95 (dq, 1H, $J_{4',5'}$ = 9.6 Hz, $J_{5',6'}$ = 6.2 Hz, H-5′), 3.82 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.77 (s, 3H, OCH_3), 3.75–3.74 (m, 1H, H-2), 3.72–3.71 (m, 1H, H-2′), 3.56–3.52 (m, 1H, H-4), 3.51 (s, 3H, OCH_3), 3.56–3.45 (m, 1H, H-4′), 3.37 (s, 3H, OCH_3), 3.33 (dd, 1H, $J_{1'',2''}$ = 3.2 Hz, $J_{2'',3''}$ = 8.9 Hz, H-2″), 3.24 (s, 3H, OCH_3), 1.54 (s, 3H, (CH_3)$_2$C), 1.35–1.34 (m, 6H, (CH_3)$_2$C, H-6′), 1.29 (d, 3H, $J_{5'',6''}$ = 6.3 Hz, H-6″), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.5 (Ar), 139.0 (Ar), 138.3 (Ar), 128.4 (Ar x 2), 128.2 (Ar x 2), 127.9 (Ar x 2), 127.7 (Ar), 127.4 (Ar), 127.3 (Ar x 2), 117.5 (Ar x 2), 114.6 (Ar x 2), 108.8, 99.3, 98.7, 95.4, 81.8, 80.5, 80.3, 80.1, 79.9,

79.5, 79.4, 76.1, 75.6 75.2, 75.2, 68.7, 68.5, 63.6, 58.8 (O*C*H$_3$), 58.4 (O*C*H$_3$), 57.6 (O*C*H$_3$), 55.6 (O*C*H$_3$), 28.4, 26.4, 18.2, 18.0 , 16.6. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{45}H_{60}NaO_{14}$: 847.3875. Found 847.3867.

_p_-Methoxyphenyl 2-_O_-acetyl-4-_O_-benzyl-3-_O_-_p_-methoxybenzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (S28)

To a solution of donor **S3** (0.47 g, 0.91 mmol) and acceptor **S2** (0.31 g, 1.01 mmol) in CH_2Cl_2 (30 mL) was added crushed 4 Å molecular sieves (200 mg). After the reaction mixture was stirred at rt for 30 min, it was cooled to –20 ºC, and then NIS (209 mg, 0.93 mmol) and AgOTf (61.6 mg, 0.24 mmol) were added. The reaction mixture was stirred for additional 30 min before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was purified by chromatography (3:1 hexane–EtOAc) to give **S28** (0.53 g, 85%) as an amorphous solid: R_f 0.29 (3:1 hexane–EtOAc); R_f 0.31 (3:1 hexane–EtOAc); $[\alpha]_D$ –6.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.37–7.25 (m, 5H, Ar), 7.27–7.25 (m, 2H, Ar), 7.00–6.96 (m, 2H, Ar), 6.85–6.81 (m, 4H, Ar), 5.46 (dd, 1H, $J_{1',2'}$ = 1.8 Hz, $J_{2',3'}$ = 3.3 Hz, H-2′), 5.37 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.08 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 4.94, 4.50 (ABq, 2H, J = 11.0 Hz, ArC*H*$_2$), 4.65, 4.63 (ABq, 2H, J = 11.2 Hz, Ar-C*H*$_2$), 4.10 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.99–3.93 (m, 2H, H-3′, H-5′), 3.79 (s, 3H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 3.68 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.65 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 3.52 (s, 3H, OC*H*$_3$), 3.49 (s, 3H, OC*H*$_3$), 3.47–3.45 (m, 1H, H-4′), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 2.17 (s, 3H, C*H*$_3$CO), 1.36 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6′), 1.26 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.3 (*C*=O), 159.3 (Ar), 154.9 (Ar), 150.4 (Ar), 138.6 (Ar), 130.1 (Ar), 129.7 (Ar x 2), 128.4 (Ar x 2), 128.0 (Ar x 2), 127.7 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 113.8 (Ar x 2), 99.7, 95.9, 82.4, 80.2, 80.1, 78.3, 77.4, 75.4, 71.5, 69.4, 68.8, 68.4, 61.1 (O*C*H$_3$), 59.1 (O*C*H$_3$), 55.7 (O*C*H$_3$), 55.3 (O*C*H$_3$), 21.1, 18.2, 17.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{38}H_{48}NaO_{12}$: 719.3038. Found 719.3030.

***p*-Methoxyphenyl 3,4-*O*-isopropylidene-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*- methyl-α-L-rhamnopyranoside (S29)**

Two solutions were prepared. Solution A was prepared by dissolving donor **S4** (25 mg, 0.08 mmol) in CH_2Cl_2 (10 mL); containing crushed 4 Å molecular sieves (100 mg). Solution B was prepared by dissolving acceptor **19** (38 mg, 0.07 mmol) in CH_2Cl_2 (10 mL); containing crushed 4 Å molecular sieves (100 mg). Both solutions A and B were stirred for 30 min at rt and then Solution B was cooled to –40 ºC before NIS (18 mg, 0.08 mmol) and AgOTf (5 mg, 0.02 mmol) were added. Solution A was then added to Solution B dropwise over 5 min while stirring. The reaction mixture was stirred for additional 30 min at –40 ºC before it was neutralized by the addition of Et_3N (1 mL). The solution was filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give **S29** (43.5 mg, 83%) as a colorless oil: R_f 0.36 (2:1 hexane–EtOAc); $[\alpha]_D$ +89.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.39–7.55 (m, 5H, Ar), 7.00–6.89 (m, 2H, Ar), 6.83–6.81 (m, 2H, Ar), 5.43–5.42 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.17 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.14 (d, 1H, $J_{1'',2''}$ = 3.5 Hz, H-1″), 5.15, 4.53 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.45 (dq, 1H, $J_{4'',5''}$ = 2.8 Hz, $J_{5'',6''}$ = 6.4 Hz, H-5″), 4.34 (dd, 1H, $J_{2'',3''}$ = 9.8 Hz, $J_{3'',4''}$ = 2.8 Hz, H-3″), 4.47–4.44 (m, 2H, H-3, H-4″), 4.01 (dd, 1H, $J_{2',3'}$ = 3.2 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 3.93 (dq, 1H, $J_{4',5'}$ = 9.4 Hz, $J_{5',6'}$ = 6.4 Hz, H-5′), 3.84–3.79 (m, 1H, H-5), 3.77 (s, 3H, OCH_3), 3.71–3.66 (m, 2H, H-2, H-2′), 3.55 (s, 3H, OCH_3), 3.51–3.47 (m, 7H, H-4′, OCH_3 x 2), 3.38 (s, 3H, OCH_3), 3.35 (dd, 1H, $J_{1'',2''}$ = 3.1 Hz, $J_{2'',3''}$ = 9.8 Hz, H-2″), 3.22 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 1.54 (s, 3H, (CH_3)$_2$C), 1.36–1.34 (m, 9H, (CH_3)$_2$C, H-6′, H-6″), 1.26 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 154.9 (Ar), 150.5 (Ar), 139.0 (Ar), 128.2 (Ar x 2), 127.9 (Ar x 2), 127.4 (Ar), 117.5 (Ar x 2), 114.6 (Ar x 2), 108.8, 99.3, 98.7, 95.6, 82.1, 80.5, 80.3, 80.1, 79.9, 79.5, 79.4, 76.1, 75.6, 75.2, 68.7, 68.5, 63.6, 61.3 (O*C*H$_3$), 58.8 (O*C*H$_3$), 58.4 (O*C*H$_3$), 57.6 (O*C*H$_3$), 55.6 (O*C*H$_3$), 28.4, 26.4, 18.2, 18.0, 16.6. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{39}H_{56}NaO_{14}$: 771.3562. Found 771.3562.

***p*-Methoxyphenyl 3-*O*-*p*-methoxybenzyl-2-*O*-methyl-α-L-fucopyranosyl-(1→3)-4-*O*-benzyl-2′-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranoside (S30)**

To a solution of donor **25** (70 mg, 0.16 mmol) in CH_2Cl_2 (10 mL), crushed 4 Å molecular sieves (100 mg) was added (Solution A). To another solution, containing acceptor **26** (72 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was added crushed 4 Å molecular sieves (100 mg) (Solution B). Both solutions were then stirred for 30 min at rt. After 30 min, Solution A was cooled to –40 ºC. To solution B was added NIS (36 mg, 0.16 mmol) and AgOTf (10 mg, 0.04 mmol) and it was then added dropwise to Solution A over 5 min while stirring. The reaction mixture was stirred for additional 30 min at –40 ºC before Et_3N (1 mL) was added. The solution was filtered, concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in AcOH (4 mL) and $(Ph_3P)_4Pd$ (18 mg, 20% w/w) was added. The reaction mixture was stirred overnight at rt before it was filtered, concentrated and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to give **S30** (76.4 mg, 71%) as colorless oil: R_f 0.52 (1:1 hexane–EtOAc); $[\alpha]_D$ +0.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.26 (m, 7H, Ar), 7.00–6.97 (m, 2H, Ar), 6.86–6.81 (m, 4H, Ar), 5.39 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.19, 4.55 (ABq, 2H, J = 11.0 Hz, ArCH_2), 5.20–5.17 (m, 2H, H-1′, H-1″), 4.72, 4.64 (ABq, 2H, J = 11.0 Hz, ArCH_2), 4.18 (dq, 1H, $J_{4'',5''}$ = 2.7 Hz, $J_{5'',6''}$ = 6.3 Hz, H-5″), 4.20–4.06 (m, 2H, H-3′, H-4″), 3.96–3.90 (m, 2H, H-3, H-5′), 3.86–3.84 (m, 1H, H-4′), 3.77 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.75–3.67 (m, 4H, H-2, H-2′, H-3″, H-5), 3.59 (dd, 1H, $J_{1'',2''}$ = 3.3 Hz, $J_{2'',3''}$ = 9.7 Hz, H-2″), 3.44 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.23 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 1.75 (br s, 1H, OH-3″), 1.33 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.29 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.27 (d, 1H, $J_{5'',6''}$ = 6.3 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.3 (Ar), 154.9 (Ar), 150.5 (Ar), 139.1 (Ar), 130.3 (Ar x 2), 129.3 (Ar x 2), 128.2 (Ar x 2), 127.8 (Ar x 2), 117.5 (Ar x 2), 114.6 (Ar x 2), 113.9 (Ar x 2), 99.8, 98.5, 95.6, 82.0, 80.7, 80.2, 79.9, 79.6, 77.7, 77.1, 75.1, 72.0, 70.1, 68.8, 68.6, 65.7, 61.2, 59.2 (O*C*H$_3$), 59.1 (O*C*H$_3$), 58.9 (O*C*H$_3$), 57.8 (O*C*H$_3$), 55.7 (O*C*H$_3$), 55.2 (O*C*H$_3$), 18.2, 17.9, 16.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{44}H_{60}NaO_{15}$: 851.3824. Found 851.3809.

Methyl 2,3-*O*-isopropylidene-6-*O*-tosyl-α-D-mannopyranoside (S32)

To a solution of methyl α-D-mannopyranoside (**S31**, 2 g, 10.3 mmol) in pyridine (15 mL), DMAP (0.19 g, 0.1% w/w) and TsCl (2.04 g, 10.92 mmol) were added and the reaction mixture was stirred overnight at rt. Water (50 mL) was then added and the mixture was diluted with CH_2Cl_2 (60 mL), washed with water (2 × 60 mL), 1M HCl soln (2 x 60 mL), and finally brine (2 x 60 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in acetone (30 mL) and DMP (2 mL) and *p*-TSA (20 mg) were added. The reaction mixture was stirred for 2 h at rt and then Et_3N (1 mL) was added. The solution was concentrated and the resulting residue was purified by chromatography (4:1 hexane–EtOAc) to give **S32** (3.12 g, 78%) as a colorless oil: R_f 0.49 (3:1 hexane–EtOAc); $[\alpha]_D$ –11.0 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.81–7.97 (m, 2H, Ar), 7.35–7.33 (m, 2H, Ar), 4.83 (br s, 1H, H-1), 4.28 (app d, 2H, $J_{5,6}$ = 4.0 Hz, H-6), 4.10–4.09 (m, 2H, H-2, H-3), 3.74–3.70 (m, H, H-5), 3.62–3.55 (m, 1H, H-4), 3.33 (s, 3H, OCH_3), 2.83 (d, 1H, $J_{4,OH-4}$ = 5.0 Hz, OH-4), 2.44 (s, 3H, ArCH_3), 1.47 (s, 3H, (CH_3)$_2$C), 1.32 (s, 3H, (CH_3)$_2$C); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 144.9 (Ar), 132.9 (Ar), 129.8 (Ar x 2), 128.0 (Ar x 2), 109.8, 98.3, 78.0, 75.4, 69.2, 68.6, 68.3, 55.2 (O*C*H$_3$), 27.8, 26.0, 21.7. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{17}H_{24}NaO_8S$: 411.1084. Found 411.1086.

Methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methyl-α-D-mannopyranoside (S33)

To a solution of **S32** (1.5 g, 3.86 mmol) in DMSO (30 mL) was added $NaBH_4$ (0.18 g, 4.63 mmol) and the reaction mixture was stirred for 8 h at 80 ºC. The solution was cooled to 0 ºC before the addition of water (30 mL). The mixture was diluted with CH_2Cl_2 (50 mL), washed with water (2 x 50 mL), 1M HCl soln (2 x 50 mL) and brine (50 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in DMF (10 mL) and CH_3I (0.30 mL, 4.63 mmol) was added. To this solution, NaH (60% in mineral oil, 0.18 g, 6.2 mmol) was added at 0 ºC and then the reaction mixture was stirred for 1 h at rt. Then, chilled water (20 mL) was added and then mixture was diluted with CH_2Cl_2 (40

mL), washed with water (2 x 30 mL), 1M HCl soln (2 x 30 mL) and brine (30 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated, and the resulting residue was purified by chromatography (5:1 hexane–EtOAc) to give **S33** (0.62 g, 69%) as a colorless oil: R_f 0.65 (5:1 hexane–EtOAc); $[\alpha]_D$ +29.1 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 4.84 (br s, 1H, H-1), 4.14–4.09 (m, 2H, H-2, H-3), 3.57 (dq, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.53 (s, 3H, OC*H*$_3$), 3.36 (s, 3H, OC*H*$_3$), 2.97 (dd, 1H, $J_{3,4}$ = 6.5 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 1.55 (s, 3H, (C*H*$_3$)$_2$C), 1.35 (s, 3H, (C*H*$_3$)$_2$C), 1.28 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 109.3, 98.3, 83.8, 78.5, 76.2, 64.7, 59.6 (O*C*H$_3$), 55.0 (O*C*H$_3$), 28.3, 26.5, 17.9. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{11}H_{20}NaO_5$: 255.1203. Found 255.1206.

Methyl 2-*O*-acetyl-3-*O*-benzyl-6-deoxy-4-*O*-methyl-α-D-mannopyranoside (S34)

To a solution of **S33** (0.5 g, 2.16 mmol) in 3:1 CH_3OH–CH_2Cl_2 (20 mL), *p*-TSA (10 mg) was added. The reaction mixture was stirred for 4 h at rt before the addition of Et_3N (1 mL). The reaction mixture was then concentrated and the resulting residue was dissolved in toluene (30 mL) and *n*-Bu_2SnO (0.53 g, 2.16 mmol) was added. The reaction mixture was heated at 120 ºC for 1 h. Then, it was cooled to 62 ºC, and *n*-Bu_4NI (0.6 g, 2.4 mmol) and BnBr (0.28 mL, 2.4 mmol) were added. The reaction mixture was stirred for additional 7 h at 62 ºC and then cooled and concentrated. The resulting residue was purified by chromatography (3:1 hexane–EtOAc) to give an oil. This oil was dissolved in pyridine (5 mL), before Ac_2O (2 mL) was added. The reaction mixture was stirred for 1 h at rt before the addition of water (20 mL). Dilution of the mixture with CH_2Cl_2 (40 mL) was followed by separation of the organic layer, which was washed with water (2 x 30 mL), 1M HCl soln (2 x 30 mL), brine (30 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (6:1 hexane–EtOAc) to give **S34** (0.53 g, 79%) as a colorless oil: R_f 0.39 (6:1 hexane–EtOAc); $[\alpha]_D$ +22.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.38–7.28 (m, 5H, Ar-H), 5.33 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 4.68, 4.54 (ABq, 2H, *J* = 11.4 Hz, ArC*H*$_2$), 4.61 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 3.80 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.63 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.4 Hz,

H-5), 3.58 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.15 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 2.14 (s, 3H, CH_3CO), 1.34 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.6 (*C*=O), 138.4 (Ar), 128.6 (Ar x 2), 128.1 (Ar x 2), 127.9 (Ar), 98.9, 82.1, 78.0, 71.9, 69.2, 67.8, 61.3 (O*C*H$_3$), 55.1 (O*C*H$_3$), 21.3, 18.1. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{17}H_{24}NaO_6$: 347.1465. Found 347.1469.

Methyl 2,3-*O*-isopropylidene-6-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (S35)

To a solution of methyl α-D-mannopyranoside, (**S31**, 3 g, 15.05 mmol) in pyridine (20 mL) and Et_3N (2.5 mL), TBDPSCl (4.96 g, 18.06 mmol) was added and the reaction mixture was heated at 60 ºC for 3 h. Water (50 mL) was added and then solution was diluted with CH_2Cl_2 (80 mL), washed with water (2 × 60 mL), 1M soln HCl (2 x 60 mL) and brine (2 x 60 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in acetone (30 mL) before DMP (4 mL) and *p*-TSA (100 mg) were added. The reaction mixture was stirred for 3 h at rt before Et_3N (1 mL) was added. The reaction mixture was concentrated and the resulting crude product was purified by chromatography (4:1 hexane–EtOAc) to give **S35** (6.25 g, 88%) as a colorless oil: R_f 0.78 (4:1 hexane–EtOAc); $[\alpha]_D$ –0.13 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.75–7.73 (m, 4H, Ar), 7.48–7.41 (m, 6H, Ar), 4.91 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 4.19–4.13 (m, 2H, H-2, H-3), 3.98–3.90 (m, 2H, H-6 x 2), 3.85–3.81 (m, 1H, H-4), 3.68–3.64 (m, 1H, H-5), 3.37 (s, 3H, OCH_3), 2.82 (s, 1H, OH-4), 1.53 (s, 3H, (CH_3)$_2$C), 1.37 (s, 3H, (CH_3)$_2$C), 1.10 (s, 9H, (CH_3)$_3$C); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 135.7 (Ar x 2), 135.6 (Ar x 2), 133.1 (Ar), 133.0 (Ar), 129.8(3) (Ar), 129.8(1) (Ar), 127.7(8) (Ar x 2), 127.7(4) (Ar x 2), 109.5, 98.3, 78.2, 75.3, 70.6, 69.5, 64.7, 54.9 (O*C*H$_3$), 27.9, 26.1, 26.8, 19.2. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{26}H_{36}NaO_6Si$: 495.2173. Found 495.2171.

Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside (S36)

To a solution of **S35** (3 g, 6.35 mmol) in THF (40 mL), TBAF (7.75 mL of 1M soln in THF, 7.75 mmol) was added and the reaction mixture was stirred for 2 h at rt before water (60 mL) was added. The solution was diluted with CH_2Cl_2 (100 mL) and washed with 1M soln HCl (2 x 80 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in DMF (20 mL) and BnBr (2 mL, 15.5 mmol) was added. To this solution, NaH (60% in mineral oil, 0.6 g, 20.64 mmol) was added portionwise over 2 min at 0 ºC and it was then stirred for additional 2 h at rt before chilled water (30 mL) and CH_2Cl_2 (60 mL) were added. The organic layer was washed with water (2 x 50 mL), satd. aq. $NaHCO_3$ soln (2 x 50 mL), brine (50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by chromatography (4:1 hexane–EtOAc) to give a syrup. To the solution of this syrup in 2:1 CH_3OH–CH_2Cl_2 (30 mL), *p*-TSA (100 mg) was added. The reaction mixture was stirred overnight at rt before Et_3N (1 mL) was added. The solution was then concentrated and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to give **S36** (1.76 g, 74%) as a colorless oil: *Rf* 0.45 (1:1 hexane–EtOAc); $[\alpha]_D$ +39.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.46–7.25 (m, 10H, Ar), 4.75, 4.57 (ABq, 2H, J = 12.1 Hz, ArCH_2), 4.76 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.69, 4.59 (ABq, 2H, J = 12.2 Hz, ArCH_2), 3.95–3.89 (m, 2H, H-2, H-3), 3.83–3.73 (m, 4H, H-4, H-5, H-6 x 2), 3.39 (s, 3H, OCH_3), 2.66 (d, 1H, $J_{2,OH\text{-}2}$ = 5.2 Hz, OH-2), 2.49 (d, 1H, $J_{3,OH\text{-}3}$ = 6.0 Hz, OH-3); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 138.6 (Ar), 138.2 (Ar), 135.8 (Ar), 135.0 (Ar), 129.8 (Ar), 128.8 (Ar), 128.6 (Ar), 18.2(2) (Ar), 128.1(6) (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 100.9, 77.0, 74.9, 73.8, 72.1, 71.2, 70.9, 69.1, 55.2 (OCH_3). HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{21}H_{26}NaO_6$: 397.1622. Found 397.1625.

Methyl 2-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (S37)

To a solution of **S36** (1.6 g, 4.27 mmol) in toluene (40 mL), *n*-Bu_2SnO (1.17 g, 4.70 mmol) was added and the reaction mixture was heated at 120 ºC for 1 h. The solution was then cooled to 62 ºC, *n*-Bu_4NI (1.9 g,

5.19 mmol) and BnBr (0.62 mL, 5.14 mmol) were added and the reaction mixture was stirred overnight at 62 ºC. The reaction mixture was then concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in pyridine (10 mL) and Ac_2O (2 mL) was added. The reaction mixture was stirred for 1 h at rt before the addition of water (30 mL) and CH_2Cl_2 (50 mL). The organic layer was separated, washed with water (2 x 50 mL), 1M HCl soln (2 x 50 mL), brine (50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by chromatography (6:1 hexane–EtOAc) to give **S37** (1.81 g, 84%) as a colorless oil: R_f 0.52 (6:1 hexane–EtOAc); $[\alpha]_D$ +24.3 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.40–7.28 (m, 13H, Ar), 7.21–7.17 (m, 2H, Ar), 5.39 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 4.89, 4.51 (ABq, 2H, J = 10.5 Hz, ArCH_2), 4.76 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 4.74, 4.55 (ABq, 2H, J = 10.5 Hz, ArCH_2), 4.72, 4.57 (ABq, 2H, J = 10.5 Hz, ArCH_2), 3.99 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.90 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 3.88–3.73 (m, 3H, H-5, H-6 x 2), 3.38 (s, 3H, OCH_3), 2.17 (s, 3H, CH_3CO); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.7 (*C*=O), 138.7 (Ar), 138.5 (Ar), 138.2 (Ar), 128.6 (Ar x 2), 128.6 (Ar x 2), 128.3 (Ar x 2), 128.1 (Ar x 2), 128.0(0) (Ar x 2), 127.9(6) (Ar), 127.8(2) (Ar x 2), 127.8(1) (Ar x 2), 99.0, 78.4, 75.4, 74.6, 73.7, 72.0, 71.5, 69.17, 68.9, 55.2 (O*C*H$_3$), 21.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{30}H_{34}NaO_7$: 529.2197. Found 529.2189.

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-4-*O*-methyl-α-D-mannopyranoside (S38)

To a solution of compound **S35** (3.05 g, 6.45 mmol) and CH_3I (0.6 mL, 7.75 mmol) in DMF (20 mL), NaH (60% in mineral oil, 0.25 g, 10.3 mmol) was added at 0 ºC portionwise over 2 min. The reaction mixture was stirred for 1 h at rt before the addition of water (30 mL). The solution was concentrated, diluted with CH_2Cl_2 (60 mL) and washed with water (2 × 50 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated. The resulting residue was dissolved in THF (20 mL), TBAF (7.75 mL of 1M soln in THF, 7.75 mmol) was added and the reaction mixture was stirred for 2 h at rt. Water (50 mL) was added and the solution was diluted with CH_2Cl_2 (60 mL) and washed with 1M soln HCl (2 x 50 mL). The organic layer was

separated, dried (Na_2SO_4), filtered and concentrated. The resulting crude product was purified by chromatography (2:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in DMF (20 mL) and BnBr (1.9 mL, 15.48 mmol) was added. To this solution, NaH (60% in mineral oil, 0.5 g, 20.65 mmol) was added portionwise over 2 min at 0 ºC and the reaction mixture was stirred for additional 3 h at rt before chilled water (40 mL) and CH_2Cl_2 (60 mL) were added. The organic layer was washed with water (2 x 50 mL), dried (Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (5:1 hexane–EtOAc) to give **S38** (1.7 g, 78%) as a colorless oil: R_f 0.54 (5:1 hexane–EtOAc); $[\alpha]_D$ +30.6 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.39–7.27 (m, 5H, Ar), 4.95 (br s, 1H, H-1), 4.68, 4.58 (ABq, 2H, J = 11.5 Hz, ArCH_2), 4.22–4.18 (m, 1H, H-3), 4.13 (d, 1H, $J_{2,3}$ = 3.5 Hz, H-2), 3.77–3.64 (m, 3H, H-5, H-6 x 2), 3.41 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.34 (dd, 1H, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 8.9 Hz, H-4), 1.56 (s, 3H, (CH_3)$_2$C), 1.37 (s, 3H, (CH_3)$_2$C); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 138.7 (Ar), 128.5 (Ar x 2), 127.8 (Ar x 2), 127.7 (Ar), 109.5, 98.6, 78.9, 78.1, 76.1, 73.7, 69.6, 68.6, 59.4 (O*C*H$_3$), 55.1 (O*C*H$_3$), 28.2, 26.5. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{18}H_{26}NaO_6$: 361.1622. Found 361.1621.

Methyl 2-*O*-acetyl-3,6-di-*O*-benzyl-4-*O*-methyl-α-D-mannopyranoside (S39)

To a solution of **S38** (3 g, 8.9 mmol) in 3:1 CH_3OH–CH_2Cl_2 (50 mL), *p*-TSA (100 mg) was added and the mixture was stirred for 4 h at rt before Et_3N (2 mL) was added. The solution was concentrated and the resulting residue was dissolved in toluene (70 mL) and *n*-Bu_2SnO (2.19 g, 8.87 mmol) was added. The reaction mixture was heated at 120 ºC for 1 h. Then, it was cooled to 62 ºC before *n*-Bu_4NI (3.59 g, 9.76 mmol) and BnBr (1.15 mL, 9.76 mmol) were added and the reaction mixture was stirred for additional 7 h at 62 ºC. The solution was then concentrated and the resulting residue was purified by chromatography (3:1 hexane–EtOAc) to give a syrup. This syrup was dissolved in pyridine (10 mL), Ac_2O (5 mL) was added and the reaction mixture was stirred for 1 h at rt before water (40 mL) and and CH_2Cl_2 (60 mL) were added. The organic layer was separated, washed with water (2 x 50 mL), 1M HCl soln (2 x 50 mL), brine (50 mL), dried

(Na_2SO_4), filtered and concentrated. The resulting residue was purified by chromatography (6:1 hexane–EtOAc) to give **S39** (2.79 g, 73%) as a colorless oil: R_f 0.45 (6:1 hexane–EtOAc); $[\alpha]_D$ +29.8 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.40–7.27 (m, 10H, Ar), 5.33 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 4.73, 4.68 (ABq, 2H, J = 10.1 Hz, ArCH_2), 4.72 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.58, 4.51 (ABq, 2H, J = 10.1 Hz, ArCH_2), 3.86 (dd, 1H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 3.82–3.78 (m, 1H, H-5), 3.74–3.36 (m, 2H, H-6 x 2), 3.59 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.51 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.14 (s, 3H, CH_3CO); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.7 (*C*=O), 138.6 (Ar), 138.4 (Ar), 128.6 (Ar x 2), 128.5 (Ar x 2), 128.1 (Ar x 2), 127.9 (Ar x 2), 127.8 (Ar x 2), 99.0, 78.2, 76.7, 73.7, 72.0, 71.6, 69.3, 69.0, 61.1, 21.4. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{24}H_{30}NaO_7$: 453.1884. Found 453.1885.

_p_-Methoxyphenyl 2-_O_-benzoyl-3,4,6-tri-_O_-benzyl-α-D-mannopyranosyl-(1→3)-4-_O_-allyl-2-_O_-methyl-α-L-fucopyranosyl-(1→3)-4-_O_-benzyl-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (S40)

To a solution of donor **S5** (360 mg, 0.55 mmol) and acceptor **27** (240 mg, 0.32 mmol) in CH_2Cl_2 (30 mL), crushed 4 Å molecular sieves (300 mg) were added. After the reaction mixture was stirred at rt for 30 min, it was cooled to –20 ºC, NIS (103.5 mg, 0.46 mmol) and AgOTf (30.8 mg, 0.12 mmol) were added. The reaction mixture was stirred for additional 30 min at –20 ºC before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was purified by chromatography (2:1 hexane–EtOAc) to give **S40** (259 mg, 63%) as a colorless oil: R_f 0.55 (2:1 hexane–EtOAc); $[\alpha]_D$ +0.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.08–8.06 (m, 2H, Ar), 7.57–7.53 (m, 1H, Ar), 7.50–7.711 (m, 22H, Ar), 7.00–6.97 (m, 2H, Ar), 6.84–6.81 (m, 2H, Ar), 5.93–5.86 (m, 1H, =C*H*), 5.73–5.72 (m, 1H, H-2‴), 5.39 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.36 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.27–5.23 (m, 1H, CH_2=), 5.18 (d, 1H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 5.16–5.13 (m, 3H, H-1‴, =CH_2, ArCH_2), 4.92, 4.52 (ABq, 2H, J = 11.2 Hz, ArCH_2), 4.80, 4.55 (ABq, 2H, J = 11.2 Hz, ArCH_2), 4.70, 4.53 (ABq, 2H, J = 10.8 Hz, ArCH_2), 4.59 (d, 1H, J = 11.3 Hz, ArCH_2), 4.34–4.30

(m, 1H, CH_2O), 4.25 (dd, 1H, $J_{2'',3''}$ = 9.8 Hz, $J_{3'',4''}$ = 2.8 Hz, H-3″), 4.18 (dq, 1H, $J_{4'',5''}$ = 2.7 Hz, $J_{5'',6''}$ = 6.4 H, H-5″), 4.12–4.03 (m, 4H, CH_2O, H-6‴ x 2, H-5′), 4.01–3.92 (m, 3H, H-5‴, H-3, H-5), 3.87 (dd, 1H, $J_{2',3'}$ = 3.3 Hz, $J_{3',4'}$ = 9.5 Hz, H-3′), 3.81–3.77 (m, 4H, OCH_3, H-2), 3.74–3.67 (m, 4H, H-2′, H-2″, H-3‴, H-4″), 3.57–3.54 (m, 4H, H-4‴, OCH_3), 3.50–3.46 (m, 4H, H-4′, OCH_3), 3.44 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.22 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 1.33 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6′), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.20 (d, 3H, $J_{5'',6''}$ = 6.4 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.5 (*C*=O), 154.9 (Ar), 150.5 (Ar), 139.1 (Ar), 138.6 (Ar), 138.6 (Ar), 137.9 (Ar), 135.2 (=*C*H), 133.0(2) (Ar), 130.0(3) (Ar), 130.0 (Ar), 129.1 (Ar), 128.4 (Ar x 2), 128.4 (Ar x 2), 128.3 (Ar x 2), 128.3 (Ar x 2), 128.1 (Ar x 2), 127.8 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4(3) (Ar), 127.3(8) (Ar), 127.1 (Ar), 126.3 (Ar), 117.5 (Ar), 117.4 (*C*H_2=), 114.6 (Ar x 2), 99.6, 99.3, 98.5, 95.6, 82.0, 81.4, 80.6, 80.0, 79.4, 79.3, 79.3, 78.9, 77.8, 75.9, 75.1, 75.1, 74.3(9), 74.3(6), 73.5, 72.6, 71.4, 69.4, 68.9, 68.7(3), 68.6(7), 66.9, 61.2 (O*C*H_3), 58.9 (O*C*H_3), 38.6 (O*C*H_3), 57.8 (O*C*H_3), 55.7 (O*C*H_3), 18.2(1), 18.1(7), 16.8. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{73}H_{88}NaO_{20}$: 1307.5761. Found 1307.5746.

_p_-Methoxyphenyl 2-_O_-benzoyl-3,6-di-_O_-benzyl-4-_O_-methyl-α-D-mannopyranosyl-(1→3)-4-_O_-allyl-2-_O_-methyl-α-L-fucopyranosyl-(1→3)-4-_O_-benzyl-2-_O_-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-_O_-methyl-α-L-rhamnopyranoside (S41)

To a solution of donor **S6** (158 mg, 0.27 mmol) and acceptor **27** (120 mg, 0.16 mmol) in CH_2Cl_2 (30 mL), crushed 4 Å molecular sieves (200 mg) were added. After the mixture was stirred at rt for 30 min, it was cooled to –20 ºC, NIS (52 mg, 0.23 mmol) and AgOTf (15.4 mg, 0.06 mmol) were added and the reaction mixture was stirred for additional 30 min at –20 ºC before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was purified by chromatography (2:1 hexane–EtOAc) to give **S41** (122 mg, 63%) a colorless oil: R_f 0.49 (4:1 hexane–EtOAc); $[\alpha]_D$ –23.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.11–8.03 (m, 3H, Ar), 7.59–7.10 (m, 17H, Ar), 6.99–6.96 (m, 2H, Ar), 6.83–6.80 (m, 2H, Ar),

5.93–5.85 (m, 1H, =C*H*), 5.67–5.66 (m, 1H, H-2‴), 5.38 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 5.32 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.27–5.23 (m, 1H, =CH_2), 5.16–5.14 (m, 3H, H-1″, H-1‴, =CH_2), 5.11, 4.66 (ABq, 2H, *J* = 11.8 Hz, ArCH_2), 4.78, 4.50 (ABq, 2H, *J* = 12.0 Hz, ArCH_2), 4.73, 4.53 (ABq, 2H, *J* = 11.75 Hz, ArCH_2), 4.68–4.61 (m, 1H, H-5″), 4.59 (dd, 1H, $J_{2'',3''}$ = 9.7 Hz, $J_{3'',4''}$ = 2.7 Hz, H-3″), 4.33–4.29 (m, 1H, CH_2O), 4.23–4.18 (m, 2H, H-5′, CH_2O), 4.09–4.04 (m, 2H, H-6‴ x 2), 3.99–3.94 (m, 2H, H-3, H-5), 3.88–3.84 (m, 2H, H-3′, H-5‴), 3.76 (s, 3H, OCH_3), 3.73–3.67 (m, 4H, H-2, H-2′, H-2″, H-3‴), 3.54 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.37–3.32 (m, 2H, H-4′, H-4″), 3.30 (s, 3H, OCH_3), 3.24–3.16 (m, 2H, H-4, H-4‴), 1.31 (d, 3H, $J_{6',5'}$ = 6.2 Hz, H-6′), 1.26 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.19 (d, 3H, $J_{6'',5''}$ = 6.5 Hz, H-6″); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 165.5 (*C*=O), 154.9 (Ar), 150.5 (Ar), 139.1 (Ar), 138.6 (Ar), 138.0 (Ar), 135.1 (=*C*H), 133.3 (Ar), 130.0 (Ar), 129.9 (Ar), 128.4 (Ar x 2), 128.3 (Ar), 128.2(9) (Ar), 128.2(6) (Ar), 128.1 (Ar x 2), 128.0 (Ar), 127.9 (Ar), 127.6 (Ar), 127.4 (Ar x 2), 127.4 (Ar x 2), 127.3 (Ar x 2), 127.1 (Ar), 126.3 (Ar), 117.4(9) (Ar x 2), 117.4(8) (=*C*H_2), 114.6 (Ar x 2), 99.7, 99.3, 98.5, 95.6, 82.0, 80.7, 80.2, 80.0, 79.8, 79.5, 79.4, 78.9, 77.6, 76.3, 75.9, 74.4, 74.1, 73.9, 73.5, 71.7, 71.4, 71.1, 69.5, 68.9, 68.7, 61.2 (O*C*H_3), 58.9 (O*C*H_3), 58.6 (O*C*H_3), 57.7 (O*C*H_3), 57.4 (O*C*H_3), 55.7 (O*C*H_3), 18.1(9), 18.1(6), 16.7. HRMS (ESI) Calcd. for $(M + Na)^+$ $C_{67}H_{84}NaO_{20}$: 1231.5448. Found 1231.5437.

4-(1-Hydroxynonadecyl) anisole (S42)

To a solution of mechanically activated magnesium turnings (1.07 g, 44.98 mmol) in anhydrous THF (2 mL) in a three-necked rounded bottom flask was added 1-bromooctadecane (1 mL from a solution of 5 g in 20 mL anhydrous THF, 14.99 mmol) and the solution was gently warmed until it started to reflux by itself. The remained of 1-bromooctadecane solution (19 mL) was added dropwise over 20 min while the reaction mixture continued to reflux. After the addition was complete, the reaction mixture was heated at reflux for an 1 h. After 1 h, the reaction mixture was cooled to rt and *p*-anisaldehyde (2.75 mL, 22.48 mmol) was added dropwise over 10 min. After the addition was complete, the reaction mixture was heated at reflux for 1 h.

Then, the solution was cooled to rt and the excess Grignard reactant was quenched carefully by the addition of ice-cold water (50 mL). The solution was then diluted with CH_2Cl_2 (100 mL), washed with 1M HCl soln (2 x 50 mL), water (2 x 50 mL) and brine (75 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (7:1 hexane–EtOAc) to afford **S42** (4.38 g, 75%) as an amorphous solid: R_f 0.48 (7:1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.30–7.27 (m, 2H, Ar-2,6), 6.92–6.89 (m, 2H, Ar-3,5), 4.63 (dt, 1H, J = 7.1 Hz, J = 3.1 Hz, H-1′), 3.83 (s, 3H, OCH_3), 1.85–1.79 (m, 1H, H-2′a), 1.78 (d, 1H, J = 2.6 Hz, OH), 1.73–1.76 (m, 1H, H-2′b), 1.43–1.27 (m, 32H, CH_2 x 16), 0.91 (t, 3H, $J_{18',19'}$ = 7.0 Hz, CH_3-19′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 159.0 (Ar), 137.1 (Ar), 127.2 (Ar x 2), 113.8 (Ar x 2), 74.3, 55.3 (O*C*H$_3$), 39.0, 32.0, 29.7(2) (CH_2 x 8), 29.6(8), 29.6(2), 29.5(8), 29.5(6), 29.4, 25.9, 22.7, 14.2. HRMS (ESI) Calcd for $(M–H_2O)^+$ $C_{26}H_{44}O$: 372.3392. Found 372.3393

4-Nonadecylanisole (S43)

To a solution of **S42** (0.78 g, 2 mmol) and Me_3SiH (0.5 mL, 4 mmol) in dry CH_2Cl_2 (4 mL) at 0°C, $BF_3{\cdot}Et_2O$ (0.5 mL, 4 mmol) was added and the reaction mixture was stirred for 1 h. The Lewis acid was quenched by the addition of sat. aq. $NaHCO_3$ soln (10 mL), and the mixture was diluted with CH_2Cl_2 (20 mL), and then washed with water (2 x 10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated and the resulting residue was purified by chromatography (10:1 hexane–EtOAc) to afford **S43** (0.71 g, 94%) as an amorphous solid: R_f 0.51 (10:1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.11–7.07 (m, 2H, Ar-3,5), 6.84–6.80 (m, 2H, Ar-2,6), 3.79 (s, 3H, OCH_3), 2.54 (t, 2H, $J_{1',2'}$ = 7.6 Hz, CH_2-1′), 1.59–1.54 (m, 2H, CH_2-2′), 1.31–1.26 (m, 32H, CH_2 x 16), 0.89 (t, 3H, $J_{18',19'}$ = 7.0 Hz, CH_3-19′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 157.2 (Ar), 134.7 (Ar), 128.8 (Ar x 2), 113.2 (Ar x 2), 54.9 (OCH_3), 34.7, 31.5, 31.4, 29.3 (CH_2 x 11), 29.2, 20.1, 29.0, 28.9, 22.3. HRMS Calcd for (ESI) $(M)^+$ $C_{26}H_{46}O$: 374.3549. Found 374.3546.

***p*-Tolyl 4-*O*-methyl-1-thio-α-L-rhamnopyranoside (S44)**

To a solution of **S18** (0.64 g, 2.1 mmol) in DMF (10 mL) and CH_3I (0.21 mL, 3.32 mmol), NaH (60% in mineral oil, 106 mg, 4.43 mmol) was added at 0 ºC and then the reaction mixture was stirred for additional 1 h at rt. The mixture was diluted with chilled water (30 mL) and CH_2Cl_2 (30 mL) and the organic layer was washed with water (2 x 20 mL) and brine (20 mL) before being dried ($NaSO_4$), filtered and concentrated. The resulting oil was dissolved 1:1 CH_3OH–CH_2Cl_2 (10 mL) and *p*-TSA (20 mg) was added. The reaction mixture was stirred for 3 h at rt before Et_3N (0.5 mL) was added. The solution was concentrated, and the resulting residue was purified by chromatography (1:1 hexane–EtOAc) to afford **S44** (0.53 g, 84%) as an amorphous solid: R_f 0.29 (1:1 hexane–EtOAc); $[\alpha]_D$ –28.9 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.37–7.34 (m, 2H, Ar-2,6), 7.13–7.11 (m, 2H, Ar-3,5), 5.41 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.20 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 4.15 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.89 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.59 (s, 3H, OC*H*$_3$), 3.18 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 2.34 (s, 3H, ArC*H*$_3$), 1.34 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 137.9 (Ar), 132.3 (Ar x 2), 130.5 (Ar), 130.07 (Ar x 2), 88.1, 83.7, 72.8, 71.9, 68.8, 61.0 (O*C*H$_3$), 21.4, 18.1. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{14}H_{20}O_4NaS$: 307.0975. Found 307.0977.

***p*-Tolyl 2-*O*-acetyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (S45)**

To a solution of **S19** (0.99 g, 2.75 mmol) and triethyl orthoacetate (1.02 mL, 5.55 mmol) in CH_2Cl_2 (20 mL) was added CSA (128 mg, 0.55 mmol). The reaction mixture was stirred for 2 h at rt before it was concentrated and dissolved in 80% HOAc and stirred for additional 30 min at rt. Water (10 mL) was added and the mixture was concentrated, diluted with CH_2Cl_2 (20 mL) and washed with water (2 × 20 mL). The organic layer was separated, dried (Na_2SO_4), filtered and concentrated to a syrup, which was purified by chromatography (4:1 hexane–EtOAc) to give **S45** (0.96 g, 87%) as a colorless oil: R_f 0.31 (1:2 hexane–EtOAc); $[\alpha]_D$ –133.4 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.39–7.28 (m, 7H, Ar), 7.13 (d, 2H, *J* =

8.1 Hz, Ar-2,6), 5.40–5.37 (m, 2H, H-1, H-2), 4.79, 4.68 (ABq, J = 11.2 Hz, ArCH_2), 4.26 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 4.16–4.10 (m, 1H, H-3), 3.46 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 2.36 (s, 3H, ArCH_3), 2.28 (d, 1H, $J_{3,OH-3}$ = 5.1 Hz, OH-3), 2.16 (s, 3H, CH_3CO), 1.37 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.9 (C=O), 138.4 (Ar), 138.2 (Ar), 132.6 (Ar x 2), 130.3 (Ar), 130.1 (Ar), 128.8 (Ar x 2), 128.3 (Ar), 128.2(2) (Ar), 128.1(4) (Ar x 2), 86.5, 82.2, 75.5, 74.6, 71.0, 68.9, 21.4, 21.3, 18.1. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{22}H_{26}O_5NaS$: 425.1393. Found 425.1405.

4-Nonadecylphenyl 2-*O*-acetyl-4-*O*-methyl-α-L-rhamnopyranoside (S46)

To a solution of **S7** (385 mg, 0.91 mmol) and **35** (396 mg, 1.1 mmol) in CH_2Cl_2 (20 mL) were added crushed 4 Å molecular sieves (200 mg). After stirring at rt for 30 min, the solution was cooled to –20 ºC and then NIS (206 mg, 0.92 mmol) and AgOTf (62 mg, 0.24 mmol) were added. The reaction mixture was then stirred for another 30 min before the addition of Et_3N (1 mL). The solution was concentrated to a crude residue that was dissolved in CH_2Cl_2 (20 mL) and NH_2NH_2·HOAc (126 mg, 1.36 mmol) was added. The reaction mixture was stirred for 5h at rt before it was concentrated and the resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give **S46** (337 mg, 66%) as a colorless oil: R_f 0.28 (2:1 hexanes–EtOAc); $[\alpha]_D$ –3.6 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.08–7.05 (m, 2H, Ar-2,6), 6.94–6.91 (m, 2H, Ar-3,5), 5.40 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.26 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.6 Hz, H-2), 4.22 (dd, 1H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.79 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.59 (s, 3H, OCH_3), 3.13 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.53 (t, 2H, $J_{1',2'}$ = 7.6 Hz, CH_2-1′), 2.18 (s, 3H, CH_3CO), 1.59–1.53 (m, 2H, CH_2-2′), 1.26 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 1.29–1.24 (m, 32H, CH_2 x 16), 0.87 (t, 3H, $J_{18',19'}$ = 6.6 Hz, CH_3-19′); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 170.7 (C=O), 154.2 (Ar), 137.0 (Ar), 129.3 (Ar x 2), 116.3 (Ar x 2), 95.8, 83.3, 72.5, 69.8, 68.1, 60.9 (OCH$_3$), 35.1, 31.9, 31.6, 29.7 (CH$_2$ x 10), 29.6, 29.5, 29.4, 29.3, 22.7, 21.0, 18.0, 14.1. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{34}H_{58}O_6Na$: 585.4126. Found 585.4122.

***p*-Nonadecylphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-levulinoyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-methyl-α-L-rhamnopyranoside(S47)**

To a solution of **S8** (225 mg, 0.45 mmol) and **S46** (309.1 mg, 0.55 mmol) in CH_2Cl_2 (20 mL), crushed 4Å molecular sieves (200 mg) were added. After the reaction mixture was stirred at rt for 30 min, it was cooled to –20 ºC, and then NIS (103.5 mg, 0.46 mmol) and AgOTf (30.8 mg, 0.12 mmol) were added. The reaction mixture was stirred for 30 min before the addition of Et_3N (1 mL). The solution was filtered and concentrated to a crude residue that was purified by chromatography (2:1 hexane–EtOAc) to give **S47** (333 mg, 79%) as a colorless oil: R_f 0.45 (2:1 hexane–EtOAc); $[\alpha]_D$ –39.7 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.36–7.25 (m, 5H, Ar), 7.07–7.04 (m, 2H, Ar-2,6), 6.92–6.90 (m, 2H, Ar-3,5), 5.36 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.30–5.26 (m, 3H, H-2, H-2′, H-3′), 5.02 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 4.72, 4.63 (ABq, 2H, J = 11.4 Hz, ArCH_2), 4.16 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.87 (dq, 1H, $J_{4',5'}$ = 9.5 Hz, $J_{5',6'}$ = 6.3 Hz, H-5′), 3.75 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.56 (s, 3H, OCH_3), 3.51 (app t, 1H, $J_{3',4'} = J_{4',5'}$ = 9.5 Hz, H-4′), 3.21 (app t, 1H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 2.76–2.63 (m, 2H, CH_2-1″), 2.54–2.44 (m, 4H, CH_2CO, CH_2COO), 2.17 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3CO), 2.14 (s, 3H, CH_3CO), 1.57–1.54 (m, 2H, CH_2-2$_{agly}$), 1.31–1.24 (m, 38H, H-6 x 3, H-6′ x 3, CH_2 x 16), 0.87 (t, 3H, $J_{18,19}$ = 7.0 Hz, CH_3-19$_{agly}$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 206.1 (*C*=O), 171.8 (*C*=O), 170.4 (*C*=O), 170.0 (*C*=O), 154.1 (Ar), 138.2 (Ar), 137.0 (Ar), 129.3 (Ar x 2), 128.4 (Ar x 2), 127.8 (Ar x 2), 127.7 (Ar), 116.3 (Ar x 2), 99.5, 95.6, 82.1, 78.4, 77.3, 74.6, 71.9, 71.8, 70.4, 68.5, 68.5, 37.9, 35.1, 31.9, 31.6, 29.8, 29.7 (*C*H$_2$ x 10), 29.6, 29.5, 29.4, 29.3, 28.0, 22.7, 21.0, 20.9, 17.9, 17.8, 14.1. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{54}H_{82}O_{13}Na$: 961.5640. Found 961.5648.

***p*-Nonadecylphenyl 2,4-di-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-methyl-α-L-rhamnopyranoside (S48)**

To a solution of **S47** (150 mg, 0.16 mmol) in CH_2Cl_2 (20 mL) was added NH_2NH_2·HOAc (22 mg, 0.24 mmol) and the reaction mixture was stirred for 5 h at rt. The solution was filtered, concentrated and the

resulting residue was purified by chromatography (2:1 hexane–EtOAc) to give a colorless oil. Next, two solutions were prepared. Solution A was prepared by dissolving the product of the NH_2NH_2·HOAc reaction in CH_2Cl_2 (10 mL) and crushed 4Å molecular sieves (100 mg) was added. Solution B was prepared by dissolving **S9** (87 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) containing crushed 4Å molecular sieves (100 mg). Both solutions A and B were stirred for 30 min at rt and then solution A was cooled to –40 ºC before NIS (51.8 mg, 0.23 mmol) and AgOTf (15.4 mg, 0.06 mmol) were added. Solution B was then added dropwise to solution A over 10 min while stirring. The reaction mixture was stirred for additional 30 min at –40 ºC before Et_3N (0.25 mL) was added. The solution was filtered, concentrated and the resulting residue was dissolved in CH_2Cl_2 (20 mL). To this solution at 0 ºC, TFA (1 mL, 5 % v/v) was added and the reaction mixture was stirred for 45 min. To this solution was added Et_3N (2 mL) and the mixture was then concentrated, and the resulting crude product was purified by chromatography (1:1 hexane–EtOAc) to give **S48** (63 mg, 39 %) as a colorless oil: R_f 0.49 (1:1 hexane–EtOAc); $[\alpha]_D$ –29.8 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.34–7.25 (m, 5H, Ar), 7.06 (d, 2H, J = 8.6 Hz, Ar-2,6), 6.91 (d, 2H, J = 8.6 Hz, Ar-3,5), 5.36 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 5.27 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 5.19 (dd, 1H, $J_{2',3'}$ = 3.1 Hz, $J_{3',4'}$ = 1.9 Hz, H-2′), 5.10 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1′), 5.06 (d, 1H, $J_{1'',2''}$ = 3.5 Hz, H-1″), 4.67, 4.64 (ABq, 2H, J = 12.0 Hz, ArCH_2), 4.17 (dd,1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 4.07–4.06 (m, 1H, H-3′), 4.02–3.99 (m, 2H, H-3″, H-5″), 3.84 (dq, 1H, $J_{4',5'}$ = 9.4 Hz, $J_{5',6'}$ = 6.3 Hz, H-5′), 3.75 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.63–3.59 (m, 1H, H-2″), 3.62 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.49–3.46 (m, 1H, H-4′), 3.47 (s, 3H, OCH_3), 3.99–3.98 (m, 1H, H-4″), 3.21 (app t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.52 (t, 2H, $J_{1,2}$ = 8.0 Hz, CH_2-1$_{agly}$), 2.17 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO), 1.57–1.54 (m, 2H, CH_2-2‴), 1.29–1.23 (m, 41H, H-6 x 3, H-6′ x 3, H-6″ x 3, CH_2 x 16), 0.87 (t, 3H, $J_{18,19}$ = 6.8 Hz, CH_3-19$_{agly}$); ^{13}C NMR (125.7 MHz, $CDCl_3$, δ_C) 167.9 (*C*=O), 167.7 (*C*=O), 151.6 (Ar), 135.9 (Ar), 134.5 (Ar), 126.7 (Ar x 2), 125.8 (Ar x 2), 125.1 (Ar x 3), 113.8 (Ar x 2), 98.0, 95.4, 93.2, 80.0, 79.4, 76.2, 75.9, 74.4, 73.8, 72.2, 70.8, 69.3, 67.3, 66.2, 66.0, 64.3, 59.7(4) (OCH_3),

58.7(9) (O*C*H$_3$), 54.7 (O*C*H$_3$), 32.6, 29.4, 29.1, 27.2 (*C*H$_2$ x 10), 27.1, 27.0, 26.7(8), 26.7(4), 22.2, 21.0, 20.8, 17.9, 17.7, 16.5, 13.9. HRMS (ESI) Calcd for $(M + Na)^+$ $C_{57}H_{90}O_{15}Na$: 1037.6178. Found 1037.6177.

Immunological Evaluation

Immunoinhibition assay of compounds **1–17**

Pam3CSK4 [TLR2 agonist] as stimulant

1. IL-6

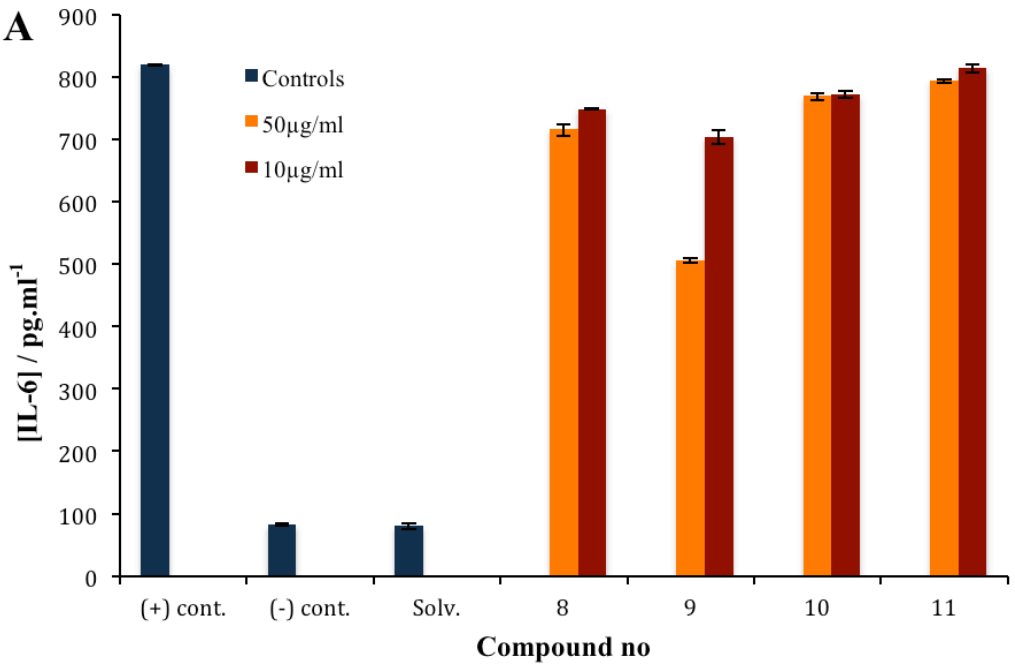


Figure S1. IL-6 immunoinhibition assay of compounds **8–11**.

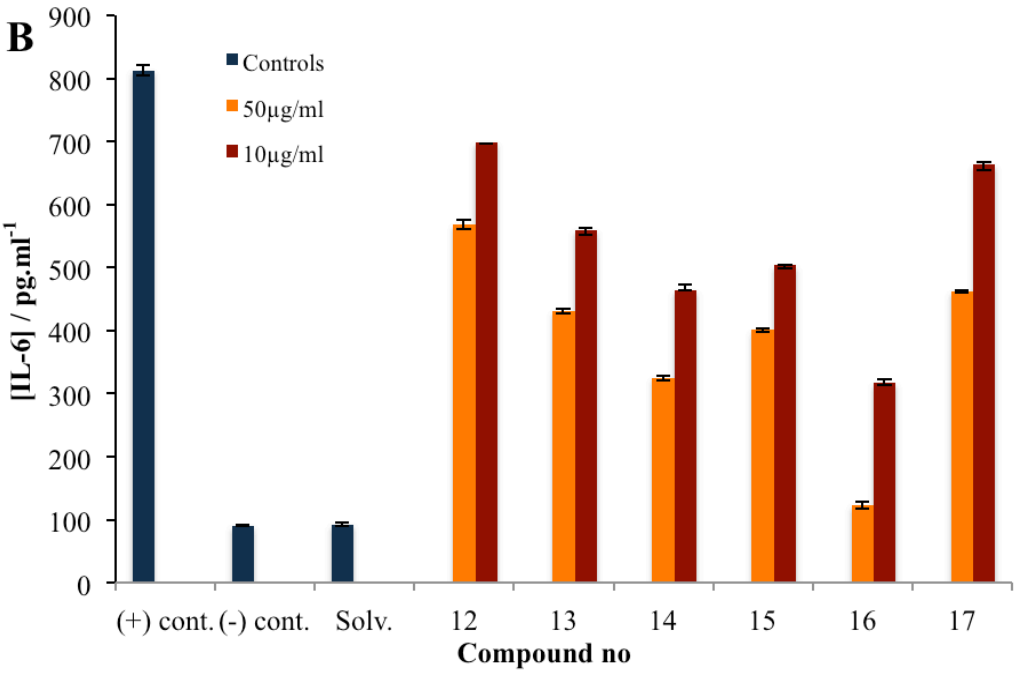


Figure S2. IL-6 immunoinhibition assay of compounds **12–17**.

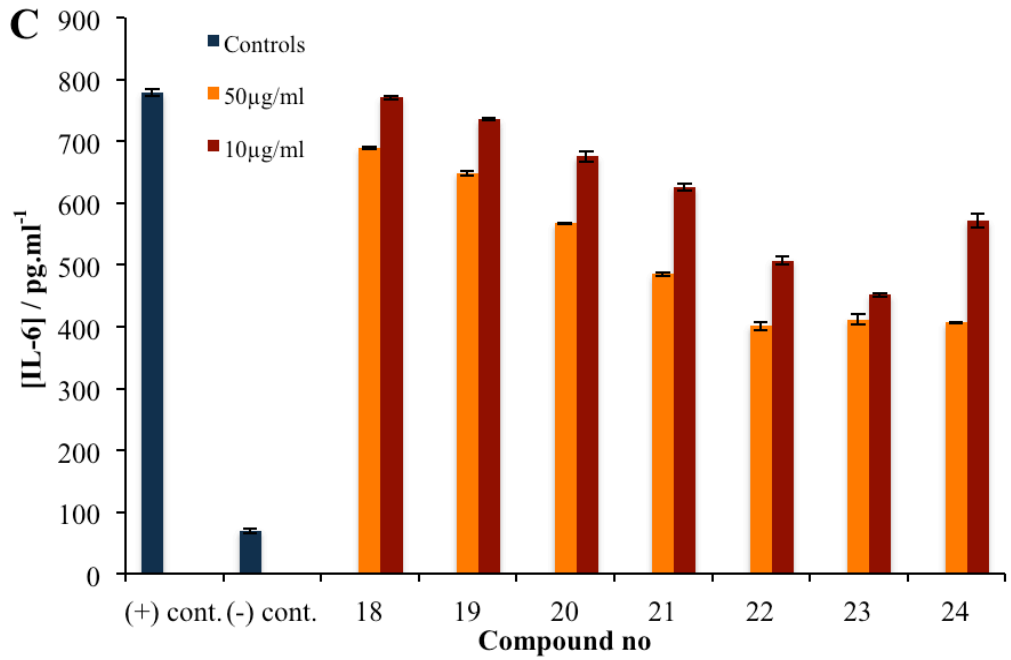


Figure S3. IL-6 immunoinhibition assay of compounds **18**–**24**.

2. IL-1ß

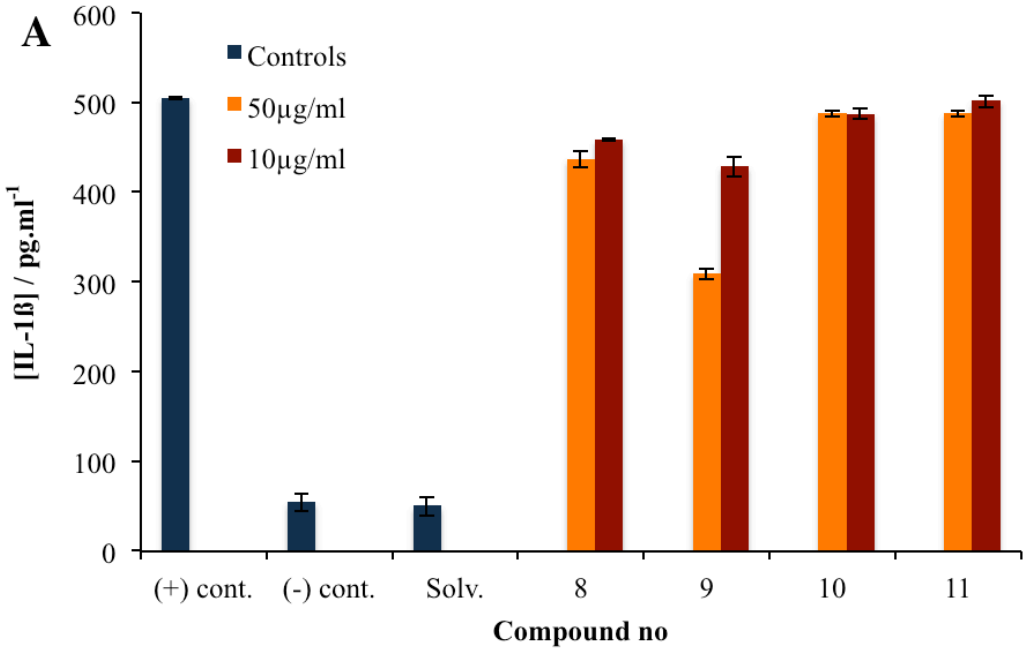


Figure S4. IL-1ß immunoinhibition assay of compounds **8**–**11**.

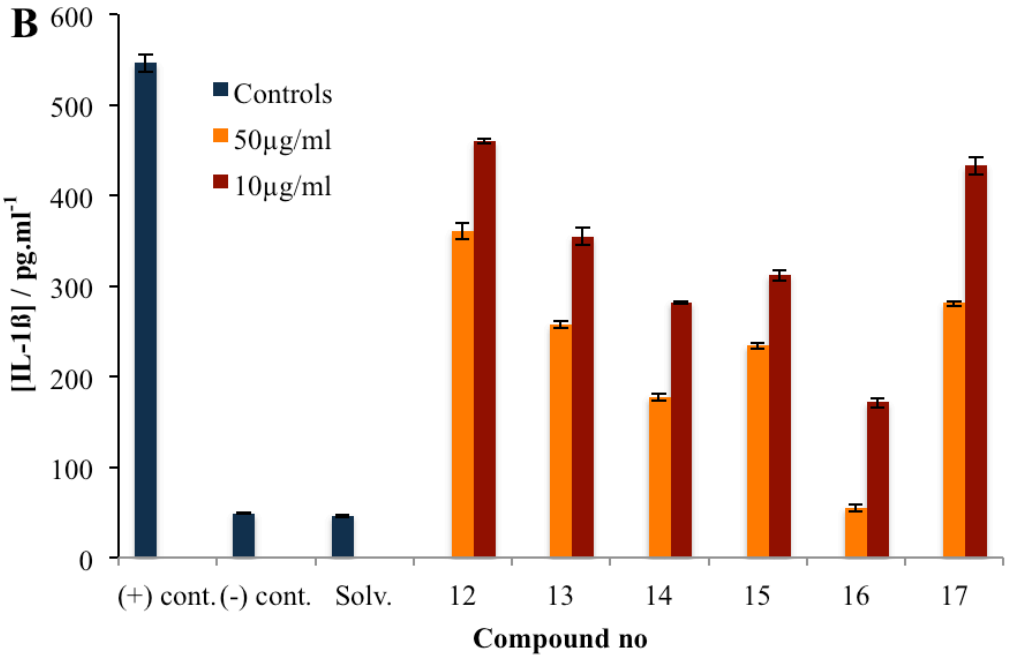


Figure S5. IL-1ß immunoinhibition assay of compounds **12**–**17**.

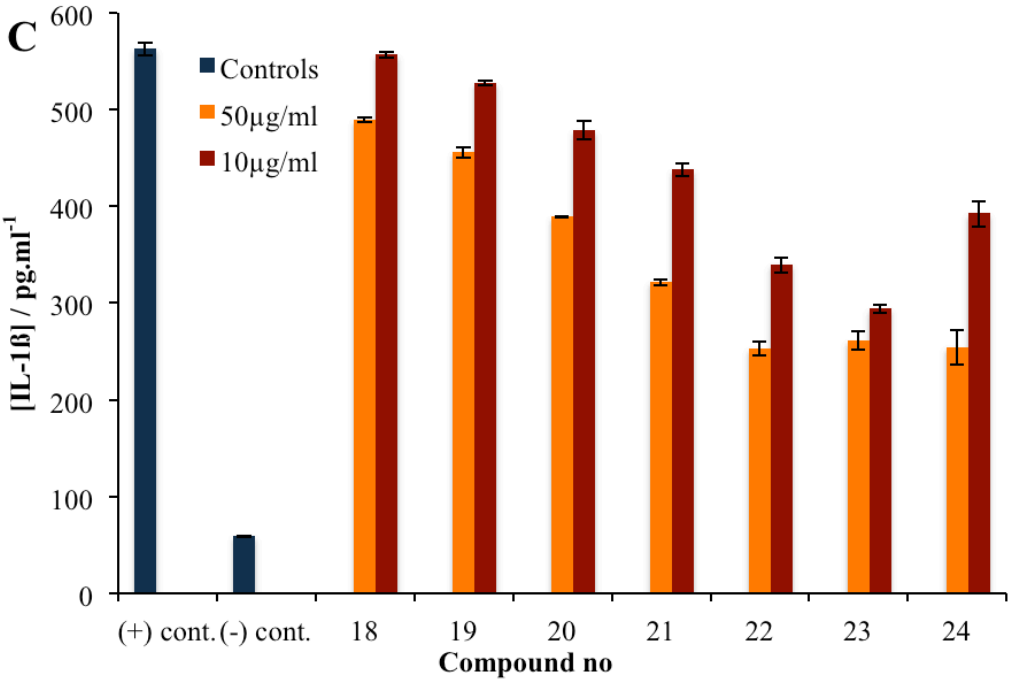


Figure S6. IL-1ß immunoinhibition assay of compounds **18**–**24**.

3. MCP-1

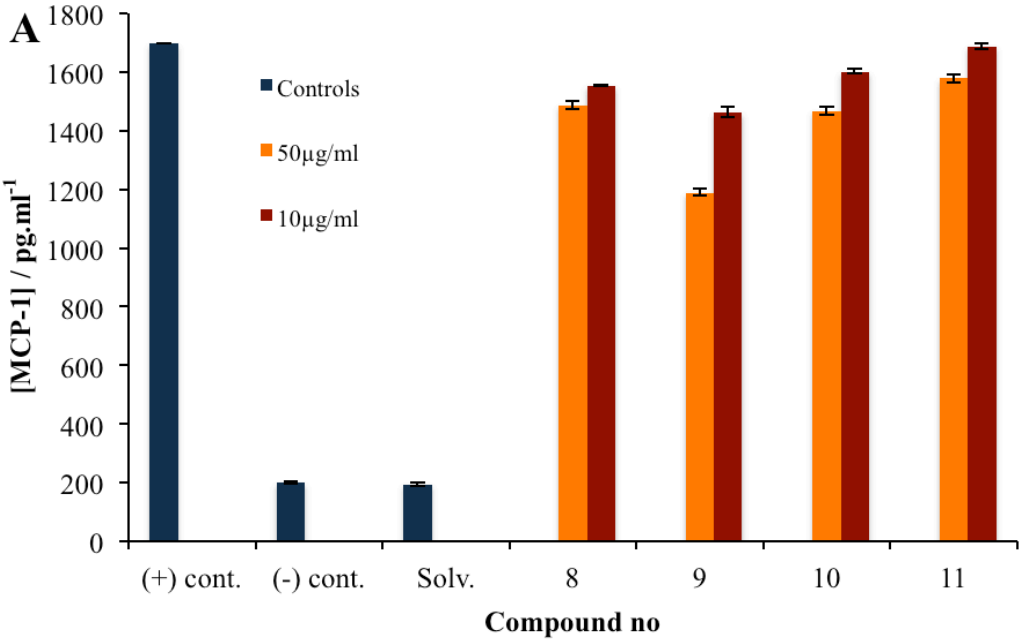


Figure S7. MCP-1 immunoinhibition assay of compounds **8–11**.

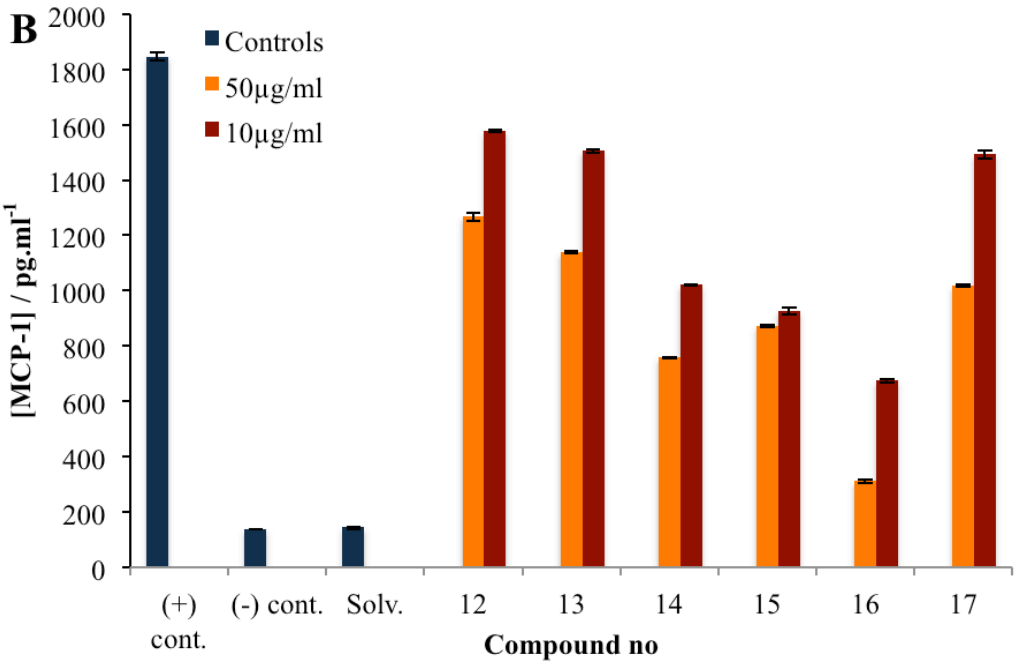


Figure S8. MCP-1 immunoinhibition assay of compounds **12–17**.

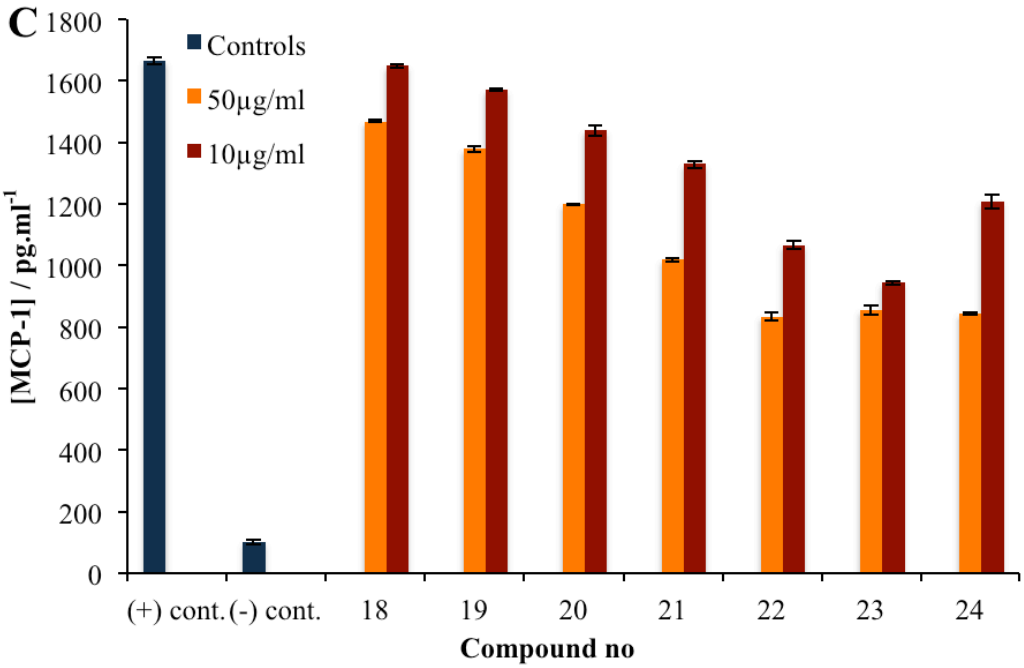


Figure S9. MCP-1 immunoinhibition assay of compounds **18**–**24**.

4. NO

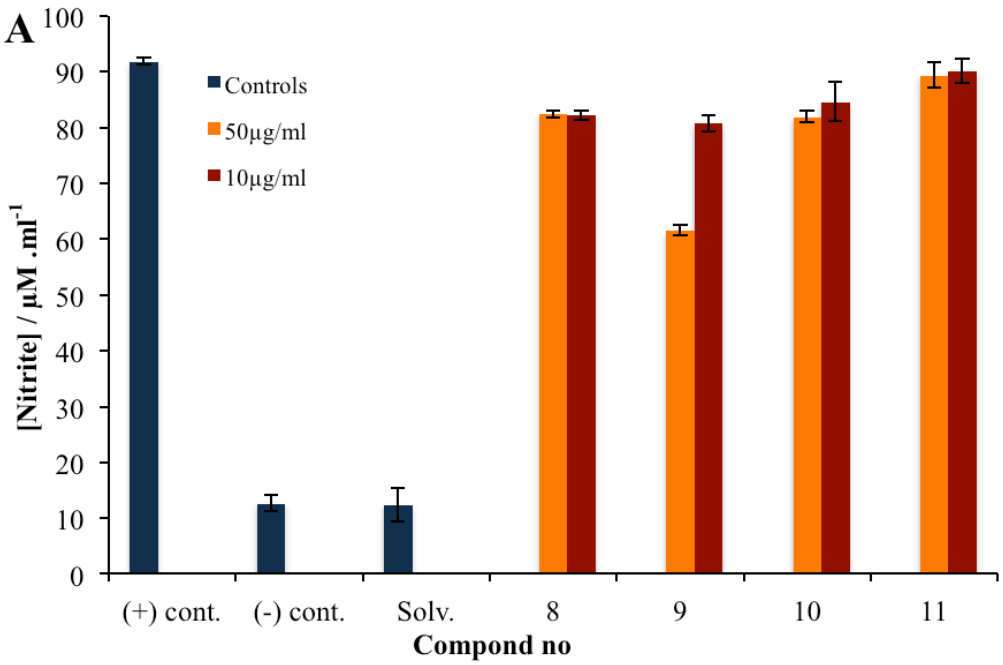


Figure S10. Nitric oxide immunoinhibition assay of compounds **8**–**11**.

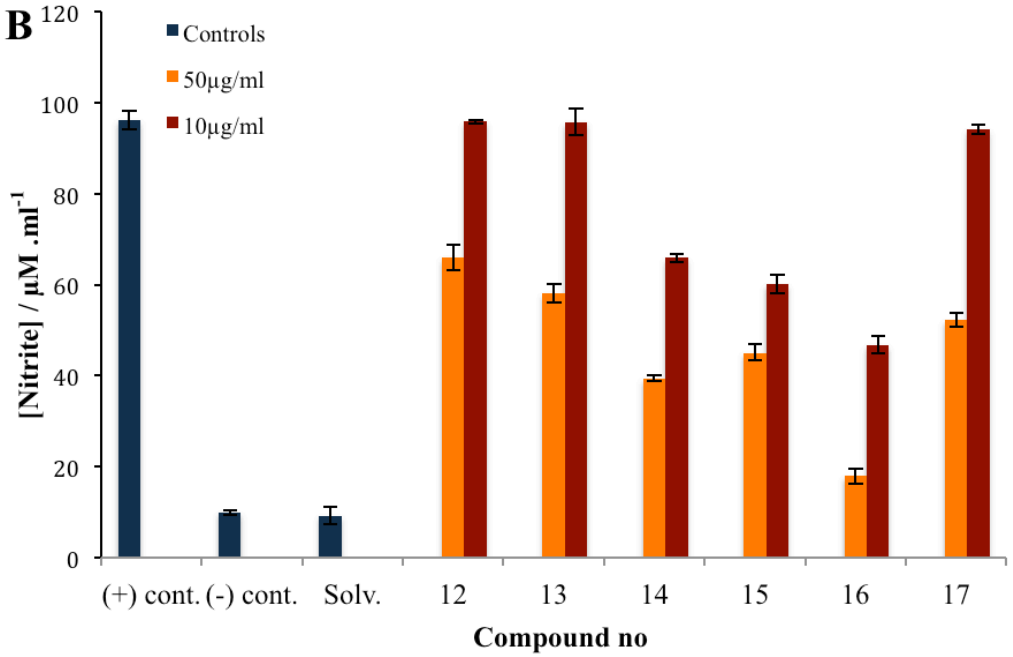


Figure S11. Nitric oxide immunoinhibition assay of compounds **12**–**17**.

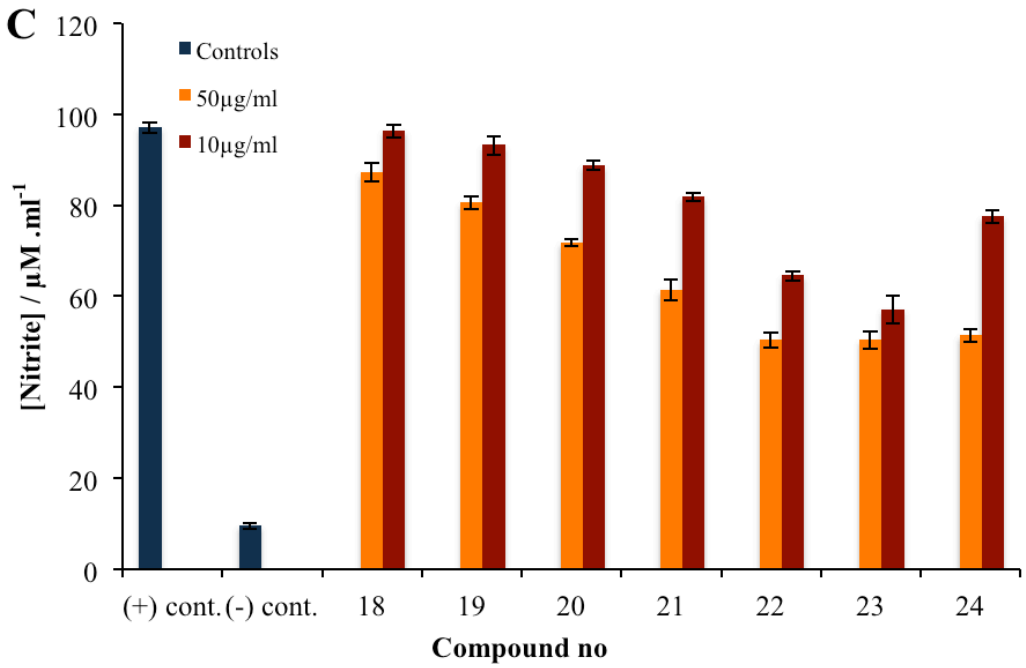


Figure S12. Nitric oxide immunoinhibition assay of compounds **18**–**24**.

Immunoinhibition assay of compounds **1–17**
Ultra pure LPS [TLR4 agonist] as stimulant

1. IL-6

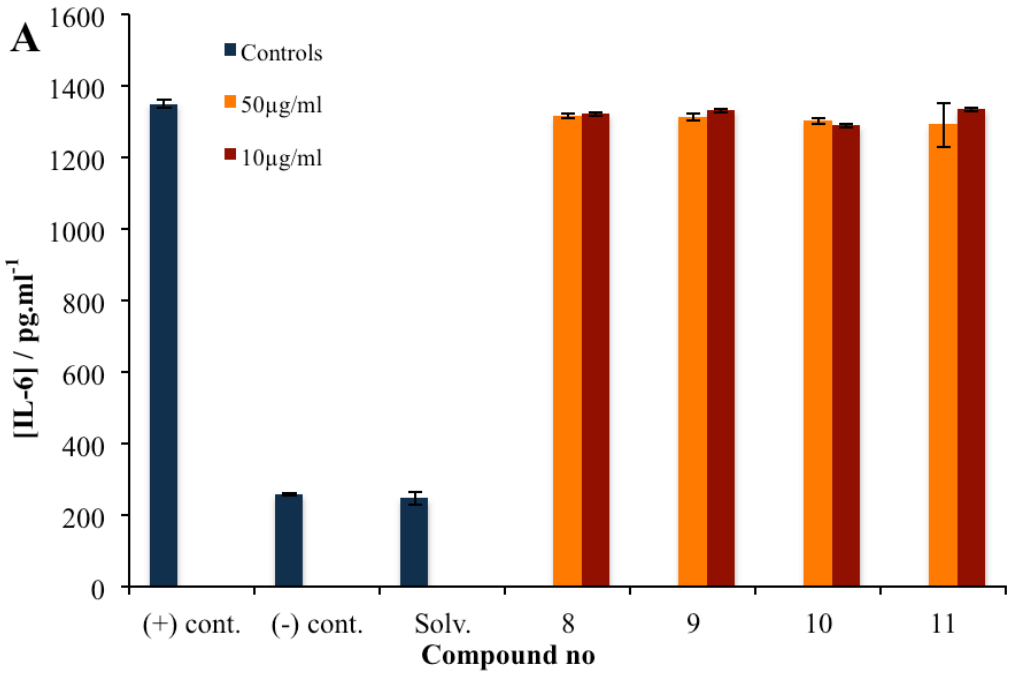


Figure S13. IL-6 immunoinhibition assay of compounds **8–11**.

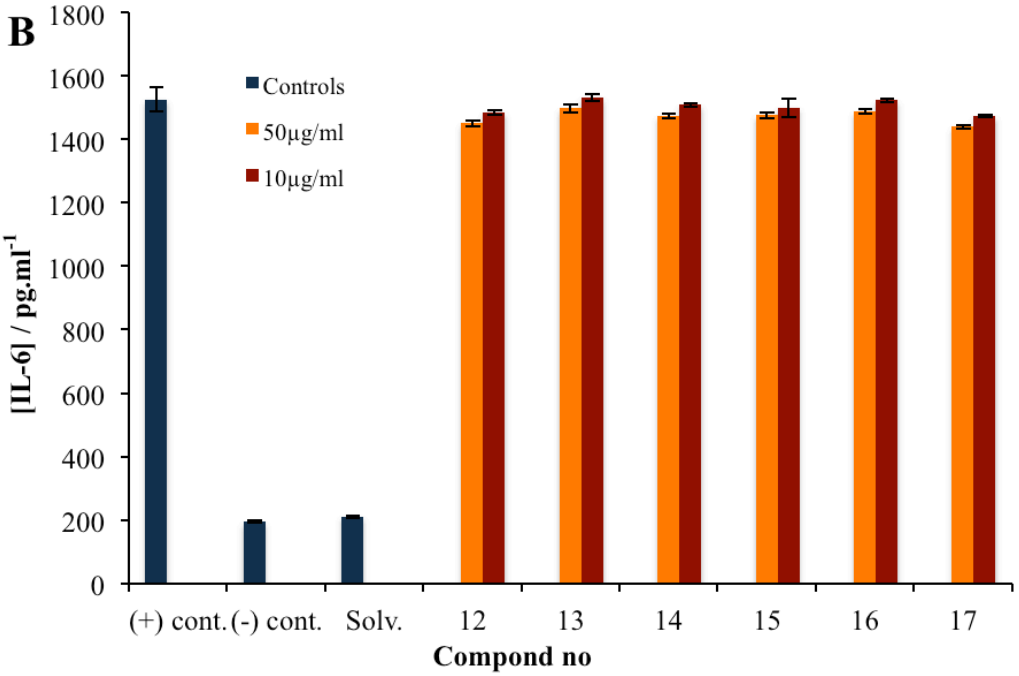


Figure S14. IL-6 immunoinhibition assay of compounds **12–17**.

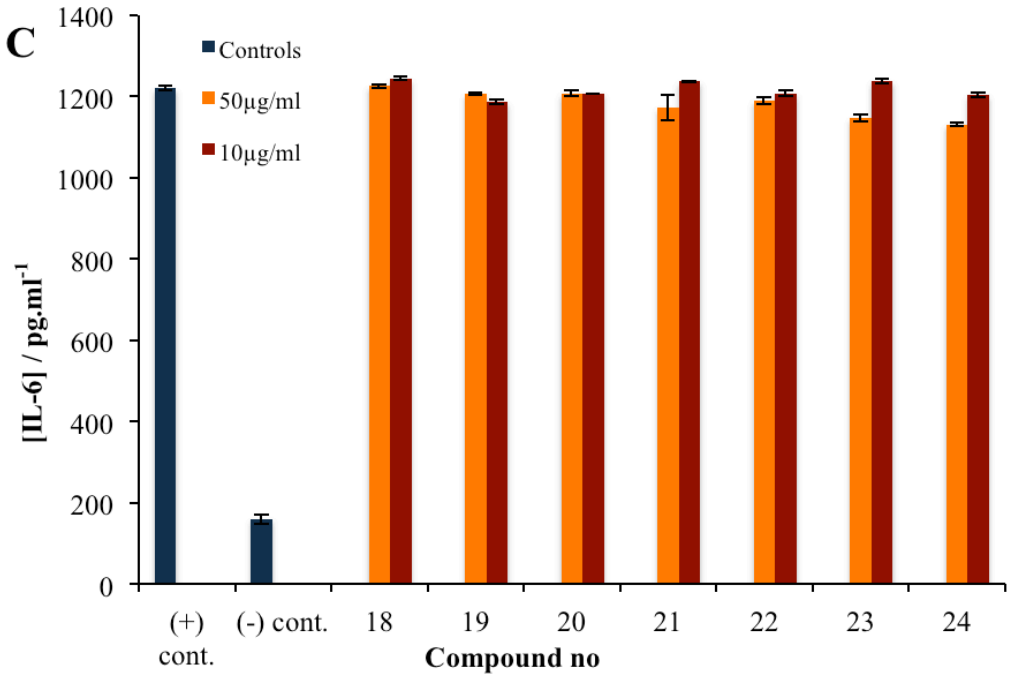


Figure S15. IL-6 immunoinhibition assay of compounds **18**–**24**.

2. IL-1ß

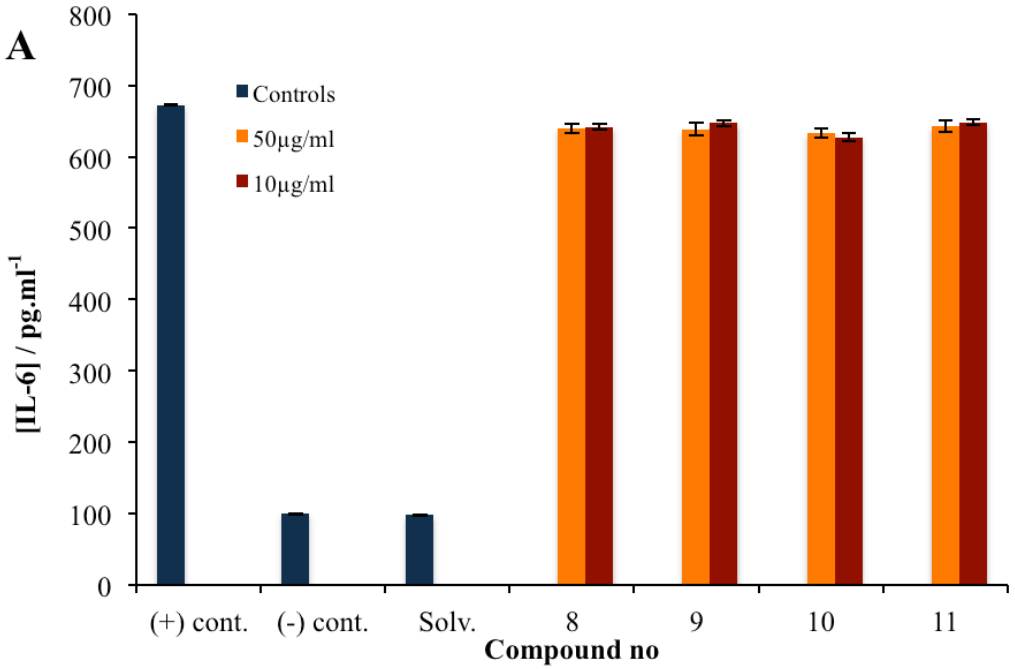


Figure S16. IL-1ß immunoinhibition assay of compounds **8**–**11**.

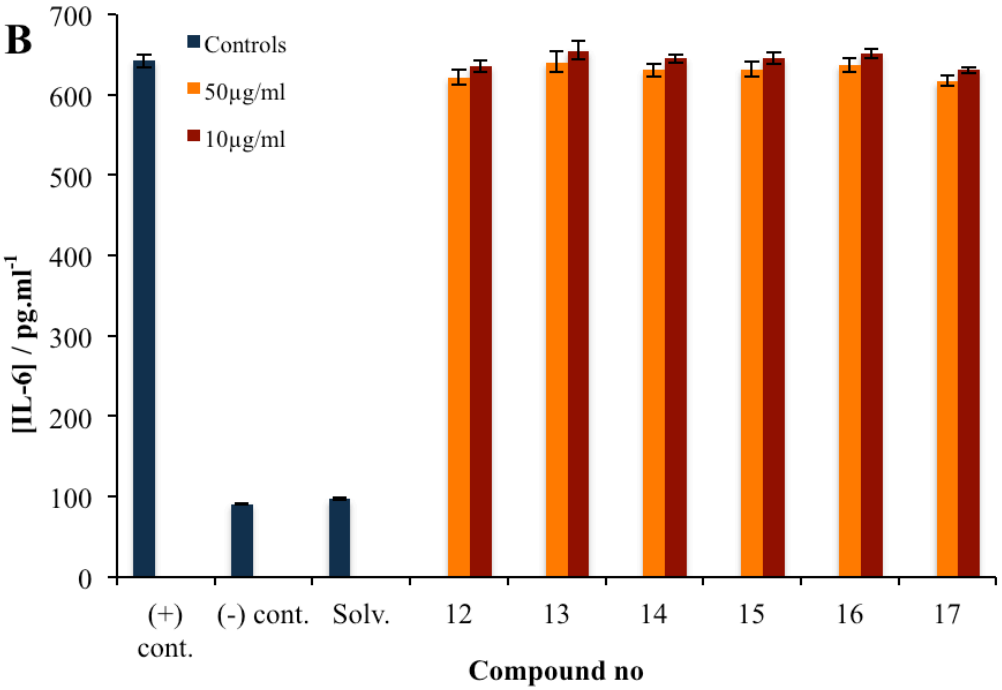


Figure S17. IL-1ß immunoinhibition assay of compounds **12**–**17**.

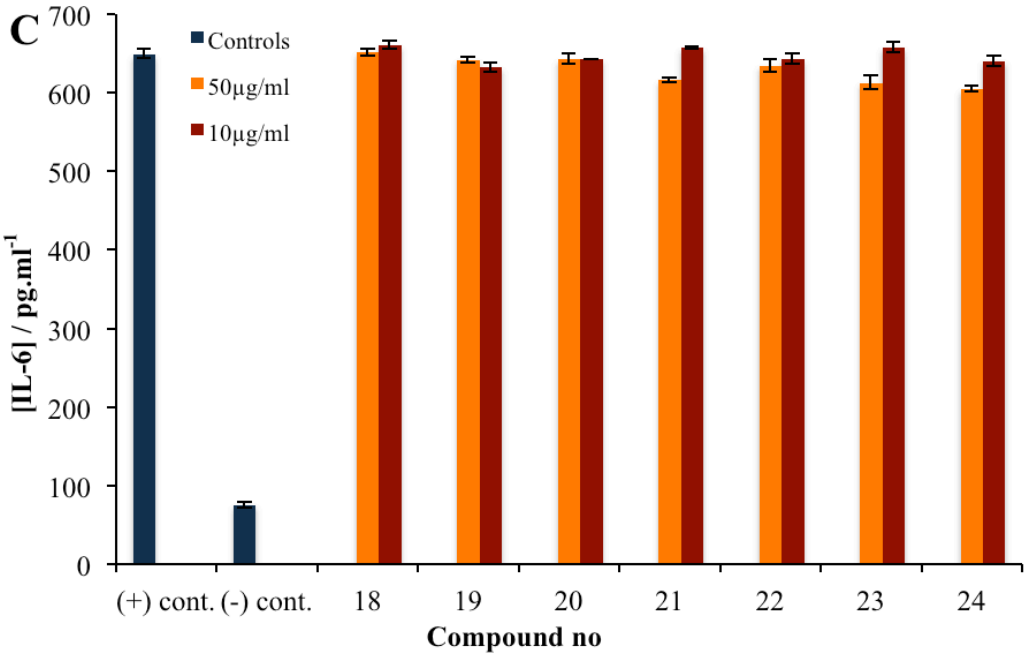


Figure S18. IL-1ß immunoinhibition assay of compounds **18**–**24**.

3. MCP-1

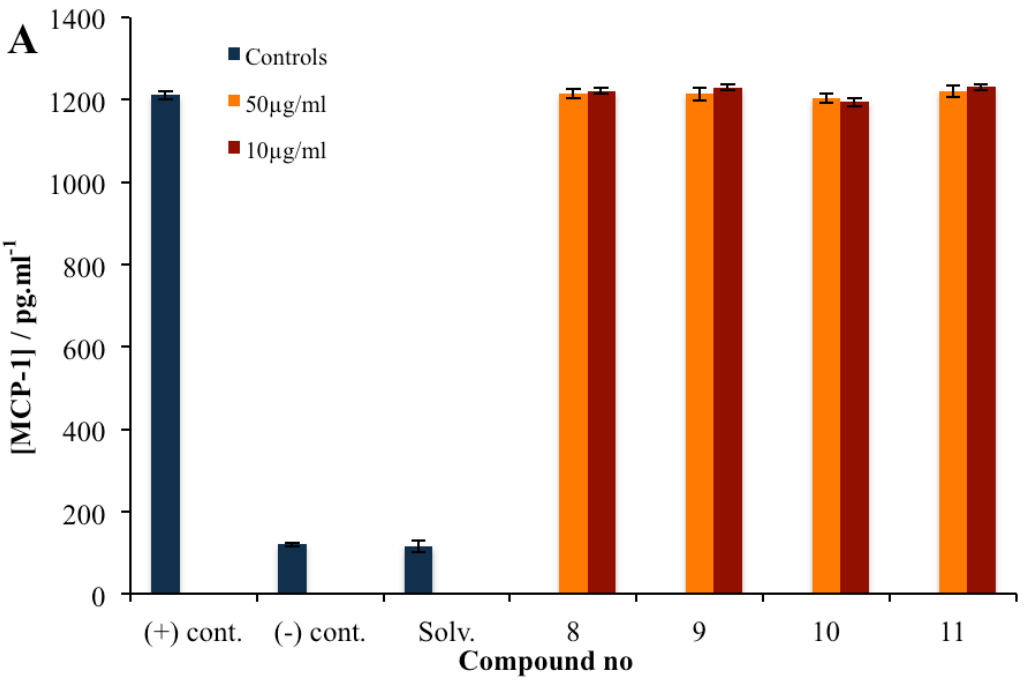


Figure S19. MCP-1 immunoinhibition assay of compounds **8**–**11**.

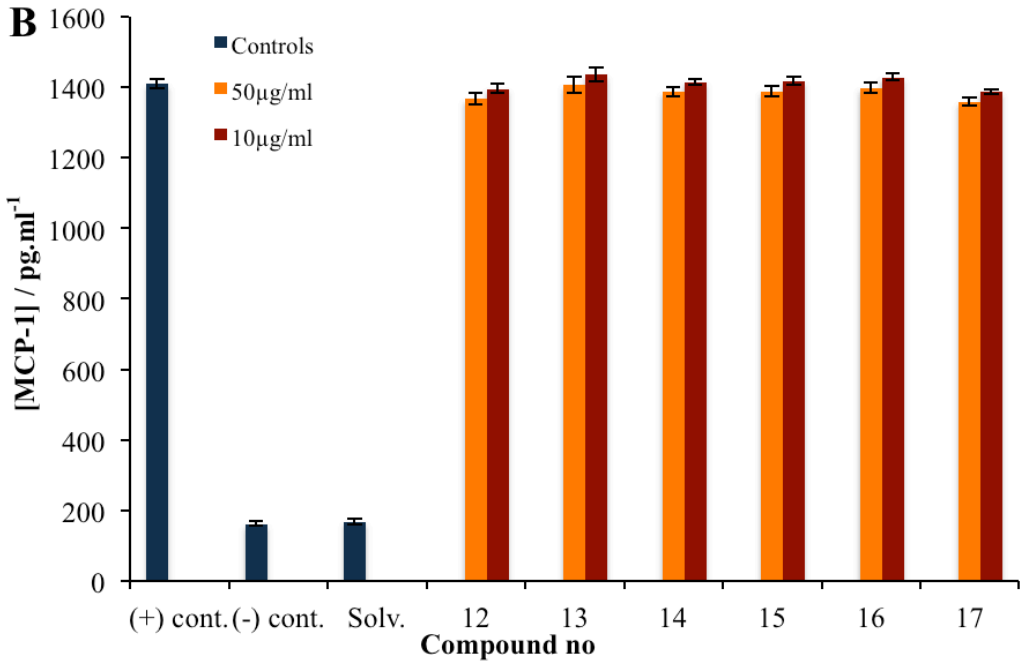


Figure S20. MCP-1 immunoinhibition assay of compounds **12**–**17**.

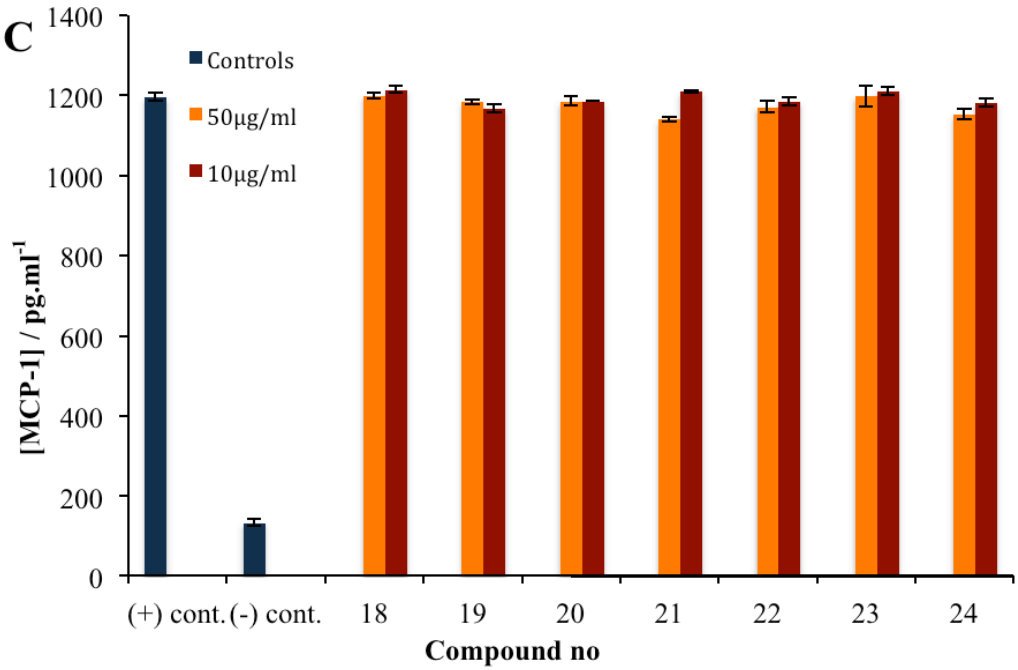


Figure S21. MCP-1 immunoinhibition assay of compounds **18**–**24**.

4. NO

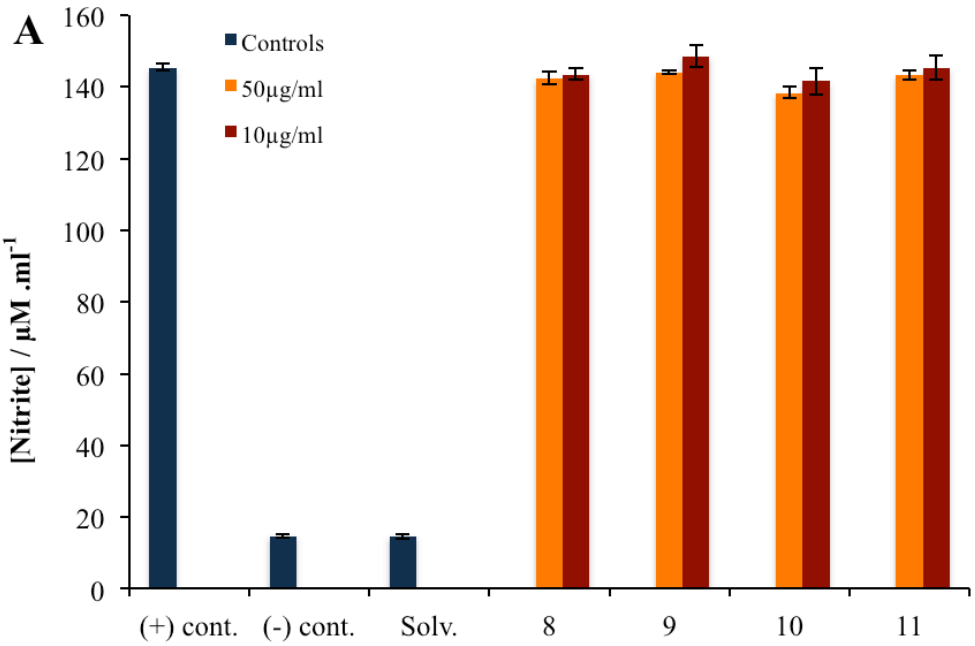


Figure S22. Nitric oxide immunoinhibition assay of compounds **8**–**11**.

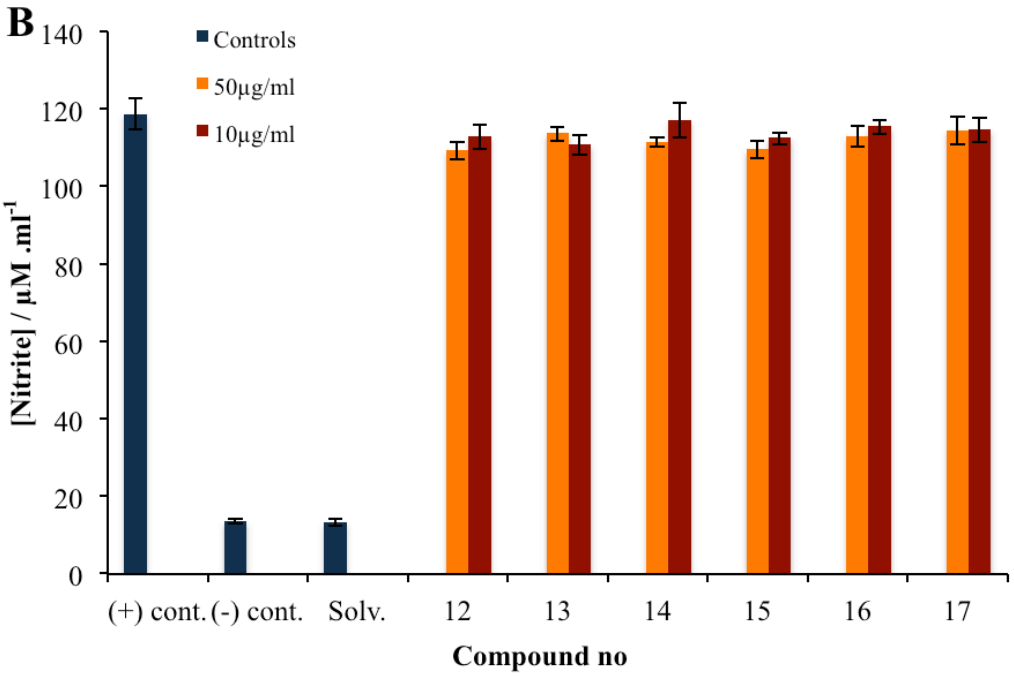


Figure S23. Nitric oxide immunoinhibition assay of compounds **12**–**17**.

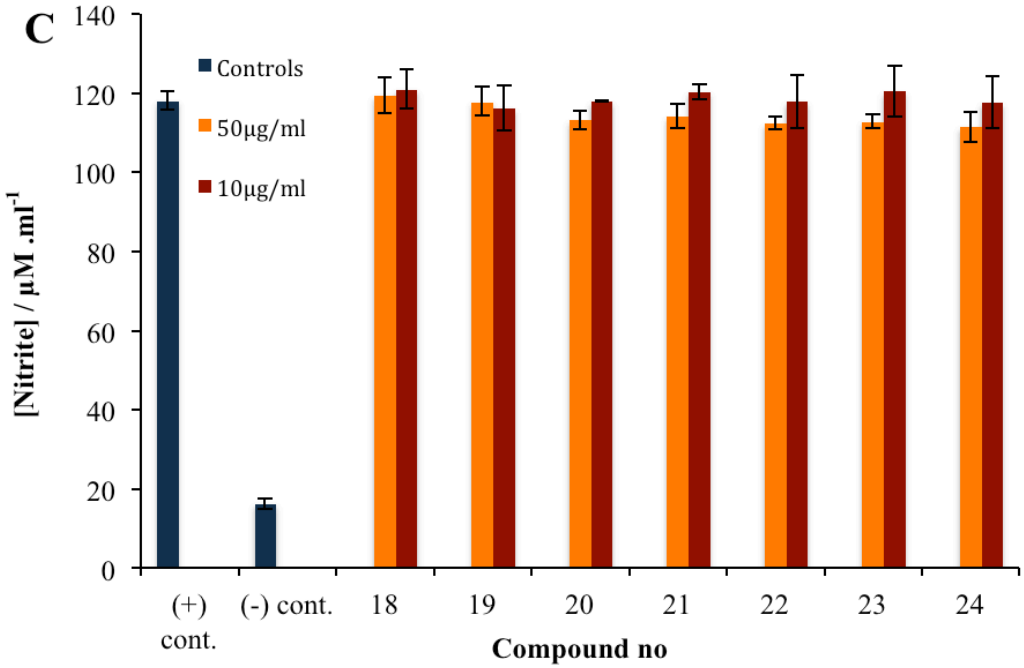


Figure S24. Nitric oxide immunoinhibition assay of compounds **18**–**24**.

Glycolipids 16, 34 and 35.

1. Pam3CSK4 as stimulant

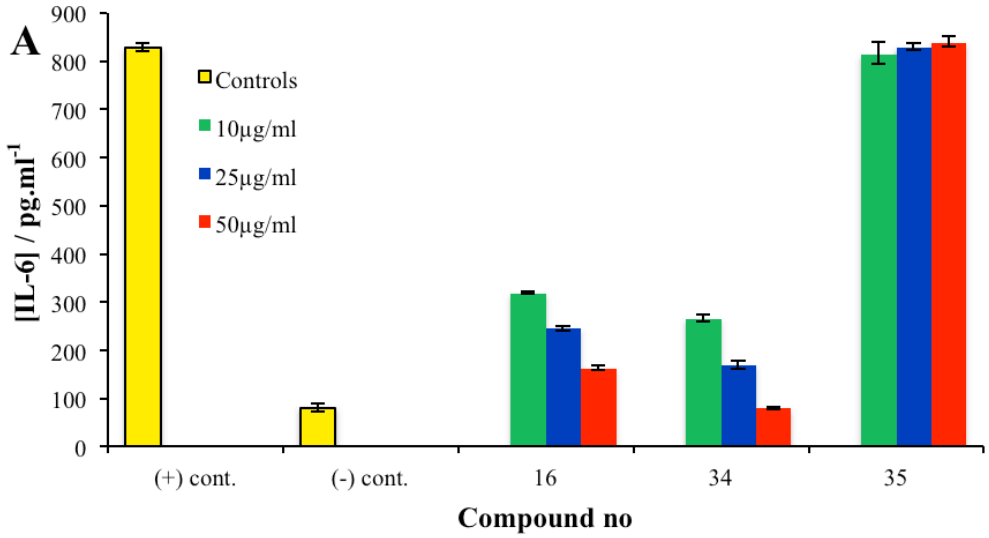


Figure S25. IL-6 immunoinhibition assay of compounds **16, 34** and **35**.

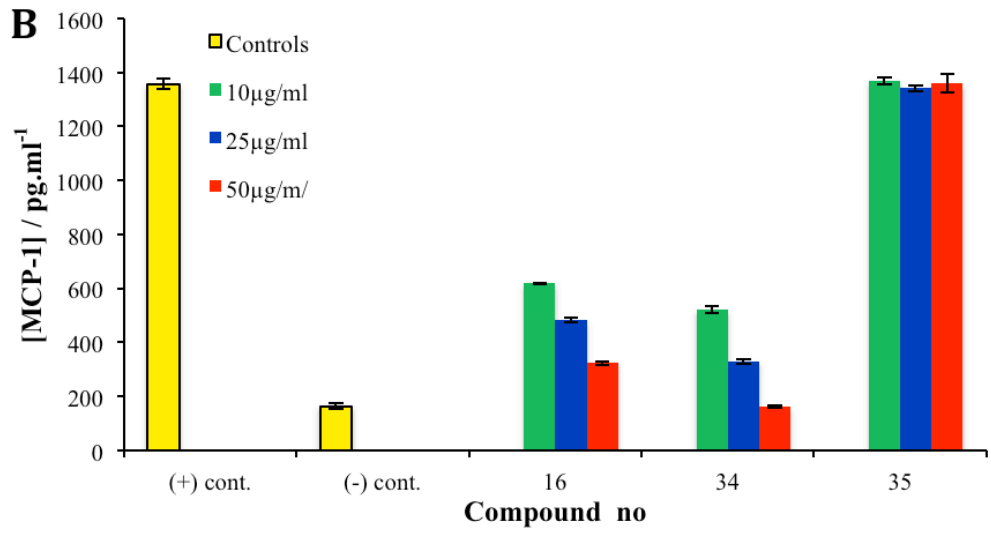


Figure S26. MC-1 immunoinhibition assay of compounds **16, 34** and **35**.

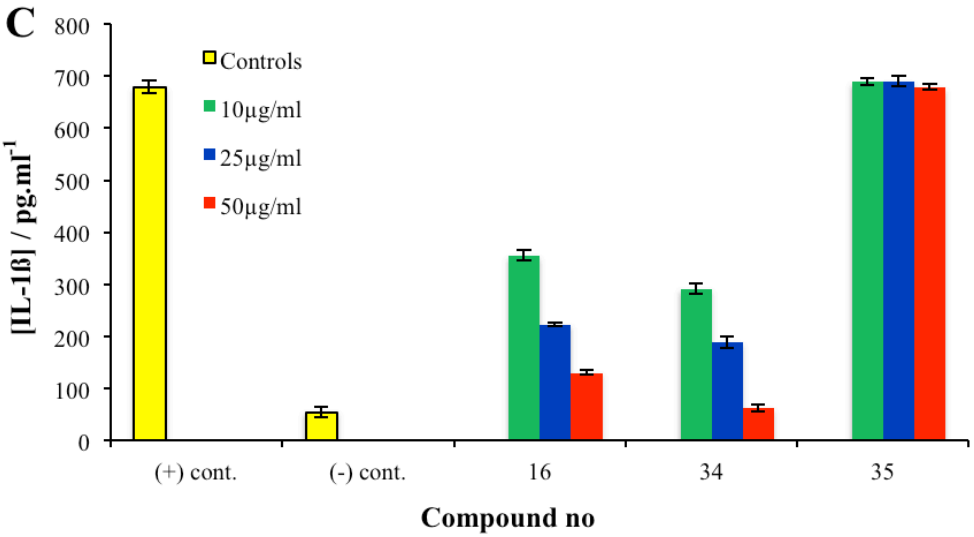


Figure S27. IL-1ß immunoinhibition assay of compounds **16, 34** and **35**.

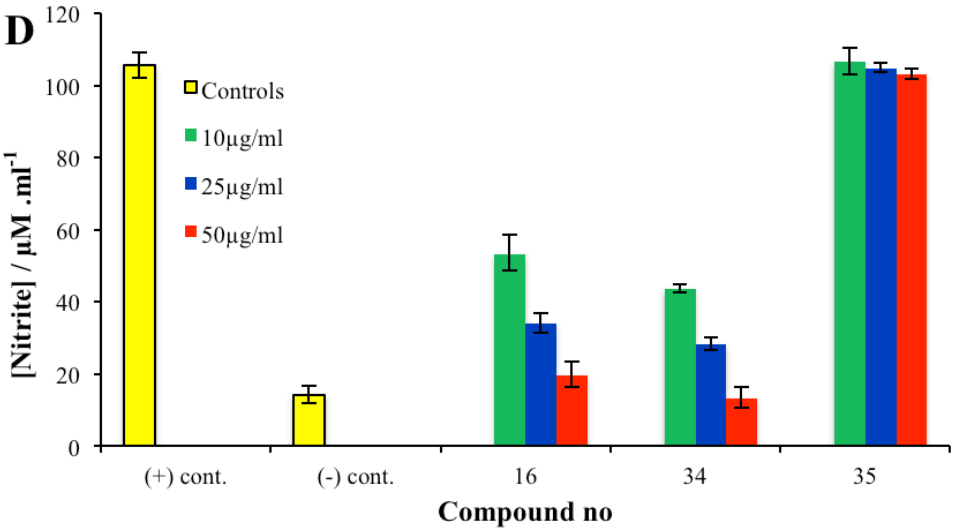


Figure S28. Nitric oxide immunoinhibition assay of compounds **16, 34** and **35**.

2. Ultrapure LPS

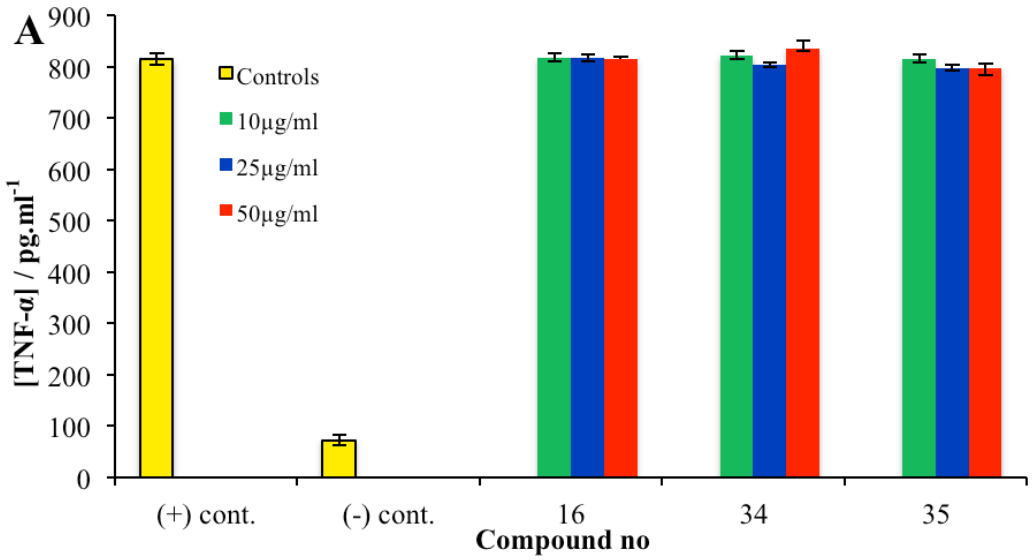


Figure S29. TNF-α immunoinhibition assay of compounds **16, 34** and **35**.

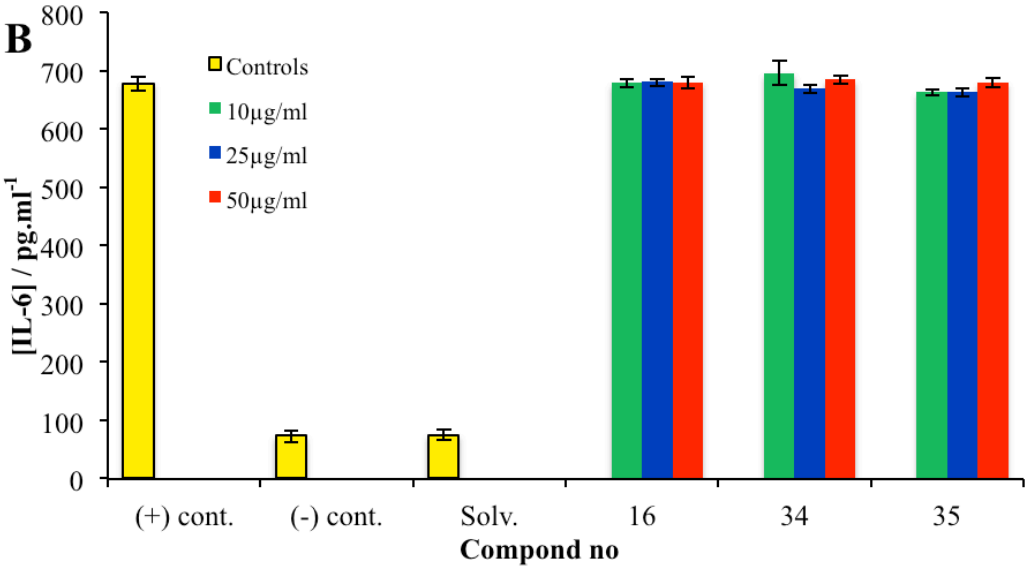


Figure S30. IL-6 immunoinhibition assay of compounds **16, 34** and **35**.

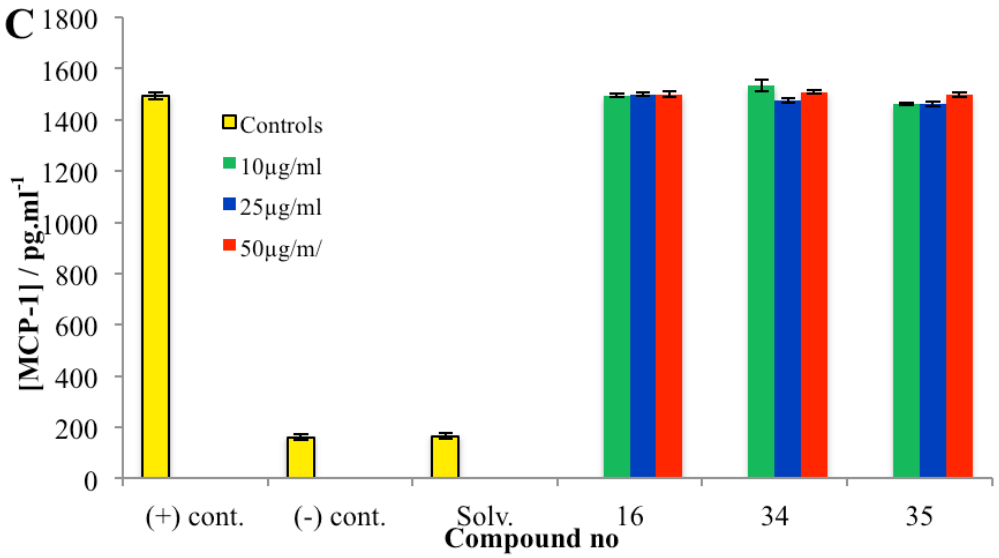


Figure S31. MCP-1 immunoinhibition assay of compounds **16, 34** and **35**.

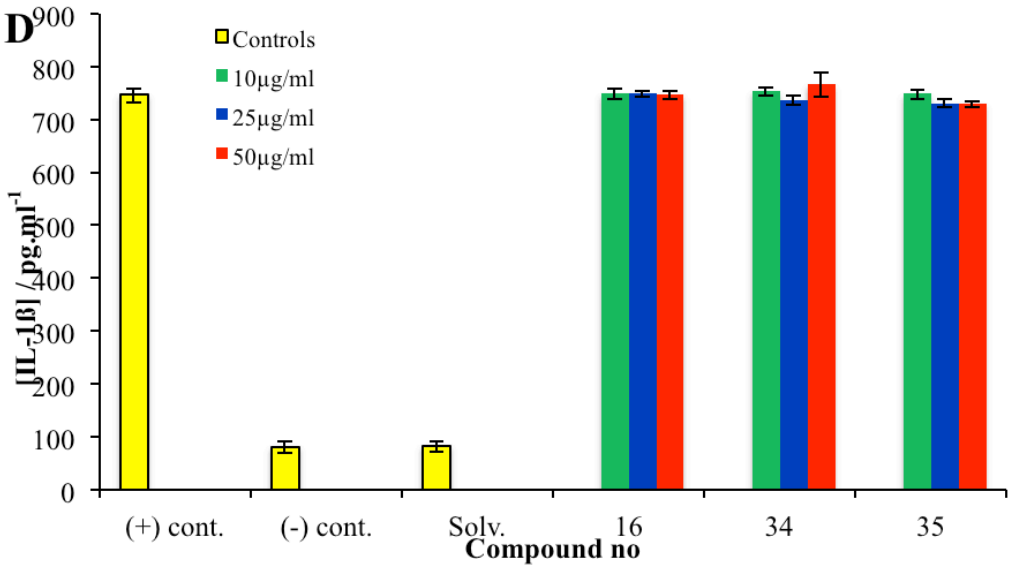


Figure S32. IL-1ß immunoinhibition assay of compounds **16, 34** and **35**.

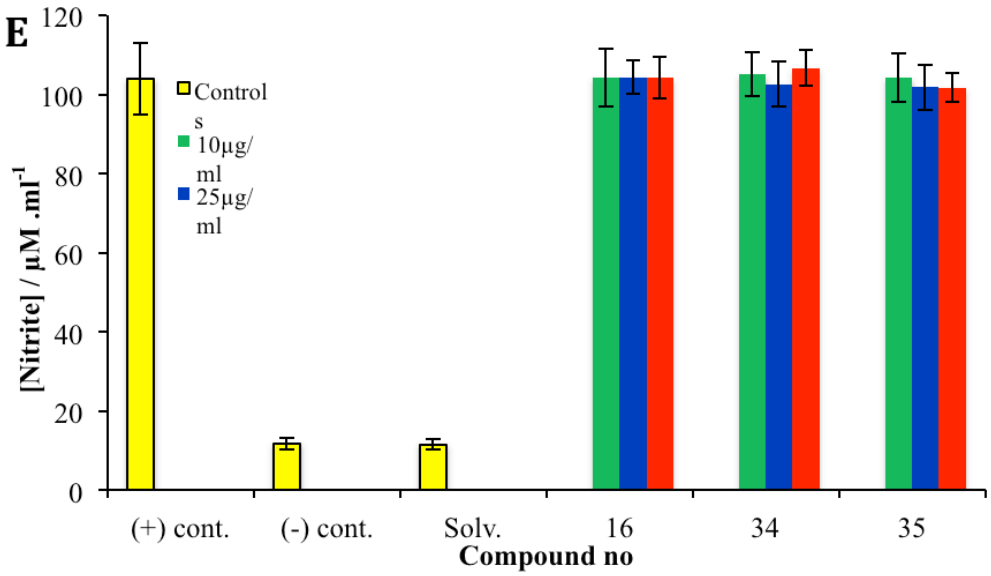
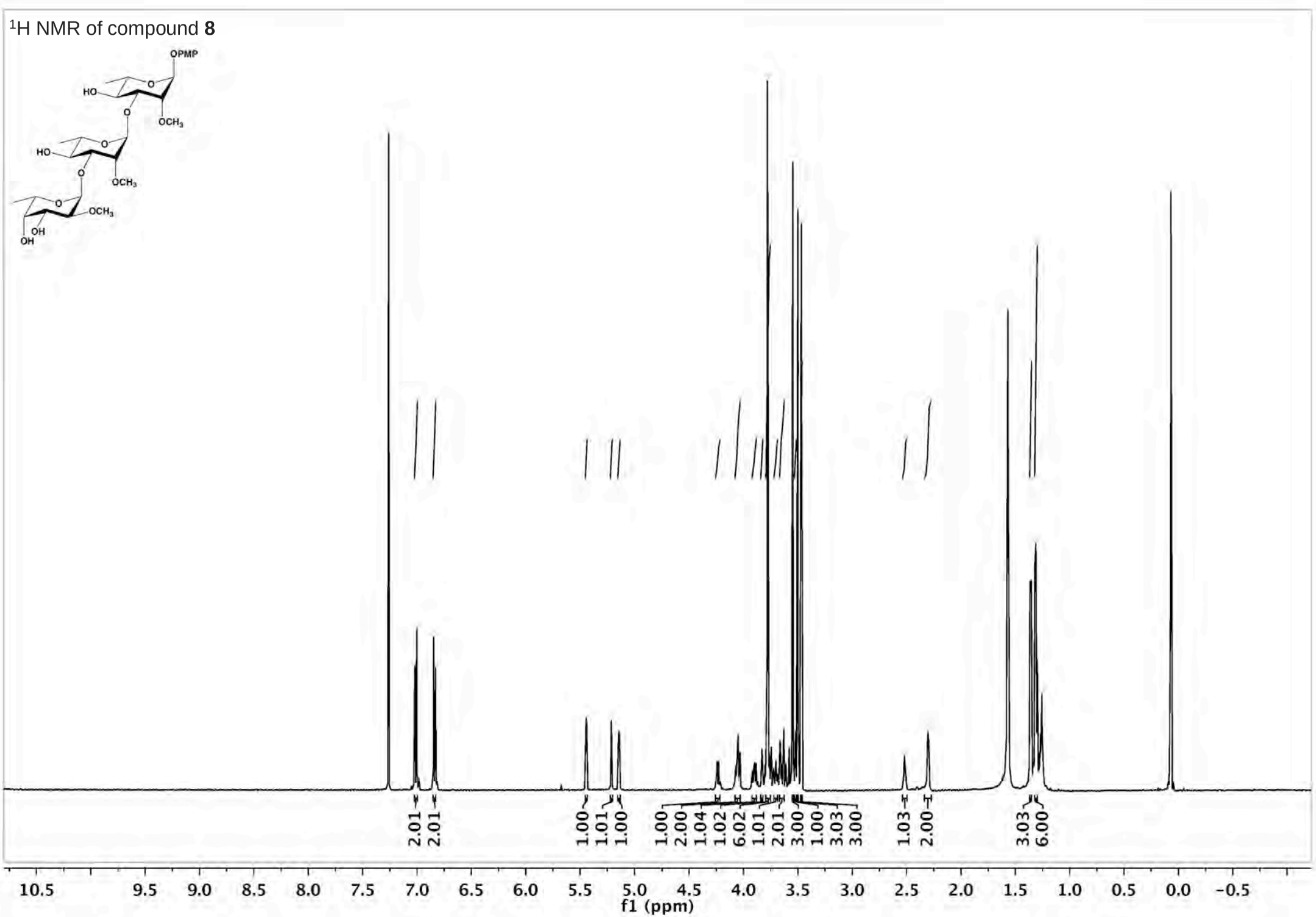
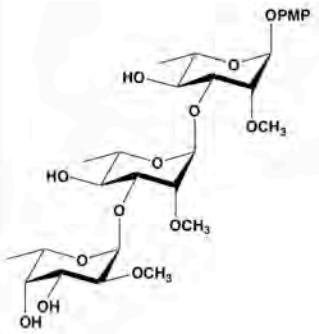


Figure S33. Nitric oxide immunoinhibition assay of compounds **16, 34** and **35**.

^{1}H NMR of compound **8**



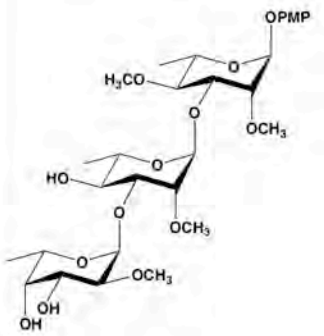
^{13}C NMR of compound **8**

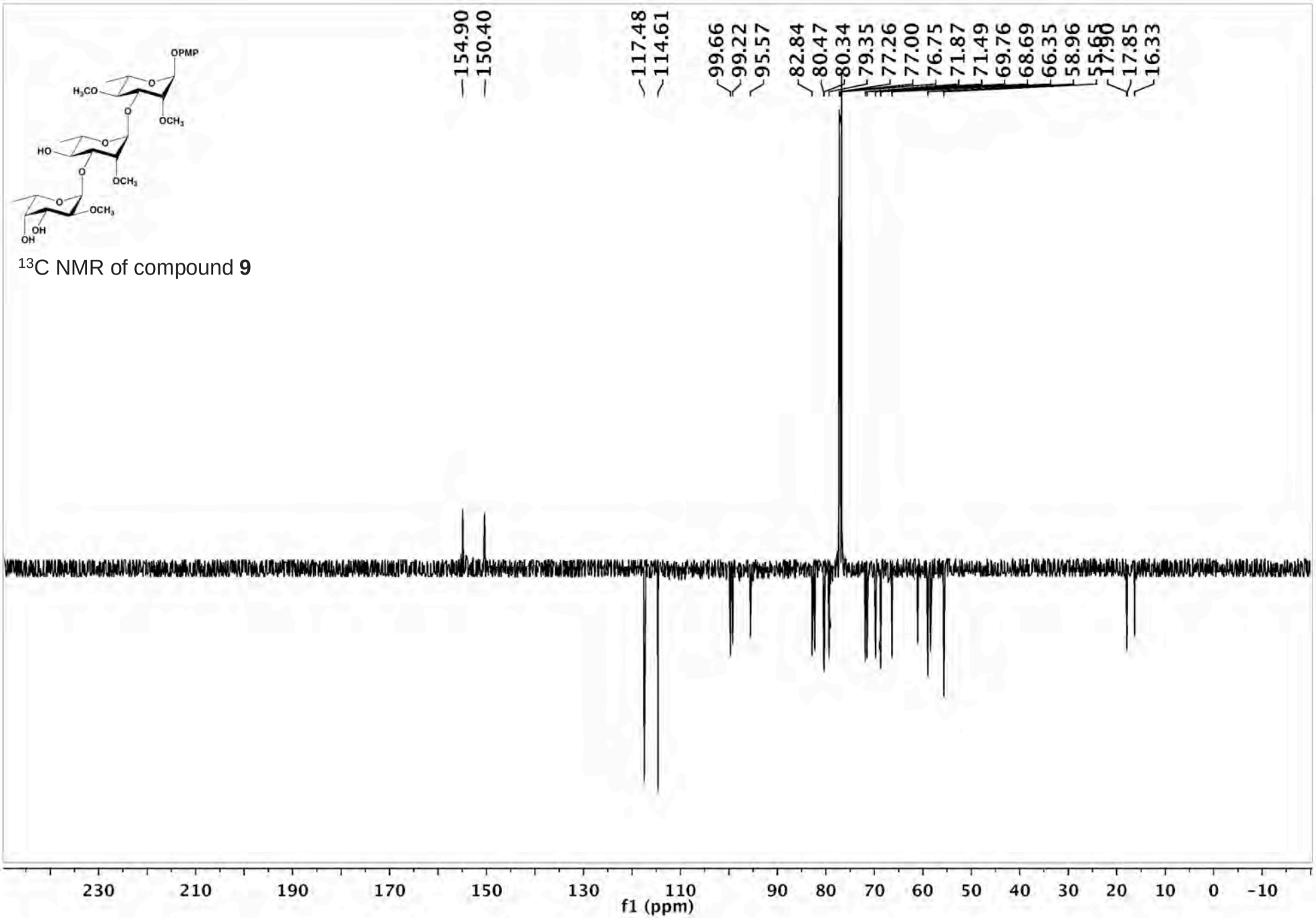


154.96
150.48
117.50
114.65
99.81
99.17
95.53
80.22
80.14
80.07
79.44
77.25
77.00
76.74
71.51
71.51
69.02
69.02
58.58
58.58
55.67
55.67
17.98
17.76
16.35

230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

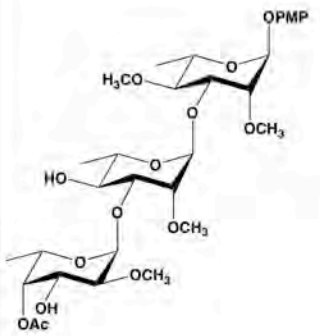
^{1}H NMR of compound **9**



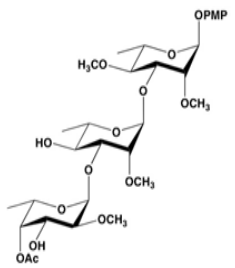


^{13}C NMR of compound **9**

^{1}H NMR of compound **10**



^{13}C NMR of compound **10**

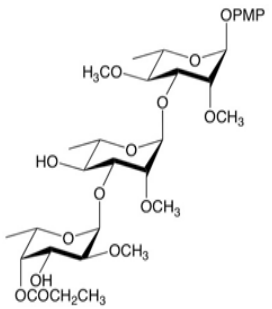


171.32
154.91
150.40
117.48
114.61
100.00
99.19
95.55
83.03
82.28
80.50
80.33
79.37
77.26
77.00
76.75
73.40
71.51
68.67
55.65
55.53
20.83
17.89
17.85
16.34

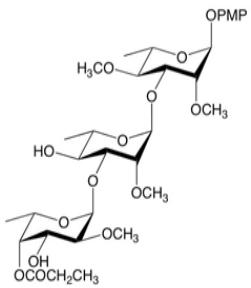
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

^{1}H NMR of compound **11**



^{13}C NMR of compound **11**

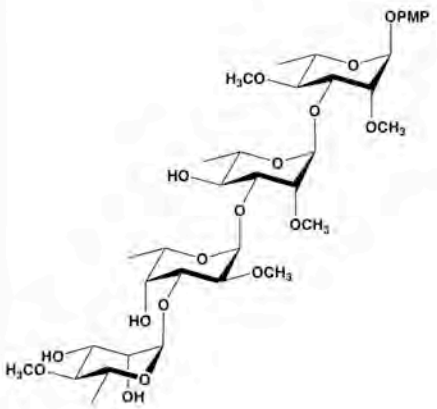


174.83
154.91
150.40
117.48
114.61
100.03
99.16
95.58
82.29
80.51
80.33
79.40
73.22
71.48
68.94
65.57
59.34
58.97
58.46
55.65
27.54
17.89
17.84
16.33
9.30

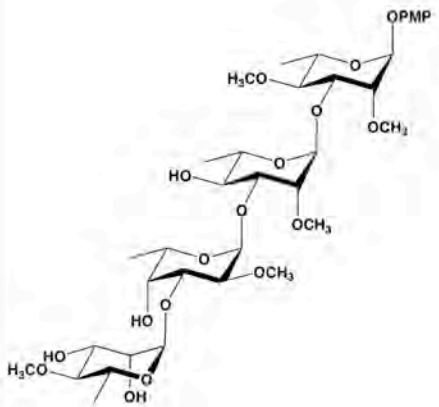
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

^{1}H NMR of compound **12**



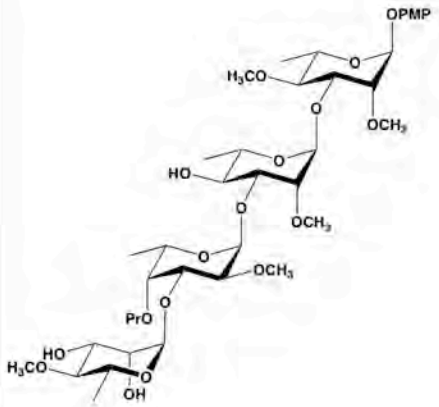
^{13}C NMR of compound **12**



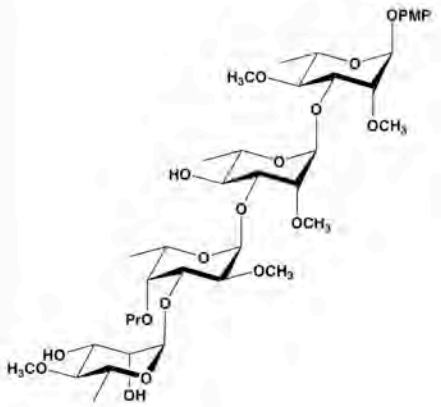
154.90
150.40
117.49
114.61
101.19
100.25
99.12
95.59
83.10
82.26
80.33
77.44
77.26
71.39
71.10
68.69
61.06
59.62
58.98
58.36
55.65
18.01
17.91
17.84
16.29

230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of compound **13**



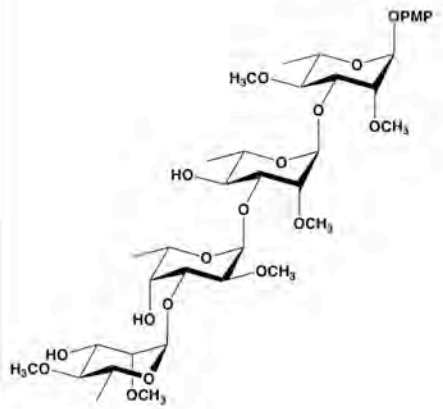
^{13}C NMR of compound **13**



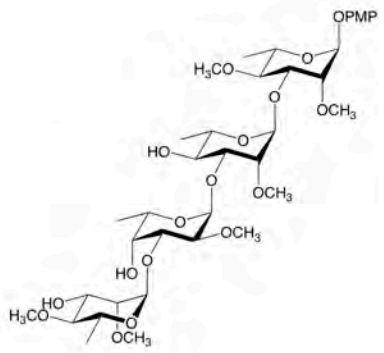
154.89
150.42
117.49
114.61
101.19
100.23
99.26
95.58
82.16
80.74
80.28
77.27
77.02
76.77
71.37
71.34
71.30
68.68
61.10
59.36
58.92
55.65
29.88
18.04
17.94
17.83
16.61
10.78

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **14**



^{13}C NMR of compound **14**

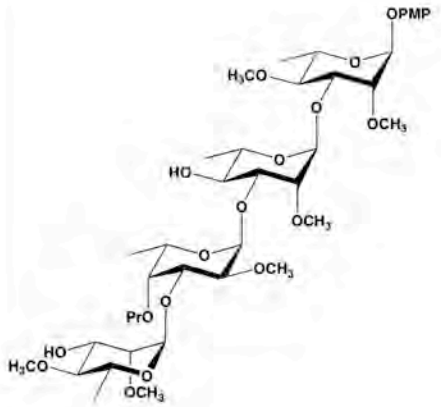


154.9014
150.4062
117.4824
114.6093
100.5830
99.3429
97.8722
95.6071
80.6551
78.8762
77.2606
77.0064
76.7522
71.6297
68.1777
66.2635
61.0444
58.9975
58.7467
58.6202
55.6534
29.6887
17.9595
17.9412
17.8639
16.2646

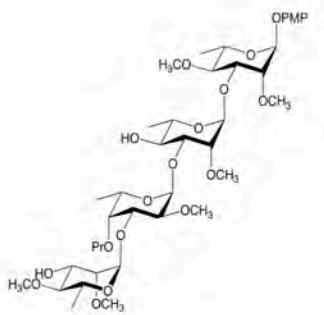
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

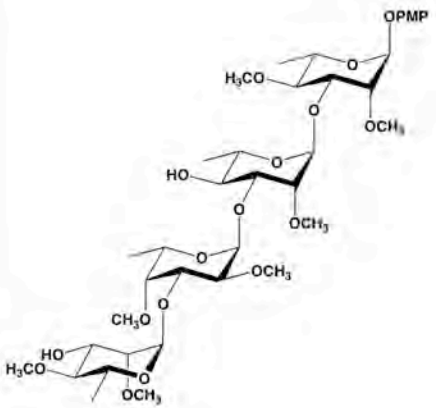
^{1}H NMR of compound **15**



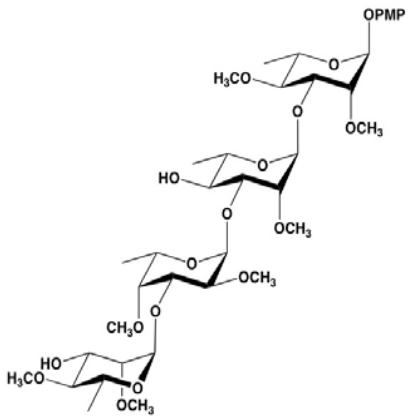
^{13}C NMR of compound **15**



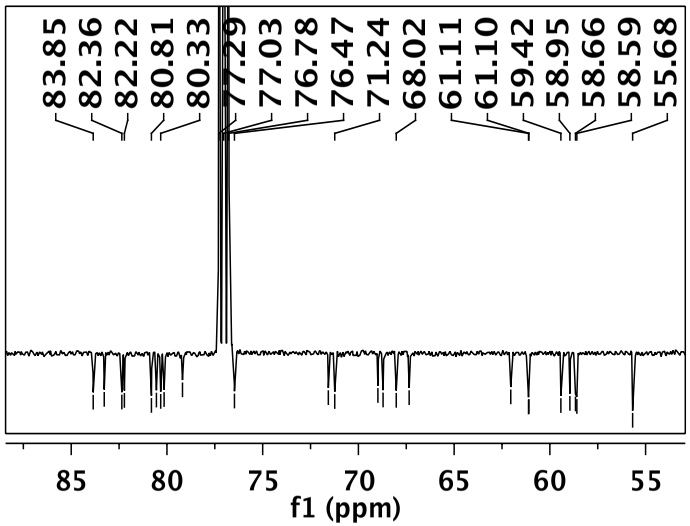
^{1}HNMR of Compound **16**



^{13}C NMR of compound **16**



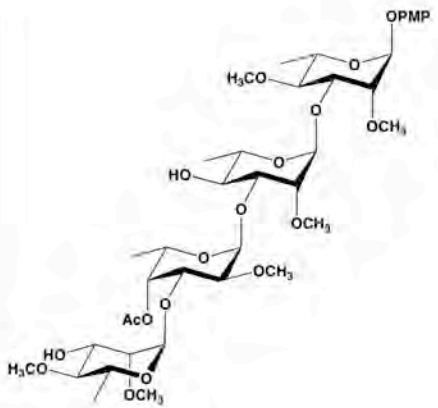
154.92
150.44
117.49
114.63
100.50
99.49
97.71
95.56
83.85
82.36
80.81
80.33
77.29
77.03
76.78
71.24
61.11
61.10
59.42
58.95
58.66
58.59
55.68
18.01
17.91
17.88
16.45

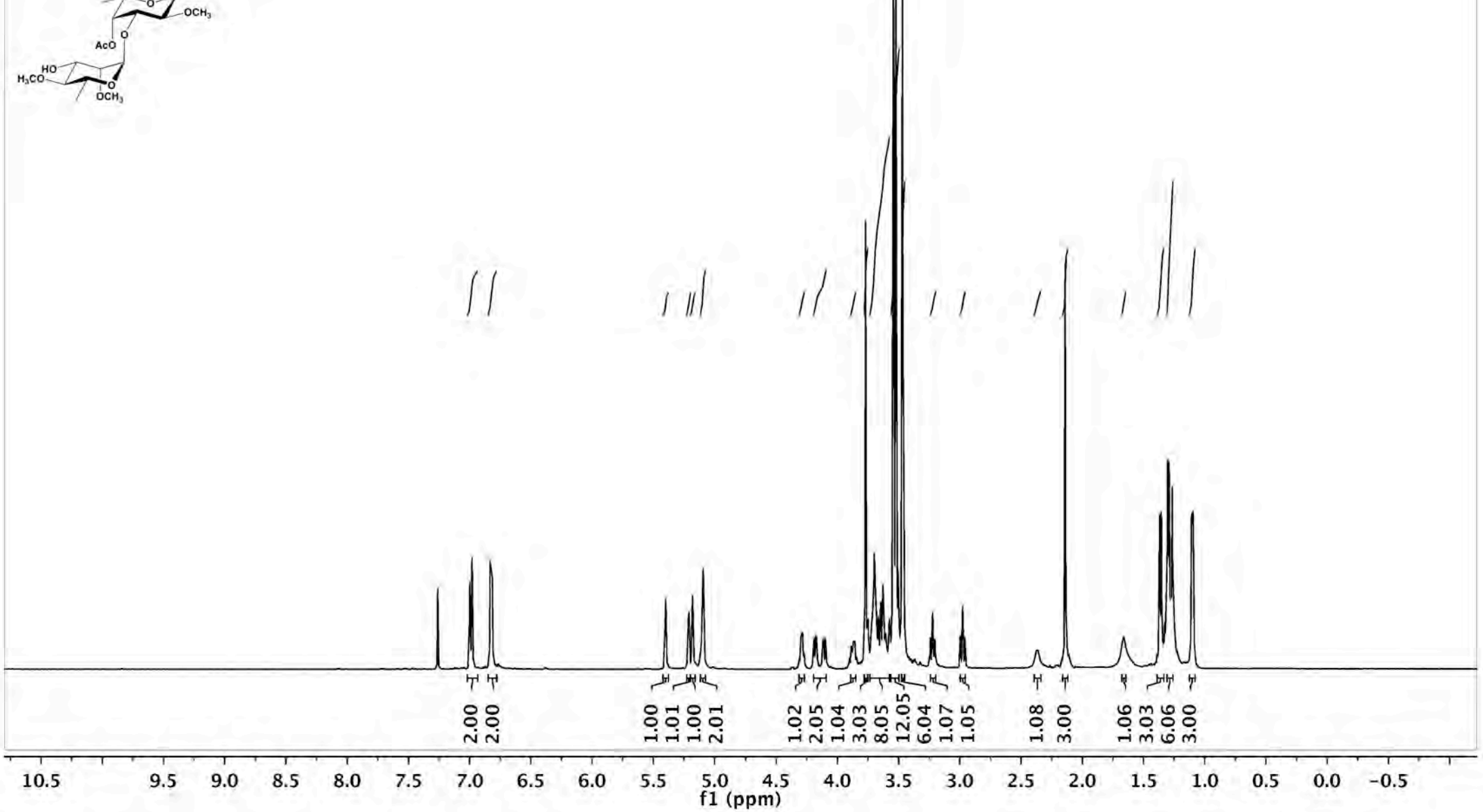


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

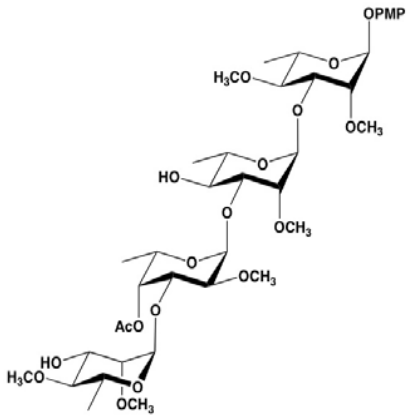
f1 (ppm)

^{1}H NMR of compound **17**

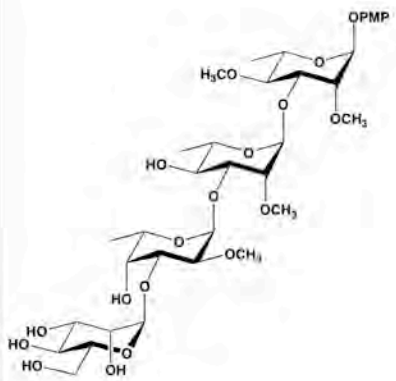




^{13}C NMR of compound **17**



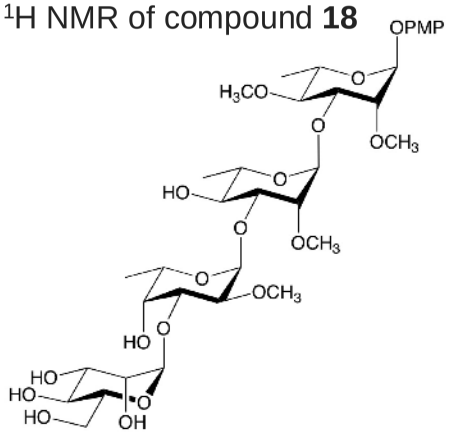
^{13}C NMR of compound **18**



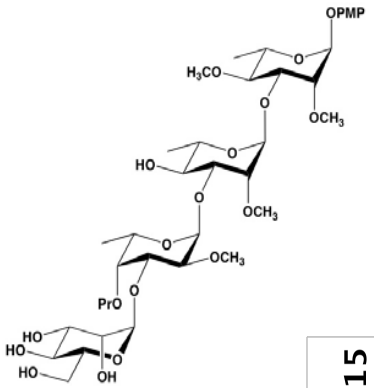
154.91
150.38
117.50
114.61
101.80
100.11
98.86
95.58
82.23
80.32
79.17
77.25
77.00
76.74
71.32
68.68
61.08
59.20
58.98
58.27
55.64
17.98
17.84
16.37

230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of compound **18**



^{13}C NMR of compound **19**



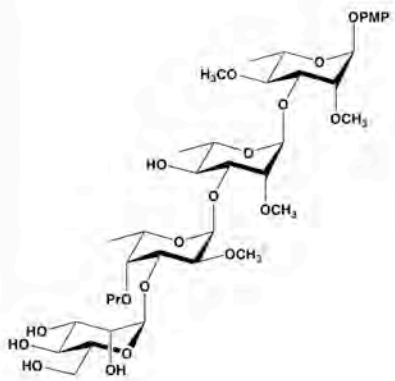
154.90
150.40
117.48
114.61
100.25
99.25
97.75
95.54
80.57
80.53
80.29
77.27
77.02
76.77
68.68
61.09
59.13
58.90
58.49
55.65
23.52
17.91
17.84
16.51
10.77

82.15
80.57
80.53
80.29
80.24
79.33
77.27
77.02
76.77
71.47
68.68
67.54
61.09
59.13
58.90
58.65
58.49
55.65

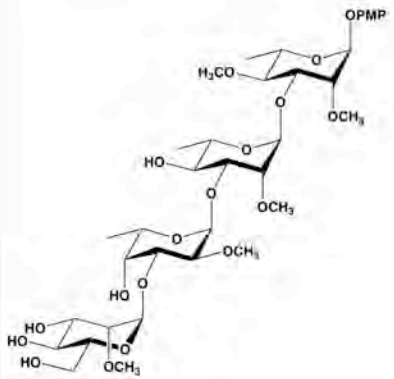
80 75 70 65 60 55
f1 (ppm)

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of compound **19**



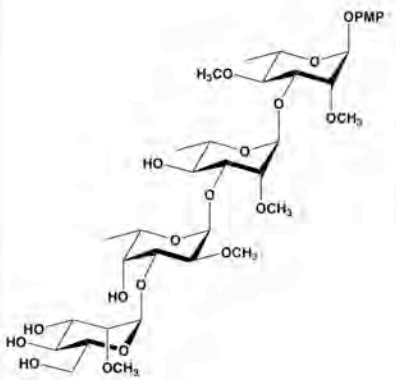
^{13}C NMR of compound **20**

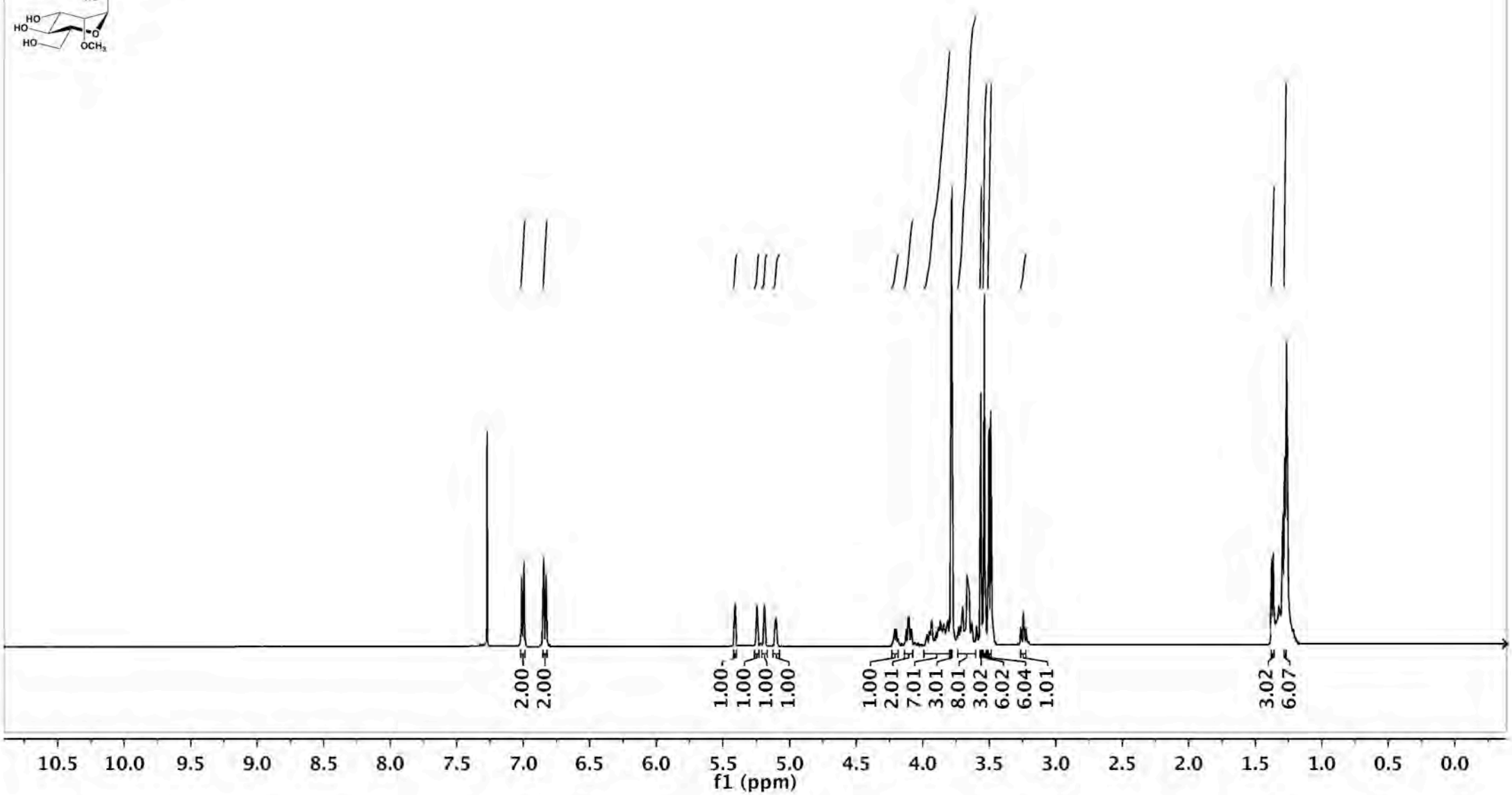


154.91
150.41
117.49
114.62
100.71
99.30
97.80
95.62
80.34
77.25
77.00
76.75
71.69
71.62
71.46
68.71
61.05
59.01
58.82
58.63
55.66
17.87
17.85
16.33

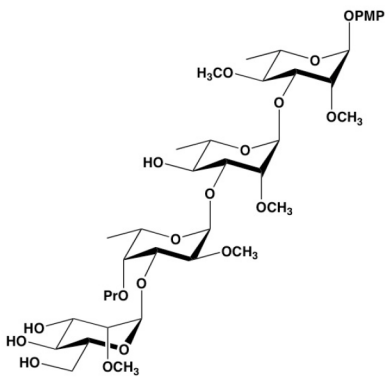
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **20**





^{13}C NMR of compound **21**

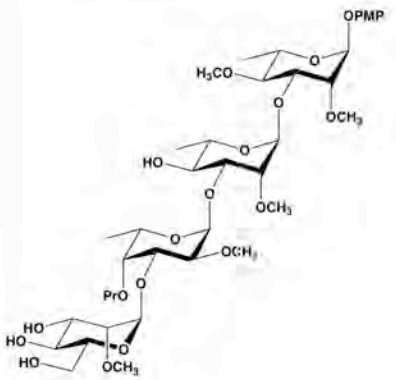


154.90
150.40
117.48
114.61
100.25
99.25
97.75
95.55
80.57
80.53
80.29
77.27
77.02
76.77
68.69
61.09
59.13
58.90
58.49
55.65
55.52
17.91
17.84
16.51
10.77

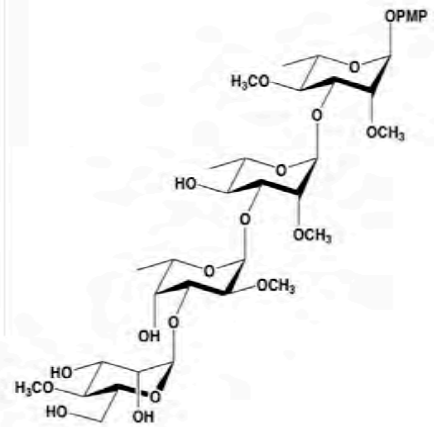
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

^{1}H NMR of compound **21**



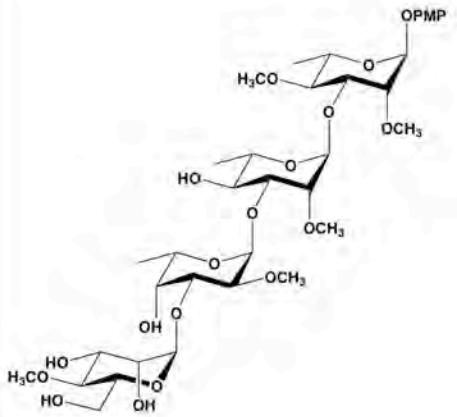
^{13}C NMR of compound **22**



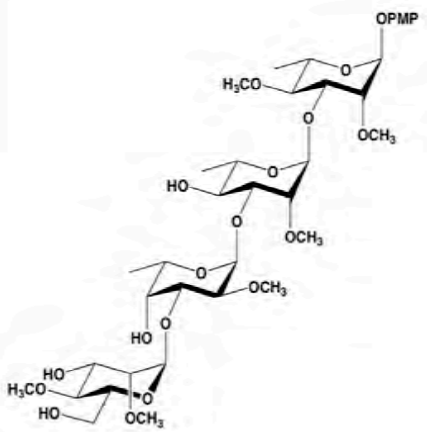
154.91
150.40
117.49
114.62
101.03
100.14
98.89
95.58
82.76
82.23
80.33
79.21
78.51
77.26
77.00
76.75
72.69
71.08
68.98
68.70
61.09
58.97
58.16
55.66
17.95
17.84
16.32

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **22**



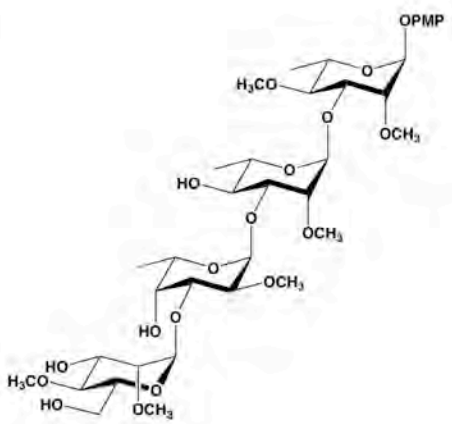
^{13}C NMR of compound **23**



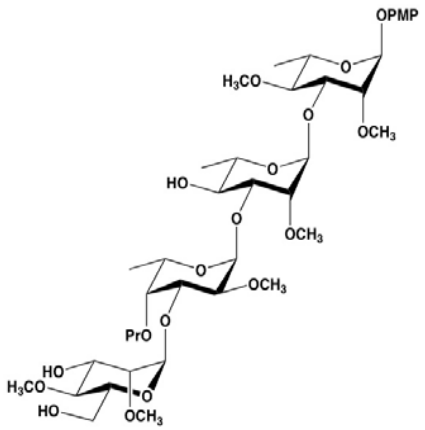
154.90
150.40
117.49
114.61
100.73
99.32
97.72
95.62
82.30
80.63
80.60
78.41
78.33
77.26
77.01
76.75
72.31
71.69
71.56
71.42
68.71
59.92
59.01
58.81
58.63
55.66
17.87
17.85
16.33

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **23**



^{13}C NMR of compound **24**

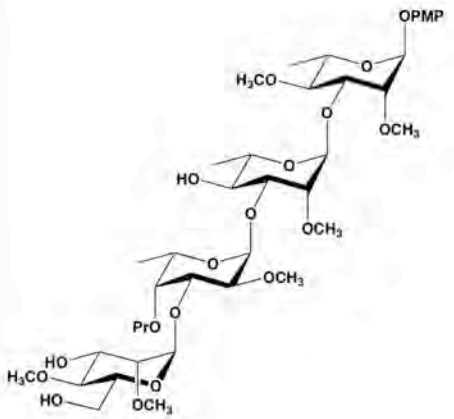


154.90
150.41
117.47
114.61
100.38
99.39
97.52
95.54
82.17
80.60
80.51
80.37
80.29
78.32
77.26
77.00
76.75
71.36
68.69
59.27
58.90
58.58
55.65
55.52
23.52
17.90
17.85
16.51
10.79

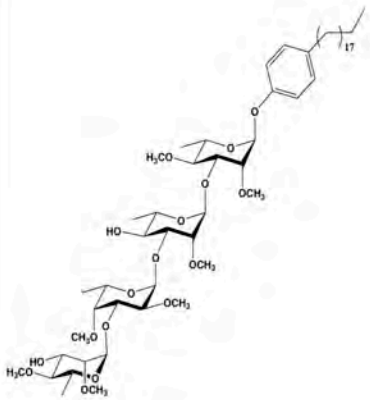
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

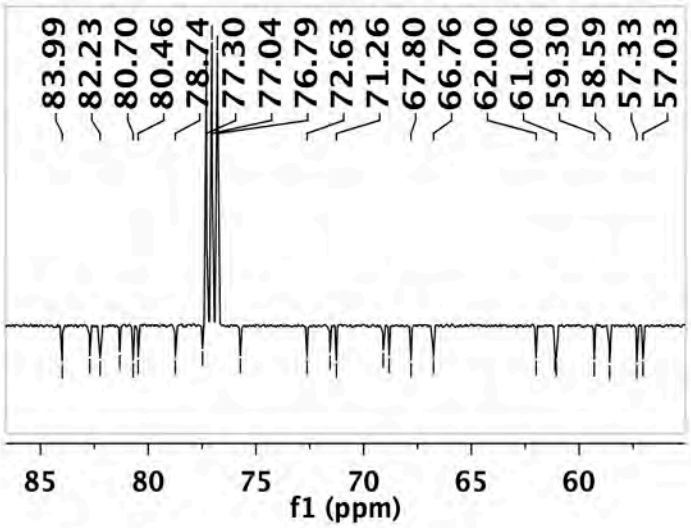
f1 (ppm)

^{1}H NMR of compound **24**



^{13}C NMR of compound **34**

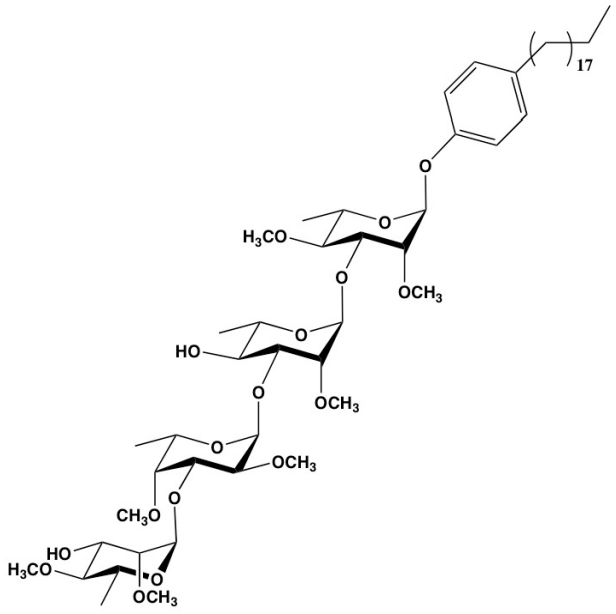




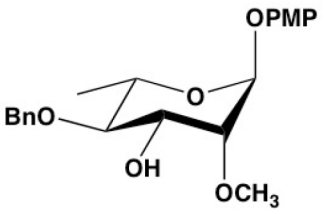
154.48
136.81
129.31
128.39
126.29
116.13
101.40
97.70
97.61
95.34
83.99
80.70
77.30
77.04
76.79
71.26
67.80
58.59
57.33
31.94
29.71
29.67
29.63
29.55
29.38
29.33
22.71
18.04
17.87
17.85
16.17
14.14

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

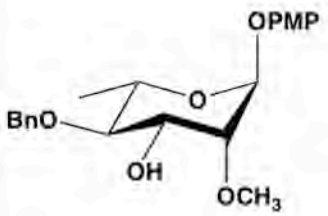
^{1}H NMR of compound **34**



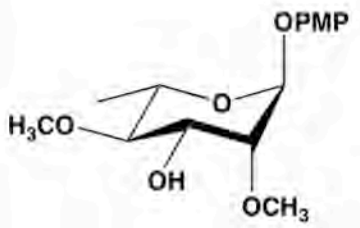
^{13}C NMR of compound **S1**



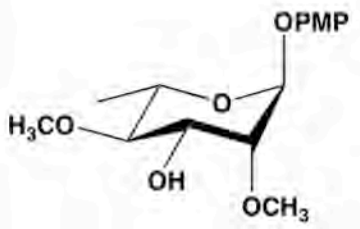
^{1}H NMR of compound **S1**



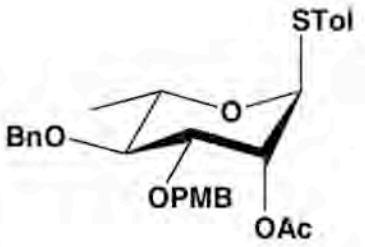
^{13}C NMR of compound **S2**



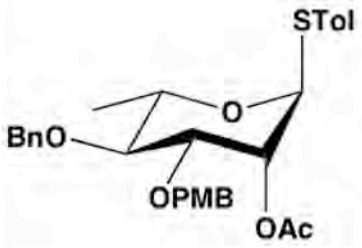
^{1}H NMR of compound **S2**



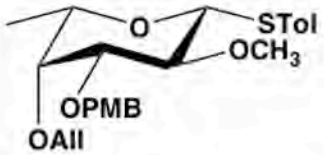
^{13}C NMR of compound **S3**



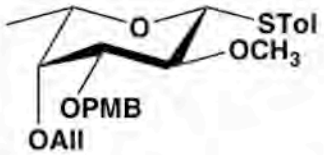
^{1}H NMR of compound **S3**



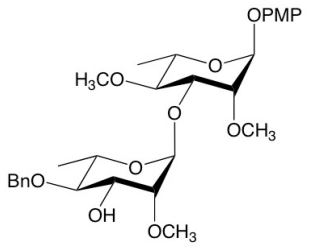
^{13}C NMR of compound **25**



^{1}H NMR of compound **25**



^{13}C NMR of compound **26**

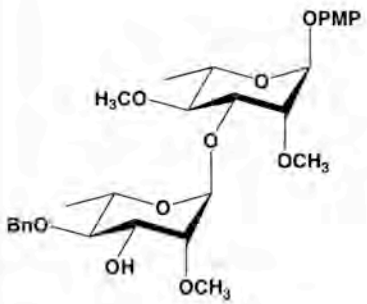


154.9285
150.4358
138.5412
138.3703
128.4343
128.0122
127.1290
117.5496
114.6419
98.6416
95.8213
80.9933
80.3885
77.3401
77.0856
76.8301
75.1086
59.0840
58.5667
55.6689
18.1615
18.0210

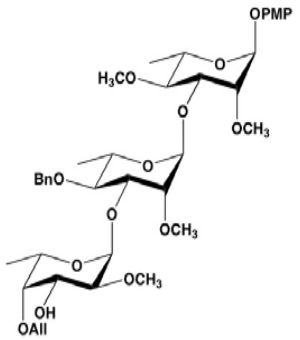
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

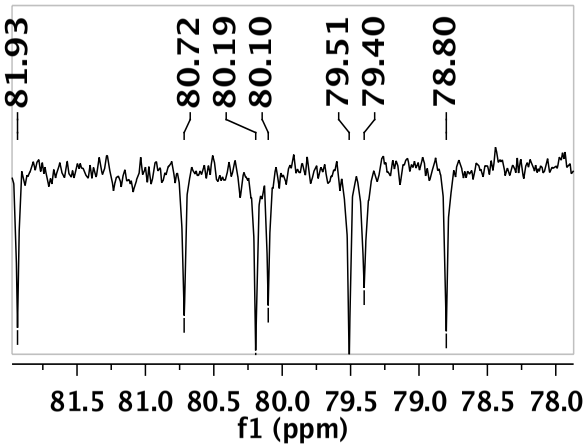
^{1}H NMR of compound **26**

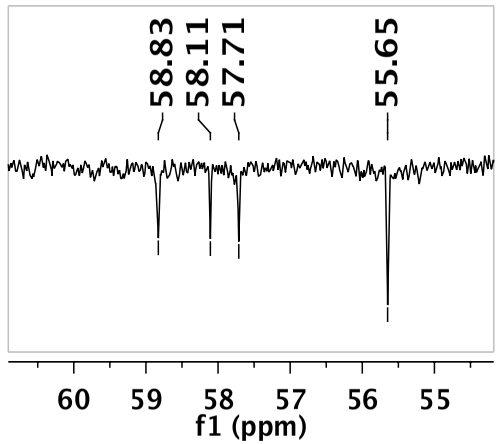


^{13}C NMR of compound **27**



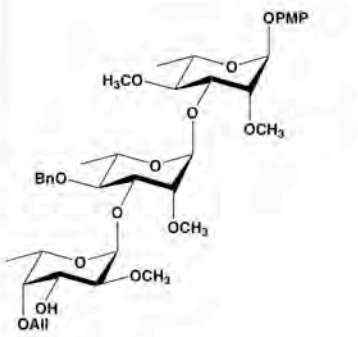
154.89 150.47 139.09 134.97 128.17 127.41 127.27 117.48 117.44 114.61 99.13 98.55 95.55 81.93 80.72 80.19 80.10 79.51 78.80 77.29 77.03 76.78 74.86 70.18 68.71 68.68 66.52 61.24 55.65 18.25 17.84 16.93



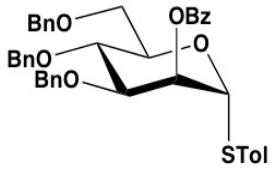


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **27**



^{13}C NMR of compound **S5**

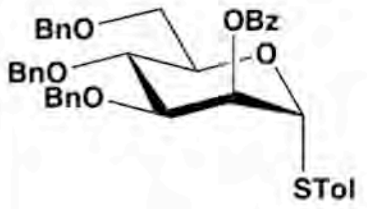


165.60
162.37
134.54
132.40
130.58
129.96
129.85
128.89
128.41
128.40
128.35
128.32
128.17
128.00
127.53
86.70
78.60
77.30
77.05
76.79
75.35
74.60
73.40
72.62
71.69
70.65
69.13
21.12

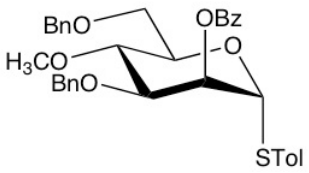
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

^{1}H NMR of compound **S5**



^{13}C NMR of compound **S6**

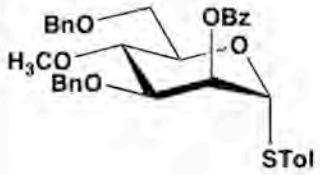


165.5952
133.1432
132.3640
129.9328
129.8402
128.3815
128.3666
128.2974
127.9915
127.7247
127.4741
127.4409
86.6400
78.3957
77.3070
77.0534
76.7970
76.3102
73.4134
72.6496
71.6577
70.6787
69.2345
61.0585
21.1179

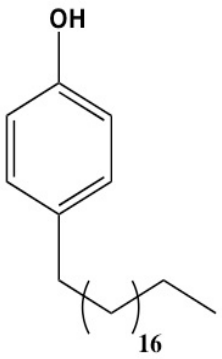
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2

f1 (ppm)

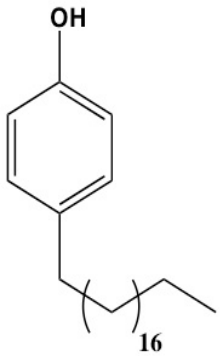
^{1}H NMR of compound **S6**

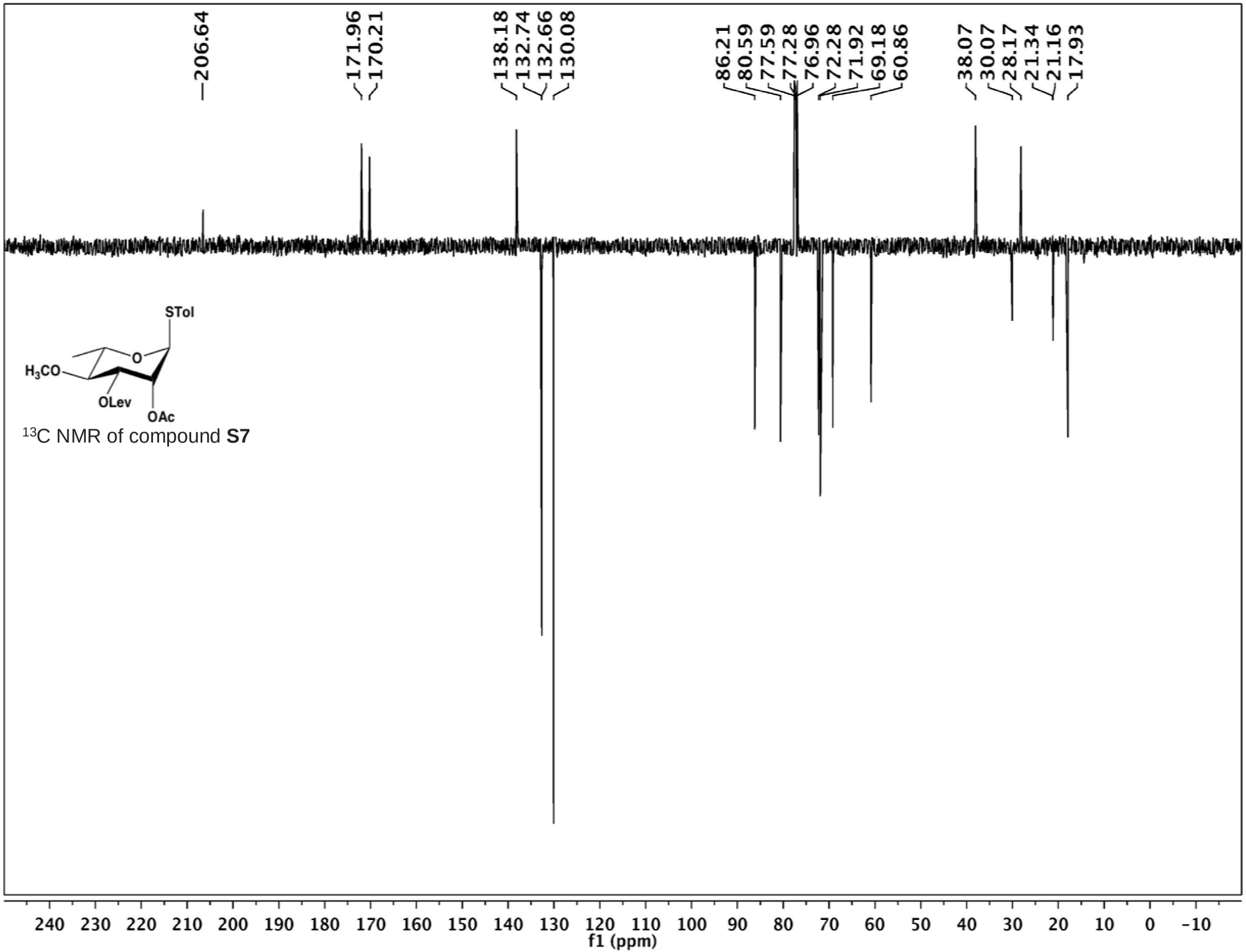


^{13}C NMR of compound **35**



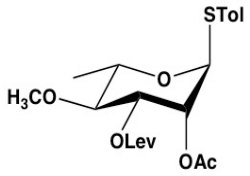
^{1}H NMR of compound **35**

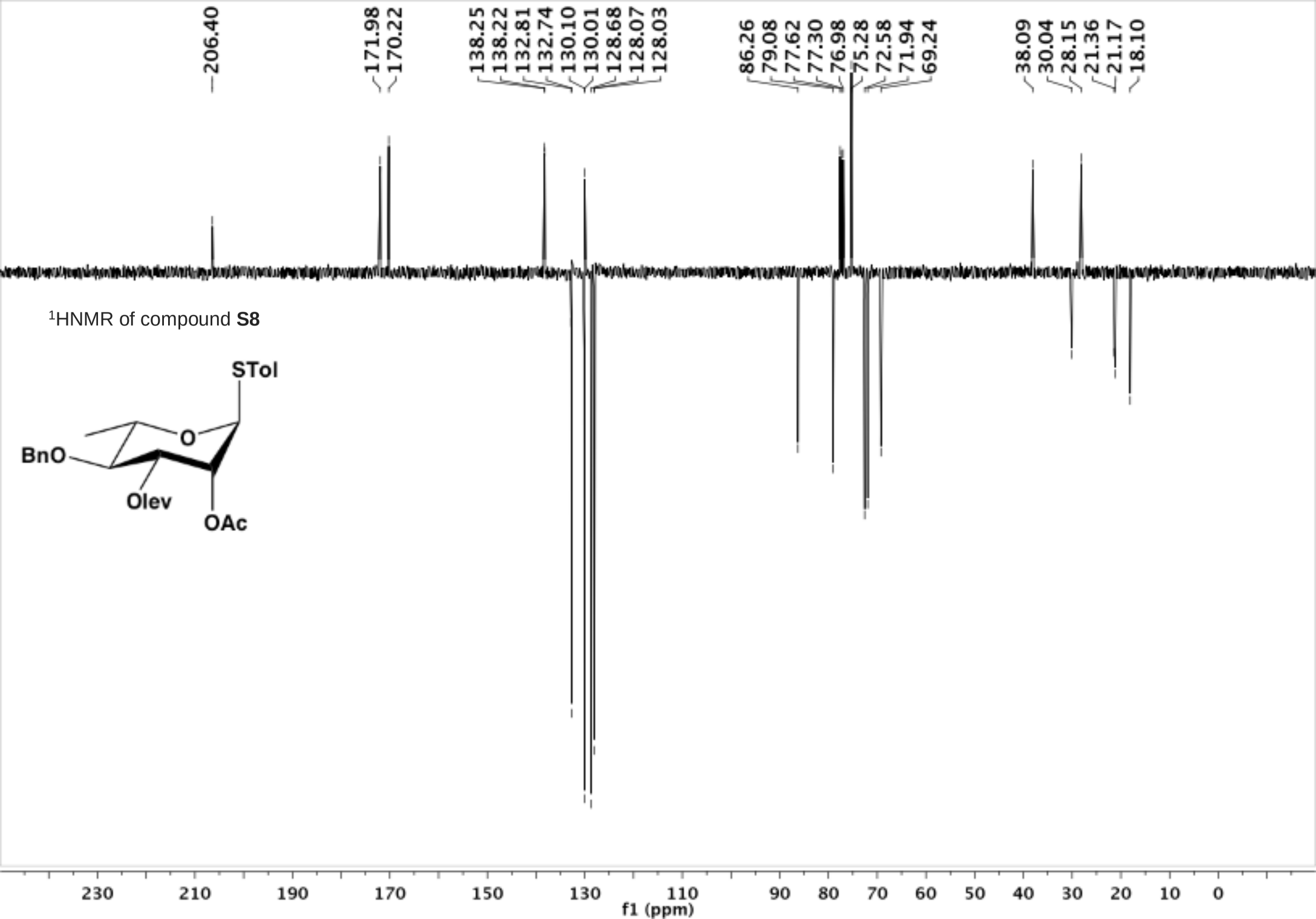




^{13}C NMR of compound **S7**

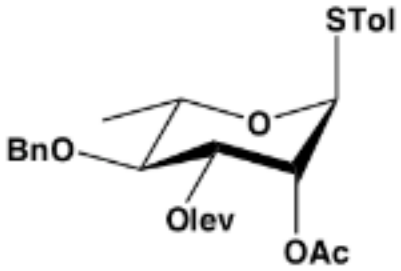
^{1}H NMR of compound **S7**



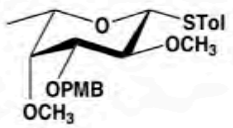


^{1}HNMR of compound **S8**

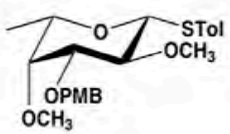
^{1}HNMR of compound **S8**



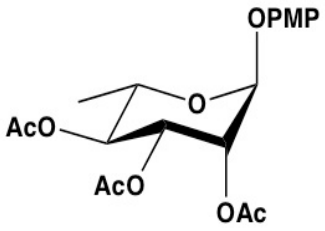
^{13}C NMR of compound **S9**



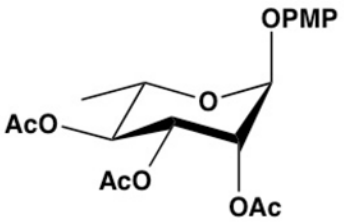
^{1}H NMR of compound **S9**



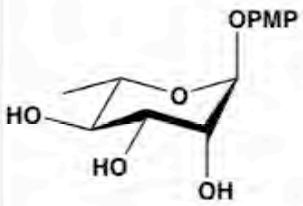
^{13}C NMR of Compound **S10**

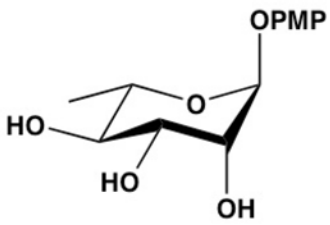


^{1}H NMR of compound **S10**

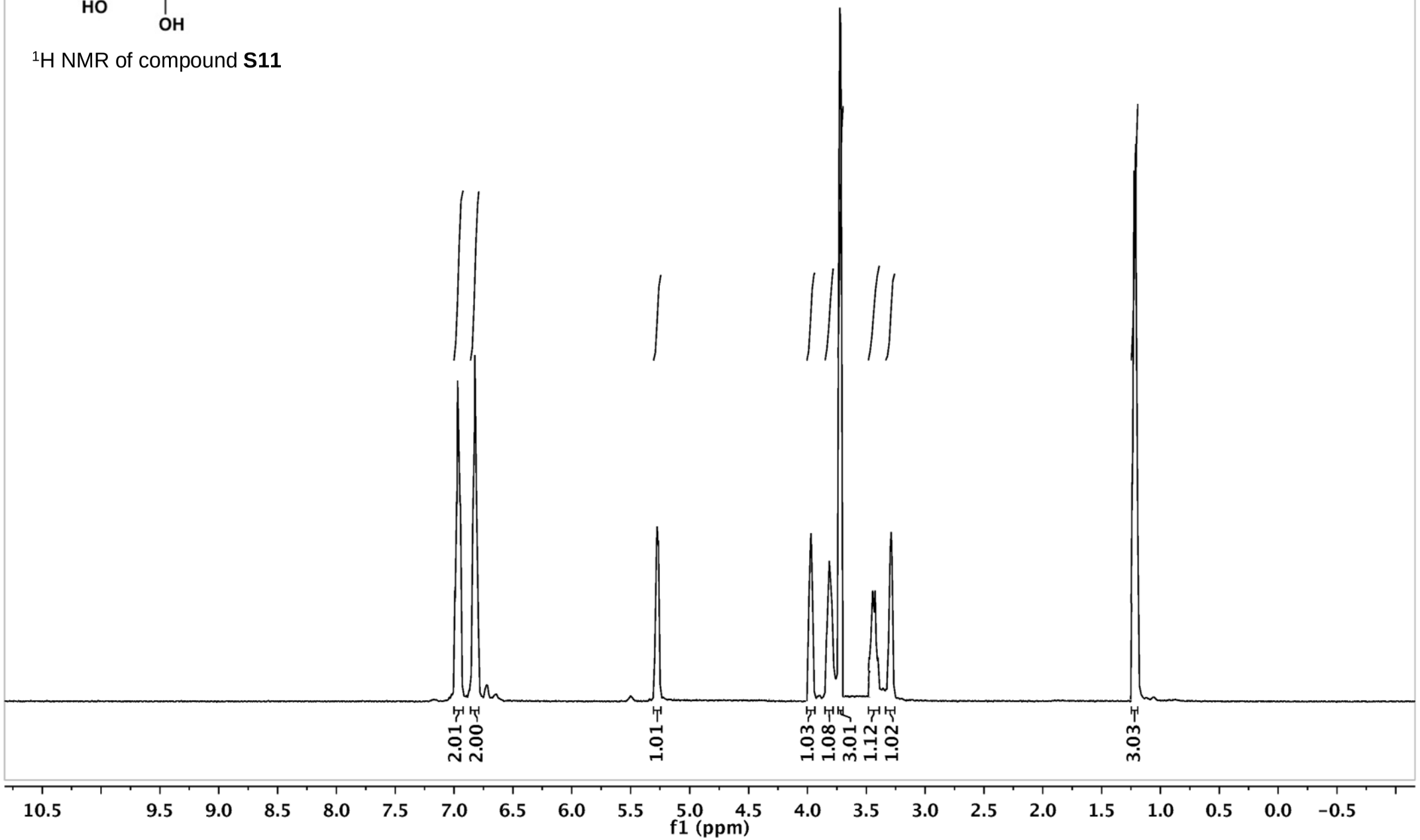


^{13}C NMR of compound **S11**

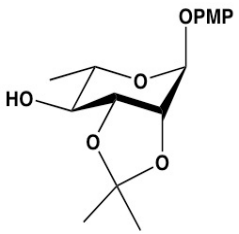




^{1}H NMR of compound **S11**



^{13}C NMR of compound **S12**

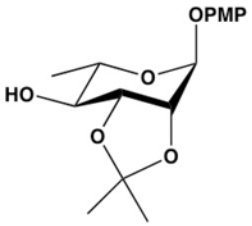


154.34
149.26
118.13
114.31
108.17
95.71
77.77
75.00
73.00
66.36
55.06
39.50 dmso
39.29 dmso
39.08 dmso
38.88 dmso
27.74
26.05
17.08

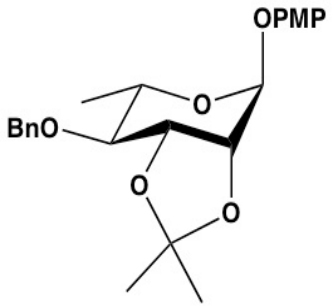
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

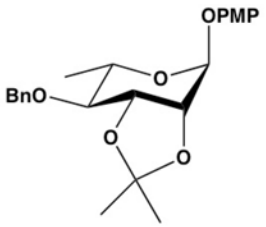
^{1}H NMR of compound **S12**



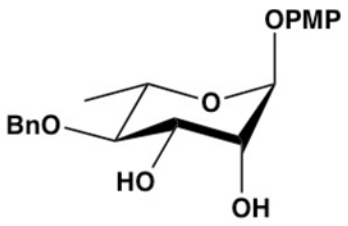
^{13}C NMR of compound **S13**



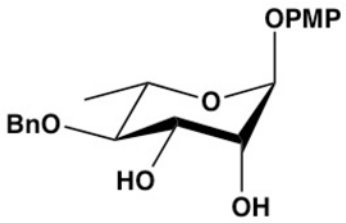
^{1}H NMR of compound **S13**



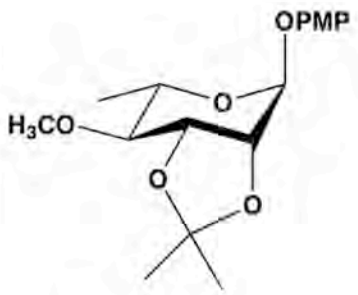
^{13}C NMR of compound **S14**



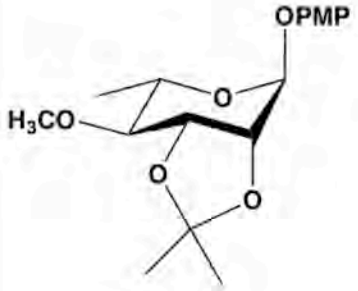
^{1}H NMR of compound **S14**



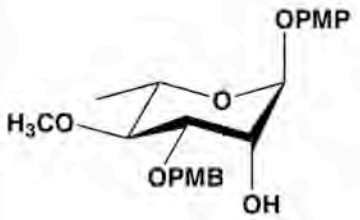
^{13}C NMR of compound **S15**



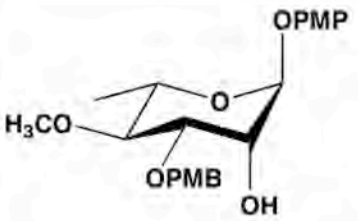
^{1}H NMR of compound **S15**



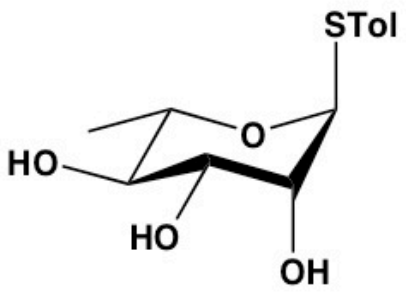
^{13}C NMR of compound **S16**



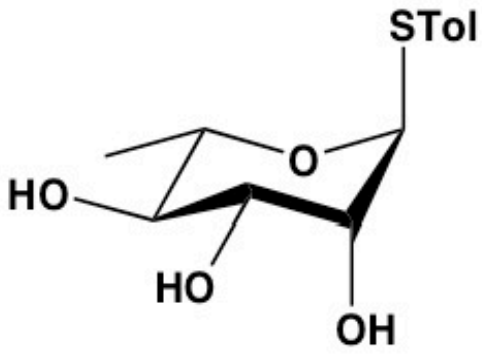
^{1}H NMR of compound **S16**



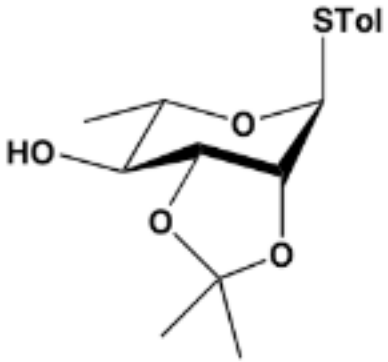
^{13}C NMR of compound **S17**



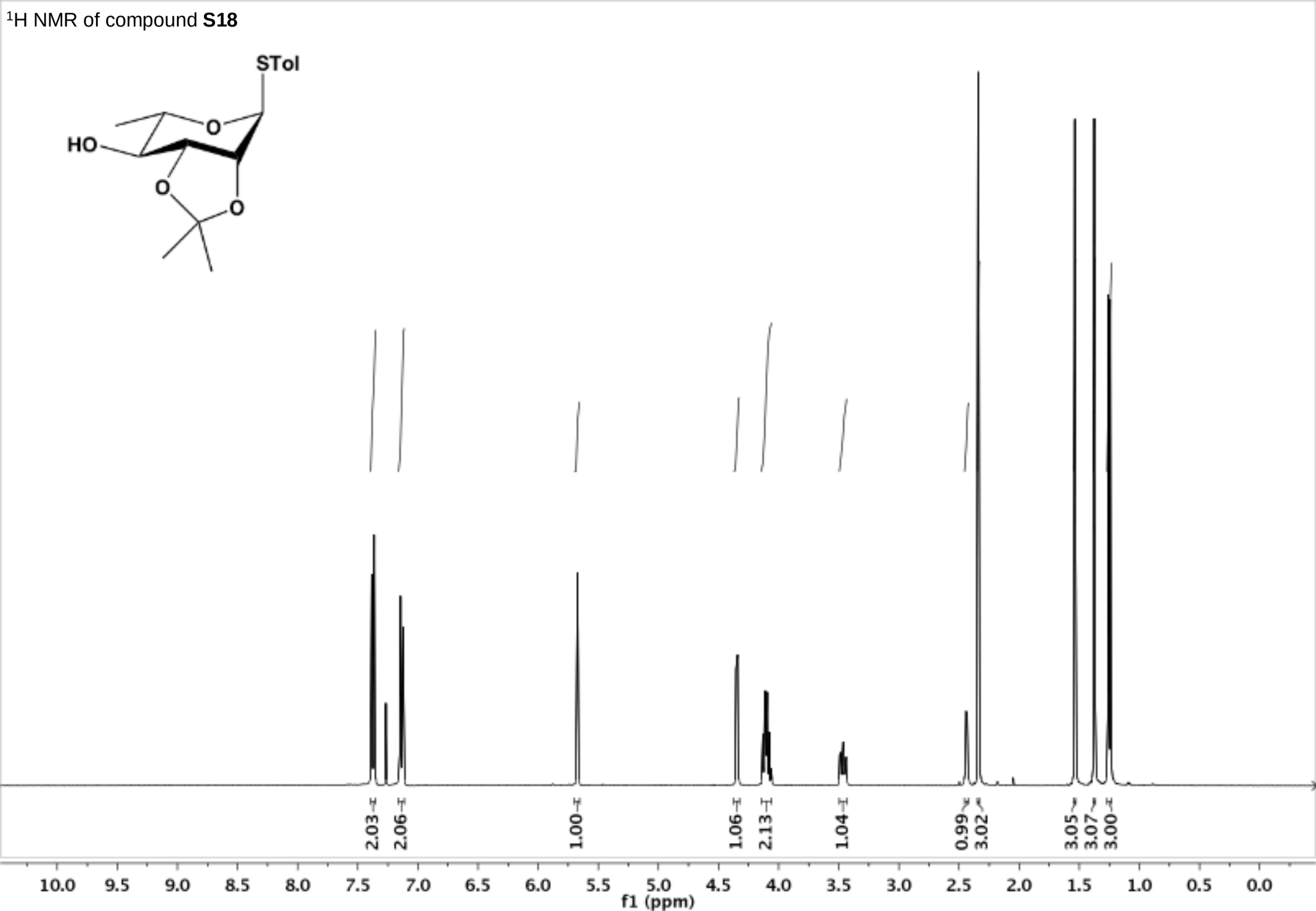
^{1}H NMR for compound **S17**



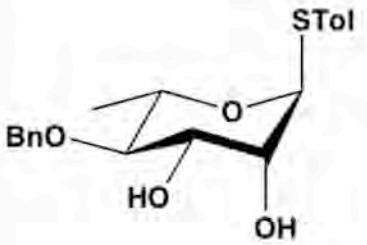
^{13}C NMR of compound **S18**



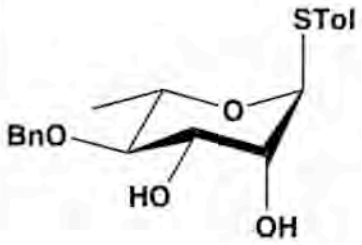
^{1}H NMR of compound **S18**



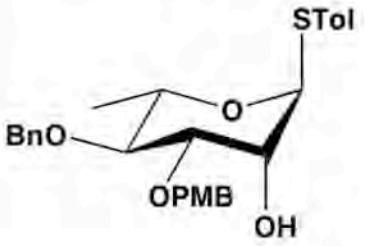
^{13}CNMR of compound **S19**



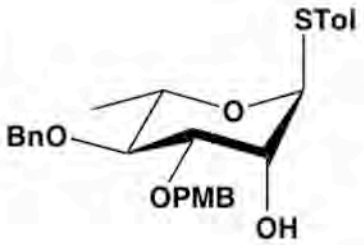
^{1}H NMR of compound **S19**



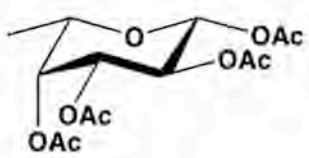
^{13}C NMR of compound **S20**



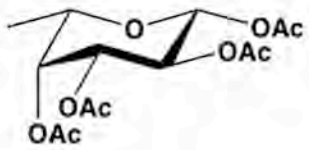
^{1}H NMR of compound **S20**



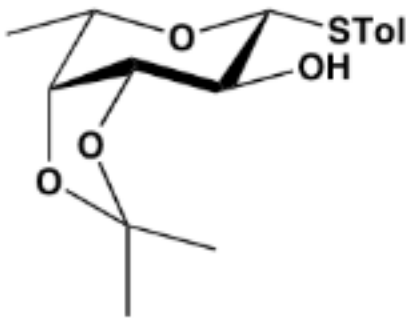
^{13}C NMR of compound **S21**



^{1}H NMR of compound **S21**

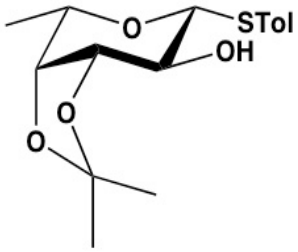


^{13}C NMR of compound **S22**

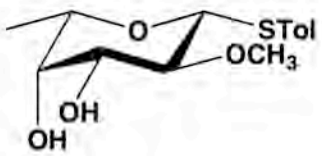


^{1}H NMR of compound

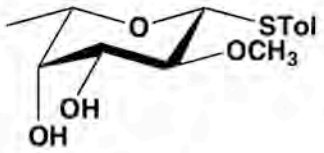
S22



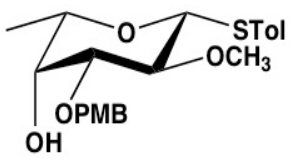
^{13}C NMR of compound **S23**



^{1}H NMR of compound **S23**



^{13}C NMR of compound **S24**

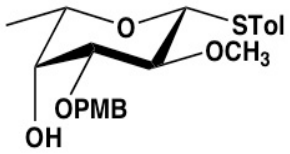


159.42
137.57
132.70
129.89
129.82
129.53
129.48
113.91
87.53
82.50
78.42
77.34
77.02
76.70
74.13
71.80
69.50
61.16
55.27
21.10
16.70

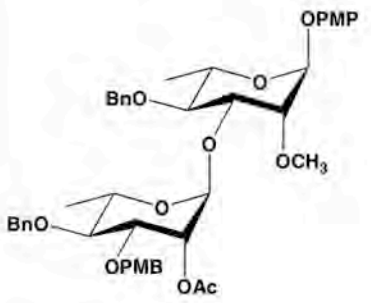
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

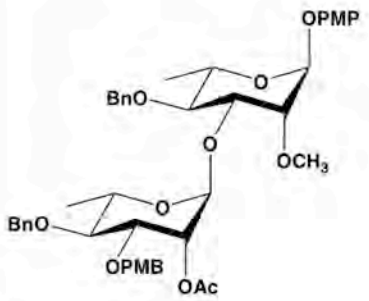
^{1}H NMR of compound **S24**



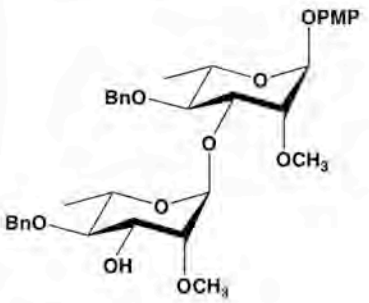
^{13}C NMR of compound **S25**



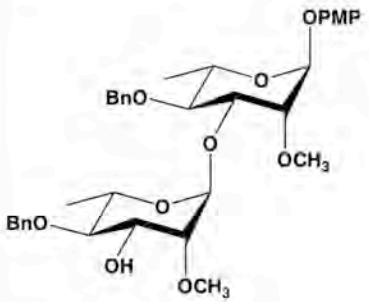
^{1}H NMR of compound **S25**



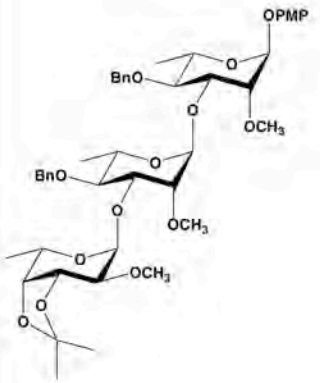
^{1}HNMR of compound **S26**



^{1}H NMR of compound **S26**



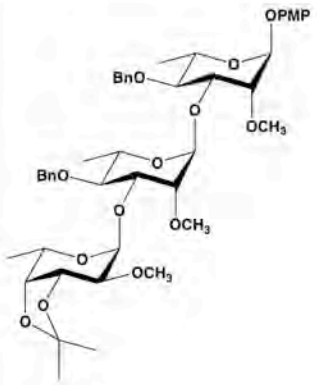
^{13}C NMR of compound **S27**



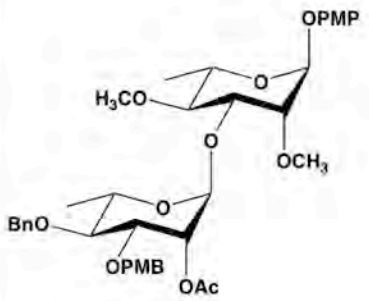
154.89
150.45
138.94
128.19
127.85
127.39
117.49
114.60
108.82
99.33
98.50
95.58
80.20
79.36
77.28
77.02
76.77
76.04
75.60
58.88
58.44
57.83
55.65
55.41
26.37
18.20
17.83
16.62

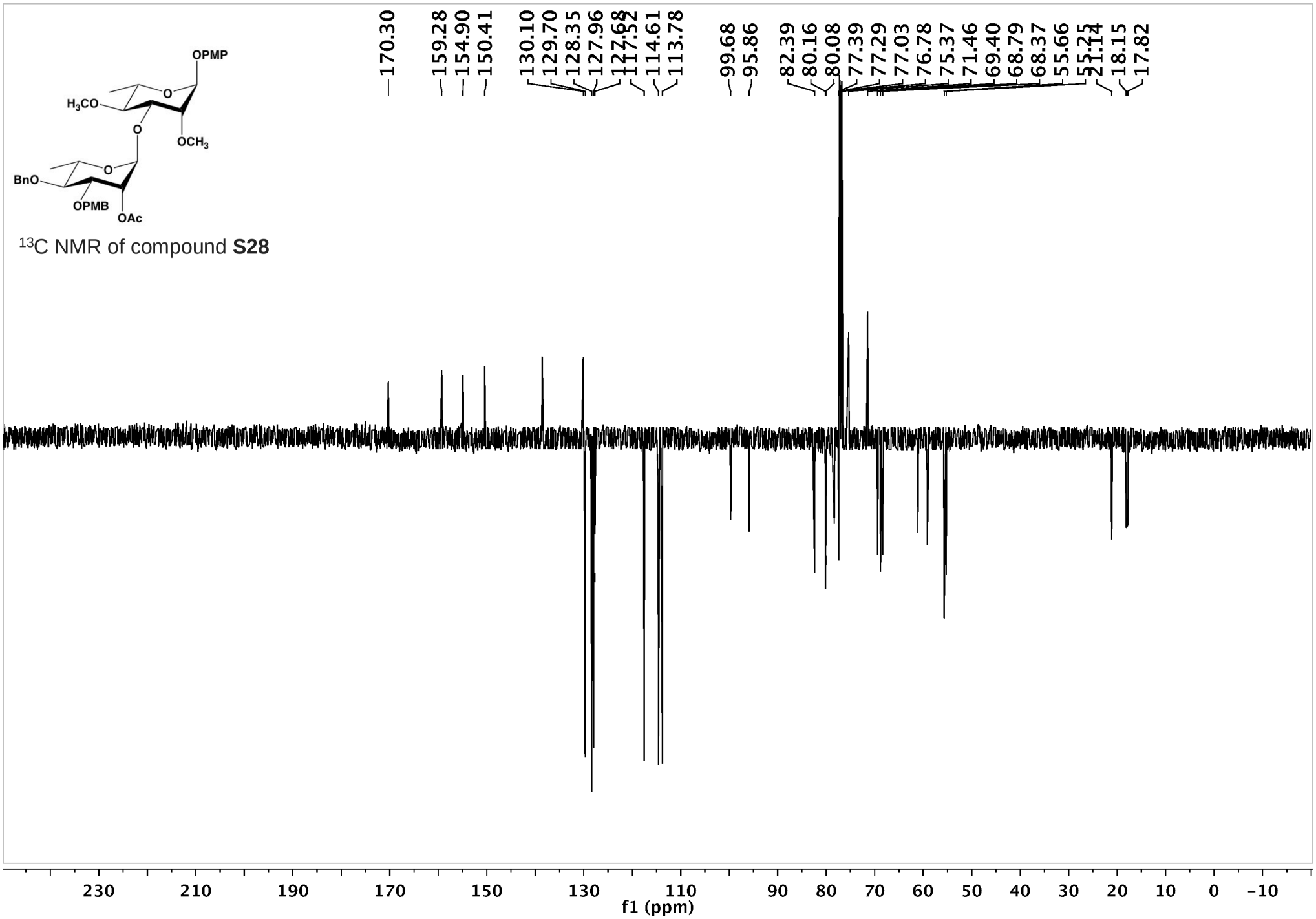
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of compound **S27**



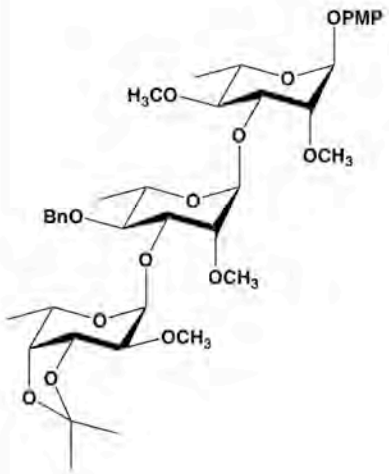
^{1}H NMR of compound **S28**



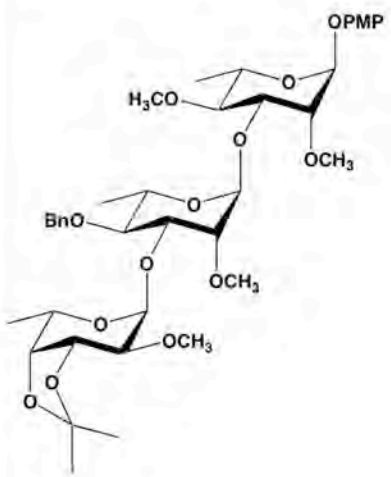


^{13}C NMR of compound **S28**

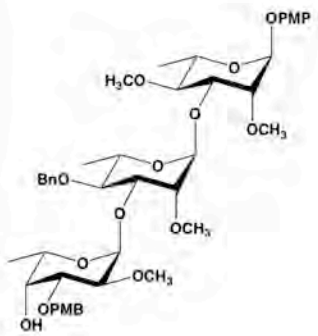
^{13}C NMR of compound **S29**



^{1}H NMR of compound **S29**



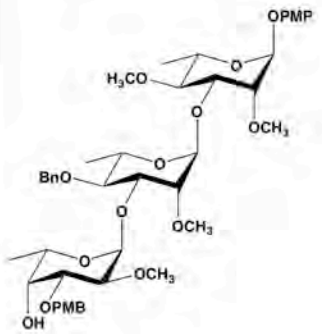
^{13}C NMR of compound **S30**



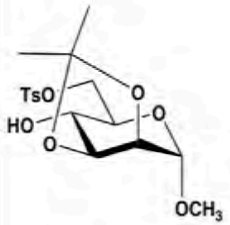
159.32
154.90
150.47
130.30
129.34
128.22
127.76
127.39
127.30
114.61
113.89
99.77
98.51
95.61
80.72
80.20
77.68
77.30
77.05
76.79
71.96
68.74
68.62
65.73
59.03
57.84
55.66
55.24
18.23
17.84
16.43

230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

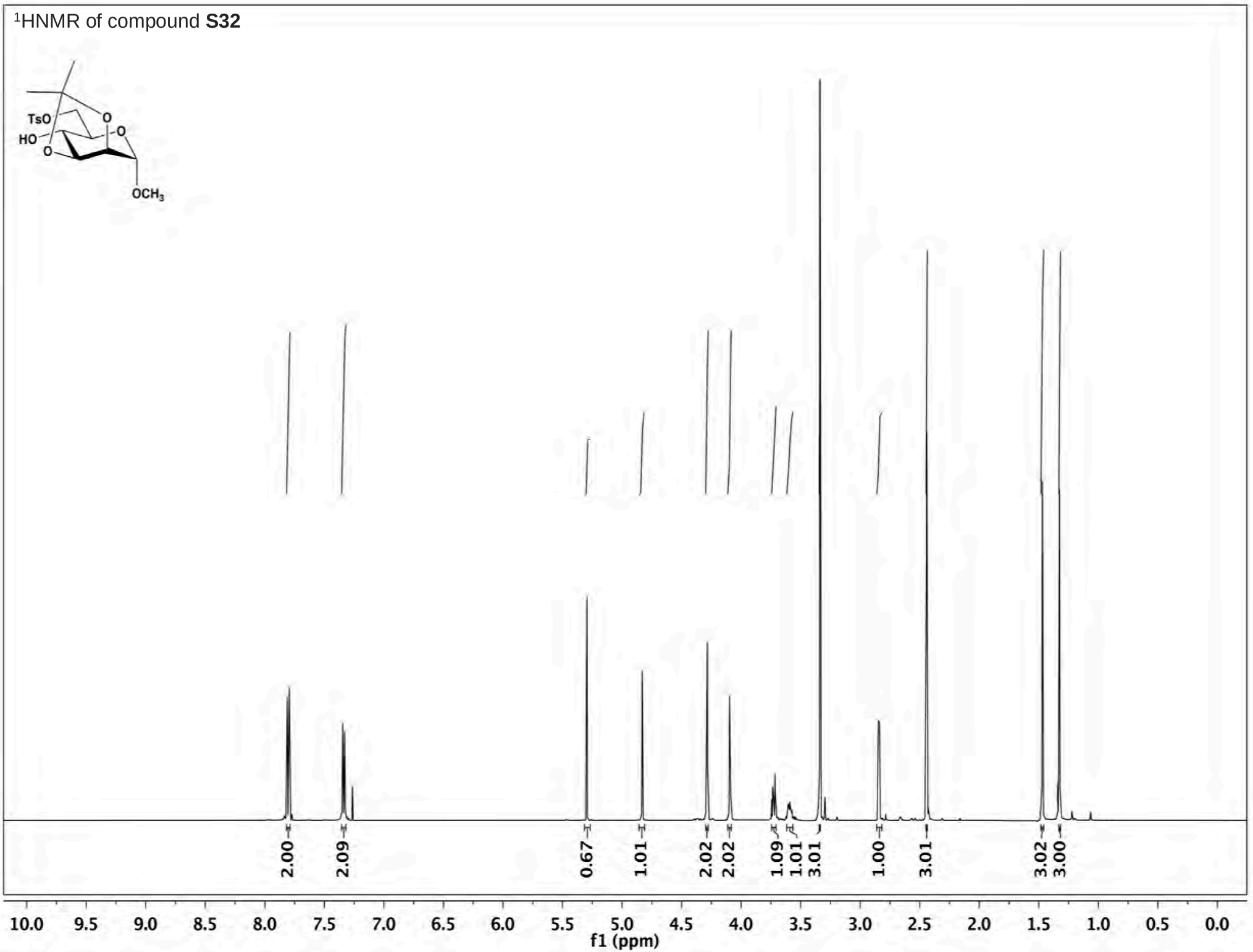
^{1}H NMR of compound **S30**



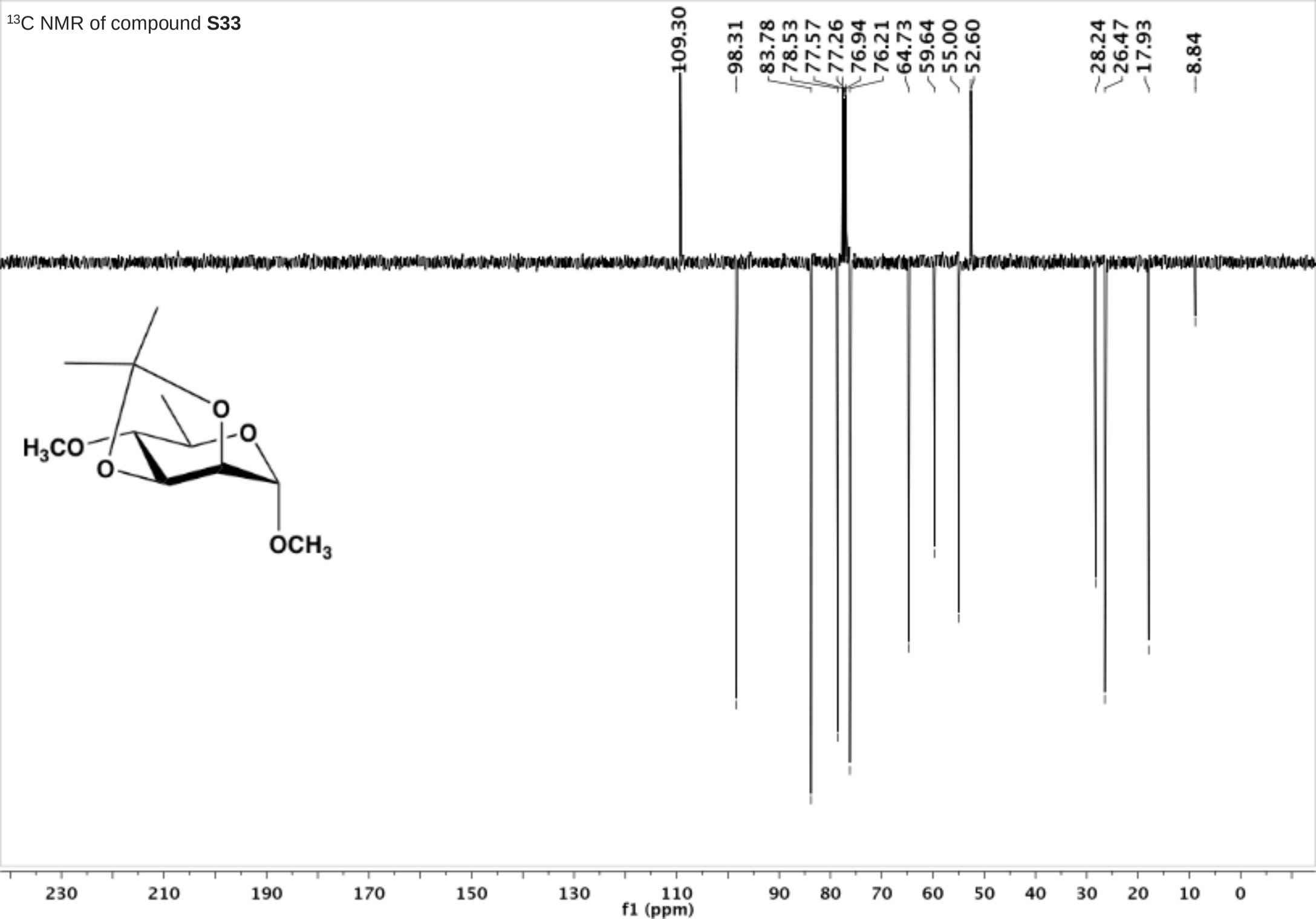
^{1}HNMR of compound **S32**



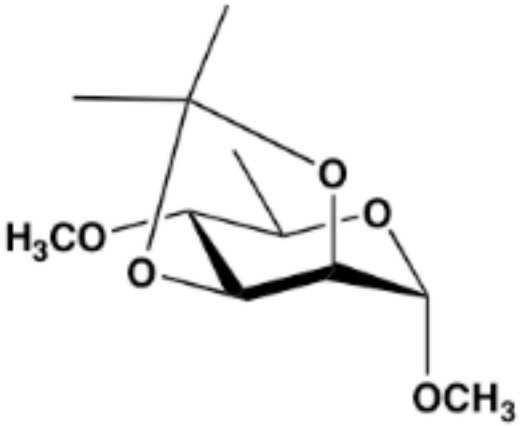
[1]HNMR of compound **S32**



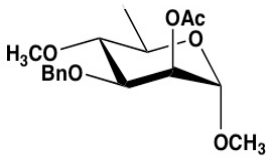
^{13}C NMR of compound **S33**



^{1}H NMR of compound **S33**



^{13}C NMR of compound **S34**

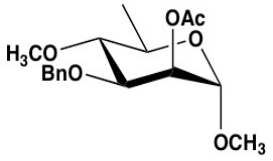


170.62
138.43
128.56
128.07
127.84
98.90
82.11
77.94
77.59
77.28
76.96
71.93
69.20
67.79
61.33
55.08
21.32
18.07

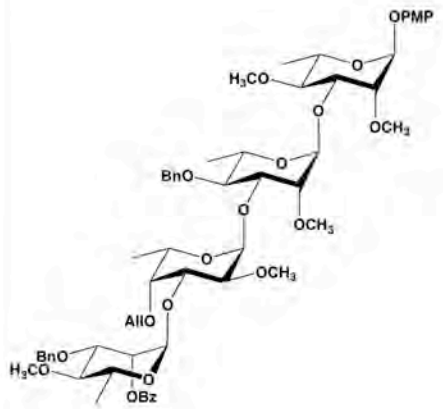
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

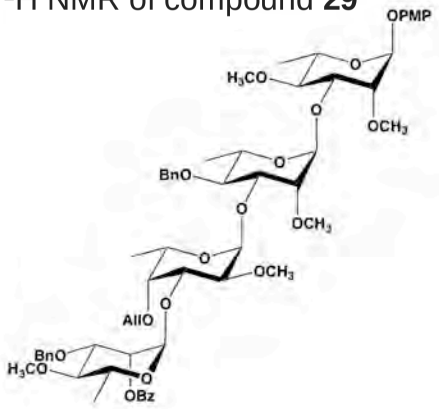
^{1}H NMR of compound **S34**



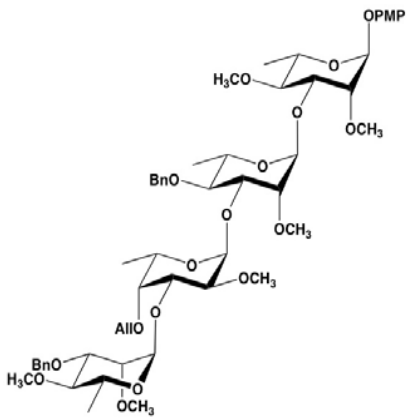
^{13}C NMR of compound **29**

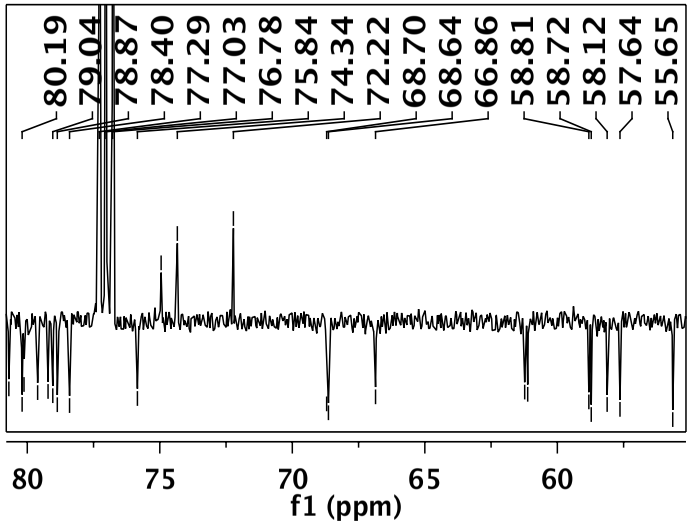


^{1}H NMR of compound **29**



^{13}C NMR of compound **30**



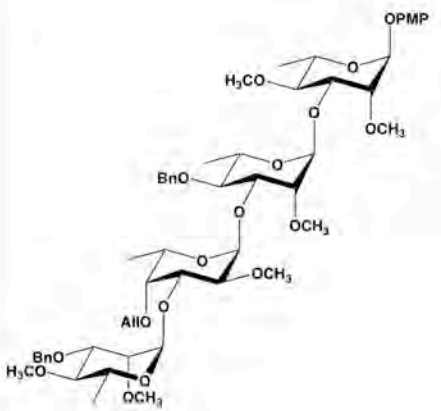


154.89 150.46 128.32 128.08 127.85 127.61 127.26 117.48 117.25 114.60 99.62 98.51 98.43 78.87 78.40 77.29 77.03 76.78 74.34 72.22 68.64 58.72 58.12 57.64 55.65 18.20 17.92 17.84 16.75

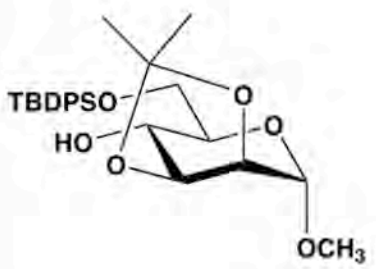
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

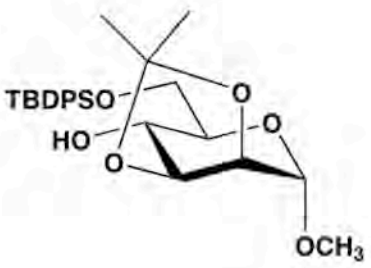
^{1}HNMR of compound **30**



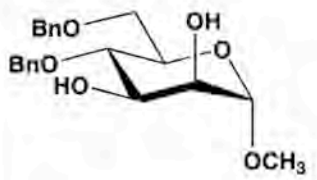
^{13}C NMR of compound **S35**



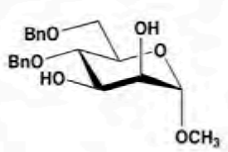
^{1}H NMR of compound **S35**

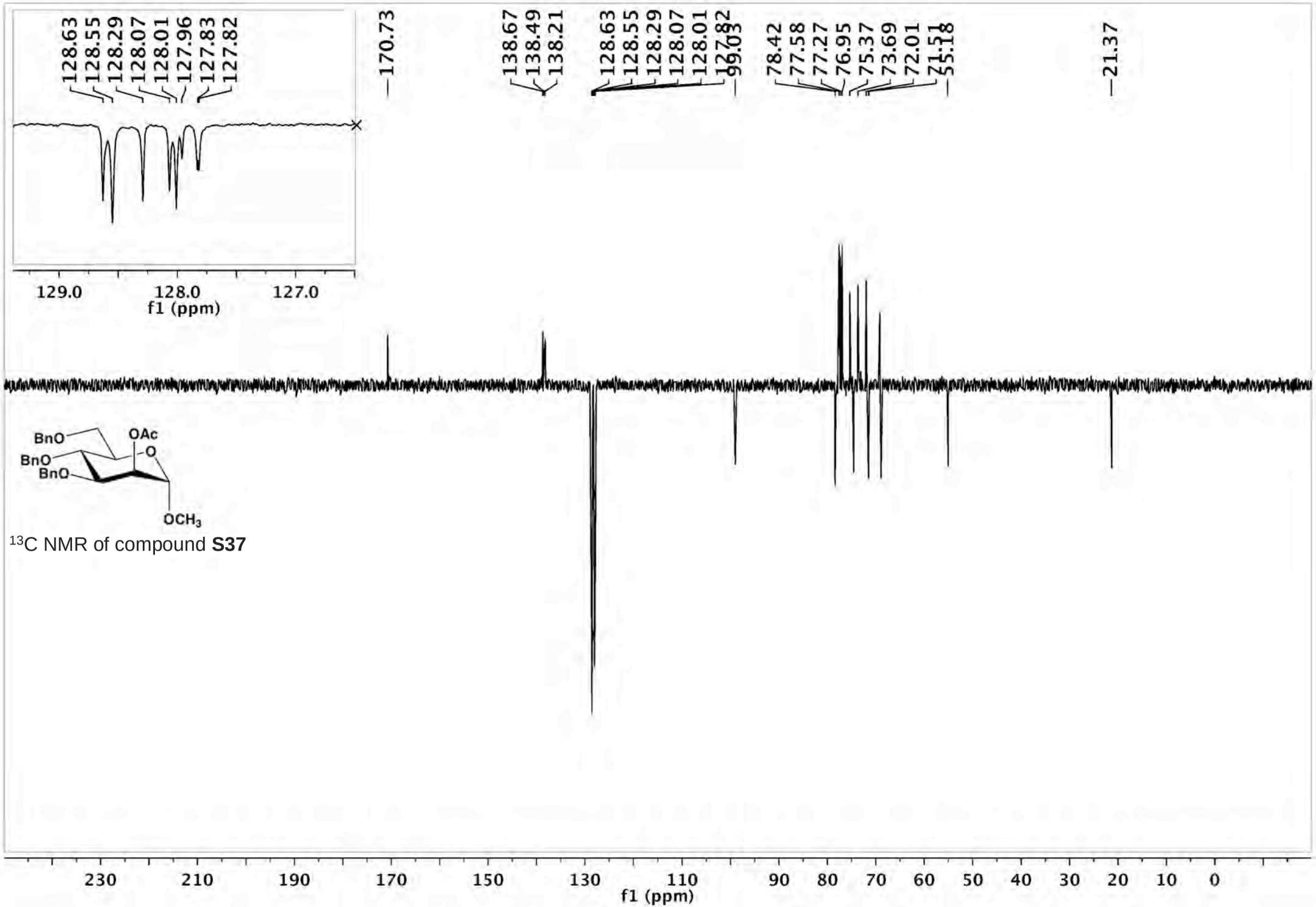


^{13}C NMR of compound **S36**



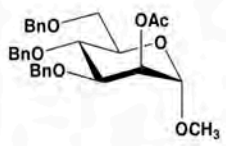
^{1}H NMR of compound **S36**



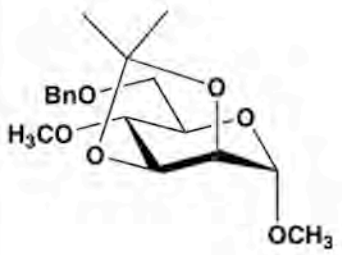


^{13}C NMR of compound **S37**

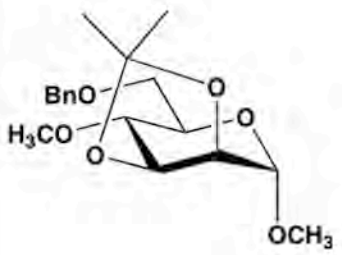
^{1}H NMR of compound **S37**



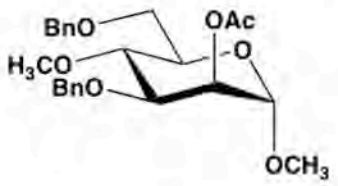
^{13}C NMR of compound **S38**



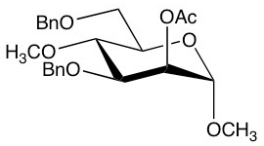
^{1}H NMR of compound **S38**

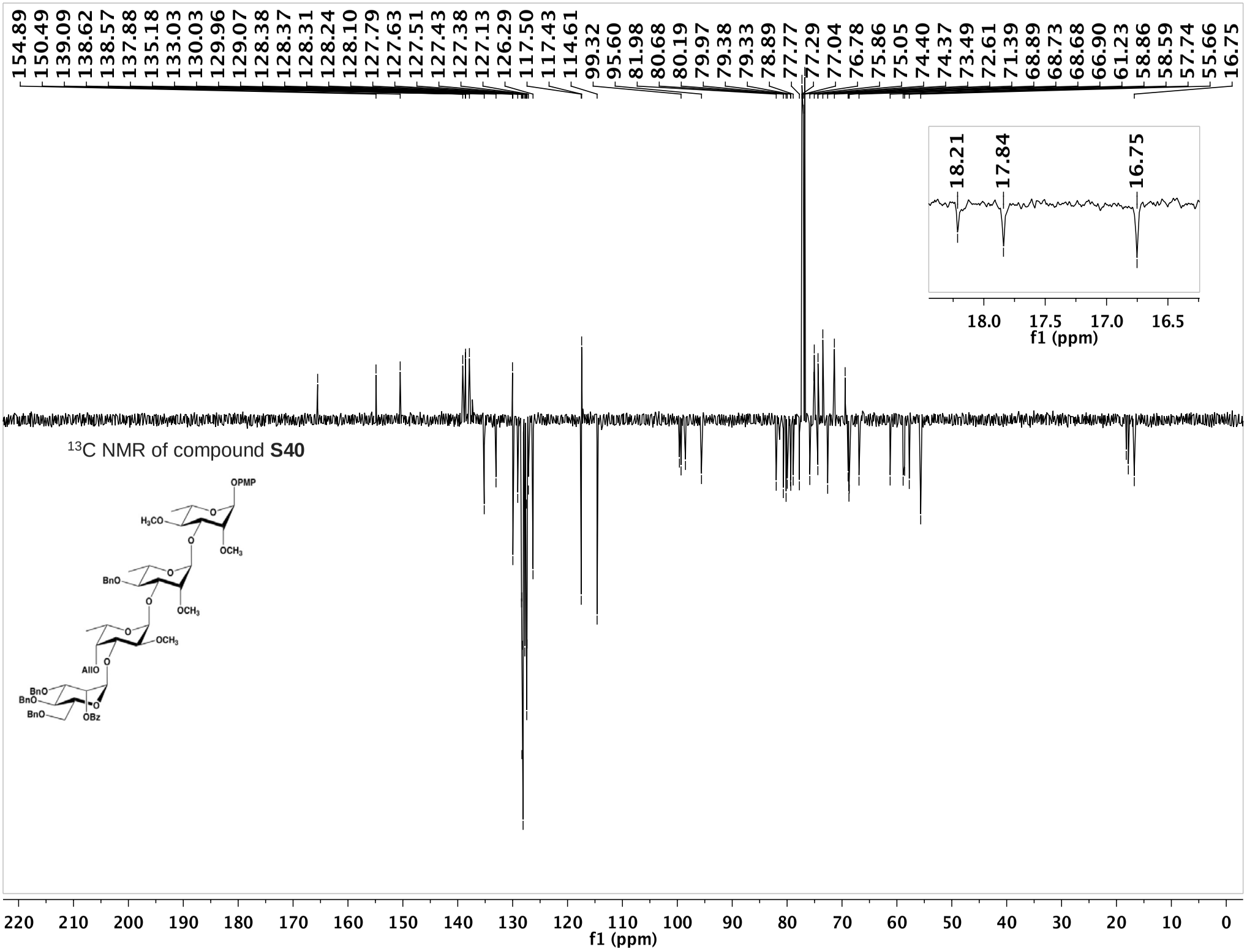


^{13}C NMR of compound **S39**



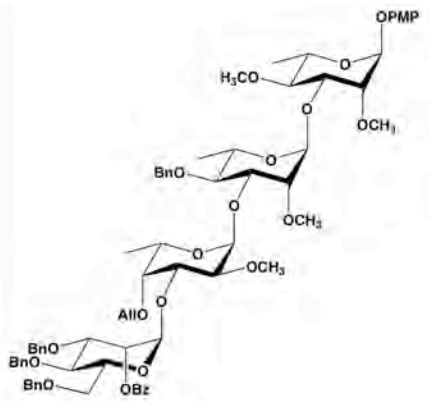
^{1}H NMR of compound **S39**



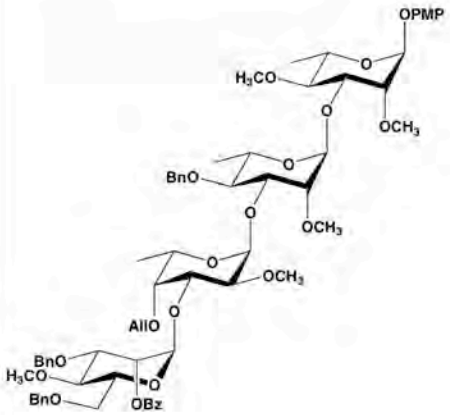


^{13}C NMR of compound **S40**

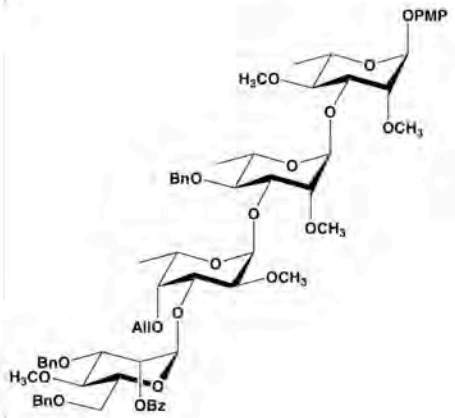
^{1}H NMR of compound **S40**



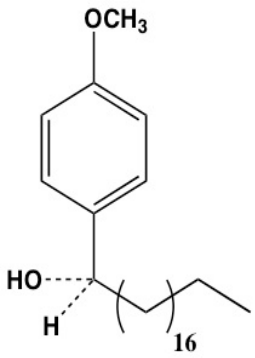
^{13}C NMR of compound **S41**



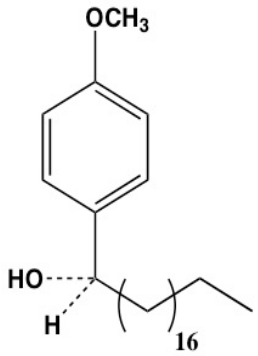
^{1}H NMR of compound **S41**



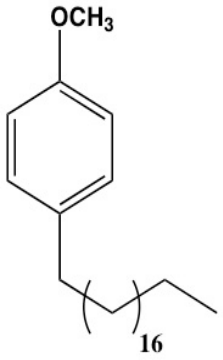
^{13}C NMR of compound **S42**



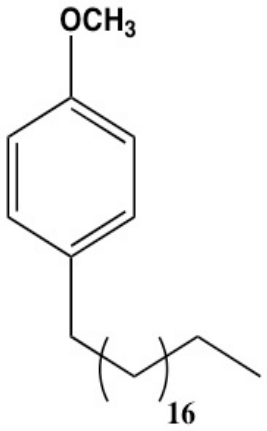
^{1}H NMR of compound **S42**



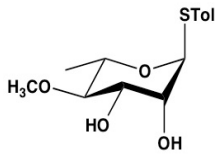
^{13}C NMR of compound **S43**



^{1}H NMR of compound **S43**



^{1}H NMR of compound **S44**

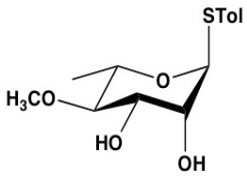


137.86
132.25
130.52
130.07
88.14
83.73
77.61
77.29
76.98
72.76
71.94
68.76
61.00
21.34
18.11

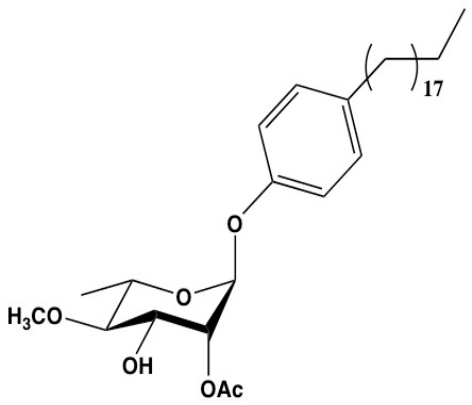
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

^{1}H NMR of compound **S44**



^{13}C NMR of compound **S46**

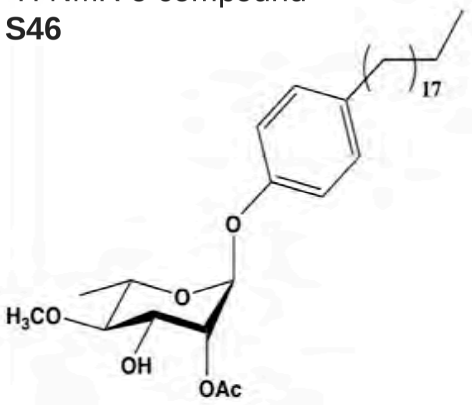


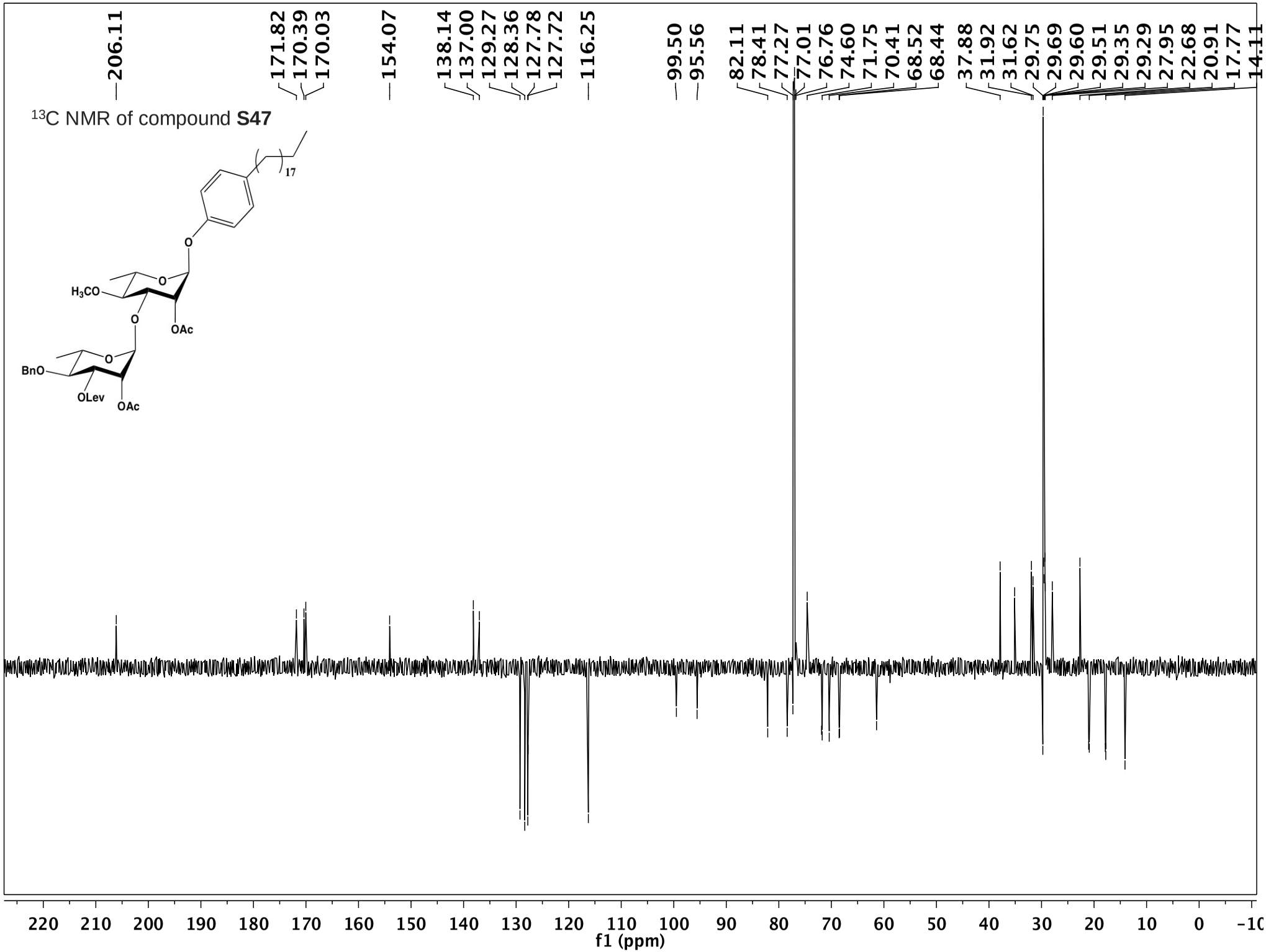
170.69
154.14
137.02
129.28
116.24
95.83
83.27
72.49
69.79
68.12
60.92
35.11
31.92
31.63
29.69
29.60
29.51
29.35
29.29
22.68
21.03
17.98
14.11

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

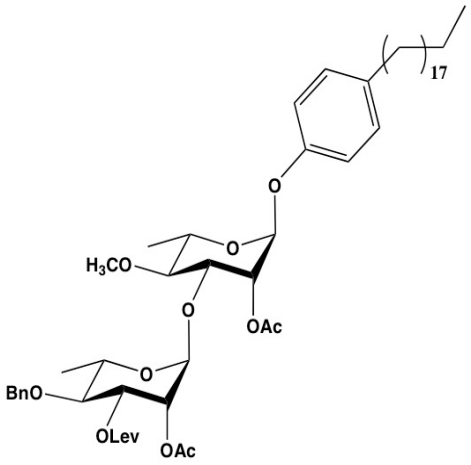
f1 (ppm)

^{1}H NMR o compound
S46

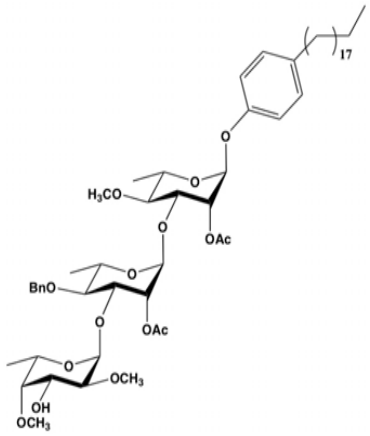



206.11
171.82
170.39
170.03
154.07
138.14
137.00
129.27
128.36
127.78
127.72
116.25
99.50
95.56
82.11
78.41
77.27
77.01
76.76
74.60
71.75
70.41
68.52
68.44
37.88
31.92
31.62
29.75
29.69
29.60
29.51
29.35
29.29
27.95
22.68
20.91
17.77
14.11
13C NMR of compound S47
17
O
O
H3CO
O
OAc
O
BnO
OLev
OAc
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

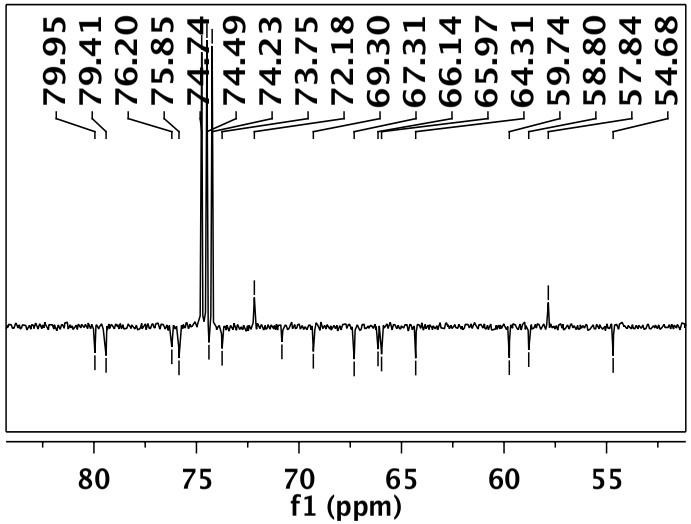
^{1}H NMR of compound **S47**



^{13}C NMR of compound **S48**



167.84
167.67
151.60
135.89
134.47
126.74
125.81
125.08
113.76
97.95
95.42
93.18
75.85
74.74
74.49
74.23
72.18
67.31
64.31
59.74
54.68
32.59
29.39
29.10
27.16
27.08
26.99
26.83
26.77
20.16
18.53
18.45
11.58



250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of compound **S48**