SUPPLEMENTARY INFORMATION

Supplementary tables and table legends 1-5

Supplementary figures 1 (raw gel data) and 2 (FACS gating strategies for immune cell analysis)

Raw data (weight monitoring over disease time course) of *in vivo* experiment (oxazolone colitis)

Total organic synthesis of BfaGC analogue (SB2201-SB2223) library

Name	Molecular Weight	Sphingosine Structure	Fatty Acyl Structure	MS2 Fingerprint	Retention Time
SB2201	717.58	n18	3-OH-n16	504	8.47
SB2202	703.56	n18	3-OH-n15	504	8.05
SB2203	731.59	n18	3-OH-i17	504	8.72
SB2204	731.59	n18	3-OH-a17	504	8.72
SB2205	731.59	n19	3-OH-n16	518	8.84
SB2206	717.58	n19	3-OH-n15	518	8.45
SB2207	745.61	n19	3-OH-i17	518	9.08
SB2208	745.61	n19	3-OH-a17	518	9.06
SB2209	703.56	i17	3-OH-n16	490	7.92
SB2210	689.54	i17	3-OH-n15	490	7.40
SB2211	717.58	i17	3-OH-i17	490	8.24
SB2212	717.58	i17	3-OH-a17	490	8.23
SB2213	703.56	a17	3-OH-n16	490	7.87
SB2214	689.54	a17	3-OH-n15	490	7.35
SB2215	717.58	a17	3-OH-i17	490	8.23
SB2216	717.58	a17	3-OH-a17	490	8.20
SB2217	717.58	i17	3-OH-n17	490	8.33
SB2218	717.58	a17	3-OH-n17	490	8.33
SB2219	717.58	n17	3-OH-n17	490	8.42
SB2220	717.58	n17	3-OH-i17	490	8.35
SB2221	717.58	n17	3-OH-a17	490	8.33
SB2222	701.58	i17	n17	538*	8.91
SB2223	703.56	n16	3-OH-n17	476	8.06

n	straight-chain
i	Isomethyl (omega-2)-branching
a	Ante-isomethyl (omega-3)-branching

***does not have acyl 3-OH: fingerprint ion is [M-H-162]**

Supplementary Table 1. Molecular weight and sphingolipid structure information for 23 synthetic BfaGCs.

Name	Sequence
pNJR6_3671_L-F	AAC GAA AAA TTT AAA CAA ATT ATT AAT CAG AGT CTG TAT TGG CTG CCC T
pNJR6_3671-L-R	ATC GAA CGT ATC GTT AGT TAT TAG TTA TTT TCG ATT GAG C
pNJR6_3671-Rg-F	CTA ATA ACT AAC GAT ACG TTC GAT AAA TGA ACT ACA AAA TAA CAA CCC
pNJR6_3671-Rg-R	CGG ATC CCC GGG TAC TCG CCA CGT CCG CAA CCC
3671-500F (1F)	GAC GCT TCG CCT CAG AAA C
3671+1520R (1R)	TTC AAA AGT ATC GGG ACG CAT C
pNBU2-3671F (2F)	AAA GAC ATA TAA AAG AAA AGA CAC CAT GAA AGA AAT AGA CTG GGC TAA TCT G
pNBU2-3671R (2R)	CAC TGG AAG ATA GGC AAT TAG TTA TTC AAC AAT AGT CAC CCA TCC G

Name	Sequence
Leu-3	CAC TTG ACT GTT GTA GAT AAA GC
Leu-4	CAT CTT CAT TGC AGC ATT ATC C
BACT1369F	CGG TGA ATA CGT TCY CGG
PROK1492R	GGW TAC CTT GTT ACG ACT T

Supplementary Table 2. Primer sequences used for the *B. fragilis* KO generation (top) and abundance analysis in HMB stool samples by qPCR (bottom).

	2C12 TCR-mCD1d-SB2217	2C12 TCR-mCD1d-SB2219
Data collection		
Temperature	100K	100K
Resolution limits (Å)	76.79-2.4 (2.5-2.4)	48.56-2.8 (2.9-2.8)
Space Group	$P2_12_12_1$	$P2_12_12_1$
Cell dimensions (Å)	a=58.5, b=80.9, c=243.3	a=58.3, b=80.6, c=242.8
	$\alpha=\beta=\gamma=90°$	$\alpha=\beta=\gamma= 90°$
Total $N^{o.}$ observations	299101 (44393)	267870 (36163)
$N^{o.}$ unique observations	46370 (6678)	29106 (4070)
Multiplicity	6.5 (6.6)	9.2 (8.9)
Data completeness	100 (100)	99.2 (97)
Wilson B-factors ($Å^2$)	62.1	82.7
I/σ_1	7.2 (1.9)	10.8 (2.1)
$R_{p.i.m}$ [1] (%)	5.5 (36.6)	4.2 (28.3)
Refinement statistics		
R_{factor} [2] (%)	18.4	20.1
R_{free} [3] (%)	23	27.4
Non-hydrogen atoms		
- Protein	6530	6542
- Water	226	152
- Heterogen	152	155
Ramachandran plot (%)		
- Allowed region	99.52	99.52
- Disallowed region	0.48	0.48
rmsd bonds (Å)	0.010	0.008
rmsd angles (°)	1.15	1.03

[1] $R_{p.i.m} = \Sigma_{hkl} [1/(N-1)]^{1/2} \Sigma i \mid I_{hkl}, i - \langle I_{hkl} \rangle \mid / \Sigma_{hkl} \langle I_{hkl} \rangle$

[2] $R_{factor} = (\Sigma \mid |Fo| - |Fc| \mid) / (\Sigma |Fo|)$ - for all data except as indicated in footnote 3.

[3] 5% of data was used for the R_{free} calculation.

Values in the parentheses refer to the highest resolution shell.

Supplementary Table 3. Data collection and refinement statistics of X-ray crystallography study.

TCR gene	TCR residues	CD1d residues	Bond type
CDR3α	Asp94-Oδ1	Arg79-Nη2	HB
CDR3α	Asp94-Oδ2	Arg79-Nη1	HB
CDR3α	Asp94	Arg79	VDW
CDR3α	Arg95-Nε	Asp80-Oδ1, Asp80-Oδ2	HB
CDR3α	Arg95-Nη1	Arg79-Nε	HB
CDR3α	Arg95-Nη2	Arg79-Nη2	HB
CDR3α	Arg95	Ser76, Arg79, Asp80	VDW
CDR3α	Gly96-O	Ala152-O	HB
CDR3α	Gly96	Ala152, Asp153	VDW
CDR3α	Ser97	Arg79, Val149, Ala152, Asp153	VDW
CDR3α	Leu99-O	Arg79-Nη2	HB
CDR3α	Leu99	Asp80, Leu84, Met87, Val149	VDW
CDR3α	Gly100	Arg79	VDW
CDR3α	Arg103	Arg79, Glu83	VDW
CDR2β	Tyr48-Oη	Glu83-Oε2	HB
CDR2β	Tyr48	Glu83, Lys86	VDW
CDR2β	Tyr50-Oη	Glu83-Oε2	HB
CDR2β	Tyr50	Glu83, Met87, Lys86	VDW
CDR2β	Glu56	Lys86	VDW
CDR3β	Glu97-Oδ2	Lys148-Nς	HB
CDR3β	Glu97	Ala152, Lys148	VDW
TCR gene	**TCR residues**	**SB2217 atoms**	**Bond type**
CDR1α	Pro28	C1, O5''	VDW
CDR1α	Asn30-Nδ2	3''-OH	HB
CDR1α	Asn30	4''-OH, C3, 3''-OH	VDW
CDR3α	Arg95	C1, C2, 2''-OH, O3	VDW
CDR3α	Gly96-N	2''-OH	HB
CDR3α	Gly96	C2, 3''-OH	VDW

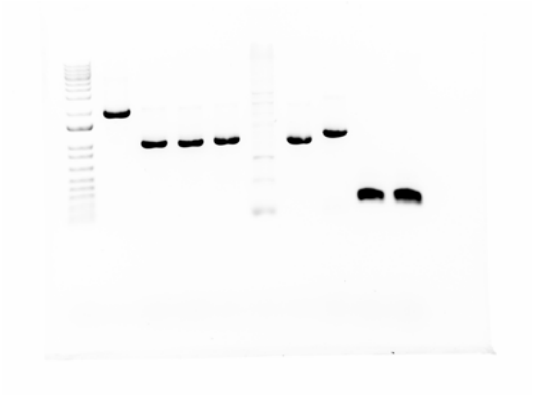
HB: Hydrogen bond, VDW: van der Waals, Cut-off at 4 Å for VDW interactions and 3.5 Å for HB.

Supplementary Table 4. 2C12 TCR contacts with SB2217 and mCD1d.

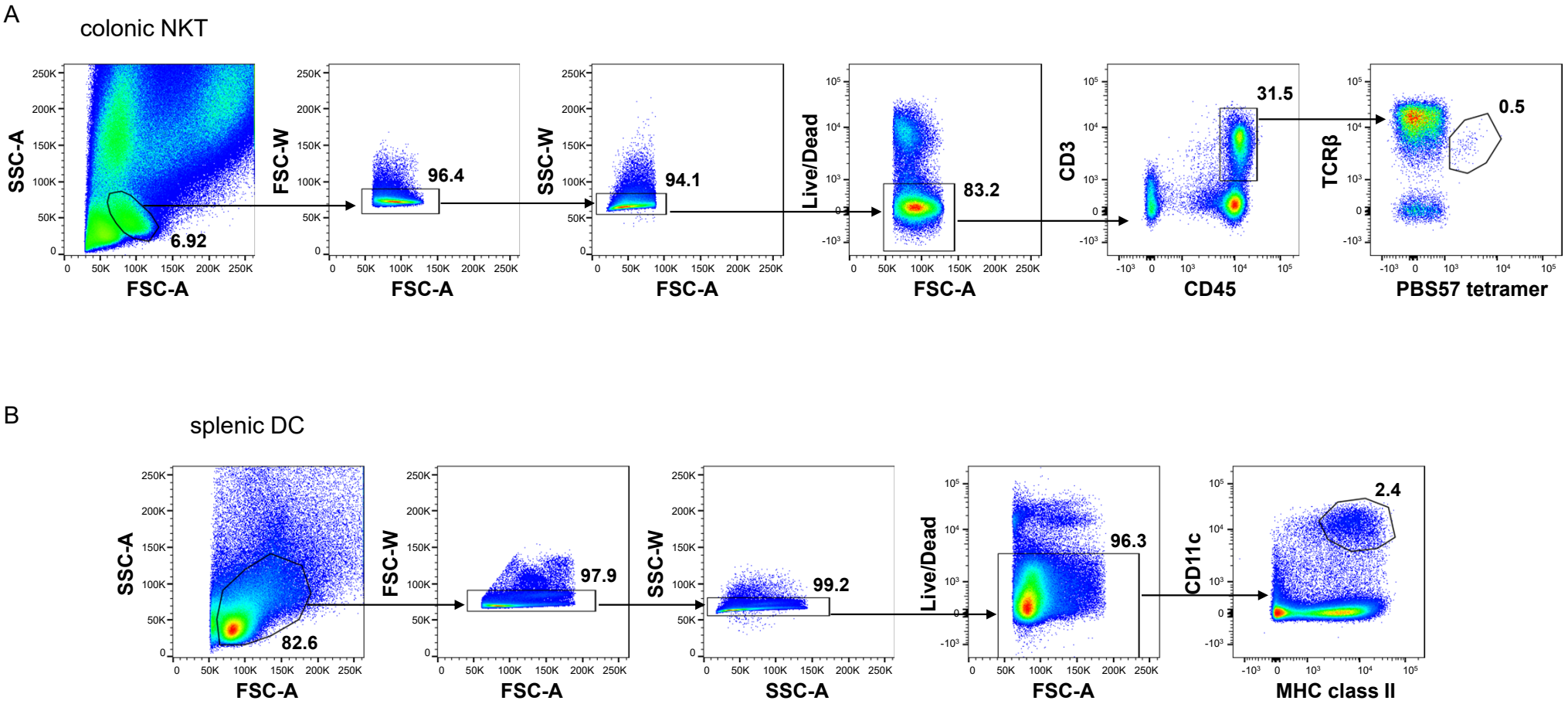
TCR gene	TCR residues	CD1d residues	Bond type
CDR1α	Thr27	Val72	VDW
CDR1α	Pro28	Ser76	VDW
CDR3α	Asp94-Oδ1	Arg79-Nη1, Nη2	HB
CDR3α	Asp94	Arg79	VDW
CDR3α	Arg95-Nε	Asp80-Oδ1	HB
CDR3α	Arg95	Ser76, Arg79, Asp80	VDW
CDR3α	Gly96-O	Ala152-O	HB
CDR3α	Gly96	Ala152, Asp153	VDW
CDR3α	Ser97	Val149, Ala152	VDW
CDR3α	Leu99-O	Arg79-Nη2	HB
CDR3α	Leu99	Asp80, Glu83, Leu84, Met87, Val149	VDW
CDR3α	Gly100	Arg79	VDW
CDR3α	Arg101	Arg79, Glu83	VDW
CDR2β	Tyr48-Oη	Glu83-Oε1, Glu83-Oε2, Lys86-Nζ	HB
CDR2β	Tyr48	Glu83, Lys86	VDW
CDR2β	Tyr50-Oη	Glu83-Oε2	HB
CDR2β	Tyr50	Glu83, Met87	VDW
CDR2β	Glu56-Oε1	Arg21-Nη1	HB
CDR2β	Glu56	Lys86	VDW
CDR3β	Glu96	Lys148, Val149, Ala152	VDW
TCR gene	**TCR residues**	**SB2219 atoms**	**Bond type**
CDR1α	Pro28	O5'', C6, C1	VDW
CDR1α	Asn30-Nδ2	3''-OH	HB
CDR1α	Asn30	C3, 4''-OH, C2, 3''-OH	VDW
CDR1α	Asn30-Nδ2	4''-OH	HB
CDR3α	Asp94, Arg95	C1	VDW
CDR3α	Arg95, Gly96	C2, 3''-OH	VDW
CDR3α	Gly96-N	2''-OH	HB
CDR3α	Arg95	C1, O1, O3, 2''-OH	VDW

HB: Hydrogen bond, VDW: van der Waals, Cut-off at 4 Å for VDW interactions and 3.5 Å for HB.

Supplementary table 5. 2C12 TCR contacts with SB2219 and mCD1d.



Supplementary Figure 1. Raw gel image for Extended figure 8A.



Supplementary Figure 2. Gating and sorting strategies of (A) colonic NKT cells and (B) splenic DCs.

Day after challenge	Vehicle					
0	100	100	100	100	100	100
1	93.5115	82.963	94.9807	89.1975	89.5604	86.6883
2	88.5496	81.4815	99.2278	84.8765	81.8681	80.1948
3	deceased	80	98.4556	83.0247	78.022	82.7922

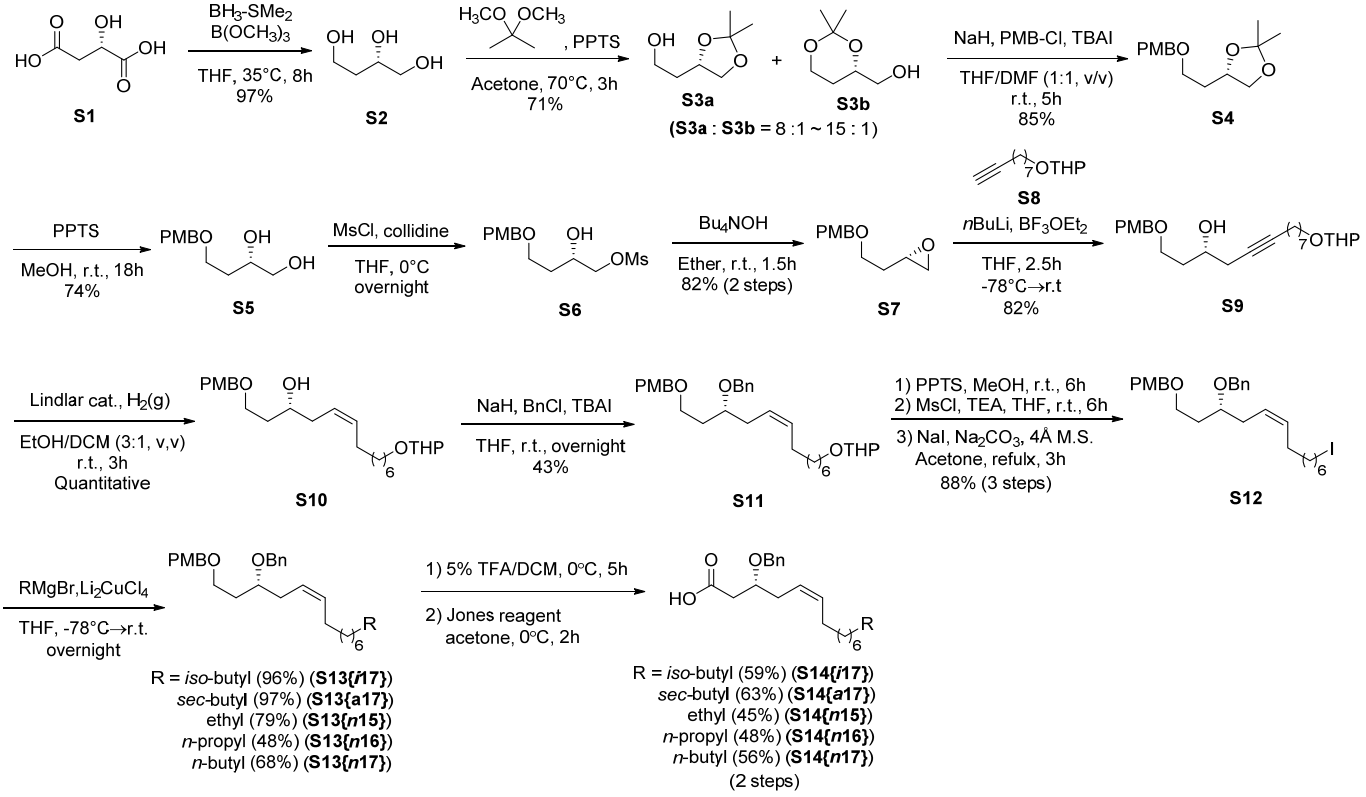
SB2217					
100	100	100	100	100	100
99.5851	98.8372	96.9231	93.5211	94.2197	102.907
105.3942	101.1628	100.3846	89.8592	94.2197	103.7791
108.7137	106.2016	101.9231	87.8873	98.8439	103.7791

All data are weight(%) based on day 0 measurement of individual animal as 100%.

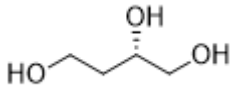
Supplemental Material for Oh *et al*. : Synthesis of BfaGC analog library

A. Synthesis of carboxylic acid building blocks

For the preparation of acyl building blocks, we first synthesized C_{13} alkyl iodide having diol at 1,3 position (**S12**) from L-(–)-malic acid. Then we obtained acyl building blocks (**S14{*i*17}**–**S14{*n*16}**) as a carboxylic acid form after the introduction of various normal and branch structure via sp^3–sp^3 cross-coupling followed by oxidation.

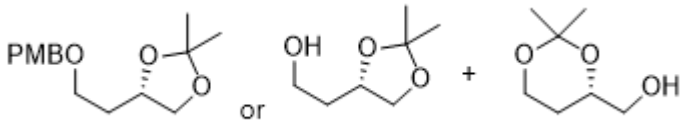


Synthesis of S2, (S)-butane-1,2,4-triol



To a solution of boron dimethyl sulfide complex (157 mmol) and trimethyl borate (269 mmol) in dry THF (70 mL) under Ar(g) was added **S1** (L-(-)-malic acid, 44.8 mmol) in dry THF (20 mL) dropwise for 1 hr at water bath, then the reaction mixture was stirred at 35 ℃ for overnight. After the completion of the reaction monitored by TLC, the reaction was quenched by slow adding of MeOH (10 mL) at water bath and stirred for additional 4 hr at room temperature (r.t.). Solvent was evaporated under reduced pressure and azeotroped with MeOH 3 times. The residue was purified by silica-gel flash column chromatography (MeOH:DCM = 1:10 to 1:6 gradient elution) to provide the desired product (41.0 mmol, 91.6%). LRMS(ESI) *m/z* for $C_4H_{11}O_3$ $[M + H]^+$ calcd: 107.06, found: 107.10.

Synthesis of S3a, S3b, and S4, (S)-2-(2,2-dimethyl-1,3-dioxolan-4-yl)ethan-1-ol, (S)-(2,2-dimethyl-1,3-dioxan-4-yl)methanol, and (S)-4-(2-((4-methoxybenzyl)oxy)ethyl)-2,2-dimethyl-1,3-dioxolane

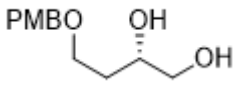


To a solution of **S2** (63.8 mmol) in acetone (300 mL) were added 2,2-dimethoxypropane (191.3 mmol), pyridinium-*p*-toluene sulfonate (5.10 mmol), then the reaction mixture was stirred at 70 ℃ (reflux) for overnight. After the completion of the reaction

monitored by TLC, solvent was evaporated under reduced pressure and the resultant was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:2 to 1.5:1 gradient elution) to provide the inseparable mixture of 5-membered and 6-membered as 9:1 ratio (45.5 mmol, 71%).

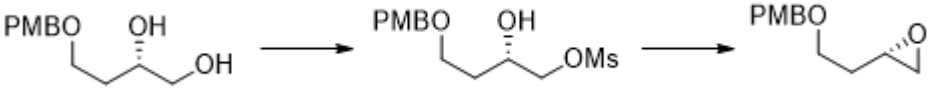
To a solution of NaH (8.89 mmol) in dry THF (60 mL) under Ar(g) was added resulting inseparable mixture (**S3a** and **S3b**, 6.84 mmol) at 0 ℃ slowly and the reaction mixture was stirred for 30 min at r.t. *p*-Methoxybenzyl chloride (8.89 mmol), tetrabutylammonium iodide (0.889 mmol) were added to the reaction mixture, then the reaction mixture was stirred at 60 ℃ for overnight. After the completion of reaction monitored by TLC, the reaction mixture was diluted with EtOAc (100 mL) and washed with brine. Resulting organic layer was dried over anhydrous Na_2SO_4(s) and solvent was evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:15 to 1:5 gradient elution) to provide the desired product (1.55 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.25 (d, J = 8.1, Hz, 2H), 6.87 (d, J = 8.7, Hz, 2H), 4.43 (s, 2H), 4.20 (quin, J = 6.6 Hz, 1H), 4.05 (dd, J = 8.1, 6.0 Hz, 1H), 3.80 (s, 3H), 3.59–3.51 (m, 3H), 1.96–1.79 (m, 2H), 1.34 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 130.6, 129.4, 114.0, 108.7, 74.1, 73.0, 70.0, 67.0, 55.5, 34.1, 27.1, 26.0; LRMS(ESI) *m/z* for $C_7H_{15}O_3$ $[M + H]^+$ calcd: 147.09, found: 147.10.

Synthesis of S5, (S)-4-((4-methoxybenzyl)oxy)butane-1,2-diol



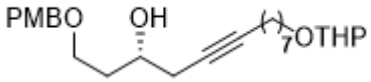
To a solution of **S4**(14.1 mmol) in MeOH (100 mL) was added pyridinium-*p*-toluenesulfonate (1.41 mmol) and the reaction mixture was stirred at r.t. for 18 hr. Solvent was evaporated under reduced pressure and the residue was purified by silica-gel flash column chromatography (MeOH:DCM = 1:40 to 1:18 gradient elution) to provide the desired product (2.99 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.25 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.46 (s, 2H), 3.90 (m, 1H), 3.81 (s, 3H), 3.69–3.60 (m, 3H), 3.49 (dd, J = 11.4, 6.2 Hz, 1H), 1.87–1.78 (m, 1H), 1.75–1.68 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 130.0, 129.6, 114.1, 73.2, 71.6, 68.2, 66.8, 55.5, 33.0, 14.4; LRMS(ESI) *m/z* for $C_{12}H_{18}NaO_4$ $[M + Na]^+$ calcd: 249.11, found: 249.05.

Synthesis of S6 and S7, (S)-2-hydroxy-4-((4-methoxybenzyl)oxy)butyl methanesulfonate and (S)-2-(2-((4-methoxybenzyl)oxy)ethyl)oxirane



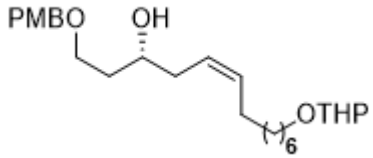
To a solution of **S5** (5.46 mmol) and collidine (54.6 mmol) in dry DCM (100 mL) was added methanesulfonyl chloride (6.56 mmol) dropwise over 1 hr under Ar(g) at 0 ℃ and the reaction mixture was stirred for 12 hr. Then, the reaction mixture was diluted with DCM (100 mL) and washed with brine. Organic layer was dried over anhydrous Na_2SO_4(s) and solvent was evaporated under reduced pressure. Then, to a solution of **S6** in dry diethylether (60 mL) was added tetrabutylammonium hydroxide (1M solution in MeOH, 7.10 mmol) under Ar(g) at 0 ℃ slowly. The reaction mixture was stirred at 0 ℃ for 6 hr. After the completion of the reaction monitored by TLC, the reaction mixture was diluted with EtOAc (100 mL) and washed with NH_4Cl(aq.) and organic layer was dried over anhydrous Na_2SO_4(s) and solvent was evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:10 to 1:5 gradient elution) to provide the desired product (932 mg, 82% as 2 step yield). ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.26 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.61–3.57 (m, 2H),, 3.07–3.04 (m, 1H), 2.78 (t, J = 4.5 Hz, 1H), 2.52 (dd, J = 4.5, 3.0 Hz, 1H), 1.92–1.87 (m, 1H), 1.80–1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4 129.5, 127.2, 114.0, 73.0, 66.9, 55.5, 50.3, 47.3, 33.2; LRMS(ESI) *m/z* for $C_{12}H_{16}NaO_3$ $[M + Na]^+$ calcd: 231.10, found: 231.00.

Synthesis of S9, (3R)-1-((4-methoxybenzyl)oxy)-13-((tetrahydro-2H-pyran-2-yl)oxy)tridec-5-yn-3-ol



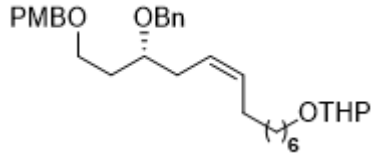
To a solution of **S8** (non-8-ynoxycyclohexane, 15.6 mmol) in dry THF was added *n*-butyllithium (17.6 mmol) under Ar(g) at -78 ℃ slowly and reaction mixture was stirred for 15 min at -78 ℃. **S7** (13.5 mmol), boron trifluoride diethyl etherate (14.9 mmol) in dry THF were added to the reaction mixture at -78 ℃ slowly and the reaction mixture was stirred at ambient temperature. After the completion of the reaction monitored by TLC, the reaction mixture was diluted with EtOAc (100 mL) and washed with NH_4Cl (aq.) and organic layer was dried over anhydrous Na_2SO_4(s). Solvent was evaporated under reduced pressure and the residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:10 to 1:3 gradient elution) to provide the desired product (4.79 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.25 (d, J = 14.0 Hz, 2H), 6.87 (d, J = 14.5 Hz, 2H), 4.57 (t, J = 6.0 Hz, 1H), 4.45 (s, 2H), 3.87–3.82 (m, 1H), 3.80 (s, 4H), 3.76–3.60 (m, 3H), 3.53–3.48 (m, 1H), 3.41–3.34 (m, 1H), 2.98 (d, J = 6.0 Hz, 1H), 2.36–2.34 (m, 2H), 2.17–2.11 (m, 2H), 2.04–1.99 (m, 1H), 1.89–1.79 (m, 3H), 1.61–1.43 (m, 6H), 1.37–1.08 (m, 8H); LRMS(ESI) *m/z* for $C_{26}H_{40}NaO_5$ [M + Na]$^+$ calcd: 455.28, found: 455.20.

Synthesis of S10, (3R,Z)-1-((4-methoxybenzyl)oxy)-13-((tetrahydro-2H-pyran-2-yl)oxy)tridec-5-en-3-ol



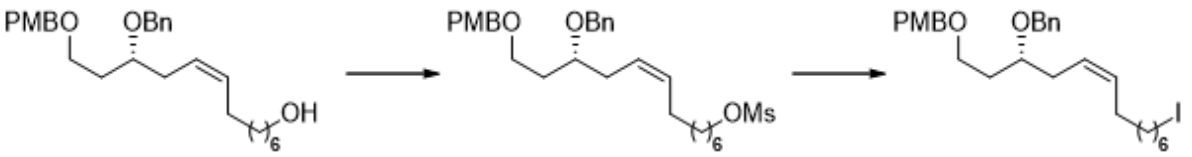
To a solution of **S9** (7.40 mmol) in EtOH/DCM (3:1, v/v) was added Lindlar catalyst (450 mg, 20 wt%) and the reaction mixture was stirred under H_2(g) at r.t. for 8 hr. After the completion of the reaction monitored by TLC, the reaction mixture was filtered through celite and solvent was evaporated under reduced pressure to provide the desired product (3.14 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.25 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.54–5.44 (m, 1H), 5.41–5.36 (m, 1H), 4.57 (t, J = 4.4 Hz, 1H), 4.45 (s, 2H), 3.90–3.80 (m, 1H), 3.78 (s, 4H), 3.76–3.66 (m, 2H), 3.64–3.58 (m, 1H), 3.52–3.47 (m, 1H), 3.40–3.35 (m, 1H), 2.89 (t, J = 3.0 Hz, 1H), 2.30–2.15 (m, 2H), 2.05–1.97 (m, 1H), 1.86–1.78 (m, 1H), 1.77–1.66 (m, 3H), 1.62–1.49 (m, 6H), 1.38–1.26 (m, 8H); LRMS(ESI) *m/z* for $C_{26}H_{42}NaO_5$ [M + Na]$^+$ calcd: 457.29, found: 457.20.

Synthesis of S11, 2-(((R,Z)-11-(benzyloxy)-13-((4-methoxybenzyl)oxy)tridec-8-en-1-yl)oxy)tetrahydro-2H-pyran



To a solution of NaH (5.06 mmol) in dry DMF (40 mL) was added **S10** (3.89 mmol) under Ar(g) slowly at 0℃. After stirring at 0 ℃ for 1 hr, benzyl chloride (5.06 mmol), tetrabutylammonium iodide (1.01 mmol) were added to the reaction mixture. Then, the reaction mixture was stirred at 60 ℃ for overnight. After the completion of the reaction monitored by TLC, reaction was quenched by adding NH_4Cl (aq.) (40 mL) at water bath. Organic layer was extracted with EtOAc (20 mL × 3) and dried over anhydrous Na_2SO_4(s) and solvent was evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:12 to 1:3 gradient elution) to provide the desired product (875 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.23 (m, 7H), 6.86 (d, J = 8.4 Hz, 2H), 5.50–5.39 (m, 2H), 4.60–4.56 (m, 2H), 4.45–4.36 (m, 3H), 3.87 (dt, J = 7.6, 2.8 Hz, 1H), 3.79 (s, 3H), 3.73 (q, J = 6.8 Hz, 1H), 3.64–3.47 (m, 4H), 3.41–3.35 (m, 1H), 2.39–2.25 (m, 2H), 1.86–1.77 (m, 2H), 1.74–1.68 (m, 1H), 1.61–1.50 (m, 9H), 1.36–1.25 (m, 15H); LRMS(ESI) *m/z* for $C_{33}H_{48}NaO_5$ [M + Na]$^+$ calcd: 547.34, found: 547.30.

Synthesis of S12, (R,Z)-1-(((3-(benzyloxy)-13-iodotridec-5-en-1-yl)oxy)methyl)-4-methoxybenzene

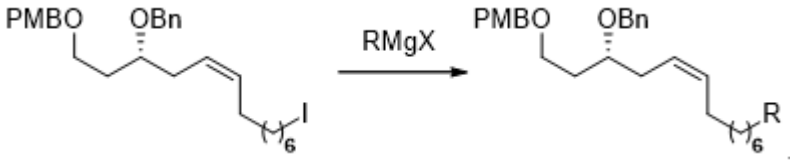


Pyridinium-*p*-toluenesulfonate (0.431 mmol) was added to a solution of **S11** (4.31 mmol) in MeOH (30 mL) and the reaction mixture was stirred at r.t. for overnight. After the completion of the reaction monitored by TLC, solvent was evaporated under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:5 to 1:2.5 gradient elution) to give the hydroxy product (1.90 g, quantitative). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.22 (m, 7H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.56–5.38 (m, 2H), 4.58 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.49–4.44 (m, 1H), 4.41–4.35 (m, 2H), 3.79 (s, 3H), 3.64–3.51 (m, 5H), 2.35–2.24 (m, 2H), 2.04–1.96 (m, 2H), 1.84–1.77 (m, 2H), 1.58–1.50 (m, 2H), 1.37–1.23 (m, 10H); LRMS(ESI) *m/z* for $C_{28}H_{41}O_4$ $[M + H]^+$ calcd: 441.29, found: 441.25.

OH-S11 (4.31 mmol) and methanesulfonyl chloride (6.46 mmol) were dissolved in dry THF under Ar(g), then dry triethylamine (8.61 mmol) was added to the reaction mixture. After stirring at r.t. for 4 hr, solvent was evaporated under reduced pressure and the residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:5 to 1:2.5 gradient elution) to give mesylated product (2.21 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.23 (m, 7H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.49–5.38 (m, 2H), 4.54 (ddd, *J* = 28.0, 11.2, 4.0 Hz, 1H), 4.45–4.36 (m, 3H), 4.20 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 3.64–3.50 (m, 3H), 2.98 (s, 3H), 2.37–2.26 (m, 2H), 2.04–2.96 (m, 2H), 1.85–1.77 (m, 2H), 1.76–1.69 (m, 2H), 1.41–1.25 (m, 10H); LRMS(ESI) *m/z* for $C_{29}H_{43}O_6S$ $[M + H]^+$ calcd: 519.27, found: 519.20.

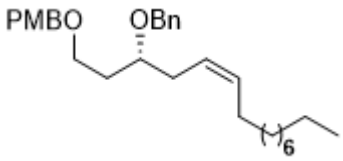
O-mesylated S11 (4.24 mmol), sodium iodide (3.86 g) and sodium carbonate (41.6 mg) were dissolved in acetone and the reaction mixture was stirred at reflux. After the completion of the reaction monitored by TLC, the reaction mixture was condensed under reduced pressure and the residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:20 to 1:7 gradient elution) to give iodinated product (2.19 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.12 (m, 7H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.49–5.38 (m, 2H), 4.54 (ddd, *J* = 28.0, 12.0, 4.4 Hz, 1H), 4.45–4.39 (m, 3H), 3.79 (s, 3H), 3.64–3.50 (m, 3H), 3.17 (quin, *J* = 4.6 Hz, 2H), 2.38–2.25 (m, 2H), 2.04–1.96 (m, 2H), 1.85–1.74 (m, 4H), 1.39–1.23 (m, 8H); LRMS(ESI) *m/z* for $C_{28}H_{40}IO_3$ $[M + H]^+$ calcd: 573.18, found: 573.10.

General procedure of the $Cu^{(I)}$-mediated sp^3-sp^3 cross coupling



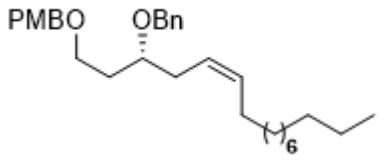
To a solution of **S12** (1.0 equiv.) in dry THF (0.1 M for **S12**) were added alkylmagnesium halide (4.0 equiv.) and dilithium tetrachlorocuprate (0.4 equiv.) successively at 0 ℃. The reaction mixture was stirred at 0 ℃ for overnight. After the completion of the reaction monitored by TLC, the reaction was quenched by adding NH_4Cl(aq.) and organic layer was extracted with EtOAc (30 mL × 3) and dried over anhydrous Na_2SO_4(s). The resultant was condensed under reduced pressure and the residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:25 to 1:12 gradient elution) to provide the desired product.

Synthesis of S13{n15}, (R,Z)-1-(((3-(benzyloxy)pentadec-5-en-1-yl)oxy)methyl)-4-methoxybenzene



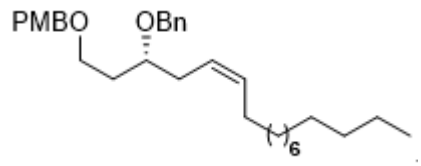
Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.23 (m, 7H), 6.86 (d, J = 8.8 Hz, 2H), 5.51–5.39 (m, 2H), 4.59 (d, J = 11.2 Hz, 1H), 4.45–4.36 (m, 3H), 3.79 (s, 3H), 3.66–3.50 (m, 3H), 2.38–2.27 (m, 2H), 2.02 (q, J = 6.4 Hz, 2H), 1.86–1.78 (m, 2H), 1.32–1.26 (m, 12H), 0.88 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 139.1, 132.4, 130.9, 129.5, 128.5, 128.0, 127.7, 125.2, 113.9, 76.3, 72.8, 71.5, 71.4, 66.9, 55.5, 34.7, 32.1, 32.1, 29.8, 29.8, 29.6, 29.5, 29.4 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{30}H_{44}NaO_3$ $[M + Na]^+$ calcd: 475.32, found: 475.25.

Synthesis of S13{n16}, (R,Z)-1-(((3-(benzyloxy)hexadec-5-en-1-yl)oxy)methyl)-4-methoxybenzene



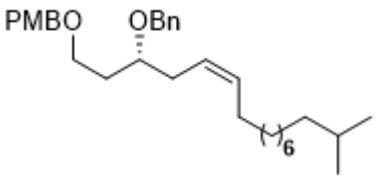
Yield: 48%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.35–7.21 (m, 7H), 6.86 (d, J = 8.7 Hz, 2H), 5.52–5.37 (m, 2H), 4.59 (d, J = 11.4 Hz, 1H), 4.45–4.35 (m, 3H), 3.79 (s, 3H), 3.67–3.51 (m, 3H), 2.38–2.24 (m, 2H), 2.02 (q, J = 6.6 Hz, 2H), 1.85–1.76 (m, 2H), 1.26 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H)x; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 138.9, 132.2, 130.7, 129.3, 128.3, 127.8, 127.5, 125.0, 113.8, 76.1, 72.6, 71.3, 66.7, 55.3, 34.5, 31.9, 31.9, 29.7, 29.6, 29.4, 29.3, 27.5, 22.7, 14.1; LRMS(ESI) *m/z* for $C_{31}H_{46}NaO_3$ $[M + Na]^+$ calcd: 489.33, found: 489.30.

Synthesis of S13{n17}, (R,Z)-1-(((3-(benzyloxy)heptadec-5-en-1-yl)oxy)methyl)-4-methoxybenzene



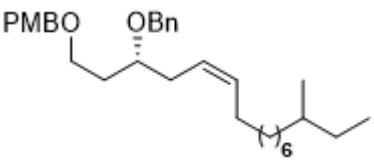
Yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.22 (m, 7H), 6.86 (d, J = 8.8 Hz, 2H), 5.50–5.38 (m, 2H), 4.59 (d, J = 4.0 Hz, 1H), 4.44–4.36 (m, 3H), 3.78 (s, 3H), 3.65–3.50 (m, 3H), 2.39–2.26 (m, 2H), 2.01 (q, J = 6.4 Hz, 2H), 1.81 (quint, J = 6.4 Hz, 2H), 1.26 (bs, 18H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 139.1, ,132.4, 130.9, 129.5, 128.5, 128.0, 127.7, 125.2, 114.0, 76.3, 72.8, 71.5, 66.9, 55.4, 34.7, 32.1, 32.1, 29.9, 29.9, 29.8, 29.6, 29.6, 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{32}H_{49}O_3$ $[M + H]^+$ calcd: 503.35, found: 503.25.

Synthesis of S13{i17}, (R,Z)-1-(((3-(benzyloxy)-15-methylhexadec-5-en-1-yl)oxy)methyl)-4-methoxybenzene



Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.23 (m, 7H), 6.86 (d, J = 8.8 Hz, 2H), 5.51–5.39 (m, 2H), 4.58 (d, J = 11.6 Hz, 1H), 4.44–4.36 (m, 3H), 3.79 (s, 3H), 3.66–3.50 (m, 3H), 2.39–2.25 (m, 2H), 2.02 (q, J = 6.8 Hz, 2H), 1.81 (quin, J = 6.6 Hz, 2H), 1.51 (sep, J = 6.6 Hz, 1H), 1.33–1.26 (m, 12H), 1.17–1.12 (m, 2H), 0.86 (d, J = 6.4 Hz, 6H); LRMS(ESI) *m/z* for $C_{32}H_{49}O_3$ $[M + H]^+$ calcd: 503.35, found: 503.25.

Synthesis of S13{a17}, 1-((((3R,Z)-3-(benzyloxy)-14-methylhexadec-5-en-1-yl)oxy)methyl)-4-methoxybenzene



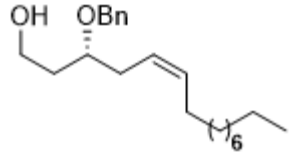
Yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.22 (m, 7H), 6.87 (d, J = 8.5 Hz, 2H), 5.49–5.39 (m, 2H), 4.58 (d, J = 17.0 Hz, 1H), 4.44–4.37 (m, 3H), 3.79 (s, 3H), 3.64–3.60 (m, 1H), 3.60–3.51 (m, 2H), 2.37–2.27 (m, 2H), 2.02 (q, J = 7.0 Hz, 2H), 1.84–1.78 (m, 2H), 1.35–1.23 (m, 14H), 1.16–1.08 (m, 1H), 0.87–0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 139.1,

132.4, 130.9, 129.5, 128.5, 128.0, 127.7, 125.2, 114.0, 76.3, 72.8, 71.5, 66.9, 55.5, 36.9, 34.7, 34.6, 32.1, 30.2, 29.9, 29.8, 29.7, 29.6, 27.7, 27.3, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{32}H_{49}O_3$ $[M + H]^+$ calcd: 503.35, found: 503.25.

General procedure of PMB deprotection

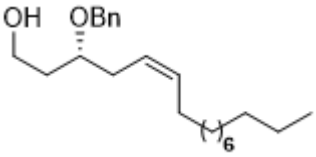
S13 was dissolved in TFA/DCM (1:20, v/v, 0.1 M for **S13**) at 0 ℃ and the reaction mixture was stirred for 4 hr. After the completion of reaction monitored by TLC, reaction mixture was diluted with EtOAc and washed with $NaHCO_3$(aq.). Organic layer was dried over anhydrous Na_2SO_4(s) and condensed under reduced pressure. The residue was and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:10 to 1:5 gradient elution) to provide the desired product.

Synthesis of OH-S13{n15}, (R,Z)-3-(benzyloxy)pentadec-5-en-1-ol



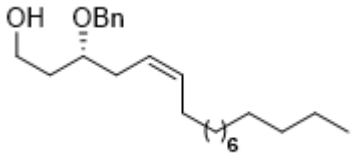
Yield: 59%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.38–7.27 (m, 5H), 5.54–5.46 (m, 1H), 5.42–5.34 (m, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 3.34–3.64 (m, 3H), 2.50–2.28 (m, 3H), 2.07–1.99 (m, 2H), 1.84–1.76 (m, 1H), 1.27 (bs, 14H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.5, 132.8, 128.7, 128.1, 127.9, 124.7, 78.7, 71.3, 61.2, 36.3, 32.1, 31.5, 29.8, 29.8, 29.6, 29.6, 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{22}H_{37}O_2$ $[M + H]^+$ calcd: 332.27, found: 333.20.

Synthesis of OH-S13{n16}, (R,Z)-3-(benzyloxy)hexadec-5-en-1-ol



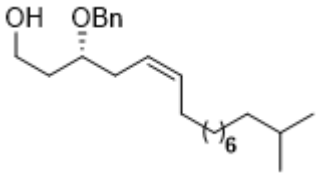
Yield: 77% ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.25 (m, 5H), 5.53–5.47(m, 1H), 5.41–5.35(m, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 3.78–3.67 (m, 3H), 2.48–2.42 (m, 1H), 2.36–2.28 (m, 2H), 2.06–1.99 (m, 2H), 1.83–1.72 (m, 2H), 1.26 (bs, 16H), 0.88 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.5, 132.8, 128.7, 128.1, 128.0, 124.7, 78.7, 71.3, 61.2, 36.3, 32.1, 31.5, 29.9, 29.8, 29.8, 29.6, 29.6, 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{23}H_{39}O_2$ $[M + H]^+$ calcd: 347.29, found: 347.25.

Synthesis of OH-S13{n17}, (R,Z)-3-(benzyloxy)heptadec-5-en-1-ol



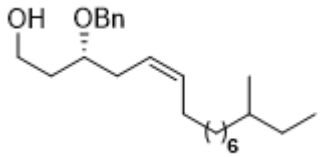
Yield: 74%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.35–7.28 (m, 5H), 5.54–5.46 (m, 1H), 5.42–5.34 (m, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 3.76–3.64 (m, 3H), 2.50–2.27 (m, 3H), 2.04 (q, *J* = 6.6 Hz, 2H), 1.81–1.73 (m, 2H), 1.26 (bs, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.5, 132.8, 128.7, 128.1, 128.0, 124.7, 78.7, 71.3, 61.1, 36.3, 32.1, 31.5, 29.9, 29.9, 29.8, 29.8, 29.6, 29.4, 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{24}H_{41}O_2$ $[M + H]^+$ calcd: 361.30, found: 361.25.

Synthesis of OH-S13{i17}, (R,Z)-3-(benzyloxy)-15-methylhexadec-5-en-1-ol



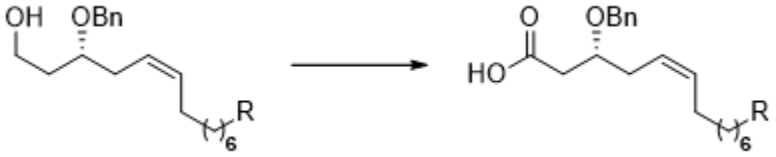
Yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.26 (m, 5H), 5.57–5.49 (m, 1H), 5.43–5.34 (m, 1H), 4.60 (q, J = 10.8 Hz, 2H), 3.97–3.87 (m, 1H), 2.58 (d, J = 5.1 Hz, 2H), 2.48–2.29 (m, 2H), 2.05–1.97 (m, 2H), 1.51 (sep, J = 6.6 Hz, 1H), 1.26 (m, 12H), 1.17–1.12 (m, 2H), 0.86 (d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 138.1, 133.4, 128.4, 127.8, 127.7, 123.8, 75.6, 71.7, 39.1, 31.7, 30.0, 29.7, 29.6, 29.4, 29.3, 28.0, 27.5, 27.4, 22.7; LRMS(ESI) *m/z* for $C_{24}H_{41}O_2$ $[M + H]^+$ calcd: 361.30, found: 361.25.

Synthesis of OH-S13{a17}, (3R,Z)-3-(benzyloxy)-14-methylhexadec-5-en-1-ol



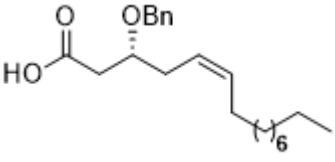
Yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.26 (m, 5H), 5.57–5.49 (m, 1H), 5.42–5.34 (m, 1H), 4.60 (q, J = 11.7 Hz, 2H), 3.93 (quint, J = 6.0 Hz, 1H), 2.59 (d, J = 5.7 Hz, 2H), 2.54–2.29 (m, 2H), 2.02 (q, J = 6.9 Hz, 2H), 1.27 (bs, 13H), 1.16–1.07 (m, 2H), 0.85 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 138.2, 133.6, 128.6, 128.0, 128.0, 123.9, 75.8, 71.9, 39.4, 36.9, 34.6, 31.8, 30.2, 29.8, 29.8, 29.7, 29.6, 27.7, 27.3, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{24}H_{41}O_2$ $[M + H]^+$ calcd: 361.30, found: 361.25.

General procedure of oxidation



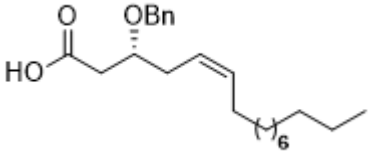
To a solution of **OH-S13** (1.0 equiv.) in acetone (0.1 M for **OH-S13**) was added Jones reagent (2.0 equiv.) at 0 ℃, then the reaction mixture was stirred for 2.5 hr. After the completion of the reaction monitored by TLC, the reaction mixture was diluted with EtOAc (2 mL) and washed with 1N HCl (3 mL). Organic layer was dried over anhydrous Na_2SO_4(s) and condensed under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:8 to 1:5 gradient elution with 0.5% AcOH) to provide the desired product.

Synthesis of S14{n15}, (R,Z)-3-(benzyloxy)pentadec-5-enoic acid



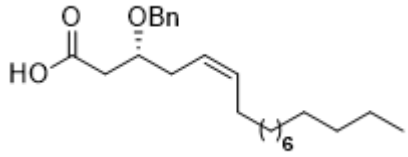
Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.26 (m, 5H), 5.56–5.49 (m, 1H), 5.41–5.35 (m, 1H), 4.60 (q, J = 11.8 Hz, 2H), 3.93 (quint, J = 6.0 Hz, 1H), 2.60–2.57 (m, 2H), 2.46–2.38 (m, 1H), 2.35–2.31 (m, 1H), 2.02 (q, J = 7.2 Hz, 2H), 1.26 (bs, 14H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 138.3, 133.6, 128.6, 128.0, 127.9, 124.0, 75.8, 71.9, 39.5, 32.1, 31.8, 29.8, 29.8, 29.5, 27.7, 22.9, 14.3.

Synthesis of S14{n16}, (R,Z)-3-(benzyloxy)hexadec-5-enoic acid



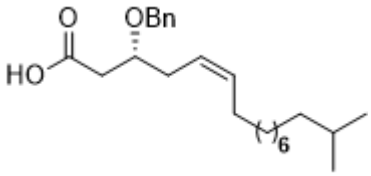
Yield: 61%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.28 (m, 5H), 5.57–5.49 (m, 1H), 5.42–5.34 (m, 1H), 4.60 (q, J = 11.4 Hz, 2H), 3.93 (quint, J = 6.0 Hz, 1H), 2.58 (d, J = 5.1 Hz, 2H), 2.49–2.29 (m, 2H), 2.02 (q, J = 6.6 Hz, 2H), 1.26 (bs, 16H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 138.3, 133.6, 128.6, 128.0, 127.9, 124.0, 75.8, 71.9, 39.5, 32.1, 31.9, 29.9, 29.8, 29.6, 27.7, 22.9, 14.3.

Synthesis of S14{n17}, (R,Z)-3-(benzyloxy)heptadec-5-enoic acid



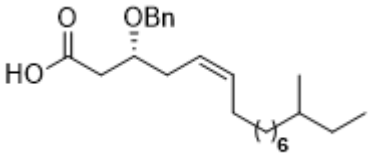
Yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.25 (m, 5H), 5.57–5.49 (m, 1H), 5.42–5.34 (m, 1H), 4.60 (q, J = 10.8 Hz, 2H), 3.93 (quint, J = 6.0 Hz, 1H), 2.58 (dd, J = 6.3, 2.4 Hz, 2H), 2.46–2.29 (m, 2H), 2.02 (q, J = 6.9 Hz, 2H), 1.26 (bs, 18H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3 138.3, 133.6, 128.6, 128.0, 127.9, 124.0, 75.8, 71.9, 39.5, 32.1, 31.9, 29.9, 29.9, 29.8, 29.6, 27.7, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{24}H_{37}O_3$ $[M - H]^-$ calcd: 373.28, found: 373.10.

Synthesis of S14{i17}, (R,Z)-3-(benzyloxy)-15-methylhexadec-5-enoic acid



Yield: 96%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.26 (m, 5H), 5.57–5.49 (m, 1H), 5.43–5.34 (m, 1H), 4.60 (q, J = 10.8 Hz, 2H), 3.97–3.87 (m, 1H), 2.58 (d, J = 5.1 Hz, 2H), 2.48–2.29 (m, 2H), 2.05–1.97 (m, 2H), 1.51 (sep, J = 6.6 Hz, 1H), 1.26 (m, 12H), 1.17–1.12 (m, 2H), 0.86 (d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 138.1, 133.4, 128.4, 127.8, 127.7, 123.8, 75.6, 71.7, 39.1, 31.7, 30.0, 29.7, 29.6, 29.4, 29.3, 28.0, 27.5, 27.4, 22.7; LRMS(ESI) *m/z* for $C_{24}H_{37}O_3$ $[M - H]^-$ calcd: 373.28, found: 373.10.

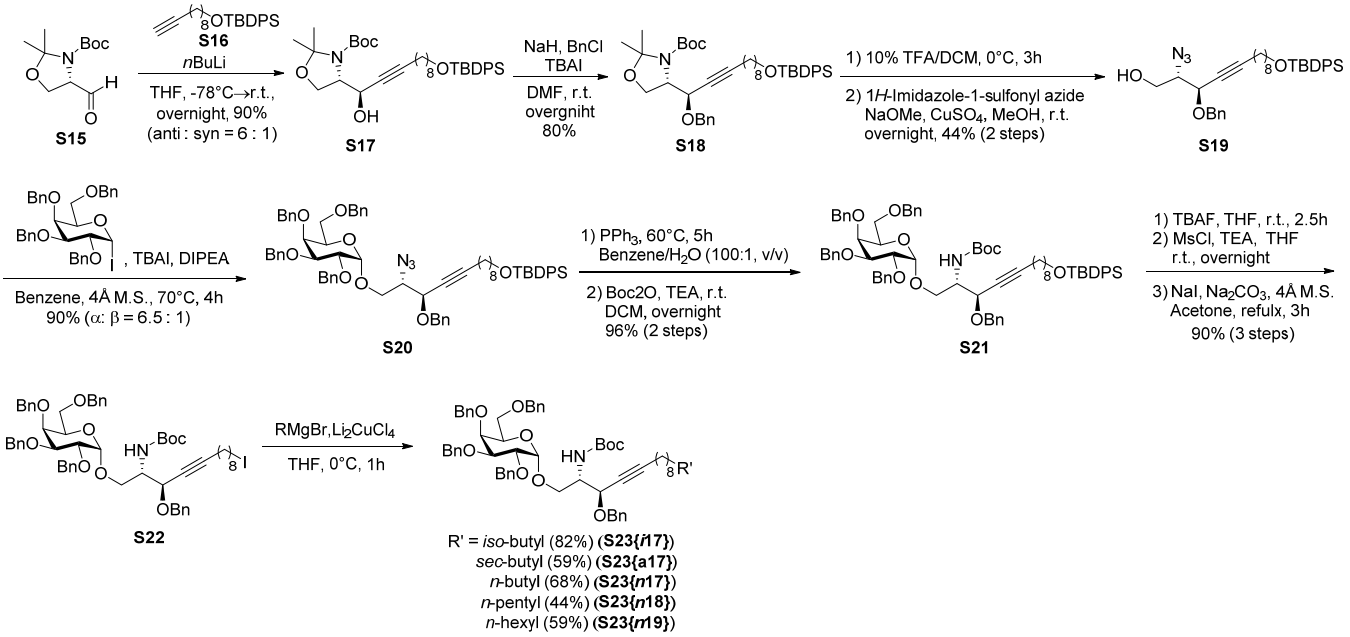
Synthesis of S14{a17}, (3R,Z)-3-(benzyloxy)-14-methylhexadec-5-enoic acid



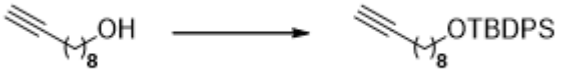
Yield: 75%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.26 (m, 5H), 5.57–5.49 (m, 1H), 5.42–5.34 (m, 1H), 4.60 (q, J = 11.7 Hz, 2H), 3.93 (quint, J = 6.0 Hz, 1H), 2.59 (d, J = 5.7 Hz, 2H), 2.54–2.29 (m, 2H), 2.02 (q, J = 6.9 Hz, 2H), 1.27 (bs, 13H), 1.16–1.07 (m, 2H), 0.85 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 138.2, 133.6, 128.6, 128.0, 128.0, 123.9, 75.8, 71.9, 39.4, 36.9, 34.6, 31.8, 30.2, 29.8, 29.8, 29.7, 29.6, 27.7, 27.3, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{24}H_{37}O_3$ $[M - H]^-$ calcd: 373.28, found: 373.10.

B. Synthesis of *α*-galactosylsphingoid building blocks

In the case of sphinganine building blocks, α-galactosylsphinganine having iodide (S22) was prepared from Garner aldehyde. In a similar manner as acyl building blocks, sphingoid building blocks (**S23{*i*17}**–**S23{*n*18}**) were generated by decoration of terminal structures via sp^3–sp^3 cross-coupling.

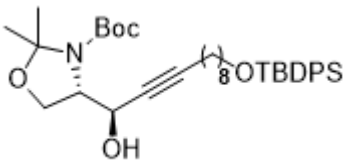


Synthesis of S16, *tert*-butyl(dec-9-yn-1-yloxy)diphenylsilane



To a solution of 9-decyne-1-ol (25.9 mmol) in dry DCM (150 mL) were added *tert*-butyl(chloro)diphenylsilane (33.7 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (33.7 mmol) under Ar(g) at 0 ℃. After being stirred for 1 hr at 0 ℃, the reaction was warmed up to ambient temperature and stirred for 4 hr. After the completion of the reaction monitored by TLC, the reaction mixture was diluted with EtOAc (100 mL) and washed with brine. Organic layer was dried over anhydrous Na_2SO_4 (s) and condensed under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:80 to 1:40 gradient elution) to provide the desired product (9.78g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.68–7.66 (m, 4H), 7.44–7.36 (m, 6H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.18 (td, *J* = 7.0, 2.5 Hz, 2H), 1.94 (t, *J* = 2.5 Hz, 1H), 1.58–1.49 (m, 4H), 1.39–1.31 (m, 4H), 1.28–1.26 (m, 4H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 135.8, 134.4, 129.7, 127.8, 85.0, 68.3, 64.2, 32.8, 29.4, 29.3, 28.9, 28.7, 27.1, 25.9, 19.4, 18.6; LRMS(ESI) *m/z* for $C_{26}H_{37}OSi$ $[M + H]^+$ calcd: 393.25, found: 393.20.

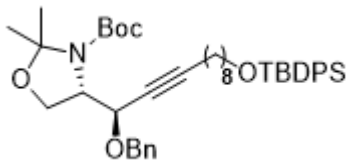
Synthesis of S17, *tert*-butyl (S)-4-((R)-11-((*tert*-butyldiphenylsilyl)oxy)-1-hydroxyundec-2-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate



To a solution of **S16** (10.7 mmol) in dry THF (80 mL) was added *n*-butyllithium (12.9 mmol) slowly under Ar(g) at -78 ℃ and the reaction mixture was stirred for 45 min at -78 ℃. Garner's aldehyde (11.8 mmol) in dry THF (20 mL) was added to reaction mixture dropwise at -78 ℃. The reaction mixture was stirred at ambient temperature for overnight. After the completion of the reaction monitored by TLC, the reaction was quenched by adding NH_4Cl(aq.) (50 mL) and organic layer was extracted with

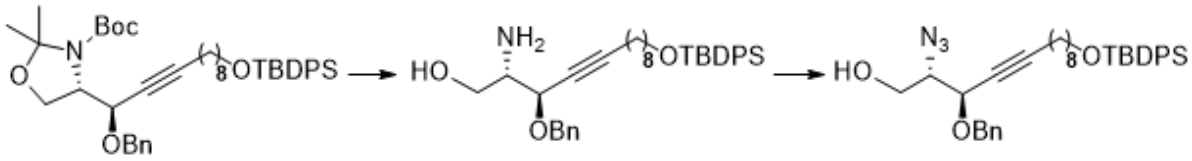
EtOAc (50 mL × 3). Organic layer was dried over anhydrous Na_2SO_4 (s) and condensed under reduced pressure. The residue purified by silica-gel flash column chromatography (EtOAc:Hex = 1:10 to 1:5 gradient elution) to provide the desired product (5.65g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm) δ 7.68–7.66 (m, 4H), 7.44–7.35 (m, 6H), 4.74 (d, J = 7.6 Hz, 1H), 4.51 (d, J = 7.6 Hz, 1H), 4.13–4.06 (m, 2H), 3.90 (bs, 1H), 3.65 (t, J = 6.4 Hz, 2H), 2.19 (td, J = 7.2, 1.6 Hz, 2H), 1.58–1.45 (m, 20H), 1.38–1.31 (m, 4H), 1.28–1.24 (m, 4H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 135.8, 134.4, 129.7, 127.8, 95.2, 64.2, 32.8, 29.5, 29.3, 29.1, 28.8, 28.6, 27.1, 26.0, 19.4, 19.0; LRMS(ESI) *m/z* for $C_{37}H_{55}NaNO_5Si$ [M + Na]$^+$ calcd: 644.37, found: 644.30.

Synthesis of S18, *tert*-butyl (S)-4-((R)-1-(benzyloxy)-11-((*tert*-butyldiphenylsilyl)oxy)undec-2-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate



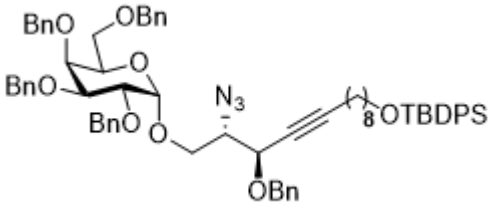
Sodium hydride (13.0 mmol) was dissolved in dry DMF (50 mL) under Ar(g) at 0 ℃. **S17** in dry DMF (10 mL) was added to the reaction mixture slowly and the reaction mixture was stirred at 0 ℃ for 30 min. Tetrabutylammonium iodide (1.30 mmol) and benzyl chloride (13.0 mmol) were added to the reaction mixture and the reaction mixture was stirred at r.t. for overnight. After the completion of the reaction monitored by TLC, the reaction was quenched by adding NH_4Cl(aq.) (50 mL) at 0 ℃ and organic layer was extracted with EtOAc (40 mL × 3). The resultant was dried over anhydrous Na_2SO_4(s) and condensed under reduced pressure. The residue purified by silica-gel flash column chromatography (EtOAc:Hex = 1:20 to 1:15 gradient elution) to provide the desired product (5.73g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak CDCl3 at 7.26 ppm) δ 7.68–7.66 (m, 4H), 7.42–7.32 (m, 11H), 4.82 (dd, J = 12.3, 5.1 Hz, 1H), 4.54 (d, J = 72 Hz, 1H), 4.52 (dd, J = 12.3, 5.1 Hz, 1H), 4.30–4.25 (m, 1H), 4.03 (d, J = 40.5 Hz, 1H), 4.01 (t, J = 7.8 Hz, 1H), 3.65 (t, J = 6.6 Hz, 2H), 2.24–2.17 (m, 2H), 1.62–1.47 (m, 15H), 1.36–1.26 (m, 12H), 1.05 (s, 9H); LRMS(ESI) *m/z* for $C_{44}H_{61}NNaO_5Si$ [M + Na]$^+$ calcd: 734.42, found: 734.50.

Synthesis of S19, (2S,3R)-2-azido-3-(benzyloxy)-13-((*tert*-butyldiphenylsilyl)oxy)tridec-4-yn-1-ol



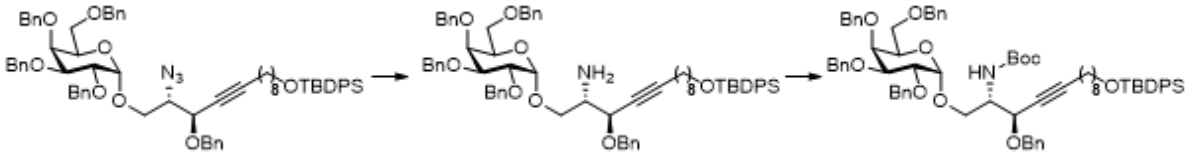
S18 (3.62 mmol) was dissolved in HCl (4 M in dioxane)/THF (9 mL/9 mL) under Ar(g) and the reaction mixture was stirred at 0 ℃. After the completion of the reaction monitored by TLC, the reaction mixture was poured to sat. $NaHCO_3$ (aq.) (40 mL) and organic layer was extracted with EtOAc (40 mL × 3). The organic layer was dried over anhydrous Na_2SO_4(s) and condensed under reduced pressure. The resultant, 4-(dimethylamino)pyridine (5.43 mmol) and imidazole-1-sulfonylazide[1)] (7.25 mmol) were dissolved in MeOH (40 mL) and the reaction mixture was stirred at r.t. for overnight. After the completion of reaction monitored by TLC, the reaction mixture was diluted with DCM (50 mL) and washed with sat. NH_4Cl(aq.). The resulting organic layer was dried with anhydrous Na_2SO_4(s) and condensed under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:12 to 1:5 gradient elution) to provide the desired product (2.18g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.68–7.66 (m, 4H), 7.43–7.27 (m, 11H), 4.84 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.28–4.26 (m, 1H), 3.82 (bs, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.60 (q, J = 5.2 Hz, 1H), 2.27 (td, J = 7.2, 1.6 Hz, 2H), 2.05 (bs, 1H), 1.58–1.51 (m, 4H), 1.41–1.32 (m, 4H), 1.29–1.26 (m, 4H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.6, 134.1, 129.5, 128.5, 128.0, 128.0, 127.6, 89.8, 75.3, 70.7, 69.8, 65.6, 64.0, 62.3, 32.5, 29.2, 29.1, 28.8, 28.4, 26.9, 25.7, 19.2, 18.8; LRMS(ESI) *m/z* for $C_{36}H_{48}N_3O_3Si$ [M + H]$^+$ calcd: 598.34, found: 598.20.

Synthesis of S20, (((11R,12S)-12-azido-11-(benzyloxy)-13-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tridec-9-yn-1-yl)oxy)(*tert*-butyl)diphenylsilane



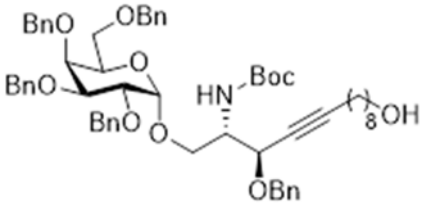
To a solution of 1-*O*-acetyl-2,3,4,6-tetra-O-benzyl-D-galactopyranoside (6.14 mmol) in dry DCM (50 mL) at 0 ℃ was added trimethylsilyl iodide (TMSI, 7.37 mmol). After being stirred for 30 min at 0 ℃, the reaction was stopped by adding anhydrous toluene (30 mL) and residual TMSI was removed by azeotropic evaporation with anhydrous toluene 3 times. The resultant (slight yellow) was dissolved in anhydrous benzene (15 mL) and kept under Ar(g). In a separate round-bottom flask, molecular sieve (4 Å, 1 g), tetrabutylammonium iodide (TBAI, 22.1 mmol), **S19** (2.46 mmol) and diisopropylethylamine (7.37 mmol) were added into dry benzene (55 mL). The reaction mixture was stirred under Ar(g) at 65 ℃ for 10 min. As the complete dissolution of TBAI, the galactosyl iodide in dry benzene was added into this flask and the reaction mixture was stirred at 65 ℃ for 2 hr. After the completion of reaction monitored by TLC, the reaction mixture was poured into cold sat. $NaHCO_3$(aq.). Organic layer was extracted with EtOAc (50 mL × 3) and dried over anhydrous Na_2SO_4(s). The resulting mixture was condensed under reduced pressure and purified by silica-gel column chromatography (EtOAc:Hex = 1:20 to 1:3 gradient elution) to provide the desired product (1.49g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.66 (dd, *J* = 7.6, 1.6 Hz, 4H), 7.41–7.23 (m, 26H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 4.83–4.75 (m, 3H), 4.73–4.65 (m, 2H), 4.56 (d, *J* = 12 Hz, 1H), 4.48–4.42 (m, 2H), 4.40–4.36 (m, 1H), 4.31–4.30 (m, 1H), 4.04 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.98–3.86 (m, 4H), 3.80–3.76 (m, 1H), 3.67–3.62 (m, 3H), 3.53–3.50 (m, 2H), 2.21 (td, *J* = 7.2, 1.6 Hz, 2H), 1.53 (septet, *J* = 7.2 Hz, 4H), 1.42–1.21 (m, 8H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.0, 138.8, 138.2, 137.7, 135.8, 134.4, 129.7, 128.6, 128.5, 128.5, 128.4, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6 98.8, 89.7, 79.0, 76.6, 75.2, 75.2, 75.0, 73.7, 73.4, 70.8, 69.9, 69.4, 69.1, 67.6, 64.2, 64.1, 32.8, 29.9, 29.5, 29.3, 29.1, 28.8, 27.1, 26.0, 19.4, 19.0; LRMS(ESI) *m/z* for $C_{70}H_{82}N_3O_8Si$ $[M + H]^+$ calcd: 1120.58, found: 1120.30.

Synthesis of S21, *tert*-butyl ((2S,3R)-3-(benzyloxy)-13-((*tert*-butyldiphenylsilyl)oxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tridec-4-yn-2-yl)carbamate



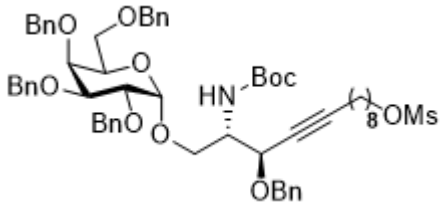
To a solution of **S20** (1.33 mmol) in benzene/H_2O (10 mL/0.1 mL) was added triphenylphosphine (2.67 mmol) and the reaction mixture was stirred at 60 ℃ for 3 hr. After the completion of reaction monitored by TLC, solvent was evaporated under reduced pressure and residual H_2O was removed by azeotropic evaporation with toluene three times. The resulting mixture was dissolved in DCM (10 mL) then di-*tert*-butyl dicarbonate (2.67 mmol), triethylamine (4.69 mmol) were added to the reaction mixture. After being stirred at r.t. for overnight, solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography (EtOAc:Hex = 1:10 to 1:5 gradient elution) to provide the desired product (1.28g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.81–7.65 (m, 4H), 7.40–7.22 (m, 31H), 5.07 (d, *J* = 9.3 Hz, 1H), 4.92 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 3.0 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.76–4.68 (m, 3H), 4.64–4.50 (m, 3H), 4.46–4.35 (m, 3H), 4.15–4.07 (m, 1H), 4.00 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.92–3.83 (m, 3H), 3.76 (d, *J* = 5.1 Hz, 1=2H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.48 (d, *J* = 6.6 Hz, 2H), 2.16 (td, *J* = 6.9, 1.5 Hz, 2H), 1.56–1.50 (m, 4H), 1.42 (s, 9H), 1.34–1.24 (m, 8H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 135.8, 134.4, 129.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 98.7, 88.7, 79.4, 79.1, 75.2, 75.0, 73.7, 73.3, 70.7, 69.7, 69.2, 69.0, 67.9, 64.2, 53.9, 32.8, 29.5, 29.3, 29.2, 28.9, 28.6, 27.1, 26.0, 19.4, 19.0; LRMS(ESI) *m/z* for $C_{75}H_{91}NaNO_{10}Si$ $[M + Na]^+$ calcd: 1216.63, found: 1216.45.

Synthesis of OH-S21, *tert*-butyl ((2S,3R)-3-(benzyloxy)-13-hydroxy-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tridec-4-yn-2-yl)carbamate



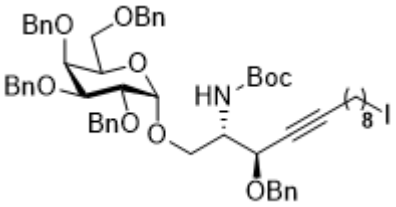
To a solution of **S20** (0.228 mmol) at r.t. in THF (2 mL) was added TBAF (1 M in THF, 0.274 mL), then stirred at r.t. for 2.5 hr. When the reaction was completed checked by TLC, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (20% EA in hexane gradient to 33.33%) to obtain the desired product (0.218g, quantitative). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.39–7.20 (m, 25H), 5.25 (d, J = 9.3 Hz, 1H), 4.93–4.89 (m, 1H), 4.86 (d, J = 3.0 Hz, 1H), 4.80 (m, 1H), 4.78–4.68 (m, 3H), 4.68–4.63 (m, 1H), 4.59–4.34 (m, 5H), 4.12–4.07 (m, 1H), 4.03–3.76 (m, 6H), 3.58 (t, J = 6.3 Hz, 2H), 3.49 (d, J = 6.6 Hz, 2H), 2.19–2.15 (m, 2H), 1.53–1.25 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 139.0, 138.8, 138.7, 138.2, 138.1, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 98.6, 88.5, 79.3, 79.1, 76.8, 75.1, 74.9, 73.6, 73.3, 73.2, 70.6, 69.6, 69.1, 68.9, 67.8, 63.0, 53.9, 32.8, 29.2, 28.9, 28.7, 28.6, 25.7, 18.8.

Synthesis of O-mesylated S21, (11R,12S)-11-(benzyloxy)-12-((*tert*-butoxycarbonyl)amino)-13-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tridec-9-yn-1-yl methanesulfonate



To a solution of **OH-S21** (1.24 mmol) in THF were added methanesulfonyl chloride (1.87 mmol) and triethylamine (2.49 mL) and the reaction mixture was stirred at r.t. for 3 hr. After the completion of the reaction monitored by TLC, solvent was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (EtOAc:Hex = 1:5 to 1:2 gradient elution) to provide the desired product (1.28g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.39–7.21 (m, 25H), 5.08 (d, J = 9.0 Hz, 1H), 4.92 (d, J = 11.4 Hz, 1H), 4.85 (d, J = 3.0 Hz, 1H), 4.81 (d, J = 11.7 Hz, 1H), 4.76–4.69 (m, 3H), 4.64 (s, 1H), 4.58 (d, J = 12.6 Hz, 1H), 4.51 (d, J = 5.7 Hz, 1H), 4.43 (dd, J = 15.6, 3.3 Hz, 2H), 4.35 (quint, J = 2.4 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 4.13–4.09 (m, 1H), 4.00 (dd, J = 9.9, 3.6 H, 1H), 3.921 (bs, 1H), 3.87–3.83 (m, 2H), 3.77 (d, J = 5.1 Hz, 2H), 3.48 (d, J = 6.3 Hz, 2H), 2.97 (s. 3H), 2.17 (td, J = 6.9, 1.8 Hz, 2H), 1.72 (quint, J = 6.9 Hz, 2H), 1.52–1.46 (m, 2H), 1.42 (s, 9H), 1.40–1.21 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.5, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 98.8, 86.6, 79.4, 79.1, 76.8, 75.2, 75.0, 73.7, 73.3, 70.7, 70.3, 69.7, 69.2, 69.0, 67.9, 53.9, 37.5, 29.3, 29.1, 29.0, 28.8, 28.6, 25.6, 18.9; LRMS(ESI) *m/z* for $C_{60}H_{75}NaNO_{12}S$ $[M + Na]^+$ calcd: 1056.49, found: 1056.30.

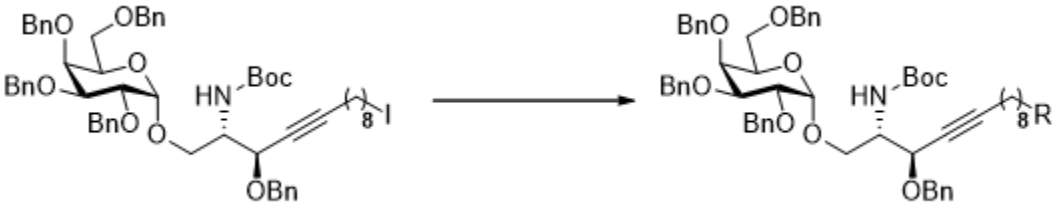
Synthesis of S22, *tert*-butyl ((2S,3R)-3-(benzyloxy)-13-iodo-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)tridec-4-yn-2-yl)carbamate



To a solution of **O-mesylated S21** (1.23 mmol) in acetone were added sodium iodide (6.17 mmol) and sodium carbonate (0.25 mmol), then the reaction mixture was stirred at 65 ℃ for 3 hr. After the completion of reaction monitored by TLC, solvent was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (EtOAc:Hex = 1:10 to 1:5 gradient elution) to provide the desired product (1.26g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.39–7.21 (m, 25H), 5.07 (d, J = 9.3 Hz, 1H), 4.92 (d, J = 11.4 Hz, 1H), 4.85 (d, J = 3.0 Hz, 1H), 4.81 (d, J = 11.7 Hz, 1H), 4.76–4.69 (m, 3H), 4.66 (s, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 6.3 Hz, 1H), 4.46–4.40 (m, 2H), 4.37–4.36 (m, 1H), 4.12 (q, J = 7.2 Hz, 1H), 4.01 (dd, J = 10.2, 3.6 Hz, 1H), 3.92 (bs, 1H), 3.90–3.83 (m, 2H), 3.77 (d, J = 5.1 Hz, 2H), 3.48 (d, J = 6.6 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.17 (t, J = 6.9 Hz, 2H), 1.79 (quint, J = 7.2 Hz, 2H), 1.58–1.26 (m, 19H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 98.8,

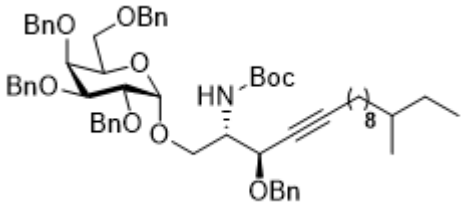
88.6, 79.4, 79.1, 75.2, 75.0, 73.7, 73.3, 70.7, 69.7, 69.2, 69.0, 67.9, 53.9, 33.7, 30.7, 29.1, 29.0, 28.8, 28.6, 18.9, 7.5; LRMS(ESI) *m/z* for $C_{59}H_{72}INaNO_9$ $[M + Na]^+$ calcd: 1088.41, found: 1088.30.

General procedure of the $Cu^{(I)}$-mediated sp^3–sp^3 cross coupling



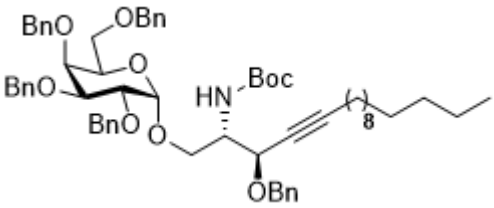
To a solution of **S22** (1.0 equiv.) in dry THF (0.1 M for **S22**) under Ar(g) were added alkylmagnesium halide (4.0 equiv.) and dilithium tetrachlorocuprate (0.4 equiv.) successively at 0 ℃. The reaction mixture was stirred for 1.5 hr at 0 ℃. After the completion of reaction monitored by TLC, the reaction was quenched by adding sat. $NaHCO_3$ (aq.) and organic layer was extracted with EtOAc three times and dried over anhydrous Na_2SO_4(s). Resulting mixture was condensed under reduced pressure and purified by silica-gel flash column chromatography (EtOAc:Hex = 1:10 to 1:6 gradient elution) to provide the desired product.

Synthesis of S23{a17}, *tert*-butyl ((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)carbamate



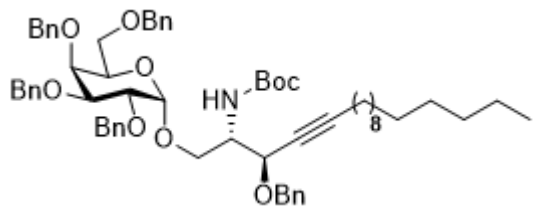
Yield: 59%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.38–7.25 (m, 25H), 5.07 (d, *J* =9.0 Hz, 1H), 4.92 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 2.7 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.76–4.68 (m, 3H), 4.64 (s, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.51 (d, *J* = 6.3 Hz, 1H), 4.46 (s, 1H), 4.39 (dd, *J* = 12.6, 5.4 Hz, 2H), 4.14–3.90 (m, 1H), 4.00 (dd, *J* =9.9, 3.6 Hz, 1H), 3.92 (bs, 1H), 3.90–3.83 (m, 2H), 3.76 (d, *J* = 4.8 Hz, 2H), 3.49 (d, *J* =6.6 Hz, 2H), 2.17 (td, *J* = 6.9 Hz, 1.5 Hz, 2H), 1.48–1.42 (m,11H), 1.36–1.23 (m, 13H), 1.16–1.06 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.7, 127.6, 98.7, 88.8, 79.4, 79.1, 75.2, 75.0, 73.7, 73.3, 70.7, 69.7, 69.2, 69.0, 67.9, 53.9, 36.9, 34.6, 30.2, 29.8, 29.7, 29.4, 28.9, 28.6, 27.3, 19.4, 19.0, 11.6; LRMS(ESI) *m/z* for $C_{63}H_{81}NaNO_9$ $[M + Na]^+$ calcd: 1018.58, found: 1018.35.

Synthesis of S23{n17}, *tert*-butyl ((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)heptadec-4-yn-2-yl)carbamate



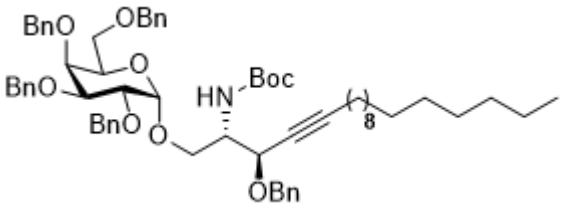
Yield: 68%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.39–7.22 (m, 25H), 5.07 (d, *J* = 8.7 Hz, 1H), 4.92 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 3.0 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.76–4.69 (m, 3H), 4.64 (s, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.51 (d, *J* = 6.3 Hz, 1H), 4.64 (s, 1H), 4.42–4.36 (m, 2H), 4.16–4.09 (m, 1H), 4.01 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.92 (bs, 1H), 3.90–3.83 (m, 2H), 3.76 (d, *J* = 5.1 Hz, 2H), 3.48 (d, *J* = 6.3 Hz, 2H), 2.16 (td, *J* = 7.2, 1.8 Hz, 2H), 1.51–1.42 (m, 11H), 1.36–1.25 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.6, 128.5, 128.5, 1284, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 98.7, 88.8, 79.4, 79.1, 75.2, 75.0, 73.7, 73.3, 70.7, 69.6, 69.1, 69.0, 67.9, 53.9, 32.1, 29.9, 29.8, 29.7, 29.6, 29.3, 29.2, 28.6, 28.0, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{63}H_{81}NaNO_9$ $[M + Na]^+$ calcd: 1018.58, found: 1018.35.

Synthesis of S23{n18}, *tert*-butyl ((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-4-yn-2-yl)carbamate



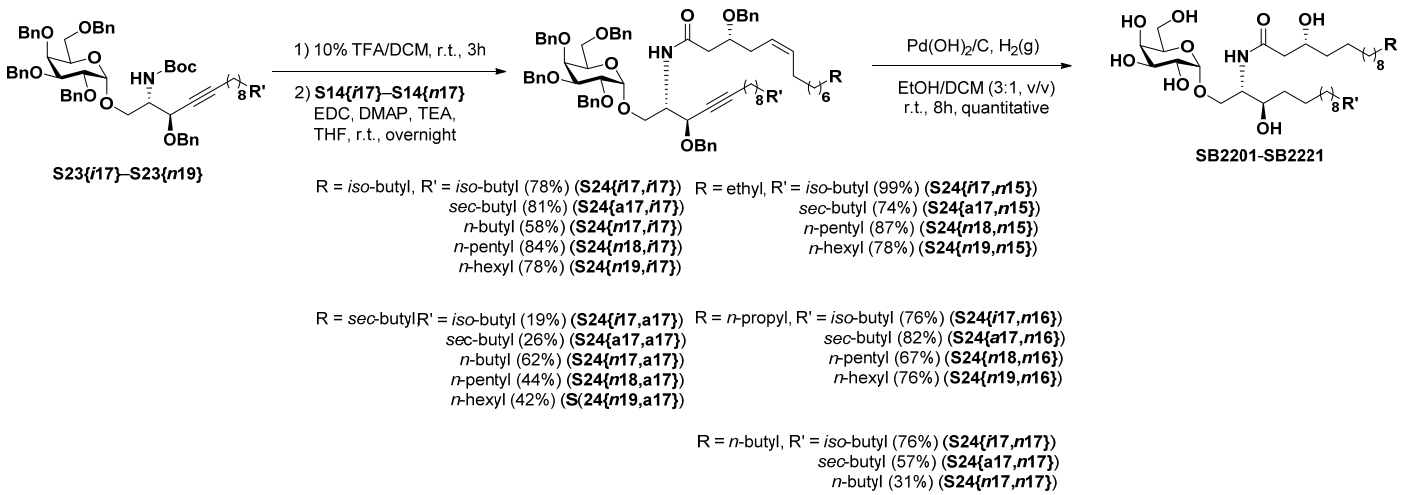
Yield: 44%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.39–7.22 (m, 25H), 5.07 (d, J = 8.7 Hz, 1H), 4.92 (d, J = 11.4 Hz, 1H), 4.85 (d, J = 3.0 Hz, 1H), 4.81 (d, J = 11.7 Hz, 1H), 4.76–4.69 (m, 3H), 4.64 (s, 1H), 4.59 (d, J = 5.7 Hz, 1H), 4.51 (d, J = 6.3 Hz, 1H), 4.64 (s, 1H), 4.42–4.36 (m, 2H), 4.16–4.09 (m, 1H), 4.01 (dd, J = 9.9, 3.6 Hz, 1H), 3.92 (bs, 1H), 3.90–3.83 (m, 2H), 3.76 (d, J = 5.1 Hz, 2H), 3.48 (d, J = 6.3 Hz, 2H), 2.16 (td, J = 7.2, 1.8 Hz, 2H), 1.51–1.42 (m, 11H), 1.36–1.25 (m, 20H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.6, 128.5, 128.5, 1284, 128.4, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 98.7, 88.8, 79.4, 79.1, 75.2, 75.0, 73.7, 73.3, 70.7, 69.6, 69.1, 69.0, 67.9, 53.9, 32.1, 29.9, 29.8, 29.6, 29.4, 29.2, 28.9, 28.6, 22.9, 19.0, 14.4; LRMS(ESI) *m/z* for $C_{64}H_{83}NaNO_9$ [M + Na]$^+$ calcd: 1032.60, found: 1032.40.

Synthesis of S23{n19}, *tert*-butyl ((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)nonadec-4-yn-2-yl)carbamate

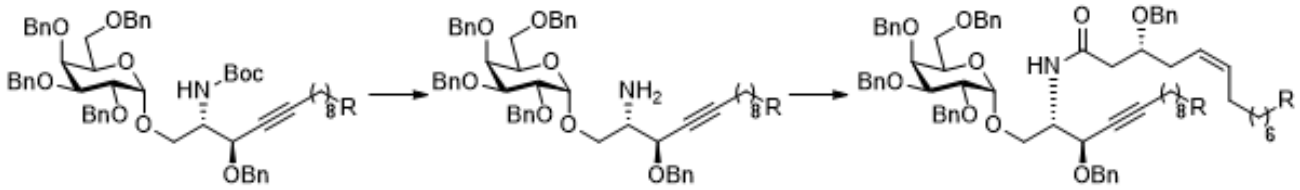


Yield: 59%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.38–7.25 (m, 25H), 5.07 (d, J = 9.0 Hz, 1H), 4.92 (d, J = 11.1 Hz, 1H), 4.85 (d, J = 2.7 Hz, 1H), 4.81 (d, J = 11.7 Hz, 1H), 4.76–4.69 (m, 3H), 4.64 (s, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 6.0 Hz, 1H), 4.46 (s, 1H), 4.42–4.36 (m, 2H), 4.13–4.09 (m, 1H), 4.01 (dd, J = 10.2, 3.6 Hz, 1H), 3.92 (bs, 1H), 3.90–3.83 (m, 2H), 3.76 (d, J = 4.8 Hz, 2H), 3.49 (d, J = 6.6 Hz, 2H), 2.16 (td, J = 6.9, 1.5 Hz, 2H), 1.51–1.46 (m, 2H), 1.42 (s, 9H), 1.37–1.25 (m, 22H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 139.1, 138.9, 138.8, 138.2, 138.1, 128.6, 128.5, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 98.7, 88.8, 79.4, 79.1, 76.8, 75.9, 75.2, 75.0, 73.7, 73.3, 70.7, 69.7, 69.1, 69.0, 67.9, 53.9, 32.1, 29.9, 29.9, 29.8, 29.6, 29.4, 29.2, 28.9, 28.6, 22.9, 19.0, 14.3; LRMS(ESI) *m/z* for $C_{65}H_{85}NaNO_9$ [M + Na]$^+$ calcd: 1046.61, found: 1046.40.

C. Construction of *α*-GalCer library

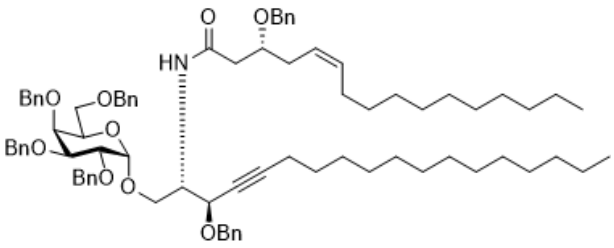


General procedure of Boc deprotection and amide coupling



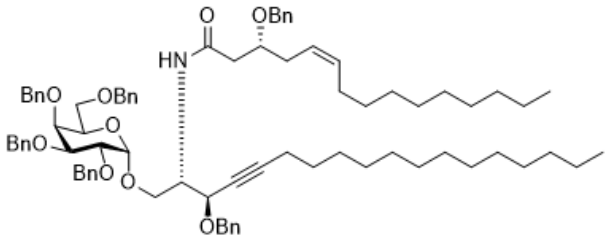
S23 (1.0 equiv.) was dissolved in TFA/DCM (0.2 mL/2 mL) and the reaction mixture was stirred at r.t. for 3 hr. After the completion of reaction monitored by TLC, the reaction was quenched by adding sat. $NaHCO_3$(aq.) and organic layer was extracted with EtOAc (10 mL × 3) and dried over anhydrous Na_2SO_4(s). The resulting mixture, **S14** (1.0 equiv.), *N*-3-dimethylaminopropyl-*N'*-ethylcarbodiimde hydrochloride (2.5 equiv.) and 4-(dimethylamino)pyridine (0.1 equiv.) were dissolved in dry THF (2 mL) and the reaction mixture was stirred at r.t. for overnight. After the completion of reaction monitored by TLC, the reaction mixture was diluted with EtOAc and was washed with brine. The resulting mixture was dried with anhydrous Na_2SO_4(s) and condensed under reduced pressure. The residue was purified by silica-gel flash column chromatography (EtOAc:Hex = 1:8 to 1:5 gradient elution) to provide the desired product.

Synthesis of S24{n18/n16}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-4-yn-2-yl)hexadec-5-enamide



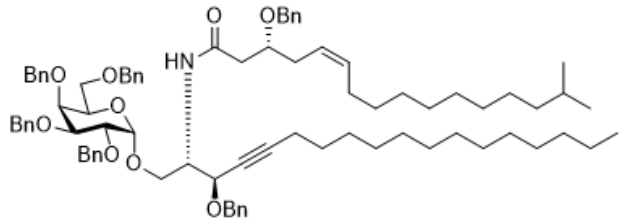
Yield: 67%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.35–7.18 (m, 30H), 6.61 (d, *J* = 8.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.37–5.32 (m, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 3.5 Hz, 1H), 4.75–4.69 (m, 3H), 4.60 (t, *J* = 12.5 Hz, 2H), 4.53–4.43 (m, 5H), 4.41–4.36 (m, 2H), 3.98 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.88–3.84 (m, 3H), 3.80–3.73 (m, 3H), 3.46 (dd, *J* = 7.5, 3.0 Hz, 2H), 2.35–2.25 (m, 4H), 2.10 (t, *J* = 7.0 Hz, 2H), 1.97 (q, *J* = 7.0 Hz, 2H), 1.44 (quint, *J* = 7.5 Hz, 2H), 1.29–125 (m, 36H), 0.88 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.1, 79.1, 75.8, 75.1, 74.9, 73.6, 73.5, 73.5, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 32.1, 32.1, 31.9, 29.9, 29.9, 29.8, 29.6, 29.4, 29.2, 28.9, 27.7, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{110}NO_9$ $[M + Na]^+$ calcd: 1252.81, found: 1252.60.

Synthesis of S24{n18/n15}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-4-yn-2-yl)pentadec-5-enamide



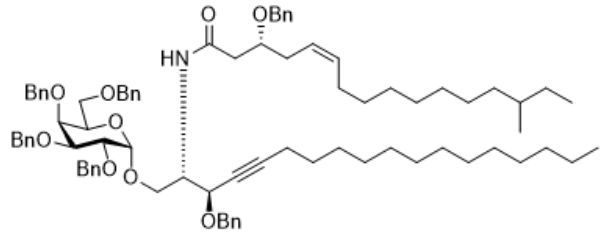
Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.18 (m, 30H), 6.62 (d, J = 8.4 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, J = 11.6 Hz, 1H), 4.82 (d, J = 3.2 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 11.2 Hz, 2H), 4.53–4.44 (m, 5H), 4.39–4.33 (m, 2H), 3.98 (dd, J = 9.6, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.76 (m, 3H), 3.46 (d, J = 6.4 Hz, 2H), 2.36–2.26 (m, 4H), 2.10 (t, J = 6.8 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.44 (quint, J = 7.2 Hz, 2H), 1.25 (bs, 34H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 52.5, 41.7, 32.1, 32.1, 31.9, 29.9, 29.9, 29.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.4, 29.2, 28.9, 27.7, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{81}H_{108}NO_9$ [M + H]$^+$ calcd: 1238.79, found: 1238.25.

Synthesis of S24{n18/i17}, (R,Z)-3-(benzyloxy)-*N*-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-4-yn-2-yl)-15-methylhexadec-5-enamide



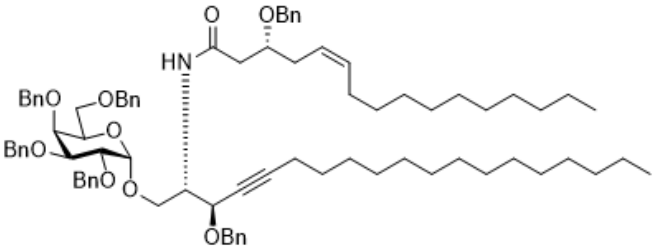
Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.59 (d, J = 8.8 Hz, 1H), 4.88 (d, J = 11.2 Hz, 1H), 4.80 (t, J = 2.8 Hz, 1H), 4.80 (d, J = 2.8 Hz, 1H), 4.73–4.67 (m, 3H), 4.63–4.56 (m, 3H), 4.52–4.42 (m, 5H), 4.39–4.34 (m, 2H), 3.97 (dt, J = 10.0, 3.2 Hz, 1H), 3.85–3.83 (m, 3H), 3.78–3.74 (m, 3H), 3.44 (d, J = 6.0 Hz, 2H), 2.34–2.22 (m, 4H), 2.08 (t, J = 6.8 Hz, 2H), 1.96 (q, J = 6.8 Hz, 2H), 1.53–1.39 (m, 4H), 1.23 (bs, 31H), 1.15–1.13 (m, 2H), 0.88–0.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.1, 79.2, 76.8, 76.7, 75.8, 75.1, 75.0, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 31.9, 31.2, 30.2, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.6, 22.9, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{83}H_{111}NaNO_9$ [M + Na]$^+$ calcd: 1288.82, found: 1288.50.

Synthesis of S24{n18/a17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-4-yn-2-yl)-14-methylhexadec-5-enamide



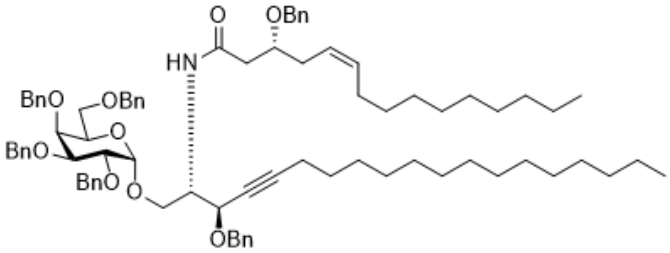
Yield: 44%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.62 (d, J = 8.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 3.0 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 12.5 Hz, 2H), 4.53–4.43 (m, 5H), 4.38 (t, J = 12.5 Hz, 2H), 3.98 (d, J = 7.5 Hz, 1H), 3.85 (bs, 3H), 3.79–3.76 (m, 3H), 3.46 (d, J = 4.0 Hz, 2H), 2.35–2.25 (m, 4H), 2.10 (t, J = 6.5 Hz, 2H), 1.97 (q, J = 6.5 Hz, 2H), 1.45–1.42 (m, 2H), 1.24 (bs, 33H), 1.13–1.08 (m, 2H), 0.88–0.84 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 138.8, 138.6, 138.5, 138.4, 137.9, 137.7, 132.7, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 124.4, 98.6, 88.8, 78.9, 76.6, 76.5, 75.6, 74.7, 73.4, 73.2, 72.9, 71.4, 70.5, 69.5, 68.8, 68.5, 67.4, 52.3, 41.5, 36.6, 34.4, 31.9, 31.7, 30.0, 29.7, 29.6, 29.5, 29.4, 29.4, 29.2, 29.0, 28.7, 27.5, 27.1, 22.7, 19.2, 18.7, 14.1, 11.4; LRMS(ESI) *m/z* for $C_{83}H_{111}NaNO_9$ [M + Na]$^+$ calcd: 1288.82, found: 1288.50.

Synthesis of S24{n19/n16}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)nonadec-4-yn-2-yl)hexadec-5-enamide



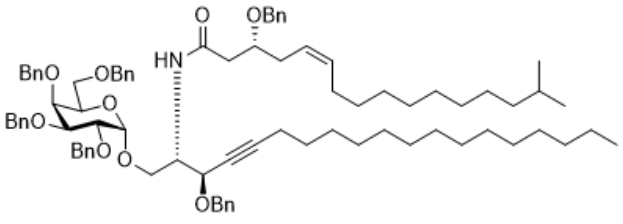
Yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.18 (m, 30H), 6.62 (d, J = 8.4 Hz, 1H), 5.50–5.42 (m, 1H), 5.39–5.31 (m, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.82 (d, J = 3.3 Hz, 1H), 4.75–4.68 (m, 3H), 4.65–4.59 (m, 2H), 4.57–4.44 (m, 5H), 4.40–4.35 (m, 2H), 3.98 (dd, J = 10.2, 3.6 Hz, 1H), 3.87–3.84 (m, 3H), 3.81–3.71 (m, 3H), 3.47 (d, J = 6.0 Hz, 2H), 2.36–2.26 (m, 4H), 2.10 (t, J = 6.6 Hz, 2H), 1.97 (q, J = 6.6 Hz, 2H), 1.48–1.41 (m, 2H), 1.25 (bs, 38H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 75.8, 75.1, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 32.1, 31.9, 29.9, 29.9, 29.6, 29.4, 29.2, 28.9, 27.7, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{83}H_{111}NO_9$ [M + Na]$^+$ calcd: 1288.82, found: 1288.55.

Synthesis of S24{n19/n15}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)nonadec-4-yn-2-yl)pentadec-5-enamide



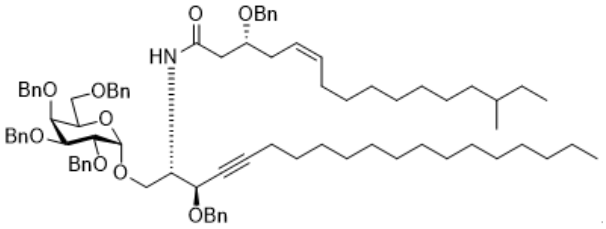
Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.17 (m, 30H), 6.62 (d, J = 8.8 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 3.2 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 11.2 Hz, 2H), 4.53–4.41 (m, 5H), 4.39–4.33 (m, 2H), 3.98 (dd, J = 9.6, 3.2 Hz, 1H), 3.87–3.74 (m, 3H), 3.80–3.75 (m, 3H), 3.46 (d, J = 6.0 Hz, 2H), 2.36–2.24 (m, 4H), 2.10 (t, J = 6.8 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.44 (quint, J = 7.2 Hz, 2H), 1.25 (bs, 36H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 52.5, 41.7, 32.1, 32.1, 31.9, 29.9, 29.9, 29.9, 29.8, 29.6, 29.5, 29.4, 29.4, 29.2, 28.9, 27.7, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{109}NaNO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.80.

Synthesis of S24{n19/i17}, (*R,Z*)-3-(benzyloxy)-*N*-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)nonadec-4-yn-2-yl)-15-methylhexadec-5-enamide



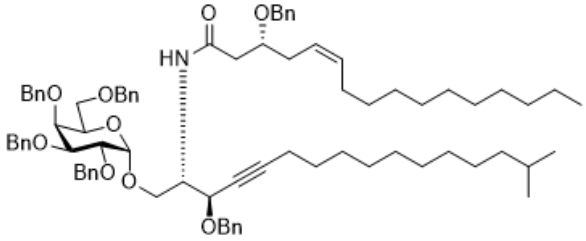
Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.59 (d, J = 8.8 Hz, 1H), 5.47–5.41 (m, 1H), 5.37–5.30 (m, 1H), 4.88 (d, J = 11.2 Hz, 1H), 4.80 (d, J = 2.4 Hz, 1H), 4.73–4.6 (m, 3H), 4.59 (t, J = 11.2 Hz, 2H), 4.52–4.42 (m, 5H), 4.39–4.34 (m, 2H), 3.97 (ddd, J = 9.6, 3.4, 1.2 Hz, 1H), 3.85–3.83 (m, 3H), 3.78 (bs, 1H), 3.76–3.73 (m, 2H), 3.45 (d, J = 6.0 Hz, 2H), 2.34–2.23 (m, 4H), 2.08 (t, J = 6.8 Hz, 2H), 1.96 (q, J = 6.8 Hz, 2H), 1.51–1.39 (4H), 1.23 (bs, 33H), 1.16–1.01 (m, 2H), 0.88–0.84 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.1, 79.2, 76.8, 76.7, 75.8, 75.1, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 31.9, 31.2, 30.2, 29.9, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.7, 22.9, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{84}H_{114}NO_9$ [M + H]$^+$ calcd: 1280.84, found: 1280.60.

Synthesis of S24{n19/a17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)nonadec-4-yn-2-yl)-14-methylhexadec-5-enamide



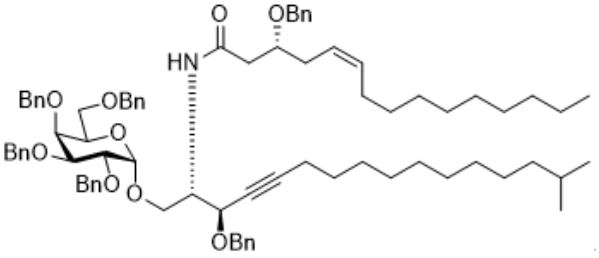
Yield: 42%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.62 (d, J = 8.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.37–5.32 (m, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 2.5 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 12.5 Hz, 2H), 4.53–4.43 (m, 5H), 4.38 (t, J = 12.5 Hz, 2H), 3.98 (dd, J = 9.5, 2.5 Hz, 1H), 3.85 (bs, 3H), 3.80–3.76 (m, 3H), 3.46 (d, J = 5.0 Hz, 2H), 2.35–2.26 (m, 4H), 2.09 (t, J = 6.5 Hz, 2H), 1.97 (q, J = 6.5 Hz, 2H), 1.45–1.41 (m, 2H), 1.25 (bs, 35H), 1.14–1.10 (m, 2H), 0.89–0.84 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.1, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 36.9, 34.6, 32.1, 31.9, 30.2, 29.9, 29.9, 29.8, 29.7, 29.6, 29.6, 29.4, 29.2, 29.9, 27.7, 27.3, 22.9, 19.4, 18.9, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{84}H_{114}NO_9$ $[M + H]^+$ calcd: 1280.84, found: 1280.60.

Synthesis of S24{i17/n16}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-15-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)hexadec-5-enamide



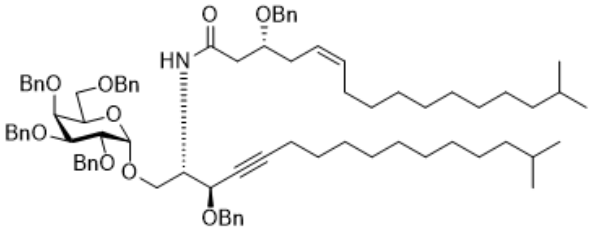
Yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.18 (m, 30H), 6.61 (d, J = 8.4 Hz, 1H), 5.50–5.42 (m, 1H), 5.39–5.32 (m, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.82 (d, J = 3.3 Hz, 1H), 4.75–4.97 (m, 3H), 4.64 (d, J = 5.1 Hz, 2H), 4.57–4.41 (m, 5H), 4.40–4.35 (m, 2H), 3.98 (dd, J = 9.9, 3.6 Hz, 1H), 3.87–3.84 (m, 3H), 3.81–3.68 (m, 3H), 3.71–3.46 (d, J = 6.0 Hz, 2H), 2.36–2.23 (m, 4H), 2.10 (t, J = 6.6 Hz, 2H), 1.97 (q, J = 6.6 Hz, 2H), 1.55–1.40 (m, 4H), 1.25 (bs, 27H), 1.17–1.13 (m, 2H), 0.88–0.75 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 75.8, 75.1, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 31.9, 30.1, 29.9, 29.9, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 28.2, 27.6, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{81}H_{107}NO_9$ $[M + Na]^+$ calcd: 1260.78, found: 1260.70.

Synthesis of S24{i17/n15}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-15-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)pentadec-5-enamide



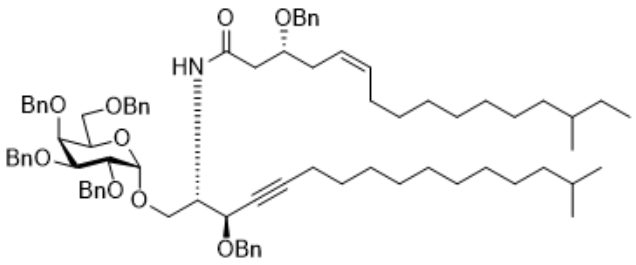
Yield: 99%; ^{1}H NMR (300 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.18 (m, 30H), 6.61 (d, J = 8.4 Hz, 1H), 5.50–5.42 (m, 1H), 5.39–5.31 (m, 1H), 4.892 (d, J = 11.4 Hz, 1H), 4.82 (d, J = 3.3 Hz, 1H), 4.75–4.68 (m, 3H), 4.62 (d, J = 8.1 Hz, 2H), 4.55 (d, J = 8.1 Hz, 1H), 4.50–4.42 (m, 4H), 4.40–4.35 (m, 2H), 3.98 (dd, J = 9.9, 3.3 Hz, 1H), 3.87–3.84 (m, 3H), 3.81–3.75 (m, 3H), 3.46 (d, J = 6.3 Hz, 2H), 2.36–2.26 (m, 4H), 2.10 (t, J = 6.6 Hz, 2H), 1.97 (q, J = 6.6 Hz, 2H), 1.55–1.39 (m, 4H), 1.25 (bs, 27H), 1.17–1.13 (m, 2H), 0.90–0.85 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.2, 75.8, 75.1, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 32.1, 31.9, 30.2, 29.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.2, 28.9, 28.2, 27.6, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{111}NaNO_9$ $[M + Na]^+$ calcd: 1246.77, found: 1246.35.

Synthesis of S24{i17/i17}, (R,Z)-3-(benzyloxy)-*N*-((2S,3R)-3-(benzyloxy)-15-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-*2H*-pyran-2-yl)oxy)hexadec-4-yn-2-yl)-15-methylhexadec-5-enamide



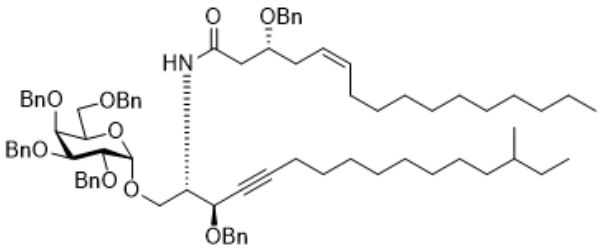
Yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.38–7.17 (m, 30H), 6.61 (d, J = 8.5 Hz, 1H), 5.45 (m, 1H), 5.35 (m, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 3.5 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 12.5 MHz, 2H), 4.53–4.43 (m, 5H), 4.38 (t, J = 13.0 Hz, 3H), 3.98 (dd, J = 10.5, 3.5 Hz, 1H), 3.87–3.82 (m, 3H), 3.80–3.75 (m, 3H), 3.48–3.44 (m, 2H), 2.35–223 (m, 4H), 2.10 (t, J = 7.0 Hz, 2H), 1.97 (q, J = 7.0 Hz, 2H), 1.54–1.47 (m, 1H), 1.45–1.41 (m, 1H), 1.24 (m, 26H), 1.14 (m, 4H), 0.86 (dd, J = 6.5, 2.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 171.0, 138.9, 138.7, 138.5, 138.5, 138.0, 137.8, 132.7, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 127.3, 124.4, 98.6, 88.9, 79.0, 75.6, 74.9, 74.8, 73.5, 73.3, 73.0, 71.5, 70.6, 69.6, 68.9, 68.5, 67.4, 52.3, 41.6, 39.1, 31.7, 30.0, 29.7, 29.6, 29.4, 29.2, 29.0, 28.7, 28.0, 27.4, 22.7, 18.7; LRMS(ESI) *m/z* for $C_{82}H_{109}NaNO_9$ $[M + Na]^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{i17/a17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-15-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)-14-methylhexadec-5-enamide



Yield: 19%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.62 (d, J = 8.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.37–5.36 (m, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 3.0 Hz, 1H), 4.74–4.69 (m, 3H), 4.60 (t, J = 12.5 Hz, 2H), 4.55–4.43 (m, 5H), 4.38 (t, J = 12.5 Hz, 2H), 3.98 (dd, J = 9.5, 3.0 Hz, 1H), 3.85 (bs, 3H), 3.77–3.73 (m, 3H), 3.46 (d, J = 5.0 Hz, 2H), 2.35–2.25 (m, 4H), 2.09 (t, J = 6.0 Hz, 2H), 1.99–1.95 (m, 2H), 1.53–1.41 (m, 4H), 1.25 (bs, 28H), 1.15–1.10 (m, 2H), 0.86 (d, J = 6.5 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.2, 138.0, 132.9, 128.6, 128.5, 128.5, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 124.6, 98.8, 89.1, 79.1, 75.8, 75.0, 75.0, 73.7, 73.5, 73.2, 71.7, 70.8, 69.8, 69.0, 68.7, 67.6, 52.5, 41.8, 39.3, 36.9, 34.6, 31.9, 30.2, 30.2, 29.9, 29.9, 29.7, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.3, 22.9, 19.4, 18.9, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{109}NaNO_9$ $[M + Na]^+$ calcd: 1274.80, found: 1274.60.

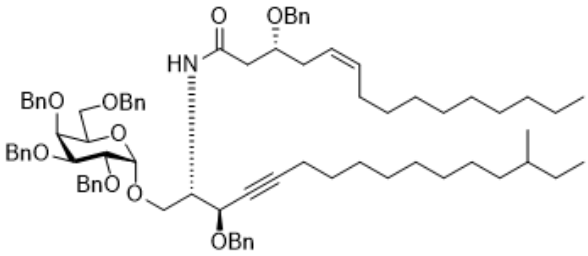
Synthesis of S24{a17/n16}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)hexadec-5-enamide



Yield: 82%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.35–7.18 (m, 30H), 6.62 (d, J = 8.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.37–5.32 (m, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 3.5 Hz, 1H), 4.74–4.69 (m, 3H), 4.66–4.58 (m, 2H), 4.53–4.43 (m, 5H), 4.41–4.36 (m, 2H), 3.98 (dd, J = 10.0, 3.5 Hz, 1H), 3.38–3.84 (m, 3H), 3.80–3.74 (m, 3H), 3.47–3.45 (m, 2H), 2.35–2.26 (m, 4H), 2.10 (t, J = 6.5 Hz, 2H), 1.97 (q, J = 6.5 Hz, 2H), 1.44 (quint, J = 7.0 Hz, 2H), 1.25 (bs, 29H), 1.15–1.08 (m, 2H), 0.89–0.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 75.8, 75.1, 75.0, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.8, 52.5, 41.7, 36.9, 34.6, 32.1, 32.1, 31.9, 20.2, 29.9, 29.7, 29.6,

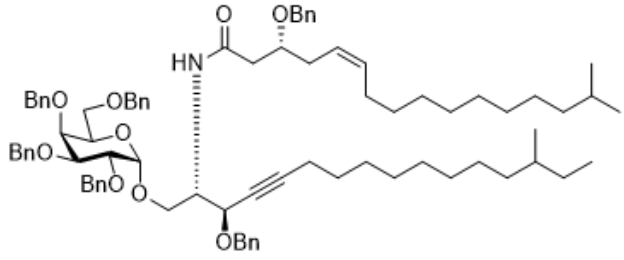
29.6, 29.4, 29.2, 28.9, 27.7, 27.3, 22.9, 19.4, 18.9, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{81}H_{107}NO_9$ [M + Na]$^+$ calcd: 1260.78, found: 1260.70.

Synthesis of S24{a17/n15}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)pentadec-5-enamide



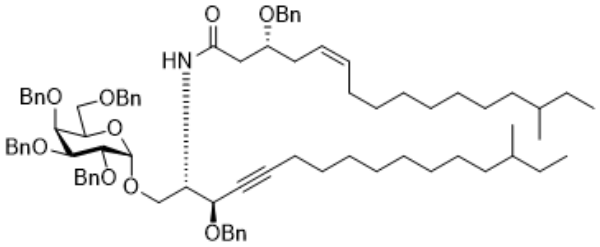
Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.18 (m, 30H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.74–4.69 (m, 3H), 4.66–4.55 (m, 2H), 4.53–4.44 (m, 5H), 4.01–4.35 (m, 2H), 3.98 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.66 (m, 3H), 3.46 (d, *J* = 5.6 Hz, 2H), 2.36–2.26 (m, 4H), 2.10 (t, *J* = 6.4 Hz, 2H), 1.97 (q, *J* = 6.8 Hz, 2H), 1.46–1.40 (m, 2H), 1.25 (bs, 27H), 1.14–1.10 (m, 2H), 0.89–0.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.5, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 52.5, 41.7, 36.9, 34.6, 32.1, 32.1, 31.9, 30.2, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 28.9, 27.7, 27.3, 22.8, 19.4, 18.9, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{111}NaNO_9$ [M + Na]$^+$ calcd: 1246.77, found: 1246.35.

Synthesis of S24{a17/i17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)-15-methylhexadec-5-enamide



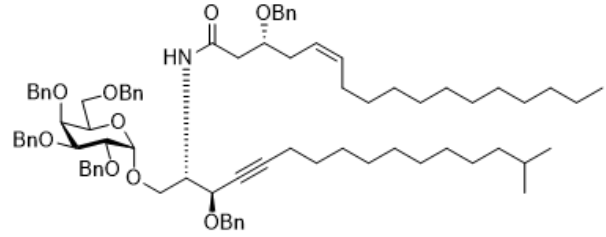
Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) *δ* 7.34–7.18 (m, 30H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.74–4.68 (m, 3H), 4.66–4.57 (m, 3H), 4.53–4.44 (m, 5H), 4.41–4.36 (m, 2H), 3.98 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.75 (m, 3H), 3.49–3.86 (m, 2H), 2.36–2.24 (m, 4H), 2.10 (t, *J* = 6.8 Hz, 2H), 1.97 (q, *J* = 6.4 Hz, 2H), 1.54–1.40 (m, 4H), 1.25 (bs, 25H), 1.15–1.07 (m, 4H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.85–0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 171.2, 139.1, 138.9, 138.7, 138.7, 138.2, 138.0, 132.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 128.5, 124.6, 98.8, 89.1, 79.2, 75.8, 75.1, 75.0, 73.7, 73.5, 73.2, 71.7, 70.8, 69.8, 69.1, 68.8, 67.6, 52.5, 41.8, 39.3, 36.9, 34.6, 31.9, 31.1, 30.3, 30.2, 29.9, 29.8, 29.7, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.6, 27.3, 22.9, 19.4, 18.9, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{109}NaNO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{a17/a17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)-14-methylhexadec-5-enamide



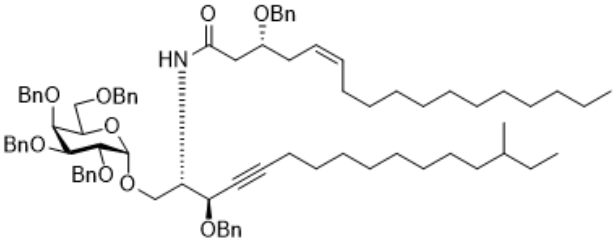
Yield: 26%; ^{1}H NMR (500 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.33–7.18 (m, 30H), 6.62 (d, J = 8.5 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.85 (d, J = 4.0 Hz, 1H), 4.78–4.69 (m, 3H), 4.66–4.58 (m, 3H), 4.54–4.43 (m, 5H), 4.38 (t, J = 12.5 Hz, 2H), 3.98 (dd, J = 10.0, 3.5 Hz, 1H), 3.85 (bs, 3H), 3.80–3.73 (m, 3H), 3.46 (d, J = 6.0 Hz, 2H), 2.35–2.25 (m, 4H), 2.10 (t, J = 6.0 Hz, 2H), 1.97 (q, J = 6.5 Hz, 2H), 1.47–1.41 (m, 2H), 1.26 (bs, 28H), 1.13–1.07 (m, 2H), 0.86–0.83 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2 139.1, 138.9, 138.7, 138.7, 138.2, 138.0, 132.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 124.6, 98.8, 89.1, 79.2, 85.8, 75.1, 75.0, 73.7, 73.5, 73.2, 71.7, 70.8, 69.8, 69.0, 68.7, 67.6, 52.5, 41.8, 36.9, 34.6, 31.9, 30.2, 30.2, 29.9, 29.9, 29.7, 29.6, 29.4, 29.2, 28.9, 27.7, 27.3, 19.4, 18.9, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{109}NaNO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{i17/n17}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-15-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)heptadec-5-enamide



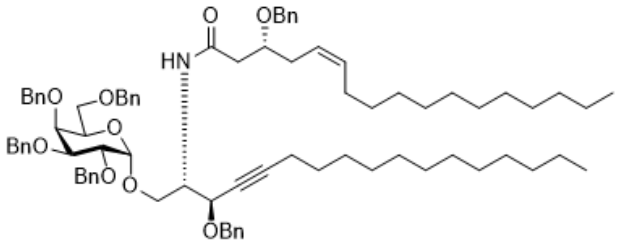
Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.20 (m, 30H), 6.62 (d, J = 8.4 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.33 (m, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 2.8 Hz, 1H), 4.74–4.68 (m, 3H), 4.65–4.57 (m, 2H), 4.53–4.44 (m, 5H), 4.41–4.36 (m, 2H), 3.98 (dd, J = 9.6, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.76 (m, 3H), 3.46 (d, J = 6.0 Hz, 2H), 2.37–2.26 (m, 4H), 2.09 (t, J = 6.4 Hz, 2H), 1.97 (q, J = 6.4 Hz, 2H), 1.54–1.41 (m, 3H), 1.25 (bs, 30H), 1.46 (bs, 2H), 0.88–0.85 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 124.6, 98.8, 89.1, 79.1, 76.8, 76.7, 75.8, 75.0, 75.0, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 31.9, 30.1, 29.9, 29.9, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.6, 22.9, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{109}NO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{a17/n17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-14-methyl-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexadec-4-yn-2-yl)heptadec-5-enamide



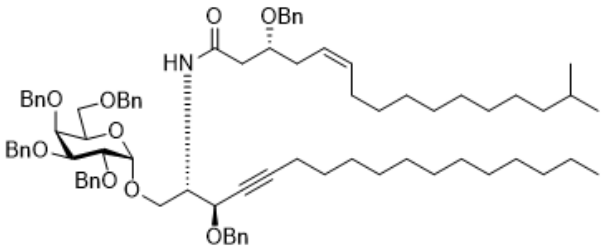
Yield: 57%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.20 (m, 30H), 6.63 (d, J = 8.4 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.29 (m, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 3.2 Hz, 1H), 4.74–4.69 (m, 3H), 4.66–4.57 (M, 3H), 4.53–444 (m, 4H), 4.41–4.36 (m, 2H), 3.98 (dd, J = 9.6, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.86 (m, 3H), 3.46 (d, J = 6.4 Hz, 2H), 2.36–2.24 (m, 4H), 2.10 (t, J = 6.8 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.44 (quint, J = 6.8 Hz, 3H), 1.25 (bs, 30H), 1.14–1.09 (m, 2H), 0.89–0.83 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.1, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.8, 69.0, 68.7, 67.6, 53.6, 52.5, 41.7, 36.9, 34.6, 32.1, 31.9, 30.2, 29.9, 29.9, 29.8, 29.7, 29.6, 29.6, 29.4, 29.2, 28.9, 27.7, 27.3, 22.9, 19.4, 18.9, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{109}NO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{n17/n17}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)heptadec-4-yn-2-yl)heptadec-5-enamide



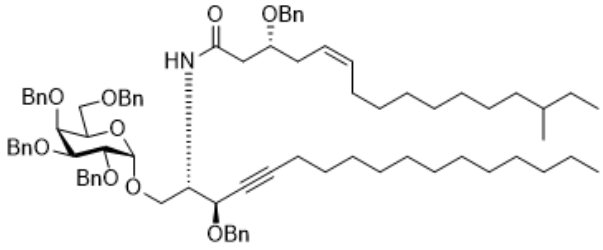
Yield: 31%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.36–7.20 (m, 30H), 6.63 (d, J = 8.8 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 3.2 Hz, 1H), 4.74–4.68 (m, 3H), 4.60 (t, J = 11.2 Hz, 2H), 4.56–4.44 (m, 5H), 4.41–4.36 (m, 2H), 3.98 (dd, J = 10.0, 3.2 Hz, 1H), 3.87–3.84 (m, 3H), 3.77 (s, 1H), 3.76–3.72 (m, 2H), 3.46 (d, J = 6.0 Hz, 2H), 2.36–2.26 (m, 4H), 2.10 (t, J = 6.8 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.44 (quint, J = 6.8 Hz, 2H), 1.26 (bs, 36H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 60.6, 52.5, 41.7, 32.1, 31.9, 29.9, 29.9, 29.8, 29.8, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 27.7, 22.9, 21.3, 18.9, 14.4, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{109}NO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

Synthesis of S24{n17/i17}, (R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)heptadec-4-yn-2-yl)-15-methylhexadec-5-enamide



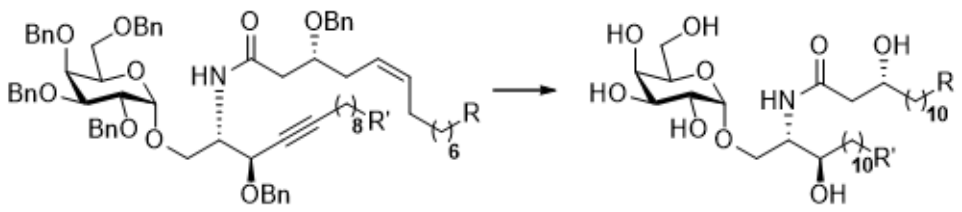
Yield: 58%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.34–7.19 (m, 30H), 6.62 (d, J = 8.8 Hz, 1H), 5.49–5.43 (m, 1H), 5.38–5.32 (m, 1H), 4.89 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 3.6 Hz, 1H), 4.74–4.68 (m, 3H), 4.60 (t, J = 11.2 Hz, 2H), 4.53–4.44 (m, 5H), 4.41–4.35 (m, 2H), 3.98 (dd, J = 10.0, 3.6 Hz, 1H), 3.87–3.84 (m, 3H), 3.80–3.72 (m, 3H), 3.46 (dd, J = 6.6, 2.0 Hz, 2H), 2.36–2.26 (m, 4H), 2.01 (t, J = 6.4 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.54–1.40 (m, 3H), 1.24 (bs, 30H), 1.15–1.12 (m, 2H), 0.89–0.85 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.1, 79.1, 76.7, 75.8, 75.0, 74.9, 73.2, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 52.5, 41.7, 39.3, 32.1, 31.9, 30.2, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.4, 29.2, 28.9, 28.2, 27.7, 27.6, 22.9, 22.9, 18.9, 14.3; LRMS(ESI) *m/z* for $C_{82}H_{109}NO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60

Synthesis of S24{n17/a17}, (3R,Z)-3-(benzyloxy)-N-((2S,3R)-3-(benzyloxy)-1-(((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)heptadec-4-yn-2-yl)-14-methylhexadec-5-enamide



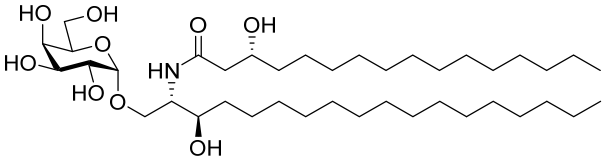
Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm) δ 7.38–7.16 (m, 30H), 6.62 (d, J = 8.4 Hz, 1H), 5.49–5.42 (m, 1H), 5.38–5.31 (m, 1H), 4.89 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 3.2 Hz, 1H), 4.74–4.68 (m, 3H), 4.60 (t, J = 11.2 Hz, 2H), 4.53–4.43 (m, 5H), 4.40–4.35 (m, 2H), 3.98 (dd, J = 10.0, 3.2 Hz, 1H), 3.86–3.84 (m, 3H), 3.80–3.74 (m, 3H), 3.44 (d, J = 5.6 Hz, 2H), 2.36–2.24 (m, 4H), 2.09 (t, J = 6.8 Hz, 2H), 1.97 (q, J = 6.8 Hz, 2H), 1.44 (quint, J = 7.2 Hz, 2H), 1.24 (bs, 31H), 1.15–1.08 (m, 2H), 0.89–0.83 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.9, 138.7, 138.6, 138.2, 138.0, 132.9, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 124.6, 98.8, 89.0, 79.1, 76.8, 76.7, 75.8, 75.0, 74.9, 73.6, 73.5, 73.2, 71.7, 70.7, 69.7, 69.0, 68.7, 67.6, 52.5, 41.7, 36.9, 34.6, 32.1, 31.9, 30.2, 29.9, 29.9, 29.8, 29.7, 29.6, 29.6, 29.4, 29.2, 28.9, 27.7, 27.3, 22.9, 19.4, 18.9, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{82}H_{109}NO_9$ [M + Na]$^+$ calcd: 1274.80, found: 1274.60.

General procedure of benzyl deprotection and triple bond reduction via catalytic hydrogenation



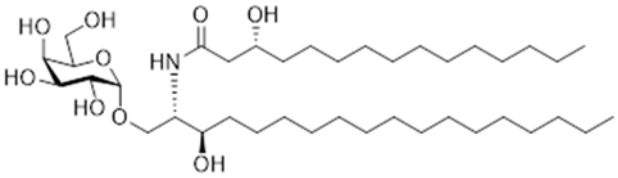
To a solution of **S24** (1.0 equiv.) in MeOH/DCM (1.5/0.5 mL) was added $Pd(OH)_2/C$ (100 wt%) and the reaction mixture was stirred under H_2 atmosphere (1 atm) for 10 hr. After the completion of reaction monitored by TLC, catalyst was removed by filtration through 0.45 μm PTFE syringe filter and washed with MeOH/DCM (3:1, v/v) solution. The resulting filtrate was concentrated under reduced pressure to provide desired products as white solid.

Synthesis of SB2201, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)octadecan-2-yl)hexadecanamide



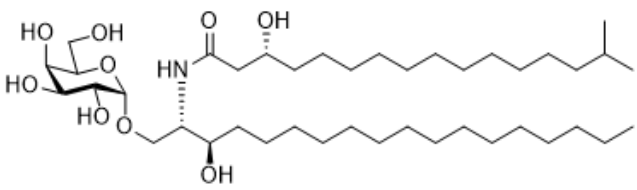
Yield: quantitative; ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) δ 4.85 (d, J = 3.6 Hz, 1H), 3.99–3.97 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.28 (m, 2H), 1.55–1.41 (m, 6H), 1.35–1.27 (m, 46H), 0.90–0.86 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) δ 173.6, 100.4, 71.6, 71.5, 70.9, 70.4, 69.8, 69.3, 68.0, 62.3, 54.4, 44.4, 37.9, 34.6, 32.6, 30.3, 30.3, 30.0, 26.5, 26.2, 23.3, 14.4; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2202, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)octadecan-2-yl)pentadecanamide



Yield: quantitative; ^{1}H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.63 (t, J = 6.9 Hz, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.41 (m, 4H), 1.35–1.27 (m, 46H), 0.89 (t, J = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 173.6, 100.3, 71.6, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 37.9, 34.5, 32.5, 30.3, 30.2, 29.9, 26.4, 26.2, 23.2, 14.3; LRMS(ESI) *m/z* for $C_{39}H_{77}NaNO_9$ $[M + Na]^+$ calcd: 726.55, found: 726.60.

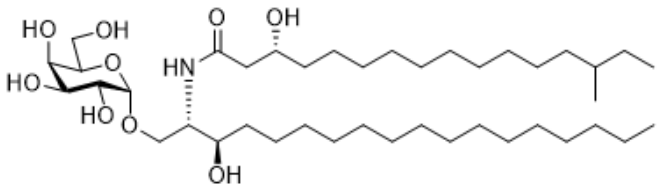
Synthesis of SB2203, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)octadecan-2-yl)-15-methylhexadecanamide



Yield: quantitative; ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) δ 4.85 (d, J = 4.2 Hz, 1H), 4.00–3.95 (m, 2H), 3.92 (dd, J = 3.0, 1.2 Hz, 1H), 3.86 (dd, J = 10.2, 3.0 Hz, 1H), 3.83 (t, J = 6.6 Hz, 1H), 3.80–3.72 (m, 4H), 3.69 (dd, J = 10.2, 4.8 Hz, 1H), 3.63 (td, J = 7.5, 2.4 Hz, 1H), 2.38 (dd, J = 14.4, 3.0 Hz, 1H), 2.30 (dd, J = 14.4, 7.8 Hz, 1H), 1.56–1.13 (m, 5H), 1.27 (bs, 44H), 1.16 (q, J = 7.2 Hz, 2H), 0.88 (dd, J = 15.0, 6.6 Hz, 9H); ^{13}C NMR

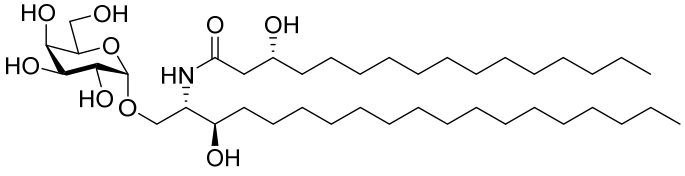
(125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) δ 173.5, 100.2, 71.6, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 39.6, 37.8, 34.5, 32.5, 30.9, 30.5, 30.2, 29.9, 28.5, 28.0, 26.4, 26.1, 23.2, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{41}H_{81}NaNO_9$ $[M + Na]^+$ calcd: 754.58, found: 754.60.

Synthesis of SB2204, (3R)-3-hydroxy-N-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)octadecan-2-yl)-14-methylhexadecanamide



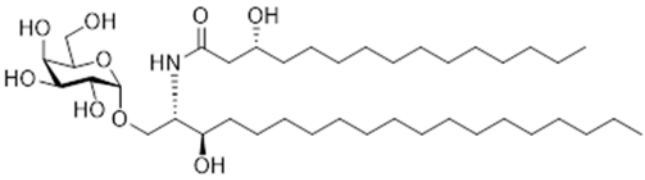
Yield: quantitative; ^1H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, *J* = 3.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.41 (m, 7H), 1.36–1.27 (m, 42H), 1.17–1.11 (m, 2H), 0.90–0.84 (m, 9H); ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 173.5, 100.2, 71.5, 70.3, 69.6, 69.2, 62.2, 54.3, 44.2, 37.8, 37.2, 35.0, 34.5, 32.4, 30.5, 30.2, 30.2, 30.0, 29.9, 27.6, 26.4, 26.1, 23.2, 19.4, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{41}H_{81}NaNO_9$ $[M + Na]^+$ calcd: 754.58, found: 754.60.

Synthesis of SB2205, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)nonadecan-2-yl)hexadecanamide



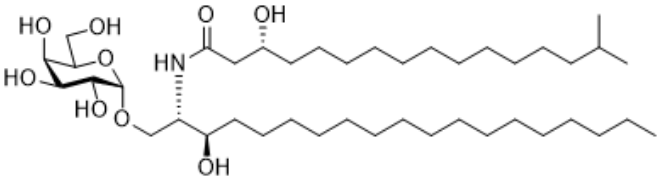
Yield: quantitative; ^1H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) δ 4.85 (d, *J* = 3.6 Hz, 1H), 4.01–3.97 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.28 (m, 2H), 1.56–1.40 (m, 7H), 1.35–1.27 (m, 47H), 0.90–0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) δ 173.6, 100.4, 71.7, 70.9, 70.4, 69.8, 69.3, 68.0, 62.3, 54.4, 44.4, 37.9, 34.6, 32.6, 30.3, 30.3, 30.0, 26.3, 26.2, 23.3, 14.4; LRMS(ESI) *m/z* for $C_{41}H_{81}NaNO_9$ $[M + Na]^+$ calcd: 754.58, found: 754.60.

Synthesis of SB2206, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)nonadecan-2-yl)pentadecanamide



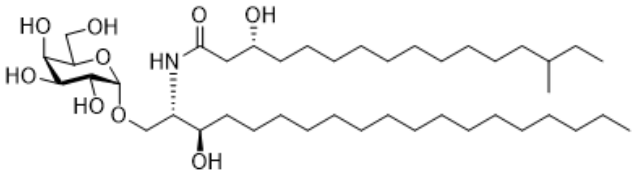
Yield: quantitative; ^1H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, *J* = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.63 (t, *J* = 6.9 Hz, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.41 (m, 4H), 1.38–1.27 (m, 48H), 0.89 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 173.6, 100.3, 71.5, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 37.9, 34.5, 32.5, 30.2, 30.2, 29.9, 26.4, 26.2, 23.2, 14.3; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2207, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)nonadecan-2-yl)-15-methylhexadecanamide



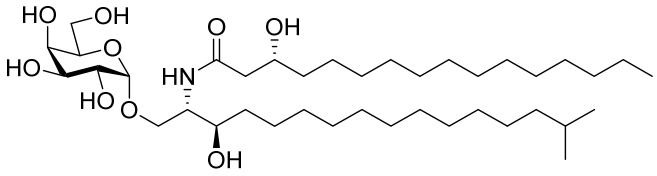
Yield: quantitative; ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) δ 4.85 (d, J = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.91 (dd, J = 2.4, 1.2 Hz, 1H), 3.86 (dd, J = 10.8, 3.6 Hz, 1H), 3.83 (t, J = 6.6 Hz, 1H), 3.80–3.76 (m, 2H), 3.75–3.72 (m, 2H), 3.69 (dd, J = 10.2, 5.4 Hz, 1H), 3.63 (td, J = 8.1, 3.0 Hz, 1H), 2.39 (dd, J = 14.4, 3.0 Hz, 1H), 2.30 (dd, J = 14.4, 9.0 Hz, 1H), 1.56–1.46 (m, 5H), 1.27 (bs, 46H), 1.16 (q, J = 7.2 Hz, 2H), 0.88 (dd, J = 14.4, 6.6 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) δ 173.5, 100.2, 71.4, 70.7, 70.2, 69.6, 69.2, 67.8, 62.1, 54.2, 44.2, 39.6, 37.8, 34.5, 32.4, 30.9, 30.4, 30.2, 29.8, 28.4, 27.9, 26.3, 26.1, 23.1, 22.8, 14.3; LRMS(ESI) *m/z* for $C_{42}H_{83}NaNO_9$ $[M + Na]^+$ calcd: 768.60, found: 768.65.

Synthesis of SB2208, (3R)-3-hydroxy-N-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)nonadecan-2-yl)-14-methylhexadecanamide



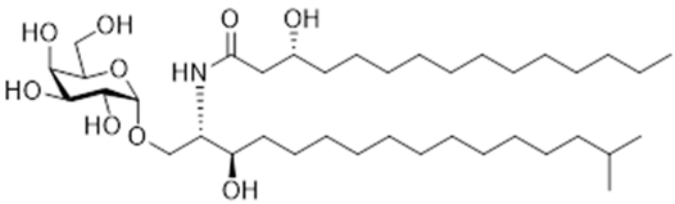
Yield: quantitative; ^{1}H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.43 (m, 7H), 1.36–1.27 (m, 44H), 1.17–1.11 (m, 2H), 0.90–0.84 (m, 9H); ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 173.5, 100.2, 71.5, 70.7, 70.2, 69.9, 69.2, 62.1, 54.2, 44.2, 37.8, 37.1, 34.9, 34.5, 32.4, 30.5, 30.2, 30.1, 30.0, 29.8, 27.6, 26.3, 26.1, 23.1, 19.4, 14.3, 11.6;LRMS(ESI) *m/z* for $C_{42}H_{83}NaNO_9$ $[M + Na]^+$ calcd: 768.60, found: 768.65.

Synthesis of SB2209, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-15-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)hexadecanamide



Yield: quantitative; ^{1}H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.28 (m, 2H), 1.56–1.40 (m, 7H), 1.35–1.27 (m, 38H), 1.18–1.14 (m, 2H), 0.90–0.86 (m, 9H); ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 173.7, 100.4, 78.5, 78.3, 78.1, 71.6, 70.9, 70.4, 69.8, 69.3, 62.3, 54.4, 44.4, 39.7, 38.0, 34.6, 32.6, 30.6, 30.4, 30.3, 30.0, 28.6, 28.1, 26.5, 26.2, 23.3, 23.0, 14.4; LRMS(ESI) *m/z* for $C_{39}H_{77}NaNO_9$ $[M + Na]^+$ calcd: 726.55, found: 726.60.

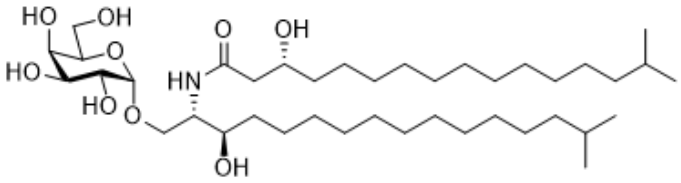
Synthesis of SB2210, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-15-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)pentadecanamide



Yield: quantitative; ^{1}H NMR (600 MHz, CD_3OD/$CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.63 (t, J = 6.9 Hz, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.41 (m, 5H), 1.35–1.27 (m, 38H), 1.18–1.14 (m, 2H), 0.90–0.86 (m, 9H); ^{13}C NMR

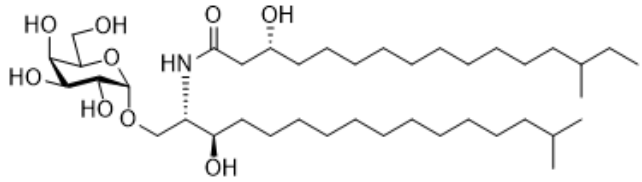
(150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): *δ* 173.6, 100.3, 71.5, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 39.6, 37.9, 34.5, 32.5, 30.5, 30.3, 30.2, 30.2, 30.2, 29.9, 28.5, 28.0, 26.4, 26.1, 23.2, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{38}H_{75}NaNO_9$ $[M + Na]^+$ calcd: 712.53, found: 712.60.

Synthesis of SB2211, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-15-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)-15-methylhexadecanamide



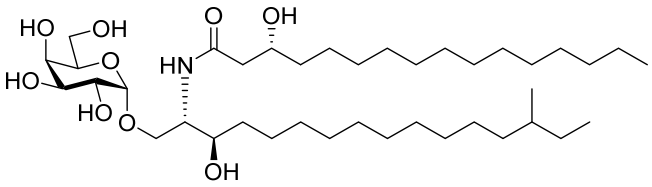
Yield: quantitative; ^1H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) *δ* 4.85 (d, *J* = 3.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.92 (d, *J* = 3.0 Hz, 1H), 3.86 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, H), 3.80–3.76 (m, 2H), 3.75–3.72 (m, 2H), 3.71–3.68 (m, 1H), 3.62 (td, *J* = 7.8, 2.4 Hz, 1H), 2.38 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.30 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.56–1.46 (m, 6H), 1.28 (bs, 36H), 1.16 (q, *J* = 6.6 Hz, 4H), 0.87 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) *δ* 173.6, 100.3, 71.6, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 39.7, 37.9, 32.5, 30.5, 30.3, 30.3, 30.2, 30.2, 28.5, 28.0, 26.4, 26.2, 22.9; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2212, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-15-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)-14-methylhexadecanamide



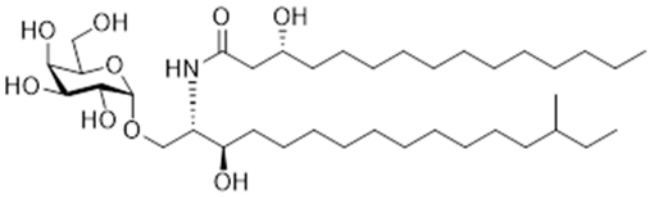
Yield: quantitative; ^1H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) *δ* 4.85 (d, *J* = 3.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.92 (dd, *J* = 2.7, 1.8 Hz, 1H), 3.86 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.80–3.76 (m, 2H), 3.75–3.72 (m, 2H), 3.71–3.68 (m, 1H), 3.63 (td, *J* = 7.8, 2.4 Hz, 1H), 2.38 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.30 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.56–1.44 (m, 6H), 1.27 (bs, 36H), 1.16 (q, *J* = 7.2 Hz, 4H), 0.90–0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) *δ* 173.5, 100.2, 71.5, 70.7, 70.2, 69.6, 69.2, 62.2, 54.3, 44.2, 39.6, 37.8, 37.2, 35.0, 34.5, 30.5, 30.4, 30.2, 30.2, 30.0, 28.5, 27.9, 27.6, 26.4, 26.1, 23.1, 22.8, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2213, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-14-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)hexadecanamide



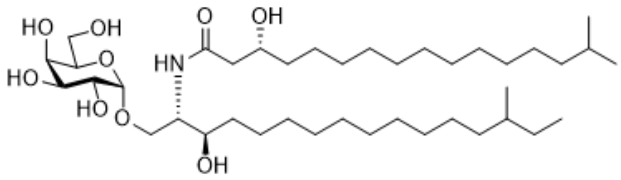
Yield: quantitative; ^1H NMR (600 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): *δ* 4.85–4.83 (m, 1H), 3.99–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 6H), 3.62 (m, 1H), 2.40–2.28 (m, 2H), 1.55–1.41 (m, 6H), 1.37–1.27 (m, 38H), 1.15–1.14 (m, 2H), 0.90–0.84 (m, 9H); ^{13}C NMR (150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); *δ* 173.7, 100.4, 71.6, 70.9, 70.4, 69.8, 69.3, 62.3, 54.4, 44.4, 38.0, 37.3, 35.1, 34.6, 32.6, 30.7, 30.4, 30.3, 30.3, 30.1, 30.0, 27.8, 26.5, 26.2, 23.3, 19.6, 14.4, 11.7; LRMS(ESI) *m/z* for $C_{39}H_{77}NaNO_9$ $[M + Na]^+$ calcd: 726.55, found: 726.60.

Synthesis of SB2214, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-14-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)pentadecanamide



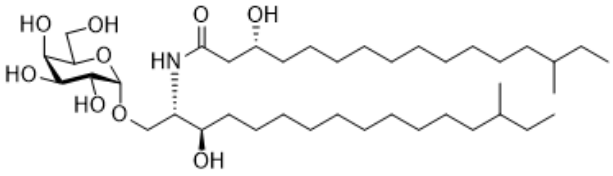
Yield: quantitative; ^{1}H NMR (600 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): *δ* 4.85 (d, *J* = 3.6 Hz, 1H), 4.00–3.96 (m, 2H), 3.93–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.63 (t, *J* = 6.9 Hz, 1H), 2.40–2.37 (m, 1H), 2.32–2.28 (m, 1H), 1.55–1.43 (m, 7H), 1.36–1.28 (m, 36H), 1.15–1.08 (m, 2H), 0.93–0.84 (m, 9H); ^{13}C NMR (150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): *δ* 173.6, 100.3, 71.6, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 37.9, 37.2, 35.0, 34.5, 32.5, 30.6, 30.3, 30.3, 30.2, 30.2, 30.0, 29.9, 27.7, 26.4, 26.2, 23.2, 19.5, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{38}H_{75}NaNO_9$ [M + Na]$^+$ calcd: 712.53, found: 712.60.

Synthesis of SB2215, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-14-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)-15-methylhexadecanamide



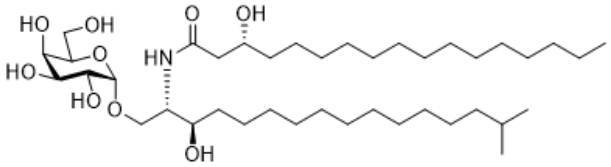
Yield: quantitative; ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) *δ* 4.85 (d, *J* = 3.0 Hz, 1H), 4.01–3.96 (m, 2H), 3.93 (d, *J* = 1.8 Hz, 1H), 3.86 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.78–3.72 (m, 4H), 3.71–3.68 (m, 1H), 3.63 (td, *J* = 8.1, 2.4 Hz, 1H), 2.39 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.30 (dd, *J* = 14.4, 9.0 Hz, 1H), 1.56–1.43 (m, 6H), 1.28 (bs, 36H), 1.18–1.11 (m, 4H), 1.88–1.84 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) *δ* 173.5, 100.2, 71.5, 70.7, 70.2, 69.6, 69.2, 62.1, 54.2, 39.6, 37.8, 37.2, 34.9, 37.8, 37.2, 34.9, 30.5, 30.4, 30.2, 30.1, 30.0, 28.5, 27.9, 27.6, 26.4, 26.1, 22.8, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ [M + Na]$^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2216, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-14-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)-14-methylhexadecanamide



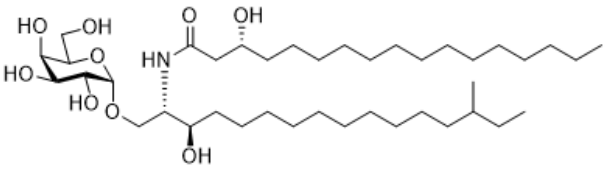
Yield: quantitative; ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 0.00 ppm) *δ* 4.85 (d, *J* = 3.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.92 (dd, *J* = 3.0, 1.2 Hz, 1H), 3.86 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, 1H), 3.80–3.76 (m, 2H), 3.75–3.72 (m, 2H), 3.71–3.68 (m, 1H), 3.63 (td, *J* = 7.8, 2.4 Hz, 1H), 2.38 (dd, *J* = 13.8, 3.6 Hz, 1H), 2.30 (dd, *J* = 14.4, 9.0 Hz, 1H), 1.55–1.51 (m, 2H), 1.50–1.44 (m, 4H), 1.27 (bs, 36H), 1.17–1.08 (m, 4H), 0.90–0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$:CD_3OD = 1:1, reference peak CD_3OD at 49.0 ppm) *δ* 173.5, 100.2, 71.5, 70.7, 70.2, 69.6, 69.2, 62.1, 54.3, 44.2, 37.8, 37.2, 34.9, 34.5, 32.4, 30.5, 30.2, 30.2, 30.1, 27.6, 26.4, 26.1, 23.1, 19.4, 11.6; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ [M + Na]$^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2217, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-15-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)heptadecanamide



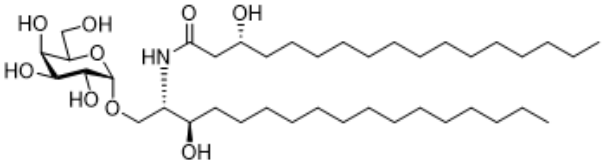
Yield: 98%; ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.2 Hz, 1H), 4.00–3.95 (m, 2H), 3.93–3.92 (m, 1H), 3.88–3.67 (m, 7H), 3.64–3.60 (m, 1H), 2.41–2.36 (m, 1H), 2.32–2.26 (m, 1H), 1.57–1.41 (m, 5H), 1.33–1.27 (m, 42H), 1.18–1.13 (m, 2H), 0.90–0.86 (m, 9H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 173.5, 100.3, 71.5, 71.4, 70.8, 70.3, 69.7, 69.2, 67.9, 62.2, 54.3, 44.3, 39.6, 37.9, 34.5, 32.5, 30.5, 30.2, 30.2, 29.9, 28.5, 28.0, 26.4, 26.1, 23.2, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2218, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-14-methyl-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)hexadecan-2-yl)heptadecanamide



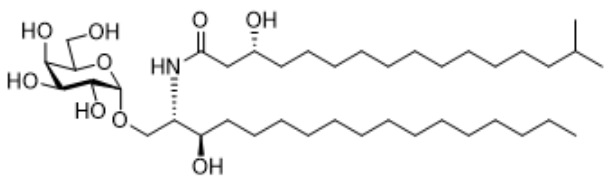
Yield: quantitative; ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85–4.84 (m, 1H), 3.99–3.60 (m, 12H), 2.40–2.27 (m, 2H), 1.55–1.39 (m, 6H), 1.36–1.23 (m, 37H), 1.17–1.07 (m, 3H), 0.94–0.80 (m, 9H); ^{13}C NMR (150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 173.5, 100.2, 71.5, 71.3, 70.7, 70.2, 69.6, 69.2, 67.8, 62.1, 54.3, 44.2, 37.8, 37.2, 35.0, 34.5, 32.4, 30.5, 30.2, 30.2, 30.2, 30.0, 29.9, 27.6, 26.4, 26.1, 23.1, 19.4, 14.3, 11.6; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2219, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)heptadecan-2-yl)heptadecanamide



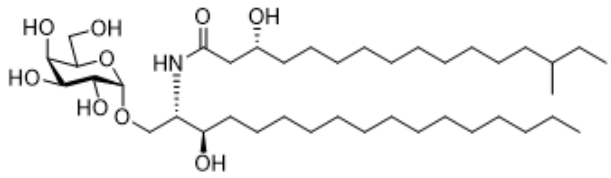
Yield: quantitative; ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.6 Hz, 1H), 3.99–3.97 (m, 2H), 3.96–3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.63–3.61 (m, 1H), 2.40–2.27 (m, 2H), 1.55–1.39 (m, 7H), 1.35–1.27 (m, 49H), 0.90–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 173.5, 100.2, 71.5, 71.3, 70.7, 70.2, 69.6, 69.2, 67.8, 62.1, 54.3, 44.2, 37.8, 34.5, 32.4, 32.4, 30.2, 30.2, 29.9, 26.3, 26.1, 23.1, 14.3; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2220, (R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)heptadecan-2-yl)-15-methylhexadecanamide



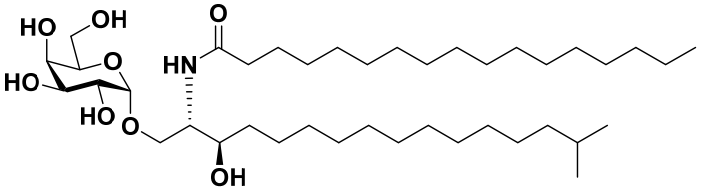
Yield: quantitative; ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.87 (d, J = 3.6 Hz, 1H), 3.97 (m, 2H), 3.92 (m, 1H), 3.87–3.67 (m, 7H), 3.64–3.60 (m, 1H), 2.40–2.26 (m, 2H), 1.63–1.40 (m, 4H), 1.27 (m, 43H), 1.16–1.13 (m, 2H), 0.94–0.86 (m, 9H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 173.5, 100.2, 71.5, 71.3, 70.7, 70.2, 69.6, 69.2, 62.1, 54.3, 44.2, 39.6, 37.8, 34.5, 30.4, 30.2, 30.2, 29.9, 28.5, 27.9, 26.3, 26.1, 23.2, 22.9, 14.3; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2221, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)heptadecan-2-yl)-14-methylhexadecanamide



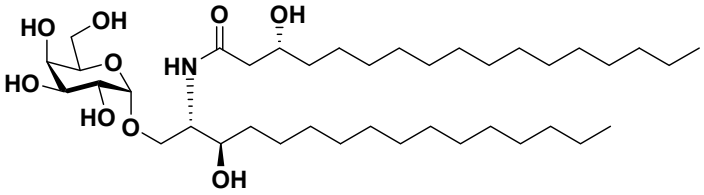
Yield: quantitative; ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.87–4.83 (m, 1H), 3.97 (m, 2H), 3.92 (m, 1H), 3.87–3.68 (m, 7H), 3.64–3.60 (m, 1H), 2.40–2.20 (m, 2H), 1.61–1.40 (m, 5H), 1.27 (m, 38H), 1.18–1.09 (m, 2H), 0.90–0.84 (m, 9H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 172.8, 99.5, 70.8, 70.6, 70.0, 69.5, 68.9, 68.4, 61.4, 53.5, 43.5, 37.1, 36.4, 34.2, 33.7, 31.7, 29.8, 29.5, 29.4, 29.3, 29.1, 26.9, 25.6, 25.4, 22.4, 18.7, 13.5, 10.9; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_9$ $[M + Na]^+$ calcd: 740.56, found: 740.60.

Synthesis of SB2222, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)heptadecan-2-yl)-14-methylhexadecanamide



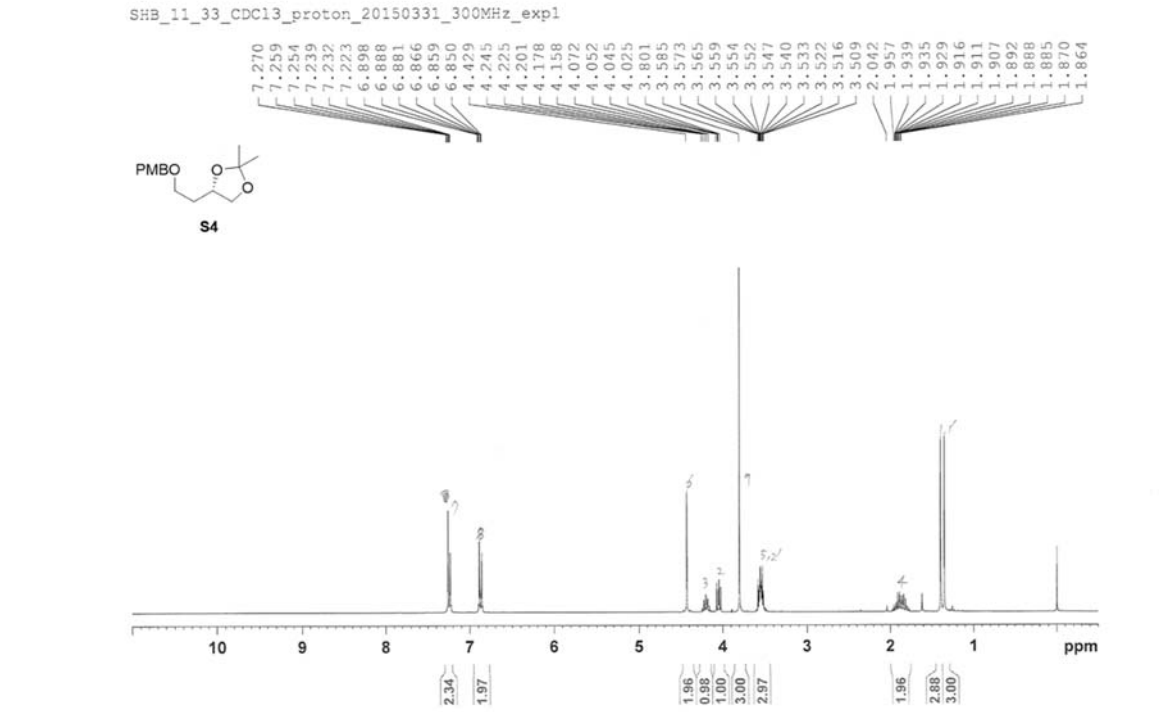
Yield: 74%; ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.87 (d, J = 3.75 Hz, 1H), 3.97–3.90 (m, 2H), 3.82–3.70 (m, 7H), 3.63–3.59 (m, 1H), 2.23 (t, J = 7.55 Hz, 2H), 1.63–1.48 (m, 5H), 1.43–1.27 (m, 44H), 1.18–1.14 (m, 2H), 0.90–0.86 (m, 9H); ^{13}C NMR (150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 175.43, 100.52, 71.49, 71.36, 70.82, 70.34, 69.66, 68.20, 62.26, 54.48, 39.63, 36.96, 34.51, 32.47, 30.49, 30.27, 30.26, 30.23, 30.20, 30.19, 30.14, 29.99, 29.89, 28.51, 27.97, 26.54, 26.29, 23.18, 22.90, 14.31; LRMS(ESI) *m/z* for $C_{40}H_{79}NaNO_8$ $[M + Na]^+$ calcd: 724.57, found: 724.45.

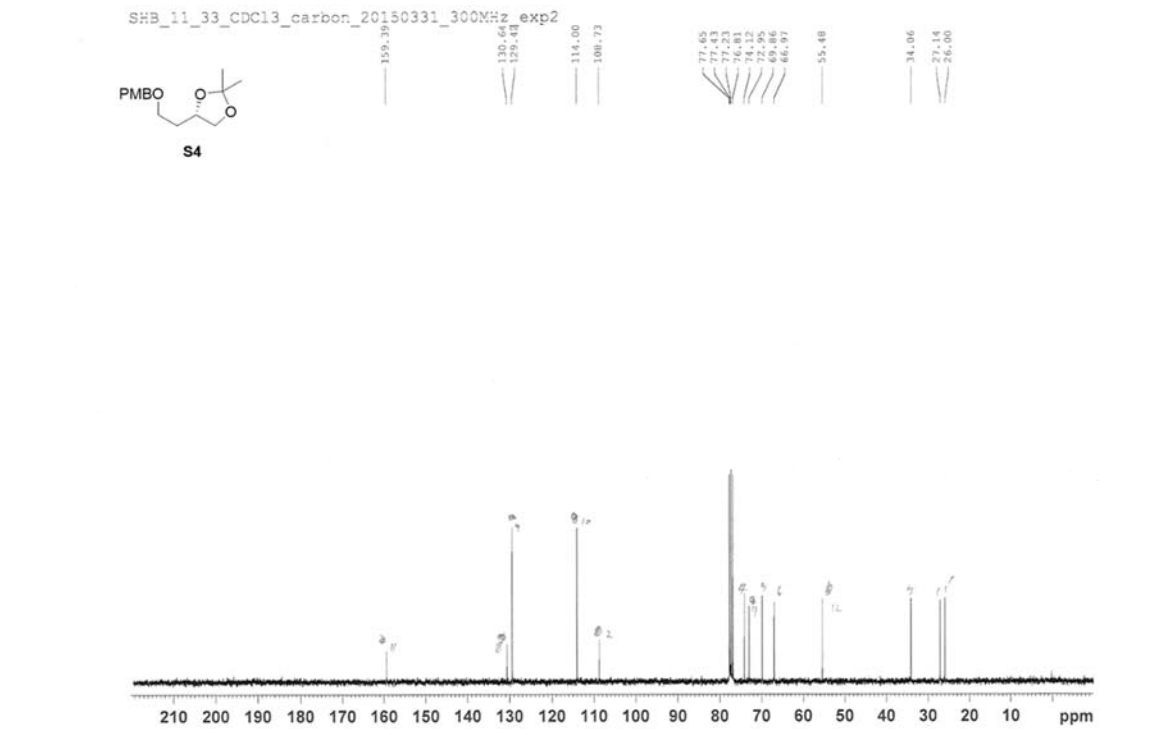
Synthesis of SB2223, (3R)-3-hydroxy-*N*-((2S,3R)-3-hydroxy-1-(((2S,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)heptadecan-2-yl)-14-methylhexadecanamide

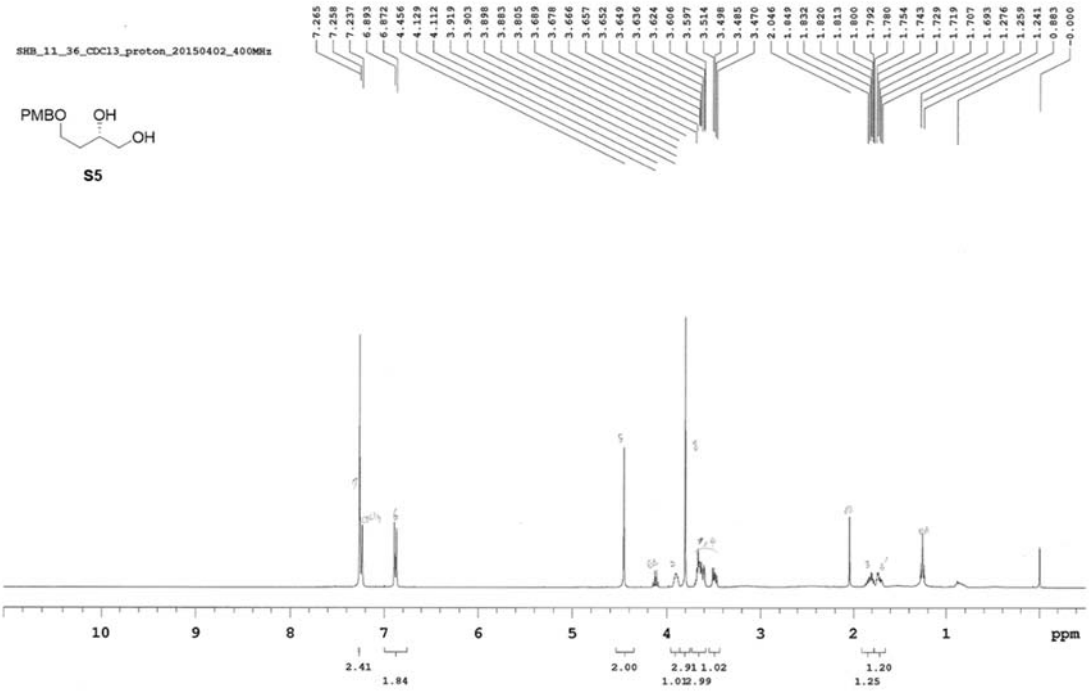


Yield: 83%; ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.85 (d, J = 3.5 Hz, 1H), 3.99–3.95 (m, 2H), 3.92 (m, 1H), 3.87–3.67 (m, 7H), 3.64–3.61 (m, 1H), 2.40–2.36 (m, 1H), 2.32–2.27 (m, 1H), 1.55–1.41 (m, 6H), 1.32–1.27 (m, 44H), 0.89 (t, J = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm); δ 173.53, 100.26, 71.54, 71.43, 70.79, 70.26, 69.68, 69.20, 67.91, 62.18, 54.29, 44.26, 37.84, 34.51, 32.47, 30.24, 30.22, 30.19, 29.89, 26.40, 26.13, 23.18, 14.30; LRMS(ESI) *m/z* for $C_{39}H_{77}NaNO_9$ $[M + Na]^+$ calcd: 726.55, found: 726.45.

2. ^{1}H and ^{13}C NMR spectra






SHB_11_36_CDCl3_proton_20150402_400MHz
PMBO OH
OH
S5
7.265
7.258
7.237
6.893
6.872
4.456
4.129
4.112
3.919
3.903
3.898
3.883
3.805
3.689
3.678
3.666
3.657
3.652
3.649
3.636
3.624
3.606
3.597
3.514
3.498
3.485
3.470
2.046
1.849
1.832
1.820
1.813
1.800
1.792
1.780
1.754
1.743
1.729
1.719
1.707
1.693
1.276
1.259
1.241
0.883
0.000
10
9
8
7
6
5
4
3
2
1
ppm
2.41
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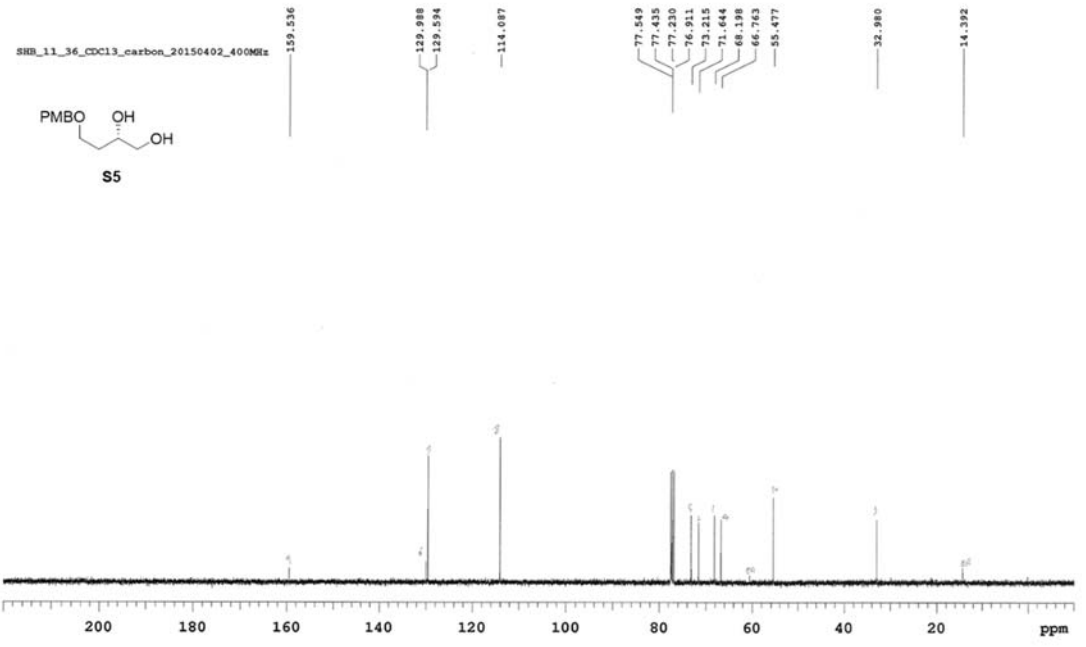
2.00
2.91
1.02
1.03
2.99
1.20
1.25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PMBO OH
OH
S5
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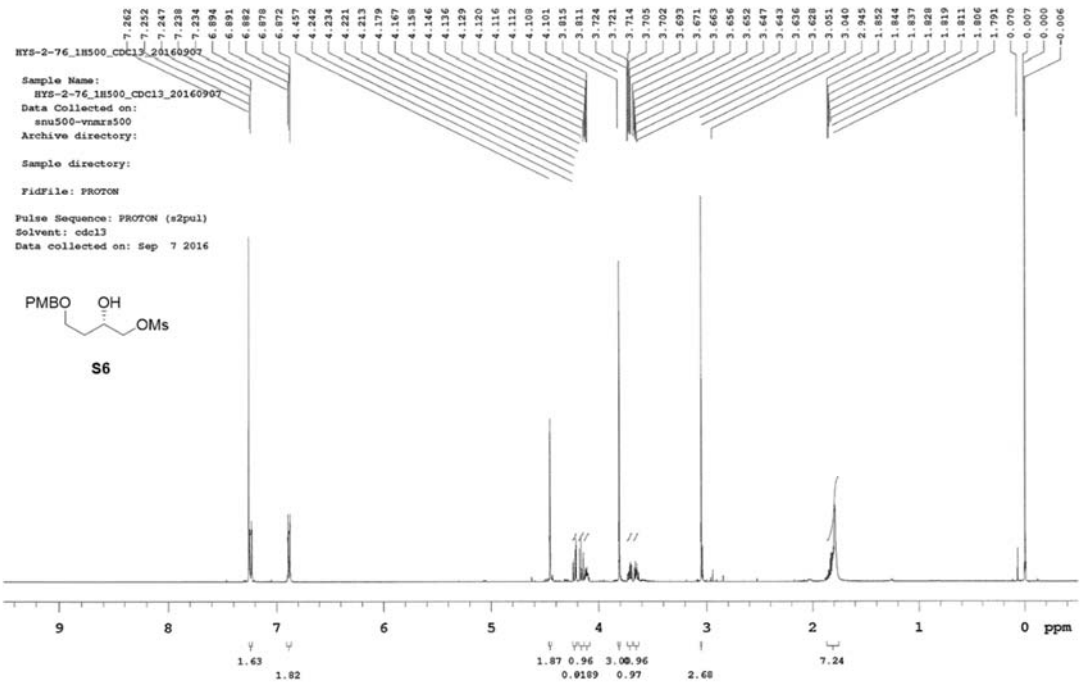
129.594
114.087
77.549
77.435
77.230
76.911
73.215
71.644
68.198
66.763
55.477
32.980
14.392
200
180
160
140
120
100
80
60
40
20
ppm


HYS-2-76_1H500_CDCl3_20160907
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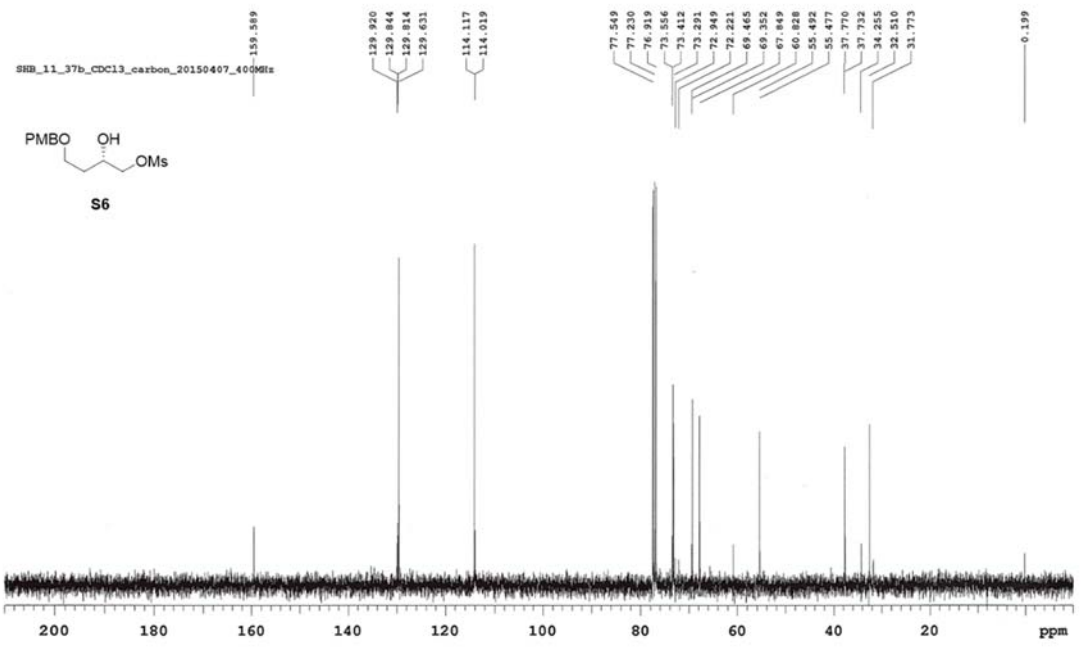
HYS-2-76_1H500_CDCl3_20160907
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 7 2016
PMBO
OH
OMs
S6
ppm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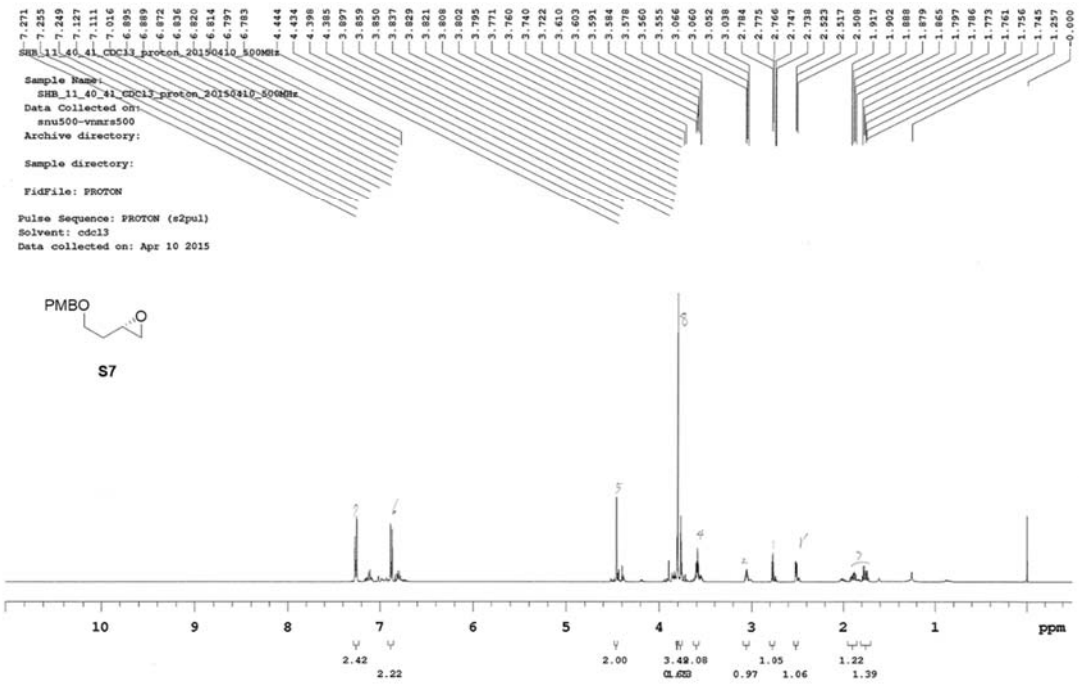
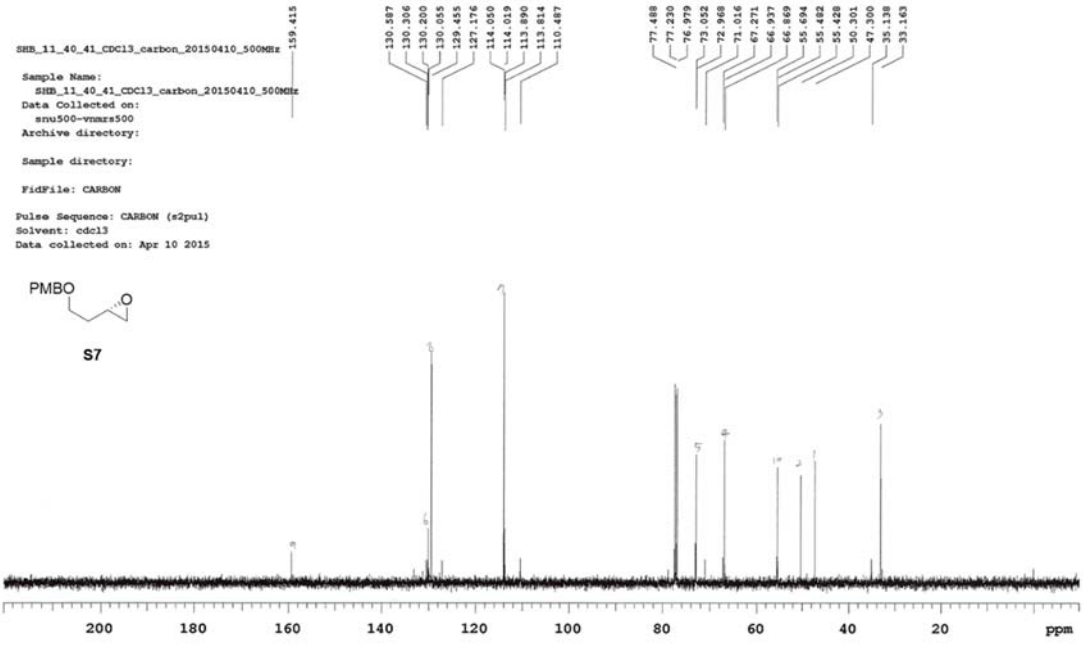
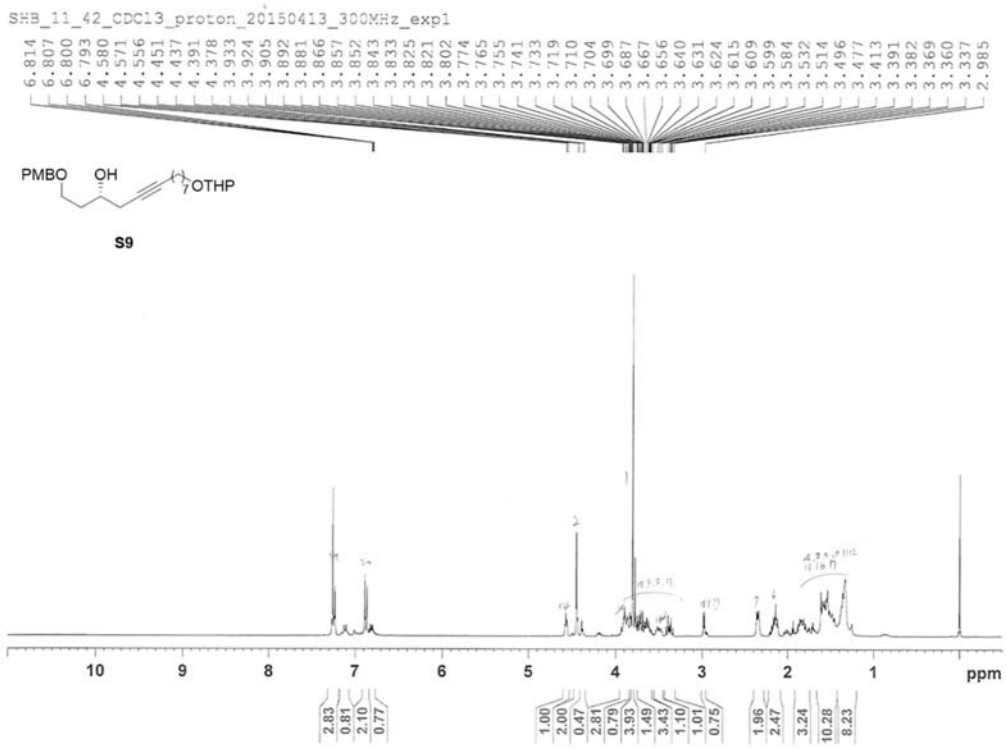
PMBO
OH
OMs
S6
ppm


SHB_11_40_41_CDCl3_proton_20150410_500MHz
Sample Name:
SHB_11_40_41_CDCl3_proton_20150410_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 10 2015
PMBO
S7
ppm


SHB_11_40_41_CDCl3_carbon_20150410_500MHz
Sample Name:
SHB_11_40_41_CDCl3_carbon_20150410_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 10 2015
PMBO
S7
ppm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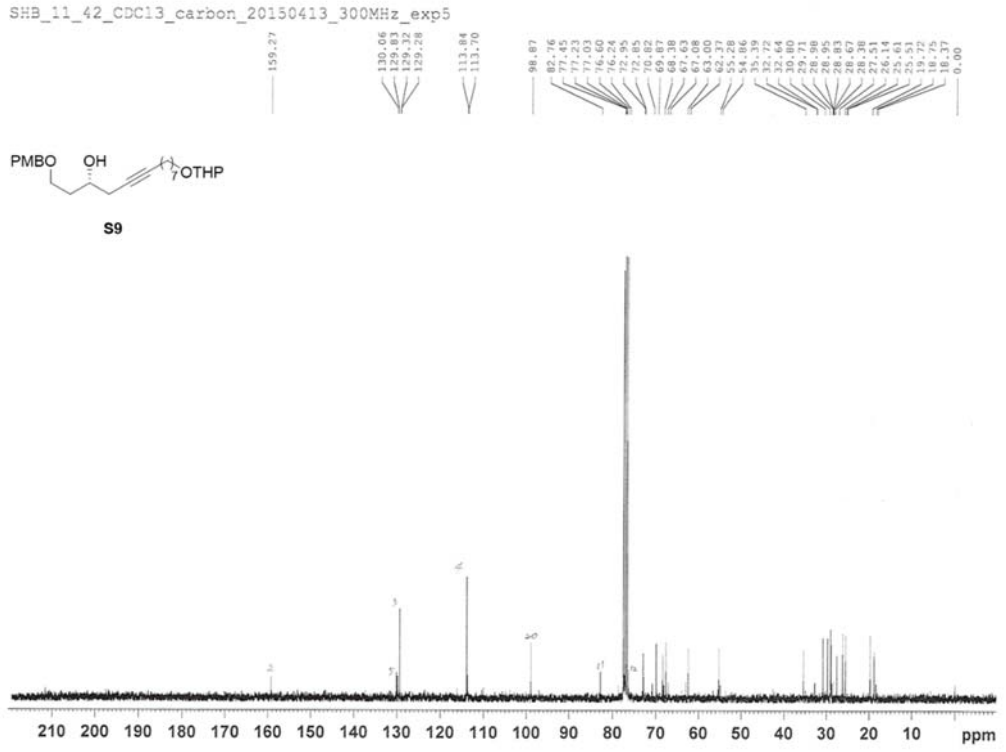
OH
OTHP
S9
ppm


SHB_11_42_CDCl3_carbon_20150413_300MHz_exp5
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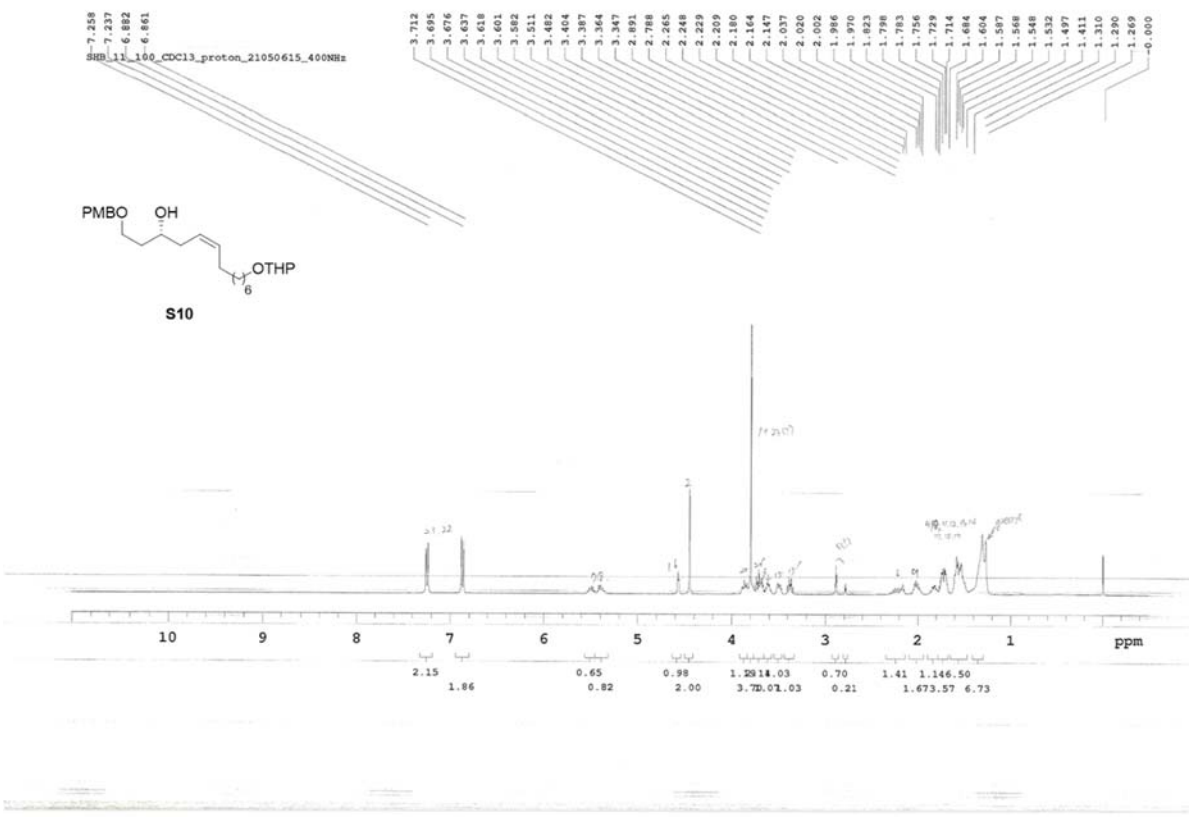
OH
OTHP
S9
ppm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OH
OTHP
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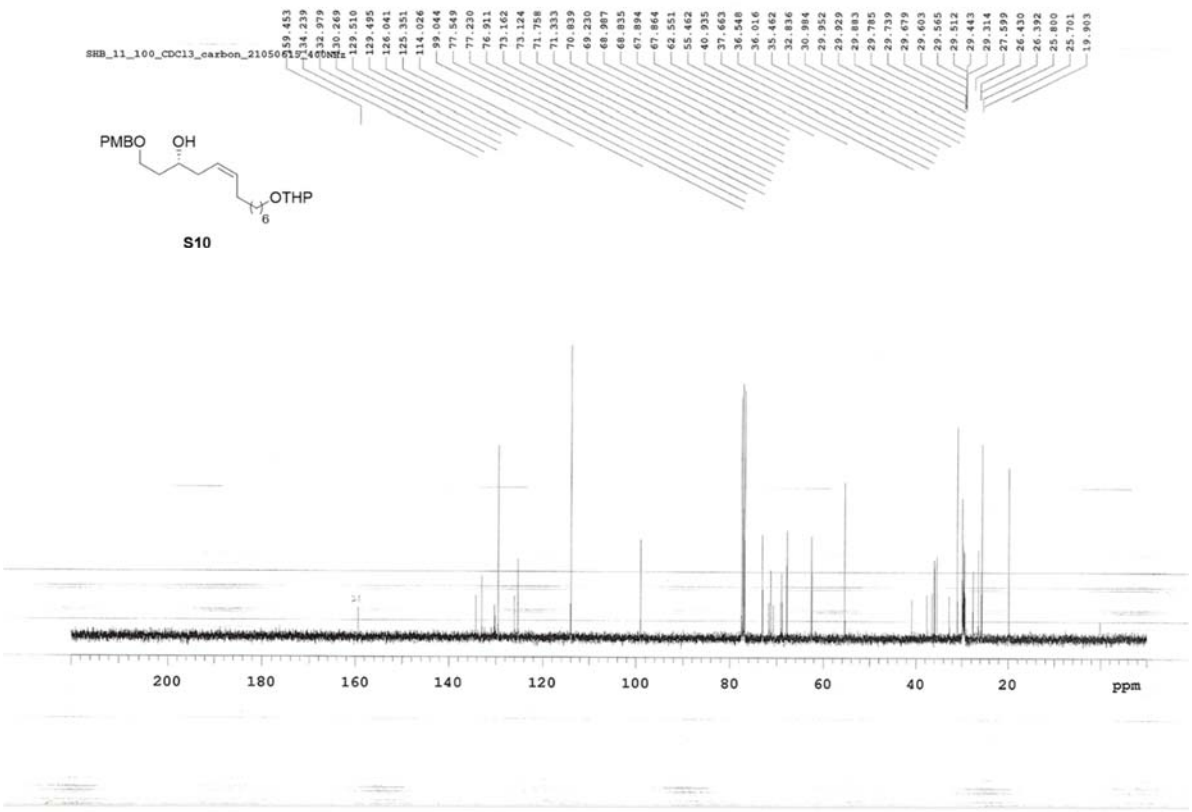
S10
ppm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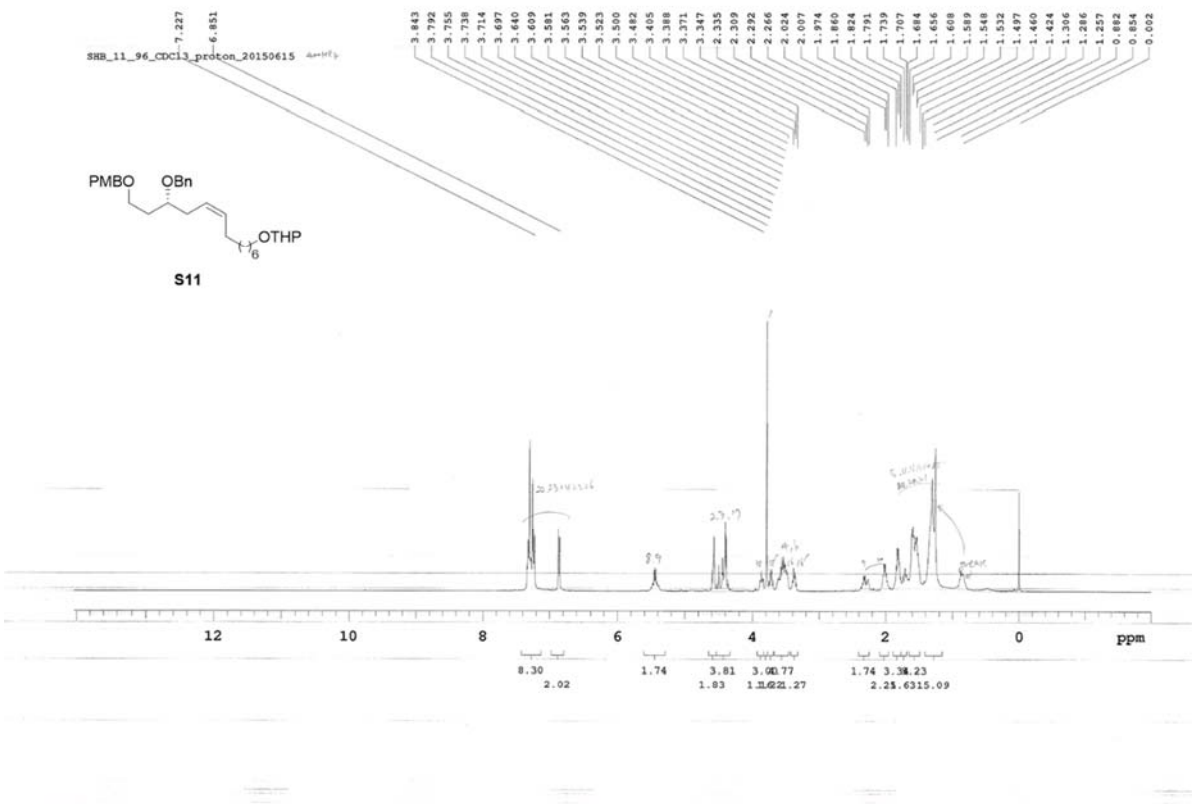
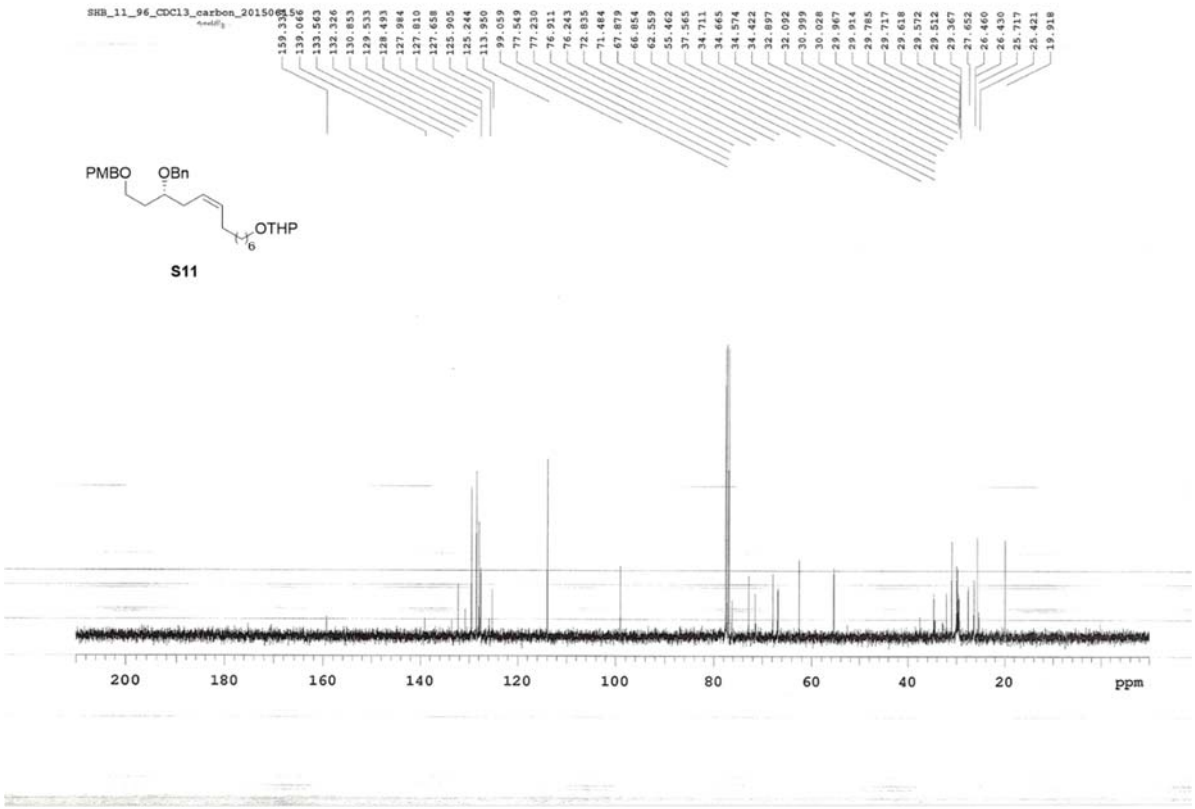
PMBO
OH
OTHP
6
S10
ppm


SHB_11_96_CDCl3_proton_20150615
PMBO
OBn
OTHP
6
S11
12
10
8
6
4
2
0
ppm


SHB_11_96_CDCl3_carbon_20150615
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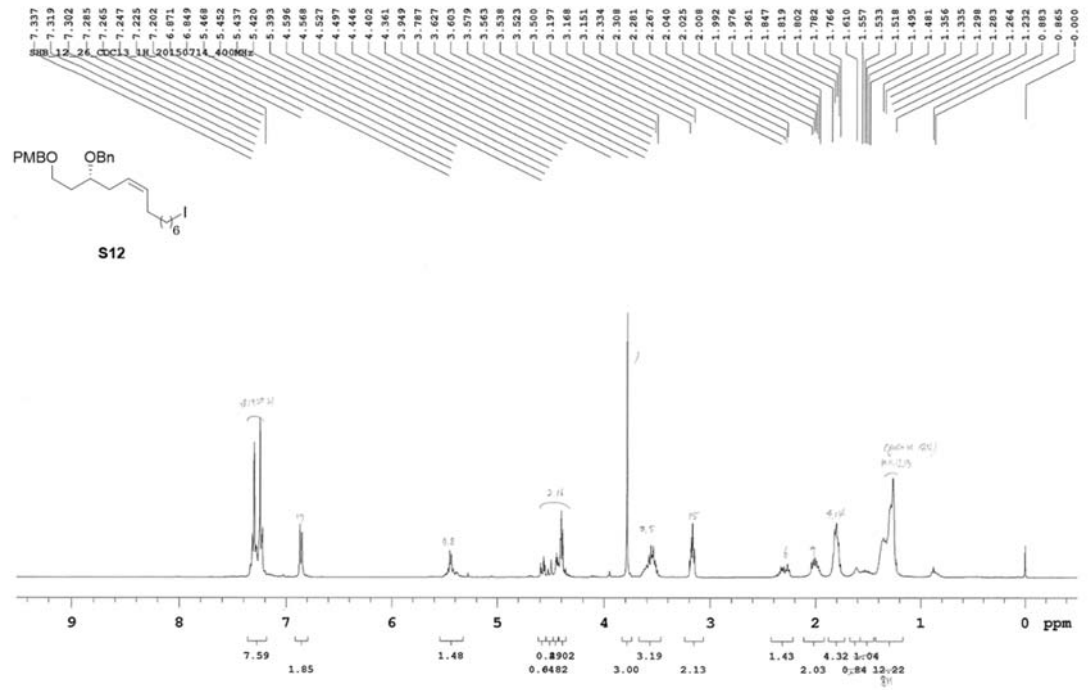
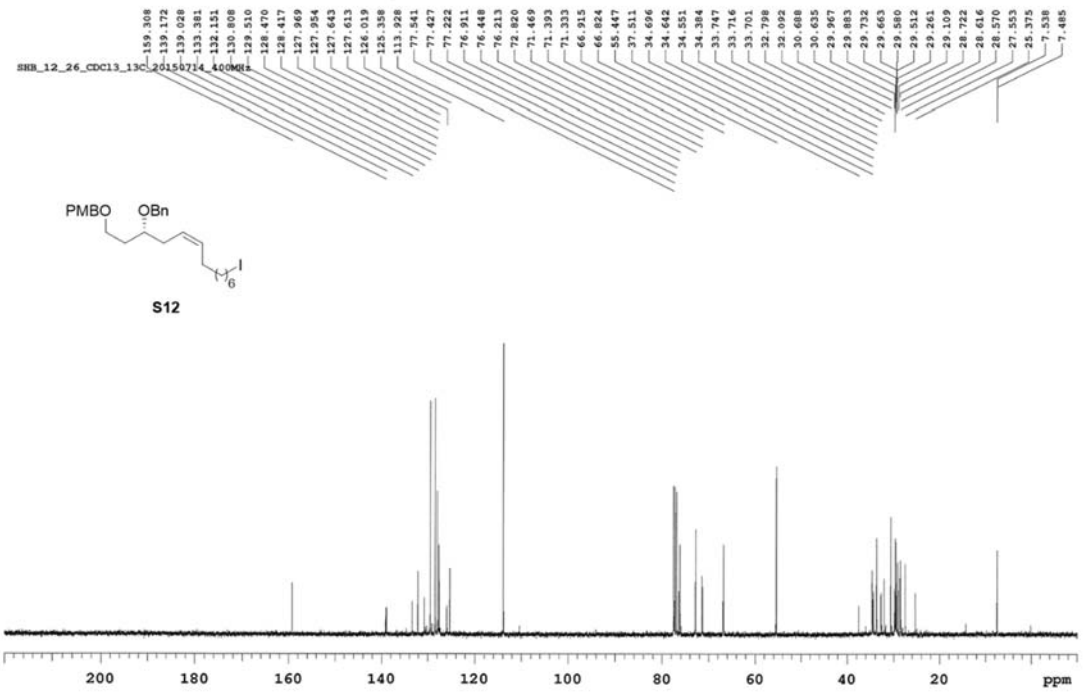
OBn
OTHP
6
S11
200
180
160
140
120
100
80
60
40
20
ppm


PMBO
OBn
I
6
S12
9
8
7
6
5
4
3
2
1
0 ppm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OBn
I
6
S12
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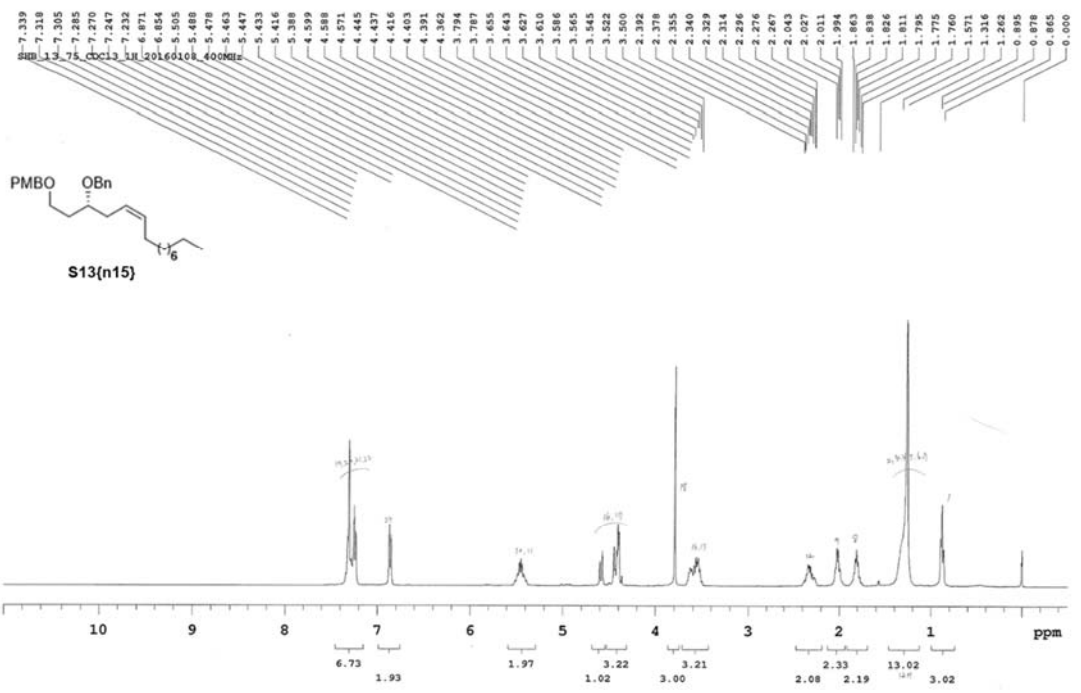
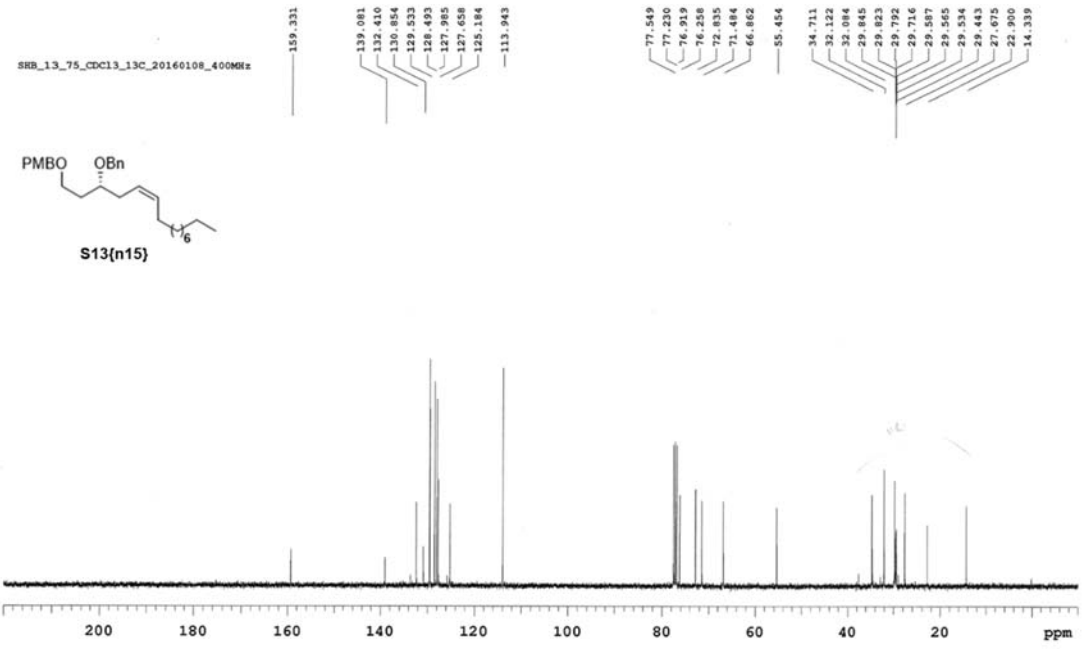
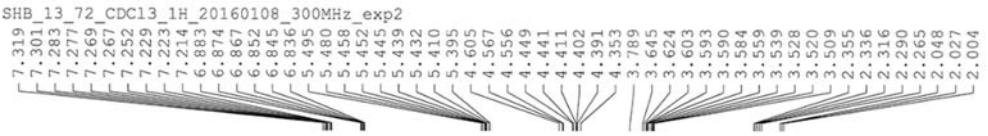
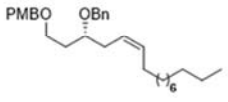
180
160
140
120
100
80
60
40
20
ppm

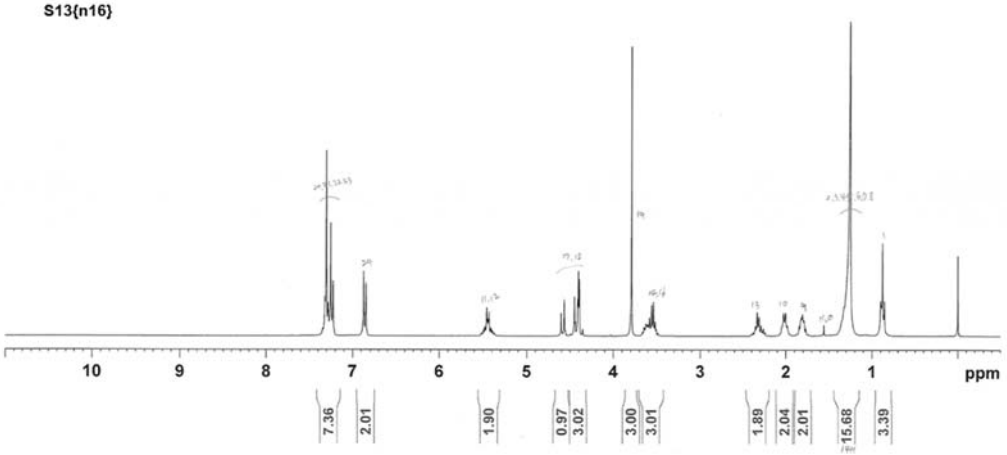

SRB_13_75_CDCl3_1H_20160108_400MHz
PMBO
OBn
6
S13{n15}
10
9
8
7
6
5
4
3
2
1
ppm
6.73
1.93
1.97
3.22
1.02
3.21
3.00
2.33
2.08
2.19
13.02
3.02

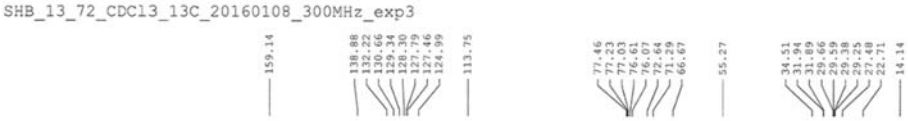

SRB_13_75_CDCl3_13C_20160108_400MHz
PMBO
OBn
6
S13{n15}
200
180
160
140
120
100
80
60
40
20
ppm

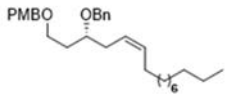




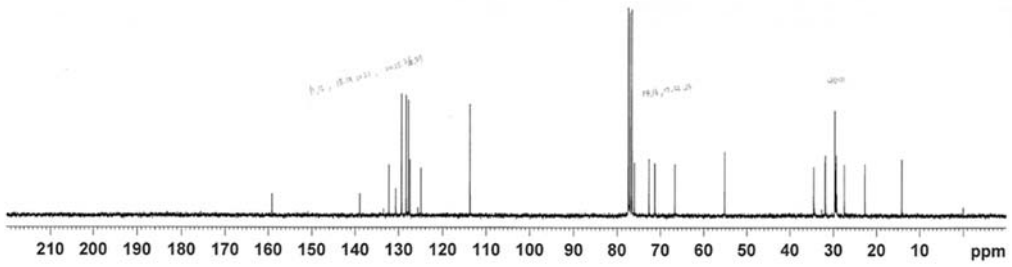
S13{n16}

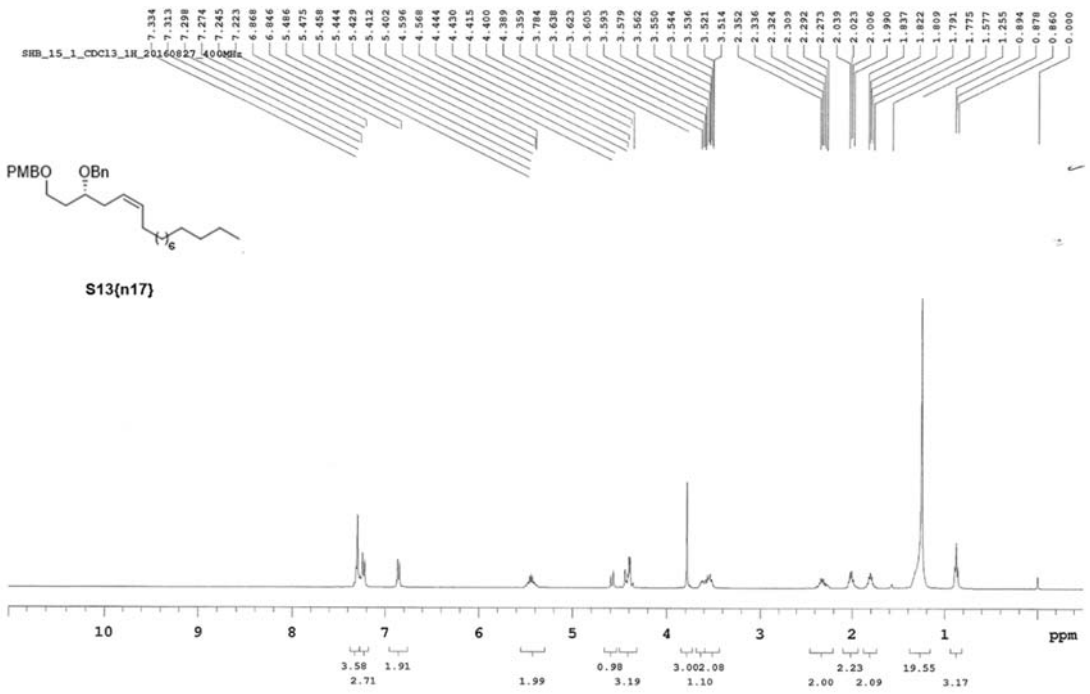




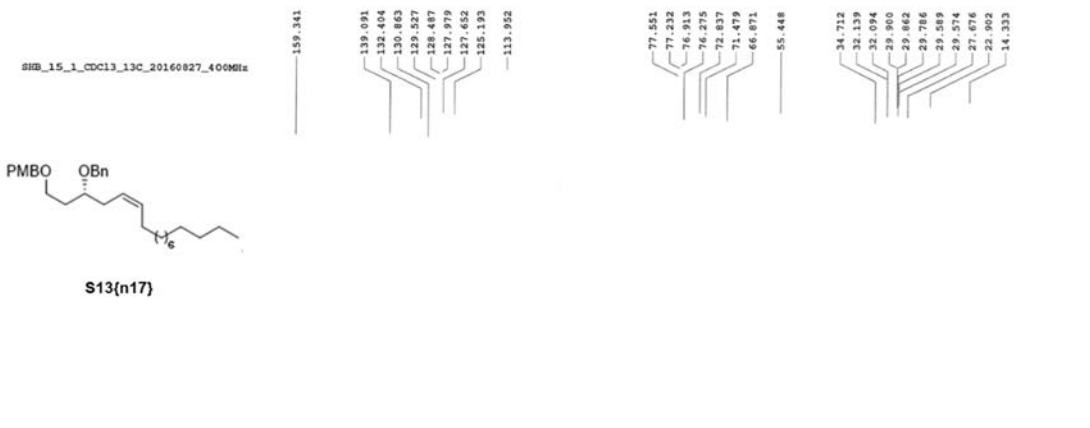


S13{n16}

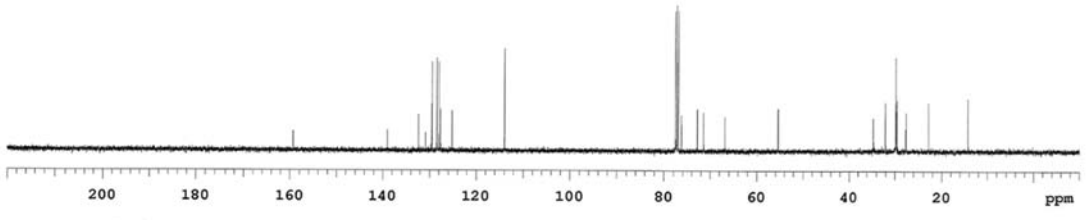


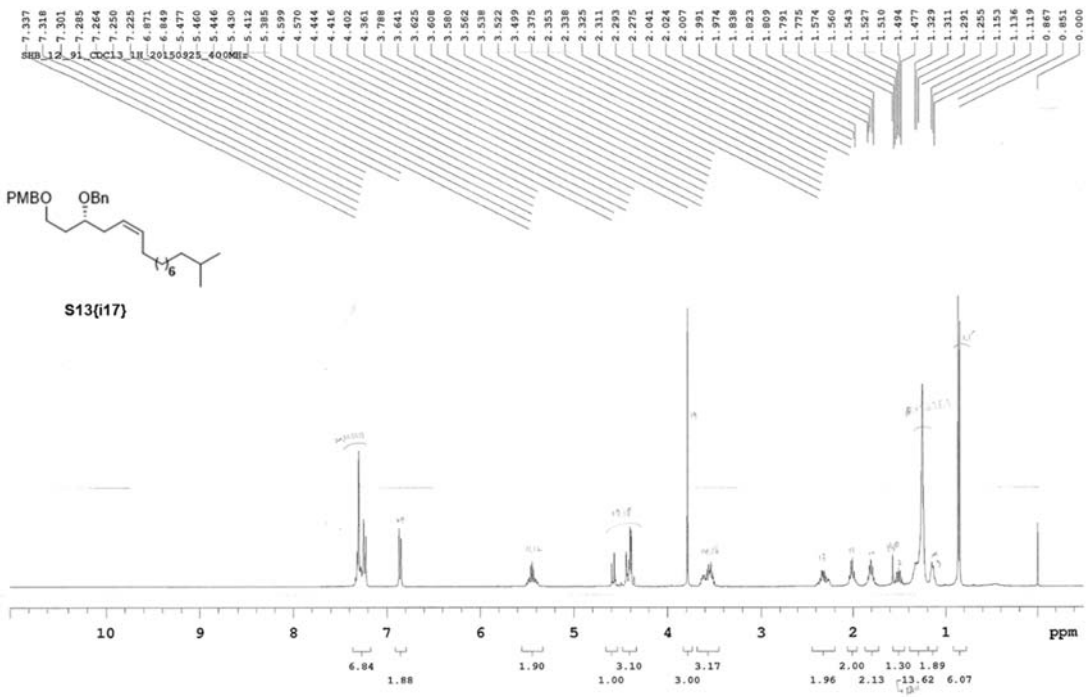


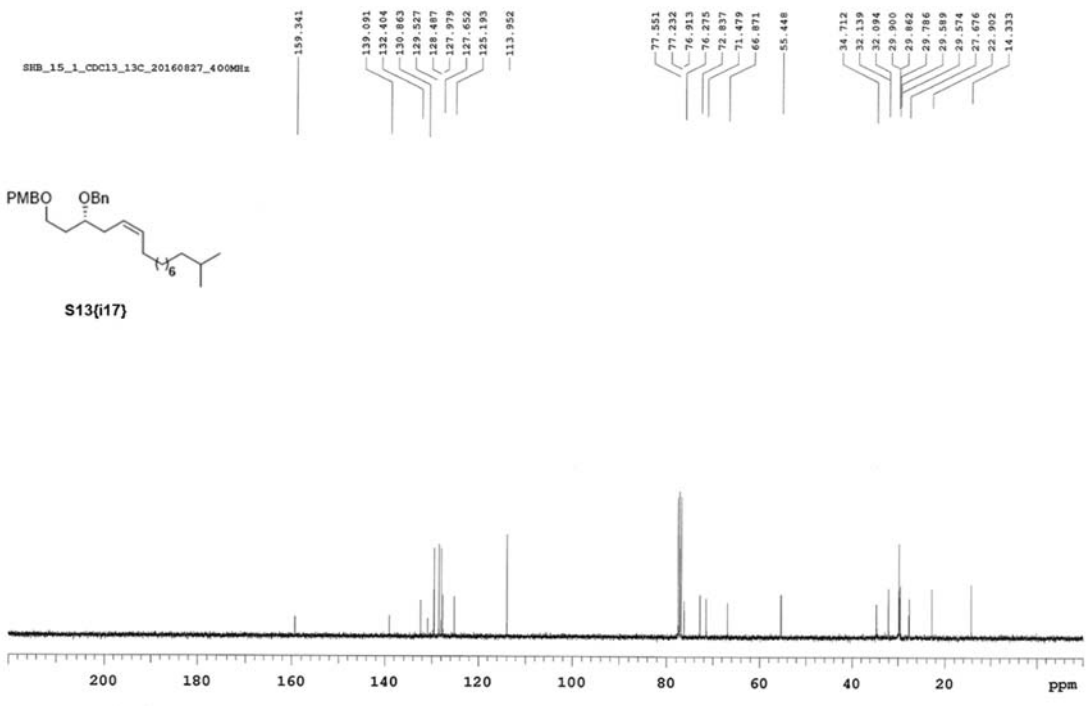
S13{n17}



S13{n17}




SHB_12_91_CDCl3_1H_20150925_400MHz
PMBO
OBn
6
S13{i17}
10
9
8
7
6
5
4
3
2
1
ppm
6.84
1.88
1.90
1.00
3.10
3.00
3.17
1.96
2.00
2.13
1.30
13.62
1.89
6.07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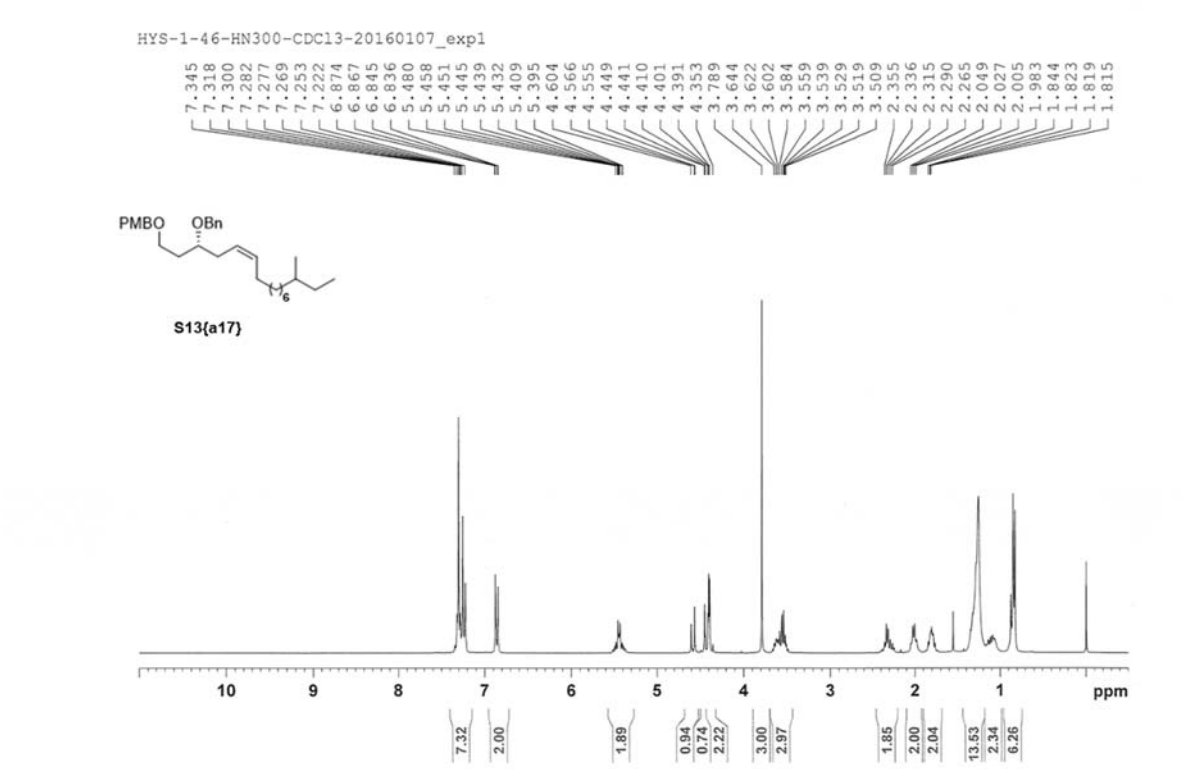
OBn
6
S13{i17}
200
180
160
140
120
100
80
60
40
20
ppm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7.318
7.300
7.282
7.277
7.269
7.253
7.222
6.874
6.867
6.845
6.836
5.480
5.458
5.451
5.445
5.439
5.432
5.409
5.395
4.604
4.566
4.555
4.449
4.441
4.410
4.401
4.391
4.353
3.789
3.644
3.622
3.602
3.584
3.559
3.539
3.529
3.519
3.509
2.355
2.336
2.315
2.290
2.265
2.049
2.027
2.005
1.983
1.844
1.823
1.819
1.815
PMBO
OBn
6
S13{a17}
10
9
8
7
6
5
4
3
2
1
ppm
7.32
2.00
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2.22
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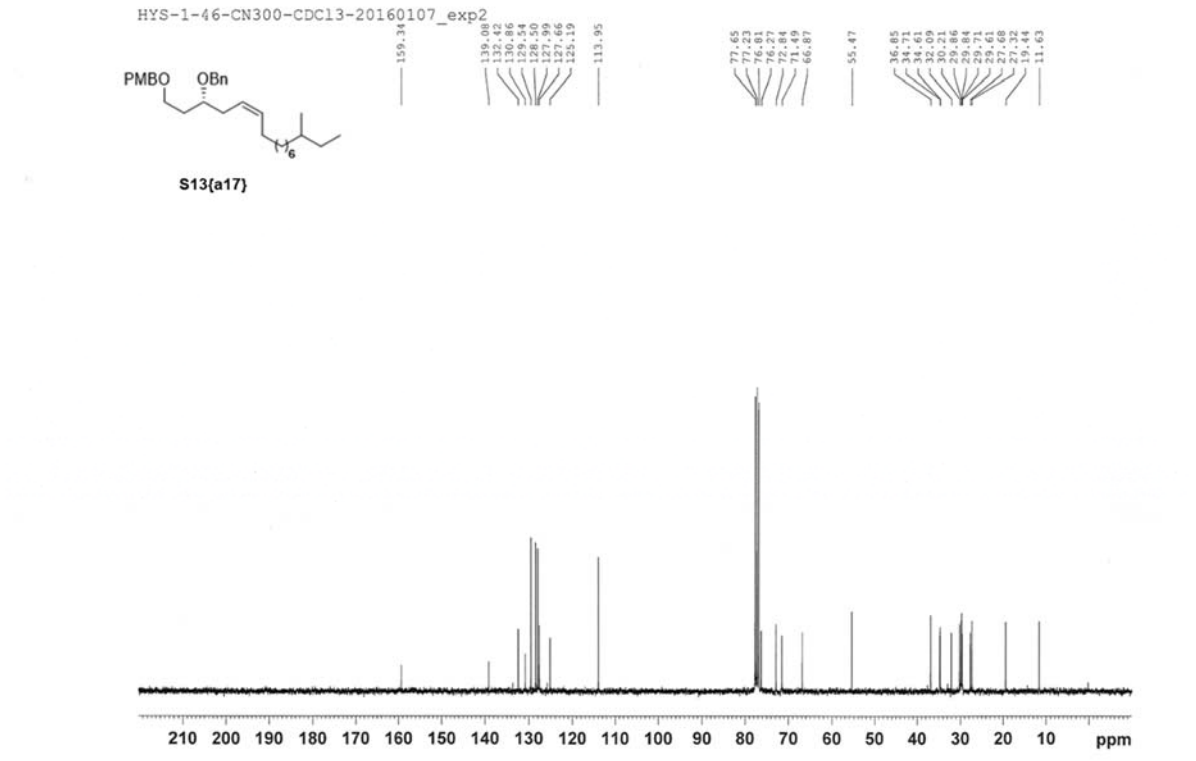
2.97
1.85
2.00
2.04
13.53
2.34
6.26


HYS-1-46-CN300-CDCl3-20160107_exp2
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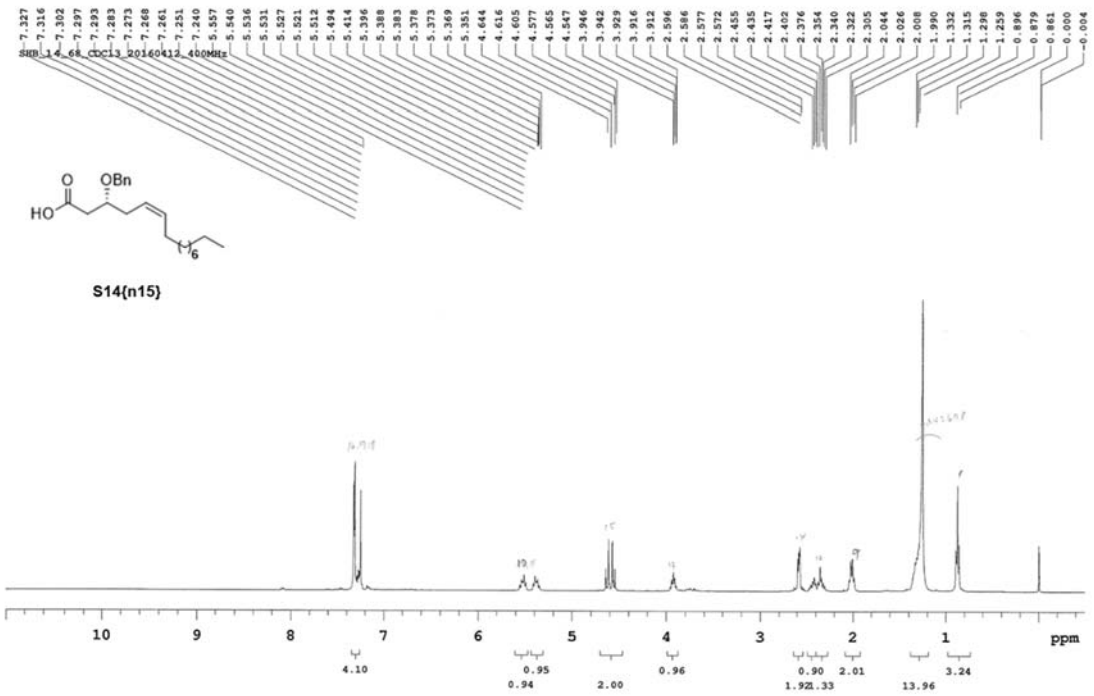
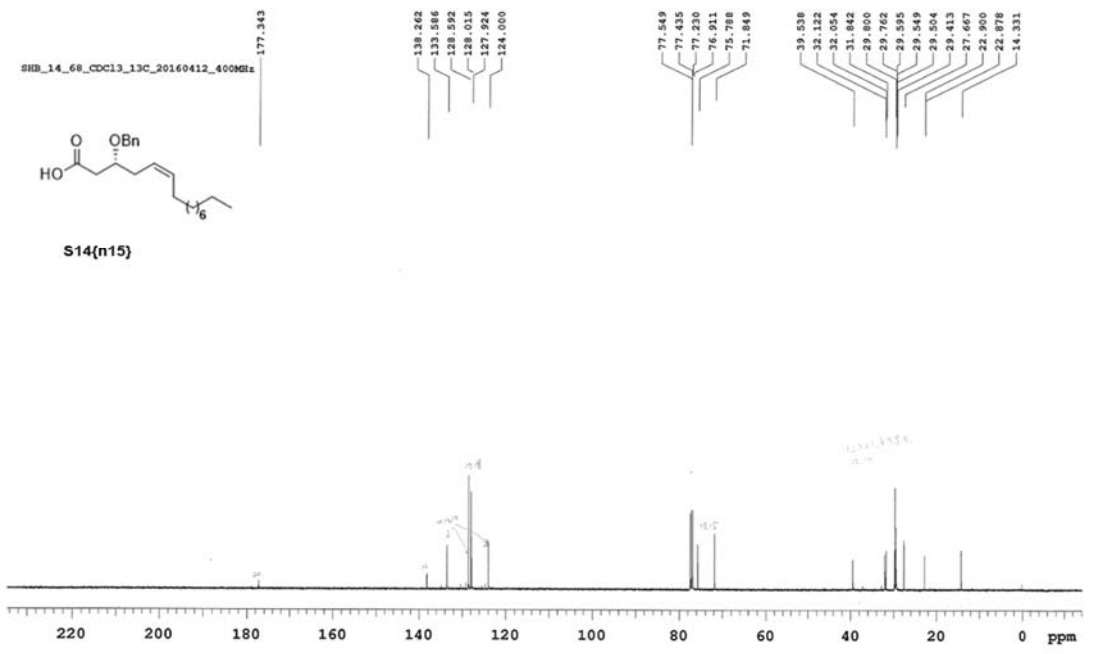
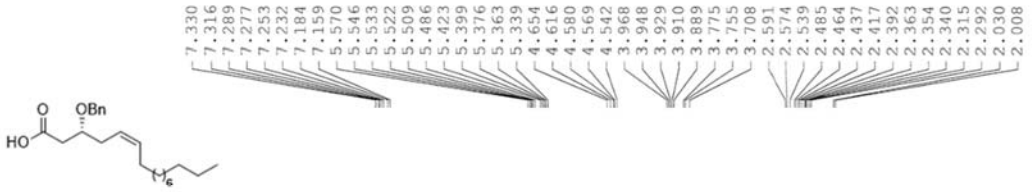
139.08
132.42
130.86
129.54
128.50
127.99
127.66
125.19
113.95
77.65
77.23
76.81
76.27
72.84
71.49
66.87
55.47
36.85
34.71
34.61
32.09
30.21
29.86
29.84
29.71
29.61
27.68
27.32
19.44
11.63
PMBO
OBn
6
S13{a17}
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

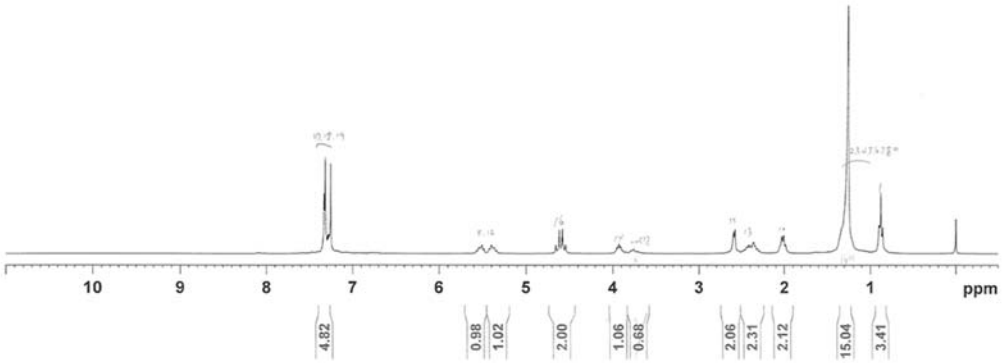

SHB_14_68_CDCl3_20160412_400MHz
7.327 7.316 7.302 7.297 7.293 7.283 7.273 7.268 7.261 7.251 7.240 5.557 5.540 5.536 5.531 5.527 5.521 5.512 5.494 5.414 5.396 5.388 5.383 5.378 5.373 5.369 5.351 4.644 4.616 4.605 4.577 4.565 4.547 3.946 3.942 3.929 3.916 3.912 2.596 2.586 2.577 2.572 2.455 2.435 2.417 2.402 2.376 2.354 2.340 2.322 2.305 2.044 2.026 2.008 1.990 1.332 1.315 1.298 1.259 0.896 0.879 0.861 0.000 -0.004
O
OBn
HO
6
S14{n15}
10 9 8 7 6 5 4 3 2 1 ppm
4.10 0.95 0.94 2.00 0.96 0.90 1.92 1.33 2.01 13.96 3.24


SHB_14_68_CDCl3_13C_20160412_400MHz
177.343
138.262 133.586 128.592 128.015 127.924 124.000
77.549 77.435 77.230 76.911 75.788 71.849
39.538 32.122 32.054 31.842 29.800 29.762 29.595 29.549 29.504 29.413 27.667 22.900 22.878 14.331
O
OBn
HO
6
S14{n15}
220 200 180 160 140 120 100 80 60 40 20 0 ppm

SHB_14_74_CDCl3_1H_20160415_300MHz_exp1

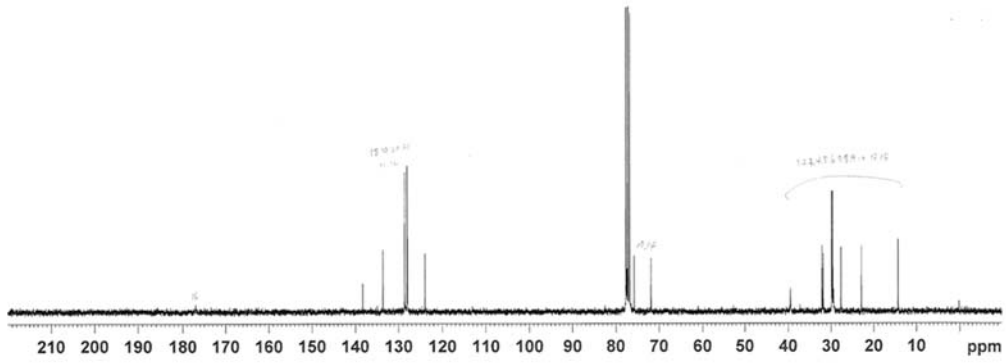


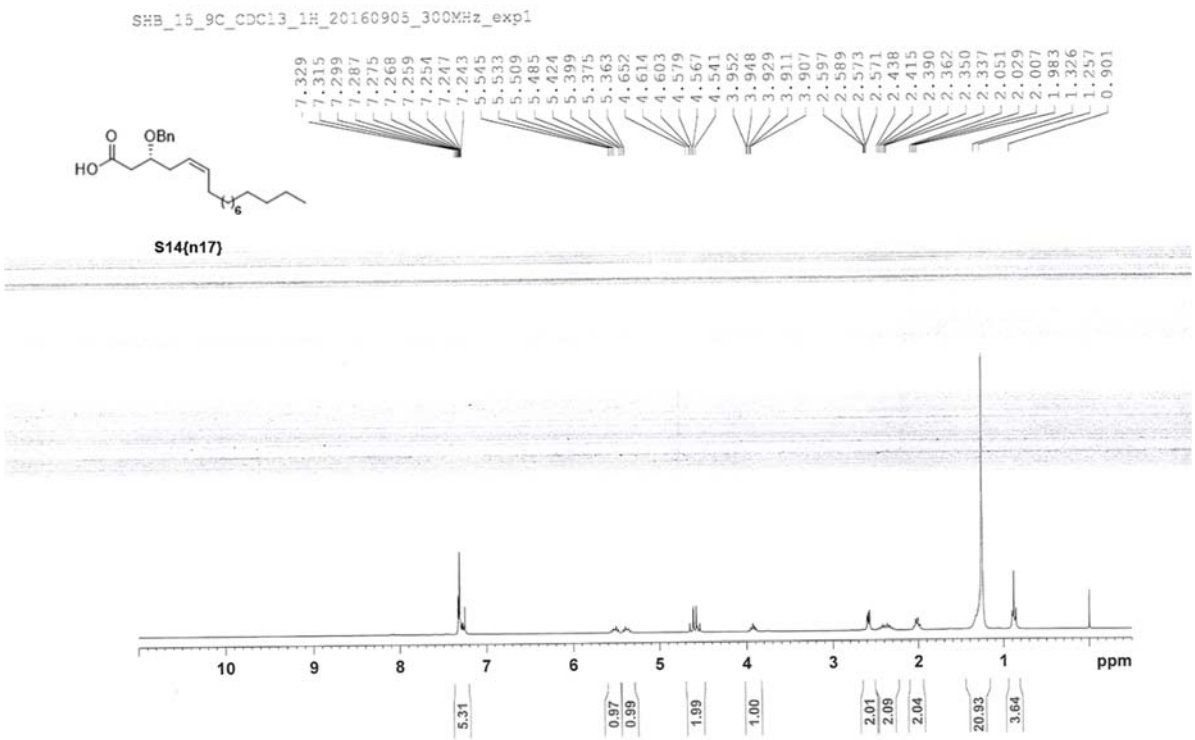
S14{n16}

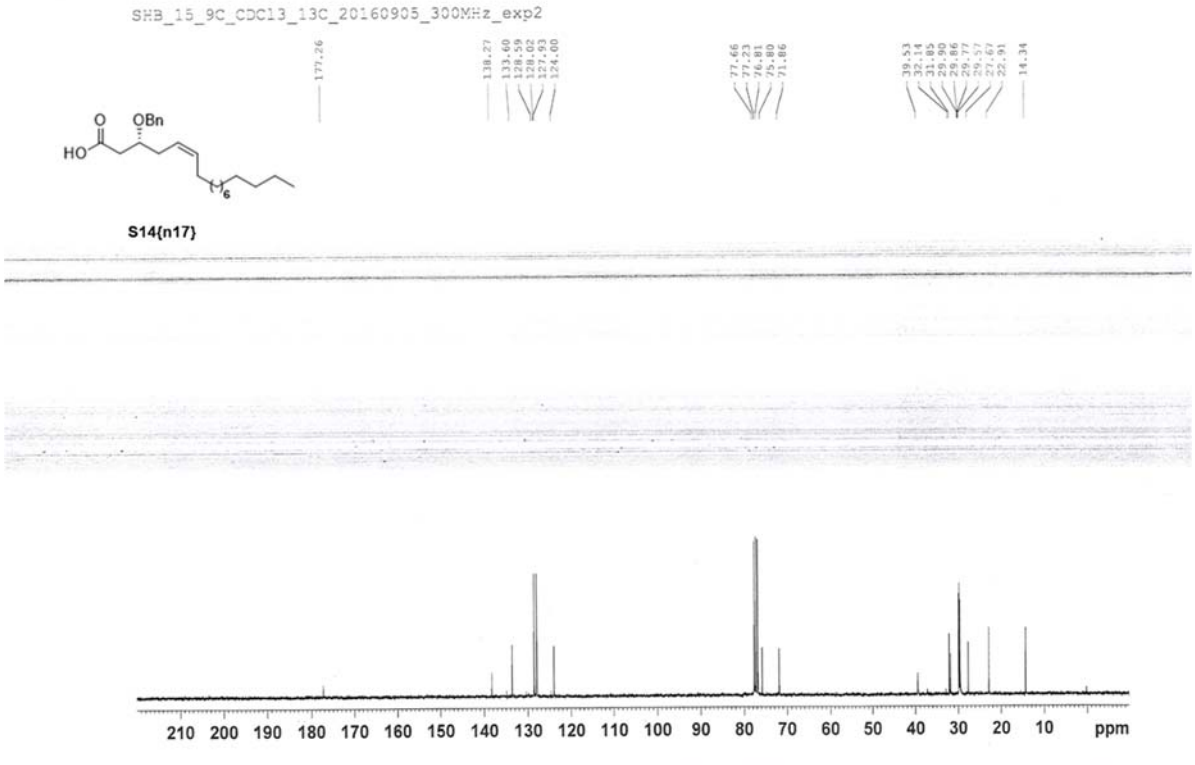


SHB_14_74_CDCl3_13C_20160415_300MHz_exp2

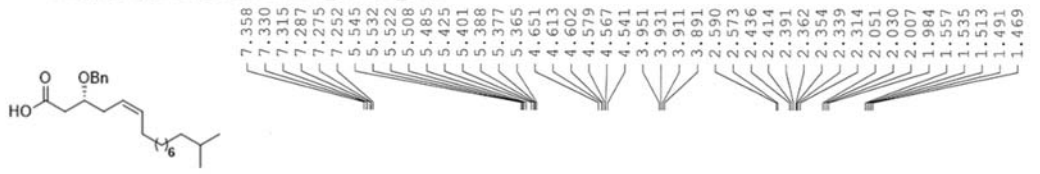
S14{n16}



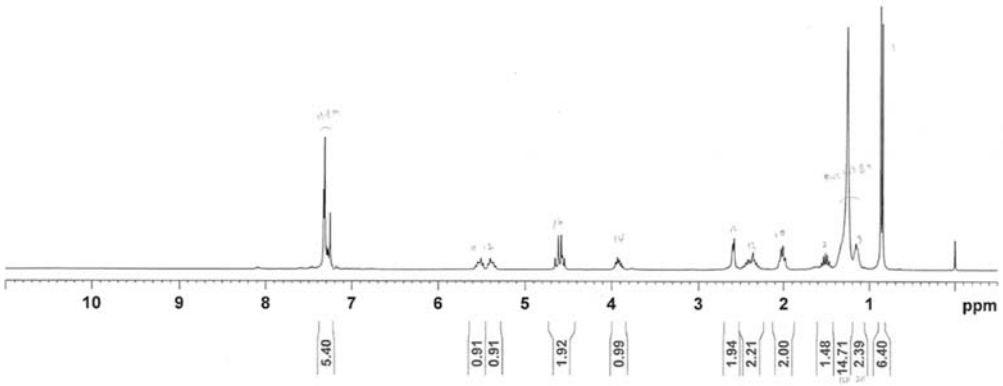

SHB_15_9C_CDCl3_1H_20160905_300MHz_exp1
7.329
7.315
7.299
7.287
7.275
7.268
7.259
7.254
7.247
7.243
5.545
5.533
5.509
5.485
5.424
5.399
5.375
5.363
4.652
4.614
4.603
4.579
4.567
4.541
3.952
3.948
3.929
3.911
3.907
2.597
2.589
2.573
2.571
2.438
2.415
2.390
2.362
2.350
2.337
2.051
2.029
2.007
1.983
1.326
1.257
0.901
O
OBn
HO
6
S14{n17}
10
9
8
7
6
5
4
3
2
1
ppm
5.31
0.97
0.99
1.99
1.00
2.01
2.09
2.04
20.93
3.64


SHB_15_9C_CDCl3_13C_20160905_300MHz_exp2
177.26
138.27
133.60
128.59
128.02
127.93
124.60
77.66
77.23
76.81
75.80
71.86
39.53
32.14
31.85
29.90
29.86
29.77
29.57
27.67
22.91
14.34
O
OBn
HO
6
S14{n17}
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

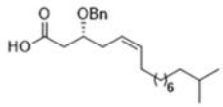
SHB_13_96_CDCl3_1H_20160126_300MHz_exp1



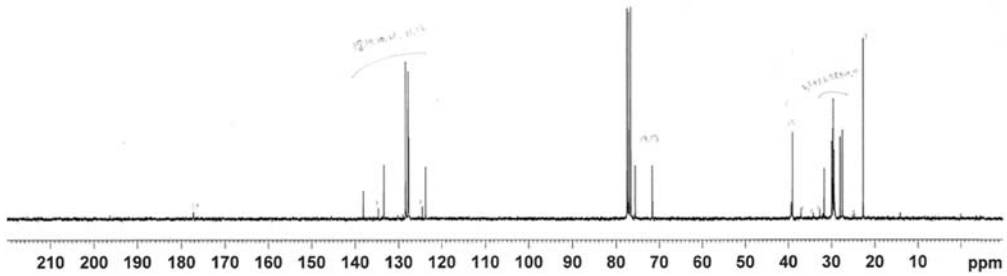
S14{i17}

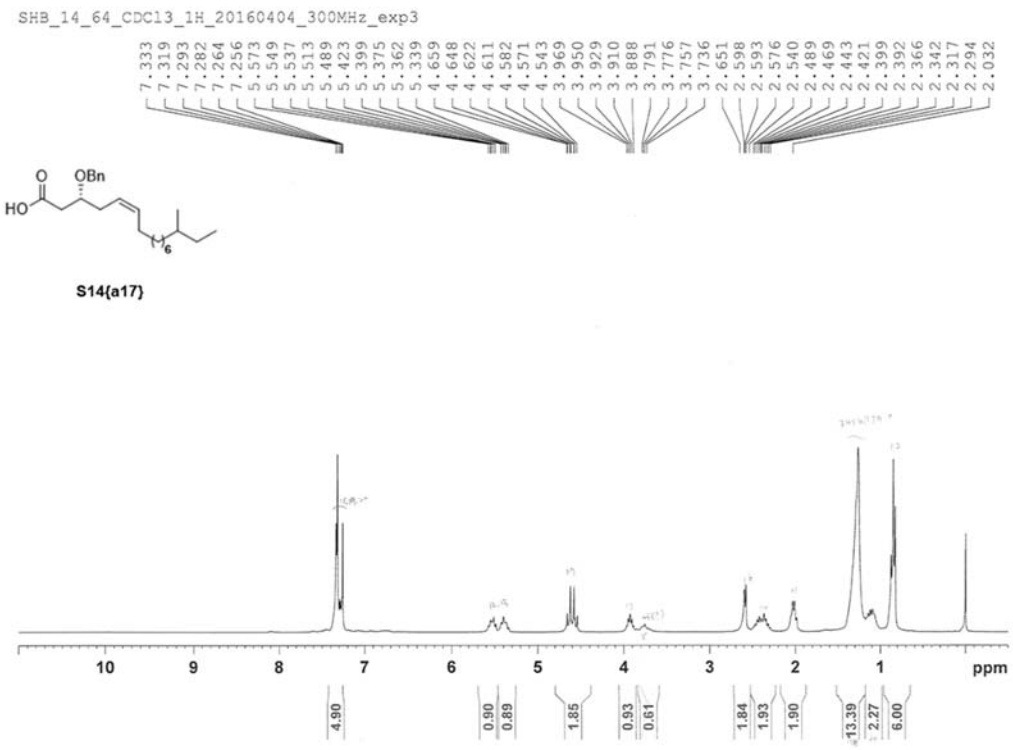


SHB_13_96_CDCl3_13C_20160126_300MHz_exp2

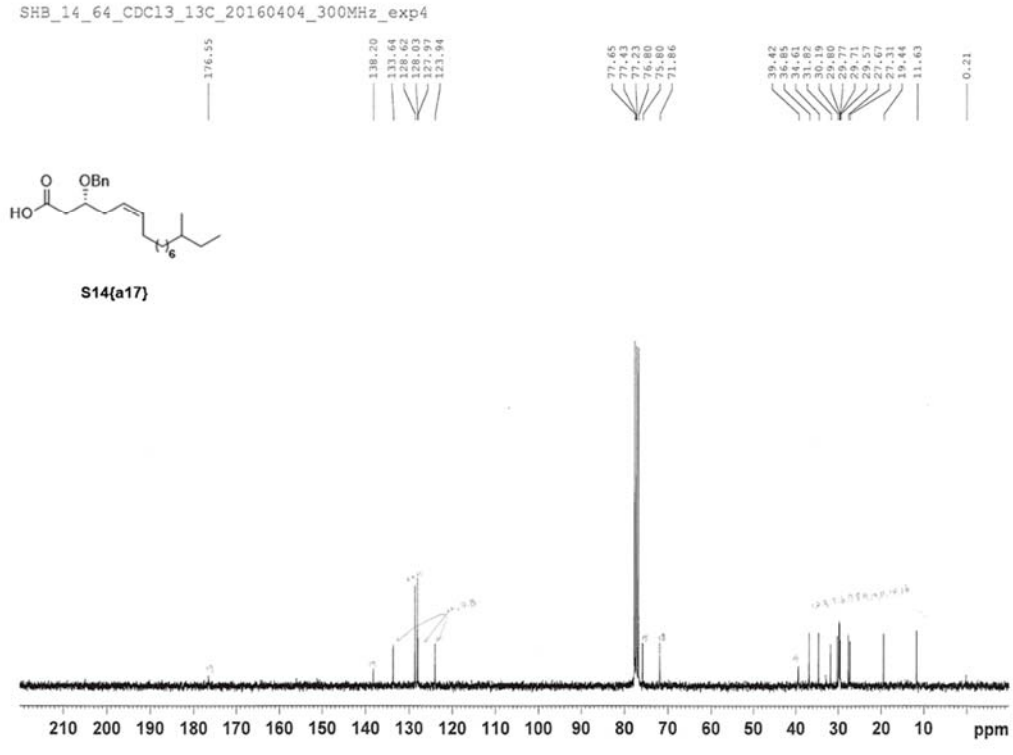


S14{i17}

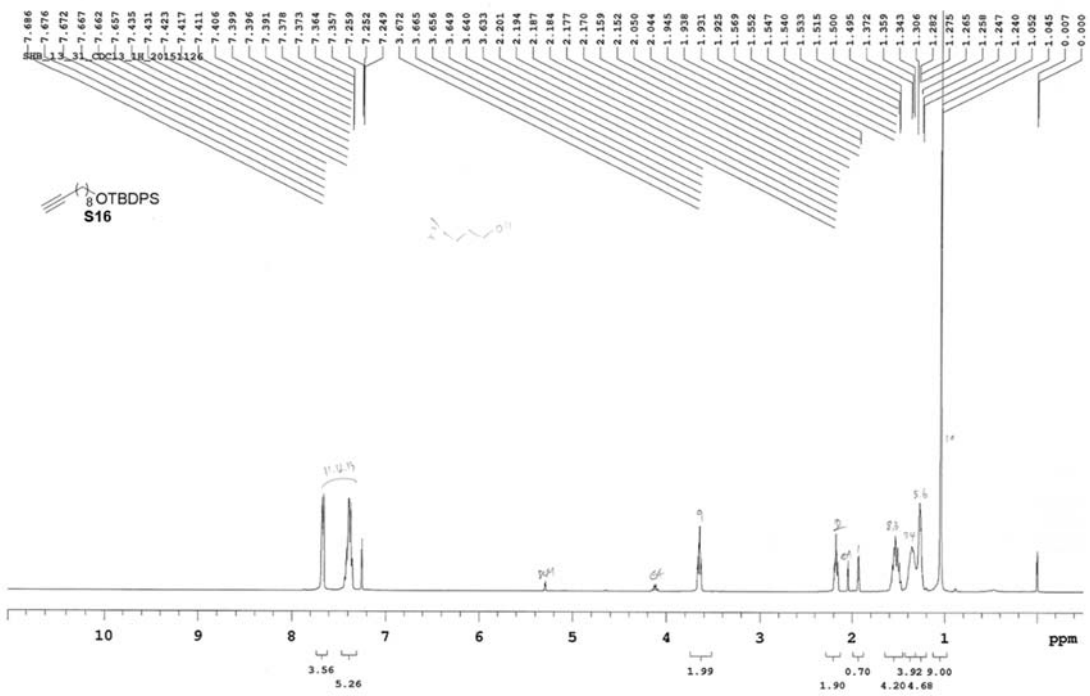


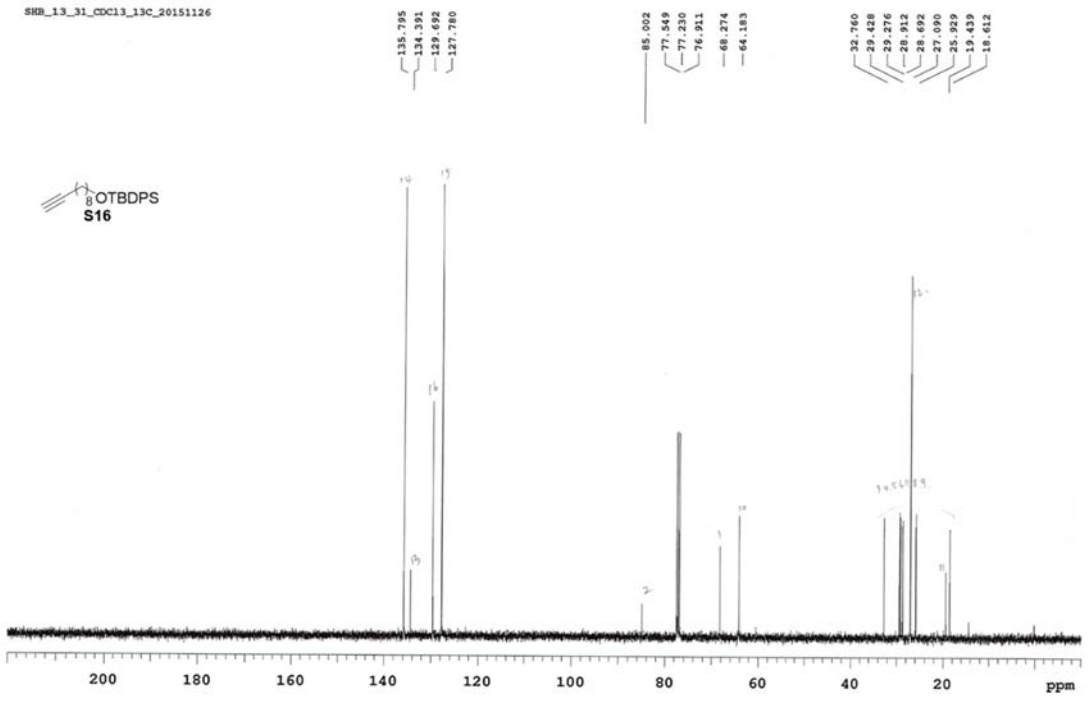


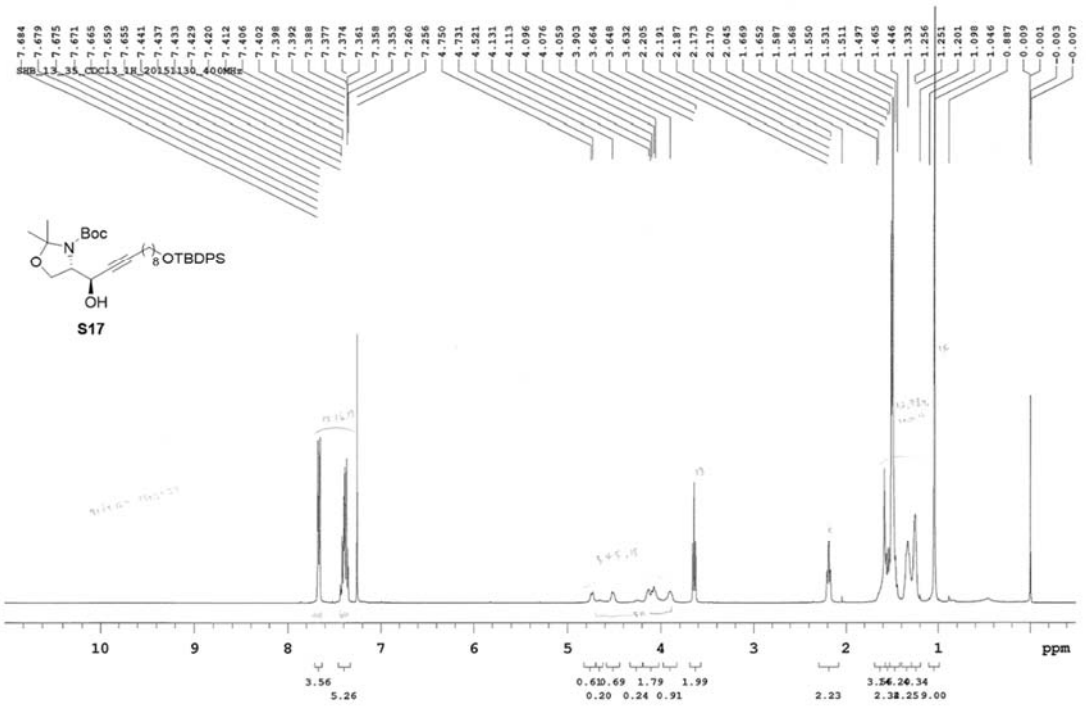
S14{a17}

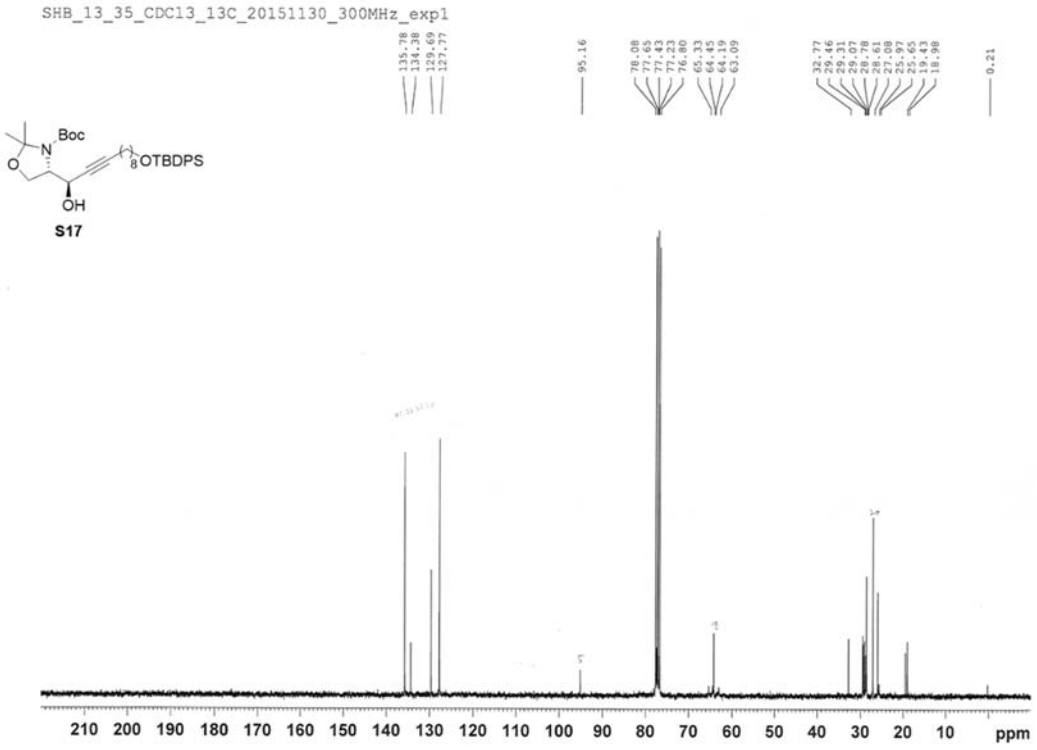


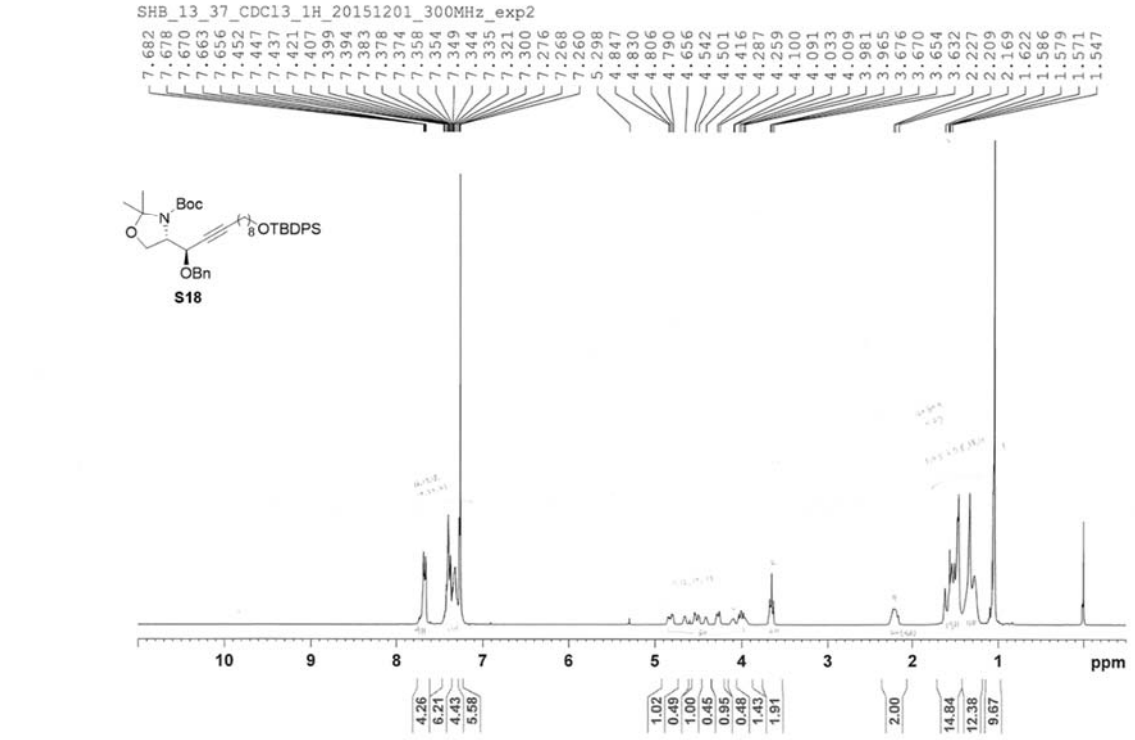
S14{a17}

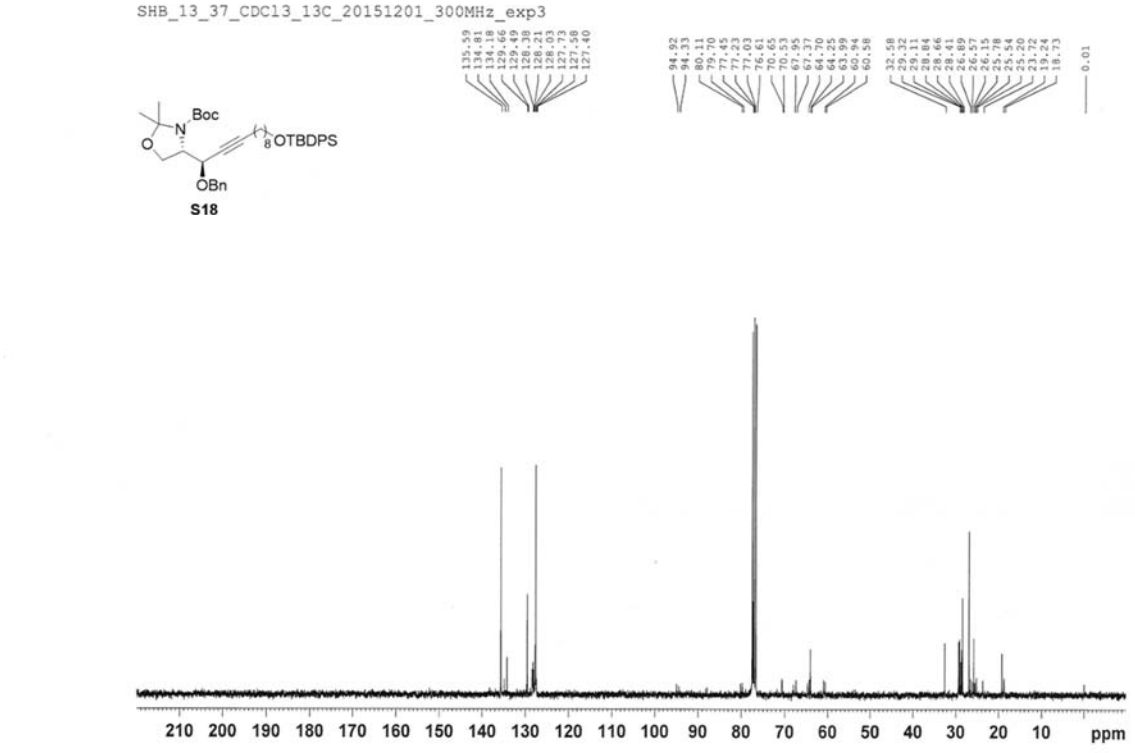

SHB_13_31_CDCl3_1H_20151126
OTBDPS
S16
ppm
3.56
5.26
1.99
1.90
0.70
4.20
3.92
4.68
9.00

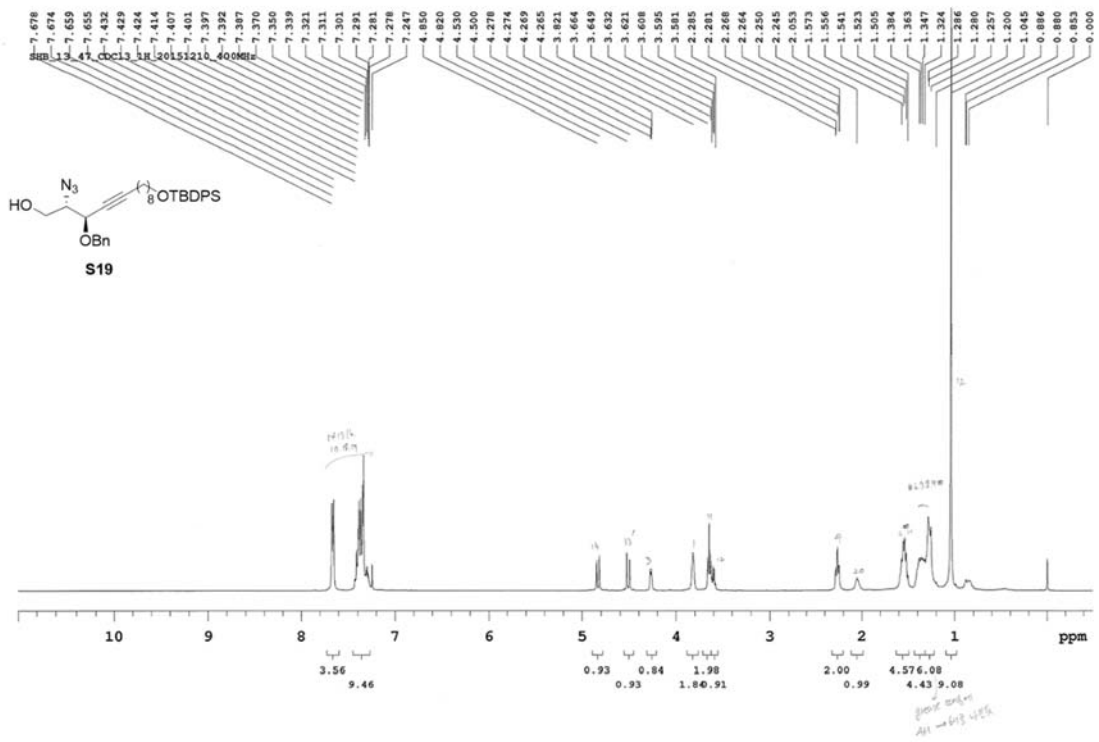

SHB_13_31_CDCl3_13C_20151126
OTBDPS
S16
ppm

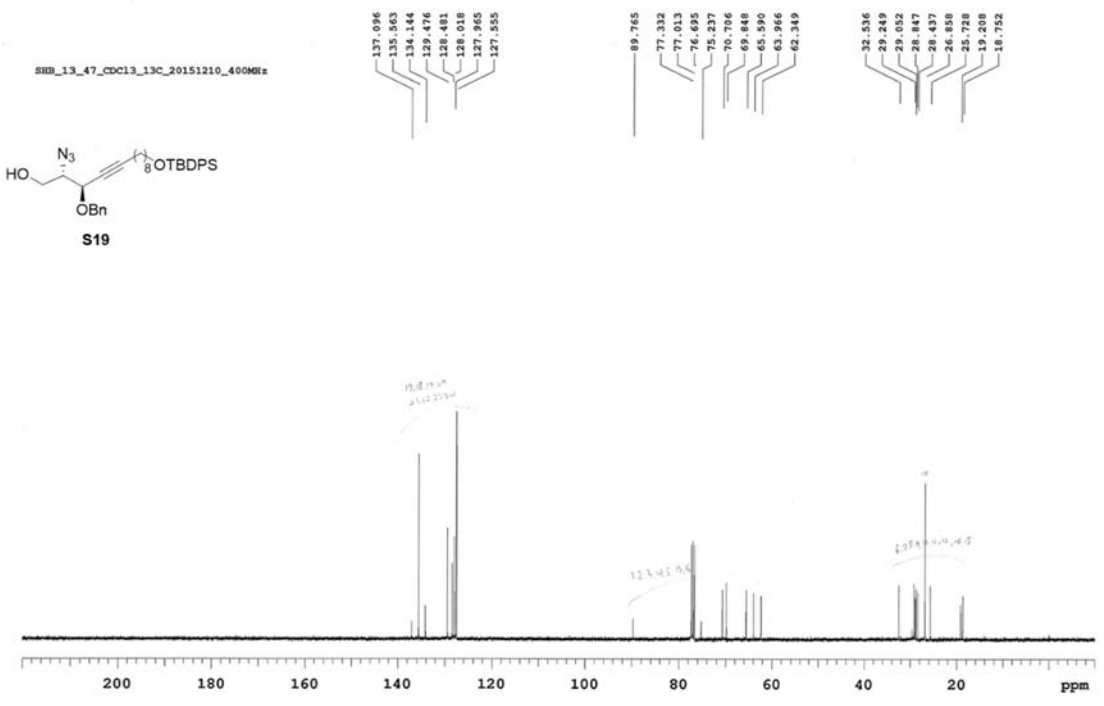

SHB_13_35_CDCl3_1H_20151130_400MHz
Boc
OTBDPS
OH
S17
ppm

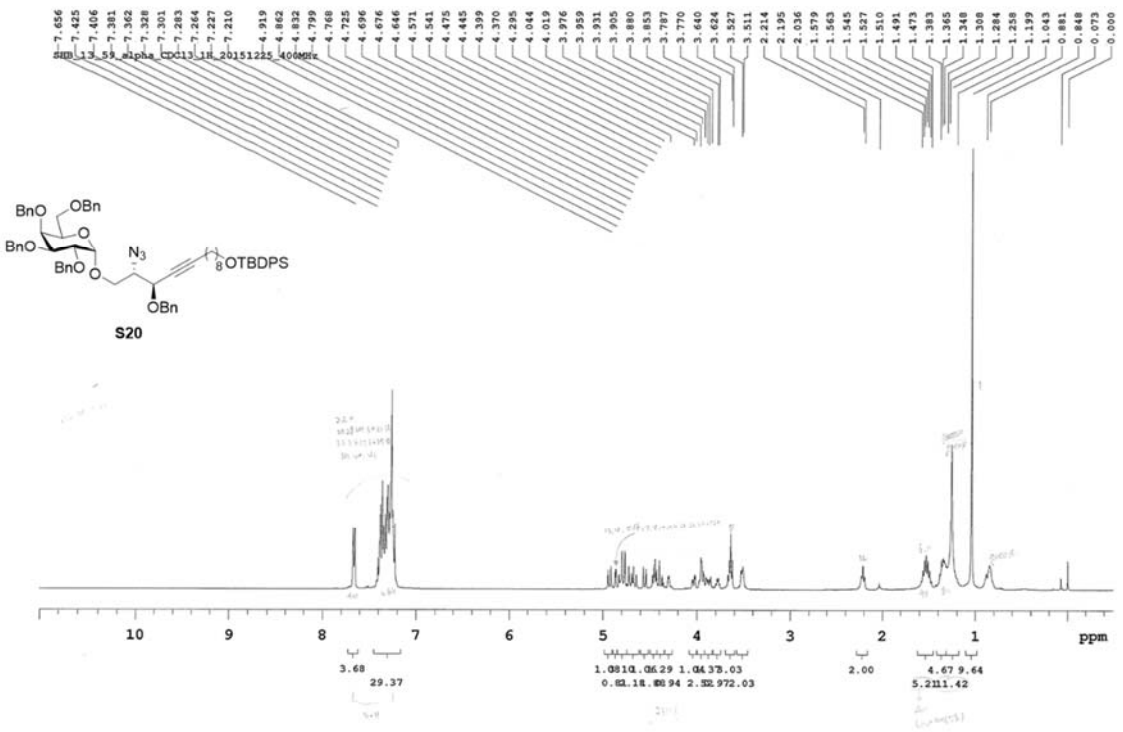

SHB_13_35_CDCl3_13C_20151130_300MHz_exp1
Boc
OTBDPS
OH
S17
ppm

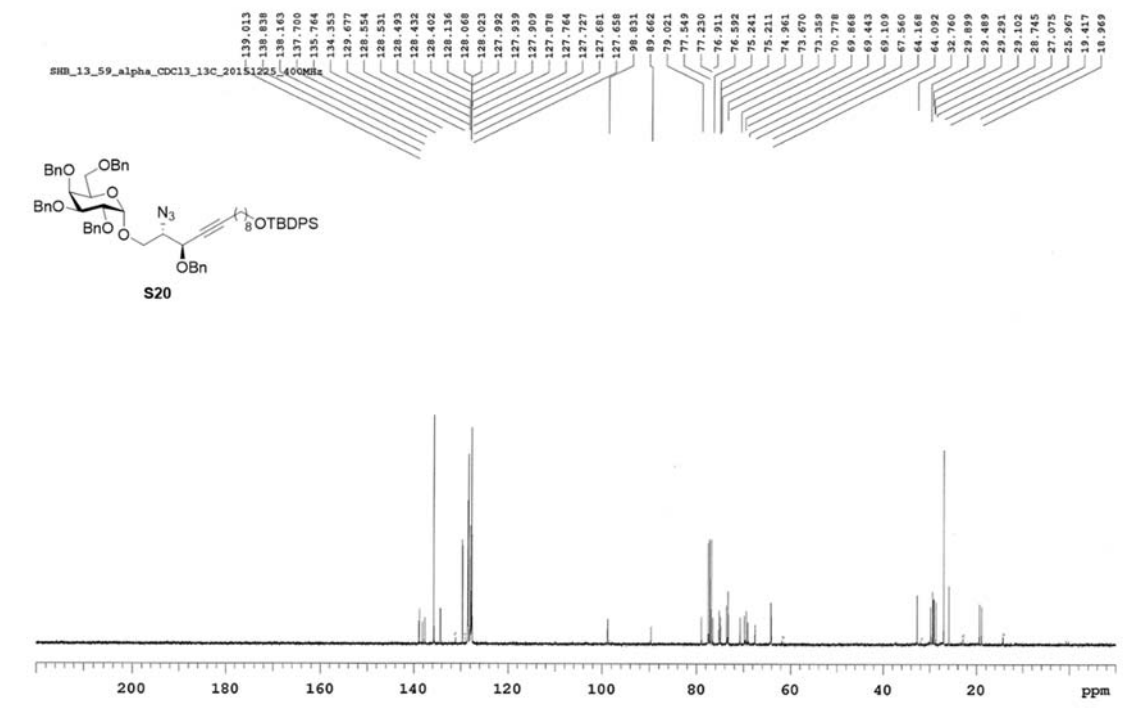

SHB_13_37_CDCl3_1H_20151201_300MHz_exp2
Boc
OTBDPS
OBn
S18
ppm


SHB_13_37_CDCl3_13C_20151201_300MHz_exp3
Boc
OTBDPS
OBn
S18
ppm

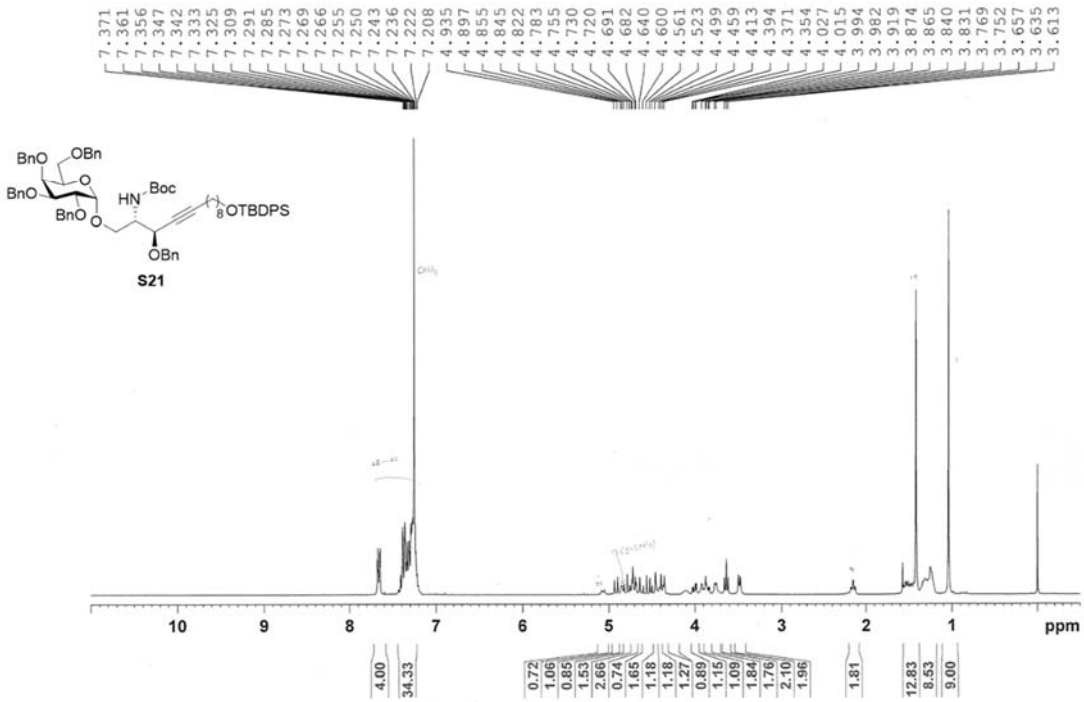

SHB_13_47_CDCl3_1H_20151210_400MHz
HO
N3
OBn
8OTBDPS
S19
ppm


SHB_13_47_CDCl3_13C_20151210_400MHz
HO
N3
OBn
8OTBDPS
S19
ppm

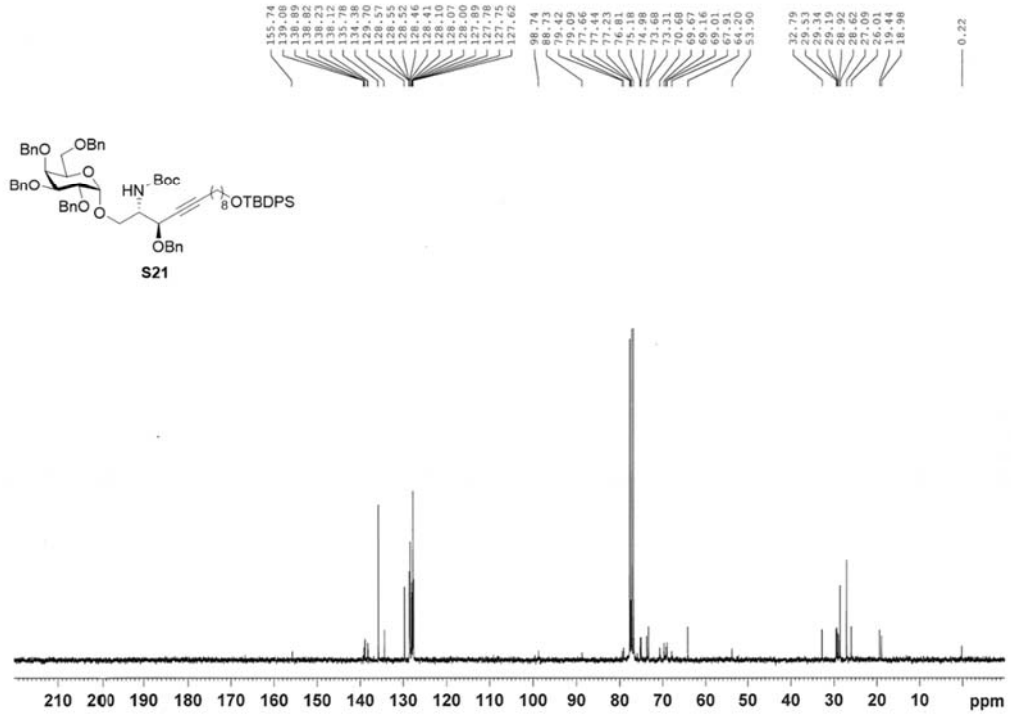

SHB_13_59_alpha_CDCl3_1H_20151225_400MHz
BnO
OBn
BnO
BnO
O
N3
8OTBDPS
OBn
S20
ppm

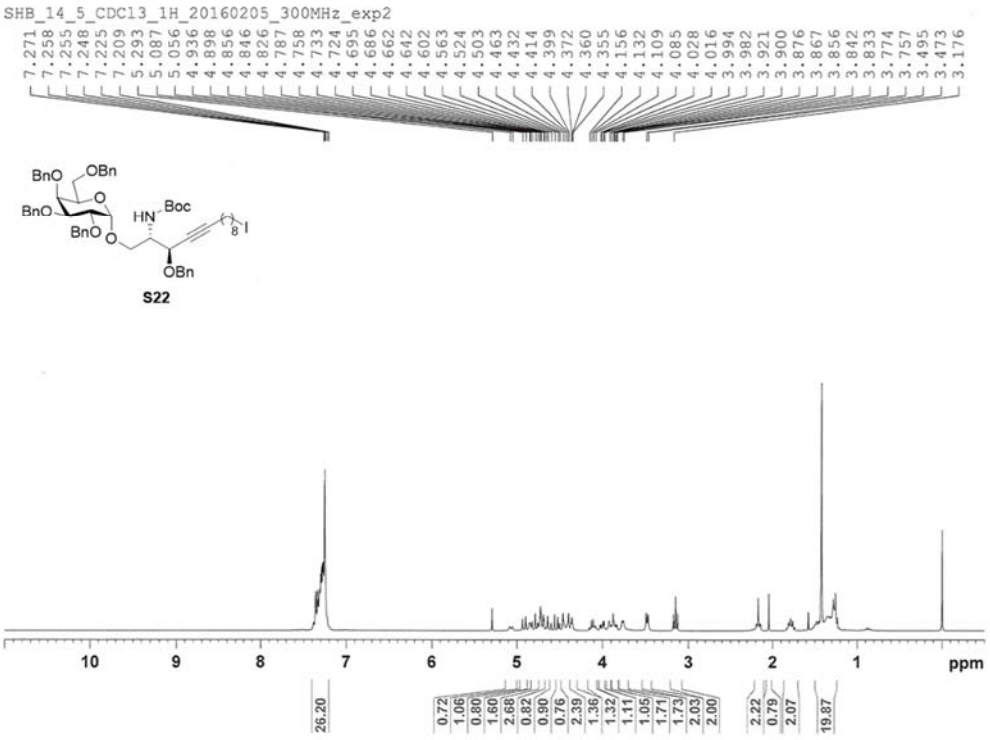

SHB_13_59_alpha_CDCl3_13C_20151225_400MHz
BnO
OBn
BnO
BnO
O
N3
8OTBDPS
OBn
S20
ppm

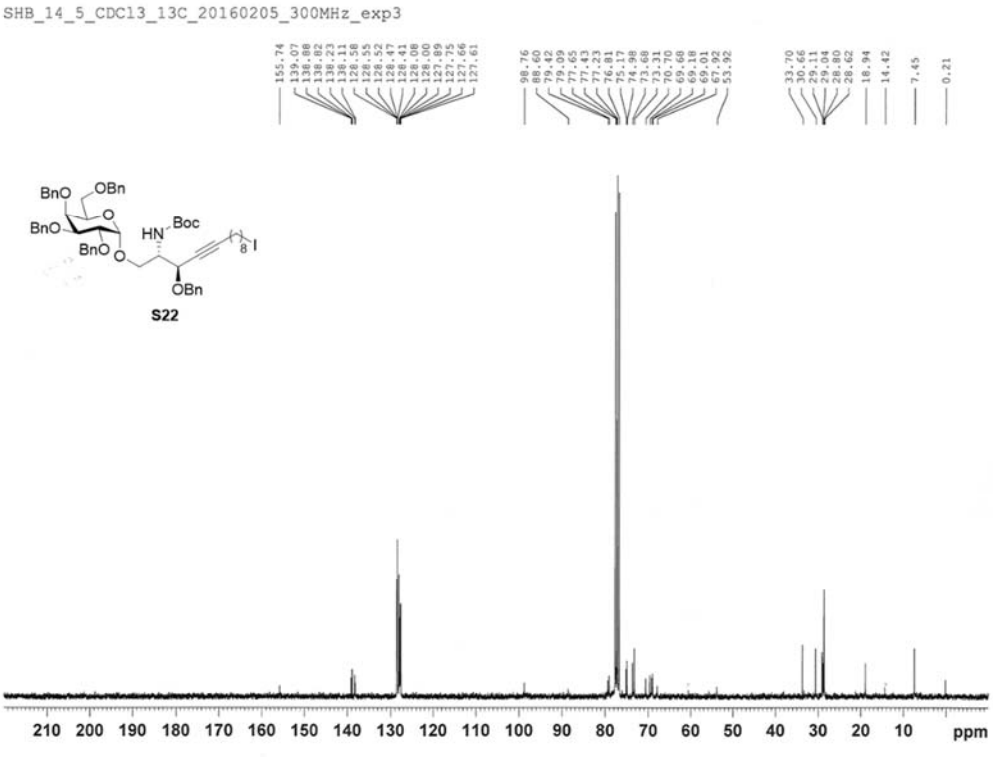
SHB_13_100_CDCl3_1H_20160129_300MHz_exp4



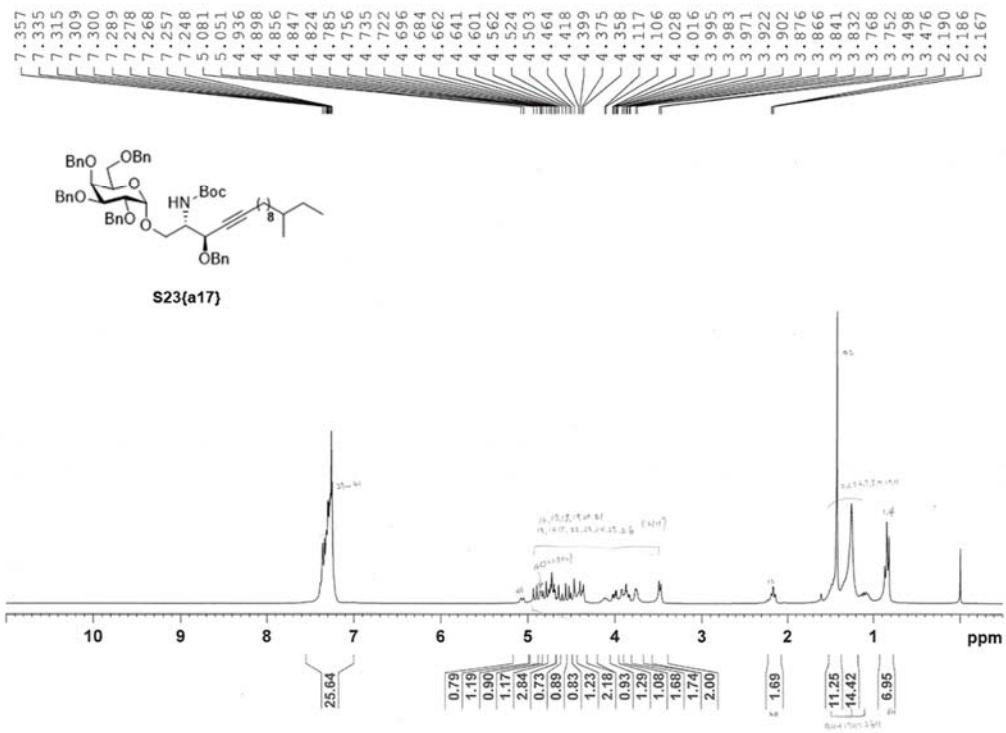
SHB_13_100_CDCl3_13C_20160129_300MHz_exp5




SHB_14_5_CDCl3_1H_20160205_300MHz_exp2
7.271
7.258
7.255
7.248
7.225
7.209
5.293
5.087
5.056
4.936
4.898
4.856
4.846
4.826
4.787
4.758
4.733
4.724
4.695
4.686
4.662
4.642
4.602
4.563
4.524
4.503
4.463
4.432
4.414
4.399
4.372
4.360
4.355
4.156
4.132
4.109
4.085
4.028
4.016
3.994
3.982
3.921
3.900
3.876
3.867
3.856
3.842
3.833
3.774
3.757
3.495
3.473
3.176
BnO
OBn
BnO
HN
Boc
BnO
O
8
I
OBn
S22
10
9
8
7
6
5
4
3
2
1
ppm
26.20
0.72
1.06
0.80
1.60
2.68
0.82
0.90
0.76
2.39
1.36
1.32
1.11
1.05
1.71
1.73
2.03
2.00
2.22
0.79
2.07
19.87

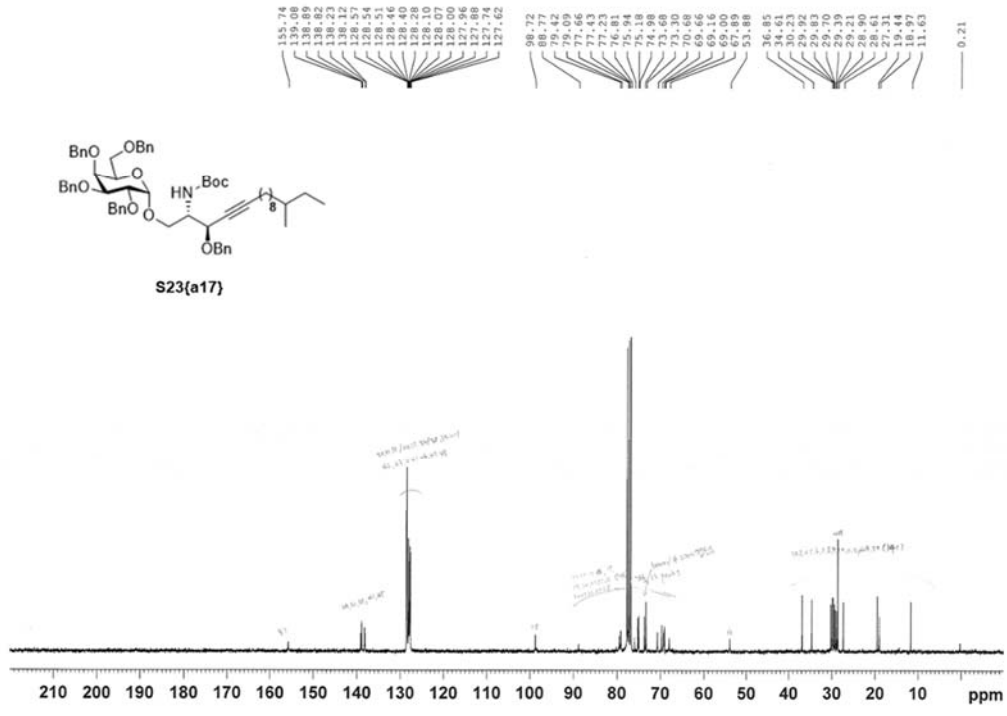

SHB_14_5_CDCl3_13C_20160205_300MHz_exp3
155.74
139.07
138.88
138.82
138.23
138.11
128.58
128.55
128.52
128.47
128.41
128.11
128.08
128.00
127.89
127.75
127.66
127.61
90.76
88.60
79.42
79.09
77.65
77.43
77.23
76.81
75.17
74.98
73.68
73.31
70.70
69.68
69.18
69.01
67.92
53.92
33.70
30.66
29.11
29.04
28.80
28.62
18.94
14.42
7.45
0.21
BnO
OBn
BnO
HN
Boc
BnO
O
8
I
OBn
S22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

SHB_14_6_CDCl3_1H_20160210_300MHz_exp1

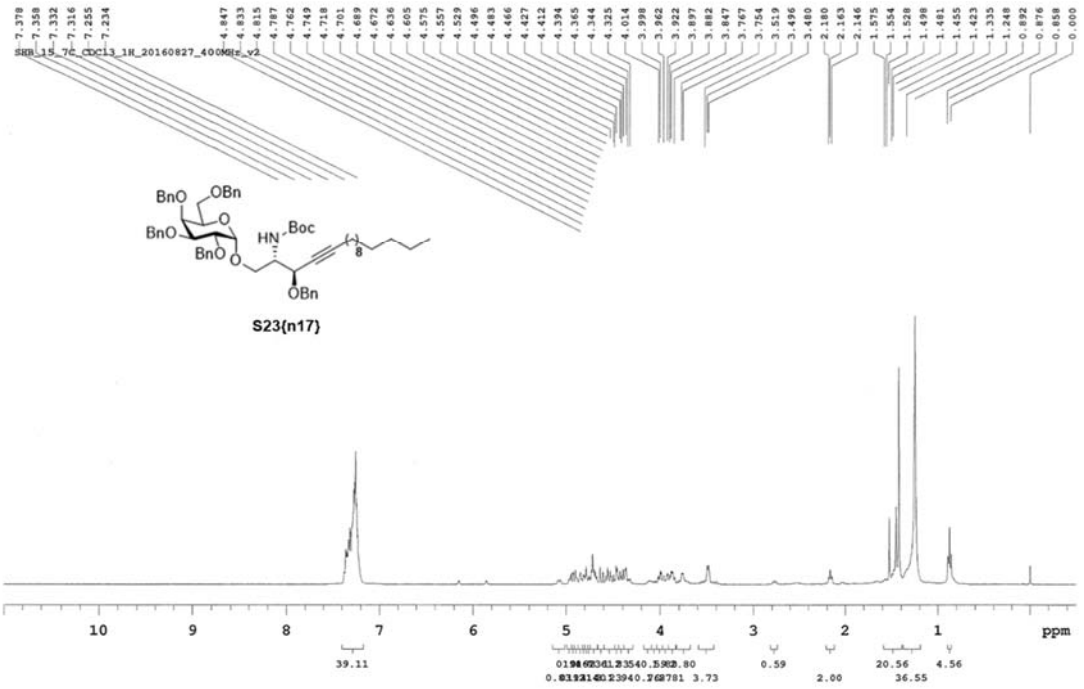


S23{a17}

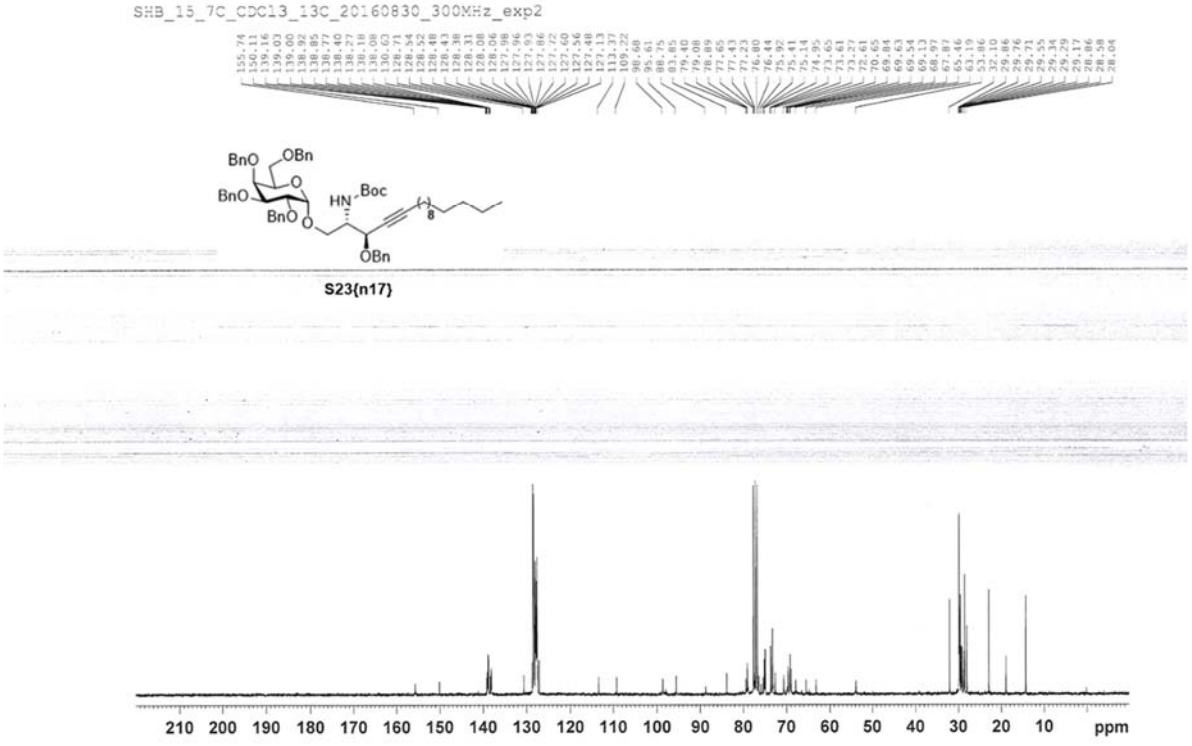
SHB_14_6_CDCl3_13C_20160210_300MHz_exp2



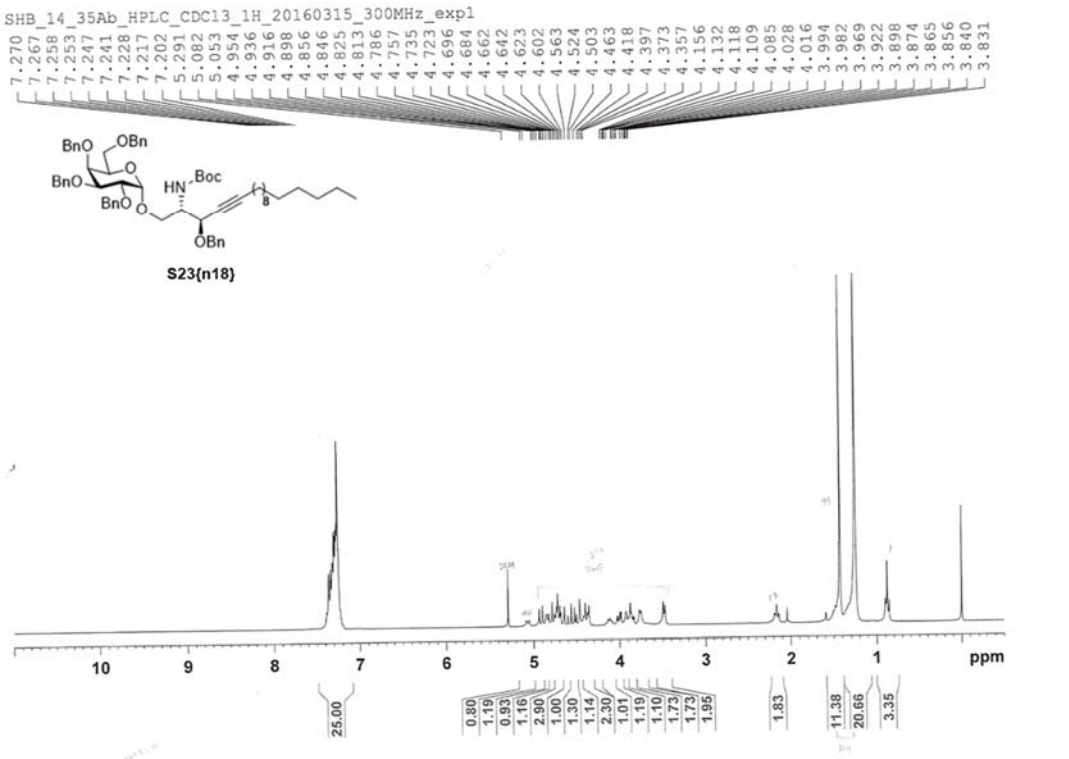
S23{a17}

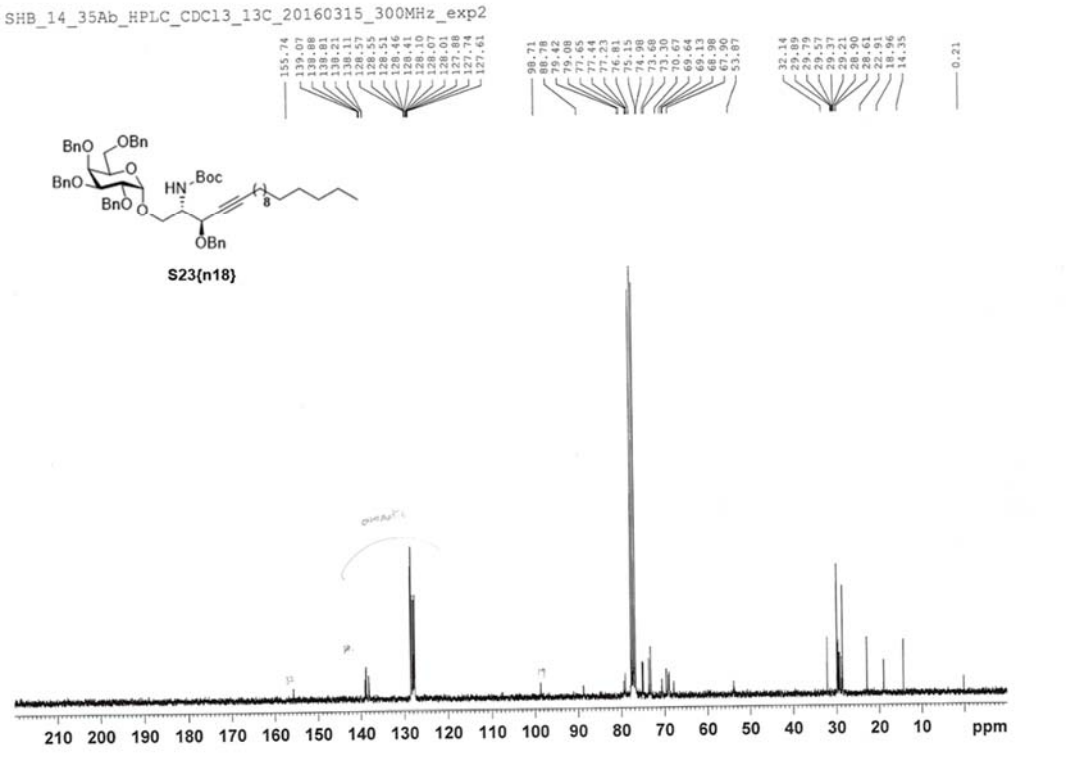


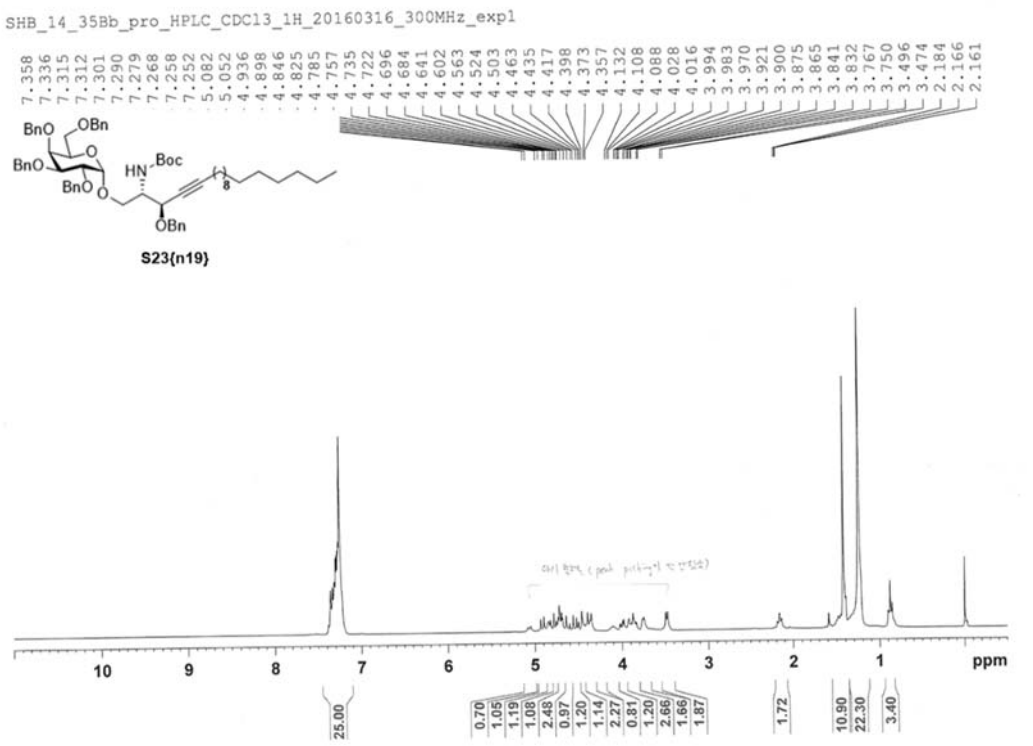
S23{n17}

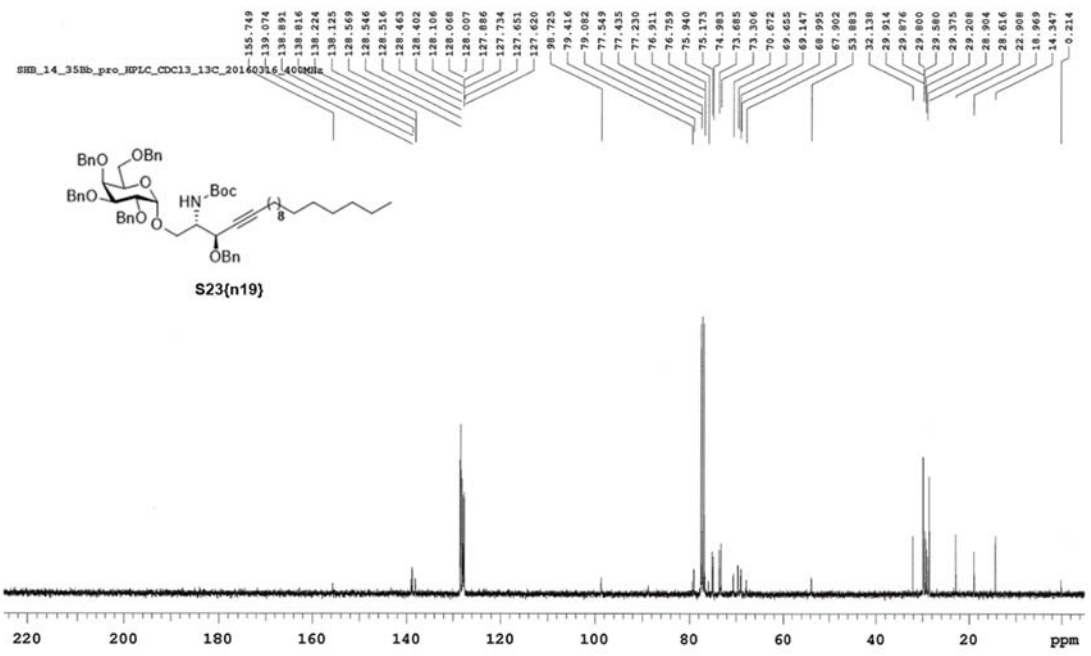


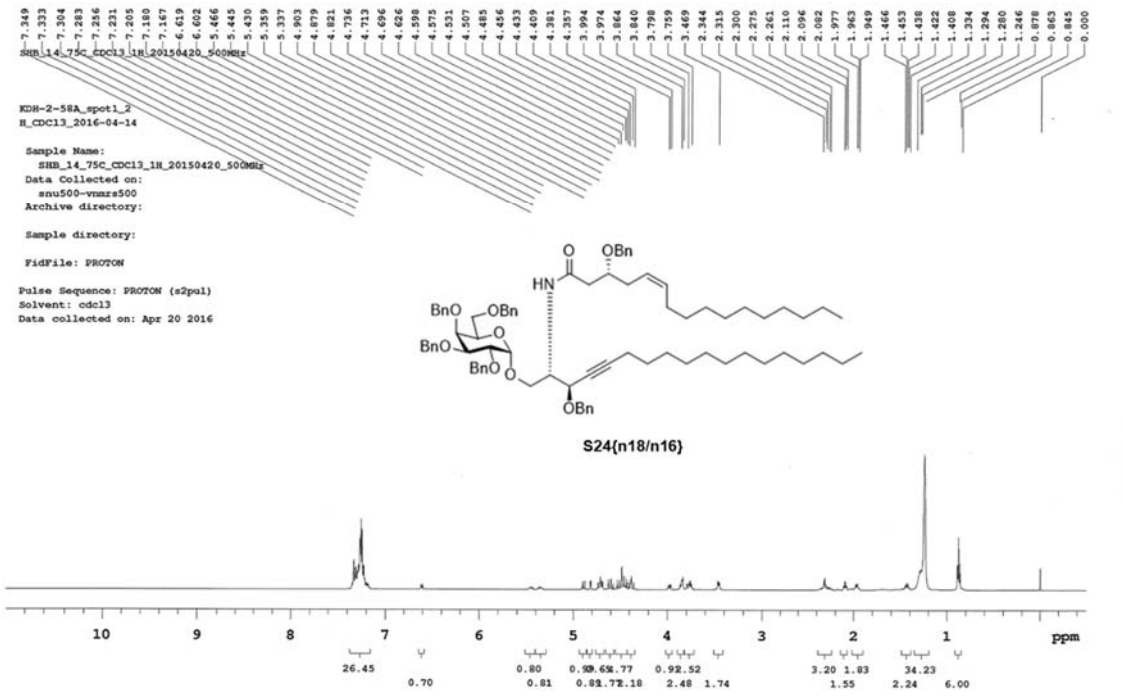
S23{n17}

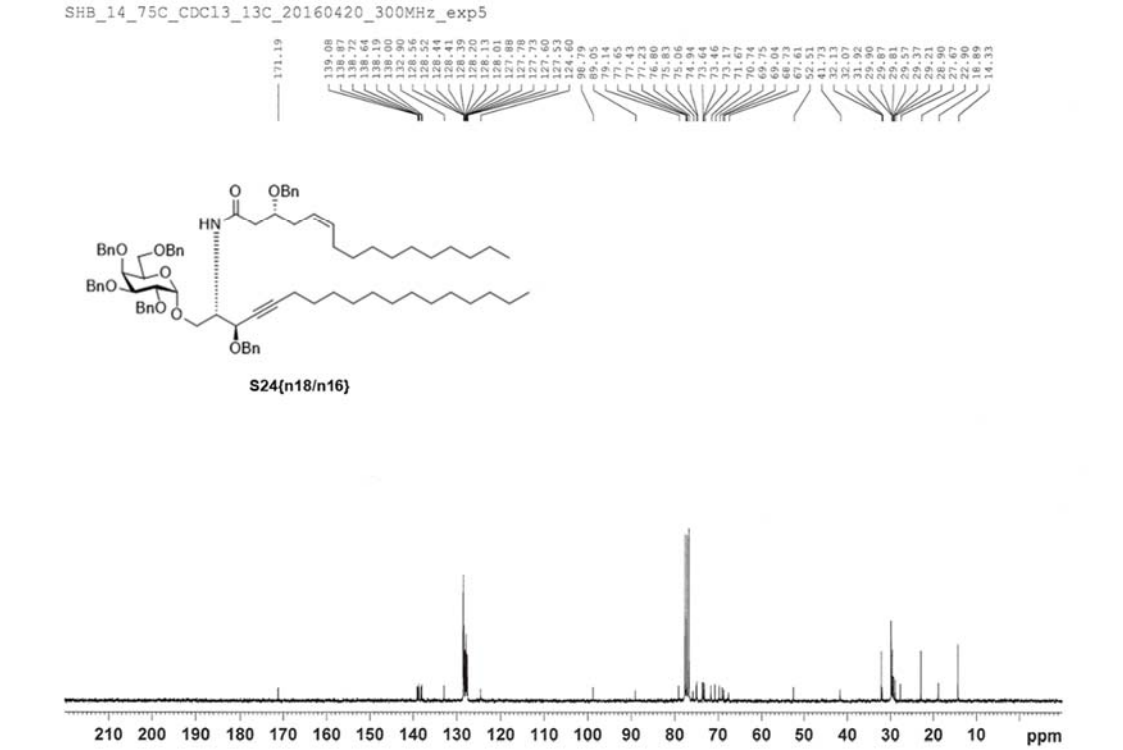

SHB_14_35Ab_HPLC_CDCl3_1H_20160315_300MHz_exp1
BnO
OBn
BnO
BnO
O
HN
Boc
8
OBn
S23{n18}
ppm

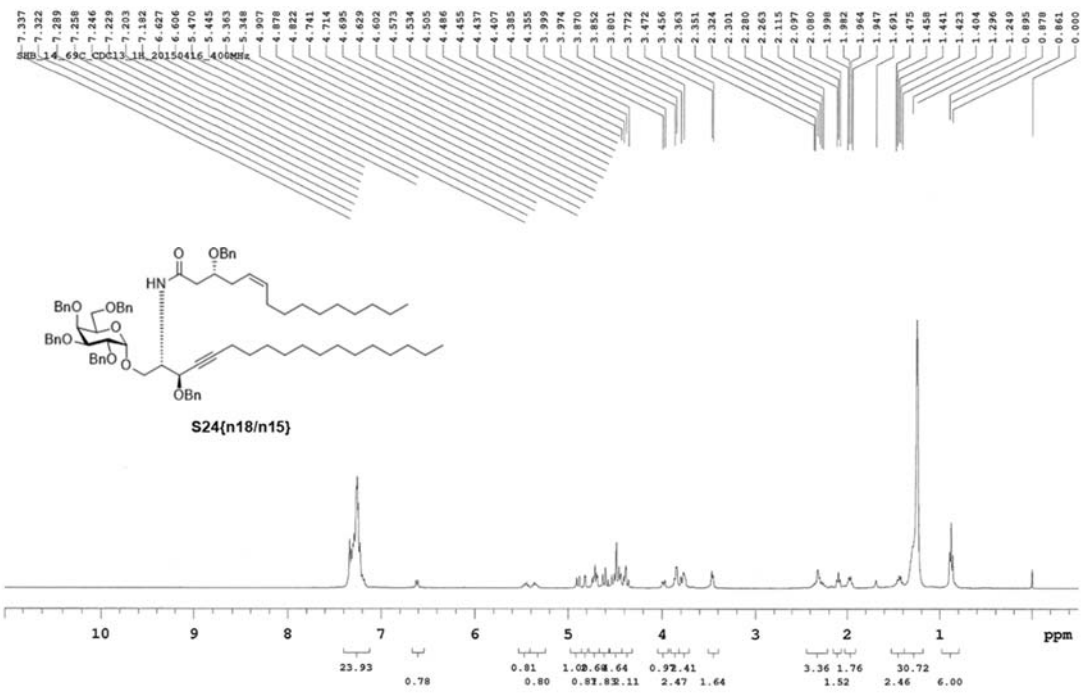

SHB_14_35Ab_HPLC_CDCl3_13C_20160315_300MHz_exp2
BnO
OBn
BnO
BnO
O
HN
Boc
8
OBn
S23{n18}
ppm

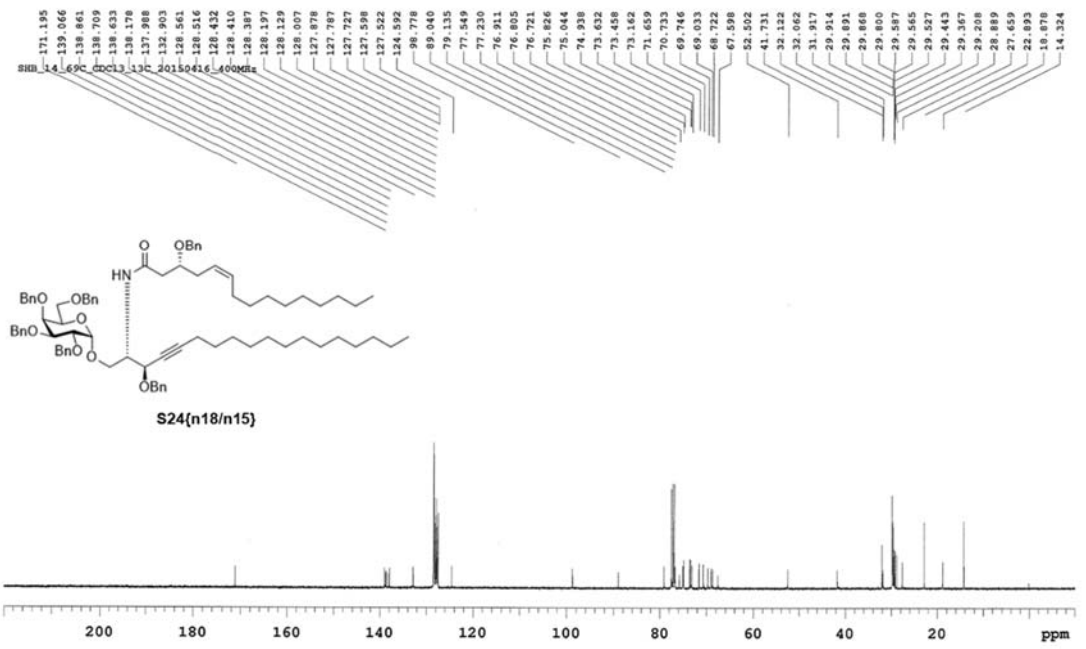

SHB_14_35Bb_pro_HPLC_CDCl3_1H_20160316_300MHz_exp1
S23{n19}
ppm

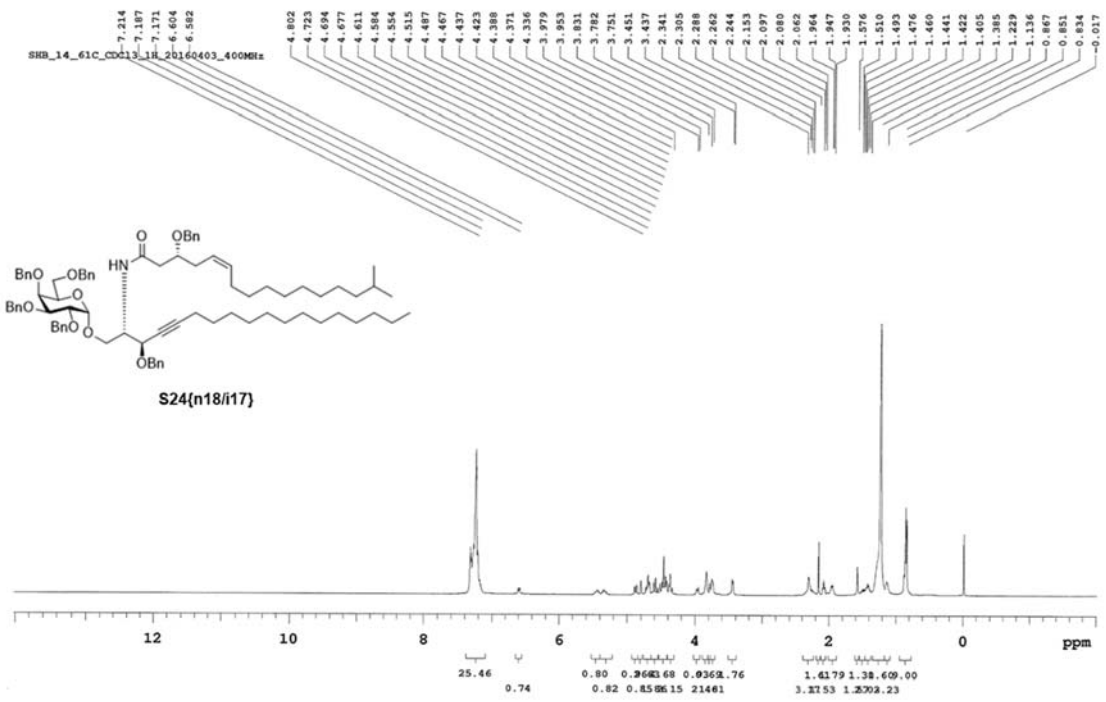

SHB_14_35Bb_pro_HPLC_CDCl3_13C_20160316_400MHz
S23{n19}
ppm

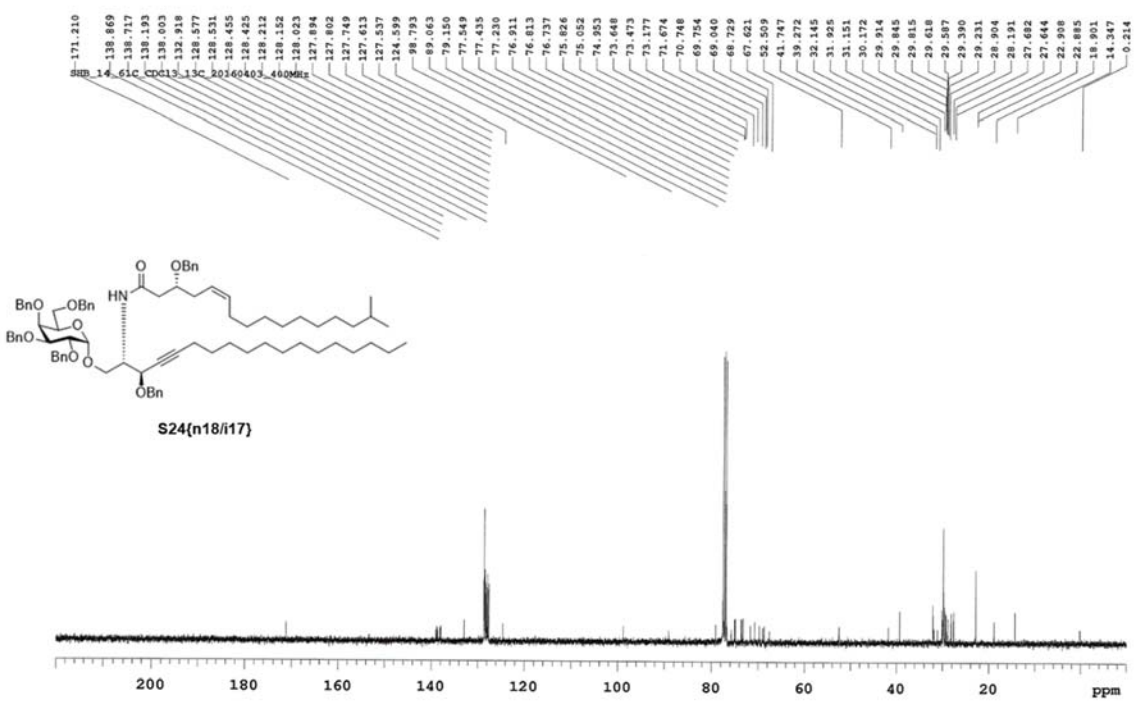

SHB_14_75C_CDC13_1H_20150420_500MHz
KDH-2-58A_spot1_2
H_CDCl3_2016-04-14
Sample Name:
SHB_14_75C_CDCl3_1H_20150420_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 20 2016
S24{n18/n16}
ppm

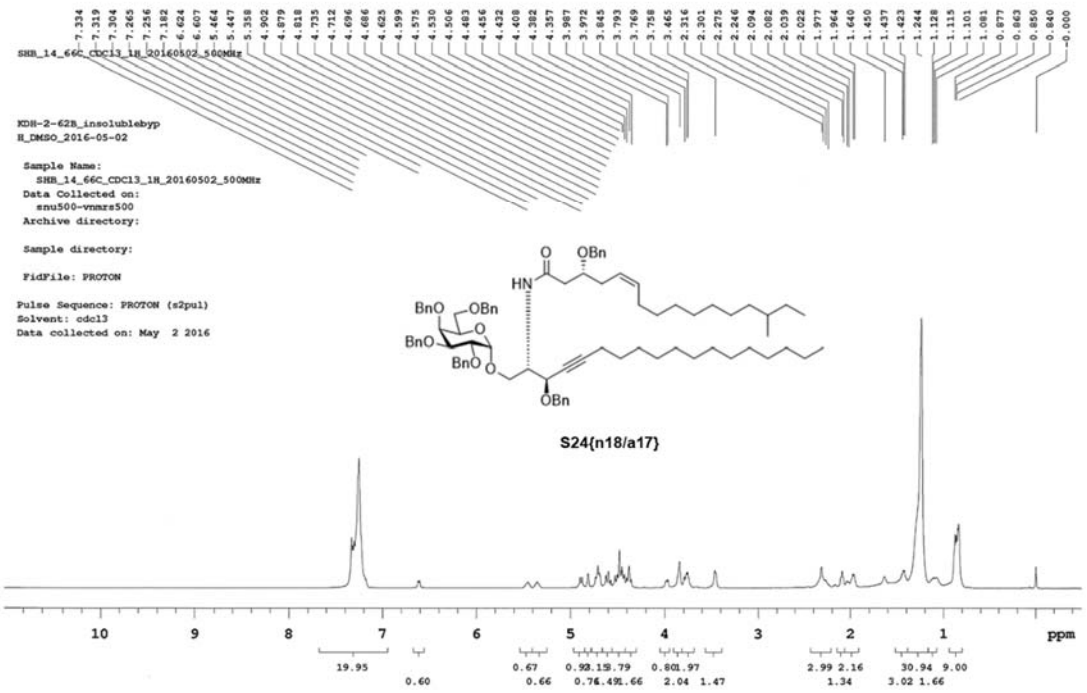

SHB_14_75C_CDCl3_13C_20160420_300MHz_exp5
S24{n18/n16}
ppm

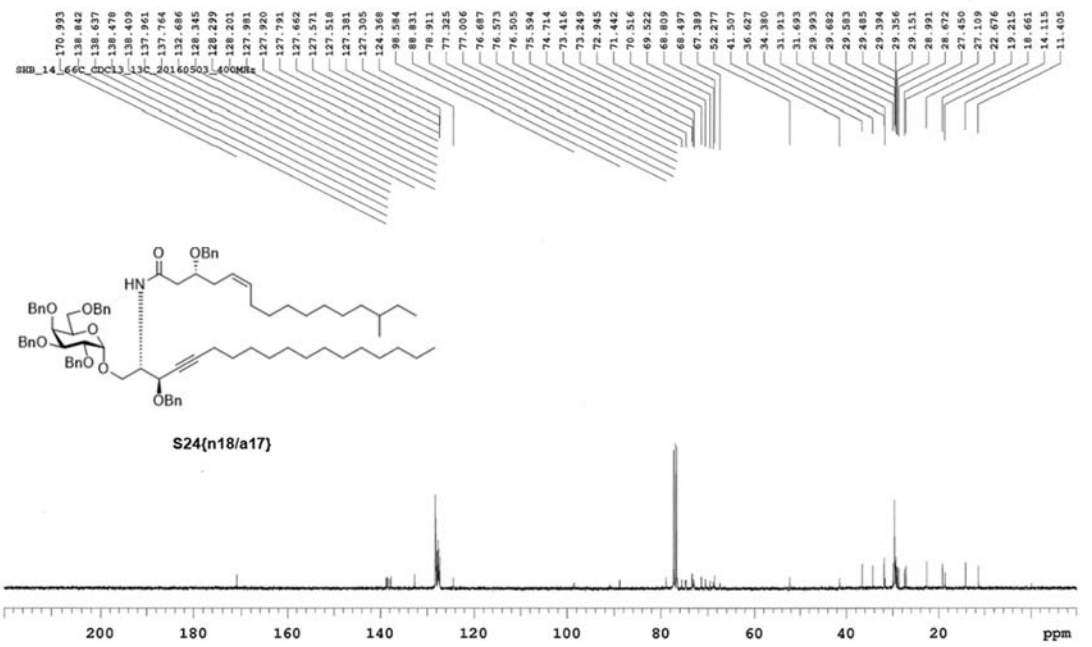

SHB_14_69C_CDCl3_1H_20150416_400MHz
S24{n18/n15}
ppm

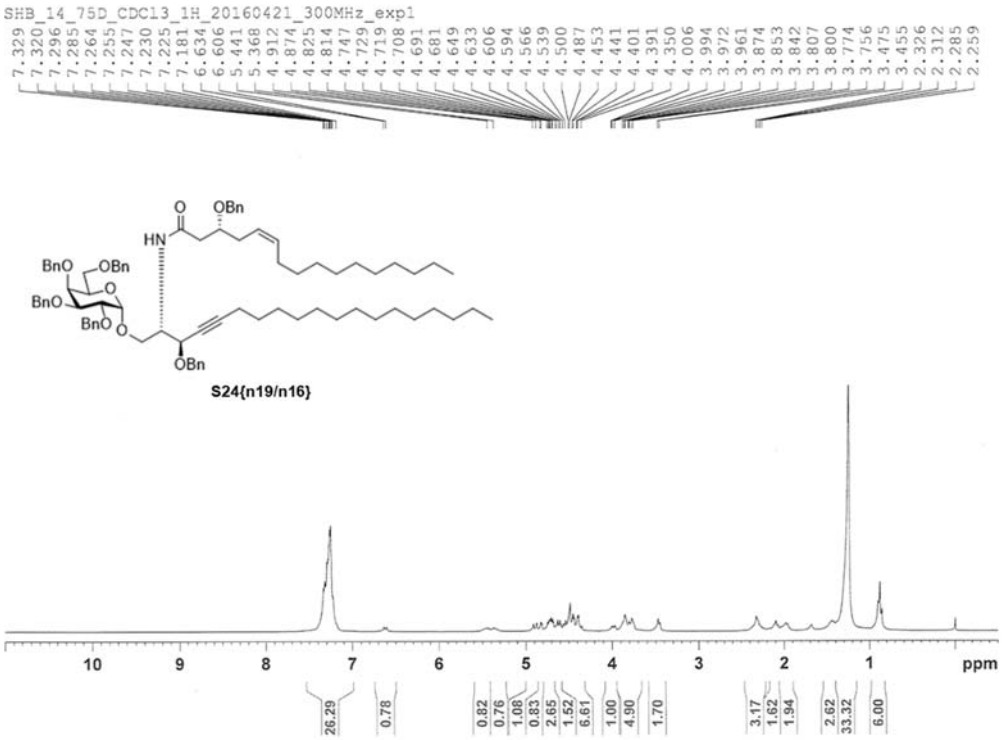

SHB_14_69C_CDCl3_13C_20150416_400MHz
S24{n18/n15}
ppm

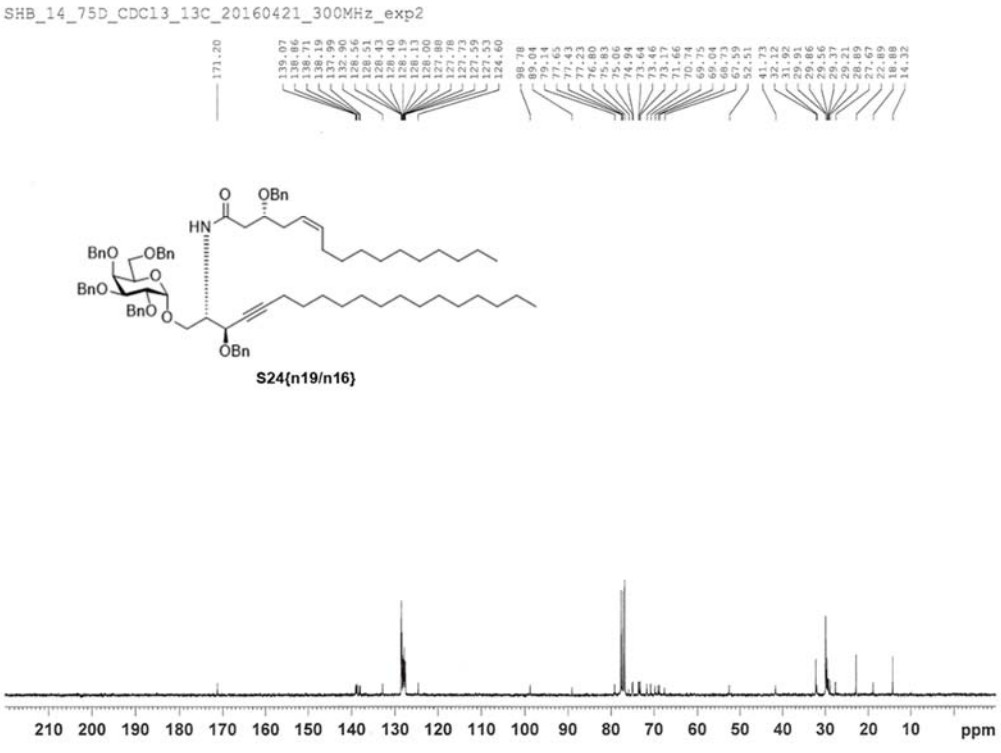

SHB_14_61C_CDCl3_1H_20160403_400MHz
S24{n18/i17}
ppm

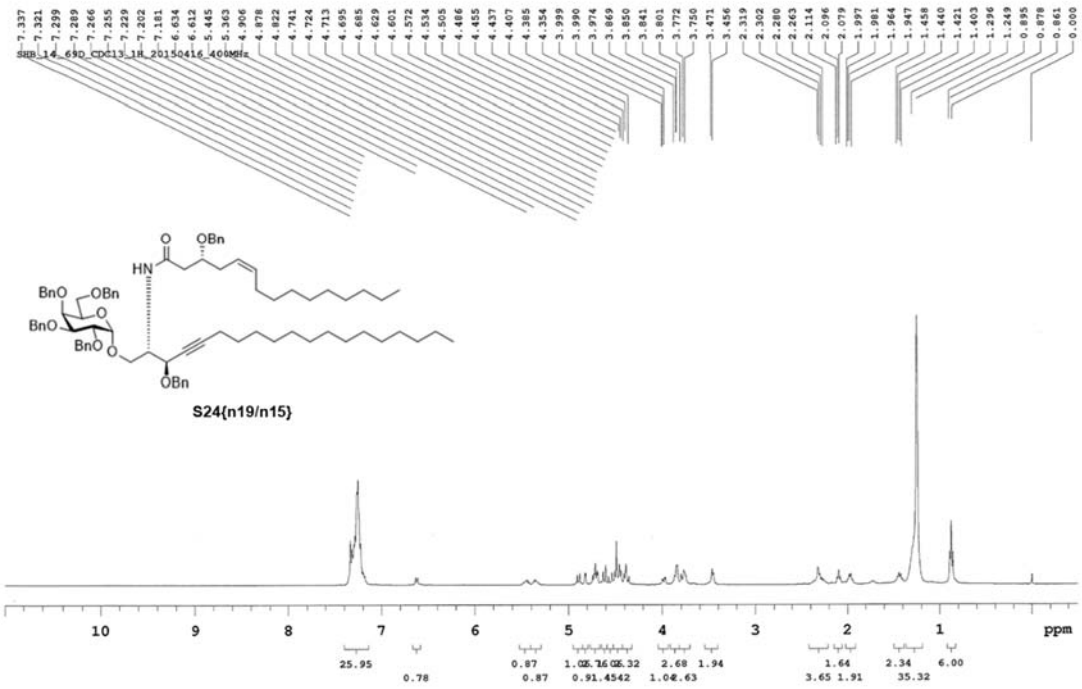

SHB_14_61C_CDCl3_13C_20160403_400MHz
S24{n18/i17}
ppm

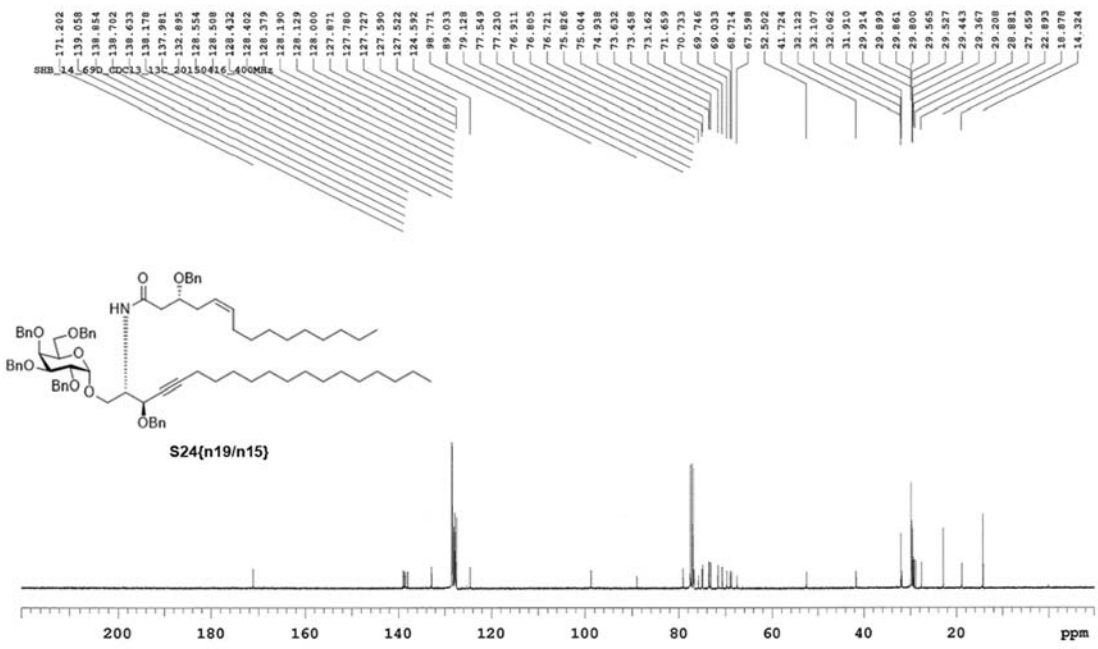

SHB_14_66C_CDCl3_1H_20160502_500MHz
KDH-2-62B_insolublebyp
H_DMSO_2016-05-02
Sample Name:
SHB_14_66C_CDCl3_1H_20160502_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 2 2016
S24{n18/a17}
ppm

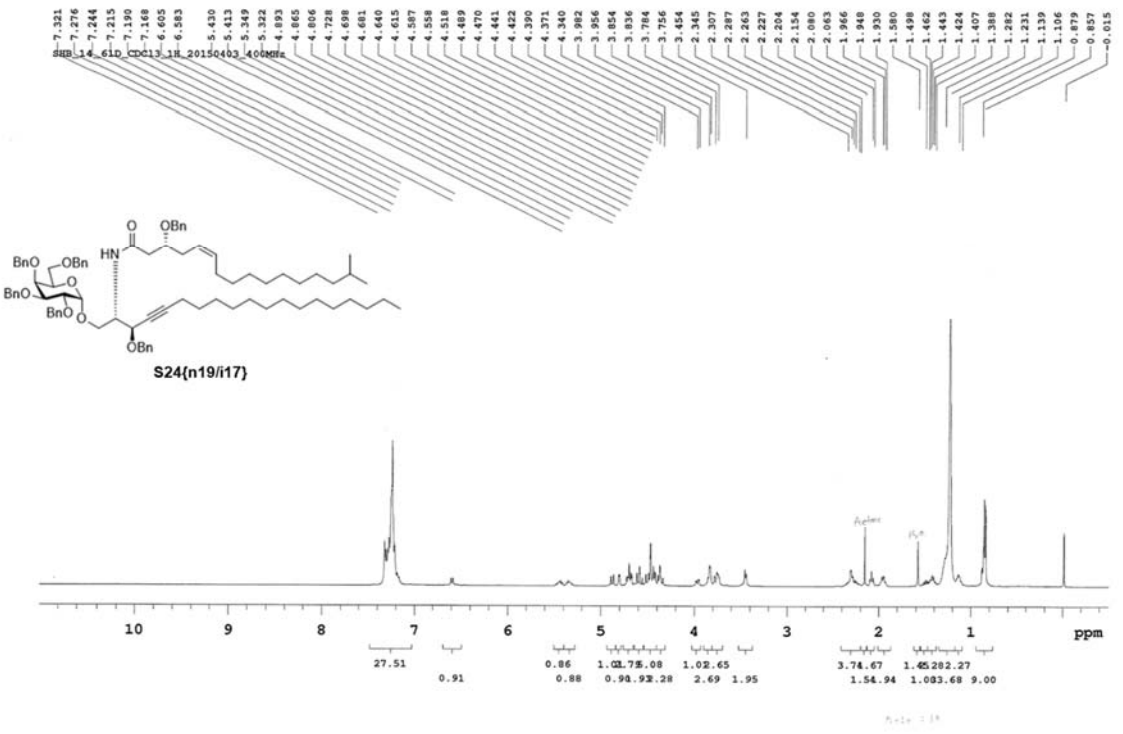

SHB_14_66C_CDCl3_13C_20160503_40CMHz
S24{n18/a17}
ppm

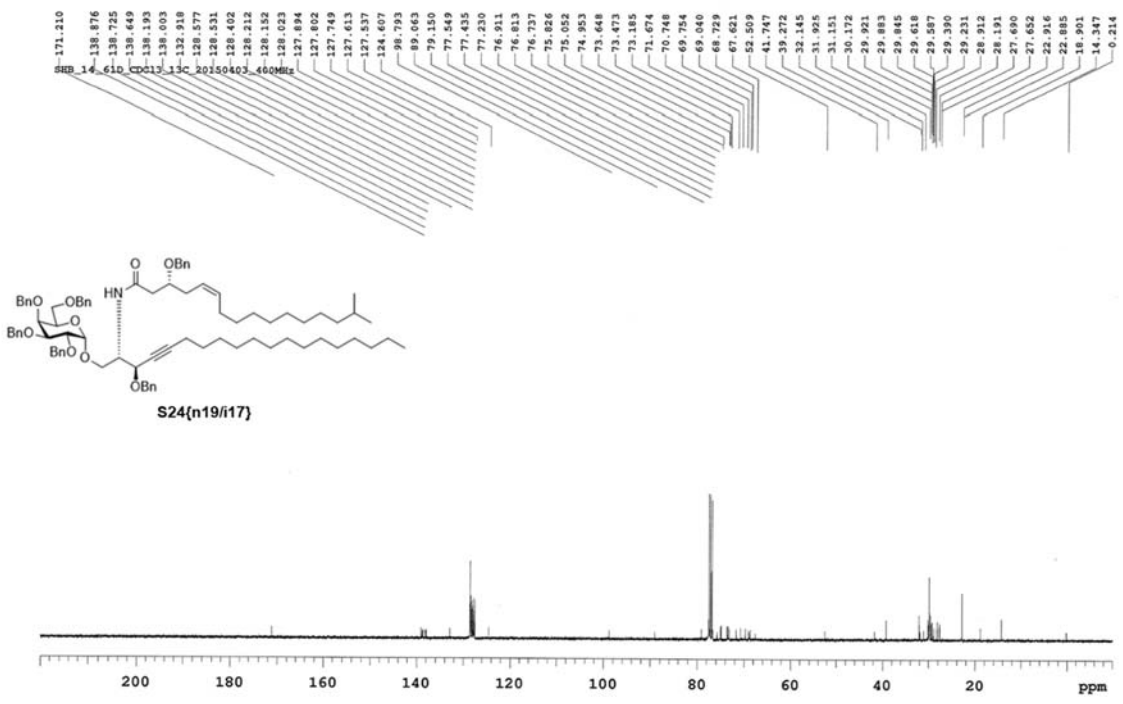

SHB_14_75D_CDCl3_1H_20160421_300MHz_exp1
7.329
7.320
7.296
7.285
7.264
7.255
7.247
7.230
7.225
7.181
6.634
6.606
5.441
5.368
4.912
4.874
4.825
4.814
4.747
4.729
4.719
4.708
4.691
4.681
4.649
4.633
4.606
4.594
4.566
4.539
4.500
4.487
4.453
4.441
4.401
4.391
4.350
4.006
3.994
3.972
3.961
3.874
3.853
3.842
3.807
3.800
3.774
3.756
3.475
3.455
2.326
2.312
2.285
2.259
O
OBn
HN
BnO
OBn
BnO
O
BnO
O
OBn
S24{n19/n16}
10
9
8
7
6
5
4
3
2
1
ppm
26.29
0.78
0.82
0.76
1.08
0.83
2.65
1.52
6.61
1.00
4.90
1.70
3.17
1.62
1.94
2.62
33.32
6.00

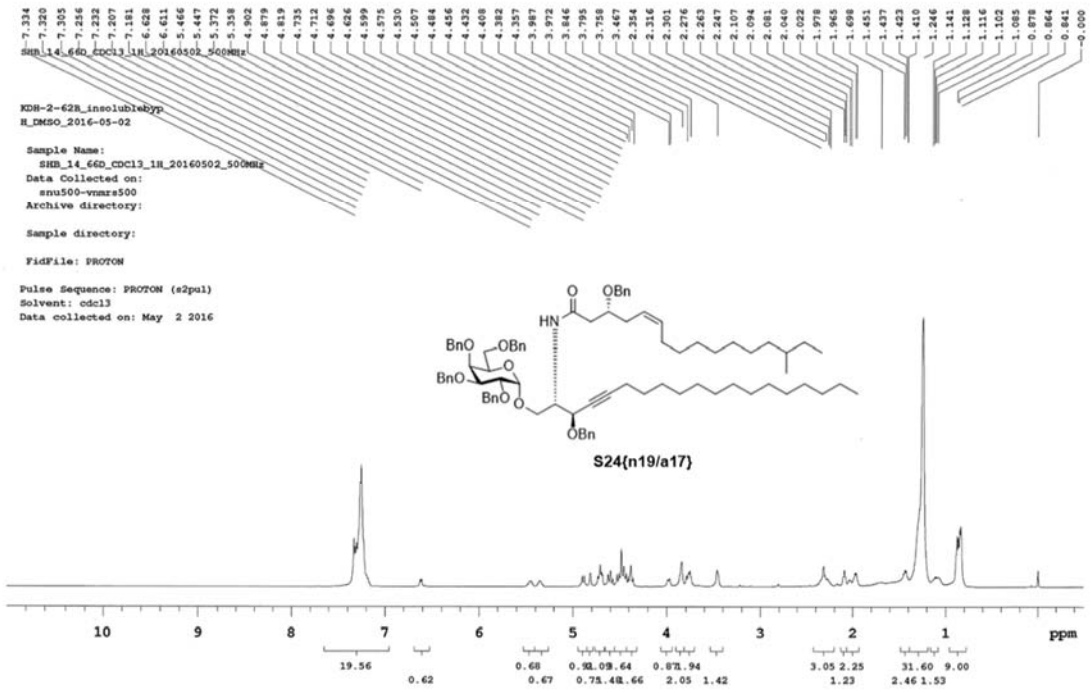

SHB_14_75D_CDCl3_13C_20160421_300MHz_exp2
O
OBn
HN
BnO
OBn
BnO
O
BnO
O
OBn
S24{n19/n16}
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

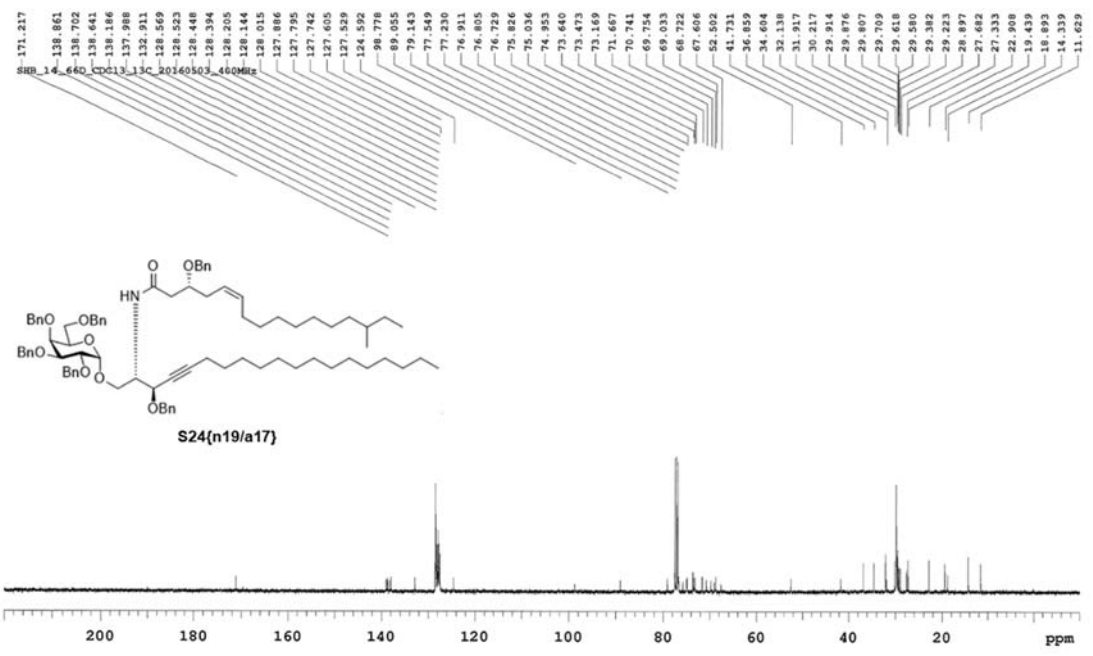

SKB_14_69D_CDCl3_1H_20150416_400MHz
S24{n19/n15}
ppm


SKB_14_69D_CDCl3_13C_20150416_400MHz
S24{n19/n15}
ppm

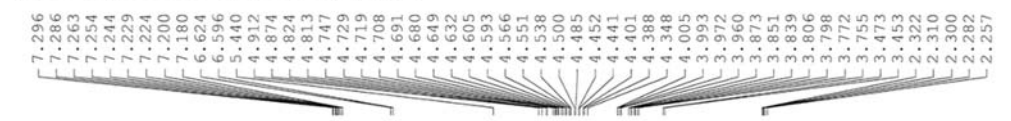

SHB_14_61D_CDCl3_1H_20150403_400MHz
S24{n19/i17}
ppm

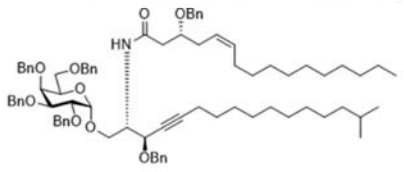

SHB_14_61D_CDCl3_13C_20150403_400MHz
S24{n19/i17}
ppm


SHB_14_66D_CDCl3_1H_20160502_500MHz
KDR-2-62R_insolublebyp
H_DMSO_2016-05-02
Sample Name:
SHB_14_66D_CDCl3_1H_20160502_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 2 2016
S24{n19/a17}
ppm

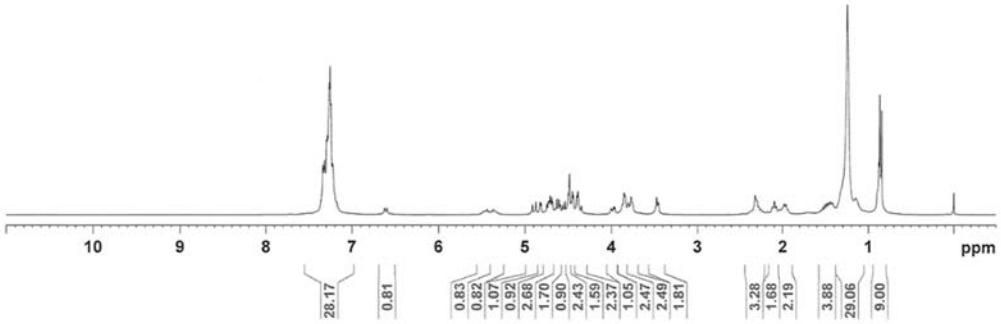

SHB_14_66D_CDCl3_13C_20160503_400MHz
S24{n19/a17}
ppm

SHB_14_75A_CDCl3_1H_20160420_300MHz_exp2

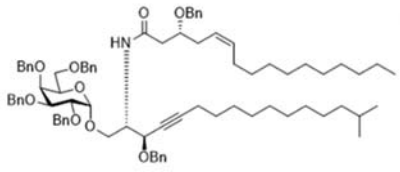




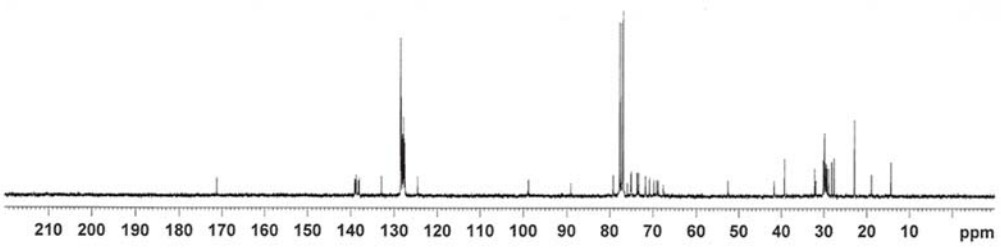
S24{i17/n16}

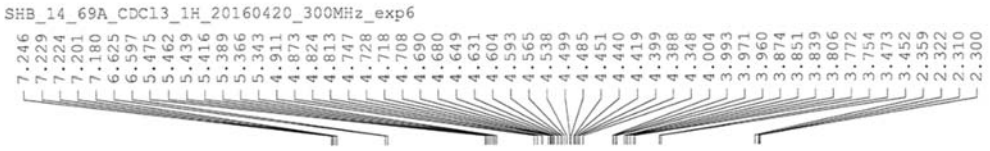


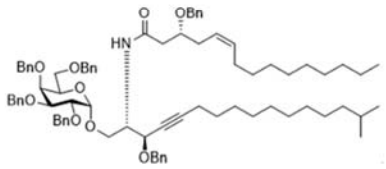
SHB_14_75A_CDCl3_13C_20160420_300MHz_exp1



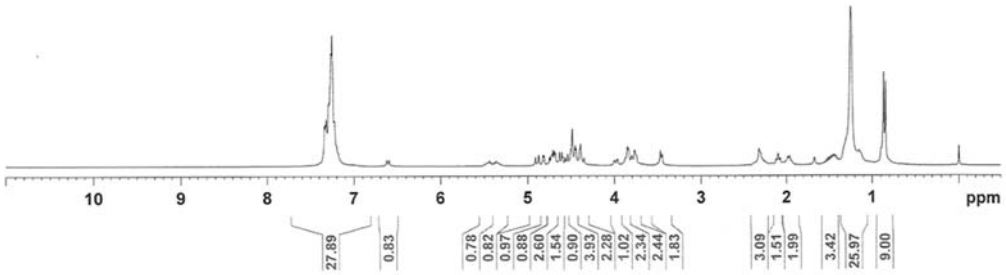
S24{i17/n16}

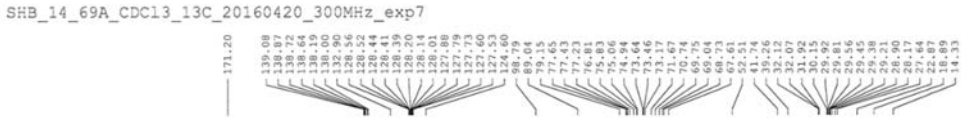


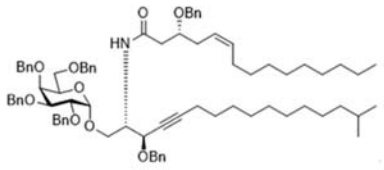




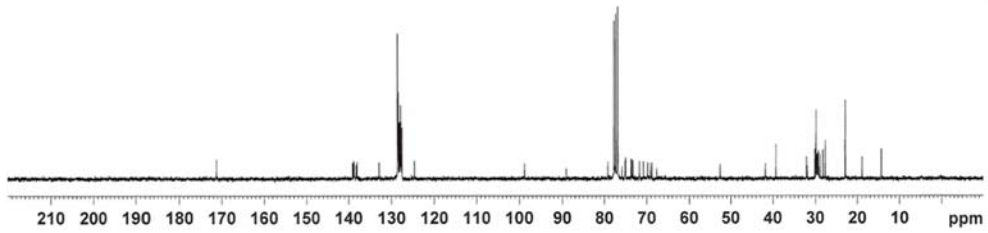
S24{i17/n15}

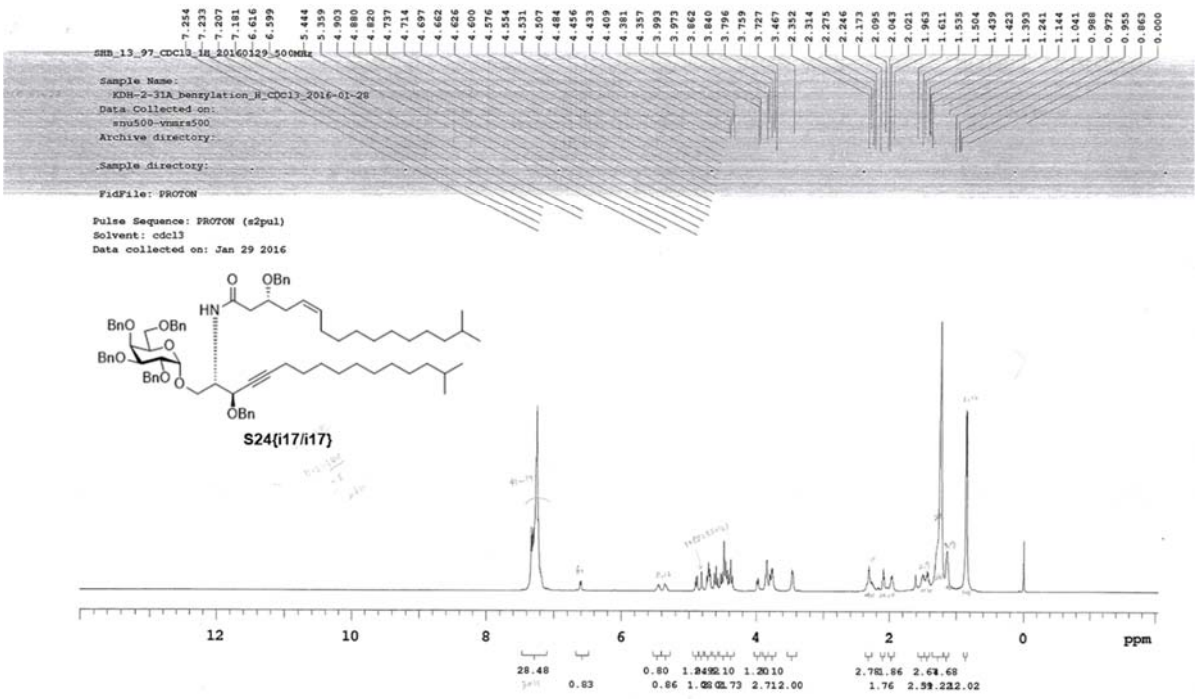


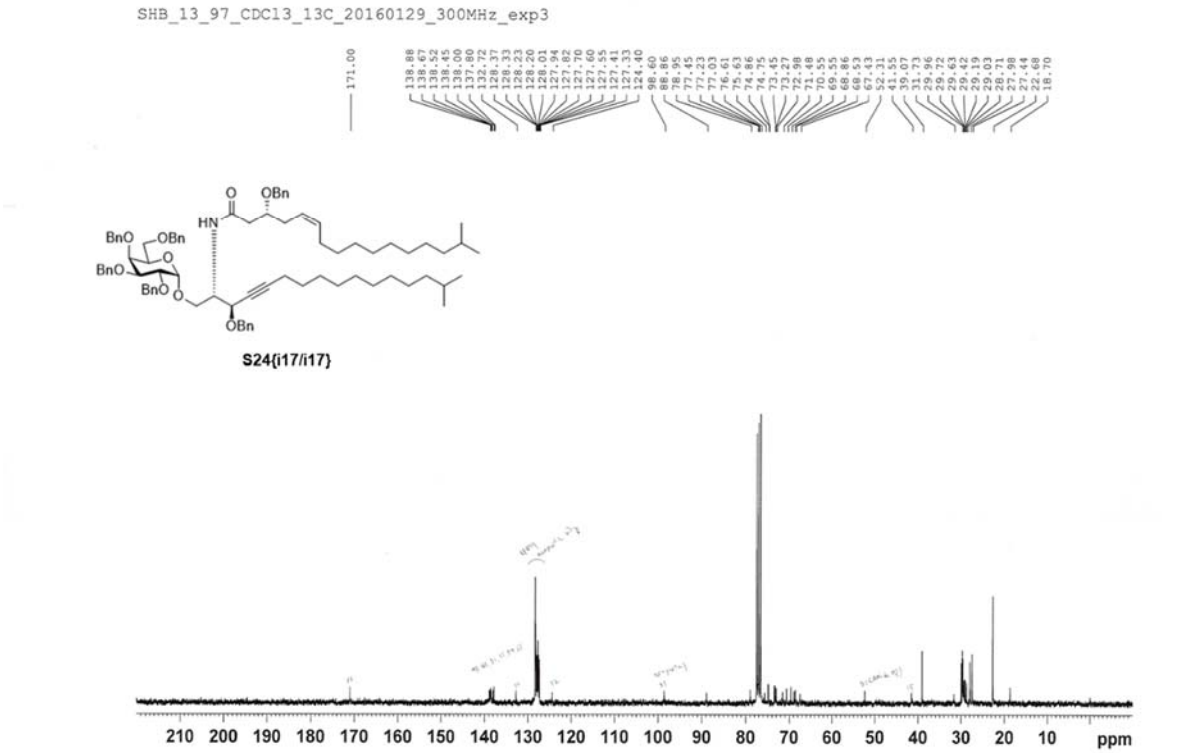


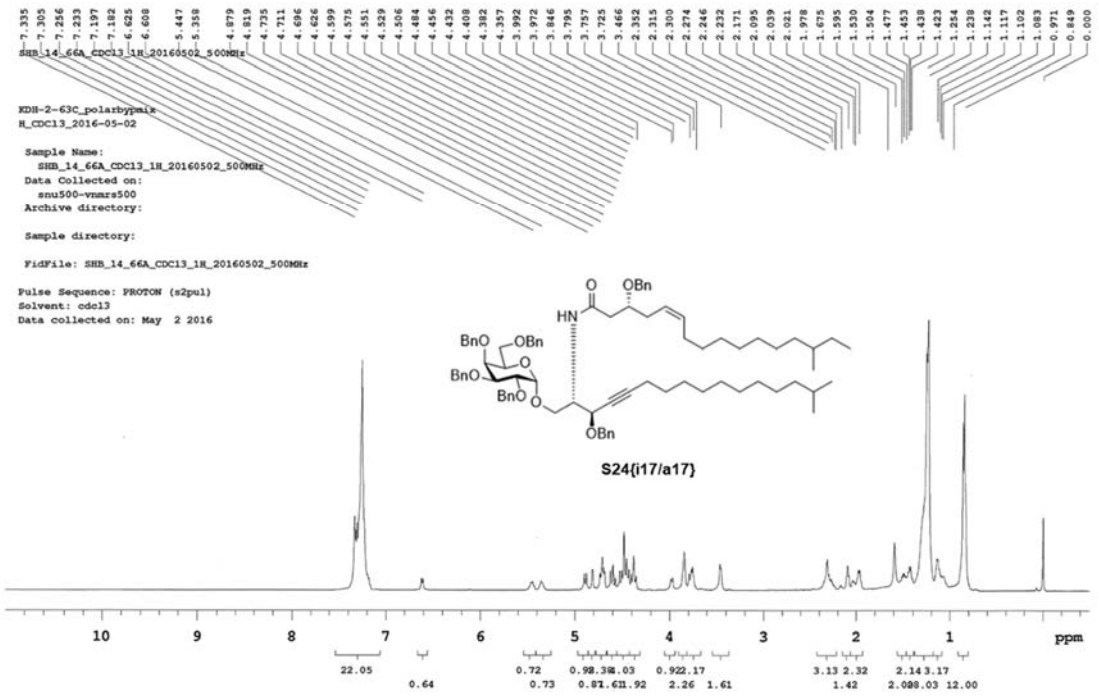


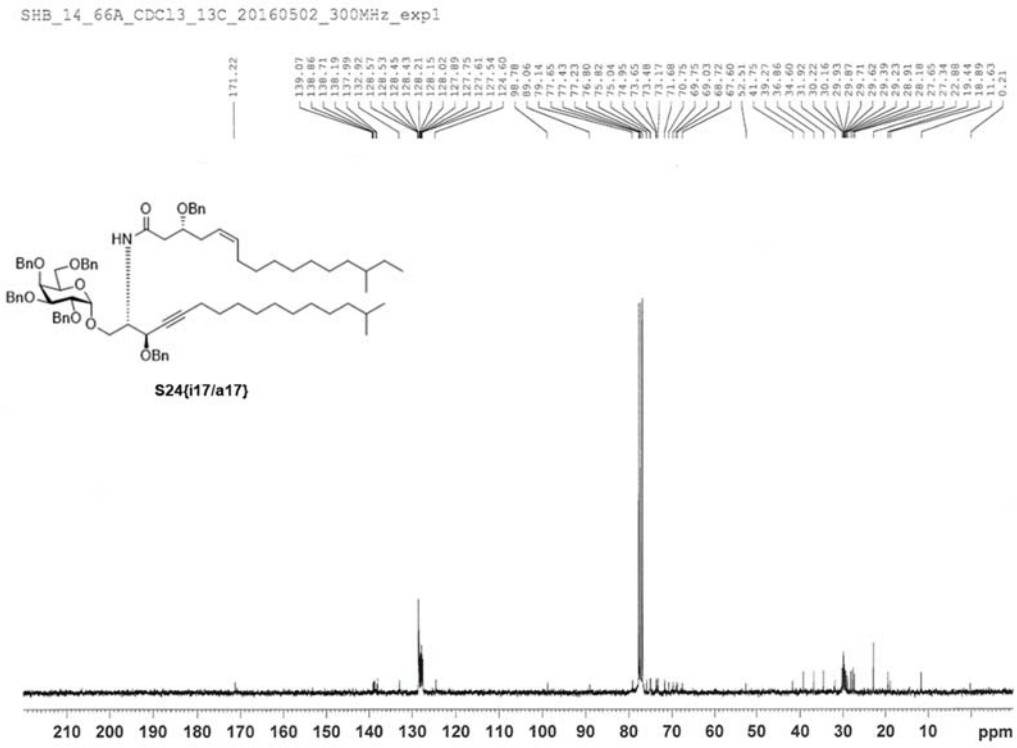
S24{i17/n15}

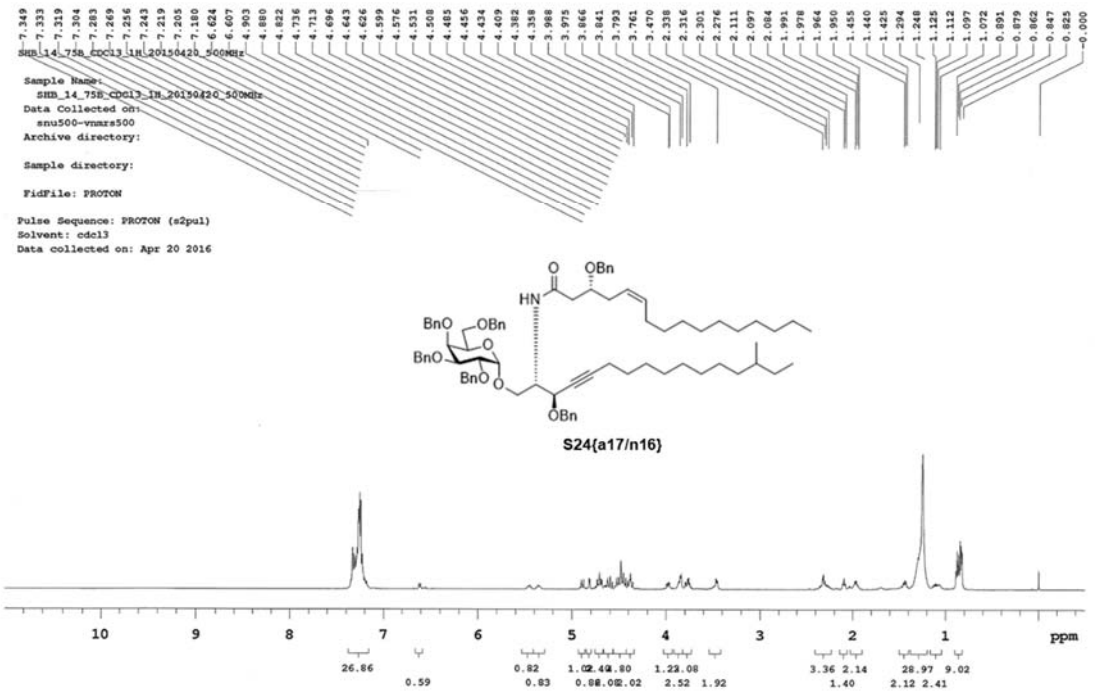


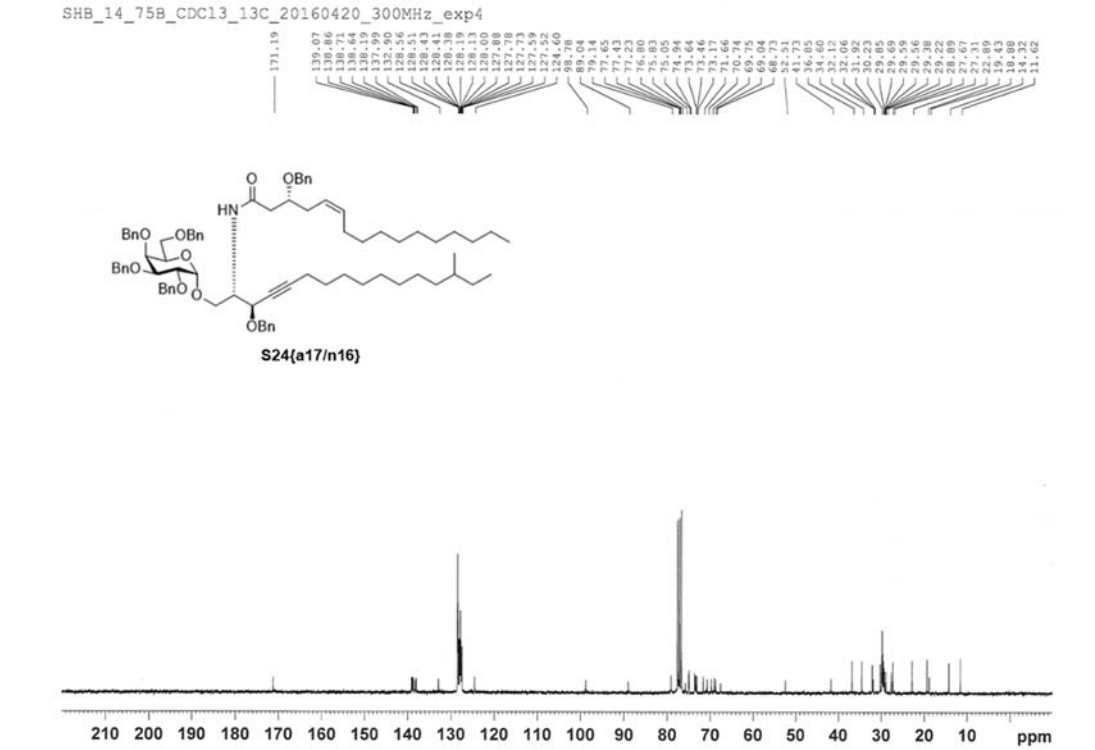

SHB_13_97_CDCl3_1H_20160129_500MHz
Sample Name:
KDH-2-31A_benzylation_H_CDCl3_2016-01-28
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 29 2016
S24{i17/i17}
ppm

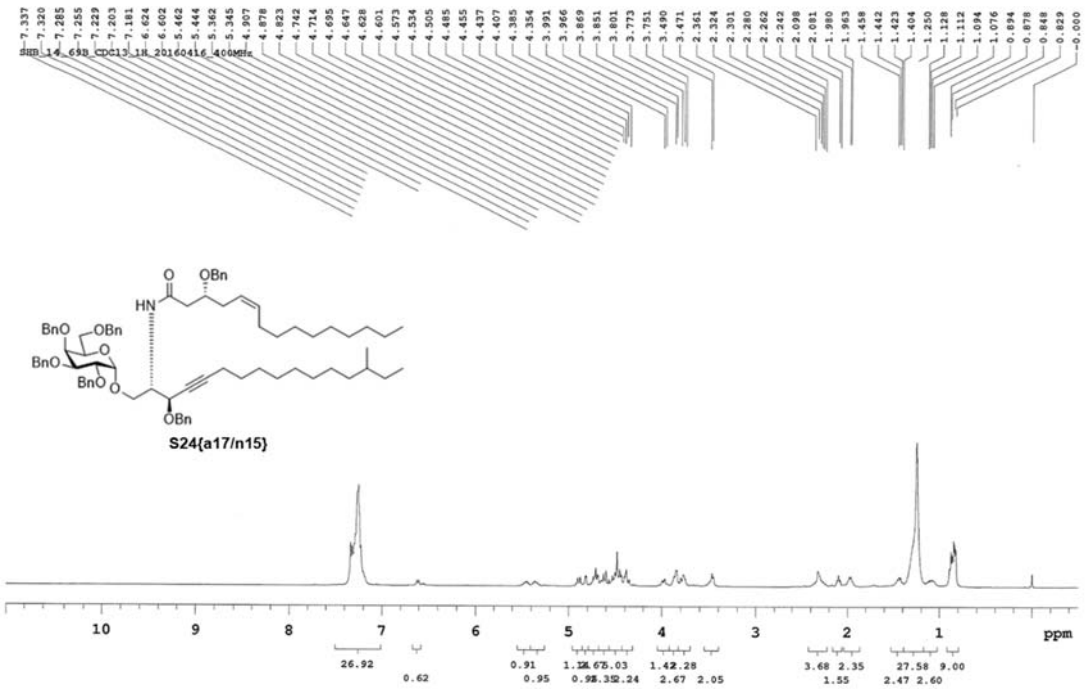

SHB_13_97_CDCl3_13C_20160129_300MHz_exp3
S24{i17/i17}
ppm

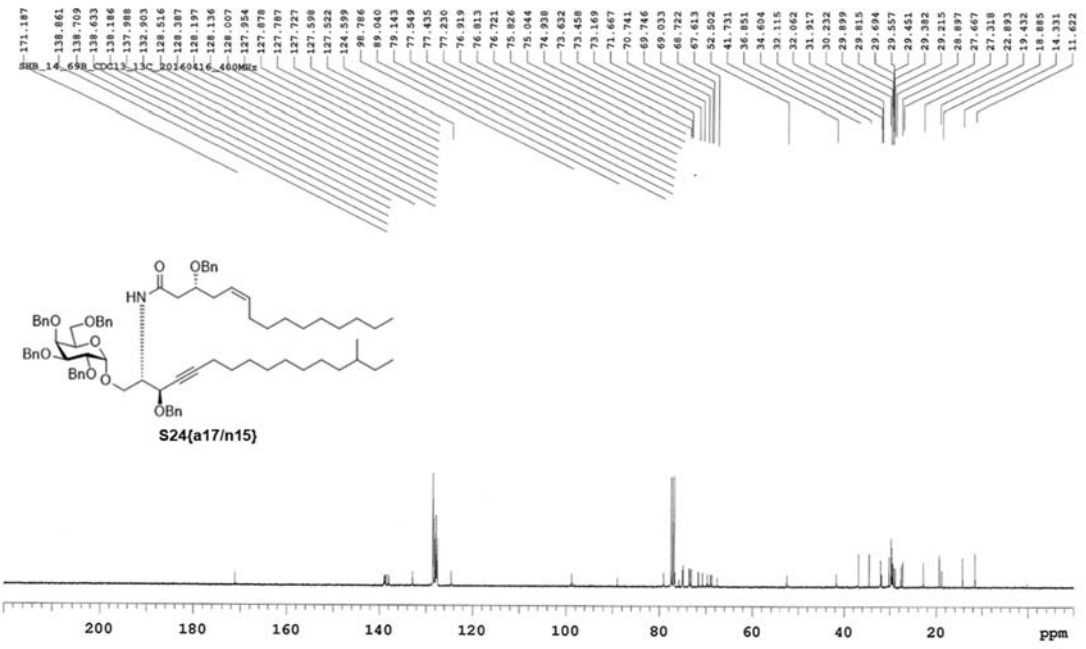

SHB_14_66A_CDCl3_1H_20160502_500MHz
KDH-2-63C_polarbypmix
H_CDCl3_2016-05-02
Sample Name:
SHB_14_66A_CDCl3_1H_20160502_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: SHB_14_66A_CDCl3_1H_20160502_500MHz
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 2 2016
S24{i17/a17}
ppm

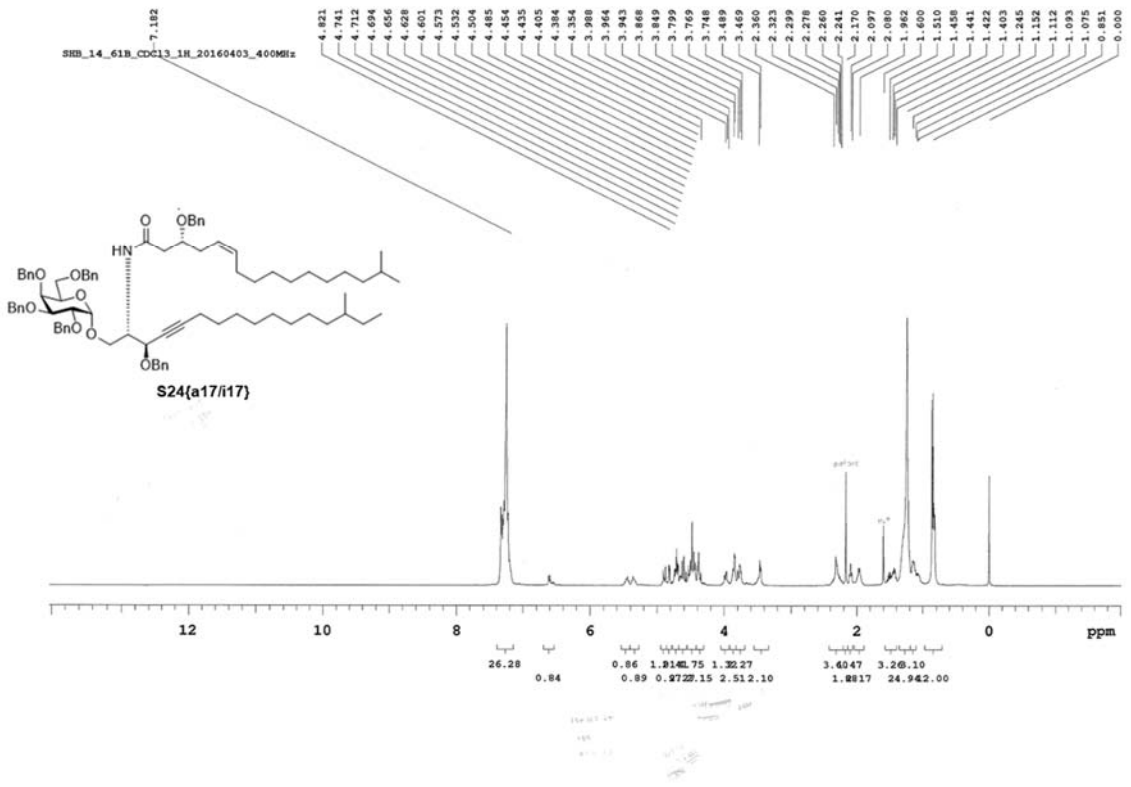

SHB_14_66A_CDCl3_13C_20160502_300MHz_exp1
S24{i17/a17}
ppm

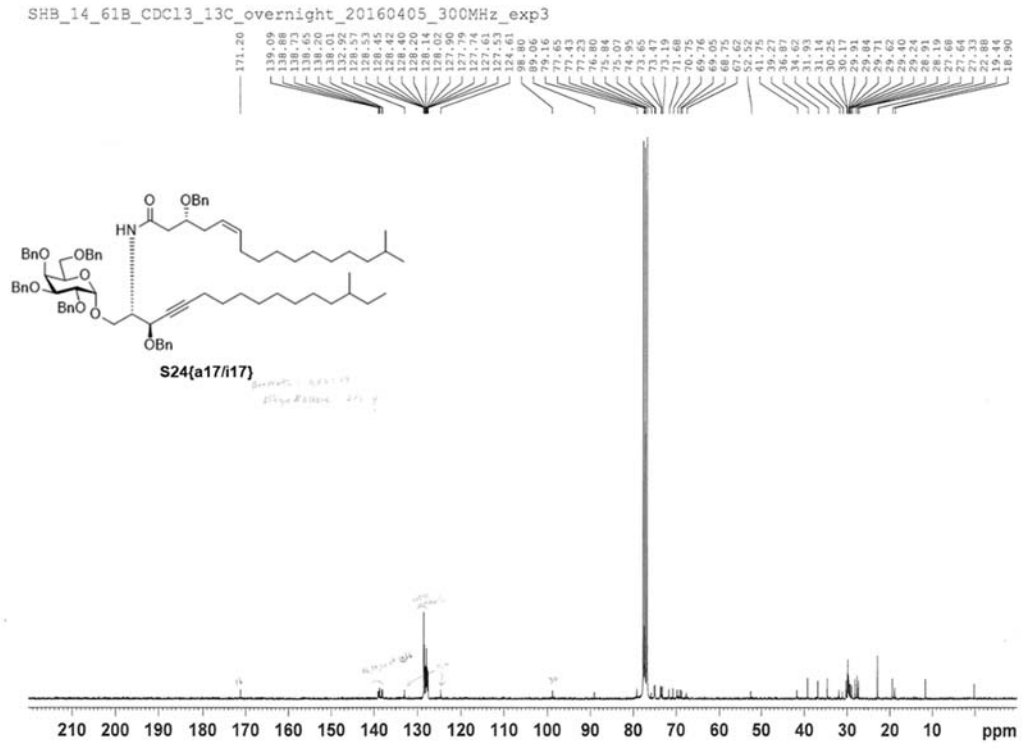

Sample Name:
SHB_14_75B_CDCl3_1H_20150420_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 20 2016
S24{a17/n16}
ppm

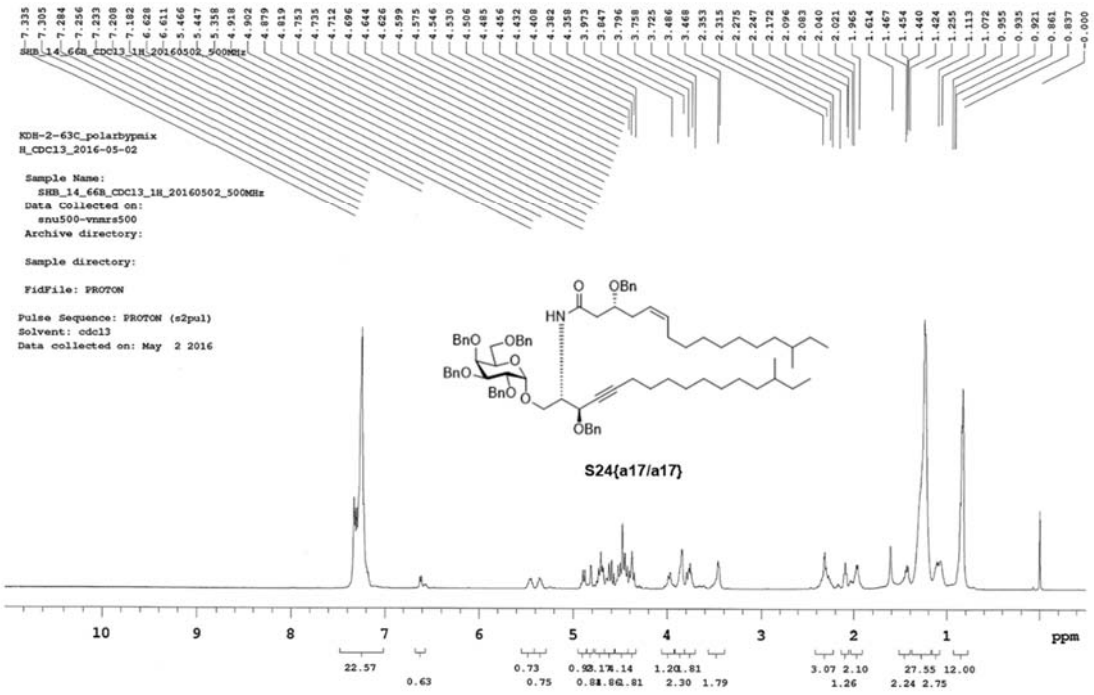

SHB_14_75B_CDCl3_13C_20160420_300MHz_exp4
S24{a17/n16}
ppm

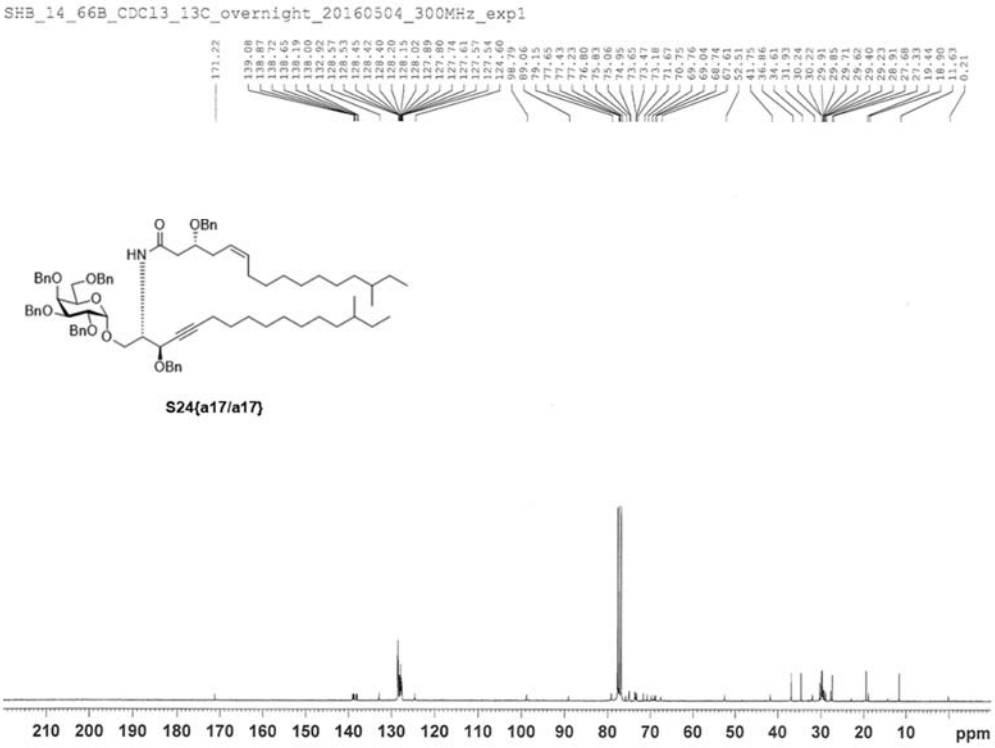

SHB_14_69B_CDCl3_1H_20160416_400MHz
S24{a17/n15}
ppm

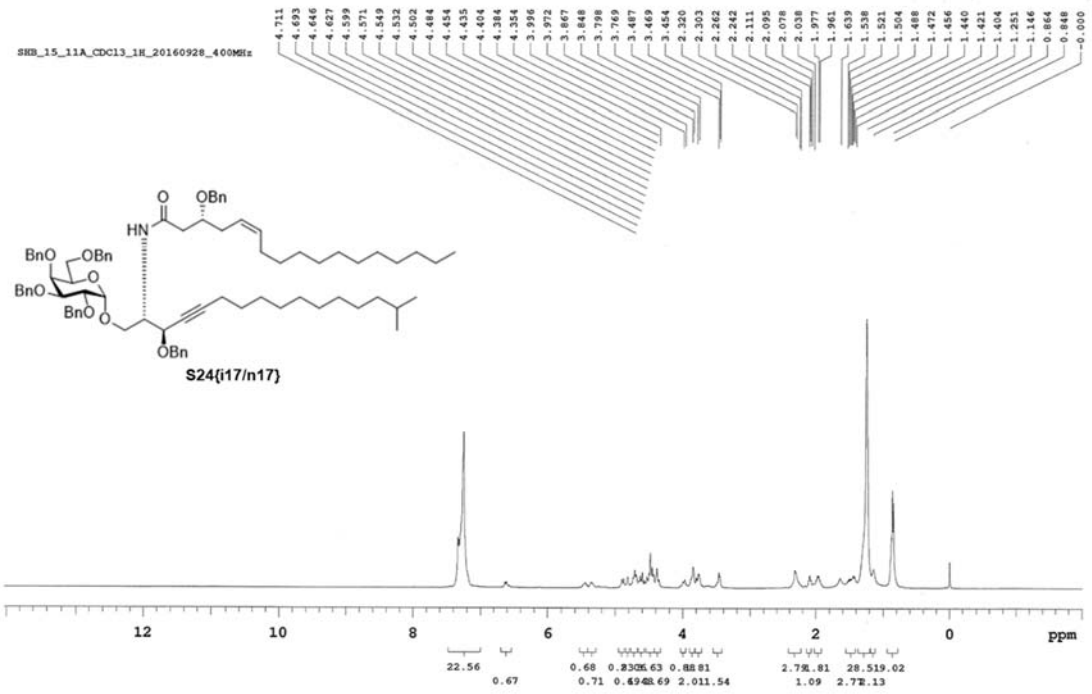

SHB_14_69B_CDCl3_13C_20160416_400MHz
S24{a17/n15}
ppm

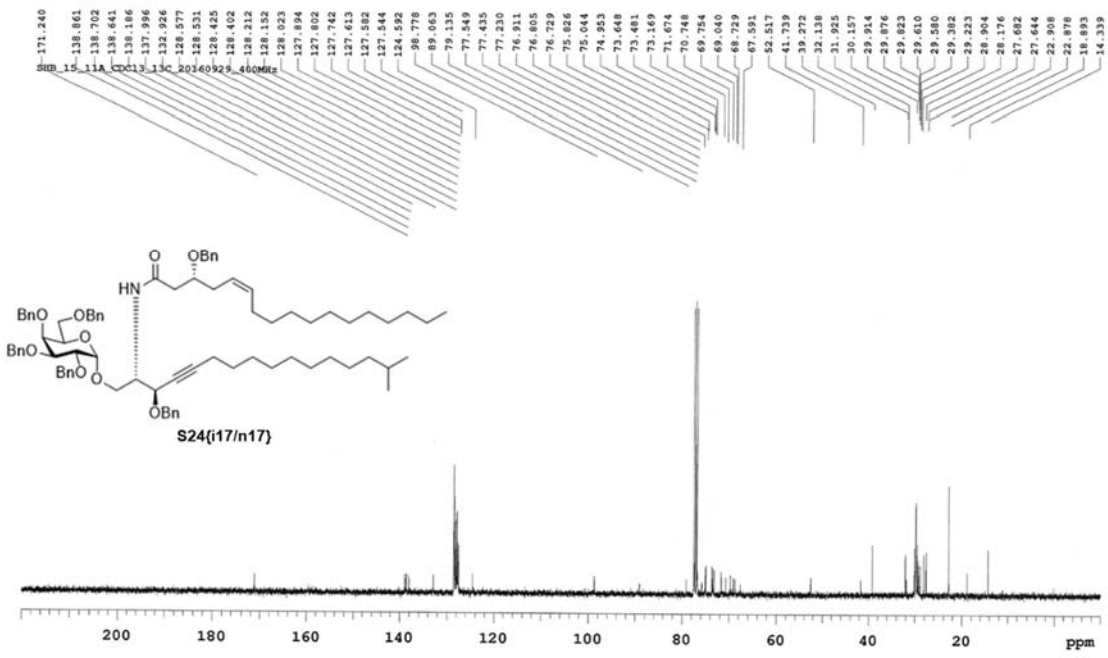

SHB_14_61B_CDCl3_1H_20160403_400MHz
S24{a17/i17}
ppm

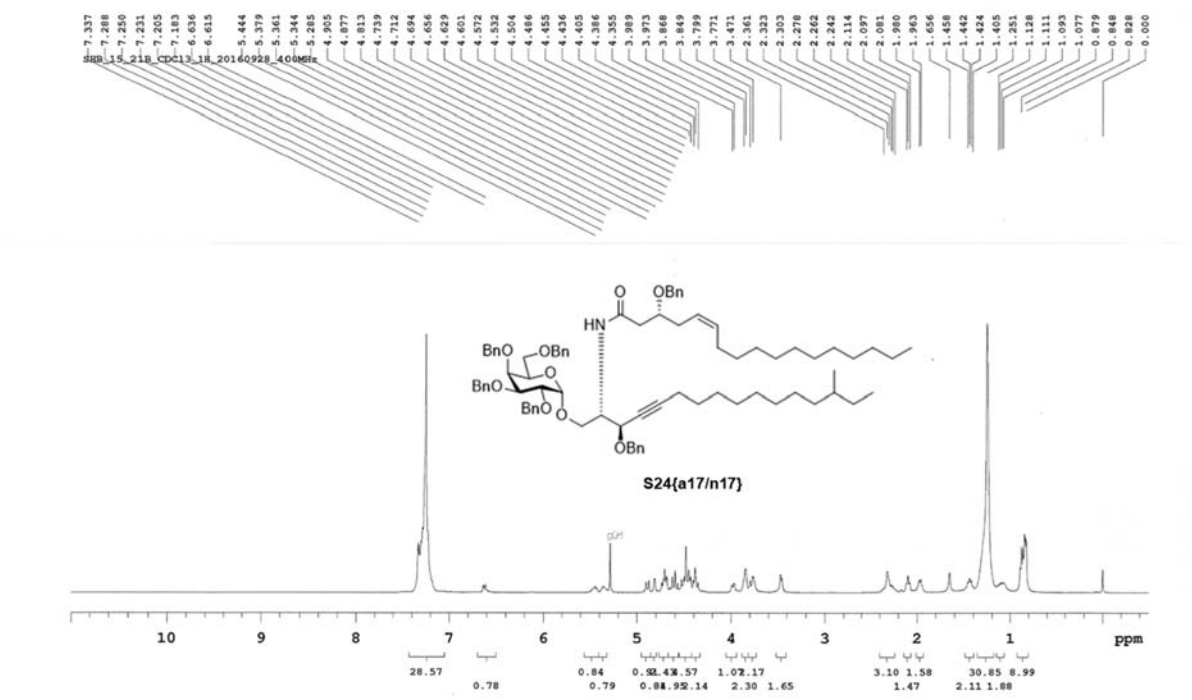

SHB_14_61B_CDCl3_13C_overnight_20160405_300MHz_exp3
S24{a17/i17}
ppm

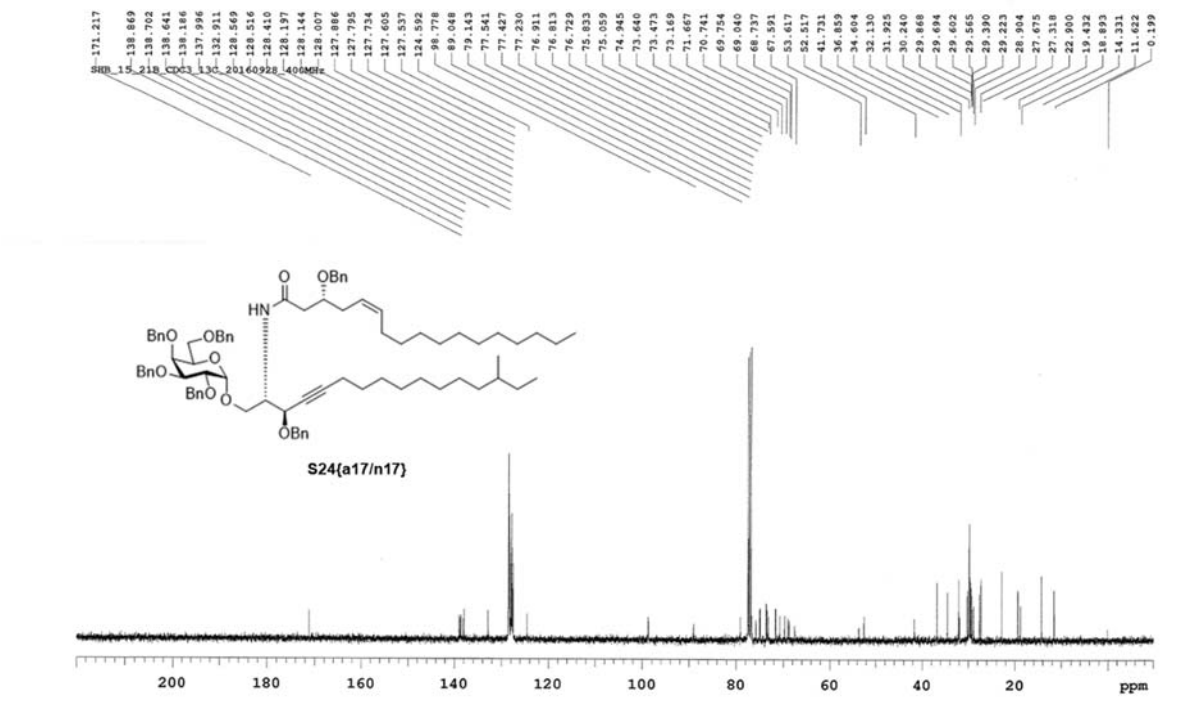

SHB_14_66B_CDCl3_1H_20160502_500MHz
KDH-2-63C_polarbypmix
H_CDCl3_2016-05-02
Sample Name:
SHB_14_66B_CDCl3_1H_20160502_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 2 2016
S24{a17/a17}
ppm

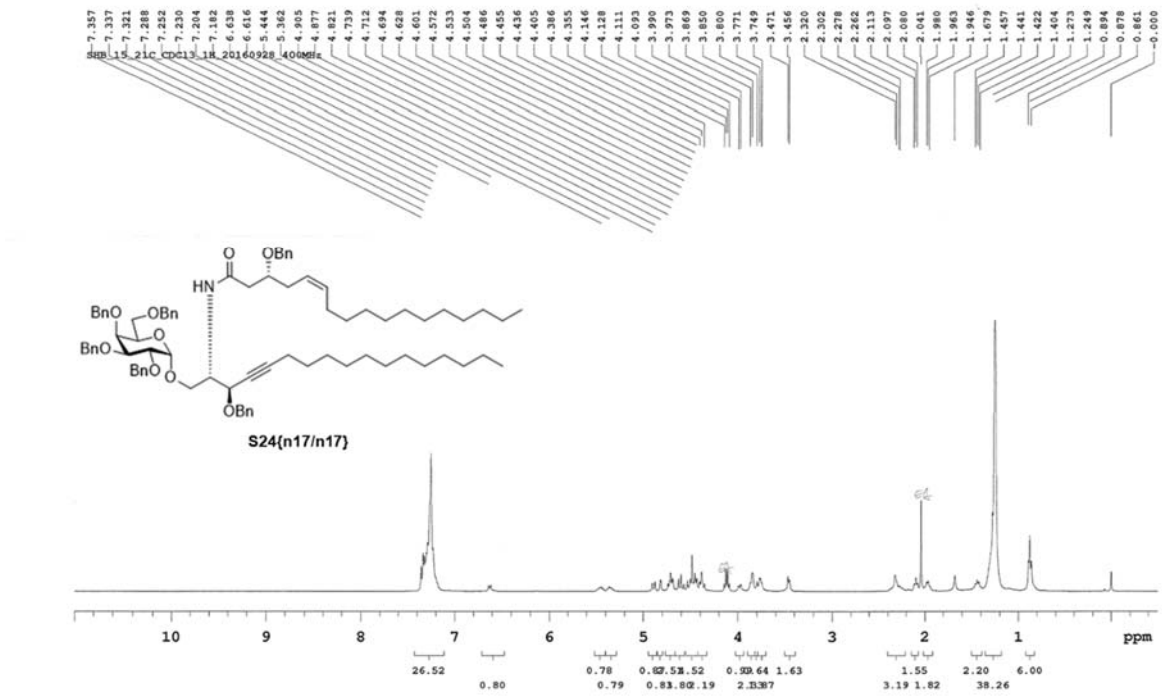

SHB_14_66B_CDCl3_13C_overnight_20160504_300MHz_exp1
S24{a17/a17}
ppm

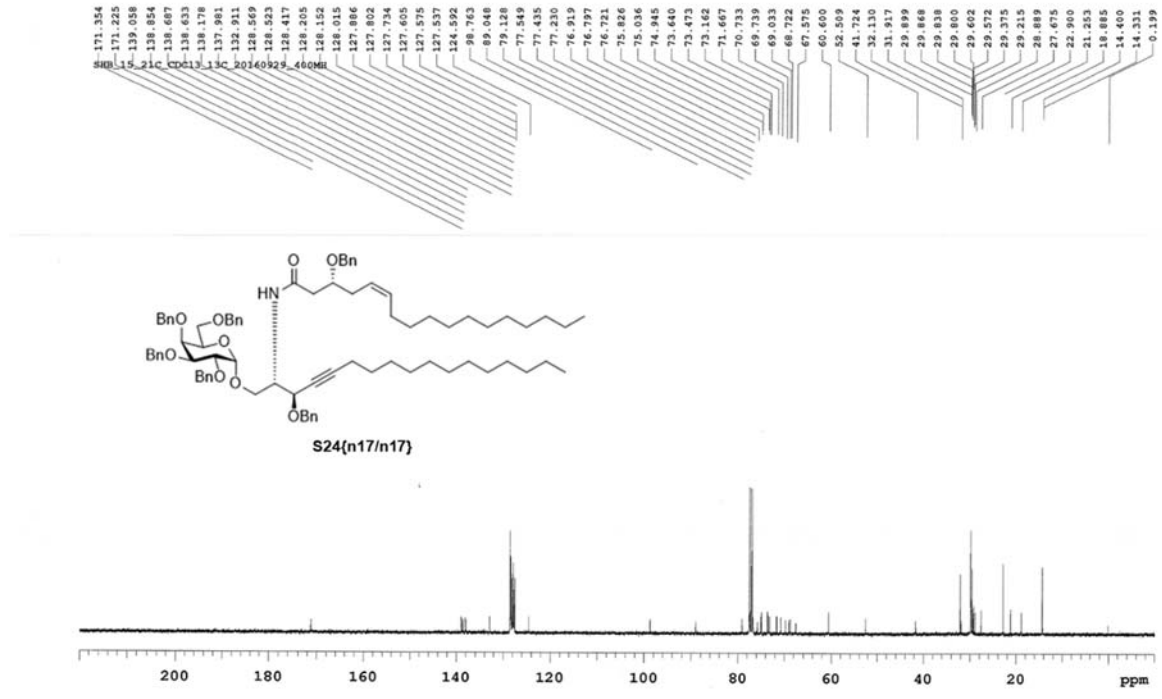

SHB_15_11A_CDCl3_1H_20160928_400MHz
S24{i17/n17}
ppm

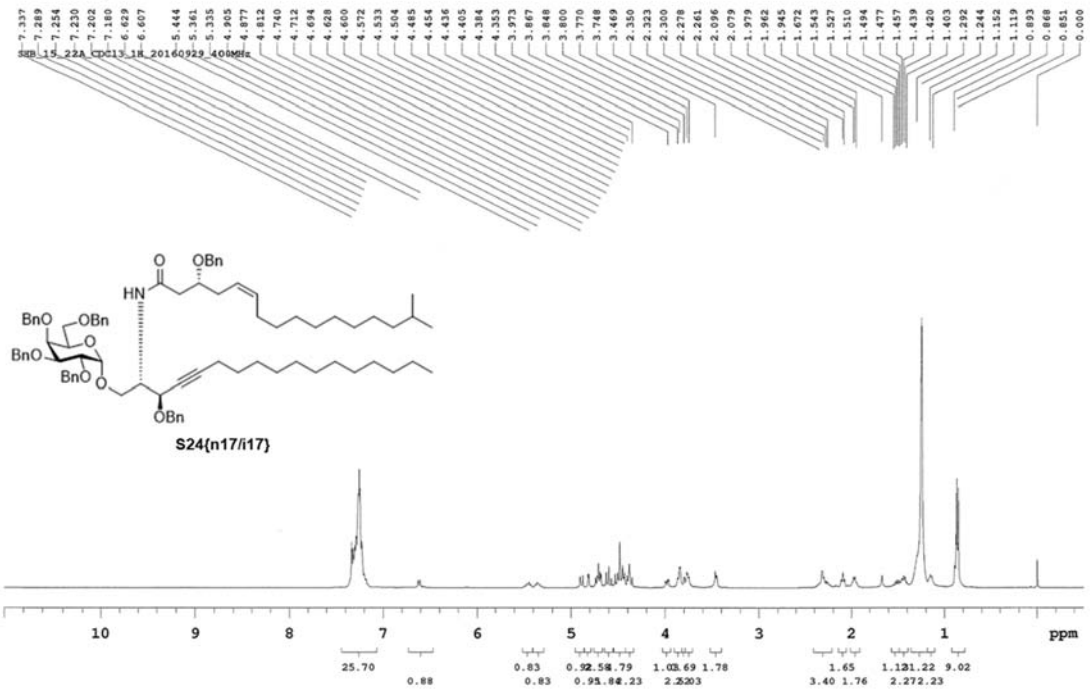

SHB_15_11A_CDCl3_13C_20160929_400MHz
S24{i17/n17}
ppm

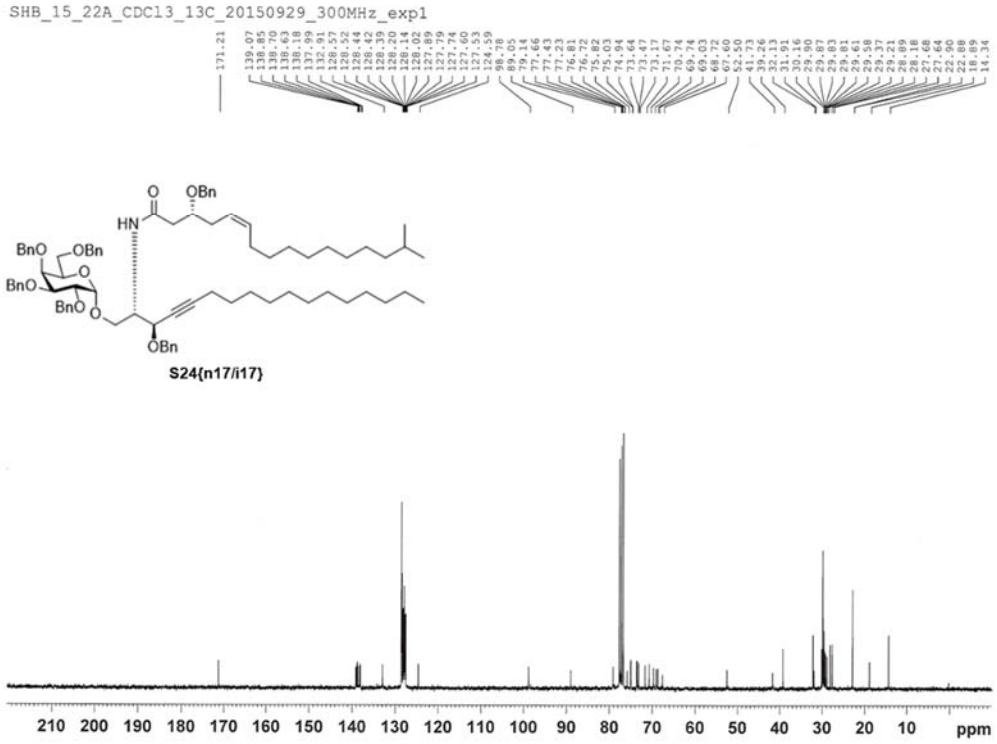

S24{a17/n17}
ppm

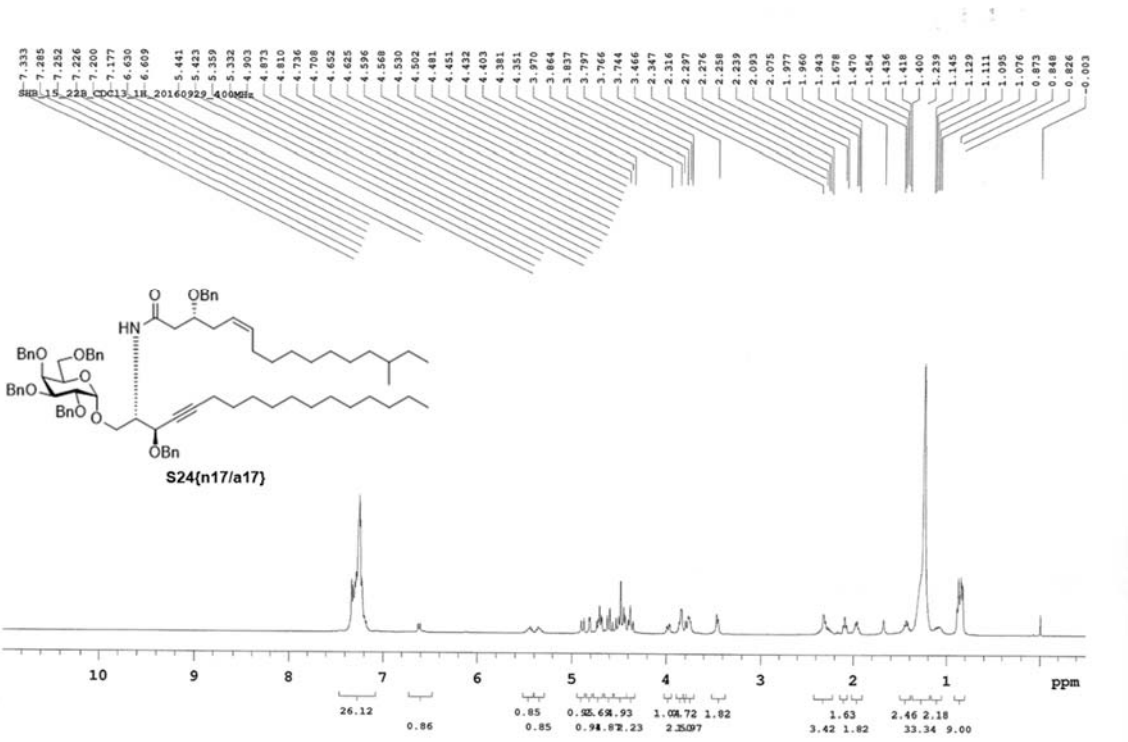

S24{a17/n17}
ppm

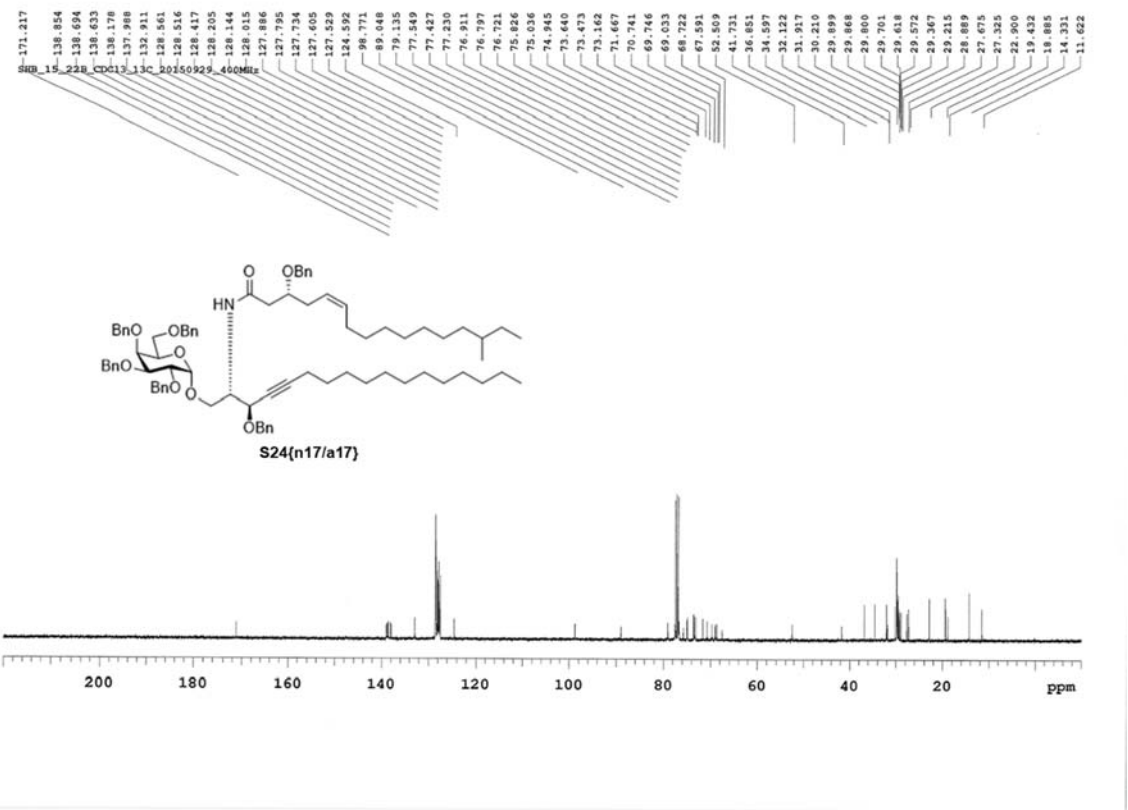

S24{n17/n17}
ppm

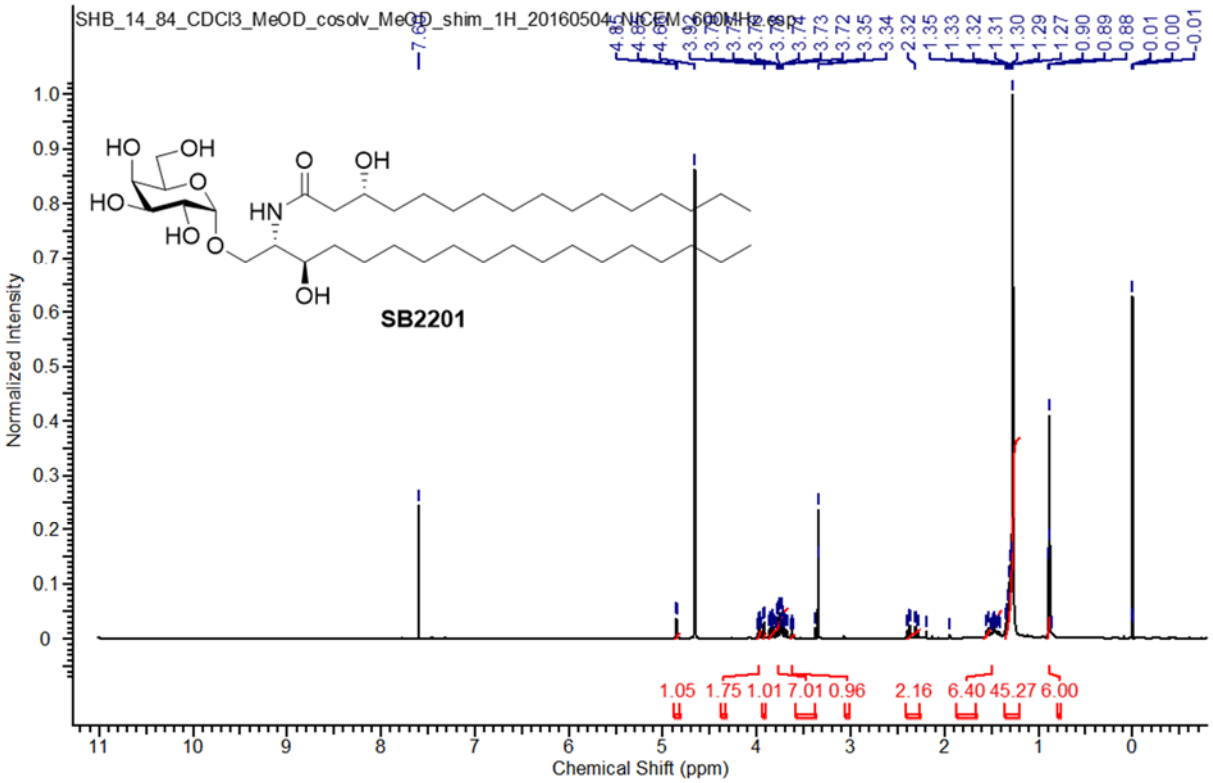

S24{n17/n17}
ppm

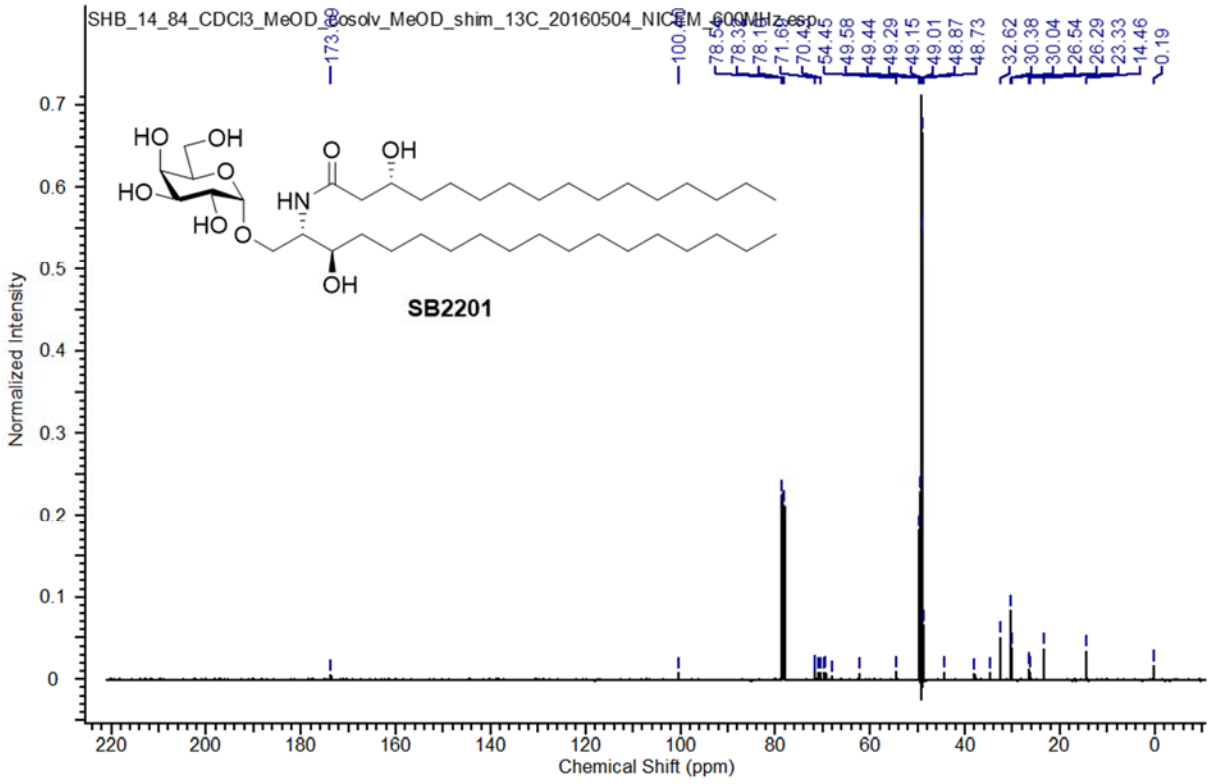

SHB_15_22A_CDCl3_1H_20160929_400MHz
BnO
OBn
HN
OBn
S24{n17/i17}
ppm

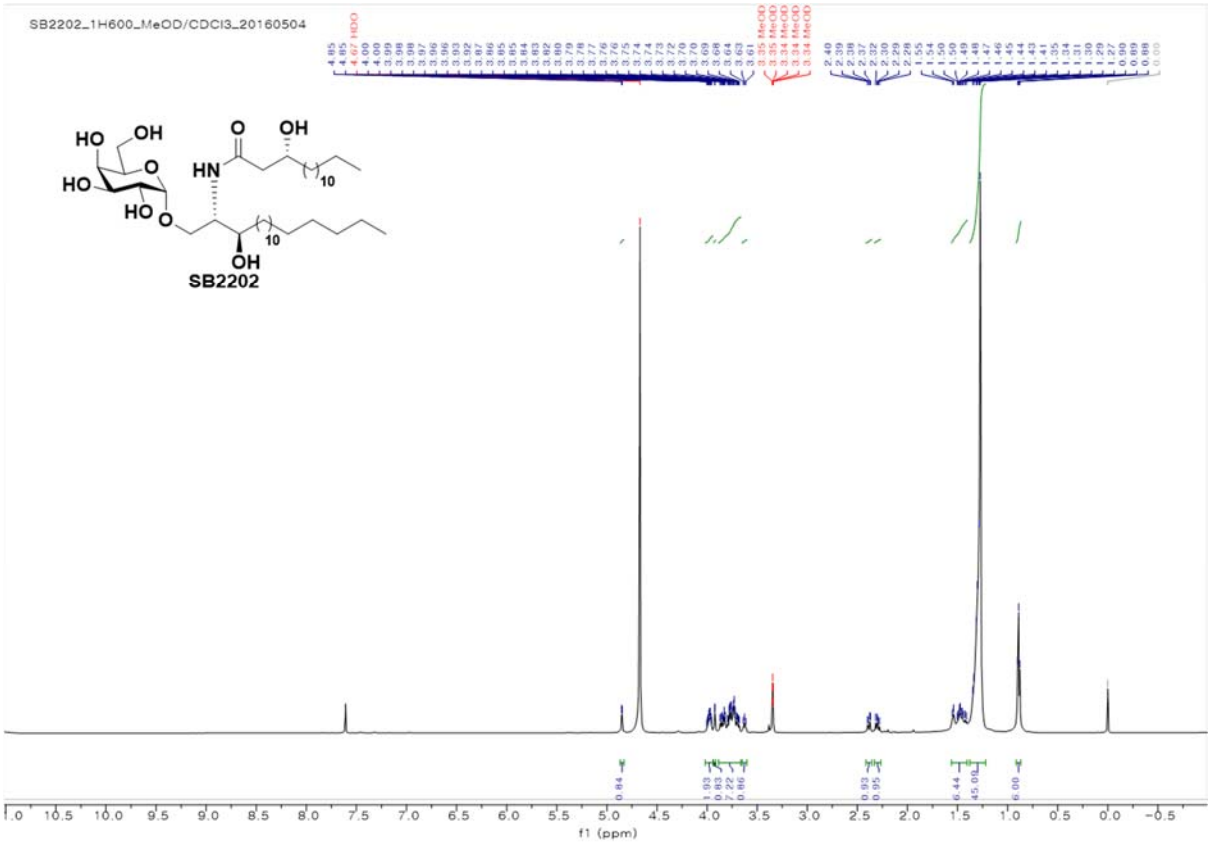

SHB_15_22A_CDCl3_13C_20150929_300MHz_exp1
BnO
OBn
HN
OBn
S24{n17/i17}
ppm

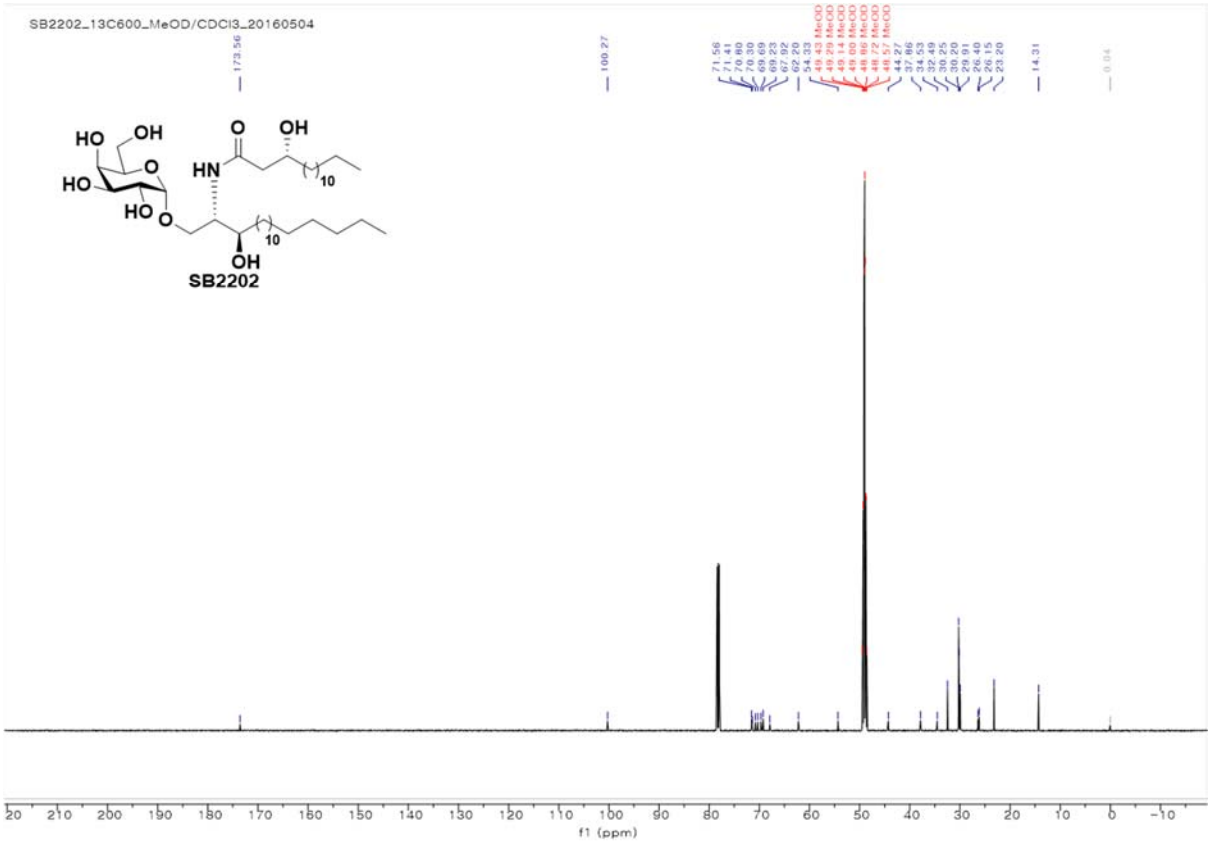

SKB_15_22B_CDCl3_1H_20160929_400MHz
S24{n17/a17}
ppm


SKB_15_22B_CDCl3_13C_20150929_400MHz
S24{n17/a17}
ppm


SHB_14_84_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160504_NICEM_600MHz.esp
SB2201
Normalized Intensity
Chemical Shift (ppm)
1.05 1.75 1.01 7.01 0.96 2.16 6.40 45.27 6.00


SHB_14_84_CDCl3_MeOD_cosolv_MeOD_shim_13C_20160504_NICEM_600MHz.esp
SB2201
Normalized Intensity
Chemical Shift (ppm)


SB2202_1H600_MeOD/CDCl3_20160504
SB2202
f1 (ppm)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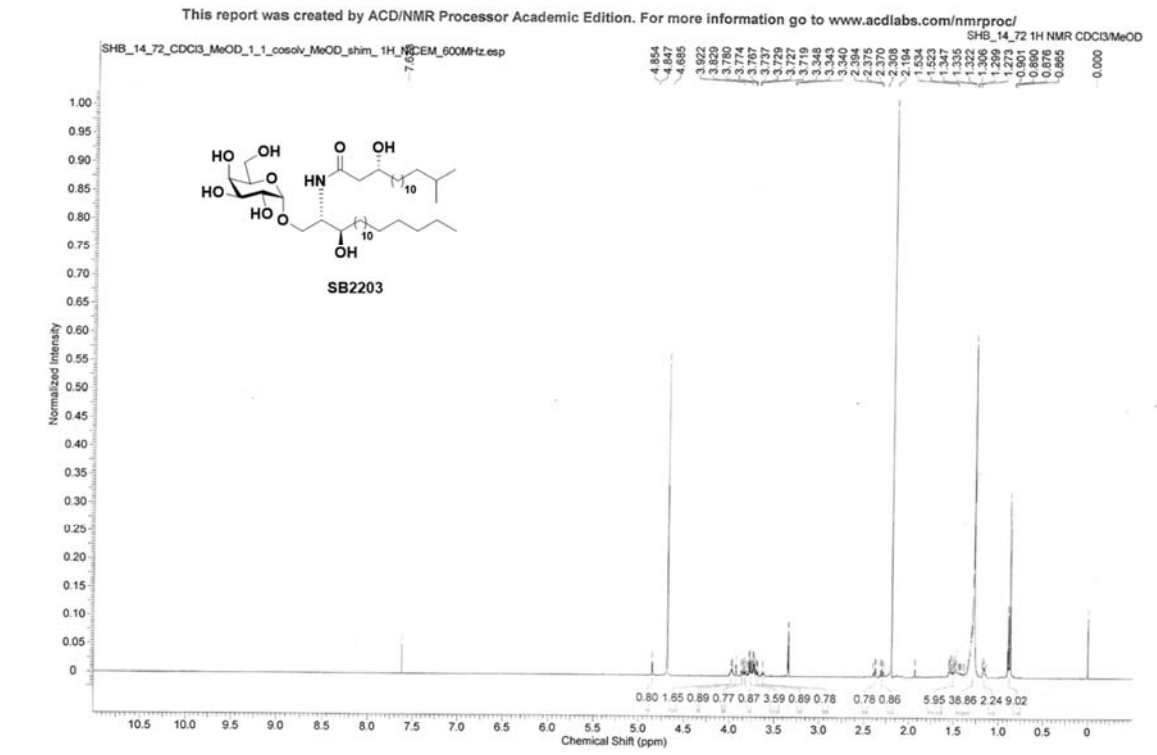
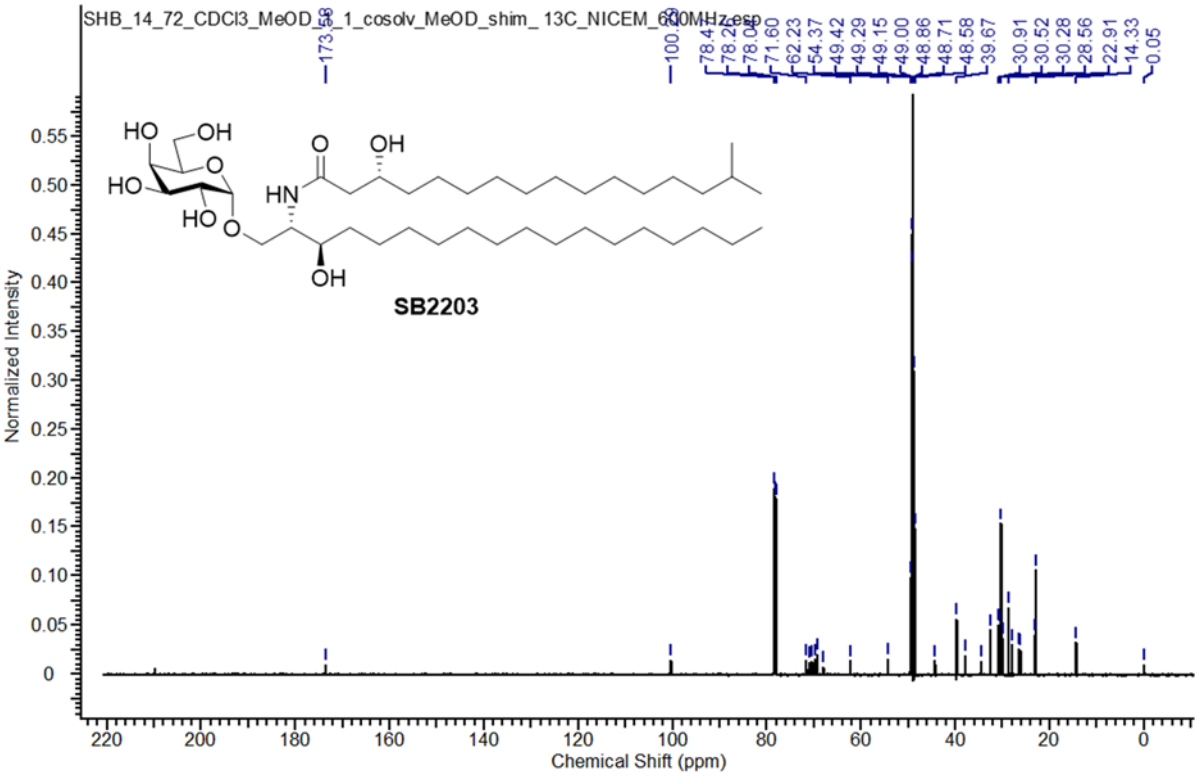
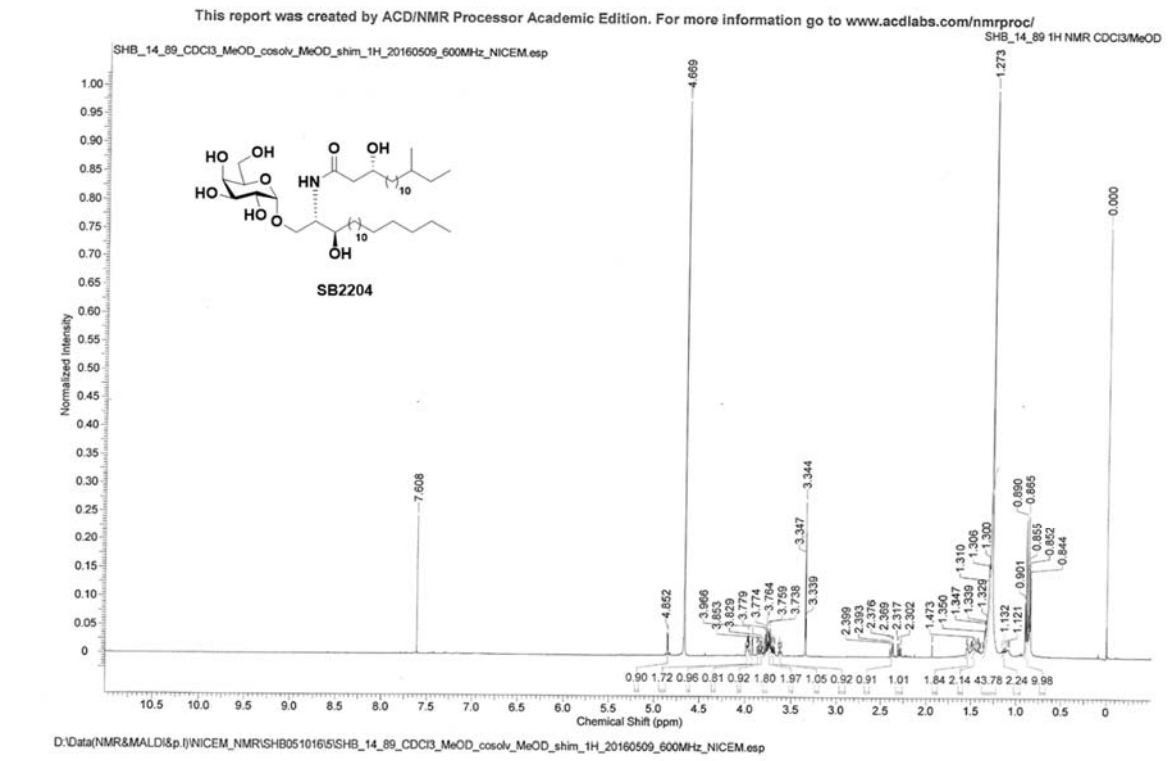
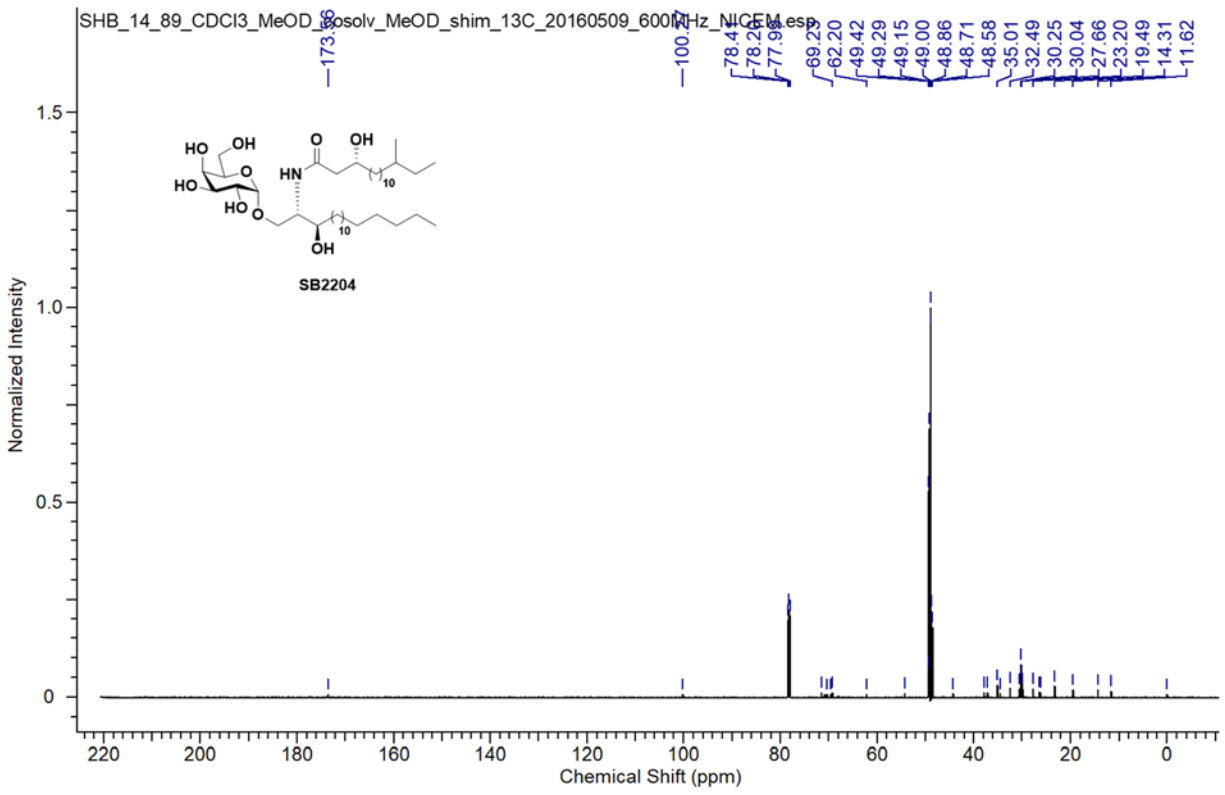
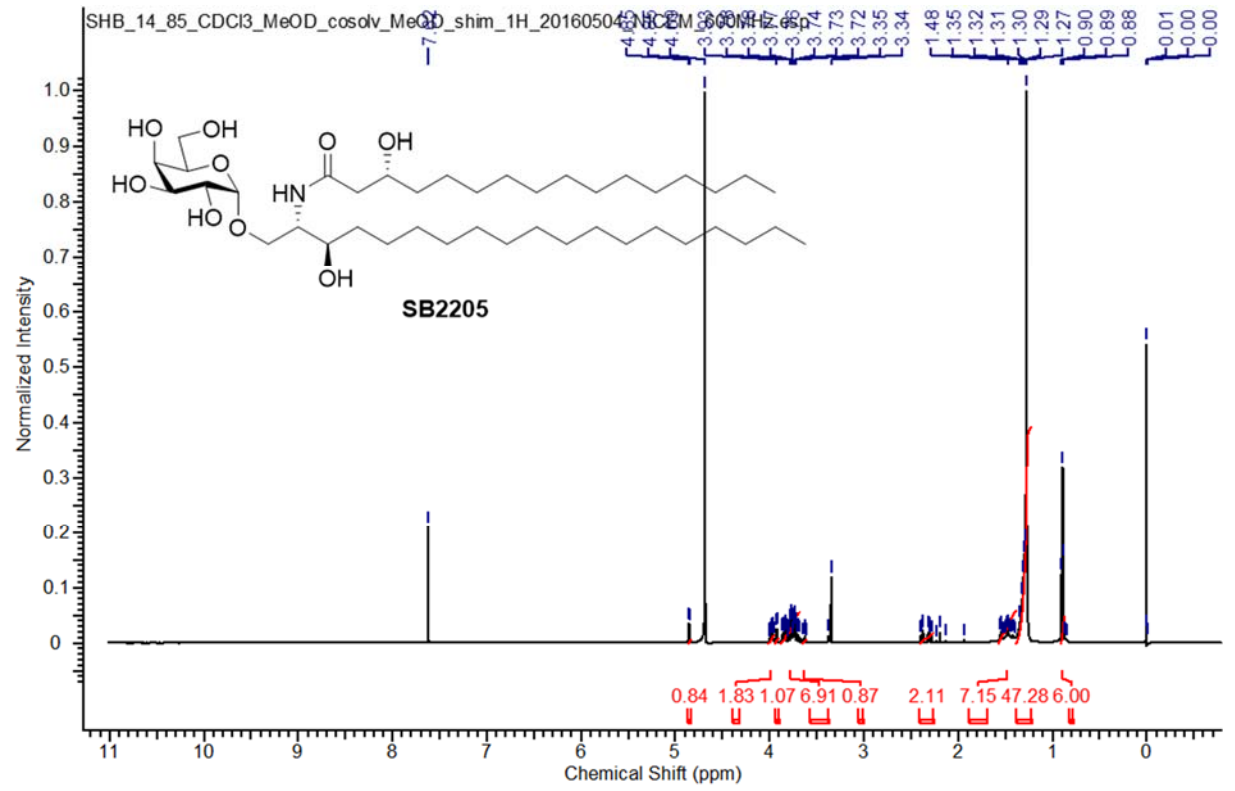
SB2202
f1 (ppm)

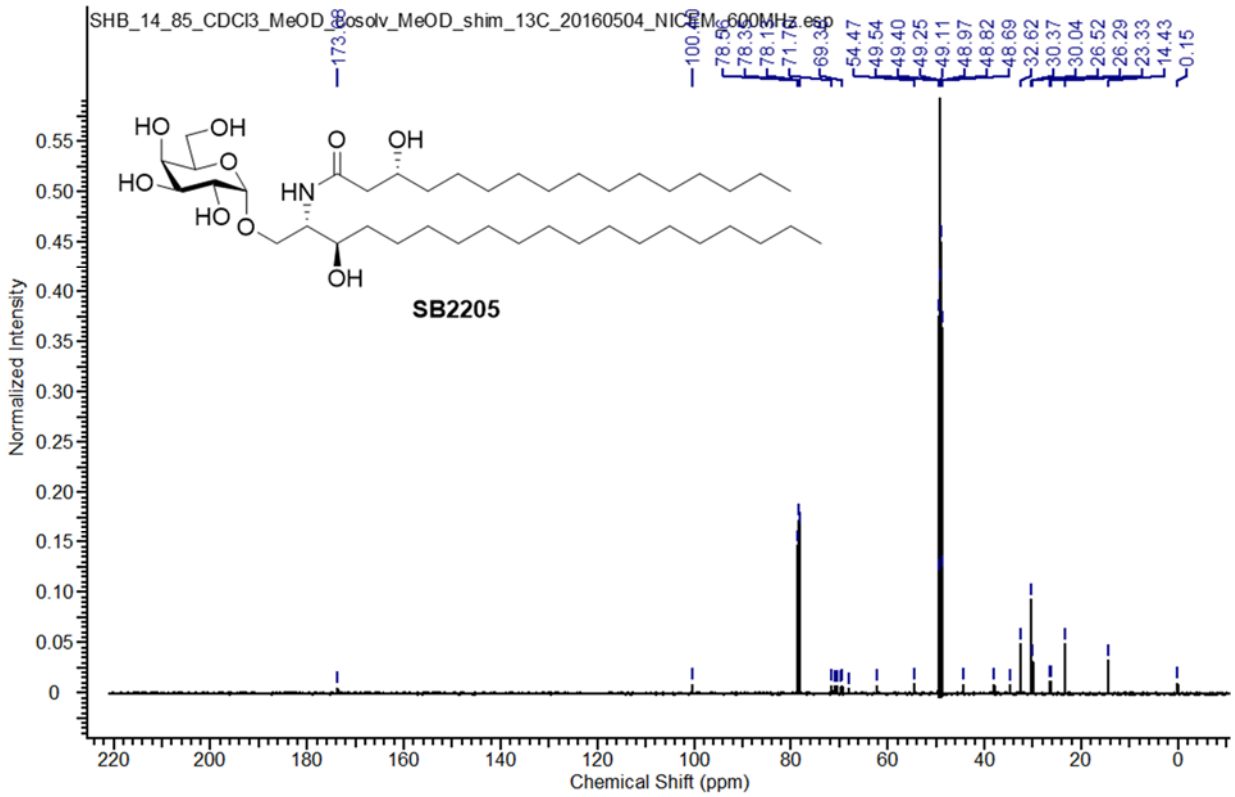

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_72 1H NMR CDCl3/MeOD
SB2203
Normalized Intensity
Chemical Shift (ppm)


SB2203
Normalized Intensity
Chemical Shift (ppm)

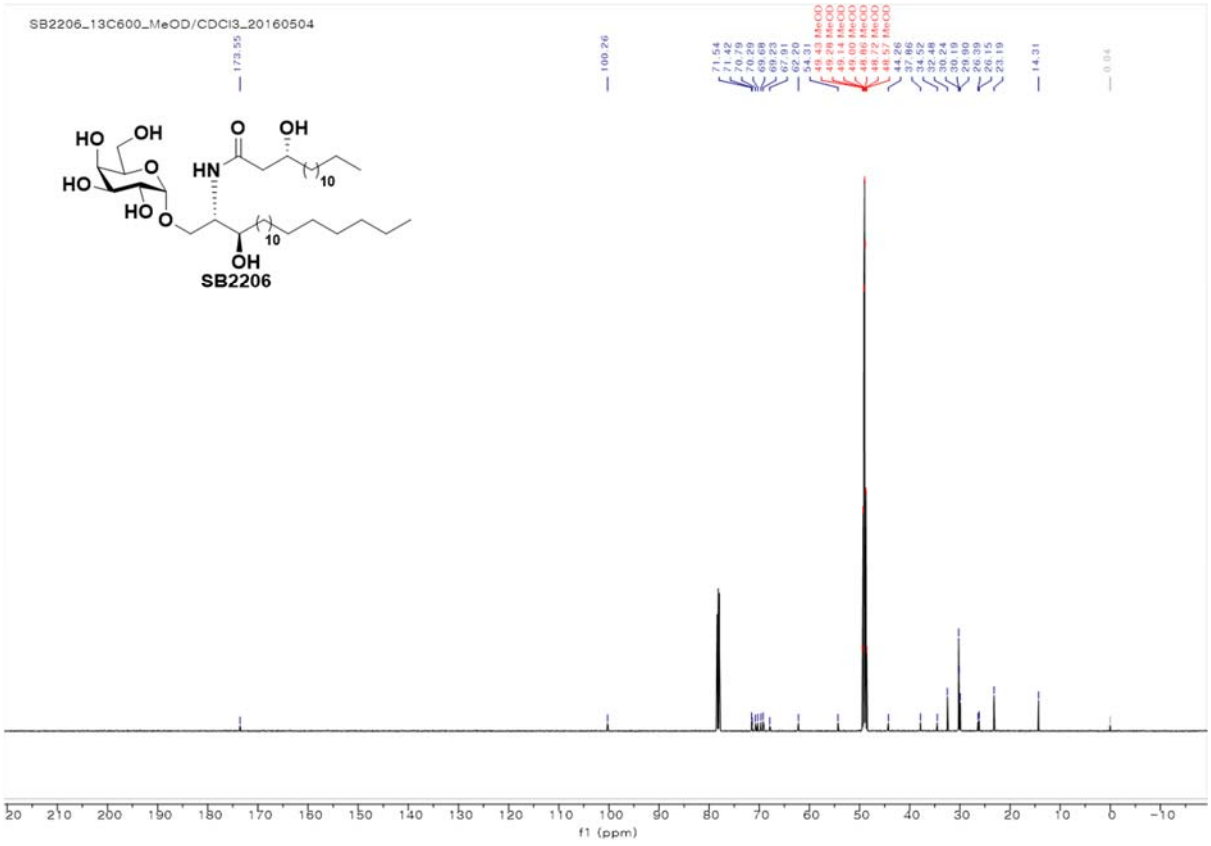

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_89_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp
SHB_14_89 1H NMR CDCl3/MeOD
SB2204
Normalized Intensity
Chemical Shift (ppm)
D:\Data(NMR&MALDI&p.I)\NICEM_NMR\SHB051016\5\SHB_14_89_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp

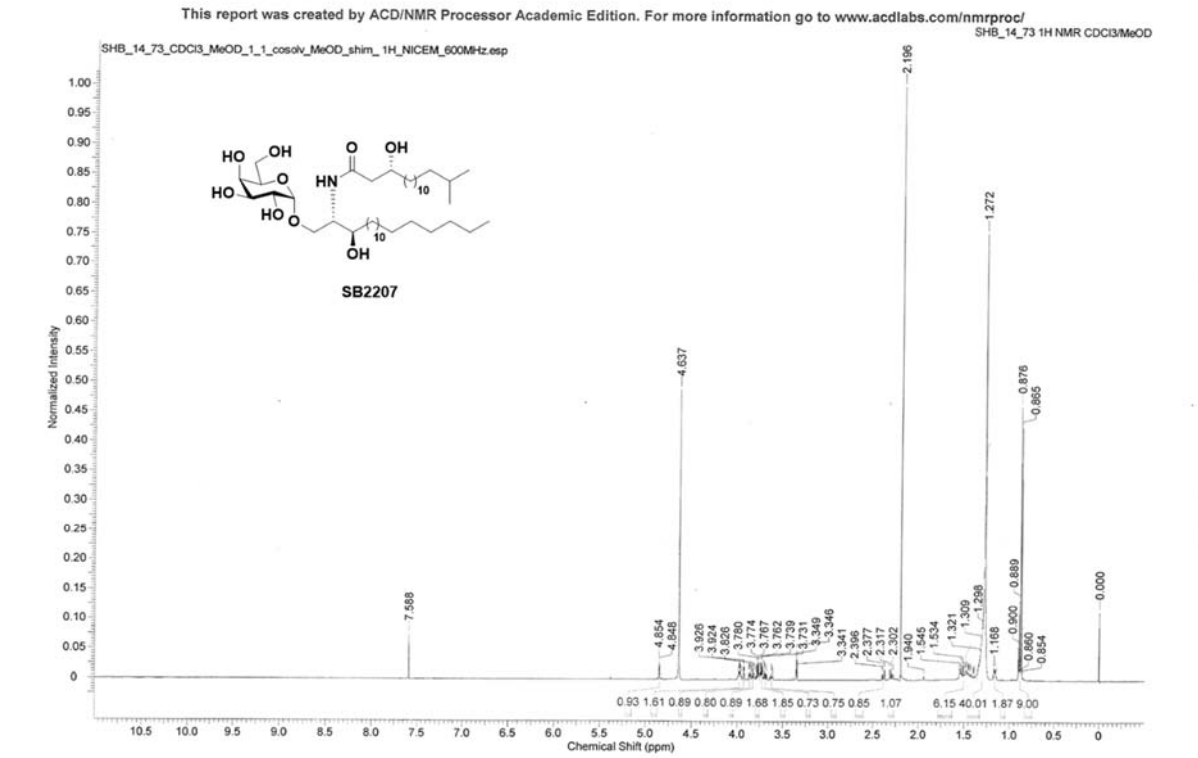

SHB_14_89_CDCl3_MeOD_cosolv_MeOD_shim_13C_20160509_600MHz_NICEM.esp
SB2204
Normalized Intensity
Chemical Shift (ppm)

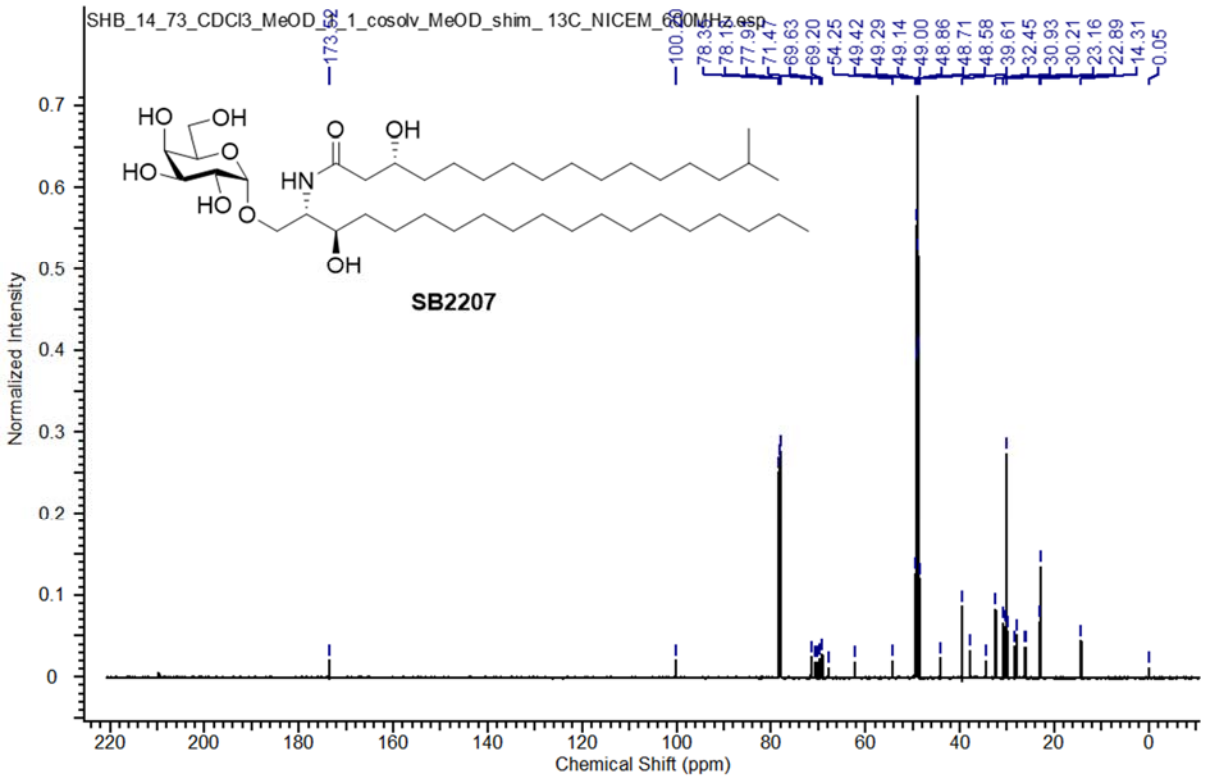

SHB_14_85_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160504_NICEM_600MHz.esp
SB2205
Normalized Intensity
Chemical Shift (ppm)
0.84 1.83 1.07 6.91 0.87 2.11 7.15 47.28 6.00


SHB_14_85_CDCl3_MeOD_cosolv_MeOD_shim_13C_20160504_NICEM_600MHz.esp
SB2205
Normalized Intensity
Chemical Shift (ppm)


SB2206_1H600_MeOD/CDCl3_20160504
HO
OH
O
HO
HN
OH
HO
O
10
10
OH
SB2206
f1 (ppm)


SB2206_13C600_MeOD/CDCl3_20160504
HO
OH
O
HO
HN
OH
HO
O
10
10
OH
SB2206
f1 (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_73_CDCl3_MeOD_1_1_cosolv_MeOD_shim_ 1H_NICEM_600MHz.esp
SHB_14_73 1H NMR CDCl3/MeOD
SB2207
Normalized Intensity
Chemical Shift (ppm)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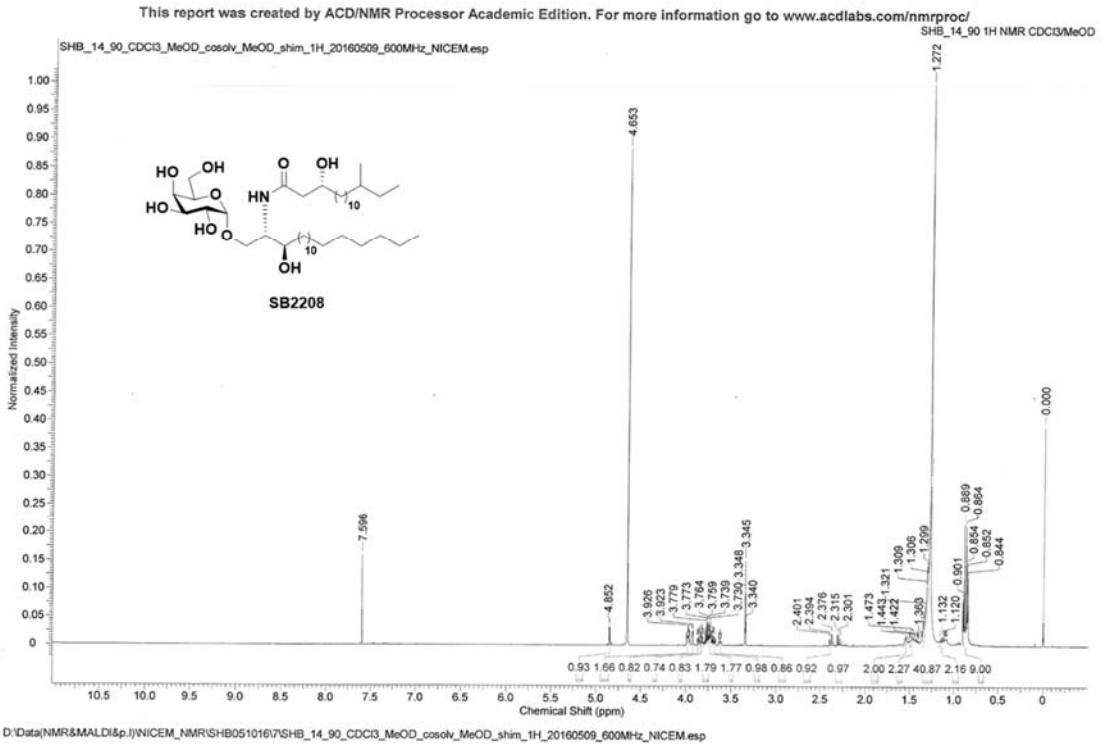
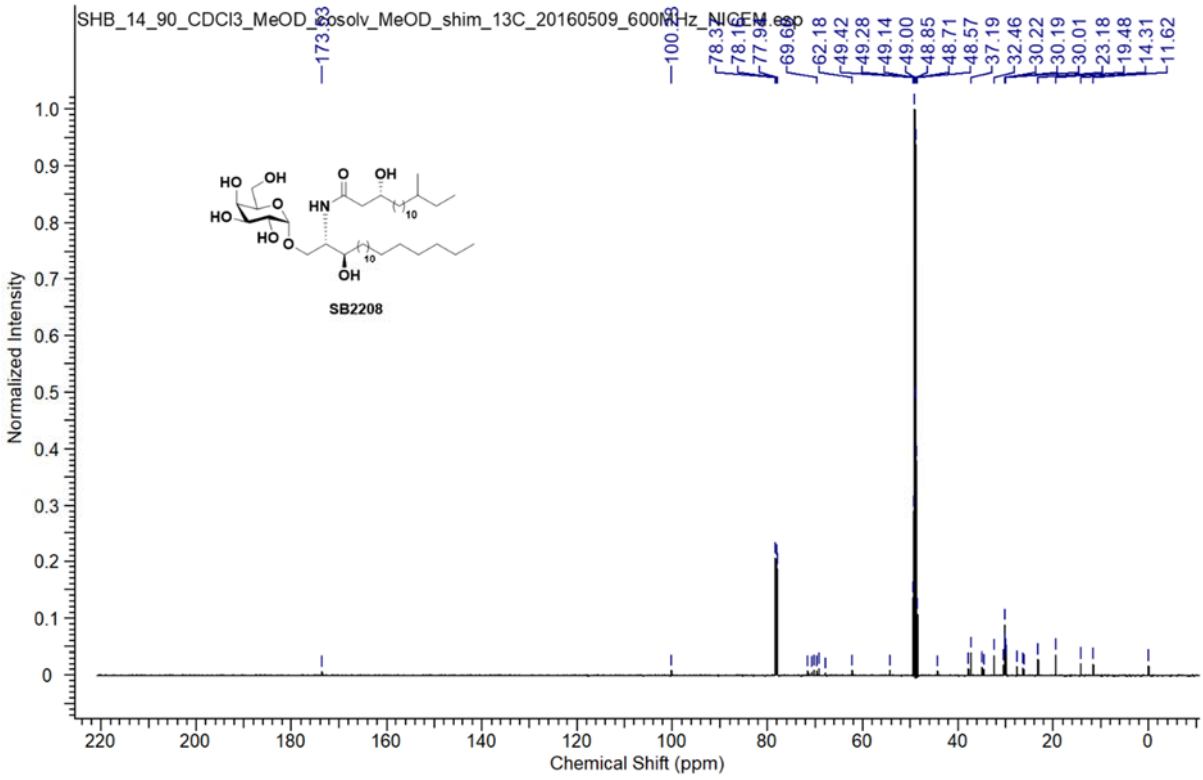
SB2207
Normalized Intensity
Chemical Shift (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_90_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp
SHB_14_90 1H NMR CDCl3/MeOD
SB2208
Normalized Intensity
Chemical Shift (ppm)
D:\Data(NMR&MALDI&p.I)\NICEM_NMR\SHB051016\7\SHB_14_90_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp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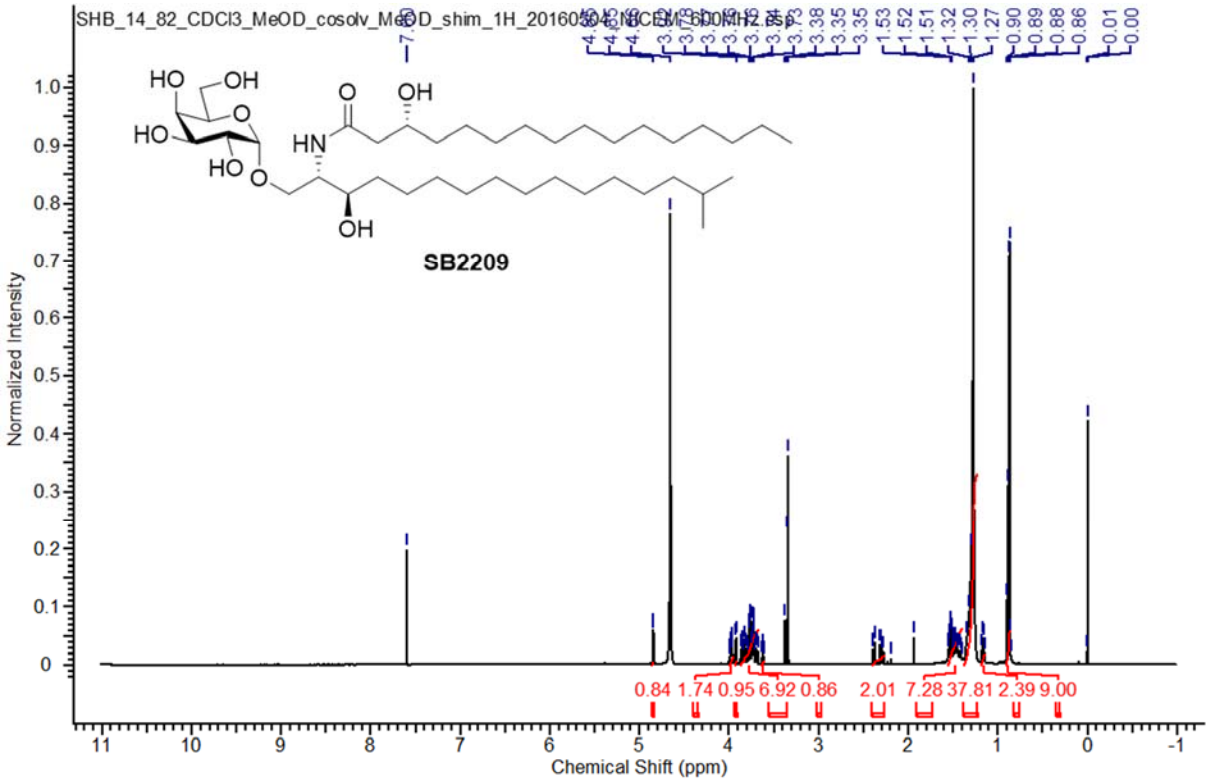
SB2208
Normalized Intensity
Chemical Shift (ppm)


SHB_14_82_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160504_NICEM_600MHz.esp
SB2209
Normalized Intensity
Chemical Shift (ppm)
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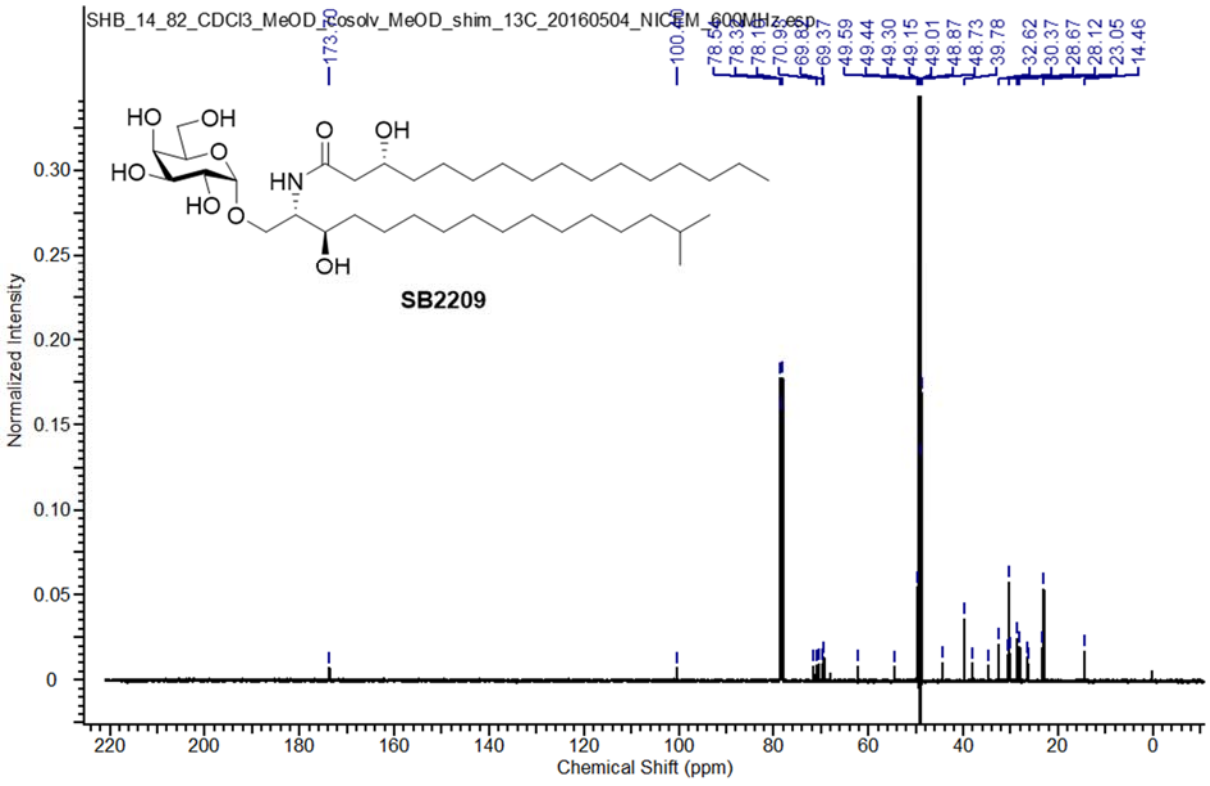
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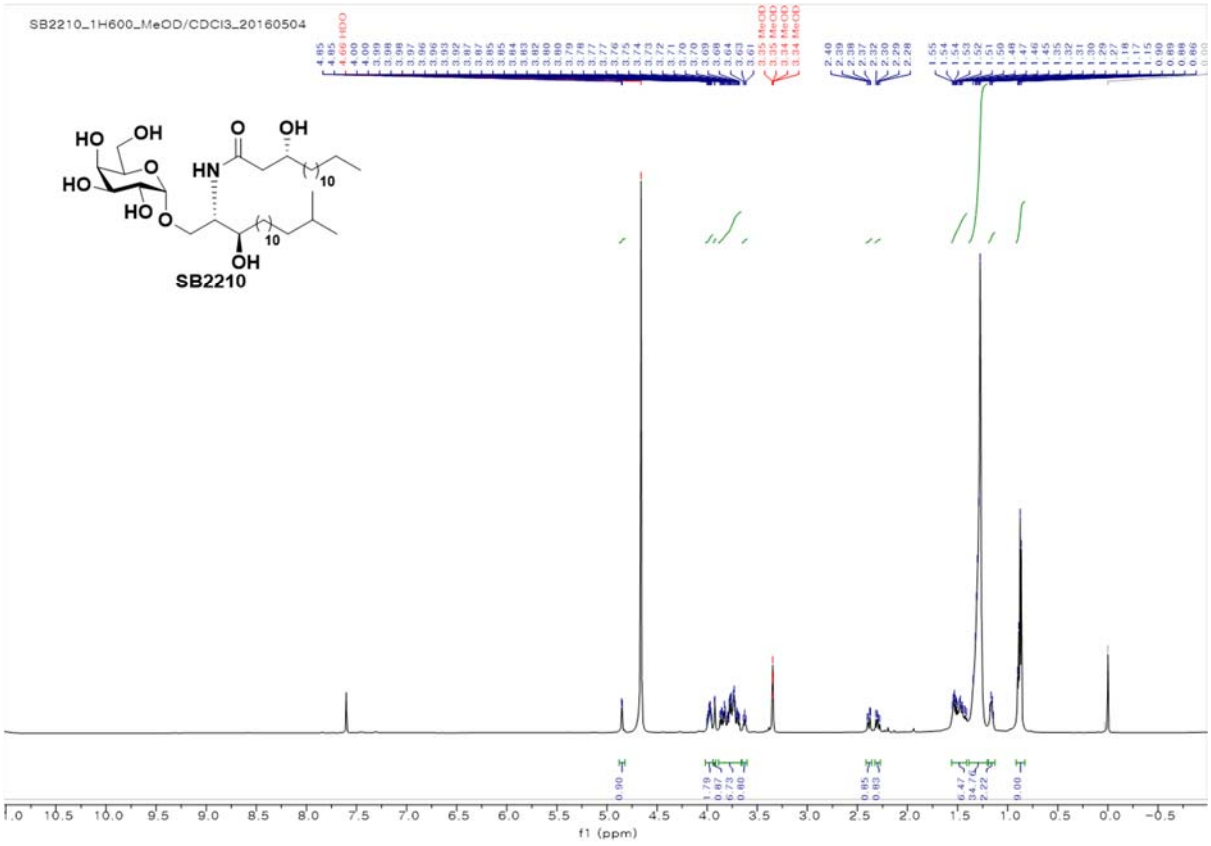
SB2209
Normalized Intensity
Chemical Shift (ppm)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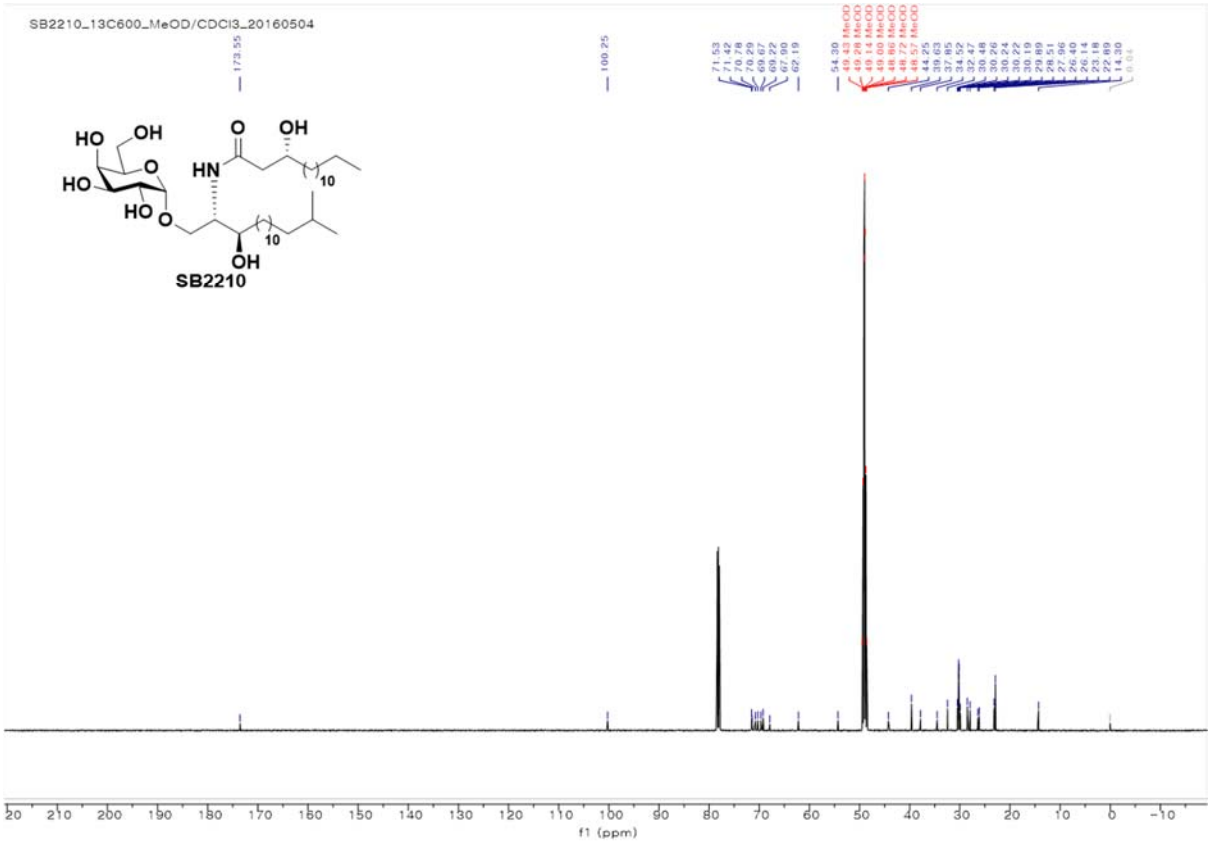
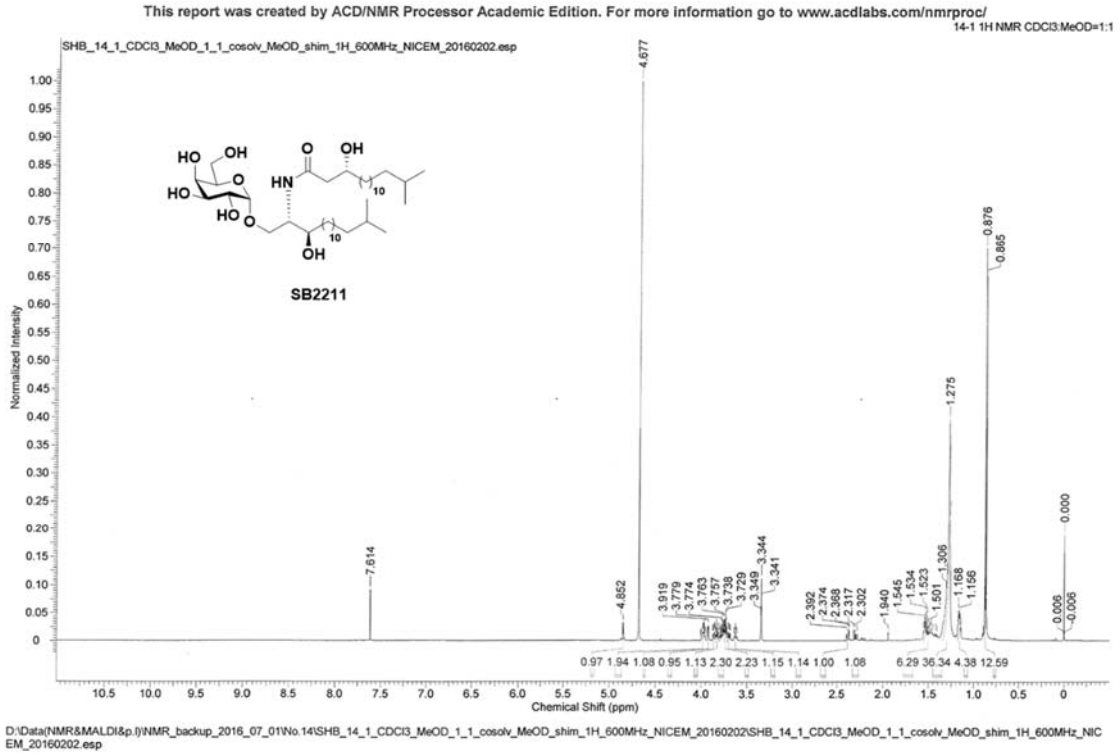
SB2210
f1 (ppm)


SB2210_13C600_MeOD/CDCl3_20160504
SB2210
f1 (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
14-1 1H NMR CDCl3:MeOD=1:1
SHB_14_1_CDCl3_MeOD_1_1_cosolv_MeOD_shim_1H_600MHz_NICEM_20160202.esp
SB2211
Normalized Intensity
Chemical Shift (ppm)
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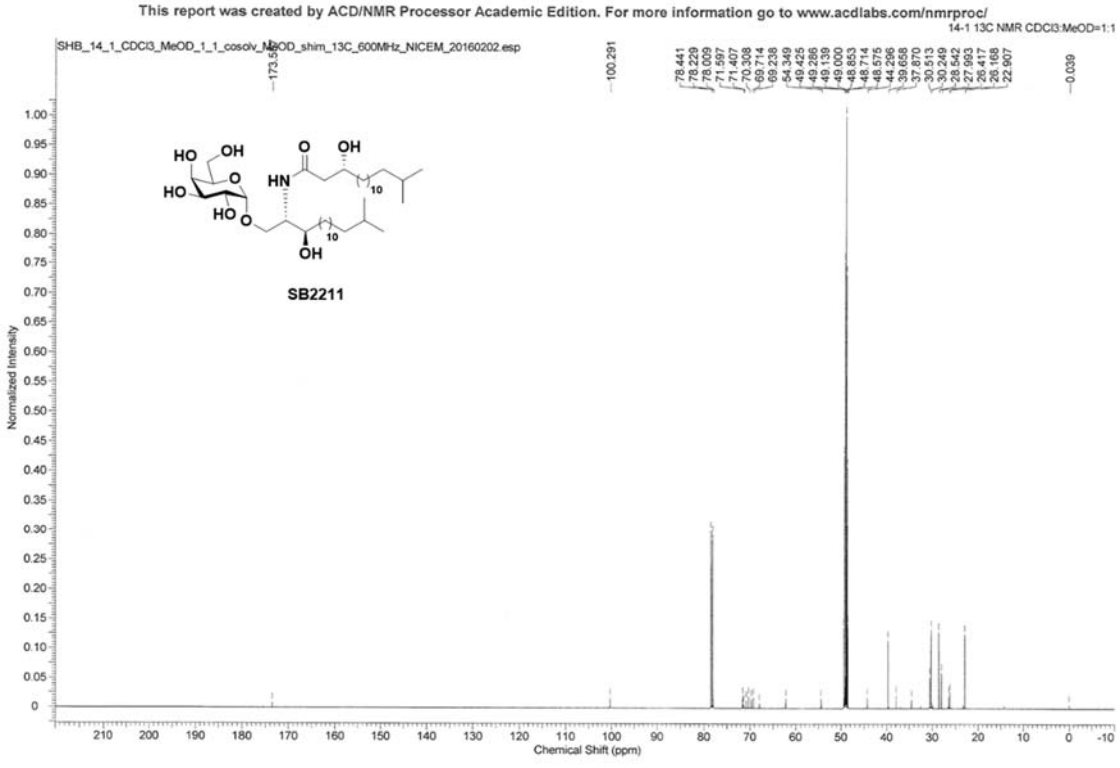
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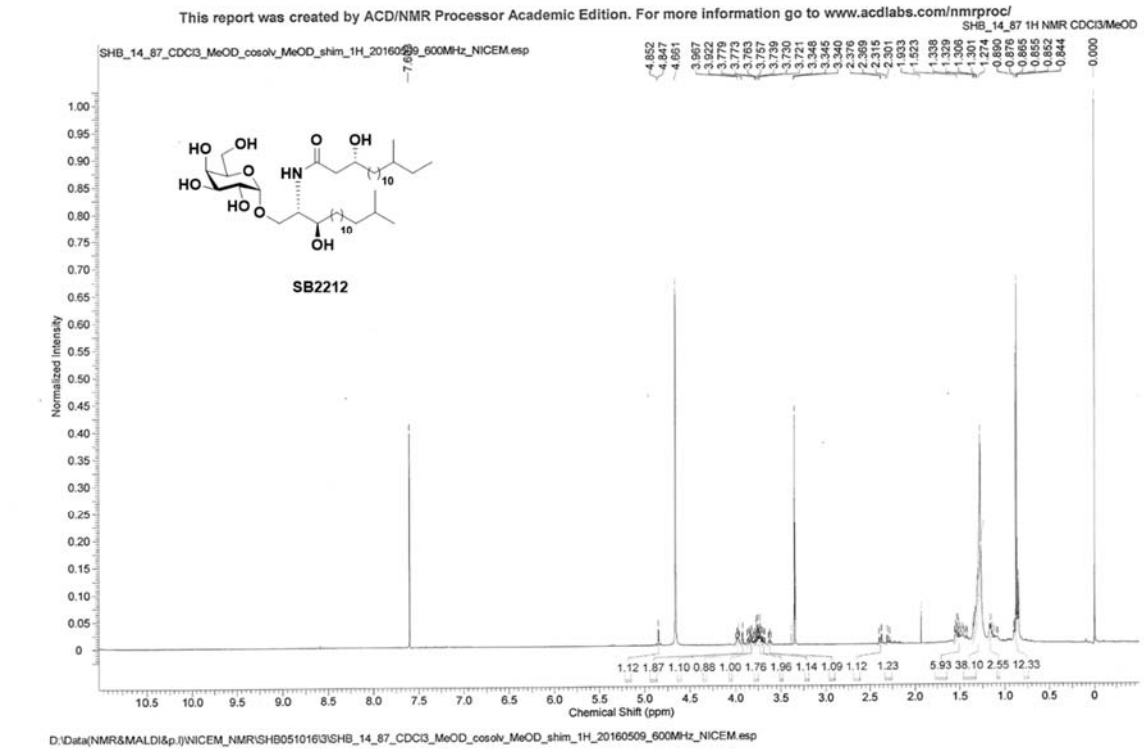
14-1 13C NMR CDCl3:MeOD=1:1
SHB_14_1_CDCl3_MeOD_1_1_cosolv_MeOD_shim_13C_600MHz_NICEM_20160202.esp
SB2211
Normalized Intensity
Chemical Shift (ppm)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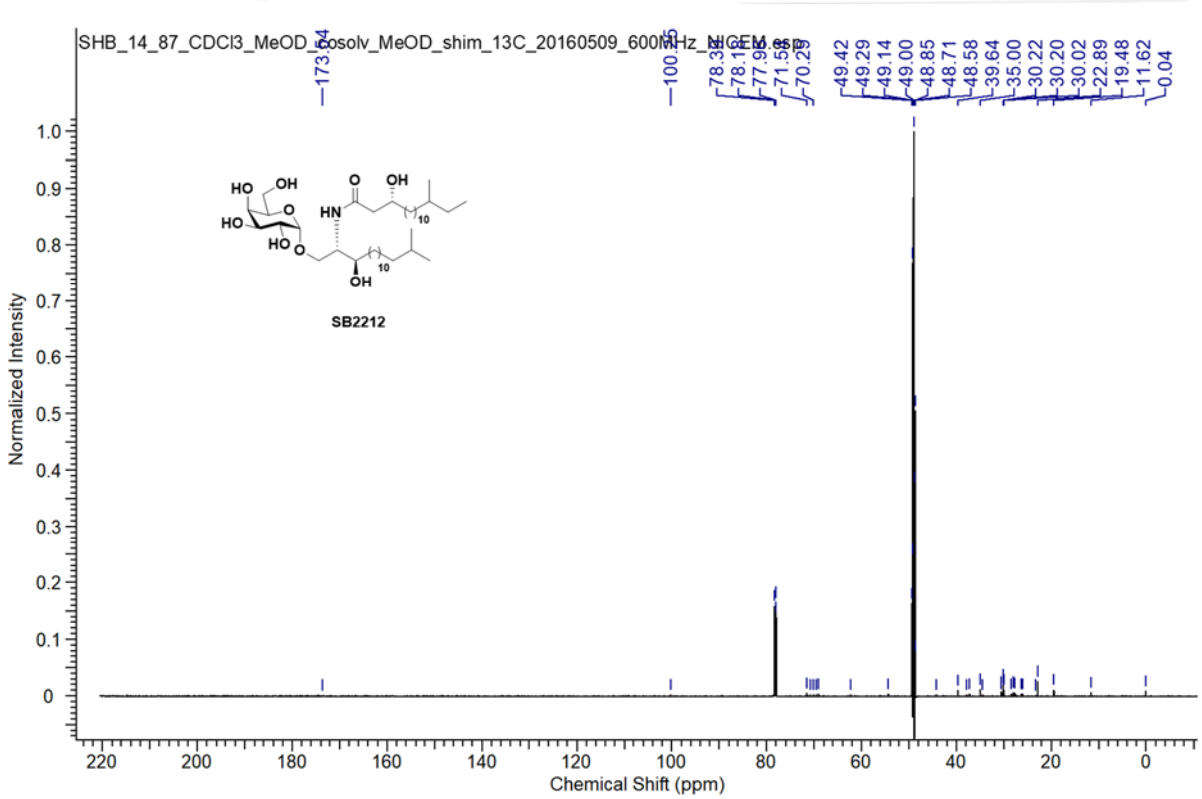
SHB_14_87 1H NMR CDCl3/MeOD
SHB_14_87_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp
SB2212
Normalized Intensity
Chemical Shift (ppm)
1.12 1.87 1.10 0.88 1.00 1.76 1.96 1.14 1.09 1.12 1.23 5.93 38.10 2.55 12.33
D:\Data(NMR&MALDI&p.l)\NICEM_NMR\SHB051016\3\SHB_14_87_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp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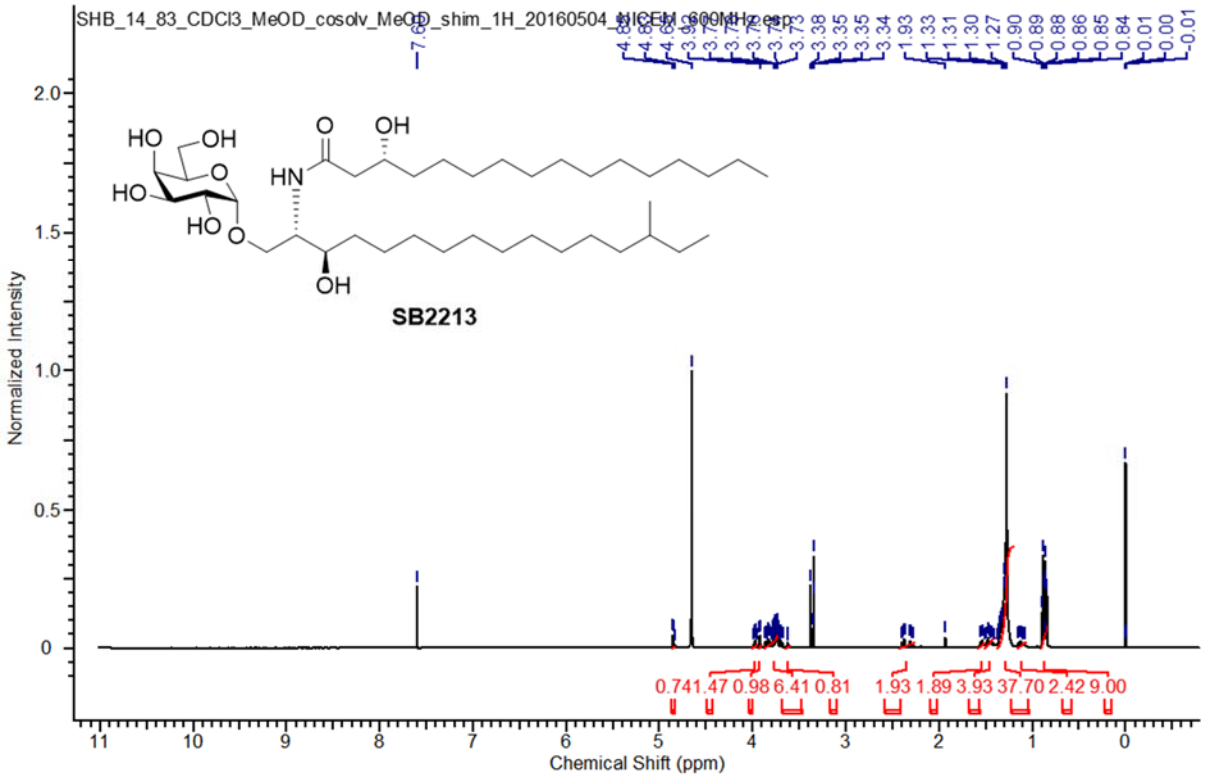
SB2212
Normalized Intensity
Chemical Shift (ppm)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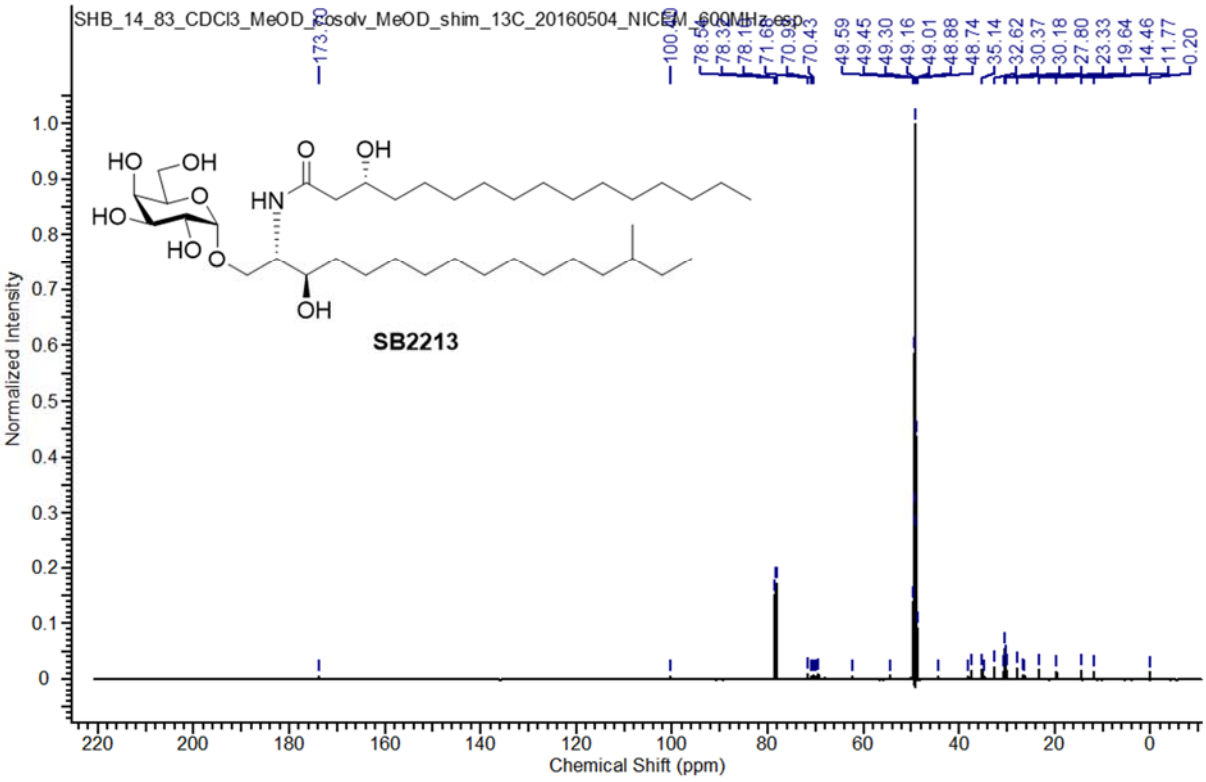
SB2213
Normalized Intensity
Chemical Shift (ppm)
0.74 1.47 0.98 6.41 0.81 1.93 1.89 3.93 37.70 2.42 9.00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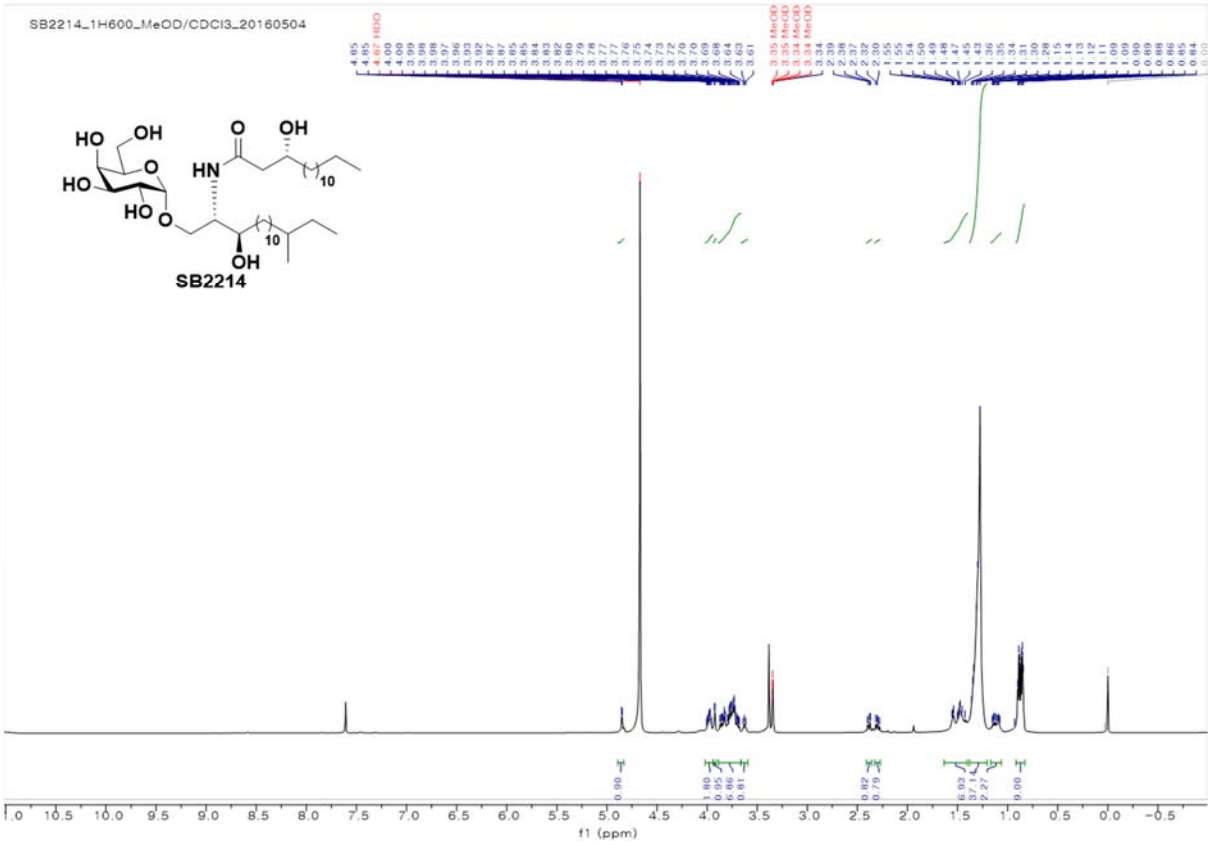
SB2213
Normalized Intensity
Chemical Shift (ppm)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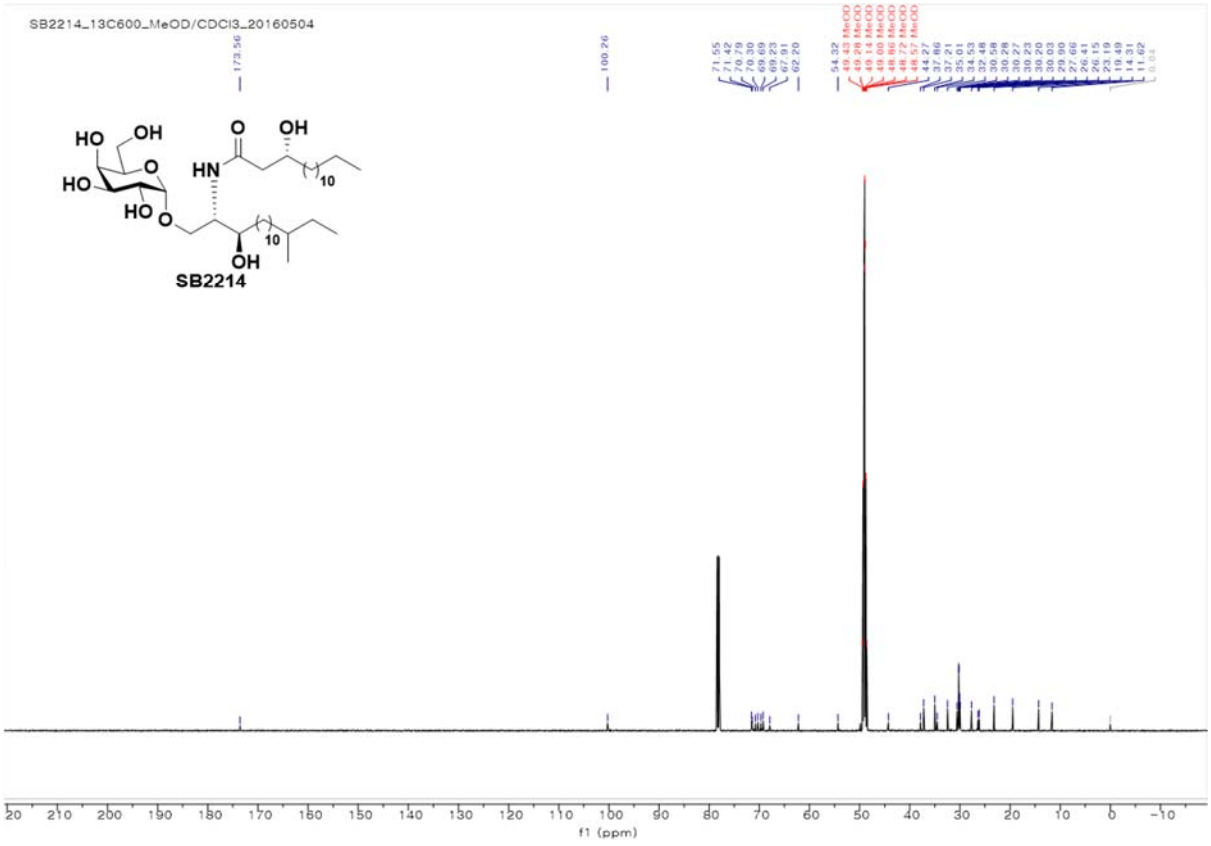
SB2214
f1 (ppm)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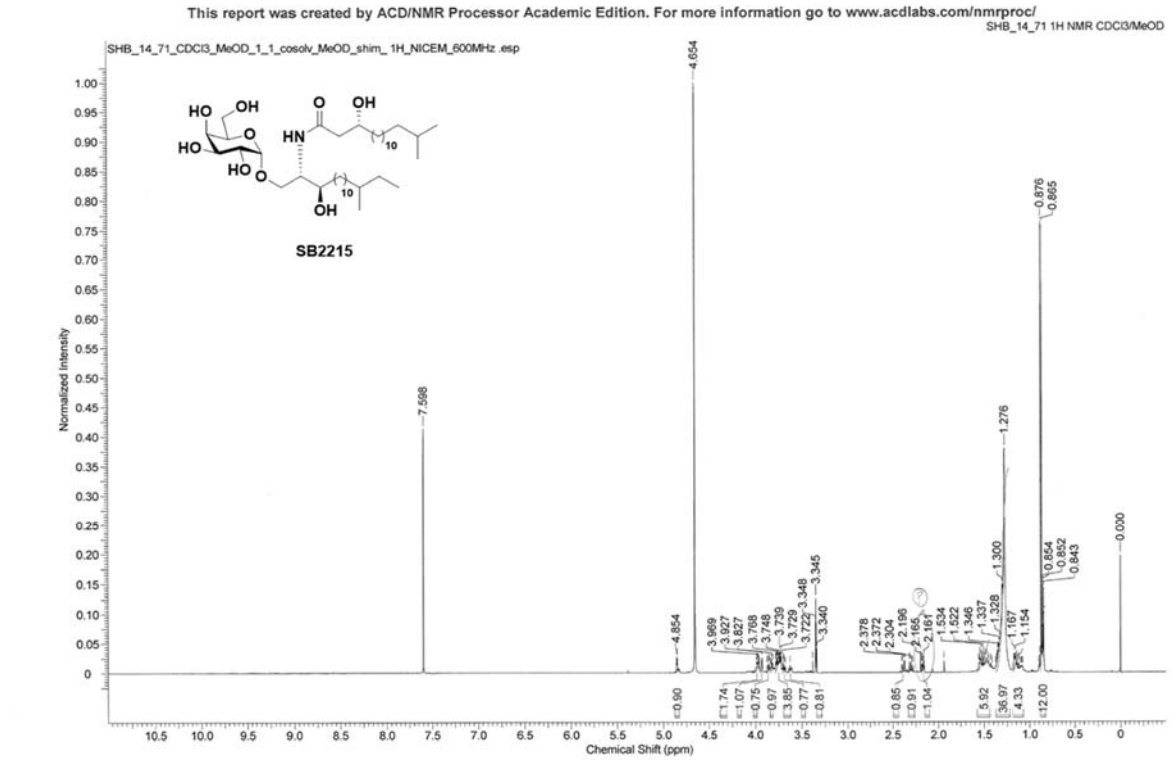
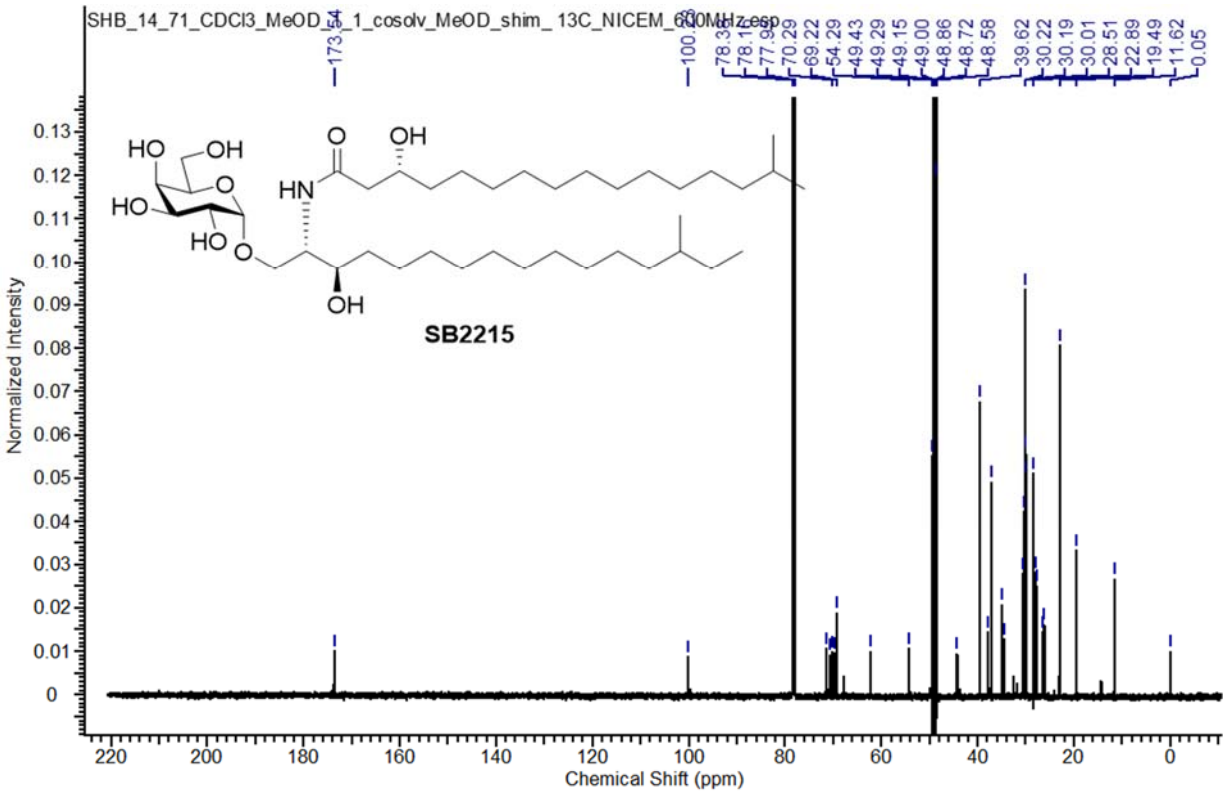
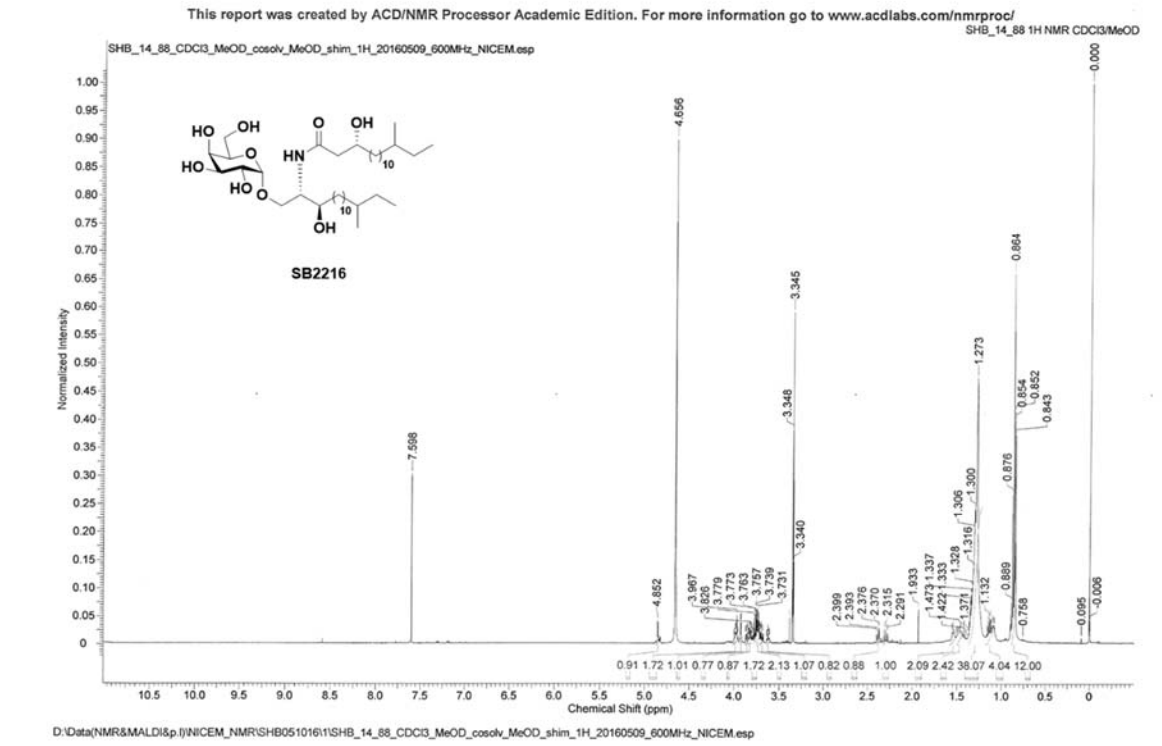
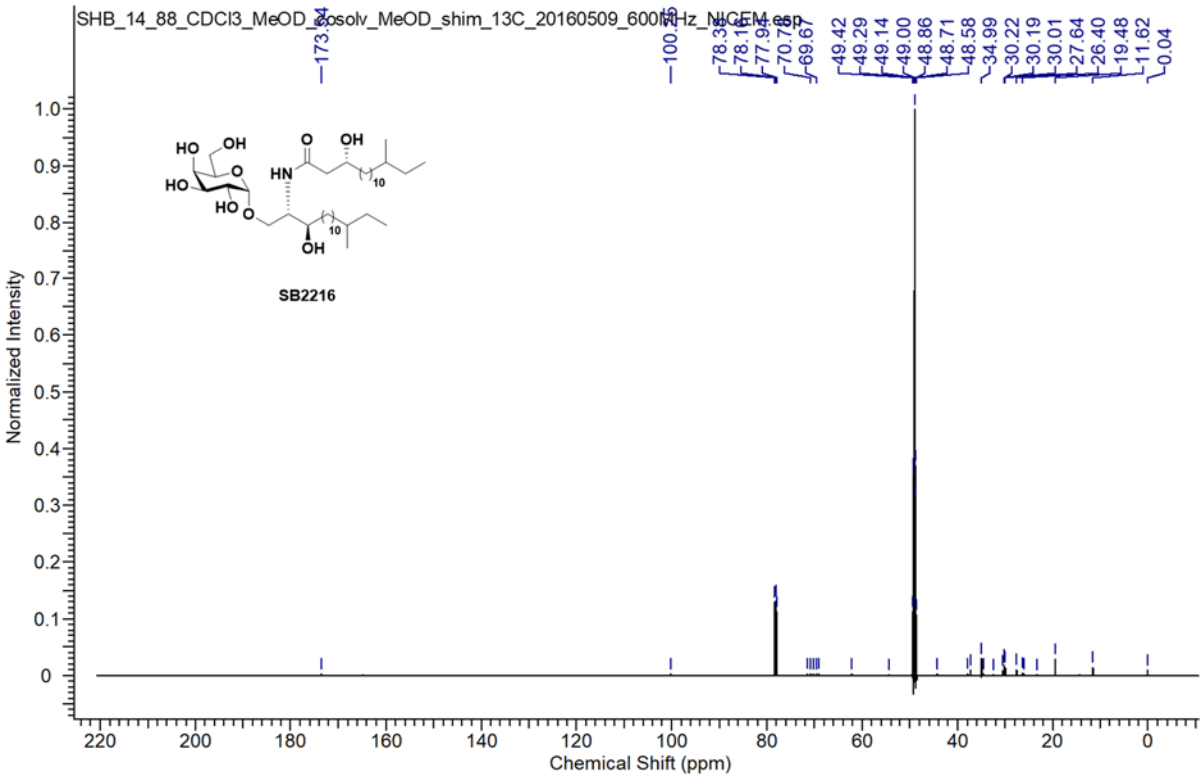
SB2214
f1 (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_71 1H NMR CDCl3/MeOD
SHB_14_71_CDCl3_MeOD_1_1_cosolv_MeOD_shim_ 1H_NICEM_600MHz .esp
SB2215
Normalized Intensity
Chemical Shift (ppm)


SHB_14_71_CDCl3_MeOD_1_1_cosolv_MeOD_shim_ 13C_NICEM_600MHz.esp
SB2215
Normalized Intensity
Chemical Shift (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
SHB_14_88 1H NMR CDCl3/MeOD
SHB_14_88_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp
SB2216
Normalized Intensity
Chemical Shift (ppm)
D:\Data(NMR&MALDI&p.I)\NICEM_NMR\SHB051016\1\SHB_14_88_CDCl3_MeOD_cosolv_MeOD_shim_1H_20160509_600MHz_NICEM.esp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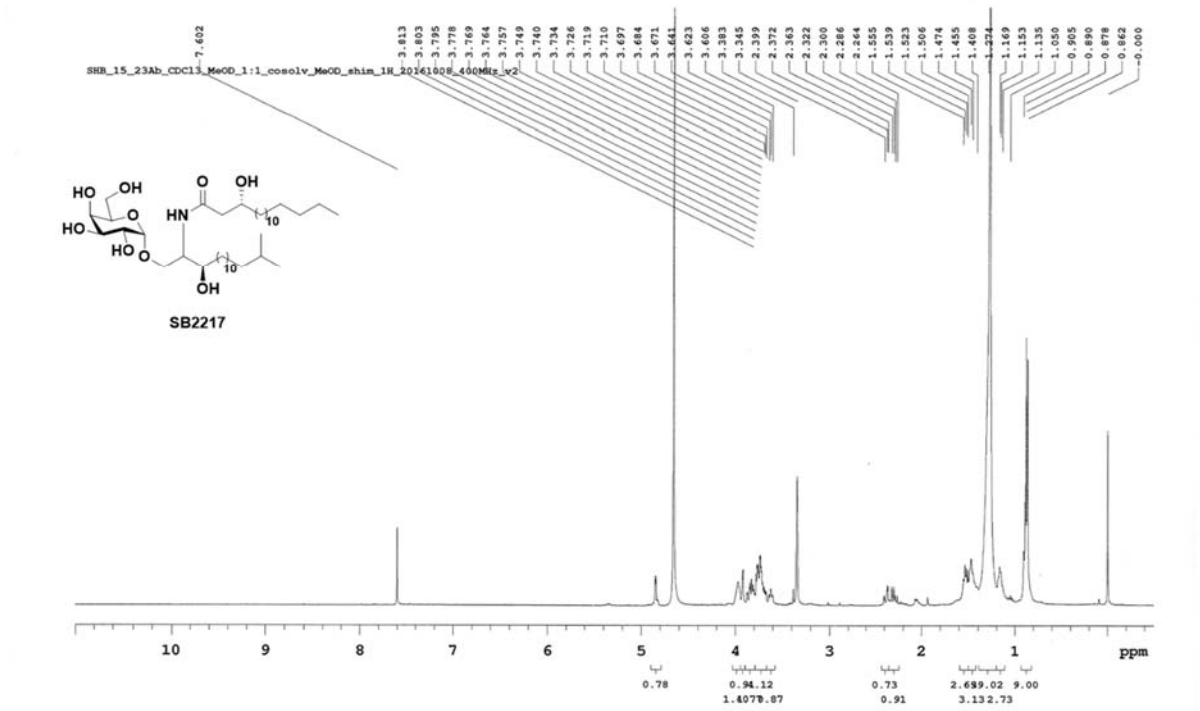
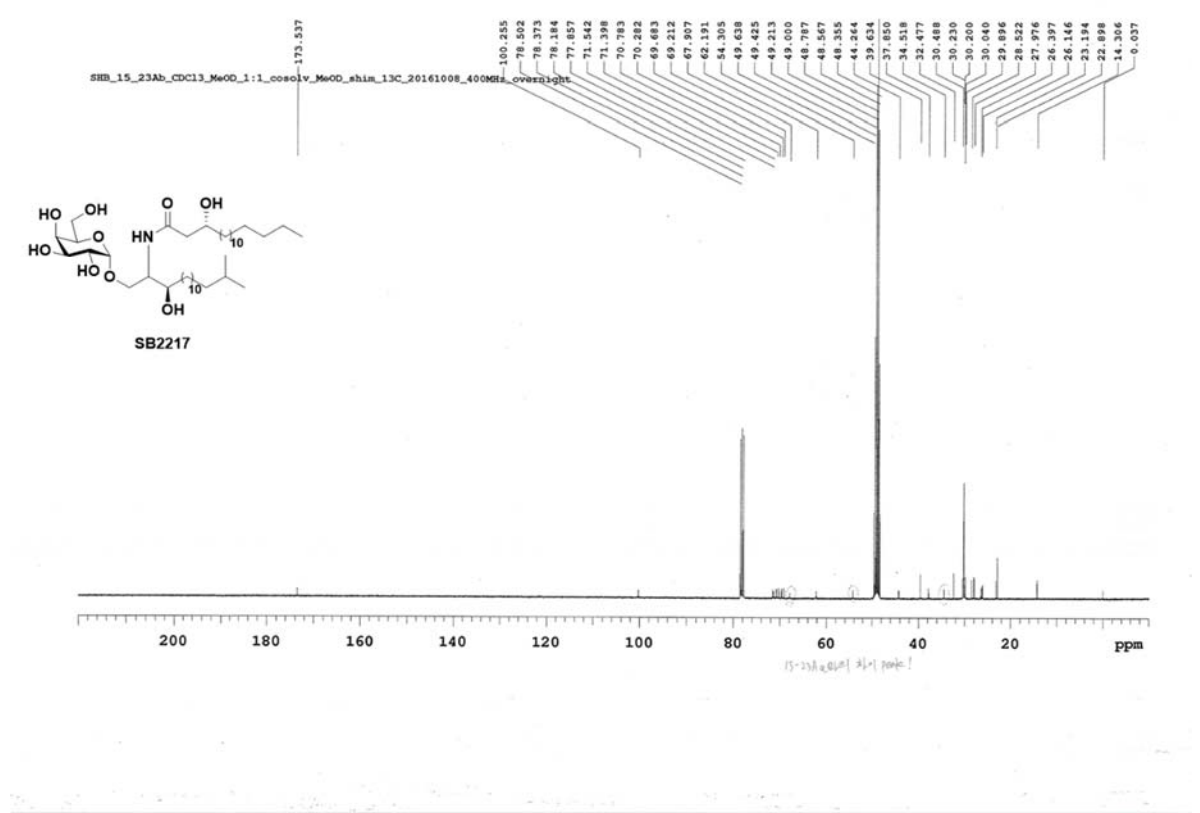
SB2216
Normalized Intensity
Chemical Shift (ppm)


SB2217
ppm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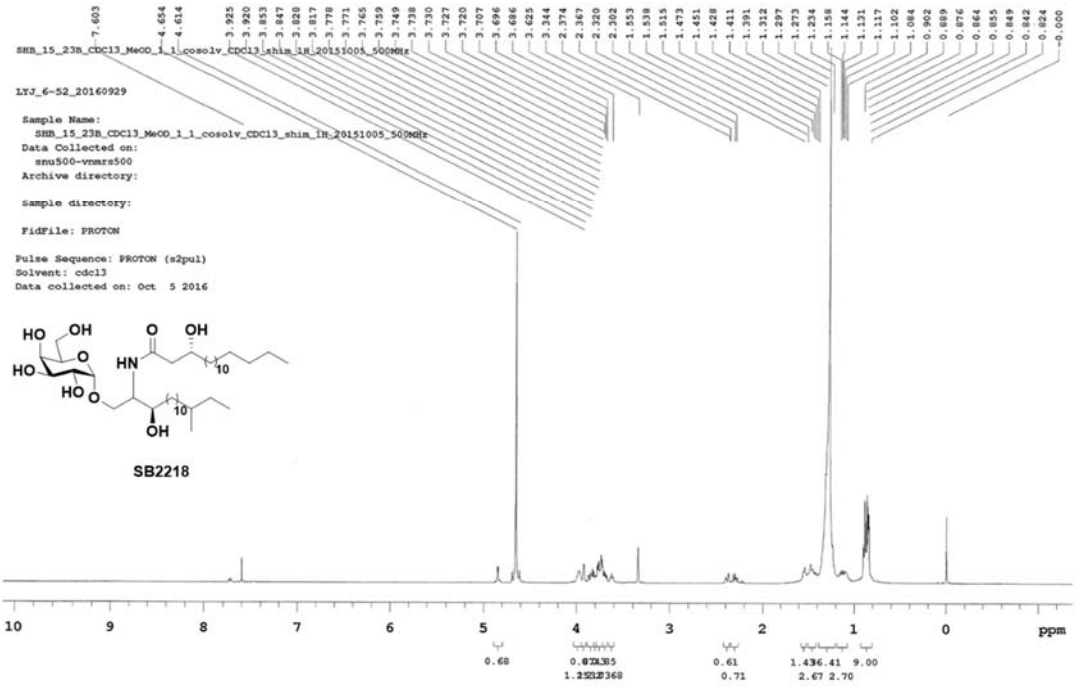
ppm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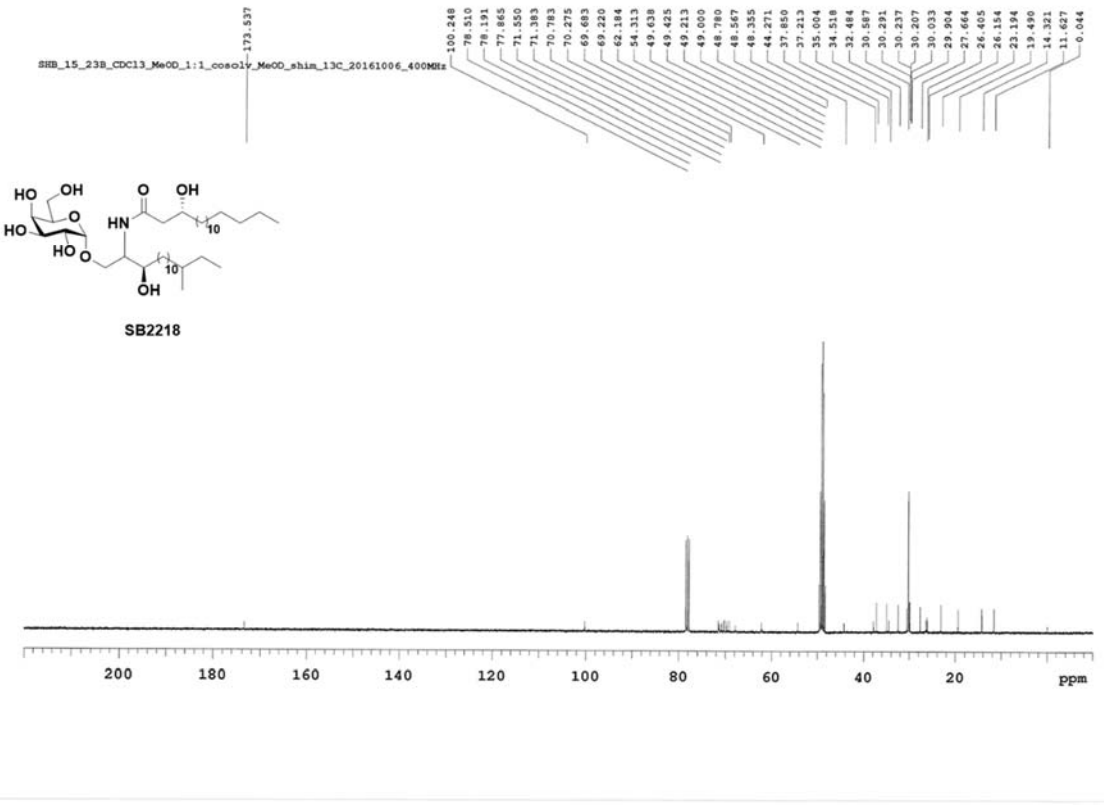
LYJ_6-52_20160929
Sample Name:
SHB_15_23B_CDCl3_MeOD_1_1_cosolv_CDCl3_shim_1H_20151005_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 5 2016
SB2218
ppm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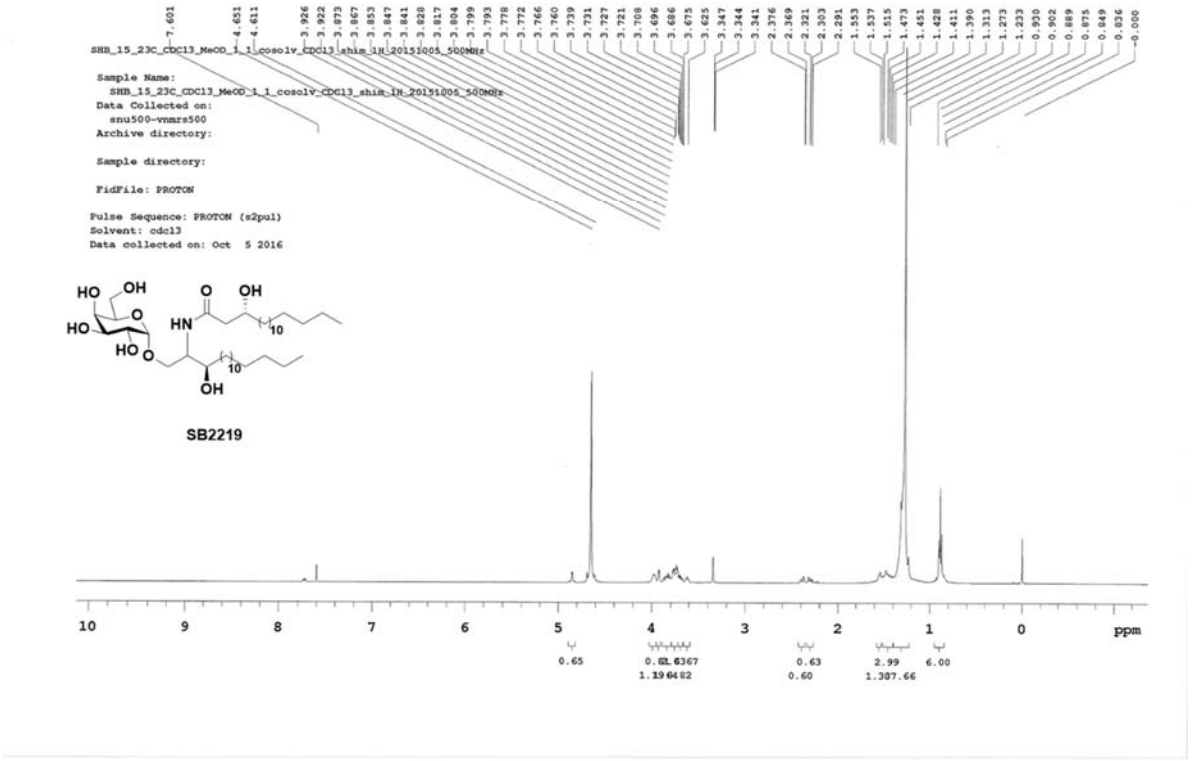
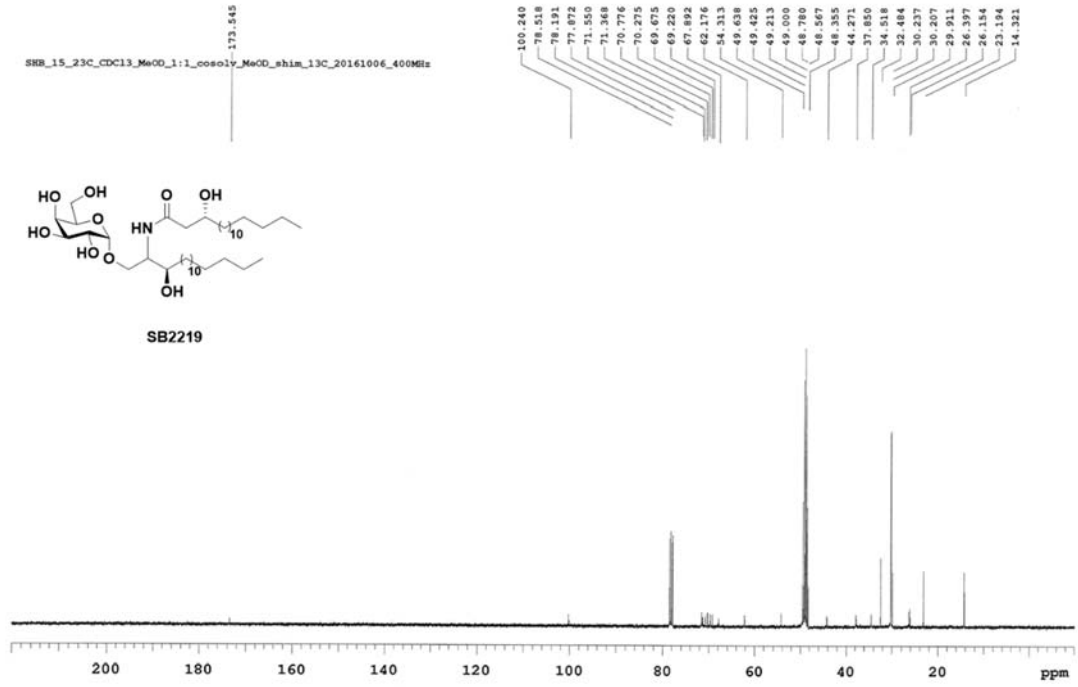
SB2218
ppm


SHB_15_23C_CDCl3_MeOD_1_1_cosolv_CDCl3_shim_1H_20151005_500MHz
Sample Name:
SHB_15_23C_CDCl3_MeOD_1_1_cosolv_CDCl3_shim_1H_20151005_500MHz
Data Collected on:
snu500-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 5 2016
SB2219
ppm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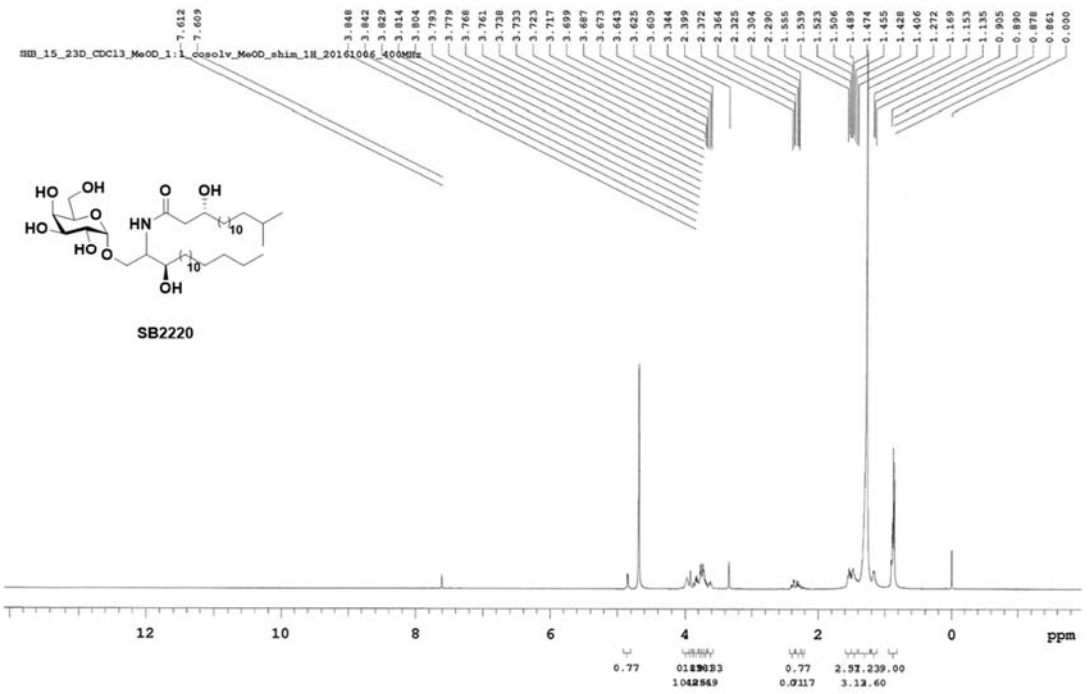
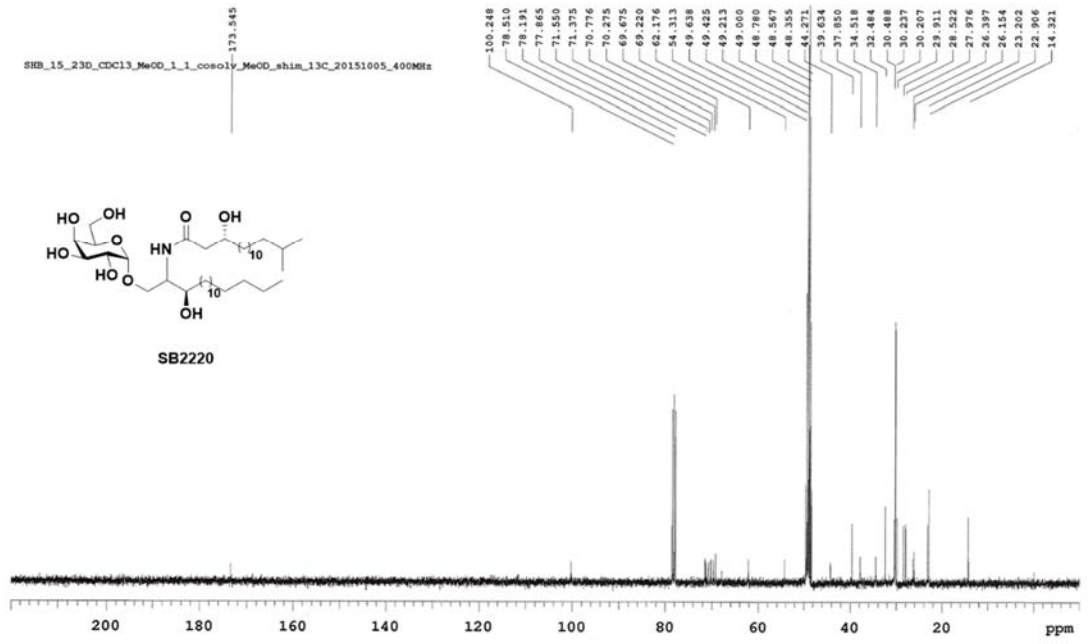
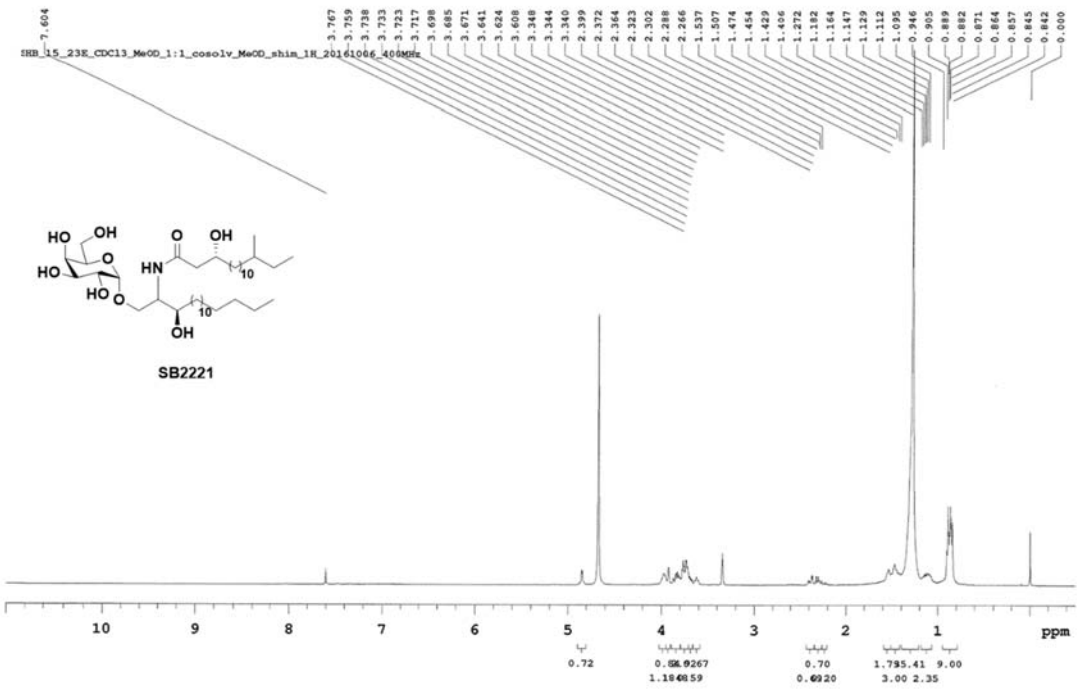
SB2219
ppm


SB2220
ppm


SB2220
ppm


SB2221
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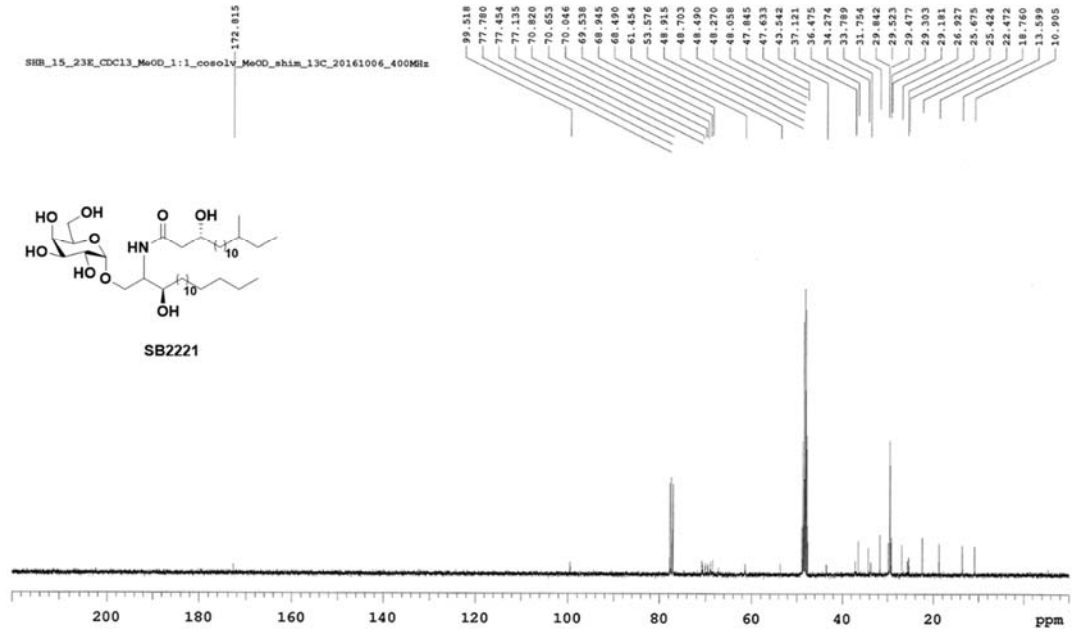
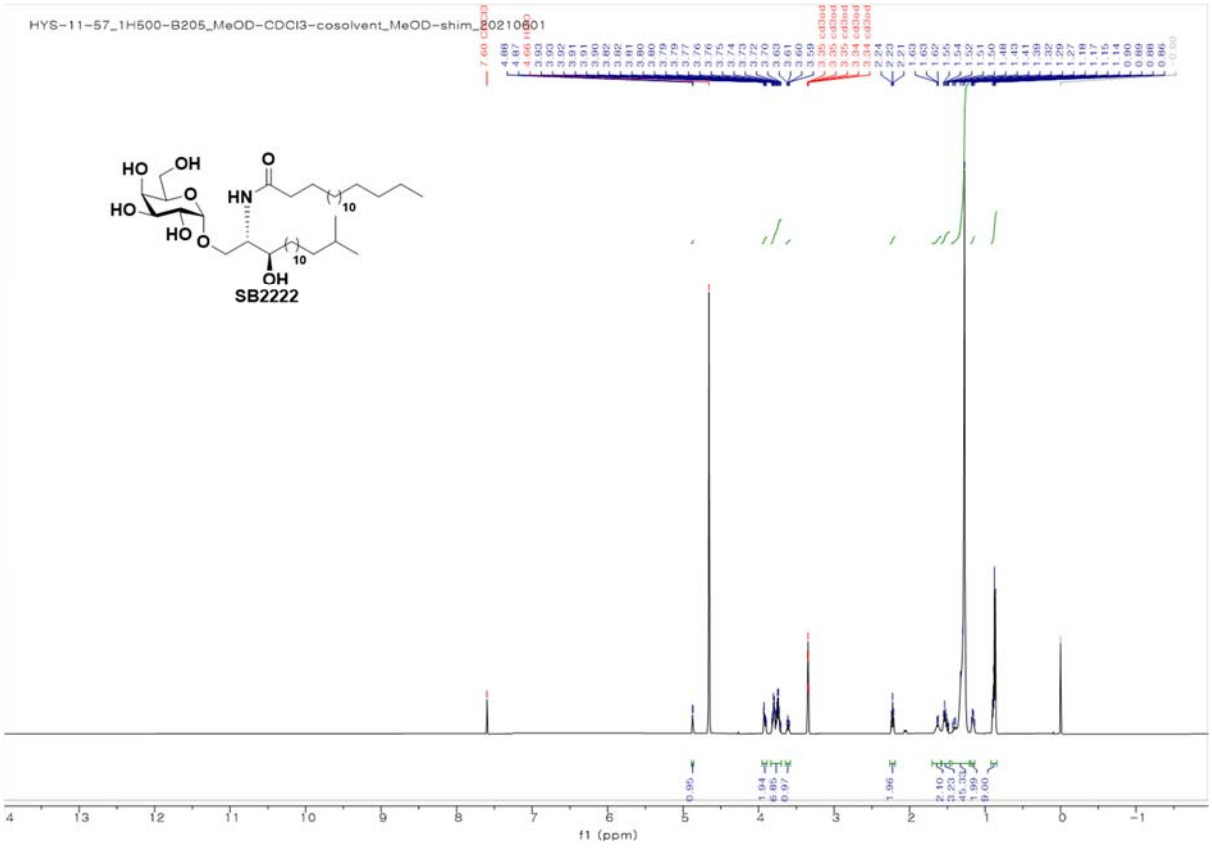
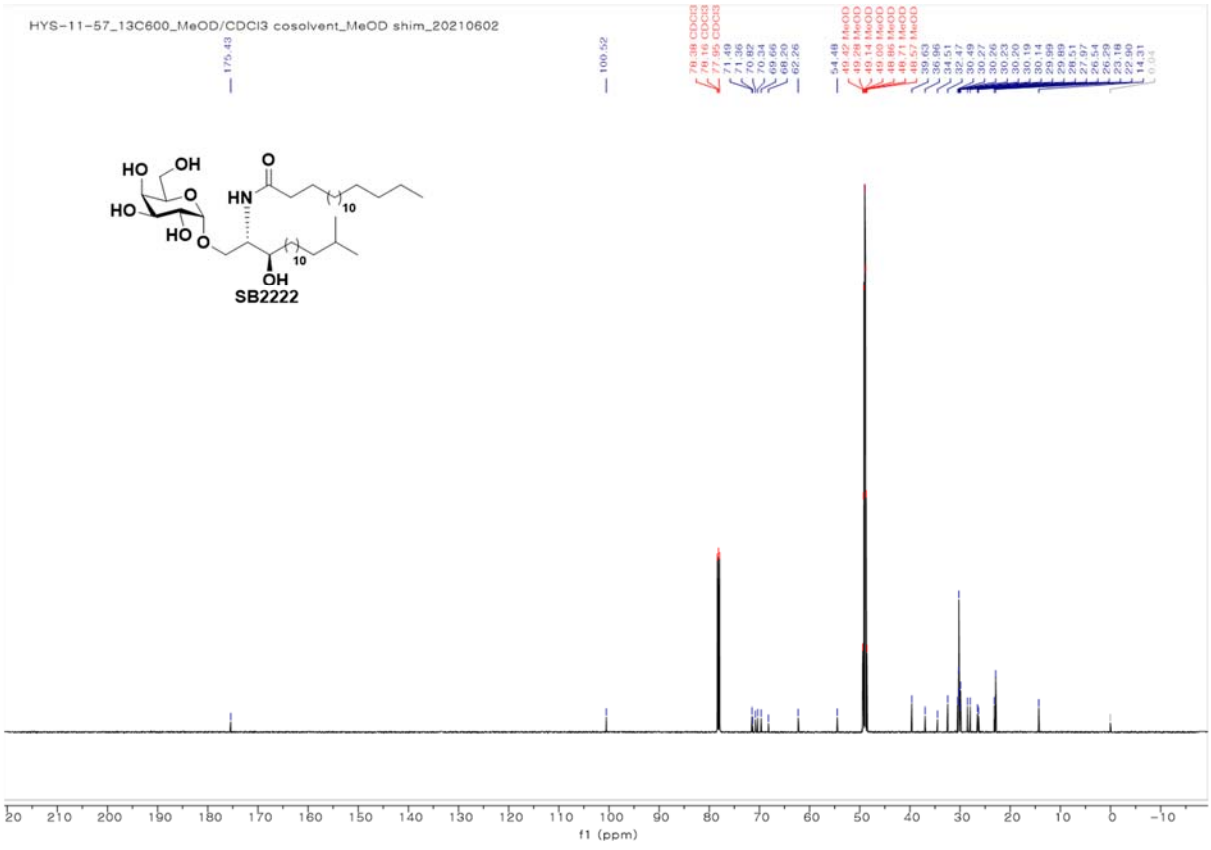
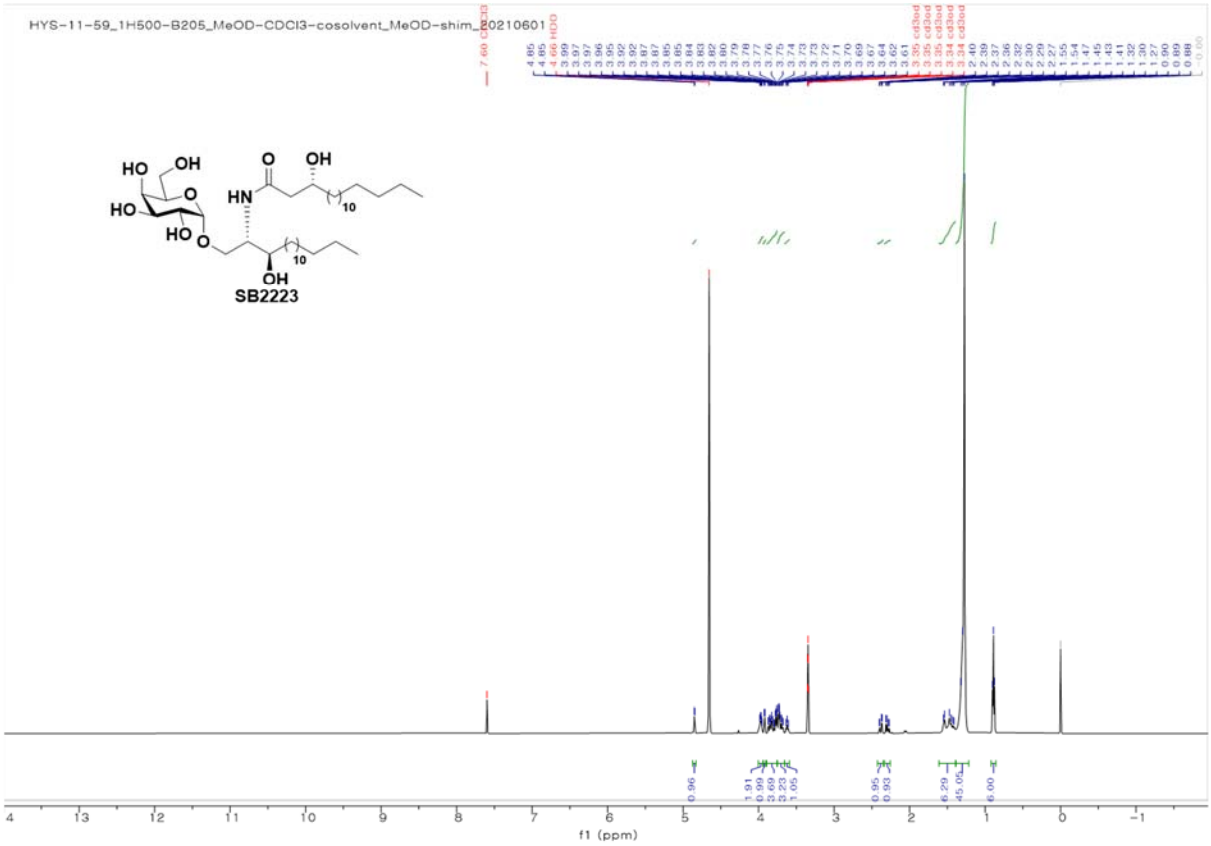
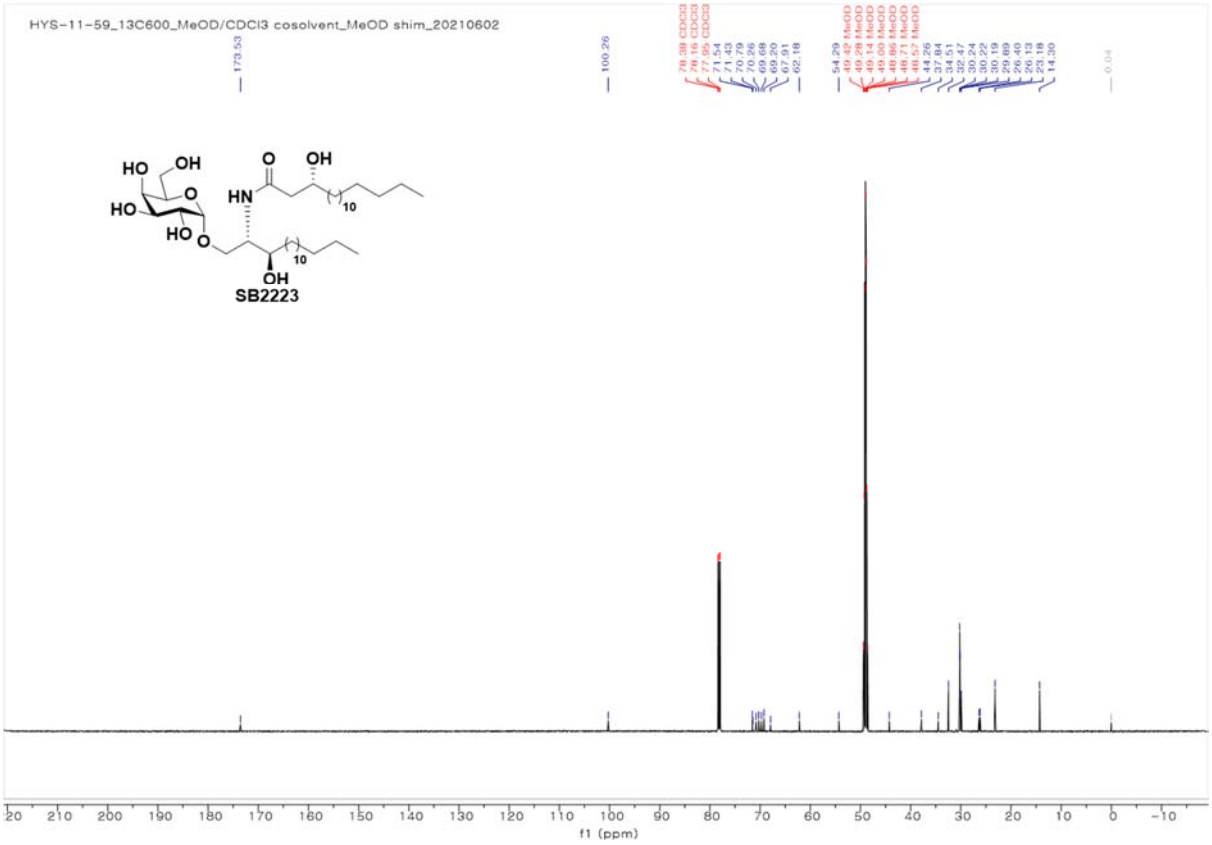

SB2221
ppm


HYS-11-57_1H500-B205_MeOD-CDCl3-cosolvent_MeOD-shim_20210601
HO
OH
O
HO
HO
O
HN
10
10
OH
SB2222
f1 (ppm)


HYS-11-57_13C600_MeOD/CDCl3 cosolvent_MeOD shim_20210602
HO
OH
O
HO
HO
O
HN
10
10
OH
SB2222
f1 (ppm)


HYS-11-59_1H500-B205_MeOD-CDCl3-cosolvent_MeOD-shim_20210601
SB2223
f1 (ppm)


HYS-11-59_13C600_MeOD/CDCl3 cosolvent_MeOD shim_20210602
SB2223
f1 (ppm)