< Supporting Information >

Improved Th17 Selectivity of *α*-Galactosylceramide via Noncovalent Interactions with Diether Moiety

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1. Supplementary Figure and Table

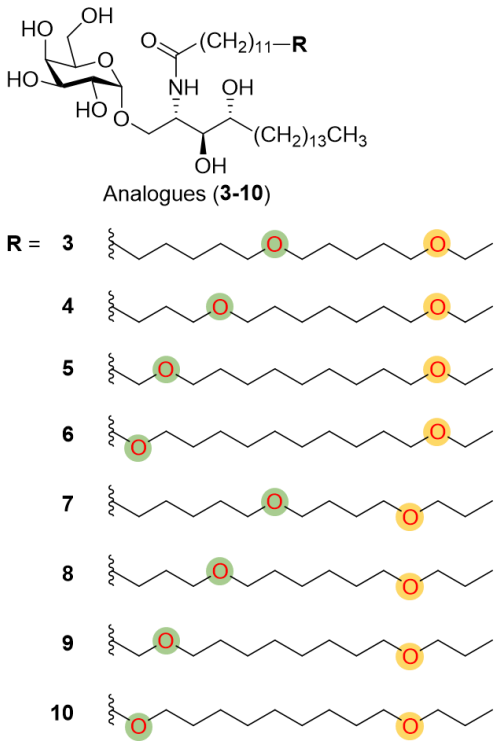


Table S1. Docking score of compounds **1**–**10** via molecular modeling

Compound	Docking score[a]
6	-39.7129
5	-38.8957
10	-38.8436
9	-31.5776
4	-29.9297
8	-27.7277
1 (KRN7000)	-25.5371
3	-24.2426
7	-21.5563
2 (OCH)	N/A[b]

[a]Docking score by CDOCKER interaction energy
[b]**2** (OCH) was filtered or failed to dock.

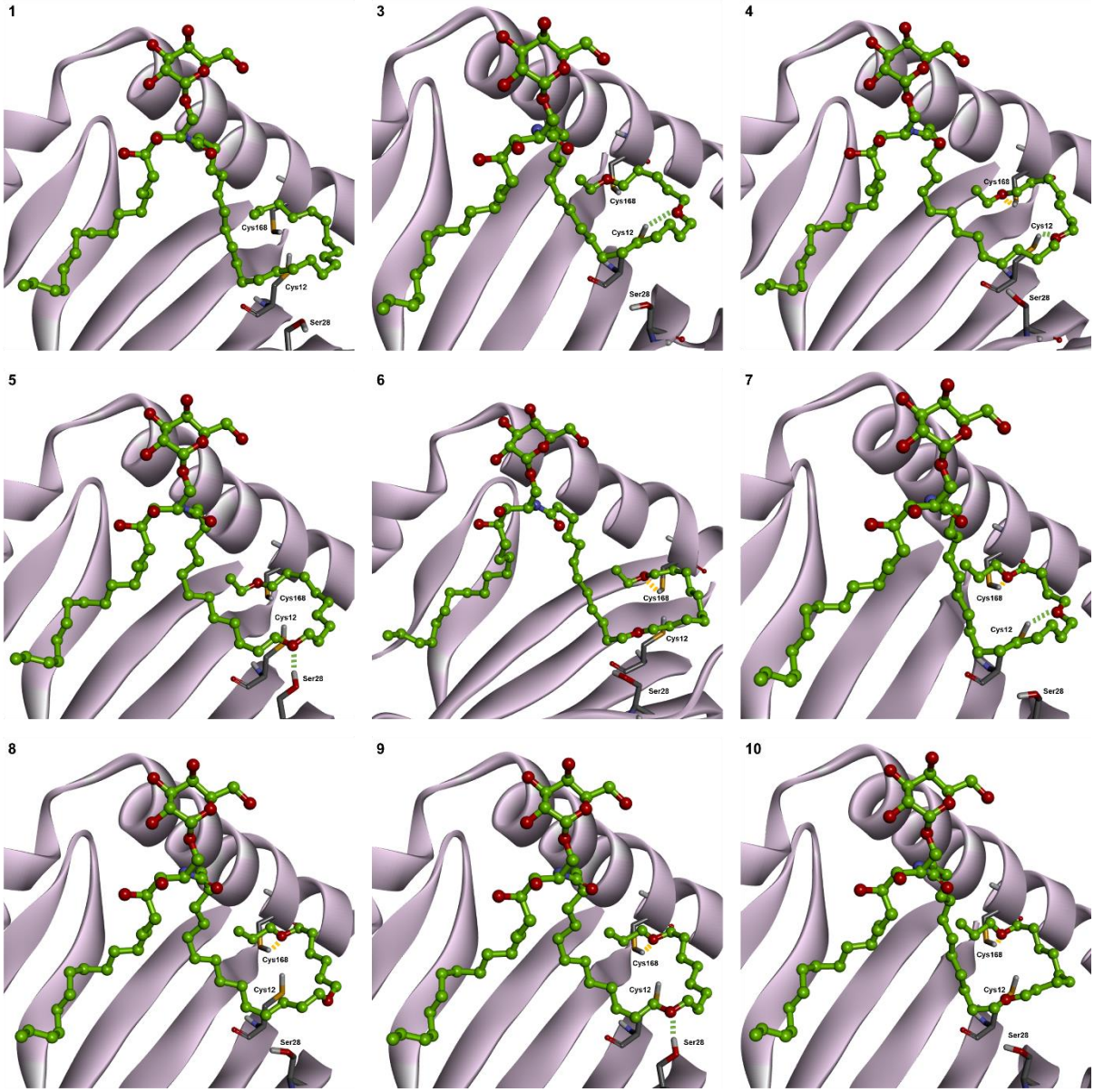


Figure S1. Optimized binding modes of compounds **1** and **3–10** within the binding pocket of mCD1d via *in situ* ligand minimization (PDB code: 3HE6). The potential hydrogen-bonding interactions are presented with green and yellow dotted lines.

2. General Experimental Information

A. Molecular modeling

Preliminary evaluation of α-GalCer analogues (**3–10**) was performed with Discovery Studio Client v16.1.0.15350. The co-crystal structure of mCD1d and KRN7000 (**1**) (PDB code: 3HE6) was utilized. Polar hydrogens in the side chain of Cys12, Ser28 and Cys168 were rotated to induce hydrogen-bonding interactions with ligands. The binding site was defined from receptor cavities. LigandFit module was used for docking and docking scores of each compound were summarized in Table S1. With ligands docked by LigandFit module, *in situ* ligand minimization protocol was performed to get the optimized binding mode of ligands within the binding pocket of mCD1d and find out potential hydrogen-bonding interactions between ligands and mCD1d.

B. Materials

KRN7000 (**1**) (Purity ≥ 96% by ^{1}H NMR) and OCH (**2**) (Purity ≥ 95% by ^{1}H NMR) were purchased from AdipoGen Life Sciences. All commercially available reagents for organic synthesis were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd, or ThermoFisher Scientific and used without further purification unless otherwise specified. Solvents were purchased from commercial vendors and used without further purification unless otherwise mentioned. Dry solvents were prepared using ultimate solvent purification system CT-SPS-SA [Glass Contour]. The progress of reaction was monitored using thin-layer chromatography (TLC) (silica gel 60, F_{254} 0.25 mm). Components on TLC were visualized by treating the TLC plates with *p*-anisaldehyde, $KMnO_4$, or phosphomolybdic acid followed by heating. The compounds were purified by flash column chromatography on silica-gel (230–400 mesh). The eluent used for purification is reported in parentheses.

C. Compound characterization

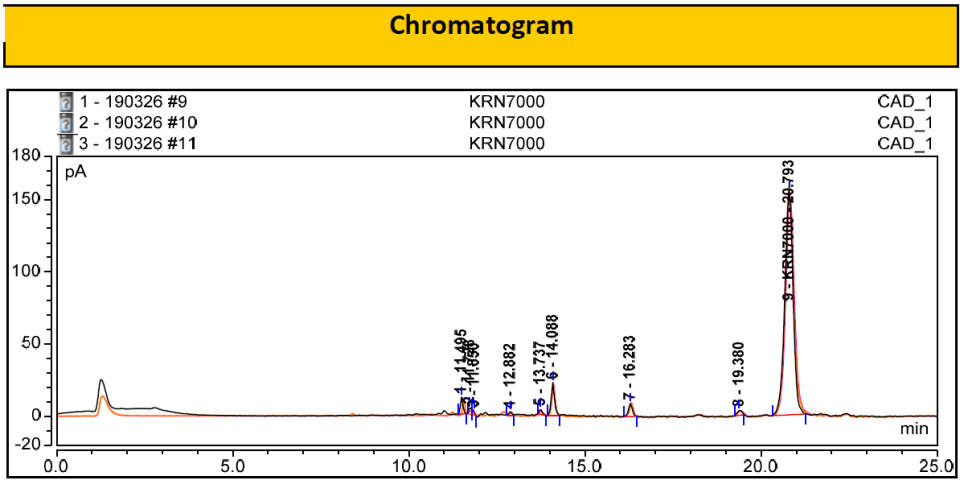
The optical rotations were measured by JP/P-1030 [JASCO] using a sodium lamp (D line, 589 nm). ^{1}H and ^{13}C NMR spectra were obtained on Bruker DRX-300 [Bruker Biospin], Agilent 400-MR DD2 [Agilent Technologies], or Varian Inova-500 [Varian Associates]. Chemical shifts were reported in parts per million (δ, ppm). ^{1}H NMR spectra were calibrated using the residual solvent peak ($CDCl_3$ 7.26 ppm; CD_2Cl_2 5.32 ppm) or tetramethylsilane (TMS, 0.00 ppm) as an internal standard. ^{13}C NMR spectra were calibrated using the residual solvent peak ($CDCl_3$ 77.16 ppm or 77.23 ppm; CD_2Cl_2 53.84 ppm; CD_3OD 49.00 ppm). Multiplicity was noted as: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublet); dt (doublet of triplet); td (triplet of doublet); br s (broad singlet), etc. Coupling constants were reported in Hz. Low-resolution mass spectrometry (LRMS) was obtained by LCMS-2020 [Shimadzu] and LTQ [Thermo Fisher Scientific] using electron spray ionization (ESI). High-resolution mass spectrometry (HRMS) of final compounds (**3–10**) was confirmed by Ultra High Resolution ESI Q-TOF mass spectrometer [Bruker] from *Organic Chemistry Research Center* at Sogang University. The purity of KRN7000 (**1**) and OCH (**2**) was measured by Vanquish DUO Flex [ThermoFisher Scientific].

D. Purity of compounds 1–10

The purity of α-GalCer analogues (**3–10**) was ≥ 95% based on ^{1}H NMR spectra. The purity of KRN7000 (**1**) and OCH (**2**) from AdipoGen Life Sciences was claimed as ≥ 96% and ≥ 95% by ^{1}H NMR, respectively. To check the purity of the commercial KRN7000 (**1**) and OCH (**2**), HPLC equipped with charged aerosol detector (CAD) was used. Chromatograms of KRN7000 (**1**) and OCH (**2**) are shown with detailed conditions of HPLC and CAD. In average, KRN7000 (**1**) showed 87.3% purity and OCH (**2**) showed 79.5% purity from three independent measurements. Although the purity of the commercial KRN7000 (**1**) and OCH (**2**) was less than ≥ 95%, the active ingredient of the compounds was still major (around 80% or higher). Thus, we used the commercial KRN7000 (**1**) and OCH (**2**) without further purification and the biological evaluations using these commercial compounds with that purity still provided the desired activity for our study.

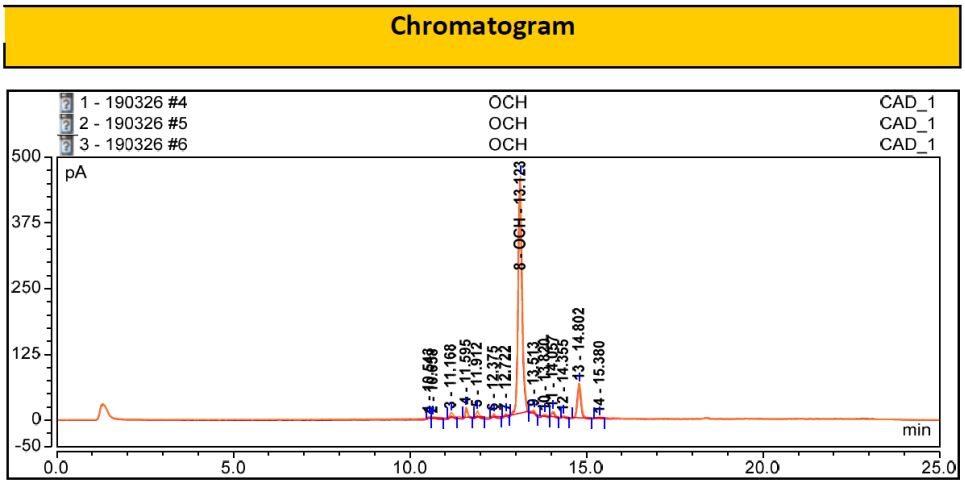
Chromatograms

KRN7000 (**1**)



No.	Injection Name	Ret.Time min CAD_1 KRN7000	Area pA*min CAD_1 KRN7000	Height pA CAD_1 KRN7000	Amount CAD_1 KRN7000	Rel.Area % CAD_1 KRN7000	Peak Type CAD_1 KRN7000
9	KRN7000	20.793	42.573	155.510	n.a.	87.69	BMB
10	KRN7000	20.815	43.938	151.537	n.a.	87.51	BMB
11	KRN7000	20.793	44.273	159.803	n.a.	86.77	BMB
	Average:	20.801	43.595	155.617	#DIV/0!	87.322	#DIV/0!
	Rel.Std.Dev:	0.060 %	2.066 %	2.657 %	#DIV/0!	0.560 %	#DIV/0!

OCH (**2**)



No.	Injection Name	Ret.Time min CAD_1 OCH	Area pA*min CAD_1 OCH	Height pA CAD_1 OCH	Amount CAD_1 OCH	Rel.Area % CAD_1 OCH	Peak Type CAD_1 OCH
4	OCH	13.112	56.474	445.752	n.a.	79.59	BMB
5	OCH	13.113	57.011	447.781	n.a.	80.16	BMB
6	OCH	13.123	57.468	450.318	n.a.	78.65	BMB
	Average:	13.116	56.984	447.950	#DIV/0!	79.467	#DIV/0!
	Rel.Std.Dev:	0.048 %	0.874 %	0.511 %	#DIV/0!	0.954 %	#DIV/0!

Conditions of HPLC

* Column: Acclaim™ 120 C18, 2.1 × 150 mm, 2.2 μm [ThermoFisher Scientific]

* Mobile phase

  - A: 0.05% TFA in H_2O

  - B: 0.05% TFA in MeOH

  - 60% ~ 100% of % B gradient

No	Time	Flow [ml/min]	%B	%C	Curve
1	0.000	Run			
2	0.000	0.400	60.0	0.0	5
3	8.000	0.400	100.0	0.0	5
4	20.000	0.400	100.0	0.0	5
5	21.000	0.400	60.0	0.0	5
6	25.000	0.400	60.0	0.0	5
7	*New Row*				
8	25.000	Stop Run			

* Flow rate: 0.4 mL/min

* Injection volume: 5 μL

* Column oven temperature: 40 ℃ (Active pre-heater 40 ℃, Forced mode)

Conditions of CAD

* Evaporation temperature: 70 ℃

* Filter: 5.0 s

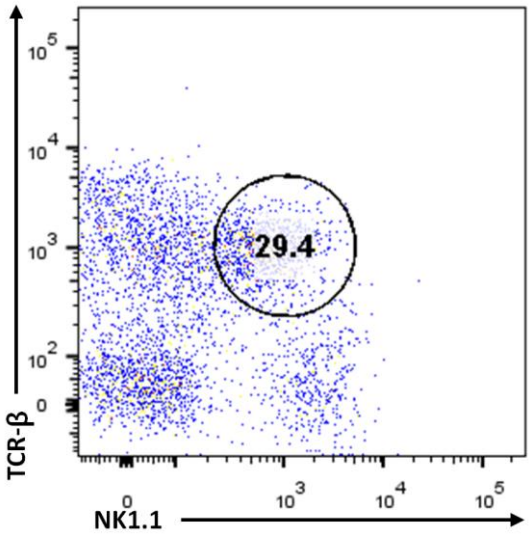
* Data collection rate: 10 Hz

* Power function: 1.0

E. Biological methods

***In vitro* stimulation of NKT cells.** Murine hepatic mononuclear cells (HMNC) from wild-type C57BL/6 mice [CRJ, Yokohama, Japan] were isolated using Percoll [GE Healthcare, 17-0891-01] gradients. Cells (2×10^5 cells) were stimulated with DMSO, KRN7000 (**1**), OCH (**2**) and α-GalCer analogues (**3–10**) in a 96-well treated multiwell tissue culture U-BottomPlates [Falcon, 353077] for 24 or 72 h. Supernatants were collected and assayed to quantify secreted cytokines by ELISA. All assays were performed in duplicate (technical replicates) and repeated three or five times under independent conditions (biological replicates). Data are presented as mean ± SEM.

Flow cytometry. Murine HMNCs were incubated with mAbs to mouse NK1.1 and TCR-β that were conjugated to PE [BD Biosciences, 557391] or PE-Cyanine5 [eBioscience, 15-5961-82]. Cells were analyzed using a BD FACSDIVA™ v6.1 [BD Biosciences, San Jose, CA], and FlowJo software v10 [Tree Star, Ashland, OR]. About 25–30% of the total cells were $NK1.1^+TCR^+$ cells.

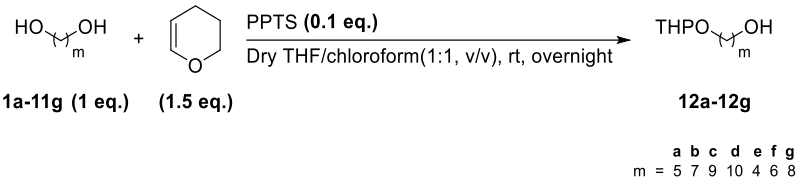


Enzyme-linked immunosorbent assay (ELISA).

Nunc clear polystyrene 96-well microwell plate with maxisorp surface plates [Thermo, 439454] was coated overnight with capture antibody from each ELISA Kit at room temperature (r.t.). All procedures were followed by manufacture's protocol. ELISA kit for IL-2 [R&D Systems, DY402] was used for quantifying 24 h incubated samples, and ELISA kits for IL-4 [R&D Systems, DY404], IFN-γ [R&D Systems, DY485], IL-17 [R&D Systems, DY421] were used for quantifying 72 h incubated samples. The color was developed by using TMB solution [Thermo, 002023], and absorbance was observed at 450, 540 nm with Synergy HT [Biotek, Winooski, VT], and Gen5 v1.01.14 [Biotek, Winooski, VT]. Technical replicates

3. Synthetic Procedures and Characterization of Compounds

A. General synthetic procedure and characterization for compounds 12a–12g



To a solution of **11a–11g** (1 equiv.) and pyridinium *p*-toluenesulfonate (PPTS) (0.1 equiv.) in dry tetrahydrofuran (THF)/chloroform (1:1, v/v) at room temperature (r.t.) was added 3,4-dihydro-2*H*-pyran (1.5 equiv.) in dry THF/chloroform (1:1, v/v) over 4 h under Ar(g). The concentration of the reaction mixture was 0.1 M for **11a–11g**. After being stirred at r.t. for overnight, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (16.7% ethyl acetate (EA) in hexane gradient to 25%) to obtain the desired compounds **12a–12g**.

Compound 12a: Compound **12a** was synthesized from **11a** (1 g, 9.60 mmol) with the procedure A and obtained as colorless oil. Yield: 51% (916.5 mg, 4.87 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.56 (m, 1H), 3.89–3.83 (m, 1H), 3.75 (dt, J = 9.6, 6.8 Hz, 1H), 3.65 (t, J = 6.2 Hz, 2H), 3.52–3.47 (m, 1H), 3.40 (dt, J = 9.6, 6.4 Hz, 1H), 1.85–1.78 (m, 1H), 1.74–1.41 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.1, 67.7, 63.0, 62.5, 32.7, 30.9, 29.6, 25.6, 22.6, 19.8; LRMS (ESI) m/z calcd for $C_{10}H_{20}NaO_3$ $[M+Na]^+$: 211.1, found: 211.3.

Compound 12b: Compound **12b** was synthesized from **11b** (1 g, 7.56 mmol) with the procedure A and obtained as colorless oil. Yield: 50% (817 mg, 3.78 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.84 (m, 1H), 3.73 (dt, J = 9.6, 6.8 Hz, 1H), 3.65 (td, J = 6.2, 5.6 Hz, 2H), 3.52–3.47 (m, 1H), 3.38 (dt, J = 9.2, 6.8 Hz, 1H), 1.85–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.60–1.50 (m, 8H), 1.35–1.30 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 67.7, 63.2, 62.5, 32.9, 30.9, 29.8, 29.4, 26.4, 25.8, 25.6, 19.8; LRMS (ESI) m/z calcd for $C_{12}H_{24}NaO_3$ $[M+Na]^+$: 239.2, found: 239.3.

Compound 12c: Compound **12c** was synthesized from **11c** (1 g, 6.24 mmol) with the procedure A and obtained as colorless oil. Yield: 47% (716.5 mg, 2.93 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.8 Hz, 1H), 3.63 (t, J = 6.6 Hz, 2H), 3.52–3.46 (m, 1H), 3.37 (dt, J = 9.6, 6.8 Hz, 1H), 1.85–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.60–1.49 (m, 8H), 1.36–1.31 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 67.8, 63.2, 62.5, 32.9, 30.9, 29.9, 29.7, 29.53, 29.49, 26.3, 25.8, 25.6, 19.8; LRMS (ESI) m/z calcd for $C_{14}H_{28}NaO_3$ $[M+Na]^+$: 267.2, found: 267.3.

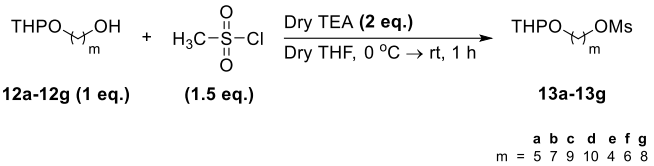
Compound 12d: Compound **12d** was synthesized from **11d** (300 mg, 1.72 mmol) with the procedure A and obtained as colorless oil. Yield: 49% (219.6 mg, 0.85 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.56 (m, 1H), 3.90–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.9 Hz, 1H), 3.63 (t, J = 6.75 Hz, 2H), 3.53–3.46 (m, 1H), 3.38 (dt, J = 9.6, 6.6 Hz, 1H), 1.85–1.79 (m, 1H), 1.75–1.68 (m, 1H), 1.65–1.49 (m, 8H), 1.36–1.29 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 67.9, 63.3, 62.6, 33.0, 31.0, 29.9, 29.73, 29.70, 29.66, 29.6, 26.4, 25.9, 25.7, 19.9; LRMS (ESI) m/z calcd for $C_{15}H_{30}NaO_3$ $[M+Na]^+$: 281.2, found: 281.4.

Compound 12e: Compound **12e** was synthesized from **11e** (1.014 g, 11.25 mmol) with the procedure A and obtained as colorless oil. Yield: 41% (802.2 mg, 4.60 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.60–4.58 (m, 1H), 3.89–3.76 (m, 2H), 3.66 (m, 2H), 3.54–3.39 (m, 2H), 2.25 (br s, 1H), 1.84–1.65 (m, 6H), 1.63–1.48 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 67.7, 62.9, 62.5, 30.8, 30.3, 26.8, 25.6, 19.8; LRMS (ESI) m/z calcd for $C_9H_{18}NaO_3$ $[M+Na]^+$: 197.1, found: 197.3.

Compound 12f: Compound **12f** was synthesized from **11f** (1 g, 8.46 mmol) with the procedure A and obtained as colorless oil. Yield: 45% (763 mg, 3.77 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.55 (m, 1H), 3.88–3.83 (m, 1H), 3.73 (dt, J = 9.6, 6.8 Hz, 1H), 3.63 (t, J = 6.6 Hz, 2H), 3.51–3.46 (m, 1H), 3.38 (dt, J = 9.6, 6.8 Hz, 1H), 1.85–1.77 (m, 1H), 1.74–1.66 (m, 1H), 1.62–1.47 (m, 9H), 1.43–1.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 67.7, 63.1, 62.6, 32.9, 31.0, 29.9, 26.2, 25.75, 25.68, 19.9; LRMS (ESI) m/z calcd for $C_{11}H_{22}NaO_3$ $[M+Na]^+$: 225.1, found: 225.3.

Compound 12g: Compound **12g** was synthesized from **11g** (1 g, 6.84 mmol) with the procedure A and obtained as colorless oil. Yield: 50% (784.0 mg, 3.40 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.83 (m, 1H), 3.72 (dt, J = 9.2, 6.8 Hz, 1H), 3.63 (t, J = 5.6 Hz, 2H), 3.50–3.46 (m, 1H), 3.37 (dt, J = 9.6, 6.8 Hz, 1H), 1.85–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.60–1.51 (m, 8H), 1.37–1.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 67.9, 63.2, 62.6, 33.0, 31.0, 29.9, 29.6, 29.5, 26.4, 25.9, 25.7, 19.9; LRMS (ESI) m/z calcd for $C_{13}H_{26}NaO_3$ $[M+Na]^+$: 253.2, found: 253.3.

B. General synthetic procedure and characterization for compounds 13a–13g



To a solution of **12a–12g** (1 equiv.) in dry THF (0.1 M for **12a–12g**) at 0 °C were added methanesulfonyl chloride (MsCl, 1.5 equiv.) and dry triethylamine (TEA, 2 equiv.) under Ar(g), then stirred at r.t. for 1 h. After reaction completion checked by TLC, the reaction mixture was filtered with EA and concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (20% EA in hexane gradient to 25%) to obtain the desired compounds **13a–13g**.

Compound 13a: Compound **13a** was synthesized from **12a** (900 mg, 4.78 mmol) with the procedure B and obtained as colorless oil. Yield: 96% (1.2182 g, 4.57 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.56–4.55 (m, 1H), 4.23 (t, J = 6.6 Hz, 2H), 3.87–3.82 (m, 1H), 3.75 (dt, J = 9.6, 6.8 Hz, 1H), 3.52–3.47 (m, 1H), 3.39 (dt, J = 9.6, 6.8 Hz, 1H), 3.00 (s, 3H), 1.84–1.75 (m, 3H), 1.74–1.67 (m, 1H), 1.65–1.60 (m, 2H), 1.58–1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.1, 70.1, 67.2, 62.6, 37.5, 30.9, 29.3, 29.1, 25.6, 22.5, 19.8; LRMS (ESI) m/z calcd for $C_{11}H_{22}NaO_5S$ $[M+Na]^+$: 289.1, found: 289.3.

Compound 13b: Compound **13b** was synthesized from **12b** (809.2 mg, 3.74 mmol) with the procedure B and obtained as colorless oil. Yield: 99% (1.0858 g, 3.69 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.56–4.54 (m, 1H), 4.20 (t, J = 6.4 Hz, 2H), 3.87–3.82 (m, 1H), 3.71 (dt, J = 9.2, 6.8 Hz, 1H), 3.51–3.45 (m, 1H), 3.36 (dt, J = 9.2, 6.8 Hz, 1H), 2.98 (s, 3H), 1.84–1.67 (m, 4H), 1.59–1.48 (m, 6H), 1.44–1.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 70.2, 67.6, 62.5, 37.4, 30.9, 29.7, 29.2, 28.9, 26.2, 25.6, 25.5, 19.8; LRMS (ESI) m/z calcd for $C_{13}H_{26}NaO_5S$ $[M+Na]^+$: 317.1, found: 317.3.

Compound 13c: Compound **13c** was synthesized from **12c** (716.5 mg, 2.93 mmol) with the procedure B and obtained as colorless oil. Yield: 97% (920.1 mg, 2.85 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.56–4.55 (m, 1H), 4.21 (t, J = 6.6 Hz, 2H), 3.89–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.8 Hz, 1H), 3.50–3.46 (m, 1H), 3.37 (dt, J = 9.6, 6.4 Hz, 1H), 2.99 (s, 3H), 1.85–1.79 (m, 1H), 1.77–1.68 (m, 3H), 1.60–1.51 (m, 6H), 1.39–1.31 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 70.3, 67.8, 62.5, 37.5, 30.9, 29.8, 29.5, 29.2, 29.1, 26.3, 25.6, 25.5, 19.9; LRMS (ESI) m/z calcd for $C_{15}H_{30}NaO_5S$ $[M+Na]^+$: 345.2, found: 345.4.

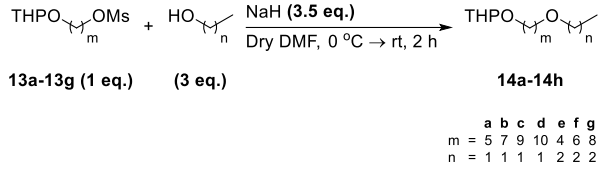
Compound 13d: Compound **13d** was synthesized from **12d** (219.6 mg, 0.85 mmol) with the procedure B and obtained as colorless oil. Yield: 98% (279.6 mg, 0.83 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.56 (m, 1H), 4.22 (t, J = 6.6 Hz, 2H), 3.90–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.9 Hz, 1H), 3.53–3.46 (m, 1H), 3.38 (dt, J = 9.6, 6.6 Hz, 1H), 3.00 (s, 3H), 1.87–1.65 (m, 4H), 1.63–1.48 (m, 6H), 1.41–1.29 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 70.4, 67.9, 62.6, 37.6, 31.0, 29.9, 29.6, 29.5, 29.3, 29.2, 26.4, 25.7, 25.6, 19.9; LRMS (ESI) m/z calcd for $C_{16}H_{32}NaO_5S$ $[M+Na]^+$: 359.2, found: 359.5.

Compound 13e: Compound **13e** was synthesized from **12e** (785 mg, 4.50 mmol) with the procedure B and obtained as colorless oil. Yield: quantitative (1.144 g, 4.53 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 4.28 (t, J = 6.4 Hz, 2H), 3.87–3.75 (m, 2H), 3.53–3.48 (m, 1H), 3.42 (dt, J = 9.6, 6.4 Hz, 1H), 3.00 (s, 3H), 1.91–1.77 (m, 3H), 1.75–1.67 (m, 3H), 1.60–1.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.1, 70.1, 66.7, 62.6, 37.5, 30.8, 26.5, 25.9, 25.6, 19.8; LRMS (ESI) m/z calcd for $C_{10}H_{20}NaO_5S$ $[M+Na]^+$: 275.1, found: 275.3.

Compound 13f: Compound **13f** was synthesized from **12f** (750 mg, 3.71 mmol) with the procedure B and obtained as colorless oil. Yield: quantitative (1.0371 g, 3.70 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.55 (m, 1H), 4.22 (t, J = 6.8 Hz, 2H), 3.88–3.83 (m, 1H), 3.73 (dt, J = 9.2, 6.8 Hz, 1H), 3.51–3.47 (m, 1H), 3.38 (dt, J = 9.6, 6.8 Hz, 1H), 3.00 (s, 3H), 1.85–1.68 (m, 4H), 1.64–1.50 (m, 6H), 1.48–1.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.2, 70.2, 67.6, 62.7, 37.6, 31.0, 29.7, 29.3, 26.0, 25.7, 25.5, 19.9; LRMS (ESI) m/z calcd for $C_{12}H_{24}NaO_5S$ $[M+Na]^+$: 303.1, found: 303.4.

Compound 13g: Compound **13g** was synthesized from **12g** (760 mg, 3.30 mmol) with the procedure B and obtained as colorless oil. Yield: quantitative (1.0348 g, 3.36 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 4.21 (t, J = 6.4 Hz, 2H), 3.89–3.84 (m, 1H), 3.72 (dt, J = 9.6, 6.8 Hz, 1H), 3.52–3.47 (m, 1H), 3.37 (dt, J = 9.6, 6.8 Hz, 1H), 3.00 (s, 3H), 1.85–1.79 (m, 1H), 1.78–1.68 (m, 3H), 1.61–1.50 (m, 6H), 1.39–1.33 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 70.3, 67.8, 62.6, 37.6, 31.0, 29.9, 29.5, 29.3, 29.2, 26.3, 25.7, 25.6, 19.9; LRMS (ESI) m/z calcd for $C_{14}H_{28}NaO_5S$ $[M+Na]^+$: 331.2, found: 331.4.

C. General synthetic procedure and characterization for compounds 14a–14h



To a solution of NaH (3.5 equiv.) in dry dimethylformamide (DMF) at 0 °C was added ethanol or propanol (3 equiv.) under Ar(g), then stirred at 0 °C for 5 min. To the reaction mixture was added **13a–13g** (1 equiv.) in dry DMF, then stirred at r.t. for 2 h. The concentration of the reaction mixture was 0.1 M for **13a–13g**. After reaction completion checked by TLC, the reaction mixture was quenched with saturated NH_4Cl(aq.). The resultant was extracted with EA three times. The combined organic layer was dried over anhydrous Na_2SO_4(s) and concentrated *in vacuo* after filtration. The resultant was evaporated with toluene twice to remove DMF. The residue was purified by silica-gel flash column chromatography (6.25% EA in hexane gradient to 7.69%) to obtain the desired compounds **14a–14h**.

Compound 14a: Compound **14a** was synthesized from **13a** (500 mg, 1.88 mmol) with the procedure C and obtained as colorless oil. Yield: 88% (356.5 mg, 1.65 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.83 (m, 1H), 3.74 (dt, J = 10, 6.8 Hz, 1H), 3.52–3.36 (m, 6H), 1.85–1.79 (m, 1H), 1.74–1.68 (m, 1H), 1.66–1.49 (m, 8H), 1.46–1.38 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 70.7, 67.7, 66.2, 62.5, 30.9, 29.8, 29.7, 25.6, 23.0, 19.8, 15.4; LRMS (ESI) m/z calcd for $C_{12}H_{24}NaO_3$ $[M+Na]^+$: 239.2, found: 239.3.

Compound 14b: Compound **14b** was synthesized from **13b** (500 mg, 1.70 mmol) with the procedure C and obtained as colorless oil. Yield: 93% (385.9 mg, 1.58 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.84 (m, 1H), 3.72 (dt, J = 9.2, 6.8 Hz, 1H), 3.52–3.35 (m, 6H), 1.85–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.62–1.49 (m, 8H), 1.40–1.28 (m, 6H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 70.9, 67.8, 66.2, 62.5, 30.9, 29.9, 29.8, 29.5, 26.35, 26.31, 25.6, 19.8, 15.4; LRMS (ESI) m/z calcd for $C_{14}H_{28}NaO_3$ $[M+Na]^+$: 267.2, found: 267.3.

Compound 14c: Compound **14c** was synthesized from **13c** (500 mg, 1.55 mmol) with the procedure C and obtained as colorless oil. Yield: 91% (385.4 mg, 1.41 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.84 (m, 1H), 3.72 (dt, J = 9.2, 7.0 Hz, 1H), 3.51–3.43 (m, 3H), 3.41–3.34 (m, 3H), 1.86–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.58–1.50 (m, 8H), 1.30 (m, 10H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 70.9, 67.8, 66.2, 62.5, 30.9, 30.0, 29.9, 29.7, 29.59, 29.56, 26.4, 26.3, 25.6, 19.8, 15.4; LRMS (ESI) m/z calcd for $C_{16}H_{32}NaO_3$ $[M+Na]^+$: 295.2, found: 295.4.

Compound 14d: Compound **14d** was synthesized from **13d** (313.9 mg, 0.93 mmol) with the procedure C and obtained as colorless oil. Yield: 97% (259.7 mg, 0.91 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.56 (m, 1H), 3.90–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.9 Hz, 1H), 3.53–3.45 (m, 3H), 3.42–3.33 (m, 3H), 1.87–1.77 (m, 1H), 1.75–1.65 (m, 1H), 1.61–1.48 (m, 8H), 1.40–1.28 (m, 12H), 1.19 (t, J = 7.05 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 71.0, 67.9, 66.3, 62.6, 31.0, 30.04, 29.97, 29.8, 29.71, 29.69, 26.5, 26.4, 25.7, 19.9, 15.5; LRMS (ESI) m/z calcd for $C_{17}H_{34}NaO_3$ $[M+Na]^+$: 309.2, found: 309.4.

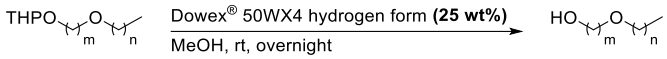
Compound 14e: Compound **14e** was synthesized from **13e** (500 mg, 1.98 mmol) with the procedure C and obtained as colorless oil. Yield: 75% (319.7 mg, 1.48 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.55 (m, 1H), 3.88–3.80 (m, 1H), 3.77–3.70 (m, 1H), 3.51–3.32 (m, 6H), 1.85–1.75 (m, 1H), 1.73–1.62 (m, 5H), 1.60–1.46 (m, 6H), 0.89 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.0, 72.7, 70.8, 67.5, 62.4, 30.9, 26.8, 26.7, 25.7, 23.1, 19.8, 10.8; LRMS (ESI) m/z calcd for $C_{12}H_{24}NaO_3$ $[M+Na]^+$: 239.2, found: 239.3.

Compound 14f: Compound **14f** was synthesized from **13f** (400 mg, 1.43 mmol) with the procedure C and obtained as colorless oil. Yield: 96% (333.3 mg, 1.36 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.55 (m, 1H), 3.90–3.82 (m, 1H), 3.73 (dt, J = 9.6, 6.9 Hz, 1H), 3.53–3.45 (m, 1H), 3.42–3.33 (m, 5H), 1.86–1.77 (m, 1H), 1.75–1.67 (m, 1H), 1.66–1.48 (m, 10H), 1.43–1.35 (m, 4H), 0.91 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 72.8, 71.0, 67.8, 62.6, 31.0, 29.9, 26.4, 26.3, 25.7, 23.2, 19.9, 10.8; LRMS (ESI) m/z calcd for $C_{14}H_{28}NaO_3$ $[M+Na]^+$: 267.2, found: 267.4.

Compound 14g: Compound **14g** was synthesized from **13g** (400 mg, 1.30 mmol) with the procedure C and obtained as colorless oil. Yield: 93% (329.4 mg, 1.21 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.58–4.55 (m, 1H), 3.90–3.83 (m, 1H), 3.72 (dt, J = 9.6, 6.9 Hz, 1H), 3.53–3.47 (m, 1H), 3.41–3.33 (m, 5H), 1.85–1.79 (m, 1H), 1.75–1.67 (m, 1H), 1.64–1.48 (m, 10H), 1.32 (m, 8H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 99.1, 72.8, 71.1, 67.9, 62.6, 31.0, 29.98, 29.95, 29.7, 26.39, 26.36, 25.7, 23.2, 19.9, 10.8; LRMS (ESI) m/z calcd for $C_{16}H_{32}NaO_3$ $[M+Na]^+$: 295.2, found: 295.5.

Compound 14h: Compound **14h** was synthesized from **13c** (335 mg, 1.04 mmol) with the procedure C and obtained as colorless oil. Yield: 90% (268.9 mg, 0.94 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.57–4.56 (m, 1H), 3.89–3.84 (m, 1H), 3.72 (dt, J = 9.6, 6.8 Hz, 1H), 3.52–3.47 (m, 1H), 3.40–3.34 (m, 5H), 1.86–1.78 (m, 1H), 1.74–1.68 (m, 1H), 1.63–1.49 (m, 10H), 1.33–1.30 (m, 10H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 99.0, 72.7, 71.1, 67.8, 62.5, 30.9, 29.93, 29.89, 29.7, 29.59, 29.56, 26.4, 26.3, 25.7, 23.1, 19.8, 10.7; LRMS (ESI) m/z calcd for $C_{17}H_{34}NaO_3$ $[M+Na]^+$: 309.2, found: 309.4.

D. General synthetic procedure and characterization for compounds 15a–15h



14a-14h (1 eq.) **15a-15h**

	a	b	c	d	e	f	g	h
m =	5	7	9	10	4	6	8	9
n =	1	1	1	1	2	2	2	2

To a solution of **14a–14h** (1 equiv.) in MeOH (0.1 M for **14a–14h**) at r.t. was added Dowex® 50WX4 hydrogen form (hydrogen form, 100–200 mesh) (25 wt%), then stirred at r.t. for overnight. After reaction completion checked by TLC, the reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (11.11% EA in hexane gradient to 22.22%) to obtain the desired compounds **15a–15h**.

Compound 15a: Compound **15a** was synthesized from **14a** (380.2 mg, 1.76 mmol) with the procedure D and obtained as colorless oil. Yield: 72% (166.5 mg, 1.26 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.66–3.65 (m, 2H), 3.50–3.41 (m, 4H), 1.65–1.56 (m, 4H), 1.47–1.38 (m, 3H), 1.20 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.7, 66.3, 63.0, 32.7, 29.6, 22.6, 15.4; LRMS (ESI) m/z calcd for $C_7H_{17}O_2$ $[M+H]^+$: 133.1, found: 133.2.

Compound 15b: Compound **15b** was synthesized from **14b** (371.4 mg, 1.52 mmol) with the procedure D and obtained as colorless oil. Yield: 64% (156.5 mg, 0.98 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.64 (td, J = 6.4, 4.4 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.59–1.56 (m, 4H), 1.40–1.35 (m, 7H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.9, 66.2, 63.2, 32.9, 29.9, 29.4, 26.3, 25.8, 15.4; LRMS (ESI) m/z calcd for $C_9H_{21}O_2$ $[M+H]^+$: 161.2, found: 161.2.

Compound 15c: Compound **15c** was synthesized from **14c** (275.2 mg, 1.01 mmol) with the procedure D and obtained as colorless oil. Yield: 94% (178.5 mg, 0.95 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (m, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 7.0 Hz, 2H), 1.58–1.53 (m, 4H), 1.30 (m, 11H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.9, 66.2, 63.2, 32.9, 30.0, 29.7, 29.6, 29.5, 26.3, 25.9, 15.4; LRMS (ESI) m/z calcd for $C_{11}H_{25}O_2$ $[M+H]^+$: 189.2, found: 189.2.

Compound 15d: Compound **15d** was synthesized from **14d** (290 mg, 1.01 mmol) with the procedure D and obtained as colorless oil. Yield: 96% (196.3 mg, 0.97 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.4 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.39 (t, J = 7.0 Hz, 2H), 1.57–1.52 (m, 4H), 1.34–1.29 (m, 13H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 71.0, 66.3, 63.3, 33.0, 30.0, 29.73, 29.71, 29.69, 29.6, 26.4, 25.9, 15.4; LRMS (ESI) m/z calcd for $C_{12}H_{27}O_2$ $[M+H]^+$: 203.2, found: 203.2.

Compound 15e: Compound **15e** was synthesized from **14e** (290 mg, 1.3222 mmol) with the procedure D and obtained as colorless oil. Yield: 90% (157.9 mg, 1.1944 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (m, 2H), 3.47–3.43 (m, 2H), 3.39 (t, J = 6.75 Hz, 2H), 2.73 (br s, 1H), 1.70–1.53 (m, 6H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 73.0, 71.1, 62.9, 30.7, 27.2, 23.0, 10.8; LRMS (ESI) m/z calcd for $C_7H_{17}O_2$ $[M+H]^+$: 133.1, found: 133.2.

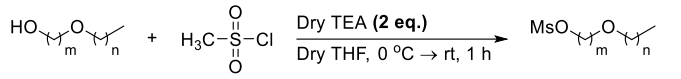
Compound 15f: Compound **15f** was synthesized from **14f** (320 mg, 1.31 mmol) with the procedure D and obtained as colorless oil. Yield: 97% (204.2 mg, 1.27 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.6 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 6.8 Hz, 2H), 1.62–1.54 (m, 6H), 1.41–1.36 (m, 5H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.8, 71.0, 63.1, 32.9, 29.9, 26.2, 25.8, 23.1, 10.8; LRMS (ESI) m/z calcd for $C_9H_{21}O_2$ $[M+H]^+$: 161.2, found: 161.2.

Compound 15g: Compound **15g** was synthesized from **14g** (315 mg, 1.16 mmol) with the procedure D and obtained as colorless oil. Yield: 92% (201.1 mg, 1.07 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.6 Hz, 2H), 3.41–3.34 (m, 4H), 1.63–1.53 (m, 6H), 1.32 (m, 9H), 0.91 (t, J = 7.6 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.8, 71.1, 63.2, 33.0, 30.0, 29.65, 29.57, 26.3, 25.9, 23.1, 10.8; LRMS (ESI) m/z calcd for $C_{11}H_{25}O_2$ $[M+H]^+$: 189.2, found: 189.2.

Compound 15h: Compound **15h** was synthesized from **14h** (335.7 mg, 1.17 mmol) with the procedure D and obtained as colorless oil. Yield: 83% (195.9 mg, 0.97 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (td, J = 6.2, 4.8 Hz, 2H), 3.41–3.34 (m, 4H), 1.63–1.53 (m, 6H), 1.30 (m, 11H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 72.7, 71.1, 63.2, 32.9, 29.9, 29.7, 29.6, 29.5, 26.3, 25.9, 23.1, 10.7; LRMS (ESI) m/z calcd for $C_{12}H_{27}O_2$ $[M+H]^+$: 203.2, found: 203.2.

E. General synthetic procedure and characterization for compounds 16a–16h



15a-15h (1 eq.) **(1.5 eq.)** **16a-16h**

	a	b	c	d	e	f	g	h
m =	5	7	9	10	4	6	8	9
n =	1	1	1	1	2	2	2	2

To a solution of **15a–15h** (1 equiv.) in dry THF (0.1 M for **15a–15h**) at 0 °C were added MsCl (1.5 equiv.) and dry TEA (2 equiv.) under Ar(g), then stirred at r.t. for 1 h. After reaction completion checked by TLC, the reaction mixture was filtered with EA and concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (25% EA in hexane gradient to 33%) to obtain the desired compounds **16a–16h**.

Compound 16a: Compound **16a** was synthesized from **15a** (160.9 mg, 1.22 mmol) with the procedure E and obtained as colorless oil. Yield: quantitative (259.1 mg, 1.23 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.23 (t, J = 6.6 Hz, 2H), 3.49–3.40 (m, 4H), 3.00 (s, 3H), 1.82–1.75 (m, 2H), 1.63–1.58 (m, 2H), 1.52–1.46 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.3, 70.1, 66.3, 37.5, 29.3, 29.1, 22.4, 15.4; LRMS (ESI) m/z calcd for $C_8H_{19}O_4S$ $[M+H]^+$: 211.1, found: 211.1.

Compound 16b: Compound **16b** was synthesized from **15b** (151 mg, 0.94 mmol) with the procedure E and obtained as colorless oil. Yield: 99% (223.4 mg, 0.94 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.22 (t, J = 6.6 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 3.00 (s, 3H), 1.78–1.71 (m, 2H), 1.60–1.54 (m, 2H), 1.44–1.35 (m, 6H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.7, 70.2, 66.2, 37.5, 29.8, 29.2, 29.0, 26.2, 25.5, 15.4; LRMS (ESI) m/z calcd for $C_{10}H_{23}O_4S$ $[M+H]^+$: 239.1, found: 239.2.

Compound 16c: Compound **16c** was synthesized from **15c** (178.5 mg, 0.95 mmol) with the procedure E and obtained as colorless oil. Yield: quantitative (262.2 mg, 0.98 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.22 (t, J = 6.6 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 3.00 (s, 3H), 1.78–1.71 (m, 2H), 1.58–1.53 (m, 2H), 1.41–1.31 (m, 10H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 70.9, 70.3, 66.2, 37.5, 29.9, 29.5, 29.3, 29.1, 26.3, 25.5, 15.4; LRMS (ESI) m/z calcd for $C_{12}H_{27}O_4S$ $[M+H]^+$: 267.2, found: 267.2.

Compound 16d: Compound **16d** was synthesized from **15d** (185 mg, 0.91 mmol) with the procedure E and obtained as colorless oil. Yield: quantitative (256.3 mg, 0.91 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.21 (t, J = 6.6 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.39 (t, J = 6.75 Hz, 2H), 3.00 (s, 3H), 1.79–1.69 (m, 2H), 1.60–1.51 (m, 2H), 1.41–1.25 (m, 12H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 71.0, 70.4, 66.3, 37.6, 30.0, 29.6, 29.5, 29.3, 29.2, 26.4, 25.6, 15.5; LRMS (ESI) m/z calcd for $C_{13}H_{29}O_4S$ $[M+H]^+$: 281.2, found: 281.2.

Compound 16e: Compound **16e** was synthesized from **15e** (147 mg, 1.11 mmol) with the procedure E and obtained as colorless oil. Yield: 98% (230 mg, 1.09 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.27 (t, J = 6.3 Hz, 2H), 3.44 (t, J = 6.0 Hz, 2H), 3.36 (t, J = 6.75 Hz, 2H), 3.00 (s, 3H), 1.90–1.81

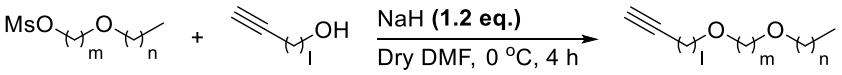
(m, 2H), 1.73–1.52 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.9, 70.2, 70.0, 37.6, 26.5, 25.9, 23.1, 10.8; LRMS (ESI) m/z calcd for $C_8H_{19}O_4S$ $[M+H]^+$: 211.1, found: 211.1.

Compound 16f: Compound **16f** was synthesized from **15f** (194 mg, 1.21 mmol) with the procedure E and obtained as colorless oil. Yield: 99% (285.5 mg, 1.20 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.22 (t, J = 6.6 Hz, 2H), 3.42–3.33 (m, 4H), 2.99 (s, 3H), 1.80–1.71 (m, 2H), 1.64–1.52 (m, 4H), 1.45–1.37 (m, 4H), 0.91 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.8, 70.7, 70.3, 37.6, 29.8, 29.3, 25.9, 25.5, 23.1, 10.8; LRMS (ESI) m/z calcd for $C_{10}H_{23}O_4S$ $[M+H]^+$: 239.1, found: 239.2.

Compound 16g: Compound **16g** was synthesized from **15g** (259.3 mg, 1.38 mmol) with the procedure E and obtained as colorless oil. Yield: 98% (360.9 mg, 1.35 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.21 (t, J = 6.6 Hz, 2H), 3.41–3.33 (m, 4H), 3.00 (s, 3H), 1.79–1.69 (m, 2H), 1.64–1.52 (m, 4H), 1.42–1.33 (m, 8H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.8, 71.0, 70.4, 37.6, 29.9, 29.5, 29.3, 29.2, 26.3, 25.6, 23.1, 10.8; LRMS (ESI) m/z calcd for $C_{12}H_{27}O_4S$ $[M+H]^+$: 267.2, found: 267.2.

Compound 16h: Compound **16h** was synthesized from **15h** (186.5 mg, 0.92 mmol) with the procedure E and obtained as colorless oil. Yield: quantitative (281 mg, 1.00 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.22 (t, J = 6.4 Hz, 2H), 3.41–3.34 (m, 4H), 3.00 (s, 3H), 1.78–1.71 (m, 2H), 1.63–1.53 (m, 4H), 1.41–1.31 (m, 10H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 72.7, 71.0, 70.3, 37.5, 29.9, 29.5, 29.3, 29.1, 26.3, 25.5, 23.1, 10.7; LRMS (ESI) m/z calcd for $C_{13}H_{29}O_4S$ $[M+H]^+$: 281.2, found: 281.2.

F. General synthetic procedure and characterization for compounds 18a–18h



16a-16h (1 eq.) **17a-17h (1.5 eq.)** **18a-18h**

l + m + n = 12

	a	b	c	d	e	f	g	h
l =	6	4	2	1	6	4	2	1
m =	5	7	9	10	4	6	8	9
n =	1	1	1	1	2	2	2	2

To a solution of NaH (1.2 equiv.) in dry DMF at 0 °C was added **17a–17h** (1.5 equiv.) in dry DMF under Ar(g), then stirred at 0 °C for 5 min. To the reaction mixture was added **16a–16h** (1 equiv.) in dry DMF. The concentration of the reaction mixture was 0.1 M for **16a–16h**. After being stirred at 0 °C for 4 h, the reaction mixture was quenched with saturated NH_4Cl(aq.). The resultant was extracted with EA three times. The combined organic layer was dried over anhydrous Na_2SO_4(s) and concentrated *in vacuo* after filtration. The resultant was evaporated with toluene twice to remove DMF. The residue was purified by silica-gel flash column chromatography (4.76% EA in hexane gradient to 33.33%) to obtain the desired compounds **18a–18h** and recover starting materials **16a–16h**.

Compound 18a: Compound **18a** was synthesized from **16a** (259.1 mg, 1.23 mmol) with the procedure F and obtained as colorless oil. Yield: 47% (137.6 mg, 0.57 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.49–3.37 (m, 8H), 2.18 (td, J = 7.0, 2.4 Hz, 2H), 1.93 (t, J = 2.4 Hz, 1H), 1.63–1.50 (m, 8H), 1.45–1.31 (m, 6H), 1.19 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 84.8, 70.97, 70.95, 70.8, 68.3, 66.2, 29.78, 29.75, 28.7, 28.6, 25.9, 23.0, 18.5, 15.4; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.2.

Compound 18b: Compound **18b** was synthesized from **16b** (156.3 mg, 0.66 mmol) with the procedure F and obtained as colorless oil. Yield: 51% (81.1 mg, 0.34 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.49–3.37 (m, 8H), 2.22 (td, J = 6.8, 2.4 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 1.72–1.54 (m, 8H), 1.33–1.28 (m, 6H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 84.6, 71.1, 70.9, 70.3, 68.5, 66.2, 29.9, 29.8, 29.5, 28.9, 26.31, 26.29, 25.4, 18.4, 15.4; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.3.

Compound 18c: Compound **18c** was synthesized from **16c** (249.3 mg, 0.94 mmol) with the procedure F and obtained as colorless oil. Yield: 76% (172.2 mg, 0.72 mmol); ^{1}H NMR (500 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.54 (t, J = 7.0 Hz, 2H), 3.47–3.42 (m, 4H), 3.38 (t, J = 7.0 Hz, 2H), 2.45 (td, J = 7.0, 2.5 Hz, 2H), 1.96 (t, J = 2.5 Hz, 1H), 1.58–1.52 (m, 4H), 1.33–1.28 (m, 10H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 81.6, 71.3, 70.9, 69.3, 68.9, 66.2, 30.0, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2, 20.0, 15.4; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.2.

Compound 18d: Compound **18d** was synthesized from **16d** (192 mg, 0.69 mmol) with the procedure F and obtained as colorless oil. Yield: 90% (156.7 mg, 0.65 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.13 (d, J = 2.4 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 3.39 (t, J = 6.75 Hz, 2H), 2.41 (t, J = 2.4 Hz, 1H), 1.63–1.51 (m, 4H), 1.28 (m, 12H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 80.3, 74.2, 71.0, 70.5, 66.3, 58.2, 30.0, 29.7, 29.6, 26.4, 26.3, 15.5; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.2.

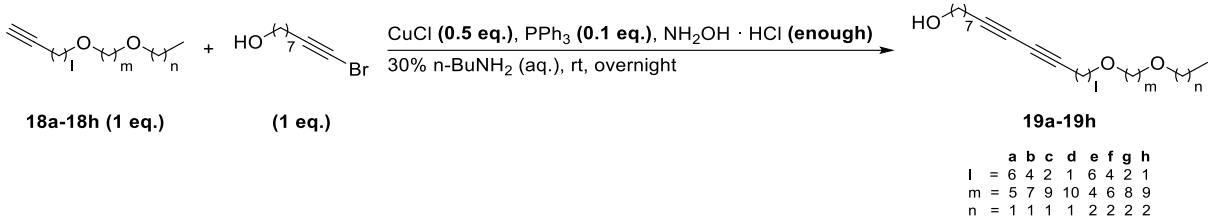
Compound 18e: Compound **18e** was synthesized from **16e** (220 mg, 1.05 mmol) with the procedure F and obtained as colorless oil. Yield: 29% (72.1 mg, 0.30 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.42–3.34 (m, 8H), 2.18 (td, J = 7.0, 2.8 Hz, 2H), 1.93 (t, J = 2.8 Hz, 1H), 1.64–1.50 (m, 10H), 1.45–1.34 (m, 4H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 84.9, 72.8, 71.0, 70.9, 70.8, 68.3, 29.9, 28.8, 28.6, 26.7, 25.9, 23.2, 18.6, 10.8; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.2.

Compound 18f: Compound **18f** was synthesized from **16f** (241.9 mg, 1.02 mmol) with the procedure F and obtained as colorless oil. Yield: 48% (117.8 mg, 0.49 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.44–3.33 (m, 8H), 2.21 (td, J = 6.9, 2.7 Hz, 2H), 1.94 (t, J = 2.7 Hz, 1H), 1.73–1.52 (m, 10H), 1.38–1.33 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 84.6, 72.8, 71.1, 71.0, 70.4, 68.5, 30.0, 29.0, 26.3, 25.5, 23.2, 18.5, 10.8; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.3.

Compound 18g: Compound **18g** was synthesized from **16g** (200 mg, 0.75 mmol) with the procedure F and obtained as colorless oil. Yield: 36% (80.1 mg, 0.33 mmol); ^{1}H NMR (500 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.54 (t, J = 7.25 Hz, 2H), 3.44 (t, J = 7.0 Hz, 2H), 3.38 (t, J = 7.0 Hz, 2H), 3.35 (t, J = 7.0 Hz, 2H), 2.45 (td, J = 7.25, 2.5 Hz, 2H), 1.97 (t, J = 2.5 Hz, 1H), 1.61–1.53 (m, 6H), 1.34–1.28 (m, 8H), 0.91 (t, J = 7.25 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 81.6, 72.8, 71.4, 71.1, 69.4, 69.0, 30.0, 29.8, 29.64, 29.61, 26.4, 26.2, 23.2, 20.1, 10.8; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.3.

Compound 18h: Compound **18h** was synthesized from **16h** (269.1 mg, 0.96 mmol) with the procedure F and obtained as colorless oil. Yield: 81% (187.5 mg, 0.78 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.13 (d, J = 2.4 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H), 3.41–3.34 (m, 4H), 2.41 (t, J = 2.4 Hz, 1H), 1.63–1.52 (m, 6H), 1.30 (m, 10H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 80.2, 74.2, 72.7, 71.1, 70.4, 58.1, 29.9, 29.65, 29.57, 29.5, 26.3, 26.2, 23.1, 10.7; LRMS (ESI) m/z calcd for $C_{15}H_{29}O_2$ $[M+H]^+$: 241.2, found: 241.2.

G. General synthetic procedure and characterization for compounds 19a–19h



To a solution of CuCl (0.5 equiv.) and PPh_3 (0.1 equiv.) in 30% *n*-$BuNH_2$(aq.) with $NH_2OH{\cdot}HCl$ at r.t. was added **18a–18h** (1 equiv.) in 30% *n*-$BuNH_2$(aq.) with $NH_2OH{\cdot}HCl$ under Ar(g). To the reaction mixture was added 9-bromonon-8-yn-1-ol[1)] (1 equiv.) in 30% *n*-$BuNH_2$(aq.) with $NH_2OH{\cdot}HCl$ over 4 h, then 30% *n*-$BuNH_2$(aq.) with $NH_2OH \cdot HCl$ was added over overnight to prevent Cu (I) oxidation. The concentration of the reaction mixture was 0.05 M for **18a–18h**. After reaction completion checked by TLC, the reaction mixture was neutralized with 2N HCl and checked by pH paper until pH became below 7. The resultant was extracted with EA three times. The combined organic layer was dried over anhydrous Na_2SO_4(s) and concentrated *in vacuo* after filtration. The residue was purified by silica-gel flash column chromatography (4.76% EA in hexane gradient to 33.33%) to obtain the desired compounds **19a–19h**.

Compound 19a: Compound **19a** was synthesized from **18a** (193 mg, 0.80 mmol) with the procedure G and obtained as white solid. Yield: 44% (133 mg, 0.35 mmol); ^{1}H NMR (400 MHz, CD_2Cl_2, reference peak CD_2Cl_2 at 5.32 ppm): δ 3.58 (t, J = 6.6 Hz, 2H), 3.45–3.36 (m, 8H), 2.24 (t, J = 6.8 Hz, 4H), 1.54–1.51 (m, 13H), 1.38–1.33 (m, 12H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, reference peak CD_2Cl_2 at 53.84 ppm): δ 77.9, 71.09, 71.05, 70.9, 66.3, 65.5, 63.1, 33.2, 30.1, 30.0, 29.3, 29.2, 29.1, 28.8, 28.7, 26.1, 26.0, 23.3, 19.5, 19.4, 15.5; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.4.

Compound 19b: Compound **19b** was synthesized from **18b** (95.8 mg, 0.44 mmol) with the procedure G and obtained as white solid. Yield: 27% (44.6 mg, 0.12 mmol); ^{1}H NMR (400 MHz, CD_2Cl_2, reference peak CD_2Cl_2 at 5.32 ppm): δ 3.58 (t, J = 6.4 Hz, 2H), 3.45–3.34 (m, 8H), 2.29–2.22 (m, 4H), 1.64–1.48 (m, 13H), 1.42–1.32 (m, 12H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, reference peak CD_2Cl_2 at 53.84 ppm): δ 78.0, 77.7, 71.2, 71.0, 70.4, 66.3, 65.7, 65.5, 63.1, 33.2, 30.2, 30.1, 29.7, 29.31, 29.26, 29.2, 28.7, 26.58, 26.56, 26.0, 25.6, 19.4, 19.3, 15.5; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.3.

Compound 19c: Compound **19c** was synthesized from **18c** (171.1 mg, 0.71 mmol) with the procedure G and obtained as white solid. Yield: 37% (100.4 mg, 0.27 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.6 Hz, 2H), 3.53 (t, J = 7.0 Hz, 2H), 3.49–3.38 (m, 6H), 2.52 (t, J = 7.0 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H), 1.58–1.48 (m, 8H), 1.43–1.29 (m, 17H), 1.19 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 78.0, 74.2, 71.3, 70.9, 68.6, 66.4, 66.2, 65.3, 63.1, 32.8, 29.9, 29.74, 29.66, 29.6, 29.5, 29.0, 28.9, 28.3, 26.3, 26.2, 25.7, 20.8, 19.3, 15.4; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.4.

Compound 19d: Compound **19d** was synthesized from **18d** (180 mg, 0.75 mmol) with the procedure G and obtained as white solid. Yield: 75% (212.8 mg, 0.56 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.17 (s, 2H), 3.63 (t, J = 6.6 Hz, 2H), 3.51–3.42 (m, 4H), 3.39 (t, J = 6.75 Hz, 2H), 2.27 (t, J = 6.9 Hz, 2H), 1.58–1.48 (m, 8H), 1.45–1.28 (m, 19H), 1.19 (t, J = 7.05 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 81.2, 72.4, 71.2, 71.0, 70.6, 66.3, 64.8, 63.1, 58.8, 32.9, 30.0, 29.7, 29.6, 29.0, 28.9, 28.3, 26.4, 26.3, 25.8, 19.4, 15.5; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.3.

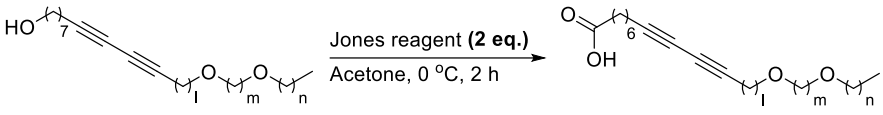
Compound 19e: Compound **19e** was synthesized from **18e** (61 mg, 0.25 mmol) with the procedure G and obtained as white solid. Yield: 67% (61.2 mg, 0.16 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (td, J = 6.3, 3.9 Hz, 2H), 3.44–3.34 (m, 8H), 2.24 (t, J = 6.9 Hz, 4H), 1.66–1.48 (m, 14H), 1.45–1.25 (m, 11H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 72.8, 71.0, 70.9, 70.8, 65.5, 63.2, 32.9, 29.8, 29.1, 29.0, 28.9, 28.5, 28.4, 26.7, 25.9, 25.8, 23.2, 19.39, 19.37, 10.8; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.4.

Compound 19f: Compound **19f** was synthesized from **18f** (55 mg, 0.23 mmol) with the procedure G and obtained as white solid. Yield: 58% (47.7 mg, 0.13 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.8 Hz, 2H), 3.41–3.34 (m, 8H), 2.24 (m, 4H), 1.70–1.48 (m, 15H), 1.43–1.27 (m, 10H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 77.6, 77.3, 72.7, 71.0, 70.9, 70.3, 65.6, 65.4, 63.1, 32.8, 29.9, 29.8, 29.0, 28.9, 28.3, 26.2, 25.7, 25.3, 23.1, 19.3, 19.2, 10.7; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.4.

Compound 19g: Compound **19g** was synthesized from **18g** (75 mg, 0.31 mmol) with the procedure G and obtained as white solid. Yield: 70% (78.9 mg, 0.21 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 3.63 (t, J = 6.45 Hz, 2H), 3.53 (t, J = 7.05 Hz, 2H), 3.45–3.33 (m, 6H), 2.52 (t, J = 7.05 Hz, 2H), 2.24 (t, J = 6.75 Hz, 2H), 1.64–1.47 (m, 10H), 1.44–1.31 (m, 15H), 0.91 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 78.1, 74.2, 72.8, 71.4, 71.1, 68.7, 66.5, 65.4, 63.2, 32.9, 30.0, 29.8, 29.64, 29.61, 29.1, 28.9, 28.4, 26.3, 26.2, 25.8, 23.2, 20.8, 19.4, 10.8; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.4.

Compound 19h: Compound **19h** was synthesized from **18h** (179.2 mg, 0.75 mmol) with the procedure G and obtained as white solid. Yield: 53% (149.1 mg, 0.39 mmol); ^{1}H NMR (500 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 4.18 (s, 2H), 3.64 (t, J = 6.5 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 3.39 (t, J = 6.5 Hz, 2H), 3.36 (t, J = 6.75 Hz, 2H), 2.27 (t, J = 7.0 Hz, 2H), 1.62–1.50 (m, 10H), 1.43–1.29 (m, 17H), 0.91 (t, J = 7.75 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 81.1, 72.7, 72.3, 71.2, 71.1, 70.5, 64.8, 63.1, 58.7, 32.8, 29.9, 29.7, 29.6, 29.5, 29.0, 28.9, 28.2, 26.3, 26.2, 25.7, 23.1, 19.4, 10.7; LRMS (ESI) m/z calcd for $C_{24}H_{43}O_3$ $[M+H]^+$: 379.3, found: 379.3.

H. General synthetic procedure and characterization for compounds 20a–20h



19a-19h (1 eq.) **20a-20h**

	a	b	c	d	e	f	g	h
l =	6	4	2	1	6	4	2	1
m =	5	7	9	10	4	6	8	9
n =	1	1	1	1	2	2	2	2

To a solution of **19a–19h** (1 equiv.) in acetone (0.1 M for **19a–19h**) at 0 °C was added Jones reagent (2 equiv.), then stirred at 0 °C for 2 h. After reaction completion checked by TLC, the reaction mixture was quenched with 2N HCl and saturated NH_4Cl(aq.). The resultant was extracted with EA five times. The combined organic layer was dried over anhydrous Na_2SO_4(s) and concentrated *in vacuo* after filtration. The residue was purified by silica-gel flash column chromatography (14.29% EA in hexane with 1% AcOH gradient to 22.22%) to obtain the desired compounds. **20a–20h**.

Compound 20a: Compound **20a** was synthesized from **19a** (106.8 mg, 0.28 mmol) with the procedure H and obtained as white solid. Yield: 77% (84.8 mg, 0.22 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.15 (br s, 1H), 3.49–3.37 (m, 8H), 2.35 (m, 2H), 2.24 (t, J = 6.6 Hz, 4H), 1.65–1.48 (m, 12H), 1.40–1.33 (m, 10H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 179.4, 77.6, 77.3, 70.9, 70.7, 66.2, 65.5, 65.4, 34.1, 29.8, 29.65, 29.62, 28.7, 28.6, 28.5, 28.3, 28.2, 25.8, 24.6, 22.9, 19.23, 19.21, 15.3; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20b: Compound **20b** was synthesized from **19b** (67 mg, 0.18 mmol) with the procedure H and obtained as white solid. Yield: 48% (33.1 mg, 0.08 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.24 (br s, 1H), 3.46 (q, J = 6.8 Hz, 2H), 3.41–3.36 (m, 6H), 2.33 (t, J = 7.2 Hz, 2H), 2.29–2.22 (m, 4H), 1.69–1.48 (m, 12H), 1.44–1.32 (m, 10H), 1.19 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference

peak $CDCl_3$ at 77.16 ppm): δ 179.3, 77.4, 77.3, 71.1, 70.8, 70.2, 66.2, 65.6, 65.5, 34.1, 29.81, 29.77, 29.4, 28.9, 28.6, 28.5, 28.2, 26.3, 26.2, 25.2, 24.6, 19.2, 19.1, 15.3; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20c: Compound **20c** was synthesized from **19c** (91.7 mg, 0.24 mmol) with the procedure H and obtained as white solid. Yield: 57% (54.2 mg, 0.14 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.50 (br s, 1H), 3.52 (t, J = 6.8 Hz, 2H), 3.49–3.38 (m, 6H), 2.50 (t, J = 6.8 Hz, 2H), 2.34 (m, 2H), 2.23 (t, J = 6.6 Hz, 2H), 1.62–1.49 (m, 8H), 1.39–1.28 (m, 14H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 179.4, 77.7, 74.2, 71.3, 70.9, 68.6, 66.4, 66.2, 65.4, 34.0, 29.8, 29.7, 29.6, 29.54, 29.49, 28.6, 28.5, 28.1, 26.3, 26.2, 24.6, 20.7, 19.2, 15.3; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20d: Compound **20d** was synthesized from **19d** (200 mg, 0.53 mmol) with the procedure H and obtained as white solid. Yield: 68% (141.2 mg, 0.36 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 8.37 (br s, 1H), 4.18 (s, 2H), 3.51–3.44 (m, 4H), 3.40 (t, J = 6.75 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 2.28 (t, J = 6.9 Hz, 2H), 1.69–1.49 (m, 8H), 1.47–1.28 (m, 16H), 1.20 (t, J = 7.05 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 179.2, 81.0, 72.4, 71.2, 71.0, 70.6, 66.3, 64.9, 58.8, 34.1, 30.0, 29.71, 29.69, 29.6, 28.7, 28.6, 28.1, 26.4, 26.3, 24.7, 19.4, 15.4; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

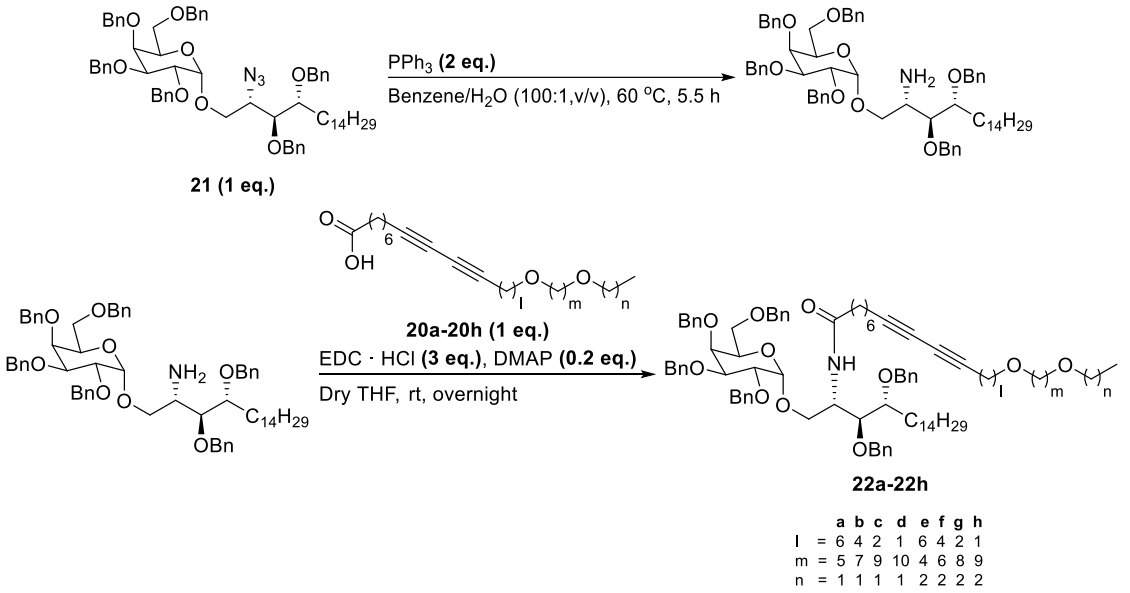
Compound 20e: Compound **20e** was synthesized from **19e** (56.9 mg, 0.15 mmol) with the procedure H and obtained as white solid. Yield: 83% (49.2 mg, 0.13 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.35 (br s, 1H), 3.42–3.34 (m, 8H), 2.33–2.31 (m, 2H), 2.23 (t, J = 6.6 Hz, 4H), 1.62–1.60 (m, 6H), 1.58–1.48 (m, 8H), 1.39–1.33 (m, 8H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 179.6, 77.7, 77.4, 72.7, 70.9, 70.8, 70.7, 65.6, 65.5, 34.2, 29.7, 28.8, 28.7, 28.6, 28.4, 28.3, 26.6, 25.9, 24.7, 23.1, 19.33, 19.31, 10.8; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20f: Compound **20f** was synthesized from **19f** (46.5 mg, 0.12 mmol) with the procedure H and obtained as white solid. Yield: 96% (46.1 mg, 0.12 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.32 (br s, 1H), 3.41–3.34 (m, 8H), 2.33 (t, J = 7.4 Hz, 2H), 2.28–2.22 (m, 4H), 1.68–1.48 (m, 14H), 1.44–1.33 (m, 8H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 179.4, 77.4, 77.3, 72.7, 71.0, 70.9, 70.2, 65.6, 65.5, 34.0, 29.8, 28.9, 28.6, 28.5, 28.2, 26.2, 25.2, 24.6, 23.0, 19.2, 19.1, 10.7; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20g: Compound **20g** was synthesized from **19g** (70 mg, 0.18 mmol) with the procedure H and obtained as white solid. Yield: 64% (46.3 mg, 0.12 mmol); ^{1}H NMR (300 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.56 (br s, 1H), 3.52 (t, J = 7.05 Hz, 2H), 3.44–3.33 (m, 6H), 2.51 (t, J = 7.05 Hz, 2H), 2.33 (t, J = 7.2 Hz, 2H), 2.23 (t, J = 6.75 Hz, 2H), 1.65–1.47 (m, 10H), 1.45–1.30 (m, 12H), 0.90 (t, J = 7.35 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 179.7, 77.8, 74.2, 72.7, 71.3, 71.1, 68.7, 66.4, 65.5, 34.2, 29.9, 29.7, 29.60, 29.57, 28.7, 28.6, 28.2, 26.3, 26.2, 24.7, 23.1, 20.8, 19.3, 10.8; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

Compound 20h: Compound **20h** was synthesized from **19h** (136 mg, 0.36 mmol) with the procedure H and obtained as white solid. Yield: 61% (86.2 mg, 0.22 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak $CDCl_3$ at 7.26 ppm): δ 10.39 (br s, 1H), 4.18 (s, 2H), 3.49 (t, J = 6.6 Hz, 2H), 3.42–3.35 (m, 4H), 2.36 (t, J = 6.8 Hz, 2H), 2.28 (t, J = 6.8 Hz, 2H), 1.66–1.51 (m, 10H), 1.46–1.30 (m, 14H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 179.5, 80.9, 72.7, 72.3, 71.1, 71.0, 70.5, 64.8, 58.7, 34.0, 29.8, 29.6, 29.54, 29.49, 28.6, 28.5, 28.0, 26.3, 26.2, 24.6, 23.0, 19.3, 10.7; LRMS (ESI) m/z calcd for $C_{24}H_{41}O_4$ $[M+H]^+$: 393.3, found: 393.3.

I. General synthetic procedure and characterization for compounds 22a–22h



To a solution of **21**[2] (1 equiv.) at r.t. in benzene (2 mL) and H_2O (20 μL) was added PPh_3 (2 equiv.), then stirred at 60 °C for 5.5 h. After reaction completion checked by TLC, the reaction mixture was concentrated *in vacuo*. The residue was evaporated with dry toluene three times to remove H_2O. **20a–20h** (1 equiv.), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 3 equiv.) and 4-dimethylaminopyridine (DMAP) (0.2 equiv.) were added to the corresponding mixture and dissolved in dry THF (2 mL) under Ar(g), then stirred at r.t. for overnight. After reaction completion checked by TLC, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (16.67% EA in hexane gradient to 25%) to obtain the desired compounds **22a–22h**.

Compound 22a: Compound **22a** was synthesized from **21** (78.4 mg, 0.075 mmol) and **20a** (29.4 mg, 0.075 mmol) with the procedure I and obtained as colorless gel. Two step yield: 75% (78.8 mg, 0.056 mmol); $[\alpha]_D^{25}$ +16.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.12 (d, J = 8.8 Hz, 1H), 4.92 (d, J = 11.6 Hz, 1H), 4.85 (d, J = 3.6 Hz, 1H), 4.81–4.73 (m, 4H), 4.65–4.35 (m, 7H), 4.20–4.13 (m, 1H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, J = 10.8, 3.2 Hz, 1H), 3.52–3.36 (m, 11H), 2.23–2.17 (m, 4H), 1.95–1.86 (m, 2H), 1.68–1.16 (m, 51H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 172.7, 138.8, 138.7, 138.57, 138.56, 137.7, 128.52, 128.48, 128.46, 128.44, 128.42, 128.39, 128.3, 128.01, 127.97, 127.9, 127.81, 127.76, 127.66, 127.65, 127.6, 127.5, 99.7, 80.2, 79.0, 78.8, 77.6, 77.39, 77.36, 76.8, 74.9, 74.8, 73.7, 73.6, 73.0, 71.8, 70.9, 70.7, 70.1, 69.5, 69.4, 66.2, 65.6, 65.4, 50.5, 36.6, 32.0, 30.0, 29.9, 29.84, 29.78, 29.75, 29.71, 29.5, 28.9, 28.8, 28.7, 28.4, 28.3, 26.2, 25.8, 25.5, 23.0, 22.8, 19.2, 15.4, 14.2; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.2.

Compound 22b: Compound **22b** was synthesized from **21** (75.6 mg, 0.072 mmol) and **20b** (28.4 mg, 0.072 mmol) with the procedure I and obtained as colorless gel. Two step yield: 64% (64.4 mg, 0.046 mmol); $[\alpha]_D^{25}$ +16.6 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.12 (d, J = 8.4 Hz, 1H), 4.92 (d, J = 11.6 Hz, 1H), 4.85 (d, J = 3.6 Hz, 1H), 4.81–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.20–4.13 (m, 1H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, J = 11.0, 3.4 Hz, 1H), 3.52–3.35 (m, 11H), 2.25 (t, J = 6.8 Hz, 2H), 2.18 (t, J = 6.8 Hz, 2H), 1.95–1.86 (m, 2H), 1.68–1.18 (m, 51H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 172.7, 138.79, 138.78, 138.7, 138.58, 138.56, 137.7, 128.53, 128.49, 128.47, 128.45, 128.43, 128.39, 128.36, 128.01, 127.98, 127.9, 127.81, 127.76, 127.67, 127.65, 127.6, 127.5, 99.7, 80.2, 79.0, 78.8, 77.4, 76.8, 74.9, 74.8, 73.7, 73.6, 73.0, 71.8, 71.1, 70.8, 70.2, 70.1, 69.5, 69.4, 66.2, 65.7, 65.6, 50.5, 36.6, 32.0, 30.0, 29.93, 29.87, 29.84, 29.80, 29.49, 29.46, 29.0, 28.9, 28.7, 28.3, 26.28, 26.25, 26.2, 25.5, 25.3, 22.8, 19.2, 19.1, 15.4, 14.3; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.3.

Compound 22c: Compound **22c** was synthesized from **21** (76.7 mg, 0.073 mmol) and **20c** (28.8 mg, 0.073 mmol) with the procedure I and obtained as colorless gel. Two step yield: 67% (68.6 mg, 0.049 mmol); $[\alpha]_D^{25}$ +17.5 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.39–7.21 (m, 30H), 6.13 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.81–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.20–4.13 (m, 1H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.52–3.38 (m, 11H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.93–1.88 (m, 2H), 1.68–1.16 (m, 51H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 172.7, 138.78, 138.77, 138.7, 138.6, 138.5, 137.7, 128.53, 128.49, 128.47, 128.44, 128.42, 128.39, 128.3, 128.01, 127.97, 127.9, 127.81, 127.76, 127.7, 127.65, 127.63, 127.5, 99.7, 80.2, 79.0, 78.8, 77.8, 77.4, 76.8, 74.9, 74.8, 74.1, 73.69, 73.68, 73.6, 73.0, 71.8, 71.3, 70.9, 70.1, 69.5, 69.4, 68.6, 66.4, 66.1, 65.4, 50.5, 36.6, 32.0, 30.0, 29.9, 29.84, 29.81, 29.79, 29.7, 29.6, 29.55, 29.50, 29.49, 28.9, 28.6, 28.2, 26.3, 26.2, 25.5, 22.8, 20.7, 19.2, 15.4, 14.2; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.3.

Compound 22d: Compound **22d** was synthesized from **21** (100 mg, 0.096 mmol) and **20d** (37.5 mg, 0.096 mmol) with the procedure I and obtained as colorless gel. Two step yield: 75% (99.8 mg, 0.072 mmol); $[\alpha]_D^{25}$ +14.9 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.12 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 4.82–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.19–4.13 (m, 3H), 4.06–4.00 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.52–3.38 (m, 9H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.95–1.86 (m, 2H), 1.68–1.18 (m, 53H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 172.8, 138.88, 138.86, 138.8, 138.7, 137.8, 128.64, 128.60, 128.57, 128.55, 128.53, 128.50, 128.46, 128.11, 128.07, 128.0, 127.91, 127.87, 127.8, 127.7, 127.6, 99.8, 81.0, 80.3, 79.1, 78.9, 77.4, 76.9, 75.0, 74.9, 73.8, 73.7, 73.1, 72.4, 71.9, 71.2, 71.0, 70.6, 70.2, 69.7, 69.5, 66.3, 64.9, 58.8, 50.6, 36.6, 32.1, 30.1, 30.0, 29.94, 29.89, 29.73, 29.71, 29.69, 29.64, 29.59, 28.9, 28.8, 28.2, 26.4, 26.3, 25.6, 22.9, 19.4, 15.5, 14.3; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.1.

Compound 22e: Compound **22e** was synthesized from **21** (81 mg, 0.077 mmol) and **20e** (30.4 mg, 0.077 mmol) with the procedure I and obtained as colorless gel. Two step yield: 69% (74.4 mg, 0.053 mmol); $[\alpha]_D^{25}$ +15.0 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.09 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 4.82–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.19–4.13 (m, 1H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.52–3.34 (m, 11H), 2.24–2.17 (m, 4H), 1.95–1.85 (m, 2H), 1.68–1.18 (m, 48H), 0.93–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 172.8, 138.89, 138.88, 138.8, 138.7, 137.8, 128.63, 128.59, 128.56, 128.54, 128.52, 128.49, 128.4, 128.11, 128.07, 128.0, 127.90, 127.86, 127.8, 127.7, 127.6, 99.8, 80.3, 79.1, 78.9, 77.7, 77.4, 76.9, 75.0, 74.9, 73.8, 73.7, 73.1, 72.8, 71.9, 71.0, 70.9, 70.8, 70.2, 69.7, 69.5, 65.6, 65.5, 50.6, 36.7, 32.1, 30.1, 30.0, 29.94, 29.89, 29.8, 29.6, 29.0, 28.9, 28.8, 28.5, 28.4, 26.7, 26.3, 25.9, 25.6, 23.2, 22.9, 19.4, 14.3, 10.8; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.2.

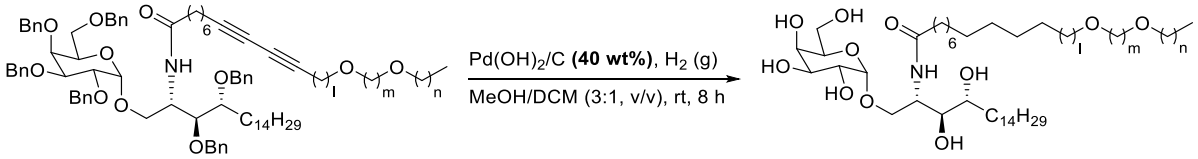
Compound 22f: Compound **22f** was synthesized from **21** (92.2 mg, 0.088 mmol) and **20f** (34.6 mg, 0.088 mmol) with the procedure I and obtained as colorless gel. Two step yield: 60% (74.1 mg, 0.053 mmol); $[\alpha]_D^{25}$ +16.6 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.09 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 4.82–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.19–4.13 (m, 1H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.52–3.34 (m, 11H), 2.26 (t, *J* = 7.0 Hz, 2H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.95–1.85 (m, 2H), 1.69–1.16 (m, 48H), 0.93–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 172.8, 138.89, 138.88, 138.8, 138.7, 137.8, 128.63, 128.59, 128.56, 128.54, 128.52, 128.49, 128.4, 128.11, 128.07, 128.0, 127.90, 127.86, 127.8, 127.75, 127.73, 127.6, 99.8, 80.3, 79.1, 78.9, 77.5, 76.9, 75.0, 74.9, 73.8, 73.7, 73.1, 72.8, 71.9, 71.1, 71.0, 70.3, 70.2, 69.7, 69.5, 65.7, 65.6, 50.6, 36.7, 32.1, 30.1, 30.0, 29.94, 29.89, 29.6, 29.1, 29.0, 28.8, 28.4, 26.7, 26.3, 25.6, 25.3, 23.2, 22.9, 19.3, 19.2, 14.3, 10.8; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.2.

Compound 22g: Compound **22g** was synthesized from **21** (104 mg, 0.099 mmol) and **20g** (39 mg, 0.099 mmol) with the procedure I and obtained as colorless gel. Two step yield: 68% (94.3 mg, 0.068 mmol); $[\alpha]_D^{25}$ +14.8 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.09 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 4.82–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.19–4.13 (m, 1H), 4.06–4.00 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.52–3.34 (m, 11H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 1.95–1.85 (m, 2H), 1.66–1.16 (m, 48H), 0.93–0.86 (m, 6H); ^{13}C NMR (100

MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.23 ppm): δ 172.8, 138.88, 138.87, 138.8, 138.7, 137.8, 128.63, 128.58, 128.56, 128.54, 128.52, 128.49, 128.4, 128.10, 128.07, 128.0, 127.90, 127.86, 127.8, 127.7, 127.6, 99.8, 80.3, 79.1, 78.9, 77.9, 76.9, 75.0, 74.9, 74.2, 73.8, 73.7, 73.1, 72.8, 71.9, 71.4, 71.1, 70.2, 69.7, 69.5, 68.7, 66.5, 65.5, 50.6, 36.7, 32.1, 30.1, 30.03, 29.97, 29.94, 29.88, 29.8, 29.63, 29.60, 29.58, 29.0, 28.8, 28.3, 26.34, 26.28, 26.2, 25.6, 23.2, 22.9, 20.8, 19.3, 14.3, 10.8; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.3.

Compound 22h: Compound **22h** was synthesized from **21** (104 mg, 0.099 mmol) and **20g** (39.0 mg, 0.099 mmol) with the procedure I and obtained as colorless gel. Two step yield: 50% (70 mg, 0.050 mmol); $[\alpha]_D^{25}$ +15.4 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, reference peak TMS at 0.00 ppm): δ 7.38–7.21 (m, 30H), 6.13 (d, J = 8.4 Hz, 1H), 4.92 (d, J = 11.6 Hz, 1H), 4.85 (d, J = 3.6 Hz, 1H), 4.81–4.72 (m, 4H), 4.65–4.35 (m, 7H), 4.19–4.15 (m, 3H), 4.06–3.99 (m, 2H), 3.94–3.84 (m, 4H), 3.74 (dd, J = 11.0, 3.4 Hz, 1H), 3.52–3.34 (m, 9H), 2.21 (t, J = 7.0 Hz, 2H), 1.95–1.86 (m, 2H), 1.68–1.16 (m, 50H), 0.93–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, reference peak $CDCl_3$ at 77.16 ppm): δ 172.7, 138.78, 138.77, 138.7, 138.565, 138.556, 137.7, 128.53, 128.49, 128.47, 128.45, 128.42, 128.39, 128.36, 128.01, 127.97, 127.9, 127.81, 127.76, 127.67, 127.65, 127.6, 127.5, 99.7, 80.9, 80.2, 79.0, 78.8, 76.8, 74.9, 74.8, 73.70, 73.68, 73.6, 73.0, 72.7, 72.3, 71.8, 71.1, 71.0, 70.5, 70.1, 69.6, 69.4, 64.8, 58.7, 50.5, 36.5, 32.0, 30.0, 29.93, 29.89, 29.84, 29.79, 29.6, 29.53, 29.49, 28.8, 28.7, 28.1, 26.3, 26.2, 25.5, 23.1, 22.8, 19.3, 14.2, 10.7; LRMS (ESI) m/z calcd for $C_{90}H_{123}NNaO_{11}$ $[M+Na]^+$: 1416.9, found: 1417.2.

J. General synthetic procedure and characterization for compounds 3–10



	a	b	c	d	e	f	g	h
l =	6	4	2	1	6	4	2	1
m =	5	7	9	10	4	6	8	9
n =	1	1	1	1	2	2	2	2

To a solution of **22a–22h** (1 equiv.) in MeOH (3 mL) and DCM (1 mL) at r.t. was added $Pd(OH)_2/C$ (40 wt%), then stirred at r.t. for 8 h under H_2(g). After reaction completion checked by TLC, the reaction mixture was filtered through celite with MeOH/DCM (4:1, v/v). The resultant was concentrated *in vacuo* to obtain the desired compounds **3–10**.

Compound 3: Compound **3** was synthesized from **22a** (78.1 mg, 0.056 mmol) with the procedure J and obtained as white solid. Yield: 90% (43.3 mg, 0.050 mmol); $[\alpha]_D^{25}$ +55.1 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.20 (q, J = 4.4 Hz, 1H), 3.93 (d, J = 2.8 Hz, 1H), 3.89 (dd, J = 10.6, 4.6 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.68 (m, 4H), 3.59–3.42 (m, 10H), 2.22 (t, J = 7.6 Hz, 2H), 1.66–1.54 (m, 8H), 1.45–1.27 (m, 52H), 1.21 (t, J = 6.8 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.2, 100.4, 75.0, 72.5, 71.6, 71.5, 71.3, 71.2, 70.8, 70.4, 69.5, 67.8, 66.7, 62.3, 51.1, 36.9, 32.8, 32.5, 30.33, 30.31, 30.25, 30.22, 30.21, 30.16, 30.1, 30.0, 29.93, 29.92, 29.91, 26.6, 26.5, 26.4, 23.25, 23.19, 15.3, 14.3; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6794.

Compound 4: Compound **4** was synthesized from **22b** (52.9 mg, 0.038 mmol) with the procedure J and obtained as white solid. Yield: quantitative (35 mg, 0.0401 mmol); $[\alpha]_D^{25}$ +52.9 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.21 (q, J = 4.4 Hz, 1H), 3.93 (d, J = 2.8 Hz, 1H), 3.89 (dd, J = 10.4, 4.8 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.68 (m, 4H), 3.59–3.42 (m, 10H), 2.22 (t, J = 7.6 Hz, 2H), 1.67–1.56 (m, 8H), 1.38–1.27 (m, 52H), 1.21 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ

175.2, 100.4, 75.1, 72.4, 71.54, 71.45, 71.3, 70.8, 70.3, 69.5, 67.8, 66.7, 62.3, 51.1, 36.9, 32.8, 32.5, 30.32, 30.30, 30.25, 30.22, 30.19, 30.17, 30.11, 30.07, 30.04, 30.02, 29.99, 29.9, 29.8, 26.64, 26.59, 26.5, 26.4, 23.2, 15.3, 14.3; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6800.

Compound 5: Compound **5** was synthesized from **22c** (56 mg, 0.040 mmol) with the procedure J and obtained as white solid. Yield: 95% (33 mg, 0.038 mmol); $[\alpha]_D^{25}$ +59.8 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.21 (q, J = 4.4 Hz, 1H), 3.93 (d, J = 2.8 Hz, 1H), 3.89 (dd, J = 10.6, 4.6 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.68 (m, 4H), 3.57–3.42 (m, 10H), 2.22 (t, J = 7.6 Hz, 2H), 1.67–1.54 (m, 8H), 1.36–1.27 (m, 52H), 1.21 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.1, 100.3, 75.1, 72.4, 71.53, 71.51, 71.3, 70.8, 70.3, 69.5, 67.8, 66.7, 62.3, 51.1, 36.9, 32.8, 32.5, 30.32, 30.29, 30.25, 30.21, 30.19, 30.16, 30.12, 30.09, 30.05, 30.03, 29.99, 29.91, 26.64, 26.59, 26.5, 26.4, 23.2, 15.3, 14.3; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6798.

Compound 6: Compound **6** was synthesized from **22d** (40 mg, 0.029 mmol) with the procedure J and obtained as white solid. Yield: 95% (23.5 mg, 0.027 mmol); $[\alpha]_D^{25}$ +51.1 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.21 (q, J = 4.4 Hz, 1H), 3.93 (d, J = 2.4 Hz, 1H), 3.89 (dd, J = 10.6, 4.6 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.68 (m, 4H), 3.59–3.42 (m, 10H), 2.22 (t, J = 7.6 Hz, 2H), 1.70–1.54 (m, 8H), 1.36–1.27 (m, 52H), 1.21 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.2, 100.4, 75.1, 72.5, 71.59, 71.55, 71.4, 70.9, 70.4, 69.6, 67.8, 66.7, 62.3, 51.1, 36.9, 32.9, 32.5, 30.34, 30.31, 30.27, 30.21, 30.18, 30.15, 30.12, 30.10, 30.07, 30.05, 29.99, 29.98, 29.9, 26.7, 26.6, 26.5, 26.4, 23.2, 15.3, 14.3; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6796.

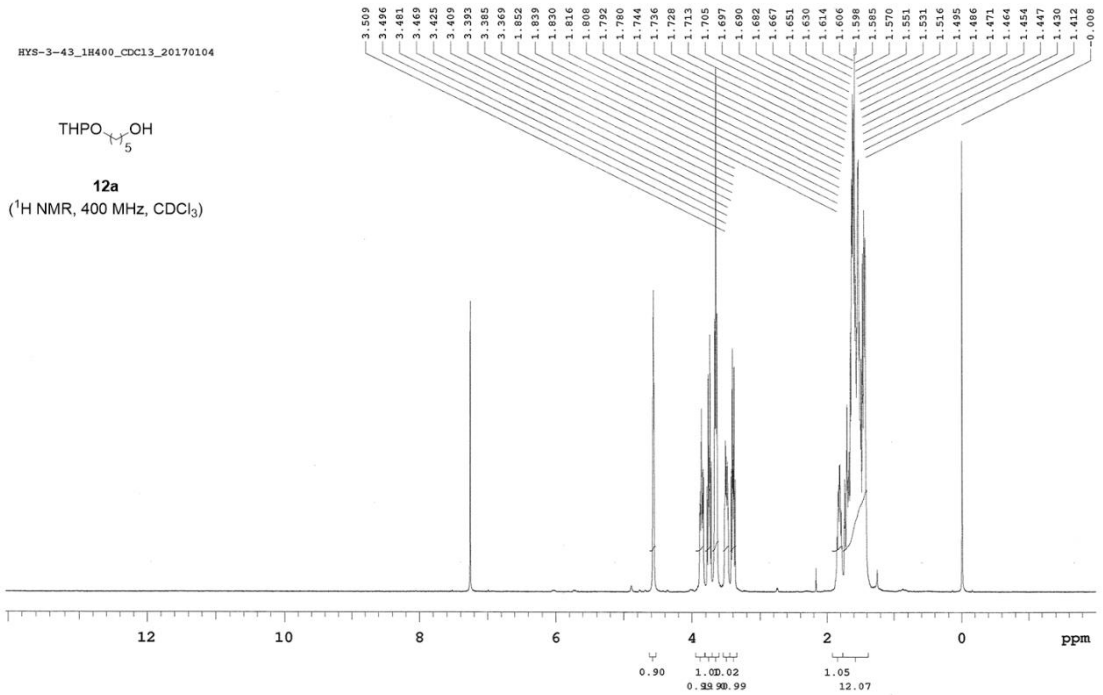
Compound 7: Compound **7** was synthesized from **22e** (40 mg, 0.029 mmol) with the procedure J and obtained as white solid. Yield: 88% (21.8 mg, 0.25 mmol); $[\alpha]_D^{25}$ +60.0 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (300 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.24–4.17 (m, 1H), 3.93 (d, J = 2.4 Hz, 1H), 3.88 (dd, J = 10.95, 4.65 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.67 (m, 4H), 3.61–3.53 (m, 2H), 3.47–3.38 (m, 8H), 2.22 (t, J = 7.65 Hz, 2H), 1.69–1.54 (m, 10H), 1.44–1.27 (m, 50H), 0.96–0.87 (m, 6H); ^{13}C NMR (75 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.3, 100.4, 75.0, 73.2, 72.4, 71.6, 71.2, 70.9, 70.4, 69.6, 67.8, 62.3, 51.2, 37.0, 32.8, 32.5, 30.34, 30.28, 30.19, 30.15, 30.0, 29.9, 26.9, 26.8, 26.7, 26.53, 26.46, 23.3, 23.2, 14.3, 10.8; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6801.

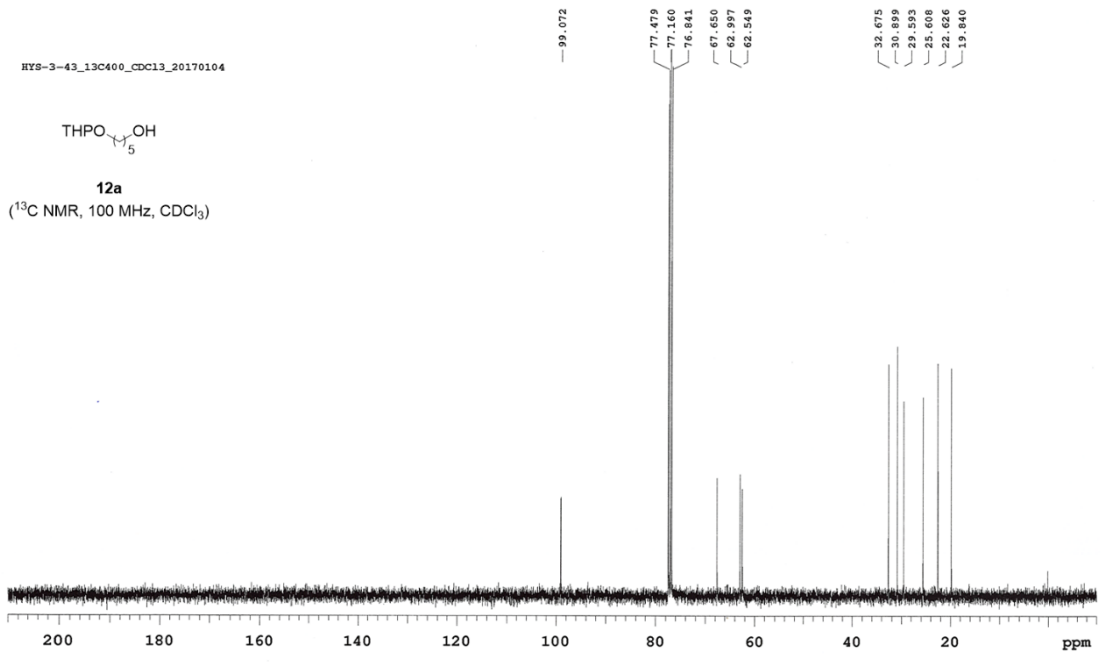
Compound 8: Compound **8** was synthesized from **22f** (40 mg, 0.029 mmol) with the procedure J and obtained as white solid. Yield: 94% (23.2 mg, 0.27 mmol); $[\alpha]_D^{25}$ +61.6 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (300 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.3 Hz, 1H), 4.20 (q, J = 4.5 Hz, 1H), 3.94–3.93 (m, 1H), 3.88 (dd, J = 10.95, 4.65 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.67 (m, 4H), 3.61–3.53 (m, 2H), 3.47–3.38 (m, 8H), 2.22 (t, J = 7.5 Hz, 2H), 1.66–1.56 (m, 10H), 1.41–1.27 (m, 50H), 0.96–0.87 (m, 6H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.2, 100.4, 75.1, 73.2, 72.5, 71.6, 71.40, 71.38, 70.9, 70.4, 69.6, 67.8, 62.3, 51.1, 37.0, 32.8, 32.5, 30.34, 30.32, 30.27, 30.24, 30.21, 30.19, 30.14, 30.09, 30.04, 30.02, 29.94, 29.92, 26.7, 26.50, 26.49, 26.4, 23.3, 23.2, 14.3, 10.7; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6796.

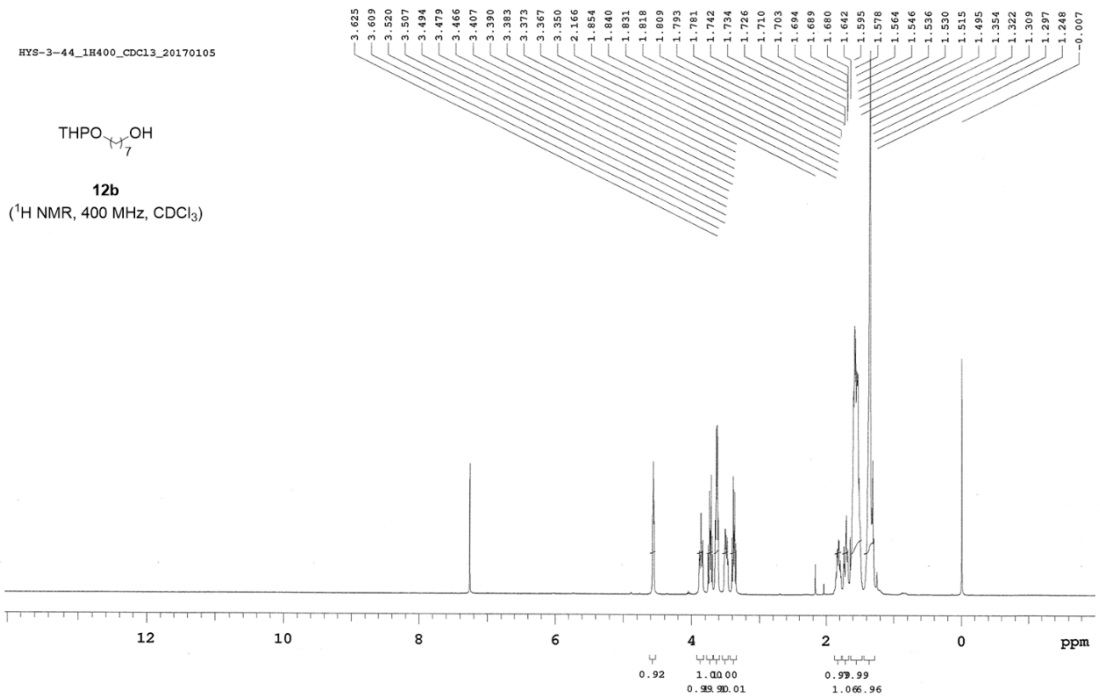
Compound 9: Compound **9** was synthesized from **22g** (40 mg, 0.027 mmol) with the procedure J and obtained as white solid. Yield: 64% (15.9 mg, 0.18 mmol); $[\alpha]_D^{25}$ +57.9 (c = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^{1}H NMR (300 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, J = 3.6 Hz, 1H), 4.21 (q, J = 4.5 Hz, 1H), 3.93 (d, J = 2.4 Hz, 1H), 3.89 (dd, J = 10.95, 4.65 Hz, 1H), 3.84–3.78 (m, 2H), 3.76–3.67 (m, 4H), 3.60–3.52 (m, 2H), 3.46–3.38 (m, 8H), 2.22 (t, J = 7.5 Hz, 2H), 1.66–1.54 (m, 10H), 1.34–1.27 (m, 50H), 0.95–0.87 (m, 6H); ^{13}C NMR (75 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.2, 100.4, 75.1, 73.2, 72.4, 71.6, 71.51, 71.49, 70.9, 70.4, 69.5, 67.8, 62.3, 51.1, 36.9, 32.8, 32.5, 30.33, 30.32, 30.27, 30.23, 30.21, 30.19, 30.14, 30.10, 30.05, 30.01, 29.95, 29.9, 26.7, 26.6, 26.5, 26.4, 23.3, 23.2, 14.3, 10.7; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6799.

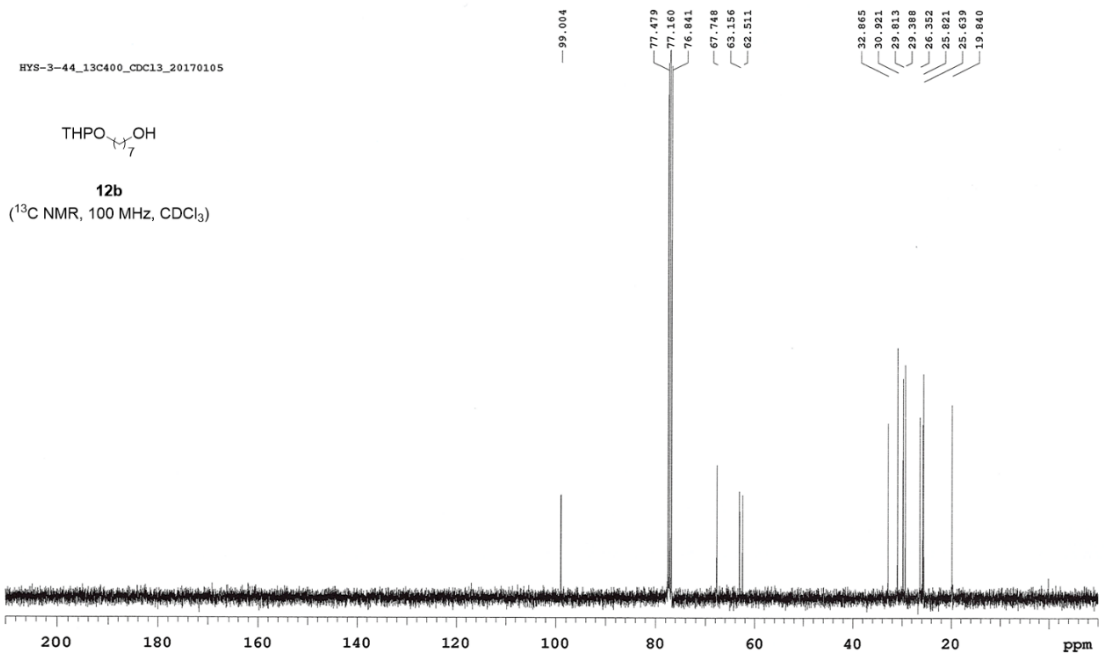
Compound 10: Compound **10** was synthesized from **22h** (57.8 mg, 0.041 mmol) with the procedure J and obtained as white solid. Yield: 89% (31.7 mg, 0.37 mmol); $[\alpha]_D^{25}$ +56.2 (*c* = 0.50, MeOH/$CHCl_3$ (1:1, v/v)); ^1H NMR (400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak TMS at 0.00 ppm): δ 4.91 (d, *J* = 3.6 Hz, 1H), 4.21 (q, *J* = 4.4 Hz, 1H), 3.93 (d, *J* = 2.8 Hz, 1H), 3.89 (dd, *J* = 10.6, 4.6 Hz, 1H), 3.84–3.79 (m, 2H), 3.76–3.68 (m, 4H), 3.59–3.53 (m, 2H), 3.46–3.38 (m, 8H), 2.22 (t, *J* = 7.6 Hz, 2H), 1.67–1.54 (m, 10H), 1.36–1.27 (m, 50H), 0.95–0.87 (m, 6H); ^{13}C NMR (100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v), reference peak CD_3OD at 49.00 ppm): δ 175.1, 100.3, 75.1, 73.1, 72.4, 71.53, 71.52, 71.48, 70.8, 70.3, 69.5, 67.8, 62.3, 51.0, 36.9, 32.8, 32.5, 30.32, 30.29, 30.24, 30.19, 30.16, 30.12, 30.09, 30.06, 30.03, 29.98, 29.91, 29.89, 26.65, 26.59, 26.5, 26.4, 23.3, 23.2, 14.3, 10.7; HRMS (ESI) m/z calcd for $C_{48}H_{95}NNaO_{11}$ $[M+Na]^+$: 884.6797, found: 884.6796.

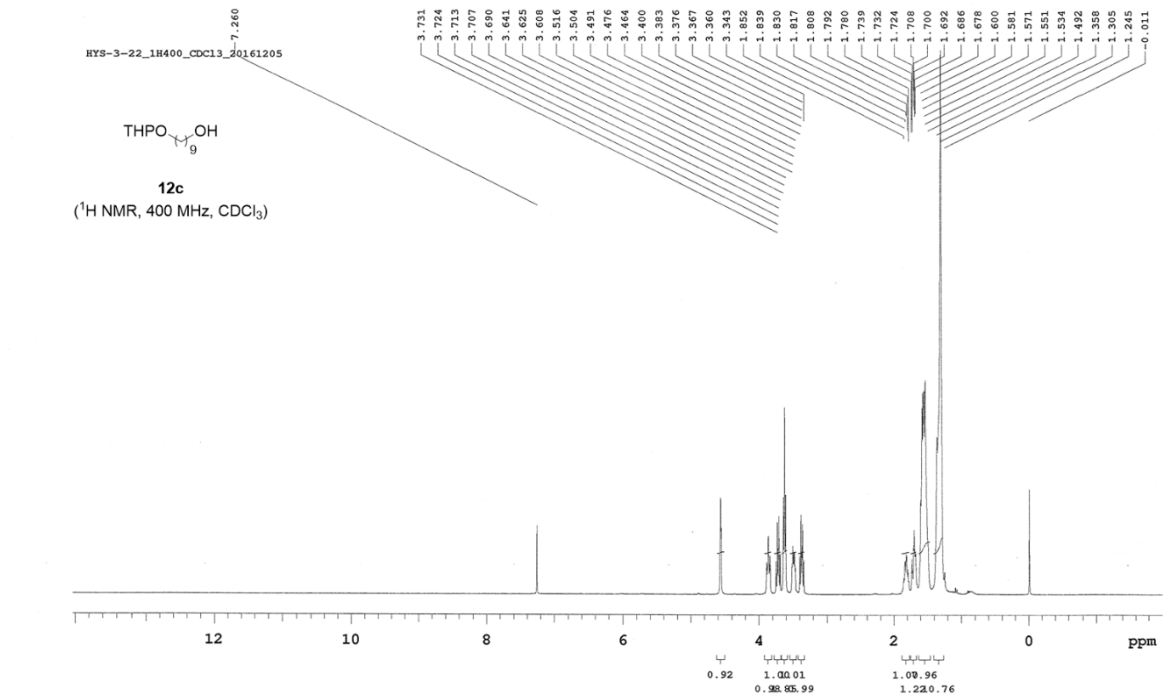
4. ^{1}H and ^{13}C NMR Spectra

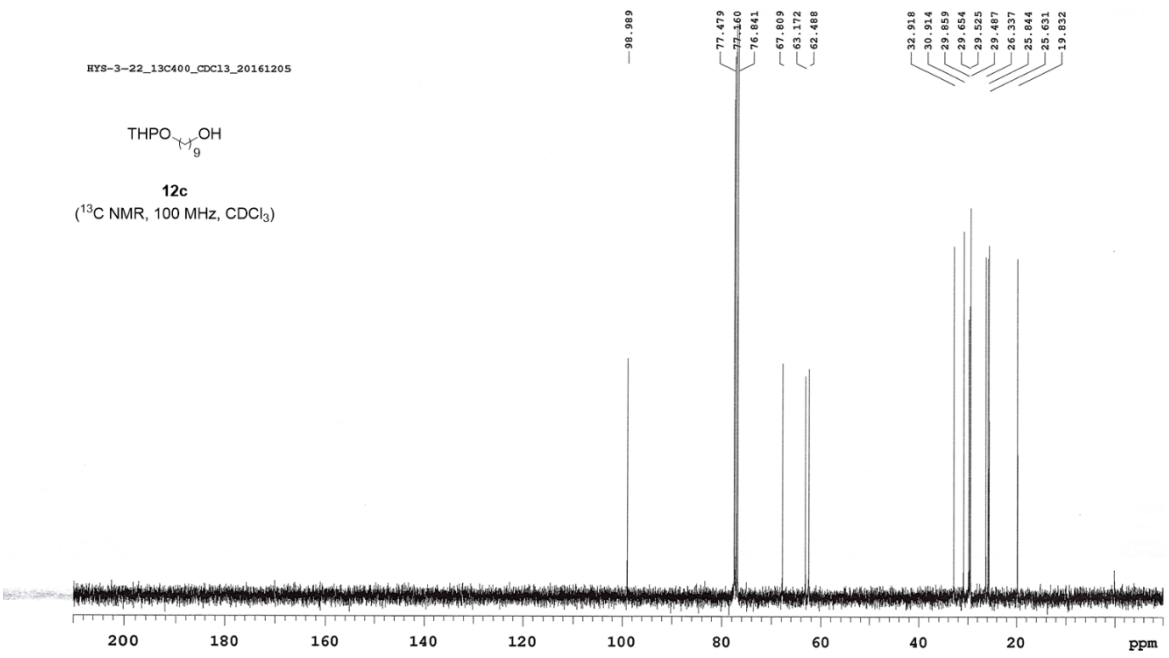


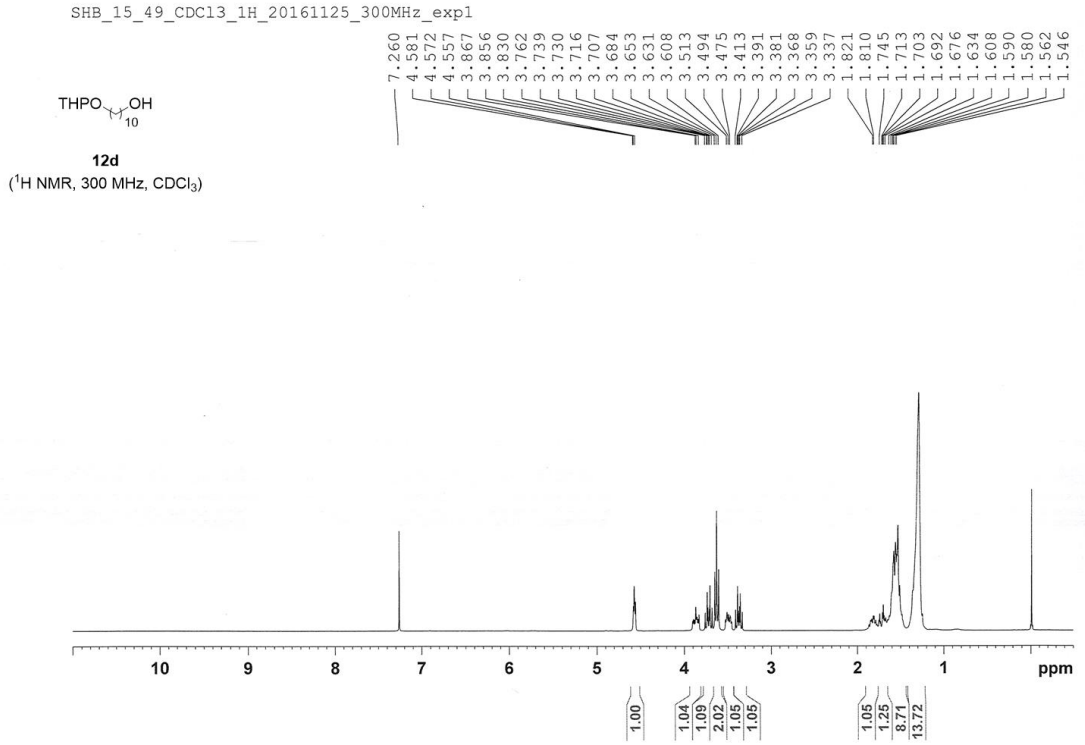



HYS-3-44_1H400_CDCl3_20170105
THPO
OH
7
12b
(1H NMR, 400 MHz, CDCl3)
3.625
3.609
3.520
3.507
3.494
3.479
3.466
3.407
3.390
3.383
3.373
3.367
3.350
2.166
1.854
1.840
1.831
1.818
1.809
1.793
1.781
1.742
1.734
1.726
1.710
1.703
1.694
1.689
1.680
1.642
1.595
1.578
1.564
1.546
1.536
1.530
1.515
1.495
1.354
1.322
1.309
1.297
1.248
0.007
12
10
8
6
4
2
0
ppm
0.92
1.00
0.99
0.01
0.97
9.99
1.06
6.96


HYS-3-44_13C400_CDCl3_20170105
THPO
OH
7
12b
(13C NMR, 100 MHz, CDCl3)
99.004
77.479
77.160
76.841
67.748
63.156
62.511
32.865
30.921
29.813
29.388
26.352
25.821
25.639
19.840
200
180
160
140
120
100
80
60
40
20
ppm

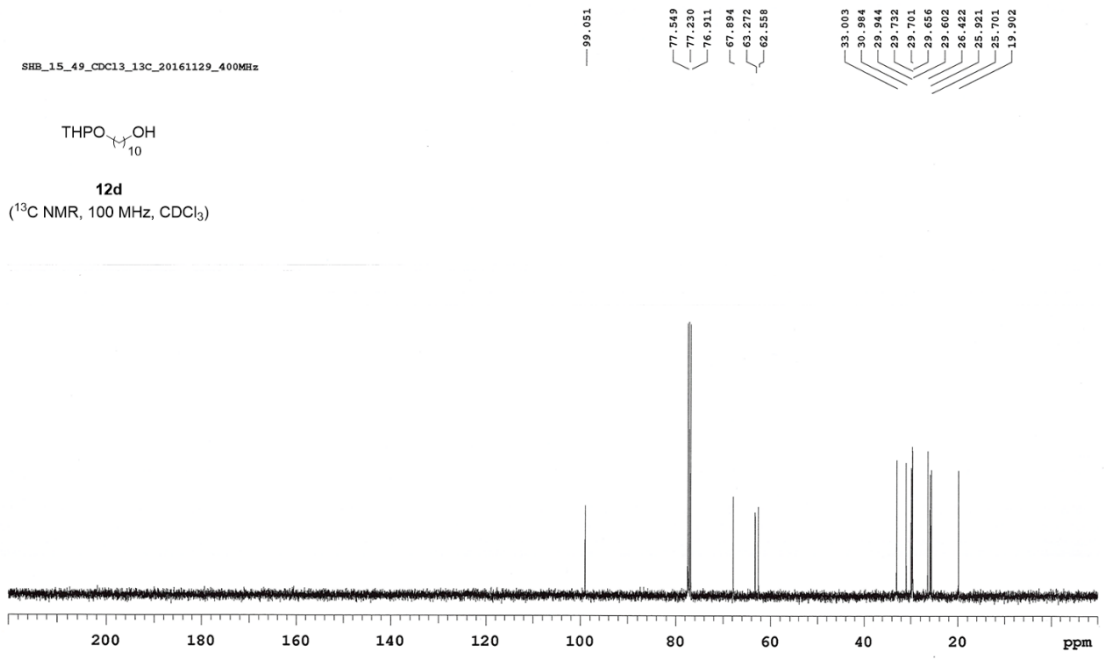

HYS-3-22_1H400_CDCl3_20161205
THPO
OH
9
12c
(1H NMR, 400 MHz, CDCl3)
7.260
3.731
3.724
3.713
3.707
3.690
3.641
3.625
3.608
3.516
3.504
3.491
3.476
3.464
3.400
3.383
3.376
3.367
3.360
3.343
1.852
1.839
1.830
1.817
1.808
1.792
1.780
1.739
1.732
1.724
1.708
1.700
1.692
1.686
1.678
1.600
1.581
1.571
1.551
1.534
1.492
1.358
1.305
1.245
0.011
12
10
8
6
4
2
0
ppm
0.92
1.00
0.98
1.01
5.99
1.09
1.22
0.96
0.76


HYS-3-22_13C400_CDCl3_20161205
THPO
OH
9
12c
(13C NMR, 100 MHz, CDCl3)
98.989
77.479
77.160
76.841
67.809
63.172
62.488
32.918
30.914
29.859
29.654
29.525
29.487
26.337
25.844
25.631
19.832
200
180
160
140
120
100
80
60
40
20
ppm



12d

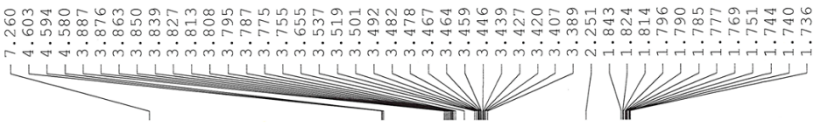
(^{1}H NMR, 300 MHz, $CDCl_3$)



12d

(^{13}C NMR, 100 MHz, $CDCl_3$)

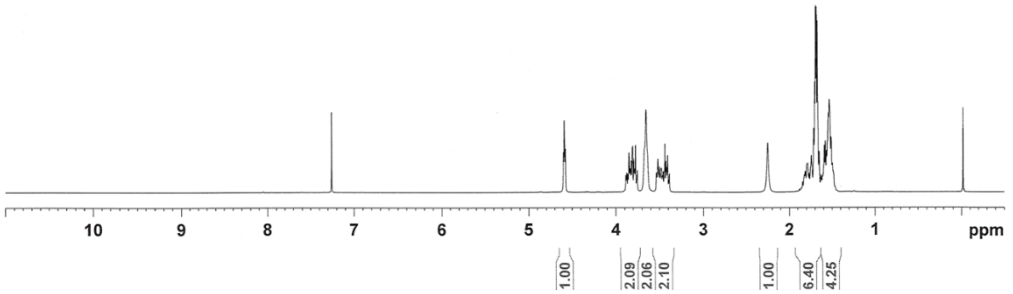
SHB_16_21_CDCl3_1H_20170216_300MHz_exp1



THPO–(CH2)4–OH

12e

(^{1}H NMR, 300 MHz, $CDCl_3$)



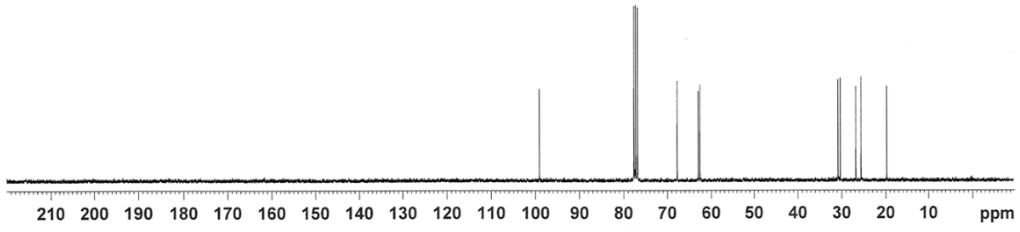
SHB-16-21 - CDCl3 - 13C - 20170216 - 300MHz - exp2

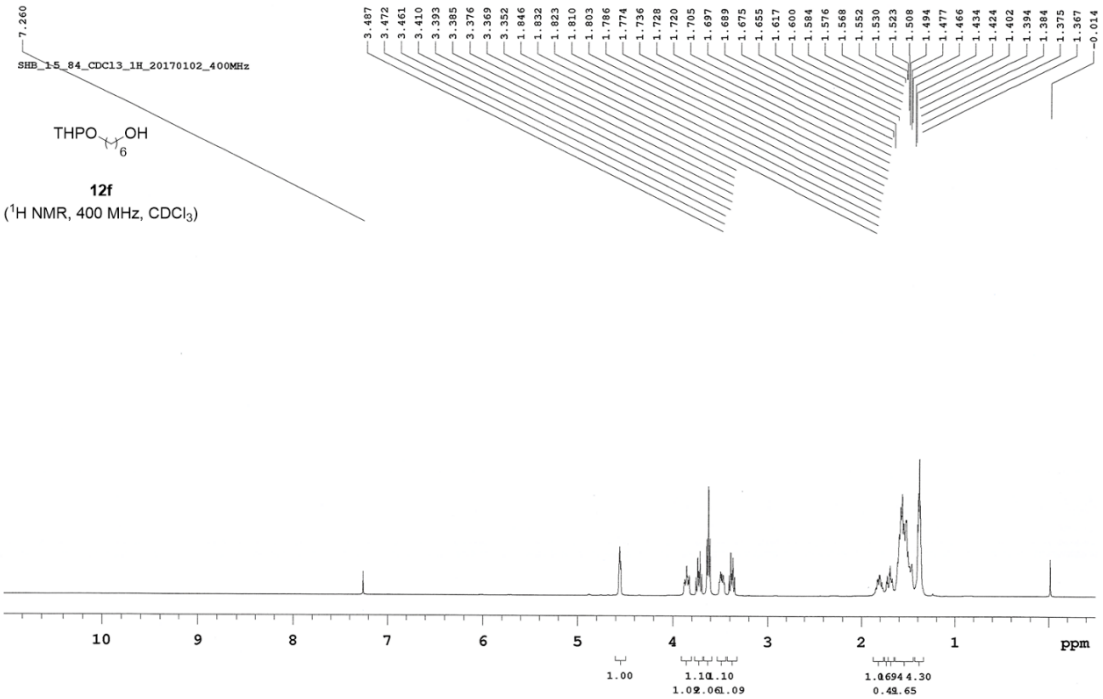
13C expt.

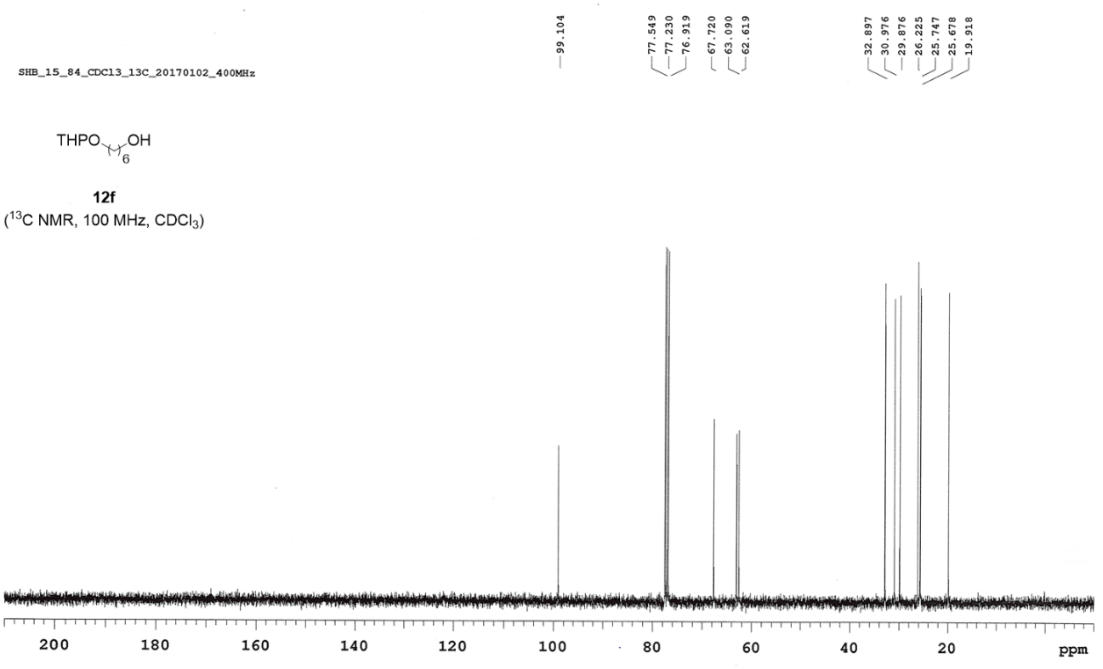
THPO–(CH2)4–OH

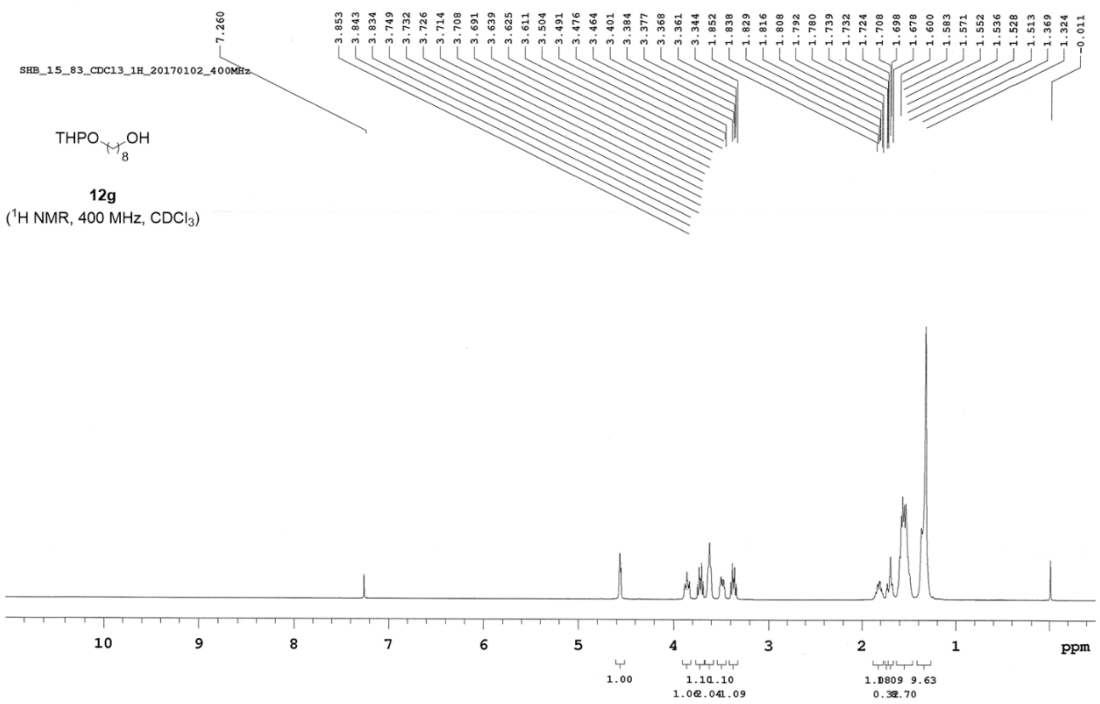
12e

(^{13}C NMR, 75 MHz, $CDCl_3$)



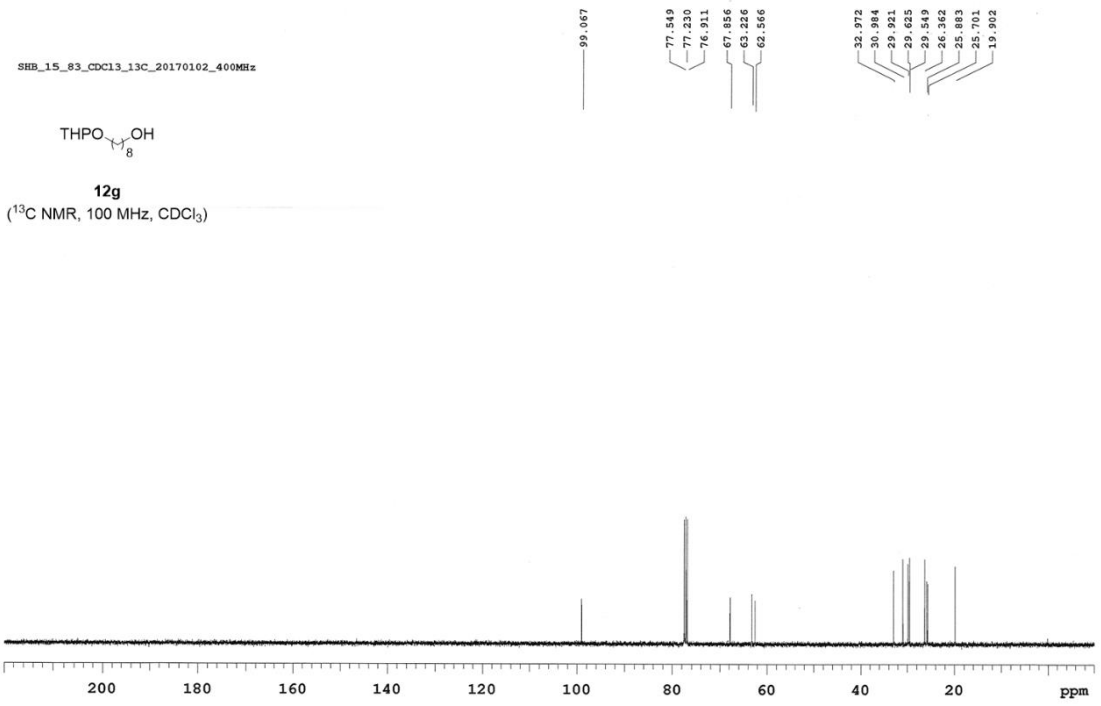

SHB_15_84_CDCl3_1H_20170102_400MHz
THPO
OH
6
12f
(1H NMR, 400 MHz, CDCl3)
ppm


SHB_15_84_CDCl3_13C_20170102_400MHz
THPO
OH
6
12f
(13C NMR, 100 MHz, CDCl3)
ppm



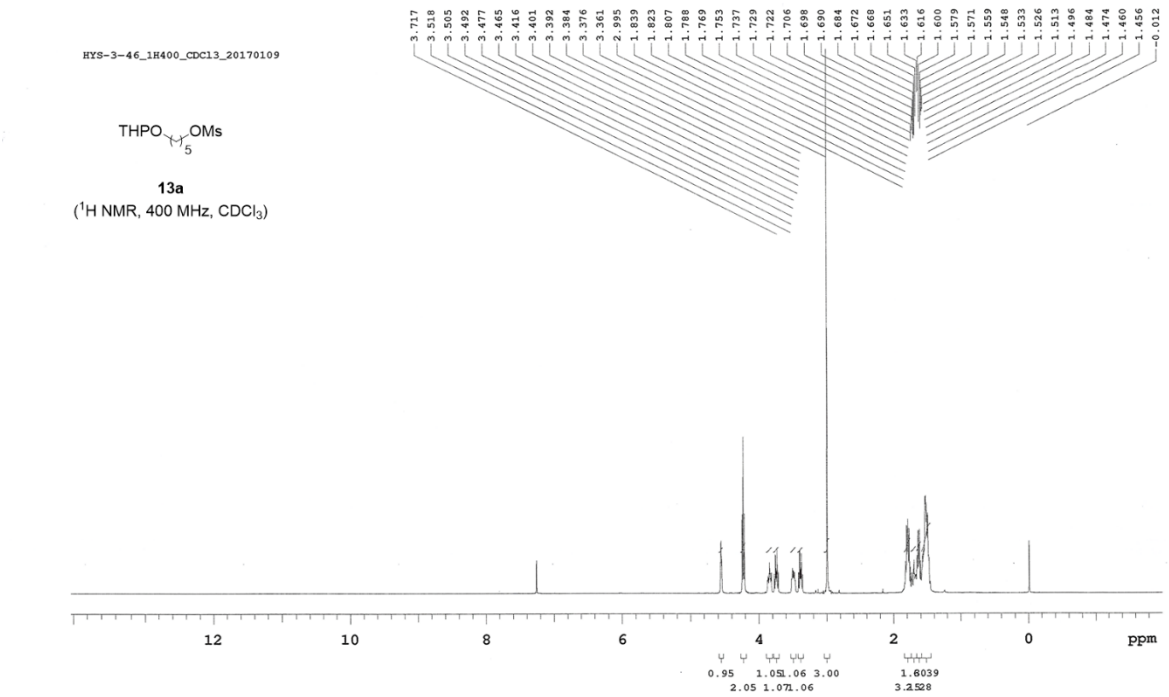
12g

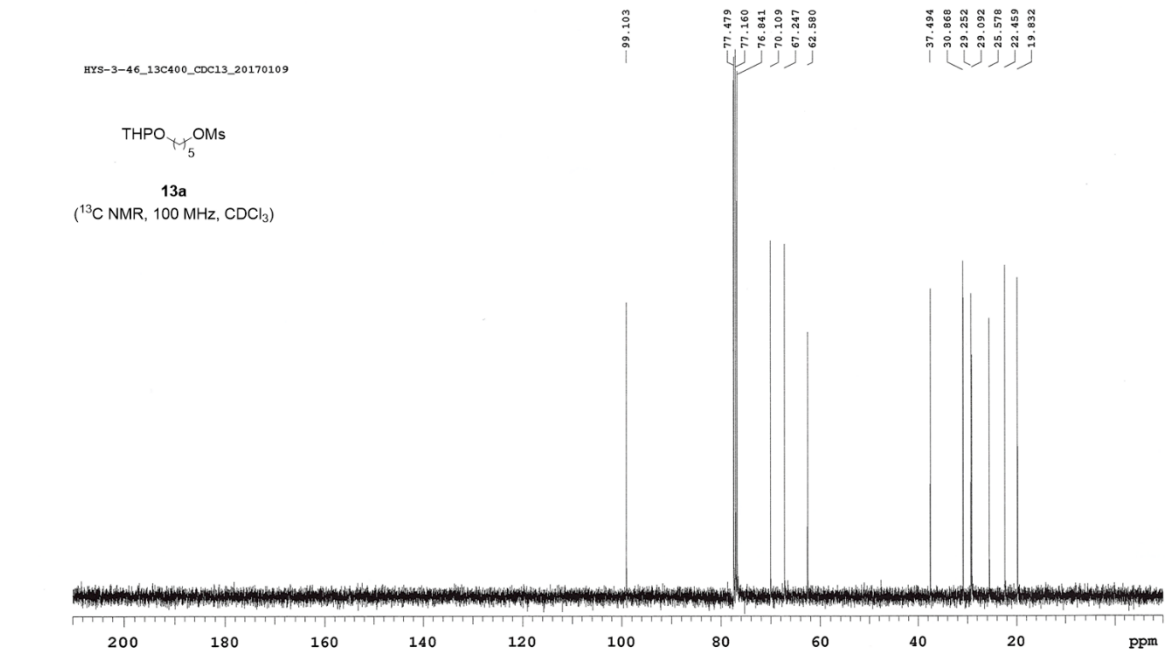
(^{1}H NMR, 400 MHz, $CDCl_3$)

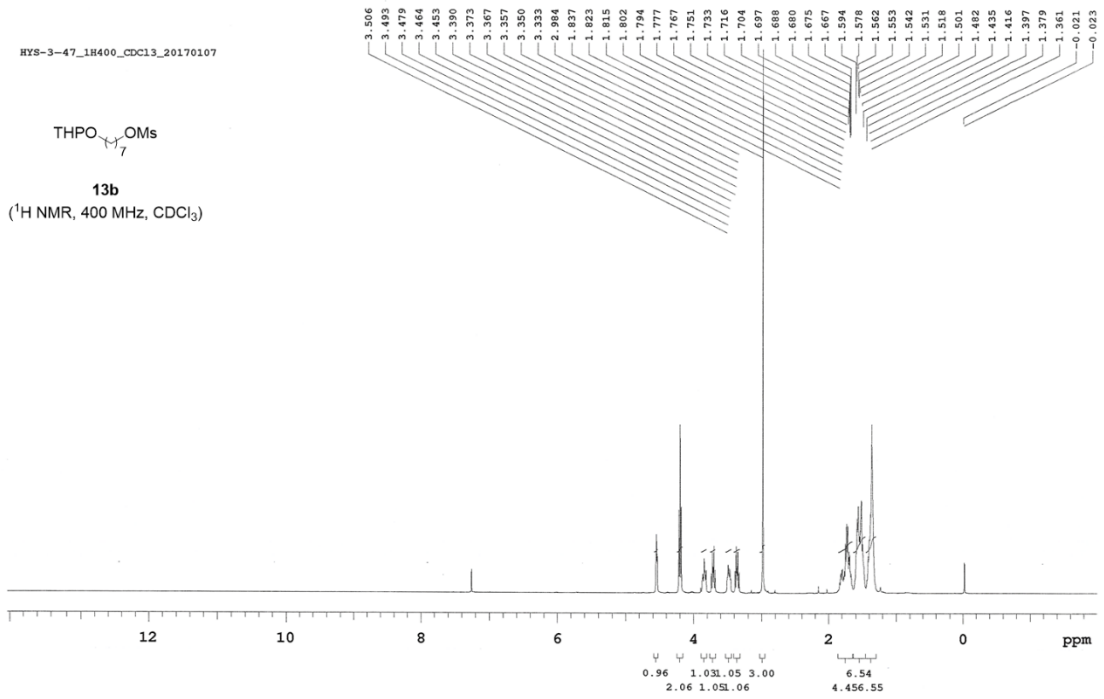


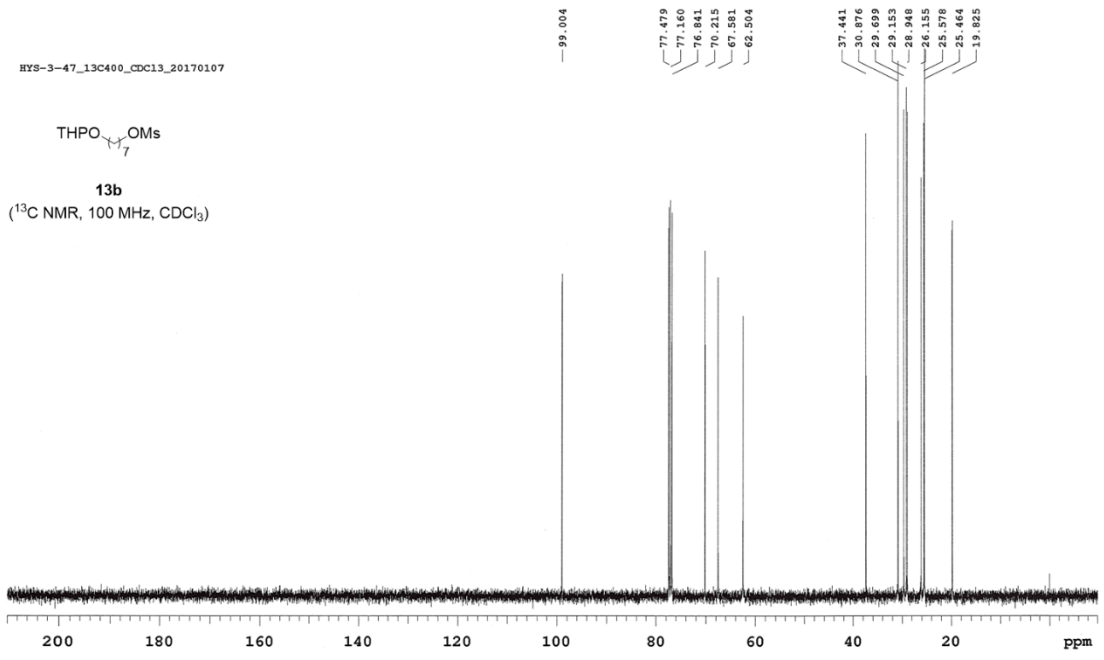
12g

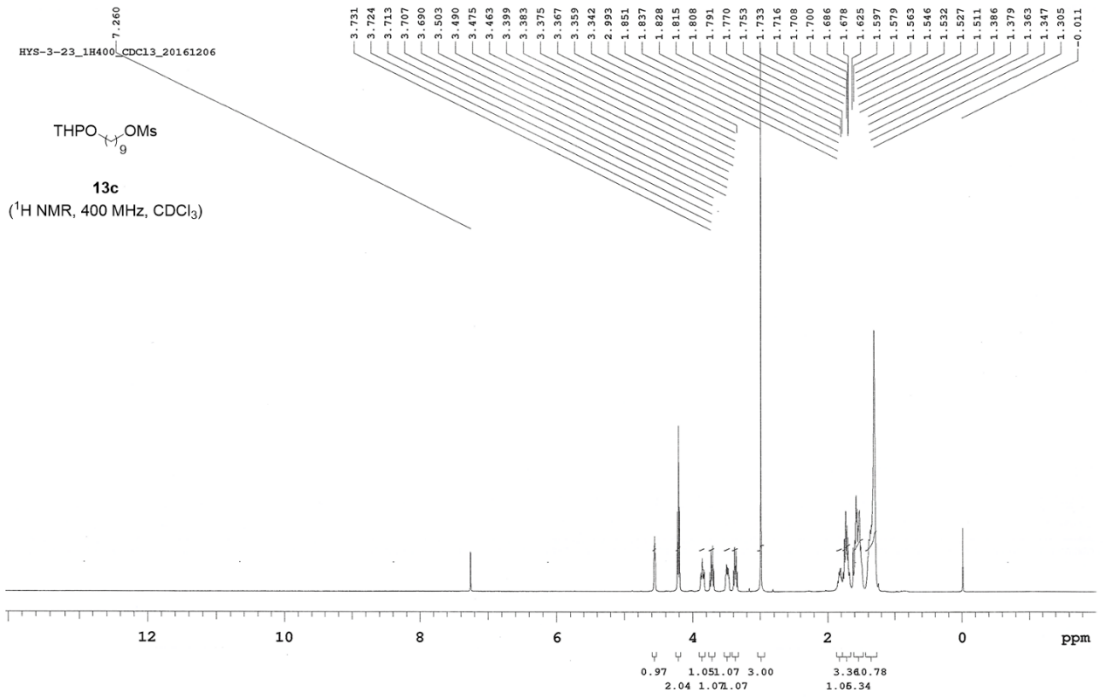
(^{13}C NMR, 100 MHz, $CDCl_3$)

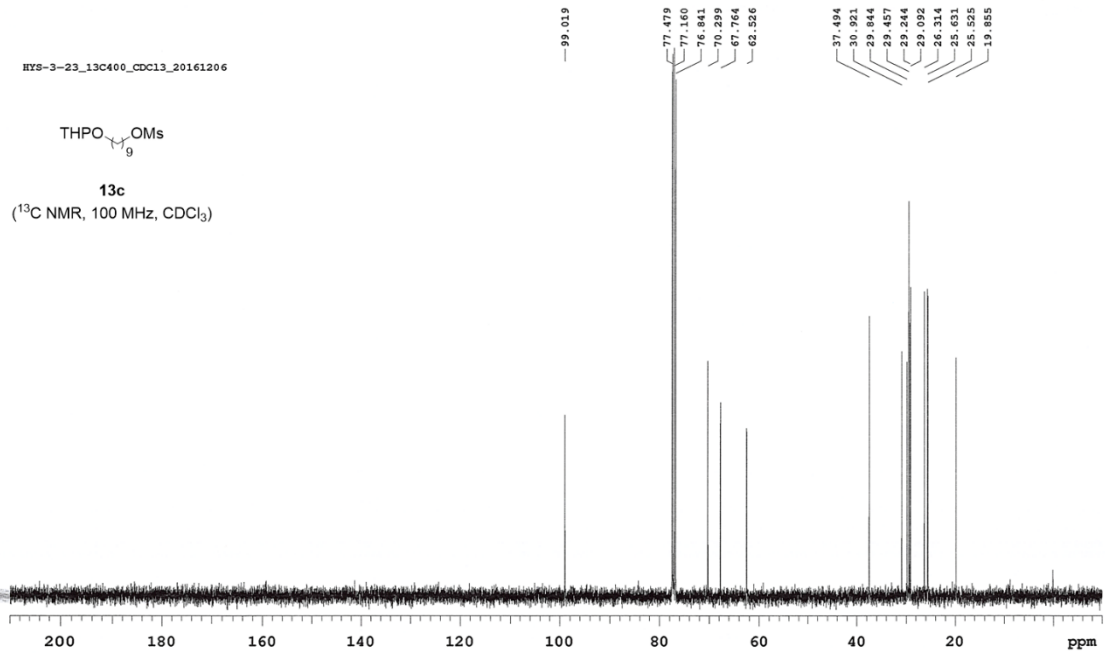

HYS-3-46_1H400_CDCl3_20170109
THPO OMs
5
13a
(1H NMR, 400 MHz, CDCl3)
3.717
3.518
3.505
3.492
3.477
3.465
3.416
3.401
3.392
3.384
3.376
3.361
2.995
1.839
1.823
1.807
1.788
1.769
1.753
1.737
1.729
1.722
1.706
1.698
1.690
1.684
1.672
1.668
1.651
1.633
1.616
1.600
1.579
1.571
1.559
1.548
1.533
1.526
1.513
1.496
1.484
1.474
1.460
1.456
-0.012
12
10
8
6
4
2
0
ppm
0.95
1.05
1.06
3.00
1.6039
2.05
1.07
1.06
3.2528


HYS-3-46_13C400_CDCl3_20170109
THPO OMs
5
13a
(13C NMR, 100 MHz, CDCl3)
99.103
77.479
77.160
76.841
70.109
67.247
62.580
37.494
30.868
29.252
29.092
25.578
22.459
19.832
200
180
160
140
120
100
80
60
40
20
ppm


HYS-3-47_1H400_CDCl3_20170107
THPO
OMs
7
13b
(1H NMR, 400 MHz, CDCl3)
3.506
3.493
3.479
3.464
3.453
3.390
3.373
3.367
3.357
3.350
3.333
2.984
1.837
1.823
1.815
1.802
1.794
1.777
1.767
1.751
1.733
1.716
1.704
1.697
1.688
1.680
1.675
1.667
1.594
1.578
1.562
1.553
1.542
1.531
1.518
1.501
1.482
1.435
1.416
1.397
1.379
1.361
-0.021
-0.023
12
10
8
6
4
2
0
ppm
0.96
1.03
1.05
3.00
6.54
2.06
1.05
1.06
4.45
6.55


HYS-3-47_13C400_CDCl3_20170107
THPO
OMs
7
13b
(13C NMR, 100 MHz, CDCl3)
99.004
77.479
77.160
76.841
70.215
67.581
62.504
37.441
30.876
29.699
29.153
28.948
26.155
25.578
25.464
19.825
200
180
160
140
120
100
80
60
40
20
ppm

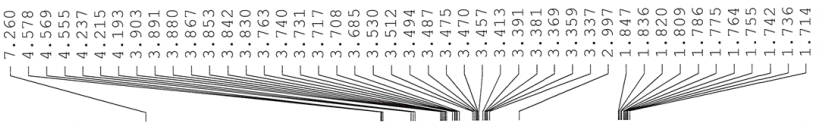

HYS-3-23_1H400_CDCl3_20161206
THPO OMs
9
13c
(1H NMR, 400 MHz, CDCl3)
7.260
3.731
3.724
3.713
3.707
3.690
3.503
3.490
3.475
3.463
3.399
3.383
3.375
3.367
3.359
3.342
2.993
1.851
1.837
1.828
1.815
1.808
1.791
1.770
1.753
1.733
1.716
1.708
1.700
1.686
1.678
1.625
1.597
1.579
1.563
1.546
1.532
1.527
1.511
1.386
1.379
1.363
1.347
1.305
0.011
12
10
8
6
4
2
0
ppm
0.97
1.05
1.07
3.00
2.04
1.07
1.07
3.36
0.78
1.05
0.34

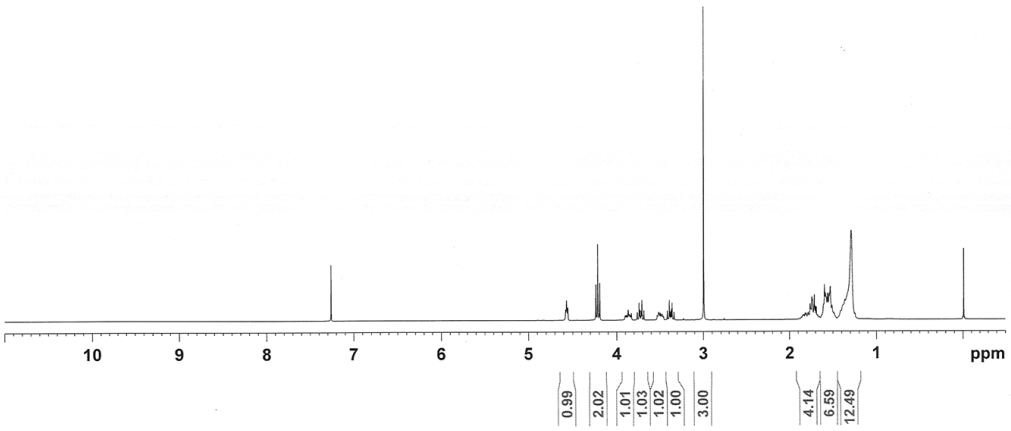

HYS-3-23_13C400_CDCl3_20161206
THPO OMs
9
13c
(13C NMR, 100 MHz, CDCl3)
99.019
77.479
77.160
76.841
70.299
67.764
62.526
37.494
30.921
29.844
29.457
29.244
29.092
26.314
25.631
25.525
19.855
200
180
160
140
120
100
80
60
40
20
ppm

SHB_15_51_CDCl3_1H_20161125_400MHz_exp2

13d

(^{1}H NMR, 300 MHz, $CDCl_3$)

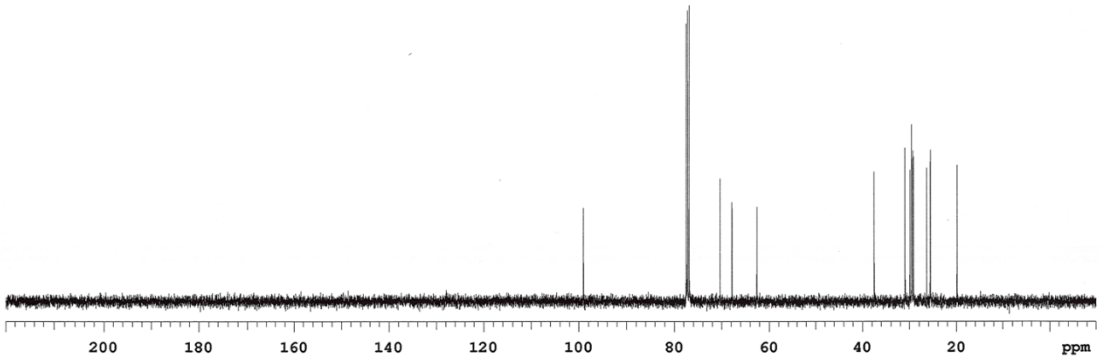


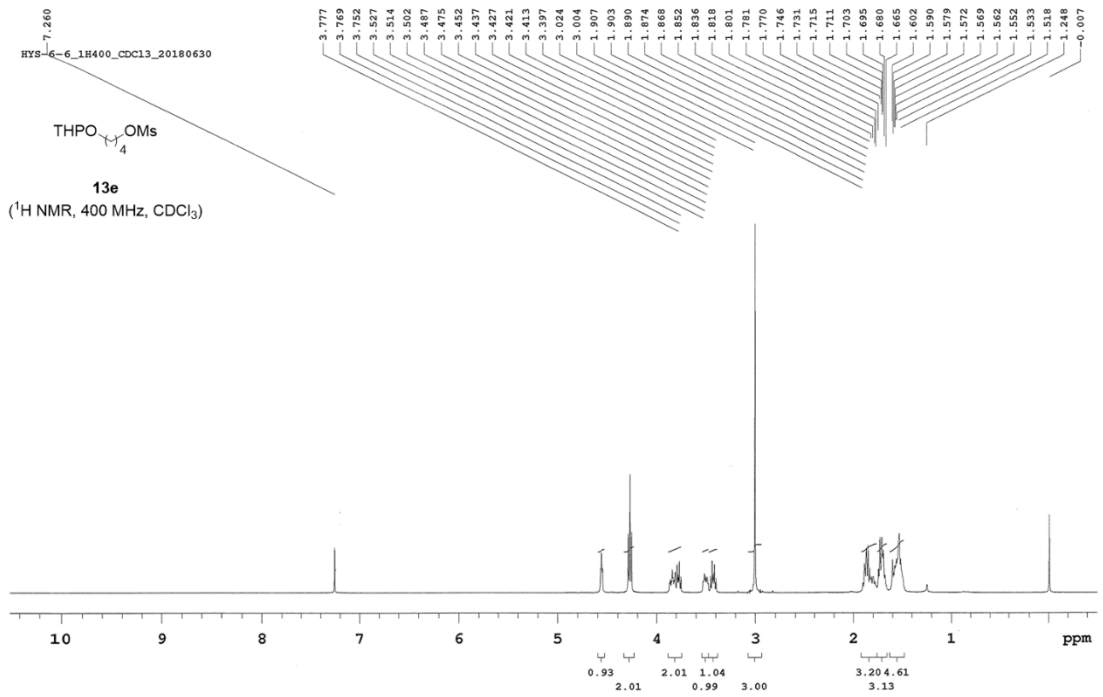


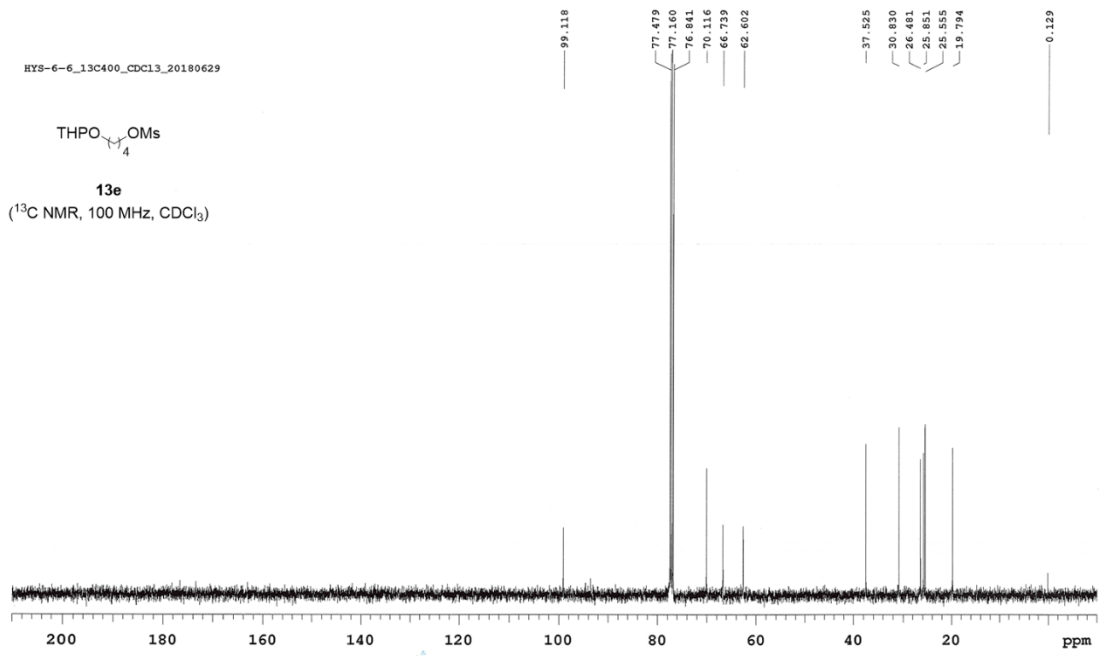
SHB_15_51_CDCl3_13C_20161129_400MHz

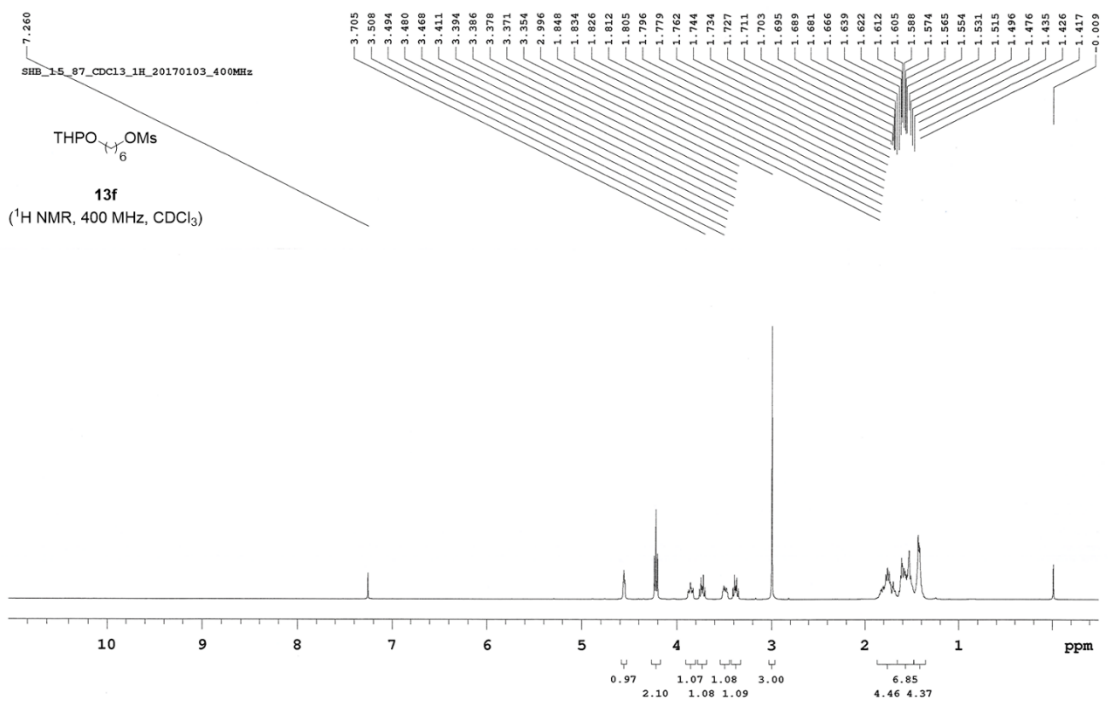
13d

(^{13}C NMR, 100 MHz, $CDCl_3$)




HYS-6-6_1H400_CDCl3_20180630
THPO OMs
4
13e
(1H NMR, 400 MHz, CDCl3)
7.260
3.777
3.769
3.752
3.527
3.514
3.502
3.487
3.475
3.452
3.437
3.427
3.421
3.413
3.397
3.024
3.004
1.907
1.903
1.890
1.874
1.868
1.852
1.836
1.818
1.801
1.781
1.770
1.746
1.731
1.715
1.711
1.703
1.695
1.680
1.665
1.602
1.590
1.579
1.572
1.569
1.562
1.552
1.533
1.518
1.248
0.007
10
9
8
7
6
5
4
3
2
1
ppm
0.93
2.01
2.01
1.04
0.99
3.00
3.20
4.61
3.13

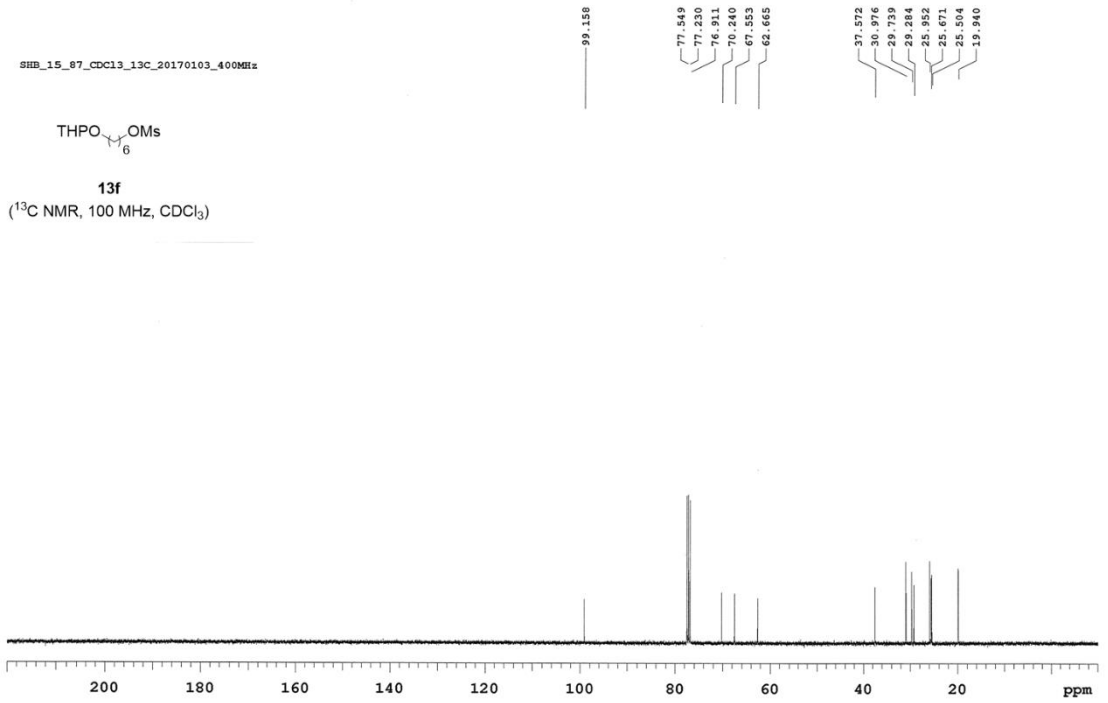

HYS-6-6_13C400_CDCl3_20180629
THPO OMs
4
13e
(13C NMR, 100 MHz, CDCl3)
99.118
77.479
77.160
76.841
70.116
66.739
62.602
37.525
30.830
26.481
25.851
25.555
19.794
0.129
200
180
160
140
120
100
80
60
40
20
ppm



THPO–(CH2)6–OMs

13f

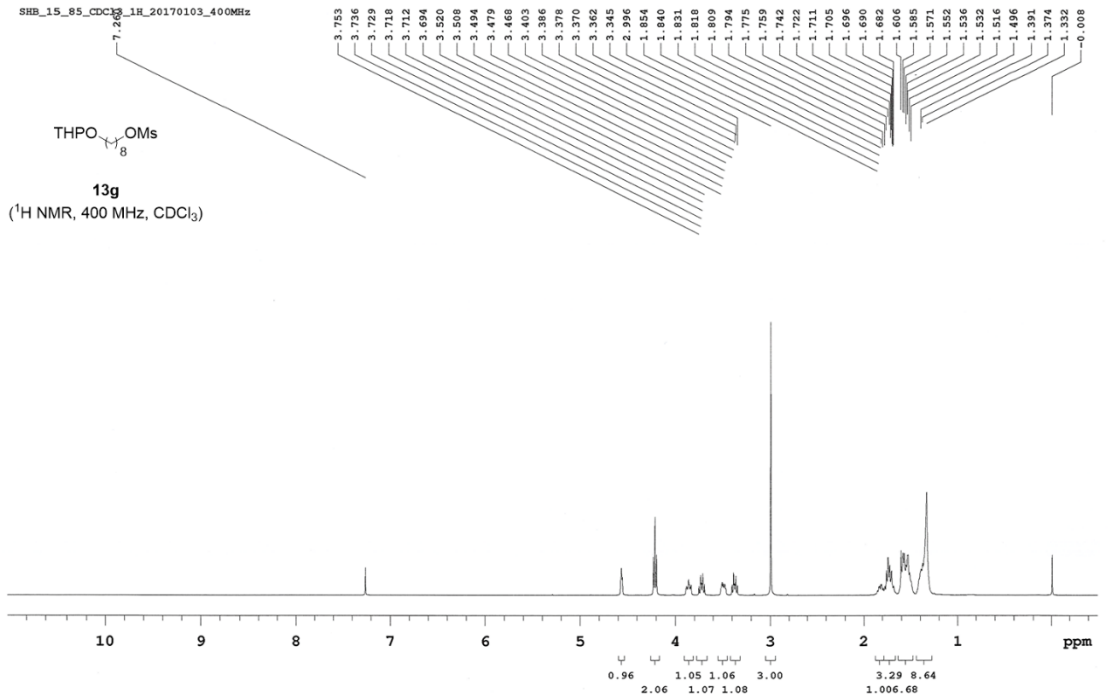
(^{1}H NMR, 400 MHz, $CDCl_3$)



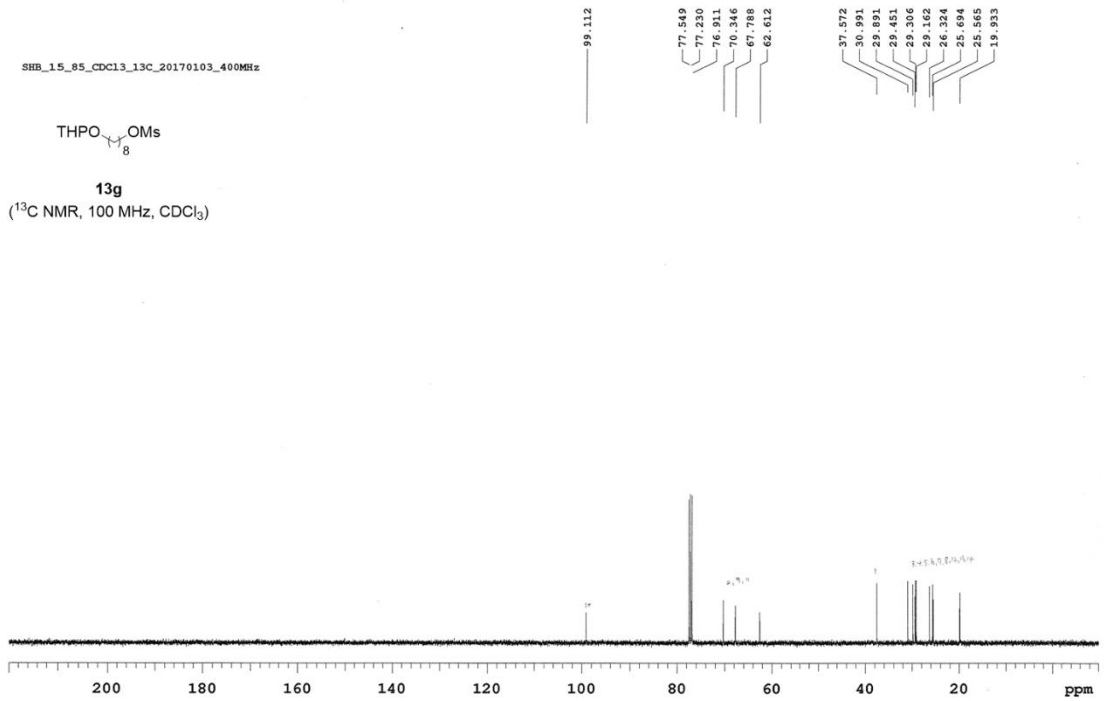
THPO–(CH2)6–OMs

13f

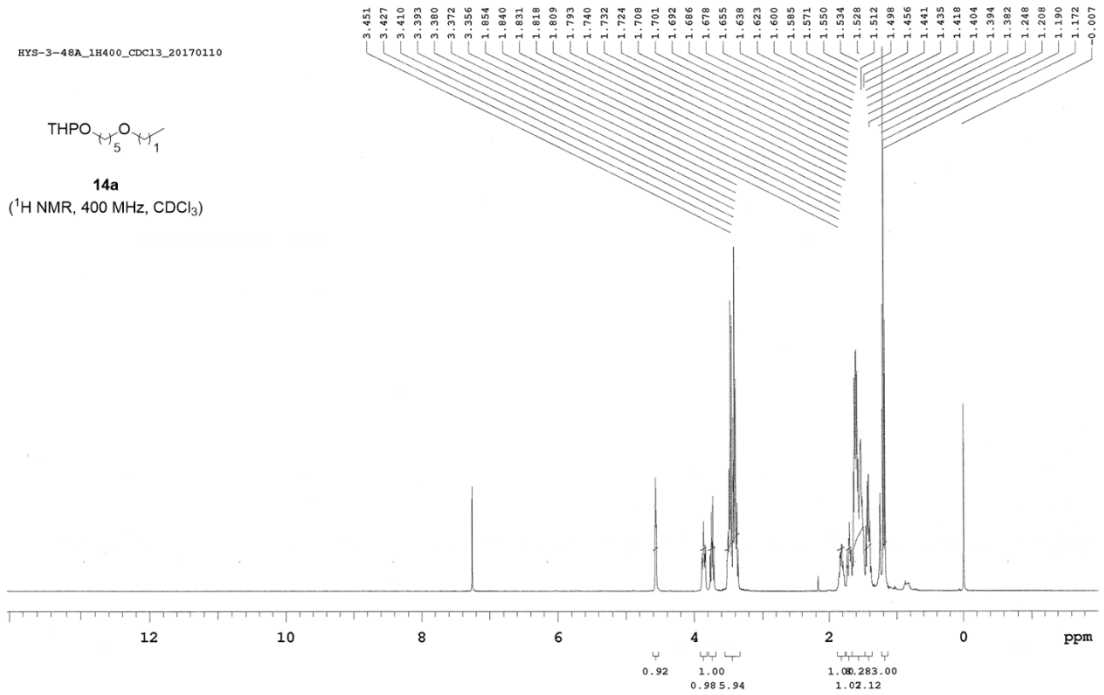
(^{13}C NMR, 100 MHz, $CDCl_3$)

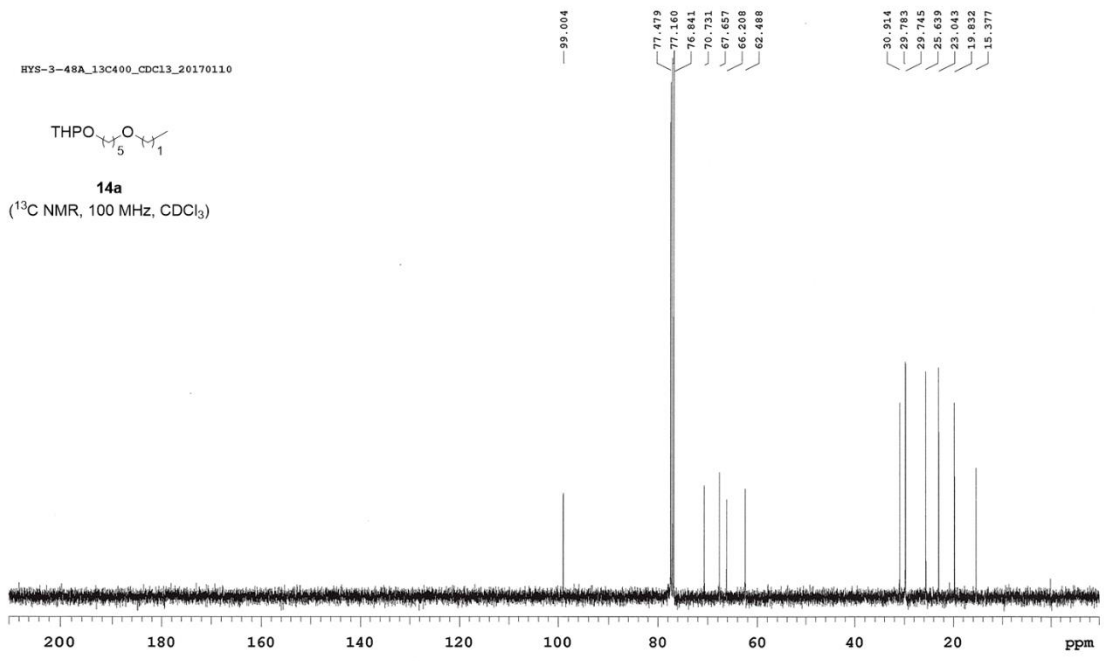


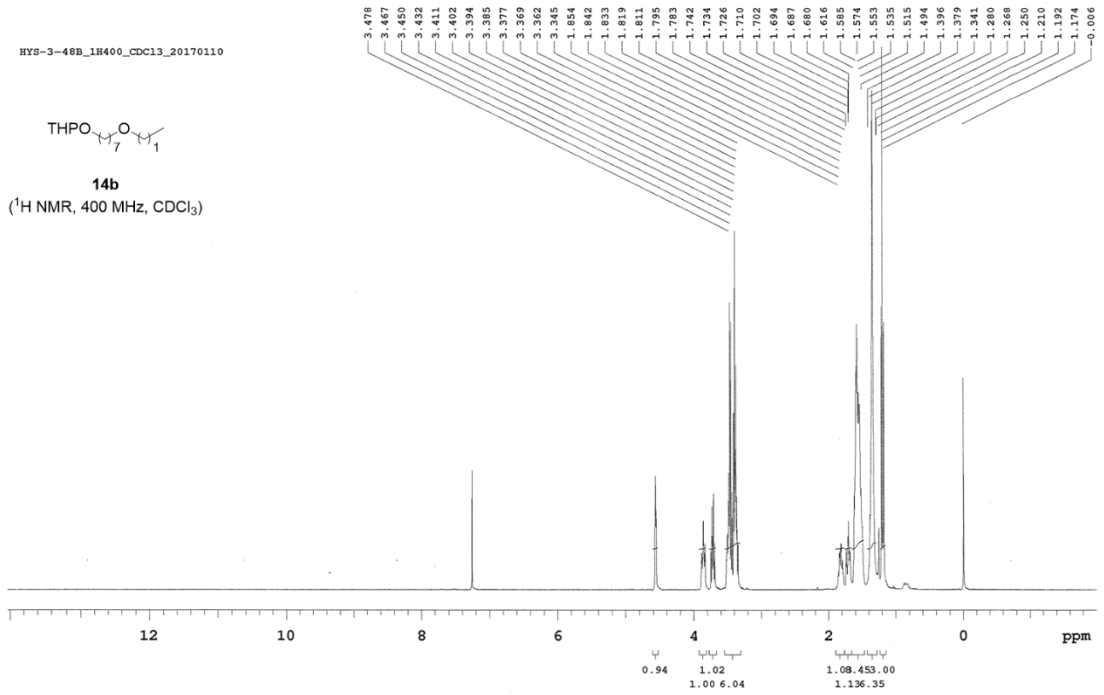
13g
(^{1}H NMR, 400 MHz, $CDCl_3$)

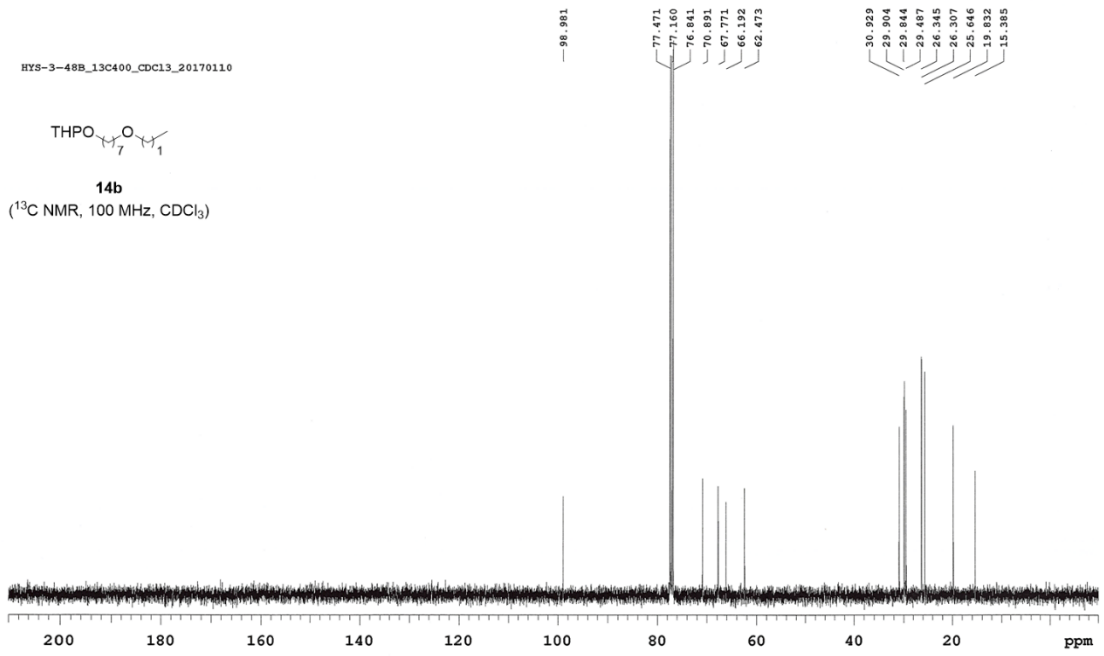


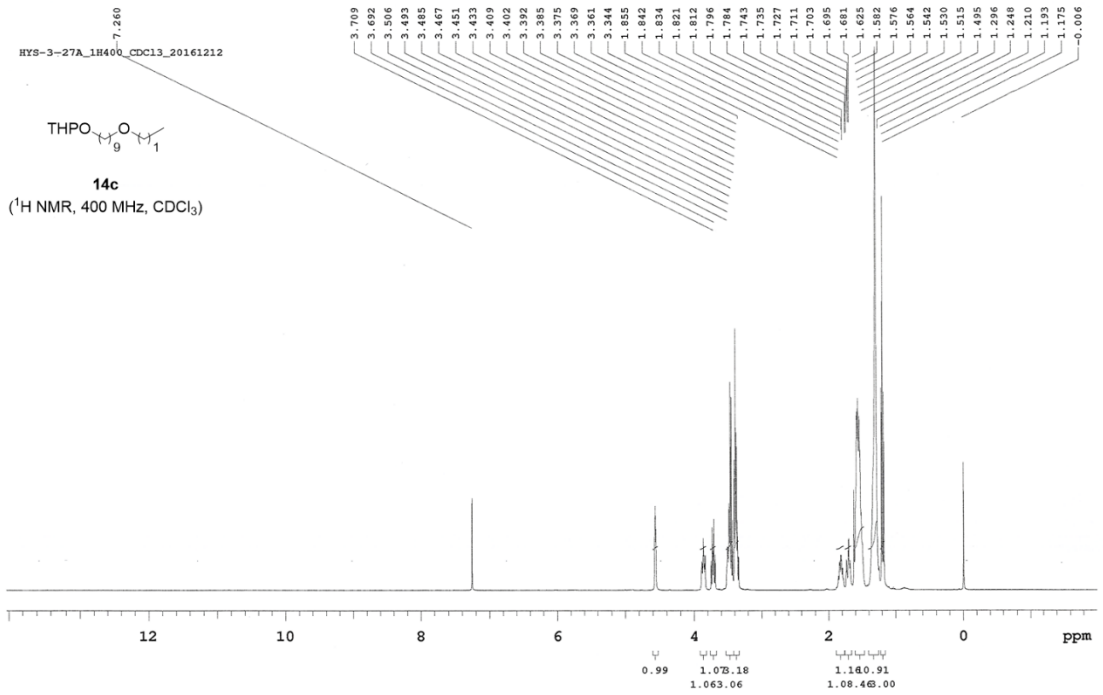
13g
(^{13}C NMR, 100 MHz, $CDCl_3$)

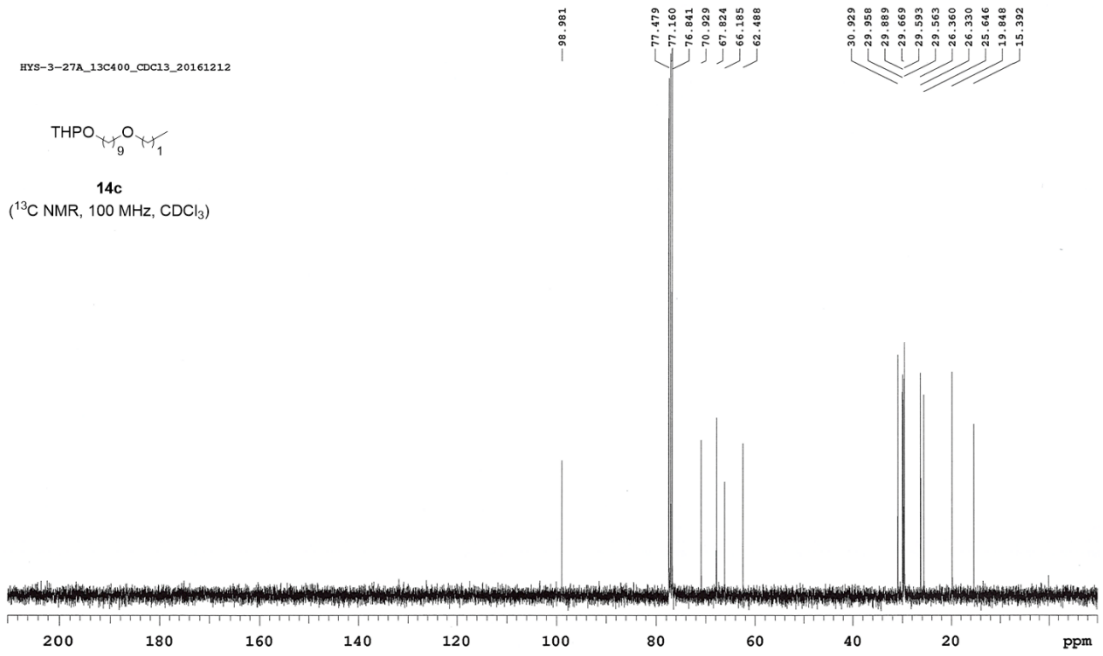

HYS-3-48A_1H400_CDCl3_20170110
THPO
5
O
1
14a
(1H NMR, 400 MHz, CDCl3)
3.451
3.427
3.410
3.393
3.380
3.372
3.356
1.854
1.840
1.831
1.818
1.809
1.793
1.740
1.732
1.724
1.708
1.701
1.692
1.686
1.678
1.655
1.638
1.623
1.600
1.585
1.571
1.550
1.534
1.528
1.512
1.498
1.456
1.441
1.435
1.418
1.404
1.394
1.382
1.248
1.208
1.190
1.172
-0.007
12
10
8
6
4
2
0
ppm
0.92
1.00
0.98
5.94
1.08
0.28
3.00
1.02
12

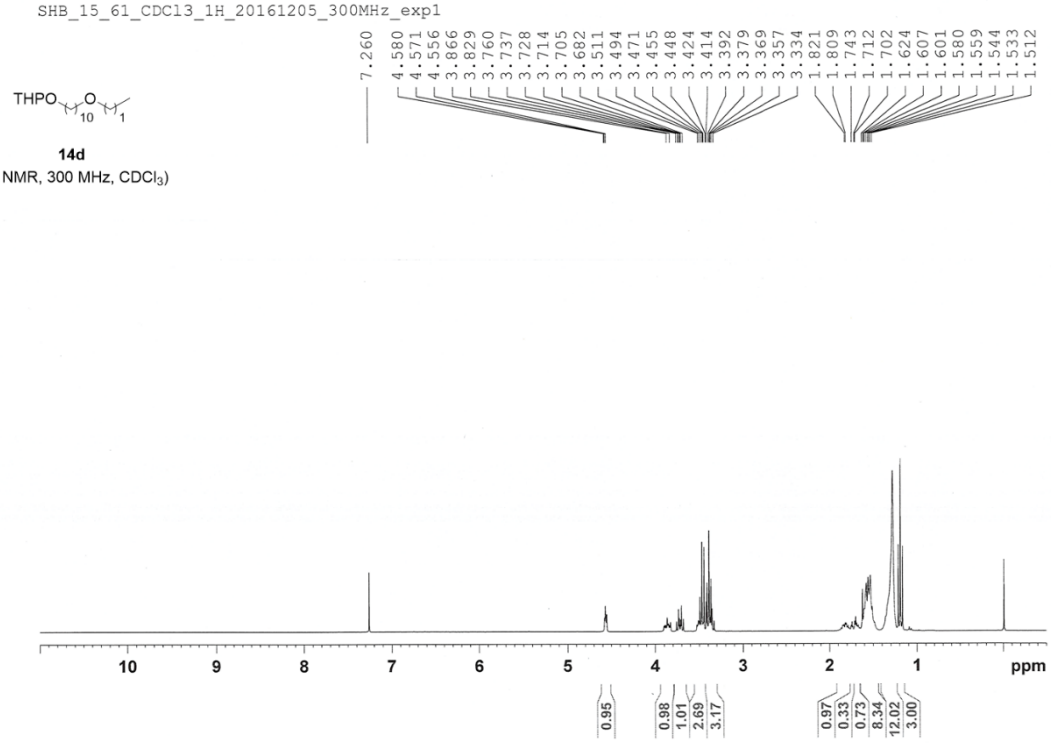

HYS-3-48A_13C400_CDCl3_20170110
THPO
5
O
1
14a
(13C NMR, 100 MHz, CDCl3)
99.004
77.479
77.160
76.841
70.731
67.657
66.208
62.488
30.914
29.783
29.745
25.639
23.043
19.832
15.377
200
180
160
140
120
100
80
60
40
20
ppm

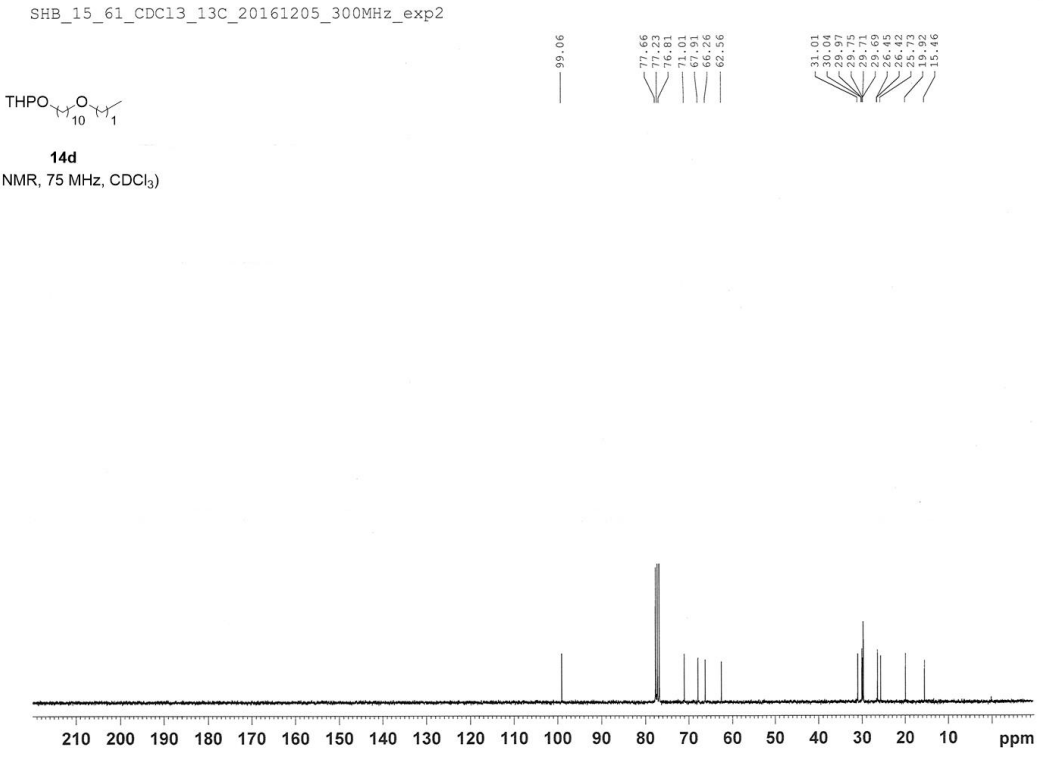

HYS-3-48B_1H400_CDCl3_20170110
THPO
O
7
1
14b
(1H NMR, 400 MHz, CDCl3)
3.478
3.467
3.450
3.432
3.411
3.402
3.394
3.385
3.377
3.369
3.362
3.345
1.854
1.842
1.833
1.819
1.811
1.795
1.783
1.742
1.734
1.726
1.710
1.702
1.694
1.687
1.680
1.616
1.585
1.574
1.553
1.535
1.515
1.494
1.396
1.379
1.341
1.280
1.268
1.250
1.210
1.192
1.174
0.006
12
10
8
6
4
2
0
ppm
0.94
1.02
1.00 6.04
1.08 4.53 3.00
1.13 6.35

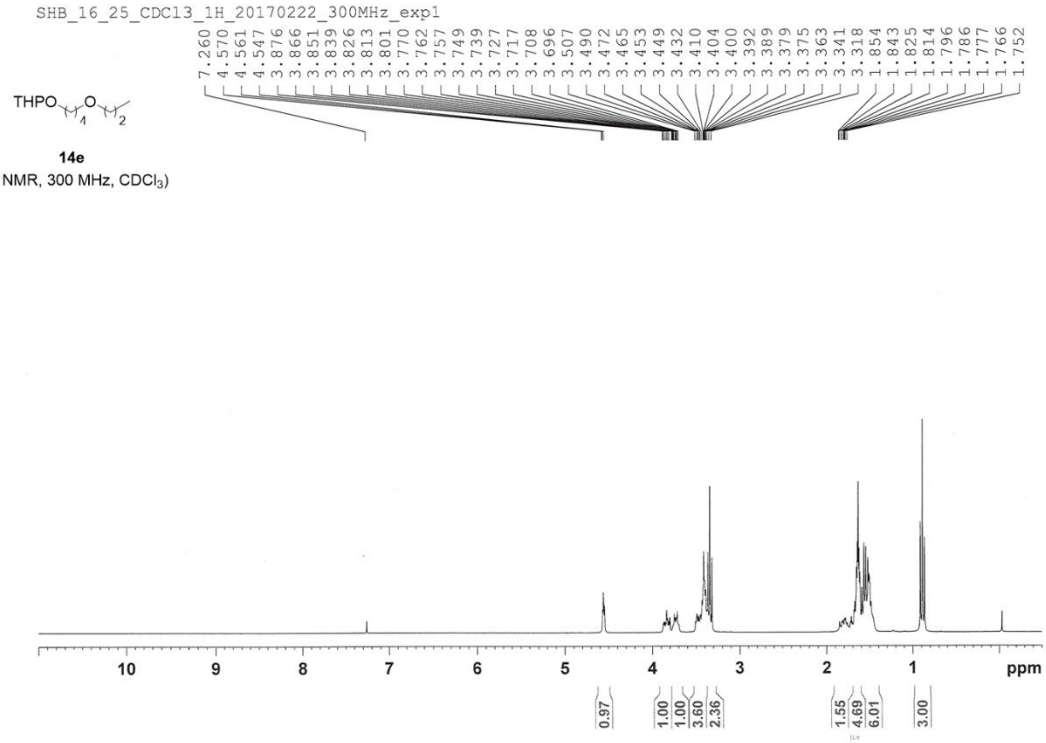

HYS-3-48B_13C400_CDCl3_20170110
THPO
O
7
1
14b
(13C NMR, 100 MHz, CDCl3)
98.981
77.471
77.160
76.841
70.891
67.771
66.192
62.473
30.929
29.904
29.844
29.487
26.345
26.307
25.646
19.832
15.385
200
180
160
140
120
100
80
60
40
20
ppm


HYS-3-27A_1H400_CDCl3_20161212
THPO
9
O
1
14c
(1H NMR, 400 MHz, CDCl3)
7.260
3.709
3.692
3.506
3.493
3.485
3.467
3.451
3.433
3.409
3.402
3.392
3.385
3.375
3.369
3.361
3.344
1.855
1.842
1.834
1.821
1.812
1.796
1.784
1.743
1.735
1.727
1.711
1.703
1.695
1.681
1.625
1.582
1.576
1.564
1.542
1.530
1.515
1.495
1.296
1.248
1.210
1.193
1.175
0.006
12
10
8
6
4
2
0
ppm
0.99
1.07
3.18
1.063.06
1.16
0.91
1.08.46
3.00

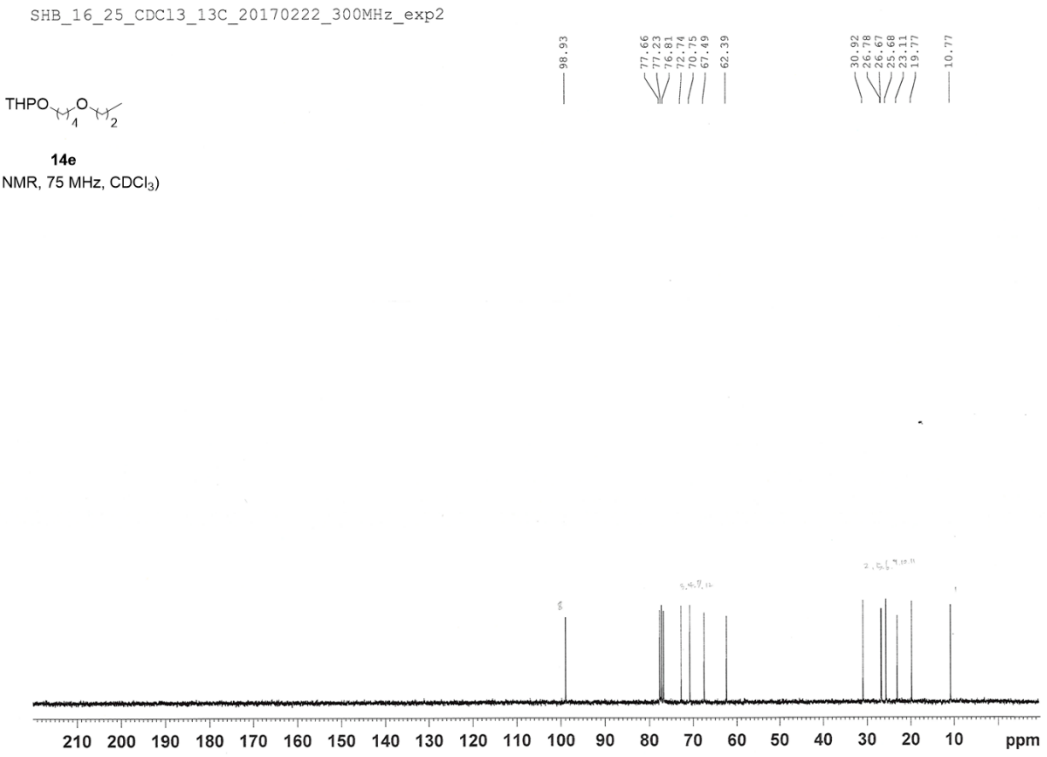

HYS-3-27A_13C400_CDCl3_20161212
THPO
9
O
1
14c
(13C NMR, 100 MHz, CDCl3)
98.981
77.479
77.160
76.841
70.929
67.824
66.185
62.488
30.929
29.958
29.889
29.669
29.593
29.563
26.360
26.330
25.646
19.848
15.392
200
180
160
140
120
100
80
60
40
20
ppm


SHB_15_61_CDCl3_1H_20161205_300MHz_exp1
7.260
4.580
4.571
4.556
3.866
3.829
3.760
3.737
3.728
3.714
3.705
3.682
3.511
3.494
3.471
3.455
3.448
3.424
3.414
3.392
3.379
3.369
3.357
3.334
1.821
1.809
1.743
1.712
1.702
1.624
1.607
1.601
1.580
1.559
1.544
1.533
1.512
THPO
10
1
14d
(1H NMR, 300 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
ppm
0.95
0.98
1.01
2.69
3.17
0.97
0.33
0.73
8.34
12.02
3.00

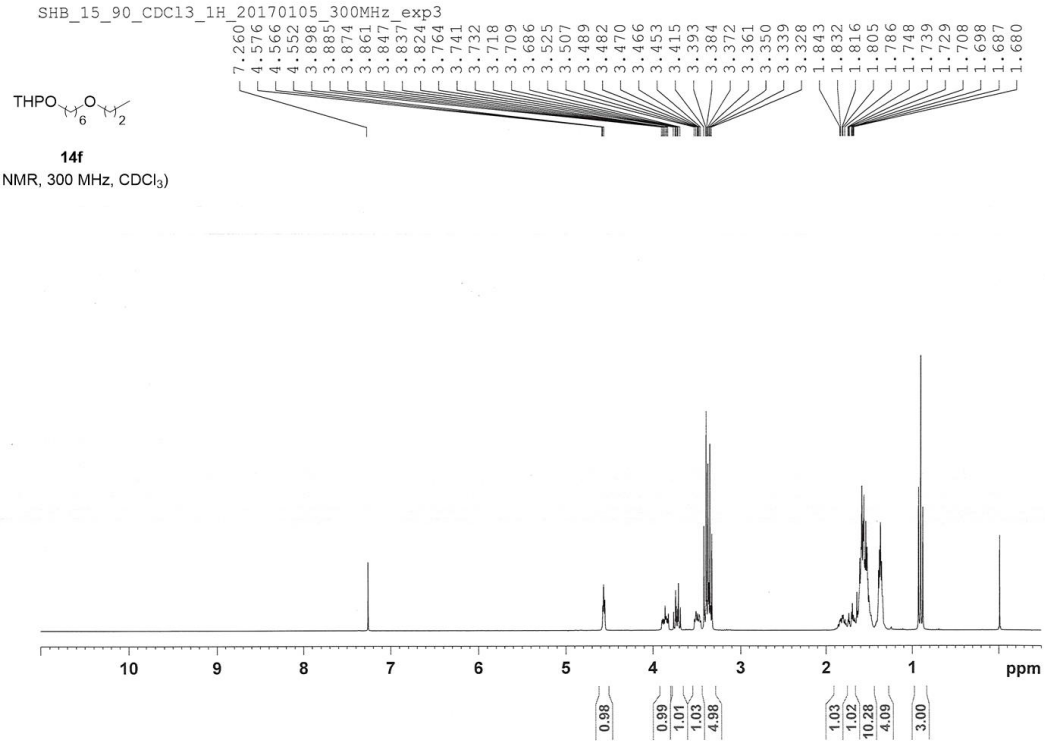

SHB_15_61_CDCl3_13C_20161205_300MHz_exp2
99.06
77.66
77.23
76.81
71.01
67.91
66.26
62.56
31.01
30.04
29.97
29.75
29.71
29.69
26.45
26.42
25.73
19.92
15.46
THPO
10
1
14d
(13C NMR, 75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



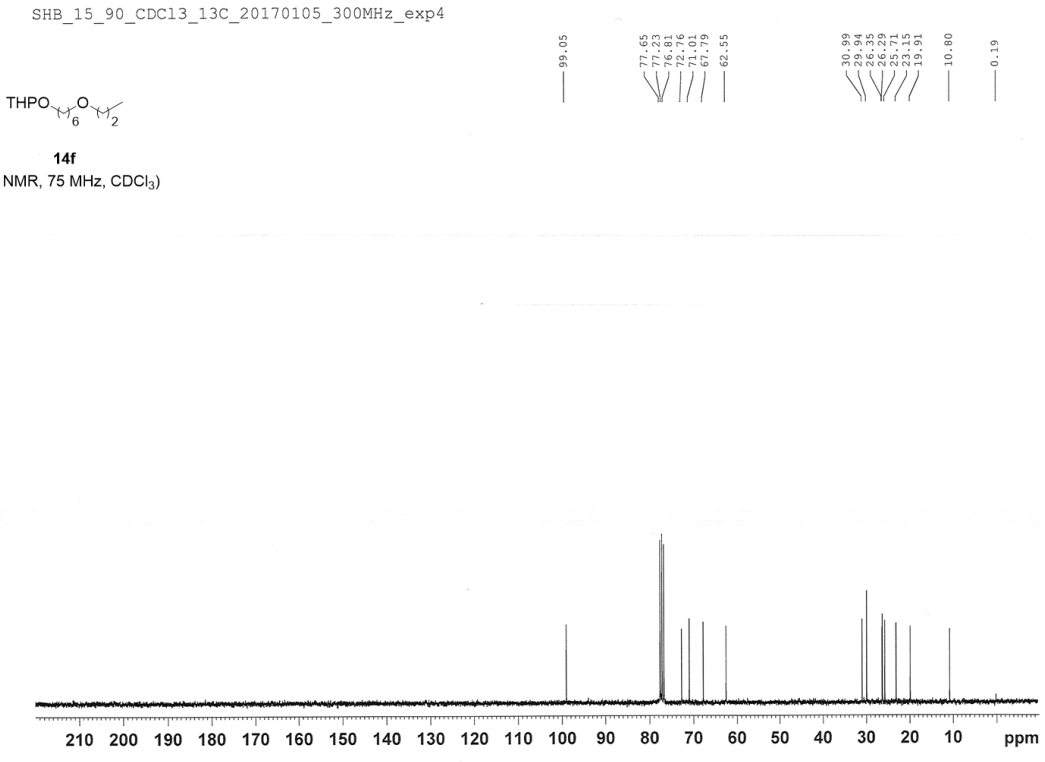
14e
(^{1}H NMR, 300 MHz, $CDCl_3$)



14e
(^{13}C NMR, 75 MHz, $CDCl_3$)

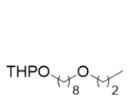


14f
(^{1}H NMR, 300 MHz, $CDCl_3$)

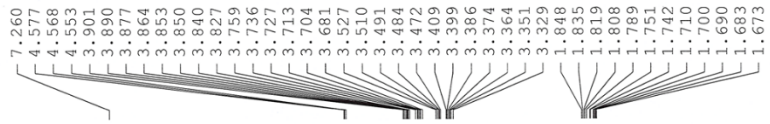


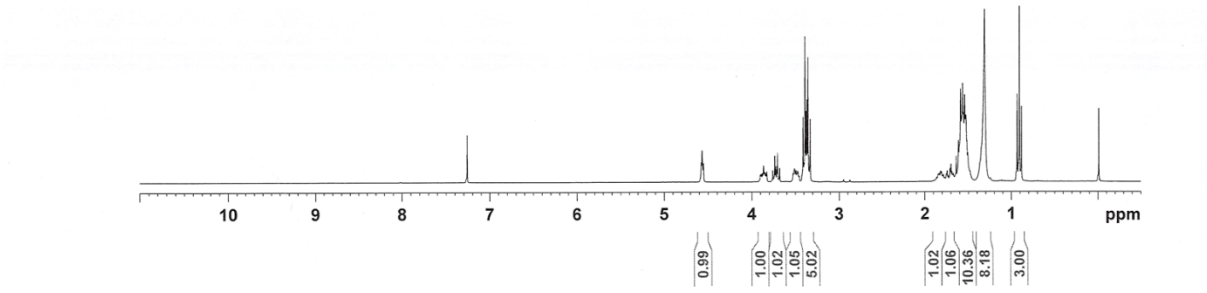
14f
(^{13}C NMR, 75 MHz, $CDCl_3$)

SHB_15_89_CDCl3_1H_20170105_300MHz_exp1



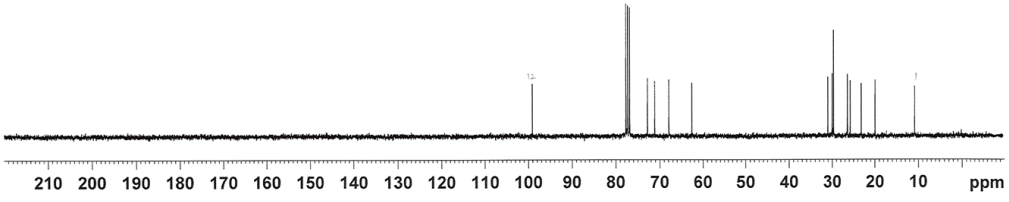
14g
(^{1}H NMR, 300 MHz, $CDCl_3$)

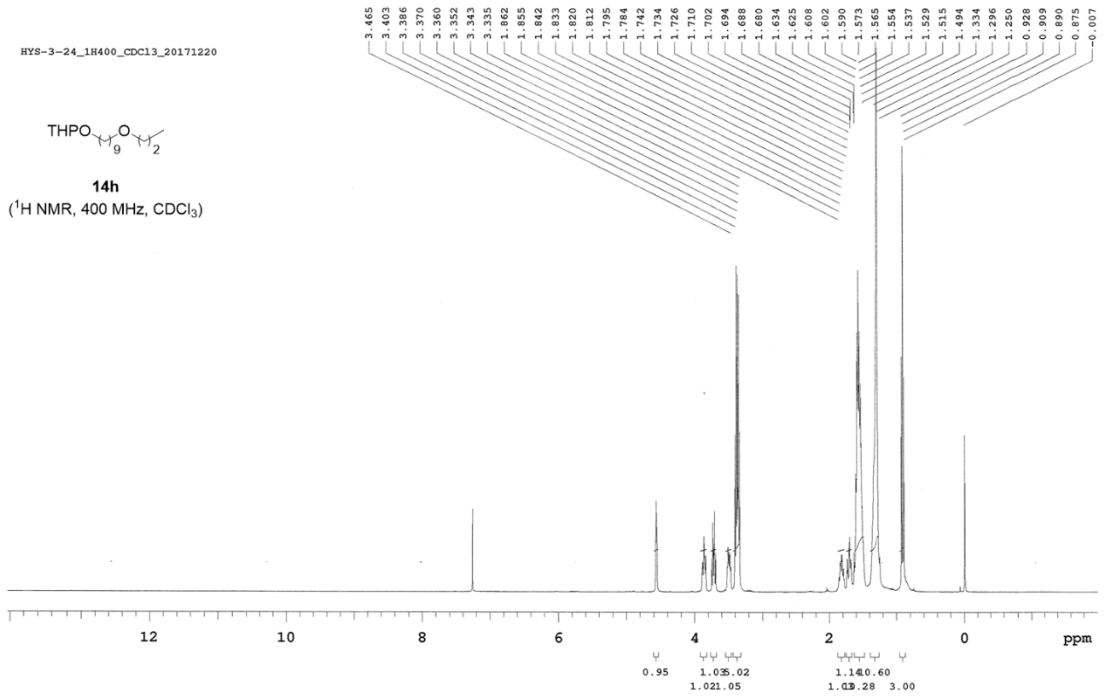


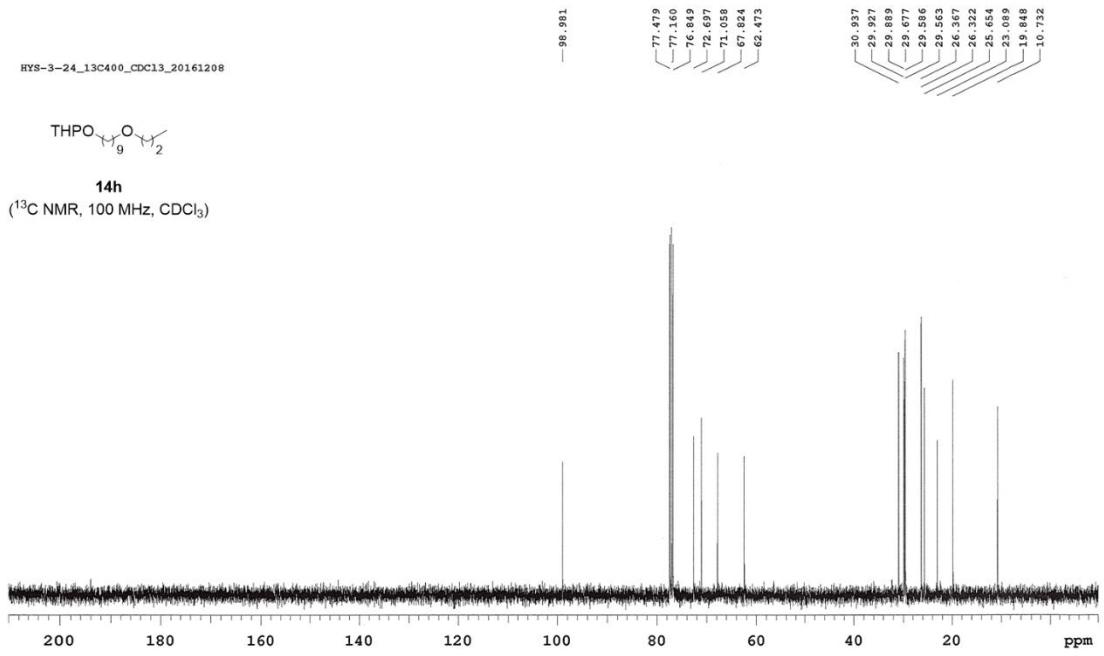


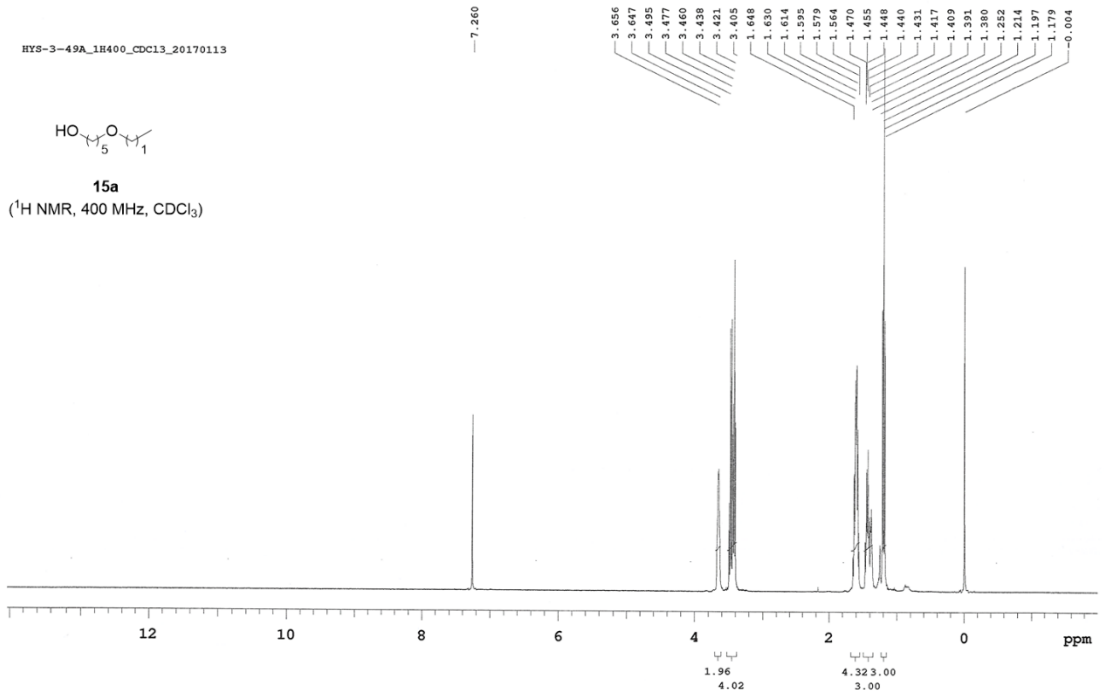
SHB_15_89_CDCl3_13C_20170105_300MHz_exp2

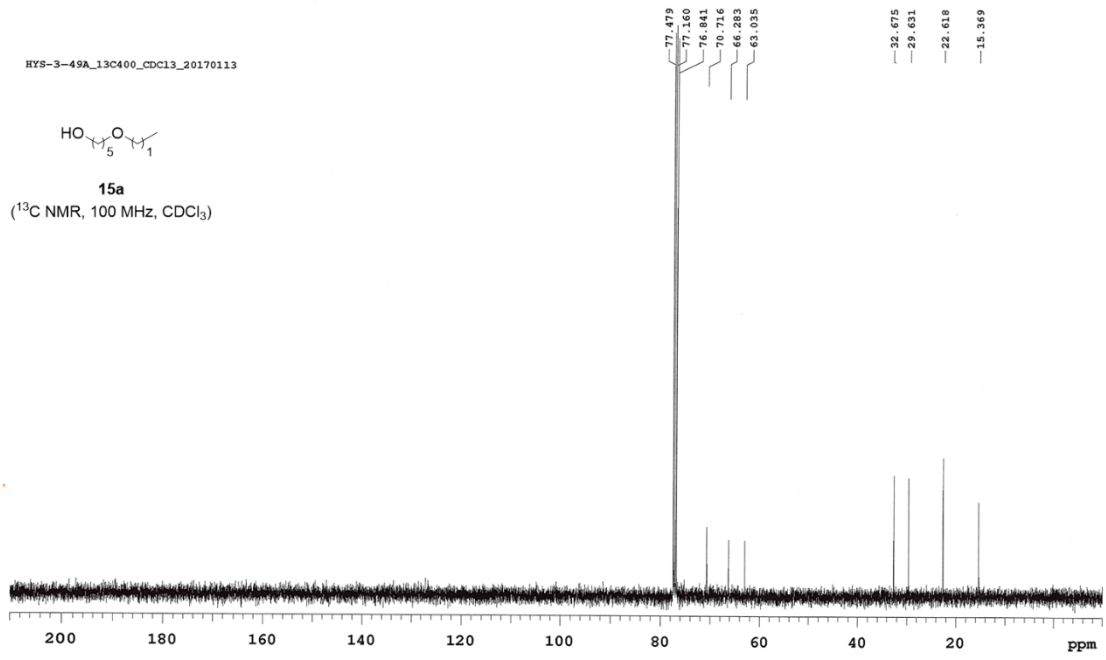
14g
(^{13}C NMR, 75 MHz, $CDCl_3$)

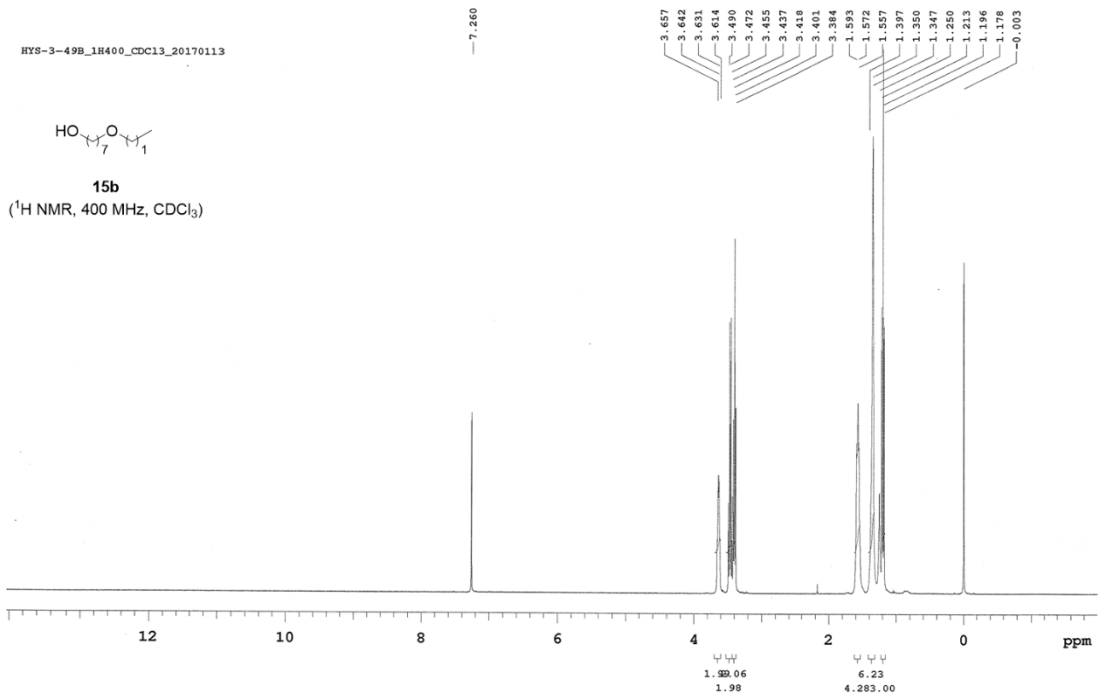


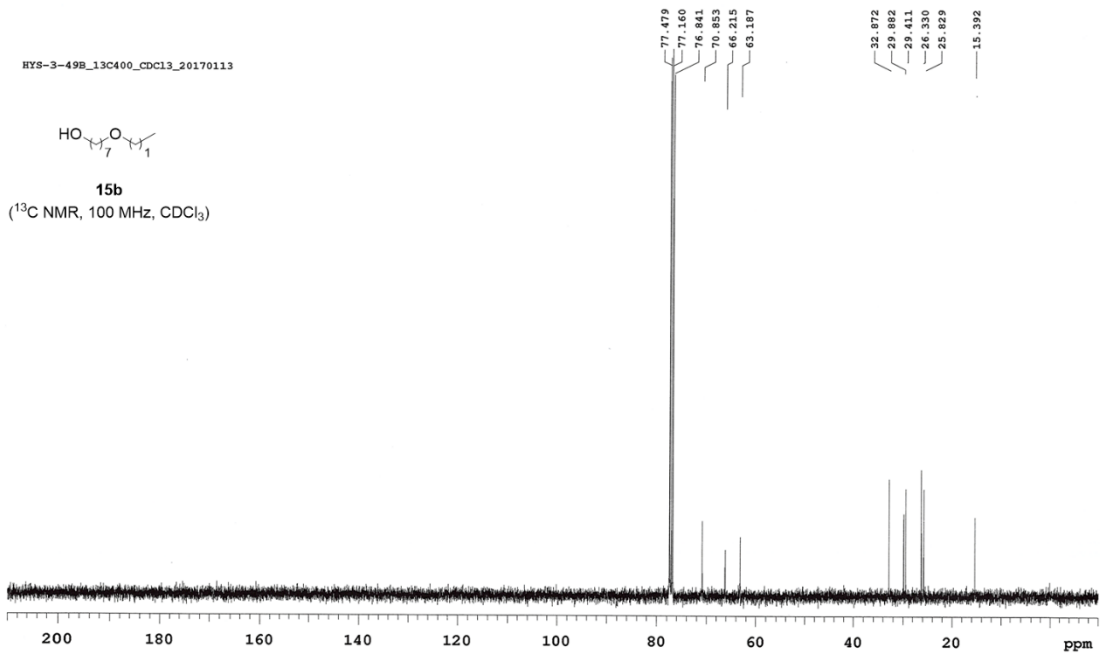

HYS-3-24_1H400_CDCl3_20171220
THPO
9
2
14h
(1H NMR, 400 MHz, CDCl3)
3.465
3.403
3.386
3.370
3.360
3.352
3.343
3.335
1.862
1.855
1.842
1.833
1.820
1.812
1.795
1.784
1.742
1.734
1.726
1.710
1.702
1.694
1.688
1.680
1.634
1.625
1.608
1.602
1.590
1.573
1.565
1.554
1.537
1.529
1.515
1.494
1.334
1.296
1.250
0.928
0.909
0.890
0.875
0.007
12
10
8
6
4
2
0
ppm
0.95
1.03
5.02
1.02
1.05
1.14
0.60
1.01
3.28
3.00

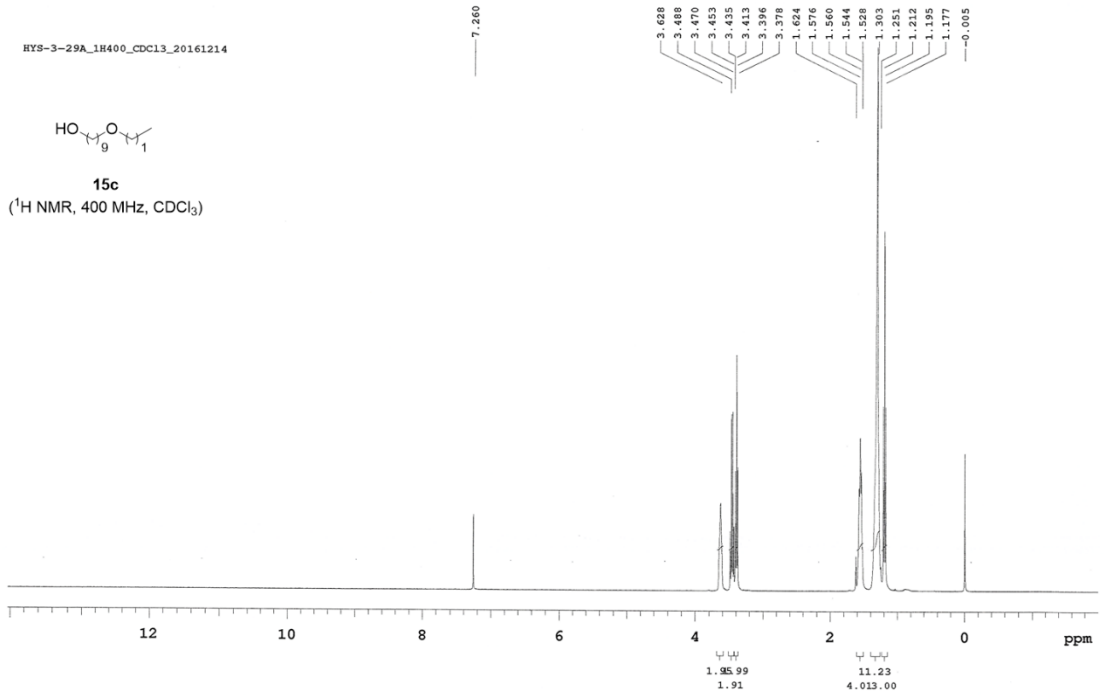

HYS-3-24_13C400_CDCl3_20161208
THPO
9
2
14h
(13C NMR, 100 MHz, CDCl3)
98.981
77.479
77.160
76.849
72.697
71.058
67.824
62.473
30.937
29.927
29.889
29.677
29.586
29.563
26.367
26.322
25.654
23.089
19.848
10.732
200
180
160
140
120
100
80
60
40
20
ppm

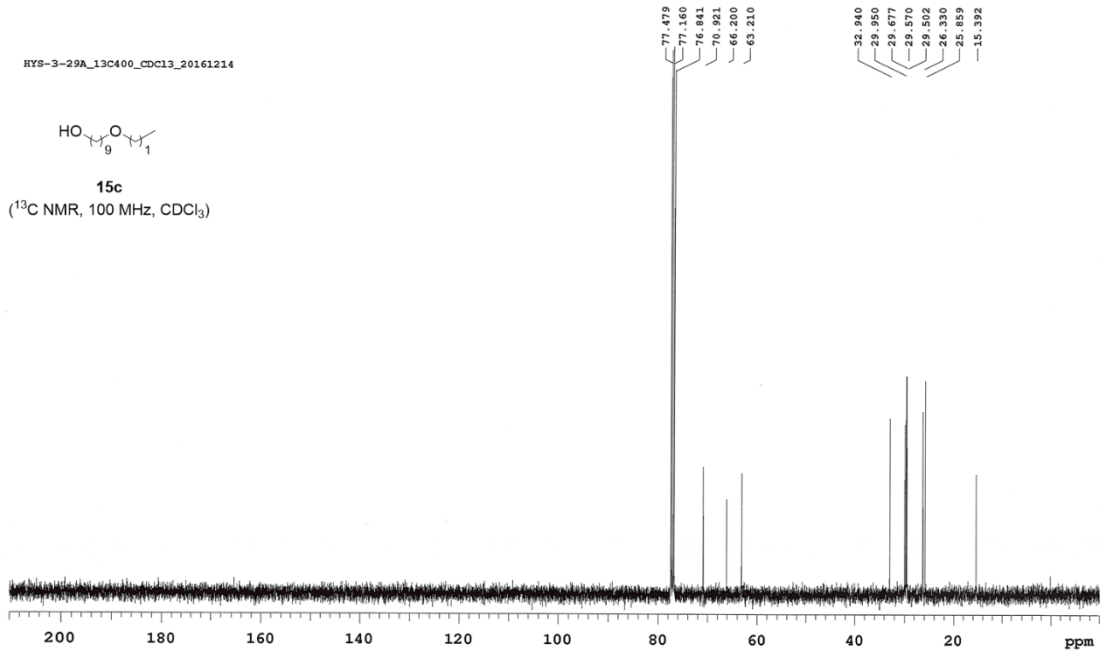

HYS-3-49A_1H400_CDCl3_20170113
HO
O
5
1
15a
(1H NMR, 400 MHz, CDCl3)
7.260
3.656
3.647
3.495
3.477
3.460
3.438
3.421
3.405
1.648
1.630
1.614
1.595
1.579
1.564
1.470
1.455
1.448
1.440
1.431
1.417
1.409
1.391
1.380
1.252
1.214
1.197
1.179
0.004
12
10
8
6
4
2
0
ppm
1.96
4.02
4.32
3.00
3.00

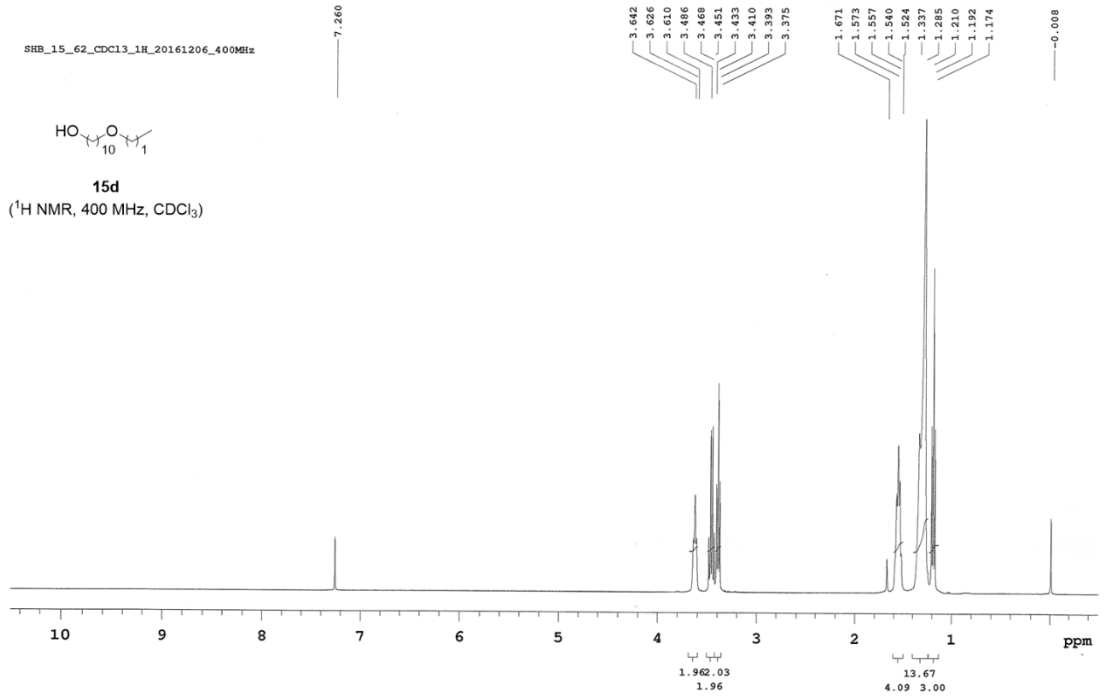

HYS-3-49A_13C400_CDCl3_20170113
HO
O
5
1
15a
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.716
66.283
63.035
32.675
29.631
22.618
15.369
200
180
160
140
120
100
80
60
40
20
ppm


HYS-3-49B_1H400_CDCl3_20170113
HO
O
7
1
15b
(1H NMR, 400 MHz, CDCl3)
7.260
3.657
3.642
3.631
3.614
3.490
3.472
3.455
3.437
3.418
3.401
3.384
1.593
1.572
1.557
1.397
1.350
1.347
1.250
1.213
1.196
1.178
0.003
12
10
8
6
4
2
0
ppm
1.98
6.23
4.283.00

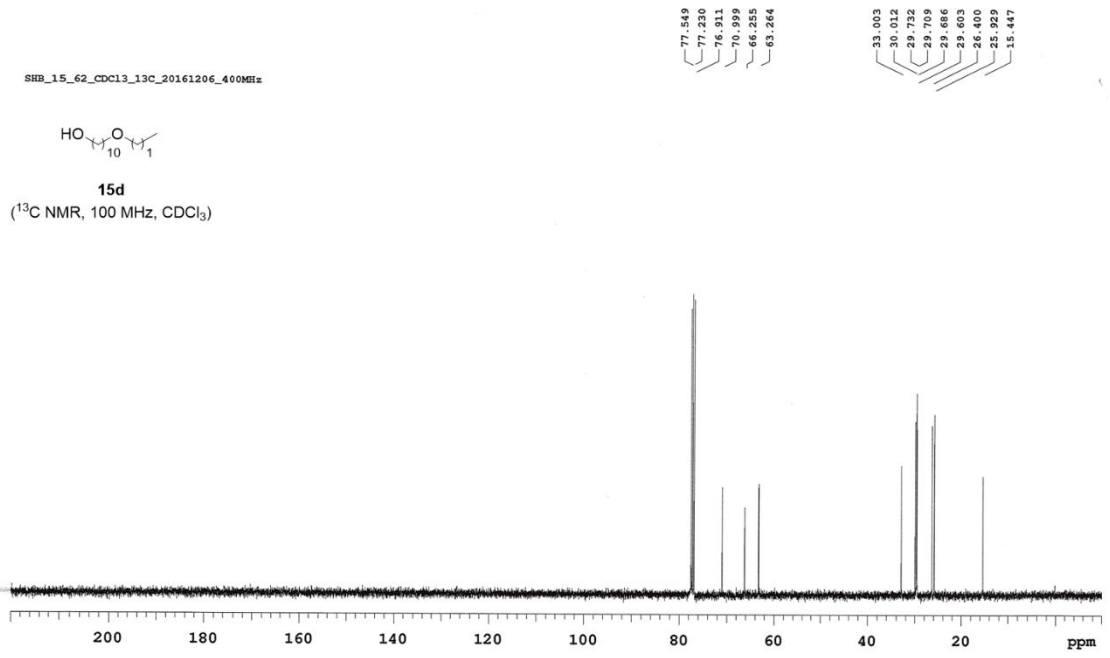

HYS-3-49B_13C400_CDCl3_20170113
HO
O
7
1
15b
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.853
66.215
63.187
32.872
29.882
29.411
26.330
25.829
15.392
200
180
160
140
120
100
80
60
40
20
ppm


HYS-3-29A_1H400_CDCl3_20161214
HO
9
O
1
15c
(1H NMR, 400 MHz, CDCl3)
7.260
3.628
3.488
3.470
3.453
3.435
3.413
3.396
3.378
1.624
1.576
1.560
1.544
1.528
1.303
1.251
1.212
1.195
1.177
0.005
12
10
8
6
4
2
0
ppm
1.99
5.99
1.91
11.23
4.013.00

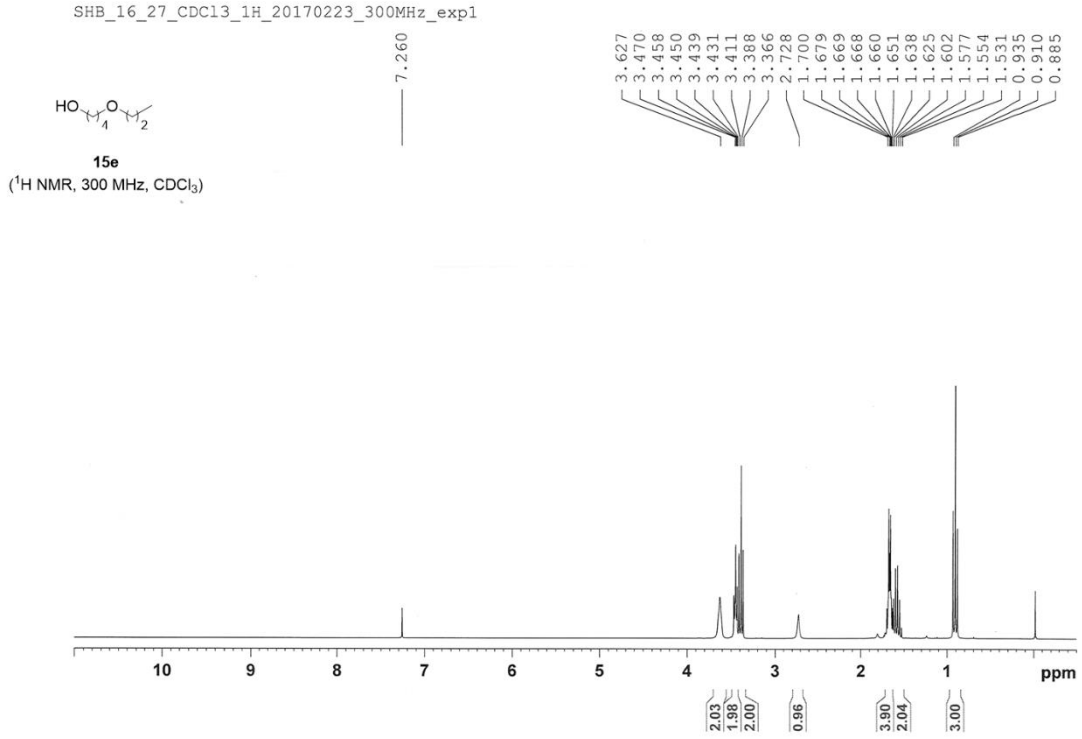

HYS-3-29A_13C400_CDCl3_20161214
HO
9
O
1
15c
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.921
66.200
63.210
32.940
29.950
29.677
29.570
29.502
26.330
25.859
15.392
200
180
160
140
120
100
80
60
40
20
ppm



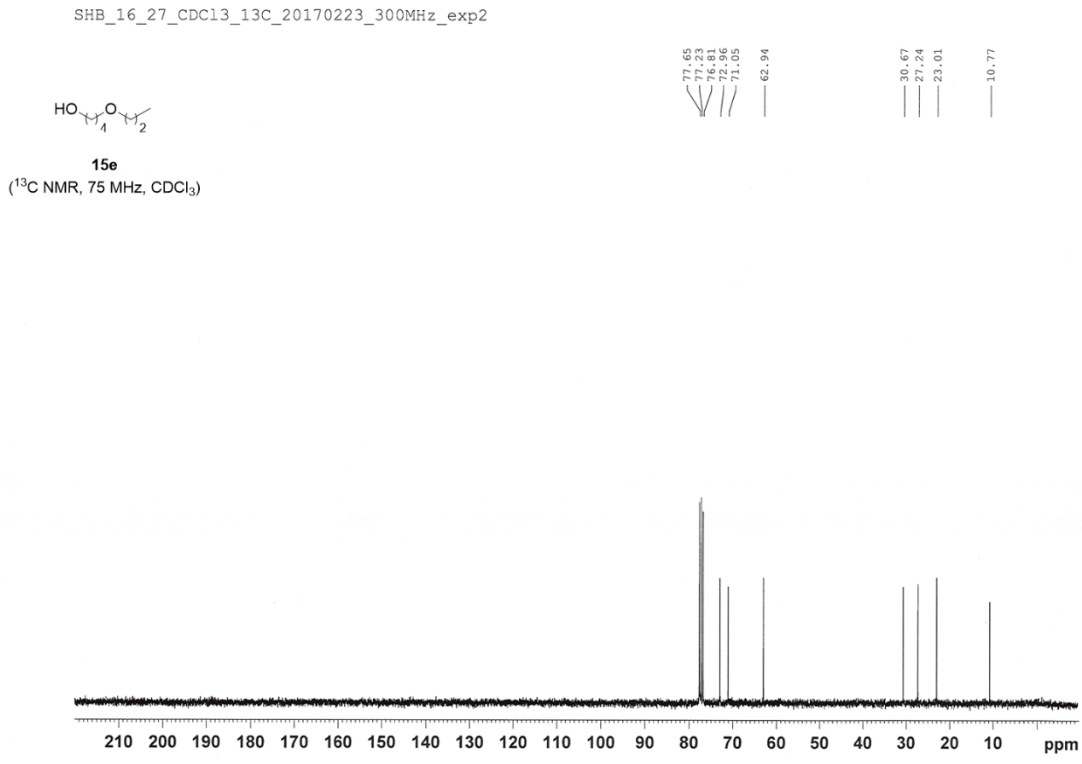
15d
(^{1}H NMR, 400 MHz, $CDCl_3$)



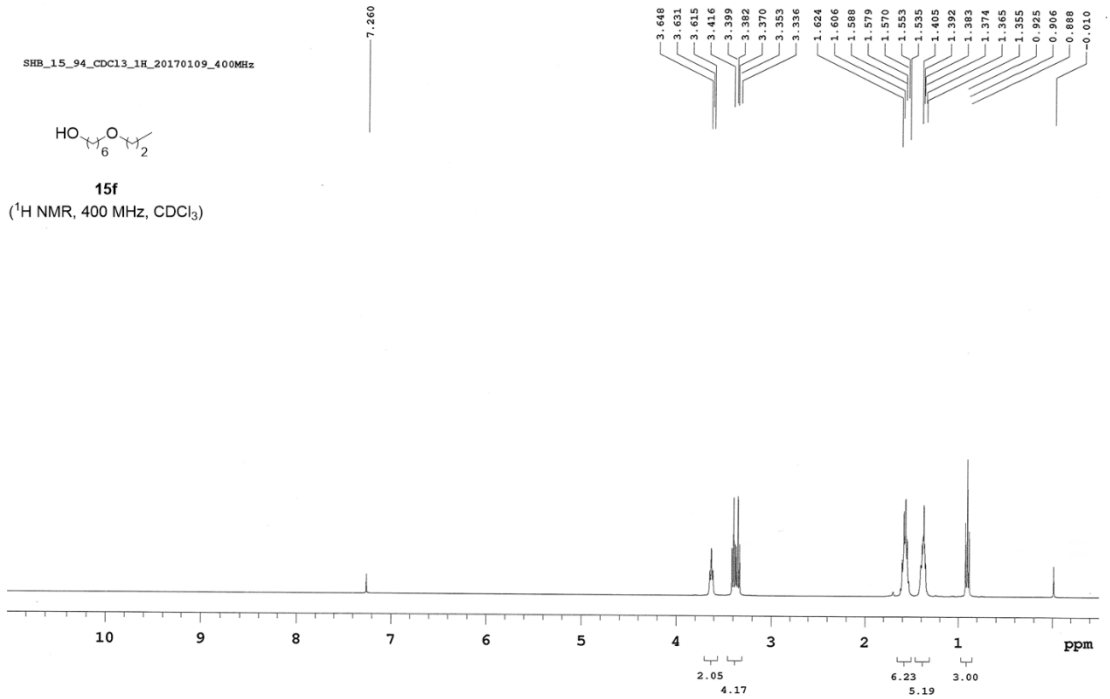
15d
(^{13}C NMR, 100 MHz, $CDCl_3$)



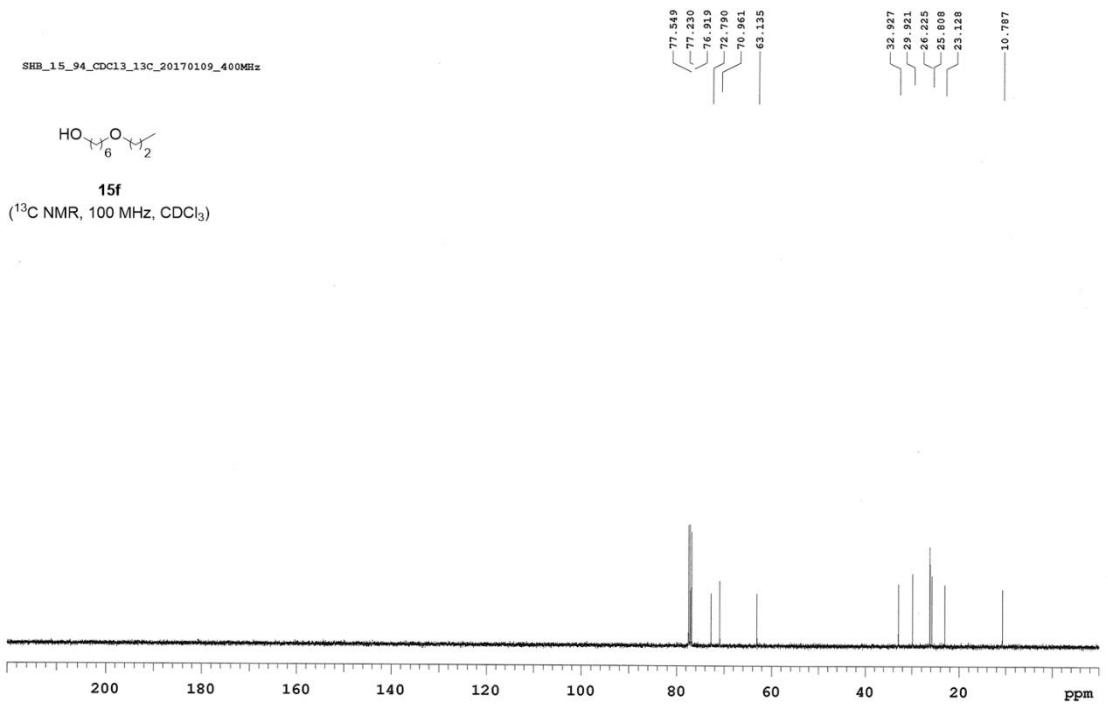
15e
(^{1}H NMR, 300 MHz, $CDCl_3$)



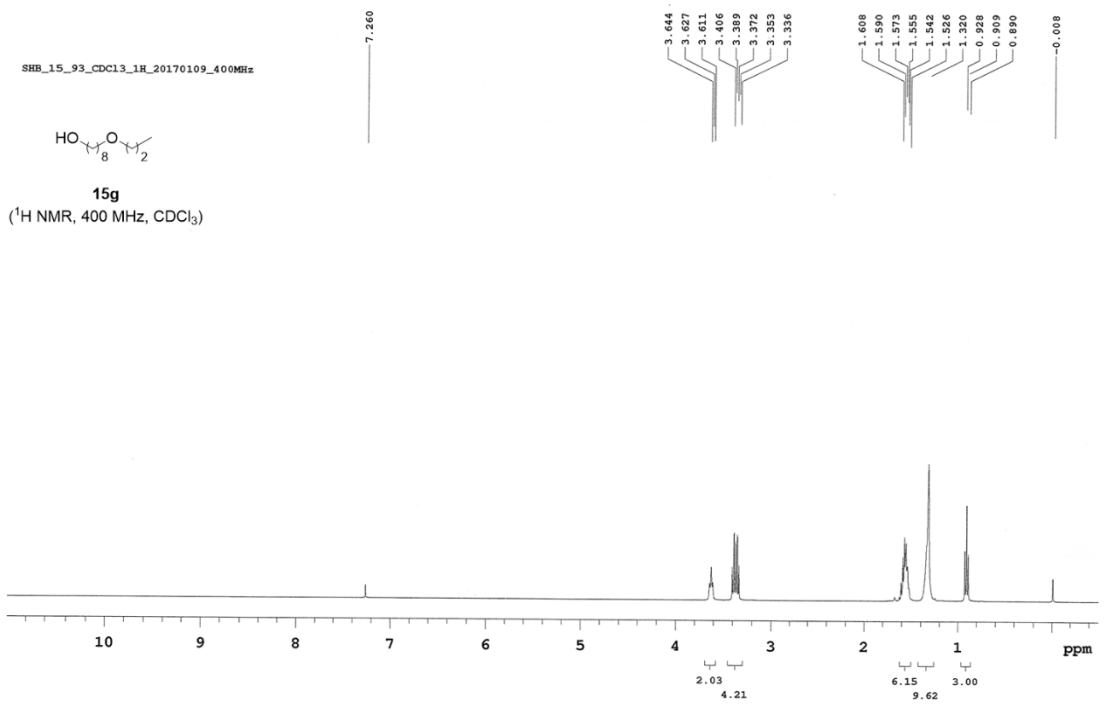
15e
(^{13}C NMR, 75 MHz, $CDCl_3$)



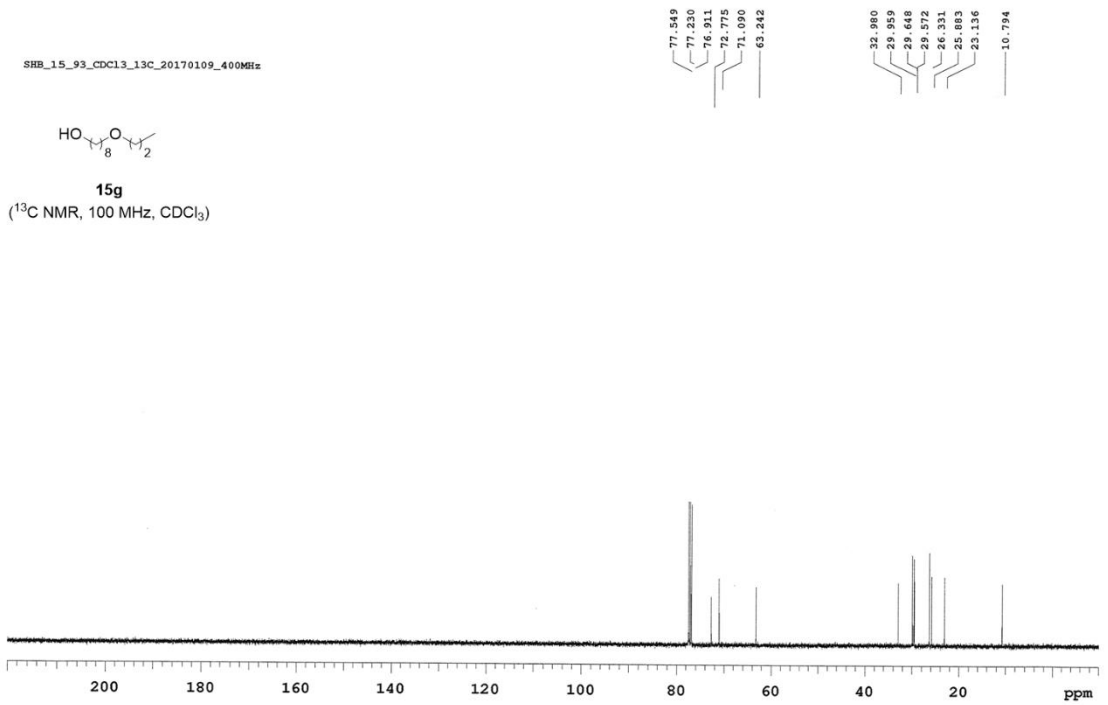
15f
(^{1}H NMR, 400 MHz, $CDCl_3$)



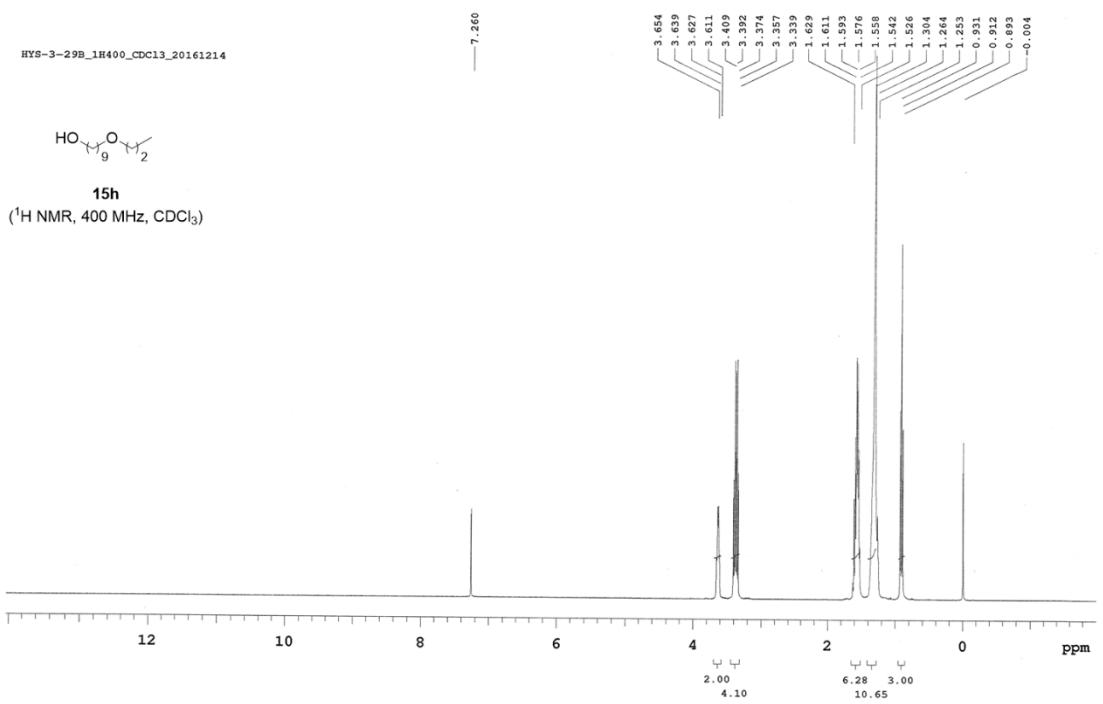
15f
(^{13}C NMR, 100 MHz, $CDCl_3$)

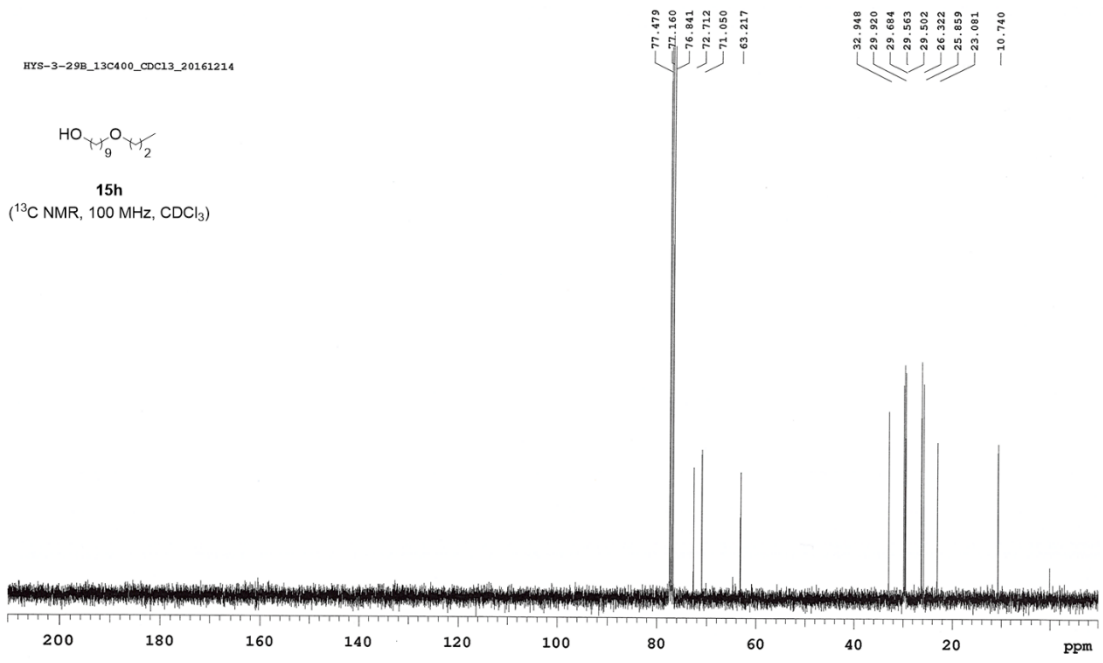


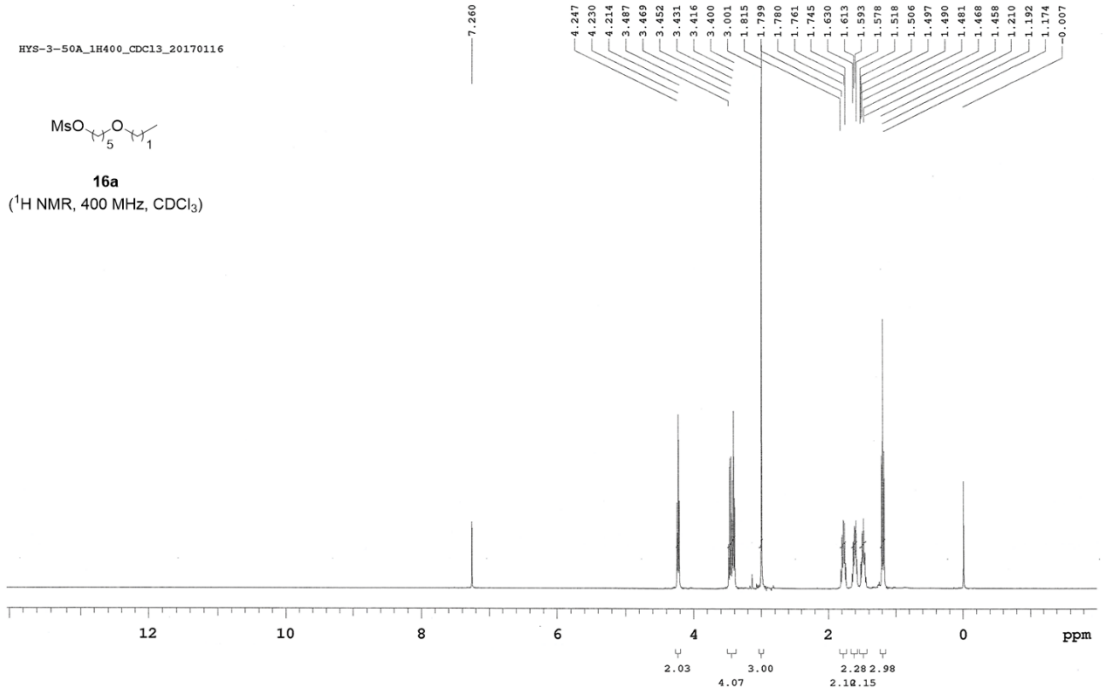
15g
(^{1}H NMR, 400 MHz, $CDCl_3$)

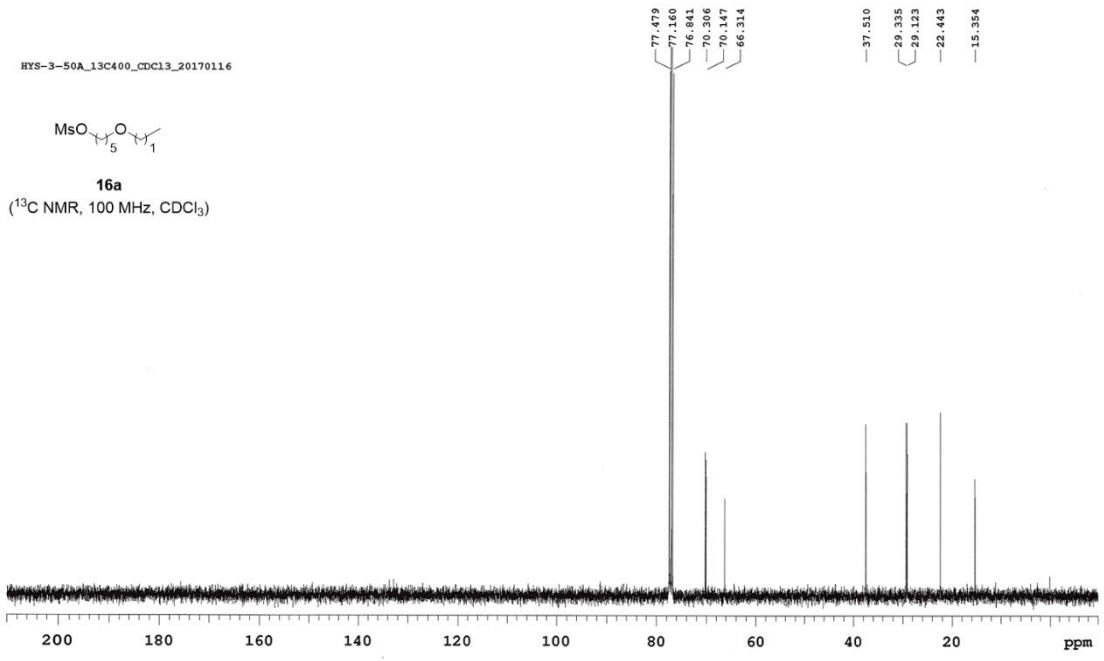


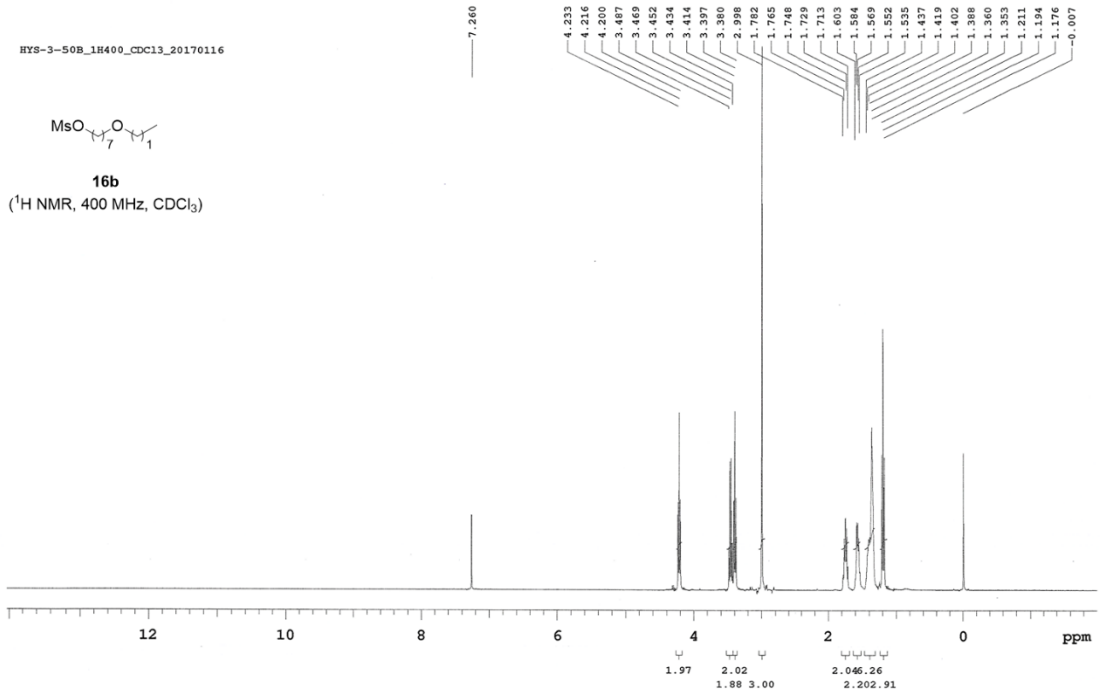
15g
(^{13}C NMR, 100 MHz, $CDCl_3$)

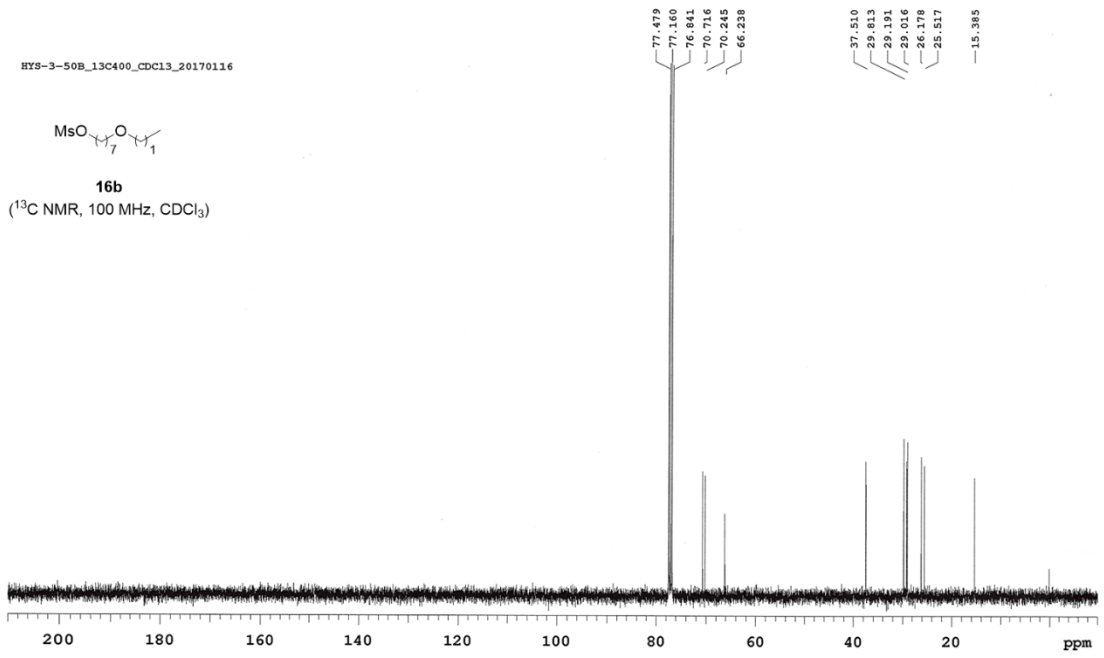

HYS-3-29B_1H400_CDCl3_20161214
HO
9
O
2
15h
(1H NMR, 400 MHz, CDCl3)
7.260
3.654
3.639
3.627
3.611
3.409
3.392
3.374
3.357
3.339
1.629
1.611
1.593
1.576
1.558
1.542
1.526
1.304
1.264
1.253
0.931
0.912
0.893
0.004
12
10
8
6
4
2
0
ppm
2.00
4.10
6.28
3.00
10.65

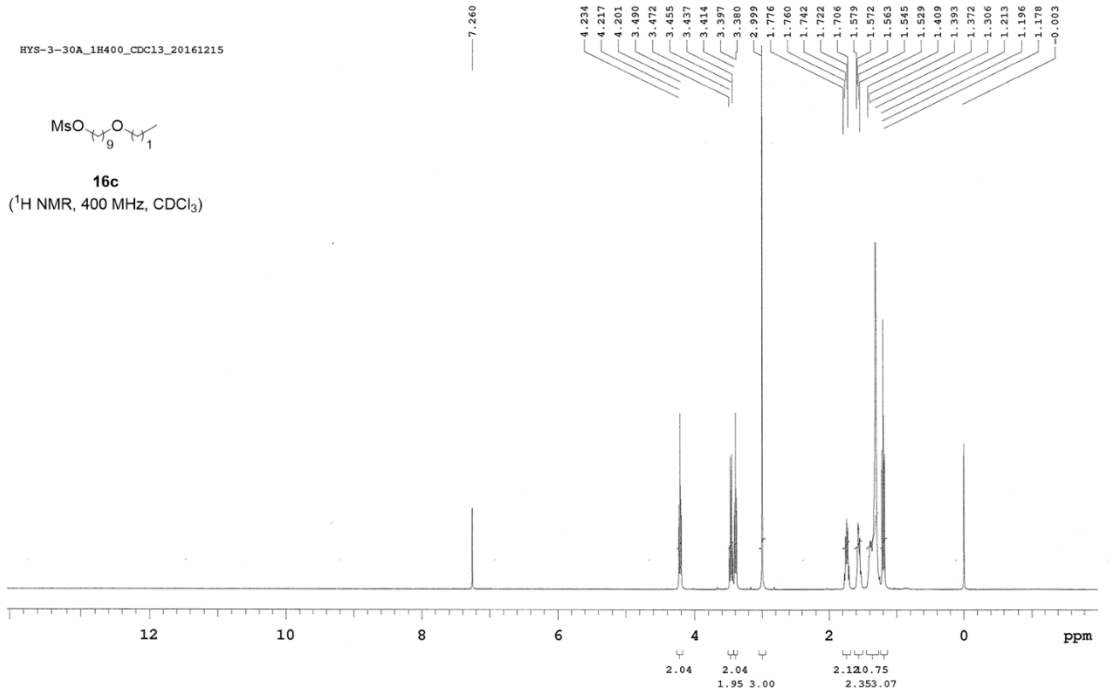

HYS-3-29B_13C400_CDCl3_20161214
HO
9
O
2
15h
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
72.712
71.050
63.217
32.948
29.920
29.684
29.563
29.502
26.322
25.859
23.081
10.740
200
180
160
140
120
100
80
60
40
20
ppm

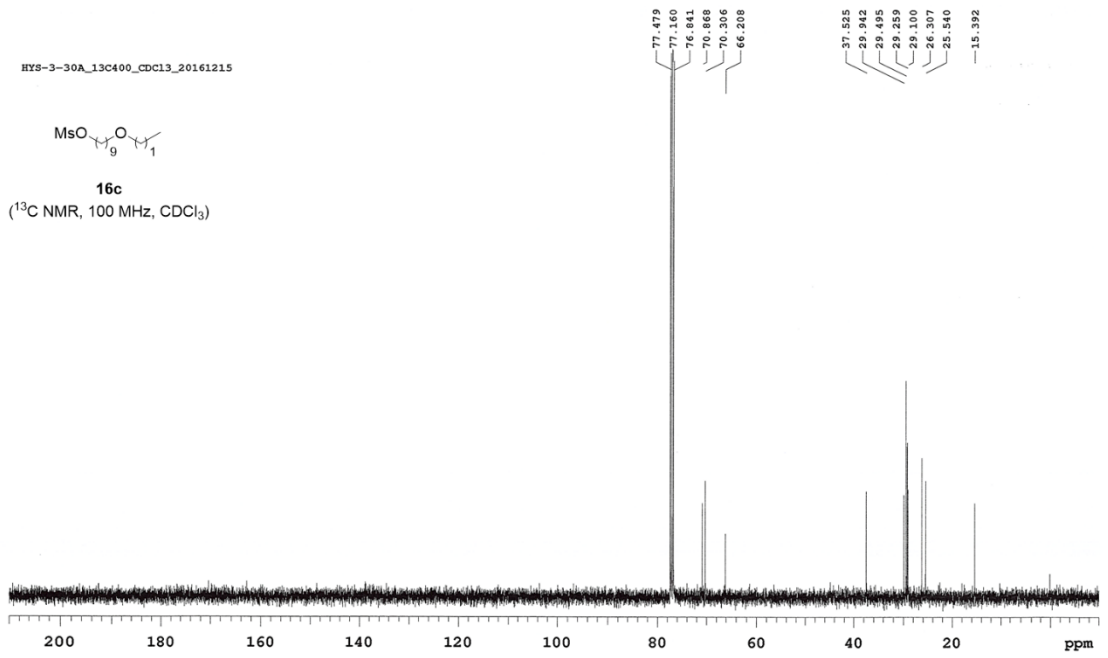

HYS-3-50A_1H400_CDCl3_20170116
MsO
O
5
1
16a
(1H NMR, 400 MHz, CDCl3)
7.260
4.247
4.230
4.214
3.487
3.469
3.452
3.431
3.416
3.400
3.001
1.815
1.799
1.780
1.761
1.745
1.630
1.613
1.593
1.578
1.518
1.506
1.497
1.490
1.481
1.468
1.458
1.210
1.192
1.174
0.007
12
10
8
6
4
2
0
ppm
2.03
4.07
3.00
2.28
2.98
2.10
2.15


HYS-3-50A_13C400_CDCl3_20170116
MsO
O
5
1
16a
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.306
70.147
66.314
37.510
29.335
29.123
22.443
15.354
200
180
160
140
120
100
80
60
40
20
ppm

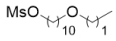

HYS-3-50B_1H400_CDCl3_20170116
MsO
7
O
1
16b
(1H NMR, 400 MHz, CDCl3)
7.260
4.233
4.216
4.200
3.487
3.469
3.452
3.434
3.414
3.397
3.380
2.998
2.782
1.765
1.748
1.729
1.713
1.603
1.584
1.569
1.552
1.535
1.437
1.419
1.402
1.388
1.360
1.353
1.211
1.194
1.176
0.007
12
10
8
6
4
2
0
ppm
1.97
2.02
1.88 3.00
2.046.26
2.202.91


HYS-3-50B_13C400_CDCl3_20170116
MsO
7
O
1
16b
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.716
70.245
66.238
37.510
29.813
29.191
29.016
26.178
25.517
15.385
200
180
160
140
120
100
80
60
40
20
ppm

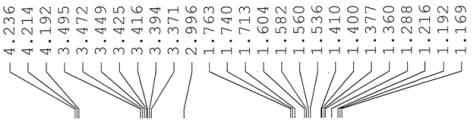

HYS-3-30A_1H400_CDCl3_20161215
MsO
9
O
1
16c
(1H NMR, 400 MHz, CDCl3)
7.260
4.234
4.217
4.201
3.490
3.472
3.455
3.437
3.414
3.397
3.380
2.999
1.776
1.760
1.742
1.722
1.706
1.579
1.572
1.563
1.545
1.529
1.409
1.393
1.372
1.306
1.213
1.196
1.178
0.003
12
10
8
6
4
2
0
ppm
2.04
2.04
1.95
3.00
2.12
0.75
2.35
3.07

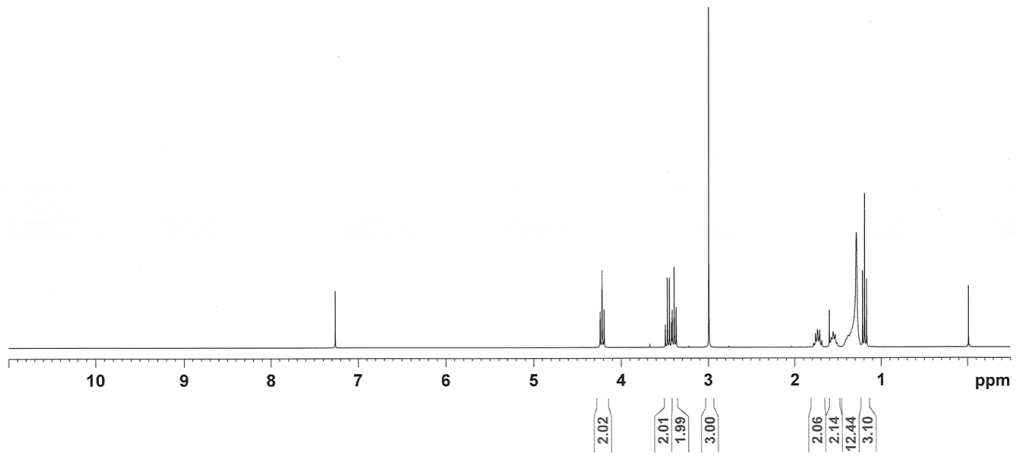

HYS-3-30A_13C400_CDCl3_20161215
MsO
9
O
1
16c
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
70.868
70.306
66.208
37.525
29.942
29.495
29.259
29.100
26.307
25.540
15.392
200
180
160
140
120
100
80
60
40
20
ppm

SHB_15_63_CDCl3_1H_20161207_300MHz_exp1

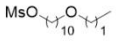


16d
(^{1}H NMR, 300 MHz, $CDCl_3$)

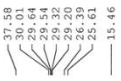


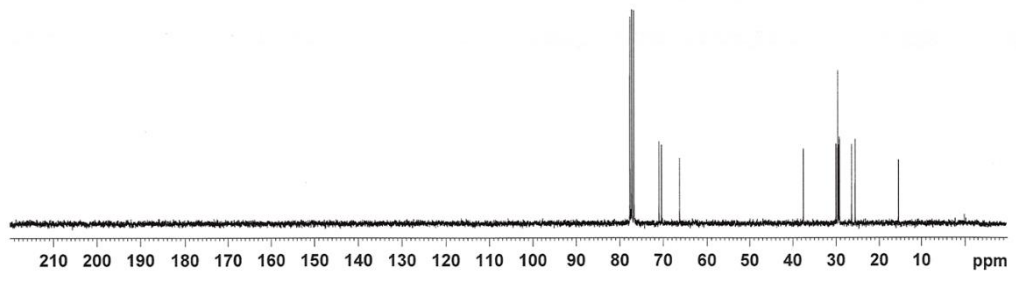


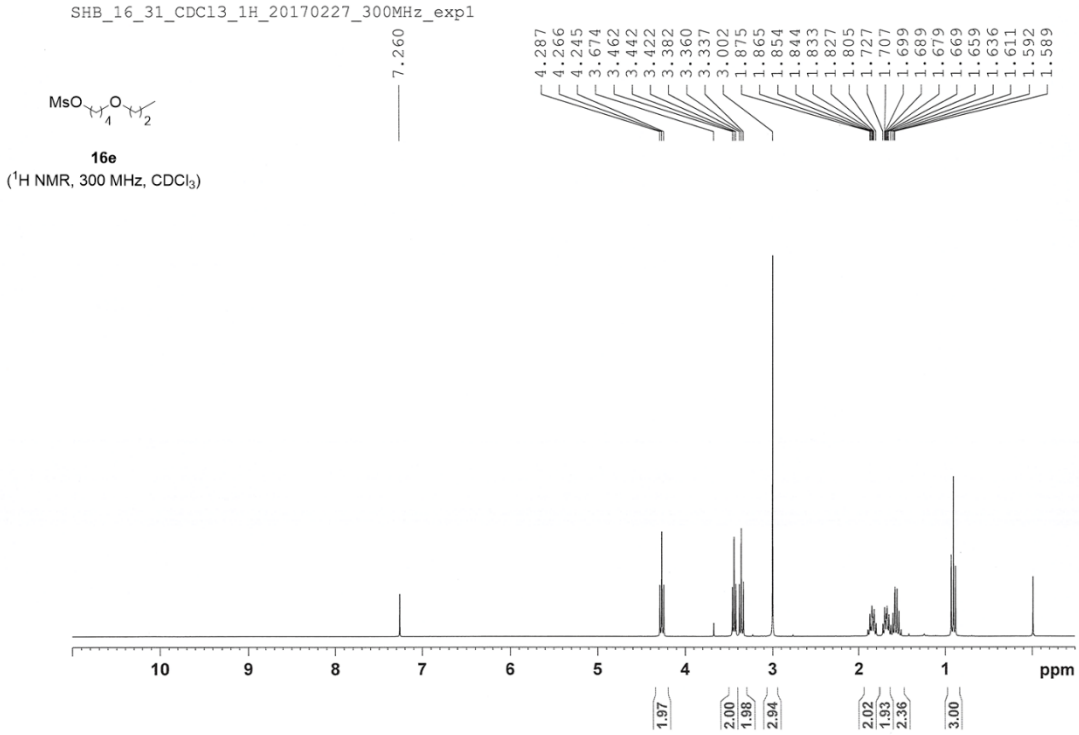
SHB_15_63_CDCl3_13C_20161207_300MHz_exp2



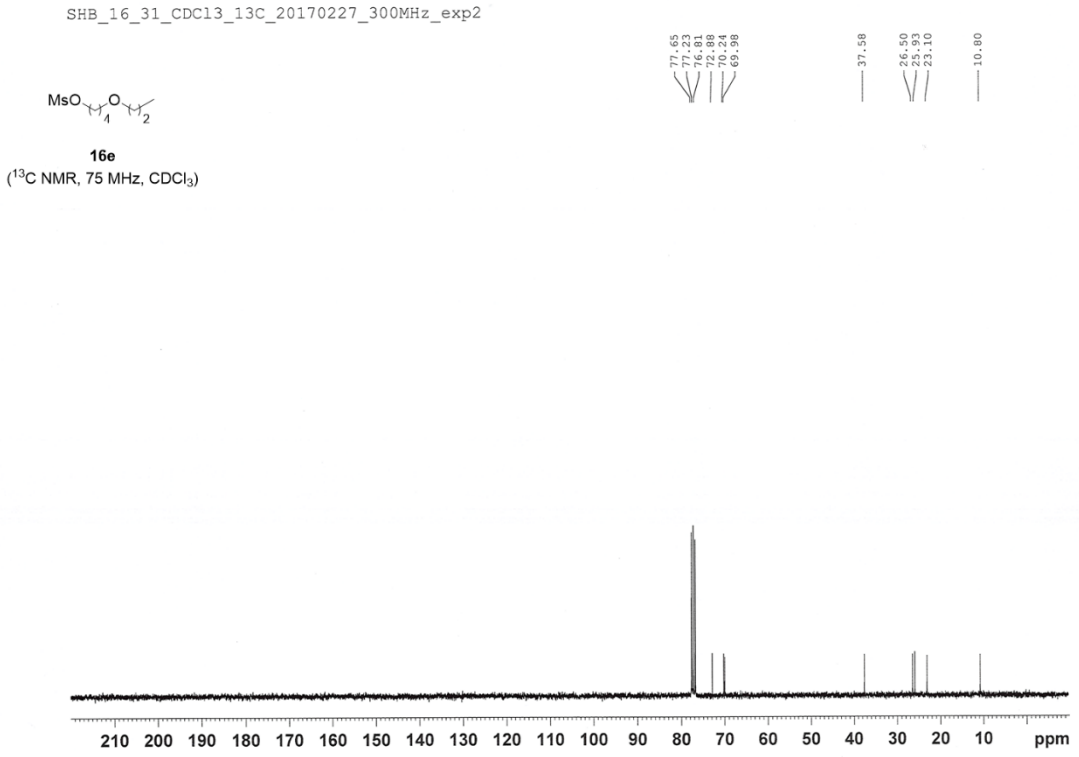
16d
(^{13}C NMR, 75 MHz, $CDCl_3$)





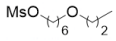


16e
(^{1}H NMR, 300 MHz, $CDCl_3$)



16e
(^{13}C NMR, 75 MHz, $CDCl_3$)

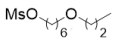
SHB_15_97_CDCl3_1H_20170111_300MHz_exp3



16f

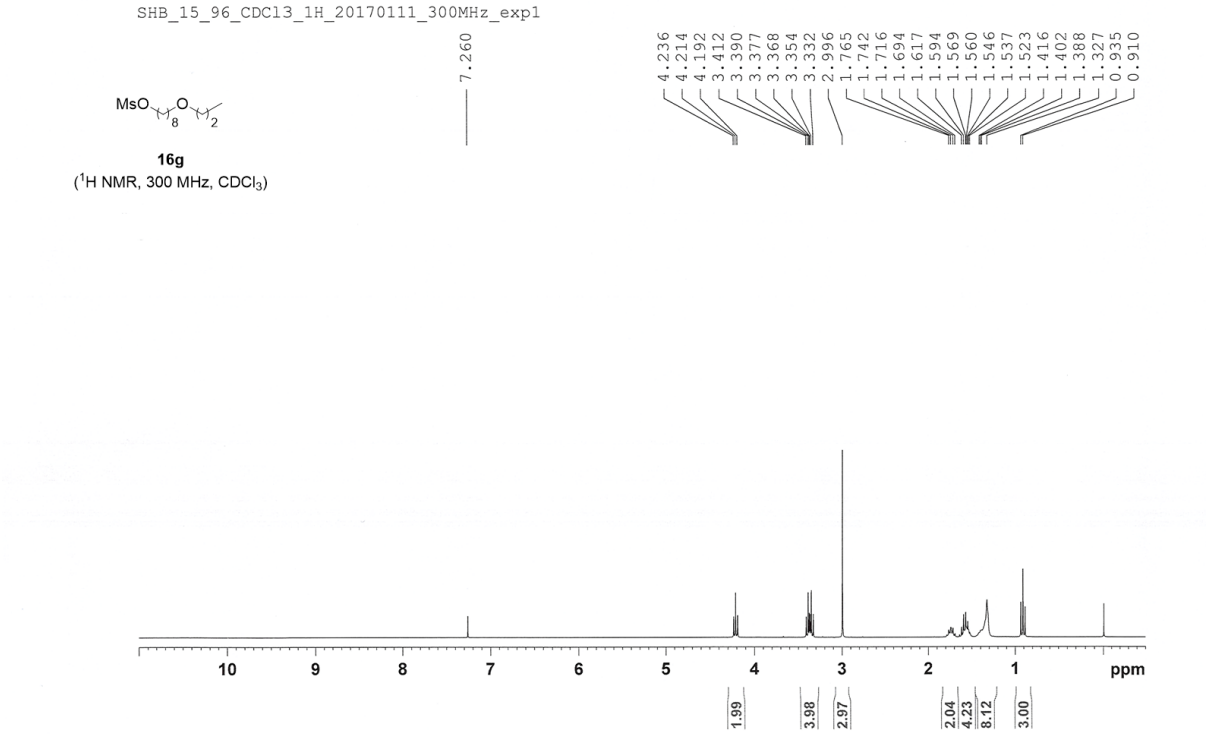
(^{1}H NMR, 300 MHz, $CDCl_3$)

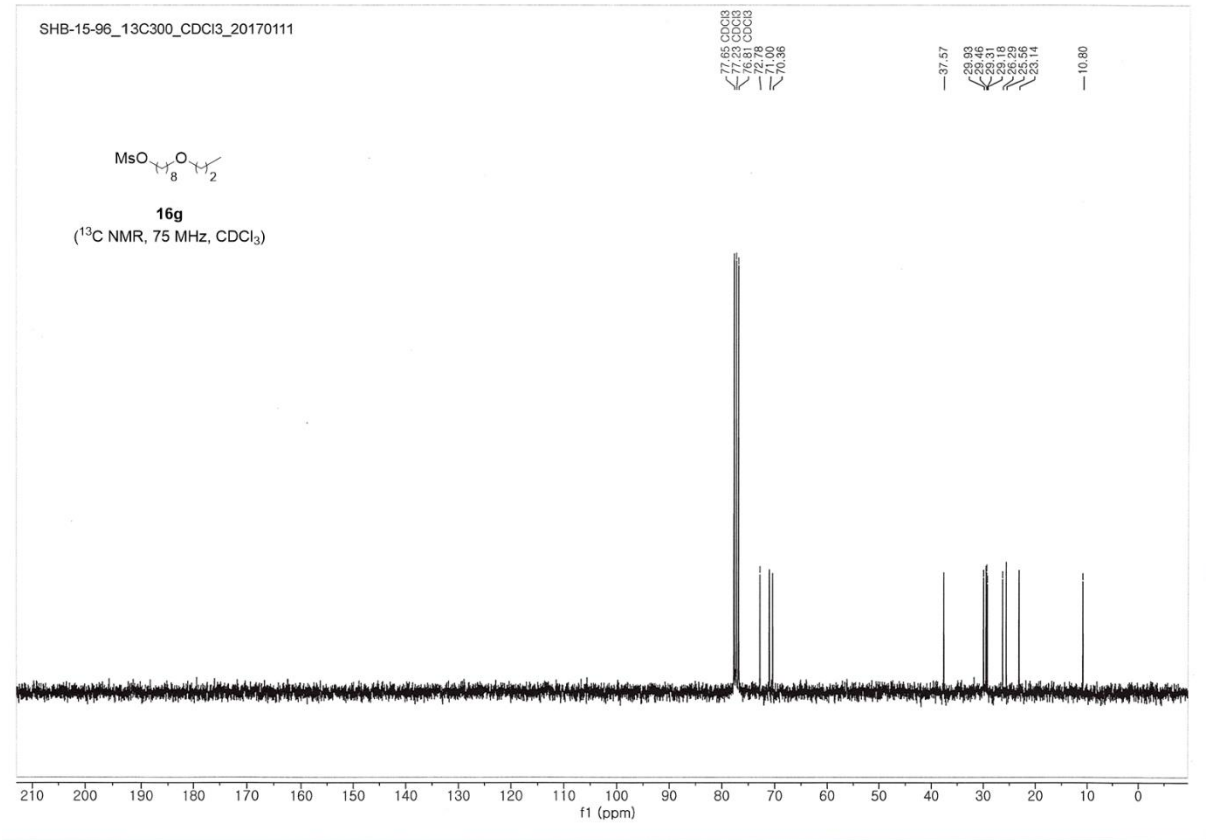
SHB_15_97_CDCl3_13C_20170111_300MHz_exp4

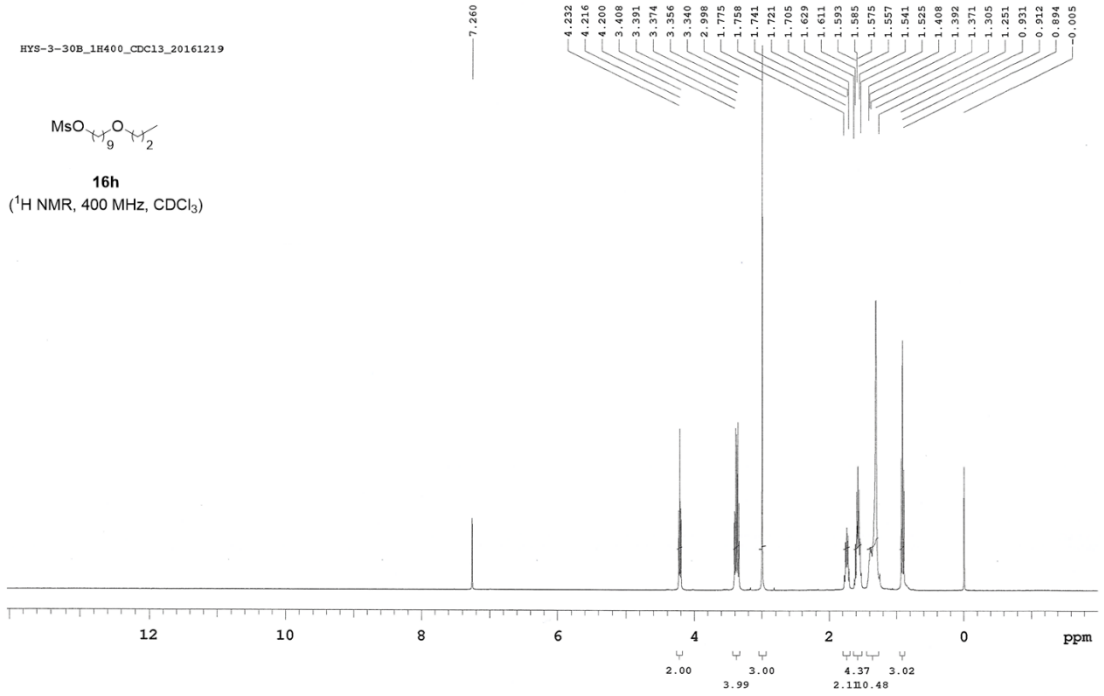


16f

(^{13}C NMR, 75 MHz, $CDCl_3$)


SHB_15_96_CDCl3_1H_20170111_300MHz_exp1
7.260
4.236
4.214
4.192
3.412
3.390
3.377
3.368
3.354
3.332
2.996
1.765
1.742
1.716
1.694
1.617
1.594
1.569
1.560
1.546
1.537
1.523
1.416
1.402
1.388
1.327
0.935
0.910
MsO
8
O
2
16g
(1H NMR, 300 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
ppm
1.99
3.98
2.97
2.04
4.23
8.12
3.00


SHB-15-96_13C300_CDCl3_20170111
77.65 CDCl3
77.23 CDCl3
76.81 CDCl3
72.78
71.00
70.36
37.57
29.93
29.46
29.31
26.19
26.02
25.56
23.14
10.80
MsO
8
O
2
16g
(13C NMR, 75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HYS-3-30B_1H400_CDCl3_20161219
MsO
9
O
2
16h
(1H NMR, 400 MHz, CDCl3)
7.260
4.232
4.216
4.200
3.408
3.391
3.374
3.356
3.340
2.998
1.775
1.758
1.741
1.721
1.705
1.629
1.611
1.593
1.585
1.575
1.557
1.541
1.525
1.408
1.392
1.371
1.305
1.251
0.931
0.912
0.894
0.005
12
10
8
6
4
2
0
ppm
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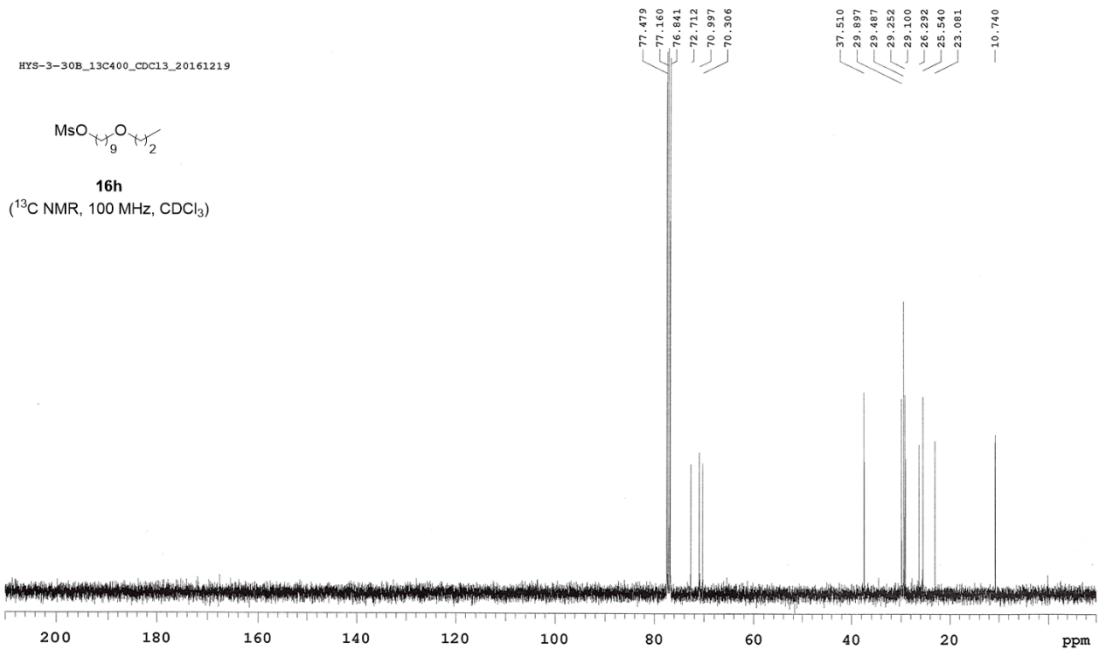
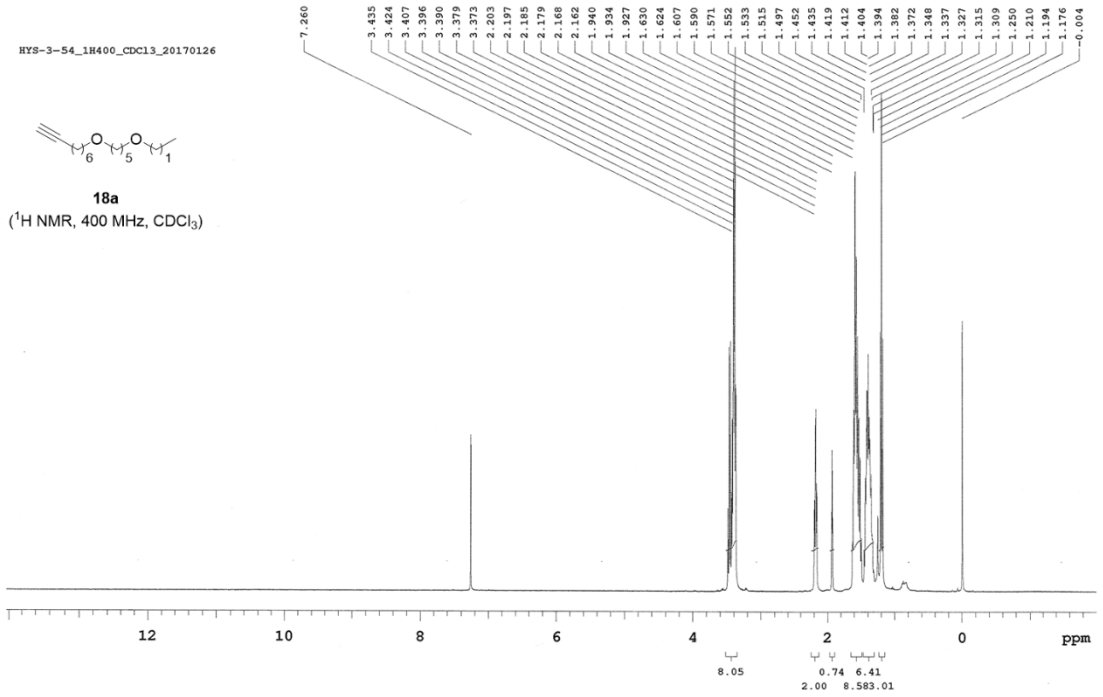
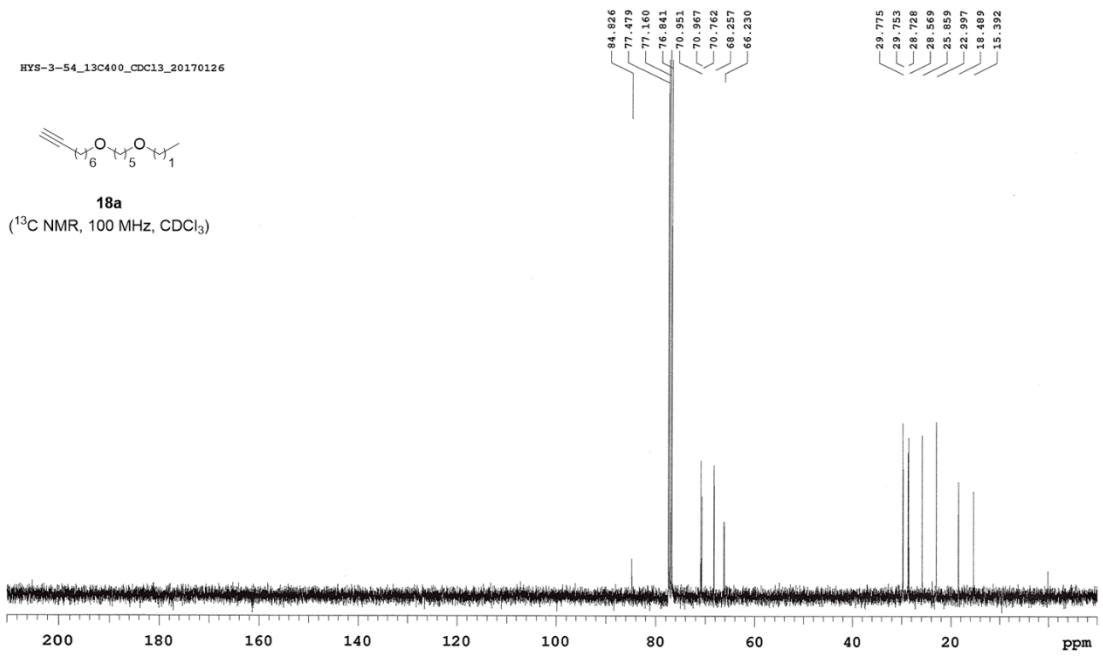
3.00
4.37
3.02
3.99
2.11
0.48

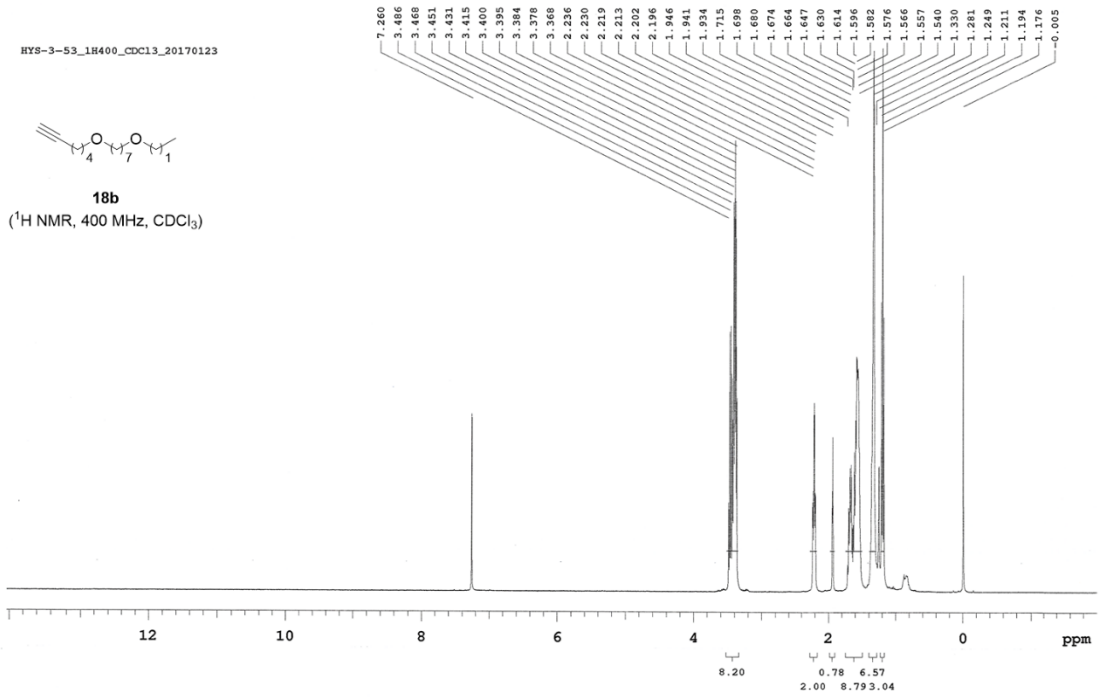

HYS-3-30B_13C400_CDCl3_20161219
MsO
9
O
2
16h
(13C NMR, 100 MHz, CDCl3)
77.479
77.160
76.841
72.712
70.997
70.306
37.510
29.897
29.487
29.252
29.100
26.292
25.540
23.081
10.740
200
180
160
140
120
100
80
60
40
20
ppm



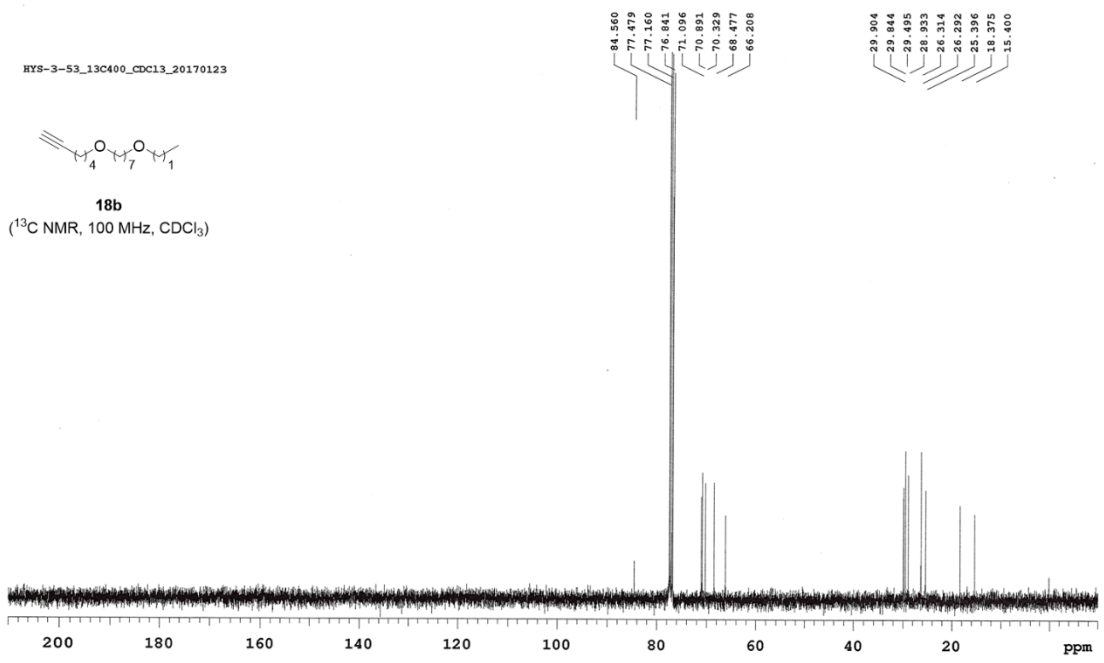
18a
(^{1}H NMR, 400 MHz, $CDCl_3$)



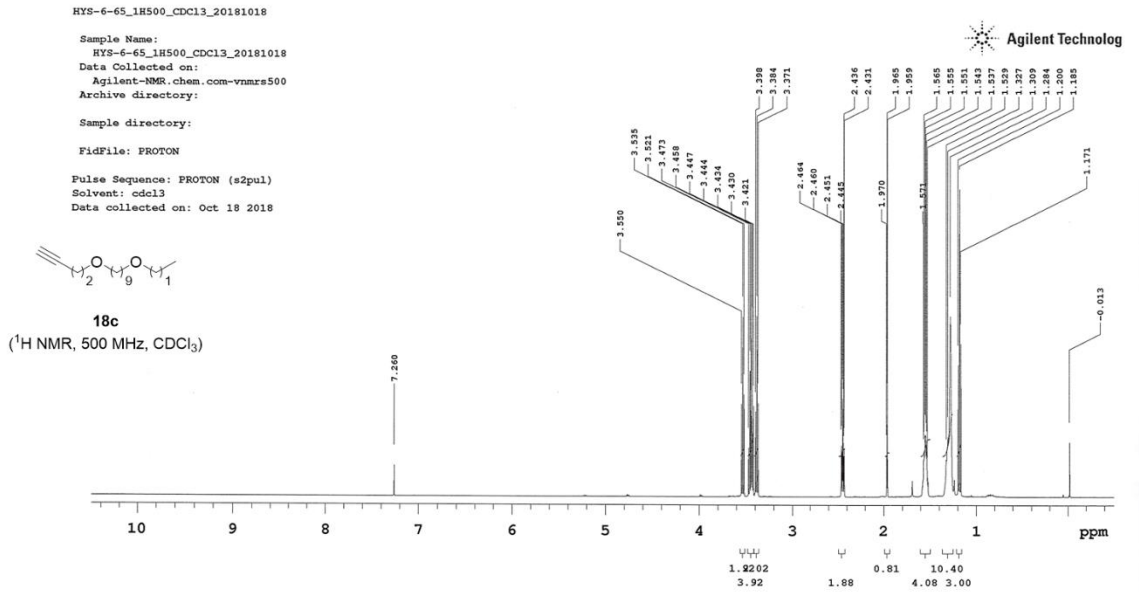
18a
(^{13}C NMR, 100 MHz, $CDCl_3$)



18b
(^{1}H NMR, 400 MHz, $CDCl_3$)

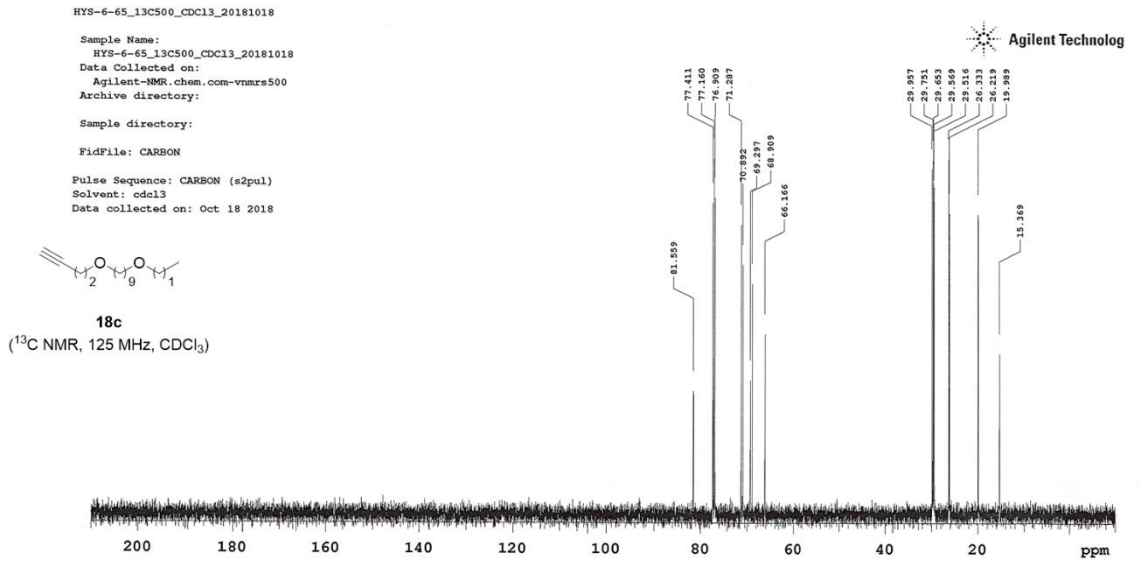


18b
(^{13}C NMR, 100 MHz, $CDCl_3$)



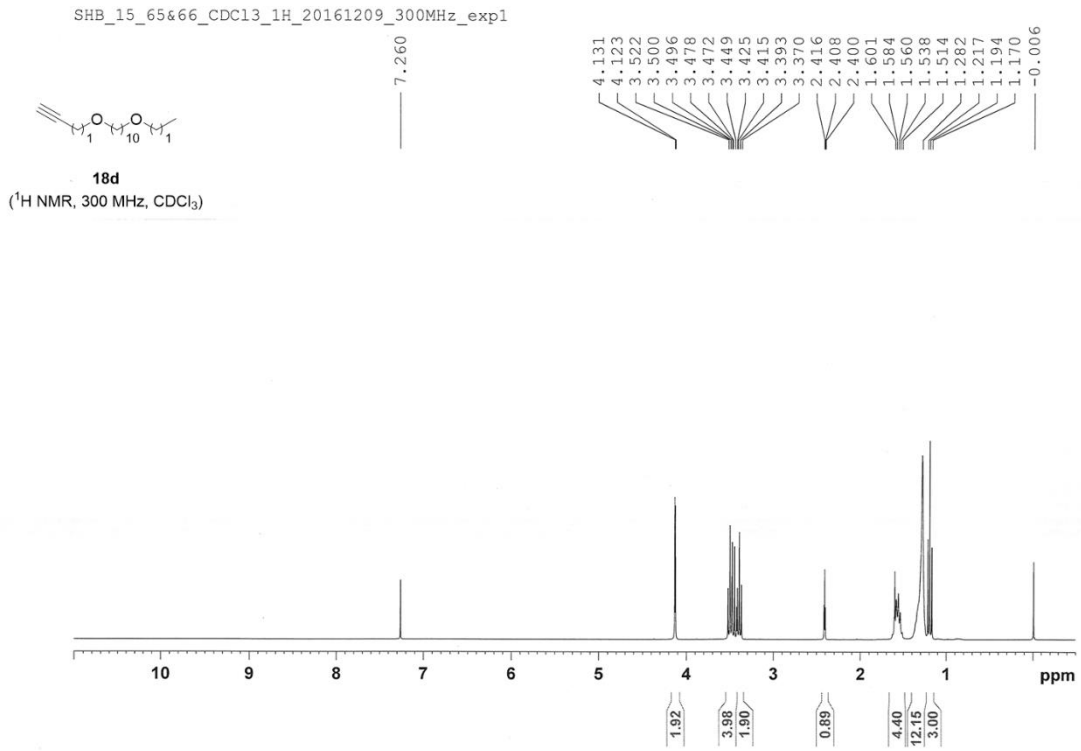
18c

(^{1}H NMR, 500 MHz, $CDCl_3$)

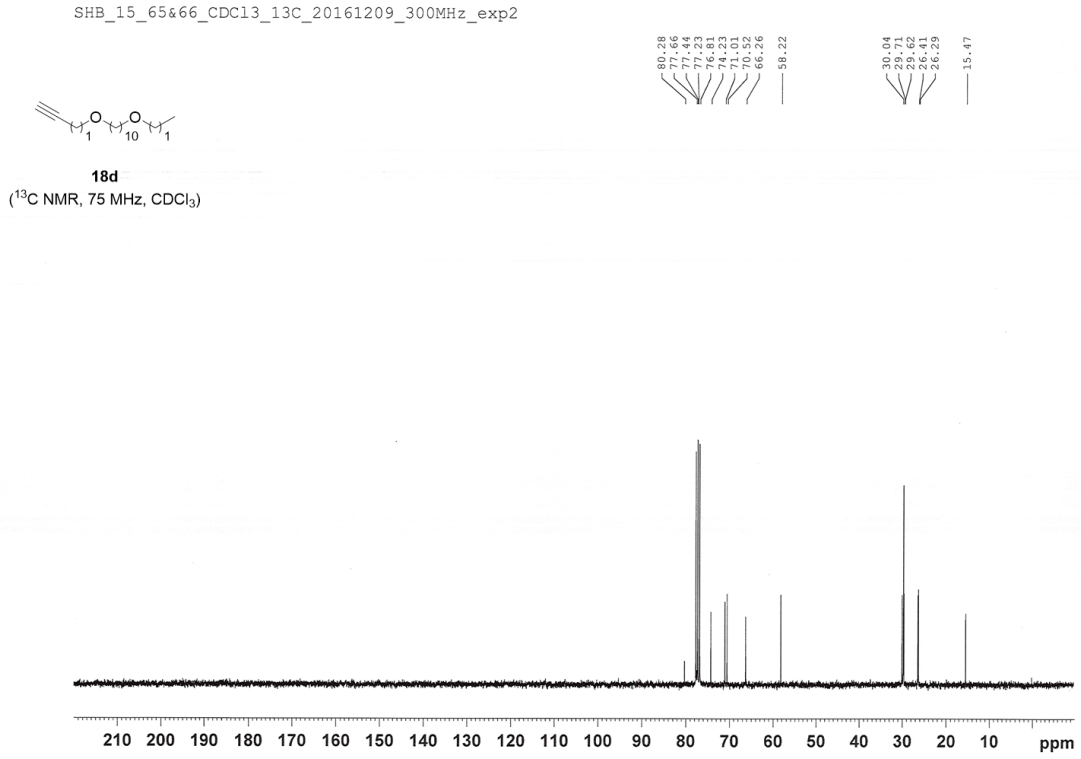


18c

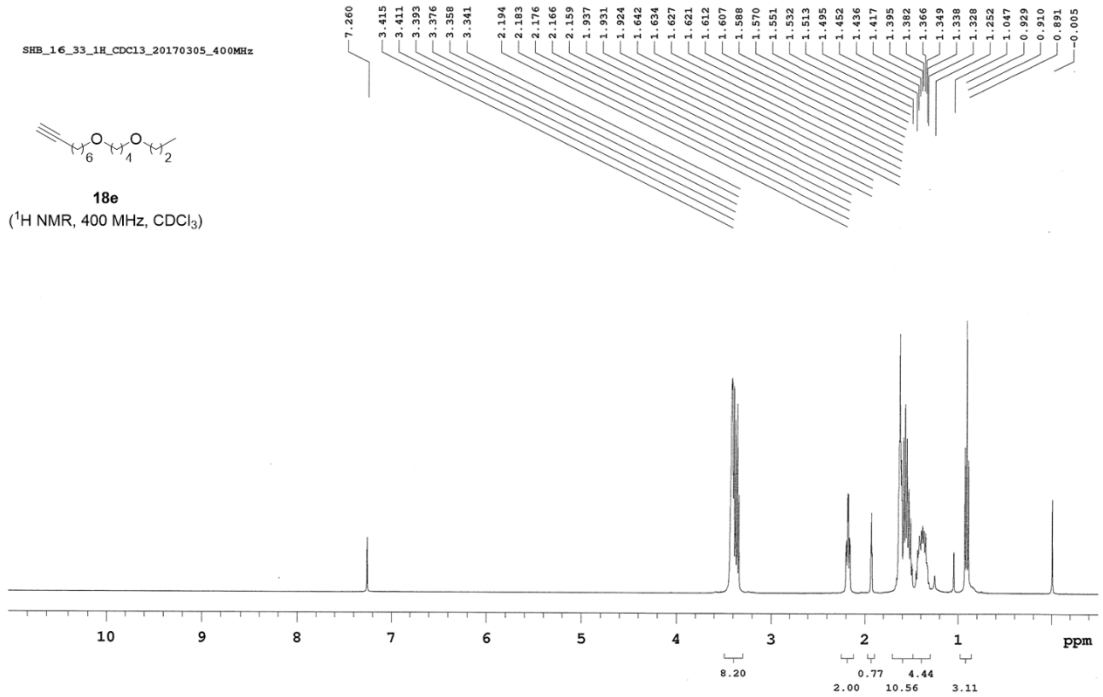
(^{13}C NMR, 125 MHz, $CDCl_3$)



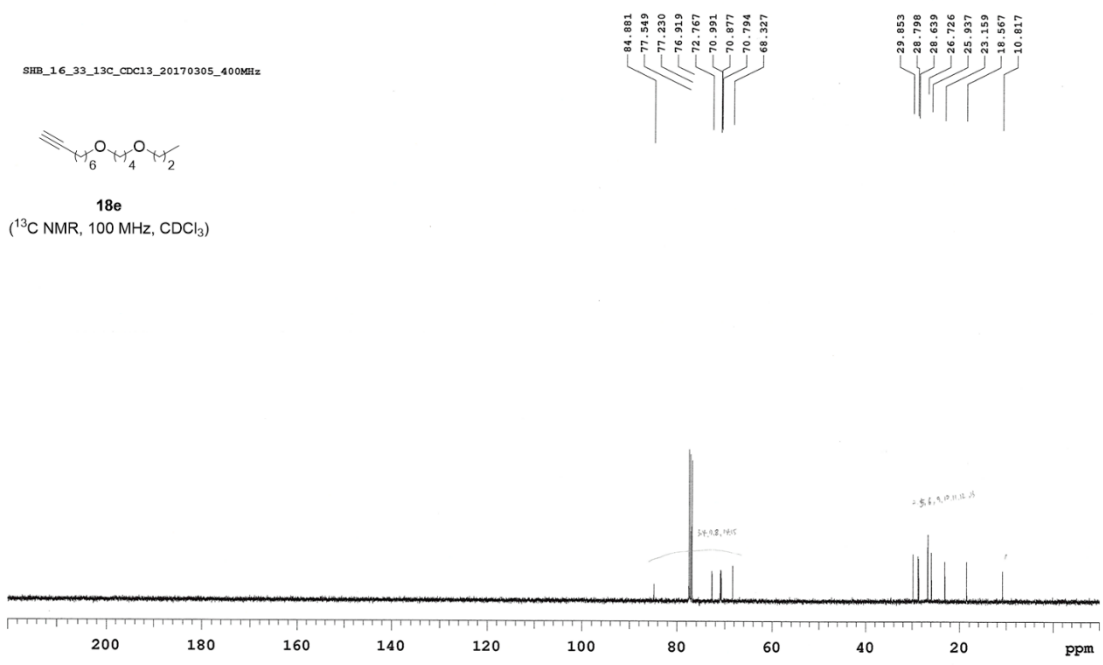
18d
(^{1}H NMR, 300 MHz, $CDCl_3$)



18d
(^{13}C NMR, 75 MHz, $CDCl_3$)

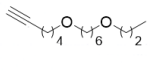


18e
(^{1}H NMR, 400 MHz, $CDCl_3$)



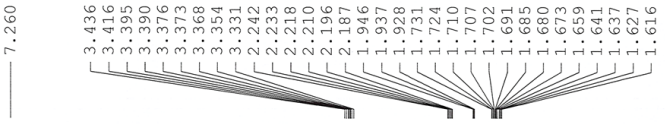
18e
(^{13}C NMR, 100 MHz, $CDCl_3$)

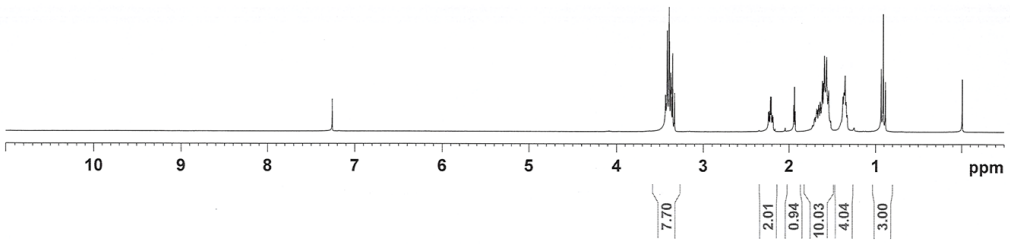
SHB_16_4&5_CDCl3_1H_20170119_300MHz_exp3



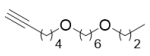
18f

(^{1}H NMR, 300 MHz, $CDCl_3$)



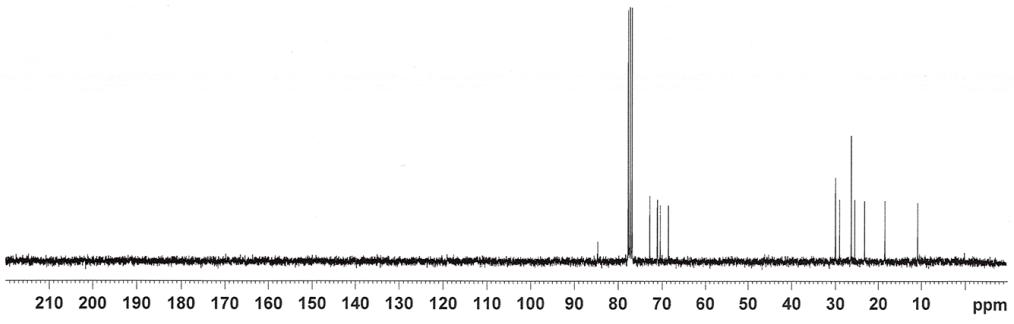


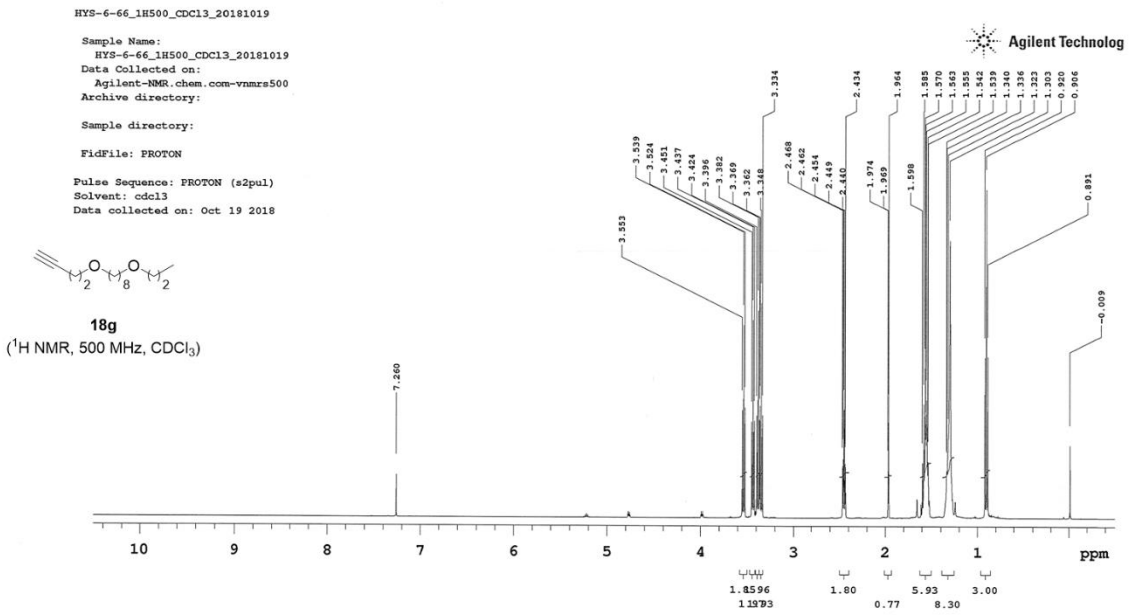
SHB_16_4&5_CDCl3_13C_20170119_300MHz_exp4



18f

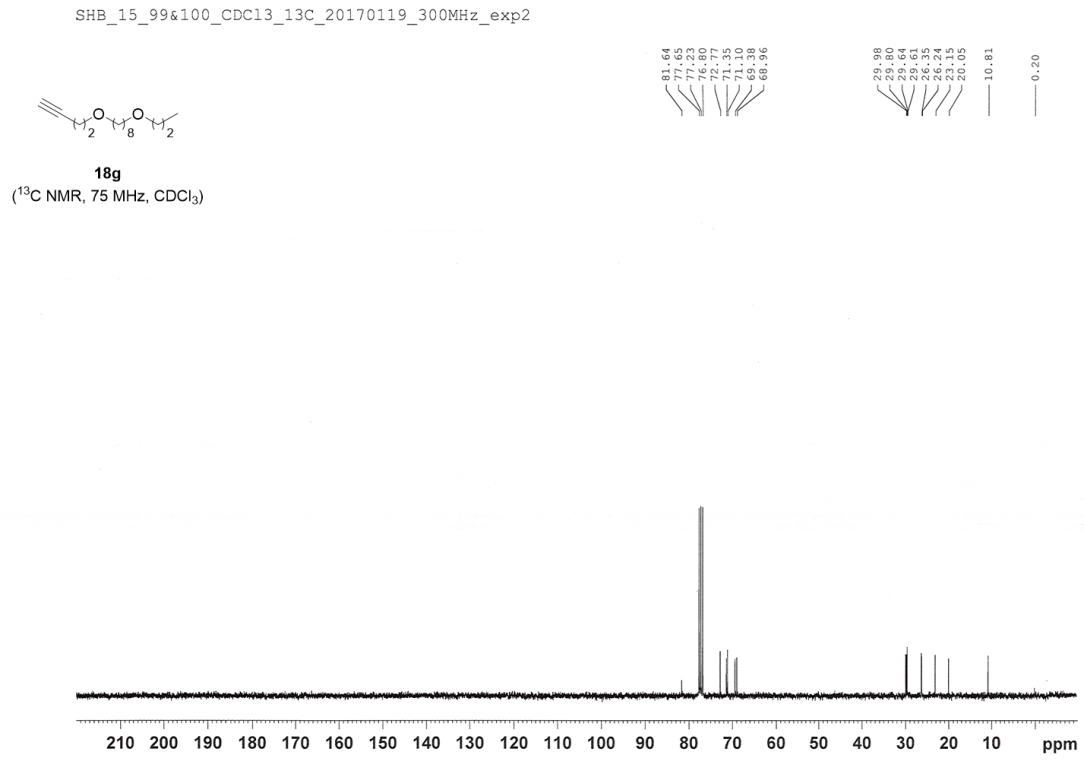
(^{13}C NMR, 75 MHz, $CDCl_3$)





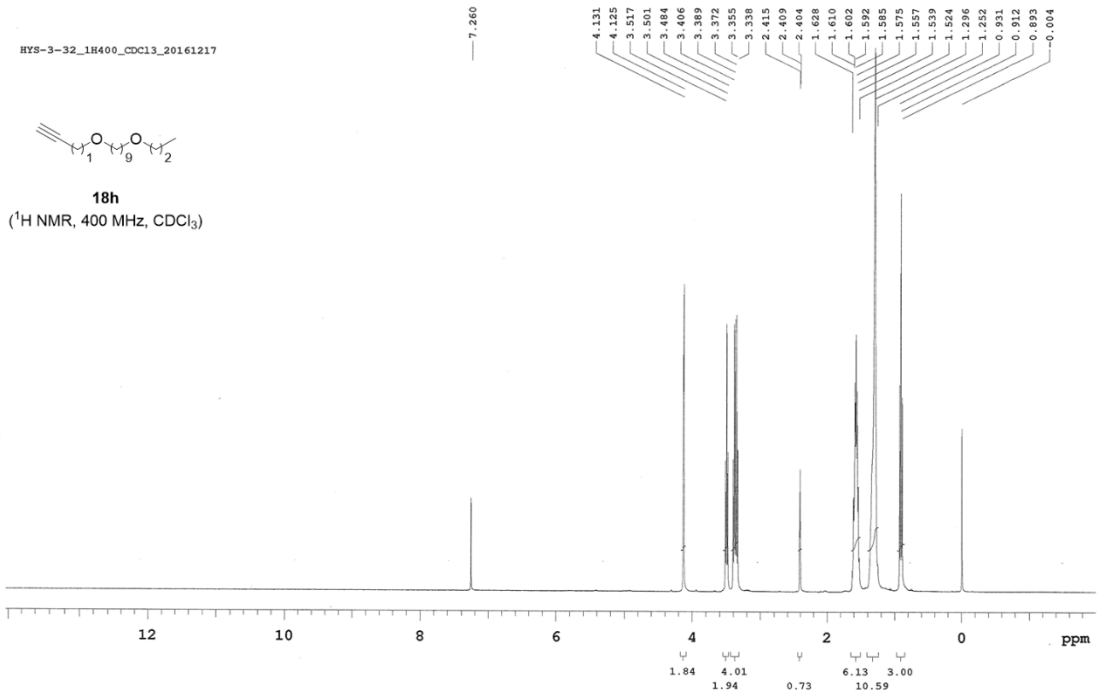
18g

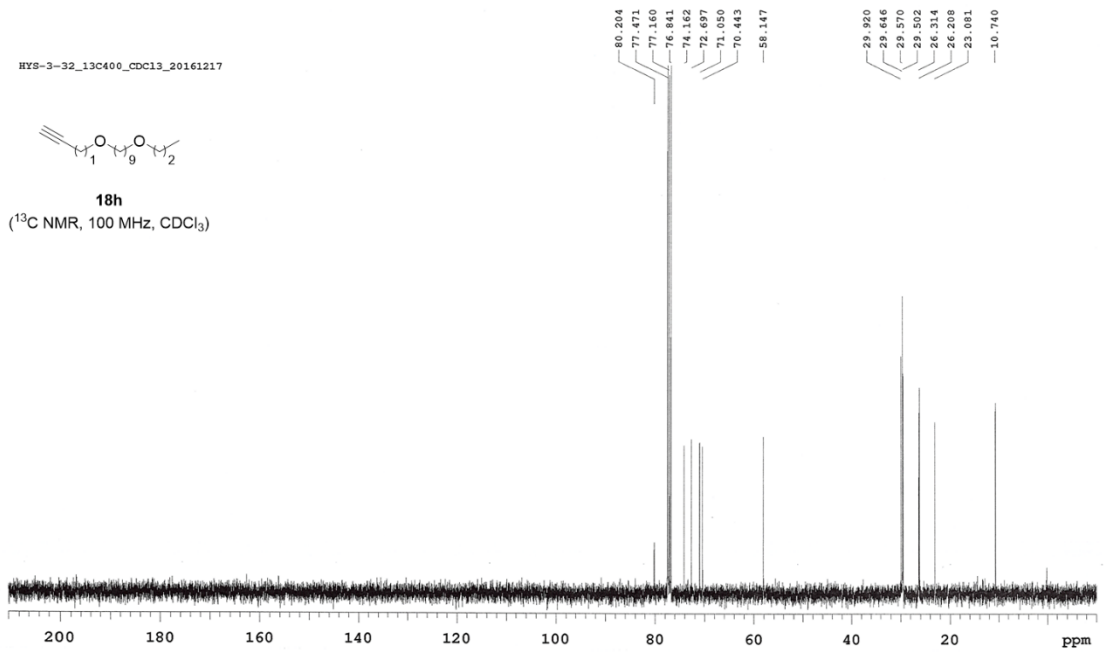
(^{1}H NMR, 500 MHz, $CDCl_3$)

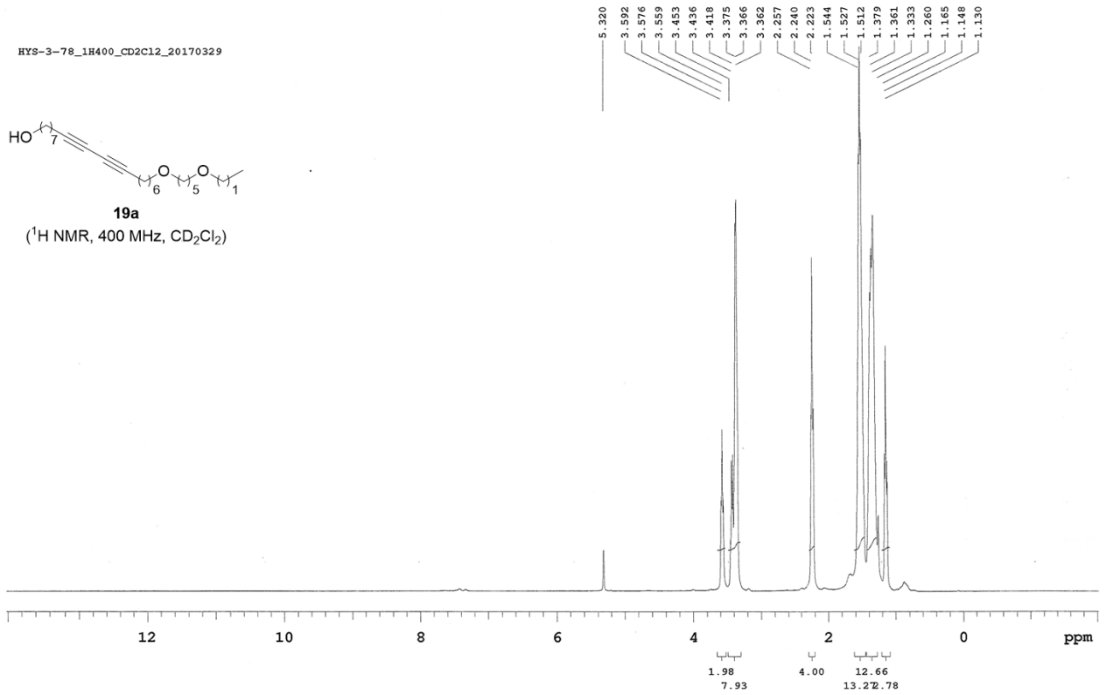


18g

(^{13}C NMR, 75 MHz, $CDCl_3$)

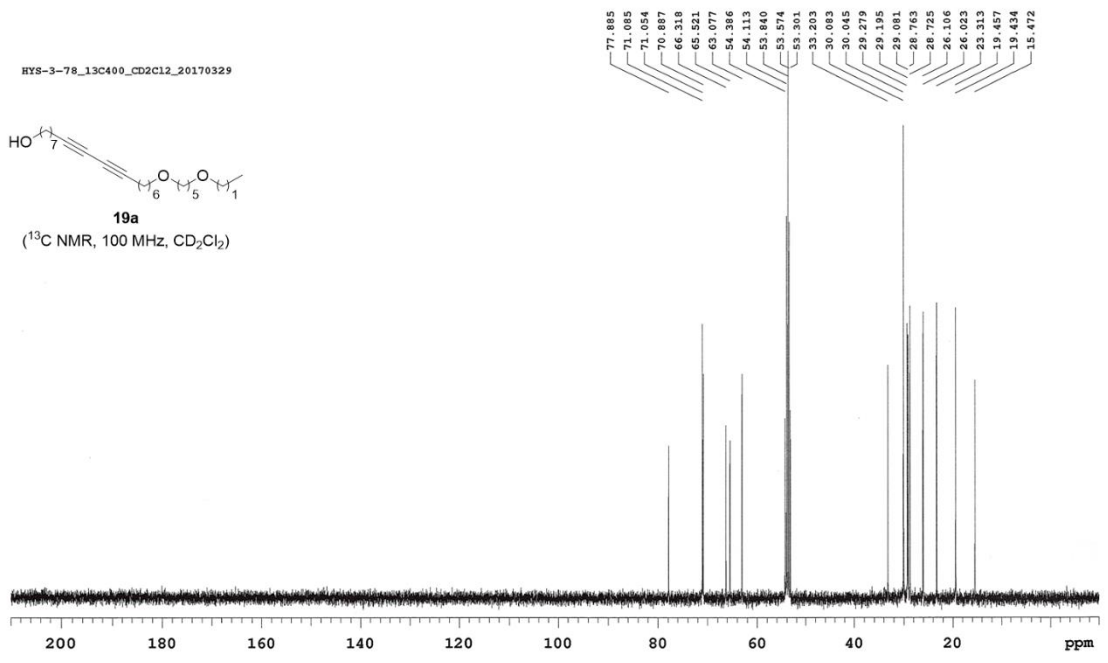

HYS-3-32_1H400_CDCl3_20161217
7.260
4.131
4.125
3.517
3.501
3.484
3.406
3.389
3.372
3.355
3.338
2.415
2.409
2.404
1.628
1.610
1.602
1.592
1.585
1.575
1.557
1.539
1.524
1.296
1.252
0.931
0.912
0.893
0.004
18h
(1H NMR, 400 MHz, CDCl3)
12
10
8
6
4
2
0
ppm
1.84
4.01
1.94
0.73
6.13
3.00
10.59


HYS-3-32_13C400_CDCl3_20161217
80.204
77.471
77.160
76.841
74.162
72.697
71.050
70.443
58.147
29.920
29.646
29.570
29.502
26.314
26.208
23.081
10.740
18h
(13C NMR, 100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm



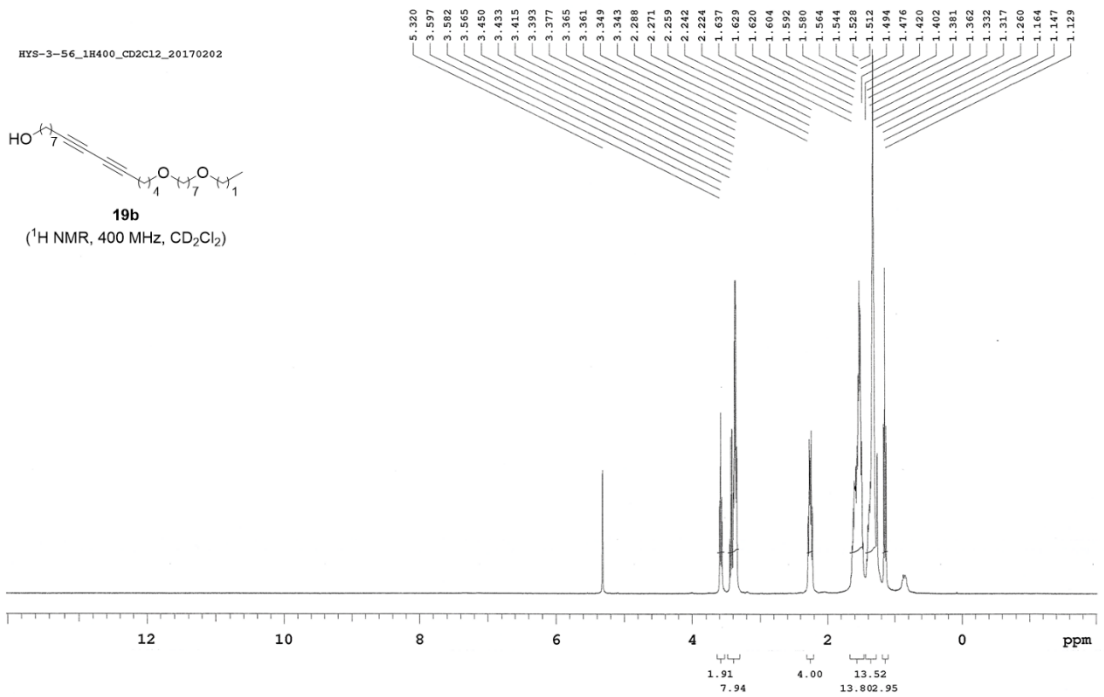
19a

(^{1}H NMR, 400 MHz, CD_2Cl_2)



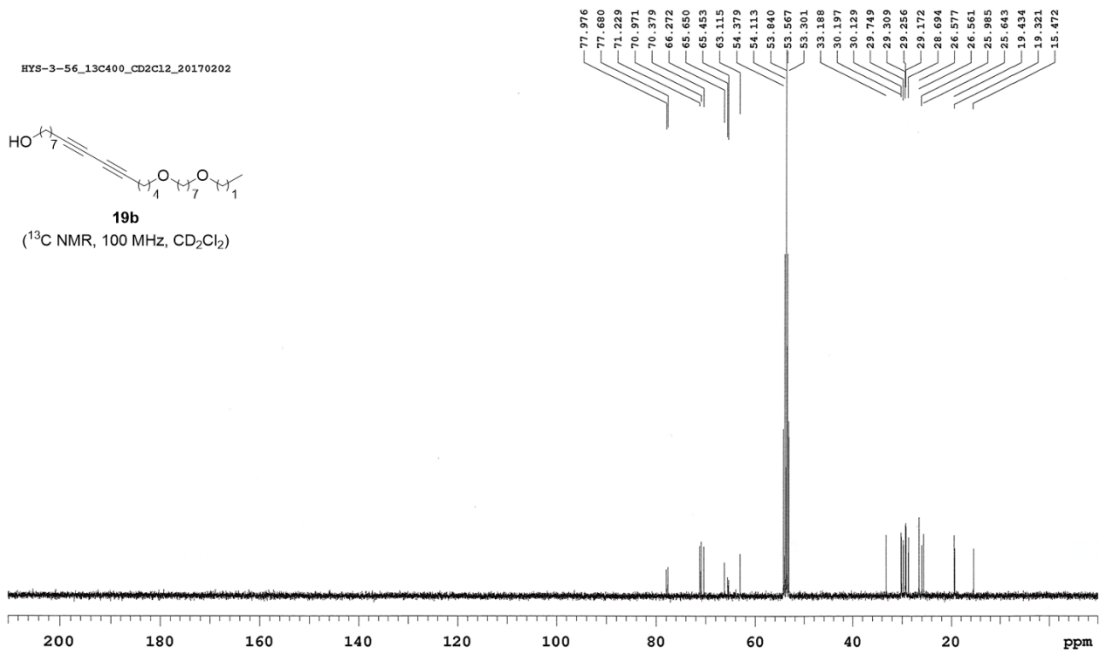
19a

(^{13}C NMR, 100 MHz, CD_2Cl_2)



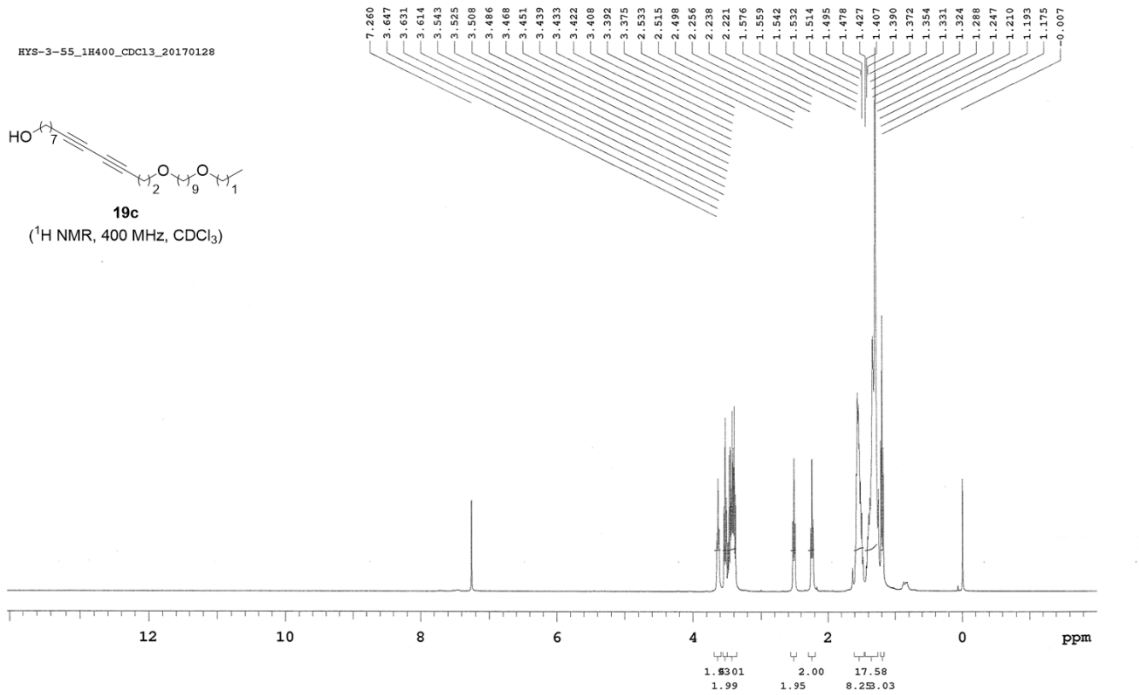
19b

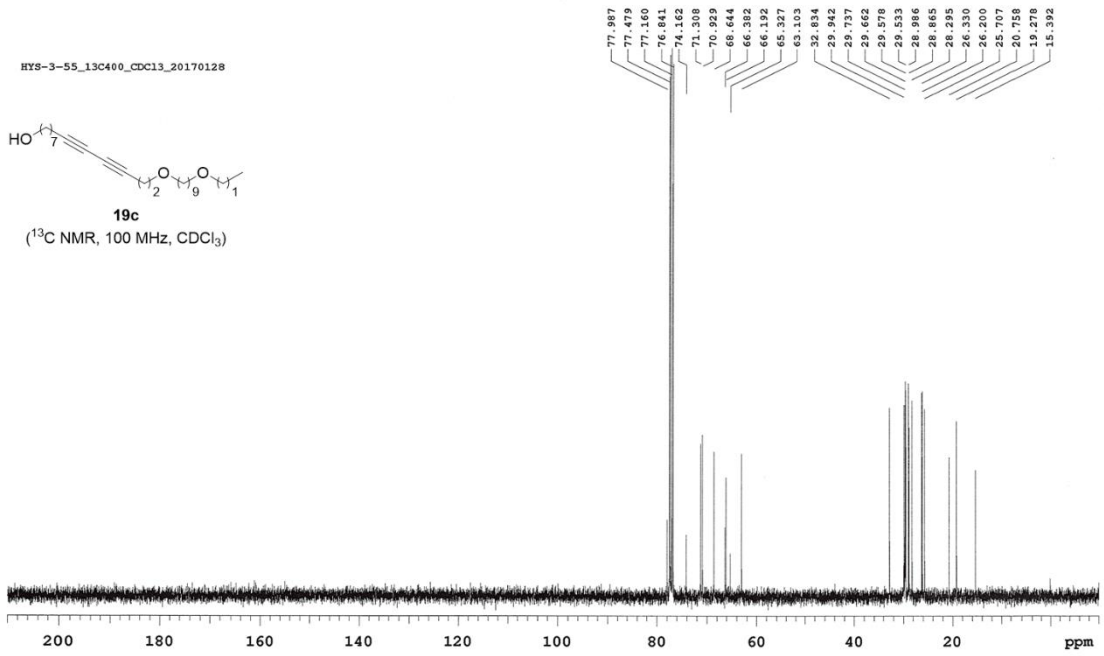
(^{1}H NMR, 400 MHz, CD_2Cl_2)



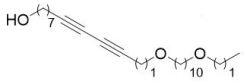
19b

(^{13}C NMR, 100 MHz, CD_2Cl_2)


HYS-3-55_1H400_CDCl3_20170128
HO
7
2
9
1
19c
(1H NMR, 400 MHz, CDCl3)
7.260
3.647
3.631
3.614
3.543
3.525
3.508
3.486
3.468
3.451
3.439
3.433
3.422
3.408
3.392
3.375
2.533
2.515
2.498
2.256
2.238
2.221
1.576
1.559
1.542
1.532
1.514
1.495
1.478
1.427
1.407
1.390
1.372
1.354
1.331
1.324
1.288
1.247
1.210
1.193
1.175
0.007
12
10
8
6
4
2
0
ppm
1.99
2.00
1.95
17.58
8.25
3.03

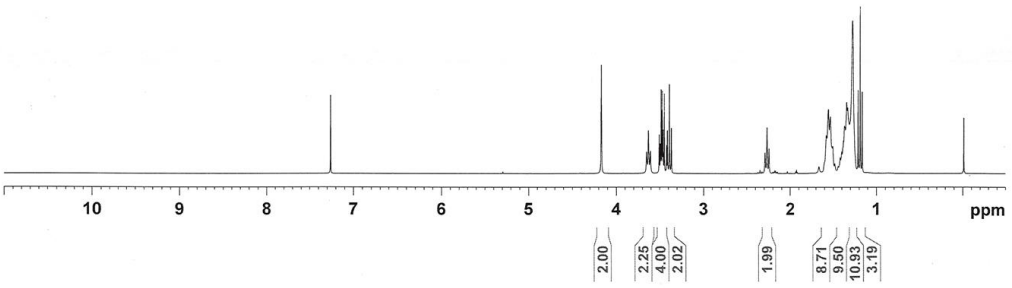

HYS-3-55_13C400_CDCl3_20170128
HO
7
2
9
1
19c
(13C NMR, 100 MHz, CDCl3)
77.987
77.479
77.160
76.841
74.162
71.308
70.929
68.644
66.382
66.192
65.327
63.103
32.834
29.942
29.737
29.662
29.578
29.533
28.986
28.865
28.295
26.330
26.200
25.707
20.758
19.278
15.392
200
180
160
140
120
100
80
60
40
20
ppm

SHB_15_69_CDCl3_1H_20161212_300MHz_exp2

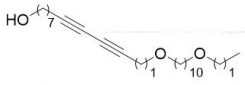


19d

(^{1}H NMR, 300 MHz, $CDCl_3$)

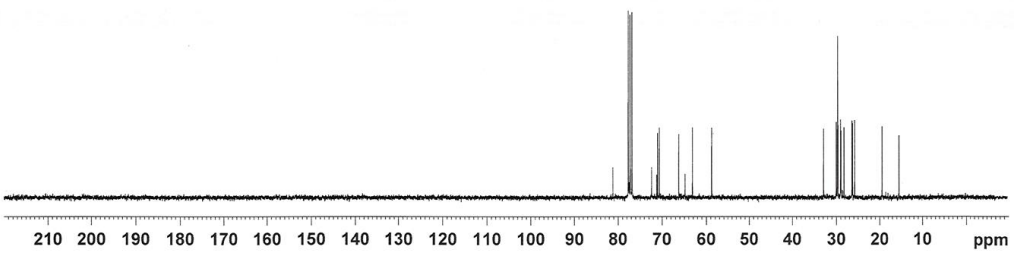


SHB_15_69_CDCl3_13C_20161212_300MHz_exp1

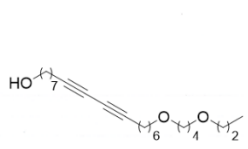


19d

(^{13}C NMR, 75 MHz, $CDCl_3$)



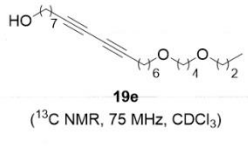
SHB_16_40_CDCl3_1H_20170309_300MHz_exp1



19e

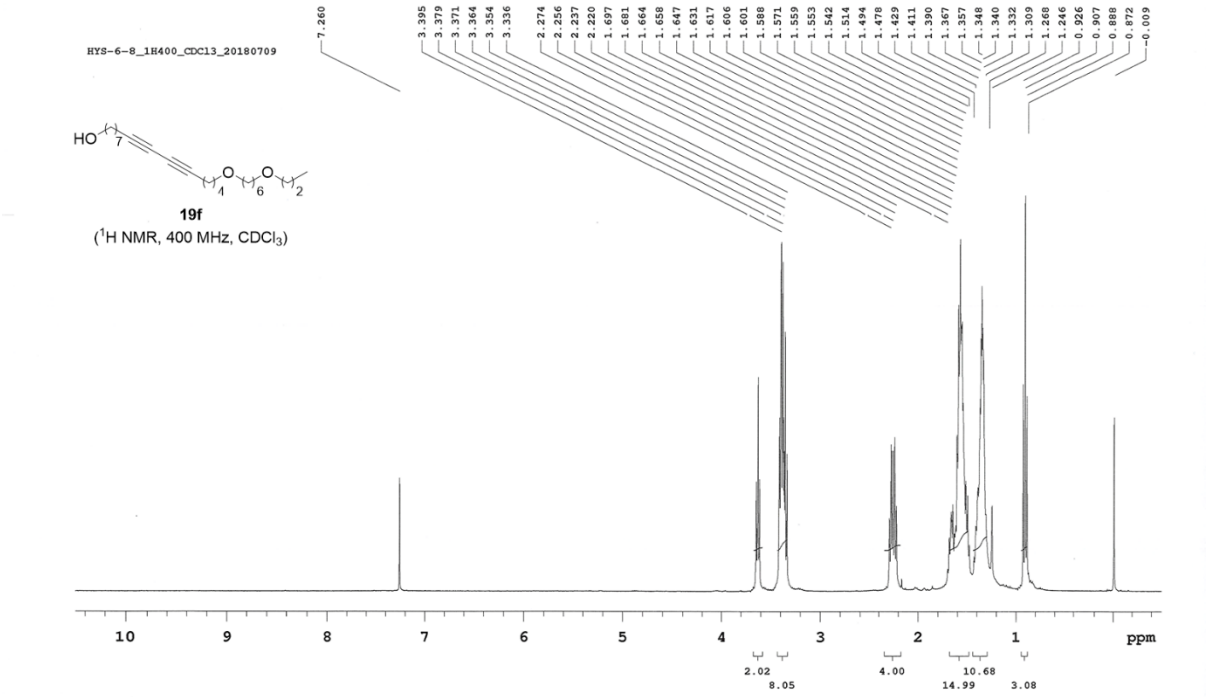
(^{1}H NMR, 300 MHz, $CDCl_3$)

SHB_16_40_CDCl3_13C_20160326_300MHz_exp3



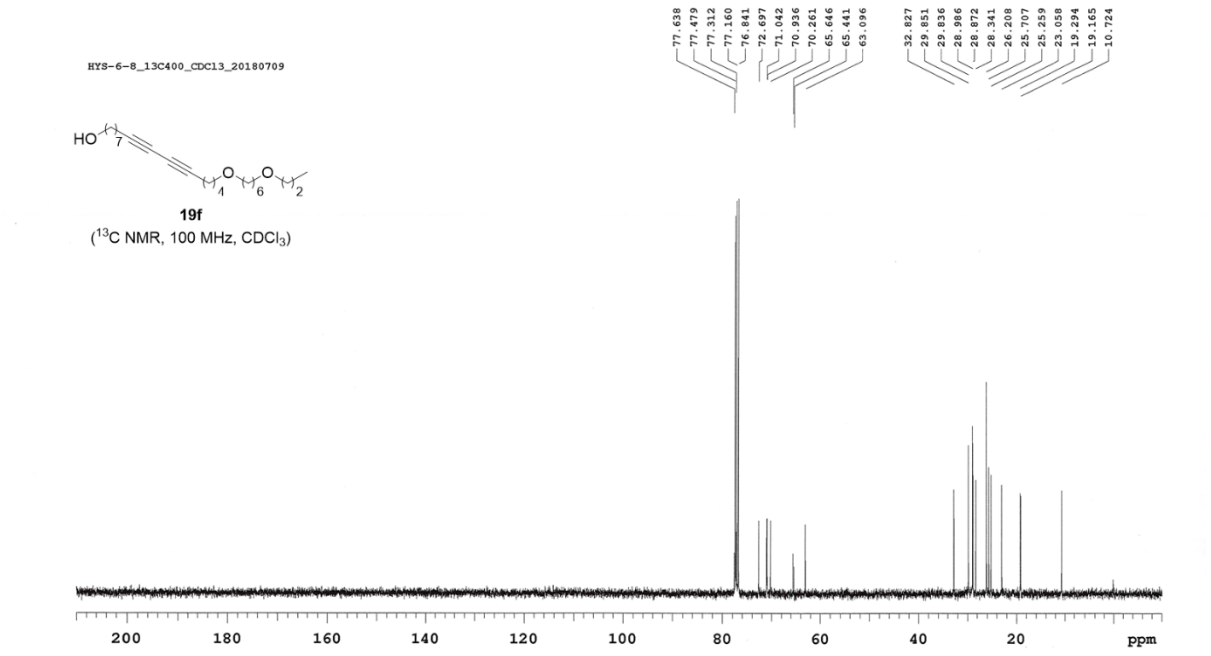
19e

(^{13}C NMR, 75 MHz, $CDCl_3$)



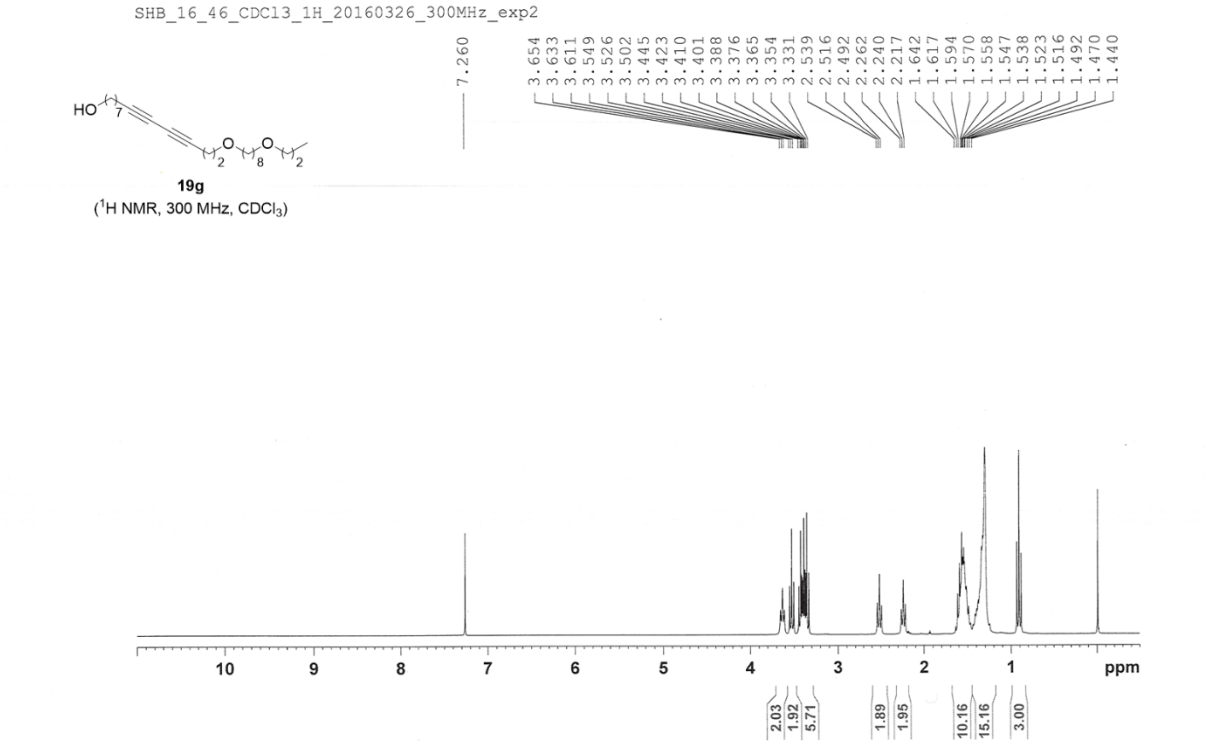
19f

(^{1}H NMR, 400 MHz, $CDCl_3$)



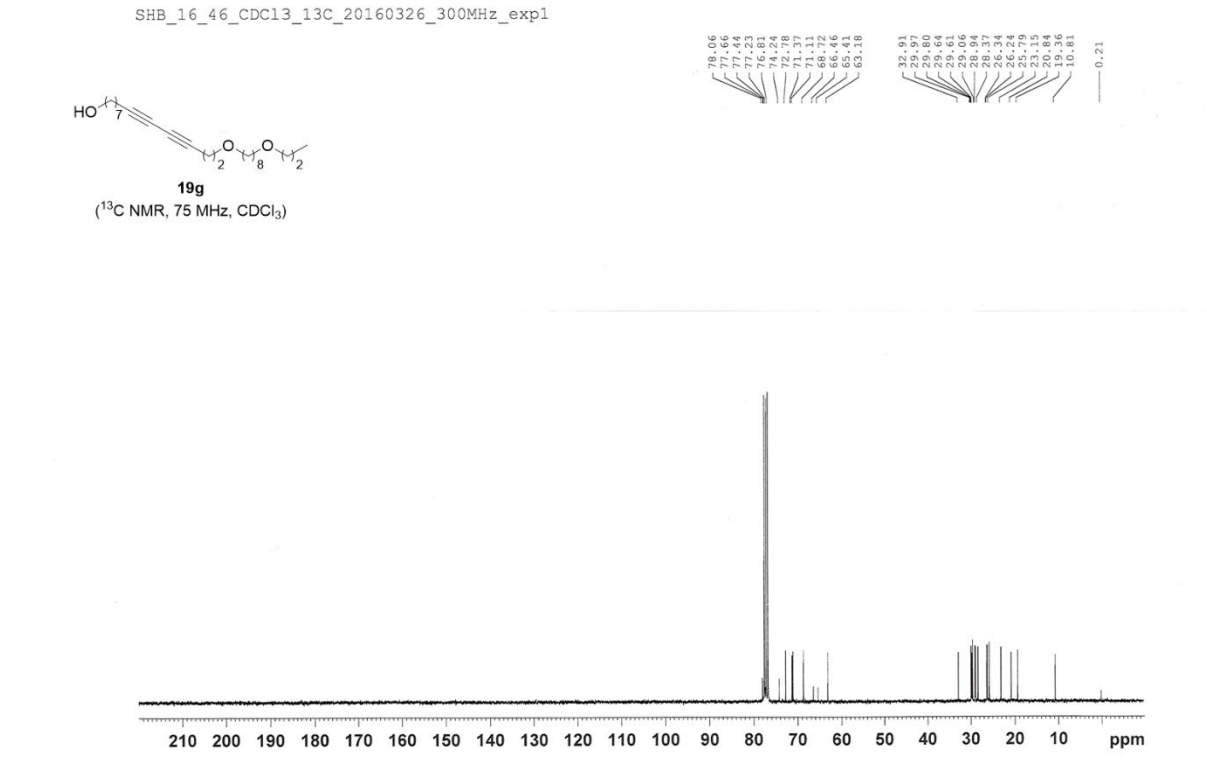
19f

(^{13}C NMR, 100 MHz, $CDCl_3$)



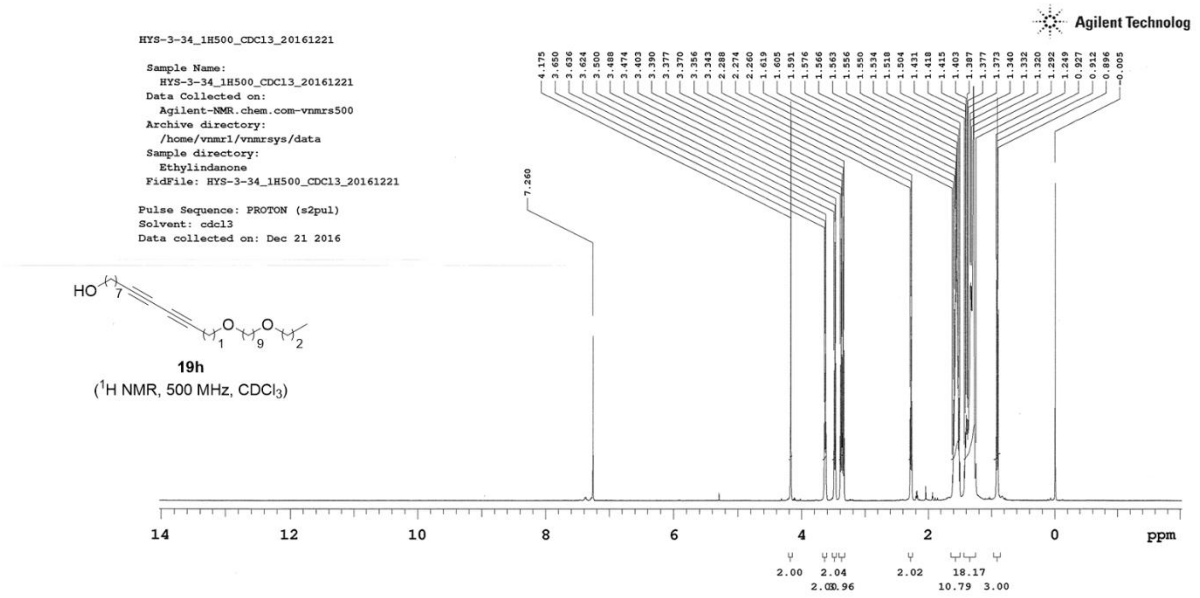
19g

(^{1}H NMR, 300 MHz, $CDCl_3$)



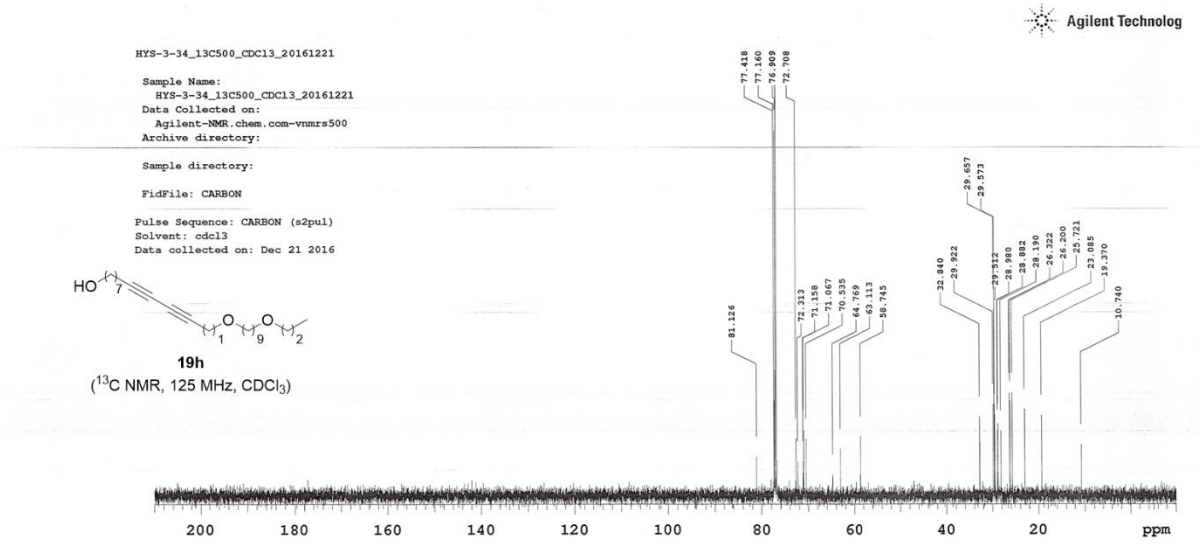
19g

(^{13}C NMR, 75 MHz, $CDCl_3$)



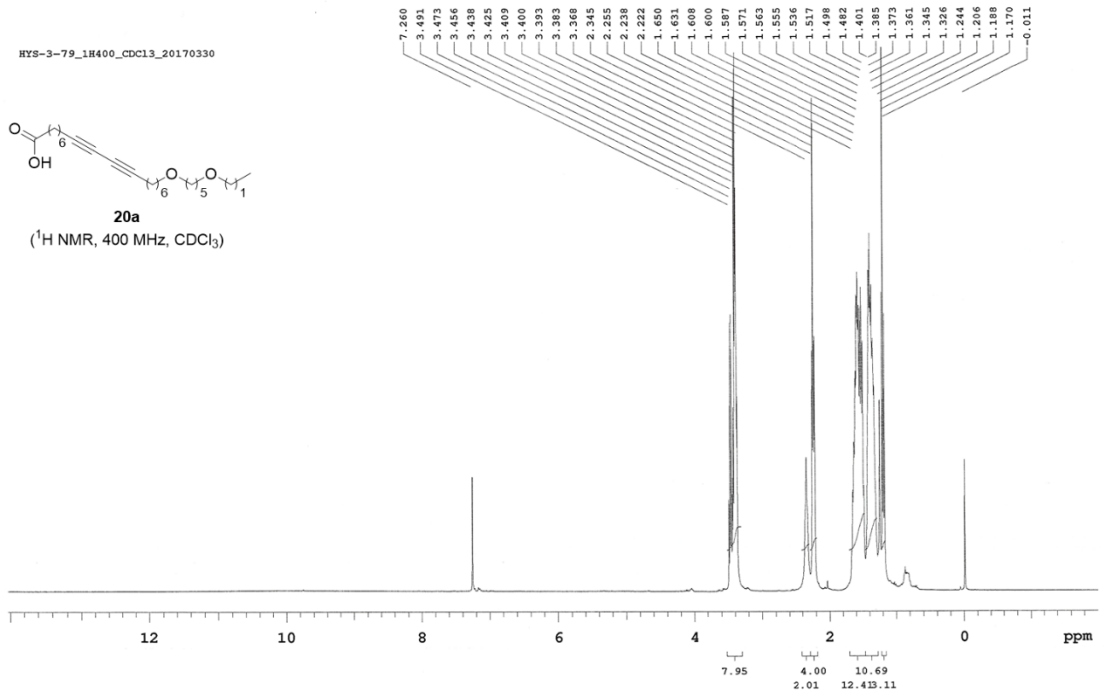
19h

(^{1}H NMR, 500 MHz, $CDCl_3$)



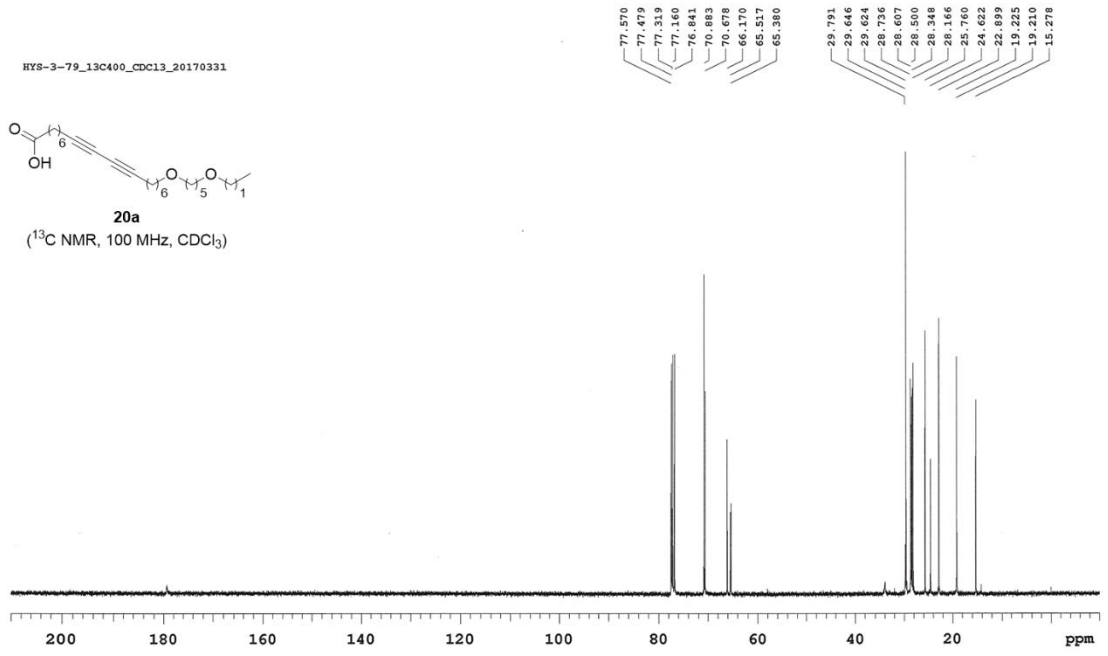
19h

(^{13}C NMR, 125 MHz, $CDCl_3$)



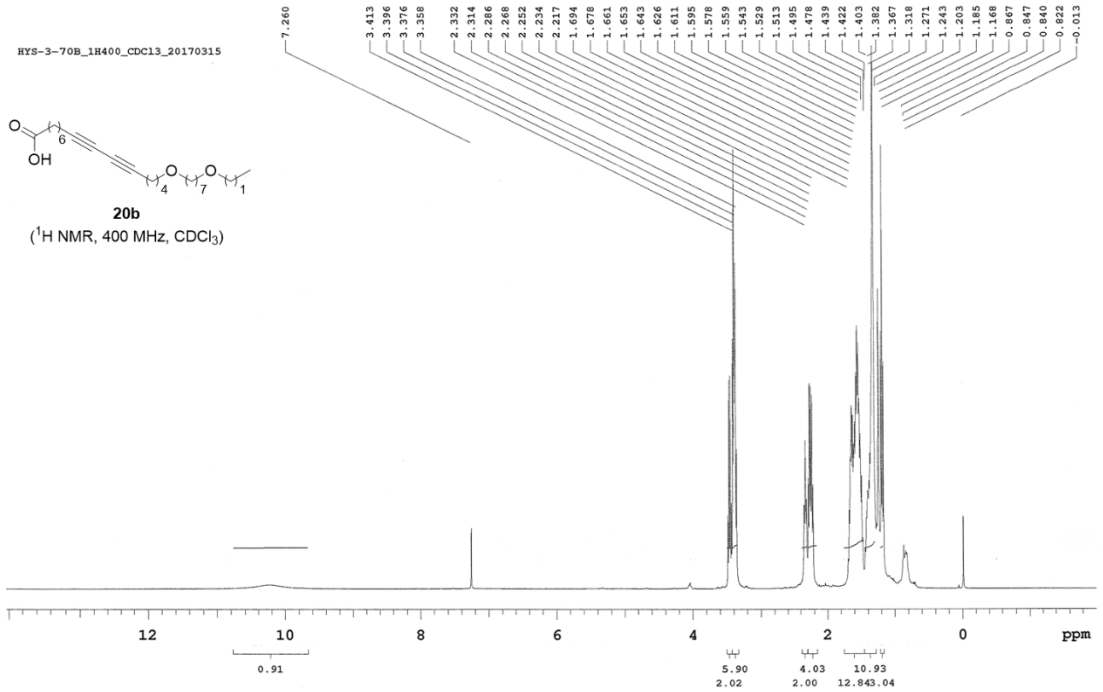
20a

(^{1}H NMR, 400 MHz, $CDCl_3$)



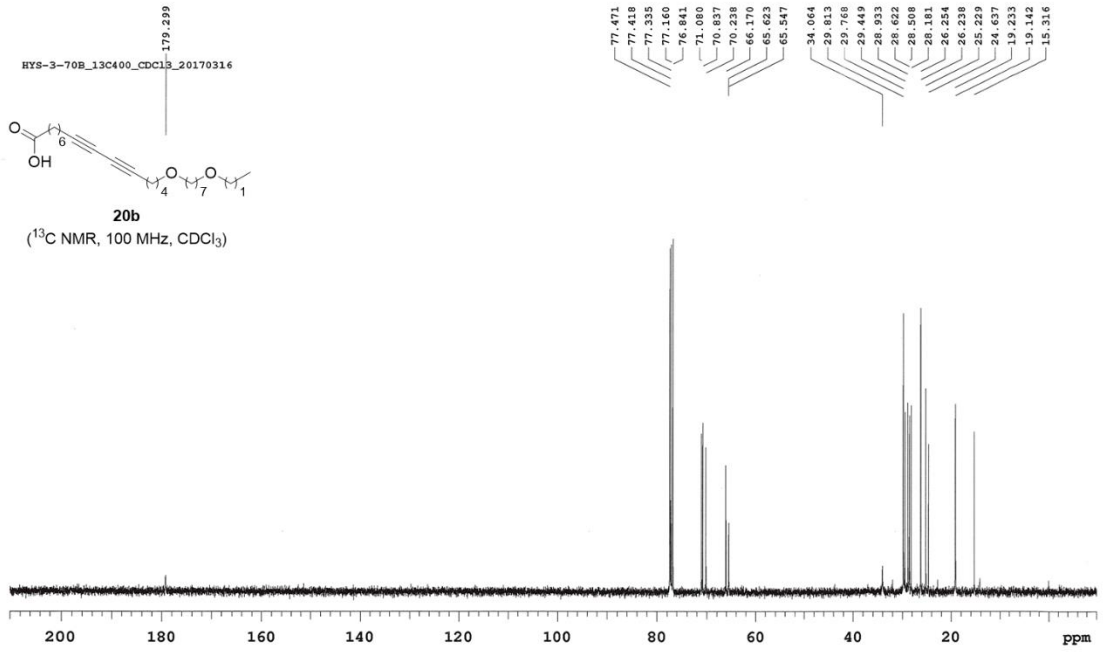
20a

(^{13}C NMR, 100 MHz, $CDCl_3$)



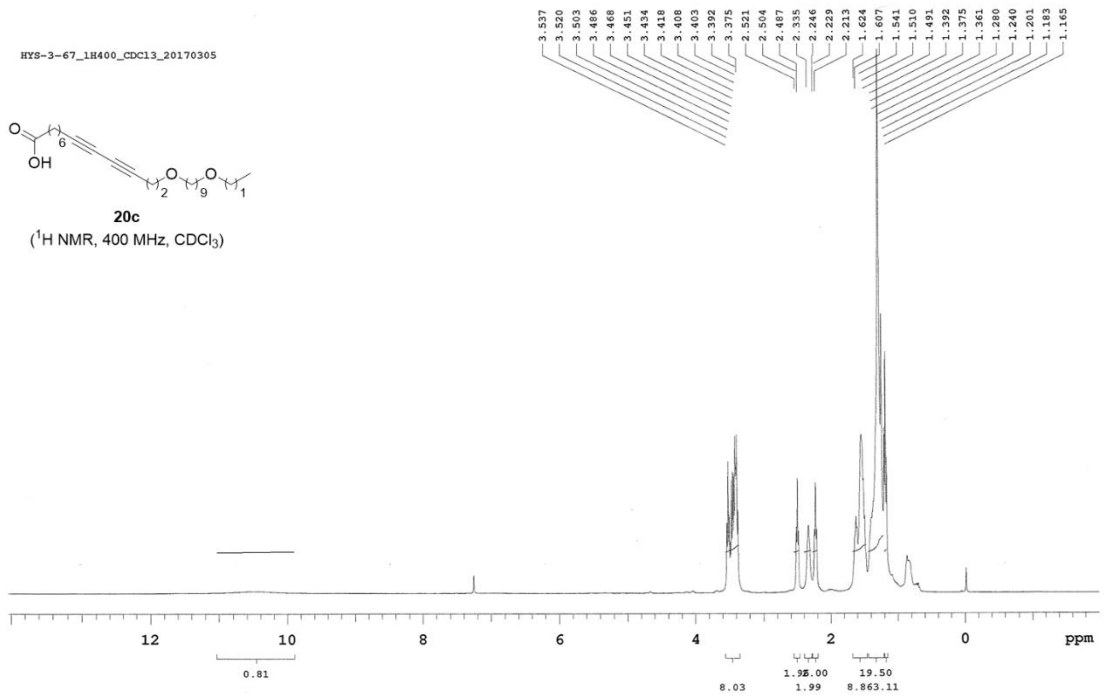
20b

(^{1}H NMR, 400 MHz, $CDCl_3$)



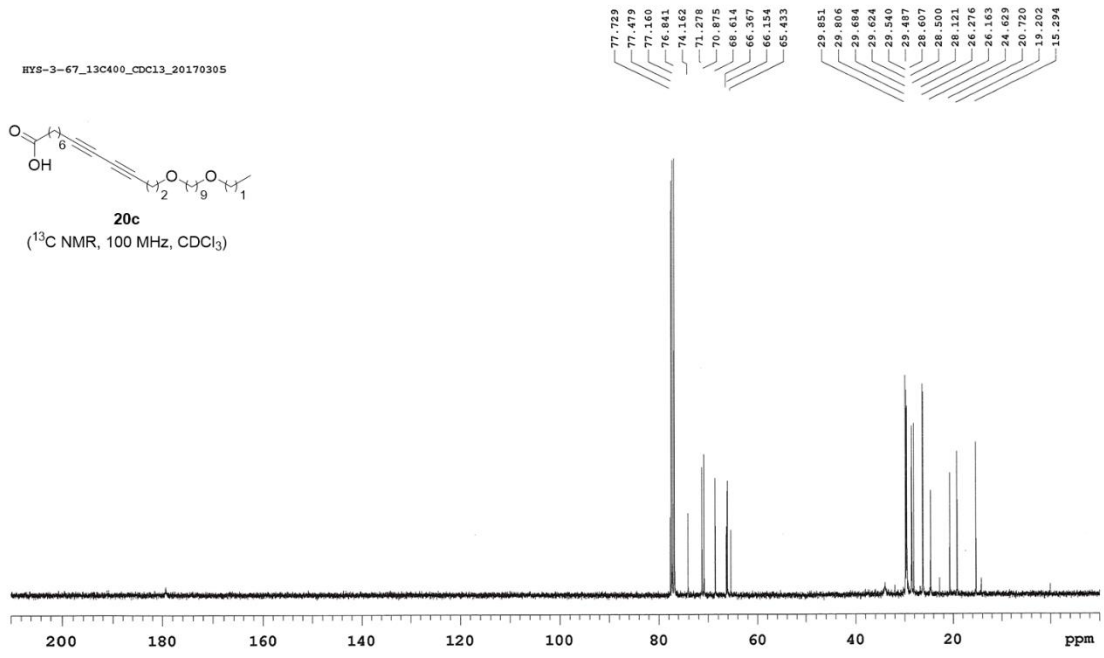
20b

(^{13}C NMR, 100 MHz, $CDCl_3$)



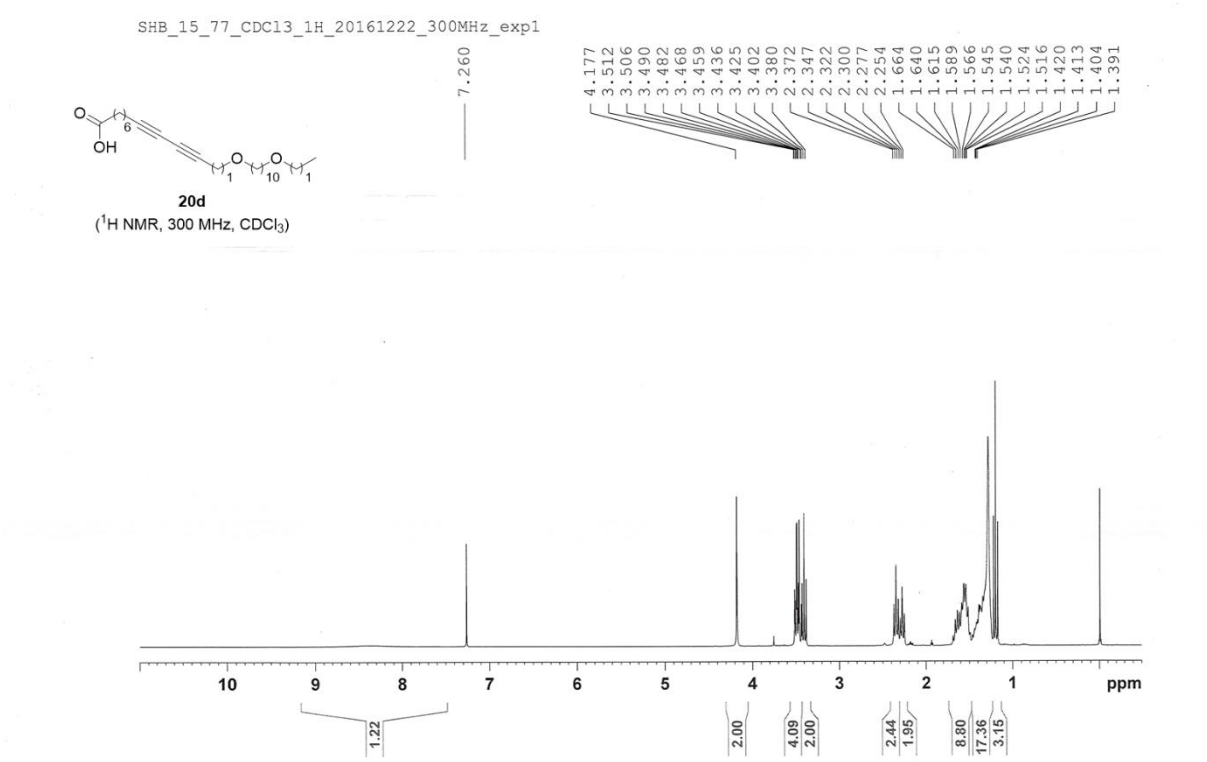
20c

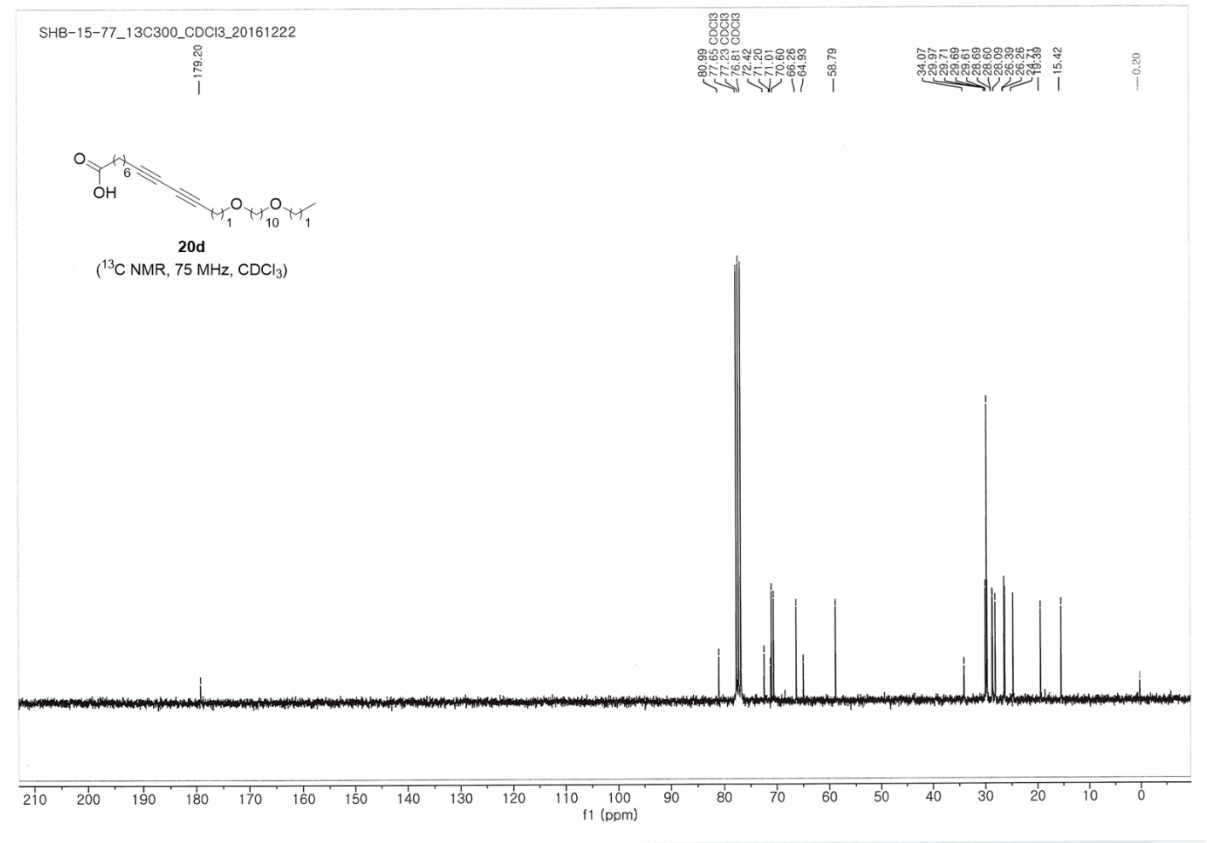
(^{1}H NMR, 400 MHz, $CDCl_3$)

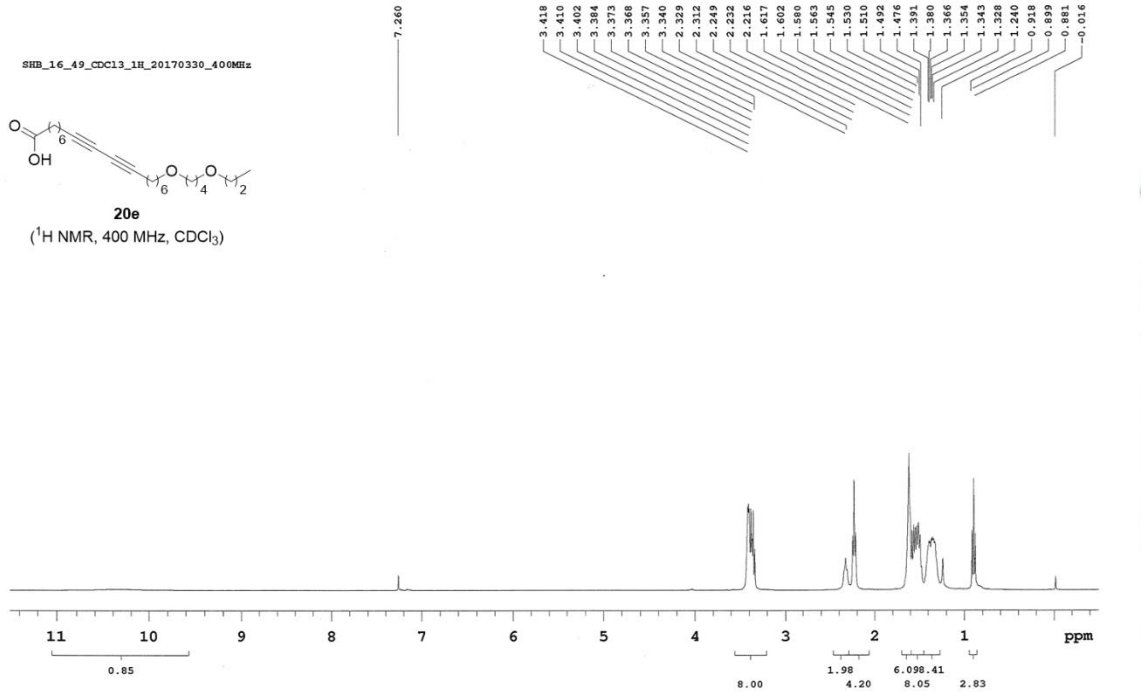


20c

(^{13}C NMR, 100 MHz, $CDCl_3$)

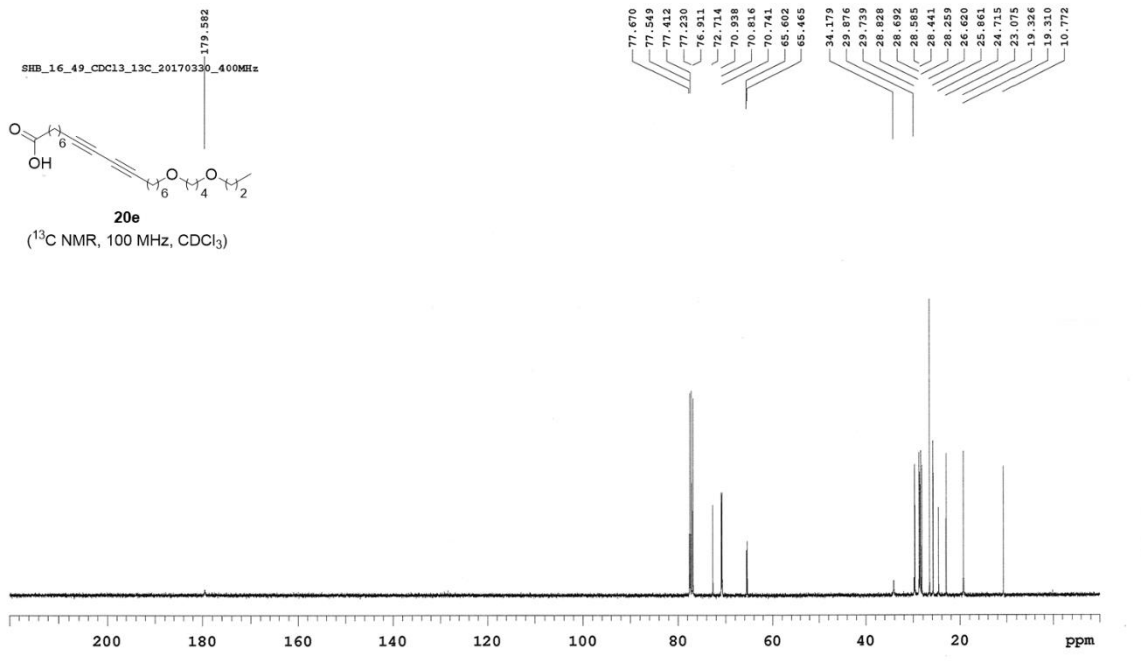

SHB_15_77_CDCl3_1H_20161222_300MHz_exp1
7.260
4.177
3.512
3.506
3.490
3.482
3.468
3.459
3.436
3.425
3.402
3.380
2.372
2.347
2.322
2.300
2.277
2.254
1.664
1.640
1.615
1.589
1.566
1.545
1.540
1.524
1.516
1.420
1.413
1.404
1.391
20d
(1H NMR, 300 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
ppm
1.22
2.00
4.09
2.00
2.44
1.95
8.80
17.36
3.15


SHB-15-77_13C300_CDCl3_20161222
179.20
80.99
77.65 CDCl3
77.23 CDCl3
76.81 CDCl3
72.42
71.26
71.01
70.60
68.86
64.83
58.79
34.07
29.97
29.71
29.69
29.61
28.69
28.60
28.09
26.39
26.26
14.31
14.28
15.42
0.20
20d
(13C NMR, 75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



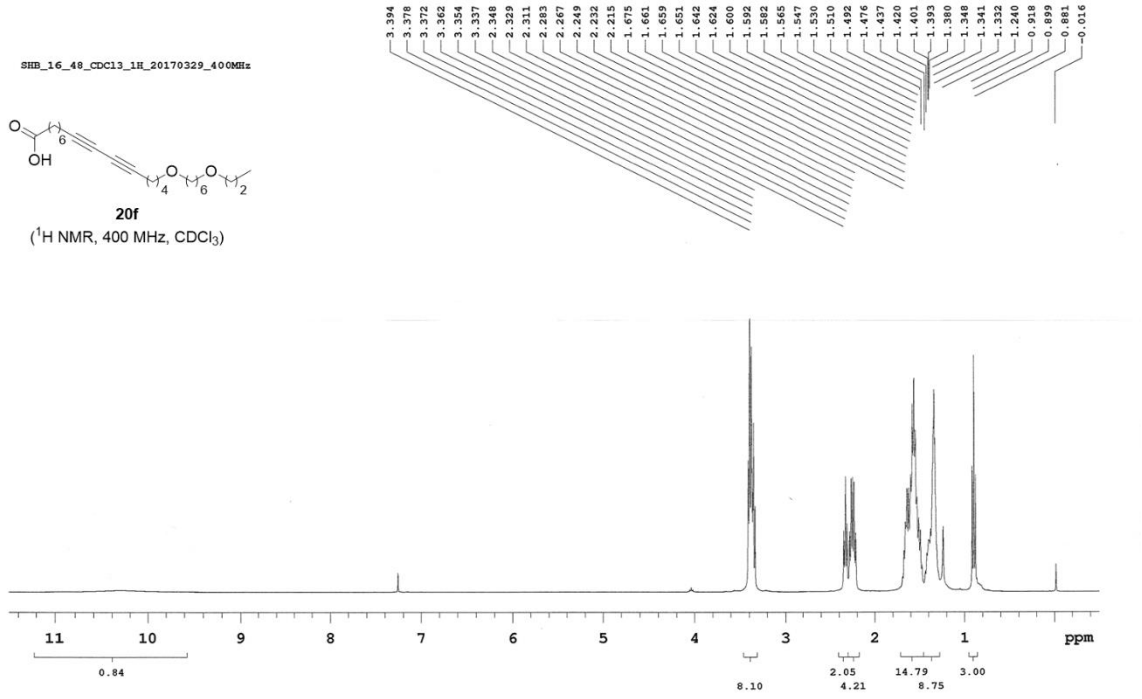
20e

(^{1}H NMR, 400 MHz, $CDCl_3$)



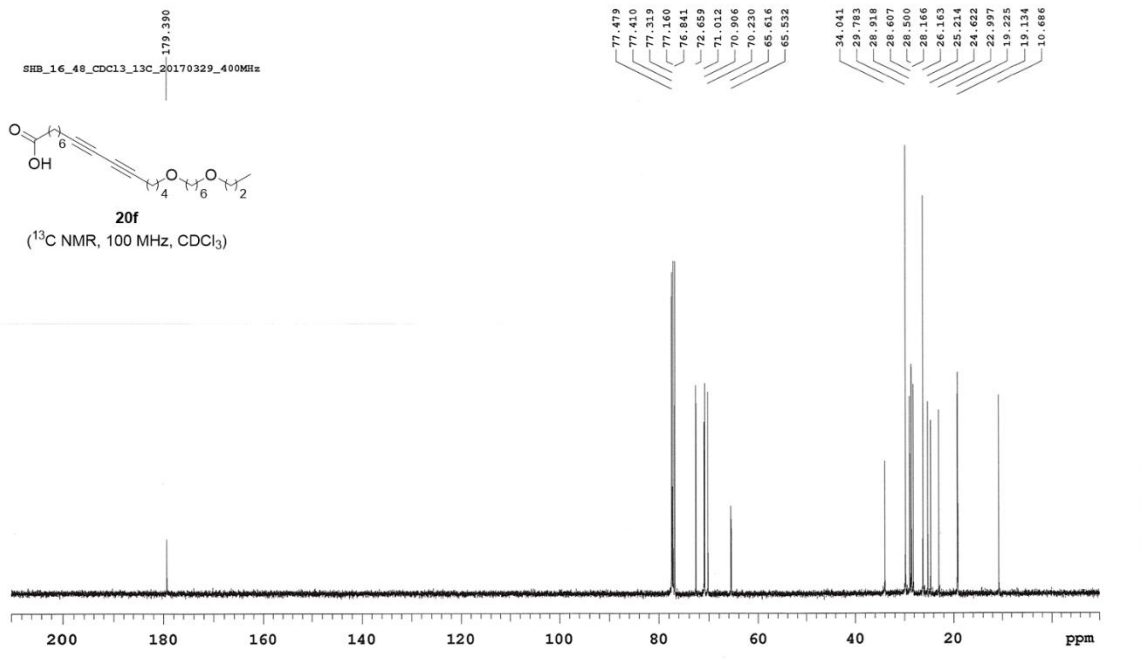
20e

(^{13}C NMR, 100 MHz, $CDCl_3$)



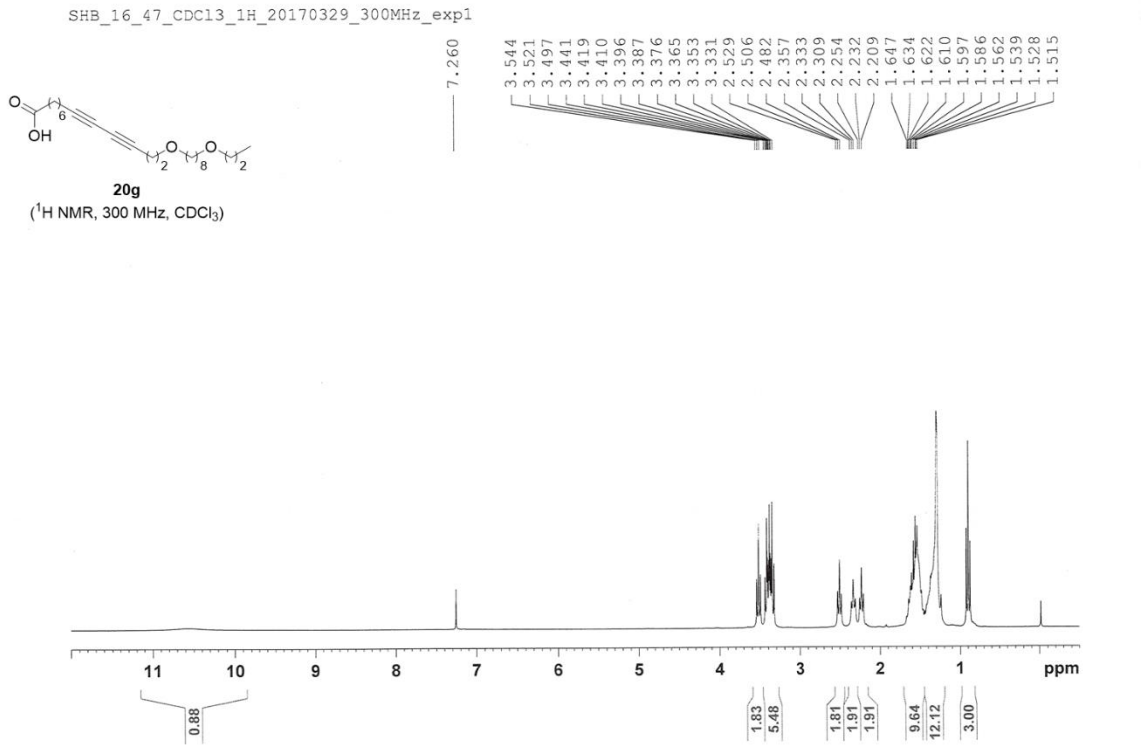
20f

(^{1}H NMR, 400 MHz, $CDCl_3$)



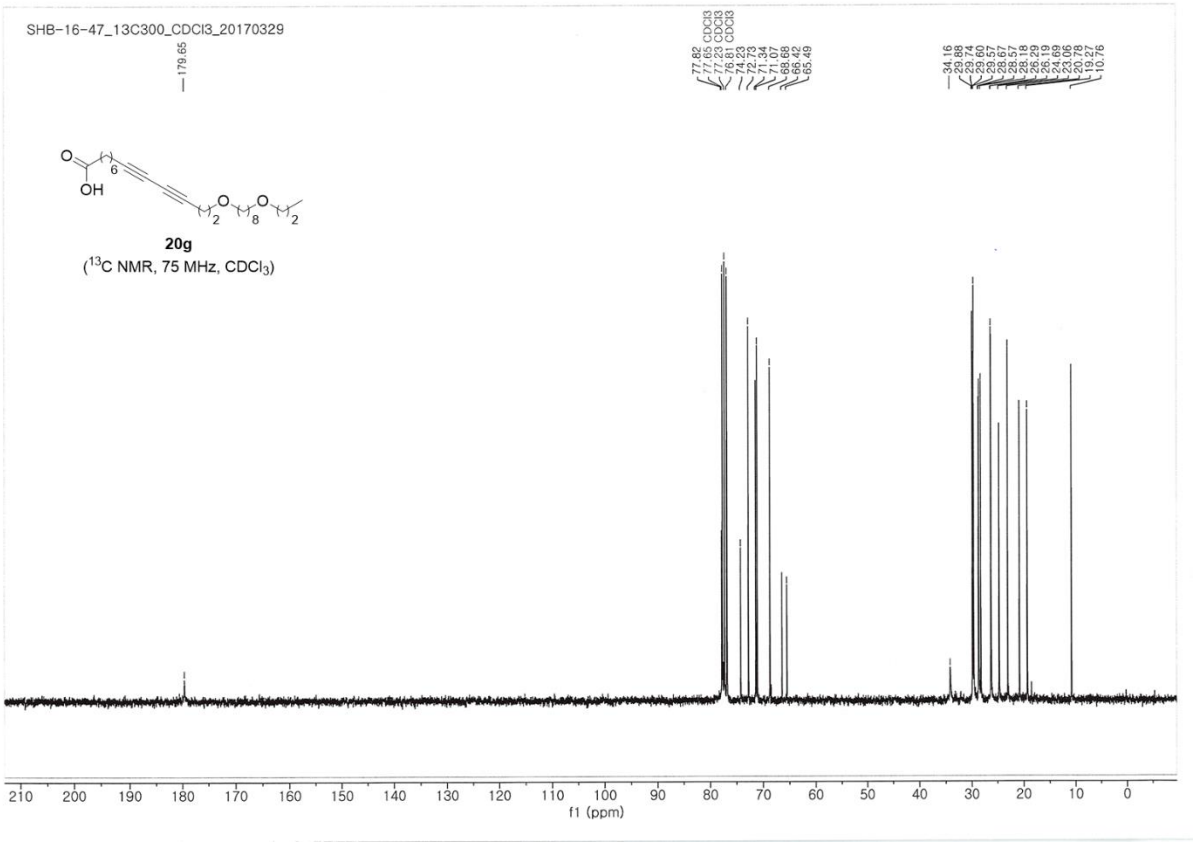
20f

(^{13}C NMR, 100 MHz, $CDCl_3$)



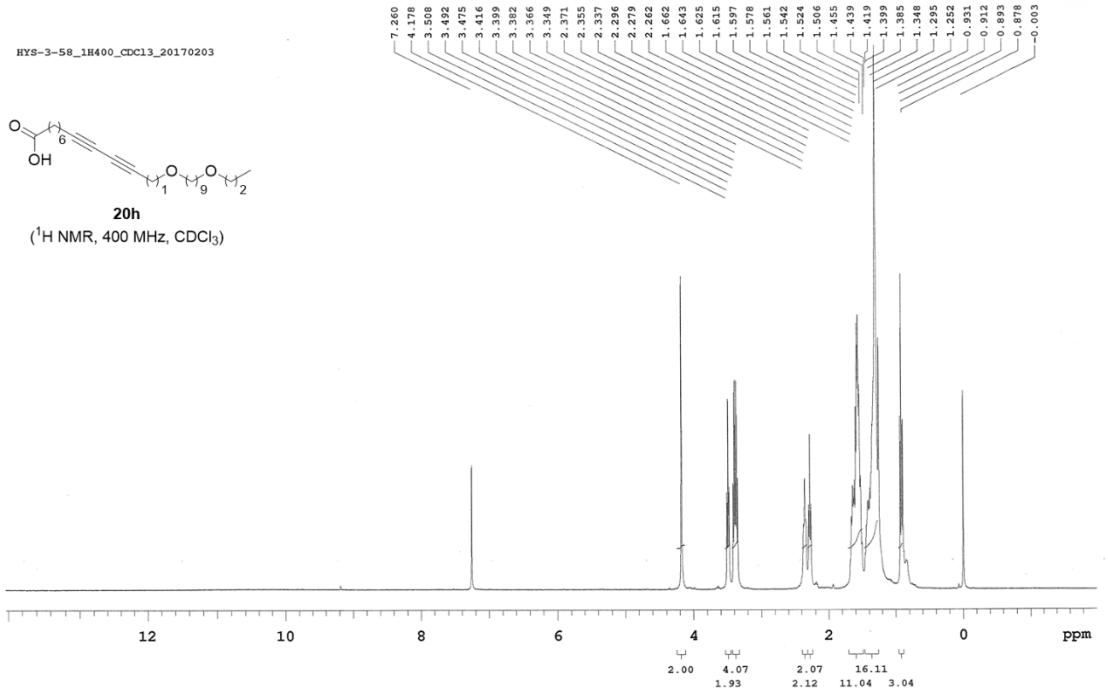
20g

(^{1}H NMR, 300 MHz, $CDCl_3$)



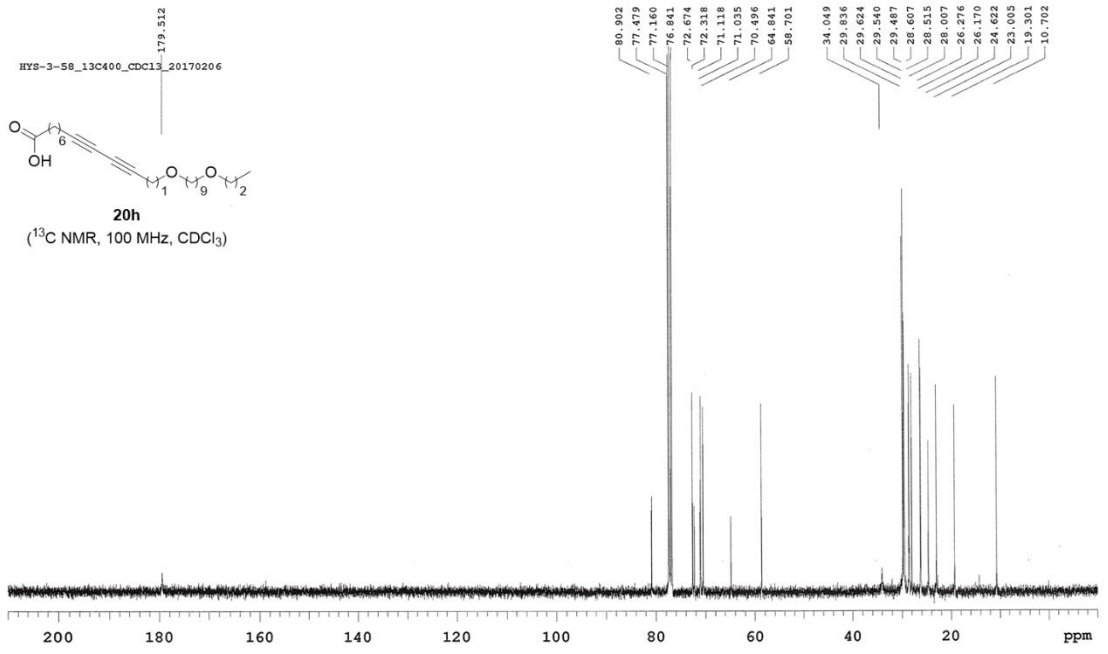
20g

(^{13}C NMR, 75 MHz, $CDCl_3$)



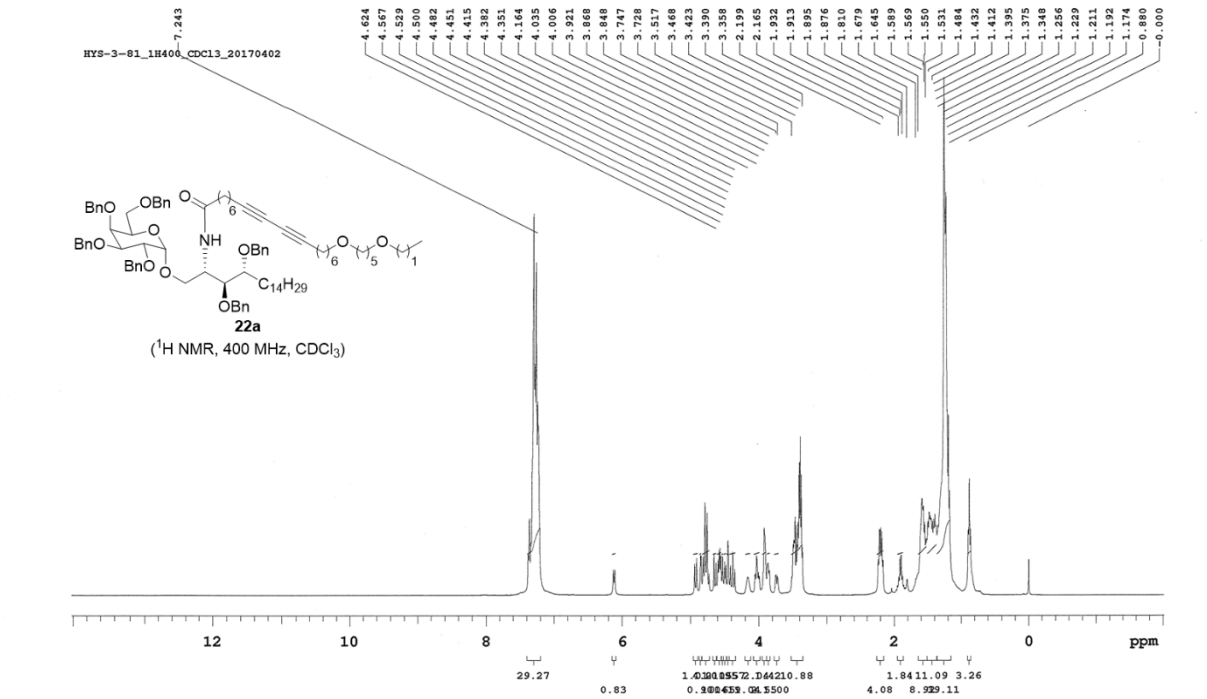
20h

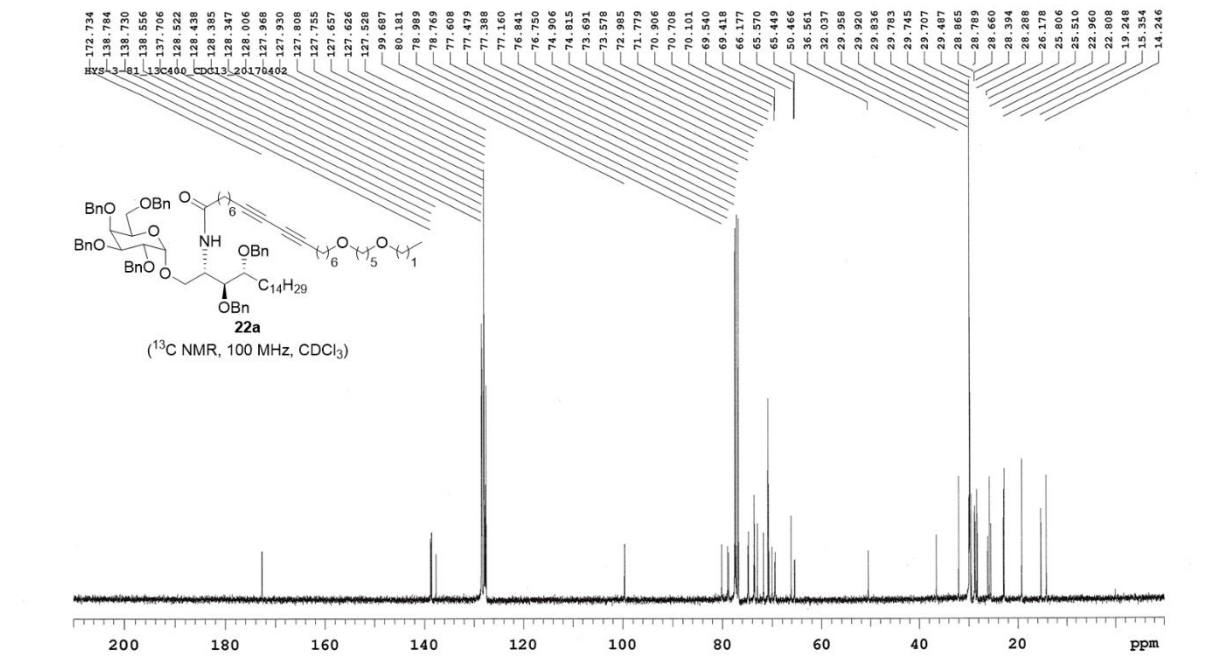
(^{1}H NMR, 400 MHz, $CDCl_3$)

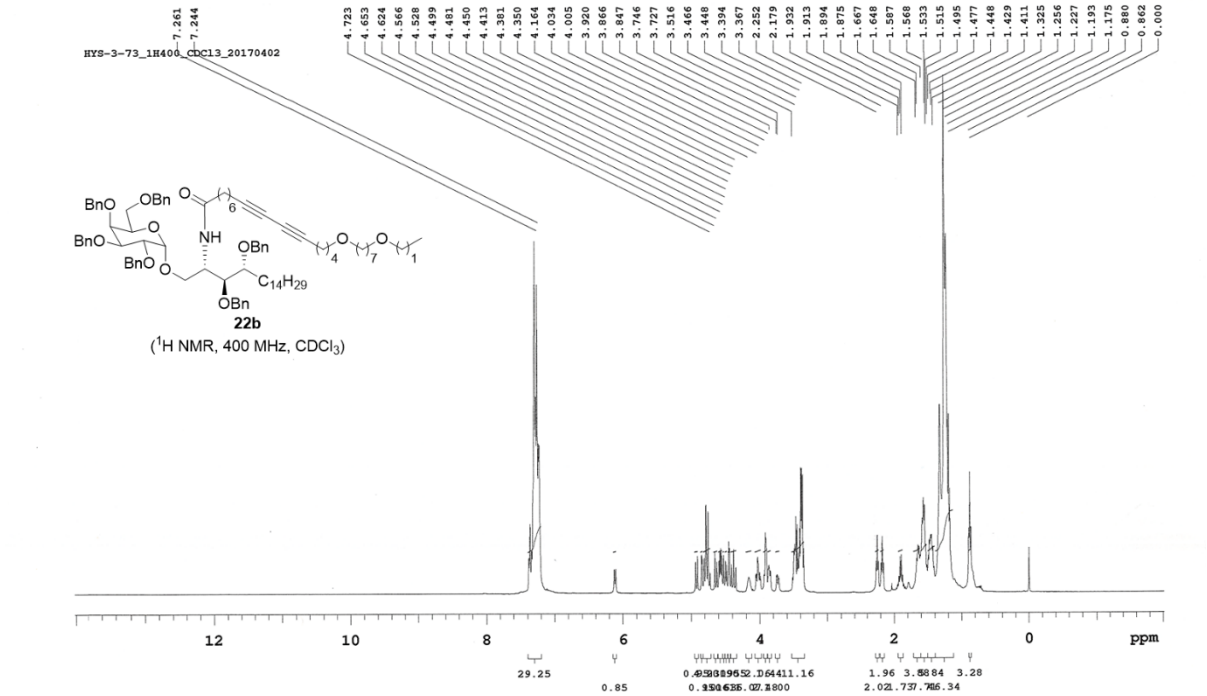


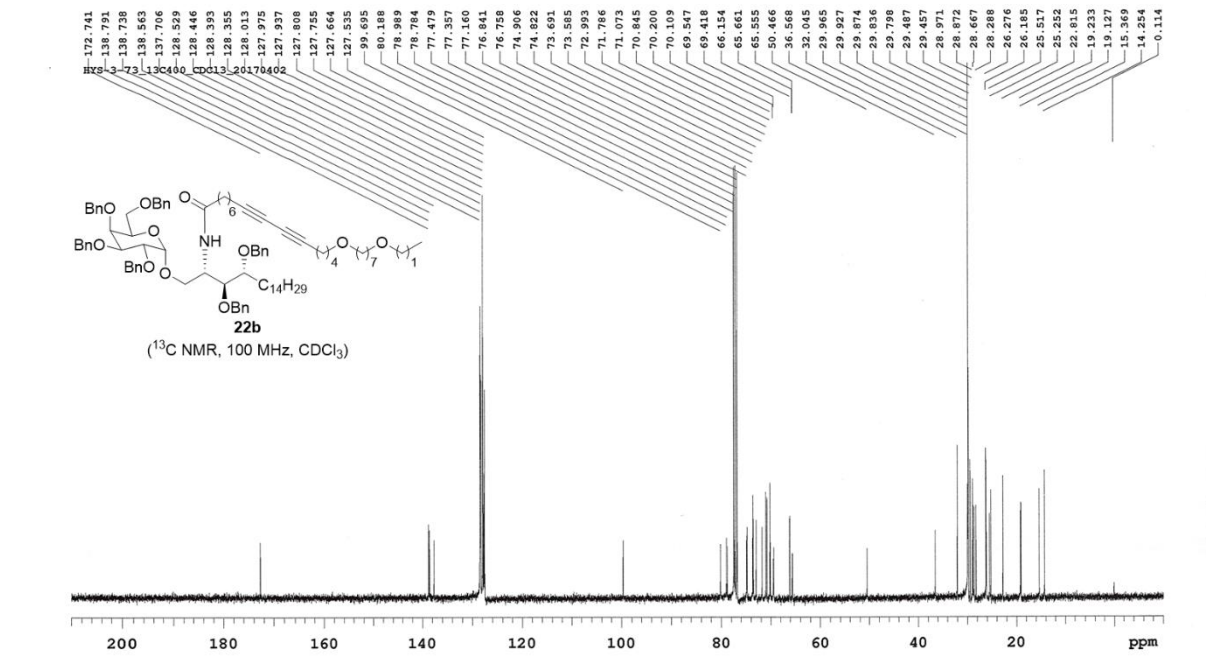
20h

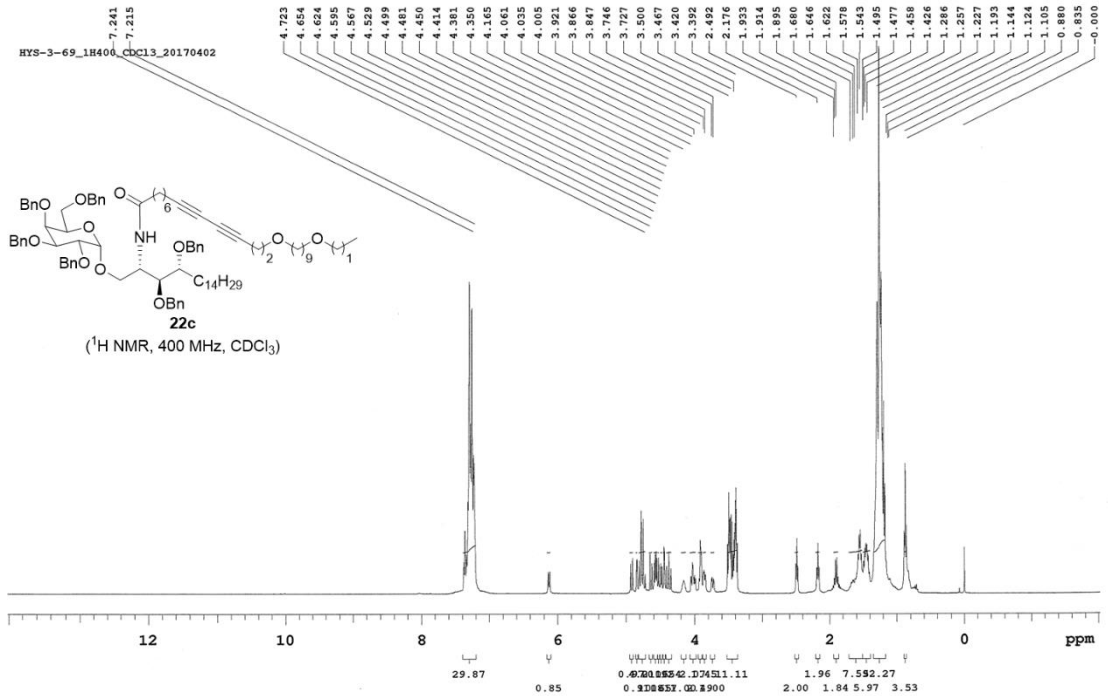
(^{13}C NMR, 100 MHz, $CDCl_3$)

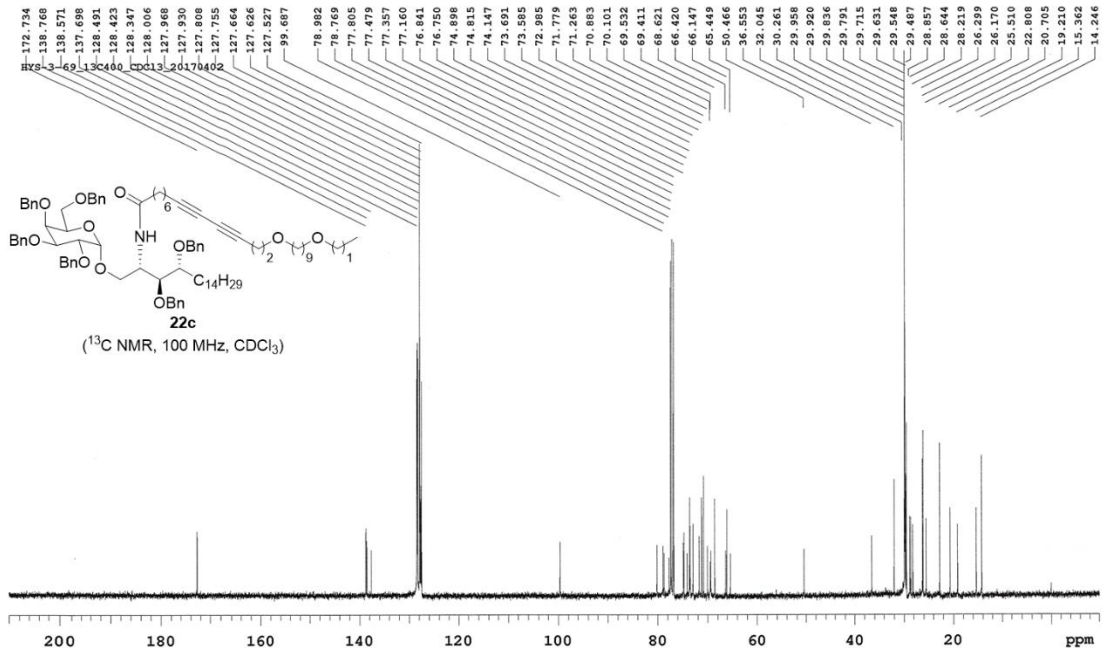

HYS-3-81_1H400_CDCl3_20170402
22a
(1H NMR, 400 MHz, CDCl3)
ppm

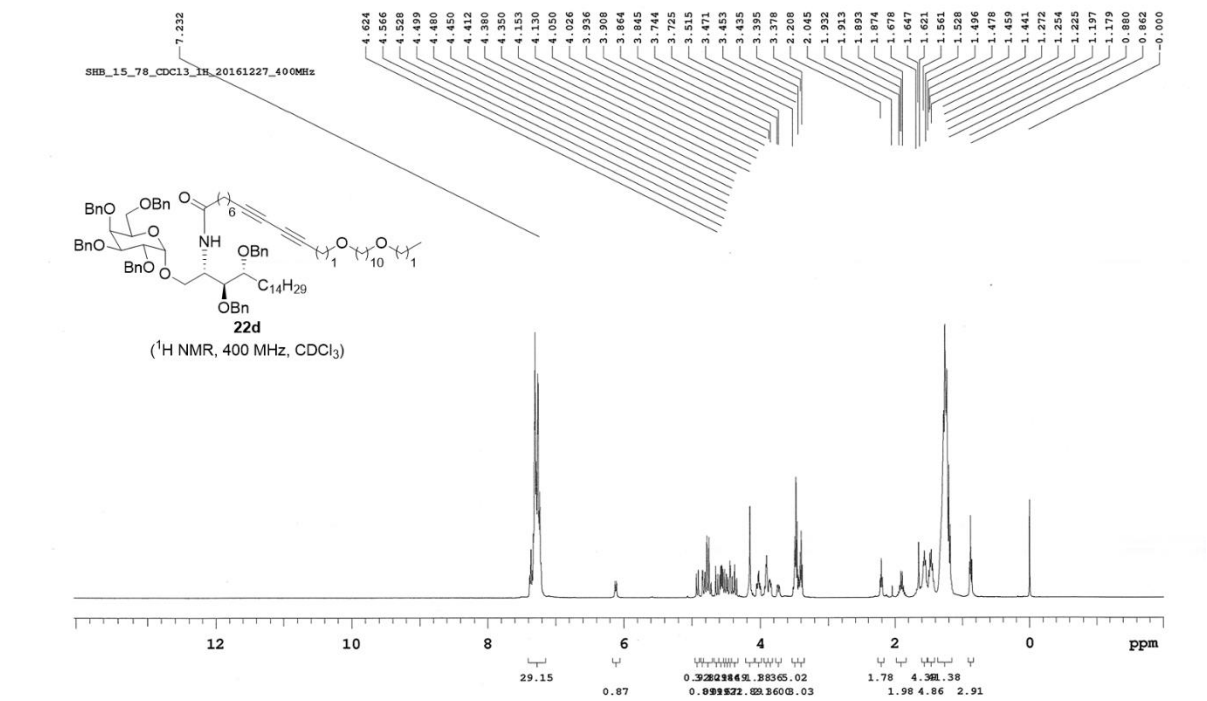

HYS-3-81_13C400_CDCl3_20170402
22a
(13C NMR, 100 MHz, CDCl3)
ppm

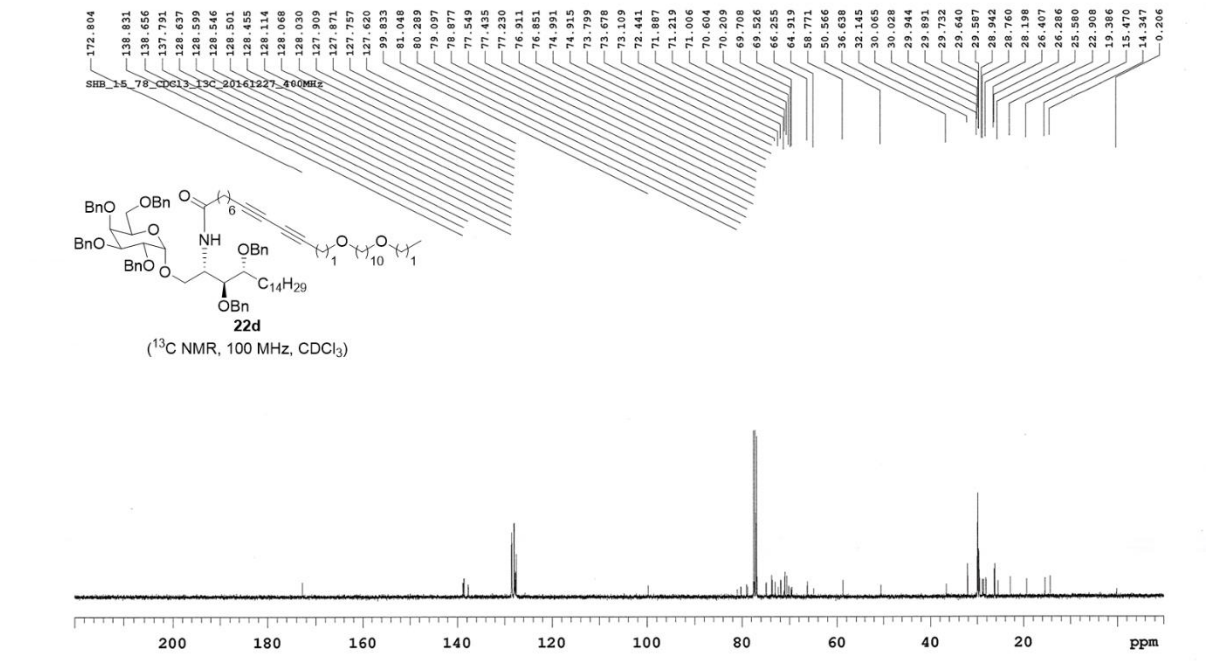

HYS-3-73_1H400_CDCl3_20170402
22b
(1H NMR, 400 MHz, CDCl3)
ppm

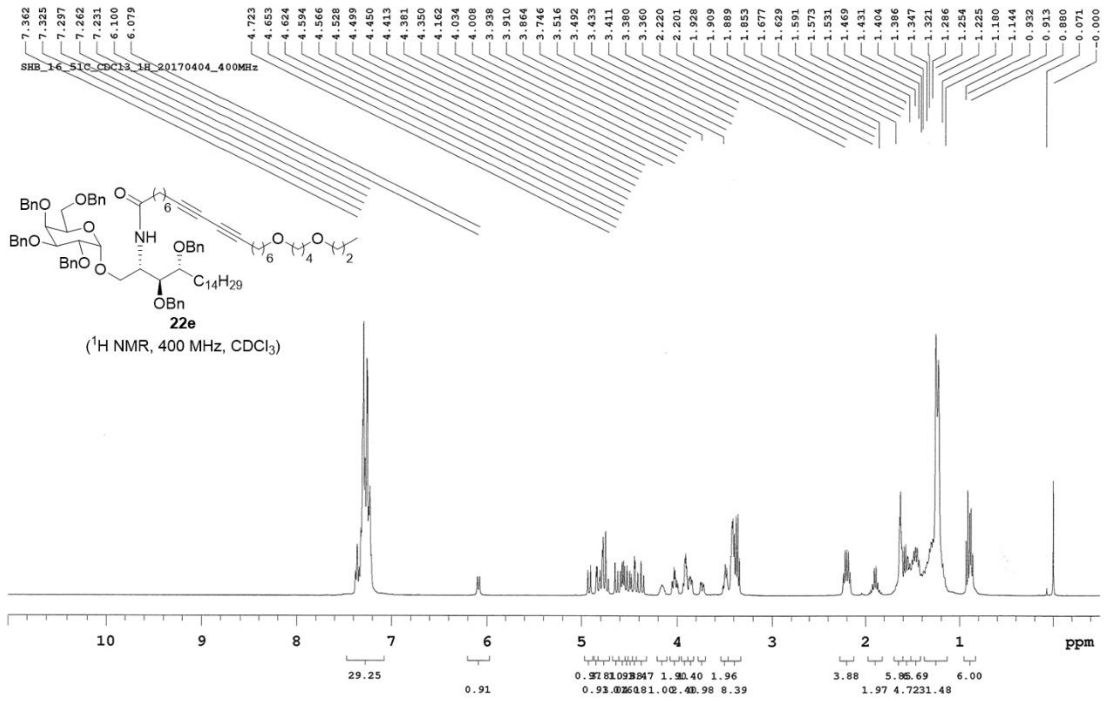

HYS-3-73_13C400_CDCl3_20170402
22b
(13C NMR, 100 MHz, CDCl3)
ppm

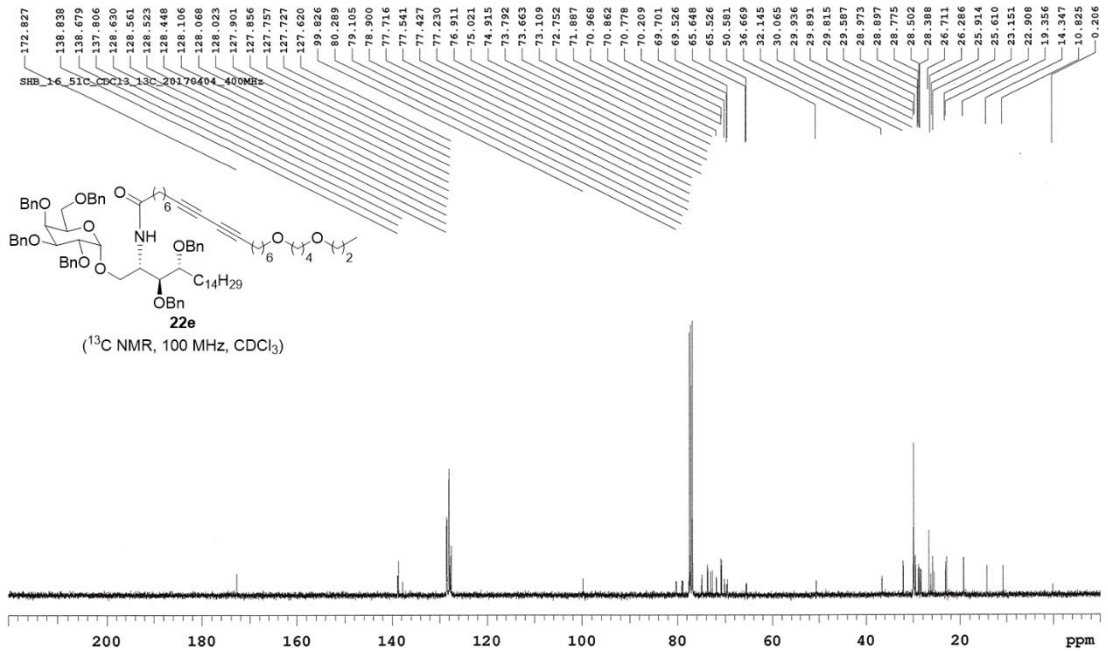

HYS-3-69_1H400_CDCl3_20170402
BnO
OBn
BnO
BnO
O
NH
OBn
C14H29
OBn
22c
(1H NMR, 400 MHz, CDCl3)
12
10
8
6
4
2
0
ppm

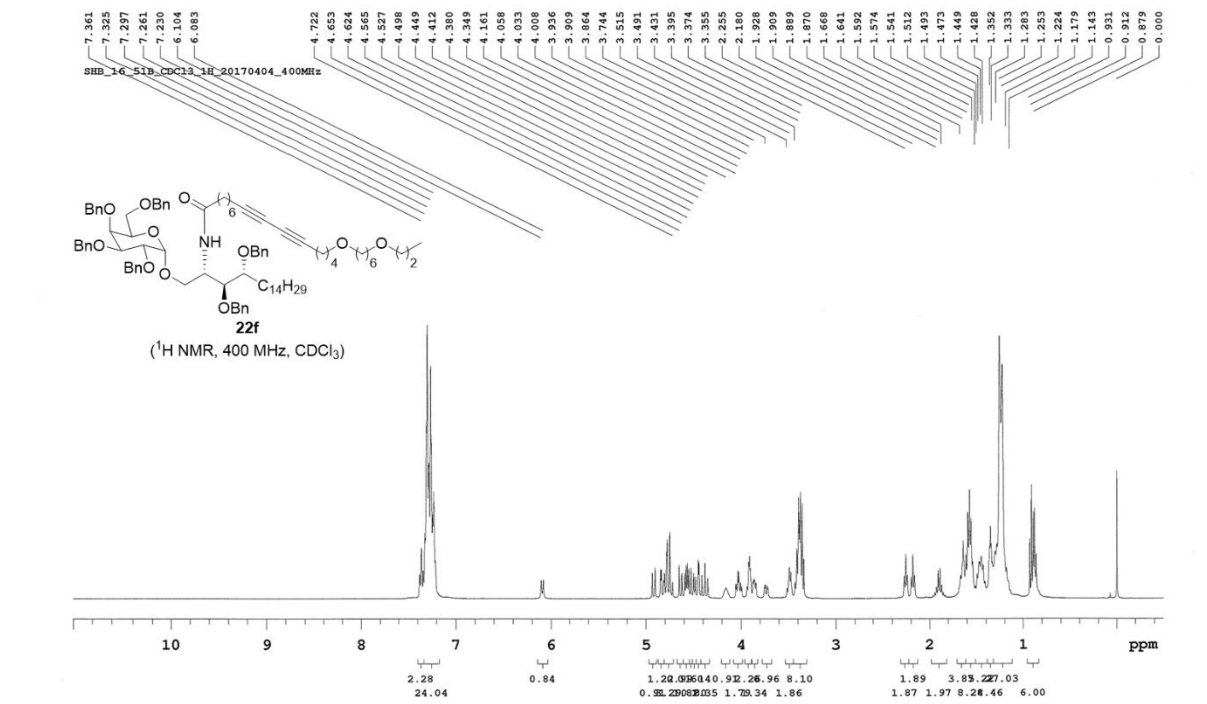

HYS-3-69_13C400_CDCl3_20170402
BnO
OBn
BnO
BnO
O
NH
OBn
C14H29
OBn
22c
(13C NMR, 100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm

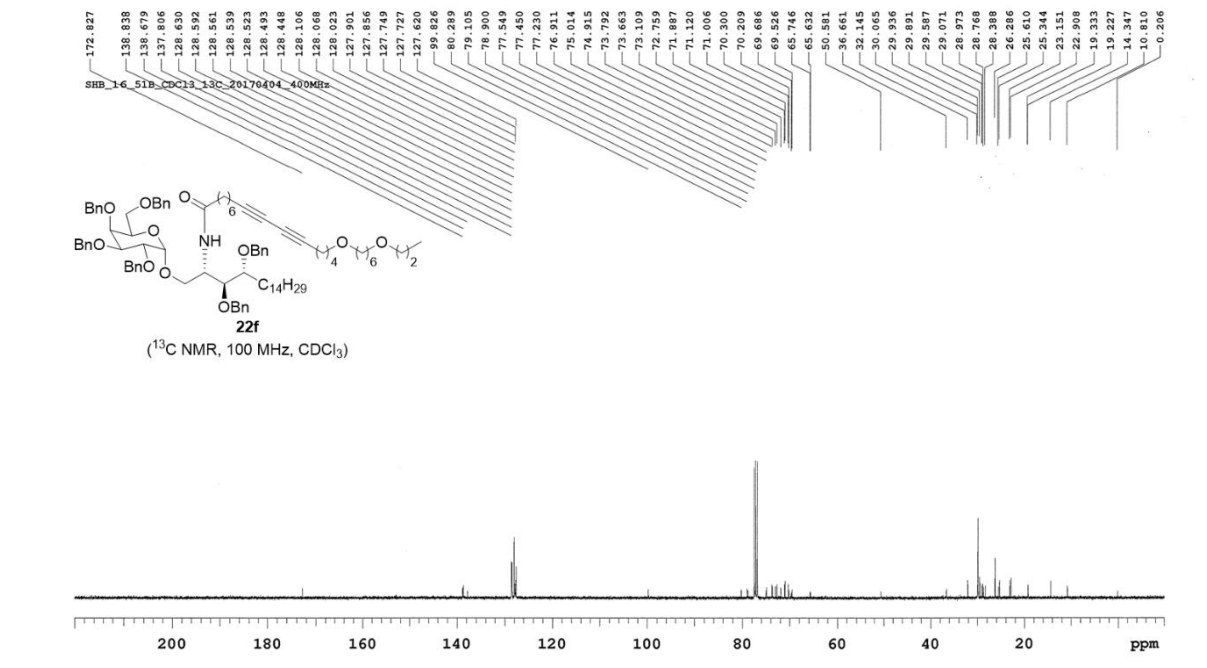

SHB_15_78_CDCl3_1H_20161227_400MHz
22d
(1H NMR, 400 MHz, CDCl3)
ppm

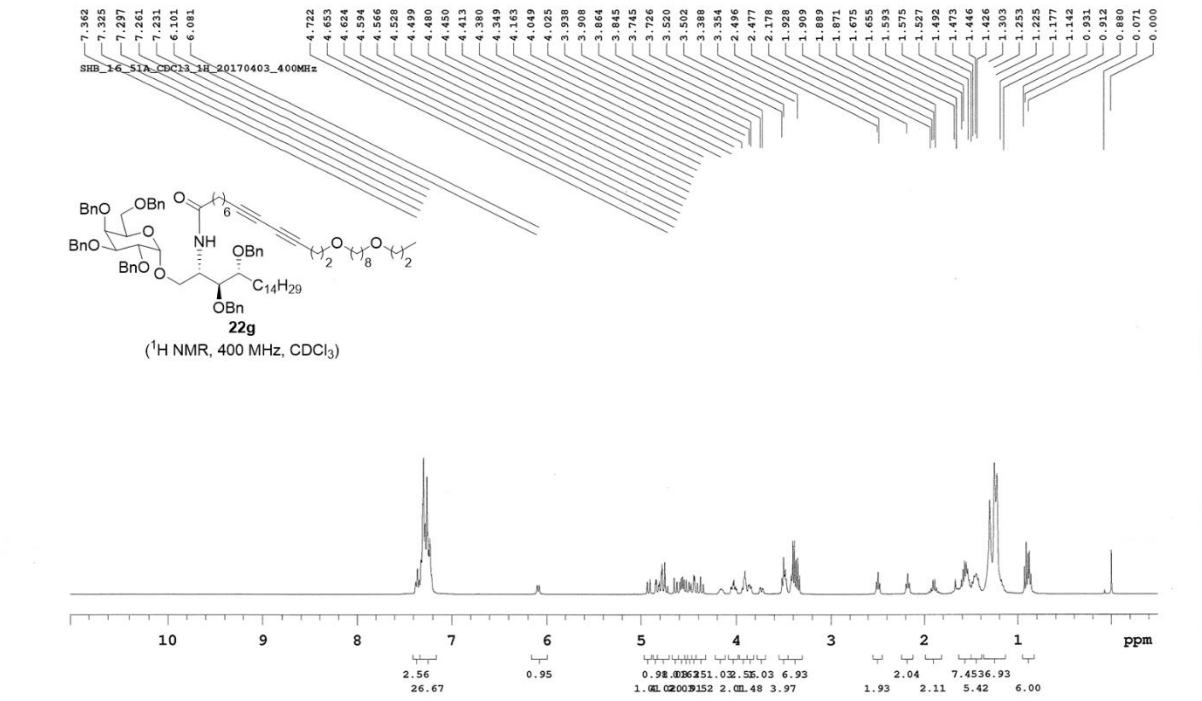

SHB_15_78_CDCl3_13C_20161227_400MHz
22d
(13C NMR, 100 MHz, CDCl3)
ppm

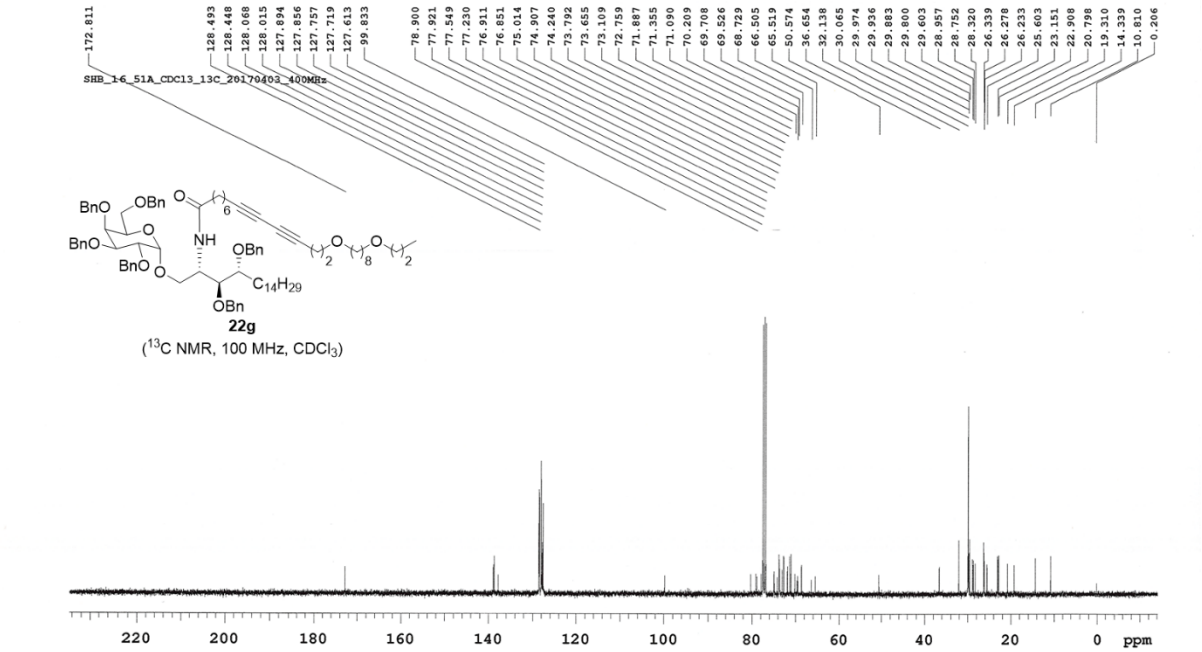

SHB_16_51C_CDCl3_1H_20170404_400MHz
22e
(1H NMR, 400 MHz, CDCl3)
ppm

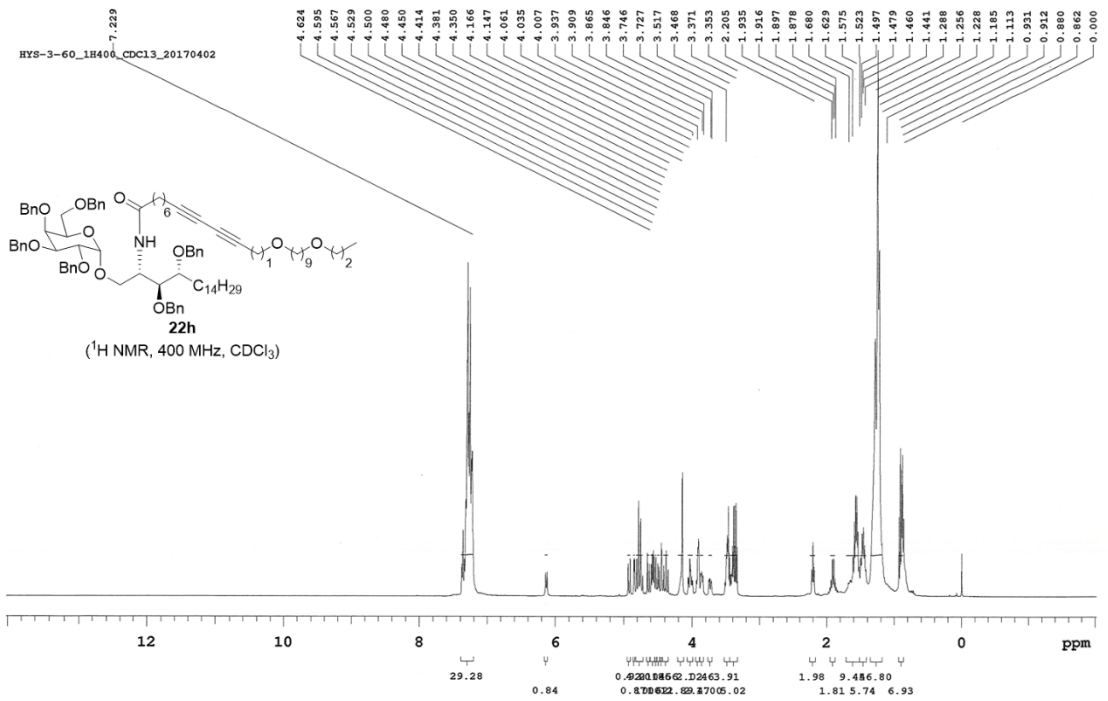

SHB_16_51C_CDCl3_13C_20170404_400MHz
22e
(13C NMR, 100 MHz, CDCl3)
ppm

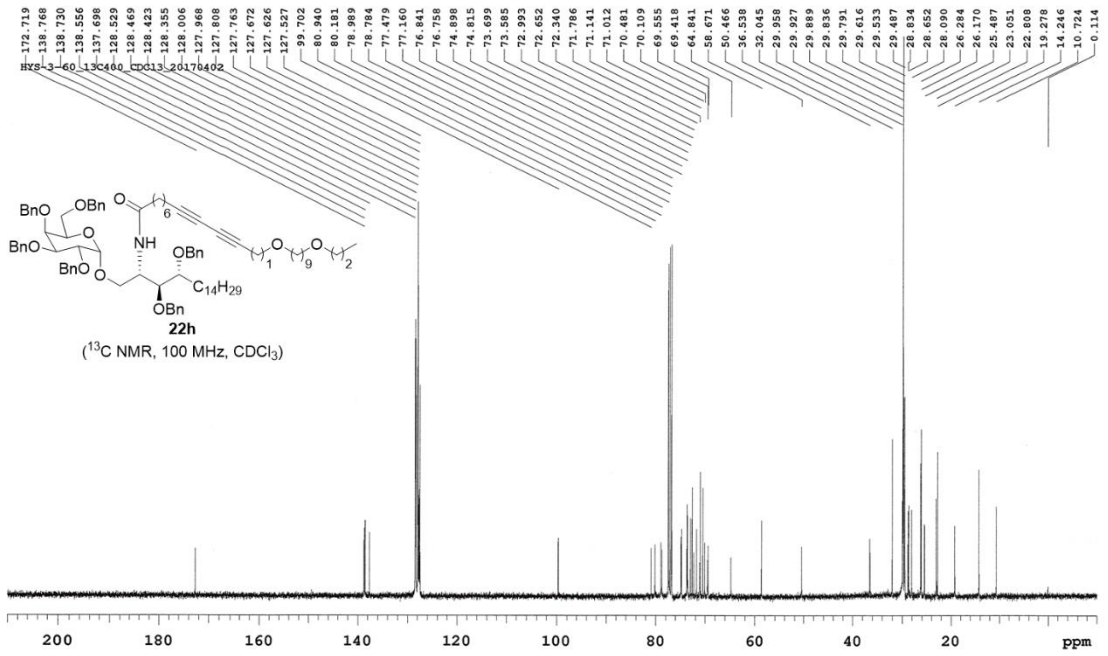

SHB_16_51B_CDCl3_1H_20170404_400MHz
22f
(1H NMR, 400 MHz, CDCl3)
ppm

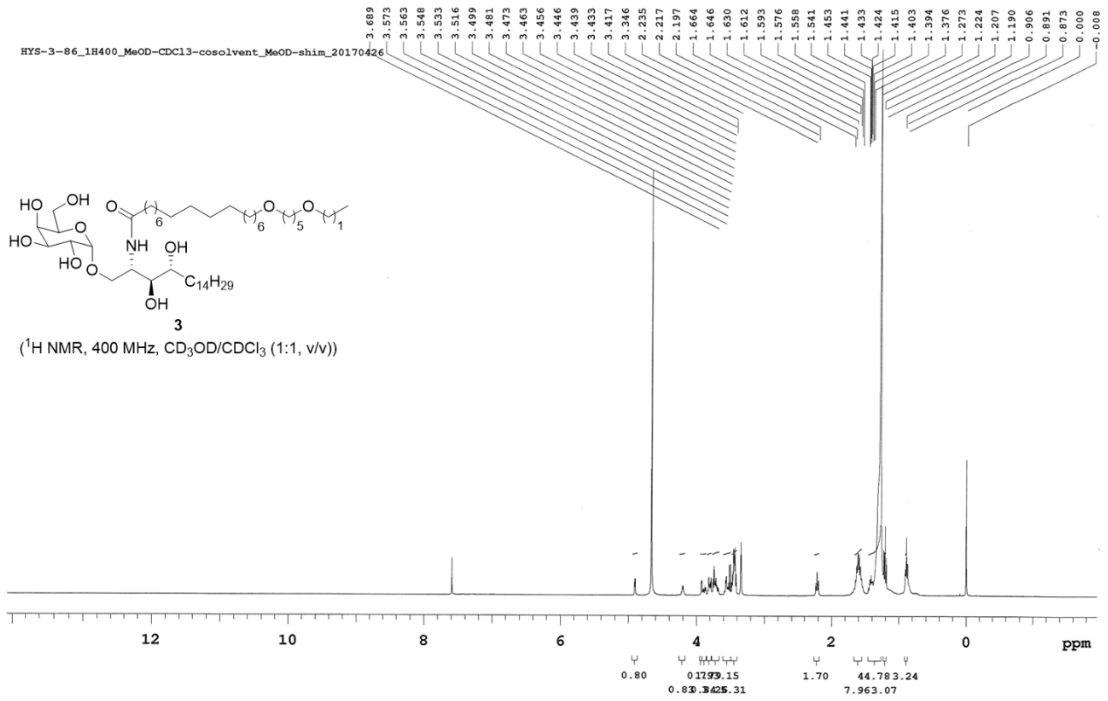

SHB_16_51B_CDCl3_13C_20170404_400MHz
22f
(13C NMR, 100 MHz, CDCl3)
ppm


SHB_16_51A_CDCl3_1H_20170403_400MHz
BnO
OBn
BnO
BnO
O
NH
OBn
$C_{14}H_{29}$
OBn
22g
(^{1}H NMR, 400 MHz, $CDCl_3$)
ppm


SHB_16_51A_CDCl3_13C_20170403_400MHz
BnO
OBn
BnO
BnO
O
NH
OBn
$C_{14}H_{29}$
OBn
22g
(^{13}C NMR, 100 MHz, $CDCl_3$)
ppm

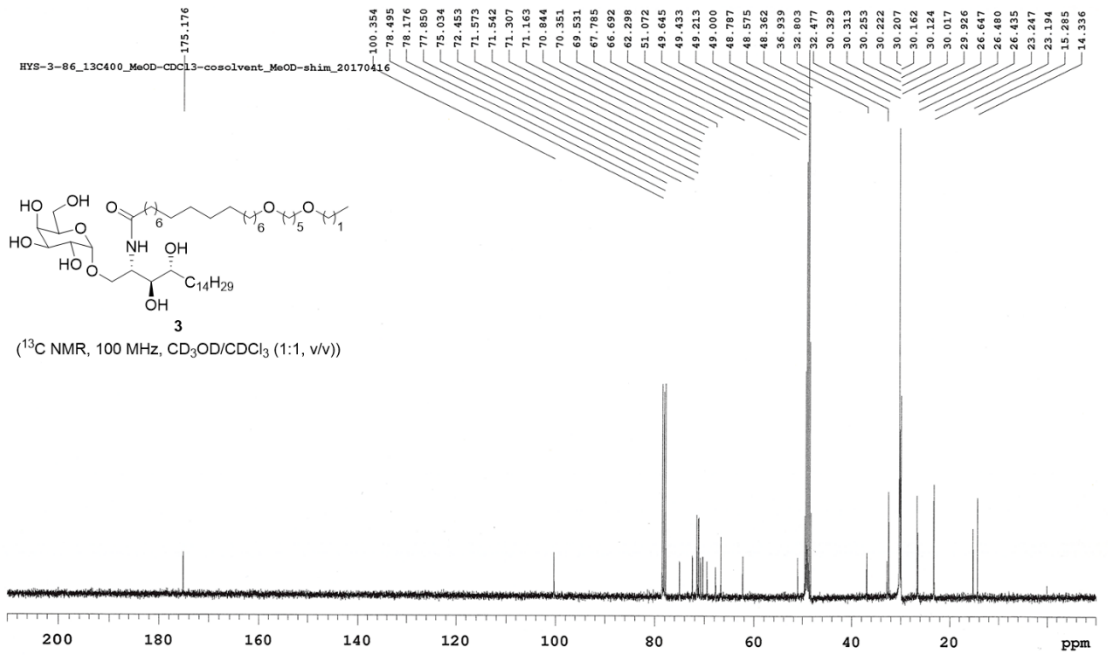

HYS-3-60_1H400_CDCl3_20170402
22h
(1H NMR, 400 MHz, CDCl3)
ppm


HYS-3-60_13C400_CDCl3_20170402
22h
(13C NMR, 100 MHz, CDCl3)
ppm



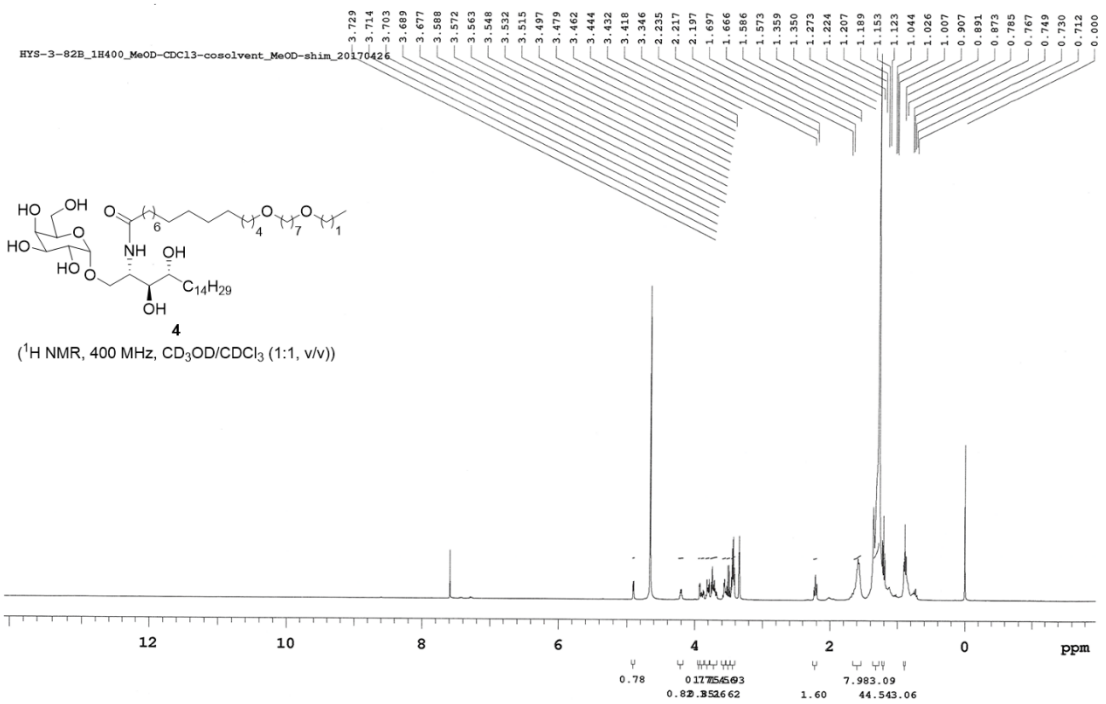
3

(^{1}H NMR, 400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))



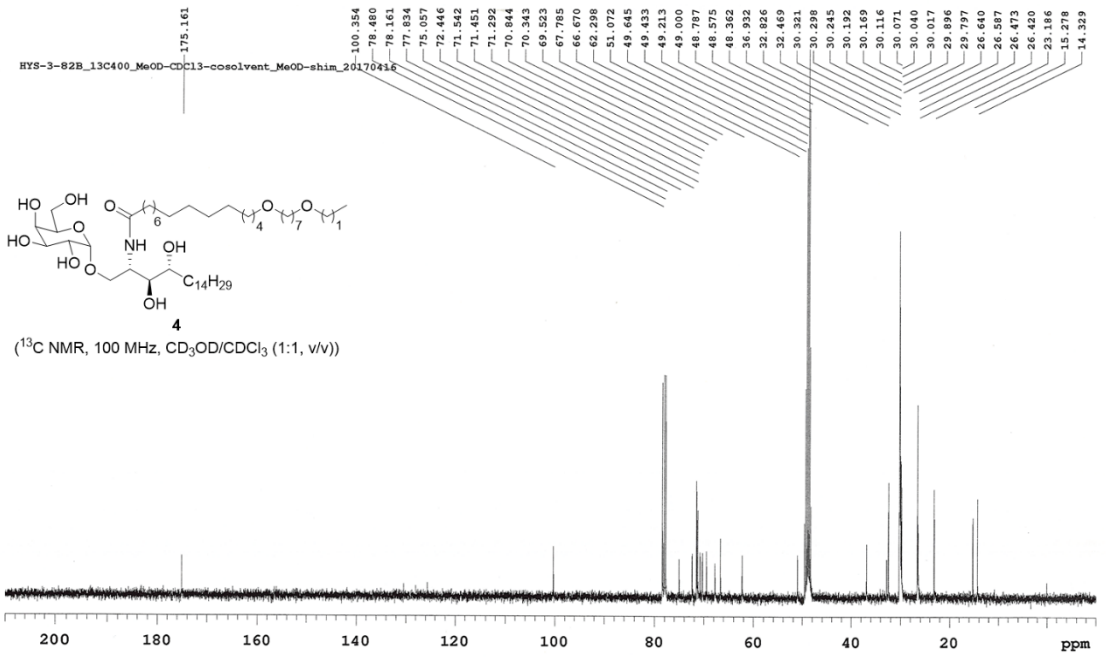
3

(^{13}C NMR, 100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))



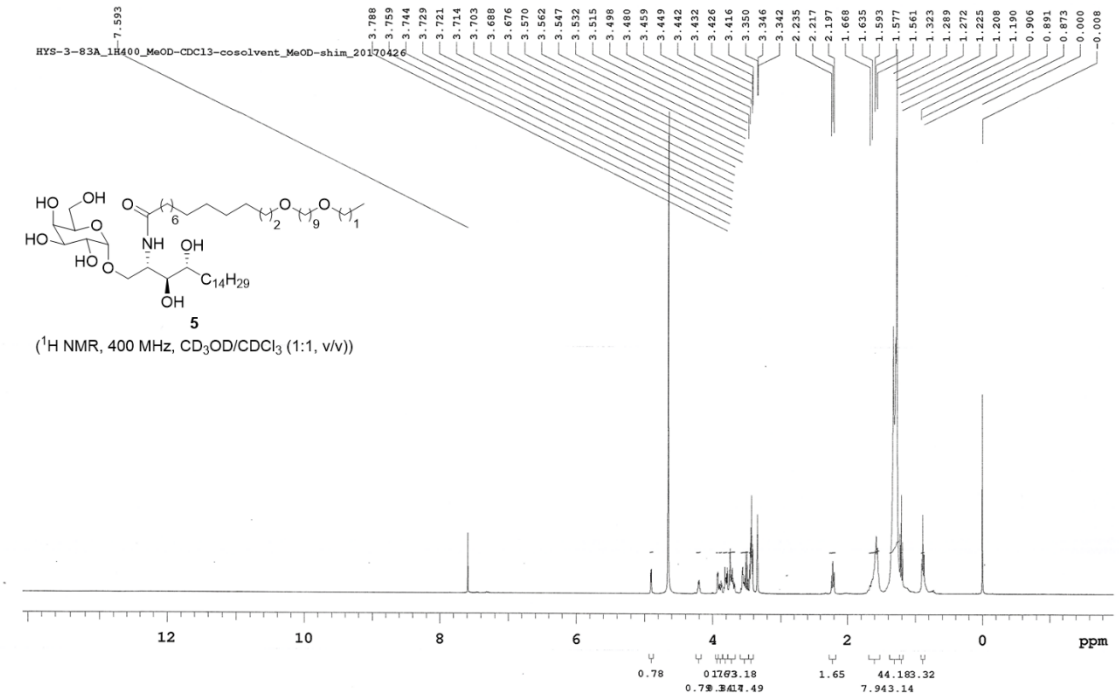
4

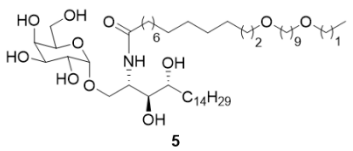
(^{1}H NMR, 400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))



4

(^{13}C NMR, 100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))



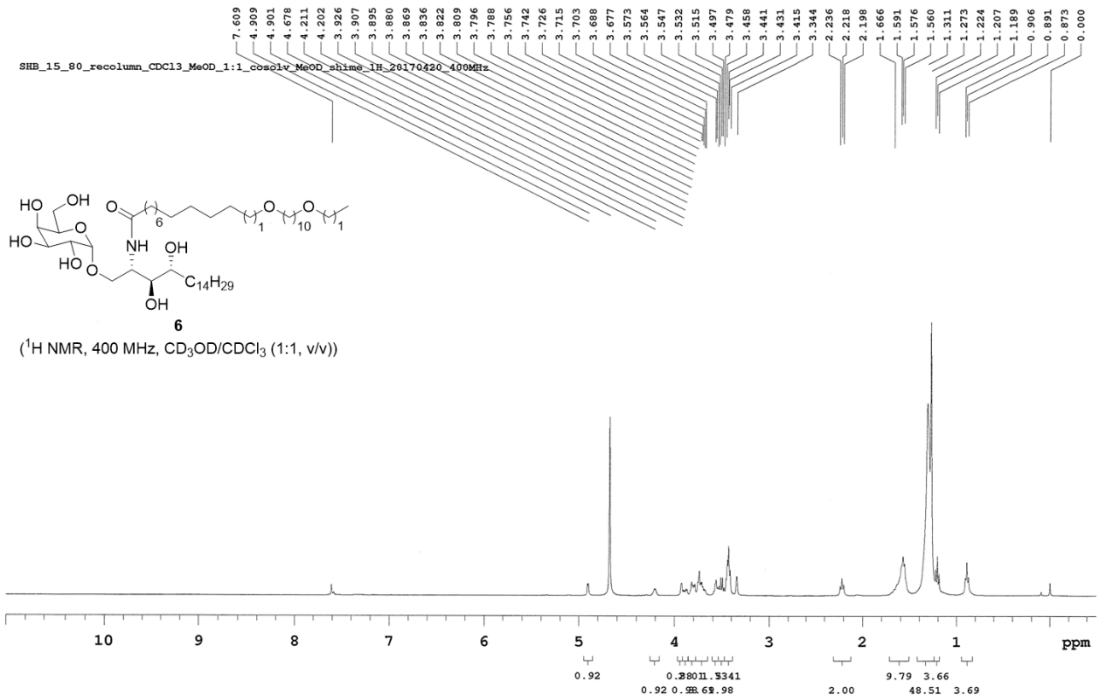


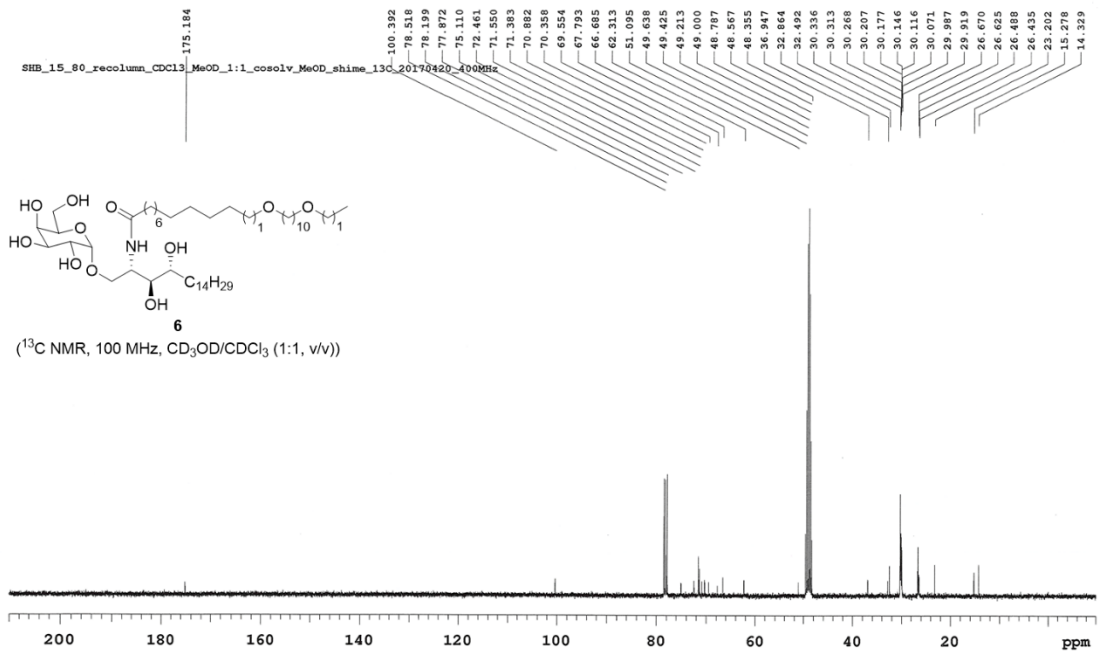
5

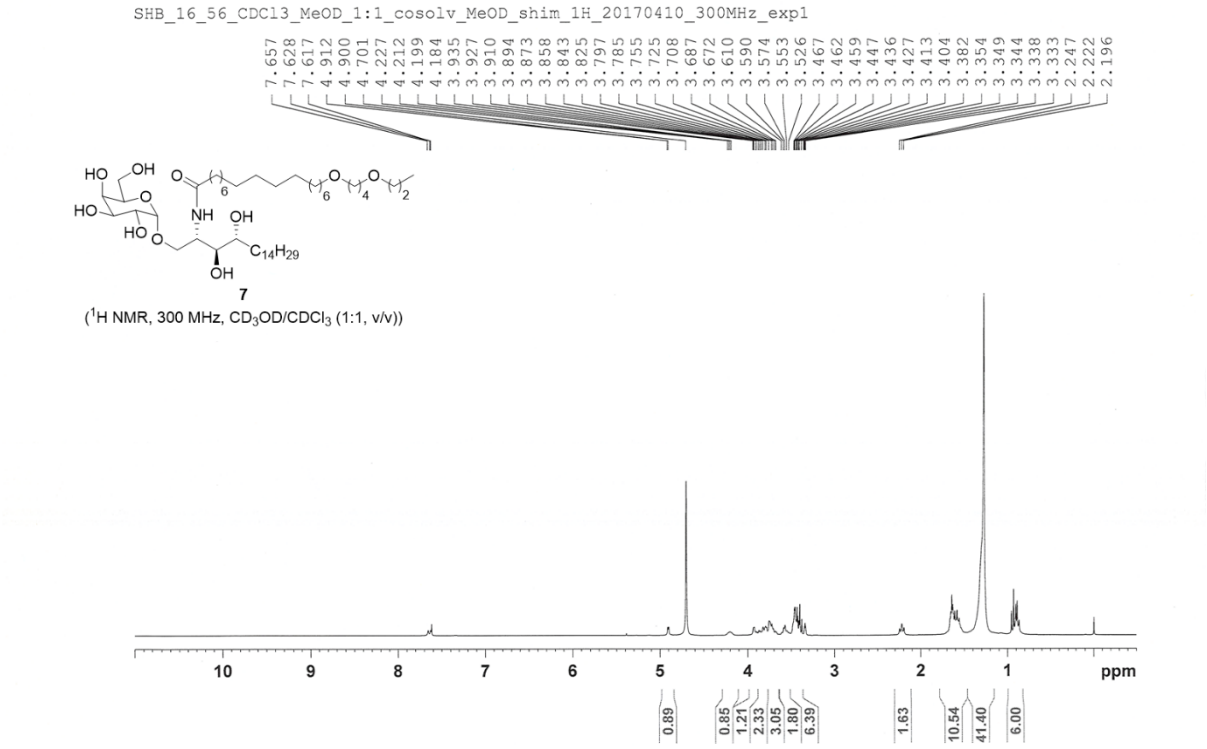
(^{1}H NMR, 400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))

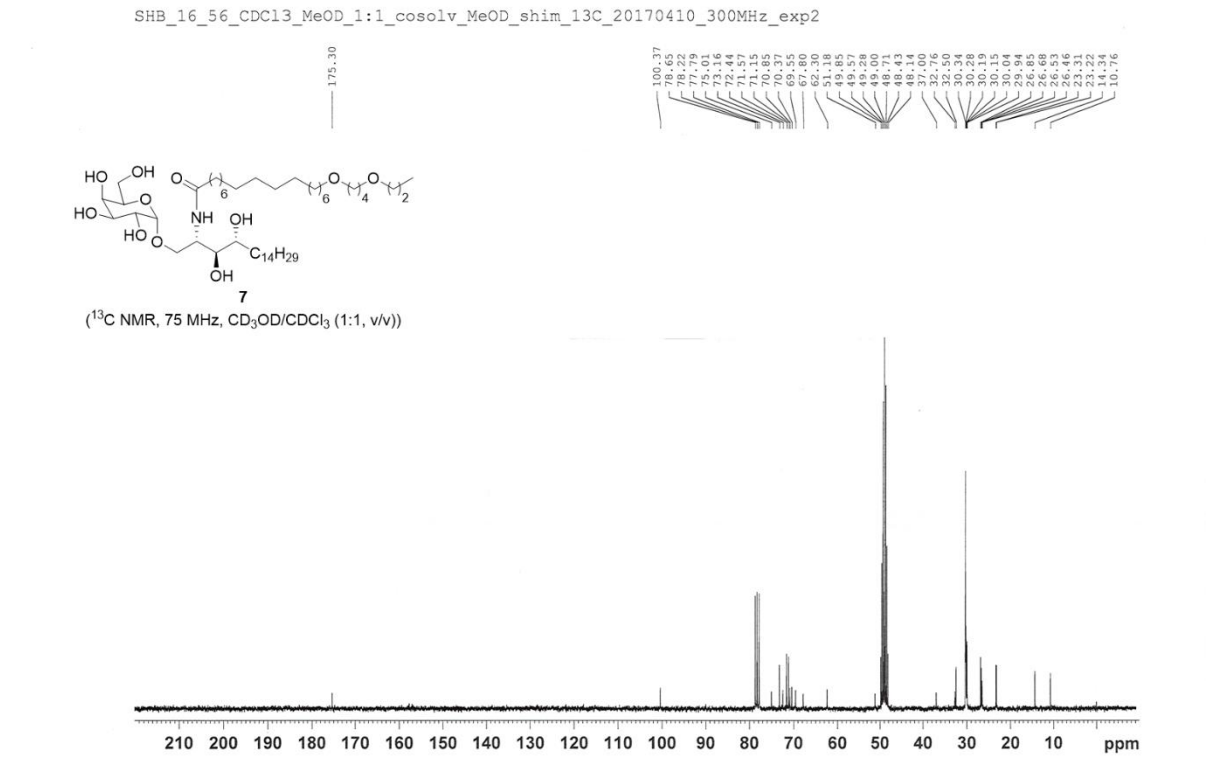
5

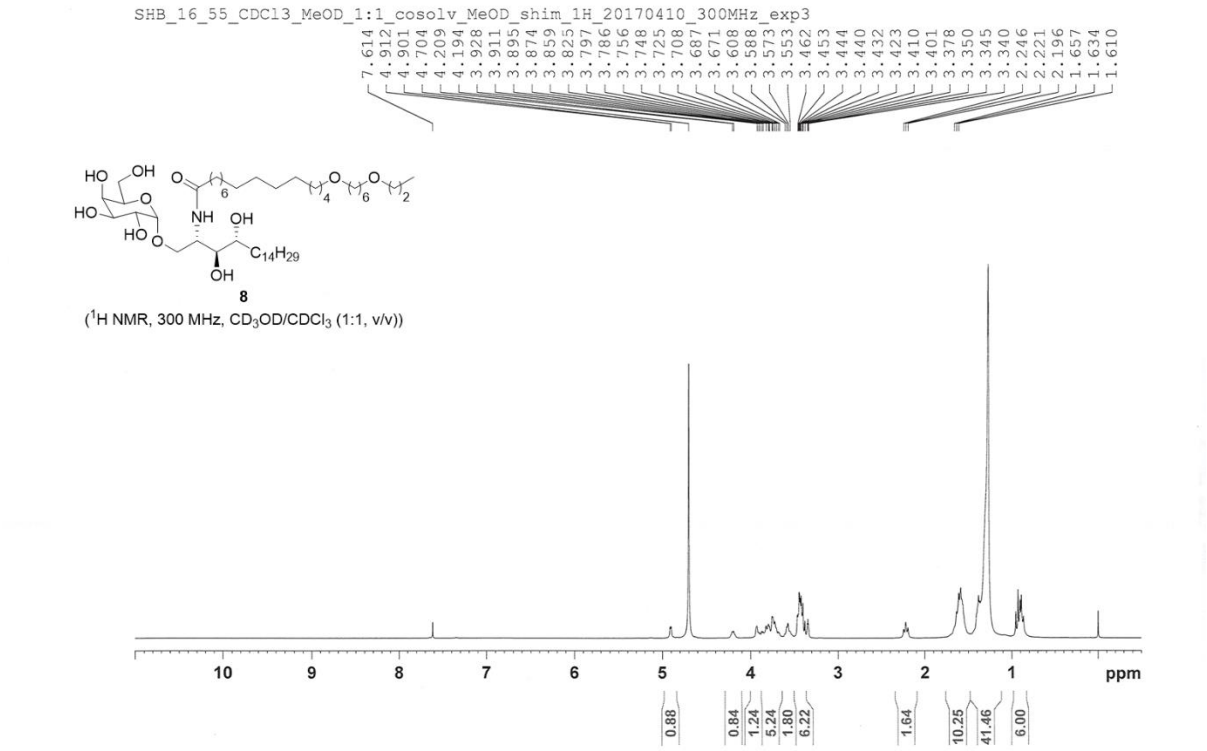
(^{13}C NMR, 100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))

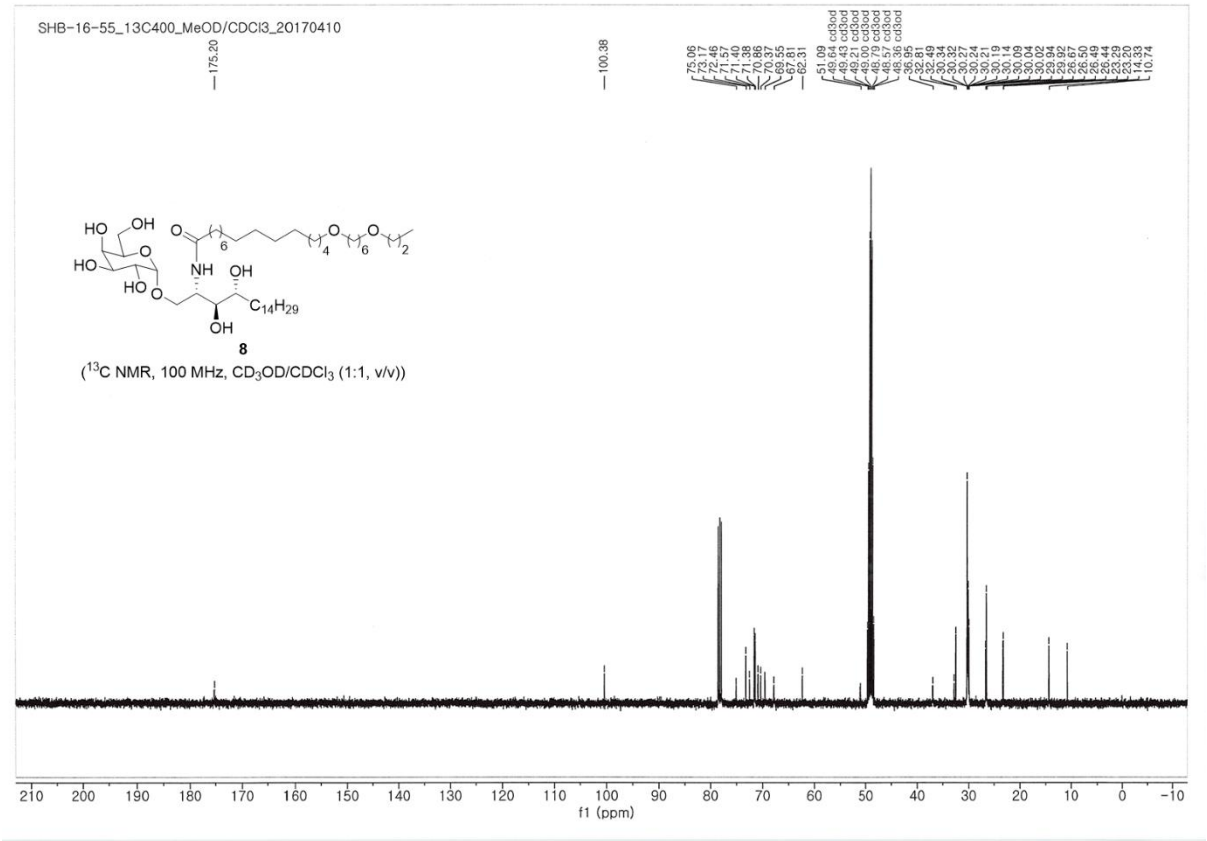

SHB_15_80_recolumn_CDCl3_MeOD_1:1_cosolv_MeOD_shime_1H_20170420_400MHz
7.609 4.909 4.901 4.678 4.211 4.202 3.926 3.907 3.895 3.880 3.869 3.836 3.822 3.809 3.796 3.788 3.756 3.742 3.726 3.715 3.703 3.688 3.677 3.573 3.564 3.547 3.532 3.515 3.497 3.479 3.458 3.441 3.431 3.415 3.344 2.236 2.218 2.198 1.666 1.591 1.576 1.560 1.311 1.273 1.224 1.207 1.189 0.906 0.891 0.873 0.000
HO OH O 6 O 1 O 10 O 1 HO O NH OH HO O C14H29 OH
6
(1H NMR, 400 MHz, CD3OD/CDCl3 (1:1, v/v))
10 9 8 7 6 5 4 3 2 1 ppm
0.92 2.00 9.79 3.66 48.51 3.69

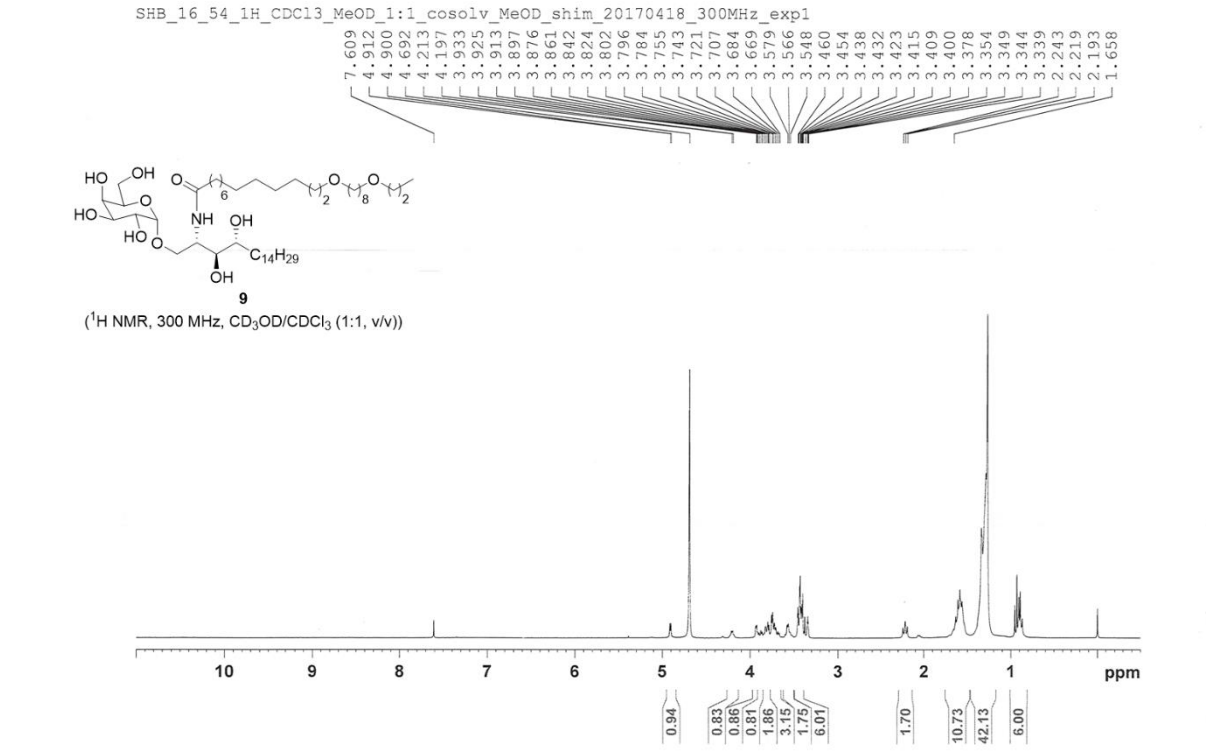

SHB_15_80_recolumn_CDCl3_MeOD_1:1_cosolv_MeOD_shime_13C_20170420_400MHz
175.184
100.392 78.518 78.199 77.872 75.110 72.461 71.550 71.383 70.882 70.358 69.554 67.793 66.685 62.313 51.095 49.638 49.425 49.213 49.000 48.787 48.567 48.355 36.947 32.864 32.492 30.336 30.313 30.268 30.207 30.177 30.146 30.116 30.071 29.987 29.919 26.670 26.625 26.488 26.435 23.202 15.278 14.329
HO OH O 6 O 1 O 10 O 1 HO O NH OH HO O C14H29 OH
6
(13C NMR, 100 MHz, CD3OD/CDCl3 (1:1, v/v))
200 180 160 140 120 100 80 60 40 20 ppm

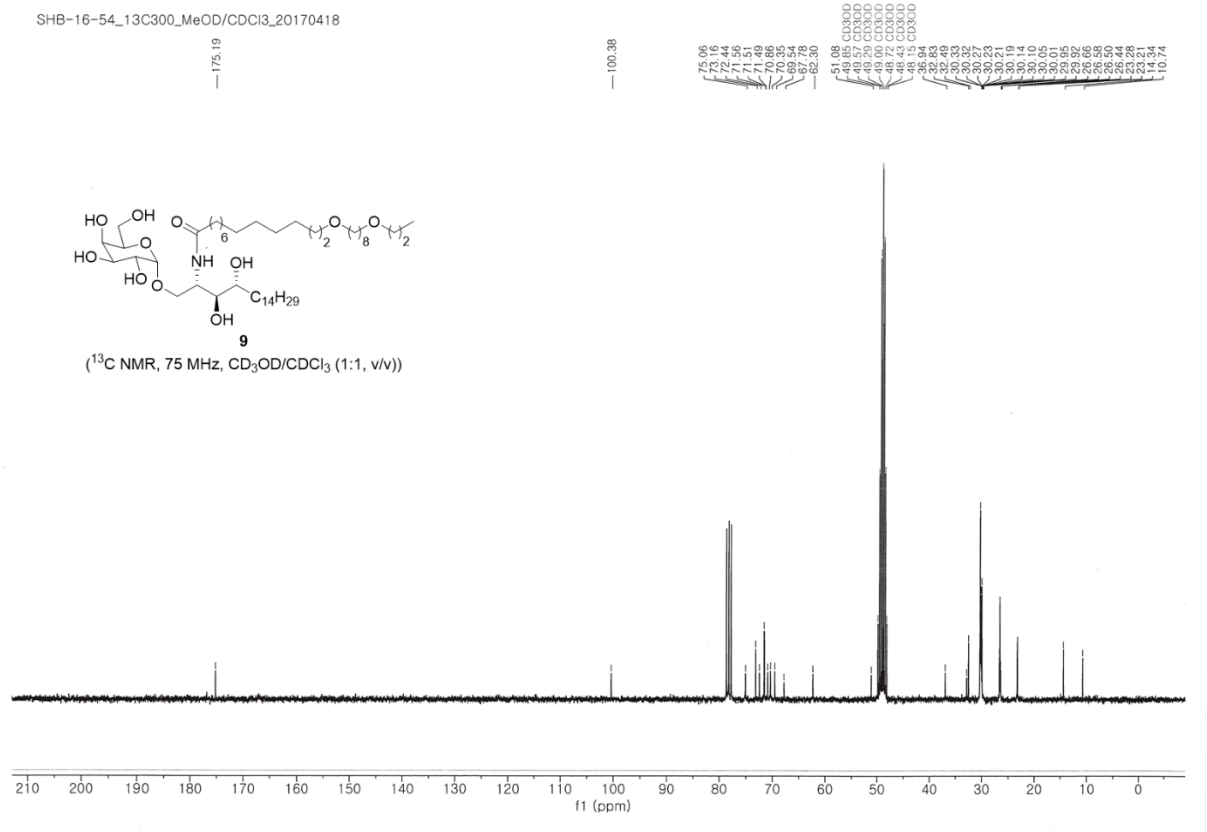

SHB_16_56_CDCl3_MeOD_1:1_cosolv_MeOD_shim_1H_20170410_300MHz_exp1
7.657
7.628
7.617
4.912
4.900
4.701
4.227
4.212
4.199
4.184
3.935
3.927
3.910
3.894
3.873
3.858
3.843
3.825
3.797
3.785
3.755
3.725
3.708
3.687
3.672
3.610
3.590
3.574
3.553
3.526
3.467
3.462
3.459
3.447
3.436
3.427
3.413
3.404
3.382
3.354
3.349
3.344
3.338
3.333
2.247
2.222
2.196
HO
OH
O
HO
HO
O
NH
OH
OH
C14H29
7
(1H NMR, 300 MHz, CD3OD/CDCl3 (1:1, v/v))
10
9
8
7
6
5
4
3
2
1
ppm
0.89
0.85
1.21
2.33
3.05
1.80
6.39
1.63
10.54
41.40
6.00

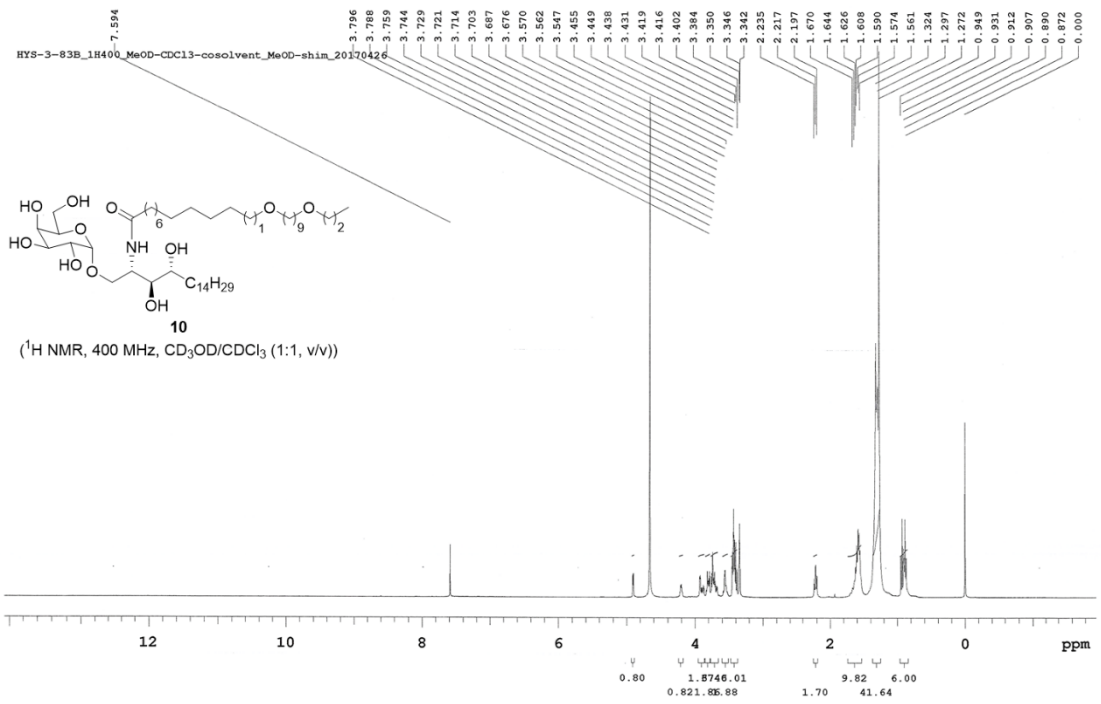

SHB_16_56_CDCl3_MeOD_1:1_cosolv_MeOD_shim_13C_20170410_300MHz_exp2
175.30
100.37
78.65
78.22
77.79
77.01
73.16
72.44
71.57
71.15
70.85
70.37
69.55
69.30
62.30
51.18
49.85
49.57
49.28
49.00
48.71
48.43
48.14
37.00
32.76
32.50
30.34
30.28
30.19
30.15
30.04
29.94
26.85
26.68
26.53
26.46
23.31
23.22
14.34
10.76
HO
OH
O
HO
HO
O
NH
OH
OH
C14H29
7
(13C NMR, 75 MHz, CD3OD/CDCl3 (1:1, v/v))
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

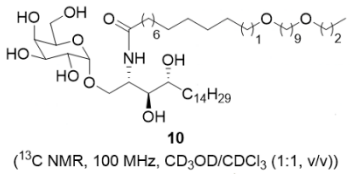

SHB_16_55_CDCl3_MeOD_1:1_cosolv_MeOD_shim_1H_20170410_300MHz_exp3
7.614
4.912
4.901
4.704
4.209
4.194
3.928
3.911
3.895
3.874
3.859
3.825
3.797
3.786
3.756
3.748
3.725
3.708
3.687
3.671
3.608
3.588
3.573
3.553
3.462
3.453
3.444
3.440
3.432
3.423
3.410
3.401
3.378
3.350
3.345
3.340
2.246
2.221
2.196
1.657
1.634
1.610
HO
OH
O
NH
OH
HO
HO
C14H29
OH
8
(1H NMR, 300 MHz, CD3OD/CDCl3 (1:1, v/v))
10
9
8
7
6
5
4
3
2
1
ppm
0.88
0.84
1.24
5.24
1.80
6.22
1.64
10.25
41.46
6.00


SHB-16-55_13C400_MeOD/CDCl3_20170410
175.20
100.38
75.06
73.17
72.46
71.57
71.40
71.38
70.86
70.37
69.55
67.81
62.31
51.09
49.64
49.43
49.21
49.00
48.79
48.57
48.36
36.95
32.81
32.49
30.34
30.32
30.27
30.24
30.21
30.19
30.14
30.09
30.04
30.02
29.94
29.92
26.67
26.50
26.49
26.44
23.29
23.20
14.33
10.74
HO
OH
O
NH
OH
HO
HO
C14H29
OH
8
(13C NMR, 100 MHz, CD3OD/CDCl3 (1:1, v/v))
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


SHB_16_54_1H_CDCl3_MeOD_1:1_cosolv_MeOD_shim_20170418_300MHz_exp1
7.609
4.912
4.900
4.692
4.213
4.197
3.933
3.925
3.913
3.897
3.876
3.861
3.842
3.824
3.802
3.796
3.784
3.755
3.743
3.721
3.707
3.684
3.669
3.579
3.566
3.548
3.460
3.454
3.438
3.432
3.423
3.415
3.409
3.400
3.378
3.354
3.349
3.344
3.339
2.243
2.219
2.193
1.658
HO
OH
O
6
2
O
8
O
2
HO
O
NH
OH
HO
O
C14H29
OH
9
(1H NMR, 300 MHz, CD3OD/CDCl3 (1:1, v/v))
10
9
8
7
6
5
4
3
2
1
ppm
0.94
0.83
0.86
0.81
1.86
3.15
1.75
6.01
1.70
10.73
42.13
6.00


SHB-16-54_13C300_MeOD/CDCl3_20170418
175.19
100.38
75.06
73.16
72.44
71.56
71.51
71.49
70.86
70.35
69.54
69.28
62.30
51.08
49.57 CD3OD
49.29 CD3OD
49.00 CD3OD
48.72 CD3OD
48.43 CD3OD
48.15 CD3OD
36.94
32.83
32.49
30.33
30.32
30.27
30.23
30.21
30.19
30.14
30.10
30.05
30.01
29.95
29.92
26.66
26.58
26.50
26.44
23.28
14.31
14.14
10.74
HO
OH
O
6
2
O
8
O
2
HO
O
NH
OH
HO
O
C14H29
OH
9
(13C NMR, 75 MHz, CD3OD/CDCl3 (1:1, v/v))
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)





10

(^{1}H NMR, 400 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))

10

(^{13}C NMR, 100 MHz, $CD_3OD/CDCl_3$ (1:1, v/v))

5. References

1) *J. Org. Chem.*, **2013**, *78*, 378 –3801.

2) *Tetrahedron*, **2005**, *61*, 1855–1862.