Supplementary Information

Polyurethanes based on renewable polyols from bioderived lactones.

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Synthesis and spectroscopic characterization data for model amide/esters:

Characterization data for PU films in entries 1-8, Table 3 in manuscript

Copies of NMR Spectra

General Experimental Information

Materials and Methods

(note: the first five paragraphs below are identical to those in the published manuscript)

All glassware was dried in an oven at 150 °C prior to use. All air/moisture sensitive experiments were carried out under a static pressure of dry nitrogen in a glove box. Anhydrous dichloromethane (DCM) and toluene were obtained by passing the commercial grade solvent through an activated alumina column. Toluene was degassed using a freeze-pump-thaw method. Ethanol, chloroform, starting materials, and reagents were used as received from the commercial sources unless indicated otherwise.

NMR spectra were recorded on a 500 or 300 MHz Varian Inova NMR spectrometers. Proton chemical shifts are referenced to internal TMS (δ 0.00) for spectra recorded in $CDCl_3$ and to residual CHD_5 (δ 7.16) for spectra recorded d_6-benzene. Carbon chemical shifts are referenced to $^{13}CDCl_3$ (δ 77.0) for spectra recorded in $CDCl_3$. Molar masses determined by NMR analysis were calculated as shown in Figure S2. Infrared spectra were recorded on a MIDAC 2000 FTIR spectrometer in ATR mode.

Molar masses (M_N and M_w) determined by SEC analysis are based on polystyrene standards. Chloroform was the mobile phase and the flow rate was 1.0 mL/min at 35 ºC using three Jordi poly(divinylbenzene) columns of 100, 100, and 500 Å pore size and a differential refractometer. The differential refractive index increment (dn/dc) was determined by pumping chloroform solutions of the polymers of known concentration through the Wyatt Technology Corp. Optilab DSP interferometric refractometer, with a wavelength of 633 nm and a temperature of 25 ºC throughout the measurement.

GC-MS experiments were conducted on an Agilent Technologies 6890N GC system and 5975 inert XL mass selective detector. Differential scanning calorimetry (DSC) measurements were performed using a Discovery DSC Instrument under a nitrogen atmosphere. The polymer samples were heated to 200 °C, held for 5 min, cooled to -50 °C, held for 5 min, and then reheated to 200 °C. The rate of both heating and cooling was 10 °C/min. The values reported were obtained from the second heating cycle. An indium standard was used for calibration. Samples weighing 2.0-7.0 mg were loaded into aluminum pans.

(–)-Menthide (**1**) and carvomenthide (**2**) were synthesized by Baeyer-Villiger oxidation of menthone and carvomenthone, respectively, according to a literature protocol. Dihydrocarvone, *m*-chloroperoxybenzoic acid (MCPBA), and diethylene glycol were commercial samples and were used as received. Tin(II) octoate [$Sn(O_2CCH(Et)Bu)_2$] was obtained from Aldrich and doubly vacuum distilled prior to use. Methylenediphenyl diisocyanate (MDI; Suprasec 3050; ca. 50:50 4,4'- and 2,4'-isomers with a few% of the 2,2'-isomer) and polymeric-MDI [PMDI; Rubinate® M; MW ca. 325 (i.e., functionality ca. 2.6); specified equiv wt: 135] were obtained from Huntsman.

ESI-MS data were collected from a Bruker-BioTof II (ESI-TOF) mass spectrometer using PEG as an internal standard. Samples were prepared from a solution of polyol in chloroform diluted with methanol and filtered through a PTFE (0.45 μm) syringe filter before injection.

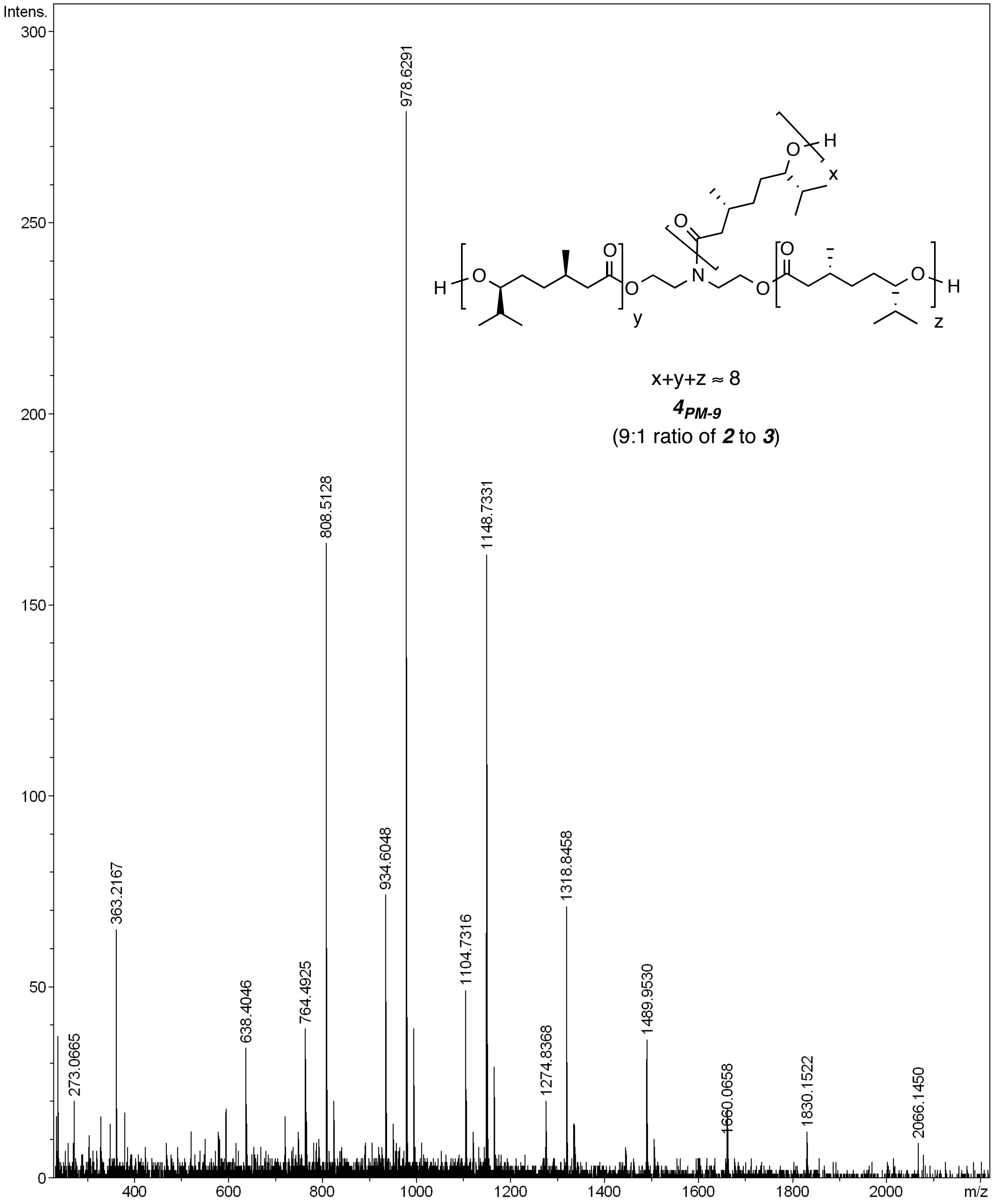
MALDI-TOF MS data were collected from a Bruker Reflex III MALDI-TOF instrument operating in the reflectron mode. Each higher molecular weight (i.e., ca. 3 kg•mol^{-1}) polyol sample was dissolved in chloroform (ca. 5 mg•mL^{-1}). The matrix material (2,5-dihydroxy benzoic acid) was dissolved in methanol (ca. 1 M). Solutions of matrix (10 µL) and sample (5 µL) were mixed with a micropipette and a drop was placed in a well of a MALDI target sample holder and allowed to evaporate.

Dynamic mechanical analysis of the PU films was measured with an RSA-2 rheometer (Rheometric Scientific, Piscataway, NJ). Films (ca. 0.5 mm thick) were cut to a rectangular shape (ca. 35 mm long and ca. 5 mm wide). A dynamic strain sweep test was performed at ambient temperature and a dynamic temperature ramp test was then carried out across a temperature range of -60 to 160 °C with a ramp rate of 3 °C min^{-1}. The T_g value was measured from the graph of T vs. loss modulus (E”). The software Origin 8.5 version was used to plot the data collected from this study.

Tensile testing of PU films was conducted using a MiniMat material tester (Rheometrics Scientific). A dogbone-shaped sample having an area of analysis of ca. 12 x 3 mm l x w and ca. 0.5 mm thickness was mounted between the stable and mobile grip. Tensile testing was carried out at a cross-head speed of 36 mm•min^{-1}. Reported values are averages and standard deviations of at least three samples. MiniMat software was used to calculate the parameters provided in Table 3.

ESI-MS characterization data for each of the two lower MW polyols 4_{PM-9} and 8_{PCM-9}. pp S5-S6

ESI-4_{PM-9}



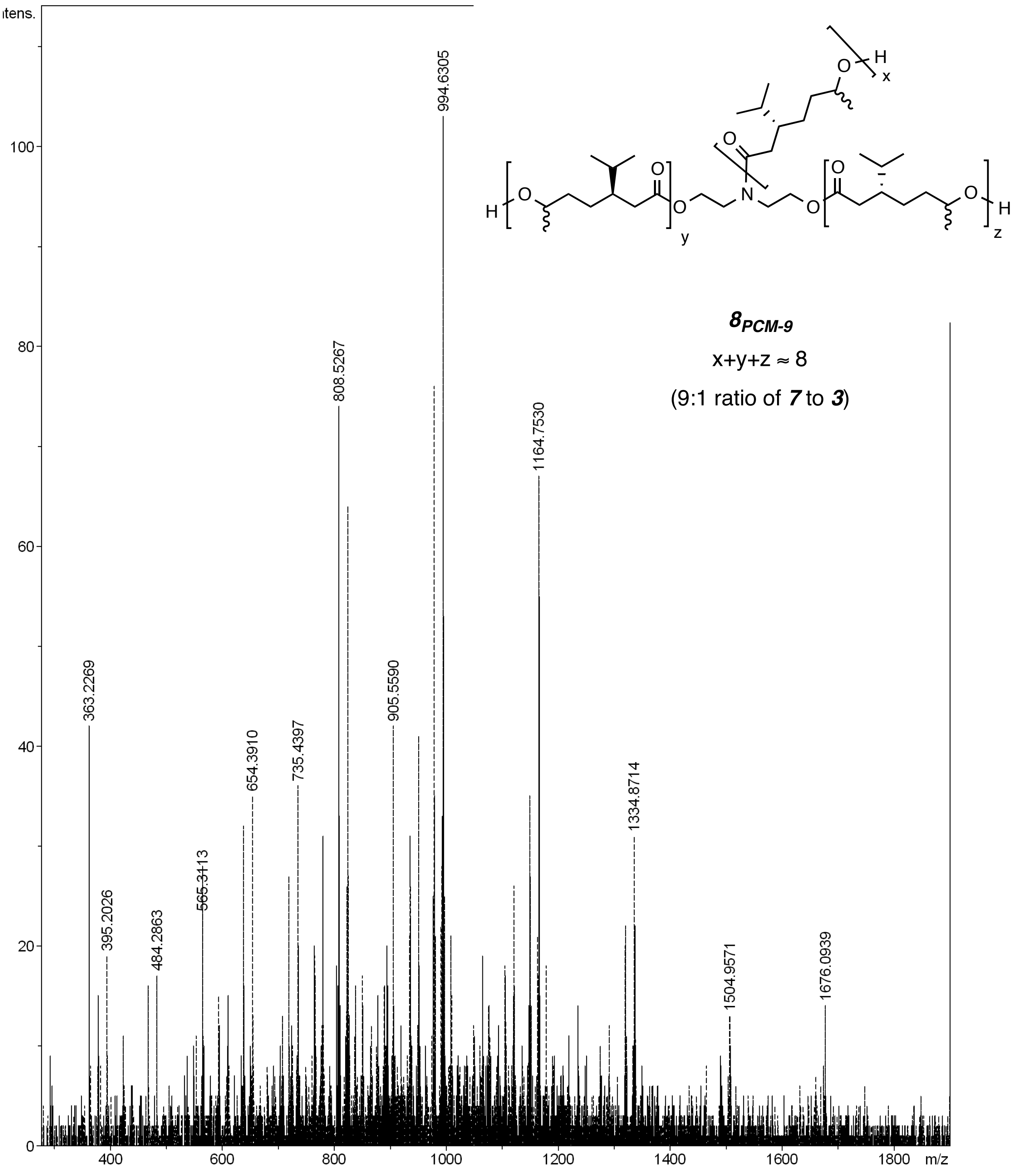
x+y+z ≈ 8

4_{PM-9}

(9:1 ratio of ***2*** to ***3***)

Bruker Daltonics DataAnalysis 3.4 printed: 4/10/2012 2:56:39 PM Page 1 of 1

ESI-8_{PCM-9}



8_{PCM-9}

x+y+z ≈ 8

(9:1 ratio of ***7*** to ***3***)

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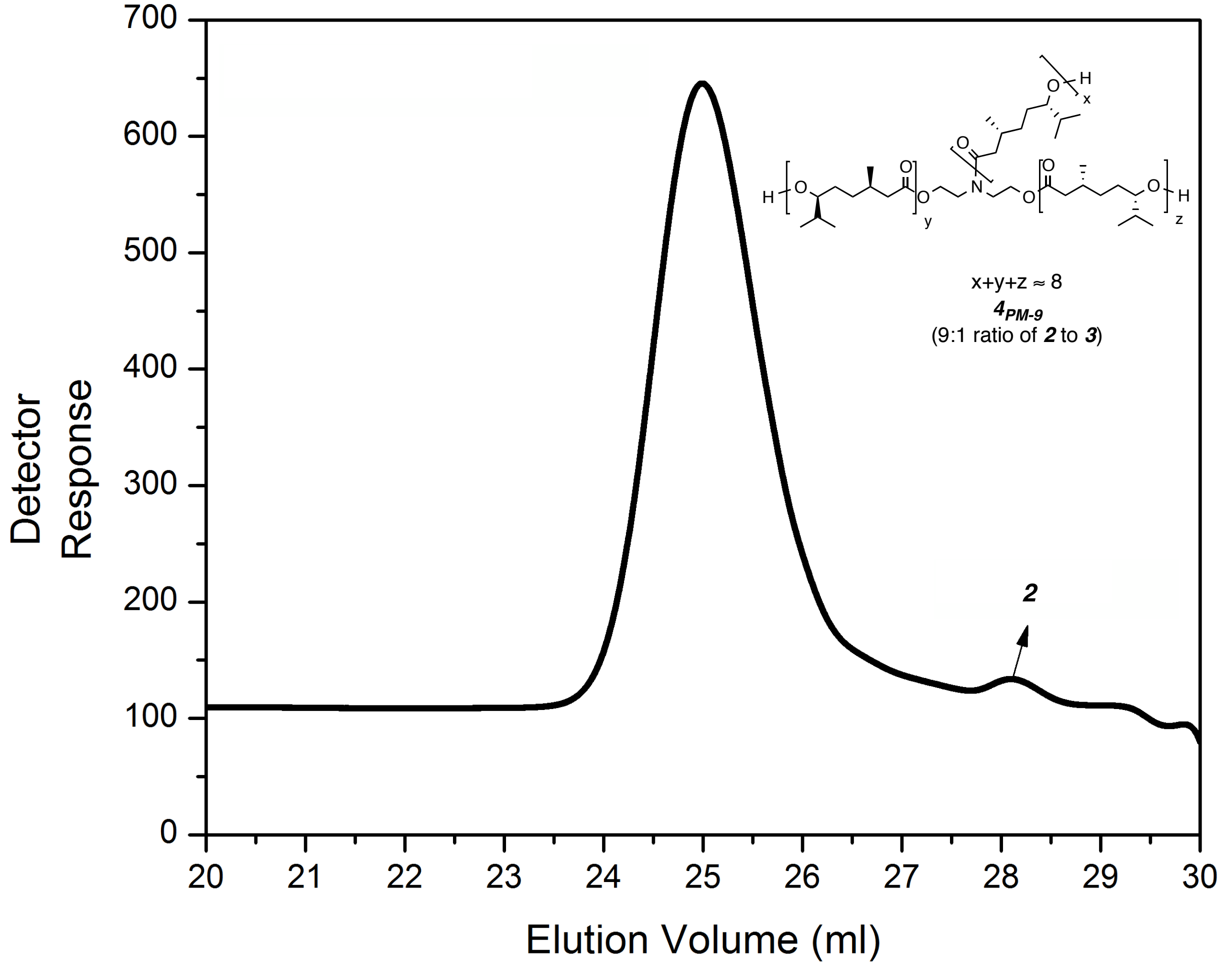
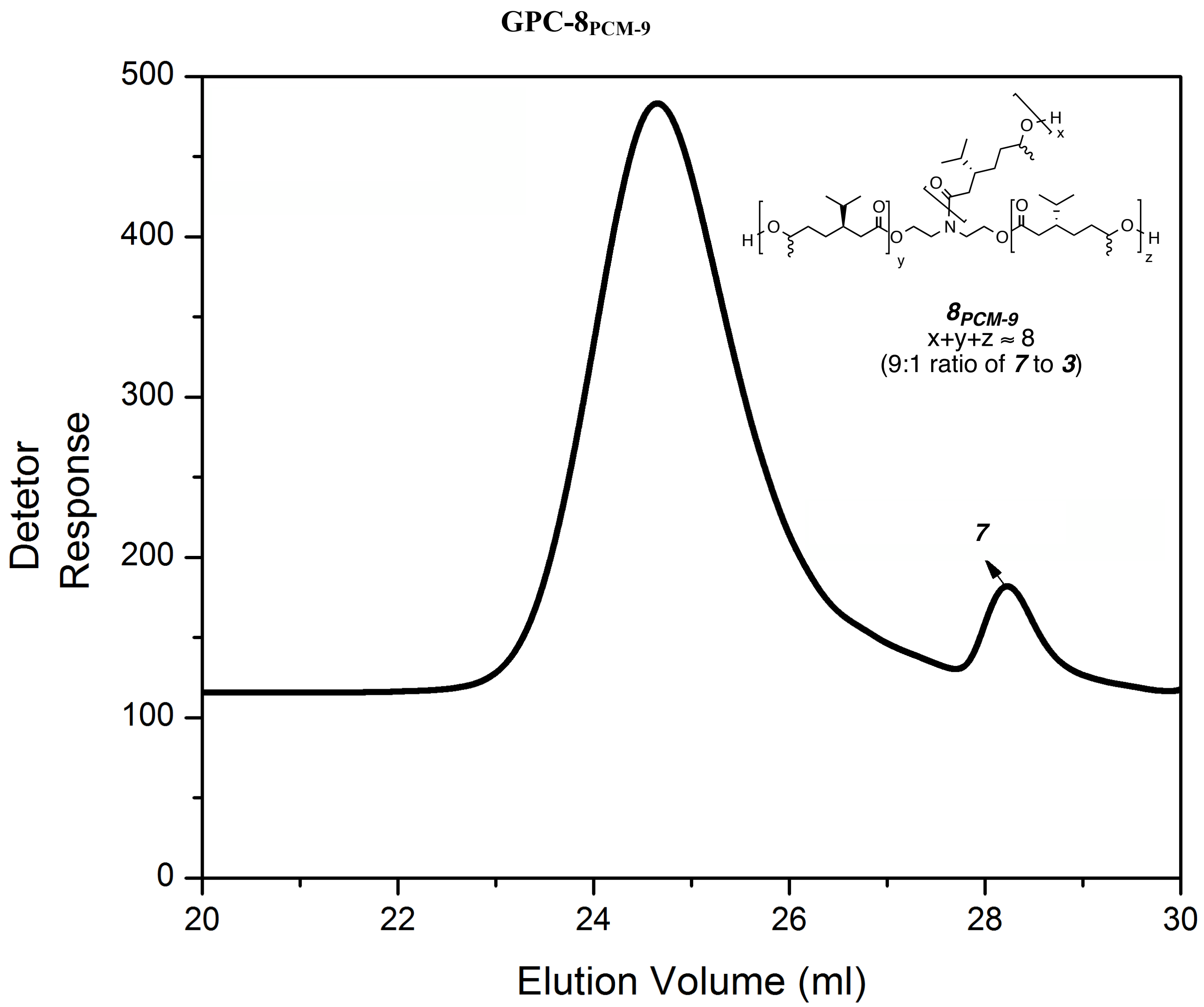
GPC characterization data for each of the two lower MW polyols 4_{PM-9} and 8_{PCM-9}. pp S7-S8

GPC-4_{PM-9}

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500
400
300
200
100
0
Detetor Response
20
22
24
26
28
30
Elution Volume (ml)
7
H
O
O
O
N
O
O
O
H
O
O
H
x
y
z
8PCM-9
x+y+z ≈ 8
(9:1 ratio of 7 to 3)

Synthesis of higher MW polyols 4_{PM-18} and 8_{PCM-18}

Synthesis of (–)-menthide-based polyol 4_{PM-18}

A glass pressure vessel was charged with an 18:1 molar ratio of (–)-menthide (**2**, 6.0 g, 35 mmol) and distilled diethanolamine (**3**, 0.21 g, 2.0 mmol) under a nitrogen atmosphere in a glove box. A solution of distilled tin(II) octoate (57 mg, 0.14 mmol) dissolved in anhydrous toluene (1.1 mL) was added. The vessel was closed and removed from the glove box. The reaction mixture was stirred and heated in an oil bath maintained at 140 ºC for 48 h and then cooled to room temperature. Pentane (5 mL) was added, the resulting mixture was triturated for several minutes, and the top pentane layer was removed with a pipette. This pentane washing procedure was repeated three times. The resulting viscous liquid was dissolved in anhydrous methylene chloride (3 mL) and magnetically stirred. Pentane (30 mL) was slowly added. The top transparent layer was carefully separated from the denser layer; the latter was dried under vacuum (several h at ambient temperature) to afford polyol $\mathbf{4}_{PM-18}$ (5.0 g, 77 %) as a transparent viscous liquid. By ^{1}H NMR analysis, this sample was estimated to contain ca. 6% of the unreacted monomer **2**.

Spectral data for 4_{PM-18}:

^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.75-4.69 (m), 4.24-4.11 (m), 3.66-3.54 (m), 3.36-3.31 (m), 2.36-2.27 (m), 2.14-2.05 (m, 9H), 2.00-1.89 (m), 1.86-1.77 (m), 1.69-1.62 (m) 1.60-1.45 (m), 1.39-1.11 (m), and 0.98-0.87 (m).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.8, 78.2, 76.8, 41.9, 41.86, 33.3, 33.0, 32.5, 32.4, 31.4, 31.1, 31.0, 30.5, 30.26, 30.17, 28.4, 19.8, 19.7, 18.9, 18.6, 17.5, 17.4, and 17.0. (only resonances that are >10% of the intensity of the tallest are reported here).

Synthesis of carvomenthide-based polyol 8_{PCM-18}

A glass pressure vessel was charged with a 18:1 molar ratio of a mixture of trans- and cis-carvomenthide (**7**, 6.0 g, 35 mmol) and distilled diethanolamine (**3**, 0.21 g, 2.0 mmol) under a nitrogen atmosphere in a glove box. A solution of distilled tin(II) octoate (57 mg, 0.14 mmol) dissolved in anhydrous toluene (1.1 mL) was added. The vessel was closed and removed from the glove box. The reaction mixture was stirred and heated in an oil bath maintained at 140 ºC for 72 h and then cooled to room temperature. Pentane (7 mL) was added, the resulting mixture was triturated for several minutes, and the top pentane layer was removed via a pipette. This pentane washing procedure was repeated three times. The resulting viscous liquid was dissolved in anhydrous methylene chloride (3 mL) and added dropwise to pentane (30 mL) that was being magnetically stirred at ambient temperature. Stirring was stopped after ca. 30 min and the resulting suspension was allowed to settle for ca. 1 h. The top transparent layer was carefully separated from the denser bottom layer; the latter was dried under vacuum (several hours at ambient temperature) to afford polyol $\mathbf{8}_{PCM-18}$ (4.8 g, 75%) as a viscous liquid. This sample contained ca. 10% of the unreacted monomer **7**.

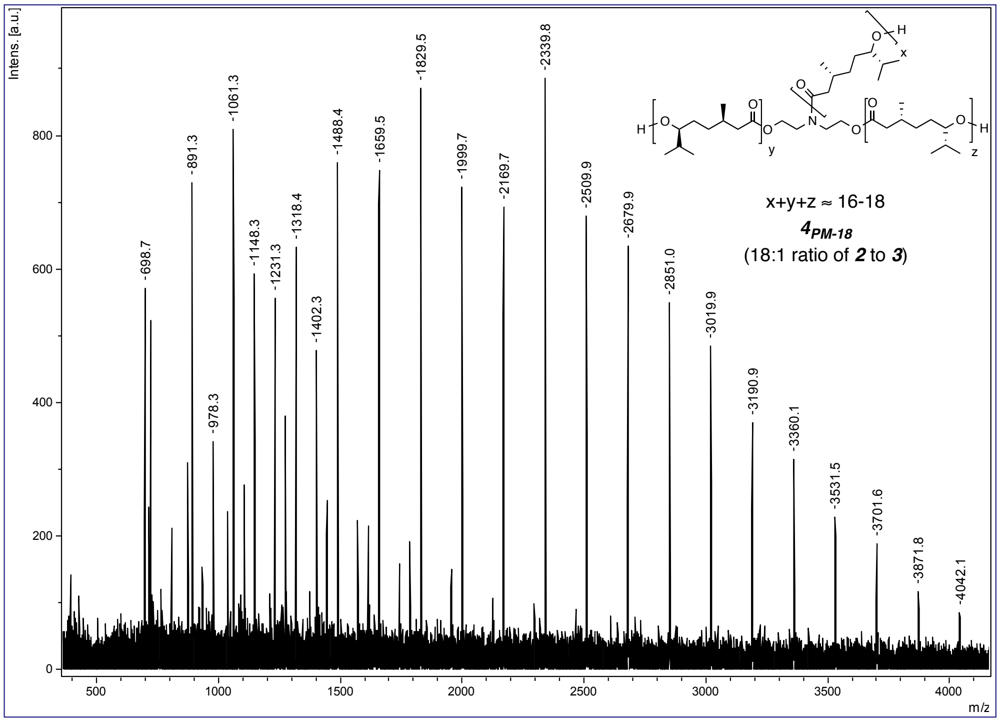
Spectral data for 8_{PCM-18}:

^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.91-4.79 (m), 4.29-3.93 (m), 3.82-3.72 (m), 3.68-3.42 (m), 2.31-2.20 (m), 2.16-2.08 (m), 1.80-1.66 (m), 1.63-1.53 (m), 1.51-1.12 (m), and 0.90-0.82 (m).

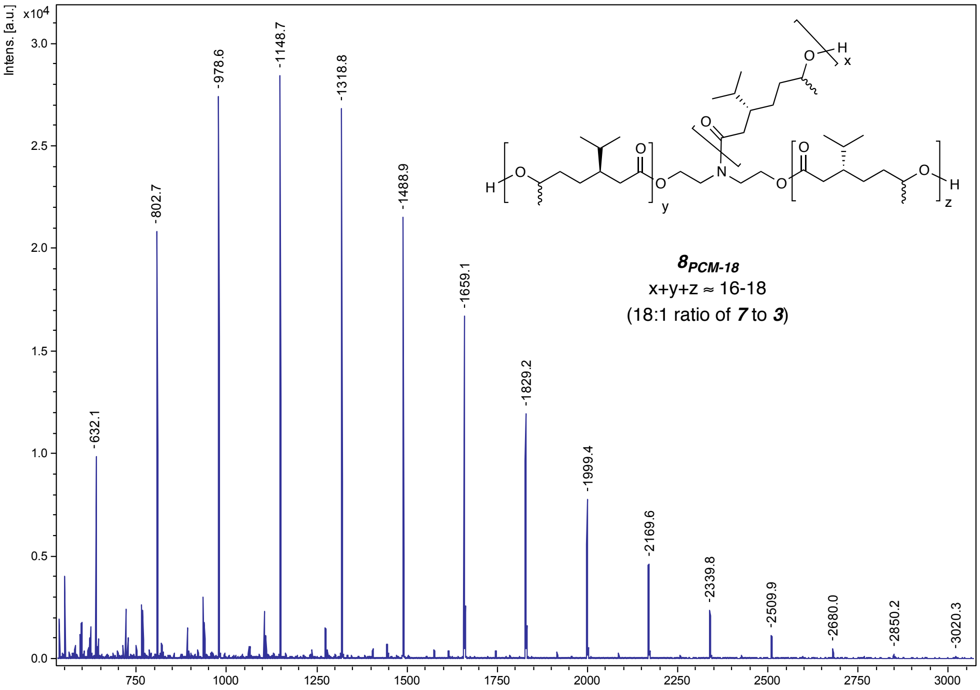
^{13}C-NMR (75 MHz, $CDCl_3$) δ 173.4, 70.8, 40.7, 40.6, 40.5, 40.4, 36.8, 36.2, 33.4, 29.7, 29.6, 29.5, 26.5, 26.4, 23.4, 19.88, 19.85, 19.3, 19.2, 19.1, 18.6, 18.5, and 18.4. (only resonances that are >10% of the intensity of the tallest are reported here.)

MALDI-MS characterization data for each of the two higher MW polyols (i.e., 4_{PM-18} and 8_{PCM-18}). p S10

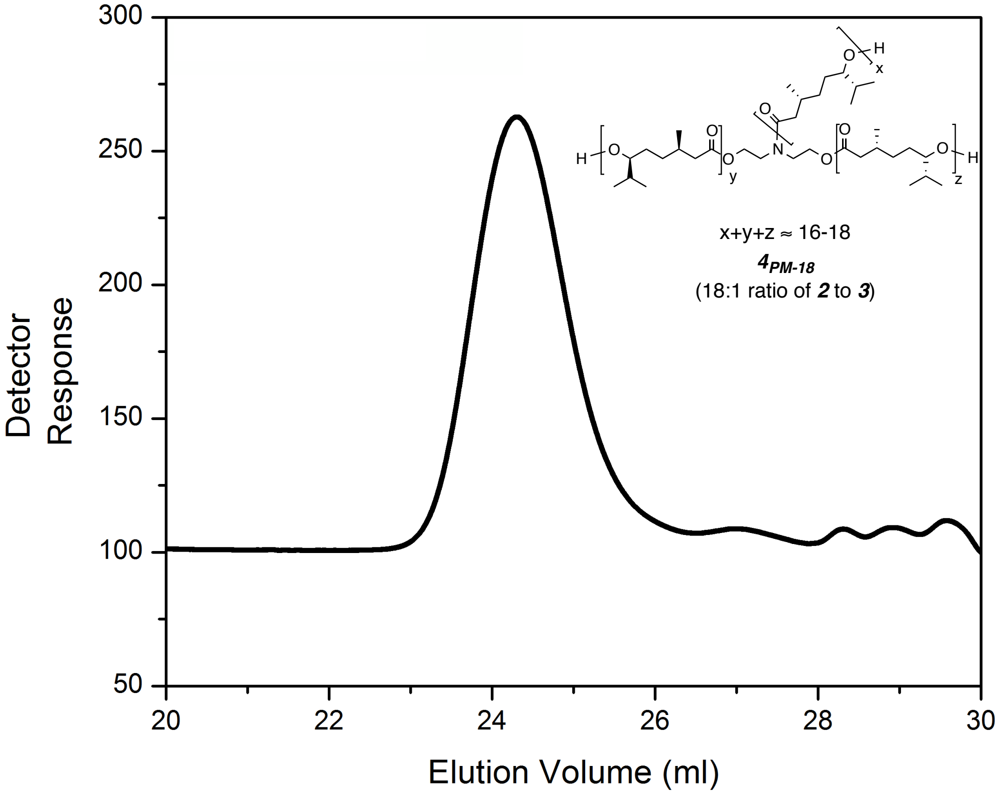
MALDI-4_{PM-18}



MALDI-8_{PCM-18}



GPC characterization data for each of the two higher MW polyols (i.e., $4_{PM\text{-}18}$ and $8_{PCM\text{-}18}$). pp S11-S12


GPC-$4_{PM\text{-}18}$

GPC-8_{PCM-18}

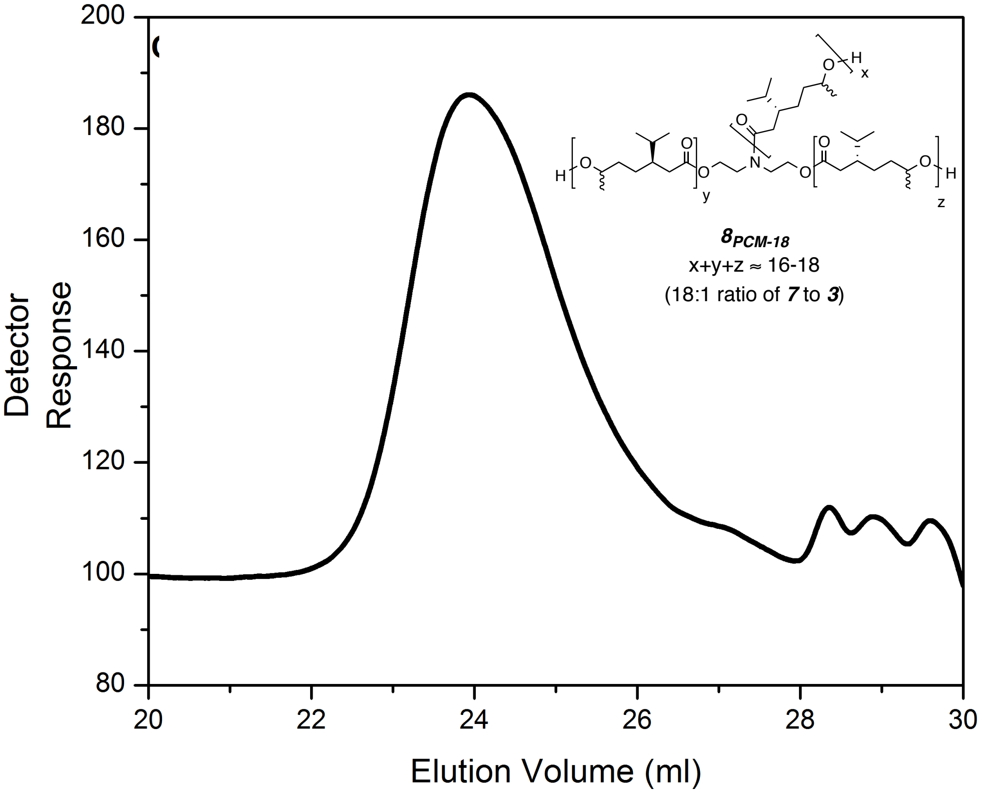
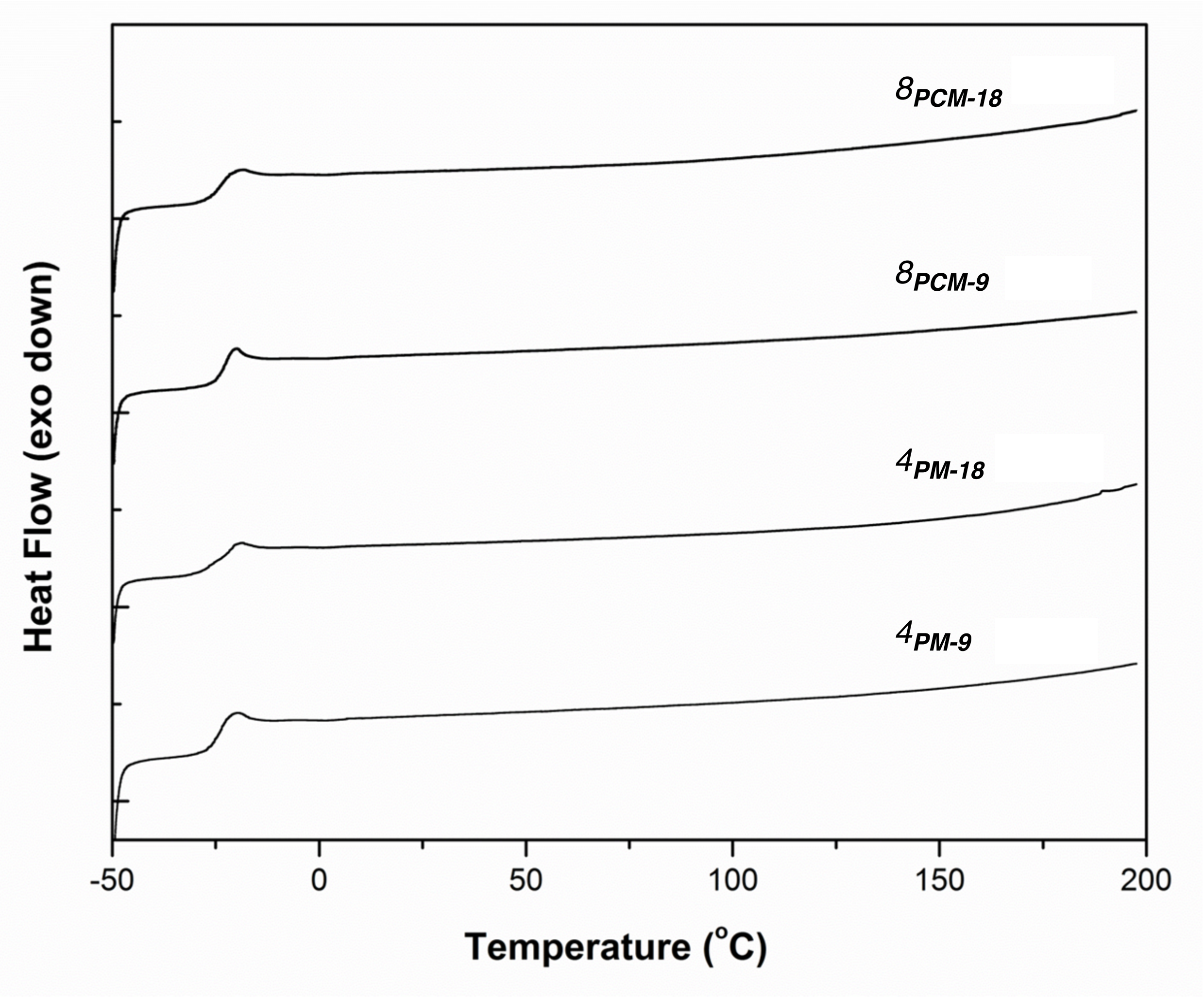

200
180
160
140
120
100
80
Detector Response
20
22
24
26
28
30
Elution Volume (ml)
H
O
O
O
N
O
O
O
H
O
H
x
y
z
8_{PCM-18}
x+y+z ≈ 16-18
(18:1 ratio of 7 to 3)

Figure S1. Differential scanning calorimetry (DSC) data for the lower and the higher molar mass polyols **4**$_{\mathrm{PM}}$ and **8**$_{\mathrm{PCM}}$.



Protocol for NMR-based determination of molar mass of polyols 4 and 8

We used the following procedure to calculate the molar mass of each polyol. It corrects for the incomplete initiation of the diethanolamine initiator. The protocol is described here for one representative sample–namely, **4**$_{\mathbf{PM\text{-}9}}$.

1. The ratio of polyols having a fully functionalized (**4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{tris}}$) vs. a non-fully functionalized (**4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$) initiator unit was determined as follows:

   Integration (Figure S2) of H1' for **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$ = 0.64
   Net integration of H1/1' for **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{tris}}$ = 3.64-0.64 = 3.00
   Molar ratio of **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{tris}}$ to **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$ = (3.00/2) : (0.64/1) = 1.50 : 0.64.
   Thus, the sample of polyol **4**$_{\mathbf{PM\text{-}9}}$ contained 30% of **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$.

2. The molar mass of **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$ was calculated as:

   $[1+(H_n/H_e)]\bullet 2\bullet$(MW of monomer **2)** + (MW of initiator **3**) = $(1 + 6.09/3)\bullet 2\bullet 170 + 105 = 1140$

3. The molar mass of **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{tris}}$ was calculated as:

   $[1+(H_n/H_e)]\bullet 3\bullet$(MW of monomer **2)** + (MW of initiator **3**) = $(1 + 6.09/3)\bullet 3\bullet 170 + 105 = 1650$

4. The molar mass of the sample of **4**$_{\mathbf{PM\text{-}9}}$ that comprises 30% of **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{bis}}$ and 70% **4**$_{\mathbf{PM\text{-}9\text{-}}\boldsymbol{tris}}$ is:

   $(1140\bullet 0.30) + (1650\bullet 0.70) = 340 + 1160 = 1500$

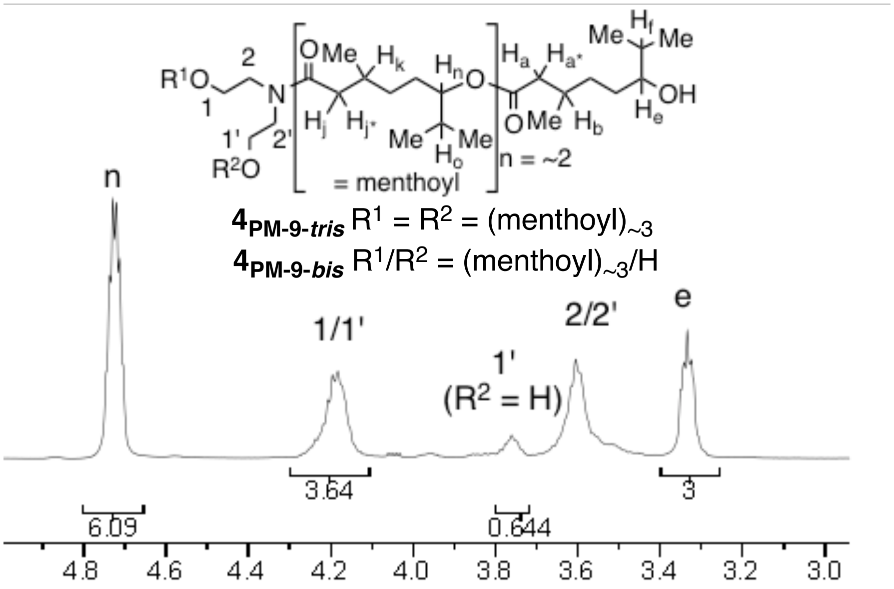
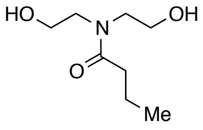


Figure S2. Region of the ^{1}H NMR spectrum of the **4**$_{\mathbf{PM\text{-}9}}$ used to determine the effective molar mass of that polyol.

Synthesis of monoamide 9a



9a

A capped vial was charged with diethanolamine (1.0 g, 9.5 mmol) in anhydrous DCM (47 mL). To the above solution was added methyl butyrate[1] (0.88 g, 8.6 mmol) and pyridine (0.7 mL, 8.4 mmol). The latter mixture was heated at 70 ºC overnight. Upon completion the reaction mixture was cooled to room temperature and the solvent was evaporated. The resulting crude material was passed through a plug of silica gel buffered with triethylamine (2% in hexane) and eluted with EtOAc to yield the monoamide **9a** (350 mg) as a transparent oil.

Spectral data for **9a**:

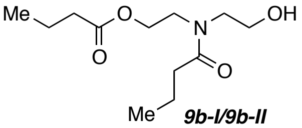
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (t, 2H, J = 4.7 Hz, CH_2OH), 3.80 (t, 2H, J = 4.9 Hz, CH_2OH), 3.57 (t, 2H, J = 5.2 Hz, CH_2N), 3.51 (t, 2H, J = 5.4 Hz, CH_2N), 3.33 (bs, 1H, O*H*), 3.21 (bs, 1H, O*H*), 2.39 (t, 2H, J = 7.4 Hz, CH_2C=O), 1.68 (sextet, 2H, J = 7.6 Hz, CH_2Me), and 0.96 (t, 2H, J = 7.4 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 61.9, 60.9, 52.1, 50.4, 35.5, 18.6, and 13.9.

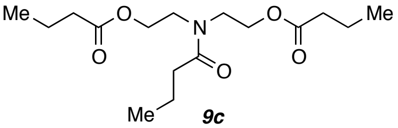
IR (neat) 3391, 2935, 2875, 1616, 1471, 1422, 1207, 1070, and 913 cm^{-1}.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_8H_{17}NO_3Na]^+$ 198.1101, found 198.1096.

Synthesis of monoester 9b-I/9b-II and diester 9c.



9b-I/9b-II



9c

Butyric anhydride (1.9 mL, 11.8 mmol) and pyridine (1.1 mL, 13.1 mmol) were added to a Teflon sealed tube charged with diethanolamine (0.7 g, 6.6 mmol) and anhydrous DCM (33 mL). The resulting solution was stirred at room temperature for 6 h and the reaction mixture was subjected to rotary evaporation. The ^{1}H NMR spectrum of the resulting crude material revealed an ca. 3:1 mixture of the monoester **9b** and diester **9c**. This mixture was purified via MPLC using hexane:ethyl acetate (2:1) to afford the monoester **9b-I/9b-II** (0.63 g) and the diester **9c** (0.56 g) as colorless oils.

Spectral data for 9b-I/9b-II (ca. 2:1 ratio):

^{1}H NMR (500 MHz, $CDCl_3$) (Major rotamer): δ 4.21 (t, 2H, J = 5.9 Hz, CH_2O_2C), 3.782 (t, 2H, J = 5.1 Hz, CH_2OH), 3.618 (t, 2H, J = 5.9 Hz CH_2N), 3.58 (t, 2H, J = 5.3 Hz, CH_2N), 2.376 [t, 2H, J = 7.3 Hz, CH_2C(=O)N], 2.307 [t, 2H, J = 7.4 Hz, CH_2C(=O)O], 1.692 (sextet, 2H, J = 7.4 Hz, CH_2Me), 1.656 (sextet, 2H, J = 7.4 Hz, CH_2Me), 0.978 (t, 3H, J = 7.4 Hz, CH_3), and 0.956 (t, 3H, J = 7.4 Hz, CH_3); (Minor rotamer): δ 4.27 (t, 2H, J = 5.6 Hz, CH_2O_2C), 3.779 (t, 2H, J =

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[1] Westaway, K. C.; Lai, Z. G. *Can. J. Chem.* **1988**, *66*, 1263-1271.

5.9 Hz, C*H*$_2$OH), 3.623 (t, 2H, *J* = 5.6 Hz, C*H*$_2$N), 3.51 (t, 2H, *J* = 5.5 Hz, C*H*$_2$N), 2.367 [t, 2H, *J* = 7.5 Hz, C*H*$_2$C(=O)N], 2.292 [t, 2H, *J* = 7.4 Hz, C*H*$_2$C(=O)O], 1.648 (sextet, 2H, *J* = 7.4 Hz, C*H*$_2$Me), 1.663 (sextet, 2H, *J* = 7.4 Hz, C*H*$_2$Me), 0.956 (t, 3H, *J* = 7.4 Hz, C*H*$_3$), and 0.948 (t, 3H, *J* = 7.4 Hz, C*H*$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ 175.3, 174.1, 173.5, 173.3, 62.1, 61.5, 60.4, 50.9, 50.0, 47.7, 45.5, 36.0, 35.9, 35.1, 34.9, 18.61, 18.57, 18.25, 18.22, 13.8, and 13.6.

IR (neat) 3413, 2963, 2876, 1736, 1624, 1462, 1421, 1176, 1075, and 748 cm^{-1}.

HRMS (ESI) (m/z): [M+Na]$^+$ calculated for [C$_{12}$H$_{23}$NO$_4$Na]$^+$ 268.1519, found 268.1547.

Spectral data for 9c:

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.22 (t, 2H, *J* = 5.6 Hz, C*H*$_2$O$_2$C), 4.20 (t, 2H, *J* = 5.9 Hz, C*H*$_2$O$_2$C), 3.62 (t, 2H, *J* = 5.7 Hz, C*H*$_2$N), 3.61 (t, 2H, *J* = 6.1 Hz, C*H*$_2$N), 2.34 [t, 2H, *J* = 7.3 Hz, C*H*$_2$C(=O)N], 2.30 [t, 2H, *J* = 7.3 Hz, C*H*$_2$C(=O)O], 2.28 [t, 2H, *J* = 7.5 Hz, C*H*$_2$C(=O)O], 1.674 (sextet, 2H, *J* = 7.4 Hz, C*H*$_2$Me), 1.650 (sextet, 2H, *J* = 7.4 Hz, C*H*$_2$Me), 1.644 (sextet, 2H, *J* = 7.4 Hz, C*H*$_2$Me), 0.96 (t, 3H, *J* = 7.3 Hz, C*H*$_3$), 0.95 (t, 3H, *J* = 7.3 Hz, C*H*$_3$), and 0.94 (t, 2H, *J* = 7.4 Hz, C*H*$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ 173.32, 173.30, 173.22, 62.0, 61.5, 47.1, 45.2, 35.9, 35.8, 34.8, 18.5, 18.24, 18.20, 13.8, and 13.6.

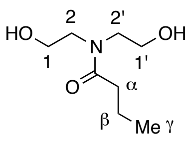
IR (neat) 2964, 1738, 1649, 1468, 1176, 913, and 746 cm^{-1}.

HRMS (ESI) (m/z): [M+Na]$^+$ calculated for [C$_{16}$H$_{29}$NO$_5$Na]$^+$ 338.1938, found 338.1923.

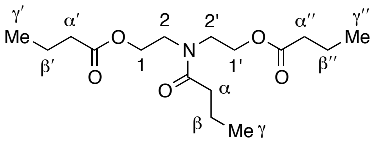
Interpretation of ^{1}H NMR data for the model compounds 9a-c

The two amide rotamers for each of the symmetrical compounds **9a** and **9c** are degenerate (and, therefore, equally populated). The former, a monoamide diol, gives rise to seven distinct sets of proton resonances. The latter, a monoamide diester, shows 13 unique resonances, albeit some having nearly identical proton chemical shifts. The unsymmetrical monamide/monoester **9b-I/9b-II** comprises a pair of energetically non-degenerate (and, therefore, non-equally populated–an ca. 2:1 ratio) rotamers. Twenty chemically distinct sets of protons (16 methylene pairs and 4 methyl groups) are present in the spectrum of this pair of rotamers, and all but two sets were identifiable. With respect to understanding the spectra of the deithanolamine-initiated polyol **4** (and **8**), the most essential points taken from the chemical shifts observed for this set of model amide/alcohol/esters are: i) slow amide rotation leads to a doubling of the resonances for each of the otherwise identical set of methylene or methyl protons, ii) esterified methylene protons in the initiator moiety (H1 and H1’) have chemical shifts in the range of δ 4.20-4.30 ppm, iii) amido-bearing methylene protons in the initiator moiety (H2 and H2’) have chemical shifts in the range of δ 3.50-3.65 ppm, and iv) free carbinol methylene protons in the initiator moiety (H1 and H1’) have chemical shifts in the range of δ 3.75-3.90 ppm.

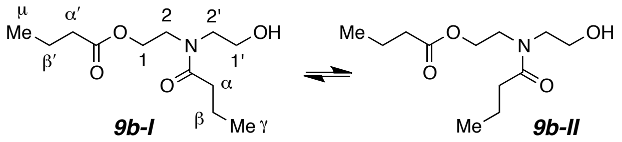
Table S1. Proton NMR data and assignments for the model butanoylated amide/esters **9a-9c**. The two amide rotamers are of identical energy for the symmetrical diol **9a** and diester **9c**, but are unequally populated for the mono-ester **9b-I/9b-II**.



9a



9c



9b-I ***9b-II***

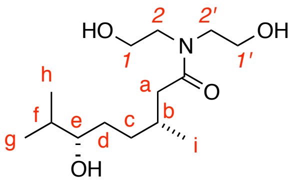
		major	minor	
Proton #	**9a**	**9b-I** or **9b-II**	**9b-I** or **9b-II**	**9c**
1 / 1’	3.87/3.80	4.21/3.782	4.27/3.779	4.22/4.20
2 / 2’	3.57/3.51	3.618/3.58	3.623/3.51	3.62/3.61
α	2.39	2.307[a]	2.292[d]	2.28[g]
β	1.68	1.656[b]	1.648	1.644[h]
γ	0.96	0.956[c]	0.948[f]	0.94[i]
α’/α”		2.376[a]	2.367[d]	2.34[g]/2.30[g]
β’/β”		1.692[b]	1.663[e]	1.674[h]/1.650[h]
γ’/γ”		0.978[c]	0.956[f]	0.95[i]/0.96[i]

[a-i] The assignments of resonances carrying the same lettered superscript are uncertain with respect to one another.

Synthesis of model amide esters 10a-c derived from diethanolamine (3) and menthide (2)

In a typical experiment, the appropriate quantities of diethanolamine (1 equiv) and lactone (3 equiv) were weighed directly into a culture tube. The vessel was then sealed and heated for 2-4 hours (conversion was monitored by LC/MS). The crude reaction mixture was loaded directly onto an MPLC column and eluted with ethyl acetate containing 1% methanol. The compounds eluted in the following order and had the indicated composition: unreacted lactone (~30-45%), the monoamide diester (~5-10%), the monoamide monoester (~20-25%), and the monoamide diol (~20-25%).

Spectral data for monoamide 10a



10a

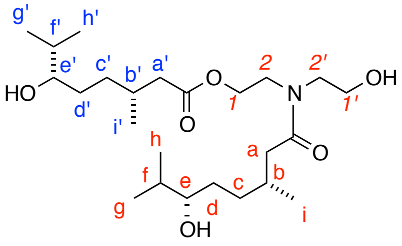
^{1}H NMR (500 MHz, CDCl$_3$) δ 3.81 (ddd, *J* = 11.0, 6.8, 3.7 Hz, 1H, H1), 3.77 (ddd, *J* = 11.6, 5.9, 3.9 Hz, 1H, H1*), 3.74 (br t, *J* = 5.1 Hz, 2H, H1'), 3.56 (ddd, *J* = 14.2, 5.7, 3.7 Hz, 1H, H2), 3.54 (ddd, *J* = 15.2, 5.2, 5.2 Hz, 1H, H2*), 3.48 (ddd, *J* = 14.2, 6.8, 3.9 Hz, 1H, H2'), 3.43 (ddd, *J* = 15.1, 5.2, 5.2 Hz, 1H, H2'*), 3.27 (ddd, *J* = 7.9, 5.2, 2.6 Hz, 1H, H_e), 2.36 (dd, *J* = 15.0, 7.6 Hz, 1H, H_a), 2.26 (dd, *J* = 15.0, 6.5 Hz, 1H, H_{a*}), 2.08-1.99 (m, 1H, H_b), 1.63 (dqq, *J* = 6.8, 6.8, 6.8 Hz, 1H, H_f), 1.56-1.52 (m, 2H, H_c/H_d), 1.33-1.24 (m, 1H, H_{c*}), 1.15-1.08 (m, 1H, H_{d*}), 0.94 (d, *J* = 6.8 Hz, 3H, H_i), 0.89 (d, *J* = 6.8 Hz, 3H, H_h), and 0.88 (d, *J* = 6.8 Hz, 3H, H_g). Proton assignments were based upon and/or are consistent with the COSY spectral data (copy provided below).

^{13}C NMR (125 MHz, CDCl$_3$) δ 175.0, 77.2, 60.9, 60.7, 52.4, 50.5, 41.1, 33.9, 33.5, 31.8, 31.0, 20.4, 19.0, and 17.5.

IR (neat): 3550-3250, 2956, 2874, 1617, 1465, 1421, and 1054.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{14}H_{29}NO_4Na]^+$ 298.1989, found 298.1959.

Spectral data for monoester 10b



10b

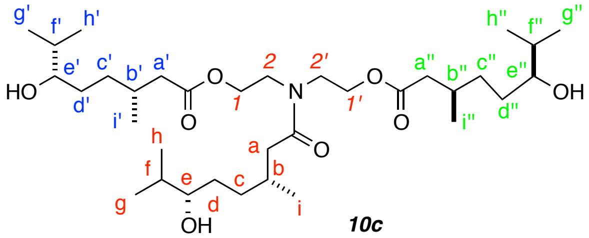
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.25 (ddd, *J* = 11.1, 5.6, 5.6 Hz, 1H, H1), 4.21 (ddd, *J* = 11.1, 5.9, 5.9 Hz, 1H, H1*), 3.77+ (ddd, *J* = 12.1, 5.6, 5.6 Hz, 1H, H1'), 3.77- (ddd, *J* = 12.1, 5.8, 5.8 Hz, 1H, H1'*), 3.70-3.46 (m, 4H, H2/H2*/H2'/H2'*), 3.32+ (ddd, *J* = 8.6, 5.2, 2.6 Hz, 1H, $H_{e'}$), 3.32- (ddd, *J* = 8.6, 5.2, 2.7 Hz, 1H, H_e), 2.39 (dd, *J* = 15.1, 6.7 Hz, 1H, H_a), 2.30, (dd, *J* = 14.9, 6.7 Hz, 1H, $H_{a'}$), 2.26 (dd, J = 15.5, 7.5 Hz, 1H, $H_{a'*}$), 2.20, (dd, J = 15.8, 7.3 Hz, 1H, H_{a*}), 2.10-2.02 (m, 1H, H_b), 1.99-1.91 (m, 1H, $H_{b'}$), 1.68-1.61 (m, 2H, $H_f/H_{f'}$), 1.60-1.49 (m, 4H, $H_c/H_d/H_{c'}/H_{d'}$), 1.38-1.25 (m, 2H, $H_{c*}/H_{c'*}$), 1.23-1.12 (m, 2H, $H_{d*}/H_{d'*}$), 0.98 (d, J = 6.6 Hz, 3H, $H_{i'}$), 0.96 (d, J = 6.7 Hz, 3H, H_i), 0.92 (d, J = 6.8, 6H, H_g, $H_{g'}$), and 0.91 (d, J = 6.9 Hz, 6H, $H_h/H_{h'}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 173.7, 173.2, 173.0, 77.0, 76.8, 76.7, 62.3, 61.6, 61.2, 60.2, 51.0, 49.5, 47.9, 45.8, 41.82, 41.76, 40.5, 40.4, 33.64, 33.61, 33.6, 33.4, 33.1, 31.7, 31.64, 31.60, 31.55, 30.9, 30.69, 30.67, 30.62, 20.3, 20.2, 19.99, 19.94, 18.97, 18.94, 17.35, 17.29, and 17.24.

IR (neat) 3600-3200 (OH), 2957, 2873 (NH), 1734 (ester CO), 1623 (amide CO), 1461, 1419, 1383 (OH), 1201, 1201, 1163, 1058, and 999 cm^{-1}.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{14}H_{47}NO_6Na]^+$ 468.3295, found 468.3345.

Spectral data for diester 10c



10c

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22 (t, J =5.6 Hz, 2H, H1/H1*), 4.21 (dd, J = 11.6, 5.8 Hz, 1H, H1'), 4.18 (dd, J = 11.7, 5.9 Hz, 1H, H1'*), 3.61 (t, J = 5.6 Hz, 4H, H2/H2'/H2*/H2'*), 3.36-3.28 (m, 3H, $H_e/H_{e'}/H_{e''}$), 2.39 (dd, J = 15.1, 6.7 Hz, 1H, H_a), 2.34 (dd, J = 14.9, 6.7 Hz, 1H, $H_{a'}/H_{a''}$), 2.24 (dd, J = 15.5, 7.5 Hz, 1H, $H_{a'*}$), 2.21 (dd, J = 15.8, 7.3 Hz, 1H, $H_{a''*}$), 2.18 (dd, J = 15.8, 7.3 Hz, 1H, H_{a*}), 2.10-2.02 (m, 1H, H_b), 1.98-1.89 (m, 2H, $H_{b'}/H_{b''}$), 1.68-1.62 (m, 3H, $H_f/H_{f'}/H_{f''}$), 1.59-1.48 (m, 6H, $H_c/H_d/H_{c'}/H_{d'}/H_{c''}/H_{d''}$), 1.38-1.27 (m, 3H, $H_{c*}/H_{c'*}/H_{c''*}$), 1.22-1.12 (m, 3H, $H_{d*}/H_{d'*}/H_{d''*}$), 0.96 (d, J = 6.6 Hz, 3H, $H_{i'}$), 0.95 (d, J = 6.7 Hz, 3H, H_i), 0.92 (d, J = 6.8, 9H, H_g, $H_{g'}$, $H_{g''}$), and 0.91 (d, J = 6.9 Hz, 9H, H_h, $H_{h'}$, $H_{h''}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 173.1, 173.0, 77.2, 76.93, 76.88, 62.1, 61.6, 47.3, 45.4, 41.8, 41.7, 40.5, 33.7, 33.66, 33.63, 33.23, 33.21, 31.8, 31.7, 31.6, 30.75, 30.71, 31.66, 20.3, 20.1, 20.0, 19.1, 19.0, 17.34, 17.30, and 17.27.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{34}H_{65}NO_8Na]^+$ 638.4602, found 638.4630.

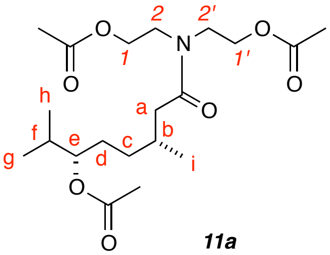
Discussion of additional details associated with the interpretation of ^{1}H NMR data for the model compounds 10a-c.

General features are: i) overlapping resonances arising from the diastereotopic sets of protons alpha to the amide moiety are centered at δ 2.39, δ 2.18 (H_a, H_{a*}), and those from the ester range between δ 2.34-2.21 ($H_{a'}$, $H_{a*'}$ and $H_{a''}$, $H_{a*''}$). ii) broad multiplets ranging between δ 2.10-2.03 (H_b) and 1.99-1.91 ($H_{b'}$ and $H_{b''}$) result from the β-methine protons embedded in different environments iii) diastereotopic protons γ and δ to the carbonyls give rise to the overlapping multiplets ranging between δ 1.59-1.48 (H_c-$H_{c''}$, H_d-$H_{d''}$), 1.38-1.27 (H_{d*}-$H_{d*''}$), and 1.22-1.12 (H_{c*}-$H_{c*''}$). iv) isopropyl methine protons lead to the overlapping resonances ranging from δ 1.68–1.62 (H_f-$H_{f''}$). v) and methyl protons in the backbone give rise to the resonances ranging from δ 0.91-0.96.

Acetylation of amide alcohols.

In a typical experiment the isolated model triol (~50 mg) was dissolved in pyridine and acetic anhydride (1:1, 0.5 mL). The reaction mixture was stirred at rt for 30 minutes and then partitioned between water and ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by MPLC (ca. 1:1 Hexanes:EtOAc) to give the acetylated derivatives (yields ca. 80%).

Spectral data for monoamide triacetate 11a



11a

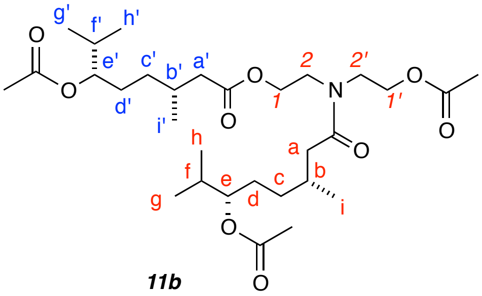
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (dddd, *J* = 13.8, 11.7, 4.7, 4.7 Hz, 1H, H$_e$), 4.21+ (dt, *J* = 11.3, 5.7 Hz, 1H, H1), 4.21- (dt, *J* = 11.3, 5.6 Hz, 1H, H1'), 4.18+ (dt, *J* = 11.6, 6.1 Hz, 1H, H1*), 4.18- (dt, *J* = 11.6, 5.9 Hz, 1H, H1'*), 3.61 (brt, *J* = 5.5 Hz, 2H, H2/H2*), 3.60 (brt, *J* = 6 Hz, 2H, H2'/H2'*), 2.31 (dd, *J* = 15.1, 5.5 Hz, 1H, H$_a$), 2.18 (dd, *J* = 15.1, 8.2 Hz, 1H, H$_{a*}$), 2.08 (s, 3H, $–O_2CCH_3$), 2.06 (s, 3H, $–O_2CCH_3$), 2.05 (s, 3H, $–O_2CCH_3$), 2.04-1.98 (m, 1H, H$_b$), 1.81 (dsept, *J* = 6.6 Hz, 1H, H$_f$), 1.59 (dddd, *J* = 13.8, 11,7, 4.7, 4.7 Hz, 1H, H$_d$), 1.49 (dddd, *J* = 13.6, 11.4, 8.5, 4.7 Hz, 1H, H$_{d*}$), 1.35 (dddd, *J* = 13.3, 11.8, 5.0, 5.0, 1H, H$_c$), 1.14 (dddd, *J* = 13.0, 11.4, 7.9, 4.9 Hz, 1H, H$_{c*}$), 0.94 (d, *J* = 6.6 Hz, 3H, H$_i$), 0.89 (d, *J* = 6.8 Hz, 3H, H$_g$), and 0.885 (d, *J* = 6.8 Hz 3H, H$_h$).Proton assignments were based upon and/or are consistent with the COSY spectral data (copy provided below).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 171.3, 171.0, 170.8, 78.8, 62.5, 62.0, 47.5, 45.7, 40.4, 33.1, 31.5, 30.6, 29.0, 21.4, 21.1, 21.0, 20.1, 18.8, and 17.7.

IR (neat) 2960, 1738, 1646, 1460, 1421, 1371, 1236, 1047, and 1027 cm^{-1}.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{20}H_{35}NO_7Na]^+$ 424.2305, found 424.2311.

Spectral data for monoester triacetate 11b



11b

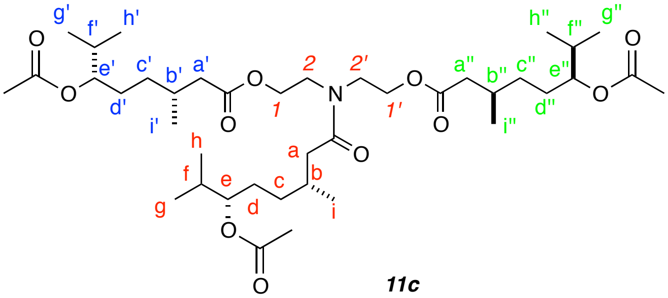
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74-4.68 (m, 2H, H$_e$/H$_{e'}$), 4.21 (ddd, *J* = 5.7, 5.7, 2.2, 2H, H1/H1*), 4.18 (ddd, *J* = 6.3, 6.3, 2.8, 2H, H1'/H1'*), 3.66-3.54 (m, 4H, H2/H2*/H2'/H2*), 2.32 (dd, *J* = 15.0, 5.7 Hz, 1H, H$_a$), 2.31 (dd, *J* = 15.1, 5.7 Hz, 1H, H$_{a'}$), 2.18 (dd, *J* = 15.0, 8.4 Hz, 1H, H$_{a*}$), 2.12 (dd, *J* = 15.1, 8.4 Hz, 1H, H$_{a'*}$), 2.05 (2, 9H, $-CO_2CH_3$), 2.04-1.98 (m, 1H, H$_b$), 1.95-1.88 (m, 1H, $H_{b'}$), 1.85-1.77 (m, 2H, $H_f/H_{f'}$), 1.63-1.53 (m, 2H, $H_d/H_{d'}$), 1.52-1.44 (m, 2H, $H_{d*}/H_{d'*}$), 1.40-1.25 (m, 2H, $H_c/H_{c'}$), 1.22-1.11 (m, 2H, $H_{c*}/H_{c'*}$), 0.94 (d, J = 6.6 Hz, 3H, H_i), 0.93 (d, J = 6.6 Hz, 3H, $H_{i'}$), 0.89 (d, J = 6.8 Hz, 6H, $H_g/H_{g'}$), and 0.88 (d, J = 6.8 Hz, 6H, $H_h/H_{h'}$)

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.92, 172.87, 172.8, 171.2, 171.14, 171.13, 170.9, 170.7, 78.7, 78.6, 78.5, 62.4, 62.2, 61.9, 61.7, 47.42, 47.40, 45.70, 45.65, 41.6, 41.5, 40.31, 40.27, 33.0, 32.99, 32.6, 31.4, 31.3, 30.6, 30.5, 30.43, 30.41, 28.92, 28.91, 28.6, 21.2, 21.0, 20.9, 19.98, 19.97, 19.8, 18.75, 18.72, and 17.6.

IR (neat) 2960, 2876, 1733, 1649, 1460, 1419, 1372, 1240, 1048, and 1022 cm^{-1}.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{30}H_{53}NO_9Na]^+$ 594.3612, found 594.3645.

Spectral data for diester triacetate 11c



11c

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74-4.68 (m, 3H, $H_e/H_{e'}/H_{e''}$), 4.20 (app q, J = 5.8 Hz, 2H, H1/H1*), 4.18 (app q, J = 6 Hz, 2H, H1'/H1'*), 3.61 (t, J = 5.8 Hz, 2H, H2/H2*), 3.60 (app q, J = 6.1 Hz, 2H, H2'/H2'*), 2.32 (dd, J = 15.1, 5.6 Hz, 1H, H_a), 2.306 (dd, J = 15.1, 5.5 Hz, 1H, $H_{a'}$), 2.301 (dd, J = 15.1, 5.5 Hz, 1H, $H_{a''}$), 2.18 (dd, J = 15.1, 8.4 Hz, 1H, H_{a*}), 2.10 (dd, J = 15.1, 8.5 Hz, 1H, $H_{a'*}$), 2.09 (dd, J = 15.0, 8.5 Hz, 1H, $H_{a''*}$), 2.05 (s, 9H, $–O_2CCH_3$), 2.04-1.97 (m, 1H, H_b), 1.96-1.88 (m, 2H, $H_{b'}/H_{b''}$), 1.86-1.77 (m, 3H, $H_f/H_{f'}/H_{f''}$), 1.63-1.53 (m, 3H, $H_d/H_{d'}/H_{d''}$), 1.52-1.43 (m, 3H, $H_{d*}/H_{d'*}/H_{d''*}$), 1.40-1.27 (m, 3H, $H_c/H_{c'}/H_{c''}$), 1.22-1.11 (m, 3H, $H_{c*}/H_{c'*}/H_{c''*}$), 0.94 (d, J = 6.6 Hz, 3H, H_i), 0.93 (d, J = 6.6 Hz, 6H, $H_i/H_{i''}$), 0.890 (d, J = 6.8 Hz, 9H, H_g, $H_{g'}/H_{g''}$), and 0.887 (d, J = 6.8 Hz, 9H, $H_h/H_{h'}/H_{h''}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 172.84, 172.81, 171.22, 171.18, 171.64, 78.8, 78.62, 78.59, 62.2, 61.8, 47.4, 45.7, 41.6, 41.5, 40.4, 33.1, 32.6, 31.43, 31.40, 30.6, 30.50, 30.47, 29.0, 28.7, 21.34, 21.33, 20.0, 19.9, 18.82, 18.79, and 17.6.

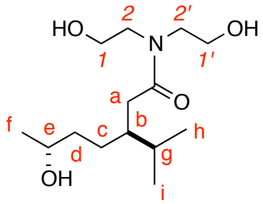
IR (neat) 2961, 2875, 1733, 1650, 1461, 1373, 1243, 1167, and 1021 cm^{-1}.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $[C_{40}H_{71}NO_{11}Na]^+$ 764.4919, found 764.4949.

The remaining compounds–S1 to S4–are unique to the SI; that is, they were not specifically shown in the manuscript.

Synthesis of model amide esters S1a-c derived from diethanolamine (3) and *cis*-carvomenthide (cis-7).

Spectral data for S1a (monoamide derived from cis carvomenthide)



S1a

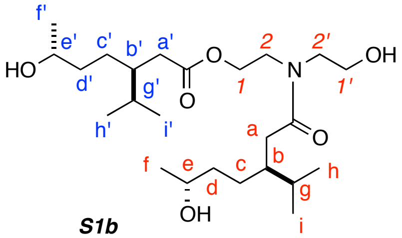
^{1}H NMR (500 MHz, CDCl$_3$) δ 3.92 (ddd, *J* = 11.0, 7.3, 3.3 Hz, 1H, H1), 3.89-3.84 (m, 1H, H$_e$), 3.81 (ddd, *J* = 11.0, 6.0, 3.5 Hz, 1H, H1*), 3.79 (t, *J* = 5.1 Hz, 2H, H1'/H1'*), 3.67 (ddd, *J* = 14.4, 6.1, 3.3 Hz, 1H, H2), 3.62 (ddd, *J* = 15.1, 5.2, 5.2 Hz, 1H, H2'), 3.46 (ddd, *J* = 14.2, 7.3, 3.4 Hz, 1H, H2*), 3.42 (ddd, *J* = 15.1, 5.0, 5.0 Hz, 1H, H2'*), 2.35 (dd, *J* = 15.5, 3.8 Hz, 1H, H$_a$), 2.26 (dd, *J* = 15.5, 9.9 Hz, 1H, H$_{a*}$), 1.99-1.93 (m, 1H, H$_b$), 1.72 (dsept, *J* = 4.3, 6.8 Hz, 1H, H$_g$), 1.50-1.34 (m, 4H, H$_c$/H$_{c*}$/H$_d$/H$_{d*}$), 1.17 (d, *J* = 7.3 Hz, 3H, H$_f$), 0.91 (d, *J* = 6.9 Hz, 3H, H$_h$), and 0.85 (d, *J* = 6.8 Hz, 3H, H$_i$).

^{13}C NMR (125 MHz, CDCl$_3$) δ 175.7, 66.9, 60.8, 60.7, 52.4, 50.6, 39.2, 36.0, 34.5, 29.6, 26.9, 23.2, 20.5, and 18.4.

IR (neat): 3530-3100, 2959, 1617, 1464, 1421, 1368, 1128, and 1055 cm^{-1}.

Exact mass calc. for [C$_{14}$H$_{29}$NO$_4$Na]$^+$ 298.1989, found 298.1996.

Spectral data for S1b (monoamide monoester derived from cis-carvomenthide)



S1b

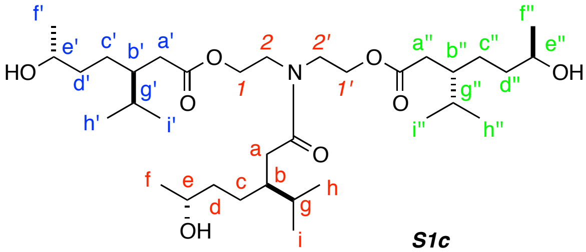
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.34-4.10 (m, 2H, H1/H1*), 3.91-3.84 (m, 1H, H2), 3.82-3.43 (m, 7H, H1'/H1'*/H2*/H2'/H2'*/H$_e$/H$_{e'}$), 2.37 (dd, *J* = 15.5, 4.0 Hz, 1H, H$_a$), 2.35 (dd, *J* = 15.5, 4.9 Hz, 1H, H$_{a'}$), 2.22 (dd, *J* = 15.5, 9.6 Hz, 1H, H$_{a*}$), 2.12 (dd, *J* = 15.3, 9.1 Hz, 1H, H$_{a'*}$), 1.97-1.91 (m, 1H, H$_b$), 1.81-1.68 (m, 3H, H$_b$/H$_g$/H$_{g'}$), 1.49-1.21 (m, 8H, H$_c$/H$_{c*}$/H$_d$/H$_{d*}$/H$_{c'}$/H$_{c'*}$/H$_{d'}$ H$_{d'*}$), 1.178 (d, *J* = 6.2 Hz, 3H, H$_f$ or H$_{f'}$), 1.176 (d, *J* = 6.2 Hz, 3H, H$_f$ or H$_{f'}$), 0.888 (d, *J* = 6.8 Hz, 3H, H$_h$ or H$_{h'}$), 0.886 (d, *J* = 6.9 Hz, 3H, H$_h$ or H$_{h'}$), 0.86 (d, *J* = 6.9 Hz, 3H, H$_i$ or H$_{i'}$), and 0.83 (d, *J* = 6.8 Hz, 3H, H$_i$ or H$_{i'}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ the spectral data for this mixture of two (inequivalently populated) rotamers is sufficiently complex that it is difficult to determine with confidence the appropriate set of resonances; a PDF copy of this spectrum is provided below.

IR (neat): 3580-3200, 2960, 1734, 1623, 1462, 1370, 1161, 1111, and 1066 cm^{-1}.

Exact mass calc. for $[C_{14}H_{47}NO_6Na]^+$ 468.3296, found 468.3294.

Spectral data for S1c (monoamide bisester derived from cis-carvomenthide)



S1c

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32-4.10 (m 4H, H1/H1*/H1’/H1’*), 3.91-3.84 (m, 1H, H_e), 3.82-3.49 (m, 6H, H2/H2*/H2’/H2’*/$H_{e'}$/$H_{e''}$), 2.343 (dd, *J* = 15.3, 5.1 Hz, 1H, H_a), 2.338 (dd, *J* = 15.5, 4.6 Hz, 1H, $H_{a'}$), 2.31 (dd, *J* = 15.1, 5.1 Hz, 1H, $H_{a''}$), 2.16 (dd, *J* = 15.9, 8.4 Hz, 1H, H_{a*}), 2.13 (dd, *J* = 15.5, 8.4 Hz, 1H, $H_{a'*}$), 2.10 (dd *J* = 15.2, 8.4 Hz, 1H, $H_{a''*}$), 1.95 (ddddd, *J* = 8.4, 8.4, 4.2, 4.2, 4.2 Hz, 1H, H_b), 1.80-1.69 (m, 5H, $H_{b'}$/$H_{b''}$/H_g/$H_{g'}$/$H_{g''}$), 1.49-1.22 (m, 12H, H_c/H_{c*}/H_d/H_{d*}/$H_{c'}$/$H_{c'*}$/$H_{d'}$/$H_{d'*}$/$H_{c''}$/$H_{c''*}$/$H_{d''}$/$H_{d''*}$), 1.182 (d, *J* = 6.2 Hz, 6H, two of H_f/$H_{f'}$/$H_{f''}$), 1.176 (d, *J* = 6.2 Hz, 3H, one of H_f/$H_{f'}$/$H_{f''}$), 0.92 (d, *J* = 6.8 Hz, 3H, H_h) 0.885 (d, *J* = 6.7 Hz, 3H, $H_{h'}$), 0.881 (d, *J* = 6.8 Hz, 3H, $H_{h''}$), 0.85 (d, *J* = 6.8 Hz, 3H, H_i, $H_{i'}$, or $H_{i''}$), 0.84 (d, *J* = 6.5 Hz, 3H, H_i, $H_{i'}$, or $H_{i''}$), and 0.82 (d, *J* = 6.2 Hz, 3H, H_i, $H_{i'}$, or $H_{i''}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ the spectral data for this mixture of two (inequivalently populated) rotamers is sufficiently complex that it is difficult to determine with confidence the appropriate set of resonances; a PDF copy of this spectrum is provided below.

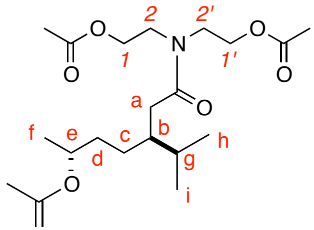
IR (neat): 3600-3300, 2960, 1735, 1631, 1461, 1370, 1275, 1159, 1113, and 1070 cm^{-1}.

Exact mass calc. $[C_{34}H_{65}NO_8Na]^+$ 638.4602, found 638.4648.

Acetate derivatives S2a-c of model amide esters S1a-c from *cis*-carvomenthide.

These tris-acetate derivatives were synthesized in analogous manner to the acetates **11a-c**, as described directly above.

Spectral data for S2a (acetylated **S1a**)



S2a

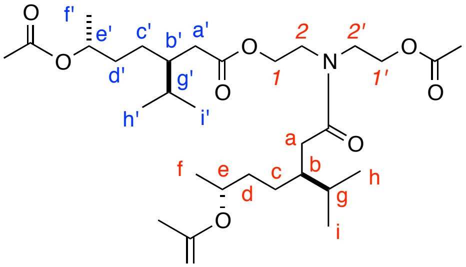
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.84 (sextet, *J* = 6.3 Hz, 1H, $\mathrm{H_e}$), 4.22 (t, *J* = 5.6 Hz, 2H, H1/H1*), 4.20 (t, *J* = 5.9 Hz, 2H, H1'/H1'*), 3.65-3.55 (4 overlapping dts, 4H, H2/H2*/H2'/H2'*), 2.32 (dd, *J* = 15.6, 5.5 Hz, 1H, $\mathrm{H_a}$), 2.15 (dd, *J* = 15.6, 7.7 Hz, 1H, $\mathrm{H_{a*}}$), 2.08 (s, 3H, -$\mathrm{O_2CCH_3}$), 2.06 (s, 3H, -$\mathrm{O_2CCH_3}$), 2.02 (s, 3H, -$\mathrm{O_2CCH_3}$), 1.91 (ddddd, *J* = 6.8, 6.8, 6.8, 5.5, 3.8 Hz, 1H, $\mathrm{H_b}$), 1.76 (dqq, *J* = 4.0, 6.8, 6.8 Hz, 1H, $\mathrm{H_g}$), 1.60 (dddd, *J* = 13.5, 11.8, 7.3, 4.8, 1H, $\mathrm{H_d}$), 1.48 (dddd, *J* = 13.7, 11.0, 5.3, 5.3 Hz, 1H, $\mathrm{H_{d*}}$), 1.34 (dddd, *J* = 13.4, 11.1, 6.4, 4.7 Hz 1H, $\mathrm{H_c}$), 1.20 (dddd, *J* = 13.4, 11.7, 6.5, 5.1 Hz, 1H, $\mathrm{H_{c*}}$), 1.20 (d, *J* = 6.3 Hz, 3H, $\mathrm{H_f}$), 0.88 (d, *J* = 6.9 Hz, 3H, $\mathrm{H_h}$), and 0.85 (d, *J* = 6.8 Hz, 3H, $\mathrm{H_i}$).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.4, 170.99, 170.98, 170.8, 71.5, 62.5, 62.1, 47.5, 45.1, 40.3, 34.3, 34.0, 29.6, 27.2, 21.6, 21.1, 21.0, 20.2, 19.6, and 18.7.

IR (neat): 2957, 1738, 1648, 1371, 1236, and 1047 cm^{-1}.

Exact mass calc. for $[\mathrm{C_{20}H_{35}NO_7Na}]^+$ 424.2306, found 424.2308.

Spectral data for S2b (acetylated **S1b**)



S2b

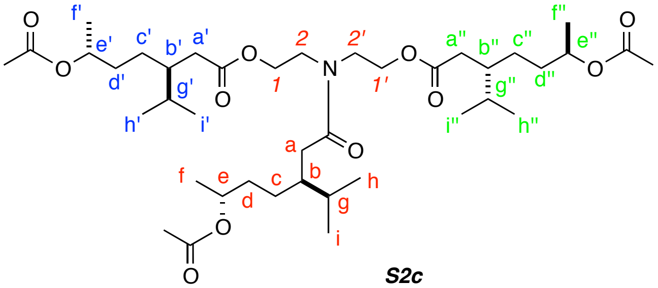
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.85 (sextet, *J* = 6.1 Hz, 1H, $\mathrm{H_e}$), 4.84 (sextet, *J* = 6.2 Hz, 1H, $\mathrm{H_{e'}}$), 4.14-4.21 (m, *4*H, H1/H1*/H1'/H1'*), 3.68-3.53 (m, 4H, H2/H2*/H2'/H2'*), 2.31 (dd, *J* = 15.2, 5.8 Hz, 1H, $\mathrm{H_a}$), 2.29 (dd, *J* = 15.6, 6.2 Hz, 1H, $\mathrm{H_{a'}}$), 2.16 (dd, *J* = 15.0, 7.7 Hz, 1H, $\mathrm{H_{a*}}$), 2.15 (dd, *J* = 15.3, 7.8 Hz, 1H, $\mathrm{H_{a'*}}$), 2.09 (s, 3H, -$\mathrm{O_2CCH_3}$), 2.03 (s, 3H, -$\mathrm{O_2CCH_3}$), 2.02 (s, 3H, -$\mathrm{O_2CCH_3}$), 1.95-1.87 (m, 1H, $\mathrm{H_b}$), 1.65-1.53 (m, 2H, $\mathrm{H_d/H_{d'}}$), 1.52-1.43 (m, 2H, $\mathrm{H_{d*}/H_{d'*}}$), 1.40-1.31 (m, 2H, $\mathrm{H_c/H_{c'}}$), 1.25-1.15 (m, 2H, $\mathrm{H_{c*}/H_{c'*}}$), 1.204 (d, *J* = 6.2 Hz, 3H, $\mathrm{H_f}$), 1.20 (d, *J* = 6.2 Hz, 3H, $\mathrm{H_{f'}}$), 0.87 (d, *J* = 6.8 Hz, 3H, $\mathrm{H_h}$), 0.86 (d, *J* = 6.6 Hz, 3H, $\mathrm{H_{h'}}$), 0.85 (d, *J* = 6.8 Hz, 3H, $\mathrm{H_i}$), and 0.83 (d, *J* = 6.7 Hz, 3H, $\mathrm{H_{i'}}$).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.74, 173.65, 173.5, 173.4, 171.0, 170.98, 170.96, 170.8, 71.48, 71.46, 71.3, 71.2, 62.4, 62.3, 62.1, 62.0, 47.51, 47.50, 45.9, 45.8, 40.72, 40.70, 40.4, 40.3, 35.9. 35.8, 34.33, 34.27, 34.0, 33.8, 33.7, 29.7, 29.63, 29.60, 27.13, 27.08, 26.98, 26.97, 26.90, 21.58, 21.57, 21.1, 21.0, 20.8, 20.1, 19.73, 19.70, 19.64, 19.60, 19.58, 18.7, 18.6, and 18.5.

IR (neat): 2958, 1734, 1649, 1371, 1243, 1050, and 753 cm^{-1}.

Exact mass calc. for [C$_{30}$H$_{53}$NO$_9$Na]$^+$ 594.3613, found 594.3626.

Spectral data for S2c (acetylated **S1c**)



S2c

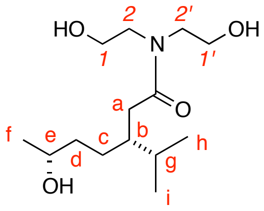
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.85 [sextets, J = 6.0 Hz, 3H, H$_e$/H$_{e'}$/H$_{e''}$], 4.23-4.15 (m, *4*H, H1/H1*/H1'/H1'*), 3.68-3.57 (m, 4H, H2/H2*H2'/H2'*), 2.36-2.26 (3H, H$_a$/H$_{a'}$/H$_{a''}$), 2.17-2.1 (3H, H$_{a*}$/H$_{a'*}$/H$_{a''*}$), 2.03 (s, 6H, -COCH$_3$), 2.02 (s, 3H, -COCH$_3$), 1.93-1.87 (m, 1H, H$_b$), 1.78-1.68 (m, 5H, H$_{b'}$/H$_{b''}$/H$_g$/H$_{g'}$/H$_{g''}$), 1.63-1.54 (m, 3H, H$_d$/H$_{d'}$/H$_{d''}$), 1.51-1.43 (m, 3H, H$_{d*}$/H$_{d'*}$/H$_{d''*}$), 1.41-1.31 (m, 3H, H$_c$/H$_{c'}$/H$_{c''}$), 1.29-1.14 (m, 3H, H$_{c*}$/H$_{c'*}$/H$_{c''*}$), 1.204 (d, J = 6.3 Hz, 6H, H$_{f'}$/H$_{f''}$), 1.20 (d, J = 6.3 Hz, 3H, H$_f$), 0.88 (d, J = 6.8 Hz, 3H, H$_h$), 0.86 (d, J = 6.6 Hz, 6H, H$_{h'}$/H$_{h''}$), 0.85 (d, J = 6.7 Hz, 3H, H$_i$). 0.833 (d, J = 6.7 Hz, 3H, H$_{i'}$), and 0.831 (d, J = 6.7 Hz, 3H, H$_{i''}$).

IR (neat): 2958, 1734, 1651, 1461, 1371, 1244, 1164, and 1022 cm^{-1}.

Exact mass calc. for [C$_{40}$H$_{71}$NO$_{11}$Na]$^+$ 764.4919, found 764.4951.

Synthesis of model amide esters S3a-c derived from diethanolamine (3) *trans*-carvomenthide (trans-7).

Spectral data for S3a (monoamide derived from *trans*-carvomenthide)



S3a

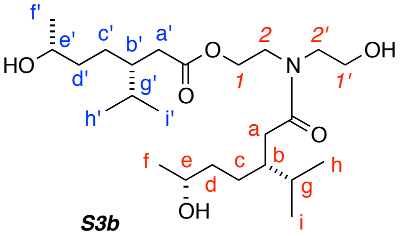
^{1}H NMR (500 MHz, CDCl$_3$) δ 3.91 (ddd, *J* = 11.3, 7.3, 3.3 Hz, 1H, H1), 3.82 (ddd, *J* = 11.3, 6.1, 3.4 Hz, 1H, H1*), 3.80 (app t, *J* = 5.1 Hz, 2H, H1'/H1'*), 3.77-3.70 (m, 1H, H_e), 3.67 (ddd, *J* = 14.2, 5.9, 3.2 Hz, 1H, H2), 3.61 (ddd, *J* = 15.1, 5.0, 5.0 Hz, 1H, H2'), 3.48 (ddd, *J* = 14.2, 7.2, 3.4 Hz, 1H, H2*), 3.45 (ddd, *J* = 15.0, 5.1, 5.1 Hz, 1H, H2'*), 2.34 (dd, *J* = 15.1, 4.4 Hz, 1H, H_a), 2.25 (dd, *J* = 15.1, 9.3 Hz, 1H, H_{a*}), 1.94 (nfom, 1H, H_b), 1.74 (dsextet, *J* = 4.2, 6.8 Hz, 1H, H_g), 1.51-1.44 (m, 1H, H_d), 1.43-1.29 (m, 3H, H_c/H_{c*}/H_{d*}), 1.17 (d, *J* = 6.2 Hz, 3H, H_f), 0.90 (d, *J* = 6.8 Hz, 3H, H_h), and 0.85 (d, *J* = 6.8 Hz, 3H, H_i). Proton assignments were based upon and/or are consistent with the COSY spectral data (copy provided below).

^{13}C NMR (125 MHz, CDCl$_3$) δ 175.7, 68.7, 60.9, 60.8, 52.5, 50.7, 41.0, 37.4, 34.9, 30.2, 27.9, 23.7, 20.0, and 18.5.

IR (neat): 3550-3200, 2959, 2873, 1617, 1464, 1420, and 1054 cm^{-1}.

Exact mass calc. for $[C_{14}H_{29}NO_4Na]^+$, 298.1989, found 298.1988.

Spectral data for S3b (monoamide monoester derived from trans carvomenthide)



S3b

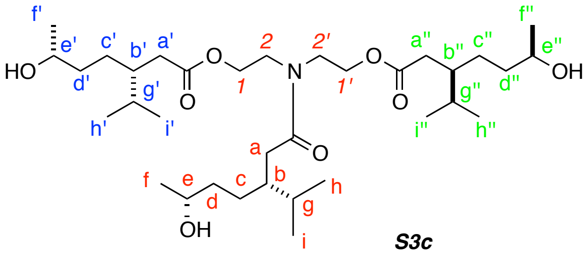
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.33-4.2 (m, 1H, H1), 4.2-4.10 (m, 1H, H1*), 3.89-3.39 (m, 8H, H1'/H1'*/H2/H2*/H2'/H2'*/H_e/$H_{e'}$), 2.36 (dd, *J* = 15.3, 4.8 Hz, 1H, H_a), 2.34 (dd, *J* = 15.4, 5.1 Hz, 1H, $H_{a'}$) 2.24 (dd, *J* = 15.2, 8.9 Hz, 1H, H_{a*}), 2.12 (dd, *J* = 15.3, 8.4 Hz, 1H, $H_{a'*}$), 1.95-1.88 (m, 1H, H_b), 1.80-1.69 (m, 3H, $H_{b'}$/H_g/$H_{g'}$), 1.51-1.3 (m, 4H, H_c/H_d/$H_{c'}$/$H_{d'}$), 1.19 (d, *J* = 6.0 Hz, 3H, $H_{\text{f or f'/minor}}$), 1.182 (d, *J* = 6.2 Hz, 3H, $H_{\text{f or f'/major}}$), 1.176 (d, *J* = 6.2 Hz, $H_{\text{f or f'/major}}$), 1.17 (d, *J* = 6.1 Hz, $H_{\text{f or f'/minor}}$), 0.92-0.82 (overlapping ds, 12H, $H_{h'}$/H_h/$H_{i'}$/H_i).

^{13}C NMR (125 MHz, CDCl$_3$) δ the spectral data for this mixture of two (inequivalently populated) rotamers is sufficiently complex that it is difficult to determine with confidence the appropriate set of resonances; a PDF copy of this spectrum is provided below. ^{13}C NMR (125 MHz, CDCl$_3$) δ 175.6, 174.4, 174.2, 174.0, 68.74, 68.67, 68.4, 68.3, 62.6, 61.7, 61.5, 60.5, 51.2, 49.9, 48.2, 46.2, 41.10, 41.08, 40.6, 37.5, 37.2, 36.1, 36.0, 34.64, 34.57, 30.1, 30.0, 29.9, 29.8, 27.84, 27.75, 23.74, 23.71, 20.0, 19.9, 19.8, 18.7, 18.5, 18.3, and 18.2.

IR (neat): 3500-3300, 2960, 2874, 1734, 1623, 1462, 1370, 1275, 1162, 1113, and 1066 cm^{-1}.

Exact mass calc. for $[C_{14}H_{47}NO_6Na]^+$, 468.3296, found 468.3315.

Spectral data for S3c (monoamide bisester derived from trans carvomenthide)



S3c

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.29 (ddd, J = 11.6, 6.8, 5.5 Hz, 1H, H1), 4.22 (t, J = 5.6 Hz, 2H, H1'/H1'*), 4.13 (ddd, J = 11.6, 5.7, 5.7 Hz, 1H, H1*), 3.8-3.7 (m, 3H, $H_e/H_{e'}/H_{e''}$), 3.66-3.58 (m, 4H, H2/H2*/H2'/H2'), 2.35 (dd, J = 15.7, 5.0 Hz, 1H, H_a), 2.33 (dd, J = 15.4, 5.1 Hz, 1H, $H_{a'}$), 2.31 (dd, J = 15.4, 5.4 Hz, 1H, $H_{a''}$), 2.18 (dd, J = 15.7, 8.3 Hz, 1H, H_{a*}), 2.133 (dd, J = 15.4, 7.8 Hz, 1H, $H_{a'*}$), 2.129 (dd, J = 15.4, 8.3 Hz, 1H, $H_{a''*}$), 1.93-1.88 (m, 1H, H_b), 1.80-1.69 (m, 5H, $H_{b'}/H_{b''}/H_g/H_{g'}/H_{g''}$), 1.49-1.29 (m, 12H, $H_c/H_{c*}/H_d/H_{d*}/H_{c'}/H_{c'*}/H_{d'}/H_{d'*}/H_{c''}/H_{c''*}/H_{d''}/H_{d''*}$), 1.183 (d, J = 6.2 Hz, 3H, $H_{f'}$), 1.181 (d, J = 6.2 Hz, 3H, $H_{f''}$), 1.17 (d, J = 6.2 Hz, 3H, H_f), 0.90 (d, J = 6.8 Hz, 3H, H_h), 0.881 (d, J = 6.7 Hz, 3H, $H_{h'}$), 0.878 (d, J = 6.7 Hz, 3H, $H_{h''}$), 0.86 (d, J = 6.8 Hz, 3H, H_i), 0.84 (d, J = 6.6 Hz, 3H, $H_{i'}$), and 0.83 (d, J = 6.7 Hz, 3H, $H_{i''}$). Proton assignments were based upon and/or are consistent with the COSY spectral data (copy provided below).

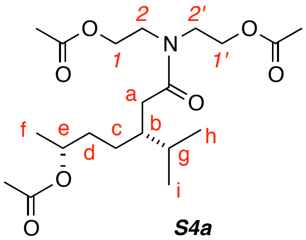
^{13}C NMR (125 MHz, CDCl$_3$) δ 174.1, 173.99, 173.97, 68.7, 68.4, 68.3, 62.2, 61.6, 47.3, 45.6, 41.0, 40.5, 37.3, 36.1, 35.9, 34.5, 30.0, 29.9, 29.8, 27.81, 27.76, 27.6, 23.79, 23.77, 23.75, 23.7, 19.92, 19.86, 19.8, 18.7, 18.6, and 18.3.

IR (neat): 3550-3250, 2960, 2874, 1734, 1630, 1461, 1370, 1274, 1160, and 1115 cm^{-1}.

Exact mass calc. for $[C_{34}H_{65}NO_8Na]^+$, 638.4602, found 638.4649.

Synthesis of acetate derivatives S4a-c of model amide/esters S3a-c from *trans*-carvomenthide.

Spectral data for S4a (acetylated **S3a**)



S4a

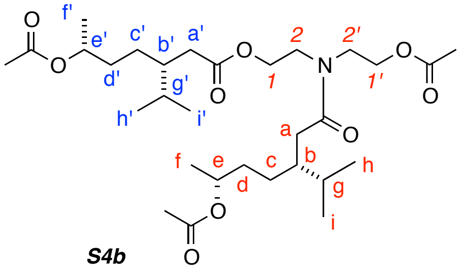
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.85 (sextet, J = 6.3 Hz, 1H, H_e), 4.21 (t, J = 5.6 Hz, 2H, H1/H1*), 4.20 (t, J = 5.9 Hz, 2H, H1'/H1'*), 3.63 (t, J = 6.6 Hz, 2H, H2'/H2'*), 3.61, (t, J = 5.9 Hz, 2H, H2/H2*), 2.33 (dd, J = 15.6, 5.6 Hz, 1H, H_a), 2.14 (dd, J = 15.6, 7.5 Hz, 1H, H_{a*}), 2.08 (s, 3H, -C1O$_2$CCH$_3$), 2.06 (s, 3H,-C1'O$_2$CCH$_3$), 2.02 [s, 3H, -R$_2$C(H)O$_2$CCH$_3$], 1.95-1.88 (m, 1H, H_b), 1.75 (dsept, J = 6.9, 4 Hz, 1H, H_g), 1.57 (dddd, J = 13.4, 11.0, 7.2, 5.3 Hz, 1H, H_d), 1.49 (dddd, J = 13.4, 10.9, 5.4, 5.4 Hz, 1H, H_{d*}), 1.34-1.2 (m, 2H, H_c/H_{c*}), 1.20 (d, J = 6.2 Hz, 3H, H_f), 0.87 (d, J = 6.9 Hz, 3H, H_h), and 0.85 (d, J = 6.9 Hz, 3H, H_i). Proton assignments were based upon and/or are consistent with the COSY spectral data (copy provided below).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.5, 170.99, 170.98, 170.9, 71.4, 62.4, 62.1, 47.5, 45.9, 40.2, 34.3, 33.9, 29.8, 27.0, 21.6, 21.1, 21.0, 20.1, 19.6, and 18.8.

IR (neat): 2958, 2873, 1734, 1622, 1461, 1419, 1251, 1163, 1058, and 1029 cm^{-1}.

Exact mass calc. for $[C_{20}H_{35}NO_7Na]^+$, 424.2306, found 424.2260.

Spectral data for S4b (acetylated **S3b**)



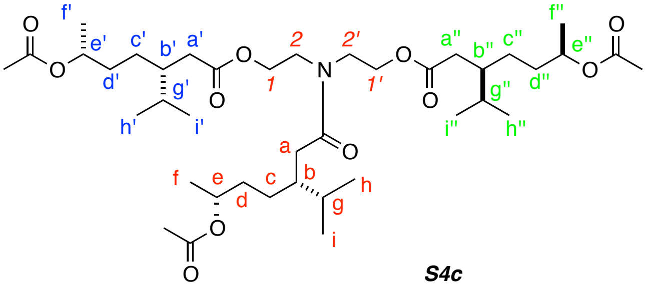
S4b

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.858 (app sextet, J = 6.2 Hz, 1H, H_e or $H_{e'}$), 4.856 (app sextet, J = 6.2 Hz, 1H, H_e or $H_{e'}$), 4.22-4.17 (m, 4H, H1/H1*/H1'/H1'*), 3.66-3.56 (m, 4H, H2/H2*/H2'/H2'*), 2.33 (dd, J = 15.4, 5.5 Hz, 0.5H, H_a), 2.32 (dd, J = 15.4, 5 Hz, 0.5H, H_a), 2.31 (dd, J = 15.6, 6.1 Hz, 0.5H, $H_{a'}$), 2.29 (dd, J = 15.4, 6.1 Hz, 0.5H, $H_{a'}$), 2.15 (two dds, J = 15.7, 7.1 Hz, 1H, H_{a*}), 2.14 (dd, J = 15.4, 7.3 Hz, 0.5H, $H_{a'*}$), 2.13 (dd, J = 15.5, 7.0 Hz, 0.5H, $H_{a'*}$), 2.08 (s, 1.5H, -C1'O$_2$CCH$_3$), 2.06 (s, 1.5H, -C1'O$_2$CCH$_3$), 2.025 (s, 3H, $-C_{e\text{ or }e'}O_2CCH_3$), 2.019 (s, 3H, $-C_{e\text{ or }e'}O_2CCH_3$), 1.94-1.87 (m, 1H, H_b), 1.79-1.67 (m, 3H, $H_{b'}/H_g/H_{g'}$), 1.62-1.53 (m, 2H, $H_d/H_{d'}$), 1.53-1.43 (m, 2H, $H_{d*}/H_{d'*}$), 1.37-1.2 (m, 4H, H_c/ $H_{c*}/H_{c'}/H_{c'*}$), 1.20 (br d, J = 6.3 Hz, 6H, $H_f/H_{f'}$), 0.876 (d, J = 6.6 Hz, 1.5H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$), 0.871 (d, J = 6.9 Hz, 1.5H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$), 0.865 (d, J = 6.6 Hz, 1.5H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$), 0.863 (d, J = 6.6 Hz, 1.5H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$), 0.850 (d, J = 6.6 Hz, 3H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$), and 0.833 (d, J = 7.0 Hz, 3H, $H_{i\text{ or }i'\text{ of }h\text{ or }h'}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.53, 173.46, 173.2, 170.7, 71.18, 71.16, 71.0, 70.9, 62.2, 62.1, 61.9 61.8, 47.34, 47.31, 47.28, 47.26, 45.7, 45.6, 40.5, 40.4, 40.1, 39.9, 35.84, 35.84, 35.76, 34.24, 34.19, 33.8, 33.7, 33.48, 33.46, 29.7, 29.61, 29.58, 26.80, 26.76, 26.7, 26.6, 21.8, 21.39, 21.38, 20.9, 20.81, 20.78, 20.75, 20.3, 20.25, 19.99, 19.96, 19.94, 19.92, 19.43, 19.37, 19.32, 19.27, 19.25, 18.81, 18.78, 18.64, 18.6, 18.5, 18.44, and 18.43. IR (neat): 2957, 2873, 1734, 1649, 1460, 1371, 1242, 1164, 1131, and 1050 cm^{-1}.

Exact mass calc. for $[C_{30}H_{53}NO_9Na]^+$, 594.3613, found 594.3639.

Spectral data for S4c (acetylated **S3c**)



S4c

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (sextet, J = 6.2 Hz, 3H, $H_e/H_{e'}/H_{e''}$), 4.24-4.15 (m, 4H, H1/H1*/H1’/H1’*), 3.67-3.57 (m, 4H, H2/H2*/H2’/H2’*), 2.34 (dd, J = 15.5, 5.7 Hz, 1H, H_a), 2.31 (dd, J = 15.3, 5.9 Hz, 1H, $H_{a'}$), 2.28 (dd, J = 15.4, 6.1 Hz 1H, $H_{a''}$), 2.15 (dd, J = 15.4, 6.9 Hz, 1H, H_{a*}), 2.14 (dd, J = 15.5, 7.4 Hz, 1H, $H_{a'*}$), 2.13 (dd, J = 15.5, 7.2 Hz, 1H, $H_{a''*}$), 2.025 (s, 3H, -O_2CCH_3), 2.024 (s, 3H, -O_2CCH_3), 2.02 (s, 3H, -O_2CCH_3), 1.94-1.87 (nfom, 1H, H_b), 1.80-1.66 (m, 5H, $H_g/H_{b'}/H_{b''}/H_{g'}/H_{g''}$), 1.62-1.53 (m, 3H, $H_d/H_{d'}/H_{d''}$), 1.52-1.43 (m, 3H, $H_{d*}/H_{d'*}/H_{d''*}$), 1.37-1.20 (m, 6H, $H_c/H_{c'}/H_{c''}/H_{c*}/H_{c'*}/H_{c''*}$), 1.206 (d, J = 6.3 Hz, 6H, $H_{f'}H_{f''}$), 1.204 (d, J = 6.3 Hz, 3H, H_f), 0.874 (d, J = 6.7 Hz, 3H, H_g), 0.863 (d, J = 6.4 Hz, 3H, $H_{g'}$), 0.862 (d, J = 6.3 Hz, 3H, $H_{g''}$), 0.850 (d, J = 6.7 Hz, 3H, H_h), 0.833 (d, J = 6.7 Hz, 3H, $H_{h'}$), and 0.832 (d, J = 6.7 Hz, 3H, $H_{h''}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 173.6, 173.4, 170.94, 170.91, 71.4, 71.2, 71.1, 62.3, 62.0, 47.5, 45.8, 40.7, 40.6, 40.2, 36.0, 35.9, 34.4, 33.9, 33.7, 33.6, 30.0, 29.9 29.8, 26.94, 26.87, 26.83, 21.60, 21.58, 20.2, 20.1, 19.7, 19.6, 19.5, 18.8, 18.7, and 18.66.

IR (neat): 2958, 2874, 1734, 1650, 1461, 1371, 1244, 1163, 1132, and 1021 cm^{-1}.

Exact mass calc. for $[C_{40}H_{71}NO_{11}Na]^+$, 764.4919, found 764.4958.

Preparation procedures for PU films (entries 2-8, Table 3 in manuscript)

PU[$\mathbf{8}_{\mathbf{PCM\text{-}9}}$/MDI] (entry 3)

This carvomenthide-based PU film was prepared by a procedure entirely analogous to that described in the manuscript [Experimental: **PU[$\mathbf{4}_{\mathbf{PM\text{-}9}}$/MDI]** (entry 1, Table 3)]. The differences were that polyol $\mathbf{8}_{\mathbf{PCM\text{-}9}}$ was used instead of $\mathbf{4}_{\mathbf{PM\text{-}9}}$ and that the resulting film was amber-colored instead of clear.

PU[$\mathbf{4}_{\mathbf{PM\text{-}9}}$/PMDI] (entry 2) and PU[$\mathbf{8}_{\mathbf{PCM\text{-}9}}$/PMDI] (entry 4)

A similar procedure was employed for the fabrication of the PU films derived from either the (–)-menthide-based or carvomenthide-based polyols $\mathbf{4}_{\mathbf{PM\text{-}9}}$ or $\mathbf{8}_{\mathbf{PCM\text{-}9}}$, respectively. The only difference in this compositon is that PMDI (0.190 g, 1.4 mmol) was used instead of MDI.

PU[$\mathbf{4}_{\mathbf{PM\text{-}18}}$/MDI] (entry 5)

Anhydrous acetone (2 mL) was added to a mixture of (–)-menthide-based polyol (**8**, 600 mg, 0.19 mmol, assuming a theoretical MW of 3165 amu for an 18:1 oligomer) and diethylene glycol (8 μL, 9 mg, 0.1 mmol) to form a homogenous solution. Diphenylmethane diisocyanate (MDI, a mixture of positional isomers, 90 μL, 110 mg, 0.42 mmol) was quickly added (≤1 min) and the resulting solution quickly mixed to homogeneity using a glass pipette. The resulting viscous mixture was immediately layered into a polyethylene cap (5 cm diameter, ca. 4 mm height), which was placed in a desiccator (ca. 250 cm d) connected to a vacuum source. A mild vacuum (ca. 200 torr) was applied periodically every few hours to remove the headspace solvent, thereby facilitating the formation of a bubble-free film. After one week at ambient temperature the film was subjected to an annealing process at 80 ºC in a vacuum oven (ca. 1 torr) for 3 days. The resulting essentially colorless film (ca. 4 mm final thickness) was removed from the cap and was characterized by ATR-IR spectroscopy, DSC, and dynamic mechanical and tensile strength measurements.

PU[$\mathbf{8}_{\mathbf{PCM\text{-}18}}$/MDI] (entry 7)

This carvomenthide-based PU film was prepared by a procedure entirely analogous to that detailed in the paragraph immediately above [for **PU[$\mathbf{4}_{\mathbf{PM\text{-}18}}$/MDI]** (entry 5)**]**. The differences were that polyol $\mathbf{8}_{\mathbf{PCM\text{-}18}}$ was used instead of $\mathbf{4}_{\mathbf{PM\text{-}18}}$ and that the resulting film was amber-colored instead of clear.

PU[$\mathbf{4}_{\mathbf{PM\text{-}18}}$/PMDI] (entry 6) and PU[$\mathbf{8}_{\mathbf{PCM\text{-}18}}$/PMDI] (entry 8)

A similar procedure was employed for the fabrication of the PU films derived from either the (–)-menthide-based or carvomenthide-based polyols $\mathbf{4}_{\mathbf{PM\text{-}18}}$ or $\mathbf{8}_{\mathbf{PCM\text{-}18}}$, respectively. The only difference was that PMDI (0.100 g, 0.75 mmol) was used in both of these preparations.

Representative ATR-IR spectrum of a film (**PU[4_{PM-9}/MDI]**, entry 1, Table 3 in manuscript). No residual isocyanate functionality is observable.

PU[4_{PM-9}/MDI]

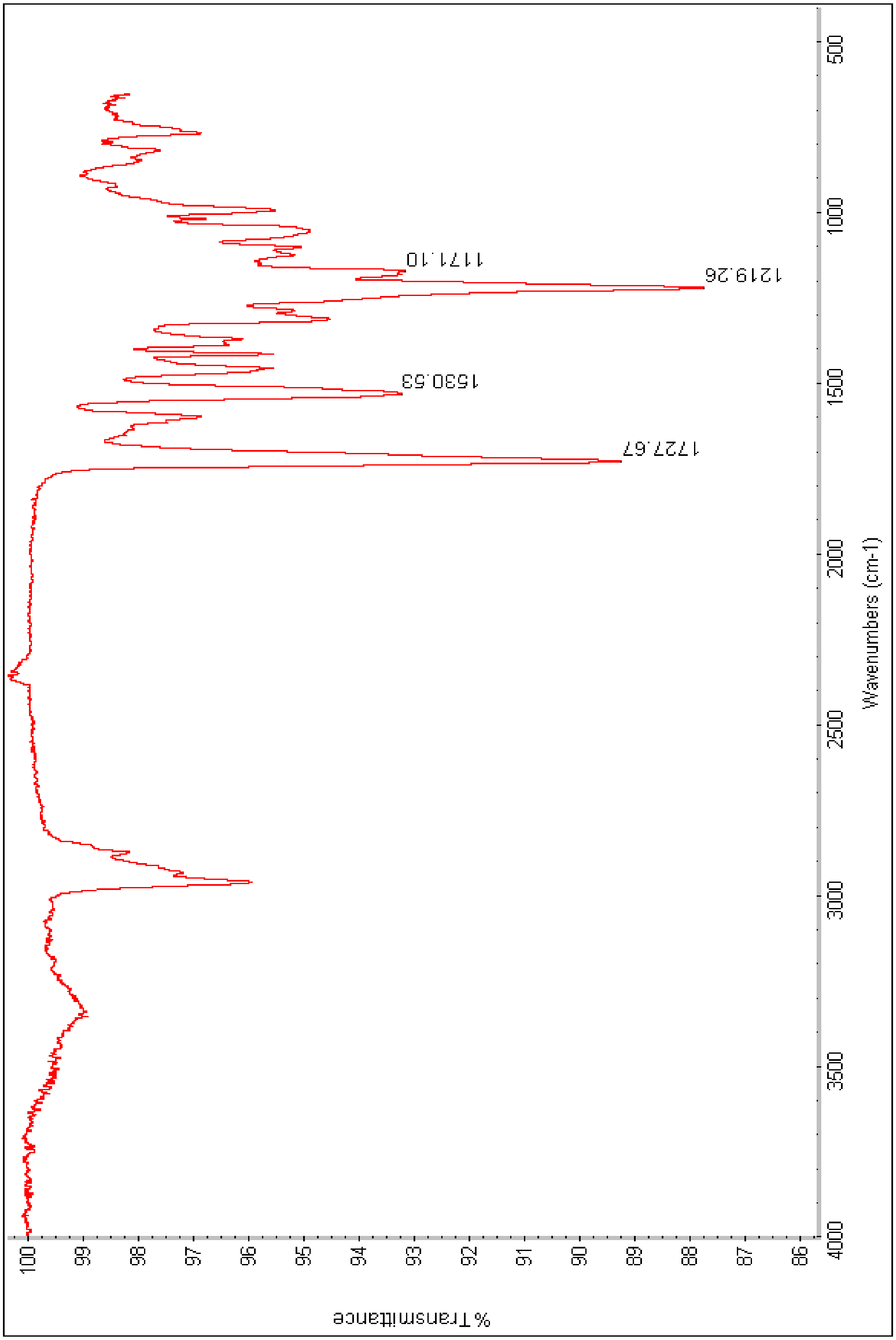
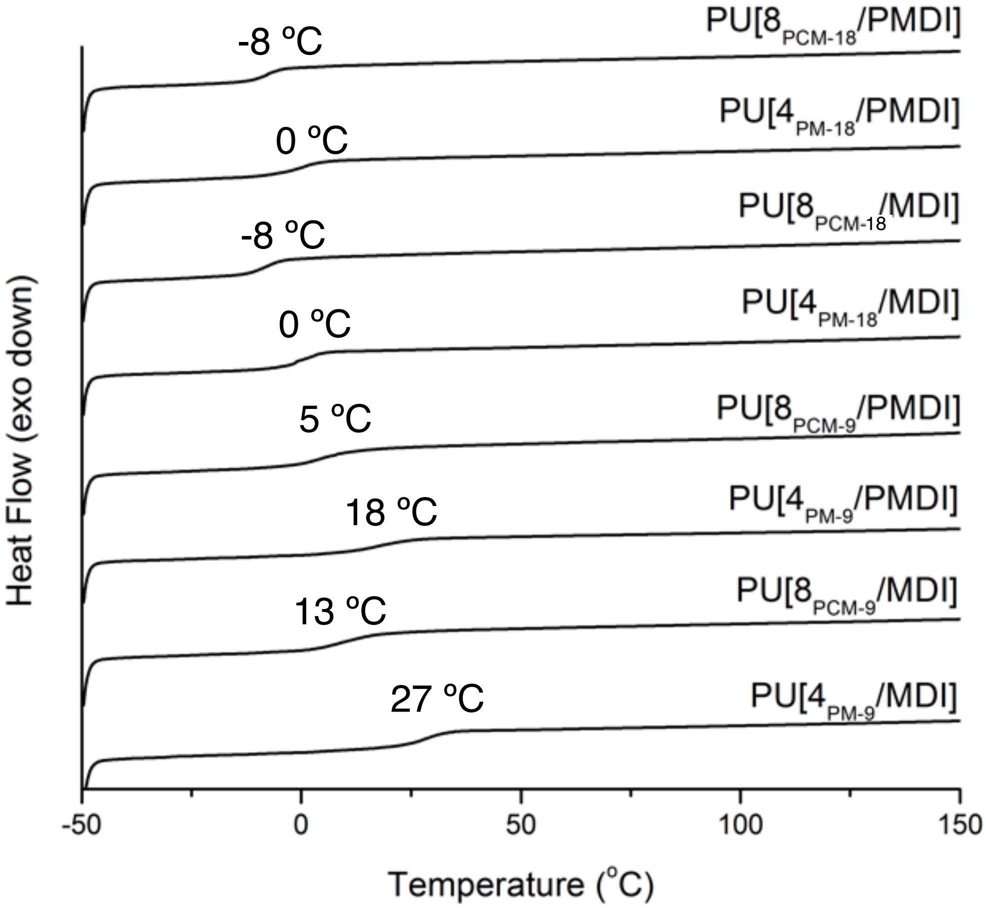
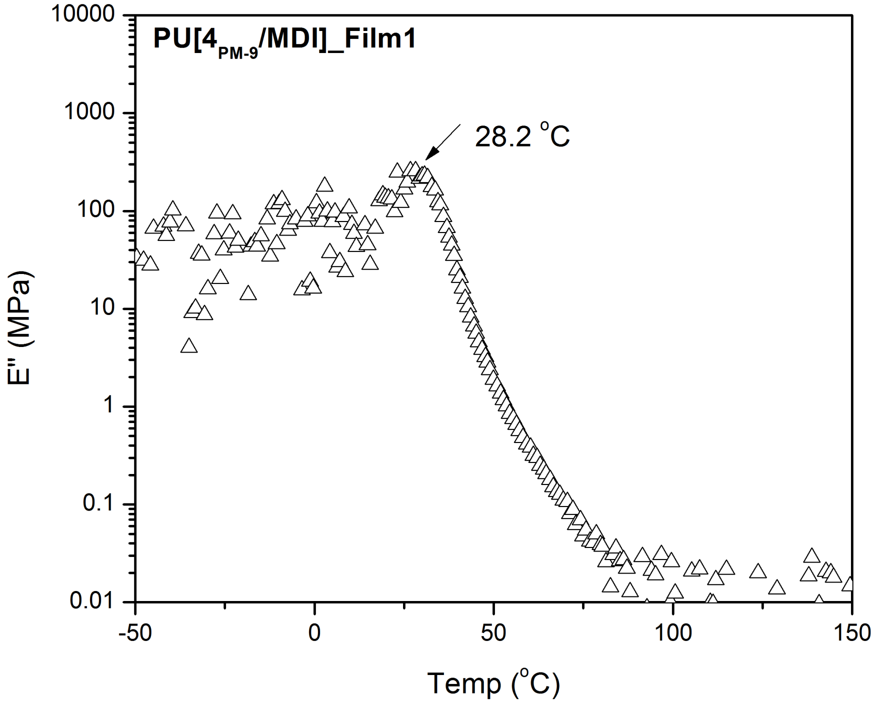


Figure S3. Differential Scanning Calorimetry (DSC) data for all 8 films.

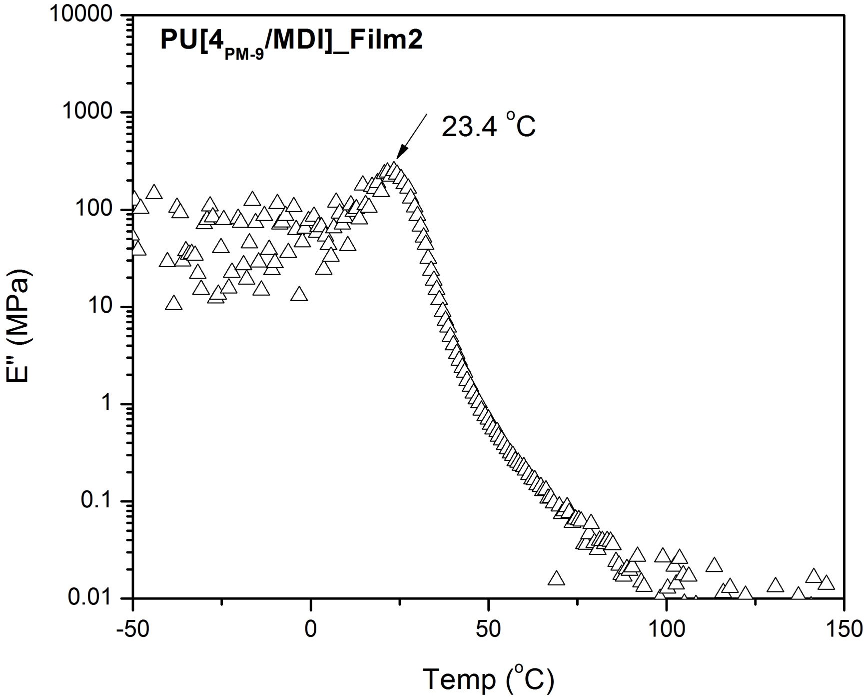


Dynamic Mechanical Analysis (DMA; T *vs.* E''). Glass transition temperature (T_g) [peak maximum for loss modulus (E'')] measured from DMA data for each PU film.

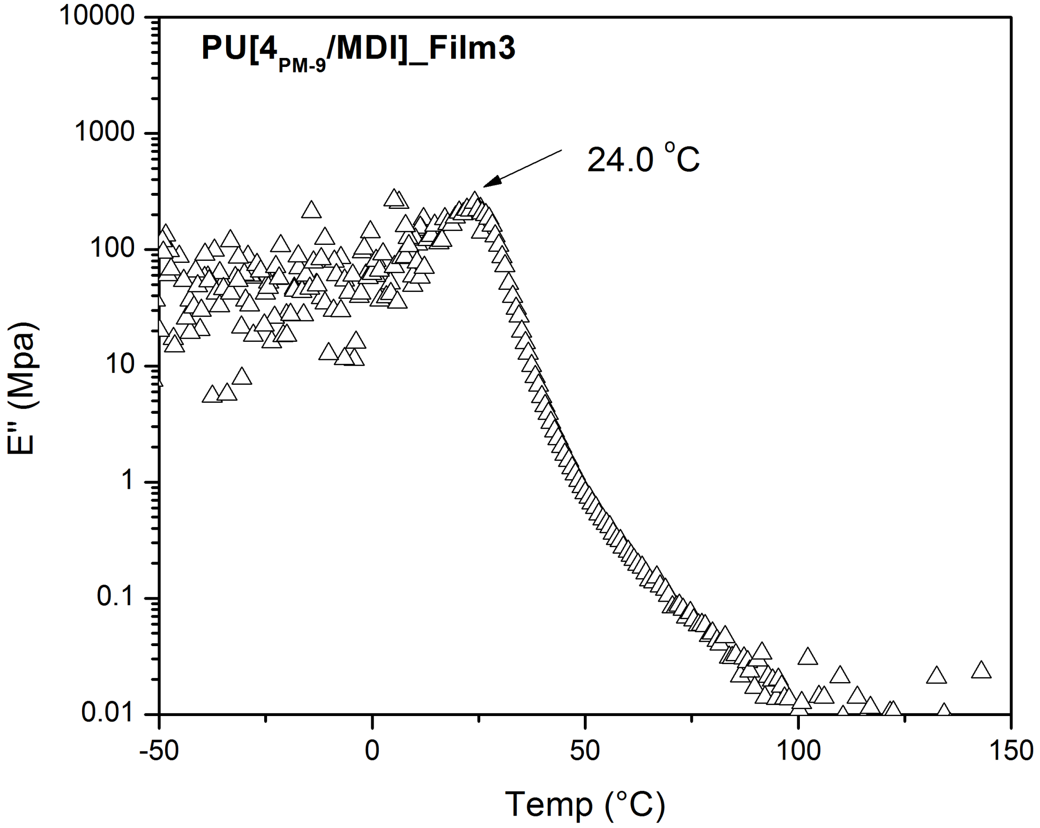
PU[4_{PM-9}/MDI]_Film1



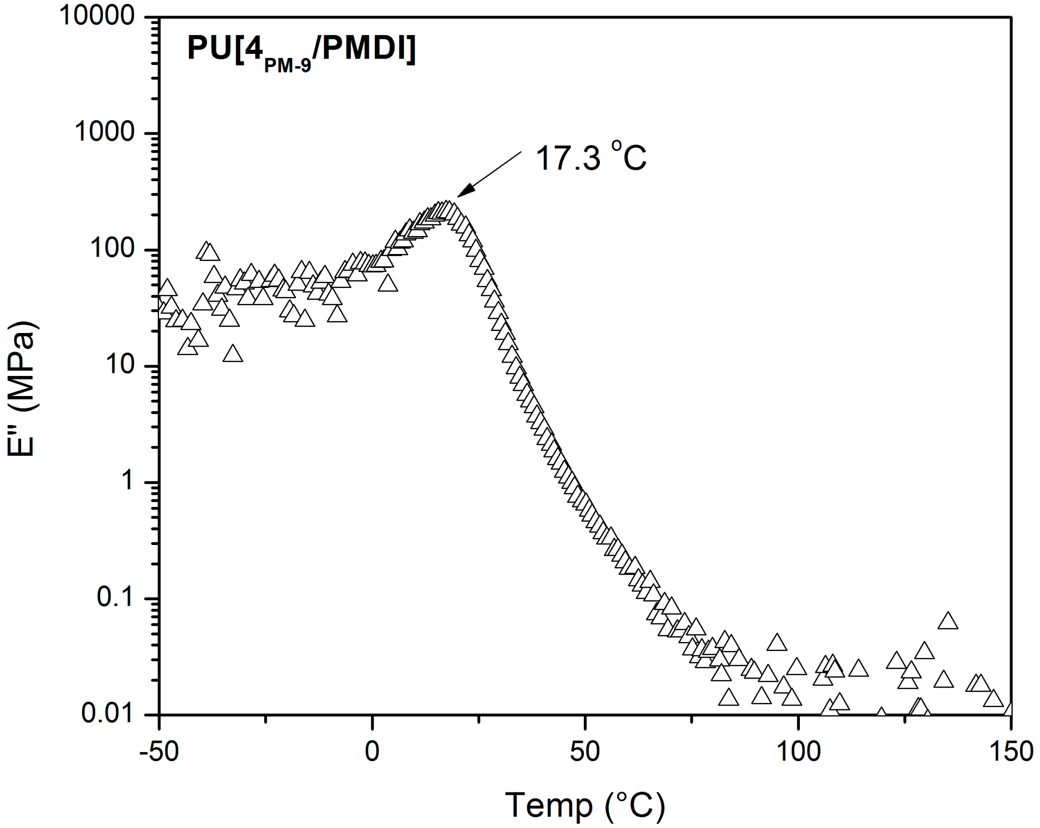
PU[4_{PM-9}/MDI]_Film2



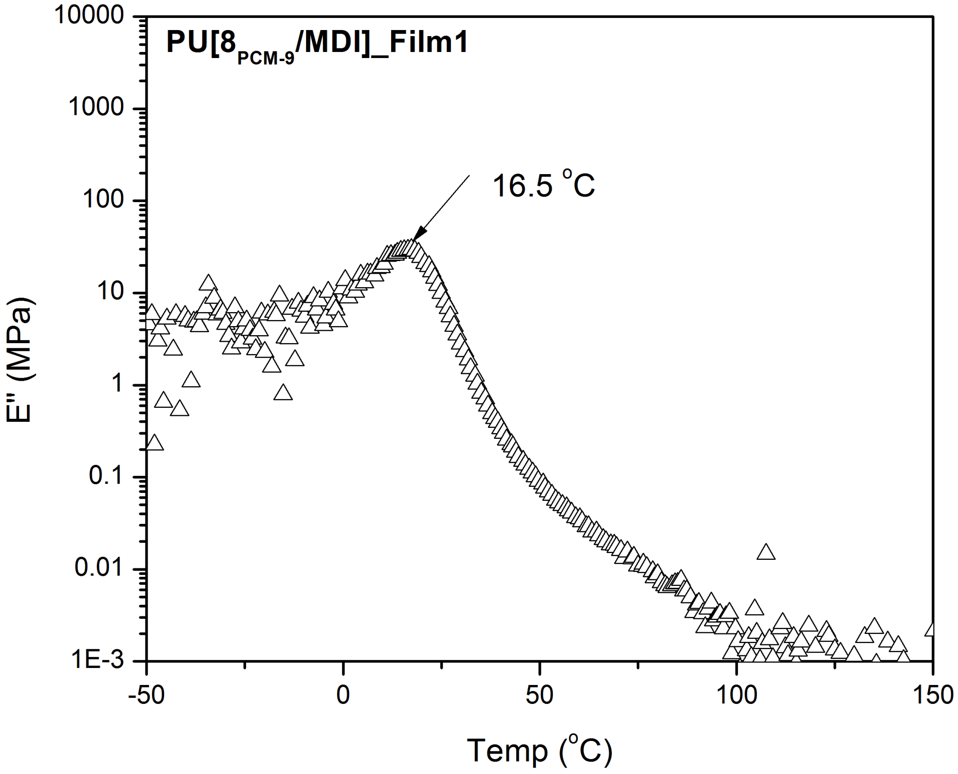
PU[4_{PM-9}/MDI]_Film3



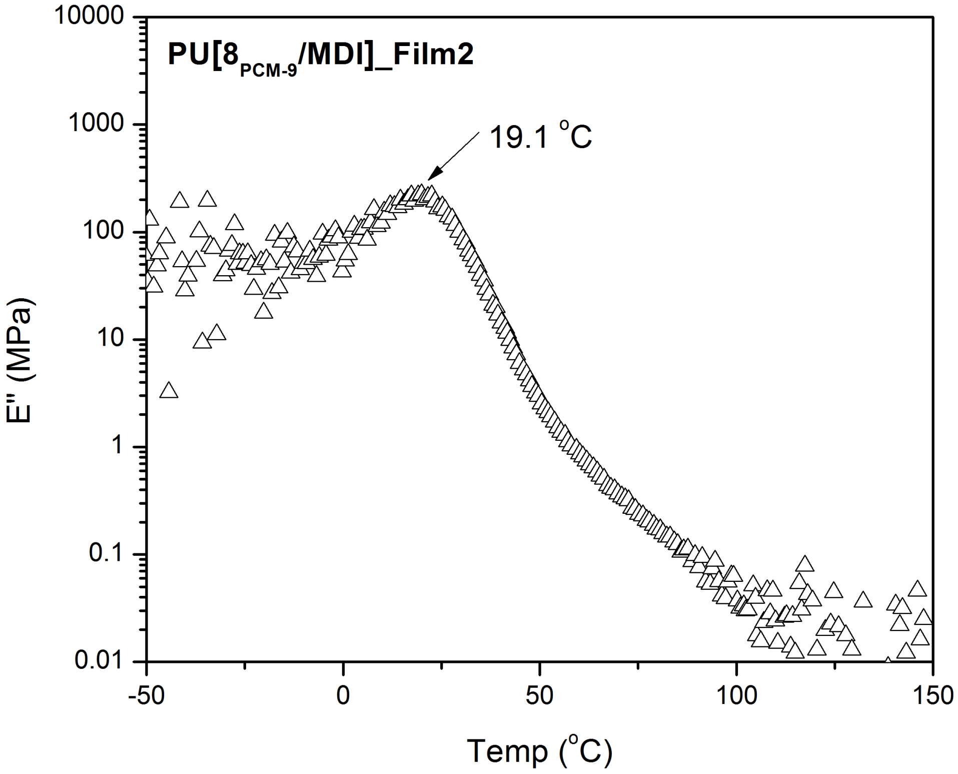
PU[4_{PM-9}/PMDI]


PU[4PM-9/PMDI]
17.3 °C
E" (MPa)
Temp (°C)
10000
1000
100
10
1
0.1
0.01
-50
0
50
100
150

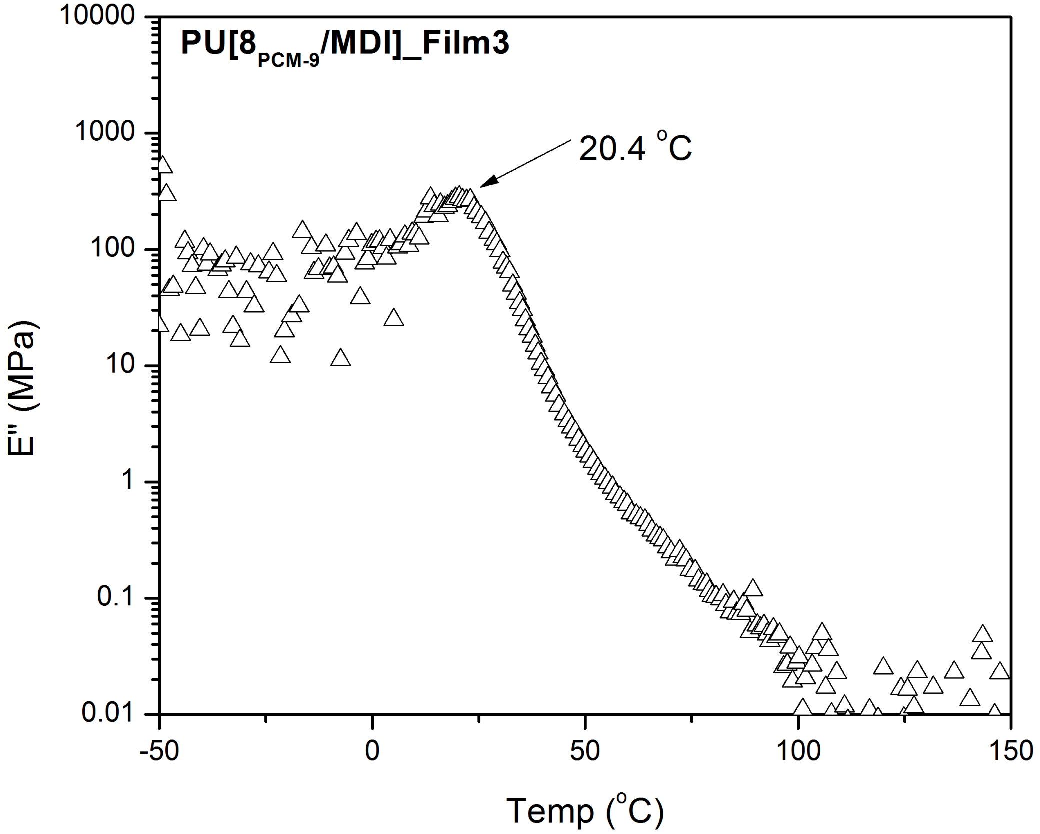
PU[8_{PCM-9}/MDI]_Film1



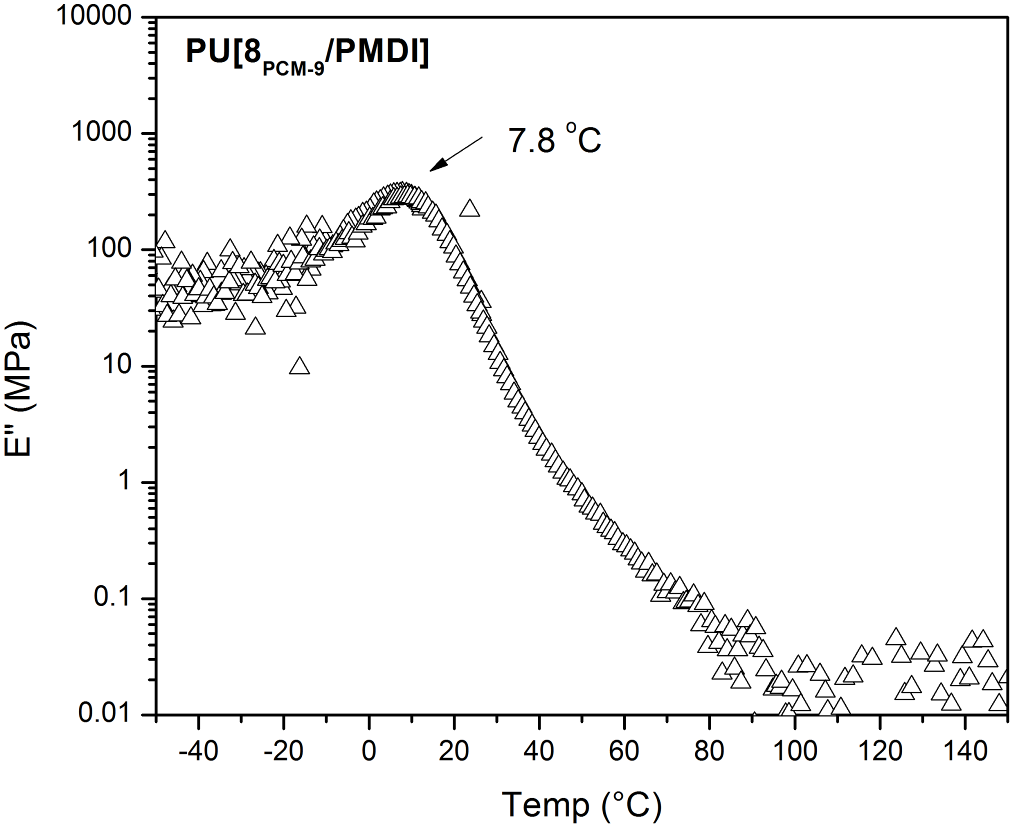
PU[8_{PCM-9}/MDI]_Film2



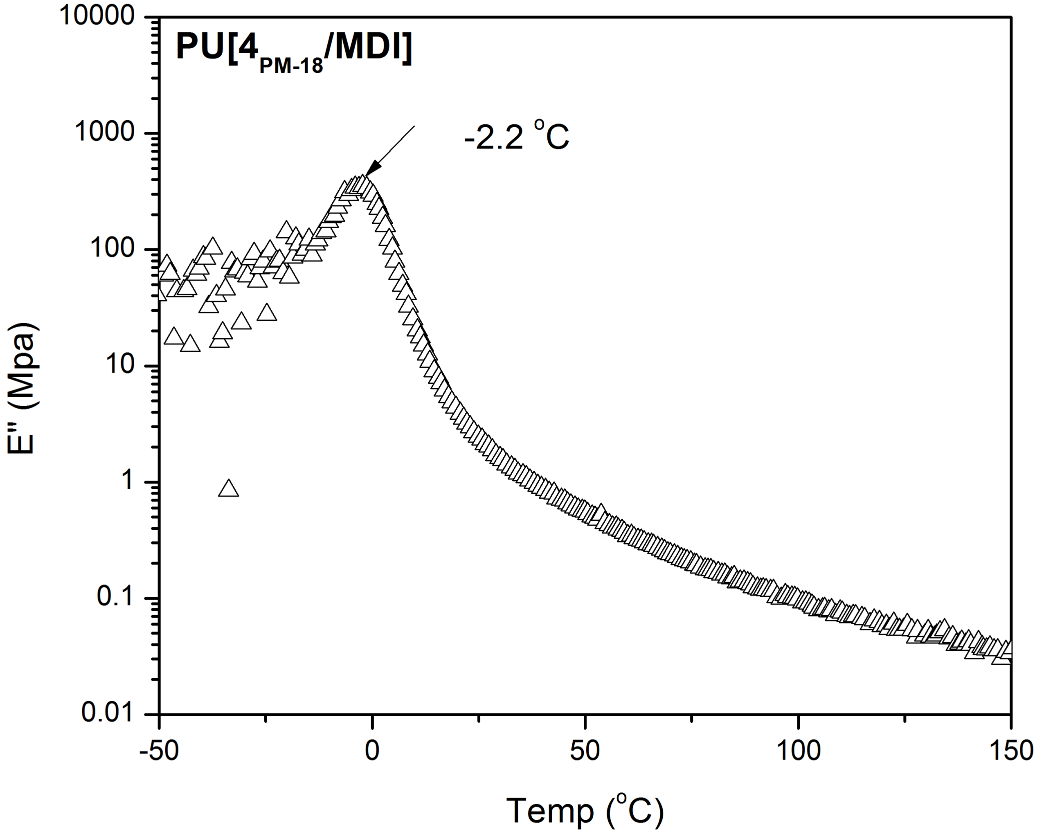
PU[8_{PCM-9}/MDI]_Film3



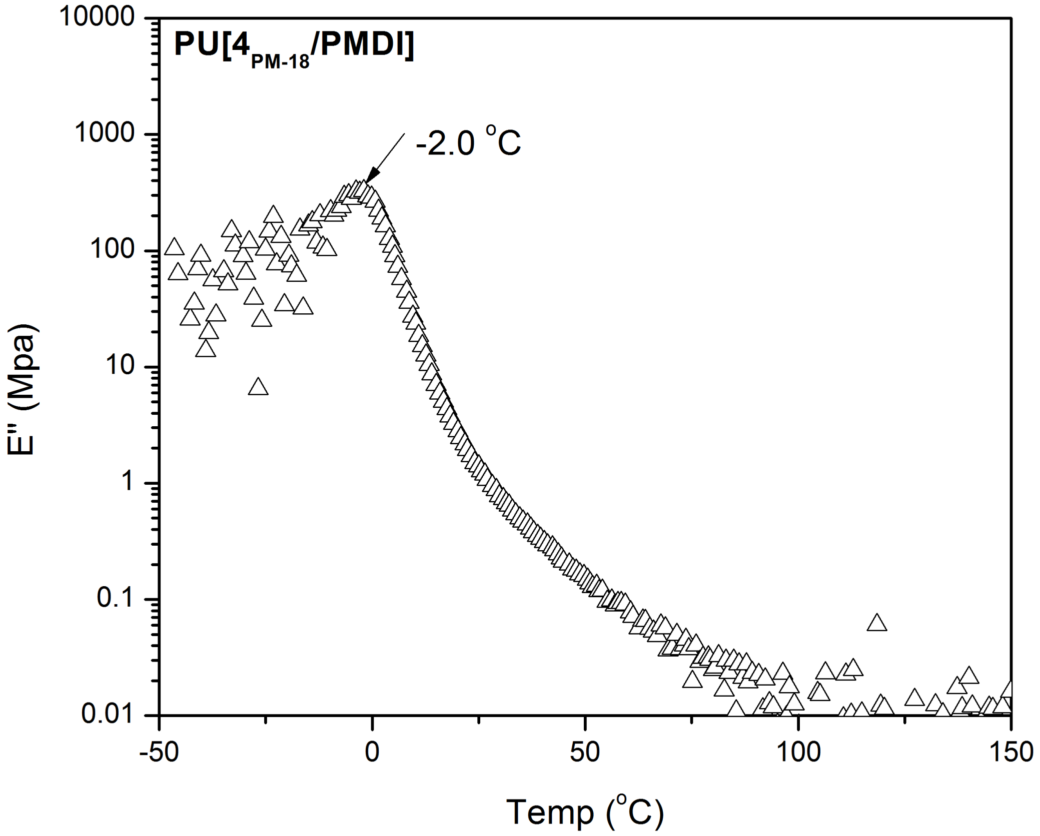
PU[$8_{PCM\text{-}9}$/PMDI]



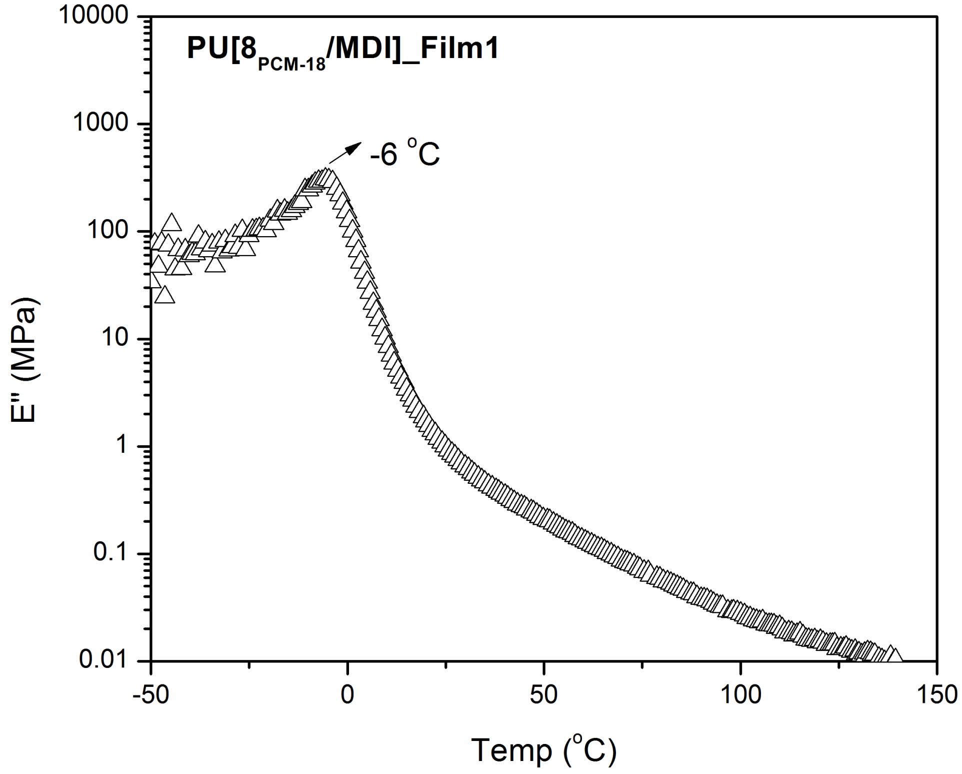
PU[4_{PM-18}/MDI]


PU[4_{PM-18}/MDI]
-2.2 °C
10000
1000
100
10
1
0.1
0.01
E'' (Mpa)
-50
0
50
100
150
Temp (°C)

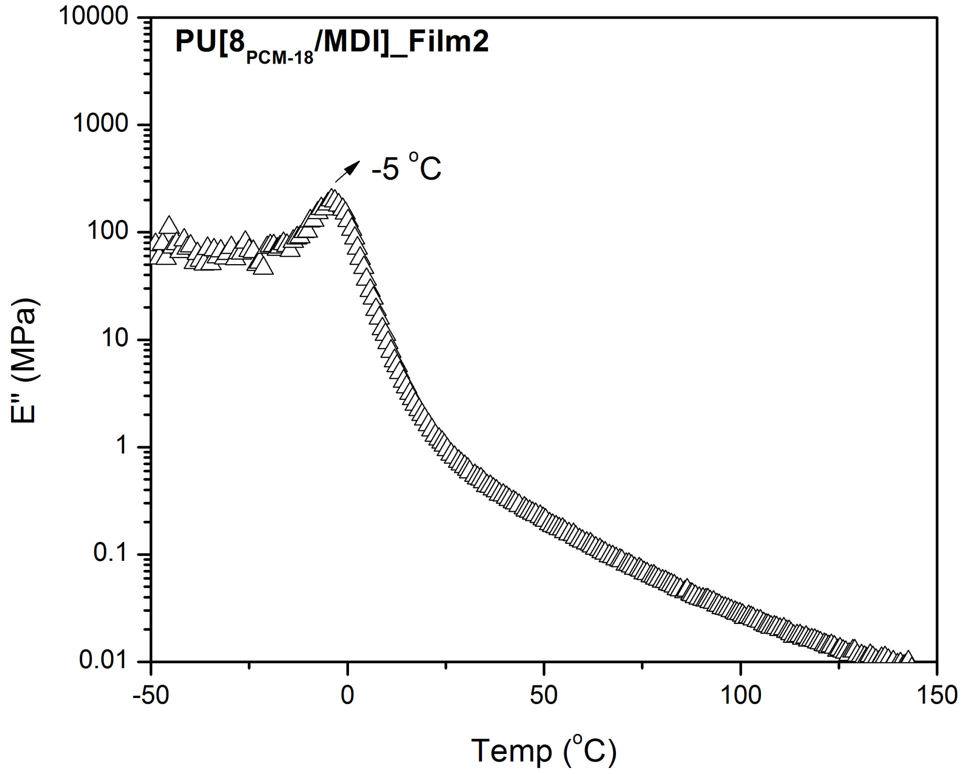
PU[4_{PM-18}/PMDI]



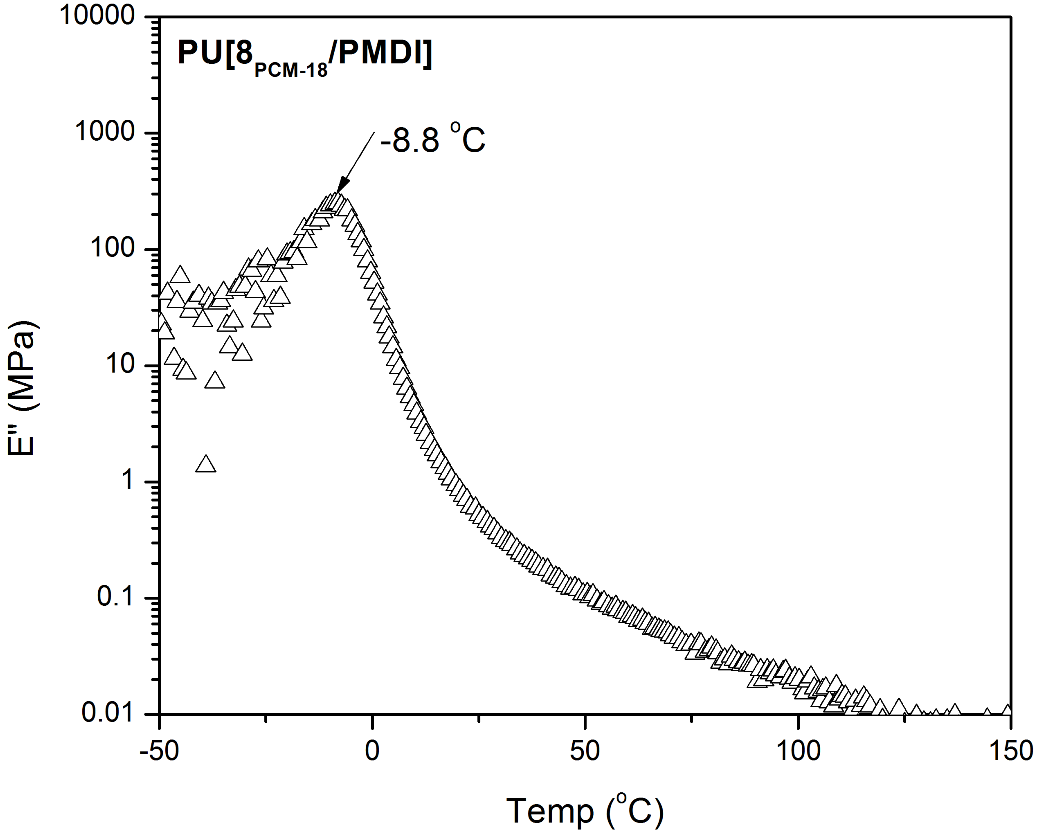
PU[8_{PCM-18}/MDI]_Film1



PU[8_{PCM-18}/MDI]_Film2

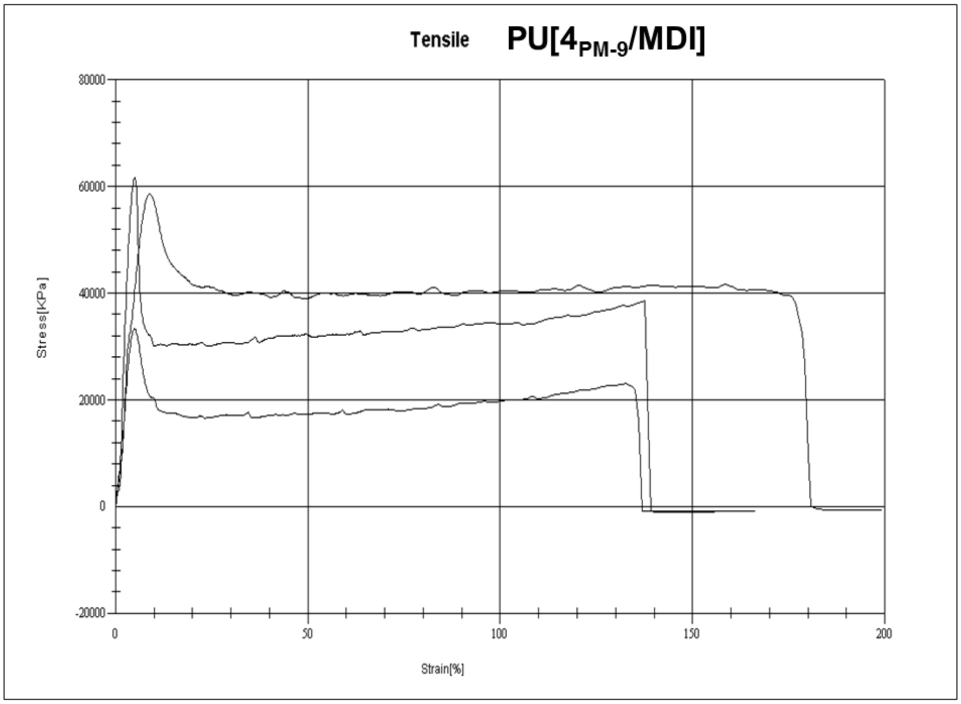


PU[8_{PCM-18}/PMDI]

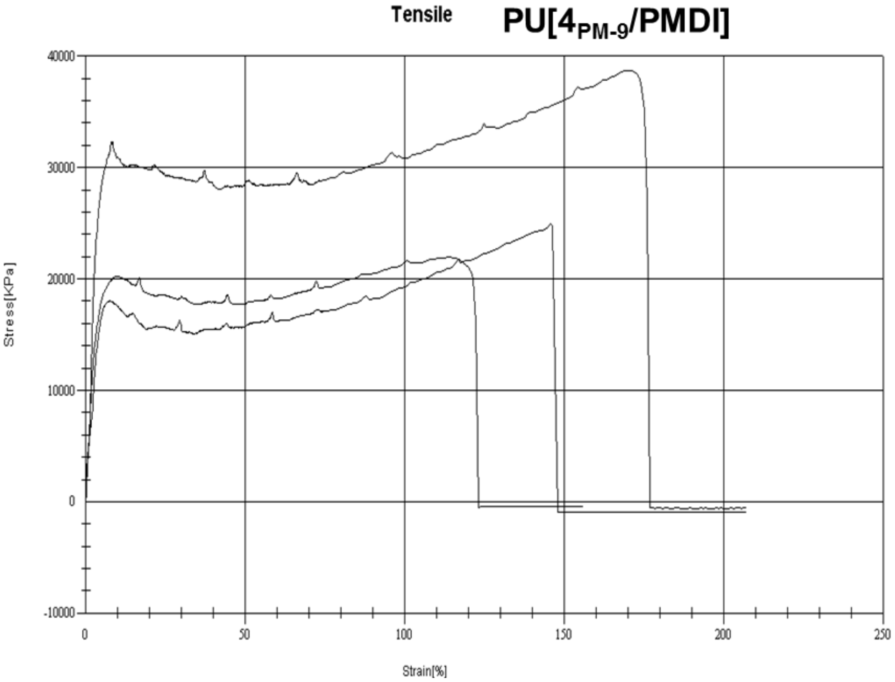


Tensile Strength. Stress vs. strain data for each PU film.

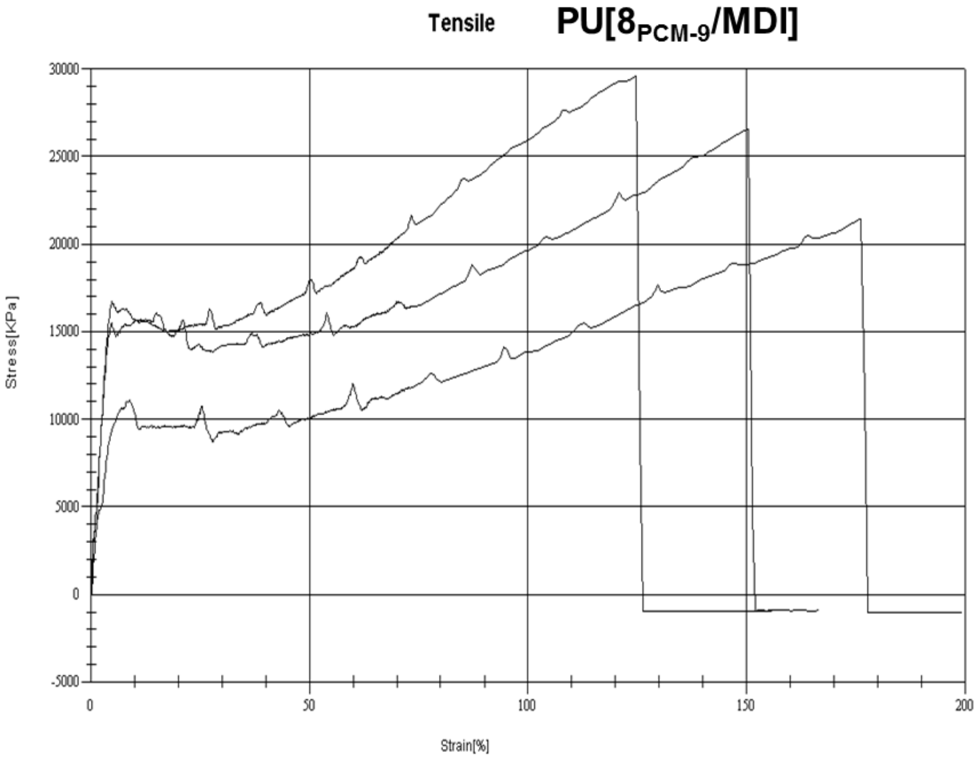
PU[4_{PM-9}/MDI]

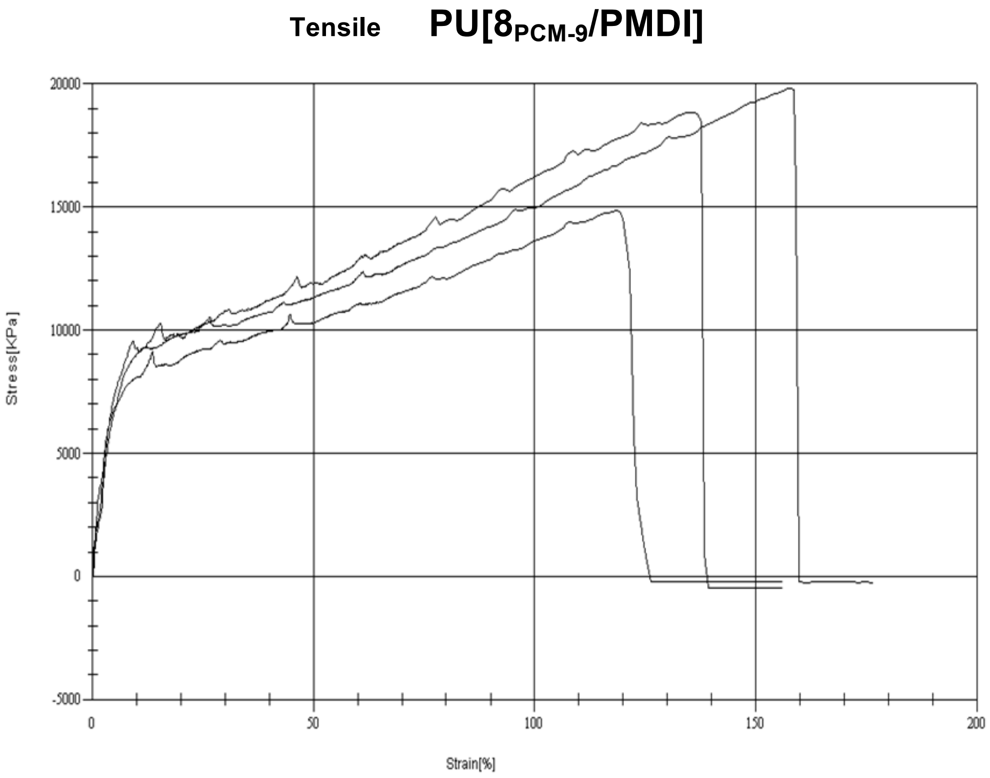


PU[4_{PM-9}/PMDI]

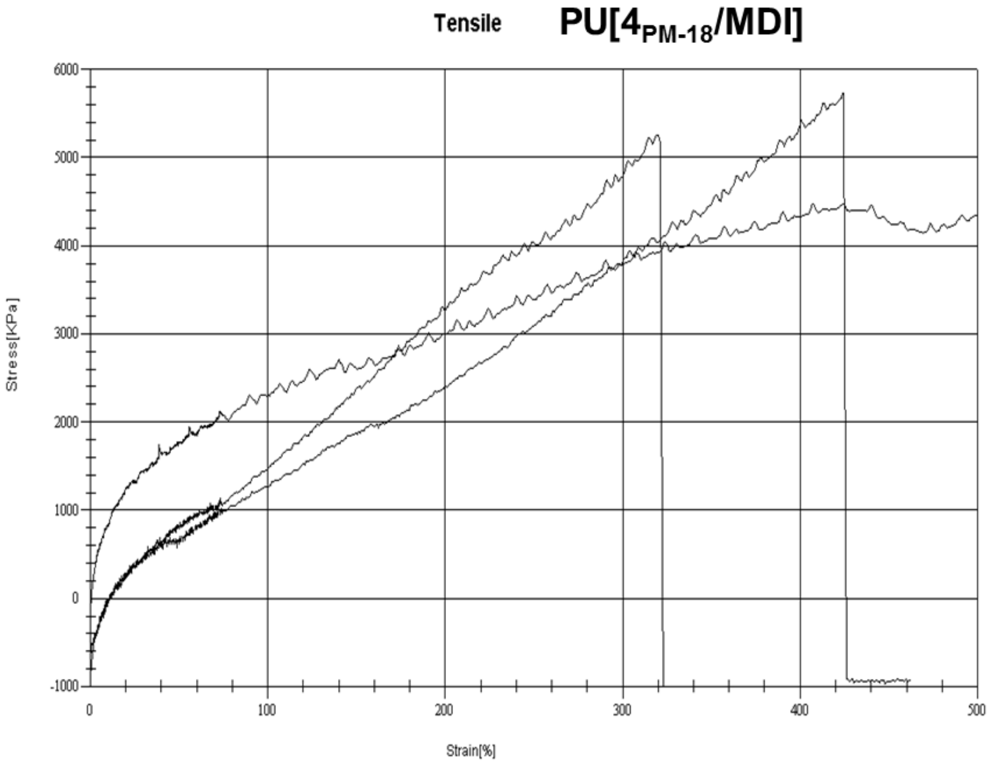


PU[8_{PCM-9}/MDI]

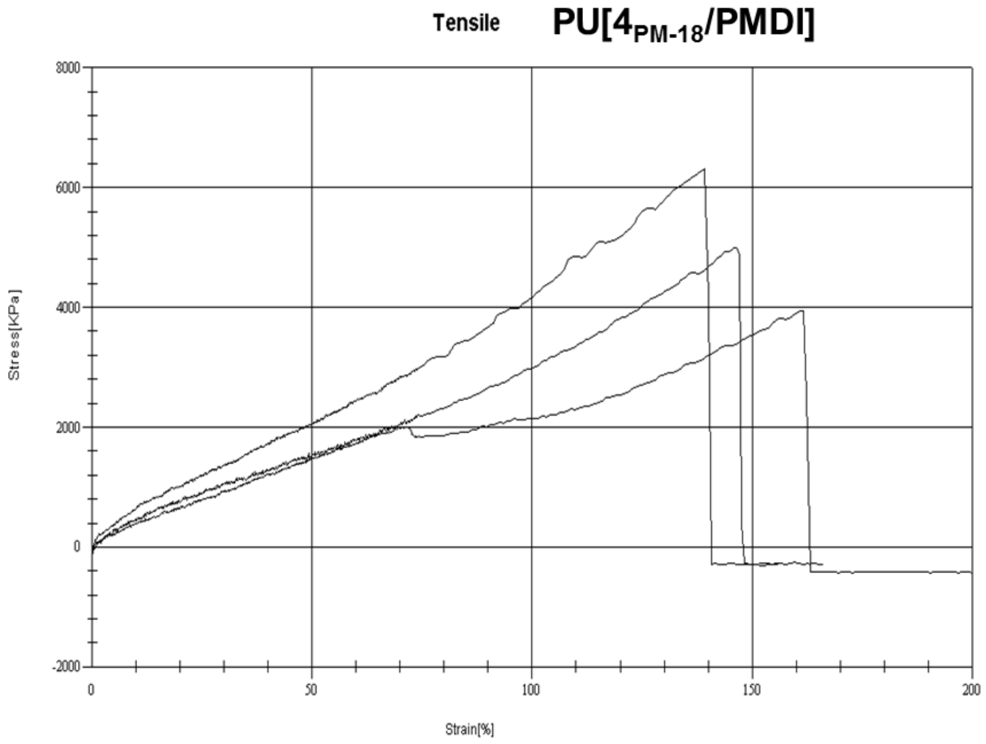

Tensile
PU[8PCM-9/MDI]
30000
25000
20000
15000
10000
5000
0
-5000
Stress[KPa]
0
50
100
150
200
Strain[%]


Tensile
PU[8PCM-9/PMDI]
20000
15000
10000
5000
0
-5000
Stress[KPa]
0
50
100
150
200
Strain[%]

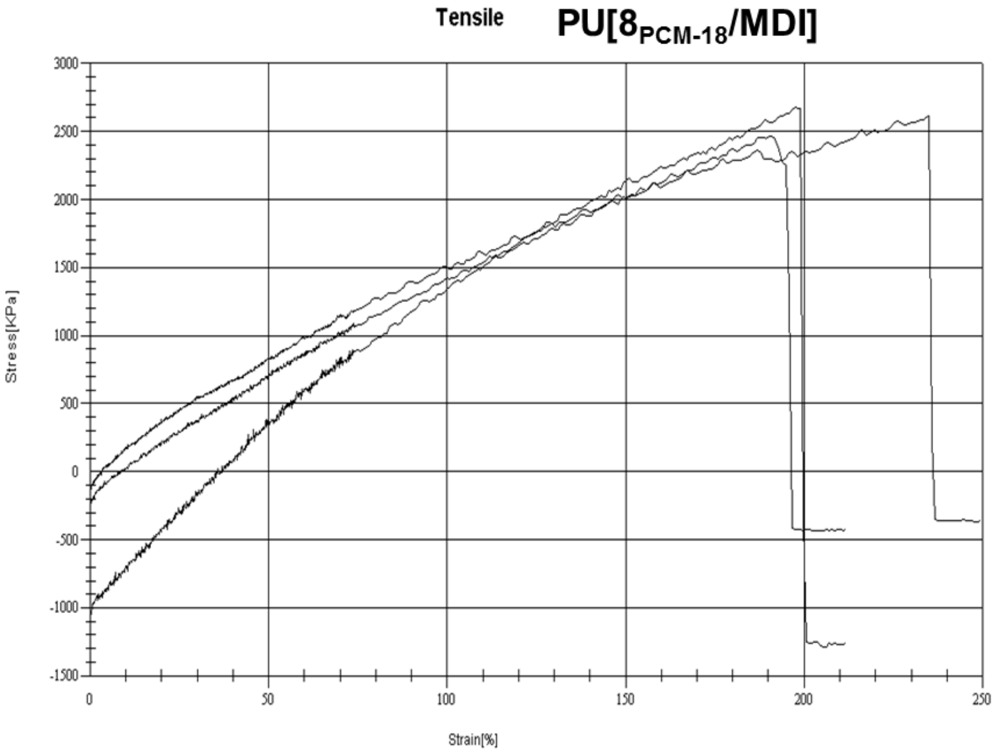
PU[4_{PM-18}/MDI]



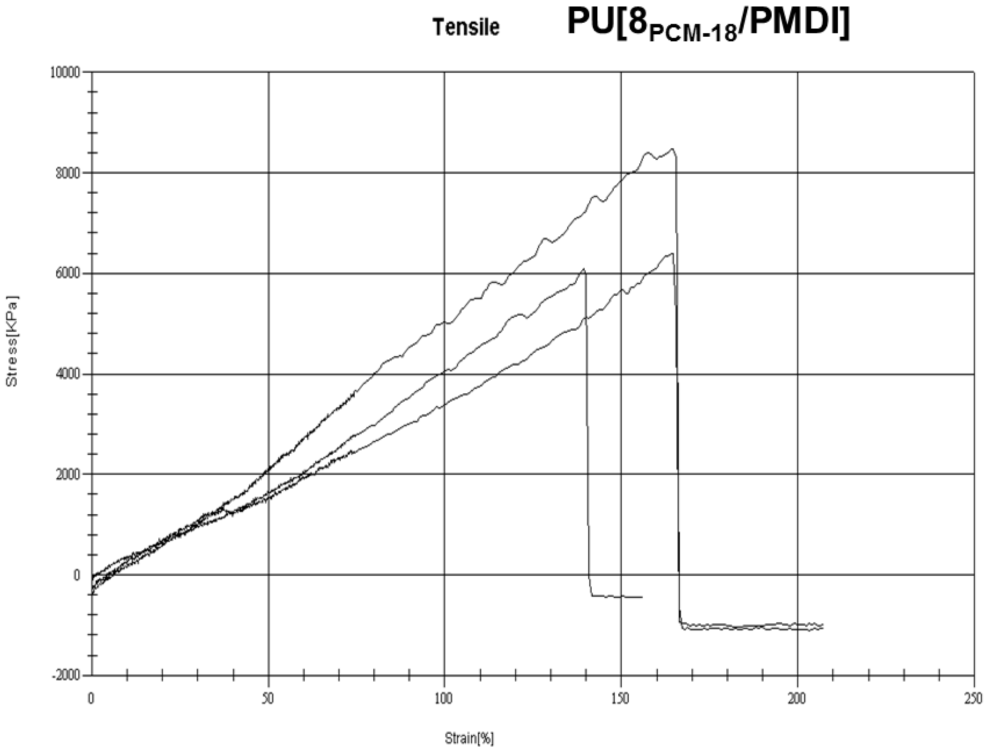
PU[4_{PM-18}/PMDI]

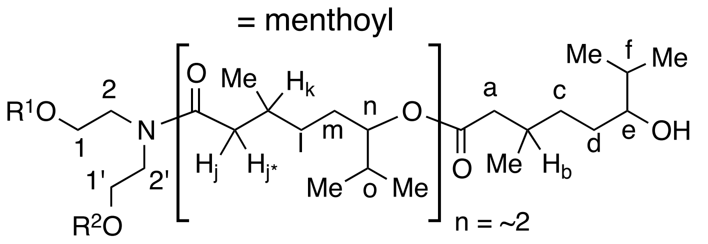


PU[8_{PCM-18}/MDI]



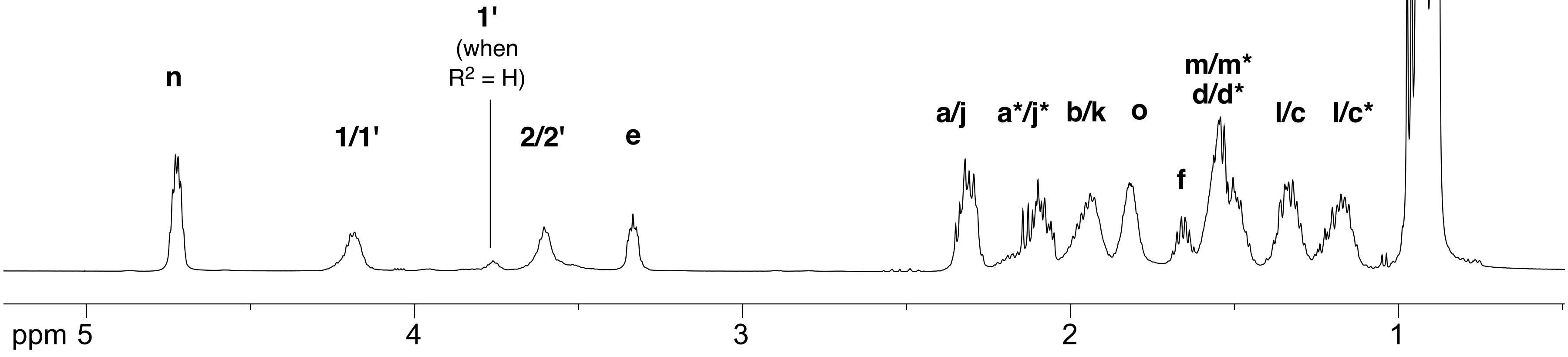
PU[8_{PCM-18}/PMDI]

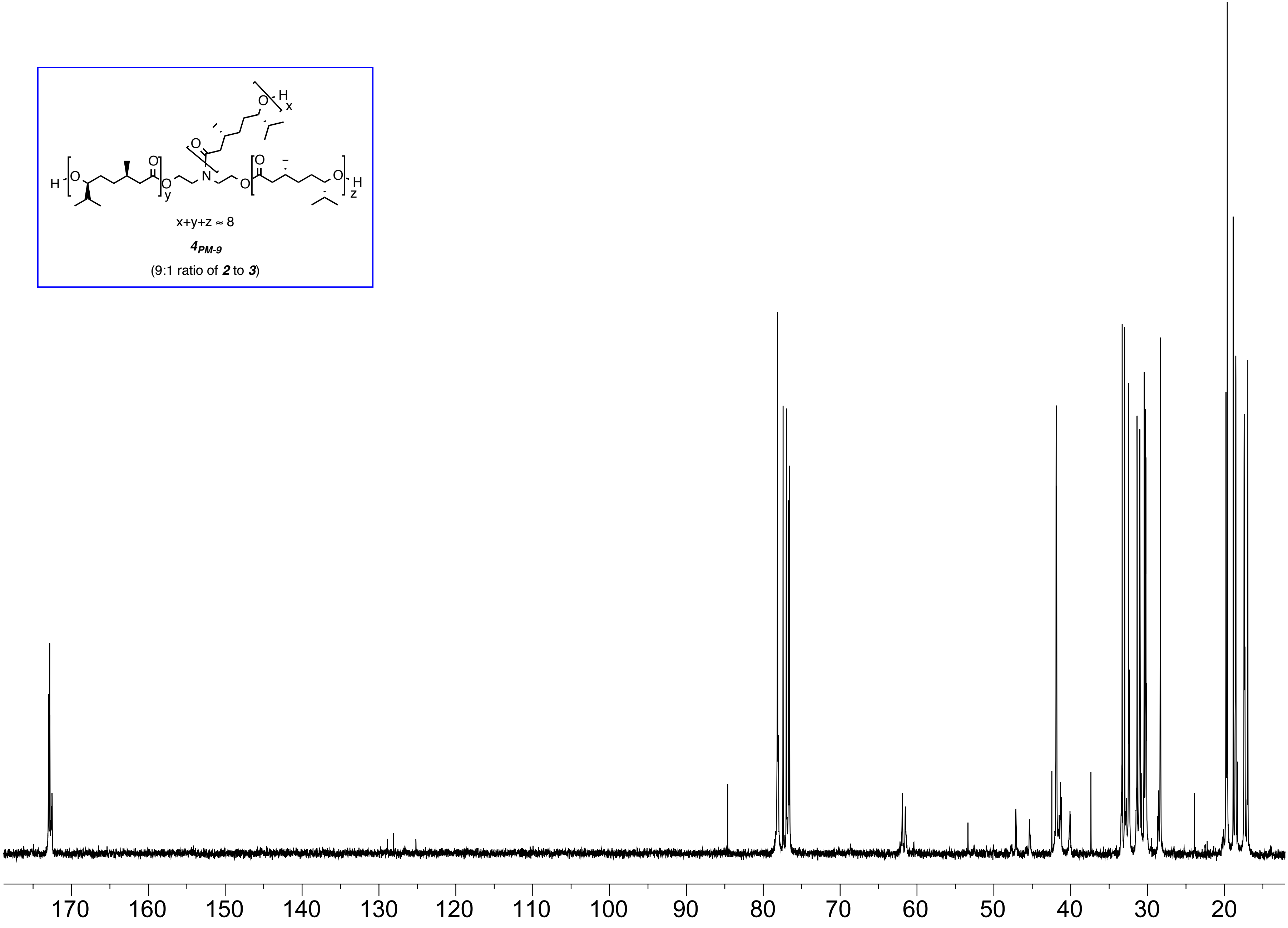


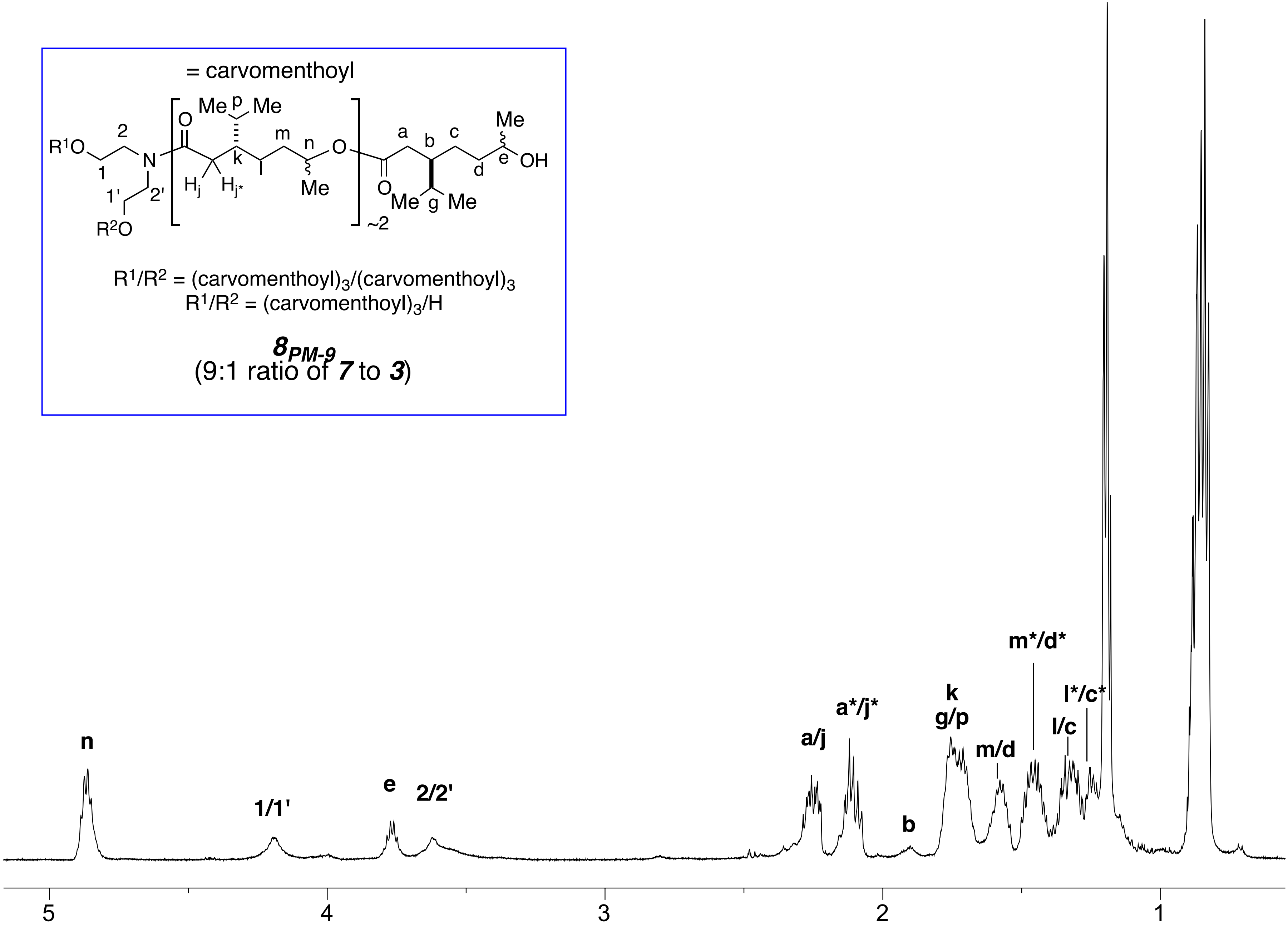


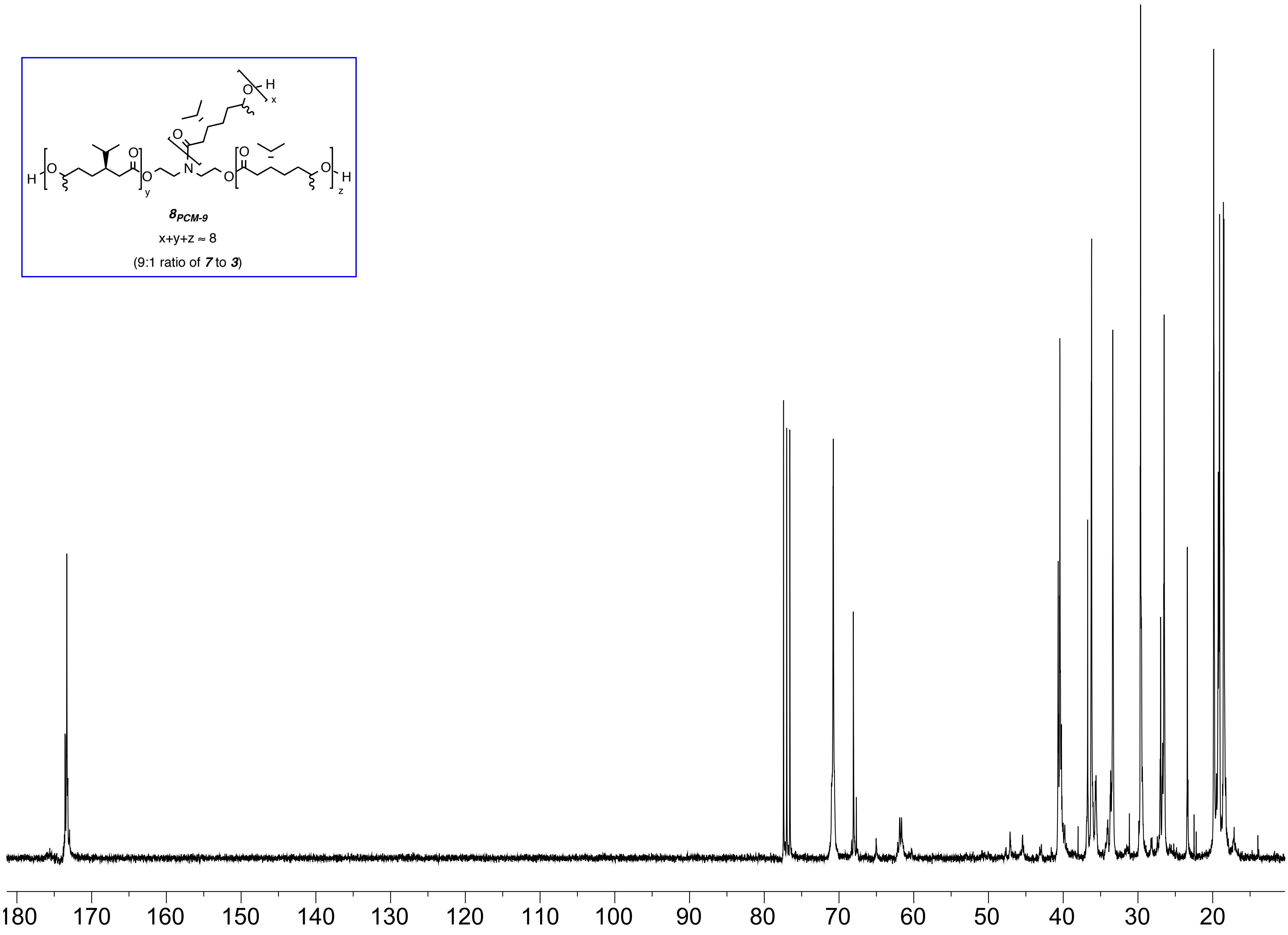
R^1/R^2 = (menthoyl)$_3$/(menthoyl)$_3$
R^1/R^2 = (menthoyl)$_3$/H

***4**$_{PM\text{-}9}$*
(9:1 ratio of ***2*** to ***3***)




x+y+z ≈ 8
4$_{PM\text{-}9}$
(9:1 ratio of **2** to **3**)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

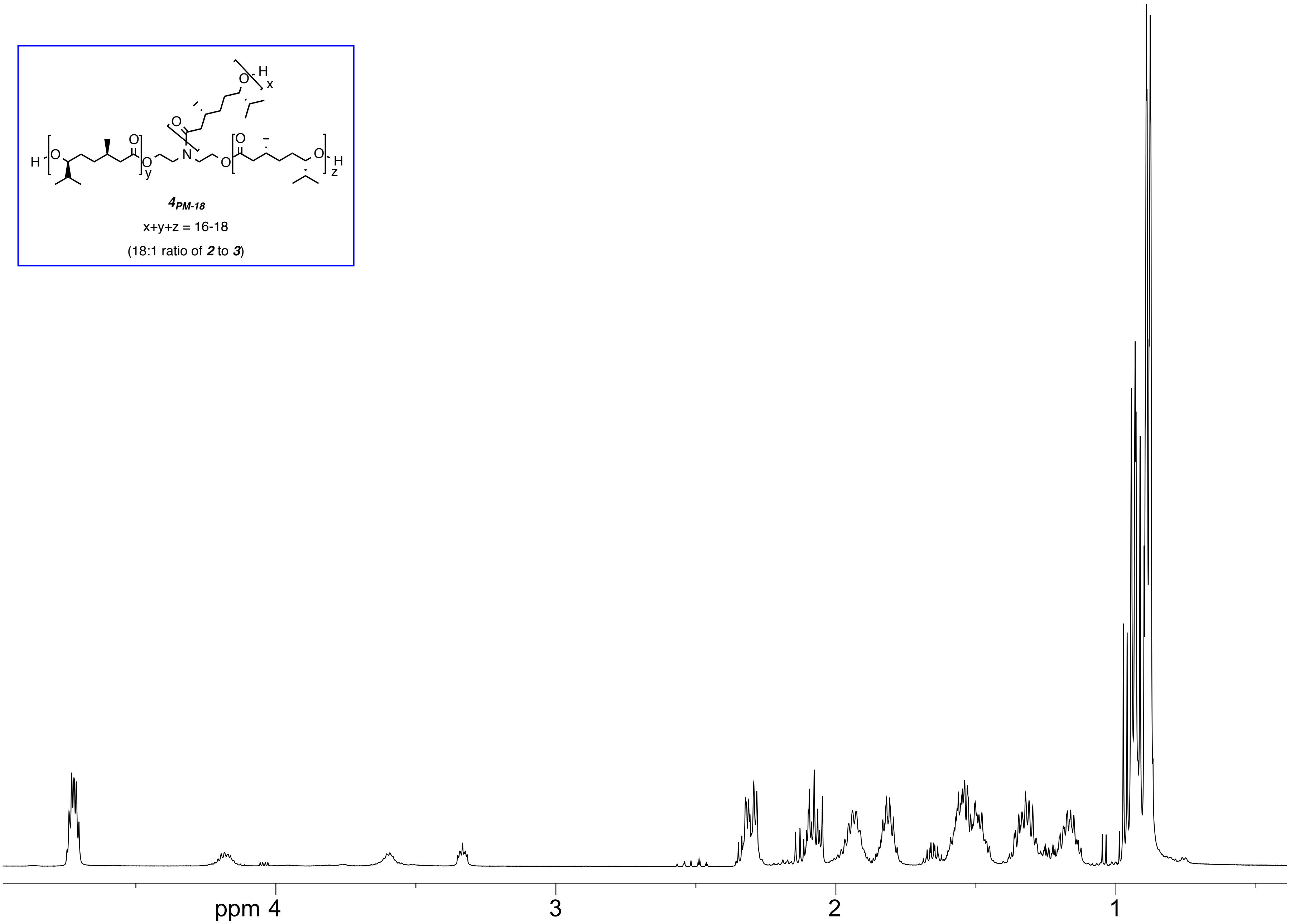

= carvomenthoyl
R1O
2
1
N
1'
2'
R2O
O
Me
p
Me
k
Hj
Hj*
l
m
n
Me
O
~2
a
b
c
d
e
Me
OH
O
Me
g
Me
R1/R2 = (carvomenthoyl)3/(carvomenthoyl)3
R1/R2 = (carvomenthoyl)3/H
8PM-9
(9:1 ratio of 7 to 3)
n
1/1'
e
2/2'
a/j
a*/j*
b
k
g/p
m/d
m*/d*
l/c
l*/c*
5
4
3
2
1

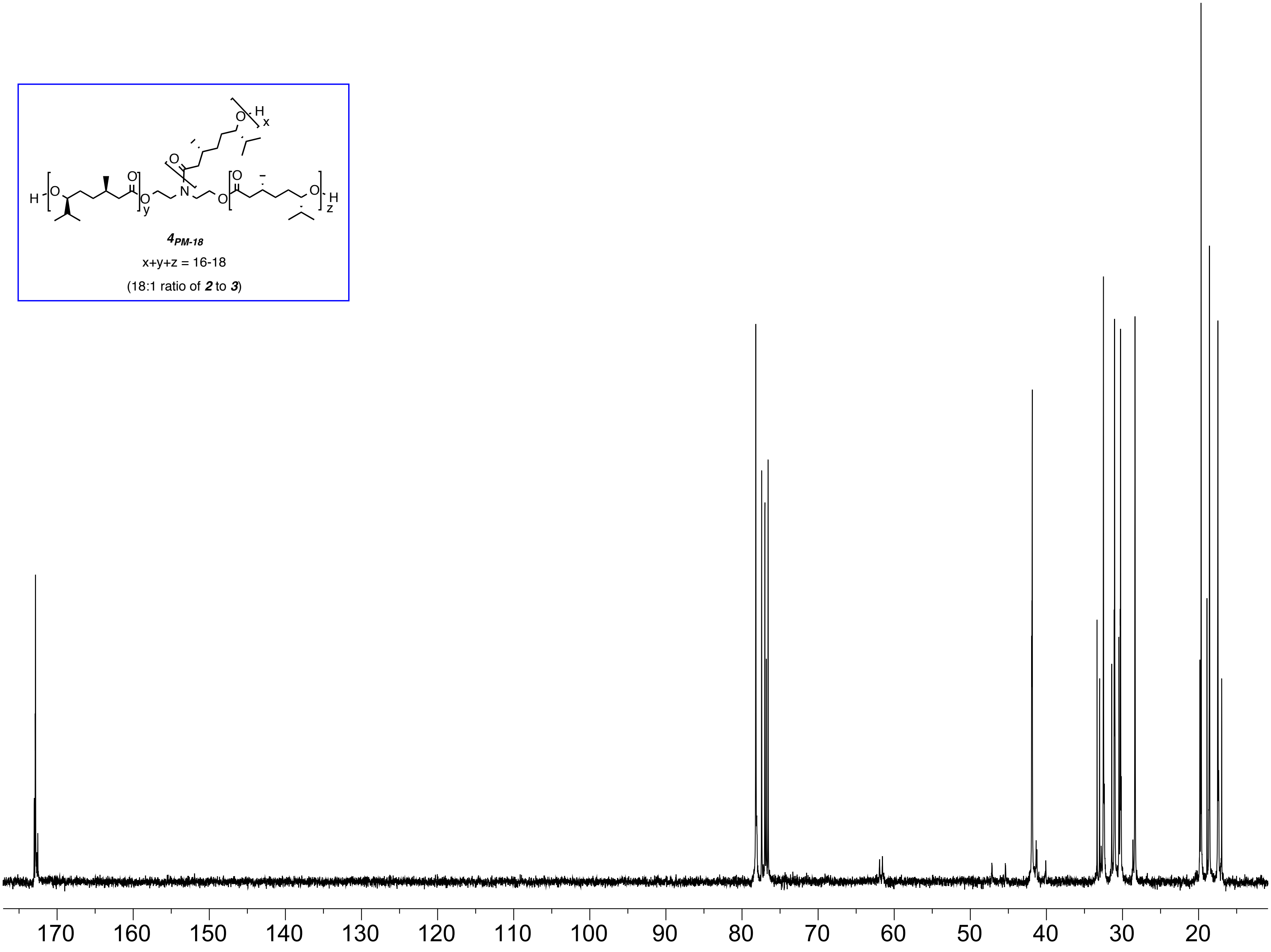


8_{PCM-9}

x+y+z ≈ 8

(9:1 ratio of ***7*** to ***3***)

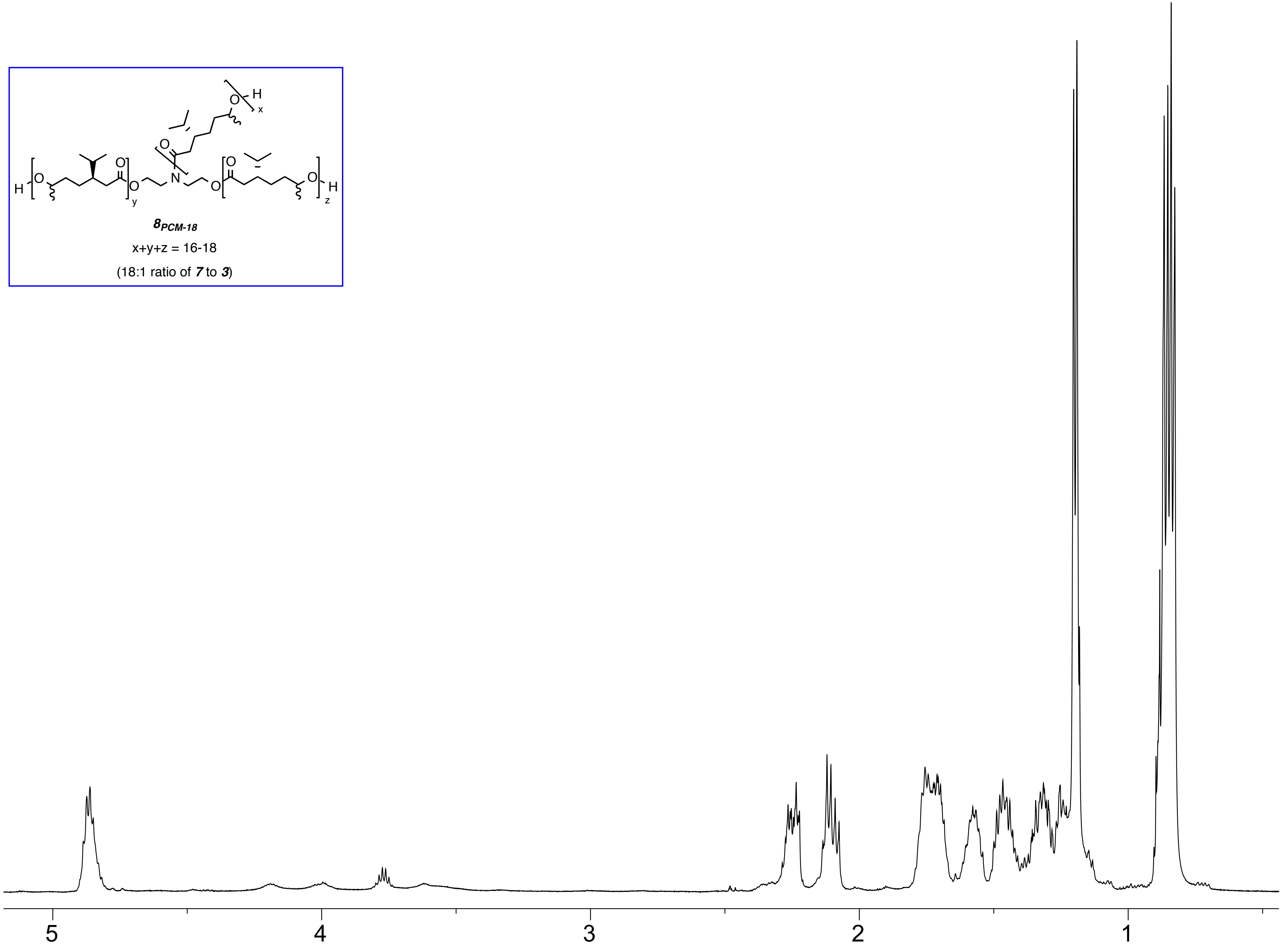

4PM-18
x+y+z = 16-18
(18:1 ratio of 2 to 3)
ppm 4
3
2
1



***4**$_{PM-18}$*

x+y+z = 16-18

(18:1 ratio of ***2*** to ***3***)

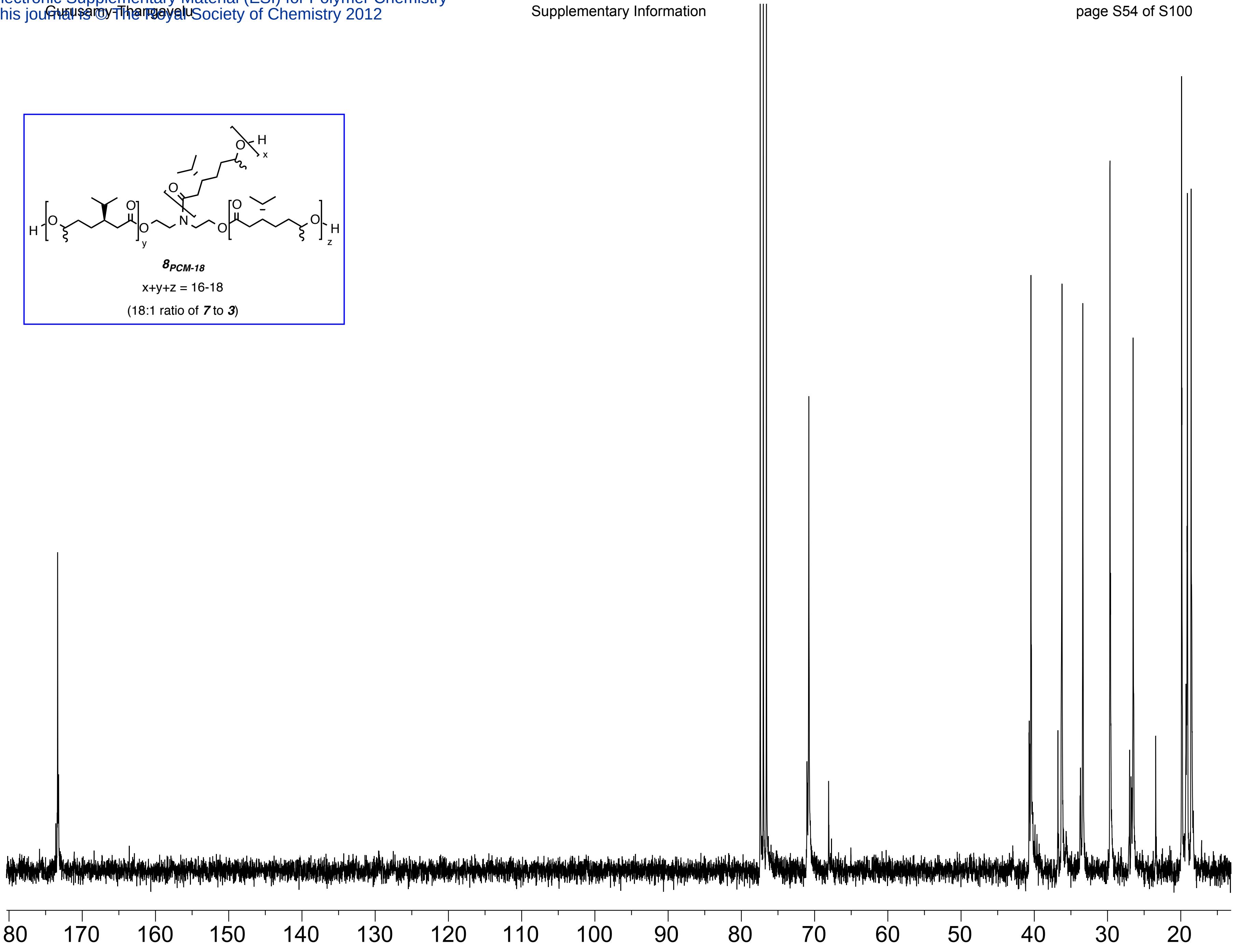


8

$\mathbf{8}_{PCM\text{-}18}$

x+y+z = 16-18

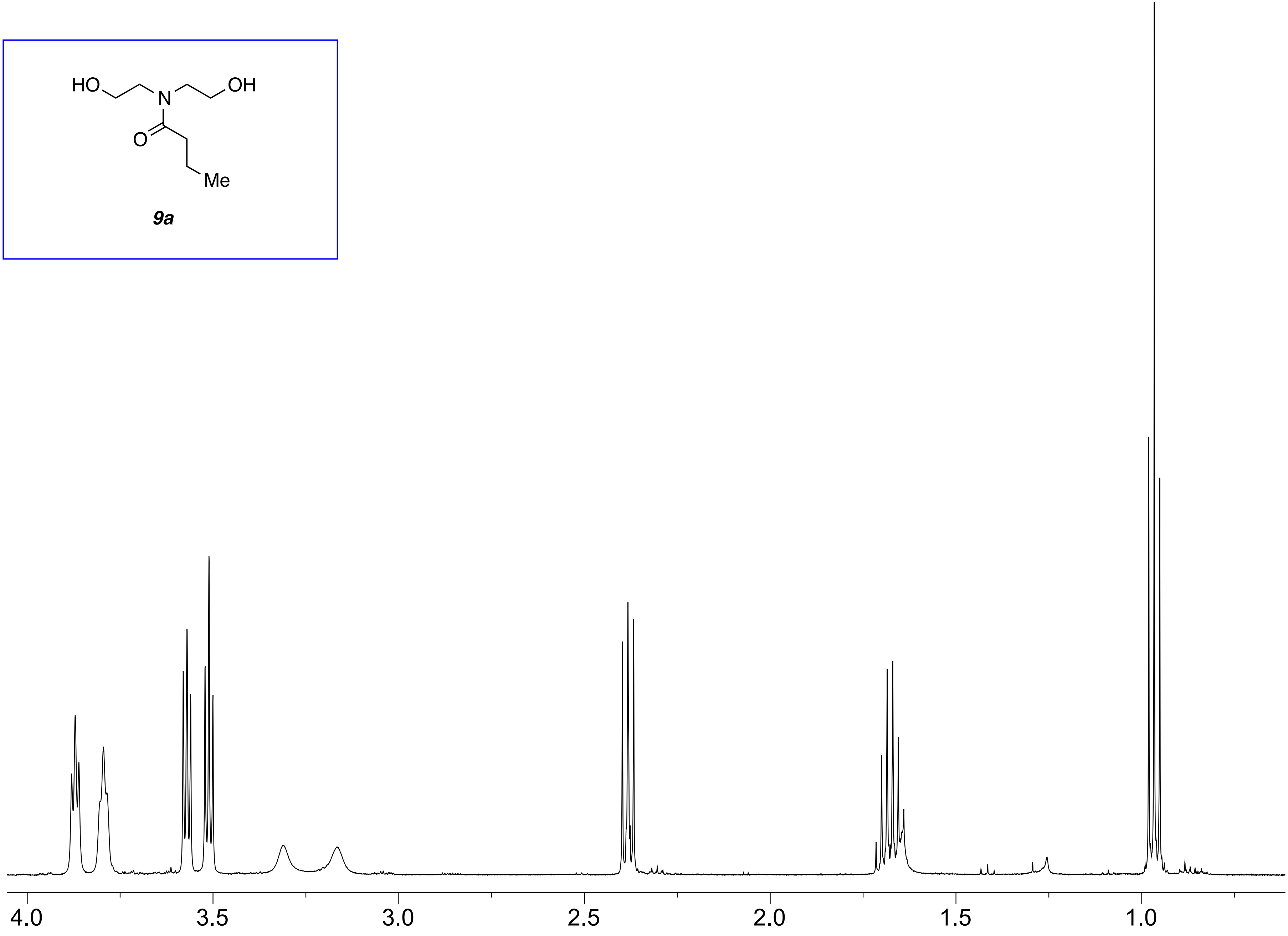
(18:1 ratio of ***7*** to ***3***)



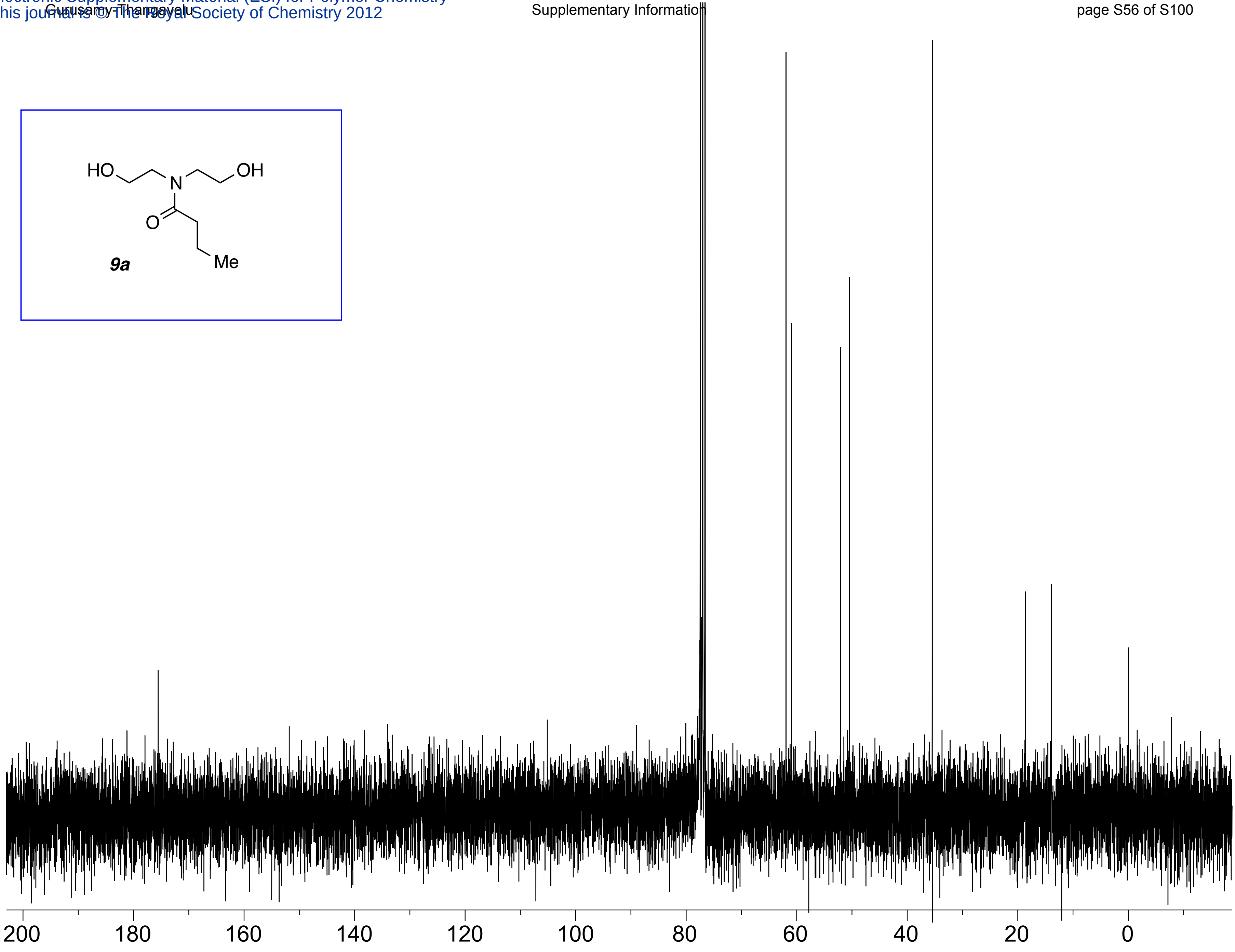
$8_{PCM\text{-}18}$

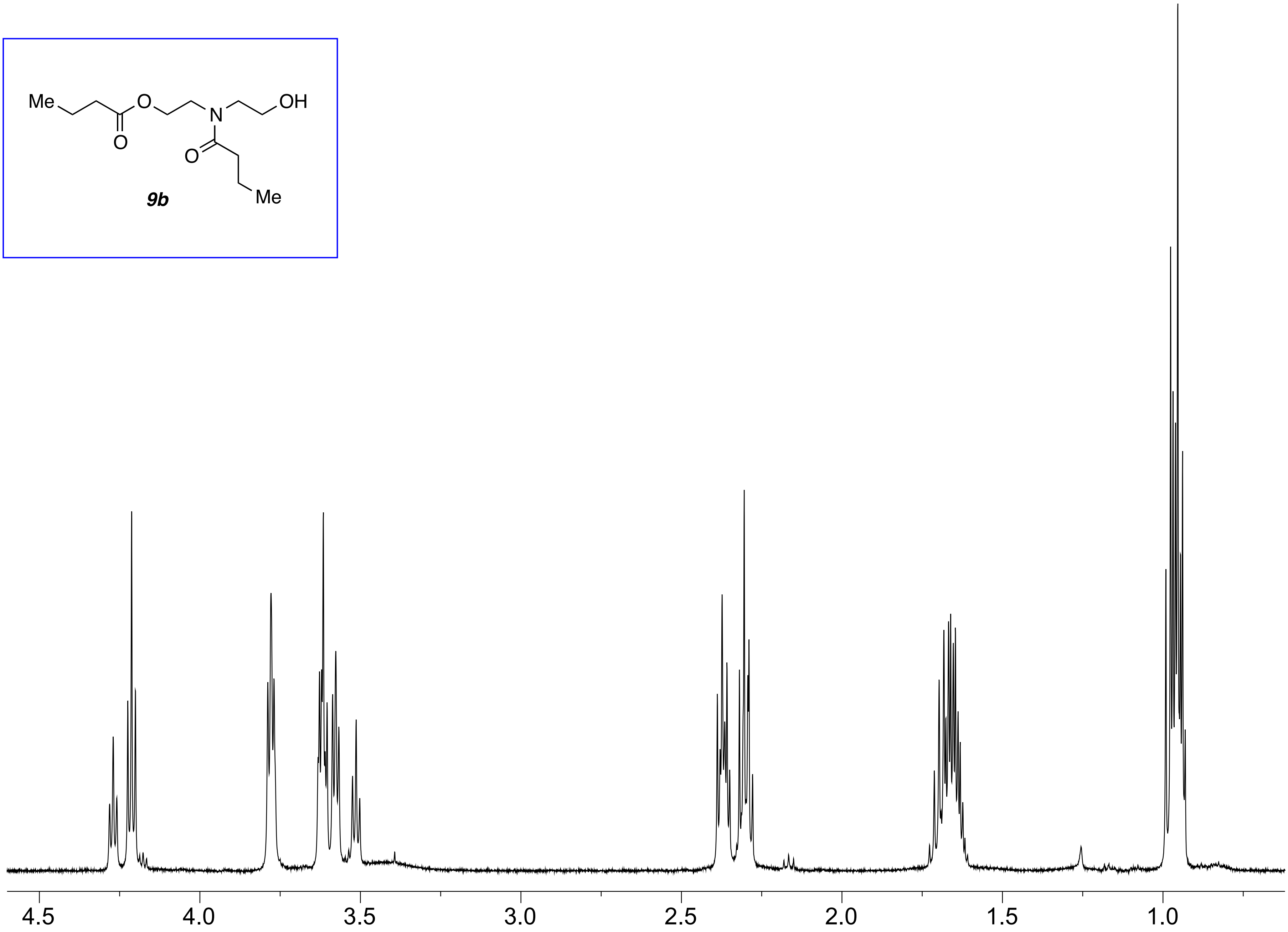
x+y+z = 16-18

(18:1 ratio of ***7*** to ***3***)

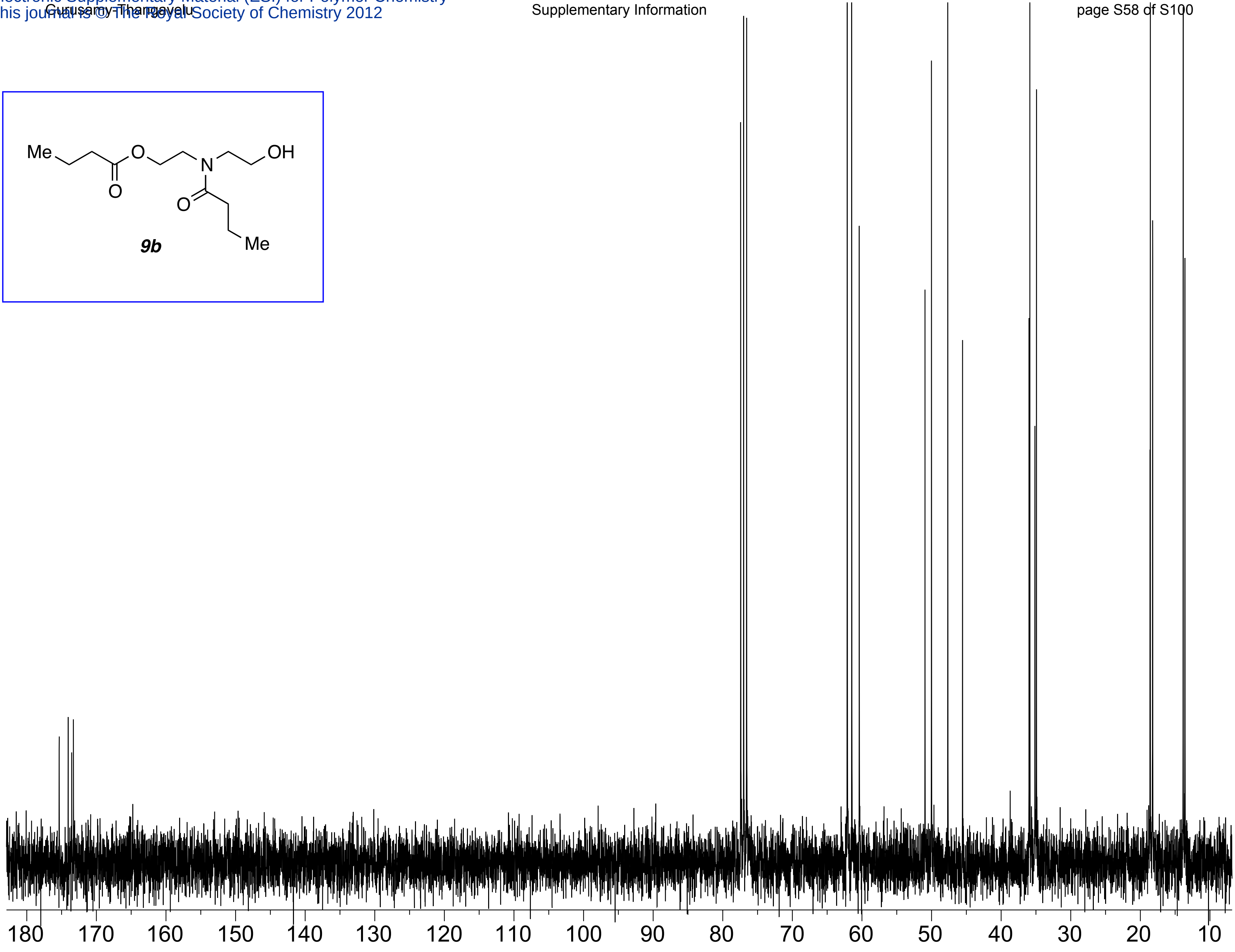


9a


HO
N
OH
O
Me
9a
200
180
160
140
120
100
80
60
40
20
0

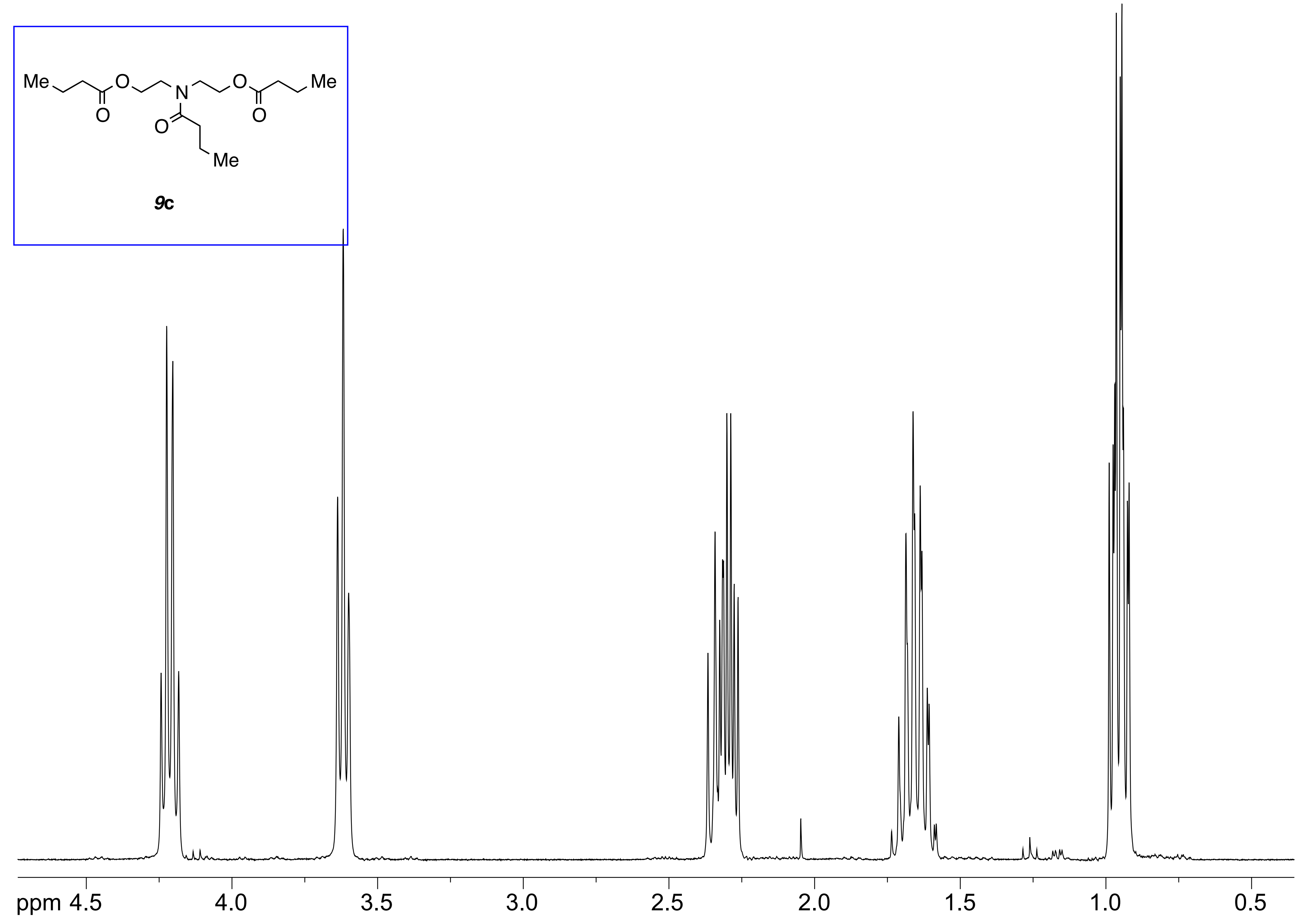


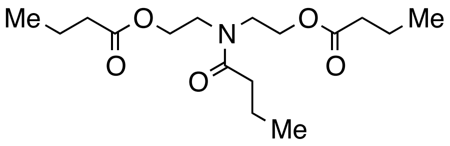
9b



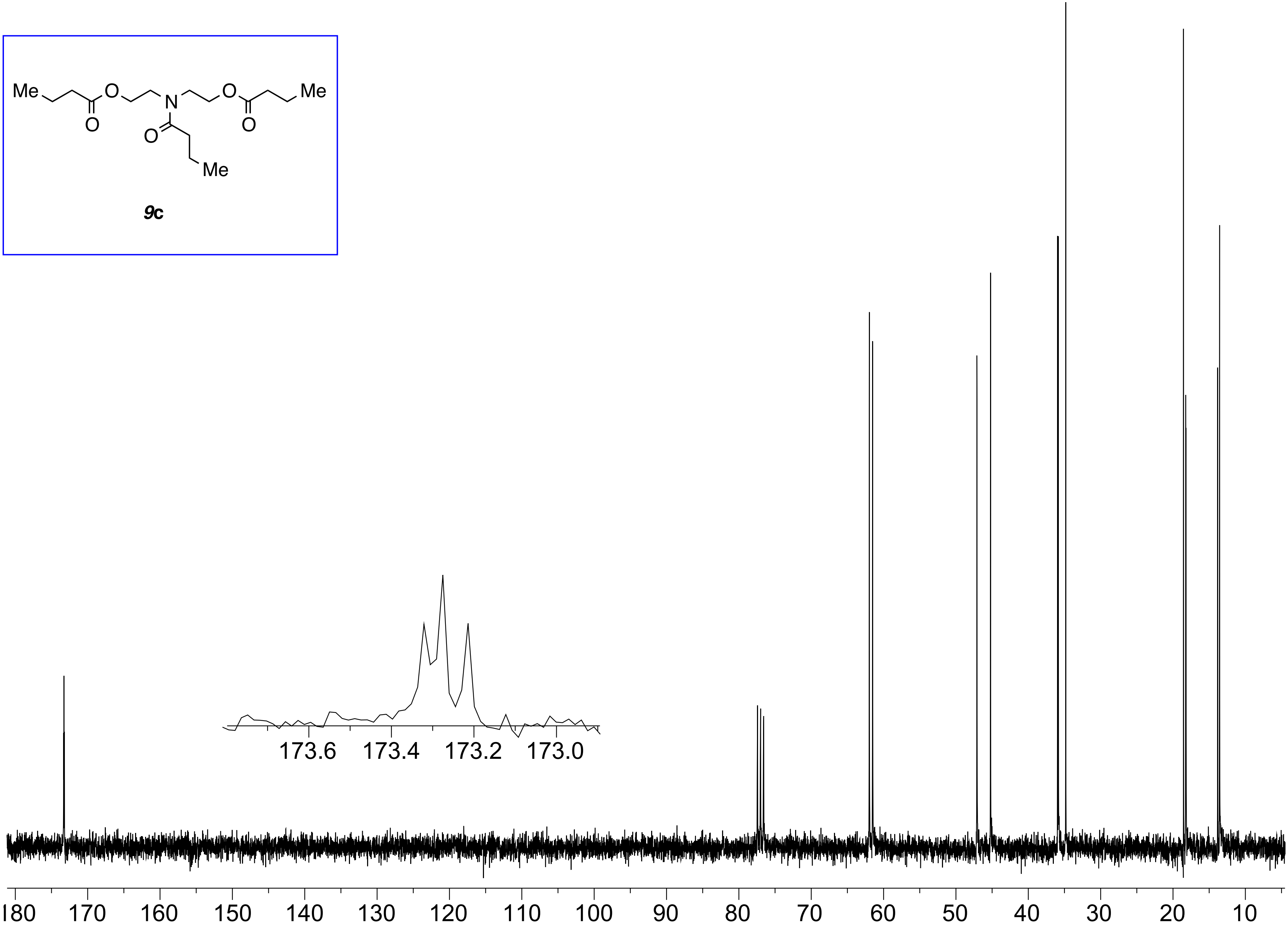
9b

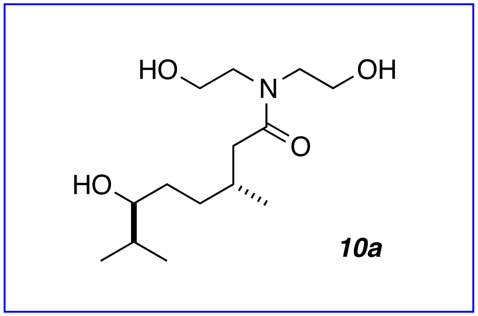
Me
O
N
OH
O
O
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Me
O
N
O
Me
O
O
O
Me
9c
ppm 4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

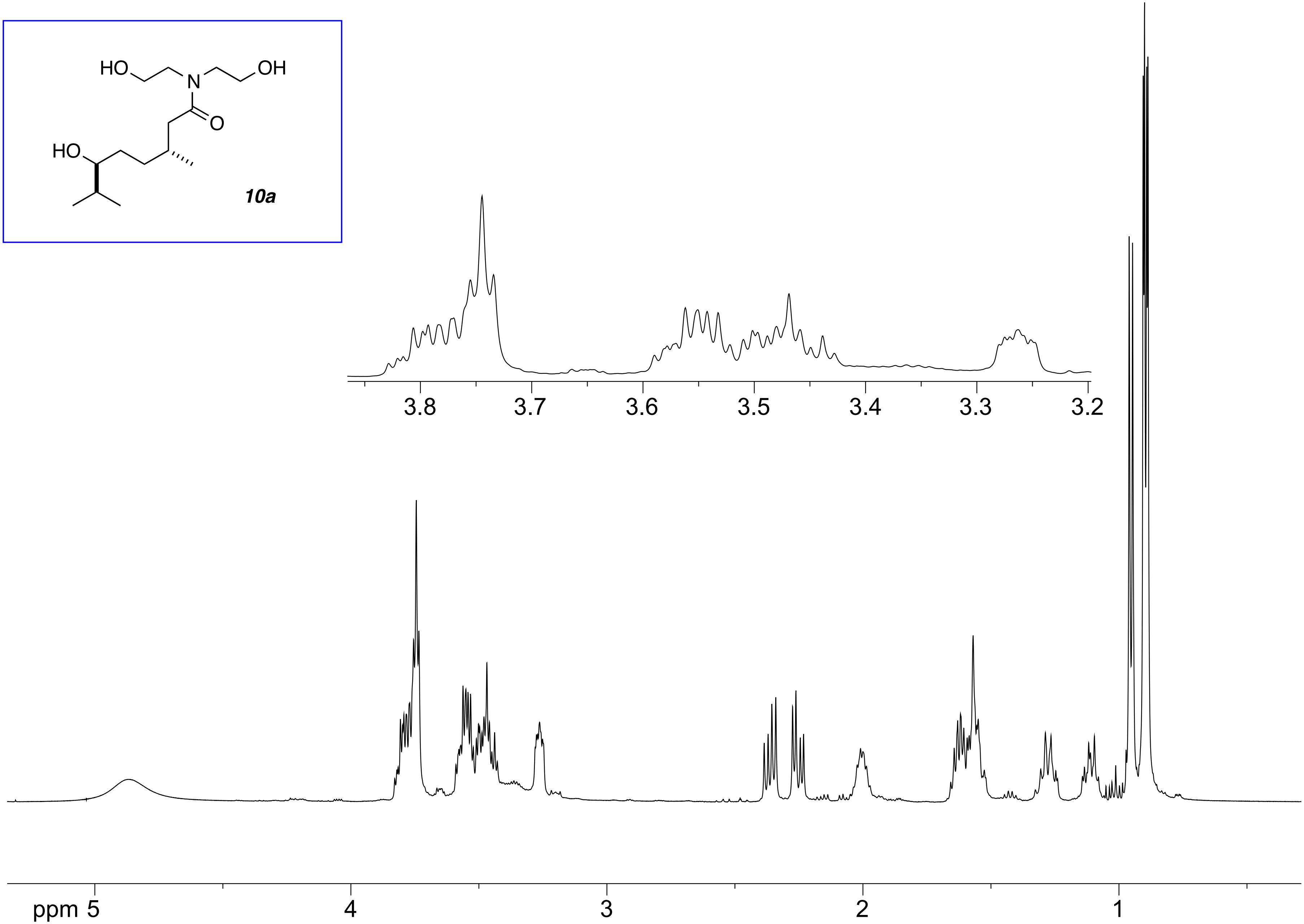

Me
O
N
O
Me
O
O
O
Me

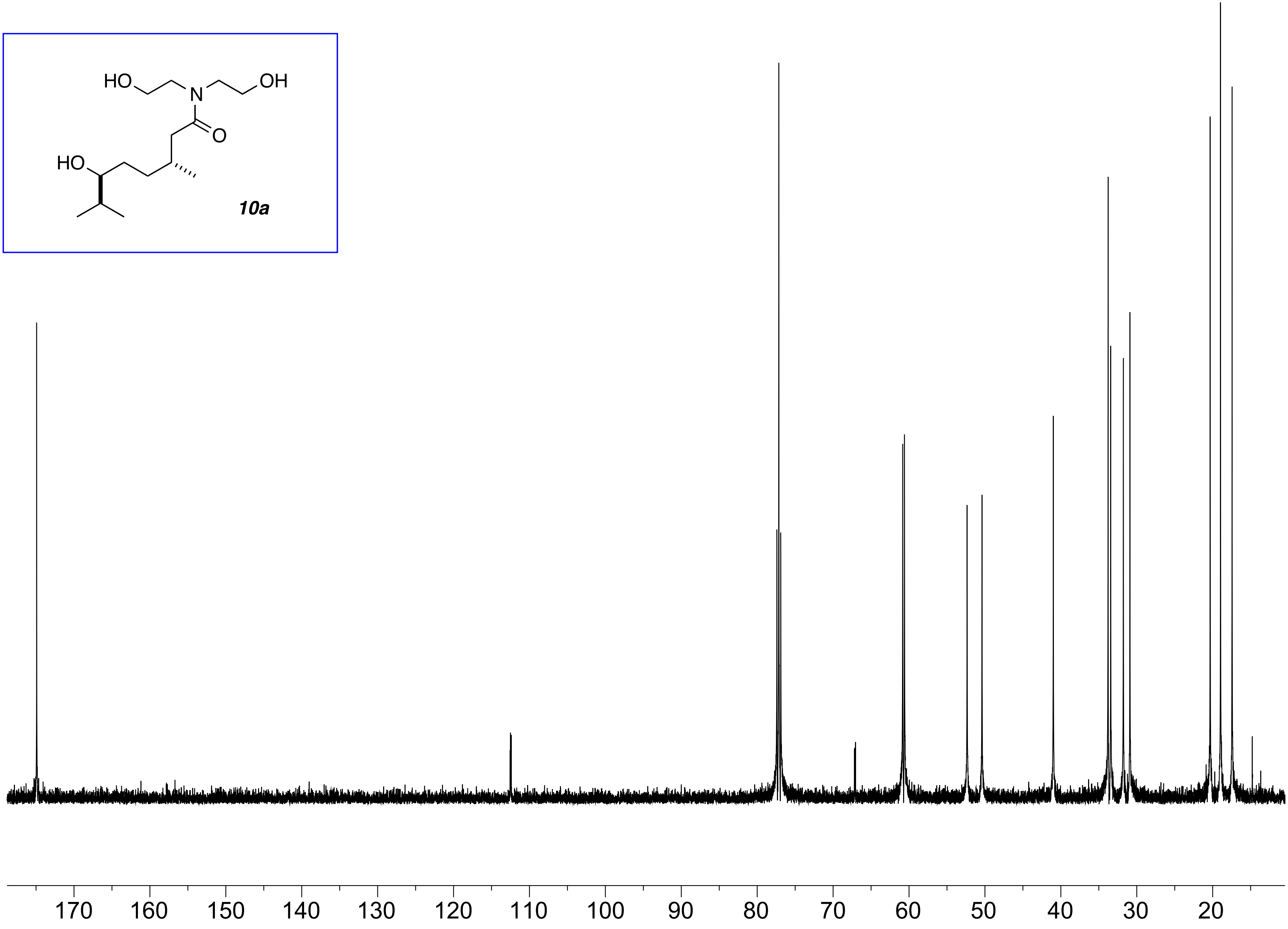
9c

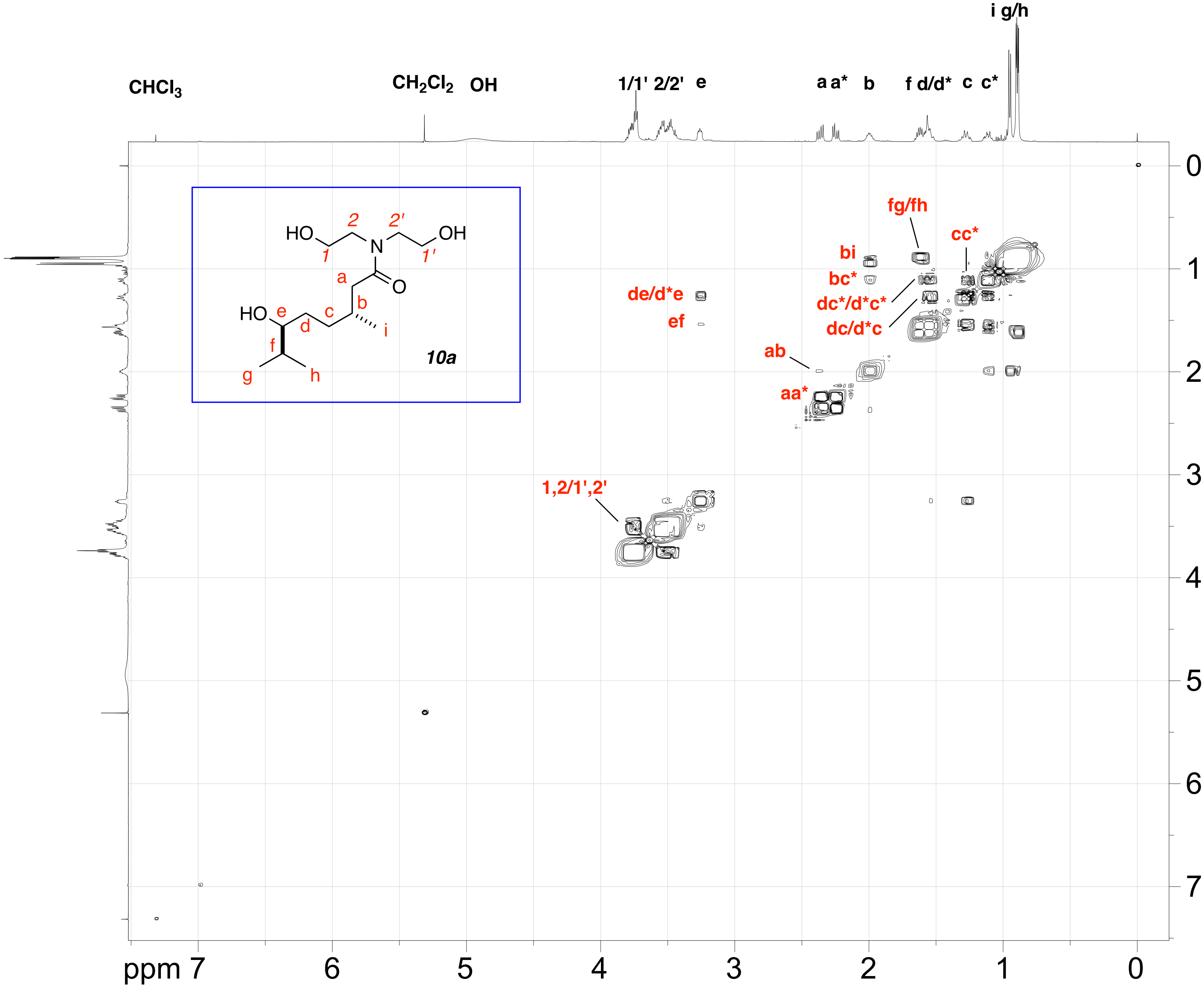

173.6
173.4
173.2
173.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

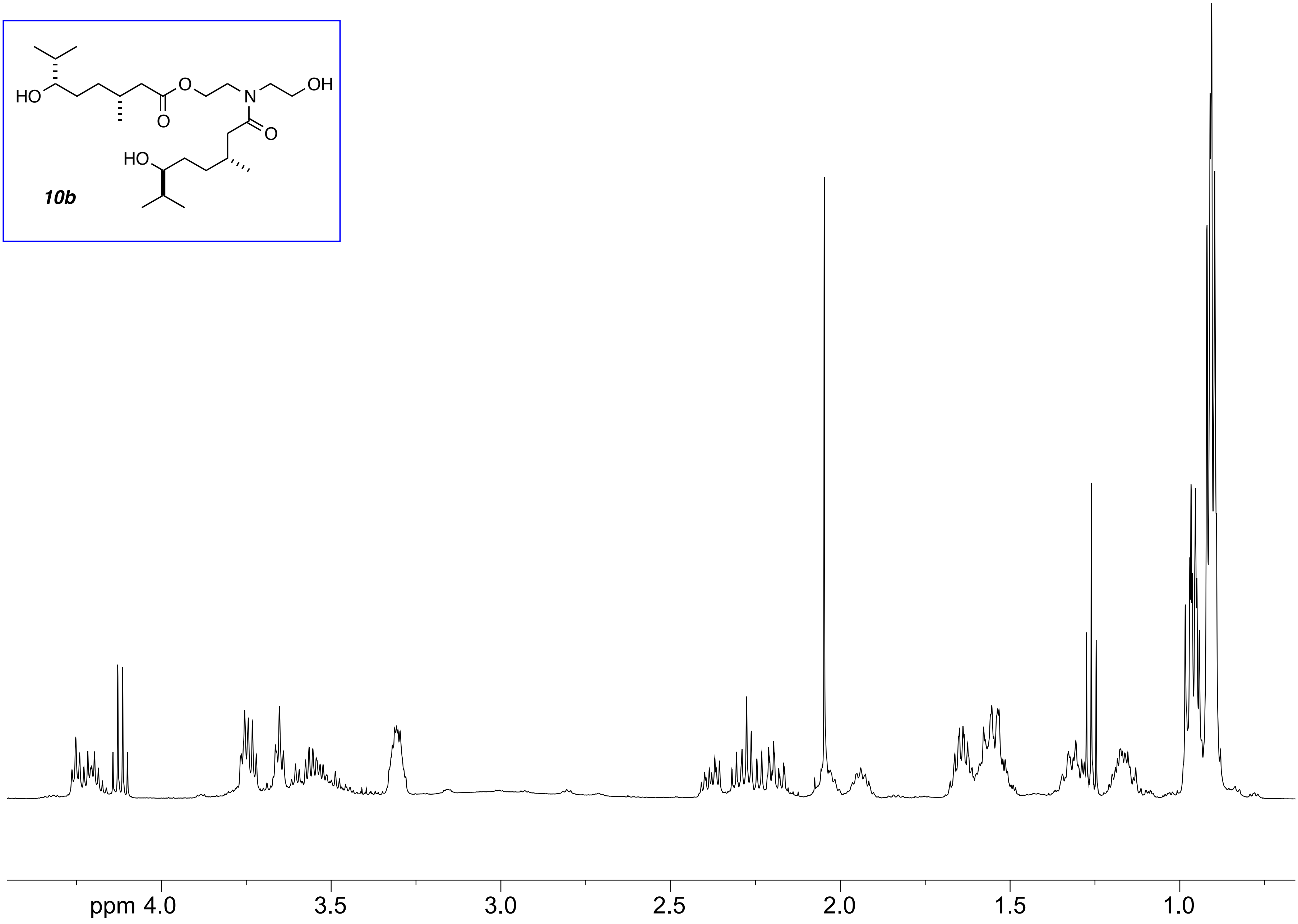


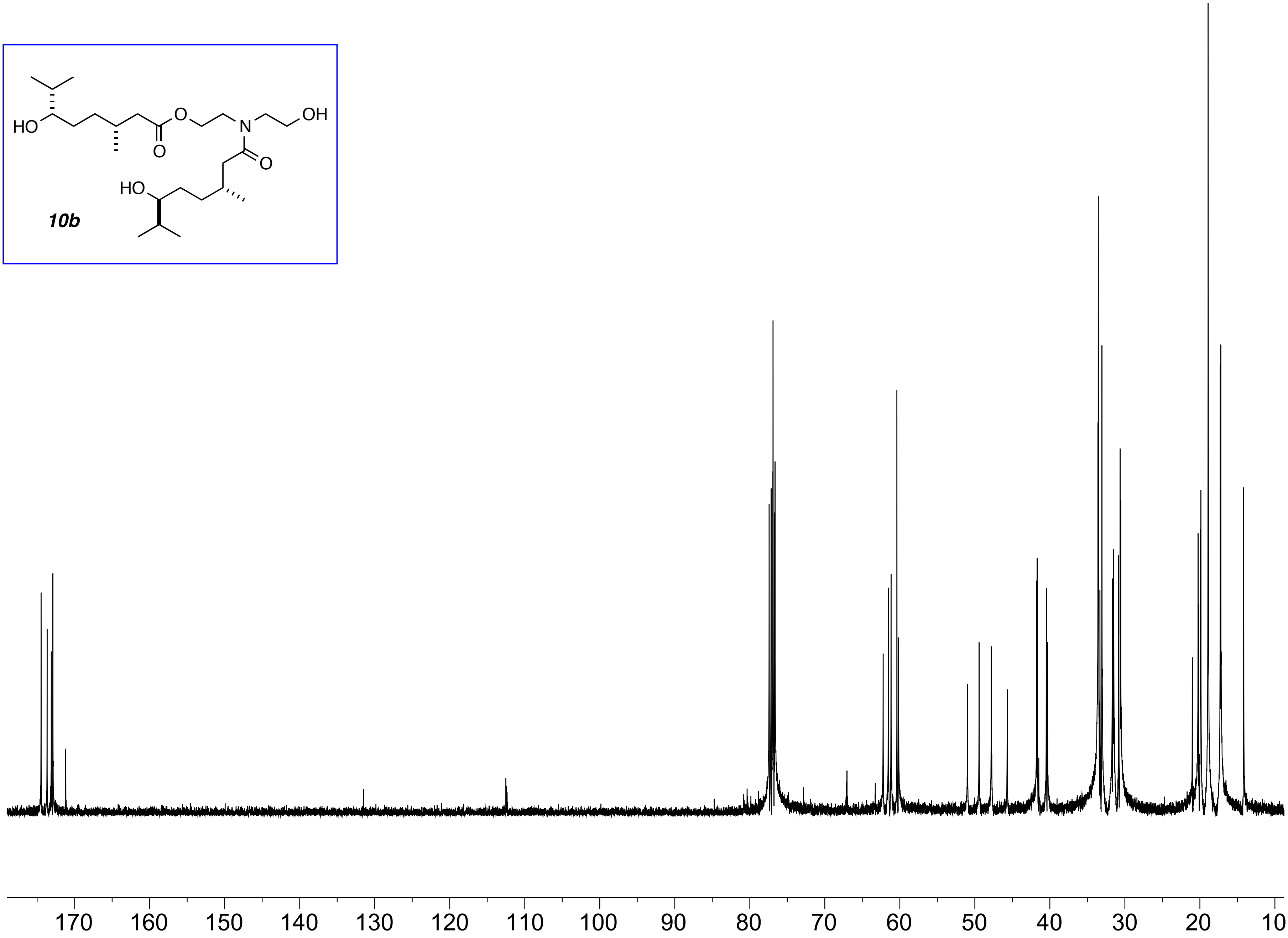
10a

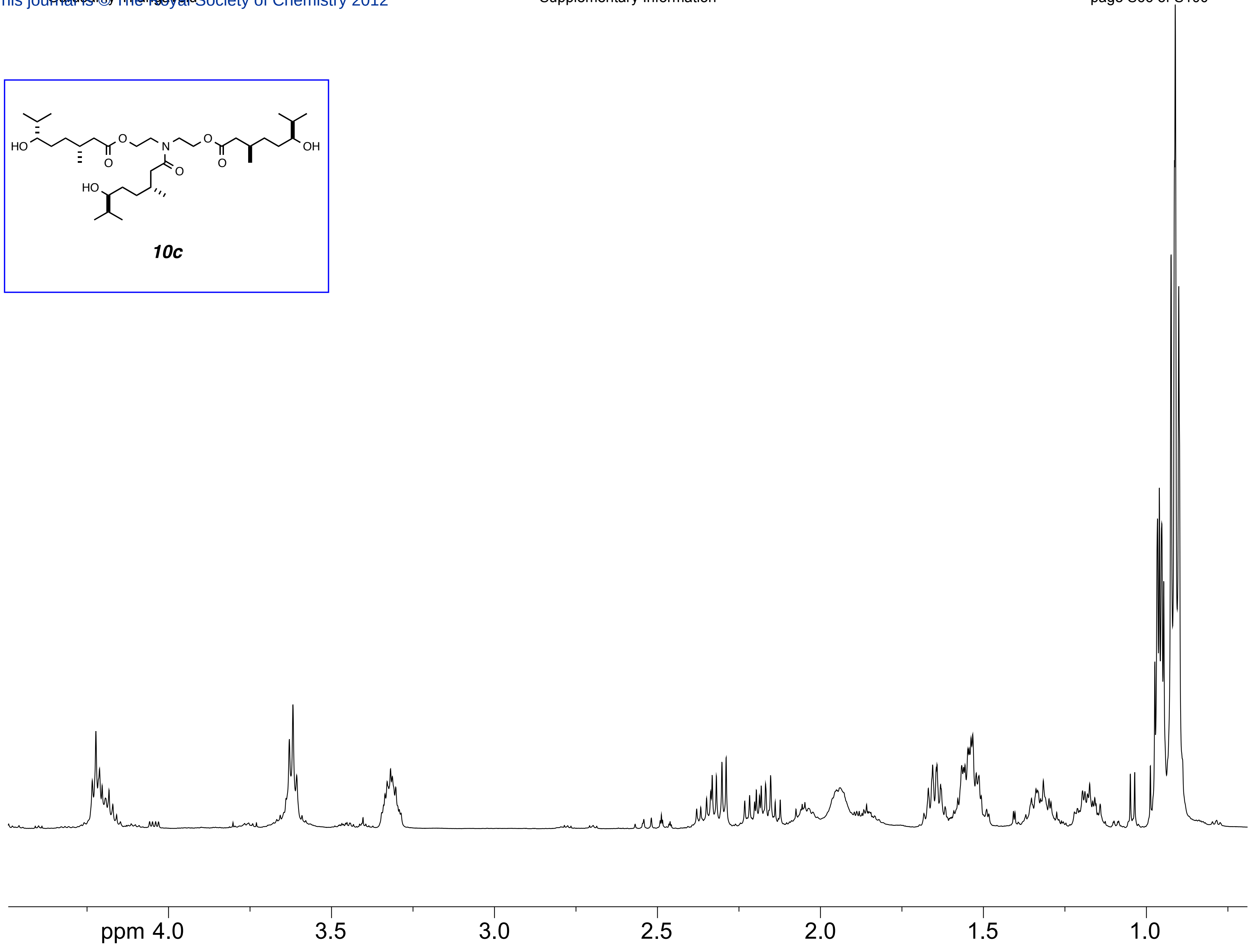



HO
N
OH
O
HO
10a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

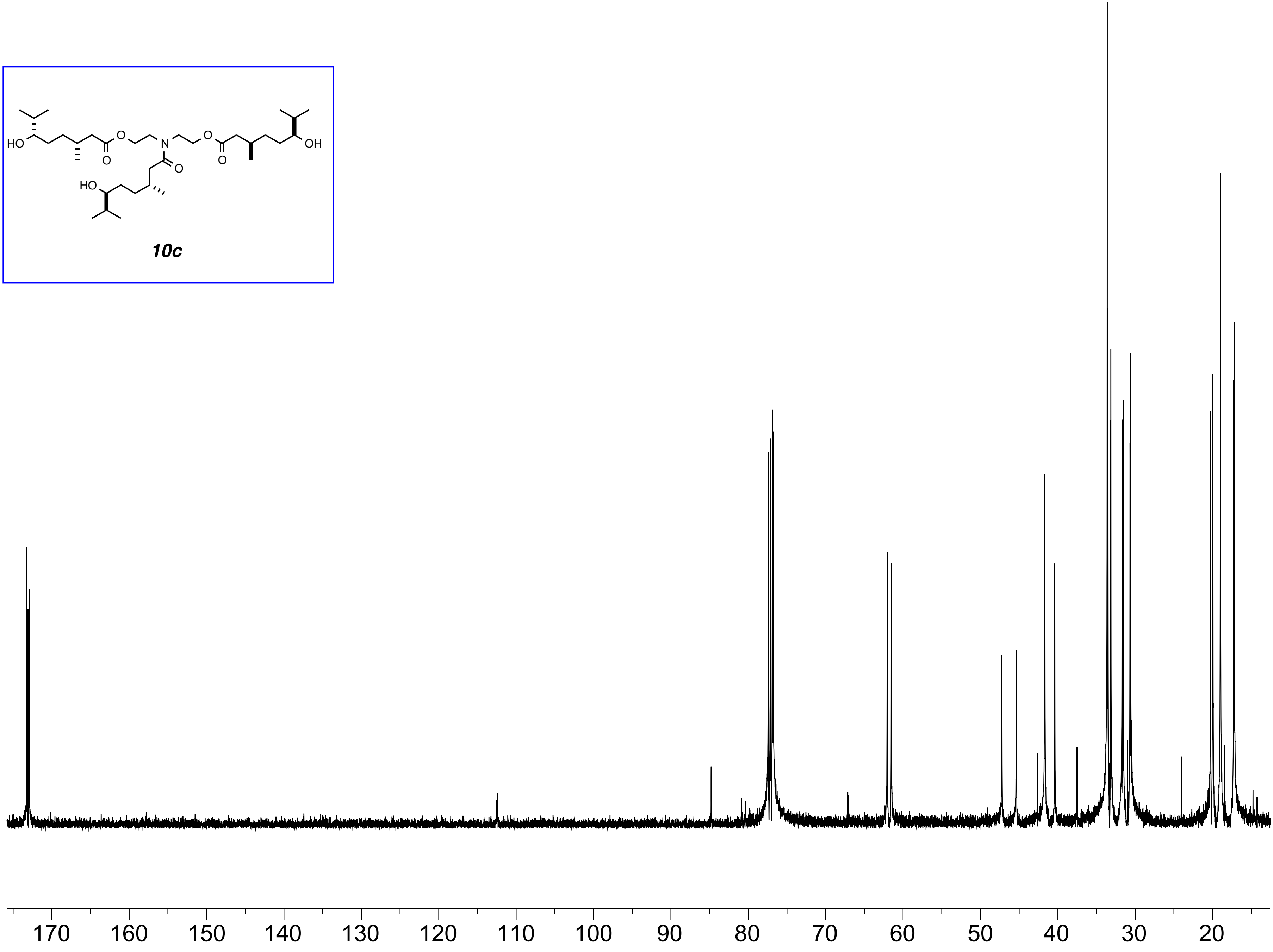

i g/h
CHCl$_3$
CH$_2$Cl$_2$
OH
1/1'
2/2'
e
a a*
b
f d/d*
c
c*
HO
2
2'
N
OH
1
1'
a
O
b
HO
e
c
d
i
f
g
h
10a
fg/fh
cc*
bi
bc*
dc*/d*c*
dc/d*c
de/d*e
ef
ab
aa*
1,2/1',2'
ppm 7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7


HO
O
N
OH
O
O
HO
10b
ppm 4.0
3.5
3.0
2.5
2.0
1.5
1.0


HO
O
O
N
OH
O
HO
10b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

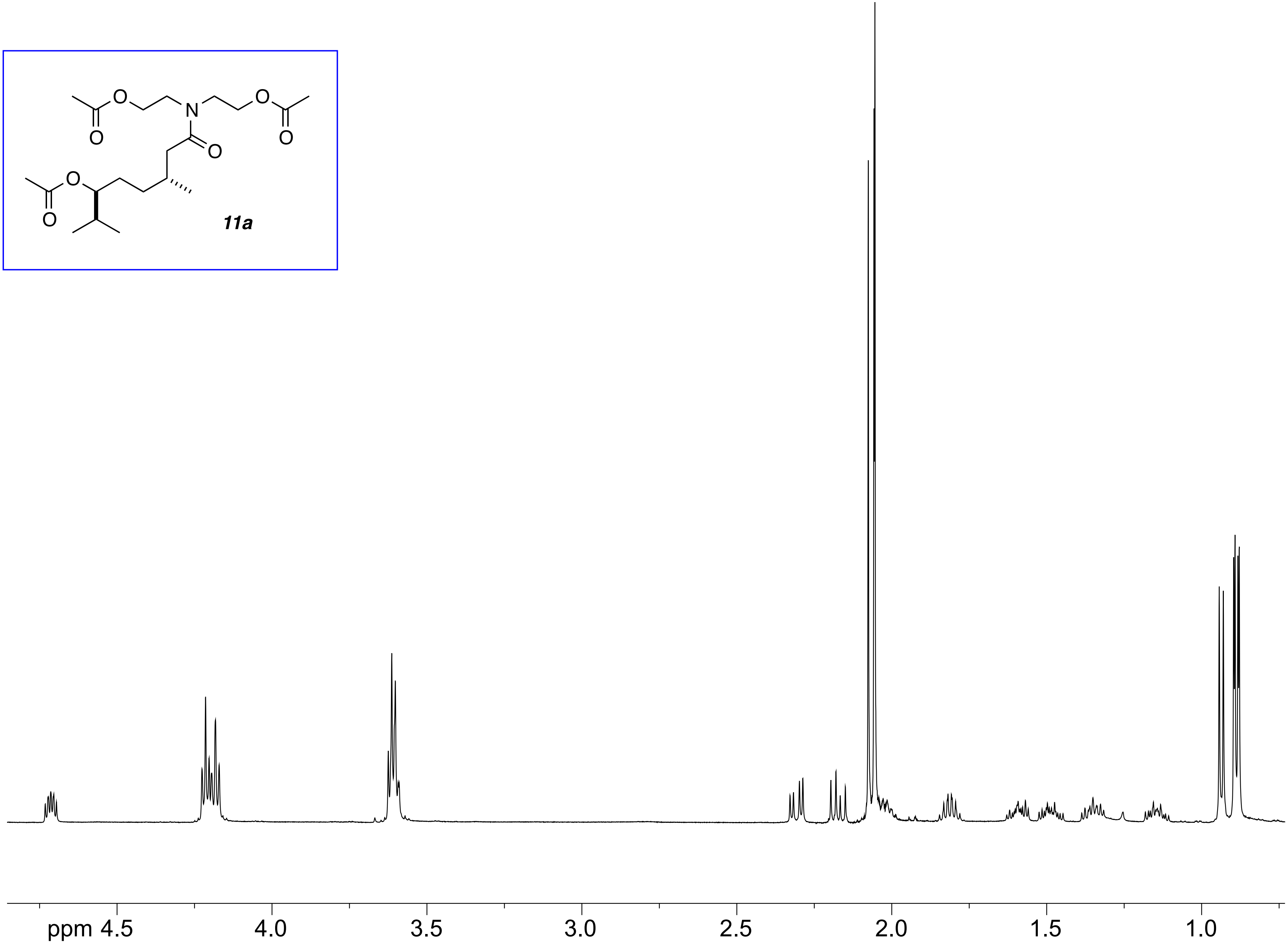


10c


HO
O
N
O
OH
O
O
O
HO

10c

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


11a
ppm 4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

Electronic Supplementary Material (ESI) for Polymer Chemistry
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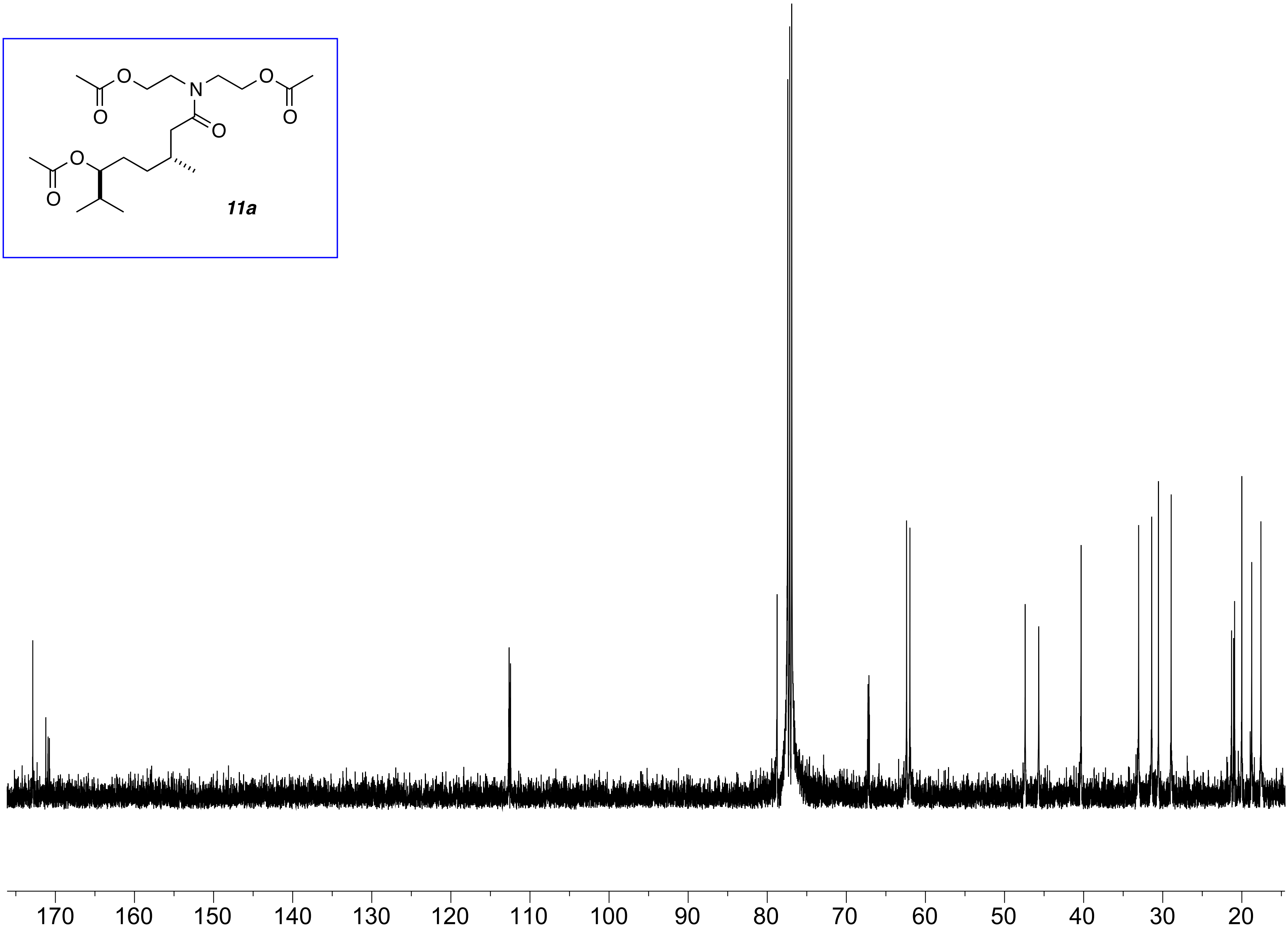
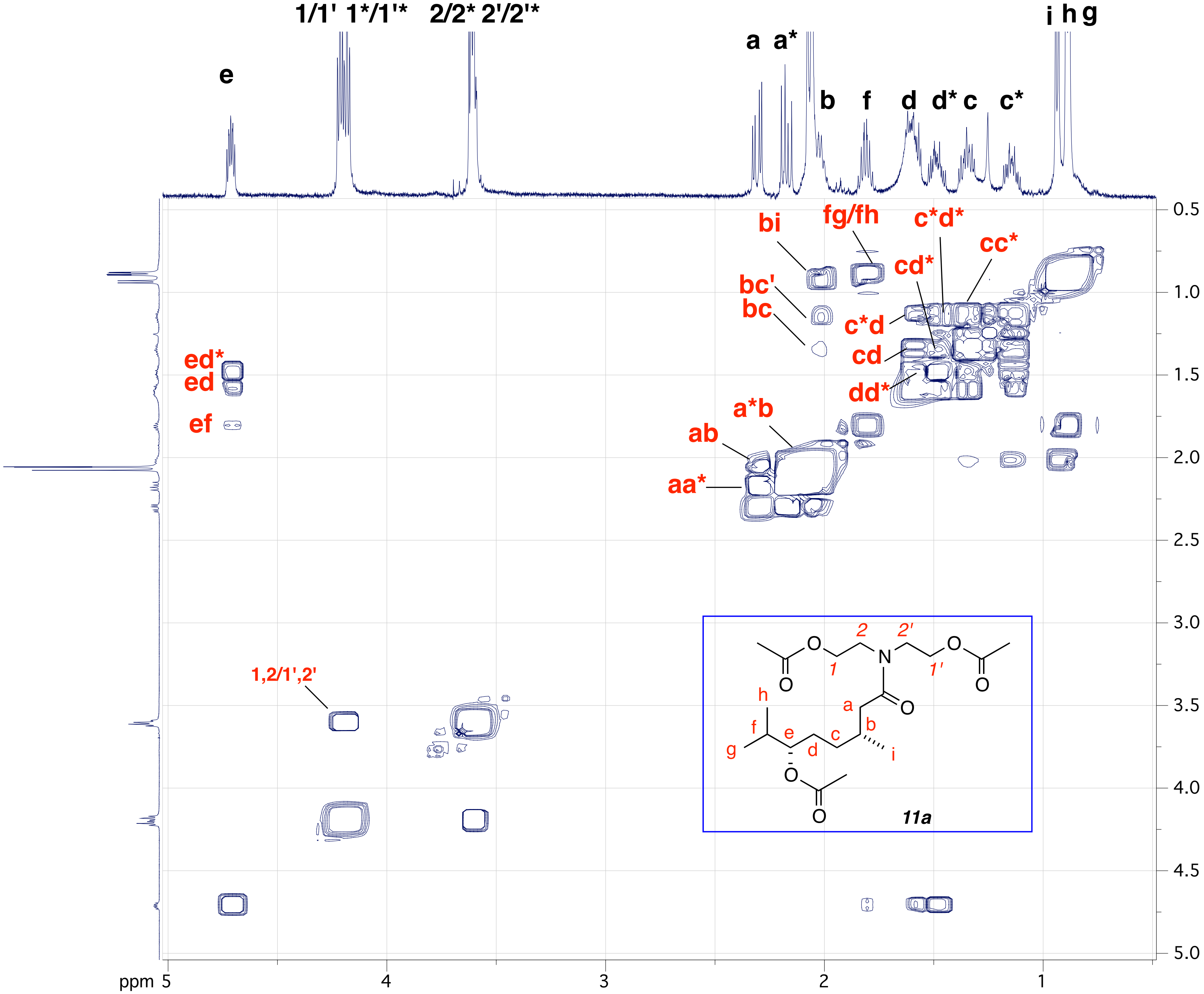
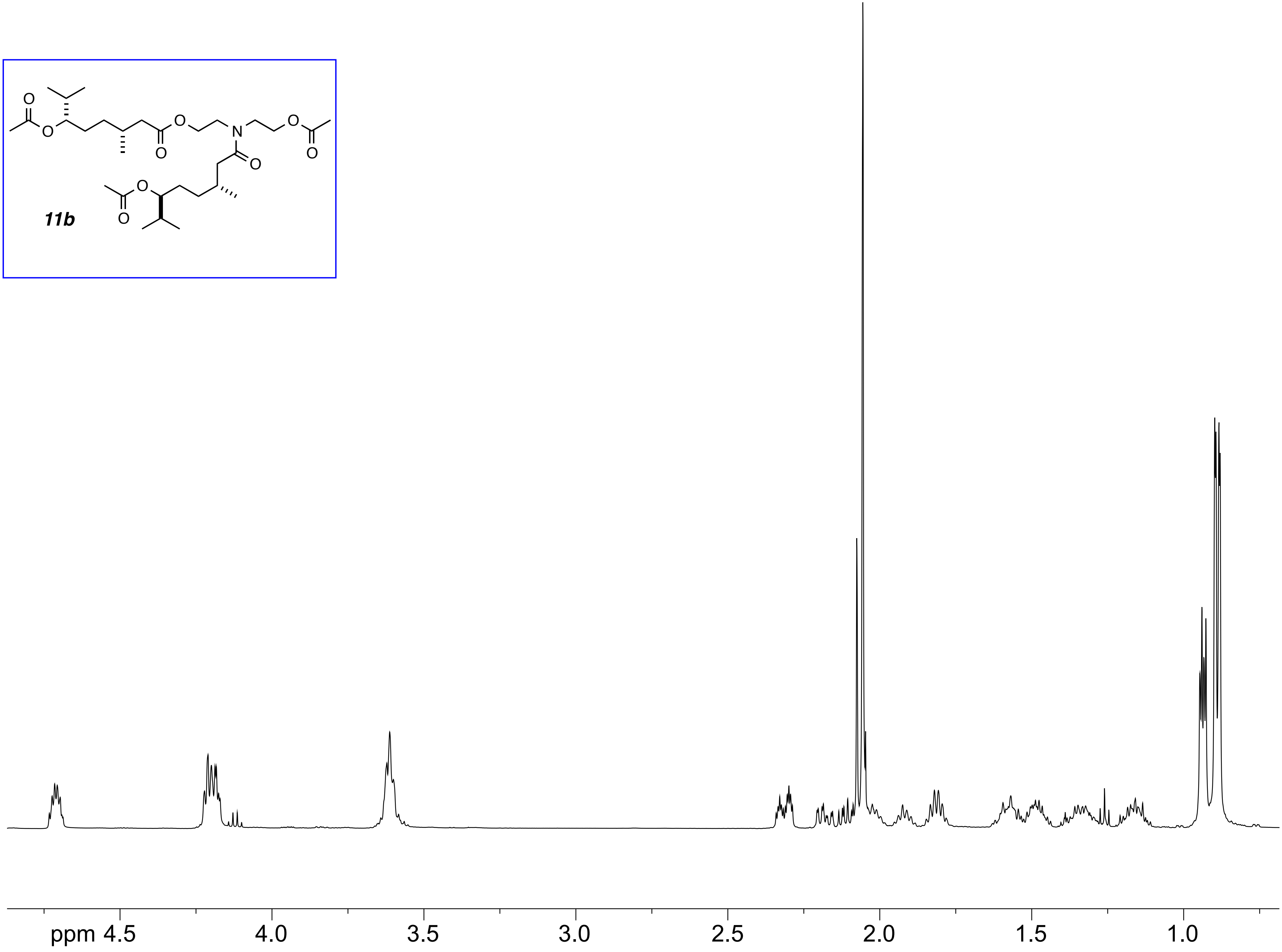
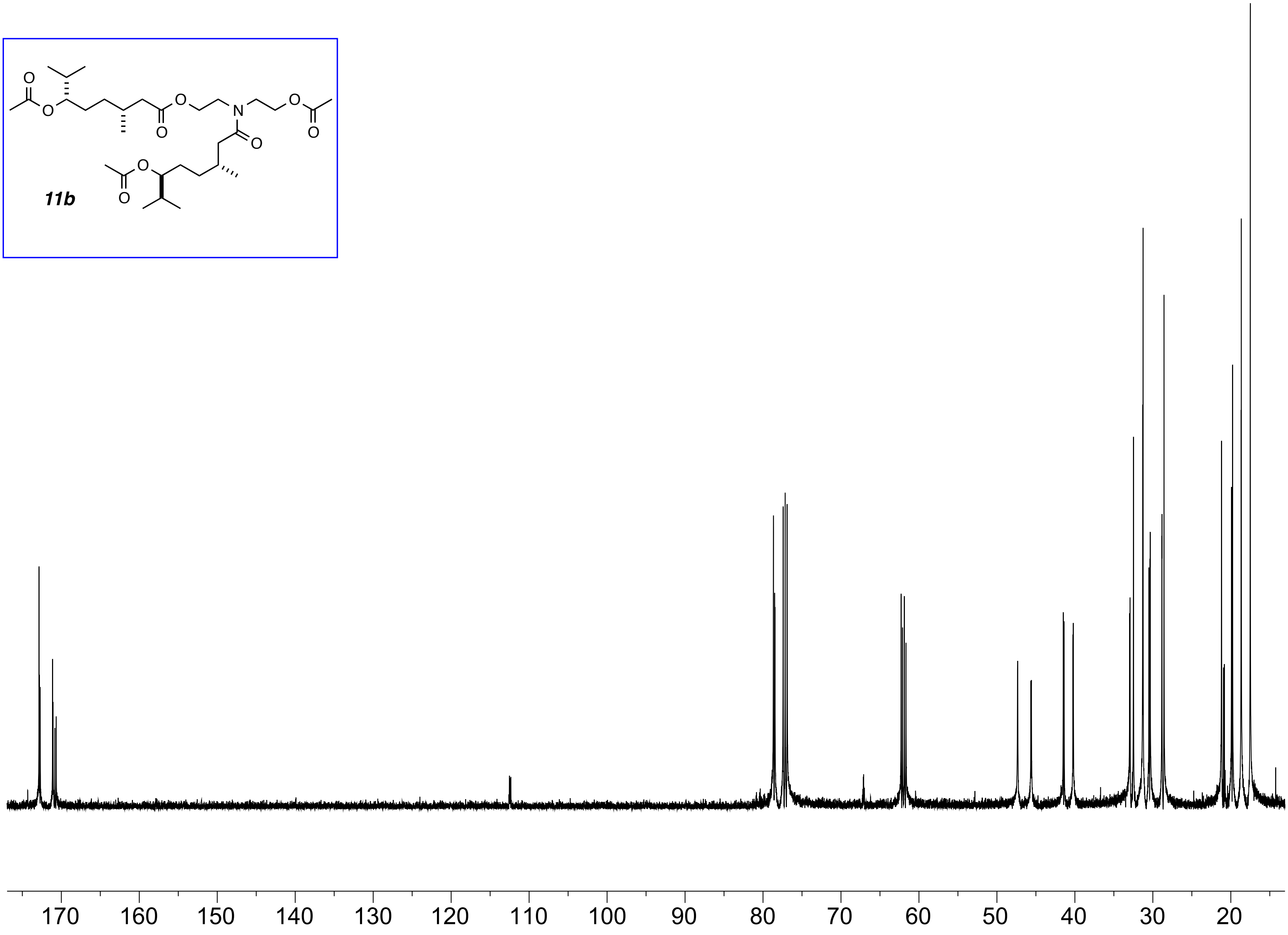


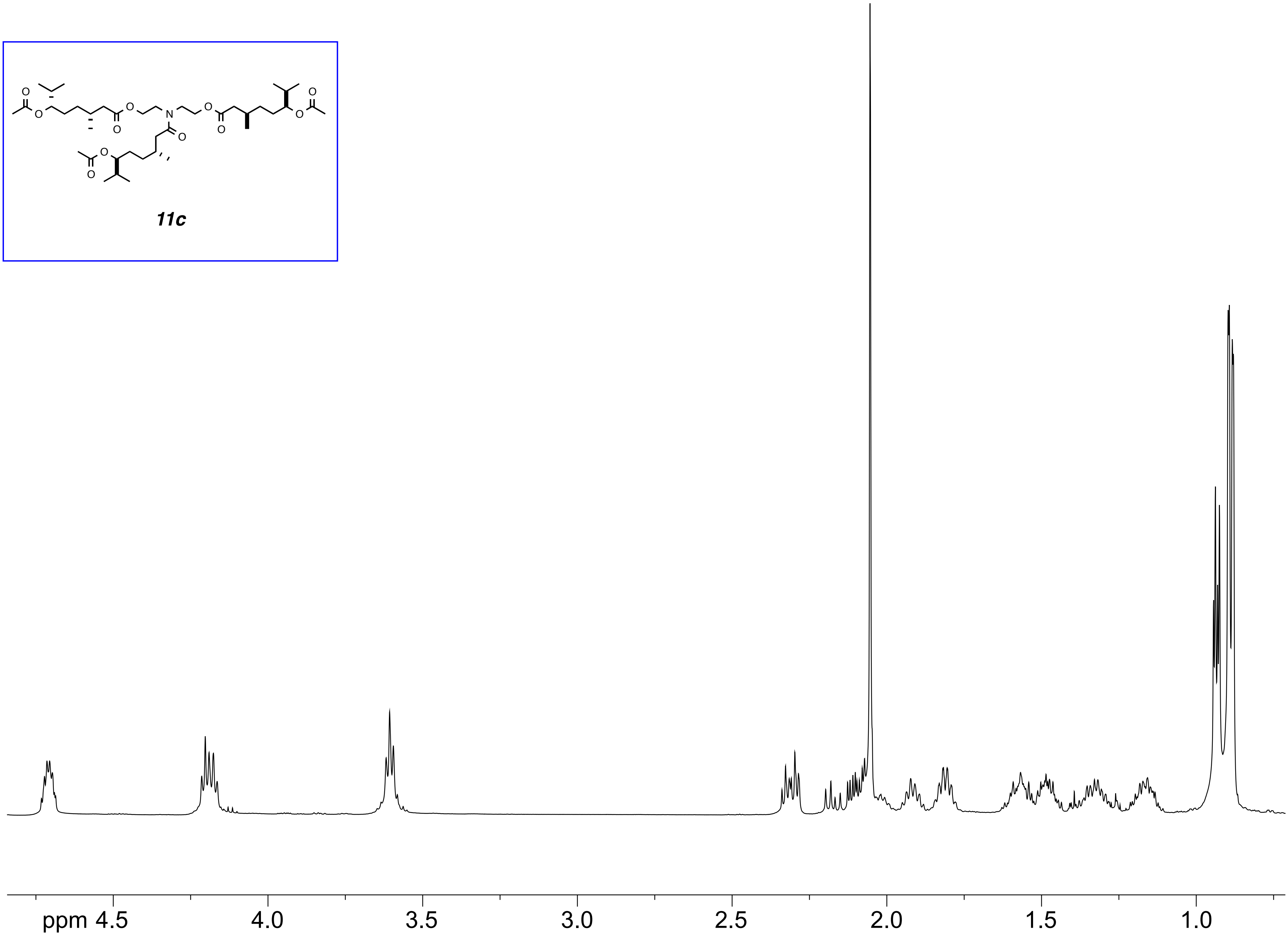

1/1' 1*/1'*
2/2* 2'/2'*
e
a a*
b
f
d d* c
c*
i h g
bi
fg/fh
c*d*
cc*
cd*
bc'
bc
c*d
cd
dd*
ed*
ed
ef
a*b
ab
aa*
1,2/1',2'
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ppm 5
4
3
2
1
2
2'
O
N
O
1
1'
O
O
h
a
O
f
e
b
c
g
d
i
O
O
11a



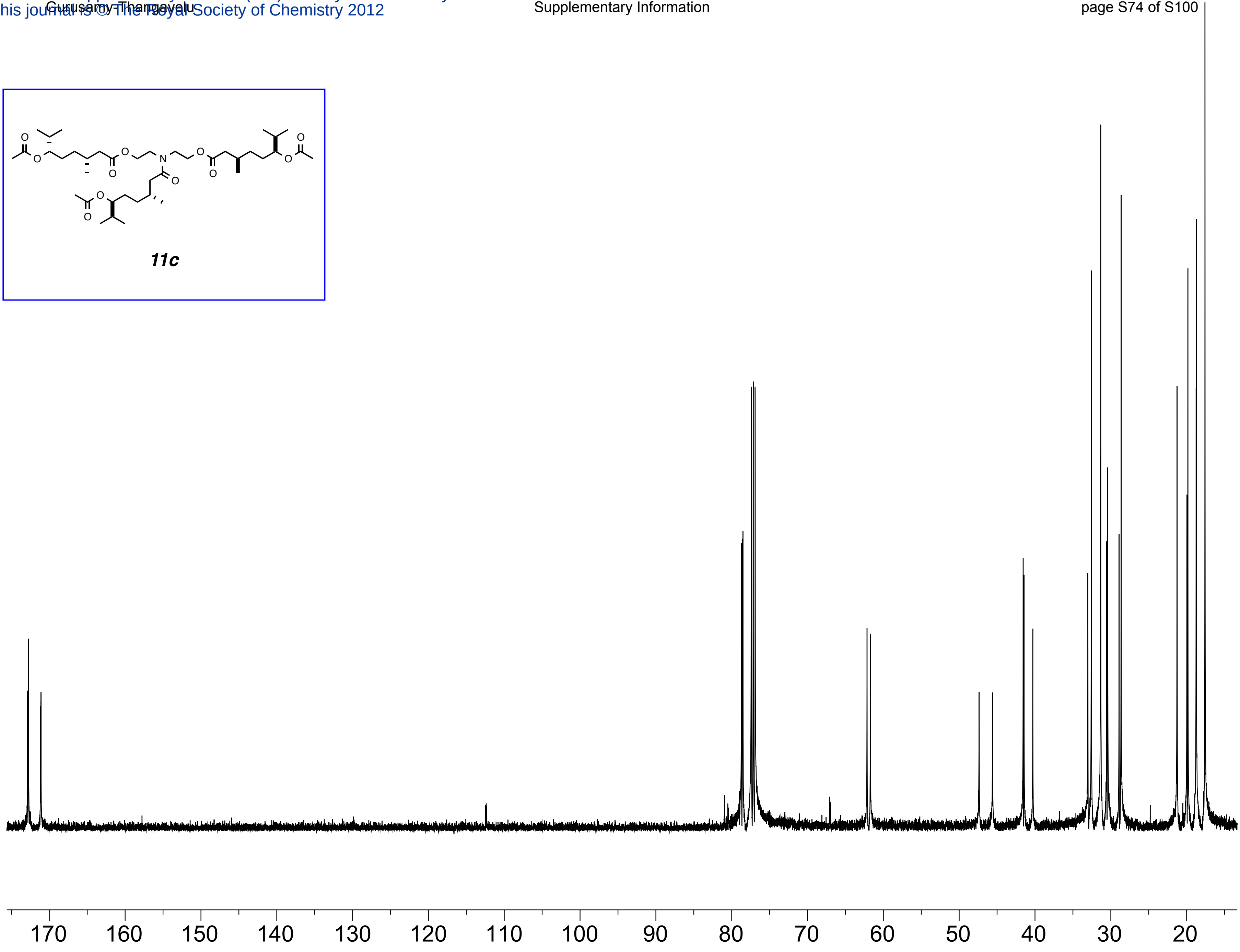
11b


O
O
O
O
N
O
O
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

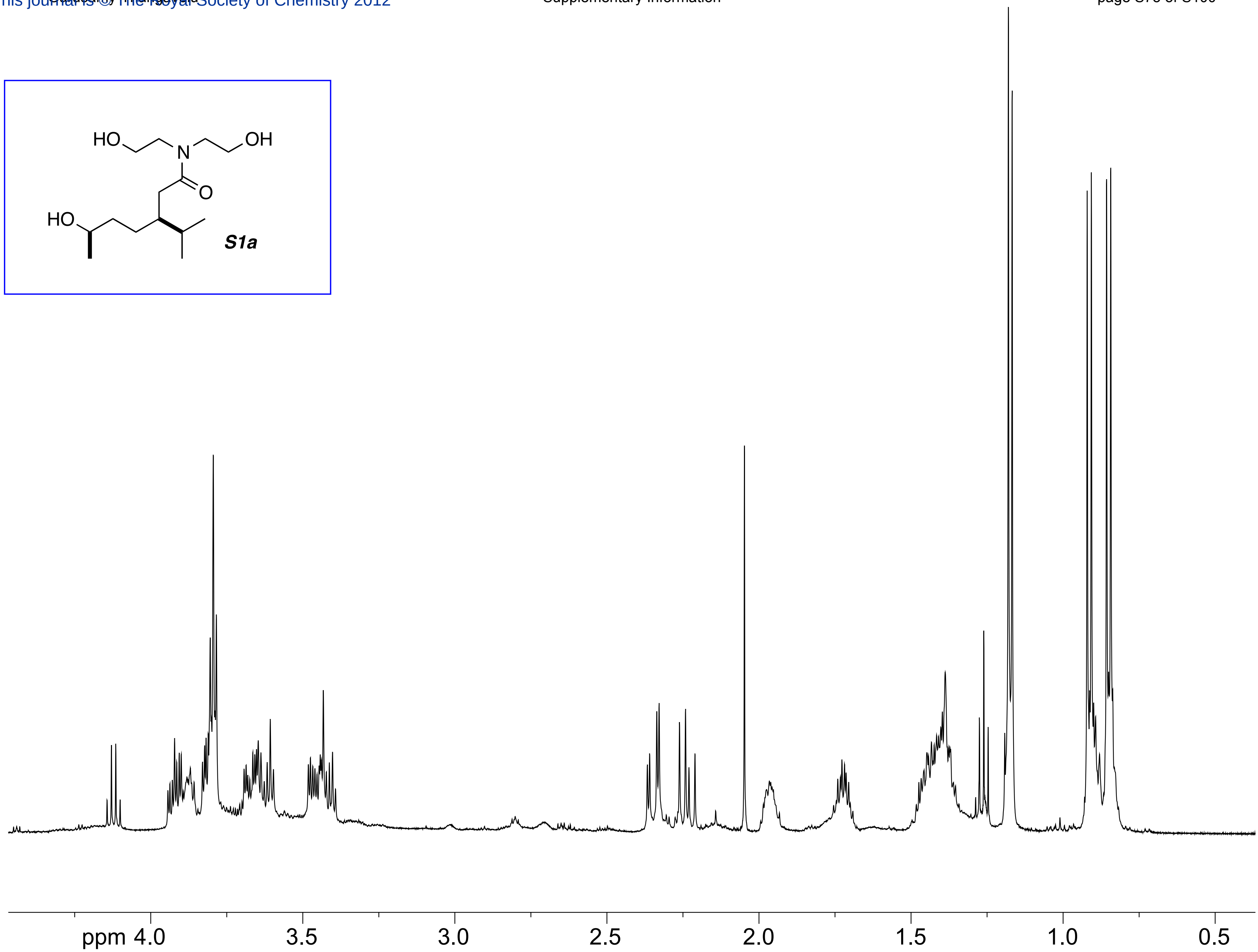
11b

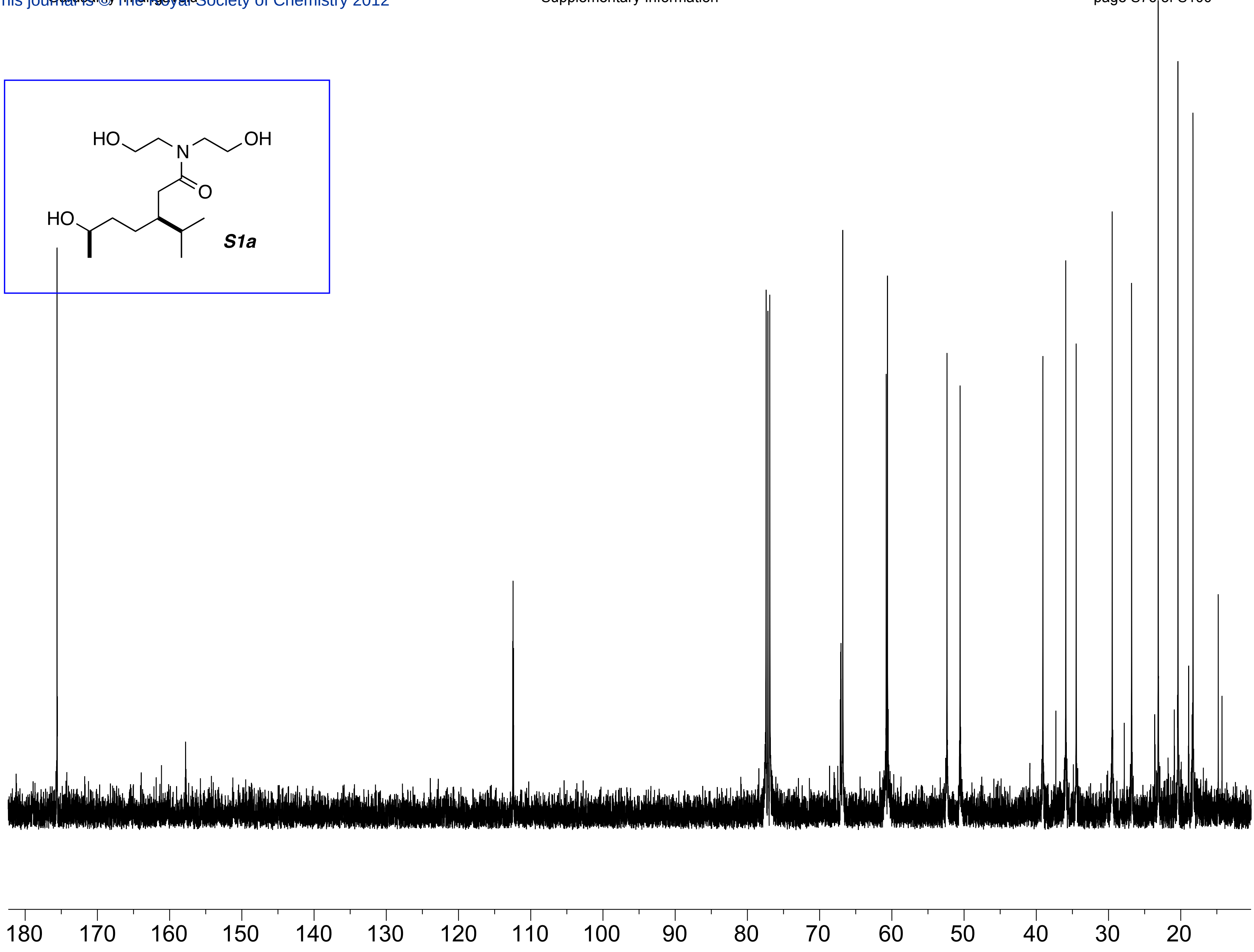


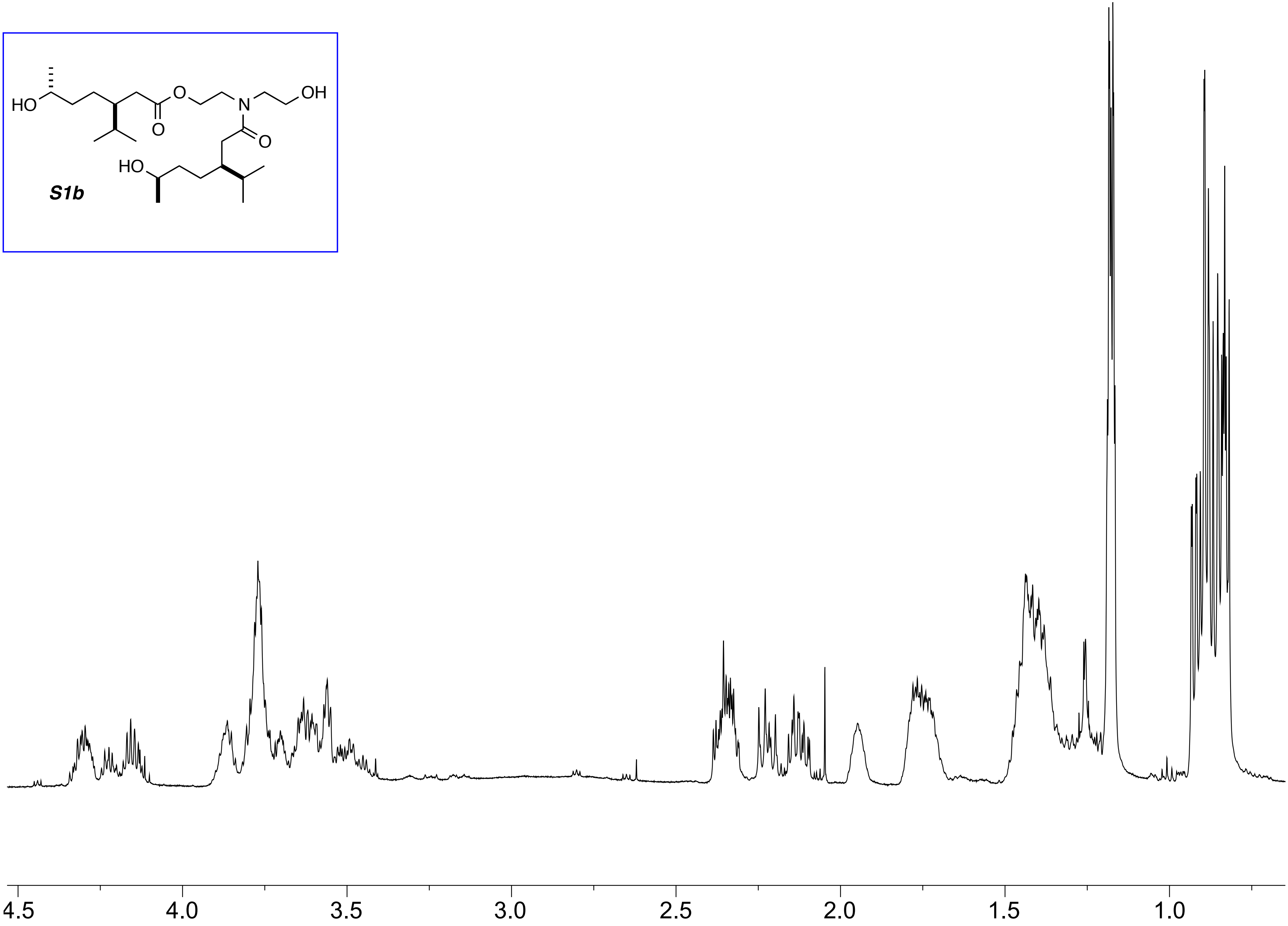
11c



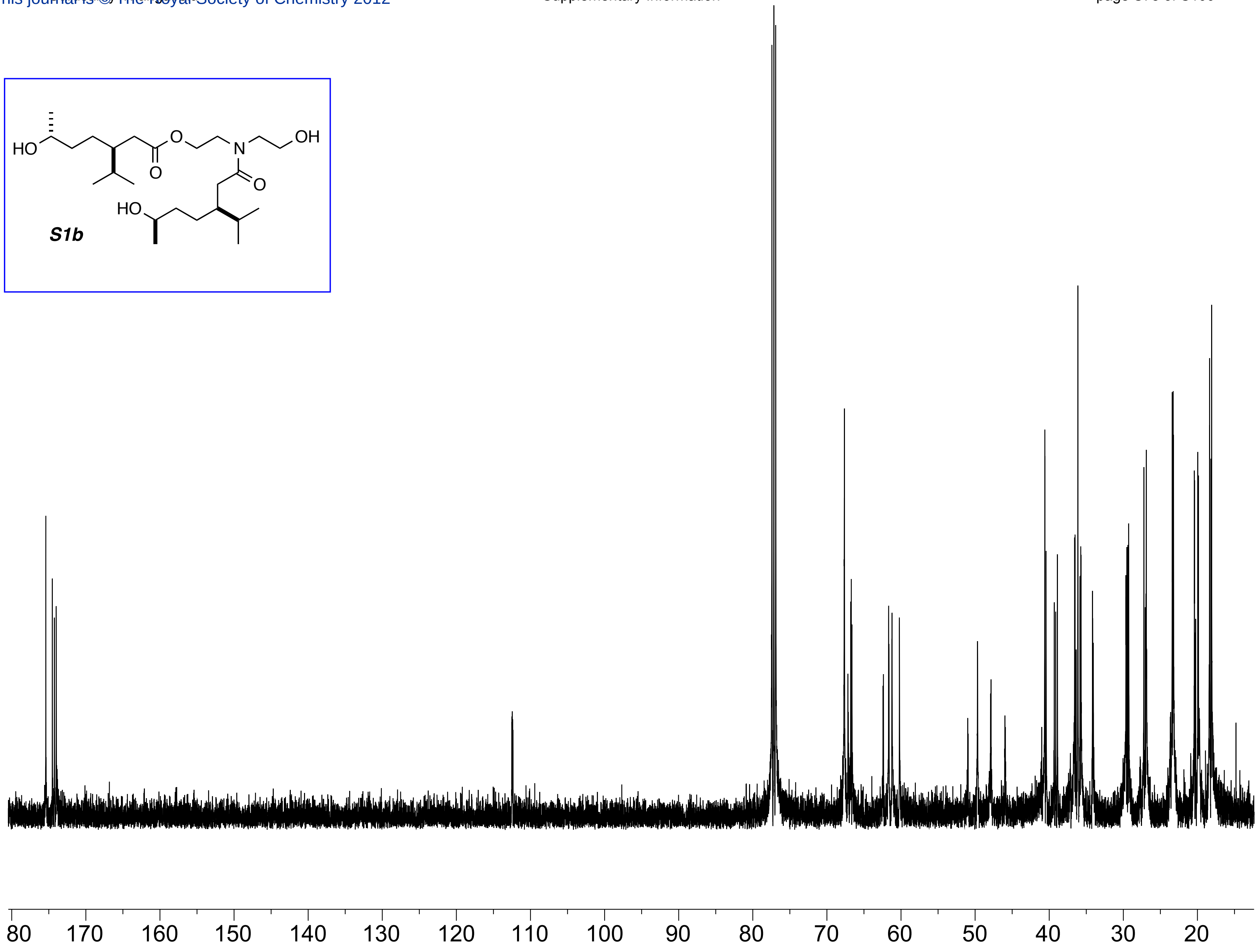
11c

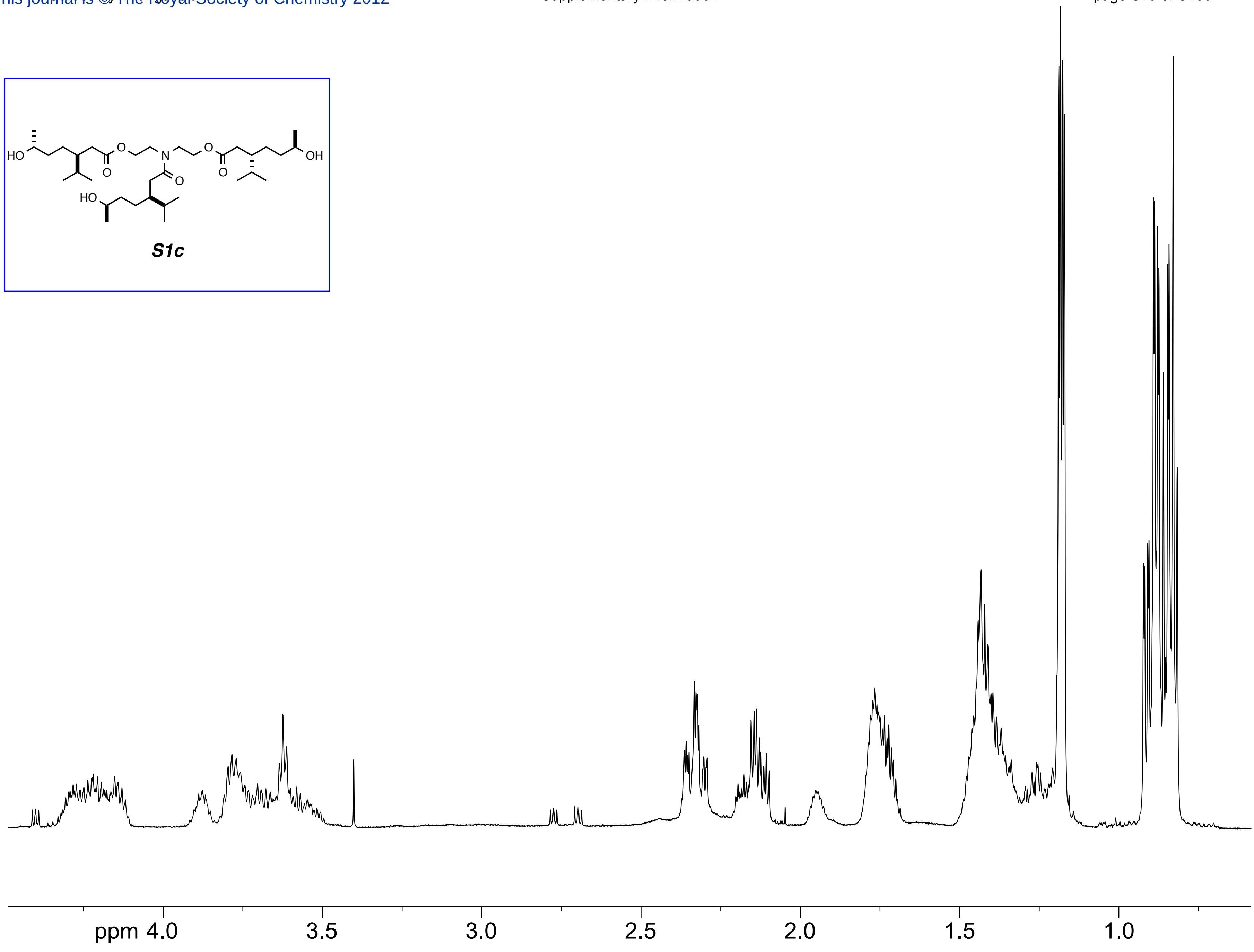

HO
N
OH
O
HO
S1a
ppm 4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


HO
N
OH
O
HO
S1a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

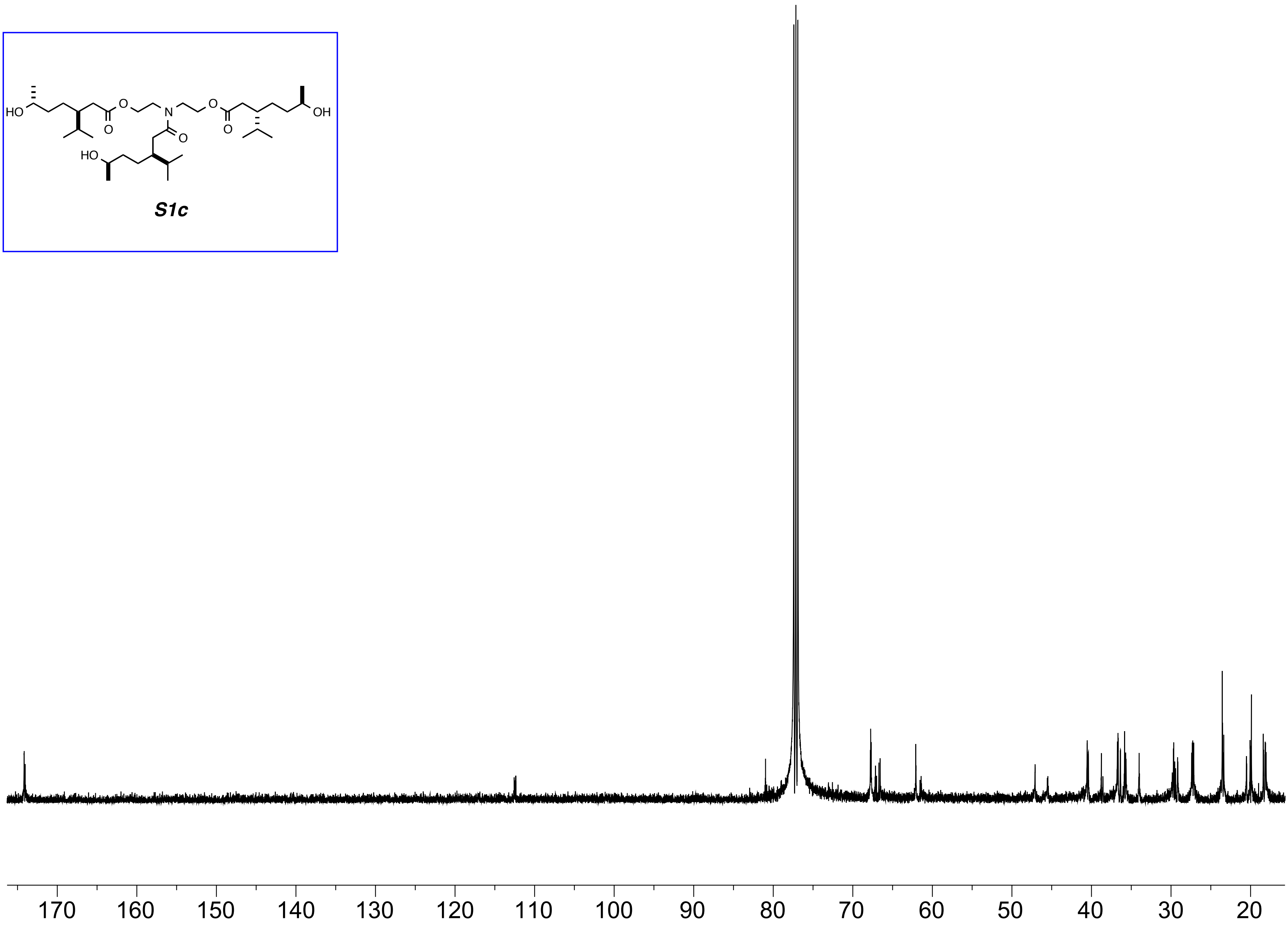


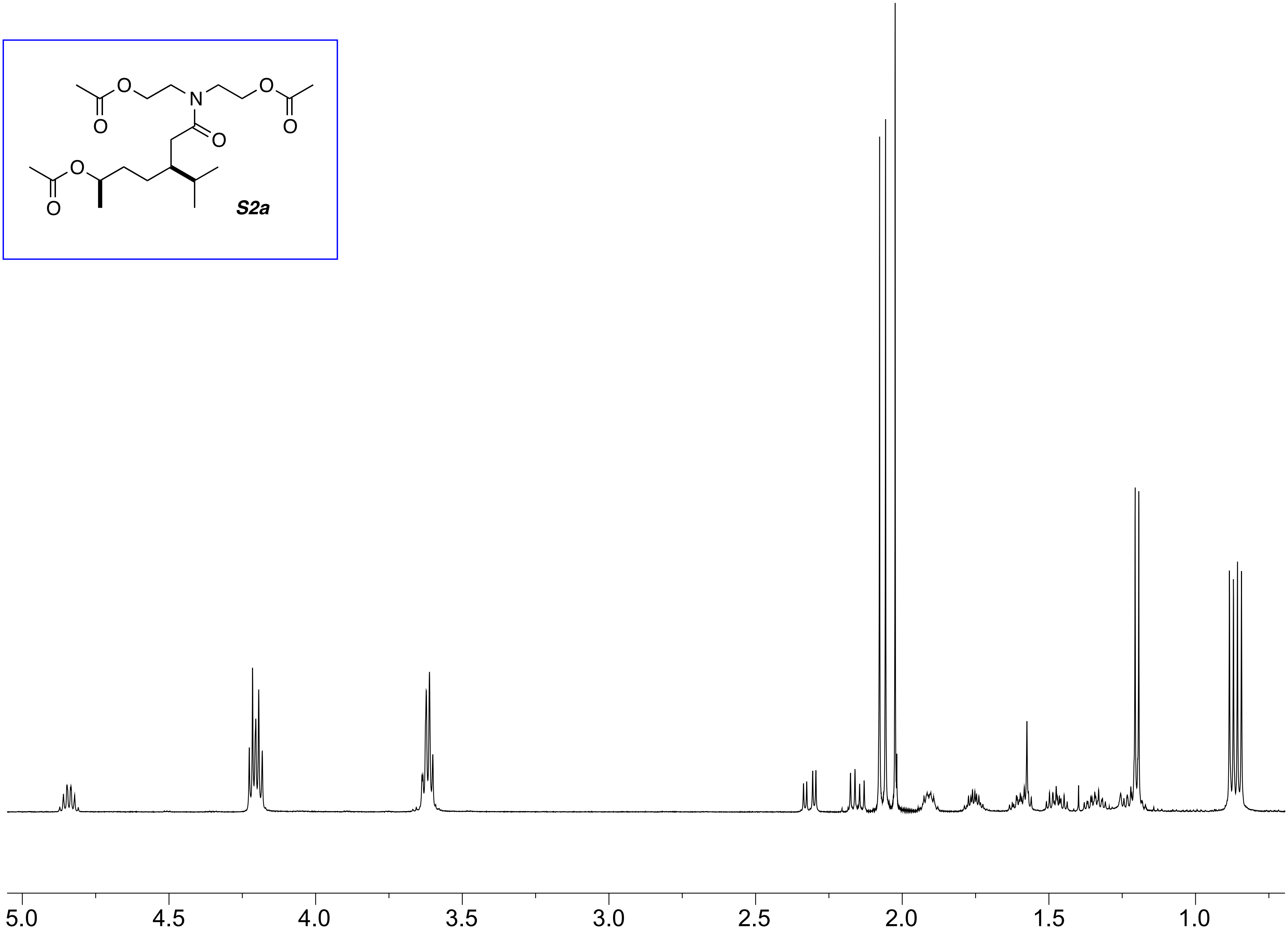
S1b


S1b
HO
O
N
OH
O
O
HO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

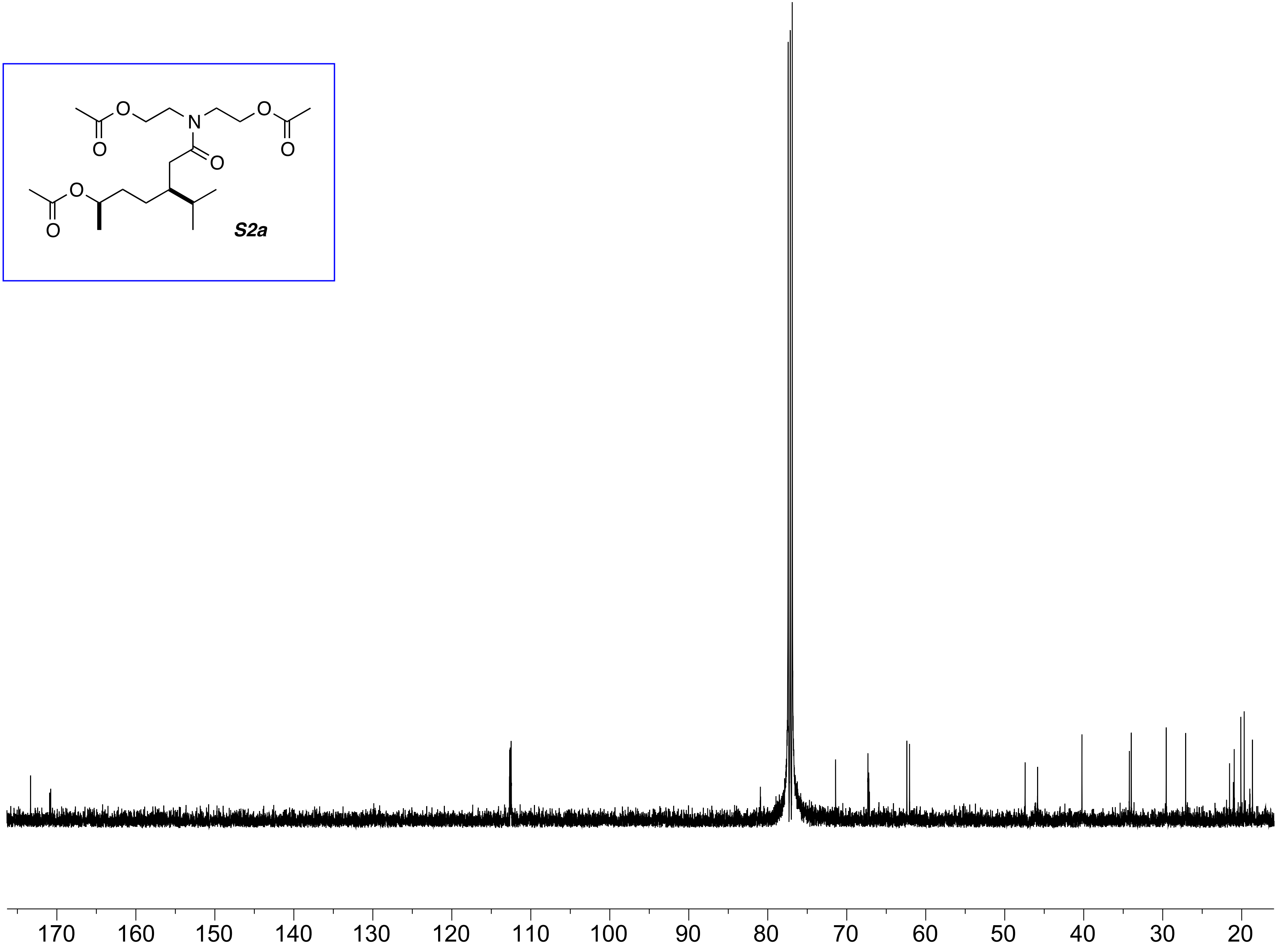


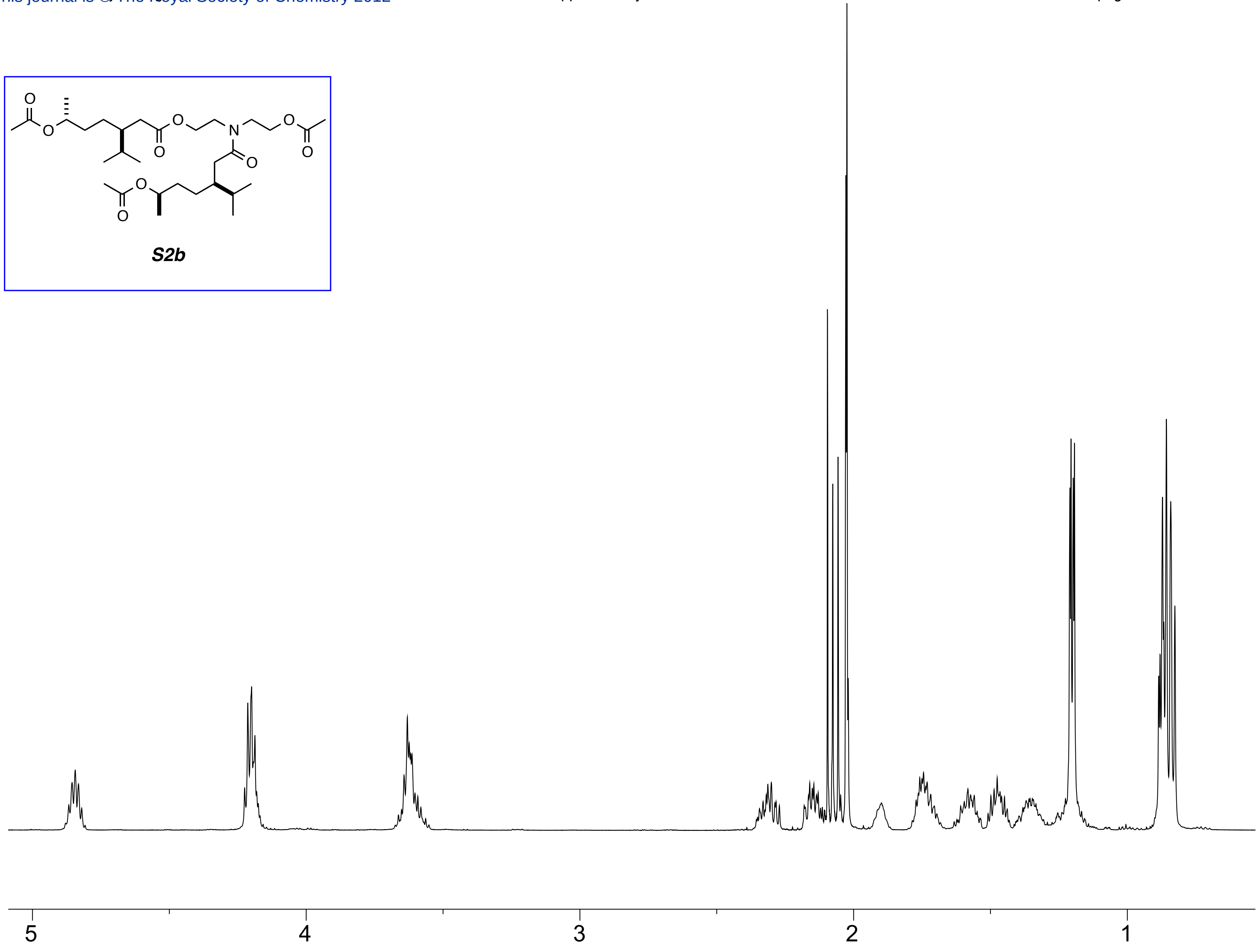
S1c


HO
O
O
N
O
O
O
OH
HO
O
S1c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

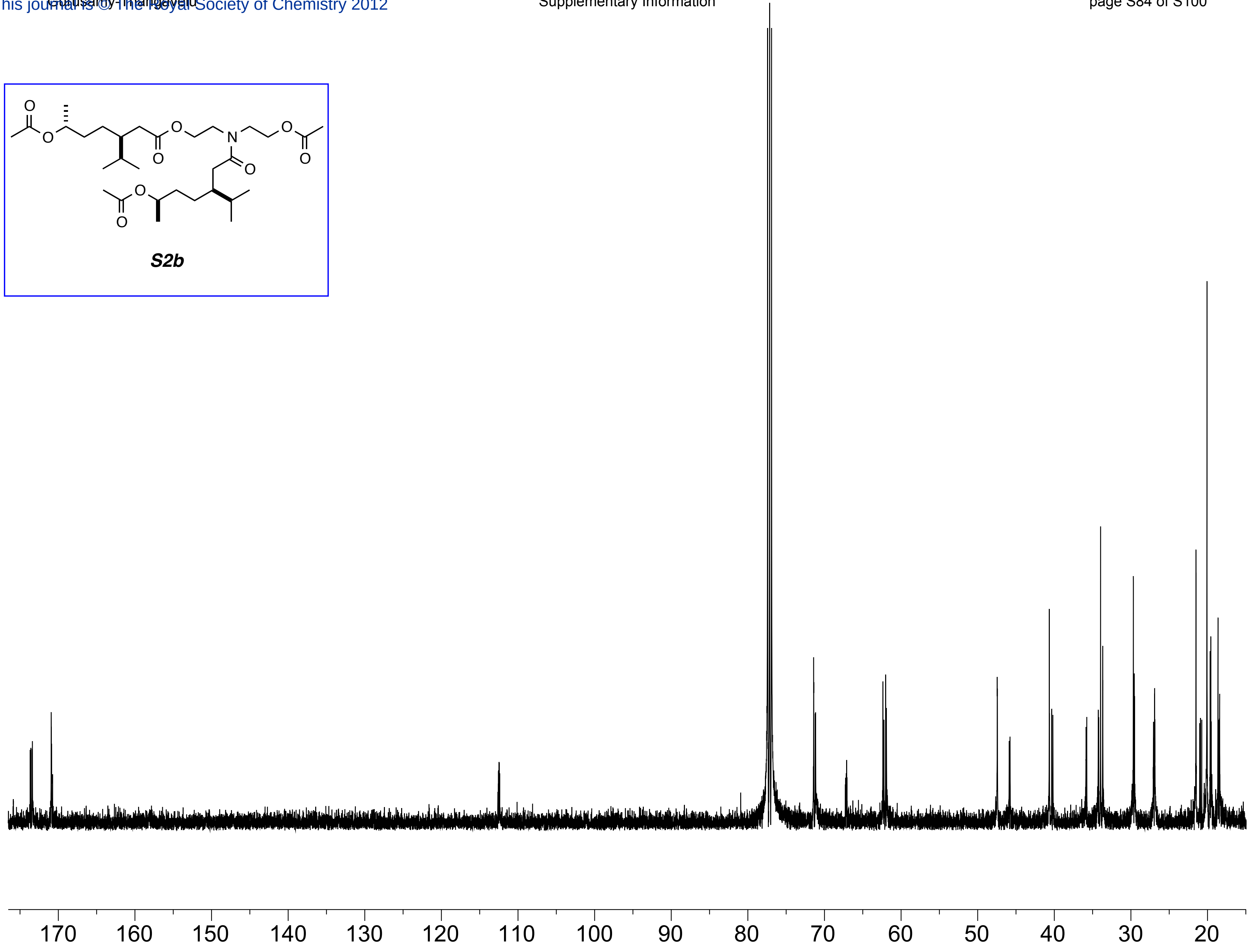


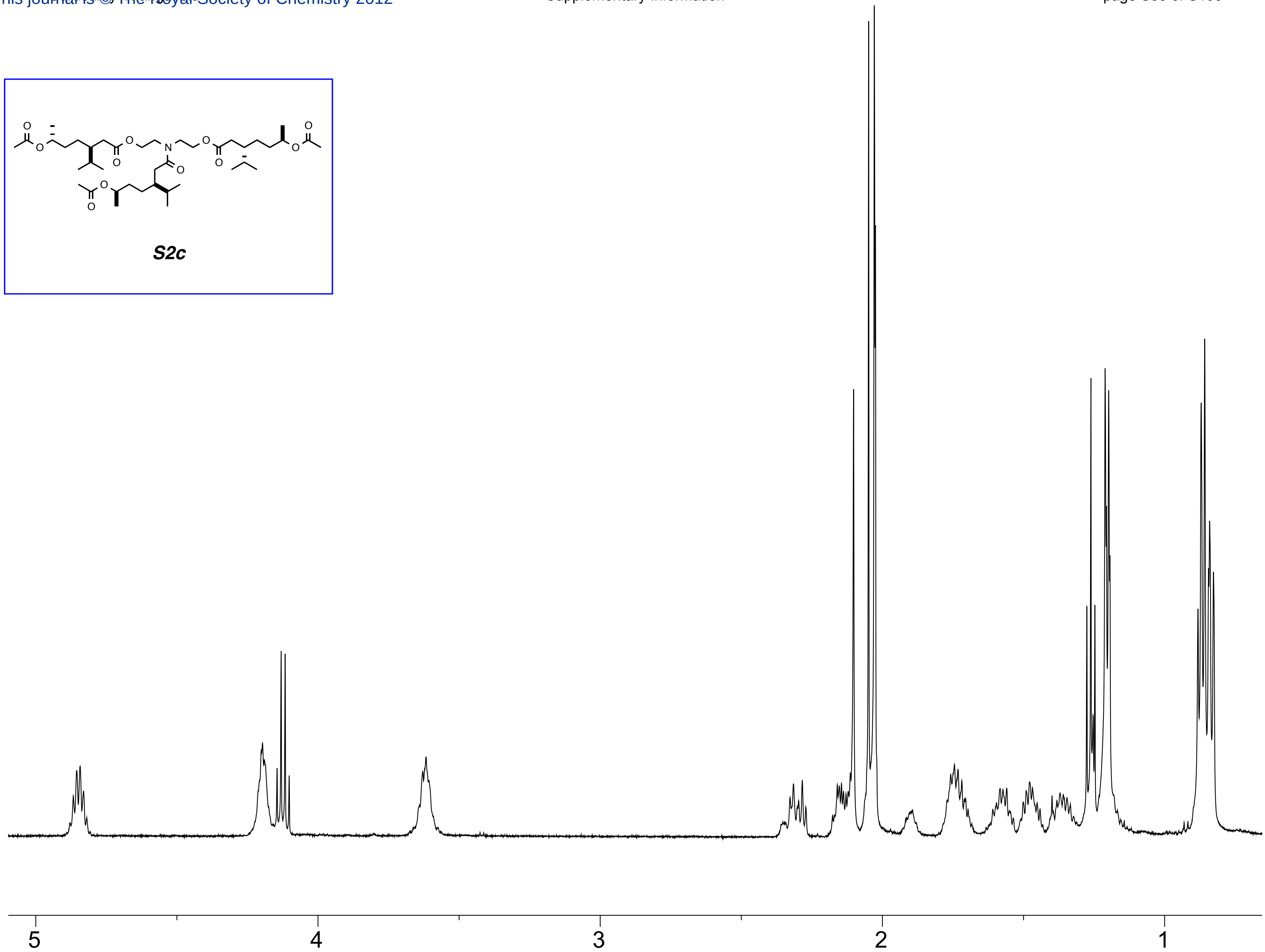
S2a


S2a
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

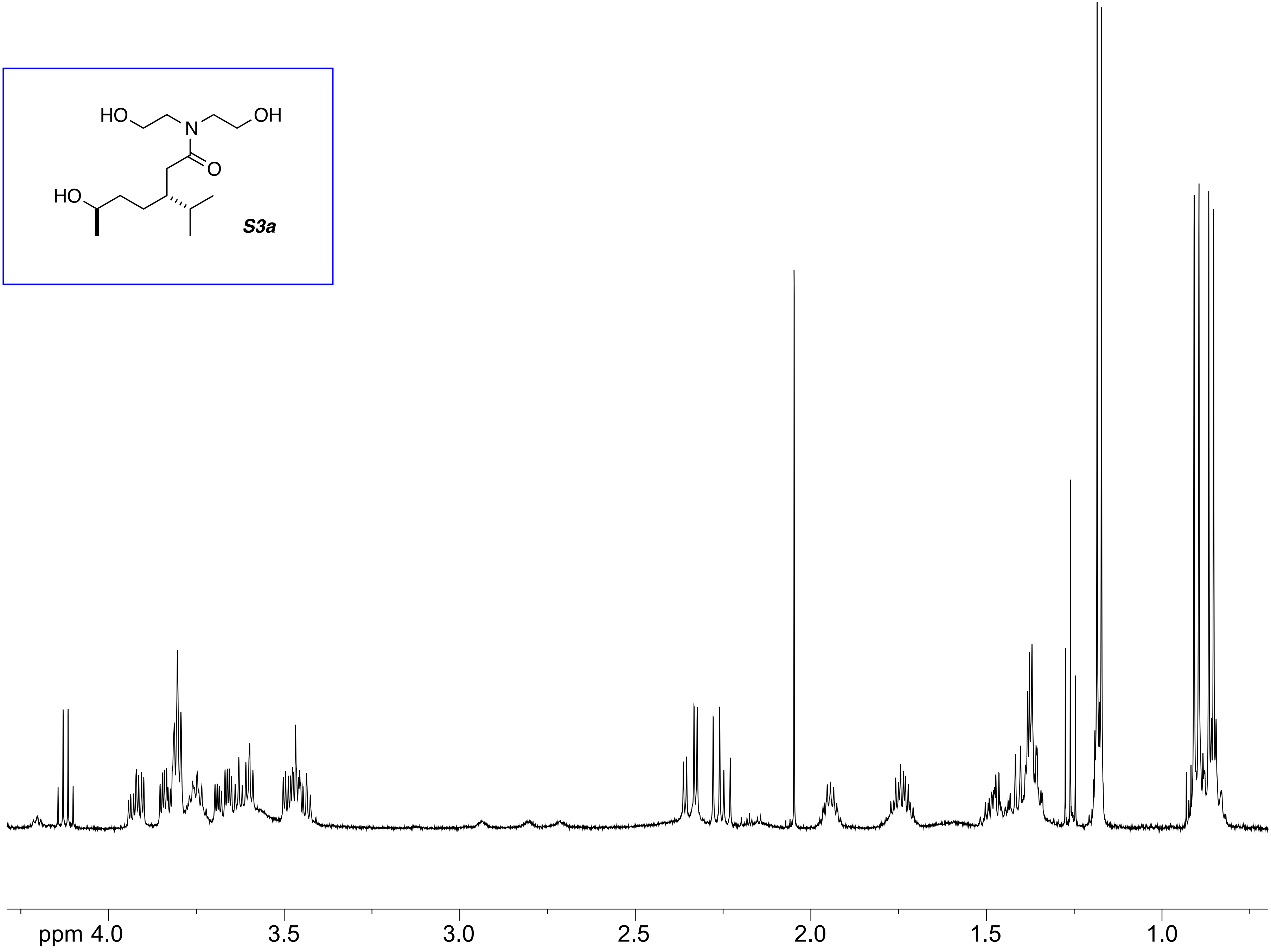


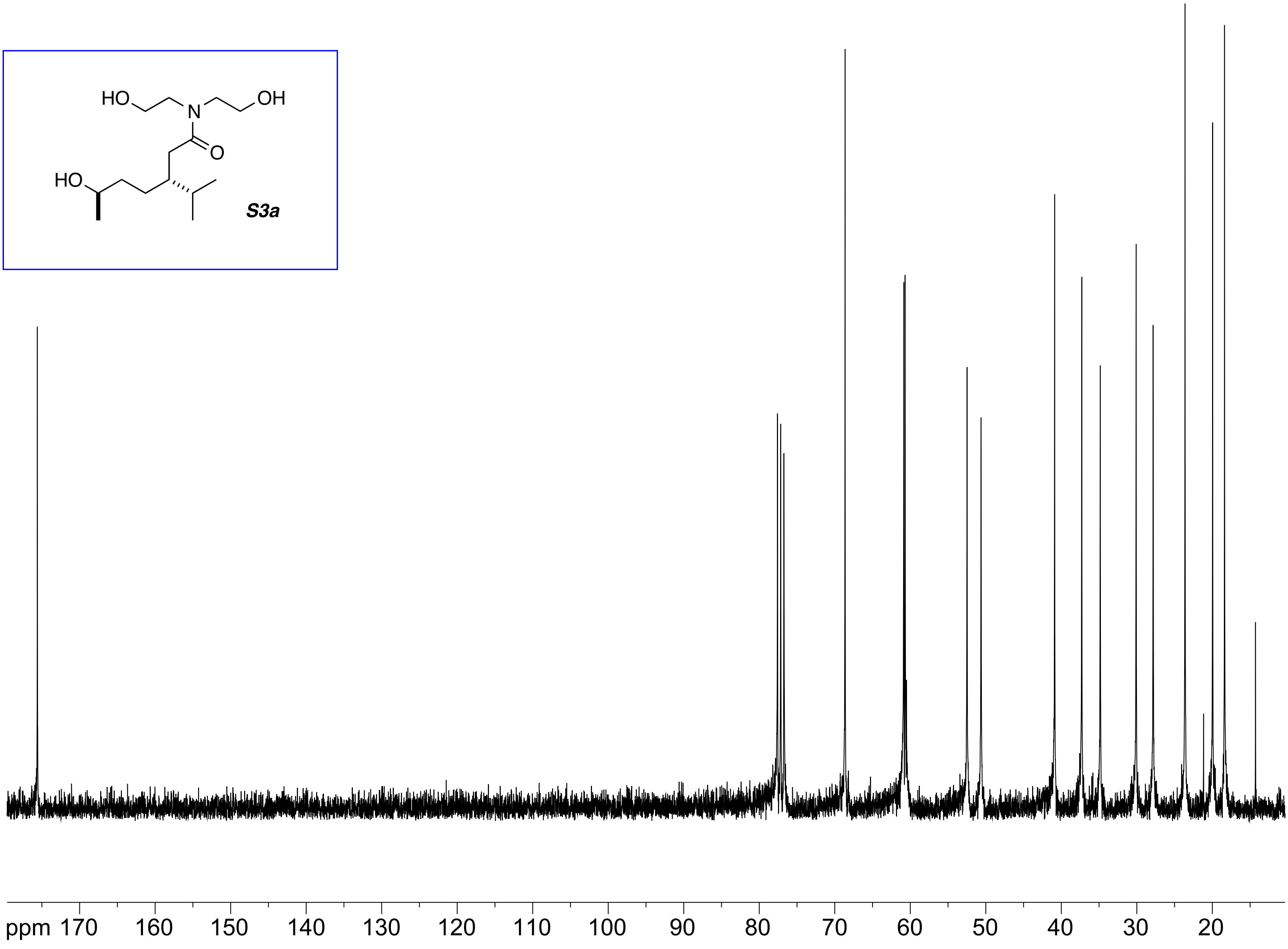
S2b

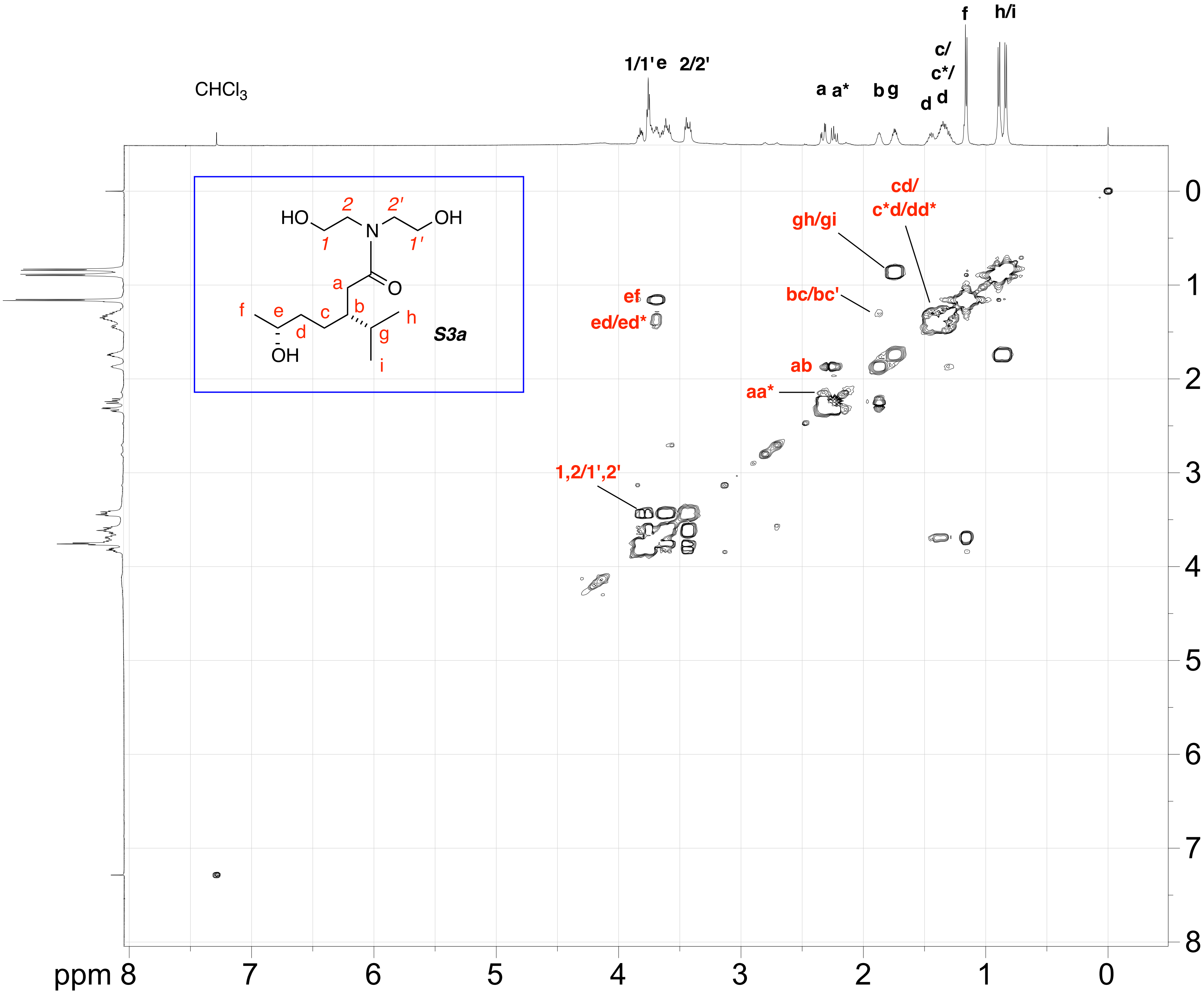

S2b

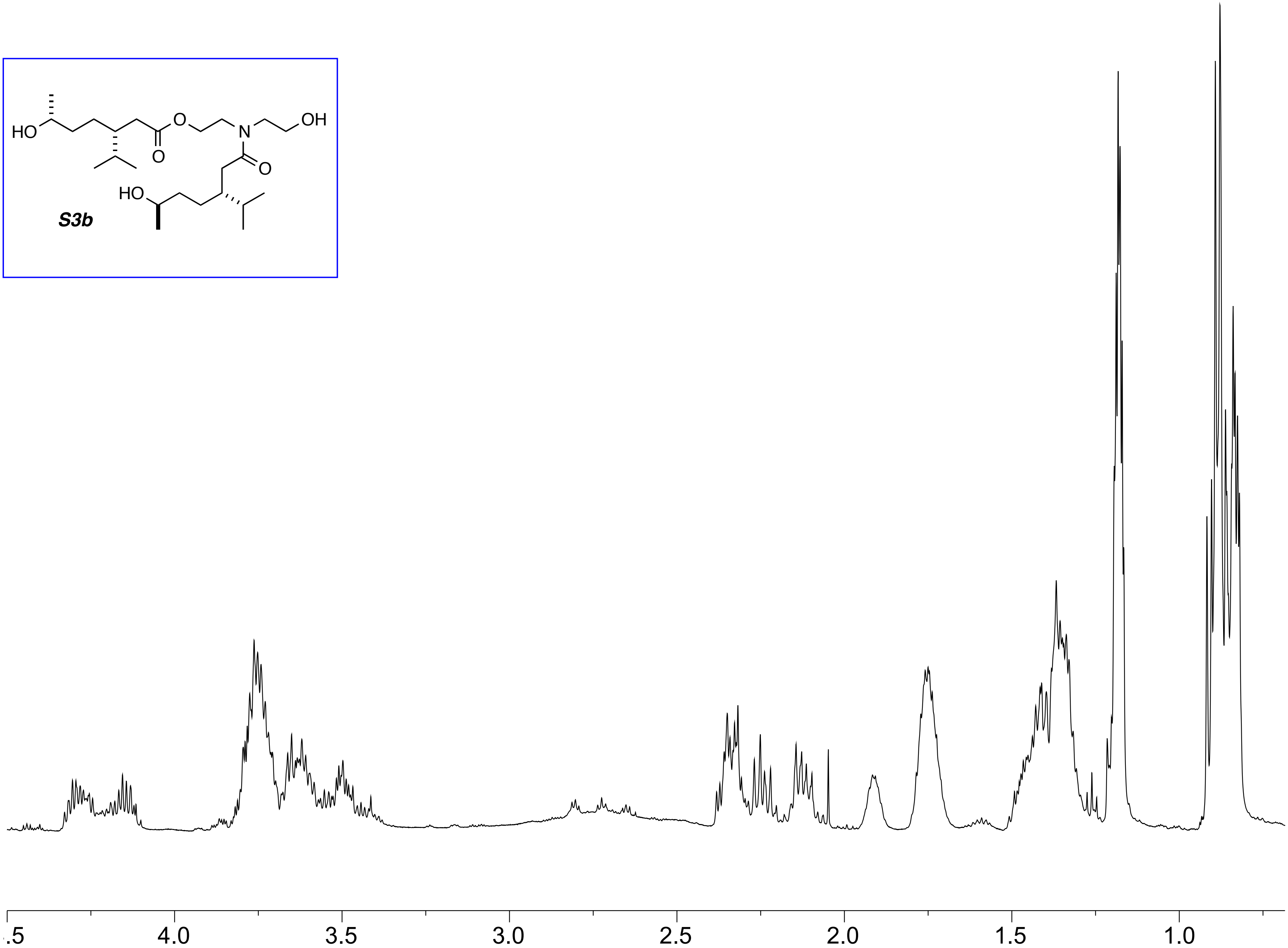


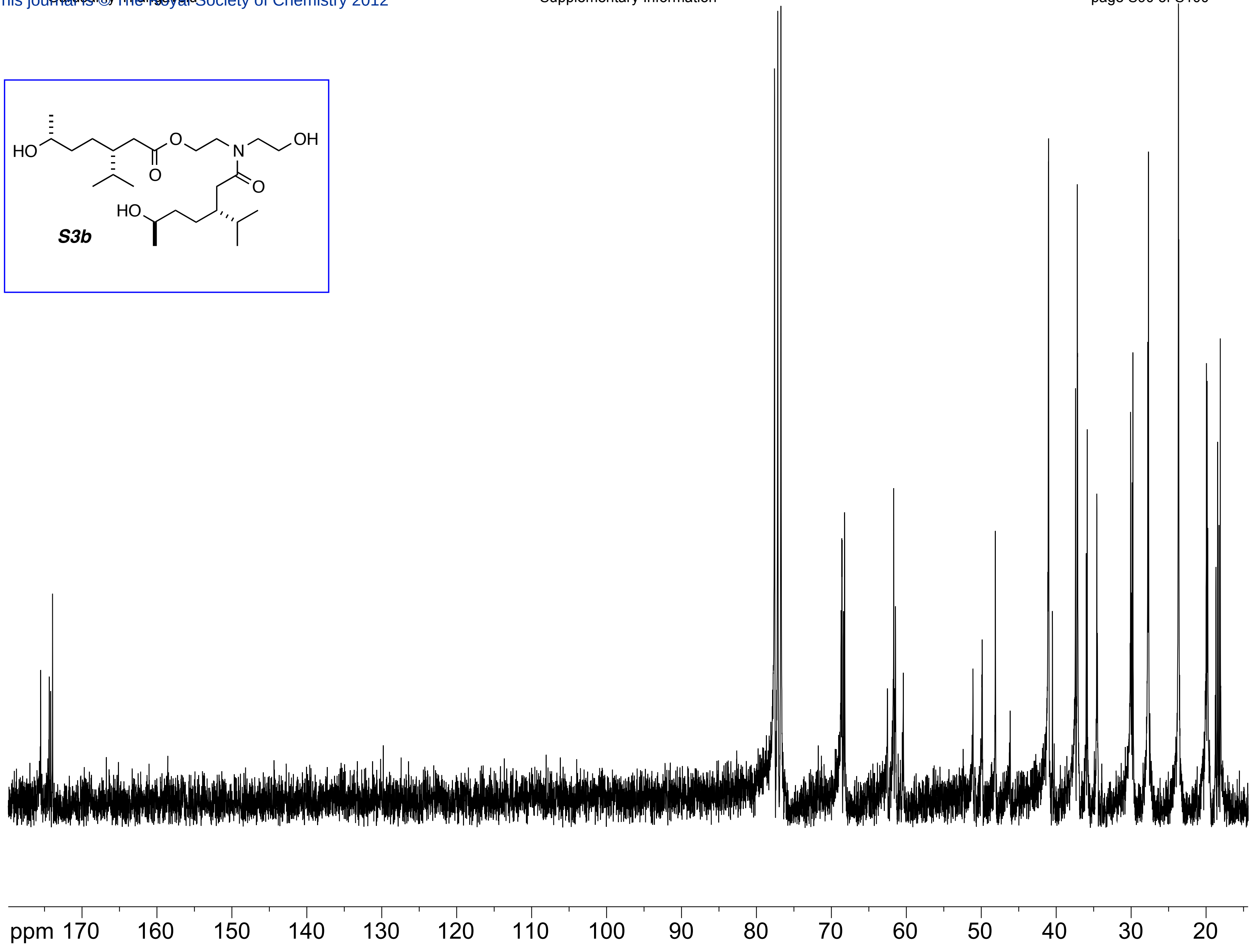
S2c


HO
N
OH
O
HO
S3a
ppm 4.0
3.5
3.0
2.5
2.0
1.5
1.0


HO
N
OH
O
HO
S3a
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

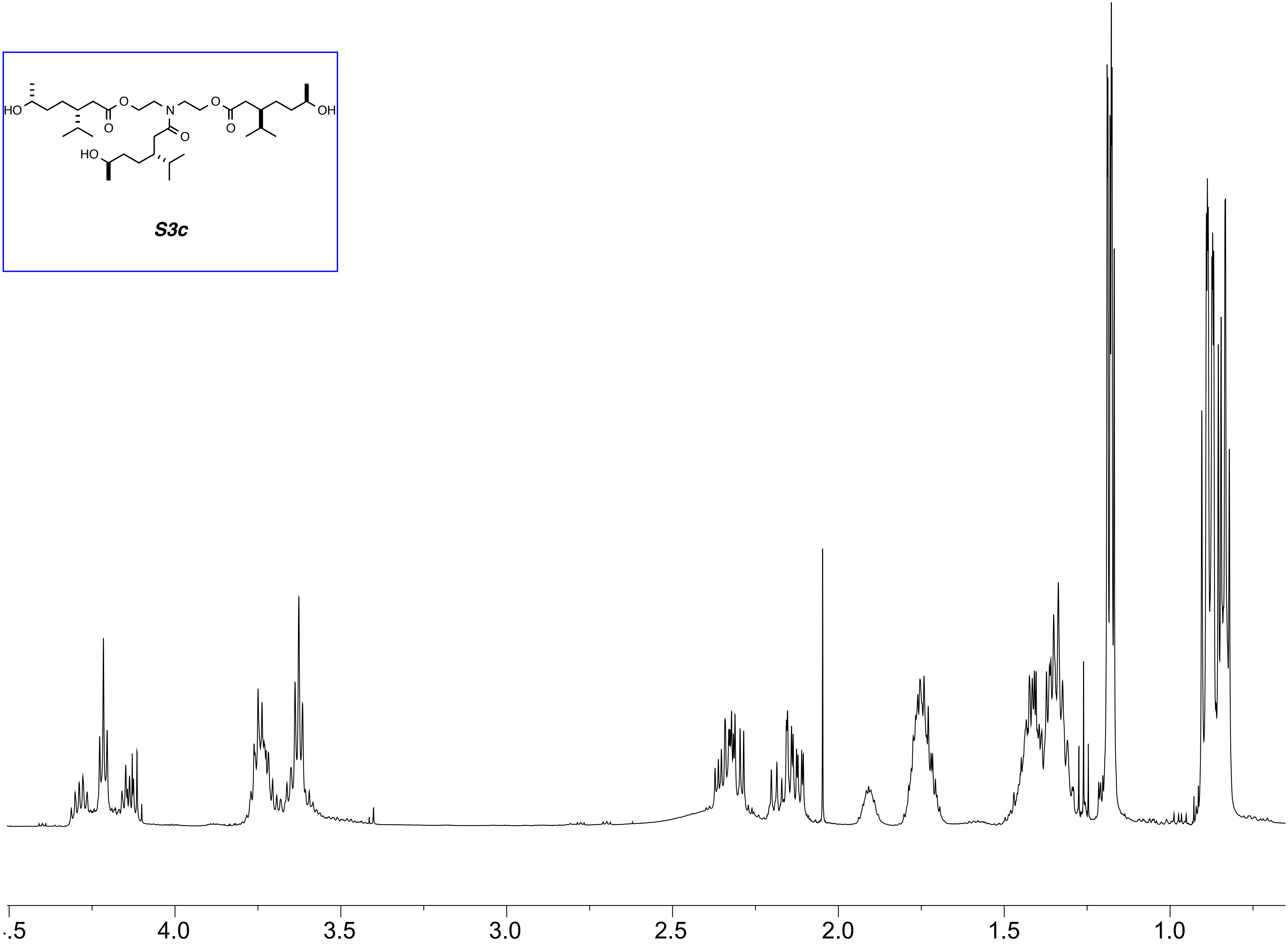

CHCl$_3$
1/1'e
2/2'
a a*
b g
d
c/
c*/
d
f
h/i
HO
OH
N
O
OH
1
2
2'
1'
a
b
c
d
e
f
g
h
i
S3a
gh/gi
cd/
c*d/dd*
bc/bc'
ef
ed/ed*
ab
aa*
1,2/1',2'
0
1
2
3
4
5
6
7
8
ppm 8
7
6
5
4
3
2
1
0


HO
O
O
N
OH
O
HO
S3b
.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

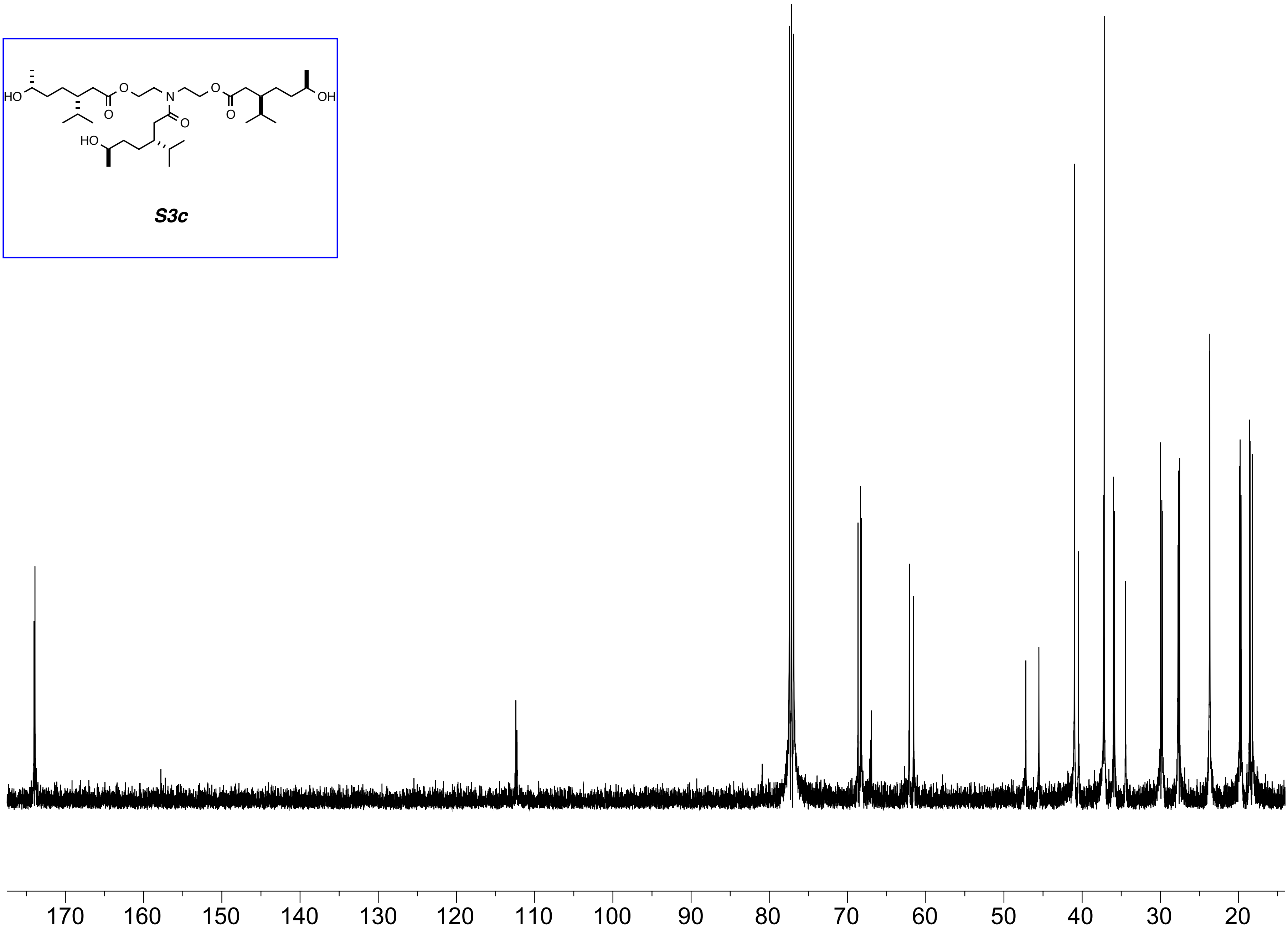


S3b

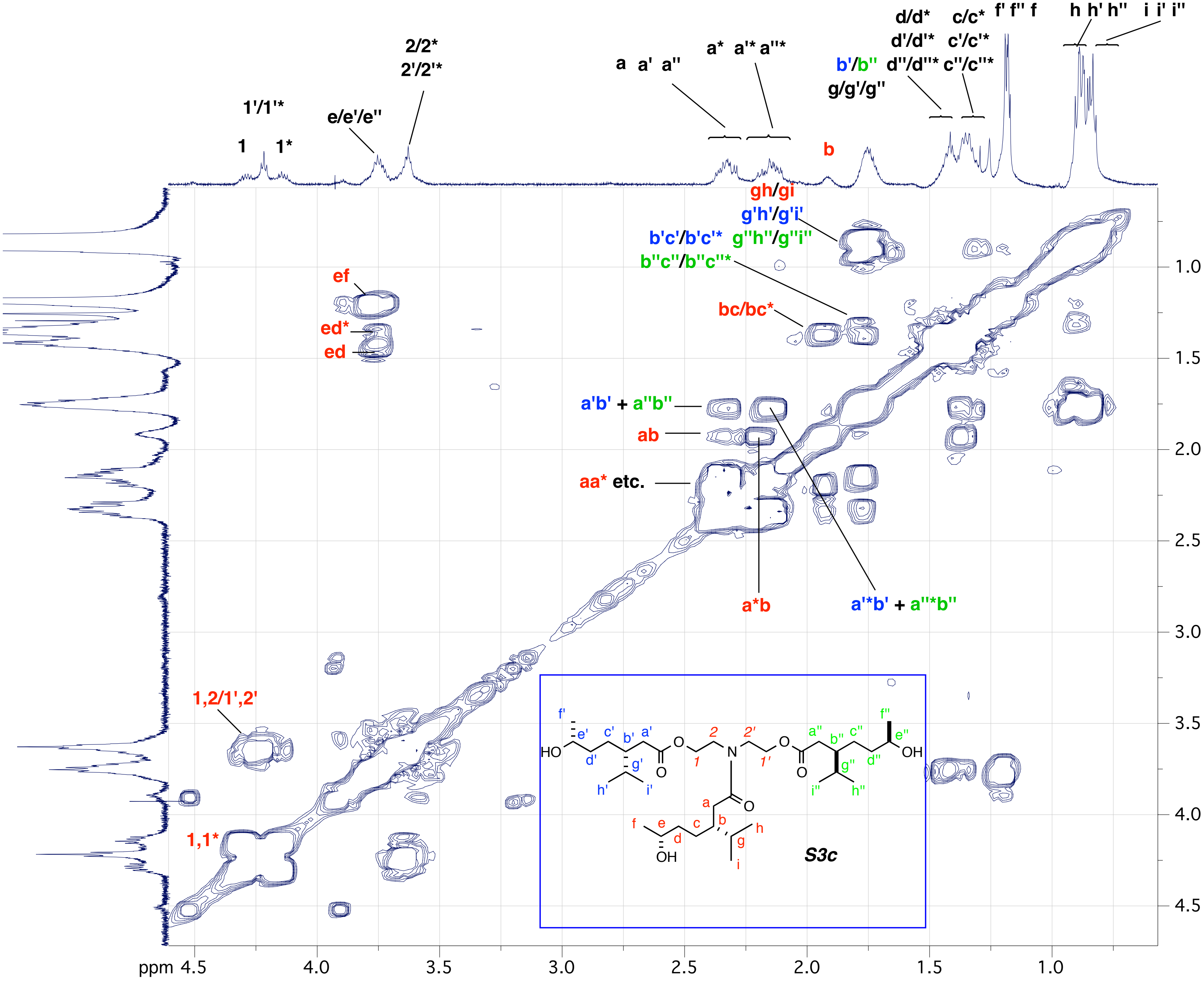
HO
O
N
OH
O
O
HO
ppm 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

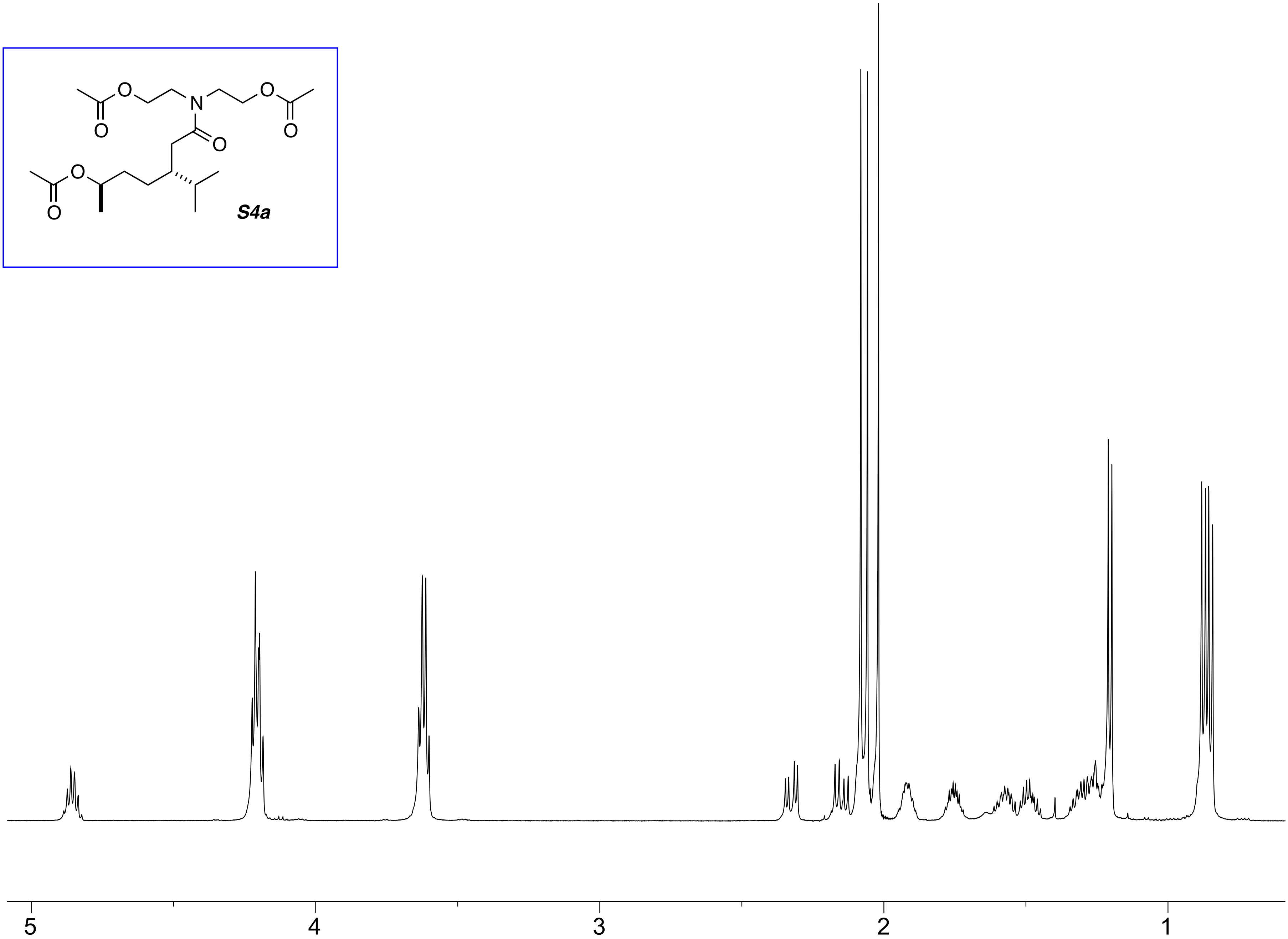


S3c


HO
O
N
O
OH
O
O
O
HO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

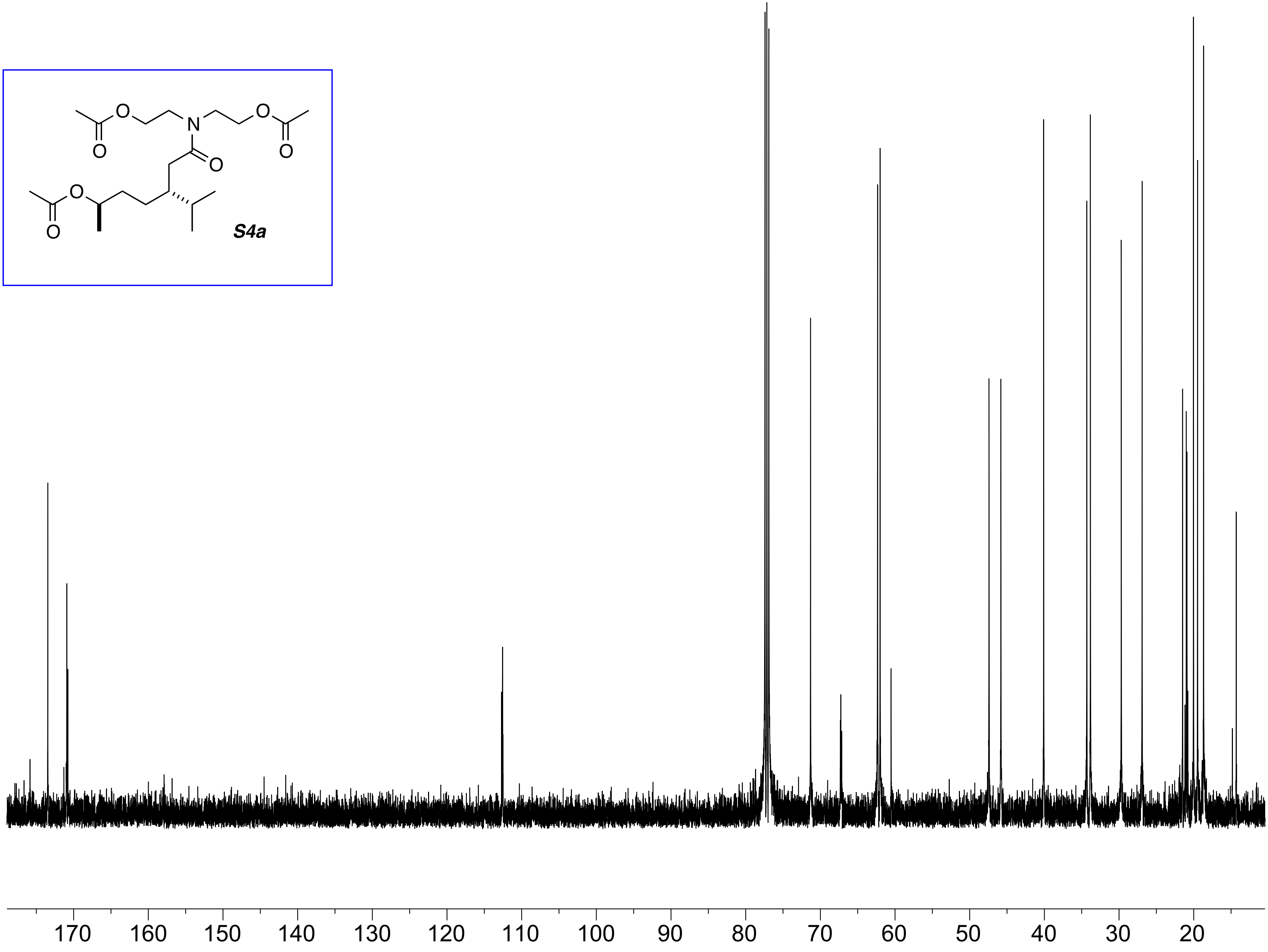
S3c

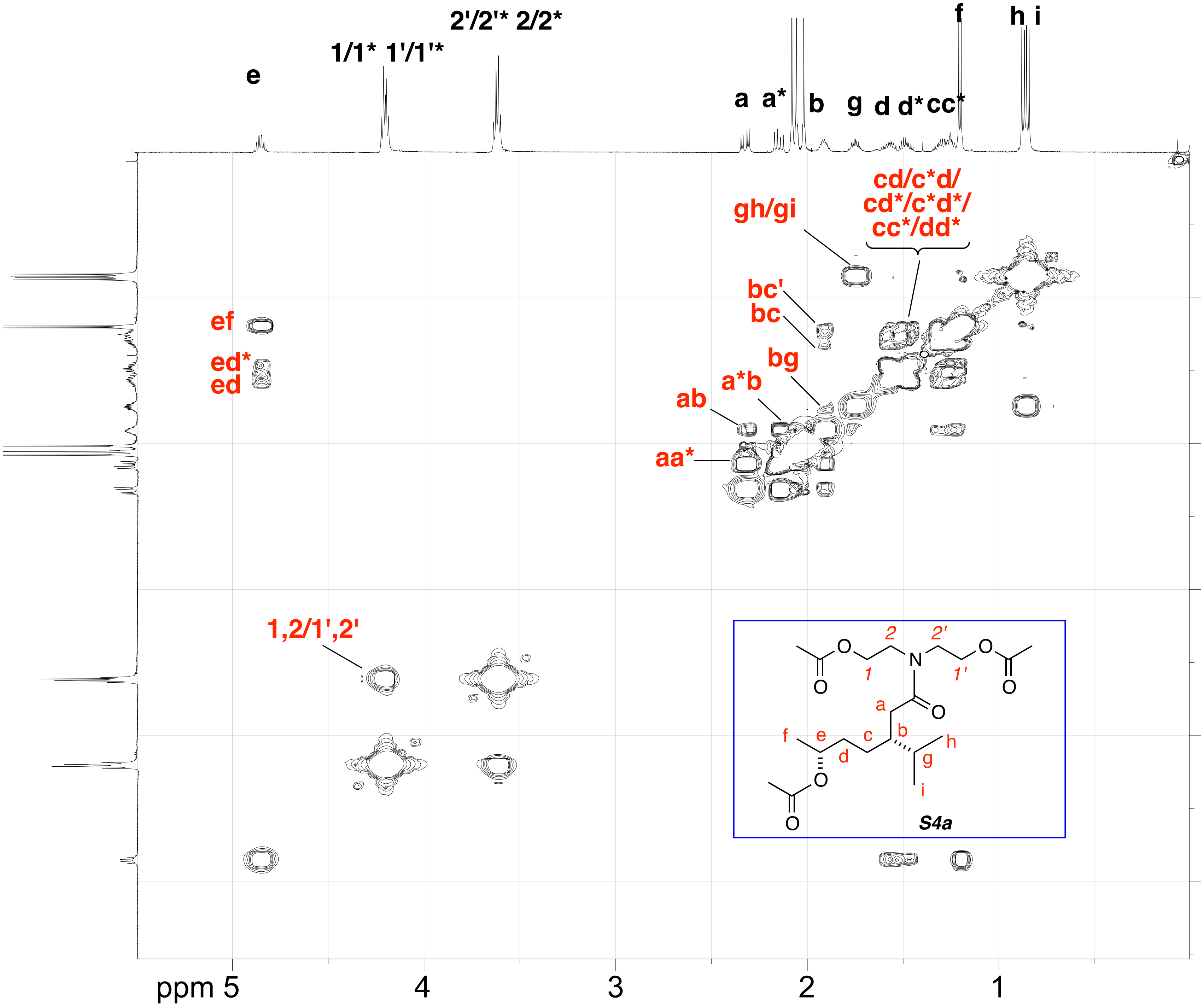

1
1*
1'/1'*
e/e'/e"
2/2*
2'/2'*
a a' a"
a* a'* a"*
b'/b"
g/g'/g"
b
d/d*
d'/d'*
d"/d"*
c/c*
c'/c'*
c"/c"*
f' f" f
h h' h"
i i' i"
gh/gi
g'h'/g'i'
b'c'/b'c'*
g"h"/g"i"
b"c"/b"c"*
ef
ed*
ed
bc/bc*
a'b' + a"b"
ab
aa* etc.
a*b
a'*b' + a"*b"
1,2/1',2'
1,1*
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
ppm 4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f'
e'
c'
b'
a'
HO
d'
g'
h'
i'
O
O
2
2'
N
1
1'
O
O
a"
b"
c"
f"
e"
OH
g"
d"
i"
h"
a
O
f
e
c
b
h
d
g
OH
i
S3c

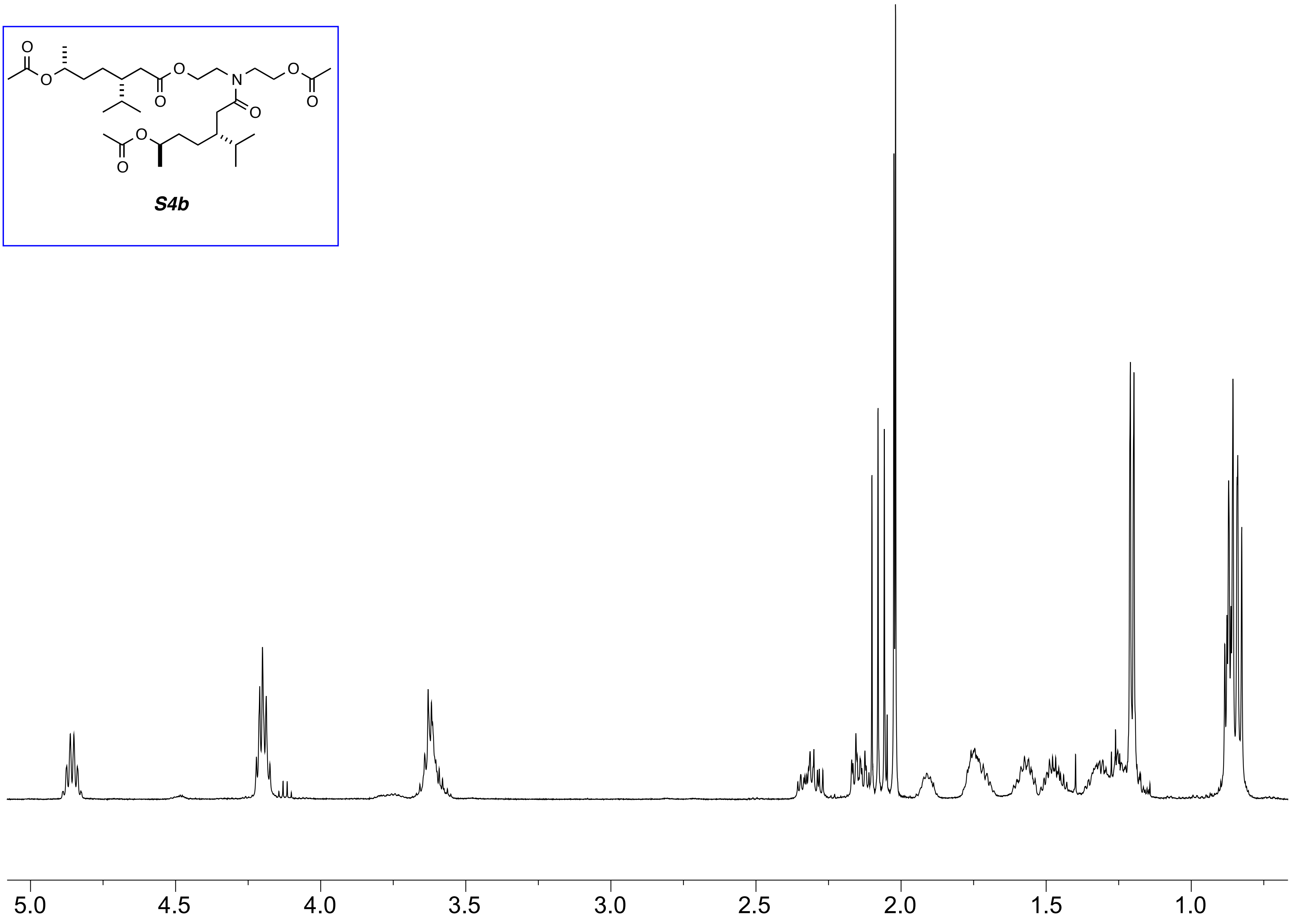


S4a

S4a




e
1/1* 1'/1'*
2'/2'* 2/2*
a a*
b
g
d d*
cc*
f
h i
gh/gi
cd/c*d/
cd*/c*d*/
cc*/dd*
bc'
bc
bg
a*b
ab
aa*
ef
ed*
ed
1,2/1',2'
ppm 5
4
3
2
1
1
2
3
4
5
2
2'
O
O
N
1
1'
O
O
a
O
f
e
c
b
h
d
g
O
i
O
S4a



S4b

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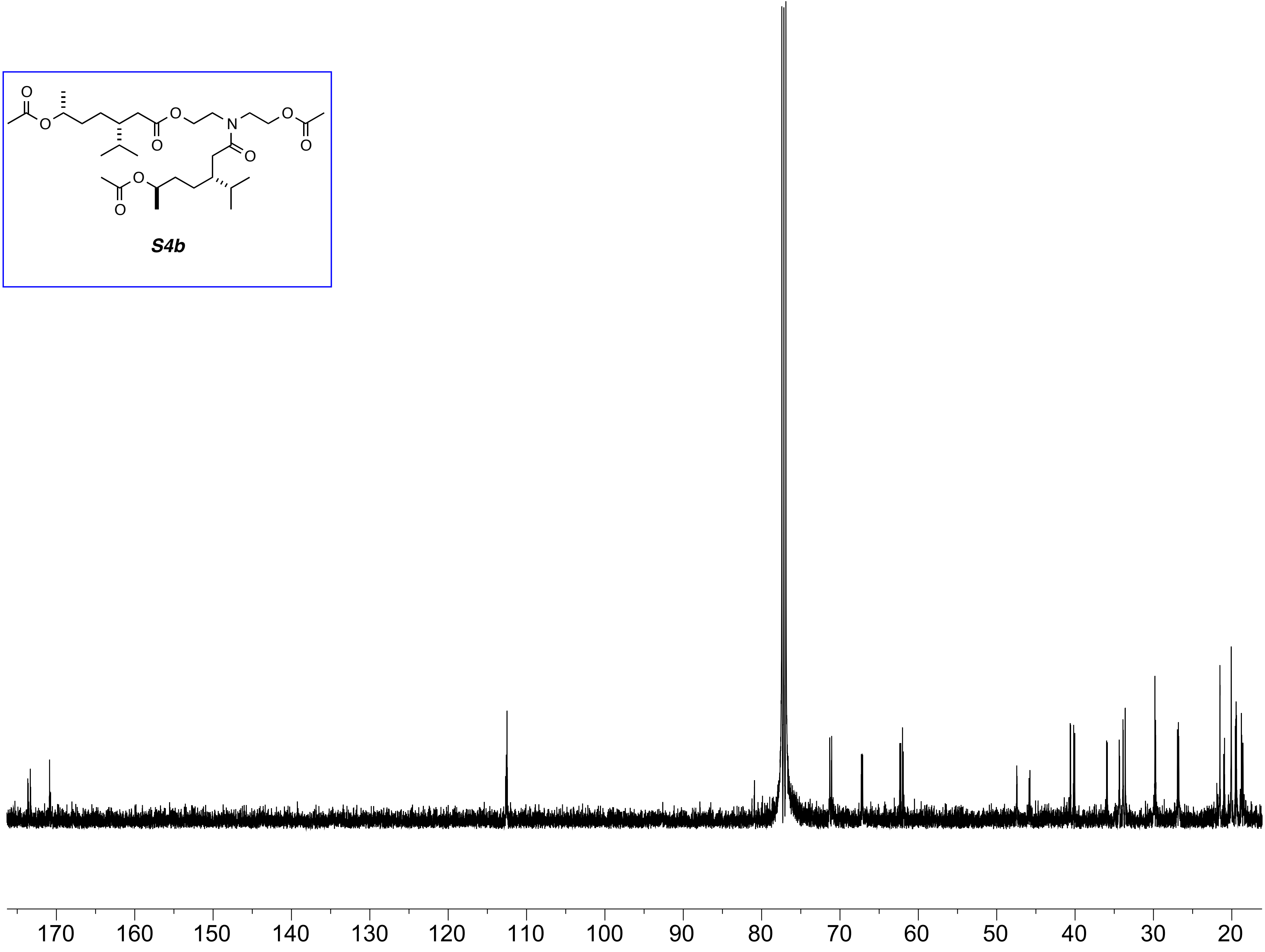
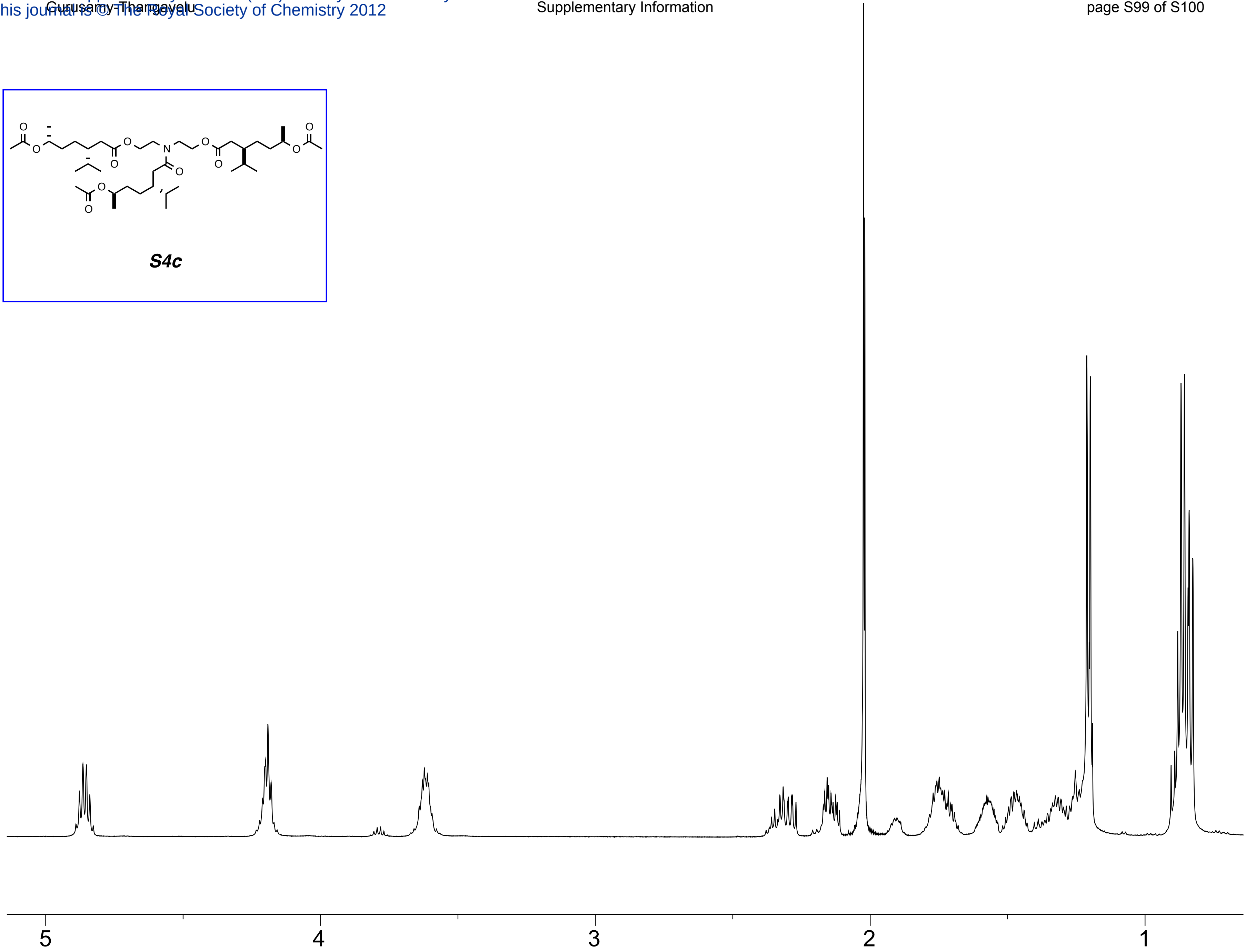


S4b



S4c

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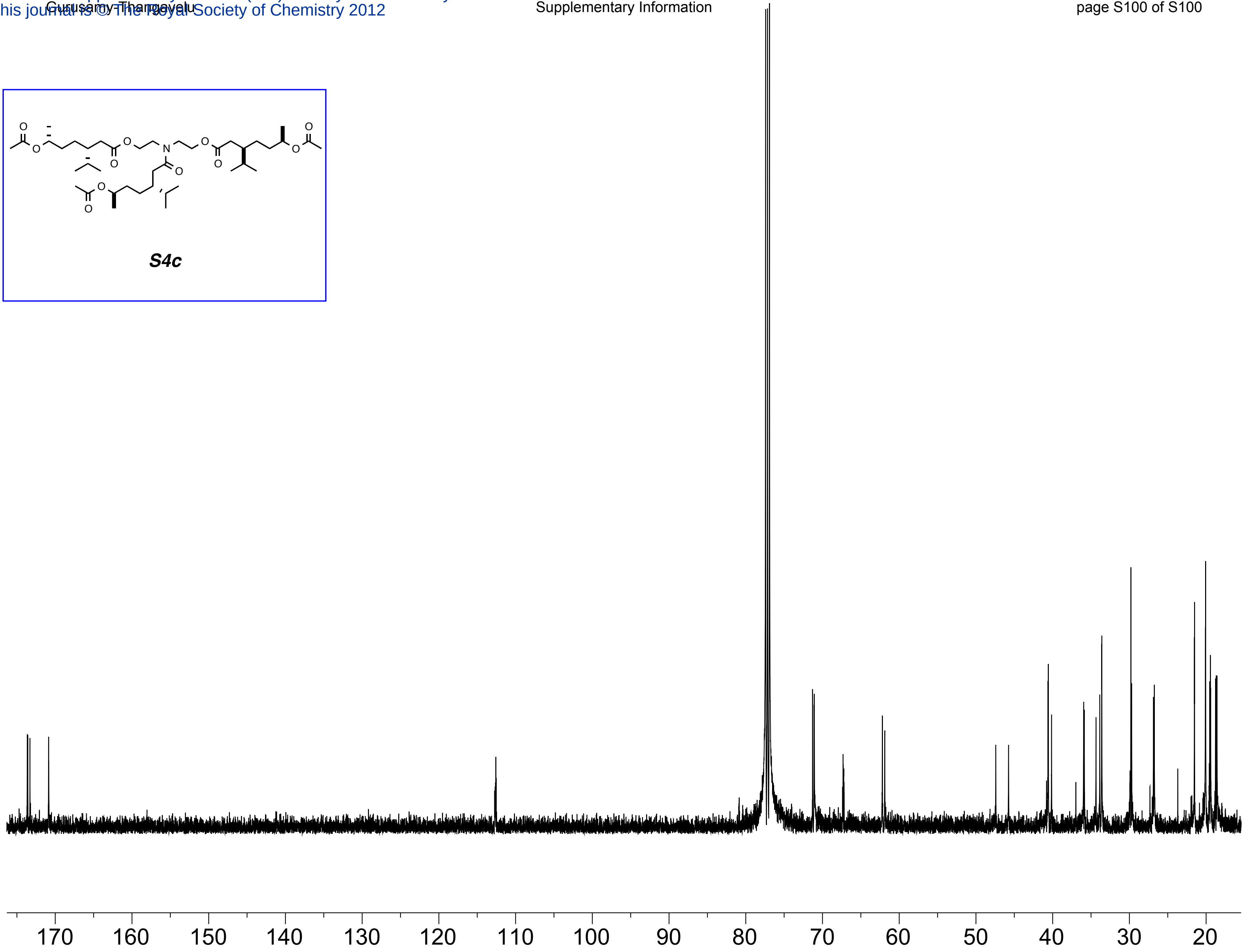

S4c