ELECTRONIC SUPPLEMENTARY INFORMATION

Towards Life in Hydrocarbons: Aggregation Behaviour of "Reverse" surfactants in Cyclohexane

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Synthesis of amphiphiles 1 and 2:

Materials.

All the reagents were purchased from Aldrich and used without further purification. Cyclohexane was dehydrated with molecular sieves.

TLC analysis were performed on TLC Sil G/UV254 of 0.25 mm thickness and flash column chromatography (FCC) separations were performed on silica gel Aldrich, pore size 60 Å, 70-230 mesh, 63-200 µm.

Experimental procedures.

2-(2-(2-hydroxyethoxy)ethoxy)ethyl adamantane-1-carboxylate (1):

in a round-bottomed flask topped with a reflux condenser were added 10 mmol (1.80g) of 1-adamantanecarboxylic acid, 25 mmol (3.74 g) TEG and 0.7 mmol of sulfuric acid in cyclohexane (10 mL). The reaction mixture was heated at the reflux temperature and stirred overnight. The reaction mixture was cooled to ambient temperature, quenched with saturated K_2CO_3, then extracted with cyclohexane (5x5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and evaporated to give a crude oil that was purified by FCC (silica gel, diethyl ether as the eluent). Isolated Yield 74%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21 (m, 2H, -*CH_2OH*), 3.76 – 3.58 (m, 10H, -*$COOCH_2CH_2O$-CH_2CH_2O-CH_2-*), 2.04 – 1.97 (br, 3H, *CH bridged adam.*), 1.92 (br, 6H, *$COOC(CH_2$-$)_3$ adam.*), 1.74 – 1.58 (br, 6H, (-*$CH_2)_3C$ adam.*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.8 (C=O), 72.8 (-*OCH_2-*), 70.8 (-*OCH_2-*), 70.6 (-*OCH_2-*), 69.4 (-*OCH_2-*), 63.3 (-*CH_2OH*), 63.3 (-*OCH_2-*), 61.8 (-*OCH_2-*), 40.8 (*C ipso adam*), 38.9 (*$COOC(CH_2$-$)_3$ adam*), 36.6 (6H, (-*$CH_2)_3C$ adam.*), 28.1 (*CH bridged adam*).

GC/MS (relative intensity, 70 eV) m/z: 312.2 ([M+],1.0), 207.10 (41.0), 136.00 (12.0), 135.05 (100.0), 93.05 (12.0), 91.05 (8.0), 89.10 (28.0), 88.05 (10.0), 79.05 (13.0), d=1.03 g/cm^3 at 25 °C.

2-(2-(2-hydroxyethoxy)ethoxy)ethyl2-((2-isopropyl-5-methylcyclohexyl)oxy)acetate (2):

in a round-bottomed flask topped with a reflux condenser were added 10 mmol (2.14g) of menthyloxyacetic acid, 25 mmol (3.74 g) TEG and 0.7 mmol of sulfuric acid in cyclohexane (10mL). The reaction mixture was heated at the reflux temperature and stirred overnight. The reaction mixture was cooled to ambient temperature, quenched with saturated K2CO3, then extracted with cyclohexane (5x5 mL). The combined organic layers were dried with anhydrous Na2SO4, filtered and evaporated to give a crude oil that was purified by FCC (silica gel, diethyl ether as the eluent). Isolated Yield 68%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (m, 2H, -*CH_2OH*), 4.19 (d, 2H, J=16.3 Hz, O-CH_2-CO), 4.11 (d, 2H, J=16.3 Hz, *O-CH_2-CO*), 3.77-3.57 (m, 10H, -*$COOCH_2CH_2O$-CH_2CH_2O-CH_2-*), 3.16 (td, 1H, J=10.6 Hz, 4.2 Hz, -*CHOH*), 2.3-2.2 (m, 4H,), 2.05 (m, 1H, -CH_2-CHOH), 1.66 (m, 4H, -*CH2CH2- cyclohexyl*), 1.31 (m, 1H, *CH-CH3 cyclohexyl*), 0.92 (d, J=6.9 Hz, 3H, *CH_3 iPr*); 0.90 (d, J=6.9 Hz, 3H, *CH_3 iPr*); 0.79 (d, J=6.9 Hz, 3H, *cyclohexyl-CH_3*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0 (C=O), 80.4 (-*cyclohexylCHOH*), 72.7 (*O-CH_2*), 70.7 (*O-CH_2*), 70.5(*O-CH_2*), 69.1(*O-CH_2*), 66.1 (*O-CH_2-COO*), 63.7(-*CH_2OH*), 61.9 (-*OCH_2*), 48.2 (*CH cyclohexyl*), 40.1 (*CH_2 cyclohexyl*), 34.5 (*CH_2 cyclohexyl*), 31.6 (*CH cyclohexyl*), 25.6 (*CH iPr*), 23.4 (*CH_2 cyclohexyl*), 22.4(*CH_3 iPr*), 21.1(*cyclohexyl-CH_3*), 16.4 (*CH_3 iPr*).

GC/MS (relative intensity, 70 eV) m/z: 346.30 ([M]+,2.0), 177.05 (4.0), 151.00 (31.0),149.00 (13.0), 139.15 (18.0), 138.15 (34.0), 133.00 (12.0), 123.10 (23.0), 103 (55.0), 102.00 (20.0),97.10 (15.0), 96.05 (11.0), 95.05 (48.0), 89.05 (37.0), 88.00 (18.0), 87.00 (100.0), 86.00 (30.0), 83.10 (72.0), 82.05 (20.0), 81.05 (60.0), 69.10 (33.0), 67.10 (17.0), 57.10 (21.0), 55.10 (39.0), 45.10 (81.0), 44.05 (10.0), 43.10 (20.0); d=0.967 g/cm3 at 25 °C.

ELECTRONIC SUPPLEMENTARY INFORMATION

Characterization: NMR

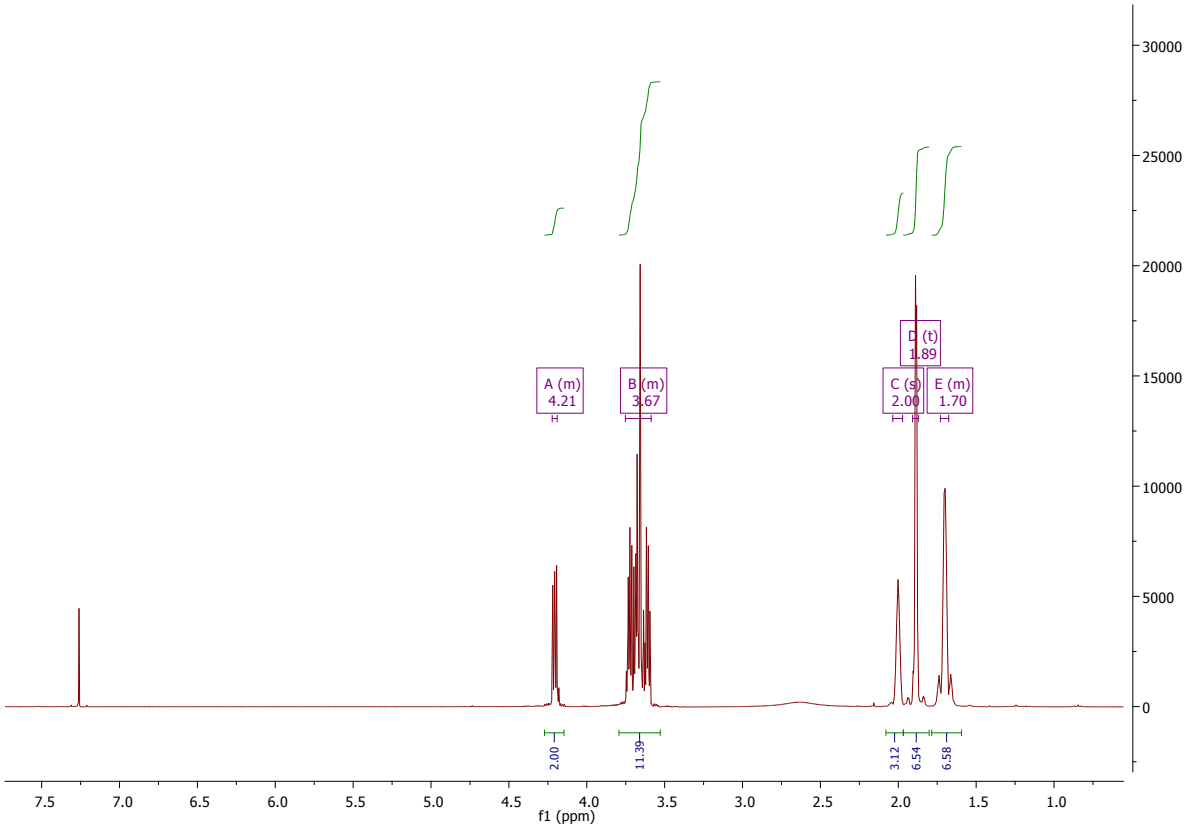
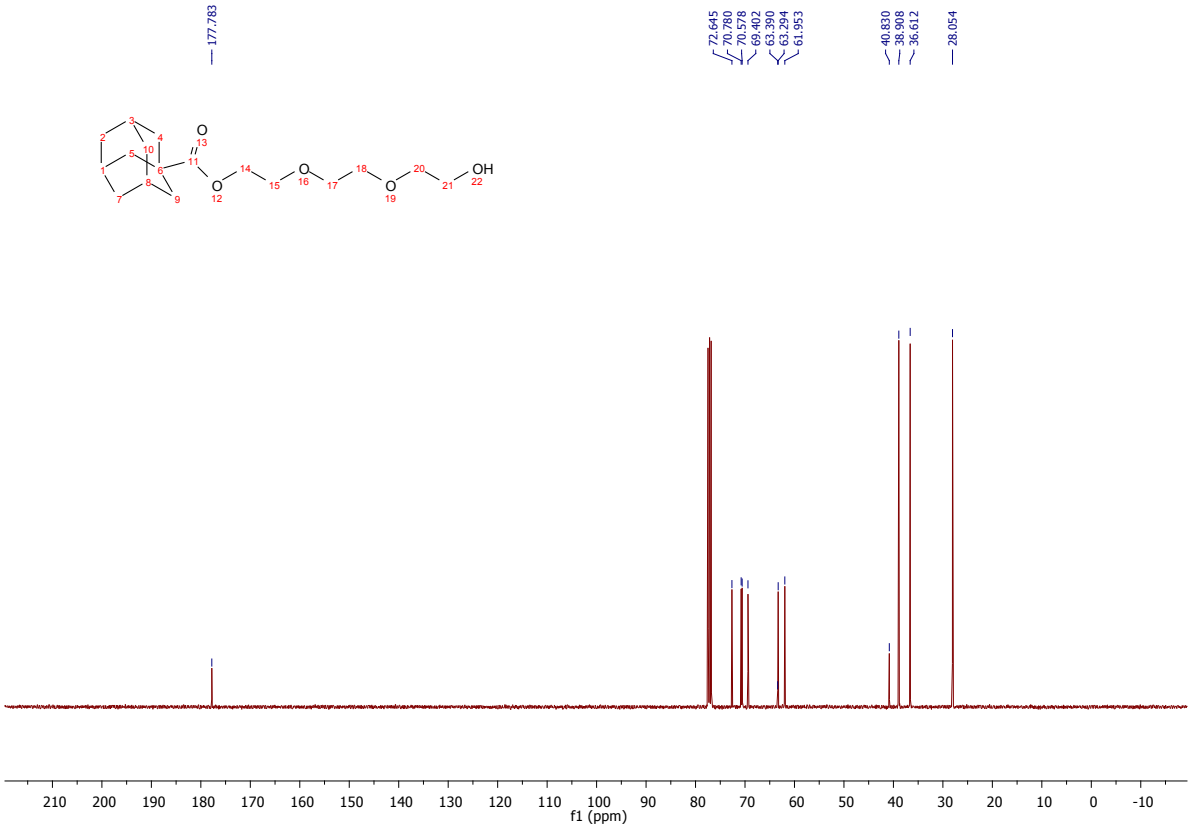


Figure S1. ^{1}H-NMR spectrum of compound $\mathbf{1_{OH}}$



ELECTRONIC SUPPLEMENTARY INFORMATION

Figure S2. 13C-NMR spectrum of compound $\mathbf{1_{OH}}$

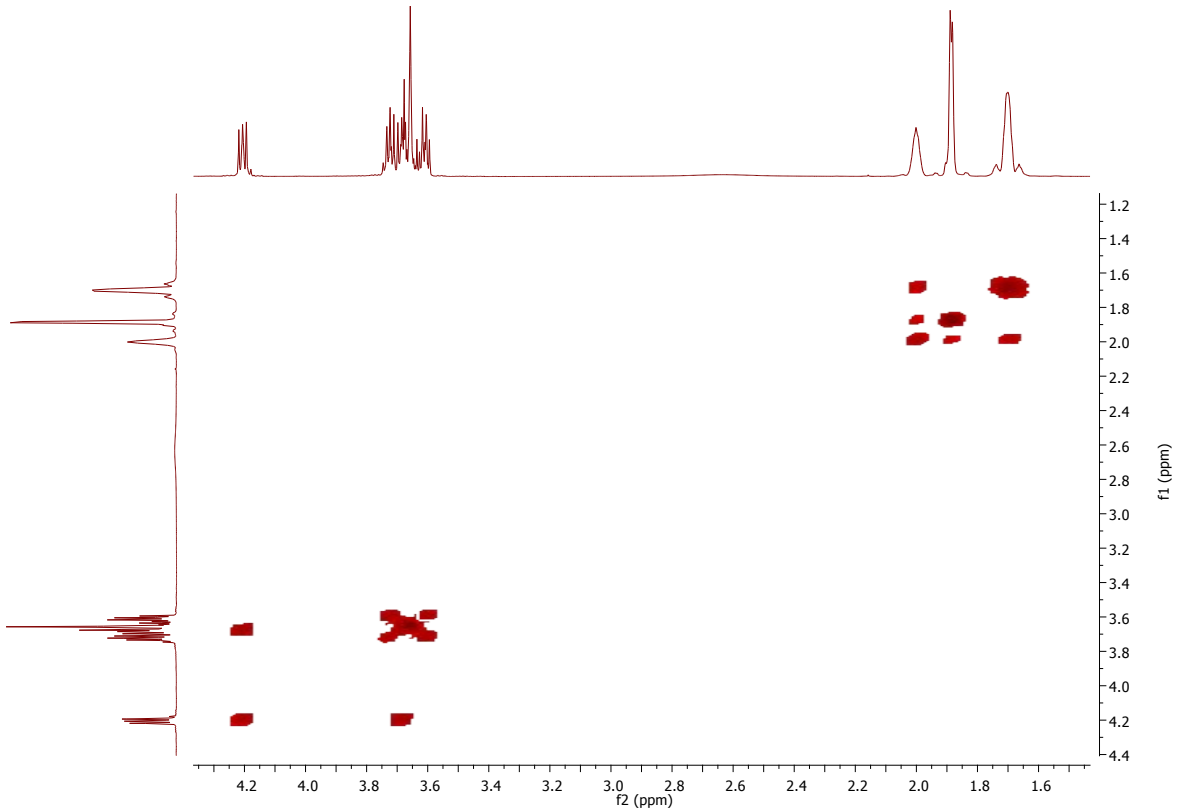


Figure S3. COSY spectrum of compound $\mathbf{1_{OH}}$

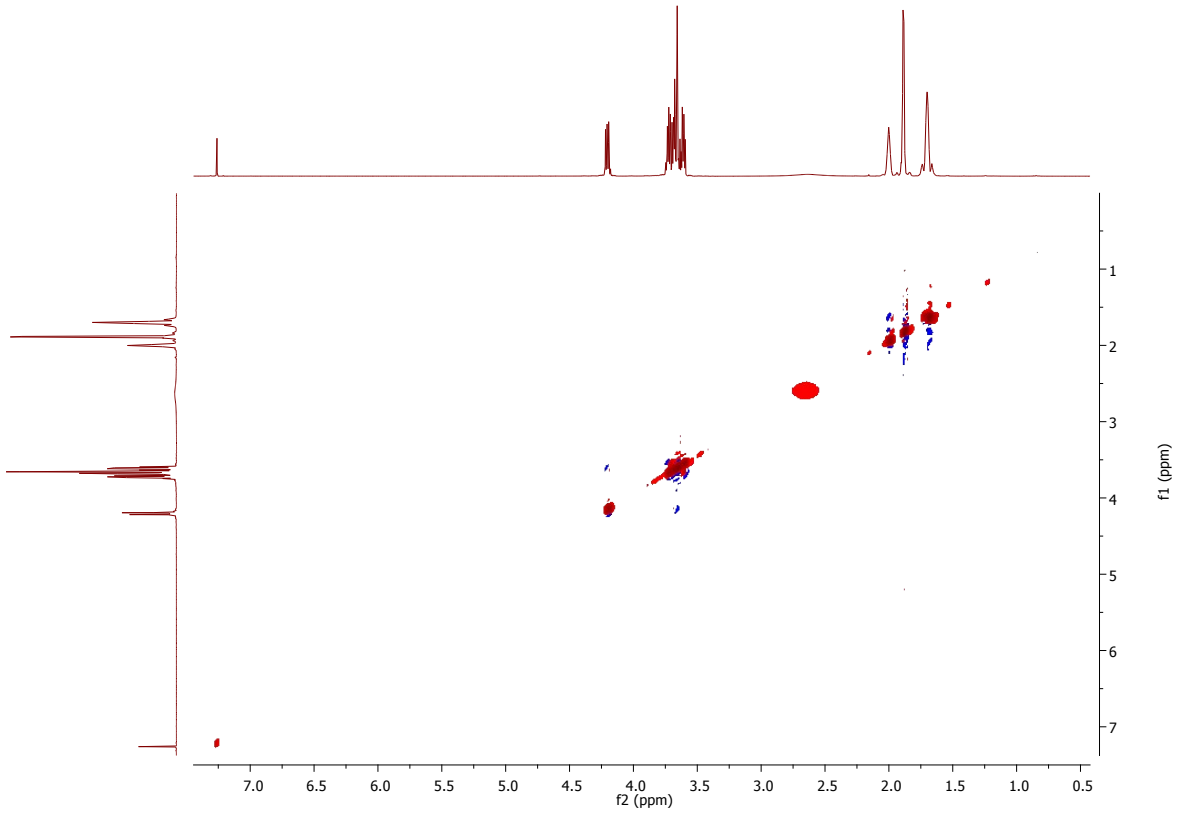


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Figure S4. NOESY spectrum of compound $\mathbf{1_{OH}}$

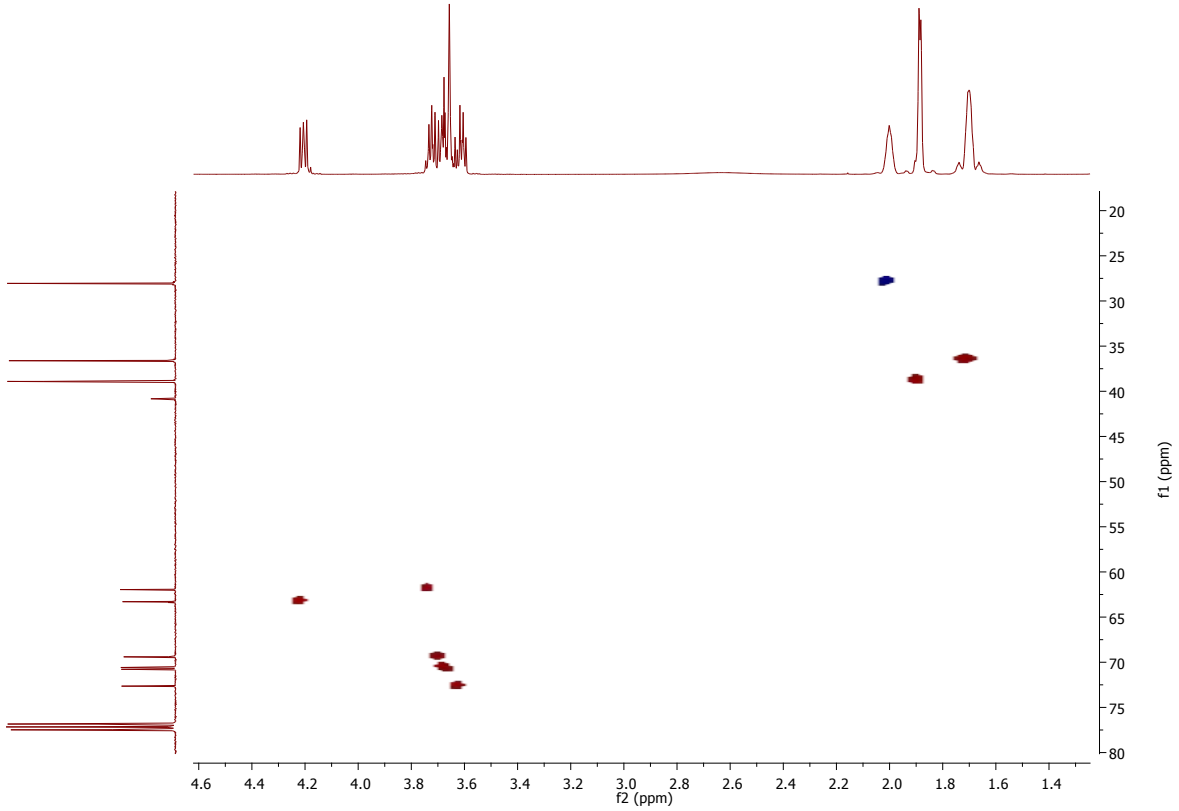

Figure S5. HSQC spectrum of compound $\mathbf{1_{OH}}$

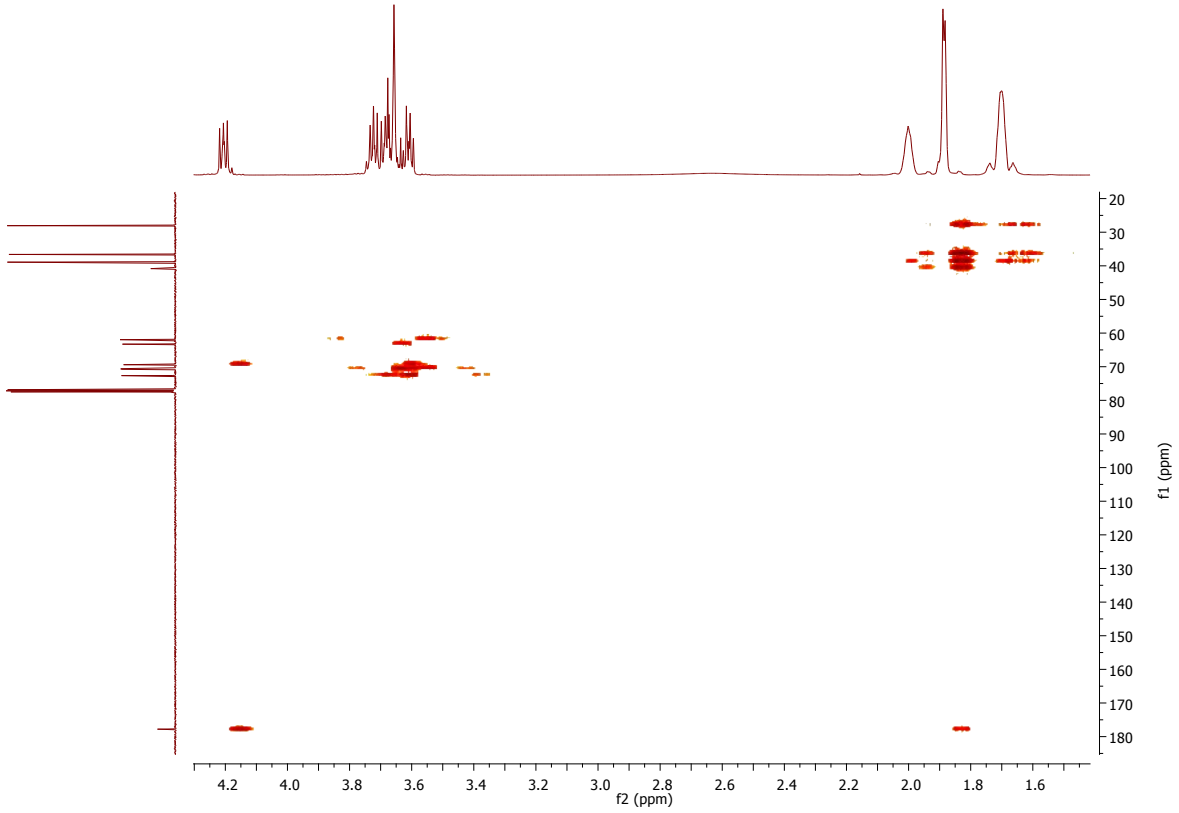

Figure S6. HMBC spectrum of compound $\mathbf{1_{OH}}$

ELECTRONIC SUPPLEMENTARY INFORMATION

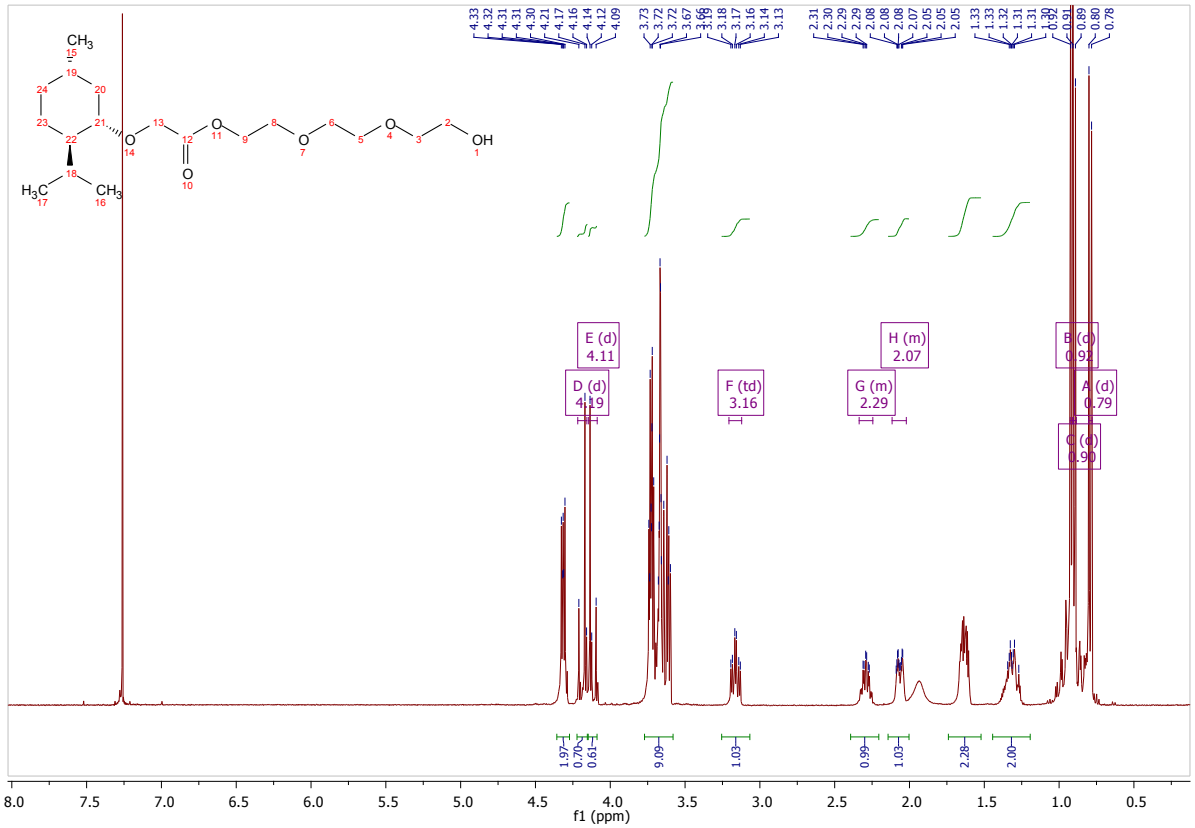

Figure S7. ^{1}HNMR spectrum of compound $\mathbf{2_{OH}}$

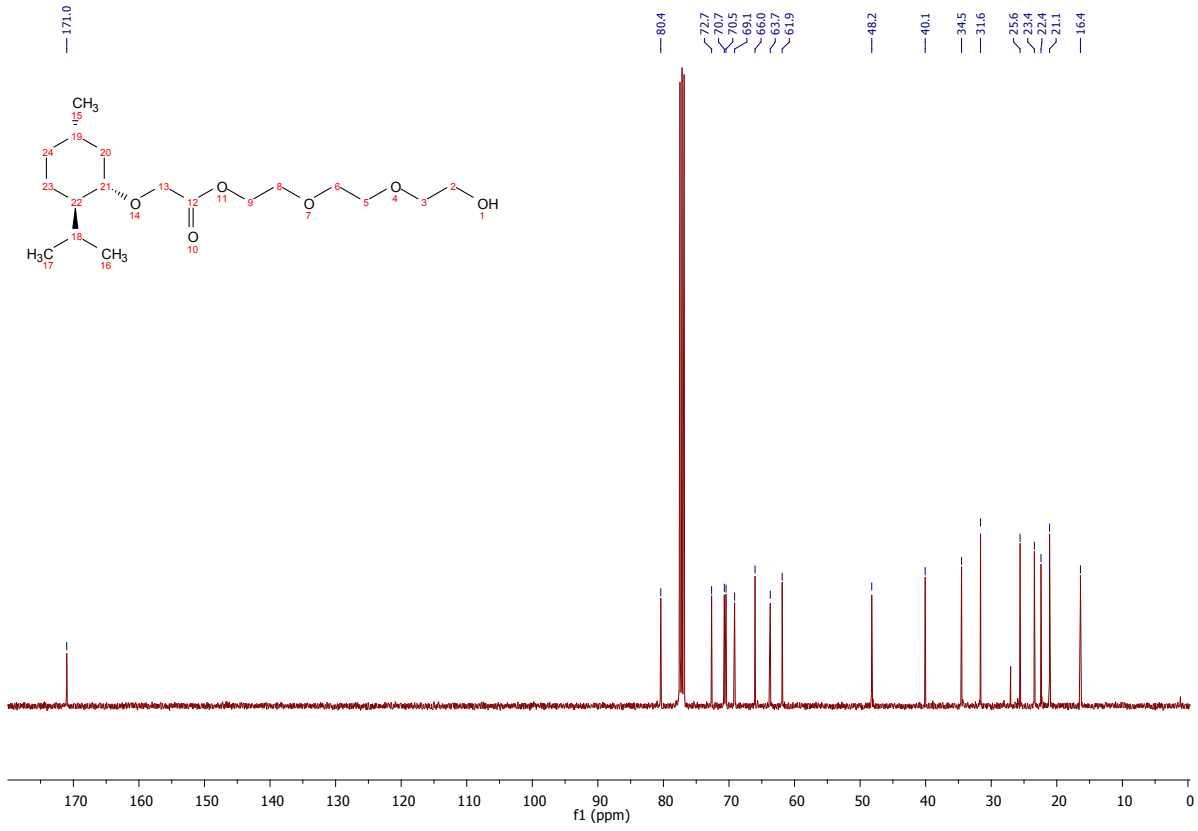

Figure S8. 13C-NMR spectrum of compound $\mathbf{2_{OH}}$

ELECTRONIC SUPPLEMENTARY INFORMATION

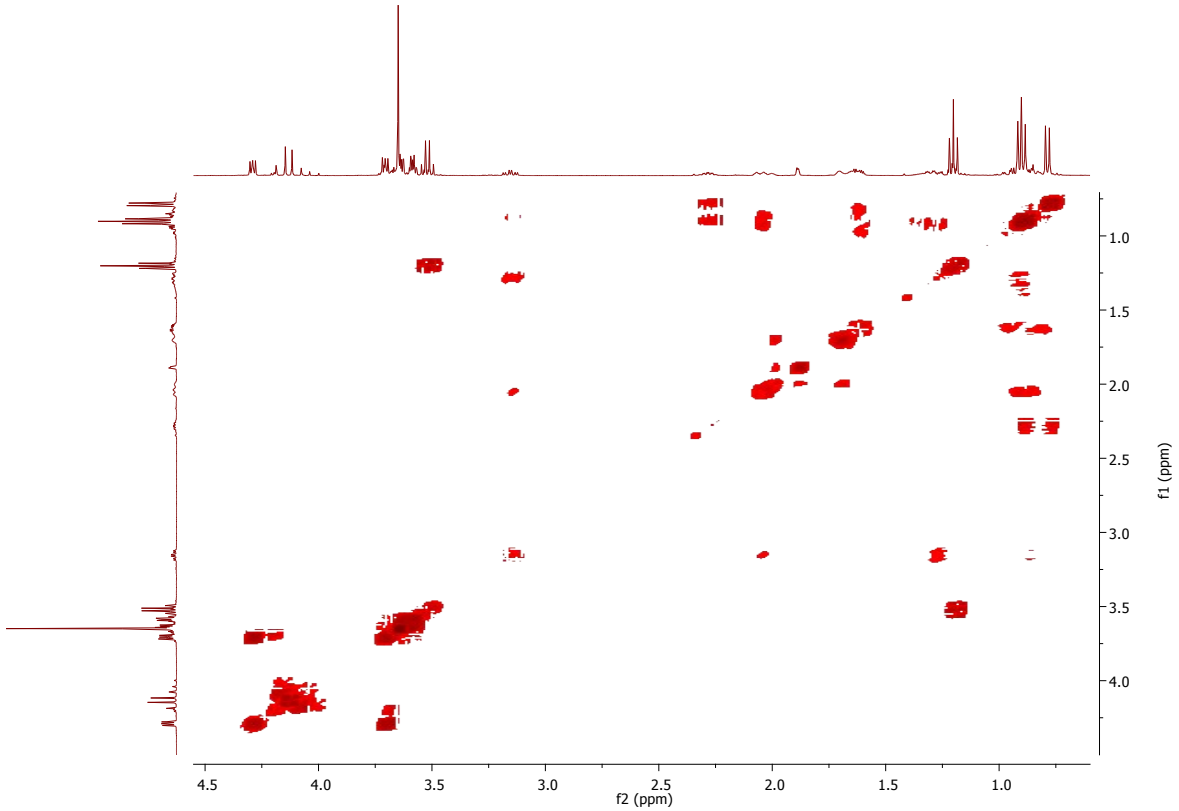

Figure S9. COSY spectrum of compound $\mathbf{2_{OH}}$

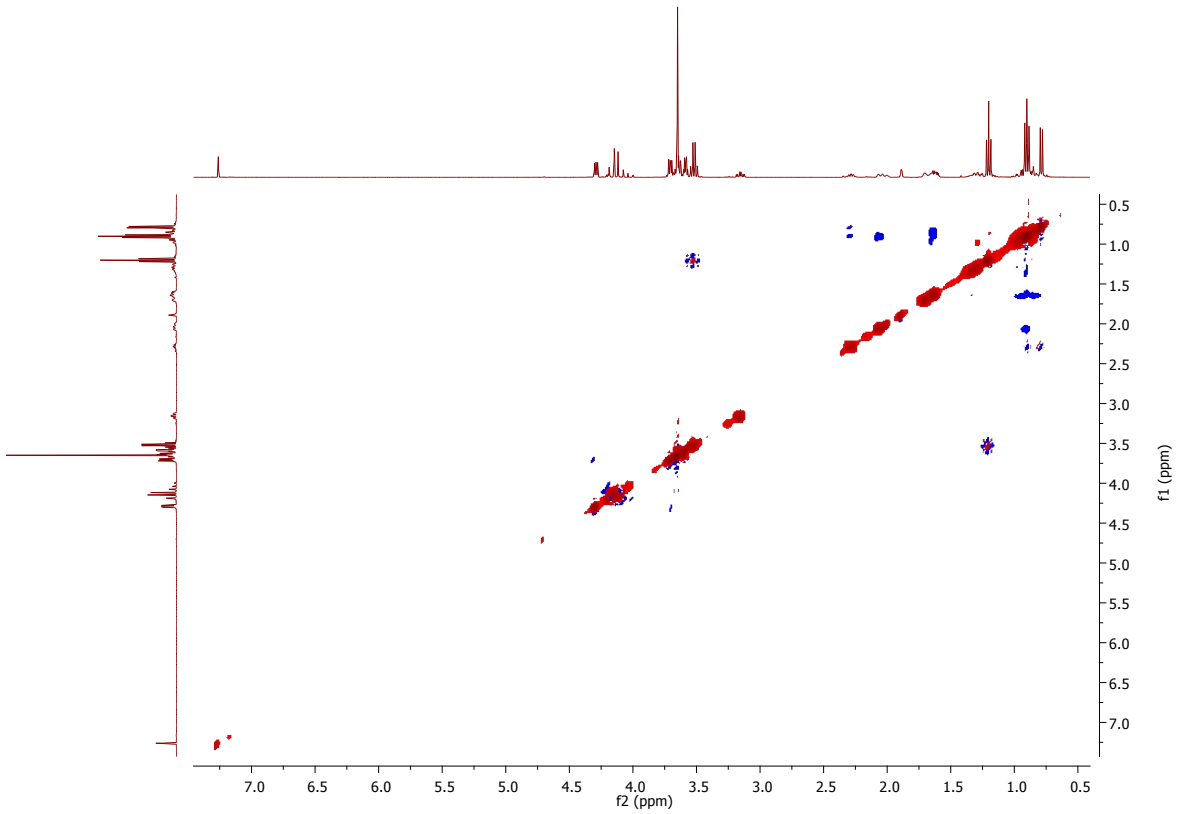

Figure S10. NOESY spectrum of compound $\mathbf{2_{OH}}$

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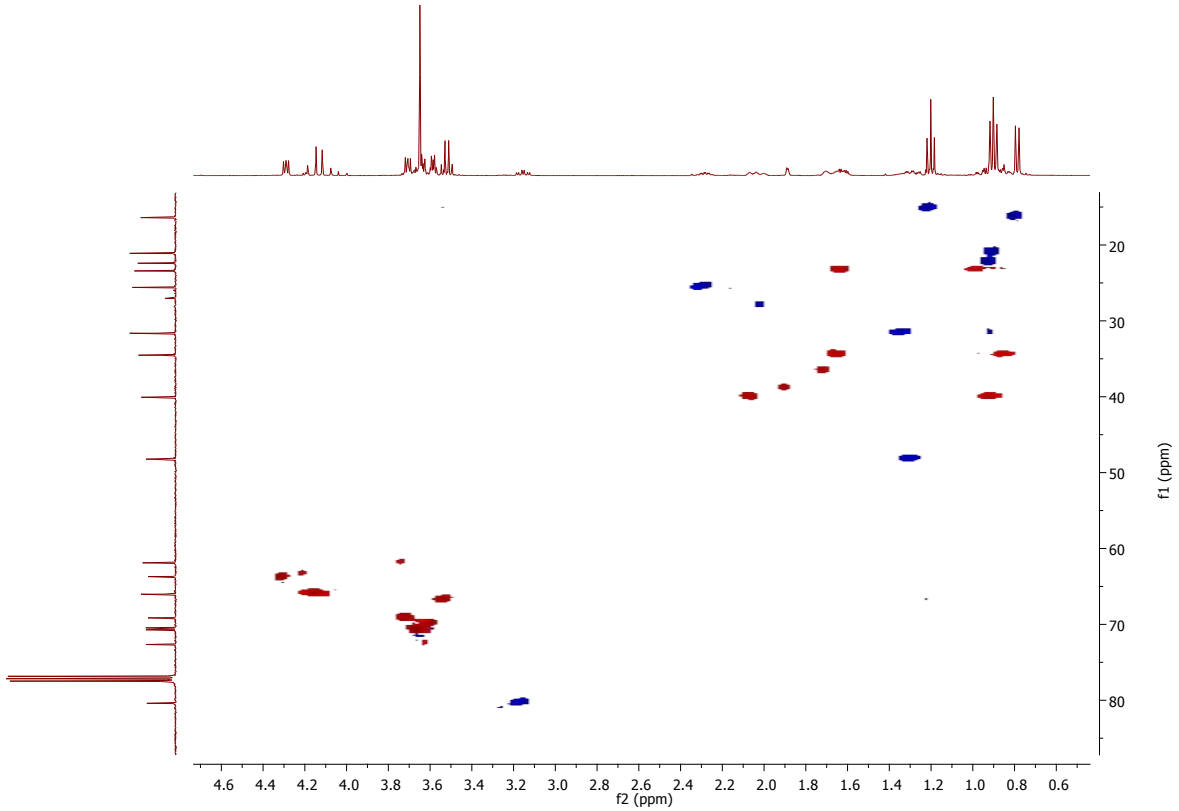

Figure S11. HSQC spectrum of compound $\mathbf{2_{OH}}$

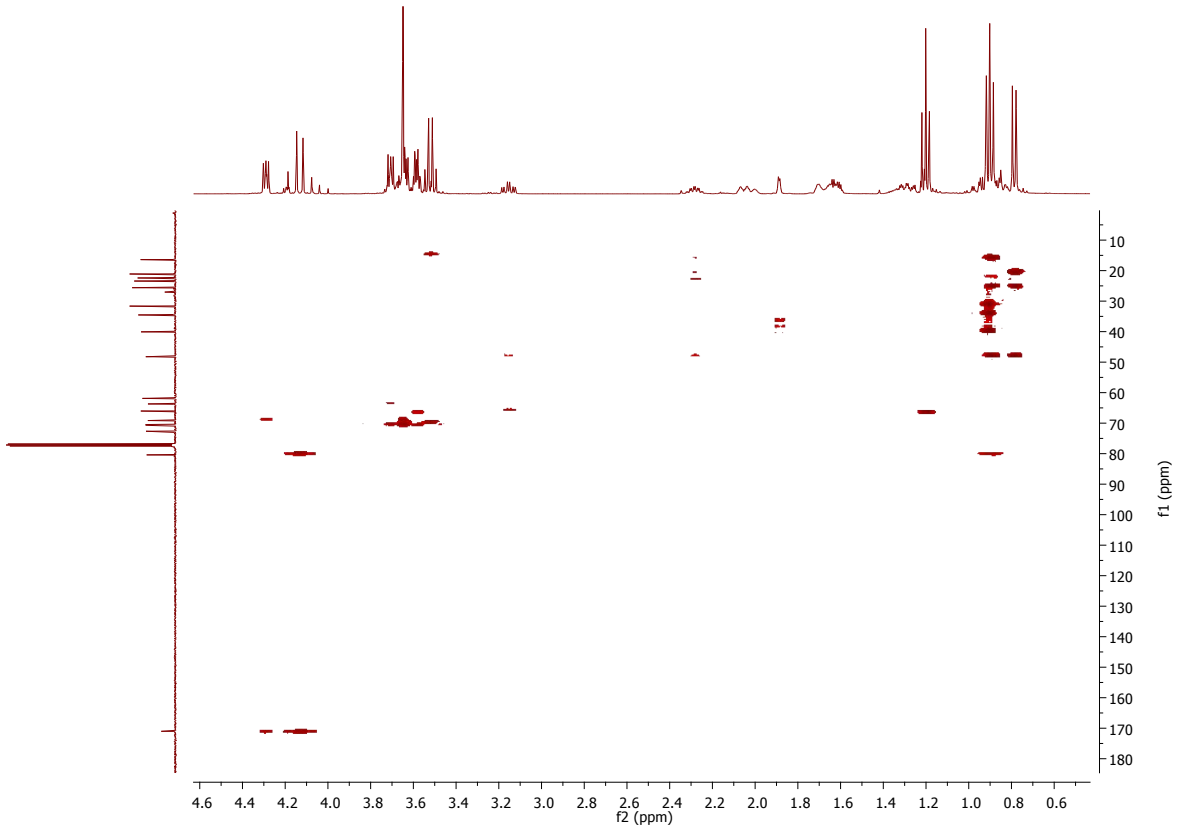

Figure S12. HMBC spectrum of compound $\mathbf{2_{OH}}$

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Characterization: GC-MS

GC/MS (EI, 70 eV) analyses were run using a Agilent 5975c-7890 mounting a HP5-MS capillary column (30 m).

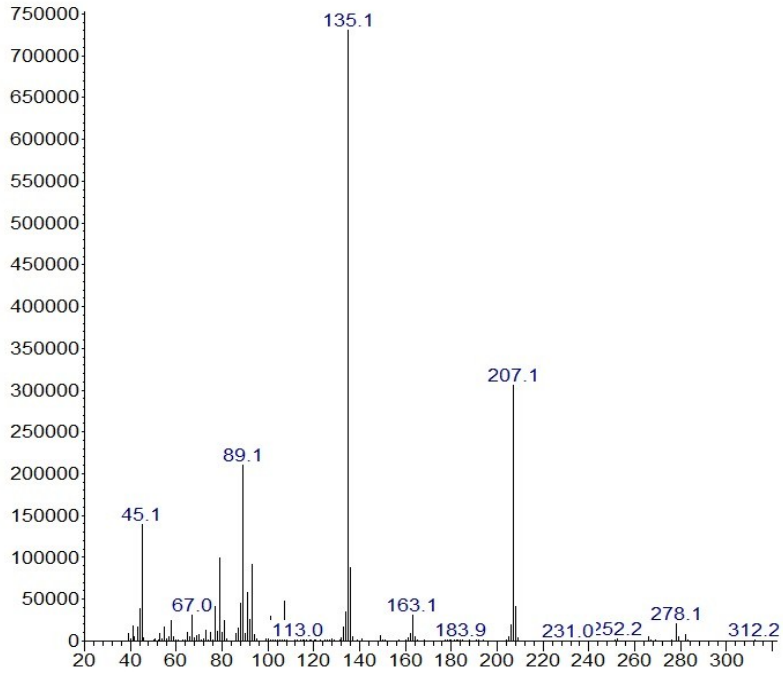

Figure S5. MS spectrum of compound $\mathbf{1_{OH}}$

GC/MS (relative intensity, 70 eV) m/z: 312.2 ([M+],1.0), 207.10 (41.0), 136.00 (12.0), 135.05 (100.0), 93.05 (12.0), 91.05 (8.0), 89.10 (28.0), 88.05 (10.0), 79.05 (13.0)

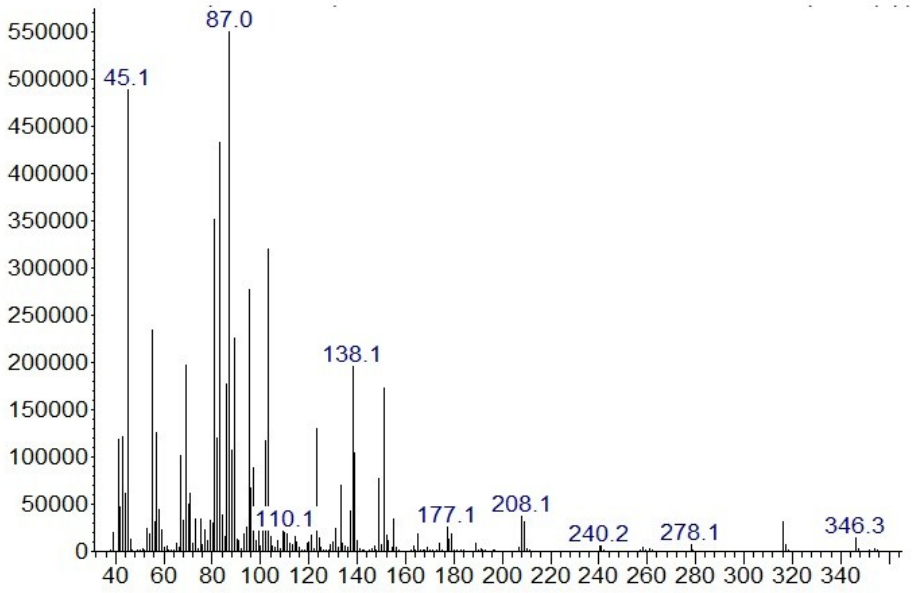

Figure S6. MS spectrum of compound $\mathbf{2_{OH}}$

GC/MS (relative intensity, 70 eV) m/z: 346.30([M]+,2.0), 177.05 (4.0), 151.00 (31.0), 149.00 (13.0), 139.15 (18.0), 138.15 (34.0), 133.00 (12.0), 123.10 (23.0), 103 (55.0), 102.00 (20.0), 97.10 (15.0), 96.05 (11.0), 95.05 (48.0),

89.05 (37.0), 88.00 (18.0), 87.00 (100.0), 86.00 (30.0), 83.10 (72.0), 82.05 (20.0), 81.05 (60.0), 69.10 (33.0), 67.10 (17.0), 57.10 (21.0), 55.10 (39.0), 45.10 (81.0), 44.05 (10.0), 43.10 (20.0);

Aggregation analysis

2D-DOSY experiments acquisition and processing

2D DOSY were carried out on freshly prepared solutions of the two amphiphiles at different concentrations in the range 5-260 mM in cyclohexane. In order to ensure locking of the systems, a coaxial tube containing 98% dmso-d6 was employed and locking was performed on the protonic residual dmso. For each sample, before running the 2D DOSY experiment, simple 1D DOSY were recorder in order to optimize the magnetic field pulse gradients (δ) and diffusion time (Δ)values to ensure proper signal abatement during the 2D experiment.

^{1}H-NMR were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 MHz. δ values in ppm are relative to $SiMe_4$. 2D-DOSY spectrum were recorded on the same instrument equipped with a PABBO BB-1H Z GRD probe head. Pulse sequence used was ledbpgp2s 2D sequence for diffusion measurements using stimulated echo and LED using bipolar gradient pulses using 2 spoil gradients. In order to select proper magnetic field pulse gradients (δ) and diffusion time (Δ) parameters for the DOSY experiment, prior 1D DOSY experiments were carried out. The amplitude of the field gradient was varied from 2 to 95% of its maximum value over 32 increments, while the gradient recovery delay (τ) and the eddy current delay (te) were fixed at 0.1 and 5 ms, respectively. The diffusion delay (Δ) was set to 50 ms and the corresponding gradient pulse duration (δ) 1-1.5 ms, in order to achieve an intensity attenuation range of at least 95%. The number of number of scans was set in the range 8-32 depending on the concentration of the amphiphile, with a recycling delay D1 of 5 s. Without sample spinning, a series of 32 spectra on 16K data points were collected with 32 transients, total measuring time was ca. 1 h. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Xwin-NMR software package.

SAXS measures and data processing

Al the amphiphiles and cyclohexane were dehydrated before the measures with molecular sieves. The amphiphile was dissolved in cyclohexane at different concentrations (50, 75, 100, 200, 300 500 mM). A SAXS Kratky camera (Cu Kαλ = 0.154 nm) equipped with a proportional detector for intensity recording was used. Solutions were held in a 1.5 mm kapton capillary at room temperature. Data were acquired as a function of the scattering vector modulus $q = (4\pi \sin\theta)/\lambda$ where 2θ is the angle between the incident and scattered photons. The SAXS curves were obtained by step scanning in the range from q = 0.07 to q = 4 nm^{-1}. In this range several angular regions, having different step intervals, were chosen.

To determine the Radius Gyration (Rg) it was used the approximation expressed by the Guinier Law which applies only at the very beginning of the scattering curve when $qR_g<1$:

$$ln(I(q)) = \ln[I(0)] - \frac{q^2 R_g^{\,2}}{3}$$

where R_g is the gyration radius of the aggregate.

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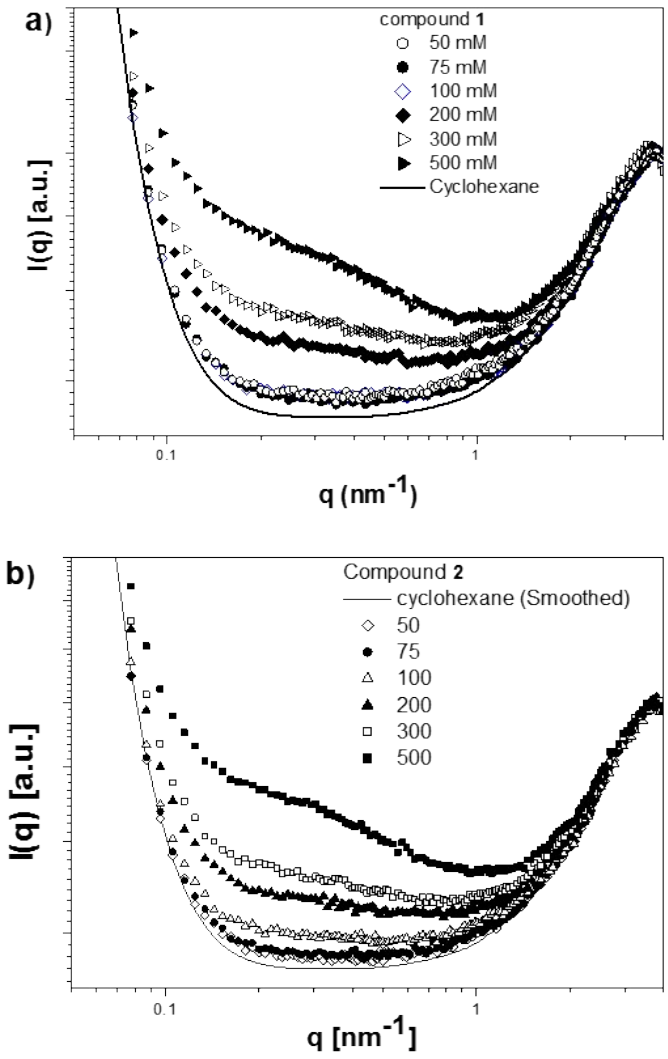

Figure S10. SAXS intensities of compound $\mathbf{1}_{OH}$ (a) and $\mathbf{2}_{OH}$ (b) (absolute units) at different concentrations compared to cyclohexane SAXS curve.