

Supporting Information

Glycerol Ethers as Hydrotropes and their use to Enhance the Solubility of Phenolic Acids in Water

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Number of Pages: 27

Number of Tables: 18

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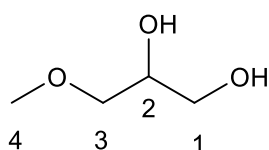
S1. Product characterization

The water content of the synthesised monoalkyl glycerol ethers was measured using a Metrohm 831 Karl Fisher coulometer (results reported in Table S1).

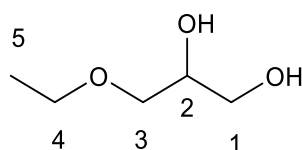
Table S1. Water content (mass percentage) and standard deviation (s) of the glycerol ethers synthesised in this work.

Substance	wt % H ₂ O ± s
[1.0.0]	1.1884 ± 0.0061
[2.0.0]	0.6230 ± 0.0030
[3.0.0]	0.6133 ± 0.0254
[4.0.0]	0.8893 ± 0.0092
[5.0.0]	0.3026 ± 0.0010
[6.0.0]	0.2139 ± 0.0163
[1.0.1]	0.0786 ± 0.0021
[2.0.2]	0.0468 ± 0.0017

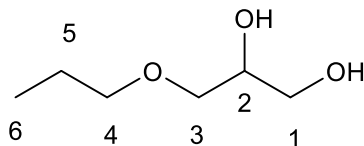
Gas chromatography was carried out in a Hewlett Packard 7890 series II Gas Chromatograph using a column of phenyl silicone 5.5% (Zebron Inferno 30 m x 0.25 mm x 0.25 μm) and Helium as carrier gas. The conditions and method used in the equipment were: 280 °C injector temperature, 250 °C detector temperature. Temperature program: 80 °C for 3 min., temperature gradient 5 °C min⁻¹ until 110 °C, temperature gradient 20 °C min⁻¹ until 230 °C, 230 °C isotherm for 5 min. The ¹H- and ¹³C-NMR spectra ([d₆]DMSO, δ ppm, J Hz) were obtained using a Bruker AV-400 instrument with tetramethylsilane (TMS) as standard.



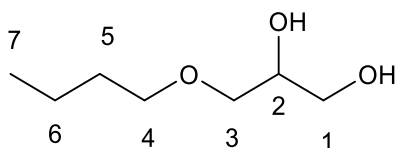
3-Methoxypropan-1,2-diol [1.0.0]: ¹H RMN (400 MHz, [d₆]DMSO): δ 4.61 (d, 1H, J = 5.1 Hz, OH₂), 4.46 (t, 1H, J = 5.7 Hz, OH₁), 3.56 (sext, 1H, J = 5.1 Hz, H₂), 3.18-3.36 (m, 4H, H₁, H₃), 3.23 (s, 3H, H₄). ¹³C RMN (100 MHz, [d₆]DMSO): δ 74.2 (CH₂, C₃), 70.3 (CH, C₂), 62.9 (CH₂, C₁), 58.3 (CH₃, C₄).



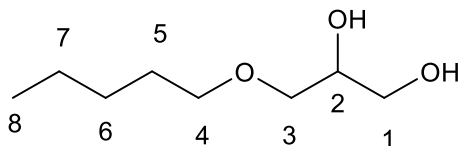
3-ethoxypropan-1,2-diol [2.0.0]: ^1H RMN (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.59 (d, 1H, $J = 5.1$ Hz, OH_2), 4.45 (t, 1H, $J = 5.7$ Hz, OH_1), 3.55 (sext, 1H, $J = 5.3$ Hz, H_2), 3.42 (q, 2H, $J = 7.0$ Hz, H_4), 3.21-3.37 (m, 4H, H_1 , H_3), 1.10 (t, 3H, $J = 7.0$ Hz, H_5). ^{13}C RMN (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 72.3 (CH_2 , C_3), 70.8 (CH , C_2), 66.0 (CH_2 , C_4), 63.4 (CH_2 , C_1), 15.4 (CH_3 , C_5).



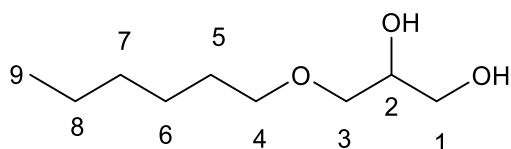
3-propoxypropan-1,2-diol [3.0.0]: ^1H RMN (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.57 (d, 1H, $J = 5.1$ Hz, OH_2), 4.44 (t, 1H, $J = 5.7$ Hz, OH_1), 3.55 (sext, 1H, $J = 5.3$ Hz, H_2), 3.22-3.38 (m, 6H, H_1 , H_3H_4), 1.48 (sext, 2H, $J = 6.7$ Hz, H_5), 0.85 (t, 3H, $J = 7.4$ Hz, H_6). ^{13}C RMN (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 72.2 (CH_2 , C_3), 72.1 (CH_2 , C_4), 70.5 (CH , C_2), 63.2 (CH_2 , C_1), 22.4 (CH_2 , C_5), 10.5 (CH_3 , C_6).



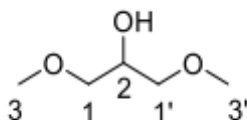
3-butoxypropan-1,2-diol [4.0.0]: ^1H RMN (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.54 (d, 1H, $J = 5.1$ Hz, OH_2), 4.41 (t, 1H, $J = 5.7$ Hz, OH_1), 3.53 (sext, 1H, $J = 5.2$ Hz, H_2), 3.34 (t, 2H, $J = 6.7$ Hz, H_4), 3.19-3.32 (m, 4H, H_1 , H_3), 1.44 (quint, 2H, $J = 7.6$ Hz, H_5), 1.29 (sext, 2H, $J = 7.3$ Hz, H_6), 0.85 (t, 3H, $J = 7.4$ Hz, H_7). ^{13}C RMN (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 72.3 (CH_2 , C_3), 70.6 (CH , C_2), 70.2 (CH_2 , C_4), 63.2 (CH_2 , C_1), 31.4 (CH_2 , C_5), 18.9 (CH_2 , C_6), 13.8 (CH_3 , C_7).



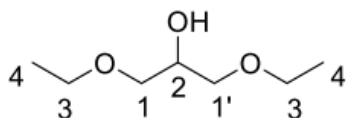
3-pentiloxopropan-1,2-diol [5.0.0]: ^1H RMN (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.56 (d, 1H, $J = 5.1$ Hz, OH_2), 4.43 (t, 1H, $J = 5.7$ Hz, OH_1), 3.55 (sext, 1H, $J = 5.3$ Hz, H_2), 3.35 (t, 2H, $J = 6.6$ Hz, H_4), 3.25-3.37 (m, 3H, H_1 , H_{3a}), 3.24 (dd, 1H, $J = 9.8$ Hz, $J = 6.0$ Hz, H_{3b}), 1.48 (quint, 2H, $J = 7.0$ Hz, H_5), 1.22-1.32 (m, 4H, H_6 , H_7), 0.86 (t, 3H, $J = 7.0$ Hz, H_8). ^{13}C RMN (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 72.3 (CH_2 , C_3), 70.6 (CH , C_2), 70.5 (CH_2 , C_4), 63.2 (CH_2 , C_1), 28.9 (CH_2 , C_5), 27.9 (CH_2 , C_6), 22.0 (CH_2 , C_7), 13.9 (CH_3 , C_8).



3-hexyloxypropan-1,2-diol [6.0.0]: ^1H RMN (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.56 (d, 1H, $J = 5.0$ Hz, OH₂), 4.43 (t, 1H, $J = 5.7$ Hz, OH₂), 3.55 (sext, 1H, $J = 5.3$ Hz, H₂), 3.36 (t, 2H, $J = 6.6$ Hz, H₄), 3.22-3.36 (m, 3H, H₁, H_{3a}), 3.24 (dd, 1H, $J = 9.8$ Hz, $J = 6.0$ Hz, H_{3b}), 1.43-1.52 (m, 2H, H₅), 1.20-1.33 (m, 6H, H₆, H₇, H₈), 0.85 (t, 3H, $J = 7.0$ Hz, H₉) ^{13}C RMN (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 77.3 (CH₂, C₃), 70.6 (CH, C₂), 70.6 (CH₂, C₄), 63.2 (CH₂, C₁), 31.2 (CH₂, C₅), 29.3 (CH₂, C₆), 25.4 (CH₂, C₇), 22.1 (CH₂, C₈), 13.9 (CH₃, C₉).



1,3-dimethoxypropan-2-ol [1.0.1]: ^1H NMR (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.79 (d, 1H, $J = 5.2$ Hz, OH₂), 3.70 (sext, 1H, $J = 5.1$ Hz, H₂), 3.28 (dd, 2H, $J = 9.8$ Hz, $J = 5.0$ Hz, H_{1a}, H_{1'a}), 3.23 (dd, 2H, $J = 9.9$ Hz, $J = 5.6$ Hz, H_{1b}, H_{1'b}), 3.24 (s, 6H, H₃, H_{3'}). ^{13}C NMR (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 74.2 (CH₂, C₁), 68.2 (CH, C₂), 58.4 (CH₃, C₃).



1,3-diethoxypropan-2-ol [2.0.2]: ^1H NMR (400 MHz, $[\text{d}_6]\text{DMSO}$): δ 4.72 (d, 1H, $J = 5.2$ Hz, OH₂), 3.67 (sext, 1H, $J = 5.1$ Hz, H₂), 3.42 (c, 4H, $J = 7.0$ Hz, H₃), 3.32 (dd, 2H, $J = 9.8$ Hz, $J = 5.0$ Hz, H_{1a}, H_{1'a}), 3.26 (dd, 2H, $J = 9.9$ Hz, $J = 5.9$ Hz, H_{1b}, H_{1'b}), 1.09 (t, 6H, $J = 7.0$ Hz, H₄). ^{13}C NMR (100 MHz, $[\text{d}_6]\text{DMSO}$): δ 72.2 (CH₂, C₁), 68.6 (CH, C₂), 65.8 (CH₂, C₃), 15.1 (CH₃, C₄).

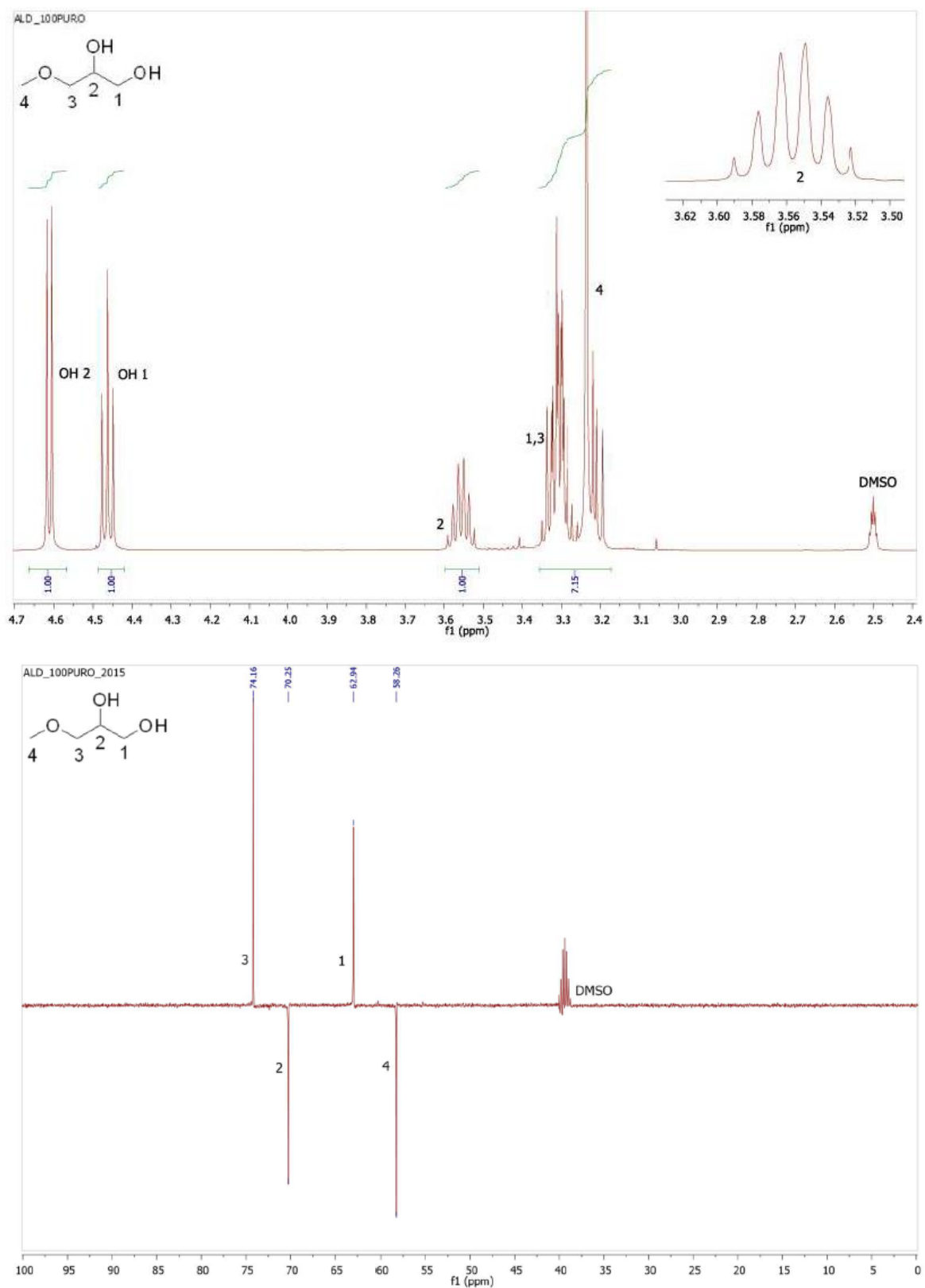


Figure S1. ¹H-RMN and ¹³C-RMN (APT) of 3-methoxypropan-1,2-diol [1.0.0].

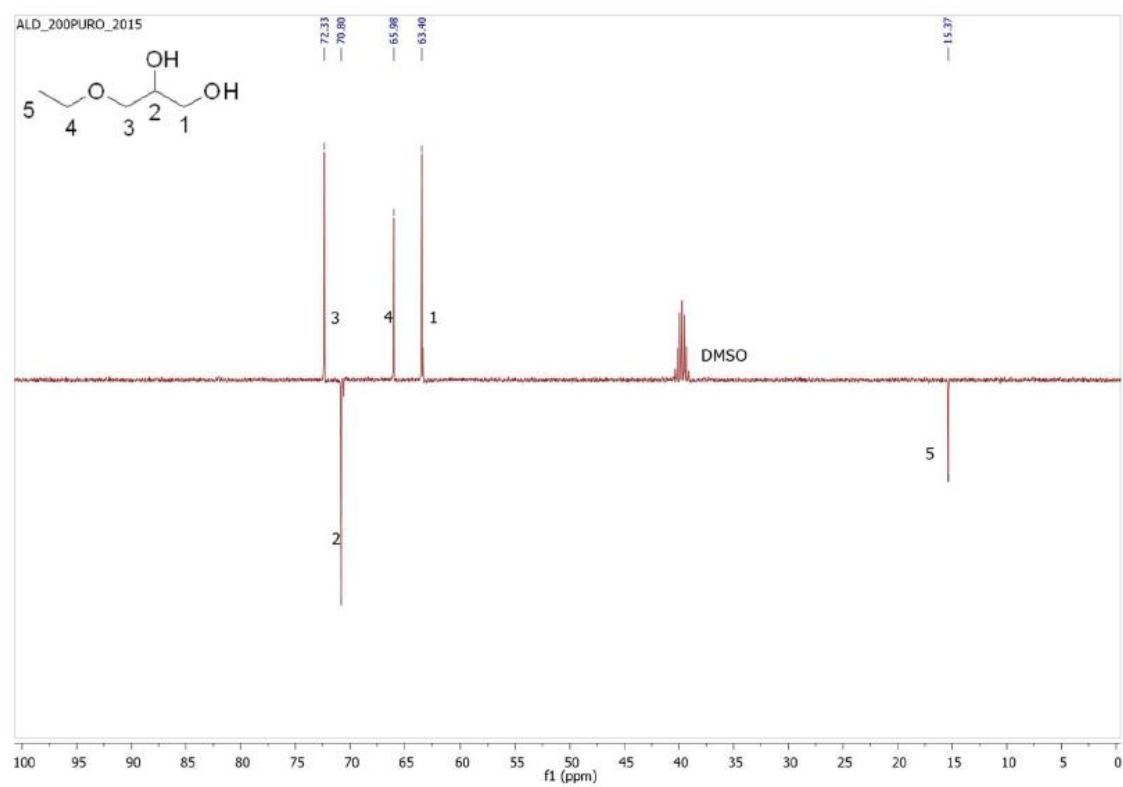
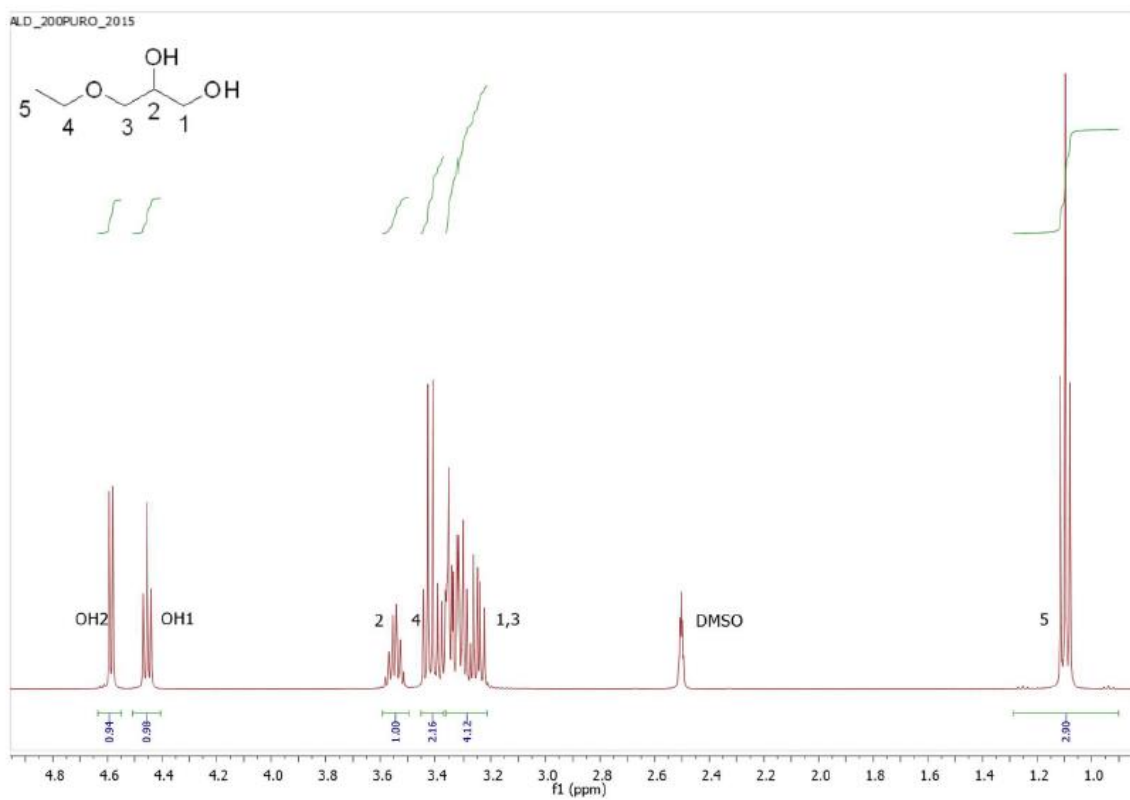


Figure S2. ^1H -RMN and ^{13}C -RMN (APT) of 3-ethoxypropan-1,2-diol [2.0.0].

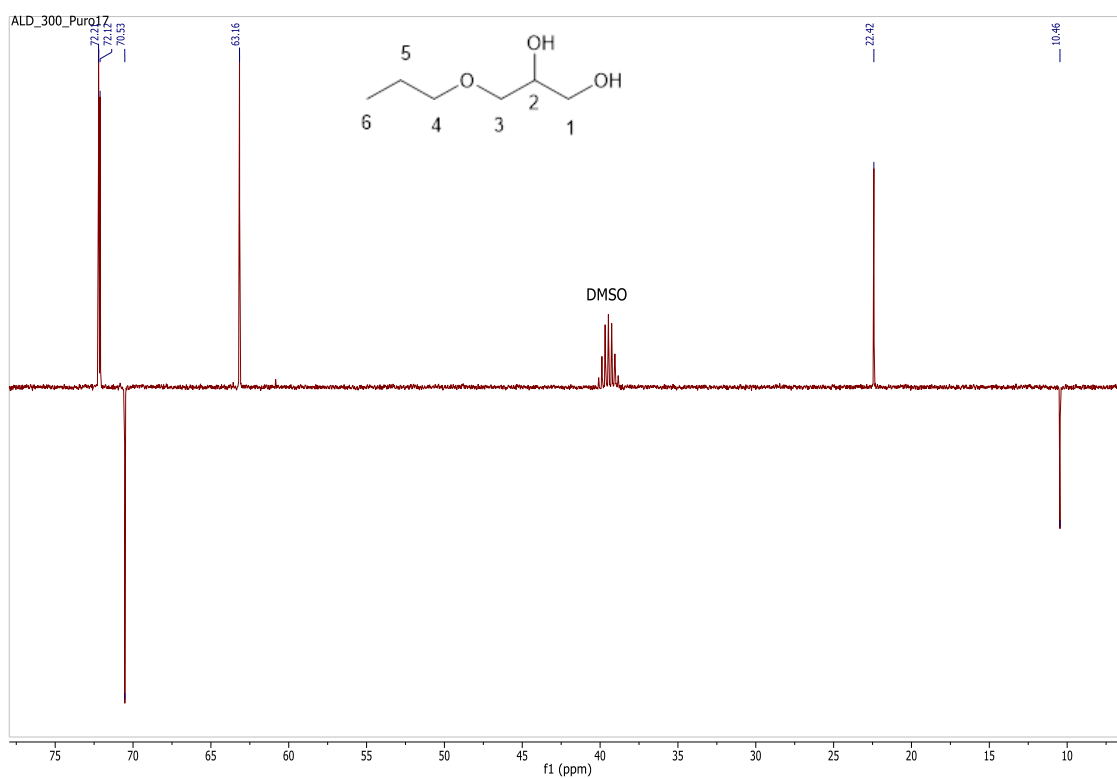
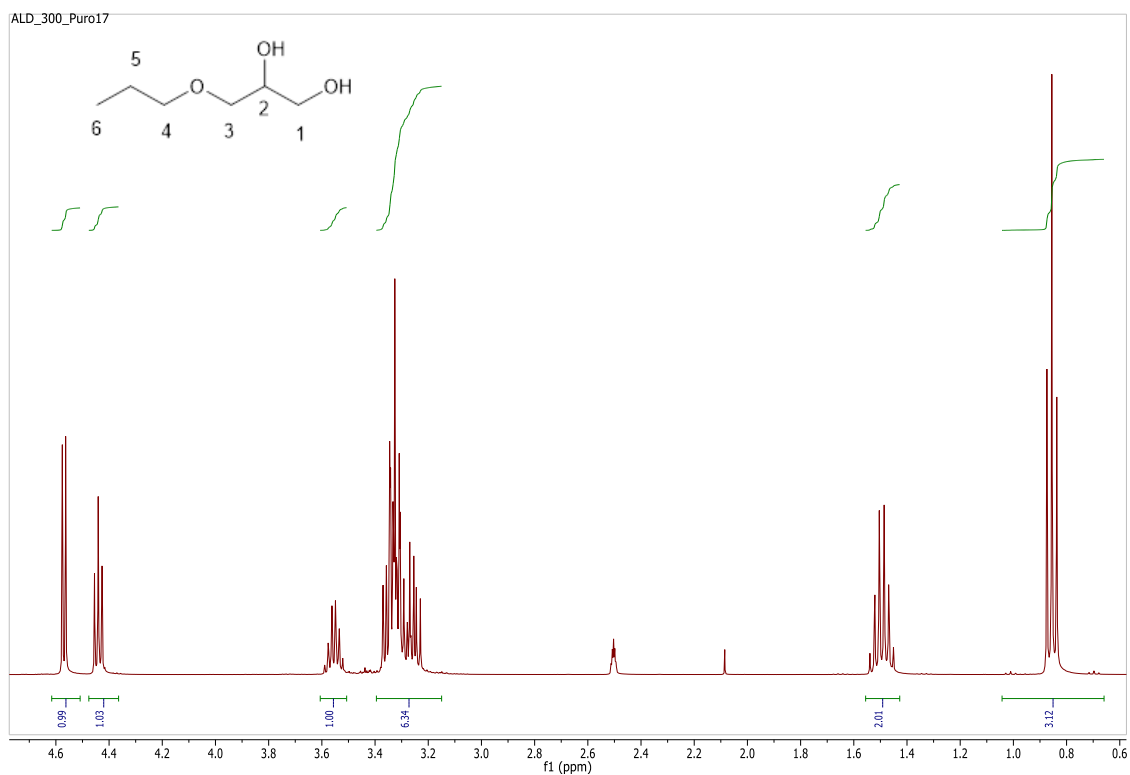


Figure S3. ^1H -RMN and ^{13}C -RMN (APT) of 3-propoxypropan-1,2-diol [3.0.0].

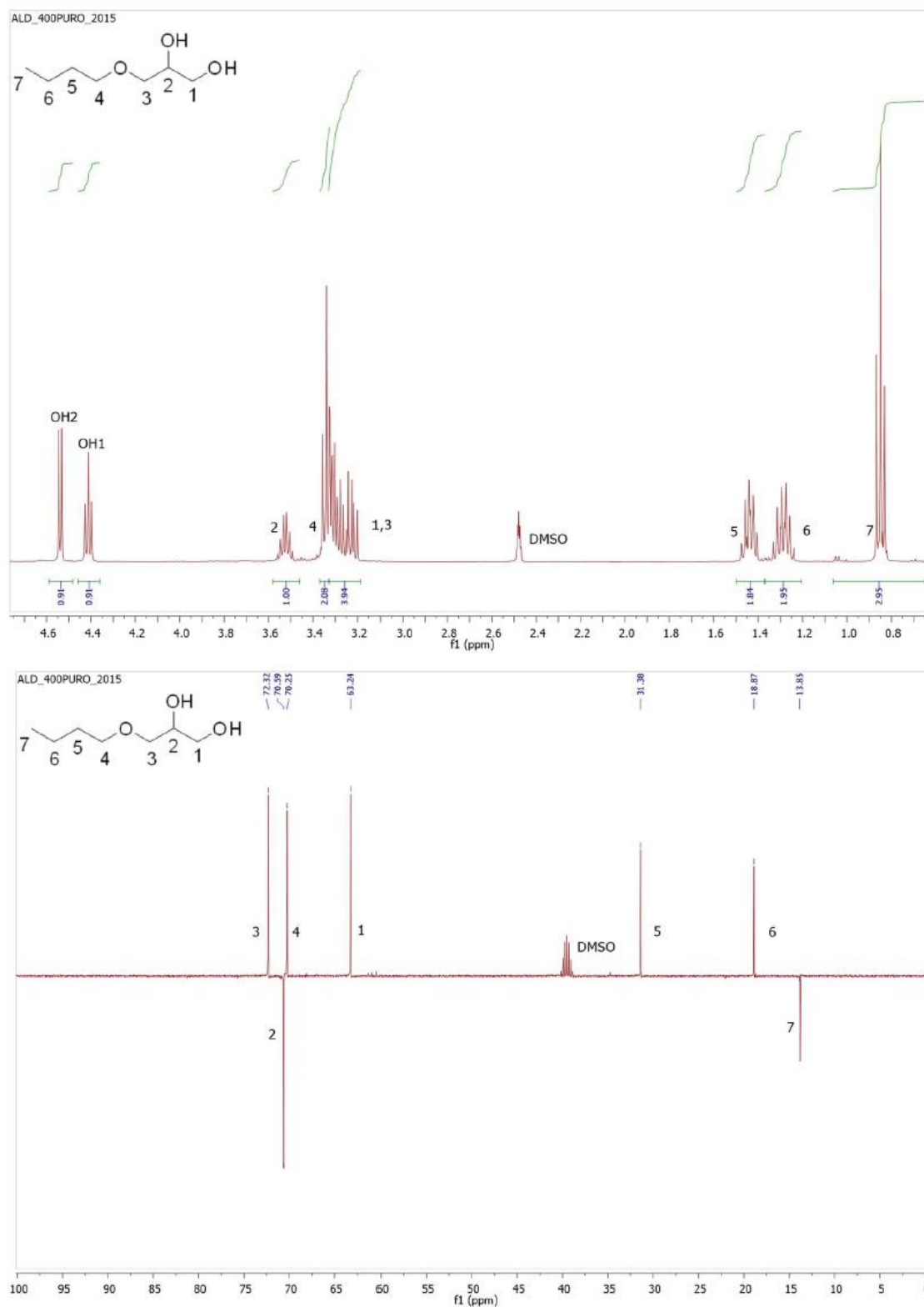


Figure S4. ¹H-RMN and ¹³C-RMN (APT) of 3-butoxypropan-1,2-diol [4.0.0].

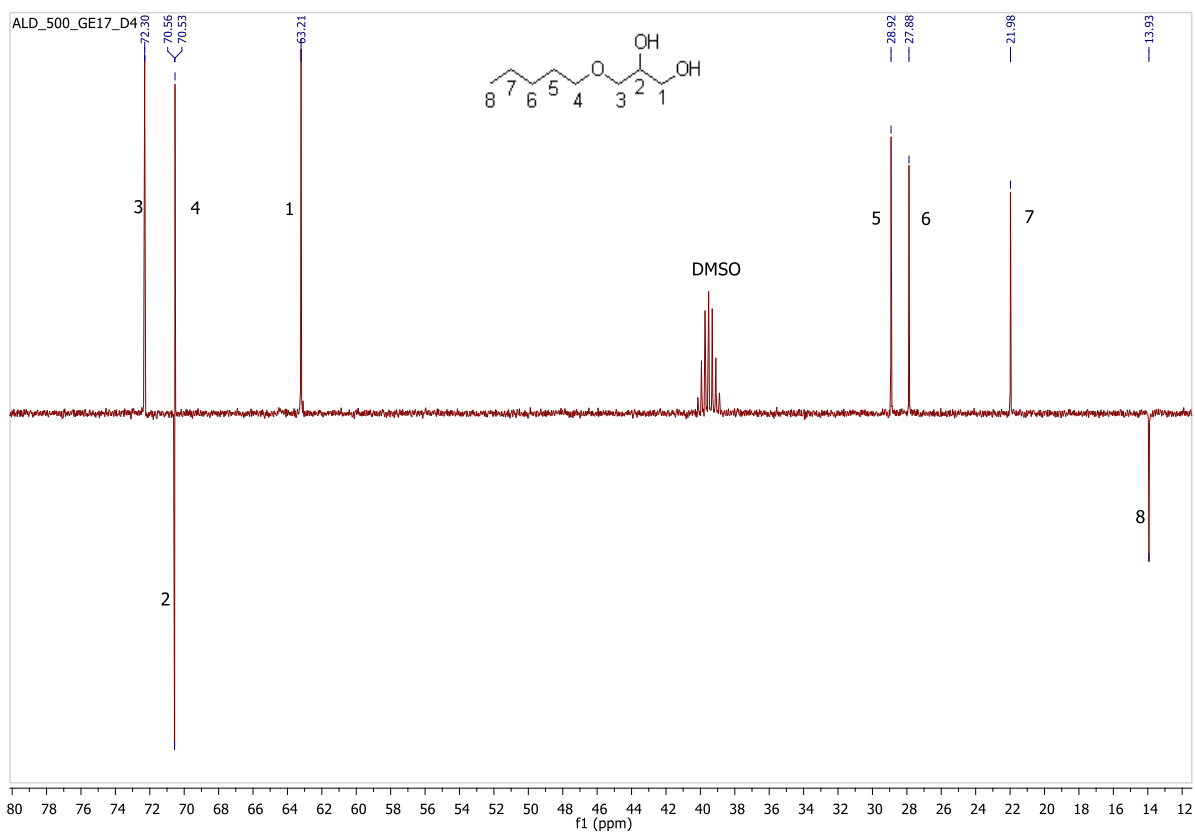
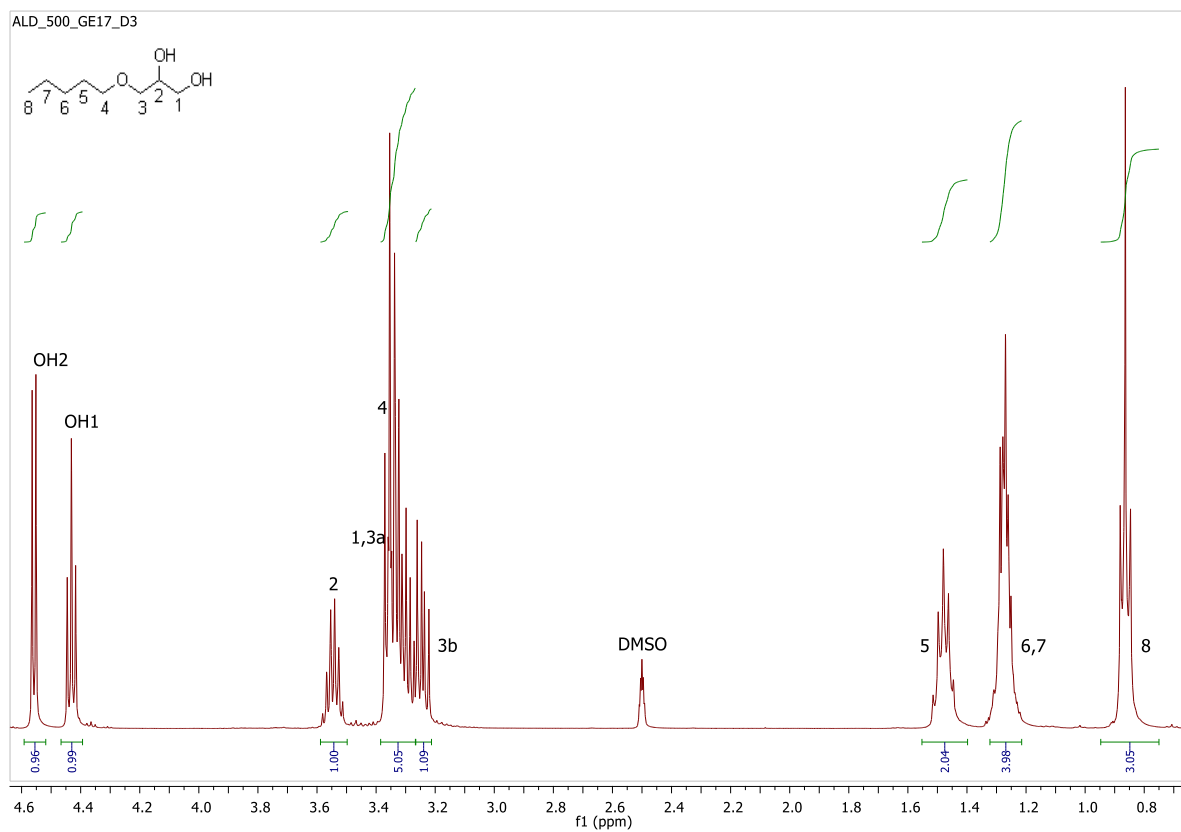


Figure S5. ^1H -RMN and ^{13}C -RMN (APT) of 3-pentoxypropan-1,2-diol [5.0.0].

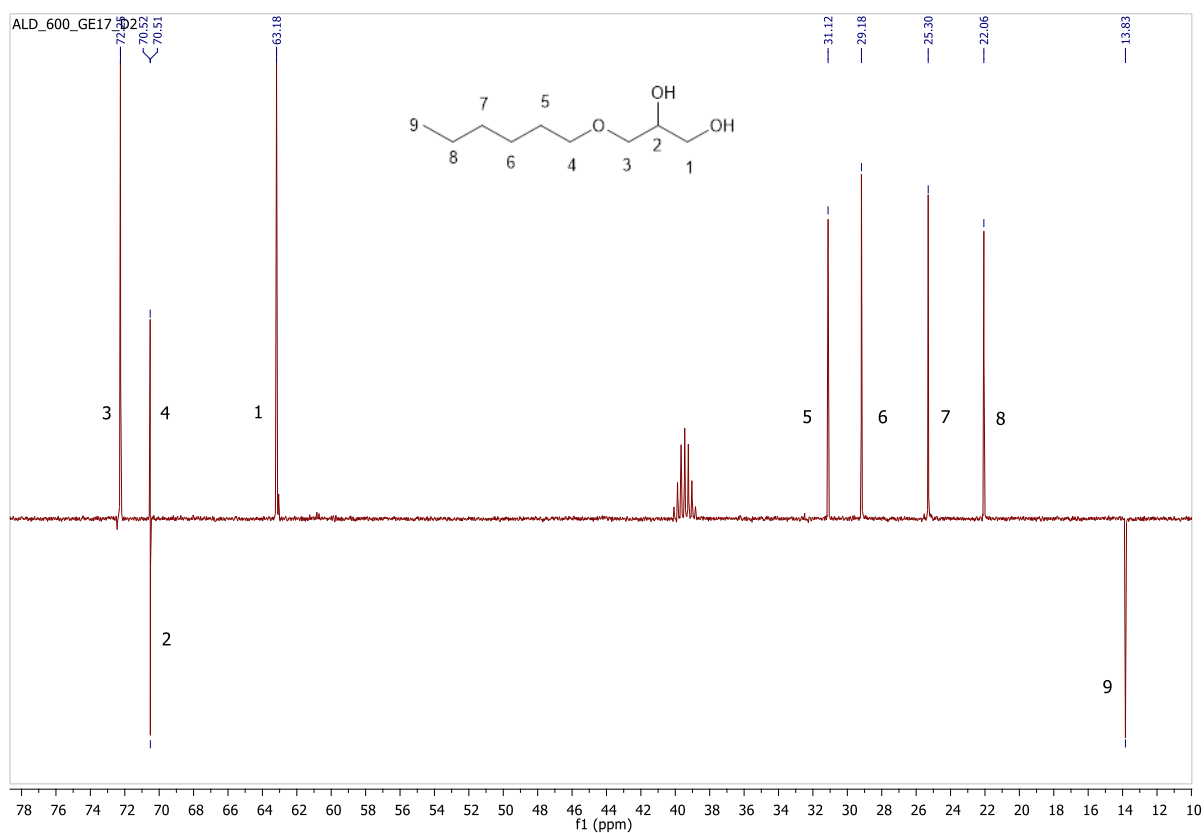
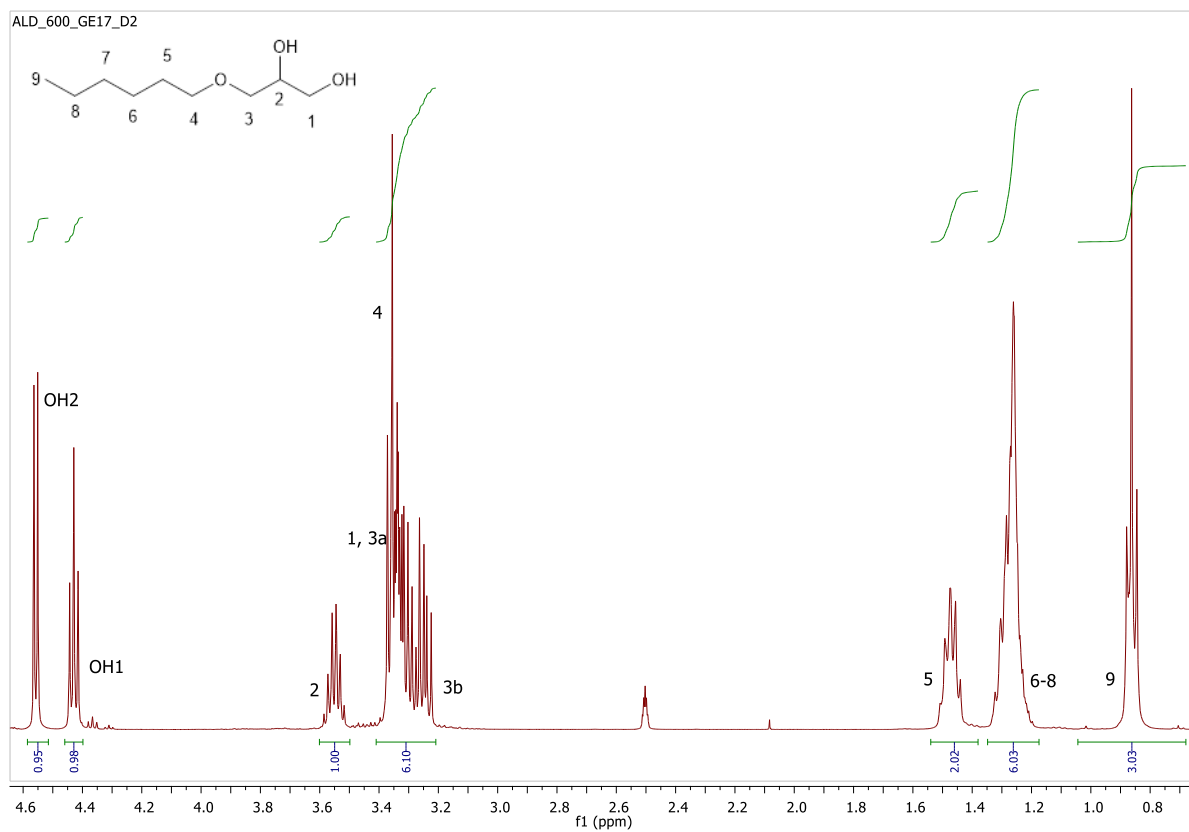


Figure S6. ^1H -RMN and ^{13}C -RMN (APT) of 3-hexyloxypropan-1,2-diol [6.0.0].

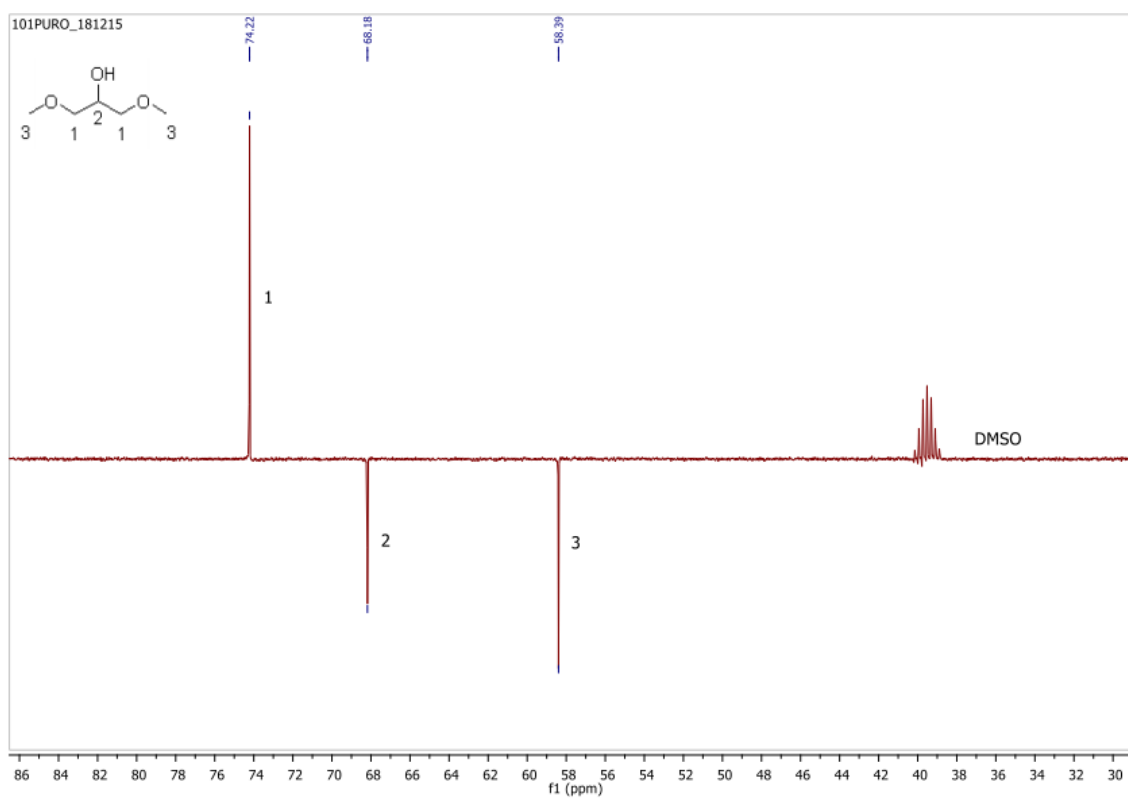
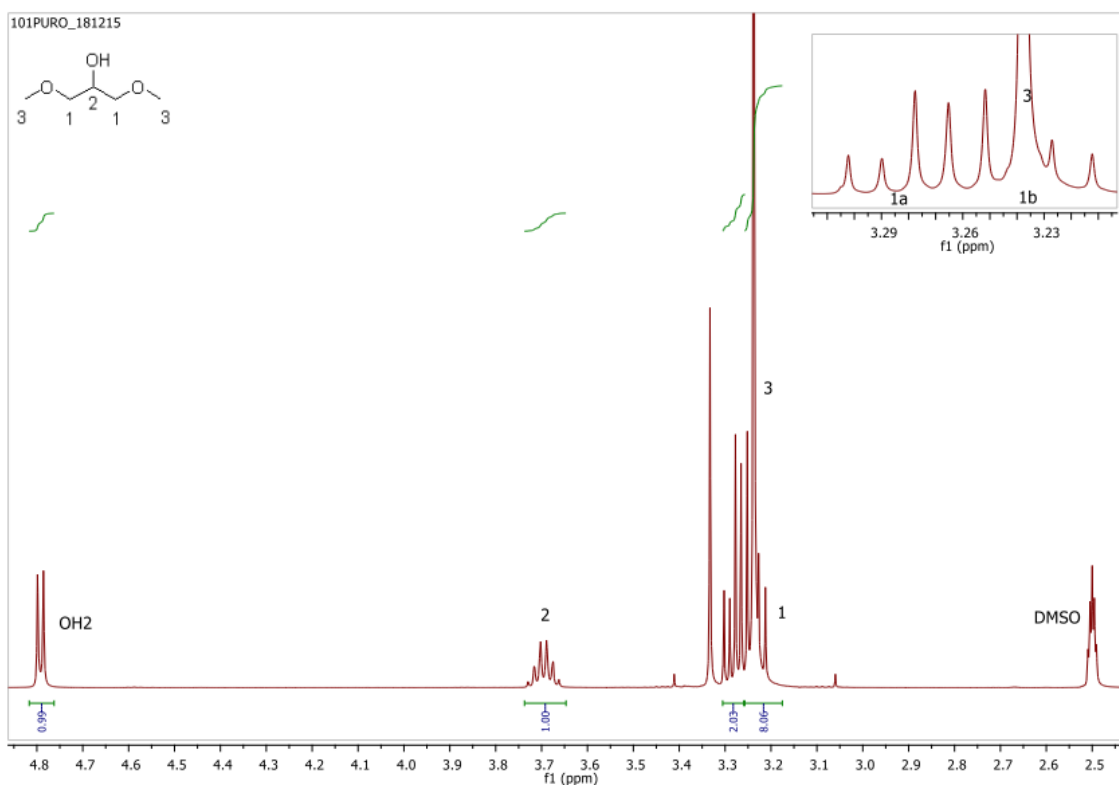


Figure S7. ^1H -RMN and ^{13}C -RMN (APT) of 1,3-Dimethoxypropan-2-ol [1.0.1].

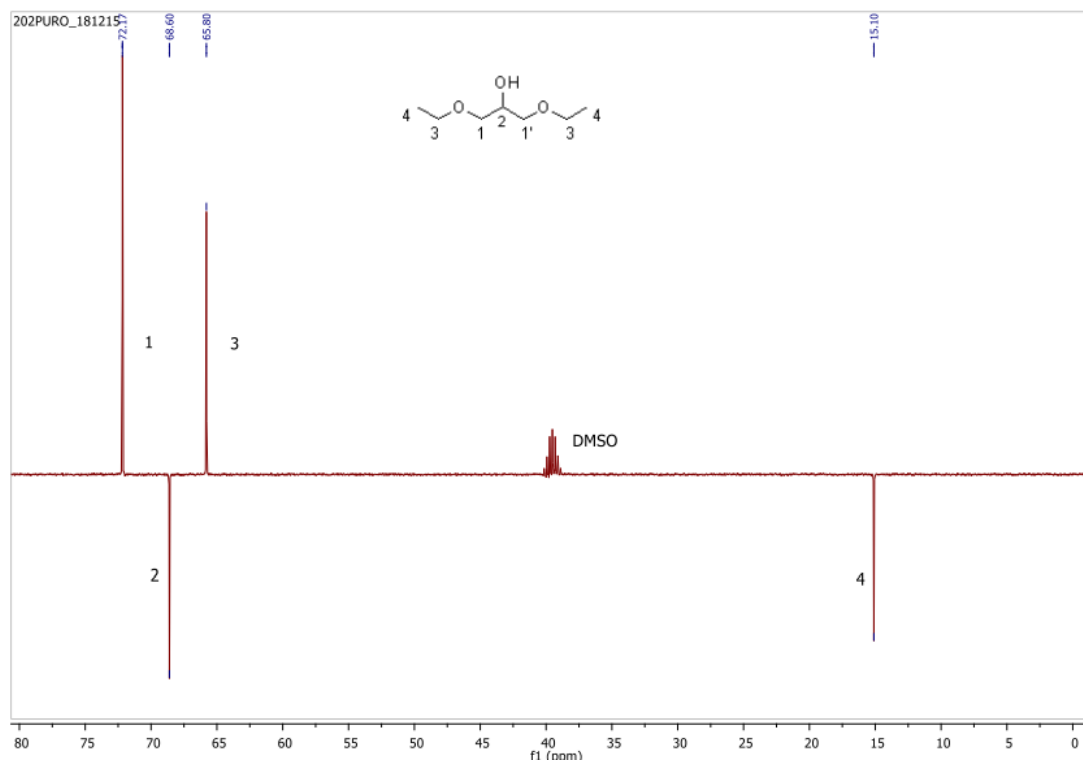
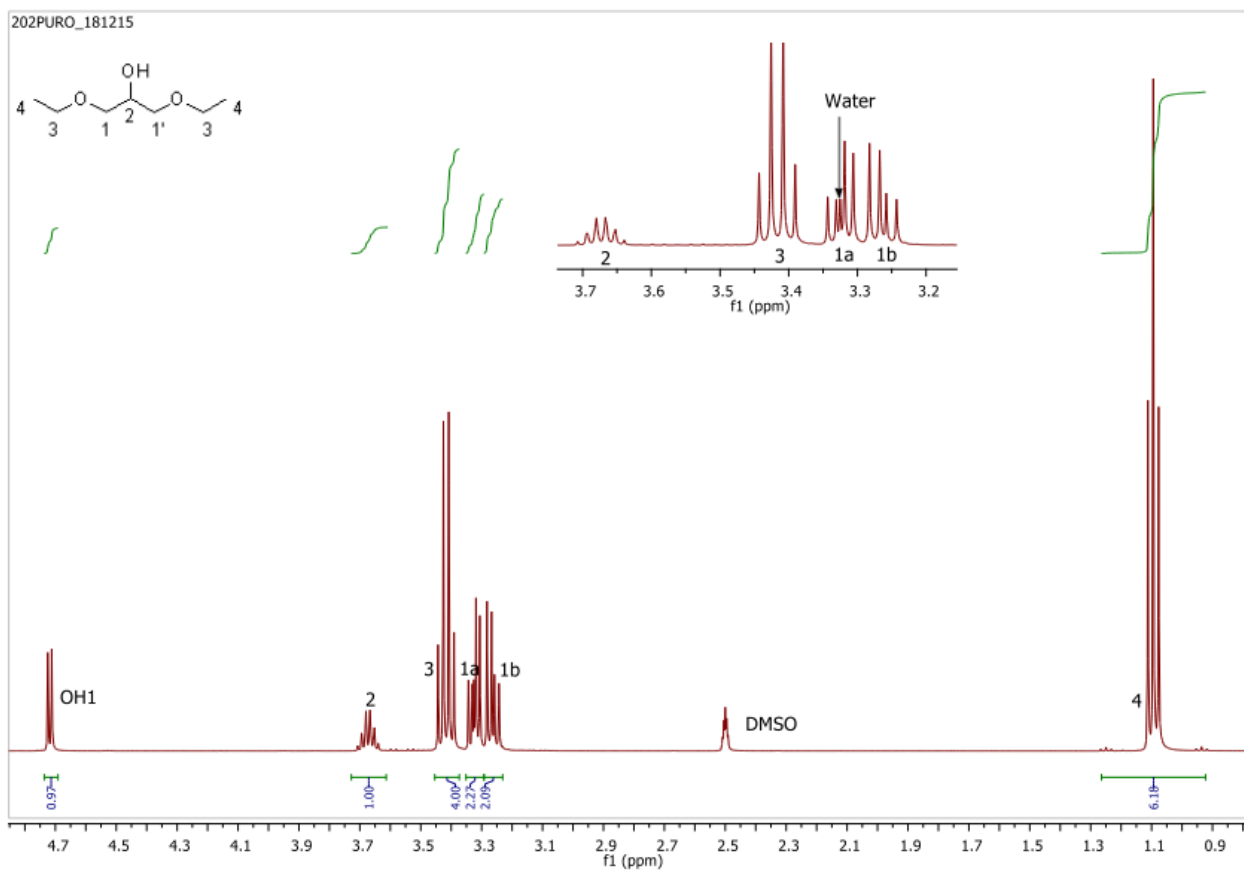


Figure S8. ^1H -RMN and ^{13}C -RMN (APT) of 1,3-Diethoxypropan-2-ol [2.0.2].

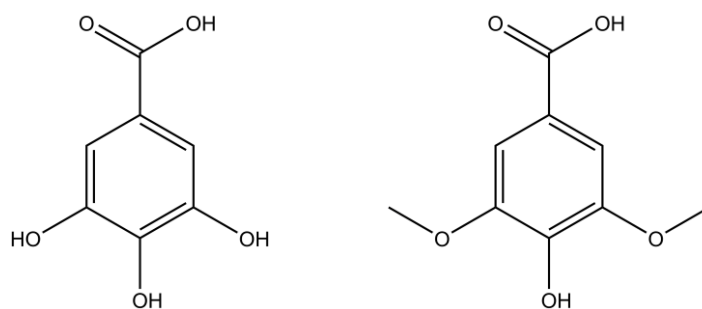


Figure S9. Chemical structure of gallic acid (left) and syringic acid (right).

S2 Solubility Data

Gallic Acid

Table S2. Gallic acid solubility in water and aqueous solutions of [0.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
0	0.0919	0.0045
1.02	0.0937	0.0009
2.19	0.0989	0.0016
3.06	0.0967	0.0009
5.03	0.1020	0.0088
10.12	0.1261	0.0031
20.04	0.1572	0.0052
30.12	0.2003	0.0106
40.04	0.2686	0.0108
59.96	0.4711	0.0065
79.40	0.7119	0.0416
99.63	1.3762	0.0260

Table S3. Gallic acid solubility in aqueous solutions of [1.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.00	0.0975	0.0002
3.01	0.1091	0.0005
5.04	0.1343	0.0055
9.8	0.1823	0.0026
20.7	0.3315	0.0173
29.56	0.5211	0.0282
49.15	0.8818	0.0106
59.65	1.1346	0.0328
71.99	1.4183	0.0293
78.98	1.5740	0.0234
89.19	1.8729	0.0259
98.81	1.9177	0.0200

Table S4. Gallic acid solubility in aqueous solutions of [2.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.02	0.0975	0.0023
1.94	0.1093	0.0033
3.05	0.1158	0.0013
4.88	0.1269	0.0006
9.86	0.1716	0.0053
19.56	0.2358	0.0175
29.65	0.4716	0.0251
39.18	0.6334	0.0341
58.85	1.0318	0.0456
78.50	1.2626	0.0603
99.38	1.6179	0.0373

Table S5. Gallic acid solubility in aqueous solutions of [3.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.04	0.0988	0.0022
1.98	0.1100	0.0057
3.04	0.1212	0.0032
4.95	0.1326	0.0120
10.22	0.2018	0.0044
20.18	0.3192	0.0063
30.10	0.5457	0.0157
39.62	0.7886	0.0150
59.82	1.0213	0.0290
78.72	1.0803	0.0269
99.39	1.2681	0.0516

Table S6. Gallic acid solubility in aqueous solutions of [4.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.04	0.1009	0.0019
2.03	0.1144	0.0025
3.02	0.1237	0.0050
5.02	0.1466	0.0019
9.98	0.2185	0.0046
19.98	0.3877	0.0113
29.80	0.5311	0.0230
39.60	0.7103	0.0347
49.48	0.8006	0.0127
60.04	0.8433	0.0057
70.28	0.8748	0.0052
79.88	0.8685	0.0088
89.93	0.9110	0.0019
99.11	1.0273	0.0521

Table S7. Gallic acid solubility in aqueous solutions of [5.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.02	0.1016	0.0003
2.09	0.1204	0.0052
3.08	0.1328	0.0009
5.03	0.1632	0.0015
9.92	0.2070	0.0033
19.94	0.2808	0.0129
29.99	0.3424	0.0236
39.60	0.4334	0.0072
50.67	0.5985	0.0033
59.37	0.6123	0.0065
79.48	0.6270	0.0345
99.70	0.8001	0.0098

Table S8. Gallic acid solubility in aqueous solutions of [6.0.0] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
38.24	0.3454	0.0055
44.92	0.3901	0.0146
49.26	0.4569	0.0187
59.53	0.5373	0.0288
64.89	0.4949	0.0183
69.00	0.5113	0.0259
73.88	0.4980	0.0017
79.98	0.4814	0.0243
83.67	0.5309	0.0019
99.79	0.6272	0.0068

Table S9. Gallic acid solubility in aqueous solutions of [1.0.1] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.00	0.1051	0.0006
3.01	0.1238	0.0014
5.02	0.1434	0.0023
10.19	0.2180	0.0020
20.36	0.4297	0.0192
29.88	0.6336	0.0022
39.99	0.9839	0.0393
50.17	1.1893	0.0281
59.89	1.4312	0.0177
69.39	1.5821	0.0088
79.96	1.8102	0.0016
99.92	1.8623	0.0902

Table S10. Gallic acid solubility in aqueous solutions of [2.0.2] at 303.2 K.

wt% Hydrotrope	Solubility /M	s /M
1.06	0.1039	0.0013
3.06	0.1265	0.0003
5.01	0.1502	0.0062
10.03	0.2289	0.0015
20.21	0.4602	0.0102
30.05	0.6837	0.0299
39.97	0.9669	0.0071
50.06	1.1384	0.0131
59.26	1.3351	0.0163
69.85	1.4111	0.0313
79.97	1.4256	0.0400
99.95	1.3826	0.0810

Syringic Acid

Table S11. *Syringic acid solubility in water and aqueous solutions of [0.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
0	0.0085	0.00002
1.04	0.0086	0.0003
3.03	0.0090	0.00001
2.02	0.0091	0.0001
5.11	0.0236	0.0006
10.05	0.0110	0.0002
19.90	0.0119	0.0007
29.74	0.0154	0.0003
39.77	0.0183	0.0002
49.70	0.0206	0.0002
59.91	0.0232	0.0002
69.43	0.0254	0.0005
79.10	0.0291	0.0000
89.40	0.0327	0.0002
99.63	0.0386	0.0026

Table S12. *Syringic acid solubility in aqueous solutions of [1.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.00	0.0089	0.0002
3.01	0.0112	0.0000
6.19	0.0147	0.0006
10.14	0.0187	0.0022
19.95	0.0345	0.0003
29.62	0.0552	0.0004
39.83	0.0842	0.0007
59.62	0.1824	0.0006
69.52	0.2534	0.0018
79.06	0.3343	0.0008
98.81	0.4367	0.0021

Table S13. *Syringic acid solubility in aqueous solutions of [2.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.02	0.0091	0.0006
3.05	0.0103	0.0004
5.46	0.0126	0.0001
10.21	0.0160	0.0008
19.78	0.0309	0.0002
29.81	0.0607	0.0019
39.68	0.1083	0.0028
59.64	0.2629	0.0036
69.44	0.3358	0.0009
80.33	0.4023	0.0038
99.38	0.3234	0.0064

Table S14. *Syringic acid solubility in aqueous solutions of [3.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.04	0.0091	0.0001
3.04	0.0110	0.0001
5.16	0.0125	0.0001
10.29	0.0216	0.0002
20.14	0.0552	0.0003
30.20	0.1214	0.0037
39.77	0.1952	0.0016
57.22	0.3222	0.0014
69.45	0.3843	0.0014
79.43	0.3911	0.0007
99.39	0.2428	0.0085

Table S15. *Syringic acid solubility in aqueous solutions of [4.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.04	0.0091	0.00003
3.02	0.0117	0.0004
5.02	0.0171	0.0001
10.03	0.0301	0.0003
20.19	0.0888	0.0004
30.02	0.1489	0.0008
40.48	0.2127	0.0080
59.64	0.3054	0.0046
68.33	0.3281	0.0050
78.87	0.3356	0.0022
99.11	0.1971	0.0010

Table S16. *Syringic acid solubility in aqueous solutions of [5.0.0] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.02	0.0093	0.0003
3.08	0.0134	0.0001
5.07	0.0201	0.0008
9.96	0.0373	0.0012
19.96	0.0727	0.0020
29.77	0.1088	0.0029
39.35	0.1449	0.0011
59.90	0.2199	0.0022
70.11	0.2435	0.0053
79.92	0.2548	0.0028
99.70	0.1554	0.0017

Table S17. *Syringic acid solubility in aqueous solutions of [1.0.1] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.00	0.0093	0.0002
3.01	0.0120	0.0004
5.02	0.0126	0.0002
10.09	0.0185	0.0006
20.36	0.0453	0.0014
29.88	0.0839	0.0029
39.99	0.1691	0.0033
49.72	0.2930	0.0093
59.89	0.4393	0.0070
69.84	0.5407	0.0043
79.96	0.6568	0.0175
99.92	0.4597	0.0228

Table S18. *Syringic acid solubility in aqueous solutions of [2.0.2] at 303.2 K.*

wt% Hydrotrope	Solubility /M	s /M
1.06	0.0094	0.0003
3.06	0.0120	0.0004
5.01	0.0145	0.0005
10.08	0.0236	0.0006
20.21	0.0702	0.0043
30.13	0.1585	0.0035
39.97	0.2999	0.0109
50.04	0.3744	0.0085
59.26	0.5044	0.0101
69.96	0.5293	0.0157
79.97	0.5299	0.0068
99.95	0.1863	0.0094

S3. Cooperative Hydrotropy Model

In order to use the cooperative hydrotropy model to fit the experimental data, it was necessary to convert the concentration of hydrotrope in the solute (free-solute basis) to its mole fraction in the ternary system ($x_{Hydrotrope}$), as well as the solubility of the solute to mole fraction in the ternary system (x_{Solute}). It was assumed that the density of the system is equal to that of water. Hence, Equations S1 and S2 were used:

$$x_{Hydrotrope} = \frac{\frac{(1000-S_3) \cdot w_2}{M_2}}{\frac{(1000-S_3) \cdot w_1}{M_1} + \frac{(1000-S_3) \cdot w_2}{M_2} + \frac{S_3}{M_3}} \quad (S1)$$

$$x_{Solute} = \frac{\frac{S_3}{M_3}}{\frac{(1000-S_3) \cdot w_1}{M_1} + \frac{(1000-S_3) \cdot w_2}{M_2} + \frac{S_3}{M_3}} \quad (S2)$$

where w_1 and w_2 are the mass fractions of water and hydrotrope in the solvent (free-solute basis), respectively, M_1 , M_2 and M_3 are the molar masses of water, hydrotrope and solute, respectively, and S_3 is the solubility of the solute in the hydrotropy system (mol/L).

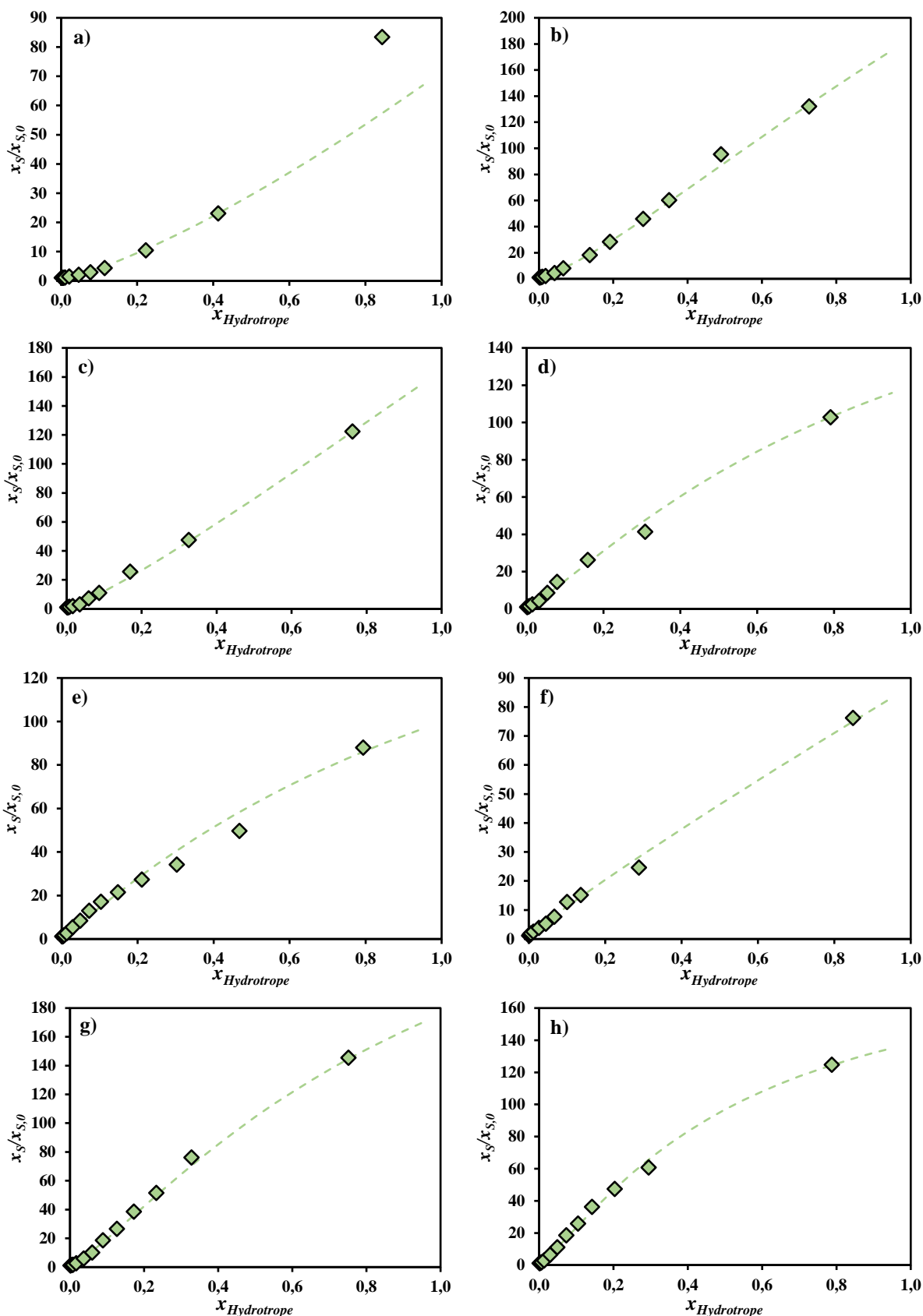


Figure S10. Experimental solubility data, \blacklozenge , for gallic acid in aqueous solutions of a) [0.0.0], b) [1.0.0], c) [2.0.0], d) [3.0.0], e) [4.0.0], f) [5.0.0], g) [1.0.1] and h) [2.0.2], fitted using the cooperative hydrotrophy model (---). The x-axis represents the mole fraction of the hydrotropic in the ternary system (as opposed to its mole fraction in the solvent free of solute).

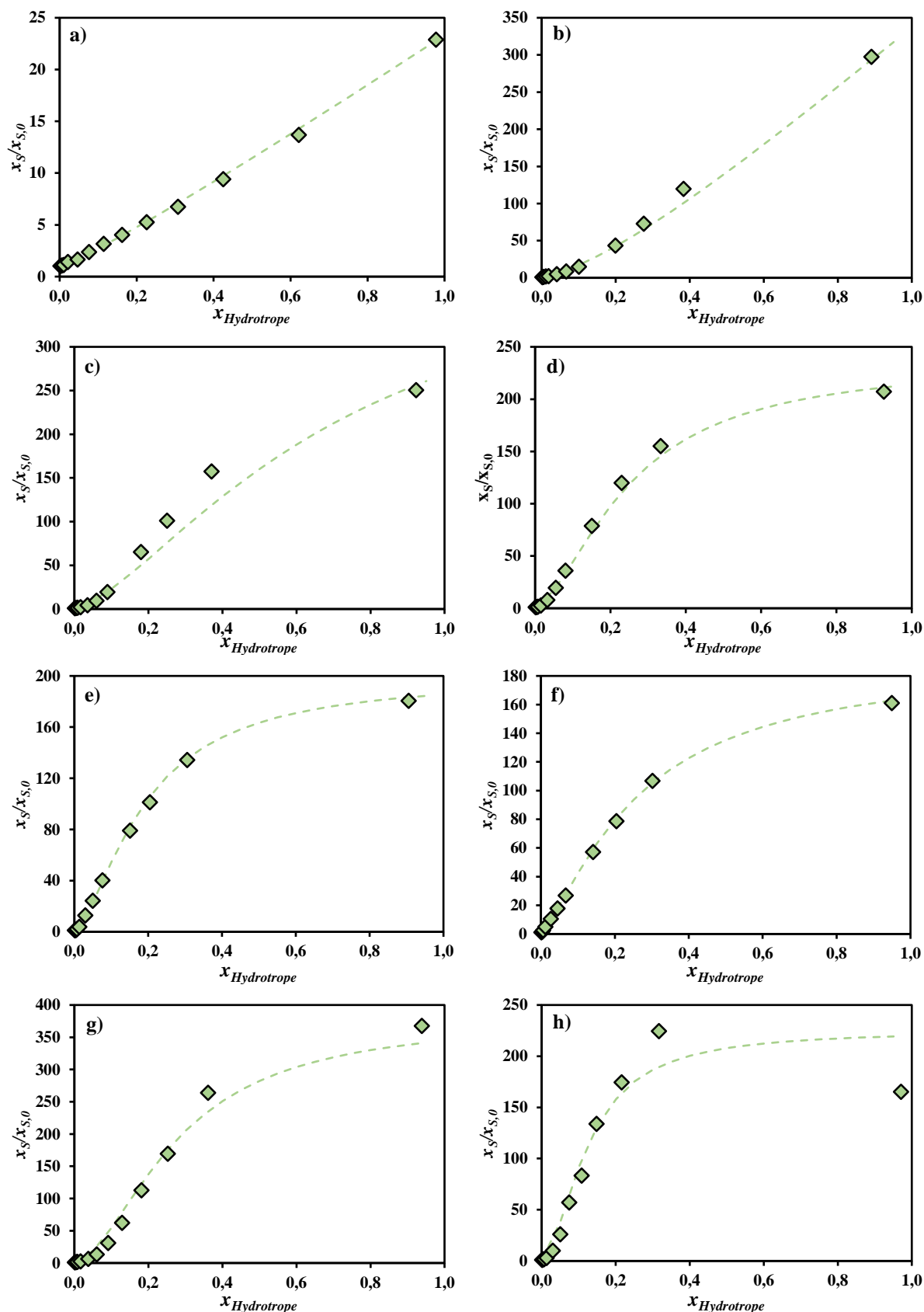


Figure S11. Experimental solubility data, \blacklozenge , for syringic acid in aqueous solutions of a) [0.0.0], b) [1.0.0], c) [2.0.0], d) [3.0.0], e) [4.0.0], f) [5.0.0], g) [1.0.1] and h) [2.0.2], fitted using the cooperative hydrotropy model (---). The x-axis represents the mole fraction of the hydrotropic component in the ternary system (as opposed to its mole fraction in the solvent free of solute).

Table S19. Parameters of the cooperative hydrotrophy model for the solubility of gallic and syringic acids in glycerol ether-based hydrotrope solutions.

	Hydrotrope	max	m	b
Gallic acid	[0.0.0]	10000 ^{a)}	1.317	-4.949
	[1.0.0]	675	1.313	-0.988
	[2.0.0]	1606	1.208	-2.178
	[3.0.0]	236	1.200	0.013
	[4.0.0]	228	1.084	-0.259
	[5.0.0]	10000 ^{a)}	0.932	-4.746
	[1.0.1]	347	1.252	0.014
	[2.0.2]	201	1.235	0.769
Syringic acid	[0.0.0]	562	1.126	-3.183
	[1.0.0]	2371	1.382	-1.801
	[2.0.0]	432	1.482	0.490
	[3.0.0]	236	1.628	2.260
	[4.0.0]	199	1.561	2.593
	[5.0.0]	192	1.330	1.782
	[1.0.1]	379	1.782	2.299
	[2.0.2]	225	1.789	3.729

a) unbounded optimization: increasing the value *ad infinitum* decreases the quadratic error sum.

S4. Solute Recovery

The feasibility of adding water to recover dissolved solute from the hydrotropic system was preliminarily studied in this work using the solubility curves fitted with the cooperative hydrotrophy model. The concept relies on calculating the mass fraction of solute that is recovered by the addition of a given volume of water. The algorithm used to calculate the recovery curves is as follow. The hydrotropic system, with total mole number n_t^0 , is selected (solute-hydrotrope pair and hydrotrope mole fraction).

1. Select fraction of water to be added (n_{H_2O}/n_t^0).
2. Arbitrate the fraction of solute that precipitates (n_p/n_t^0).
3. Calculate increase of the new system (n_t/n_t^0):

$$\frac{n_t}{n_t^0} = 1 + \frac{n_{H_2O}}{n_t^0} - \frac{n_p}{n_t^0}$$

4. Calculate hypothetical composition of the new system (x_1, x_2, x_3) from the composition of the original system (x_1^0, x_2^0, x_3^0):

$$x_1 = \frac{x_1^0 + n_{H_2O}/n_t^0}{n_t/n_t^0}$$

$$x_2 = \frac{x_2^0}{n_t/n_t^0}$$

$$x_3 = \frac{x_3^0 - n_p/n_t^0}{n_t/n_t^0}$$

5. Calculate saturation mole fraction of solute (x_3') for the hypothetical mole fraction of hydrotrope obtained in step 3 (Equation 3 of the main text with the parameters of Table SX).
6. If $x_3 = x_3'$, stop iteration. If $x_3 > x_3'$, return to step 1 and arbitrate higher n_p . If $x_3 < x_3'$, return to step 1 and arbitrate lower n_p .

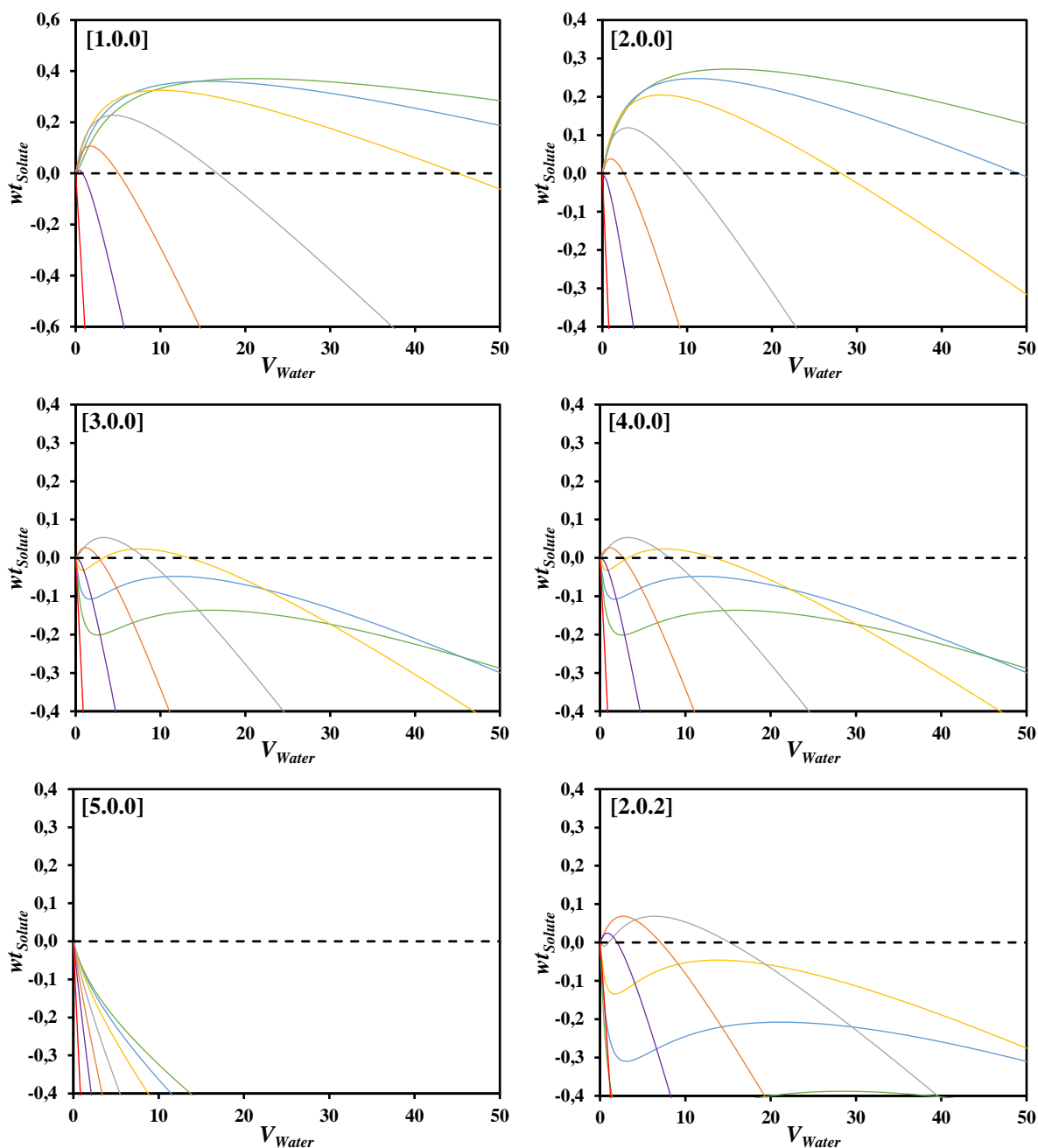


Figure S12. Estimated fraction of gallic acid (wt_{Solute}) recovered from hydrotrope solution by the addition of water (V_{Water} is the volumetric reason between added water and initial system), with an initial hydrotrope mole fraction of 0.01 —, 0.05 —, 0.1 —, 0.2 —, 0.4 —, 0.6 — and 0.8 —. A negative value indicates that no precipitation happens, with the system being able to dissolve further solute.

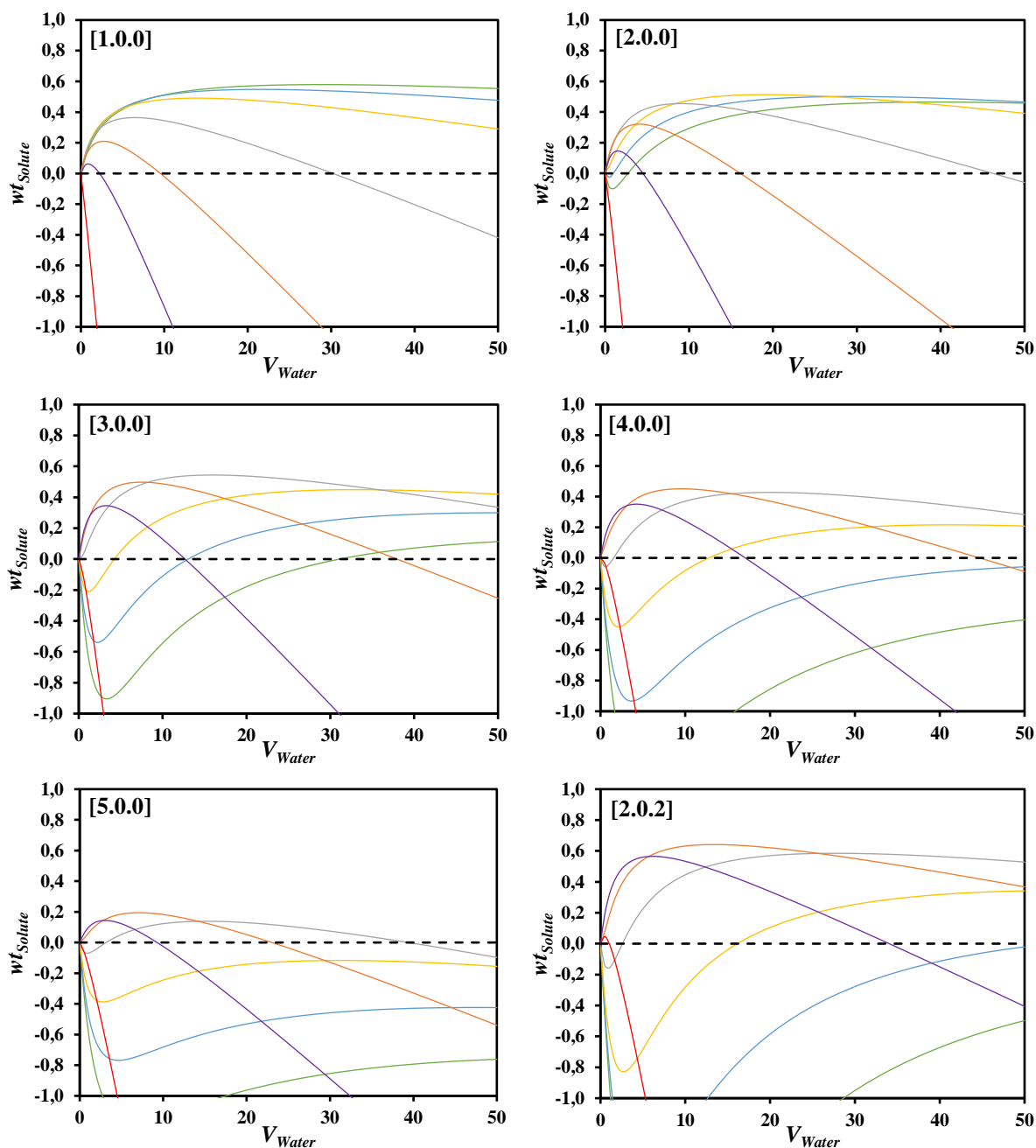


Figure S13. Estimated fraction of syringic acid (wf_{Solute}) recovered from hydrotrope solution by the addition of water (V_{Water} is the volumetric reason between added water and initial system), with an initial hydrotrope mole fraction of 0.01 —, 0.05 —, 0.1 —, 0.2 —, 0.4 —, 0.6 — and 0.8 —. A negative value indicates that no precipitation happens, with the system being able to dissolve further solute.