

Supporting Information for:

Dual High-Resolution α -Glucosidase and Radical Scavenging Profiling Combined with HPLC-HRMS-SPE-NMR for Identification of Minor and Major Constituents Directly from the Crude Extract of *Pueraria lobata*.

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Table S1: Retention time, UV, MS and ¹H NMR data obtained in the HPLC-HRMS-SPE-NMR mode after analysis of peaks 1-24 of crude methanol extract of *Pueraria lobata*.

Peak	Name	RT (min)	$\lambda_{\max}$ (nm)	m/z (MF, ppm) ^a	¹ H NMR δ (m, nH, J (in Hz)) ^b
1	3'-Hydroxypuerarin	7.4	246, 292	433.1129 [M+H] ⁺ (C ₂₁ H ₂₁ O ₁₀ ⁺ , ΔM 2.7)	8.16 (s, 1H, H-2), 8.06 (d, 1H, 8.1 Hz, H-5), 7.02 (d, 1H, 2.0 Hz, H-2'), 6.99 (1H, d, 8.8 Hz, H-5'), 6.86 (1H, dd, 2.0, 8.8 Hz, H-6'), 6.82 (1H, d, 8.0 Hz, H-6), 5.10 (d, 1H, 9.7 Hz, H-1''), 4.00 (m, 1H, H-2''), 3.89 (dd, 1H, 2.1, 12.0 Hz, H-6''B), 3.75 (dd, 1H, 5.1, 12.0 Hz, H-6''A), 3.55-3.45 (m, 3H, H-3'' to H-5'').
2	Daidzein 8-C-[β -D-xylopyranosyl-(1 $\rightarrow$ 6)]- β -D-glucopyranoside	10.6	192, 249	549.1682 [M+H] ⁺ (C ₂₆ H ₂₉ O ₁₃ ⁺ , ΔM 2.4) 417.1230 [M+H-xy] ⁺ (C ₂₁ H ₂₁ O ₉ ⁺ , ΔM -3.8)	8.21 (s, 1H, H-2), 8.09 (d, 1H, 8.9 Hz, H-5), 7.40 (d, 1H, 8.7 Hz, H-2'/6'), 7.01 (d, 1H, 8.9 Hz, H-6), 6.87 (d, 1H, 8.7 Hz, H-3'/5'), 5.10 (d, 1H, 9.7 Hz, H-1''), 4.28 (d, 1H, 7.5 Hz, H-1'''), 4.17 (dd, 1H, 1.0, 11.5 Hz, H-6''B), 4.10 (brs, 1H, H-2''), 3.87 (d, 1H, 5.4, 11.5 Hz, H-5''B), 3.83 (m, 1H, H-6''A), 3.66-3.52 (m, 3H, H-3'' to H-5''), 3.48 (ddd, 1H, 5.4, 8.6, 10.0 Hz, H-4'''), 3.29 (m, 1H, H-3'''), 3.21 (dd, 1H, 7.5, 9.8 Hz, H-2'''), 3.17 (d, 1H, 10.1, 11.5 Hz, H-5'''A)
3	Puerarin	11.3	249, 312	417.1180 [M+H] ⁺ (C ₂₁ H ₂₁ O ₉ ⁺ , ΔM 1.1)	8.19 (s, 1H, H-2), 8.06 (d, 1H, 8.8 Hz, H-5), 7.39-7.37 (m, 2H, H-2'/6'), 6.99 (d, 1H, 8.8 Hz, H-6), 6.82-6.79 (m, 2H, H-3'/5'), 5.10 (d, 1H, 9.8 Hz, H-1''), 4.11 (brs, 1H, H-2''), 3.89 (dd, 1H, 2.1, 12.0 Hz, H-6''B), 3.76 (dd, 1H, 5.1, 12.0 Hz, H-6''A), 3.55-3.45 (m, 3H, H-3'' to H-5''),
4	6''-O- α -D-Apiofuranosylpuerarin	11.8	200, 245, 303	549.1604 [M+H] ⁺ (C ₂₆ H ₂₉ O ₁₃ ⁺ , ΔM 0.4) 417.1164 [M+H-api] ⁺ (C ₂₁ H ₂₁ O ₉ ⁺ , ΔM 1.9)	8.19 (s, 1H, H-2), 8.07 (d, 1H, 8.8 Hz, H-5), 7.39 (d, 2H, 8.5 Hz, H-2'/H-6'), 6.99 (d, 1H, 8.8 Hz, H-6), 6.85 (d, 2H, 8.5 Hz, H-3'/H-5'), 5.10 (d, 1H, 10.0 Hz, H-1''), 4.97 (d, 1H, 2.4 Hz, H-1'''), 4.01 (d, 1H, 11.1 Hz, H-4''B), 3.97 (d, 1H, 9.8 Hz, H-6''B), 3.90 (d, 1H, 2.4 Hz, H-2'''), 3.76 (d, 2H, 9.8 Hz, H-6''A/H-4''A), 3.60-3.50 (m, 5H, H-2'' to H-5''/H-5''').
5	3'-Methoxypuerarin	12.6	223, 251	447.1281 [M+H] ⁺ (C ₂₂ H ₂₃ O ₁₀ ⁺ , ΔM 0.9)	8.23 (s, 1H, H-2), 8.08 (d, 1H, 8.8 Hz, H-5), 7.18 (d, 1H, 2.0 Hz, H-2'), 7.00 (d, 1H, 8.8 Hz, H-6), 6.98 (dd, 1H, 2.0, 8.2 Hz, H-6'), 6.86 (d, 1H, 8.2 Hz, H-5'), 5.11 (d, 1H, 9.8 Hz, H-1''), 4.12 (brs, 1H, H-2''), 3.90 (s, 3H, -OCH ₃), 3.89 (d, 1H, 2.2, 12.0 Hz, H-6''B), 3.76 (dd, 1H, 5.2, 12.0 Hz, H-6''A), 3.55-3.46 (m, 3H, H-3'' to H-5'').

6	3'-Methoxydaidzein 8-C-[α -D-apiofuranosyl-(1 $\rightarrow$ 6)]- β -D-glucopyranoside	13.1	197, 251	579.1770 [M+H] ⁺ (C ₂₇ H ₃₁ O ₁₄ , Δ M -2.8) 447.1230 [M+H-api] ⁺ (C ₂₂ H ₂₃ O ₁₀ ⁺ , Δ M -0.7)	8.23 (s, 1 H, H-2) 8.08 (d, 8.8 Hz, 1 H, H-5) 7.18 (d, 1 H, 1.8 Hz, H-2'), 7.10 (d, 1 H, 8.8 Hz, H-6), 6.99 (dd, 1 H, 1.8, 8.1 Hz, H-6'), 6.86 (d, 8.1 Hz, 1H, H-5'), 5.10 (d, 1H, 9.7 Hz, H-1''), 4.97 (d, 1H, 2.5 Hz, H-1'''), 4.01 (d, 11.2 Hz, H-6''B), 3.97 (d, 9.8 Hz, H-4''B), 3.90 (s, 3H, -OCH ₃), 3.88 (m, 1H, H-2'''), 3.77 (d, 1H, 9.8 Hz, H-4''A), 3.74 (m, 1H, H-6''A), 3.61 (m, 1H, H-5''), 3.59 (m, H-4''), 3.58 (m, 2H, H-5'''), 3.53(m, 1H, H-3'').
7	Daidzin	17.7	193, 248	417.1174 [M+H] ⁺ (C ₂₁ H ₂₁ O ₉ ⁺ , Δ M 3.7) 255.0652 [M+H-gluc] ⁺ (C ₁₅ H ₁₁ O ₄ ⁺ , Δ M 0.8)	8.20 (s, 1H, H-2), 8.15 (d, 1H, 8.8 Hz, H-5), 7.41-7.38 (m, 2H, H-2'/H-6'), 7.25 (d, 1H, 2.2 Hz, H-8), 7.22 (dd, 1H, 2.2, 8.8 Hz, H-6), 6.88-6.85 (m, 2H, H-3'/H-5'), 5.11 (m, 1H, H-1''), 3.93 (dd, 1H, 2.2, 12.2 Hz, H-6''B), 3.72 (dd, 1H, 5.8, 12.2 Hz, H-6''A), 3.58 - 3.46 (m, 4H, H-2'' to H-5'').
8	3'-Methoxydaidzin	19.8	199, 218	447.1339 [M+H] ⁺ (C ₂₂ H ₂₃ O ₁₀ ⁺ , 4.7) 285.0774 [M+H-gluc] ⁺ (C ₁₆ H ₁₃ O ₅ ⁺ , Δ M 3.8)	8.24 (s, 1H, H-2), 8.16 (d, 1H, 8.8 Hz, H-5), 7.26 (d, 1 H, 2.2 Hz, H-8) 7.23 (dd, 1 H, 8.8, 2.2 Hz, H-6), 7.18 (d, 1 H, 1.8 Hz, H-2'), 6.98 (dd, 1 H, 1.8, 8.1 Hz, H-6'), 6.86 (d, 1 H, 8.1 Hz, H-5'), 5.11(d, 1H, 7.5 Hz, H-1''), 3.93 (dd, 1 H, 2.0, 12.2 Hz, H-6''B), 3.72 (dd, 1 H, 5.8, 12.2 Hz, H-6''A), 3.53-3.50 (m, 4 H, H-2'' to 5'')
9	Genistein 8-C- α -D-apiosyl-(1 $\rightarrow$ 6)- β -D-glucoside	20.2	194, 260	565.1542 [M+H] ⁺ (C ₂₆ H ₂₉ O ₁₄ ⁺ , Δ M 0.4) 433.1127 [M+H-api] ⁺ (C ₂₁ H ₂₁ O ₁₀ ⁺ , Δ M 3.0)	8.13 (s, 1H, H-2), 7.39 (d, 2H, 8.0 Hz, H-2'/6'), 6.86 (d, 2H, 8.0 Hz, H-3'/5'), 6.29 (s, 1H, H-6), 5.00 (d, 1H, 10.0 Hz, H-1''), 4.96 (d, 1H, 2.4 Hz, H-1'''), 4.00 (dd, 1H, 1.2, 11.2 Hz, H-4''B), 3.96 (d, 1H, 9.6 Hz, H-6''B), 3.89 (d, 1H, 2.4 Hz, H-2'''), 3.7 (d, 1H, 9.6 Hz, H-6''A), 3.72 (dd, 1H, 5.8, 11.2 Hz, H-4''A), 3.58-3.46 (m, 5H, H-3'' to 5''/H-5'').
10	Genistein 8-C- β -D-glucoside	20.8	194, 260	433.1182 [M+H] ⁺ (C ₂₁ H ₂₁ O ₁₀ ⁺ , Δ M 4.4)	8.13 (s, 1H, H-2), 7.38(d, 2H, 8.0 Hz, H-2'/6'), 6.86 (d, 2H, 8.0 Hz, H-3'/5'), 6.29 (s, 1H, H-6), 4.94 (d, 1H, 9.8 Hz, H-1''), 4.12 (brs, 1H, H-2''), 3.89 (d, 1H, 2.5, 12.2 Hz, H-6''B), 3.73 (dd, 1H, 5.4, 12.2 Hz, H-6''A), 3.50-3.42 (m, 3H, H-3'' to H-5'').
11	Daidzein 4'- β -D-glucopyranoside	23.3	194, 216	417.1153 [M+H] ⁺ (C ₂₁ H ₂₁ O ₉ ⁺ , Δ M 0.1)	8.18 (s, 1H, H-2), 8.07 (d, 1H, 8.8 Hz, H-5), 7.49 (d, 2H, 8.2 Hz, H-2'/H-6'), 7.17 (d, 2H, 8.2 Hz, H-3'/H-5'), 6.95 (dd, 1H, 2.2, 8.8 Hz, H-6), 6.87 (d, 1H, 2.2 Hz, H-8), 4.95 (d, 1H, 7.5 Hz, H-1''), 3.91 (m, 1H, H-6''B), 3.71 (dd, 1H, 5.3, 11.7 Hz, H-6''A), 3.52-3.41

					(m, 4H, H-2" to 5")
12	Genistin	25.1	198, 218	433.1109 [M+H] ⁺ (C ₂₁ H ₂₁ O ₁₀ ⁺ , ΔM 2.8) 271.0596 [M+H-glc] ⁺ (C ₁₅ H ₁₁ O ₅ ⁺ , ΔM 2.8) 865.2162 [2M+H] ⁺ (C ₄₂ H ₄₁ O ₂₀ ⁺ , ΔM -3.4)	8.15 (s, 1H, H-2), 7.38 (d, 2H, 8.2 Hz, H-2'/H-6'), 6.85 (d, 2H, 8.2 Hz, H-3'/H-5'), 6.71 (d, 1H, 2.2 Hz, H-6), 6.53 (d, 1H, 2.2 Hz, H-8), 5.05 (d, 1H, 7.5 Hz, H-1"), 3.91 (dd, 1H, 2.3, 12.2 Hz, H-6"B), 3.72 (dd, 1H, 5.7, 12.2 Hz, H-6"A), 3.54-3.48 (m, 4H, H-2" to 5")
13	6"-O-malonyldaidzin	25.7	194, 248	503.1182 [M+H] ⁺ (C ₂₄ H ₂₃ O ₁₂ ⁺ , ΔM 0.1) 255.0648 [M+H-mal-glc] ⁺ (C ₁₅ H ₁₁ O ₄ ⁺ , ΔM -3.7)	8.22 (brs, 1H, H-2), 8.07 (d, 1H, 8.8 Hz, H-5), 7.39 (d, 2H, 8.8 Hz, H-2'/H-6'), 7.26 (d, 1H, 2.2 Hz, H-8), 7.20 (dd, 1H, 2.2, 8.8 Hz, H-6), 6.85 (d, 2H, 8.8 Hz, H-3'/5'), 5.11-5.09 (m, 1H, H-1"), 4.61 (dd, 1H, 2.0, 12.0 Hz, H-6"B), 4.26 (dd, 1H, 7.2, 12.0 Hz, H-6"A), 3.80 (m, 1H, H-5"), 3.55-3.51 (m, 2H, H-2"/H-3"), 3.40 (m, 1H, H-4")
14	6"-O-Malonyl-3'-methoxydaidzin	26.2	200, 218	533.1363 [M+H] ⁺ (C ₂₅ H ₂₅ O ₁₂ ⁺ , ΔM 1.3) 285.0817 [M+H-mal-glc] ⁺ (C ₁₆ H ₁₃ O ₅ , ΔM 2.6)	8.26 (s, 1H, H-2), 8.17 (d, 1H, 8.8 Hz, H-5), 7.27 (d, 1H, 2.2 Hz, H-8), 7.20 (dd, 1H, 2.2, 8.8 Hz, H-6), 7.18 (d, 1H, 2.4 Hz, H-2'), 6.98 (dd, 1H, 2.4, 8.0 Hz, H-6'), 6.86 (d, 1H, 8.0 Hz, H-5'), 5.10 (d, 1H, 7.5 Hz, H-1"), 4.56 (dd, 1H, 2.0, 12.4 Hz, H-6"B), 4.27 (dd, 1H, 6.7, 12.4 Hz, H-6"A), 3.88 (s, 3H, OCH ₃), 3.80 (m, 1H, H-5"), 3.54 (m, 1H, H-2"), 3.52 (m, 1H, H-3"), 3.41 (m, 1H, H-4")
15	Puerol B 2-O-β-D-glucopyranoside.	26.8	198, 200	475.1592 [M+H] ⁺ (C ₂₄ H ₂₇ O ₁₀ ⁺ , ΔM -0.6) 313.1068 [M+H-glc] ⁺ (C ₁₈ H ₁₇ O ₅ ⁺ , ΔM 1.3)	7.44 (d, 1H, 8.7 Hz, H-6'), 6.97 (d, 2H, 2.2 Hz, H-3'), 6.90 (d, 2H, 8.5 Hz, H-2"/H-6"), 6.73 (dd, 1H, 2.2, 8.7 Hz, H-5'), 6.63 (d, 2H, 8.5 Hz, H-3"/H-5"), 6.17 (d, 1H, 1.3 Hz, H-2), 6.15 (ddd, 1H, 1.3, 3.5, 6.5 Hz, H-4), 5.06 (d, 1H, 7.5 Hz, H-1"), 3.96 (dd, 1H, 2.4, 12.1 Hz, H-6"B), 3.72 (dd, 1H, 6.5, 12.1 Hz, H-6"A), 3.88 (s, 3H, OCH ₃), 3.57-3.37 (m, 4H, H-2" to H-5"), 3.22-3.17 (m, 1H, H-4aB), 2.79 (dd, 1H, 6.5, 14.7 Hz, H-4aA)
16	6"-O-Malonylgenistin	27.9	194, 260	519.1125 [M+H] ⁺	8.14 (s, 1H, H-2) 7.39 (d, 2H, 8.6 Hz, H-2'/H-6'), 6.85 (d, 2H, 8.6 Hz, H-3'/H-5') 6.71 (d,

				(C ₂₄ H ₂₃ O ₁₃ ⁺ , ΔM 1.6)	1H, 2.0 Hz, H-6'), 6.52 (d, 1H, 2.0 Hz, H-8'), 5.03 (d, 7.2 Hz, 1H, H-1''), 4.27 (dd, 1H, 7.2, 11.7 Hz, H-6''A), 3.80-3.40 (m, 4H, H-2'' to H-5'')
17	Ononin	28.2	198, 250	431.1320 [M+H] ⁺ (C ₂₂ H ₂₃ O ₉ ⁺ , ΔM 2.6) 269.0809 [M+H-glc] ⁺ (C ₁₆ H ₁₃ O ₄ ⁺ , ΔM 1.7)	8.23 (s, 1H, H-2), 8.16 (d, 1H, 8.8 Hz, H-5), 7.52-7.47 (m, 2H, H-2'/H-6'), 7.26 (d, 1H, 2.2 Hz, H-8), 7.23 (dd, 1H, 2.2, 8.8 Hz, H-6), 7.52-7.47 (m, 2H, H-3'/H-5'), 5.12 (m, 1H, H-1''), 3.93 (dd, 1H, 2.2, 12.1 Hz, H-6''B), 3.83 (s, 3H, OCH ₃), 3.72 (dd, 1H, 5.8, 12.1 Hz, H-6''A), 3.58-3.47 (m, 3H, H-2'' to H-4''), 3.36 (m, 1H, H-5'')
18	Daidzein	29.5	219, 249	255.0656 [M+H] ⁺ (C ₁₅ H ₁₁ O ₄ ⁺ , ΔM 3.2)	8.13 (s, 1H, H-2), 8.06 (d, 1H, 8.8 Hz, H-5), 7.38-7.35 (m, 2H, H-2'/H-6'), 6.94 (dd, 1H, 2.2, 8.8 Hz, H-6), 6.88-6.85 (m, 3H, H-8/H-3'/H-5').
19	6''-O-malonylononin	29.8	220, 250	517.1344 [M+H] ⁺ (C ₂₅ H ₂₅ O ₁₂ ⁺ , ΔM -0.8) 285.0760 [M+H-mal-glc] ⁺ (C ₁₆ H ₁₃ O ₅ ⁺ , ΔM -0.4)	8.23 (s, 1H, H-2) 8.16 (d, 8.8 Hz, 1H, H-5), 7.51-7.48 (m, 2H, H-2'/H-6'), 7.26 (d, 2.2 Hz, 1H, H-8) 7.23 (dd, 2.2, 8.8 Hz, 1H, H-6), 7.01-6.98 (m, 2H, H-2'/H-5'), 5.11 (d, 7.2 Hz, 1H, H-1''), 4.61 (1H, dd, 1.8, 11.7 Hz, H-6B''), 4.26 (1H, dd, 7.1, 11.7 Hz, H-6A''), 3.81-3.78 (1H, m, H-5''), 3.55-3.39 (3H, m, H-2'' to H-4'').
20	Sissotrin	30.2	197, 218, 255	447.1276 [M+H] ⁺ (C ₂₂ H ₂₃ O ₁₀ ⁺ , ΔM -0.7) 285.0751 [M+H-glc] ⁺ (C ₁₆ H ₁₃ O ₅ ⁺ , ΔM -1.8)	8.17 (brs, 1H, H-2), 7.50 (d, 2H, 8.8 Hz, H-2'/H-6'), 7.00 (d, 2H, 8.8 Hz, H-3'/H-5'), 6.72 (d, 1H, 2.2 Hz, H-6), 6.53 (d, 1H, 2.2 Hz, H-8), 3.91(s, 3H, OCH ₃), 5.06 (m, 1H, H-1''), 3.40-3.31 (m, 4H, H-2'' to 5'')
21	Biochanin A 7-O-β-D-glucoside-6''-O-malonate	31.0	220, 260	533.5169 [M+H] ⁺ (C ₂₅ H ₂₅ O ₁₃ ⁺ , ΔM 1.4) 285.3560 [M+H-mal-glc] ⁺ (C ₁₆ H ₁₃ O ₅ ⁺ , ΔM -2.1)	8.18 (s, 1H, H-2), 7.50 (d, 8.6 Hz, 1H, H-2'/H-6'), 6.99 (d, 8.6 Hz, 1H, H-3'/H-5'), 6.73 (d, 2.2 Hz, 1H, H-6), 6.52 (d, 2.2 Hz, 1H, H-8), 5.03 (m, 1H, H-1''), 4.53 (1H, dd, 1.9, 11.9 Hz, H-6B''), 4.26 (1H, dd, 7.1, 11.9 Hz, H-6A''), 3.80-3.40 (4H, m, H-2'' to H-5'')
22	Genistein	32.1	198, 217,	271.0602 [M+H] ⁺	8.06 (s, 1H, H-2), 7.37 (d, 2H, 8.8 Hz, H-2'/H-6'), 6.85 (d, 2H, 8.8 Hz, H-3'/H-5'), 6.35

			260	(C ₁₅ H ₁₁ O ₅ ⁺ , ΔM 1.7)	(d, 1H, 2.2 Hz, H-6), 6.23 (d, 1H, 2.2 Hz, H-8)
23	3'-De- <i>O</i> -methyl- puerariafuran	32.9	212, 315	271.0965 [M+H] ⁺ (C ₁₅ H ₁₁ O ₅ ⁺ , ΔM -0.2) 270.0870 [M] ⁺ (C ₁₅ H ₁₀ O ₅ ⁺ , ΔM -1.0) 254.0659 [M+H-OH] ⁺ (C ₁₅ H ₁₀ O ₄ ⁺ , ΔM 1.9) 253.0488 [M+H-H ₂ O] ⁺ (C ₁₅ H ₉ O ₄ ⁺ , ΔM 2.7)	10.07 (s, 1H, 3-CHO), 7.89 (d, 1H, 8.5 Hz, H-4), 7.42 (d, 1H, 8.2 Hz, H-6'), 6.94 (d, 1H, 2.2 Hz, H-7), 6.84 (dd, 1H, 8.5, 2.2 Hz, H-5), 6.48-6.90 (m, 2H, H-3'/5')
24	Formononetin	33.9	221	269.3536 [M+H] ⁺ (C ₁₆ H ₁₃ O ₄ ⁺ , ΔM 2.3)	8.05 (s, 1H, H-2), 8.04 (d, 1H, 8.8 Hz, H-5), 7.49 (d, 2H, 8.8 Hz, H-2'/H-6'), 6.99 (d, 2H, 8.8 Hz, H-3'/H-5'), 6.94 (dd, 1H, 2.0, 8.8 Hz, H-6), 6.88 (d, 2.0 Hz, H-8), 3.82 (s, 3H, OCH ₃).

^aMS spectra acquired in positive ion mode; ^b 600 MHz spectra in methanol-*d*₄, at 300 K.

Figure S1. ^1H NMR spectrum of **6** acquired in the HPLC-HRMS-SPE-NMR mode (600 MHz, methanol- d_4 , 300 K)

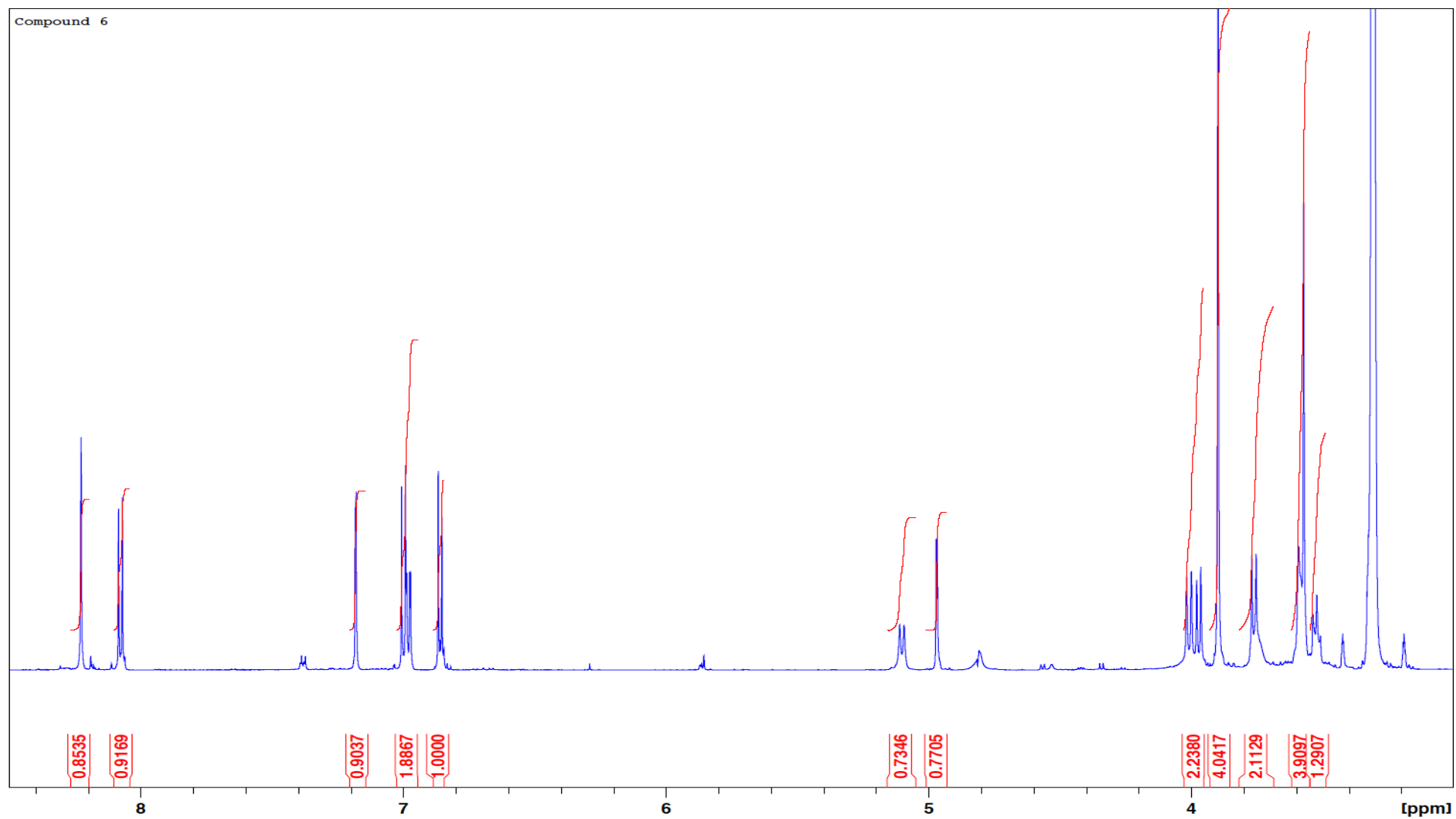


Figure S2. ^1H NMR spectrum of **14** acquired in the HPLC-HRMS-SPE-NMR mode (600 MHz, methanol- d_4 , 300 K)

