Supplementary Information

to

Conformational equilibria in the selected A-type trimeric procyanidins

by

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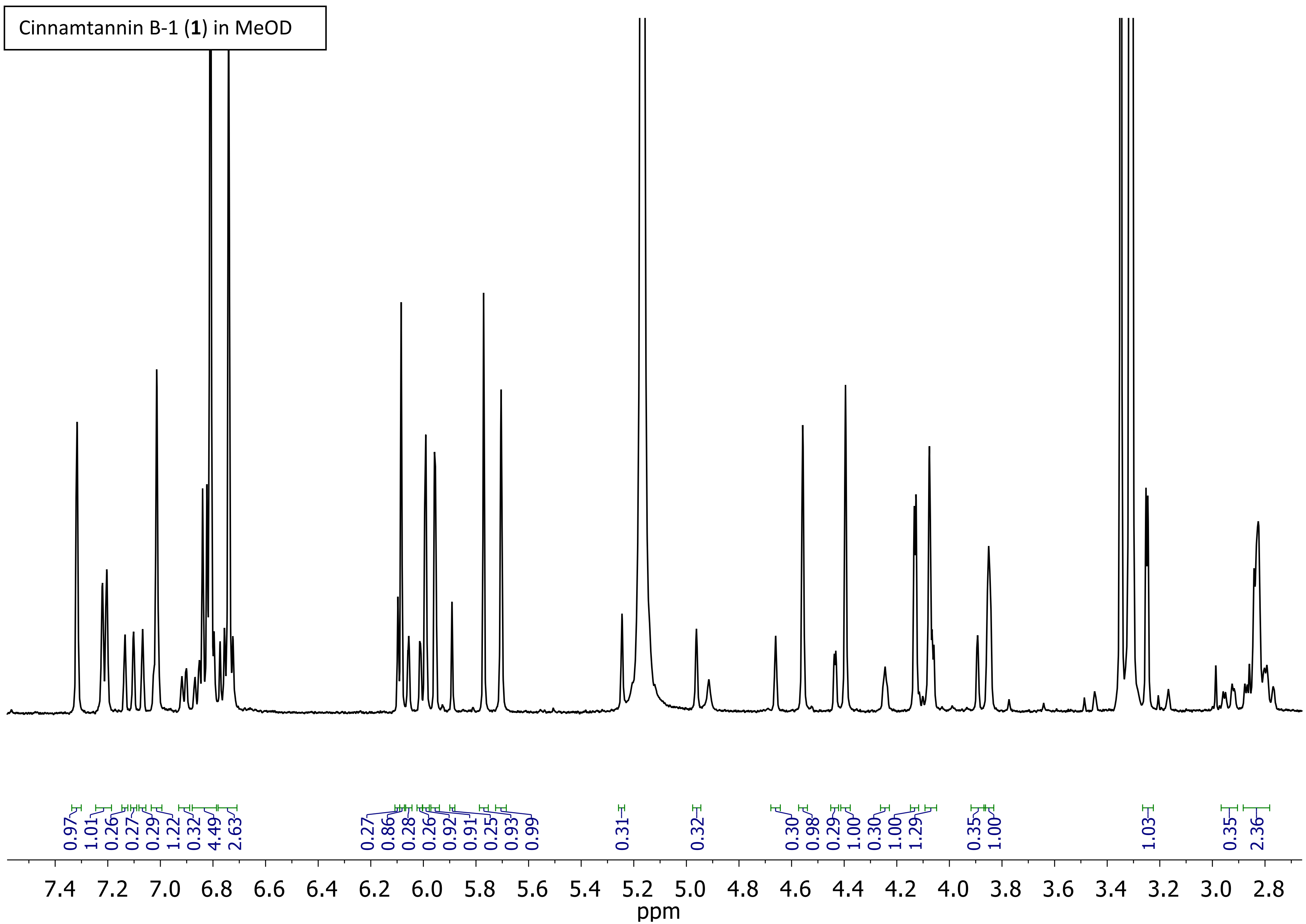

Cinnamtannin B-1 (**1**) in MeOD
0.97
1.01
0.26
0.27
0.29
1.22
0.32
4.49
2.63
0.27
0.86
0.28
0.26
0.92
0.91
0.25
0.93
0.99
0.31
0.32
0.30
0.98
0.29
1.00
0.30
1.00
1.29
0.35
1.00
1.03
0.35
2.36
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
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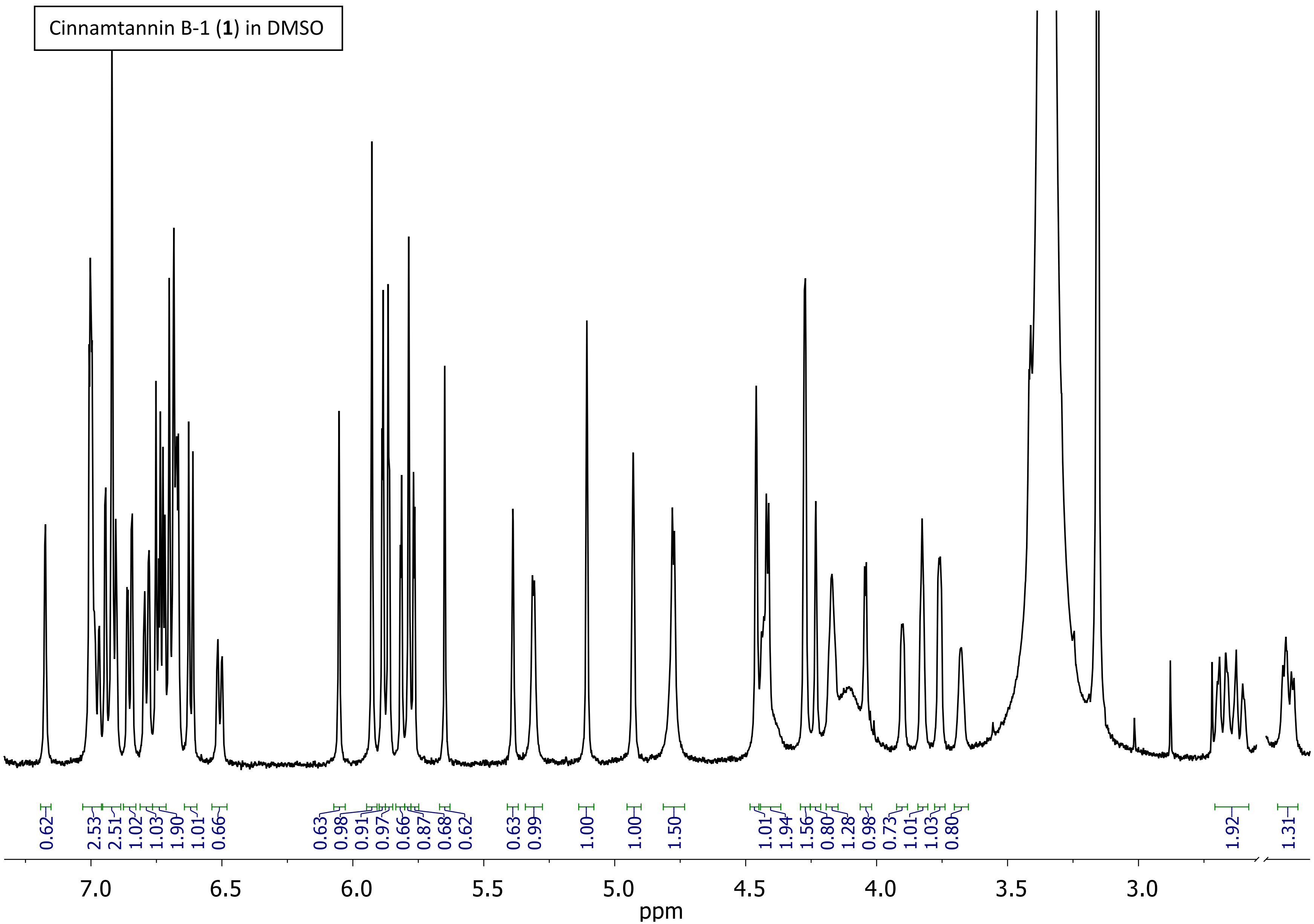
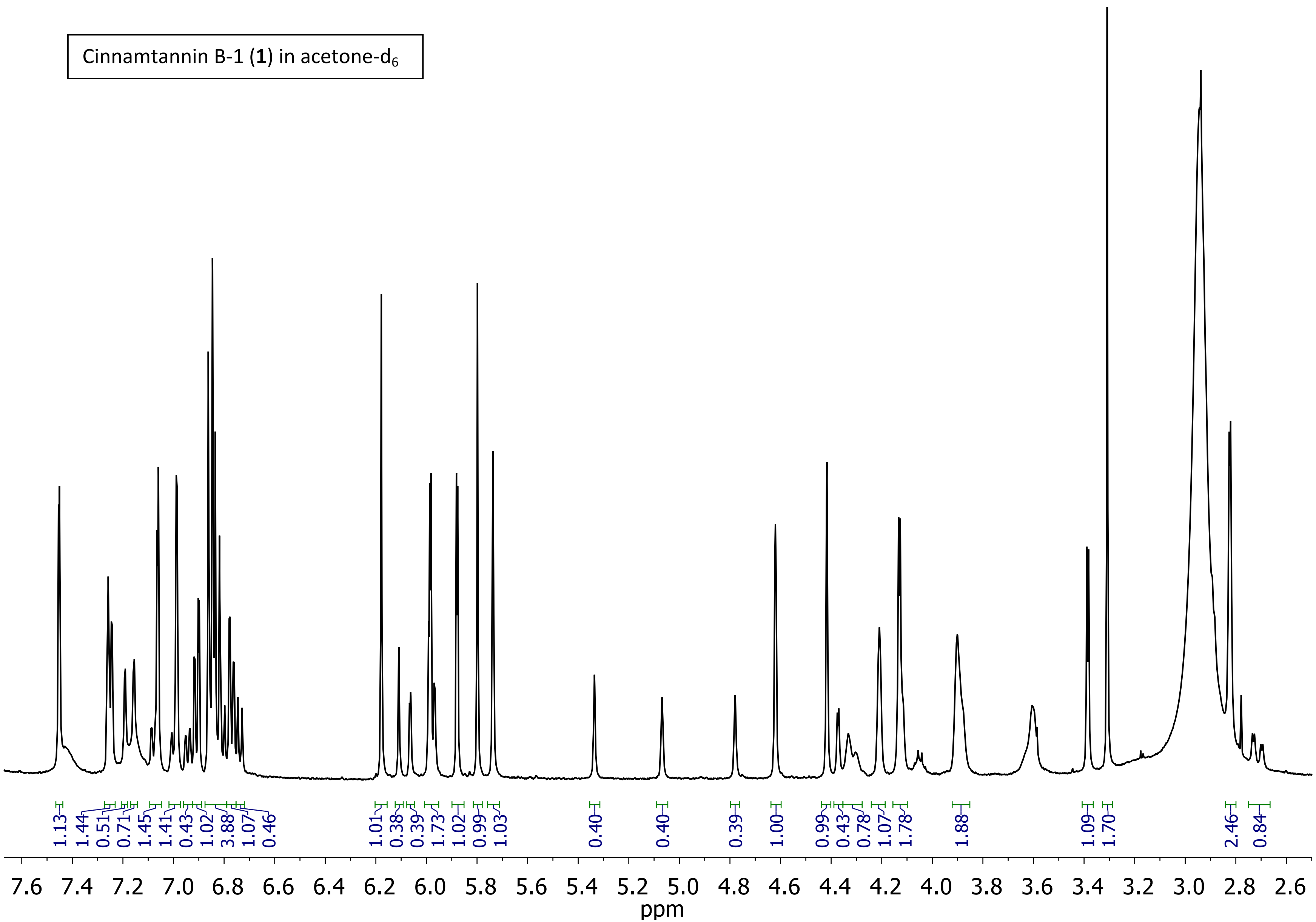
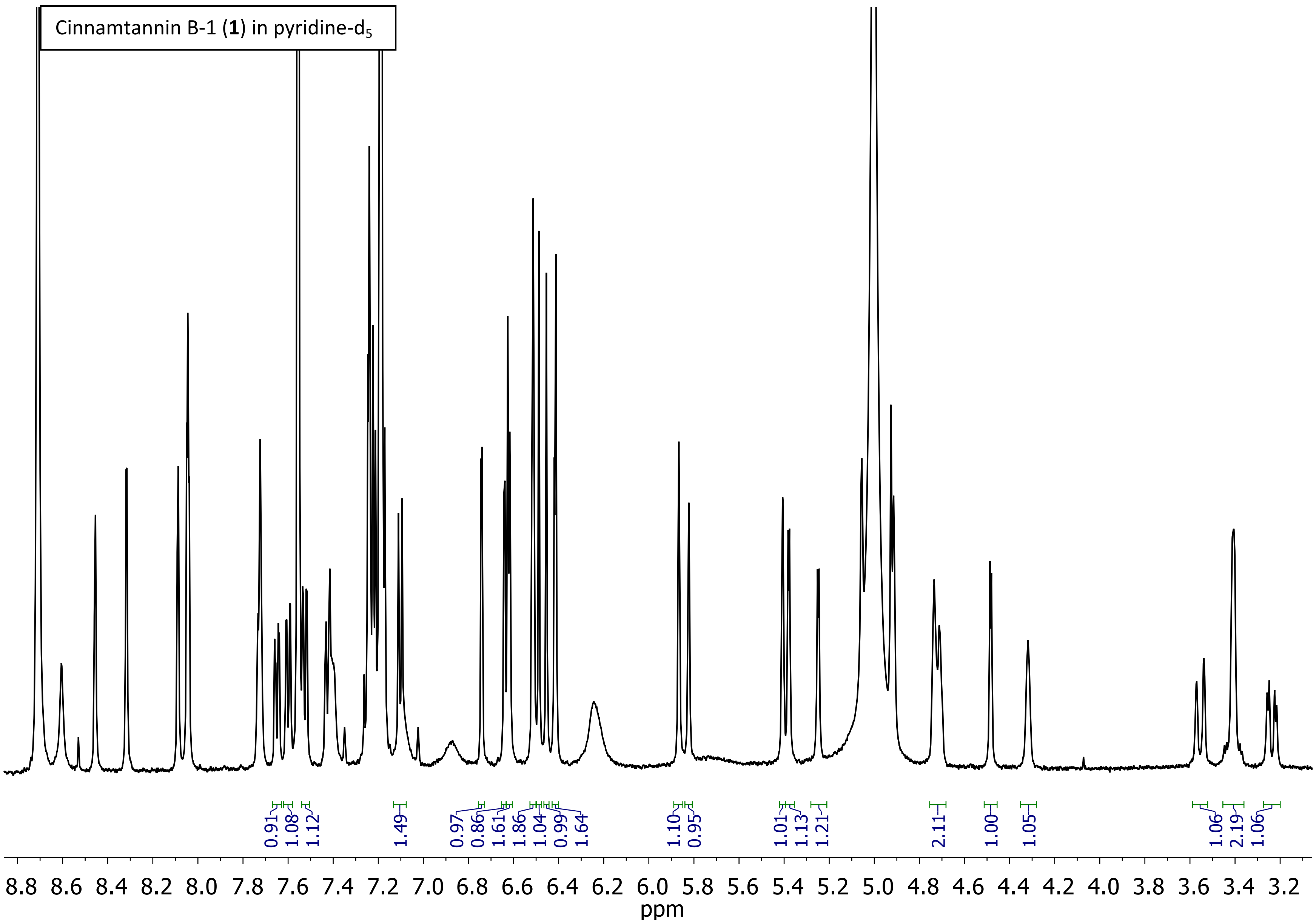
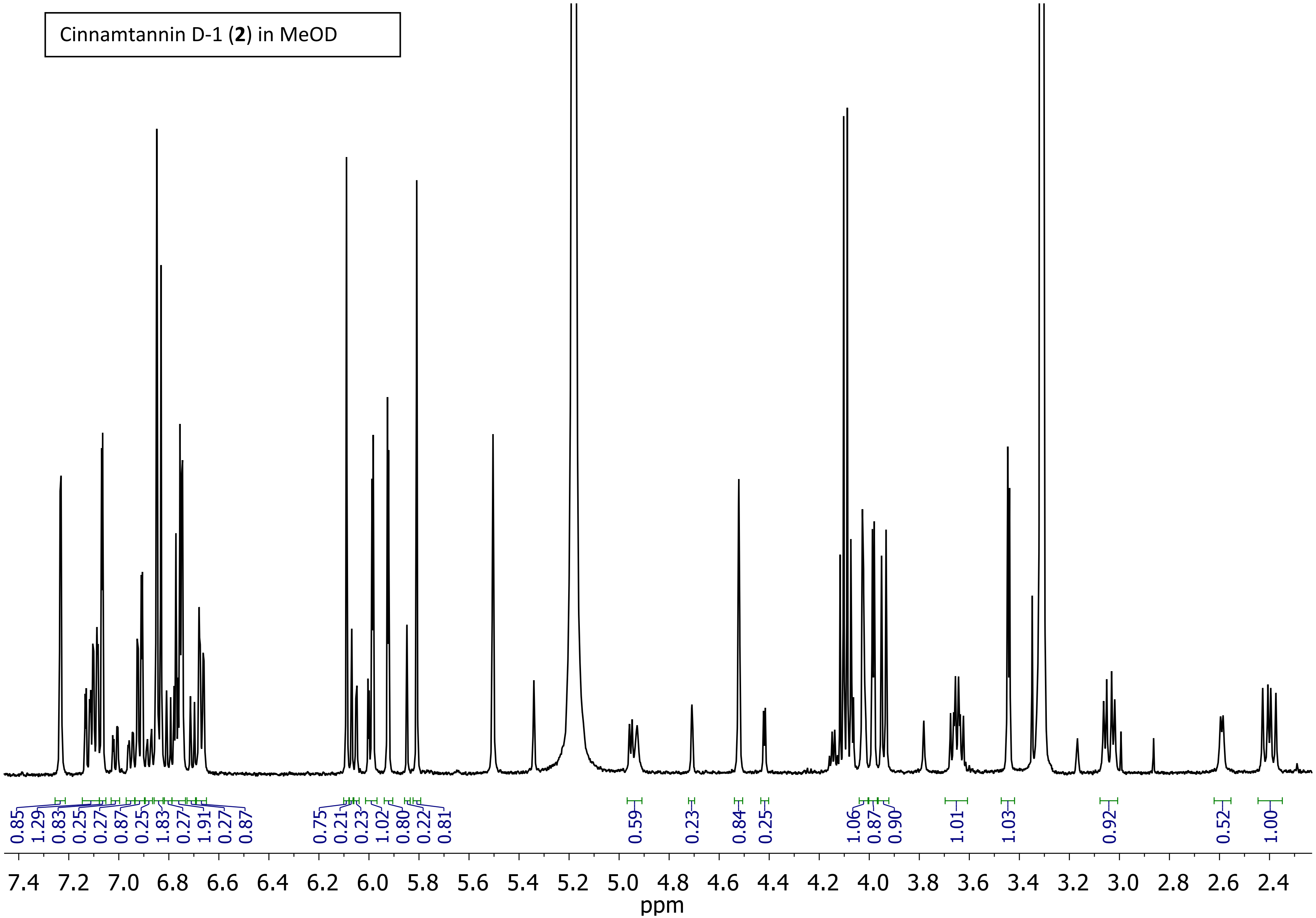
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
ppm

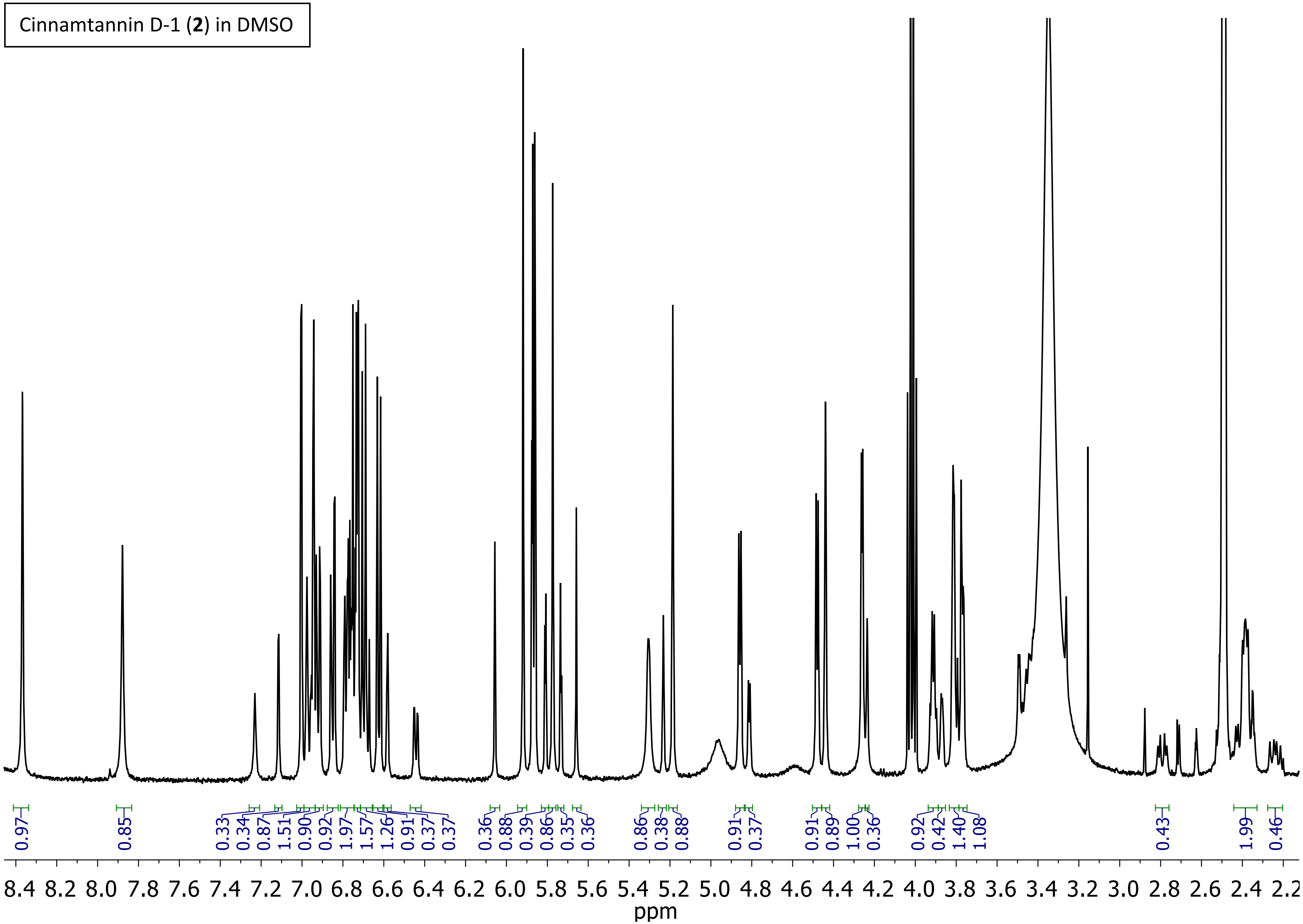

Cinnamtannin B-1 (1) in DMSO
0.62
2.53
2.51
1.02
1.03
1.90
1.01
0.66
0.63
0.98
0.91
0.97
0.66
0.87
0.68
0.62
0.63
0.99
1.00
1.00
1.50
1.01
1.94
1.56
0.80
1.28
0.98
0.73
1.01
1.03
0.80
1.92
1.31
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

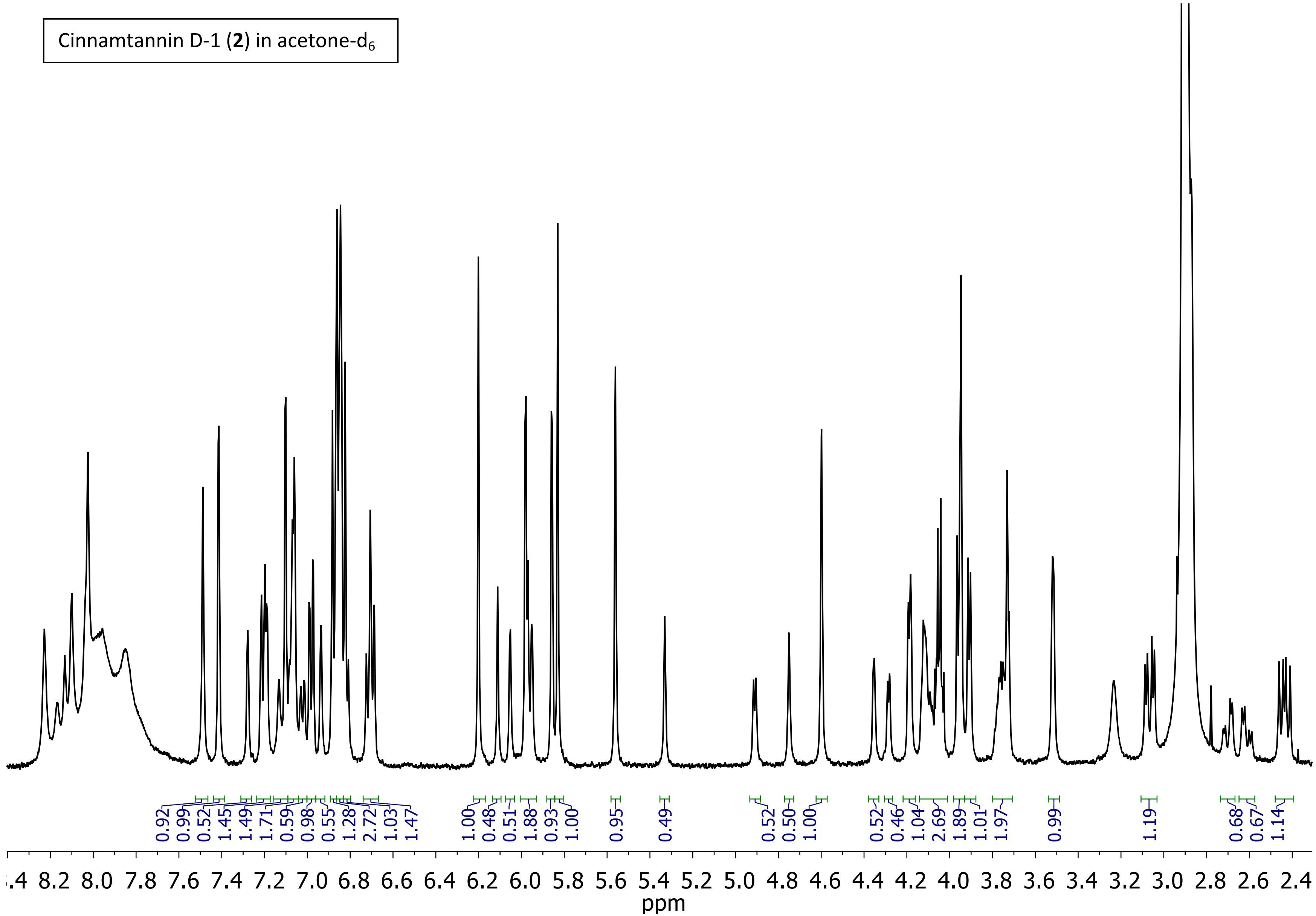

Cinnamtannin B-1 (1) in acetone-d6
1.13
1.44
0.51
0.71
1.45
1.41
0.43
1.02
3.88
1.07
0.46
1.01
0.38
0.39
1.73
1.02
0.99
1.03
0.40
0.40
0.39
1.00
0.99
0.43
0.78
1.07
1.78
1.88
1.09
1.70
2.46
0.84
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
ppm

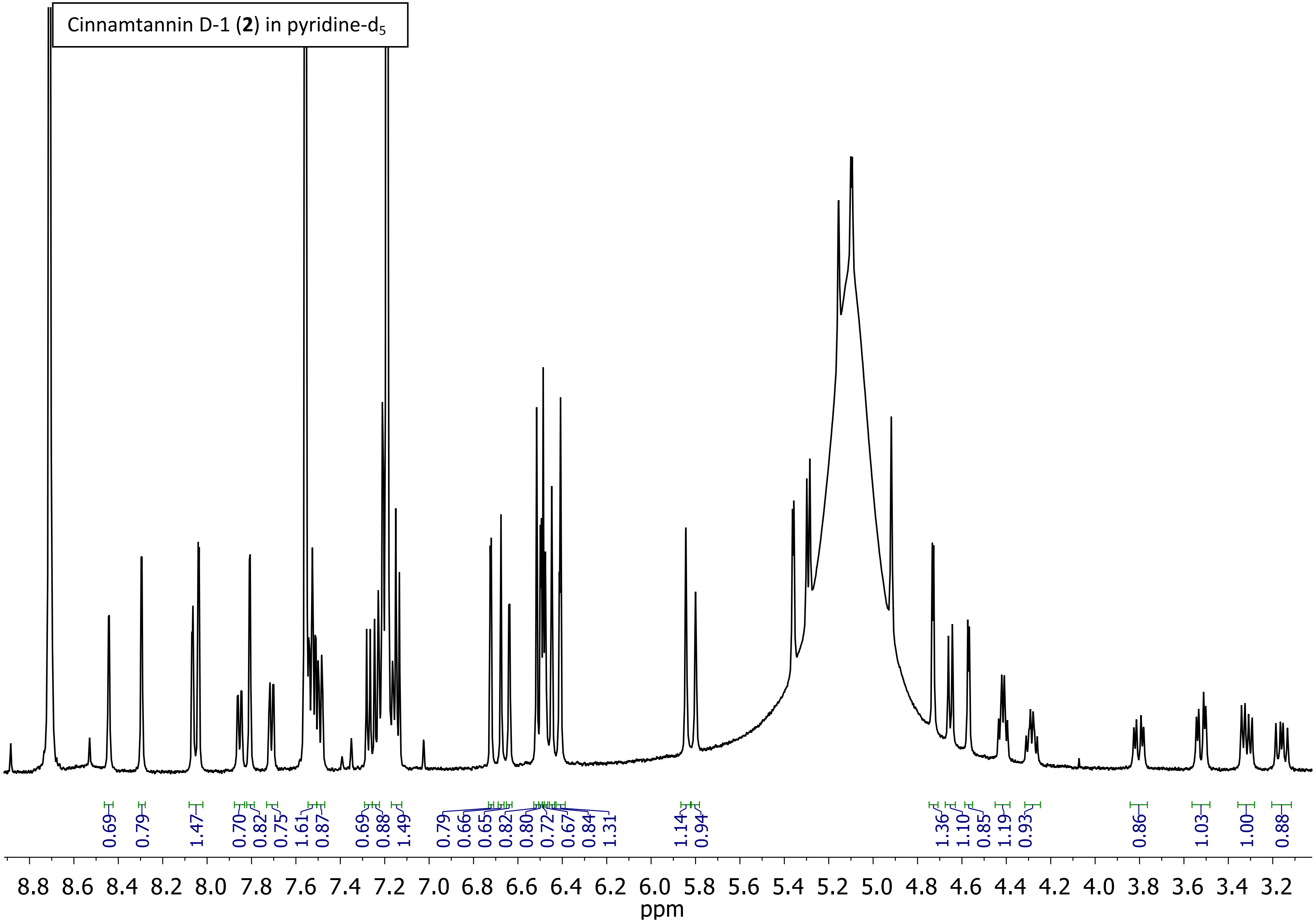

Cinnamtannin B-1 (1) in pyridine-d5
0.91
1.08
1.12
1.49
0.97
0.86
1.61
1.86
1.04
0.99
1.64
1.10
0.95
1.01
1.13
1.21
2.11
1.00
1.05
1.06
2.19
1.06
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm



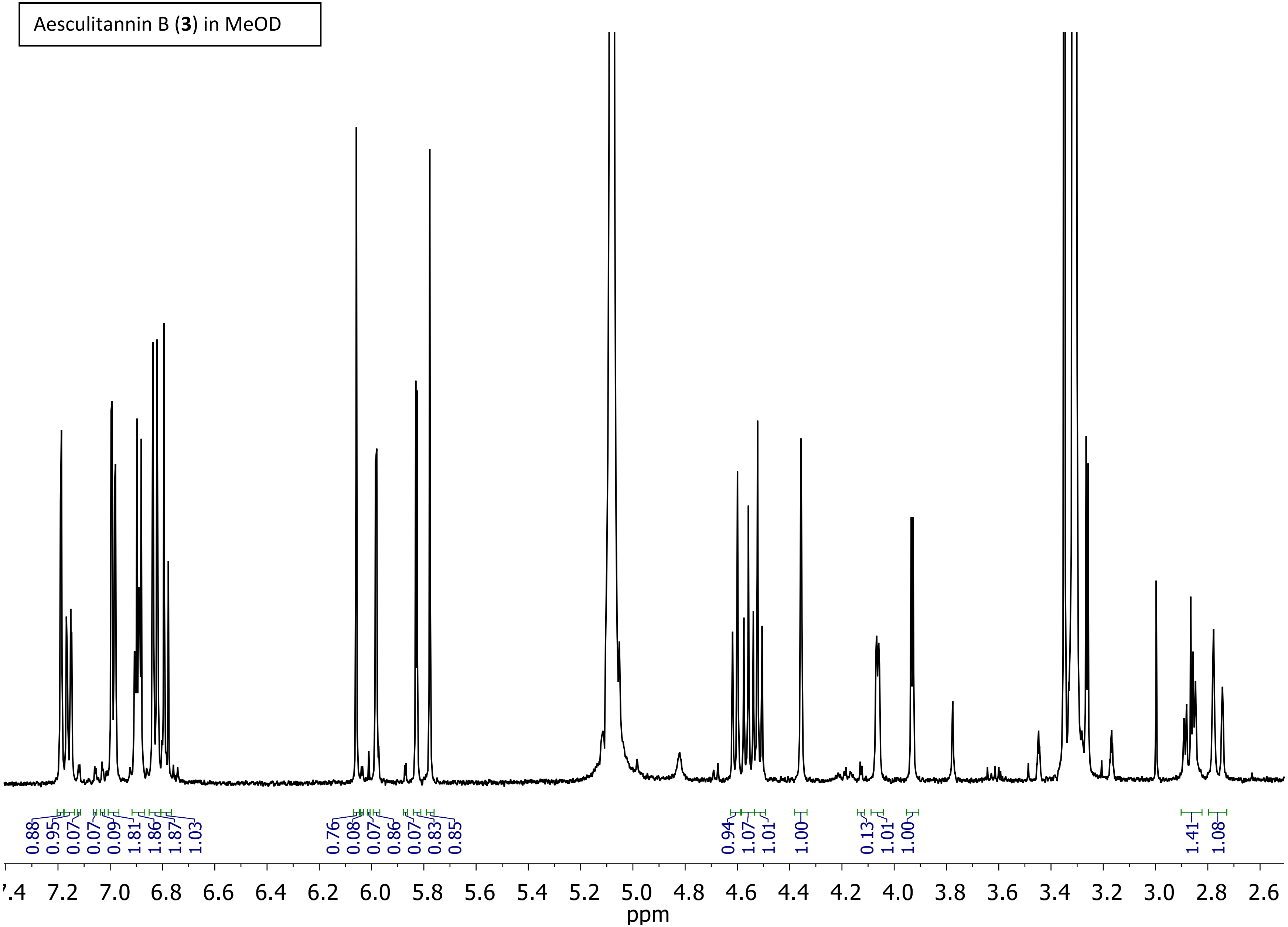
Cinnamtannin D-1 (**2**) in MeOD
0.85
1.29
0.83
0.25
0.27
0.87
0.25
1.83
0.27
1.91
0.27
0.87
0.75
0.21
0.23
1.02
0.80
0.22
0.81
0.59
0.23
0.84
0.25
1.06
0.87
0.90
1.01
1.03
0.92
0.52
1.00
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
ppm

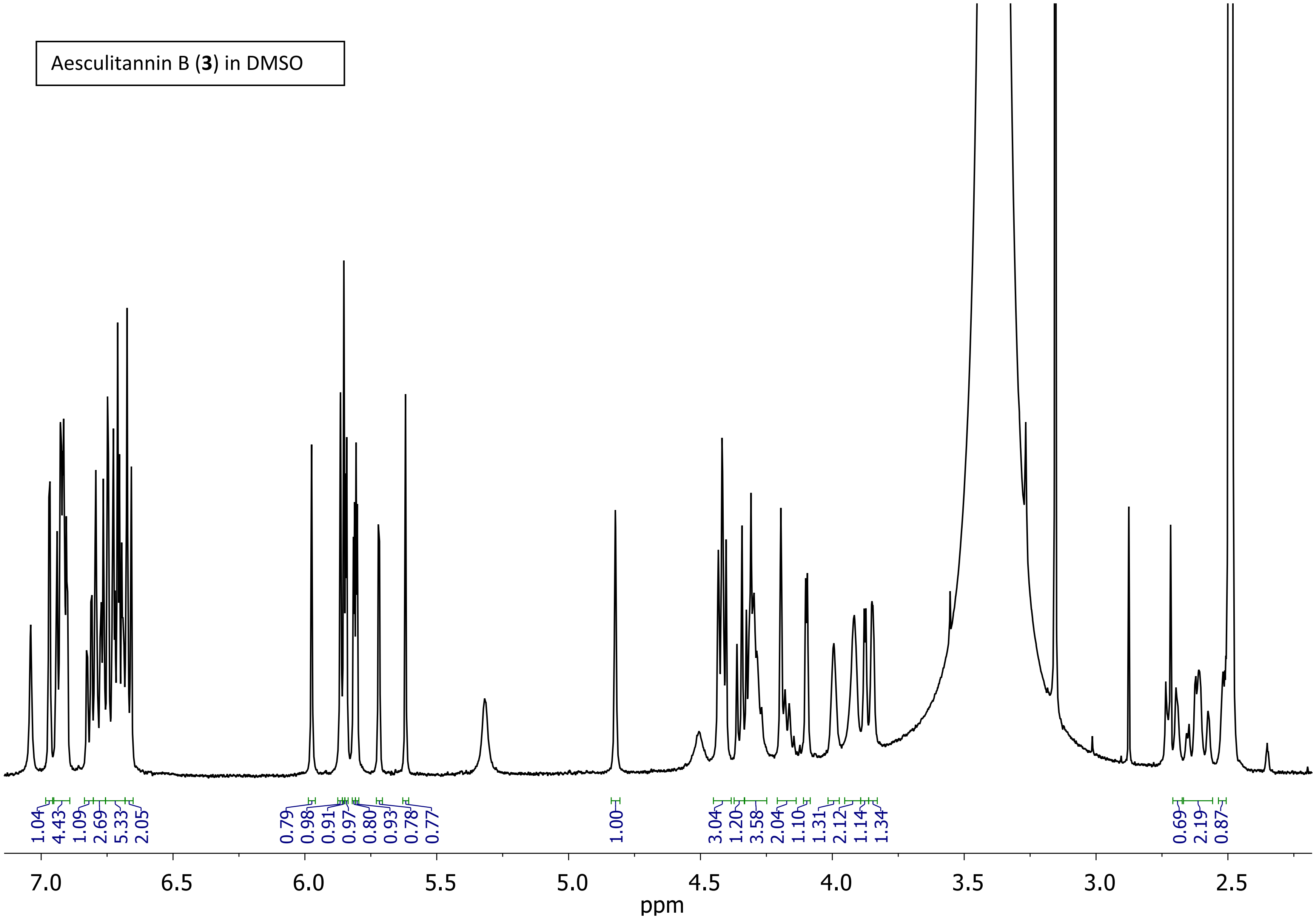

Cinnamtannin D-1 (2) in DMSO
0.97
0.85
0.33
0.34
0.87
1.51
0.90
0.92
1.97
1.57
1.26
0.91
0.37
0.37
0.36
0.88
0.39
0.86
0.35
0.36
0.86
0.38
0.88
0.91
0.37
0.91
0.89
1.00
0.36
0.92
0.42
1.40
1.08
0.43
1.99
0.46
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
ppm


Cinnamtannin D-1 (**2**) in acetone-d$_6$
0.92 0.99 0.52 1.45 1.49 1.71 0.59 0.98 0.55 1.28 2.72 1.03 1.47
1.00 0.48 0.51 1.88 0.93 1.00
0.95
0.49
0.52 0.50 1.00
0.52 0.46 1.04 2.69 1.89 1.01 1.97
0.99
1.19
0.68 0.67 1.14
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
ppm

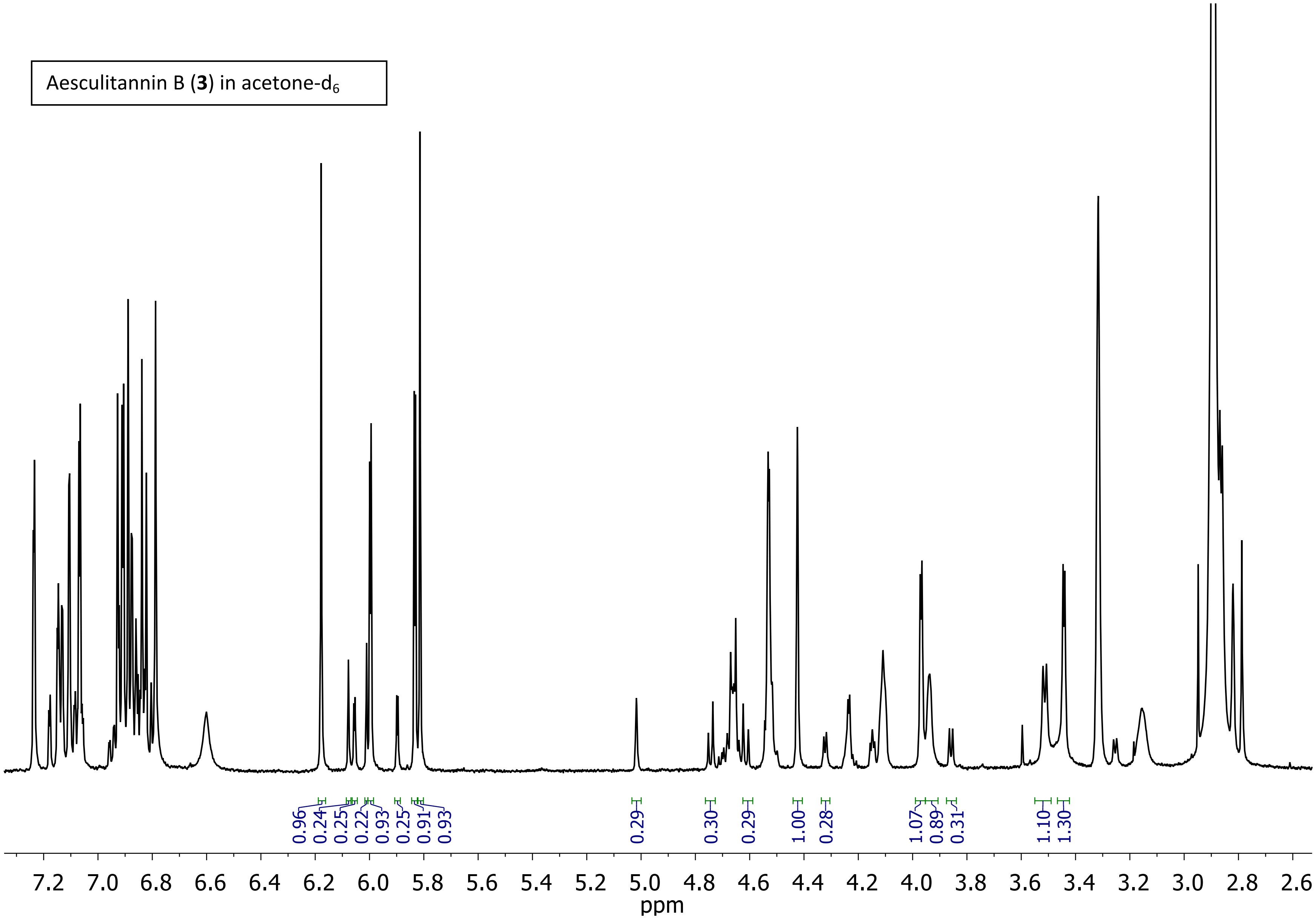


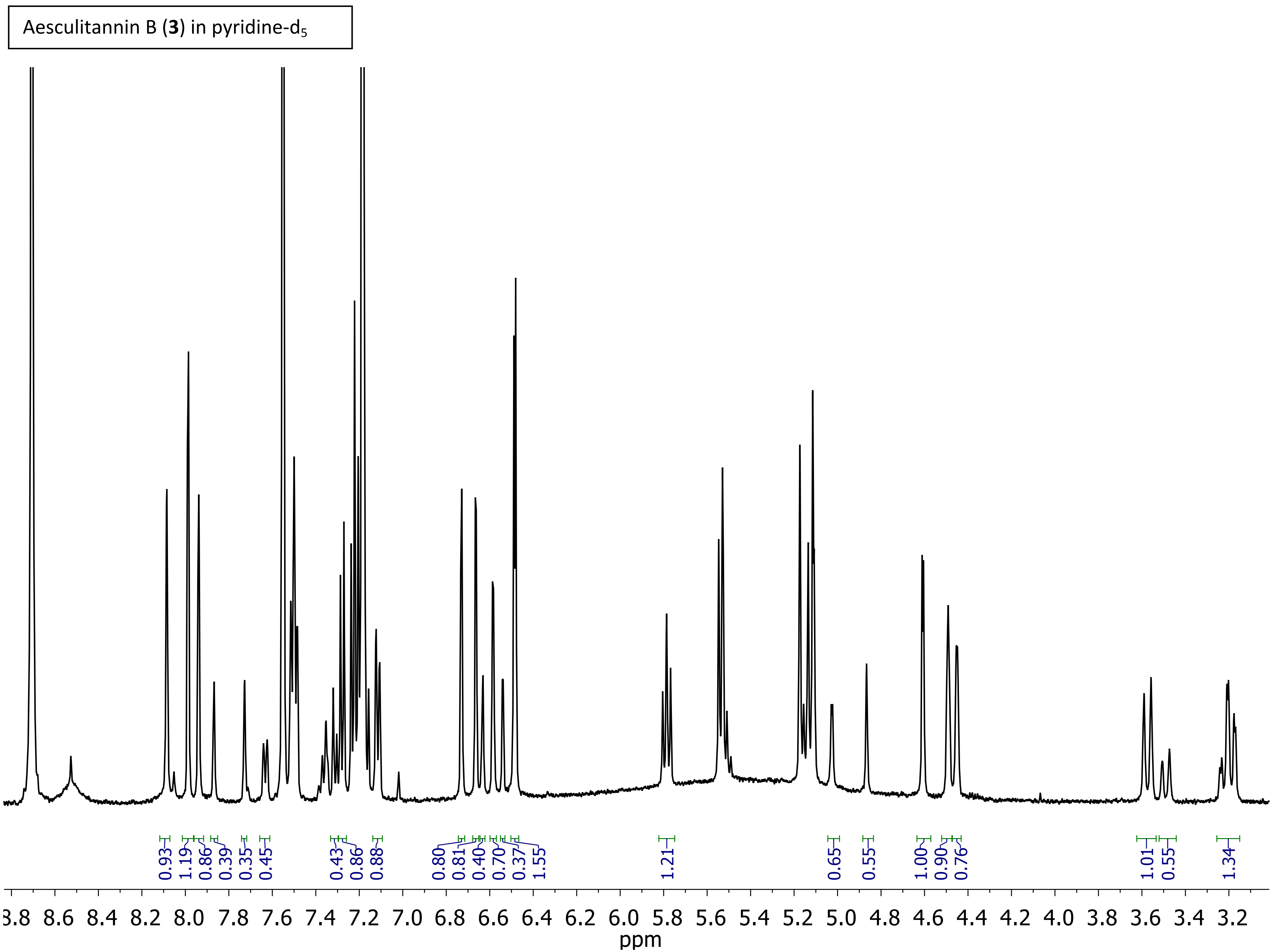
Cinnamtannin D-1 (2) in pyridine-d5
0.69
0.79
1.47
0.70
0.82
0.75
1.61
0.87
0.69
0.88
1.49
0.79
0.66
0.65
0.82
0.80
0.72
0.67
0.84
1.31
1.14
0.94
1.36
1.10
0.85
1.19
0.93
0.86
1.03
1.00
0.88
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

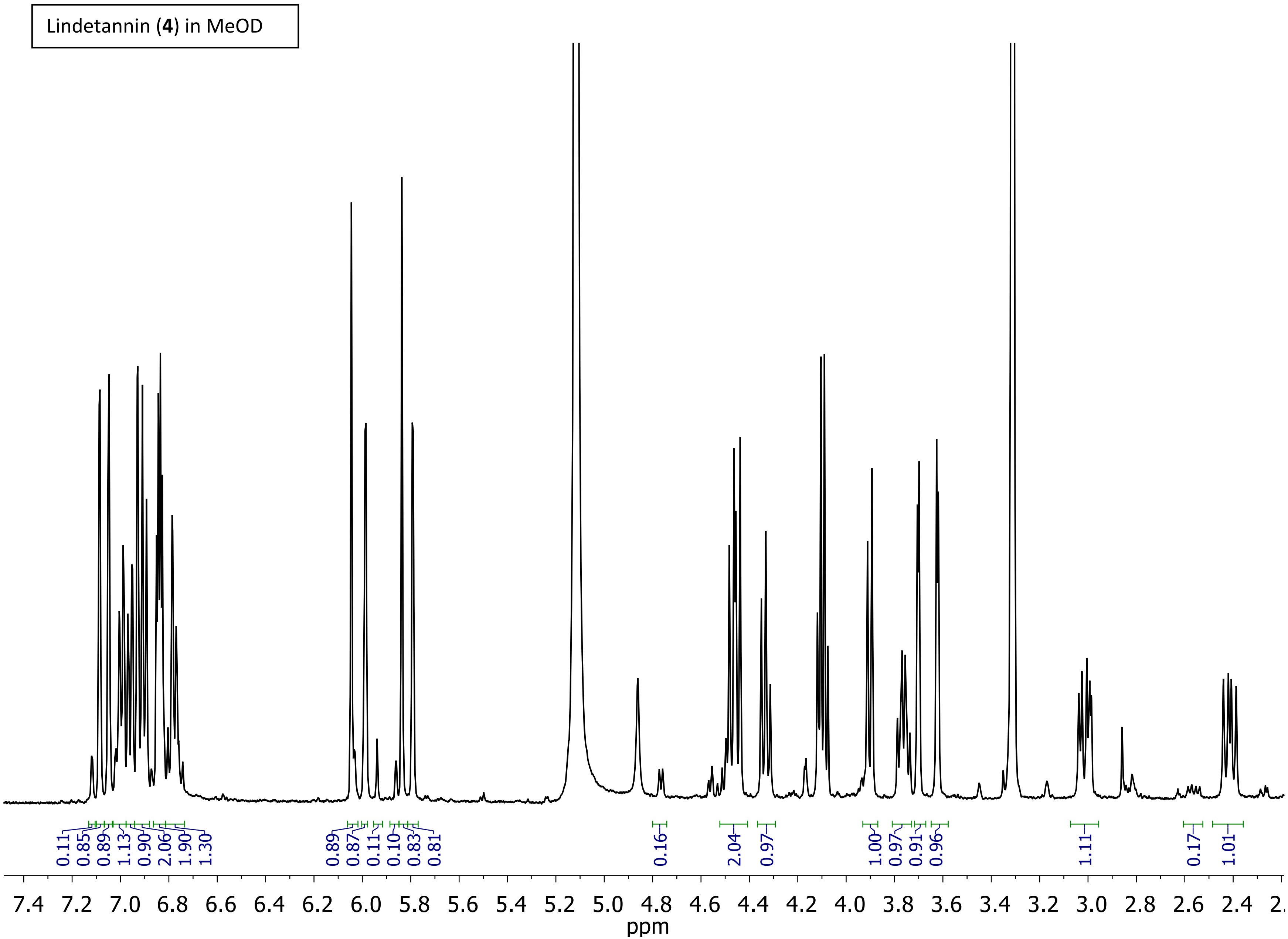

Aesculitannin B (3) in MeOD
0.88
0.95
0.07
0.07
0.09
1.81
1.86
1.87
1.03
0.76
0.08
0.07
0.86
0.07
0.83
0.85
0.94
1.07
1.01
1.00
0.13
1.01
1.00
1.41
1.08
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
ppm

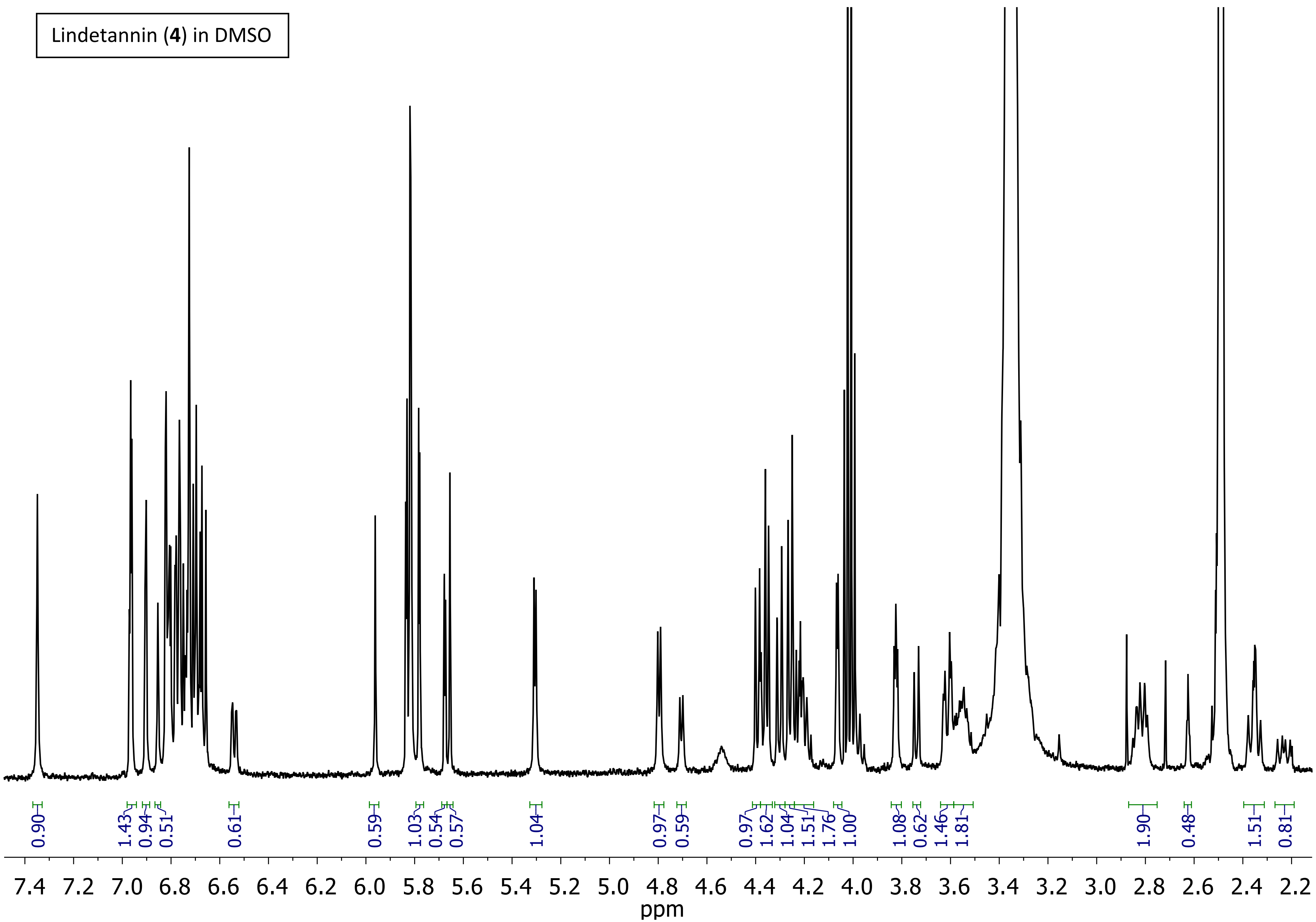


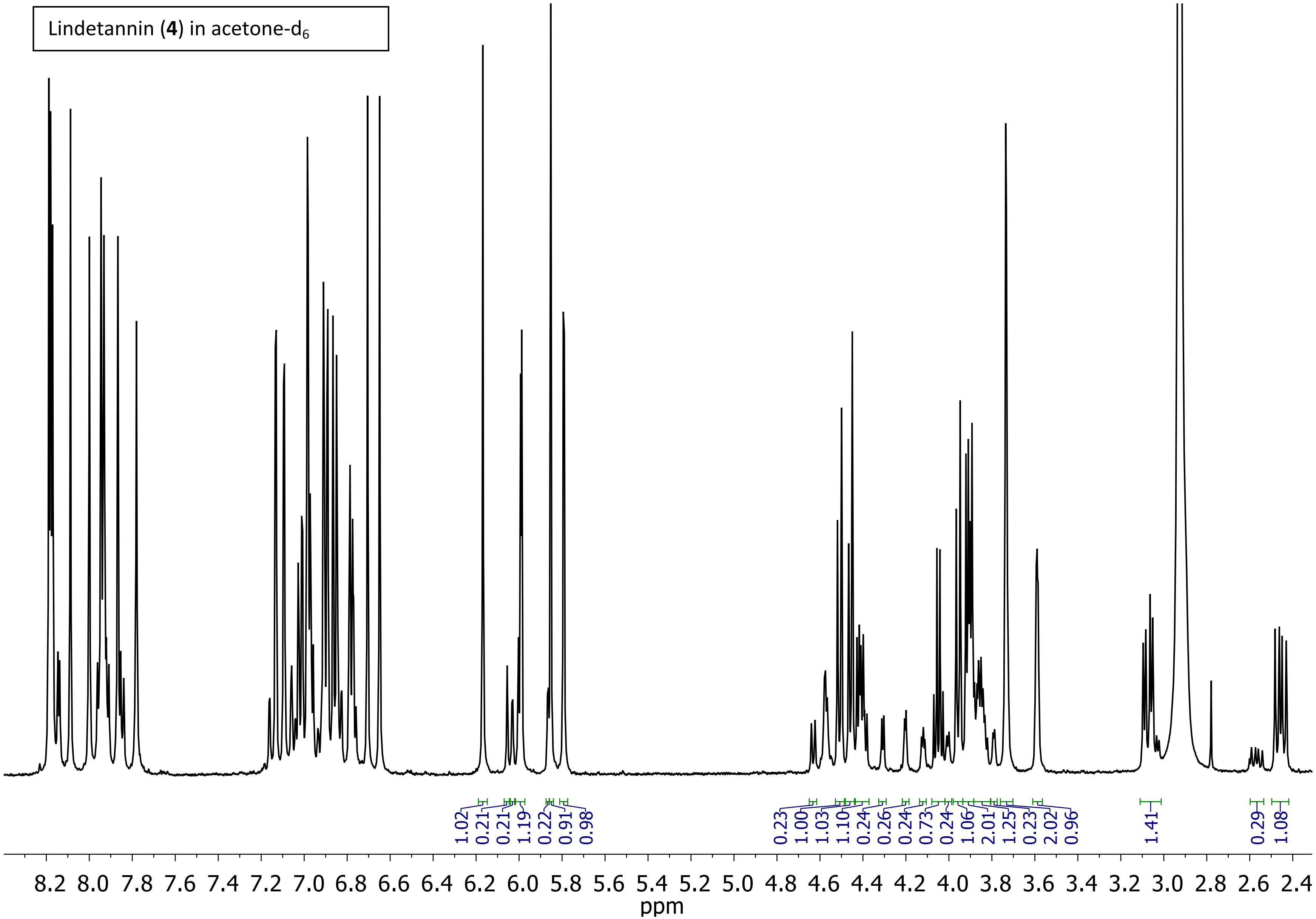
Aesculitannin B (3) in DMSO
1.04
4.43
1.09
2.69
5.33
2.05
0.79
0.98
0.91
0.97
0.80
0.93
0.78
0.77
1.00
3.04
1.20
3.58
2.04
1.10
1.31
2.12
1.14
1.34
0.69
2.19
0.87
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


Aesculitannin B (3) in acetone-d6
0.96
0.24
0.25
0.22
0.93
0.25
0.91
0.93
0.29
0.30
0.29
1.00
0.28
1.07
0.89
0.31
1.10
1.30
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
ppm


Aesculitannin B (3) in pyridine-d5
0.93
1.19
0.86
0.39
0.35
0.45
0.43
0.86
0.88
0.80
0.81
0.40
0.70
0.37
1.55
1.21
0.65
0.55
1.00
0.90
0.76
1.01
0.55
1.34
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm


Lindetannin (**4**) in MeOD
0.11
0.85
0.89
1.13
0.90
2.06
1.90
1.30
0.89
0.87
0.11
0.10
0.83
0.81
0.16
2.04
0.97
1.00
0.97
0.91
0.96
1.11
0.17
1.01
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
ppm


Lindetannin (**4**) in DMSO
0.90
1.43
0.94
0.51
0.61
0.59
1.03
0.54
0.57
1.04
0.97
0.59
0.97
1.62
1.04
1.51
1.76
1.00
1.08
0.62
1.46
1.81
1.90
0.48
1.51
0.81
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
ppm



Lindetannin (**4**) in acetone-d_6
1.02
0.21
0.21
1.19
0.22
0.91
0.98
0.23
1.00
1.03
1.10
0.24
0.26
0.24
0.73
0.24
1.06
2.01
1.25
0.23
2.02
0.96
1.41
0.29
1.08
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
ppm

Lindetannin (**4**) in pyridine-d_5

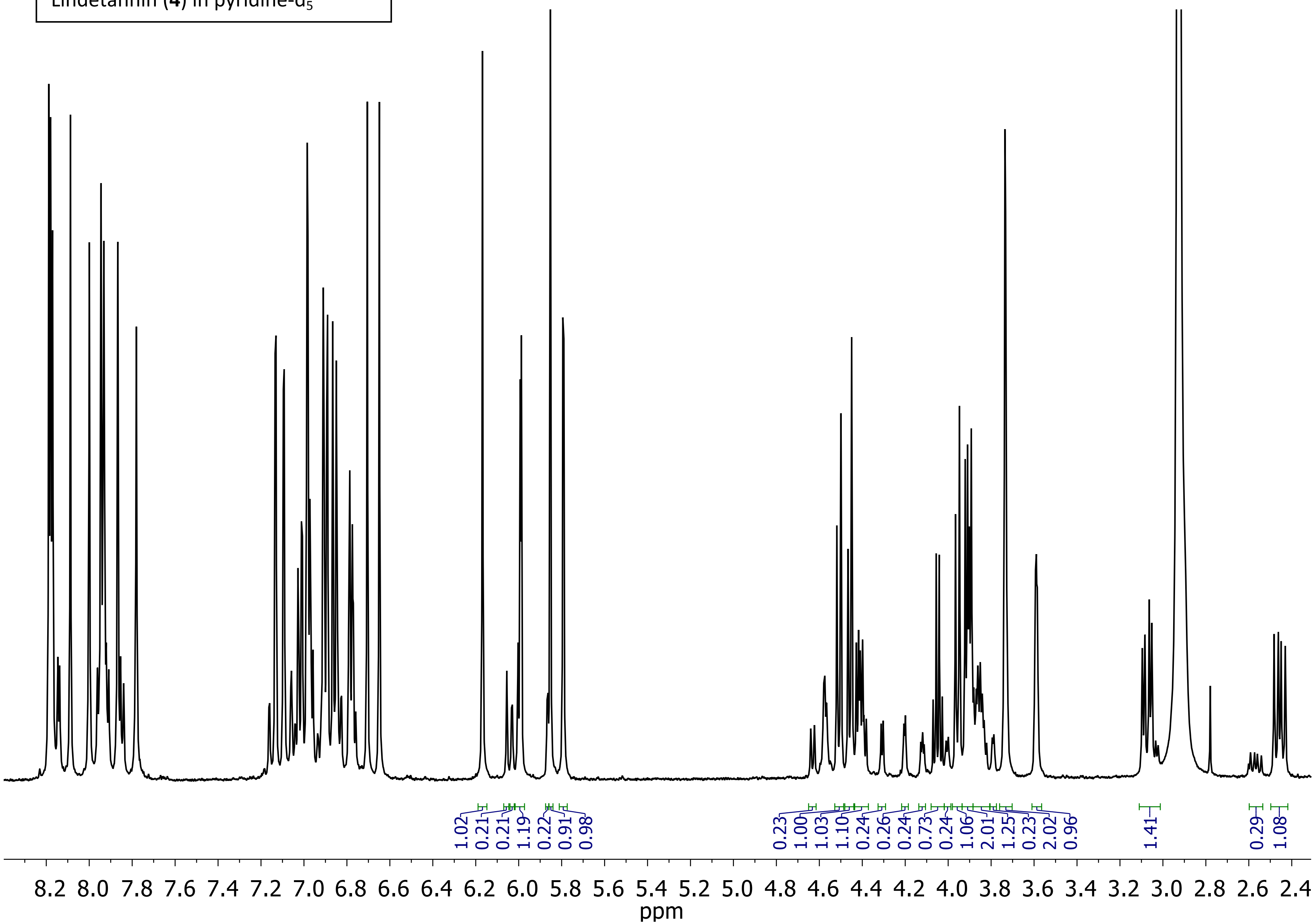


Table SI1. Internal energies (E) and Gibbs free energies (ΔG) differences between the two lowest-energy conformers of **1-4** (in kcal/mol) calculated with two functionals: B3LYP and M062X and 6-31G(d,p) basis set.

	B3LYP			**M062X**		
	ϕ [°]	E	ΔG	ϕ [°]	E	ΔG
(1)	-91.0	0.2	0	-90.3	3.6	1.7
	+89.8	0	1.7	+90.7	0	0
(2)	-95.6	2.3	0	-88.2	4.9	1.9
	+91.9	0	2.3	+92.5	0	0
(3)	-100.4	5.3	2.3	-99.1	7.0	5.1
	+85.8	0	0	+84.4	0	0
(4)	-102.5	15.1	0	-99.9	21.4	17.5
	+80.0	0	7.8	+80.1	0	0

Signal assignment for minor and major rotamers of 1-4 in MeOD and DMSO-d$_6$

Cinnamtannin B1 (1). Major rotamer in MeOD (integral 1.0): ^{1}H NMR (500 MHz, T = 270K): δ 2.83 (br, 2H, H-4"), 3.25 (d, 1H, ^3J = 3.4Hz, H-3), 3.85 (br s, 1H, H-3"), 4.08 (s, 1H, H-3'), 4.13 (d, 1H, ^3J = 3.0Hz, H-4), 4.40 (br, 1H, H-2"), 4.56 (s, 1H, H-4'), 5.70 (s, 1H, H-2'), 5.77 (s, 1H, H-6'), 5.96 (d, 1H, ^4J = 1.8Hz, H-8), 5.99 (d, 1H, ^4J = 1.8Hz, H-6), 6.08 (s, 1H, H-6"), 6.74 (br, 2H, H-15, H-16"), 6.81 (br, 3H, H-16, H-15', H-12"), 6.83 (d, 1H, ^3J = 8.0Hz, H-15"), 7.01 (H-12), 7.21 (br d, 1H, ^3J = 8.4Hz, H-16'), 7.32 (br s, 1H, H-12'); ^{13}C NMR (126 MHz): δ 29.0 (C-4), 30.0 (C-4"), 38.4 (C-4'), 67.3 (C-3), 67.7 (C-3"), 72.7 (C-3'), 79.0 (C-2'), 80.4 (C-2"), 96.2 (C-6'), 96.7 (C-6, C-6"), 98.4 (C-8), 100.1 (C-2, C-10"), 105.1 (C-10), 106.5 (C-8'), 106.8 (C-10'), 109.0 (C-8"), 115.6 (C-12"), 115.9 (C-12, C-15', C-15"), 116.1 (C-15), 116.8 (C-12'), 119.5 (C-16"), 120.0 (C-16), 121.5 (C-16'), 131.9 (C-11'), 132.5 (C-11), 133.3 (C-11"), 145.4 (C-14"), 145.6 (C-13, C-13"), 146.0 (C-13'), 146.4 (C-14'), 146.7 (C-14), 151.2 (C-7'), 151.9 (C-9'), 154.3 (C-5), 155.7 (C-9"), 155.8 (C-5'), 155.9 (C-5"), 156.1 (C-7"), 156.9 (C-9), 158.0 (C-7). Minor rotamer in MeOD (integral 0.30): ^{1}H NMR (500 MHz, T = 270K): δ 2.80 (overlapped, H-4"a), 2.94 (dd, 1H, ^2J = 17.0Hz, ^3J = 4.9Hz, H-4"b), 3.89 (br s, 1H, H-3'), 4.06 (d, 1H, ^3J = 3.4Hz, H-3), 4.24 (br, 1H, H-3"), 4.43 (d, 1H, ^3J = 3.0Hz, H-4), 4.66 (s, 1H, H-4'), 4.96 (s, 1H, H-2"), 5.25 (s, 1H, H-2'), 5.89 (s, 1H, H-6'), 6.01 (d, 1H, ^4J = 1.9Hz, H-6), 6.06 (d, 1H, ^4J = 1.9Hz, H-8), 6.10 (s, 1H, H-6"), 6.73 (overlapped, H-15), 6.76 (d, 1H, ^3J = 8.0Hz, H-15"), 6.80 (overlapped, H-15'), 6.86 (br d, 1H, ^3J = 8.4Hz, H-16"), 6.91 (br d, 1H, ^3J = 8.0Hz, H-16'), 7.02 (overlapped, H-16), 7.07 (br, 1H, H-12'), 7.10 (br, 1H, H-12"), 7.14 (br, 1H, H-12); ^{13}C NMR (126 MHz): δ 29.6 (C-4), 30.3 (C-4"), 38.4 (C-4'), 67.2 (C-3"), 68.6 (C-3), 73.3 (C-3'), 79.0 C-2'), 79.9 (C-2"), 96.8 (C-8, C-6"), 97.6 (C-6'), 98.5 (C-6), 100.3 (C-10"), 100.4 (C-2), 104.4 (C-10), 105.5 (C-8"), 107.3 (C-8'), 107.7 (C-10'), 115.3 (C-12"), 116.0 (C-12), 116.3 (C-12', C-15"), 116.4 (C-15'), 119.2 (C-16"), 119.9 (C-16), 120.7 (C-16'), 131.8 (C-11'), 132.3 (C-11"), 132.7 (C-11), 145.7

(C-13), 146.3 (C-14'), 152.6 (C-9'), 154.1 (C-5), 154.9 (C-7''), 156.6 (C-5'), 157.3 (C-9). Major rotamer in DMSO (integral 1.0): ^{1}H NMR (500 MHz): δ 2.35 (dd, 1H, ^{2}J = 16.0Hz, ^{3}J = 5.2Hz, H-4''a), 2.68 (dd, 1H, ^{2}J = 16.1Hz, ^{3}J = 3.9Hz, H-4''b), 3.76 (br, 1H, H-3'), 3.83 (br, 1H, H-3), 4.17 (br, 1H, H-3''), 4.27 (br d, 1H, ^{3}J = 2.0Hz, H-4), 4.46 (s, 1H, H-4'), 4.93 (s, 1H, H-2''), 5.11 (s, 1H, H-2'), 5.79 (s, 1H, H-6''), 5.86 (d, 1H, ^{4}J = 2.2Hz, H-8), 5.89 (d, 1H, ^{4}J = 2.2Hz, H-6), 5.93 (s, 1H, H-6'), 6.62 (d, 1H, ^{3}J = 8.3Hz, H-15'), 6.68 (br, H-15''), 6.74 (d, 1H, ^{3}J = 8.3Hz, H-15), 6.79 (dd, 1H, ^{3}J = 8.3Hz, ^{4}J = 1.6Hz, H-16), 6.85 (dd, 1H, ^{3}J = 8.0Hz, ^{4}J = 2.0Hz, H-16'), 6.91 (overlapped, H-16''), 6.92 (br, 1H, H-12'), 7.00 (d, 1H, ^{4}J = 1.8Hz, H12''), 7.01 (d, 1H, ^{4}J = 2.0Hz, H-12). Minor rotamer in DMSO (integral 0.66): ^{1}H NMR (500 MHz): δ 2.50 (overlapped, H-4''a), 2.61 (br, 1H, H-4''b), 3.42 (overlapped, H-3), 3.68 (br, 1H, H-3''), 3.90 (br, 1H, H-3'), 4.04 (d, 1H, ^{3}J = 3.3Hz, H-4), 4.23 (s, 1H, H-2''), 4.27 (overlapped, 1H, H-4'), 5.39 (s, 1H, H-2'), 5.65 (s, 1H, H-6'), 5.77 (d, 1H, ^{4}J = 2.2Hz, H-6), 5.82 (d, 1H, ^{4}J = 2.2Hz, H-8), 6.05 (s, 1H, H-6''), 6.51 (dd, 1H, ^{3}J = 8.3Hz, ^{4}J = 1.6Hz, H-16''), 6.67 (overlapped, H-15''), 6.68 (overlapped, H-16, H-12''), 6.72 (br, 1H, H-15'), 6.74 (br, 1H, H-15), 6.95 (d, 1H, ^{4}J = 1.8Hz, H-12), 6.98 (dd, 1H, ^{3}J = 8.2Hz, ^{4}J = 1.8Hz, H-16'), 7.19 (d, 1H, ^{4}J = 1.8Hz, H-12').

Cinnamtannin D1 (2). Major rotamer in MeOD (integral 1.0): ^{1}H NMR (500 MHz, T = 270K): δ 2.45 (dd, 1H, ^{2}J = 16.5Hz, ^{3}J = 10.3Hz, H-4''a), 3.05 (dd, 1H, ^{2}J = 16.5Hz, ^{3}J = 6.2Hz, H-4''b), 3.46 (d, 1H, ^{3}J =3.3Hz, H-3), 3.67 (br, 1H, H-3''), 3.96 (d, 1H, ^{3}J = 9.3Hz, H-2''), 4.00 (d, 1H, ^{3}J = 3.3Hz, H-4), 4.06 (br s, 1H, H-3'), 4.53 (s, 1H, H-4'), 5.52 (s, 1H, H-2'), 5.84 (s, 1H, H-6'), 5.94 (d, 1H, ^{4}J = 1.9Hz, H-6), 6.00 (d, 1H, ^{4}J = 1.9Hz, H-8), 6.10 (s, 1H, H-6''), 6.66 (dd, 1H, ^{3}J = 8.2Hz, ^{4}J = 1.7Hz, H-16''), 6.75 (d, 1H, ^{4}J = 1.7Hz, H-12'') 6.76 (d, 1H, ^{3}J = 8.3Hz, H-15''), 6.84 (d, 2H, ^{3}J = 8.3 Hz, H-15, H-15'), 6.94 (dd, 1H, ^{3}J = 8.6Hz, ^{4}J = 1.9Hz, H-16), 7.07 (d, 1H, ^{3}J = 2.1Hz, H-12), 7.09 (dd, 1H, ^{3}J = 8.2Hz, ^{4}J = 1.9Hz, H-16'), 7.23 (d, 1H, ^{4}J =1.3Hz, H-12'); ^{13}C NMR (126 MHz): δ 29.1 (C-4), 30.8 (C-4''), 38.4

(C-4’), 67.3 (C-3), 70.2 (C-3”), 72.6 (C-3’), 78.8 (C-2’), 83.5 (C-2”), 96.2 (C-6’), 96.6 (C-6”), 96.7 (C-8), 98.5 (C-6), 100.2 (C-2), 101.9 (C-10”), 105.2 (C-10), 106.4 (C-8’), 106.7 (C-10’), 108.8 (C-8”), 115.9 (C-12, C-15’), 116.0 (C-12”), 116.4 (C-15, C-15”), 116.7 (C-12’), 120.1 (C-16), 120.2 (C-16”), 121.2 (C-16’), 131.7 (C-11’), 132.6 (C-11), 132.8 (C-11”), 145.6 (C-13, C-13”), 145.9 (C-14”), 146.0 (C-13’), 146.4 (C-14’), 146.8 (C-14), 151.2 (C-7’), 151.9 (C-9’), 154.3 (C-5), 155.5 (C-5”, C-7”, C-9”), 156.0 (C-5’), 156.8 (C-9), 157.9 (C-7). Minor rotamer in MeOD (integral 0.24): ^{1}H NMR (500 MHz, T = 270K): δ 2.60 (dd, 1H, ^2J = 16.4Hz, ^3J = 5.6Hz, H-4”a), 2.66 (dd, 1H, ^2J = 16.4Hz, ^3J = 4.4Hz, H-4”b), 4.02 (br s, 1H, H-3’), 4.08 (d, 1H, ^3J = 3.9Hz, H-3), 4.11 (q, 1H, ^3J = 5.4Hz, H-3”), 4.44 (d, 1H, ^3J = 3.3Hz, H-4), 4.70 (s, 1H, H-4’), 4.92 (d, 1H, ^3J = 5.5Hz, H-2”), 5.33 (s, 1H, H-2’), 5.87 (s, 1H, H-6”), 6.00 (d, 1H, ^4J = 2.4Hz, H-6), 6.07 (d, 1H, ^4J = 2.4Hz, H-8), 6.09 (s, 1H, H-6’), 6.72 (d, 1H, ^3J = 8.0Hz, H-15”), 6.79 (d, 1H, ^3J = 8.0Hz, H-15’), 6.81 (d, 1H, ^3J = 8.3Hz, H-15), 6.85 (overlapped, 1H, H-12”), 6.87 (dd, 1H, ^3J = 8.3Hz, ^4J = 1.9Hz, H-16”) , 6.96 (dd, 1H, ^3J = 8.4Hz, ^4J = 1.9Hz, H-16’), 7.04 (dd, 1H, ^3J = 8.1Hz, ^4J = 2.0Hz, H-16), 7.13 (d, 1H, ^3J = 2.0Hz, H-12’), 7.16 (d, 1H, ^3J = 2.1Hz, H-12); ^{13}C NMR (126 MHz): δ 26.9 (C-4”), 29.6 (C-4), 38.0 (C-4’), 68.5 (C-3”), 68.6 (C-3), 72.8 (C-3’), 79.2 (C-2’), 82.2 (C-2”), 96.5 (C-6’), 96.8 (C-8), 97.2 (C-6”), 98.5 (C-6), 100.4 (C-2), 100.7 (C-10”), 104.3 (C-10), 105.7 (C-10’), 106.9 (C-8’), 108.3 (C-8”), 114.7 (C-12”, C-15”), 115.8 (C-15), 115.9 (C-12), 116.2 (C-15’), 116.4 (C-12’), 119.5 (C-16”), 119.9 (C-16), 120.8 (C-16’), 131.8 (C-11’), 132.8 (C-11), 145.0 (C-14”), 145.8 (C-13’), 146.2 (C-14’, C-13”), 146.8 (C-14), 152.6 (C-9’), 153.9 (C-9”), 156.0 (C-7”), 157.2 (C-5’). Major rotamer in DMSO (integral 1.0): ^{1}H NMR (500 MHz): δ 2.36 (br, 1H, H-4”a), 2.42 (br, 1H, H-4”b), 3.77 (br, 1H, H-3’), 3.81 (br d, 1H, ^3J = 2.8Hz, H-3), 3.91 (q, 1H, ^3J = 5.3Hz, H-3”), 4.26 (d, 1H, ^3J = 3.2Hz, H-4), 4.44 (br s, 1H, H-4’), 4.48 (d, 1H, ^3J = 5.3Hz, H-2”), 4.86 (d, 1H, ^3J = 5.3Hz, OH-3’), 5.19 (s, 1H, H-2’), 5.30 (br d, 1H, ^3J = 3.2Hz, OH-3), 5.77 (s, 1H, H-6”), 5.86 (d, 1H, ^4J = 2.3Hz, H-8), 5.87 (d, 1H, ^4J = 2.3Hz, H-

6), 5.92 (s, 1H, H-6'), 6.62 (d, 1H, ^3J = 7.8Hz, H-15"), 6.70 (d, 1H, ^3J = 7.8Hz, H-15'), 6.73 (d, 1H, ^4J = 2.3Hz, H-12"), 6.74 (d, 1H, ^3J = 8.5Hz, H-15), 6.78 (dd, 1H, ^3J = 8.2Hz, ^4J = 1.9Hz, H-16"), 6.85 (dd, 1H, ^3J = 7.8Hz, ^4J = 1.9Hz, H-16), 6.92 (dd, 1H, ^3J = 8.2Hz, ^4J = 1.9Hz, H-16'), 6.94 (d, 1H, ^4J = 1.9Hz, H-12'), 7.00 (d, 1H, ^4J = 1.9Hz, H-12). Minor rotamer in DMSO (integral 0.42): ^{1}H NMR (500 MHz): δ 2.24 (dd, 1H, ^2J = 16.1Hz, ^3J = 9.5Hz, H-4"a), 2.79 (dd, 1H, ^2J = 16.1Hz, ^3J = 5.6Hz, H-4"b), 3.47 (overlapped, H-3"), 3.49 (d, 1H, ^3J = 3.6Hz, H-3), 3.80 (overlapped, 1H, H-2"), 3.82 (overlapped, H-4), 3.87 (br, 1H, H-3'), 4.24 (s, 1H, H-4'), 4.81 (d, 1H, ^3J = 4.1Hz, OH-3') 5.23 (s, 1H, H-2'), 5.66 (s, 1H, H-6'), 5.73 (d, 1H, ^4J = 2.3Hz, H-6), 5.81 (d, 1H, ^4J = 2.3Hz, H-8), 6.06 (s, 1H, H-6"), 6.44 (dd, 1H, ^3J = 8.2Hz, ^4J = 1.6Hz, H-16"), 6.58 (d, 1H, ^4J = 1.6Hz, H-12"), 6.68 (d, 1H, ^3J = 8.0Hz, H-15"), 6.73 (overlapped, H-15'), 6.76 (overlapped, H-16), 6.77 (overlapped, H-15), 6.96 (overlapped, H-16'), 6.98 (d, 1H, ^4J = 2.1Hz, H-12), 7.12 (d, 1H, ^4J = 1.8Hz, H-12').

Aesculitannin B (3). Major rotamer in MeOD (integral 1.0): ^{1}H NMR (500 MHz, T = 270K): δ 2.76 (br d, 1H, ^2J = 17.2Hz, H-4"a), 2.87 (dd, 1H, ^2J = 17.2Hz, ^3J = 4.8Hz, H-4"b), 3.26 (d, 1H, ^3J = 3.4Hz, H-3), 3.94 (d, 1H, ^3J = 3.5Hz, H-4), 4.06 (br d, 1H, ^3J = 4.1Hz, H-3"), 4.36 (br s, 1H, H-2"), 4.51 (d, 1H, ^3J = 8.8Hz, H-4'), 4.56 (t, 1H, ^3J = 8.7Hz, H-3'), 4.61 (d, 1H, ^3J = 9.4Hz, H-2'), 5.78 (s, 1H, H-6'), 5.83 (d, 1H, ^4J = 2.3Hz, H-6), 5.98 (d, 1H, ^4J = 2.3Hz, H-8), 6.06 (s, 1H, H-6"), 6.79 (d, 1H, ^3J = 8.1Hz, H-15"), 6.83 (br, 2H, H-15, H-16), 6.89 (d, 1H, ^3J = 8.2Hz, H-15'), 6.90 (dd, 1H, ^3J = 8.2Hz, ^4J = 1.7Hz, H-16"), 6.98 (d, 1H, ^4J = 1.7Hz, H-12"), 6.99 (d, 1H, ^4J = 2.0Hz, H-12), 7.16 (dd, 1H, ^3J = 8.2Hz, ^4J = 2.0Hz, H-16'), 7.19 (d, 1H, ^4J = 2.0Hz, H-12'); ^{13}C NMR (126 MHz): δ 29.1 (C-4), 30.3 (C-4"), 39.2 (C-4'), 67.2 (C-3), 67.8 (C-3"), 74.1 (C-3'), 79.8 (C-2"), 84.7 (C-2'), 96.6 (C-8, C-6"), 97.3 (C-6'), 98.0 (C-6), 100.3 (C-2), 101.0 (C-10"), 104.2 (C-10), 107.0 (C-8'), 108.8 (C-8"), 109.1 (C-10'), 115.4 (C-12"), 115.8 (C-12, C-15"), 116.1 (C-15), 116.5 (C-15'), 116.7 (C-12'), 119.4 (C-16"), 120.0 (C-16), 121.3 (C-16'), 131.2 (C-11'), 132.4 (C-11), 133.1 (C-11"), 145.4 (C-13), 145.7

(C-14), 146.0 (C-13”), 146.3 (C-13’), 146.8 (C-14’), 146.9 (C-14”), 151.4 (C-7’), 152.4 (C-9’), 154.1 (C-9), 155.4 (C-9”), 155.6 (C-5’), 156.4 (C-5”, C7”), 156.7 (C-5), 158.1 (C-7).

Major rotamer in DMSO (integral 1.0): ^{1}H NMR (500 MHz): δ 2.61 (br, 1H, H-4”a), 2.71 (br, 1H, H-4”b), 3.85 (br d, 1H, ^{3}J = 3.0Hz, H-3), 4.10 (d, 1H, ^{3}J = 3.1Hz, H-4), 4.29 (br, 1H, H-3’), 4.35 (d, 1H, ^{3}J = 9.6Hz, H-2’), 4.41 (br, 1H, H-4’), 4.82 (s, 1H, H-2”), 5.80 (d, 1H, ^{4}J = 2.4Hz, H-6), 5.84 (d, 1H, ^{4}J = 2.4Hz, H-8), 5.85 (s, 1H, H-6’), 5.86 (s, 1H, H-6”), 6.65 – 6.60 (m, 5H, H-15, H-15’, H-16’, H-15”, H-16”), 6.82 (dd, 1H, ^{3}J = 8.1Hz, ^{4}J = 2.2Hz, H-16), 6.92 (d, 1H, ^{4}J = 1.9Hz, H-12”), 6.93 ((d, 1H, ^{4}J = 1.8Hz, H-12’), 6.97 ((d, 1H, ^{4}J = 2.1Hz, H-12).

Minor rotamer in DMSO (integral 0.8): ^{1}H NMR (500 MHz): δ 2.51 (overlapped, H-4”a), 2.63 (br, 1H, H-4”b), 3.36 (overlapped, H-3), 3.88 (d, 1H, ^{3}J = 3.2Hz, H-4), 3.92 (br s, 1H, H-3”), 4.17 (br, 1H, H-3’), 4.19 (s, 1H, H-2”), 4.31 (d, 1H, ^{3}J = 9.2Hz, H-4’), 4.43 (br, 1H, H-2’), 5.62 (s, 1H, H-6’), 5.72 (d, 1H, ^{4}J = 2.4Hz, H-6), 5.81 (d, 1H, ^{4}J = 2.4Hz, H-8), 5.97 (s, 1H, H-6”), 6.65 – 6.93 (9H, H-12, H-15, H-16, H-12’, H-15’, H-16’, H-12”, H-15”, H-16”).

Lindetannin (4). Major rotamer in MeOD (integral 1.0): ^{1}H NMR (500 MHz, T = 270K): δ 2.43 (dd, 1H, ^{2}J = 16.5Hz, ^{3}J = 10.0Hz, H-4”a), 3.03 (dd, 1H, ^{2}J = 16.4Hz, ^{3}J = 6.4Hz, H-4”b), 3.64 (d, 1H, ^{3}J = 3.0Hz, H-3), 3.72 (d, 1H, ^{3}J = 3.0Hz, H-4), 3.77 (br, 1H, H-3”), 3.92 (d, 1H, ^{3}J = 9.1Hz, H-2”), 4.35 (t, 1H, ^{3}J = 9.2Hz, H-3’), 4.45 (d, 1H, ^{3}J = 8.8Hz, H-4’), 4.48 (d, 1H, ^{3}J = 9.7Hz, H-2’), 5.81 (d, 1H, ^{4}J = 2.0Hz, H-6), 5.85 (s, 1H, H-6’), 6.00 (d, 1H, ^{4}J = 1.9Hz, H-8), 6.06 (s, 1H, H-6”), 6.77 (dd, 1H, ^{3}J = 7.9Hz, ^{4}J = 1.5Hz, H-16”), 6.84 (d, 2H, ^{3}J = 7.2Hz, H-15, H-15”), 6.90 (d, 1H, ^{3}J = 8.2Hz, H-15’), 6.93 (d, 1H, ^{4}J = 1.5Hz, H-12”), 6.97 (br, 1H, H-16), 6.98 (br, 1H, H-16’), 7.06 (d, 1H, ^{4}J = 1.7Hz, H-12’), 7.10 (d, 1H, ^{4}J = 1.9Hz, H-12); ^{13}C NMR (126 MHz): δ 29.0 (C-4), 31.0 (C-4”), 39.0 (C-4’), 67.4 (C-3), 69.8 (C-3”), 74.5 (C-3’), 83.0 (C-2”), 84.5 (C-2’), 96.5 (C-6”), 96.6 (C-8), 97.3 (C-6’), 98.0 (C-6), 100.4 (C-2), 102.5 (C-10”), 104.2 (C-10), 106.8 (C-8’), 108.9 (C-8”), 109.1 (C-10’), 115.8 (C-12”), 115.9 (C-12), 116.0 (C-15”), 116.3 (C-15), 116.6 (C-12’, C-15’), 120.1 (C-16), 120.9 (C-16’, C-16”), 131.4 (C-11’), 132.5 (C-11), 132.6 (C-11”), 145.8 (C-13), 146.1 (C-14, C-13’, C-13”), 146.7 (C-14’), 146.9 (C-14”), 151.3 (C-7’), 152.5 (C-9’), 154.2 (C-9), 155.1 (C-7”), 155.5 (C-9”), 155.7 (C-5”), 156.4 (C-5’), 156.6 (C-5), 158.1 (C-7). Major rotamer in DMSO (integral 1.0): ^{1}H NMR (500 MHz): δ 2.36 (br, 1H, H-4”a), 2.82 (br, 1H, H-4”b), 3.55 (br, 1H, H-3”), 3.83 (br t, 1H, ^{3}J = 3.7Hz, H-3), 4.07 (d, 1H, ^{3}J = 3.7Hz, H-4), 4.20 (br, 1H, H-3’), 4.26 (d, 1H, ^{3}J = 8.5Hz, H-4’), 4.31 (d, 1H, ^{3}J = 9.4Hz, H-2’), 4.40 (d, 1H, ^{3}J = 8.8Hz, H-2”), 5.78 (d, 1H, ^{4}J = 2.3Hz, H-6), 5.82 (s, 2H, H-6’, H6”), 5.83 (d, 1H, ^{4}J = 2.3Hz, H-8), 6.66 (d, 1H, ^{3}J = 8.2Hz, H-15”), 6.71 (br, H-15’), 6.73 (br, H-12”), 6.78 (br, H-15, H-16”), 6.81 (br, H-16’), 6.82 (br, H-16), 6.91 (d, 1H, ^{4}J = 1.7Hz, H-12’), 6.97 (br, 1H, H-12). Minor rotamer in DMSO (integral 0.6): ^{1}H NMR (500 MHz): δ 2.24 (dd, 1H, ^{2}J = 16.5Hz, ^{3}J = 10.3Hz, H-4”a), 2.82 (br, 1H, H-4”b), 3.57 (br, 1H, H-3”), 3.60 (d, 1H, ^{3}J = 3.7Hz, H-4), 3.63 (d, 1H, ^{3}J = 3.6Hz, H-3), 3.75 (d, 1H, ^{3}J = 9.6Hz, H-2”), 3.98 (overlapped, H-3’), 4.23 (d, 1H, ^{3}J = 5.9Hz, H-4’), 4.26 (overlapped, H-2’), 5.66 (s, 1H, H-6’), 5.68 (d, 1H, ^{4}J = 2.3Hz, H-6), 5.82 (overlapped, H-8), 5.97 (s, 1H, H-6”), 6.54 (dd, 1H, ^{3}J = 8.1Hz, ^{4}J = 1.6Hz, H-16”), 6.70 (overlapped, H-15, H-15”), 6.73 (overlapped, H-12), 6.75 (d, 1H, ^{4}J = 1.7Hz, H-12”), 6.78 (overlapped, H-16’), 6.81 (overlapped, H-16), 6.83 (overlapped, H-15’), 6.97 (overlapped, H-12’).

ΔG^{298} calculations procedure from the ^{1}H temperature NMR spectra

For **1-4** the ΔG values were calculated using the Eyring's equation:

$$\Delta G_{Tc} = 4.58T_c * (10.32 + \log\frac{T_c}{k_c})$$

where T_c is the coalescence temperature and k_c is the rate constant at the coalescence temperature.

In order to calculate k_c from the NMR spectra, one has to measure the separation between the NMR signals (in Hz) at temperature far away from the coalescence temperature (Δν):

$$k_c = \frac{\pi * \Delta\nu}{\sqrt{2}}$$

Here, Δν values were measured for 230K.

Coalescence temperature is different for different signals and depends on the signal separation and the differences in the chemical environment of the given nucleus in both rotamers. In many cases the coalescence temperature exceeded the boiling point of the solvent (methanol). Then, it is possible to estimate T_c from linear approximation: one has to measure signals separation values in Hz (Δν) for different temperatures and find T at which Δν=0 (coalescence temperature).

The differences in the coalescence temperatures for different signals in the same compound result in the different Gibbs free energies. In order to calculate ΔG at 298K one can take the obtained ΔG values and plot them against temperatures for which they were calculated. Then, again from linear approximation, ΔG^{298} can be calculated. The Δν, T_c, k_c, and ΔG^{Tc} values obtained in the present paper are available upon request.

The applied ΔG^{298} calculation method implies the usage of linear approximation twice and therefore, despite very good linear correlations, the obtained results are encumbered with error and, as such, are only estimated values.