Supporting Information

New Bioactive Metabolites from *Penicillium purpurogenum* MM †

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† **Dedicated to Prof. Dr. A. Zeeck on the Occasion of his 75th Birthday**

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Table S1: Specific optical rotation values of (*S*)-tenellic acid B dimethyl acetal (**1a**), calculated with Gaussian'09, using the B3LYP functional and the 6-311G(2d, p) basis set [37]; 16 conformers within **3** kcal/mol above the global minimum were averaged on basis of their Boltzmann factors. On the right side, from top to bottom: (*S)*-conformers **1**, **2**, and **3**. 5

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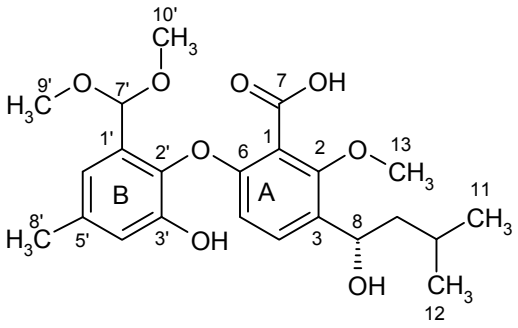
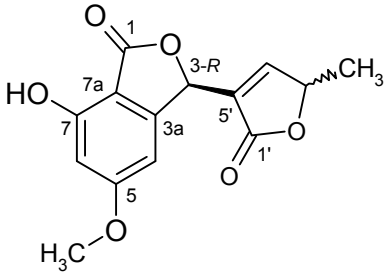


1a

1b: aldehyde at C-7'



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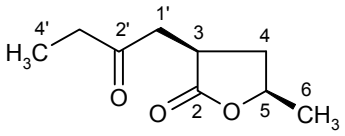

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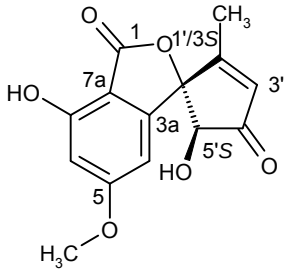


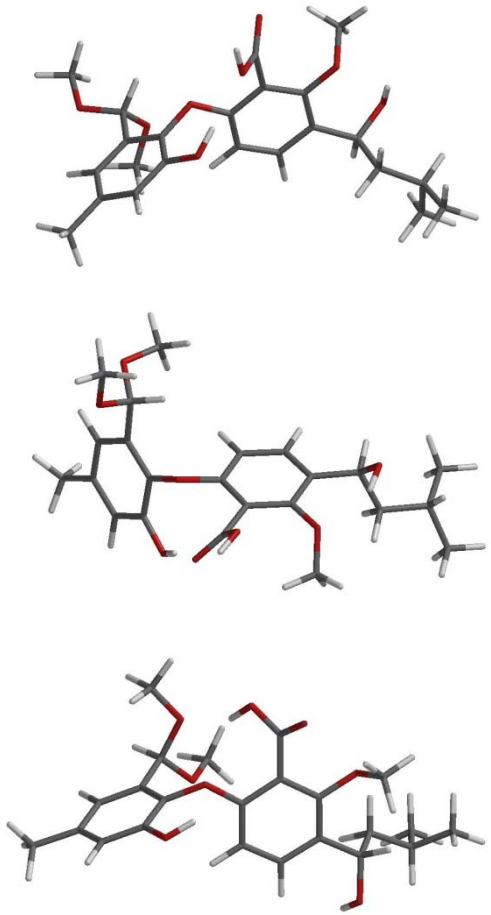
4a

4b: 5',7-diacetate

Figure S1. Chemical structures of compounds **1-4**

Table S1: Specific optical rotation values of (*S*)-tenellic acid B dimethyl acetal (**1a**), calculated with Gaussian'09, using the B3LYP functional and the 6-311G(2d, p) basis set [37]; 16 conformers within 4 kcal/mol above the global minimum were averaged on basis of their Boltzmann factors. On the right side, from top to bottom: (*S*)-conformers 1, 2, and 3.

		molar rotations of conformers				
Conformer	Boltzmann factor	λ = 589 nm	λ = 578 nm	λ = 546 nm	λ = 436 nm	λ = 365 nm
1	0.278	-349.8	-364.6	-413.7	-693.1	-1067.9
2	0.196	-445.2	-464.6	-529.3	-909.4	-1459.3
3	0.121	105.4	110.7	128.6	246.8	462.7
4	0.109	72.2	75.7	87.4	162.3	293.8
5	0.082	-402.6	-420.0	-477.8	-813.1	-1281.8
6	0.077	-331.6	-345.7	-392.7	-659.9	-1014.0
7	0.075	464.8	485.1	552.5	948.7	1527.4
8	0.041	34.4	36.3	42.9	89.5	184.4
9	0.008	194.4	202.5	229.0	374.7	549.3
10	0.005	386.0	403.0	459.9	797.5	1296.9
11	0.004	128.6	134.6	155.0	282.3	492.4
12	0.003	172.7	181.1	209.9	396.6	725.3
13	0.001	399.5	417.2	476.0	823.9	1333.3
14	0.001	305.5	318.8	362.9	619.6	982.6
15	0.000	-302.6	315.8	-359.9	-617.7	-985.7
16	0.000	151.4	158.4	182.0	327.8	561.3
molar rotation*)		**-181.85**	**-188.85**	**-214.06**	**-355.97**	**-539.77**
specific rotation*)		**-4.17**	**-4.35**	**-4.93**	**-8.19**	**-12.42**



*) Boltzmann-averaged

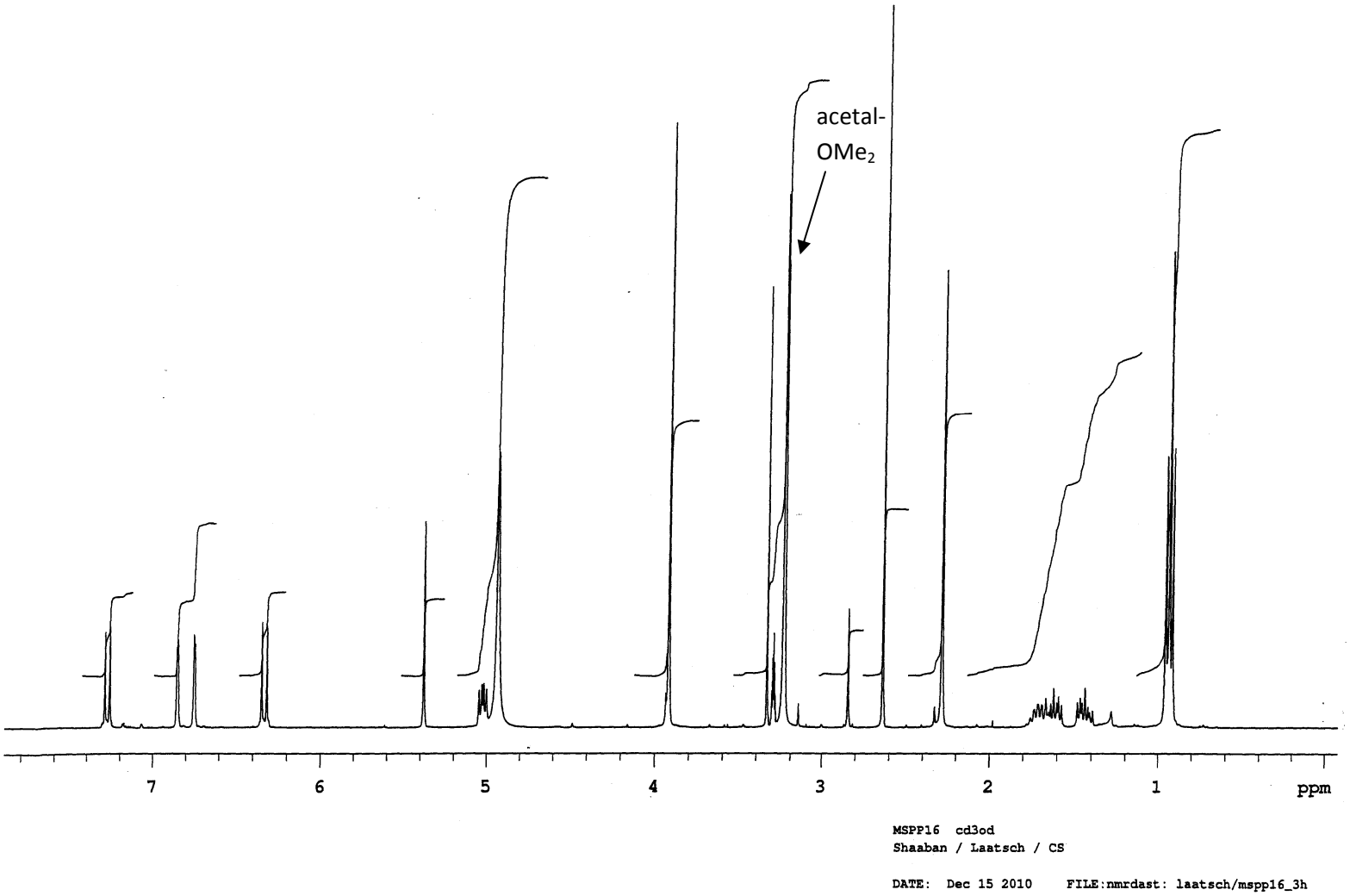


Figure S2. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of tenellic acid B dimethyl acetal (**1a**)

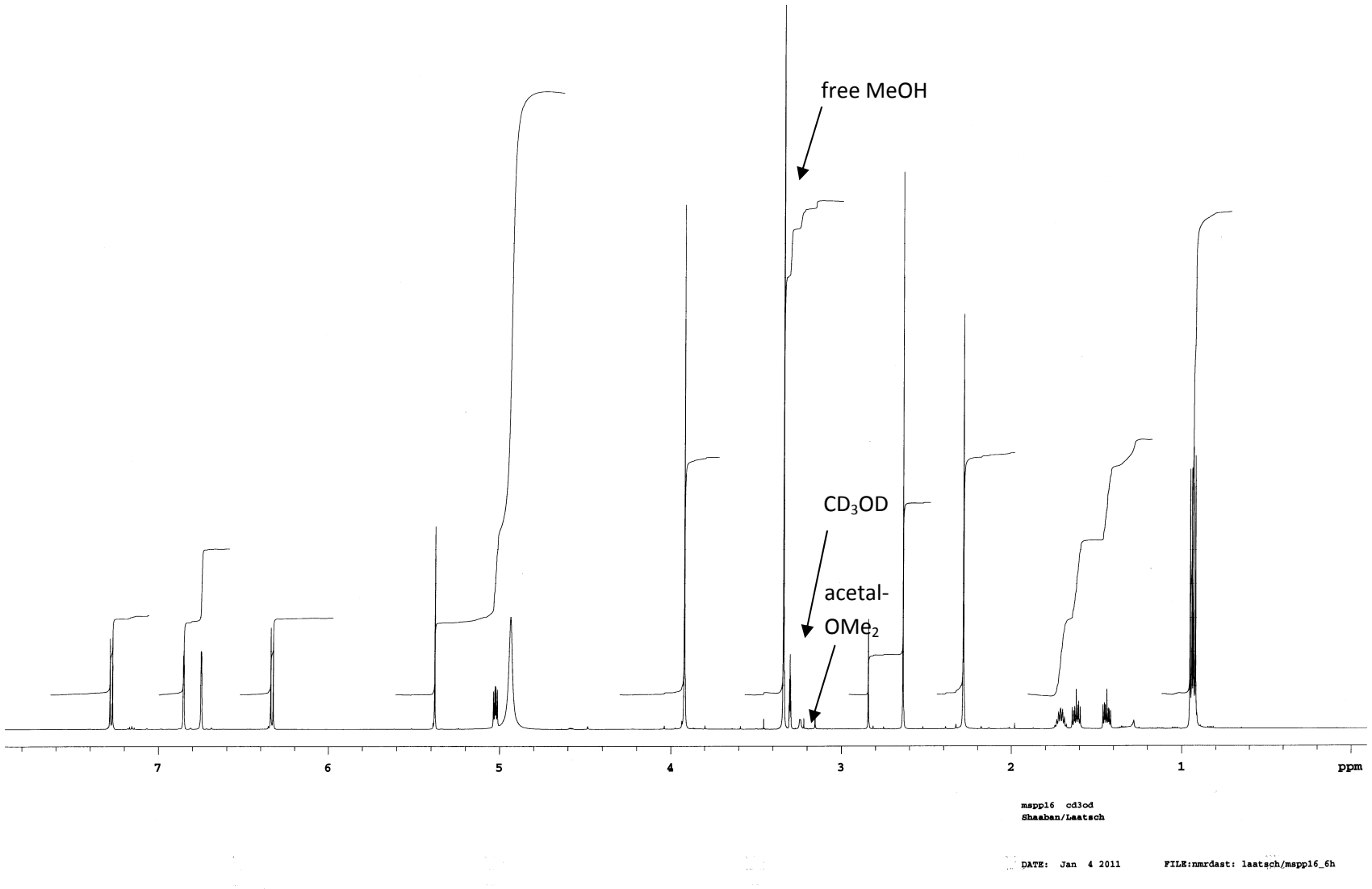


Figure S3. ^{1}H NMR spectrum (CD_3OD, 600 MHz) of tenellic acid B dimethyl acetal (**1a**) after $(OCH_3)_2/(OCD_3)_2$ exchange

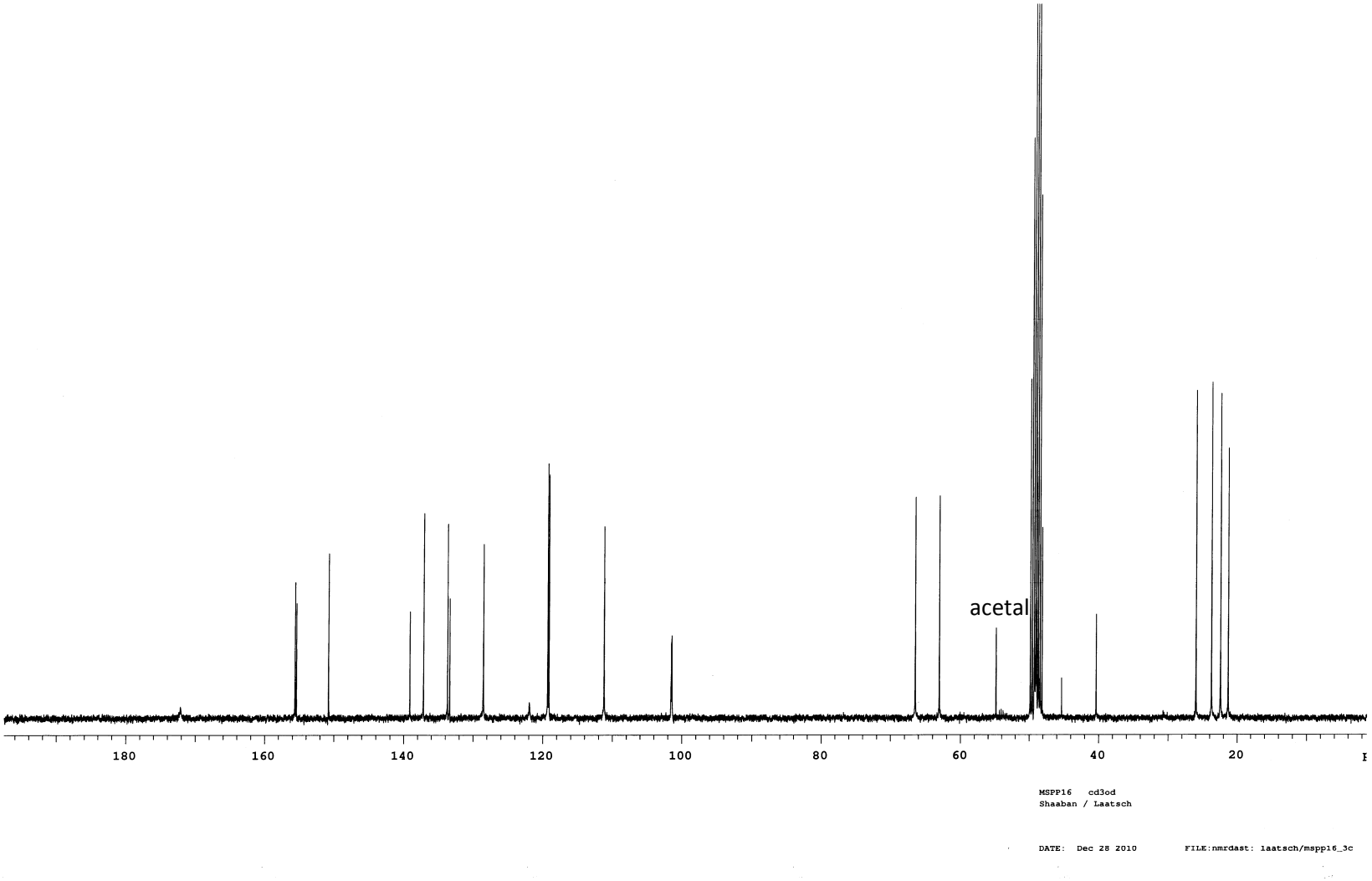


Figure S4. ^{13}C NMR spectrum (CD_3OD, 75 MHz) of tenellic acid B dimethyl acetal (**1a**)

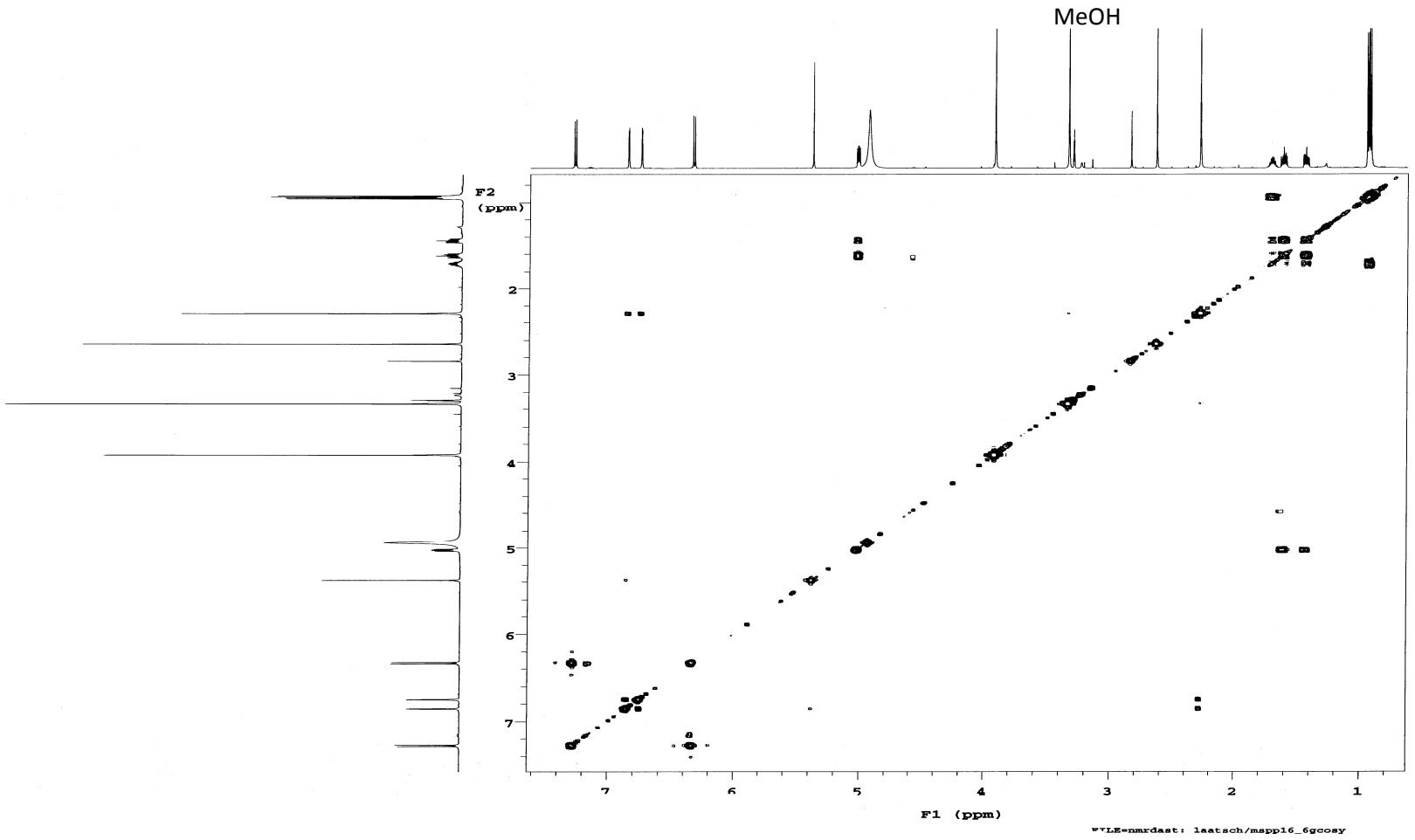


Figure S5. ^{1}H-^{1}H-COSY spectrum (CD_3OD, 600 MHz) of tenellic acid B dimethyl acetal (**1a**)

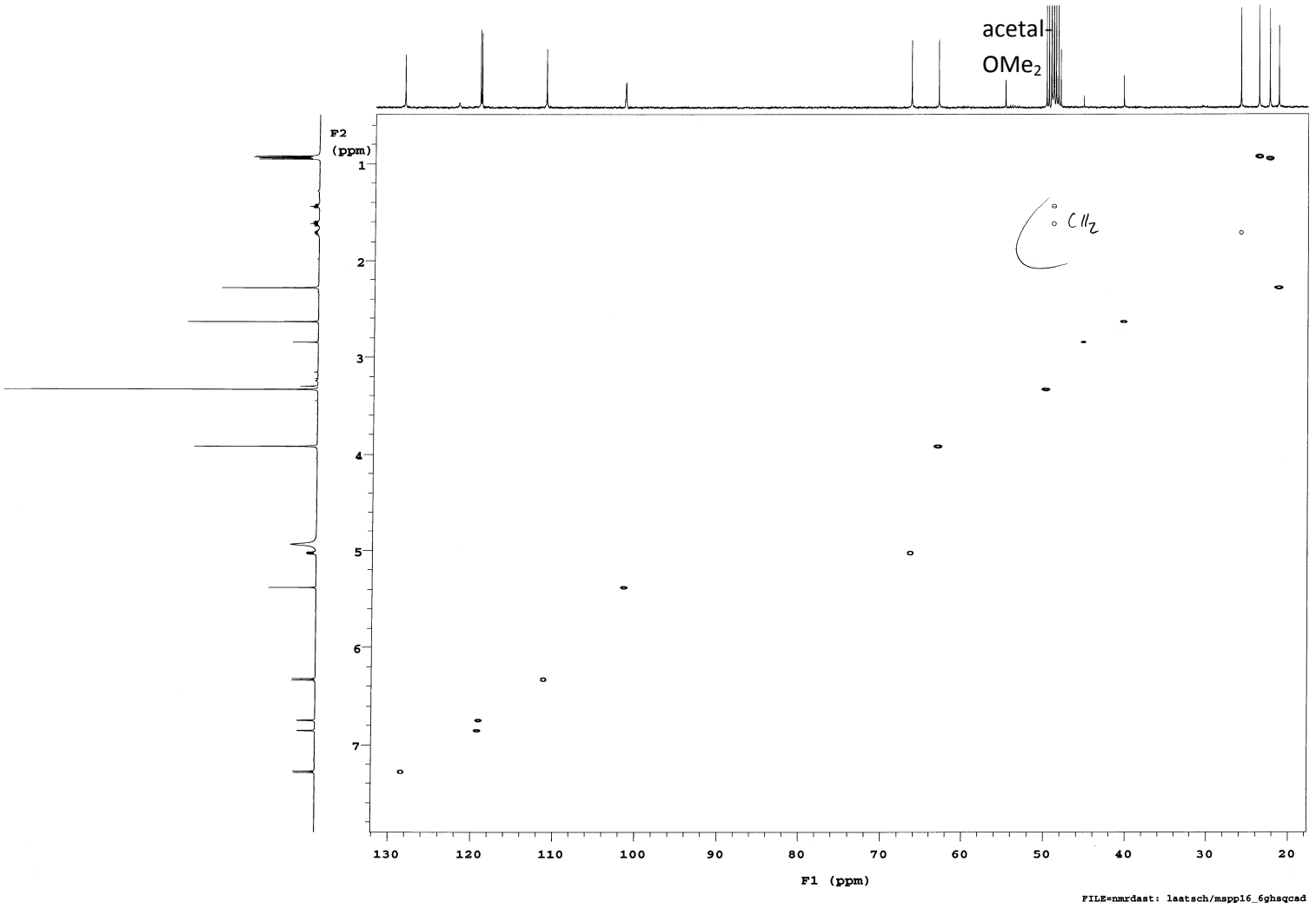


Figure S6. HSQC spectrum (CD_3OD, 600 MHz) of tenellic acid B dimethyl acetal (**1a**)

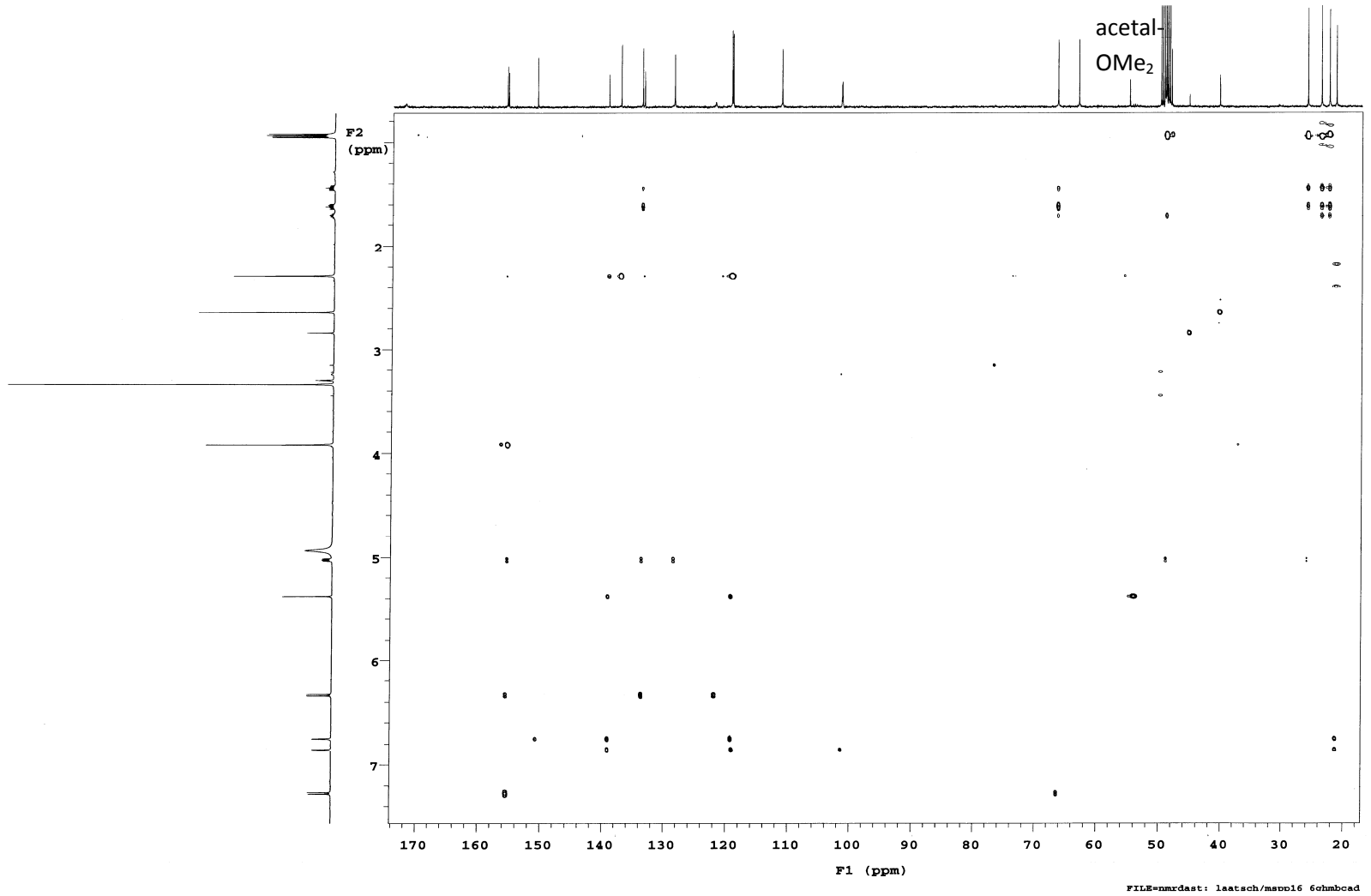


Figure S7. HMBC spectrum (CD_3OD, 600 MHz) of tenellic acid B dimethyl acetal (**1a**)

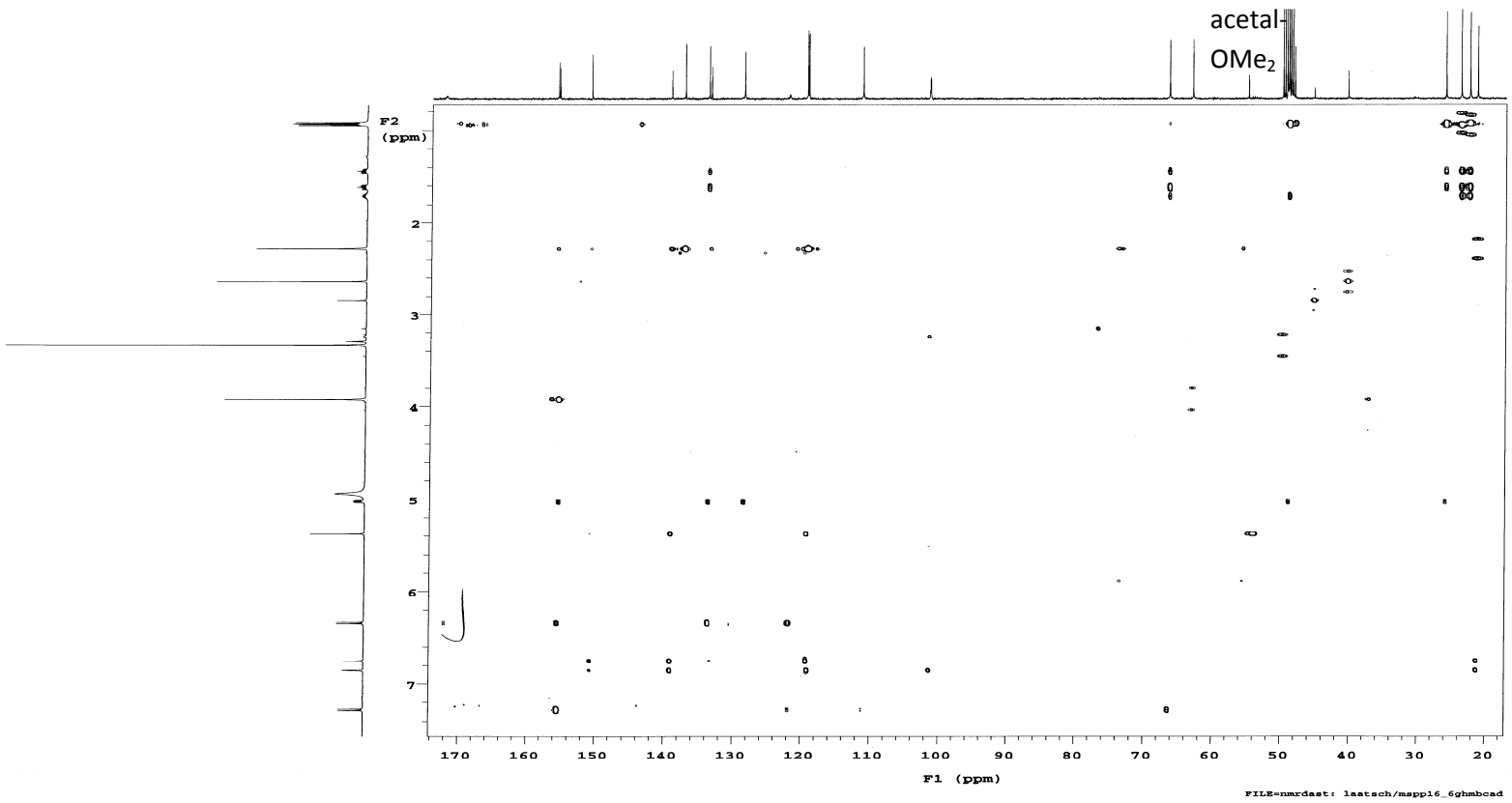
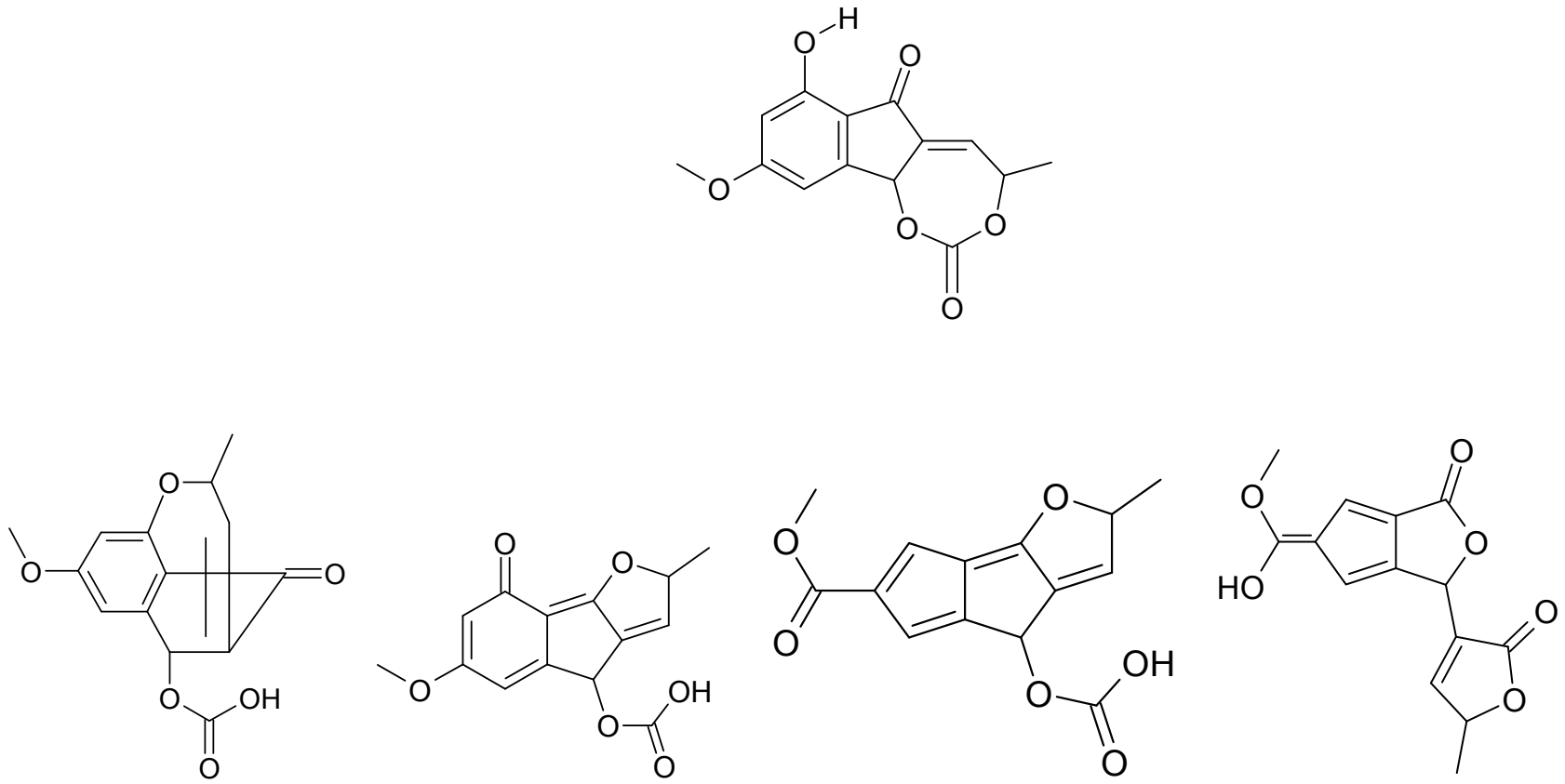


Figure S8. HMBC spectrum (CD_3OD, 600 MHz) of tenellic acid B dimethyl acetal (**1a**)



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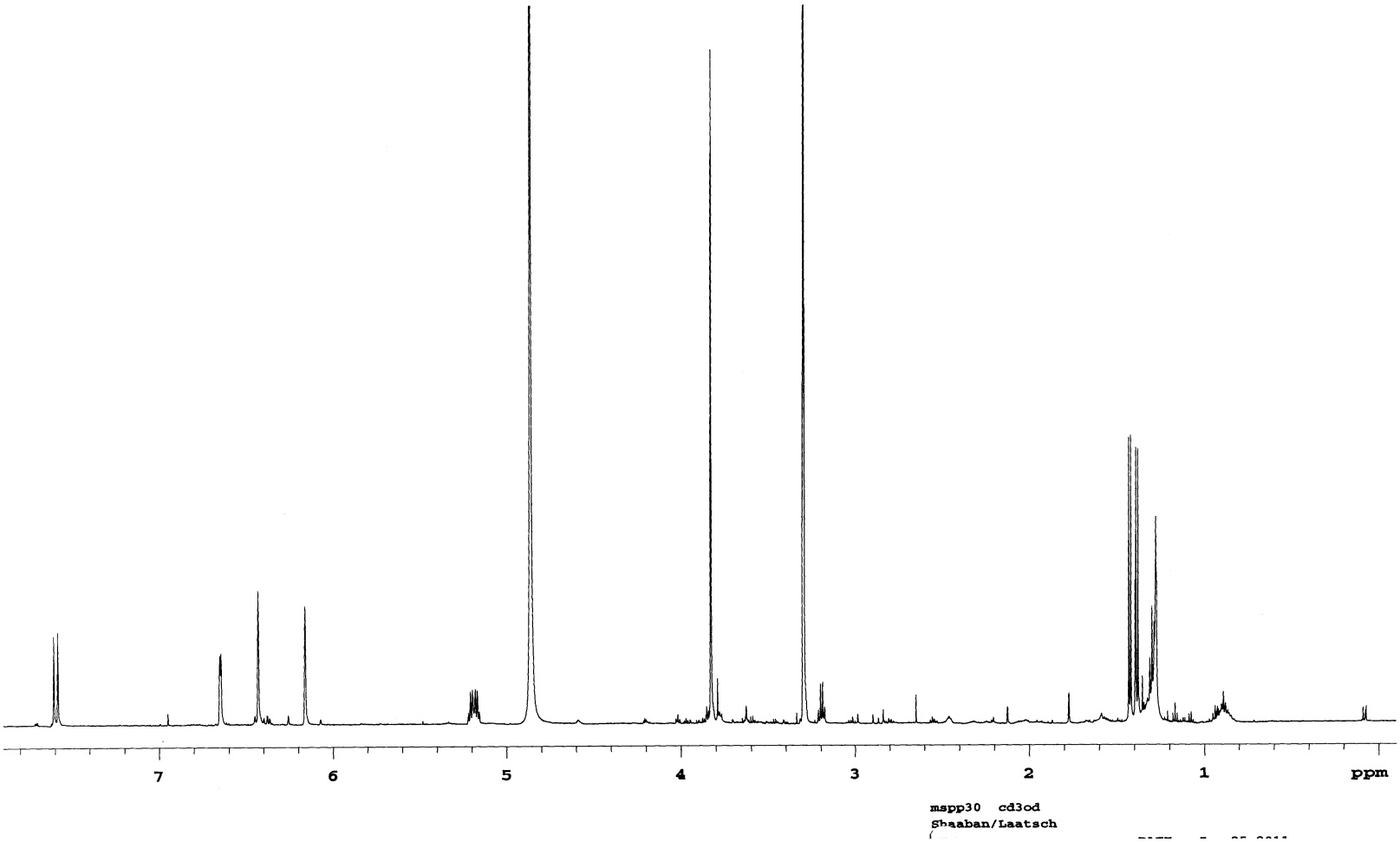


Figure S10. ^{1}H NMR spectrum (CD_3OD, 600 MHz) of isotalarone (**2**)

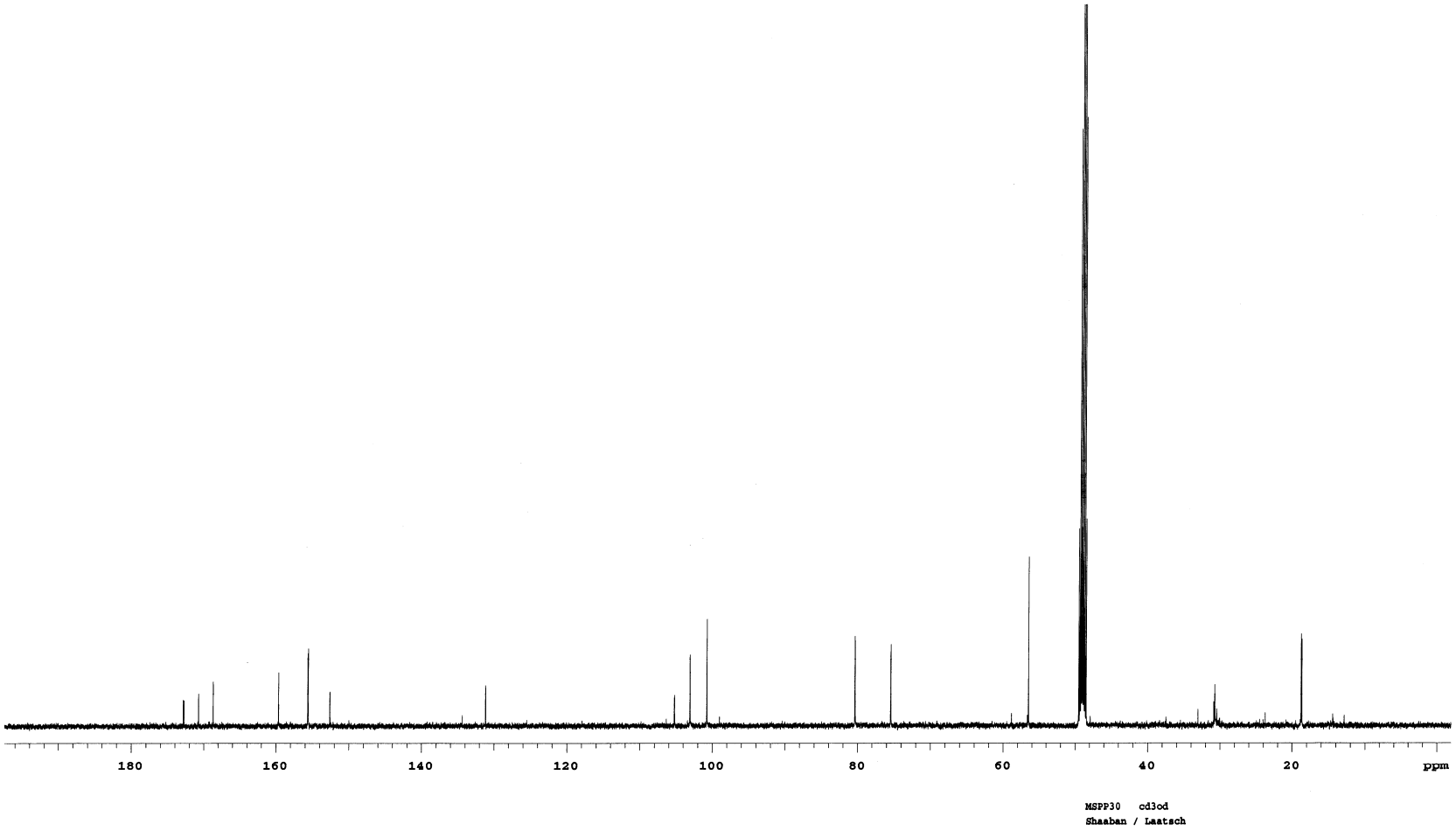


Figure S11. ^{13}C NMR spectrum (CD_3OD, 125 MHz) of isotalarone (**2**)

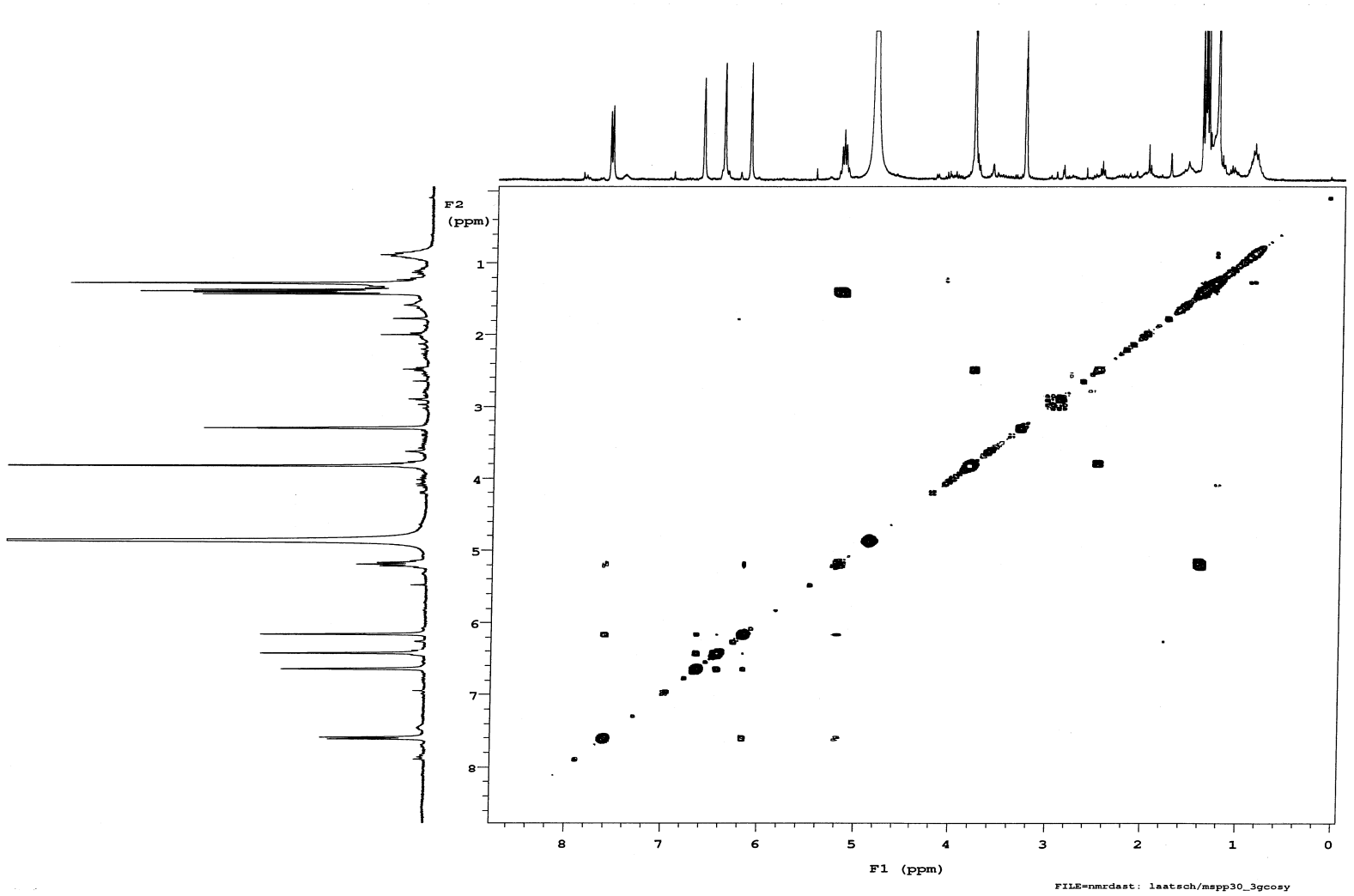


Figure S12. ^{1}H-^{1}H-COSY spectrum (CD_3OD, 300 MHz) of isotalarone (**2**)

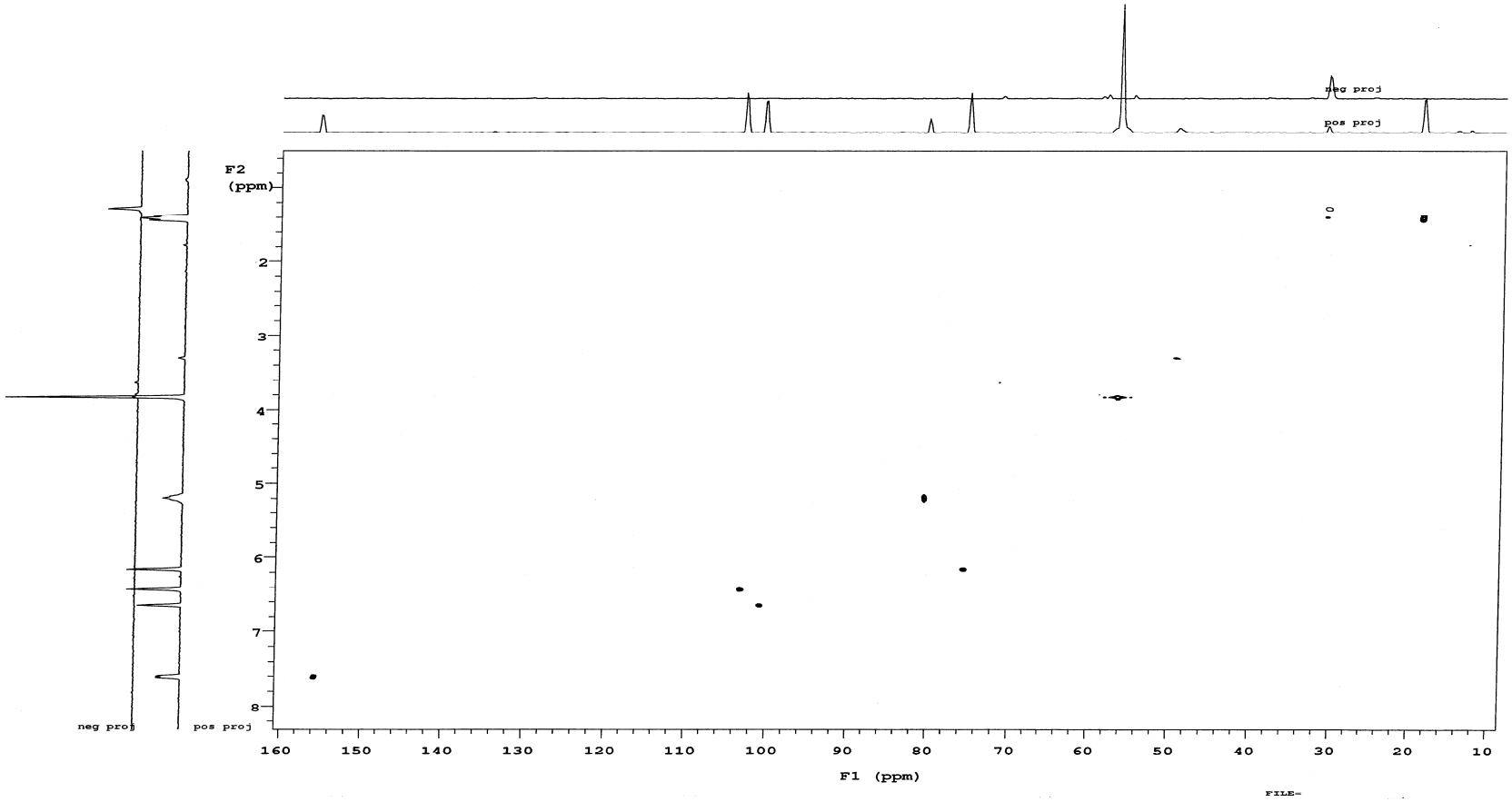


Figure S13. HSQC spectrum (CD_3OD, 300, 75 MHz) of isotalarone (**2**)

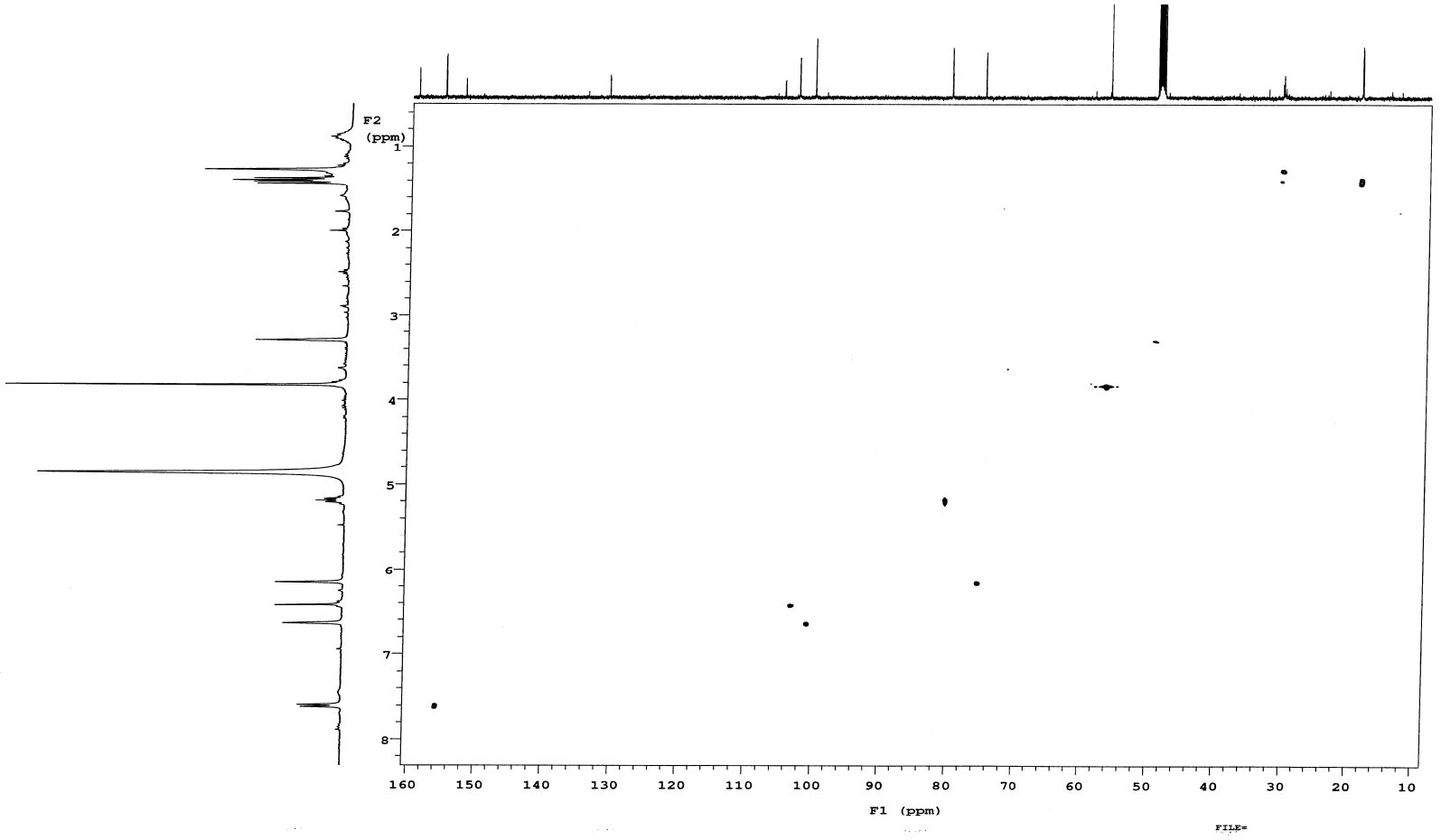


Figure S14. HSQC spectrum (CD_3OD, 300, 75 MHz) of isotalarone (**2**)

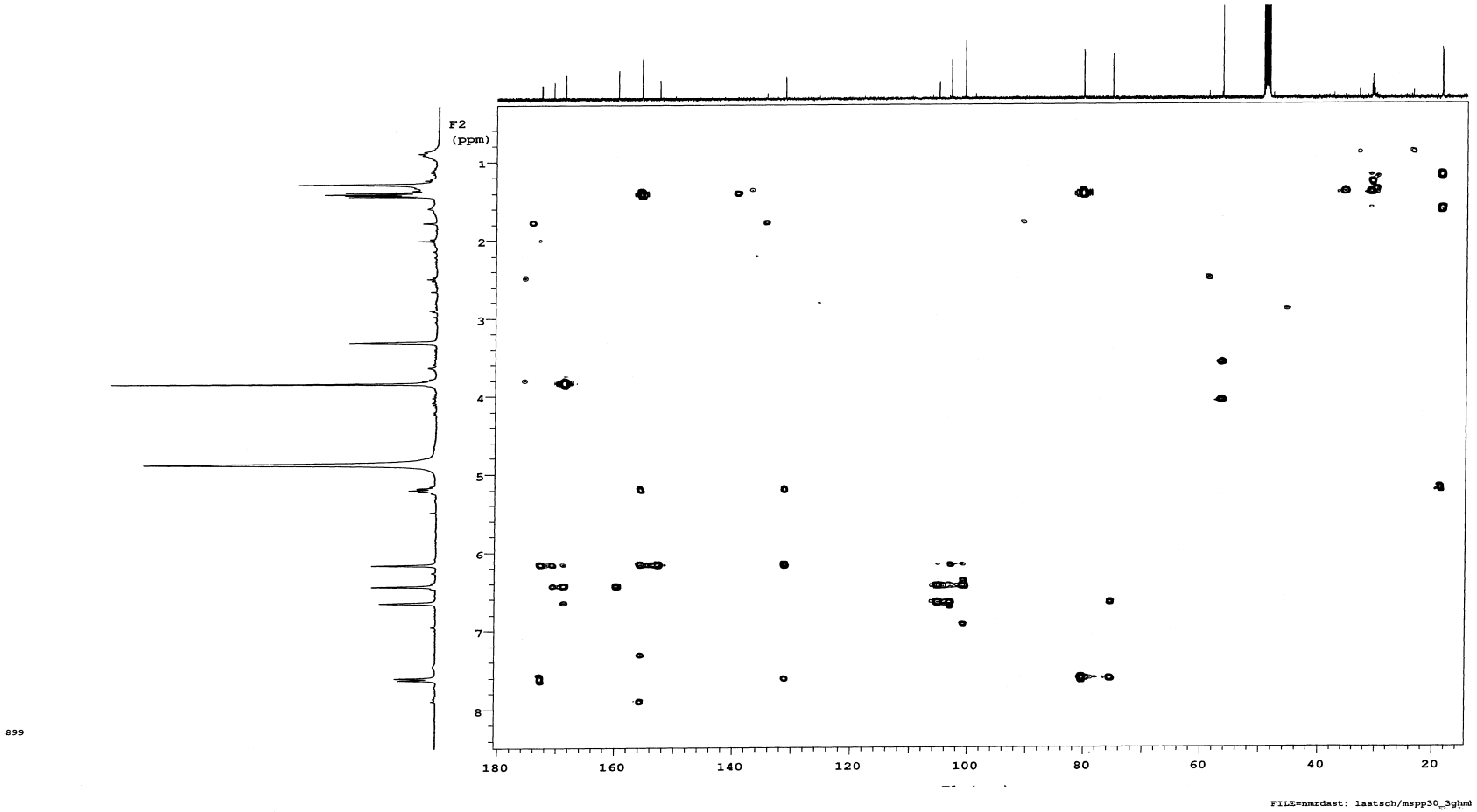


Figure S15. HMBC spectrum (CD_3OD, 300, 75 MHz) of isotalarone (**2**)

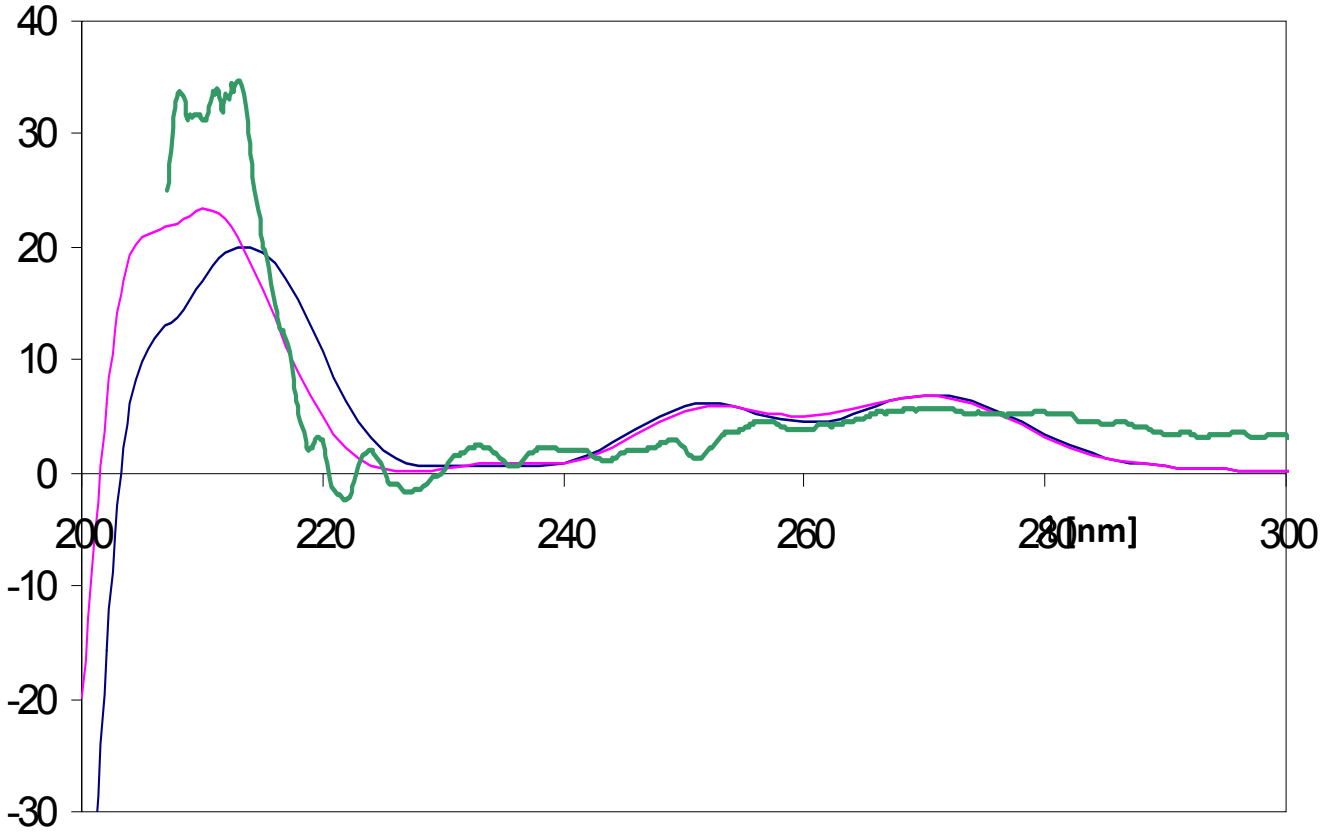
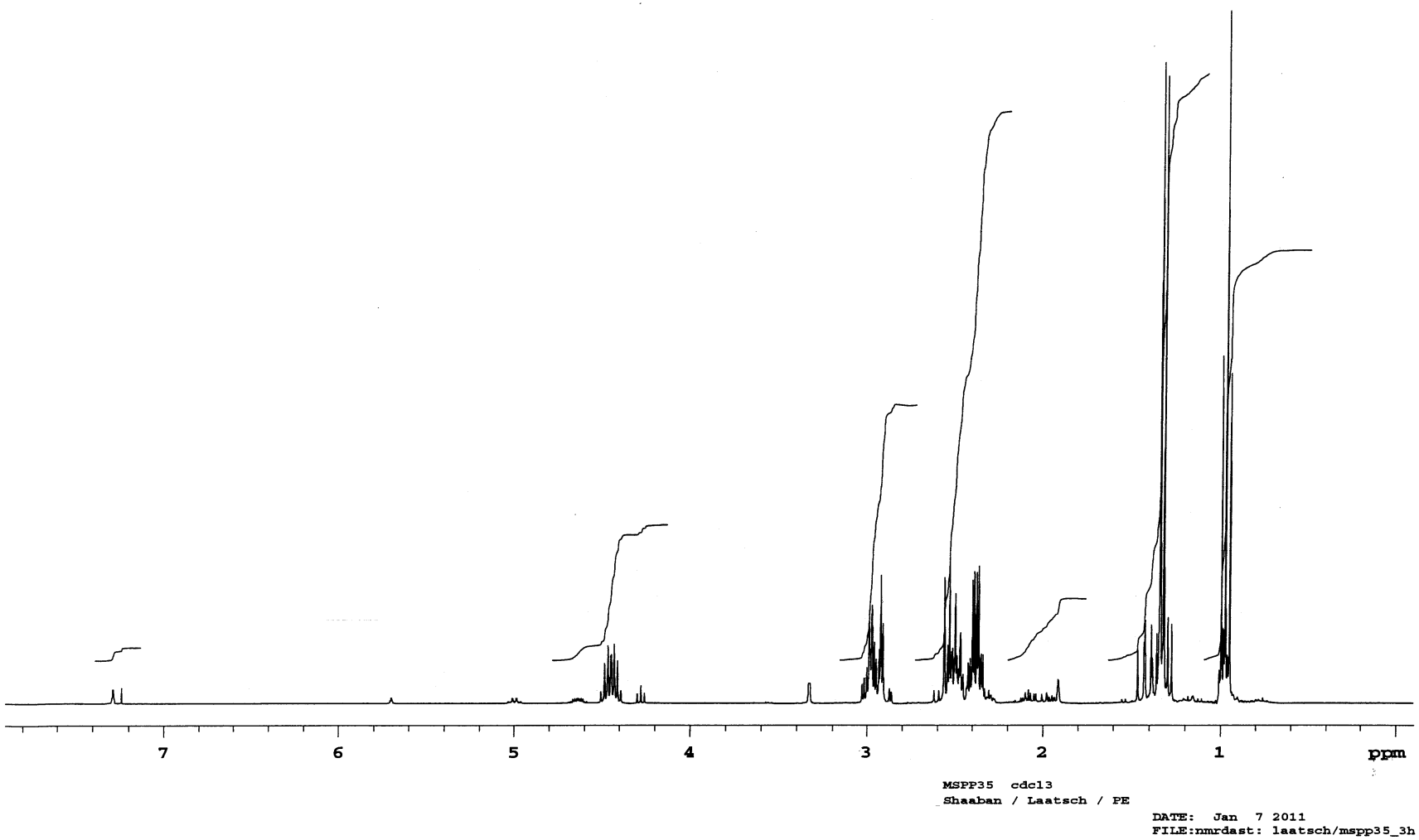


Figure S16. Experimental CD spectrum of isotalarone (**2**) in methanol (—), in comparison with the (3*R*,3'*R*) (—) and (3*R*,3'*S*) (—) isomers.



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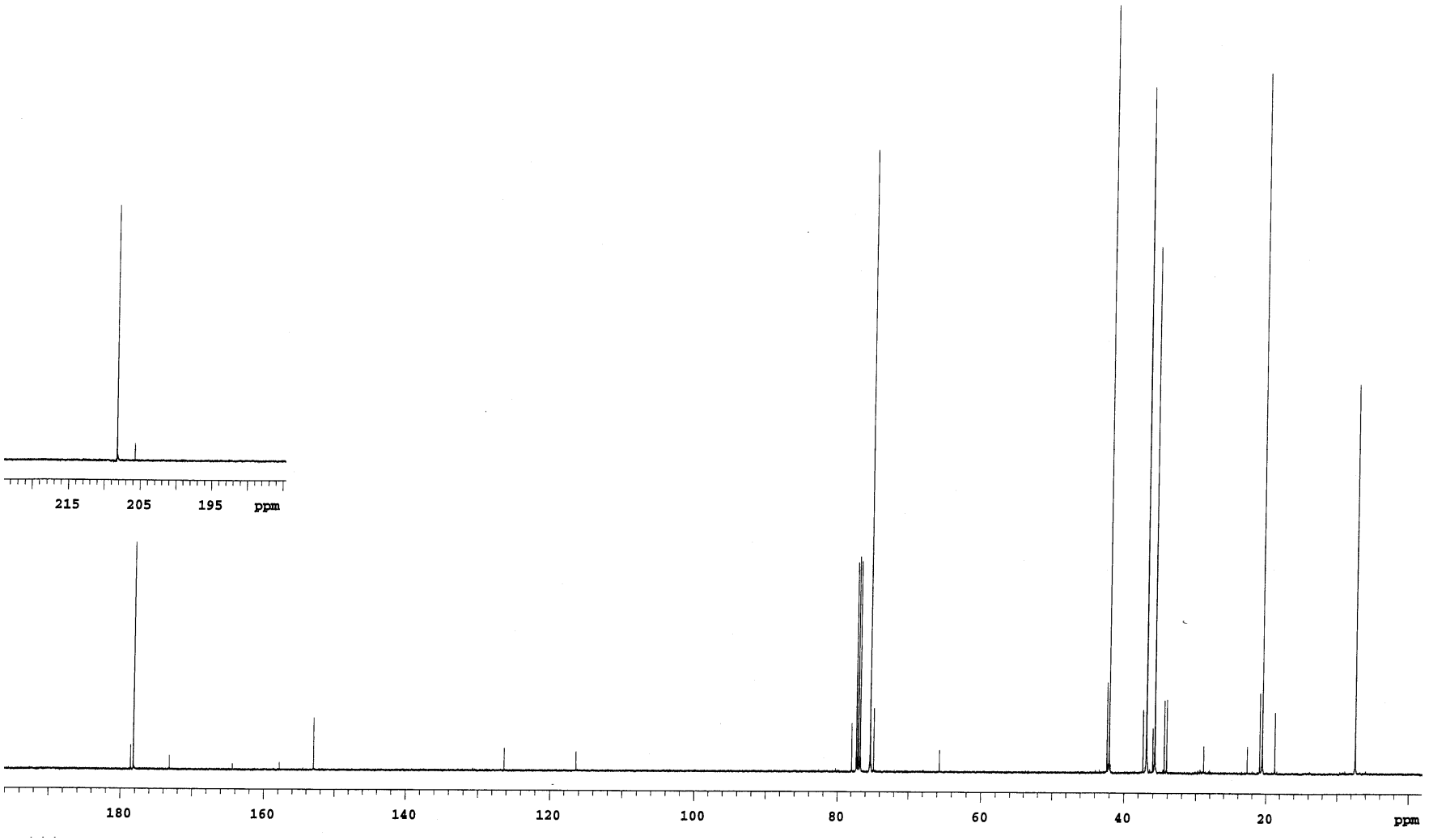
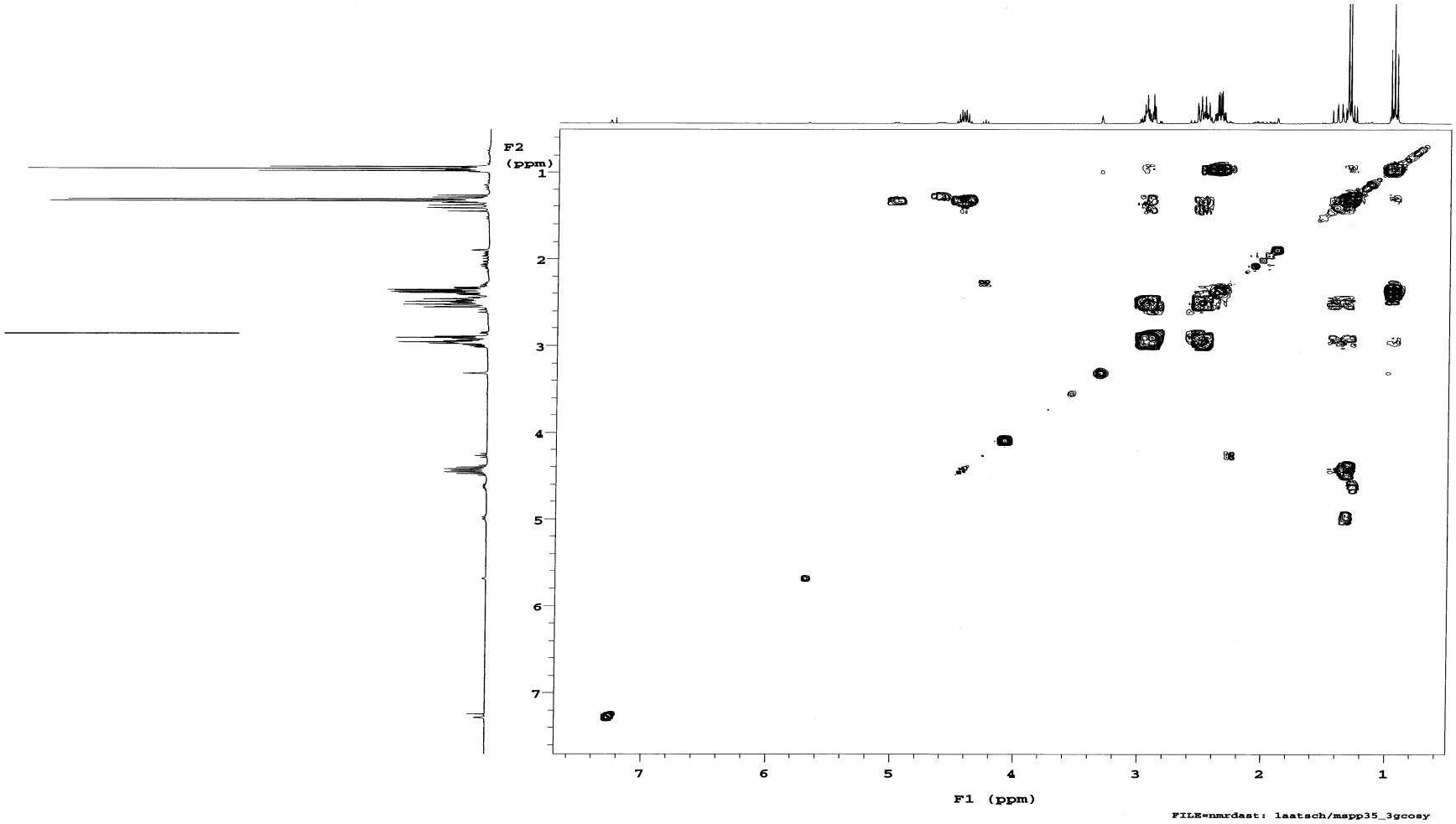


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of (3*R*,5'*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one (**3**)



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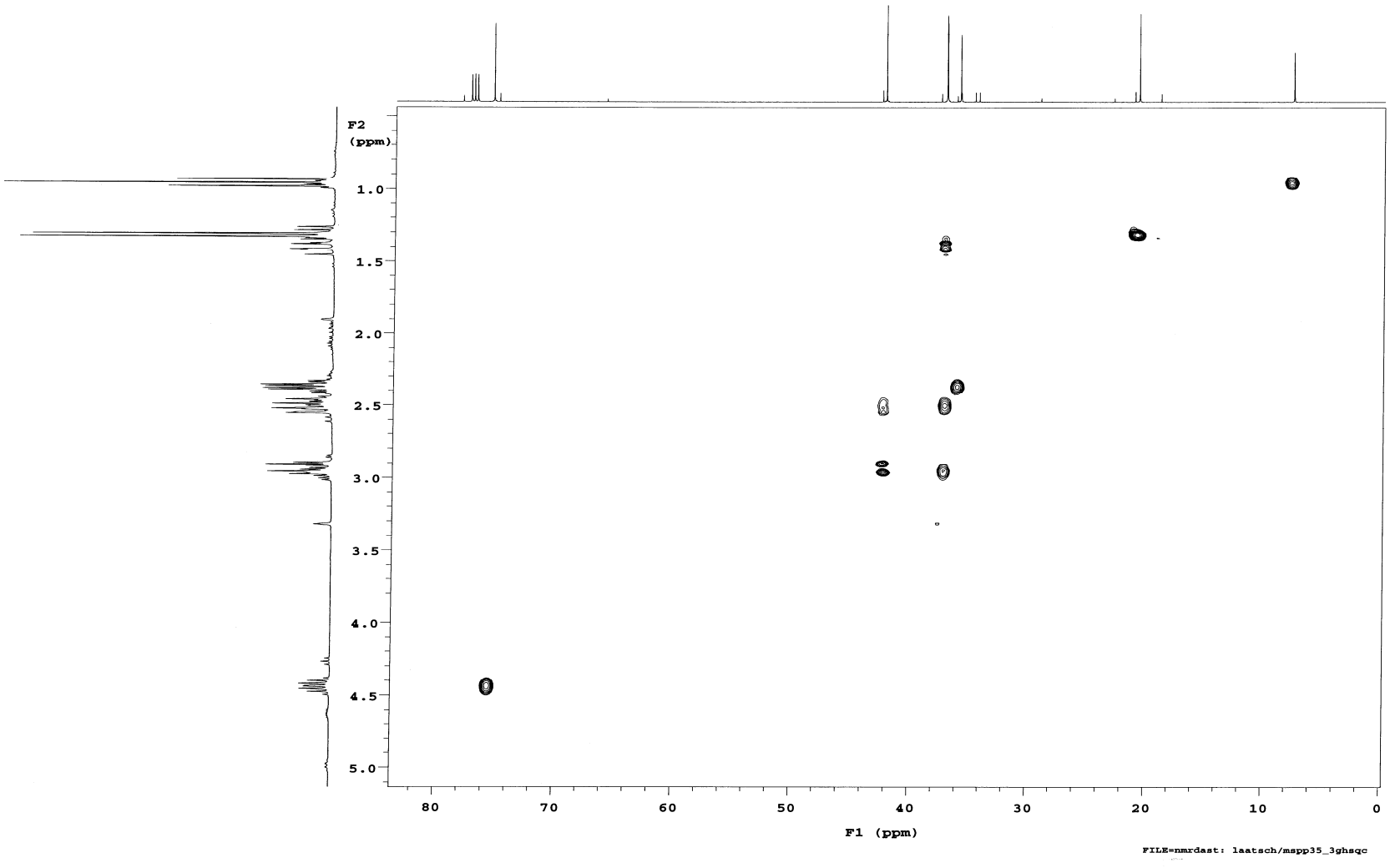


Figure S20. HSQC spectrum ($CDCl_3$, 125 MHz) of (3*R*,5'*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one (**3**)

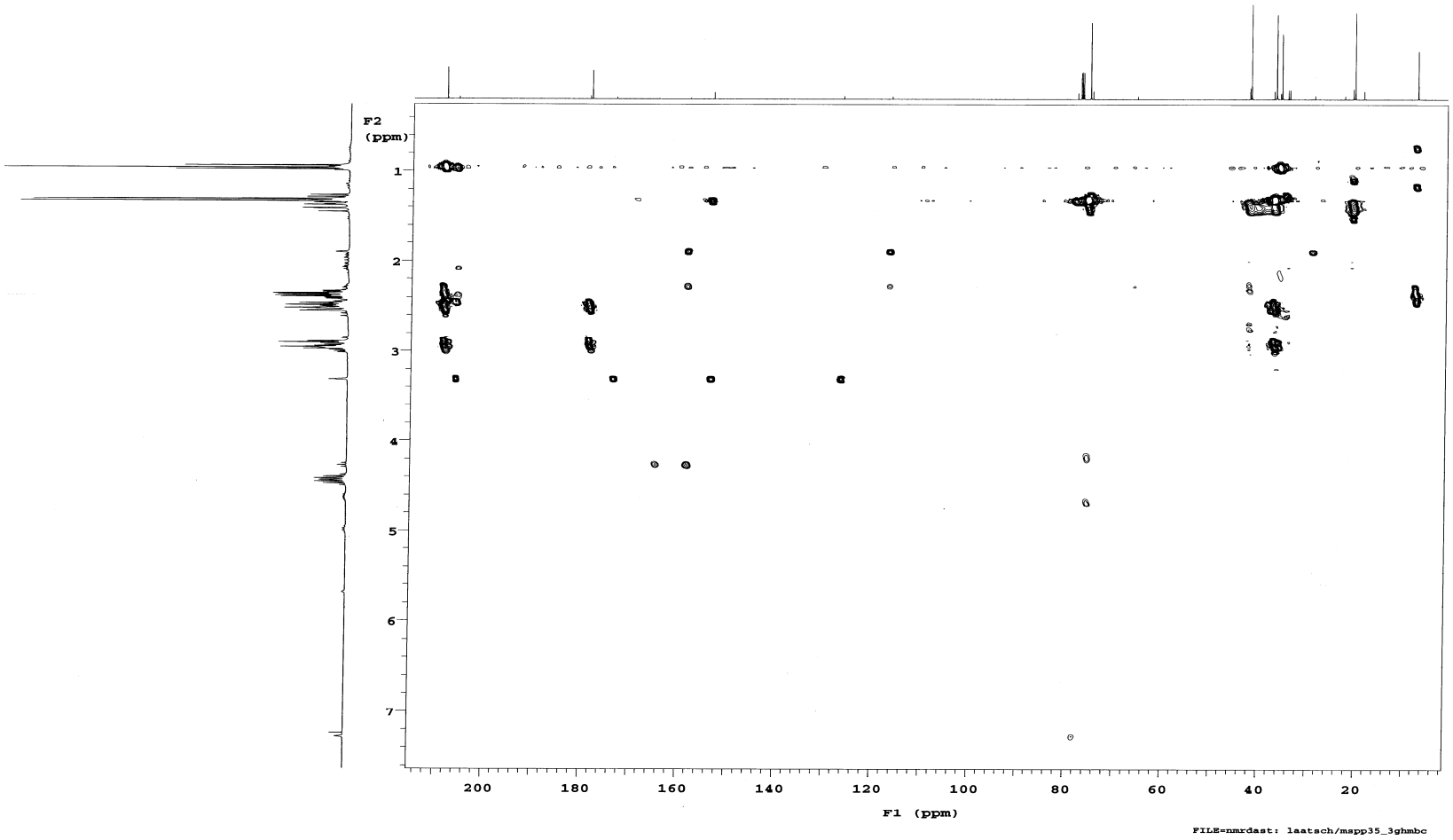


Figure S21. HMBC spectrum ($CDCl_3$, 125 MHz) of (3*R*,5'*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one (**3**)

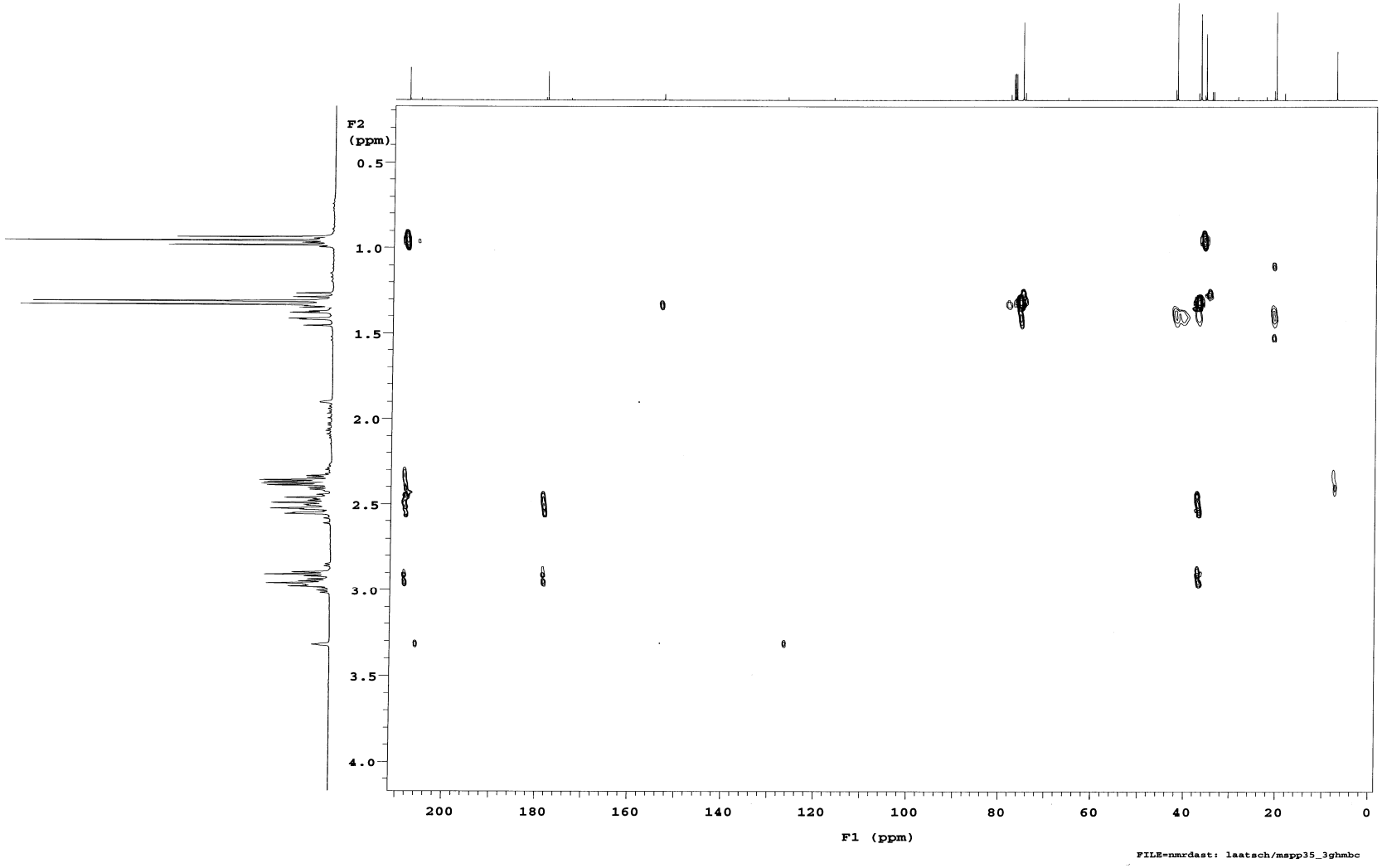


Figure S22. HMBC spectrum ($CDCl_3$, 125 MHz) of (3*R*,5'*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one (**3**)

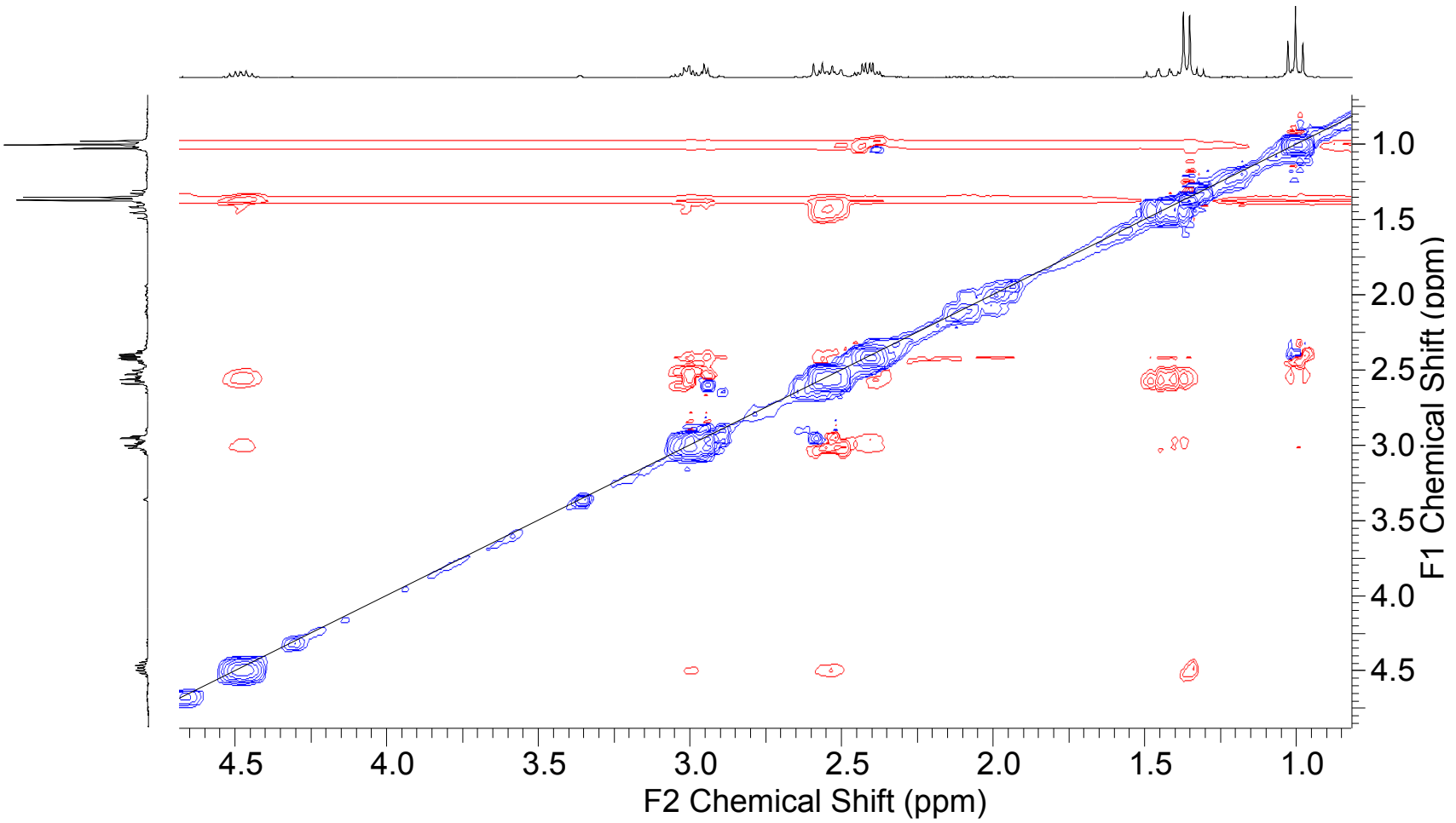


Figure S23. NOESY spectrum ($CDCl_3$, 300 MHz) of (3*R*,5'*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one (**3**)

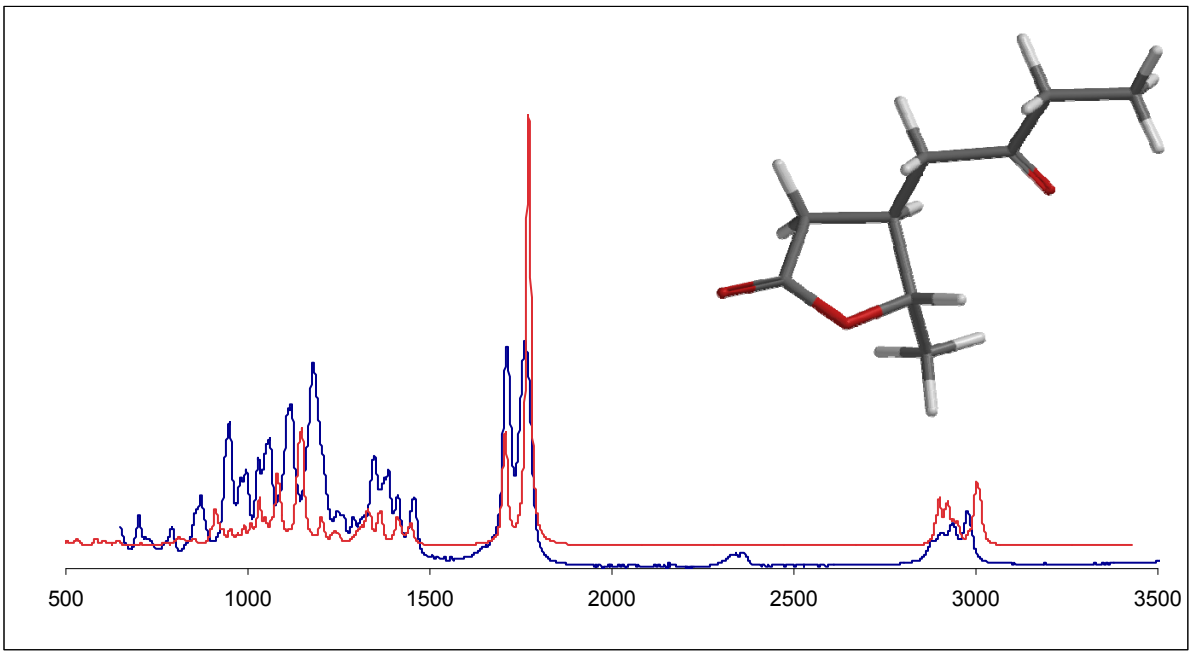


Figure S24. IR spectrum of (4*R*,5*S*)-*trans*-5-methyl-4-(2-oxo-butyl)-dihydrofuran-2-one calculated with Gaussian 09 (red line); blue line = exp. spectrum, neat **3**.

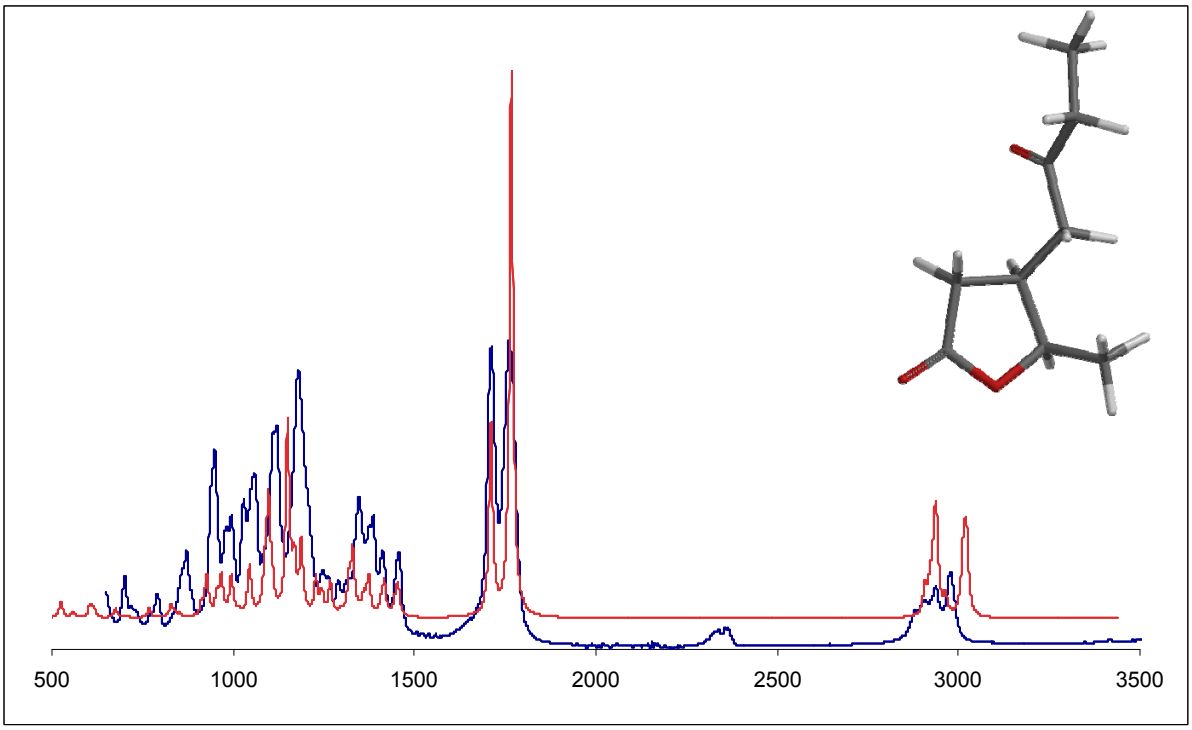


Figure S25. IR spectrum of (4*R*,5*R*)-*cis*-5-methyl-4-(2-oxo-butyl)-dihydrofuran-2-one calculated with Gaussian 09 (red line); blue line = exp. spectrum, neat **3**.

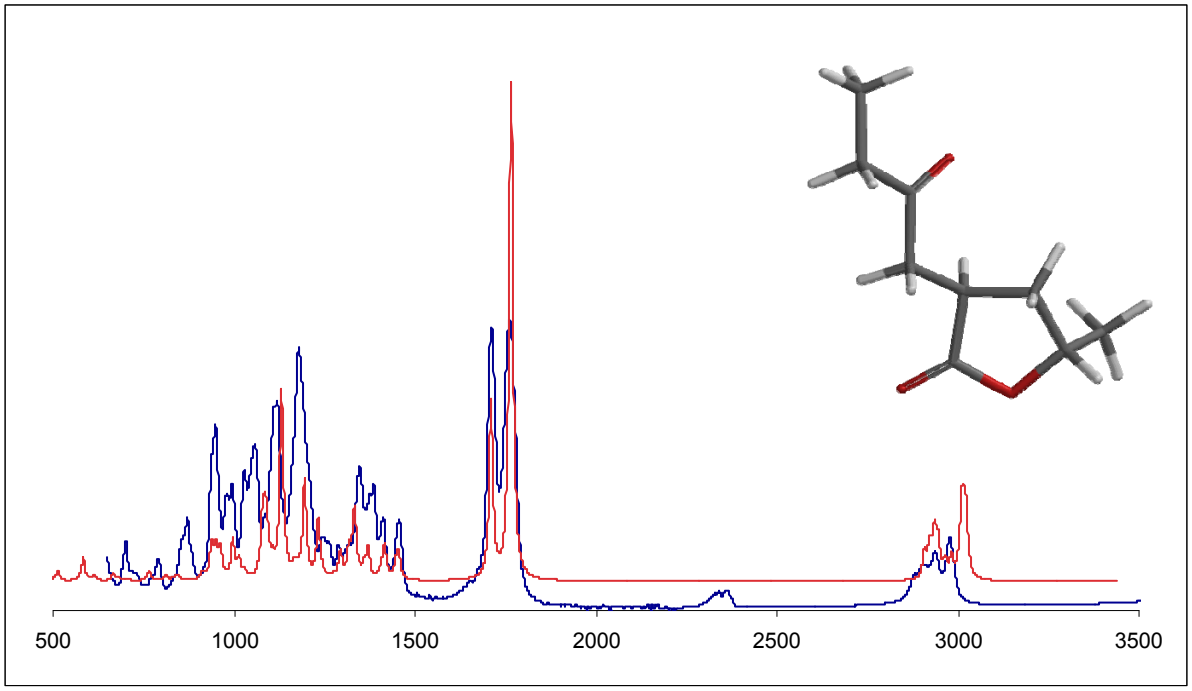


Figure S26. IR spectrum of (3*R*,5*S*)-*trans*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one, calculated with Gaussian 09 (red line); blue line = exp. spectrum, neat **3**.

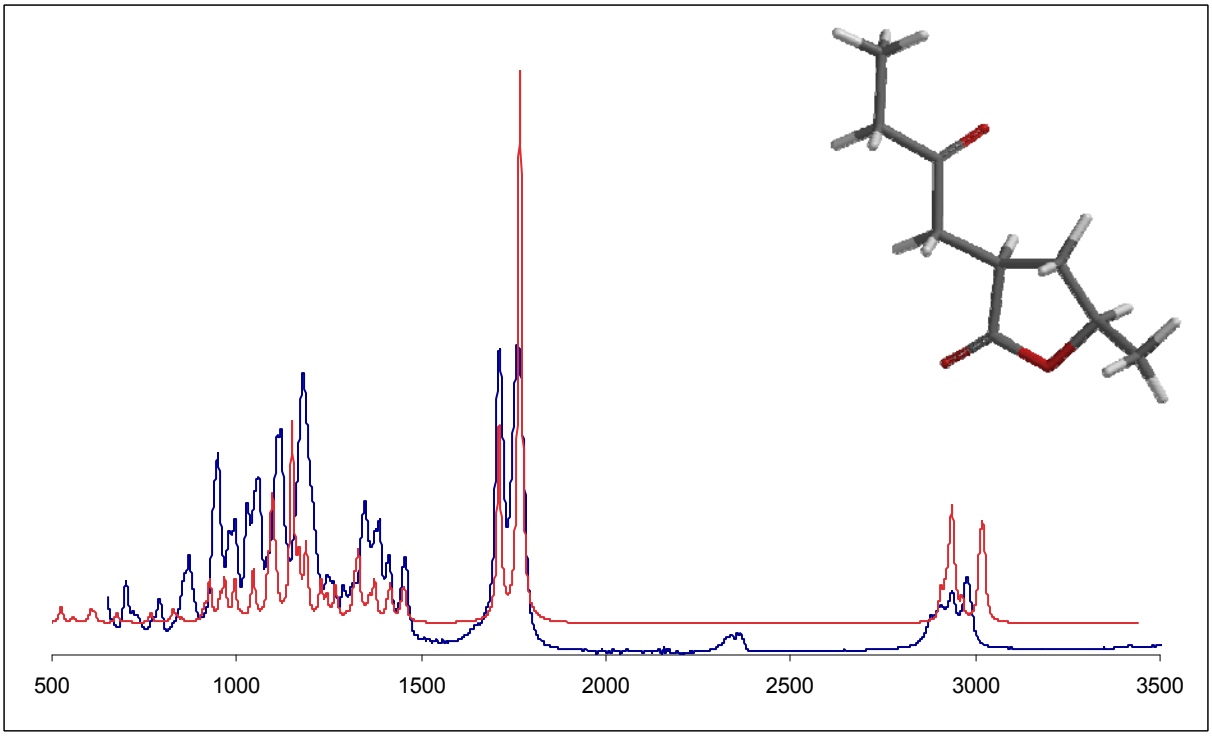


Figure S27. IR spectrum of (3*R*,5*R*)-*cis*-5-methyl-3-(2-oxo-butyl)-dihydrofuran-2-one, calculated with Gaussian 09 (red line); blue line = exp. spectrum, neat **3**.

Table S 2: Experimental ^{13}C NMR data (125 MHz, CD_3OD) and calculated shifts of (3*R*,3'*S*)-isotalarone (**2**) and its (3*R*,3'*R*) isomer (SPARTAN'14, 2014).

C	**natural 2** δ_C [a)]	(3*R*,3'*S*)-**2** δ_C [b)]	(3*R*,3'*R*)-**2** δ_C [b)]
1	**170.7**	172.2	172.2
3	**75.4**	76.6	76.6
3a	**152.6**	148.7	148.8
4	**100.7**	99.7	99.9
5	**168.7**	167.8	167.8
6	**103.1**	102.5	102.4
7	**159.1**	160.8	160.8
7a	**105.3**	101.8	101.8
OMe	**56.6**	54.9	54.9
1'	**172.9**	170.3	170.2
3'	**80.4**	76.6	76.6
4'	**155.7**	147.0	149.9
5'	**131.2**	133.8	133.9
6' (Me)	**18.8**	18.4	18.4
		$\Sigma\,|\Delta\delta_{exp\text{-}calc}|$ = 34.1	**$\Sigma\,|\Delta\delta_{exp\text{-}calc}|$ = 34.2**

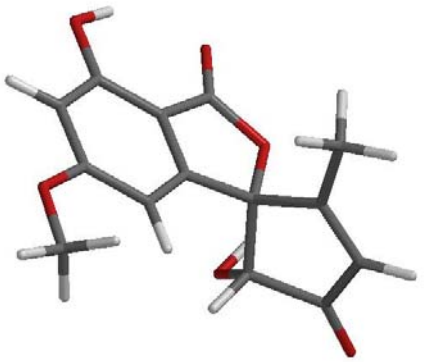
[a)] Due to the mixture of (3*R*,3'*R/S*)-diastereomers, all carbon signals appeared in duplicate with a shift difference of $\Delta\delta \approx 0.05\text{-}0.15$ ppm.

[b)] Boltzmann-averaged shifts from the main conformers (99% occupation)

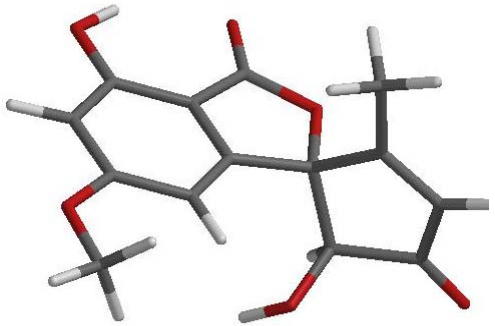
Table S3: Specific optical rotation values of (3*S*,5'*R*)- and (3*S*,5'*S*)-talaroflavones (**4**), calculated with Gaussian'09, using the WB97XD functional and the 6-311G(d,p) basis set [37]; all conformers within 4 kcal/mol above the global minimum were averaged on basis of their Boltzmann factors.

		molar rotations of conformers				
(3*S*,5'*R*)-Conformers	Boltzmann factor	λ = 589 nm	λ = 578 nm	λ = 546 nm	λ = 436 nm	λ = 365 nm
1a	0.437	36.69	37.63	40.11	21.97	-379.74
2a	0.437	36.69	37.63	40.11	21.97	-379.74
3a	0.077	295.62	310.45	361.19	710.18	1525.36
4a	0.050	321.30	337.42	392.57	770.13	1625.78
5a	0.000	53.23	54.92	59.90	56.55	-341.11
molar rotation*)		**70.76**	**73.52**	**82.34**	**112.11**	**-133.49**
specific rotation*)		**2.56**	**2.66**	**2.98**	**4.06**	**-4.83**
(3*S*. *5'S*)-Conformers						
1b	0.194	254.00	266.93	311.21	613.60	1226.89
2b	0.193	254.37	267.32	311.66	614.41	1228.29
3b	0.139	274.90	288.86	336.64	661.54	1310.38
4b	0.194	254.05	266.98	311.27	613.75	1227.20
5b	0.140	274.54	288.48	336.21	660.78	1309.09
6b	0.001	271.95	285.54	332.02	649.04	1337.89
7b	0.139	274.52	288.46	336.19	660.82	1309.32
8b	0.000	242.29	254.61	296.80	584.68	1167.84
molar rotation*)		**262.73**	**276.09**	**321.83**	**633.65**	**1261.89**
specific rotation*)		**9.51**	**9.99**	**11.65**	**22.94**	**45.68**

*) Sum of Boltzmann-averaged values



(3*S*,5'*R*)-**4**



(3*S*,5'*S*)-**4** (natural **4**)

Table S4: Experimental ^{13}C (75 MHz) and ^{1}H NMR data (300 MHz) in CD_3OD), and calculated shifts of (3*S*,5'*S*)-talaroflavone-diacetate (**4b**) and its unnatural (3*S*,5'*R*) isomer (SPARTAN'14, 2014).

C	natural **4b**		calcd. (3*S*,5*R*)-**4b**		calcd. (3*S*,5*S*)-**4b**	
	δ_C [a)]	δ_H [a)]	δ_C	δ_H	δ_C	δ_H
1	168.1		166.5		165.8	
3/1'	92.7		86.6		90.3	
3a	151.5		152.9		149.7	
4	106.7	6.61	101.5	6.56	103.3	6.64
5	167.2		166.0		165.2	
5-OMe	57.2	np	54.7	3.82	54.7	3.80
6	112.1	6.93	109.6	6.72	110.6	6.74
7	149.5		152.6		152.2	
7-OAc (CO)	170.0		171.9		169.9	
7-OAc (Me)	19.8	2.35	18.3	2.45	18.4	2.46
7a	112.4		111.1		111.4	
2'	172.0		175.5		174.3	
2'-Me	13.3	np	14.5	2.00	14.4	2.03
3'	133.2	np	132.3	6.26	129.9	6.22
4'	197.1		198.8		195.4	
5'	78.1	5.81	75.9	5.29	77.6	6.55
5'-OAc (CO)	170.8		170.2		170.2	
5'-OAc (Me)	20.4	1.82	19.3	2.15	19.3	1.88
			$\Sigma\ |\Delta\delta_{exp-calc}| = 39.5$		**$\Sigma\ |\Delta\delta_{exp-calc}| = 31.7$**	

[a)] Shift values reported by Ayer and Racok (1990); np = not published