Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Atropisomerism of a monosubstituted perfluoro[2.2]paracyclophane. A combined synthetic, kinetic, spectroscopic and computational study

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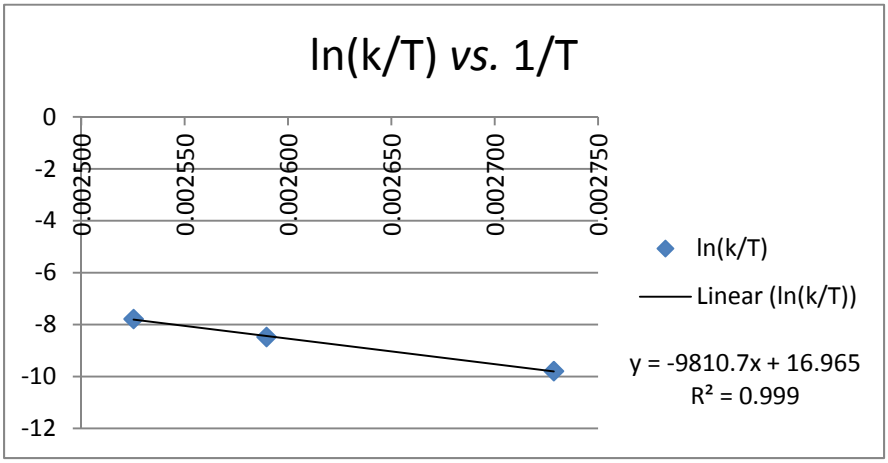
Kinetics

Measurement of barrier for rotation by nOe difference experiments

The temperature was corrected with the ethylene glycol standard. The temperature measured by the difference of the chemical shifts of the proton signals in ethylene glycol, corrected temp, and the temperature read by the thermocouple, temp, were in the linear relationship

Corrected temp = 0.9835 x temp – 0.1019

temp (°C)	temp corrected	T1 (s)	MB(∞)	k=(1-MB(∞)) /MB(∞)/T1	1/T	ln(k/T)
95	93.33	1.64	0.9675	0.0205	0.002729	-9.792
115	113.00	1.97	0.8633	0.0804	0.002590	-8.477
125	122.84	2.01	0.7511	0.1649	0.002525	-7.784



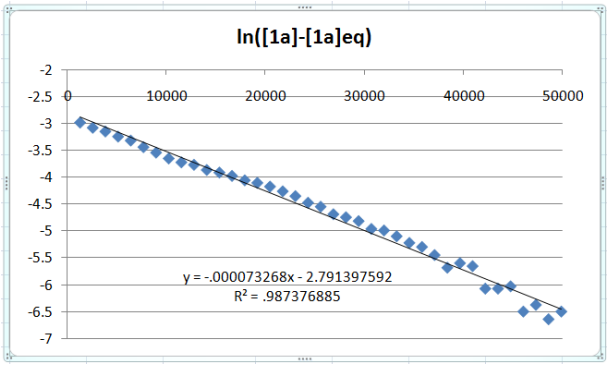
ΔH (kcal/mol)	ΔS (cal/mol/K)	ΔG (25oC)
19.49	**-13.50**	**23.51**

Standard error of ΔG_{298} = 1.1 kcal/mol.

Measurement of the rate constant of the reaction **5a** → **5b** at 25 °C

time/s	b	a+b	a	a/b	ln(a-ae)
1280	0.1977	0.5047	0.2977	1.505817	-2.98183
2560	0.2022	0.5047	0.2931	1.449555	-3.07694
3840	0.2052	0.5049	0.29	1.413255	-3.14656
5120	0.2083	0.5055	0.2861	1.3735	-3.24163
6400	0.212	0.5047	0.2833	1.336321	-3.31594
7680	0.2159	0.505	0.2791	1.292728	-3.4389
8960	0.2188	0.5052	0.276	1.261426	-3.54046
10240	0.2218	0.5052	0.273	1.230839	-3.64966
11520	0.2232	0.5056	0.2712	1.215054	-3.7214
12800	0.2252	0.5047	0.2701	1.199378	-3.76792
14080	0.2264	0.5056	0.268	1.183746	-3.86323
15360	0.228	0.505	0.267	1.171053	-3.91202
16640	0.2286	0.5056	0.2658	1.16273	-3.9739
17920	0.2301	0.5056	0.2643	1.148631	-4.05705
19200	0.2312	0.5053	0.2635	1.139706	-4.10439
20480	0.2321	0.5054	0.2624	1.130547	-4.17339
21760	0.2333	0.5056	0.2611	1.11916	-4.26158
23040	0.2346	0.5055	0.2599	1.107843	-4.35053
24320	0.2358	0.5058	0.2584	1.095844	-4.47414
25600	0.2369	0.5054	0.2576	1.087379	-4.5469
26880	0.2379	0.5059	0.2562	1.076923	-4.68855
28160	0.2388	0.5055	0.2557	1.070771	-4.74443
29440	0.2388	0.5061	0.2551	1.068258	-4.81589
30720	0.2399	0.5061	0.254	1.058774	-4.96185
32000	0.24	0.5063	0.2538	1.0575	-4.99083
33280	0.2411	0.5057	0.2531	1.049772	-5.09947
34560	0.2418	0.5057	0.2524	1.043838	-5.22136
35840	0.2423	0.5057	0.252	1.040033	-5.29832
37120	0.2429	0.5059	0.2513	1.034582	-5.44914
38400	0.2441	0.5055	0.2504	1.025809	-5.68398
39680	0.2428	0.5065	0.2507	1.032537	-5.59942
40960	0.2434	0.5061	0.2505	1.02917	-5.65499
42240	0.2442	0.5065	0.2493	1.020885	-6.07485
43520	0.2446	0.5061	0.2493	1.019215	-6.07485
44800	0.2445	0.5061	0.2494	1.020041	-6.03229
46080	0.2453	0.5062	0.2485	1.013045	-6.50229
47360	0.2453	0.506	0.2487	1.013861	-6.37713
48640	0.246	0.5057	0.2483	1.00935	-6.64539
49920	0.2454	0.5061	0.2485	1.012632	-6.50229
51200	0.2458	0.5068	0.2474	1.006509	-7.82405
52480	0.2474	0.5057	0.2469	0.997979	#NUM!
53760	0.2465	0.5057	0.2478	1.005274	-7.1309
55040	0.2469	0.5061	0.247	1.000405	#NUM!
56320	0.247	0.5054	0.2476	1.002429	-7.41858
57600	0.2467	0.5066	0.2468	1.000405	#NUM!
58880	0.2471	0.5066	0.2463	0.996762	#NUM!
60160	0.2467	0.5064	0.2469	1.000811	#NUM!
61440	0.2471	0.5062	0.2467	0.998381	#NUM!
62720	0.2475	0.5057	0.2468	0.997172	#NUM!
64000	0.2473	0.5057	0.247	0.998787	#NUM!
65280	0.2473	0.5064	0.2463	0.995956	#NUM!

The reaction **5a** → **5b** was monitored in benzene-d6 at 25 °C (reading of the thermocouple, uncorrected) by 1H NMR, for 18 hrs. Spectra were acquired in 64 transients, with a relaxation delay of 10 s and an acquisition time of 10 s, for a total of 51 spectra. Only 40 of them were taken into calculating the rate constant, because in the last ones the mixture was very close to equilibrium and the errors in ln([**5a**]-[**5a**]$_{eq}$) were large. The signals of H1'' were used for integration, after baseline correction: 4.30 – 4.19 ppm [**5b**], 4.03 – 3.84 ppm [**5a**] + [**5b**], and 3.75 – 3.63 [**5a**].



The slope of the plot ln([**5a**]-[**5a**]eq) , which is the logarithm of the difference between the concentration of **5a** at time t and the concentration at equilibrium, *vs.* time is the sum of the rate constants for the forward and backward reactions, $k_f + k_b$. The equilibrium constant, $K = k_f/k_b$ is 1, and $k_f = k_b = 3.67 \times 10^{-5}$ s^{-1}. (standard error 0.07×10^{-5} s^{-1}). This corresponds to a half-life time of 5.25 hrs.

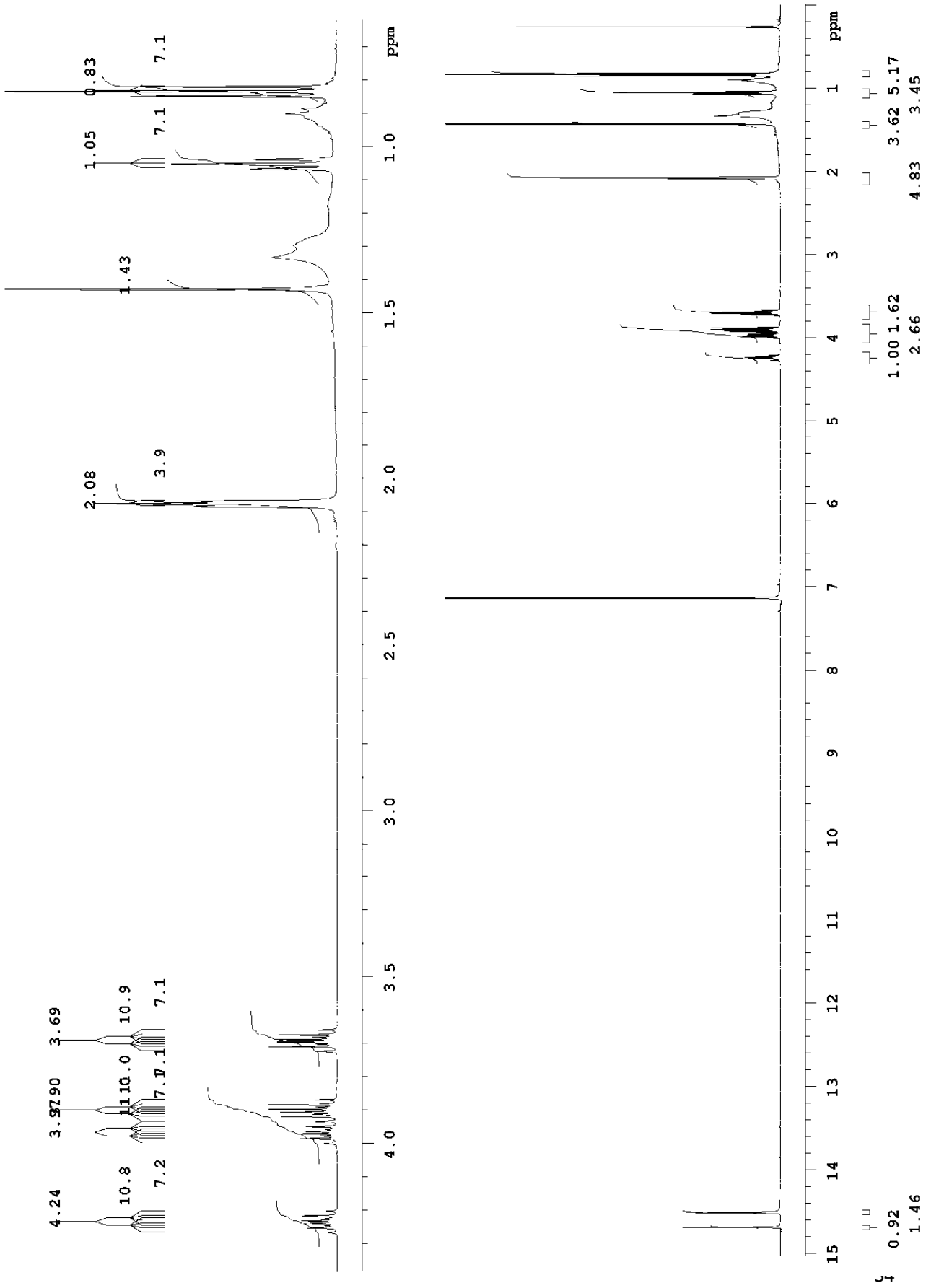


Figure 1S. ^{1}H spectrum of compound 5 in benzene-*d6* at 25 °C.

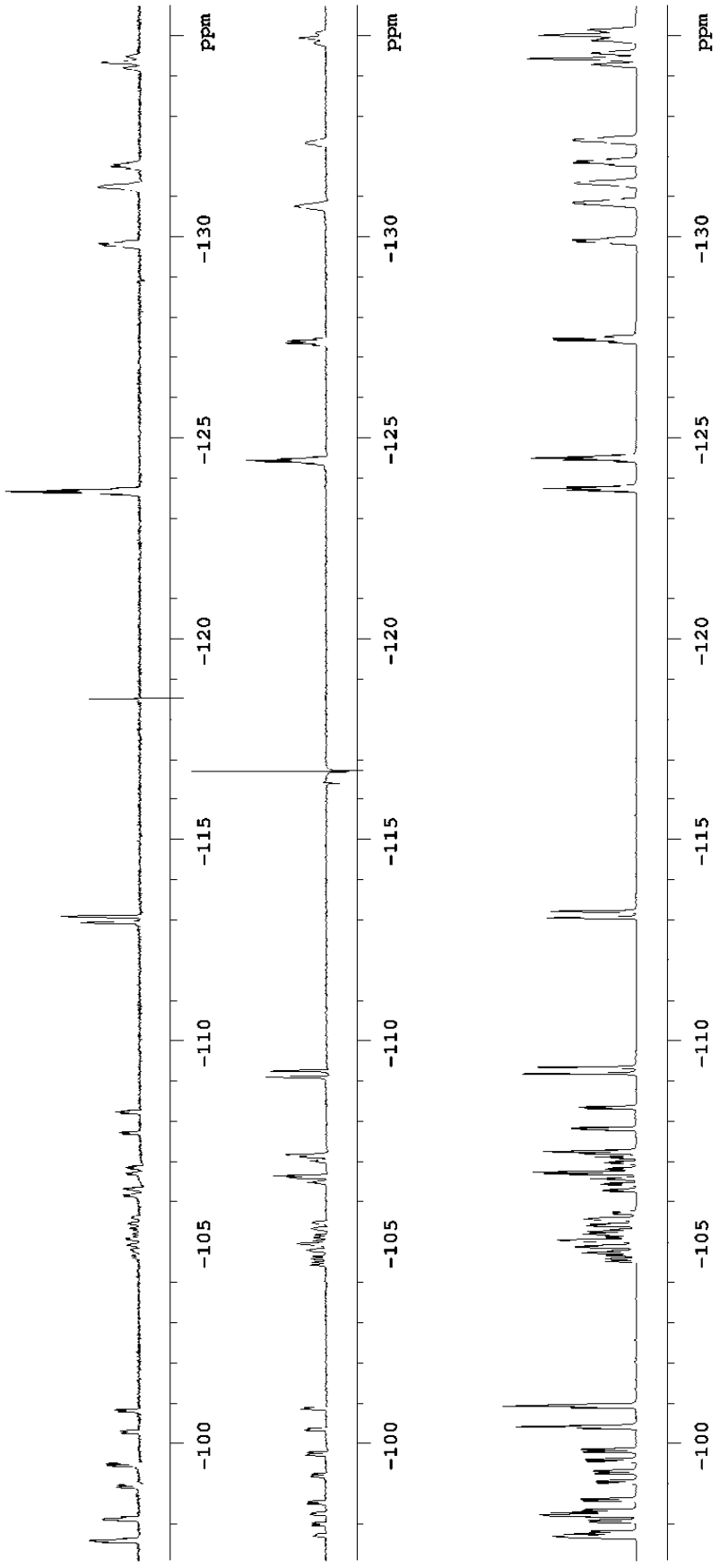


Figure 2S. ^{19}Fspectrum of compound **5** in benzene-*d6* at 25 °C. (bottom) and TOCSY1D spectra of conformers **5a** (top) and **5b.**

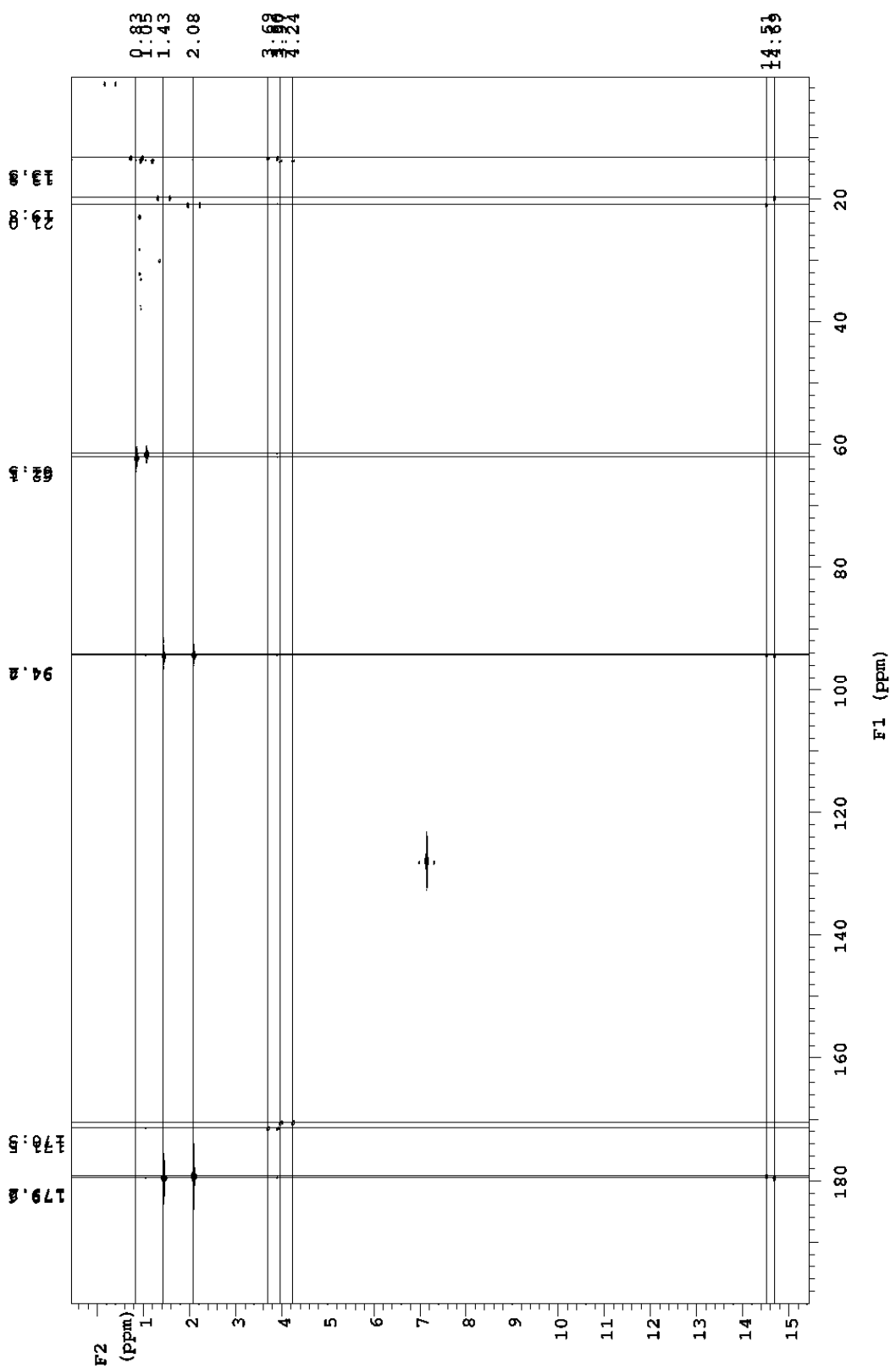


Figure 3Sa. ^{1}H-^{13}C gHMBC spectrum of compound **5** in benzene-*d6* at 25 °C.

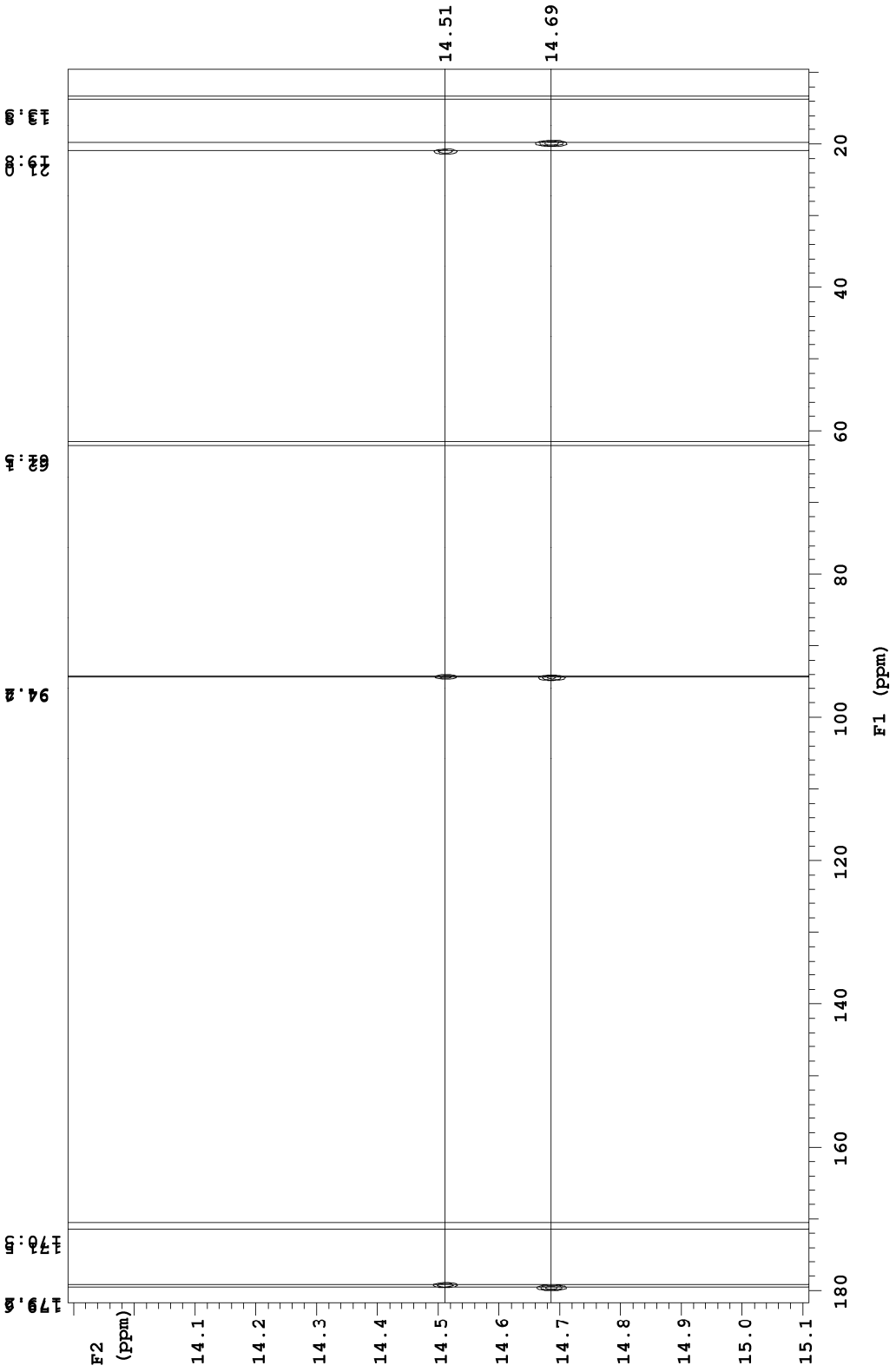


Figure 3Sb. ^{1}H-^{13}C gHMBC spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

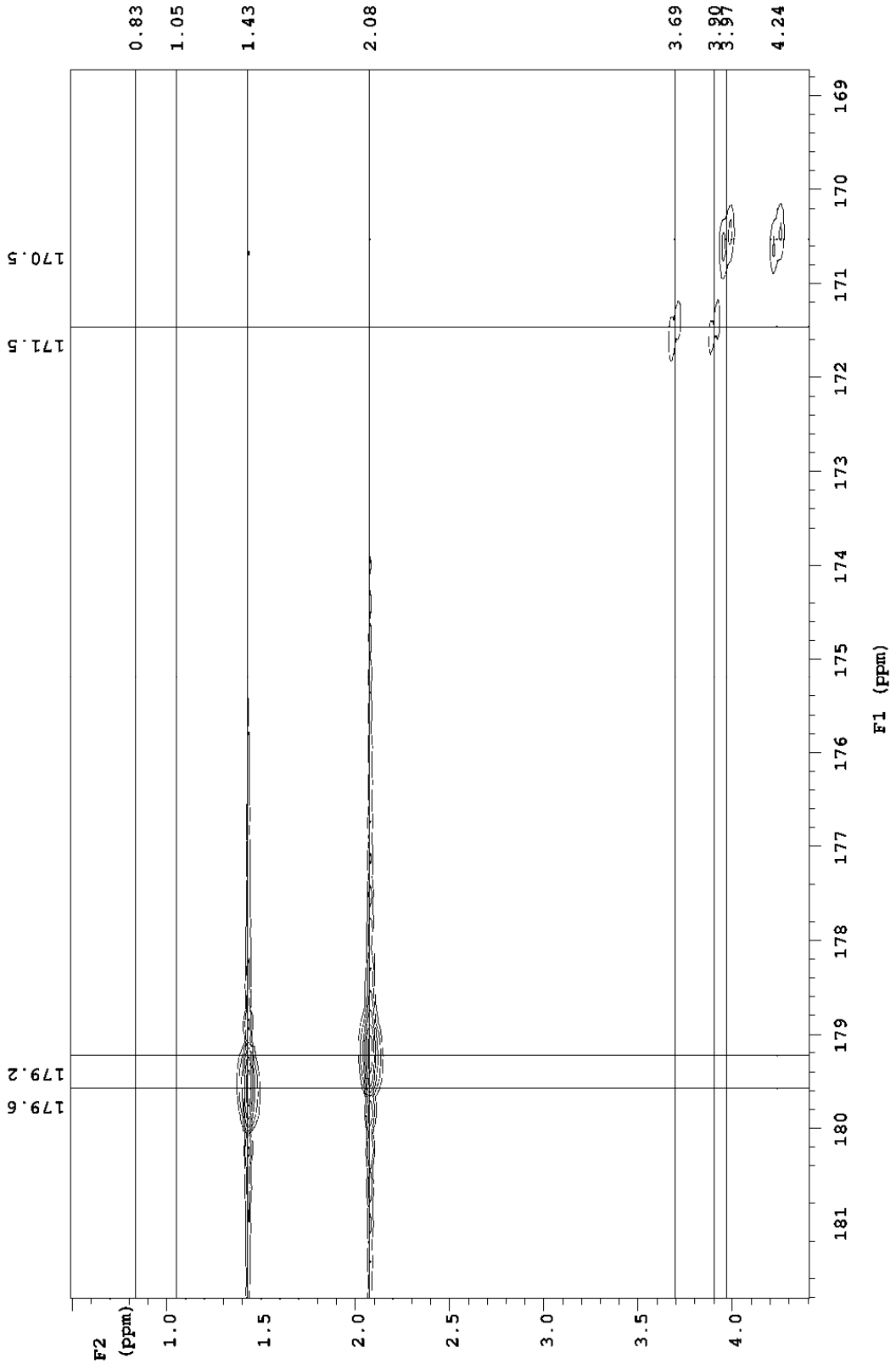


Figure 3Sc. ^{1}H-^{13}C gHMBC spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

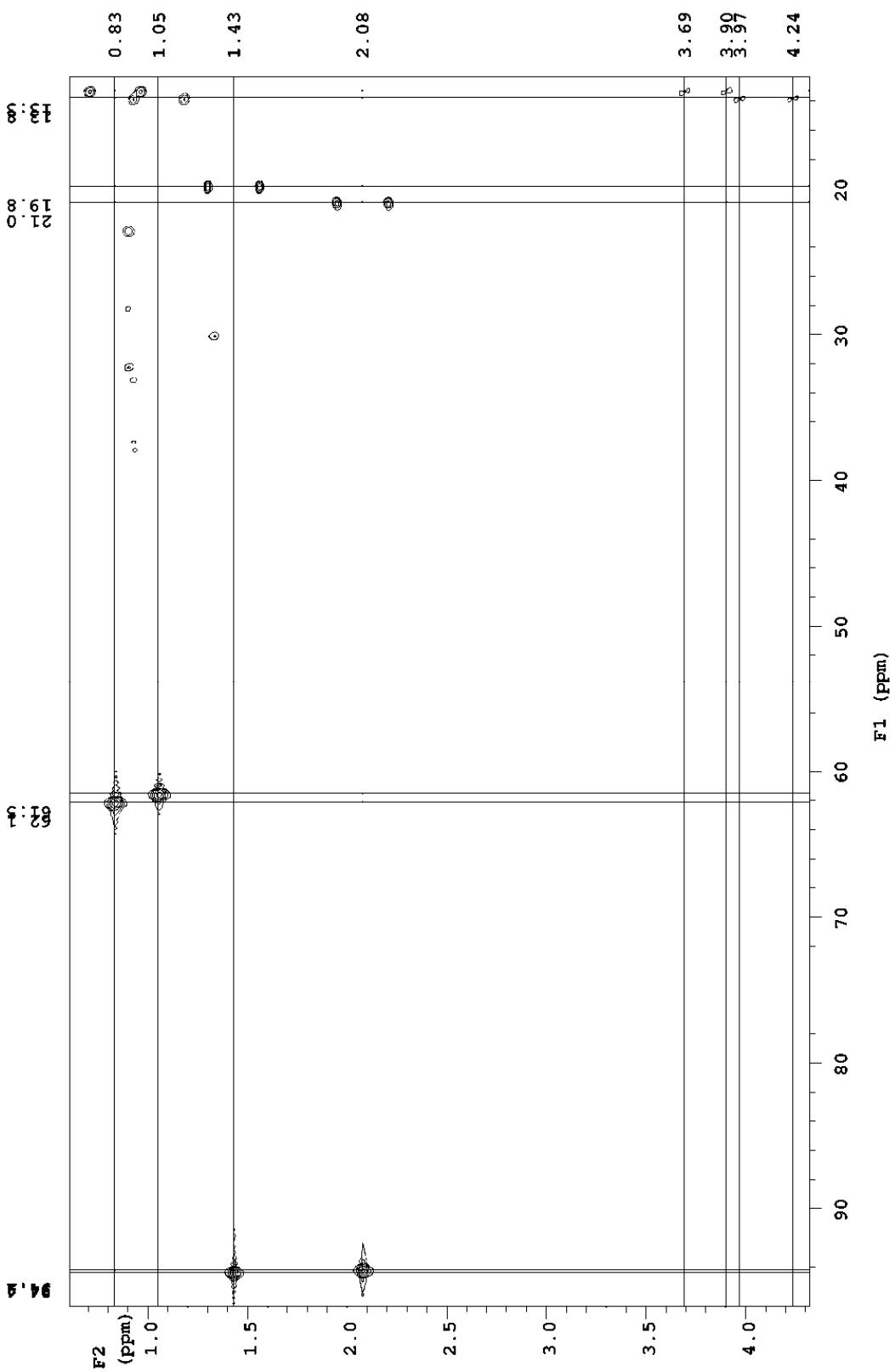


Figure 3Sd. ^{1}H-^{13}C gHMBC spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

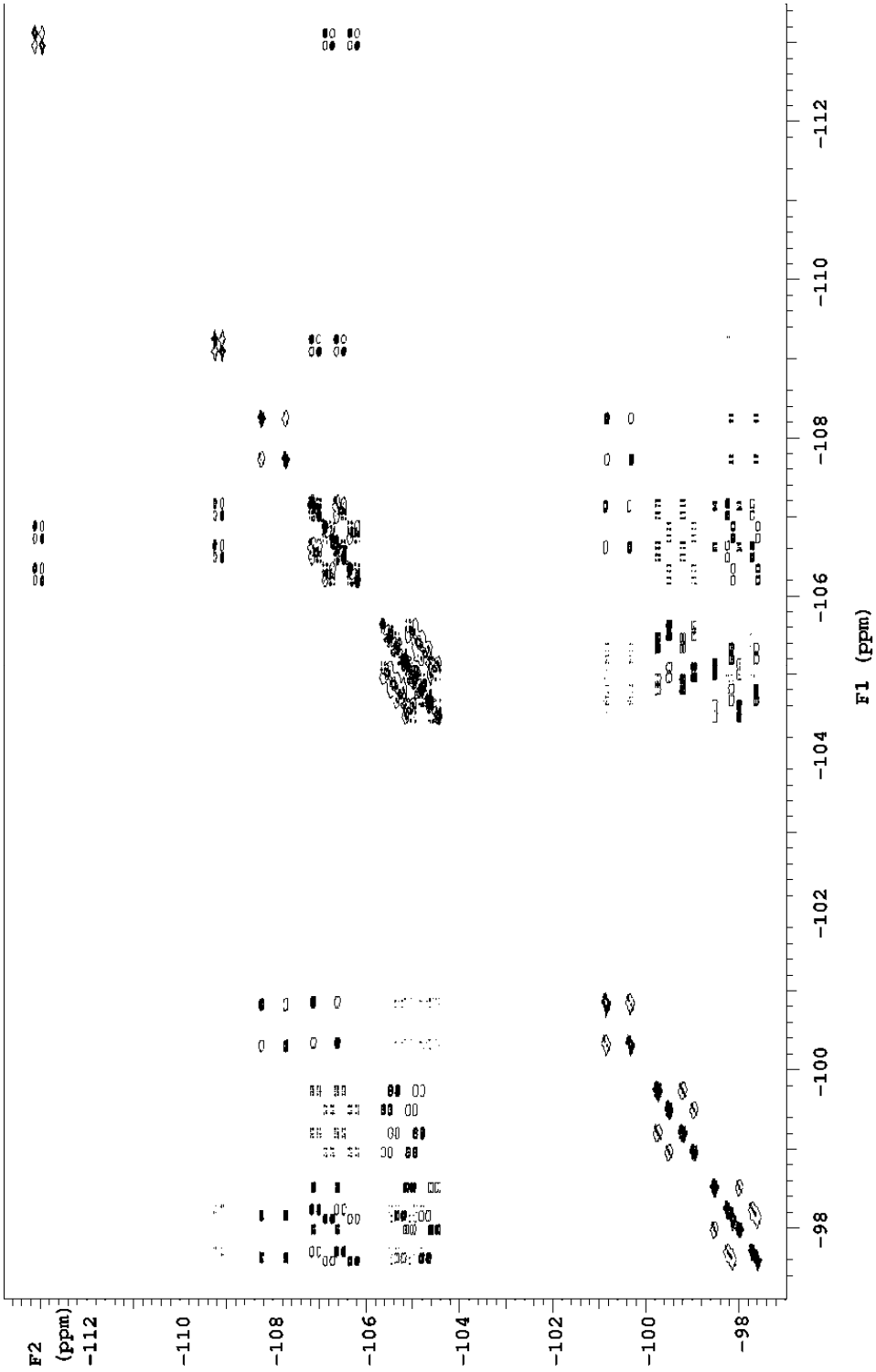


Figure 4Sa. ^{19}F-^{19}F DQCOSY spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

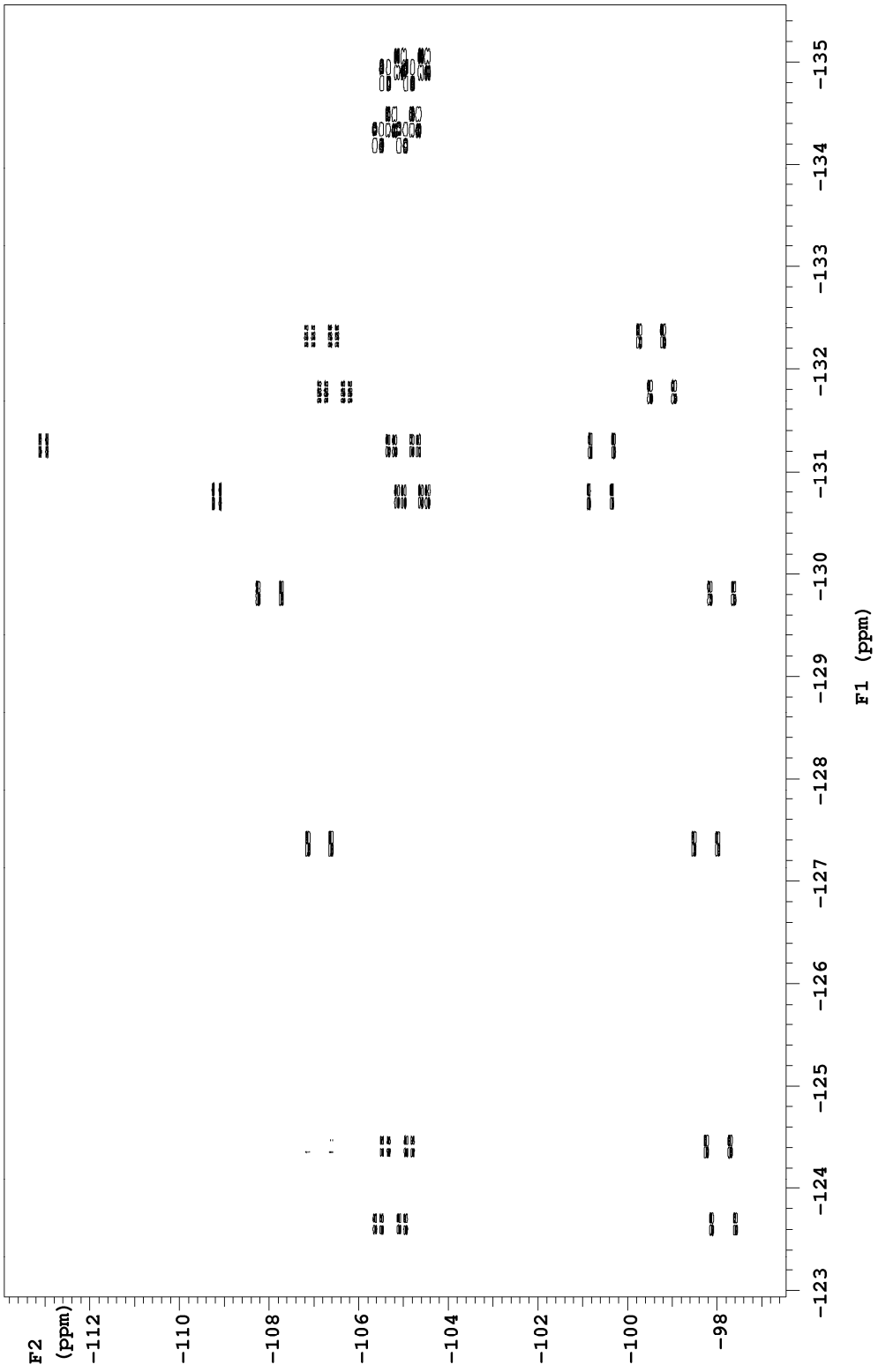


Figure 4Sb. ^{19}F-^{19}F DQCOSY spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

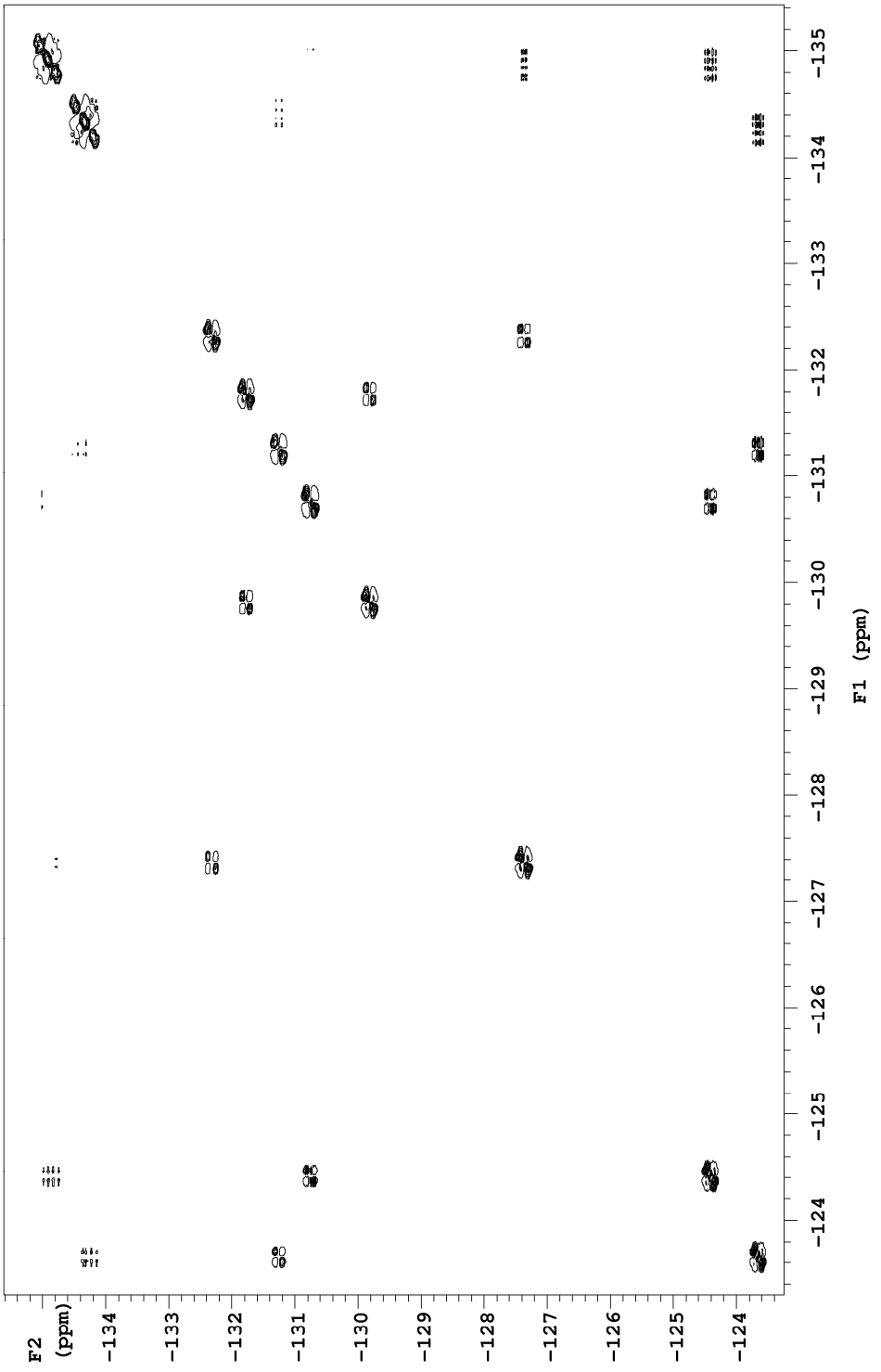


Figure 4Sc. ^{19}F-^{19}F DQCOSY spectrum of compound **5** in benzene-*d6* at 25 °C. (expansion).

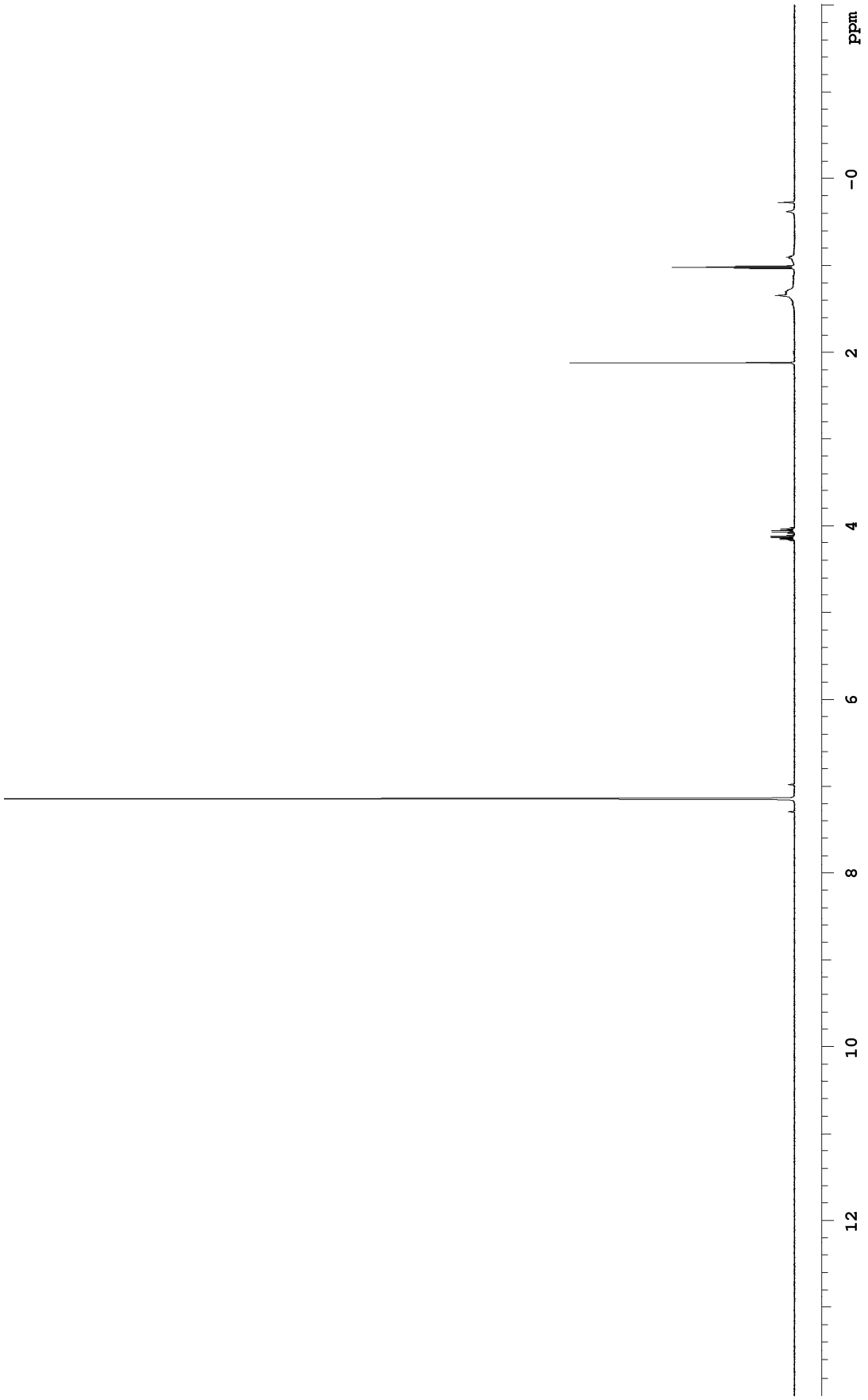


Figure 5S. ^{1}H spectrum of compound **6**in benzene-*d6* at 25 °C.

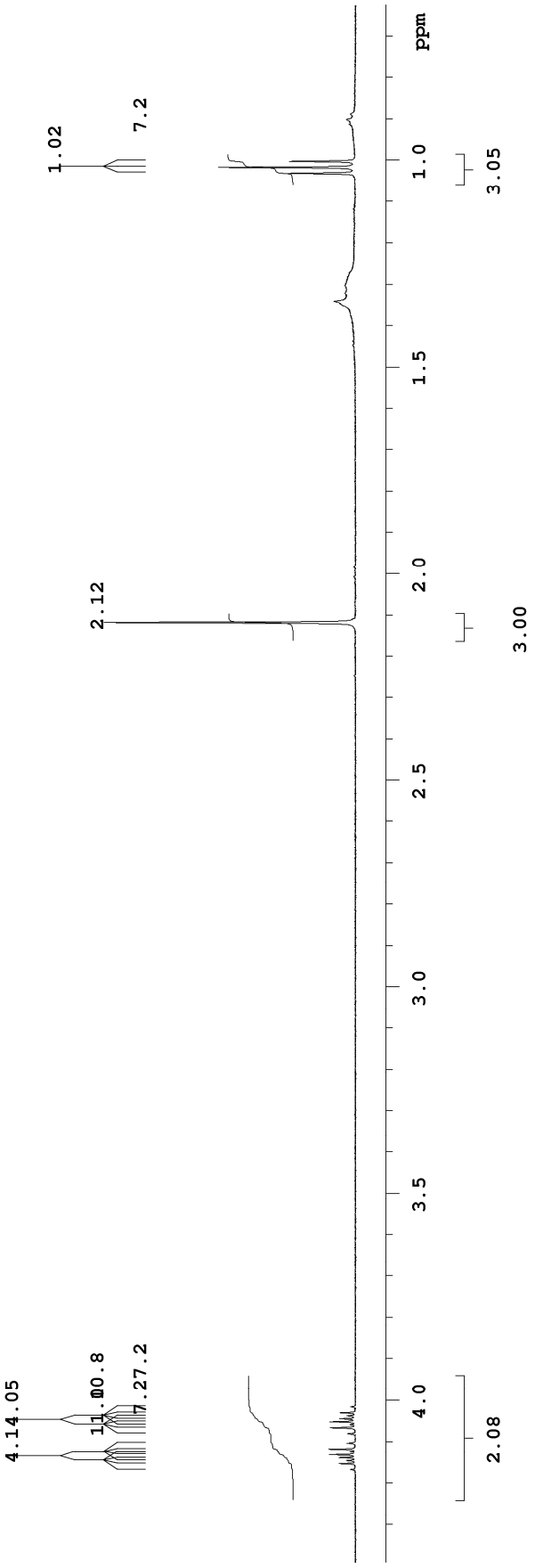


Figure 5Sa. ^{1}H spectrum of compound **6** in benzene-*d6* at 25 °C (expansion).

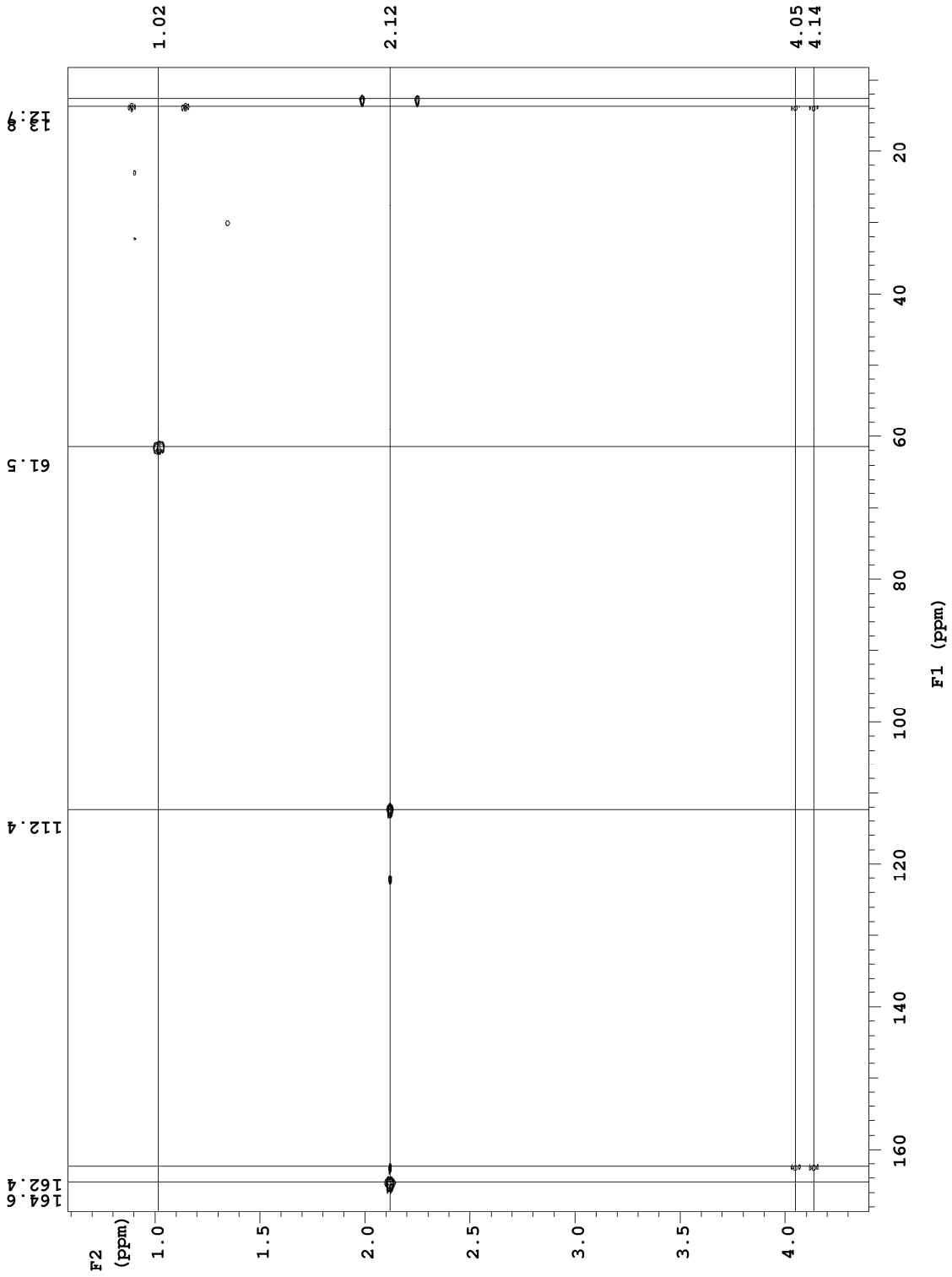


Figure 6S. ^{1}H-^{13}C gHMBC spectrum of compound **6** in benzene-*d6* at 25 °C.

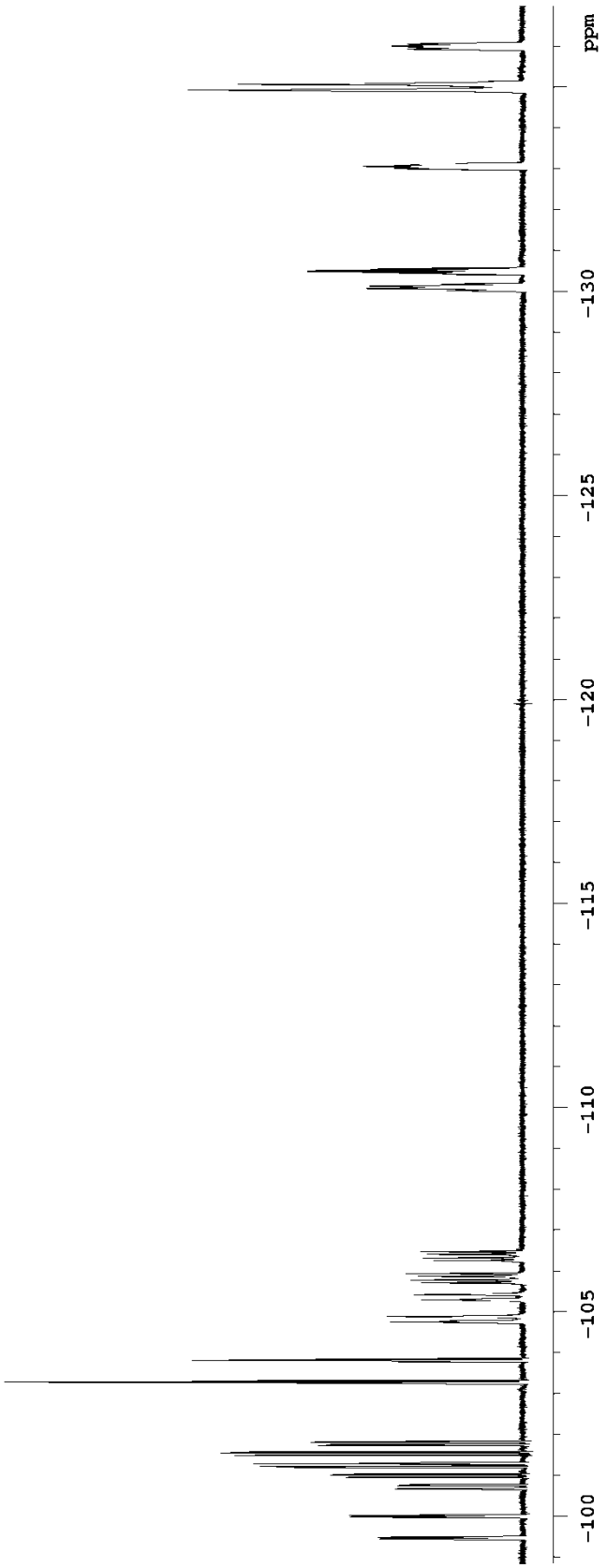


Figure 7S. ^{19}F spectrum of compound **6** in benzene-*d6* at 25 °C.

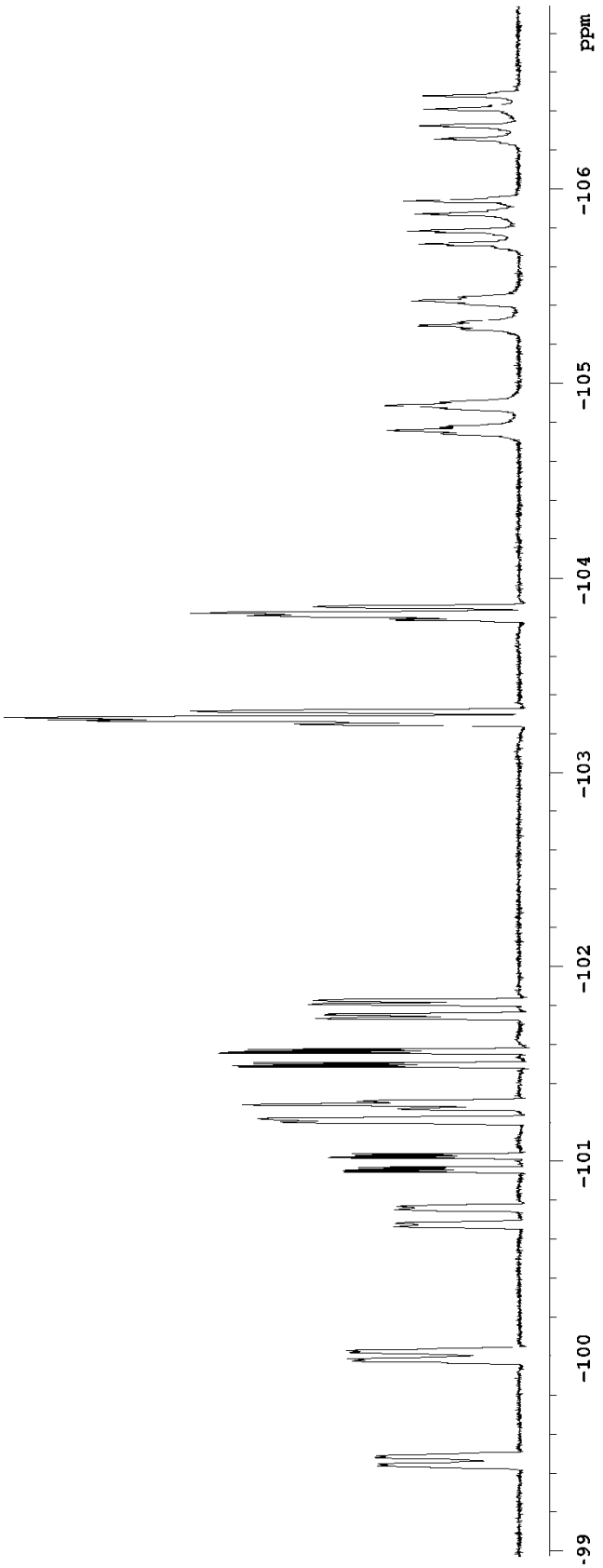


Figure 7Sa. ^{19}F spectrum of compound **6** in benzene-*d6* at 25 °C (expansion).

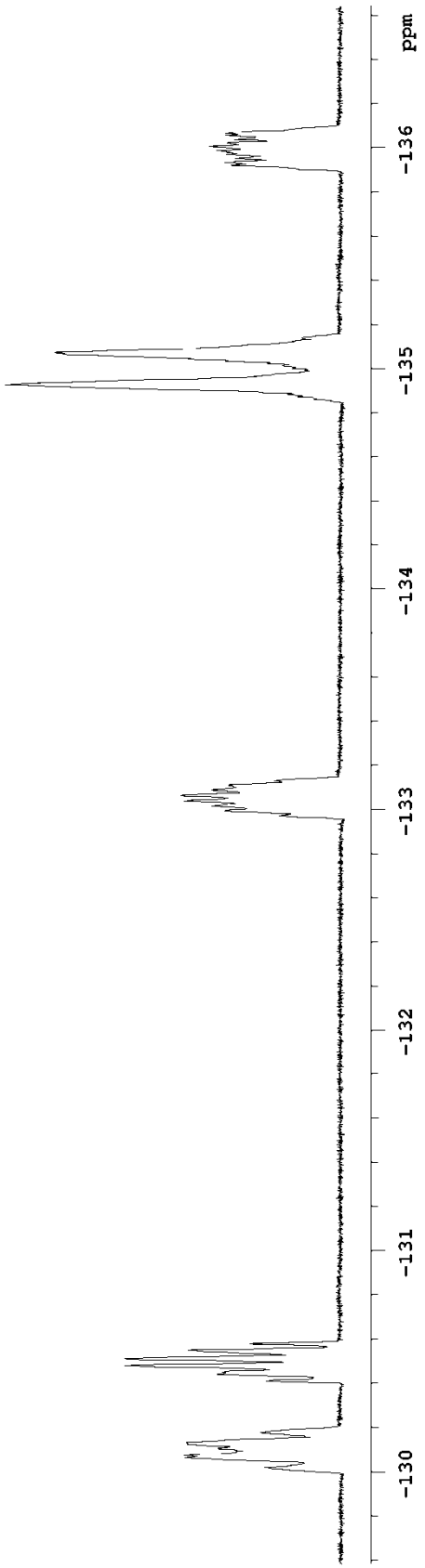


Figure 7Sb. ^{19}F spectrum of compound **6** in benzene-*d6* at 25 °C (expansion).

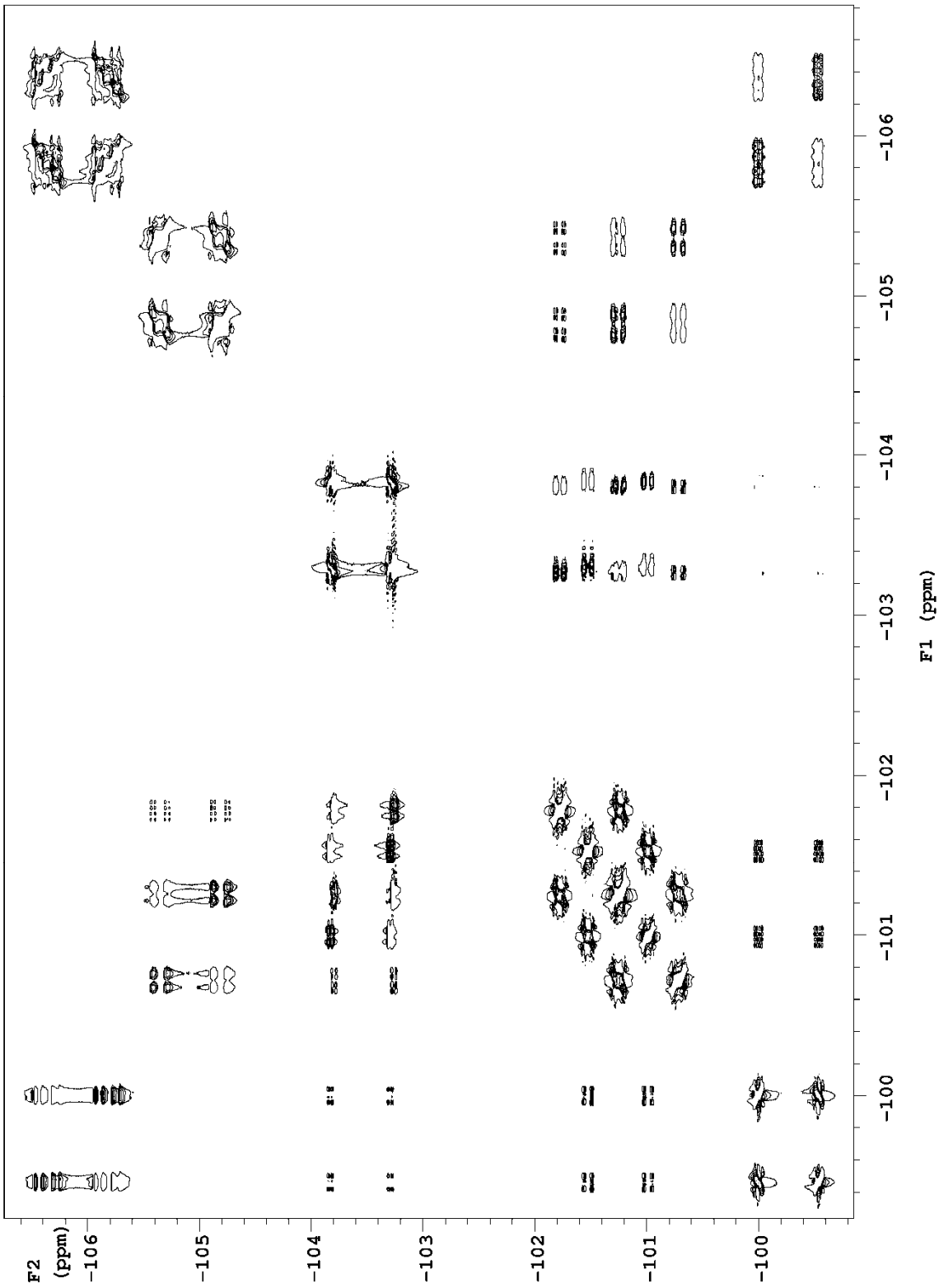


Figure 7Sa. ^{19}F-^{19}F DQCOSY spectrum of compound **6** in benzene-*d6* at 25 °C (expansion).

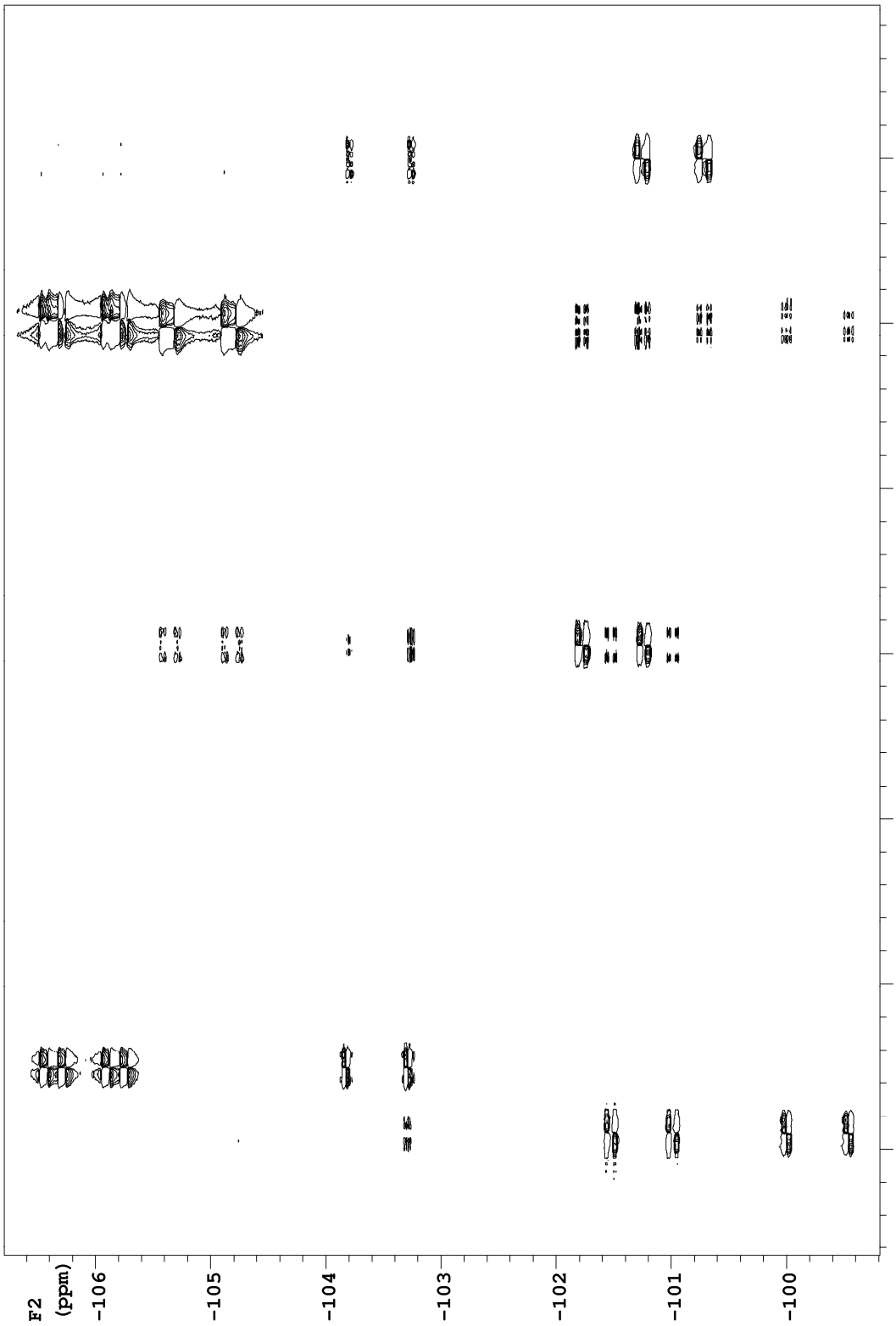


Figure 7Sb. ^{19}F-^{19}F DQCOSY spectrum of compound **6** in benzene-*d6* at 25 °C (expansion).

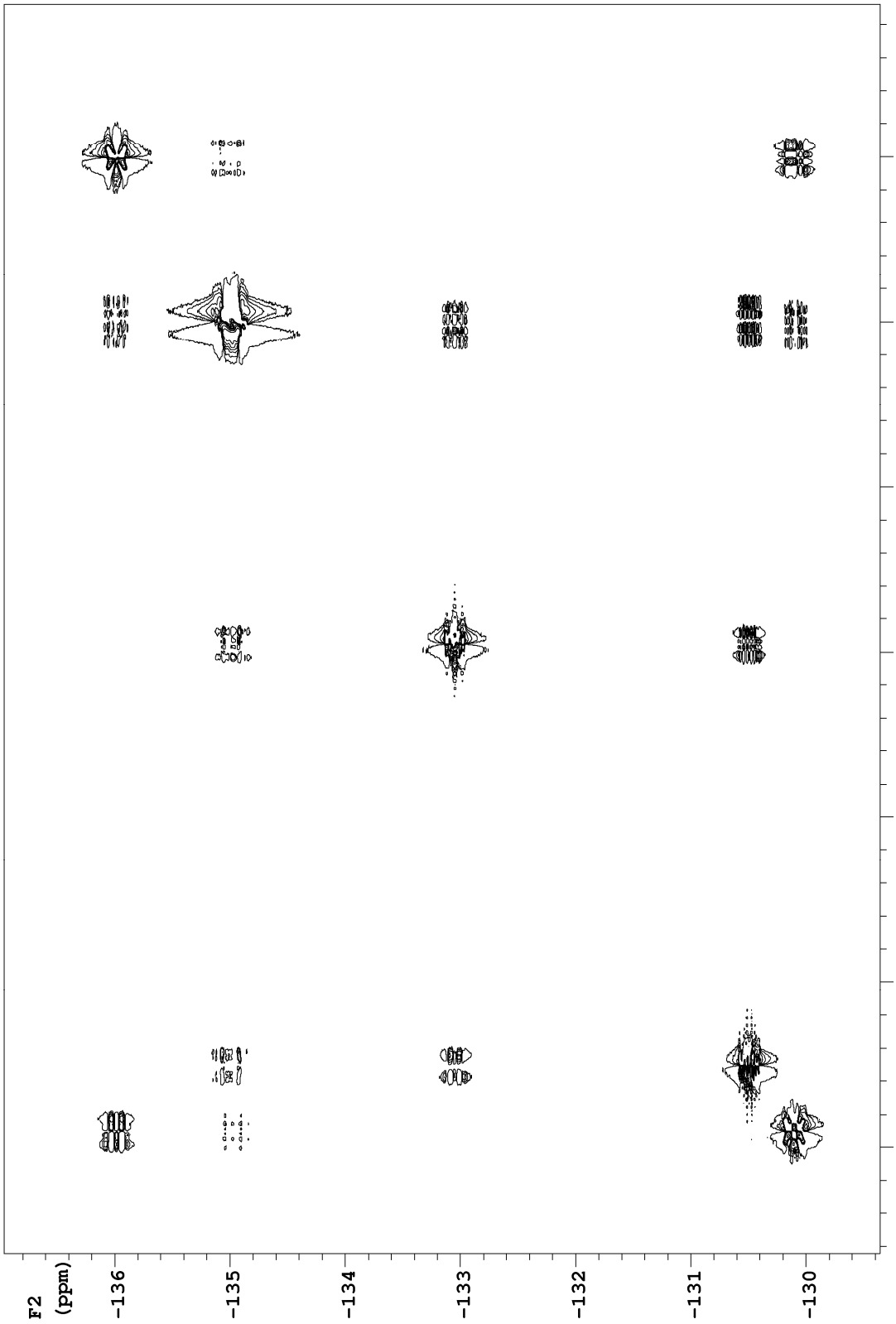


Figure 7Sc. ^{19}F-^{19}F DQCOSY spectrum of compound **6**in benzene-*d6* at 25 °C (expansion).

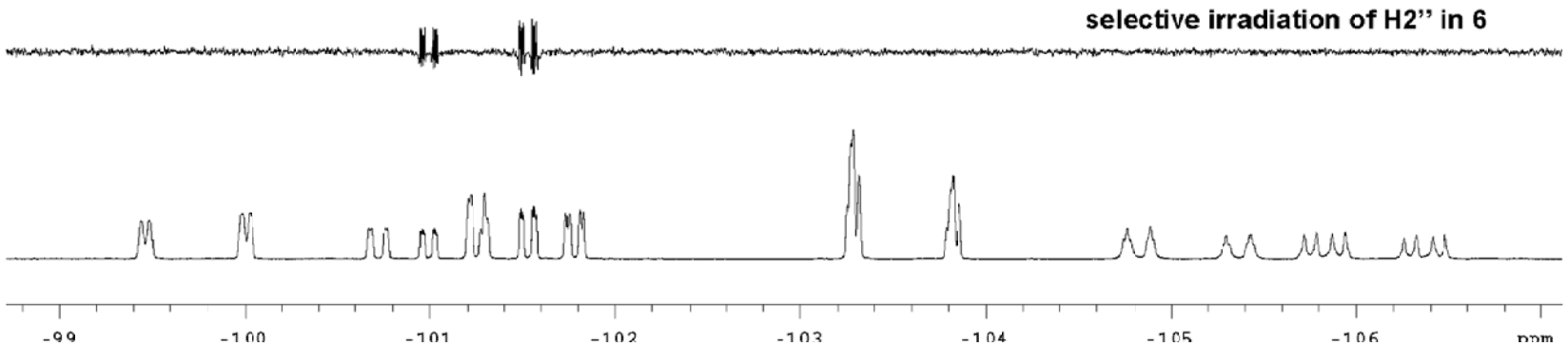


Figure 8S. ^{19}F-^{19}F nOe difference spectrum spectrum of compound **6**in benzene-*d6* at 25 °C (top). And the 19F spectrum (bottom)

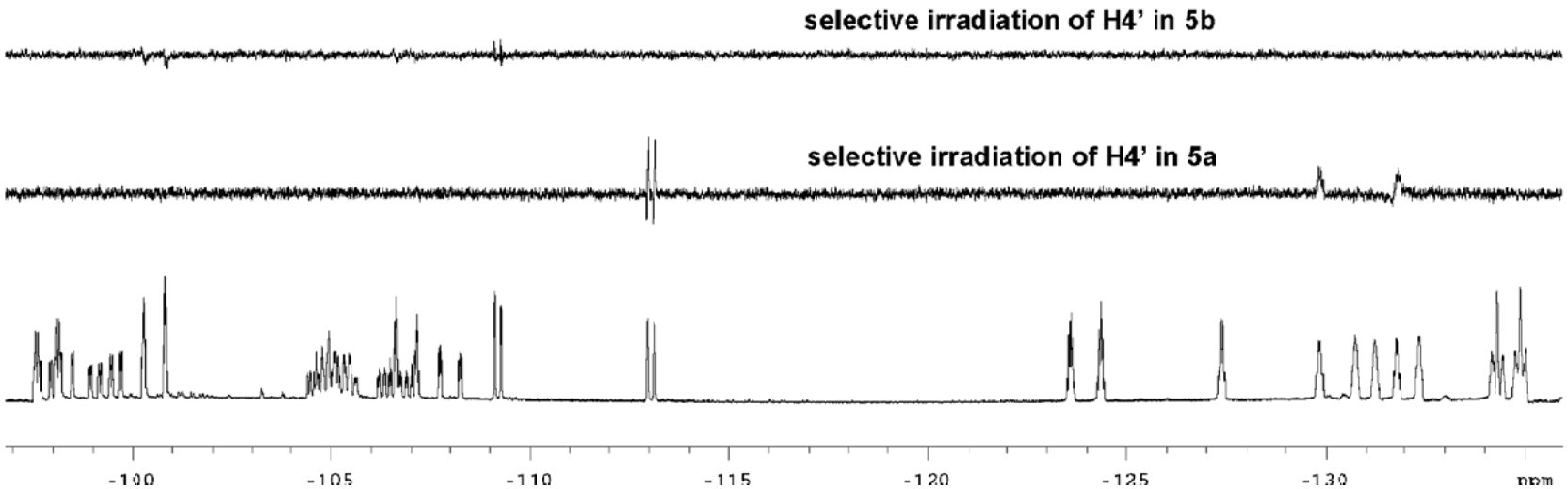


Figure 9S. ^{19}F-^{19}F nOe difference spectrum of compound **5**in benzene-*d6* at 25 °C (top) and the 19F spectrum (bottom)