SUPPORTING INFORMATION Part 2

Synthesis of New Asymmetric Xanthene Dyes *via* Catalyst free S_NAr with Sulfur Nucleophiles

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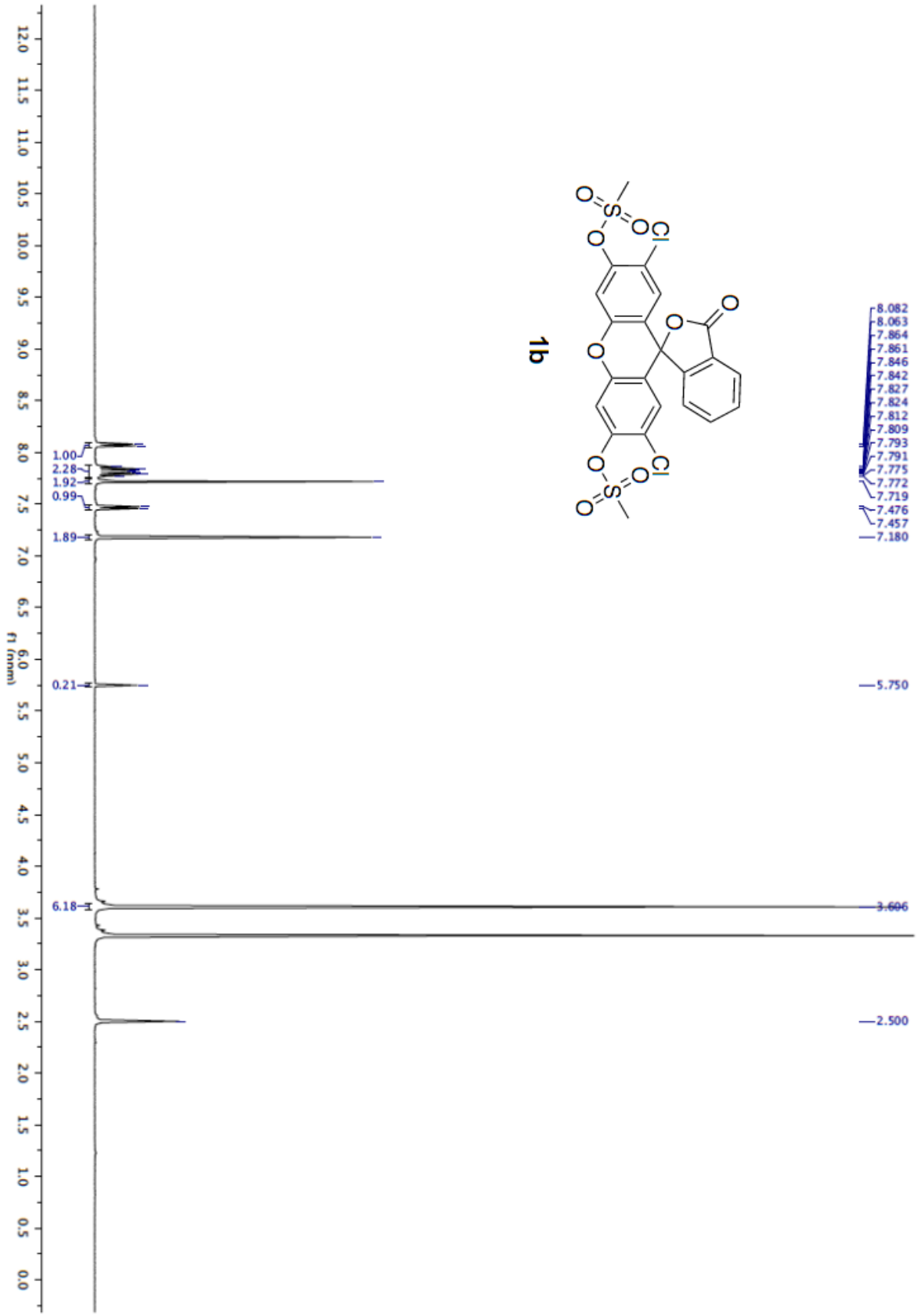
Contents Part 2: NMR Spectra

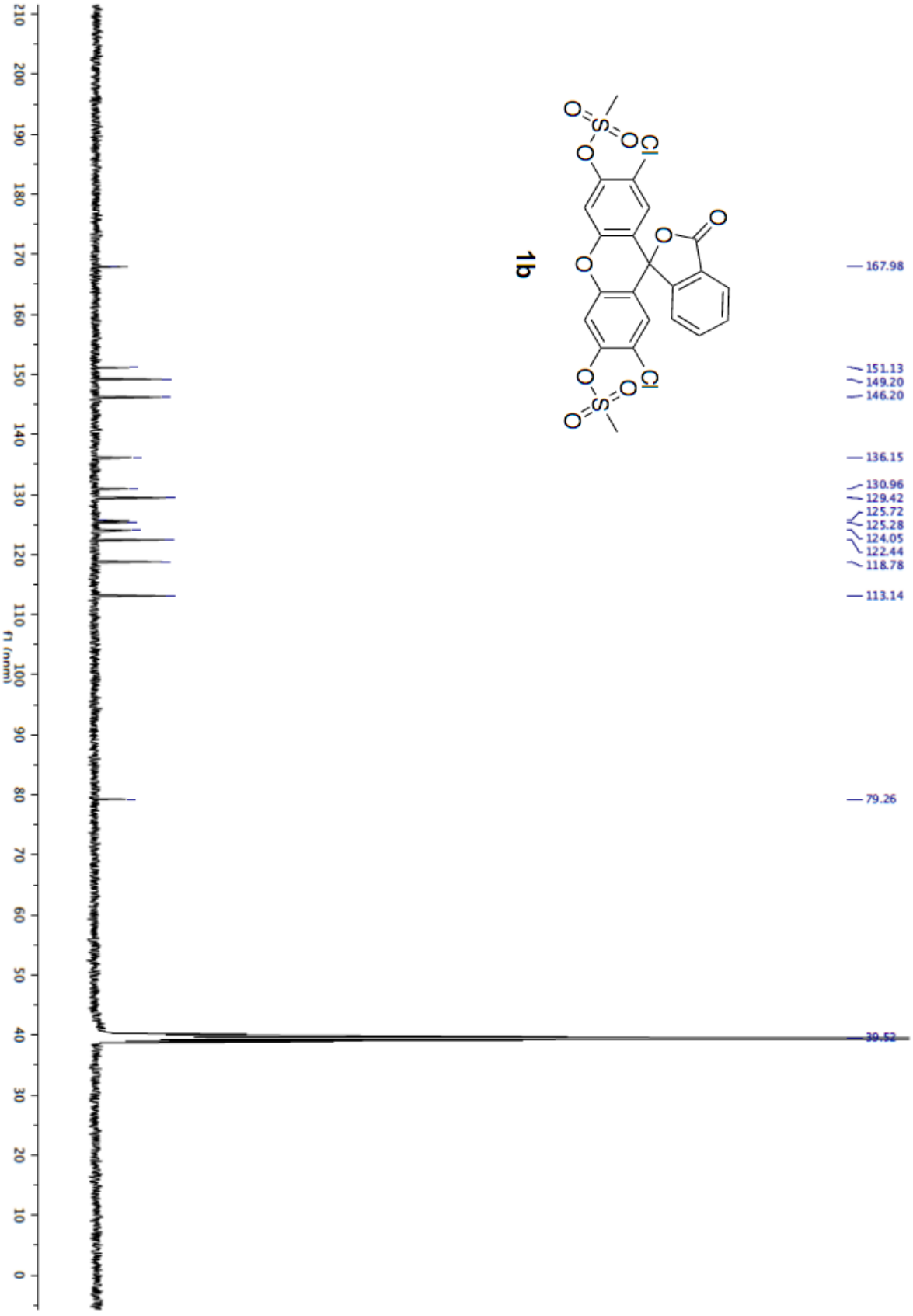
Note:

The structures are shown as open or lactonic form, respectively, depending on the presence of a signal around 80 ppm in the ^{13}C-spectra, which gives evidence for the lactonic structure.

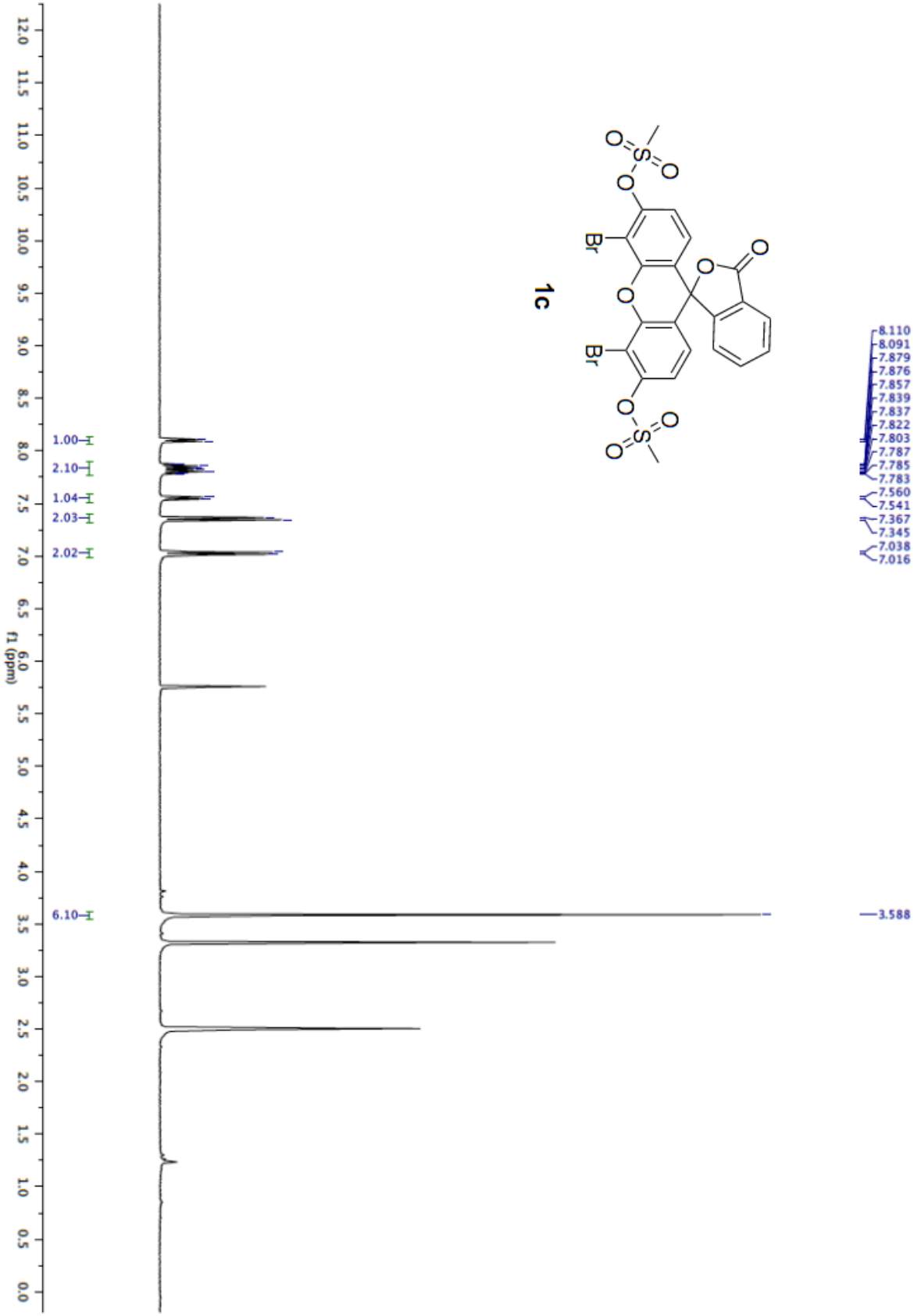
[1]H-spectrum of **1b** in DMSO-d_6



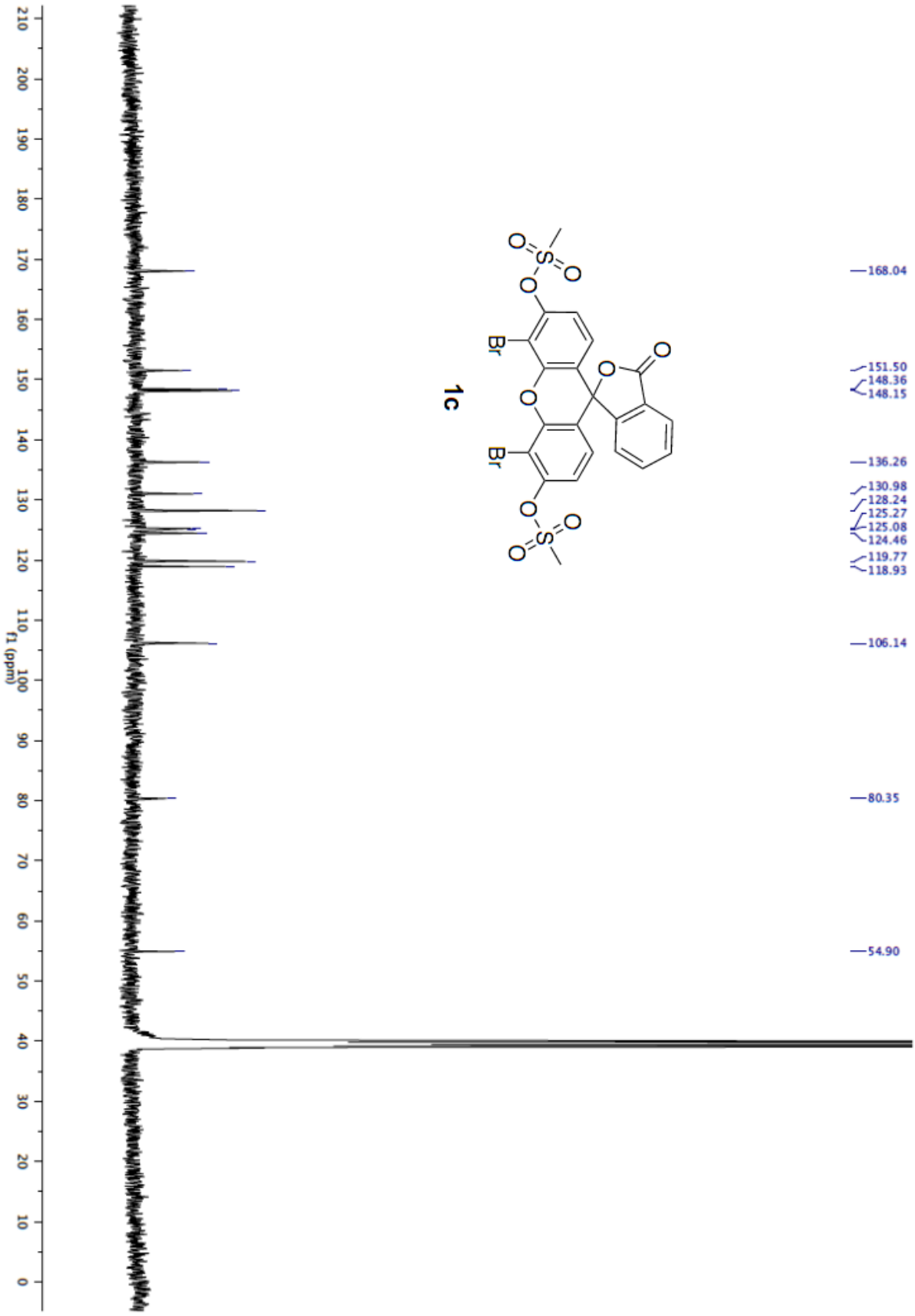
^{13}C-spectrum of **1b** in DMSO-d_6



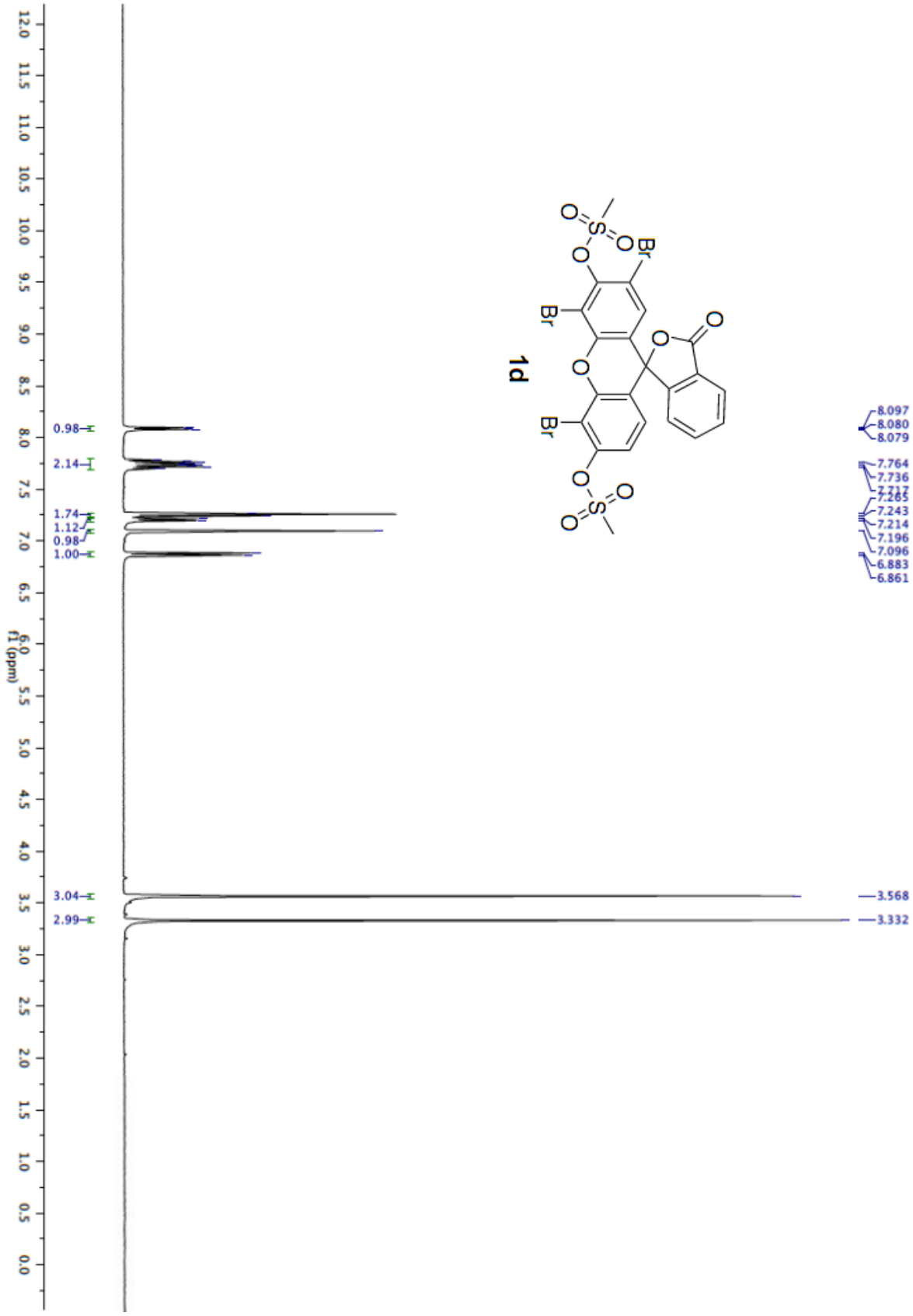
^{1}H-spectrum of **1c** in DMSO-d_6



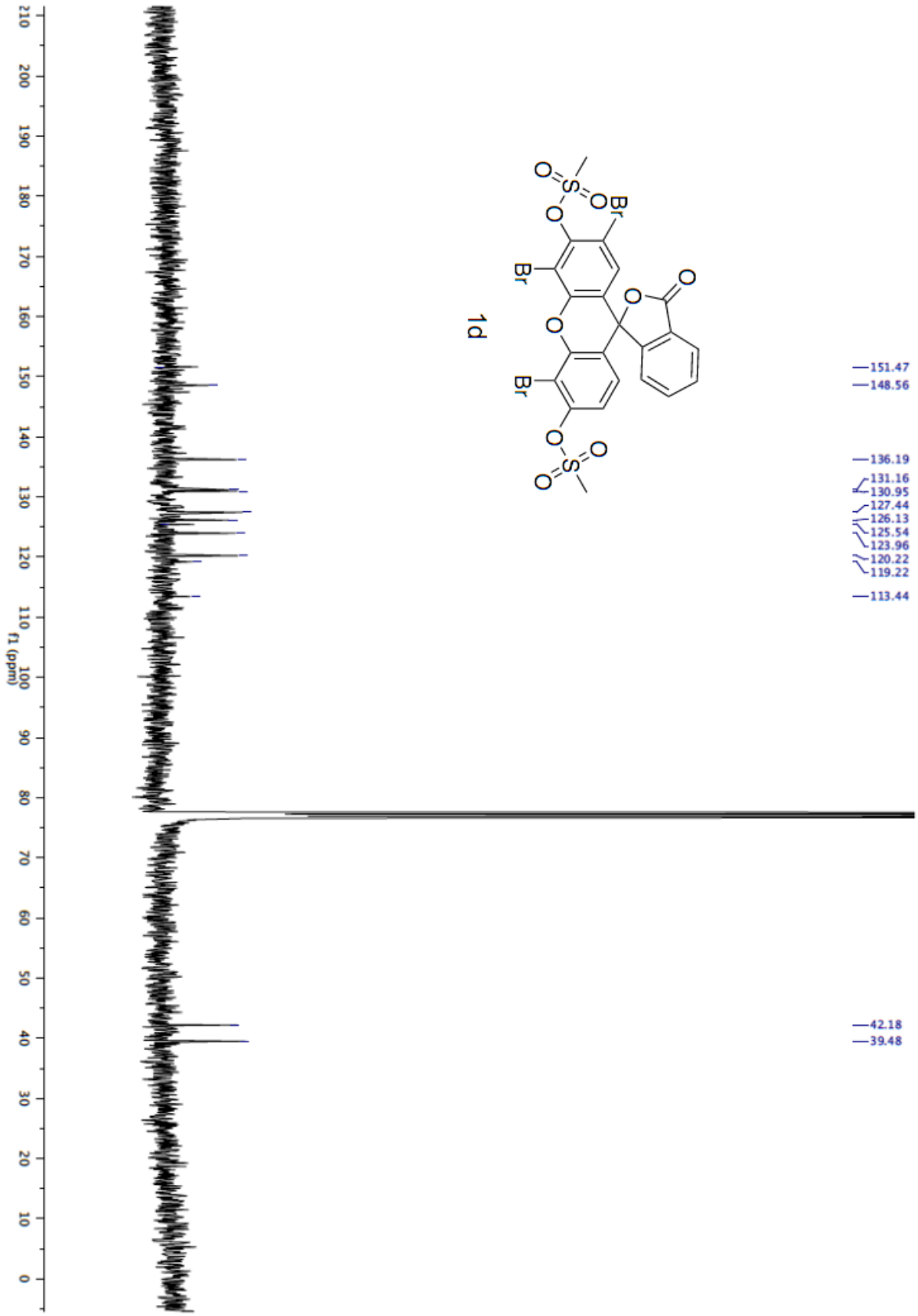
^{13}C-spectrum of **1c** in DMSO-d_6



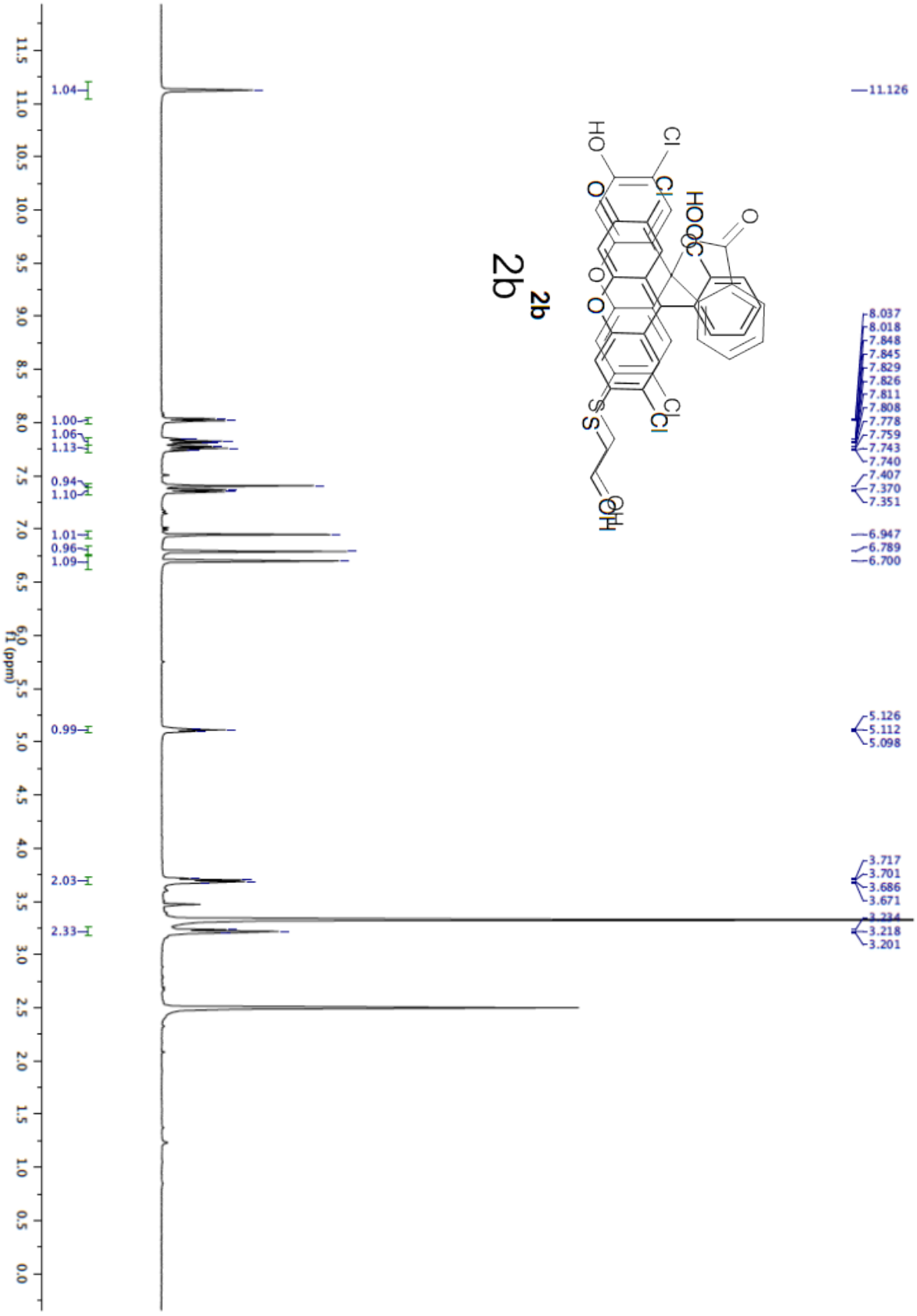
^{1}H-spectrum of **1d** in $CDCl_3$



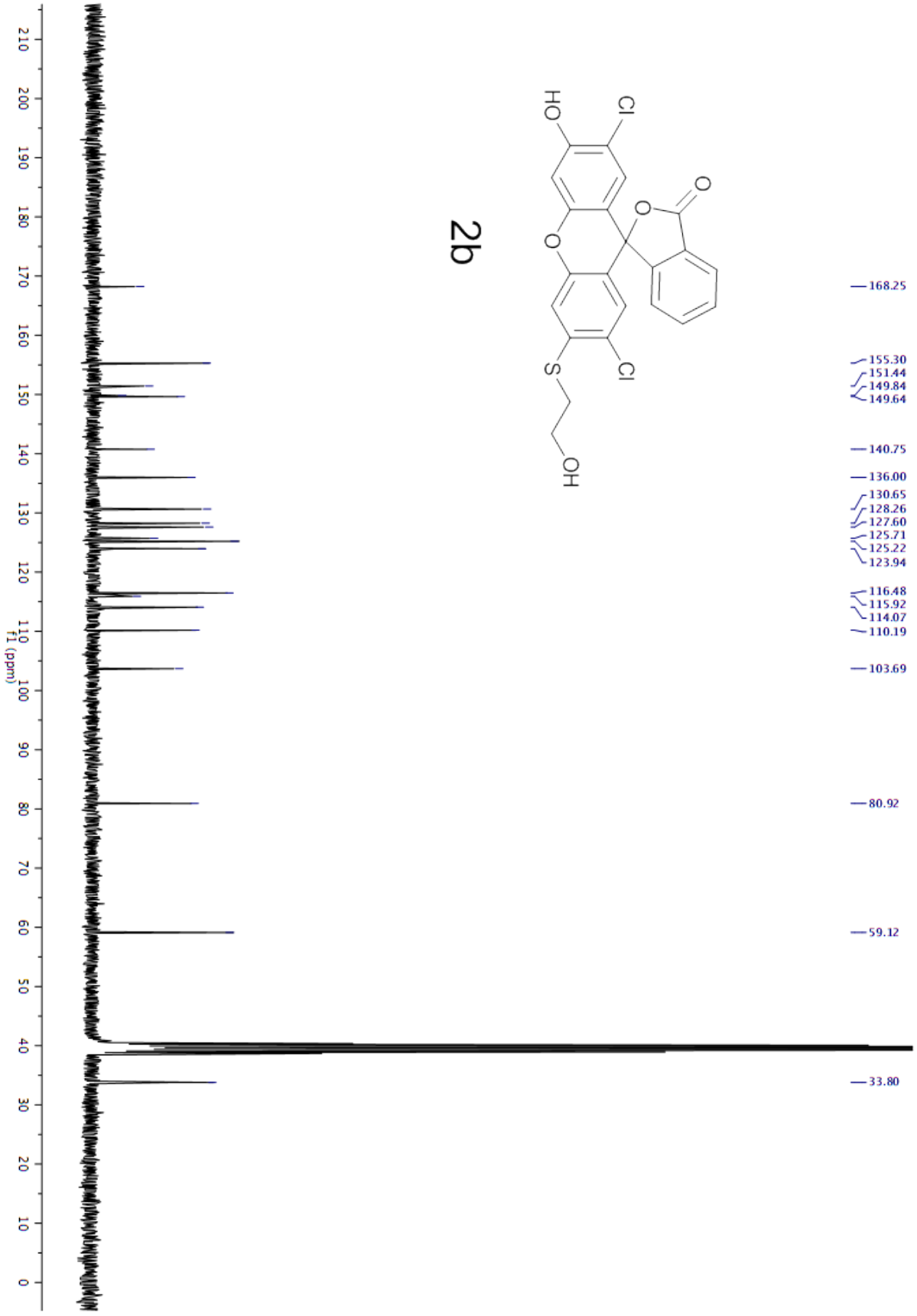
^{13}C-spectrum of **1d** in $CDCl_3$



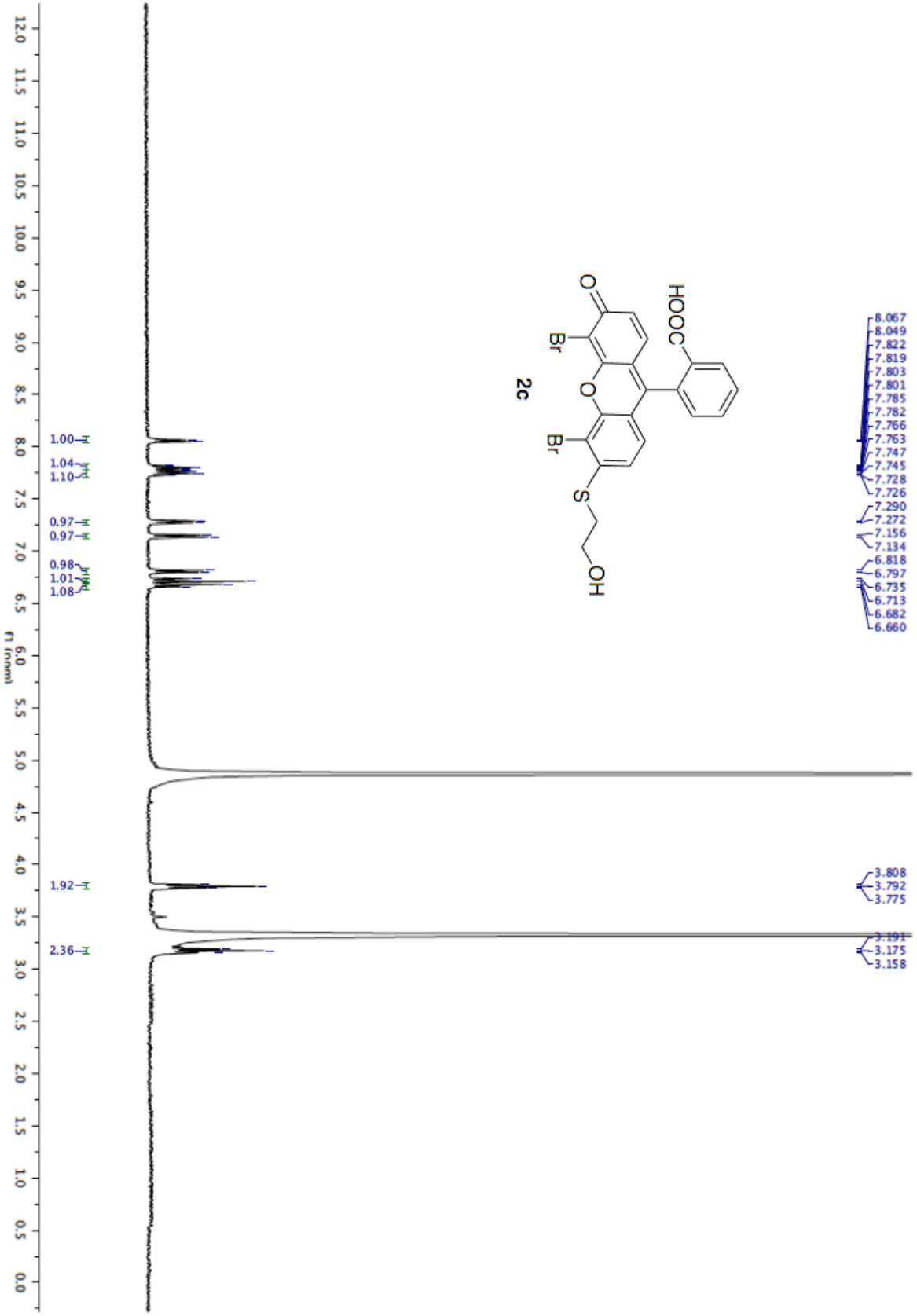
[1]H-spectrum of **2b** in DMSO-d_6



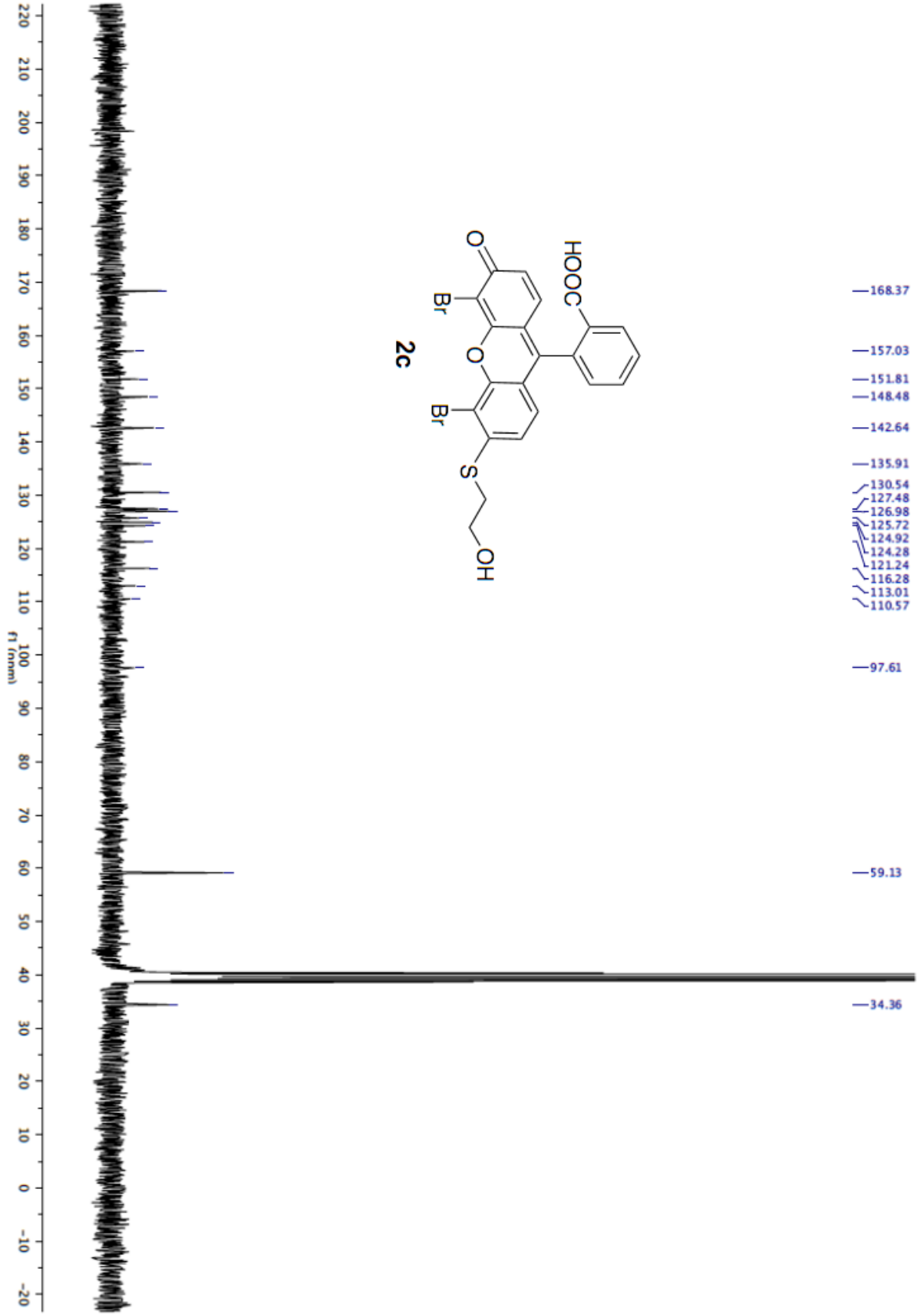
^{13}C-spectrum of **2b** in DMSO-d_6



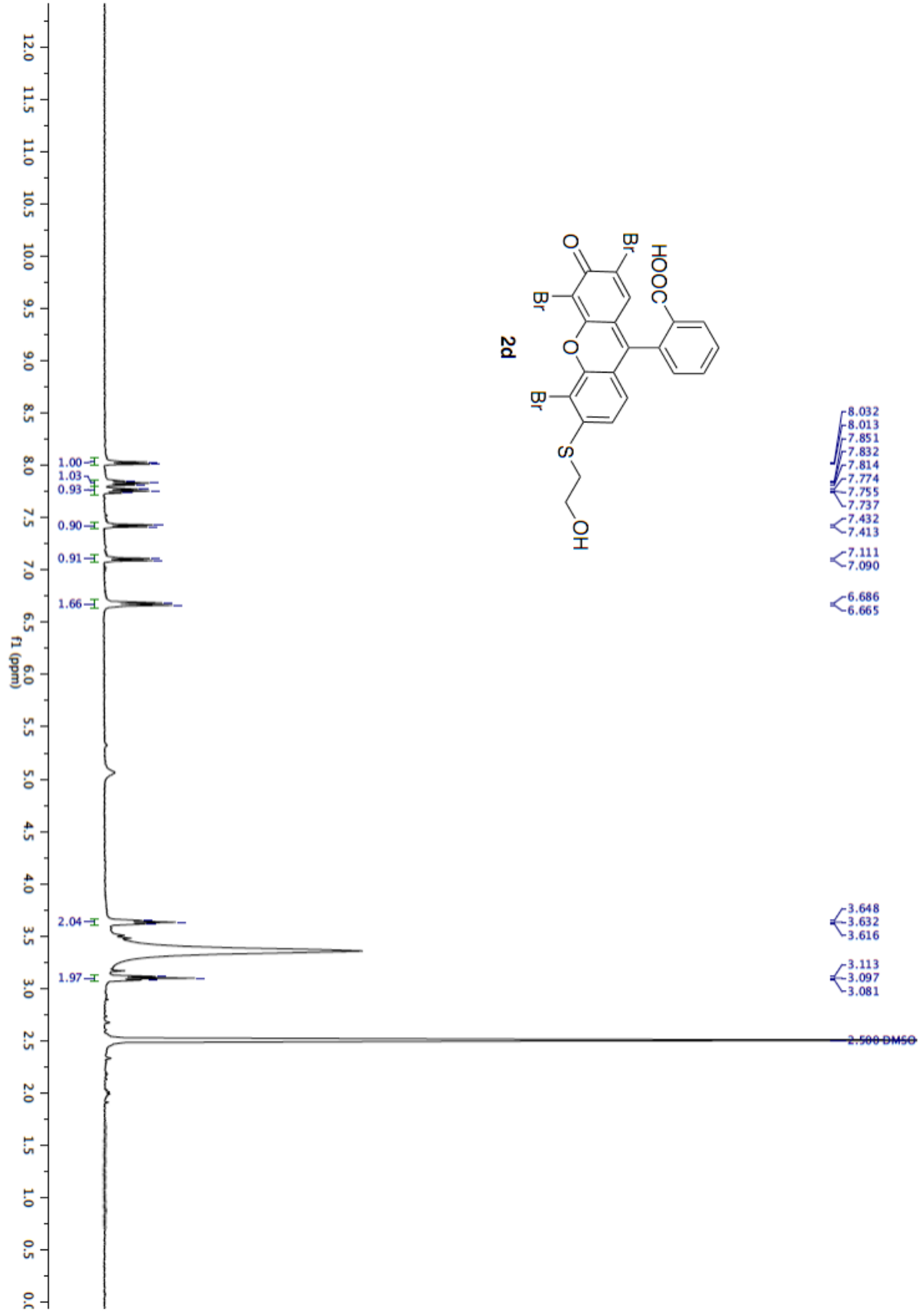
^{1}H-spectrum of **2c in** CD_3OD



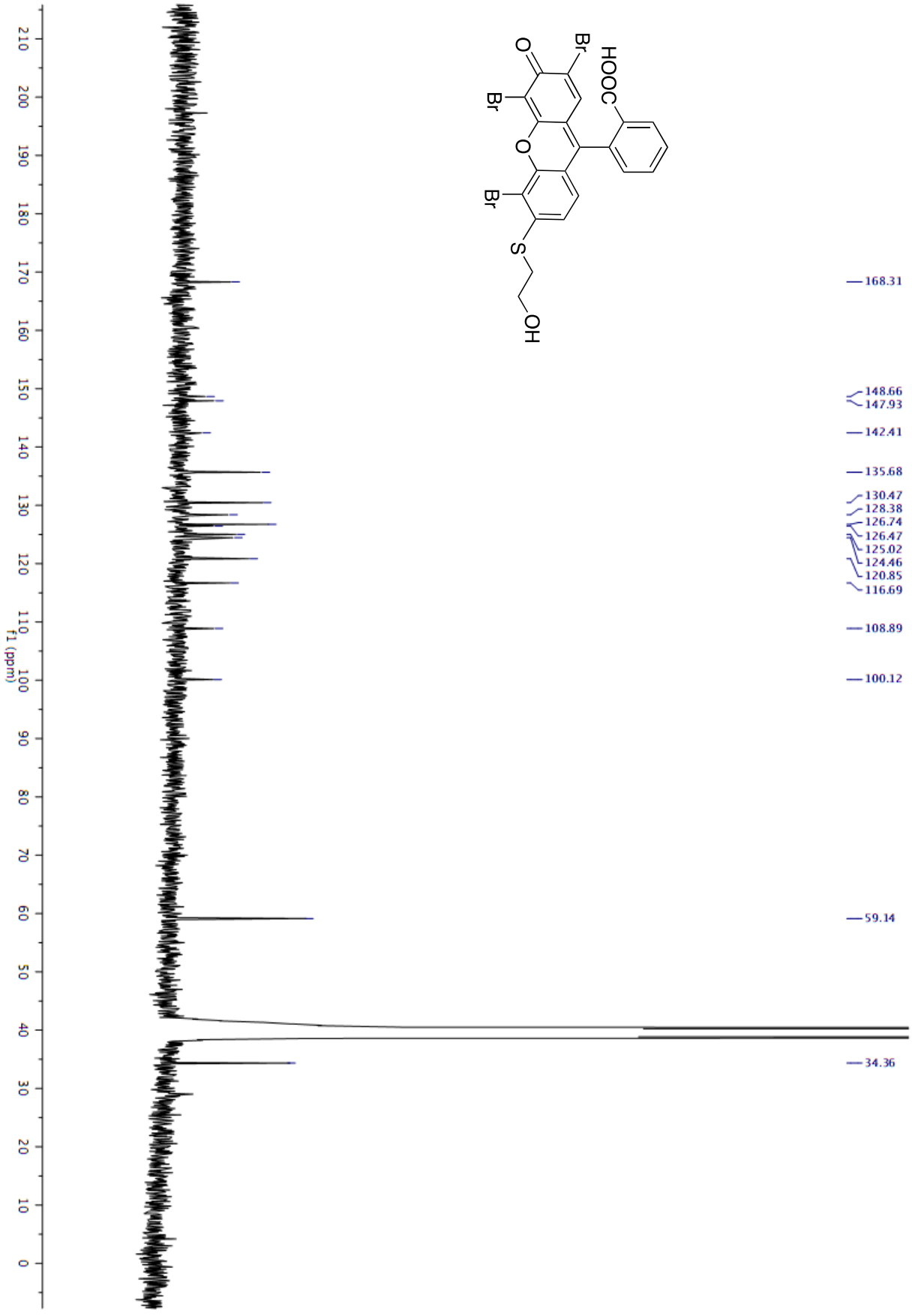
^{13}C-spectrum of **2c** in CD_3OD



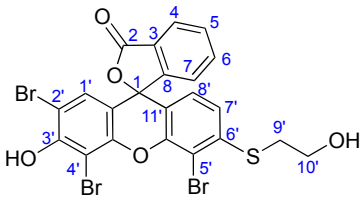
[1]H-spectrum of **2d** in DMSO-d_6



^{13}C-spectrum of **2d** in DMSO-d_6



To distinguish whether the substitution reaction took place on the 3' or 6'-position of the xanthene moiety in **2d** (MK-74-2), two-dimensional carbon-proton shift correlation *via* long-range C-H coupling was applied. In particular, the heteronuclear multiple bond correlation (HMBC) was employed (Figure S1), which identifies $^{2}J_{CH}$ and $^{3}J_{CH}$ couplings while $^{1}J_{CH}$ coupling is usually suppressed. In HMBC, a ^{1}H NMR is displayed in the f2 dimension and a ^{13}C NMR in the f1 dimension. It was observed that three protons on the xanthene moiety, corresponding to two doublets and one singlet in CD_3OD, were displayed as two doublets in DMSO. In the HMBC spectrum, grey lines show correlations from proton H-7' to carbons C-11' and C-5' (3-bond couplings). Green lines show correlations from two protons H-1' and H-8' to carbons C-3' and C-6' (all are 3-bond couplings).



MK-74-2

2d

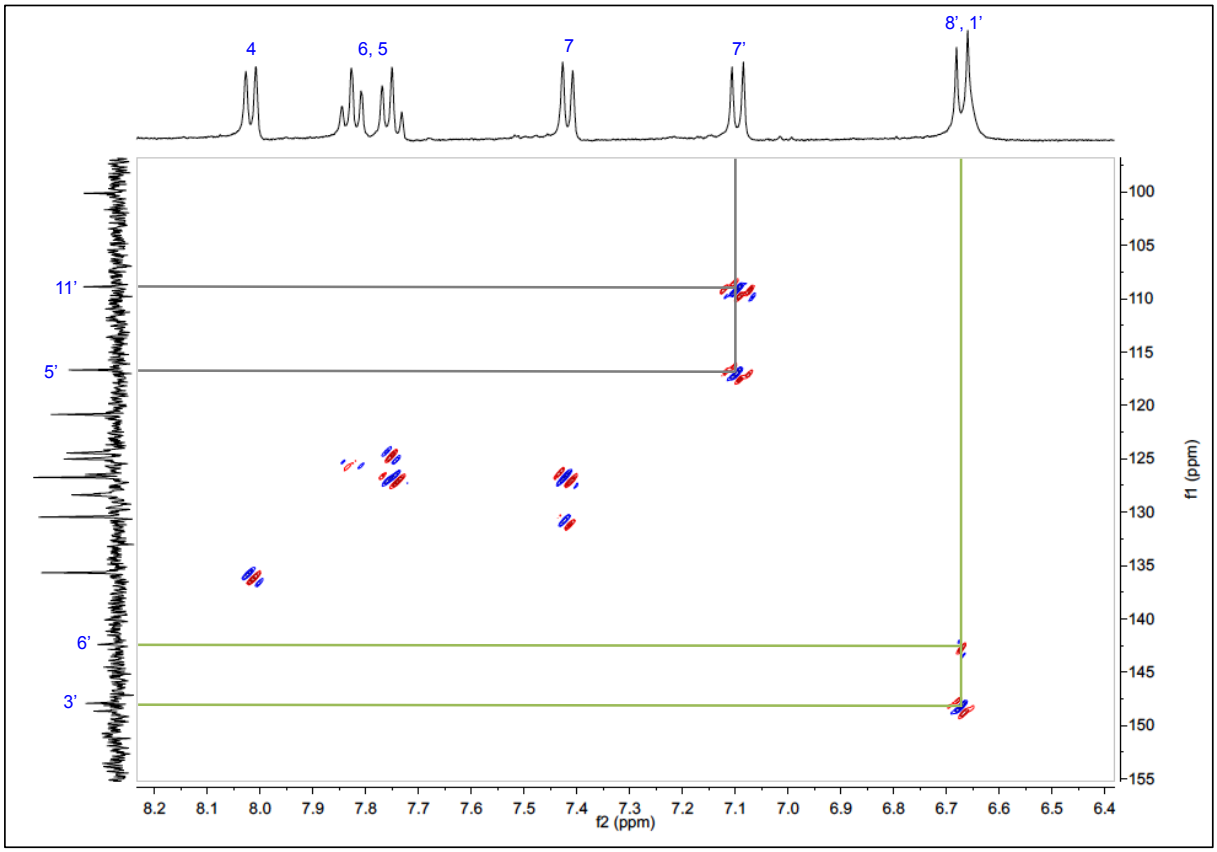
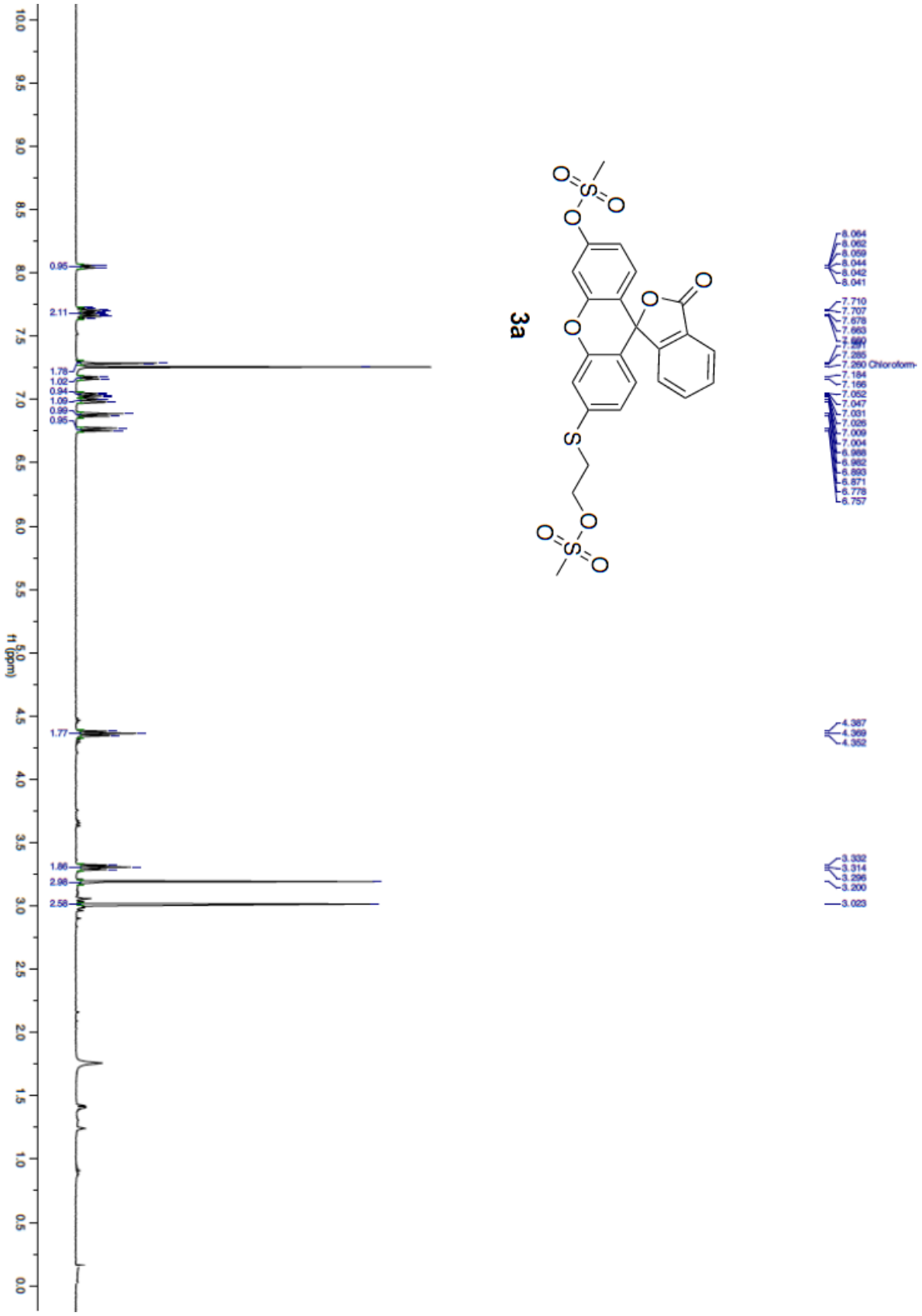
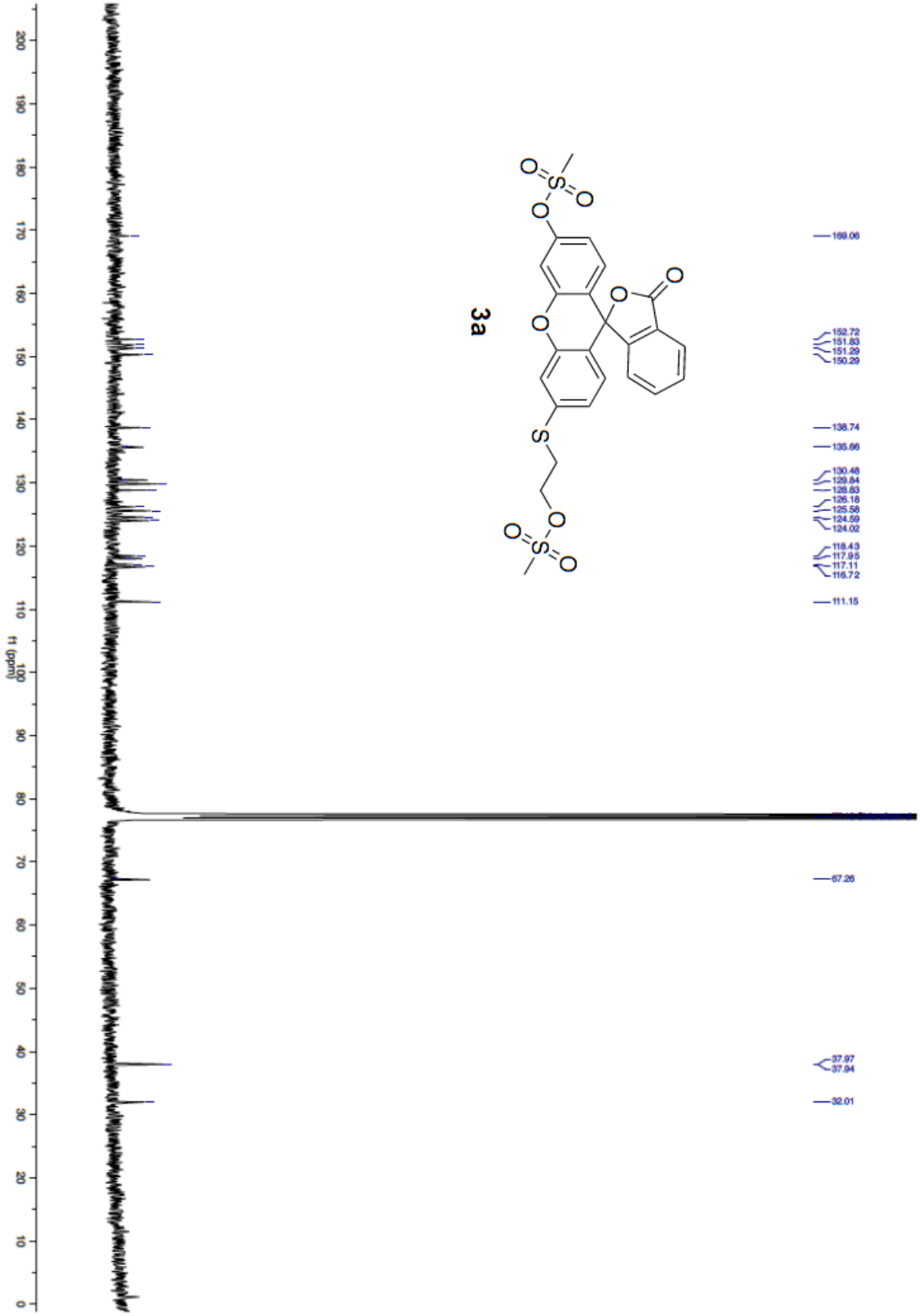


Figure S1. HMBC experiment of **2d**.

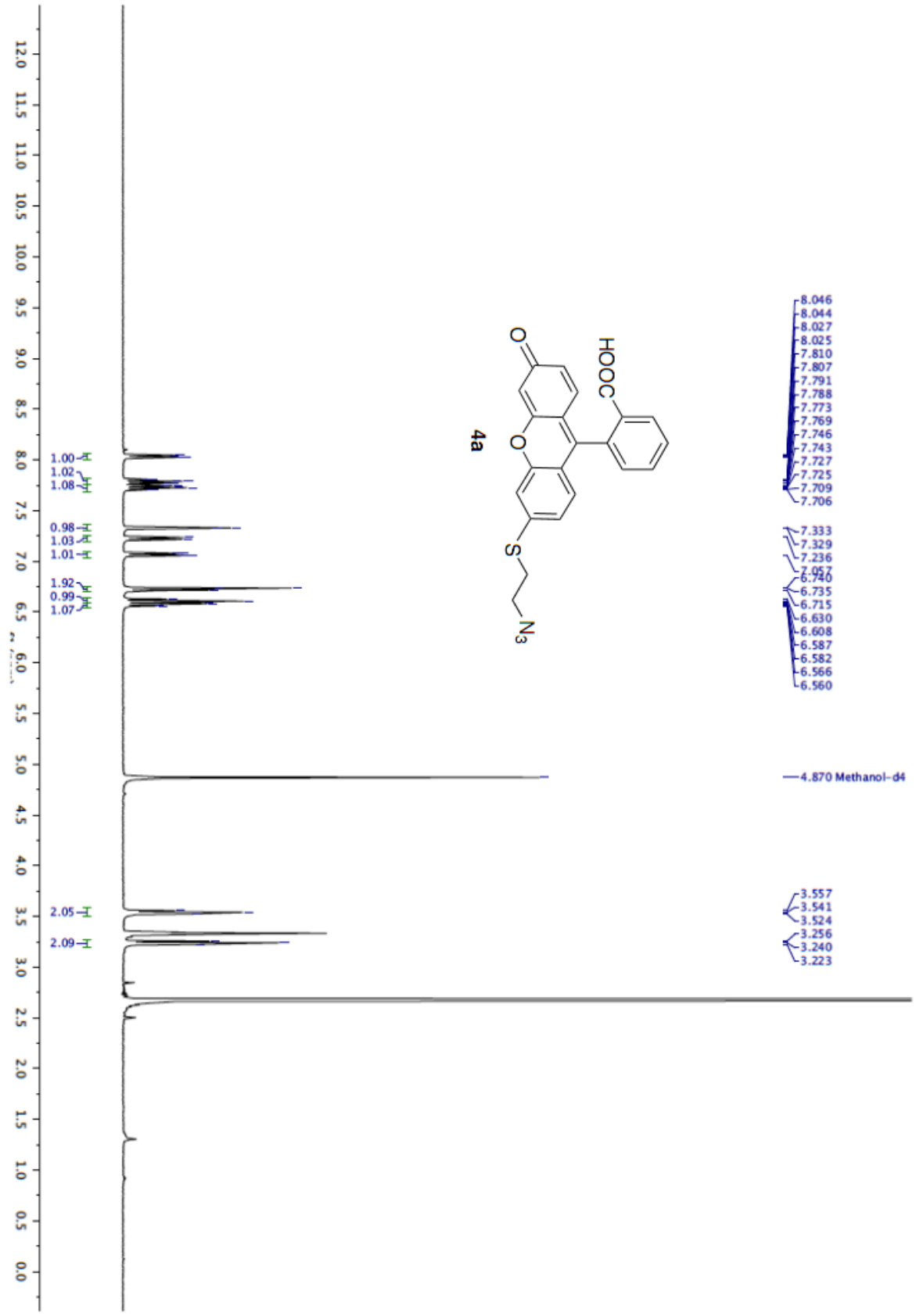
^{1}H-spectrum of **3a** in $CDCl_3$



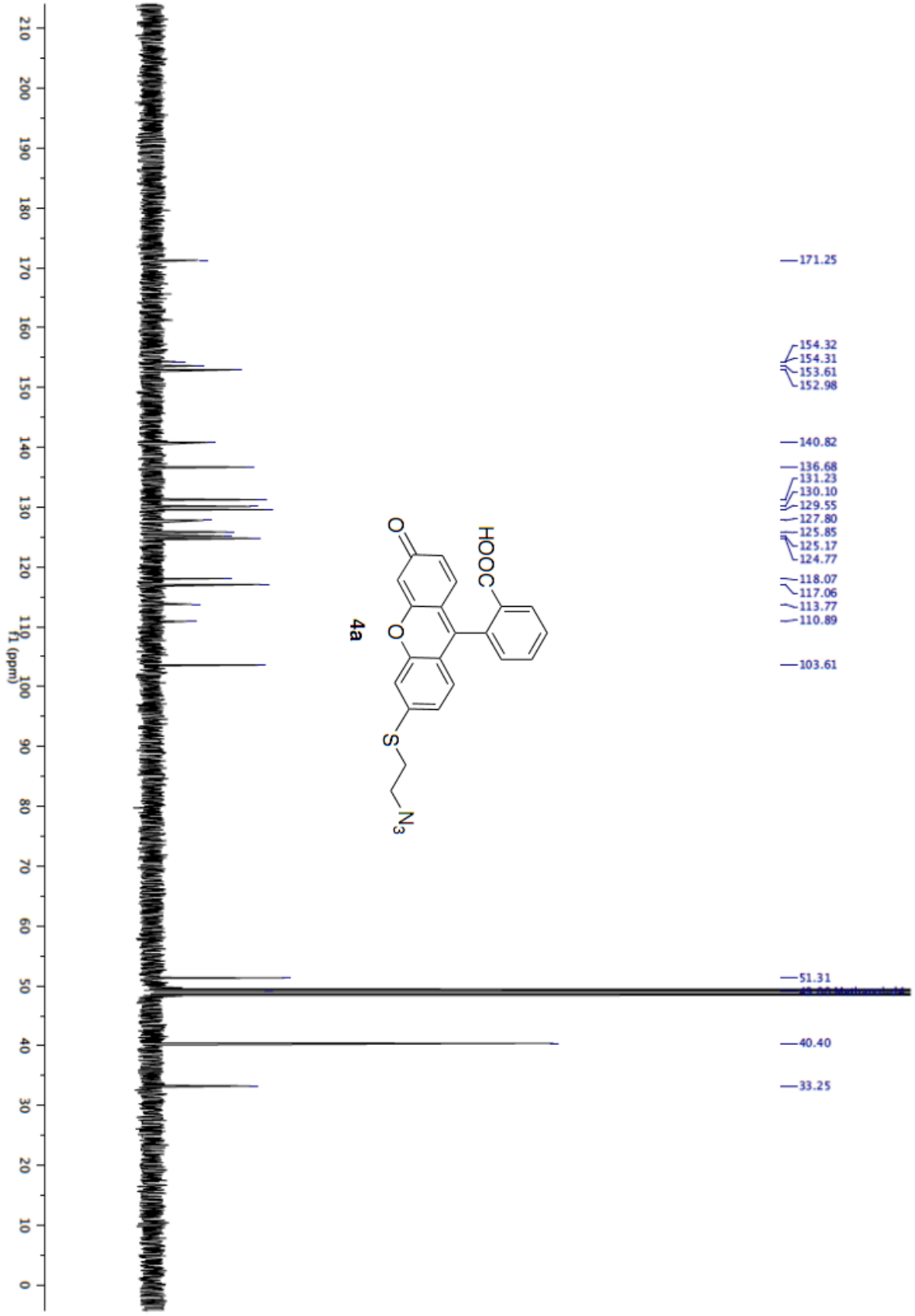
^{13}C-spectrum of **3a** in $CDCl_3$



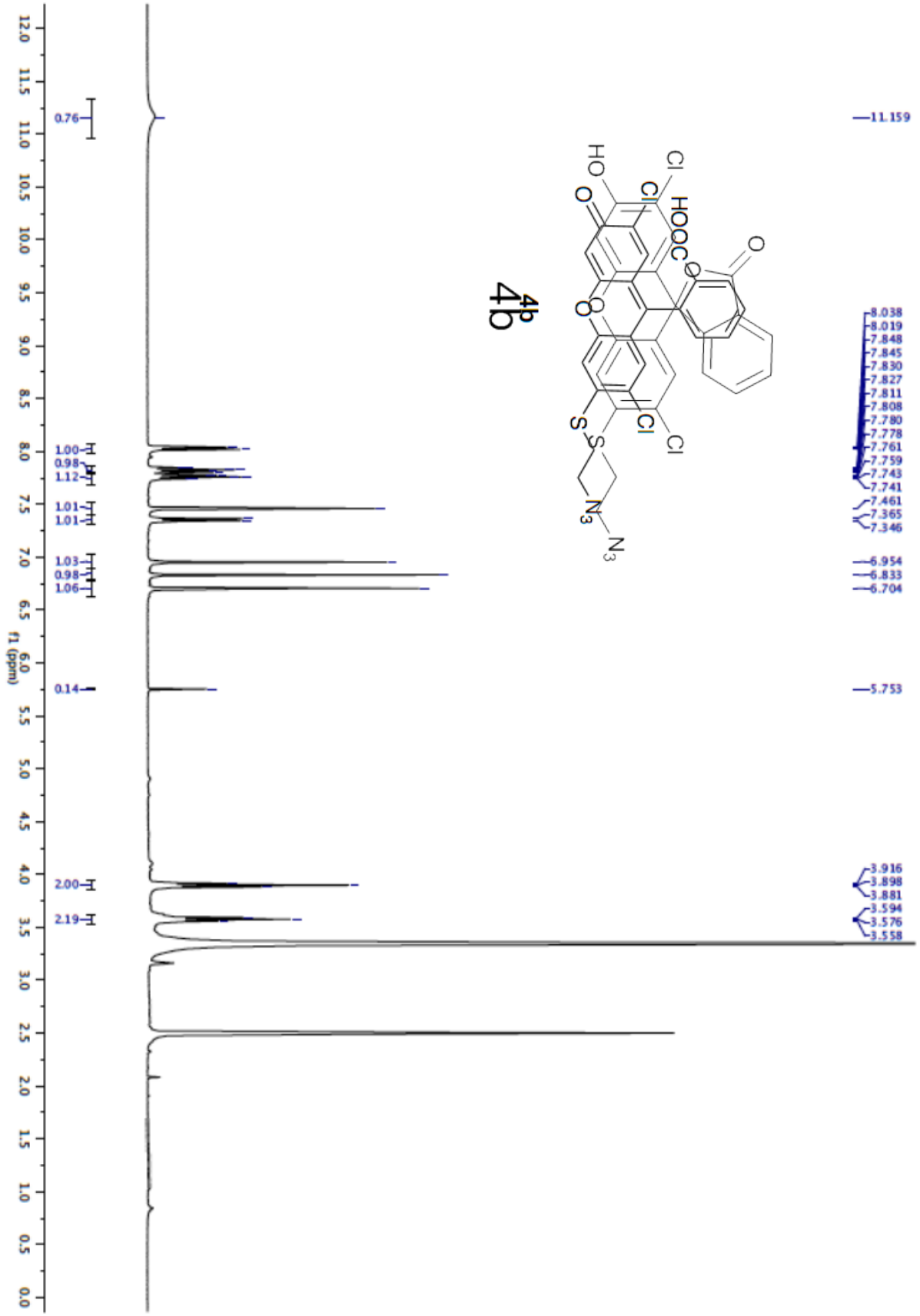
^{1}H-spectrum of **4a** in CD_3OD



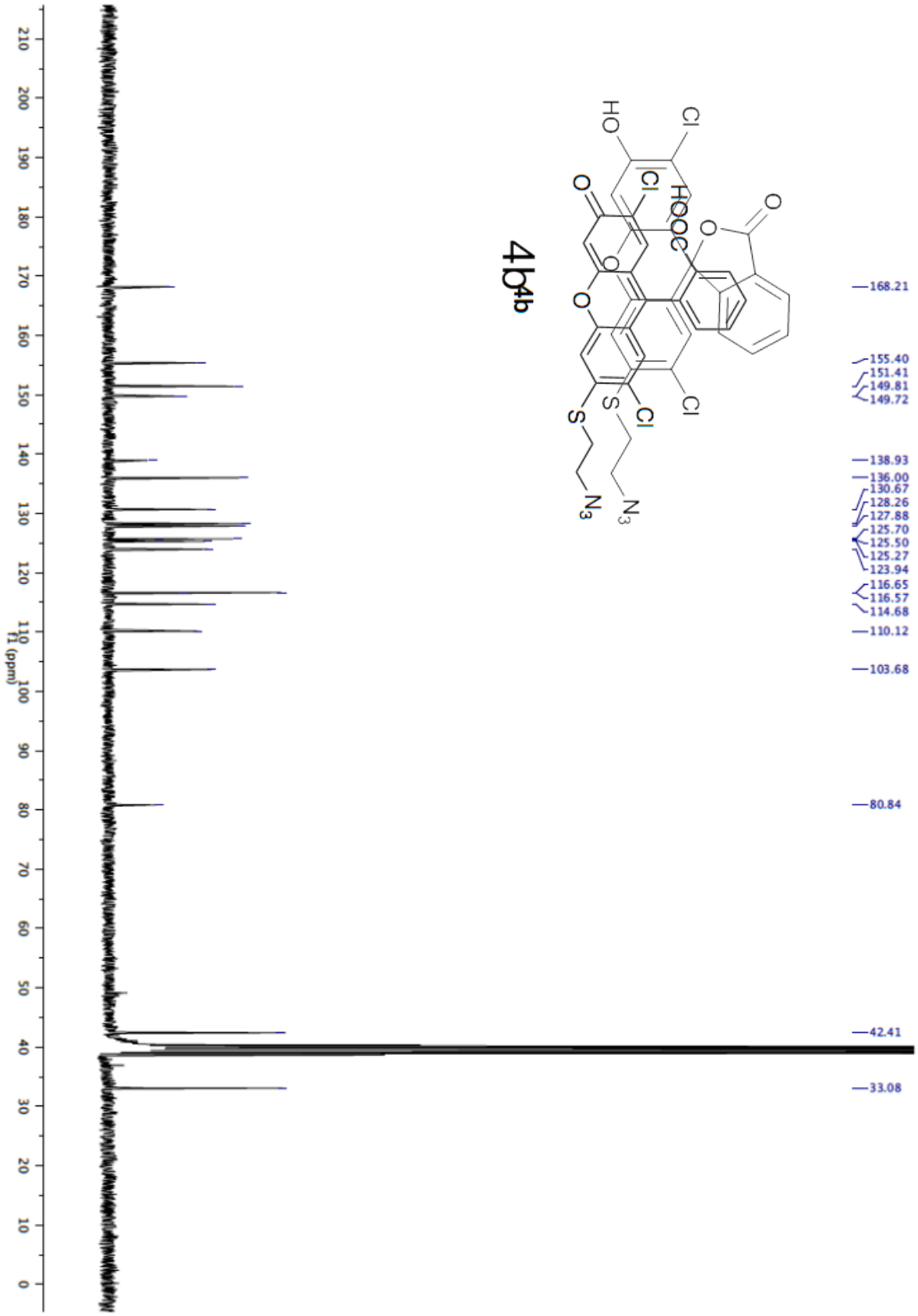
^{13}C-spectrum of **4a** in CD_3OD



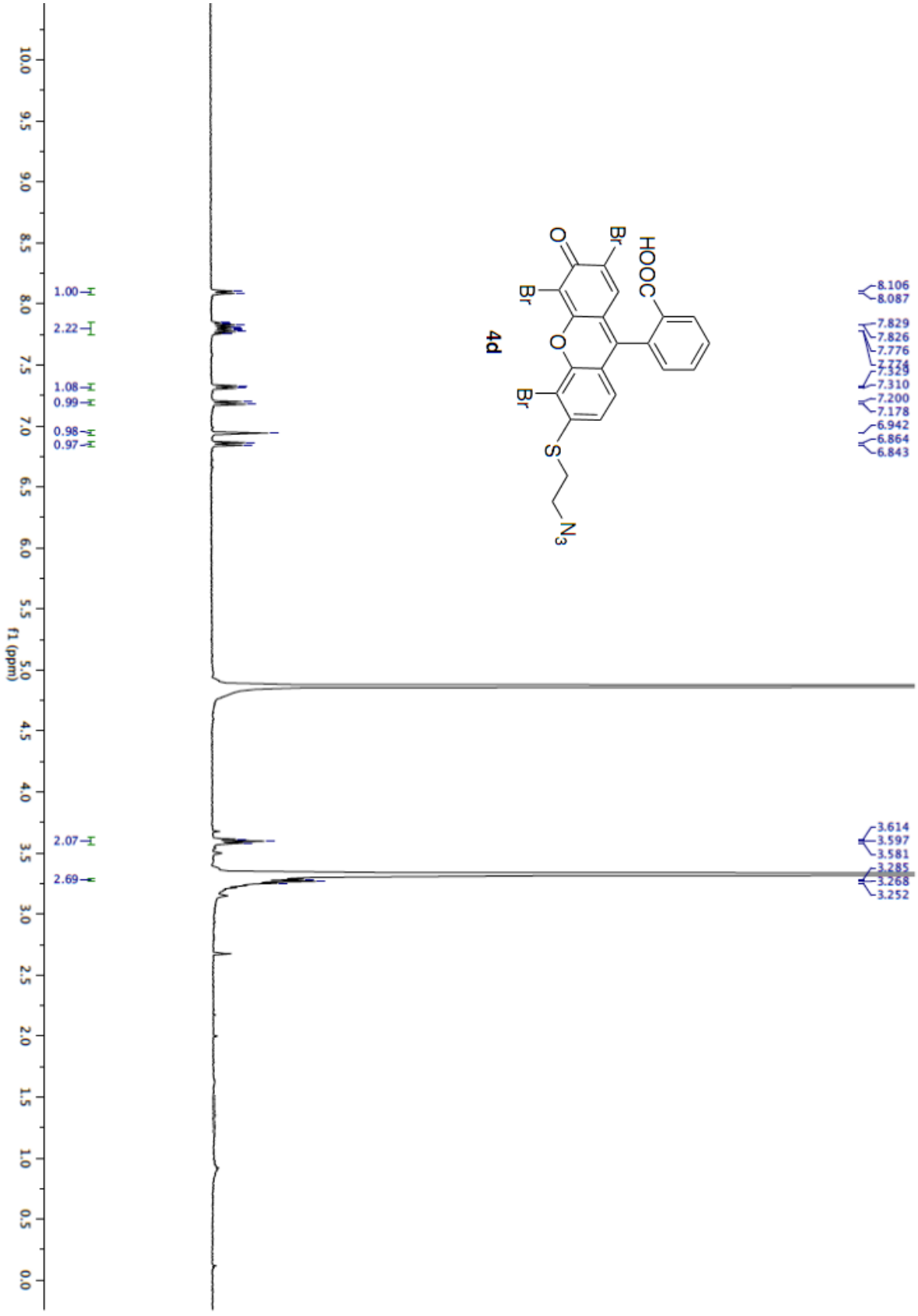
[1]H-spectrum of **4b** in DMSO-*d6*



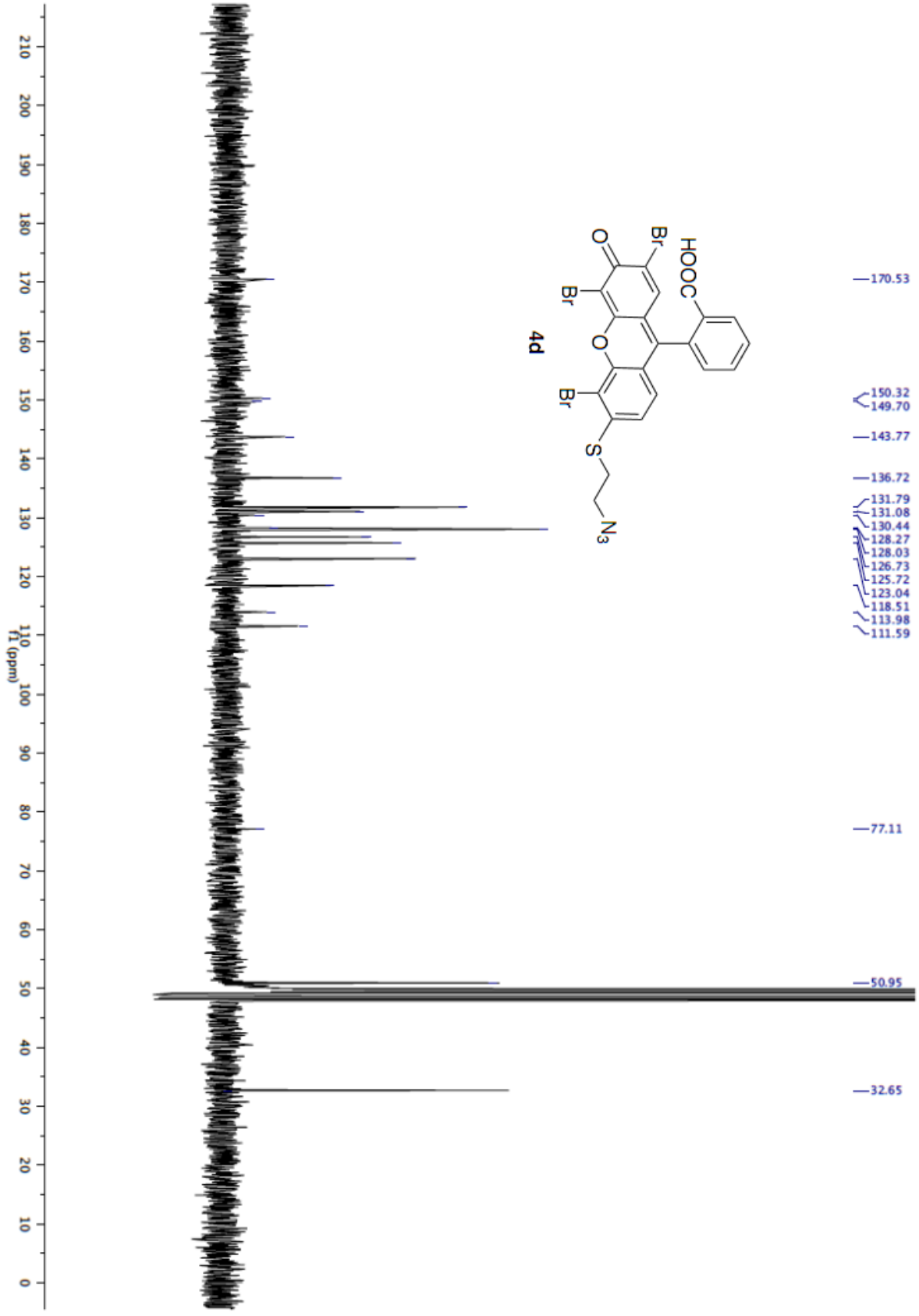
^{13}C-spectrum of **4b** in DMSO-*d6*



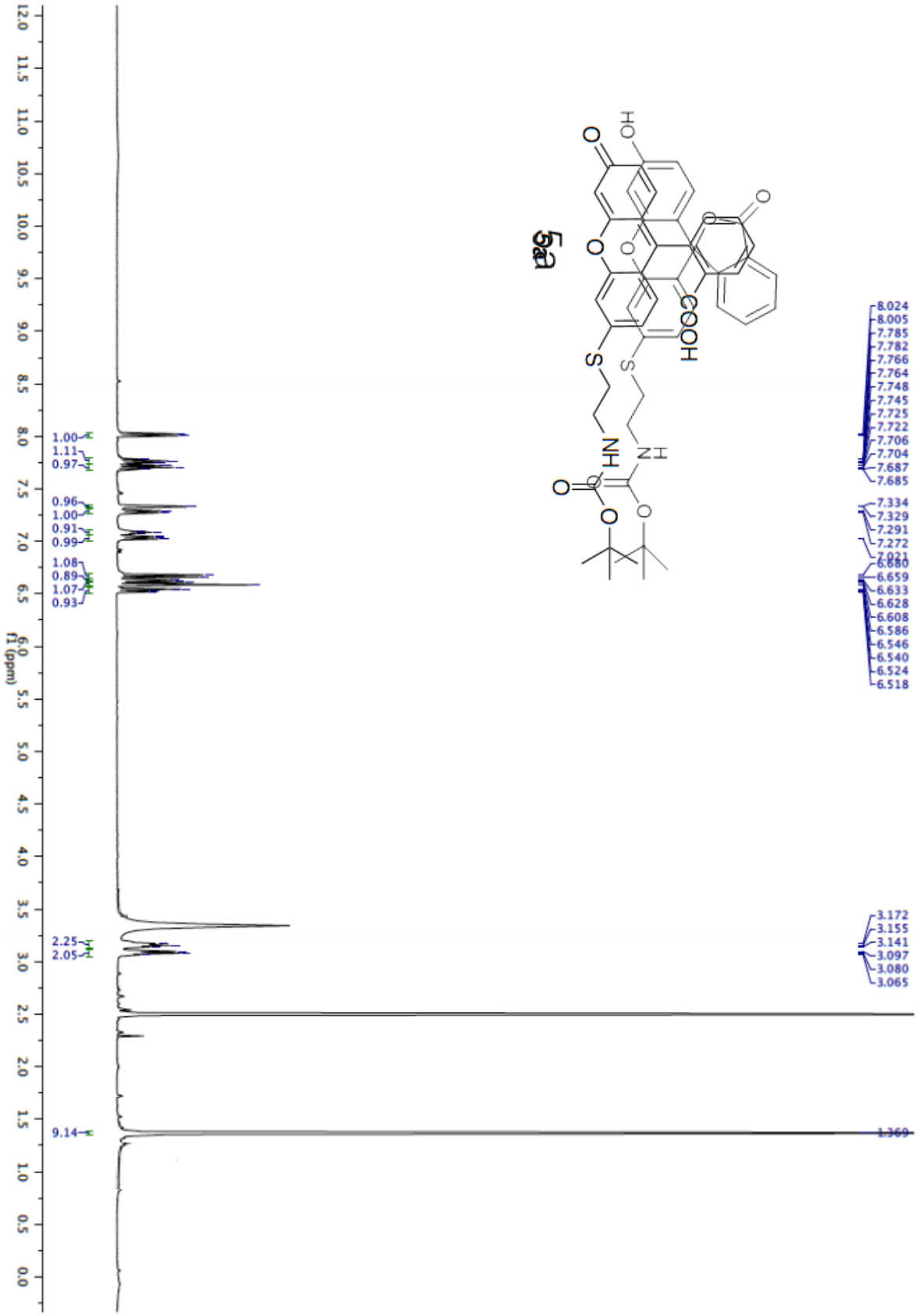
^{1}H-spectrum of **4d** in CD_3OD



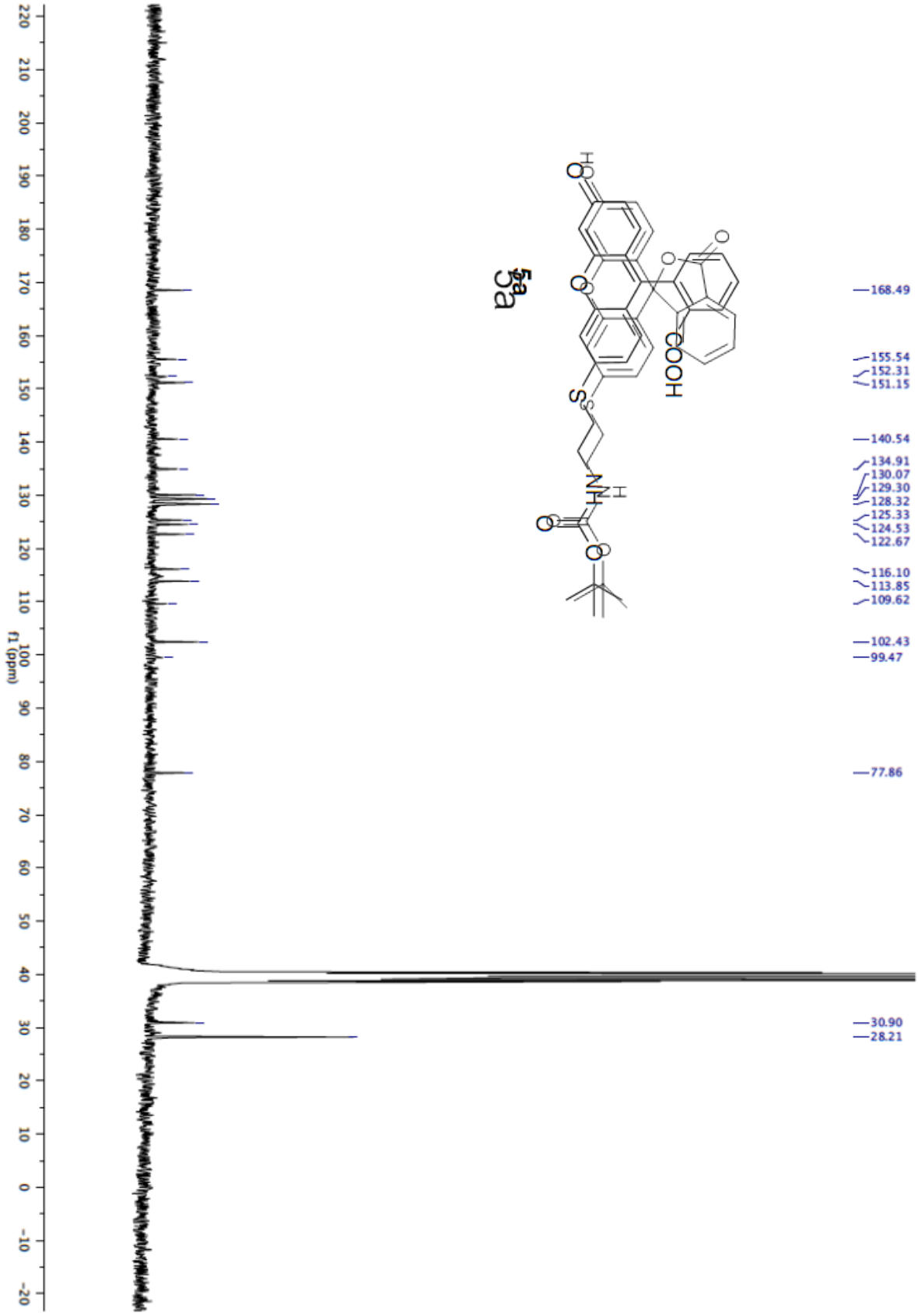
^{13}C-spectrum of **4d** in CD_3OD



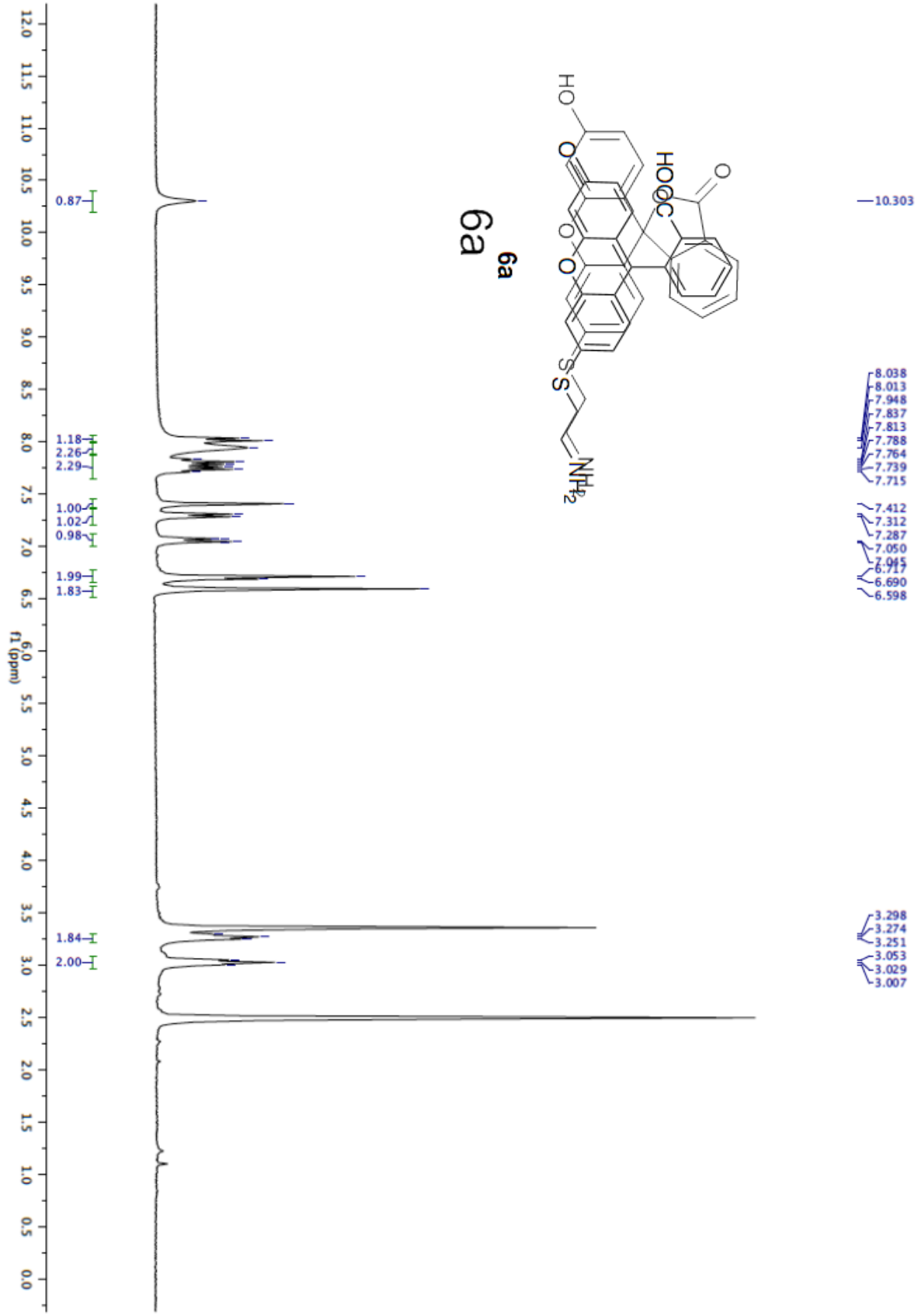
[1]H-spectrum of **5a** in DMSO-*d6*



^{13}C-spectrum of **5a** in DMSO-*d6*



[1]H-spectrum of **6a** in DMSO-*d6*



^{13}C-spectrum of **6a** in DMSO-*d6*