Electronic Supporting Information

Cyclophane-size driving the photochemical behaviour of benzophenone.

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Table of Contens

Synthesis and Characterization of 1 and 2.

Materials and method

Chemicals were used from commercial sources without any purification. Thin layer chromatography (TLC) was performed on silica gel 60 F 254 (Merck 5719) or on silica gel 60 F 254 (Merck 7747) prepared plates and revealed with a ultra-violet lamp. Column chromatography was carried out on silica gel 60 (40–63 μm) from Merck (7736) for flash chromatography or silica gel 60 (63–200 μm) from Merck (7734) for gravity columns.

Absorption spectra were recorded on a Hewlett-Packard 8452A Diode Array Spectrophotometer. Samples for absorption spectra were prepared in spectroscopic grade solvents and adjusted to a linear range response. Emission spectra were recorded in a Jasco FP-750 spectrofluorometer. Samples for emission spectra were prepared in

spectroscopic grade solvents and adjusted to a linear range response. No fluorescent contaminants were detected in the wavelength region of experimental interest upon excitation. Fluorescence quantum yields were determined by comparison with 0.1 M quinine sulphate in 0.05 M sulphuric acid as a reference, and corrected for the refractive index of the solvent. The samples were irradiated in an immersion well photo reactor (Pyrex) equipped with a 150 W medium-pressure mercury lamp.

Synthetic scheme and numbering of the molecules

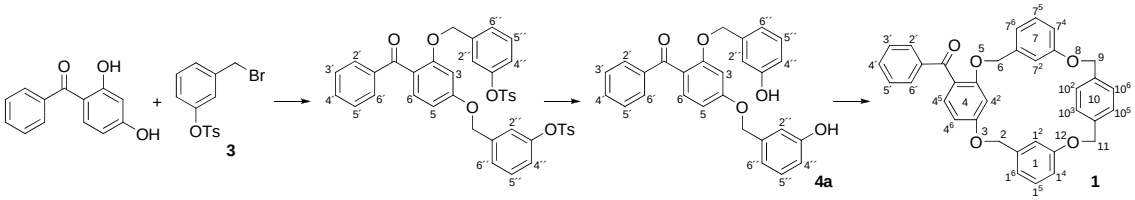

Figure **S1**. Synthetic scheme for 3,5,8,12-Tetraoxa-4^4-benzoyl-1,4,7(1,3),10(1,4)-tetrabenzenacyclododecaphane (**1**) and numbering of the molecules

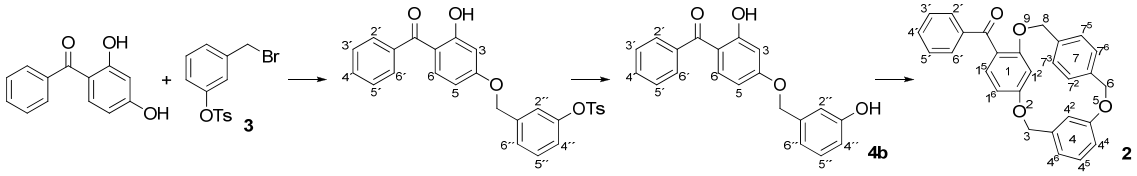

Figure **S2**. Synthetic scheme for 2,5,9-trioxa-1^4-benzoyl-1,4(1,3),7(1,4)-tribenzenacyclononaphane (**2**) and numbering of the molecules

Characterization of 1. Assignment of the signals.

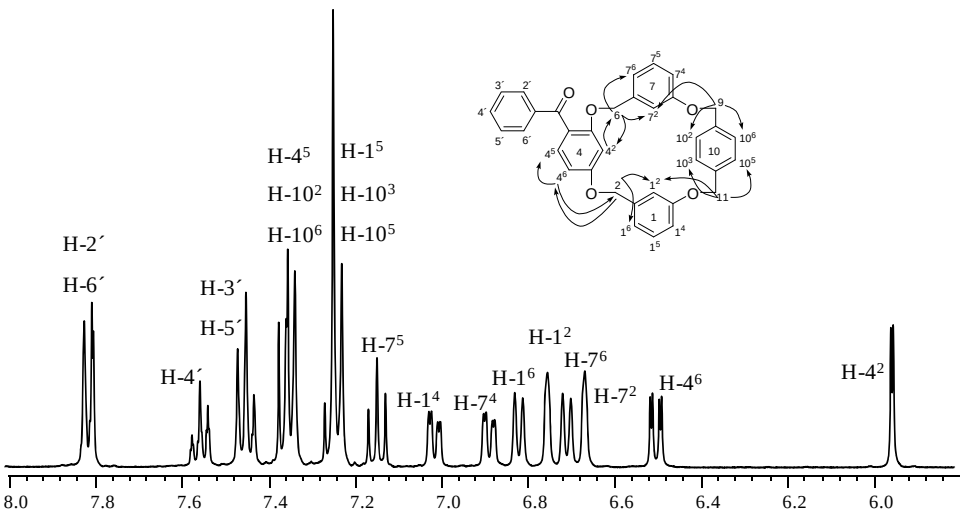

Figure **S3**. Expansion of the ^{1}H-RMN ($CDCl_3$, 400 MHz) of **1**. In the structure are shown some of nOe effects observed.

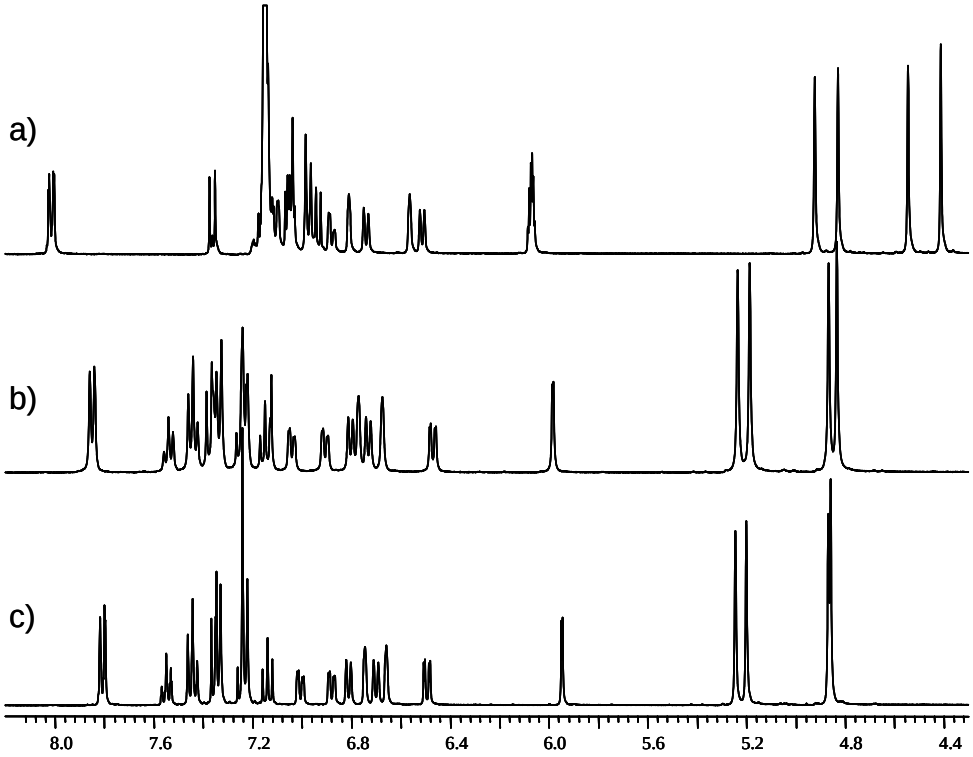

Figure **S4**. ^{1}H-RMN (400 MHz) spectra of **1** recorded in en C_6D_6 (a), $CDCl_3$:C_6D_6 (9:1) (b) and $CDCl_3$ (c).

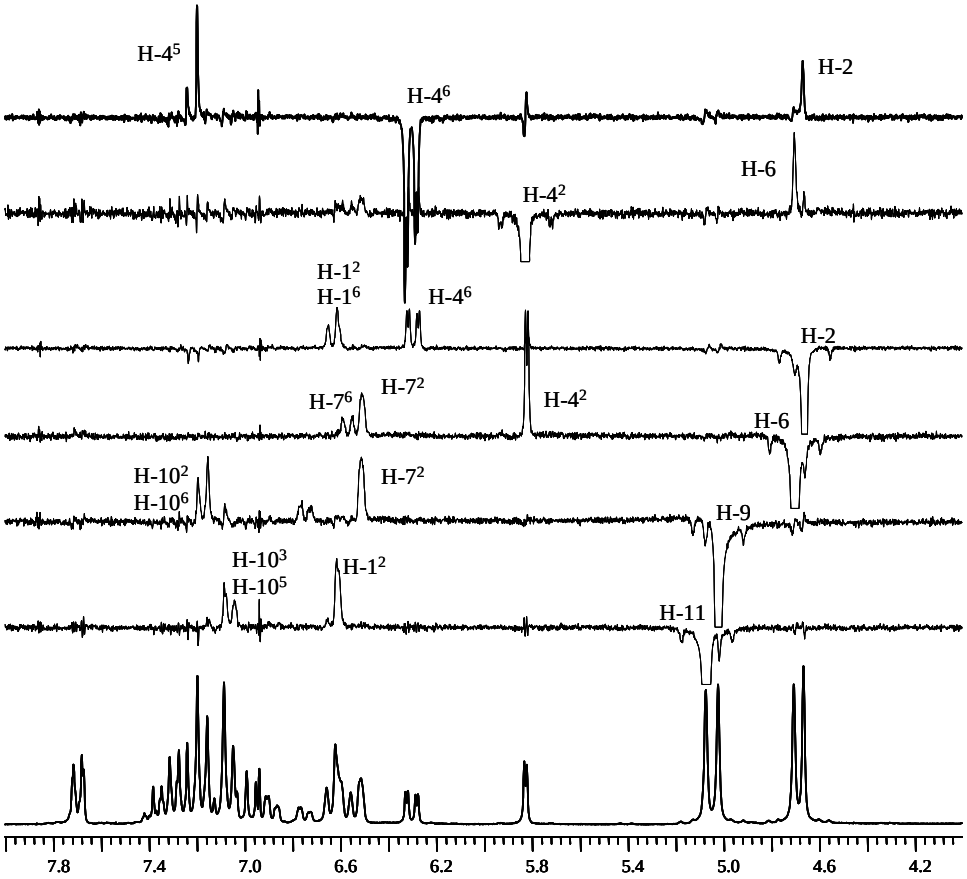

Figure **S5**. NOEDIFF experiments ($CDCl_3$:C_6D_6 (9:1), 200 MHz) of **1**.

	^{1}H-RMN (ppm)	^{13}C-RMN (ppm)	HMBC (J ^{3}) correlations
1^{2}	6.70 (s, 1H)	111.4	C-1^{4}, C-1^{6}, C-2
1^{4}	6.96 (dd, 1H, J = 7.8, 2.1 Hz)	117.7	C-1^{2}, C-1^{6}
1^{5}	7.20 (m, 3H)	129.5	C-1^{1}, C-1^{3}
1^{6}	6.77 (d, 1H, J = 7.8 Hz)	119.6	C-1^{2}, C-1^{4}, C-2
4^{2}	5.91 (d, 1H, J = 2.1 Hz)	102.3	C-4^{4}, C-4^{6}
4^{5}	7.30 (m, 3H)	131.7	C-4^{1}, C-4^{3}
4^{6}	6.45 (dd, 1H, J = 7.8, 2.1 Hz)	103.8	C-4^{2}, C-4^{4}
7^{2}	6.62 (s, 1H)	110.6	C-7^{4}, C-7^{6}, C-6
7^{4}	6.84 (dd, 1H, J = 7.8, 2.1 Hz)	116.6	C-7^{2}, C-7^{6}
7^{5}	7.10 (t, 1H, J = 7.8 Hz)	130.0	C-7^{1}, C-7^{3}
7^{6}	6.65 (d, 1H, J = 7.8 Hz)	118.3	C-7^{2}, C-7^{4}, C-6
10^{2}-10^{6}	7.30 (m, 3H)	127.3	C-10^{2},10^{6}, C-10^{4}, C-9
10^{3}-10^{5}	7.20 (m, 3H)	125.6	C-10^{3},10^{5}, C-10^{1}, C-11
2´, 6´	7.76 (d, 2H, J = 7.8 Hz)	129.7	C-2´, 6´, C-4´, CO
3´, 5´	7.40 (t, 2H, J = 7.8 Hz)	128.1	C-1´, C-3´, 5´
4´	7.51 (t, 1H, J = 7.8 Hz)	132.5	C-2´, 6´
2	4.82 (s, 4H)	69.5	C-1^{2}, C-1^{6}, C-4^{1}
6	4.82 (s, 4H)	70.3	C-4^{3}, C-7^{2}, C-7^{6}
9	5.16 (s, 2H)	68.6	C-10^{2},10^{6}, C-7^{3}
11	5.20 (s, 2H)	69.6	C-10^{3},10^{5}, C-1^{3}

Table **S1**. Spectroscopic data of **1** assigned based on the HMQC and HMBC spectra of **1**.

Characterization of 2. Assignment of the signals.

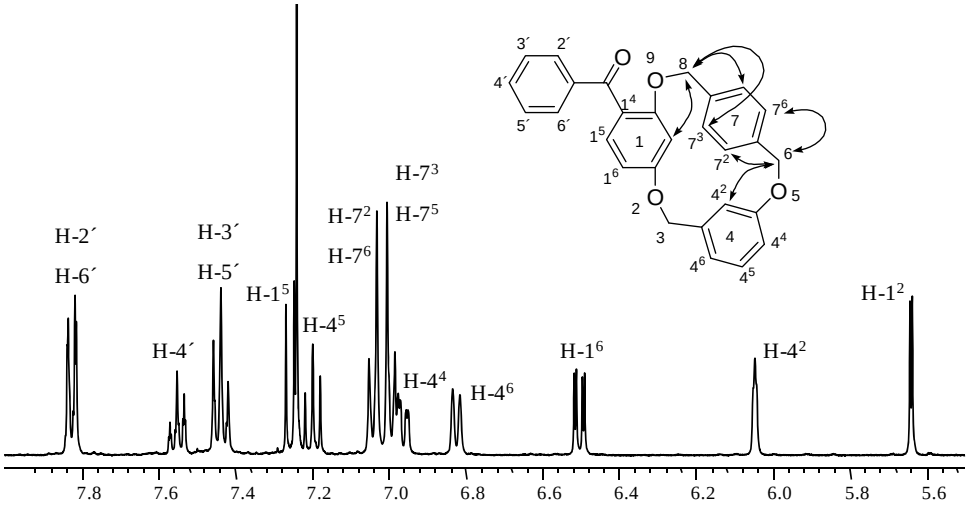

Figure **S6**. Expansion of the ^{1}H-RMN ($CDCl_3$, 400 MHz) of **2**. In the structure are shown some of nOe effects observed.

	^{1}H-RMN (ppm)	^{13}C-RMN (ppm)	HMBC (J^{3}) correlations
1^2	5.64 (d, 1H, *J* = 2.4 Hz)	109.9	C-1^4, C-1^6
1^5	7.26 (d, 1H, *J* = 7.9 Hz)	131.5	C-1^1, C-1^3, CO
1^6	6.50 (dd, 1H, *J* = 7.9, 2.4 Hz)	110.5	C-1^2, C-1^4
4^2	6.05 (sa, 1H)	117.4	C-4^4, C-4^6, C-3
4^4	6.96 (dd, 1H, *J* = 7.9, 2.4 Hz)	119.7	C-4^2, C-4^6
4^5	7.20 (t, 1H, *J* = 7.9 Hz)	129.5	C-4^1, C-4^3
4^6	6.82 (d, 1H, *J* = 7.9 Hz)	120.7	C-4^2, C-4^4, C-3
7^2-7^6	6.99 (d, 2H, *J* = 7.9 Hz)	128.4	C-7^2, 7^6, C-7^4, C-6
7^3-7^5	7.04 (d, 2H, *J* = 7.9 Hz)	129.0	C-7^3, 7^5, C-7^1, C-8
2´, 6´	7.82 (d, 2H, *J* = 7.9 Hz)	129.8	C-2´, 6´, C-4´, CO
3´, 5´	7.44 (t, 2H, *J* = 7.9 Hz)	128.1	C-1´, C-3´, 5´
4´	7.55 (t, 1H, *J* = 7.9 Hz)	132.7	C-2´, 6´
3	4.97 (s, 2H)	69.1	C-1^1, C-4^2, C-4^6
6	5.10 (s, 2H)	73.2	C-4^3, C-7^2, 7^6
8	4.82 (s, 2H)	74.7	C1^3, C-7^3, 7^5

Table **S2**. Spectroscopic data of **2** assigned based on the HMQC and HMBC spectra of **2**.

Photochemical reaction and numbering of the molecules

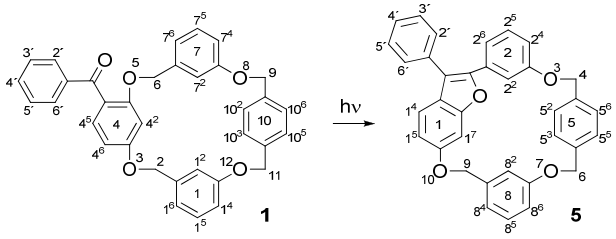

Figure **S7**. Photochemical reaction of **1** and numbering of the molecules

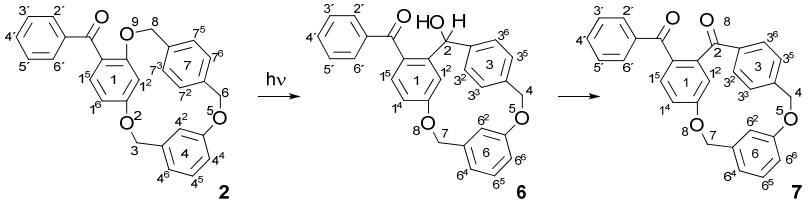

Figure **S8**. Photochemical reaction of **2** and numbering of the molecules

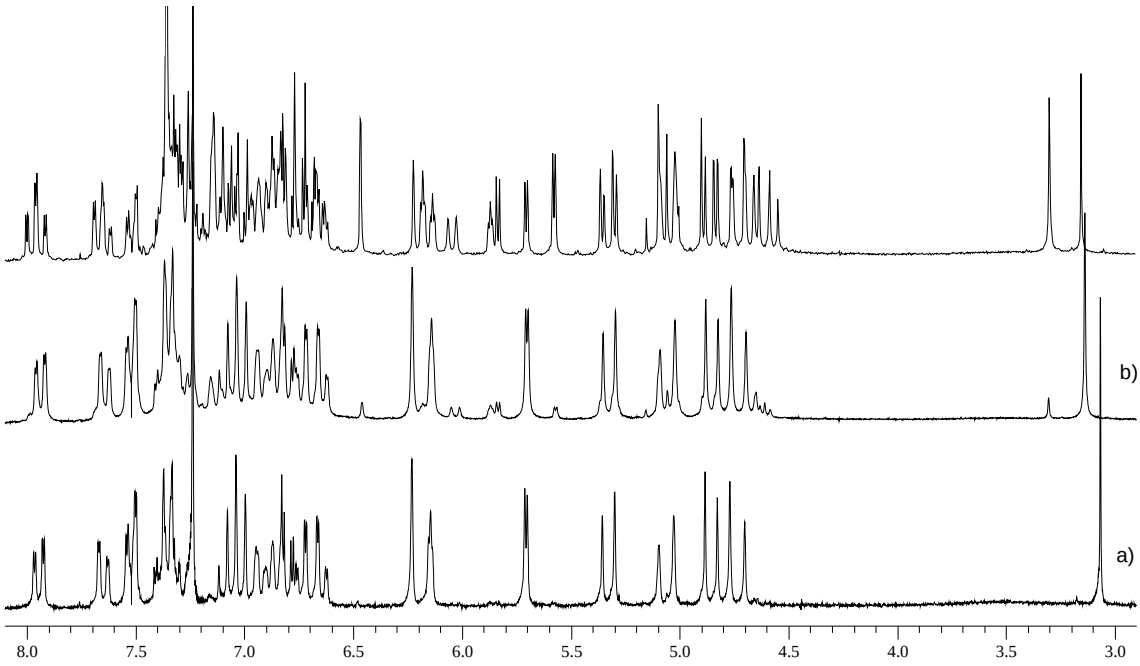

Figure **S9**. ^{1}H-RMN (200 MHz) spectra of **6** recorded in en immediately after solution preparation (a), after 15 minutes (b) and after 1 h (c).

NMR-Spectra

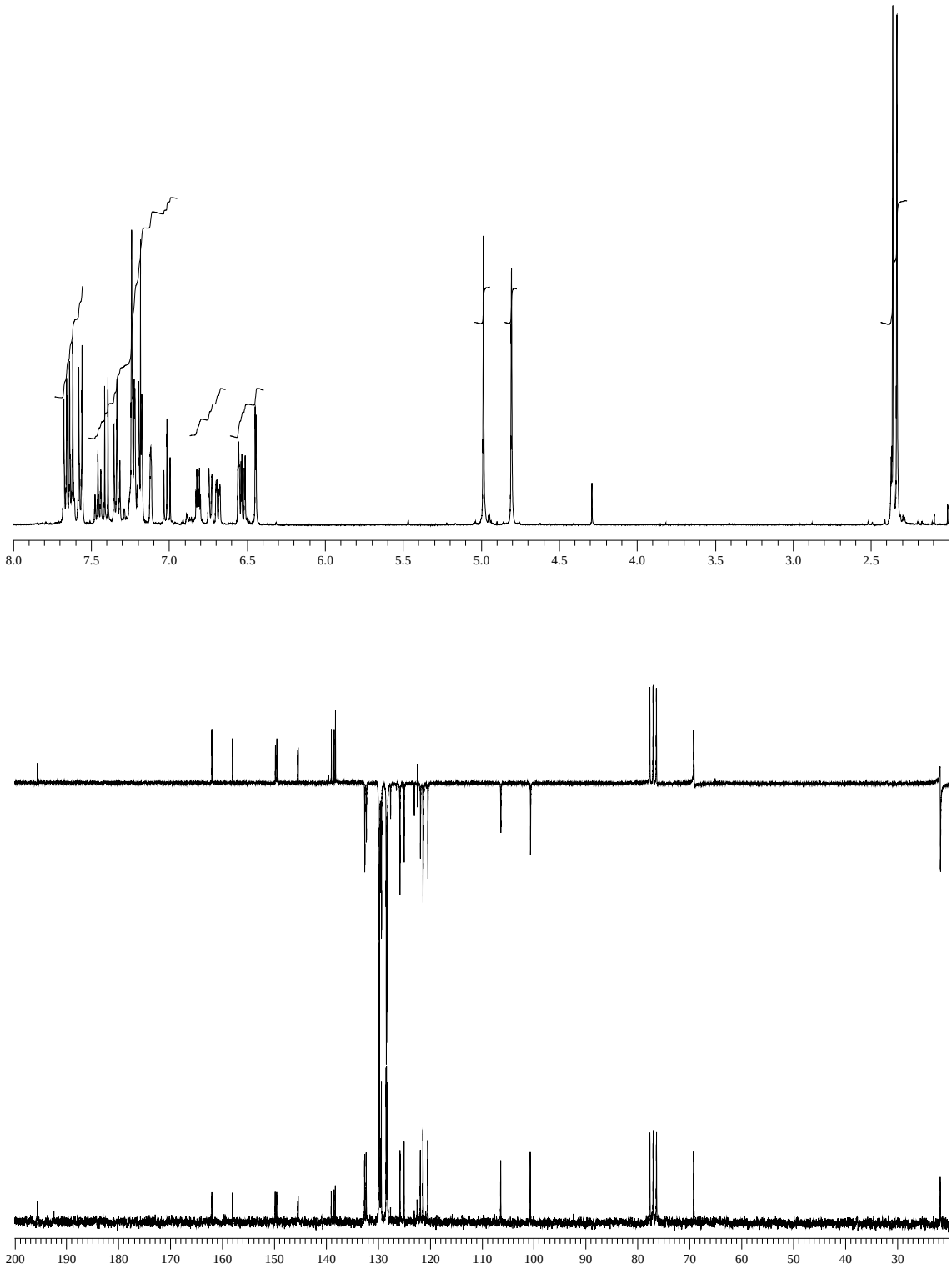

Figure **S10**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of 2,4-Bis[3'-(tosyloxy)benzyloxy] benzophenone

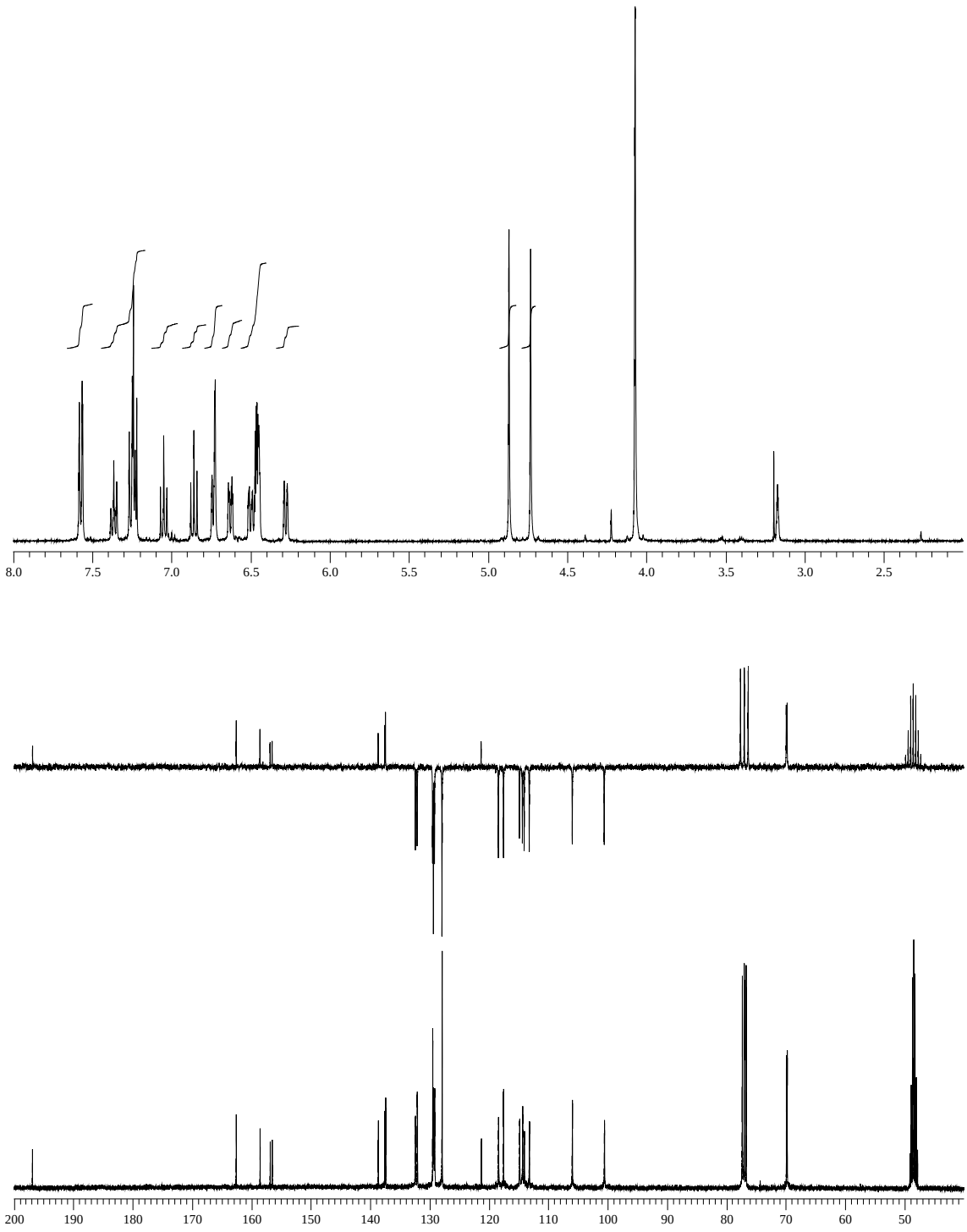

Figure **S11**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of 2,4-Bis[3'-(hydroxyl)benzyloxy] benzophenone (**4a**)

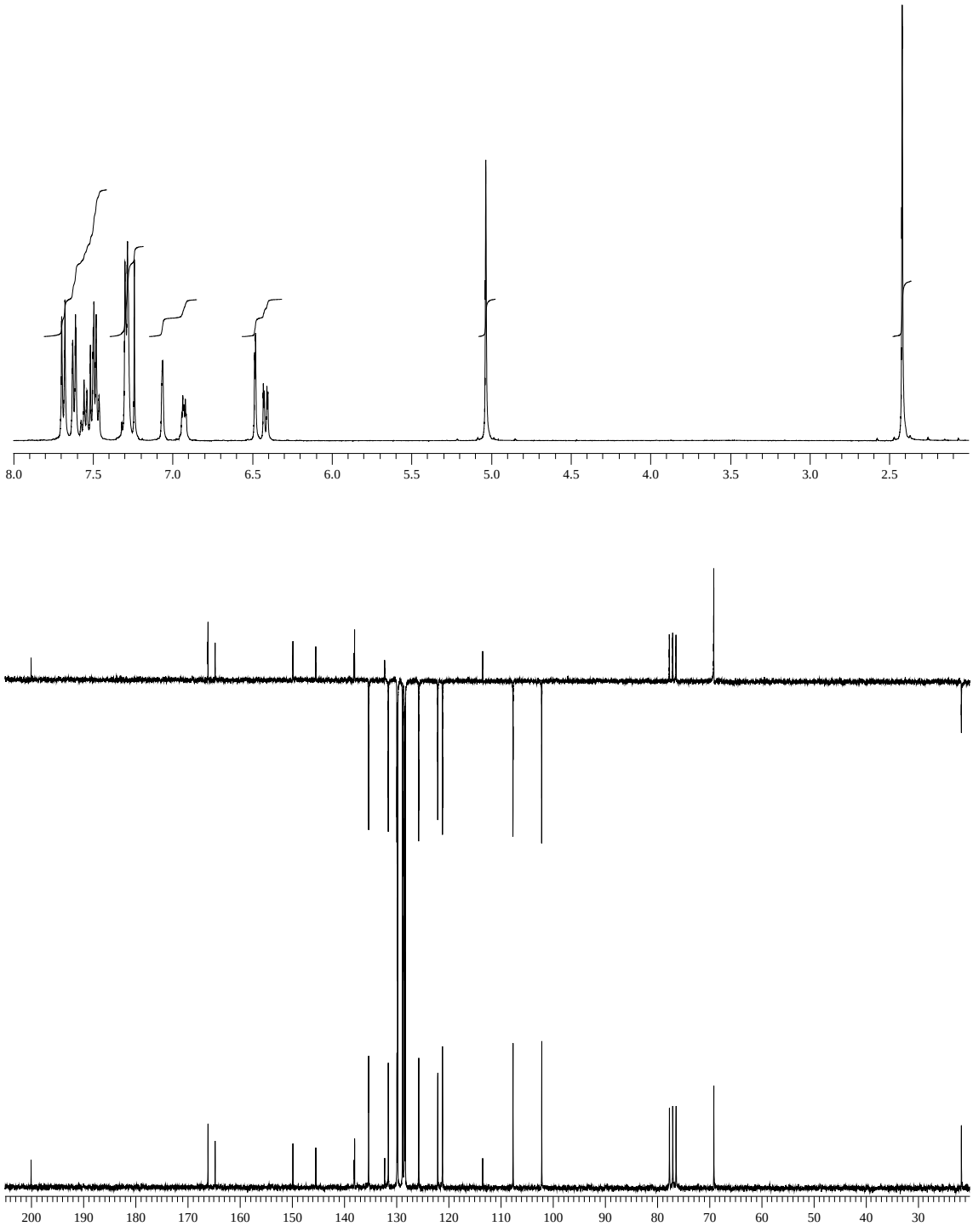

Figure **S12**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of 2-Hydroxy-4-[3'-(tosyloxy)benzyloxy] benzophenone

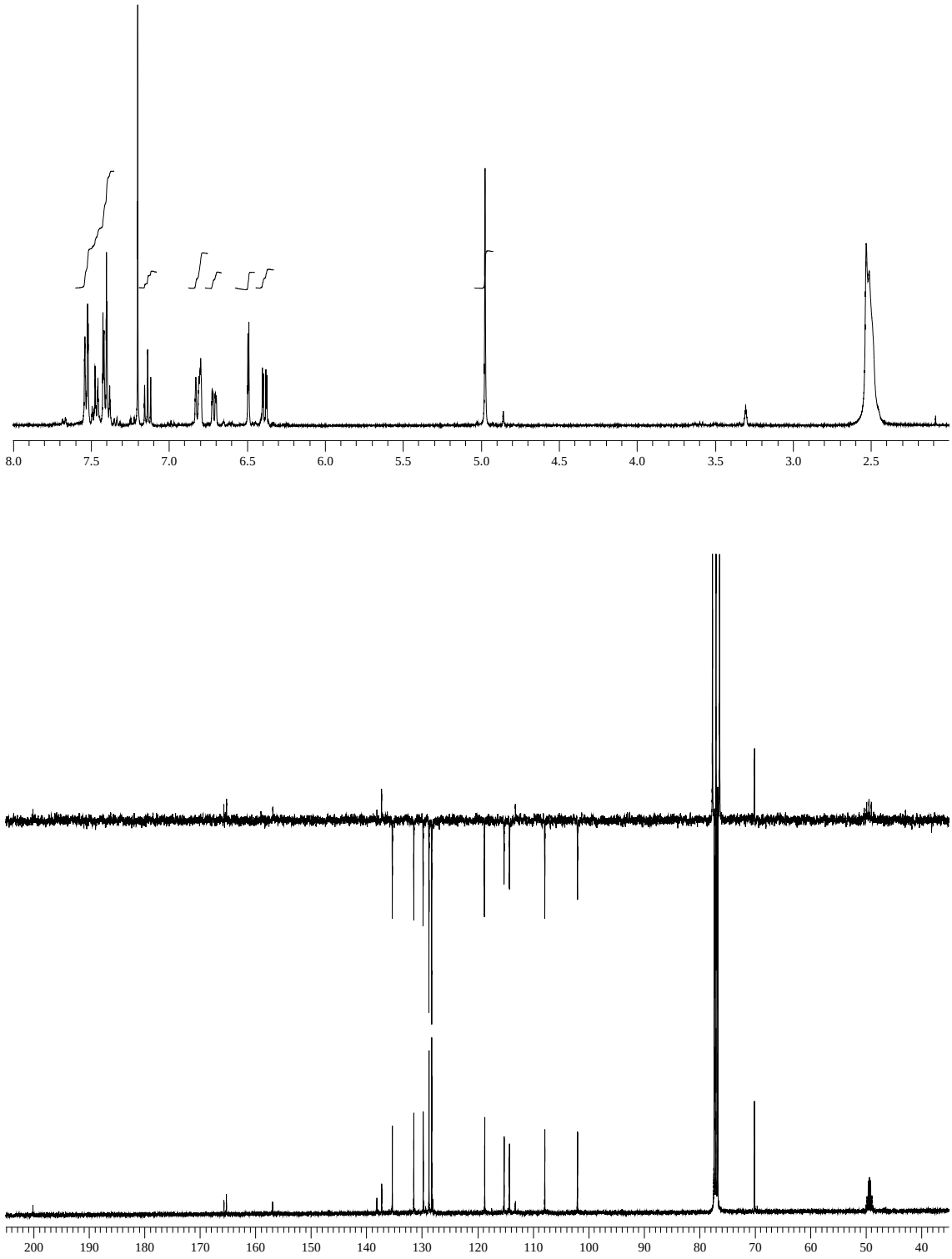

Figure **S13**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of 2-Hydroxy-4-[3'-(hydroxy)benzyloxy] benzophenone (**4b**)

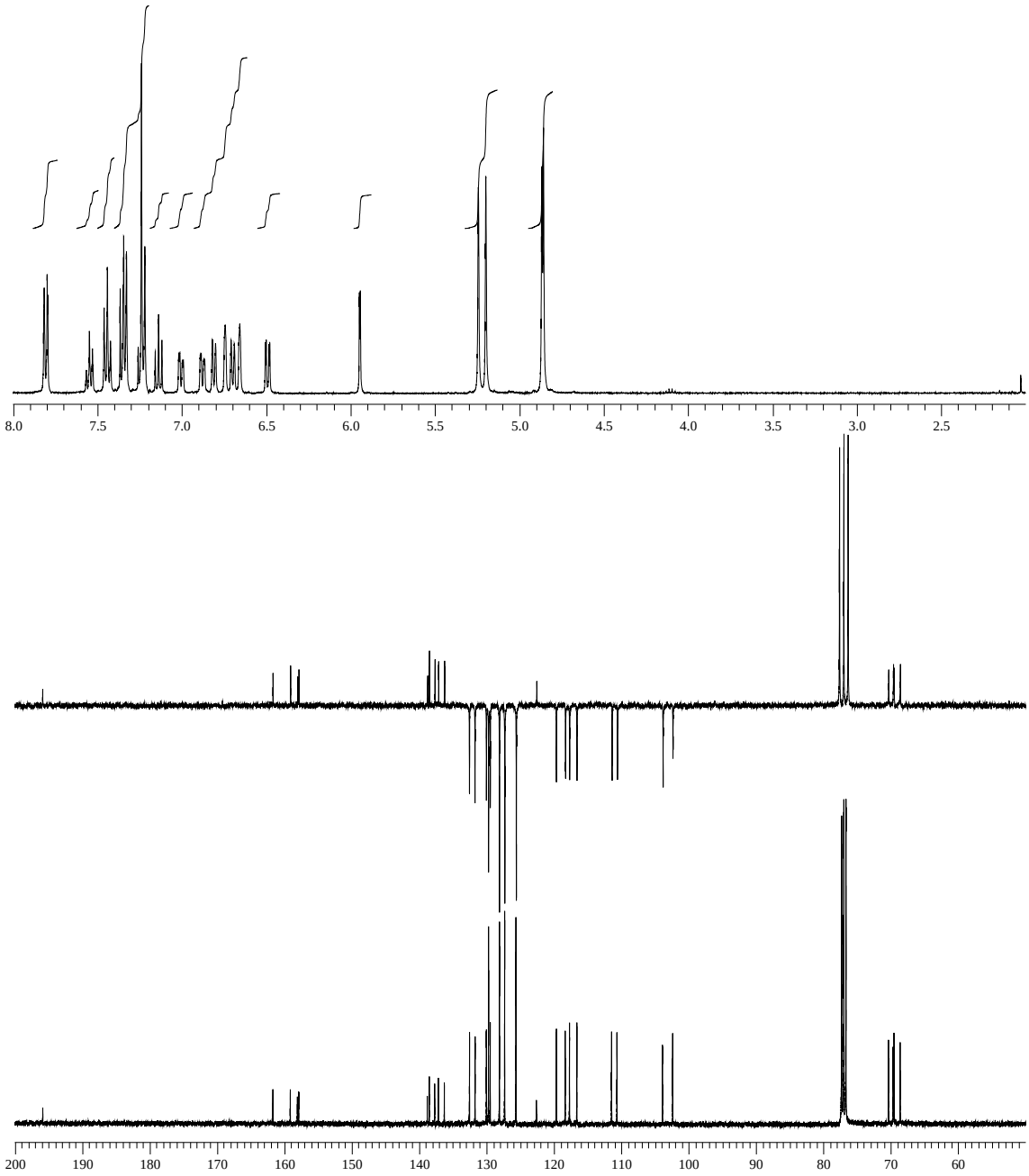

Figure **S14**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of **1**

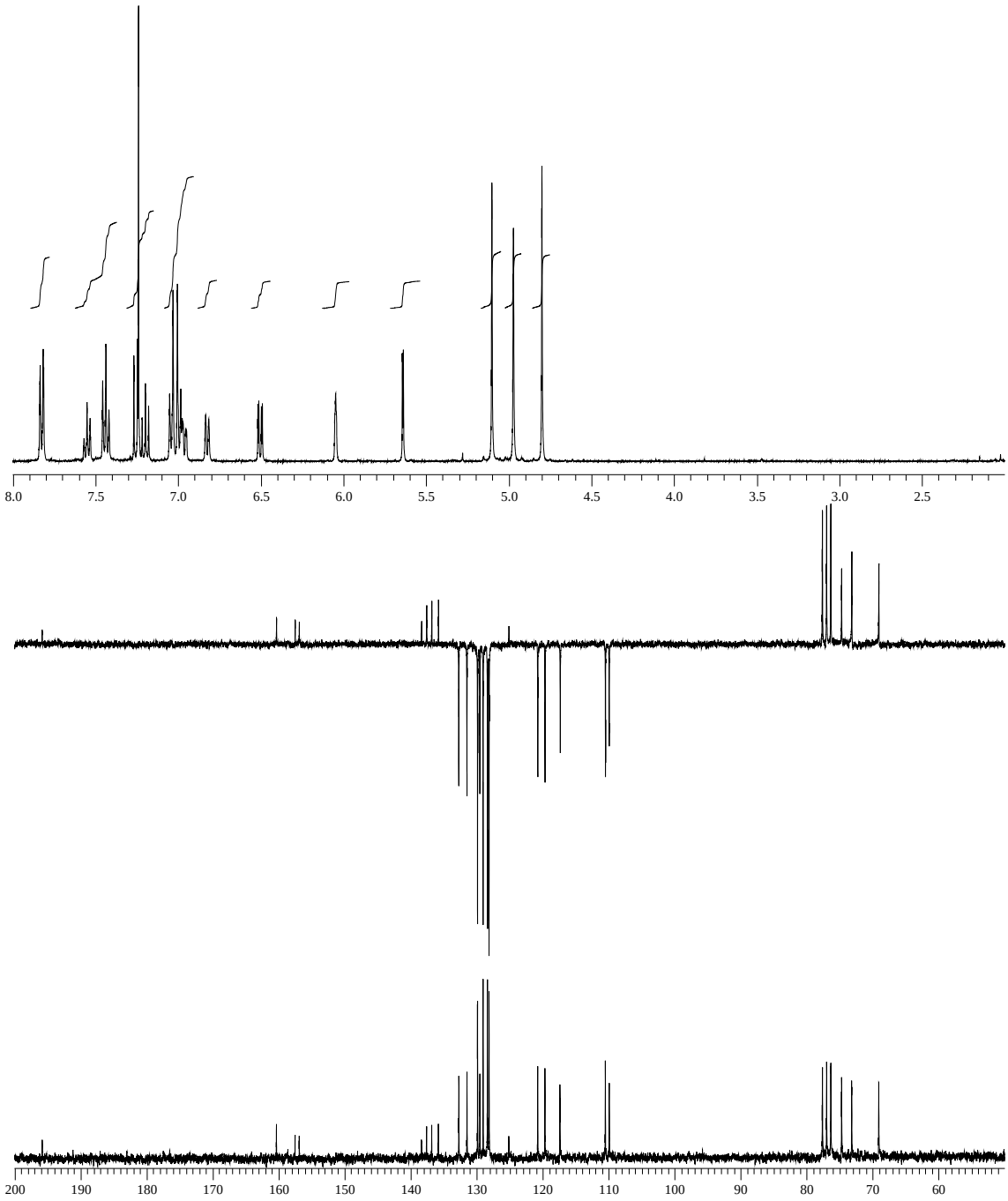

Figure **S15**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of **2**

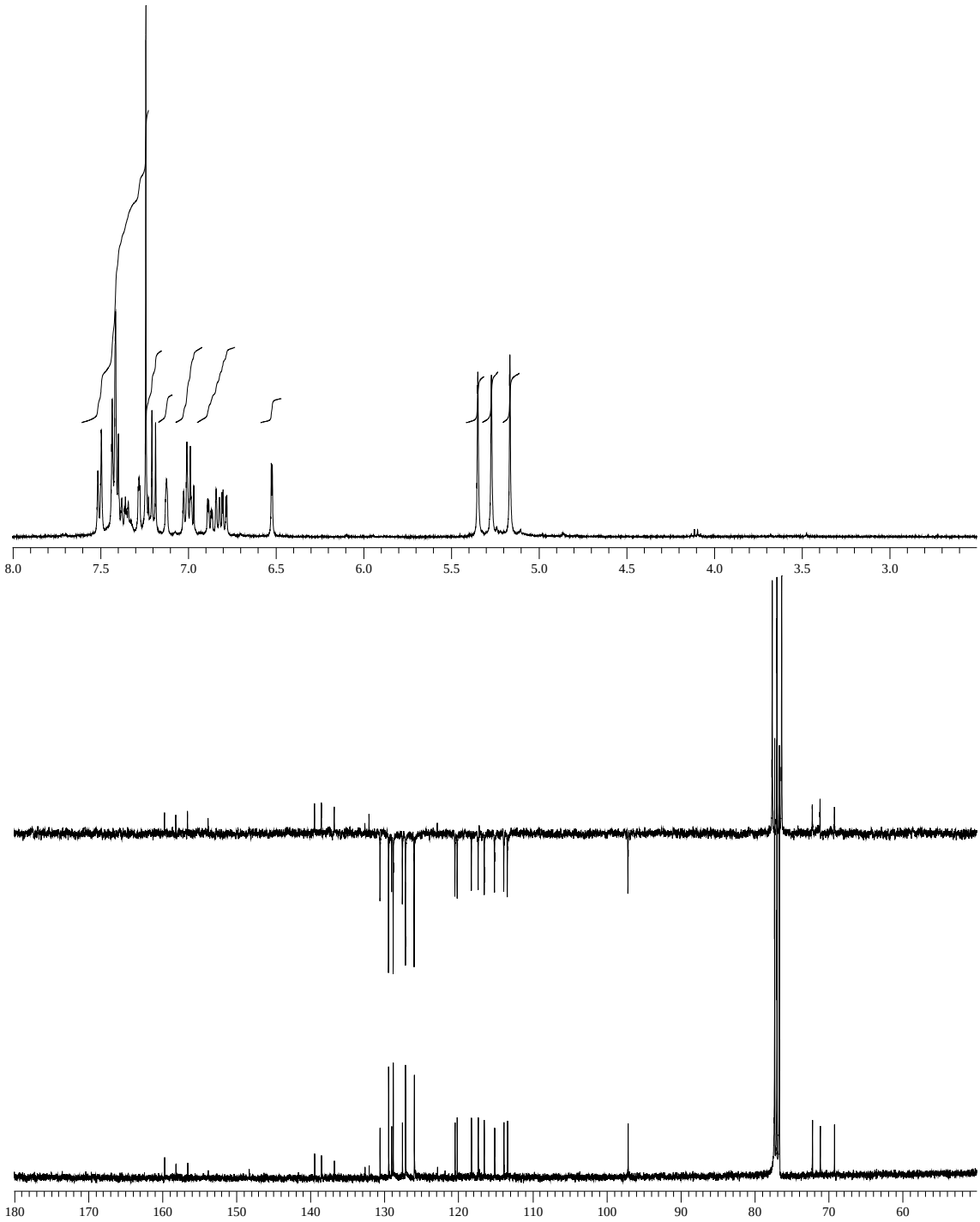

Figure **S16**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of **5**

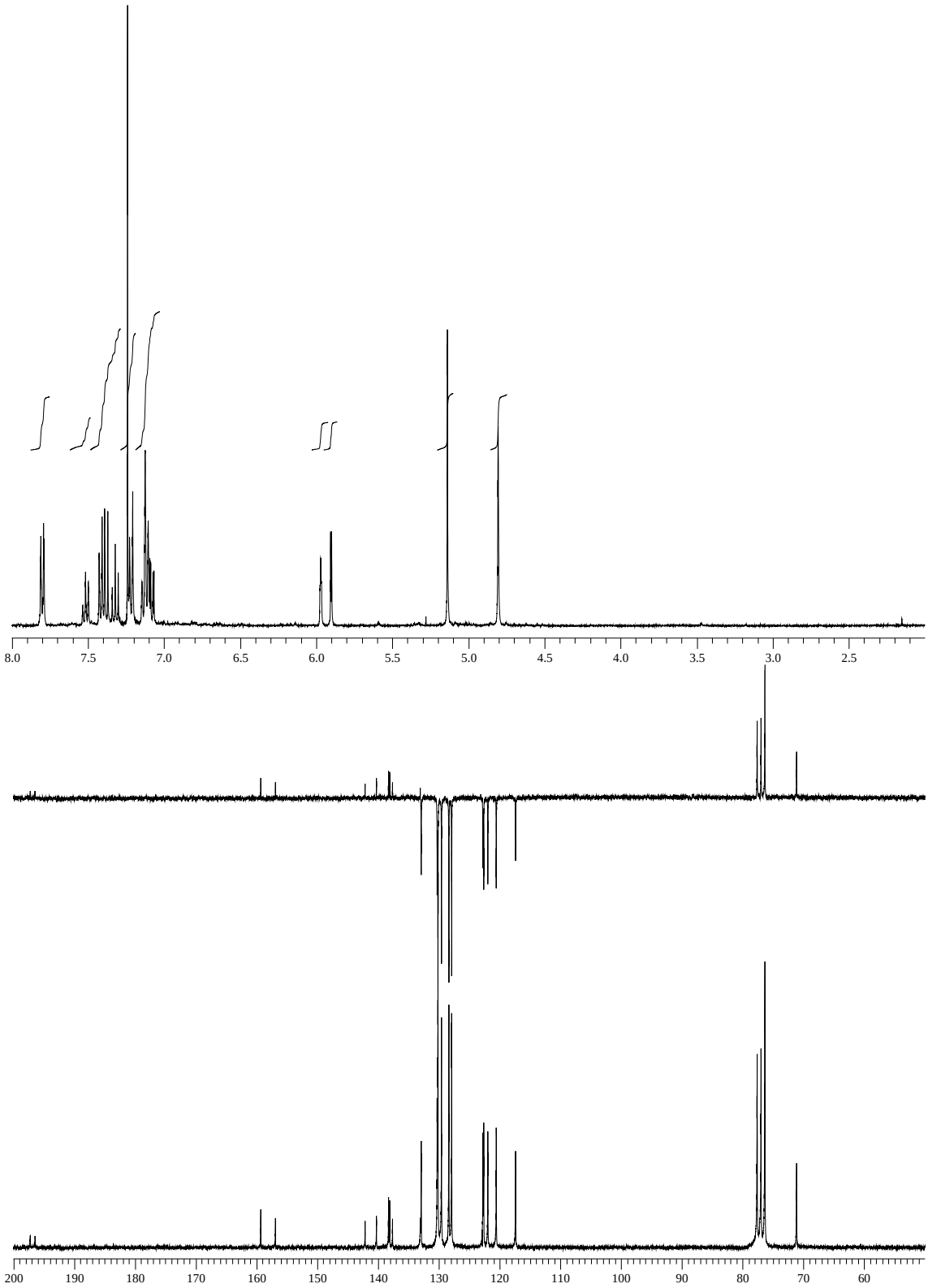

Figure **S17**. Proton, carbon and SEFT NMR spectra ($CDCl_3$) of **7**