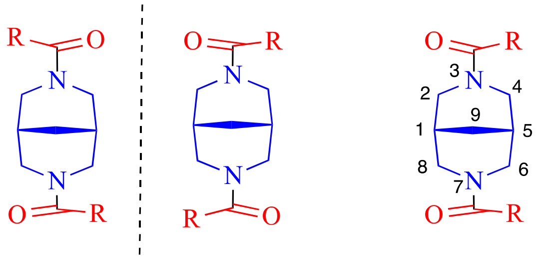
Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 352–355

First example of peroxosolvate of iodine-containing organic molecule

**Andrei V. Churakov, Aleksei V. Medved’ko, Petr V. Prikhodchenko,
Dmitry P. Krut’ko and Sergey Z. Vatsadze**

Table of contents



dl-pair (C_2-symmetry) *meso*-form (C_S-symmetry)

Scheme S1

Table S1 *syn*/*anti* Ratios for bis-amides in DMSO-d$_6$.

Entry	Bis-amide	DMSO-d$_6$
1	**2a**	0.25
2	**2'a**	0.33
3	**3a**	0.48
4	**2b**	0.39
5	**2'b**	0.54
6	**3b**	0.70

Table S2 Selected bond lengths (Å) and angles (°).

	3a	**3b**	**3b·H$_2$O$_2$**		**2'a**	**2'b**
			Molecule A	Molecule B		
O=C9	1.211(2)	–	–	–	1.209(8)	–
N–C(O)	1.349(3) 1.350(3)	1.347(3) 1.349(3)	1.342(4) 1.352(4)	1.339(4) 1.348(4)	1.346(9) 1.352(9)	1.349(2) 1.347(2)
O=C(N)	1.226(3) 1.231(2)	1.235(3) 1.239(3)	1.236(4) 1.239(4)	1.241(4) 1.242(4)	1.206(9) 1.216(8)	1.227(2) 1.227(2)
C–I	2.125(2) 2.135(2)	2.150(2) 2.166(2)	2.153(3) 2.162(3)	2.149(3) 2.149(3)	–	–
C–Br	–	–	–	–	1.908(8) 1.909(7)	1.9320(18) 1.9274(18)
O=C–C–Hal	-10.4(3) 4.3(3)	105.7(2) 109.3(2)	-97.8(3) -107.3(3)	-98.6(3) -102.9(3)	-74.9(7) 105.6(7)	-6.8(2) -8.2(2)

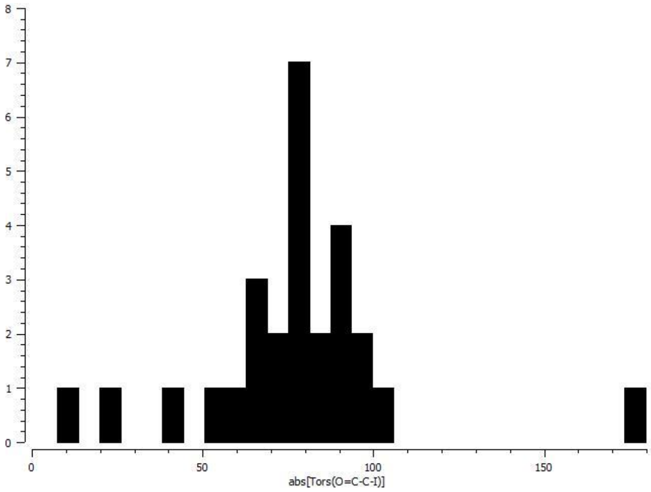


Figure S1 Distribution of O=C–C–I torsion angles in acyclic R$_2$NC(=O)–C–I groups derived from CSD (ver. 5.41, August 2020).

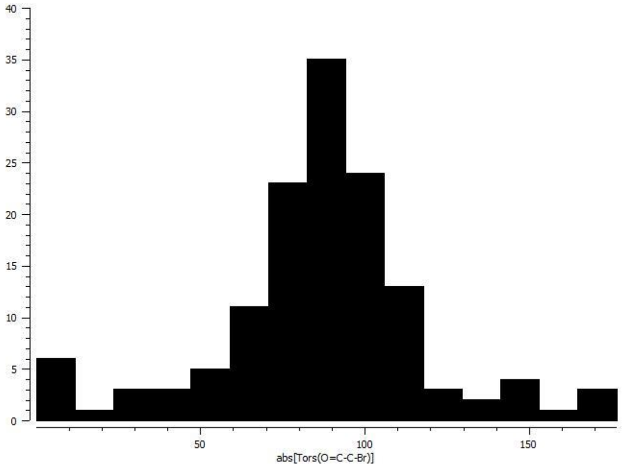


Figure S2 Distribution of O=C–C–Br torsion angles in acyclic R$_2$NC(=O)–C–Br groups derived from CSD (ver. 5.41, August 2020).

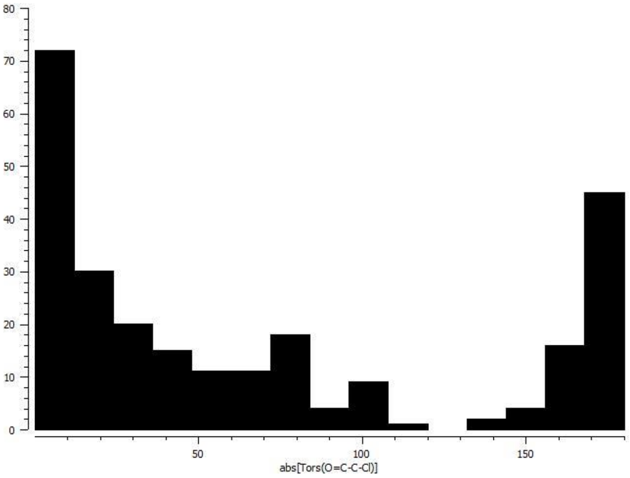


Figure S3 Distribution of O=C–C–Cl torsion angles in acyclic $R_2NC(=O)$–C–Cl groups derived from CSD (ver. 5.41, August 2020).

1. Experimental

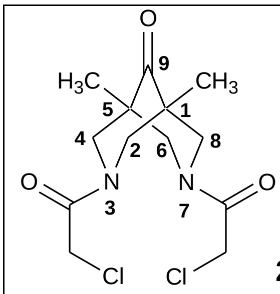
^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker Avance-400 and Bruker Avance II 600 spectrometers. The spectrometer frequency is denoted in parentheses for each spectral data set. Chemical shifts were referred to the signals of the deuterosolvents (7.26 ppm and 77.0 ppm for $CDCl_3$, 2.49 ppm and 39.5 ppm for $(CD_3)_2SO$). Lorentz-Gauss apodization was used for precise measurement of the proton coupling constants values. The ratio of *syn,anti*-isomers was determined based on the integral intensities of signals of the same type of protons. 5,7-dimethyl-1,3-diazaadamantan-6-one (**1a**) or 5,7-dimethyl-1,3-diazaadamantane (**1b**) were prepared as described [A. V. Medved'ko, B. V. Egorova, A. A. Komarova, R. D. Rakhimov, D. P. Krut'ko, S. N. Kalmykov and S. Z. Vatsadze, *ACS Omega,* 2016, **1**, 854–867].

2. Synthesis

Compounds **2a**,**b** and **2'a**,**b**. A solution of chloroacetyl chloride or bromoacetyl bromide (10 mmol) in benzene (5 ml) was added dropwise to a mixture of 5,7-dimethyl-1,3-diazaadamantan-6-one or 5,7-dimethyl-1,3-diazaadamantane (5 mmol), sodium hydrogen carbonate (10 mmol), benzene (10 ml) and water (2.5 ml) under vigorous stirring. The biphasic mixture was stirred for 1 h. The organic phase was separated, the water phase was extracted with benzene. The combined organic fractions were dried over sodium sulfate, and the solvent was removed by rotary evaporation to give white powder.

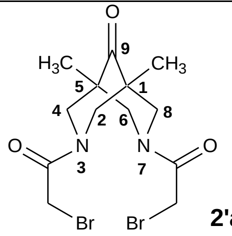
Compounds **3a,b**. Compound **2a,b** (1 mmol) was dissolved in dry acetone (40 ml for **3a** and 80 ml for **3b**, respectively), and sodium iodide (4 equiv.) was added. The solution was refluxed for 8 h. The mixture was cooled and filtered through sintered glass filter. The filtrate was evaporated to dryness and treated with DCM (20 ml) and water (4 ml). The organic phase was separated, washed with 10% aqueous sodium thiosulfate (5 ml) and dried over sodium sulfate. The solvent was removed by rotary evaporated to give beige powder.

The crystals **2'a** and **3a** were obtained by vapor diffusion of pentane (5 ml) to the solution of the compound (approx. 20 mg) in chloroform (1 ml). The crystals **2'b**, **3b** were obtained by slow diffusion of hexane (100 ml) to the solution of the compound (approx. 100 mg) in chloroform (5 ml). The crystals of **3b·H$_2$O$_2$** were obtained by cooling to -18° C of saturated solution of **3b** in 96 % hydrogen peroxide.

 **2a**	1,1'-(1,5-Dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)bis(2-chloroethan-1-one) **2a**

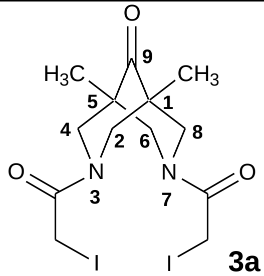
anti-**2a**. ^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm, *J*/Hz): 1.09 (s, 6 H, CH$_3$); 2.86 (dd, 2 H, $^2J_{HH}$ = 13.9, $^4J_{HH}$ = 2.4, H^{2,6}(ax) or H^{4,8}(ax)); 3.41 (dd, 2 H, $^2J_{HH}$ = 13.7, $^4J_{HH}$ = 2.4, H^{4,8}(ax) or H^{2,6}(ax)); 4.03, 4.32 (both d, 2 H, $^2J_{HH}$ = 13.0, CH$_{2b}$); 4.05 (dd, 2 H, $^2J_{HH}$ = 13.7, $^4J_{HH}$ = 3.0, H^{4,8}(eq) or H^{2,6}(eq)); 4.94 (dd, 2 H, $^2J_{HH}$ = 13.9, $^4J_{HH}$ = 3.0, H^{2,6}(eq) or H^{4,8}(eq)). ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 16.37 (CH$_3$); 40.97 (CH$_{2b}$); 46.46 (C^{1,5}); 53.64, 57.63 (CH$_2$N); 166.61 (C(O)N); 210.20 (C^9=O).

syn/anti-**2a** (4:1). ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO, δ/ppm, *J*/Hz): 0.93 (s, CH$_3$ (*syn*-, *anti*-)); 2.85 (dd, $^2J_{HH}$ = 13.5, $^4J_{HH}$ = 2.3, H^{2,6}(ax) or H^{4,8}(ax) (*anti*-), H^{2,8}(ax) or H^{4,6}(ax) (*syn*-)); 3.25 (dd, $^2J_{HH}$ = 13.6, $^4J_{HH}$ = 2.3, H^{4,8}(ax) or H^{2,6}(ax) (*anti*-)); 3.30 (br d, $^2J_{HH}$ = 13.3, H^{4,6}(ax) or H^{2,8}(ax) (*syn*-)); 4.14, 4.58 (both d, $^2J_{HH}$ = 13.5, CH$_{2b}$ (*anti*-)); 4.19 (dd, $^2J_{HH}$ = 13.6, $^4J_{HH}$ = 2.8, H^{4,8}(eq) or H^{2,6}(eq) (*anti*-)); 4.28 (br d, $^2J_{HH}$ = 13.3, H^{4,6}(eq) or H^{2,8}(eq) (*syn*-)); 4.39, 4.60 (both d, $^2J_{HH}$ = 13.5, CH$_{2b}$ (*syn*-)); 4.55 (br d, $^2J_{HH}$ = 13.5, H^{2,8}(eq) or H^{4,6}(eq) (*syn*-)); 4.84 (dd, $^2J_{HH}$ = 13.5, $^4J_{HH}$ = 2.8, H^{2,6}(eq) or H^{4,8}(eq) (*anti*-)). ^{13}C NMR (100 MHz, (CD$_3$)$_2$SO, δ/ppm): 15.70 (CH$_3$ (*anti*-)); 15.97, 16.40 (CH$_3$ (*syn*-)); 41.76 (CH$_{2b}$ (*syn*-)); 42.34 (CH$_{2b}$ (*anti*-)); 45.10, 45.32 (C^{1,5} (*syn*-)); 45.81 (C^{1,5} (*anti*-)); 52.63, 55.83 (CH$_2$N (*anti*-)); 53.89, 55.48 (CH$_2$N (*syn*-)); 164.63 (C(O)N (*syn*-)); 165.27 (C(O)N (*anti*-)); 211.27 (C^9=O (*anti*-)); 211.57 (C^9=O (*syn*-)).

 **2'a**	1,1'-(1,5-Dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)-bis(2-bromoethan-1-one) **2'a**

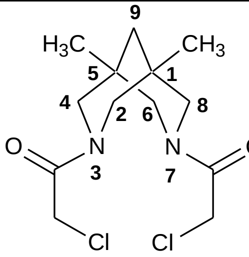
anti-**2'a**. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 1.10 (s, 6 H, CH_3); 2.86 (dd, 2 H, $^2J_{HH}$ = 14.0, $^4J_{HH}$ = 2.4, $H^{2,6}$(ax) or $H^{4,8}$(ax)); 3.39 (dd, 2 H, $^2J_{HH}$ = 13.8, $^4J_{HH}$ = 2.4, $H^{4,8}$(ax) or $H^{2,6}$(ax)); 3.78, 4.15 (both d, 2 H, $^2J_{HH}$ = 11.6, $CH_{2'b}$); 4.05 (dd, 2 H, $^2J_{HH}$ = 13.8, $^4J_{HH}$ = 2.9, $H^{4,8}$(eq) or $H^{2,6}$(eq)); 4.94 (dd, 2 H, $^2J_{HH}$ = 14.0, $^4J_{HH}$ = 2.9, $H^{2,6}$(eq) or $H^{4,8}$(eq)). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 16.37 (CH_3); 26.05 ($CH_{2'b}$); 46.45 ($C^{1,5}$); 53.61, 58.13 (CH_2N); 166.58 (C(O)N); 210.16 (C^9=O).

syn/anti-**2'a** (3:1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ/ppm, *J*/Hz): 0.94 (s, CH_3 (*syn*-, *anti*-)); 2.84 (dd, $^2J_{HH}$ = 13.5, $^4J_{HH}$ = 2.3, $H^{2,6}$(ax) or $H^{4,8}$(ax) (*anti*-), $H^{2,8}$(ax) or $H^{4,6}$(ax) (*syn*-)); 3.23 (dd, $^2J_{HH}$ = 13.6, $^4J_{HH}$ = 2.3, $H^{4,8}$(ax) or $H^{2,6}$(ax) (*anti*-)); 3.28 (br d, $^2J_{HH}$ = 13.5, $H^{4,6}$(ax) or $H^{2,8}$(ax) (*syn*-)); 3.80, 4.51 (both d, $^2J_{HH}$ = 11.6, $CH_{2'b}$ (*anti*-)); 4.01, 4.57 (both d, $^2J_{HH}$ = 11.3, $CH_{2'b}$ (*syn*-)); 4.25 (dd, $^2J_{HH}$ = 13.6, $^4J_{HH}$ = 2.9, $H^{4,8}$(eq) or $H^{2,6}$(eq) (*anti*-)); 4.36 (br d, $^2J_{HH}$ = 13.5, $H^{4,6}$(eq) or $H^{2,8}$(eq) (*syn*-)); 4.54 (br d, $^2J_{HH}$ = 13.5, $H^{2,8}$(eq) or $H^{4,6}$(eq) (*syn*-)); 4.84 (dd, $^2J_{HH}$ = 13.5, $^4J_{HH}$ = 2.9, $H^{2,6}$(eq) or $H^{4,8}$(eq) (*anti*-)). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ/ppm): 15.65 (CH_3 (*anti*-)); 15.91, 16.38 (CH_3 (*syn*-)); 27.73 ($CH_{2'b}$ (*syn*-)); 28.61 ($CH_{2'b}$ (*anti*-)); 45.13, 45.27 ($C^{1,5}$ (*syn*-)); 45.89 ($C^{1,5}$ (*anti*-)); 52.47, 56.41 (CH_2N (*anti*-)); 53.78, 56.05 (CH_2N (*syn*-)); 164.78 (C(O)N (*syn*-)); 165.44 (C(O)N (*anti*-)); 211.23 (C^9=O (*anti*-)); 211.30 (C^9=O (*syn*-)).

 **3a**	1,1'-(1,5-Dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)-bis(2-iodoethan-1-one) **3a**

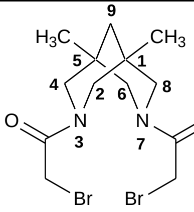
anti-**3a**. ^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 1.09 (s, 6 H, CH_3); 2.81 (d, 2 H, $^2J_{HH}$ = 13.9, $H^{2,6}$(ax) or $H^{4,8}$(ax)); 3.30 (d, 2 H, $^2J_{HH}$ = 13.6, $H^{4,8}$(ax) or $H^{2,6}$(ax)); 3.66, 4.03 (both d, 2 H, $^2J_{HH}$ = 10.8, CH_{3b}); 3.99 (d, 2 H, $^2J_{HH}$ = 13.6, $H^{4,8}$(eq) or $H^{2,6}$(eq)); 4.93 (d, 2 H, $^2J_{HH}$ = 13.9, $H^{2,6}$(eq) or $H^{4,8}$(eq)). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): -3.57 (CH_{3b}); 16.39 (CH_3); 46.31 ($C^{1,5}$); 53.75, 58.69 (CH_2N); 167.62 (C(O)N); 210.17 (C^9=O).

syn/anti-**3a** (1:0.48). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ/ppm, *J*/Hz): 0.91, 0.94 (both s, CH_3 (*syn*-)); 0.93 (s, CH_3 (*anti*-)); 2.77 (d, $^2J_{HH}$ = 13.4, $H^{2,6}$(ax) or $H^{4,8}$(ax) (*anti*-), $H^{2,8}$(ax) or $H^{4,6}$(ax) (*syn*-)); 3.13 (dd, $^2J_{HH}$ = 13.5, $^4J_{HH}$ = 2.1, $H^{4,8}$(ax) or $H^{2,6}$(ax) (*anti*-)); 3.16 (d, $^2J_{HH}$ = 13.4, $H^{4,6}$(ax) or H^{2,8}(ax) (*syn*-)); 3.52, 4.31 (both d, $^{2}J_{\mathrm{HH}}$ = 10.6, CH$_{3b}$ (*anti*-)); 3.66, 4.42 (both d, $^{2}J_{\mathrm{HH}}$ = 10.1, CH$_{3b}$ (*syn*-)); 4.22 (dd, $^{2}J_{\mathrm{HH}}$ = 13.5, $^{4}J_{\mathrm{HH}}$ = 2.8, H^{4,8}(eq) or H^{2,6}(eq) (*anti*-)); 4.33 (d, $^{2}J_{\mathrm{HH}}$ = 13.4, H^{4,6}(eq) or H^{2,8}(eq) (*syn*-)); 4.52 (d, $^{2}J_{\mathrm{HH}}$ = 13.3, H^{2,8}(eq) or H^{4,6}(eq) (*syn*-)); 4.82 (dd, $^{2}J_{\mathrm{HH}}$ = 13.4, $^{4}J_{\mathrm{HH}}$ = 2.8, H^{2,6}(eq) or H^{4,8}(eq) (*anti*-)). ^{13}C NMR (100 MHz, (CD$_3$)$_2$SO, δ/ppm): -1.49 (CH$_{3b}$ (*syn*-)); -0.11 (CH$_{3b}$ (*anti*-)); 15.67 (CH$_3$ (*anti*-)); 15.87, 16.36 (CH$_3$ (*syn*-)); 45.09, 45.22 (C^{1,5} (*syn*-)); 45.76 (C^{1,5} (*anti*-)); 52.53, 56.96 (CH$_2$N (*anti*-)); 53.74, 56.64 (CH$_2$N (*syn*-)); 166.31 (C(O)N (*syn*-)); 166.87 (C(O)N (*anti*-)); 211.35 (C^9=O (*anti*-)); 211.41 (C^9=O (*syn*-)).

 **2b**	1,1'-(1,5-Dimethyl-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)-bis(2-chloroethan-1-one) **2b**

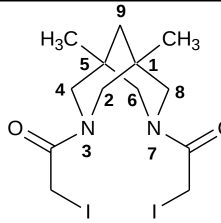
anti-**2b**. ^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm, *J*/Hz): 0.97 (s, 6 H, CH$_3$); 1.49 (s, 2 H, CH$_2$^{9}); 2.46 (dd, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.7, $^{4}J_{\mathrm{HH}}$ = 2.7, H^{2,6}(ax) or H^{4,8}(ax)); 3.01 (dd, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.5, $^{4}J_{\mathrm{HH}}$ = 2.7, H^{4,8}(ax) or H^{2,6}(ax)); 3.66 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.5, H^{4,8}(eq) or H^{2,6}(eq)); 3.93, 4.21 (both d, 2 H, $^{2}J_{\mathrm{HH}}$ = 12.8, CH$_{2b}$); 4.55 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.7, H^{2,6}(eq) or H^{4,8}(eq)). ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 24.29 (CH$_3$); 31.19 (C^{1,5}); 41.29 (CH$_{2b}$); 46.96 (CH$_2$^{9}); 51.30, 55.94 (CH$_2$N); 166.10 (C(O)N).

syn/anti-**2b** (1:0.39). ^{1}H NMR (400 MHz, (CD$_3$)$_2$SO, δ/ppm, *J*/Hz): 0.86 (s, CH$_3$ (*syn*-, *anti*-)); 1.41 (s, CH$_2$^{9} (*syn*-, *anti*-)); 2.38 (d, $^{2}J_{\mathrm{HH}}$ = 12.7, H^{2,8}(ax) or H^{4,6}(ax) (*syn*-)); 2.39 (d, $^{2}J_{\mathrm{HH}}$ = 12.8, H^{2,6}(ax) or H^{4,8}(ax) (*anti*-),); 2.85 (d, $^{2}J_{\mathrm{HH}}$ = 13.0, H^{4,8}(ax) or H^{2,6}(ax) (*anti*-), H^{4,6}(ax) or H^{2,8}(ax) (*syn*-)); 3.71 (d, $^{2}J_{\mathrm{HH}}$ = 13.1, H^{4,8}(eq) or H^{2,6}(eq) (*anti*-)); 3.81 (d, $^{2}J_{\mathrm{HH}}$ = 12.8, H^{4,6}(eq) or H^{2,8}(eq) (*syn*-)); 3.98, 4.43 (both d, $^{2}J_{\mathrm{HH}}$ = 13.3, CH$_{2b}$ (*anti*-)); 4.10 (d, $^{2}J_{\mathrm{HH}}$ = 12.7, H^{2,8}(eq) or H^{4,6}(eq) (*syn*-)); 4.22, 4.49 (both d, $^{2}J_{\mathrm{HH}}$ = 13.1, CH$_{2b}$ (*syn*-)); 4.39 (d, $^{2}J_{\mathrm{HH}}$ = 12.8, H^{2,6}(eq) or H^{4,8}(eq) (*anti*-)).

 **2'b**	1,1'-(1,5-Dimethyl-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)-bis(2-bromoethan-1-one) **2'b**

anti-**2'b**. ^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm, *J*/Hz): 0.95 (s, 6 H, CH$_3$); 1.45 (s, 2 H, CH$_2$^{9}); 2.43 (dd, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.7, $^{4}J_{\mathrm{HH}}$ = 2.5, H^{2,6}(ax) or H^{4,8}(ax)); 2.96 (dd, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.5, $^{4}J_{\mathrm{HH}}$ = 2.5, H^{4,8}(ax) or H^{2,6}(ax)); 3.64 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.5, H^{4,8}(eq) or H^{2,6}(eq)); 3.66, 4.02 (both d, 2 H, $^{2}J_{\mathrm{HH}}$ = 11.3, CH$_{2'b}$); 4.51 (d, 2 H, $^{2}J_{\mathrm{HH}}$ = 13.7, H^{2,6}(eq) or H^{4,8}(eq)). ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 24.23 (CH$_3$); 26.62 (CH$_{2'b}$); 31.19 (C^{1,5}); 46.80 (CH$_2$^{9}); 51.22, 56.39 (CH$_2$N); 165.93 (C(O)N).

syn/anti-**2'b** (1:0.54). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ/ppm, *J*/Hz): 0.87, 0.90 (both s, CH_3 (*syn*-)); 0.87 (s, CH_3 (*anti*-)); 1.40 (s, CH_2^9 (*syn*-, *anti*-)); 2.36 (d, $^2J_{HH}$ = 12.9, $H^{2,8}$(ax) or $H^{4,6}$(ax) (*syn*-)); 2.38 (d, $^2J_{HH}$ = 13.3, $H^{2,6}$(ax) or $H^{4,8}$(ax) (*anti*-)); 2.84 (br d, $^2J_{HH}$ = 13.3, $H^{4,6}$(ax) or $H^{2,8}$(ax) (*syn*-), $H^{4,8}$(ax) or $H^{2,6}$(ax) (*anti*-)); 3.68, 4.30 (both d, $^2J_{HH}$ = 11.4, $CH_{2'b}$ (*anti*-)); 3.76 (d, $^2J_{HH}$ = 13.3, $H^{4,8}$(eq) or $H^{2,6}$(eq) (*anti*-)); 3.85, 4.42 (both d, $^2J_{HH}$ = 11.3, $CH_{2'b}$ (*syn*-)); 3.88 (d, $^2J_{HH}$ = 13.1, $H^{4,6}$(eq) or $H^{2,8}$(eq) (*syn*-)); 4.10 (d, $^2J_{HH}$ = 12.9, $H^{2,8}$(eq) or $H^{4,6}$(eq) (*syn*-)); 4.39 (d, $^2J_{HH}$ = 13.3, $H^{2,6}$(eq) or $H^{4,8}$(eq) (*anti*-)). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ/ppm): 23.62 (CH_3 (*anti*-)); 23.73, 24.39 (CH_3 (*syn*-)); 28.18 ($CH_{2'b}$ (*syn*-)); 28.78 ($CH_{2'b}$ (*anti*-)); 29.91, 30.89 ($C^{1,5}$ (*syn*-)); 30.77 ($C^{1,5}$ (*anti*-)); 44.79 (CH_2^9 (*syn*-)); 45.69 (CH_2^9 (*anti*-)); 50.23, 55.07 (CH_2N (*anti*-)); 51.17, 54.35 (CH_2N (*syn*-)); 164.43 (C(O)N (*syn*-)); 164.82 (C(O)N (*anti*-)).

 **3b**	1,1'-(1,5-Dimethyl-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)-bis(2-iodoethan-1-one) **3b**

anti-**3b** (*anti*-). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 0.93 (s, 6 H, CH_3); 1.42 (s, 2 H, CH_2^9); 2.36 (dd, 2 H, $^2J_{HH}$ = 13.7, $^4J_{HH}$ = 2.4, $H^{2,6}$(ax) or $H^{4,8}$(ax)); 2.84 (dd, 2 H, $^2J_{HH}$ = 13.4, $^4J_{HH}$ = 2.4, $H^{4,8}$(ax) or $H^{2,6}$(ax)); 3.53, 3.86 (both d, 2 H, $^2J_{HH}$ = 10.5, CH_{3b}); 3.56 (d, 2 H, $^2J_{HH}$ = 13.4, $H^{4,8}$(eq) or $H^{2,6}$(eq)); 4.49 (d, 2 H, $^2J_{HH}$ = 13.7, $H^{2,6}$(eq) or $H^{4,8}$(eq)). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): -2.56 (CH_{3b}); 24.22 (CH_3); 31.09 ($C^{1,5}$); 46.60 (CH_2^9); 51.22, 56.86 (CH_2N); 166.84 (C(O)N).

syn/anti-**3b** (1:0.70). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ/ppm, *J*/Hz): 0.84, 0.90 (both s, CH_3 (*syn*-)); 0.86 (s, CH_3 (*anti*-)); 1.38 (s, CH_2^9 (*syn*-, *anti*-)); 2.28 (d, $^2J_{HH}$ = 13.0, $H^{2,8}$(ax) or $H^{4,6}$(ax) (*syn*-)); 2.31 (dd, $^2J_{HH}$ = 13.3, $^4J_{HH}$ = 2.5, $H^{2,6}$(ax) or $H^{4,8}$(ax) (*anti*-)); 2.70 (d, $^2J_{HH}$ = 12.9, $H^{4,6}$(ax) or $H^{2,8}$(ax) (*syn*-)); 2.74 (dd, $^2J_{HH}$ = 13.2, $^4J_{HH}$ = 2.5, $H^{4,8}$(ax) or $H^{2,6}$(ax) (*anti*-)); 3.42, 4.06 (both d, $^2J_{HH}$ = 10.5, CH_{3b} (*anti*-)); 3.54, 4.25 (both d, $^2J_{HH}$ = 10.0, CH_{3b} (*syn*-)); 3.70 (d, $^2J_{HH}$ = 13.2, $H^{4,8}$(eq) or $H^{2,6}$(eq) (*anti*-)); 3.84 (d, $^2J_{HH}$ = 12.9, $H^{4,6}$(eq) or $H^{2,8}$(eq) (*syn*-)); 4.08 (d, $^2J_{HH}$ = 13.0, $H^{2,8}$(eq) or $H^{4,6}$(eq) (*syn*-)); 4.36 (d, $^2J_{HH}$ = 13.3, $H^{2,6}$(eq) or $H^{4,8}$(eq) (*anti*-)). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, δ/ppm): -0.54 (CH_{3b} (*syn*-)); 0.18 (CH_{3b} (*anti*-)); 23.76 (CH_3 (*anti*-)); 23.83, 24.47 (CH_3 (*syn*-)); 30.07, 30.99 ($C^{1,5}$ (*syn*-)); 30.85 ($C^{1,5}$ (*anti*-)); 44.96 (CH_2^9 (*syn*-)); 45.71 (CH_2^9 (*anti*-)); 50.48, 55.83 (CH_2N (*anti*-)); 51.36, 55.15 (CH_2N (*syn*-)); 166.04 (C(O)N (*syn*-)); 166.37 (C(O)N (*anti*-)).

3. X-ray studies.

The experimental intensities were collected on a Bruker D8 Venture diffractometer for **3a** (150 K), on a Bruker SMART APEX II machine for **3b** (100 K) and **3b·H_2O_2** (150 K) and Enraf-Nonius CAD4 (295 K) for **2'a** using graphite monochromatized MoKα radiation, λ=0.71073 Å. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [G. M. Sheldrick, *Acta Crystallogr. A.*, 2008, **64**, 112–22]. In the structure **3b·H_2O_2** one of the two crystallographically independent peroxide molecules are cross-type disordered over two positions with occupancy ratio 0.60(1)/0.40(1). In **3a** and **3b** all hydrogen atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters. In **3b·H_2O_2**, all carbon H atoms were placed in calculated positions and refined using a riding model, while peroxide H atoms were localized objectively, and their positional parameters were refined with restrained O-H distances (SADI). As for **2'a**, all hydrogen atoms were placed in calculated positions and refined using a riding model. Structural details are given in Table S3.

The crystallographic data for **3a**, **3b**, **3b·H_2O_2**, **2'a** and **2'b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC numbers 2048266-2048268, 2049144, and 1860309, respectively.

Table S3 Crystal data and refinement details.

	3a	**3b**	**3b·H_2O_2**	**2'a**	**2'b**
Formula	$C_{13}H_{18}I_2N_2O_3$	$C_{13}H_{20}I_2N_2O_2$	$C_{13}H_{23b2}N_2O_4$	$C_{13}H_{18}Br_2N_2O_3$	$C_{13}H_{20}Br_2N_2O_2$
*F*w	504.09	490.11	524.12	410.11	396.13
colour, habit	colourless, prism	colourless, plate	colourless, needle	colourless, prism	colourless, prism
cryst size (mm)	0.30×0.20×0.15	0.45×0.40×0.10	0.50×0.10×0.02	0.30×0.25×0.20	0.20×0.20×0.08
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1$/c	*P*-1	$P2_1$/n	$P2_1$/c
a (Å)	8.0984(2)	7.7120(2)	7.7873(3)	8.111(3)	7.7677(3)
b (Å)	9.9494(3)	13.6081(3)	13.9039(6)	20.818(8)	19.8219(7)
c (Å)	11.3056(3)	15.0465(4)	16.1367(7)	9.245(2)	9.7022(3)
α (deg)	66.5477(9)	90	90.5863(15)	90	90
β (deg)	69.4791(8)	93.6593(9)	92.0803(15)	90.71(3)	103.038(1)
γ (deg)	77.5030(9)	90	99.9612(14)	90	90
V (Å^3)	779.52(4)	1575.85(7)	1719.47(12)	1560.9(9)	1455.34(9)
Z	*2*	*4*	*4*	*4*	*4*
D_c (g·cm^{-3})	2.148	2.066	2.025	1.745	1.808
μ (mm^{-1})	4.043	3.992	3.674	5.201	5.570
F(000)	480	936	1008	816	792
θ range (deg)	2.06 to 30.00	2.71 to 30.00	2.53 to 27.00	3.18 to 25.98	2.06 to 27.98
reflns collcd	12934	18684	25807	4907	13694
indep reflns/R_{int}	4527 / 0.0235	4569 / 0.0234	7471 / 0.0293	3054 / 0.0386	3518 / 0.0279
completness	0.998	0.995	0.997	0.999	0.999
reflns $I>2\sigma(I)$	4074	4341	6711	1461	3050
param/restraints	254 / 0	252 / 0	422 / 12	183 / 0	252 / 0
GOF on F^2	1.038	1.224	1.104	1.015	1.031
$R_1(I>2\sigma(I))$	0.0211	0.0242	0.0282	0.0597	0.0212
wR_2(all data)	0.0460	0.0519	0.0581	0.2233	0.0473
largest diff peak & hole, e·Å^{-3}	0.980 / -0.738	0.817 / -0.712	0.964 / -0.897	0.622 / -0.923	0.369 / -0.345

4. NMR spectra

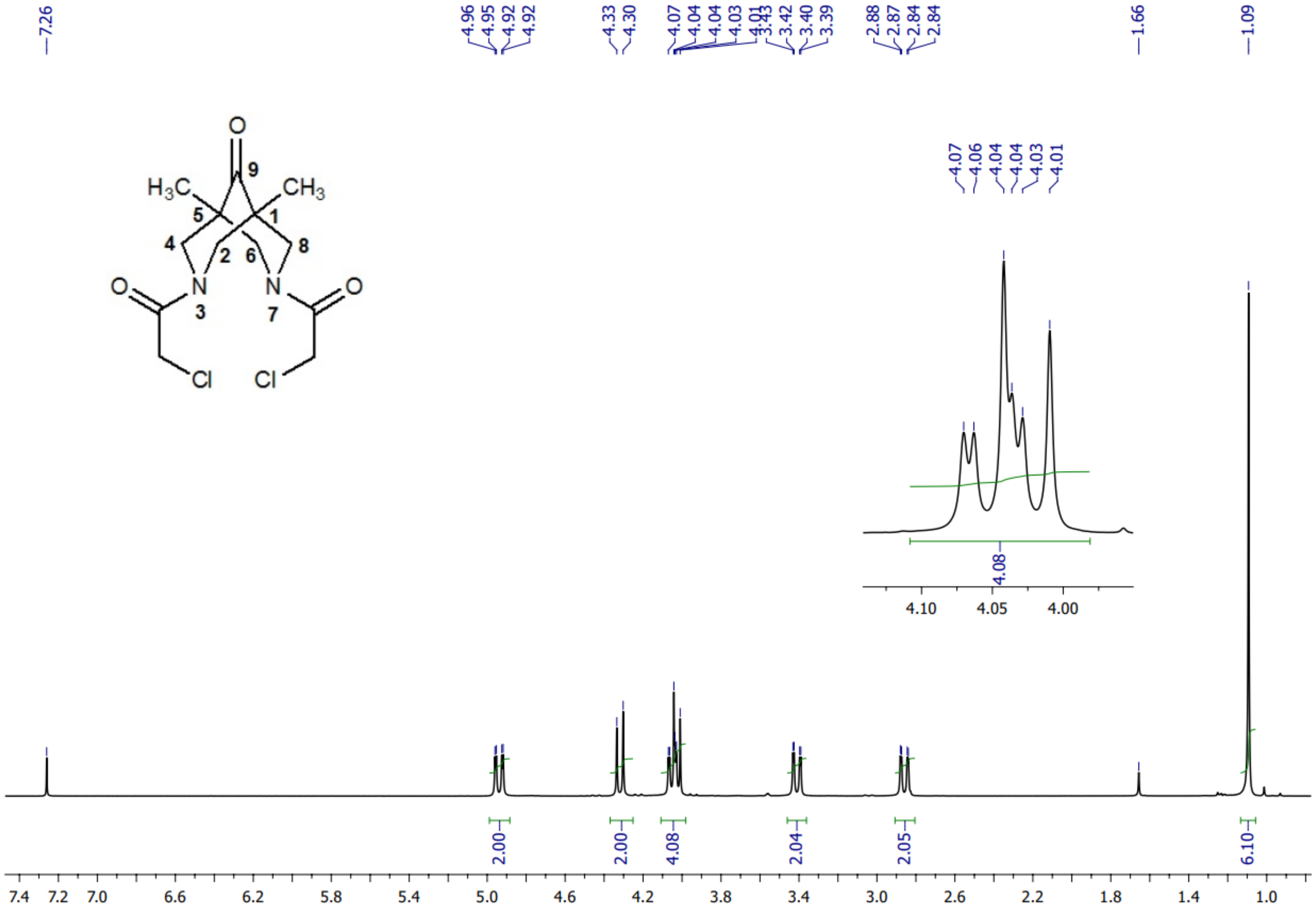


Figure S4. ^{1}H NMR spectrum of bis-amide 2a in $CDCl_3$

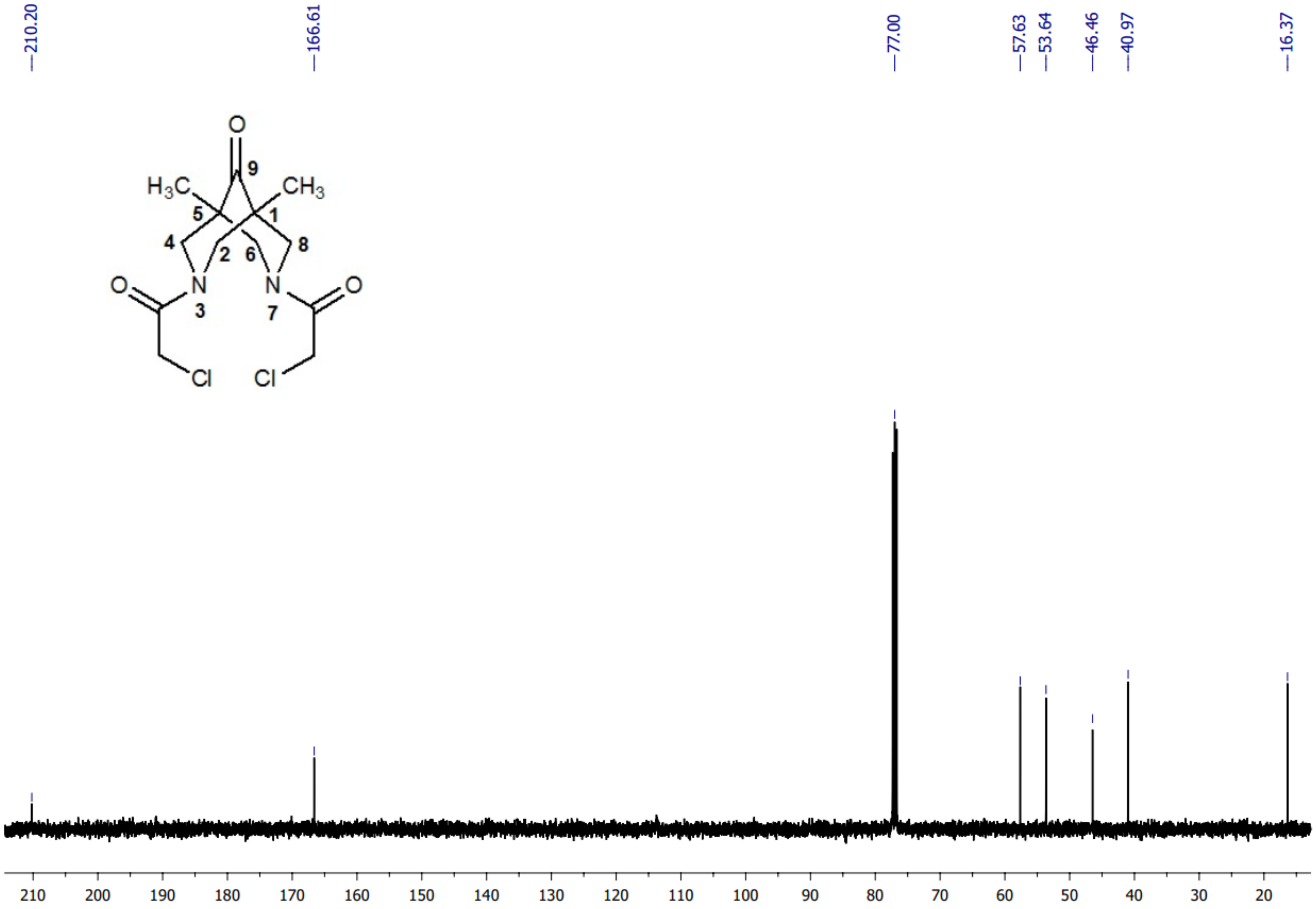


Figure S5. ^{13}C NMR spectrum of bis-amide 2a in CDCl$_3$

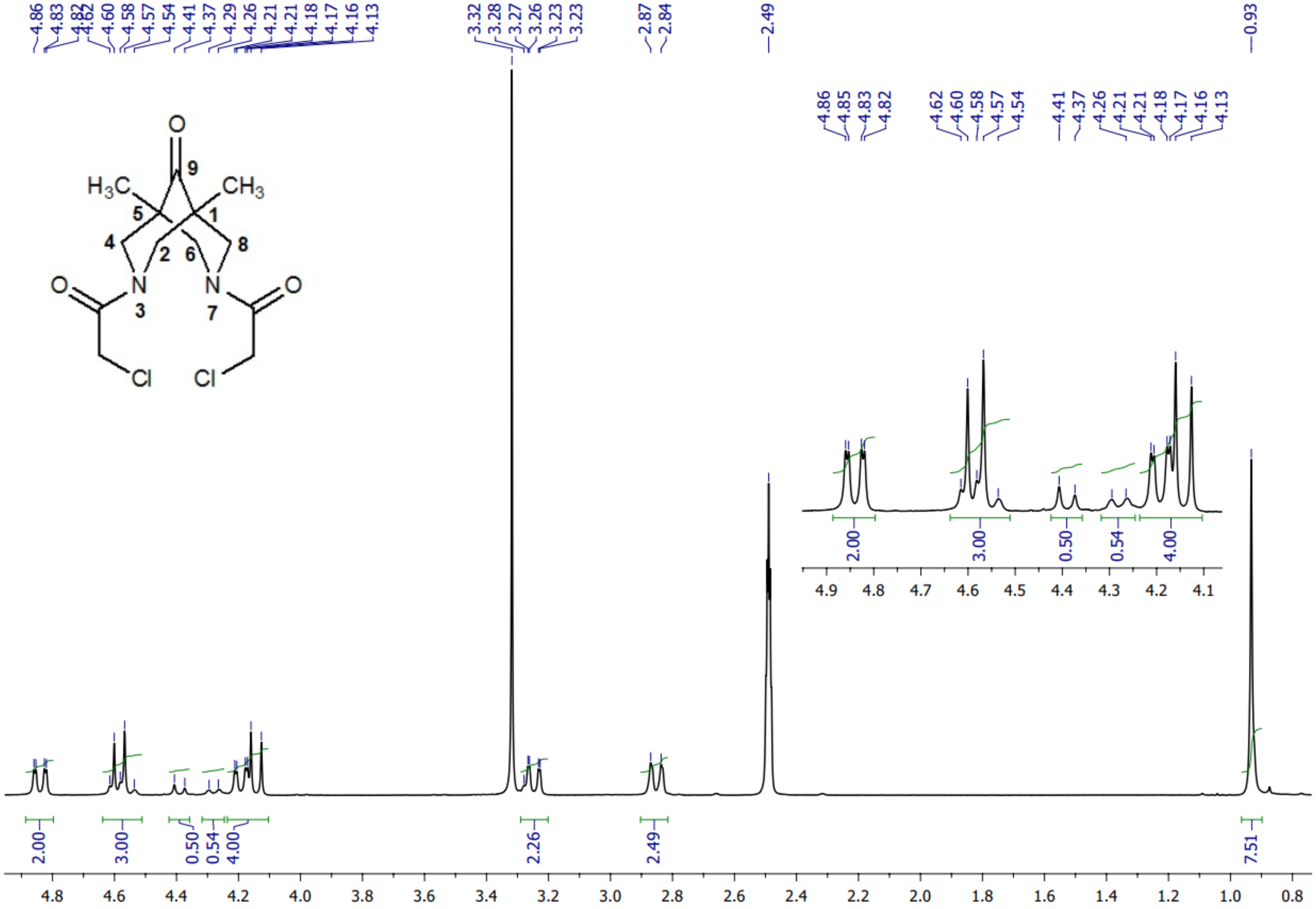


Figure S6. ^{1}H NMR spectrum of bis-amide 2a in DMSO-d$_6$.

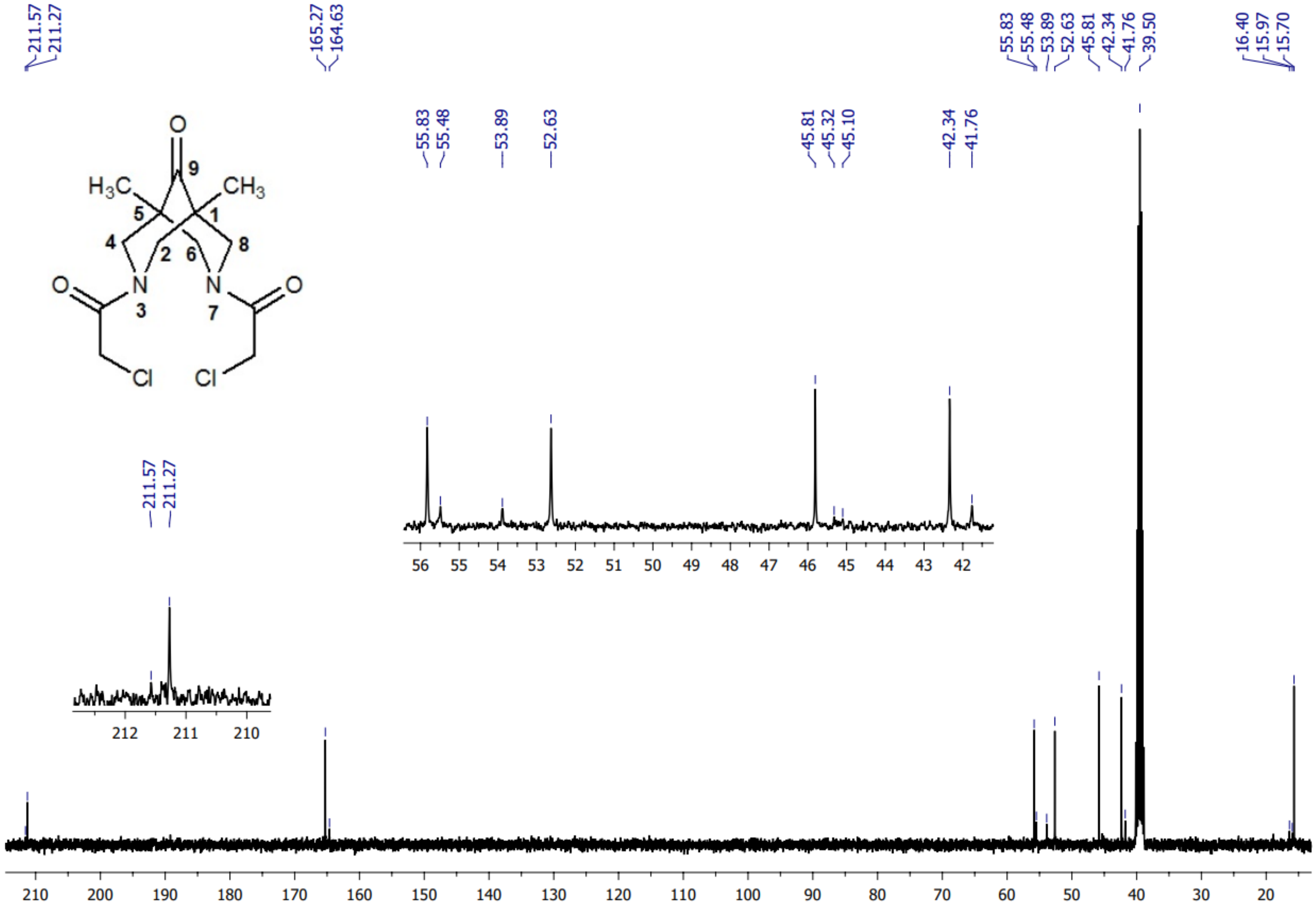


Figure S7. ^{13}**C NMR spectrum of bis-amide 2a in DMSO-d$_6$.**

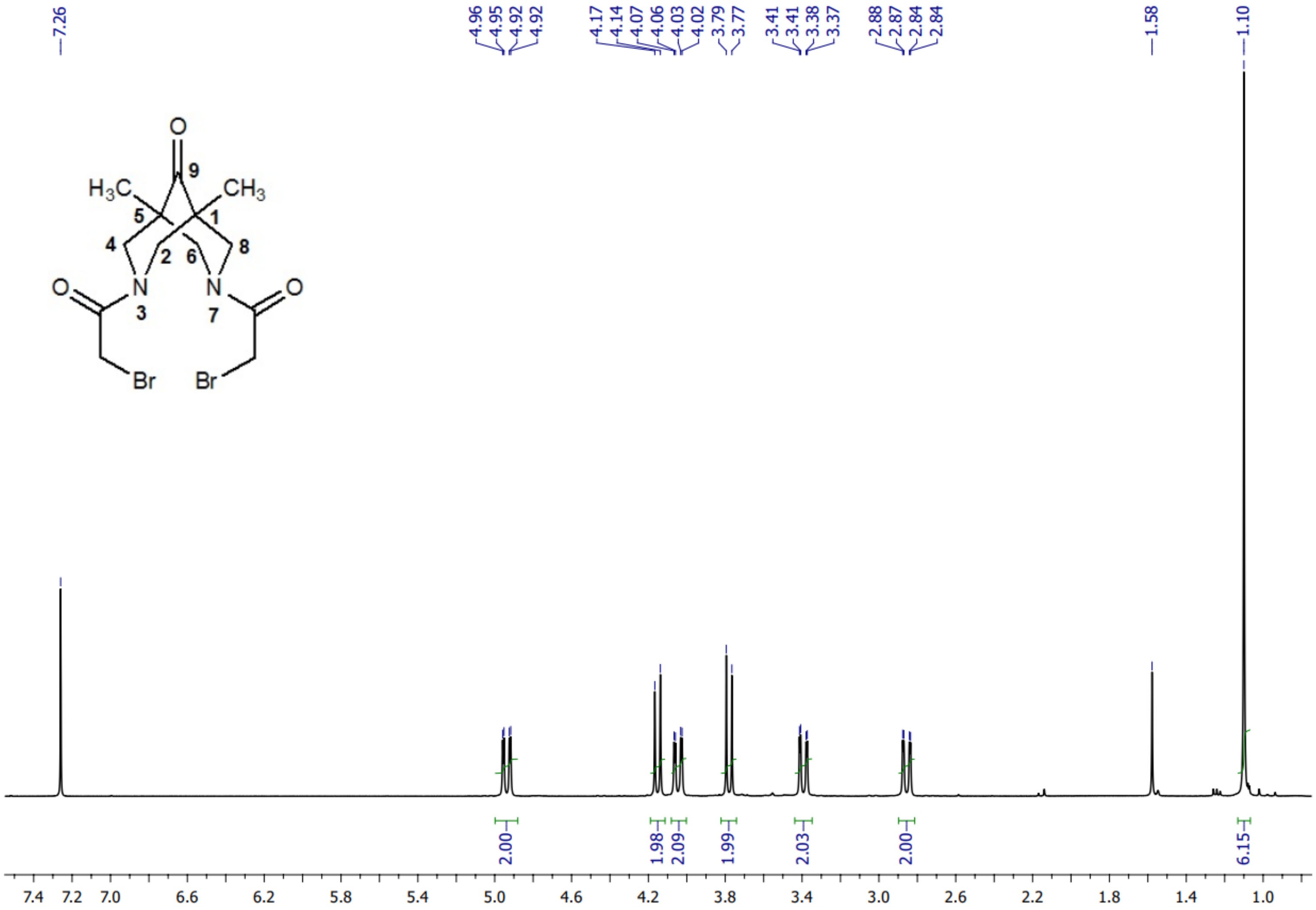


Figure S8. ^{1}**H NMR spectrum of bis-amide 2'a in** $\mathbf{CDCl_3}$**.**

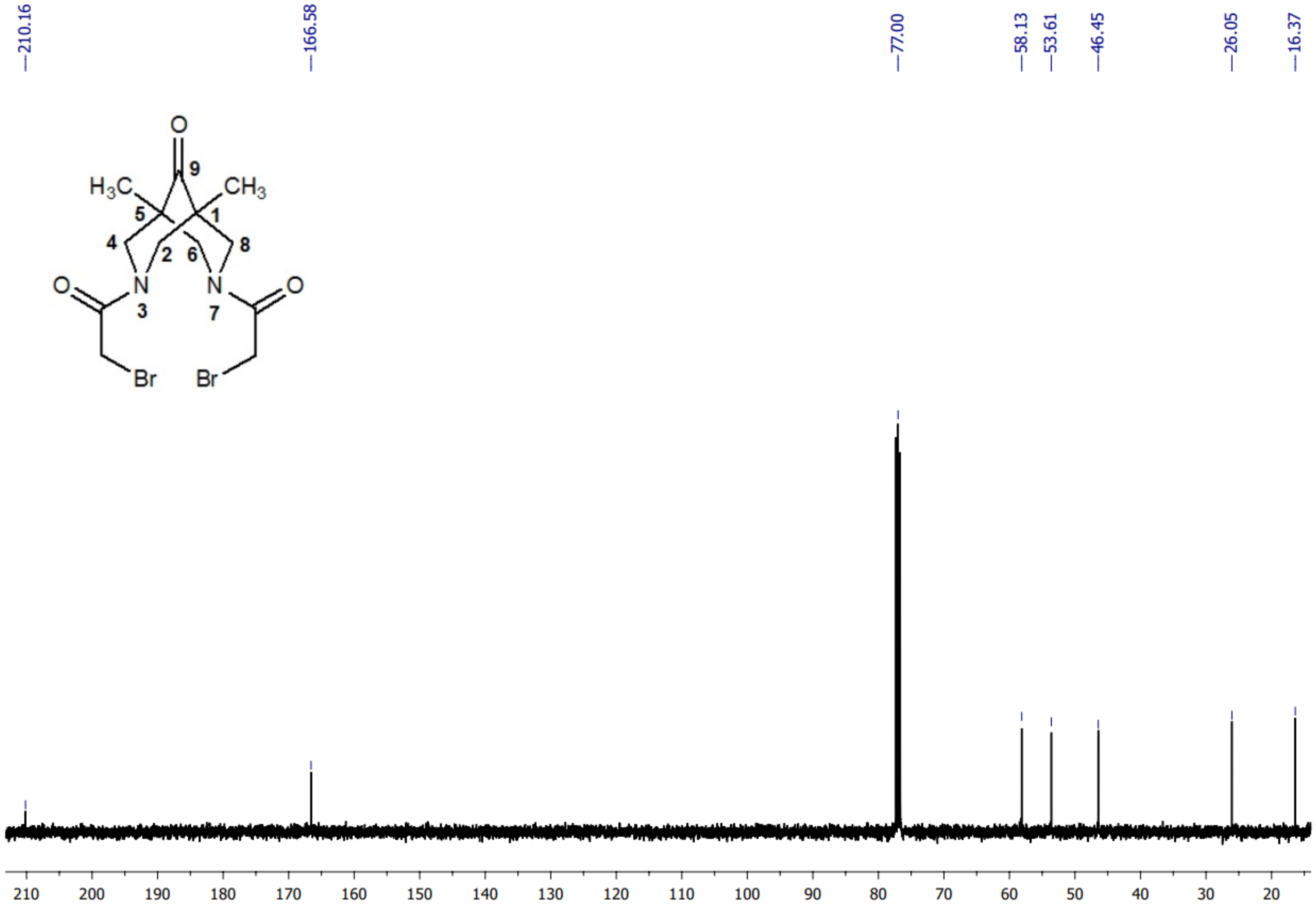


Figure S9. ^{13}**C NMR spectrum of bis-amide 2'a in CDCl$_3$.**

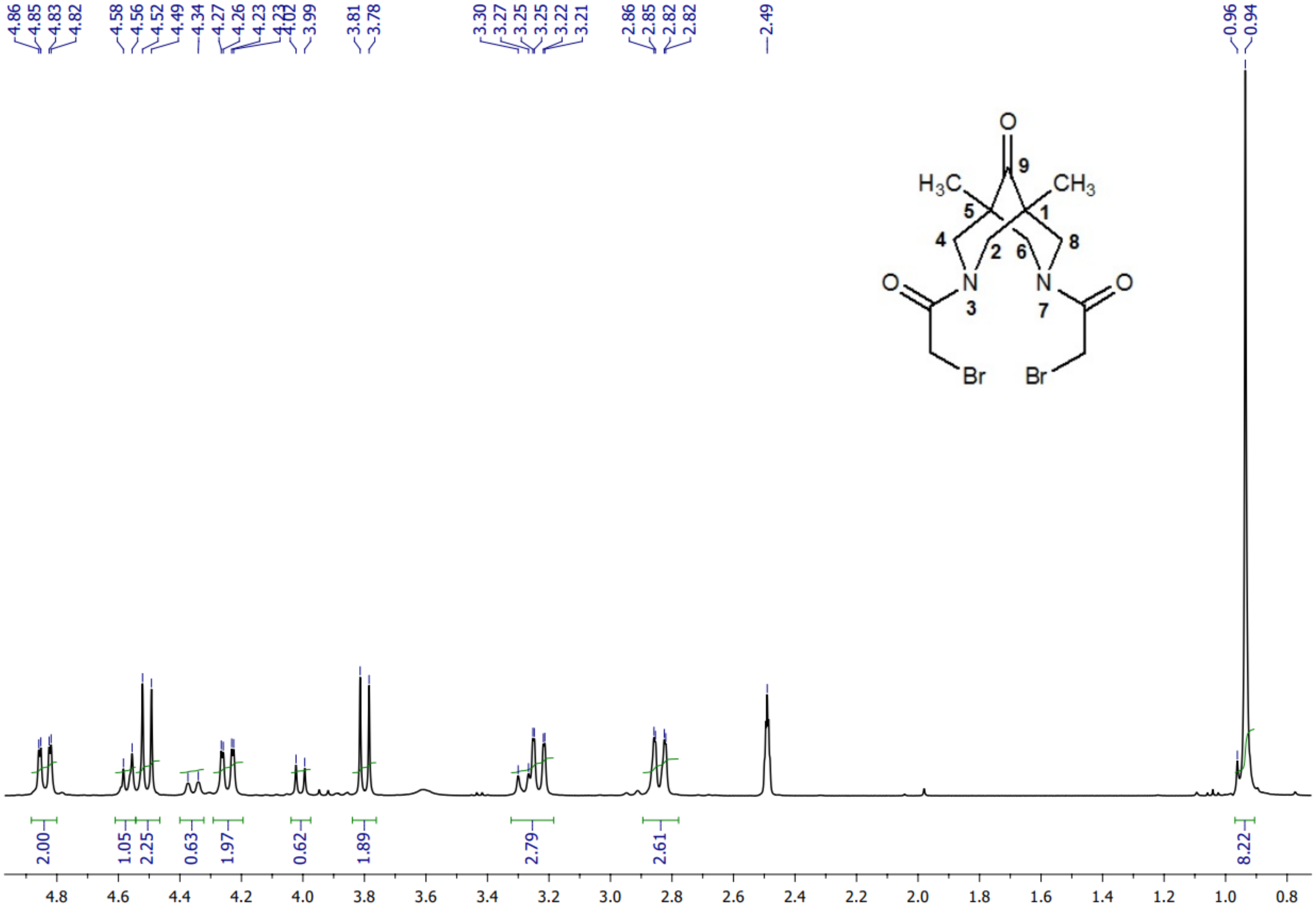


Figure S10. ^{1}H NMR spectrum of bis-amide 2’a in DMSO-d_6.

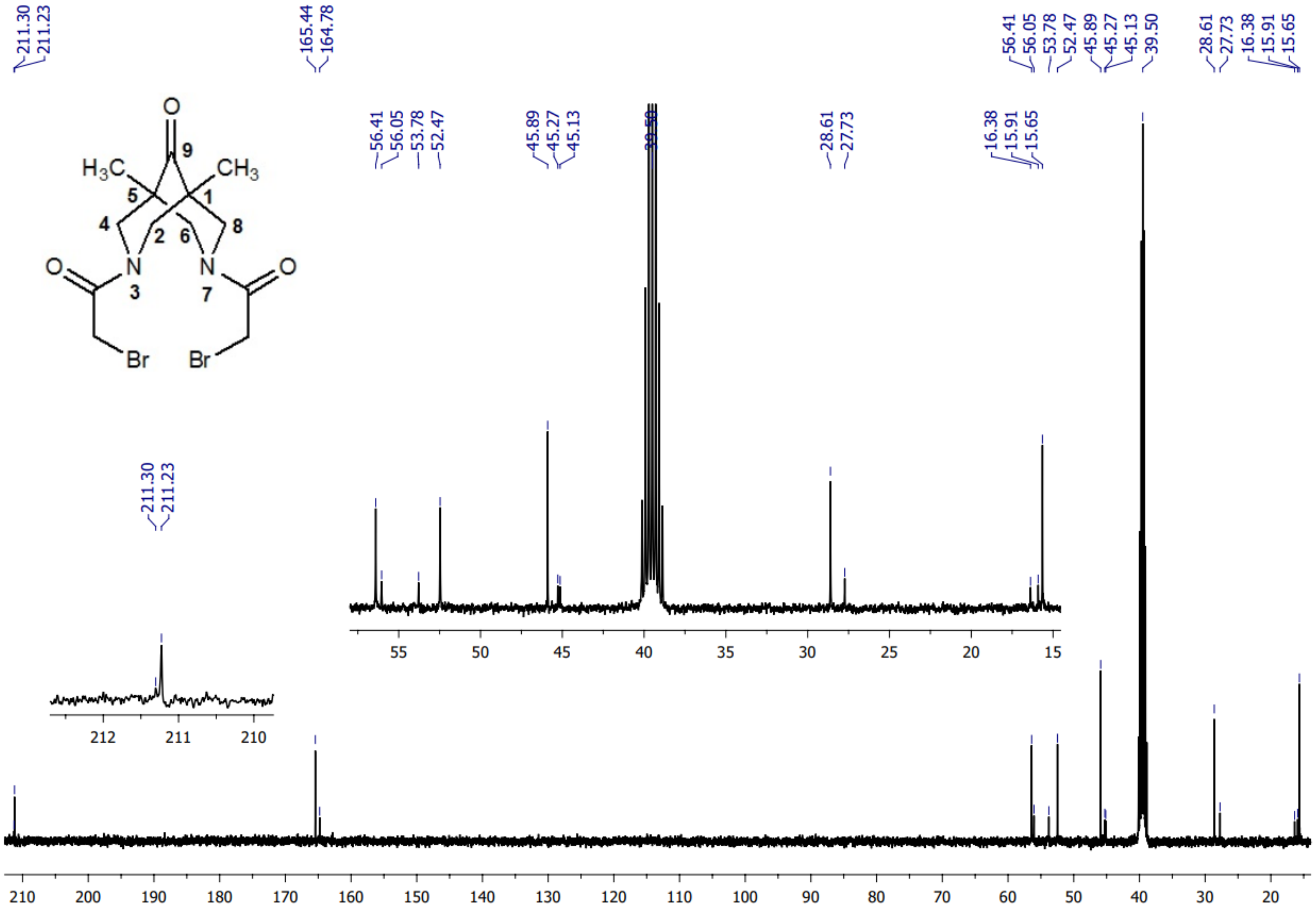


Figure S11. ^{13}C NMR spectrum of bis-amide 2'a in DMSO-d$_6$.

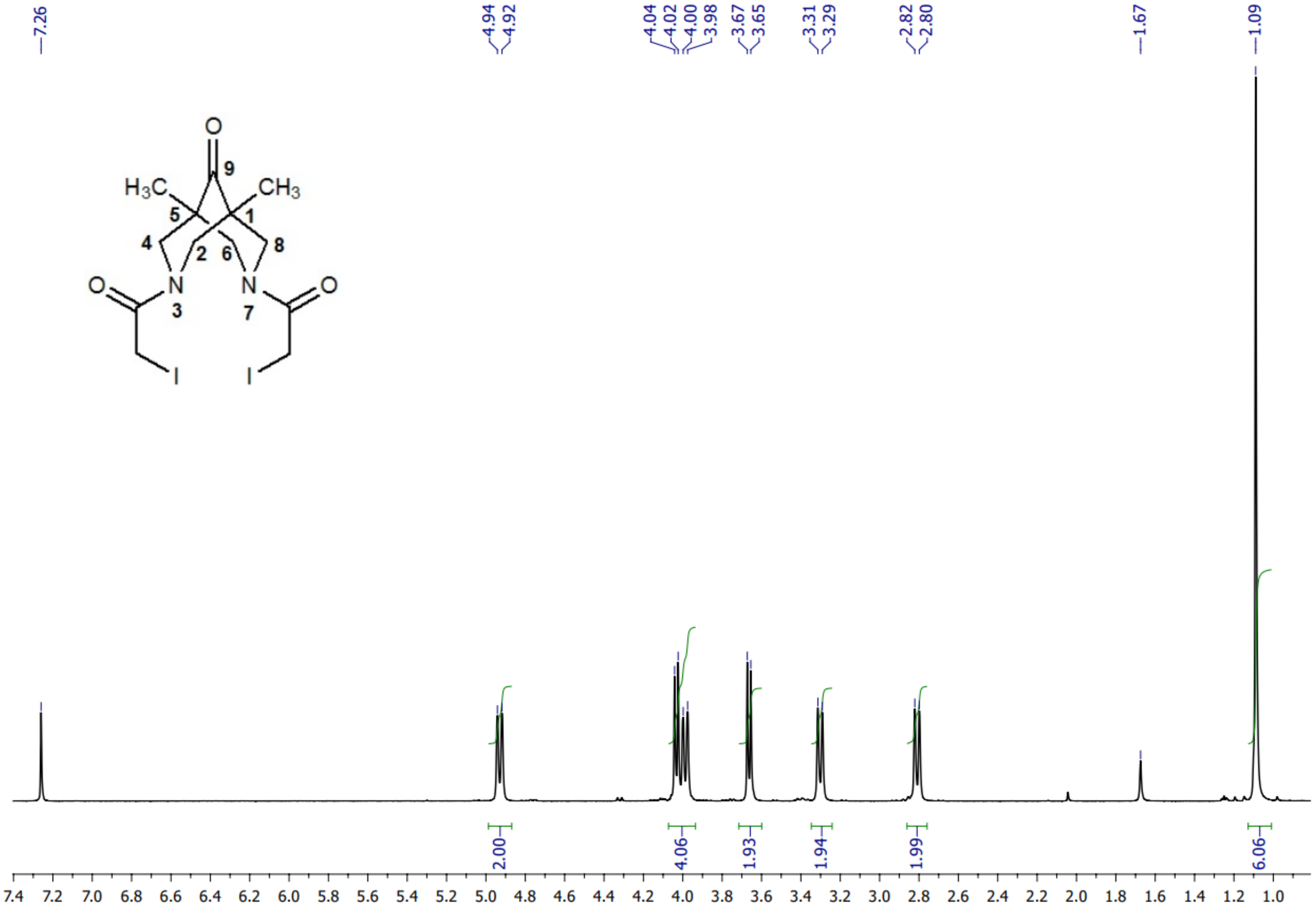


Figure S12. ^{1}H NMR spectrum of bis-amide 3a in $CDCl_3$.

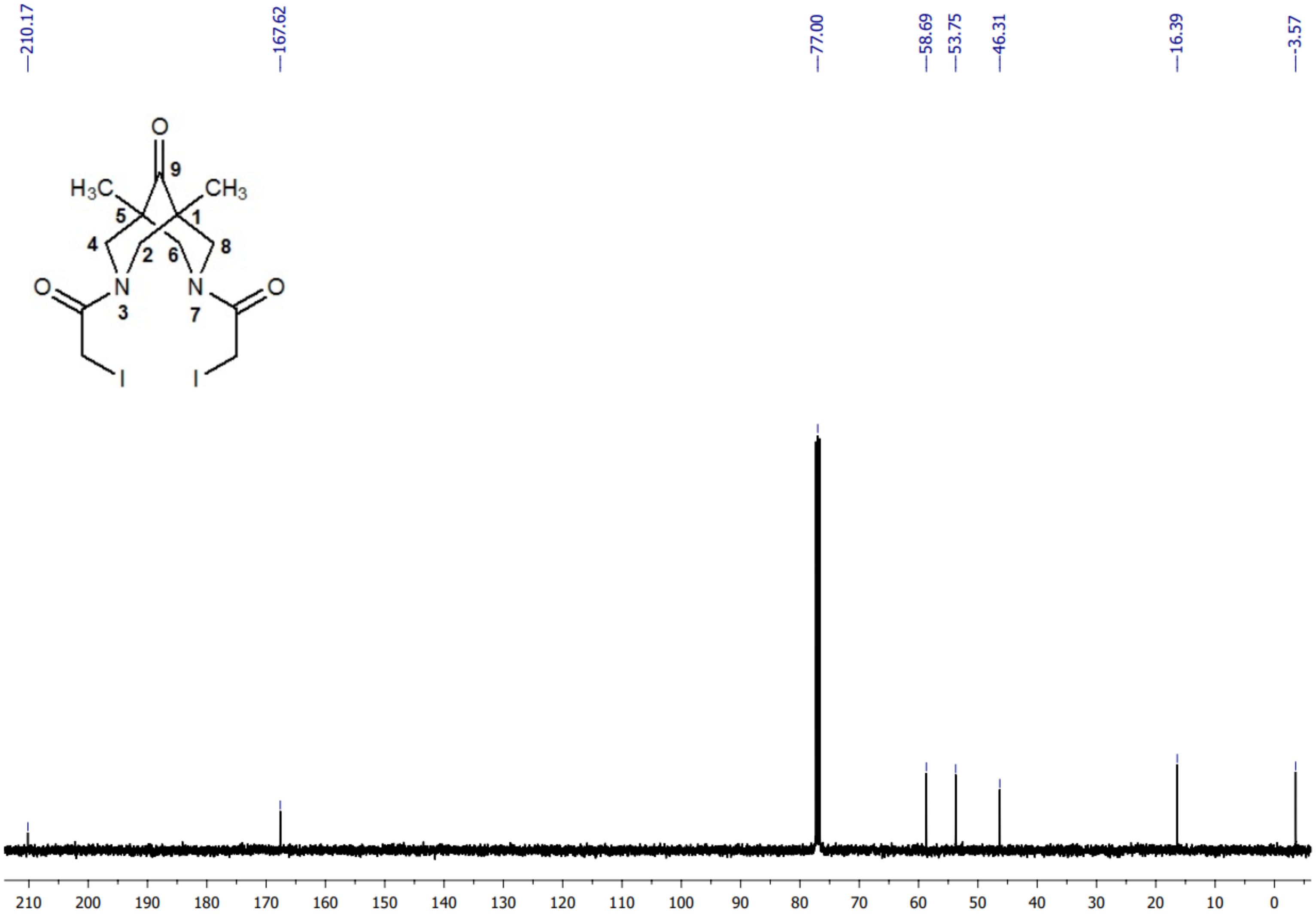


Figure S13. ^{13}**C NMR spectrum of bis-amide 3a in CDCl$_3$.**

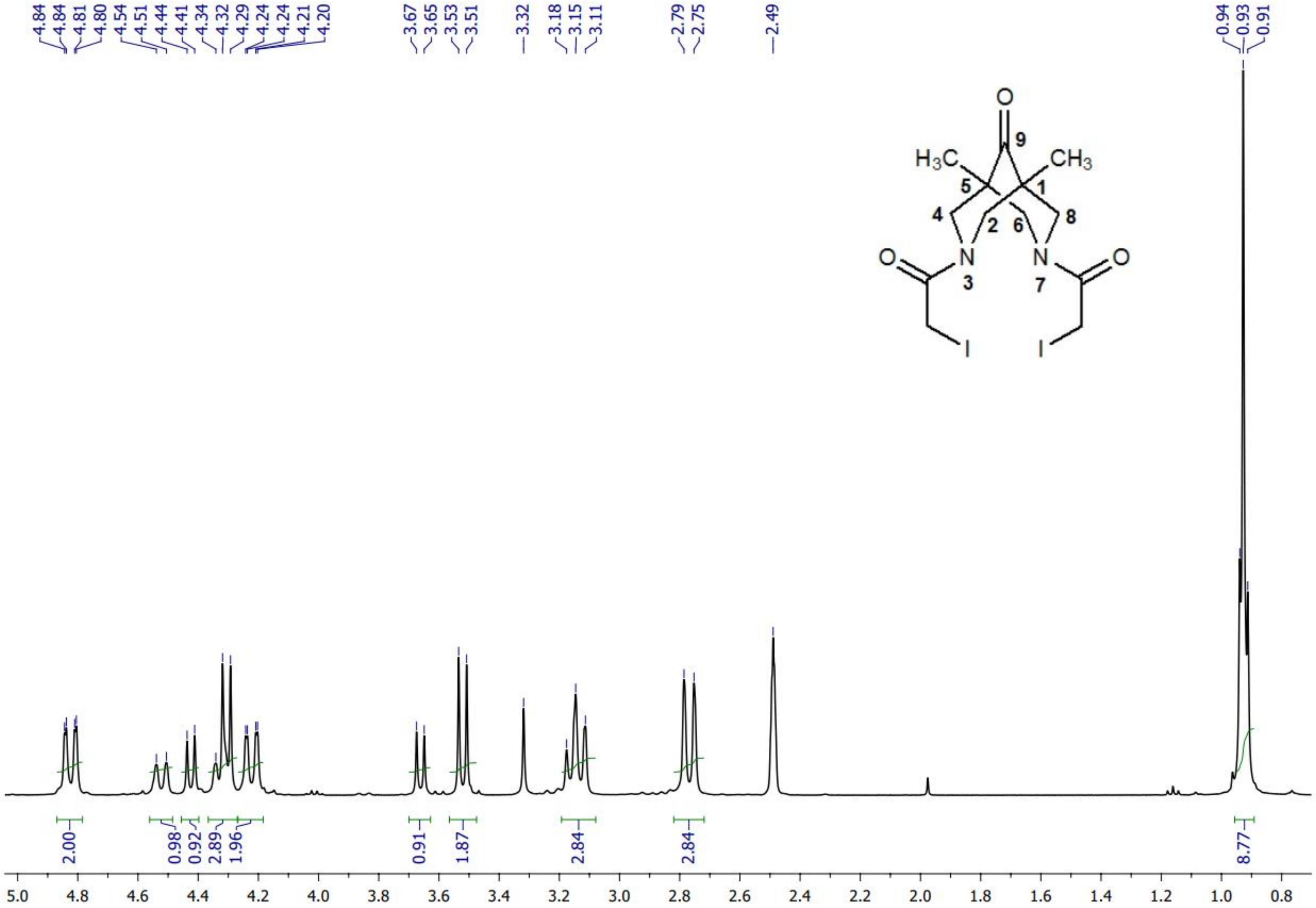


Figure S14. ^{1}H NMR spectrum of bis-amide 3a in DMSO-d_6.

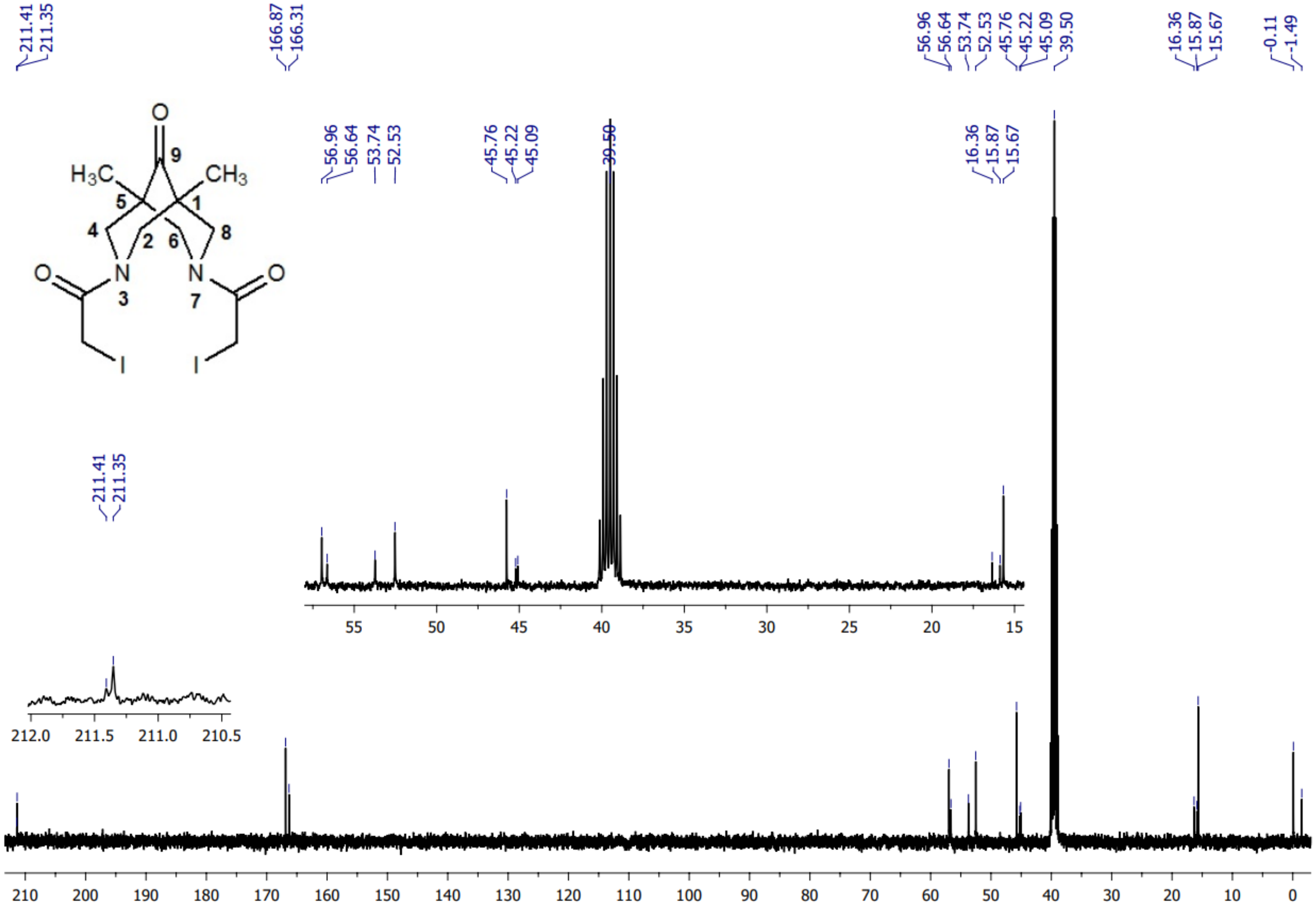


Figure S15. ^{13}C NMR spectrum of bis-amide 3a in DMSO-d$_6$.

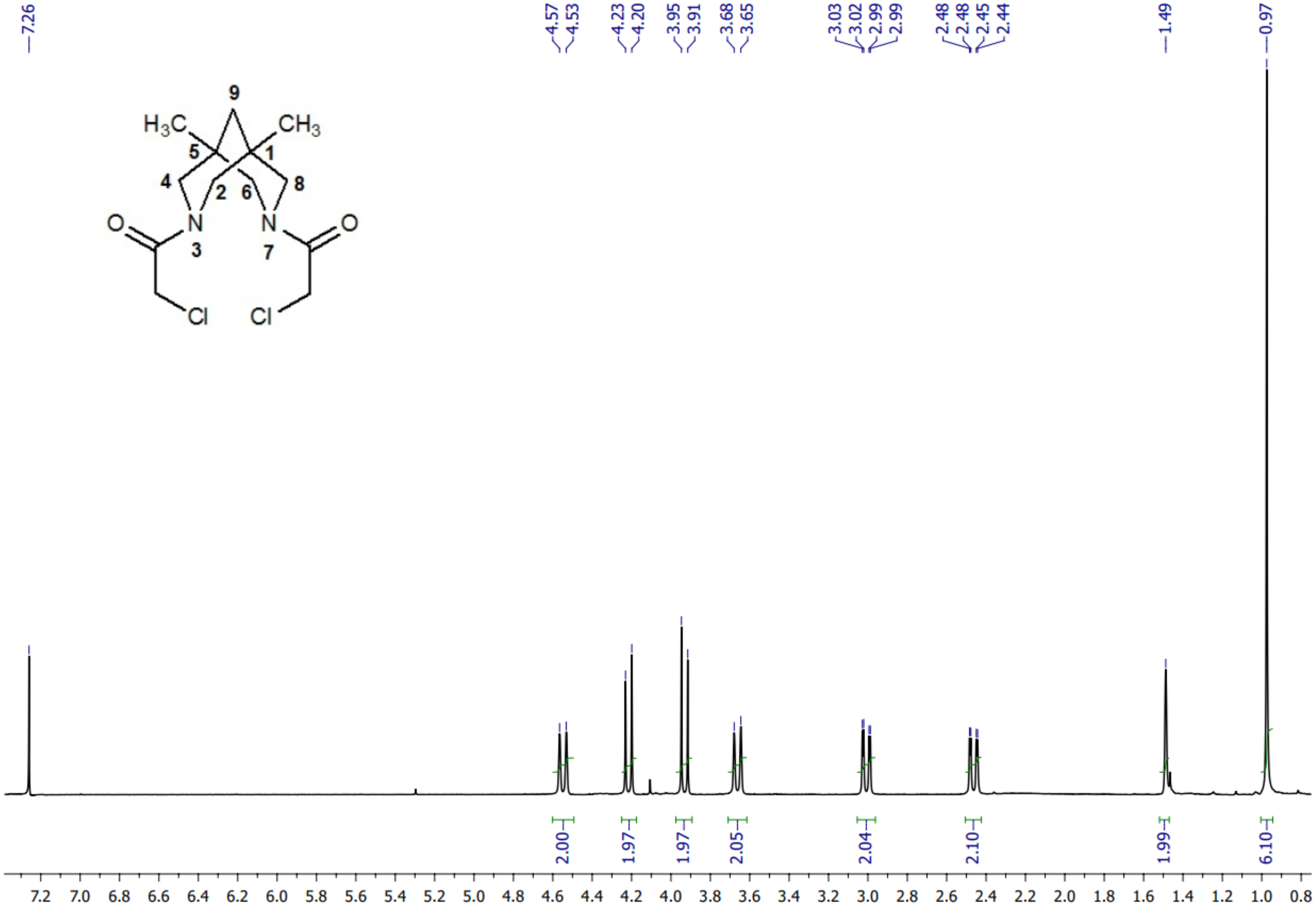


Figure S16. **^{1}H NMR spectrum of bis-amide 2b in $CDCl_3$.**

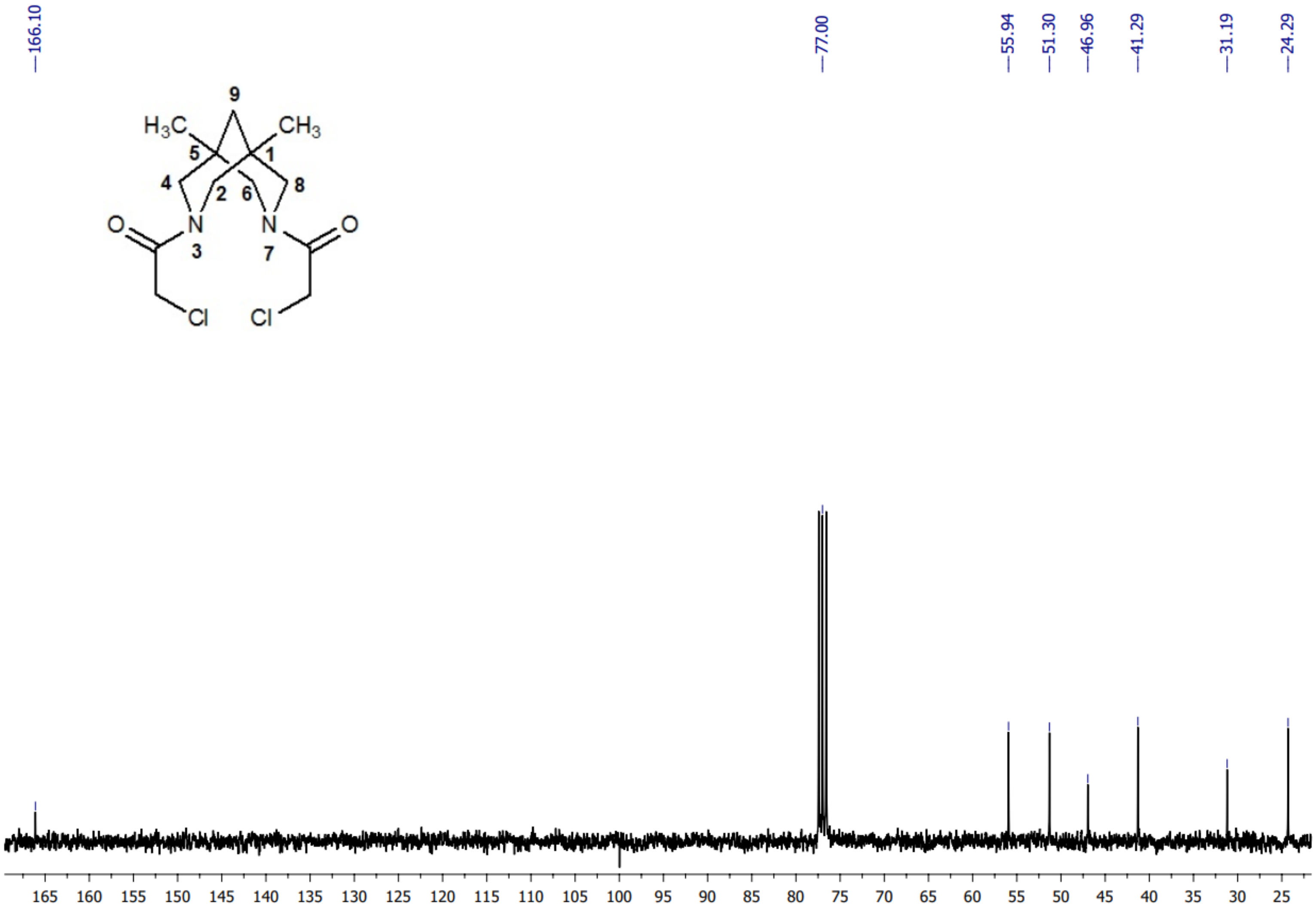


Figure S17. ^{13}C NMR spectrum of bis-amide 2b in $CDCl_3$.

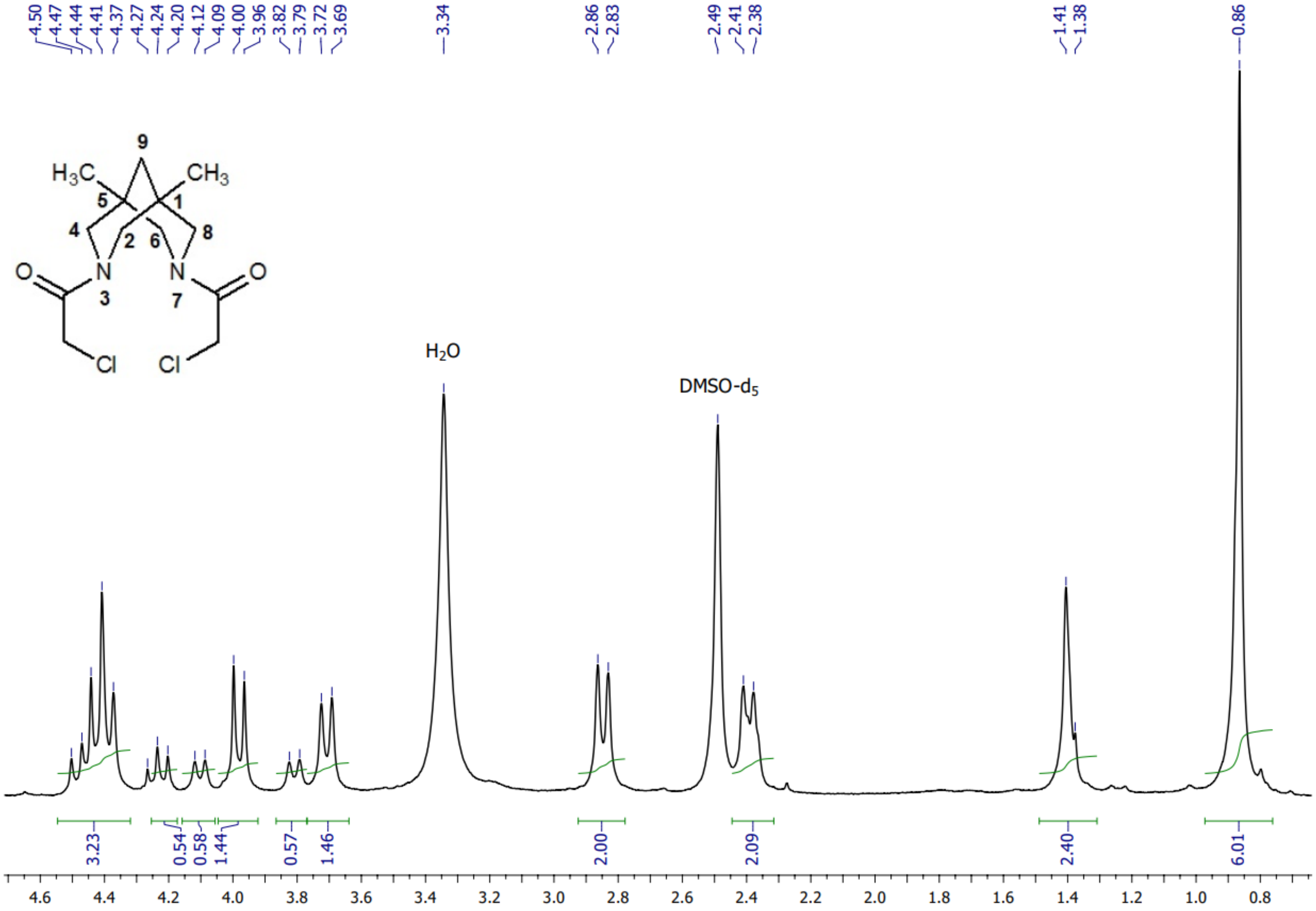


Figure S18. ^{1}H NMR spectrum of bis-amide 2b in DMSO-d_6.

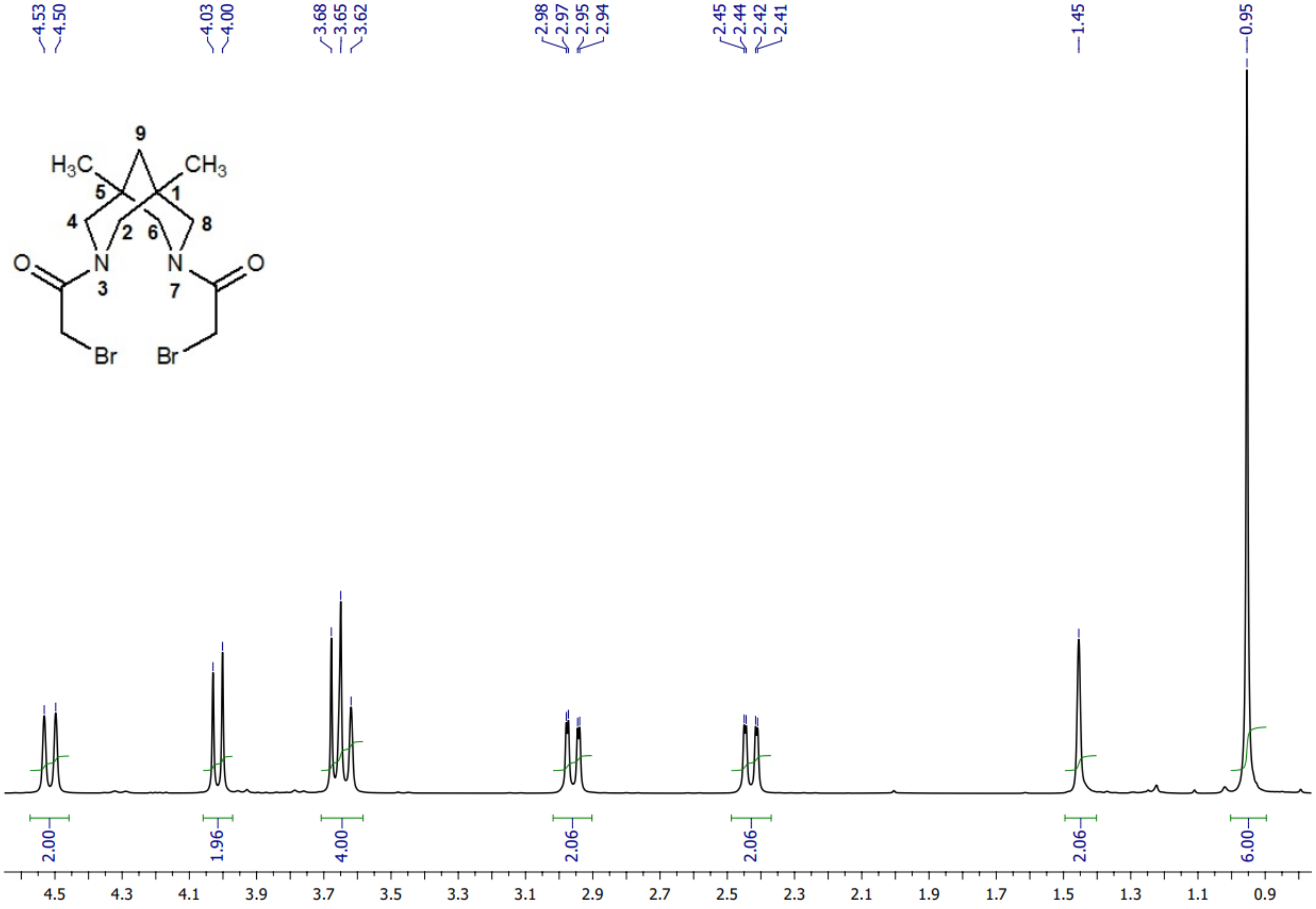


Figure S19. **^{1}H NMR spectrum of bis-amide 2'b in $CDCl_3$.**

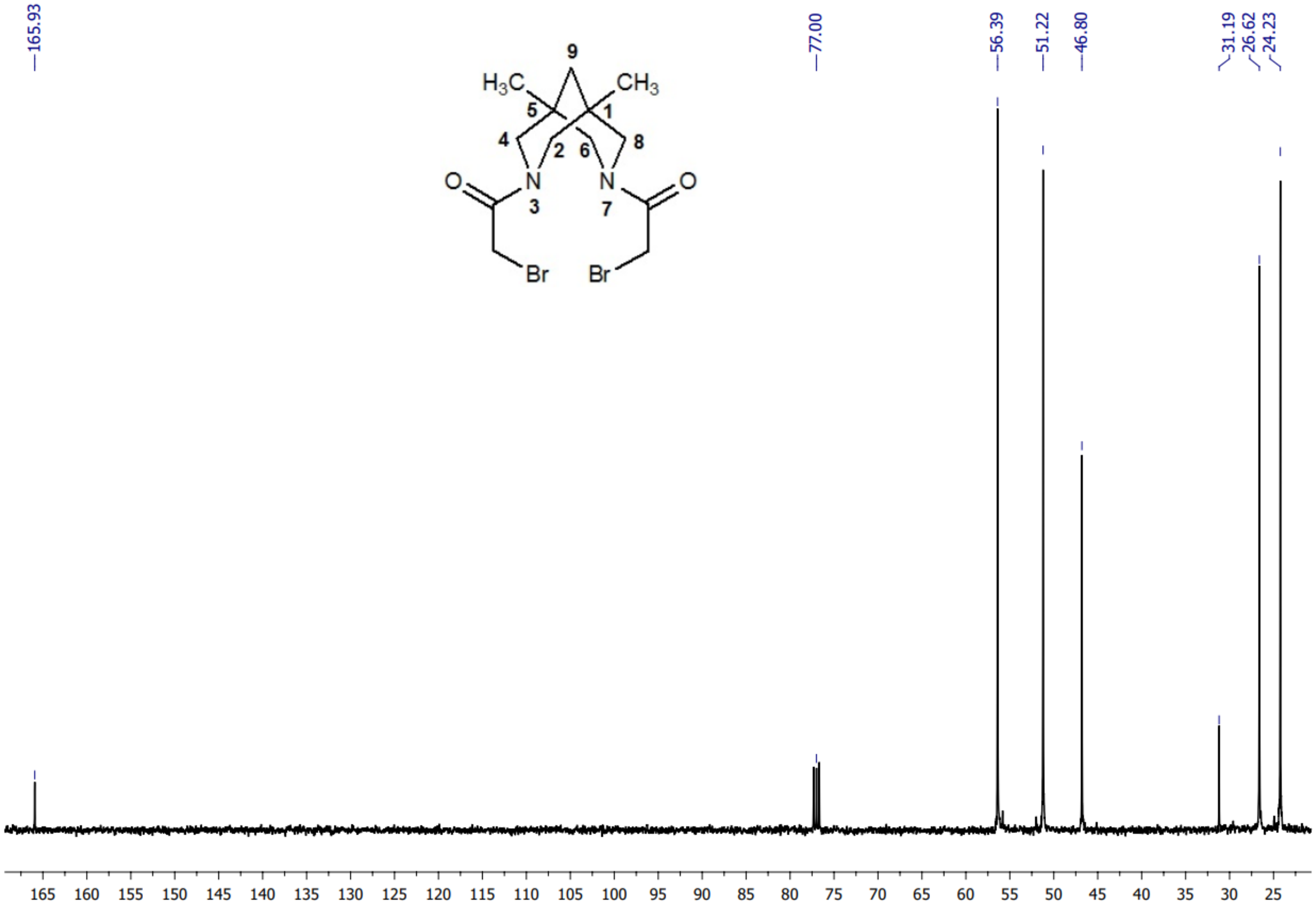


Figure S20. ^{13}C NMR spectrum of bis-amide 2’b in $CDCl_3$.

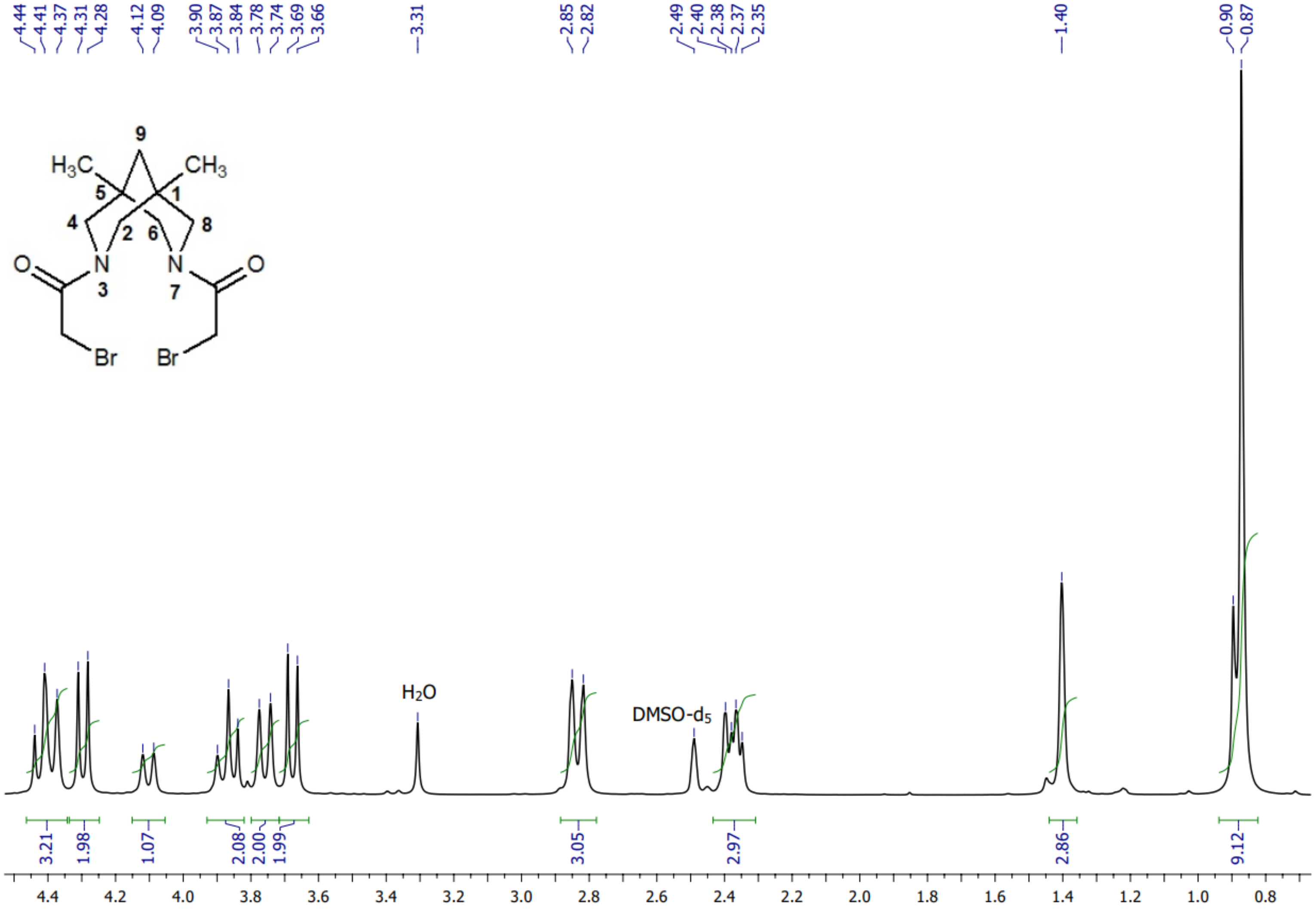


Figure S21. ^{1}H NMR spectrum of bis-amide 2’b in DMSO-d_6.

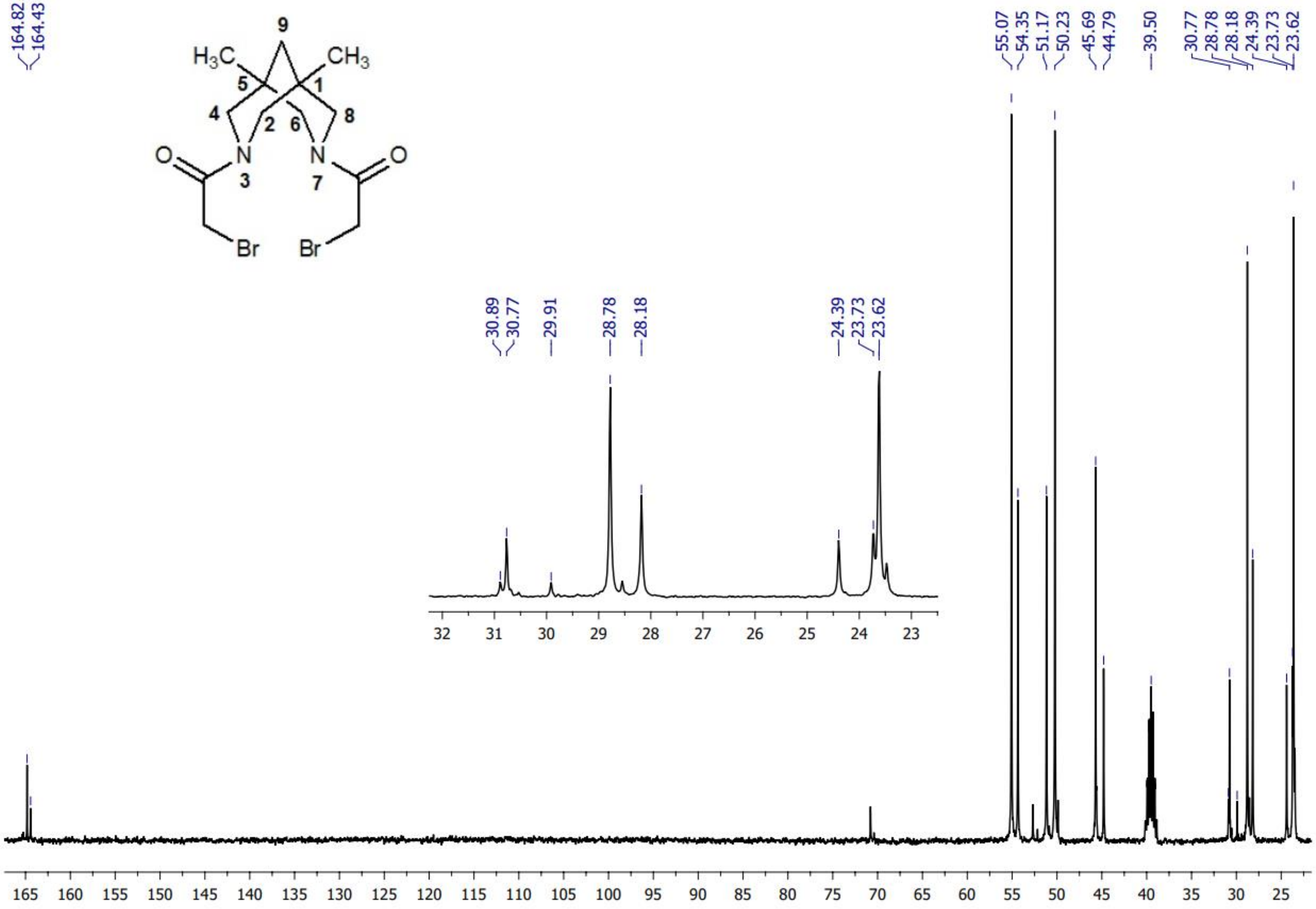


Figure S22. ^{13}C NMR spectrum of bis-amide 2'b in DMSO-d$_6$.

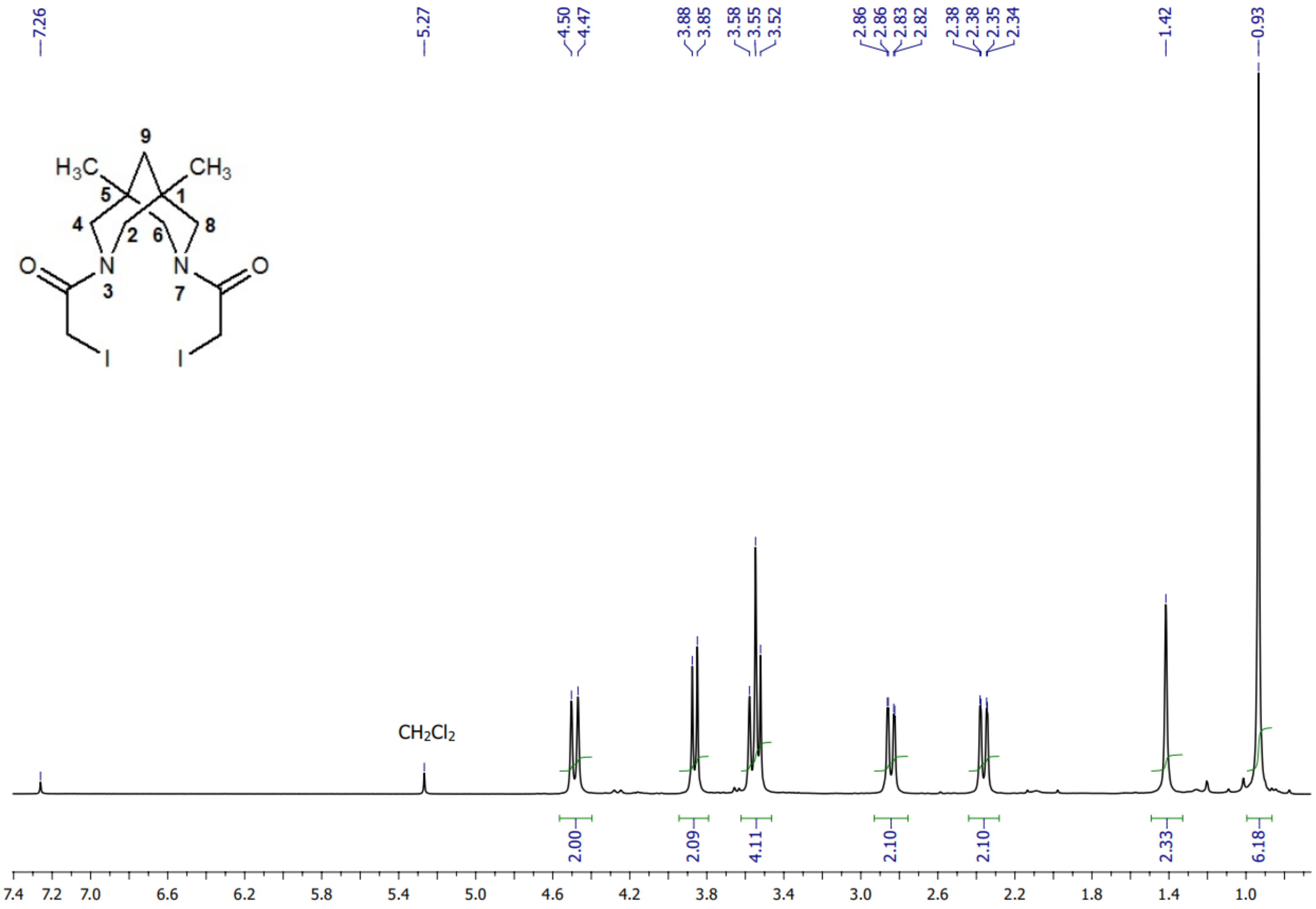


Figure S23. ^{1}H NMR spectrum of bis-amide 3b in $CDCl_3$.

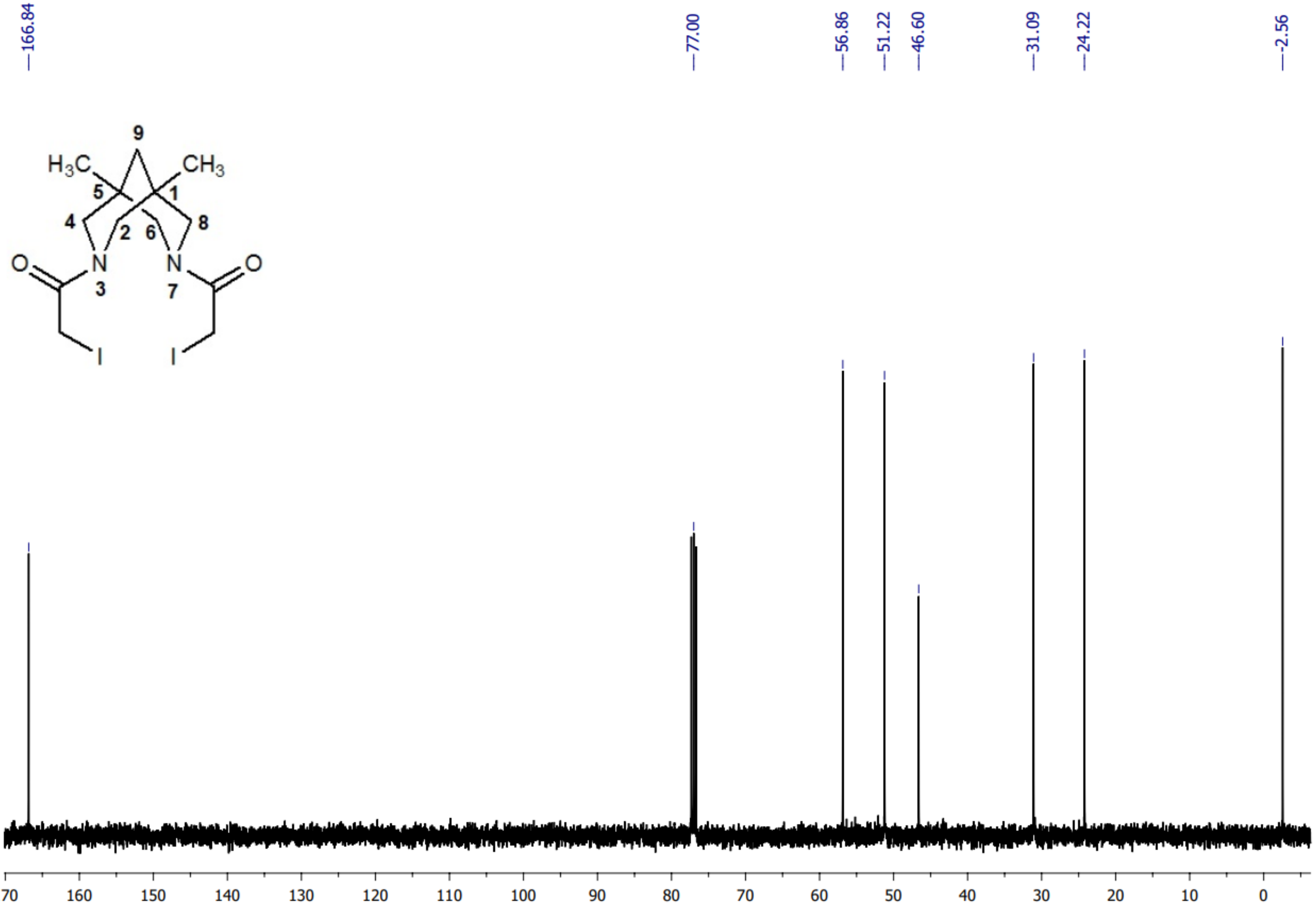


Figure S24. ^{13}C NMR spectrum of bis-amide 3b in $CDCl_3$.

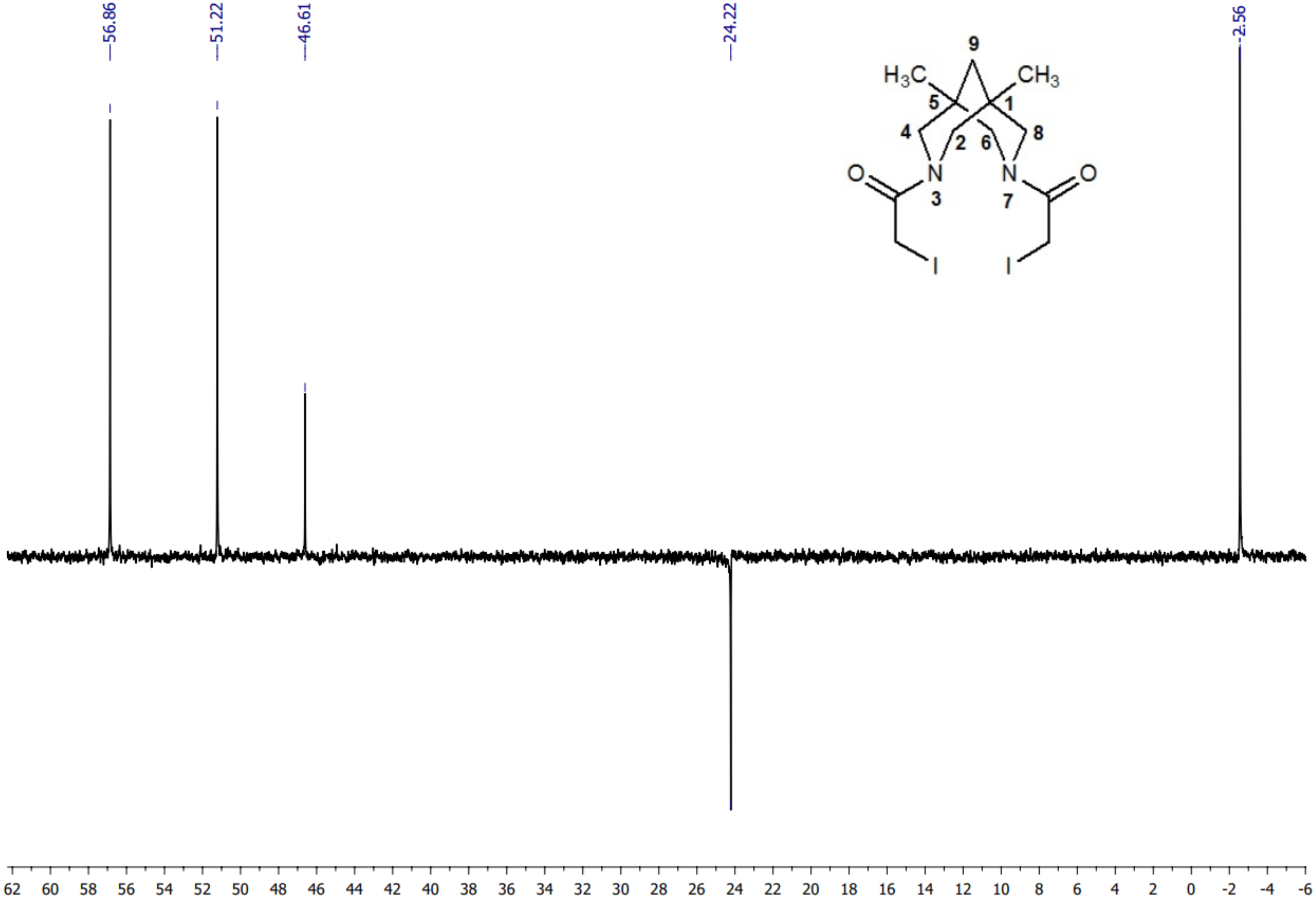


Figure S25. ***DEPT-135*** **spectrum of bis-amide 3b in** $\mathbf{CDCl_3}$**.**

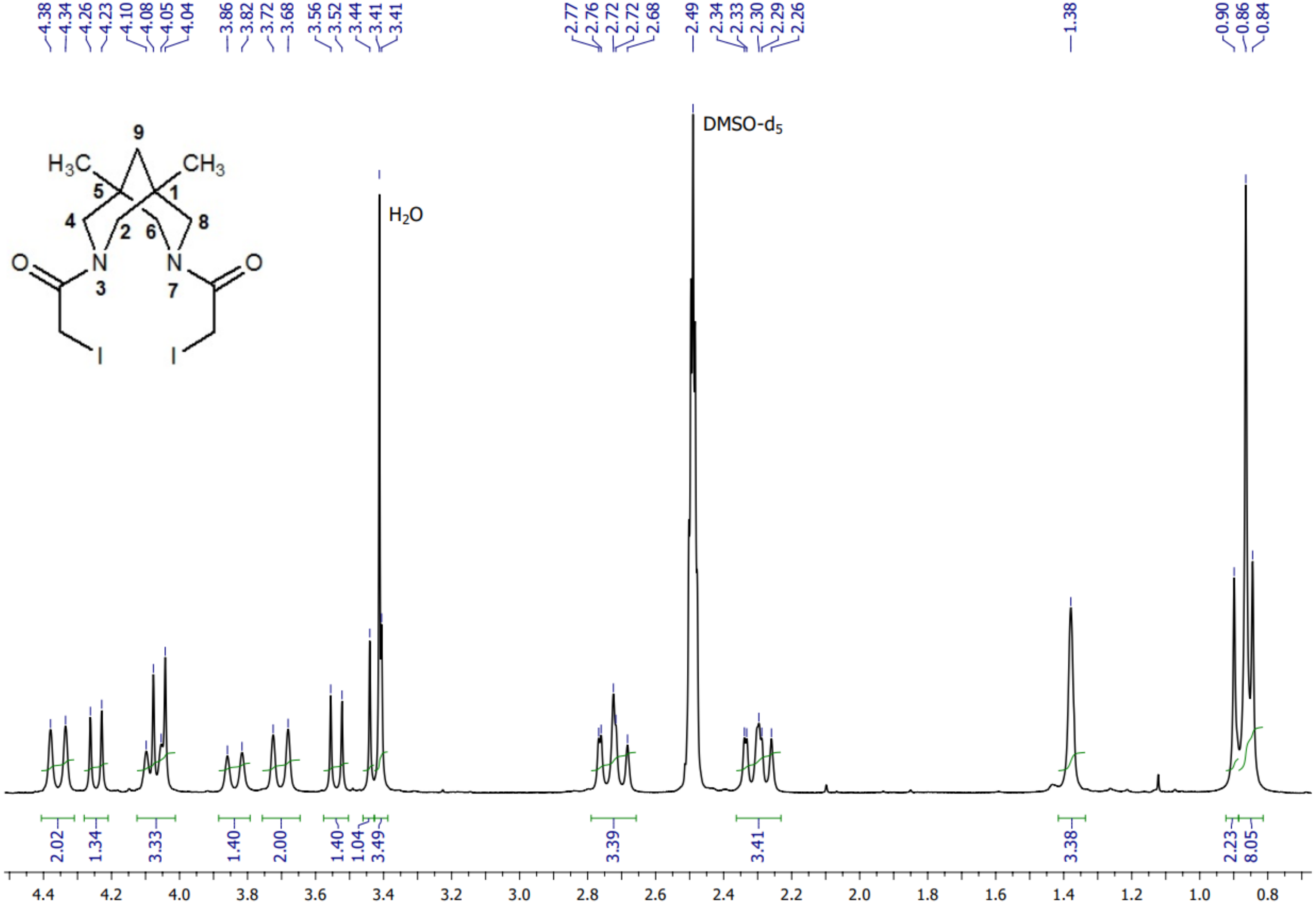


Figure S26. ^{1}H NMR spectrum of bis-amide 3b in DMSO-d_6.

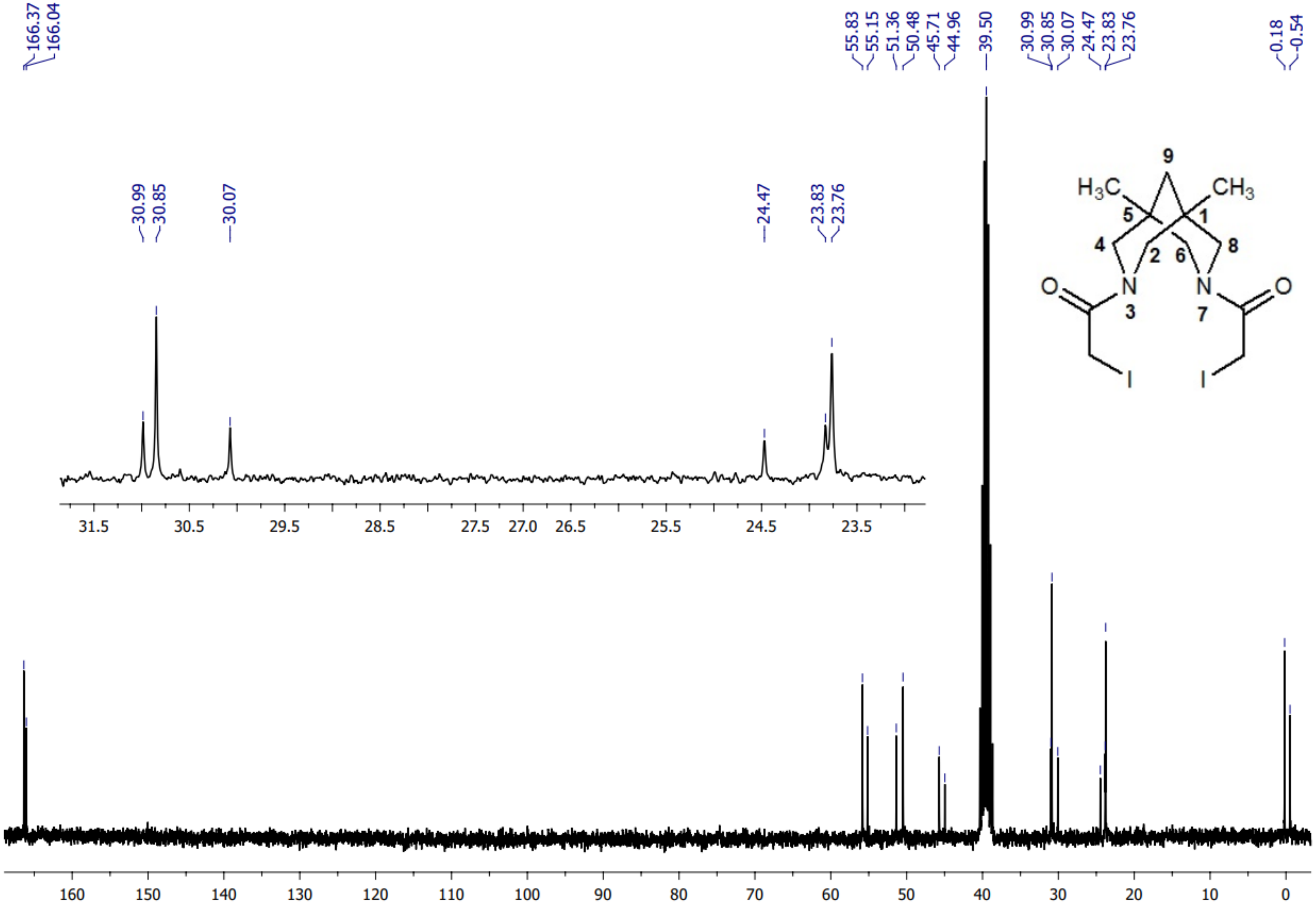


Figure S27. ^{13}C NMR spectrum of bis-amide 3b in DMSO-d$_6$.