Supplementary Material

The straightforward one-pot approach to five- and six-membered saturated heterocyclic cationic gemini-surfactants

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Reagents and Solvents

1,4-Dibromobutane (**B1**), 1,5-dibromopentane (**B2**), β-aminoethanol (**A1**), *n*-butylamine (**A2**), *n*-hexylamine (**A4**), *n*-hexadecylamine (**A6**), *n*-octadecylamine (**A7**) and oleylamine [(9Z)-octadec-9-en-1-amine] (**A8**) were purchased from Sigma-Aldrich and were utilized without further purification. 4,4,4-Trifuorobutan-1-amine (**A3**) and 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexan-1-amine (**A5**) were a gift from Dr. A. A. Tutunov. Potassium carbonate (K_2CO_3) was dried by heating above +200°C prior use. All the solvents used in the study as methanol (MeOH), ethanol (EtOH; 96%), isopropyl alcohol (*i*-PrOH), *n*-buthyl alcohol (*n*-BuOH), acetone (Me_2CO), acetonitrile (MeCN), ethyl acetate (AcOEt) and *tert*-butyl methyl ether (*t*-BuOMe) were of commercial origin and were used as received without further purification.

Analytical Techniques

All the melting points, in degrees Centigrade, of the prepared compounds were determined using a Boetius apparatus and were uncorrected. Elemental analysis was performed using a CHN combustion analyzer CarloErba model 1106; the halogens were determined by combustion-ion chromatography using an Anton Paar microwave oxygen combustion apparatus in conjunction with a Dionex ion chromatography system. All the ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 machine with the working frequency 400 MHz. Both the ^1H and ^{13}C NMR spectra are reported utilizing the δ-scale and are in ppm; a multiplication sign "×" denotes the number of functional groups whose nuclei possess the same resonance frequencies; the abbreviation "dist" indicates a distorted NMR signal. The traces of protonated solvents ($CHCl_3$; DMSO) in deuterated solvents ($CDCl_3$; DMSO-d_6) were used as internal standards during ^1H spectra acquisition, and the deuterated solvents themselves were serving as internal standards during ^{13}C spectra acquisition. All the NMR spectra of the prepared quaternary ammonium salts in deuterium oxide (D_2O) solutions were recorded using capillary tubes filled with HMDS [$(Me_3Si)_2O$] serving as an external standard, neat HMDS chemical shifts were assumed as ^1H NMR (400 MHz, $CDCl_3$): δ_H 0.06 ppm and ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 1.94 ppm, respectively,[1,2] and they were corrected: the correction value is +0.68.[3] In some of the ^1H spectra recorded in deuterium oxide a singlet of HMDS was accompanied by distorted "sidebands" arising due to intrusion of a PVC safety cap situated at the lower end of a capillary tube into the field of the detection coil. The same effect was also expressed, however in a lesser degree, in the ^{13}C NMR spectra recorded in deuterium oxide with HMDS as the external standard.

Experimental Procedures

(Z)-Octadec-9-en-1-aminium (Z)-octadec-9-enylcarbamate (Oleylaminium oleyl carbamate). To a stirred suspension of oleylamine (**A8**, 3.3 ml, 2.67 g, 10 mmole) in MeCN (20 ml) a few pieces of dry ice (solid CO_2) were carefully introduced so as to avoid excessive foaming. Immediately after that a white bulky precipitate formed, the precipitate was filtered off, it was washed on a filter with MeCN and dried in the air; this sequence of procedures afforded oleylaminium oleyl carbamate in 2.57 g (89%) yield as a white crystalline solid, mp was not determined. ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.28 (3H, br s, $^+NH_3$), 5.33 (4H, m, CH=CH × 2), 4.29 (1H, br s, CONH), 3.01 (2H, dist t, CH_2), 2.70 (2H, dist t, CH_2), 1.99 (8H, m, CH_2 × 4), 1.53 (2H, br s, CH_2), 1.40 (2H, br s, CH_2), 1.25 (44H, br s, CH_2 × 22), 0.87 (6H, dist t, CH_3 × 2).^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.3 (CONH), 129.9 (CH × 2), 129.7 (CH × 2), 41.8 (CH_2), 40.6 (CH_2), 40.5 (CH_2), 32.6 (CH_2), 31.9 (CH_2 × 2), 30.7 (CH_2 × 2), 29.7 (CH_2 × 3), 29.6 (CH_2 × 2), 29.5 (CH_2 × 3), 29.3 (CH_2 × 7), 27.2 (CH_2 × 4), 26.8 (CH_2), 22.7 (CH_2 × 2), 14.1 (CH_3 × 2).

The other amines employed in the study, except for β-aminoethanol,[4] do not form the corresponding carbamate salts on contact with carbon dioxide.

1,1′-(Butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (C1). A solution of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole) and β-aminoethanol (**A1**, 1.5 ml, 1.46 g, 24 mmole) in MeCN (20 ml) was refluxed at stirring under an argon (Ar) flow for 3 h. Then the resulting clear solution was cooled to rt. Thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) was introduced to the resulting mass, and the mixture was brought to reflux at stirring, the refluxing was continued for 12 h. After the specified time had passed, *n*-BuOH (20-30 ml) was added to the warm (+50-60°C) mixture to dissolve the deposited crystals of the product. Then the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot *n*-BuOH (20 ml), and the resulting solution was concentrated *in vacuo*. The concentrated solution was diluted with Me_2CO (100 ml), and the cloudy solution was left to stand at rt overnight. The formed precipitate was filtered off, and the crude product (**C1**) left on a filter was immediately recrystallised from a mixture of MeOH/*i*-PrOH (approximately 1:10 v/v); this sequence of procedures afforded pure (**C1**) in 1.66 g (37%) yield as white very hygroscopic crystals, mp was not determined. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 4.75 (2H, s, OH × 2), 4.02 (4H, br s, CH_2 × 2), 3.63 (8H, br s, CH_2 × 4), 3.52 (4H, dist t, CH_2 × 2), 3.46 (4H, br s, CH_2 × 2), 2.20 (8H, br s, CH_2 × 4), 1.88 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 64.3 (CH_2 × 4), 61.0 (CH_2 × 2), 59.7 (CH_2 × 2), 56.5 (CH_2 × 2), 21.9 (CH_2 × 4), 20.7 (CH_2 × 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 5.25 (2H, t, $^3J_{HH}$ 5.3 Hz, OH × 2), 3.79 (4H, br s, CH_2 × 2), 3.61 (4H, br s, CH_2 × 2), 3.57 (4H, br s, CH_2 × 2), 3.41 (8H, br s, CH_2 × 4), 2.06 (8H, br s, CH_2 × 4), 1.76 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 62.7 (CH_2 × 4), 60.0 (CH_2 × 2), 58.2 (CH_2 × 2), 55.2 (CH_2 × 2), 21.0 (CH_2 × 4), 19.7 (CH_2 × 2). Anal. calcd for $C_{16}H_{34}N_2O_2Br_2$ (446.26): C, 43.06; H, 7.68; N, 6.28; Br, 35.81. Found: C, 43.04; H, 7.70; N, 6.25; Br, 35.83.

1,1′-(Butane-1,4-diyl)bis(1-butylpyrrolidinium) dibromide (C2). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), *n*-butylamine (**A2**, 2.4 ml, 1.75 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 10 h. After the specified time had passed, *n*-BuOH (20 ml) was added to the warm (+50-60°C) mixture to dissolve the deposited crystals of the product. Then the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot *n*-BuOH (20 ml), and the resulting filtrate was diluted with Me_2CO (100-150 ml). The precipitated crystals were collected by filtration, they were washed on a filter with Me_2CO (20 ml) and dried in the air; this sequence of procedures afforded (**C2**) in 3.39 g (72%) yield as white nonhygroscopic crystals. Further recrystallisation from a mixture of EtOH/*i*-PrOH (approximately 1:10 v/v) afforded the pure product (**C2**) in 2.95 g (87%) yield, mp 283-284°C with decomposition. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 3.60 (8H, br s, CH_2 × 4), 3.42 (4H, s, CH_2 × 2), 3.33 (4H, dist t, CH_2 × 2), 2.24 (8H, br s, CH_2 × 4), 1.89 (4H, s, CH_2 × 2), 1.78 (4H, dist quint, CH_2 × 2), 1.44 (4H, sext, $^3J_{HH}$ 7.3 Hz, CH_2 × 2), 1.01 (6H, t, $^3J_{HH}$ 7.4 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 63.6 (CH_2 × 4), 60.2 (CH_2 × 2), 59.2 (CH_2 × 2), 25.3 (CH_2 × 2), 22.2 (CH_2 × 4), 20.7 (CH_2 × 2), 19.8 (CH_2 × 2), 13.6 (CH_3 × 2). Anal. calcd for $C_{20}H_{42}N_2Br_2$ (470.37): C, 51.07; H, 9.00; N, 5.96; Br, 33.98. Found: C, 51.09; H, 9.03; N, 5.99; Br, 34.01.

1,1′-(Butane-1,4-diyl)bis(1-(4,4,4-trifluorobutyl)-pyrrolidinium) dibromide (C3). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), 4,4,4-trifuorobutan-1-amine (**A3**, 2.8 ml, 3.05 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 15 h. After the specified time had passed, *n*-BuOH (20-30 ml) was added to the warm (+50-60°C) mixture to dissolve the deposited crystals of the product. Then the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot *n*-BuOH (20 ml), and the resulting solution was concentrated *in vacuo*. The concentrated solution was diluted with Me_2CO (200 ml), and the cloudy solution was left to stand at

rt overnight. The precipitated crystals were filtered off, they were washed on a filter with Me_2CO (20 ml) and dried in the air; this sequence of procedures afforded (**C3**) in 3.49 g (60%) yield as white nonhygroscopic crystals. Further recrystallisation from a mixture of MeCN/Me_2CO (approximately 1:10 v/v) afforded the pure product (**C3**) in 3.20 g (92%) yield, mp 260-261°C, it decomposes at 262°C. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 3.66 (8H, br s, CH_2 × 4), 3.46 (8H, br s, CH_2 × 4), 2.40 (4H, sext, $^3J_{HH}$ 9.4 Hz, CH_2 × 2), 2.27 (8H, br s, CH_2 × 4), 2.13 (4H, dist quint, CH_2 × 2), 1.92 (4H, br s, CH_2 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 127.3 (q, $^1J_{CF}$ 275.9 Hz; CF_3 × 2), 63.9 (CH_2 × 4), 59.3 (CH_2 × 2), 58.6 (CH_2 × 2), 30.4 (q, $^2J_{CF}$ 29.6 Hz; CH_2 × 2), 20.2 (CH_2 × 4), 20.6 (CH_2 × 2), 16.8 (q appears as d, $^3J_{CF}$ 2.7 Hz; CH_2 × 2). Anal. calcd for $C_{20}H_{36}N_2F_6Br_2$ (578.31): C, 41.54; H, 6.27; N, 4.84; F, 19.71; Br, 27.63. Found: C, 41.56; H, 6.29; N, 4.80; F 19.69; Br, 27.60.

1,1′-(Butane-1,4-diyl)bis(1-hexylpyrrolidinium) dibromide (C4). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), *n*-hexylamine (**A4**, 3.2 ml, 2.42 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 4 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (10-20 ml), and the resulting filtrate was diluted with Me_2CO (100-150 ml). The precipitated crystals were collected by filtration, they were washed on a filter with Me_2CO (20 ml) and dried in the air; this sequence of procedures afforded (**C4**) in 2.67 g (51%) yield as white moderately hygroscopic crystals. Further recrystallisation from a mixture of MeCN/Me_2CO (approximately 1:10 v/v) afforded the pure product (**C4**) in 2.34 g (88%) yield, mp 201-202°C. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 3.60 (8H, br s, CH_2 × 4), 3.42 (4H, br s, CH_2 × 2), 3.33 (4H, dist t, CH_2 × 2), 2.24 (8H, br s, CH_2 × 4), 1.89 (4H, br s, CH_2 × 2), 1.79 (4H, br s, CH_2 × 2), 1.41 (12H, br s, CH_2 × 6), 0.94 (6H, dist dt, CH_3 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 63.6 (CH_2 × 4), 60.4 (CH_2 × 2), 59.2 (CH_2 × 2), 31.1 (CH_2 × 2), 25.9 (CH_2 × 2), 23.2 (CH_2 × 2), 22.4 (CH_2 × 2), 22.2 (CH_2 × 4), 20.7 (CH_2 × 2), 13.9 (CH_3 × 2). Anal. calcd for $C_{24}H_{50}N_2Br_2$ (526.48): C, 54.75; H, 9.57; N, 5.32; Br, 30.35. Found: C, 54.77; H, 9.59; N, 5.33; Br, 30.33.

1,1′-(Butane-1,4-diyl)bis(1-hexadecylpyrrolidinium) dibromide (C6). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), *n*-hexadecylamine (**A6**, 5.78 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 15 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (20-30 ml), and the resulting filtrate was left to stand at rt for several days (1-2 days). The precipitated crystals were collected by filtration, they were washed on a filter with MeCN (20 ml) and dried in the air; this sequence of procedures afforded the crude product (**C6**) in 8.3 g (103%) yield. The crude product (**C6**) was suspended in hot (+50°C) MeCN (40 ml), and to the suspension MeOH was added dropwise until the clear solution was formed. The resulting clear solution was left to stand at rt overnight. The formed precipitate was collected by filtration, it was washed on a filter with MeCN (20 ml) and dried in the air; this sequence of procedures afforded pure (**C6**) in 6.03 g (75%) yield as a white nonhygroscopic powder, mp 197-199°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.98 (4H, dist quint, CH_2 × 2), 3.79 (4H, br s, CH_2 × 2), 3.50 (4H, dist quint, CH_2 × 2), 3.26 (4H, dist t, CH_2 × 2), 2.38 (4H, br s, CH_2 × 2), 2.13 (8H, br s, CH_2 × 4), 1.77 (4H, br s, CH_2 × 2), 1.22-1.33 (52H, br m, CH_2 × 26), 0.85 (6H, t, $^3J_{HH}$ 6.7 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 63.0 (CH_2 × 4), 60.9 (CH_2 × 2), 59.8 (CH_2 × 2), 31.8 (CH_2 × 2), 29.6 (CH_2 × 8), 29.5 (CH_2 × 4), 29.4 (CH_2 × 4), 29.3 (CH_2 × 2), 29.1 (CH_2 × 2), 26.5 (CH_2 × 2), 23.5 (CH_2× 2), 22.6 (CH_2 × 2), 22.5 (CH_2 × 4), 20.9 (CH_2 × 2), 14.1 (CH_3 × 2). Anal. calcd for $C_{44}H_{90}N_2Br_2$ (807.01): C, 65.49; H, 11.24; N, 3.47; Br, 19.80. Found: C, 65.51; H, 11.26; N, 3.45; Br, 19.78.

1,1′-(Butane-1,4-diyl)bis(1-octadecylpyrrolidinium) dibromide (C7). A mixture of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole), *n*-octadecylamine (**A7**, 6.46 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6

mmole) in MeCN (20 ml) was refluxed at stirring for 15 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (40 ml), and the resulting filtrate was left to stand at rt for several days (1-2 days). The precipitated crystals were collected by filtration, they were washed on a filter with MeCN (20 ml) and dried in the air; this sequence of procedures afforded the crude product (**C7**) in 10.55 g (122%) yield. The crude product (**C7**) was suspended in hot (+50°C) MeCN (50 ml), and to the suspension MeOH was added dropwise until the clear solution was formed. The resulting clear solution was left to stand at rt overnight. The formed precipitate was collected by filtration, it was washed on a filter with MeCN (40 ml) and dried in the air; this sequence of procedures afforded pure (**C7**) in 7.7 g (89%) yield as a white nonhygroscopic powder, mp 192-194°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.93 (4H, dist quint, CH_2 × 2), 3.75 (4H, br s, CH_2 × 2), 3.50 (4H, dist quint, CH_2 × 2), 3.25 (4H, dist t, CH_2 × 2), 2.34 (4H, br s, CH_2 × 2), 2.10 (8H, br s, CH_2 × 4), 1.73 (4H, br s, CH_2 × 2), 1.19-1.30 (60H, br m, CH_2 × 30), 0.82 (6H, t, $^3J_{HH}$ 6.6 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 62.7 (CH_2 × 4), 60.8 (CH_2 × 2), 59.6 (CH_2 × 2), 31.8 (CH_2 × 2), 29.6 (CH_2 × 14), 29.5 (CH_2× 2), 29.3 (CH_2 × 4), 29.2 (CH_2 × 2), 29.0 (CH_2 × 2), 26.4 (CH_2 × 2), 23.5 (CH_2 × 2), 22.5 (CH_2 × 2), 22.4 (CH_2 × 4), 20.8 (CH_2 × 2), 14.0 (CH_3 × 2). Anal. calcd for $C_{48}H_{98}N_2Br_2$ (863.11): C, 66.79; H, 11.44; N, 3.25; Br, 18.52. Found: C, 66.78; H, 11.41; N, 3.20; Br, 18.48.

(Z)-1,1′-(Butane-1,4-diyl)bis(1-((Z)-octadec-9-enyl)pyrrolidinium) dibromide (C8). A solution of 1,4-dibromobutane (**B1**, 4.0 ml, 7.34 g, 34 mmole) and oleylamine (**A8**, 8.0 ml, 6.4 g, 24 mmole) in MeCN (20 ml) was refluxed at stirring under an Ar flow for 3 h. Then the resulting clear solution was cooled to rt. Thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) was introduced to the resulting mass, and the mixture was brought to reflux at stirring, the refluxing was continued for 20 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (50 ml), and the resulting filtrate was diluted with *t*-BuOMe (200 ml), and the resulting cloudy solution was left to stand at +5°C overnight. The formed wax-like material was filtered off, it was washed on a filter with *t*-BuOMe (20 ml), at first it was dried in the air and later in a vacuum desiccator over P_2O_5; this sequence of procedures afforded pure (**C8**) in 6.60 g (77%) yield as a white nonhygroscopic wax-like material, mp 185-188°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.29 (4H, app q, CH=CH × 2), 3.95 (4H, dist quint, CH_2 × 2), 3.77 (4H, br s, CH_2 × 2), 3.50 (4H, dist quint, CH_2 × 2), 3.25 (4H, dist t, CH_2 × 2), 2.35 (4H, br s, CH_2 × 2), 2.12 (8H, br s, CH_2 × 4), 1.96 (8H, dist q, CH_2 × 4), 1.75 (4H, br s, CH_2 × 2), 1.21-1.32 (44H, br m, CH_2 × 22), 0.83 (6H, t, $^3J_{HH}$ 6.7 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 129.9 (CH × 2), 129.5 (CH × 2), 63.0 (CH_2 × 4), 60.9 (CH_2 × 2), 59.7 (CH_2 × 2), 31.8 (CH_2 × 2), 29.6 (CH_2 × 2), 29.5 (CH_2 × 2), 29.4 (CH_2 × 2), 29.3 (CH_2 × 2), 29.2 (CH_2 × 4), 29.0 (CH_2 × 4), 27.1 (CH_2 × 2), 27.0 (CH_2 × 2), 26.4 (CH_2 × 2), 23.5 (CH_2 × 2), 22.5 (CH_2 × 2), 22.4 (CH_2 × 4), 20.8 (CH_2 × 2), 14.0 (CH_3 × 2). Anal. calcd for $C_{48}H_{94}N_2Br_2$ (859.08): C, 67.11; H, 11.03; N, 3.26; Br, 18.60. Found: C, 66.86; H, 11.23; N, 3.20; Br, 18.57.

1,1′-(Pentane-1,5-diyl)bis(1-butylpiperidinium) dibromide (D2). A mixture of 1,5-dibromopentane (**B2**, 4.7 ml, 7.82 g, 34 mmole), *n*-butylamine (**A2**, 2.4 ml, 1.75 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 10 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (10-20 ml), and the resulting filtrate was diluted with Me_2CO (100-150 ml). The precipitated crystals were collected by filtration, they were washed on a filter with Me_2CO (20 ml) and dried in the air; this sequence of procedures afforded (**D2**) in 3.19 g (61%) yield as white nonhygroscopic crystals. Further recrystallisation from a mixture of MeCN/Me_2CO (approximately 1:10 v/v) afforded the pure product (**D2**) in 1.92 g (95%) yield, mp 265-266°C with decomposition. ^{1}H NMR (400 MHz, D_2O [HMDS]): δ_H 3.39 (16H, br m, CH_2 × 8), 1.94 (8H, br s, CH_2 × 4), 1.85 (4H, br s, CH_2 × 2), 1.74 (8H, br s, CH_2 × 4), 1.48 (6H, merged quint and sext, CH_2 × 3), 1.03 (6H, t,

$^{3}J_{HH}$ 7.3 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, D_2O [HMDS]): δ_C 60.0 (CH_2 × 4), 58.7 (CH_2 × 2), 58.6 (CH_2 × 2), 23.5 (CH_2 × 3), 21.4 (CH_2 × 2), 21.3 (CH_2 × 2), 19.8 (CH_2 × 6), 13.6 (CH_3 × 2). Anal. calcd for $C_{23}H_{48}N_2Br_2$ (512.45): C, 53.91; H, 9.44; N, 5.47; Br, 31.19. Found: C, 53.82; H, 9.38; N, 5.38; Br, 31.05.

1,1′-(Pentane-1,5-diyl)bis(1-hexadecylpiperidinium) dibromide (D6). A mixture of 1,5-dibromopentane (**B2**, 4.7 ml, 7.82 g, 34 mmole), *n*-hexadecylamine (**A6**, 5.78 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 24 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (50 ml), and the resulting filtrate was evaporated to dryness *in vacuo*. The resulting oily residue was dissolved in hot AcOEt (50-70 ml), and the resulting clear solution was left to stand at rt for several days (1-2 days). The formed precipitate was filtered off, it was washed with AcOEt (20 ml) on a filter and dried in the air; this sequence of procedures afforded pure (**D6**) in 5.40 g (64%) yield as a white nonhygroscopic powder, mp 139-141°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.79 (4H, dist t, CH_2 × 2), 3.67 (4H, dist t, CH_2 × 2), 3.50 (4H, dist d, CH_2 × 2), 3.36 (4H, dist t, CH_2 × 2), 2.02 (4H, dist t, CH_2 × 2), 1.92 (4H, br s, CH_2 × 2), 1.76 (4H, br s, CH_2 × 2), 1.68 (4H, br s, CH_2 × 2), 1.58 (6H, dist d, CH_2 × 3), 1.19-1.30 (52H, br m, CH_2 × 26), 0.81 (6H, t, $^{3}J_{HH}$ 6.6 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 60.3 (CH_2 × 2), 58.8 (CH_2 × 4), 56.5 (CH_2 × 2), 31.8 (CH_2 × 2), 29.5 (CH_2 × 16), 29.3 (CH_2 × 2), 29.2 (CH_2 × 2), 29.1 (CH_2 × 2), 26.4 (CH_2 × 2), 22.7 (CH_2), 22.5 (CH_2 × 2), 21.7 (CH_2 × 2), 20.7 (CH_2 × 2), 19.8 (CH_2 × 4), 14.0 (CH_3 × 2). Anal. calcd for $C_{47}H_{96}N_2Br_2$ (849.09): C, 66.48; H, 11.40; N, 3.30; Br, 18.82. Found: C, 66.52; H, 11.58; N, 2.27; Br, 18.90.

1,1′-(Pentane-1,5-diyl)bis(1-octadecylpiperidinium) dibromide (D7). A mixture of 1,5-dibromopentane (**B2**, 4.7 ml, 7.82 g, 34 mmole), *n*-octadecylamine (**A7**, 6.46 g, 24 mmole), and thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) in MeCN (20 ml) was refluxed at stirring for 24 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN (50 ml), and the resulting filtrate was left to stand at rt for several days (1-2 days). The formed precipitate, the mixture of the two quaternary ammonium salts, was collected by filtration, it was washed on a filter with MeCN (20 ml) and dried in the air; this sequence of procedures afforded the crude product (**D7**) in 7.8 g (82%) yield as a white nonhygroscopic powder. The powder was dissolved in hot MeCN (20-30 ml), the resulting clear solution was diluted with AcOEt (100-150 ml), and the cloudy solution was left to stand at rt overnight. The formed precipitate was collected by filtration, it was washed on a filter with AcOEt (20-30 ml) and dried in the air; this sequence of procedures afforded pure (**D7**) in 2.42 g (27%) yield as a white nonhygroscopic powder, mp 131-134°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.84 (4H, brs, CH_2 × 2), 3.71 (4H, br s, CH_2 × 2), 3.52 (4H, dist d, CH_2 × 2), 3.36 (4H, br s, CH_2 × 2), 2.05 (4H, br s, CH_2 × 2), 1.95 (4H, br s, CH_2 × 2), 1.70-1.79 (8H, br m, CH_2 × 4), 1.61 (6H, br s, CH_2 × 3), 1.22-1.33 (60H, br m, CH_2 × 30), 0.84 (6H, dist t, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 60.6 (CH_2 × 2), 58.8 (CH_2 × 4), 56.3 (CH_2 × 2), 31.8 (CH_2 × 2), 29.6 (CH_2 × 14), 29.5 (CH_2 × 2), 29.4 (CH_2 × 4), 29.3 (CH_2 × 2), 29.2 (CH_2 × 2), 26.5 (CH_2 × 2), 22.7 (CH_2), 22.6 (CH_2 × 2), 21.8 (CH_2 × 2), 20.8 (CH_2 × 2), 20.7 (CH_2 × 2), 19.9 (CH_2 × 4), 14.0 (CH_3 × 2). Anal. calcd for $C_{51}H_{104}N_2Br_2$ (905.19): C, 67.67; H, 11.58; N, 3.09; Br, 17.65. Found: C, 67.72; H, 11.71; N, 2.27; Br, 17.77.

(Z)-1,1′-(Pentane-1,5-diyl)bis(1-((Z)-octadec-9-enyl)piperidinium) dibromide (D8). A solution of 1,5-dibromopentane (**B2**, 4.7 ml, 7.82 g, 34 mmole) and oleylamine (**A8**, 8.0 ml, 6.4 g, 24 mmole) in MeCN (20 ml) was refluxed at stirring under an Ar flow for 3 h. Then the resulting clear solution was cooled to rt. Thoroughly ground K_2CO_3 (8.0 g, 57.6 mmole) was introduced to the resulting mass, and the mixture was brought to reflux at stirring, the refluxing was continued for 24 h. After the specified time had passed, the remaining inorganic materials were separated by hot filtration, the inorganic materials left on a filter were washed with hot MeCN

(50 ml), and the resulting filtrate was evaporated to dryness *in vacuo*. The resulting oily residue was dissolved in hot AcOEt (50 ml), and the resulting clear solution was left to stand at rt for several days (1-2 days). The formed wax-like material was filtered off, it was washed on a filter with AcOEt (20 ml), at first it was dried in the air and later in a vacuum desiccator over P_2O_5; this sequence of procedures afforded pure (**D8**) in 1.77 g (20%) yield as a white nonhygroscopic wax-like material, mp was not determined. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.02 (4H, s, CH=CH × 2), 3.48 (4H, br s, CH_2 × 2), 3.34 (8H, br s, CH_2 × 4), 3.16 (4H, br s, CH_2 × 2), 1.69 (16H, br s, CH_2 × 8), 1.52 (8H, br s, CH_2 × 4), 1.37 (6H, br s, CH_2 × 3), 0.94-1.06 (44H, br m, CH_2 × 22), 0.56 (6H, t, $^3J_{HH}$ 6.3 Hz, CH_3 × 2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 129.1 (CH × 2), 128.7 (CH × 2), 58.5 (CH_2 × 2), 58.1 (CH_2 × 4), 56.8 (CH_2 × 2), 31.7 (CH_2 × 2), 31.0 (CH_2 × 2), 28.8 (CH_2 × 2), 28.7 (CH_2 × 2), 28.6 (CH_2 × 2), 28.5 (CH_2 × 2), 28.4 (CH_2 × 2), 28.3 (CH_2 × 2), 26.3 (CH_2 × 2), 25.7 (CH_2 × 2), 22.3 (CH_2), 21.8 (CH_2 × 2), 21.0 (CH_2 × 4), 20.4 (CH_2 × 4), 20.0 (CH_2 × 4), 19.1 (CH_2 × 2), 13.3 (CH_3 × 2). Anal. calcd calculated for $C_{51}H_{100}N_2Br_2$ (901.16): C, 67.97; H, 11.18; N, 3.11; Br, 17.73. Found: C, 68.02; H, 11.23; N, 3.02; Br, 17.53.

References

1. Neat proton HMDS chemical shift can be found under https://sdbs.db.aist.go.jp/HNmrSpectralView.aspx?imgdir=hsp&fname=HSP43781&sdbsno=5566 (accessed 20 August 2025); Spectral Database for Organic Compounds, SDBS, by National Institute of Advanced Industrial Science and Technology (AIST), Japan.
2. Neat carbon HMDS chemical shift can be found under https://sdbs.db.aist.go.jp/CNmrSpectralView.aspx?imgdir=cds&fname=CDS09868&sdbsno=5566, (accessed 20 August 2025); Spectral Database for Organic Compounds, SDBS, by National Institute of Advanced Industrial Science and Technology (AIST), Japan.
3. Pretsch, E.; Bühlmann, P.; Badertscher, M. In *Structure Determination of Organic Compounds, Tables of Spectral Data*, 4th Edn.; Springer-Verlag: Berlin Heidelberg, 2009, pp 155, 241. https://doi.org/10.1007/978-3-540-93810-1
4. Frauenkron, M.; Melder, J.-P.; Ruider, G.; Rossbacher, R.; Höke, H. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH GmbH & Co. KGaA: Weinheim, 2012, p 406. https://doi.org/10.1002/14356007.a10_001

NMR Spectra

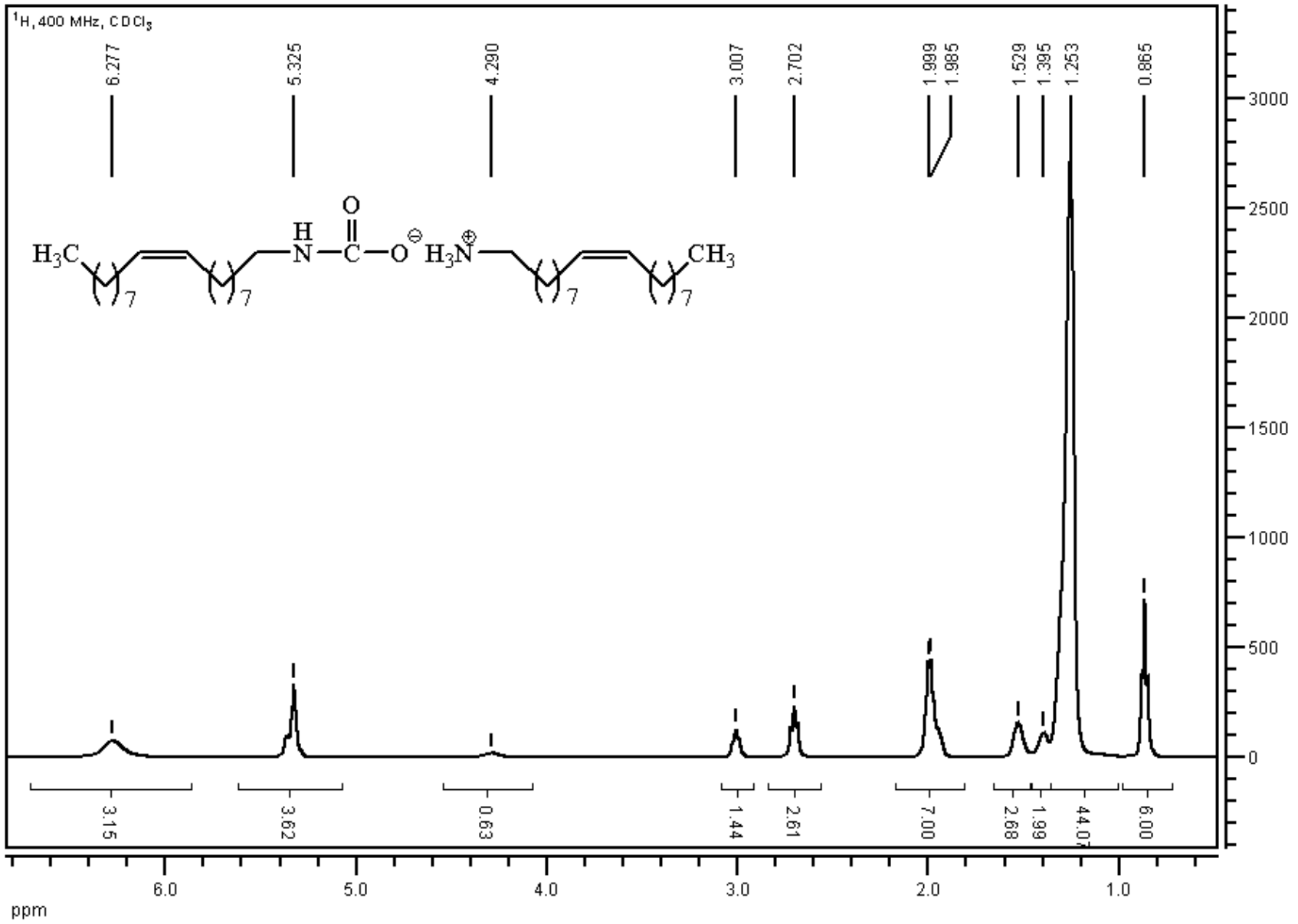

Figure S1. The ^{1}H spectrum of (Z)-octadec-9-en-1-aminium (Z)-octadec-9-enylcarbamate in $CDCl_3$ solution recorded at 400 MHz.

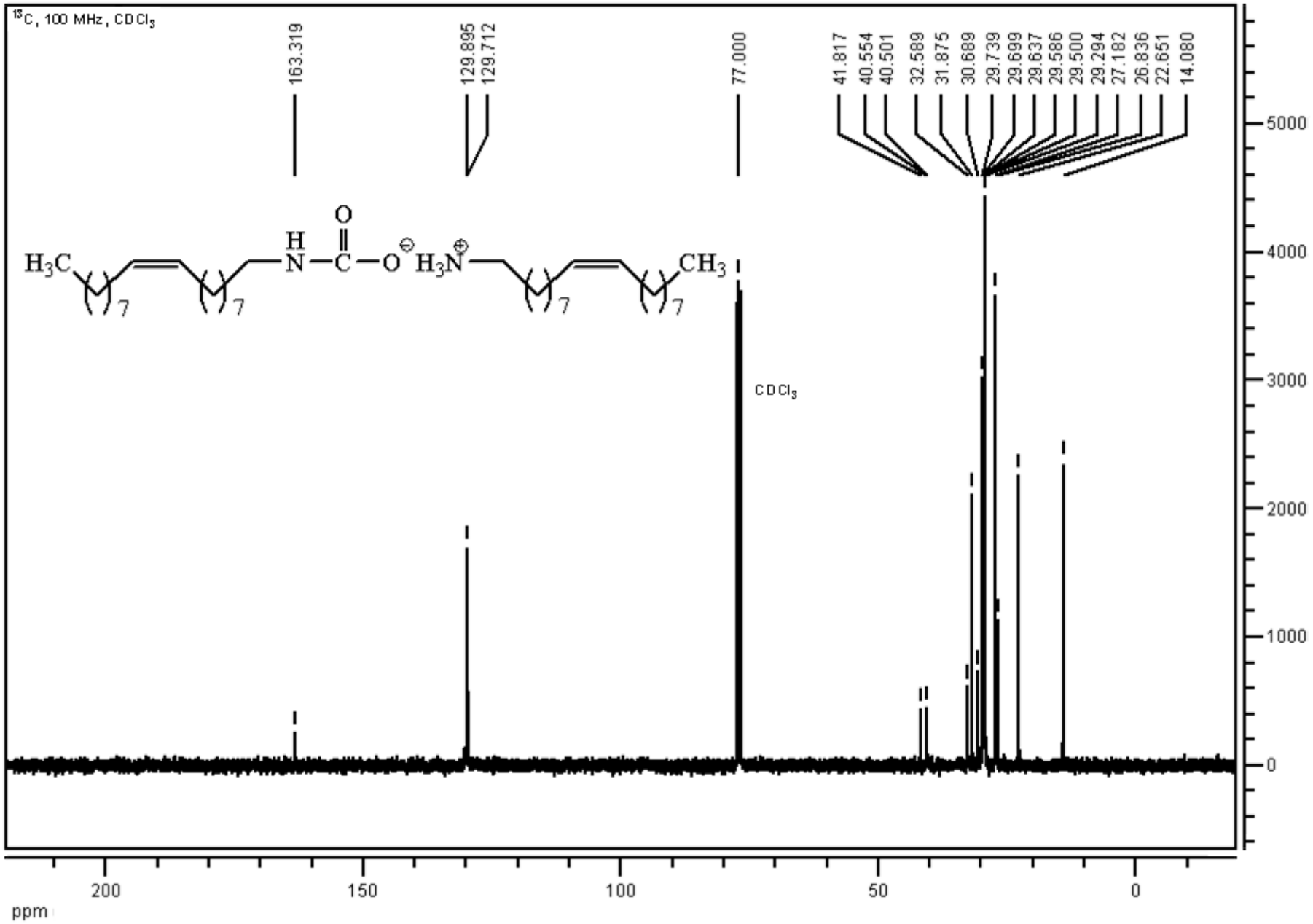

Figure S2. The ^{13}C spectrum of (Z)-octadec-9-en-1-aminium (Z)-octadec-9-enylcarbamate in $CDCl_3$ solution recorded at 100 MHz.

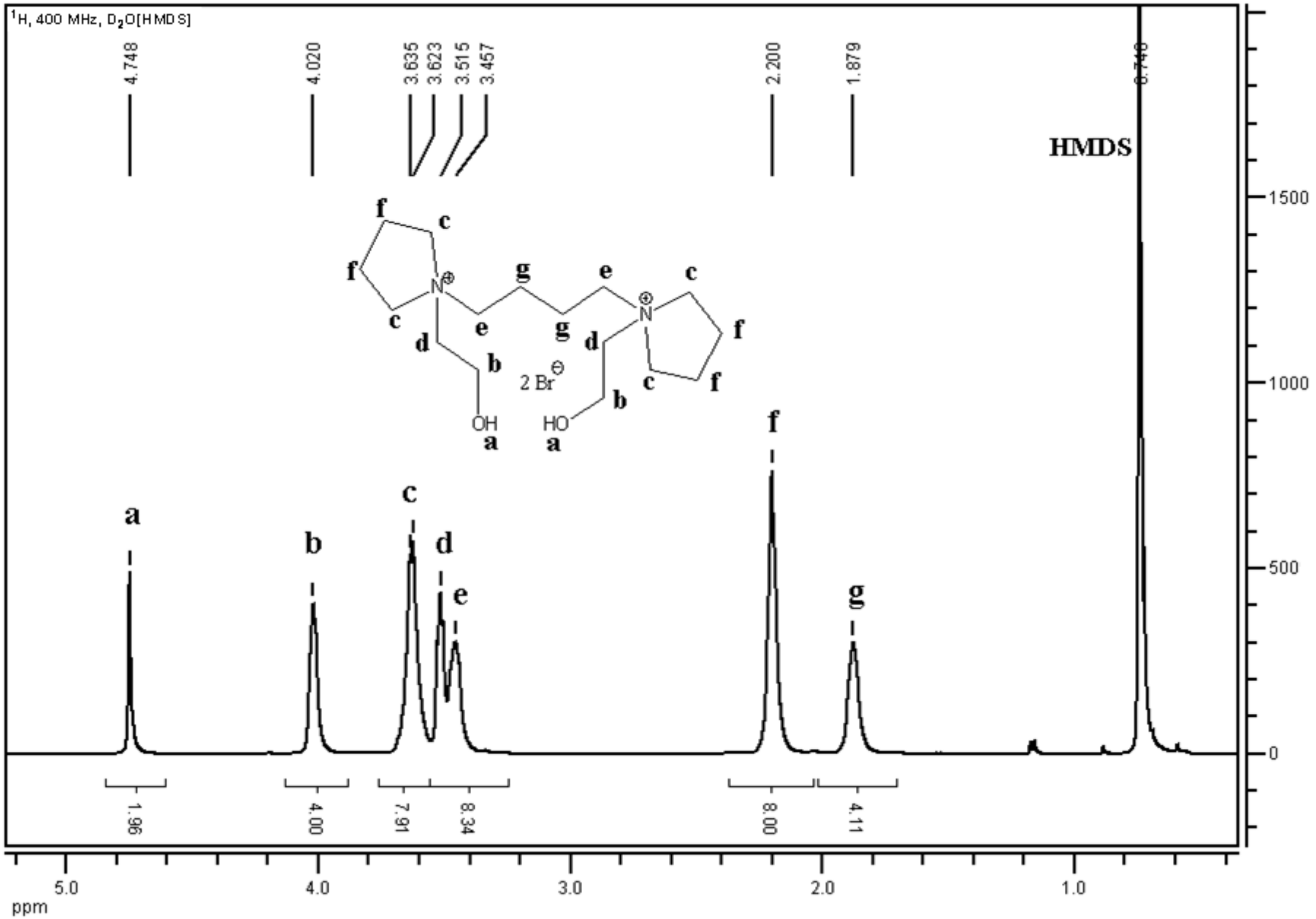

Figure S3. The ^{1}H spectrum of 1,1′-(butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (**C1**) in D_2O [HMDS] solution recorded at 400 MHz.

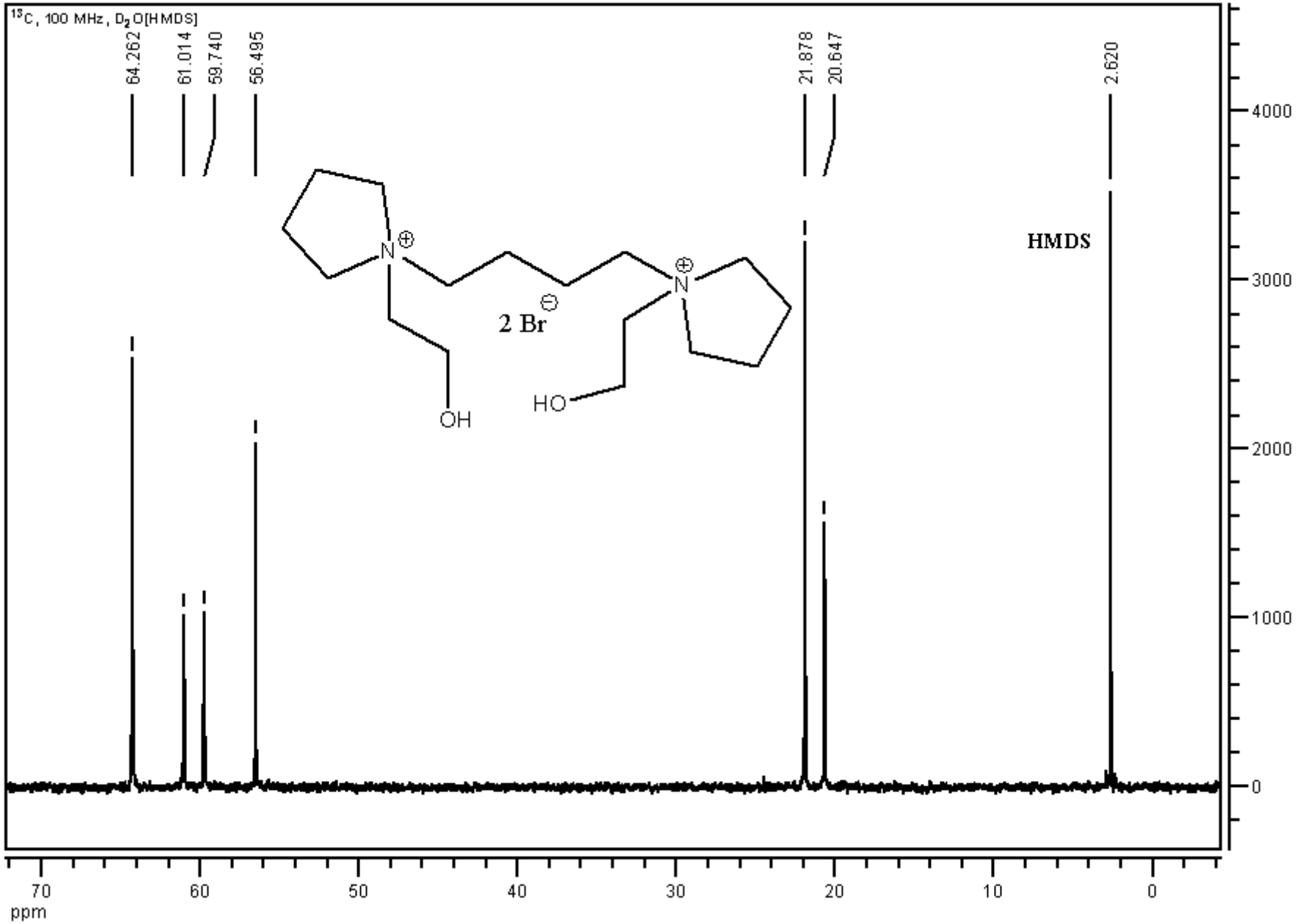

Figure S4. The ^{13}C spectrum of 1,1′-(butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (**C1**) in D_2O [HMDS] solution recorded at 100 MHz.

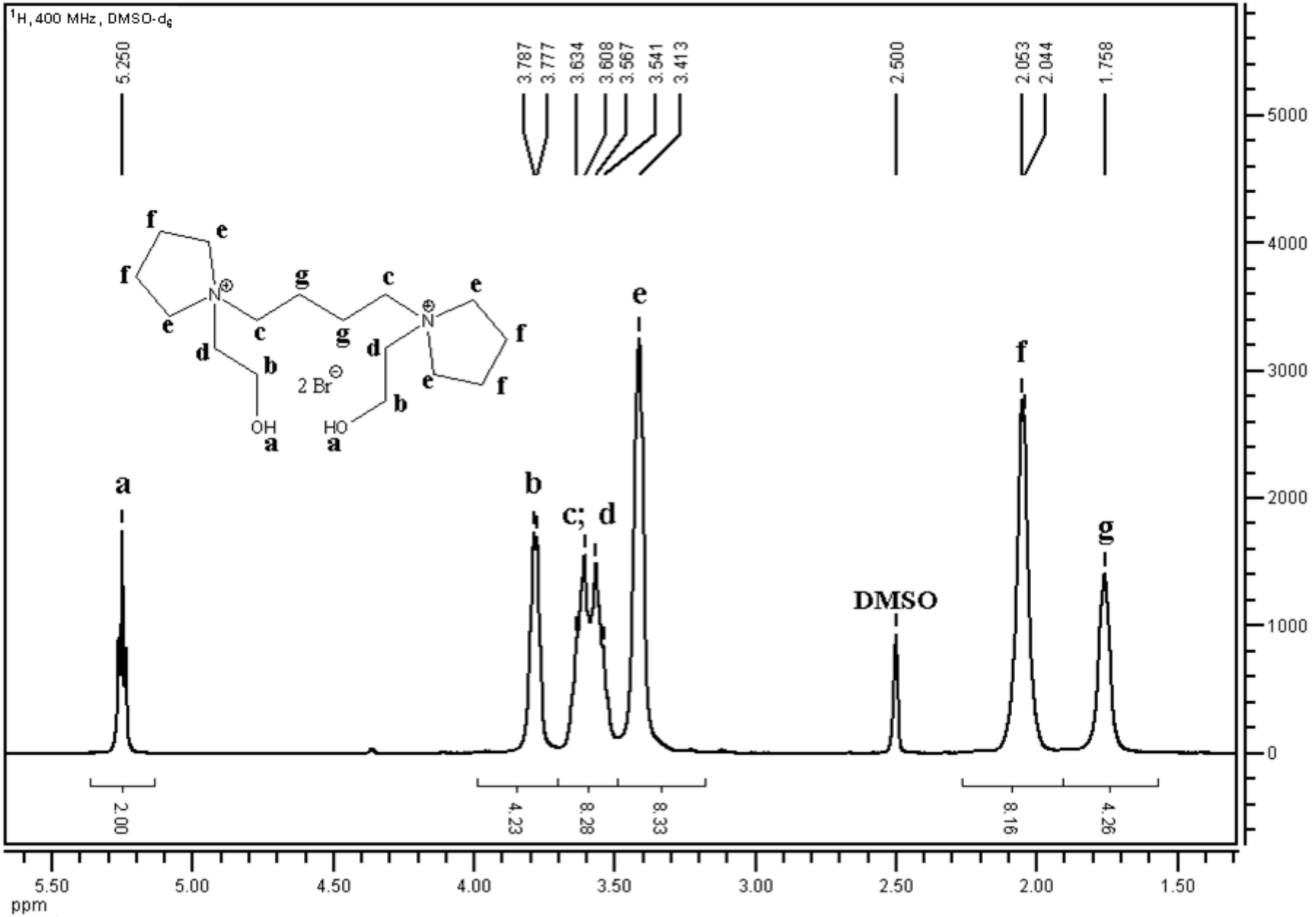

Figure S5. The ^{1}H spectrum of 1,1′-(butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (**C1**) in DMSO-d_6 solution recorded at 400 MHz.

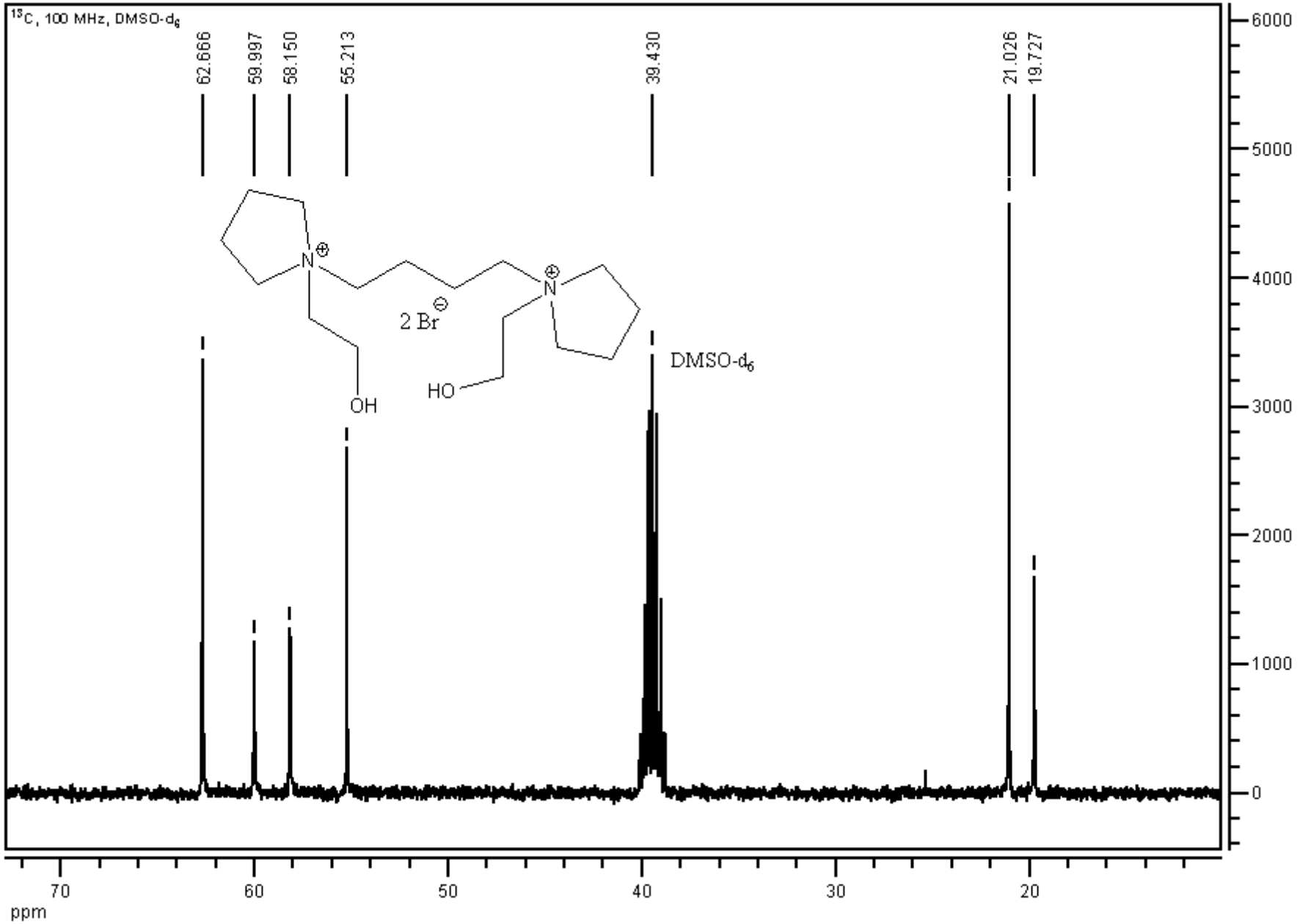

Figure S6. The ^{13}C spectrum of 1,1′-(butane-1,4-diyl)bis(1-(2-hydroxyethyl)pyrrolidinium) dibromide (**C1**) in DMSO-d$_6$ solution recorded at 100 MHz.

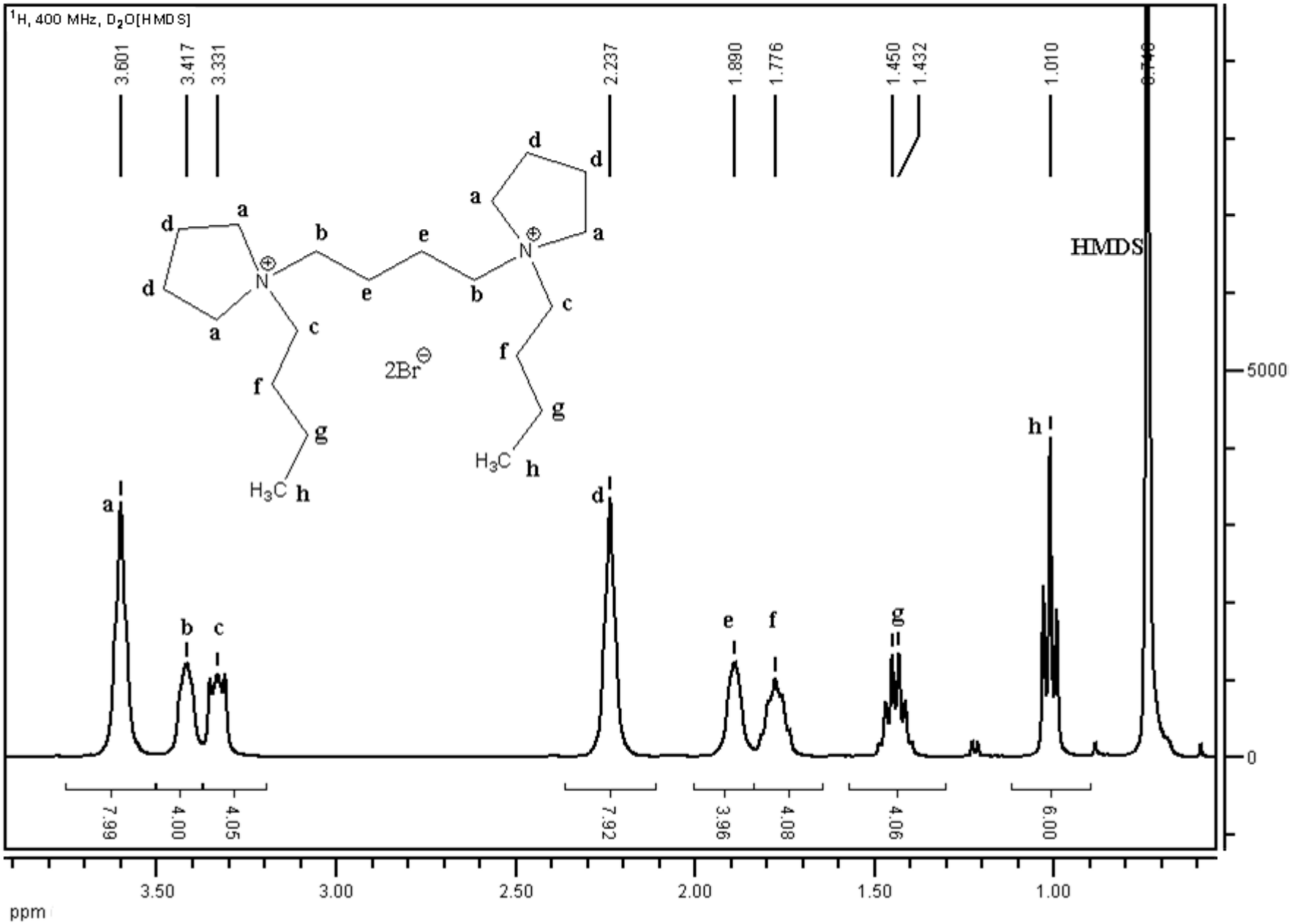

Figure S7. The ^{1}H spectrum of 1,1′-(butane-1,4-diyl)bis(1-butylpyrrolidinium) dibromide (**C2**) in D_2O [HMDS] solution recorded at 400 MHz.

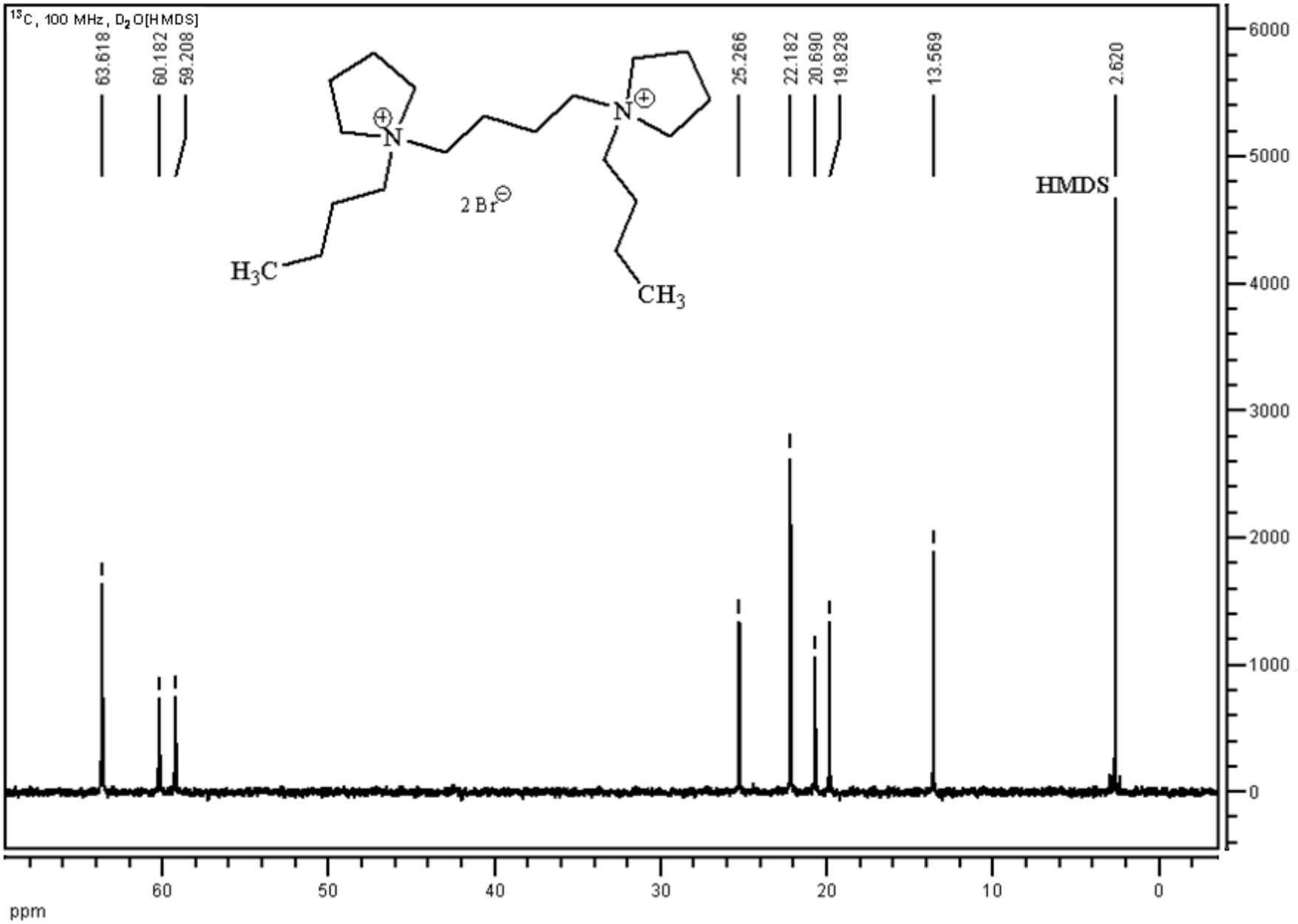

Figure S8. The ^{13}C spectrum of 1,1′-(butane-1,4-diyl)bis(1-butylpyrrolidinium) dibromide (**C2**) in D_2O [HMDS] solution recorded at 100 MHz.

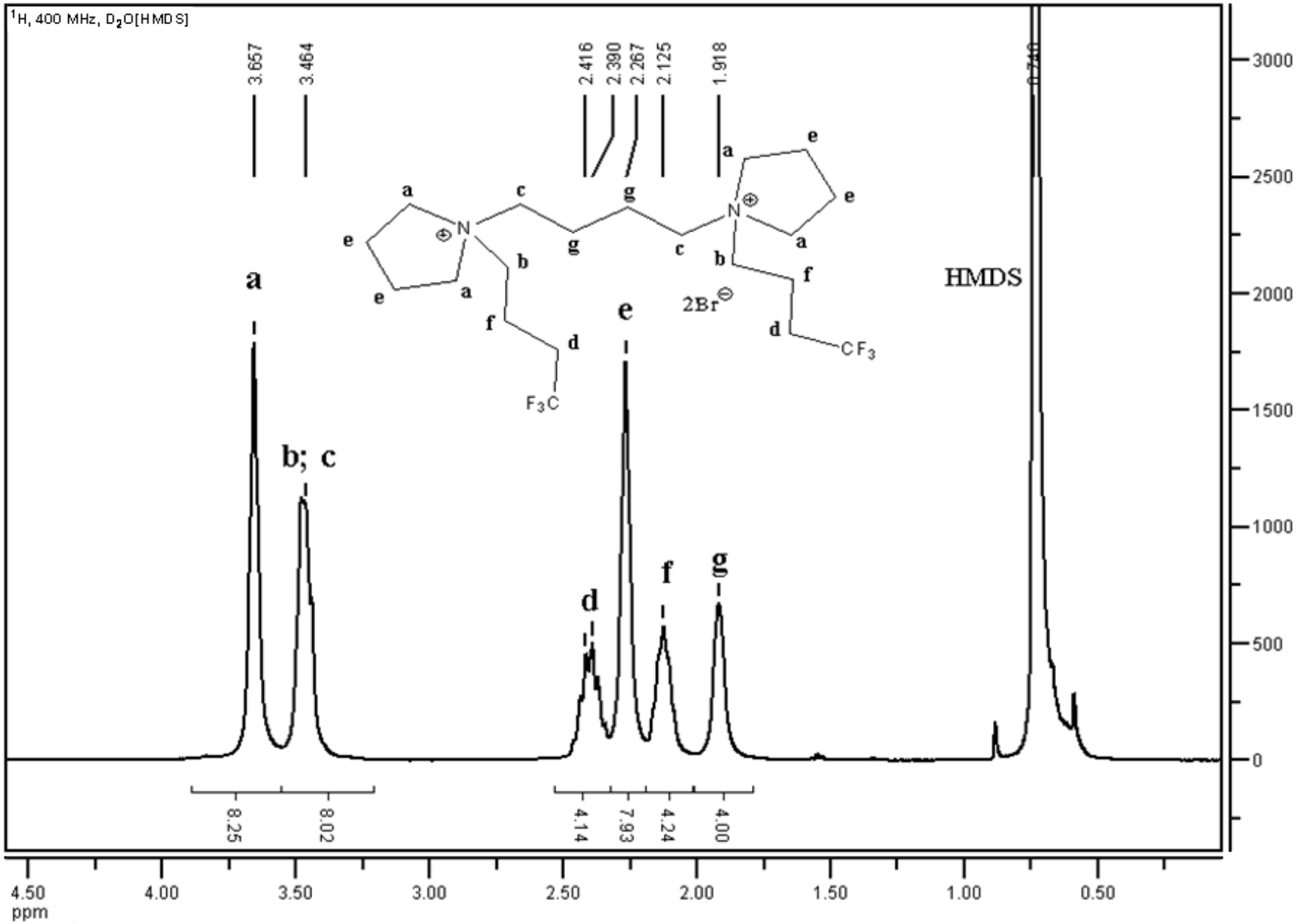

Figure S9. The ^{1}H spectrum 1,1′-(butane-1,4-diyl)bis(1-(4,4,4-trifluorobutyl)-pyrrolidinium) dibromide (**C3**) in D_2O [HMDS] solution recorded at 400 MHz.

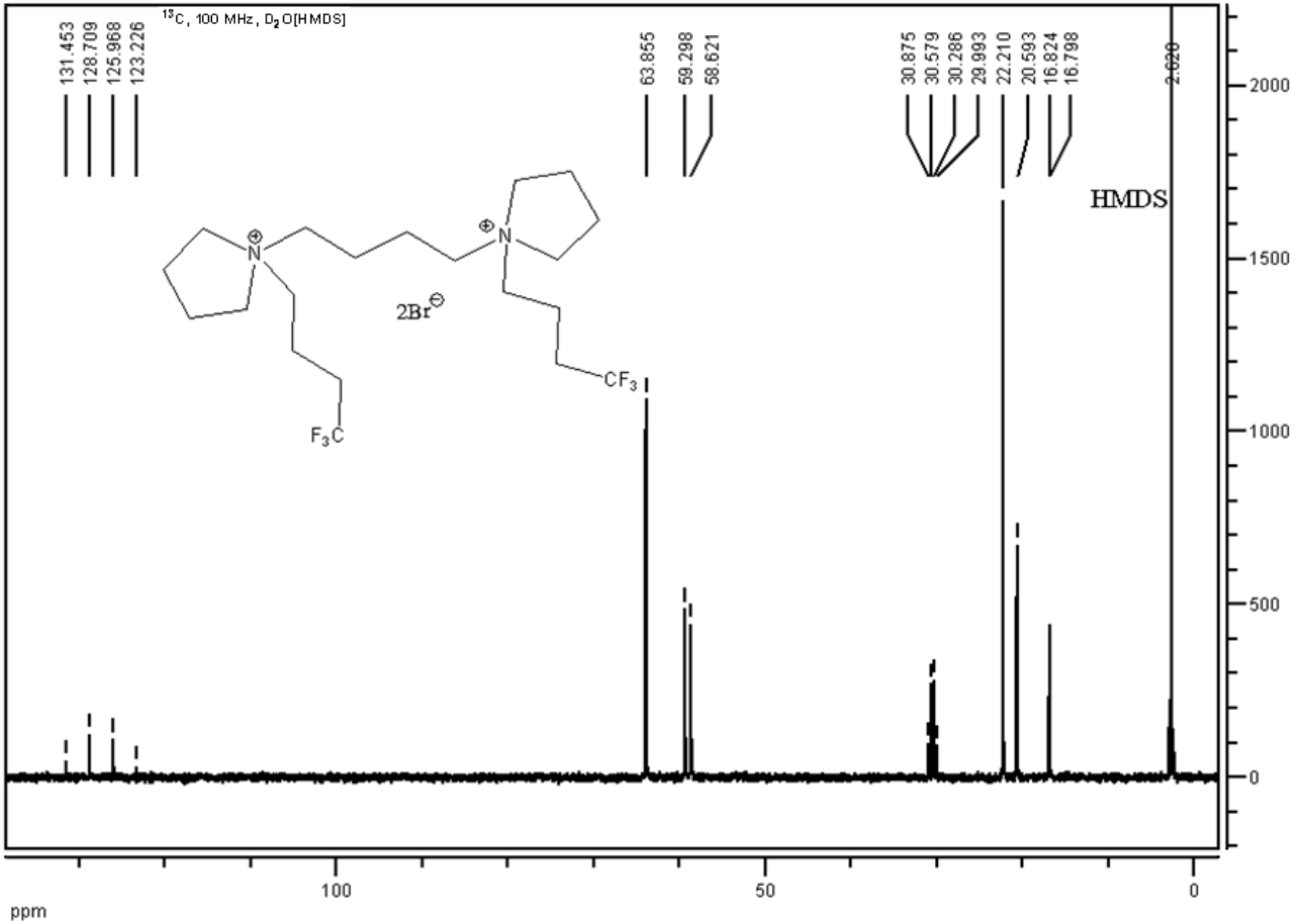

Figure S10. The ^{13}C spectrum 1,1′-(butane-1,4-diyl)bis(1-(4,4,4-trifluorobutyl)-pyrrolidinium) dibromide (**C3**) in D_2O [HMDS] solution recorded at 100 MHz.

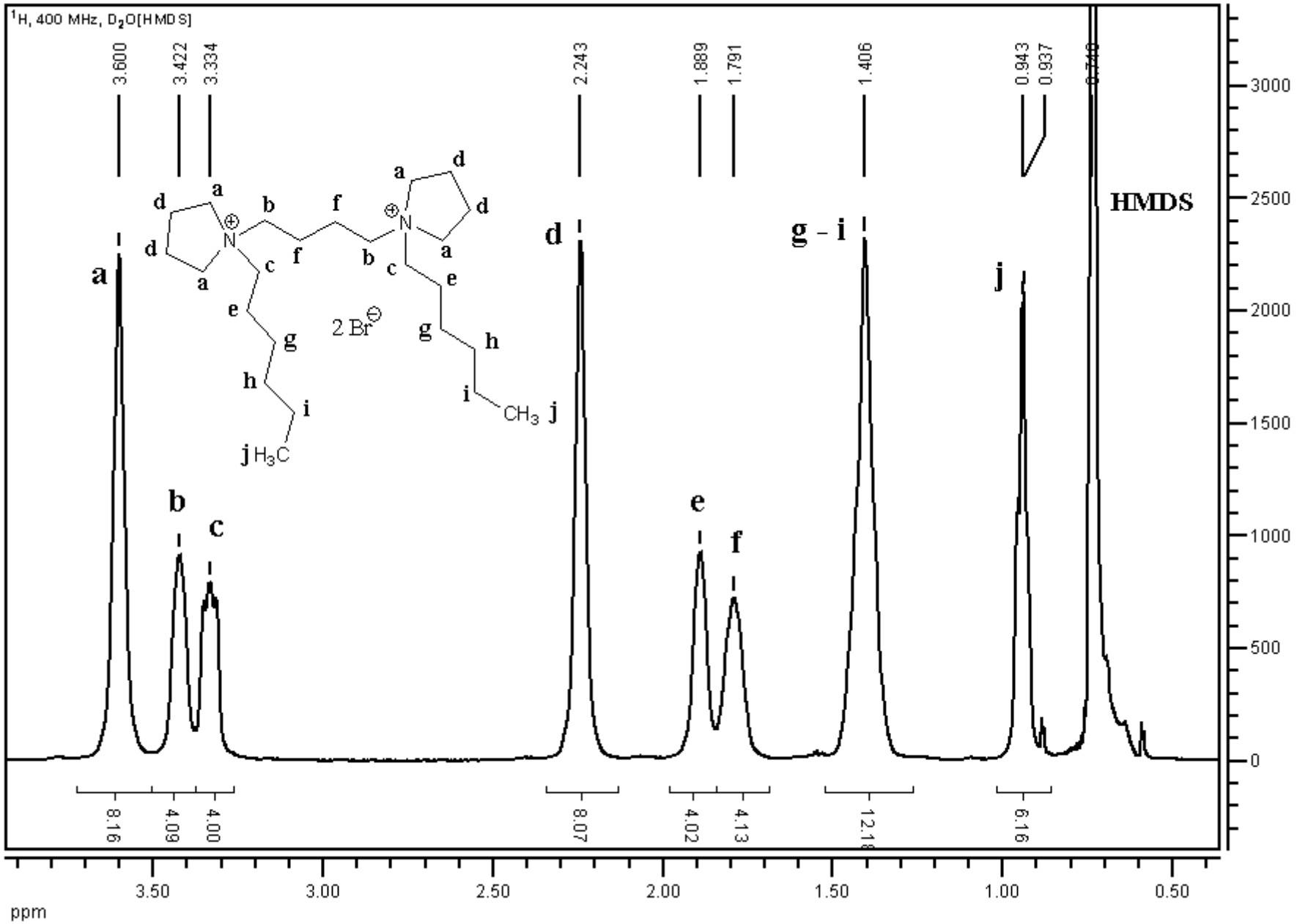

Figure S11. The ^{1}H spectrum 1,1′-(butane-1,4-diyl)bis(1-hexylpyrrolidinium) dibromide (**C4**) in D_2O [HMDS] solution recorded at 400 MHz.

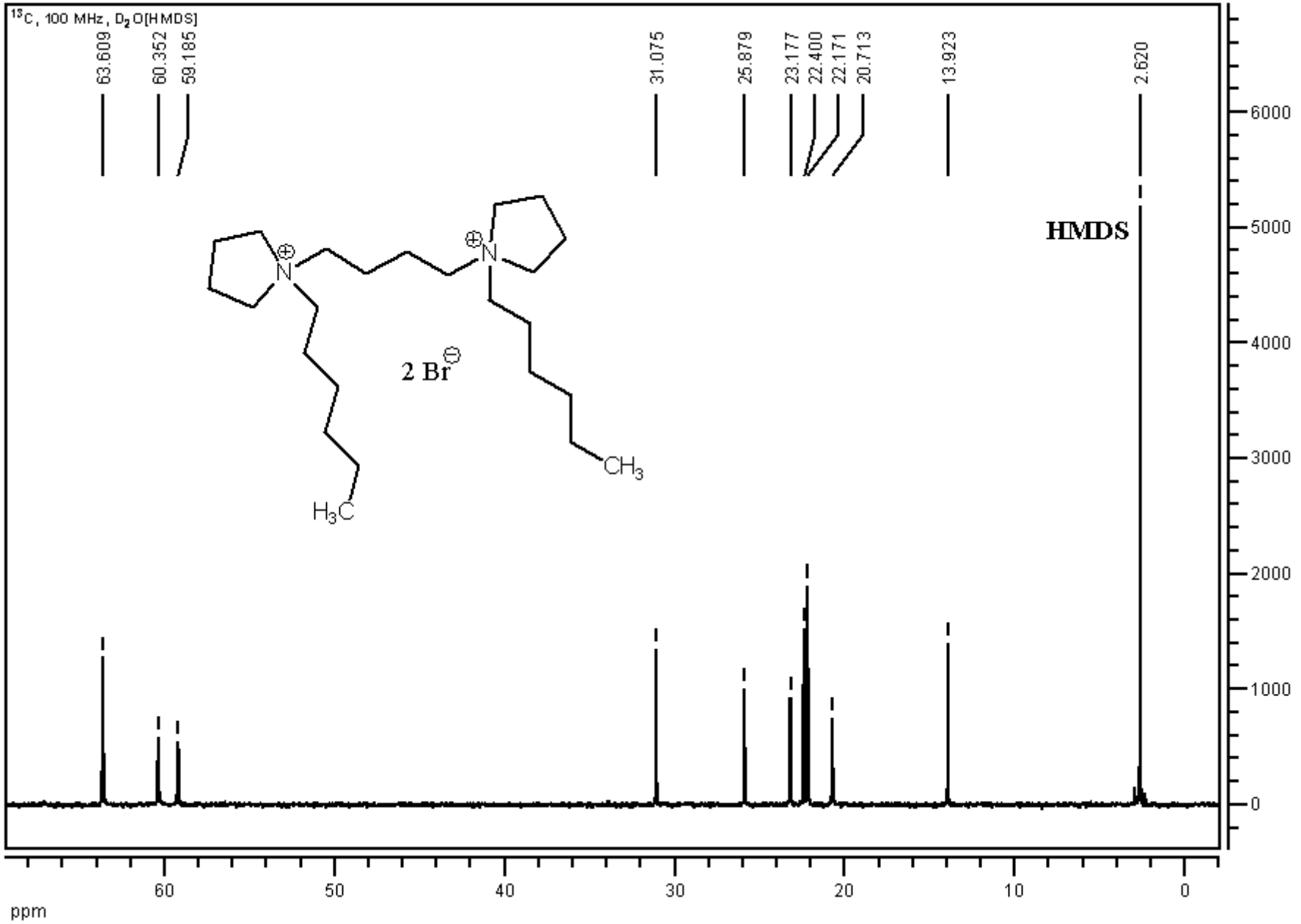

Figure S12. The ^{13}C spectrum 1,1′-(butane-1,4-diyl)bis(1-hexylpyrrolidinium) dibromide (**C4**) in D_2O [HMDS] solution recorded at 100 MHz.

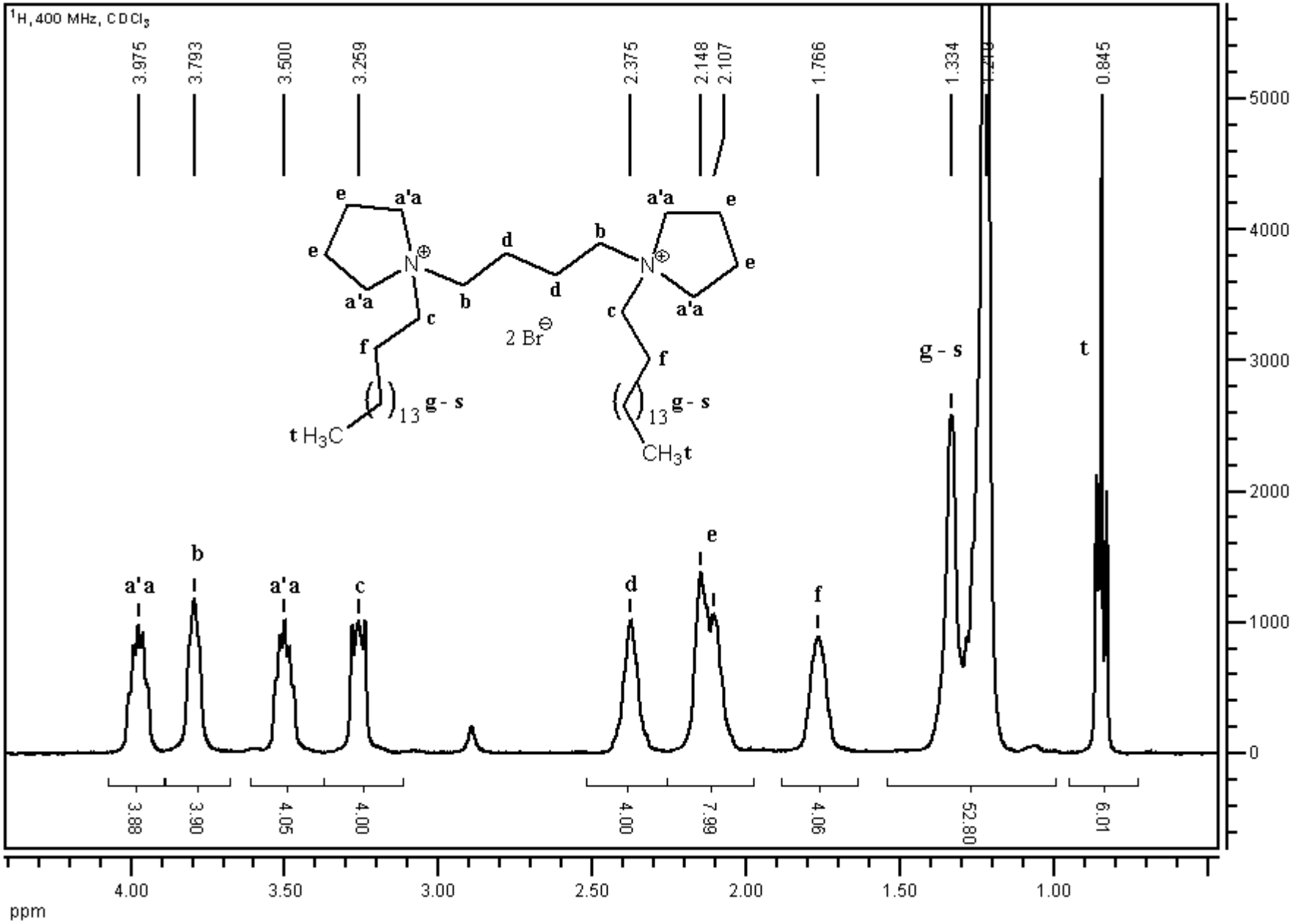

Figure S13. The ^{1}H spectrum of 1,1′-(butane-1,4-diyl)bis(1-hexadecylpyrrolidinium) dibromide (**C6**) in $CDCl_3$ solution recorded at 400 MHz.

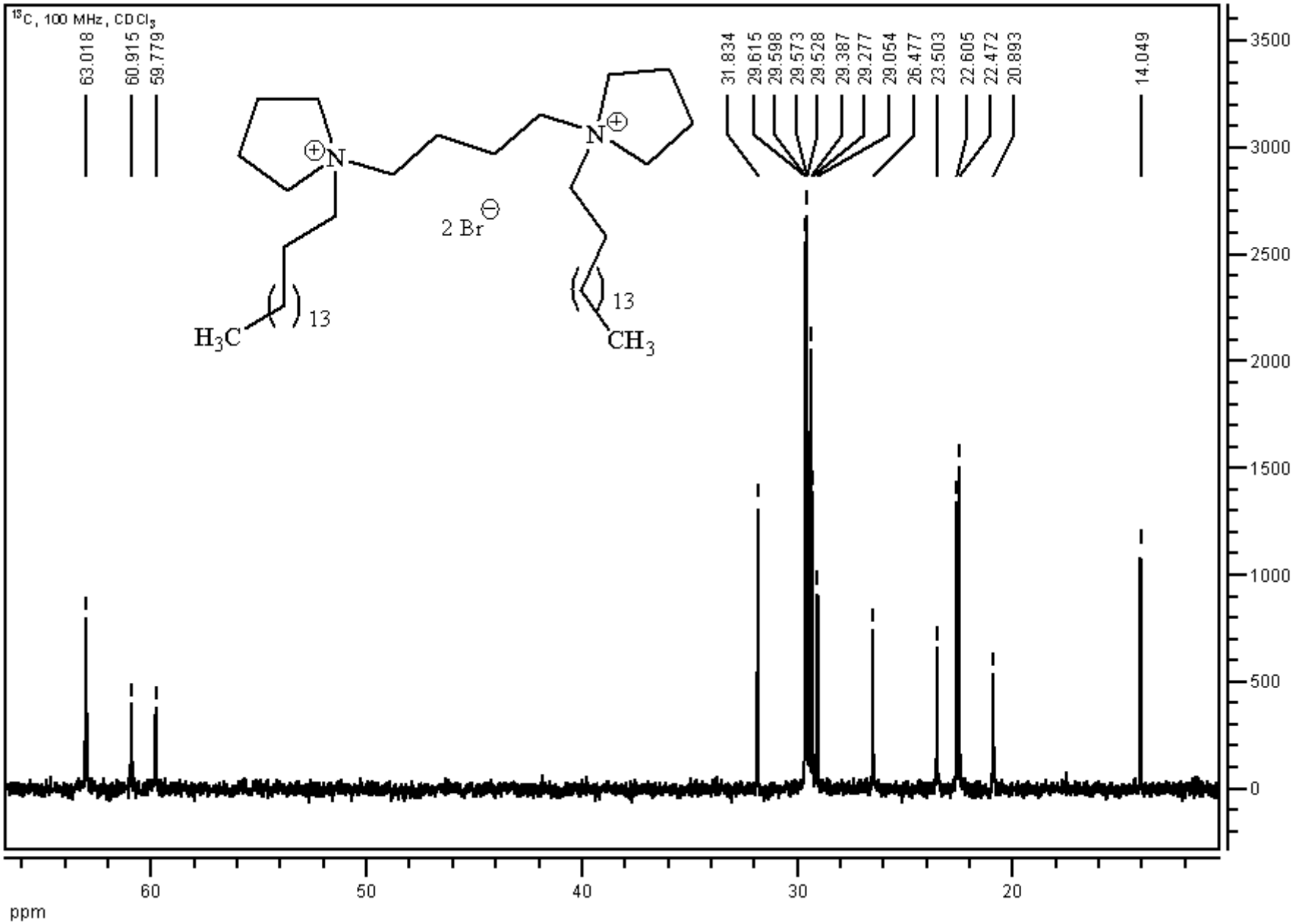

Figure S14. The ^{13}C spectrum of 1,1′-(butane-1,4-diyl)bis(1-hexadecylpyrrolidinium) dibromide (**C6**) in $CDCl_3$ solution recorded at 100 MHz.

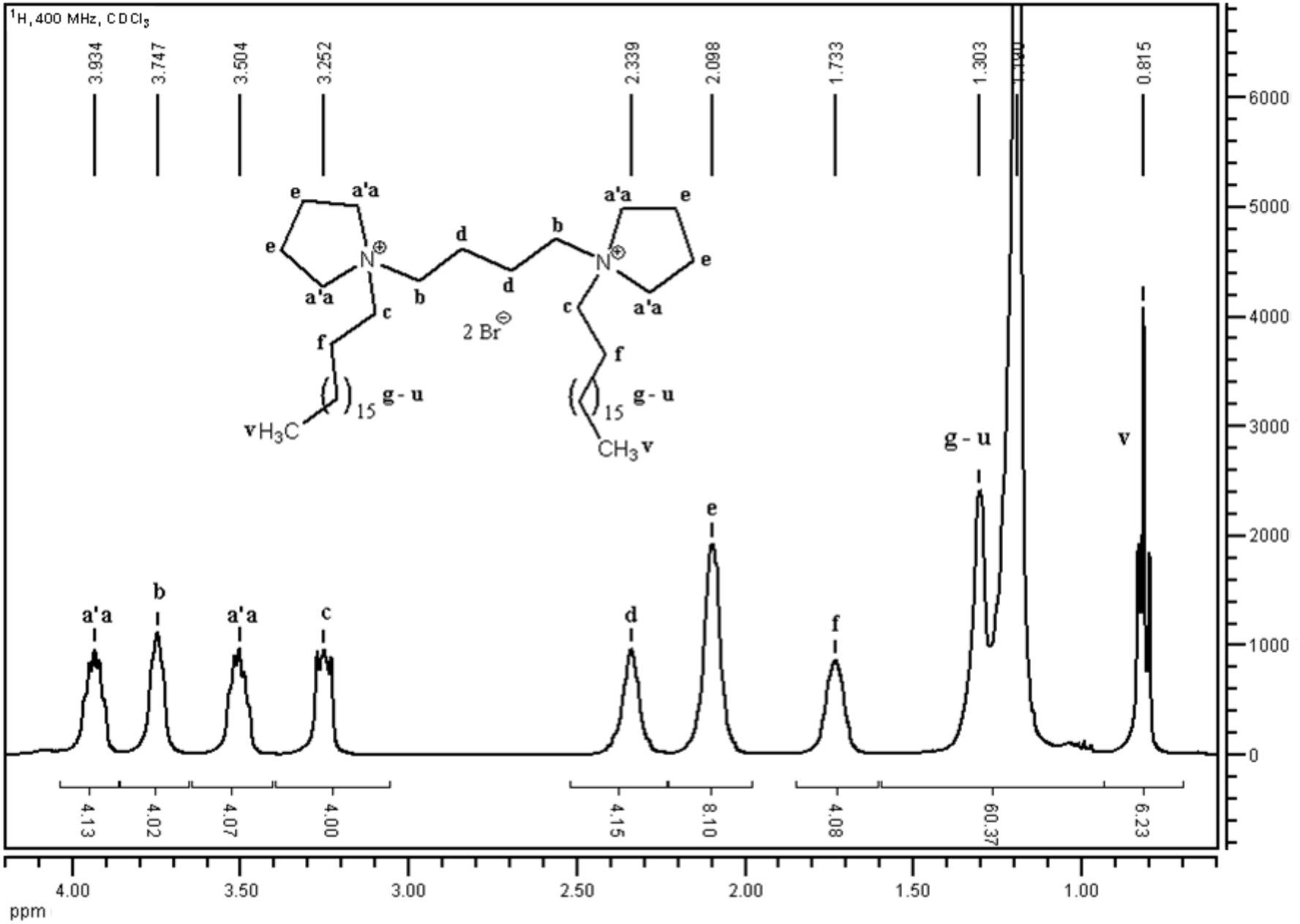

Figure S15. The ^{1}H spectrum of 1,1′-(butane-1,4-diyl)bis(1-octadecylpyrrolidinium) dibromide (**C7**) in $CDCl_3$ solution recorded at 400 MHz.

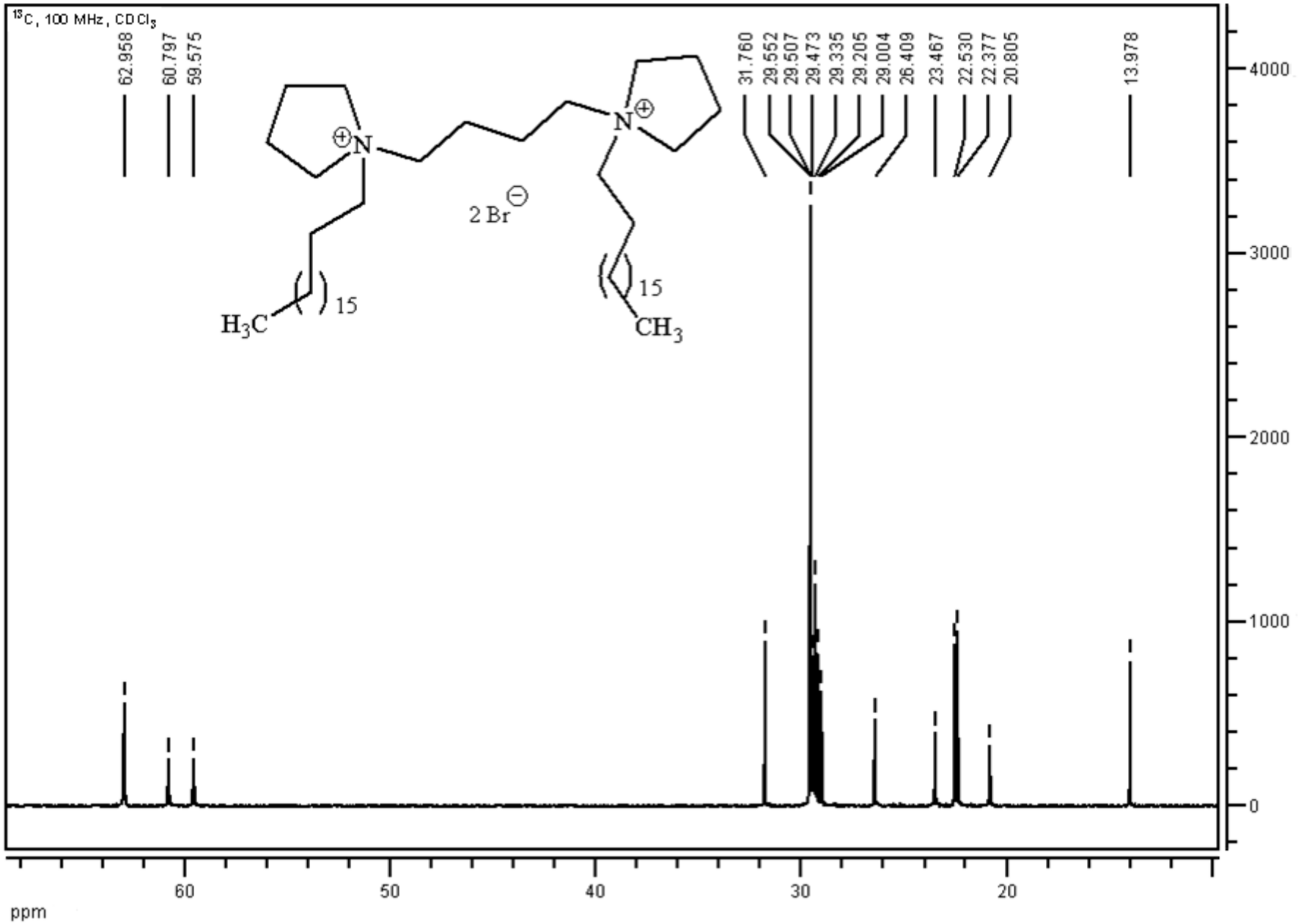

Figure S16. The ^{13}C spectrum of 1,1'-(butane-1,4-diyl)bis(1-octadecylpyrrolidinium) dibromide (**C7**) in $CDCl_3$ solution recorded at 100 MHz.

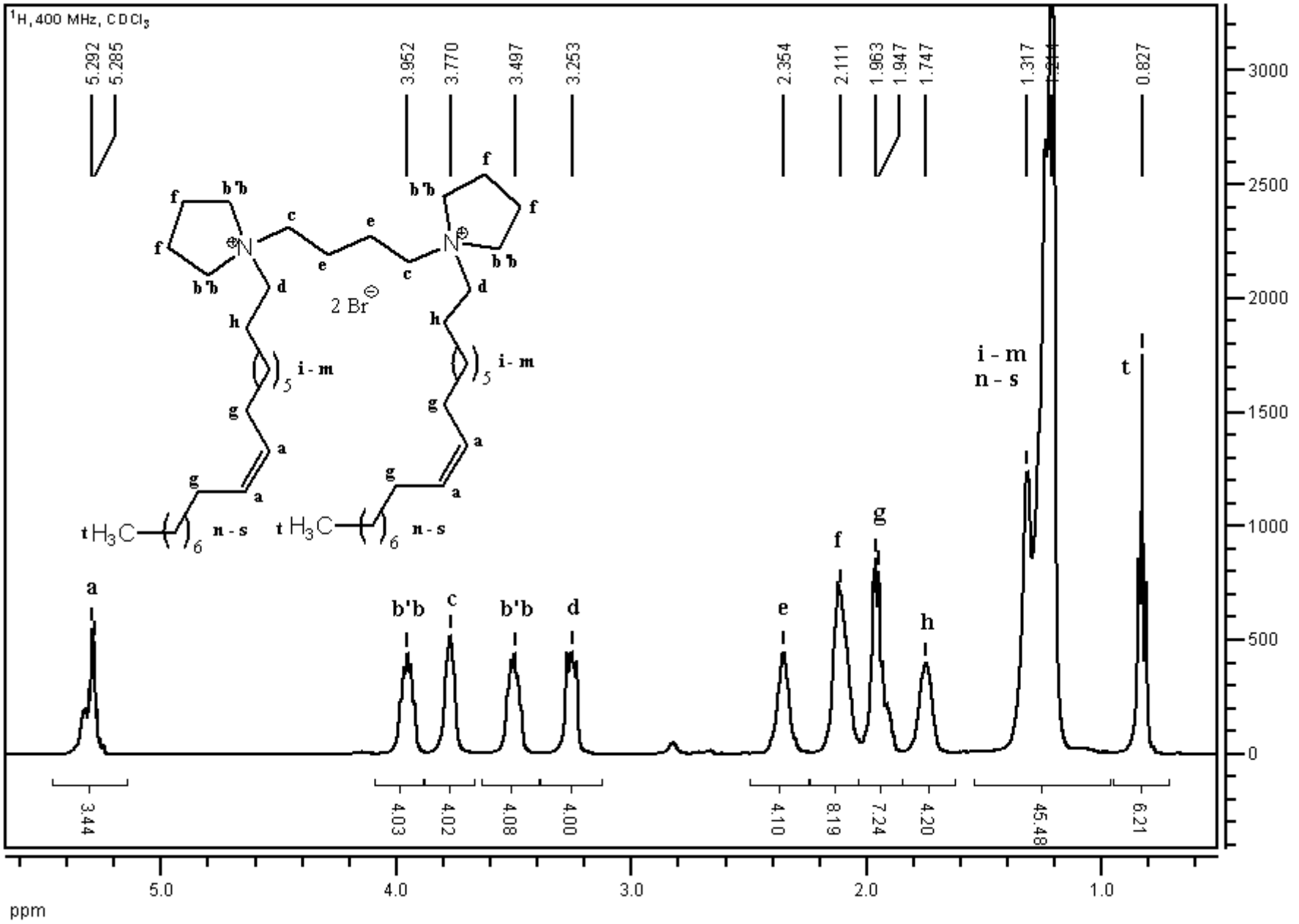

Figure S17. The ^{1}H spectrum of (Z)-1,1′-(butane-1,4-diyl)bis(1-((Z)-octadec-9-enyl)pyrrolidinium) dibromide (**C8**) in $CDCl_3$ solution recorded at 400 MHz.

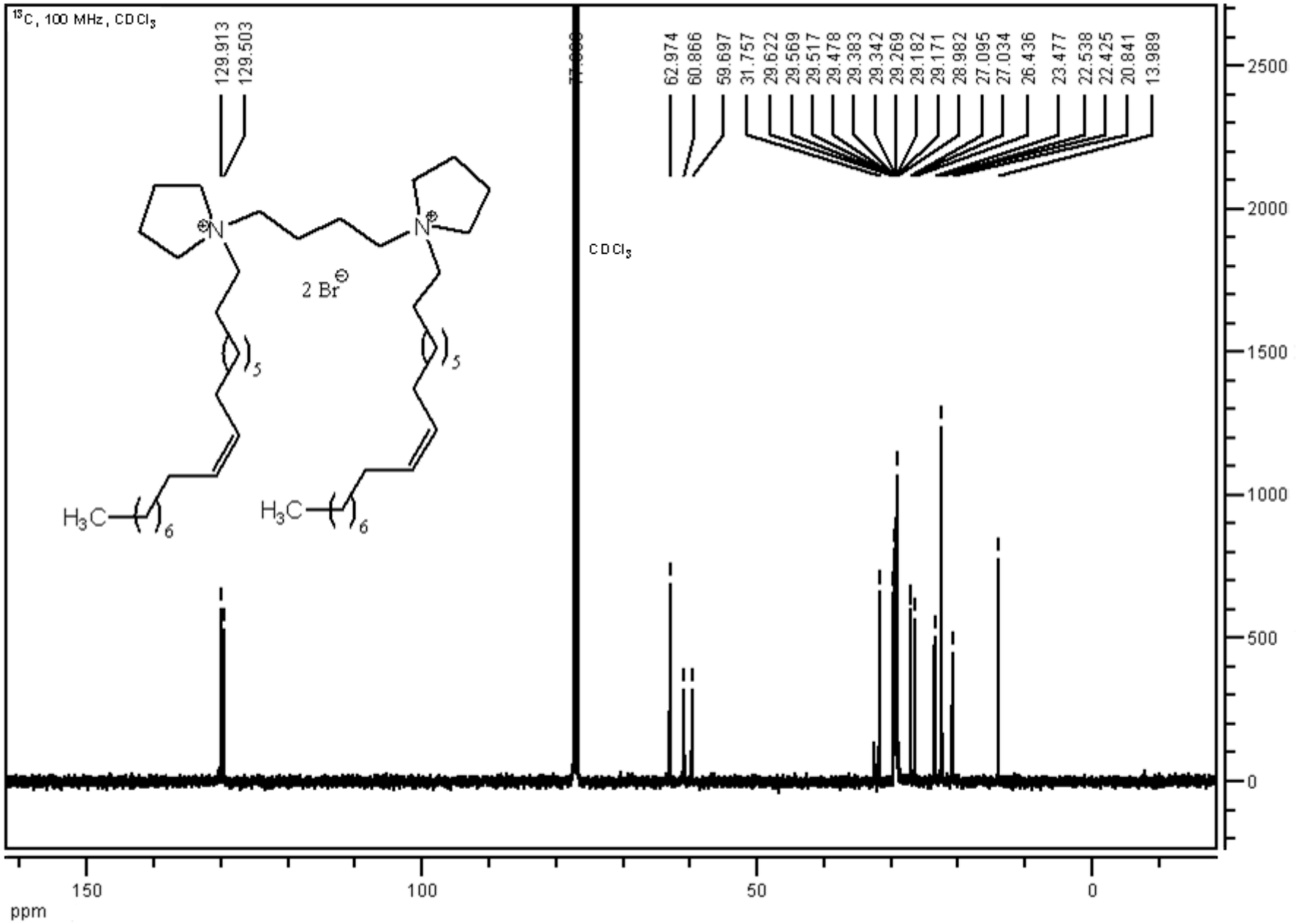

Figure S18. The ^{13}C spectrum of (Z)-1,1′-(butane-1,4-diyl)bis(1-((Z)-octadec-9-enyl)pyrrolidinium) dibromide (**C8**) in $CDCl_3$ solution recorded at 100 MHz.

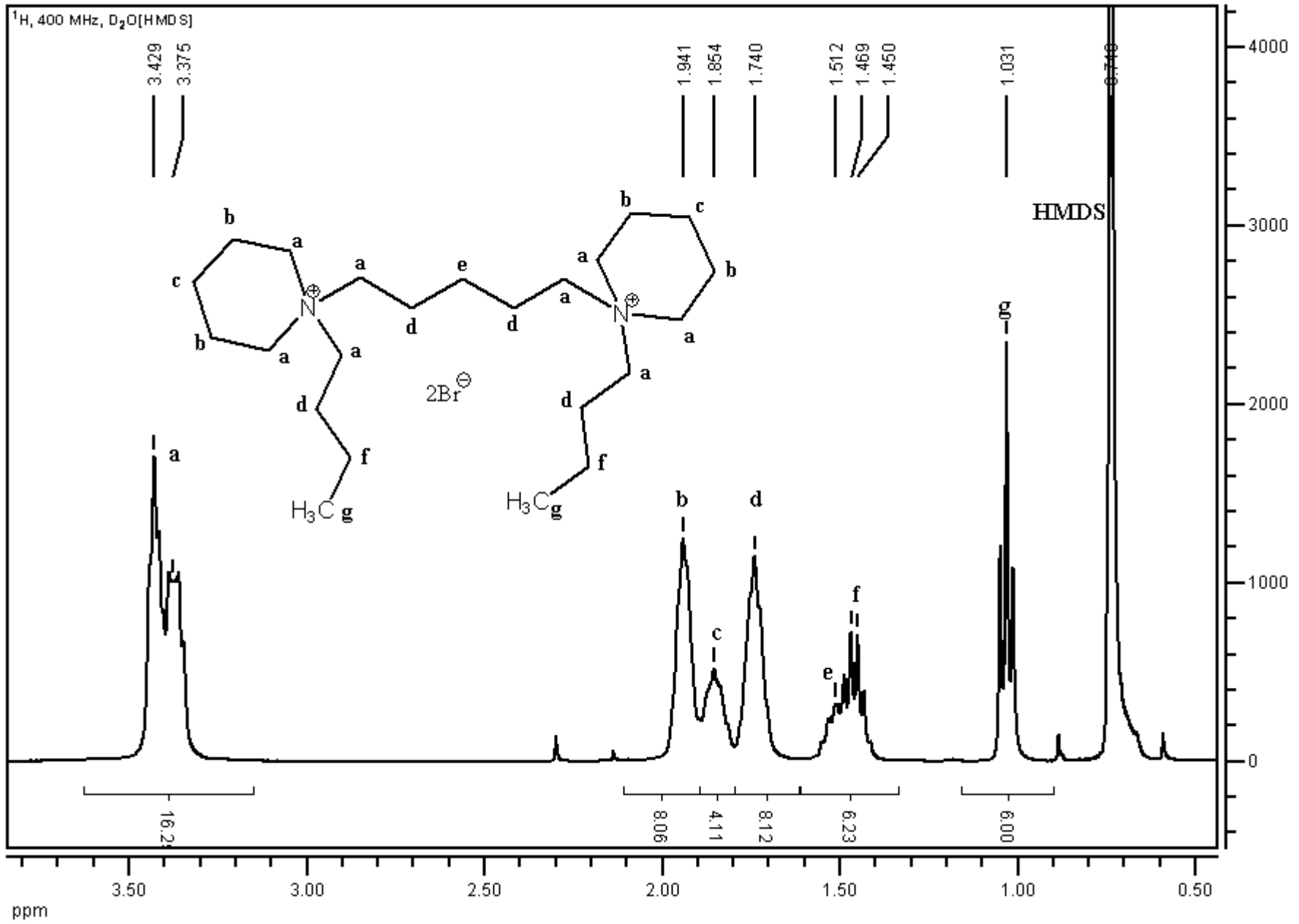

Figure S19. The ^{1}H spectrum of 1,1′-(pentane-1,5-diyl)bis(1-butylpiperidinium) dibromide (**D2**) in D_2O [HMDS] solution recorded at 400 MHz.

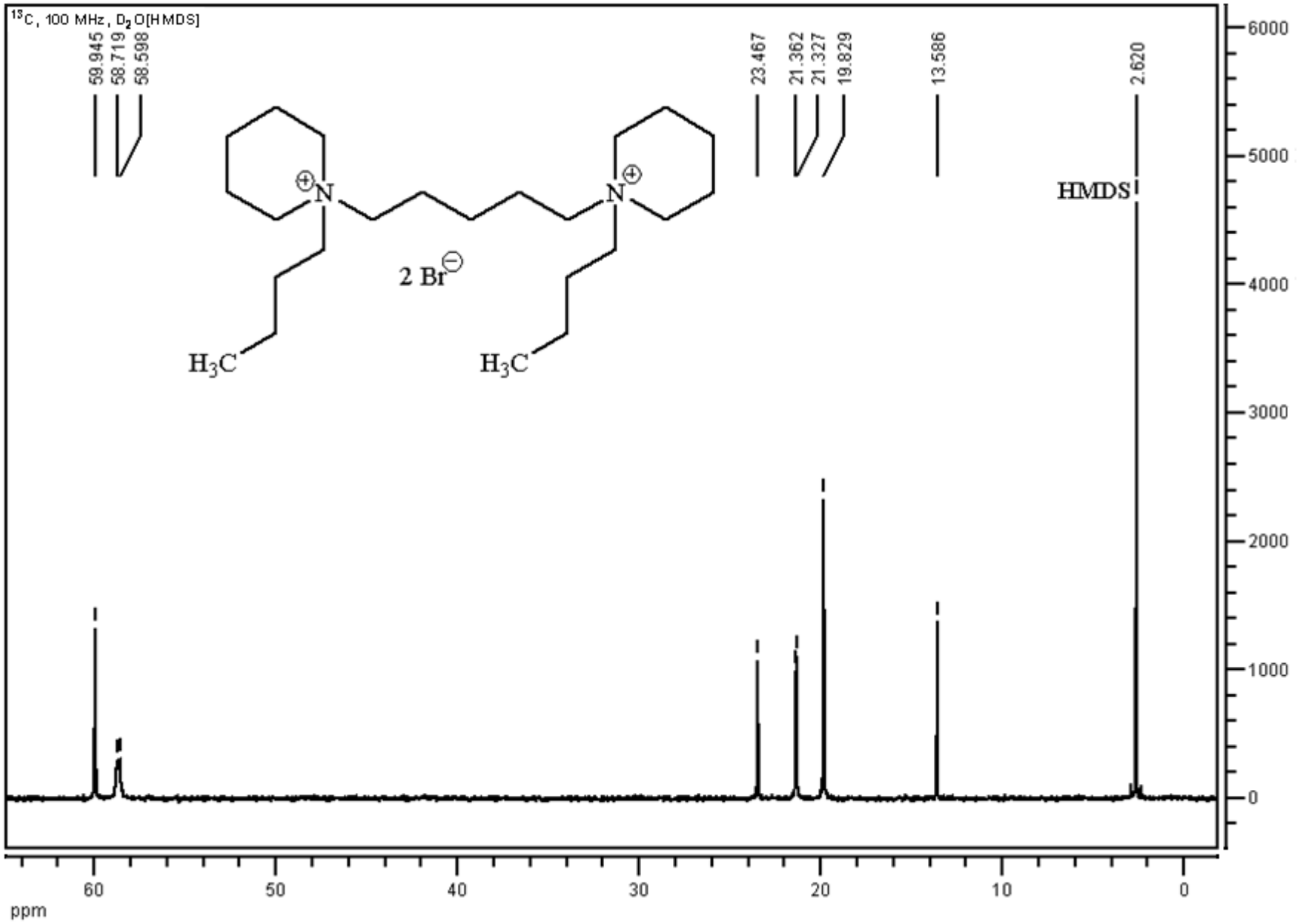

Figure S20. The ^{13}C spectrum of 1,1'-(pentane-1,5-diyl)bis(1-butylpiperidinium) dibromide (**D2**) in D_2O [HMDS] solution recorded at 100 MHz.

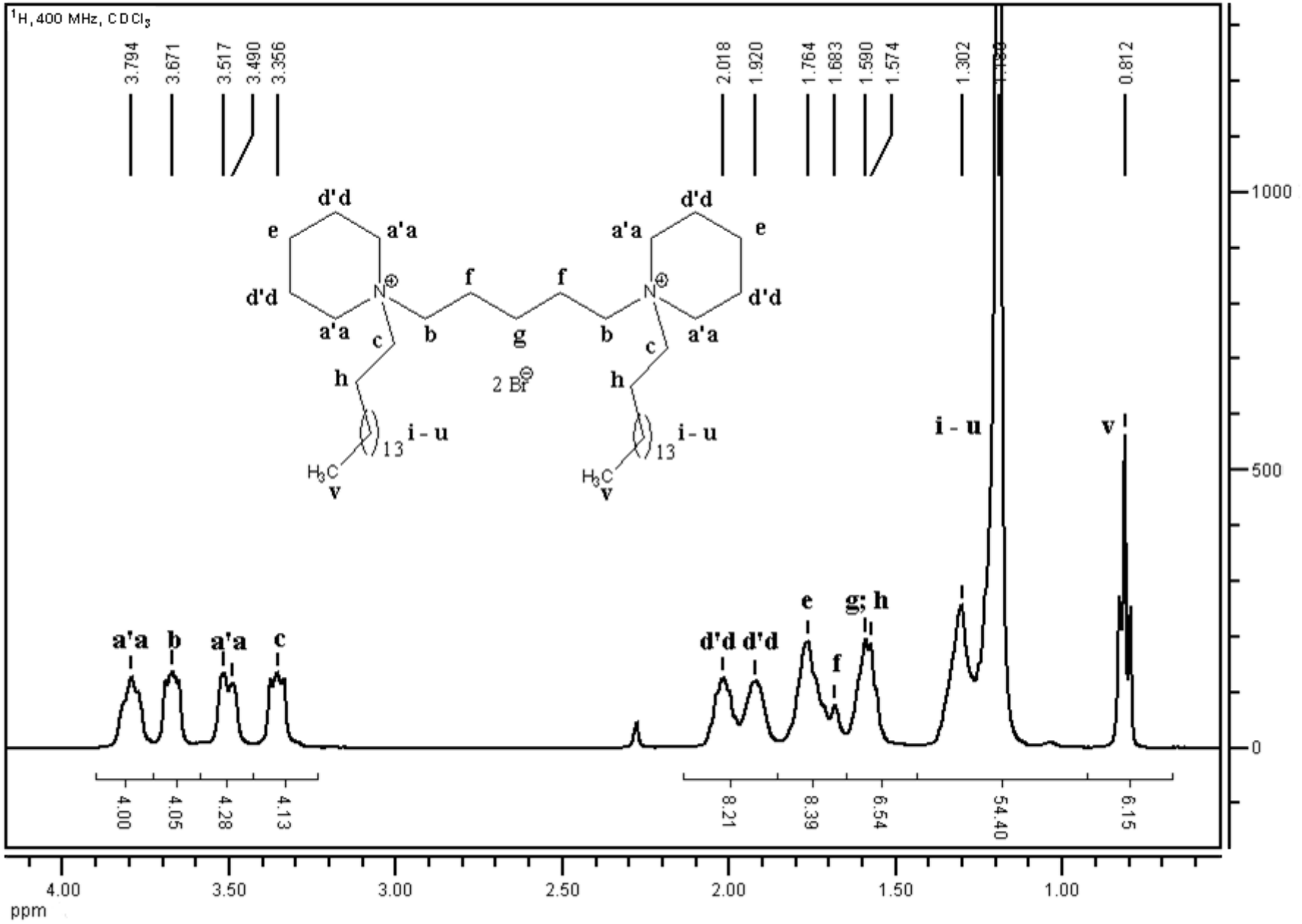

Figure S21. The ^{1}H spectrum of 1,1′-(pentane-1,5-diyl)bis(1-hexadecylpiperidinium) dibromide (**D6**) in $CDCl_3$ solution recorded at 400 MHz.

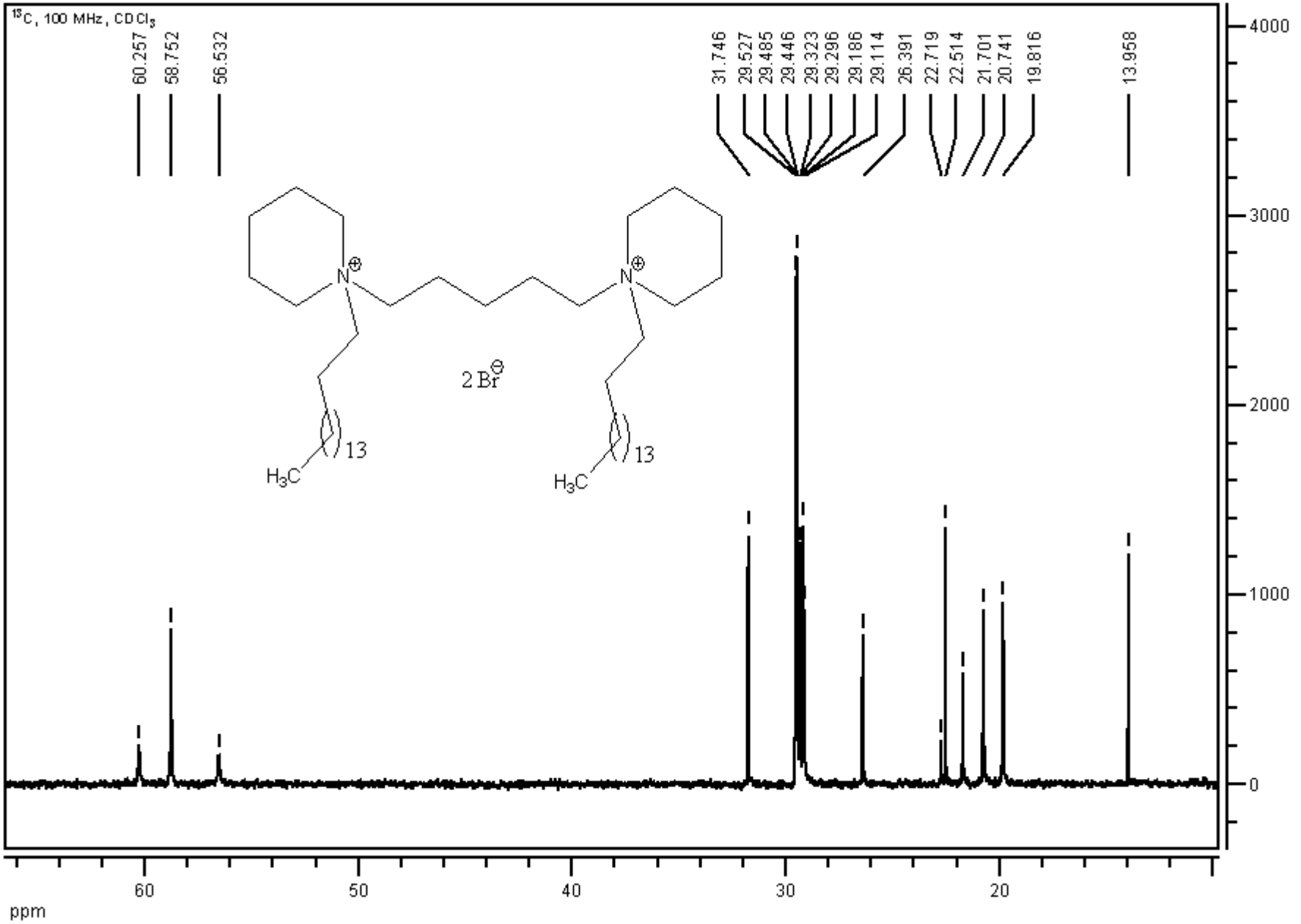

Figure S22. The ^{13}C spectrum of 1,1′-(pentane-1,5-diyl)bis(1-hexadecylpiperidinium) dibromide (**D6**) in $CDCl_3$ solution recorded at 100 MHz.

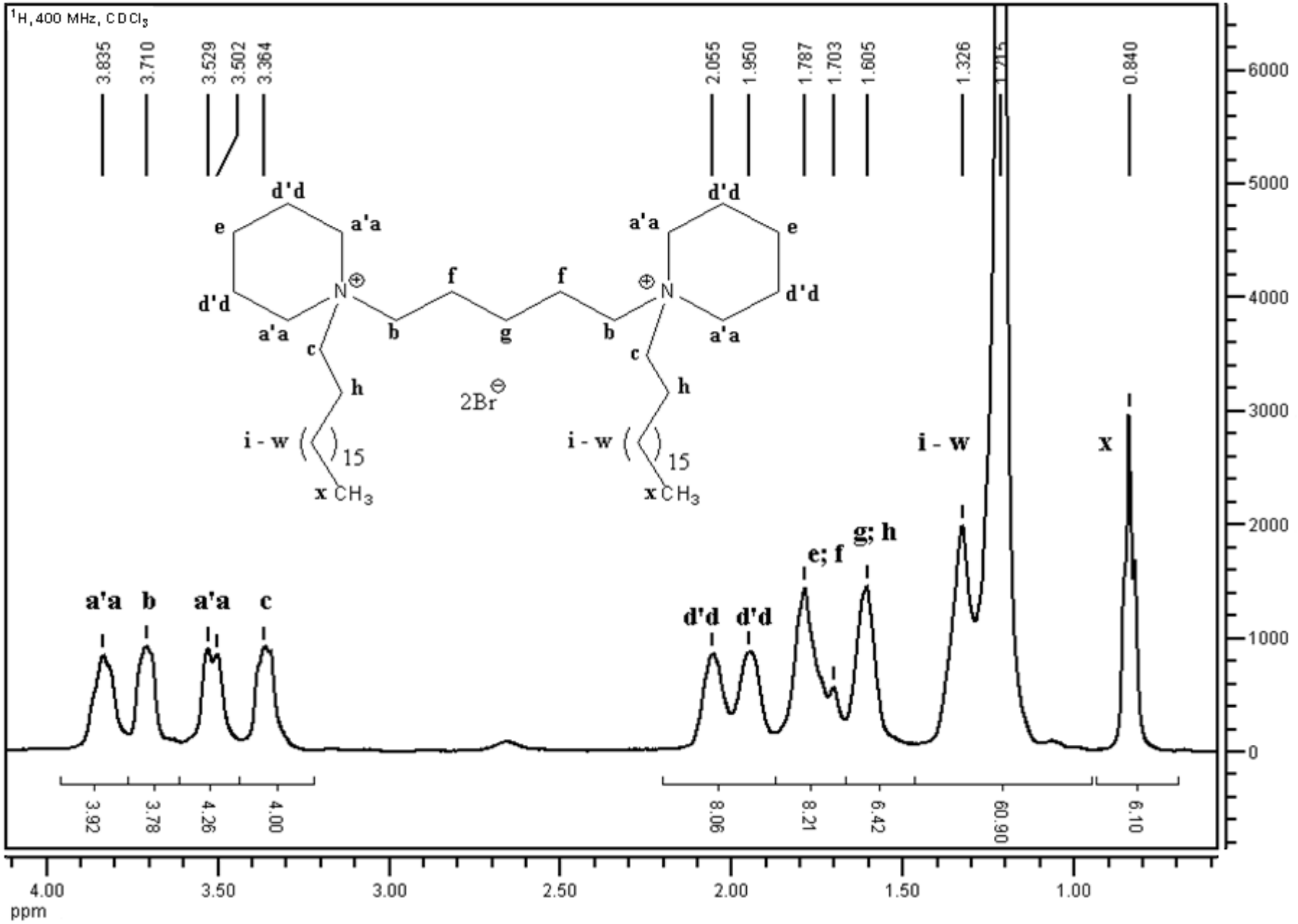

Figure S23. The ^{1}H spectrum of 1,1′-(pentane-1,5-diyl)bis(1-octadecylpiperidinium) dibromide (**D7**) in $CDCl_3$ solution recorded at 400 MHz.

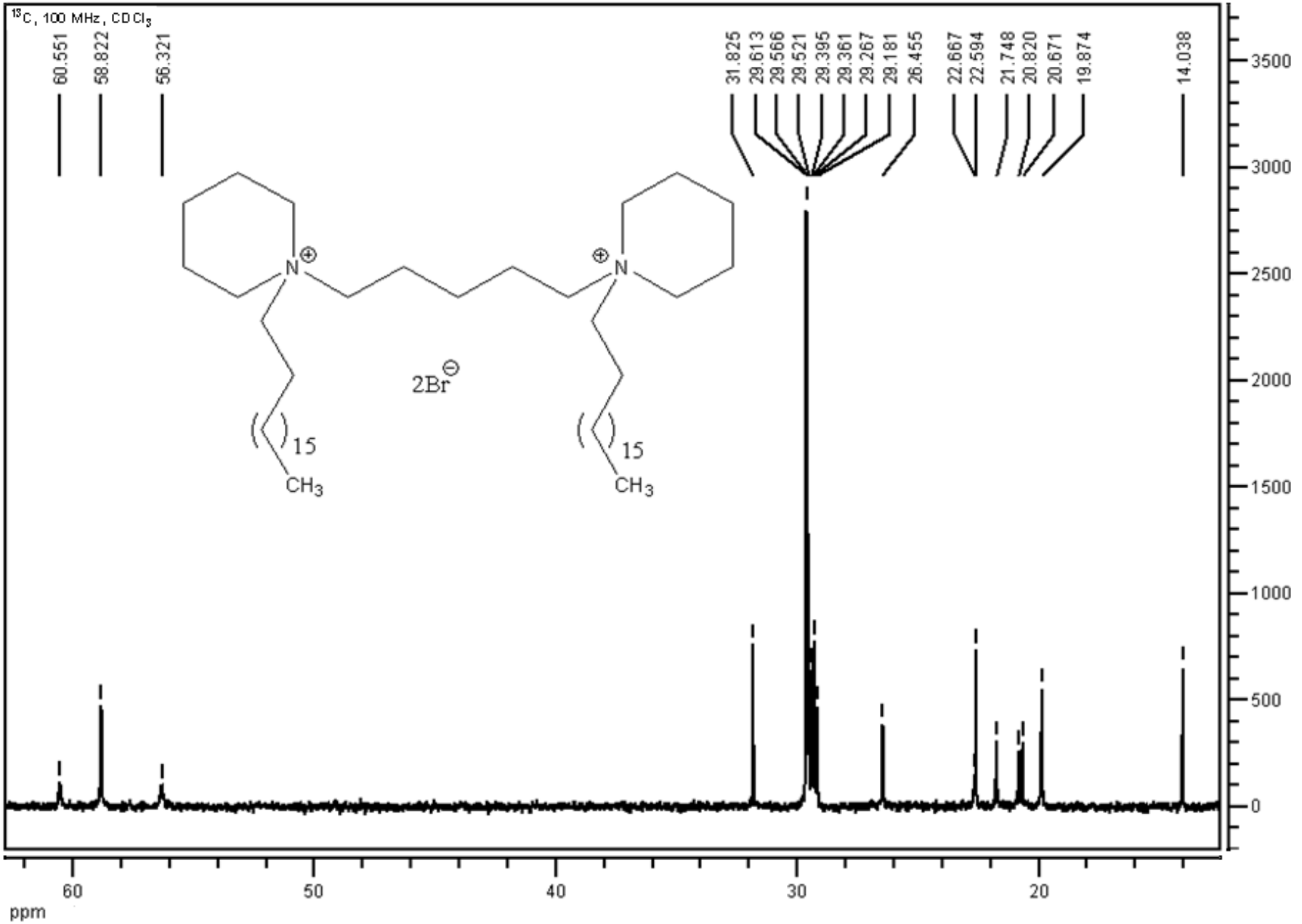

Figure S24. The ^{13}C spectrum of 1,1′-(pentane-1,5-diyl)bis(1-octadecylpiperidinium) dibromide (**D7**) in $CDCl_3$ solution recorded at 100 MHz.

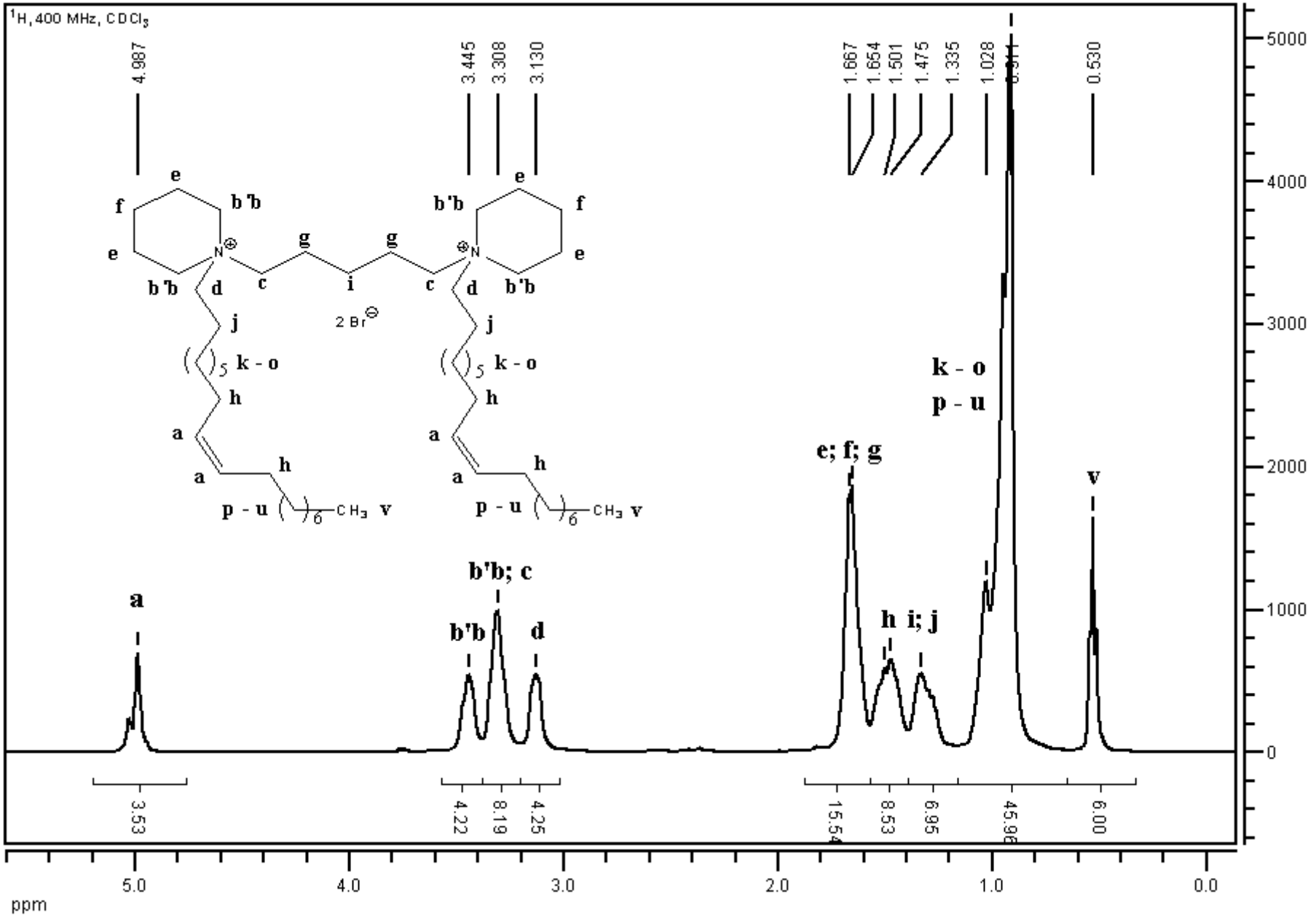

Figure S25. The ^{1}H spectrum of (Z)-1,1′-(pentane-1,5-diyl)bis(1-((Z)-octadec-9-enyl)piperidinium) dibromide (**D8**)in $CDCl_3$ solution recorded at 400 MHz.

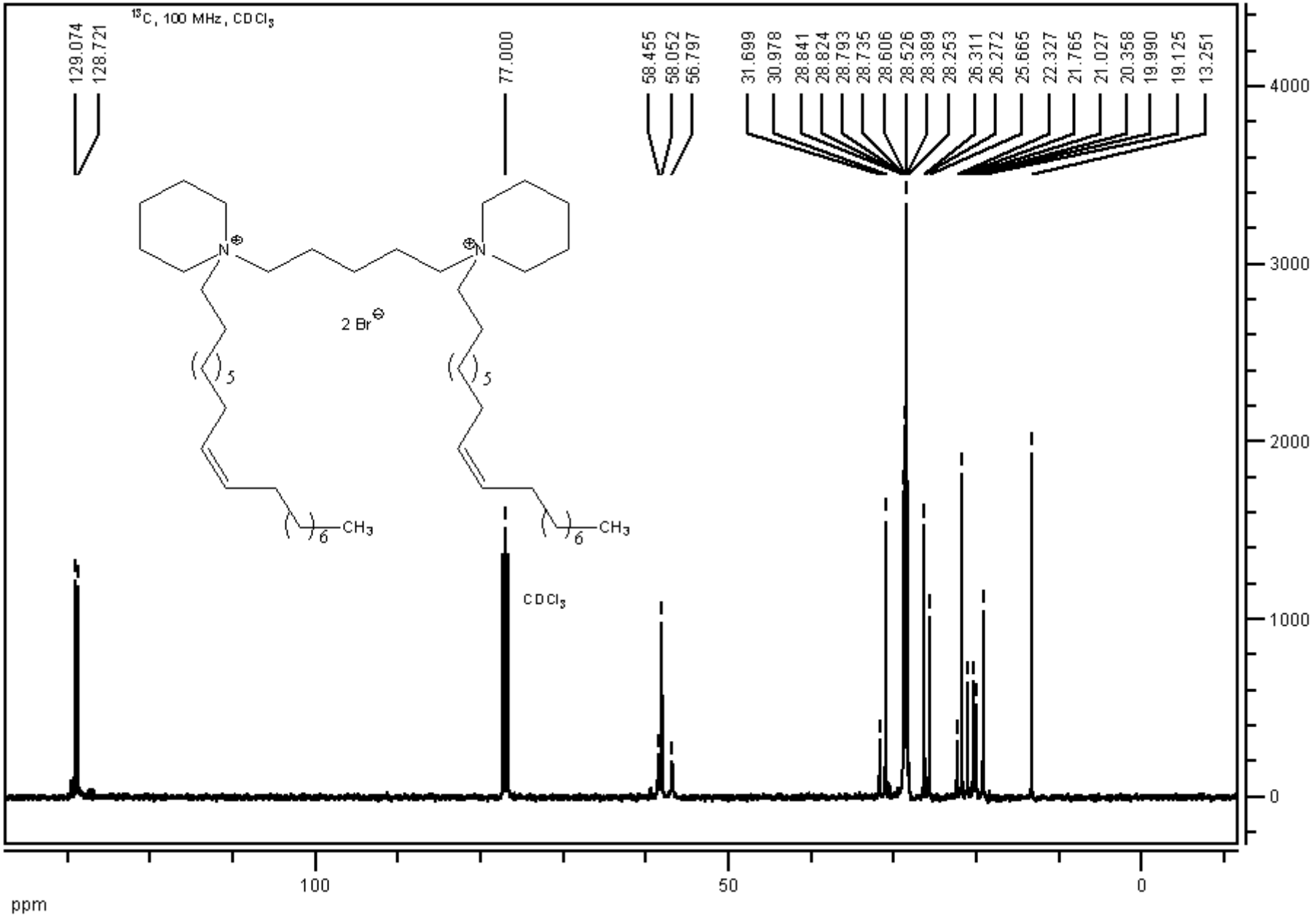

Figure S26. The ^{13}C spectrum of (Z)-1,1′-(pentane-1,5-diyl)bis(1-((Z)-octadec-9-enyl)piperidinium) dibromide (**D8**)in $CDCl_3$ solution recorded at 100 MHz.