Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 720–721

Development and synthesis of novel representatives of polyazido-substituted *N*-(alkoxymethyl)nitramines

Dmitry B. Vinogradov, Pavel V. Bulatov, Evgeny Yu. Petrov and Vladimir A. Tartakovsky

^{1}H, ^{13}C and ^{14}N NMR spectra were recorded in DMSO-d_6 on a Bruker AVANCE AM300, DRX500 and AV600 spectrometers: the quintet of residual protons of the deuterated solvent at δ 2.503 is the internal standard for ^{1}H nuclei, and the DMSO-d_6 septet at δ 39.98, for ^{13}C nuclei. IR spectra were recorded on a Bruker-Alpha spectrometer (KBr pellets). Decomposition temperatures were measured with a Stuart SMP-10 instrument at a heating rate of 2 °C/min.

1,7-Dichloro-3-oxa-5-nitrazaheptane 3a.

2-Chloroethanol (0.69 g, 8.57 mmol) was added to a solution of 1,4-dichloro-2-nitrazabutane **2a** (1.54 g, 8.90 mmol) in 1,2-dichloroethane (16 ml). The resulting solution was stirred under reflux for 37 h. After that time, dichloroethane was distilled off *in vacuo* to leave 1.78 g of crude **3a** which was intensely stirred at 75 °C for 1 h in a solution of $NaHCO_3$ (1.5 g, 17.85 mmol) in water (15 ml). Then the product was extracted with benzene (2×15 ml), and the benzene solution was washed with water (1×8 ml). The resulting benzene solution (30 ml) was then vigorously stirred at room temperature for 40 min with 15 % aq. hydrochloric acid (15 ml), then the benzene solution was washed with water (2×10 ml). Benzene was distilled off *in vacuo*. The residue of 1,7-dichloro-3-oxa-5-nitrazaheptabe **3a** (1.17 g, 5.4 mmol, 63 %) is a light yellow oil (the content is 99+ mol.%, according to ^{1}H NMR data). n_D^{22} = 1.4994; IR, ν, cm^{-1}: 1079 (C-O-C), 1300 (NNO_2 sym.), 1532 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 3.74 (t, *J*=5.9, 2H, O$\underline{CH_2}CH_2Cl$), 3.85 (m, 4H, 2×CH_2Cl), 4.15 (t, *J*=6.4, 2H, $CH_2\underline{CH_2}NNO_2$), 5.28 (s, 2H, O_2NNCH_2O) (Fig. S1); ^{13}C NMR δ (75 MHz, DMSO-d_6) 40.37 ($NCH_2\underline{C}H_2Cl$), 43.53 ($OCH_2\underline{C}H_2Cl$), 51.48 ($CH_2\underline{C}H_2NNO_2$), 69.37 (O$\underline{C}H_2CH_2Cl$), 79.65 ($NCH_2O$) (Fig. S2); Found %: C 28.06; H 4.59; N 13.33. $C_5H_{10}Cl_2N_2O_3$. Calculated %: C 27.67; H 4.64; N 12.91.

1,8-Dichloro-3-oxa-5-nitrazaoctane 3b.

A procedure similar to the synthesis of **3a** based on 1,5-dichloro-2-nitrazapentane **2b** (5.2 g, 27.8 mmol) and 2-chloroethanol (2.00 g, 24.84 mmol) gave a residue of 1,8-dichloro-3-oxa-5-nitrazaoctane **3b** (4.58 g, 19.82 mmol, 73%) as a light-yellow oil (the content is ~99 % mol. according to ^{1}H NMR spectroscopy). n_D^{22} =1.5004; IR, ν, cm^{-1}: 1083 (C-O-C), 1298 (NNO_2 sym.), 1531 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 2.11 (m, 2H, $CH_2\underline{CH_2}CH_2$), 3.72 (m, 4H, $Cl\underline{CH_2}CH_2CH_2$, $O\underline{CH_2}CH_2Cl$), 3.82 (m, 2H, $OCH_2\underline{CH_2}Cl$), 3.91 (m, 2H, $CH_2\underline{CH_2}NNO_2$), 5.25 (s, 2H, O_2NNCH_2O) (Fig. S4); ^{13}C NMR δ (75 MHz, DMSO-d_6) 29.52 ($CH_2\underline{C}H_2CH_2$), 42.56 ($Cl\underline{C}H_2CH_2CH_2$), 43.57 ($OCH_2\underline{C}H_2Cl$), 48.19 ($CH_2\underline{C}H_2NNO_2$), 69.45 ($O\underline{C}H_2CH_2Cl$), 79.44 ($NCH_2O$) (Fig. S5); Found %: C 31.45; H 5.15; N 12.18. $C_6H_{12}Cl_2N_2O_3$. Calculated %: C 31.19; H 5.23; N 12.12.

1,7-Dichloro-3-oxa-5-nitrazaoctane 3c.

A procedure similar to the synthesis of **3a** (refluxing for 70 h in DCE) based on 1,4-dichloro-2-nitrazapentane **2c** (5.27 g, 28.18 mmol) and 2-chloroethanol (2.00 g, 24.84 mmol) to give a residue of 1,7-dichloro-3-oxa-5-nitrazaoctane **3c** (4.64 g, 20.08 mmol, 81%) as a light-yellow oil (the content is ~99 % mol. according to ^{1}H NMR spectroscopy). n_D^{22} =1.4935; IR, ν, cm^{-1}: 1085 (C-O-C), 1294 (NNO_2 sym.), 1528 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.50 (d, *J*=6.6, 3H, $C\underline{CH_3}$), 3.74 (m, 2H, $O\underline{CH_2}CH_2Cl$), 3.84 (m, 2H, $OCH_2\underline{CH_2}Cl$), 4.09 (m, 2H, $C\underline{CH_2}NNO_2$), 4.49 (dq, *J*=13.0, 6.6, 1H, CHCl), 5.19 (d, *J*=11.8, 1H, O_2NNCH_2O), 5.38 (d, *J*=11.8, 1H, O_2NNCH_2O) (Fig. S7); ^{13}C NMR δ (75 MHz, DMSO-d_6) 22.09 ($\underline{C}H_3CH$), 43.57 ($OCH_2\underline{C}H_2Cl$), 54.77 ($CH\underline{C}H_2NNO_2$), 56.97 (CHCl), 69.47 ($O\underline{C}H_2CH_2Cl$), 79.94 (NCH_2O) (Fig. S8); Found %: C 31.62; H 5.23. $C_6H_{12}Cl_2N_2O_3$. Calculated %: C 31.19; H 5.23.

7,8-Dibromo-1-chloro-5-oxa-3-nitrazaoctane 3d.

A procedure similar to the synthesis of **3a** based on 1,4-dichloro-2-nitrazabutane **2a** (3.72 g, 21.5 mmol) and 2,3-dibromopropan-1-ol (4.68 g, 21.48 mmol) gave a residue of 7,8-dibromo-1-chloro-5-oxa-3-nitrazaoctane **3d** (5.70 g, 19.82 mmol, 75%) as a light-yellow oil (the content is ~99 % mol. according to ^{1}H NMR spectroscopy). n_D^{22} =1.5506; IR, ν, cm^{-1}: 1077 (C-O-C), 1281 (NNO_2 sym.), 1535 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 500.13 MHz, DMSO-d_6) 3.86 (t, *J*=6.4, 2H, $O\underline{CH_2}CH$), 3.91 (m, 2H, $CH\underline{CH_2}Br$), 3.95 (t, *J*=4.9, 2H, $Cl\underline{CH_2}CH_2NNO_2$), 4.16 (t, *J*=6.4, 2H, $ClCH_2\underline{CH_2}NNO_2$), 4.56 (dq, *J*=10.2, 5.1, 1H, CHBr), 5.32

(s, 2H, O_2NNCH_2O) (Fig. S10); ^{13}C NMR δ (75 MHz, DMSO-d_6) 29.52 ($CH_2\underline{C}H_2CH_2$), 42.56 ($Cl\underline{C}H_2CH_2CH_2$), 43.57 ($OCH_2\underline{C}H_2Cl$), 48.19 ($CH_2\underline{C}H_2NNO_2$), 69.45 ($O\underline{C}H_2CH_2Cl$), 79.44 ($NCH_2O$) (Fig. S11); Found %: C 20.62; H 3.03. $C_6H_{11}Br_2ClN_2O_3$. Calculated %: C 20.33; H 3.13.

8-Bromo-7,7-bis(bromomethyl)-1-chloro-5-oxa-3-nitrazaoctane 3e.

A procedure similar to the synthesis of **3a** (refluxing for 90 h in DCE) based on 1,4-dichloro-2-nitrazabutane **2a** (2.00 g, 11.56 mmol) and 2,2,2-tris(bromomethyl)ethanol (3.50 g, 10.77 mmol) gave a residue of 8-bromo-7,7-bis(bromomethyl)-1-chloro-5-oxa-3-nitrazaoctane **3e** (4.47 g, 9.69 mmol, 90%) as a light-yellow oil (the content is ~99 % mol. according to ^1H NMR spectroscopy). n_D^{22} =1.5607; IR, ν, cm^{-1}: 1088 (C-O-C), 1280 (NNO_2 sym.), 1535 (NNO_2 asym.); ^1H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 3.53 (s, 6H, $C(\underline{CH_2}Br)_3$), 3.61 (s, 2H, $O\underline{CH_2}C$), 3.88 (t, *J*=6.3, 2H, $Cl\underline{CH_2}CH_2NNO_2$), 4.18 (t, *J*=6.4, 2H, $ClCH_2\underline{CH_2}NNO_2$), 5.29 (s, 2H, O_2NNCH_2O) (Fig. S13); ^{13}C NMR δ (75 MHz, DMSO-d_6) 34.75 (3×CH_2Br), 40.37 ($Cl\underline{C}H_2CH_2NNO_2$), 43.19 (C tert.), 51.62 ($ClCH_2\underline{C}H_2NNO_2$), 67.64 ($O\underline{C}H_2C$), 79.64 ($NCH_2O$) (Fig. S14); Found %: C 21.02; H 3.00; N 5.97. $C_8H_{14}Br_3ClN_2O_3$. Calculated %: C 20.83; H 3.06; N 6.07.

1,2-Dibromo-9-chloro-4-oxa-6-nitrazanonane 3f.

A procedure similar to the synthesis of **3a** based on 1,5-dichloro-2-nitrazapentane **2b** (4.4 g, 23.52 mmol) and 2,3-dibromopropan-1-ol (4.68 g, 21.39 mmol) gave a residue of 1,2-dibromo-9-chloro-4-oxa-6-nitrazanonane **3f** (5.73 g, 15.55 mmol, 73%) as a light-yellow oil (the content is ~99 % mol. according to ^1H NMR spectroscopy). n_D^{22} =1.5453; IR, ν, cm^{-1}: 1085 (C-O-C), 1299 (NNO_2 sym.), 1536 (NNO_2 asym.); ^1H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 2.12 (m, 2H, $CH_2\underline{CH_2}CH_2$), 3.71 (t, *J*=6.4, 2H, $Cl\underline{CH_2}CH_2$), 3.91 (m, 6H, $CH_2\underline{CH_2}NNO_2$, $O\underline{CH_2}CH$, $CH\underline{CH_2}Br$), 4.55 (dq, *J*=10.2, 5.1, 1H, CHBr), 5.28 (s, 2H, O_2NNCH_2O) (Fig. S16); ^{13}C NMR δ (75 MHz, DMSO-d_6) 29.55 ($CH_2\underline{C}H_2CH_2$), 34.39 (CH_2Br), 42.56 ($Cl\underline{C}H_2CH_2CH_2$), 48.29 ($CH_2\underline{C}H_2NNO_2$), 50.30 (CHBr), 70.70 ($O\underline{C}H_2CH$), 79.45 ($NCH_2O$) (Fig. S17); Found %: C 22.97; H 3.51; N 7.54. $C_7H_{13}Br_2ClN_2O_3$. Calculated %: C 22.82; H 3.56; N 7.60.

1,7-Dichloro-2-chloromethyl-3-oxa-5-nitrazaoctane 3g.

A procedure similar to the synthesis of **3a** (refluxing for 90 h in DCE) based on 1,4-dichloro-2-nitrazapentane **2c** (4.5 g, 24.05 mmol) and 1,3-dichloropropan-2-ol (2.87 g, 22.25 mmol) gave a residue of

1,7-dichloro-2-chloromethyl-3-oxa-5-nitrazaoctane **3g** (4.27 g, 15.27 mmol, 69%) as a light-yellow oil (the content is ~99 % mol. according to ^{1}H NMR spectroscopy). n_D^{22} =1.5056; IR, ν, cm^{-1}: 1091 (C-O-C), 1299 (NNO_2 sym.), 1534 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-*d*$_6$) 1.51 (d, *J*=6.6, 3H, C$\underline{CH_3}$), 3.78 (m, 4H, OCH($\underline{CH_2}$Cl)$_2$), 4.11 (m, 3H, O$\underline{CH}$(CH$_2$Cl)$_2$, C$\underline{CH_2}$NNO$_2$), 4.49 (m, 1H, CHCl), 5.29 (d, *J*=12.0, 1H, O$_2$NNC$\underline{H_2}$O), 5.49 (d, *J*=12.0, 1H, O$_2$NNC$\underline{H_2}$O) (Fig. S19); ^{13}C NMR δ (75 MHz, DMSO-*d*$_6$) 22.06 ($\underline{C}$H$_3$CH), 44.22 (OCH($\underline{C}$H$_2$Cl)$_2$), 54.77 (CH$\underline{C}$H$_2$NNO$_2$), 57.03 (CHCl), 77.79 (O$\underline{C}$H(CH$_2$Cl)$_2$), 79.24 (NCH$_2$O) (Fig. S20); Found %: C 30.21; H 4.59; N 10.13. $C_7H_{13}Cl_3N_2O_3$. Calculated %: C 30.08; H 4.69; N 10.02.

1,7-Diazido-3-oxa-5-nitrazaheptane 4a.

1,7-Dichloro-3-oxa-5-nitrazaheptane **3a** (7.22 g, 33.26 mmol) was added with vigorous stirring to a solution of NaN_3 (11.23 g, 172.6 mmol) and tetramethylammonium bromide (TBAB) (2.81 g, 25.1 mmol) in water (60 ml). The reaction mixture was refluxed for 14 h with stirring. After the reaction, the reaction mixture was extracted with 1×40 ml and 1×20 ml benzene. The organic phase was washed with 2×20 ml water and benzene was distilled off *in vacuo*. The residue is 1,7-diazido-3-oxa-5-nitrazaheptane **4a** (the content is 99+ % mol. according to ^{1}H NMR spectroscopy) as a light-yellow mobile liquid (7.21 g, 31.32 mmol, 94.2 %). n_D^{22} =1.5112; Decomp. start at 185-186 °C; IR, ν, cm^{-1}: 1087 (C-O-C), 1299 (NNO_2 sym.), 1532 (NNO_2 asym.), 2103 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-*d*$_6$) 3.44 (t, *J*=5.6, 2H, OCH$_2$$\underline{CH_2}N_3$), 3.65 (t, *J*=5.9, 2H, N$_3$$\underline{CH_2}CH_2NNO_2$), 3.75 (t, *J*=5.6, 2H, O$\underline{CH_2}$CH$_2$Cl), 4.01 (t, *J*=5.9, 2H, N$_3$CH$_2$$\underline{CH_2}NNO_2$), 5.25 (s, 2H, O$_2NNC\underline{H_2}$O) (Fig. S1); ^{13}C NMR δ (75 MHz, DMSO-*d*$_6$) 47.88 (N$_3$$\underline{C}H_2CH_2NNO_2$), 49.40 (OCH$_2$$\underline{C}H_2N_3$), 50.03 (CH$_2$$\underline{C}H_2NNO_2$), 68.16 (O$\underline{C}H_2CH_2N_3$), 79.61 (NCH$_2$O) (Fig. S2); ^{14}N NMR δ (36.14 MHz, DMSO-*d*$_6$) -172.83, -132.77, -29.60 (Fig. S3); Found %: C 26.31; H 4.40; N 48.59. $C_5H_{10}N_8O_3$. Calculated %: C 26.09; H 4.38; N 48.68.

1,8-Diazido-3-oxa-5-nitrazaoctane 4b.

A procedure similar to the synthesis of **4a** (treatment time 15 h) based on 1,8-dichloro-3-oxa-5-nitrazaoctane **3b** (4.00 g, 17.31 mmol) gave a residue of 1,8-diazido-3-oxa-5-nitrazaoctane **4b** (the content is 99+ % mol. according to ^{1}H NMR spectroscopy) (4.04 g, 16.54 mmol, 96 %) as a light-yellow mobile liquid. n_D^{22} =1.5093; Decomp. start at 164-166 °C; IR, ν, cm^{-1}: 1091 (C-O-C), 1297 (NNO_2 sym.), 1528 (NNO_2 asym.), 2103 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-*d*$_6$) 1.90 (m, 2H, CH$_2$$\underline{CH_2}CH_2$), 3.44 (m, 4H, N$_3$$\underline{CH_2}CH_2CH_2$, OCH$_2$$\underline{CH_2}N_3$), 3.73 (m, 2H, O$\underline{CH_2}CH_2N_3$), 3.85 (t, *J*=7.0, 2H, CH$_2$$\underline{CH_2}NNO_2$), 5.23

(s, 2H, O_2NNCH_2O) (Fig. S4); ^{13}C NMR δ (75 MHz, DMSO-d_6) 26.01 ($CH_2\underline{C}H_2CH_2$), 48.13 ($N_3\underline{C}H_2CH_2CH_2$), 48.15 ($OCH_2\underline{C}H_2N_3$), 50.03 ($CH_2\underline{C}H_2NNO_2$), 68.15 ($O\underline{C}H_2CH_2N_3$), 79.42 ($NCH_2O$) (Fig. S5); ^{14}N NMR δ (36.14 MHz, DMSO-d_6) -172.63, -132.69, -29.35 (Fig. S6); Found %: C 29.80; H 4.67; N 45.61. $C_6H_{12}N_8O_3$. Calculated %: C 29.51; H 4.95; N 45.88.

1,7-Diazido-3-oxa-5-nitrazaoctane 4c.

A procedure similar to the synthesis of **4a** (treatment time 20 h) based on 1,7-dichloro-3-oxa-5-nitrazaoctane **3c** (5.82 g, 25.19 mmol) gave a residue of 1,7-diazido-3-oxa-5-nitrazaoctane **4c** (the content is 99+ % mol. according to ^1H NMR spectroscopy) (5.30 g, 21.70 mmol, 86 %) as a light-yellow mobile liquid. n_D^{22} =1.5043; Decomp. start at 167-169 °C; IR, ν, cm^{-1}: 1108 (C-O-C), 1278 (NNO_2 sym.), 1534 (NNO_2 asym.), 2120 (N_3); ^1H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.25 (d, *J*=6.6, 3H, $C\underline{CH_3}$), 3.44 (m, 2H, $OCH_2\underline{CH_2}N_3$), 3.76 (m, 2H, $O\underline{CH_2}CH_2N_3$), 3.88 (qd, *J*=14.9, 6.6, 2H, $C\underline{CH_2}NNO_2$), 4.03 (m, 1H, CHN_3), 5.16 (d, *J*=11.7, 1H, O_2NNCH_2O), 5.33 (d, *J*=11.7, 1H, O_2NNCH_2O) (Fig. S7); ^{13}C NMR δ (75 MHz, DMSO-d_6) 16.54 ($\underline{C}H_3CH$), 50.00 ($OCH_2\underline{C}H_2N_3$), 54.33 ($CH\underline{C}H_2NNO_2$), 55.14 (CHN_3), 68.19 ($O\underline{C}H_2CH_2N_3$), 79.86 (NCH_2O) (Fig. S8); ^{14}N NMR δ (36.14 MHz, DMSO-d_6) -171.32, -132.63, -29.50 (Fig. S9); Found %: C 29.82; H 4.80; N 46.12. $C_6H_{12}N_8O_3$. Calculated %: C 29.51; H 4.95; N 45.88.

1,7,8-Triazido-5-oxa-3-nitrazaoctane 4d.

A procedure similar to the synthesis of **4a** (treatment time 20 h) based on 7,8-dibromo-1-chloro-5-oxa-3-nitrazaoctane **3d** (4.20 g, 11.85 mmol) gave a residue of 1,7,8-triazido-5-oxa-3-nitrazaoctane **4d** (the content is 99+ % mol. according to ^1H NMR spectroscopy) (2.81 g, 9.85 mmol, 83%) as a light-yellow mobile liquid. n_D^{22} =1.5304; Decomp. start at 142-144 °C; IR, ν, cm^{-1}: 1088 (C-O-C), 1288 (NNO_2 sym.), 1526 (NNO_2 asym.), 2105 (N_3); ^1H NMR, δ (*J*, 600.13 MHz, DMSO-d_6) 3.48 (ddd, *J*=20.1, 12.9, 5.6, 2H, $CH\underline{CH_2}N_3$), 3.65 (t, *J*=5.9, 2H, $N_3\underline{CH_2}CH_2NNO_2$), 3.72 (ddd, *J*=17.4, 10.4, 5.5, 2H, $O\underline{CH_2}CH$), 3.92 (ddd, *J*=11.0, 7.3, 4.1, 1H, CHN_3), 4.01 (t, *J*=5.9, 2H, $CH_2\underline{CH_2}NNO_2$), 5.26 (s, 2H, O_2NNCH_2O) (Fig. S10); ^{13}C NMR δ (75 MHz, DMSO-d_6) 47.89 ($N_3\underline{C}H_2CH_2NNO_2$), 49.48 ($CH_2\underline{C}H_2NNO_2$), 50.79 ($CH\underline{C}H_2N_3$), 60.17 ($CHN_3$), 69.06 ($O\underline{C}H_2CH$), 79.76 ($NCH_2O$) (Fig. S11); (Fig. S11); ^{14}N NMR δ (36.14 MHz, DMSO-d_6) -173.86, -133.84, -29.79 (Fig. S12); Found %: C 26.24; H 3.97, N 53.75. $C_6H_{11}N_{11}O_3$. Calculated %: C 25.27; H 3.89, N 54.02.

1,8-Diazido-7,7-bis(azidomethyl)-5-oxa-3-nitrazaoctane 4e.

A procedure similar to the synthesis of **4a** (treatment time 15 h) based on 8-bromo-7,7-bis(bromomethyl)-1-chloro-5-oxa-3-nitrazaoctane **3e** (4.20 g, 7.52 mmol) gave a residue of 1,8-diazido-7,7-bis(azidomethyl)-5-oxa-3-nitrazaoctane **4e** (the content is 99+ % mol. according to ^{1}H NMR spectroscopy) (2.59 g, 7.31 mmol, 97%) as a light-yellow mobile liquid. n_D^{22} =1.5362; Decomp. start at 169-171 °C; IR, ν, cm^{-1}: 1091 (C-O-C), 1301 (NNO_2 sym.), 1525 (NNO_2 asym.), 2100 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-*d*$_6$) 3.38 (s, 6H, C(C<u>H$_2$</u>N$_3$)$_3$), 3.46 (s, 2H, OC<u>H$_2$</u>C), 3.65 (t, *J*=5.9, 2H, N$_3$C<u>H$_2$</u>CH$_2$NNO$_2$), 4.00 (t, *J*=5.9, 2H, N$_3$CH$_2$C<u>H$_2$</u>NNO$_2$), 5.22 (s, 2H, O$_2$NNCH$_2$O) (Fig. S13); ^{13}C NMR δ (75 MHz, DMSO-*d*$_6$) 44.01 (C tert.), 47.87 (N$_3$C<u>H$_2$</u>CH$_2$NNO$_2$), 49.49 (N$_3$CH$_2$C<u>H$_2$</u>NNO$_2$), 51.28 (3×CH$_2$N$_3$), 68.10 (OC<u>H$_2$</u>C), 79.88 (NCH$_2$O) (Fig. S14); ^{14}N NMR δ (36.14 MHz, DMSO-*d*$_6$) -175.52, -133.54, -29.54 (Fig. S15); Found %: C 27.84; H 3.85; N 54.63. $C_8H_{14}N_{14}O_3$. Calculated %: C 27.12; H 3.98; N 55.35.

1,2,9-Triazido-4-oxa-6-nitrazanonane 4f.

A procedure similar to the synthesis of **4a** based on compound **3f** (5.23 g, 14.19 mmol) gave a residue of 1,2,9-triazido-4-oxa-6-nitrazanonane **4f** (the content is 99+ % mol. according to ^{1}H NMR spectroscopy) (2.94 g, 9.82 mmol, 69%) as a light-yellow mobile liquid. n_D^{22} =1.5275; Decomp. start at 144-146 °C; IR, ν, cm^{-1}: 1087 (C-O-C), 1299 (NNO_2 sym.), 1532 (NNO_2 asym.), 2103 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-*d*$_6$) 1.91 (m, 2H, CH$_2$C<u>H$_2$</u>CH$_2$), 3.43 (m, 3H, 1/2×CHC<u>H$_2$</u>N$_3$, N$_3$C<u>H$_2$</u>CH$_2$), 3.54 (dd, *J*=13.0, 4.2, 1H, 1/2×CHC<u>H$_2$</u>N$_3$), 3.71 (ddd, *J*=17.3, 10.4, 5.5, 2H, OC<u>H$_2$</u>CH), 3.85 (t, *J*=7.1, 2H, CH$_2$C<u>H$_2$</u>NNO$_2$), 3.92 (m, 1H, CHN$_3$), 5.24 (s, 2H, O$_2$NNCH$_2$O) (Fig. S16); ^{13}C NMR δ (75 MHz, DMSO-*d*$_6$) 26.05 (CH$_2$C<u>H$_2$</u>CH$_2$), 48.19 (CH$_2$C<u>H$_2$</u>NNO$_2$, N$_3$C<u>H$_2$</u>CH$_2$), 50.79 (CHC<u>H$_2$</u>N$_3$), 60.22 (CHN$_3$), 69.11 (OC<u>H$_2$</u>CH), 79.58 (NCH$_2$O) (Fig. S17); ^{14}N NMR δ (36.14 MHz, DMSO-*d*$_6$) -170.55, -133.26, -29.37 (Fig. S18); Found %: C 28.79; H 4.28. $C_7H_{13}N_{11}O_3$. Calculated %: C 28.10; H 4.38.

1,7-Diazido-2-azidomethyl-3-oxa-5-nitrazaoctane 4g.

A procedure similar to the synthesis of **4a** (treatment time 20 h) based on 1,7-dichloro-2-chloromethyl-3-oxa-5-nitrazaoctane **3g** (3.80 g, 13.59 mmol) gave a residue of 1,7-diazido-2-azidomethyl-3-oxa-5-nitrazaoctane **4g** (the content is 99+ % mol. according to ^{1}H NMR spectroscopy) (3.44 g, 11.5 mmol, 85%) as a light-yellow mobile liquid. n_D^{22} =1.5199; Decomp. start at 170-171 °C; IR, ν, cm^{-1}: 1085

(C-O-C), 1294 (NNO_2 sym.), 1526 (NNO_2 asym.), 2102 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.26 (d, *J*=6.5, 3H, C<u>CH</u>$_3$), 3.46 (m, 4H, OCH(<u>CH</u>$_2$$N_3$)$_2$), 3.89 (m, 2H, C<u>CH</u>$_2$$NNO_2$), 3.99 (m, 2H, O<u>CH</u>(CH_2N_3)$_2$, CHN_3), 5.26 (d, *J*=11.7, 1H, O_2NNCH_2O), 5.43 (d, *J*=11.7, 1H, O_2NNCH_2O) (Fig. S19); ^{13}C NMR δ (75 MHz, DMSO-d_6) 16.54 (<u>C</u>H_3CH), 51.40 (OCH(<u>C</u>H_2N_3)$_2$), 54.57 (CH<u>C</u>H_2NNO_2), 55.23 (CHN_3), 77.16 (O<u>C</u>H(CH_2N_3)$_2$), 79.18 (NCH_2O) (Fig. S20); ^{14}N NMR δ (36.14 MHz, DMSO-d_6) -172.50, -133.40, -29.71 (Fig. S21); Found %: C 28.10; H 4.62; N 51.25. $C_7H_{13}N_{11}O_3$. Calculated %: C 28.10; H 4.38; N 51.49.

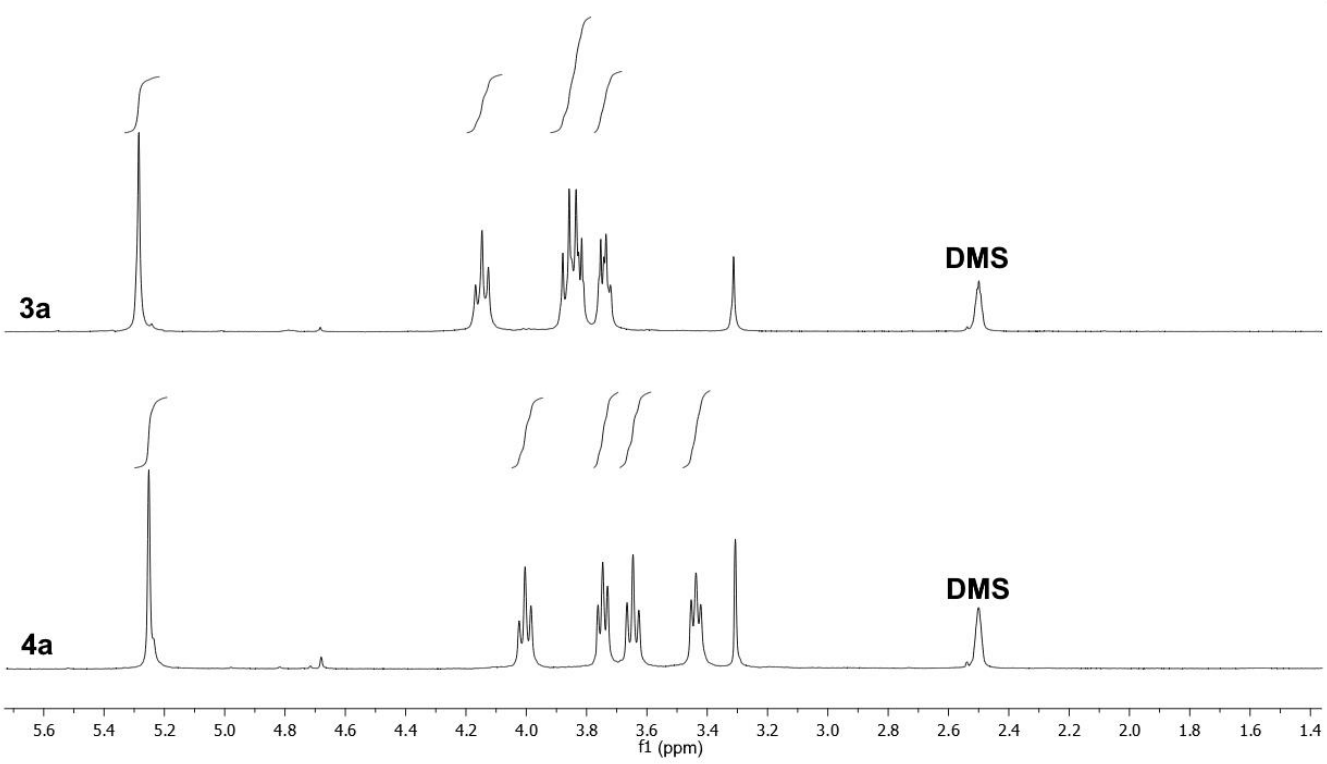

Figure S1. ^{1}H NMR spectra of compounds **3a**, **4a** in DMSO-d_6.

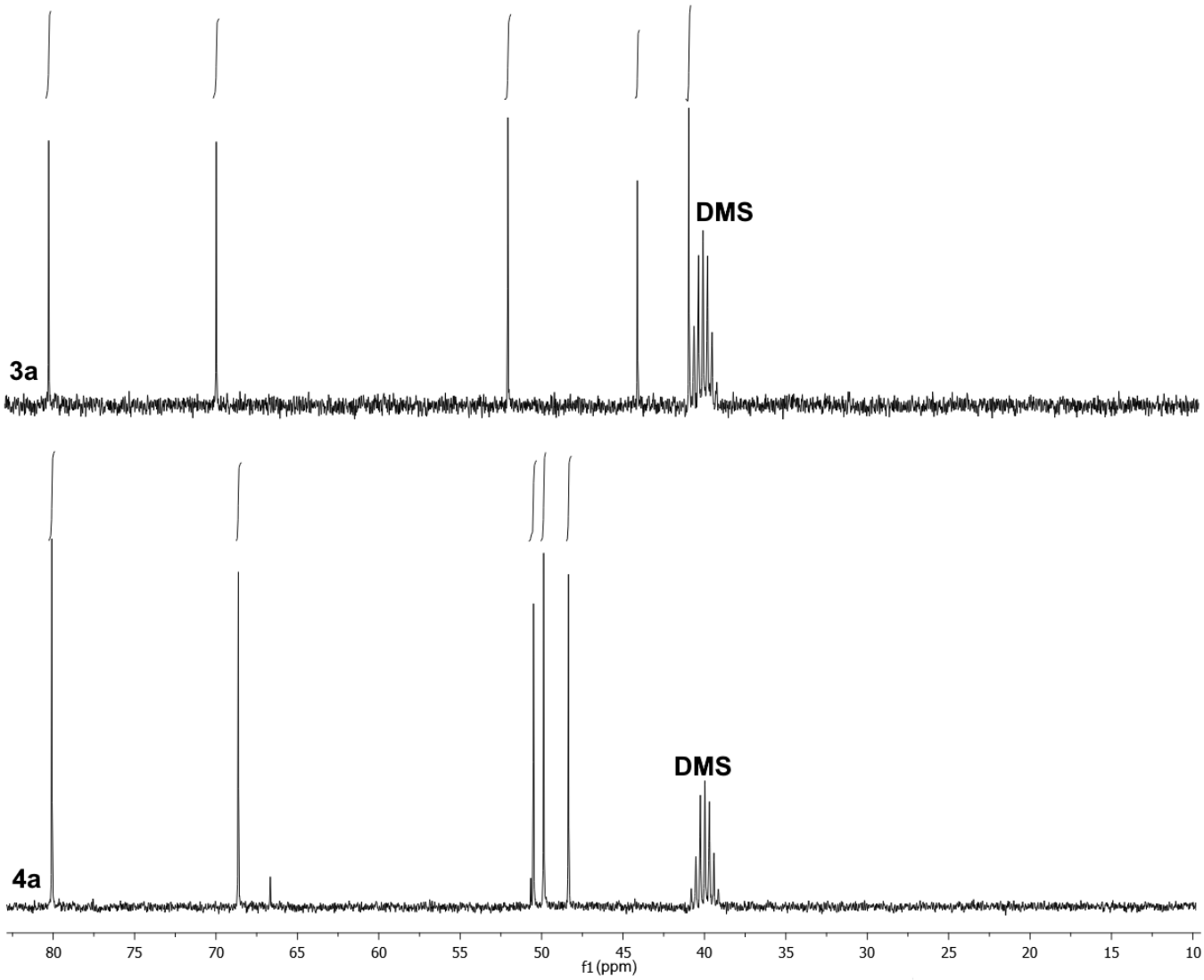

Figure S2. ^{13}C NMR spectra of compounds **3a**, **4a** in DMSO-d_6.

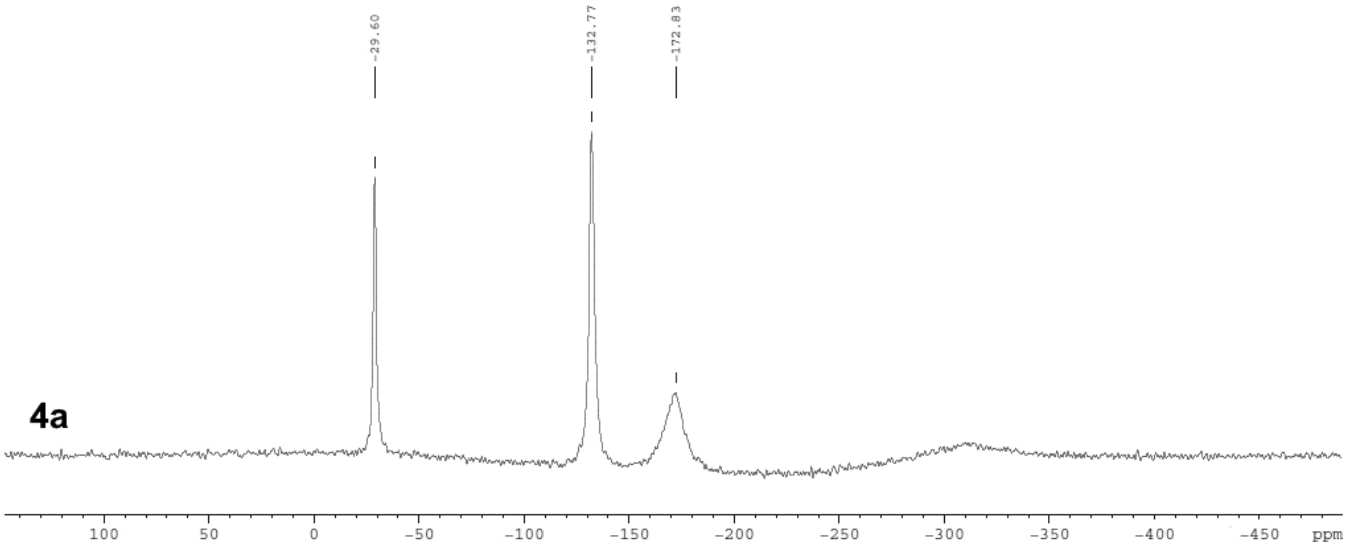

Figure S3. ^{14}N NMR spectra of compound **4a** in DMSO-d_6.

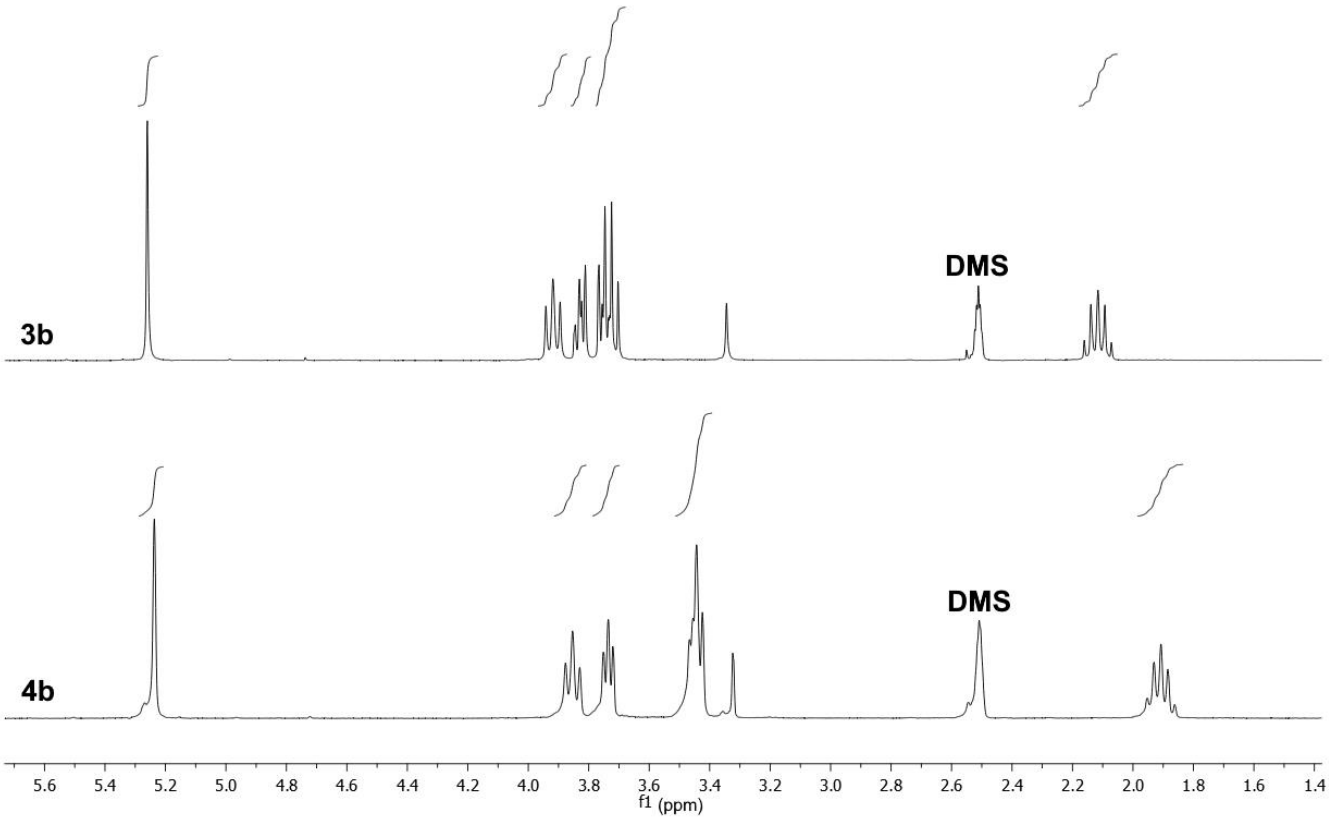

Figure S4. ^{1}H NMR spectra of compounds **3b**, **4b** in DMSO-d_6.

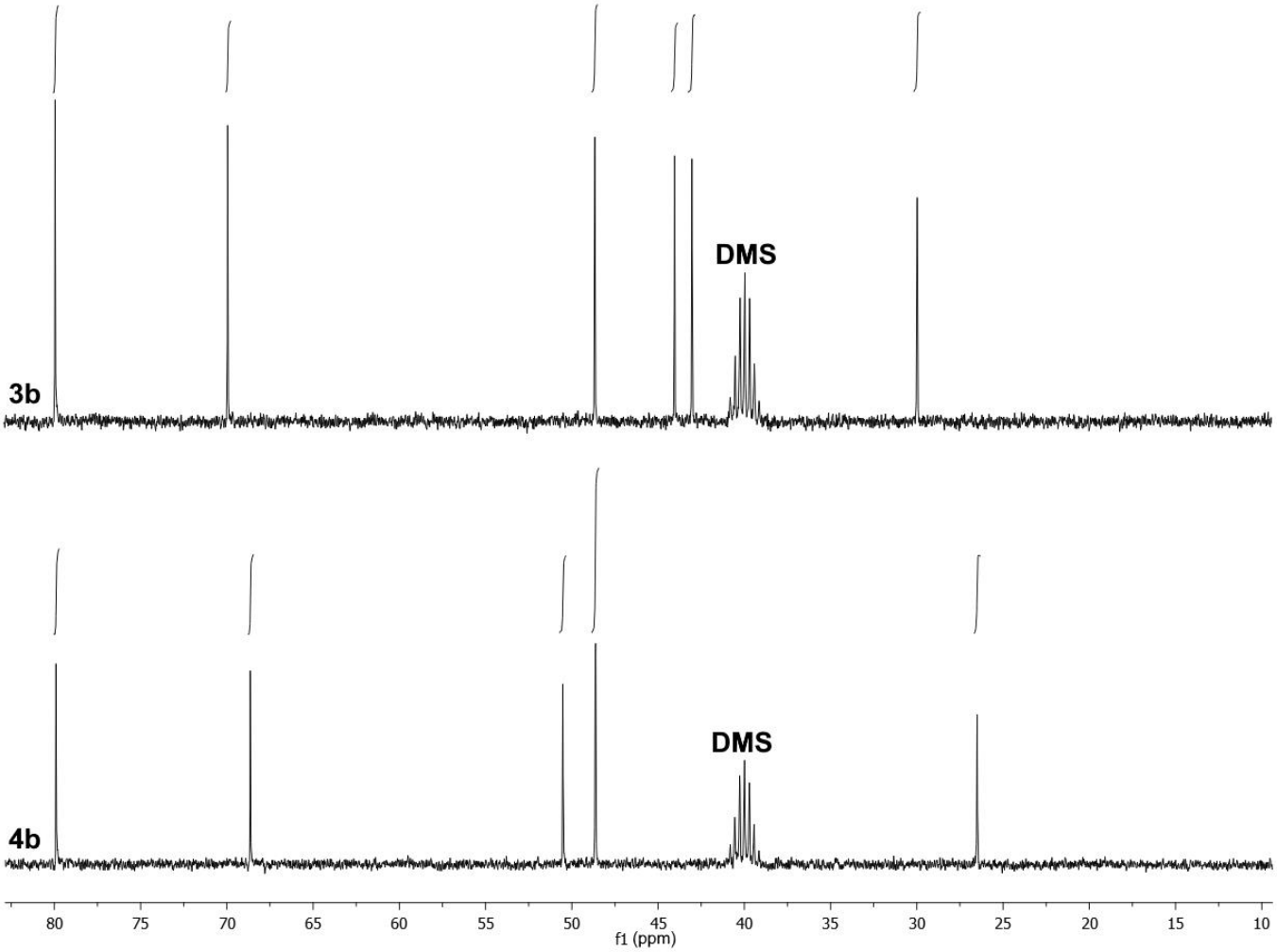

Figure S5. ^{13}C NMR spectra of compounds **3b**, **4b** in DMSO-d_6.

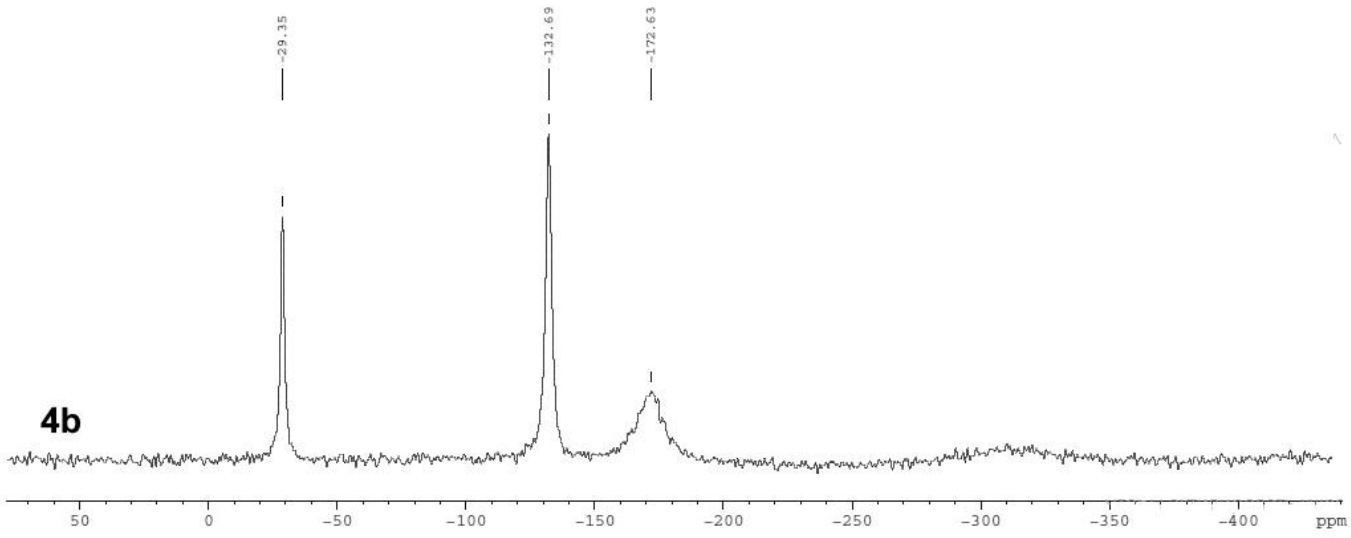

Figure S6. ^{14}N NMR spectra of compound **4b** in DMSO-d_6.

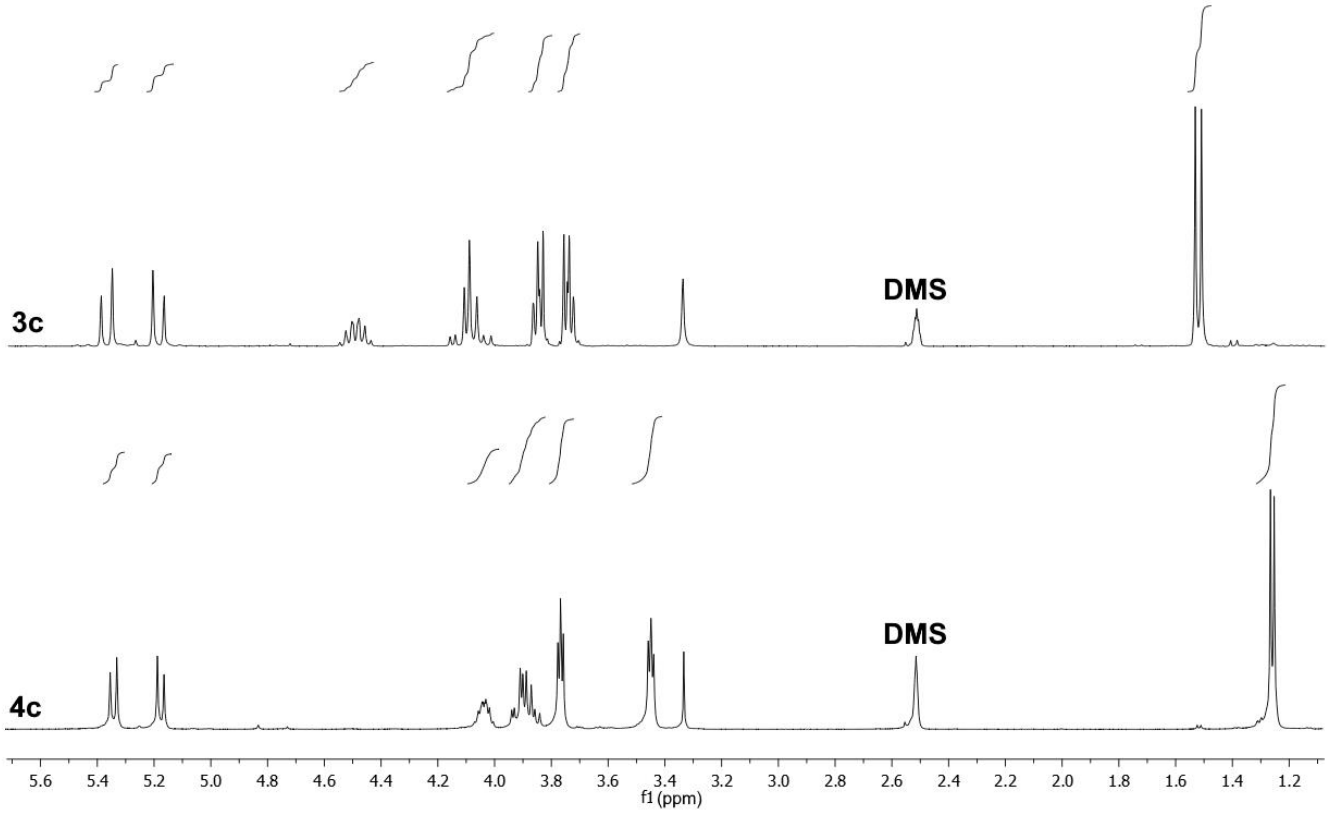

Figure S7.[1]H NMR spectra of compounds **3c**, **4c** in DMSO-d_6.

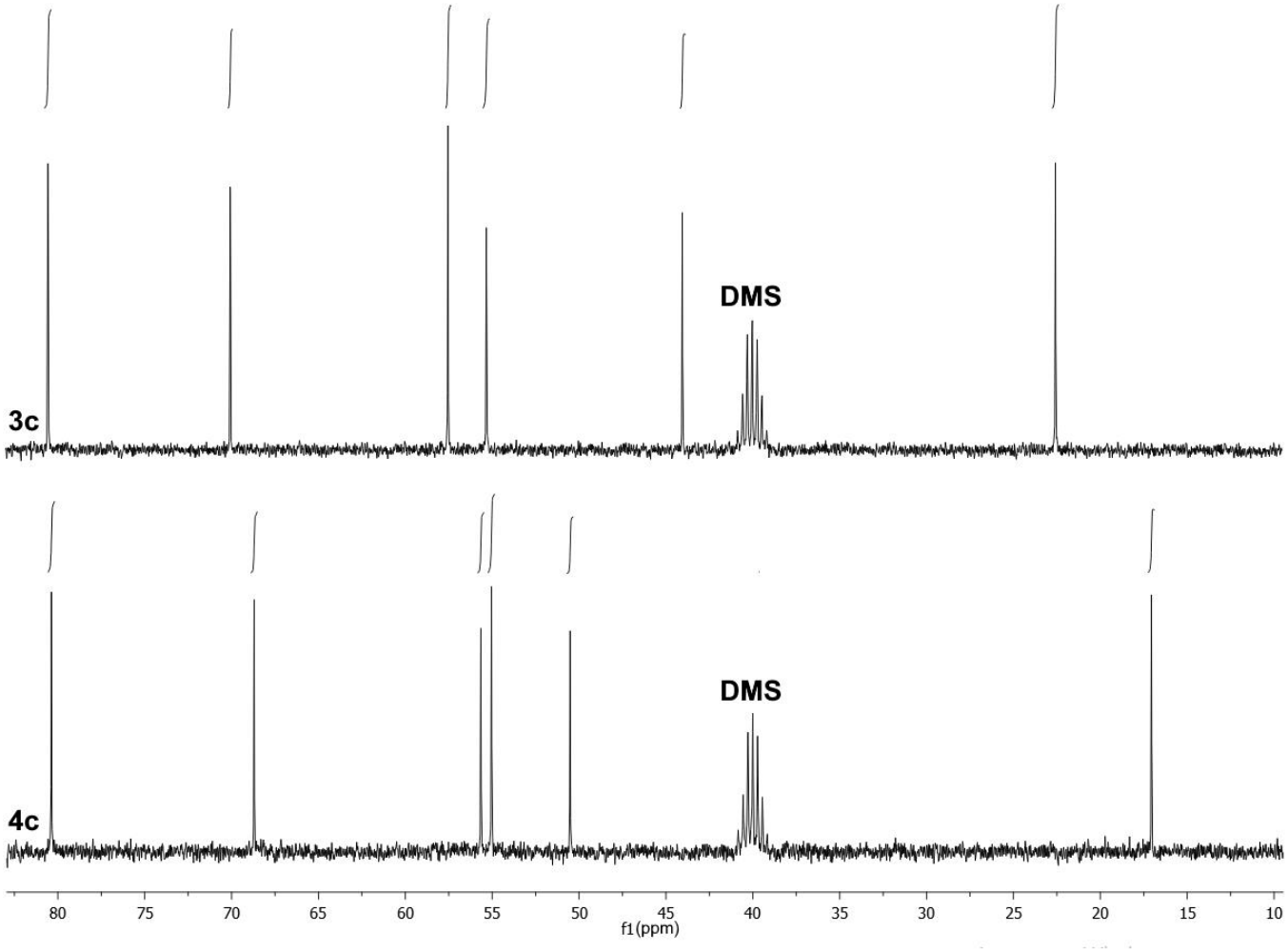

Figure S8. ^{13}C NMR spectra of compounds **3c**, **4c** in DMSO-d_6.

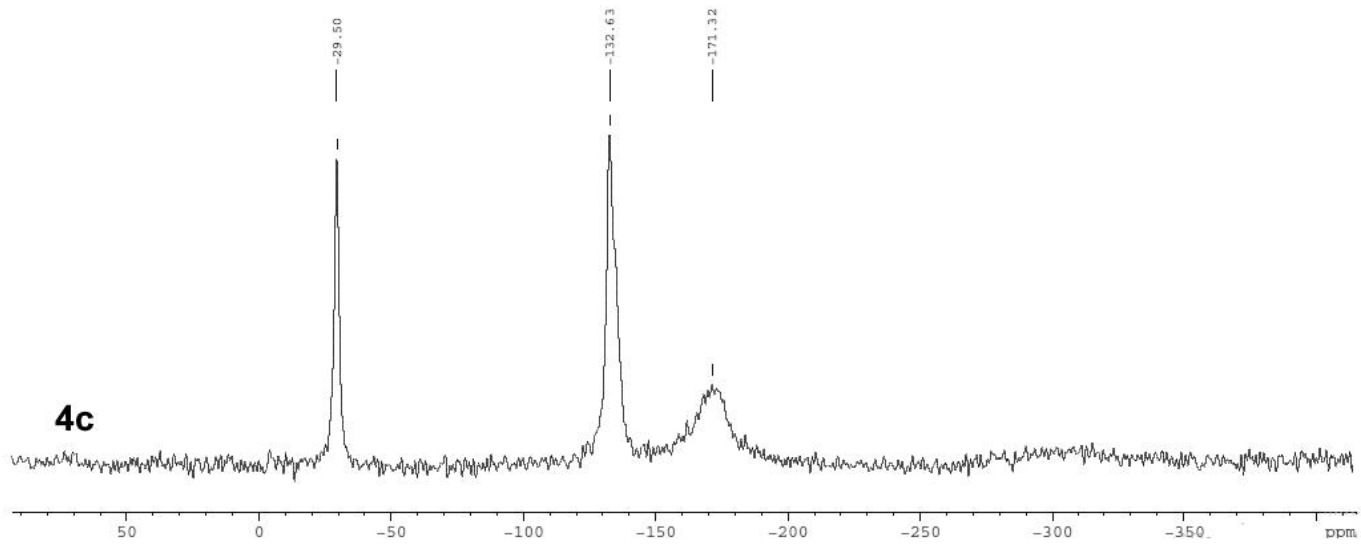

Figure S9. ^{14}N NMR spectra of compound **4c** in DMSO-d_6.

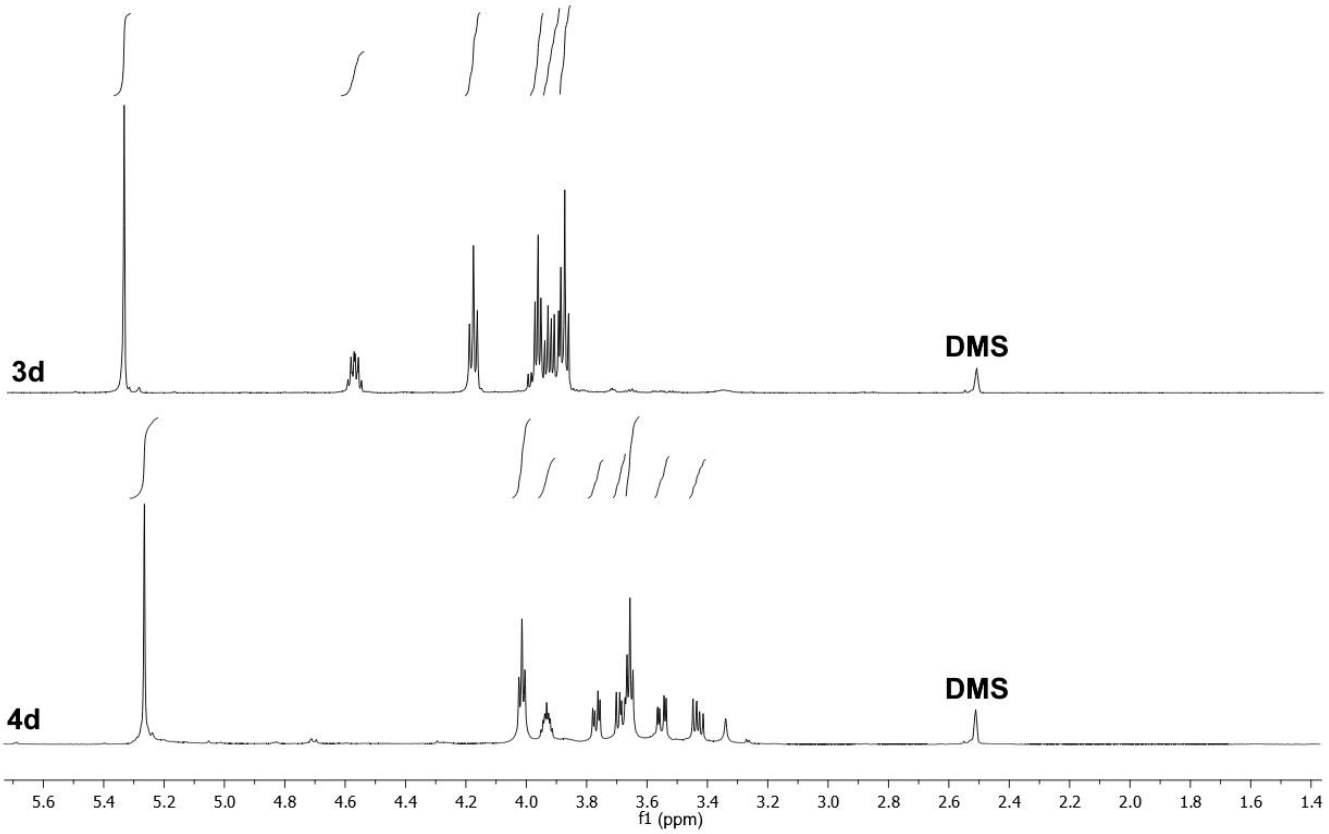

Figure S10. ^{1}H NMR spectra of compounds **3d**, **4d** in DMSO-d_6.

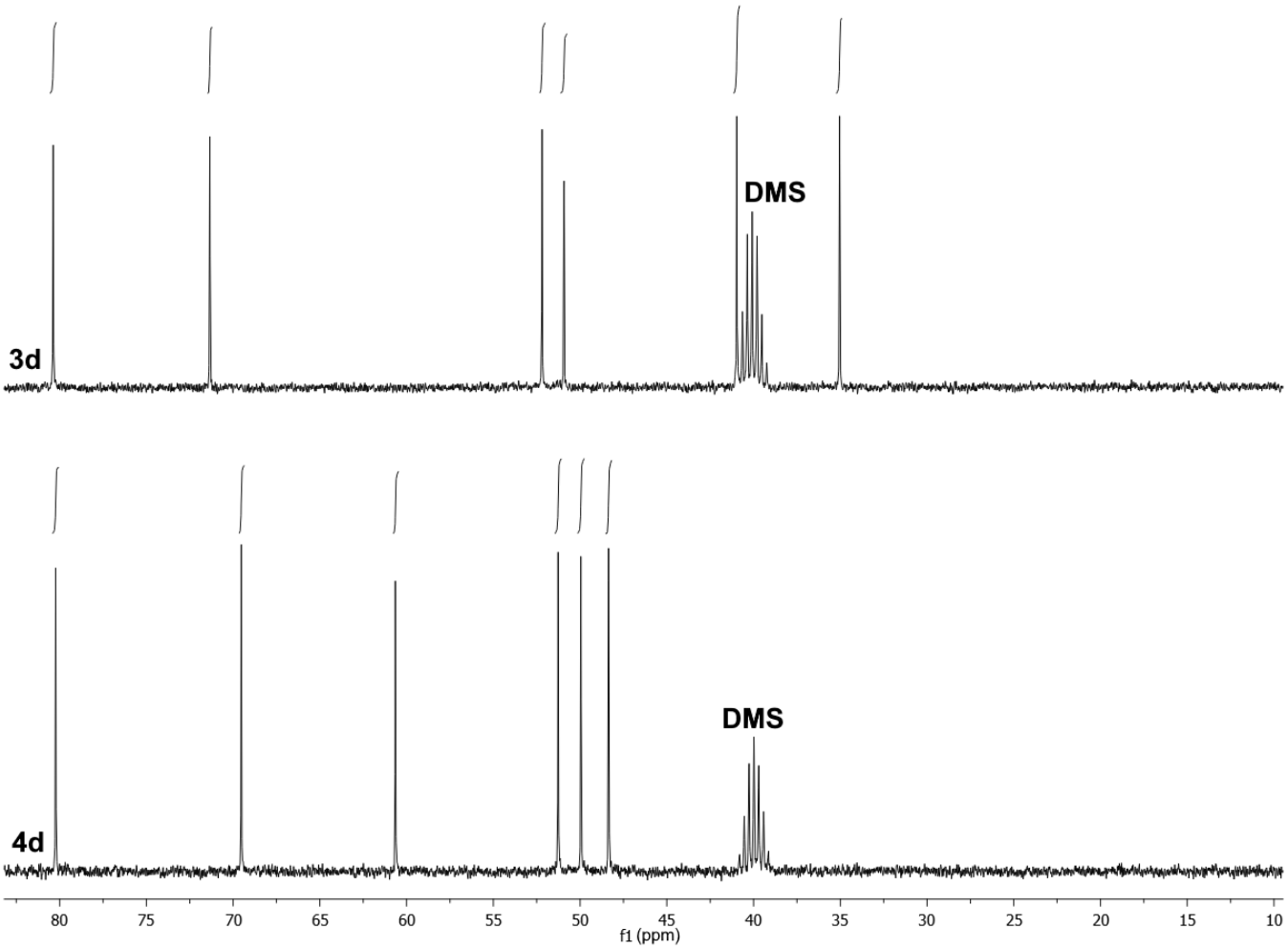

Figure S11. ^{13}C NMR spectra of compounds **3d**, **4d** in DMSO-d_6.

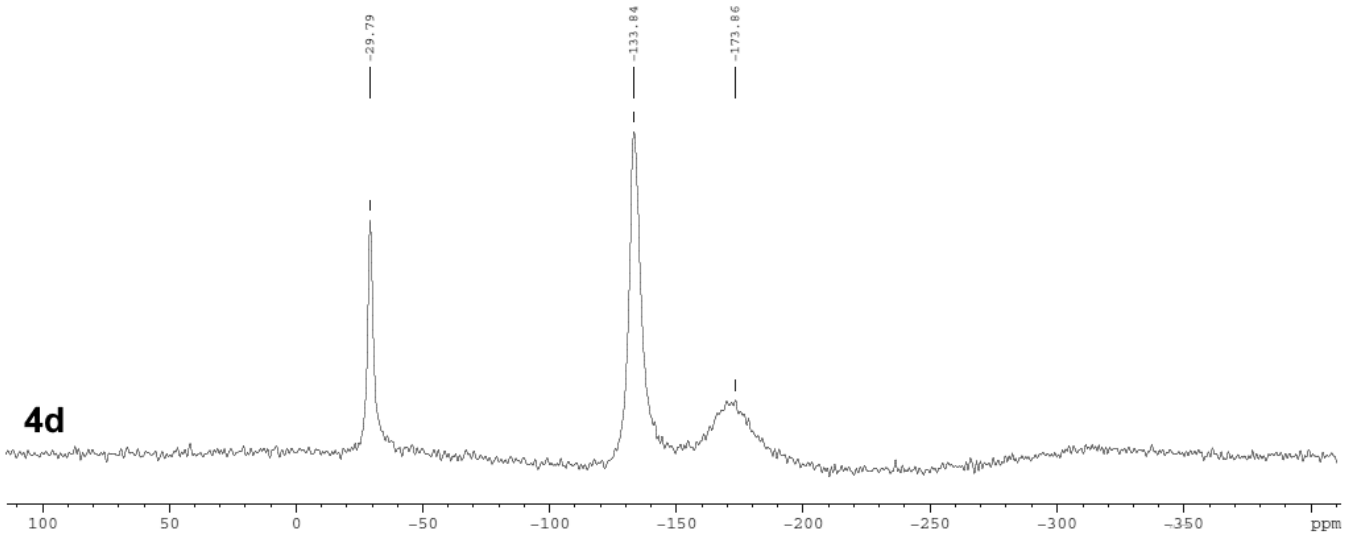

Figure S12. ^{14}N NMR spectra of compound **4d** in DMSO-d_6.

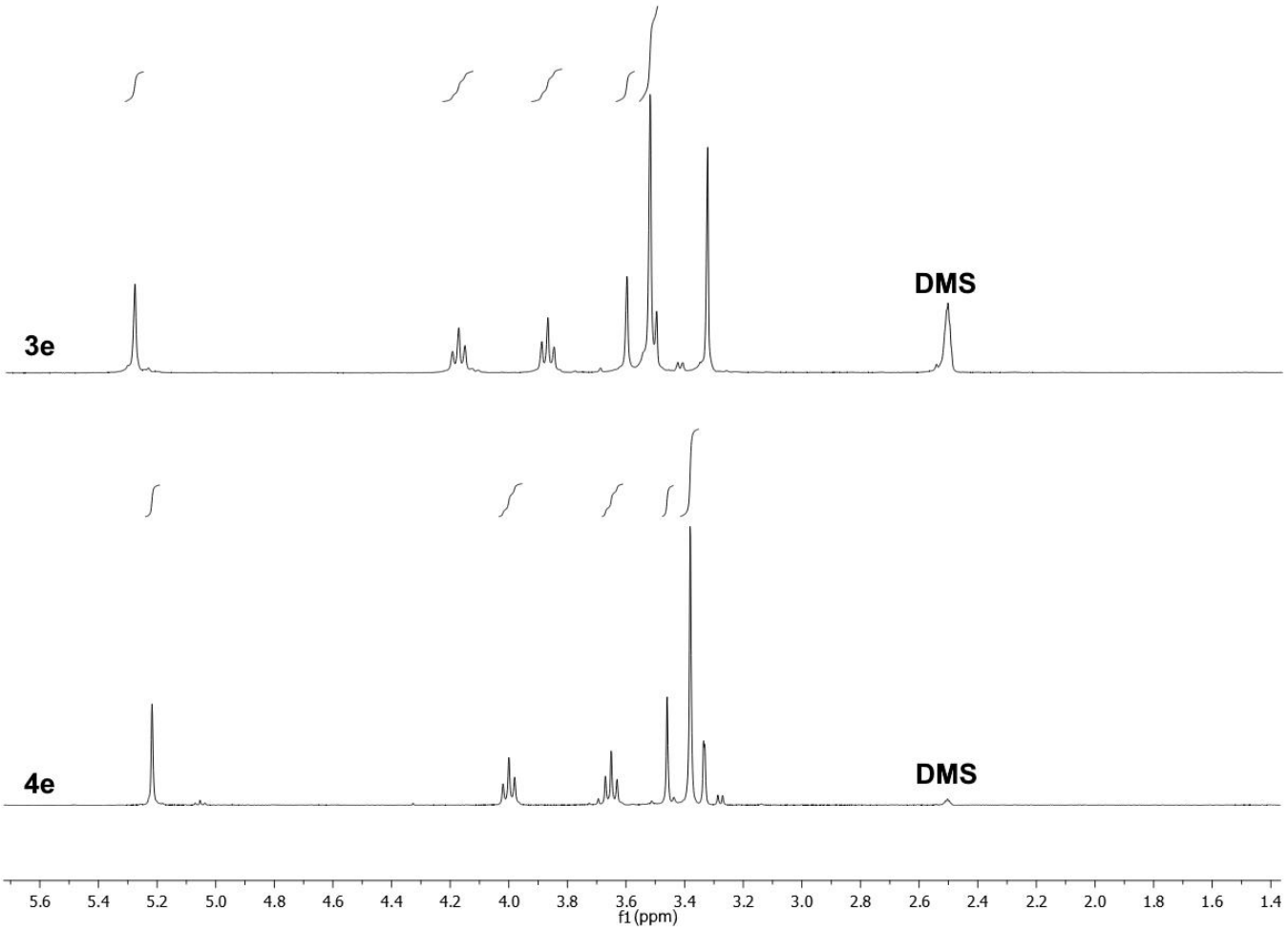

Figure S13. ^{1}H NMR spectra of compounds **3e**, **4e** in DMSO-d_6.

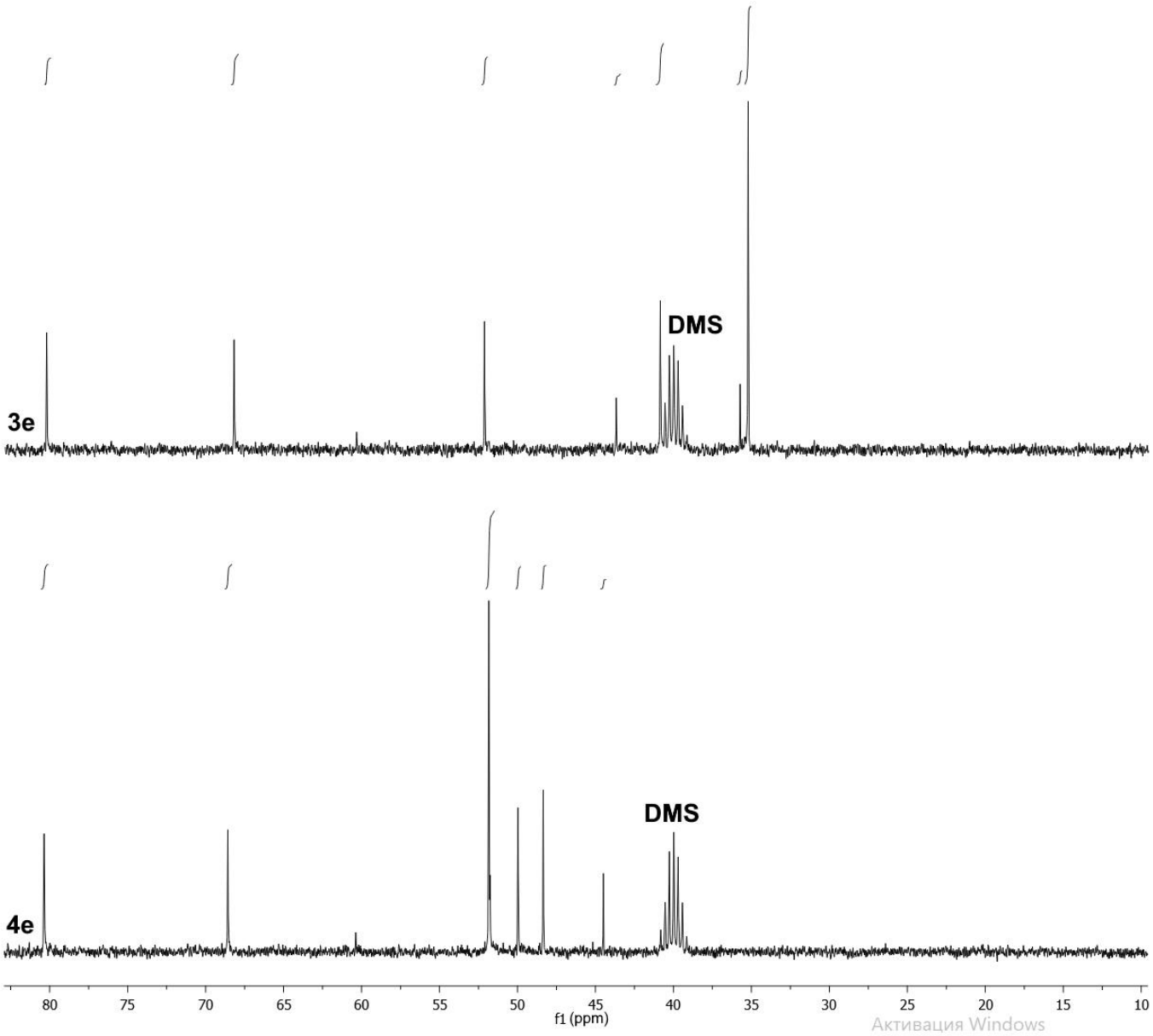

Figure S14. ^{13}C NMR spectra of compounds **3e**, **4e** in DMSO-d_6.

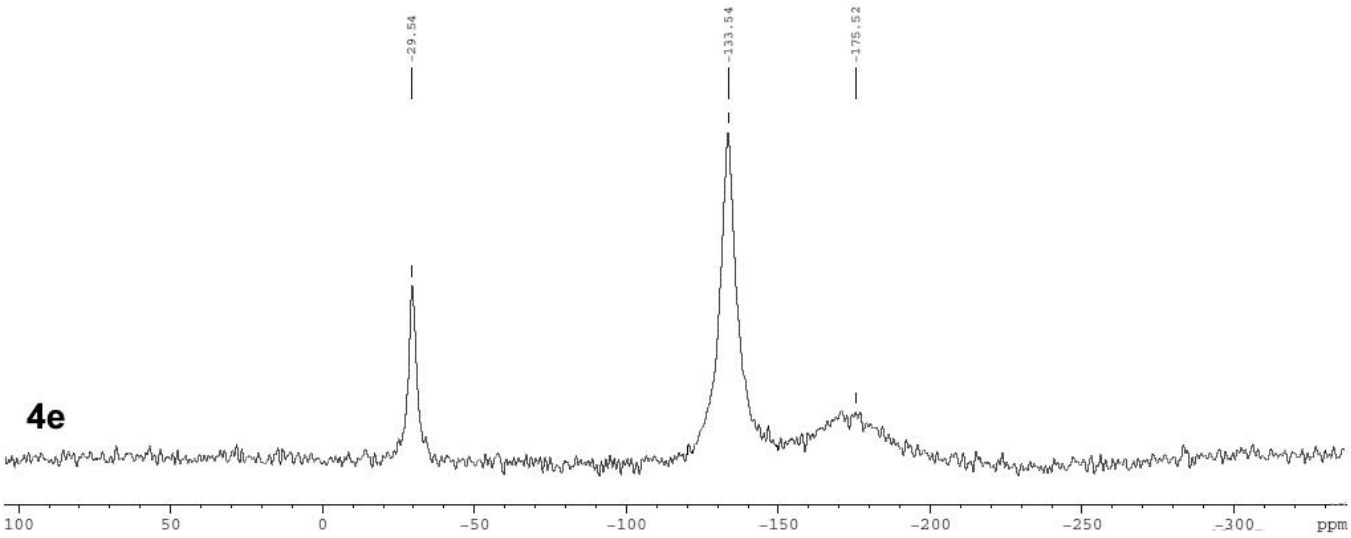

Figure S15. ^{14}N NMR spectra of compounds **4e** in DMSO-d_6.

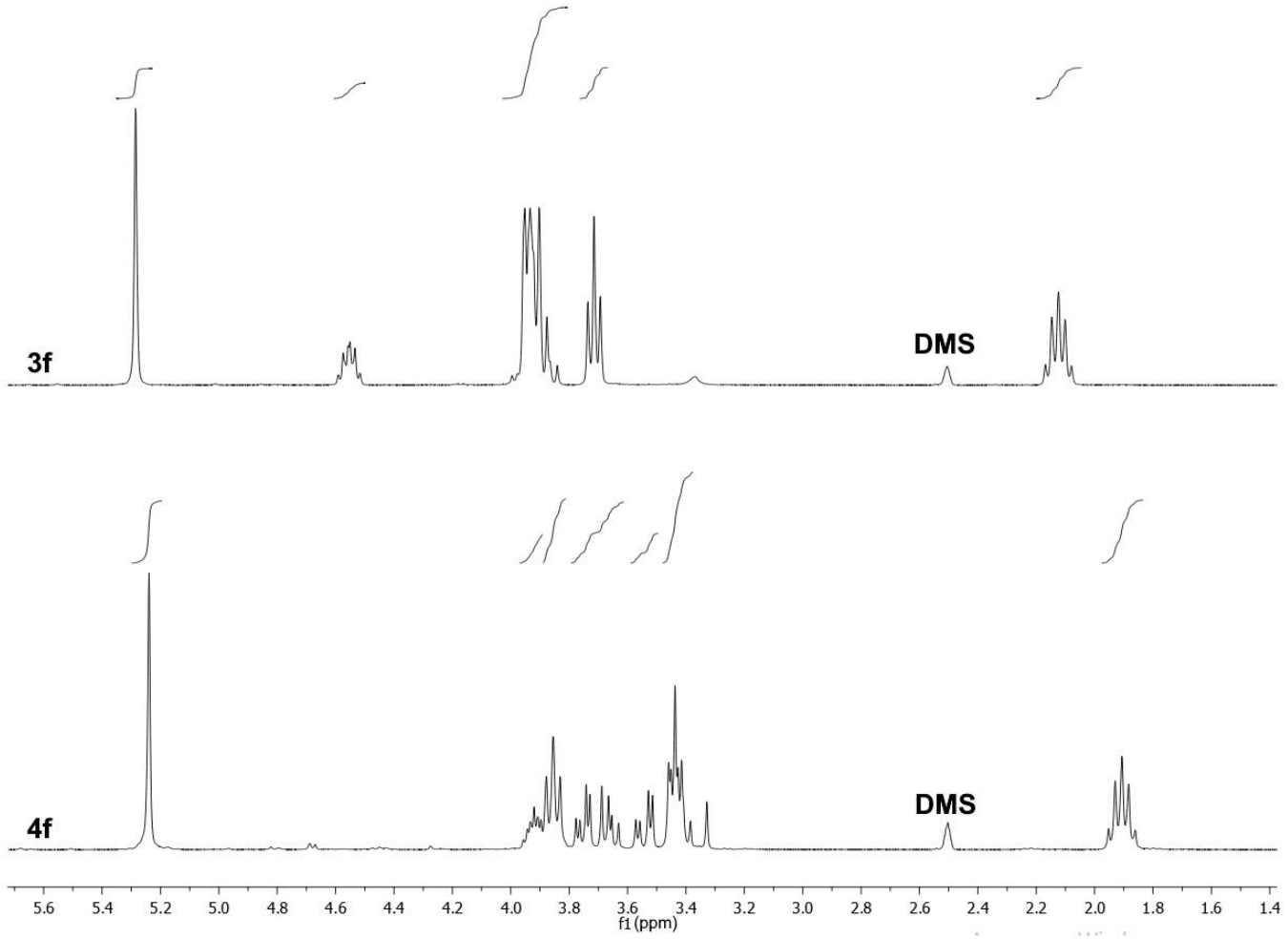

Figure S16. ^{1}H NMR spectra of compounds **3f**, **4f** in DMSO-d_6.

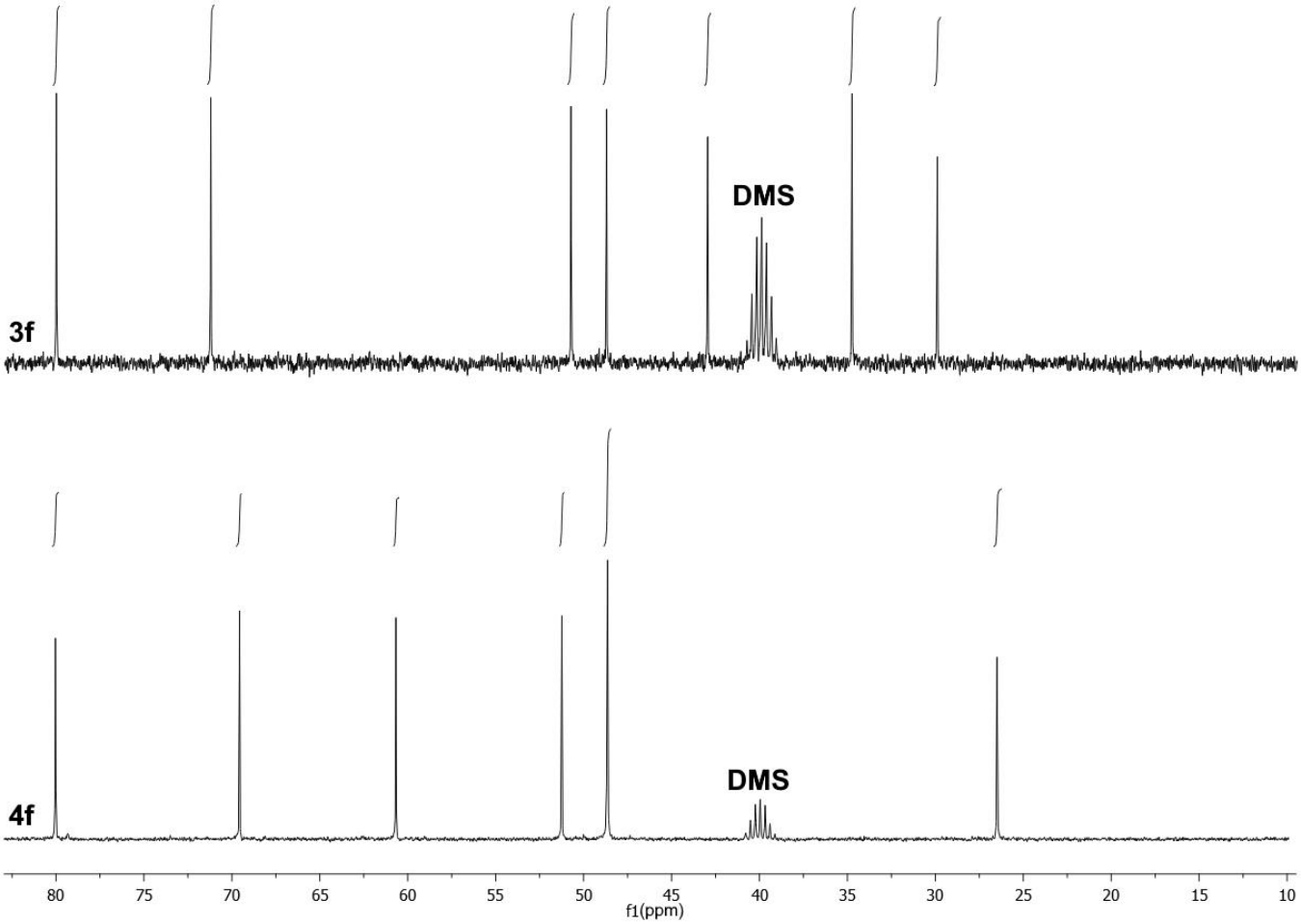

Figure S17. ^{13}C NMR spectra of compounds **3f**, **4f** in DMSO-d_6.

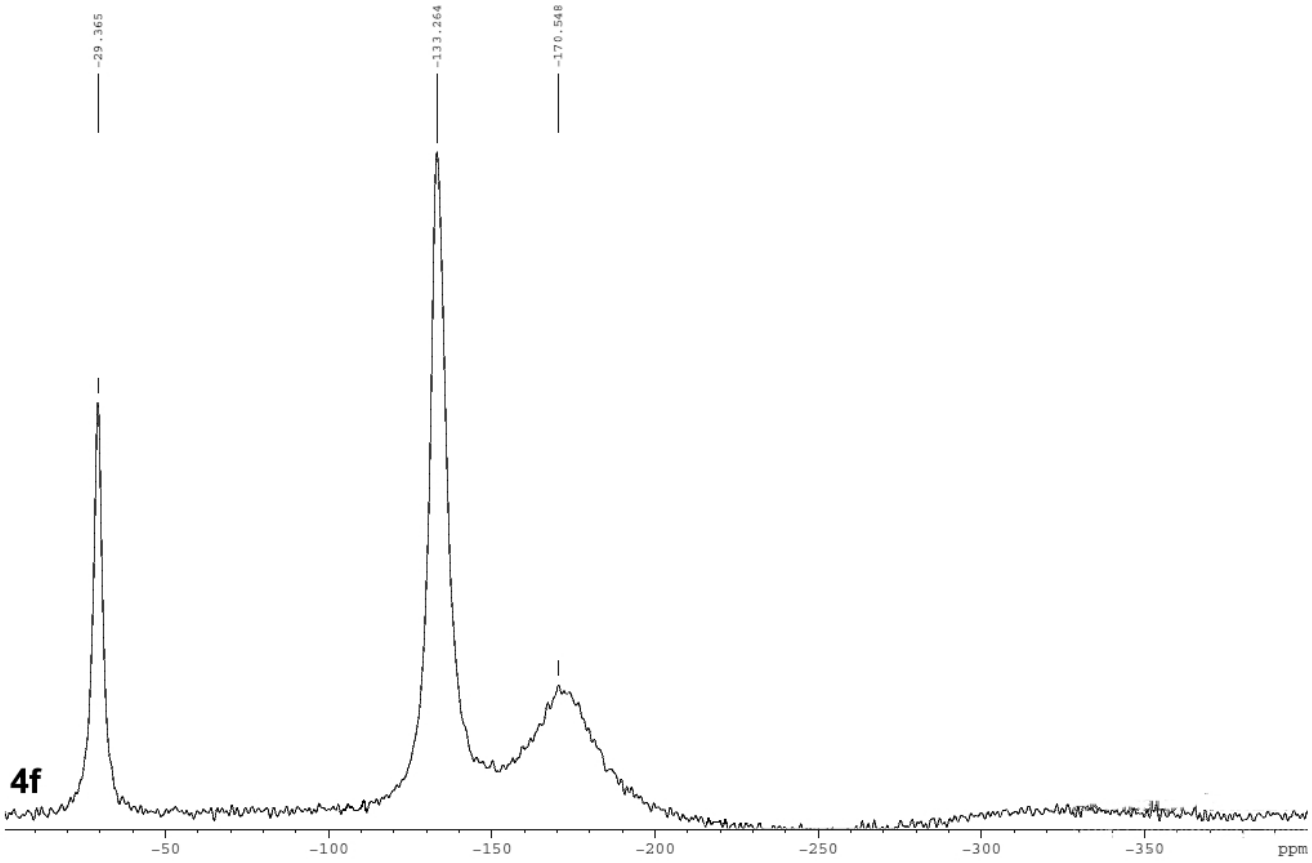

Figure S18. ^{14}N NMR spectra of compound **4f** in DMSO-d_6.

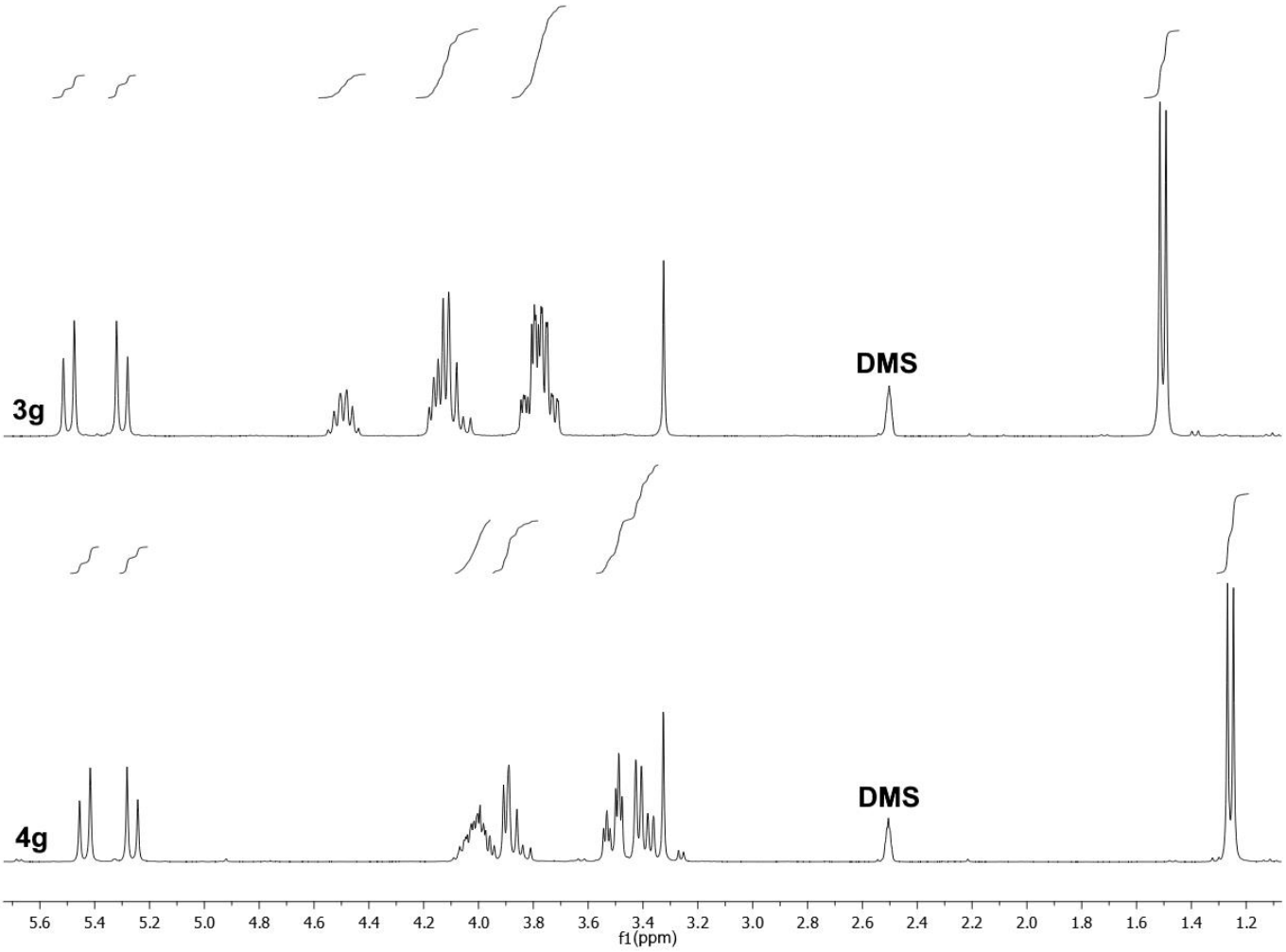

Figure S19.[1]H NMR spectra of compounds **3g**, **4g** in DMSO-d_6.

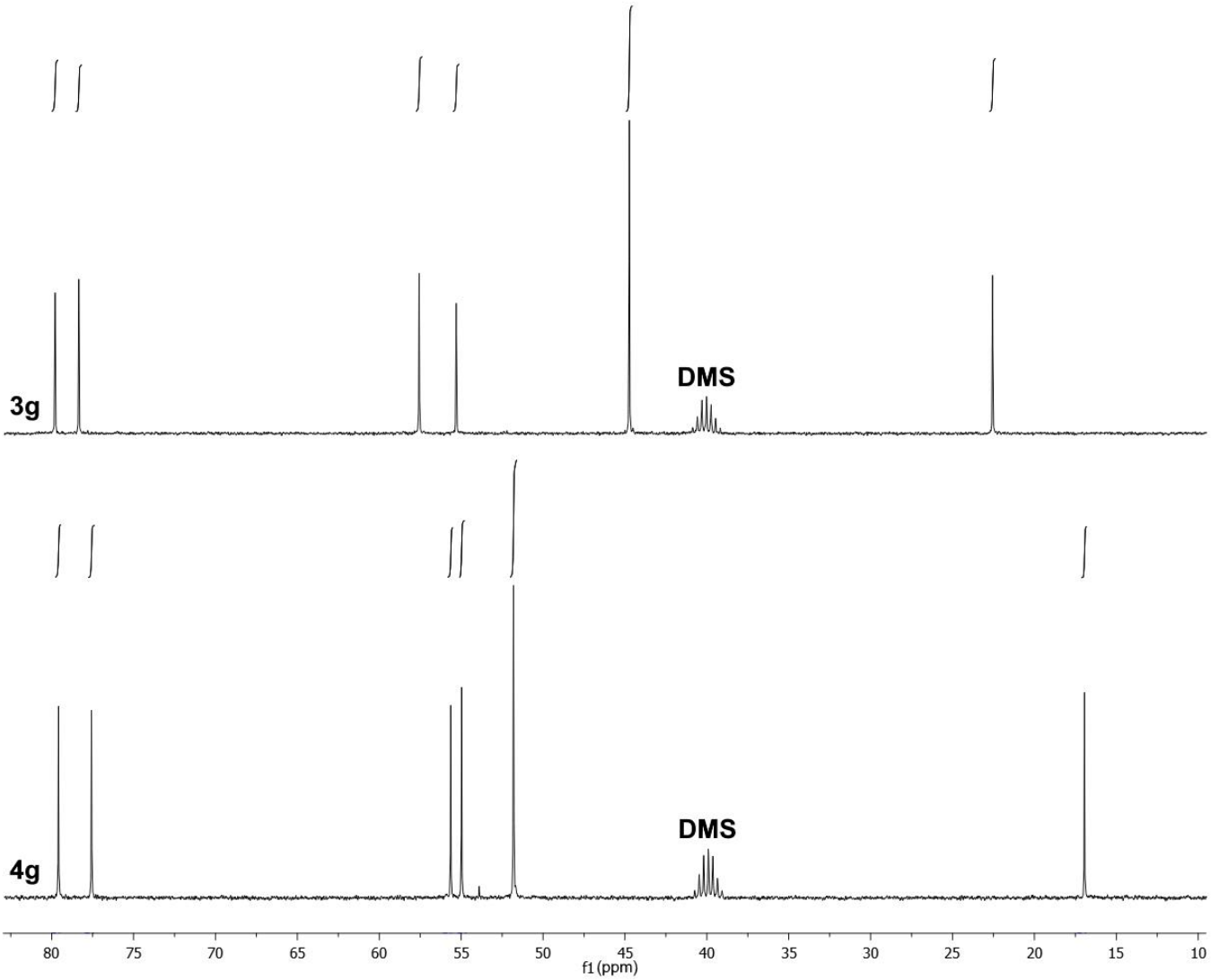

Figure S20. ^{13}C NMR spectra of compounds **3g**, **4g** in DMSO-d_6.

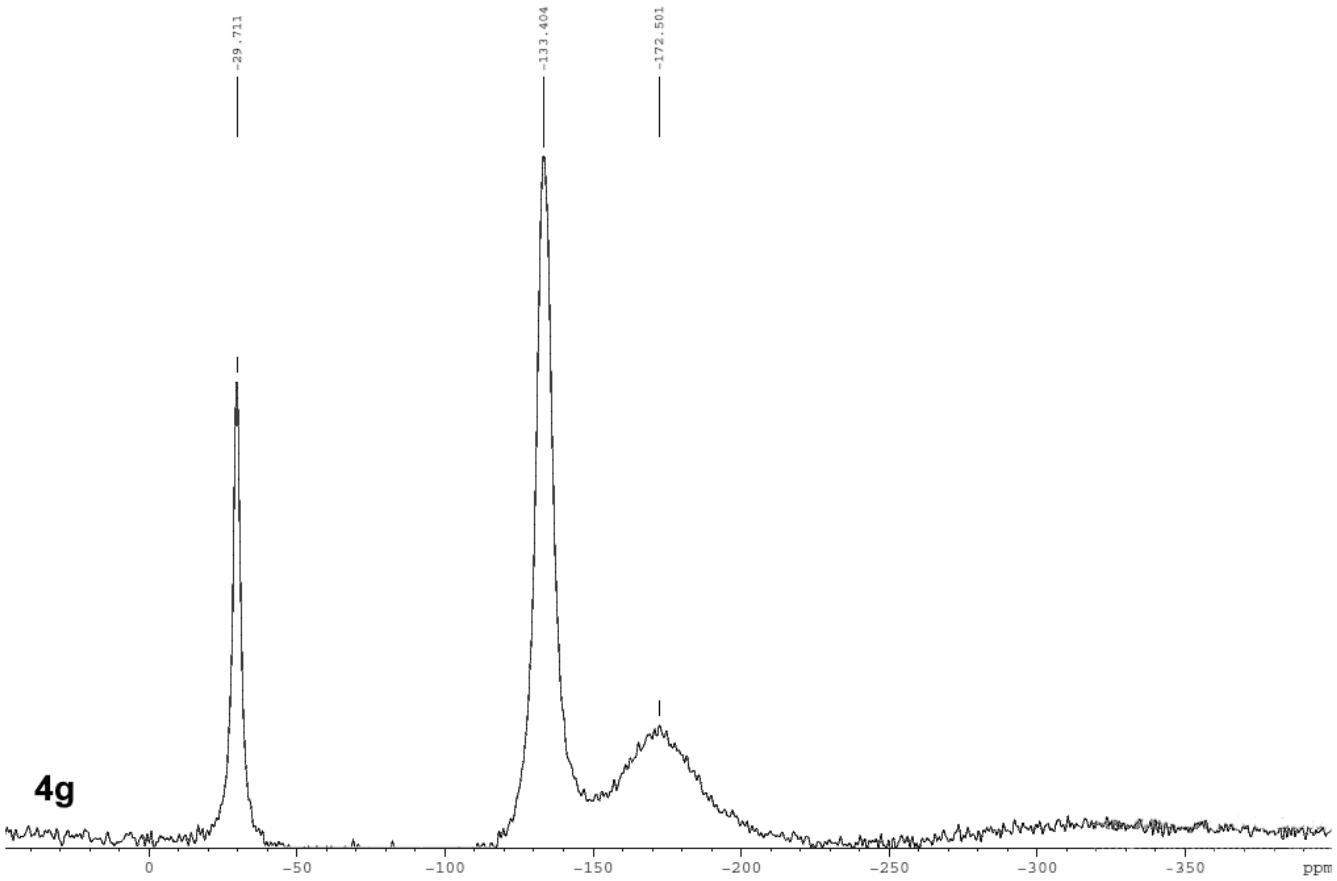

Figure S21. ^{14}N NMR spectra of compound **4g** in DMSO-d_6.