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New access to azido-substituted alkylnitramines

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^{1}H, ^{13}C and ^{14}N NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker AVANCE AM300 and DRX500 spectrometers: the quintet of residual protons of the deuterated solvent at δ 2.505 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 device at a heating rate of 2 °C/min.

1,4-Dichloro-2-nitro-2-azabutane 2a.

To thionyl chloride (250 ml, 3.45 mol) with intensive stirring in a water bath, H_2O (5.2 ml, 0.29 mol) is gradually added, and this was stirred at room temperature for 1 hour. After that, DMF (2.6 ml) and $BF_3{\times}Et_2O$ (2.6 ml) are added. To the resulting solution, under vigorous stirring, *N*-nitrooxazolidine **1a** (37.33 g, 0.32 mol) is added. The mixture is left overnight at room temperature. Then, the mixture is boiled at reflux for 25 h, and excess thionyl chloride is distilled off in vacuum. The resulting light yellow non-viscous liquid (53.70 g, 0.31 mol) (97%) is identified to be a crude 1,4-dichloro-2-nitro-2-azabutane **2a** (approx. 98% mol, according to ^{1}H NMR spectroscopy data). The material is fractionally distilled, yielding 44.98 g (0.26 mol, 81%) of product **2a** (99+% mol, according to ^{1}H NMR spectroscopy data), b.p. 62.5°C (0.29 Torr); IR, ν, cm^{-1}: 1270 (NNO_2 sym.), 1557 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, $CDCl_3$) 3.86 (t, *J*=5.8 Hz, 2H, $CH_2\underline{CH_2}Cl$), 4.00 (t, *J*=5.7 Hz, 2H, $N\underline{CH_2}CH_2Cl$), 5.69 (s, 2H, $ClCH_2NNO_2$) (Fig. S1); ^{13}C NMR δ (75 MHz, DMSO-d_6) 40.33 (CH_2Cl), 51.79 (CH_2NNO_2), 73.38 (NCH_2Cl) (Fig. S3); Found %: C 20.82; H 3.59; N 15.92. $C_3H_6Cl_2N_2O_2$. Calculated %: C 20.83; H 3.50; N 16.19.

1,4-Dichloro-2-nitro-2-azapentane 2b.

Starting from 5-methyl-*N*-nitrooxazolidine **1b** (73.51 g, 0.56 mol) by the similar procedure as for **2a**, a light yellow non-viscous liquid (99.4g, 95%) of crude material **2b** (approx. 98% mol, according to ^{1}H NMR) is obtained. The crude product **2b** is fractionally distilled to give 81.88 g (78%) of 1,4-dichloro-2-nitro-2-azapentane **2b** (approx. 99+% mol, according to ^{1}H NMR), b.p. 52.5°C (0.20 Torr); IR, ν, cm^{-1}: 1185 (NNO_2 sym.), 1557 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 500 MHz, $CDCl_3$) 1.65 (d, *J*=6.7 Hz, $\underline{CH_3}CH$), 3.77 (dd, *J*=15.2, 9.0 Hz, 1H, $N\underline{CH_2}CH$), 4.21 (dd, *J*=15.3, 3.0 Hz, 1H, $N\underline{CH_2}CH$), 4.47 (m, 1H, CHCl), 5.52 (d, *J*=11.8, 1H, $ClCH_2NNO_2$), 5.97 (d, *J*=11.9, 1H, $ClCH_2NNO_2$) (Fig. S1). ^{13}C NMR δ (75 MHz, DMSO-d_6) 21.99 ($\underline{CH_3}CH$), 56.93 (CH_2NNO_2), 60.42 (CHCl), 73.57 (NCH_2Cl) (Fig. S6); Found %: C 25.19; H 3.93; N 14.68. $C_4H_8Cl_2N_2O_2$. Calculated %: C 25.69; H 4.31; N 14.98.

1,5-Dichloro-2-nitro-2-azapentane 2c.

Starting from N-nitroperhydro-1,3-oxazine **1c**, by the similar procedure as for **2a**, light yellow non-viscous liquid (20.16 g, 99%) of crude product **2c** (approx. 99% mol, according to ^{1}H NMR) is obtained. The crude material is fractionally distilled to give 15.69 g (76.3%) of 1,5-dichloro-2-nitro-2-azapentane **2c** (approx. 99+% mol, according to ^{1}H NMR), b.p. 84.0°C (0.33 Torr); IR, ν, cm^{-1}: 1200 (NNO_2 sym.), 1550 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 500 MHz, $CDCl_3$) 2.28 (m, 2H, $CH_2\underline{CH_2}$ CH_2Cl), 3.66 (t, *J*=6.0 Hz, 2H, CH_2Cl), 3.97 (t, *J*=6.7 Hz, 2H, CH_2NNO_2), 5.65 (s, 2H, $ClCH_2NNO_2$) (Fig. S1). ^{13}C NMR δ (75 MHz, DMSO-d_6) 29.46 ($CH_2\underline{CH_2}CH_2$), 42.41 (CH_2Cl), 48.60 (CH_2NNO_2), 73.16 (NCH_2Cl) (Fig. S9); Found %: C 25.78; H 3.96; N 15.52. $C_4H_8Cl_2N_2O_2$. Calculated %: C 25.69; H 4.31; N 14.98.

1,4-Diazido-2-nitro-2-azabutane 3a.

To a solution of NaN_3 (1.70 g, 26.2 mmol) and $CaCl_2$ (0.90 g, 8.1 mmol) in DMF (10 ml), 1,4-dichloro-2-nitro-2-azabutane **2a** (2.00 g, 11.56 mmol) is added with stirring. The resulting mixture is stirred at 95-100°C for 33 hours. The mixture is poured into water (40 ml) and extracted with ethyl acetate and hexane mixture (2:1, 1x40 ml and 1x20ml). The combined extracts are washed with water (4 x 20 ml), and the solvents are distilled off in vacuum. The residue is compound **3a**, a light yellow non-viscous liquid (1.83 g, 9.83 mmol, yield 85%, purity 99+% mol, according to ^{1}H NMR. T. decomp. 151°C; IR, ν, cm^{-1}: 1286 (NNO_2 sym.), 1538 (NNO_2 asym.), 2108 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 3.63 (t, *J*=5.8 Hz, 2H, $CH_2\underline{CH_2}N_3$), 4.02 (t, *J*=5.8 Hz, 2H, $N\underline{CH_2}CH_2N_3$), 5.32 (s, 2H, $N_3CH_2NNO_2$) (Fig. S2); ^{13}C NMR δ

(75 MHz, DMSO-d_6) 47.90 (CH_2N_3), 50.34 (CH_2NNO_2), 65.41 (NCH_2N_3) (Fig. S3); ^{14}N NMR, δ (21.69 MHz, DMSO-d_6) -169.11, -134.46, -30.48 (Fig. S4); Found %: C 19.29; H 3.40; N 59.66. $C_3H_6N_8O_2$. Calculated %: C 19.36; H 3.25; N 60.20.

1,4-Diazido-2-nitro-2-azapentane 3b.

Taking 1,4-dichloro-2-nitro-2-azapentane **2b** (1.58 g, 8.45 mmol), by the similar procedure as for **3a** (the temperature and the heating time are respectively 90-95°C and 15 hours), product **3b** was obtained as a light yellow non-viscous liquid (1.5 g, 89%, purity 99+% mol, according to ^{1}H NMR. T. decomp. 158°C; IR, ν, cm^{-1}: 1281 (NNO_2 sym.), 1540 (NNO_2 asym.), 2122 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.24 (d, *J*=6.4 Hz, $\underline{CH_3}CH$), 3.88 (m, 2H, $N\underline{CH_2}CH$), 3.98 (m, CHN_3), 5.31 (dd, *J*=42.3, 13.7 Hz, 2H, $N_3CH_2NNO_2$) (Fig. S5); ^{13}C NMR, δ (125.76 MHz, DMSO-d_6) 16.56 ($\underline{CH_3}CH$), 55.24 (CHN_3), 55.37 (CH_2NNO_2), 65.84 (NCH_2N_3) (Fig. S6); ^{14}N NMR, δ (36.14 MHz, DMSO-d_6) -166.89, -134.21, -29.11 (Fig. S7); Found %: C 24.94; H 3.41; N 56.10. $C_4H_8N_8O_2$. Calculated %: C 24.00; H 4.03; N 55.98.

1,5-Diazido-2-nitro-2-azapentane 3c.

Using 1,5-dichloro-2-nitro-2-azapentane **2c** (2.00 g, 10.69 mmol), by the similar procedure as for **3a** (temperature and heating time are respectively 90-95°C and 15 hours), product **3c** was obtained as a light yellow non-viscous liquid (2.06 g, 96%, purity 99+% mol, according to ^{1}H NMR). T. decomp. 163°C; IR, ν, cm^{-1}: 1287 (NNO_2 sym.), 1536 (NNO_2 asym.), 2104 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.87 (p, *J*=6.8 Hz, 2H, $CH_2\underline{CH_2}$ CH_2N_3), 3.43 (t, *J*=6.6 Hz, 2H, CH_2N_3), 3.86 (t, *J*=7.0 Hz, 2H, CH_2NNO_2), 5.31 (s, 2H, $N_3CH_2NNO_2$) (Fig. S8); ^{13}C NMR, δ (125.76 MHz, DMSO-d_6) 26.04 ($CH_2\underline{CH_2}CH_2$), 48.14 (CH_2N_3), 49.00 (CH_2NNO_2), 65.33 (NCH_2N_3) (Fig. S9); ^{14}N NMR, δ (36.14 MHz, DMSO-d_6) -171.36, -132.83, -28.92 (Fig. S10); Found %: C 24.94; H 3.77; N 59.76. $C_4H_8N_8O_2$. Calculated %: C 24.00; H 4.03; N 55.98.

4-Chloro-1-methoxy-2-nitro-2-azabutane 4a.

1,4-Dichloro-2-nitro-2-azabutane **2a** (2.14 g, 12.37 mmol) is added to absolute MeOH (7 ml). The solution is boiled with reflux for 3 h, and methanol is distilled off in vacuum. The resude is crude product **4a**, a colourless non-viscous liquid (2.05 g, 12.16 mmol, 98%, purity approx. 98% mol, according to ^{1}H NMR). The crude material is fractionally distilled to give 1.54 g (9.12 mmol, 74%) of the title product **4a** (purity 99+% mol, according to ^{1}H NMR), b.p. 75.0 °C (0.70 Torr); IR, ν, cm^{-1}: 1079 (C-O-C), 1283 (NNO_2 sym.), 1535 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 500 MHz, DMSO-d_6) 3.34 (s, 3H, CH_3O), 3.86 (t, *J*=6.3 Hz, 2H, CH_2Cl), 4.14 (t, *J*=6.3 Hz, 2H, $CH_2\underline{CH_2}NNO_2$), 5.16 (s, 2H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S2); ^{13}C NMR δ (75 MHz, DMSO-d_6) 40.91(CH_2Cl), 52.04 (CH_2NNO_2), 57.02 (CH_3O), 81.46 (OCH_2N) (Fig. S3); Found %: C 28.29; H 5.05; N 17.49. $C_4H_9Cl_1N_2O_3$. Calculated %: C 28.50; H 5.38; N 16.62.

4-Chloro-1-methoxy-2-nitro-2-azapentane 4b.

Using 1,4-dichloro-2-nitro-2-azapentane **2b**, by the similar procedure as for **4a** (the boiling time is 20 hours), crude product **4b** as a colourless non-viscous liquid (2.92 g, 15.99 mmol, 78%, purity approx. 98% mol, according to ^{1}H NMR) is obtained. The crude material is fractionally distilled to give 2.25 g (12.32 mmol, 60%) of the title compound **4b** (99+% mol, according to ^{1}H NMR), b.p. 72.5°C (0.64 Torr); IR, ν, cm^{-1}: 1094 (C-O-C), 1279 (NNO_2 sym.), 1537 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.50 (d, *J*=6.6 Hz, 3H, $\underline{CH_3}CH$), 3.34 (s, 3H, CH_3O), 4.08 (m, 2H, $CH\underline{CH_2}NNO_2$), 4.49 (m, 1H, CH), 5.05 (d, *J*=11.5 Hz, 1H, $CH_3O\underline{CH_2}NNO_2$), 5.26 (d, *J*=11.5 Hz, 1H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S5); ^{13}C NMR δ (75 MHz, DMSO-d_6) 22.56 ($\underline{CH_3}CH$), 55.27 (CH_2NNO_2), 57.07 (CH_3O), 57.53 (CHCl), 81.68 ($O\underline{CH_2}N$) (Fig. S6); Found %: C 32.47; H 6.07; N 16.33. $C_5H_{11}Cl_1N_2O_3$. Calculated %: C 32.89; H 6.07; N 15.34.

5-Chloro-1-methoxy-2-nitro-2-azapentane 4c.

Taking 1,5-dichloro-2-nitro-2-azapentane **2c**, by the similar procedure as for **4a**, crude product **4c** as a colourless non-viscous liquid (1.60 g, 8.76 mmol, 88%, purity approx. 98% mol, according to ^{1}H NMR) is obtained. The crude material is fractionally distilled to give 1.04 g (5.70 mmol, 57%) of the title product **4c** (purity 99+% mol, according to ^{1}H NMR), b.p. 89.5°C (0.59 Torr); IR, ν, cm^{-1}: 1084 (C-O-C), 1281 (NNO_2 sym.), 1531 (NNO_2 asym.); ^{1}H NMR, δ (*J*, 500 MHz, DMSO-d_6) 2.09 (p, *J*=6.6Hz, 2H, $CH_2\underline{CH_2}CH_2$), 3.32 (s, 3H, CH_3O), 3.70 (t, *J*=6.4 Hz, 2H, CH_2Cl), 3.89 (t, *J*=7.0Hz, 2H, $CH_2\underline{CH_2}NNO_2$),

5.12 (s, 2H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S8); ^{13}C NMR δ (75 MHz, DMSO-d_6) 29.99 ($CH_2\underline{CH_2}CH_2$), 43.04(CH_2Cl), 48.63 (CH_2NNO_2), 57.03 (CH_3O), 81.19 (OCH_2N) (Fig. S9); Found %: C 32.59; H 5.89; N 15.36. $C_5H_{11}Cl_1N_2O_3$. Calculated %: C 32.89; H 6.07; N 15.34.

4-Azido-1-methoxy-2-nitro-2-azabutane 5a.

4-Chloro-1-methoxy-2-nitro-2-azabutane **4a** (1.59 g, 9.43 mmol) is added with vigorous stirring to ssolution of NaN_3 (1.86 g, 28.6 mmol) and tetrabutylammonium bromide (TBAB, 0.47 g, 4.2 mmol) in water (10 ml). The resulting mixture is refluxed with stirring for 12 hours. After cooling, the mixture is extracted with benzene (2 x 10 ml). The combined extracts is washed with water (2 x 8 ml), and benzene is distilled off in vacuum. The residue is the title compound **5a**, a light yellow non-viscous liquid (1.42 g, 8.11 mmol, 86%, purity 99+% mol, according to ^1H NMR), T. decomp. 213°C; IR, ν, cm^{-1}: 1091 (C-O-C), 1281 (NNO_2 sym.), 1536 (NNO_2 asym.), 2107 (N_3); ^1H NMR, δ (*J*, 500 MHz, DMSO-d_6) 3.34 (s, 3H, CH_3O), 3.64 (t, *J*=5.9 Hz, 2H, CH_2N_3), 3.99 (t, *J*=5.9 Hz, 2H, $CH_2\underline{CH_2}NNO_2$), 5.14 (s, 2H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S2); ^{13}C NMR δ (125.76 MHz, DMSO-d_6) 47.94(CH_2N_3), 49.47 (CH_2NNO_2), 56.62 (CH_3O), 80.93 (OCH_2N) (Fig. S3); ^{14}N NMR δ (36.14 MHz, DMSO-d_6) -171.23, -132.99, -28.80 (Fig. S4); Found %: C 27.43; H 5.15; N 39.90. $C_4H_9N_5O_3$. Calculated %: C 27.43; H 5.18; N 39.99.

4-Azido-1-methoxy-2-nitro-2-azapentane 5b.

From 4-chloro-1-methoxy-2-nitro-2-azapentane **4b**, by the similar procedure as for **5a** (the boiling time is 35 hours), the title compound **5b** as a light yellow non-viscous liquid (1.11 g, 5.87 mmol, 68%, purity 99+% mol, according to ^1H NMR) is obtained. T. decomp. 187°C; IR, ν, cm^{-1}: 1098 (C-O-C), 1279 (NNO_2 sym.), 1536 (NNO_2 asym.), 2120 (N_3); ^1H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.24 (d, *J*=6.5 Hz, 3H, $\underline{CH_3}CH$), 3.34 (s, 3H, CH_3O), 3.87 (qd, *J*=14.9, 6.6 Hz, 2H, $CH\underline{CH_2}NNO_2$), 4.02 (dq, *J*=13.0, 6.5 Hz, 1H, CHN_3), 5.13 (dd, *J*=57.3, 11.5Hz, 2H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S5); ^{13}C NMR δ (150.90 MHz, DMSO-d_6) 16.63 ($\underline{CH_3}CH$), 54.62 (CHN_3), 55.20 ($CH\underline{CH_2}NNO_2$), 56.62 (CH_3O), 81.13 (OCH_2N) (Fig. S6); ^{14}N NMR δ (43.37 MHz, DMSO-d_6) -169.49, -135.04, -29.40 (Fig. S7); Found %: C 32.26; H 5.51; N 36.38. $C_5H_{11}N_5O_3$. Calculated %: C 31.75; H 5.86; N 37.02.

5-Azido-1-methoxy-2-nitro-2-azapentane 5c.

Starting from 5-chloro-1-methoxy-2-nitro-2-azapentane **4c** (1.39 g, 7.61 mmol), by the similar procedure as for **5a**, the title compound **5c** as a light yellow non-viscous liquid (1.27 g, 6.71 mmol, 88%, purity 99+% mol, according to ^{1}H NMR) is obtained. T. decomp. 202°C; IR, ν, cm^{-1}: 1094 (C-O-C), 1284 (NNO_2 sym.), 1533 (NNO_2 asym.), 2102 (N_3); ^{1}H NMR, δ (*J*, 300.13 MHz, DMSO-d_6) 1.89 (m, 2H, $CH_2\underline{CH_2}CH_2$), 3.32 (s, 3H, CH_3O), 3.42 (t, J=6.6 Hz, 2H, CH_2N_3), 3.83 (m, 2H, $CH_2\underline{CH_2}NNO_2$), 5.11 (s, 2H, $CH_3O\underline{CH_2}NNO_2$) (Fig. S8); ^{13}C NMR δ (125.76 MHz, DMSO-d_6) 26.48 ($CH_2\underline{CH_2}CH_2$), 48.58 (CH_2N_3), 48,66 (CH_2NNO_2), 57.01 (CH_3O), 81.14 (OCH_2N) (Fig. S9); ^{14}N NMR δ (43.37 MHz, DMSO-d_6) -171.86, -132.67, -28.59 (Fig. S10); Found %: C 31.74; H 5.83; N 37.10. $C_5H_{11}N_5O_3$. Calculated %: C 31.75; H 5.86; N 37.02.

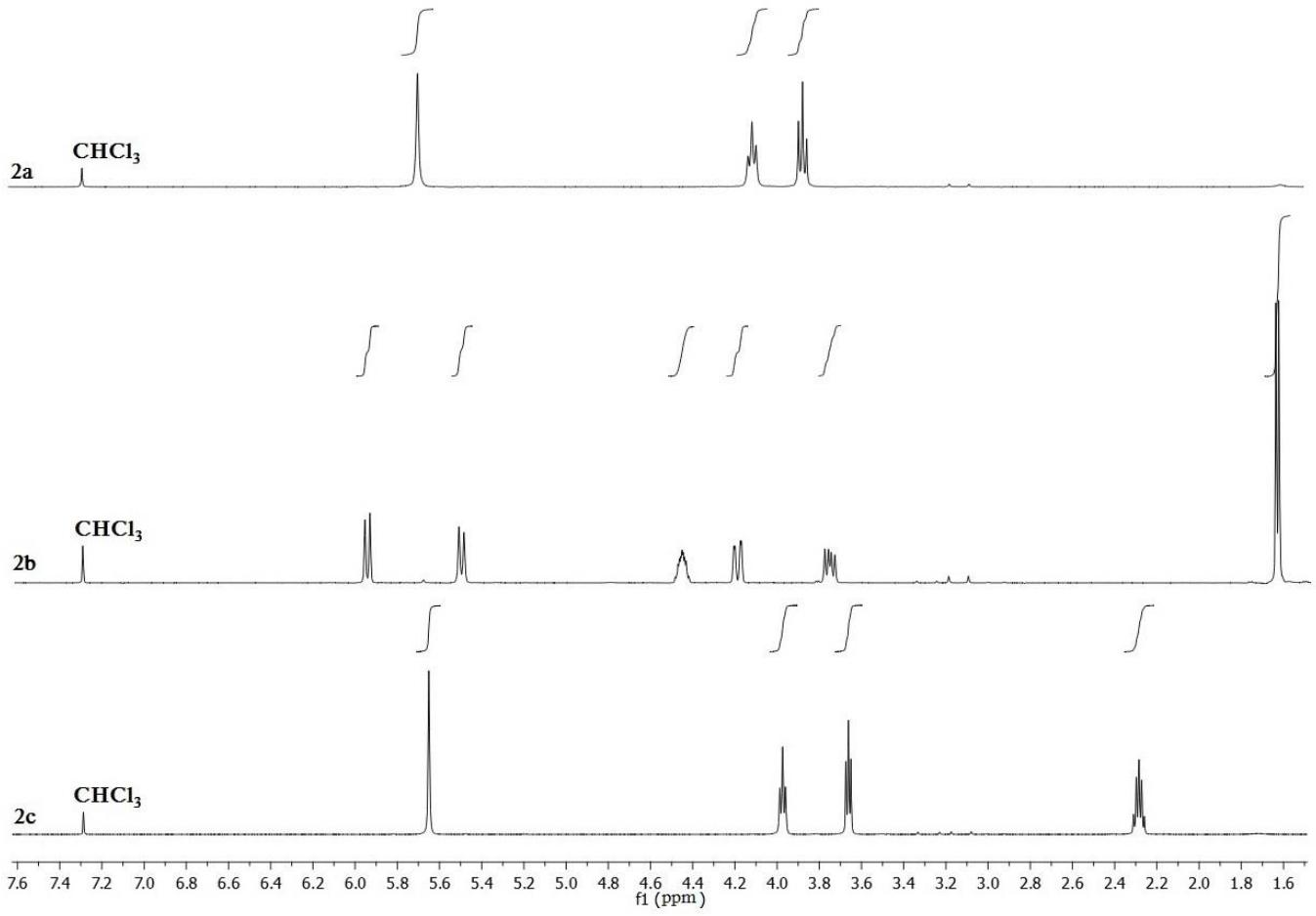

Figure S1.^{1}H NMR spectra in $CDCl_3$ of 1,4-dichloro-2-nitro-2-azabuthane **2a**; 1,4-dichloro-2-nitro-2-azapentane **2b**; 1,5-dichloro-2-nitro-2-azabuthane **2c**.

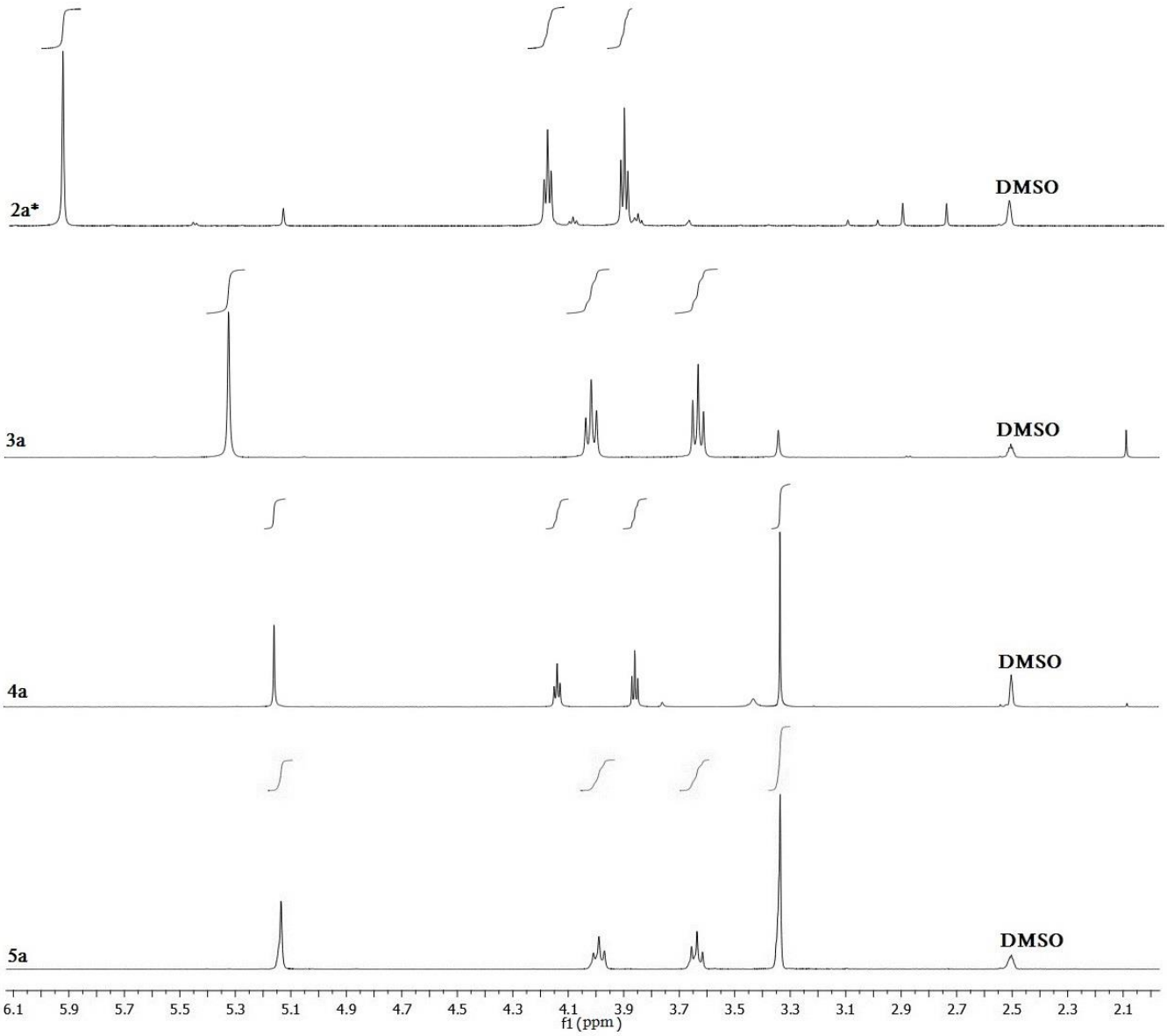

Figure S2. ^{1}H NMR spectra in DMSO-d_6 of compounds **2a-5a**. (*- **2a** in DMSO-d_6).

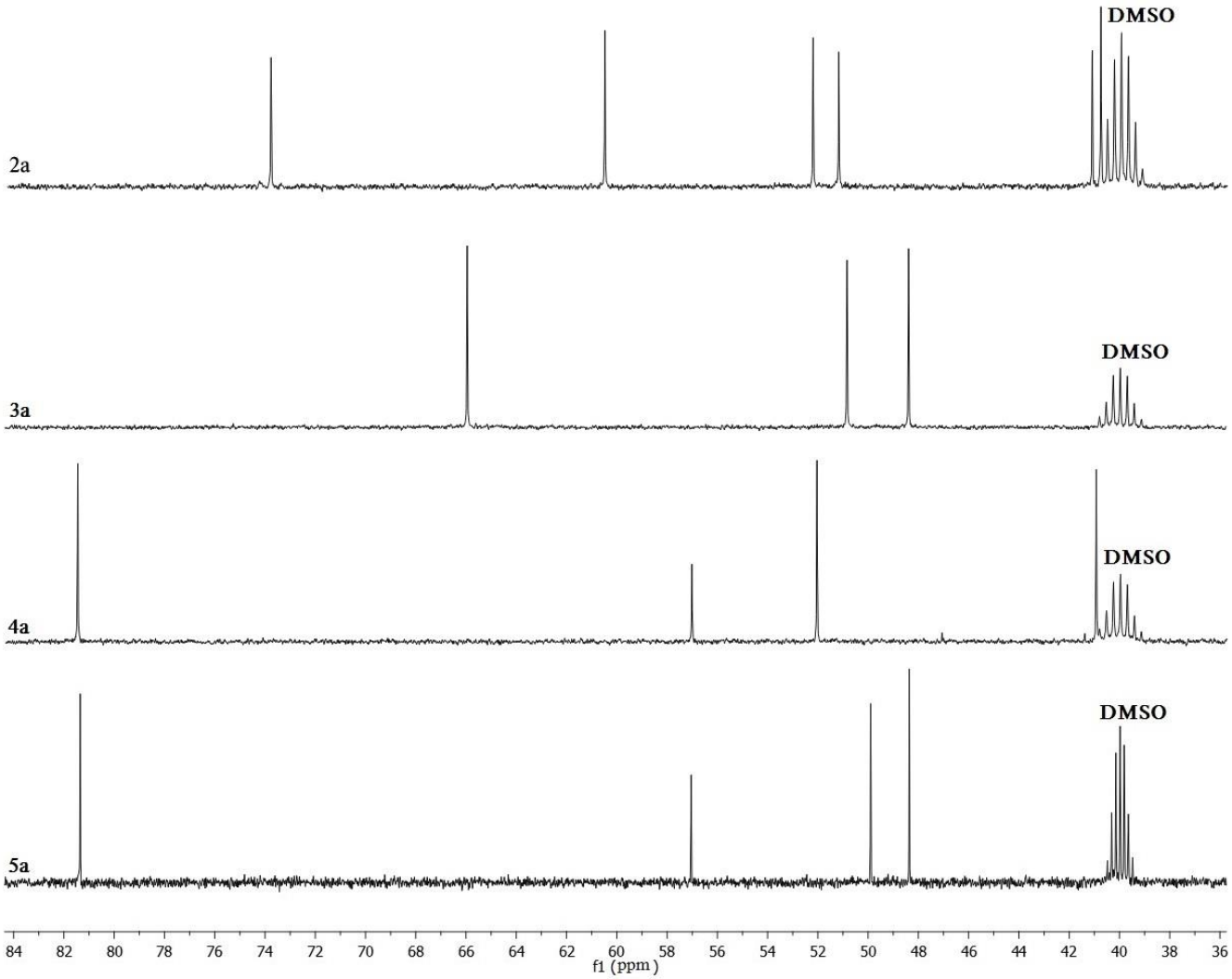

Figure S3. ^{13}C NMR spectra in DMSO-d_6 of compounds **2a-5a**.

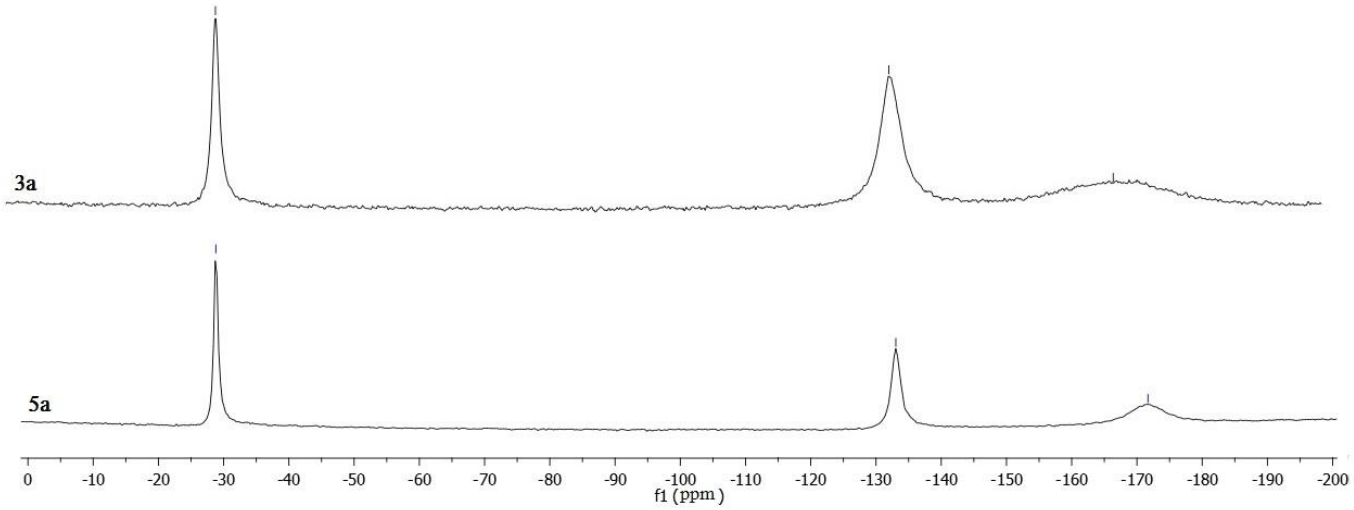

Figure S4. ^{14}N NMR spectra in DMSO-d_6 of compounds **3a**, **5a**.

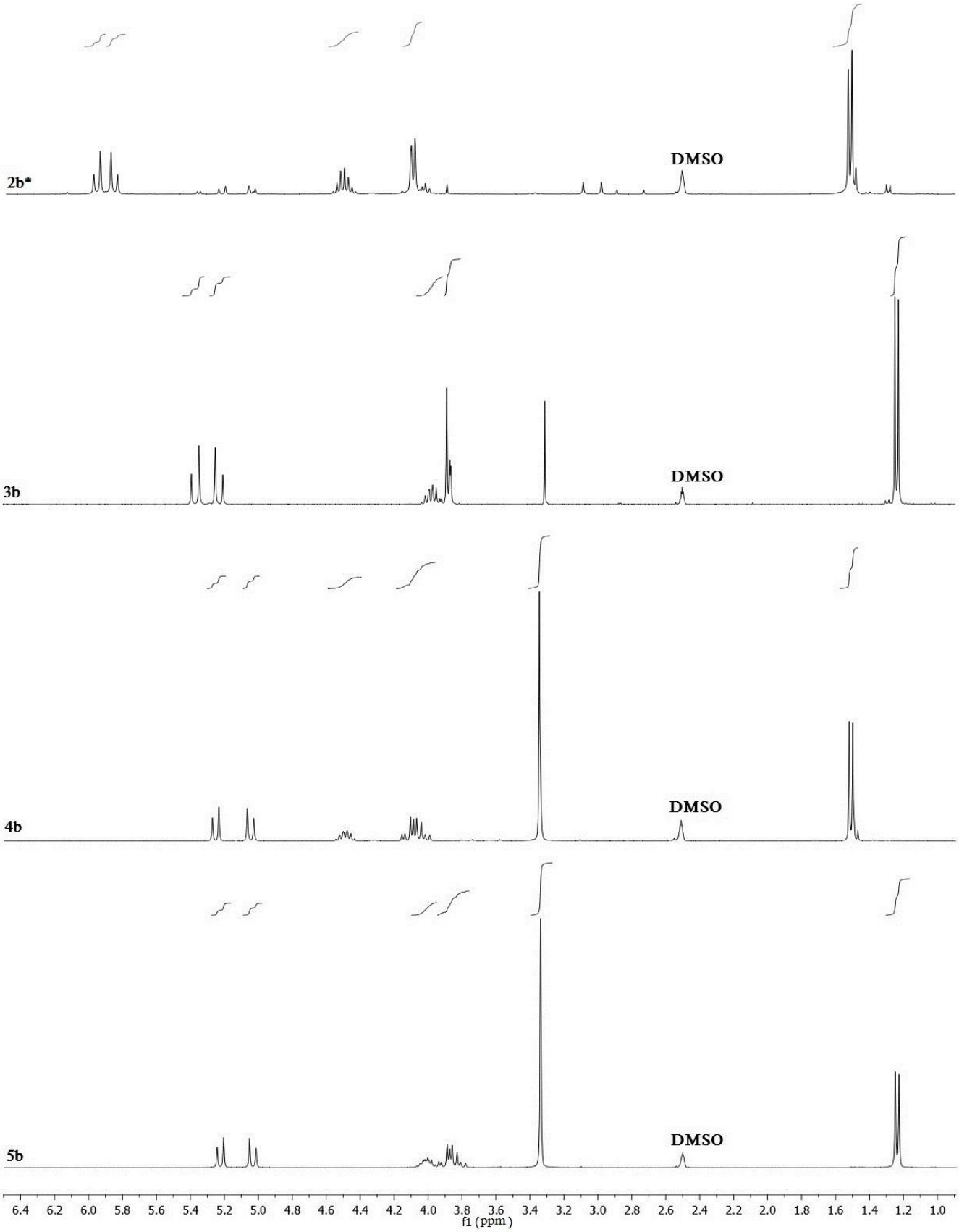

Figure S5. ^{1}H NMR spectra in DMSO-d_6 of compounds **2b-5b**. (*- **2b** in DMSO-d_6).

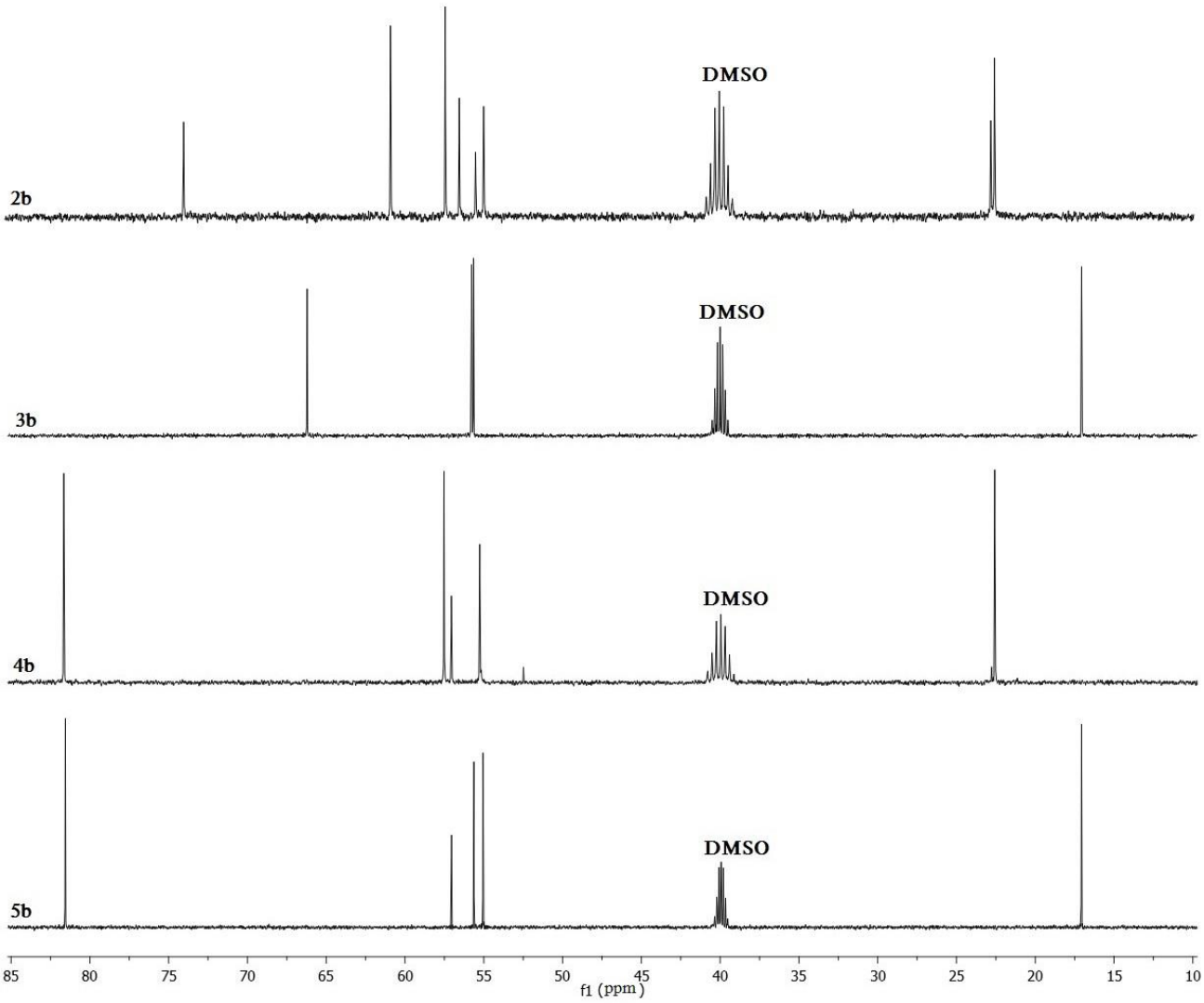

Figure S6. ^{13}C NMR spectra in DMSO-d_6 of compounds **2b**-**5b**.

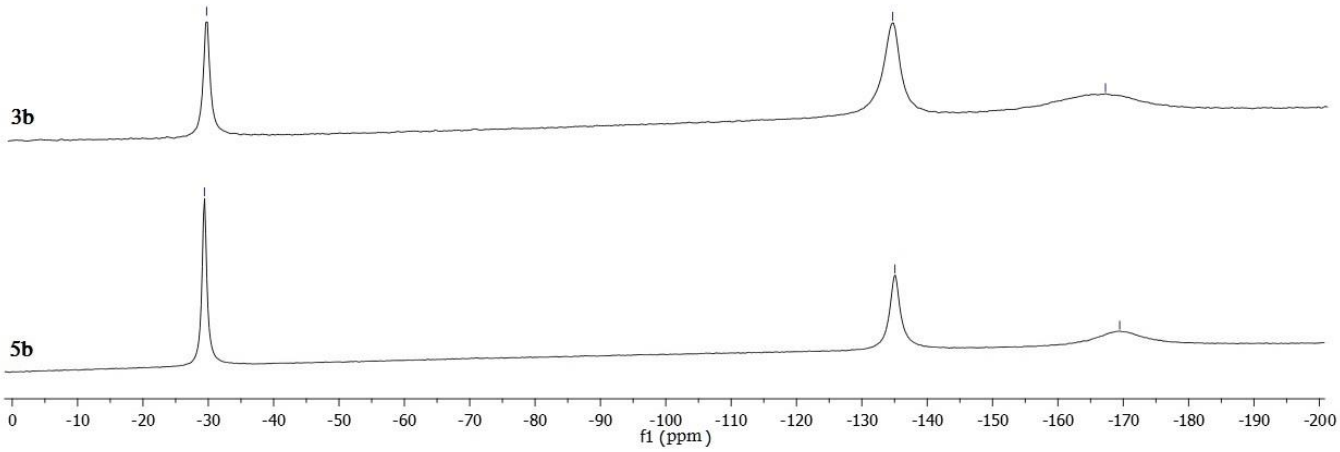

Figure S7. ^{14}N NMR spectra in DMSO-d_6 of compounds **3b**, **5b**.

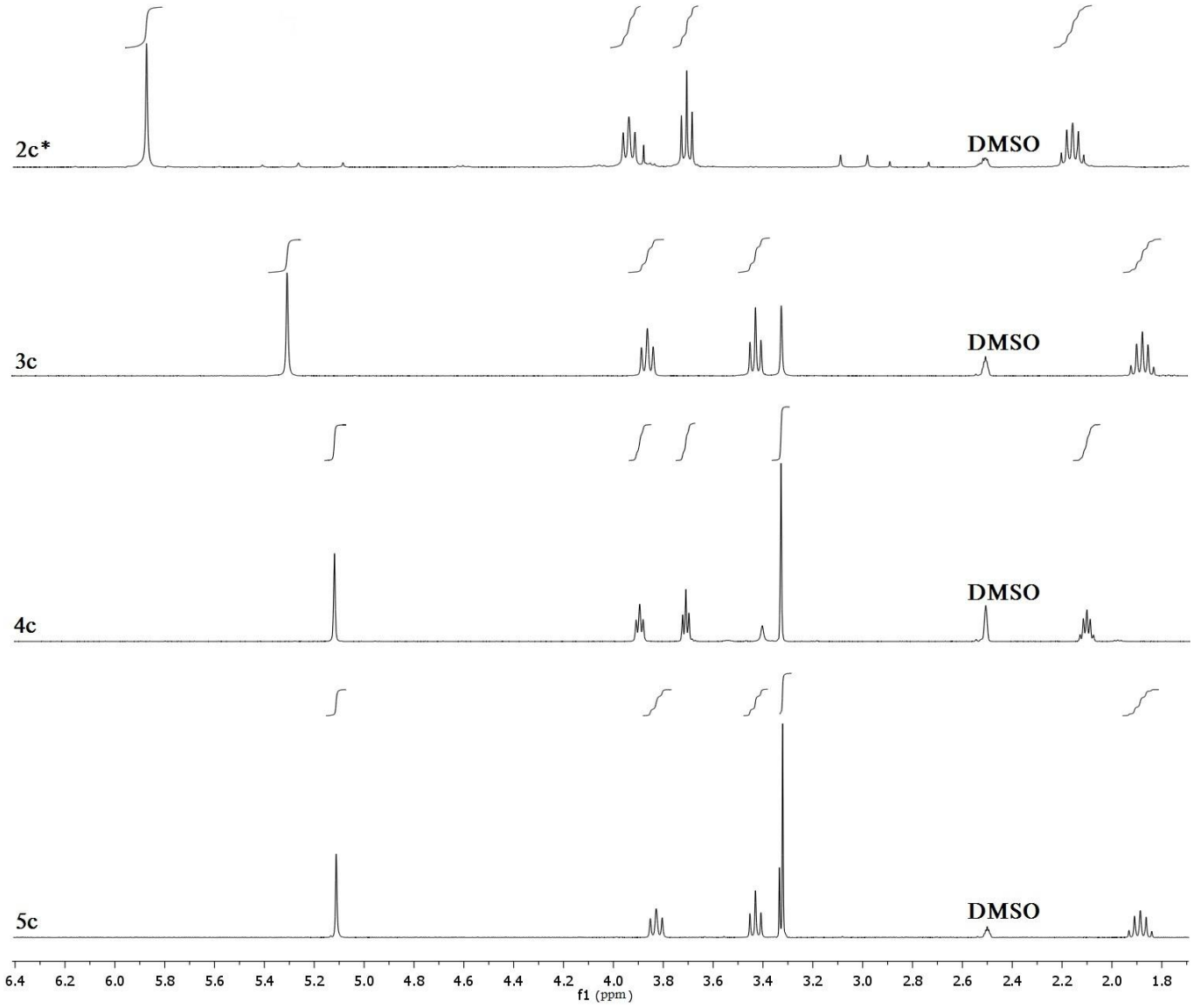

Figure S8. ^{1}H NMR spectra in DMSO-d_6 of compounds **2c**-**5c**. (*- **2c** in DMSO-d_6).

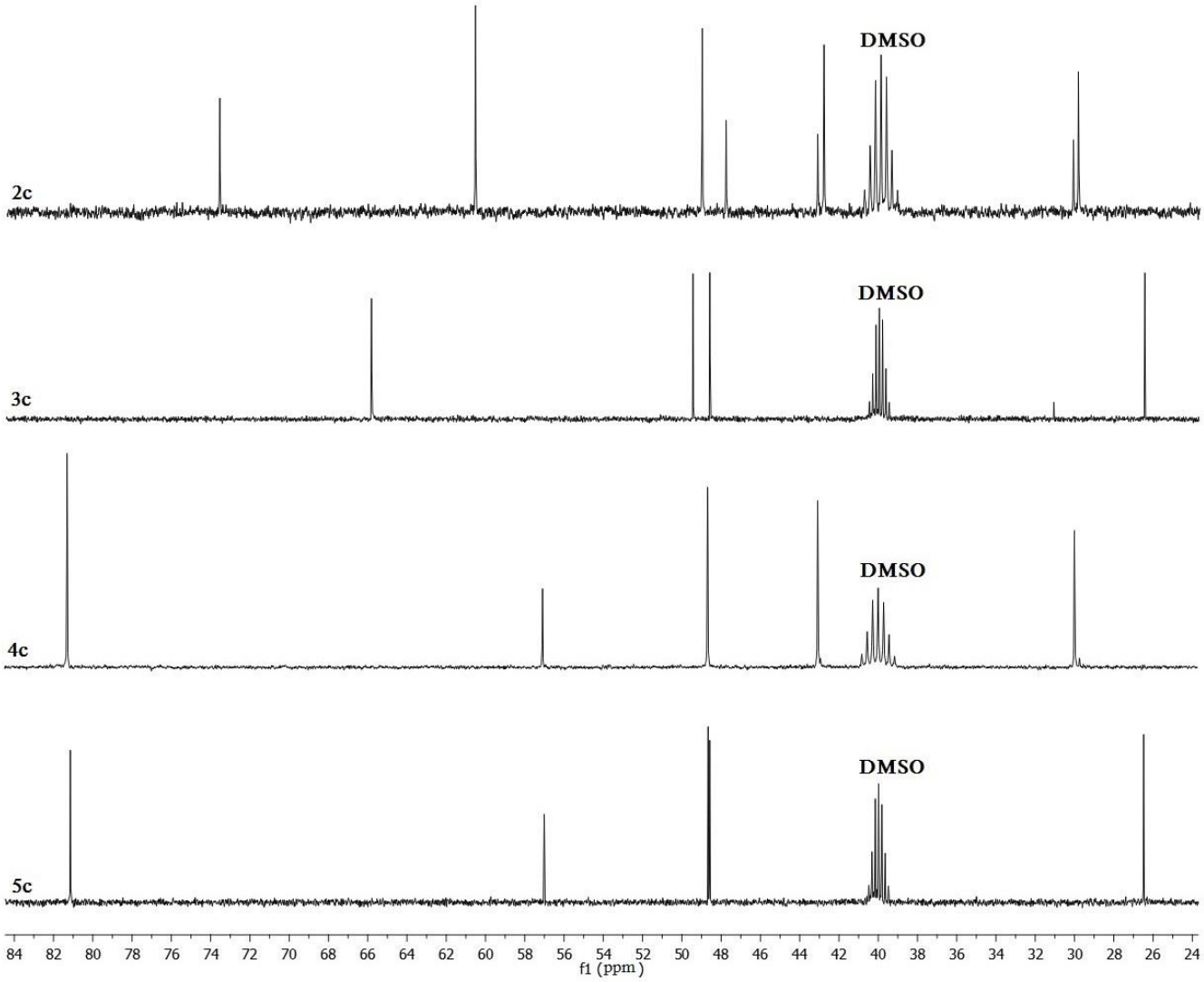

Figure S9. ^{13}C NMR spectra in DMSO-d_6 of compounds **2c-5c**.

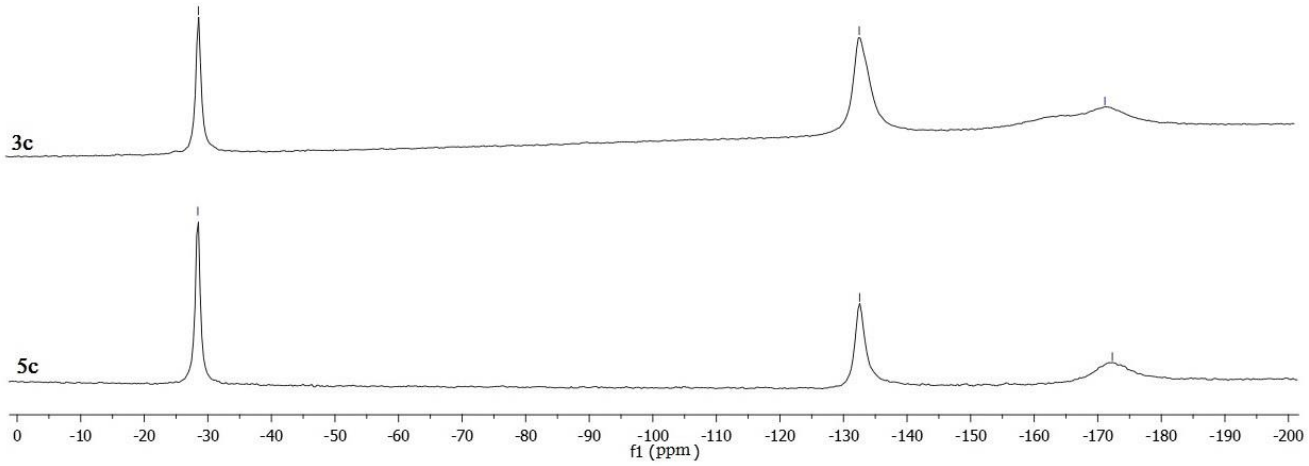

Figure S10. ^{14}N NMR spectra in DMSO-d_6 of comppounds **3c**, **5c**.