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Heterocyclization of amino alcohols into saturated cyclic quaternary ammonium salts

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^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker AVANCE AM300 spectrometer (300.13 and 75.47 MHz, respectively): 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). Melting points and decomposition temperatures were measured with a Stuart SMP-10 device at a heating rate of 2 °C/min.

Potassium *N*-(2-hydroxyethyl)sulfamate 2. Sulfamic acid (97 g, 1 mol) is dissolved with stirring in a 1 liter conical flask containing ethanolamine **1a** (187 ml, 3.1 mol). The resulting solution is heated with vigorous stirring to boiling at 178 °C and kept for 9 h under reflux. Intense evolution of ammonia accompanied by strong bubbling is observed in the first 3 hours. After this treatment, the mixture is cooled to ~60 °C, then a solution of potassium hydroxide (63.3 g, 1.13 mol) in methanol (375 ml) is added. After the mixture becomes uniform, acetone (440 ml) is added with stirring. The mixture is allowed to settle. The crystalline precipitate is filtered off and washed on a filter with a mixture of (150 ml) of methanol and (200 ml) of acetone. The solvent is distilled off from the mother liquor and then separated by fractional distillation (recycling of excess ethanolamine). The resulting white crystalline precipitate is dried *in vacuo* to give (171 g, 955 mmol) (96%) of potassium *N*-(2-hydroxyethyl)-sulfamate (99% according to ^{1}H NMR spectroscopy data) (^{1}H NMR spectroscopy data, Ref. 13).

3-Nitro-1,1-dimethylimidazolidin-1-ium nitrate 4a. Potassium *N*-(2-hydroxyethyl)sulfamate (10 g, 55.79 mmol) and paraformaldehyde (2.26 g, 75.3 mmol) are dissolved in glacial acetic acid at room temperature. The resulting solution in acetic acid is kept for 20 min at room temperature, then the prepared nitrating mixture H_2SO_4/HNO_3 (21 ml/38 ml) is added with stirring at -15 °C. The resulting mixture is stirred at -14...-16 °C for 1 h. Next, the nitrated mixture is poured into a mixture of ice (85 g) and water (250 ml). The product is extracted with ethyl acetate (4×65 ml) and washed with water (7×42 ml). The ethyl acetate solution is left for 12 h over anhydrous magnesium sulfate. Next, ethyl acetate is distilled off at a $T_{bath} \leq 50$ °C/ 15 Torr. Residue: a mixture of *N*-[(2-nitroxyethyl)nitramino]methanol **3** and ethylenedinitrate (87% and 13%, respectively, according to ^{1}H NMR spectroscopy) (9.61 g). ^{1}H NMR, δ (*J*, Hz): 4.14 (2H, t, *J*=5.1, $N\underline{CH_2}CH_2ONO_2$), 4.77 (2H, t, *J*=5.1, $NCH_2\underline{CH_2}ONO_2$), 4.88(4H, s, $O_2NO\underline{CH_2CH_2}ONO_2$), 5.12 (2H, s, OCH_2N), 6.53 (1H, s, OH).

The resulting mixture of *N*-[(2-nitroxyethyl)nitramino]methanol **3** with ethylenedinitrate (9.61 g) is added without purification to a solution of *N*,*N*,*N'*,*N'*-tetramethyldiaminomethane (2.3 g, 22.5 mmol) in acetonitrile (35 ml). The resulting solution is kept for 30 min at 45 °C. Colorless crystals precipitate from the solution, which are then filtered off. Yield: colorless crystalline 3-nitro-1,1-dimethylimidazolidin-1-ium **4a** nitrate (99% pure according to ^{1}H NMR spectroscopy) (2.30 g, 11.05 mmol) (19.8%). (M.p. 198-199 °C (decomp.)). IR, ν, cm^{-1}: 1353 (NNO_2 sym.); 1527 (NNO_2 asym.). ^{1}H NMR, δ (*J*, Hz): 3.30 (6H, s, $(CH_3)_2N$), 4.00 (2H, t, *J*=7.0, $CH_2\underline{CH_2}N(CH_3)_2$), 4.32 (2H, t, *J*=7.0, $\underline{CH_2}CH_2N(CH_3)_2$), 5.35 (2H, s, NCH_2N) (Fig. S1). ^{13}C NMR, δ: 46.55 ($(CH_3)_2N$); 50.77 ($\underline{C}H_2CH_2N(CH_3)_2$); 61.85 ($CH_2\underline{C}H_2N(CH_3)_2$); 75.97 ($NCH_2N$) (Fig. S2). Found %: C 28.89; H 5.77; N 26.87. $C_5H_{12}N_4O_5$. Calculated %: C 28.85; H 5.81; N 26.91.

3-Nitro-1,1-dimethylimidazolidin-1-ium dinitramide 4b. *Stage 1.* A solution of 3-nitro-1,1-dimethylimidazolidin-1-ium **4a** nitrate (2.30 g, 11 mmol) in distilled water (3.6 ml) is prepared in a 10 ml flask. Dowex 2x8 anion exchange resin (OH-form) (0.55 g) is added, and the mixture is stirred for 1.5 h with a magnetic stirrer. The anion exchange resin is filtered off and washed with distilled water (1 ml) on the filter. The filtrate is used at the second stage.

Stage 2. A solution of ammonium dinitramide (ADNA, 1.35 g, 11 mmol) in distilled water (1.4 ml) is added with stirring to the filtrate from the first stage. After approximately 20 minutes, a precipitate is formed. The mixture is stirred for another 20 minutes, and the precipitate is filtered off. The crystals on the filter are washed with distilled water (4 ml) and dried in open air to a constant mass. Yield: colorless crystalline 3-nitro-1,1-dimethylimidazolidin-1-ium dinitramide **4b** (99% according to ^{1}H NMR data) (1.79 g, 7.12 mmol) (64.5%). (Mp 82-83 °C, decomp. 185-190 °C). IR, ν, cm^{-1}: 1181 (NNO_2sym.); 1523 (NNO_2asym.). ^{1}H NMR, δ (*J*, Hz): 3.30 (6H, s, $(CH_3)_2N$); 4.00 (2H, t, *J* =6.8, $CH_2\underline{CH_2}N(CH_3)_2$); 4.33 (2H, t, *J* =6.6, $\underline{CH_2}CH_2N(CH_3)_2$); 5.35 (2H, s,$NCH_2N$) (Fig. S1). ^{13}C NMR, δ: 46.62 ($(CH_3)_2N$); 50.89 ($\underline{C}H_2CH_2N(CH_3)_2$); 61.97 ($CH_2\underline{C}H_2N(CH_3)_2$); 76.08 ($NCH_2N$) (Fig. S2). ^{14}N NMR, δ: -9.85 ($N(NO_2)_2$); -33.49 (NNO_2); -318.06 ($CH_2CH_2\underline{N}^{+}(CH_3)_2$) (Fig. S3). ^{15}N NMR, δ: -9.42 ($N(NO_2)_2$); -33.04 (NNO_2); -206.15 ($CH_2CH_2\underline{N}^{+}(CH_3)_2$) (Fig. S4). Found %: C 23.70; H 5.07; N 33.31. $C_5H_{12}N_6O_6$. Calculated %: C 23.81; H 4.80; N 33.32.

1-Nitro-3,3-dimethylimidazolidin-1-ium perchlorate 4c. *Stage 1.* A solution of 3-nitro-1,1-dimethylimidazolidin-1-ium **4a** nitrate (2.30 g, 11 mmol) in distilled water (3.1 ml) is prepared in a 10 ml flask. Dowex 2x8 anion exchange resin (OH-form) (0.58 g) is added, and the mixture is stirred for 1.5 h with a magnetic stirrer. The anion exchange resin is filtered off and washed with distilled water (1.33 ml) on the filter. The filtrate is used at the second stage.

Stage 2. A solution of ammonium perchlorate (APC, 1.33 g, 11 mmol) in distilled water (7 ml) is added with stirring to the filtrate from the first stage. A precipitate is formed. The mixture is kept with stirring for another 20 min, and the precipitate is filtered off. The crystals on the filter are washed with distilled

water (2×3 ml) and dried in open air to a constant weight. Yield: colorless crystalline 3-nitro-1,1-dimethylimidazolidin-1-ium perchlorate **4c** (99% according to ^{1}H NMR data) (2.03 g, 8.16 mmol) (74.2%). (Mp 215-216 °C, decomp.). IR (in KBr), ν, cm^{-1}: 1339 (NNO_2 sym.); 1529 (NNO_2 asym.). ^{1}H NMR, δ (*J*, Hz): 3.29 (6H, s, $(CH_3)_2N$); 3.99 (2H, t, *J*=7.0, $CH_2\underline{CH_2}N(CH_3)_2$); 4.32 (2H, t, *J*=7.0, $\underline{CH_2}CH_2N(CH_3)_2$); 5.34 (2H, s, NCH_2N) (Fig. S1). ^{13}C NMR, δ: 46.61 ($(CH_3)_2N$); 50.89 ($\underline{C}H_2CH_2N(CH_3)_2$); 61.95 ($CH_2\underline{C}H_2N(CH_3)_2$); 76.05 ($NCH_2N$) (Fig. S2). Found %: C 24.56; H 4.92; N 17.19. $C_5H_{12}ClN_3O_6$. Calculated %: C 24.45; H 4.92; N 17.11.

3,3-Dimethyloxazolidin-3-ium iodide 5a. Paraformaldehyde (1.5 g, 50 mmol) is added with stirring to *N*-methylethanolamine **1b** (3.7 g, 50 mmol). The mixture is heated to 40 °C and stirred for 3 h until paraformaldehyde is dissolved completely. A solution of methyl iodide (10.2 g, 4.5 ml, 71.8 mmol) in acetonitrile (12 ml) is added with stirring over a water bath to the reaction mixture. The mixture is kept for 20 h at room temperature. After that, the excess methyl iodide and acetonitrile are distilled off *in vacuo*. The residue is dissolved in methanol (30 ml) and precipitated with ether (80 ml). The crystals that precipitated are filtered off and dried. Yield: colorless crystals (prone to yellowing with time under light), 3,3-dimethyloxazolidin-3-ium iodide **5a** (99% according to ^{1}H NMR spectroscopy data) (10.5 g, 46.05 mmol) (92%). (Mp 184-185 °C, decomp. 205 °C, (189 °C Ref. 14)). IR, ν, cm^{-1}: 1120 (C-O-C). ^{1}H NMR, δ (*J*, Hz): 3.20 (6H, s, $(CH_3)_2N$); 3.71 (2H, t, *J*=7.4, $NCH_2\underline{CH_2}O$); 4.26 (2H, t, *J*=7.3, $N\underline{CH_2}CH_2O$); 4.84 (2H, s,OCH_2N) (Fig. S5). ^{13}C NMR, δ: 49.30 ($(CH_3)_2N$); 60.86 ($NCH_2\underline{C}H_2O$); 65.98 ($N\underline{C}H_2CH_2O$); 92.60 (OCH_2N) (Fig. S6).

3,3-Dimethyloxazolidin-3-ium sulfamate 5b. A solution of lead sulfamate (3.06 g, 9.03 mmol) in distilled water (25 ml) is added with stirring to a solution of 3,3-dimethyloxazolidin-3-ium iodide **5a** (4.12 g, 18.07 mmol) in distilled water (25 ml). A precipitate is formed. The suspension is stirred at room temperature for 10 min. The precipitate is filtered off. Water is distilled off *in vacuo* from the mother liquor, and the precipitate is dried with ethanol. The residue is extracted with EtOH/MeOH mixture (25 ml/10 ml) at 60–65 °C. The solution is allowed to cool to room temperature, and the precipitate of lead iodide that formed additionally is filtered off. Ethanol is distilled off *in vacuo* from the mother liquor. Acetone (10 ml) is poured over the residue, and the mixture is kept overnight. Acetone is filtered off from the precipitate that crystallized (the product is hygroscopic!). Yield: colorless crystalline 3,3-dimethyloxazolidin-3-ium sulfamate **5b** (99% according to ^{1}H NMR data) (1.94 g, 9.85 mmol) (54.5%). IR, ν, cm^{-1}: 1123 (C-O-C); 1223 (H_2NSO_3). ^{1}H NMR, δ (*J*, Hz): 3.20 (6H, s, $(CH_3)_2N$); 3.72 (2H, t, *J*=7.4, $NCH_2\underline{CH_2}O$); 4.27 (2H, t, *J*=7.3, $N\underline{CH_2}CH_2O$); 4.85 (2H, s, OCH_2N) (Fig. S5). ^{13}C NMR, δ: 49.11 ($(CH_3)_2N$); 60.81 ($NCH_2\underline{C}H_2O$); 65.98 ($N\underline{C}H_2CH_2O$); 92.53 (OCH_2N) (Fig. S6). Found %: C 29.52; H 7.12; N 13.75. $C_5H_{14}N_2O_4S$. Calculated %: C 30.29; H 7.12; N 14.13.

3,3-Dimethyloxazolidin-3-ium nitrate 5c. A solution of sodium hydroxide (0.47 g, 11.75 mmol) in ethanol (16 ml) and distilled water (16 ml) is added with stirring to a solution of 3,3-dimethyloxazolidin-3-ium sulfamate **5b** (2.30 g, 11.68 mmol) in distilled water (12 ml) and ethanol (64 ml), then THF (48 ml) is added. The resulting solution is cooled to -5...0 °C and kept for 40 min at this temperature. Sodium sulfamate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium nitrate (0.93 g, 11.68 mmol) in distilled water (10 ml) is added to the mother liquor, and the mixture is kept for 10 min. The solvent is distilled off *in vacuo*. The residue is dissolved in methanol (10 ml), diethyl ether (25 ml) is added, and the residue of inorganic compounds is filtered off. The solvent is distilled off *in vacuo* to give a viscous pale yellow oil of 3,3-dimethyloxazolidin-3-ium nitrate **5c** (1.18 g, 7.20 mmol) (61.8%, 98% pure according to ^{1}H NMR spectroscopy data). (Decomp. 230 °C). IR, ν, cm^{-1}: 1125 (C-O-C); 1389 (NO_2sym.); 1638 (NO_2asym.). ^{1}H NMR, δ (*J*, Hz): 3.18 (6H, s, $(CH_3)_2N$); 3.69 (2H, t, *J* =7.4, $NCH_2\underline{CH_2}O$); 4.24 (2H, t, *J* =7.4, $N\underline{CH_2}CH_2O$); 4.82 (2H, s, OCH_2N) (Fig. S5). ^{13}C NMR, δ: 49.25 ($(CH_3)_2N$); 60.96 ($NCH_2\underline{C}H_2O$); 66.07 ($N\underline{C}H_2CH_2O$); 92.69 (OCH_2N) (Fig. S6). Found %: N 17.04. $C_5H_{12}N_2O_4$. Calculated %: N 17.06.

3,3-Dimethyloxazolidin-3-ium dinitramide 5d (Scheme 2, conditions *iii*). A solution of silver dinitramide (1.55 g, 7.24 mmol) in distilled water (13 ml) is added with stirring to a solution of 3,3-dimethyloxazolidin-3-ium iodide **5a** (1.65 g, 7.24 mmol) in distilled water (10 ml). A precipitate is formed. The suspension is stirred at room temperature for 10 min. The precipitate is filtered off. Water is distilled off *in vacuo* from the mother liquor. The residue is dissolved in methanol (1 ml), acetone (20 ml) is added, and silver iodide that precipitated additionally is filtered off. The solvent is distilled off *in vacuo* from the mother liquor. Diethyl ether (10 ml) is poured over the residue and the mixture is kept overnight. The ether is filtered off from the precipitate that crystallized. Yield: colorless crystalline 3,3-dimethyloxazolidin-3-ium dinitramide **5d** (99% according to ^{1}H NMR data) **(**1.38 g, 6.67 mmol) (92%).

3,3-Dimethyloxazolidin-3-ium dinitramide 5d (Scheme 2, conditions *v*, *vii*). A solution of sodium hydroxide (0.32 g, 8 mmol) in ethanol (11 ml) and distilled water (2 ml) is added with stirring to a solution of 3,3-dimethyloxazolidin-3-ium sulfamate **5b** (1.57 g, 7.98 mmol) in distilled water (8.4 ml) and ethanol (44 ml), then THF (33 ml) is added. The resulting solution is cooled to -5...0 °C and kept at this temperature for 40 min. Sodium sulfamate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium dinitramide (ADNA, 0.99 g, 7.98 mmol) in distilled water (6.6 ml) is added to the mother liquor, and the mixture is kept for 10 min. The solvent is distilled off *in vacuo*. The residue is dissolved in methanol (10 ml), THF (23 ml) is added, and the solution is kept overnight. After that, inorganic residues are filtered off. The solvent is distilled off *in vacuo*. Ether is added to the viscous liquid residue, and the system is kept overnight. Ether is filtered off, and the crystalline residue is dried. Yield: pay yellow crystalline3,3-dimethyloxazolidin-3-ium dinitramide **5d** (99% according to ^{1}H NMR data) (1.50 g, 7.21 mmol) (90%). (Mp 83-84 °C, decomp. 170 °C). IR, ν, cm^{-1}: 1124 (C-O-C); 1336 (NO_2 sym.); 1538 (NO_2 asym.). ^{1}H NMR, δ (*J*, Hz): 3.18 (6H, s, $(CH_3)_2N$); 3.68 (2H, t, *J* =7.4, $NCH_2\underline{CH_2}O$); 4.25 (2H, t, *J*=7.4, $N\underline{CH_2}CH_2O$); 4.81 (2H, s,OCH_2N) (Fig. S5). ^{13}C NMR, δ: 49.35

($(CH_3)_2N$); 61.04 ($NCH_2\underline{C}H_2O$); 66.06 ($N\underline{C}H_2CH_2O$); 92.79 (OCH_2N) (Fig. S6). Found %: N 27.11. $C_5H_{12}N_4O_5$. Calculated %: N 26.91.

3,3-Dimethyloxazolidin-3-ium perchlorate 5e. A solution of sodium hydroxide (0.45 g, 11.25 mmol) in ethanol (16 ml) and distilled water (3 ml) is added with stirring to a solution of 3,3-dimethyloxazolidinium sulfamate **5b** (2.23 g, 11.32 mmol) in distilled water (12 ml) and ethanol (63 ml), then THF (47 ml) is added. The resulting solution is cooled to -5...0 °C and kept at this temperature for 40 min. Sodium sulfamate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium perchlorate (APC, 1.33 g, 11.32 mmol) in distilled water (9.4 ml) is added to the mother liquor, and the mixture is kept for 10 min. The solvent is distilled off *in vacuo*. The residue is dissolved in boiling methanol (60 ml), and the inorganic residues are filtered off. About half of the solvent is distilled off *in vacuo*, and the remaining solution is kept overnight. The suspension is filtered, and the crystalline residue is dried. Yield: colorless crystalline 3,3-dimethyloxazolidin-3-ium perchlorate **5e** (99% pure according to ^{1}H NMR data, 2.01 g, 9.97 mmol, 88%). Decomp. 270-278 °C. IR,ν, cm^{-1}: 1088 (C-O-C). ^{1}H NMR, δ (*J*, Hz): 3.17 (6H, s, $(CH_3)_2N$); 3.68 (2H, t, *J* =7.4, $NCH_2\underline{CH_2}O$); 4.26 (2H, t, *J* =7.4, $N\underline{CH_2}CH_2O$); 4.81 (2H, s, OCH_2N) (Fig. S5). ^{13}C NMR, δ: 49.29 ($(CH_3)_2N$); 60.96 ($NCH_2\underline{C}H_2O$); 66.05 ($N\underline{C}H_2CH_2O$); 92.69 (OCH_2N) (Fig. S6). ^{14}N NMR, δ: -311.84, -317.46 ($CH_2CH_2\underline{N}^+(CH_3)_2$) (Fig. S7). Found %: C 29.88; H 6.03; N 6.73. $C_5H_{12}ClNO_5$. Calculated %: C 29.79; H 6.00; N 6.95.

(4a*R,8a*R**)-4,8-Dimethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine 6.** Glyoxal dihydrate trimer (5.70 g, 27.12 mmol) is added with stirring to methylethanolamine **1b** (12.2 g, 162.43 mmol). The mixture is heated to 40 °C and stirred for 3 h until glyoxal dihydrate trimer is dissolved completely. After that, the mixture is dissolved in diethyl ether (70 ml), and the undissolved fraction is filtered off. Ether is removed *in vacuo* to approximately 15-20% of the initial volume, and a crystalline precipitate is formed. The precipitate is filtered off and dried. Yield: colorless crystalline compound **6** (99% pure according to ^{1}H NMR, 11.11 g, 64.51 mmol, 79.4%). ^{1}H NMR, δ (*J*, Hz): 2.21 (2H, dd, *J* = 11.1, 1.7, 2×CH_2N); 2.34 (6H, s, 2×CH_3N); 2.68 (2H, td, *J* = 11.5, 3.5, 2×CH_2N); 3.50 (2H, td, *J* = 11.6, 2.8,2×CH_2O); 3.80 (2H, dd, *J* = 11.6, 2.9, 2×CH_2O); 3.88 (2H, s, CHCH).

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium) diiodide 7a.** Methyl iodide (2.18 ml, 34.86 mmol) is added with stirring to a solution of 4,8-dimethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine **6** (1.5 g, 8.72 mmol) in methanol (20 ml). The mixture is heated to boiling (~42 °C) and stirred for 10 h under reflux. The mixture is allowed to cool to room temperature. The resulting crystalline precipitate that formed is filtered off and additionally washed with methanol (1×2 ml) on the filter. The precipitate is dried. Yield: colorless crystalline salt **7a** (99% pue according to ^{1}H NMR, 0.60 g, 1.32 mmol, 15%). Mp 209-210 °C (decomp.). IR,ν, cm^{-1}: 1038 (C-O-C). ^{1}H NMR, δ (*J*, Hz): 3.23 (6H, s, 2×CH_3N); 3.32 (6H, s, 2×CH_3N); 3.83–3.93 (4H, m, 2×CH_2O); 4.38 (4H, dd, *J* = 9.7, 2.8, 2×CH_2N); 5.40 (2H, s,CHCH) (Fig. S8). ^{13}C NMR, δ: 42.66 ($(CH_3)_2N$); 53.23 ($NCH_2\underline{C}H_2O$); 60.95; 61.08 ($N\underline{C}H_2CH_2O$); 86.11 ($O\underline{C}H\underline{C}HN$) (Fig. S9). Found %: C 26.34; H 4.78; N 6.14. $C_{10}H_{22}I_2N_2O_2$. Calculated %: C 26.33; H 4.86; N 6.14.

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium bis(methoxysulfonate) 7b.** Dimethyl sulfate (1.7 ml, 17.46 mmol) is added with stirring to a solution of diamine **6** (1.5 g, 8.72 mmol) in acetonitrile (10 ml). The mixture is heated to boiling (~81 °C) and stirred for 4 h under reflux. The mixture is allowed to cool to room temperature. The resulting crystalline precipitate is filtered off and additionally washed with acetonitrile (2 ml) on the filter. The precipitate is dried. Yield: colorless crystalline salt **7b** (99% pure according to ^{1}H NMR, 1.19 g, 2.81 mmol, 32%). (Decomp. >280 °C). IR,ν, cm^{-1}: 1008 (C-O-C); 1219 (CH_3OSO_3). ^{1}H NMR, δ (*J*, Hz): 3.22 (6H, s, 2×CH_3N); 3.29 (6H, s, 2×CH_3N); 3.40 (6H, s, 2×(CH_3OSO_3)) 3.81–3.90 (4H, m, 2×CH_2O); 4.28–4.41 (4H, m, 2×CH_2N); 5.29 (2H, s, CHCH) (Fig. S8). ^{13}C NMR, δ: 42.20 ((CH_3)$_2$N); 53.27 (NCH_2CH_2O); 61.02; 61.12 (NCH_2CH_2O); 86.36 (OCHCHN) (Fig. S9). ^{15}N NMR, δ: -320.38 ($CH_2CH_2N^+(CH_3)_2$) (Fig. S10). Found %: C 33.55; H 6.89; N 6.56. $C_{12}H_{28}N_2O_{10}S_2$. Calculated %: C 33.95; H 6.65; N 6.60.

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium dinitrate 7c** (Scheme 3, conditions *iii*). A solution of lead nitrate (0.6 g, 1.81 mmol) in distilled water (6 ml) is added with stirring to a solution of diiodide **7a** (0.82 g, 1.8 mmol) in distilled water (6 ml). A crystalline precipitate is formed. The suspension is stirred at room temperature for 15 min. A mixture of methanol/acetonitrile (1:1, 16 ml) is added, and the suspension is kept at room temperature for another 40 minutes. The precipitate is filtered off. The solvents are distilled off *in vacuo* from the mother liquor. Yield: colorless crystalline dinitrate **7c** (98% pure according to ^{1}H NMR, 0.5 g, 1.53 mmol. 85%).

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium dinitrate 7c** (Scheme 3, conditions *v*, *vi*). A solution of sodium hydroxide (0.22 g, 5.5 mmol) in ethanol (8 ml) and distilled water (1.5 ml) is added with stirring to a solution of bis(methoxysulfonate) **7b** (1.17 g, 2.75 mmol) in distilled water (7 ml) and ethanol (33 ml), then THF (22 ml) is added. The resulting solution is cooled to -5...0 °C and kept at this temperature for 40 min. Sodium methyl sulfate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium nitrate (0.44 g, 5.5 mmol) in distilled water (5 ml) is added to the mother liquor, and the mixture is kept for 20 min. The solvent is distilled off *in vacuo* from the solution. The residue is dissolved in ethanol (15 ml), and the inorganic residues are filtered off. The solvent is distilled off *in vacuo*. The residue is recrystallized from a methanol/acetone solution (1:3, 16 ml). A crystalline precipitate is formed which is filtered off and dried. Yield: colorless crystalline dinitrate **7c** (99% pure according to ^{1}H NMR, 0.79 g, 2.42 mmol, 88%). Mp 245-246 °C (decomp.). IR,ν, cm^{-1}: 1037 (C-O-C); 1382 (NO_2sym.); 1633 (NO_2asym.). ^{1}H NMR, δ (*J*, Hz): 3.21 (6H, s, 2×CH_3N); 3.29 (6H, s, 2×CH_3N); 3.77–3.91 (4H, m, 2×CH_2O); 4.29–4.41 (4H, m, 2×CH_2N); 5.31 (2H, s, CHCH) (Fig. S8). ^{13}C NMR, δ: 42.13 ((CH_3)$_2$N); 53.28 (NCH_2CH_2O); 61.06; 61.13 (NCH_2CH_2O); 86.38 (OCHCHN) (Fig. S9). Found %: C 36.84; H 7.01; N 16.96. $C_{10}H_{22}N_4O_8$. Calculated %: C 36.81; H 6.80; N 17.17.

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium bis(dinitramide) 7d.** A solution of sodium hydroxide (0.22 g, 5.5 mmol) in ethanol (8 ml) and distilled water (1.5 ml) is added with stirring to a solution of bis(methoxysulfonate) **7b** (1.17 g, 2.75 mmol) in

distilled water (7 ml) and ethanol (33 ml), then THF (22 ml) is added. The resulting solution is cooled to -5...0 °C and kept for 40 min at this temperature. After that, sodium methyl sulfate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium dinitramide (0.68 g, 5.48 mmol) in distilled water (5 ml) is added to the mother liquor, and the mixture is kept for 20 min. The solvent is distilled off *in vacuo*. The residue is dissolved in ethanol (15 ml), and the inorganic residues are filtered off. The solvent is distilled off *in vacuo*. The residue is recrystallized from an ethanol/acetone solution (1:5, 12 ml). A crystalline precipitate is formed which is filtered off and dried. Yield: pay yellow crystalline bis(dinitramide) **7d** (99% pure according to ^{1}H NMR, 0.97 g, 2.34 mmol, 85%). Mp 208-209 °C (decomp.). IR,ν, cm^{-1}: 1012 (C-O-C); 1530 (NNO_2asym.). ^{1}H NMR, δ (*J*, Hz): 3.20 (6H, s, 2×CH_3N); 3.28 (6H, s, 2×CH_3N); 3.77–3.88 (4H, m, 2×CH_2O); 4.28–4.40 (4H, m, 2×CH_2N); 5.26 (2H, s,CHCH) (Fig. S8). ^{13}C NMR, δ: 42.21 ($(CH_3)_2$N); 53.38 (NCH$_2$<u>C</u>H$_2$O); 61.09; 61.16 (N<u>C</u>H$_2$CH$_2$O); 86.37 (O<u>C</u>H<u>C</u>HN) (Fig. S9). ^{14}N NMR, δ: -9.21 ($N(NO_2)_2$); -319.83 (CH_2CH_2<u>N</u>$^{+}(CH_3)_2$) (Fig. S11). ^{15}N NMR, δ: -9.83 ($N(NO_2)_2$); -320.39 (CH_2CH_2<u>N</u>$^{+}(CH_3)_2$) (Fig. S12). Found %: C 29.12; H 5.49; N 27.13. $C_{10}H_{22}N_8O_{10}$. Calculated %: C 28.99; H 5.35; N 27.04.

(4a*R,8a*R**)-4,4,8,8-Tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium diperchlorate 7e.** A solution of sodium hydroxide (0.2 g, 5 mmol) in ethanol (7 ml) and distilled water (1.5 ml) of is added with stirring to a solution of bis(methoxysulfonate) **7b** (1.06 g, 2.5 mmol) in distilled water (6 ml) and ethanol (30 ml), then THF (32 ml) is added. The resulting solution is cooled to -5...0 °C and kept at this temperature for 40 min. Sodium methyl sulfate that precipitated is filtered off from the cold reaction mixture. A solution of ammonium perchlorate (APC, 0.59 g, 5.02 mmol) in distilled water (5 ml) is added to the mother liquor, and the mixture is kept for 20 min. The solvent is distilled off *in vacuo*. The residue is recrystallized from ethanol (~15 ml). The crystalline precipitate is filtered off and dried. Yield: colorless crystalline diperchlorate **7e** (99% pure according to ^{1}H NMR, 1.01 g, 2.5 mmol, 100%). Decomp. 280 °C (self-ignition). IR,ν, cm^{-1}: 1089 (C-O-C). ^{1}H NMR, δ (*J*, Hz): 3.20 (6H, s, 2×CH_3N); 3.28 (6H, s, 2×CH_3N); 3.76–3.88 (4H, m, 2×CH_2O); 4.27–4.42 (4H, m, 2×CH_2N); 5.25 (2H, s, CHCH) (Fig. S8). ^{13}C NMR, δ: 42.20 ($(CH_3)_2$N); 53.38 (NCH$_2$<u>C</u>H$_2$O); 61.07; 61.13 (N<u>C</u>H$_2$CH$_2$O); 86.35 (O<u>C</u>H<u>C</u>HN) (Fig. S9). Found %: C 30.11; H 5.73; N 7.02. $C_{10}H_{22}Cl_2N_2O_{10}$. Calculated %: C 29.94; H 5.53; N 6.98.

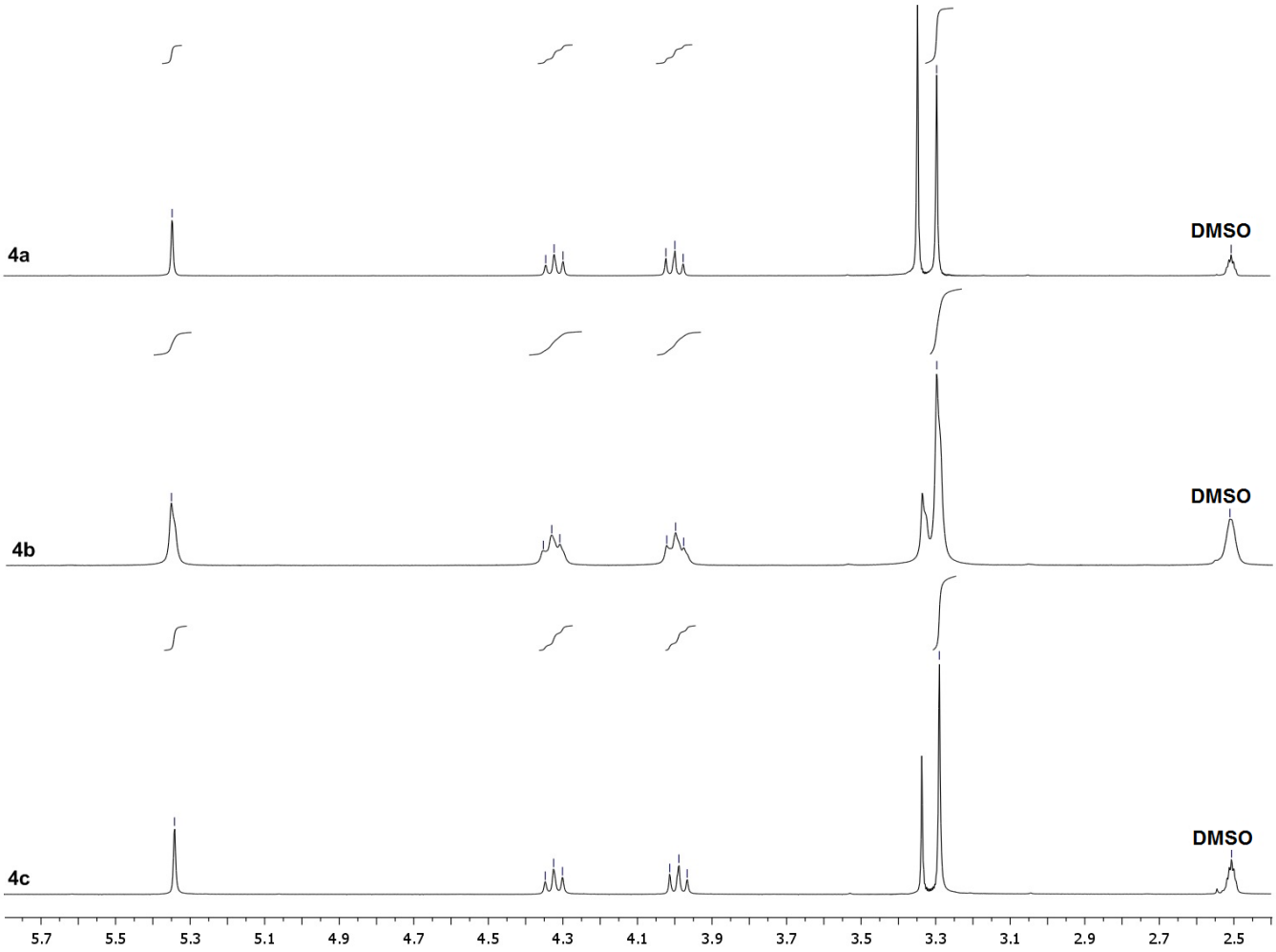

Figure S1.[1]H NMR spectra in DMSO-d_6 of 3-nitro-1,1-dimethylimidazolidin-1-ium salts (nitrate **4a**, dinitramide **4b**, perchlorate **4c**).

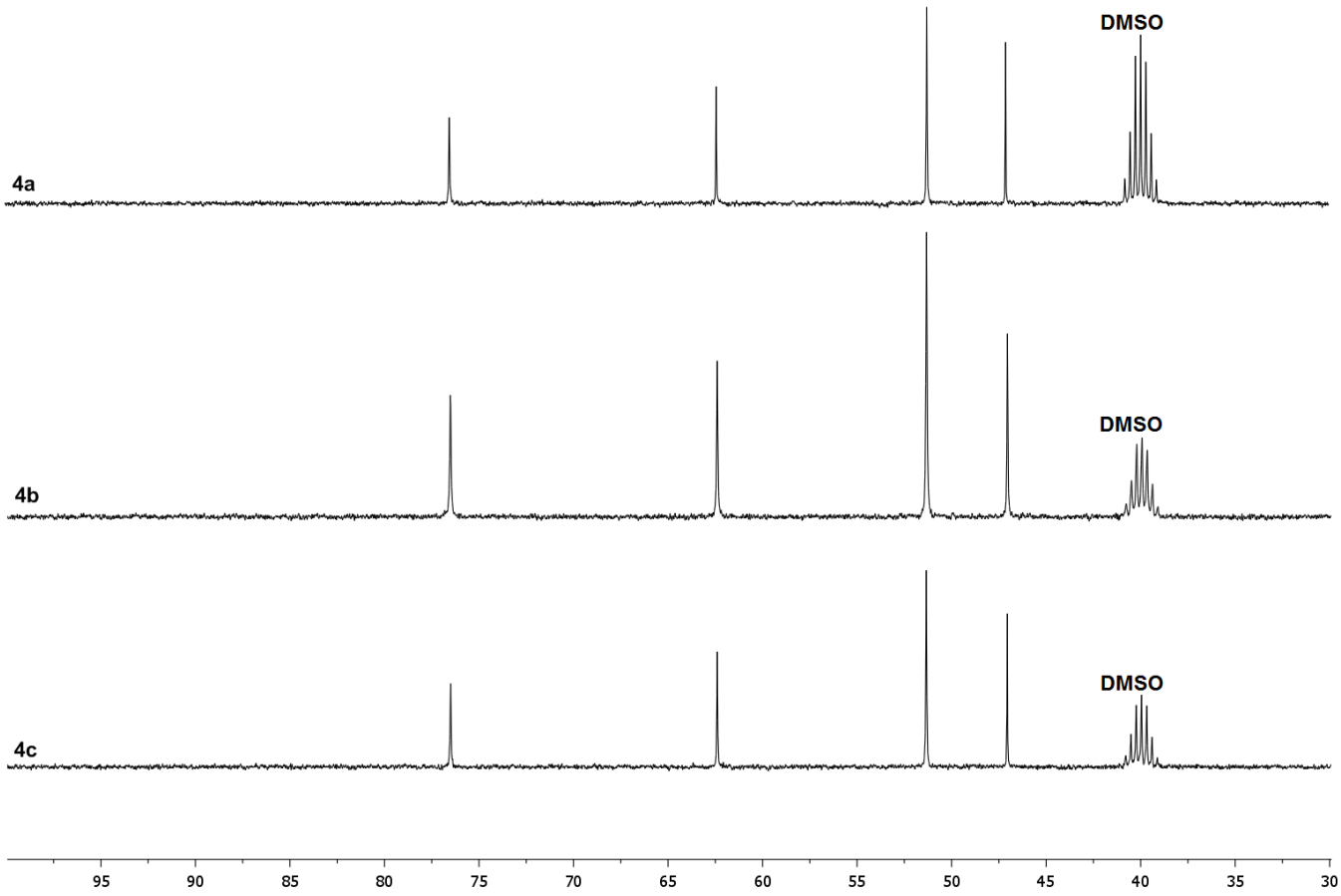

Figure S2. ^{13}C NMR spectra in DMSO-d_6 of 3-nitro-1,1-dimethylimidazolidin-1-ium salts (nitrate **4a**, dinitramide **4b**, perchlorate **4c**).

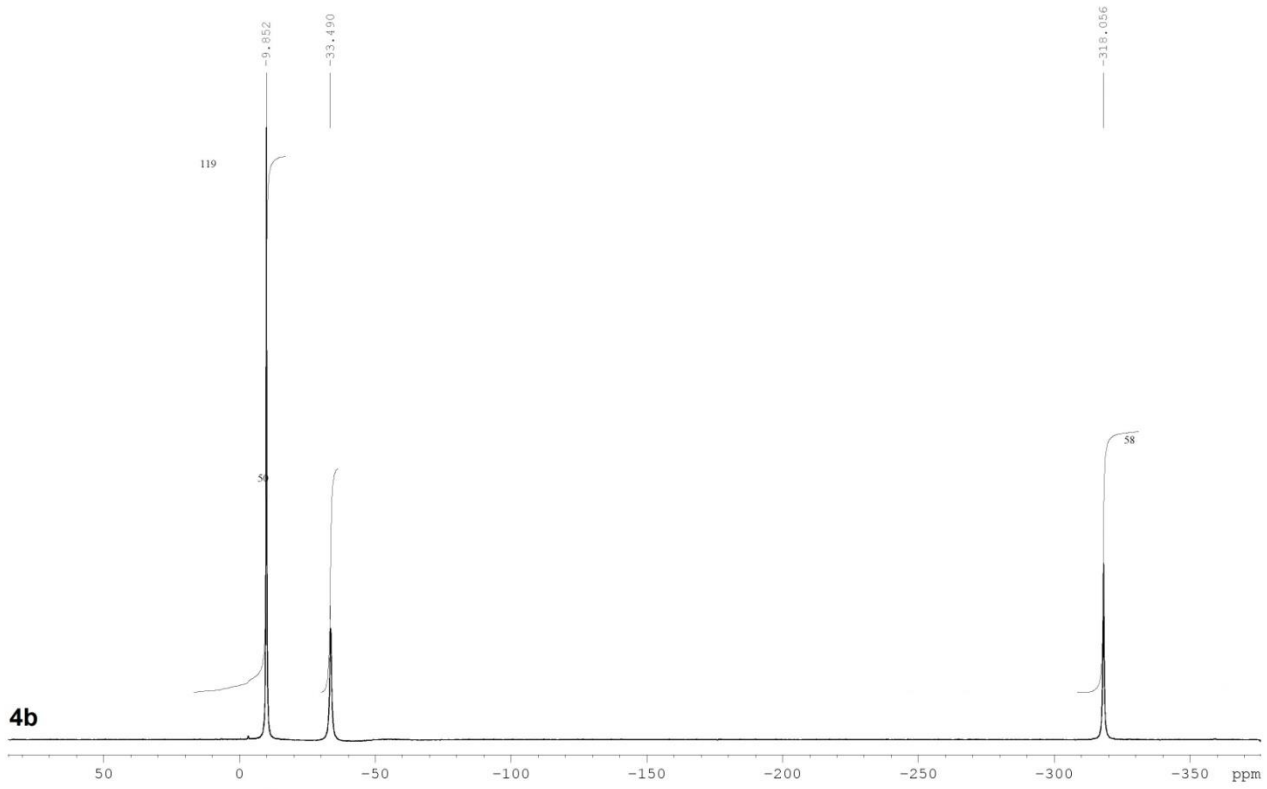

Figure S3. ^{14}N NMR spectra in DMSO-d_6 of 3-nitro-1,1-dimethylimidazolidin-1-ium dinitramide **4b**.

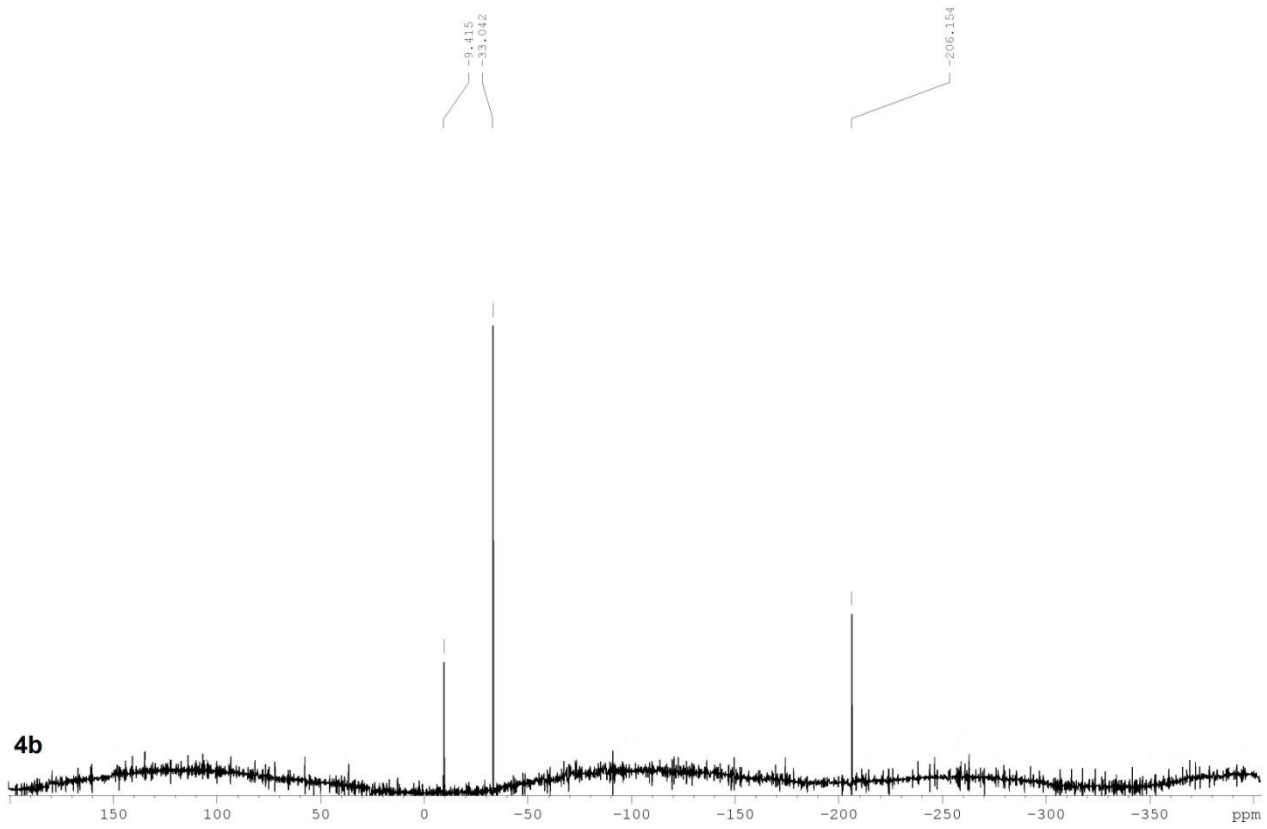

Figure S4. ^{15}N NMR spectra in DMSO-d_6 of 3-nitro-1,1-dimethylimidazolidin-1-ium dinitramide **4b**.

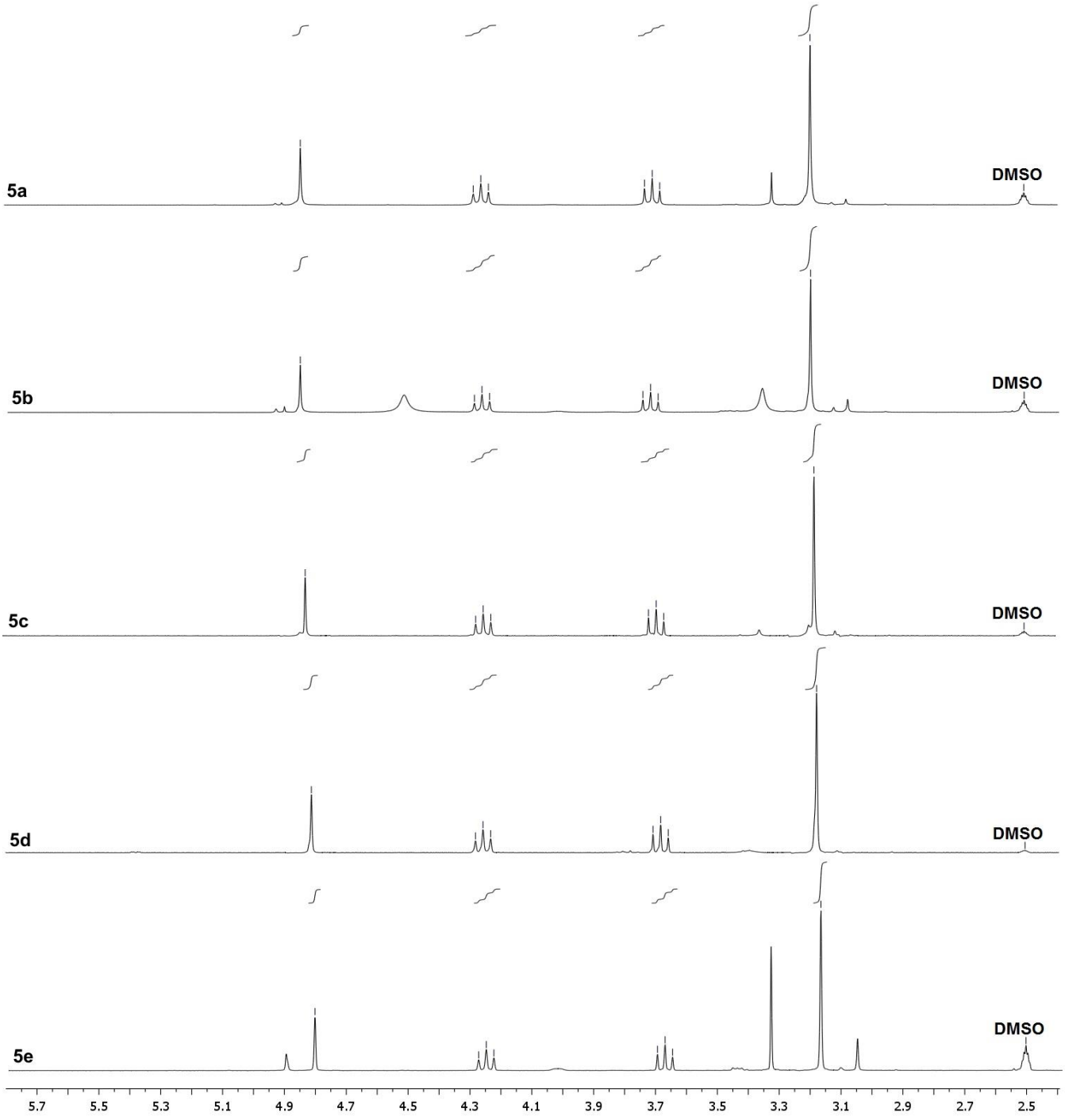

Figure S5. ^{1}H NMR spectra in DMSO-d_6 of 3,3-dimethyloxazolidin-3-ium salts (iodide **5a**, sulfamate **5b**, nitrate **5c**, dinitramide **5d**, perchlorate **5e**).

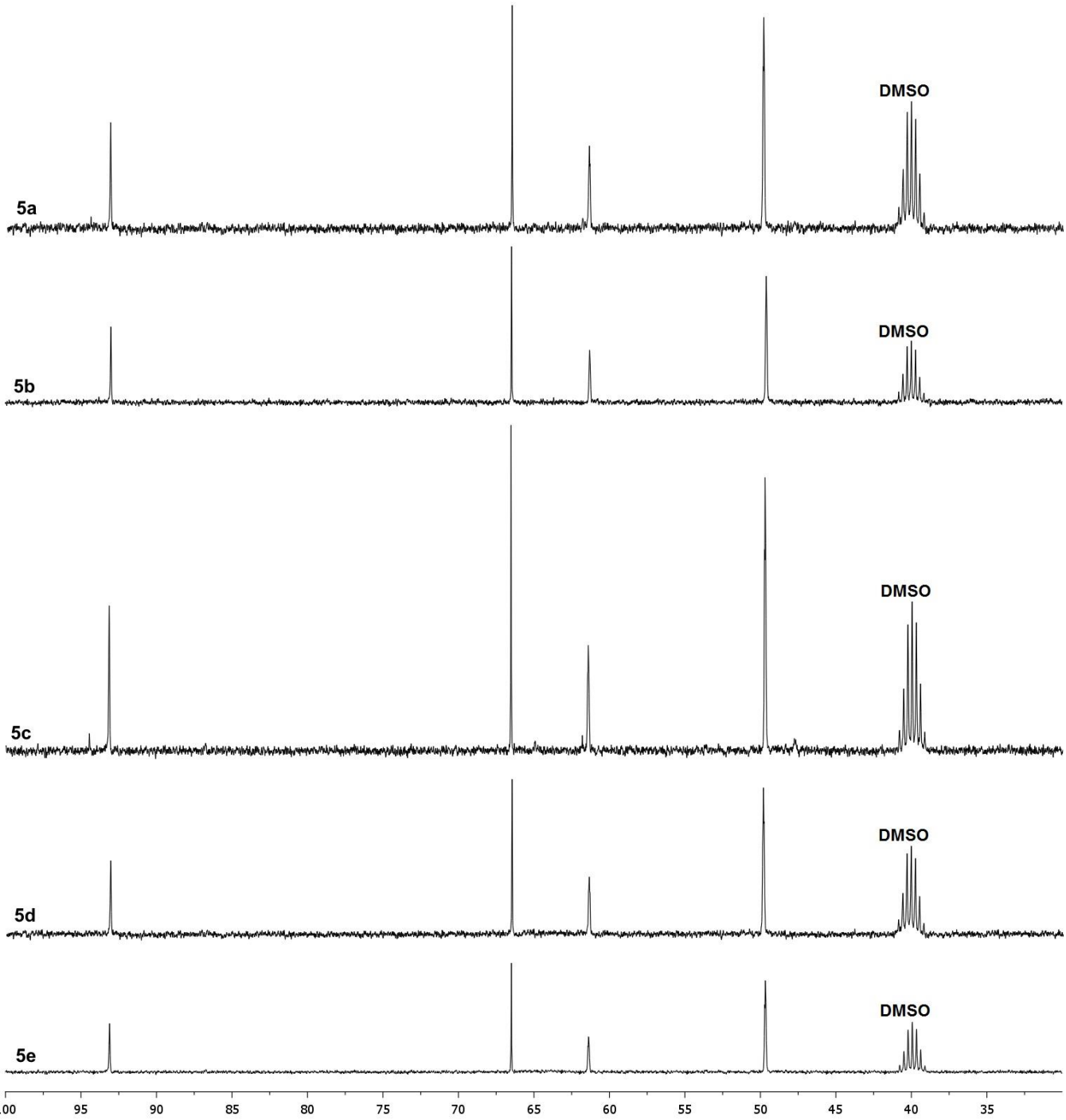

Figure S6. ^{13}C NMR spectra in DMSO-d_6 of 3,3-dimethyloxazolidin-3-ium salts (iodide **5a**, sulfamate **5b**, nitrate **5c**, dinitramide **5d**, perchlorate **5e**).

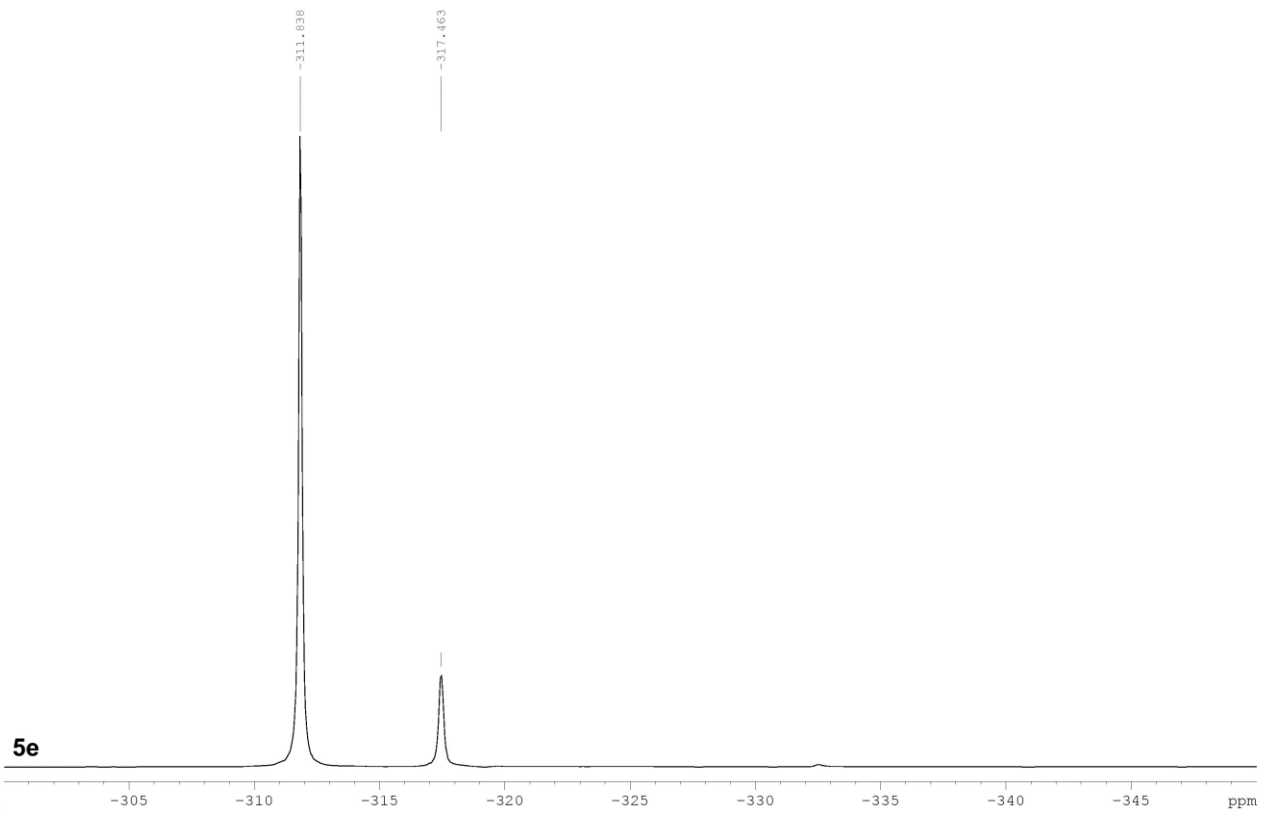

Figure S7. ^{14}N NMR spectra in DMSO-d_6 of 3,3-dimethyloxazolidin-3-ium perchlorate **5e**.

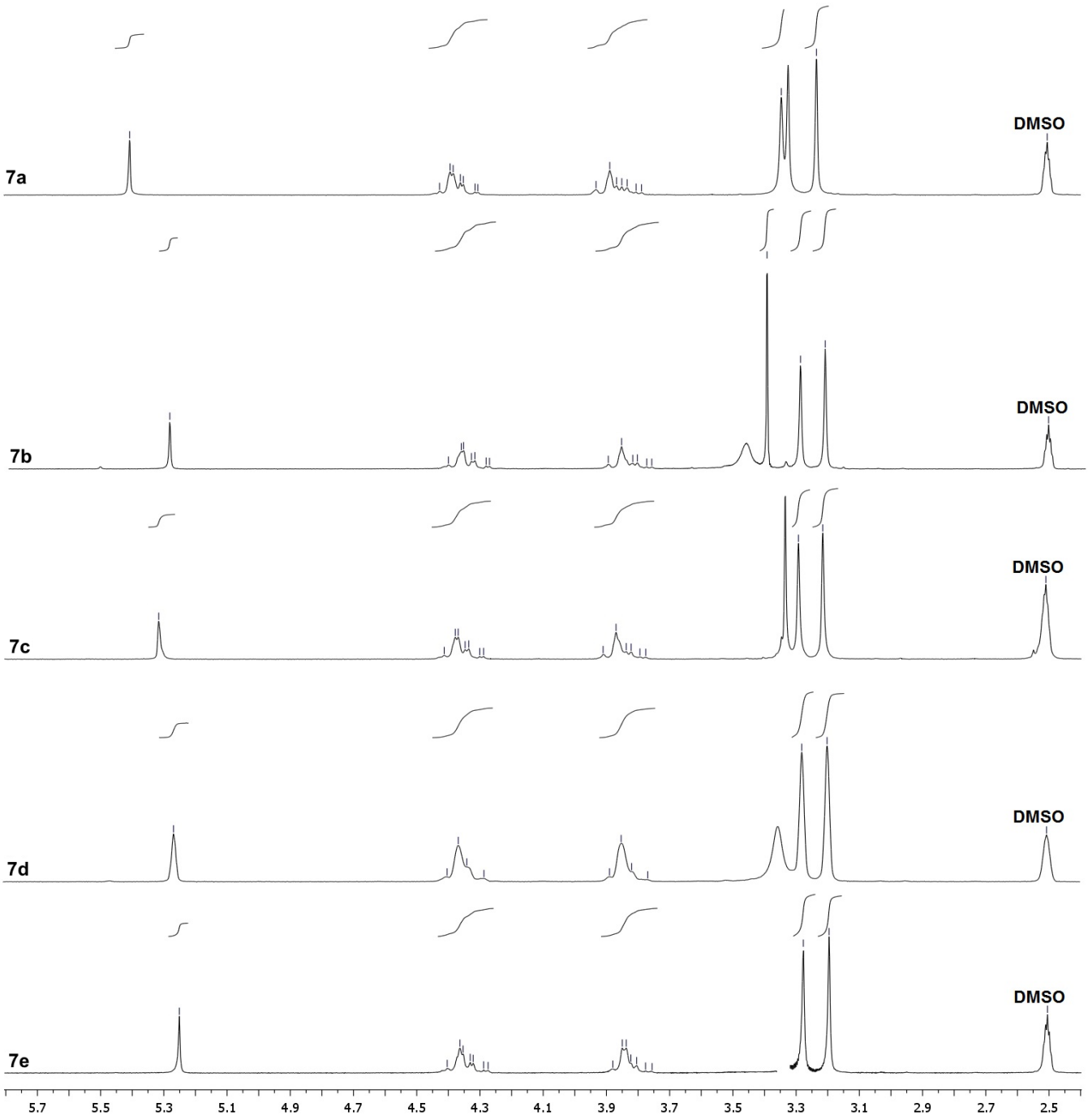

Figure S8. ^{1}H NMR spectra in DMSO-d_6 of 4,4,8,8-tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium salts (diiodide **7a**, bis(methoxysulfonate) **7b**, dinitrate **7c**, bis(dinitramide) **7d**, diperchlorate **7e**).

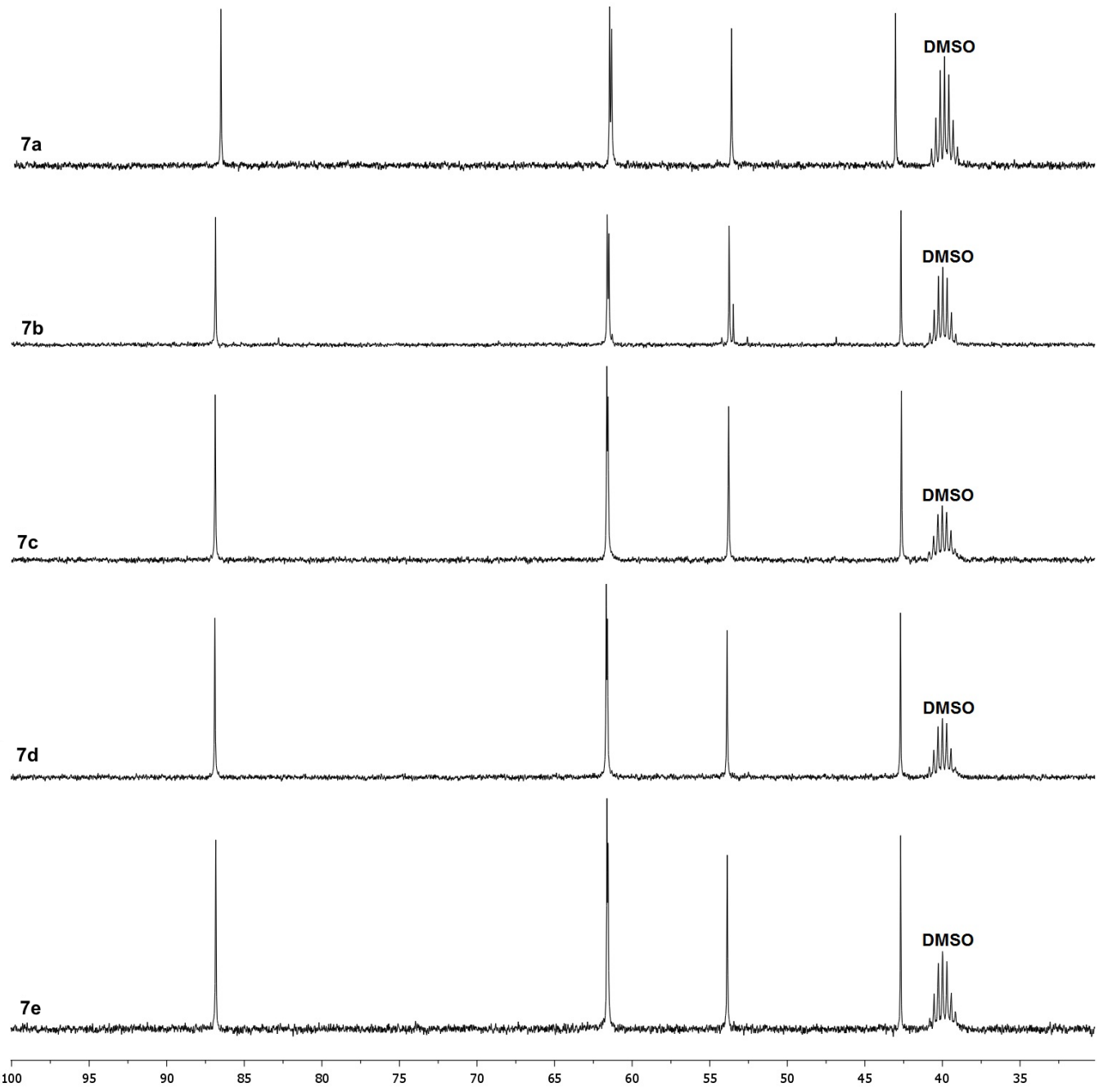

Figure S9. ^{13}C NMR spectra in DMSO-d_6 of 4,4,8,8-tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium salts (diiodide **7a**, bis(methoxysulfonate) **7b**, dinitrate **7c**, bis(dinitramide) **7d**, diperchlorate **7e**).

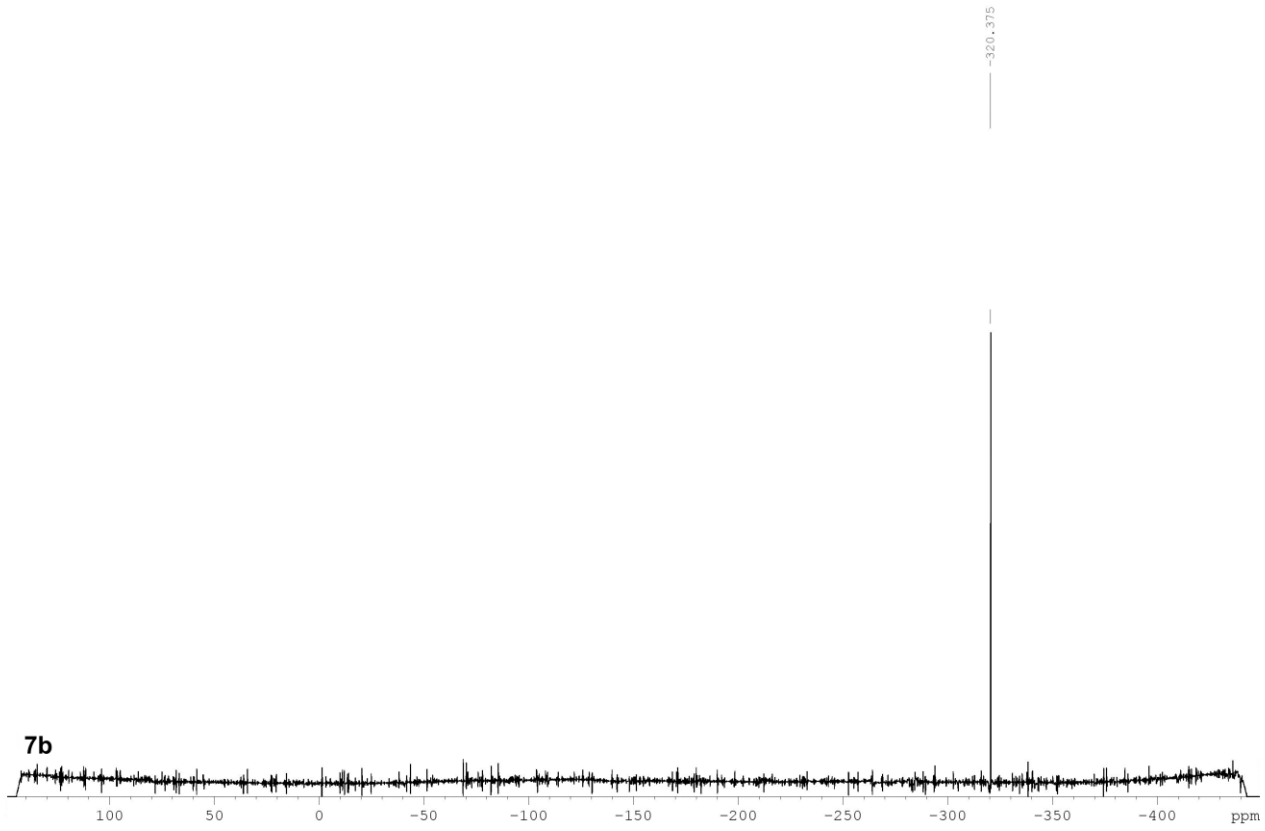

Figure S10. ^{15}N NMR spectra in DMSO-d_6 of 4,4,8,8-tetramethylperhydro[1,4]oxazino-[3,2-*b*][1,4]oxazine-4,8-diinium bis(methoxysulfonate) **7b**.

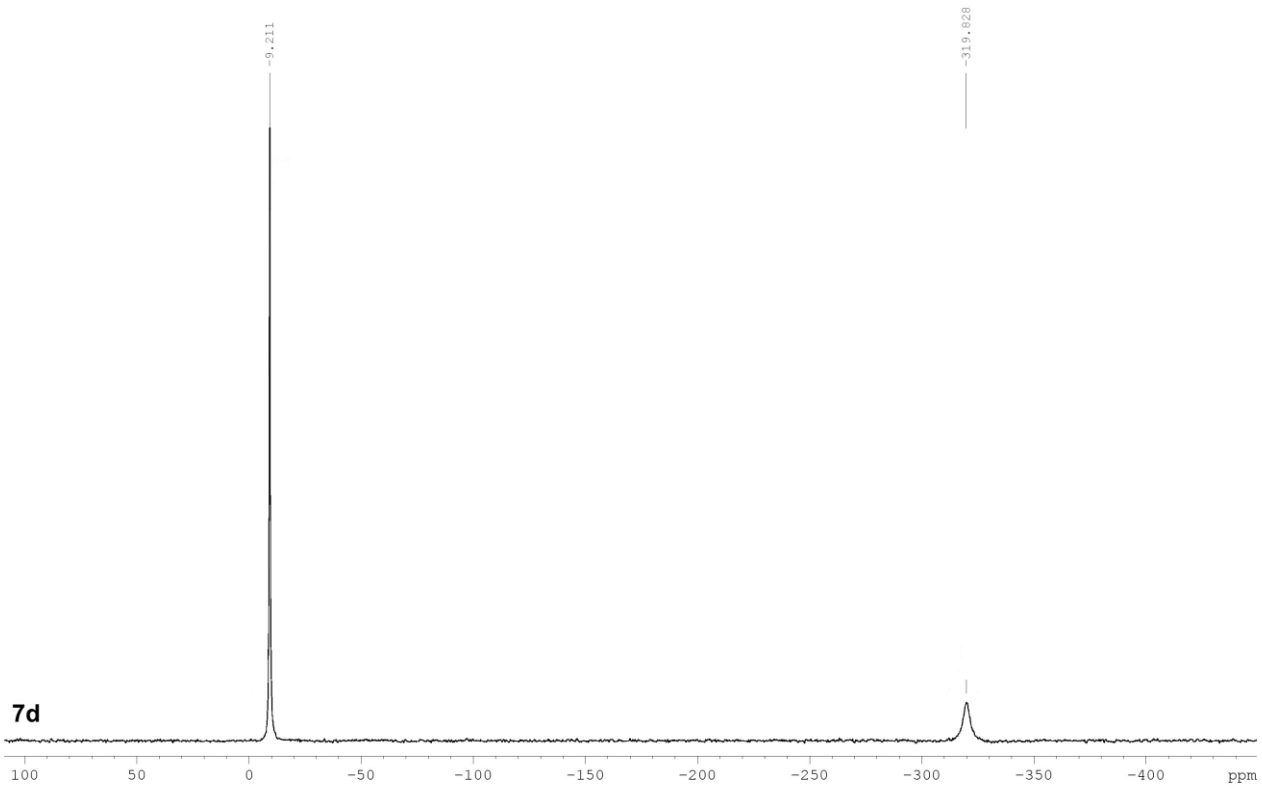

Figure S11. ^{14}N NMR spectra in DMSO-d_6 of 4,4,8,8-tetramethylperhydro[1,4]oxazino-[3,2-*b*][1,4]oxazine-4,8-diinium bis(dinitramide) **7d**.

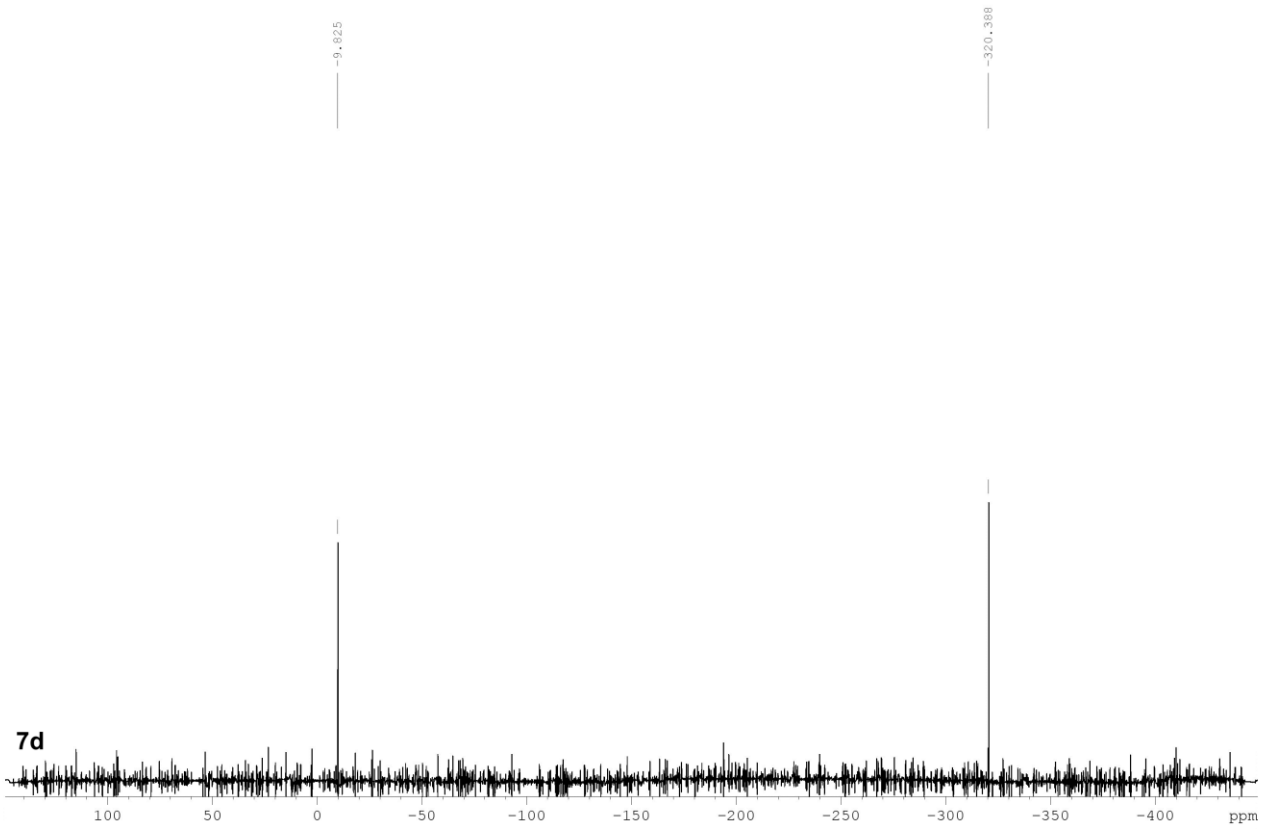

Figure S12. ^{15}N NMR spectra in DMSO-d_6 of 4,4,8,8-tetramethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine-4,8-diinium bis(dinitramide) **7d**.

X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation. The intensity data were integrated by the SAINT program[S1] and were corrected for absorption and decay using SADABS[S2]. The structure was solved by direct methods using SHELXT[S3] and refined on F^2 using SHELXL-2018[S4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Positions of all hydrogen atoms were found from the electron density-difference map, these atoms were refined with individual isotropic displacement parameters. The SHELXTL program suite[S1] was used for molecular graphics.

Acknowledgment

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

Table S1. Crystal data and structure refinement for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino [3,2-*b*][1,4]oxazine **6**.

Identification code	P2328	
Empirical formula	C8 H16 N2 O2	
Formula weight	172.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 14.2653(3) Å	α= 90°.
	b = 4.66150(10) Å	β= 90°.
	c = 13.1875(3) Å	γ = 90°.
Volume	876.94(3) $Å^3$	
Z	4	
Density (calculated)	1.304 g/cm^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	376	
Crystal size	0.59 x 0.16 x 0.08 mm^3	
Theta range for data collection	3.404 to 37.780°.	
Index ranges	-24<=h<=24, -8<=k<=8, -22<=l<=22	
Reflections collected	37616	
Independent reflections	2348 [R(int) = 0.0274]	
Observed reflections	2100	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8753 and 0.8429	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2348 / 0 / 87	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0878	
R indices (all data)	R1 = 0.0350, wR2 = 0.0913	
Largest diff. peak and hole	0.440 and -0.219 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine **6**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5411(1)	1467(1)	6475(1)	15(1)
N(1)	6042(1)	3797(1)	8329(1)	12(1)
C(1)	4936(1)	3879(1)	6923(1)	11(1)
C(2)	6381(1)	1477(1)	6730(1)	16(1)
C(3)	6521(1)	1344(1)	7866(1)	14(1)
C(4)	6206(1)	3969(1)	9421(1)	18(1)

Table S3. Bond lengths [Å] and angles [°] for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino [3,2-*b*][1,4]oxazine **6**.

O(1)-C(2)	1.4237(6)
O(1)-C(1)	1.4394(5)
N(1)-C(1)#1	1.4352(6)
N(1)-C(4)	1.4610(6)
N(1)-C(3)	1.4650(6)
C(1)-C(1)#1	1.5325(8)
C(1)-H(1)	0.974(8)
C(2)-C(3)	1.5127(7)

C(2)-H(2A)	0.977(10)
C(2)-H(2B)	0.988(10)
C(3)-H(3A)	0.973(9)
C(3)-H(3B)	0.987(10)
C(4)-H(4A)	0.990(9)
C(4)-H(4B)	0.974(11)
C(4)-H(4C)	0.976(10)

C(2)-O(1)-C(1)	110.97(3)
C(1)#1-N(1)-C(4)	112.49(4)
C(1)#1-N(1)-C(3)	112.16(3)
C(4)-N(1)-C(3)	112.29(4)
N(1)#1-C(1)-O(1)	109.97(3)
N(1)#1-C(1)-C(1)#1	110.23(4)
O(1)-C(1)-C(1)#1	110.57(3)
N(1)#1-C(1)-H(1)	109.5(5)
O(1)-C(1)-H(1)	108.2(5)
C(1)#1-C(1)-H(1)	108.3(5)
O(1)-C(2)-C(3)	111.20(4)
O(1)-C(2)-H(2A)	105.8(6)
C(3)-C(2)-H(2A)	110.5(5)
O(1)-C(2)-H(2B)	109.1(5)
C(3)-C(2)-H(2B)	110.4(5)
H(2A)-C(2)-H(2B)	109.7(8)
N(1)-C(3)-C(2)	108.64(4)
N(1)-C(3)-H(3A)	112.0(5)
C(2)-C(3)-H(3A)	109.7(5)
N(1)-C(3)-H(3B)	108.5(5)
C(2)-C(3)-H(3B)	109.2(5)
H(3A)-C(3)-H(3B)	108.8(7)
N(1)-C(4)-H(4A)	109.0(6)
N(1)-C(4)-H(4B)	113.9(6)
H(4A)-C(4)-H(4B)	108.0(8)
N(1)-C(4)-H(4C)	109.6(5)
H(4A)-C(4)-H(4C)	109.0(8)
H(4B)-C(4)-H(4C)	107.2(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	10(1)	16(1)	17(1)	-6(1)	-1(1)	2(1)
N(1)	11(1)	12(1)	12(1)	-1(1)	-2(1)	0(1)
C(1)	11(1)	10(1)	12(1)	0(1)	-1(1)	0(1)
C(2)	10(1)	20(1)	18(1)	-5(1)	0(1)	1(1)
C(3)	11(1)	12(1)	19(1)	0(1)	-2(1)	1(1)
C(4)	16(1)	25(1)	14(1)	0(1)	-3(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino[3,2-*b*][1,4]oxazine **6**.

	x	y	z	U(eq)
H(1)	5214(6)	5629(18)	6653(6)	15(2)
H(2A)	6647(7)	-220(20)	6405(7)	27(2)
H(2B)	6675(7)	3220(20)	6449(7)	23(2)
H(3A)	6286(6)	-475(19)	8124(6)	19(2)
H(3B)	7196(7)	1487(17)	8019(7)	21(2)
H(4A)	6888(7)	4170(20)	9546(7)	26(2)
H(4B)	5985(7)	2300(20)	9796(7)	29(2)
H(4C)	5884(6)	5640(20)	9697(7)	24(2)

Table S6. Torsion angles [°] for (4a*R**,8a*R**)-4,8-dimethylperhydro[1,4]oxazino [3,2-*b*][1,4]oxazine **6**.

C(2)-O(1)-C(1)-N(1)#1	-179.02(4)
C(2)-O(1)-C(1)-C(1)#1	-57.06(5)
C(1)-O(1)-C(2)-C(3)	59.51(5)
C(1)#1-N(1)-C(3)-C(2)	56.87(5)
C(4)-N(1)-C(3)-C(2)	-175.30(4)
O(1)-C(2)-C(3)-N(1)	-58.06(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

References

S1. *APEX-III*, Bruker AXS Inc., Madison, Wisconsin, USA, 2019.

S2. L. Krause, R. Herbst-Irmer, G.M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.

S3. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.

S4. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3.