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A convenient synthesis of *N,N′,N″*-trisubstituted diethylenetriamines

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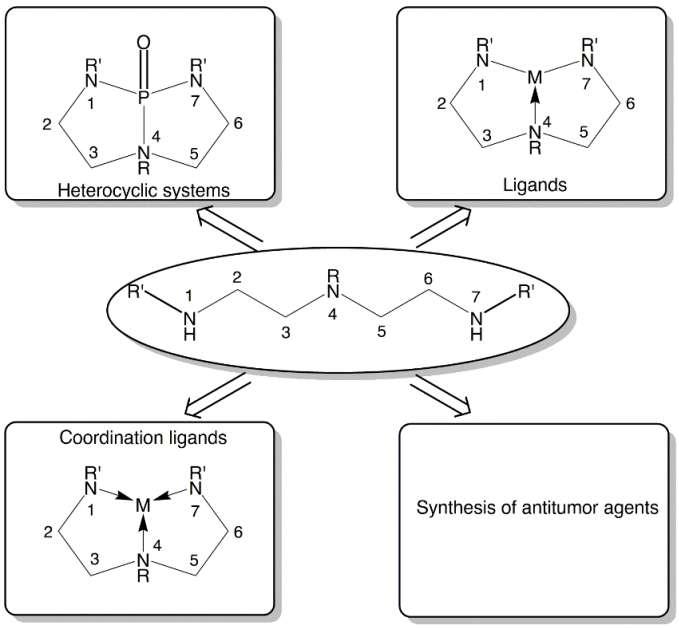
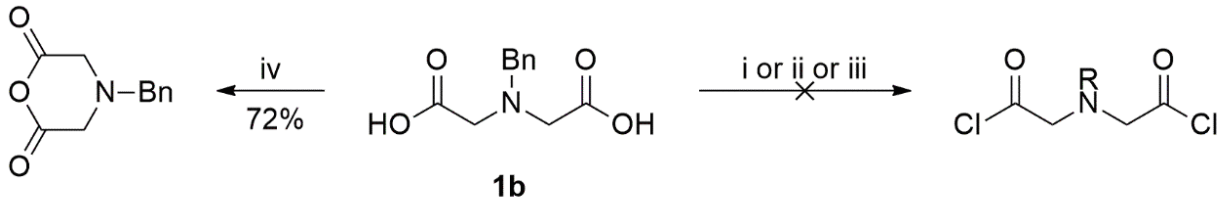
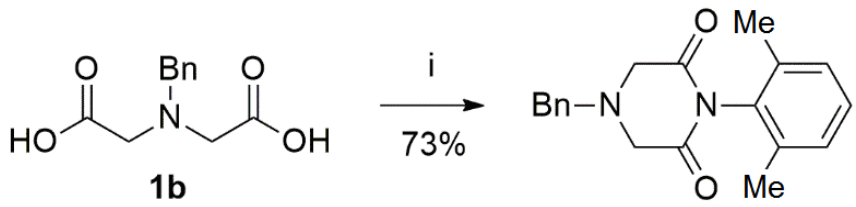


Figure S1. The scope of application of 1,4,7-trisubstituted 1,4,7-triazaheptanes.



Scheme S1. *Reagents and conditions:* i, $(COCl)_2$, DMF; ii, PCl_5, CCl4; iii, $(COCl)_2$, DMF, 2,6-dimethylaniline, Δ; iv. $SOCl_2$, DMF.



Scheme S2. *Reagents and conditions:* i, Ac_2O, Py, Δ, then 2,6-dimethylaniline, Δ.

Experimental data.

NMR spectra were recorded on a Bruker Avance 400 or Agilent 400-MR spectrometers at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Elemental analyses were carried out by the Microanalytical Laboratory of N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences. Melting points (m.p.) were measured with a Büchi B-545 melting point apparatus (Büchi, Flawil, Switzerland). Microwave activated reactions were conducted in Monowave 200 (Anton Paar, Graz, Austria). High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage 4.5 kV); mass range from *m*/*z* 50 to *m*/*z* 1600; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for the solutions in acetonitrile (flow rate 3 μl min^{-1}). Nitrogen was applied as a dry gas (flow rate 4 dm^3 min^{-1}); the interface temperature was set at 200 °C. Elemental analysis was performed using EuroEA-3000 (EuroVector) instrument. Solvents were dried by standard methods and distilled prior to use: ether were stored under KOH, refluxed under Na/benzophenone and then distilled.

*General procedure for the preparation of **1a-d***

To an aqueous solution of chloroacetic acid (19.00 g; 0.2 mol in 70.0 ml of water) at 5 °C was added dropwise an aqueous solution of NaOH (8.00 g; 0.2 mol in 40.0 ml of water). The temperature was kept that it did not exceed 20 °C. Then a solution of the corresponding amine in water was added to the resulting solution. The mixture was heated to 80 ° C, and a solution of NaOH (8.00 g; 0.2 mol in 40.0 ml of water) was added dropwise at a constant rate over 1 hour. Then the solution was refluxed for 1 hour. The mixture was poured into a flat-bottom flask, acidifed to pH = 2 with dilute HCl solution (34.0 ml, v/v = 1:1). The precipitate that formed after acidification was filtered off and washed with ice water. The product was dried in a desiccator over P_2O_5 under reduced pressure [S1]. Compounds **1a-d** were prepared according to the literature procedure, and the spectral data are consistent with the literature.

2,2'-(Ethylazanediyl)diacetic acid **1a**

The general procedure described above was followed using a solution of ethylamine in water (6.44 g, 0.1 mol, 70% solution). A white powder weighing 15.8 g was obtained (yield 98%). M_p = 135 °C. NMR ^{1}H (DMSO-d_6, δ, ppm, J/Hz): 1.00 (t, 3H, J=7.44, C**H**$_3$), 2.75 (q, 2H, J=7.44, C**H**$_2$), 3.46 (s, 4H, C**H**$_2$CO). NMR ^{13}C (DMSO-d_6, δ, ppm): 12.38 (**C**H_3), 47.90 (**C**H_2), 54.33 (**C**H_2CO), 171.96 (**C**OOH)

2,2'-(Benzylazanediyl)diacetic acid **1b**

The general procedure described above was followed using benzylamine (11.0 ml, 0.1 mol). A white powder weighing 17.9 g was obtained (yield 81%). M_p = 205 °C. NMR ^{1}H (DMSO-d_6, δ, ppm, J/Hz): 3.46 (s, 4H, C**H**$_2$CO), 3.87 (s, 2H, C**H**$_2$Ph), 7.25-7.36 (m, 5H, aromatic protons). NMR ^{13}C (DMSO-d_6, δ, ppm): 53.73 (**C**H_2), 57.21 (**C**H_2Ph), 127.28, 128.36, 128.84, 138.62 (aromatic carbon), 172.34 (**C**OOH).

2,2'-(tert-Butylazanediyl)diacetic acid **1c**

The general procedure described above was followed using *tert*-butylamine (10.5 ml, 0.1 mol). A white powder weighing 16.7 g was obtained (yield 81%). M_p = 223 °C. NMR ^{1}H (DMSO-d_6, δ,

ppm, J/Hz): 1.04 (s, 9H, C**H**$_3$), 3.45 (s, 4H, C**H**$_2$). NMR ^{13}C (DMSO-d$_6$, δ, ppm): 26.13 (**C**H$_3$), 53.32 (**C**H$_2$), 174.54 (**C**OOH).

2,2'-(Phenylazanediyl)diacetic acid **1d**

The general procedure described above was followed using phenylamine (9.2 ml, 0.1 mol). A white powder weighing 12.5 g was obtained (yield 60%). M_p = 200 °C. NMR ^{1}H (DMSO-d$_6$, δ, ppm, J/Hz): 4.02 (s, 4H, C**H**$_2$), 6.45 (d, 2H, J=8.59, ***o***-C**H**), 6.64 (t, 1H, J=7.08, 7.32, ***p***-C**H**), 7.15 (t, 2H, J=7.32, 8.59, ***m***-C**H**). NMR ^{13}C (DMSO-d$_6$, δ, ppm): 54.98 (**C**H$_2$), 111.07, 116.34, 128.99, 147.31 (aromatic carbons), 173.44 (**C**OOH).

4-Benzylmorpholine-2,6-dione (see Scheme S1)

A solution of diacid **1b** (3.00 g, 13.44 mmol) in benzene (25 ml) was placed in a 100 ml Schlenk flask under argon flow. Thionyl chloride (8.8 ml, 121.85 mmol) and a catalytic amount of DMF were added dropwise with stirring. The mixture was stirred at 35°C for 2 h, and then 12 h at room temperature. The solvent was removed under reduced pressure to leave a yellow powder weighing 2.52 g (yield 72%). M_p = 278 °C. NMR ^{1}H (DMSO-d$_6$, δ, ppm, J/Hz): 4.06 (s, 4H, C**H**$_2$CO), 4.42 (s, 2H, C**H**$_2$Ph), 7.41-7.43 (m, 3H, aromatic protons), 7.53-7.55 (m, 2H, aromatic protons). NMR ^{13}C (DMSO-d$_6$, δ, ppm): 53.36 (**C**H$_2$CO), 58.42 (**C**H$_2$Ph), 128.78, 129.67, 130.18, 131.64 (aromatic carbons), 167.71 (**C**O).

4-Benzyl-1-(2,6-dimethylphenyl)piperazine-2,6-dione (see Scheme S2)

Diacid **1b** (1.50 g, 6.72 mmol) in pyridine (28 ml) was heated at 50°C under an inert atmosphere until the acid dissolved. Acetic anhydride (2.2 ml, 23.32 mmol) was added, and this was heated at 100°C for 1 h and then left on overnight stirring at room temperature. The reaction mixture was then heated to 50°C, and 2,6-dimethylaniline (0.6 ml, 4.67 mmol) was added, and the mixture was heated at 100°C for 1 h. The solvent was removed under reduced pressure. The yellow residue was dissolved in methanol and treated with activated charcoal. After removal of the solvent, water was added, and the solution was basified to pH=10 with 1 M NaOH solution. The solution was extracted with diethyl ether, the aqueous phase was acidified to pH 7 with 2 M HCl. The organic layer was removed under reduced pressure, the resulting solid residue was recrystallized from ethanol to afford a white powder weighing 1.51 g (yield 73%). M_p = 156 °C. NMR ^{1}H (CDCl$_3$, δ, ppm, J/Hz): 2.10 (s, 6H, C**H**$_3$), 3.57 (s, 4H, C**H**$_2$CO), 3.74 (s, 2H, C**H**$_2$Ph), 7.05-7.08 (m, 1H), 7.12-7.14 (m, 1H), 7.20-7.24 (m, 1H), 7.32-7.40 (m, 5H, aromatic protons). NMR ^{13}C CDCl$_3$, δ, ppm): 17.60 (**C**H$_3$), 56.49 (**C**H$_2$CO), 60.71 (**C**H$_2$Ph), 128.06, 128.43, 128.70, 129.00, 131.84, 135.15, 135.39, 135.48 (aromatic carbons), 169.29 (**C**O). The spectral data are consistent with the literature [S2].

*General procedure for the preparation of **2ab-db** and **2ad-dd***

Compound **1a-1d** and corresponding amine were placed in a flask. The reaction was carried out under microwave irradiation for 20 minat 220 °C. Then the mixture was cooled to room temperature, CH_2Cl_2 was added, and this was washed with water. The organic phase was dried over Na_2SO_4, the solvent was removed under reduced pressure. The excess amine was distilled off under vacuum (1 mbar). The substances were purified by recrystallization from a mixture of ethyl acetate and petroleum ether or by column chromatography (petroleum ether-ethyl acetate-triethylamine).

2,2'-(Ethylazanediyl)bis(N-benzylacetamide) **2ab**

The general procedure described above was followed using **1a** (3.00 g, 18.6 mmol) and benzylamine (16.0 ml, 0.14 mol). The substance was recrystallized from a mixture of ethyl

acetate and petroleum ether. A white powder weighing 2.06 g was obtained (yield 33%). M_p = 70 °C.NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 0.96 (t, 3H, J=7.04, $CH_2C\underline{\mathbf{H}}_3$), 2.55 (q, 2H, J=7.04, $C\underline{\mathbf{H}}_2CH_3$), 3.10 (s, 4H, $C\underline{\mathbf{H}}_2CO$) 4.35(d, 4H, J=5.87, $C\underline{\mathbf{H}}_2Ph$), 7.16-7.29 (m, 10H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 12.08 ($\underline{\mathbf{C}}H_3$), 43.05 ($\underline{\mathbf{C}}H_2Ph$), 49.88 ($\underline{\mathbf{C}}H_2CO$), 58.42 ($\underline{\mathbf{C}}H_2N$), 127.35, 127.44, 128.60, 138.15 (aromatic carbon), 170.48 ($\underline{\mathbf{C}}ONH$). Elemental analysis: Theoretical (%): C, 70.77; H, 7.42; N, 12.38. Found (%) $C_{20}H_{25}N_3O_2$: C, 70.64; H, 7.49; N, 12.43.

2,2'-(Benzylazanediyl)bis(N-benzylacetamide) **2bb**

The general procedure described above was followed using **1b** (2.00 g, 8.96 mmol) and benzylamine (10.0 ml, 0.09 mol). The substance was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder weighing 2.46 g was obtained (yield 67%). M_p = 100 °C.NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 3.21 (s, 4H, $C\underline{\mathbf{H}}_2CO$), 3.68 (s, 2H, $PhC\underline{\mathbf{H}}_2N$), 4.37 (d, 4H, J=5.81, $NHC\underline{\mathbf{H}}_2Ph$), 7.16-7.32 (m, 15H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 43.16 ($\underline{\mathbf{C}}H_2Ph$), 58.15 ($\underline{\mathbf{C}}H_2N$), 59.63 ($\underline{\mathbf{C}}H_2CO$), 127.44, 127.56, 127.75, 128.59, 128.66, 129.01, 136.91, 138.04 (aromatic carbons), 170.18 ($\underline{\mathbf{C}}ONH$). Elemental analysis: Theoretical (%): C, 74.79; H, 6.78; N, 10.47. Found (%) $C_{25}H_{27}N_3O_2$: C, 74.83; H, 6.78; N, 10.39.

2,2'-(tert-Butylazanediyl)bis(N-benzylacetamide) **2cb**

The general procedure described above was followed using **1c** (1.50 g, 7.93 mmol) and benzylamine (8.0 ml, 0.07 mol). The substance was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder weighing 0.47 g was obtained (yield 16%). M_p = 79 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.03 (s, 9H, $C\underline{\mathbf{H}}_3C$), 3.18 (s, 4H, $C\underline{\mathbf{H}}_2CO$), 4.38 (d, 4H, J=5.56, $C\underline{\mathbf{H}}_2Ph$), 7.23-7.29 (m, 10H, aromatic protons), 7.90 (b.s, 2H, $N\underline{\mathbf{H}}$). NMR ^{13}C ($CDCl_3$, δ, ppm): 26.40 ($\underline{\mathbf{C}}H_3C$), 43.10 ($\underline{\mathbf{C}}H_2CO$), 55.26 ($CH_3\underline{\mathbf{C}}$), 55.77 ($\underline{\mathbf{C}}H_2Ph$), 127.12, 127.52, 128.45, 138.44 (aromatic carbons), 172.68 ($\underline{\mathbf{C}}ONH$). Elemental analysis: Theoretical (%): C, 74.79; H, 6.78; N, 10.47. Found (%) $C_{25}H_{27}N_3O_2$: C, 74.83; H, 6.78; N, 10.39.

2,2'-(Phenylazanediyl)bis(N-benzylacetamide) **2db**

The general procedure described above was followed using **1d** (2.00 g, 9.56 mmol) and benzylamine (10.0 ml, 0.09 mol). The substance was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder weighing 2.87 g was obtained (yield 78%). M_p = 83 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 3.89 (s, 4H, $C\underline{\mathbf{H}}_2CO$), 4.39 (d, 4H, J=5.50, $C\underline{\mathbf{H}}_2Ph$), 6.49 (d, 2H, J=8.07, $\underline{\mathbf{C}}H$), 6.79 (t, 1H, J=7.34, $C\underline{\mathbf{H}}$), 7.16-7.25 (m, 12H, aromatic protons), 8.36 (b.s, 2H, $N\underline{\mathbf{H}}$). NMR ^{13}C ($CDCl_3$, δ, ppm): 43.24 ($\underline{\mathbf{C}}H_2Ph$), 57.15 ($\underline{\mathbf{C}}H_2$), 111.71, 118.23, 127.21, 127.49, 128.47, 129.33, 138.11, 146.14 (aromatic carbons), 170.82 ($\underline{\mathbf{C}}ONH$). Elemental analysis: Theoretical (%): C, 74.39; H, 6.50; N, 10.84. Found (%) $C_{24}H_{25}N_3O_2$: C, 74.54; H, 6.49; N, 10.92.

2,2'-(Ethylazanediyl)bis(N-phenylacetamide) **2ad**

The general procedure described above was followed using **1a** (2.00 g, 12.41 mmol) and aniline (10.0 ml, 0.11 mol). The substance was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder weighing 1.76 g was obtained (yield 46%). M_p = 84 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.08 (t, 3H, J=7.15, $C\underline{\mathbf{H}}_3$), 2.72 (q, 2H, J=7.15, $C\underline{\mathbf{H}}_2CH_3$),3.32 (s, 4H, $C\underline{\mathbf{H}}_2CO$), 7.09 (t, 2H, J=7.40, **para**-$C\underline{\mathbf{H}}$), 7.30 (dd, 4H, J=7.70, 8.13, **meta**-$C\underline{\mathbf{H}}$), 7.60 (d, 4H, J=7.64, **ortho** –$C\underline{\mathbf{H}}$), 9.15 (b.s, 2H, $N\underline{\mathbf{H}}$). NMR ^{13}C ($CDCl_3$, δ, ppm): 12.37 ($\underline{\mathbf{C}}H_3$), 50.01 ($\underline{\mathbf{C}}H_2CH_3$), 59.15 ($\underline{\mathbf{C}}H_2CO$), 119.91, 124.38, 128.95, 137.62, (aromatic carbons), 169.50 ($\underline{\mathbf{C}}ONH$). Elemental analysis: Theoretical (%): C, 69.43; H, 6.80; N, 13.49. Found (%) $C_{18}H_{21}N_3O_2$: C, 69.39; H, 6.83; N, 13.45.

2,2'-(Benzylazanediyl)bis(N-phenylacetamide) **2bd**

The general procedure described above was followed using **1b** (1.50 g, 6.72 mmol) and aniline (7.5 ml, 0.08 mol). The substance was purified by column chromatography (ethyl acetate:petroleum ether:Et_3N= 4:1:0.02). A white powder weighing 1.37 g was obtained (yield 53%). M_p = 96 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 3.41 (s, 4H, C**H$_2$**CO), 3.83 (s, 2H, C**H$_2$**Ph), 7.10 (t, 2H, J=7.43, C**H**), 7.25-7.36 (m, 9H, aromatic protons), 7.57 (d, 4H, J=7.83, C**H**), 8.93 (b.s, 2H, N**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 58.70 (**C**H_2CO), 59.49 (**C**H_2Ph), 119.92, 124.38, 127.85, 128.67, 128.94, 136.95, 137.60 (aromatic carbons), 169.14 (**C**ONH). Elemental analysis: Theoretical (%): C, 73.97; H, 6.21; N, 8.57. Found (%) $C_{23}H_{23}N_3O_2$: C, 74.00; H, 6.19; N, 8.59.

2,2'-(tert-Butylazanediyl)bis(N-phenylacetamide) **2cd**

The general procedure described above was followed using **1c** (2.00 g, 10.57 mmol) and aniline (10.0 ml, 0.11 mol). The substance was purified by column chromatography (ethyl acetate:petroleum ether:Et_3N= 4:1:0.02).A white powder weighing 1.25 g was obtained (yield 34%). M_p = 192 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.09 (s, 9H, C**H$_3$**C), 3.36 (s, 4H, C**H$_2$**CO), 7.08 (t, 2H, J=6.99, ***p***-C**H**), 7.31 (dd, 4H, J=7.31, 8.13, ***m***-C**H**), 7.67 (d, 4H, J=7.63, ***o***–C**H**), 9.62 (b.s, 2H, N**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 26.48 (**C**H_3C), 55.44 (**C**H_2CO), 56.73 (CH_3**C**), 119.87, 124.14, 128.88, 138.04 (aromatic carbons), 171.48 (**C**ONH). Elemental analysis: Theoretical (%): C, 70.77; H, 7.42; N, 12.38. Found (%) $C_{20}H_{25}N_3O_2$: C, 70.74; H, 7.39; N, 12.43

2,2'-(Phenylazanediyl)bis(N-phenylacetamide) **2dd**

The general procedure described above was followed using **1d** (1.43 g, 6.84 mmol) and aniline (7.5 ml, 0.08 mol). The substance was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder weighing 1.03 g was obtained (yield 42%). M_p = 220 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 4.26 (s, 4H, **C**H$_2$CO), 6.62 (d, 2H, J=8.22), 6.75 (t, 1H, J=7.24), 7.10 (t, 2H, J=7.43), 7.22 (t, 2H, J=7.43), 7.34 (t, 4H, J=7.63), 7.67 (d, 4H, J=7.63) (aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 58.42 (**C**H_2CO), 112.52, 118.87, 120.45, 125.02, 129.92, 130.35, 139.46, 147.66 (aromatic carbons), 171.30 (**C**ONH). Elemental analysis: Theoretical (%): C, 73.52; H, 5.89; N, 11.69. Found (%) $C_{22}H_{21}N_3O_2$: C, 73.54; H, 5.92; N, 11.65

*General procedure for the preparation of **3a-d***

a) A solution of compound **1a-d** in ethyl alcohol, concentrated sulfuric acid was placed in a 100-ml round-bottom flask. The reaction mixture was refluxed for 5 days, then cooled to room temperature, unreacted alcohol was removed on a rotary evaporator, CH_2Cl_2 was added. The precipitate was filtered off, the filtrate was washed 3 times with a saturated $NaHCO_3$ solution and dried over Na_2SO_4, and the solvent was removed in a vacuum.

b) Ethyl chloroacetate was slowly added to a solution of amine and K_2HPO_4 $3H_2O$ in 10 ml of MeCN while cooling to 0°C. The reaction mixture was stirred at room temperature for 30 min and then refluxed for 24 h. The solvent was evaporated in vacuum, water was added and organic compounds were extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, the solvent was removed in a vacuum [S3].

Diethyl 2,2'-(ethylazanediyl)diacetate **3a**

a) The general procedure described above was followed using **1a** (6.46 g, 0.04 mol), ethanol (28.0 ml), concentrated sulfuric acid (1.1 ml, 2.0 mmol). A yellow liquid weighing 1.78 g was obtained (yield 20%).

b) The general procedure described above was followed using ethyl chloroacetate (3.43 g, 28.0 mmol), K_2HPO_4 $3H_2O$ (6.85 g, 30.0 mmol) and ethylamine (5.0 ml, 10 mmol, 2M solution in THF). A yellow liquid weighing 0.92 g was obtained (yield 42%).

NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.06 (t, 3H, J=7.20, $NCH_2C\mathbf{H_3}$), 1.23 (t, 6H, J=7.20, $OCH_2C\mathbf{H_3}$), 2.74 (q, 2H, J=7.07, $NC\mathbf{H_2}CH_3$), 3.51 (s, 4H, $C\mathbf{H_2}CO$), 4.13 (q, 4H, J=7.24, $NC\mathbf{H_2}CH_3$). NMR ^{13}C ($CDCl_3$, δ, ppm): 12.52 ($\mathbf{C}H_3$), 13.99 ($\mathbf{C}H_3$), 48.26 ($\mathbf{C}H_2$), 54.28 ($\mathbf{C}H_2$), 60.36 ($\mathbf{C}H_2CO$), 170.63 ($\mathbf{C}OO$)

Diethyl 2,2'-(benzylazanediyl)diacetate **3b**

a) The general procedure described above was followed using **1b** (4.46 g, 0.02 mol), ethanol (14.0 ml), concentrated sulfuric acid (0.5 ml, 1.0 mmol). A yellow liquid weighing 1.91 g was obtained (yield 17%).

b) The general procedure described above was followed using ethyl chloroacetate (3.43 g, 28.0 mmol), K_2HPO_4 $3H_2O$ (6.85 g, 30.0 mmol) and benzyl amine (1.08 g, 10 mmol). A yellow liquid weighing 1.46 g was obtained (yield 53%).

NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.26 (t, 6H, J=7.20, $C\mathbf{H_3}$), 3.54 (s, 4H, $C\mathbf{H_2}CO$), 3.91 (s, 2H, $PhC\mathbf{H_2}N$), 4.15 (q, 4H, J=7.20, $C\mathbf{H_2}CH_3$), 7.25-7.39 (m, 5H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.20 ($\mathbf{C}H_3$), 54.18 ($\mathbf{C}H_2CO$), 57.79 ($\mathbf{C}H_2CH_3$), 60.38 ($Ph\mathbf{C}H_2N$), 127.30, 128.31, 129.01, 138.15 (aromatic carbons), 171.16 ($\mathbf{C}OO$)

Diethyl 2,2'-(tert-butylazanediyl)diacetate **3c**

a) The general procedure described above was followed using **1c** (1.50 g, 7.93 mmol), ethanol (5.6 ml), concentrated sulfuric acid (0.2 ml, 0.38 mmol). A yellow liquid weighing 0.24 g was obtained (yield 12 %).

b) The general procedure described above was followed using ethyl chloroacetate (3.43 g, 28.0 mmol), K_2HPO_4 $3H_2O$ (6.85 g, 30.0 mmol) and *tert*-butyl amine (0.73 g, 10 mmol). A yellow liquid weighing 1.34 g was obtained (yield 48%).

NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.08 (s, 9H, $C\mathbf{H_3}C$), 1.22 (t, 6H, J=7.12, $CH_2C\mathbf{H_3}$), 3.50 (s, 4H, $C\mathbf{H_2}CO$), 4.11 (q, 4H, J=7.13, $C\mathbf{H_2}CH_3$). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.11 ($\mathbf{C}H_3CH_2$), 27.27 ($\mathbf{C}H_3C$), 51.16 ($CH_3\mathbf{C}$), 55.05 ($\mathbf{C}H_2CO$), 60.35 ($CH_3\mathbf{C}H_2$), 172.80 ($\mathbf{C}OO$)

Diethyl 2,2'-(phenylazanediyl)diacetate **3d**

a) The general procedure described above was followed using **1d** (4.00 g, 1.91 mmol), ethanol (13.5 ml), concentrated sulfuric acid (0.4 ml, 0.80 mmol). A yellow liquid weighing 0.21 g was obtained (yield 41 %).

b) The general procedure described above was followed using ethyl chloroacetate (3.43 g, 28.0 mmol), K_2HPO_4 $3H_2O$ (6.85 g, 30.0 mmol) and aniline (0.93 g, 10 mmol). A yellow liquid weighing 1.70 g was obtained (yield 64%).

NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.27 (t, 6H, J=7.20, $CH_2C\underline{\mathbf{H_3}}$), 4.13 (s, 4H, $C\underline{\mathbf{H_2}}CO$), 4.20 (q, 4H, J=7.16, $C\underline{\mathbf{H_2}}CH_3$), 6.60 (d, 2H, J=8.59, **ortho** -C**H**), 6.77 (t, 1H, J=7.33, **para**-C**H**), 7.21 (t, 2H, J=7.33, 8.84, **meta**-C**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.15 ($\underline{\mathbf{C}}H_3$), 53.43 ($\underline{\mathbf{C}}H_2CO$), 61.03 ($\underline{\mathbf{C}}H_2$), 112.41, 118.20, 129.18, 147.77(aromatic carbons), 170.88 ($\underline{\mathbf{C}}OO$)

*General procedure for the preparation of **2aa-da***

Compound **3a-d** in ethanol-ethylamine solution was placed in a 100 ml conical flask. The reaction mixture was stirred for 2 days (TLC monitoring, petroleum ether-ethyl acetate, 2: 1). Then the solvent and excess amine were evaporated in vacuum. The resulting oil was dissolved in a mixture of petroleum ether / ethyl acetate with heating, then the solution was cooled, which caused precipitation of the impurities. The precipitate was filtered off and discarded. The solution was evaporated to leave the product.

2,2'-(Ethylazanediyl)bis(N-ethylacetamide) **2aa**

The general procedure describe/d above was followed using **3a** (2.35 g, 10.80 mmol), ethanol (25.0 ml), ethylamine solution (2.09 g of 70% aqueous solution, 32.40 mmol). A yellow oil weighing 2.10 g was obtained (yield 90%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.01 (t, 3H, J=7.04, $NCH_2C\underline{\mathbf{H_3}}$), 1.10 (t, 6H, J=7.43, $NHCH_2C\underline{\mathbf{H_3}}$), 2.57 (q, 2H, J=7.04, $NC\underline{\mathbf{H_2}}CH_3$), 3.09 (s, 4H, $C\underline{\mathbf{H_2}}CO$), 3.22-3.29 (m, 4H, $NHC\underline{\mathbf{H_2}}CH_3$), 7.06 (b.s, 2H, N**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 12.05 ($NCH_2\underline{\mathbf{C}}H_3$), 14.71 ($NHCH_2\underline{\mathbf{C}}H_3$), 33.95 ($NH\underline{C}H_2CH_3$), 49.83 ($\underline{\mathbf{C}}H_2CO$), 58.47 ($N\underline{\mathbf{C}}H_2CH_3$), 170.58 ($\underline{\mathbf{C}}OO$). Elemental analysis: Theoretical (%): C, 55.79; H, 9.83; N, 19.52. Found (%) $C_{10}H_{21}N_3O_2$: C, 55.78; H, 9.90; N, 19.45

2,2'-(Benzylazanediyl)bis(N-ethylacetamide) **2ba**

The general procedure described above was followed using **3b** (3.44 g, 12.30 mmol), ethanol (30.0 ml), ethylamine solution (2.38 g of 70% aqueous solution, 36.90 mmol). A yellow oil weighing 2.00 g was obtained (yield 60%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.06 (t, 6H, J=7.33, $C\underline{\mathbf{H_3}}$), 3.12 (s, 4H, $C\underline{\mathbf{H_2}}CO$), 3.21-3.25 (m, 4H, $C\underline{\mathbf{H_2}}CH_3$), 3.65 (s, 2H, $PhC\underline{\mathbf{H_2}}N$), 6.88 (b.s, 2H, N**H**), 7.21-7.27 (m, 5H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.72 ($\underline{\mathbf{C}}H_3$), 34.05 ($\underline{\mathbf{C}}H_2CH_3$), 58.26 ($\underline{\mathbf{C}}H_2CO$), 59.63 ($\underline{\mathbf{C}}H_2N$), 127.66, 128.52, 128.96, 137.17 (aromatic carbons), 170.31 ($\underline{\mathbf{C}}OO$). Elemental analysis: Theoretical (%): C, 64.95; H, 8.36; N, 15.15. Found (%) $C_{15}H_{23}N_3O_2$: C, 65.10; H, 8.34; N, 15.08

2,2'-(tert-Butylazanediyl)bis(N-ethylacetamide) **2ca**

The general procedure described above was followed using **3c** (0.97 g, 3.95 mmol), ethanol (10.0 ml), ethylamine solution (1.20 g of 70% aqueous solution, 19.77 mmol). A yellow oil weighing 0.70 g was obtained (yield 58%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.01 (s, 9H, $C(C\underline{\mathbf{H_3}})_3$), 1.09 (t, 6H, J=7.28, $C\underline{\mathbf{H_3}}$), 3.13 (s, 4H, $C\underline{\mathbf{H_2}}CO$), 3.20-3.27 (m, 4H, $C\underline{\mathbf{H_2}}CH_3$), 7.53 (b.s, 2H, N**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.57 ($\underline{\mathbf{C}}H_3$), 26.36 ($C(\underline{\mathbf{C}}H_3)_3$), 34.08 ($\underline{\mathbf{C}}H_2CH_3$), 55.21 ($\underline{\mathbf{C}}(CH_3)_3$) 55.74 ($\underline{\mathbf{C}}H_2CO$), 172.68 ($\underline{\mathbf{C}}OO$). Elemental analysis: Theoretical (%): C, 55.79; H, 9.83; N, 14.86. Found (%) $C_{10}H_{21}N_3O_2$: C, 55.76; H, 9.84; N, 14.88

2,2'-(Phenylazanediyl)bis(N-ethylacetamide) **2da**

The general procedure described above was followed using **3d** (2.00 g, 9.56 mmol), ethanol (30.0 ml), ethylamine solution (2.38 g of 70% aqueous solution, 36.9 mmol). A yellow oil weighing 2.15 g was obtained (yield 92%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.11 (t, 6H, J=7.04, 7.44, $C\underline{\mathbf{H_3}}$), 3.25-3.32 (m, 4H, $C\underline{\mathbf{H_2}}CH_3$), 3.96 (s, 4H, $C\underline{\mathbf{H_2}}CO$), 6.49 (d, 2H, J=8.61, **ortho** –C**H**), 6.75 (t, 1H, J=7.04, 7.34, **para**-C**H**), 7.17 (t, 2H, J=7.43, 8.61, **meta**-C**H**), 7.88 (b.s, 2H, N**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.53 ($\underline{\mathbf{C}}H_3$), 34.39 ($\underline{\mathbf{C}}H_2CH_3$), 57.38 ($\underline{\mathbf{C}}H_2CO$), 111.59, 118.11,

129.28, 146.41 (aromatic carbons), 170.47 (**C**OO). Elemental analysis: Theoretical (%): C, 63.85; H, 8.04; N, 15.96. Found (%) $C_{14}H_{21}N_3O_2$: C, 65.80; H, 8.05; N, 15.98

2,2'-(Benzylazanediyl)bis(N-tert-butylacetamide) **2bc**

A solution of compound **1b** (7.35 g, 32.5 mmol), *tert*-butylamine (6.9 ml, 65.0 mmol), and HOBt H_2O (9.95 g, 65.0 mmol) in THF (300 ml) and DMF (10 ml) was placed into a round bottom flask. While stirring and cooling to 0 °C, DCC (13.41 g, 65.0 mmol) was added. The reaction mixture was stirred at room temperature for 2 days. The solvent was removed under reduced pressure, ethyl acetate was added and filtered through celite. The filtrate was washed 3 times with saturated $NaHCO_3$ solution and dried over Na_2SO_4, then the solvent was removed *in vacuo*. The material was recrystallized from a mixture of ethyl acetate and petroleum ether. A white powder was obtained, weighing 5.37 g (yield 49%). M_p = 120 °C. NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.32 (s, 18H, C**H**$_3$), 3.07 (s, 4H, C**H**$_2$CO), 3.66 (s, 2H, C**H**$_2$Ph), 6.48 (b.s, 2H, N**H**) 7.25-7.33 (m, 5H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 28.73 (**C**H$_3$), 50.93 (**C**H$_2$CO), 59.11 (**C**H$_2$Ph), 59.76 (CH$_3$**C**), 127.80, 128.73, 128.89, 137.23 (aromatic carbons), 169.14 (**C**ONH). Elemental analysis: Theoretical (%): C, 68.47; H, 9.35; N, 12.57. Found (%) $C_{19}H_{31}N_3O_2$: C, 68.43; H, 9.37; N, 12.60.

*General procedure for the preparation of diamines **4***

The corresponding diamide **2** in diethyl ether was placed in a Schlenk flask. With stirring and cooling, $LiAlH_4$ was added in portions. The reaction mixture was stirred at room temperature for 3 days. Water was added dropwise to quench the excess of $LiAlH_4$, after which 20% NaOH solution (1 ml solution per 26.35 mmol $LiAlH_4$) was added, and the mixture was stirred for 20 min. The formed precipitate was filtered off on a Buchner funnel, the precipitate was washed with ether, the organic extracts were combined and washed 3 times with water, dried over Na_2SO_4, the solvent was removed under reduced pressure.

N^1,N^2-Diethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine **4aa**

The general procedure described above was followed using **2aa** (2.02 g, 9.38 mmol), diethyl ether (75 ml) and $LiAlH_4$ (2.56 g, 67.56 mmol). A pale-yellow oil was obtained (yield 1.78 g, 90%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 0.96 (t, 3H, J=7.07, NCH$_2$C**H**$_3$), 1.06 (t, 6H, J=7.07, NHCH$_2$C**H**$_3$), 2.48-2.63 (m, 14H, C**H**$_2$CH$_2$NH, CH$_2$C**H**$_2$NH, NHC**H**$_2$CH$_3$,, NC**H**$_2$CH$_3$), 2.51 (q, 4H, , J=6.82, NHC**H**$_2$CH$_3$), 2.60 (t, 4H, J=7.07, CH$_2$C**H**$_2$NH), 2.61 (q, 4H, J=5.43, NC**H**$_2$CH$_3$). NMR ^{13}C ($CDCl_3$, δ, ppm): 11.56 (NCH$_2$**C**H$_3$), 15.22 (NHCH$_2$**C**H$_3$), 44.07 (NH**C**H$_2$CH$_3$), 47.45 (**C**H$_2$CH$_2$NH), 47.96 (N**C**H$_2$CH$_3$), 53.27 (CH$_2$**C**H$_2$NH). **HRMS** (ESI) calculated for $C_{10}H_{25}N_3$ $[M+H]^+$, *m/z* 188.2121 found $[M+H]^+$, *m/z* 188.2124.

N^1-Benzyl-N^2-ethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine **4ba**

The general procedure described above was followed using **2ba** (2.00 g, 7.21 mmol), diethyl ether (80 ml) and $LiAlH_4$ (2.12 g, 55.86 mmol). A pale-yellow oil was obtained (yield 1.50 g, 83%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.04 (t, 6H, J=7.07, C**H**$_3$), 2.52 (q, 4H, J=7.07, C**H**$_2$CH$_3$), 2.57-2.64 (m, 8H, C**H**$_2$CH$_2$NH, CH$_2$C**H**$_2$NH), 3.56 (s, 2H, NHC**H**$_2$Ph), 7.18-7.29 (m, 5H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 15.13 (**C**H$_3$), 43.85 (**C**H$_2$CH$_2$NH), 47.23 (**C**H$_2$CH$_3$) 54.04 (CH$_2$**C**H$_2$NH), 59.32 (**C**H$_2$Ph), 126.89, 128.19, 128.67, 139.56 (aromatic carbons). **HRMS** (ESI) calculated for $C_{15}H_{27}N_3$ $[M+H]^+$, *m/z* 250.2278 found $[M+H]^+$, *m/z* 250.2250.

N^1-tert-Butyl-N^2-ethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine **4ca**

The reaction mixture was stirred at room temperature for 2 weeks. The general procedure described above was followed using **2ca** (0.70 g, 2.65 mmol), diethyl ether (40 ml) and $LiAlH_4$ (0.64 g, 20.53 mmol). A yellow oil was obtained (yield 0. 58 g, 70%). 1.00 (s, 9H, C**H$_3$**C), 1.17-1.21 (m, 6H, CH_2C**H$_3$**), 2.54-2.60 (м, 12H, CH_2C**H$_2$**NH, C**H$_2$**CH_2NH, C**H$_2$**CH_3). NMR ^{13}C ($CDCl_3$, δ, ppm): 14.07(**C**H_3C), 29.65 (CH_2**C**H_3), 45.49 (N**C**H_2CH_2NH), 50.35 (**C**H_2CH_3), 53.48 (CH_2**C**H_2NH), 54.88 ((CH_3)$_3$**C**). **HRMS** (ESI) calculated for $C_{12}H_{29}N_3$ $[M+H]^+$, *m/z* 216.2434 found $[M+H]^+$, *m/z* 216.2440.

N^2-Ethyl-N^1-(2-ethylaminoethyl)-N^1-phenylethane-1,2-diamine **4da**

The general procedure described above was followed using **2da** (2.50 g, 6.25 mmol), diethyl ether (75 ml) and $LiAlH_4$ (1.80 g, 47.43 mmol). A light-yellow oil was obtained (yield 2.25 g, 95%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.12 (t, 6H, J=7.21, NCH_2C**H$_3$**), 2.67 (q, 4H, J=7.15, NHC**H$_2$**CH_3), 2.84 (t, 4H, J=6.80, C**H$_2$**CH_2NH), 3.48 (t, 4H, J=6.80, CH_2C**H$_2$**NH),6.70 (t, 1H, J=7.25, ***p***-C**H**), 6.76 (d, 2H, J=8.07, ***o***-C**H**), 7.21-7.25 (m, 2H, ***m***-C**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 15.22 (NCH_2**C**H_3), 44.19 (NH**C**H_2CH_3), 47.07 (N**C**H_2CH_2NH), 51.64 (NCH_2**C**H_2NH), 112.33, 116.32, 129.22, 148.19 (aromatic carbons). **HRMS** (ESI) calculated for $C_{14}H_{25}N_3$ $[M+H]^+$, *m/z* 236.2121 found $[M+H]^+$, *m/z* 236.2140.

N^1-Benzyl-N^1-(2-benzylaminoethyl)-N^2-ethylethane-1,2-diamine **4ab**

The general procedure described above was followed using **2ab** (0.29 g, 0.85 mmol), diethyl ether (20 ml) and $LiAlH_4$ (0.25 g, 6.59 mmol). A light-yellow oil was obtained (yield 0.19 g, 71%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 0.98 (t, 3H, J=7.07, CH_2C**H$_3$**), 2.05 (b.s, 2H, N**H**), 2.48 (q, 2H, J=6.82, C**H$_2$**CH_3), 2.58 (t, 4H, J=5.43, C**H$_2$**CH_2NH), 2.68 (t, 4H, J=5.43, CH_2C**H$_2$**NH), 3.78 (s, 4H, NHC**H$_2$**Ph), 7.24-7.30 (m, 10H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 11.61 (**C**H_3), 46.94 (**C**H_2CH_2NH), 47.82 (**C**H_2CH_3) 53.21 (CH_2**C**H_2NH), 53.91 (**C**H_2Ph), 126.78, 128.03, 128.29, 140.33 (aromatic carbons). **HRMS** (ESI) calculated for $C_{20}H_{29}N_3$ $[M+H]^+$, *m/z* 312.2434 found $[M+H]^+$, *m/z* 312.2440.

N^1, N^2-dibenzyl-N^1-(2-(benzylamino) ethyl) ethane-1,2-diamine **4bb**

The general procedure described above was followed using **2bb** (5.85 g, 14.57 mmol), diethyl ether (180 ml) and $LiAlH_4$ (4.01 g, 105.67 mmol). A light-yellow oil was obtained (yield 4.32 g, 79%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 1.74 (b.s, 2H, N**H**), 2.58 (t, 4H, J=5.43, C**H$_2$**CH_2NH), 2.65 (t, 4H, J=5.55, CH_2C**H$_2$**NH), 3.51 (s, 2H, PhC**H$_2$**N), 3.65 (s, 4H, NHC**H$_2$**Ph), 7.18-7.28 (m, 15H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 46.78 (**C**H_2CH_2NH), 53.70 (**C**H_2Ph), 53.90 (CH_2**C**H_2NH), 59.23 (**C**H_2N), 126.78, 126.90, 128.02, 128.21, 128.28, 128.76, 139.45, 140.23 (aromatic carbons). **HRMS** (ESI) calculated for $C_{25}H_{32}N_3$ $[M+H]^+$, *m/z* 374.2591 found $[M+H]^+$, *m/z* 374.2580.

N^1-tert-Butyl-N^1-(2-benzylaminoethyl)-N^2-ethylethane-1,2-diamine **4cb**

The general procedure described above was followed using **2cb** (1.74 g, 4.73 mmol), diethyl ether (65 ml) and $LiAlH_4$ (1.39 g, 36.61 mmol). A light-yellow oil was obtained (yield 1.27 g, 79%). NMR ^{1}H ($CDCl_3$, δ, ppm, J/Hz): 0.99 (s, 9H, C**H$_3$**C), 2.55-2.58 (м, 8H, C**H$_2$**C**H$_2$**NH, C**H$_2$**CH_3), 3.68 (s, 4H, NHC**H$_2$**Ph), 7.16-7.28 (m, 10H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 27.18 (**C**H_3), 50.30 (N**C**H_2CH_2NH), 50.68 (**C**H_2Ph), 53.92 (CH_2**C**H_2NH), 54.79 (**C**(CH_3)$_3$), 126.80, 128.06, 128.29 (aromatic carbons). **HRMS** (ESI) calculated for $C_{22}H_{33}N_3$ $[M+H]^+$, *m/z* 340.2747 found $[M+H]^+$, *m/z* 340.2731.

N^1-(2-Benzylaminoethyl)-N^2-ethyl-N^1-phenylethane-1,2-diamine **4db**

The general procedure described above was followed using **2db** (5.70 g, 14.71 mmol), diethyl ether (180 ml) and $LiAlH_4$ (4.14 g, 0.11 mol). A light-yellow oil was obtained (yield 5.23 g, 99%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 1.62 (b.s, 2H, N**H**), 2.79 (t, 4H, J=6.57, C**H**$_2$$CH_2NH$), 3.43 (t, 4H, J=6.71, CH_2C**H**$_2$NH), 3.72 (s, 4H, NHC**H**$_2$Ph), 6.65-6.72 (m, 3H), 7.14-7.34 (m, 12H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 46.70 (N**C**H_2CH_2NH), 51.72 (NCH_2**C**H_2NH), 53.90 (**C**H_2Ph), 112.54, 116.44, 126.69, 126.93, 127.99, 128.34, 129.18, 139.98, 143.27, 148.23 (aromatic carbons). **HRMS** (ESI) calculated for $C_{24}H_{29}N_3$ $[M+H]^+$, *m/z* 360.2434 found $[M+H]^+$, *m/z* 360.2441.

N^1-Benzyl-N^2-tert-butyl-N^1-(2-tert-butylaminoethyl)ethane-1,2-diamine **4bc**

The general procedure described above was followed using **2bc** (2.50 g, 7.49 mmol), diethyl ether (80 ml) and $LiAlH_4$ (2.20 g, 58.02 mmol). An orange oil was obtained (yield 1.25 g, 54%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 1.04 (s, 18H, C**H**$_3$), 2.54-2.62 (m, 8H, NC**H**$_2$C**H**$_2$NH), 3.55 (s, 2H, C**H**$_2$Ph), 7.18-7.30 (m, 5H, aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 28.96 (**C**H_3), 39.98 (N**C**H_2CH_2NH), 49.88 (NCH_2**C**H_2NH), 54.94 (**C**H_2Ph), 58.83 (CH_3**C**), 126.88, 128.20, 128.86, 139.43 (aromatic carbons). **HRMS** (ESI) calculated for $C_{19}H_{35}N_3$ $[M+H]^+$, *m/z* 306.2904 found $[M+H]^+$, *m/z* 360.2900.

N^1-Ethyl-N^2-phenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine **4ad**

The general procedure described above was followed using **2ad** (1.76 g, 5.65 mmol), 80.0 ml of diethyl ether (80 ml) and $LiAlH_4$ (1.55 g, 40.84 mmol). A yellow-orange oil was obtained (yield 80%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 1.06 (t, 3H, J=7.15, NCH_2C**H**$_3$), 2.62 (q, 2H, J=7.15, NC**H**$_2$$CH_3$), 2.74 (t, 4H, J=5.93, NC**H**$_2$$CH_2NH$), 3.16 (t, 4H, J=5.93, NCH_2C**H**$_2$NH), 6.58 (d, 4H, J=8.56, **ortho** –C**H**), 6.72 (t, 2H, J=7.34, **para**-C**H**), 7.17 (t, 4H, J=7.34, **meta**-C**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 11.58 (**C**H_3CH_2N), 41.56 (**C**H_2CH_2NH), 47.51 (CH_3**C**H_2N), 52.22 (CH_2**C**H_2NH), 112.95, 117.31, 129.20, 148.34 (aromatic carbons). **HRMS** (ESI) calculated for $C_{18}H_{25}N_3$ $[M+H]^+$, *m/z* 284.2121 found $[M+H]^+$, *m/z* 284.2120.

N^1-Benzyl-N^2-phenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine **4bd**

The general procedure described above was followed using **2bd** (1.33 g, 3.56 mmol), diethyl ether (50 ml) and $LiAlH_4$ (0.98 g, 25.82 mmol). A dark orange oil was obtained (yield 1.04 g, 85%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz):): 2.81 (t, 4H, J=5.99, NC**H**$_2$$CH_2NH$), 3.20 (t, 4H, J=5.99 NCH_2C**H**$_2$NH), 3.69 (s, 2H, PhC**H**$_2$N), 4.05 (b.s, 2H, N**H**), 6.55 (d, 4H, J=7.40), 6.74 (t, 2H, J=7.34), 7.19 (t, 4H, J=7.40), 7.33-7.42 (m, 5H) (aromatic protons).NMR ^{13}C ($CDCl_3$, δ, ppm): 41.49 (N**C**$H_2$$CH_2NH$), 52.72 ($NCH_2$**C**$H_2$NH), 58.67 (**C**$H_2$Ph), 112.79, 117.21, 127.30, 128.47, 128.98, 129.16, 138.96, 148.22 (aromatic carbons). **HRMS** (ESI) calculated for $C_{23}H_{27}N_3$ $[M+H]^+$, *m/z* 346.2278 found $[M+H]^+$, *m/z* 346.2267.

N^1-tert-Butyl-N^2-phenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine **4cd**

The general procedure described above was followed using **2cd** (1.21 g, 3.56 mmol), diethyl ether (50 ml) and $LiAlH_4$ (0.97 g, 25.56 mmol). An orange oil was obtained (yield 0.78 g, 70%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 1.21 (s, 9H, C**H**$_3$), 2.83 (t, 4H, J=6.30, NC**H**$_2$$CH_2NH$), 3.16 (t, 4H, J=6.30, NCH_2C**H**$_2$NH), 4.20 (b.s, 2H, N**H**), 6.57 (d, 4H, J=7.58, ***o***-C**H**), 6.76 (t, 2H, J=7.34, ***p***-C**H**), 7.21 (t, 4H, J=7.34, ***m***-C**H**). NMR ^{13}C ($CDCl_3$, δ, ppm): 27.14 (**C**H_3), 44.23 (N**C**H_2CH_2NH), 49.67 (NCH_2**C**H_2NH), 112.85, 117.10, 129.11, 148.18 (aromatic carbons). **HRMS** (ESI) calculated for $C_{20}H_{29}N_3$ $[M+H]^+$, *m/z* 312.2434 found $[M+H]^+$, *m/z* 312.2425.

N^1,N^2-Diphenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine **4dd**

The reaction mixture was stirred at room temperature for 2 weeks. The general procedure described above was followed using **2dd** (1.61 g, 4.48 mmol), diethyl ether (70 ml) and $LiAlH_4$ (1.22 g, 32.15 mmol). A light-yellow powder was obtained (yield 1.36 g, 92%). NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 3.36 (t, 4H, J=6.30, NC**H₂**CH_2NH), 3.60 (t, 4H, J=6.30, NCH_2C**H₂**NH), 4.28 (b.s, 2H, N**H**), 6.59-6.61 (m, 4H) 6.73-6.85 (m, 5H), 7.17 (t, 4H, J=7.46, ***m***-C**H**), 7.27-7.29 (m, 2H) (aromatic protons). NMR ^{13}C ($CDCl_3$, δ, ppm): 41.88 (N**C**H_2CH_2NH), 51.34 (NCH_2**C**H_2NH), 54.48 (N**C**H_2CH_2NH), 60.17 (NCH_2**C**H_2NH), 112.93, 113.26, 117.15, 117.97, 129.23, 129.30, 147.74, 147.96 (aromatic carbons). **HRMS** (ESI) calculated for $C_{22}H_{25}N_3$ $[M+H]^+$, *m/z* 332.2121 found $[M+H]^+$, *m/z* 332.2114.

References

[S1] N. Smrečki, B.M. Kukovec, M. Daković, Z. Popović, *Inorg. Chim. Acta*, 2013, **400**, 122.

[S2] C. G. Kruse, J. J. Troost, P. Cohen-Fernandes, H. van der Linden and J. D. van Loon, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 303.

[S3] N. Kumari, S. Jha, S. Bhattacharya, *Chem. Asian J.*, 2012, **7**, 2805.

Figures of ^{1}H and ^{13}C spectra

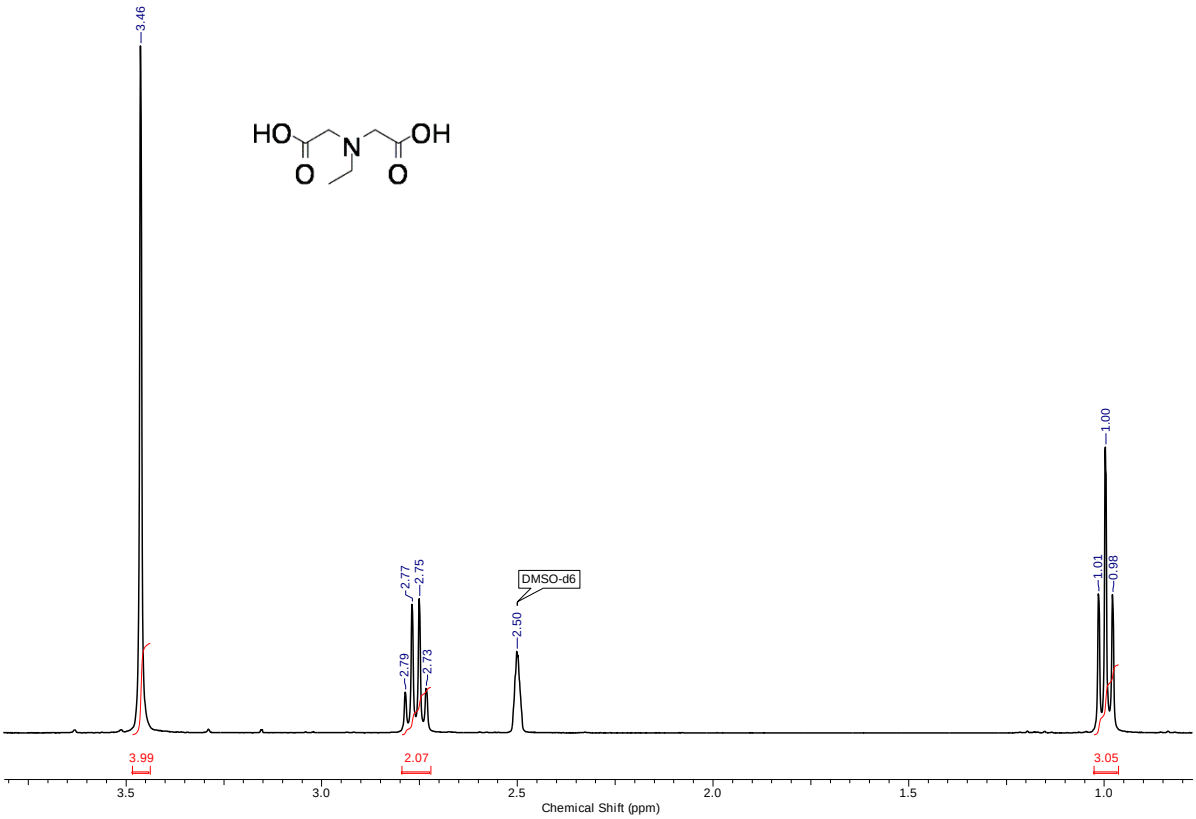


Figure S2. **^{1}H NMR** spectrum of *2,2'-(ethylazanediyl)diacetic acid* **1a**

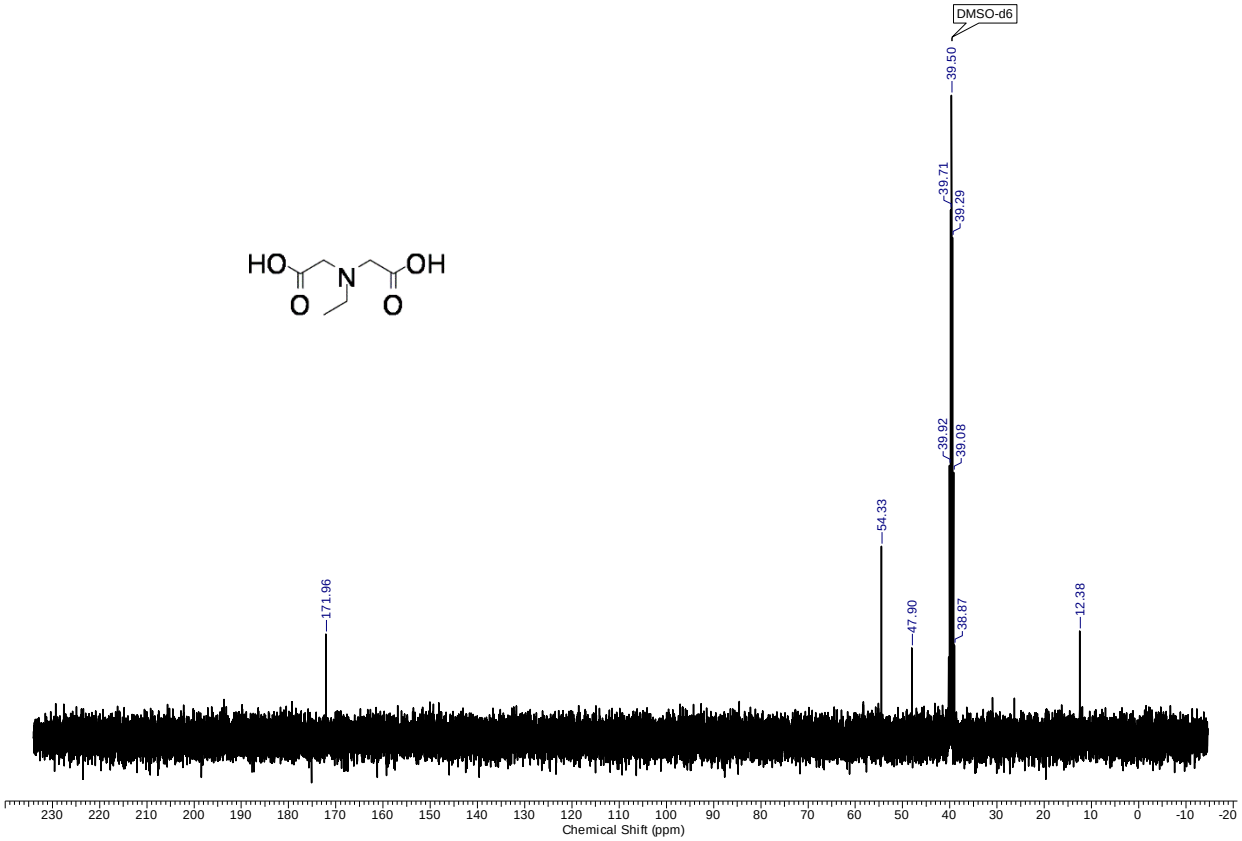


Figure S3. **^{13}C NMR** spectrum of *2,2'-(ethylazanediyl)diacetic acid* **1a**

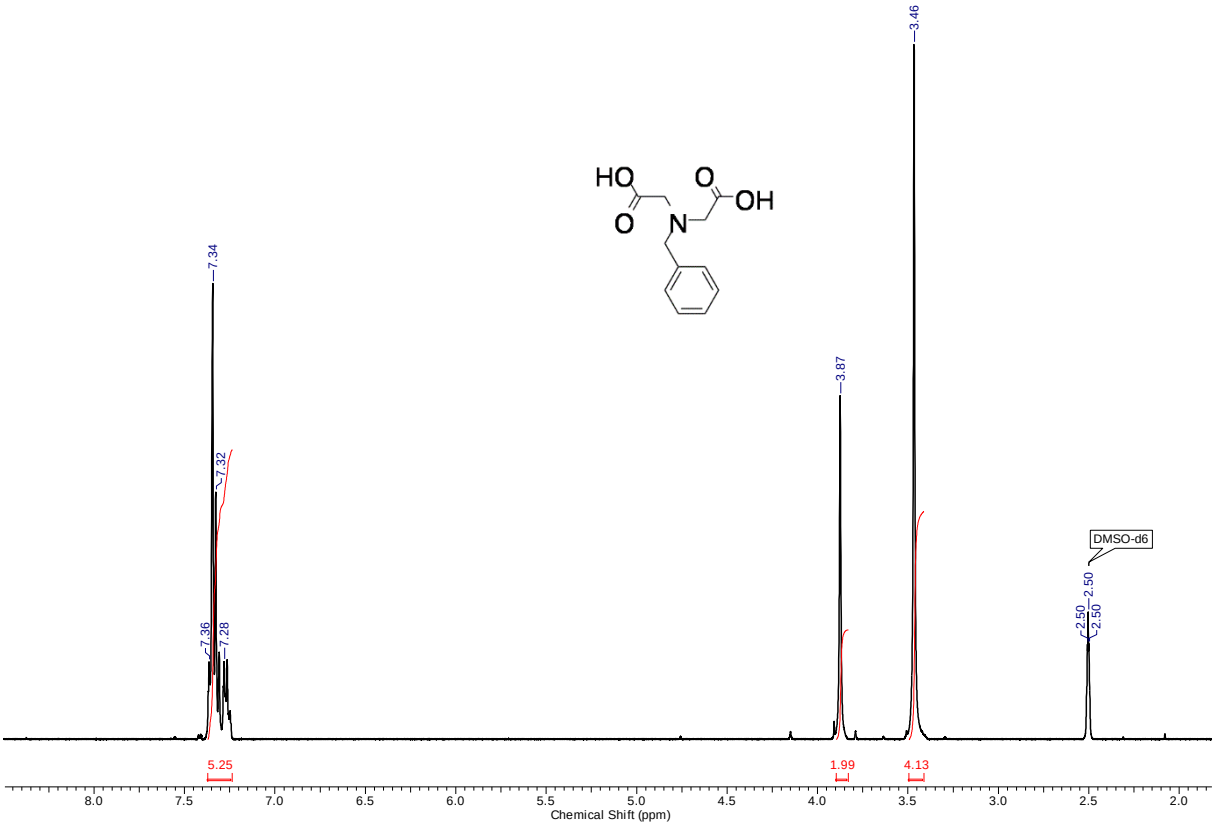


Figure S4. **^{1}H NMR** spectrum of *2,2'-(benzylazanediyl)diacetic acid* **1b**

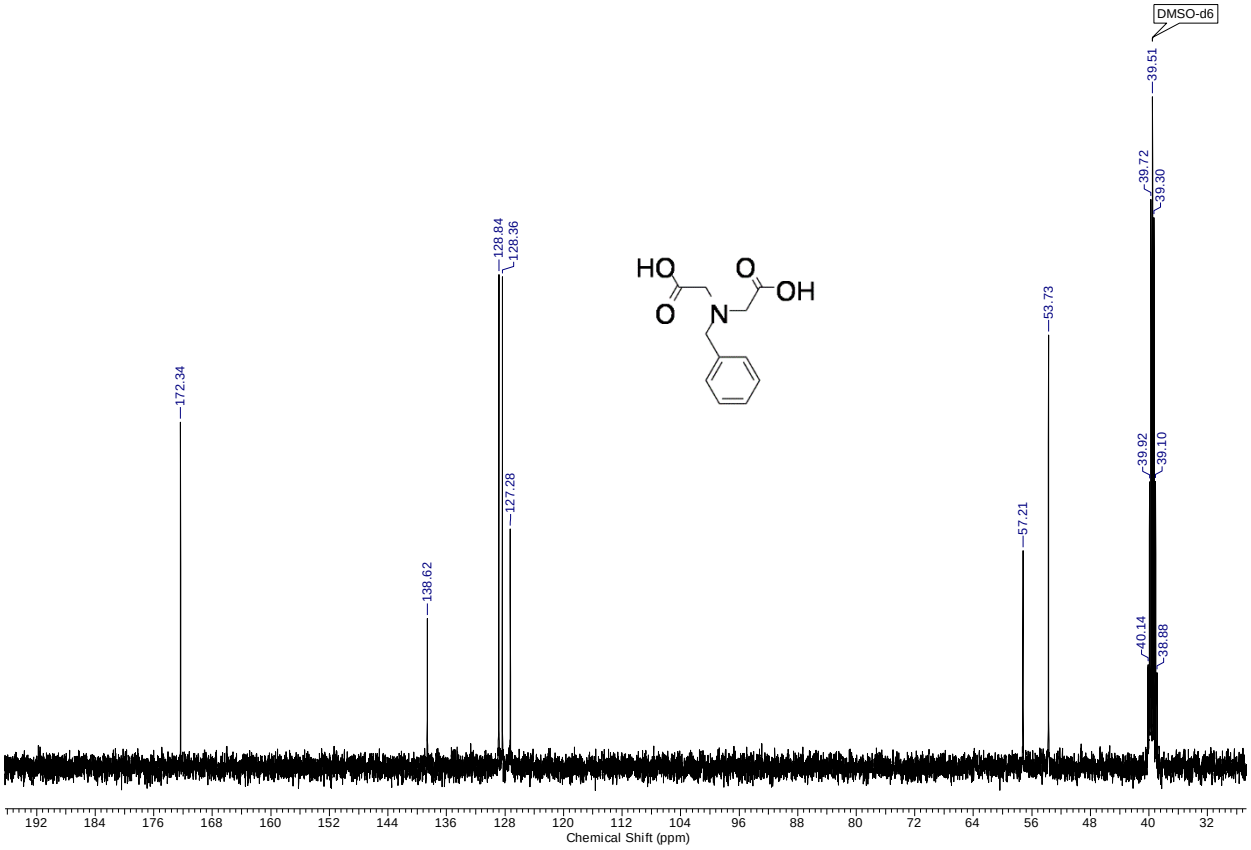


Figure S5. **^{13}C NMR** spectrum of *2,2'-(benzylazanediyl)diacetic acid* **1b**

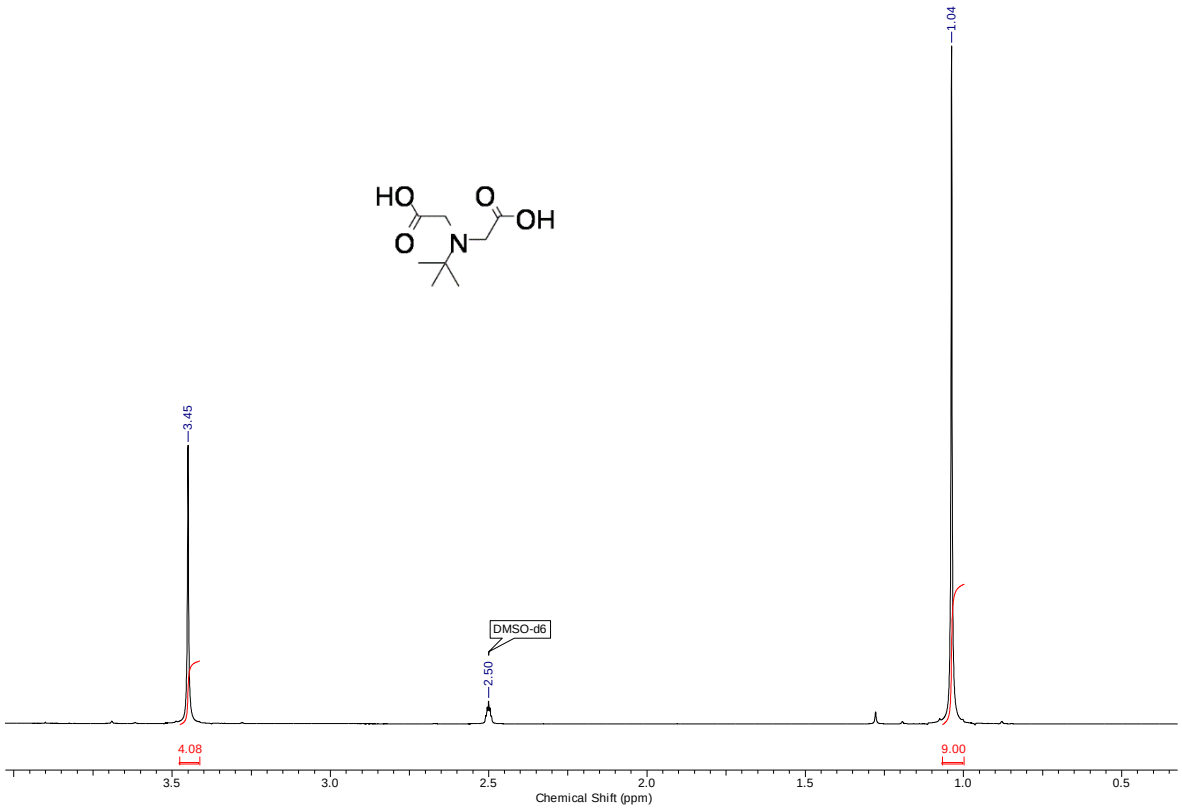


Figure S6. **^{1}H NMR** spectrum of *2,2'-(tert-butylazanediyl)diacetic acid* **1c**

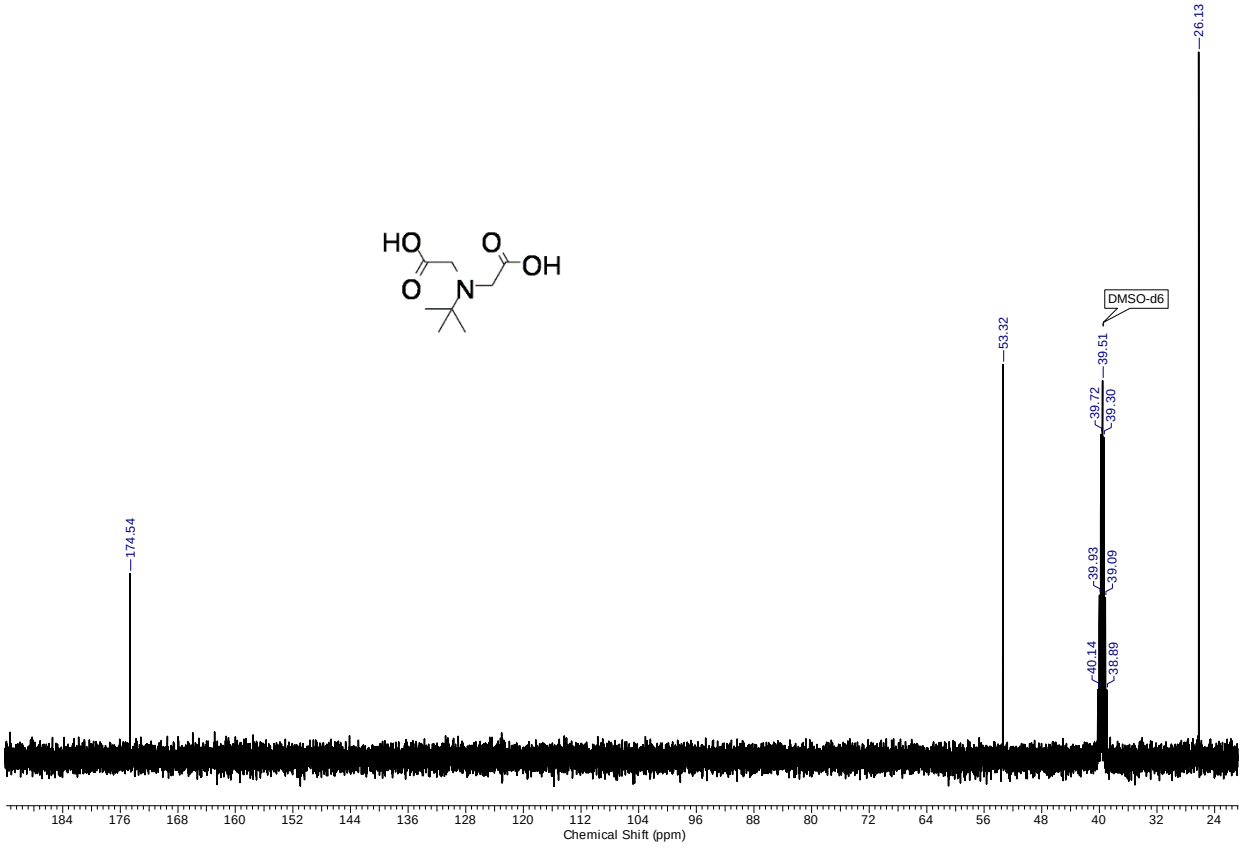


Figure S7. **^{13}C NMR** spectrum of *2,2'-(tert-butylazanediyl)diacetic acid* **1c**

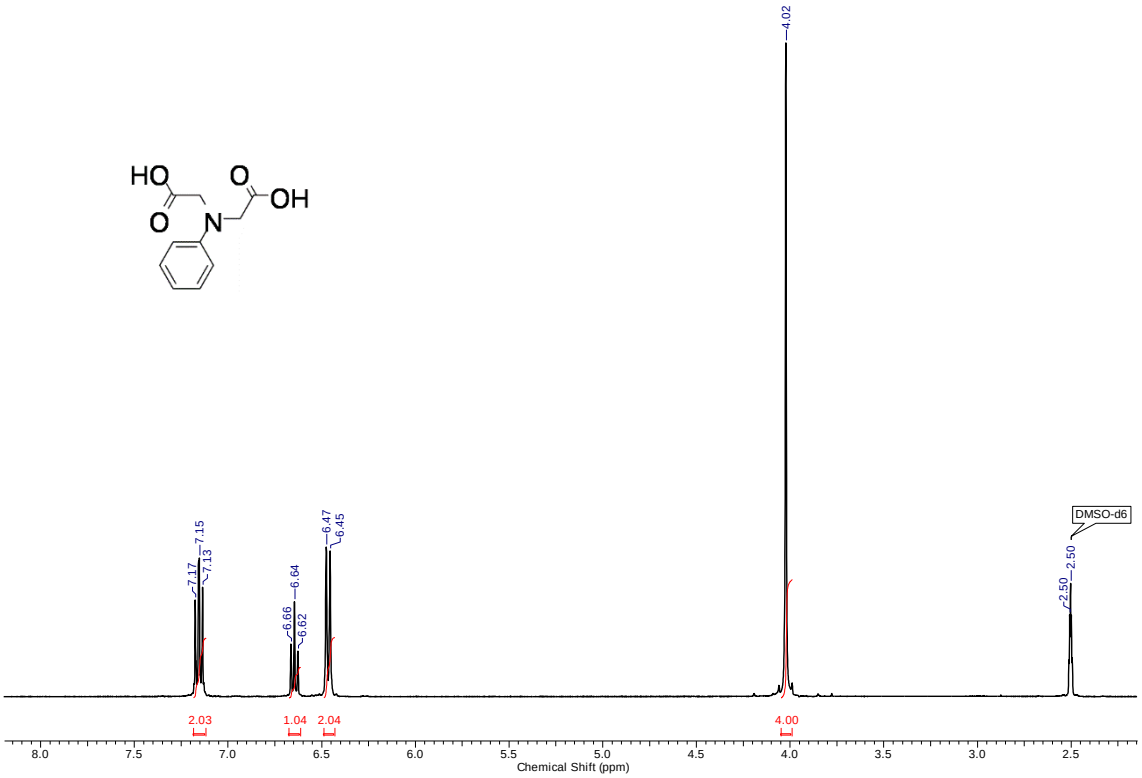


Figure S8. **^{1}H NMR** spectrum of *2,2'-(phenylazanediyl)diacetic acid* **1d**

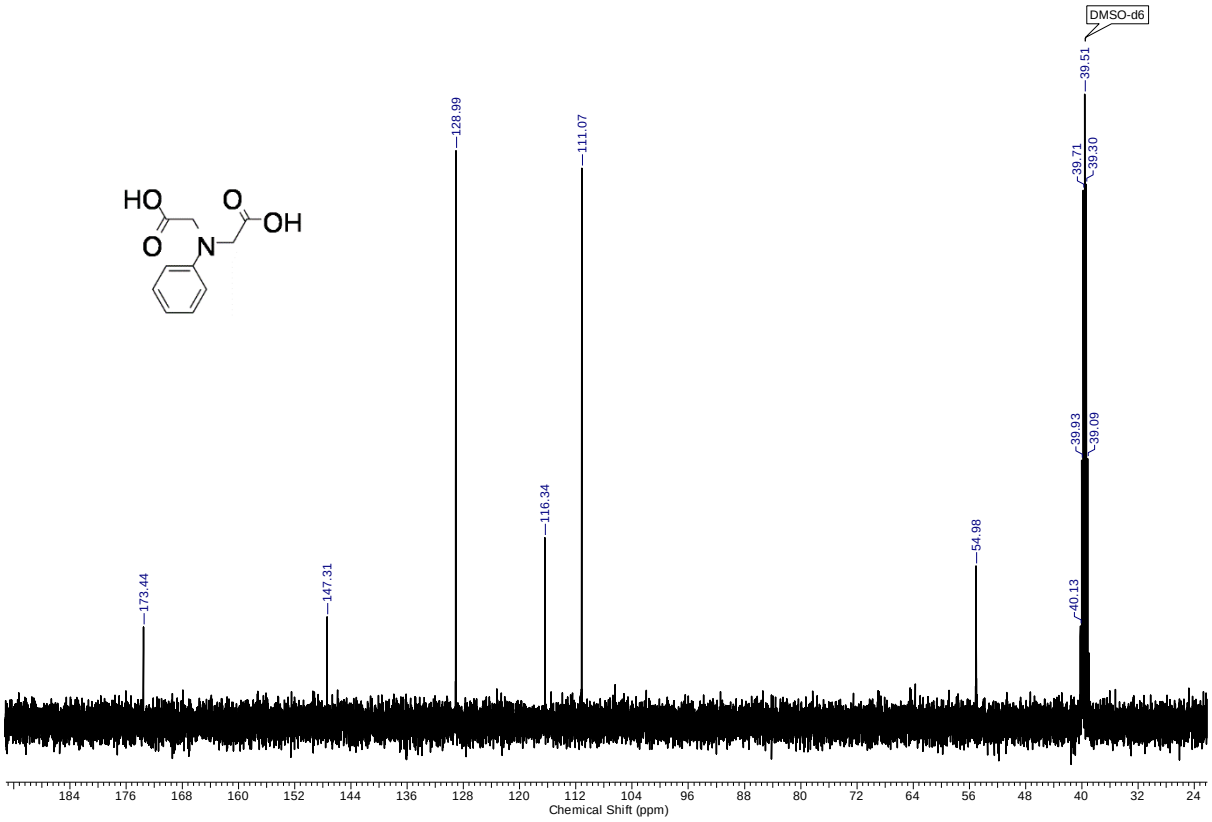


Figure S9. **^{13}C NMR** spectrum of *2,2'-(phenylazanediyl)diacetic acid* **1d**

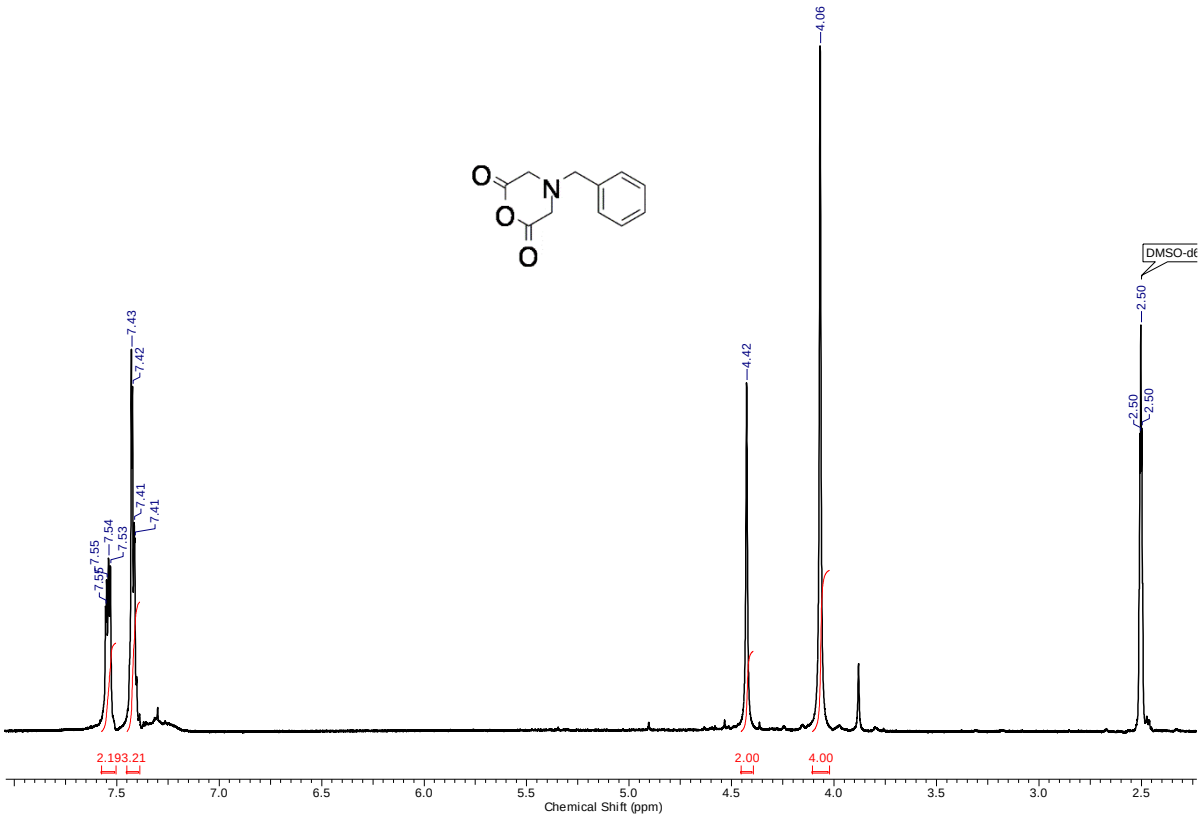


Figure S10. **^{1}H NMR** spectrum of *4-benzylmorpholine-2,6-dione*

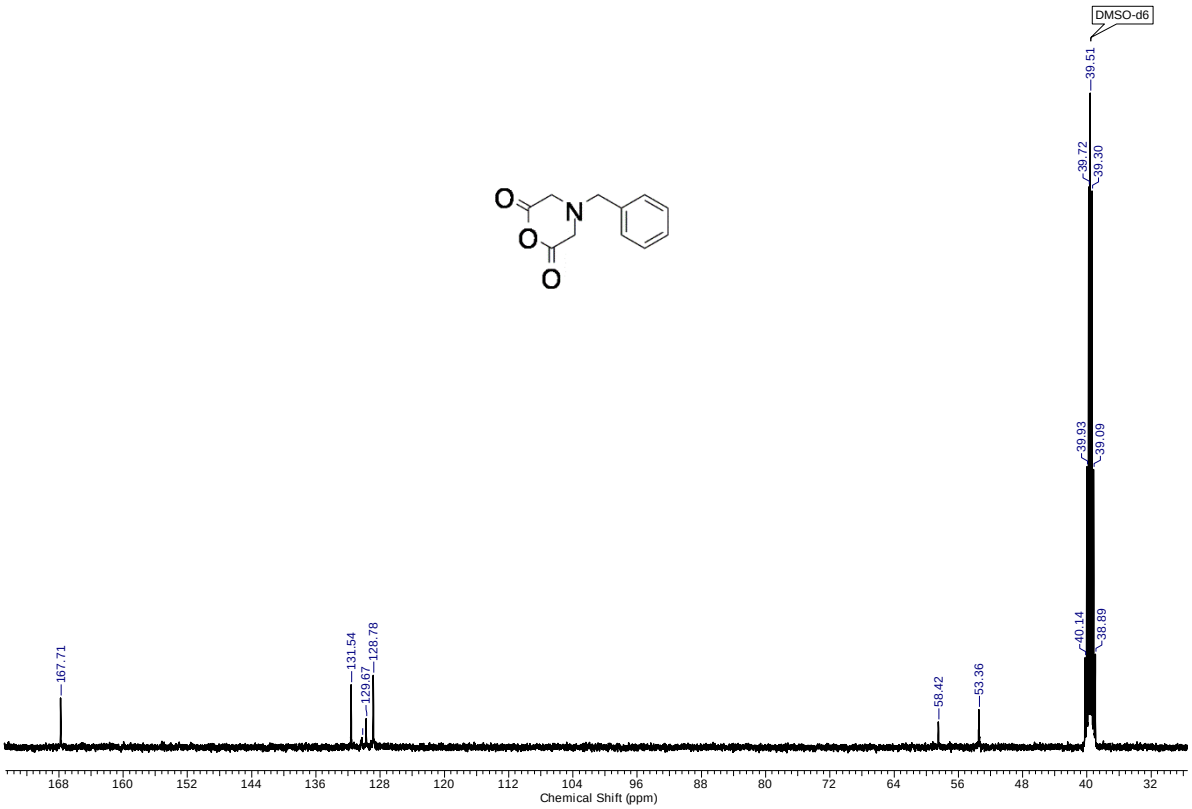


Figure S11. **^{13}C NMR** spectrum of *4-benzylmorpholine-2,6-dione*

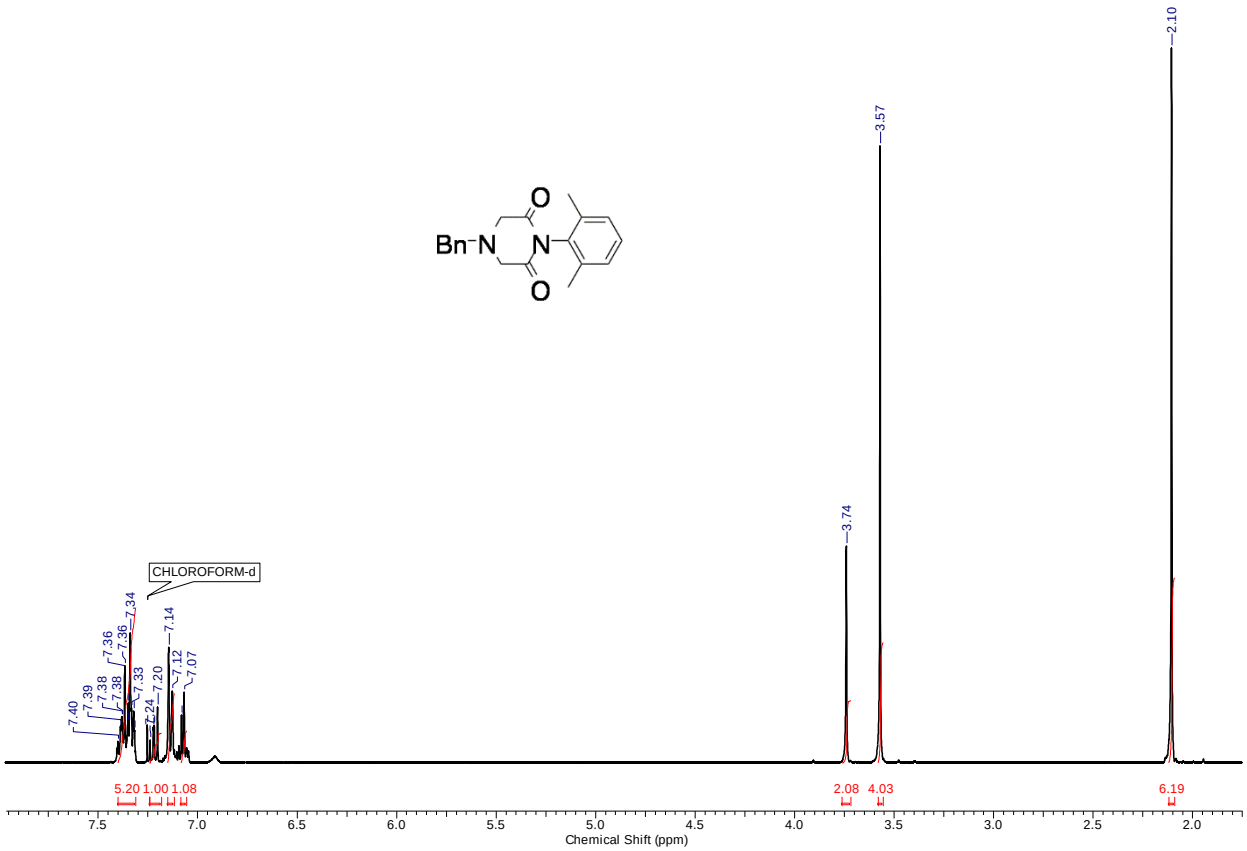


Figure S12. **^{1}H NMR** spectrum of *4-benzyl-1-(2,6-dimethylphenyl) piperazine-2,6-dione*

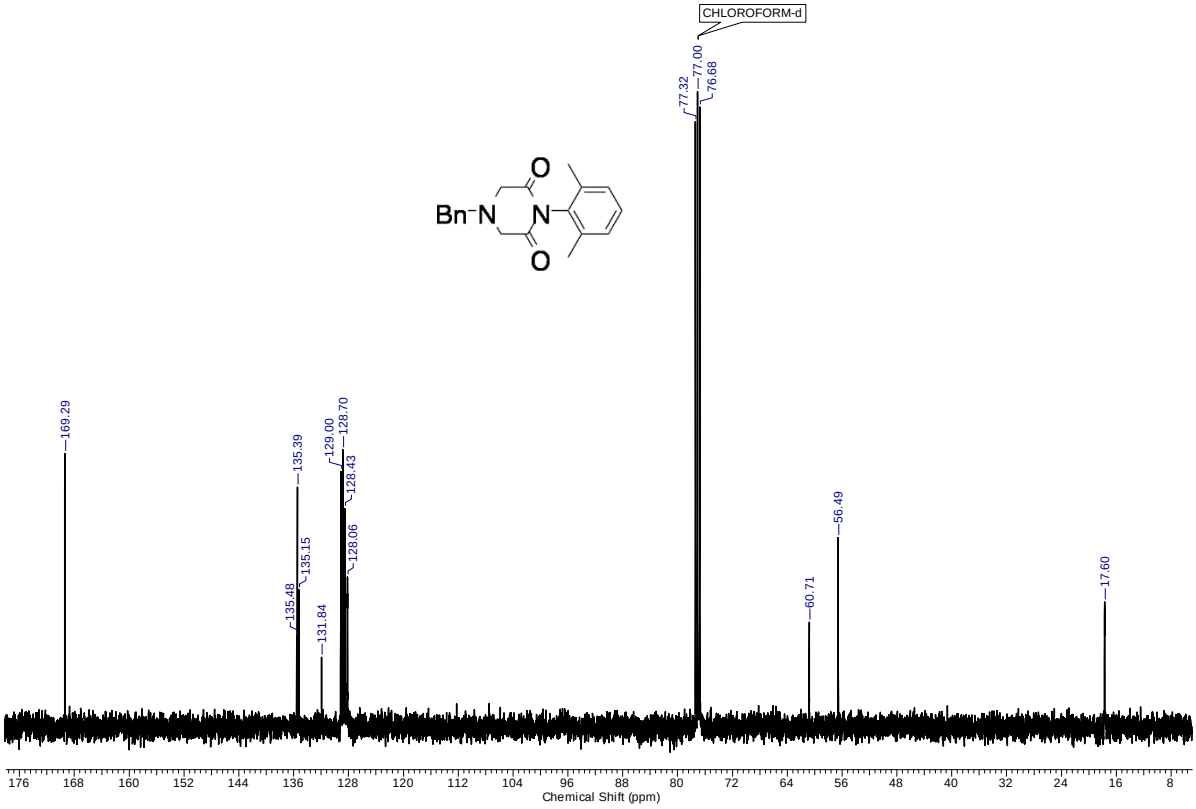


Figure S13. **^{13}C NMR** spectrum of *4-benzyl-1-(2,6-dimethylphenyl) piperazine-2,6-dione*

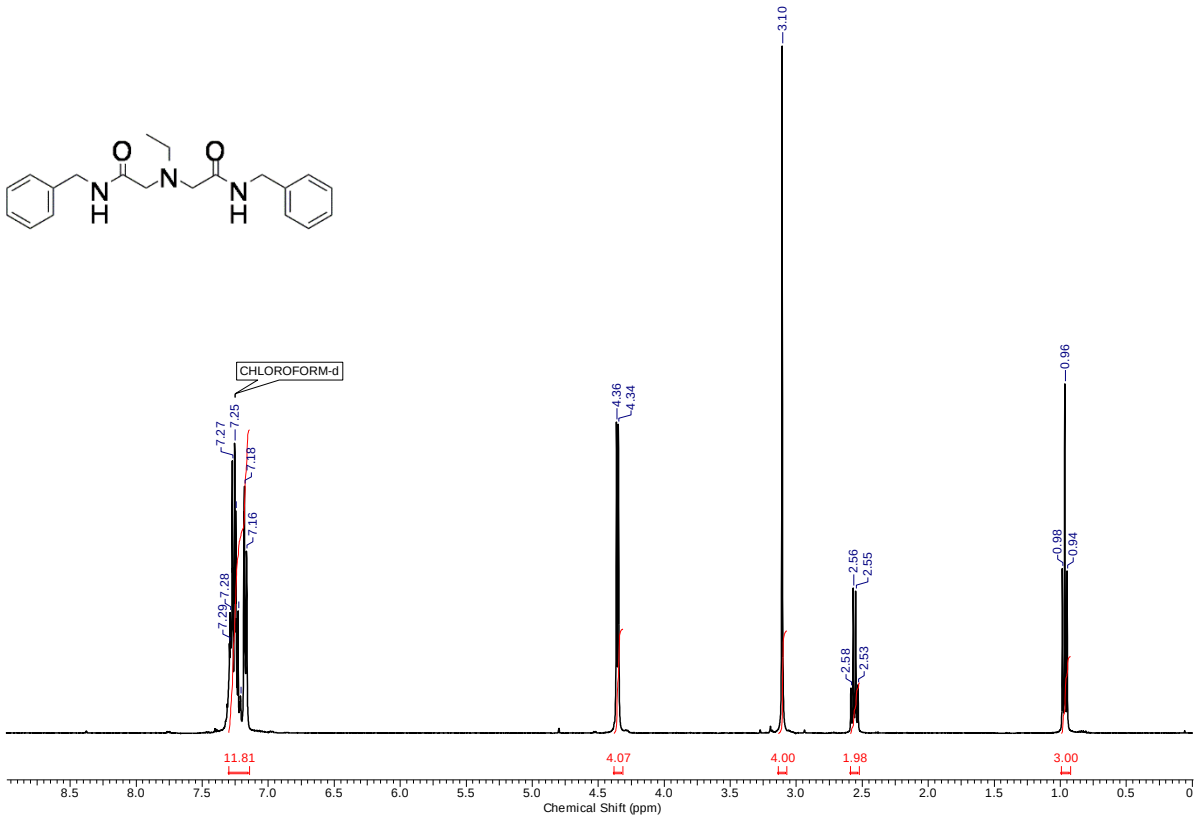


Figure S14. **^{1}H NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-benzylacetamide)* **2ab**

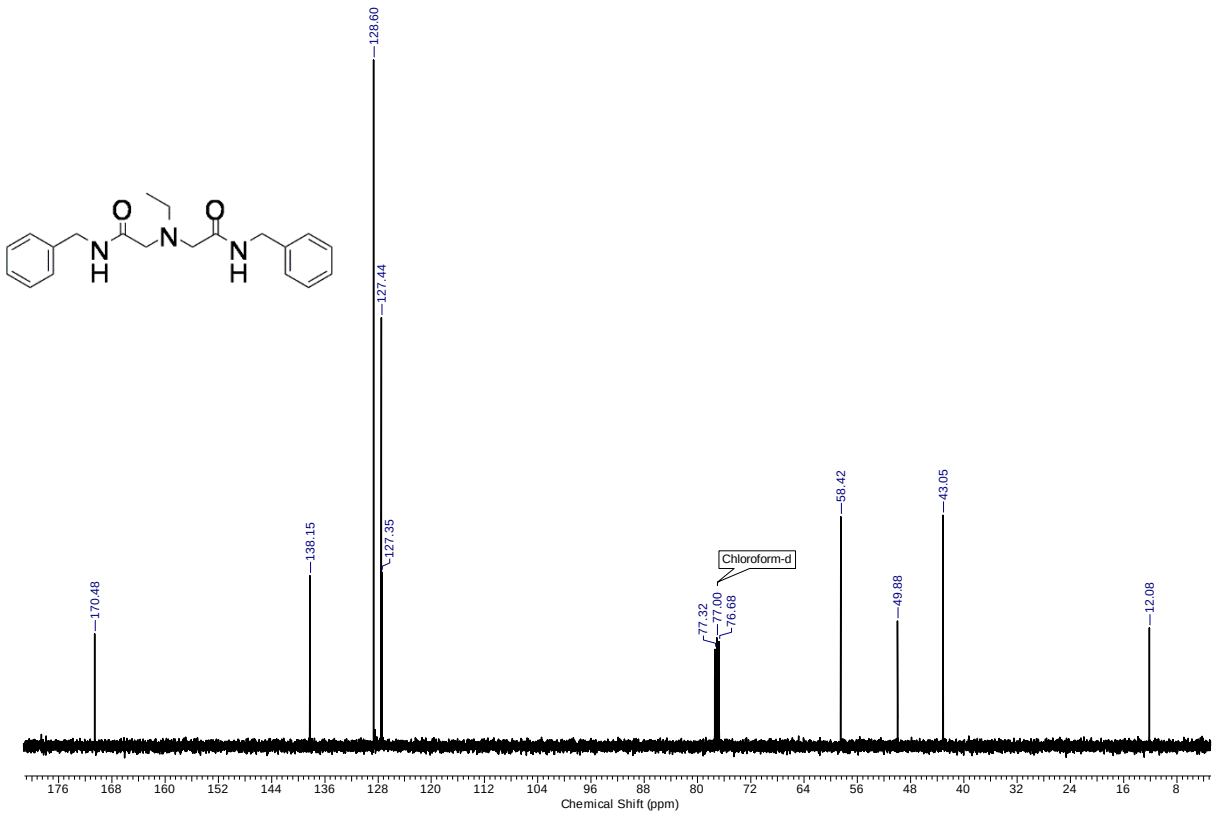


Figure S15. **^{13}C NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-benzylacetamide)* **2ab**

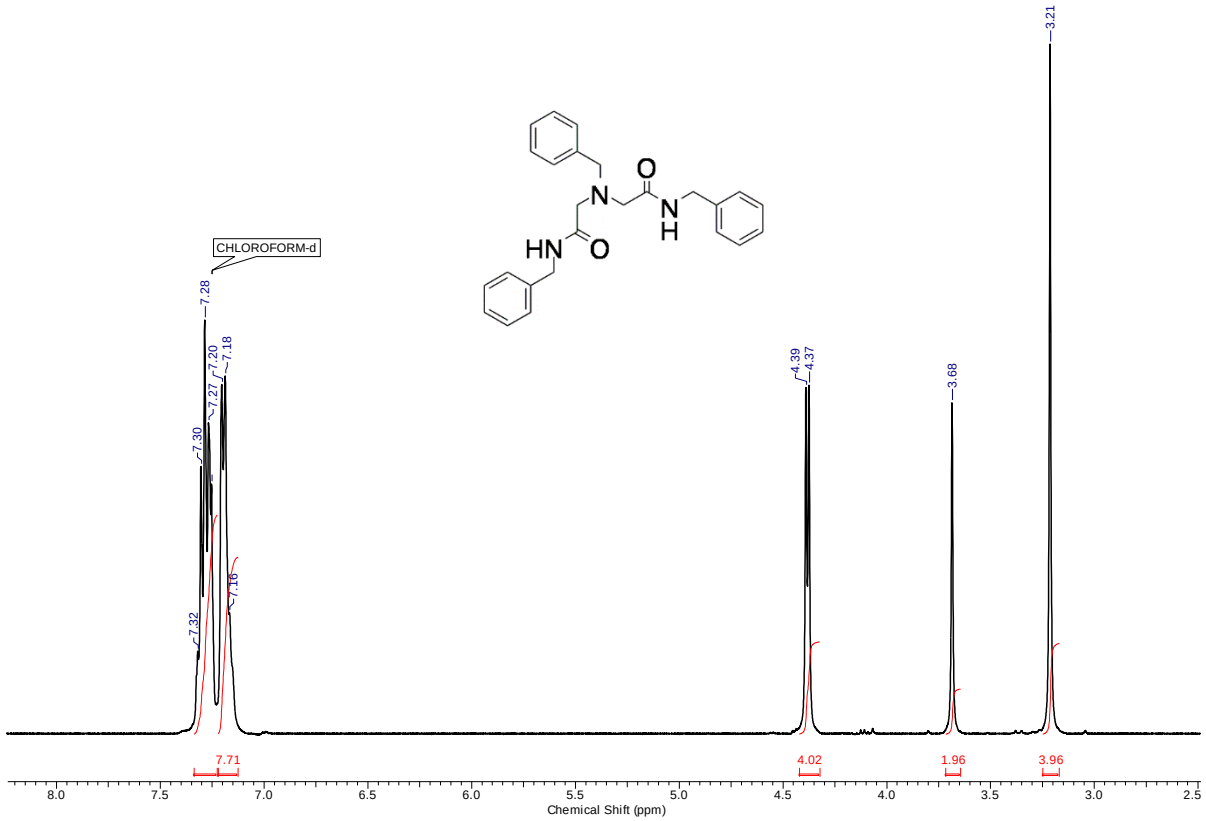


Figure S16. **^{1}H NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-benzylacetamide)* **2bb**

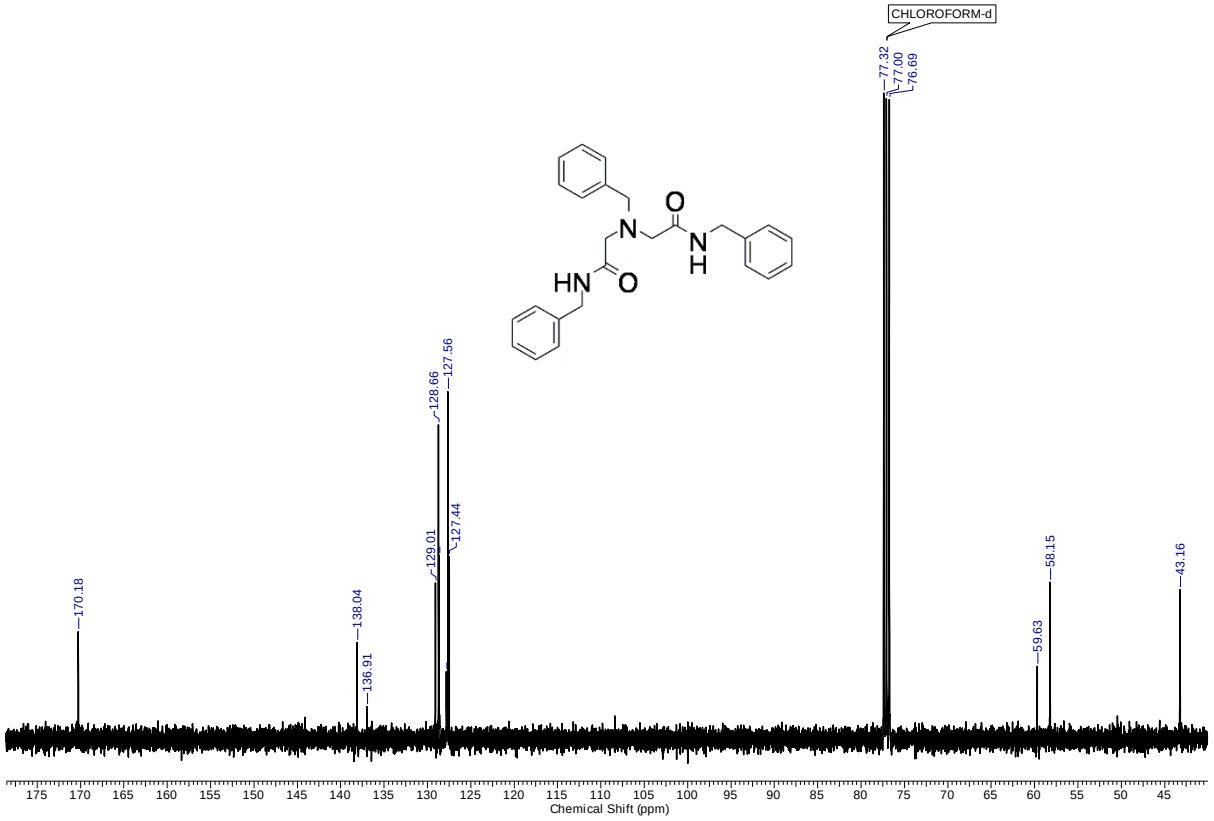


Figure S17. **^{13}C NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-benzylacetamide)* **2bb**

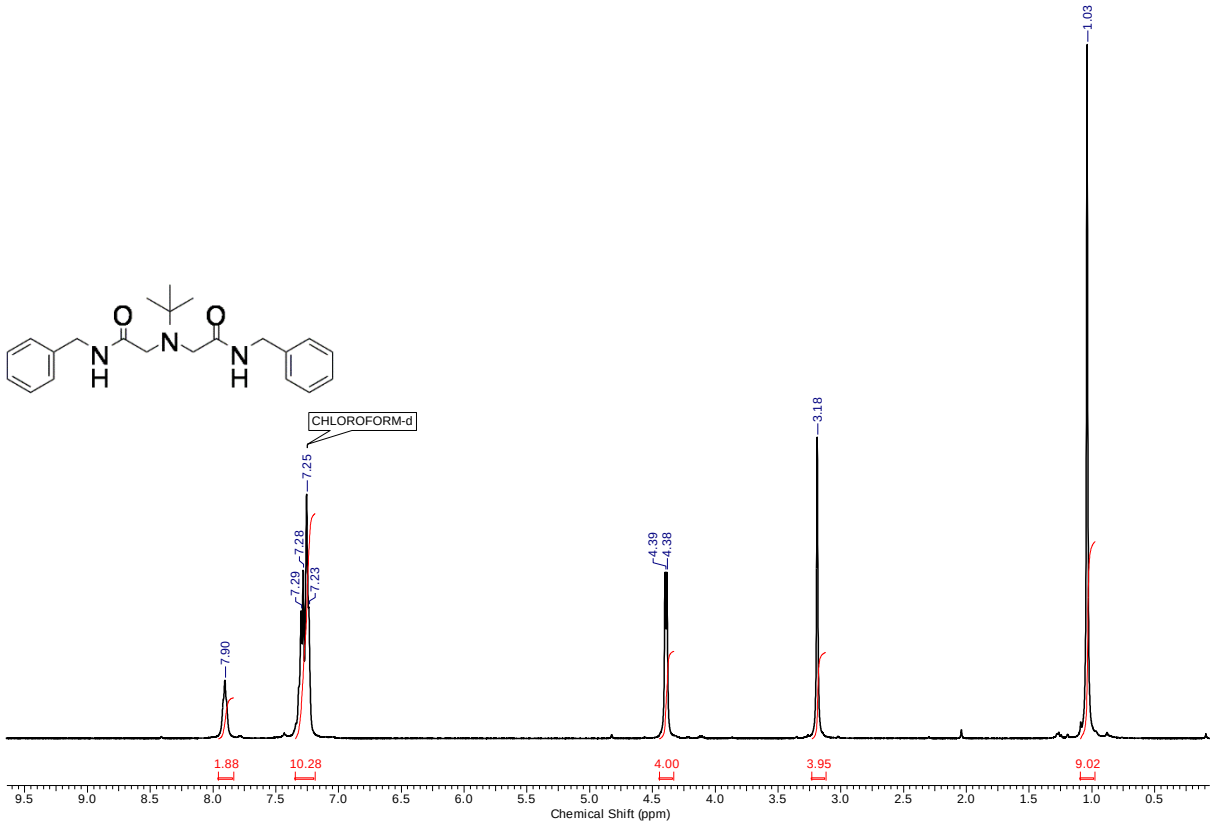


Figure S18. **^{1}H NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-benzylacetamide)* **2cb**

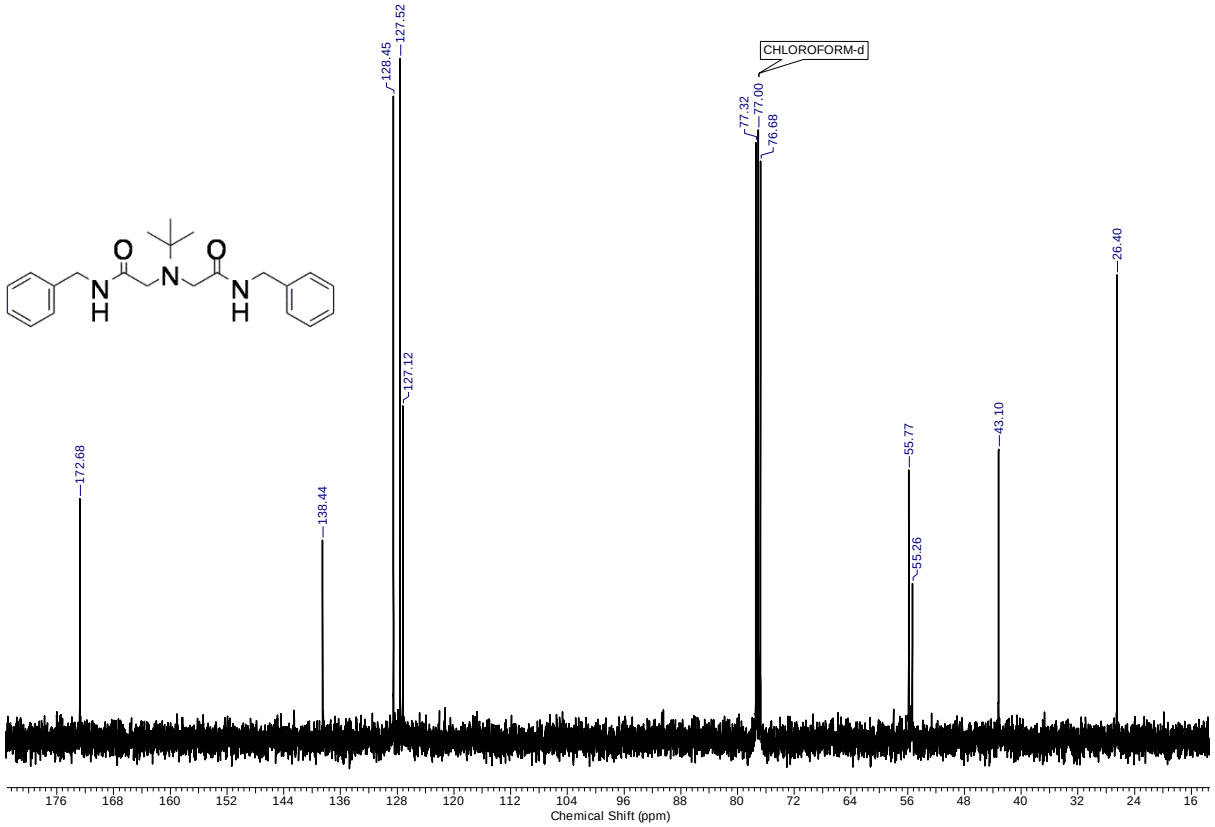


Figure S19. **^{13}C NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-benzylacetamide)* **2cb**

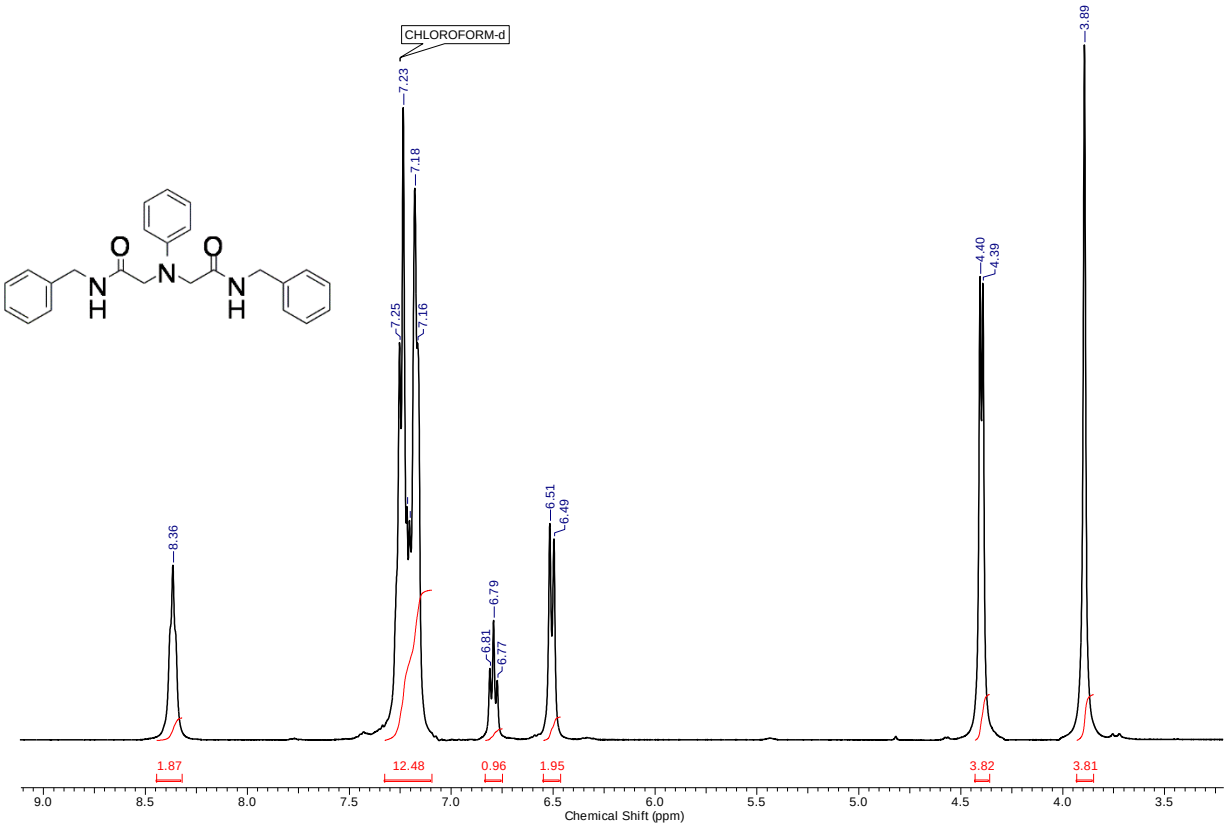


Figure S20. **^{1}H NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-benzylacetamide)* **2db**

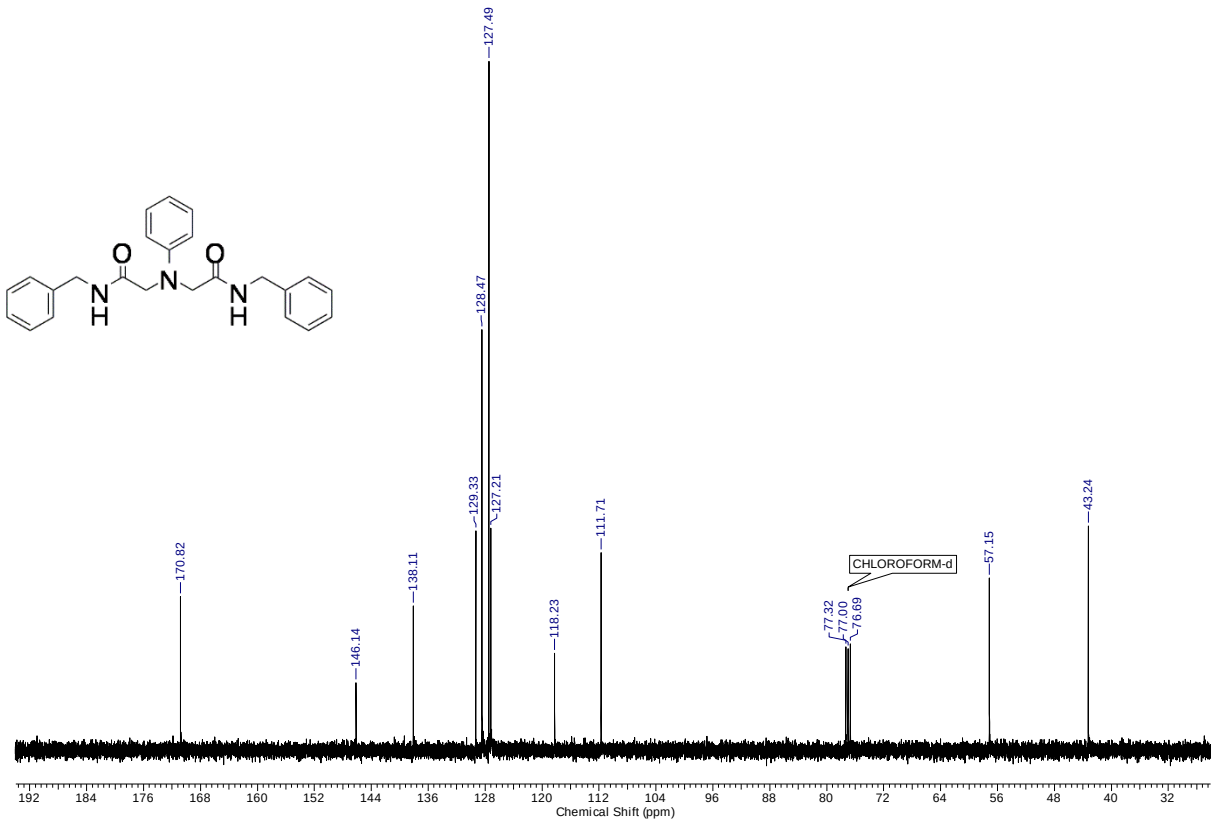


Figure S21. **^{13}C NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-benzylacetamide)* **2db**

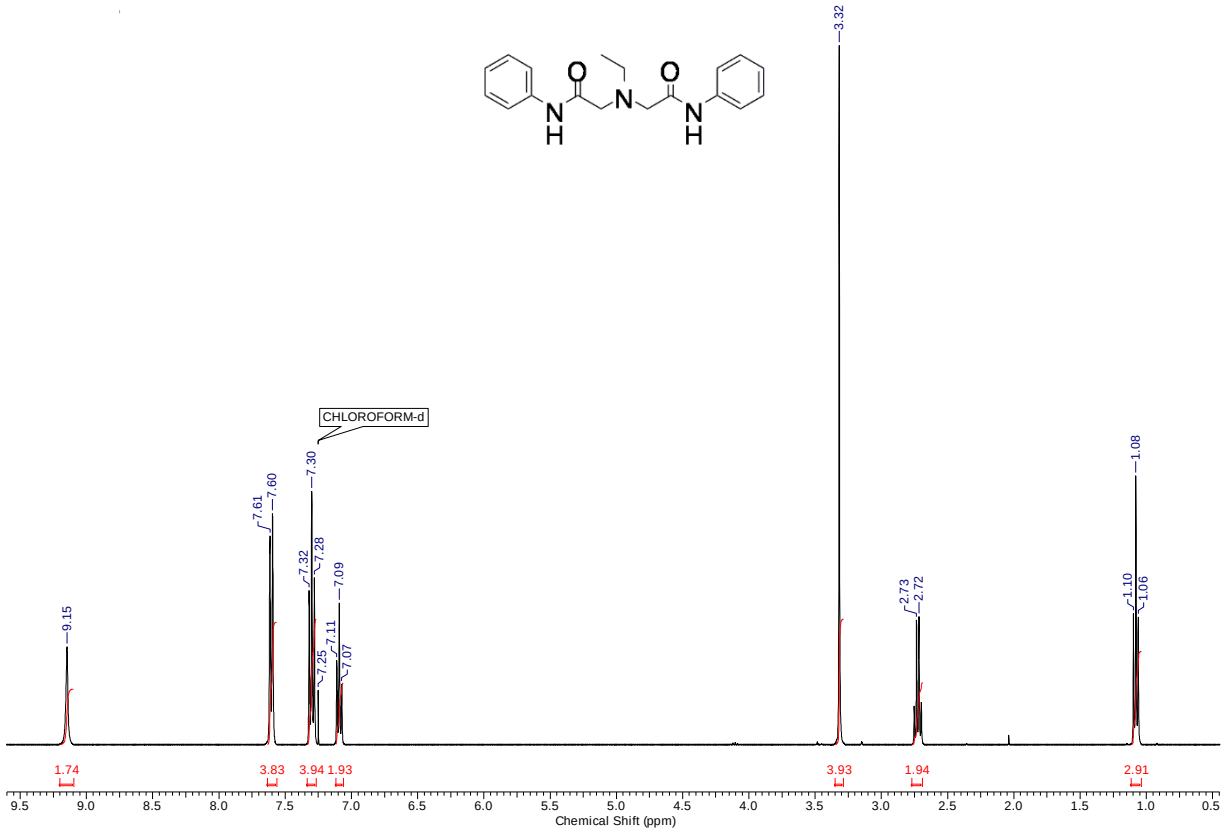


Figure S22. **^{1}H NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-phenylacetamide)* **2ad**

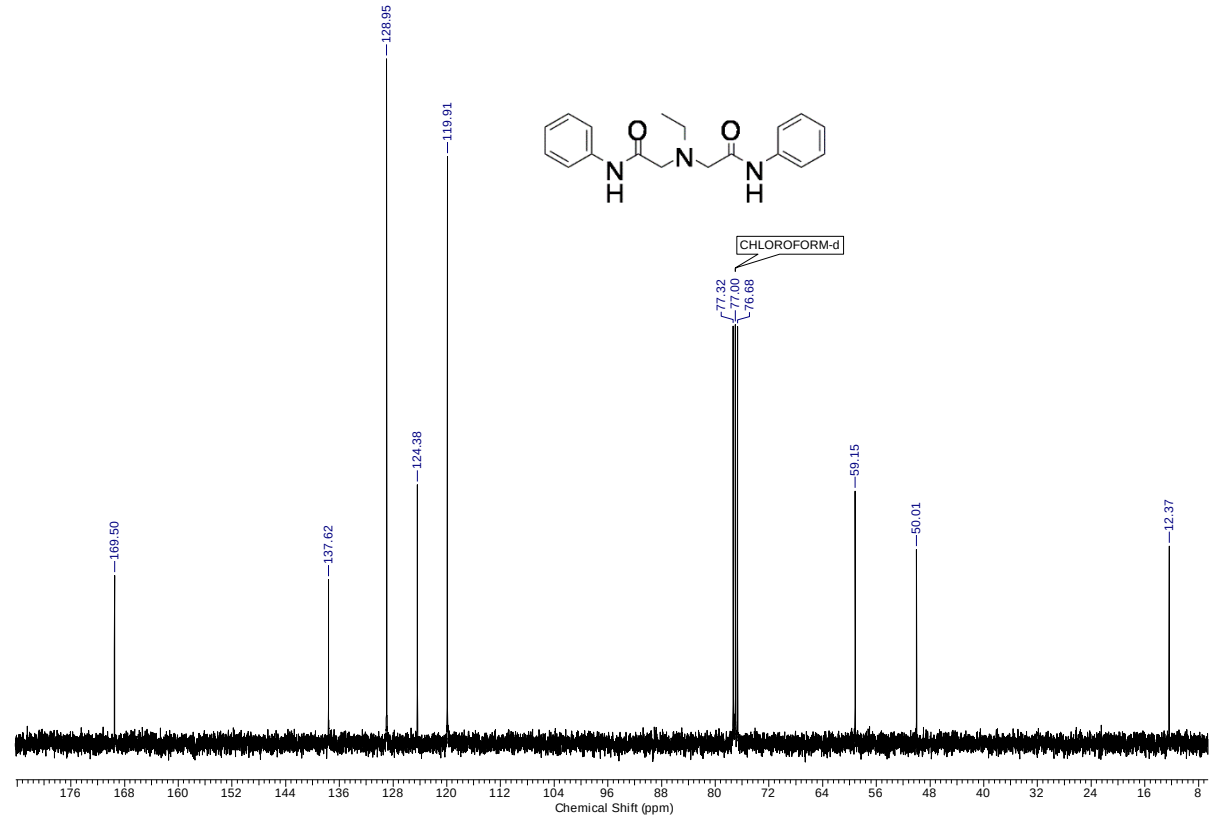


Figure S23. **^{13}C NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-phenylacetamide)* **2ad**

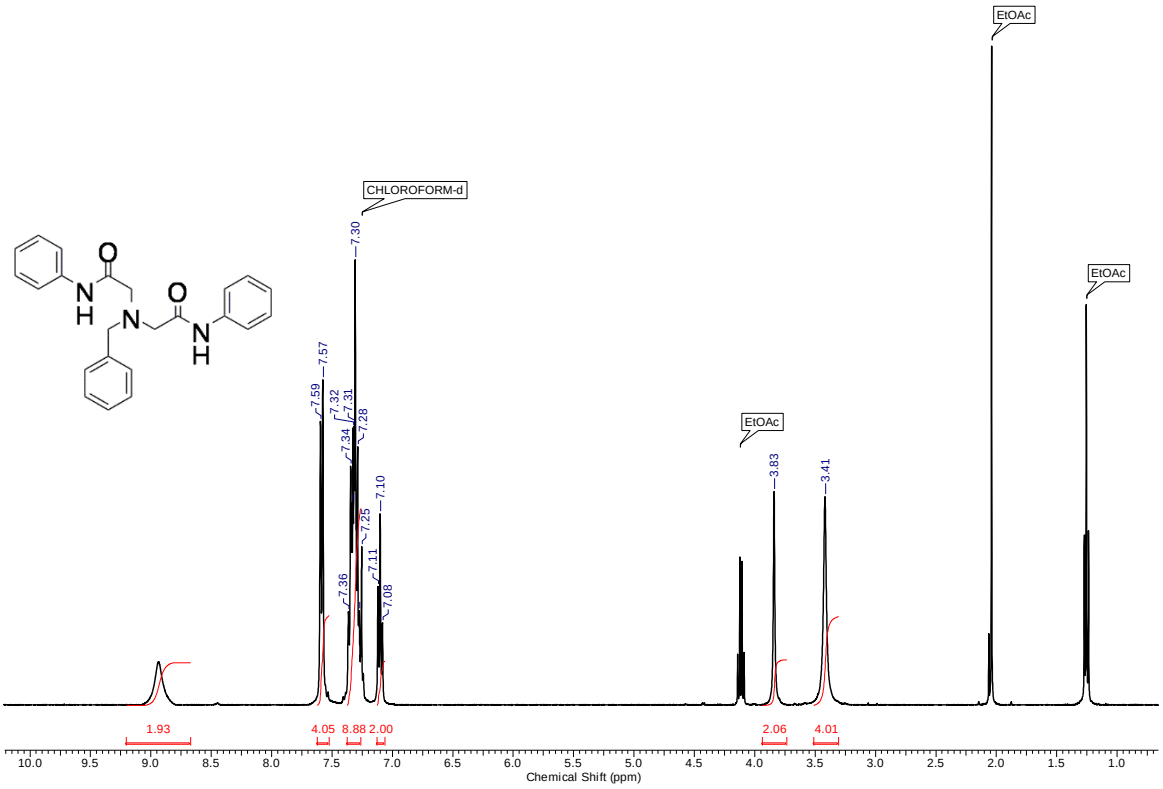


Figure S24. **^{1}H NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-phenylacetamide)* **2bd**

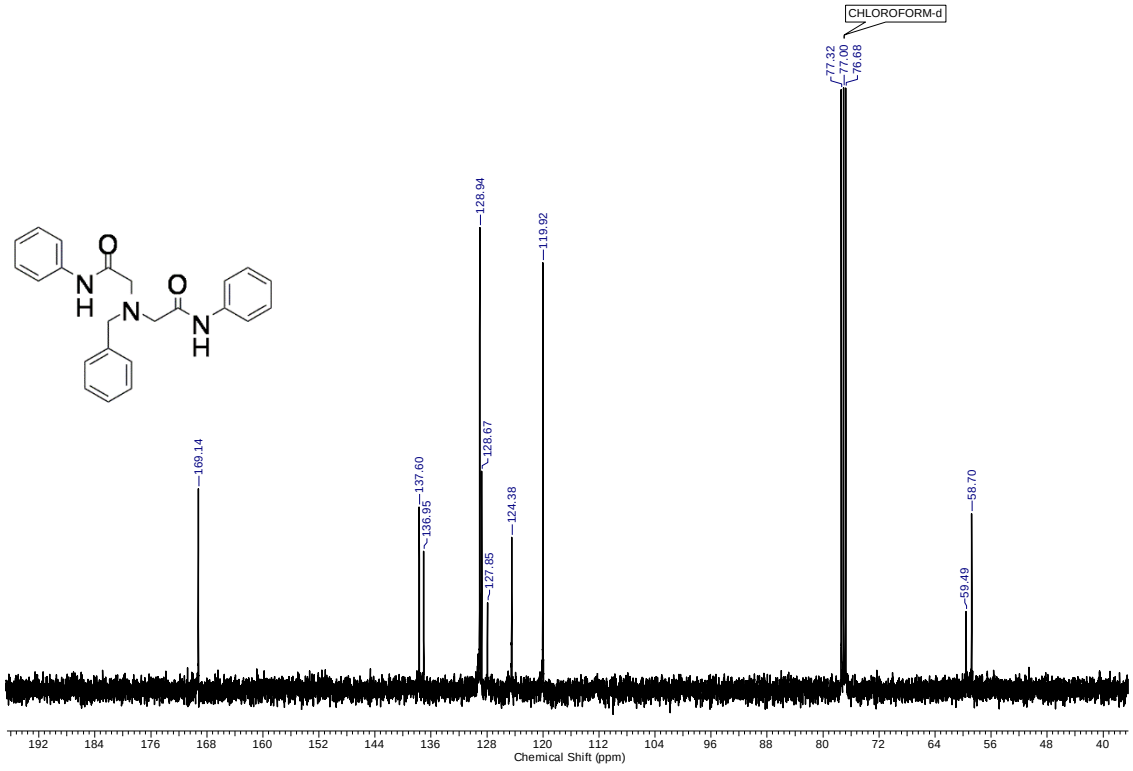


Figure S25. **^{13}C NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-phenylacetamide)* **2bd**

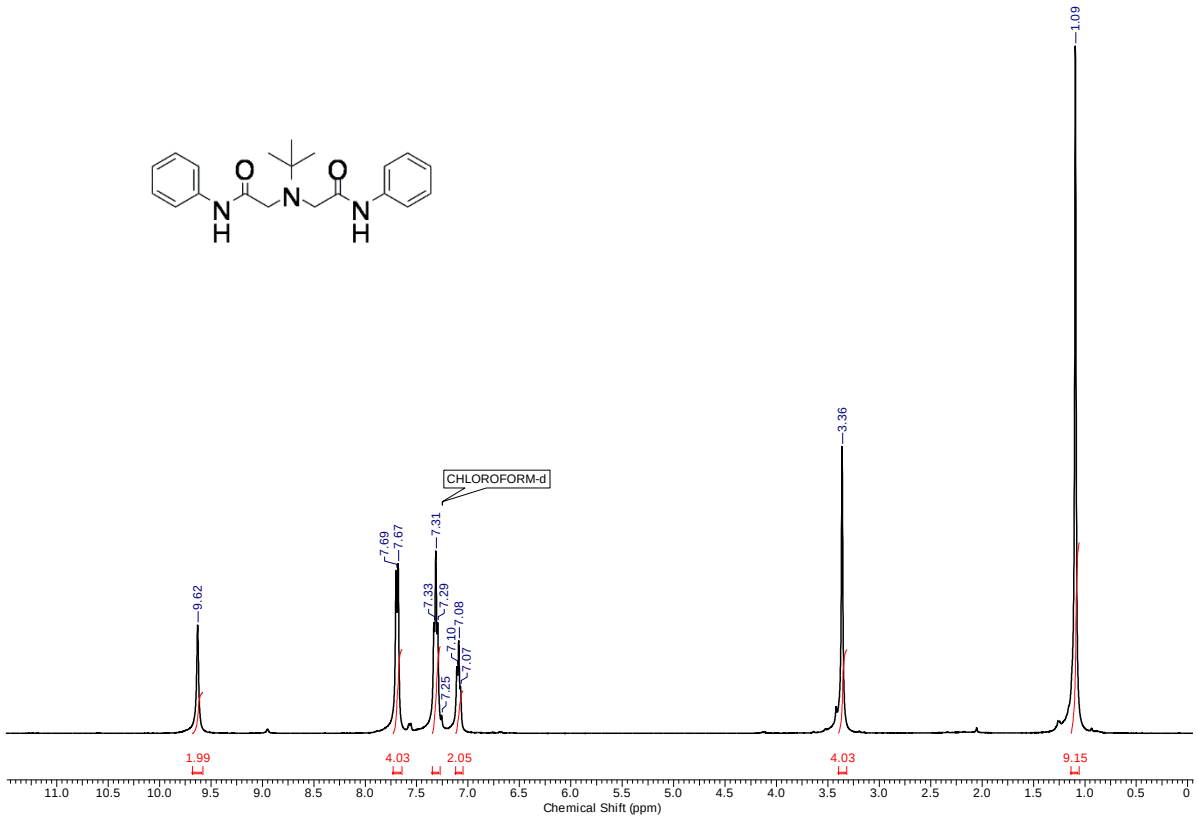


Figure S26. **^{1}H NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-phenylacetamide)* **2cd**

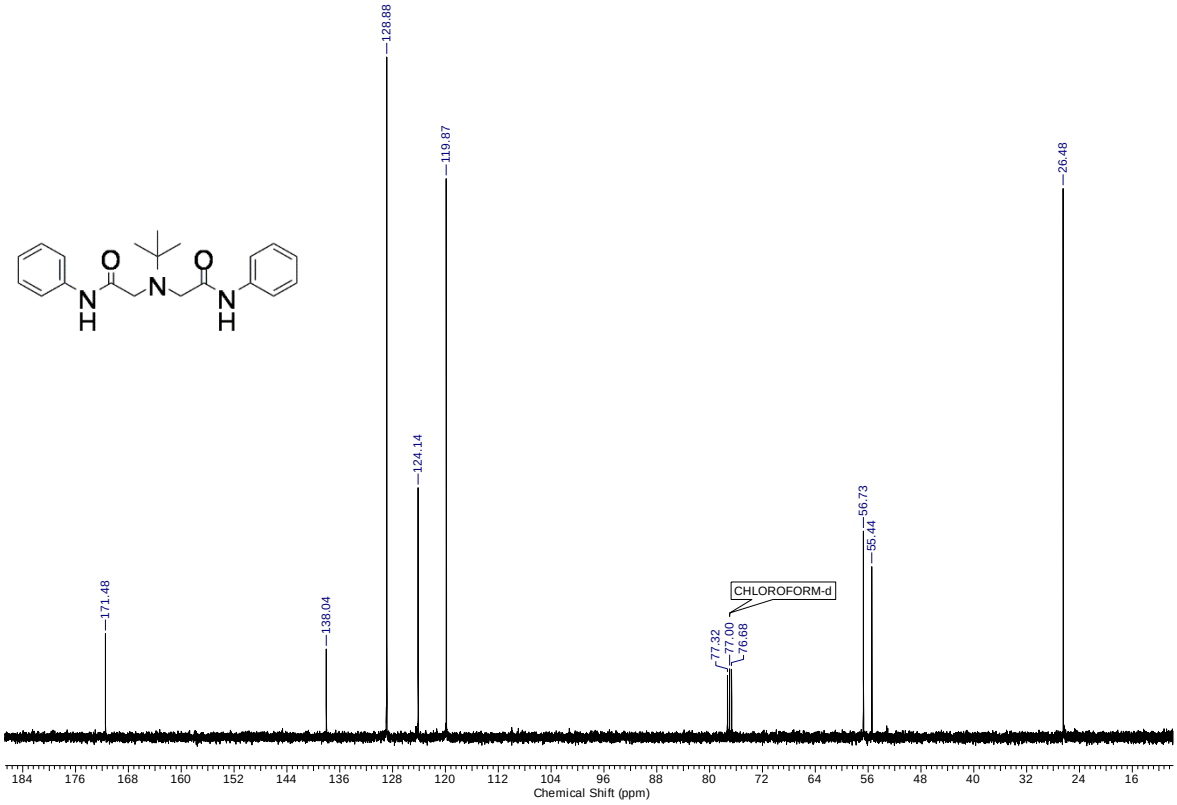


Figure S27. **^{13}C NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-phenylacetamide)* **2cd**

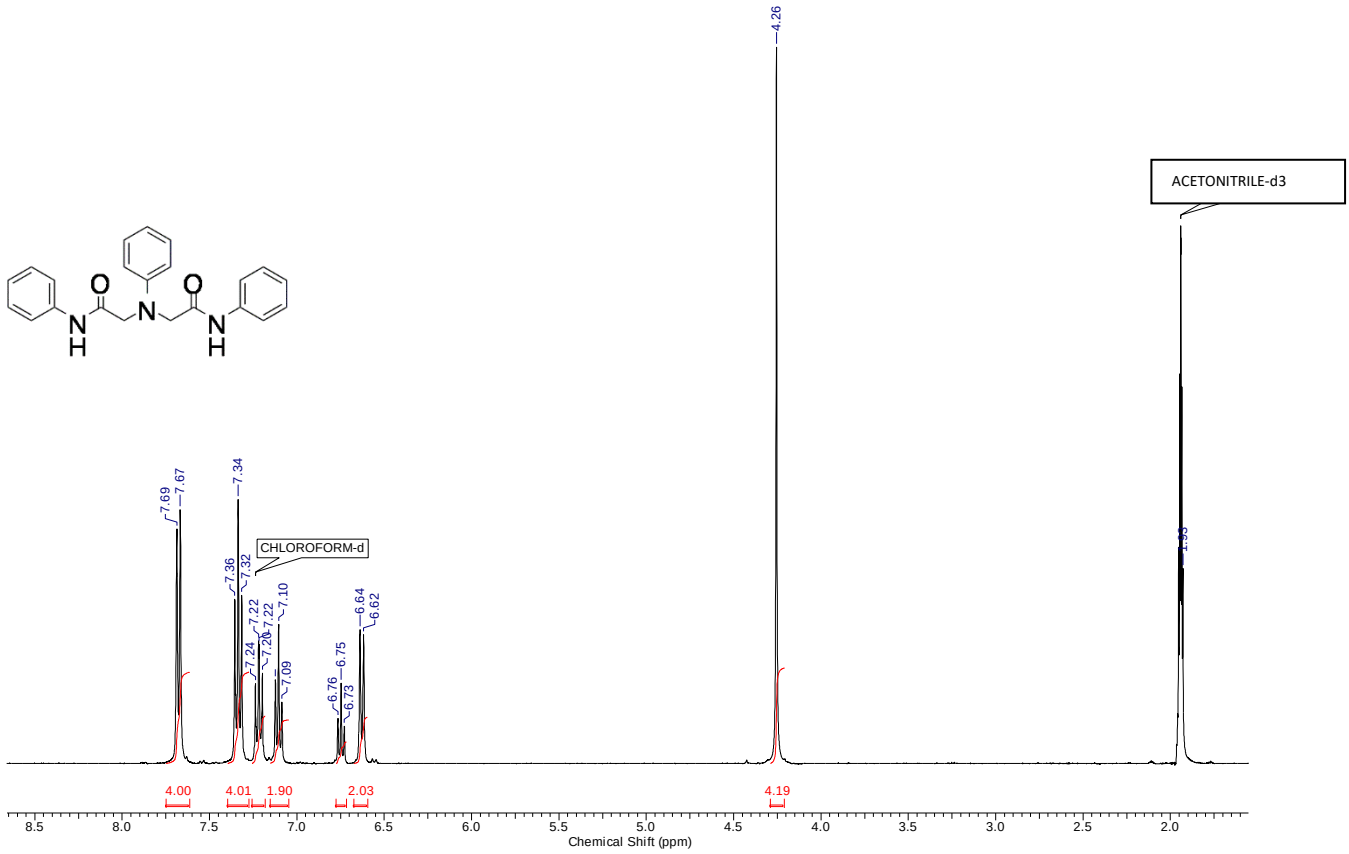


Figure S28. **^{1}H NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-phenylacetamide)* **2dd**

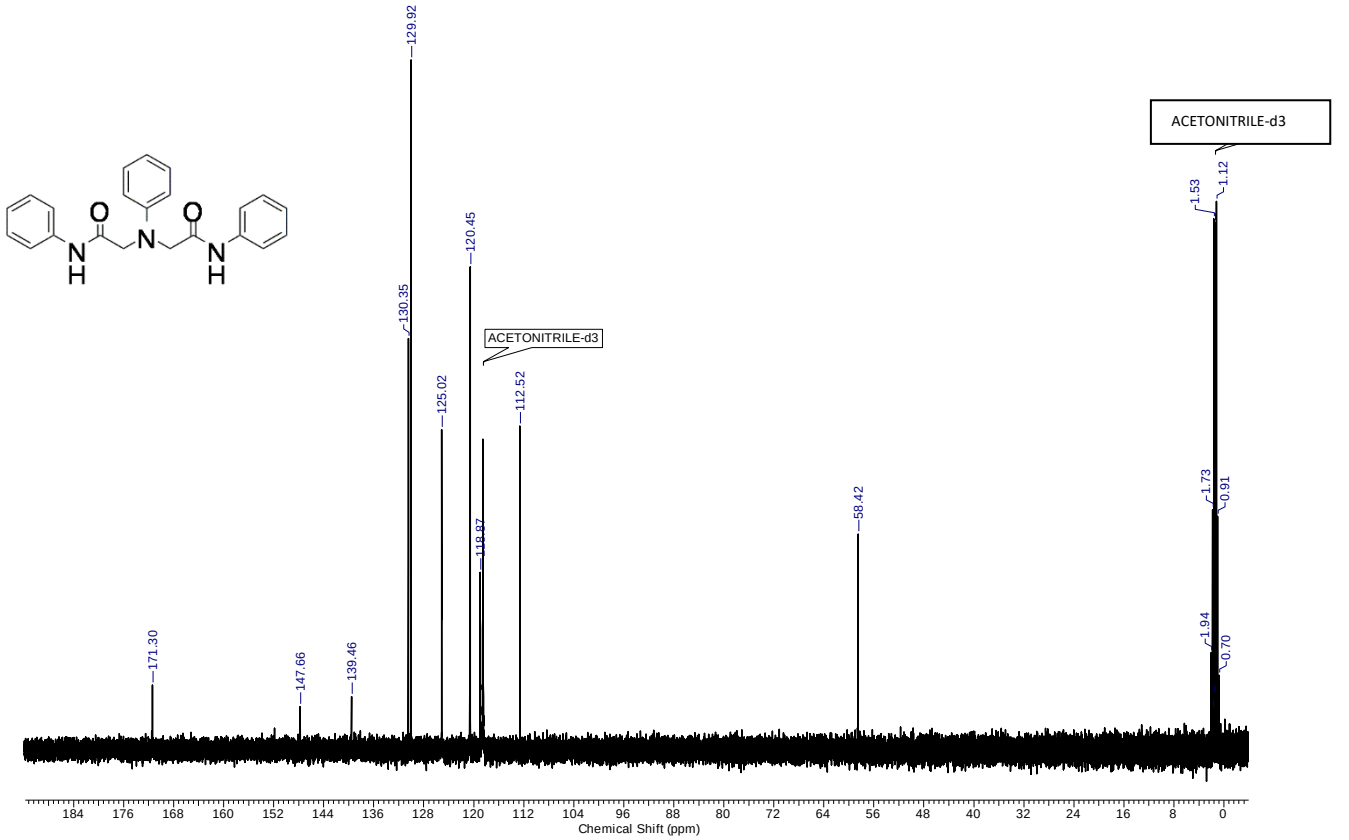


Figure S29. **^{13}C NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-phenylacetamide)* **2dd**

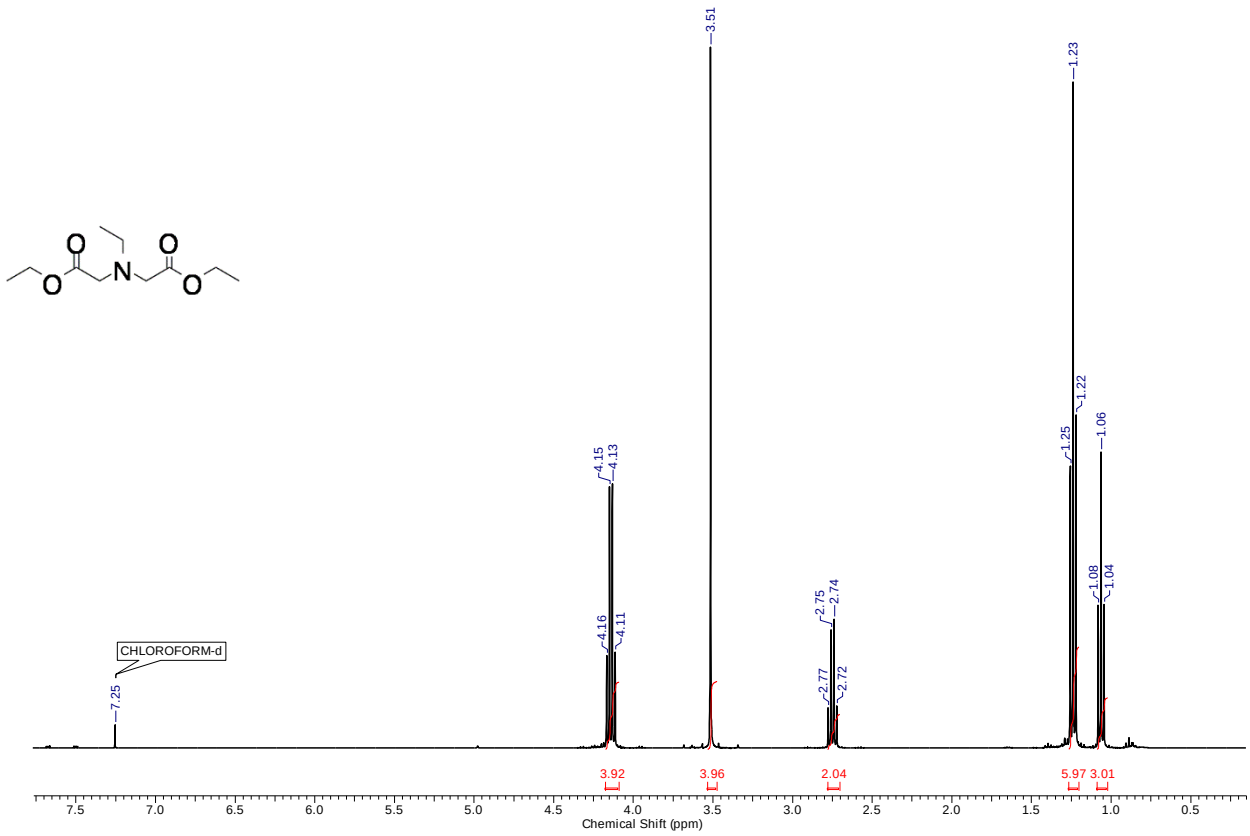


Figure S30. [1]H NMR spectrum of *diethyl 2,2'-(ethylazanediyl)diacetate* **3a**

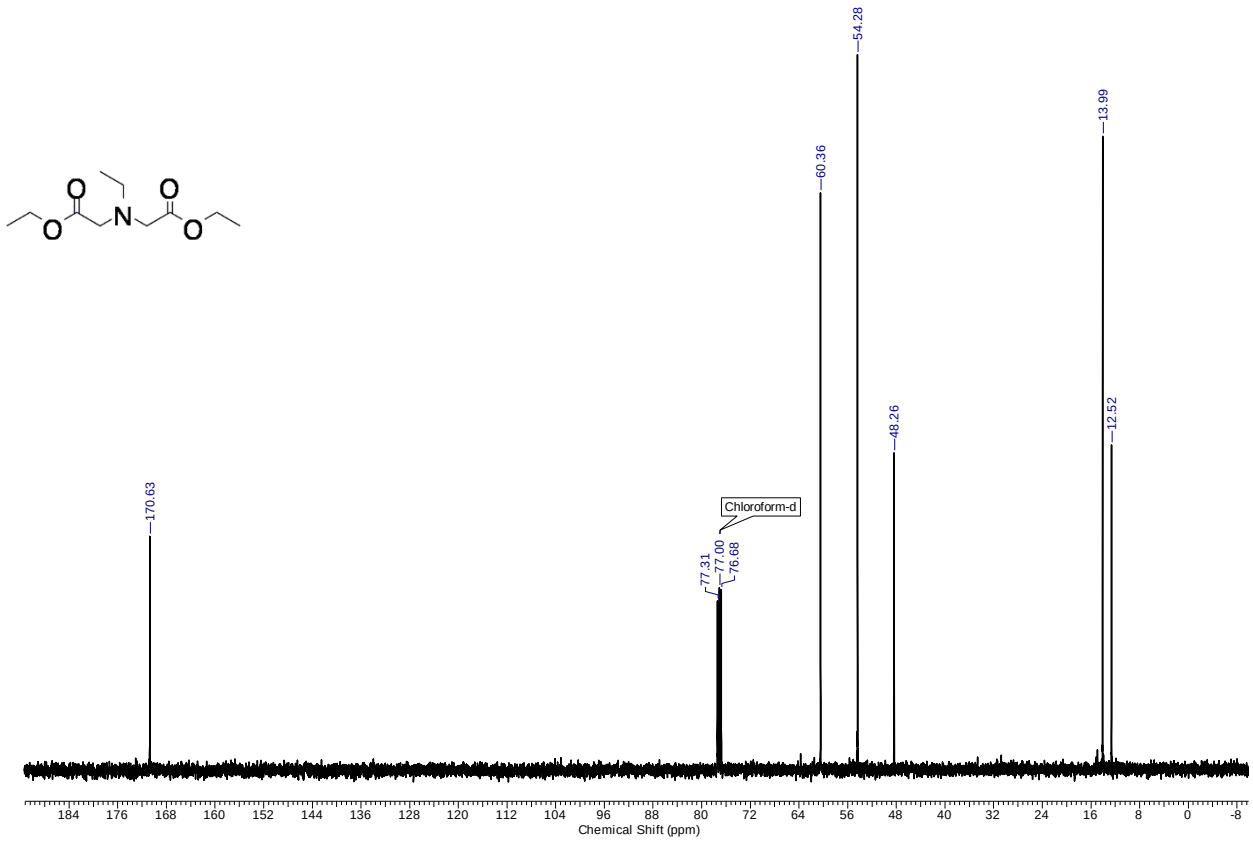


Figure S31. **[13]C NMR** spectrum of *diethyl 2,2'-(ethylazanediyl)diacetate* **3a**

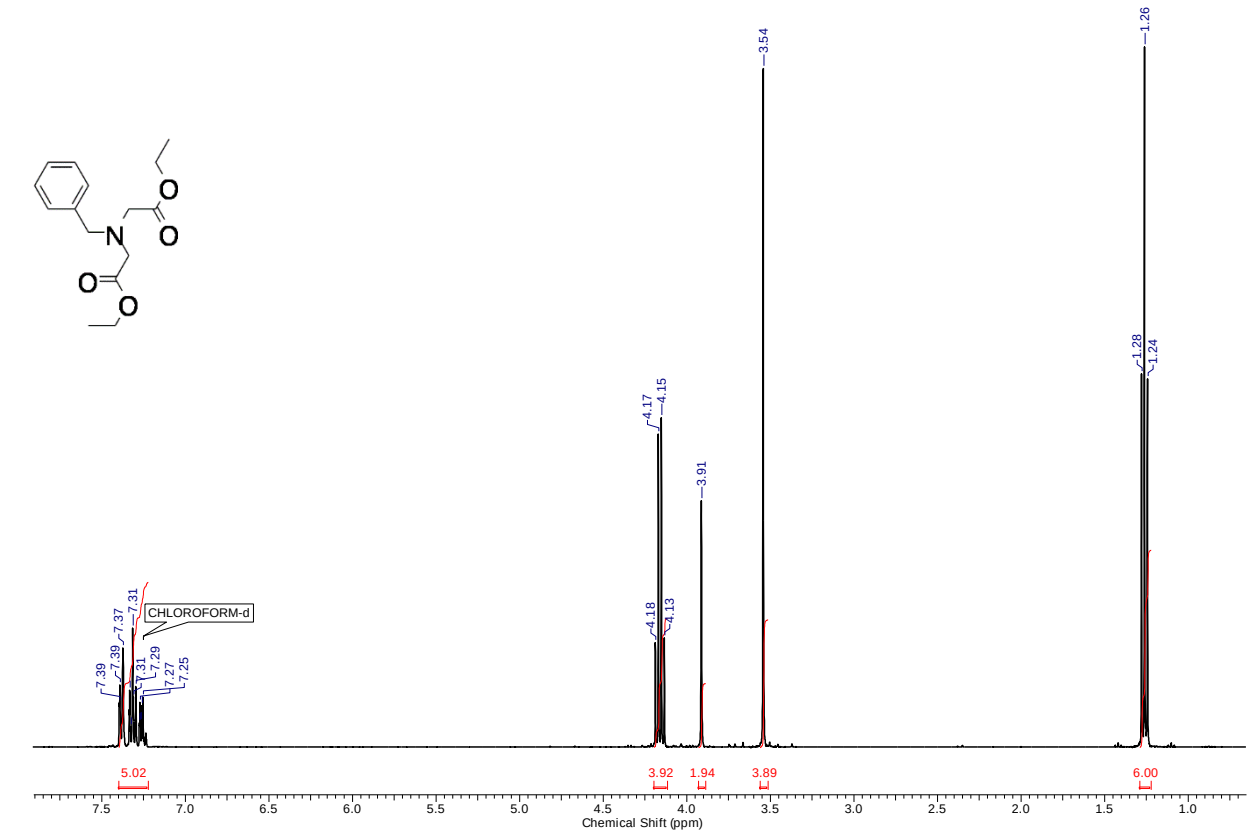


Figure S32. **^{1}H NMR** spectrum of *diethyl 2,2'-(benzylazanediyl)diacetate* **3b**

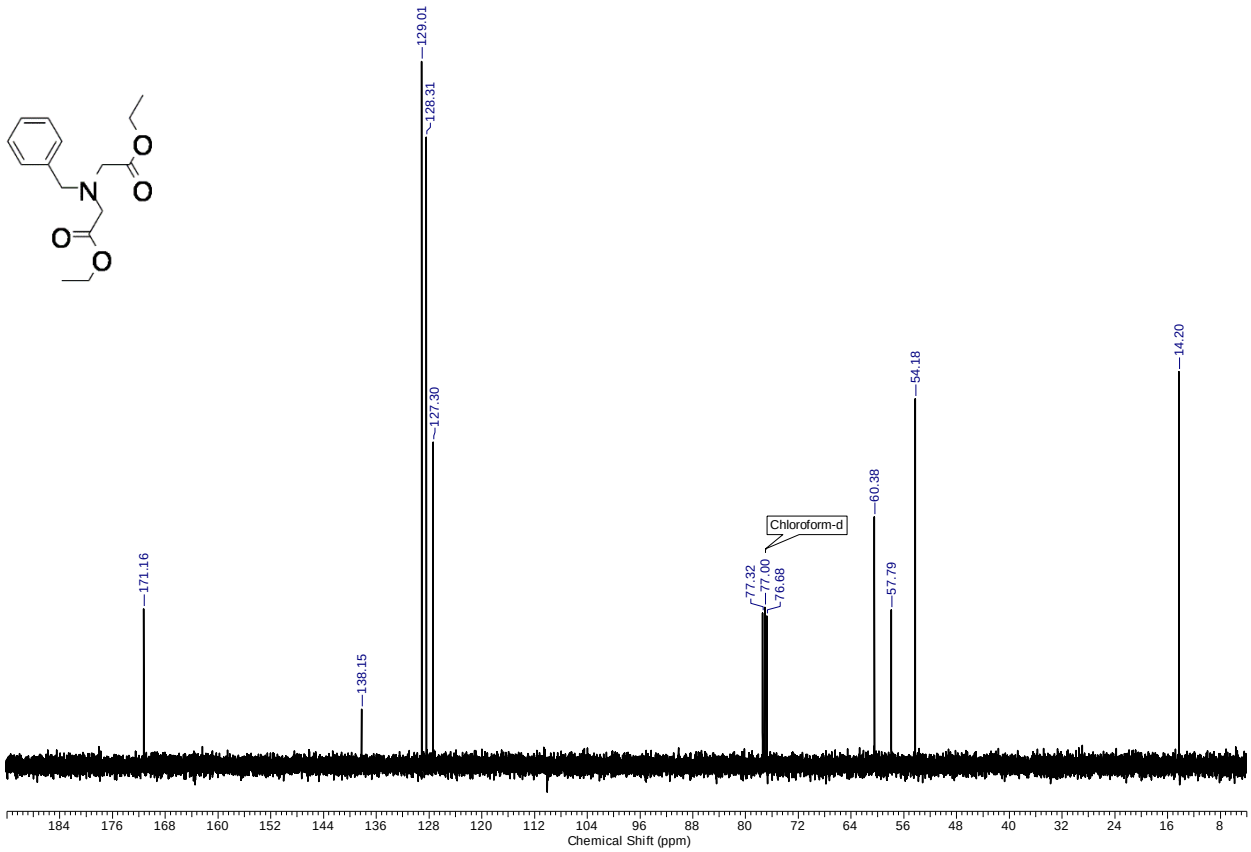


Figure S33. **^{13}C NMR** spectrum of *diethyl 2,2'-(benzylazanediyl)diacetate* **3b**

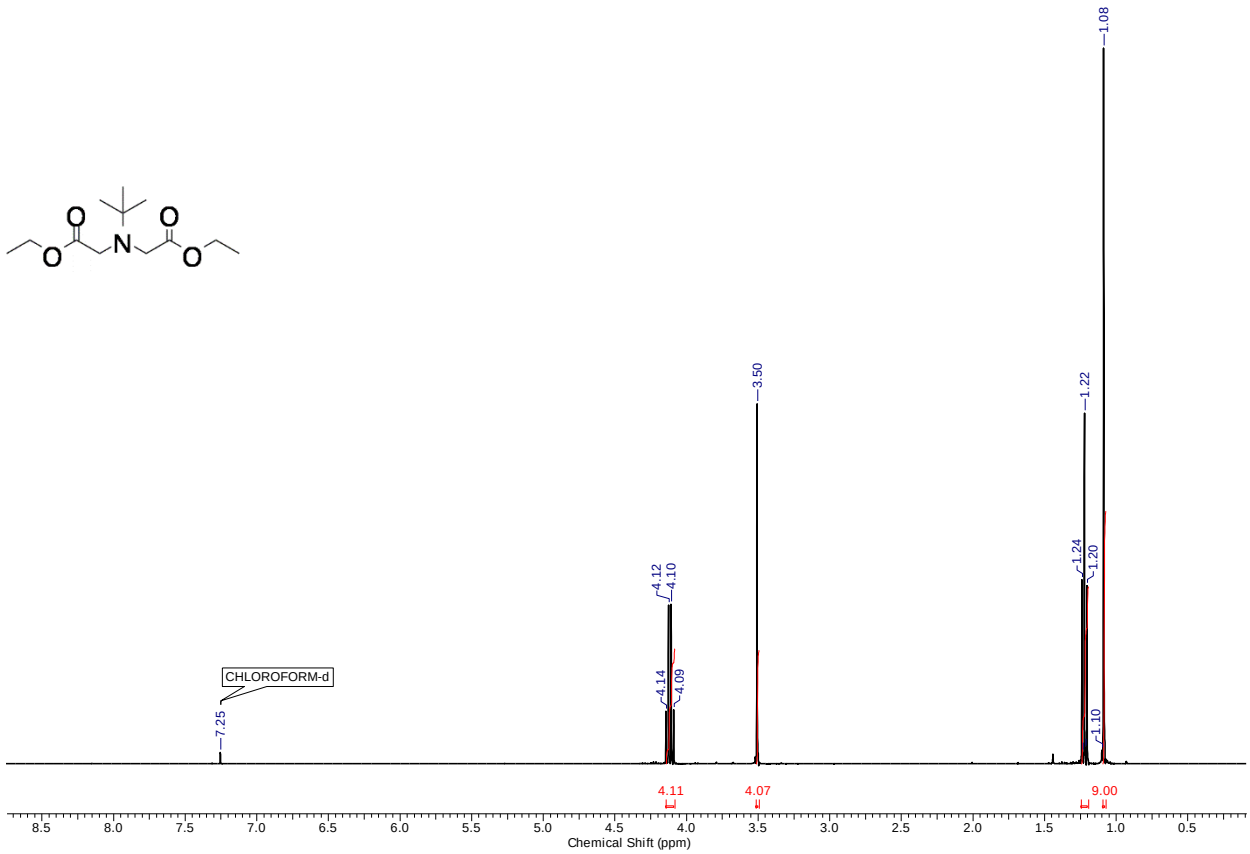


Figure S34. **^{1}H NMR** spectrum of *diethyl 2,2'-(tert-butylazanediyl)diacetate* **3c**

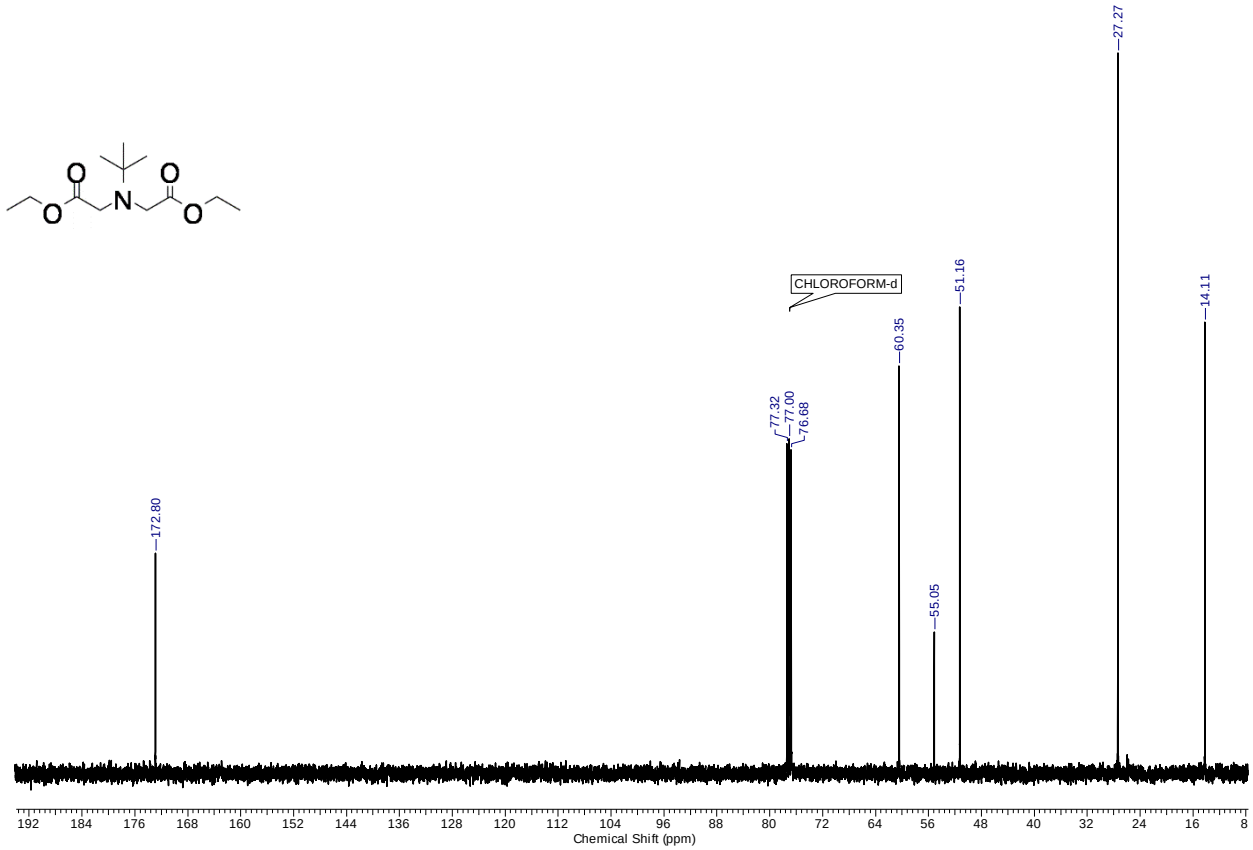


Figure S35. **^{13}C NMR** spectrum of *diethyl 2,2'-(tert-butylazanediyl)diacetate* **3c**

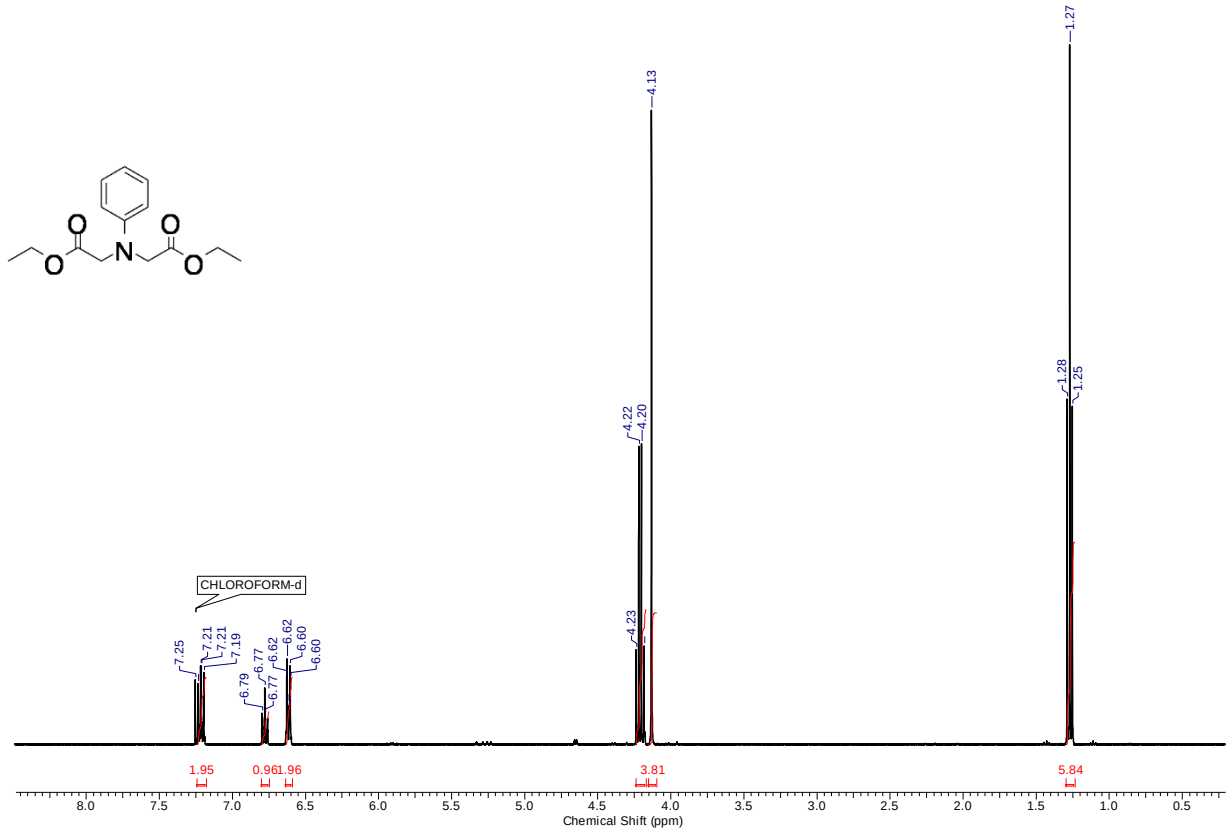


Figure S36. **^{1}H NMR** spectrum of *diethyl 2,2'-(phenylazanediyl)diacetate* **3d**

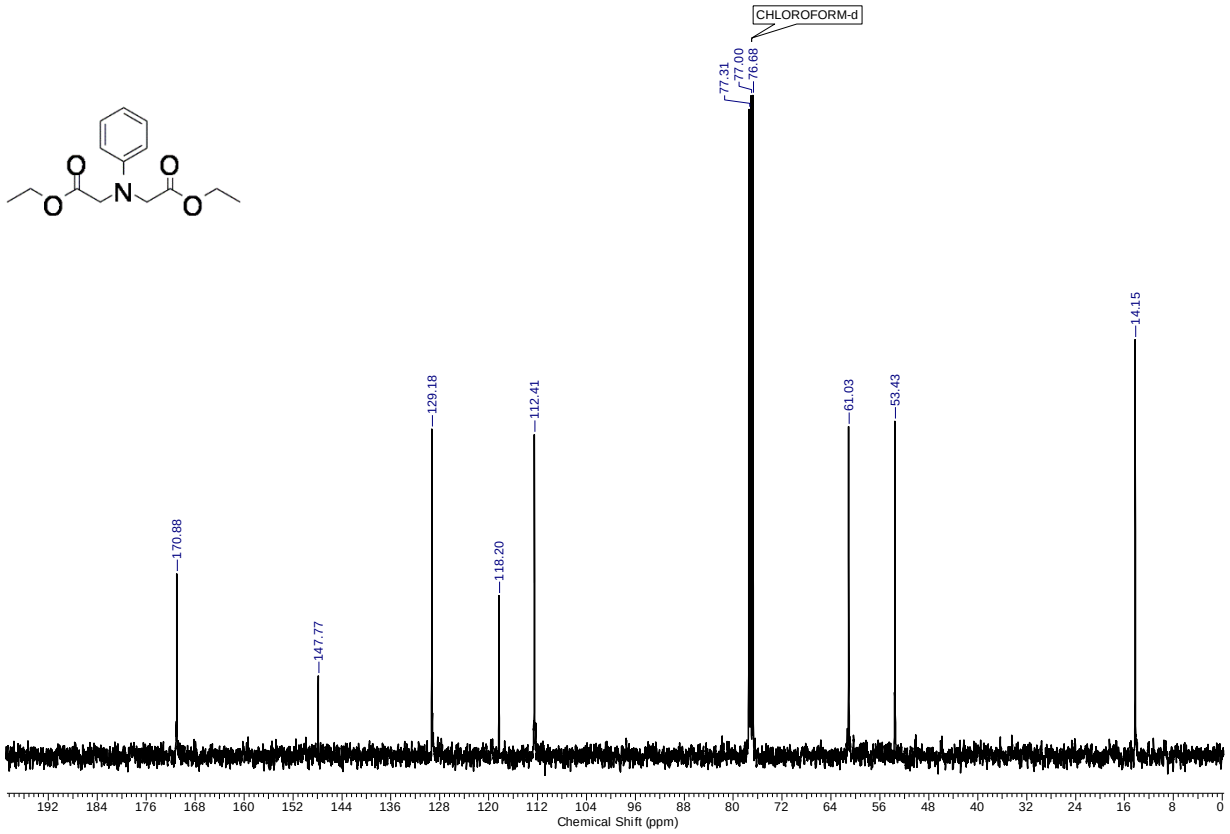


Figure S37. **^{13}C NMR** spectrum of *diethyl 2,2'-(phenylazanediyl)diacetate* **3d**

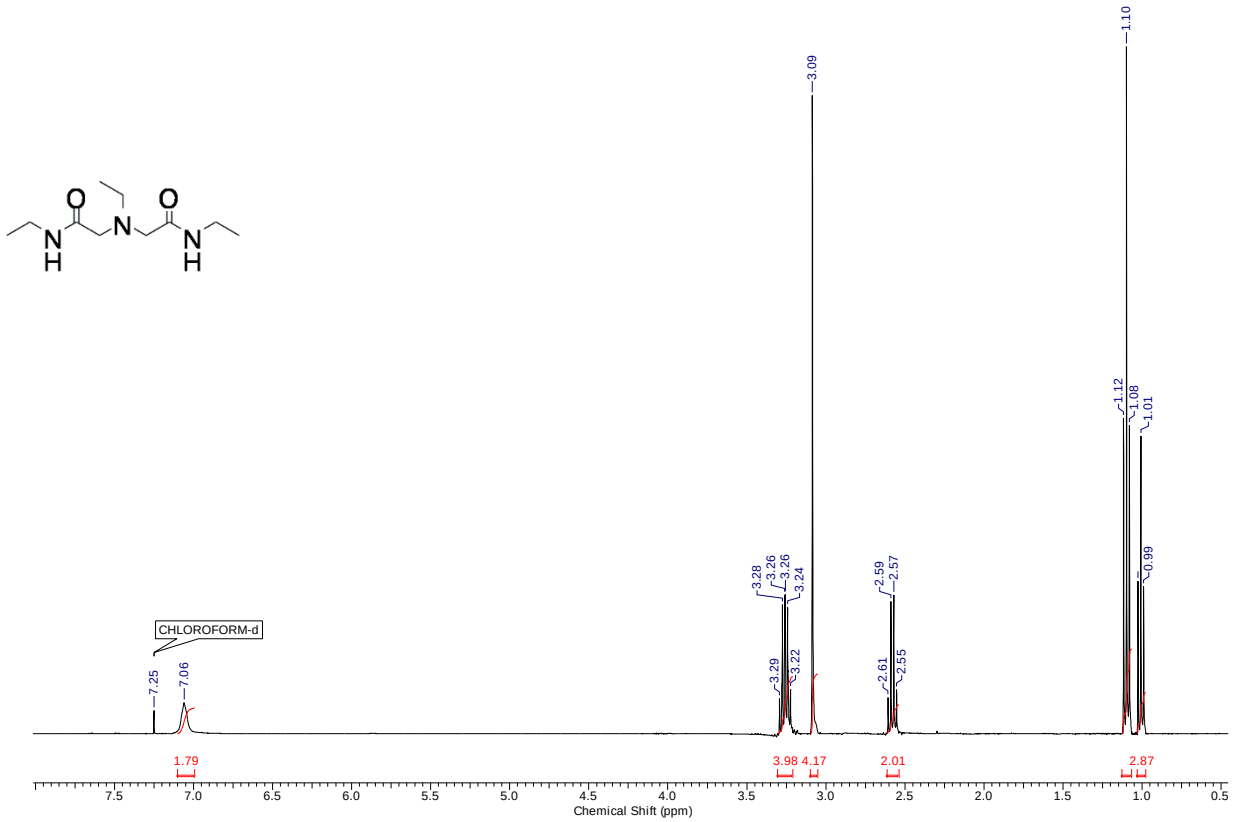


Figure S38. **^{1}H NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-ethylacetamide)* **2aa**

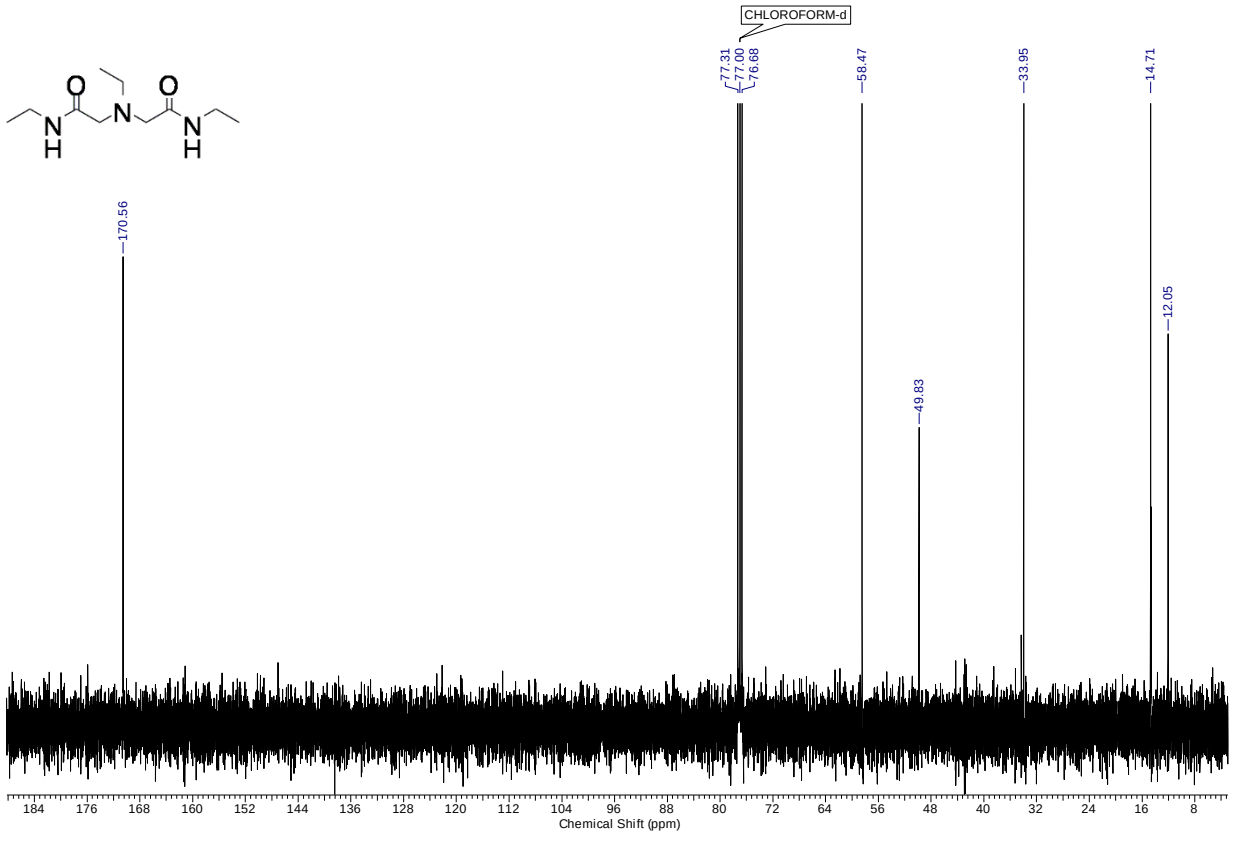


Figure S39. **^{13}C NMR** spectrum of *2,2'-(ethylazanediyl)bis(N-ethylacetamide)* **2aa**

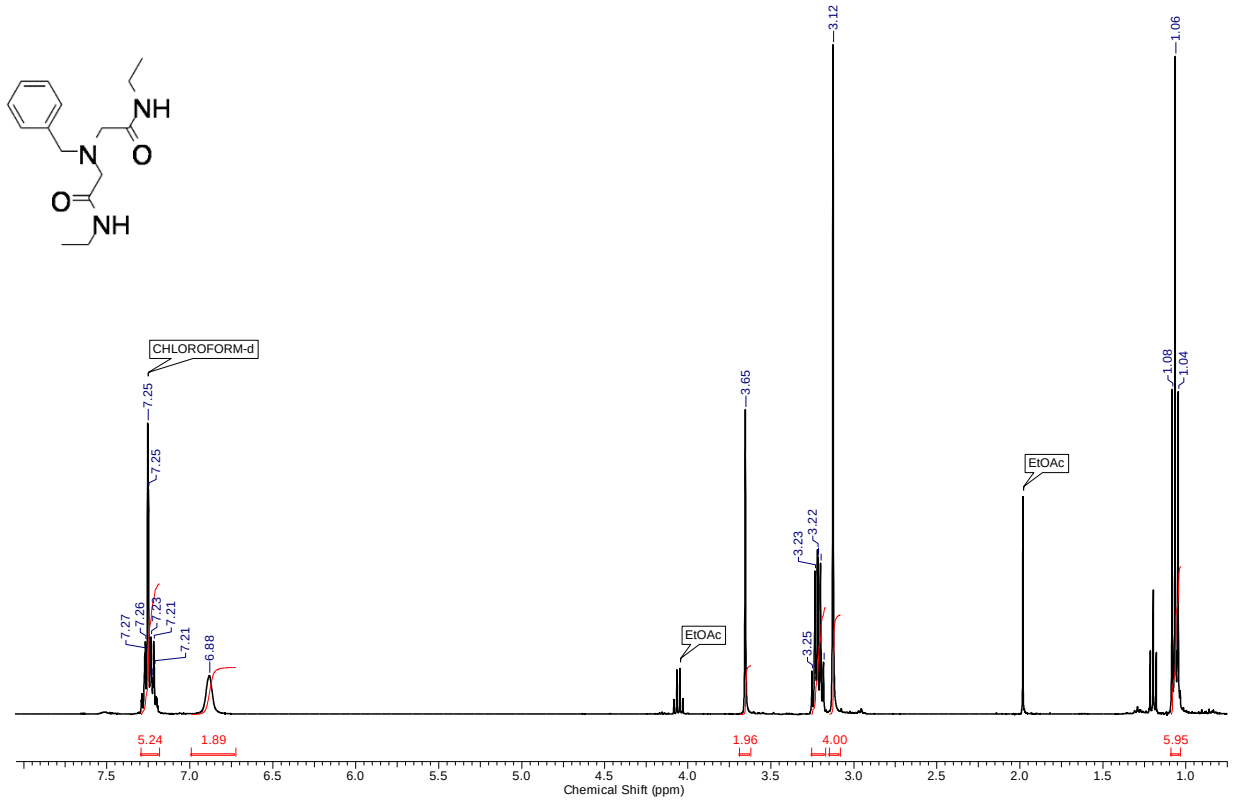


Figure S40. **^{1}H NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-ethylacetamide)* **2ba**

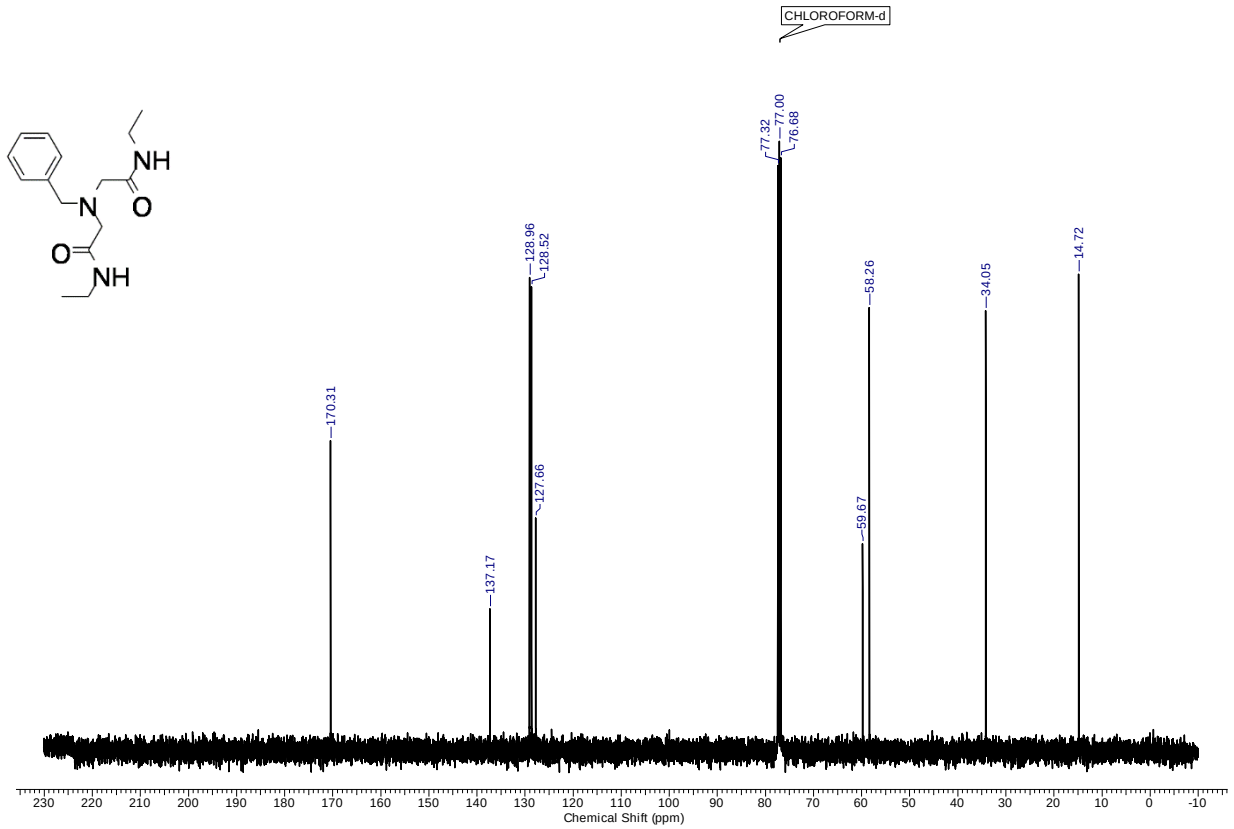


Figure S41. **^{13}C NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-ethylacetamide)* **2ba**

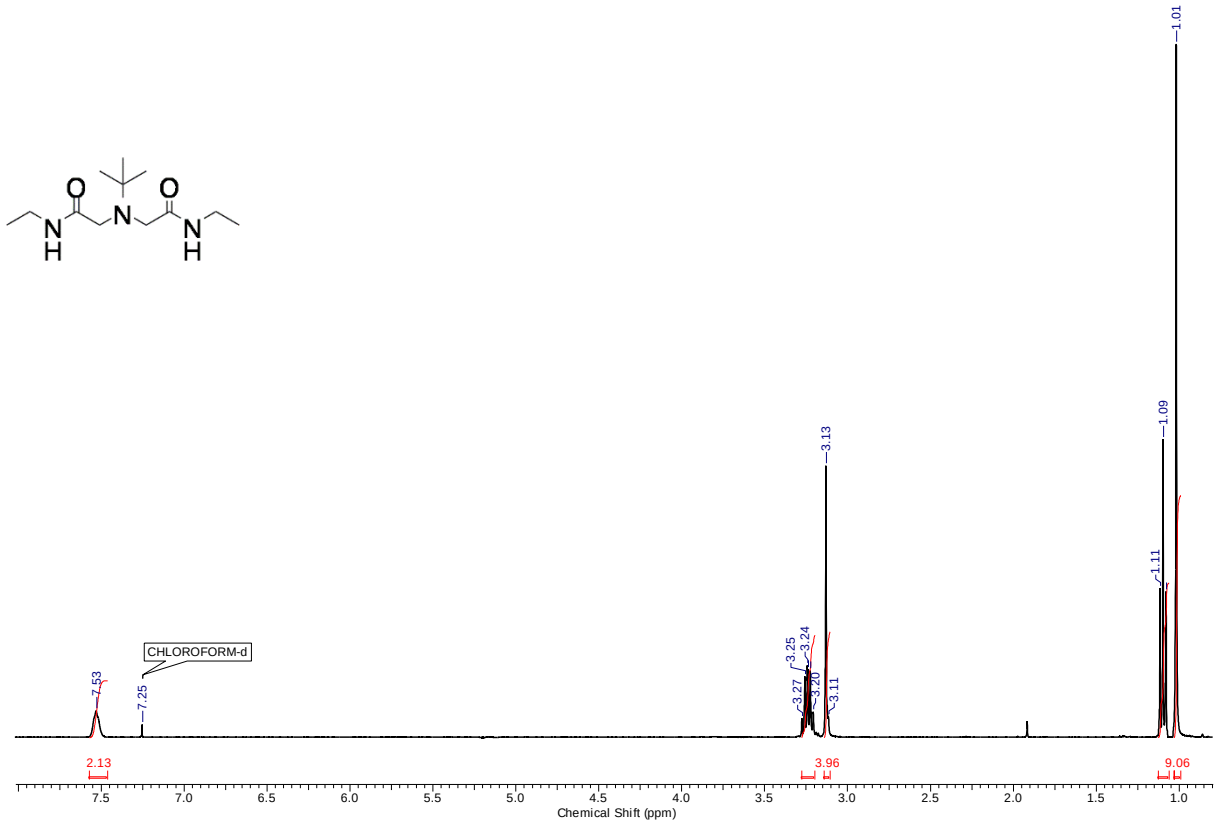


Figure S42. **^{1}H NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-ethylacetamide)* **2ca**

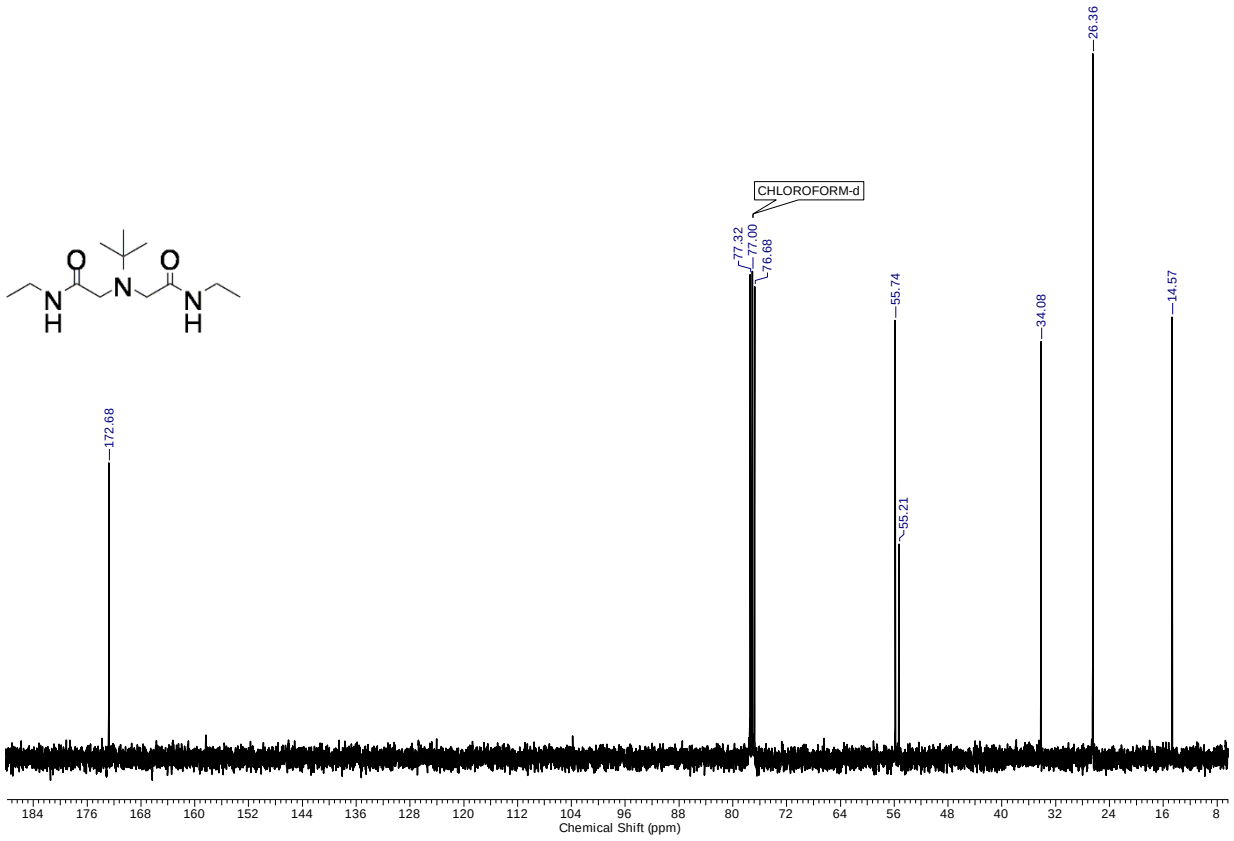


Figure S43. **^{13}C NMR** spectrum of *2,2'-(tert-butylazanediyl)bis(N-ethylacetamide)* **2ca**

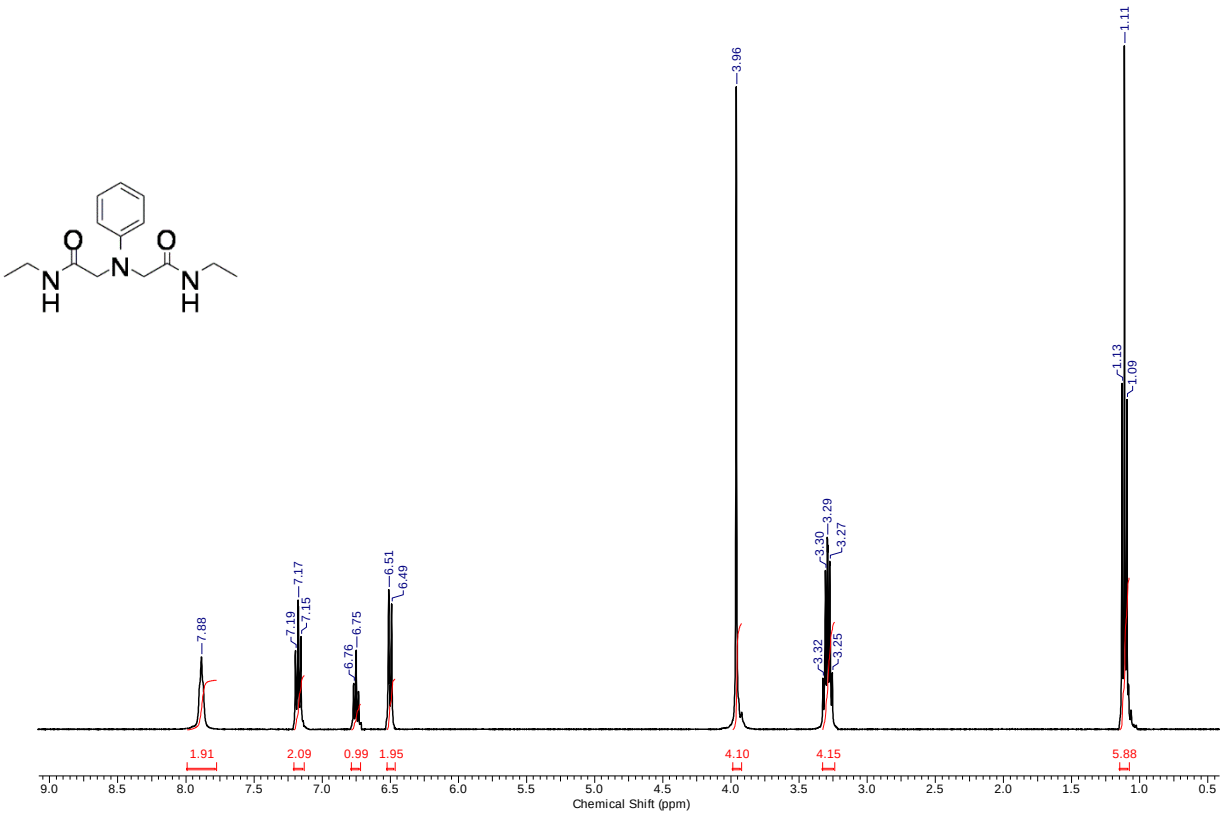


Figure S44. **^{1}H NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-ethylacetamide)* **2da**

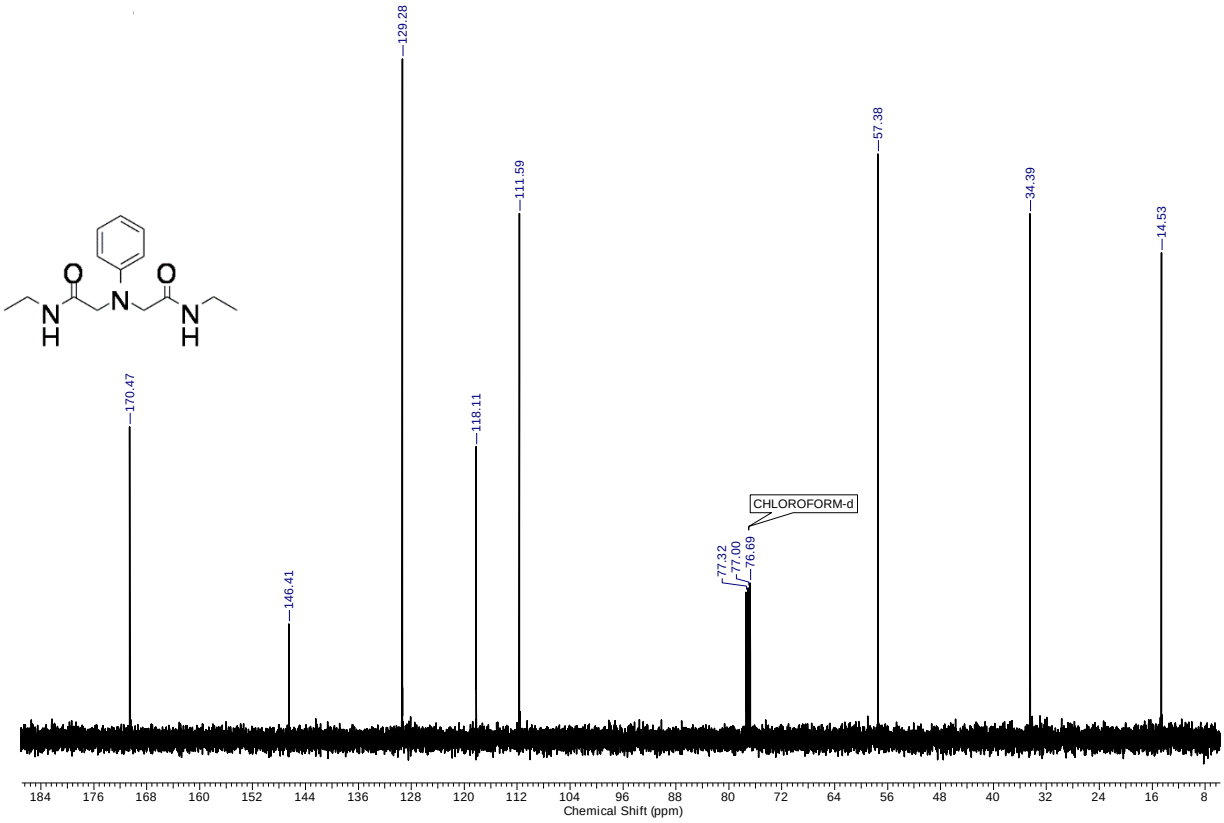


Figure S45. **^{13}C NMR** spectrum of *2,2'-(phenylazanediyl)bis(N-ethylacetamide)* **2da**

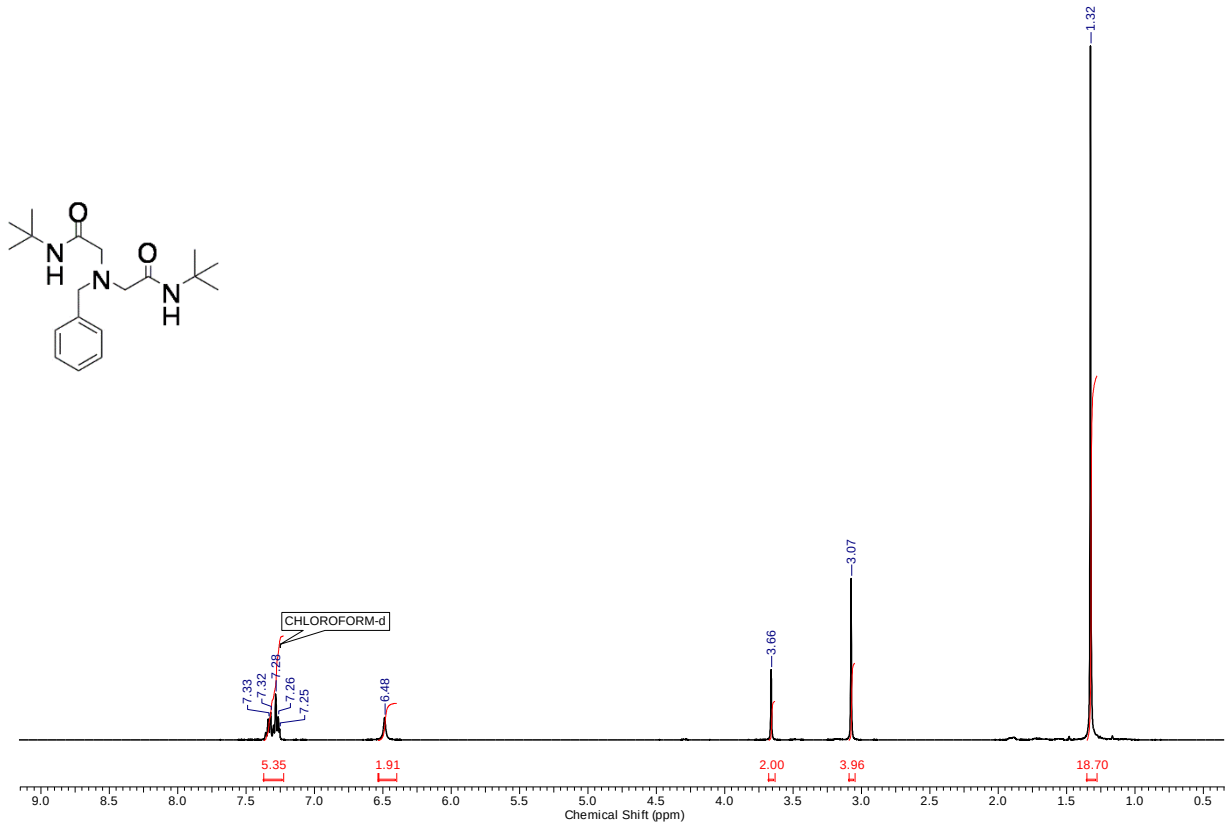


Figure S46. **^{1}H NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-tert-butylacetamide)* **2bc**

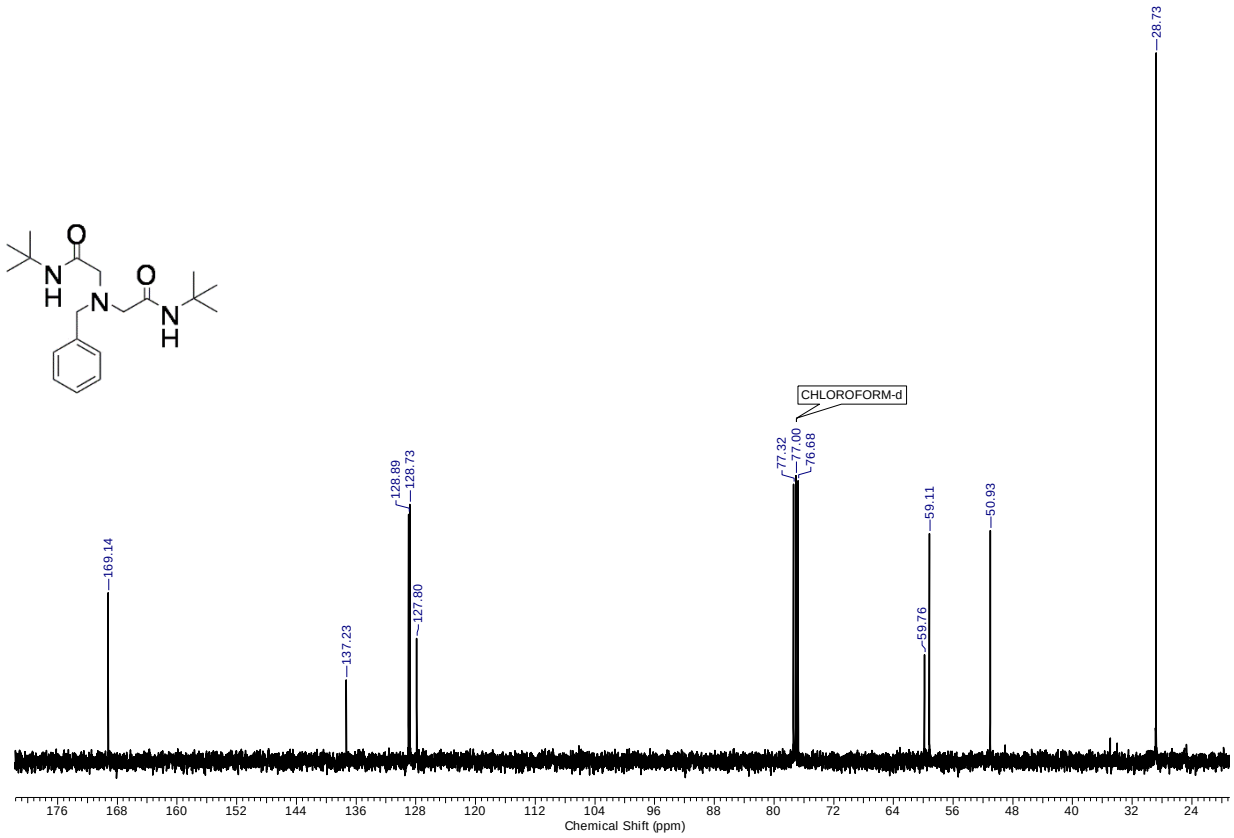


Figure S47. **^{13}C NMR** spectrum of *2,2'-(benzylazanediyl)bis(N-tert-butylacetamide)* **2bc**

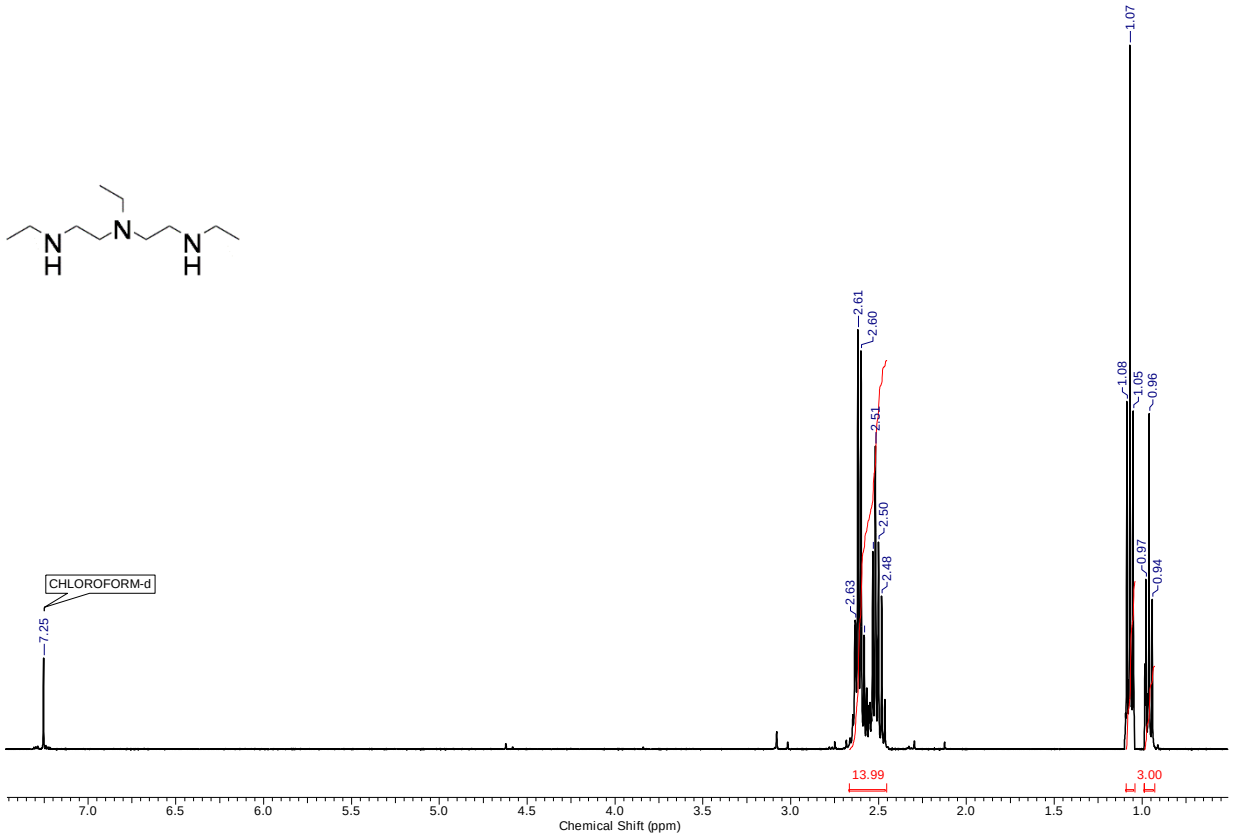


Figure S48. **^{1}H NMR** spectrum of *N^1,N^2-diethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine* **4aa**

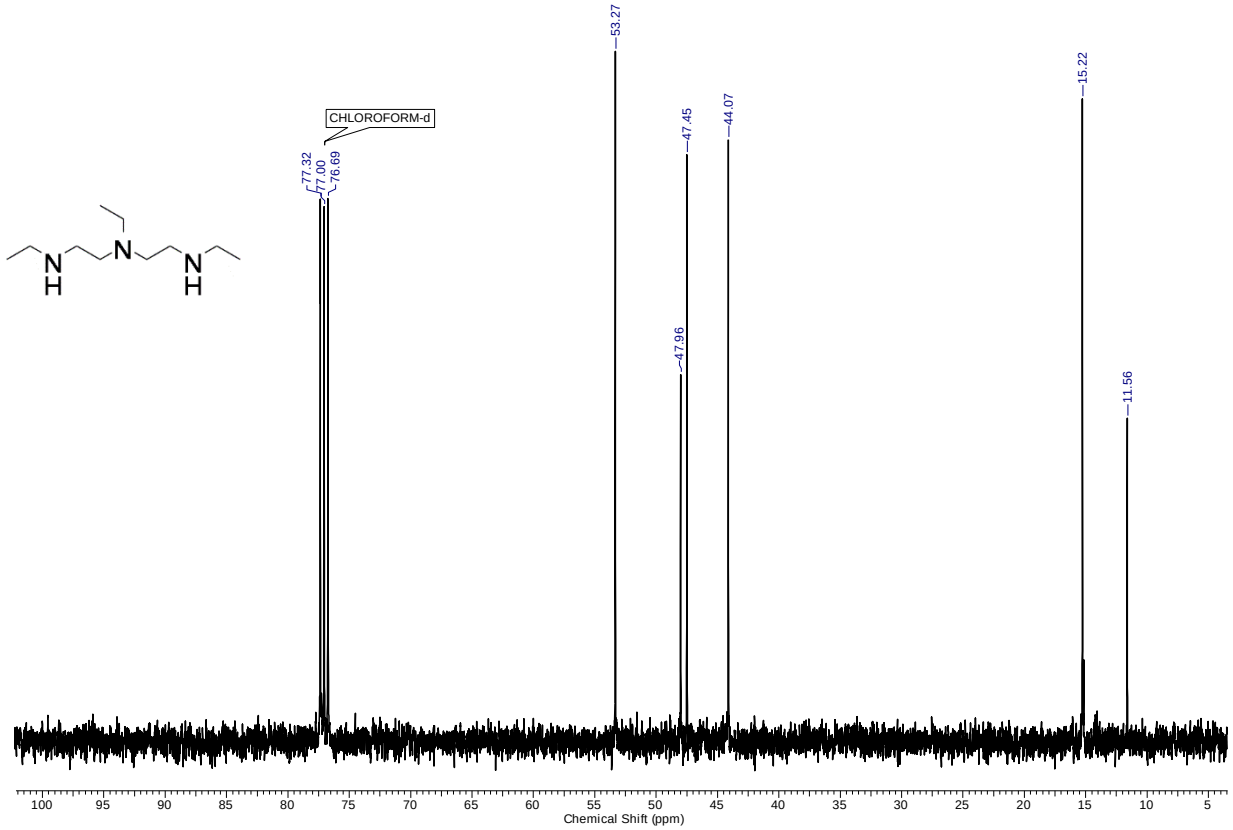


Figure S49. ^{13}C NMR spectrum of *N^1,N^2-diethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine* **4aa**

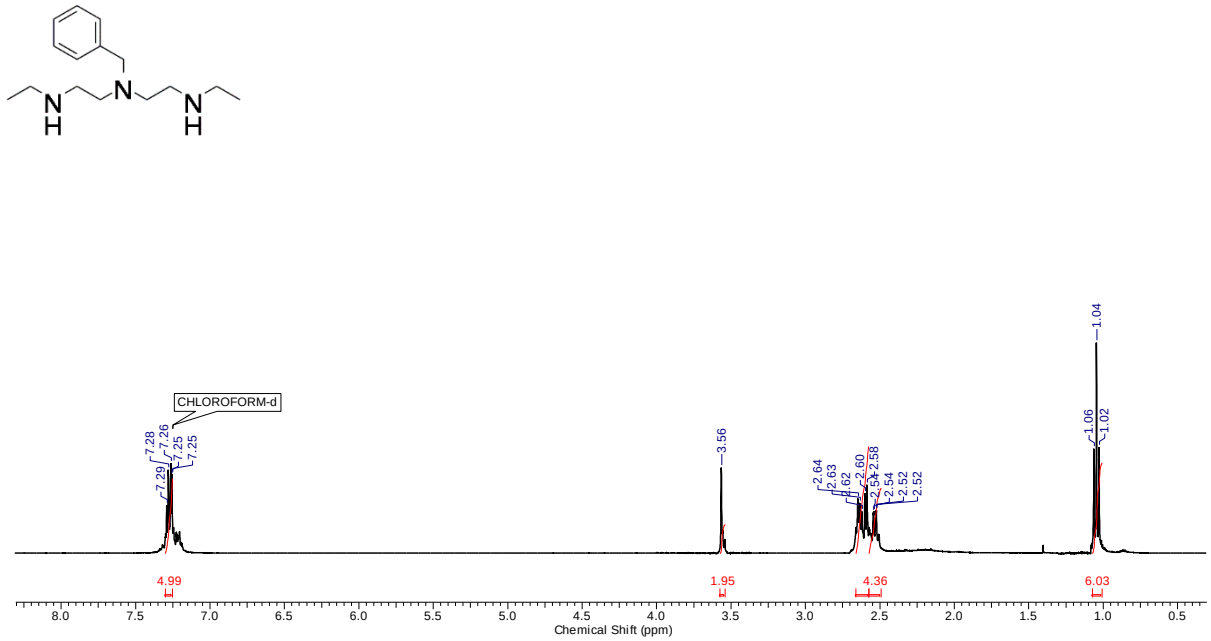


Figure S50. **^{1}H NMR** spectrum of *N^1-benzyl-N^2-ethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine* **4ba**

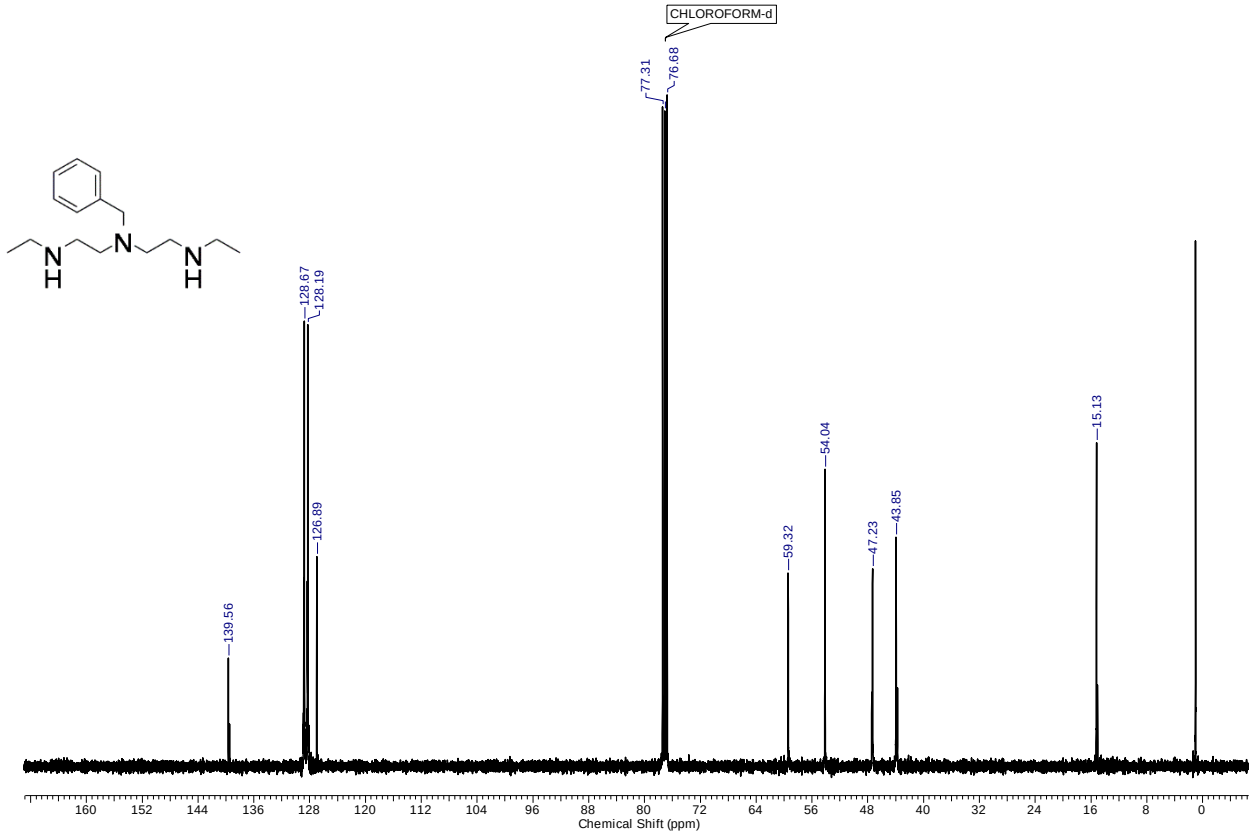


Figure S51. **^{13}C NMR** spectrum of *N^1-benzyl-N^2-ethyl-N^1-(2-ethylaminoethyl)ethane-1,2-diamine* **4ba**

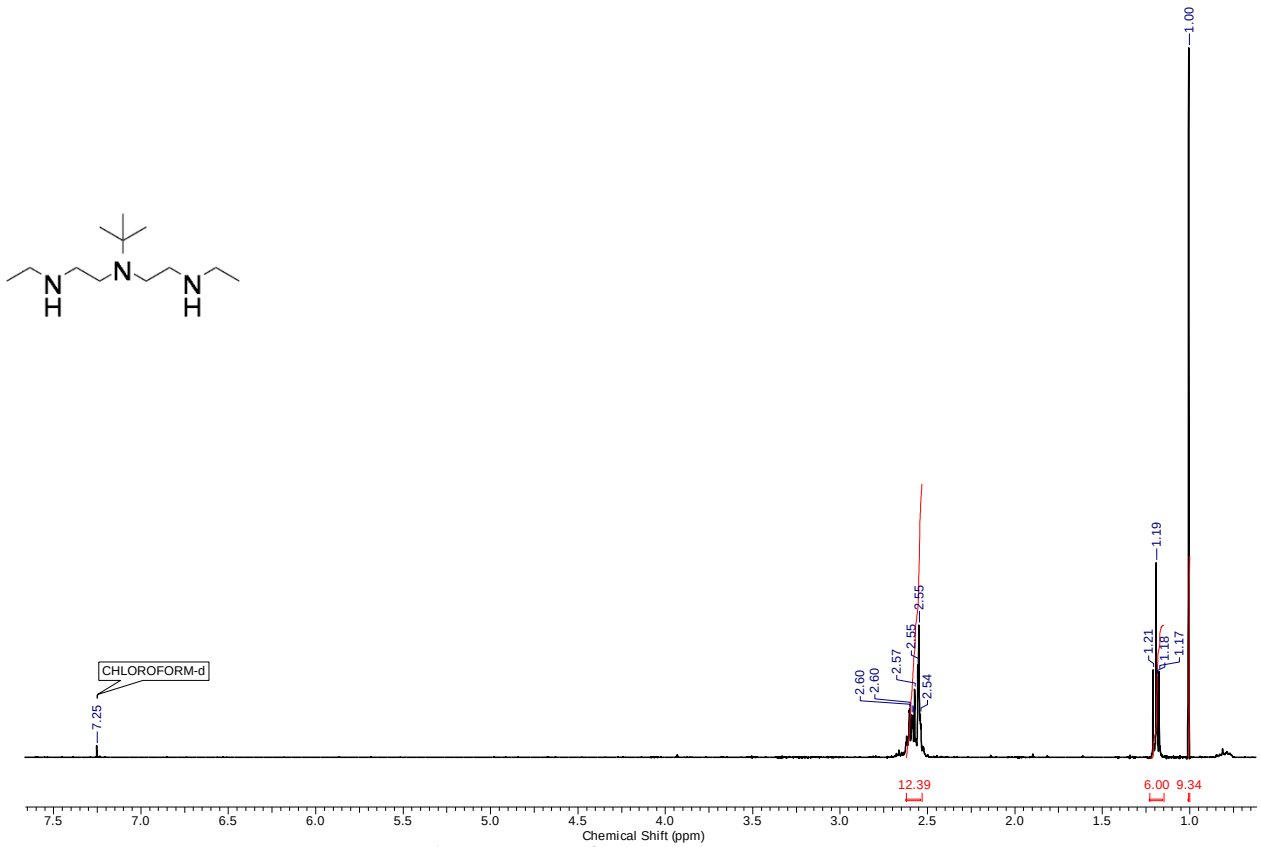


Figure S52. ^{1}H NMR spectrum of *N*^{1}*-tert-butyl-N*^{2}*-ethyl-N*^{1}*-(2-ethylaminoethyl)ethane-1,2-diamine* **4ca**

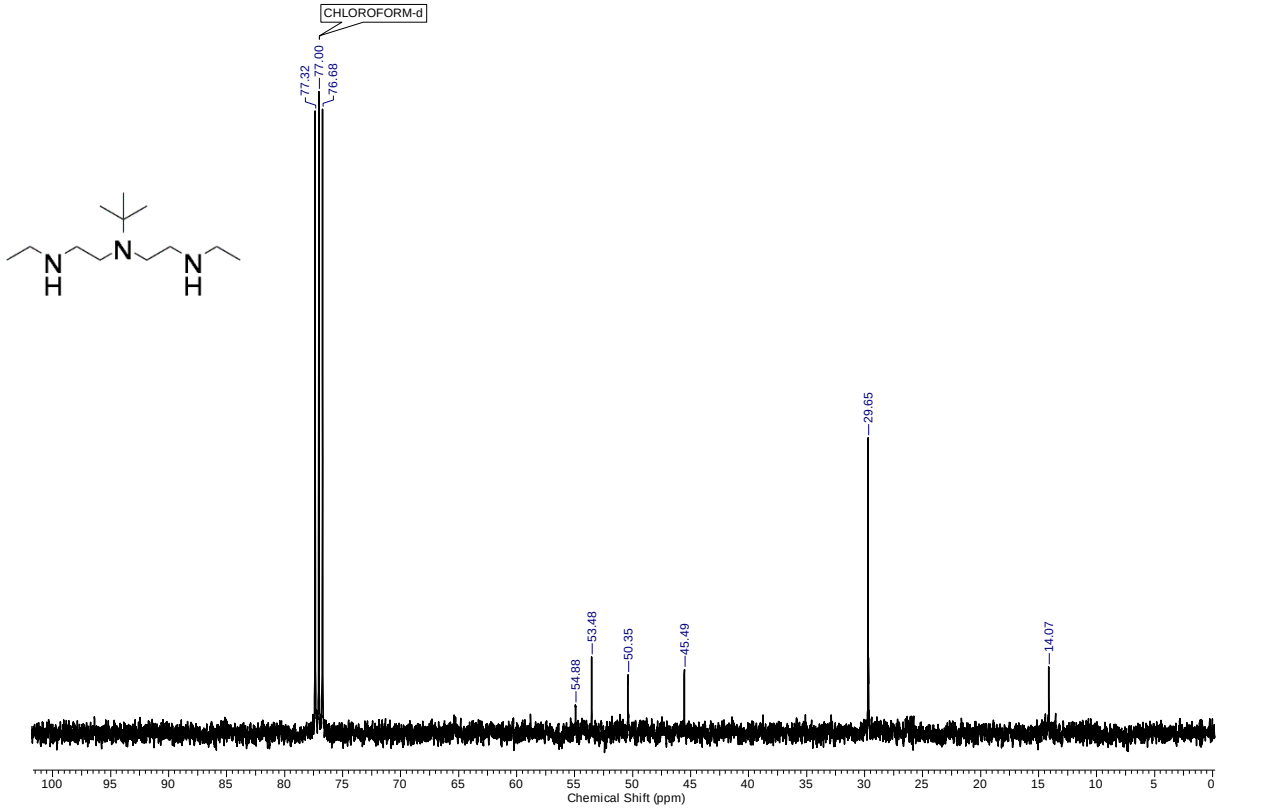


Figure S53. **^{13}C NMR** spectrum of *N*^{1}*-tert-butyl-N*^{2}*-ethyl-N*^{1}*-(2-ethylaminoethyl)ethane-1,2-diamine* **4ca**

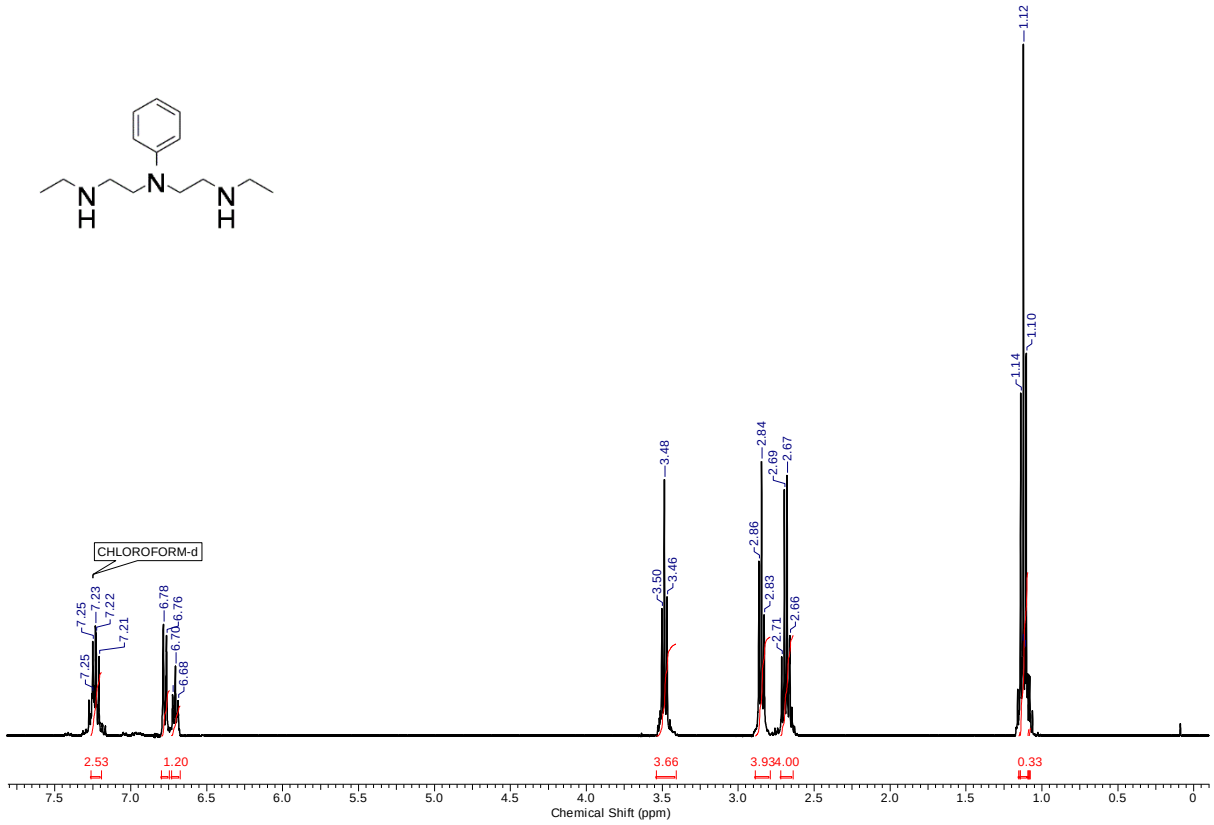


Figure S54. **^{1}H NMR** spectrum of *N^2-ethyl-N^1-(2-ethylaminoethyl)-N^1-phenylethane-1,2-diamine* **4da**

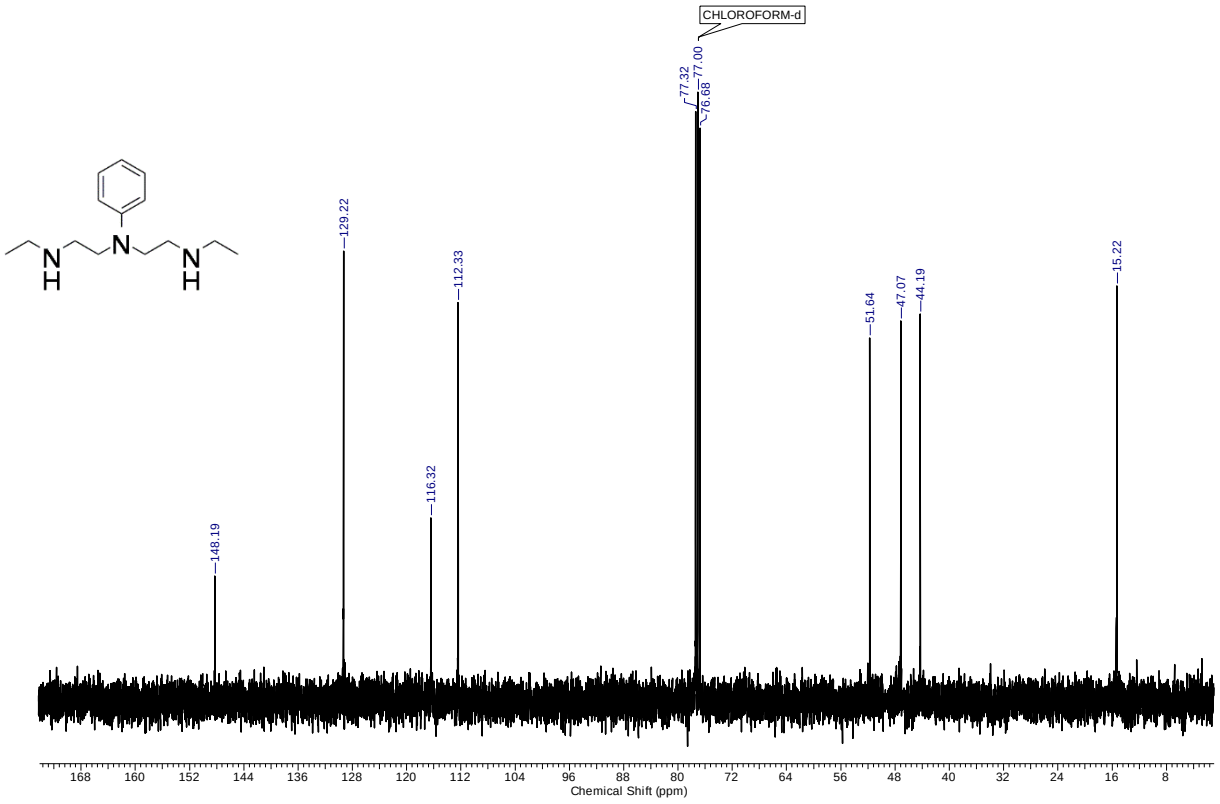


Figure S55. **^{13}C NMR** spectrum of *N^2-ethyl-N^1-(2-ethylaminoethyl)-N^1-phenylethane-1,2-diamine* **4da**

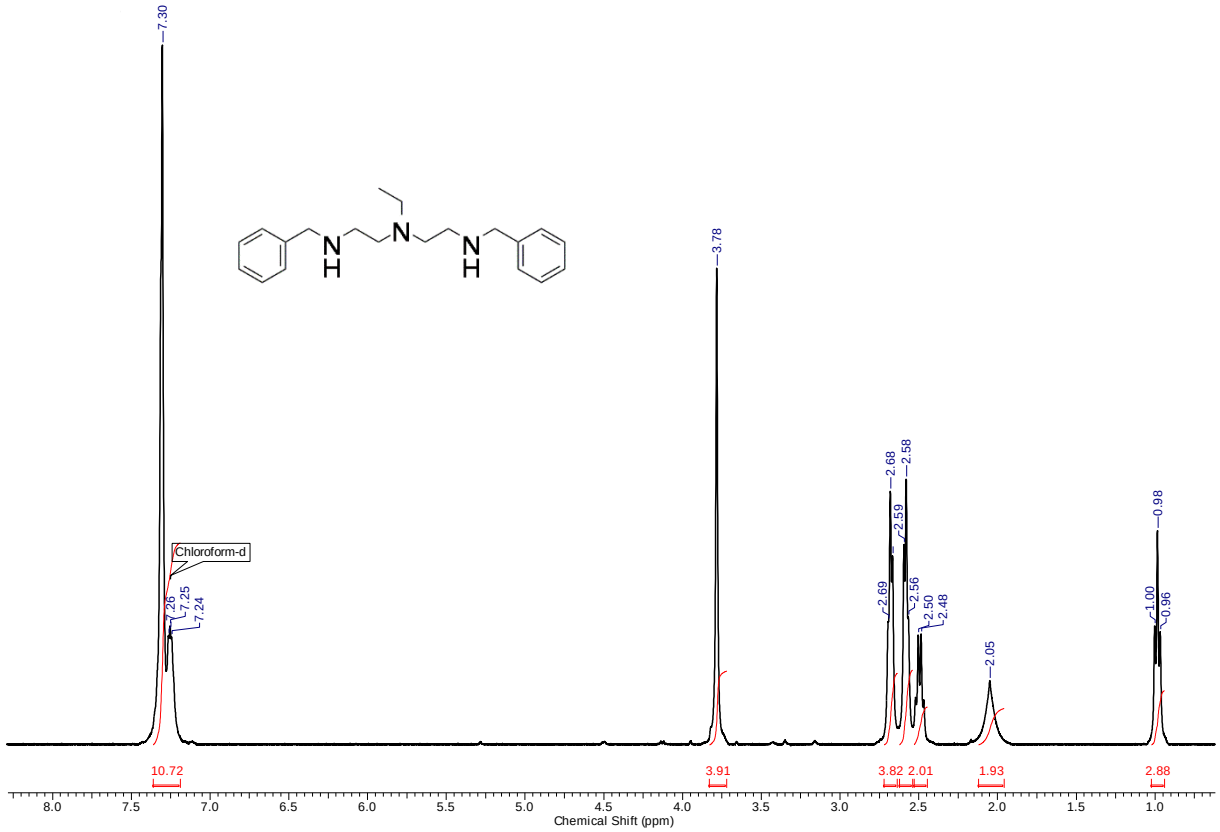


Figure S56. **^{1}H NMR** spectrum of *N^1-benzyl-N^1-(2-benzylaminoethyl)-N^2-ethylethane-1,2-diamine* **4ab**

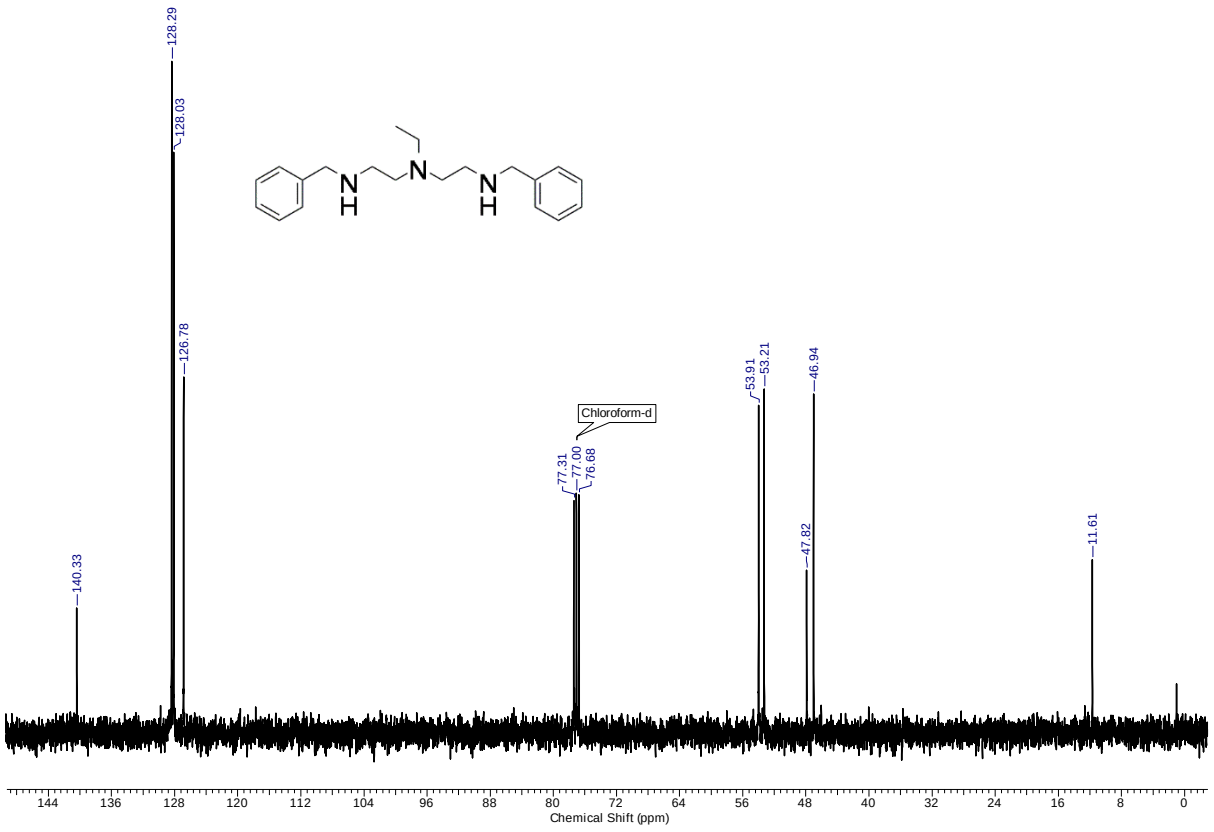


Figure S57. ^{13}C NMR spectrum of *N^1-benzyl-N^1-(2-benzylaminoethyl)-N^2-ethylethane-1,2-diamine* **4ab**

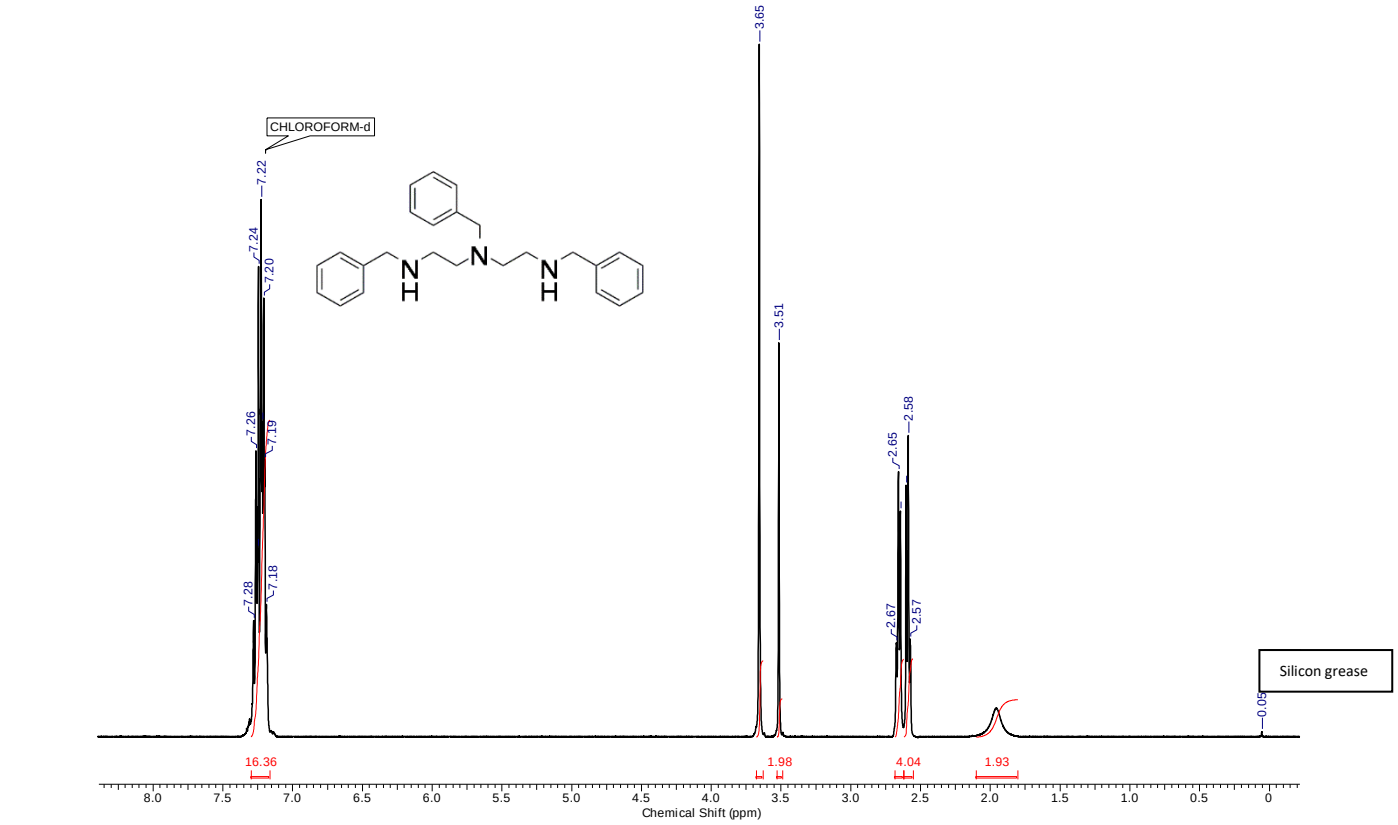


Figure S58. **^{1}H NMR** spectrum of *N^1,N^2-dibenzyl-N^1-(2-benzylaminoethyl)ethane-1,2-diamine* **4bb**

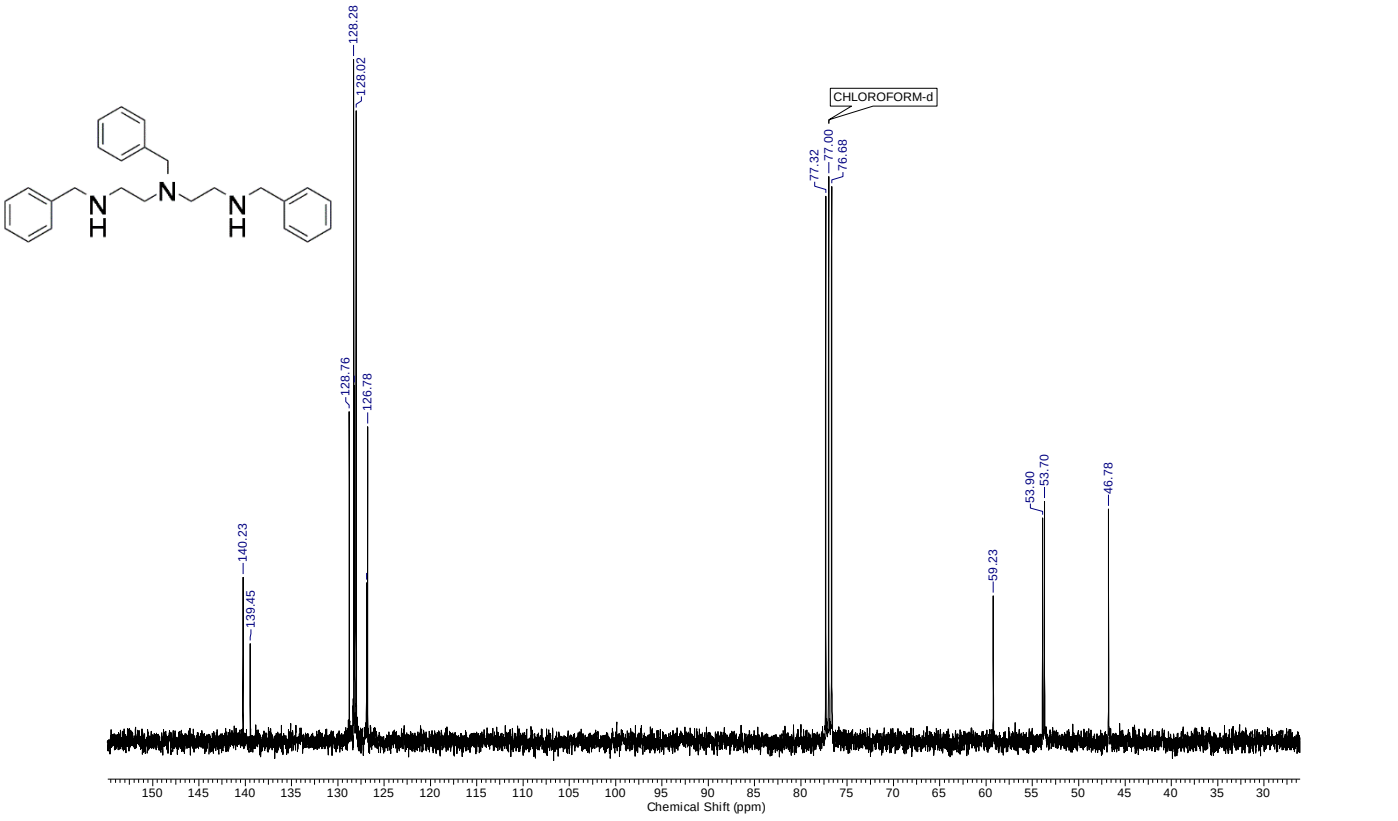


Figure S59. **^{13}C NMR** spectrum of *N^1,N^2-dibenzyl-N^1-(2-benzylaminoethyl)ethane-1,2-diamine* **4bb**

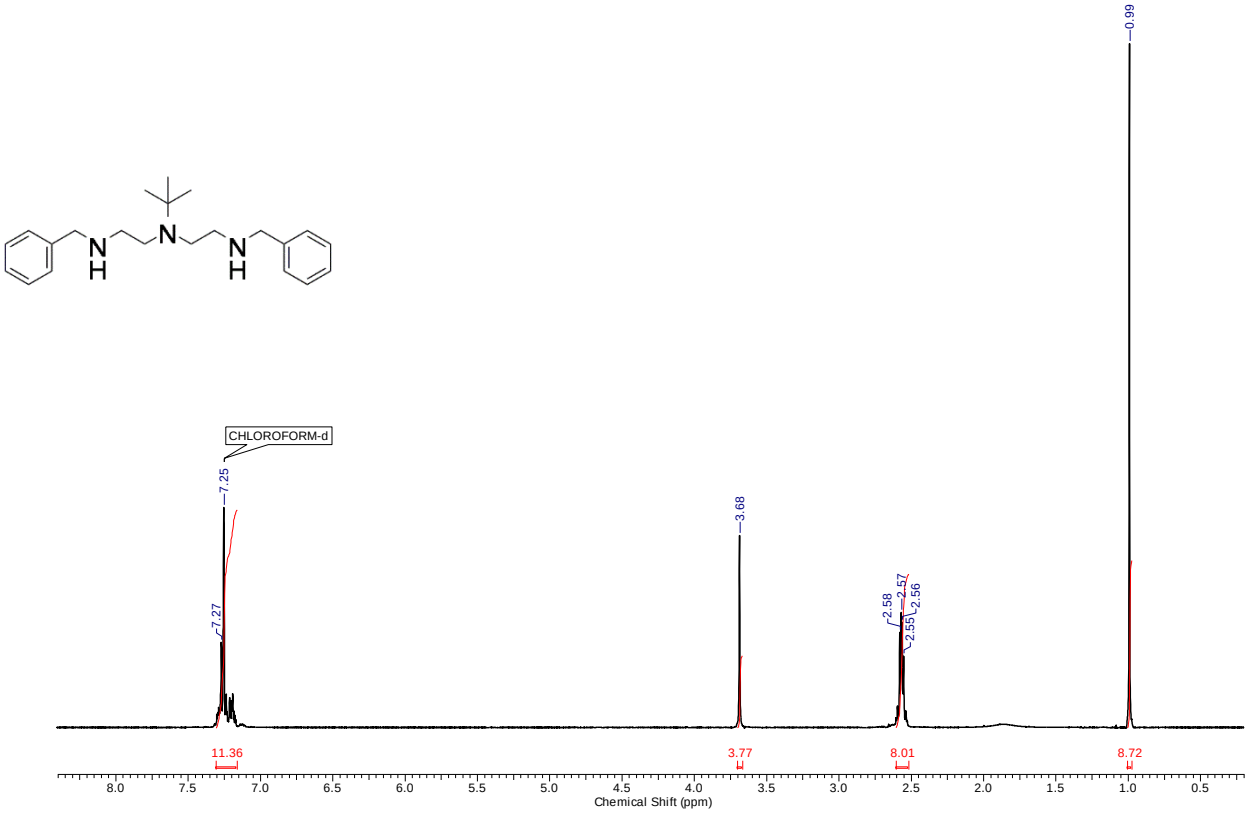


Figure S60. **^{1}H NMR** spectrum of *N^1-(2-benzylaminoethyl)-N^1-tert-butyl-N^2-ethylethane-1,2-diamine* **4cb**

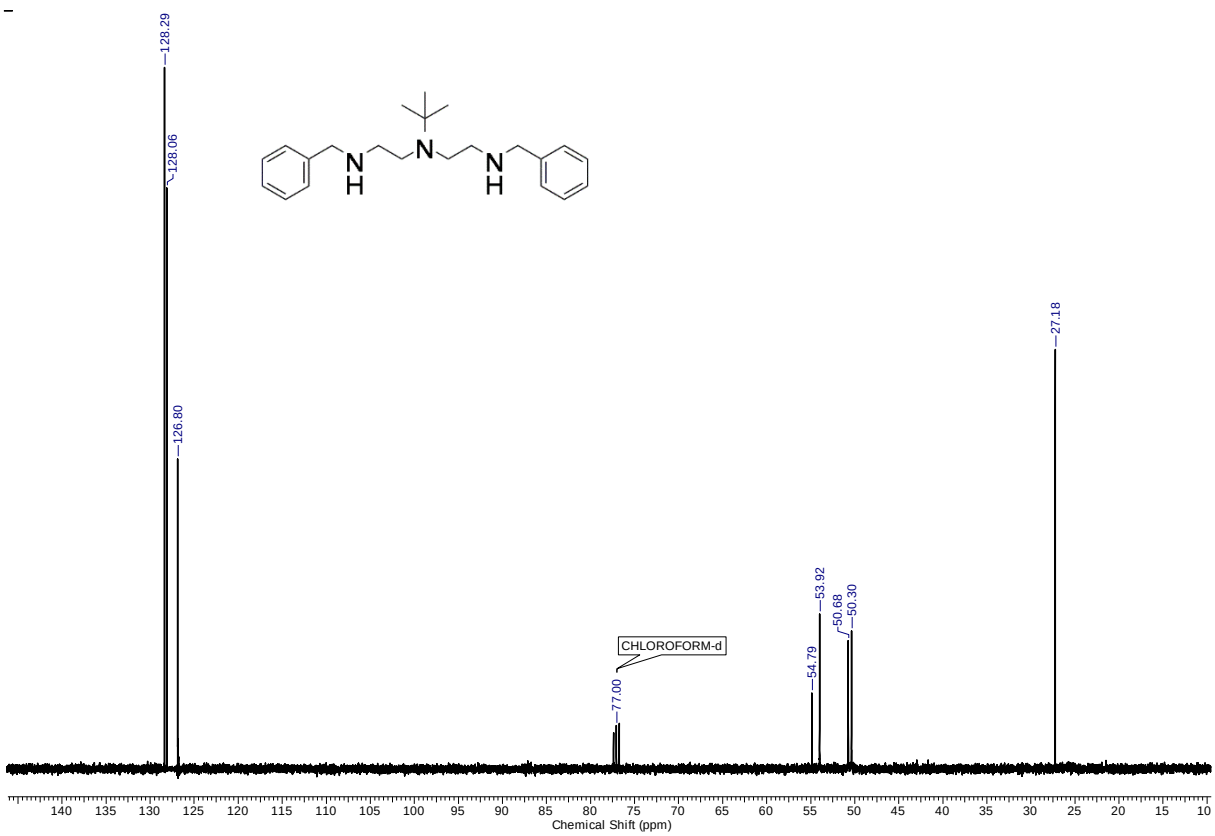


Figure S61 ^{13}C NMR spectrum of *N^1-(2-benzylaminoethyl)-N^1-tert-butyl-N^2-ethylethane-1,2-diamine* **4cb**

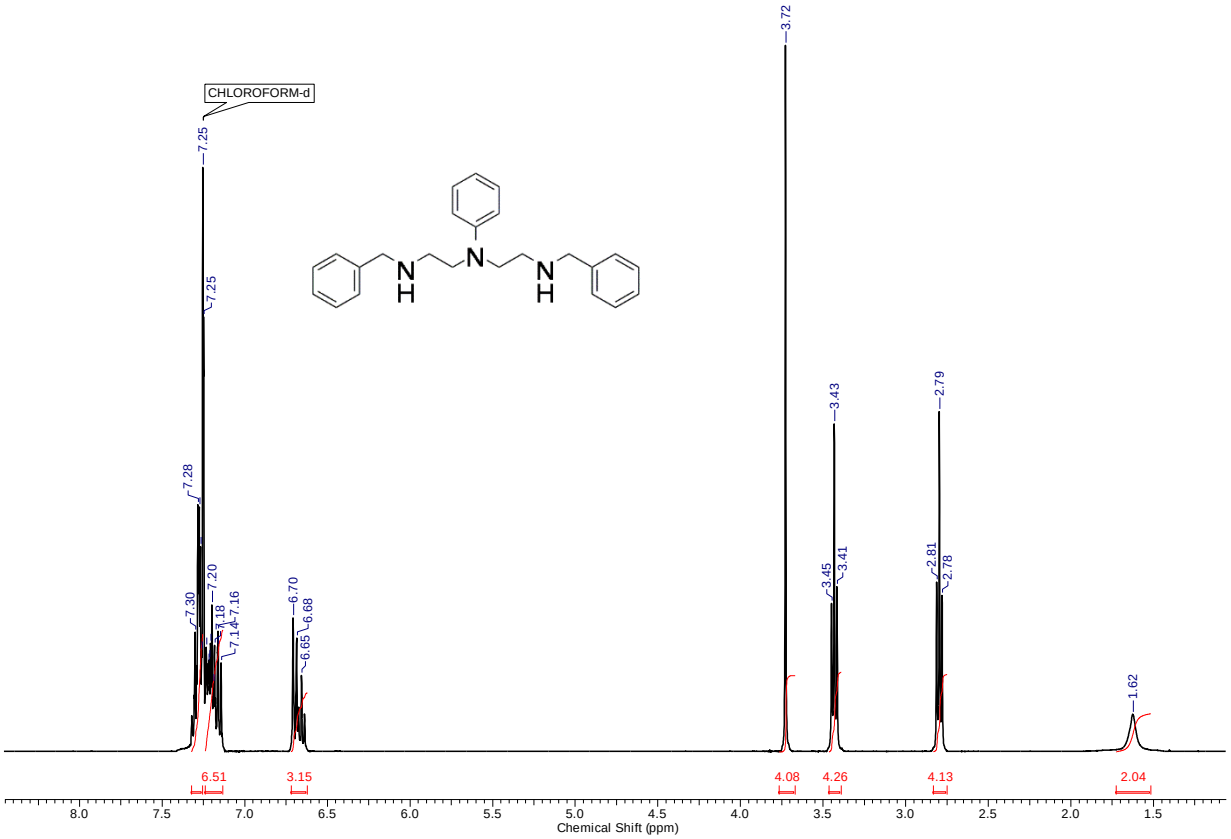


Figure S62 **^{1}H NMR** spectrum of *N^1-(2-benzylaminoethyl)-N^2-ethyl-N^1-phenylethane-1,2-diamine* **4db**

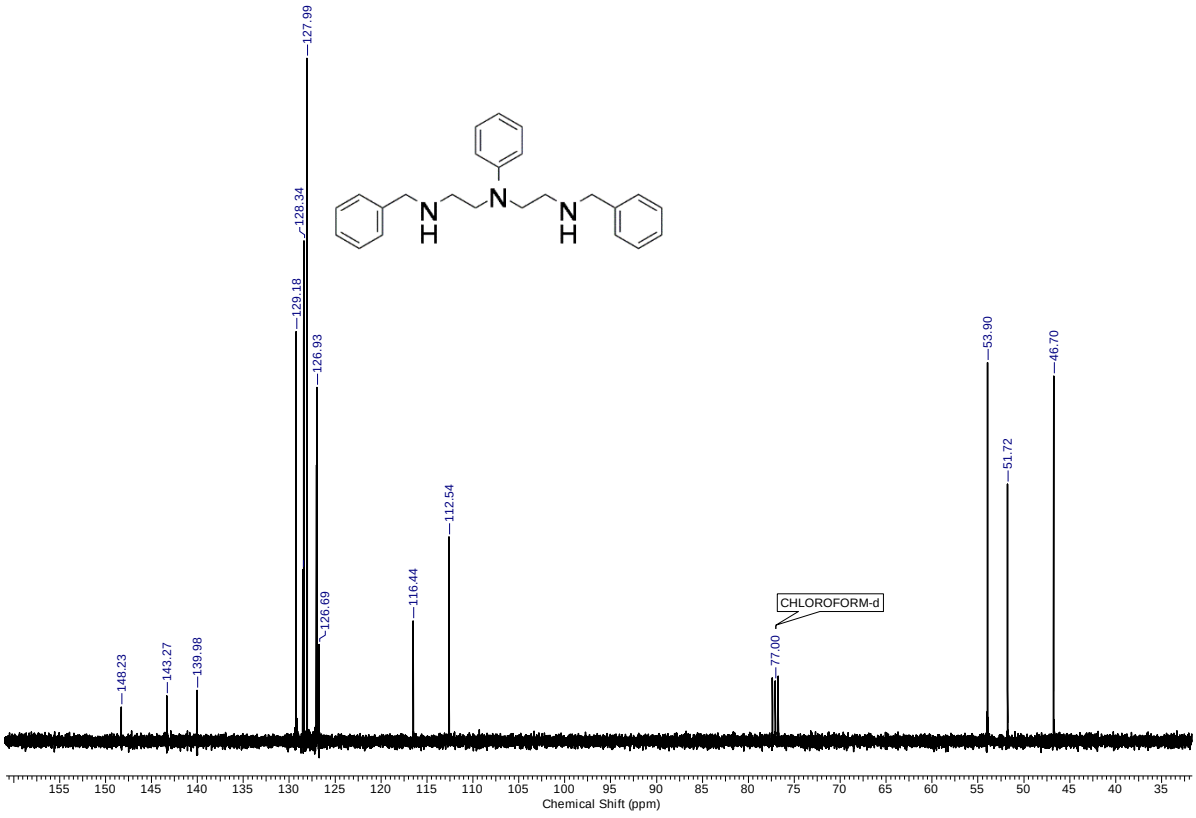


Figure S63 **^{13}C NMR** spectrum of *N^1-(2-benzylaminoethyl)-N^2-ethyl-N^1-phenylethane-1,2-diamine* **4db**

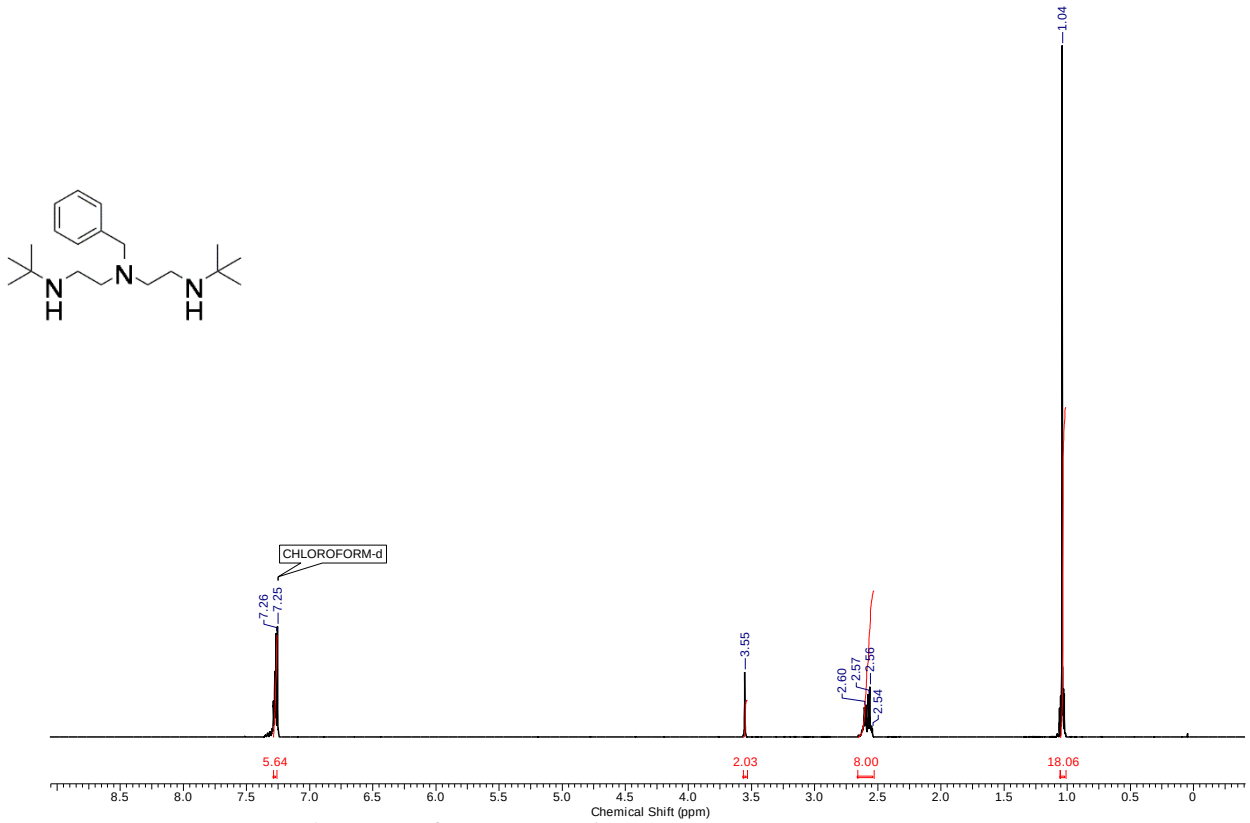


Figure S64 ^{1}H NMR of *N*^{1}*-benzyl-N*^{2}*-tert-butyl-N*^{1}*-(2-tert-butylaminoethyl)ethane-1,2-diamine* **4bc**

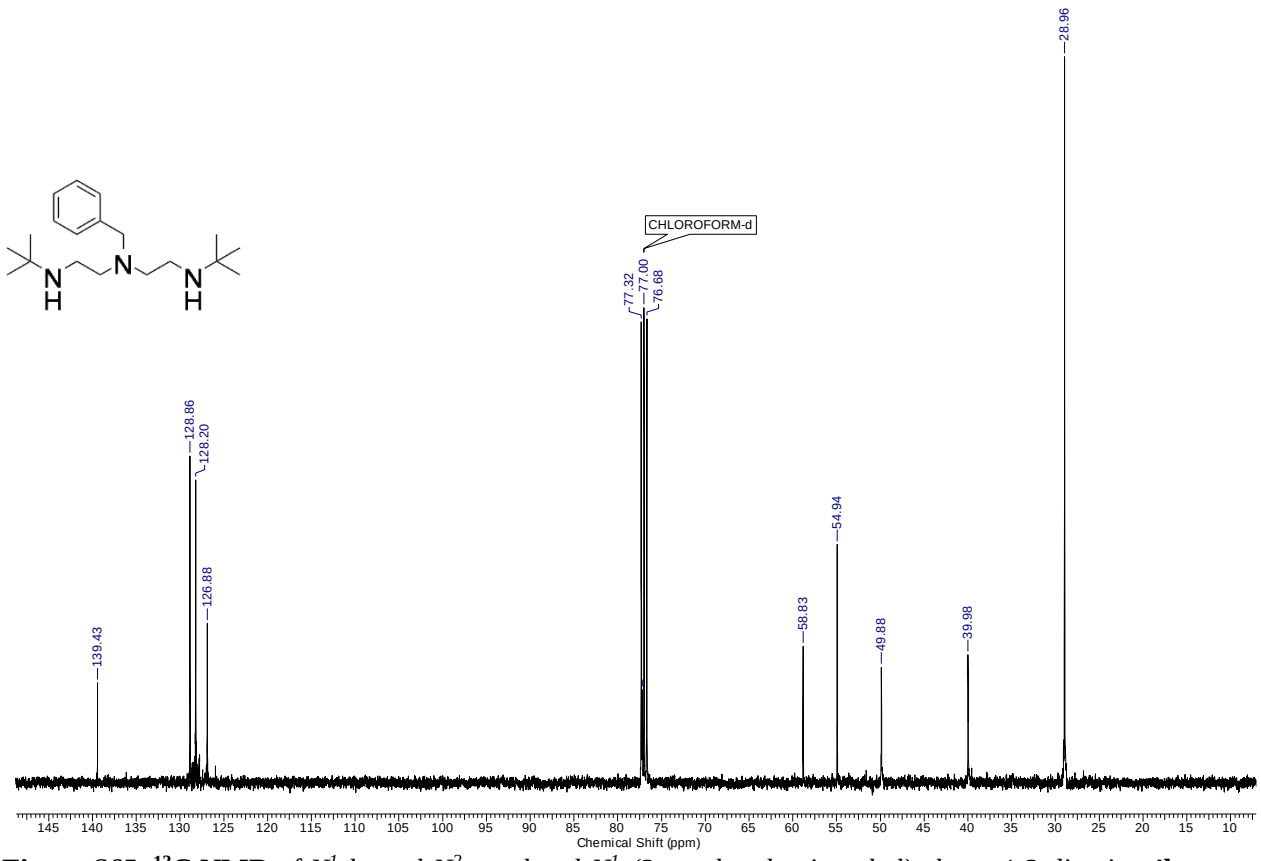


Figure S65. **^{13}C NMR** of *N*^{1}*-benzyl-N*^{2}*-tert-butyl-N*^{1}*-(2-tert-butylaminoethyl)ethane-1,2-diamine* **4bc**

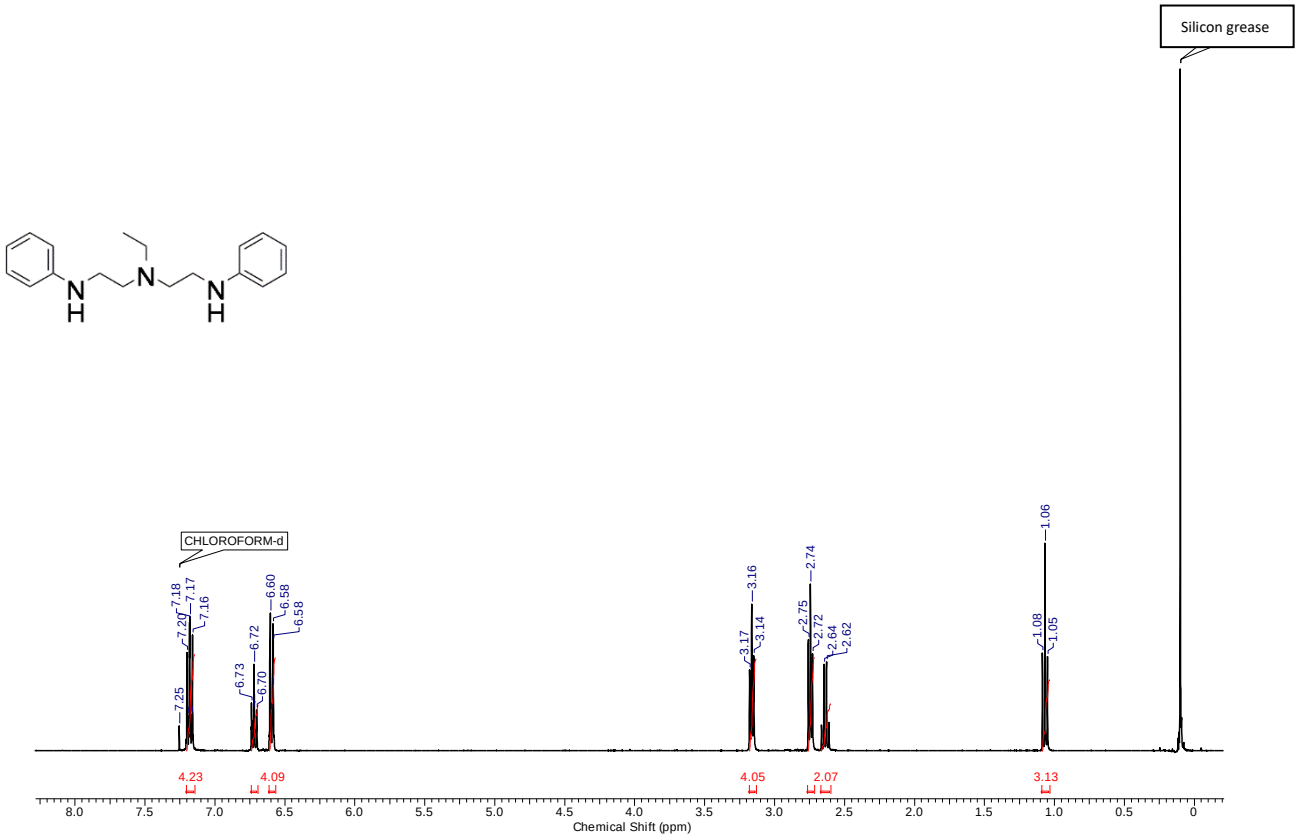


Figure S66 **^{1}H NMR** spectrum of *N^{1}-ethyl-N^{2}-phenyl-N^{1}-(2-phenylaminoethyl)ethane-1,2-diamine* **4ad**

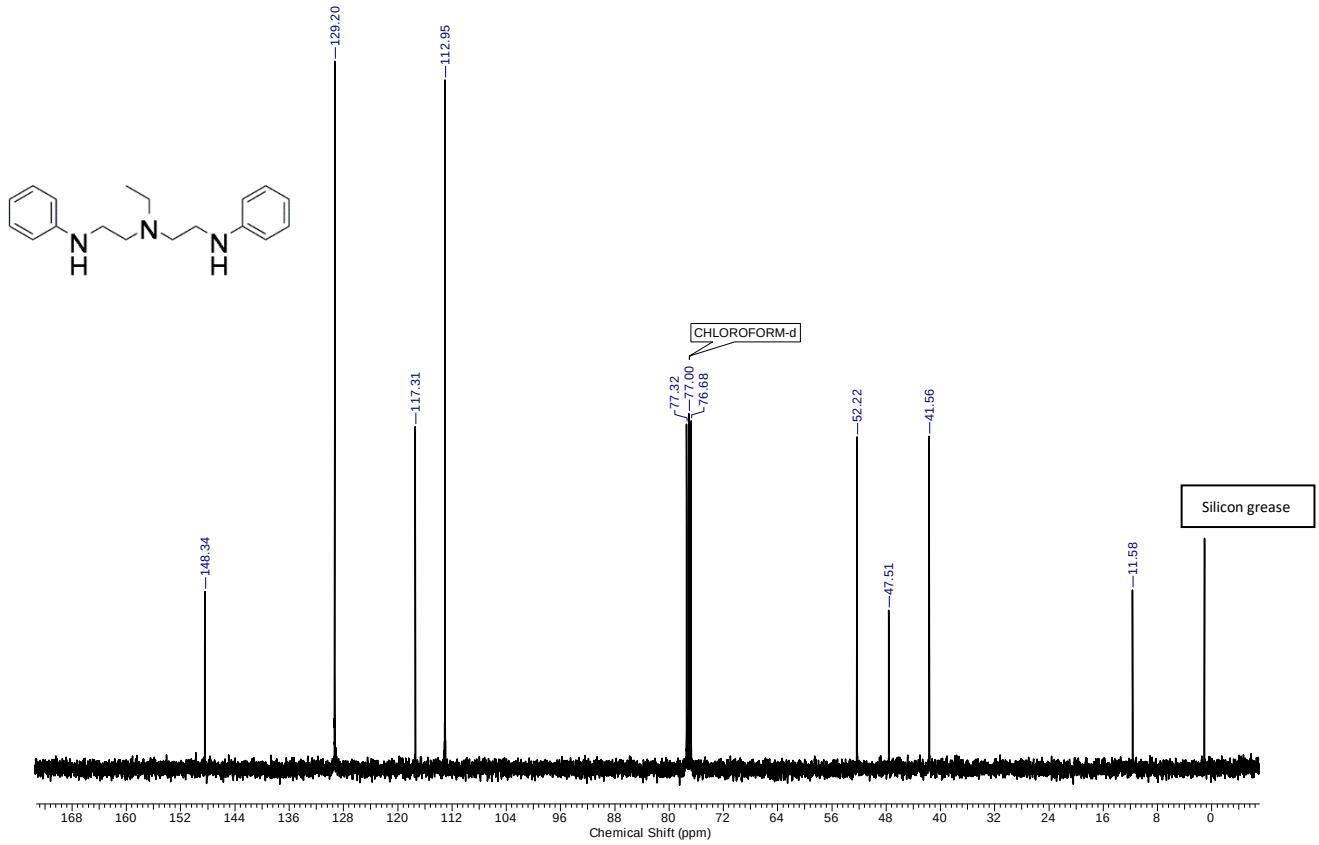


Figure S67. **^{13}C NMR** spectrum of *N^{1}-ethyl-N^{2}-phenyl-N^{1}-(2-phenylaminoethyl)ethane-1,2-diamine* **4ad**

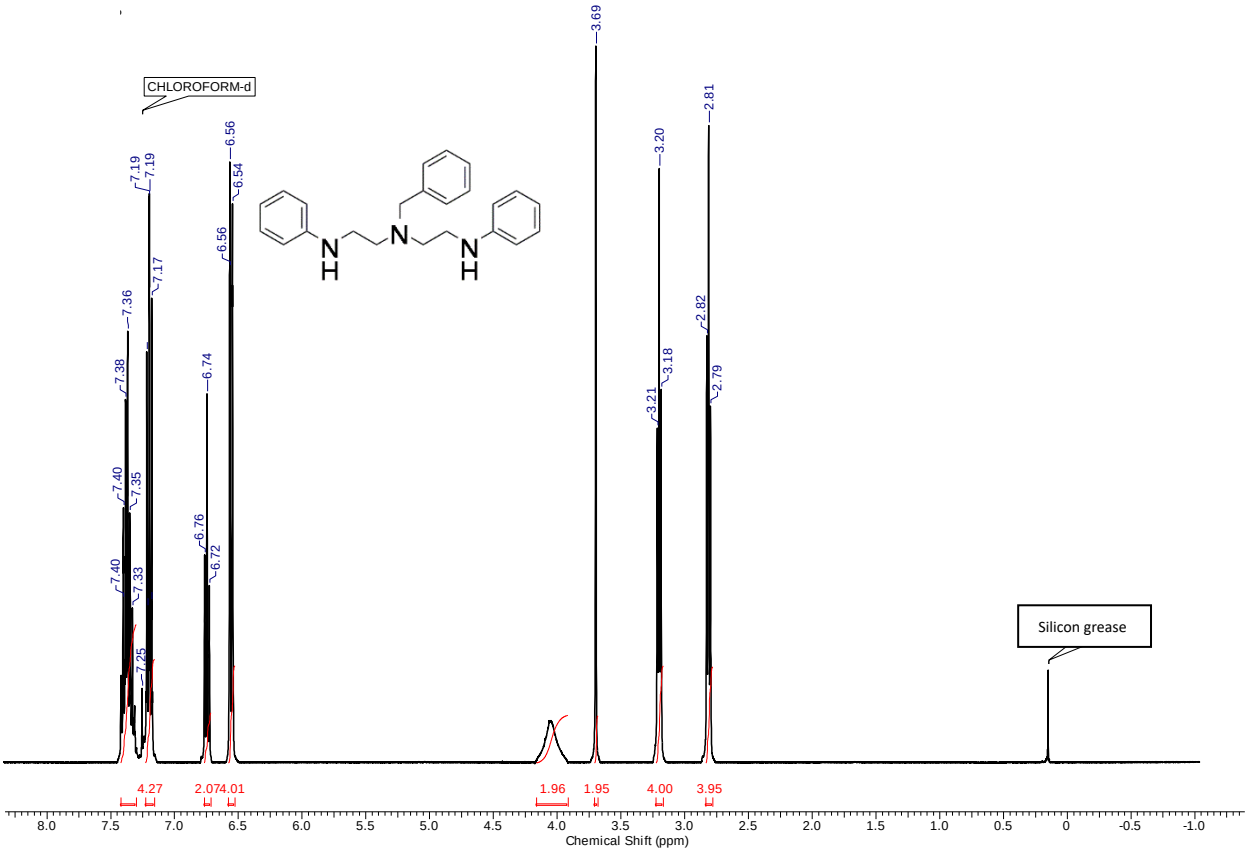


Figure S68 ^{1}H NMR spectrum of *N*^{1}*-benzyl-N*^{2}*-phenyl-N*^{1}*-(2-phenylaminoethyl)ethane-1,2-diamine* **4bd**

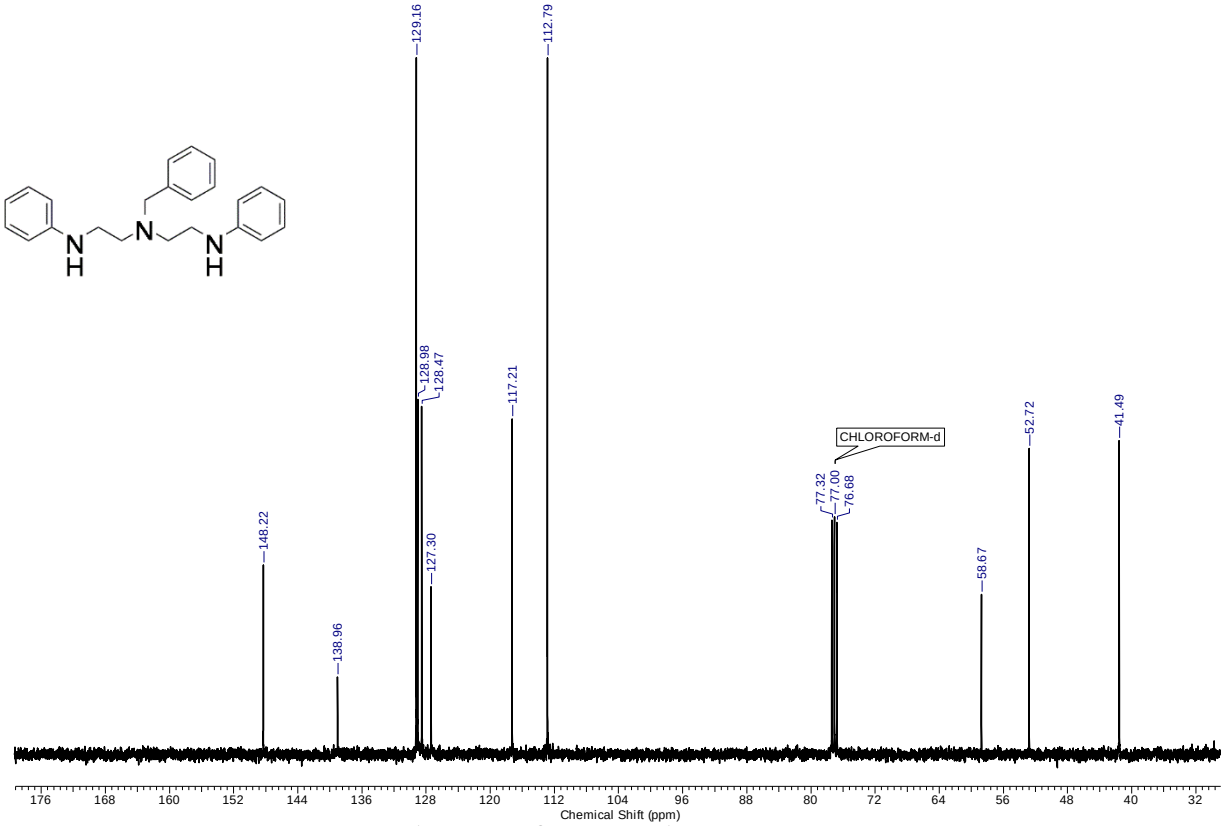


Figure S69. ^{13}C NMR spectrum of *N*^{1}*-benzyl-N*^{2}*-phenyl-N*^{1}*-(2-phenylaminoethyl)ethane-1,2-diamine* **4bd**

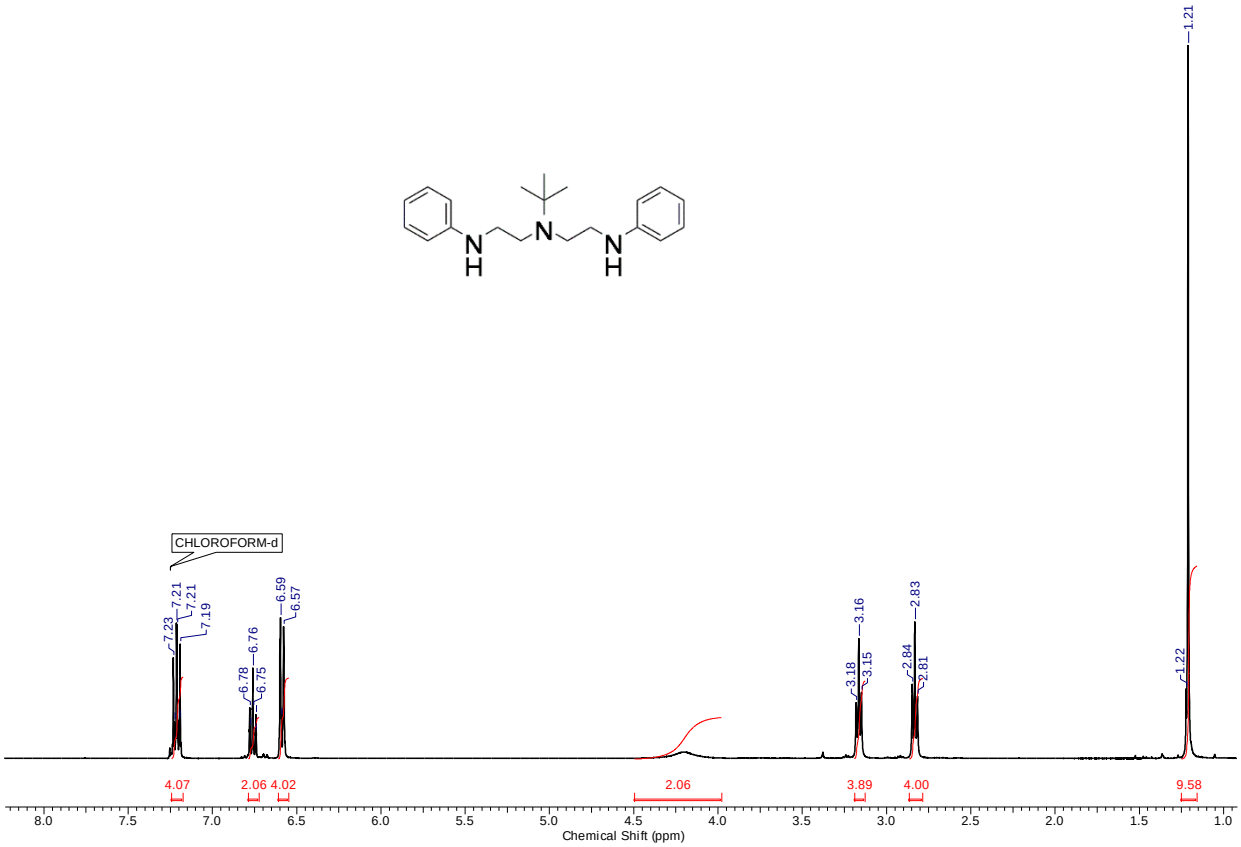


Figure S70. **^{1}H NMR** of *N^1-tert-butyl-N^2-phenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine* **4cd**

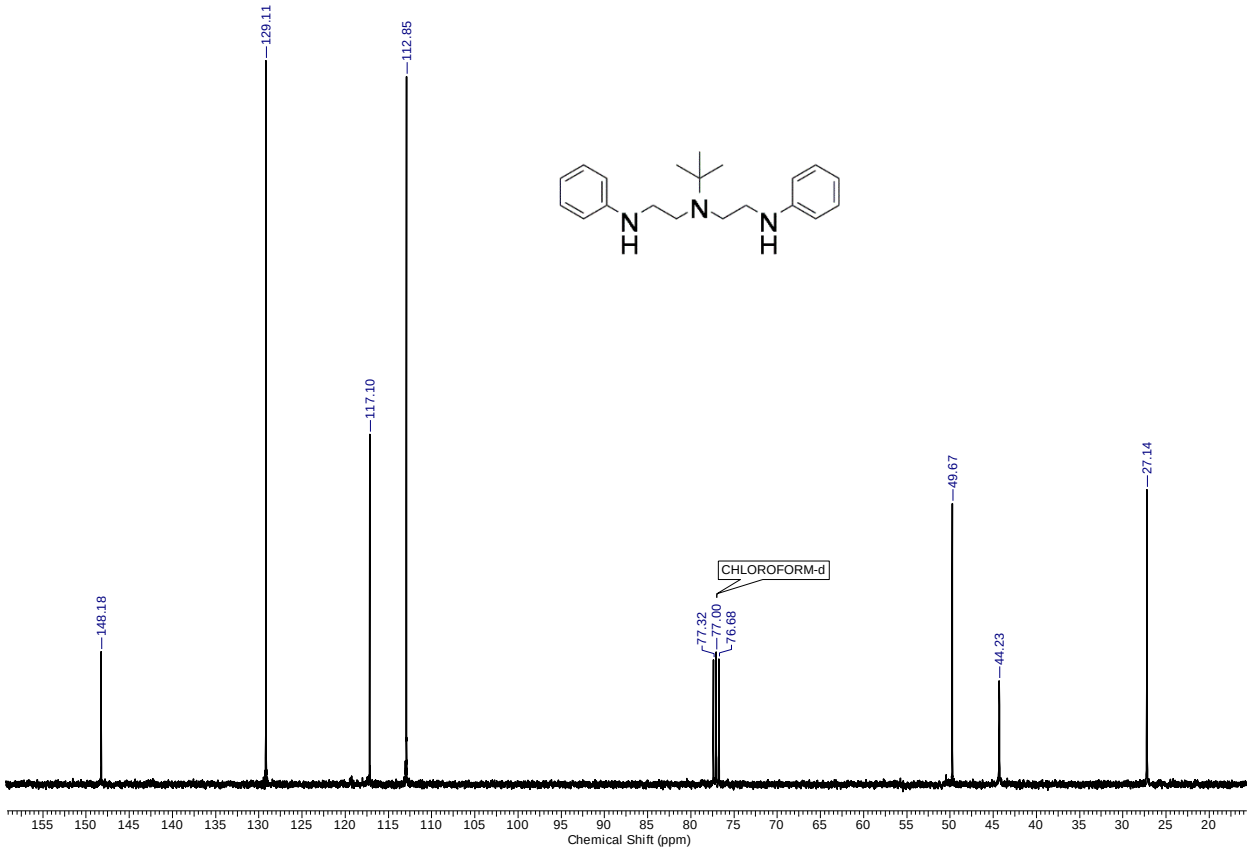


Figure S71. **^{13}C NMR** of *N^1-tert-butyl-N^2-phenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine* **4cd**

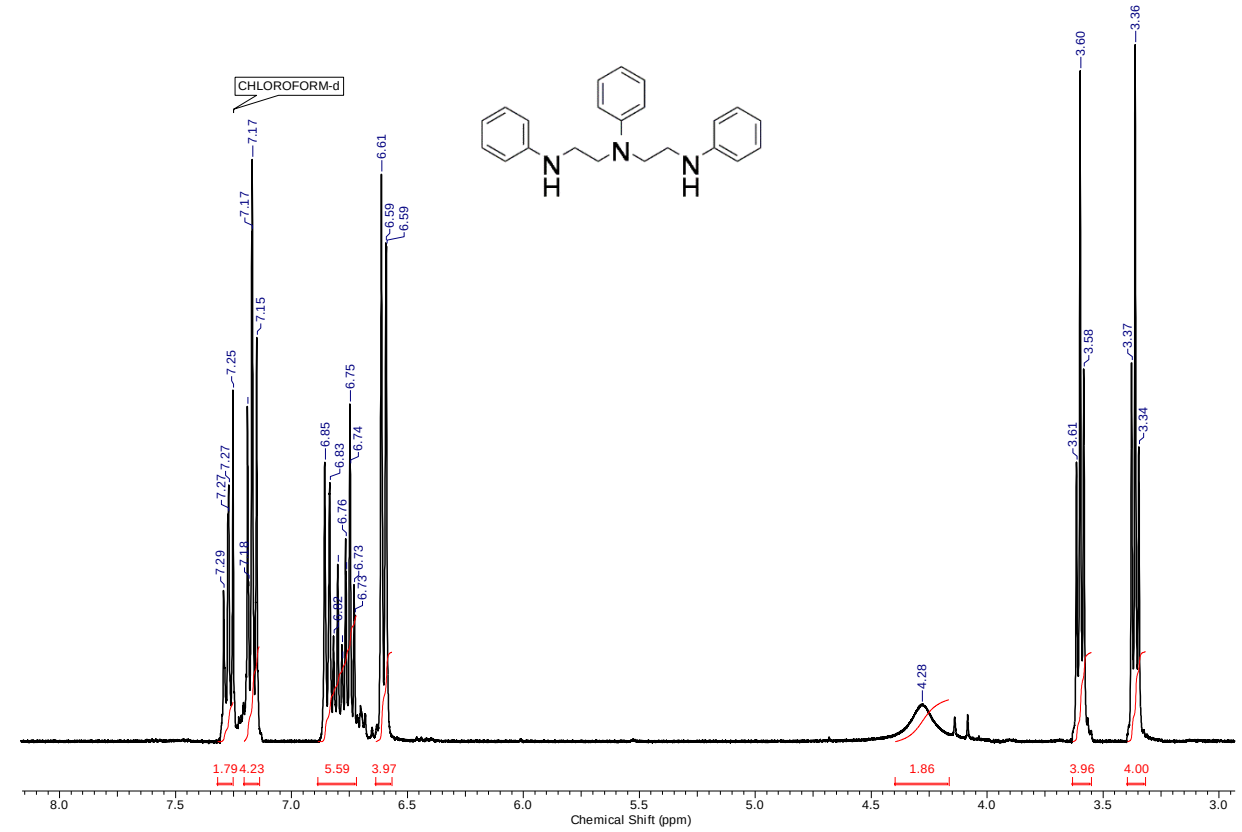


Figure S72. **^{1}H NMR** spectrum of *N^1,N^2-diphenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine* **4dd**

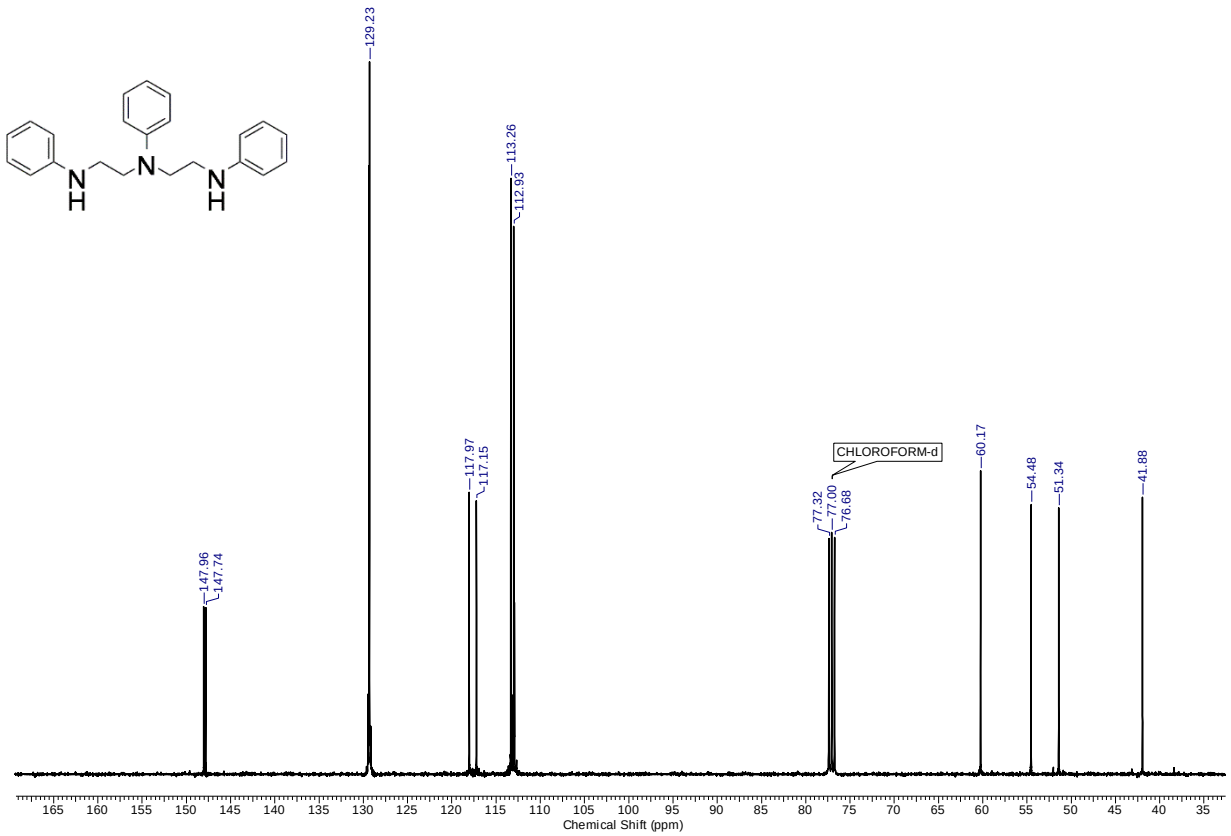


Figure S73. **^{13}C NMR** spectrum of *N^1,N^2-diphenyl-N^1-(2-phenylaminoethyl)ethane-1,2-diamine* **4dd**