# Supplementary Information
## A New Stepwise Synthesis of a Family of Propylamines Derived from Diatom Silaffins and their Activity in Silicification

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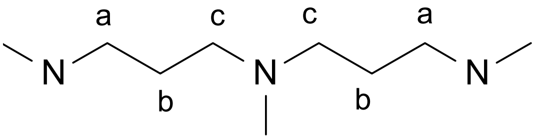
## Synthetic Procedures

### *N*-Methyl-N,N-bis[3-(methylamino)propyl]amine [tri(1-methylazetane)], N3

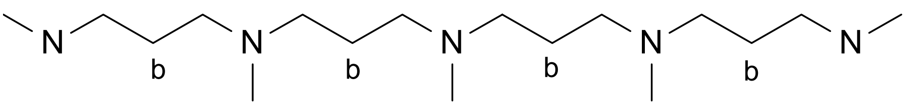


Methylamine (33%) in ethanol (94 g, 1 mole) was diluted with ethanol (40 mL) and methyl acrylate (172 g, 2 mole) diluted with ethanol (145 mL) was added to the methylamine solution in portions (~50 mL) at 20-40 °C. The mixture was left at room temperature for 5-7 days and the progress of the reaction monitored by FTIR spectroscopy. When the reaction was complete (disappearance of NH band (3300 $cm^{-1}$, thin film method)), ethanol was distilled off under reduced pressure and the residue distilled under vacuum (90 °C, 0.2 mm Hg) to give di-β-carbethoxyethylmethylamine (191g, 94%) as a colourless liquid.

Di-β-carbethoxyethylmethylamine (180g, 0.89 mole) was added to methylamine in ethanol (33%), (250 g, 2.66 mole) and the mixture left at room temperature for 3-5 days. The progress of the reaction was monitored by FTIR as before. When the reaction was complete, (disappearance of the ester C=O band (1740 $cm^{-1}$, thin film method)), ethanol was distilled off under reduced pressure and the residue dried under vacuum (70 °C, 0.2 mm Hg, 2 h) to give *N*-methyl-3-methyl[3-(methylamino)-3-oxopropyl]aminopropanamide (178g, 99%) as a viscous colourless liquid.

$LiAlH_4$ (16g, 0.42 mole) was suspended in anhydrous diethyl ether (550 mL) at room temperature. *N*-Methyl-3-methyl[3-(methylamino)-3-oxopropyl]aminopropanamide (20.1 g, 0.1 mole) was added to the suspension of $LiAlH_4$ portionwise during 6 h. The mixture was stirred for 12 h, cooled (–5 °C) and decomposed at 0-10 °C by the sequential addition of water (30 mL), a solution of KOH (22.5 g) in water (22.5 mL) followed by water alone (70 mL). The ether fraction was separated and the precipitate washed with diethyl ether (2 x 100 mL). Ether was distilled off and the residue distilled under vacuum (65 °C, 0.2 mm Hg) to give **N3** (8.5 g, 49%) as a colourless liquid. FTIR (film, $cm^{-1}$): 3292-3296, 2939-2945, 2788, 2839, 1450-1465, 1373, 1315, 1150, 1122, 1068, 733-740. $^1H$ NMR, (5% in $CDCl_3$): 1.63ppm ($5^t$, 4H, $2xCH_2$ (b)), 2.15 ($1^t$, 3H (NMe)), 2.35 ($3^t$, 4H, $2xCH_2$ (c)), 2.40 ($1^t$, 6H, $NHCH_3$), 2.58 ($3^t$, 4H, (a)). ESI-MS +ve ion. 174.3 ($[M+H]^+$).

### *N*-Methyl-*N*-[3-(methylamino)propyl]-*N*-3-[methyl(3-methyl[3-(methylamino) propyl]aminopropyl) amino]propylamine [penta(1-methylazetane)], N5

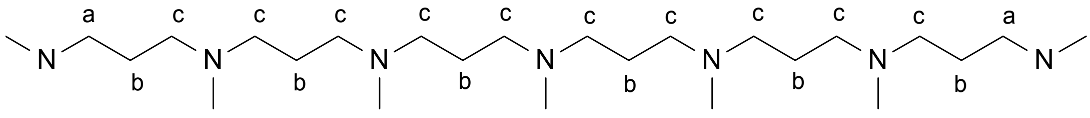


**N3** (12 g, 0.069 mole) was dissolved in ethanol (70 mL) and methyl acrylate (13.8 g, 0.16 mole). The mixture was boiled for 5-8 h, and the progress of the reaction monitored by FTIR spectroscopy. On completion of the reaction (disappearance of NH band (3300 cm$^{-1}$, thin film method)), ethanol was distilled off under reduced pressure and the residue dried under vacuum (70 $^{o}$C, 0.2 mm Hg, 2 h) to give methyl 6,10,14-trimethyl-3-oxo-2-oxa-6,10,14-triazaheptadecan-17-oate (24 g) as a colourless liquid in a near quantitative yield.

6,10,14-Trimethyl-3-oxo-2-oxa-6,10,14-triazaheptadecan-17-oate (24 g, 0.069 mole) in ethanol (12 mL) was added to methylamine in ethanol (33%) (50 g, 0.53 mole) and the mixture left at room temperature for 3-5 days. The progress of the reaction was monitored using FTIR spectroscopy. On completion of the reaction (disappearance of the ester C=O band (1740 cm$^{-1}$, thin film method)), ethanol was distilled off under reduced pressure and the residue dried under vacuum (70 $^{o}$C, 0.2 mm Hg, 2 h) to give *N*-6,10,14-tetramethyl-3-oxo-2,6,10,14-tetraazaheptadecan-17-amide (23.8 g) as a colourless liquid in near quantitative yield.

LiAlH$_4$ (7 g, 0.184 mole) was suspended in anhydrous diethyl ether (400 mL) at room temperature. *N*-6,10,14-Tetramethyl-3-oxo-2,6,10,14-tetraazaheptadecan-17-amide (23.8 g, 0.07 mole) portionwise over 6 h. The mixture was stirred for 12 h, cooled down to –5 $^{o}$C and decomposed at 0-10 $^{o}$C by the sequential addition of water (13 mL), a solution of KOH (15 g) in water (15 mL) followed by water (30 mL). The ether fraction was separated and the precipitate washed with diethyl ether (2 x 75 mL). Ether was distilled off and the residue was distilled under vacuum (142 $^{o}$C, 0.2 mm Hg) to give **N5** (12 g (55%) as a colourless liquid. FTIR (film, cm$^{-1}$): 3292-3296, 2939-2945, 2788, 2839, 1450-1465, 1373, 1315, 1150, 1122, 1068, 733-740. $^1$H NMR, 5% in CDCl$_3$. 1.62ppm (m$^t$, 8H (b)), 2.14 (1$^t$, 9H (NMe)), 2.28-2.35 (m$^t$, 12H (c)), 2.40 (1$^t$, 6H (NHMe)), 2.58 (m$^t$, 4H (a)). ESI-MS +ve ion. 316.4 ([M+H]$^+$), 245.4 ([M+H]$^+$ - C$_3$H$_5$NHMe), 174.3 ([M+H]$^+$ - C$_3$H$_5$N(Me)C$_3$H$_6$NHMe).

### *N*$^1$,*N*$^{23}$,4,8,12,16,20-heptamethyl-4,8,12,16,20-pentaazatricosane-1,23-diamine [hepta(1-methylazetane)], N7



**N5** (8 g, 0.025 mole) was dissolved in ethanol (50 mL) and methyl acrylate (7 g, 0.08 mole). The mixture was boiled for 5-8 h and the progress of the reaction monitored using FTIR spectroscopy. On completion of the reaction (disappearance of the NH band (3300 cm$^{-1}$, thin film method), ethanol was distilled off under reduced pressure and the residue dried under vacuum (70 $^{o}$C, 0.2 mm Hg, 2 h) to give dimethyl 4,8,12,16,20-pentamethyl-4,8,12,16,20-pentaazatricosane-1,23-dioate (12.1 g, ~100 %) as a colourless liquid.

4,8,12,16,20-Pentamethyl-4,8,12,16,20-pentaazatricosane-1,23-dioate (12.1 g, 0.025 mole) in ethanol (10 mL) was added to methylamine in ethanol (33%) (15g, 0.16 mole) and the mixture left at room temperature for 3-5 days. The progress of the reaction was monitored using FTIR spectroscopy. On completion of the reaction (disappearance of ester C=O band (1740 cm$^{-1}$, thin film method)), ethanol was distilled off under reduced pressure and the residue dried under vacuum (70 $^{o}$C, 0.2 mm Hg, 2 h) to give *N*$^1$,*N*$^{23}$,4,8,12,16,20-heptamethyl-4,8,12,16,20-pentaazatricosane-1,23-diamide (12 g) as a colourless liquid in near quantitative yield.

$LiAlH_4$ (2.5 g, 0.066 mole) was suspended in anhydrous diethyl ether (200 mL) at room temperature. *N*$^1$,*N*$^{23}$,4,8,12,16,20-Heptamethyl-4,8,12,16,20-pentaazatricosane-1,23-diamide (12g, 0.025 mole) was added to the suspension of $LiAlH_4$ in small portions (0.1-0.3 g) during 6 h. The mixture was stirred for 12 h, cooled down to –5 °C and decomposed at 0-10 °C by the sequential addition of water (4.6 mL), a solution of KOH (5.5 g) in water (5.5 mL) followed by water alone (11 mL) The ether fraction was separated and the precipitate washed with diethyl ether (2 x 50 mL). Ether was distilled off and the residue distilled under vacuum (185 °C, 0.2 mm Hg) to give **N7** (7.9 g, 69%) as a colourless liquid. FTIR (film, cm$^{-1}$): 3292-3296, 2939-2945, 2788, 2839, 1450-1465, 1373, 1315, 1150, 1122, 1068, 733-740. $^1$H NMR, 5% in $CDCl_3$. 1.65ppm (m$^t$, 12H (b)), 2.20 (1$^t$, 15H (NMe)), 2.30-2.40 (m$^t$, 20H (c)), 2.42 (1$^t$, 6H (NHMe)), 2.62 (3$^t$, 4H (a)). ESI-MS +ve ion. 458.5 ($[M+H]^+$), 387.5 ($[M+H]^+$ - $C_3H_5NHMe$), 316.3 ($[M+H]^+$ - $C_3H_5NMeC_3H_6NHMe$).

**SEM Silica prepared in the presence of N7 at a 1Si:1N ratio.**