SUPPORTING INFORMATION

Encapsulated Reagents for Nitrosation

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General. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 at 295 ± 1 $^\circ\text{C}$ on JEOL Eclipse 500 MHz spectrometer. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. UVvis spectra were measured on a JASCO V-530 spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. All experiments with moisture- and/or air-sensitive compounds were run in freshly distilled over P_2O_5 chloroform, under a dried nitrogen atmosphere. Parent tetrahydroxycalix[4]arene and calixarene **2** were prepared according to the published procedures.^{1,2} $\text{NO}_2/\text{N}_2\text{O}_4$ was generated from copper and conc. HNO_3 .

Caution 1: NO_2 has an irritating odor and is very toxic!

Caution 2: *N*-Nitrosoamides are carcinogens³ and should be treated with extreme care!

Preparation of Nitrosonium Complex (1): *Procedure 1.* NO₂/N₂O₄ gas was bubbled for 20 sec through the solution of calixarene **2** (25 mg, 2.5 x 10⁻⁵ mol) and SnCl₄ (3 mL, 2.6 x 10⁻⁵ mol) in dry CHCl₃ (0.5-1.0 mL). The solvent was evaporated under the steam of dry nitrogen. The dark-blue precipitate was dissolved in dry CHCl₃ (0.5-1.0 mL) and used for further reactions. *Procedure 2.* Stock solution of NO₂ (~3 eq) in CHCl₃ was added to the solution of **2** (1 eq) and SnCl₄ (1.5 eq) in CHCl₃ at rt. After 1 h, complex **1** was precipitated upon addition of hexanes, filtered off, washed with hexanes (2 x), and dried in vacuo. Yield >95%; ¹H NMR δ 7.02 (s, 8 H), 3.77 (t, *J* = 7.5 Hz, 8 H), 3.60 (s, 8 H), 1.38 (m, 32 H), 1.30 (s, 36 H), 0.92 (t, *J* = 7.5 Hz, 12 H); UVvis (CDCl₃) λ_{max} = 578 nm; FTIR (CDCl₃) ν (NO⁺) = 1934 cm⁻¹. Anal. Calcd for C₆₈H₁₀₄Cl₄N₂O₈Sn: C, 61.04; H, 7.83; N, 2.09. Found: C, 60.96; H, 7.88; N, 2.09. Calixarene **2**: ¹H NMR δ 6.95 (s, 8 H, Ar), 3.73 (s, 8 H, ArCH₂Ar), 3.38 (t, 8 H, *J* = 7.5 Hz, O-CH₂), 1.28 (s, 36 H, C(CH₃)₃), 1.26-1.12 (m, 32 H, OCH₂), 0.86 (t, 12 H, *J* = 7.5 Hz, CH₃).

Preparation of Amides (3a-q). Amides **3a-q** were synthesized by the textbook procedure upon mixing equimolar amounts of the corresponding amines and acid chlorides in H₂O-EtOAc, 1:1 in the presence of K₂CO₃, and purified by recrystallization from MeOH.⁴ No traces of the solvent were present in samples used for nitrosation (¹H NMR, CDCl₃). The corresponding ¹H NMR spectra are attached below.

N-Methylpropanoylamide (3a): Yield 50 %; ¹H NMR δ 6.12 (bs, 1 H, NH), 2.77 (bs, 3 H, NCH₃), 2.24-2.28 (q, 2 H, *J* = 8 Hz, CH₂), 1.11 (t, 3 H, *J* = 8 Hz, CH₃).

N-Methylbutyrylamide (3b): Yield 54 %; ¹H NMR δ 5.74 (bs, 1 H, NH), 2.77 (d, 3 H, *J* = 5 Hz, NCH₃), 2.12 (t, 2 H, *J* = 7.5 Hz, CH₂), 1.59-1.66 (m, 2 H, CH₂), 0.91 (t, 3 H, *J* = 7.5 Hz, CH₃).

N-Methylvalerylamide (3c): Yield 62 %; ^1H NMR δ 6.43 (bs, 1 H, NH), 2.69 (d, 3 H, $J = 5$ Hz, NCH_3), 2.09 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.48-1.54 (m, 2 H, CH_2), 1.22-1.28 (m, 2 H, CH_2), 0.81 (t, 3 H, $J = 7.5$ Hz, CH_3).

N-Methylhexanoylamide (3d): Yield 36 %; ^1H NMR δ 6.24 (bs, 1 H, NH), 2.71 (d, 3 H, $J = 5$ Hz, NCH_3), 2.10 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.51-1.58 (m, 2 H, CH_2), 1.22-1.28 (m, 4 H, 2 x CH_2), 0.81 (t, 3 H, $J = 7.5$ Hz, CH_3).

N-Methyloctanoylamide (3e): Yield 66 %; ^1H NMR δ 6.13 (bs, 1 H, NH), 2.73 (d, 3 H, $J = 5$ Hz, NCH_3), 2.12 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.53-1.58 (m, 2 H, CH_2), 1.22-1.28 (m, 8 H, 4 x CH_2), 0.83 (t, 3 H, $J = 7.5$ Hz, CH_3).

N-Methylpivaloylamide (3f): Yield 65 %; ^1H NMR δ 5.69 (bs, 1 H, NH), 2.78 (d, 3 H, $J = 5$ Hz, NCH_3), 1.15 (s, 9 H, CH_3).

N-Ethylpropanoylamide (3g): Yield 60 %; ^1H NMR δ 5.56 (bs, 1 H, NH), 3.29-3.24 (m, 2 H, CH_2), 2.17 (q, 2 H, $J = 7.5$ Hz, CH_2), 1.16 (t, 3 H, $J = 7.5$ Hz, CH_3), 1.13 (t, 3 H, $J = 7.5$ Hz, CH_3).

N-Ethylbutyrylamide (3h): Yield 44 %; ^1H NMR δ 5.52 (bs, 1 H, NH), 3.22-3.16 (m, 2 H, CH_2), 2.07 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.53-1.60 (m, 2 H, CH_2), 1.06 (t, 3 H, $J = 7.5$ Hz, CH_3), 0.86 (t, 3 H, $J = 7.5$ Hz, CH_3).

N-Ethylvalerylamide (3i): Yield 70 %; ^1H NMR δ 5.96 (bs, 1 H, NH), 3.21 (m, 2 H, CH_2), 2.10 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.53, 1.28 (2 x m, 4 H, CH_2), 1.07 (t, 3 H, $J = 7.5$ Hz, CH_3), 0.85 (t, 3 H, $J = 7.5$ Hz, CH_3).

***N*-Ethylhexanoylamide (3j):** Yield 64 %; ^1H NMR δ 5.95 (bs, 1 H, NH), 3.14 (m, 2 H, CH₂), 2.11 (t, 2 H, $J = 7.5$ Hz, CH₂), 1.56, 1.45, 1.24 (3 x m, 6 H, CH₂), 0.87, 0.84 (2 x t, 6 H, $J = 7.5$ Hz, CH₃).

***N*-propylpropanoylamide (3k):** Yield 66 %; ^1H NMR δ 5.85 (bs, 1H, NH), 3.13-3.17 (q, 2 H, $J = 8$ Hz, CH₂), 2.13-2.17 (q, 2 H, $J = 8$ Hz, NCH₃), 1.43-1.51 (m, 2 H, CH₂), 1.10 (t, 3 H, $J = 8$ Hz, CH₃), 0.86 (t, 3 H, $J = 8$ Hz, CH₃).

***N*-propylbutirylamide (3l):** Yield 50 %; ^1H NMR δ 5.52 (bs, 1 H, NH), 3.17-3.21 (q, 2 H, $J = 7.5$ Hz, CH₂), 2.14 (t, 2 H, $J = 7.5$ Hz, NCH₃), 1.61-1.68 (m, 2 H, CH₂), 1.46-1.55 (m, 2 H, CH₂), 0.95 (t, 3 H, $J = 7.5$ Hz, CH₃), 0.92 (t, 3 H, $J = 7.5$ Hz, CH₃).

***N*-propylvalerylamide (3m):** Yield 51 %; ^1H NMR δ 5.64 (bs, 1 H, NH), 3.17 (q, 2 H, $J = 7.5$ Hz, CH₂), 2.14 (t, 2 H, $J = 7.5$ Hz, NCH₃), 1.58, 1.49, 1.32 (3 x m, 6 H, CH₂), 0.91, 0.87 (2 x t, 6 H, $J = 7.5$ Hz, CH₃).

***N*-propylhexanoylamide (3n):** Yield 53 %; ^1H NMR δ 6.04 (bs, 1 H, NH), 3.14 (q, 2 H, $J = 7.5$ Hz, CH₂), 2.10 (t, 2 H, $J = 7.5$ Hz, NCH₃), 1.56, 1.45, 1.24 (3 x m, 10 H, CH₂), 0.86, 0.81 (2 x t, 6 H, $J = 7.5$ Hz, CH₃).

***N*-*i*-Propylvalerylamide (3o):** Yield 20 %; ^1H NMR (CDCl₃) δ 5.46 (bs, 1 H, NH), 3.98-4.09 (m, 1 H, CH), 2.09 (t, 2 H, $J = 7$ Hz, CH₂), 1.53-1.59 (m, 2 H, CH₂), 1.26-1.34 (m, 2 H, CH₂), 1.10 (d, 6 H, $J = 7$ Hz, CH₃), 0.87 (t, 3 H, $J = 7.5$ Hz, CH₃).

***N*-*t*-Butylpivaloylamide (3p):** Yield 45 %; ^1H NMR δ 5.39 (bs, 1 H, NH), 1.36, 1.14 (2 x s, 18 H, CH₃).

***N*-Benzylbutyrylamide (3q):** Yield 67 %; ^1H NMR δ 7.32-7.28 (m, 3 H, C_6H_5), 7.26-7.24 (m, 2 H, C_6H_5), 5.89 (bs, 1 H, NH), 4.41 (d, 2 H, $J = 6$ Hz, NCH_2), 2.17 (t, 2 H, $J = 7.5$ Hz, CH_2), 1.62-1.70 (m, 2 H, CH_2), 0.93 (t, 3 H, $J = 7.5$ Hz, CH_3).

Nitrosation Procedure with Encapsulated Reagent (1). Calixarene-nitrosonium complex **1** (1 eq) was added to the solution of amide **3a-q** (1-3 eq) in freshly distilled CHCl_3 , and the reaction mixture was stirred at rt for 5 h. The solvent was evaporated, and the residue was analyzed by ^1H NMR spectroscopy and in some cases separated by preparative TLC, resulting in *N*-nitrosoamides as orange oils. All runs were performed at least in duplicate. The spectral data for the obtained *N*-nitroso compounds **4a-e** were identical with those independently obtained from **3a-e** and $\text{NO}_2/\text{N}_2\text{O}_4$ in CHCl_3 (>95% yields) following the literature protocols.⁵⁻⁷ The corresponding ^1H NMR spectra are attached below. *N*-nitrosoamides **4f-q** cannot be obtained from **3f-q** and complex **1**. These were prepared, for spectral comparison, employing $\text{NO}_2/\text{N}_2\text{O}_4$ in CHCl_3 and used without further purification.

***N*-methyl-*N*-nitrosopropylamide (4a):**^{8,9,11} Yield 50%; ^1H NMR δ 3.14 (q, 2 H, $J = 8$ Hz, $\text{CH}_2\text{C}(\text{O})$), 3.05 (s, 3 H, $\text{N}(\text{NO})\text{CH}_3$), 1.26 (t, 3 H, $J = 8$ Hz, CH_3).

***N*-methyl-*N*-nitrosobutyramide (4b):**^{10,11} Yield 68 %; ^1H NMR δ 3.09 (t, 2 H, $J = 8$ Hz, $\text{CH}_2\text{C}(\text{O})$), 3.05 (s, 3 H, $\text{N}(\text{NO})\text{CH}_3$), 1.76-1.81 (m, 2 H, CH_2), 0.97 (t, 3 H, $J = 8$ Hz, CH_3).

***N*-methyl-*N*-nitrosovaleramide (4c):**¹¹ Yield 53 %; ^1H NMR δ 3.17 (t, 2 H, $J = 8$ Hz, $\text{CH}_2\text{C}(\text{O})$), 3.10 (s, 3 H, $\text{N}(\text{NO})\text{CH}_3$), 1.75-1.81 (m, 2 H, CH_2), 1.40-1.47 (m, 2 H, CH_2), 0.95 (t, 3 H, $J = 8$ Hz, CH_3).

***N*-methyl-*N*-nitrosohexanoylamide (4d):**^{11,12} Yield 95%; ¹H NMR δ 3.13 (t, 2 H, *J* = 8 Hz, CH₂C(O)), 3.08 (s, 3 H, N(NO)CH₃), 1.75-1.81 (m, 2 H, CH₂), 1.32-1.36 (m, 4 H, 2 x CH₂), 0.88 (t, 3 H, *J* = 8 Hz, CH₃).

***N*-methyl-*N*-nitrosooctanoylamide (4e):**^{11,12} Yield 63 %; ¹H NMR δ 3.19 (t, 2 H, *J* = 7.5 Hz, CH₂C(O)), 3.12 (s, 3 H, N(NO)CH₃), 1.72-1.81 (m, 2 H, CH₂), 1.26-1.41 (m, 8 H, (CH₂)₄), 0.86 (t, 3 H, *J* = 7.5 Hz, CH₃).

***N*-Ethyl-*N*-nitrosopropionylamide (4g):**¹³ Yield 33 % (from NO₂/N₂O₄), 10% (from NO⁺SbF₆⁻); ¹H NMR δ 3.74-3.78 (q, 2 H, *J* = 7.5 Hz, N(NO)CH₂), 3.10-3.14 (q, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.26 (t, 3 H, *J* = 7.5 Hz, CH₃), 0.92 (t, 3 H, *J* = 7.5 Hz, CH₃).

***N*-Ethyl-*N*-nitrosobutyrylamide (4h):**¹⁴ Yield >95 % (from NO₂/N₂O₄); ¹H NMR δ 3.78-3.83 (q, 2 H, *J* = 7.5 Hz, N(NO)CH₂), 3.13-3.16 (t, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.79-1.85 (m, 2 H, CH₂), 1.03 (t, 3 H, *J* = 7.5 Hz, CH₃), 0.97 (t, 3 H, *J* = 7.5 Hz, CH₃); ¹³C NMR δ 178.4, 36.7, 34.1, 18.6, 13.8, 12.0.

***N*-Propyl-*N*-nitrosopropionylamide (4k):**¹⁵ Yield 48 % (from NO₂/N₂O₄); ¹H NMR δ 3.72 (t, 2 H, *J* = 7.5 Hz, N(NO)CH₂), 3.16 (q, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.53-1.60 (m, 2 H, CH₂), 1.20 (t, 3 H, *J* = 7.5 Hz, CH₃), 0.94 (t, 3 H, *J* = 7.5 Hz, CH₃); ¹³C NMR δ 178.9, 40.3, 28.5, 22.4, 20.4, 11.6.

***N*-Propyl-*N*-nitrosobutyrylamide (4l):** Yield 95 % (from NO₂/N₂O₄); ¹H NMR δ 3.72 (t, 2 H, *J* = 7.5 Hz, N(NO)CH₂), 3.14 (t, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.79-1.86 (m, 2 H, CH₂), 1.34-1.41 (m, 2 H, CH₂), 1.03 (t, 3 H, *J* = 7.5 Hz, CH₃) 0.81 (t, 3 H, *J* = 7.5 Hz, CH₃); ¹³C NMR δ 178.8, 40.1, 36.6, 20.4, 18.7, 13.6, 11.2.

***N*-Propyl-*N*-nitrosovalerylamine (4m):** Yield 95 % (from NO₂/N₂O₄); ¹H NMR δ 3.72 (t, 2 H, *J* = 7.5 Hz, N(NO)CH₂), 3.16 (t, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.74-1.79 (m,

2H, CH₂), 1.41-1.46 (m, 2 H, CH₂), 1.34-1.40 (m, 2 H, CH₂), 0.95 (t, 3 H, *J* = 7.5 Hz, CH₃) 0.81 (t, 3 H, *J* = 7.5 Hz, CH₃); ¹³C NMR δ 178.8, 40.3, 34.6, 27.2, 22.4, 20.3, 13.8, 11.4.

***N*-Benzyl-*N*-nitrosobutyrylamide (4q):** Yield 95 % (from NO₂/N₂O₄); ¹H NMR δ 7.24-7.27 (m, 3 H, C₆H₅), 7.16-7.17 (m, 2 H, C₆H₅), 4.92 (s, 2 H, CH₂ C₆H₅), 3.19 (t, 2 H, *J* = 7.5 Hz, CH₂C(O)), 1.80-1.87 (m, 2 H, CH₂), 1.02 (t, 3 H, *J* = 7.5 Hz, CH₃).

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