Supporting Information for:

DSA: A new internal standard for NMR studies in aqueous solution

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***N*-[3-(Trimethylsilyl)propyl]phthalimide.** *N*-[3-(Trimethylsilyl)propyl]phthalimide was prepared according to the procedure of Lukevics and Voronkov;[1] spectral data were consistent with those reported by Mariano et. al.[2] A 50-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a ground glass stopper, a thermometer, and an air condenser fitted with a nitrogen inlet was charged with phthalimide (2.34 g, 15.8 mmol), anhydrous K_2CO_3 (1.3 g, 9.4 mmol), (3-chloropropyl)trimethylsilane (3.1 mL, 2.7 g, 18 mmol), and 15 mL of anhydrous DMF. The mixture was heated at 142-149 °C for 8 h. The reaction mixture was then cooled to room temperature and concentrated by rotary evaporation, and the residue was partitioned between 20 mL of H_2O and 50 mL of EtOAc. The aqueous layer was extracted with 2×25 ml of EtOAc, and the combined organic layers were washed with 10 mL of H_2O, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford a yellowish solid. Column chromatography on silica gel (gradient elution, hexanes to 20% EtOAc-hexanes) afforded 3.75 g (91%) of *N*-[3-(trimethylsilyl)propyl]phthalimide as a white solid: mp 71-72.5 °C; IR (film from CH_2Cl_2) 1766, 1709 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$) δ 7.86-7.82 (m, 2 H), 7.73-7.69 (m, 2 H), 3.66 (t, J = 7.4 Hz, 2 H), 1.70-1.63 (m, 2 H), 0.55-0.51 (m, 2 H), -0.02 (s, 9 H); ^{13}C NMR(125.7 MHz,$CDCl_3$) δ 168.4, 133.7, 132.2, 123.1, 41.0, 23.2, 13.7, -1.8.

4,4-Dimethyl-4-silapentane-1-ammonium trifluoroacetate (DSA). A 100-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar was charged with *N*-[3-(trimethylsilyl)propyl]phthalimide (0.749 g, 2.87 mmol) and 27 mL of 2-propanol. The suspension was heated to form a homogenous solution, 4.5 mL of water was added, and the solution was cooled to room temperature. Sodium borohydride (0.720g, 18.6 mmol) was added over 1 min, the flask was equipped with a nitrogen inlet adapter, and the suspension was stirred vigorously for 24 hours.[3] Glacial acetic acid (5 mL) was added in drops by Pasteur pipet, slowly and carefully to avoid spattering during the vigorous gas evolution that occurred. The flask was equipped with a condenser fitted with a gas inlet adapter and the mixture was heated at reflux for 7 h. The reaction mixture was cooled to room temperature, 6 mL of 6 M aq HCl was added, and the solution was concentrated to ca. 25% of its original volume by rotary evaporation. An additional 6-mL portion of 6 M aq HCl was added, followed by H_2O to make ca. 75 mL. The mixture was vigorously washed with three 50-mL portions of 1:1 EtOAc-hexanes in a separatory funnel, shaking each time for 5 minutes. The aqueous layer was then washed with 10 mL of hexanes, cooled in an ice bath, basified with NaOH (pellets), and extracted with hexanes (100 mL followed by 2x50 mL). The combined organic layers were washed with 20 mL of H_2O and then shaken vigorously with 2 mL of trifluoroacetic acid for 5 min. The biphasic mixture of hexanes and TFA was then transferred to a round-bottomed flask and concentrated by rotary evaporation (<40 °C). Toluene (20 mL) was then added and the solution was concentrated by rotary evaporation to afford an oil. The oil was dissolved in 20 mL of water, and the water was then removed by lyophilization (freeze-drying) to give 0.638 g of a white solid. Recrystallization from toluene afforded 0.599 g (85%) of DSA as white shiny crystals: mp 116-118 °C; IR (film from CH_2Cl_2) 3076 (br), 1682, 1595 cm^{-1}; ^1H NMR (500 MHz, D_2O, referenced against HOD) δ 2.96 (t, J = 7.4 Hz, 2 H), 1.58-1.52 (m, 2 H), 0.55-0.52 (m, 2 H), 0.00 (s, 9 H); ^{13}C NMR (125.71 MHz, D_2O, referenced against the Me_3Si resonance) δ 165.7 (q, J = 36 Hz), 119.2 (q, J = 292 Hz), 45.2, 24.5, 15.2, 0.0. Anal. Calcd for $C_8H_{18}F_3NO_2Si$: C, 39.17; H, 7.40; N, 5.71. Found: C, 39.33; H, 7.47; N, 5.71.

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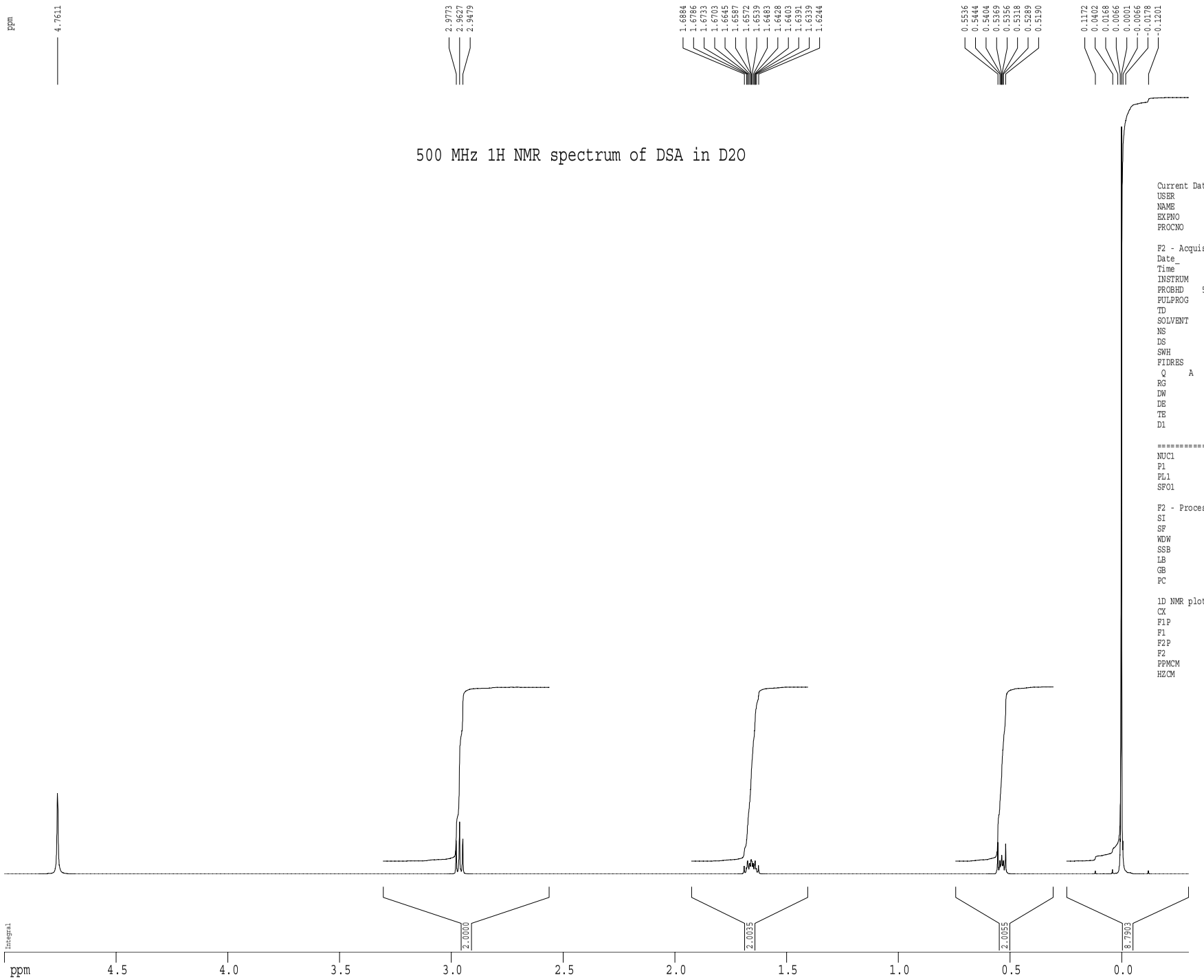
[1] Lukevics, E.; Voronkov, M. G. *Zh. Obshch. Khim.* **1968**, *38*, 2322-2324; *Chem. Abstr.* **1969**, *70*, 28982.
[2] Lee, Y. J.; Ling, R.; Mariano, P. S. *J. Org. Chem.* **1996**, *61*, 3304-3314.
[3] Osby, J. O.; Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, *25*, 2093-2096.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