

# Primary Amine Confinement at the Interface of Grafted Calixarenes and Silica

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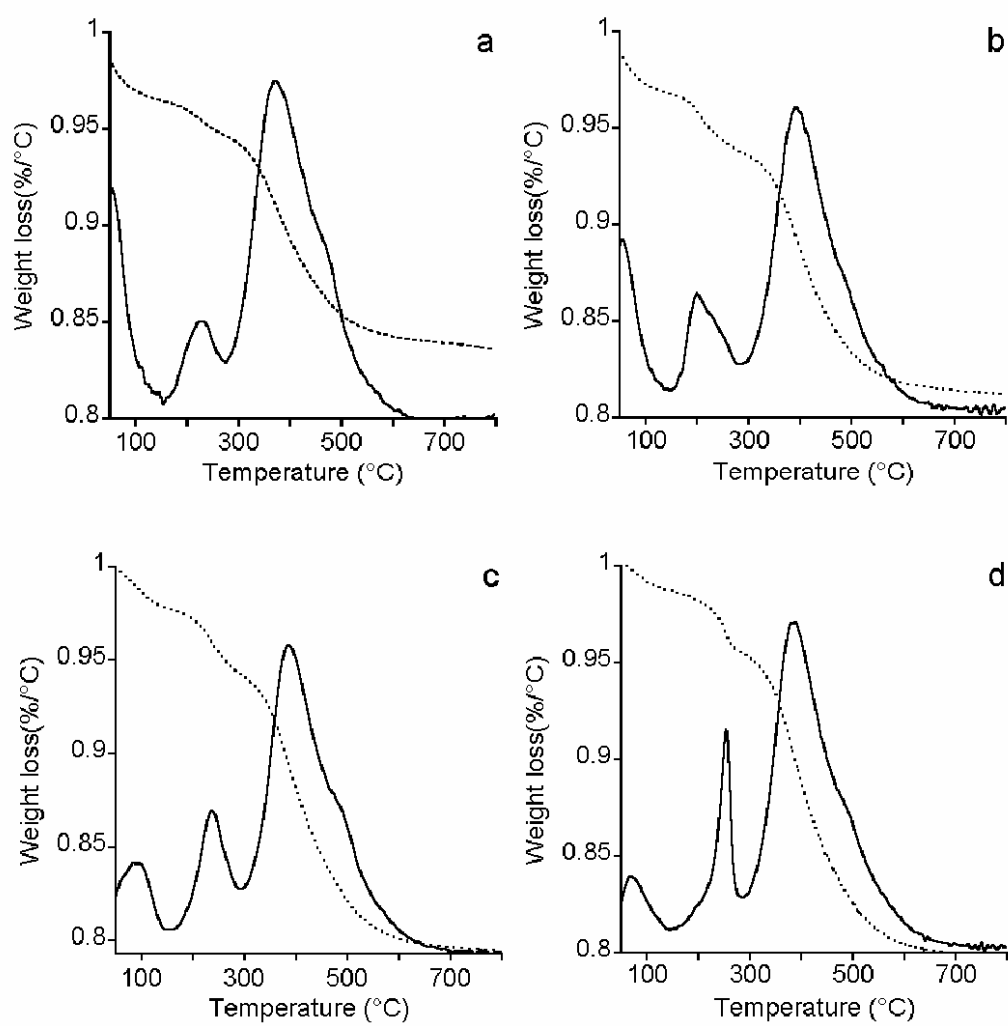
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**Figure S1.** TGA of sample **4a** (a) **4b** (b) **4c** (c) and **4d** (d) showing weight-loss upon combustion.

## General Experimental

Chemical reagents were purchased at reagent grade quality and were used without further purification unless otherwise noted. Dichloromethane was distilled over  $\text{CaH}_2$ , and benzene and toluene were distilled over sodium wire, and stored over molecular sieves in a Schlenk tube. *N*-*t*-Boc protected aminoalcohols were prepared according to established literature procedures, and calixarene **7c** was synthesized as described previously.<sup>S1</sup> Silica gel chromatography was performed using Selecto 60 silica gel (0.32-0.64 mm particle size). Reactions were monitored via TLC on Selecto silica gel coated plates. FAB mass spectra were recorded using either NBA (*m*-nitrobenzyl alcohol) or NPOE (*o*-nitro phenyl octyl ether) as matrix at the UC Berkeley Mass Spectrometry Facility. UV-Visible spectra were measured on a Cary Bio 400 instrument equipped with a Harrick Praying Mantis accessory for diffuse reflectance solid state spectra. Solution NMR spectra were recorded on either a Bruker DRX-500, AVB-400 or AV-300 instrument. Chemical shifts are reported relative to the residual solvent peak for  $\text{CHCl}_3$  at  $\delta = 7.26$  ppm. Solid-state NMR spectroscopy was performed at the Caltech Solid-State NMR Facility using a Bruker DSX500 spectrometer at 500 MHz. Calixarene surface densities were estimated by carbon content as measured using a Perkin-Elmer 2400 Series II combustion analyzer at the Berkeley Microanalytical Laboratory. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter.

## Materials Synthesis for Anchored Aminocalixarene Materials **4a-d**

The desired amount of aminocalixarene **3a-d** was dissolved in 50 mL of benzene in a round bottom flask and treated with the required amount of silica (no pretreatment). The slurry was stirred overnight open to ambient atmosphere, and afterwards the solvent was removed via rotary evaporation. The material was Soxhlet extracted in benzene for 12 hours, washed briefly with pentane, and allowed to dry at room temperature under vacuum (50 mtorr).

## Salicylaldehyde Binding for Anchored Aminocalixarene Materials **4a-d**

A 5 mM solution of salicylaldehyde containing was prepared in anhydrous toluene. Aminocalixarene material **4a-d** and molecular sieves were pretreated under vacuum (50 mtorr) for a period of 1 h at 100 °C and allowed to cool under nitrogen. Two equivalents per amine of salicylaldehyde were added via syringe, and the slurry was heated to 100 °C for a period of 8 h. Amounts of bound salicylaldehyde were estimated by leaching sites from the surface in excess acetonitrile while exposed to ambient atmosphere and performing spectrophotometry on the leached solution. The amount of Schiff base was estimated at the following wavelengths and using the following extinction coefficients measured for compounds **8a-d**: **8a** measured at  $\lambda = 315$  using  $\epsilon = 3733 \text{ M}^{-1}$ ; **8b** measured at  $\lambda = 313$  using  $\epsilon = 2851 \text{ M}^{-1}$ ; **8c** measured at  $\lambda = 315$  using  $\epsilon = 2863 \text{ M}^{-1}$ ; **8d** measured at  $\lambda = 313$  using  $\epsilon = 2836 \text{ M}^{-1}$ . The amount of bound salicylaldehyde to 3-aminopropyltriethoxysilane-treated silica was determined by gas chromatography using hexamethylbenzene as an internal standard.

### General procedure for synthesis of 1a-d.

To a mixture of *tert*-butylcalix[4]arene (3.0g, 4.63 mmol) and triphenylphosphine (1.8g, 6.9 mmol) in 50 ml dry toluene, a solution of diethylazodicarboxylate (1.2g, 6.9 mmol) in 5 ml of dry toluene was added under vigorous stirring. After 15 min, the resulting yellow solution was heated to 40 °C, and a toluene solution of N-*t*-Boc-protected alcohol (9.25 mmol) was added dropwise. The resulting mixture was heated and maintained at 70 °C for a period 2 h. Evaporation of solvent produced a light yellow colored solid. The residue was purified via column chromatography.

5,11,17,23-Tetra-*tert*-butyl-25-(*N*-*tert*-Butyloxycarbonyl)-2-Aminopropoxy-26,27,28-trihydroxycalix[4]arene (1a). After purification via column chromatography (eluent is CH<sub>2</sub>Cl<sub>2</sub>/methanol 1:0.020 v/v, R<sub>f</sub> 0.5), a white powder was obtained in 33 % yield:  $[\alpha]_D^{25} = +4.46$  (c=0.016, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.16 (s, 1H, OH), 9.54 (s, 1H, OH), 9.47 (s, 1H, OH), 7.13 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.09 (m, 3H, ArH-*m*), 7.07 (d, 2H, <sup>4</sup>J = 2.0 Hz, ArH-*m*), 7.04 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.00 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 6.59 (s, 1H, NH), 4.37 (d, 1H, <sup>2</sup>J = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.21-4.31 (m, 4H, ArCH<sub>2</sub>Ar+CH), 4.15, 4.04 (two m, 1H+1H, CH<sub>2</sub>CH), 3.40-3.51 (m, 4H, ArCH<sub>2</sub>Ar), 1.58 (d, 3H, <sup>3</sup>J = 6.8 Hz, CH<sub>3</sub>CH), 1.52 (s, 9H, OCCH<sub>3</sub>), 1.25 (s, 9H, CCH<sub>3</sub>), 1.24 (s, 9H, CCH<sub>3</sub>), 1.23 (s, 9H, CCH<sub>3</sub>), 1.20 (s, 9H, CCH<sub>3</sub>); <sup>13</sup>C NMR 156.11, 148.61, 148.47, 148.20, 147.58, 143.81, 143.52, 143.12, 133.75, 132.92, 128.73, 128.06, 127.35, 127.20, 127.02, 126.38, 126.10, 125.83, 125.75, 125.72, 80.11, 79.30, 46.79, 34.30, 34.08, 33.98, 33.94, 33.03, 32.25, 31.95, 31.54, 31.51, 31.24, 28.53, 28.42, 18.20; HR FAB MS calcd for C<sub>52</sub>H<sub>70</sub>O<sub>6</sub>N 804.520315, found 804.518150.

5,11,17,23-Tetra-*tert*-butyl-25-(*N*-*tert*-Butyloxycarbonyl)-2-Aminoethoxy-26,27,28-trihydroxycalix[4]arene (1b). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/methanol 1:0.020 v/v, R<sub>f</sub> 0.6), a white powder was obtained in 32 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.13 (s, 1H, OH), 9.60 (s, 2H, OH), 7.10 (s, 2H, ArH-*m*), 7.06 (m, 4H, ArH-*m*), 7.00 (d, 2H, <sup>4</sup>J = 2.1 Hz, ArH-*m*), 6.84 (s, 1H, NH), 4.28 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.26 (d, 2H, <sup>2</sup>J = 13.5 Hz, ArCH<sub>2</sub>Ar), 4.21 (t, 2H, <sup>3</sup>J = 4.5 Hz, OCH<sub>2</sub>), 3.80 (q, 2H, <sup>3</sup>J = 4.5 Hz, NCH<sub>2</sub>), 3.46 (d, 2H, <sup>2</sup>J = 13.5 Hz, ArCH<sub>2</sub>Ar), 3.45 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 1.51 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.22 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),

1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 149.00, 148.71, 148.47, 147.77, 143.65, 133.69, 128.52, 128.03, 127.80, 126.84, 126.17, 126.08, 126.02, 34.56, 34.31, 34.20, 33.24, 32.45, 31.74, 31.47, 28.78; HR FAB MS calcd for C<sub>51</sub>H<sub>69</sub>NO<sub>6</sub> 791.512490, found 791.514540.

5,11,17,23-Tetra-*tert*-butyl-25-(*N-tert*-Butyloxycarbonyl)-3-Aminopropoxy-26,27,28-trihydroxycalix[4]arene (**1c**). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/methanol 1:0.010 v/v, R<sub>f</sub> 0.4), a white powder was obtained in 42 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.20 (s, 1H, OH), 9.63 (s, 2H, OH), 7.10 (s, 2H, ArH-*m*), 7.08 (d, 2H, <sup>4</sup>*J* = 2.7 Hz, ArH-*m*), 7.06 (s, 2H, ArH-*m*), 7.00 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 5.77 (s, 1H, NH), 4.25-4.37 (m, 4H, ArCH<sub>2</sub>Ar), 4.15 (t, 2H, <sup>3</sup>*J* = 6.0 Hz, OCH<sub>2</sub>), 3.60 (m, 2H, NCH<sub>2</sub>), 3.45 (d, 4H, <sup>2</sup>*J* = 13.5 Hz, ArCH<sub>2</sub>Ar), 2.31 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.48 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.22 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 148.63, 148.53, 147.86, 143.63, 128.53, 128.33, 127.77, 126.81, 126.11, 126.04, 125.97, 34.52, 34.30, 34.21, 33.26, 32.43, 31.76, 31.49, 28.81; HR FAB MS calcd for C<sub>52</sub>H<sub>71</sub>NO<sub>6</sub> 805.528170, found 805.529040.

5,11,17,23-Tetra-*tert*-butyl-25-(*N-tert*-Butyloxycarbonyl)-4-Aminobutyloxy-26,27,28-trihydroxycalix[4]arene (**1d**). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/methanol 1:0.020 v/v, R<sub>f</sub> 0.8), a white powder was obtained in 48 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.18 (s, 1H, OH), 9.59 (s, 2H, OH), 7.10 (s, 2H, ArH-*m*), 7.08 (s, 2H, ArH-*m*), 7.07 (s, 2H, ArH-*m*), 7.00 (s, 2H, ArH-*m*), 4.87 (s, 1H, NH), 4.34 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.29 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.16 (t, 2H, <sup>3</sup>*J* = 6.4 Hz, OCH<sub>2</sub>), 3.46 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.44 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 3.36 (m, 2H, NCH<sub>2</sub>), 2.19 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 1.93 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 1.47 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.24 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.23 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 156.18, 149.25, 148.44, 148.24, 147.73, 143.72, 143.22, 133.49, 129.93, 128.36, 128.14, 127.63, 126.49, 125.79, 125.76, 125.70, 79.21, 38.43, 34.28, 34.05, 33.96, 33.04, 32.27, 31.53, 31.28, 28.49, 27.25, 26.55; HR FAB MS calcd for C<sub>53</sub>H<sub>73</sub>NO<sub>6</sub> 819.543790, found 819.543770.

### General procedure for synthesis of 2a-d

To a solution of **1a-d** (0.248 mmol) in 5 ml of dry benzene containing catalytic amount of DMAP, triethylamine (1.49 mmol) was added, and the solution was stirred at room temperature for 15 min. Subsequently, C<sub>2</sub>H<sub>5</sub>OSiCl<sub>3</sub> (0.347 mmol) was added dropwise during the course of 10 min. The reaction was then continued for 12 h at 40 °C. The white, solid, ammonium salt that was formed was removed via filtration, and the organic solution was evaporated to dryness. The evaporated residue was extensively washed with dry hexane, and the organic solution was isolated and evaporated to dryness. The white residue was purified with flash chromatography on dehydrated Selecto silica.

5,11,17,23-Tetra-*tert*-butyl-25-(*R*)-(N-*tert*-Butyloxycarbonyl)-2-Aminopropoxy-26,27,28-Ethoxysilylcalix[4]arene (**2a**). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethanol 1:0.020 v/v, R<sub>f</sub> 0.7), a white powder was obtained in 49 % yield:  $[\alpha]_D^{25} = +8.42$  (c=0.008, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.13 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.11 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.05 (d, 1H, <sup>4</sup>J = 2.7 Hz, ArH-*m*), 7.01-7.03 (m, 3H, ArH-*m*), 6.68 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 6.64 (d, 1H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 6.54 (m, 1H, NH), 4.60 (d, 1H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.48 (d, 1H, <sup>2</sup>J = 13.5 Hz, ArCH<sub>2</sub>Ar), 4.47 (d, 1H, <sup>2</sup>J = 13.8 Hz, ArCH<sub>2</sub>Ar), 4.42 (d, 1H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.23 (m, 2H, SiOCH<sub>2</sub>), 3.75, 4.03 (two m, 1H+1H, OCH<sub>2</sub>CH), 3.36 (d, 1H, <sup>2</sup>J = 13.8 Hz, ArCH<sub>2</sub>Ar), 3.35 (d, 1H, <sup>2</sup>J = 13.8 Hz, ArCH<sub>2</sub>Ar), 3.27 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.18 (m, 1H, CHCH<sub>3</sub>), 1.43 (t, 3H, <sup>3</sup>J = 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 1.31 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.15 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.12 (d, 3H, <sup>3</sup>J = 6.0 Hz, CH<sub>3</sub>CH), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 148.13, 146.32, 146.09, 144.84, 144.67, 132.81, 131.54, 130.22, 129.69, 126.36, 124.71, 124.49, 74.62, 61.05, 41.01, 34.81, 34.27, 33.95, 32.87, 31.77, 31.66, 31.54, 31.42, 31.11, 30.98, 30.91, 26.57, 17.99; HR FAB MS calcd for C<sub>54</sub>H<sub>72</sub>NO<sub>7</sub>Si 874.507808, found 874.505590.

5,11,17,23-Tetra-*tert*-butyl-25-(N-*tert*-Butyloxycarbonyl)-2-Aminoethoxy-26,27,28-Ethoxysilylcalix[4]arene (**2b**). After purification via flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethanol 1:0.015 v/v, R<sub>f</sub> 0.8), a white powder was obtained in 63 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.14 (d, 2H, <sup>4</sup>J = 2.0 Hz, ArH-*m*), 7.05 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.04 (s, 2H, ArH-*m*), 6.75 (s, 2H, ArH-*m*), 6.34 (s, 1H, NH), 4.50 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.45 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.25 (q, 2H, <sup>3</sup>J = 7.2 Hz, SiOCH<sub>2</sub>), 3.85 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>N), 3.61 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>N), 3.38 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar),

3.31 (d, 2H,  $^2J = 13.2$  Hz, ArCH<sub>2</sub>Ar), 1.44 (t, 3H,  $^3J = 7.2$  Hz, SiOCH<sub>2</sub>CH<sub>3</sub>), 1.42 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.31 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.18 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 148.12, 144.67, 132.79, 131.53, 130.21, 129.68, 126.36, 126.30, 124.71, 124.49, 61.05, 53.42, 34.80, 34.26, 33.95, 32.87, 31.53, 31.42, 31.11, 28.43, 17.99; HR FAB MS calcd for C<sub>53</sub>H<sub>71</sub>O<sub>7</sub>NSi 861.499983, found 861.497640.

5,11,17,23-Tetra-*tert*-butyl-25-(*N-tert*-butyloxycarbonyl)-3-Aminopropoxy-26,27,28-Ethyloxysilylcalix[4]arene (**2c**). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethanol 1:0.010 v/v, R<sub>f</sub> 0.5), a white powder was obtained in 69 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.14 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 7.05 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 7.01 (s, 2H, ArH-*m*), 6.66 (s, 2H, ArH-*m*), 5.57 (s, 1H, NH), 4.49 (d, 2H,  $^2J = 12.9$  Hz, ArCH<sub>2</sub>Ar), 4.48 (d, 2H,  $^2J = 13.5$  Hz, ArCH<sub>2</sub>Ar), 4.23 (q, 2H,  $^3J = 7.2$  Hz, SiOCH<sub>2</sub>), 3.91 (t, 2H,  $^3J = 5.4$  Hz, OCH<sub>2</sub>), 3.47 (m, 2H, NCH<sub>2</sub>), 3.35 (d, 2H,  $^2J = 13.5$  Hz, ArCH<sub>2</sub>Ar), 3.33 (d, 2H,  $^2J = 13.2$  Hz, ArCH<sub>2</sub>Ar), 2.08 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.42 (t,  $^3J = 7.2$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 1.33 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.31 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.16 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.90 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 148.35, 146.54, 146.08, 145.06, 144.71, 133.22, 132.05, 130.35, 129.96, 126.52, 124.79, 124.70, 74.81, 61.01, 53.64, 34.95, 34.47, 34.20, 34.09, 33.08, 31.80, 31.66, 31.30, 29.92, 28.51, 18.39; HR FAB MS calcd for C<sub>54</sub>H<sub>73</sub>O<sub>7</sub>NSi 875.515633, found 875.516510.

5,11,17,23-Tetra-*tert*-butyl-25-(*N-tert*-butyloxycarbonyl)-4-Aminobutyloxy-26,27,28-Ethoxysilylcalix[4]arene (**2d**). After purification via column chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethanol 1:0.020 v/v, R<sub>f</sub> 0.8), a white powder was obtained in 66 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.13 (d, 2H,  $^4J = 2.8$  Hz, ArH-*m*), 7.05 (d, 2H,  $^4J = 2.8$  Hz, ArH-*m*), 6.99 (s, 2H, ArH-*m*), 6.61 (s, 2H, ArH-*m*), 4.59 (s, 1H, NH), 4.49 (d, 2H,  $^2J = 13.0$  Hz, ArCH<sub>2</sub>Ar), 4.48 (d, 2H,  $^2J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 4.20 (q, 2H,  $^3J = 7.2$  Hz, SiOCH<sub>2</sub>), 3.85 (t, 2H,  $^3J = 6.8$  Hz, OCH<sub>2</sub>CH<sub>2</sub>), 3.34 (d, 2H,  $^2J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 3.32 (d, 2H,  $^2J = 13.0$  Hz, ArCH<sub>2</sub>Ar), 3.21 (m, 2H, CH<sub>2</sub>), 1.87 (m, 2H, CH<sub>2</sub>), 1.78 (m, 2H, CH<sub>2</sub>), 1.44 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.39 (t, 3H,  $^3J = 6.8$  Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.14 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.85 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 148.02, 145.59, 144.32, 133.04, 131.89, 130.03, 129.78, 126.19, 124.33, 63.15, 34.64, 33.89, 31.50, 31.35, 30.97, 27.48, 18.18; HR FAB MS calcd for C<sub>55</sub>H<sub>75</sub>O<sub>7</sub>NSi 889.531309, found 889.532210.

### General Synthesis of 3a-d

To a solution of **2a-d** (0.114 mmol) in 2 mL of dry dichloromethane, trimethyliodosilane (0.148 mmol) was slowly added at 0°C. The reaction was continued for 15 min and was subsequently evaporated to dryness. The residue was redissolved in dry dichloromethane (~0.5 mL) and treated with dry ethanol (1.48 mmol) for a period of 20 min. Evaporation in vacuo (50 mtorr) for 3h produced analytically pure calixarenes **3a-d**, which were used for materials synthesis without further purification.

5,11,17,23-Tetra-*tert*-butyl-25-(*R*)-2-Aminopropoxy-26,27,28-Ethoxysilylcalix[4]arene (**3a**). Evaporation produced a pale yellow solid with 89 % yield:  $[\alpha]_D^{25} = +7.80$  ( $c=0.008$ , CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.12 (s, 2H, ArH-*m*), 7.07 (s, 2H, ArH-*m*), 7.04 (m, 2H, ArH-*m*), 6.83 (s, 2H, ArH-*m*), 4.42 (m, 2H+2H, ArCH<sub>2</sub>Ar+OCH<sub>2</sub>), 4.27 (m, 2H, ArCH<sub>2</sub>Ar), 4.10, 4.00 (two m, 1H+1H, OCH<sub>2</sub>CH), 3.42 (m, 4H, ArCH<sub>2</sub>Ar), 1.92 (d, 3H, <sup>3</sup>*J* = 6.6 Hz, CH<sub>3</sub>CH), 1.54 (t, 3H, <sup>3</sup>*J* = 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.28 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.03 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>49</sub>H<sub>66</sub>O<sub>5</sub>NSi 776.471028, found 776.471860.

5,11,17,23-Tetra-*tert*-butyl-25-2-Aminoethoxy-26,27,28-Ethoxysilylcalix[4]arene (**3b**). Evaporation produced a pale yellow solid with 93 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.14 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 7.05 (d, 2H, <sup>4</sup>*J* = 2.0 Hz, ArH-*m*), 7.02 (s, 2H, ArH-*m*), 6.71 (s, 2H, ArH-*m*), 4.51 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.49 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.25 (q, 2H, <sup>3</sup>*J* = 7.2 Hz, SiOCH<sub>2</sub>), 3.89 (t, 2H, <sup>3</sup>*J* = 4.8 Hz, OCH<sub>2</sub>), 3.36 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 3.34 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.20 (t, 2H, <sup>3</sup>*J* = 4.8 Hz, NCH<sub>2</sub>), 1.44 (t, 3H, <sup>3</sup>*J* = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.31 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.16 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>48</sub>H<sub>64</sub>O<sub>5</sub>NSi 762.455400, found 762.454210.

5,11,17,23-Tetra-*tert*-butyl-25-3-Aminopropoxy-26,27,28-Ethoxysilylcalix[4]arene (**3c**). Evaporation produced a pale yellow solid with 92 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.14 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 7.05 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 6.99 (s, 2H, ArH-*m*), 6.61 (s, 2H, ArH-*m*), 4.46 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.42 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.24 (q, 2H, <sup>3</sup>*J* = 7.2 Hz, SiOCH<sub>2</sub>), 3.93 (t, 2H, <sup>3</sup>*J* = 6.0 Hz, OCH<sub>2</sub>), 3.48 (br s, 2H, NH<sub>2</sub>), 3.36 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.35 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 3.22 (t, 2H, <sup>3</sup>*J* = 6.4 Hz, NCH<sub>2</sub>), 2.12 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.40 (t, 3H, <sup>3</sup>*J* = 7.2 Hz,



CH<sub>2</sub>CH<sub>3</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.15 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.85 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>49</sub>H<sub>66</sub>O<sub>5</sub>NSi 776.471028, found 776.472060.

5,11,17,23-Tetra-*tert*-butyl-25-4-Aminobutyloxy-26,27,28-Ethoxysilylcalix[4]arene (**3d**). Evaporation produced a pale yellow solid with 89 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.14 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 7.04 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 6.98 (s, 2H, ArH-*m*), 6.60 (s, 2H, ArH-*m*), 4.46 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.40 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.20 (q, 2H, <sup>3</sup>J = 7.2 Hz, SiOCH<sub>2</sub>), 3.87 (t, 2H, <sup>3</sup>J = 6.0 Hz, SiOCH<sub>2</sub>), 3.69 (m, 2H, NH<sub>2</sub>), 3.36 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.34 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar), 3.19 (t, 2H, <sup>3</sup>J = 7.2 Hz, NCH<sub>2</sub>), 2.11 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 2.00 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 1.39 (t, 3H, <sup>3</sup>J = 7.2 Hz, SiOCH<sub>2</sub>CH<sub>3</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.14 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>50</sub>H<sub>68</sub>NO<sub>5</sub>Si 790.486678, found 790.486670.

### General Synthesis of **6a-d** and **8a-d**

A solution of aminocalixarene **3a-d**, **7a-d** (0.064 mmol) and salicylaldehyde (0.084 mmol) in 3 mL of dry toluene was refluxed for 3h over molecular sieves. After separation of molecular sieves and evaporation, the residue was subjected to flash column chromatographic purification.

5,11,17,23-Tetra-*tert*-butyl-25-(*R*)-[2-(2-Hydroxyphenylmethylenimino)propoxy]-26,27,28-Ethoxysilylcalix[4]arene (**6a**). After flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 1:0.1 v/v, R<sub>f</sub> 0.9), a yellow powder was obtained in 73 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.60 (s, 1H, CHN), 7.24 (m, 2H, ArH), 7.14 (d, 1H, <sup>4</sup>J = 2.7 Hz, ArH-*m*), 7.05 (d, 1H, <sup>4</sup>J = 2.7 Hz, ArH-*m*), 7.03 (m, 2H, ArH), 6.97 (s, 2H, ArH), 6.91 (d, 1H, <sup>3</sup>J = 8.4 Hz, ArH), 6.81 (t, 1H, <sup>3</sup>J = 8.4 Hz, ArH), 6.57 (d, 1H, <sup>4</sup>J = 2.7 Hz, ArH-*m*), 6.53 (d, 1H, <sup>4</sup>J = 2.7 Hz, ArH-*m*), 4.40-4.52 (m, 4H, ArCH<sub>2</sub>Ar), 4.09-4.23 (m, 3H, SiOCH<sub>2</sub>+CHCH<sub>3</sub>), 3.97 (m, 2H, OCH<sub>2</sub>CH), 3.21-3.38 (m, 4H, ArCH<sub>2</sub>Ar), 1.48 (d, 3H, <sup>3</sup>J = 5.7 Hz, CH<sub>3</sub>CH), 1.37 (t, 3H, <sup>3</sup>J = 6.9 Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.32 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.13 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.81 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>56</sub>H<sub>70</sub>NO<sub>6</sub>Si 880.497243, found 880.495400.

5,11,17,23-Tetra-*tert*-butyl-25-[2-(2-Hydroxyphenylmethylenimino)ethoxy]-26,27,28-Ethoxysilylcalix[4]arene (**6b**). After flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> 0.5), an

off-white powder was obtained in 77 % yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.57 (s, 1H, CHN), 7.25 (m, 2H, ArH), 7.10 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 7.04 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 6.99 (s, 2H, ArH-*m*), 6.93 (d, 1H,  $^3J = 8.4$  Hz, ArH), 6.84 (t, 1H,  $^3J = 8.4$  Hz, ArH), 6.62 (s, 2H, ArH-*m*), 4.49 (d, 2H,  $^2J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.47 (d, 2H,  $^2J = 13.6$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.21 (m, 4H,  $\text{NCH}_2+\text{OCH}_2$ ), 4.05 (t, 2H,  $\text{SiOCH}_2$ ), 3.33 (d, 2H,  $^2J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.32 (d, 2H,  $^2J = 13.6$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 1.38 (t, 3H,  $^3J = 6.8$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.30 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.14 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 0.86 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ); FAB MS  $m/z$  872.6  $[\text{M}+\text{Li}^+]$ , 866.6  $[\text{M}+\text{H}^+]$ , 802.6  $[\text{M}+\text{Li}^+-\text{SiOC}_2\text{H}_5+3\text{H}^+]$ ; HR FAB MS calcd for  $\text{C}_{55}\text{H}_{68}\text{NO}_6\text{Si}$  866.481593, found 866.481050.

5,11,17,23-Tetra-*tert*-butyl-25-[3-(2-Hydroxyphenylmethylenimino)propoxy]-26,27,28-Ethoxysilylcalix[4]arene (**6c**). Following flash chromatography (eluent  $\text{CH}_2\text{Cl}_2/\text{ethylacetate}$  1:0.05 v/v,  $R_f$  0.8), an off-white powder was obtained in 74 % yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.44 (s, 1H, CHN), 7.28 (m, 1H, ArH), 7.21 (m, 1H, ArH), 7.14 (d, 2H,  $^4J = 2.8$  Hz, ArH-*m*), 7.06 (d, 2H,  $^4J = 2.8$  Hz, ArH-*m*), 7.00 (s, 2H, ArH-*m*), 6.96 (d, 1H,  $^3J = 8.0$  Hz, ArH), 6.86 (t, 1H,  $^3J = 8.0$  Hz, ArH), 6.63 (s, 2H, ArH-*m*), 4.50 (d, 2H,  $^2J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.49 (d, 2H,  $^2J = 13.6$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.21 (m, 2H,  $\text{NCH}_2$ ), 4.03 (t, 2H,  $^3J = 6.8$  Hz,  $\text{OCH}_2$ ), 3.93 (t, 2H,  $^3J = 6.0$  Hz,  $\text{OCH}_2$ ), 3.35 (d, 2H,  $^2J = 13.6$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.33 (d, 2H,  $^2J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 2.27 (m, 2H,  $\text{CH}_2$ ), 1.39 (t, 3H,  $^3J = 7.2$  Hz,  $\text{SiOCH}_2\text{CH}_3$ ), 1.32 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.15 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 0.87 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ); FAB MS  $m/z$  886.6  $[\text{M}+\text{Li}^+]$ , 880.6  $[\text{M}+\text{H}^+]$ , 816.6  $[\text{M}+\text{Li}^+-\text{SiOC}_2\text{H}_5+3\text{H}^+]$ ; HR FAB MS calcd for  $\text{C}_{56}\text{H}_{70}\text{NO}_6\text{Si}$  880.497243, found 880.496940.

5,11,17,23-Tetra-*tert*-butyl-25-[4-(2-Hydroxyphenylmethylenimino)butyloxy]-26,27,28-Ethoxysilylcalix[4]arene (**6d**). Following flash chromatography (eluent  $\text{CH}_2\text{Cl}_2/\text{ethylacetate}$  1:0.1 v/v,  $R_f$  0.7), an off-white powder was obtained in 81 % yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.37 (s, 1H, CHN), 7.30 (t, 1H,  $^3J = 8.0$  Hz, ArH), 7.23 (d, 1H,  $^3J = 8.0$  Hz, ArH), 7.13 (d, 2H,  $^4J = 2.8$  Hz, ArH-*m*), 7.05 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 6.98 (s, 2H, ArH-*m*), 6.96 (d, 1H,  $^3J = 7.6$  Hz, ArH), 6.87 (t, 1H, 7.6 Hz, ArH), 6.60 (s, 2H, ArH-*m*), 4.50 (d, 2H,  $^2J = 14.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.47 (d, 2H,  $^2J = 14.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.19 (m, 2H,  $\text{NCH}_2$ ), 3.88 (t, 2H,  $^3J = 6.0$  Hz,  $\text{OCH}_2$ ), 3.70 (t, 2H,  $^3J = 6.0$  Hz,  $\text{SiOCH}_2$ ), 3.33

(d, 2H,  $^2J = 14.0$  Hz, ArCH<sub>2</sub>Ar), 3.32 (d, 2H,  $^2J = 13.2$  Hz, ArCH<sub>2</sub>Ar), 2.00 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 1.35 (t, 3H,  $^3J = 6.8$  Hz, SiOCH<sub>2</sub>CH<sub>3</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.14 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>57</sub>H<sub>72</sub>NO<sub>6</sub>Si 894.512920, found 894.511930.

5,11,17,23-Tetra-*tert*-butyl-25-[(*R*)-2-(2-Hydroxyphenylmethylenimino)propoxy]-26,27,28-trihydroxycalix[4]arene (**8a**). Following flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 1:0.018 v/v, R<sub>f</sub> 0.4) yellow powder was obtained in 74 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 13.2 (s, 1H, C<sub>6</sub>H<sub>4</sub>OH), 9.90 (s, 1H, OH), 9.42 (s, 1H, OH), 9.15 (s, 1H, OH), 8.83 (s, 1H, CHN), 7.53 (d, 1H,  $^3J = 9.3$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.30 (t, 1H,  $^3J = 8.7$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.17 (d, 1H,  $^4J = 2.4$  Hz, ArH-*m*), 7.07 (d, 1H,  $^4J = 2.4$  Hz, ArH-*m*), 7.05 (d, 1H,  $^4J = 2.4$  Hz, ArH-*m*), 6.87-6.97 (m, 7H, ArH-*m*+ C<sub>6</sub>H<sub>4</sub>), 4.51 (d, 1H,  $^2J = 12.6$  Hz, ArCH<sub>2</sub>Ar), 4.23-4.42 (m, 3H, OCH<sub>2</sub>+ArCH<sub>2</sub>Ar), 4.04-4.12 (m, 2H, ArCH<sub>2</sub>Ar), 3.37-3.52 (m, 4H, CHCH<sub>3</sub>+ArCH<sub>2</sub>Ar), 3.16 (d, 1H,  $^2J = 13.8$  Hz, ArCH<sub>2</sub>Ar), 1.45 (d, 3H,  $^3J = 6.6$  Hz, CH<sub>3</sub>CH), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.17 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); FAB MS m/z 811 [M+H<sup>+</sup>].

5,11,17,23-Tetra-*tert*-butyl-25-[2-(2-Hydroxyphenylmethylenimino)ethoxy]-26,27,28-trihydroxycalix[4]arene (**8b**). Following flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> 0.7), a yellow powder was obtained in 69 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.09 (s, 1H, OH), 9.40 (br s, 2H, OH), 8.80 (s, 1H, CHN), 7.51 (d, 1H,  $^3J = 8.0$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.31 (t, 1H,  $^3J = 7.2$  Hz, C<sub>6</sub>H<sub>4</sub>), 7.09 (s, 2H, ArH-*m*), 7.03 (d, 2H,  $^4J = 2.4$  Hz, ArH-*m*), 7.01 (s, 2H, ArH-*m*), 6.88-6.95 (m, 4H, ArH-*m* + C<sub>6</sub>H<sub>4</sub>), 4.45 (m, 2H, OCH<sub>2</sub>), 4.38 (m, 2H, NCH<sub>2</sub>), 4.31 (d, 2H,  $^2J = 12.8$  Hz, ArCH<sub>2</sub>Ar), 3.98 (d, 2H,  $^2J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 3.43 (d, 2H,  $^2J = 12.8$  Hz, ArCH<sub>2</sub>Ar), 3.32 (d, 2H,  $^2J = 13.6$  Hz, ArCH<sub>2</sub>Ar), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.18 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>); FAB MS m/z 796 [M+H<sup>+</sup>]; HR FAB MS calcd for C<sub>53</sub>H<sub>65</sub>NO<sub>5</sub> 795.486275, found 795.484990.

5,11,17,23-Tetra-*tert*-butyl-25-[3-(2-Hydroxyphenylmethylenimino)propoxy]-26,27,28-trihydroxycalix[4]arene (**8c**). Following separation via flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> 0.7), a yellow powder was obtained in 72 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 13.5

(br s, 1H, C<sub>6</sub>H<sub>4</sub>OH), 10.20 (s, 1H, OH), 9.59 (s, 2H, OH), 8.69 (s, 1H, CHN), 7.29-7.34 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.08 (s, 2H, ArH-*m*), 7.06 (m, 4H, ArH-*m*), 7.00 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 6.97 (d, 1H, <sup>3</sup>*J* = 8.0 Hz, C<sub>6</sub>H<sub>4</sub>), 6.88 (t, 1H, <sup>3</sup>*J* = 8.0 Hz, C<sub>6</sub>H<sub>4</sub>), 4.31 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.28 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.17 (m, 4H, OCH<sub>2</sub>+ NCH<sub>2</sub>), 3.46 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 3.42 (d, 2H, <sup>2</sup>*J* = 13.2 Hz, ArCH<sub>2</sub>Ar), 2.53 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.18 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); FAB MS *m/z* 810.5 [M+H<sup>+</sup>]; HR FAB MS calcd for C<sub>54</sub>H<sub>67</sub>NO<sub>5</sub> 809.501925, found 809.504210.

5,11,17,23-Tetra-*tert*-butyl-25-[4-(2-Hydroxyphenylmethylenimino)butyloxy]-26,27,28-trihydroxycalix[4]arene (**8d**). Following separation via flash chromatography (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 1:0.025 v/v, R<sub>f</sub> 0.5), a yellow powder was obtained in 83 % yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 13.60 (s, 1H, C<sub>6</sub>H<sub>4</sub>OH), 10.16 (s, 1H, OH), 9.56 (s, 2H, OH), 8.47 (s, 1H, CHN), 7.30 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.08 (s, 2H, ArH-*m*), 7.05 (d, 2H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 7.04 (s, 2H, ArH-*m*), 6.95-6.98 (m, 2H, ArH-*m*+C<sub>6</sub>H<sub>4</sub>), 6.87 (t, 1H, <sup>3</sup>*J* = 7.6 Hz, C<sub>6</sub>H<sub>4</sub>), 4.33 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.25 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.17 (t, 2H, <sup>3</sup>*J* = 6.8 Hz, OCH<sub>2</sub>), 3.83 (t, 2H, <sup>3</sup>*J* = 6.8 Hz, NCH<sub>2</sub>), 3.43 (d, 2H, <sup>2</sup>*J* = 13.6 Hz, ArCH<sub>2</sub>Ar), 3.41 (d, 2H, <sup>2</sup>*J* = 12.8 Hz, ArCH<sub>2</sub>Ar), 2.22 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 2.17 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>), 1.22 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.18 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); FAB MS *m/z* 825 [M+H<sup>+</sup>].

### General Calixarene Site Leaching Procedure

50 mg of materials **4a-d**, **5a-d** were suspended in 20 mL of acetonitrile. The solution was allowed to vent open to the atmosphere for 48 h. The solids were removed via filtration, washed with additional acetonitrile, and the solution was collected. The solution was evaporated to yield a slightly yellow solid that was characterized using <sup>1</sup>H NMR spectroscopy. Extraction of sites was confirmed to result in at least 85% leaching of anchored sites as ascertained via thermogravimetric analysis.

5,11,17,23-Tetra-*tert*-butyl-25-(*R*)-2-Aminopropoxy-26,27,28-trihydroxycalix[4]arene (**7a**). Slightly yellow powder: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.13 (d, 1H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 7.09 (d, 1H, <sup>4</sup>*J* = 2.4 Hz, ArH-*m*), 7.06 (m, 4H, ArH-*m*), 7.02 (d, 1H, <sup>4</sup>*J* = 2.0 Hz, ArH-*m*), 6.97 (d, 1H, <sup>4</sup>*J* = 2.0 Hz, ArH-*m*), 5.95 (br s, 5H, OH+NH<sub>2</sub>), 4.49 (d, 1H, <sup>2</sup>*J* = 12.8

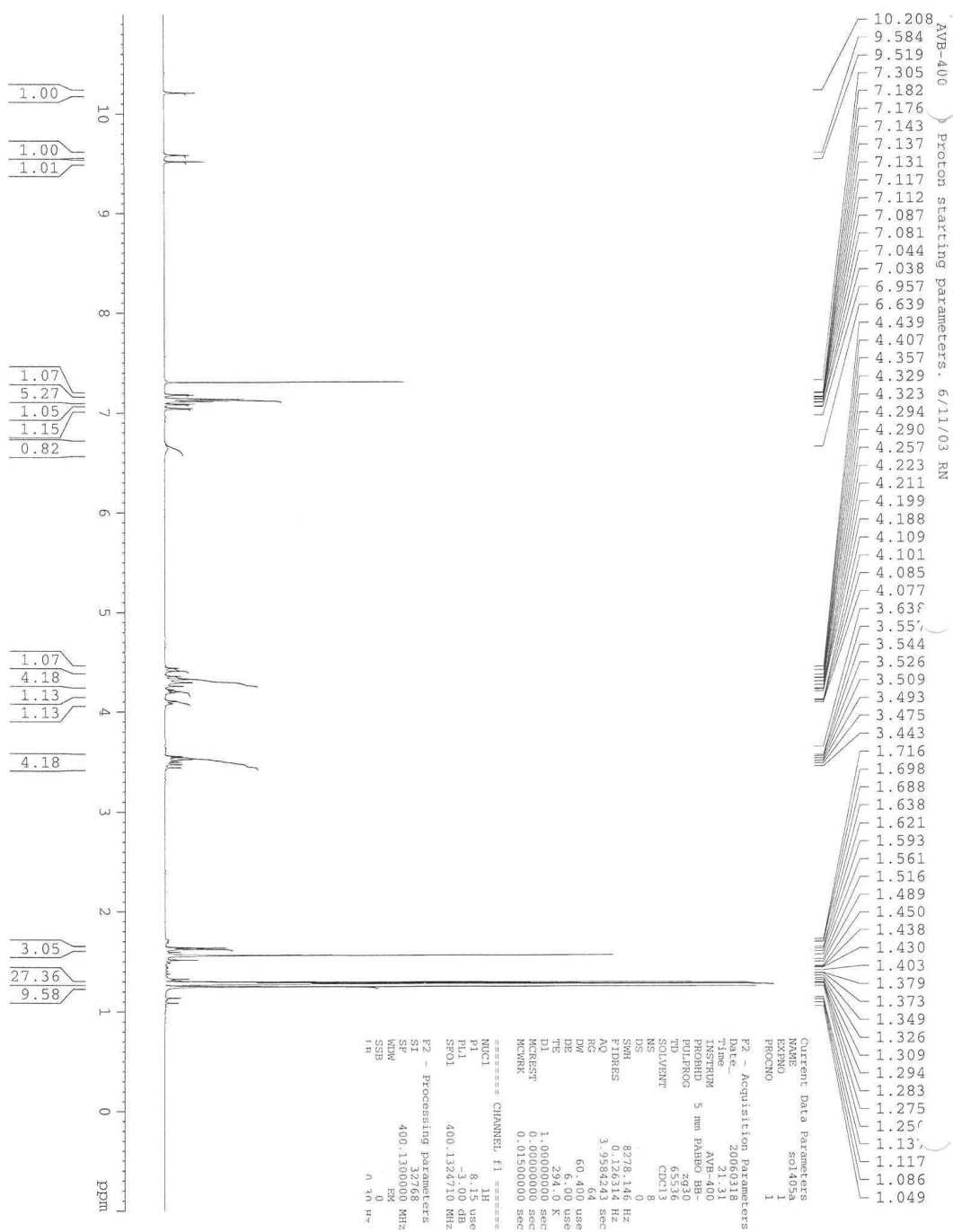
Hz, ArCH<sub>2</sub>Ar), 4.24-4.30 (m, 3H, ArCH<sub>2</sub>Ar), 3.88, 4.06 (two m, 1H each, OCH<sub>2</sub>), 3.74 (m, 1H, CHCH<sub>2</sub>O), 3.40-3.49 (m, 3H, ArCH<sub>2</sub>Ar), 2.87 (d, 1H, <sup>2</sup>J = 10.0 Hz, ArCH<sub>2</sub>Ar), 1.31 (d, 3H, <sup>3</sup>J = 6.4 Hz, CH<sub>3</sub>CH), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.22 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>47</sub>H<sub>63</sub>NO<sub>4</sub> 705.475710, found 705.473370.

5,11,17,23-Tetra-*tert*-butyl-25-2-Aminoethoxy-26,27,28-trihydroxycalix[4]arene (**7b**). White powder, 88 % of the calixarene was leached from the surface: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.10 (s, 2H, ArH), 7.07 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH), 7.06 (s, 2H, ArH), 7.05 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH), 6.99 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH), 4.39 (d, 2H, <sup>2</sup>J = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.27 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar), 4.18 (t, 2H, <sup>3</sup>J = 4.8 Hz, CH<sub>2</sub>), 3.45 (d, 2H, <sup>2</sup>J = 13.6 Hz, ArCH<sub>2</sub>Ar), 3.44 (d, 2H, <sup>2</sup>J = 12.8 Hz, ArCH<sub>2</sub>Ar), 3.36 (t, 2H, <sup>3</sup>J = 4.8 Hz, CH<sub>2</sub>), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); FAB MS m/z 692.6 [M+H<sup>+</sup>].

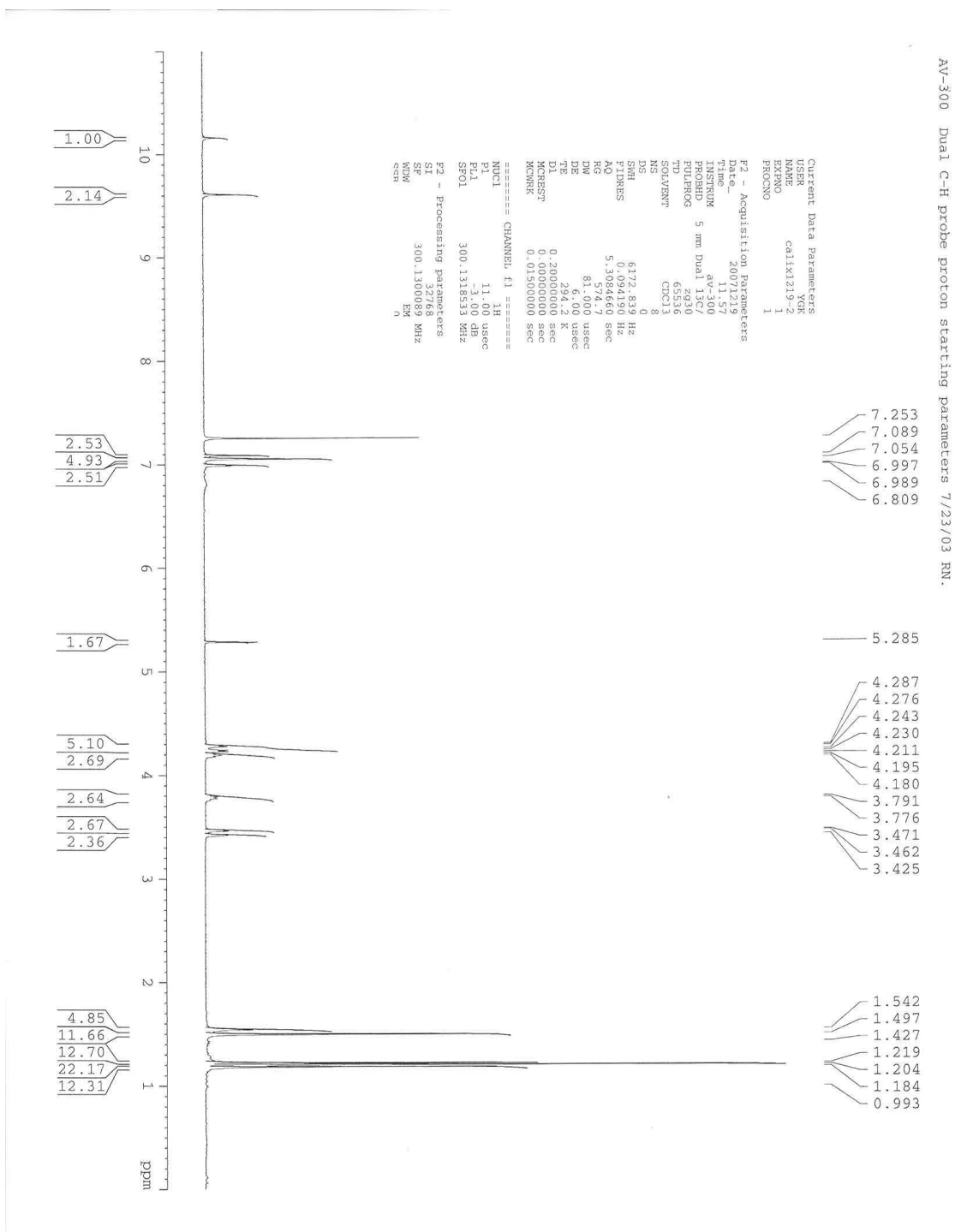
5,11,17,23-Tetra-*tert*-butyl-25-4-Aminobutyloxy-26,27,28-trihydroxycalix[4]arene (**7d**). Slightly yellow powder: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.07 (m, 4H, ArH-*m*), 7.03 (s, 2H, ArH-*m*), 6.98 (d, 2H, <sup>4</sup>J = 2.4 Hz, ArH-*m*), 4.28 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 4.25 (d, 2H, <sup>2</sup>J = 12.8 Hz, ArCH<sub>2</sub>Ar), 4.10 (m, 2H, OCH<sub>2</sub>), 3.45 (d, 2H, <sup>2</sup>J = 12.8 Hz, ArCH<sub>2</sub>Ar), 3.43 (d, 2H, <sup>2</sup>J = 13.2 Hz, ArCH<sub>2</sub>Ar), 3.29 (m, 2H, NCH<sub>2</sub>), 2.23 (m, 4H, CH<sub>2</sub>), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); HR FAB MS calcd for C<sub>48</sub>H<sub>65</sub>NO<sub>4</sub> 719.491369, found 719.490260.

## Reference

(S1) Bass, J. D.; Solovyov, A.; Pascall, A. J.; Katz, A. *J. Am. Chem. Soc.* **2006**, *128*, 3737-3747.



**Figure S2.**  $^1\text{H}$  NMR spectrum of **1a**.



**Figure S3.**  $^1\text{H}$  NMR spectrum of **1b**.

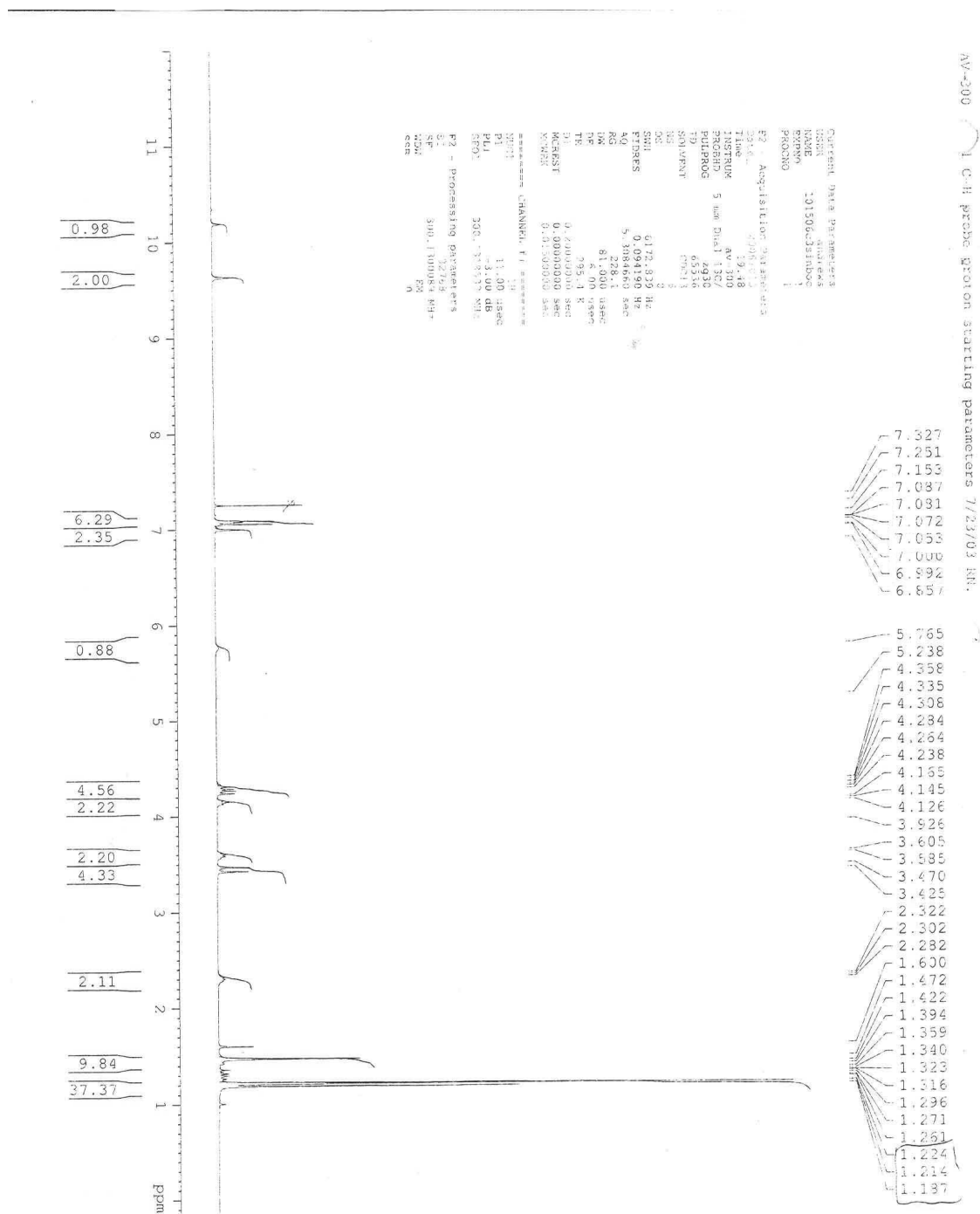
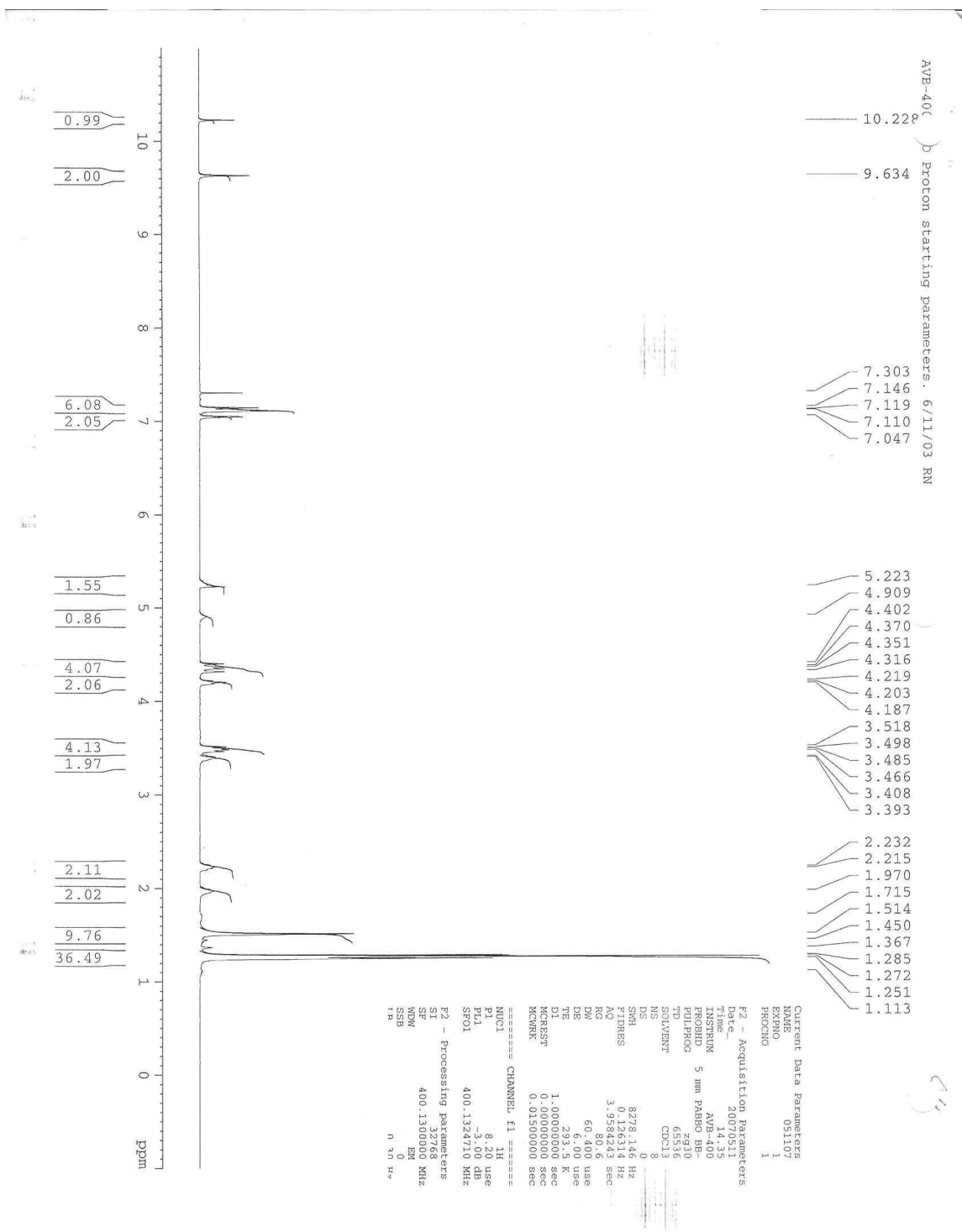


Figure S4.  $^1\text{H}$  NMR spectrum of **1c**.





**Figure S5.**  $^1\text{H}$  NMR spectrum of **1d**.



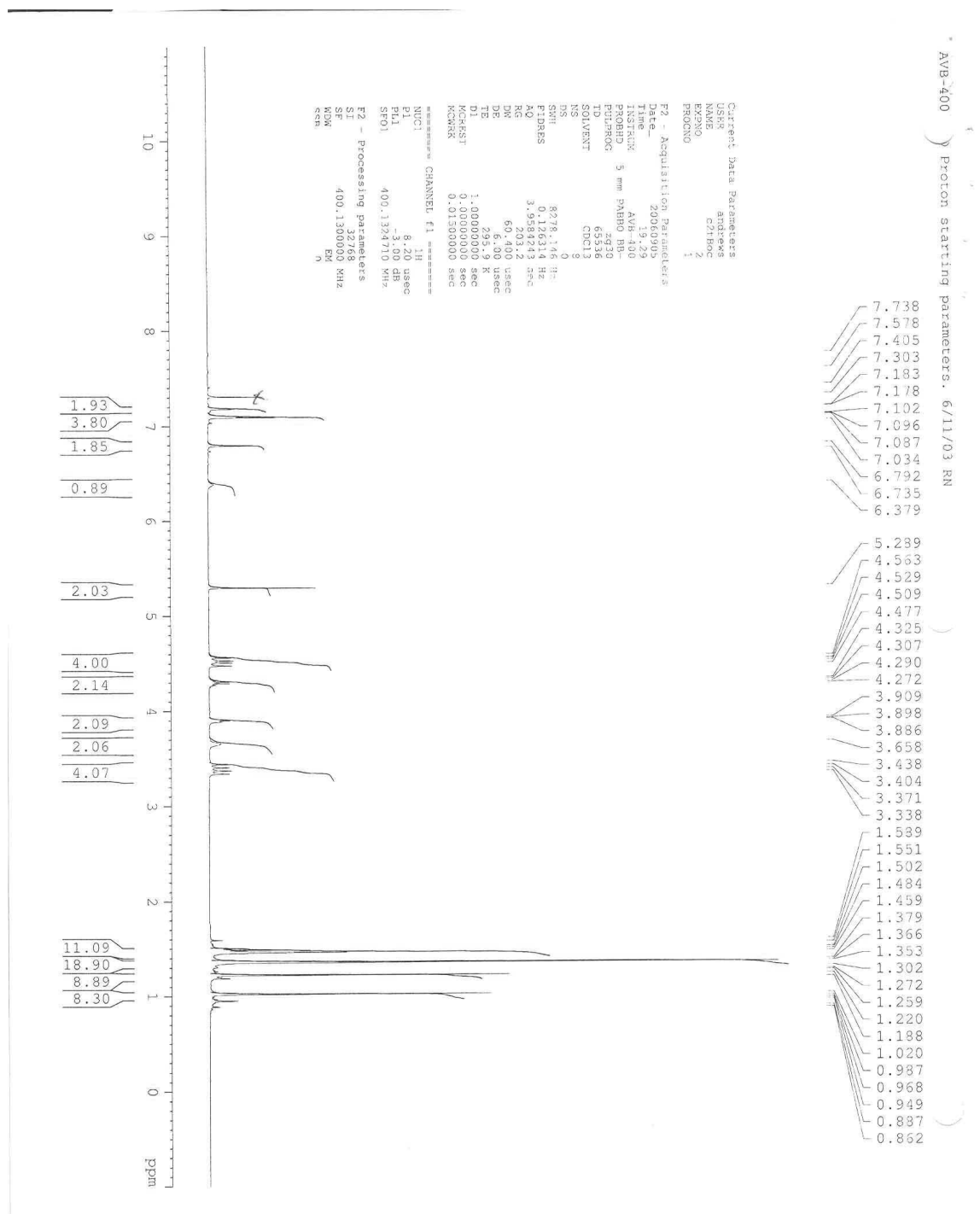


Figure S7.  $^1\text{H}$  NMR spectrum of **2b**.

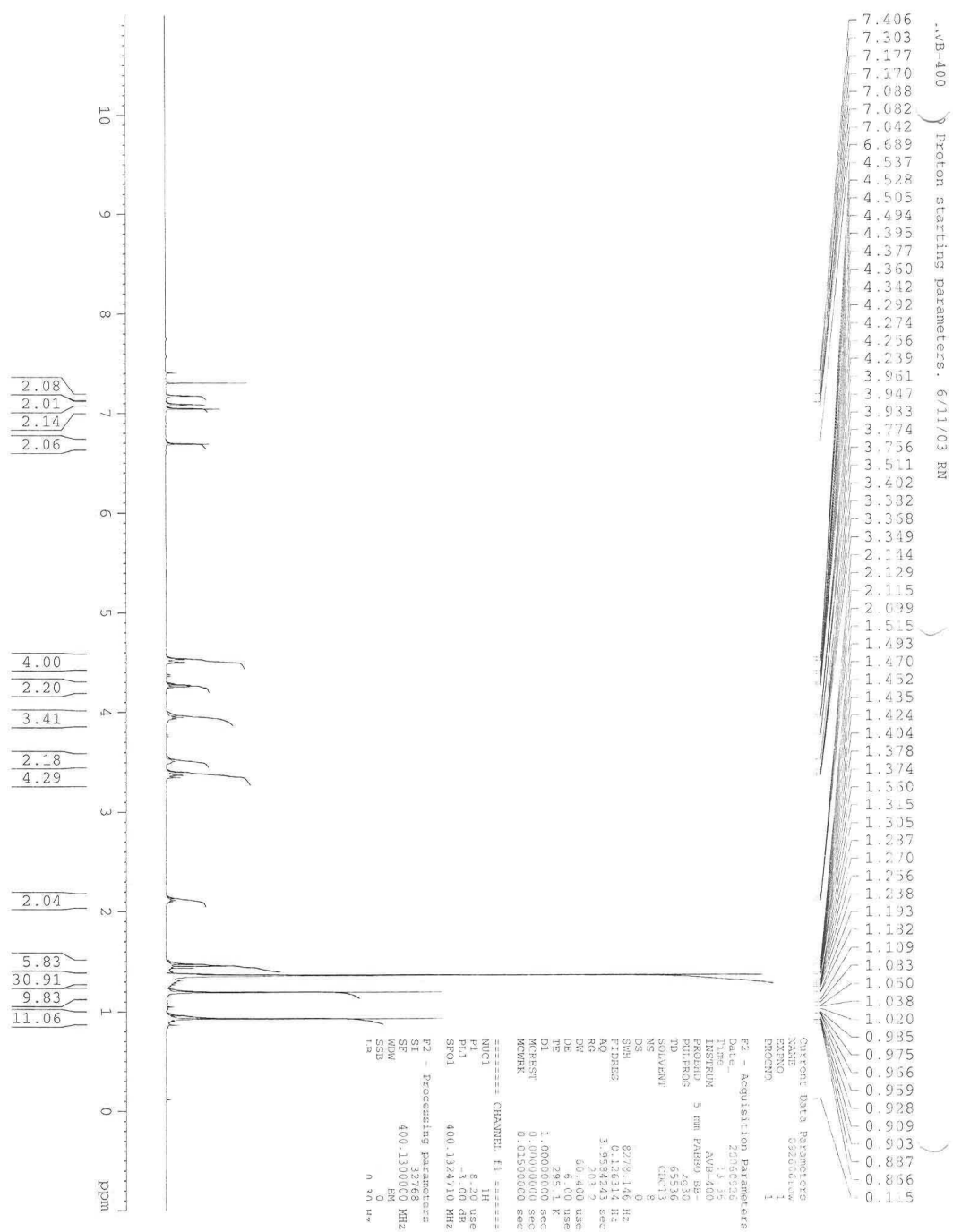
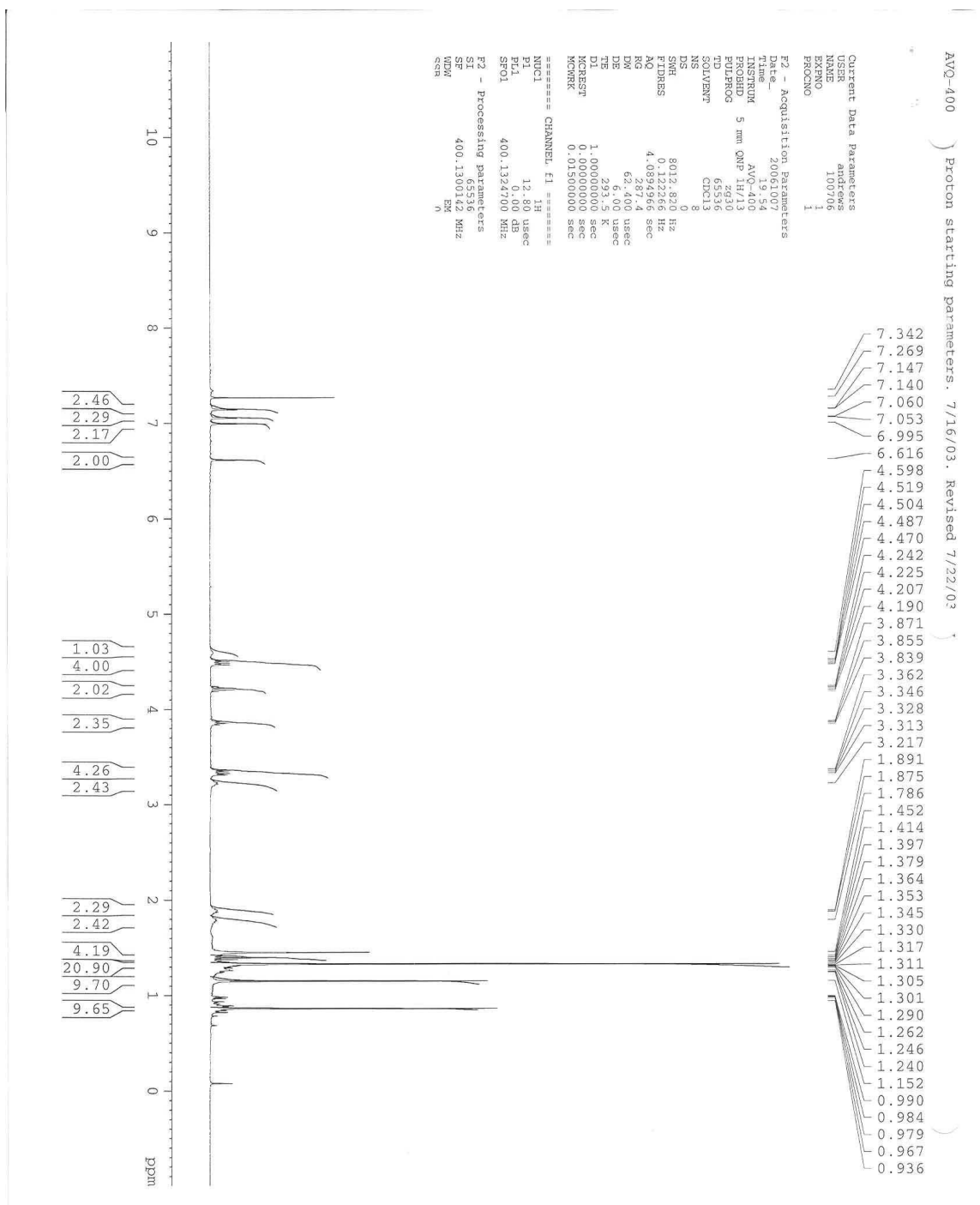


Figure S8.  $^1\text{H}$  NMR spectrum of **2c**.



**Figure S9.**  $^1\text{H}$  NMR spectrum of **2d**.

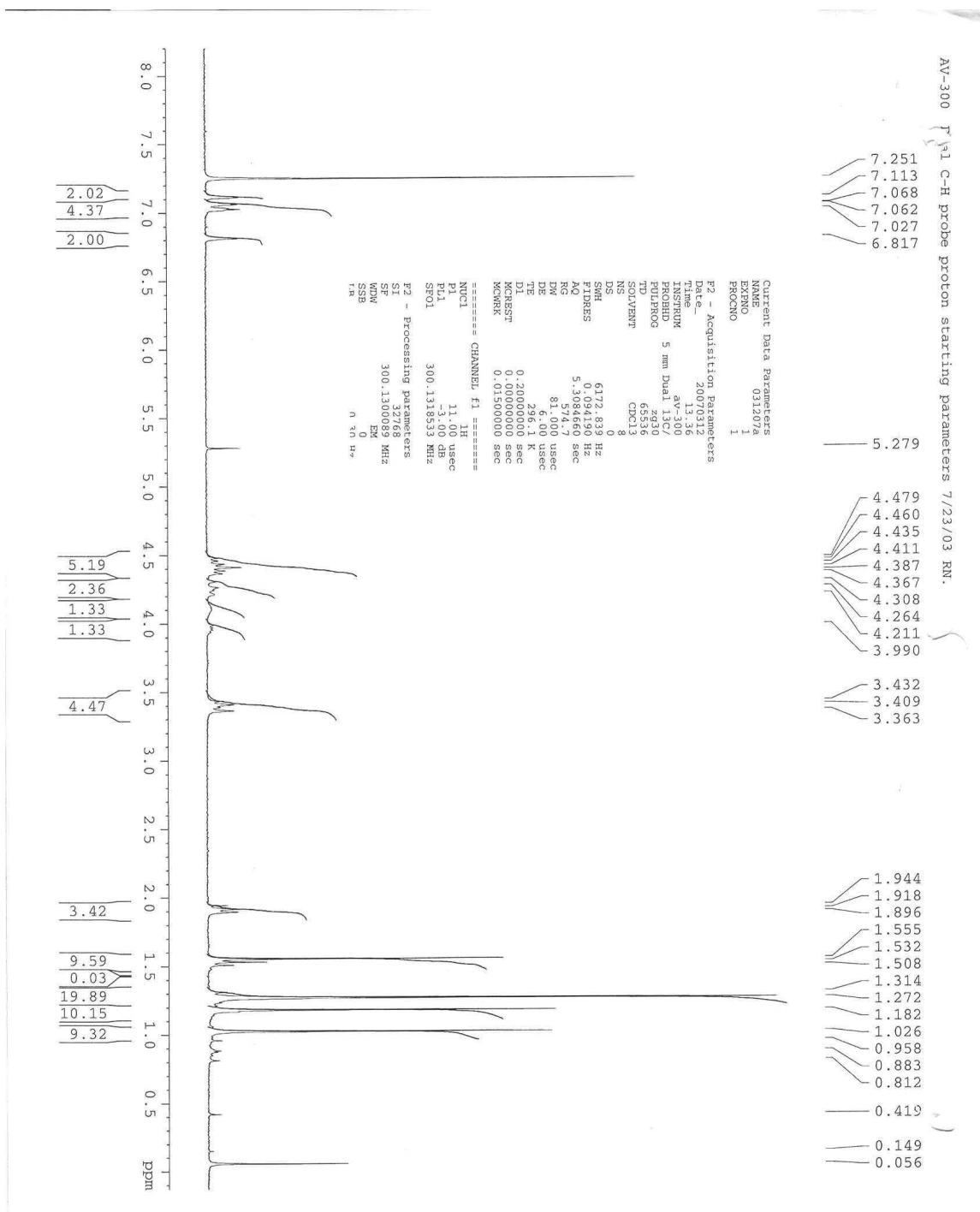


Figure S10. <sup>1</sup>H NMR spectrum of 3a.

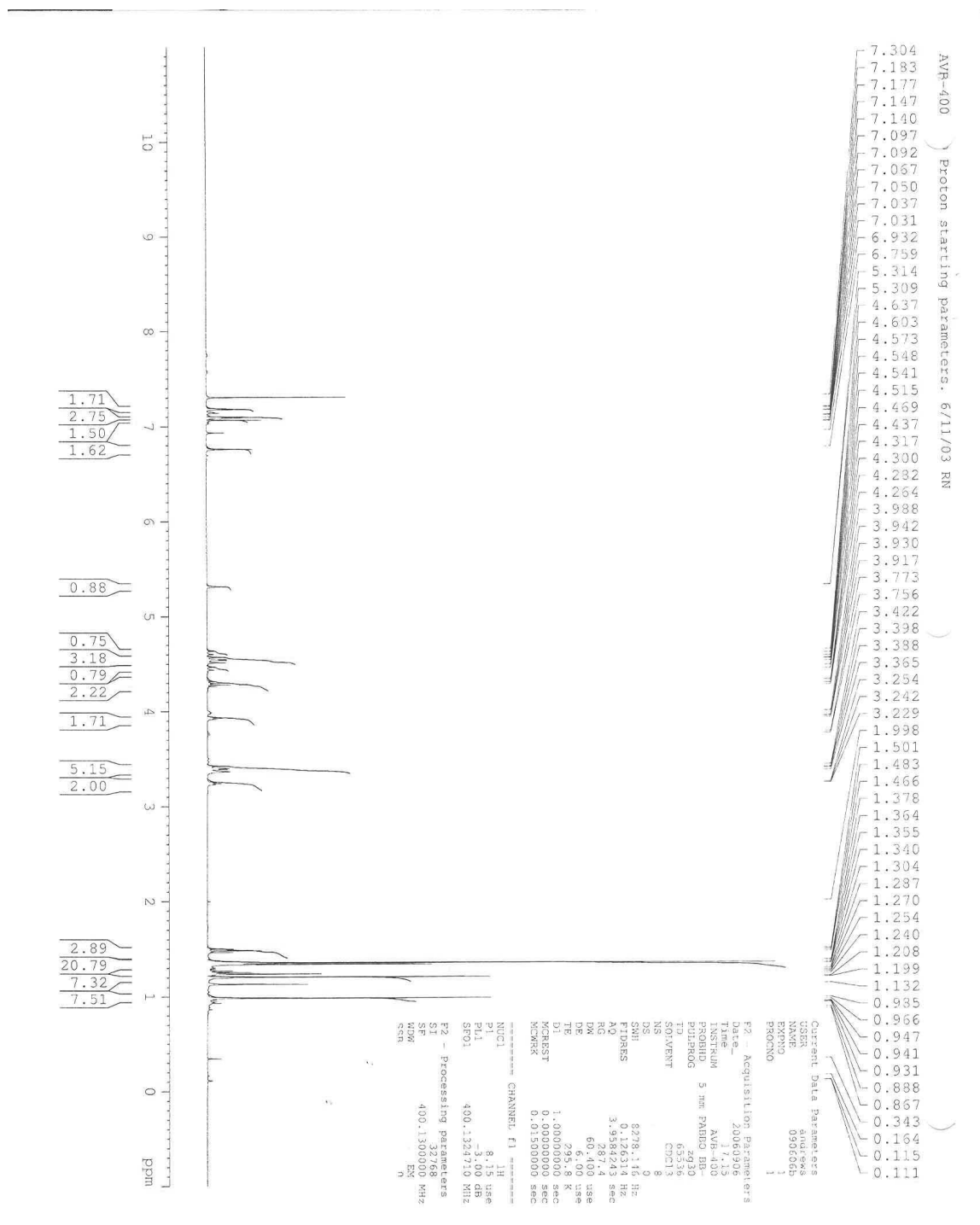


Figure S11.  $^1\text{H}$  NMR spectrum of **3b**.

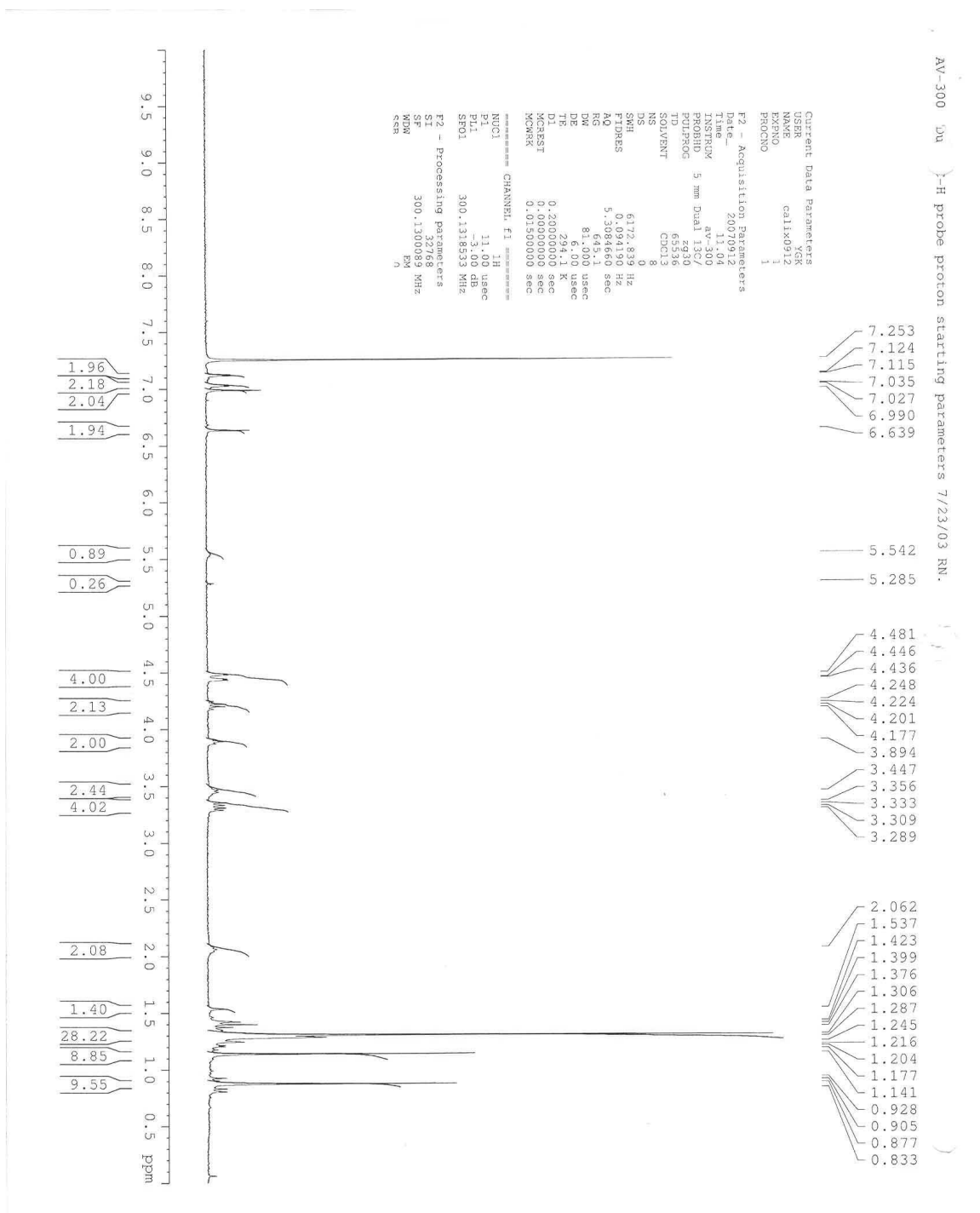


Figure S12. <sup>1</sup>H NMR spectrum of 3c.





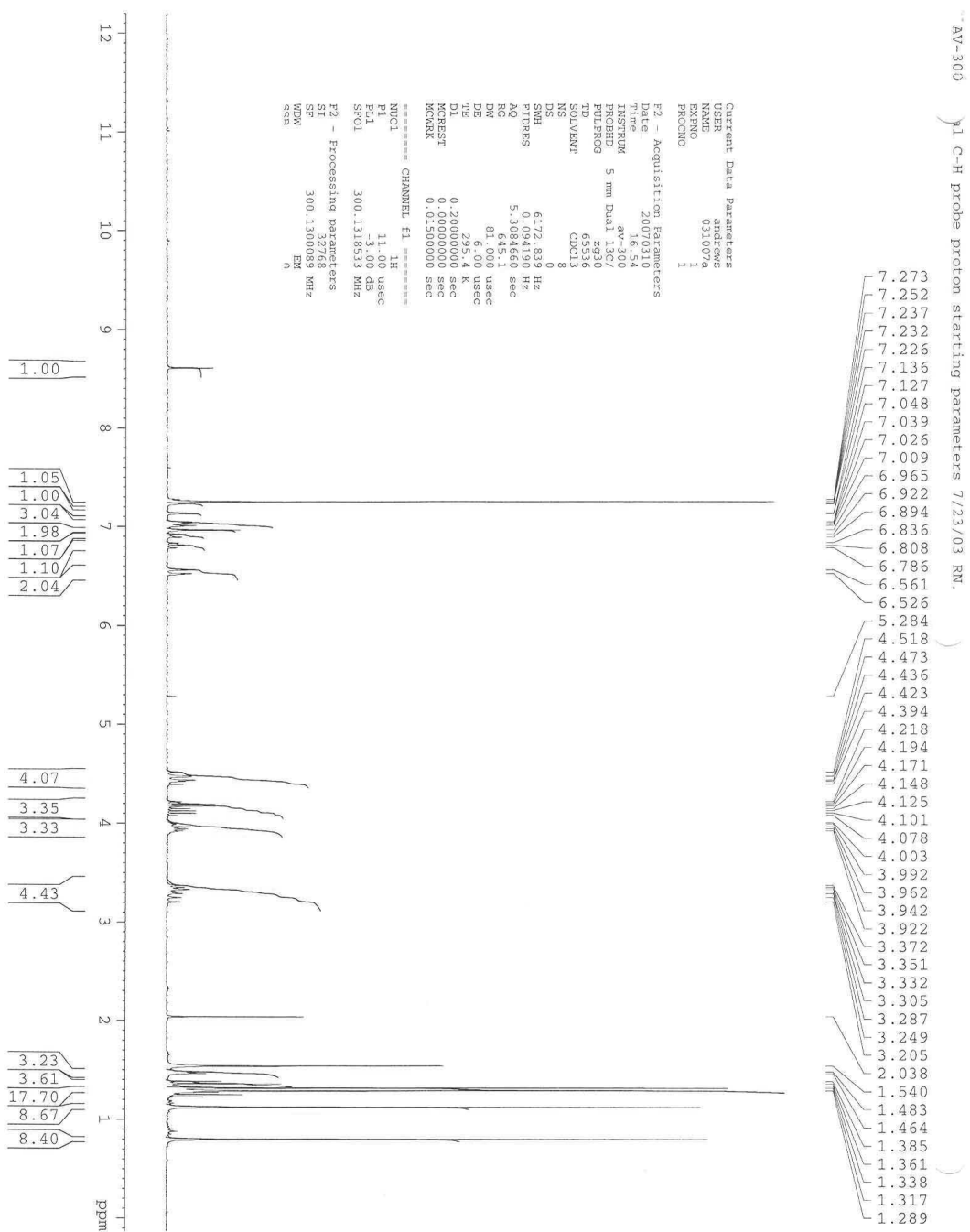


Figure S14. <sup>1</sup>H NMR spectrum of 6a.

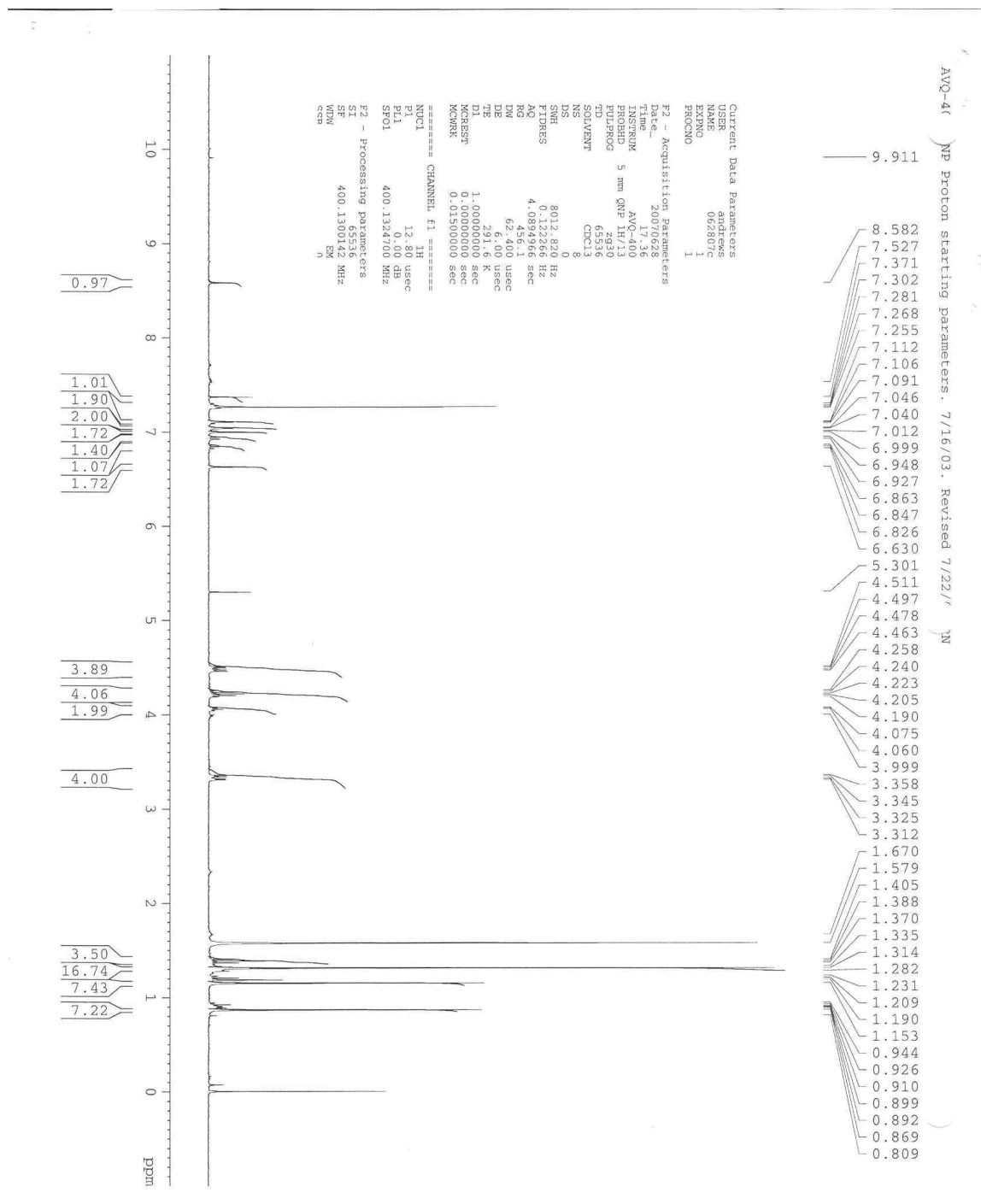


Figure S15.  $^1\text{H}$  NMR spectrum of **6b**.

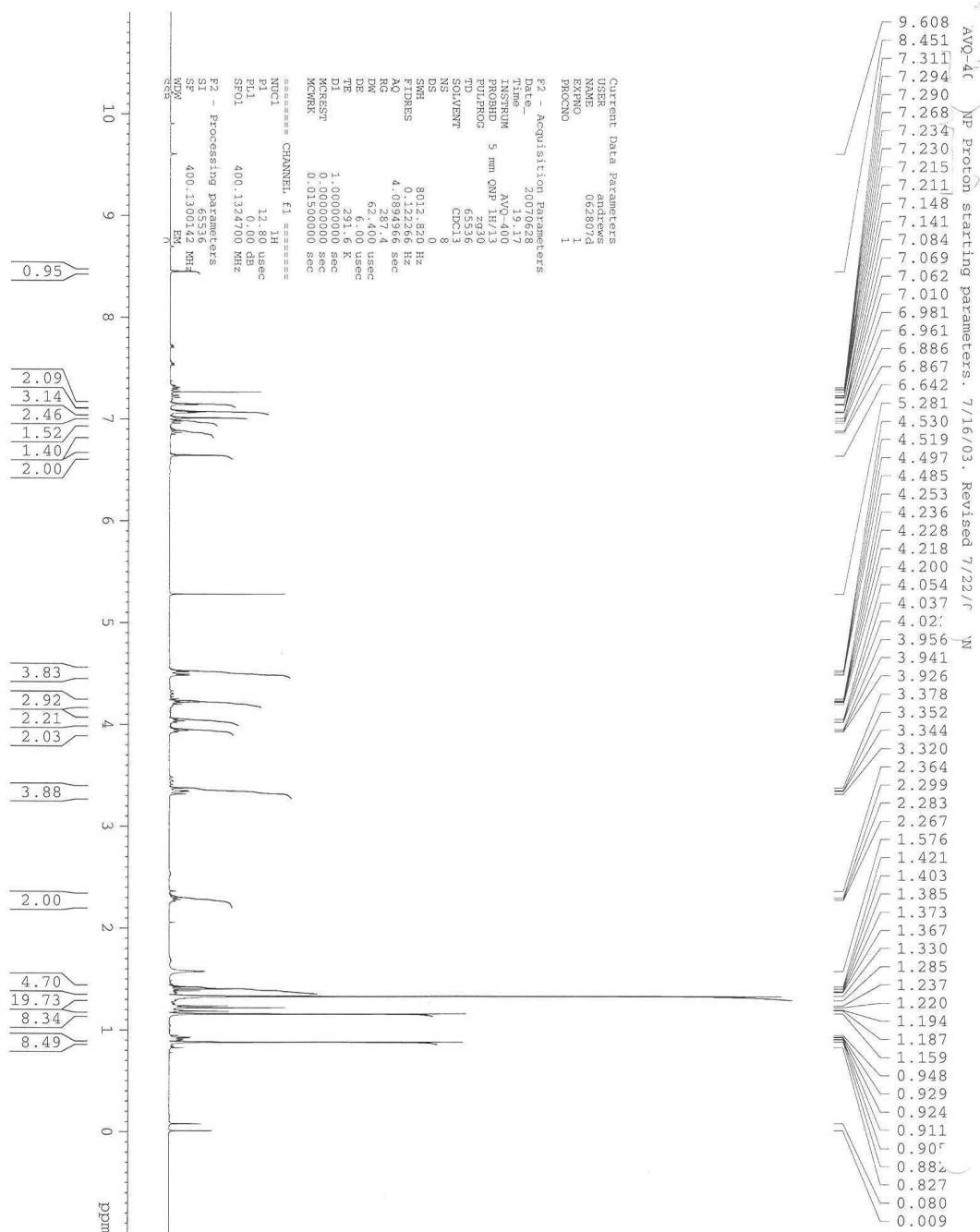


Figure S16.  $^1\text{H}$  NMR spectrum of **6c**.

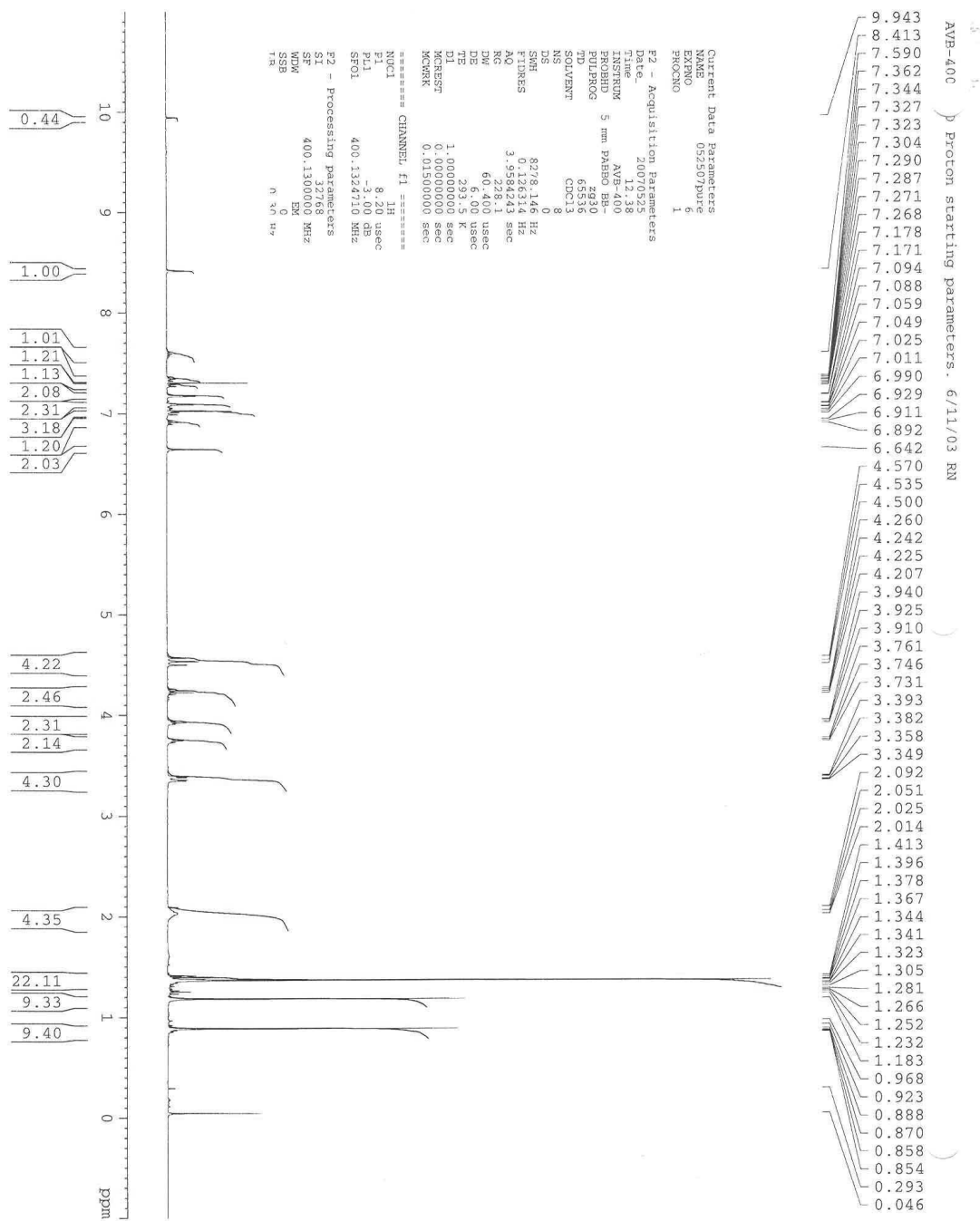


Figure S17. <sup>1</sup>H NMR spectrum of **6d**.

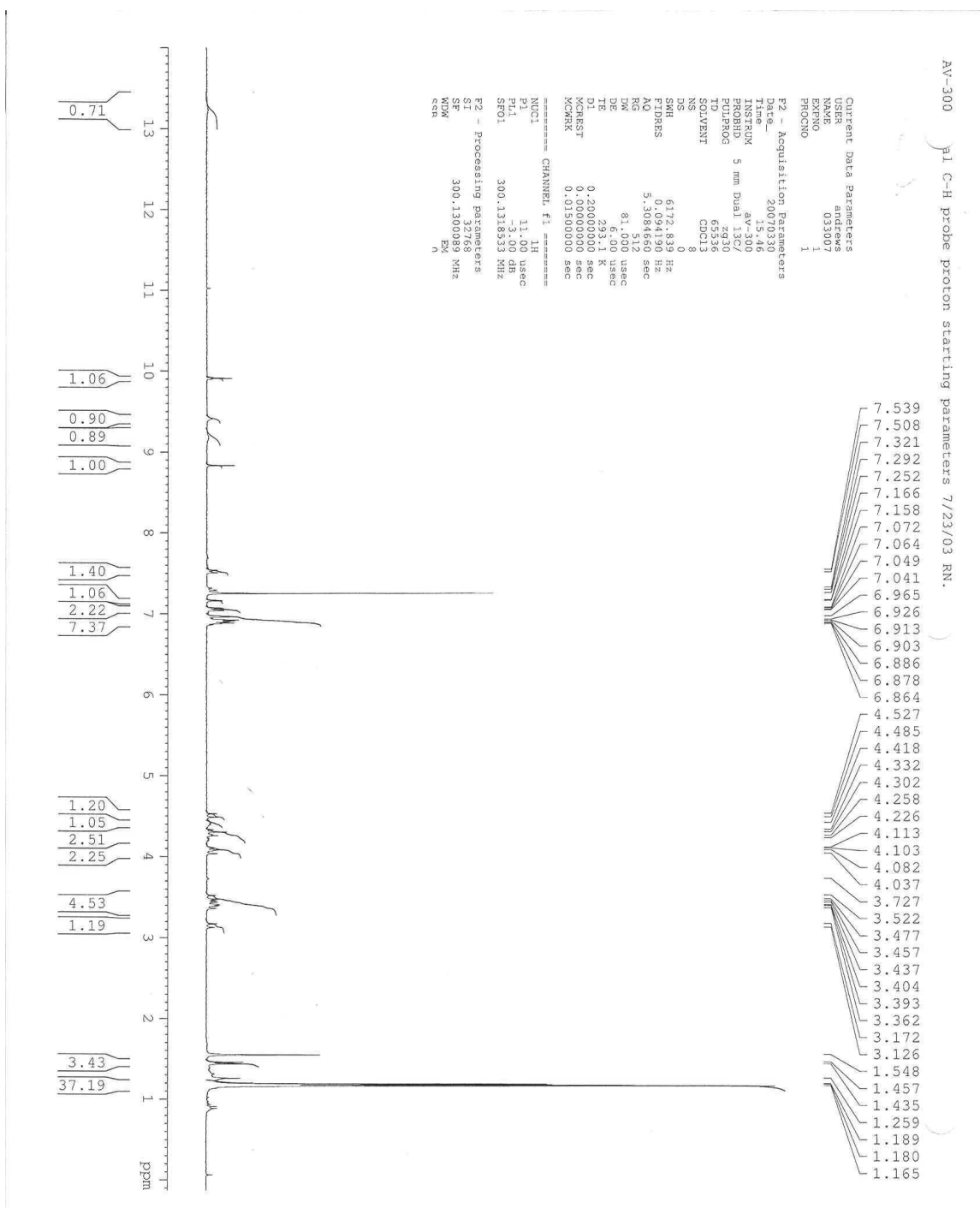


Figure S18. <sup>1</sup>H NMR spectrum of 8a.

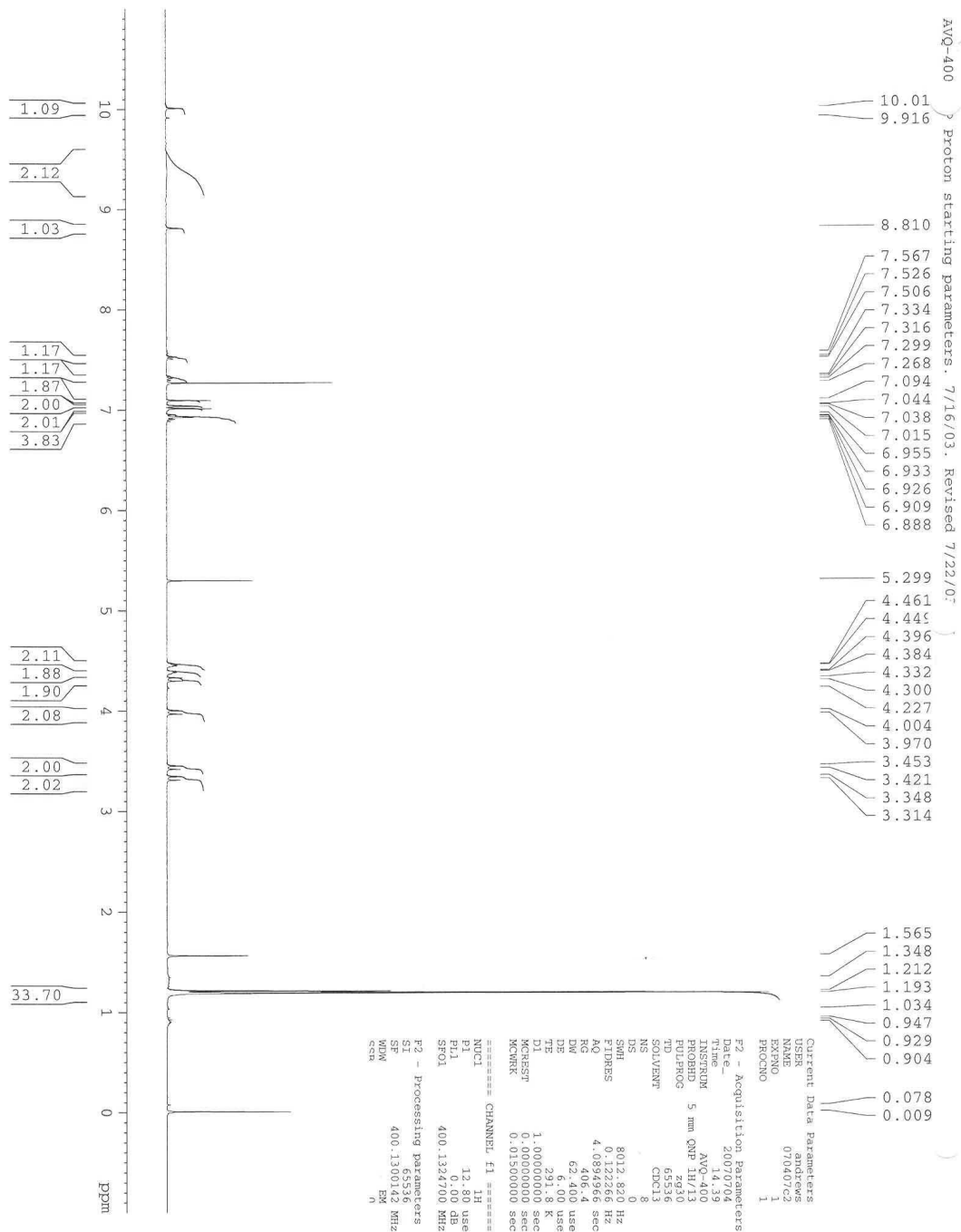


Figure S19.  $^1\text{H}$  NMR spectrum of **8b**.

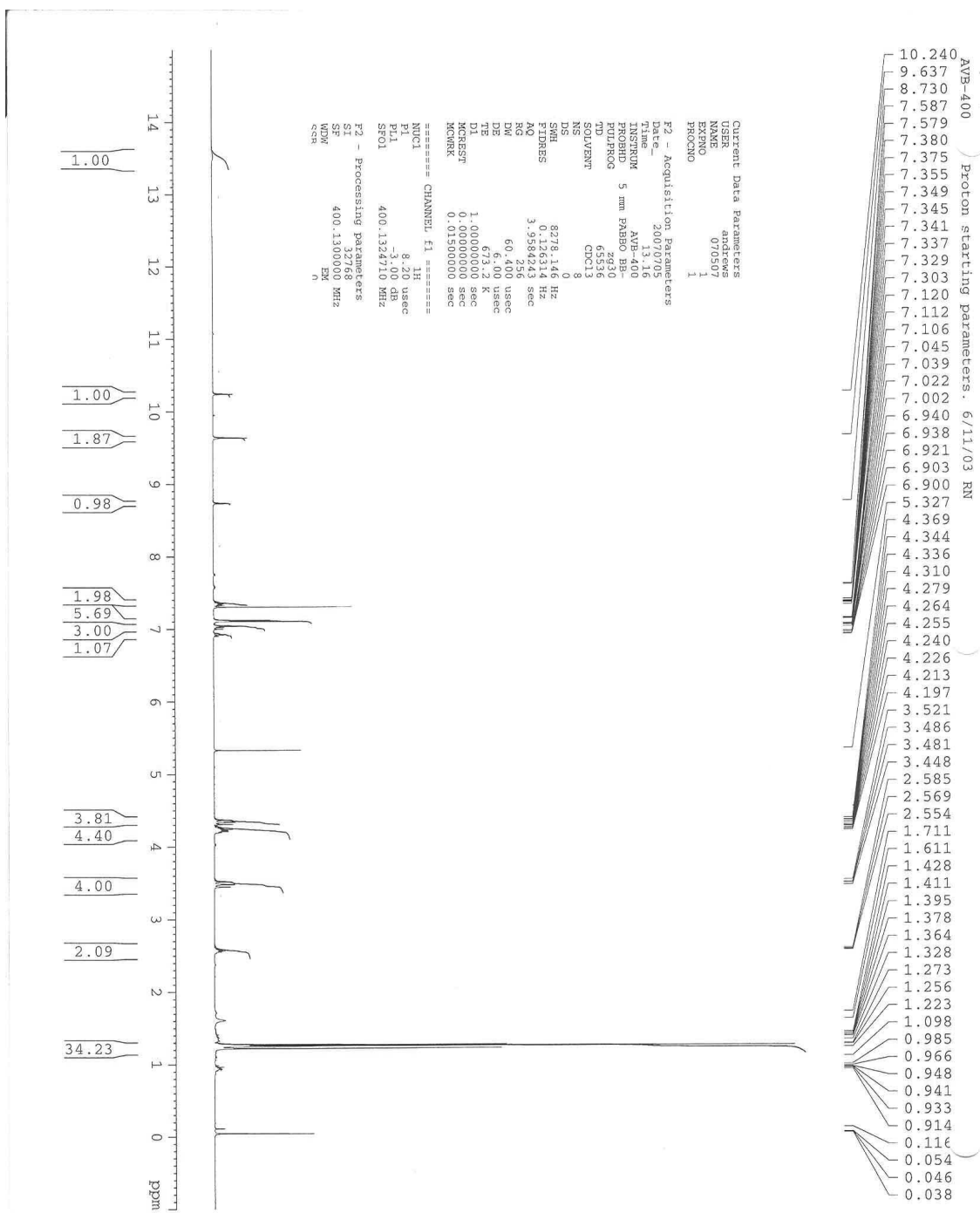


Figure S20.  $^1\text{H}$  NMR spectrum of **8c**.







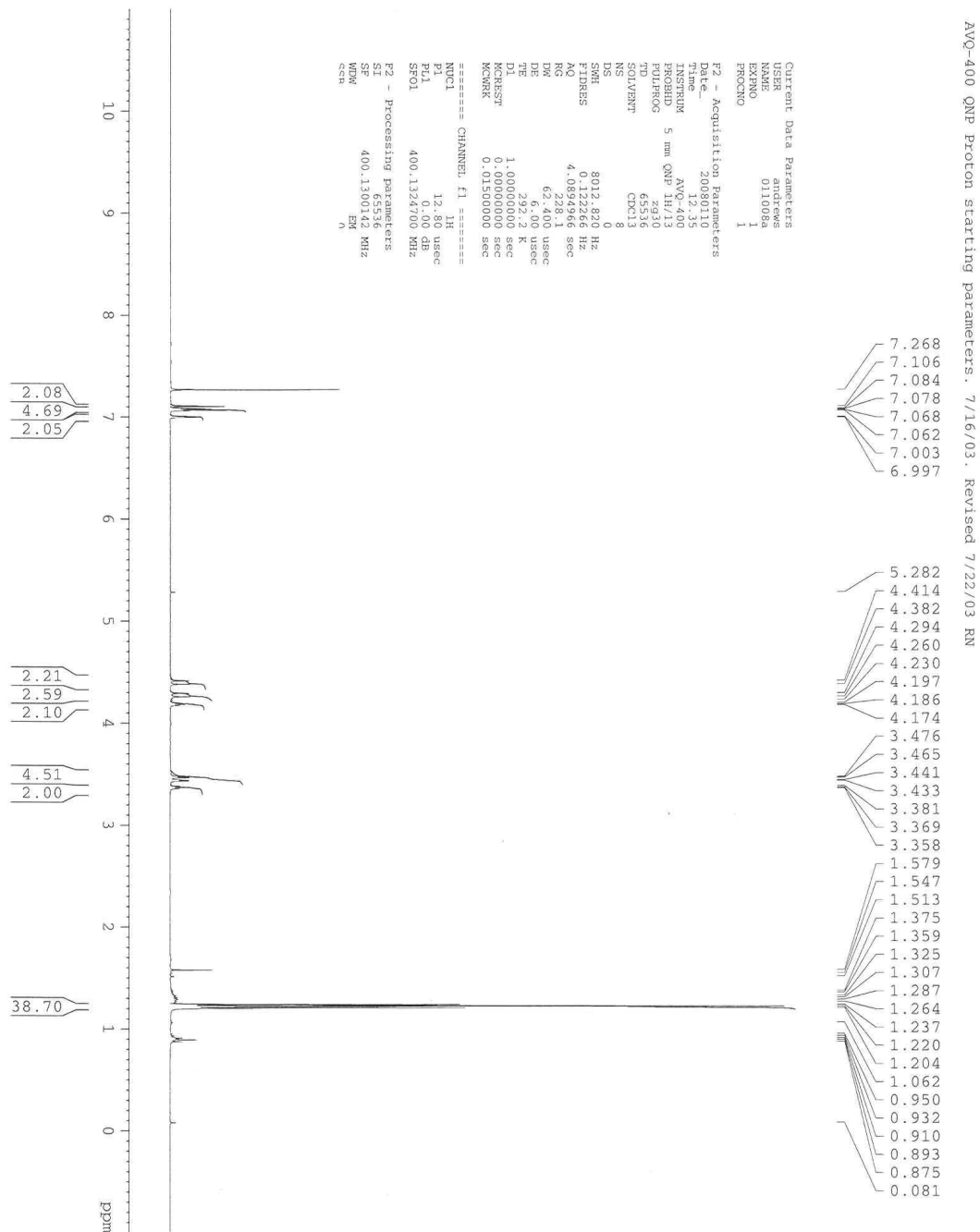


Figure S23.  $^1\text{H}$  NMR spectrum of **7b**.

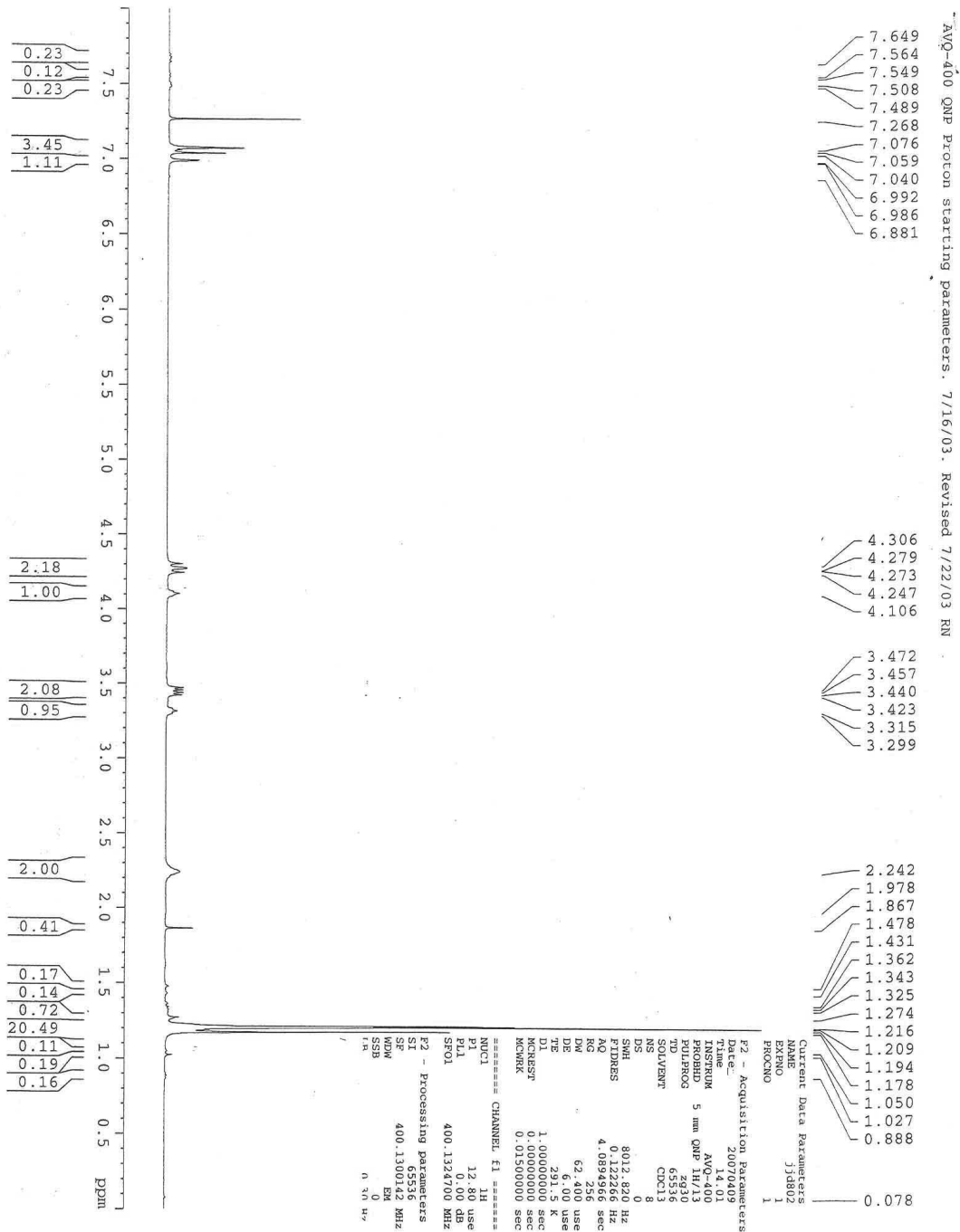


Figure S24.  $^1\text{H}$  NMR spectrum of **7d**.