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Supporting Information

5: A mixture of the tosylate **4** (6.887 g, 14.57 mmol) and thiourea (1.221 g, 16.04 mmol) in 36 mL of 95% EtOH was heated at 90°C for 20 h. After the solvent was removed and dried in vacuo, the residue was mixed with a solution of KOH (6.140 g, 93.01 mmol) in 35 mL of H₂O. The mixture was refluxed for 24 h under N₂. After cooling, the reaction mixture was acidified with 20 mL of 12N H₂SO₄ and extracted with CHCl₃ (50 mL x 3). The organic layer was dried over anhydrous MgSO₄ and then concentrated in vacuo. The crude product thus obtained was purified by silica gel column chromatography using CHCl₃/AcOEt (20 : 1) as an eluent to afford **5** (3.611 g, 74%) as a colorless oil. ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 14.15, 22.70, 24.28, 26.10, 29.36, 29.51, 29.63, 29.68, 31.93, 70.07, 70.25, 70.55, 70.70, 71.58, 72.89.

6: To a suspension of NaH (0.104 g, 2.383 mmol) in 2 mL of THF was added a solution of **5** (0.761 g, 2.275 mmol) in 2 mL of THF. After the mixture was stirred for a few minutes, ethyl 4-bromobutyrate (0.400 g, 2.05 mmol) in 2.5 mL of THF was added to the reaction mixture, which was stirred for 5 h at room temperature and then the solvent was removed under reduced pressure. The residue was mixed with 30 mL of H₂O, extracted with CHCl₃ (30 mL x 5), and dried over anhydrous MgSO₄, and then concentrated in vacuo. The crude product was purified by silica gel column chromatography using CH₂Cl₂/Et₂O (20 : 1) as an eluent to afford **6** (0.775 g, 84%) as a pale yellow oil. ¹³C NMR (100

MHz, CDCl₃) δ (ppm) 14.15, 14.24, 22.70, 24.81, 26.10, 29.37, 29.51, 29.63, 29.65, 29.68, 31.20, 31.73, 31.93, 33.01, 60.40, 70.06, 70.35, 70.59, 70.68, 70.93, 71.58, 173.11.

7: A solution of **6** (1.000 g, 2.229 mmol) in 11 mL of EtOH was treated with a solution of NaOH (0.462 g, 11.55 mmol) in 2 mL of H₂O at 80~90°C for 2 h, and then the solvent was removed in vacuo. The residue was mixed with 30 mL of H₂O and 5 mL of 3N HCl, extracted with CHCl₃ (30 mL x 3), and dried over anhydrous MgSO₄, and then concentrated in vacuo. The crude product was used without purification, because ¹H NMR spectrum of the crude **7** indicates exclusive formation of **7**. ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 14.15, 22.70, 24.58, 26.06, 29.37, 29.49, 29.52, 29.62, 29.65, 29.68, 31.12, 31.53, 31.93, 32.64, 70.02, 70.35, 70.58, 70.61, 71.19, 71.59, 177.94.

8: To a solution of **7** (1.00 g, 2.38 mmol) in 40 mL of CH₂Cl₂ and 0.4 mL of DMF was added oxalyl chloride (0.42 mL, 4.8 mmol) in one portion. The reaction mixture was heated at 50°C for 4 h. After evaporation of the solvent in vacuo, formation of **8** was ascertained by ¹H NMR ((200 MHz, CDCl₃) δ (ppm) 3.69-3.55 (m, 10H), 3.42 (t, 2H, J = 6.80 Hz), 3.02 (t, 2H, J = 7.08 Hz), 2.67 (t, 2H, J = 8.48 Hz), 2.60 (t, 2H, J = 6.96 Hz), 1.96 (m, 2H), 1.50 (m, 2H), 1.26 (s, 18H), 0.84(t, 3H)). A solution of the crude **8** (ca. 90% purity by ¹H NMR) solution in 15 mL of THF was added slowly to a mixture of 2,6-diaminopyridine (1.307 g, 11.98 mmol) and Et₃N (0.65 mL, 4.689 mmol), and then the mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo and the residue was mixed with 30 mL of H₂O and extracted with CHCl₃ (30 mL x 3). The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The crude product was purified by

silica gel column chromatography using $\text{CHCl}_3/\text{MeOH}$ (15 : 1) as an eluent to give **8** (1.01 g, 83%) as a pale yellow oil. ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.14, 22.69, 24.85, 26.07, 29.35, 29.20, 29.62, 29.67, 31.23, 31.72, 31.92, 35.93, 70.03, 70.31, 70.56, 70.63, 70.91, 71.56, 103.19, 104.23, 140.11, 149.71, 157.08, 170.67.

1: Amide **8** (2.40 g, 4.69 mmol) and Et_3N (0.97 mL, 7.0 mmol) were dissolved in THF (40 mL). Glutaryl chloride (0.40 mL, 3.1 mmol) was added dropwise to the mixture and it was stirred for 19 h at room temperature. After evaporation of the solvent, the residue was mixed with H_2O (40 mL) and extracted with CHCl_3 (40 mL x 3). The organic layers were combined and dried over anhydrous MgSO_4 . After concentration in vacuo, chromatography on SiO_2 (CHCl_3 -acetone = 3:1) gave **1** (1.98 g, 76%). M.p. 99.2-102.4°C (acetone); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.15, 20.98, 22.69, 24.69, 26.08, 29.36, 29.50, 29.62, 29.64, 29.67, 31.26, 31.72, 31.92, 35.78, 36.05, 70.01, 70.30, 70.56, 70.62, 70.86, 71.57, 109.43, 109.56, 140.68, 149.35, 149.56, 171.07, 171.20; IR (KBr): ν = 3306, 1671 cm^{-1} ; FABMS: m/z = 1119 ($[\text{M}]^+$); elemental analysis for $\text{C}_{59}\text{H}_{102}\text{N}_6\text{O}_{10}\text{S}_2$: calcd C 63.29, H 9.18, N 7.51; found C 63.00, H 9.30, N 7.42.

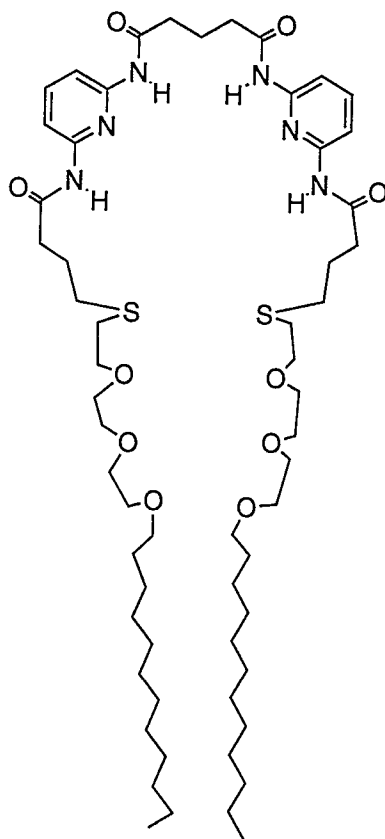
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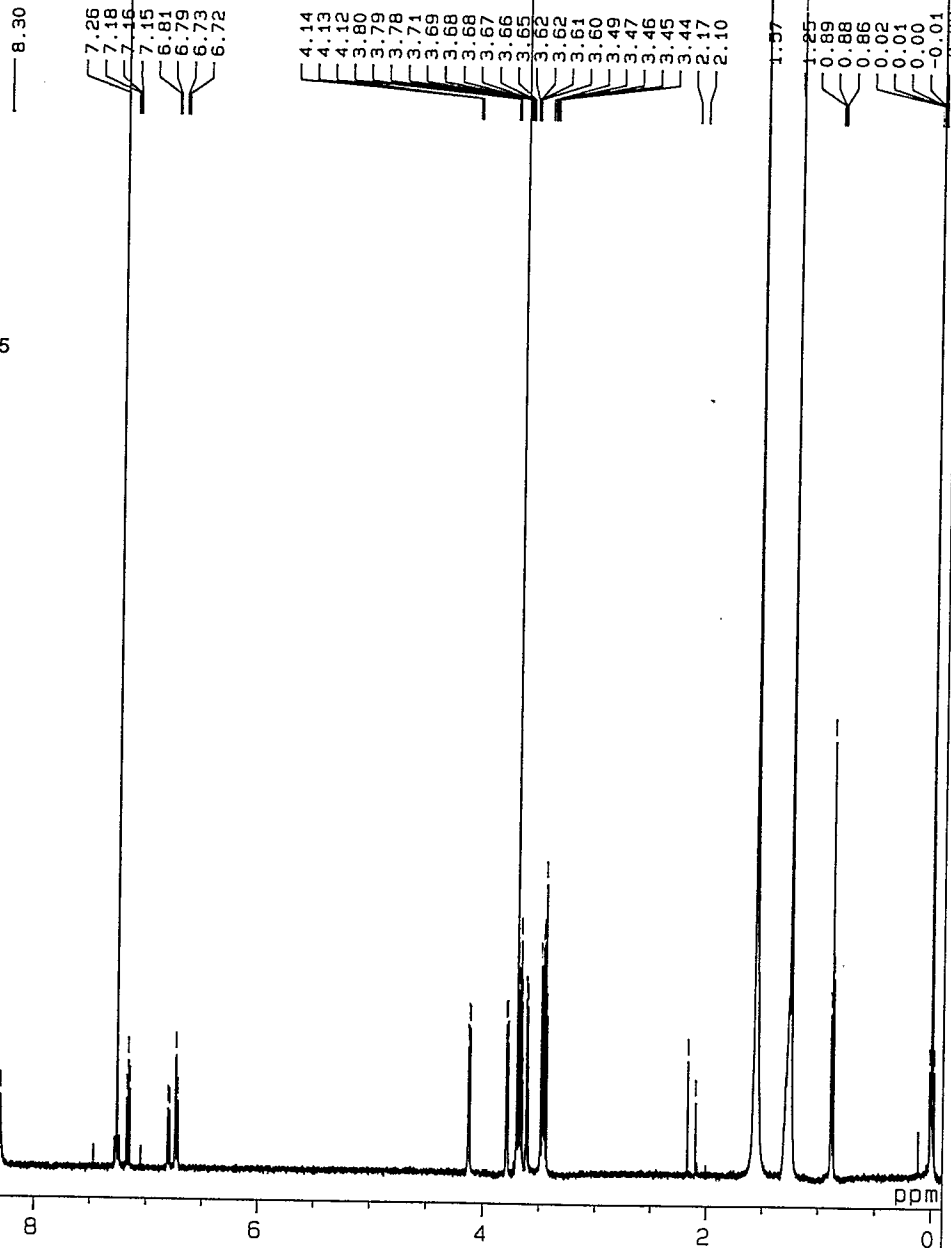
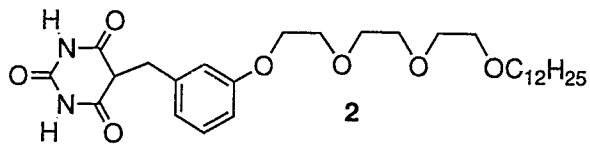
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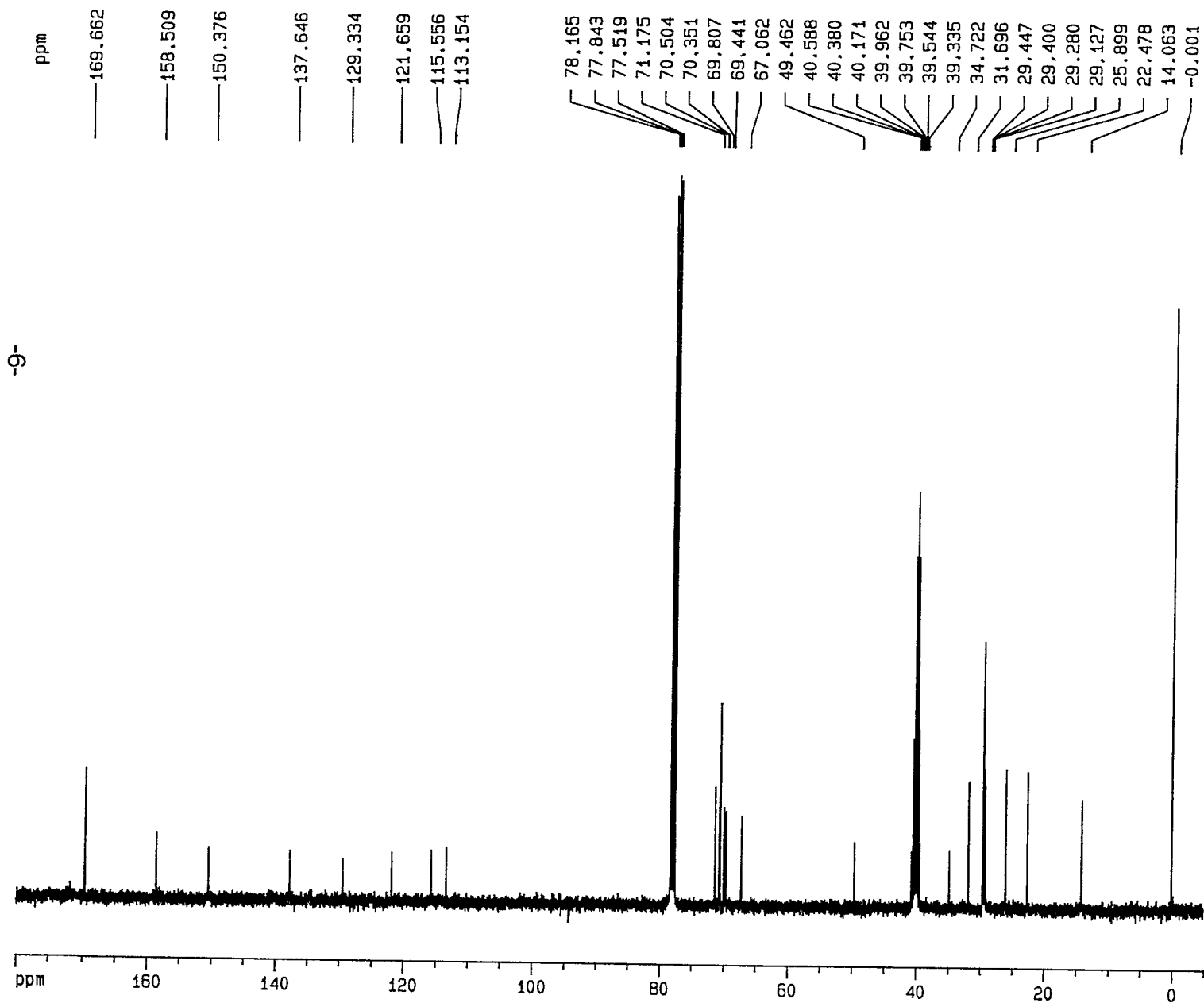
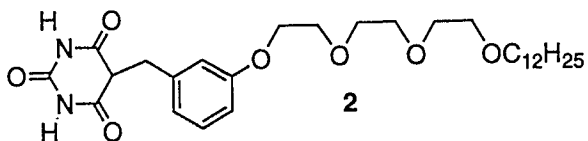
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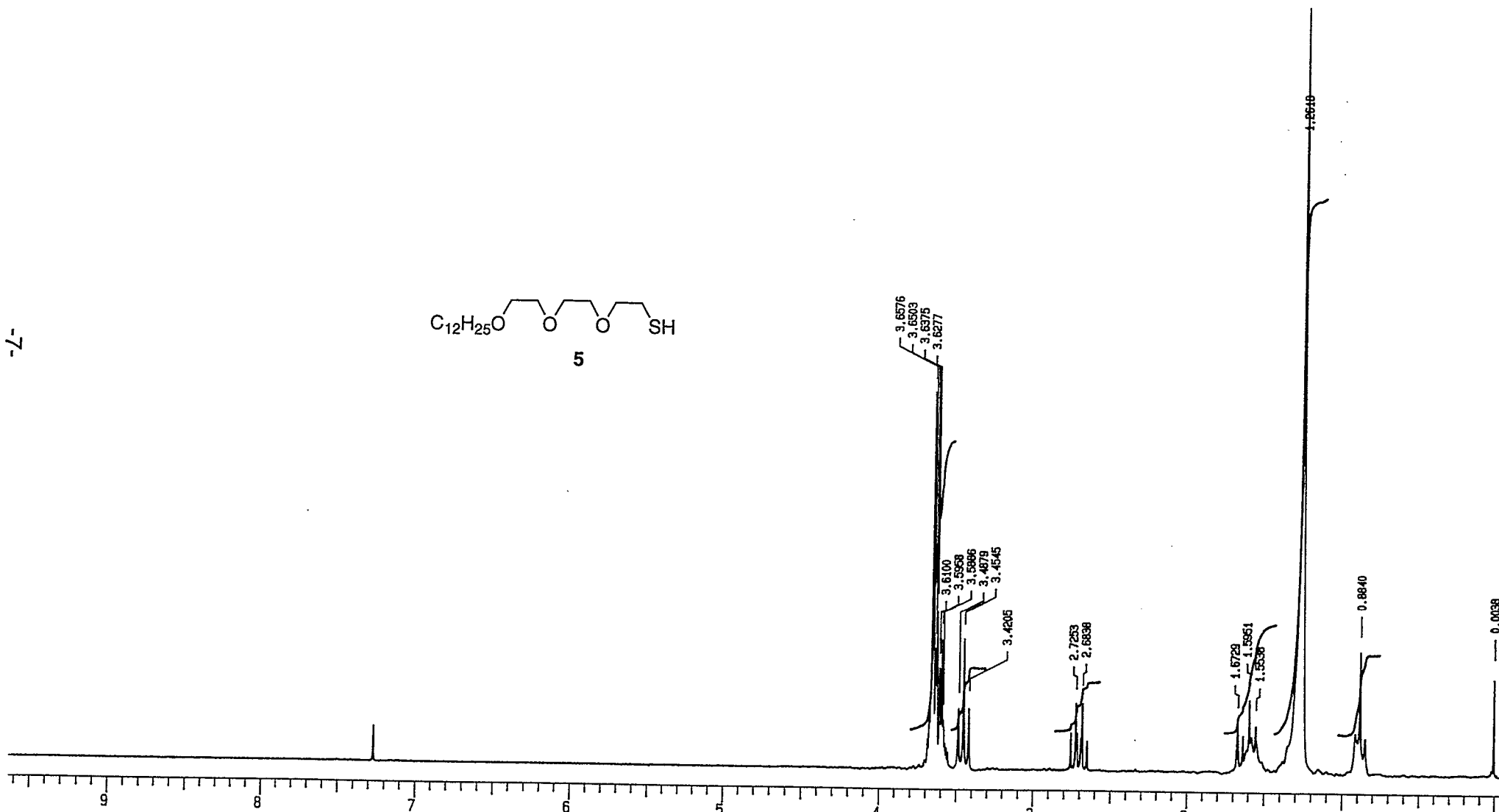
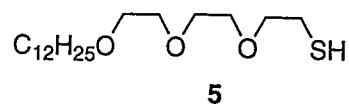
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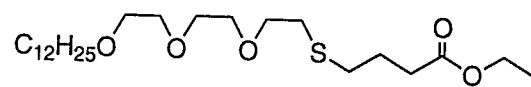
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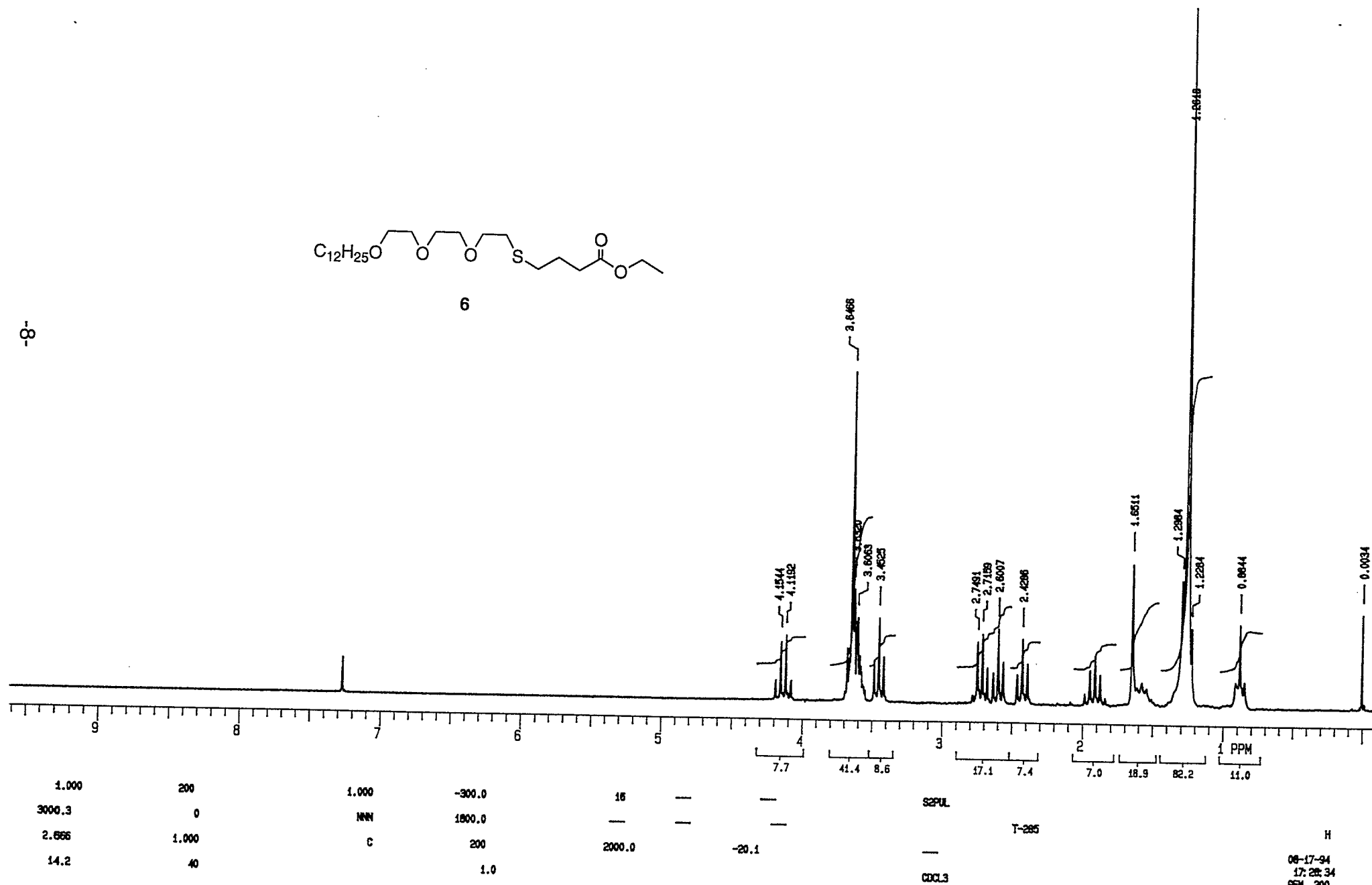
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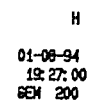
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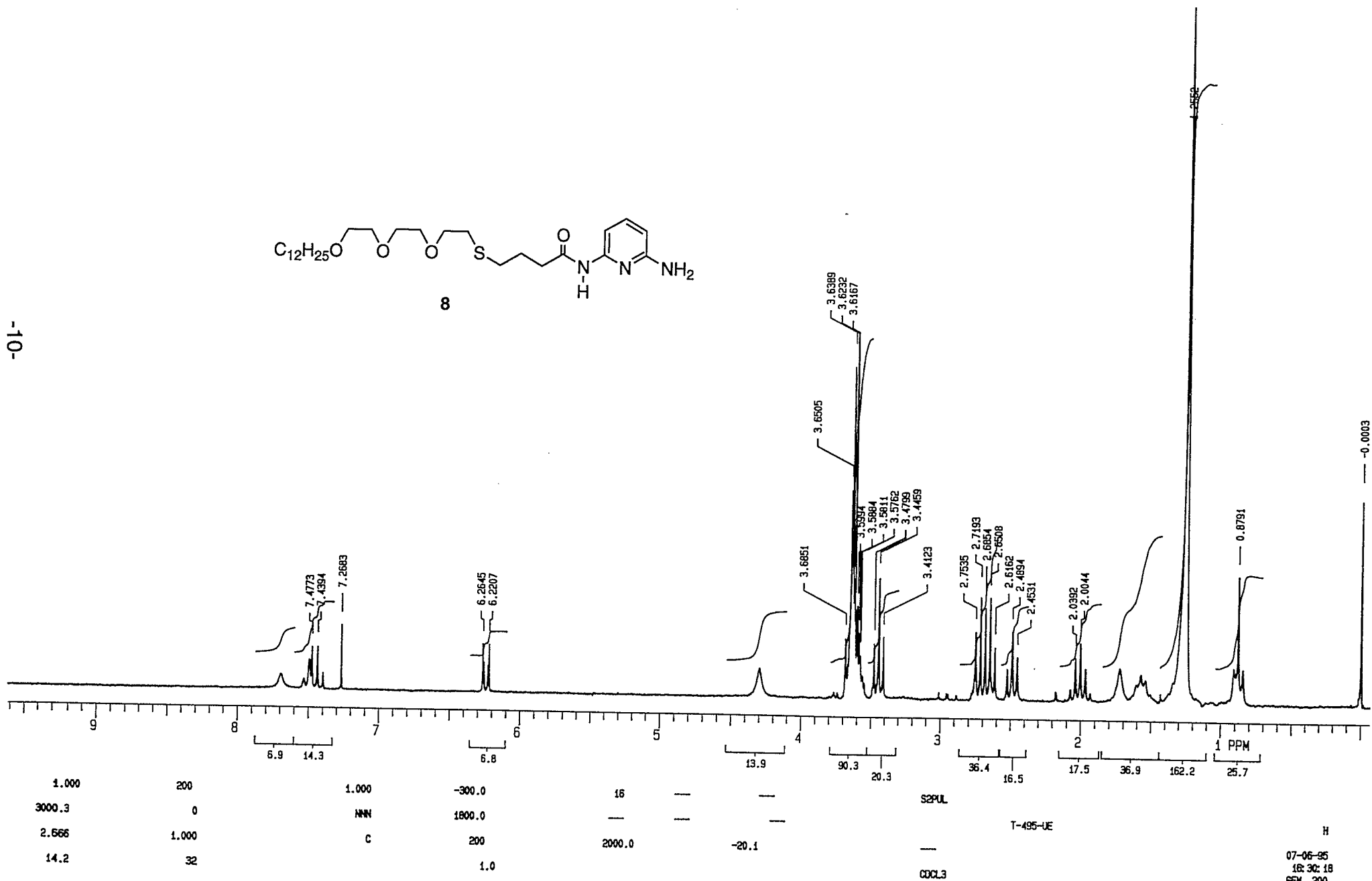
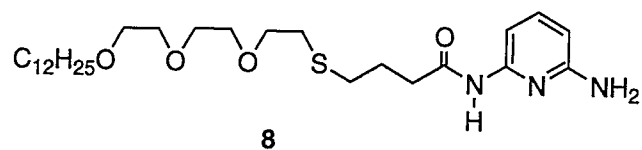
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Isotope Patterns of Observed and Calculated ESIMS Spectra
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