Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Oxidatively Stable, Aqueous Europium(II) Complexes through Steric and Electronic Manipulation of Cryptand Coordination Chemistry**

*Nipuni-Dhanesha H. Gamage, Yujiang Mei, Joel Garcia, and Matthew J. Allen**

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Materials and Methods

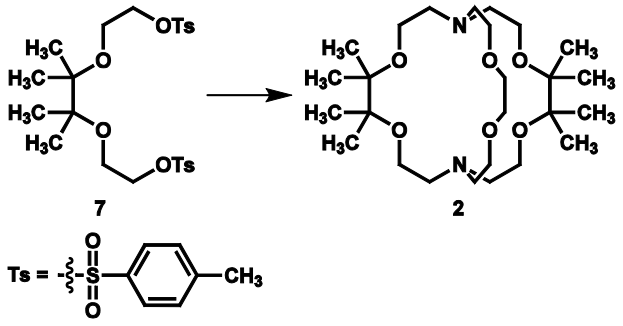
Commercially available chemicals were of reagent-grade purity or better and were used without further purification unless otherwise noted. Human hemoglobin was obtained from RayBiotech Inc. (catalog number: MD-22009P). Water was purified using a PURELAB Ultra Mk2 water purification system (ELGA). Dichloromethane was purified using a solvent purification system (Vacuum Atmospheres Company). Triethylamine was distilled from CaH_2. 2,2'-(2,3-Dimethylbutane-2,3-diyl)bis(oxy)bis(ethane-2,1-diyl)bis(4-methylbenzenesulfonate), **7**, was synthesized using a previously published procedure.[1]

Flash chromatography was performed using silica gel 60, 230–400 mesh (EMD Chemicals).[2] Analytical thin-layer chromatography (TLC) was carried out on ASTM TLC plates precoated with silica gel 60 F_{254} (250 μm layer thickness). TLC visualization was accomplished using a UV lamp followed by charring with potassium permanganate stain (3 g $KMnO_4$, 20 g K_2CO_3, 5 mL 5% w/v aqueous NaOH, 300 mL H_2O).

^{1}H NMR spectra were obtained using a Varian Unity 300 (300 MHz) spectrometer and a Mercury 400 (400 MHz) spectrometer, ^{13}C NMR spectra were obtained using a Varian Unity 300 (75 MHz) spectrometer and a Mercury 400 (101 MHz) spectrometer. ^{19}F NMR spectra were obtained using Varian Unity 300 (282 MHz) spectrometer. Chemical shifts are reported relative to residual solvent signals unless otherwise noted ($CDCl_3$: ^{1}H: δ 7.27, ^{13}C: δ 77.23; CD_3OD: ^{1}H: δ 3.31, ^{13}C: δ 49.00; $CFCl_3$ (internal standard): ^{19}F δ 0.00). NMR data are assumed to be first order, and the apparent multiplicity is reported as "s" = singlet, "d" = doublet, "dd" = doublet of doublets, "t" = triplet, "td" = triplet of doublets, "q" = quartet, "m" = multiplet, or "brs" = broad singlet. Italicized elements are those that are responsible for the shifts. High-resolution electrospray ionization mass spectra (HRESIMS) were obtained on an electrospray time-of-flight

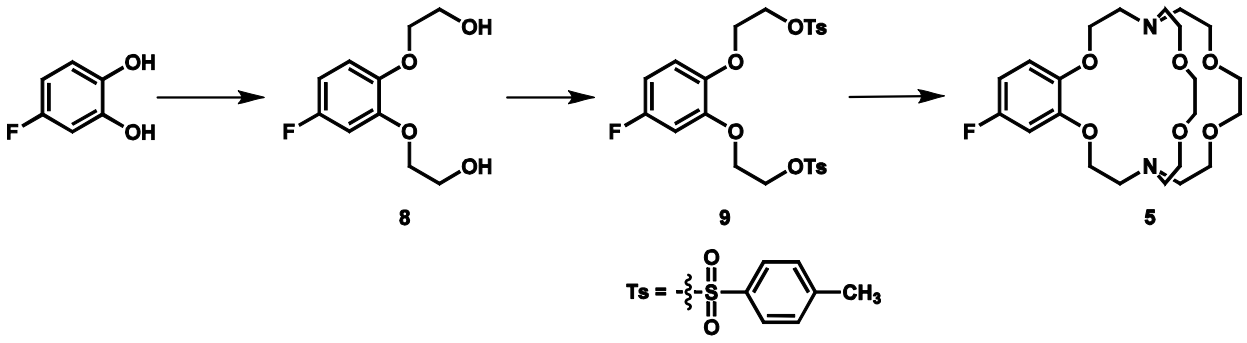
high-resolution Waters Micromass LCT Premier XE mass spectrometer. Cyclic voltammetric analyses were performed using a WaveNow USB potentiostat (Pine Research Instrumentation). A standard three-electrode cell was used with a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode (1.0 M KCl). All electrochemical experiments were performed under an Ar atmosphere at ambient temperature with Et_4NClO_4 (0.05 M) as the supporting electrolyte, an aqueous solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 0.01 M, pH 7.5) as the solvent, and the ferrocene/ferrocinium (Fc/Fc^+) redox couple as an internal standard (*3*). From the initial potential of the analysis (–1.5 V), the voltage was ramped to 0.75 V and back to –1.5 V at a scan rate of 150 mV/s. Data points were collected every 3.35 ms, and the measurements were repeated 3–6 times each with independently prepared samples. After each measurement, ferrocene (6.7 mM in acetonitrile) was added to the sample (0.13 mM ferrocene after addition) and the measurement was repeated to enable referencing to Fc/Fc^+.[3]

Synthetic Procedures and Characterization



5,5,6,6,14,14,15,15-Octamethyl-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2): To a mixture of Cs_2CO_3 (0.866 g, 2.66 mmol, 6 equiv) in acetonitrile (60 mL) at reflux was added a solution of ditosylate **7** (0.467 g, 0.907 mmol, 2.05 equiv) and 2,2'-(ethylenedioxy) bis(ethylamine) (649 μL, 0.443 mmol, 1 equiv) in acetonitrile (120 mL) dropwise over 48 h.

Upon completion of the addition, the resulting reaction mixture was heated at reflux for 48 h. Solvent was removed under reduced pressure, and purification was performed using silica gel chromatography (stepwise gradient of 50:1→10:1→8:1 dichloromethane/methanol) to yield 61 mg (28%) of **2** as a yellow oil. ^{1}H NMR (300 MHz, CD_3OD, δ): 1.23 and 1.25 (overlapping s, C*H*$_3$, 24H), 2.51–2.72 (m, C*H*$_2$, 12H), 3.42–3.82 (m, C*H*$_2$, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 20.8 (*C*H$_3$), 53.3 (*C*H$_2$), 56.9 (*C*H$_2$), 59.3 (*C*H$_2$), 67.8 (*C*H$_2$), 68.7 (*C*H$_2$), 81.1; TLC: R_f = 0.46 (8:1 dichloromethane/methanol); HRESIMS (*m*/*z*): $[M + H]^+$ calcd for $C_{26}H_{53}N_2O_6$, 489.3904; found, 489.3914.



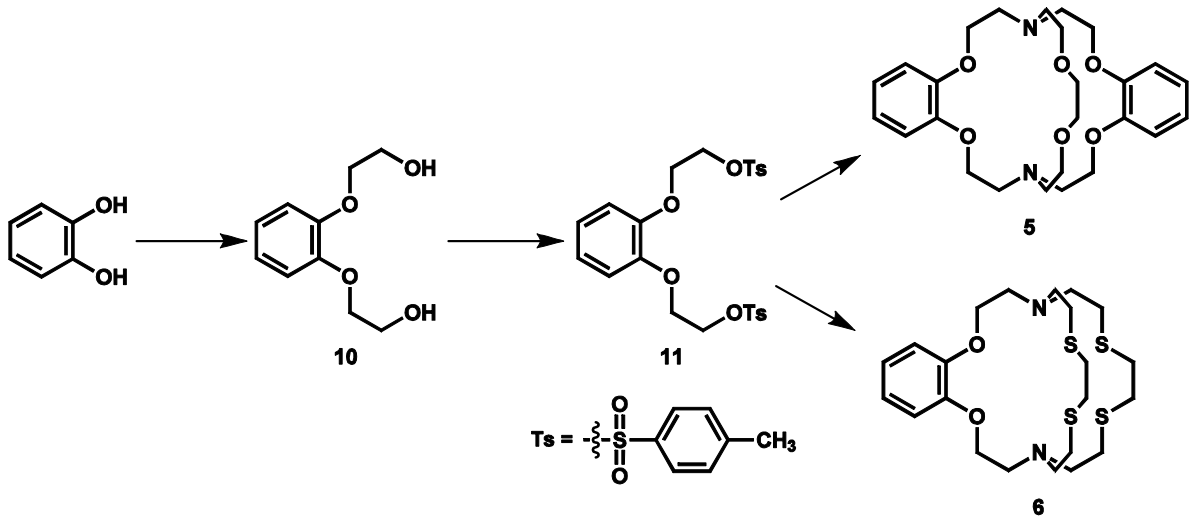
2,2'-(4-Fluoro-1,2-phenylene)bisoxydiethanol (8): To a degassed solution of water (1 mL), 1-butanol (2.5 mL), and NaOH (0.545 g, 13.6 mmol, 3 equiv) under an atmosphere of Ar was added 4-fluorobenzene-1,2-diol (0.580 g, 4.54 mmol, 1 equiv), and the resulting mixture was heated at reflux. After 5 min at reflux, a solution of 2-chloroethanol (912 μL, 13.6 mmol, 3 equiv) in degassed 1-butanol (15 mL) was added dropwise over 1 h while maintaining reflux. The resulting solution was heated at reflux for 18 h at which point the solvent was removed under reduced pressure. Purification was performed using silica gel chromatography (stepwise gradient of 1:0→40:1→20:1→5:1 dichloromethane/methanol) to yield 643 mg (66%) of **8** as a

pale brown solid. ^{1}H NMR (300 MHz, CD_3OD, δ): 3.82–3.93 (m, CH_2, 4H), 4.04 (q, J = 4.8 Hz, CH_2, 4H), 6.60 (td, J = 9.0, 3.3 Hz, C*H*, 1H), 6.79 (dd, J = 3.0, 10.5 Hz, C*H*, 1H), 6.91–6.99 (m, C*H*, 1H); ^{13}C NMR (75 MHz, CD_3OD, δ): 61.5 (*C*H_2), 61.7 (*C*H_2), 72.0 (*C*H_2), 72.9 (*C*H_2), 103.1 (d, $^{2}J_{C–F}$ = 27.2 Hz, *C*H), 107.4 (d, $^{2}J_{C–F}$ = 22.1 Hz, *C*H), 116.68 (d, $^{3}J_{C–F}$ = 10.0 Hz, *C*H), 146.4 (d, $^{4}J_{C–F}$ = 2.3 Hz), 151.4 (d, $^{3}J_{C–F}$ = 10.1 Hz) 159.1 (d, $^{1}J_{C–F}$ = 237.7 Hz, *C*F); ^{19}F NMR (282 MHz, CD_3OD, δ): –121.5 to –121.4 (m, C*F*); TLC: R_f = 0.22 (40:1 dichloromethane/methanol); HRESIMS (*m*/*z*): $[M + H]^+$ calcd for $C_{10}H_{14}O_4F$, 217.0876; found, 217.0874.

2,2'-(4-Fluoro-1,2-phenylene)bisoxybis(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (9): To a mixture of diol **8** (0.501 g, 2.30 mmol, 1 equiv) and triethylamine (3 mL) at 0 °C under an atmosphere of Ar was added a solution of 4-methylbenzene-1-sulfonyl chloride (1.32 g, 6.90 mmol, 3 equiv) in dichloromethane (9 mL) dropwise over 30 min. Upon completion of the addition, the mixture was warmed to ambient temperature and stirred for 24 h. The resulting solution was washed sequentially with water (3 × 25 mL), saturated aqueous $NaHCO_3$ (3 × 25 mL), and saturated aqueous citric acid (3 × 25 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Purification was performed using silica gel chromatography (stepwise gradient of 1:0→3:1→1:1 hexanes/ethyl acetate) to yield 0.930 g (77%) of **8** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.44 (s, CH_3, 6H), 4.08–4.18 (m, CH_2, 4H), 4.25–4.37 (m, CH_2, 4H), 6.47–6.62 (m, C*H*, 2H), 6.72–6.81 (m, C*H*, 1H), 7.34 (d, J = 7.8 Hz, C*H*, 4H), 7.80 (d, J = 7.8 Hz, C*H*, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.8 (*C*H_3), 67.4 (*C*H_2), 68.1 (*C*H_2), 68.5 (*C*H_2), 68.6 (*C*H_2), 103.7 (d, $^{2}J_{C–F}$ = 26.2 Hz, *C*H), 108.1 (d, $^{2}J_{C–F}$ = 22.2 Hz, *C*H), 118.2 (d, $^{3}J_{C–F}$ = 9.0 Hz, *C*H), 128.1 (*C*H), 130.1 (*C*H), 132.9,

144.6, 145.2, 149.7 (d, $^{3}J_{C–F}$ = 10.0 Hz), 158.3 (d, $^{1}J_{C–F}$ = 241.7 Hz, *C*F); ^{19}F NMR (282 MHz, $CDCl_3$, δ): –118.5 to –118.4 (m, C*F*); TLC: R_f = 0.27 (3:1 hexanes/ethyl acetate); HRESIMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{24}H_{25}O_8FS_2Na$, 547.0873; found, 547.0872.

5,6-(4-Fluorobenzo)-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacos-5-ene (4): To a mixture of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (0.052 g, 0.20 mmol, 1 equiv) and anhydrous Cs_2CO_3 (0.652 g, 2.00 mmol, 10 equiv) under an atmosphere of Ar was added anhydrous acetonitrile (10 mL) followed by ditosylate **9** (0.115 g, 0.220 mmol, 1.1 equiv). The reaction mixture was heated at reflux for 168 h, cooled to ambient temperature, and filtered through Whatman number 1 filter paper. The solvent was removed under reduced pressure, and purification of the resulting residue was performed using silica gel chromatography (stepwise gradient of 50:1→10:1→5:1 methanol/ammonium hydroxide (28–30% aqueous solution)) to obtain a pale yellow oil that was further purified using silica gel chromatography (9:1 dichloromethane/methanol). The resulting product was dissolved in dichloromethane and filtered through Whatman number 1 filter paper. The solvent was removed under reduced pressure to yield 10 mg (11%) of **4** as a colorless oil. ^{1}H NMR (400 MHz, CD_3OD, δ): 2.60–2.89 (m, CH_2, 12H), 3.38–3.70 (m, CH_2, 16H), 4.14–4.24 (m, CH_2, 4H), 6.63–6.75 (m, C*H*, 1H), 6.92 (d, *J* = 10.4 Hz, C*H*, 1H), 6.97–7.08 (m, C*H*, 1H); ^{13}C NMR (101 MHz, CD_3OD, δ): 53.8 (*C*H_2), 53.9 (*C*H_2), 54.3 (*C*H_2), 66.7 (*C*H_2), 66.8 (*C*H_2), 68.7 (*C*H_2), 68.8 (*C*H_2), 69.29 (*C*H_2), 69.34 (*C*H_2), 102.3 (d, $^{2}J_{C–F}$ = 27.7 Hz, *C*H), 107.4 (d, $^{2}J_{C–F}$ = 23.1 Hz, *C*H), 114.0 (d, $^{3}J_{C–F}$ = 10.5 Hz, *C*H); ^{19}F NMR (282 MHz, $CDCl_3$, δ): –120.3 to –120.1 (m, C*F*); TLC: R_f = 0.26 (5:1 methanol/ammonium hydroxide (20–30% aqueous solution)); HRESIMS (*m*/*z*): $[M + H]^+$ calcd for $C_{22}H_{36}N_2O_6F$, 443.2557; found, 443.2557.



2,2'-(1,2-Phenylenebisoxy)diethanol (10): To a degassed solution of water (1 mL), 1-butanol (2.5 mL), and NaOH (0.545 g, 13.6 mmol, 3 equiv) under an atmosphere of Ar was added catechol (0.500 g, 4.54 mmol, 1 equiv), and the resulting mixture was heated at reflux. After 5 min at reflux, a degassed solution of 2-chloroethanol (912 μL, 13.6 mmol, 3 equiv) in 1-butanol (12.5 mL) was added dropwise over 1 h while maintaining reflux. The resulting solution was heated at reflux for 18 h at which point the solvent was removed under reduced pressure. Purification was performed using silica gel chromatography (stepwise gradient of 1:1→1:3→0:1 hexanes/ethyl acetate) to yield 546 mg (61%) of **10** as a white solid. ^{1}H NMR (300 MHz, CD_3OD, δ): 3.87 (t, J = 4.6 Hz, CH_2, 4H), 4.07 (t, J = 4.6 Hz, CH_2, 4H), 6.86–7.05 (m, CH, 4H); ^{13}C NMR (75 MHz, CD_3OD, δ): 61.7 (*C*H_2), 72.0 (*C*H_2), 115.6 (*C*H), 122.7 (*C*H), 150.3; TLC: R_f = 0.14 (1:1 hexanes/ethyl acetate); HRESIMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{10}H_{14}O_4Na$, 221.0790; found, 221.0794.

2,2'-(1,2-Phenylenebisoxy)bis(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (11): To a mixture of diol **10** (2.00 g, 10.1 mmol, 1 equiv) and triethylamine (8.5 mL) at 0 °C under an atmosphere of Ar was added a solution of 4-methylbenzene-1-sulfonyl chloride (5.771 g, 30.27

mmol, 3 equiv) in dichloromethane (27.5 mL) dropwise over 2 h. Upon completion of the addition, the reaction mixture was warmed to ambient temperature and stirred for 24 h. The resulting solution was washed sequentially with water (3 × 50 mL), saturated aqueous $NaHCO_3$ (3 × 50 mL), and saturated aqueous citric acid (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Purification was performed using silica gel chromatography (stepwise gradient of 1:0→5:1→3:1→0:1 hexanes/ethyl acetate) to yield 3.72 g (73%) of **11** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.44 (s, C*H*$_3$, 6H), 4.17 (t, *J* = 4.8 Hz, C*H*$_2$, 4H), 4.33 (t, *J* = 4.8 Hz, C*H*$_2$, 4H), 6.79–6.85 (m, C*H*, 2H), 6.88–6.94 (m, C*H*, 2H), 7.34 (d, *J* = 8.0 Hz, C*H*, 4H), 7.81 (d, *J* = 8.8 Hz, C*H*, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.8 (*C*H$_3$), 67.5 (*C*H$_2$), 68.4 (*C*H$_2$), 116.5 (*C*H), 122.8 (*C*H), 128.1 (*C*H), 130.1 (*C*H), 133.1, 145.2, 148.6; TLC: R_f = 0.20 (3:1 hexanes/ethyl acetate); HRESIMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{24}H_{26}O_8S_2Na$, 529.0967; found, 529.0948.

5,6,14,15-Dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (5): To a mixture of Cs_2CO_3 (1.96 g, 6.01 mmol, 6 equiv) in acetonitrile (100 mL) at reflux was added a solution of ditosylate **11** (1.04 g, 2.05 mmol, 2.05 equiv) and 2,2'-(ethylenedioxy)bis(ethylamine) (146 μL, 1.00 mmol, 1 equiv) in acetonitrile (100 mL) dropwise over 48 h. Upon complete addition, the resulting mixture was heated at reflux for 120 h. Solvent was removed under reduced pressure, and purification was performed using silica gel chromatography (stepwise gradient of 1:0→50:1→8:1 dichloromethane/methanol) to obtain a light yellow oil that was further purified using silica gel chromatography (stepwise gradient of 20:1→5:1 methanol/ammonium hydroxide (28–30% aqueous solution)). After removing solvent under reduced pressure, the resulting product was dissolved in dichloromethane and was filtered through glass wool. The solvent was removed under reduced pressure to yield 61 mg (13%) of **5**

as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.87 (t, *J* = 5.6 Hz, C*H*$_2$, 4H), 3.02–3.20 (m, C*H*$_2$, 8H), 3.49 (s, C*H*$_2$, 4H), 3.56 (t, *J* = 5.2 Hz, C*H*$_2$, 4H), 4.13 (t, *J* = 6.2 Hz, C*H*$_2$, 8H), 6.88 (d, *J* = 2.4 Hz, C*H*, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 55.2 (*C*H$_2$), 68.3 (*C*H$_2$), 70.6 (*C*H$_2$), 70.9 (*C*H$_2$), 77.4 (*C*H$_2$), 115.2 (*C*H), 121.6 (*C*H) 149.4; TLC: R_f = 0.46 (8:1 dichloromethane/methanol); HRESIMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{26}H_{36}N_2O_6Na$, 495.2471; found, 495.2473.

5,6-(Benzo)-4,7-dioxa-13,16,21,24-tetrathia-1,10-diazabicyclo[8.8.8]hexacos-5-ene (6): To a mixture of 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (0.053 g, 0.16 mmol, 1 equiv) and anhydrous Cs_2CO_3 (0.525 g, 1.61 mmol, 10 equiv) under an atmosphere of Ar was added anhydrous acetonitrile (10 mL) followed by ditosylate **11** (0.086 g, 0.17 mmol, 1.05 equiv). The reaction mixture was heated at reflux for 120 h, cooled to ambient temperature, and filtered through Whatman number 1 filter paper. The solvent was removed under reduced pressure, and purification of the resulting residue was performed using silica gel chromatography (stepwise gradient of 1:0→30:1→20:1→10:1→5:1 dichloromethane/methanol). The resulting product was further purified using silica gel chromatography (stepwise gradient of 1:0→4:1→1:1→0:1 hexane/ethyl acetate). The solvent was removed under reduced pressure to yield 10 mg (13%) of **6** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.58–3.05 (m, C*H*$_2$, 24H), 4.20 (t, *J* = 5.0 Hz, C*H*$_2$, 4H), 6.92 (brs, C*H*, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 30.6 (*C*H$_2$), 32.8 (*C*H$_2$), 54.8 (*C*H$_2$), 57.2 (*C*H$_2$), 68.2 (*C*H$_2$), 114.9 (*C*H), 121.7 (*C*H), 149.0; TLC: R_f = 0.33 (30:1 dichloromethane/methanol), 0.22 (4:1 hexane/ethyl acetate); HRESIMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{22}H_{36}N_2O_2S_4Na$, 511.1557; found, 511.1552.

Eu^{II} Cryptate Formation

To an aqueous solution of 3-(*N*-morpholino)propanesulfonic acid (MOPS) (0.01 M, pH 7.5), Et_4NClO_4 (0.05 M), and $Eu(NO_3)_3 \cdot 5H_2O$ (1.1 mM, 1 equiv) was added a solution of the desired cryptand (12 mM, 1.2 equiv) in acetonitrile, and the resulting mixture was sparged with Ar for 5 min. The potential of the resulting solution was held at –0.8 V (30 min per 0.01 mmol of $Eu(NO_3)_3 \cdot 5H_2O$) while stirring under constant sparging with Ar.[4] Immediately after holding the potential at –0.8 V, cyclic voltammograms were obtained in the potential range of –1.5 to 0.75 V at a scan rate of 150 mV/s. After acquiring the voltammogram, ferrocene (6.7 mM in acetonitrile, 0.1 equiv) was added, and another cyclic voltammogram was obtained. These cyclic voltammetric experiments were repeated 3–7 times for each ligand. Cyclic voltammograms of ligands **1–6** were obtained using the same protocol without Eu.

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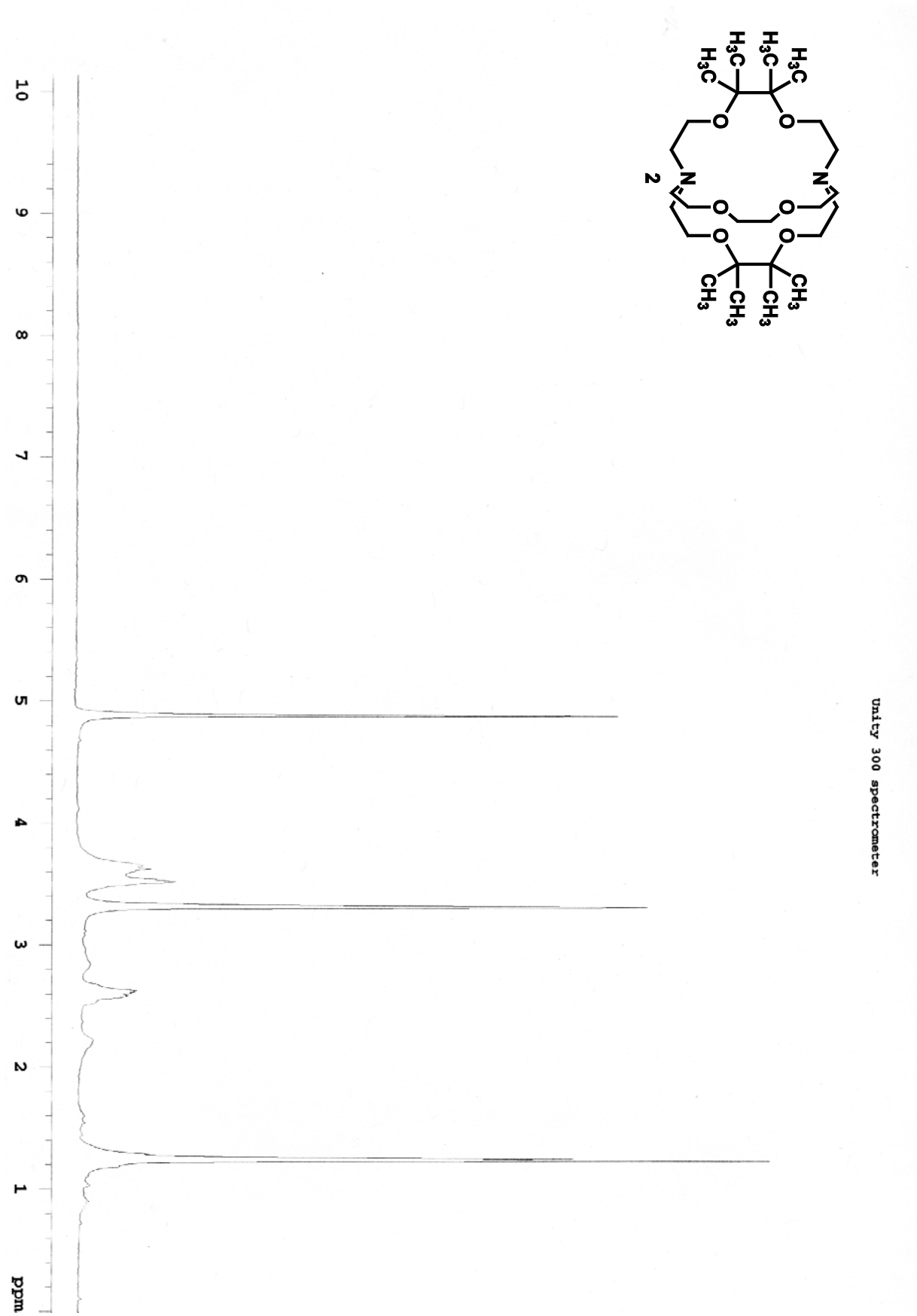
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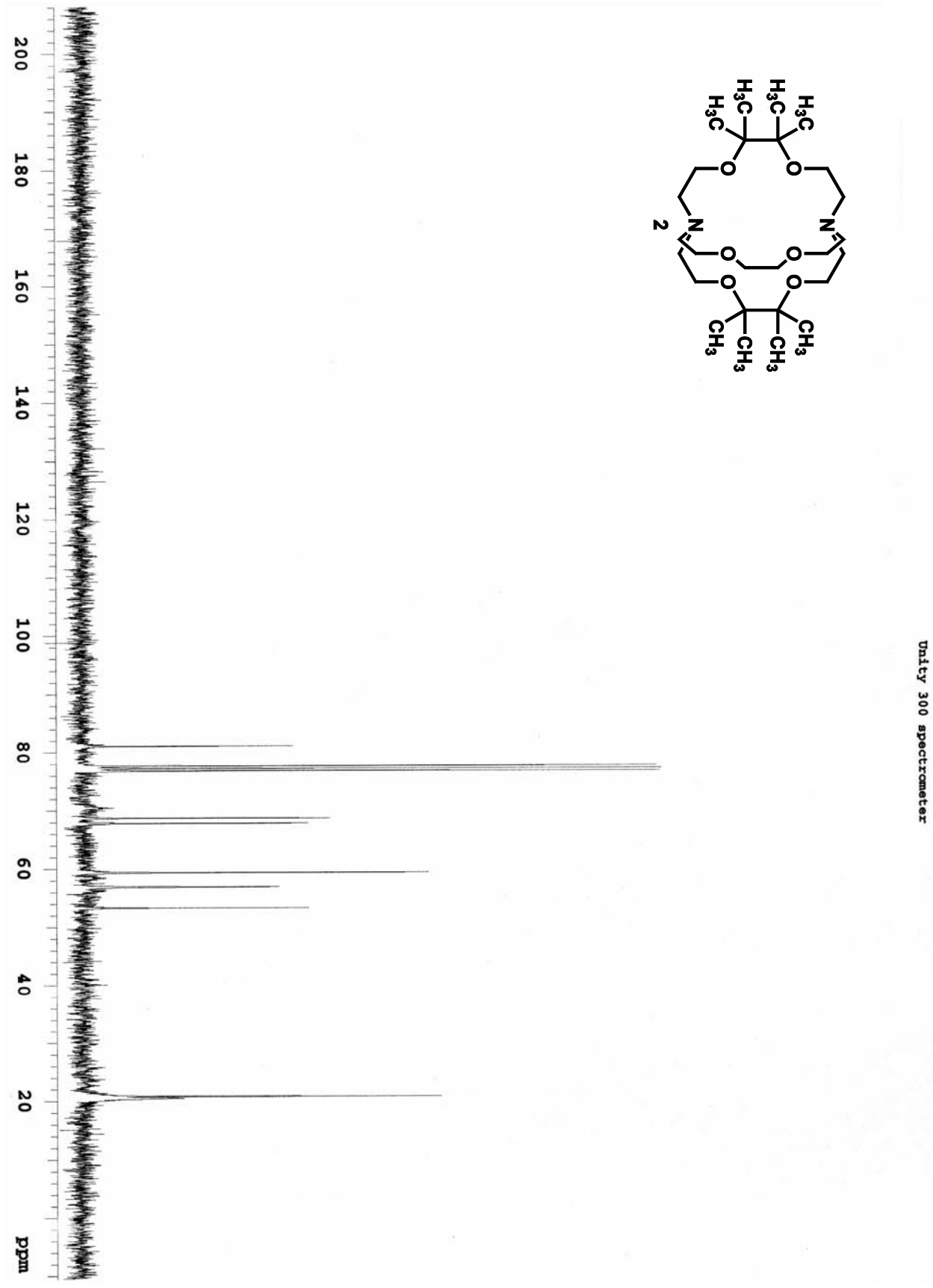
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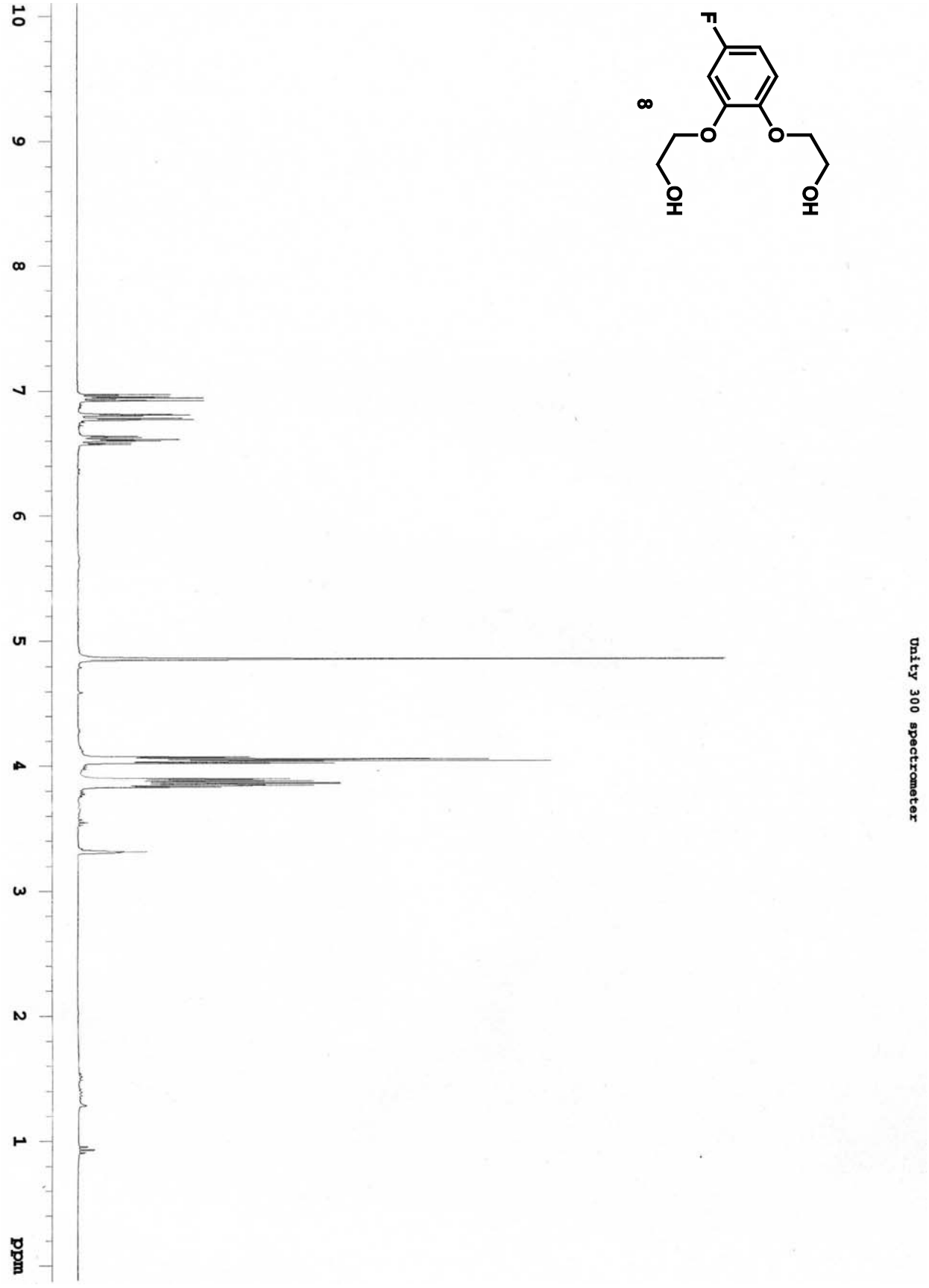
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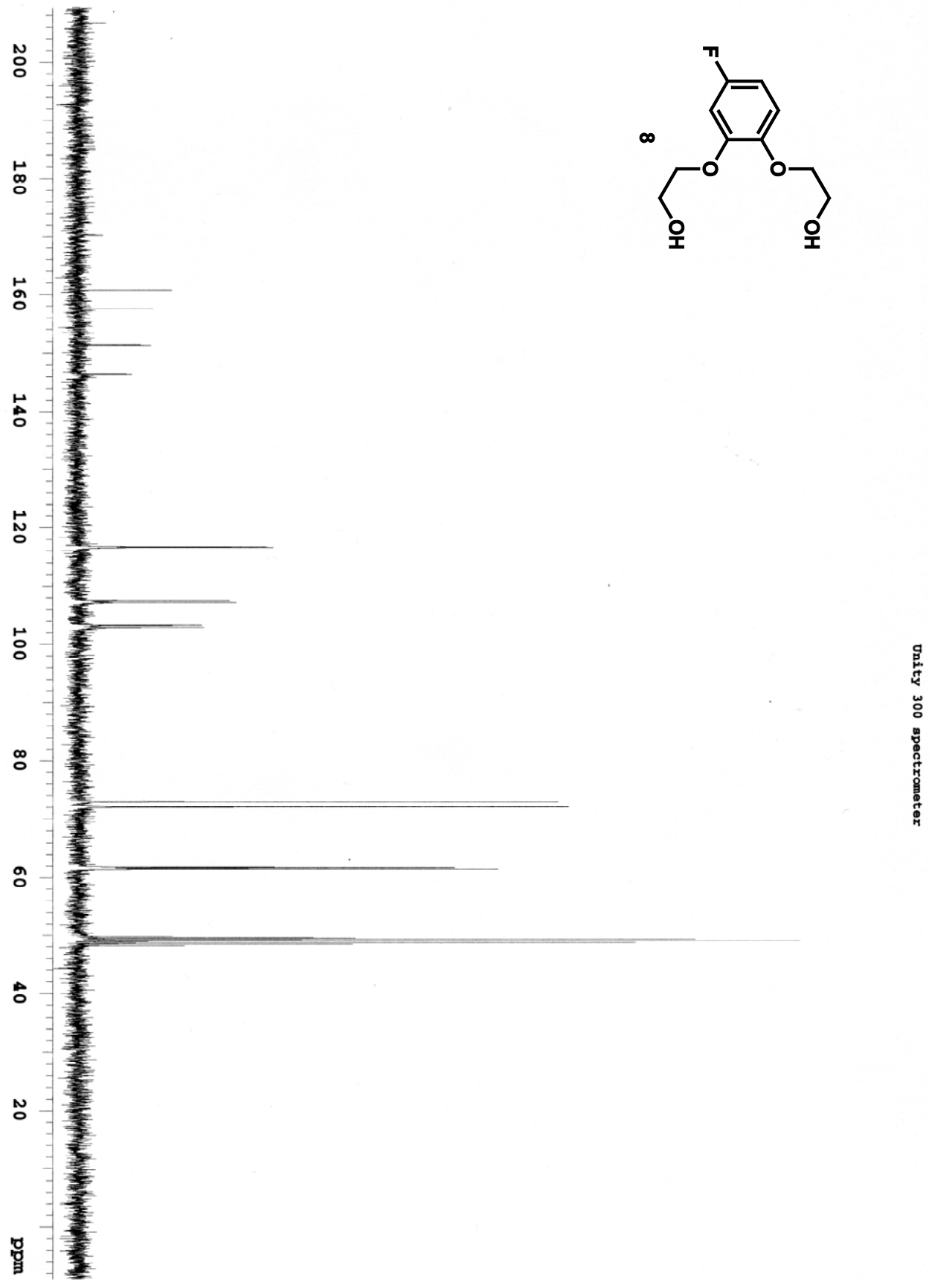
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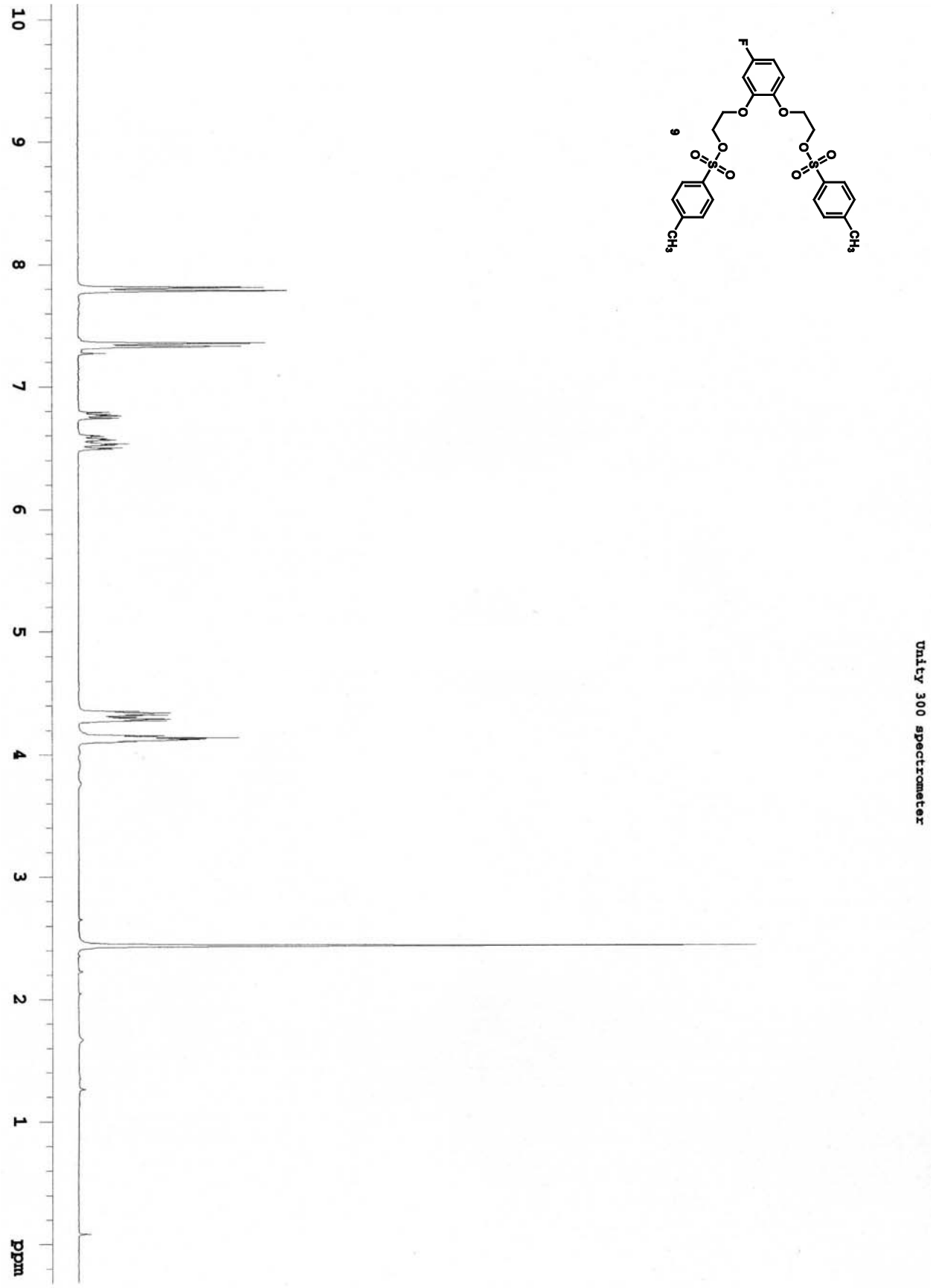
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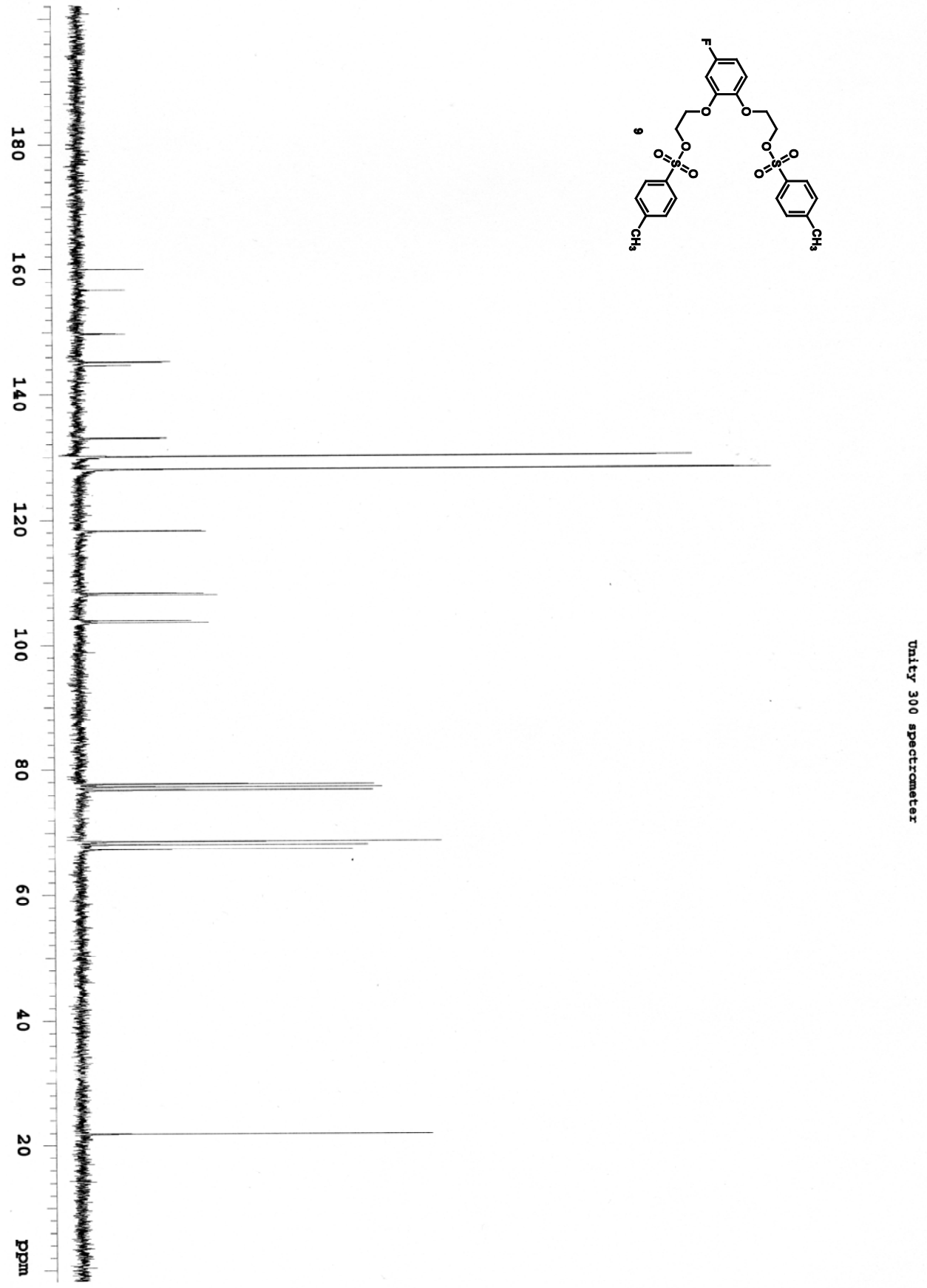
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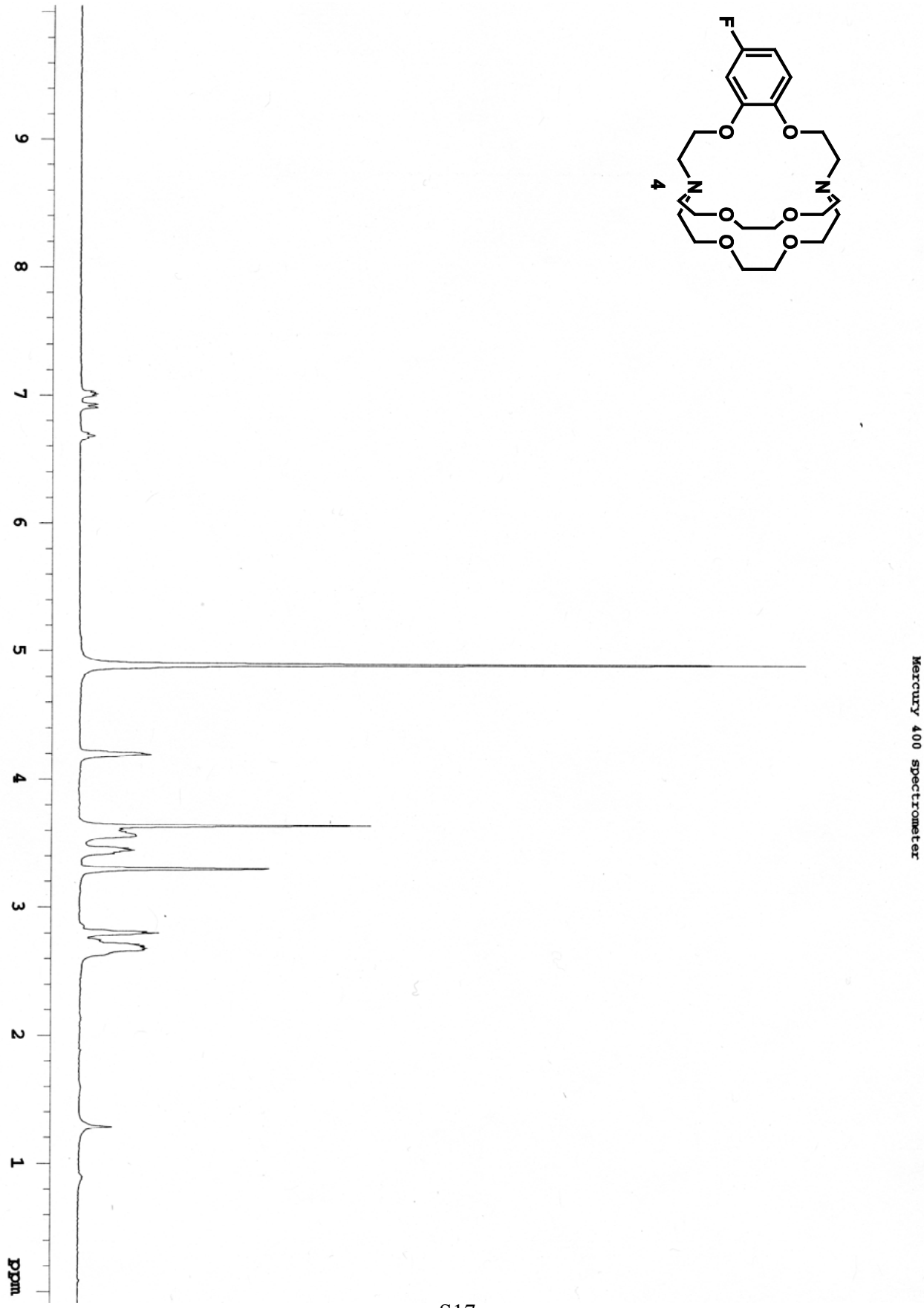
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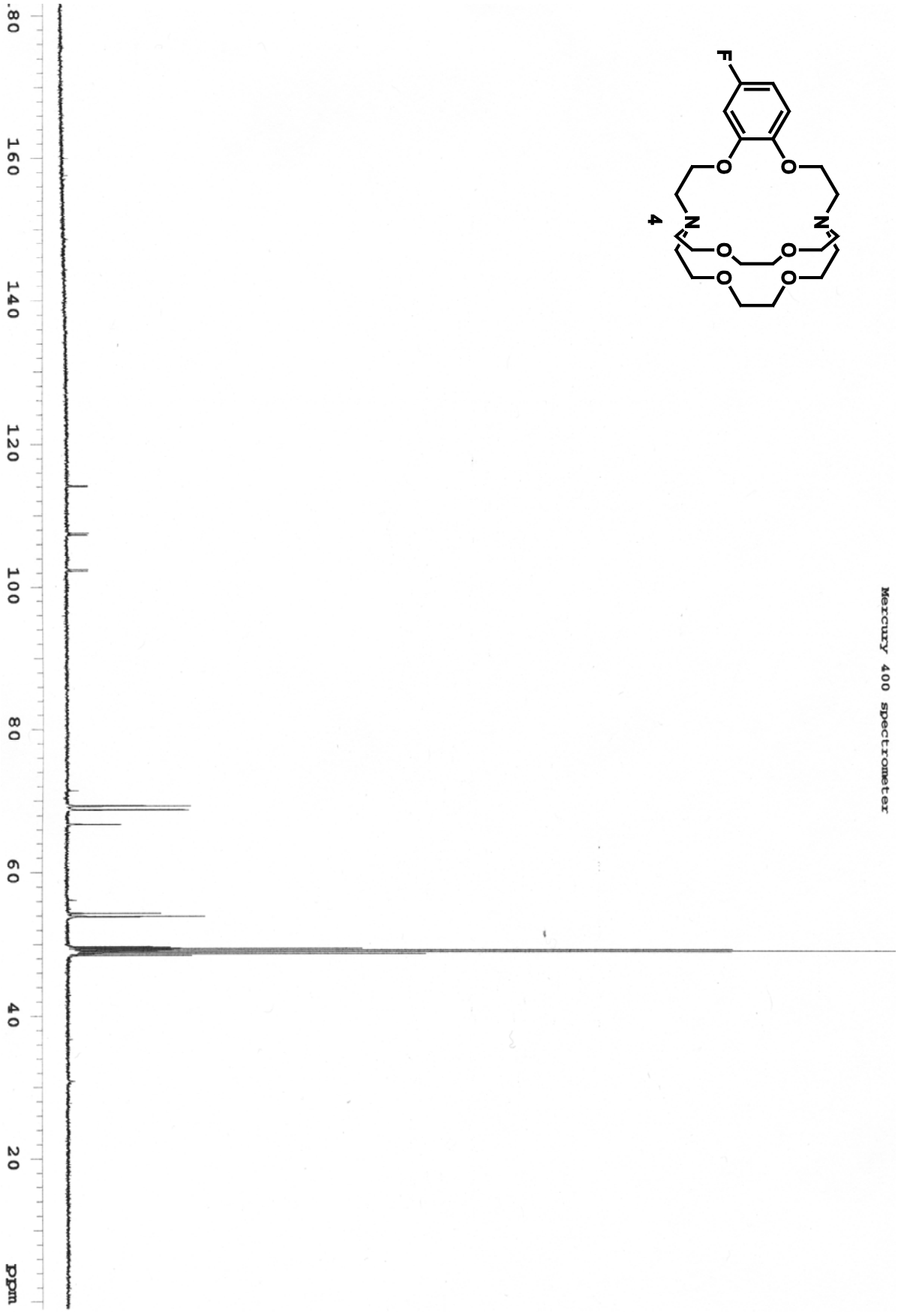
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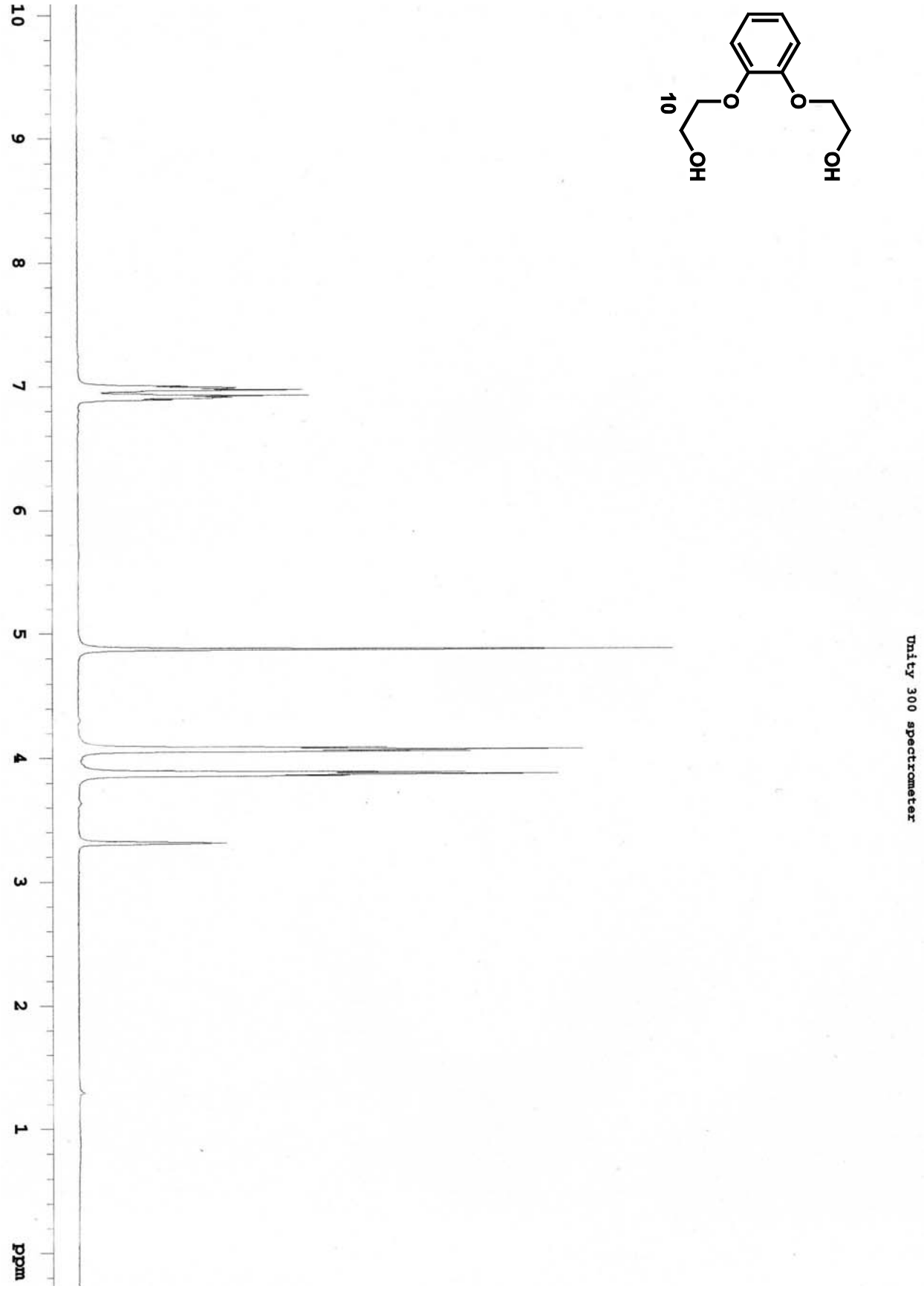
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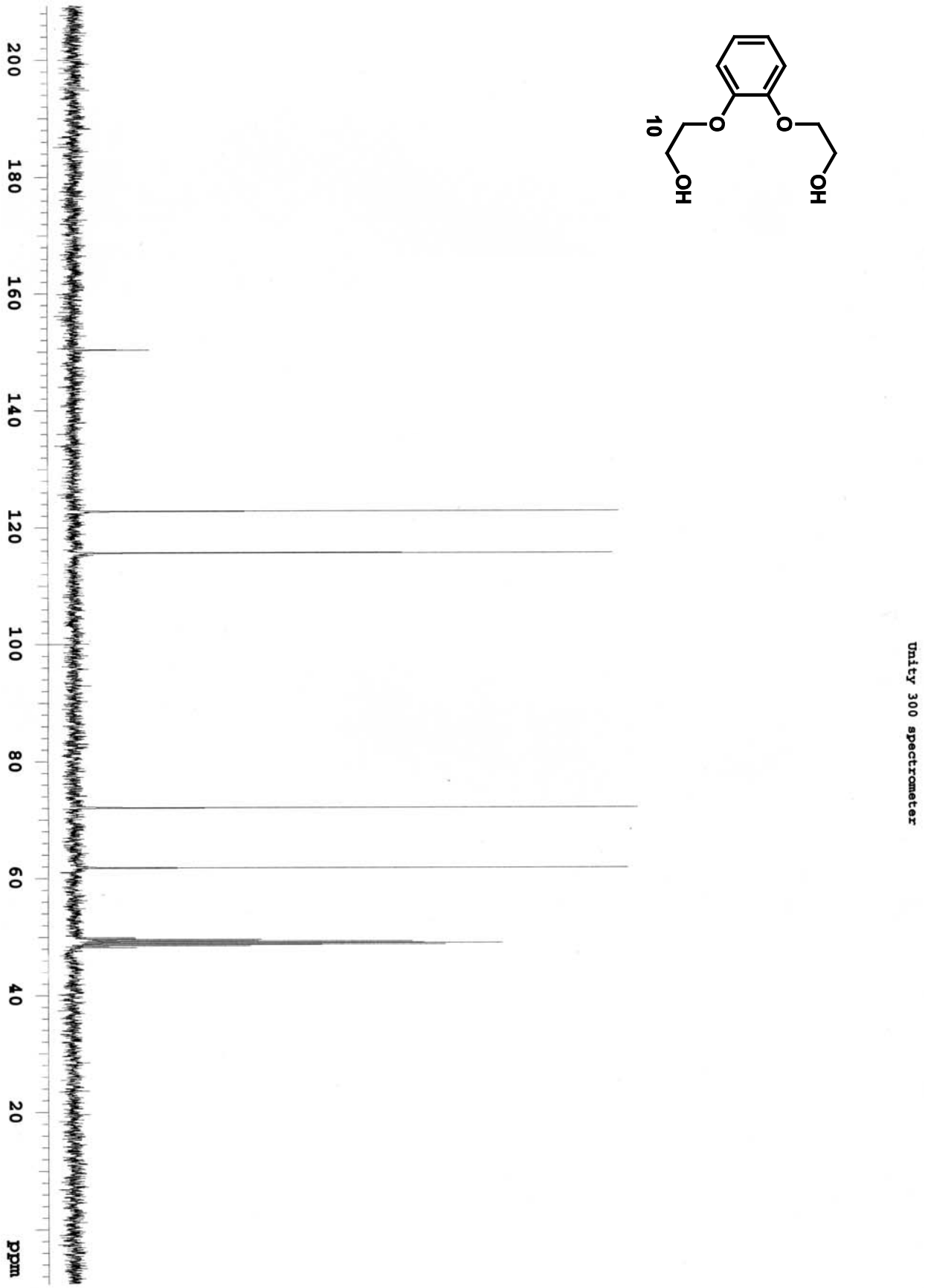
9
8
7
6
5
4
3
2
1
ppm
10
OH
OH
Unity 300 spectrometer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60
40
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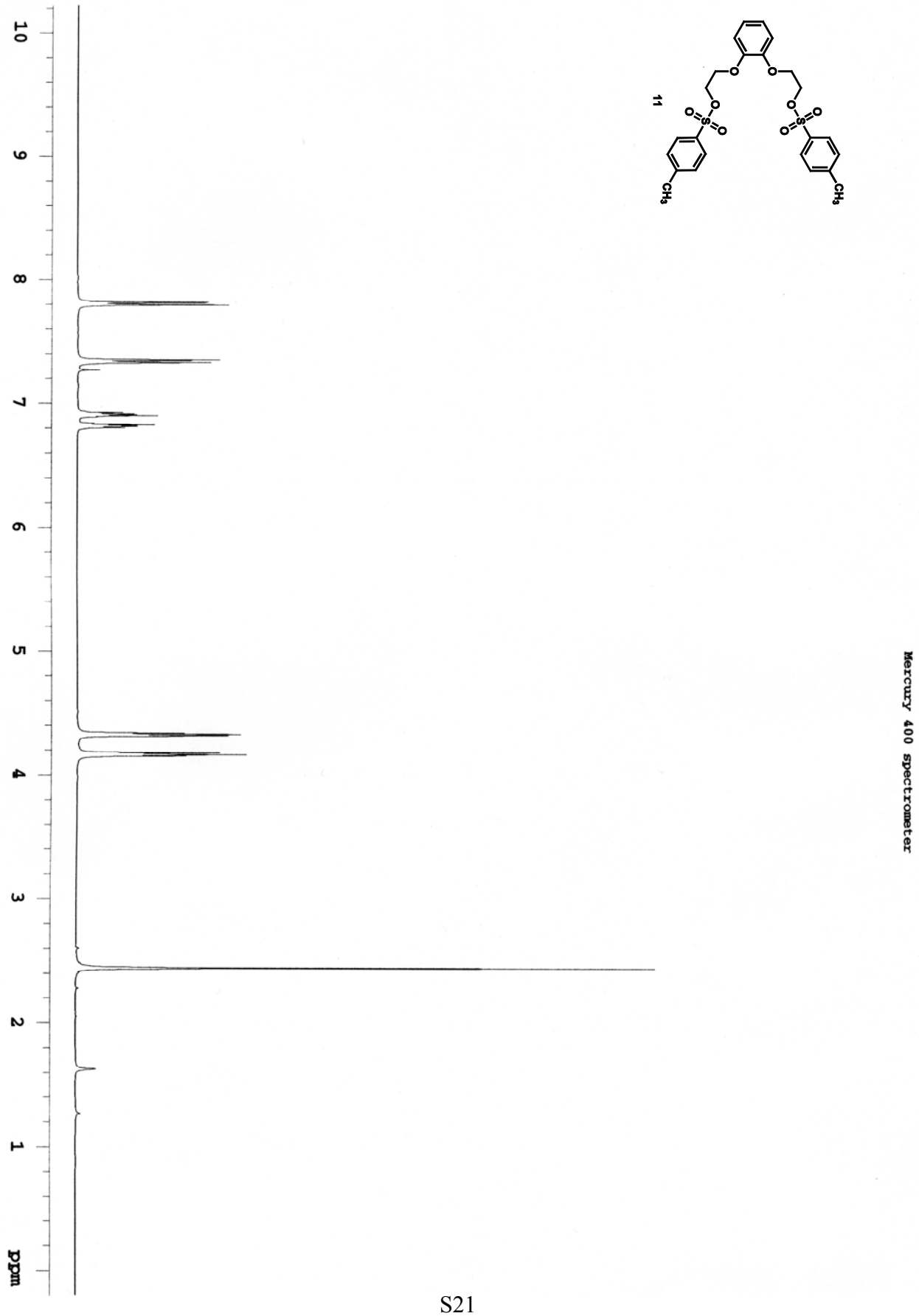
ppm
10
OH
OH
Unity 300 spectrometer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Mercury 400 spectrometer
10
9
8
7
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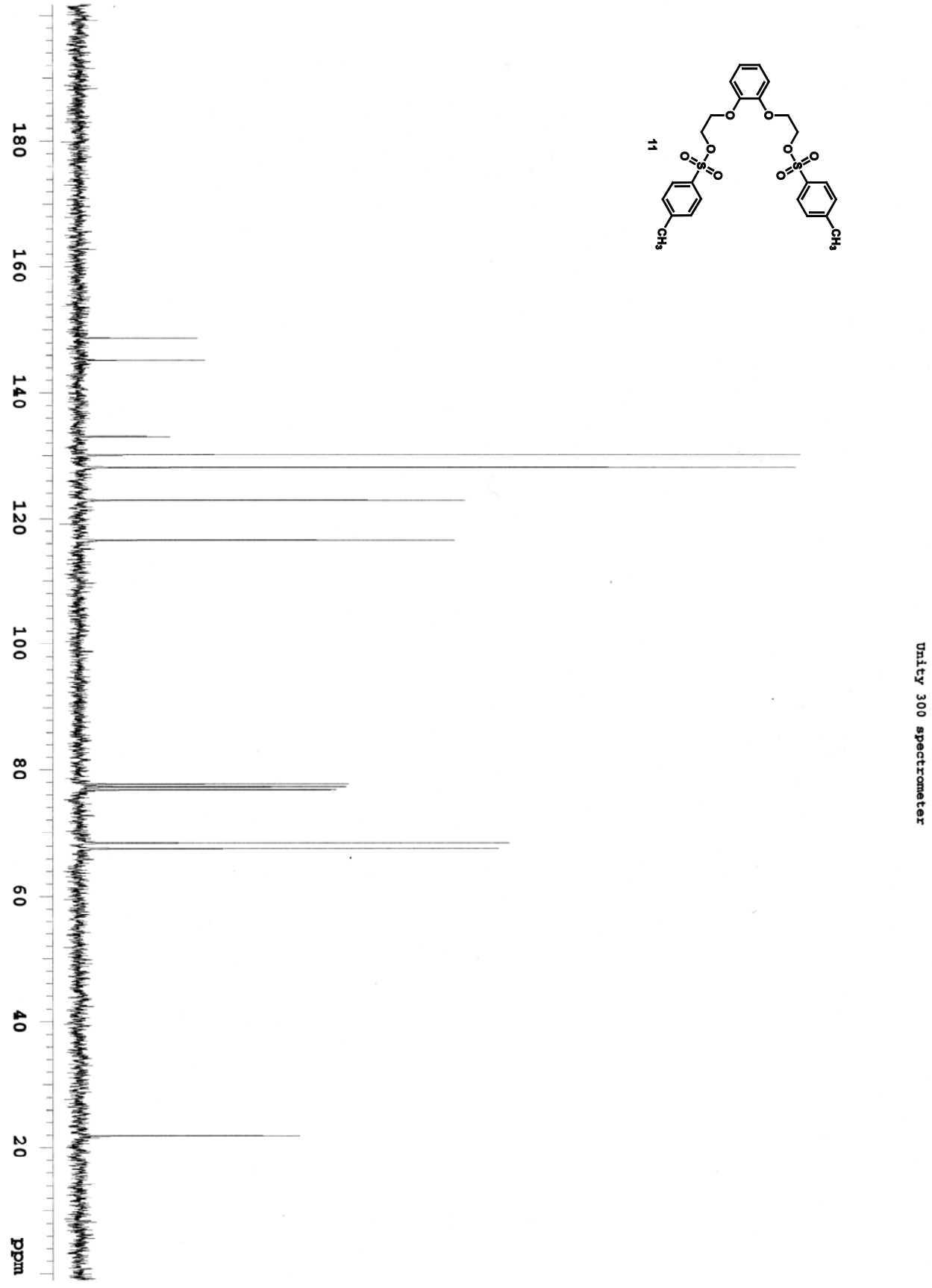
4
3
2
1
ppm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180
160
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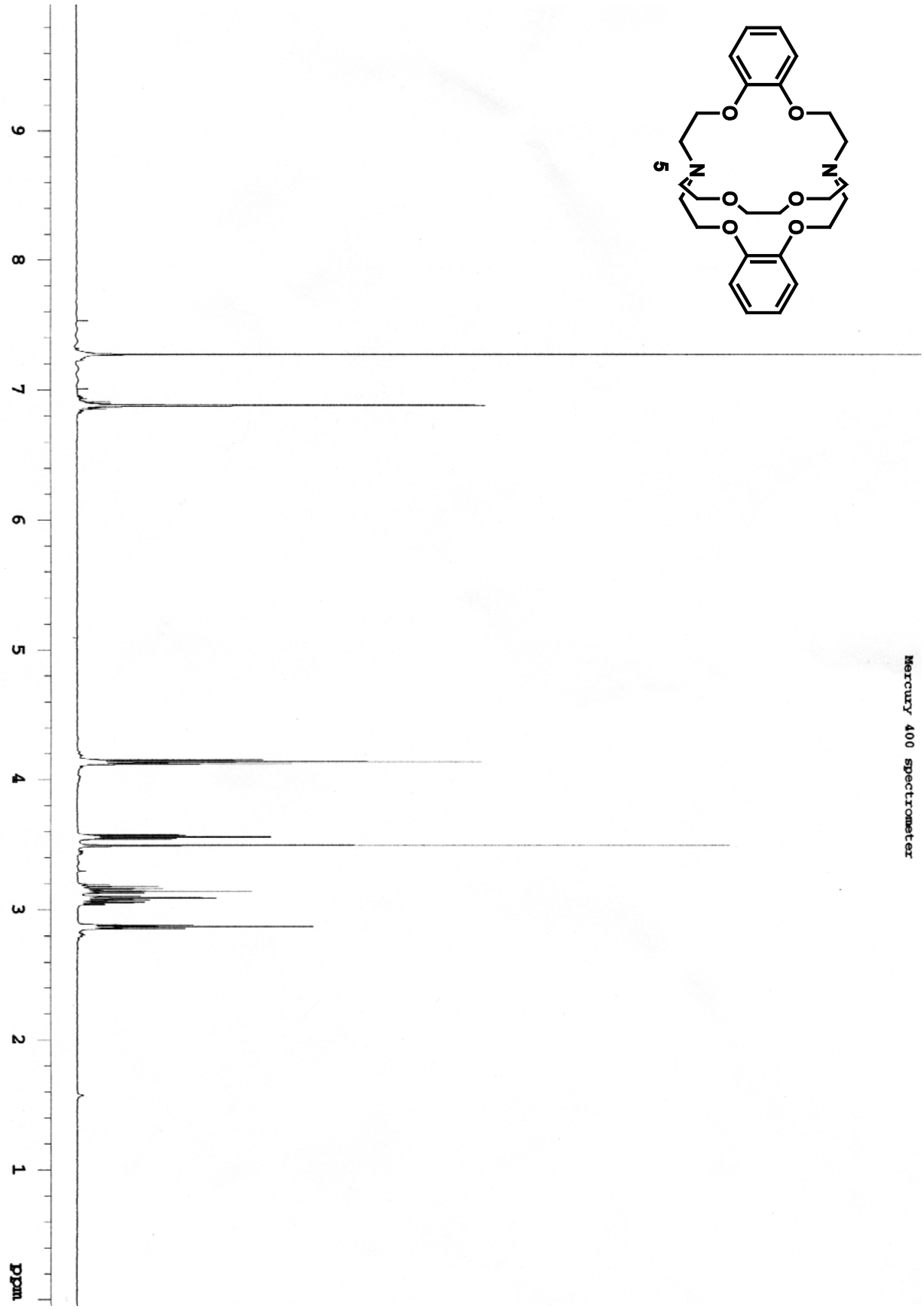
120
100
80
60
40
20
ppm
Unity 300 spectrometer


5
Mercury 400 spectrometer
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8
7
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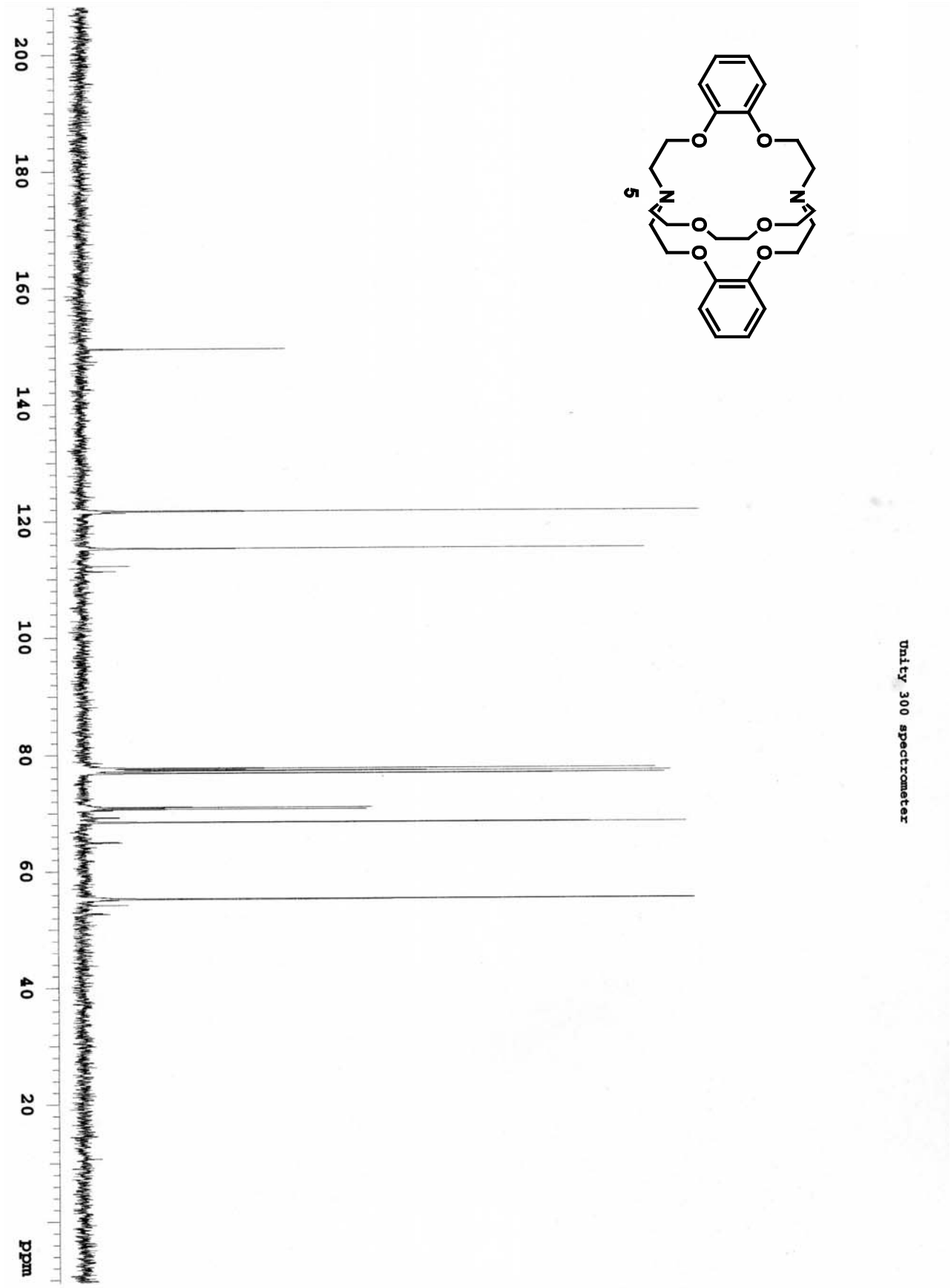
1
ppm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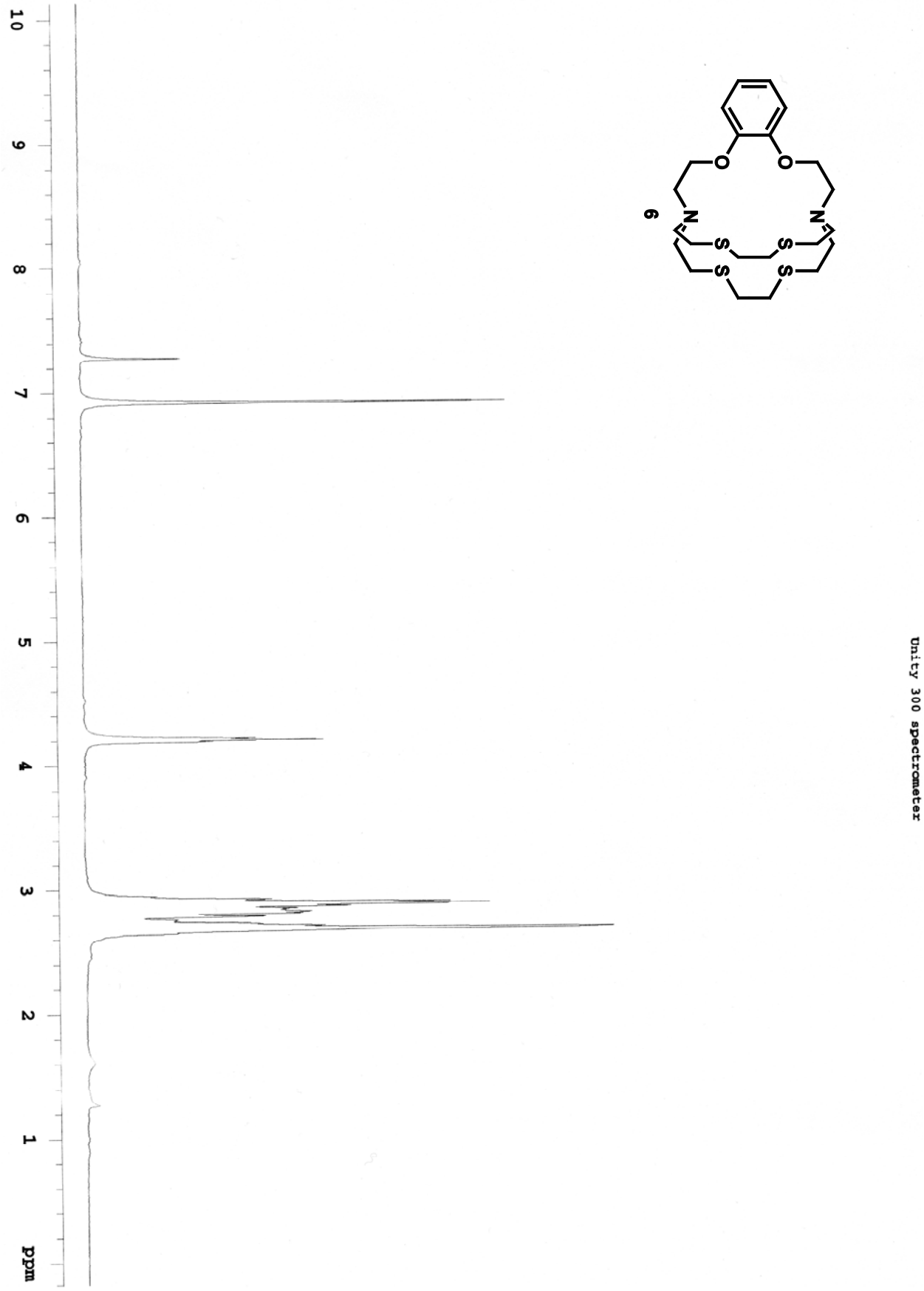
40
20
ppm
5
Unity 300 spectrometer



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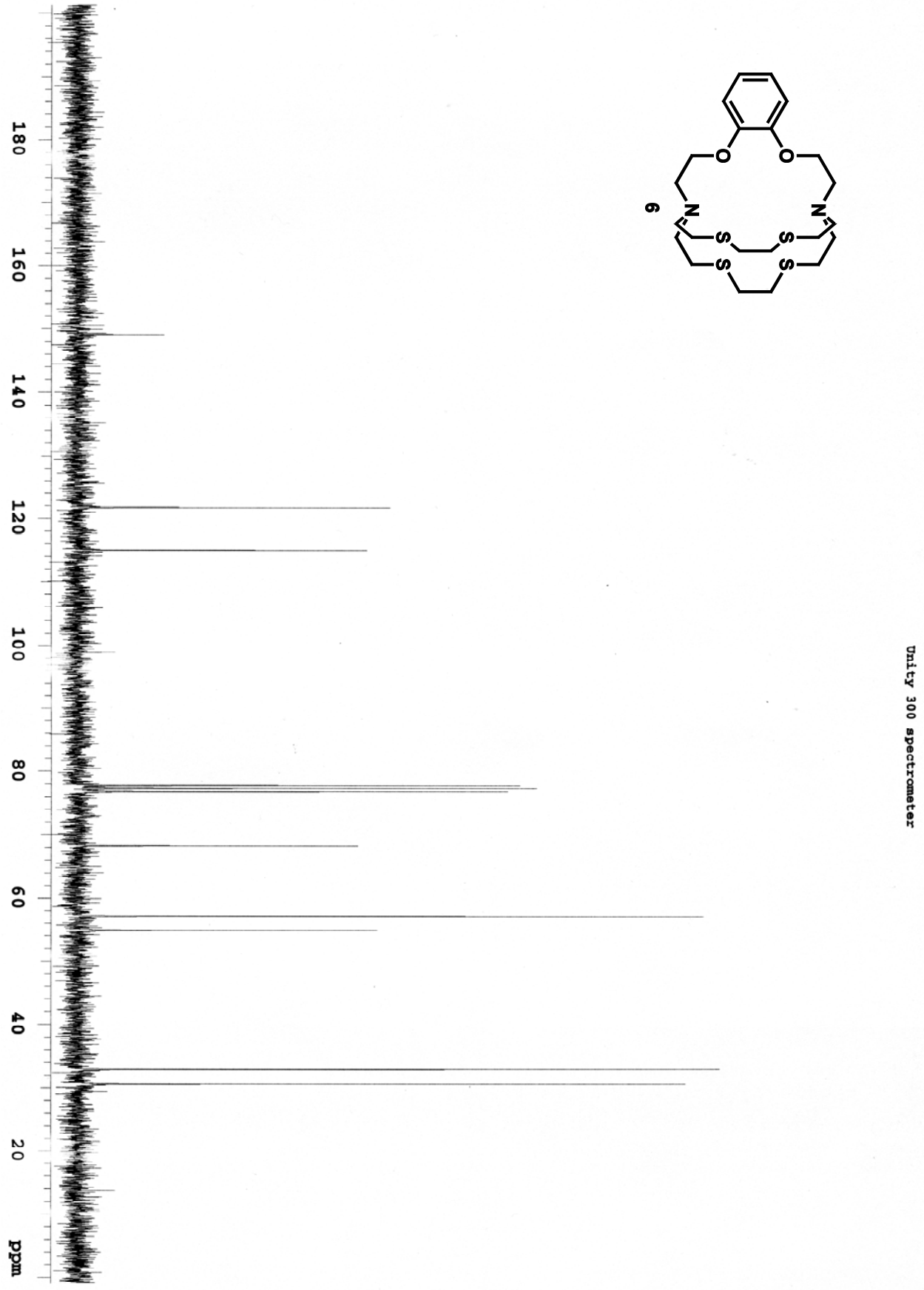
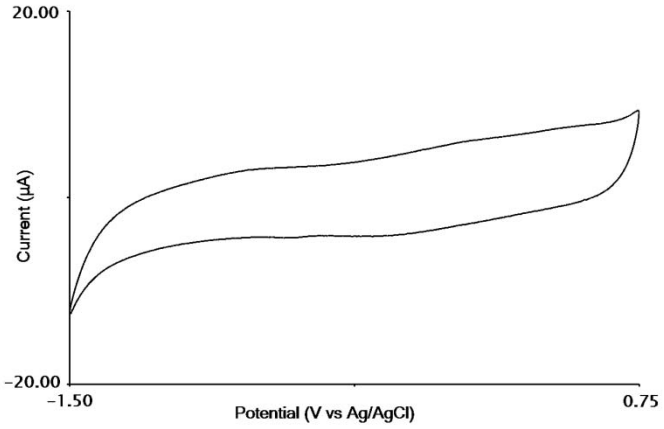

180
160
140
120
100
80
60
40
20
ppm
Unity 300 spectrometer

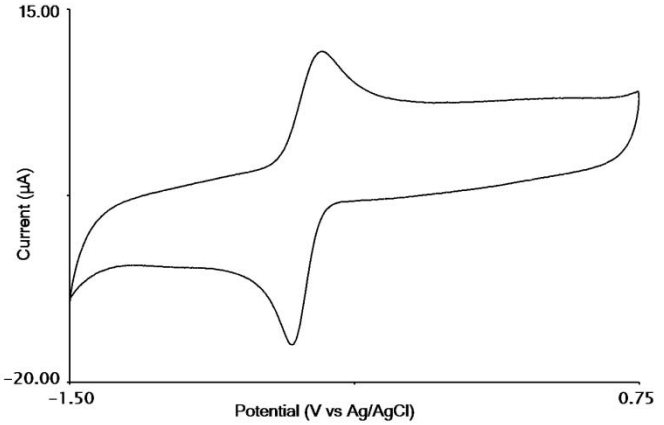
6

Representative Cyclic Voltammograms

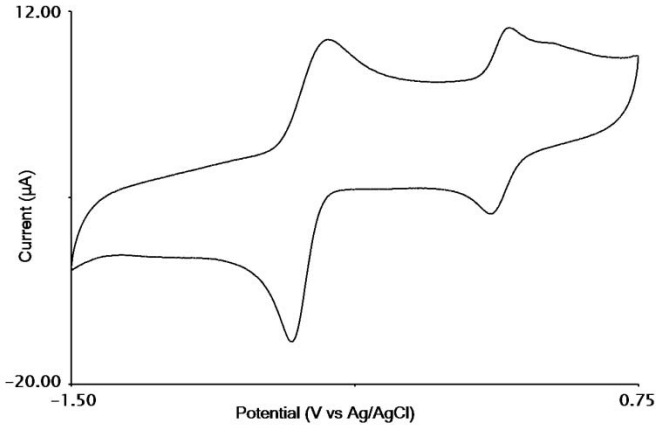
9:1 (v/v) aqueous buffer (0.01 M MOPS, 0.05 M Et_4NClO_4, pH 7.5)–acetonitrile



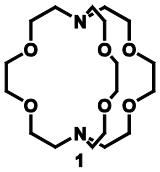
$Eu(NO_3)_3 \cdot 5H_2O$ (1.0 mM)



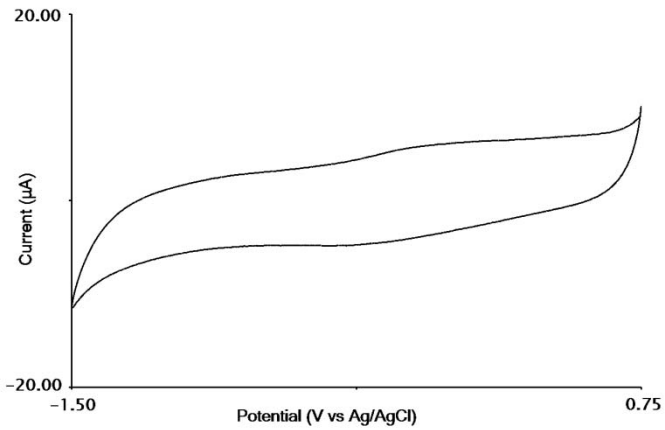
$Eu(NO_3)_3 \cdot 5H_2O$ (1.0 mM) + ferrocene (0.1 mM)



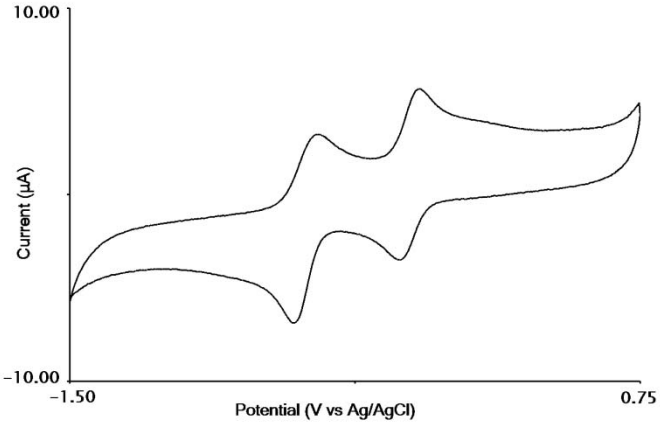
Sample	Peaks (V vs Fc/Fc^+)
$Eu(NO_3)_3$	$E_{pa} = -0.7443$ ($Eu^{II/III}$), $E_{pc} = -0.7846$ ($Eu^{III/II}$)



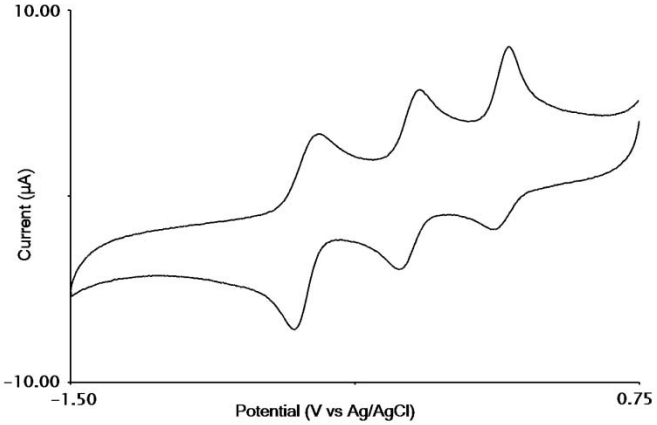
(1.2 mM)



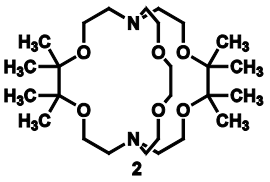
1–Eu (≤ 1.0 mM)



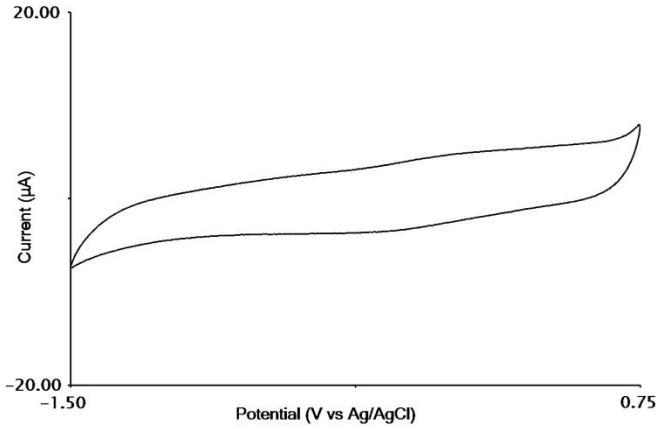
1–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)



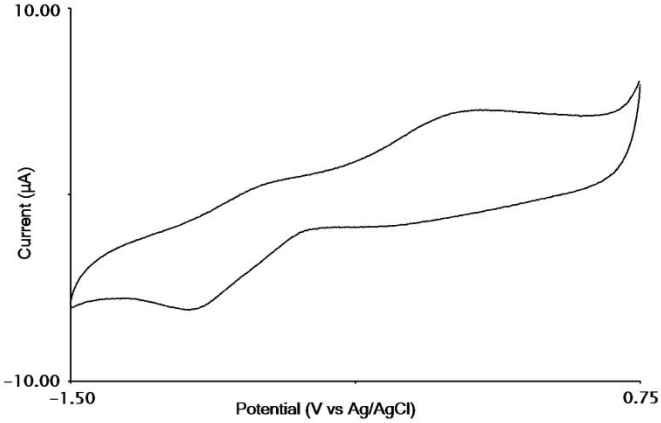
Sample	Peaks (V vs Fc/Fc^+)
1–Eu	E_{pa} = –0.7501 ($Eu^{II/III}$), E_{pa} = –0.3545 (**1–Eu**$^{II/III}$), E_{pc} = –0.3793 (**1–Eu**$^{III/II}$), E_{pc} = –0.7946 ($Eu^{III/II}$)



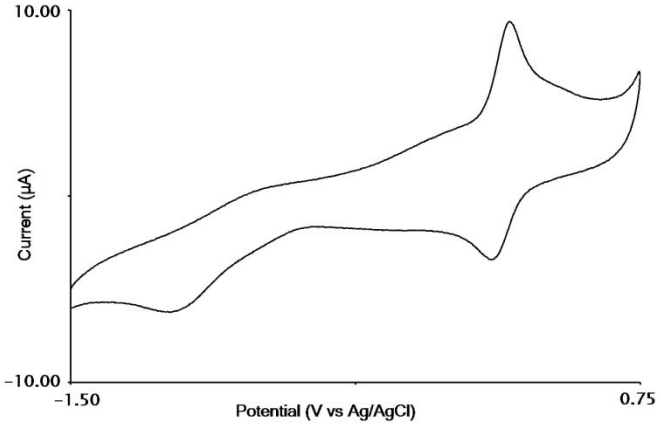
(1.2 mM)



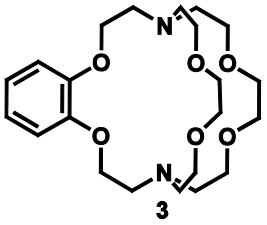
2–Eu (≤ 1.0 mM)



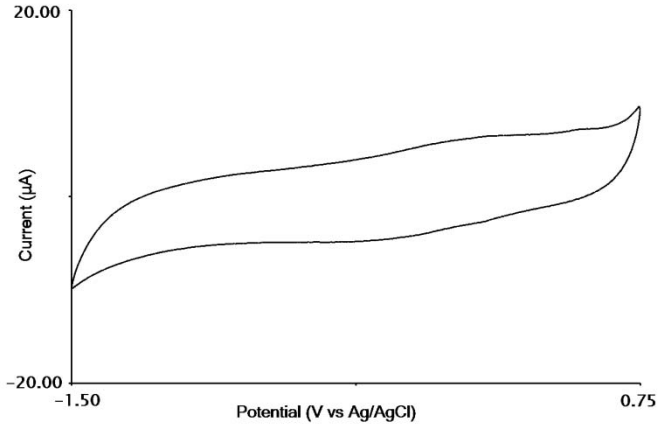
2–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)



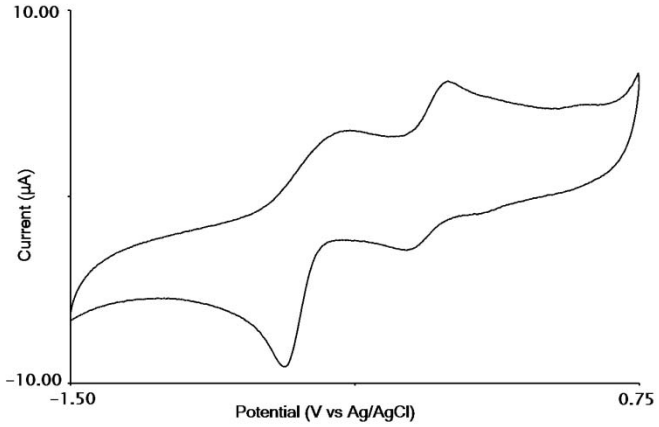
Sample	**Peaks (V vs Fc/Fc$^+$)**
2–Eu	E_{pa} = –0.1690 (**2–Eu**$^{II/III}$), E_{pc} = –1.1948 (Eu$^{III/II}$)



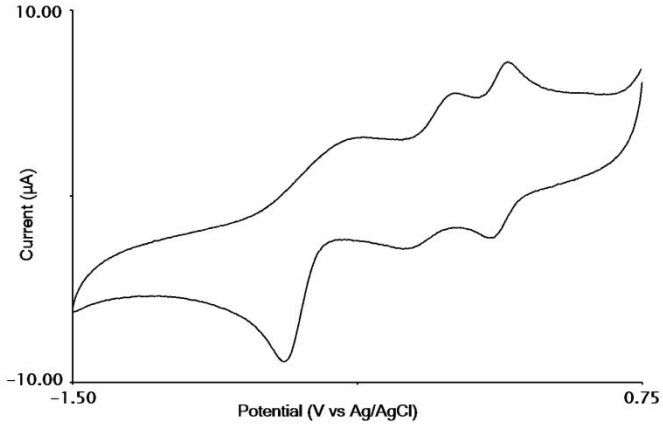
(1.2 mM)



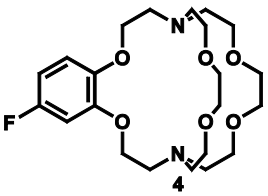
3–Eu (≤ 1.0 mM)



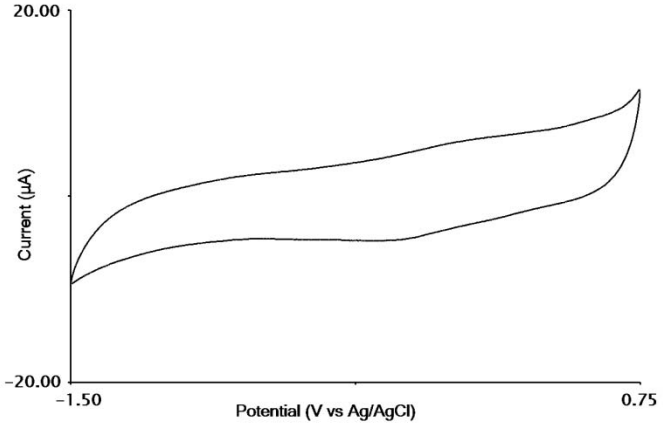
3–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)



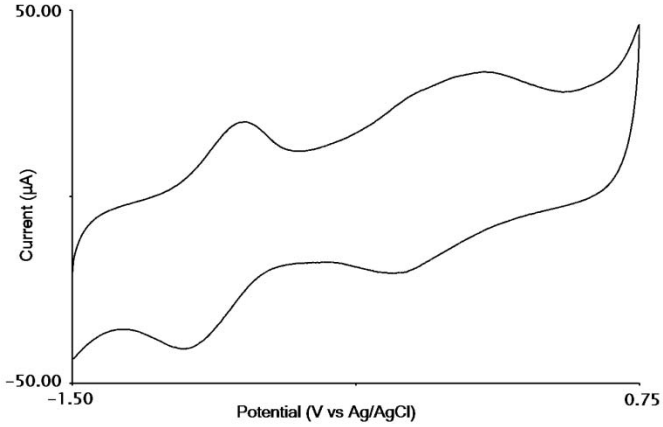
Sample	**Peaks (V vs Fc/Fc^+)**
3–Eu	E_{pa} = –0.6194 ($Eu^{II/III}$), E_{pa} = –0.2245 (**3–Eu**$^{II/III}$), E_{pc} = –0.3293 (**3–Eu**$^{III/II}$), E_{pc} = –0.8047 ($Eu^{III/II}$)



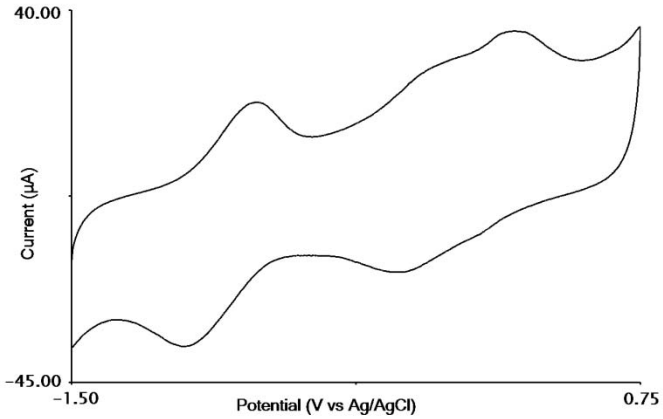
(1.2 mM)



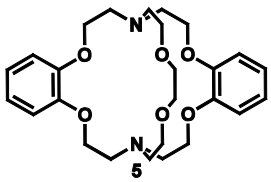
4–Eu (≤ 1.0 mM)



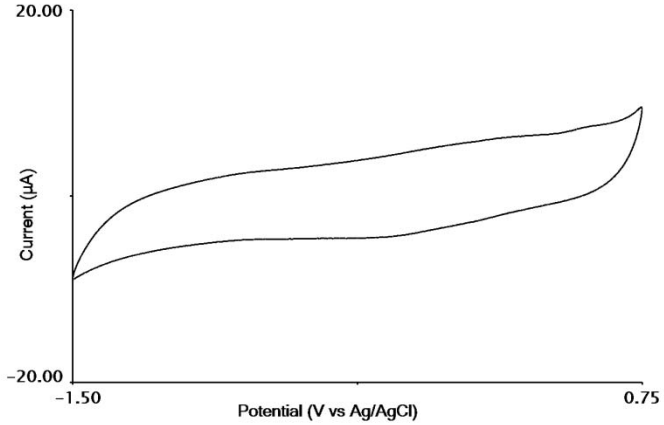
4–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)



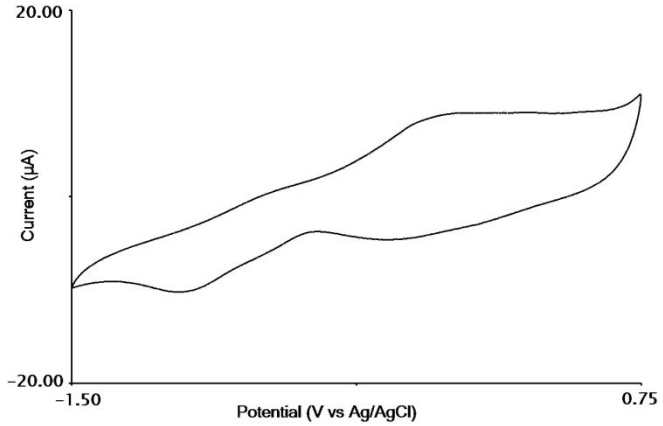
Sample	**Peaks (V vs Fc/Fc^+)**
4–Eu	$E_{pa} = -1.0696$ ($Eu^{II/III}$), $E_{pa} = -0.1052$ (**4–Eu**$^{II/III}$), $E_{pc} = -0.3595$ (**4–Eu**$^{III/II}$), $E_{pc} = -1.1846$ ($Eu^{III/II}$)



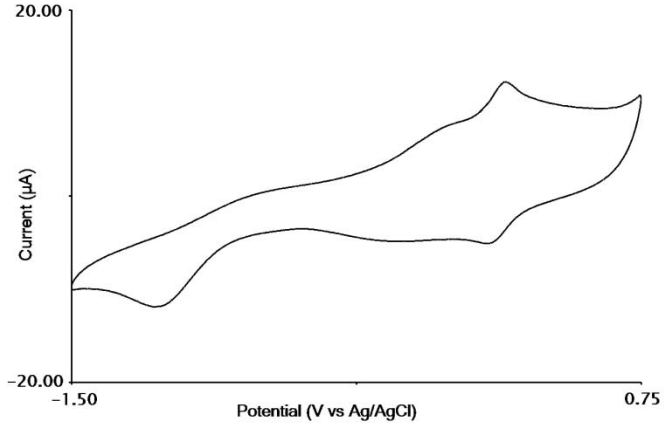
(1.2 mM)



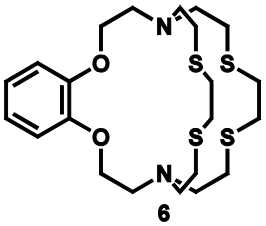
5–Eu (≤ 1.0 mM)



5–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)

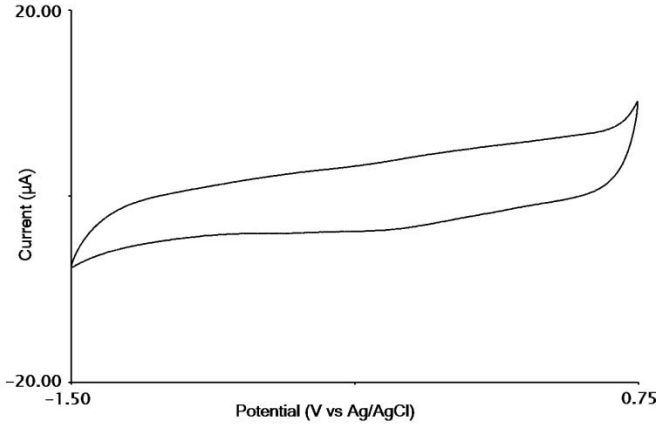


Sample	Peaks (V vs Fc/Fc^+)
5–Eu	E_{pa} = –0.2045 (**5–Eu**$^{II/III}$), E_{pc} = –0.3946 (**5–Eu**$^{III/II}$), E_{pc} = –1.2198 ($Eu^{III/II}$)

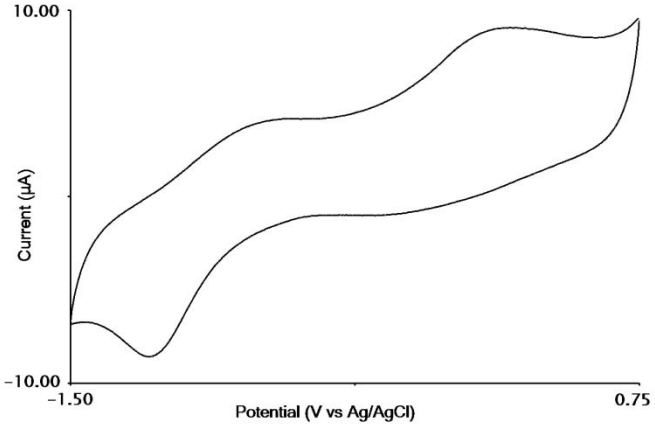


6

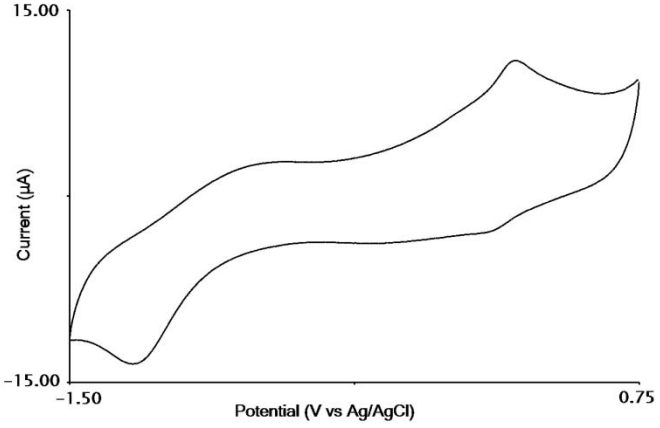
(1.2 mM)



6–Eu (≤ 1.0 mM)

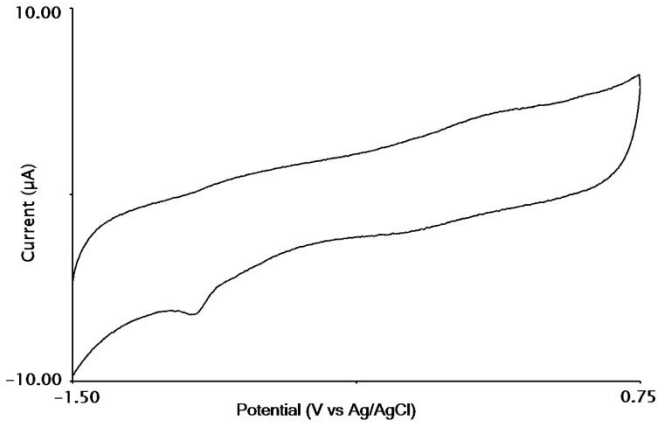


6–Eu (≤ 1.0 mM) + ferrocene (0.1 mM)

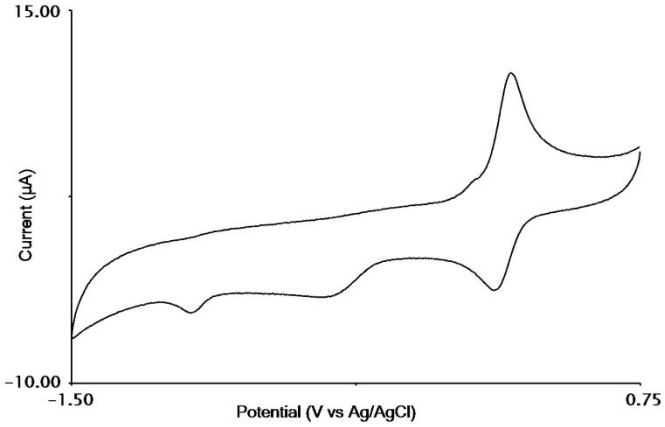


Sample	**Peaks (V vs Fc/Fc^+)**
6–Eu	E_{pa} = –0.9196 ($Eu^{II/III}$), E_{pa} = –0.0199 (**6–Eu**$^{II/III}$), E_{pc} = –0.4046 (**6–Eu**$^{III/II}$), E_{pc} = –1.3545 ($Eu^{III/II}$)

hemoglobin (1.0 mM)



hemoglobin (1.0 mM) + ferrocene (0.1 mM)



Sample	**Peaks (V vs Fc/Fc$^+$)**
hemoglobin	E_{pa} = –0.0753 ($Fe^{II/III}$), E_{pc} = –0.3991 ($Fe^{III/II}$)

Cyclic Voltammetric Data*

Sample	Anodic peak potential (V vs Ag/AgCl (1 M KCl))	Anodic peak potential (V vs Fc/Fc^+)	Anodic peak potential (V vs NHE)
$Eu(NO_3)_3$	–0.485 ± 0.012	–0.701 ± 0.030	–0.288
1–Eu	–0.110 ± 0.011	–0.336 ± 0.016	0.087
5–Eu	–0.011 ± 0.008	–0.211 ± 0.004	0.186
3–Eu	0.001 ± 0.008	–0.208 ± 0.009	0.198
2–Eu	0.043 ± 0.012	–0.169 ± 0.006	0.240
4–Eu	0.169 ± 0.009	–0.079 ± 0.007	0.366
hemoglobin	0.167 ± 0.002	–0.070 ± 0.003	0.364
6–Eu	0.260 ± 0.018	–0.035 ± 0.010	0.457

* Potentials are listed as mean ± standard error.