Metal salen complexes incorporating triphenoxymethanes: Efficient, size selective anion binding by phenolic donors with a visual report

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General Considerations. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer at 299.95 and 75.47 MHz for the proton and carbon channels. UV-Vis spectra were recorded on a Varian Cary 50 spectrometer. Elemental analyses were performed at either the in-house facility of the Department of Chemistry and the University of Florida or by Complete Analysis Laboratories Inc., Parsippany, NJ. All solvents were ACS or HPLC grade and used as purchased except for metalation reactions where the solvents were dried with a Meyer distillation system.

Experimental Procedures:

Synthesis of racemic Ligand 1

A portion of 0.63 g (5.52mmol) of 1,2-diaminocyclohexane was dissolved in 50mL absolute ethanol. To this solution a slurry of 5.00g (11.05mmol) of 3-(2,2'-Methylenebis (4-methyl-6-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde in 300mL ethanol was added. The reaction was refluxed open to the air for 12 hours. The solution was cooled to room temperature and water was added to the solution resulting in the precipitation of a bright yellow solid. The solid was filtered and dried to afforf the product in an 83% yield (4.73g).

^1H NMR: δ 8.12 (s, 2H); 7.04 (s, 4H); 6.93 (s, 2H); 6.77 (s, 2H); 6.66 (s, 4H); 5.94 (s, 2H); 5.62 (s, 2H); 5.40 (s, 2H); 3.30 (d, 2H); 2.20 (s, 6H); 2.17 (s, 6H); 2.10 (s, 6H); 2.00-1.85 (m,); 1.38 (s, 36H). ^{13}C NMR δ 165.4; 157.7; 151.4; 137.7; 134.5; 131.2; 129.2; 128.3; 127.9; 127.7; 127.5; 117.9; 72.0; 39.2; 34.9; 33.2; 30.0; 24.33; 21.3; 20.7.

Synthesis of R,R-1

A portion of 2.00g (7.57mmol) of (1R,2R)-(-)-1,2-diaminocyclohexane D-tartrate was mixed with 2.09g (15.14mmol) of potassium carbonate and dissolved in 15mL water. To this solution, 60mL of absolute ethanol was added and the solution was brought to a reflux. A slurry of 6.85g (15.14mmol) 3-(2,2'-Methylenebis (4-methyl-6-*tert*-butylphenol)-5-methyl-2-hydroxybenzaldehyde in approximately 150mL of ethanol was slowly added to the amine with an addition funnel. The solution was then refluxed for three hours. 20mL of water was added and it was cooled in the refrigerator for 12 hours. The bright yellow solid was filtered and then dissolved in methylene chloride. It was washed three times with water in a separatory funnel, dried with magnesium sulfate and the solvent was removed to afford the pure productin 78% yield (6.05g).

^1H NMR: δ 8.12 (s, 2H); 7.04 (s, 4H); 6.93 (s, 2H); 6.77 (s, 2H); 6.66 (s, 4H); 5.94 (s, 2H); 5.62 (s, 2H); 5.40 (s, 2H); 3.30 (d, 2H); 2.20 (s, 6H); 2.17 (s, 6H); 2.10 (s, 6H); 2.00-1.85 (m,); 1.38 (s, 36H). ^{13}C NMR δ 165.4; 157.7; 151.4; 137.7; 134.5; 131.2; 129.2; 128.3; 127.9; 127.7; 127.5; 117.9; 72.0; 39.2; 34.9; 33.2; 30.0; 24.33; 21.3; 20.7.

Synthesis of Ni-R,R-1

A portion of 1g (0.974mmol) R,R-1 was dissolved in dry THF. To this solution 0.27g (10.30mmol) of nickel acetate was added and it was refluxed under nitrogen for 12 hours. The solution was cooled, filtered and the solvent removed. The remaining solid was then dissolved in pentane, filtered and a dark red solid was obtained in an 87% yield (0.92g). X-ray quality crystals were grown by slow evaporation from a concentrated acetonitrile solution.

^{1}H NMR: δ 7.45 (s, 2H); 7.17 (d, 2H); 6.87 (s, 4H); 6.83 (s, 2H); 6.76 (s, 4H); 6.57 (s, 2H); 6.38 (s, 2H); 6.25 (s, 2H); 3.20-3.15 (m, 2H); 2.55-2.45 (m, 2H); 2.17 (s, 6H); 2.14 (s, 12H); 2.00-1.9 (m, 2H); 1.12 (s, 18H); 1.11 (s, 18H). ^{13}C NMR δ 158.2; 152.0; 151.8; 137.5; 137.3; 137.2; 132.2; 130.6; 128.9; 128.6; 127.4; 127.3; 126.6; 126.8; 119.6; 70.3; 36.4; 34.6; 29.5; 28.7; 24.4; 21.0; 20.4. Anal. Calc. for $C_{68}H_{86}N_2O_6Ni\cdot CH_3CN$: C, 74.77; H, 7.74; N, 3.74. Found C, 74.24; H, 7.84; N, 3.44.

Synthesis of racemic Ni-Ligand 1

A portion of 1.0g (0.974mmol) of ligand-1 was dissolved in dry THF. To this solution 0.27g (1.07 mmol) of nickel acetate was added and it was refluxed under nitrogen for 12 hours. The solution was cooled, filtered and the solvent removed. The solid was then washed with pentane and filtered producing a red solid product in a 91% yield (0.96g).

^{1}H NMR: δ 7.45 (s, 2H); 7.17 (d, 2H); 6.87 (s, 4H); 6.83 (s, 2H); 6.76 (s, 4H); 6.57 (s, 2H); 6.38 (s, 2H); 6.25 (s, 2H); 3.20-3.15 (m, 2H); 2.55-2.45 (m, 2H); 2.17 (s, 6H); 2.14 (s, 12H); 2.00-1.9 (m, 2H); 1.12 (s, 18H); 1.11 (s, 18H). ^{13}C NMR δ 158.2; 152.0; 151.8; 137.5; 137.3; 137.2; 132.2; 130.6; 128.9; 128.6; 127.4; 127.3; 126.6; 126.8; 119.6; 70.3; 36.4; 34.6; 29.5; 28.7; 24.4; 21.0; 20.4.

Synthesis of Pd Ligand 1

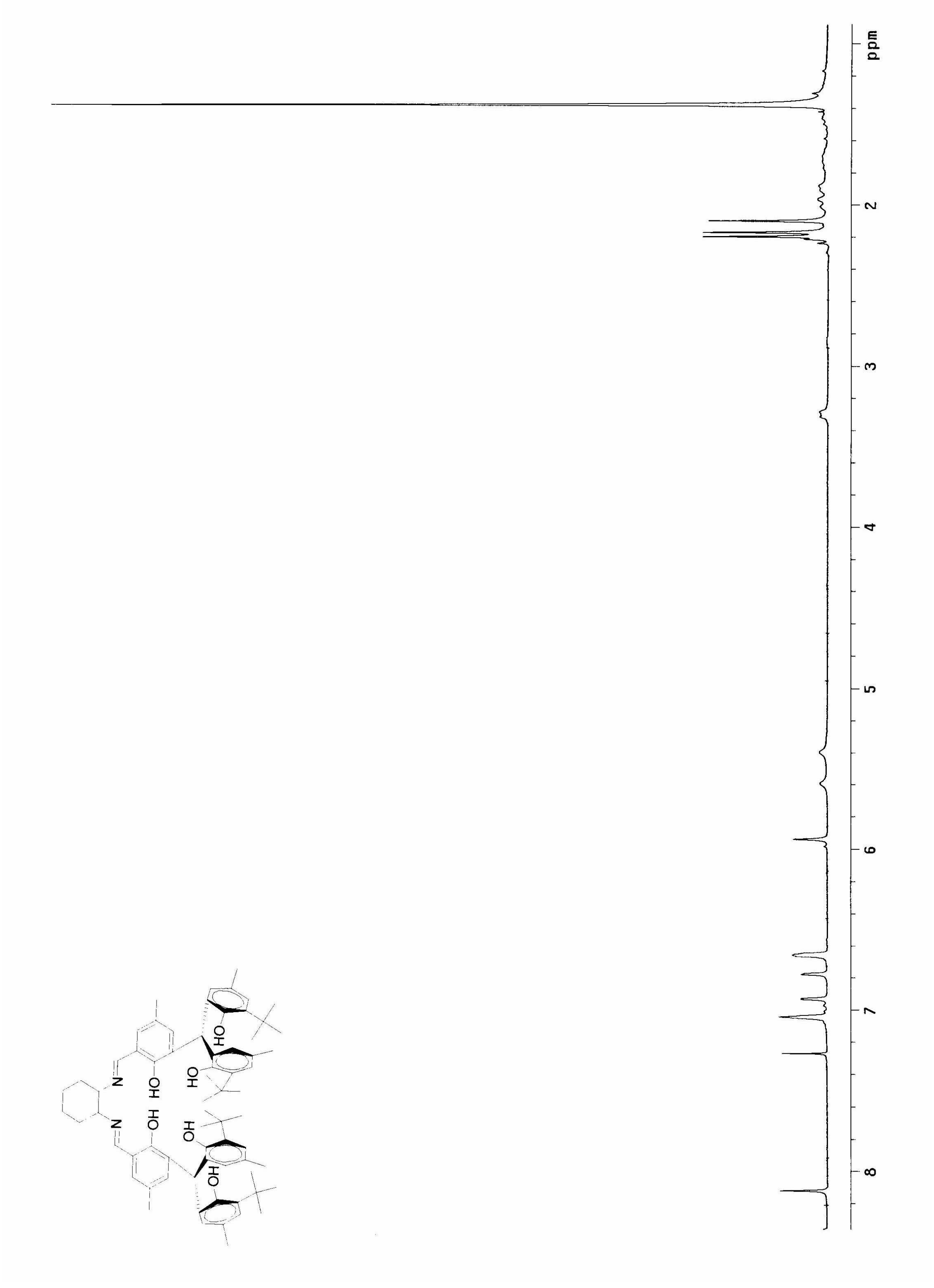
A portion of 1.00g (0.974mmol) of ligand-1 was dissolved in dry ether. To this solution 0.092g (2.14mmol) sodium methoxide was added along with 0.240g (1.07mmol) of palladium acetate. The solution was refluxed for three hours under nitrogen during which time a green precipitate formed. The solution was cooled and the precipitate was filtered. The product was redissolved in methylene chloride, filtered and then solvent was removed leaving a yellow solid in a 62% yield (0.68g). X-ray quality crystals were grown by a chloroform/pentane diffusion.

^{1}H NMR: δ 7.57 (s, 2H); 7.10 (d, 2H); 6.98 (s, 4H); 6.95 (s, 2H); 6.91 (s, 2H); 6.88 (s, 2H); 6.60 (s, 2H); 6.58 (s, 2H); 6.28 (s, 2H); 5.81 (s, 2H); 3.50-3.40 (m, 2H); 2.41 (d, 2H); 2.16 (s, 6H); 2.14 (s, 6H); 2.09 (s, 6H); 1.71 (d, 2H); 1.28 (s, 18H); 1.18 (s, 18H). ^{13}C NMR δ 160.49; 156.44; 151.26; 138.74; 137.58; 136.90; 134.04; 132.91; 130.16; 129.61; 128.60; 128.41; 128.06; 125.91; 125.08; 120.64; 72.62; 38.86; 34.89; 30.05; 28.99; 24.47; 21.47; 20.23. Anal. Calc. for $C_{68}H_{86}N_2O_6Pd$: C, 72.20; H, 7.43; N, 2.48. Found C, 72.03; H, 7.65; N, 2.51.

Synthesis of Ni-Ligand-1-Fluoride.

A portion of 0.050g (0.046mmol) of Ni-Ligand-1 along with 0.029g (0.092mmol) tetrabutyl ammonium fluoride trihydrate was dissolved in 1mL toluene. Pentane was slowly diffused into the solution forming x-ray quality crystals.

^{1}H NMR: δ 7.44 (s, 2H); 7.16 (d, 2H); 6.86 (s, 4H); 6.83 (s, 2H); 6.75 (s, 4H); 6.37 (s, 2H); 3.37 (m, 8H); 3.14 (s, 2H); 2.46 (m, 2H); 2.17 (m, 6H); 2.13 (s, 12H); 1.92 (m, 2H); 1.68 (m, 8H); 1.46 (q, 8H); 1.30 (m, 2H); 1.12 (s, 18H); 1.10 (s, 18H); 1.02 (t, 12H). Anal. Calc. for $C_{84}H_{120}N_3O_6NiF$: C, 75.03; H, 8.93; N, 3.12. Found C, 74.24; H, 8.91; N, 2.64.



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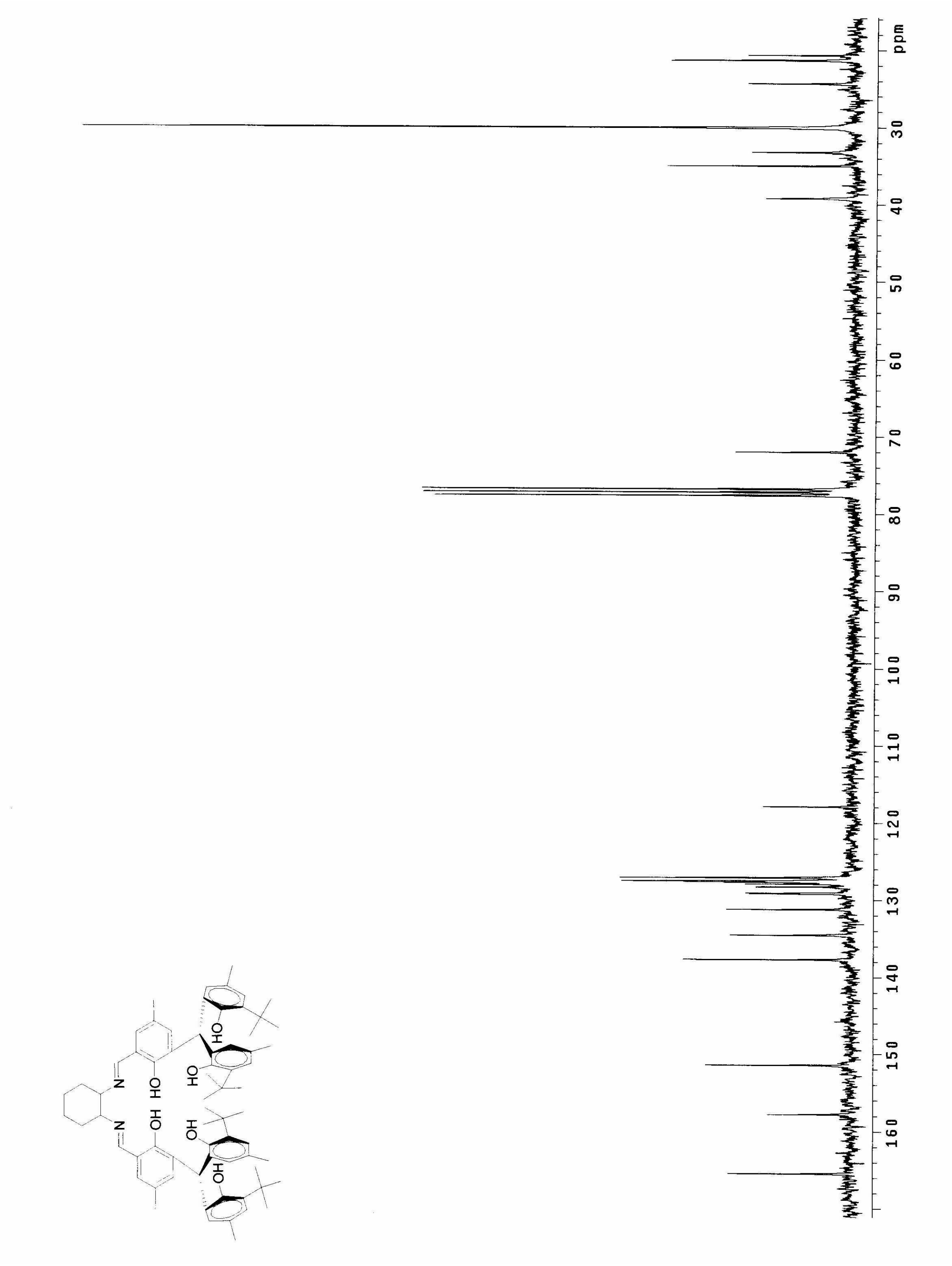

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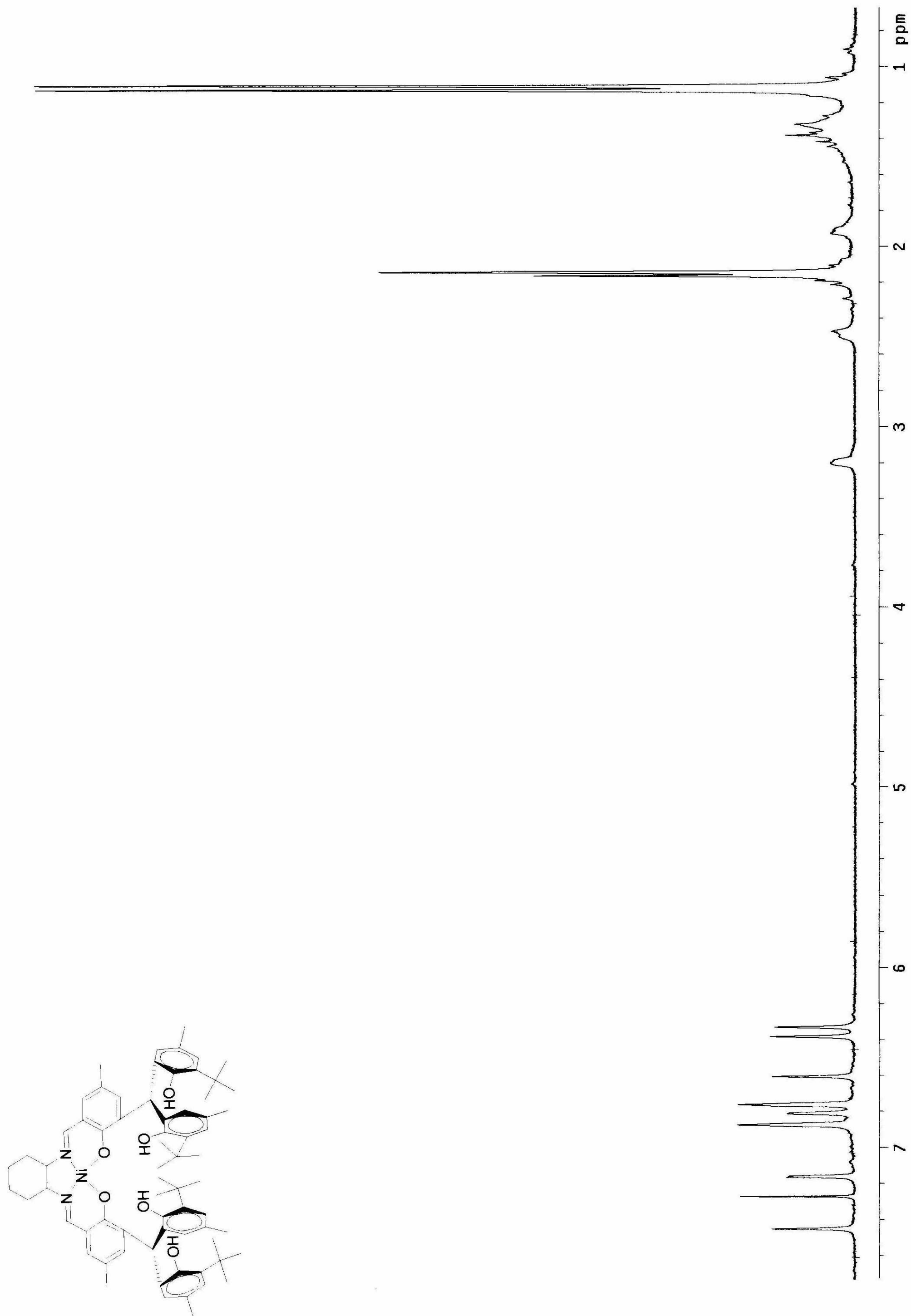

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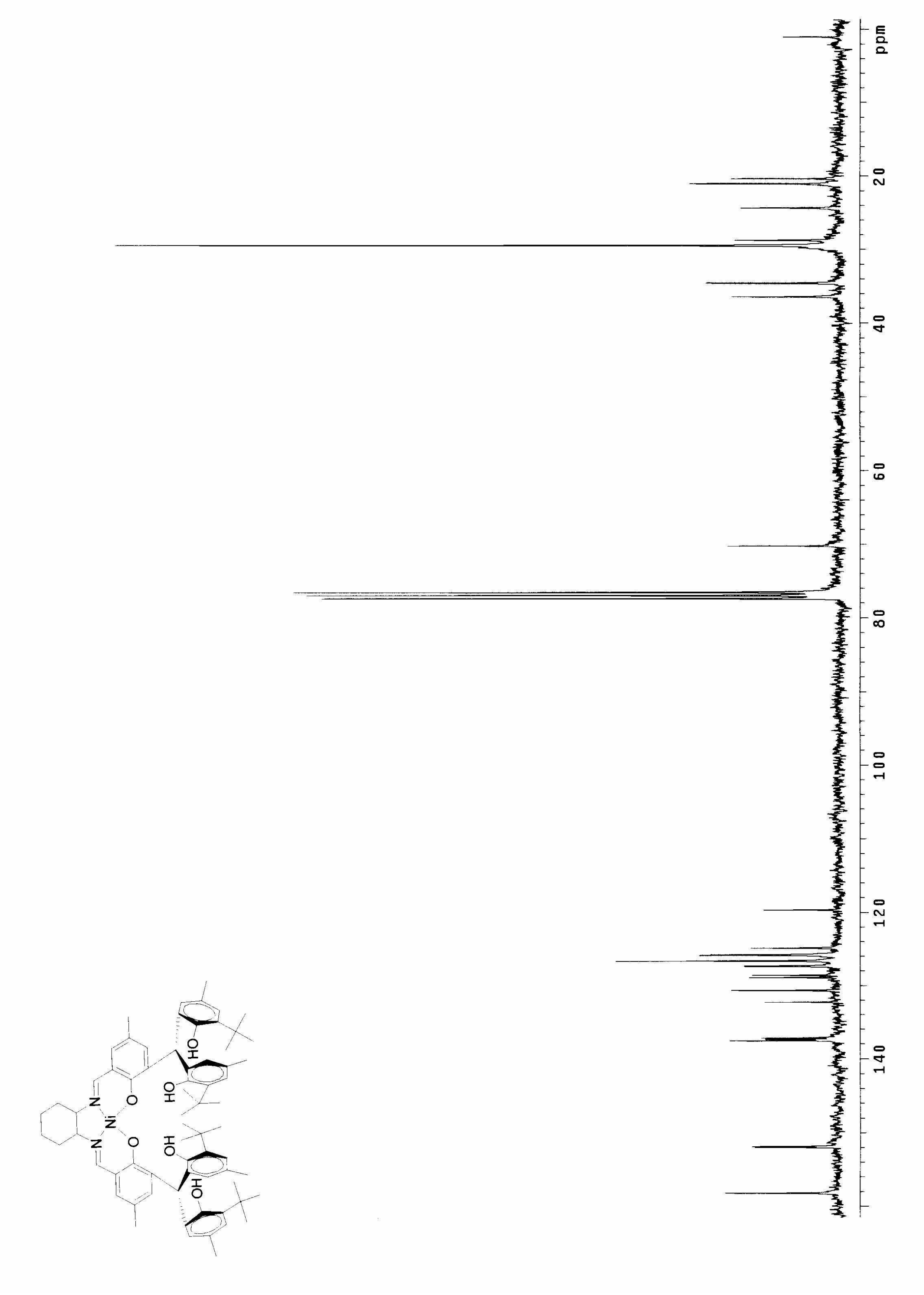

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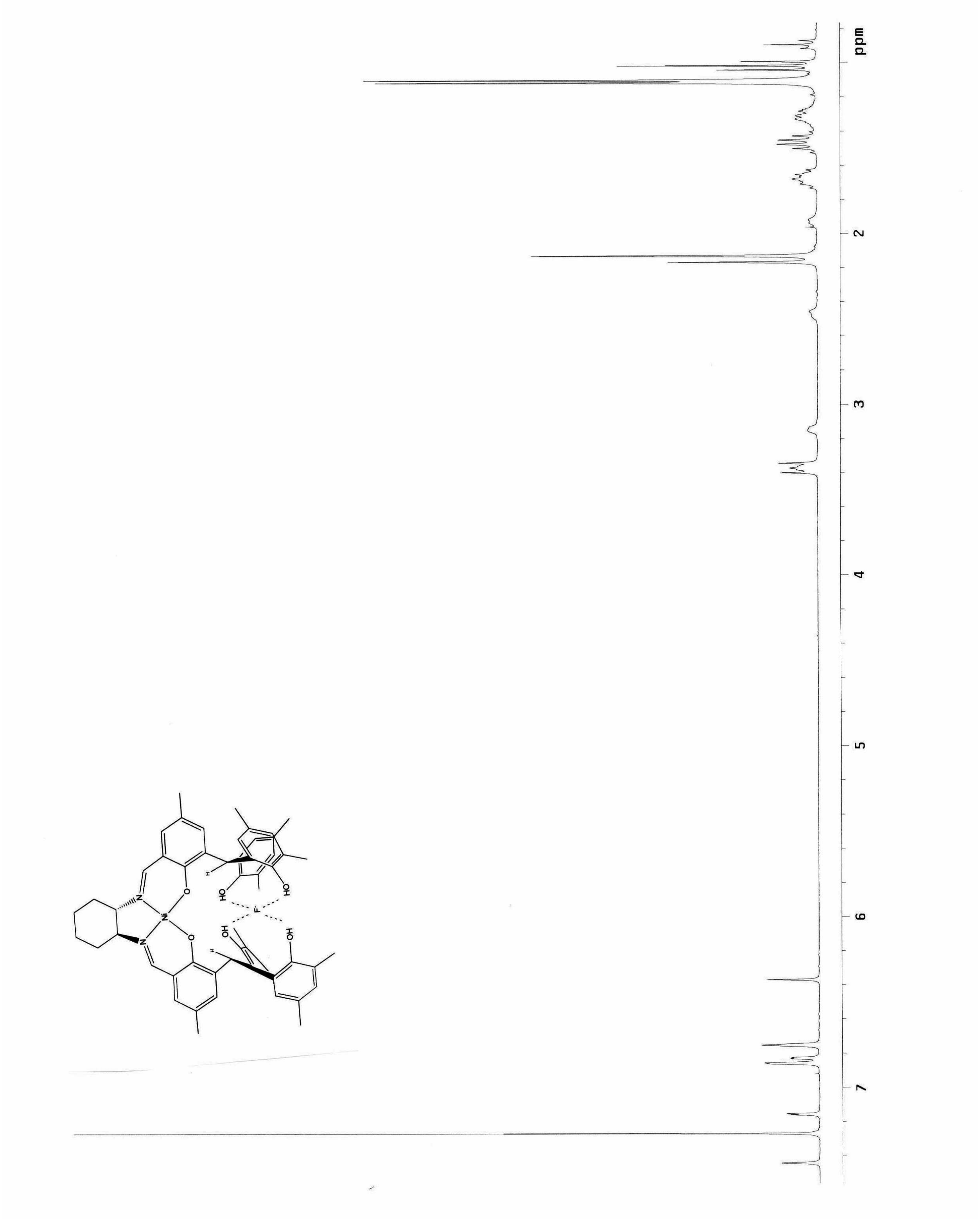

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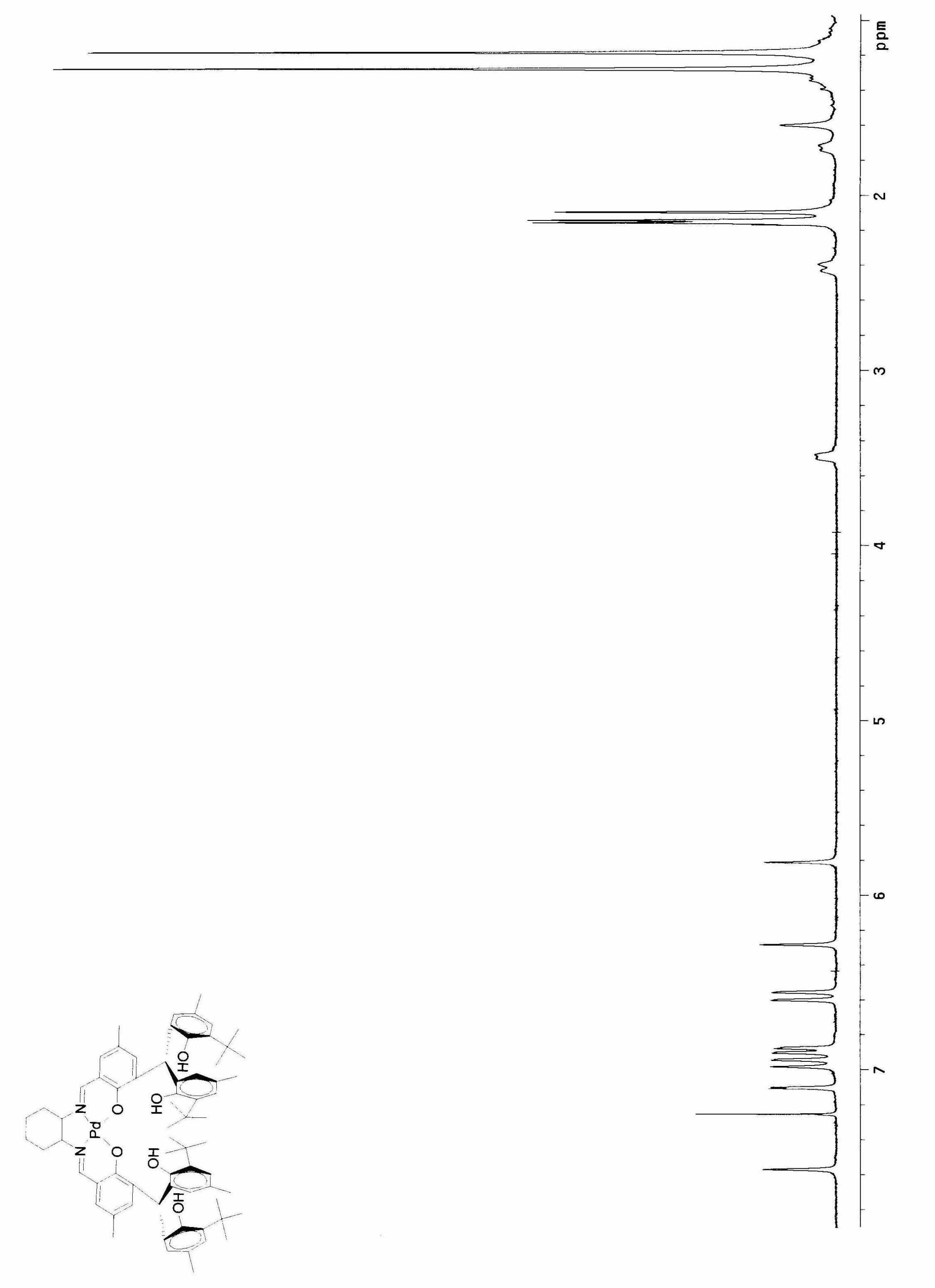

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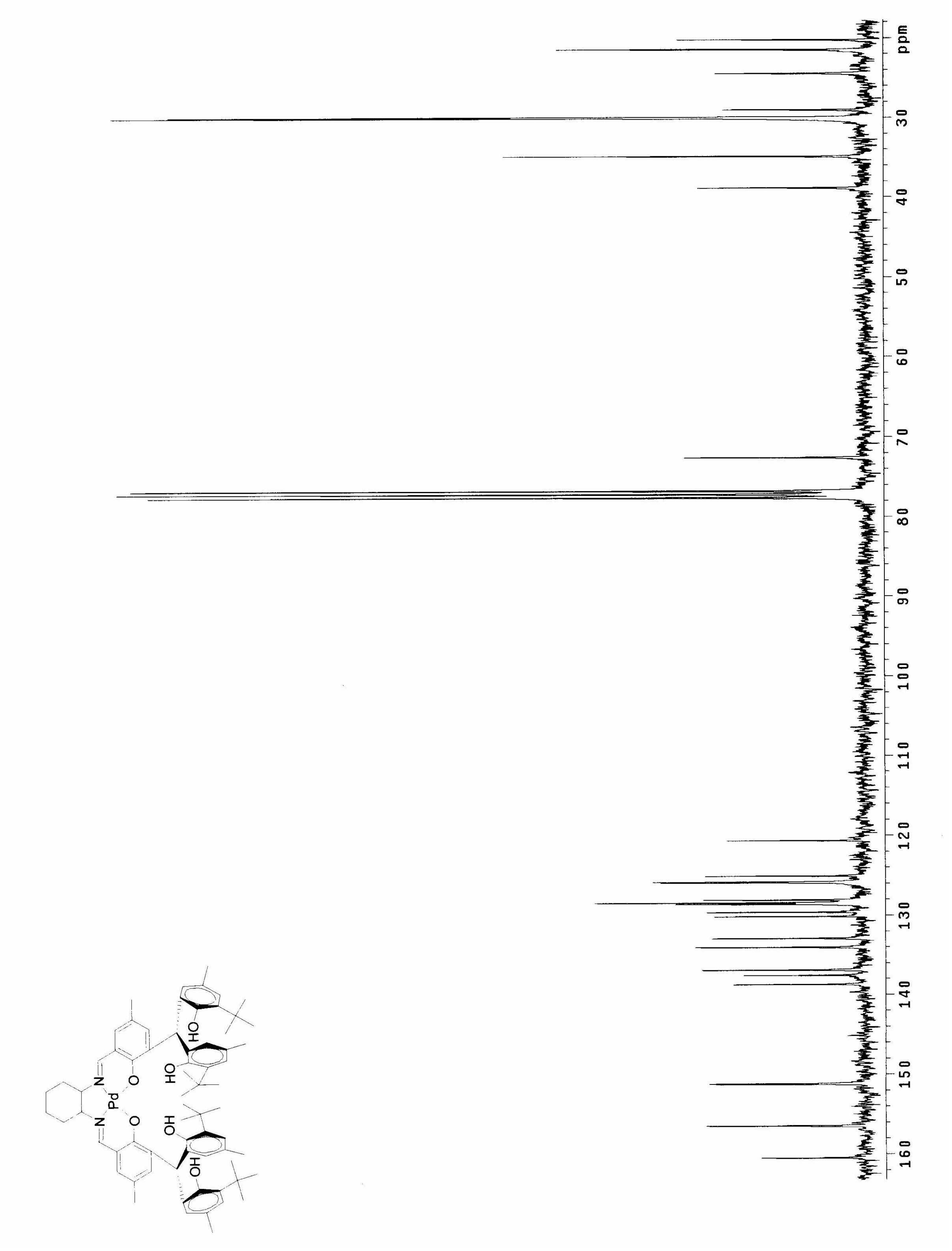

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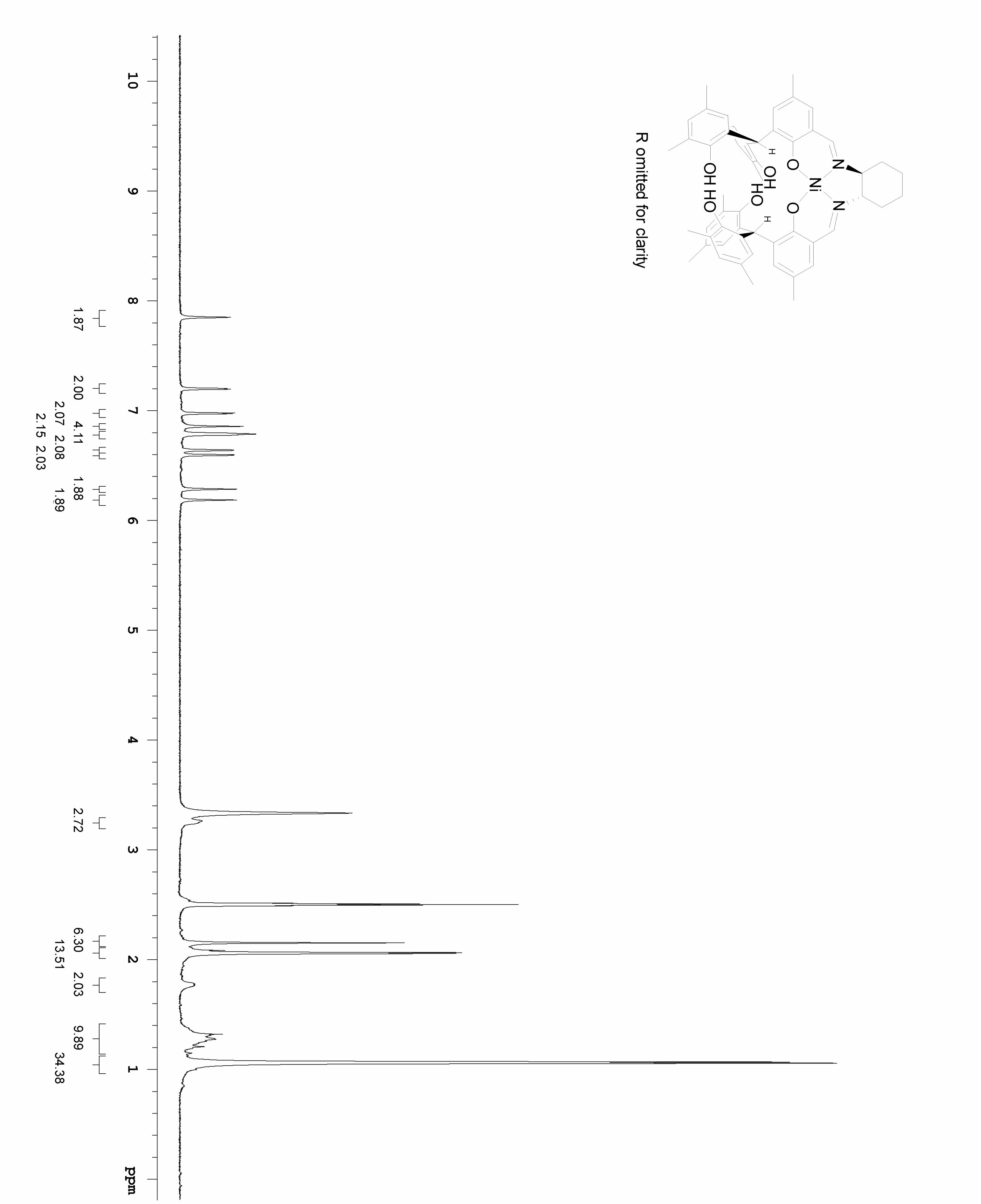

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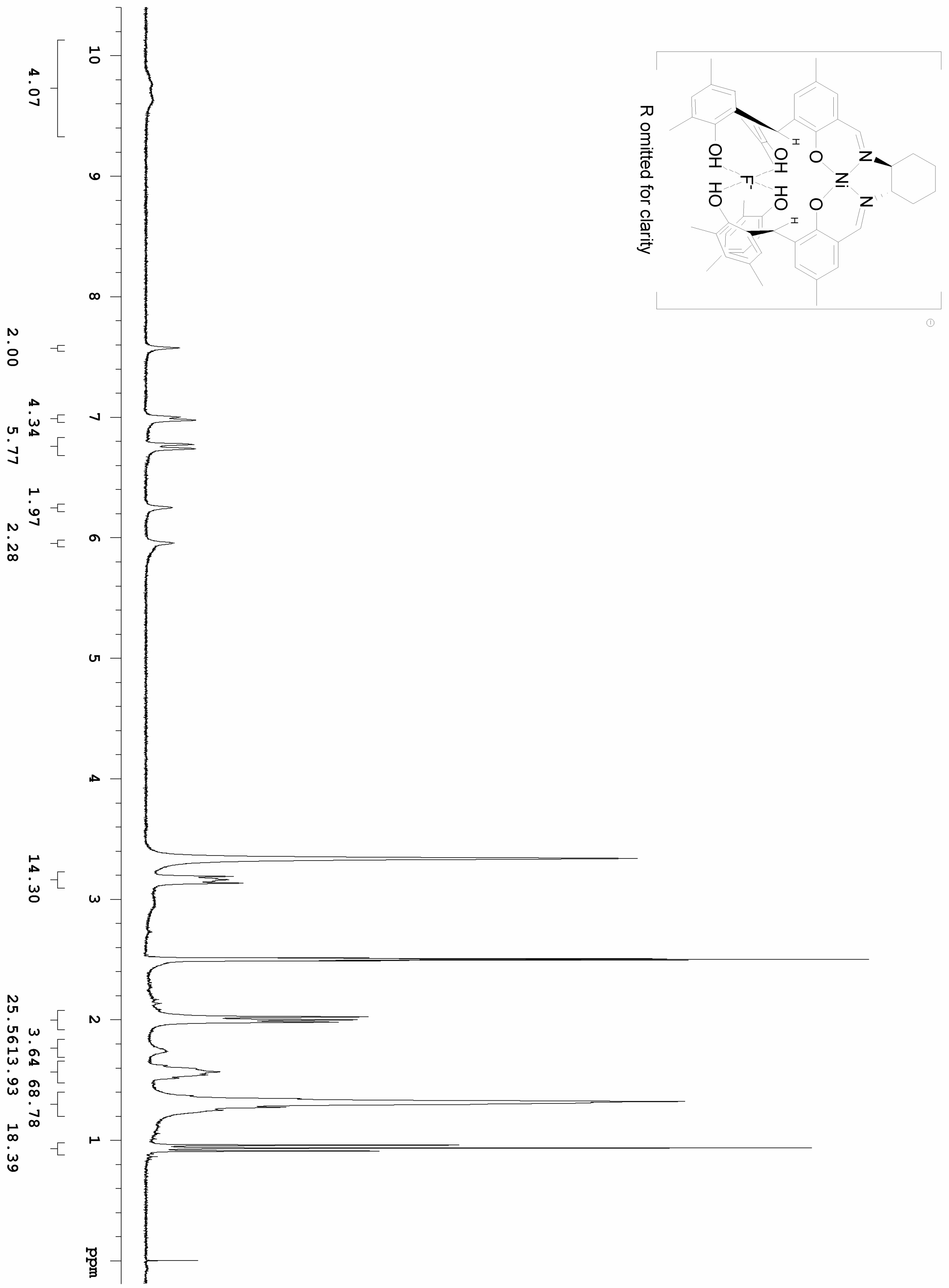

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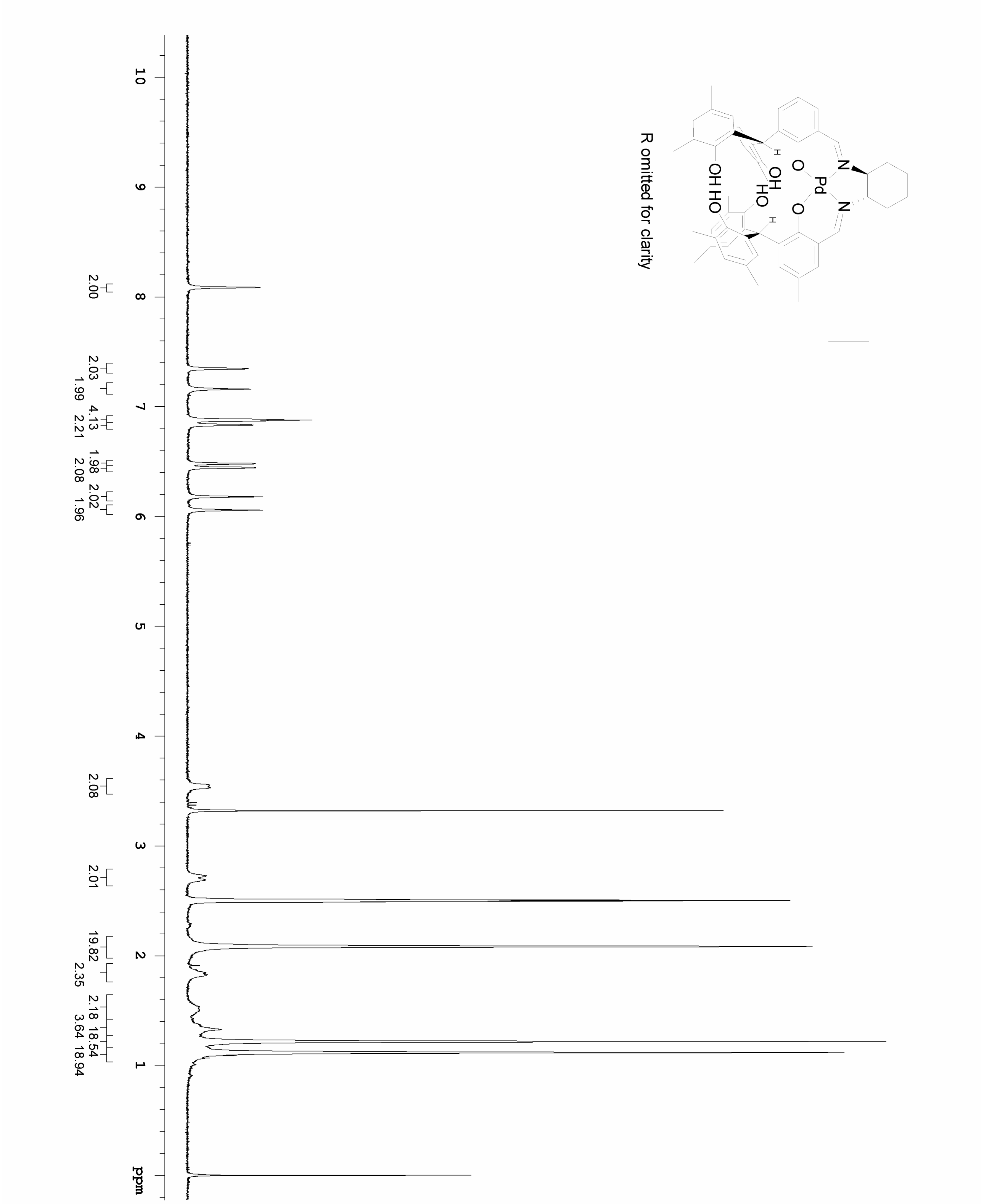

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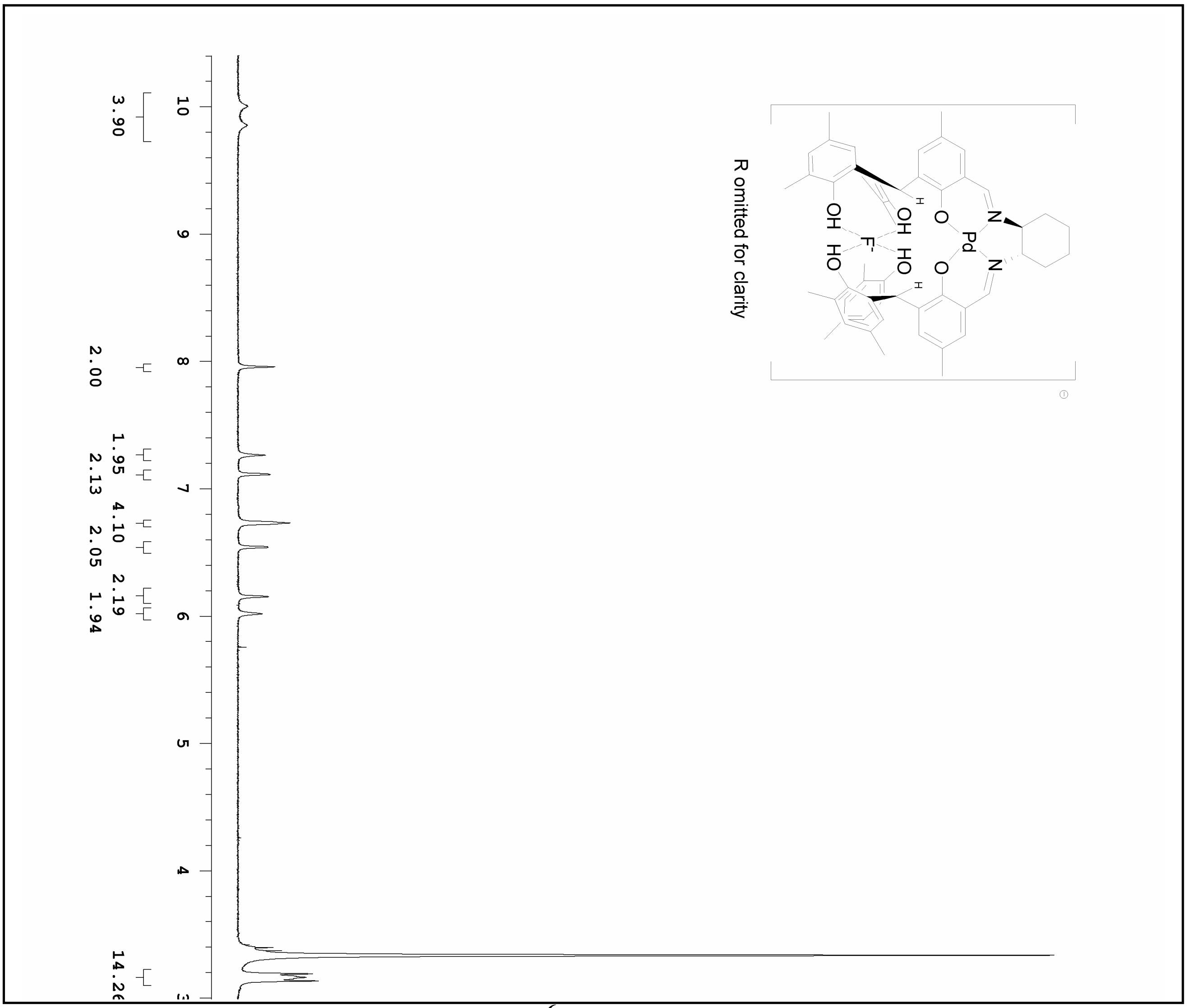
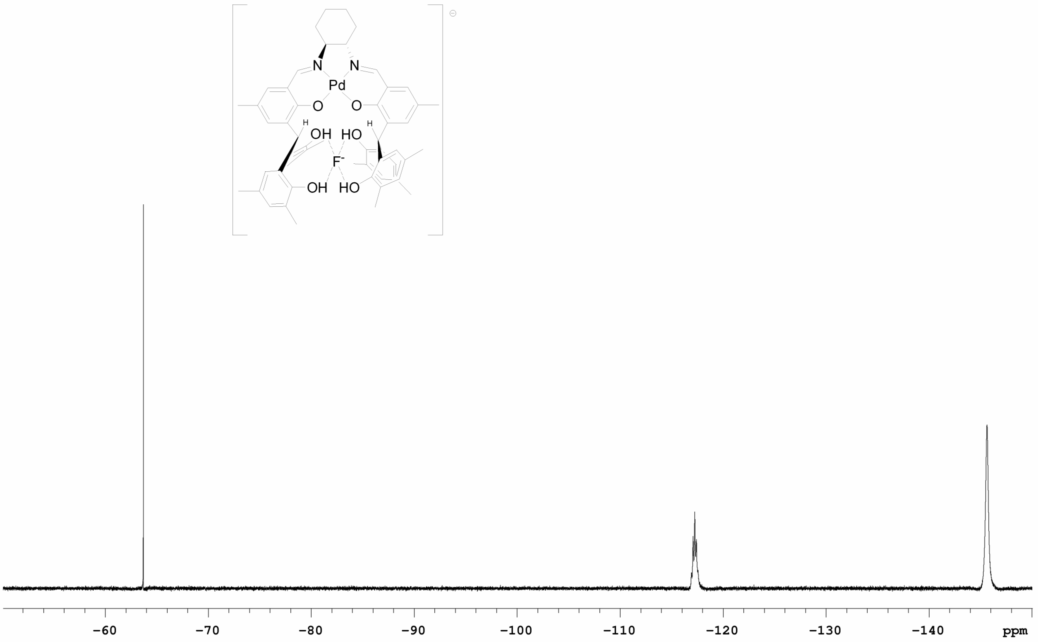
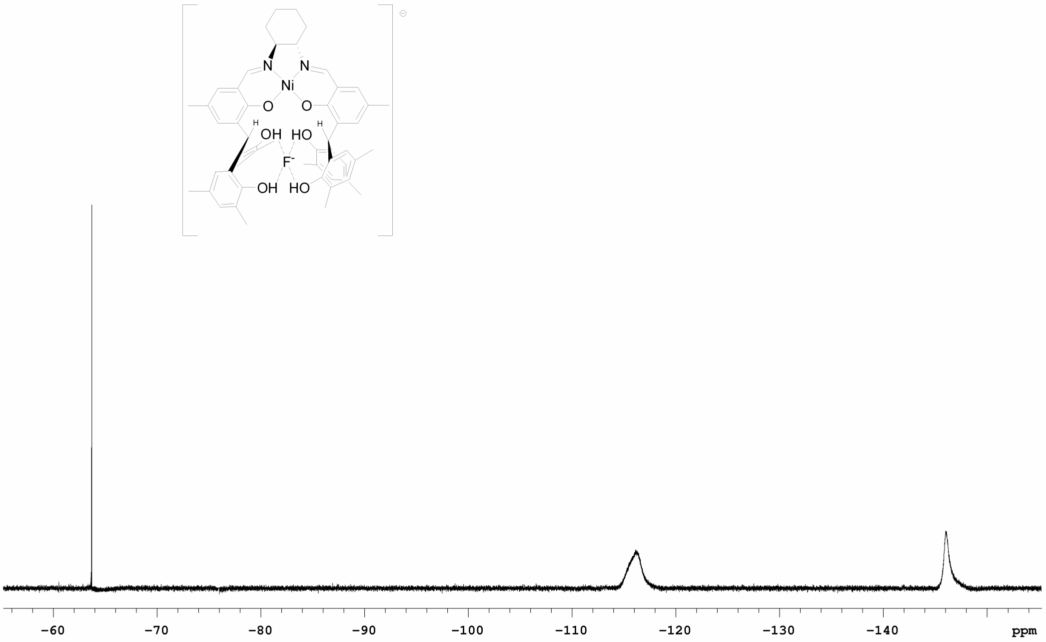


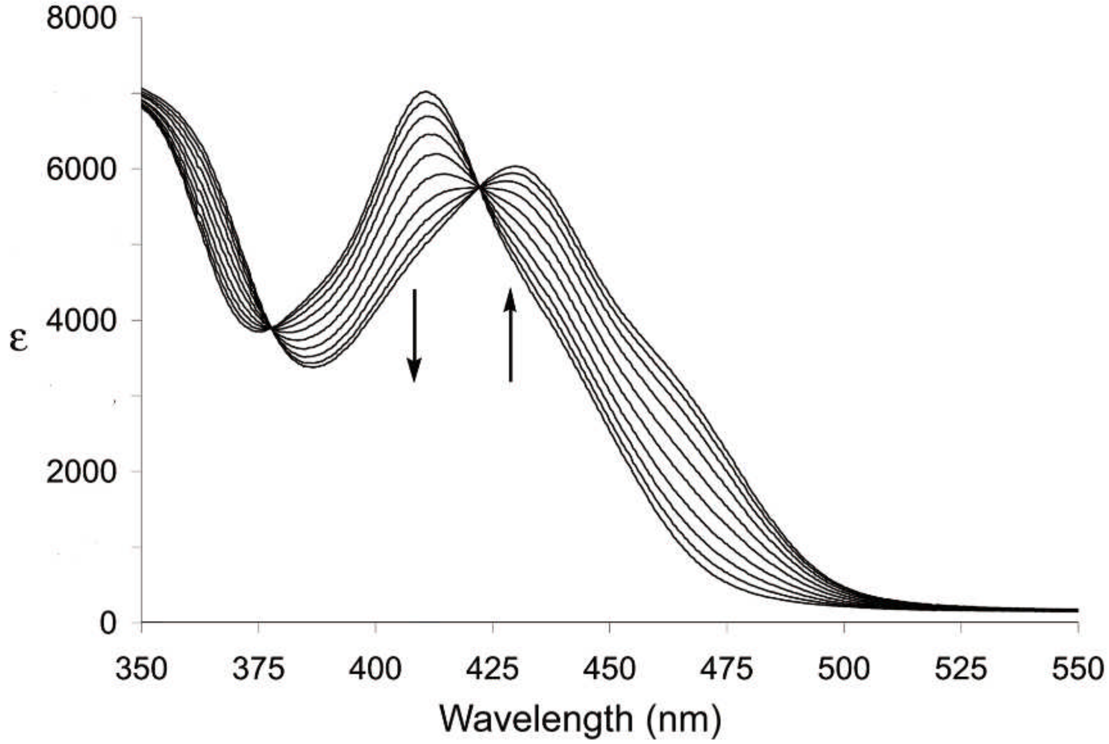
Spectrum in d^6- DMSO

^{19}F NMR **Spectrum in DMSO**

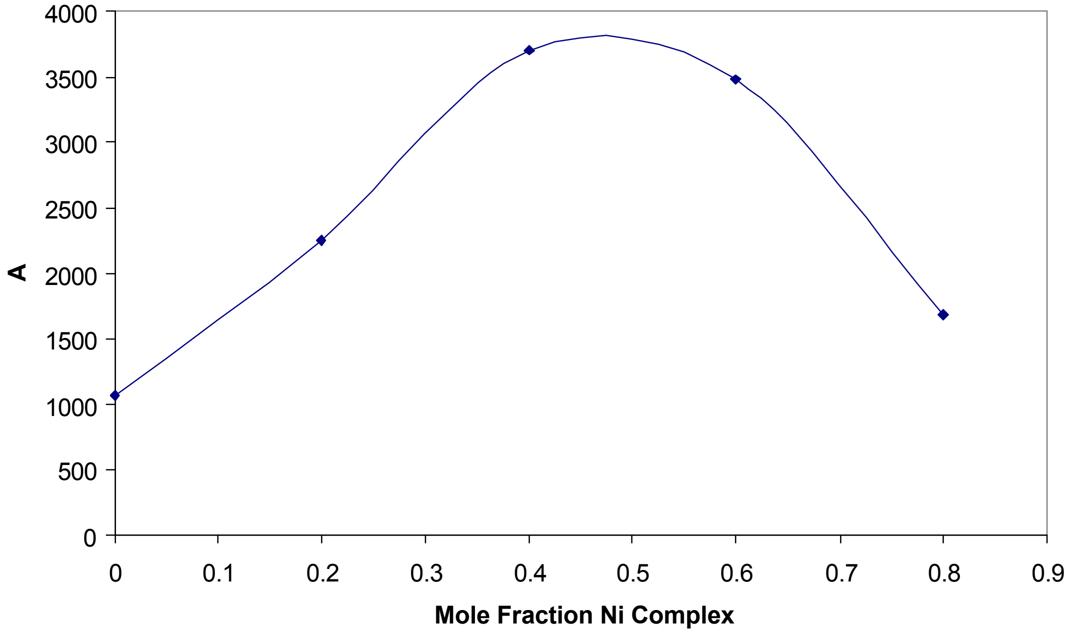


^{19}F NMR **Spectrum in DMSO**

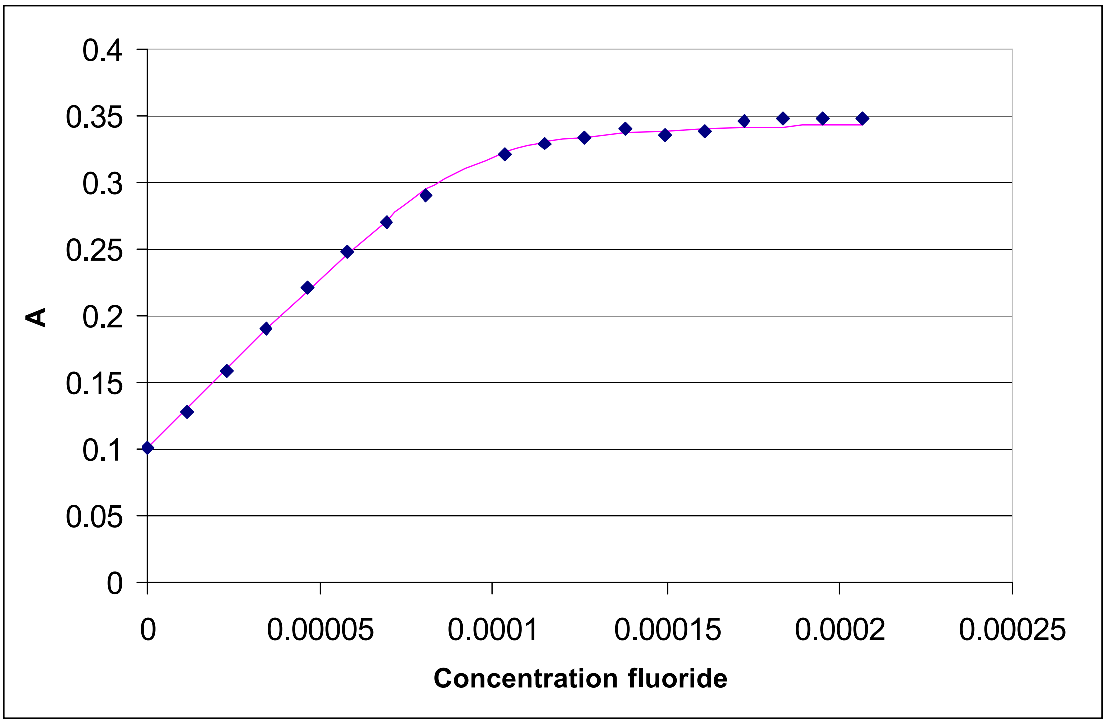




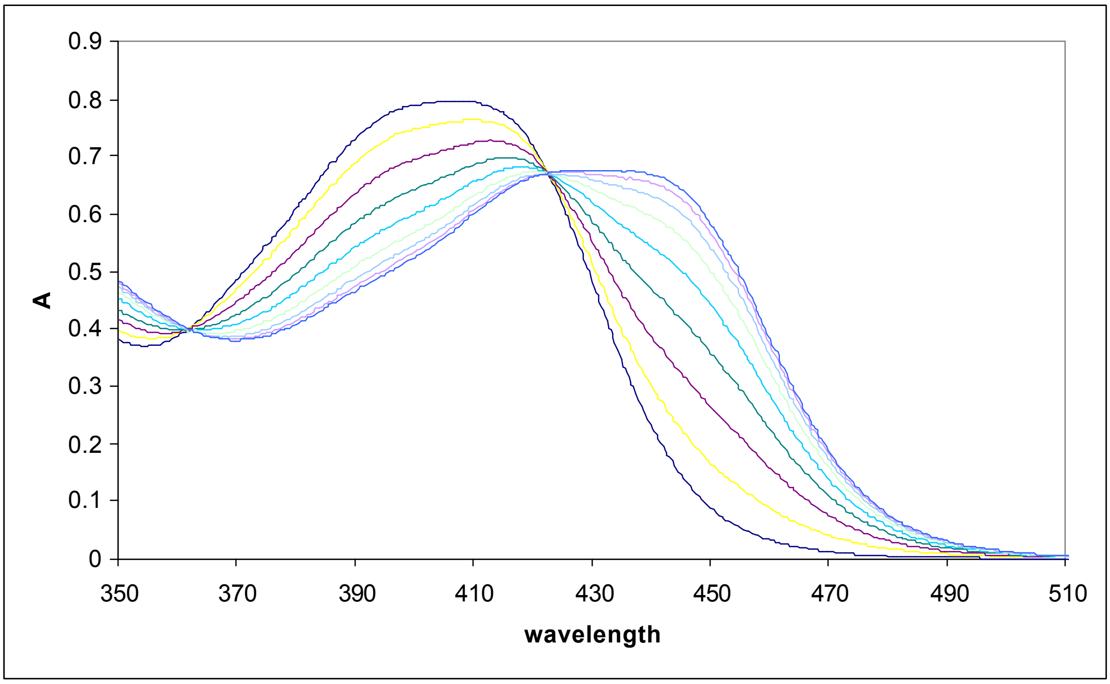
Ni complex titrated with 1M Tetrabutylammonium fluoride solution in acetone



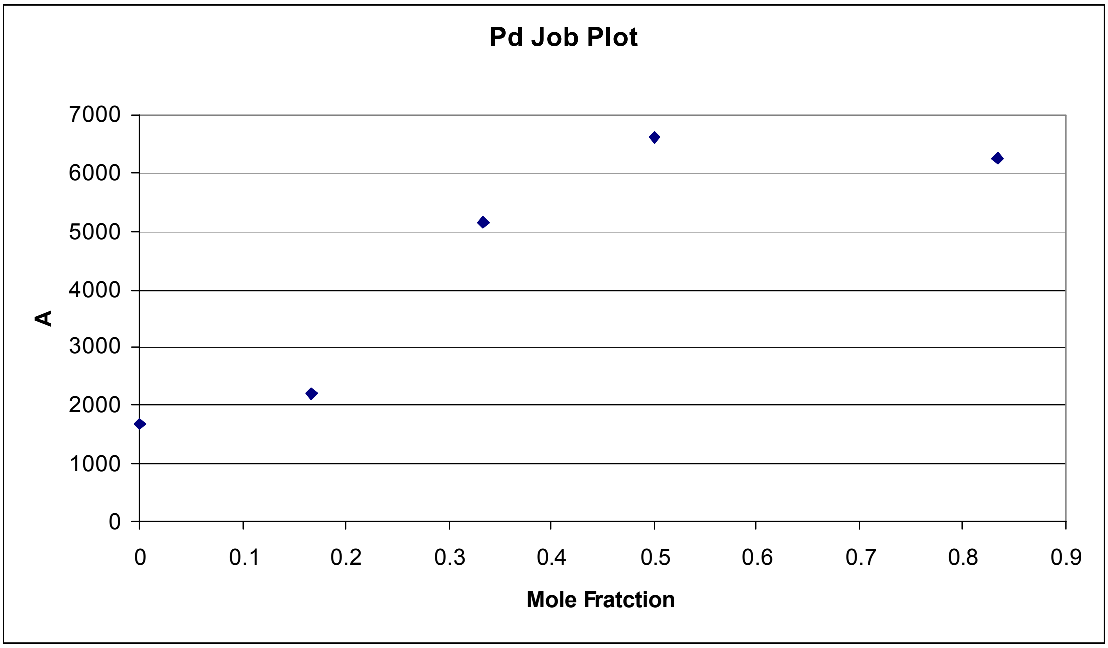
Job Plot of Ni complex titration with tetrabutyl ammonium fluoride solution

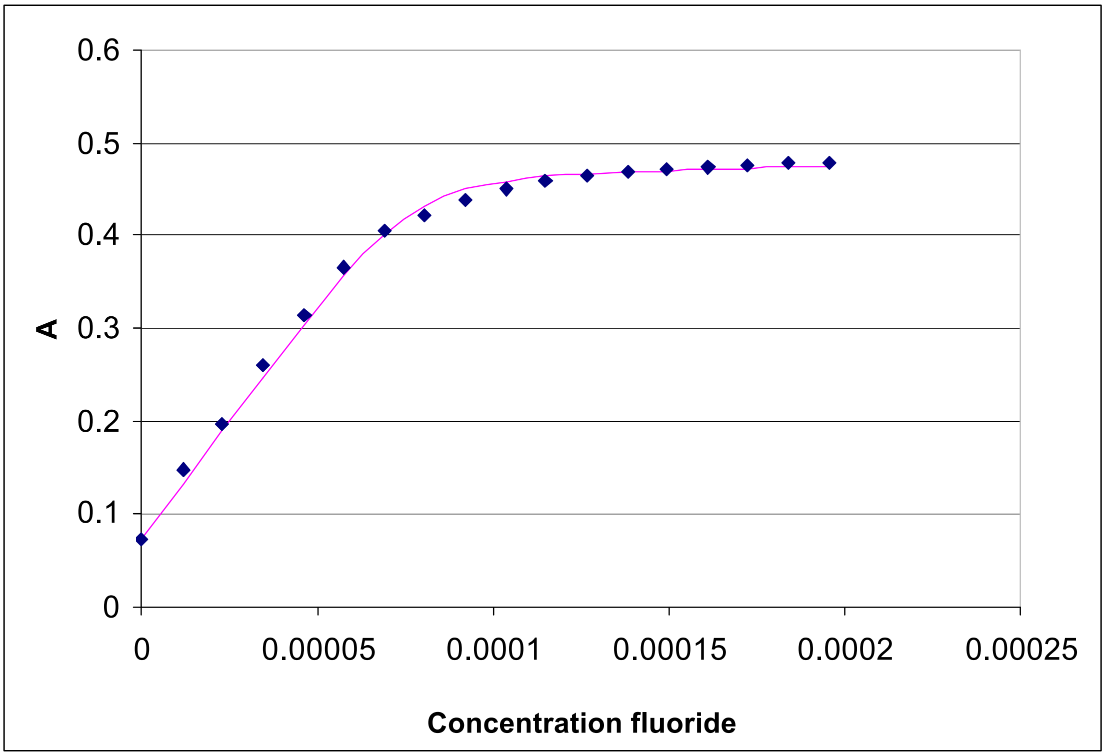


Binding constant of Fluoride to nickel complex in acetone at 450nm. **LogK = 5.64**



UV- VIS spectra of Pd complex with a 1M tetrabutyl ammonium fluoride solution in acetone





Binding constant of fluoride to palladium complex in acetone at 450nm. **LogK = 5.81**