

NH vs CH⁻anion hydrogen bond formation in platinum(tetrakispyridine) complexes

Ismael El Drubi Vega,^a Philip A. Gale*,^a, Mark E. Light^a and Stephen J. Loeb^b

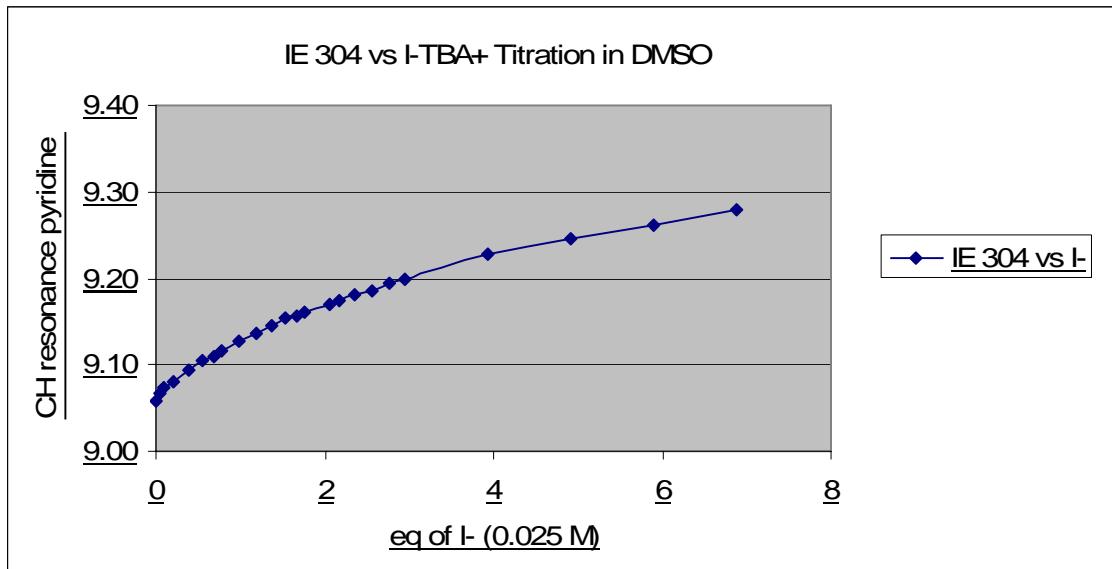
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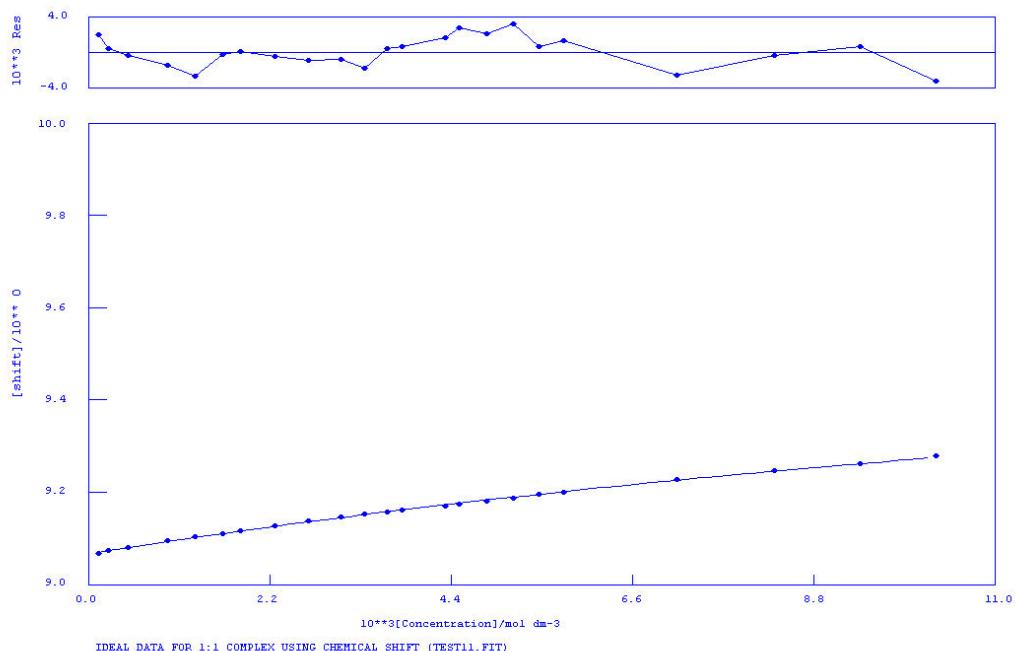
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Titrations tetrakispyridineplatinum(II) tetrafluoroborate **1**.

- Tetrabutylammonium iodide.



Graph 1 NMR titration shift graph.



Fit 1 WinNMR fit.

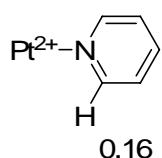
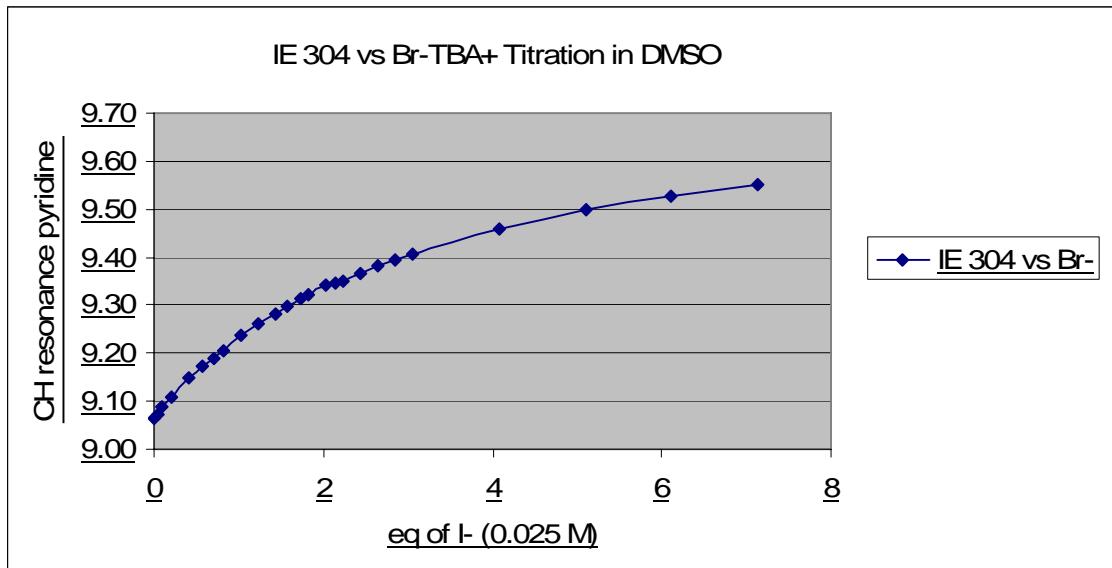
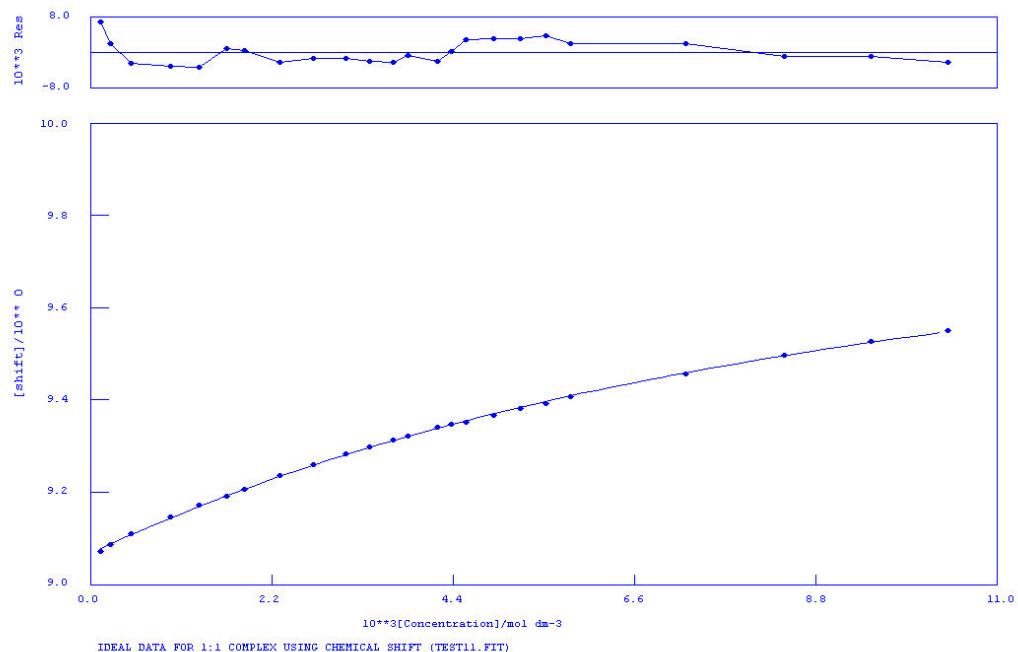


Figure 1 Shift at 3 eq.

- Tetrabutylammonium bromide.



Graph 2 NMR titration shift graph.



Fit 2 WinNMR fit.

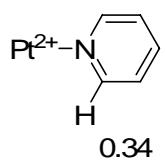
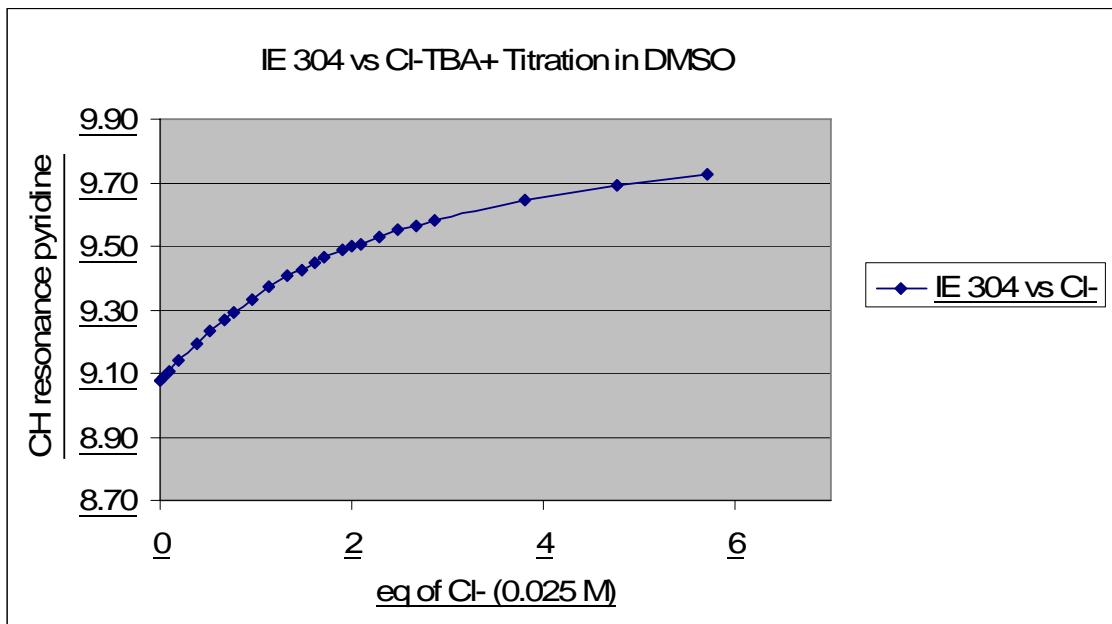
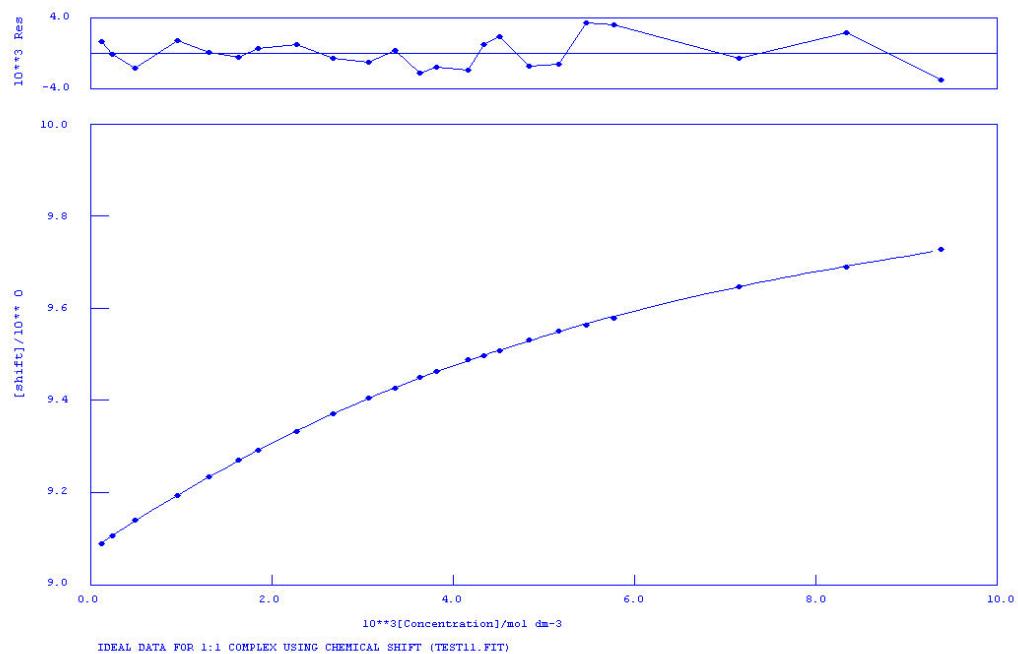


Figure 2 Shift at 3 eq.

- Tetrabutylammonium chloride.



Graph 3 NMR titration shift graph.



Fit 3 WinNMR fit.

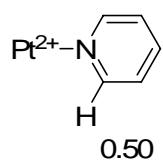
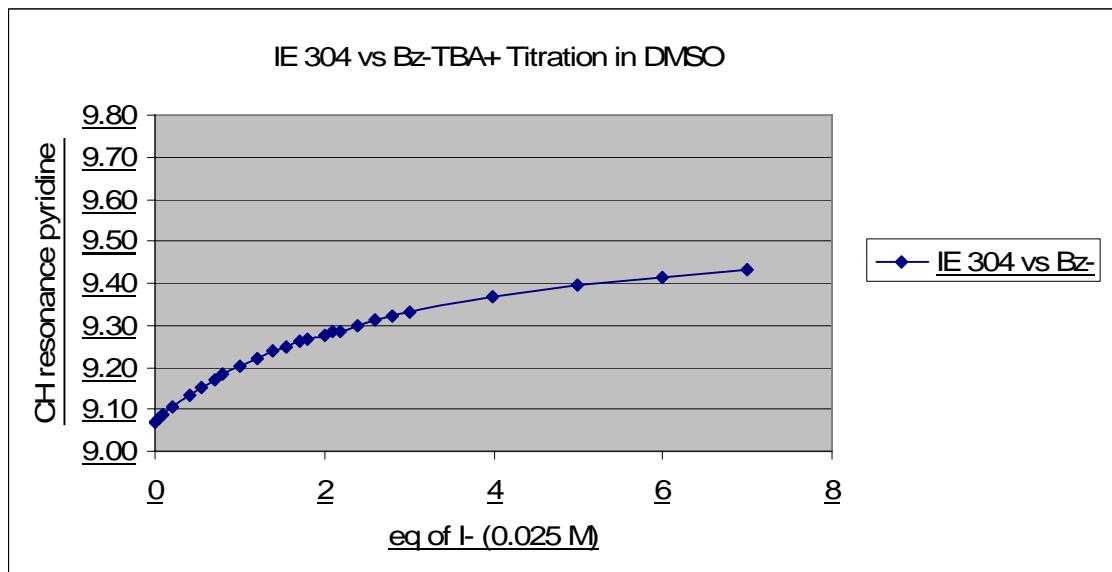
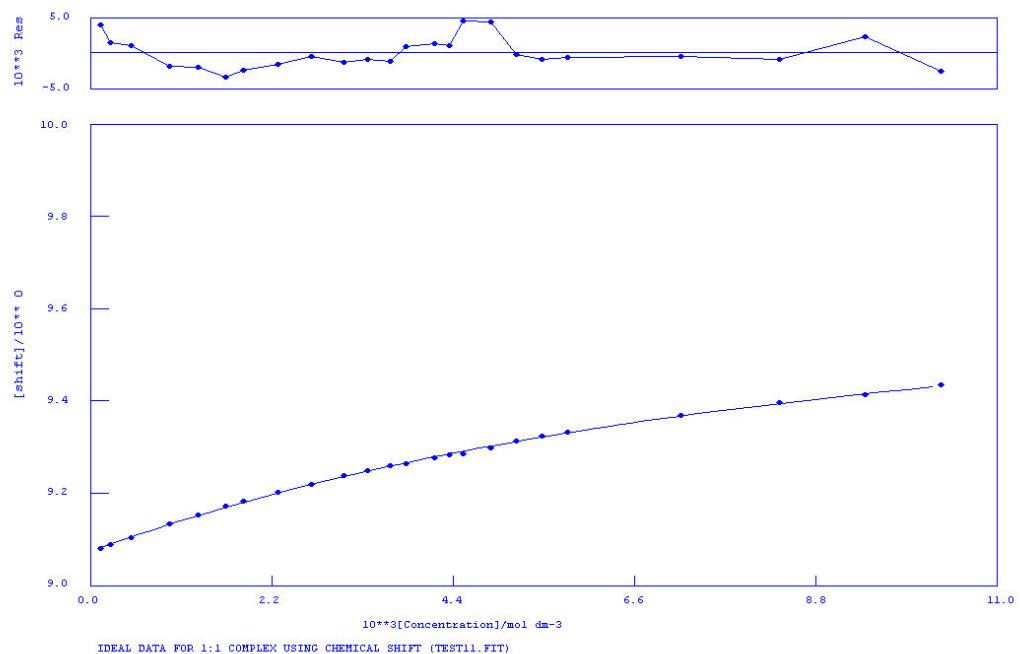


Figure 3 Shift at 3 eq.

- Tetrabutylammonium benzoate.



Graph 4 NMR titration shift graph.



Fit 4 WinNMR fit.

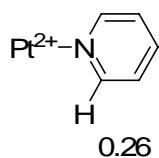
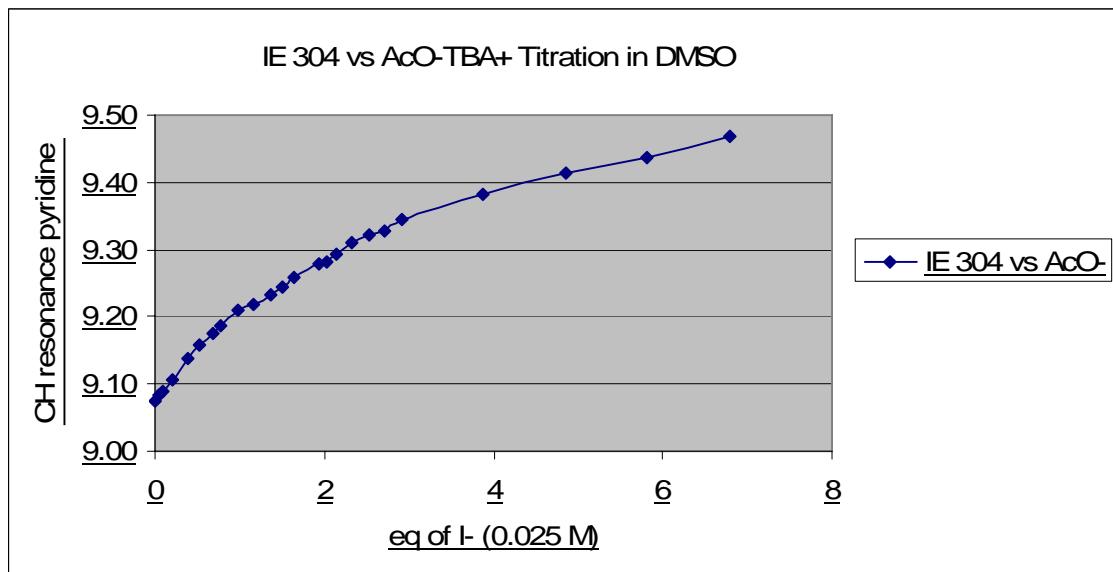
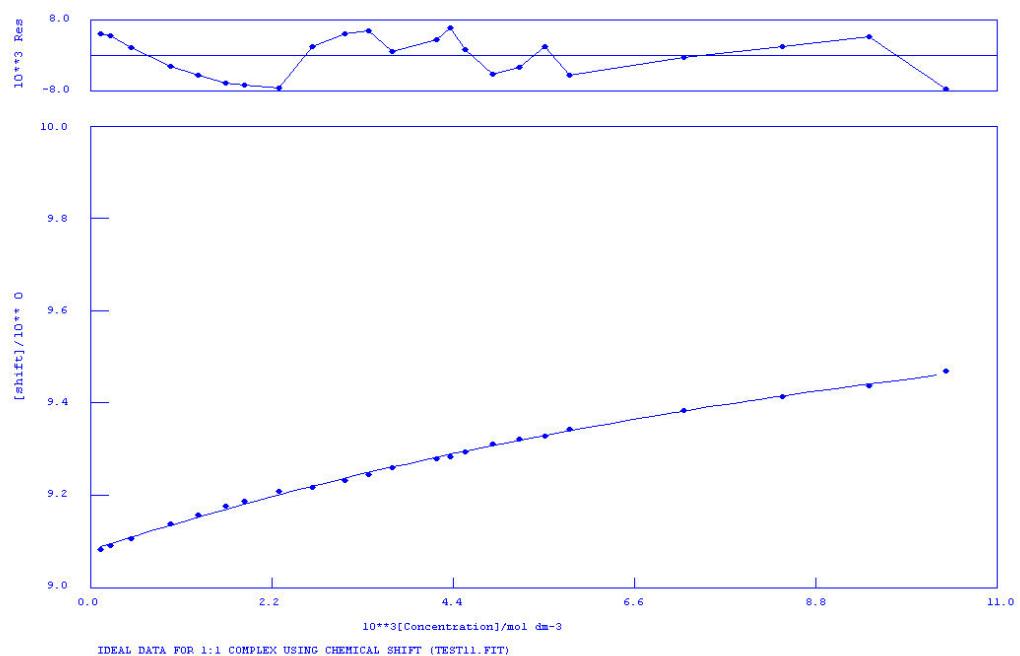


Figure 4 Shift at 3 eq.

- Tetrabutylammonium acetate.



Graph 5 NMR titration shift graph.



Fit 5 WinNMR fit.

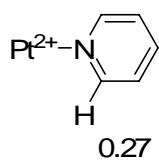
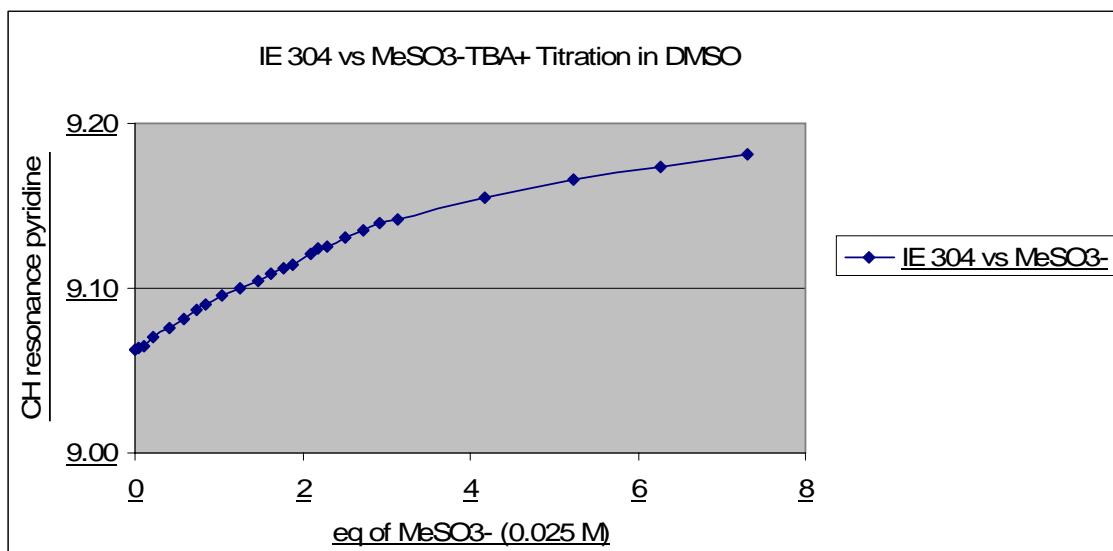
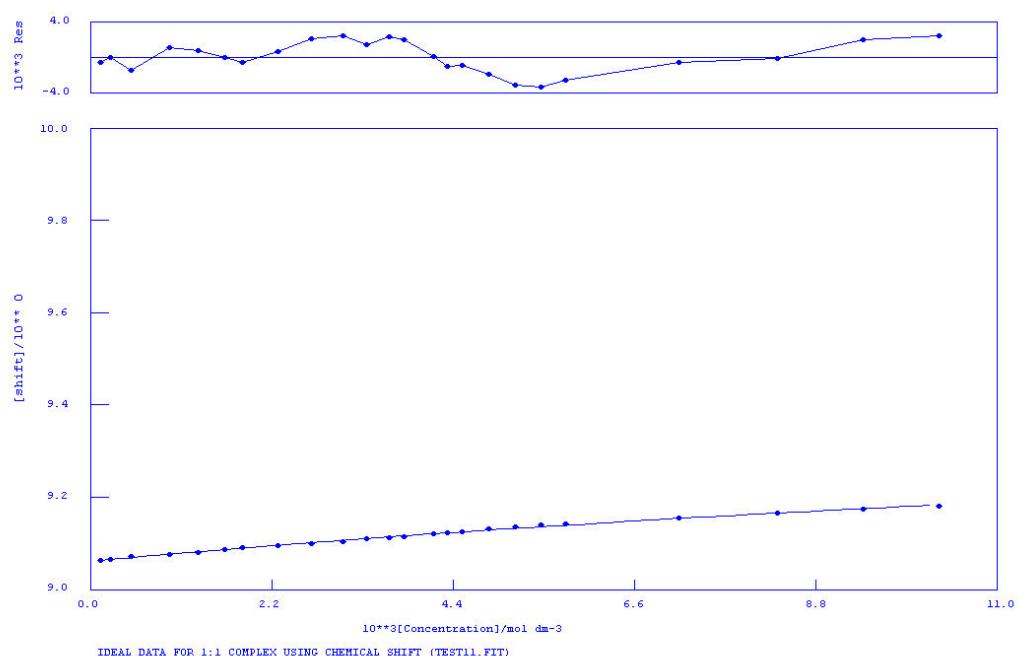


Figure 5 Shift at 3 eq.

- Tetrabutylammonium methanesulfonate.



Graph 6 NMR titration shift graph.



Fit 6 WinNMR fit.

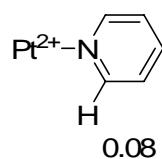
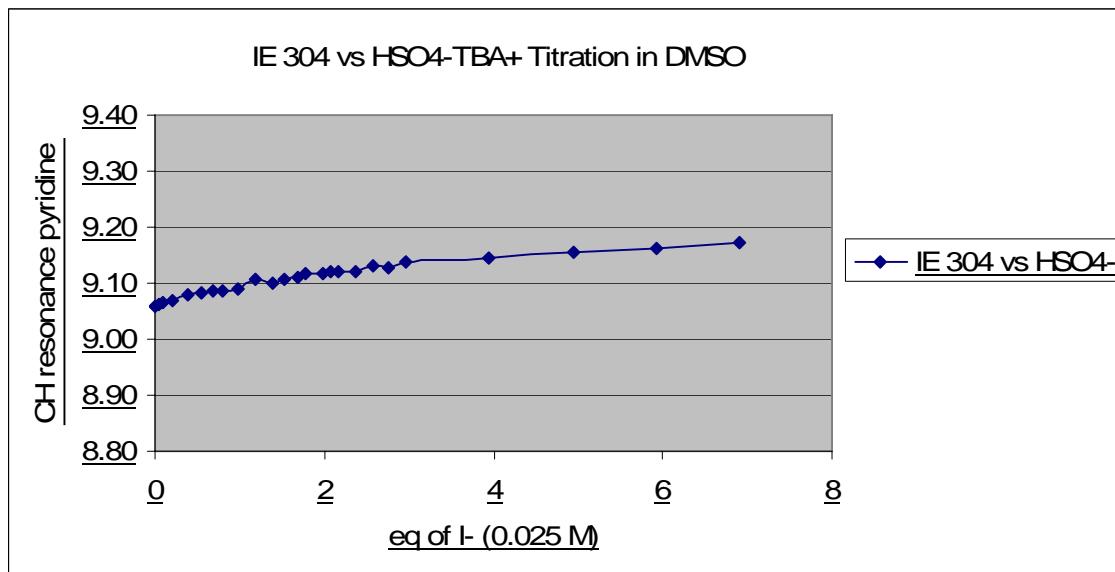
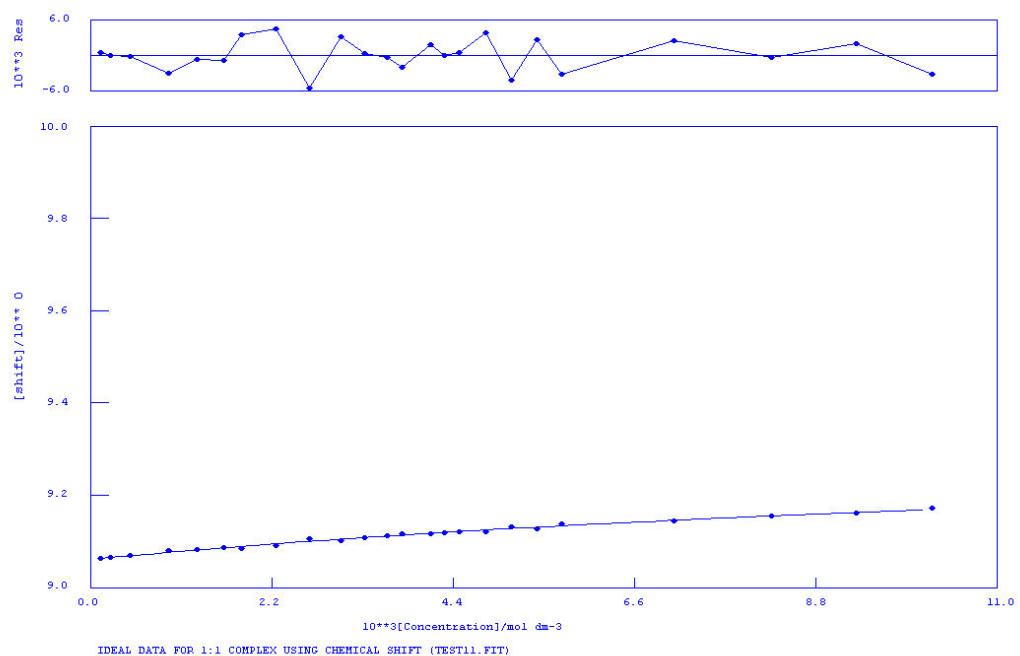


Figure 6 Shift at 3 eq.

- Tetrabutylammonium hydrogensulfate.



Graph 7 NMR titration shift graph.



Fit 7 WinNMR fit.

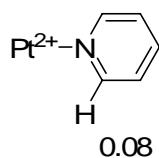
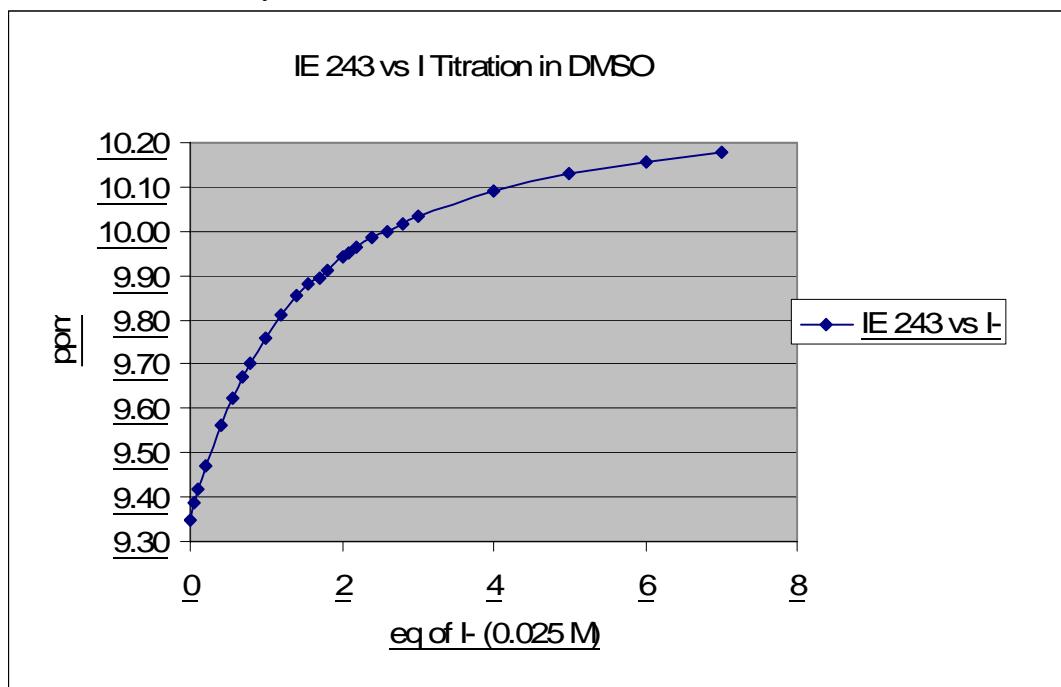


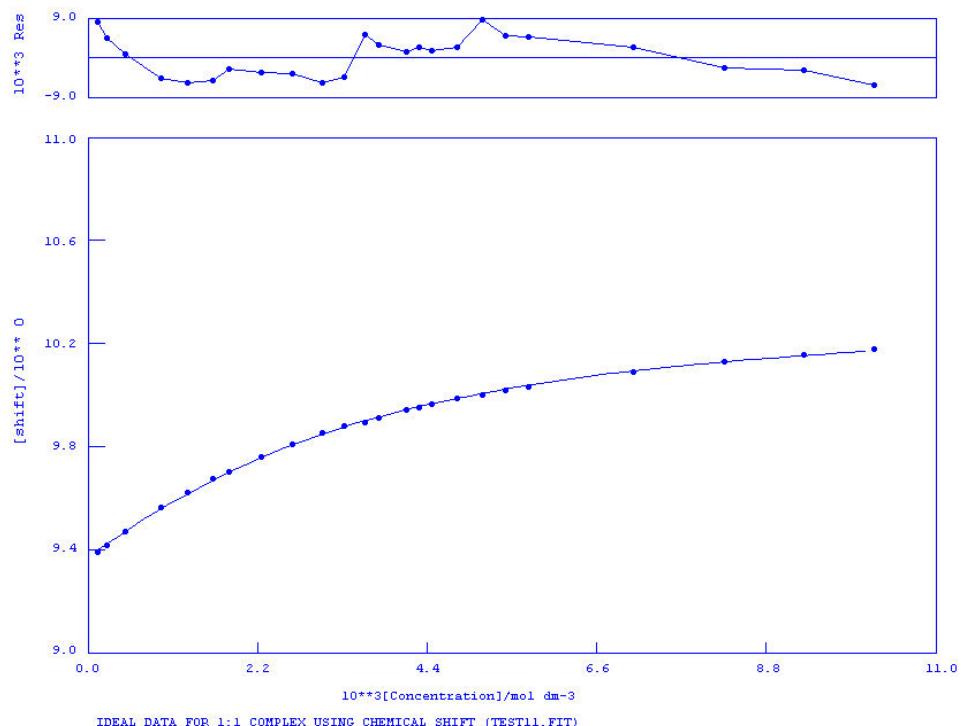
Figure 7 Shift at 3 eq.

Titrations tetrakis(m-(1H-pyrrole)pyridine)platinum(II) tetrafluoroborate **2**.

- Tetrabutylammonium iodide.
 - CH Pyridine

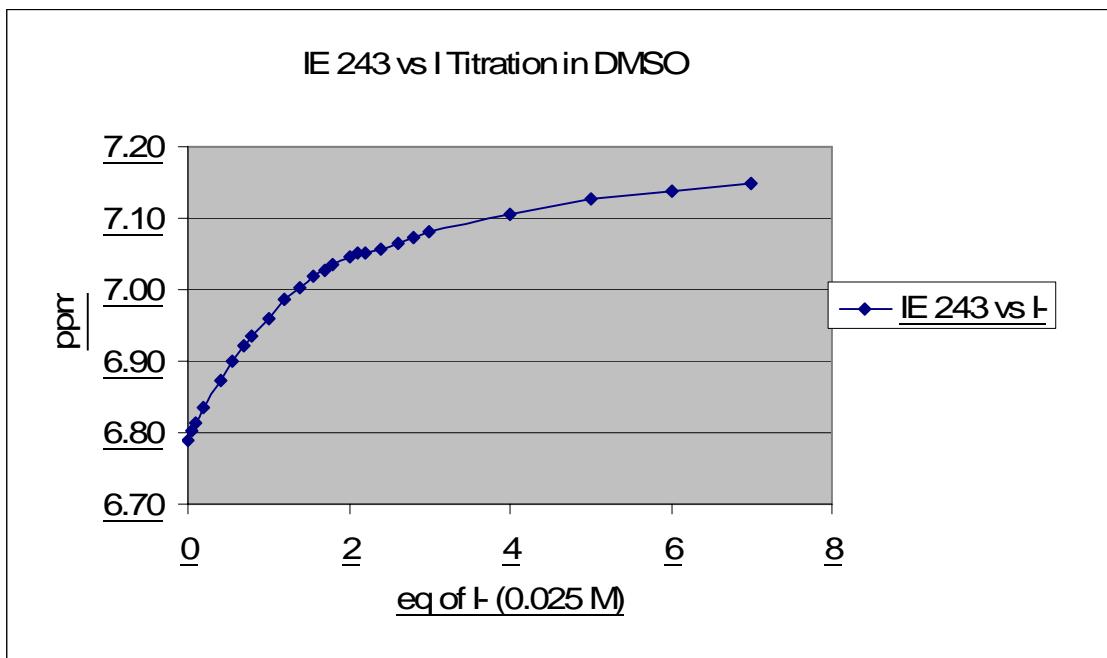


Graph 8 NMR titration shift graph.

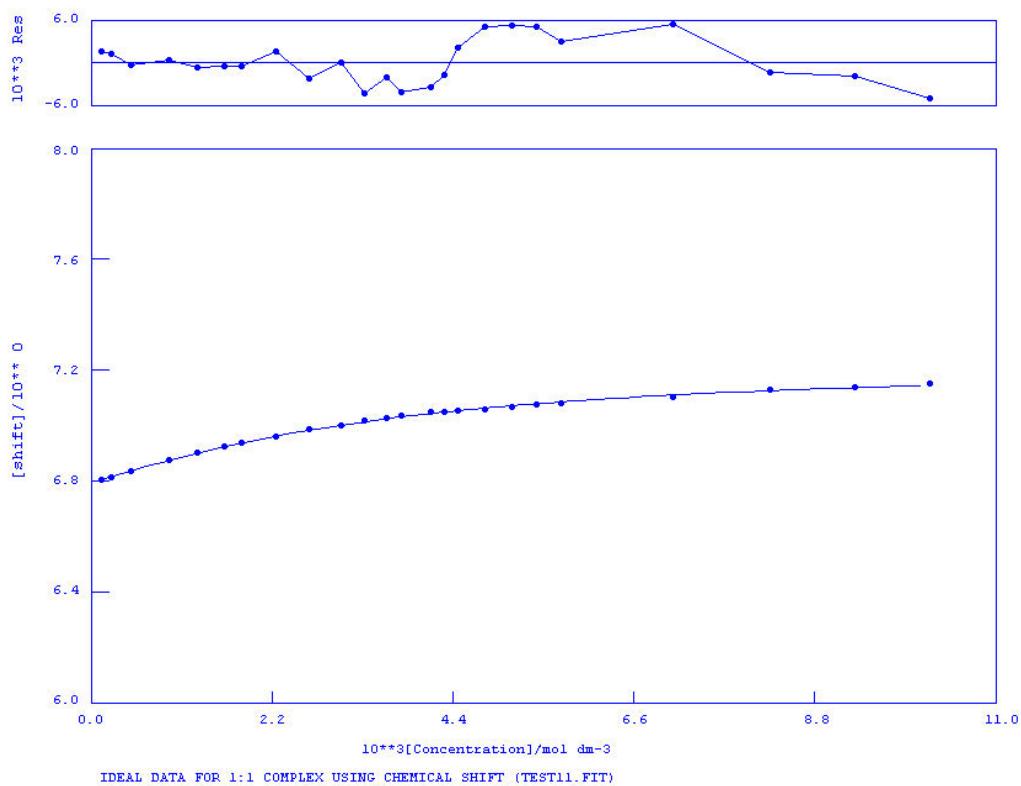


Fit 8 WinNMR fit.

➤ CH pyrrole



Graph 9 NMR titration shift graph.



Fit 9 WinNMR fit.

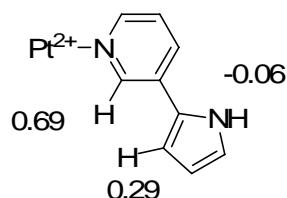
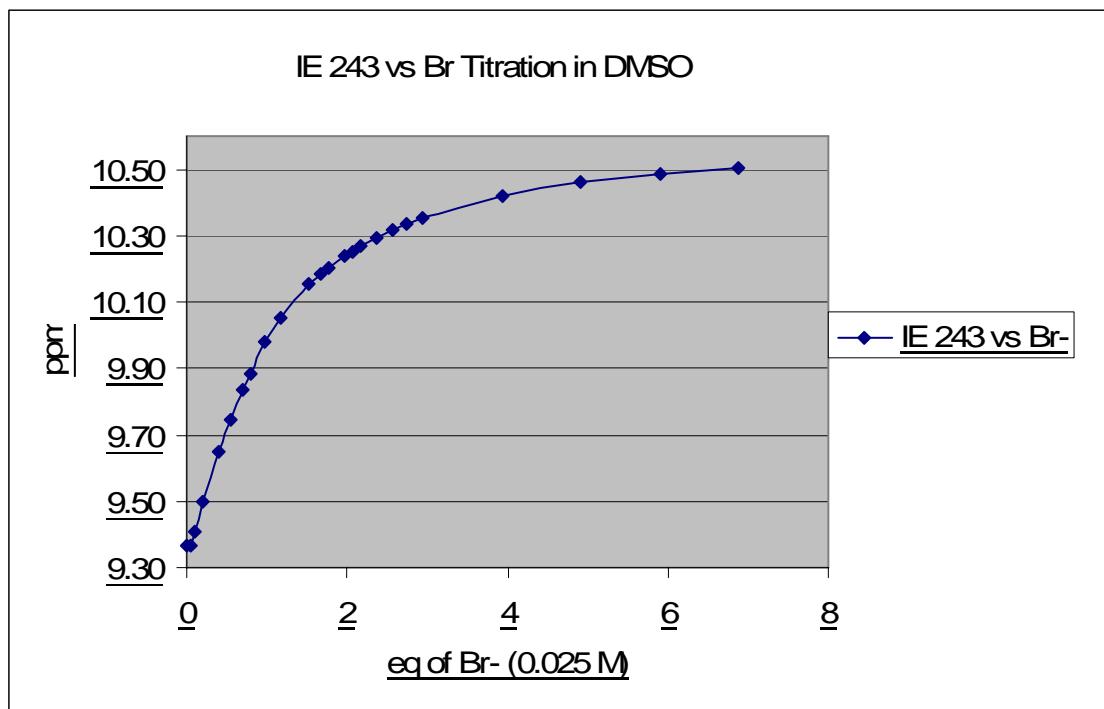
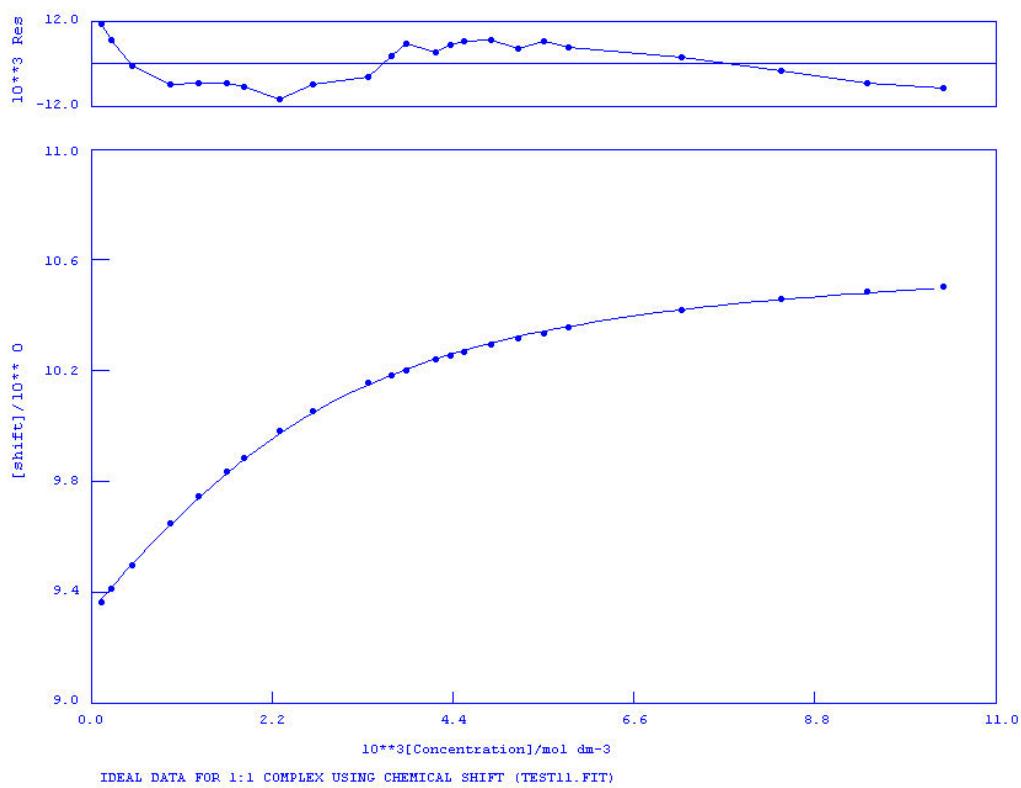


Figure 8 Shift at 3 eq.

- Tetrabutylammonium bromide.
 - CH Pyridine

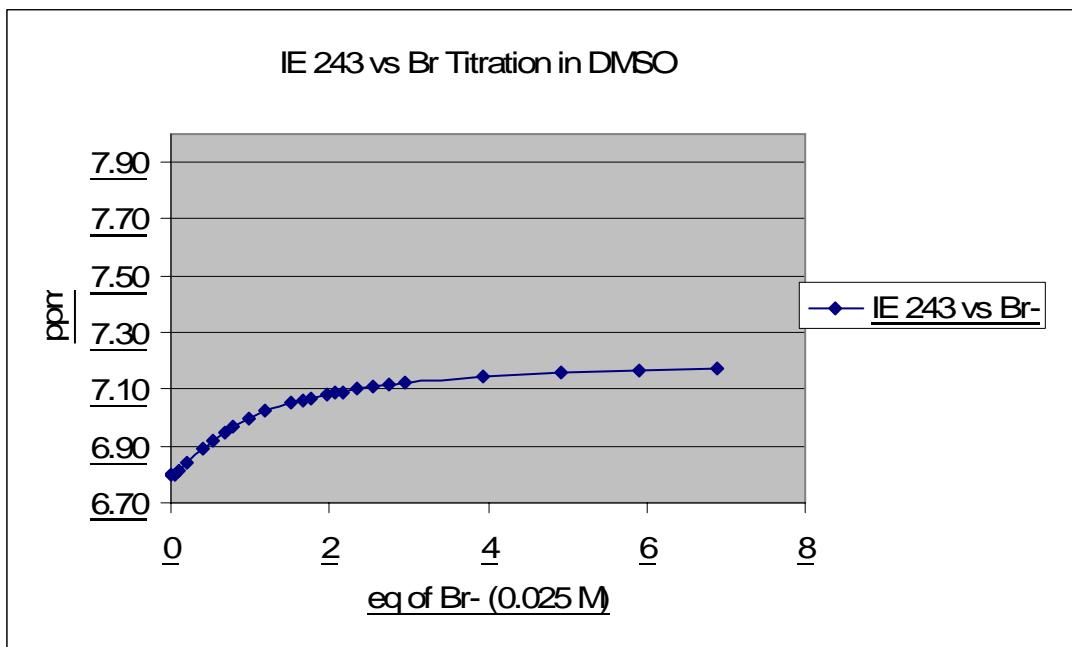


Graph 10 NMR titration shift graph.

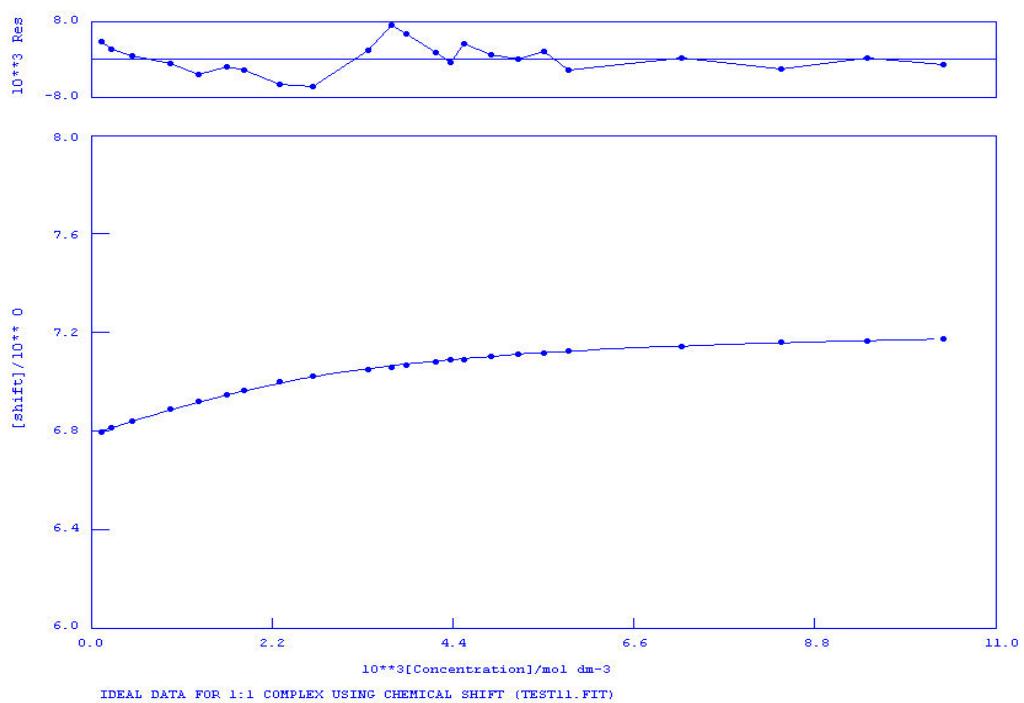


Fit 10 WinNMR fit.

➤ CH pyrrole



Graph 11 NMR titration shift graph.



Fit 11 WinNMR fit.

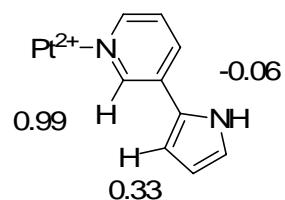
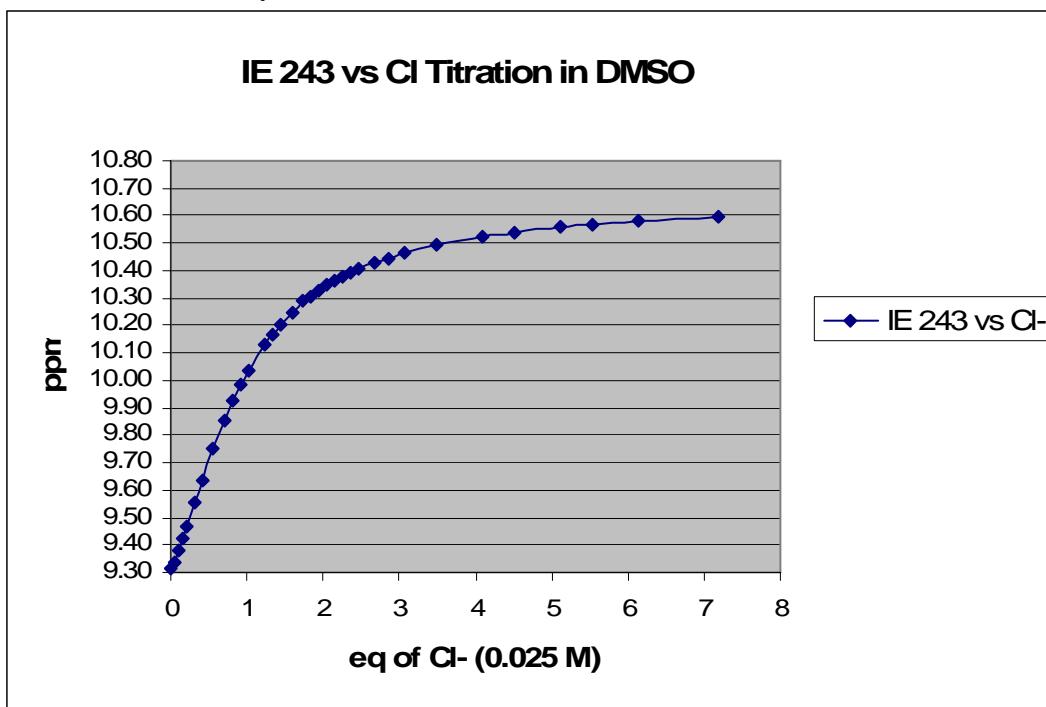
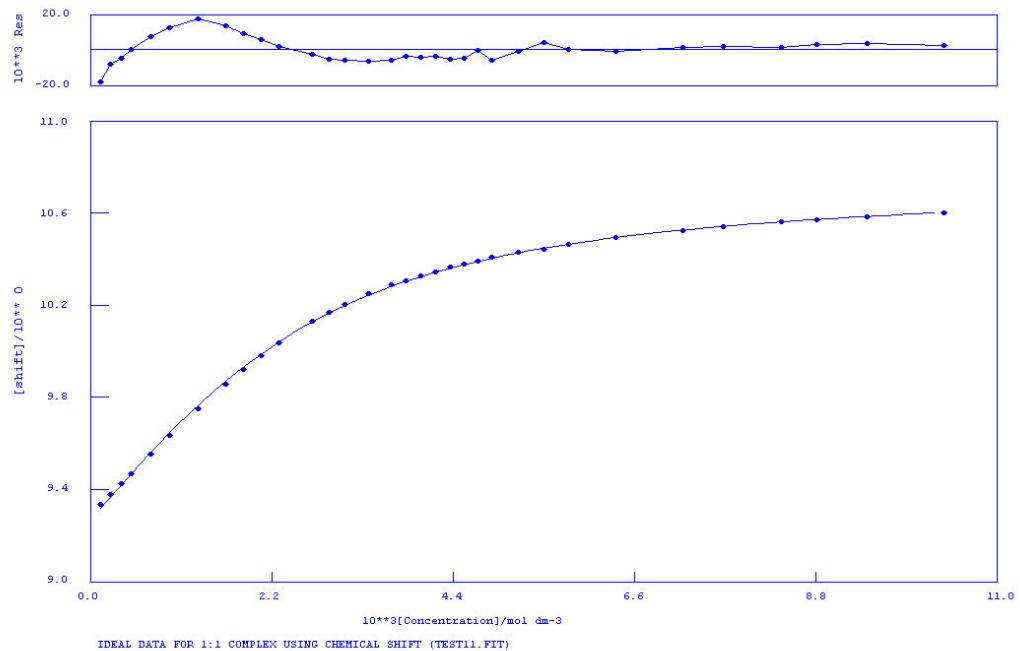


Figure 9 Shift at 3 eq.

- Tetrabutylammonium chloride.
 - CH Pyridine

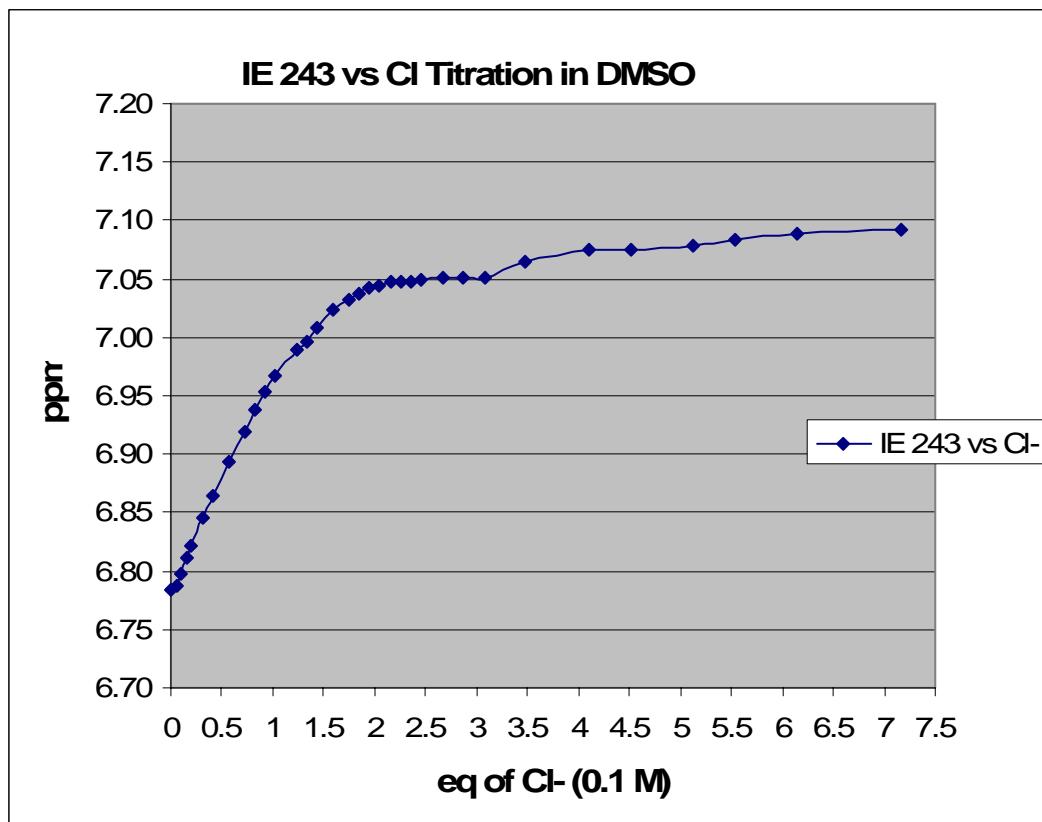


Graph 12 NMR titration shift graph.

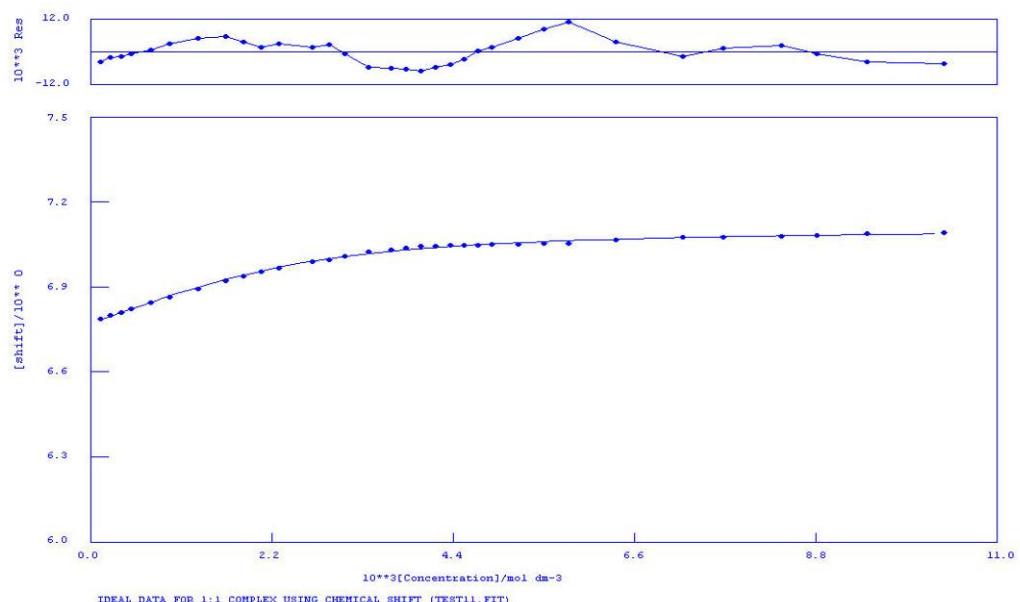


Fit 12 WinNMR fit.

➤ CH Pyrrole



Graph 13 NMR titration shift graph.



Fit 13 WinNMR fit.

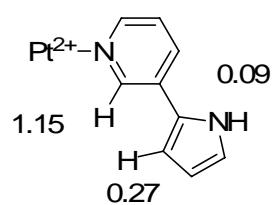
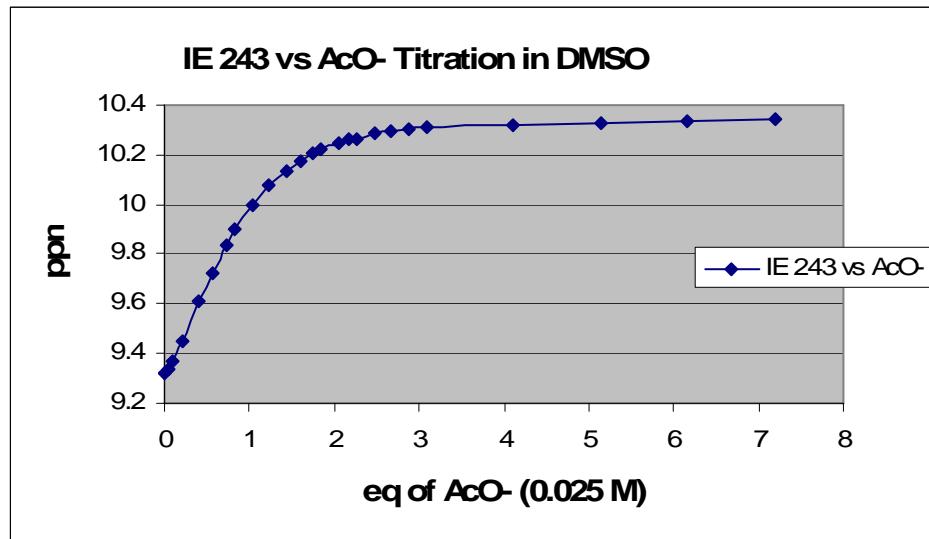


Figure 10 Shift at 3 eq.

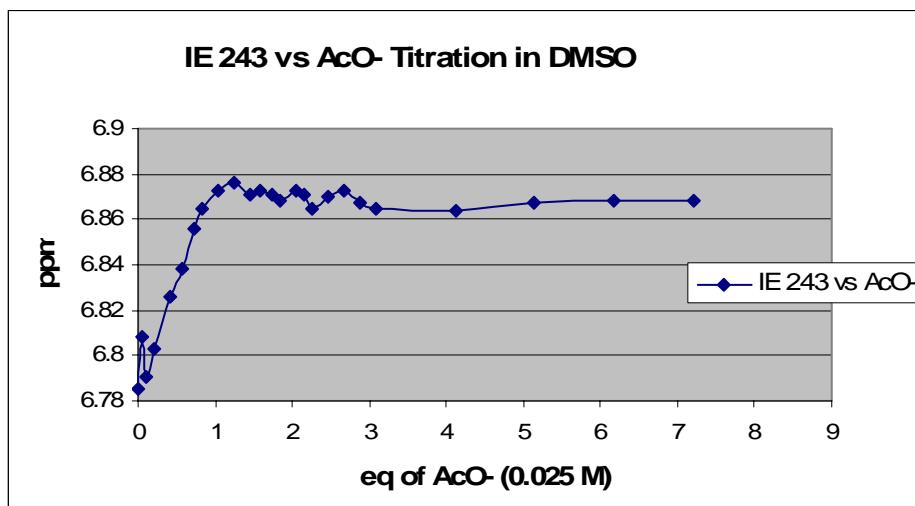
- Tetrabutylammonium acetate.

➤ CH Pyridine



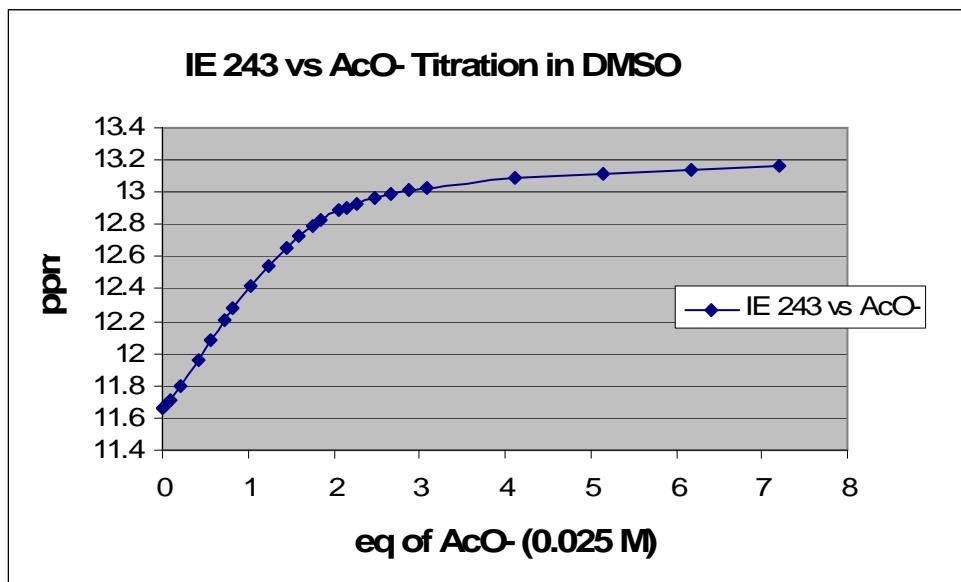
Graph 14 NMR titration shift graph.

➤ CH pyrrole

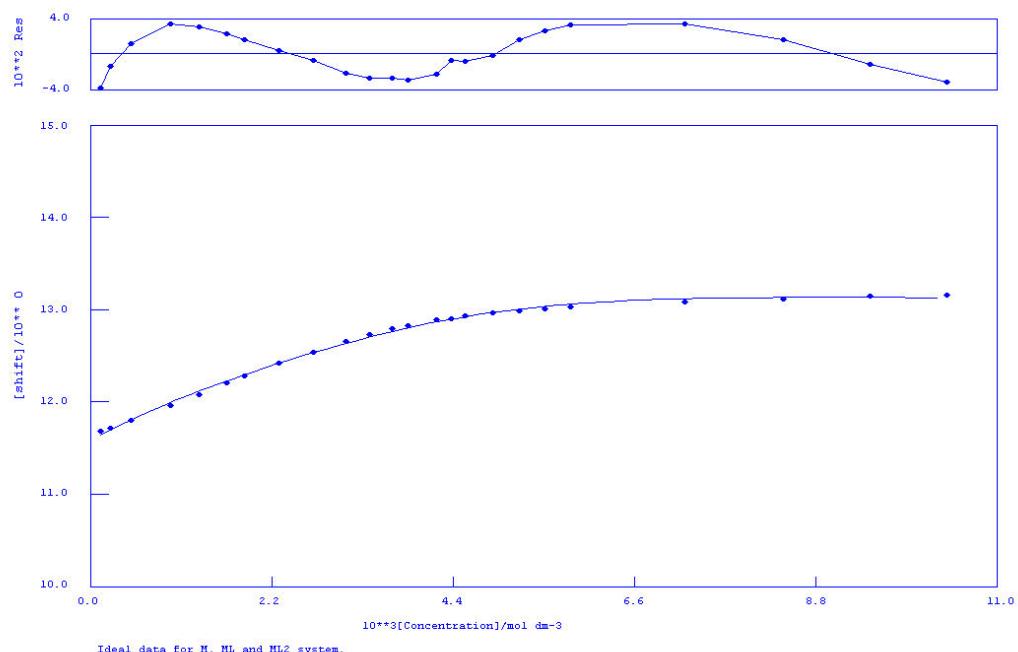


Graph 15 NMR titration shift graph.

➤ NH pyrrole



Graph 16 NMR titration shift graph.



Fit 14 WinNMR fit.

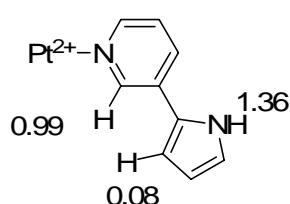
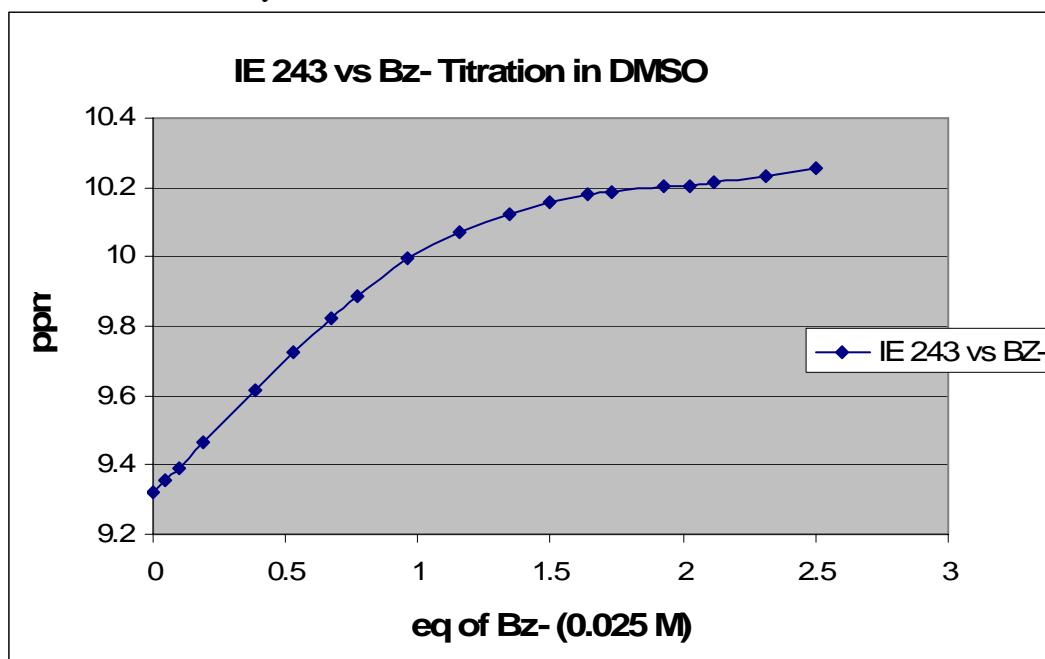


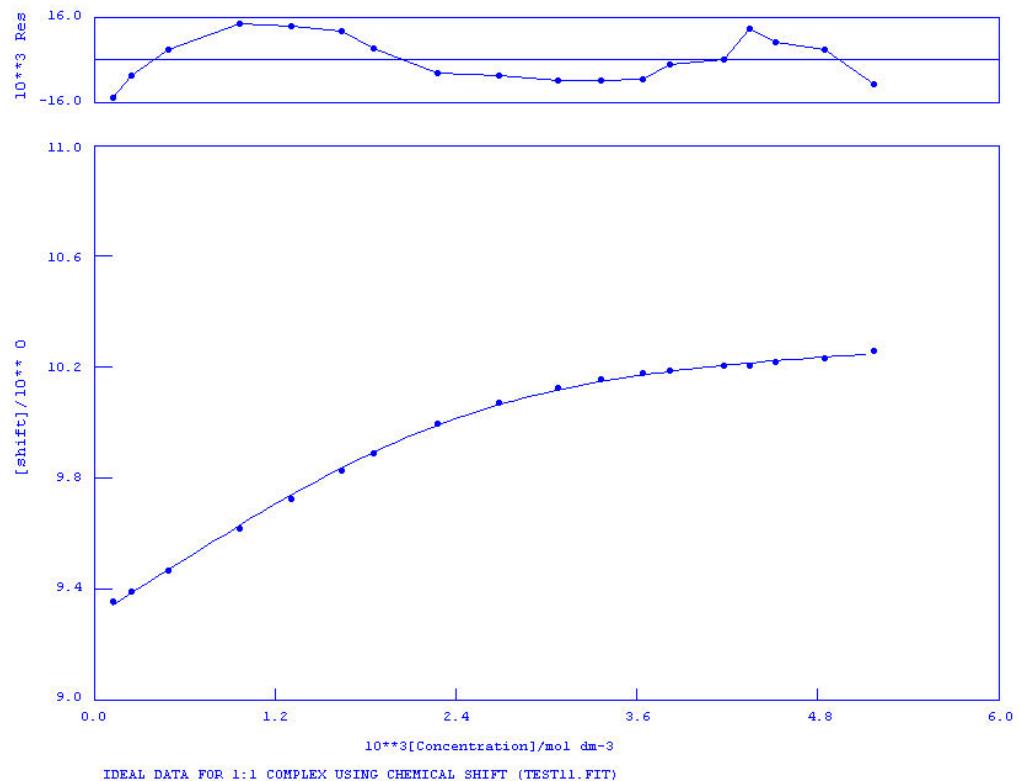
Figure 11 Shift at 3 eq.

- Tetrabutylammonium benzoate.

➤ CH Pyridine

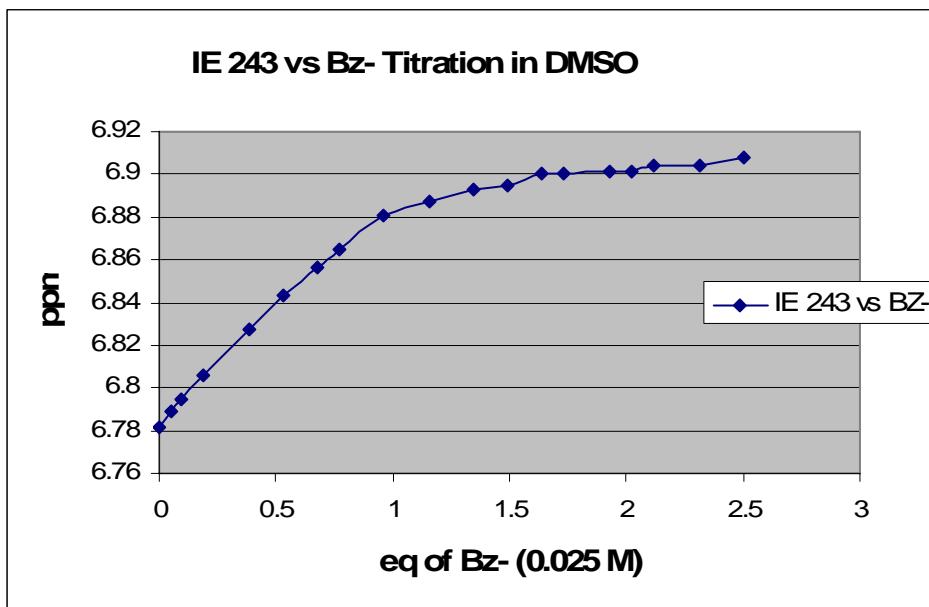


Graph 17 NMR titration shift graph.

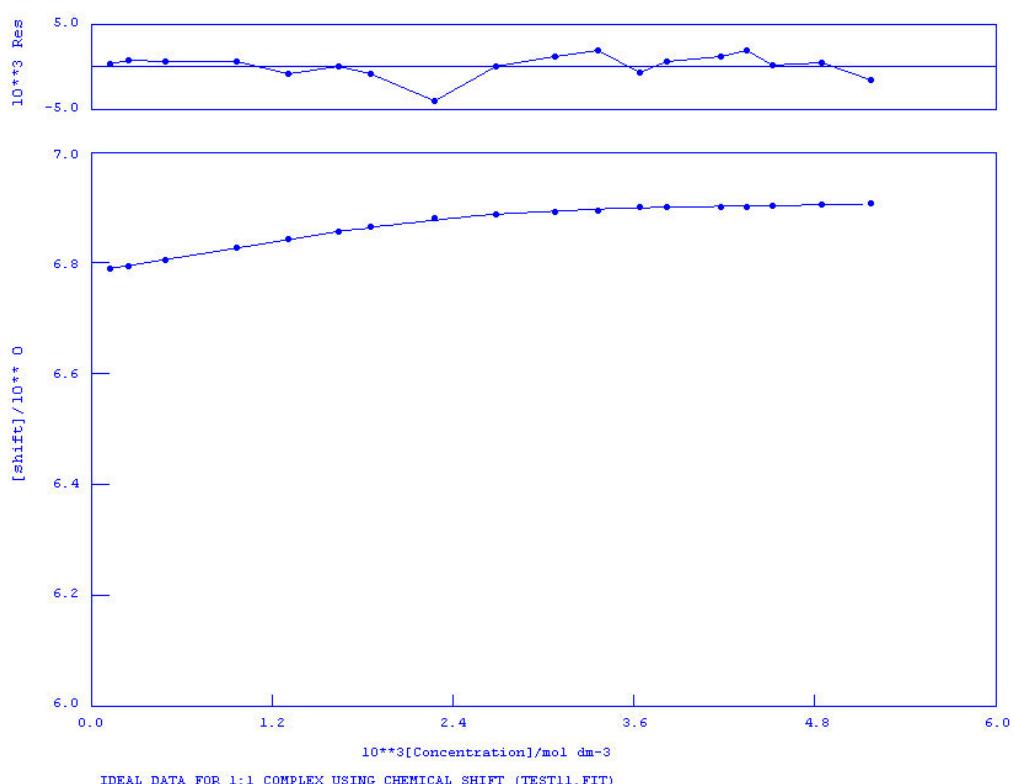


Fit 15 WinNMR fit.

➤ CH pyrrole



Graph 18 NMR titration shift graph.



Fit 16 WinNMR fit.

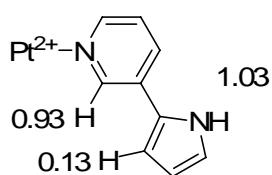
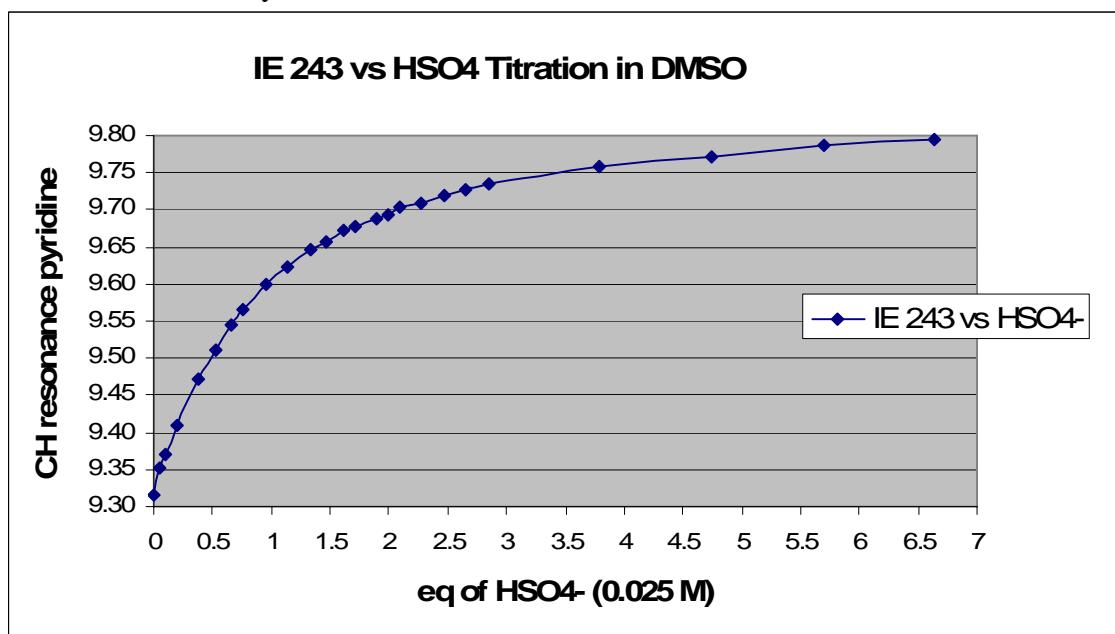
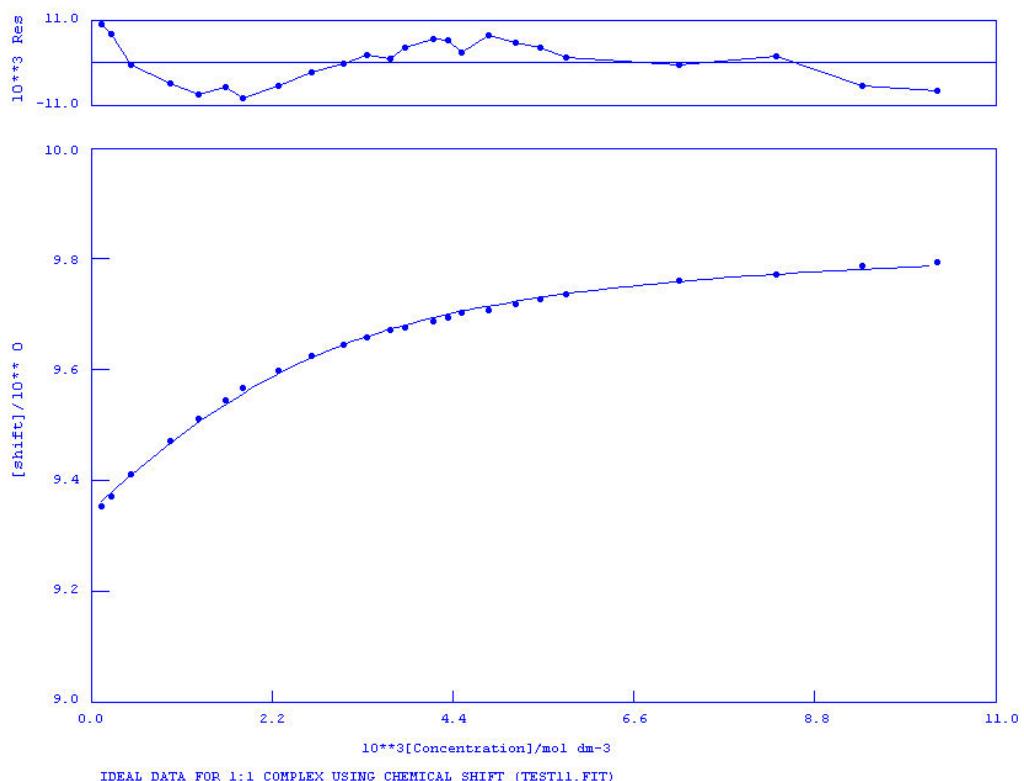


Figure 12 Shift at 2.5 eq.

- Tetrabutylammonium hydrogensulfate.
 - CH Pyridine

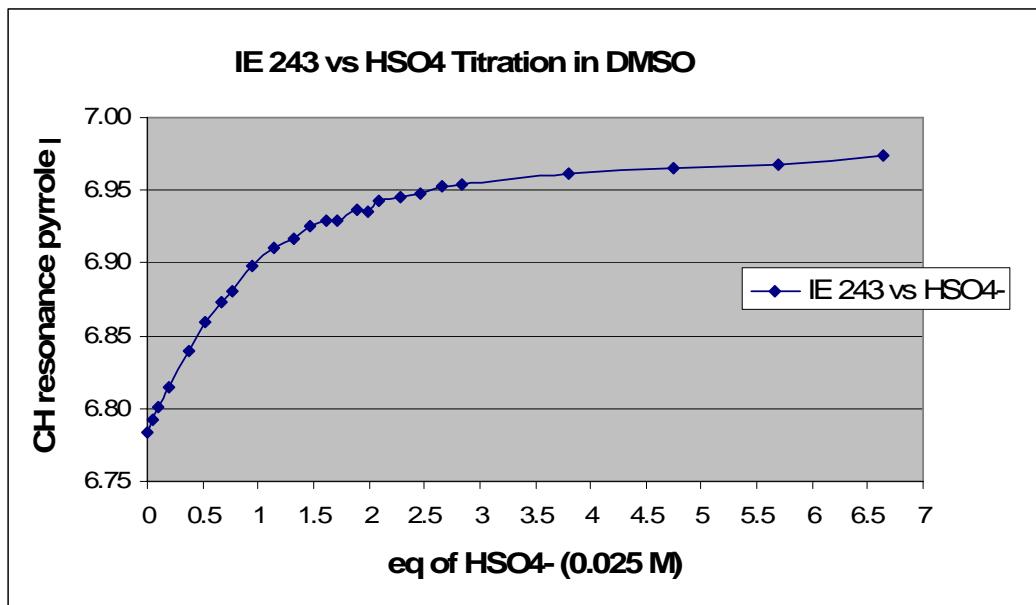


Graph 19 NMR titration shift graph.

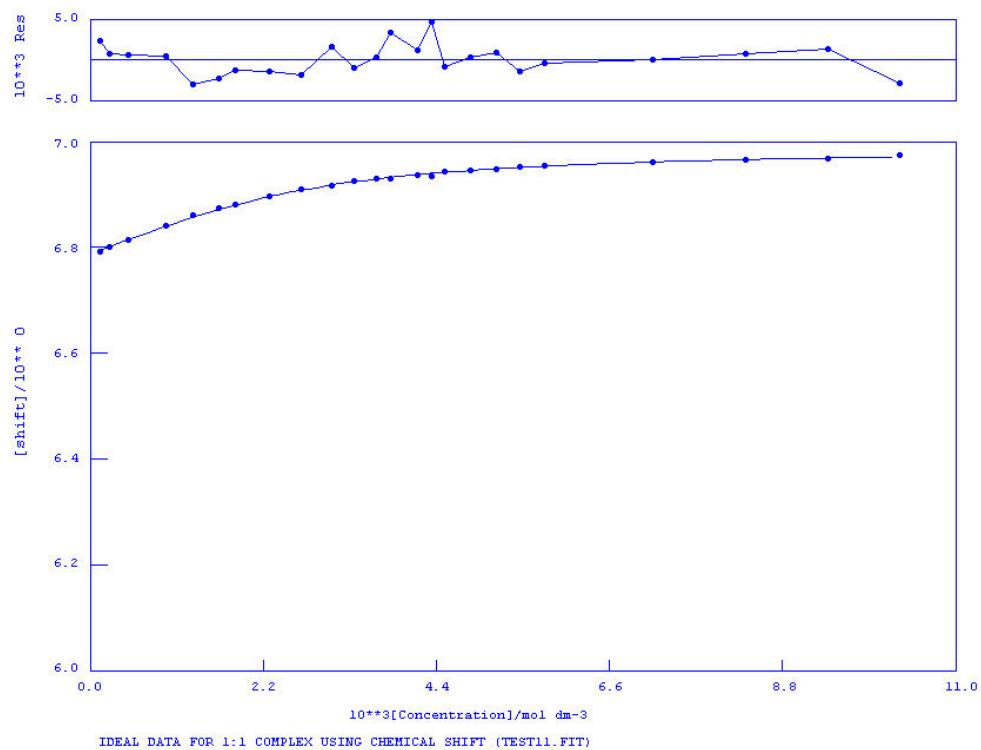


Fit 17 WinNMR fit.

➤ CH Pyrrole



Graph 20 NMR titration shift graph.



Fit 18 WinNMR fit.

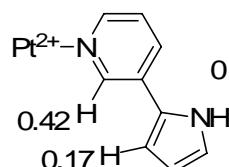
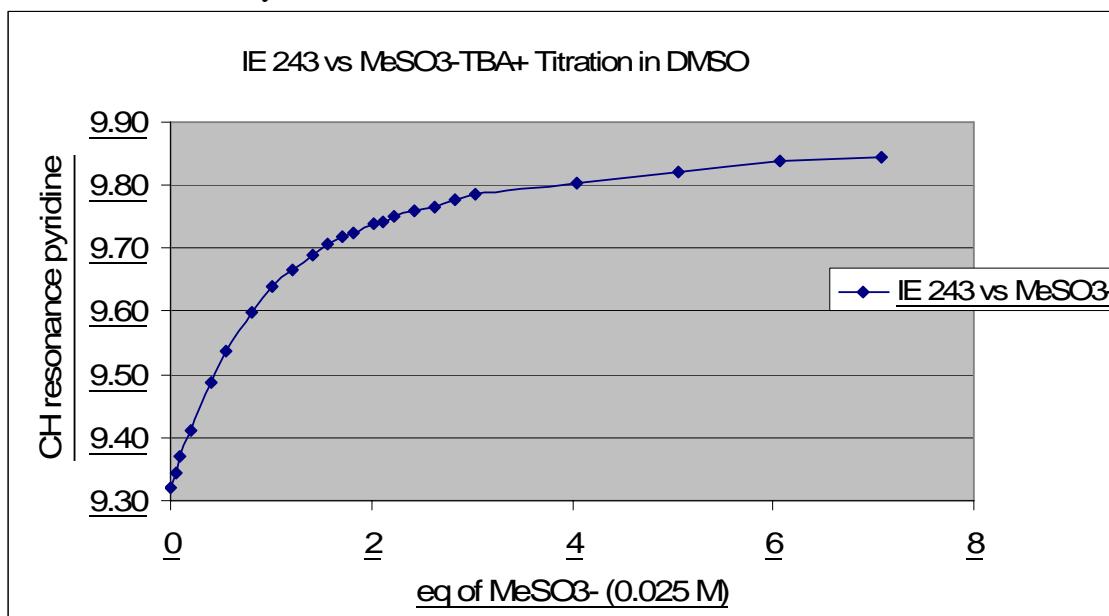


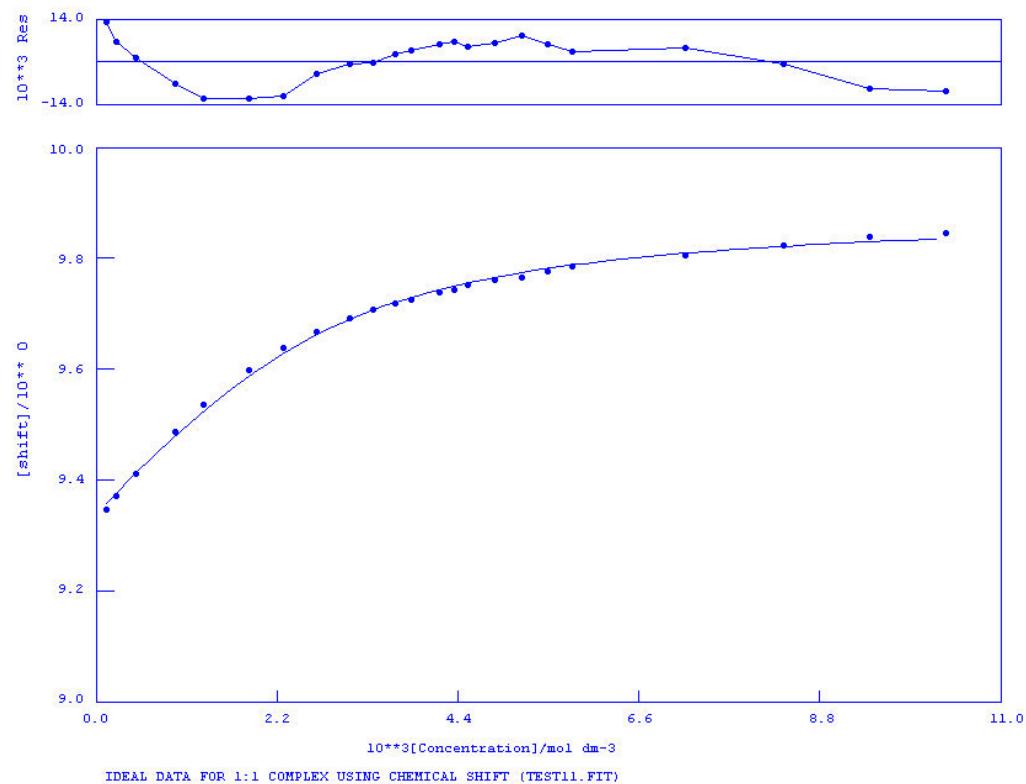
Figure 13 Shift at 3 eq.

- Tetrabutylammonium methanesulfonate.

➤ CH Pyridine

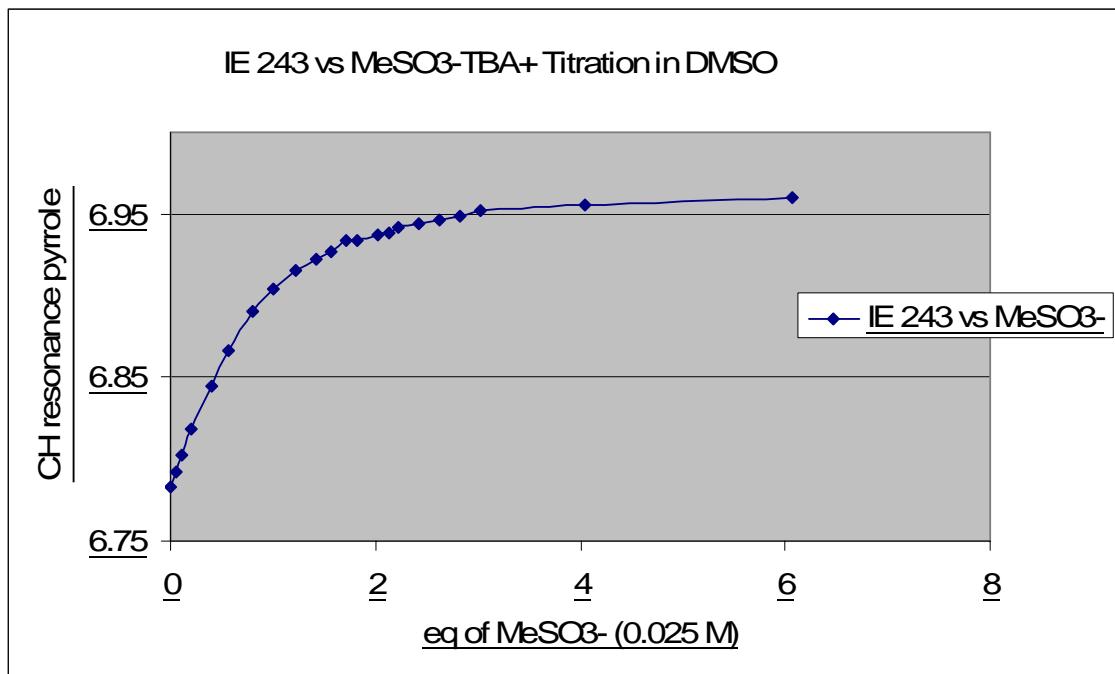


Graph 21 NMR titration shift graph.

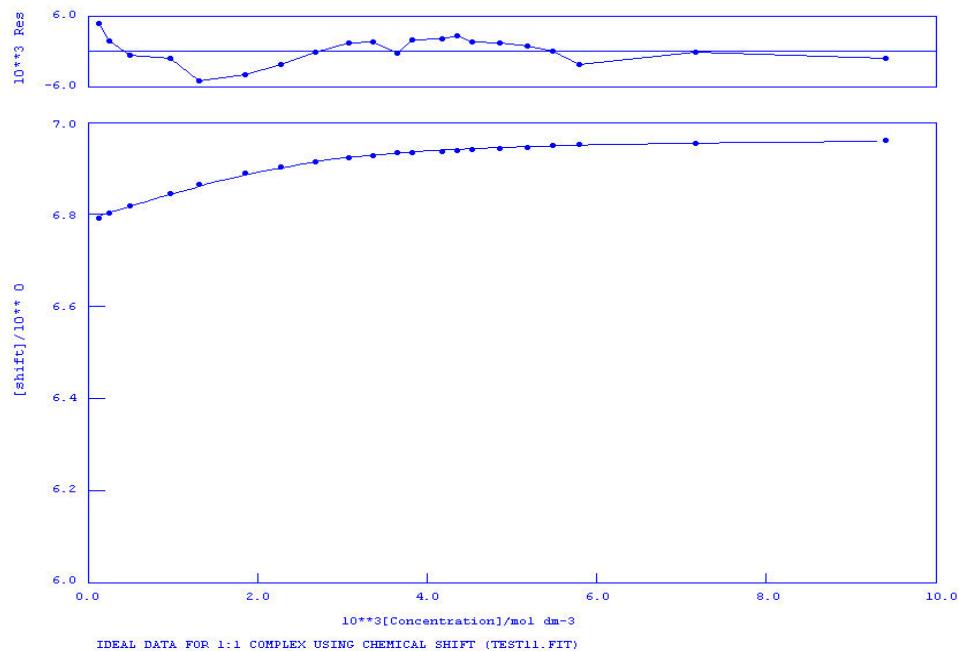


Fit 19 WinNMR fit.

➤ CH Pyrrole



Graph 22 NMR titration shift graph.



Fit 20 WinNMR fit.

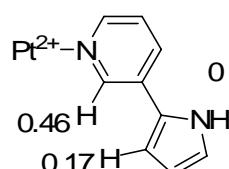
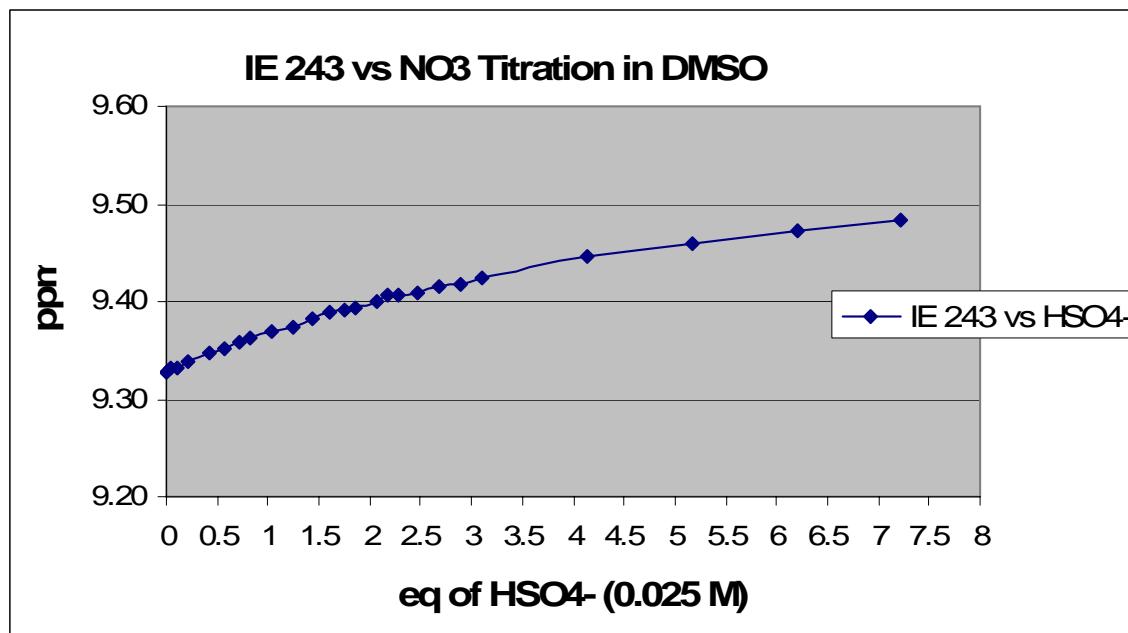


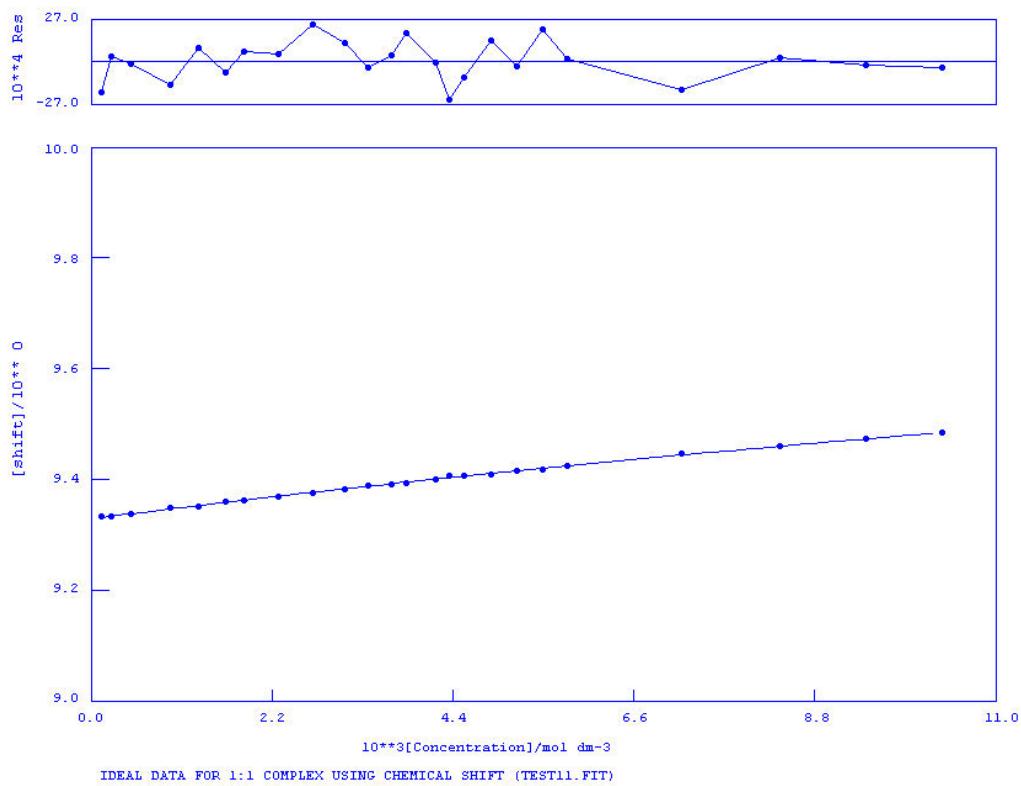
Figure 14 Shift at 3 eq.

- Tetrabutylammonium nitrate.

➤ CH Pyridine

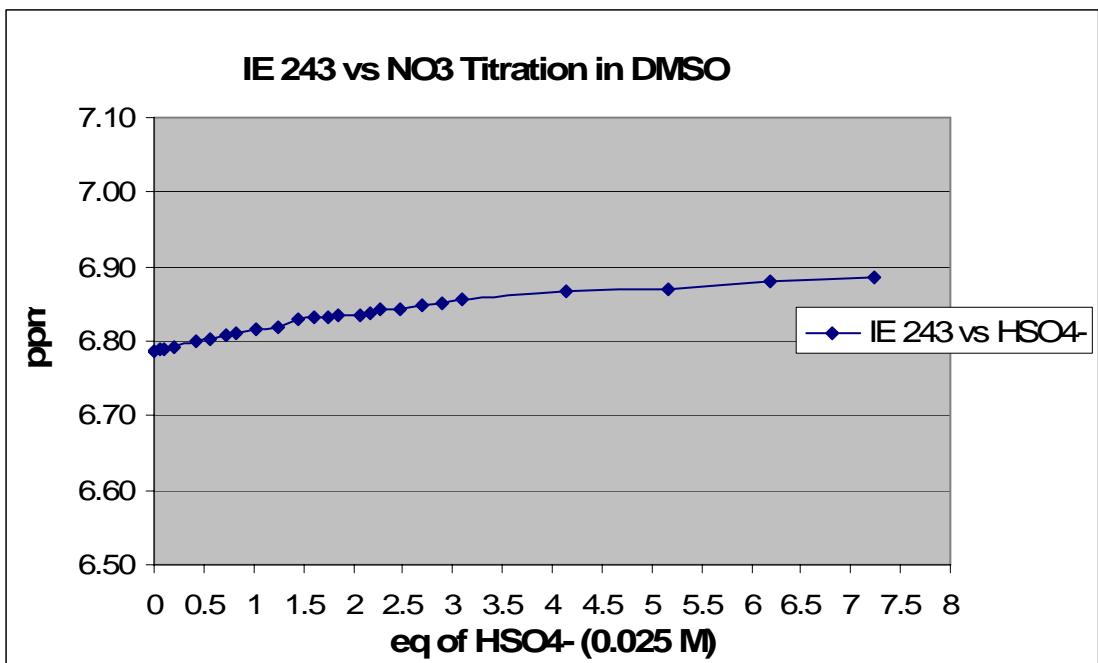


Graph 23 NMR titration shift graph.

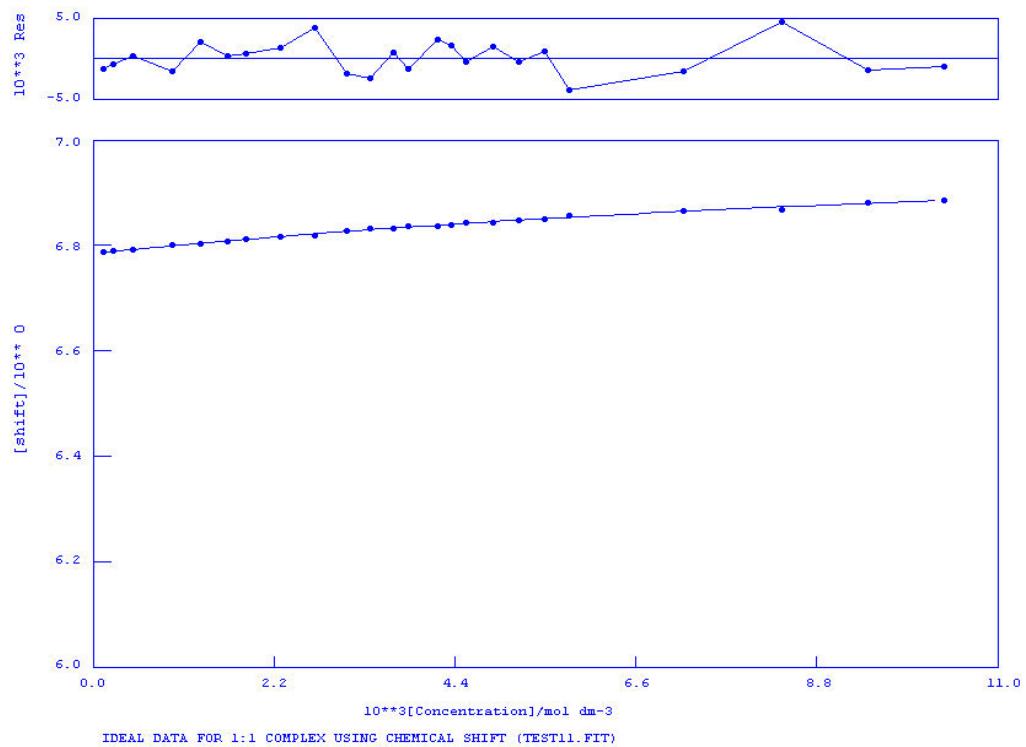


Fit 21 WinNMR fit.

➤ CH Pyrrole



Graph 24 NMR titration shift graph.



Fit 22 WinNMR fit.

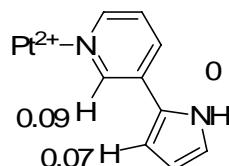
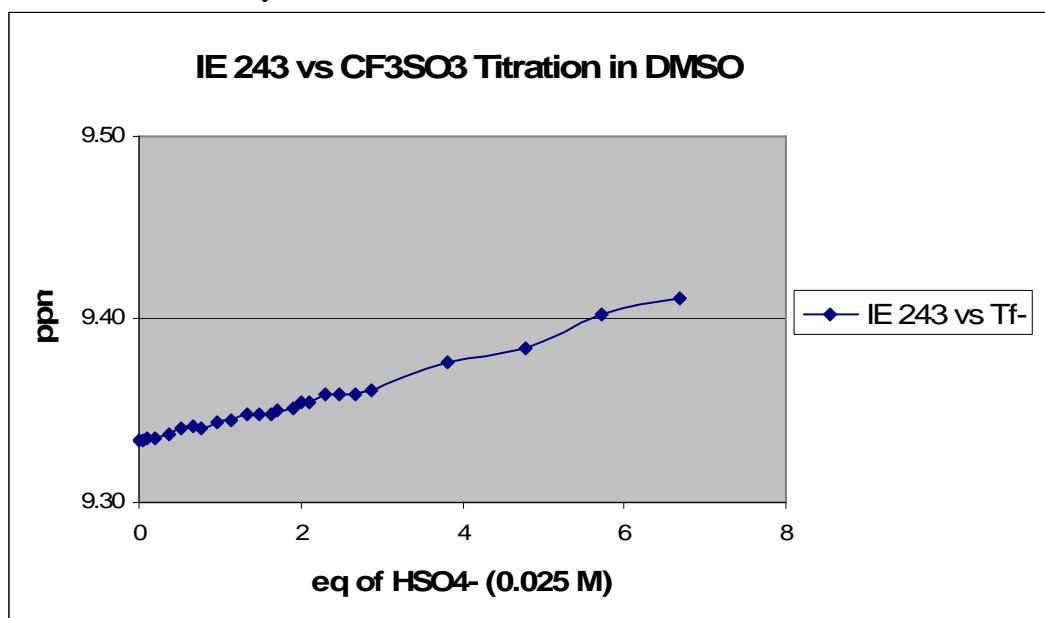


Figure 15 Shift at 3 eq.

- Tetrabutylammonium triflate.

➤ CH Pyridine



Graph 25 NMR titration shift graph.

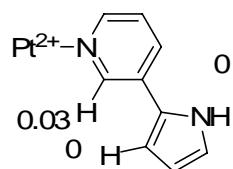
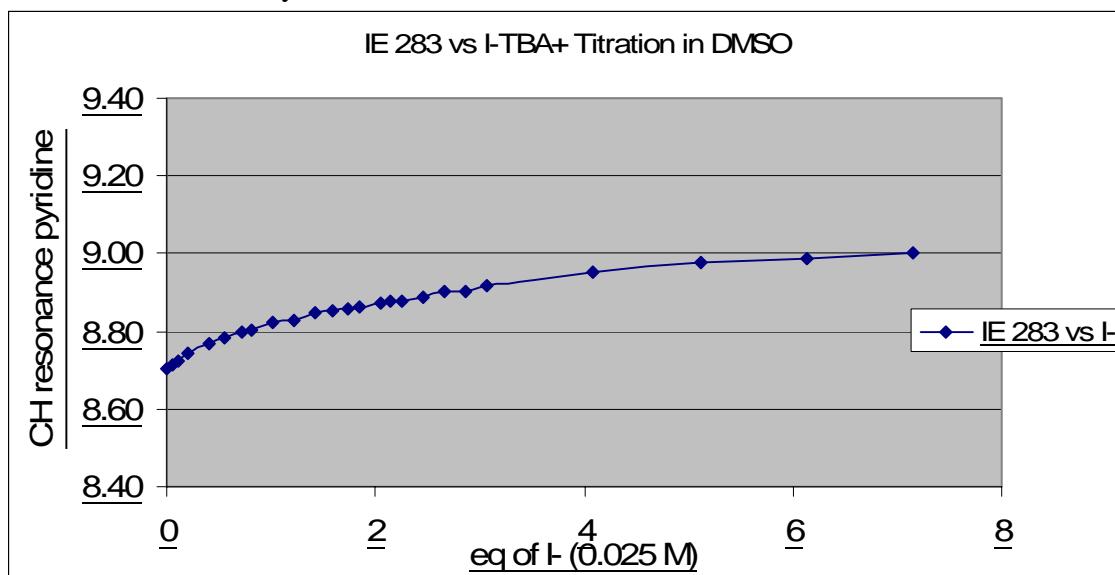


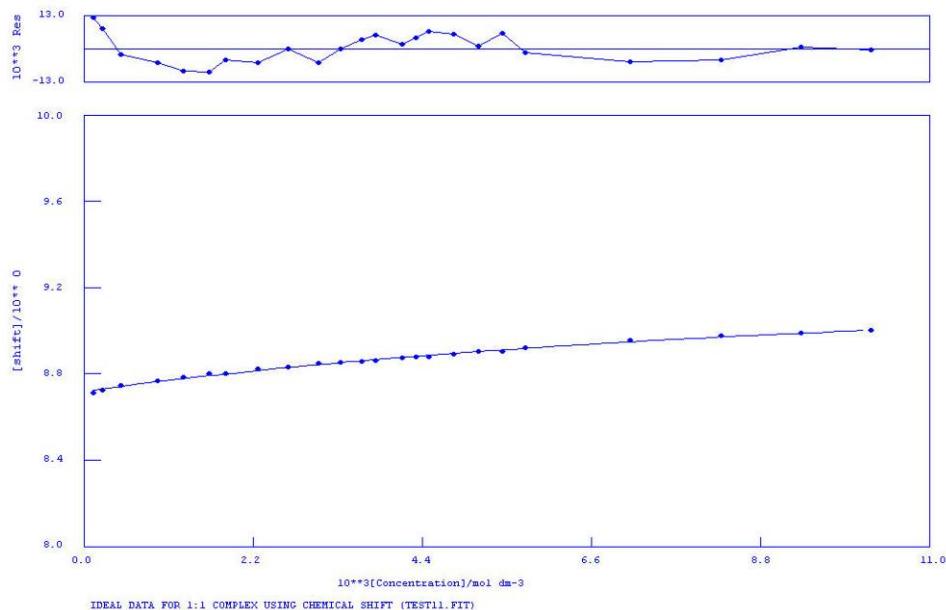
Figure 16 Shift at 3 eq.

Titrations tetrakis(p-(1H-pyrrole)pyridine)platinum(II) tetrafluoroborate **3**.

- Tetrabutylammonium iodide.
 - CH α Pyridine



Graph 26 NMR titration shift graph.



Fit 23 WinNMR fit.

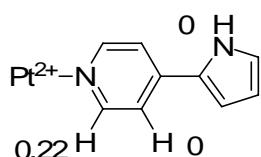
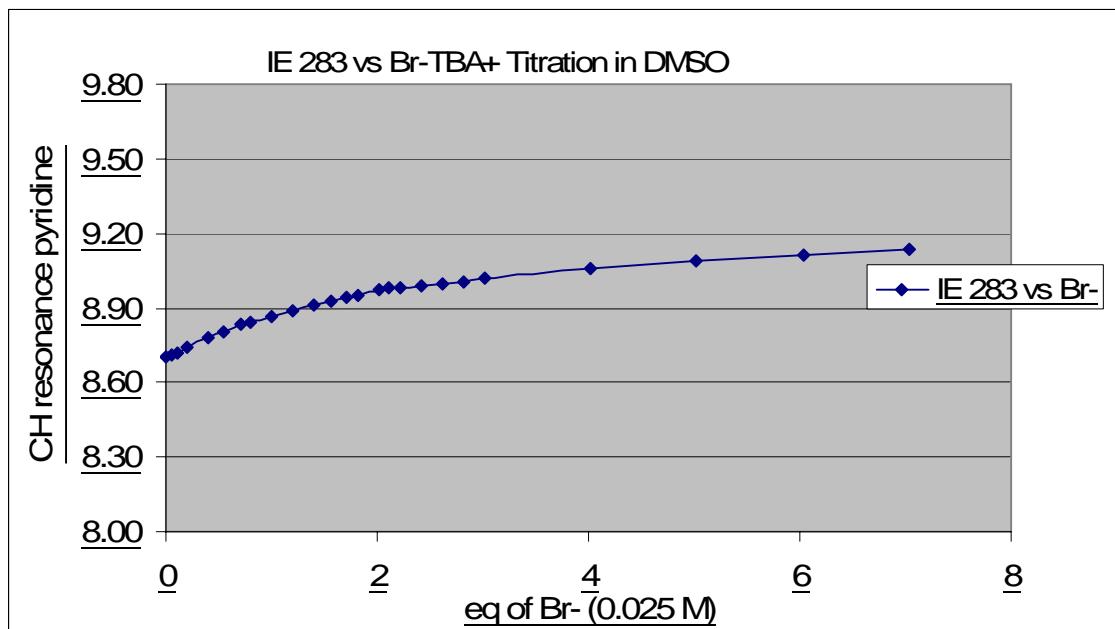


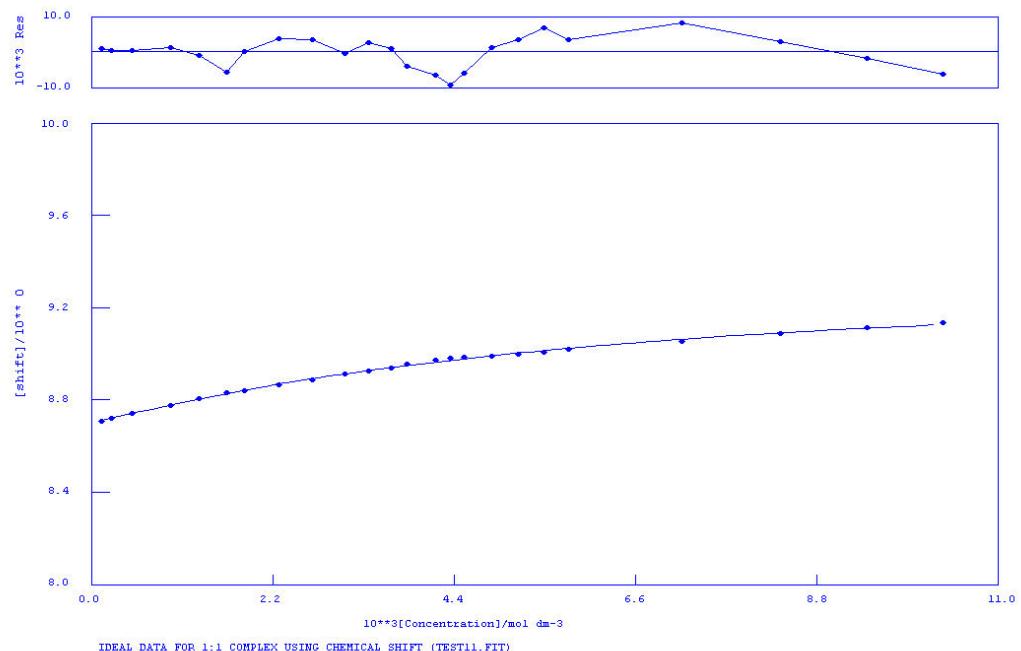
Figure 17 Shift at 3 eq.

- Tetrabutylammonium bromide.

➤ CH_α Pyridine



Graph 27 NMR titration shift graph.



Fit 24 WinNMR fit.

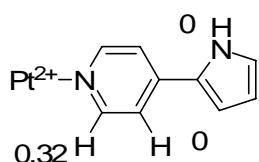
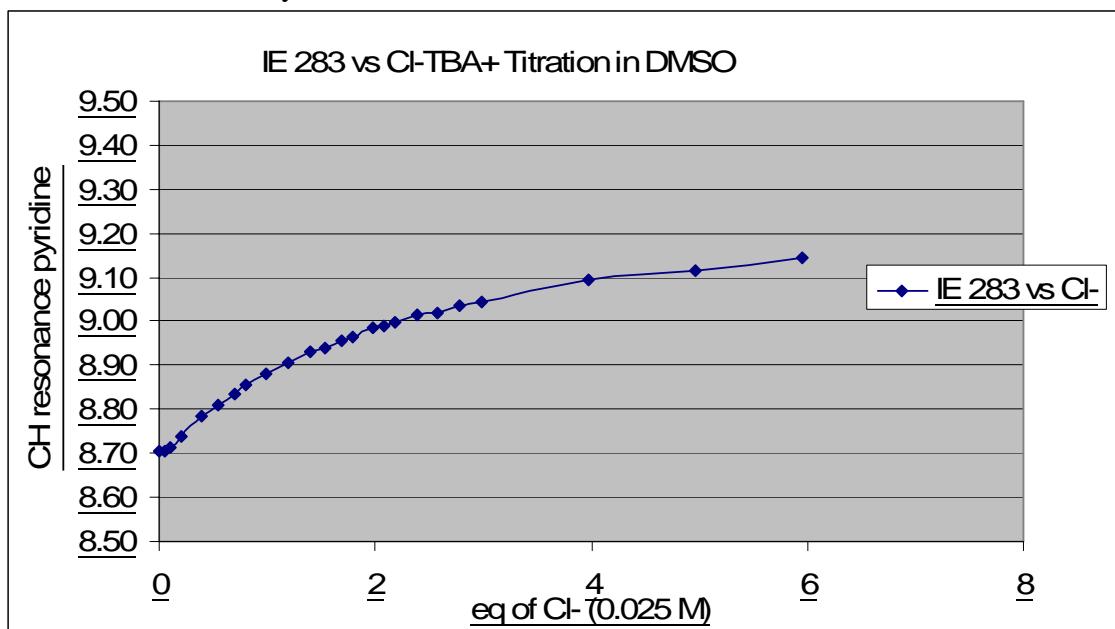


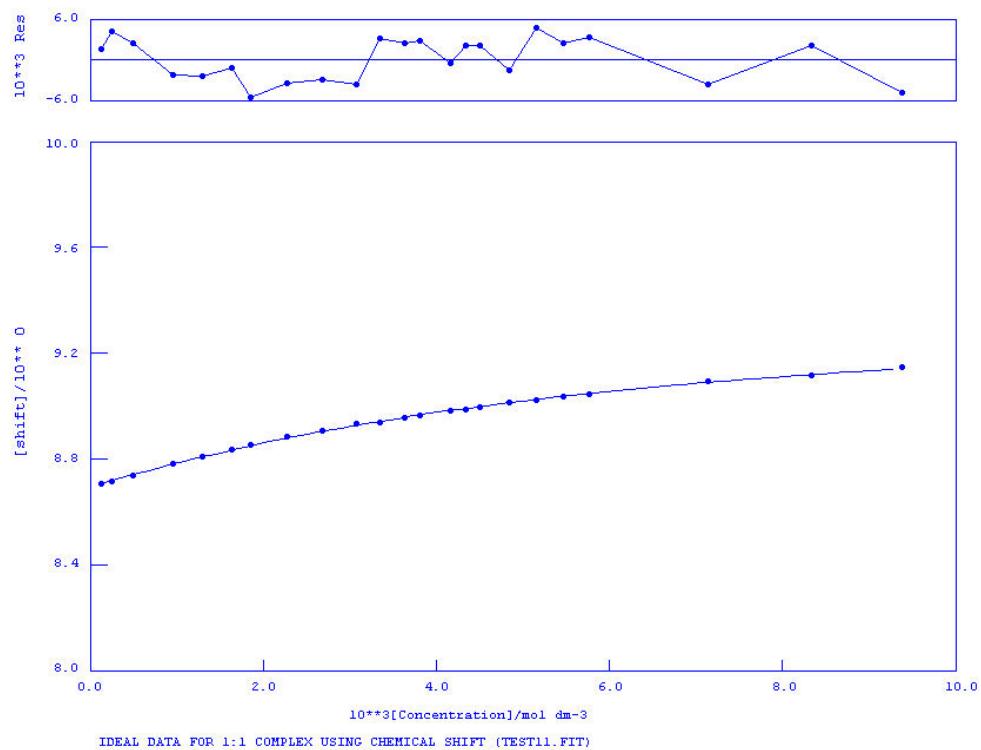
Figure 18 Shift at 3 eq.

- Tetrabutylammonium chloride.

➤ CH_α Pyridine



Graph 28 NMR titration shift graph.



Fit 25 WinNMR fit.

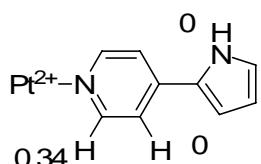
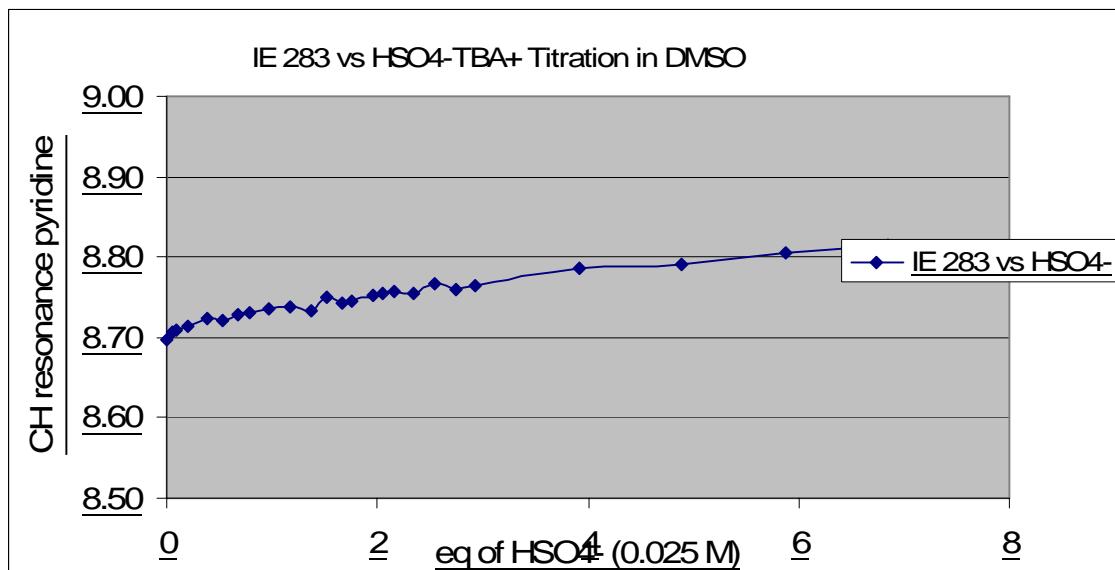


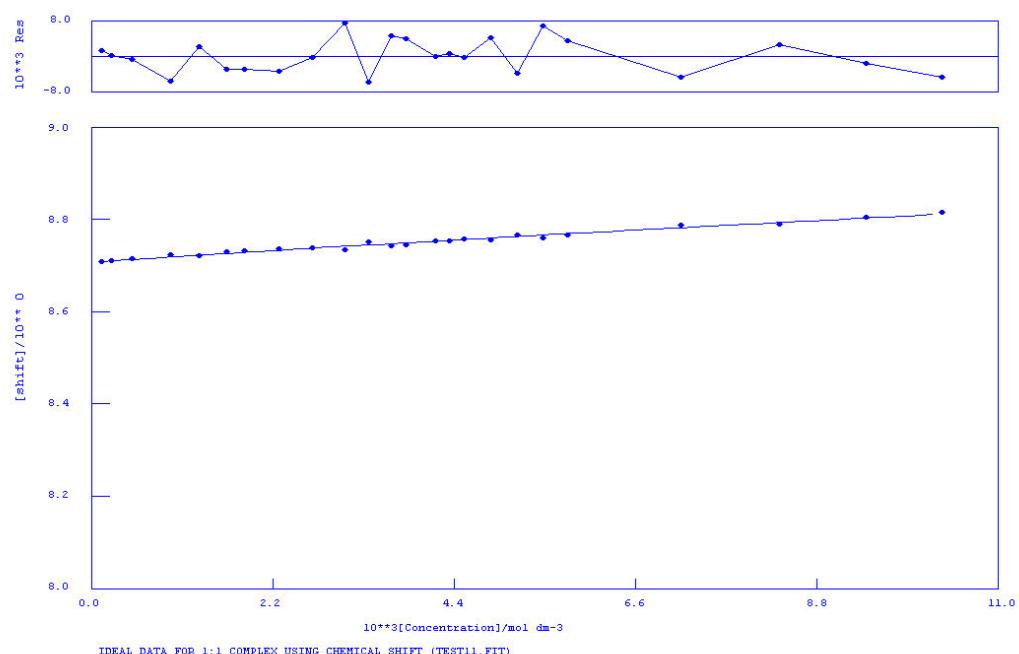
Figure 19 Shift at 3 eq.

- Tetrabutylammonium hydrogensulfate.

➤ CH_α Pyridine



Graph 29 NMR titration shift graph.



Fit 26 WinNMR fit.

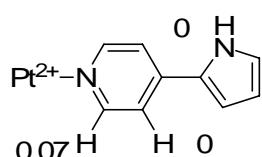
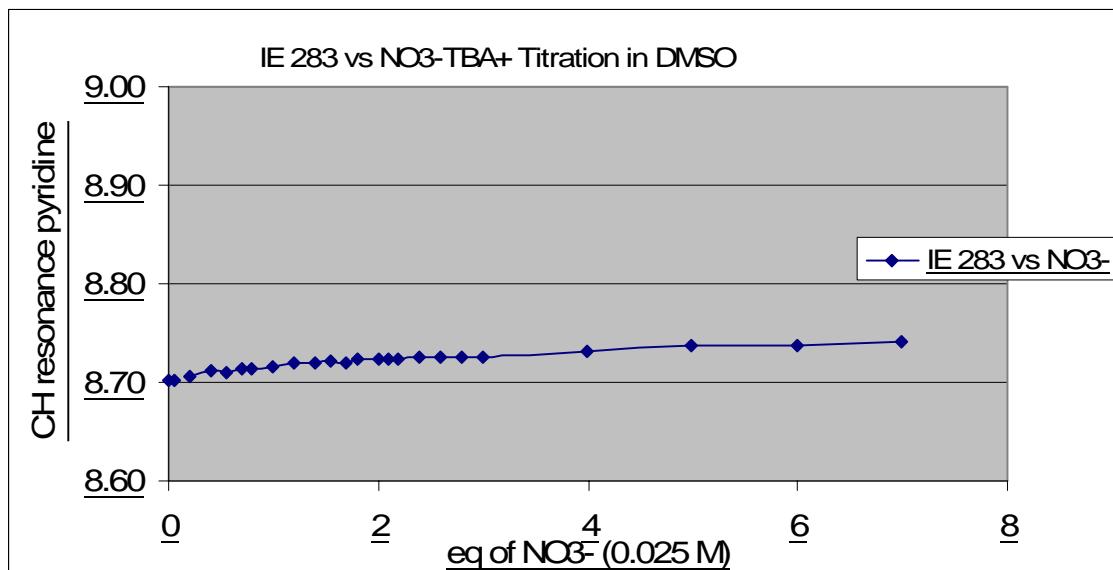


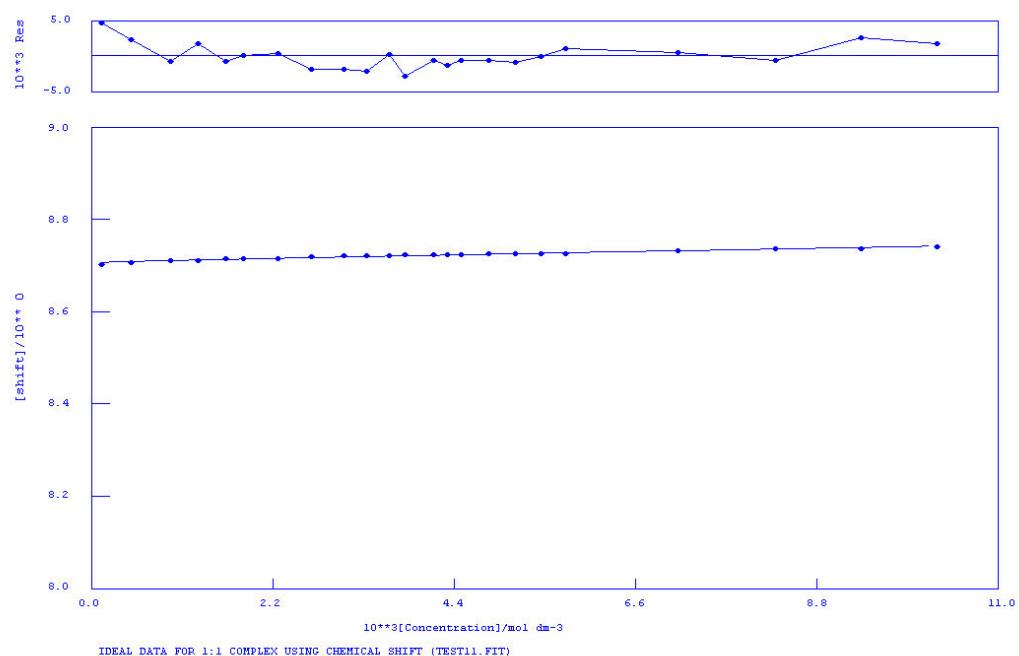
Figure 20 Shift at 3 eq.

- Tetrabutylammonium nitrate.

➤ CH_α Pyridine



Graph 30 NMR titration shift graph.



Fit 27 WinNMR fit.

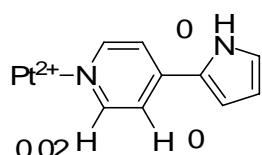
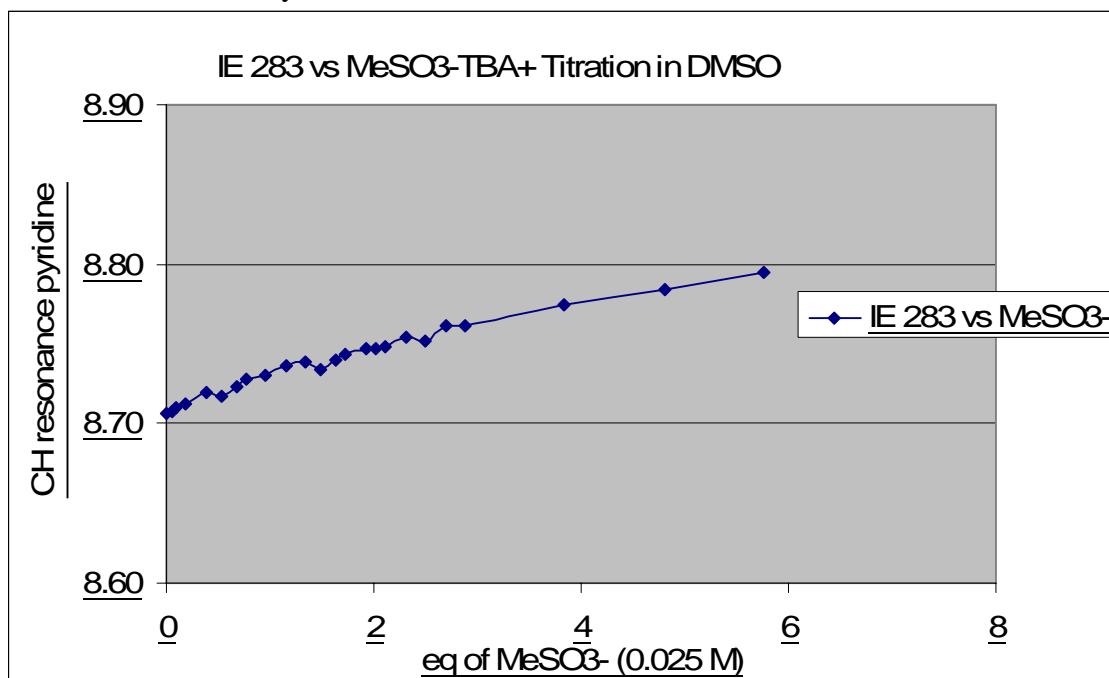


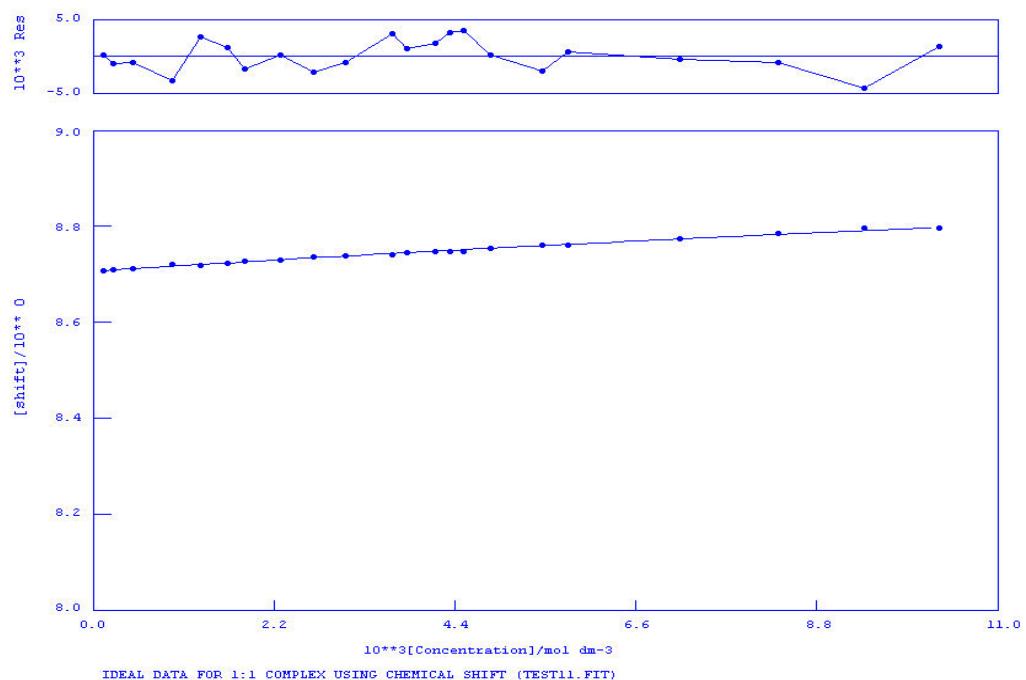
Figure 21 Shift at 3 eq.

- Tetrabutylammonium methanesulfonate.

➤ CH_α Pyridine



Graph 31 NMR titration shift graph.



Fit 28 WinNMR fit.

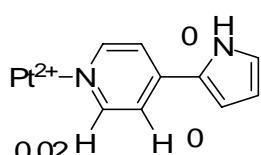
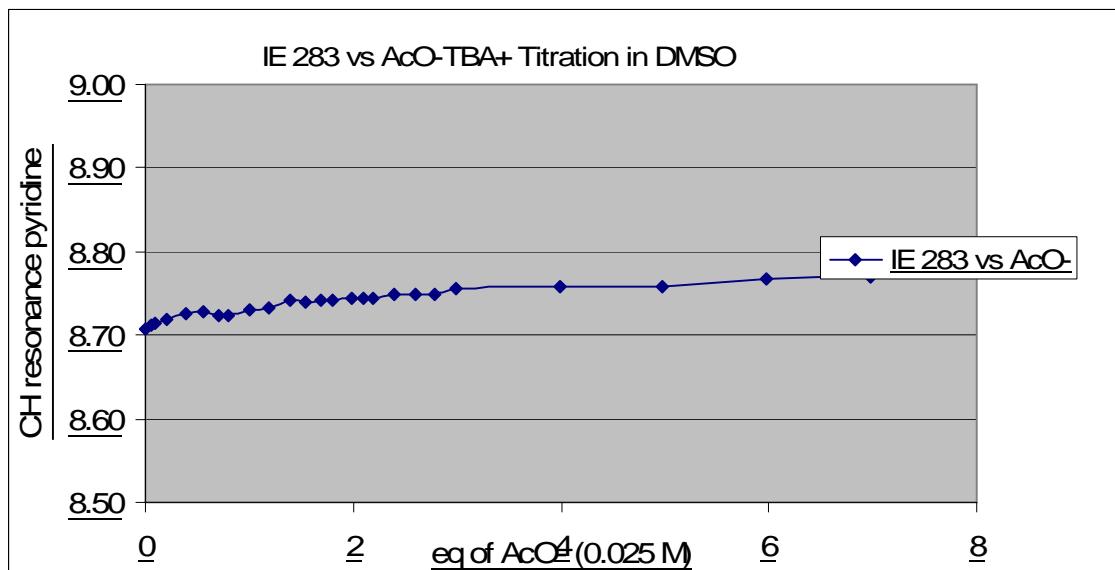


Figure 22 Shift at 3 eq.

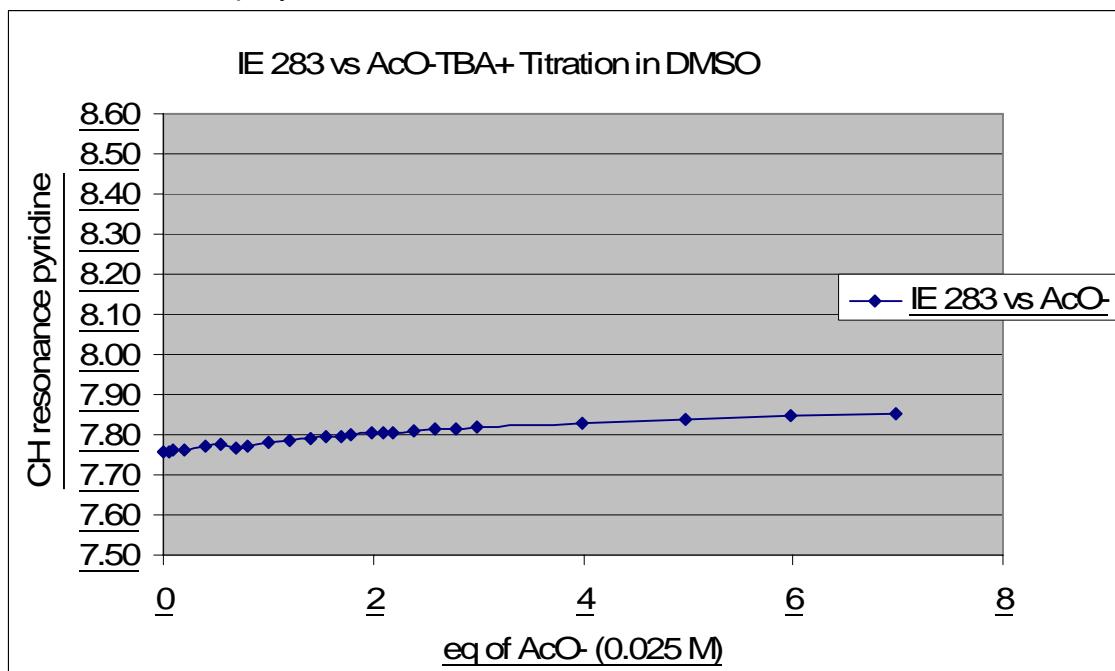
- Tetrabutylammonium acetate.

➤ CH α Pyridine



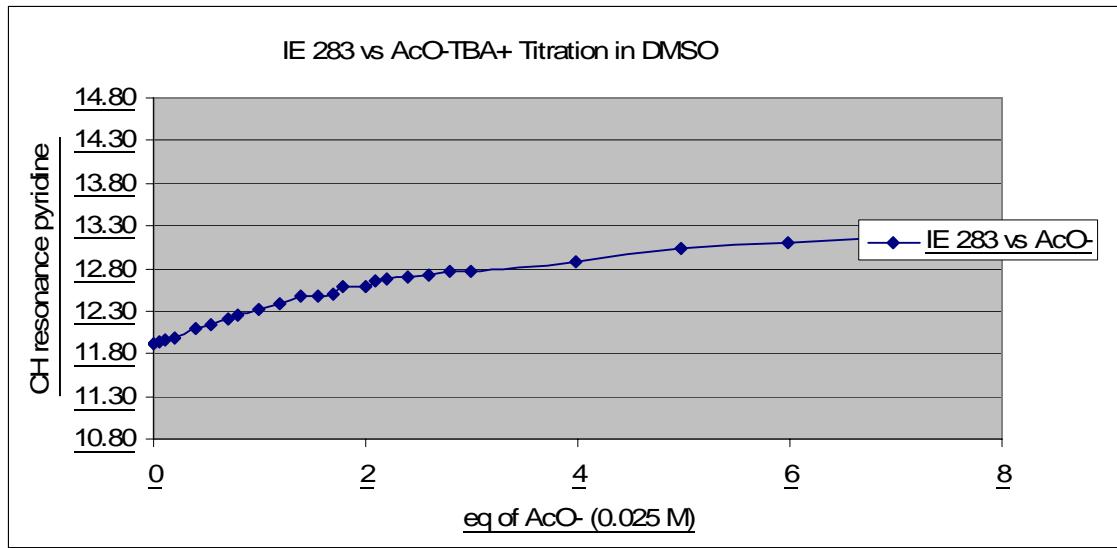
Graph 32 NMR titration shift graph.

➤ CH β Pyridine

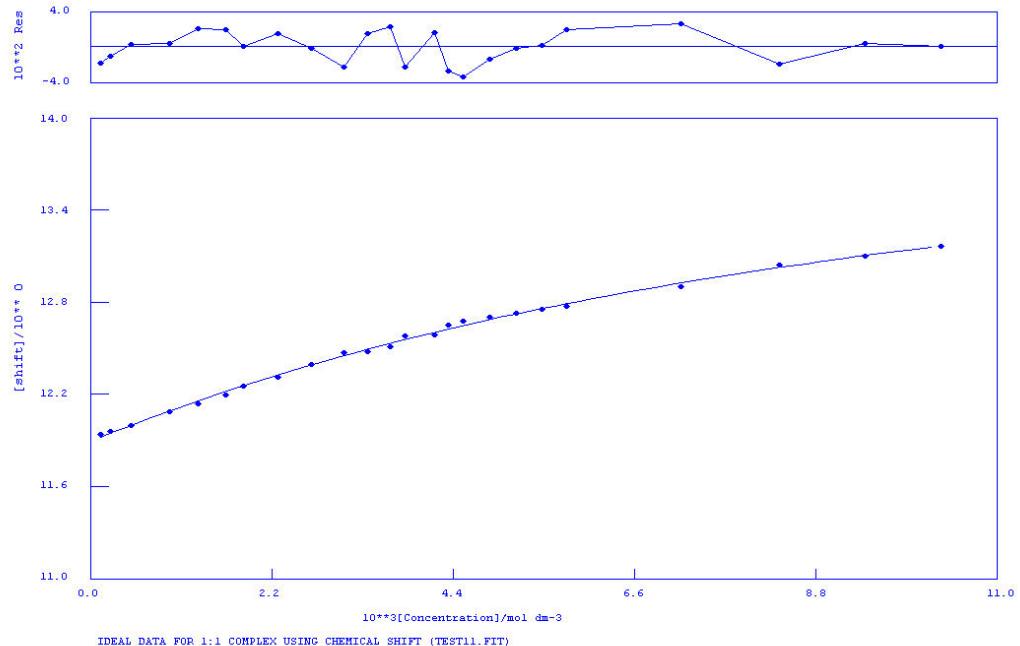


Graph 33 NMR titration shift graph.

➤ NH Pyrrole



Graph 34 NMR titration shift graph.



Fit 29 WinNMR fit.

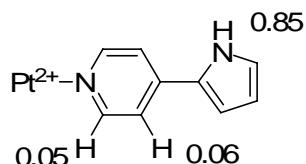
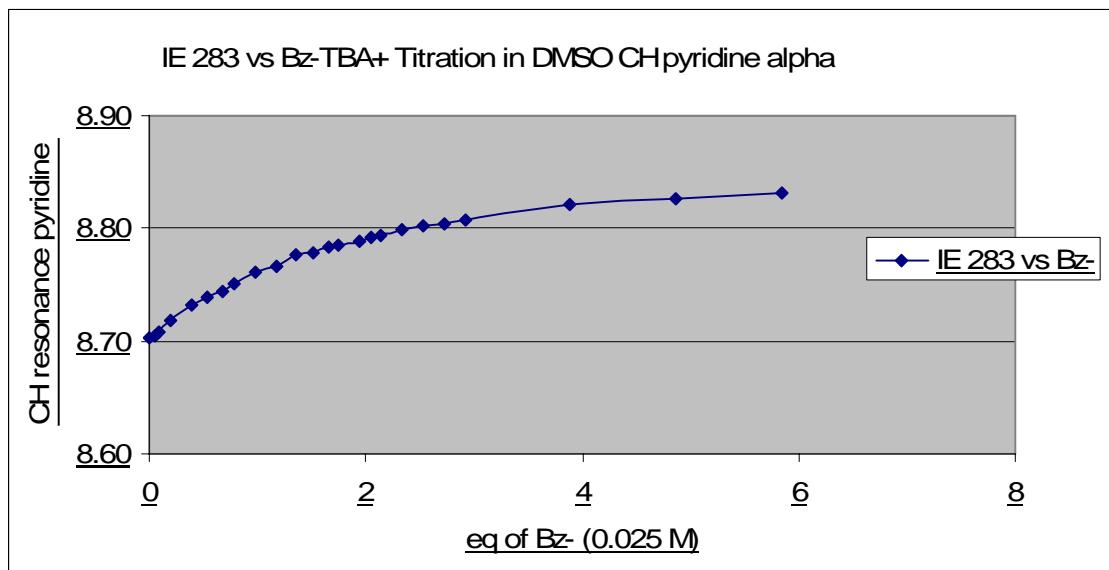


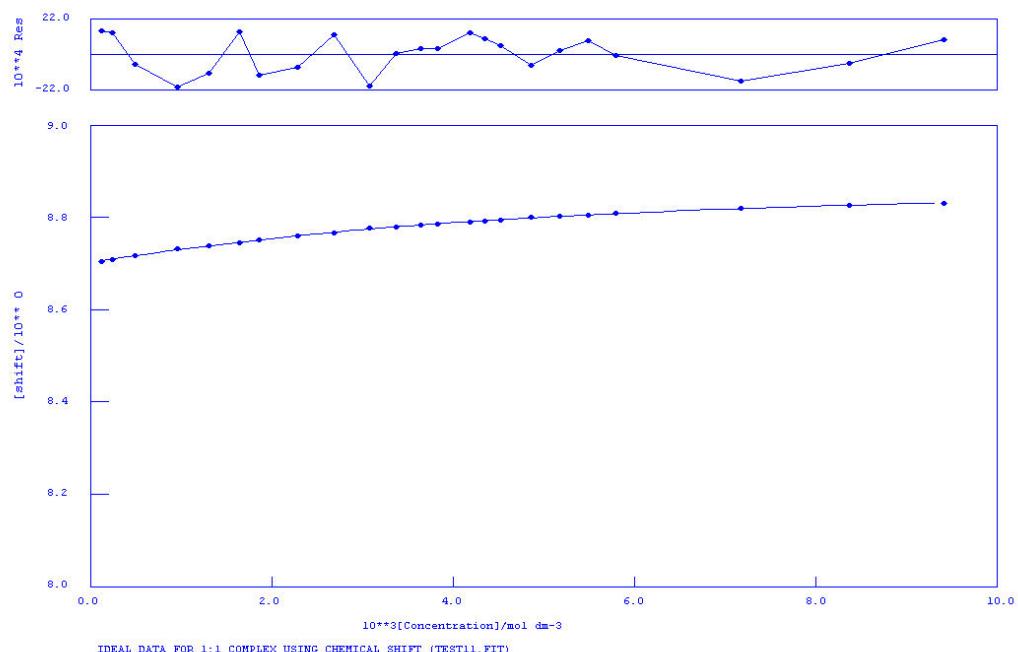
Figure 23 Shift at 3 eq.

- Tetrabutylammonium benzoate.

➤ CH_α Pyridine

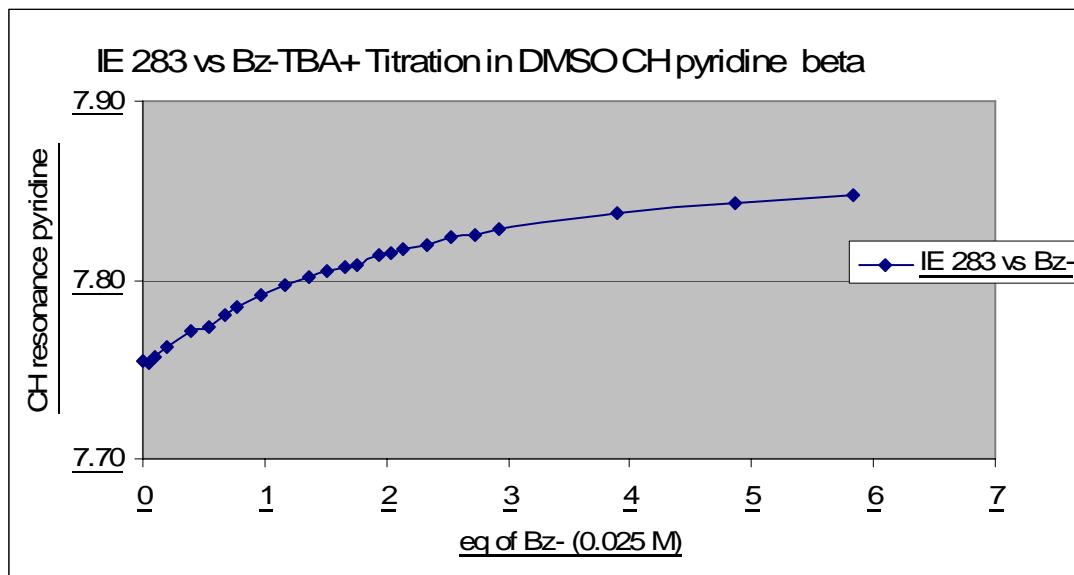


Graph 35 NMR titration shift graph.

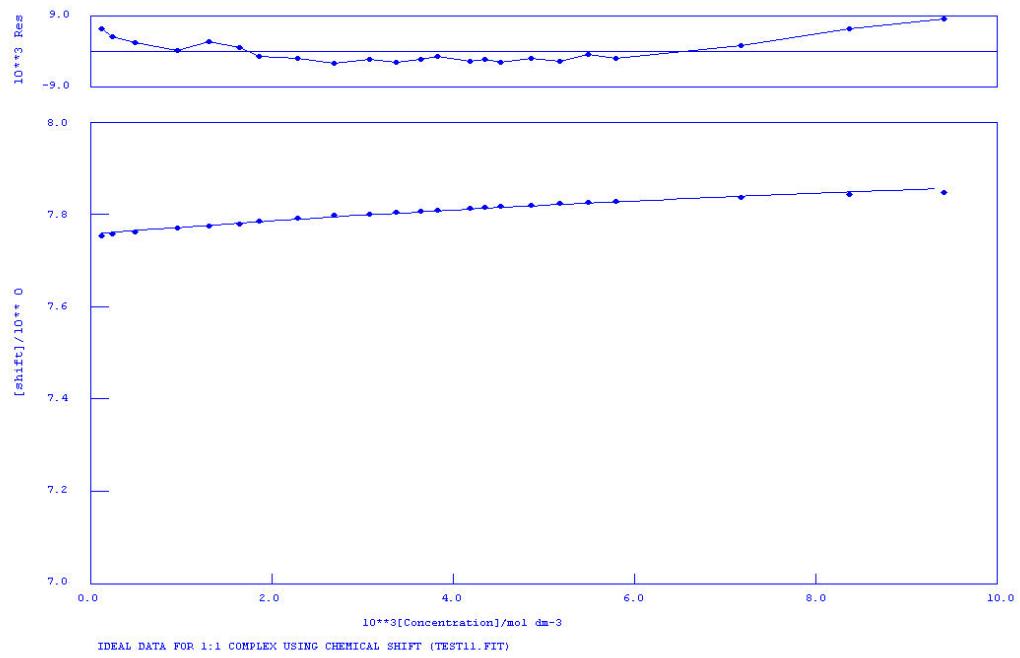


Fit 30 WinNMR fit.

➤ CH β Pyridine

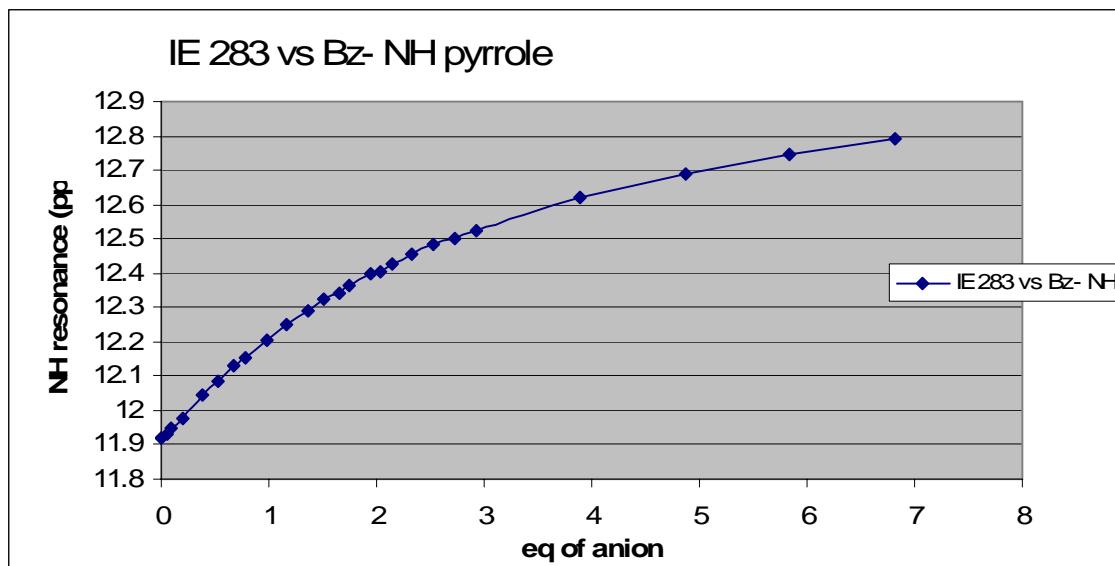


Graph 36 NMR titration shift graph.

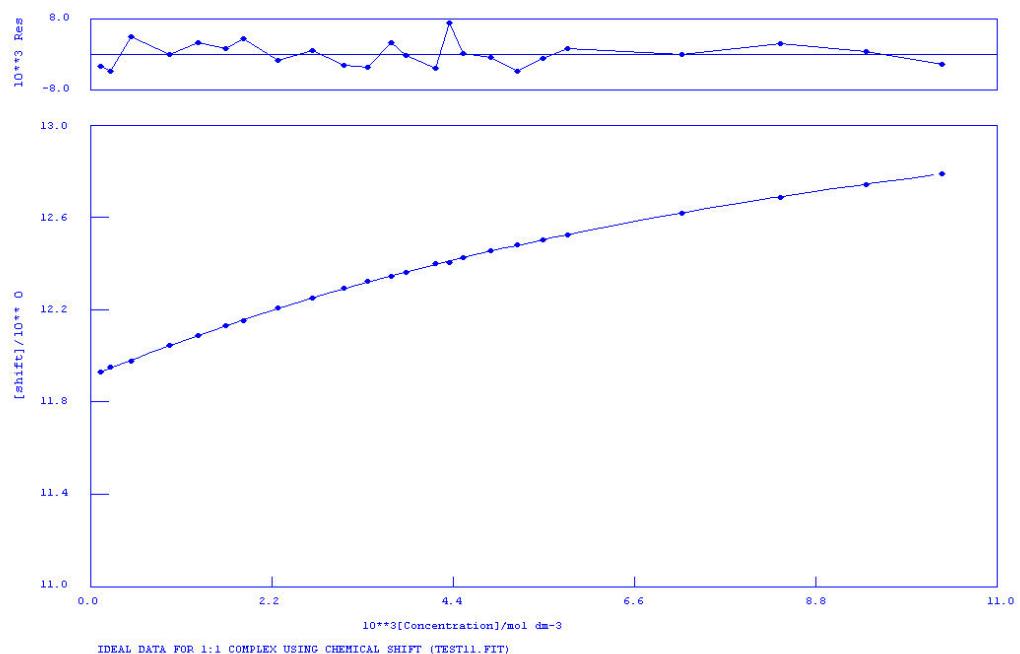


Fit 31 WinNMR fit.

➤ NH pyrrole



Graph 37 NMR titration shift graph.



Fit 32 WinNMR fit.

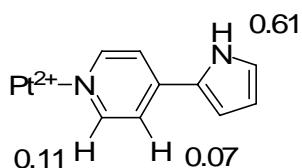
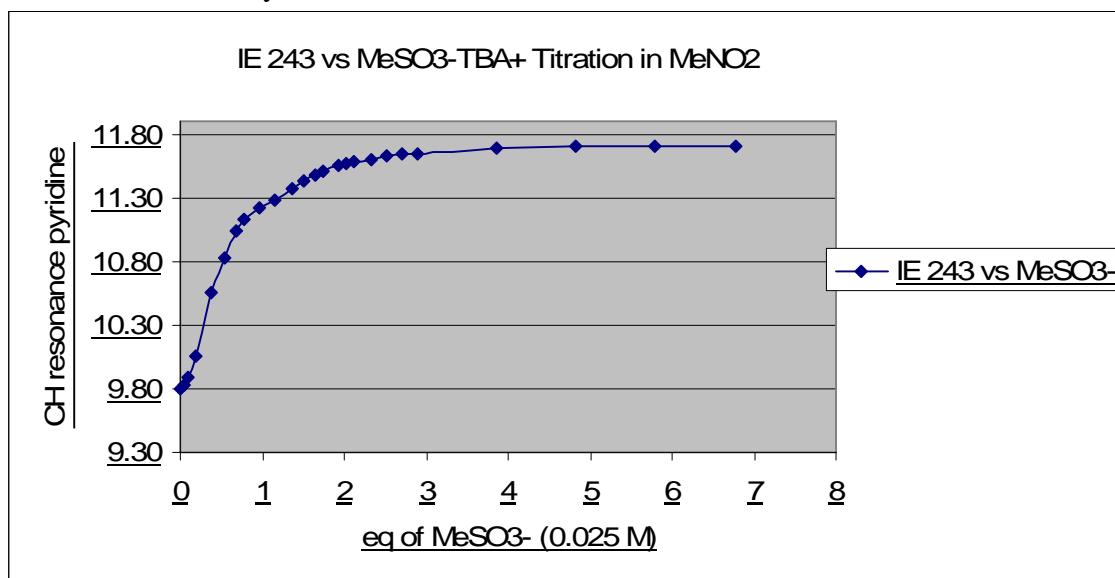


Figure 24 Shift at 3 eq.

Titrations tetrakis(m-(1H-pyrrole)pyridine)platinum(II) tetrafluoroborate **2** in other solvents.

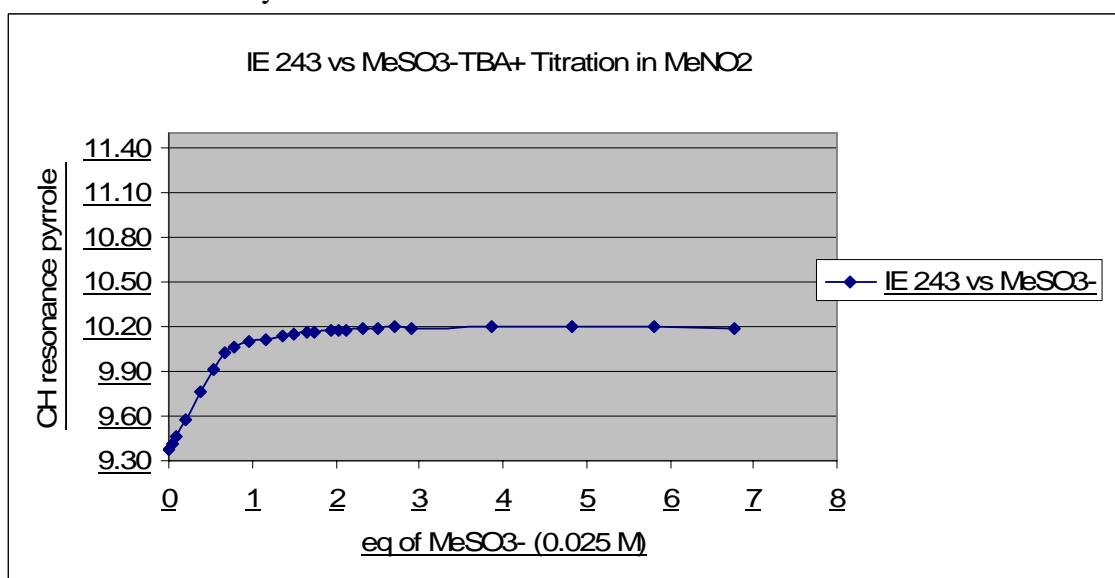
***MeNO₂-d₃*.**

- **Tetrabutylammonium methanesulfonate.**
 - NH Pyrrole



Graph 38 NMR titration shift graph.

- CH Pyridine

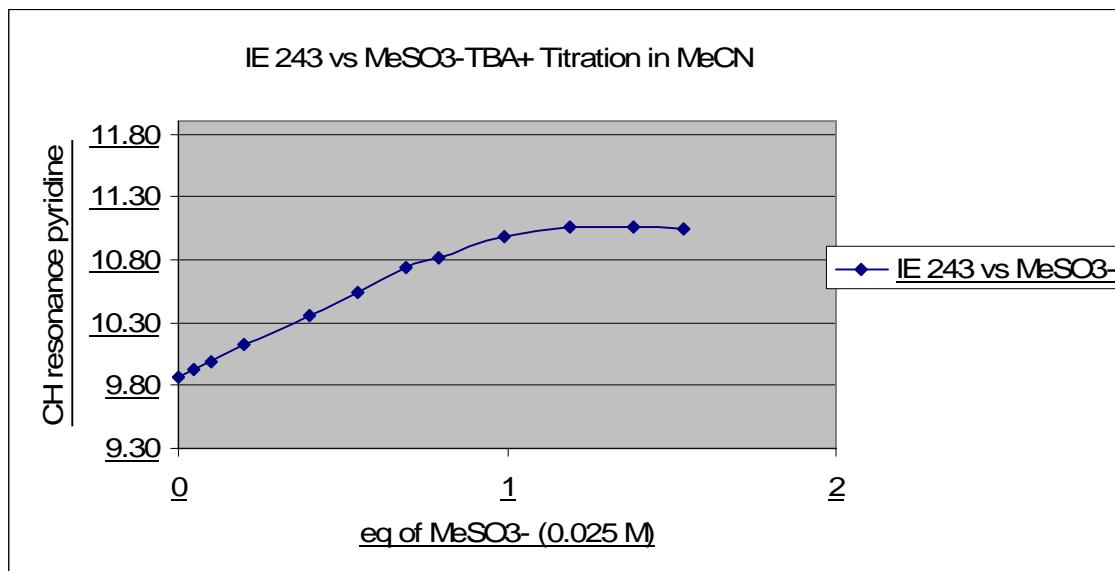


Graph 39 NMR titration shift graph.

MeCN-d₃.

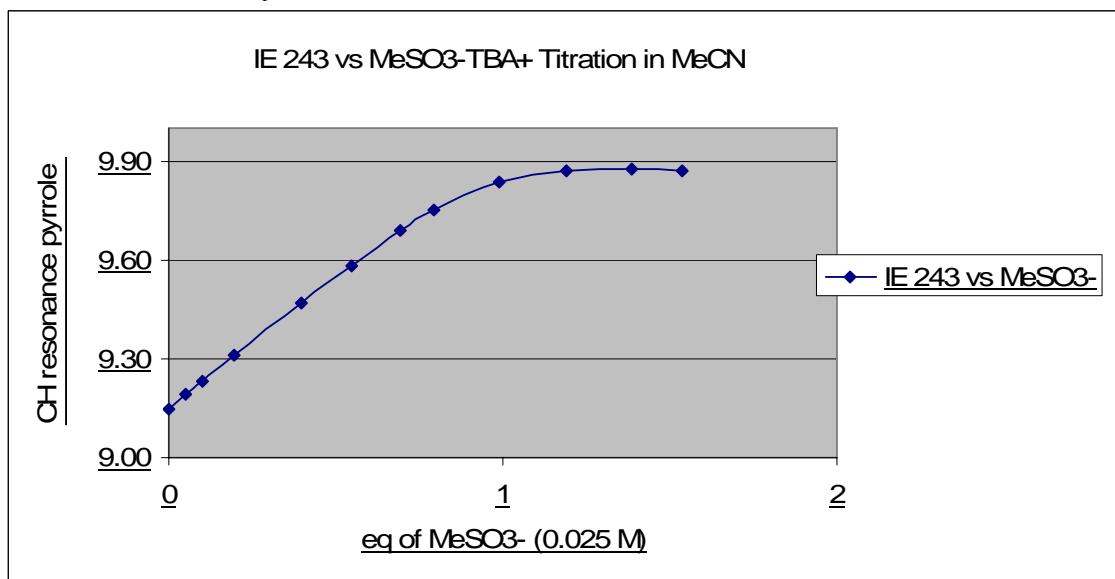
- **Tetrabutylammonium methanesulfonate.**

➤ NH Pyrrole



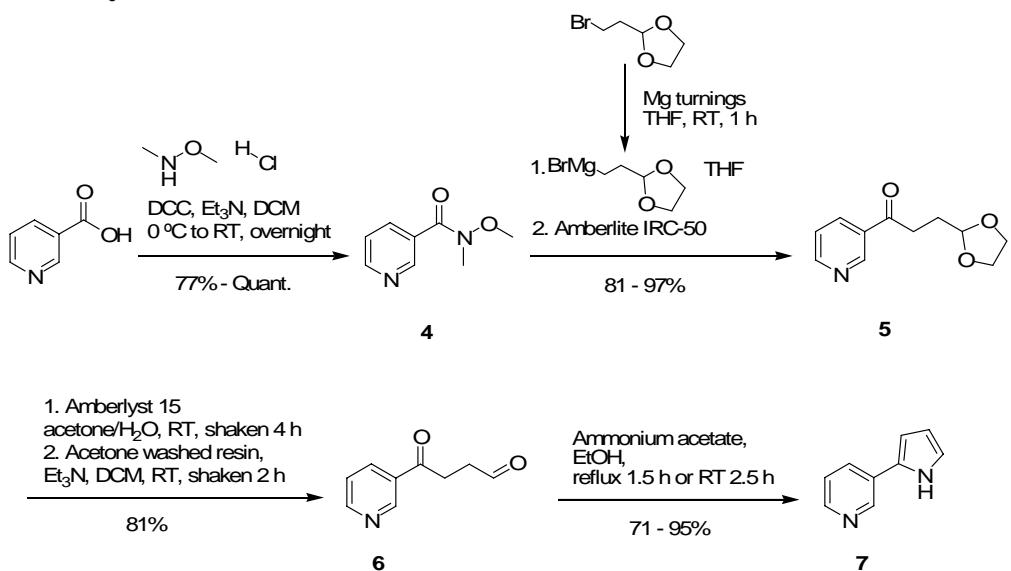
Graph 40 NMR titration shift graph.

➤ CH Pyridine

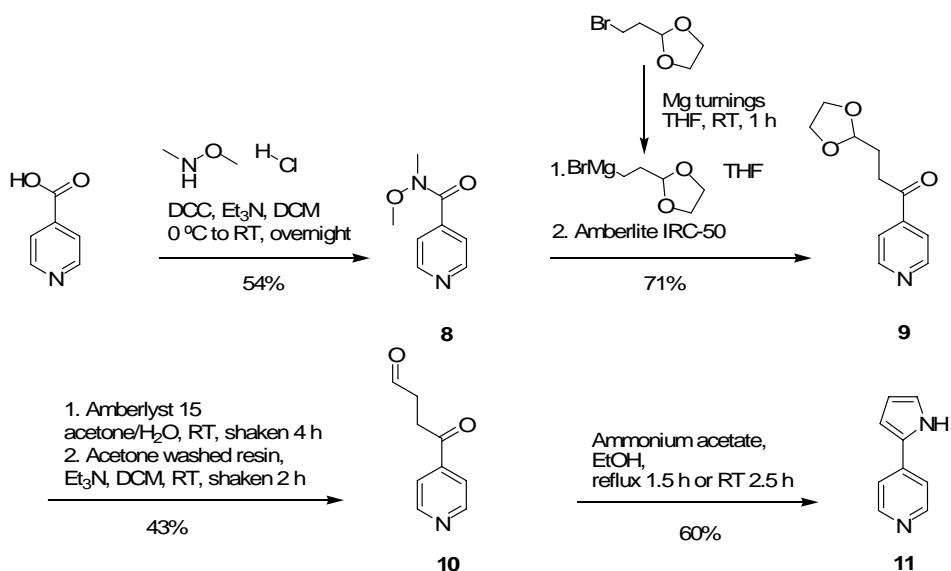


Graph 41 NMR titration shift graph.

Ligands synthesis



Scheme 1 Compounds **4**, **5** and **6** prepared from the same bibliographic source^{a1}. Final compound **7** prepared using the Paal Knoor reaction^{b2,3}.



Scheme 2 Compounds **8**, **9** and **10** prepared from the same bibliographic source¹. Final compound **11** prepared using the Paal Knoor reaction^{b2,3}.

^a 1. Baxendale, I. R.; Brusotti, G.; Matsuoka, M.; Ley, S. V., Synthesis of nornicotine, nicotine and other functionalised derivatives using solid-supported reagents and scavengers. *Journal of the Chemical Society-Perkin Transactions 1* **2002**, (2), 143-154.

^b 2. Kruse, C. G.; Bouw, J. P.; Vanhes, R.; Vandekuilen, A.; Denhartog, J. A. J., New Methods for the Synthesis of 2-Arylpyrroles. *Heterocycles* **1987**, 26, (12), 3141-3151.

3. Noland, W. E.; Cole, K. P.; Britton, D., Five (1H-pyrrol-2-yl)pyridines. *Acta Crystallographica Section C-Crystal Structure Communications* **2003**, 59, O263-O267.

N-methoxy-N-methylnicotinamide 4. This compound was prepared following the literature method¹. Yield, 8.5 g, or 54%. ¹H NMR 300 MHz in CDCl₃ (ppm): 8.83 (dd, J 2.3, J 0.8, 1H), 8.56 (dd, J 4.9, J 1.9, 1H), 7.90 (dd, J 7.9, J 2.3, 1H), 7.24 (ddd, J 7.9, J 4.9, J 0.8, 1H), 1.30 (s, 3H), 1.30 (s, 3H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 166.6 (CO), 150.6 (CH), 148.5 (CH), 135.3 (CH), 129.1 (C), 122.6 (CH), 60.5 (CH₃), 32.4 (CH₃).

3-(1,3-dioxolan-2-yl)-1-(pyridin-3-yl)propan-1-one 5. This compound was prepared following the literature method¹. Yield 2.7 g of yellow oil, or 74%. ¹H NMR 300 MHz in CDCl₃ (ppm): 9.12 (dd, J 1.5, J 0.8, 1H), 8.71 (dd, J 4.9, J 1.9, 1H), 8.18 (ddd, J 7.9, J 1.9, J 1.5, 1H), 7.36 (ddd, J 7.9, J 4.9, J 0.8, 1H), 4.95 (t, J 4.1, 1H), 3.90 (m, 2H), 3.80 (m, 2H), 3.07 (t, J 7.1, 2H), 2.15 (td, J 7.1, J 4.1, 2H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 198.2 (CO), 153.4 (CH), 149.6 (CH), 135.4 (CH), 132.2 (C), 123.6 (CH), 103.1 (CH), 65.0 (2 × CH₂), 32.7 (CH₂), 27.7 (CH₂).

4-oxo-4-(pyridin-3-yl)butanal 6. This compound was prepared following the literature method¹. Yield 0.6 g of yellow oil, or 73%. ¹H NMR 300 MHz in CDCl₃ (ppm): 9.89 (s, 1H), 9.19 (d, J 0.8, 1H), 8.78 (dd, J 0.8, J 3.6, 1H), 8.24 (dd, J 5.5, J 1.3, 1H), 7.42 (dd, J 3.6, J 5.5, 1H), 3.31 (t, J 4.5, 2H), 2.96 (t, J 4.7, 2H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 200.1 (CO), 196.8 (CO), 153.8 (CH), 149.7 (CH), 135.5 (CH), 131.9 (C), 123.8 (CH), 37.5 (CH₂), 31.3 (CH₂).

3-(1*H*-pyrrol-2-yl)pyridine 7. This compound was prepared following the literature method^{2,3}. Yield 1.2 g of white solid, or 84%. ¹H NMR 300 MHz in DMSO-d₆ (ppm): 11.43 (s, 1H), 8.87 (d, J 2.3, 1H), 8.33 (dd, J 1.5, J 4.9, 1H), 7.96 (ddd, J 7.9, J 1.5, J 2.25, 1H), 7.35 (dd, J 7.9, J 4.9, 1H), 6.92 (s, 1H), 6.63 (s, 1H), 6.15 (dd, J 3.4, J 6.0, 1H). ¹³C NMR 75.4 MHz in DMSO-d₆ (ppm): 146.5 (CH), 144.9 (CH), 131.6 (CH), 129.3 (C), 128.6 (C), 124.0 (CH), 120.5 (CH), 110.6 (CH), 107.6 (CH).

N-methoxy-N-methylisonicotinamide 8. This compound was prepared following the literature method¹. Yield 8.53 g of yellow oil, or 55%. ¹H NMR 300 MHz in CDCl₃ (ppm): 8.64 (dd, J 4.5, J 1.5, 2H), 7.45 (dd, J 4.5, J 1.5, 2H), 3.48 (s, 3H), 3.31 (s, 3H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 167.5 (CO), 1149.9 (CH), 141.7 (C), 121.9 (CH), 61.3 (2 × CH₃).

3-(1,3-dioxolan-2-yl)-1-(pyridin-4-yl)propan-1-one 9. This compound was prepared following the literature method¹. Yield 4.1 g of yellow oil, or 54%. ¹H NMR 300 MHz in CDCl₃ (ppm): 8.76 (dd, J 3.1, J 1.5, 2H), 7.70 (dd, J 3.1, J 1.5, 2H), 4.96 (t, J 3.4, 1H), 3.91 (m, 2H), 3.82 (m, 2H), 3.07 (t, J 5.3, 2H), 2.12 (m, 2H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 198.9 (CO), 150.9 (CH), 142.9 (C), 121.1 (CH), 103.1 (CH), 65.1 (CH₂), 32.7 (CH₂), 27.7 (CH₂).

4-oxo-4-(pyridin-4-yl)butanal 10. This compound was prepared following the literature method¹. Yield 1.32 g of yellow oil, or 42%. ¹H NMR 300 MHz in CDCl₃ (ppm): 9.84 (s, 1H), 8.78 (d, J 4.5, 2H), 7.72 (dd, J 3.4, J 1.1, 2H), 3.26 (t, J 4.5, 2H), 2.93 (t, J 4.9, 2H). ¹³C NMR 75.4 MHz in CDCl₃ (ppm): 206.8 (CO), 199.9 (CO), 150.9 (CH), 142.4 (C), 121.1 (CH), 37.4 (CH₂), 31.3 (CH₂).

4-(1*H*-pyrrol-2-yl)pyridine 11. This compound was prepared following the literature method^{2,3}. Yield 0.67 g of white solid, or 56%. ¹H NMR 300 MHz in DMSO-d₆ (ppm): 11.59 (s, 1H), 8.45 (d, J 4.5, 2H), 7.56 (d, J 4.5, 2H), 6.98 (s, 1H), 6.79 (s, 1H), 6.19 (s, 1H). ¹³C NMR 75.4 MHz in DMSO-d₆ (ppm): 149.9 (CH), 139.3 (C), 128.3 (C), 121.6 (CH), 117.3 (CH), 109.7 (CH), 108.7 (CH).

Stack plots

Methanesulfonate in DMSO-d₆.

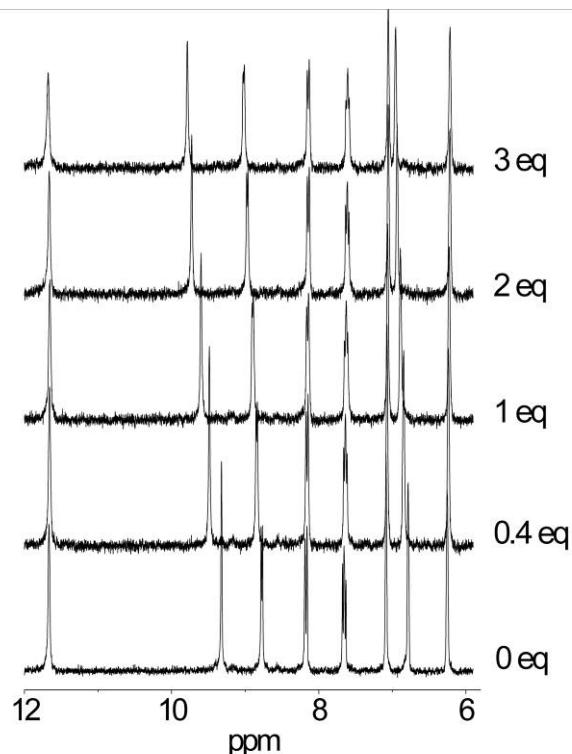


Figure 25 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium methanesulfonate in DMSO-d₆.

Iodide in DMSO-d₆.

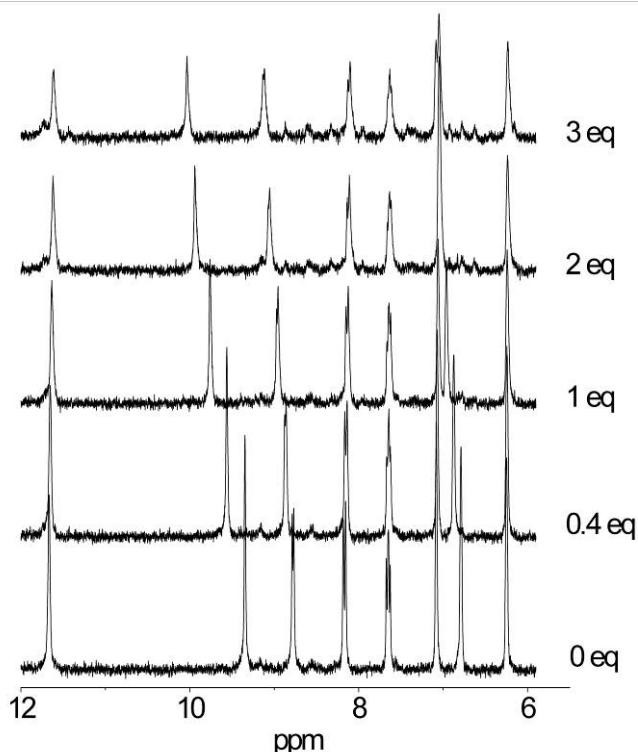


Figure 26 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium iodide in DMSO-d₆.

Bromide in DMSO-*d*₆.

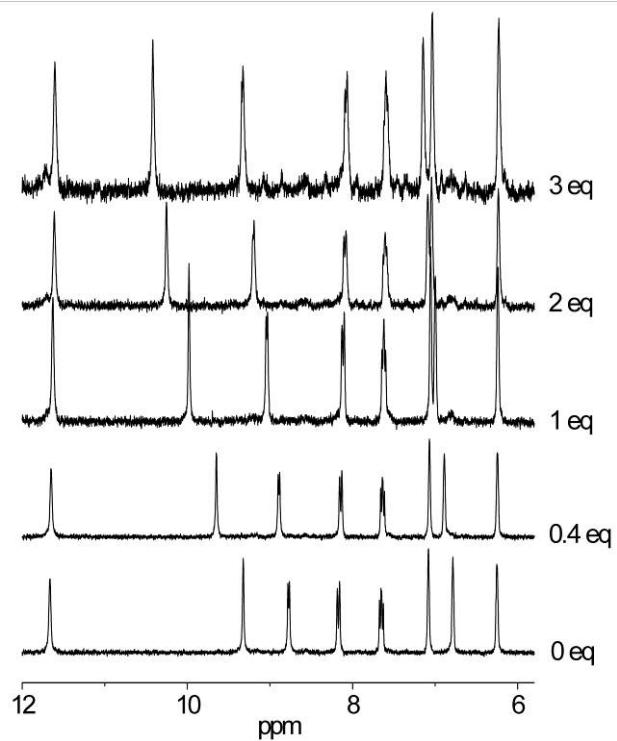


Figure 27 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium bromide in DMSO-*d*₆.

Chloride in DMSO-*d*₆.

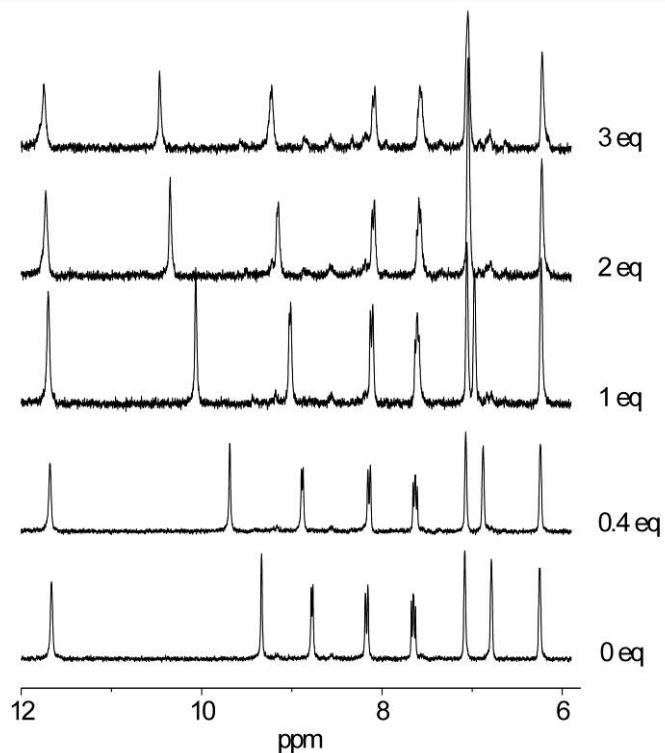


Figure 28 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium chloride in DMSO-*d*₆.

Acetate in DMSO-*d*₆.

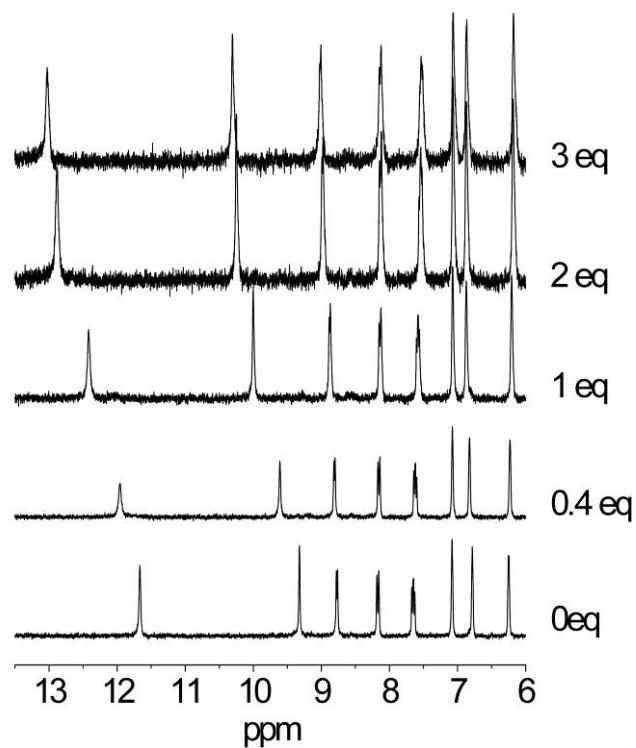


Figure 29 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium acetate in DMSO-*d*₆.

Methanesulfonate in MeNO₂-*d*₃.

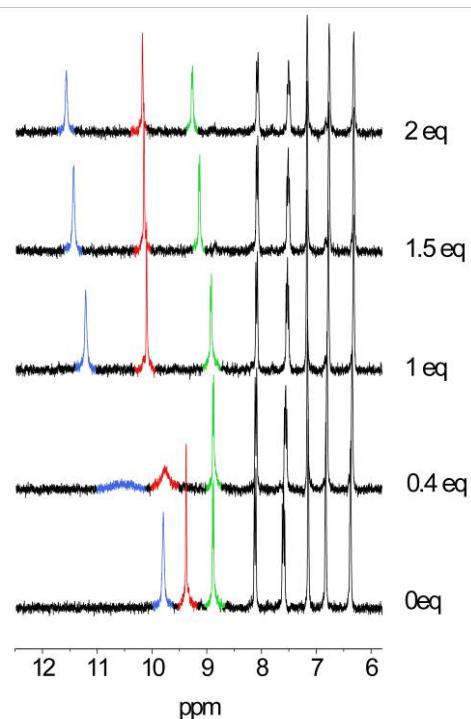


Figure 30 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium metanesulfonate in MeNO₂-*d*₃. Precipitation occurred after 2 equivalents.

Methanesulfonate in MeCN-d₃.

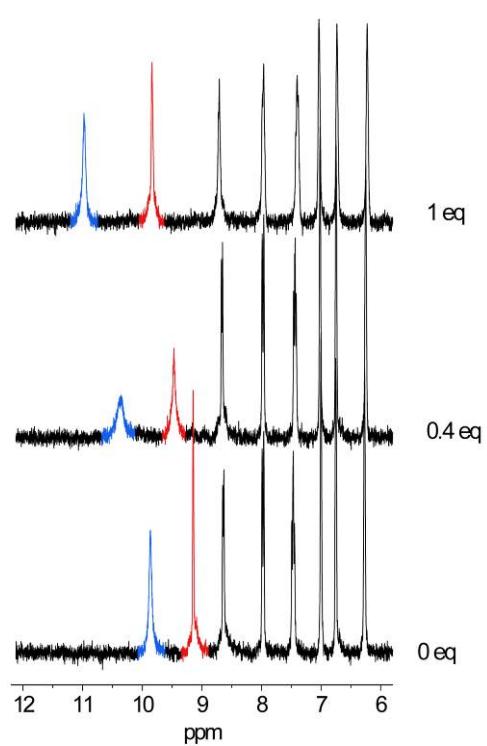


Figure 31 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium metanesulfonate in MeCN-d₃. Precipitation occurred after 1 equivalent.

Chloride in MeNO₂-d₃.

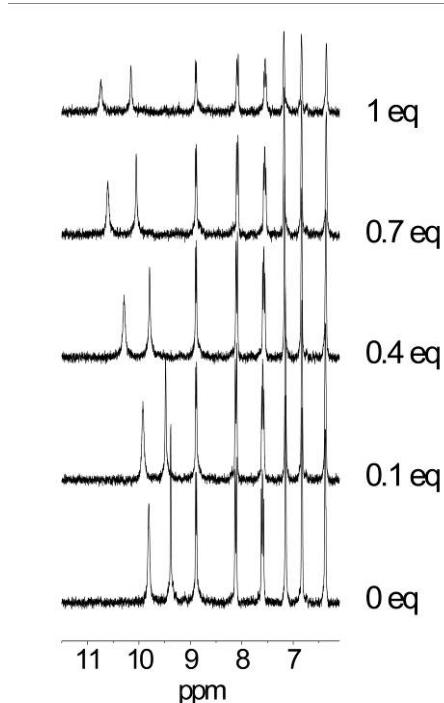


Figure 32 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium chloride in MeNO₂-d₃. Precipitation occurred after 1 equivalent.

Bromide in MeNO₂-d₃.

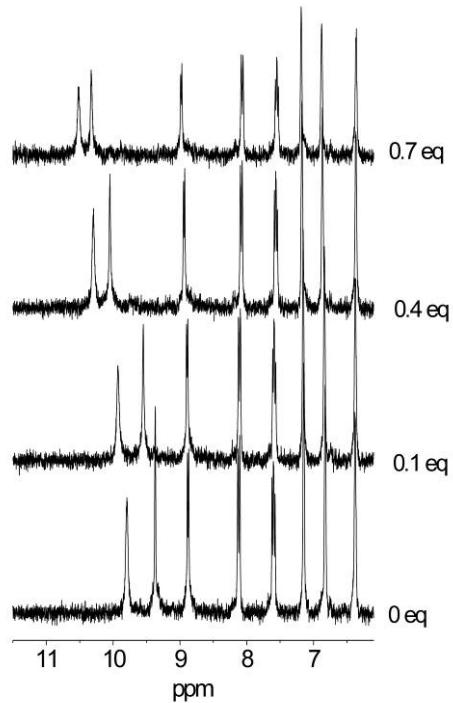


Figure 33 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium bromide in MeNO₂-d₃. Precipitation occurred after 1 equivalent.

Iodide in MeNO₂-d₃.

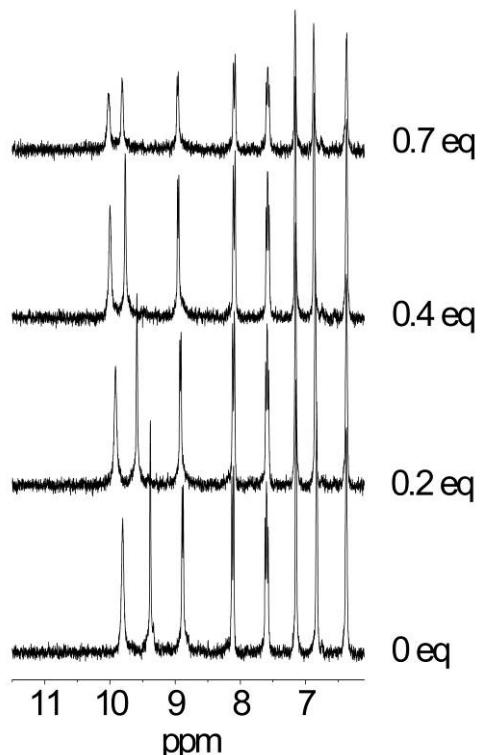


Figure 34 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium iodide in MeNO₂-d₃. Precipitation occurred after 1 equivalent.

Hydrogensulfate in $\text{MeNO}_2\text{-}d_3$.

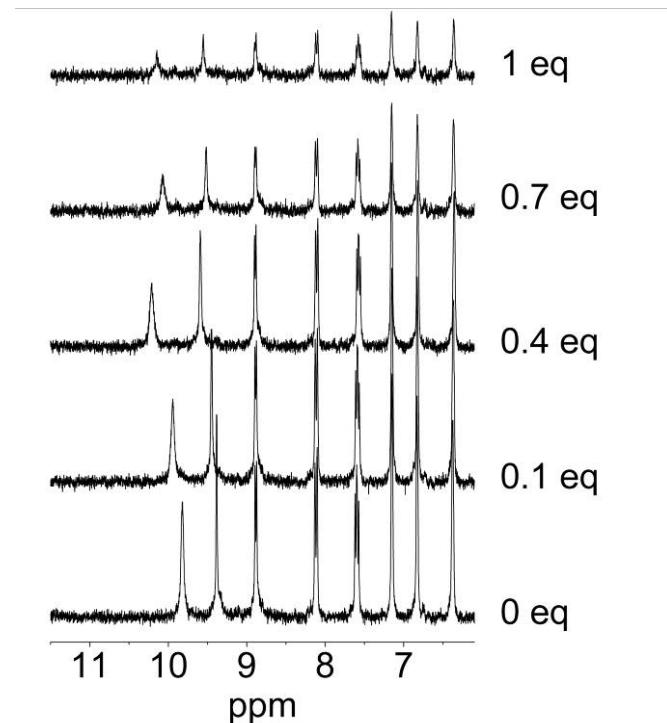


Figure 35 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate **2** with tetrabutylammonium hydrogensulfate in $\text{MeNO}_2\text{-}d_3$. Precipitation occurred after 1 equivalent.

Nitrate in $\text{MeNO}_2\text{-}d_3$.

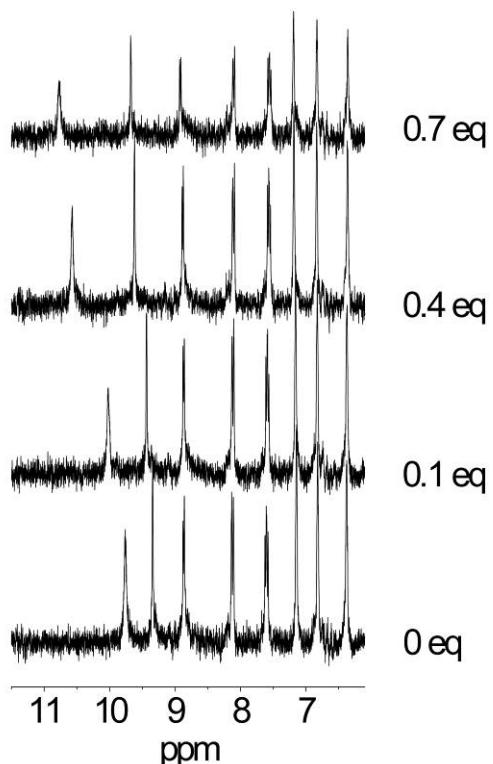
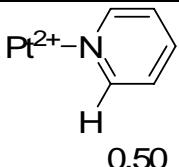
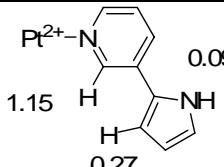
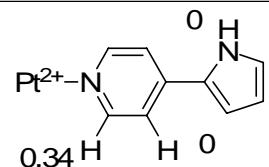
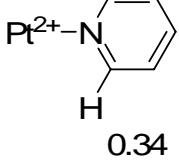
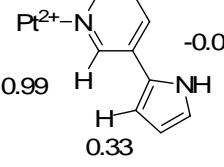
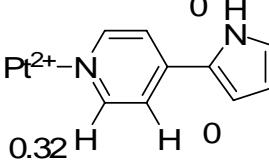
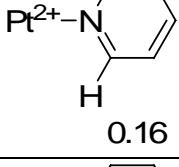
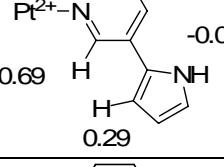
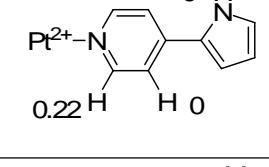
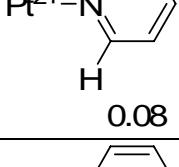
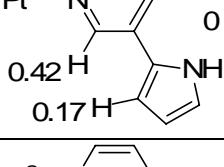
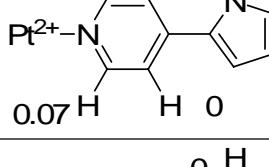
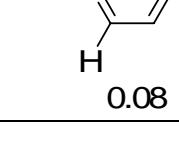
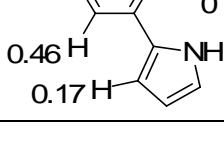
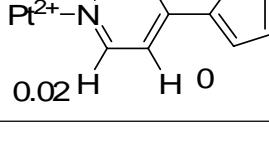
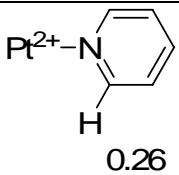
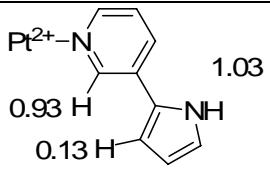
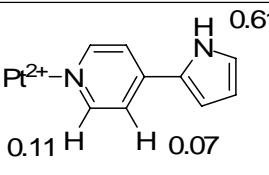
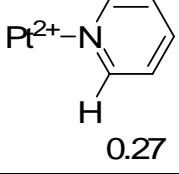
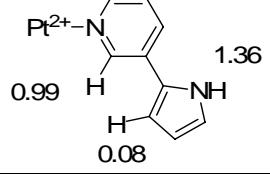
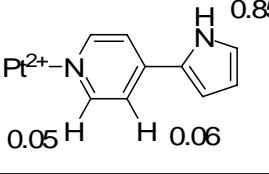
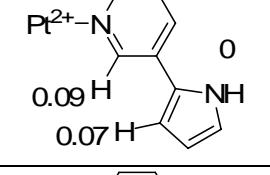
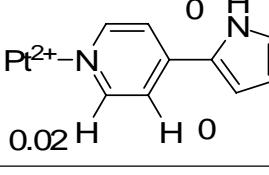
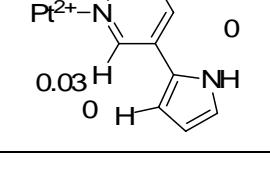


Figure 36 Stack plot tetrakis *m*-(1*H*-pyrrol-2-yl)pyridine)platinum(II) tetrafluoroborate with tetrabutylammonium nitrate in $\text{MeNO}_2\text{-}d_3$. Precipitation occurred after 1 equivalent.

Shifts overview

Table 1 Abstract of ^1H NMR shifts for compounds **1-3**.

	1	2	3
Cl ⁻	 0.50	 1.15 0.27 0.09	 0.34 0.34 0.34
Br ⁻	 0.34	 0.99 0.33 -0.06	 0.32 0.32 0.32
I ⁻	 0.16	 0.69 0.29 -0.06	 0.22 0.22 0.22
HSO ₄ ⁻	 0.08	 0.42 0.17 0	 0.07 0.07 0.07
MeSO ₃ ⁻	 0.08	 0.46 0.17 0	 0.02 0.02 0.02

Bz ⁻	 0.26		
AcO ⁻	 0.27		
NO ₃ ⁻	-	 0	 0
CF ₃ SO ₃ ⁻	-	 0	-

CH correlation experiments.

HMBQC of compound 2.

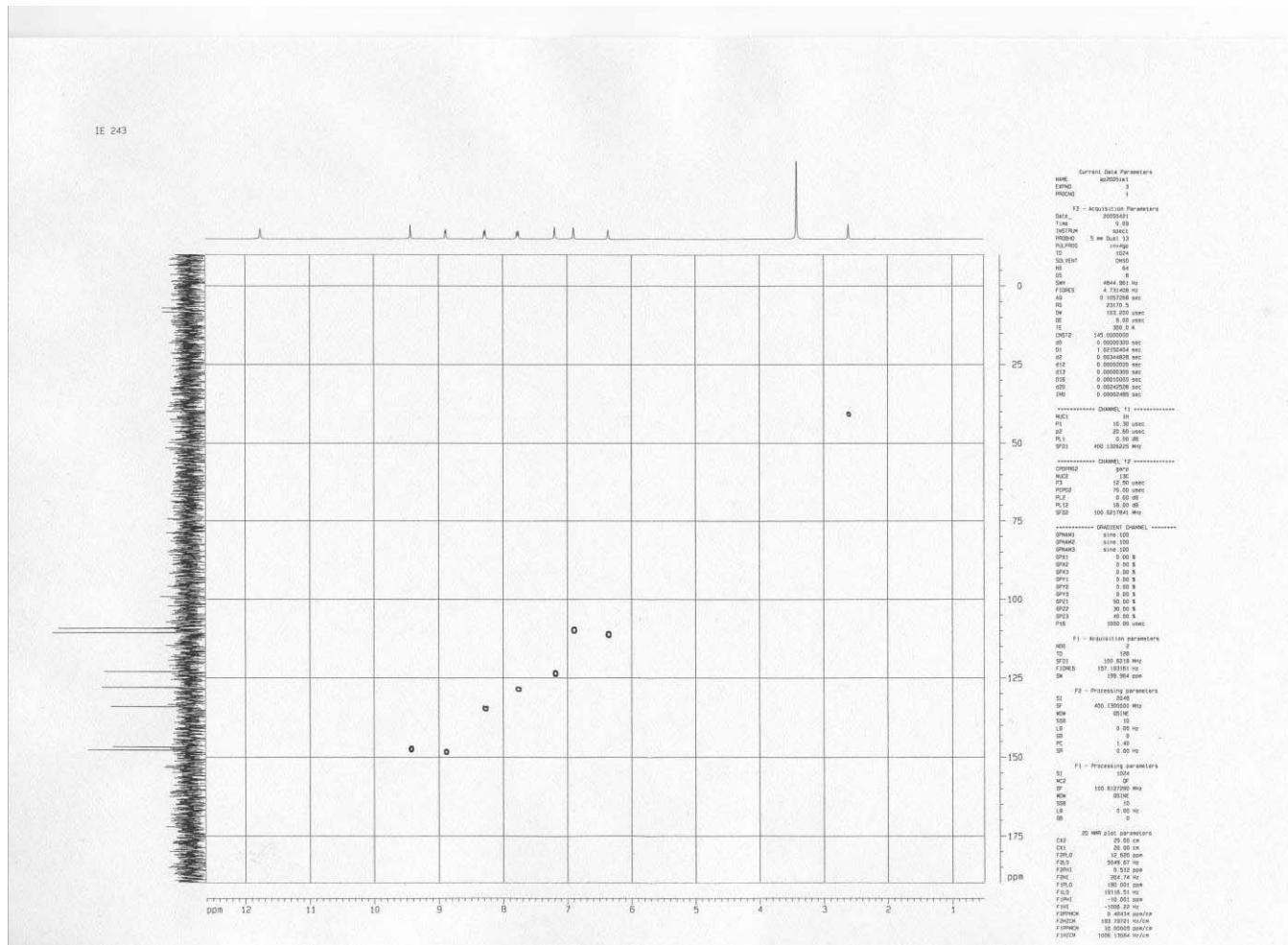


Figure 37 Compound 2 CH correlation.

HMQC of compound 3

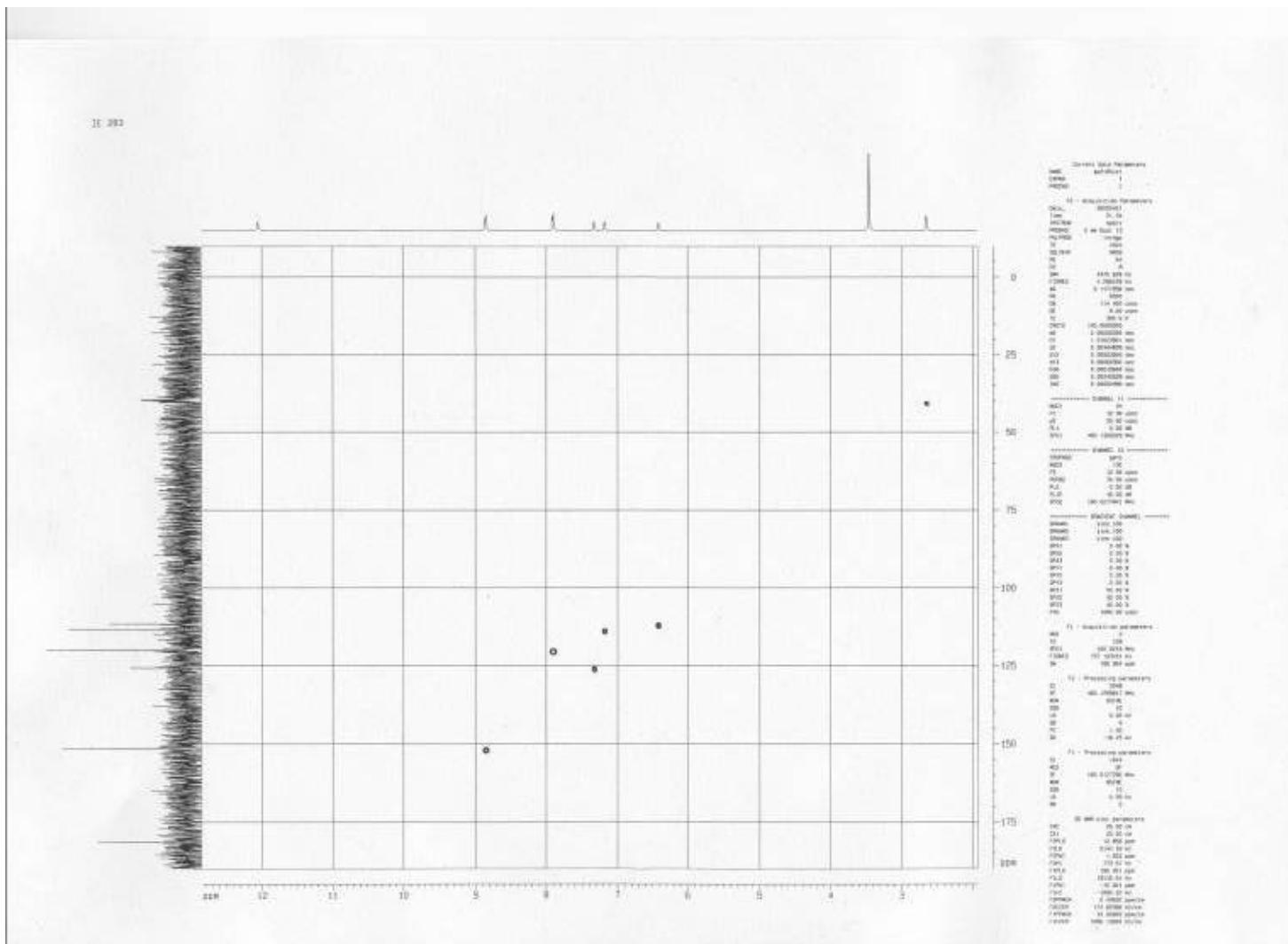


Figure 38 Compound 3 CH correlation.

Spectroscopic data.

Compound 1

¹H NMR

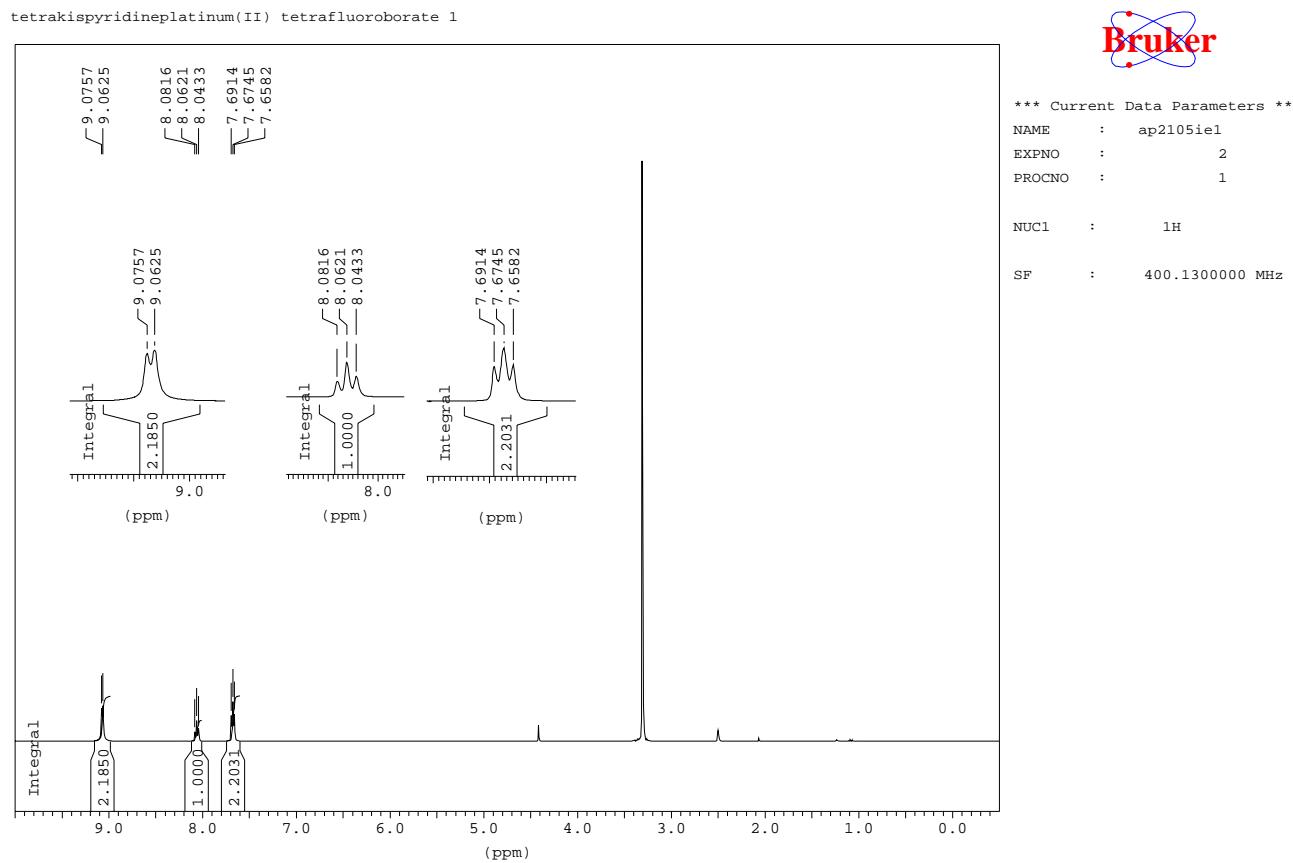


Figure 39 ^1H NMR spectra of compound **1**.

¹³C NMR

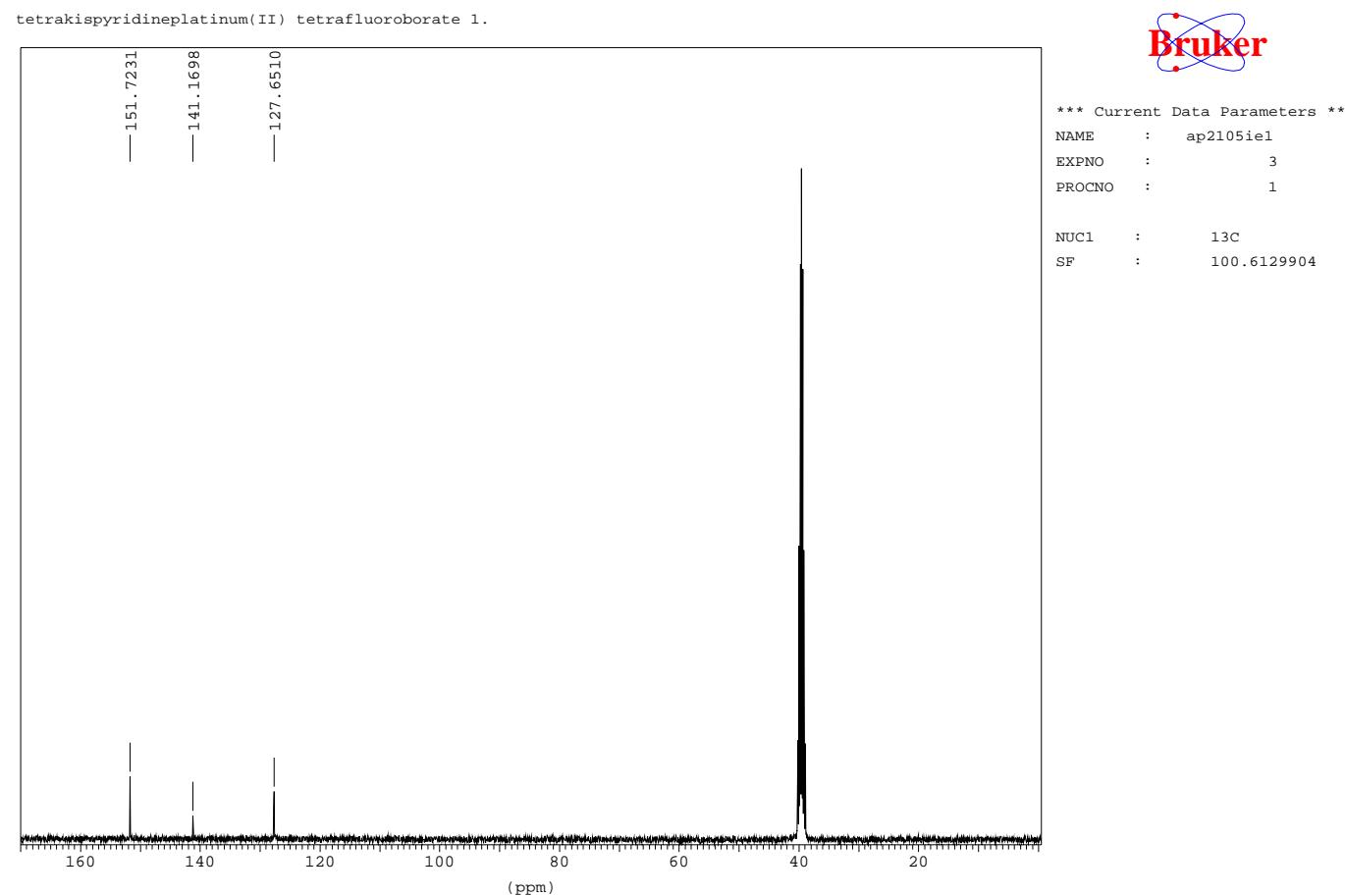


Figure 40 ¹³C NMR spectra of compound 1.

HR Mass spectrum

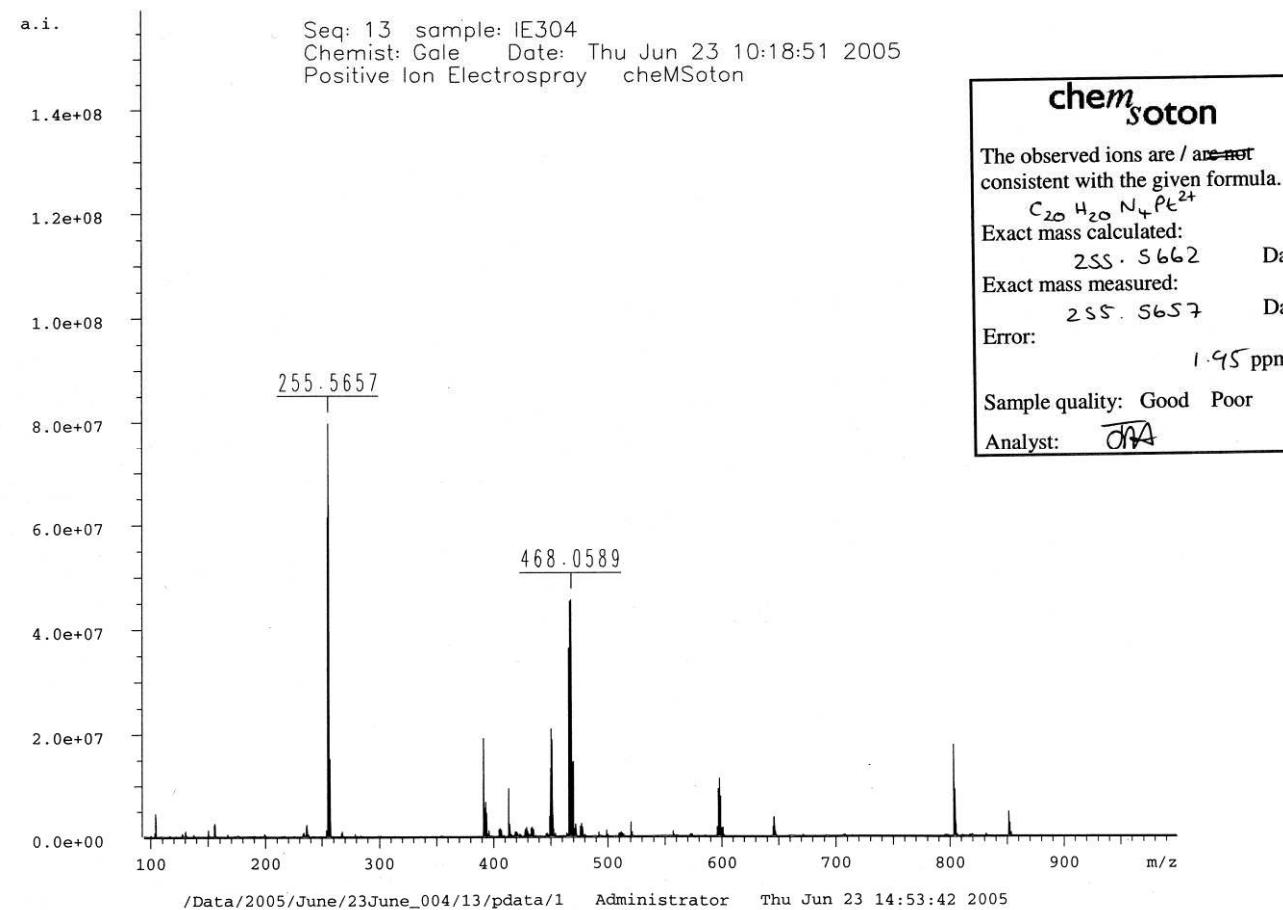


Figure 41 HRES⁺ of compound 1.

Compound 2

^1H NMR

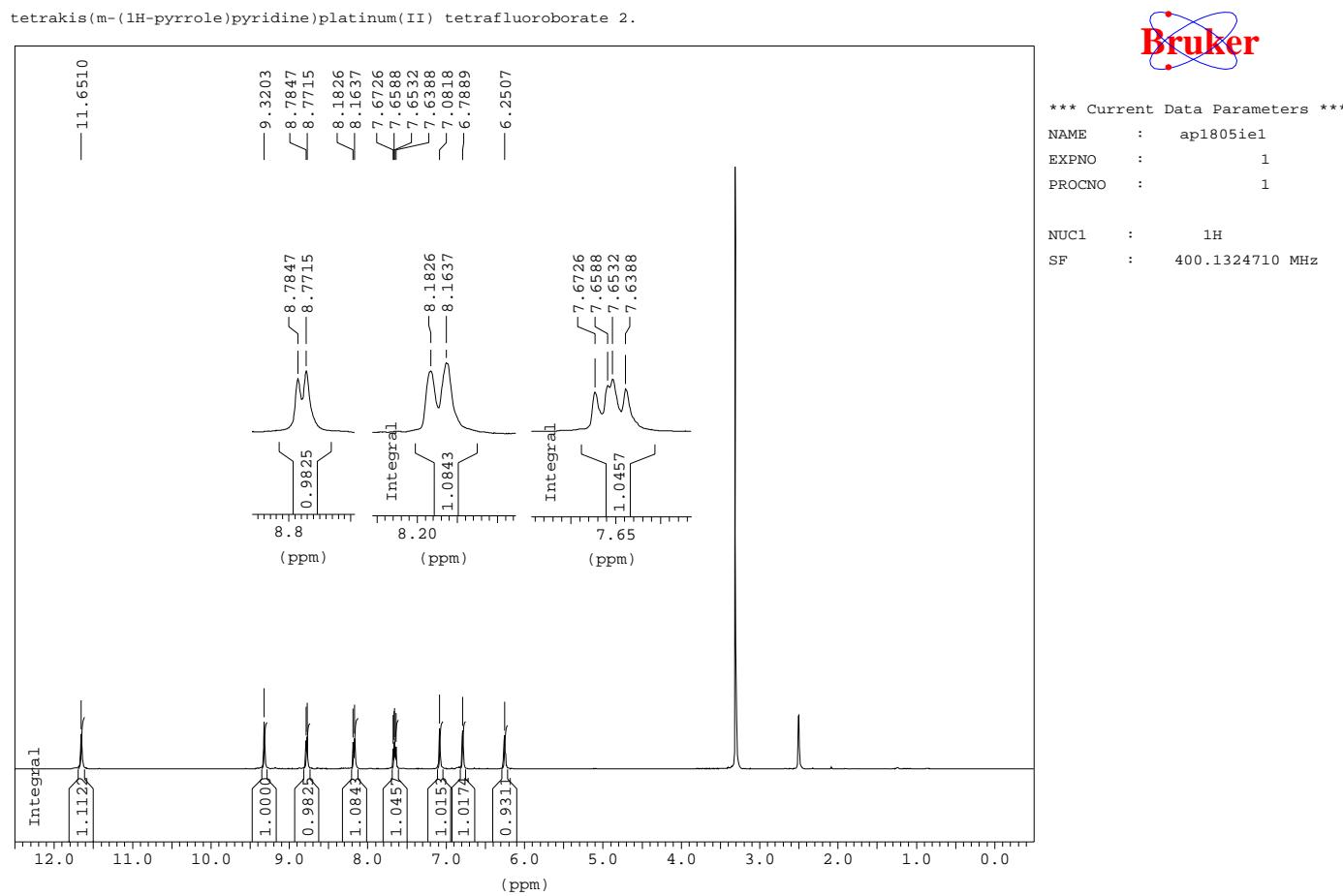


Figure 42 ^1H NMR spectra of compound 1.

¹³C NMR

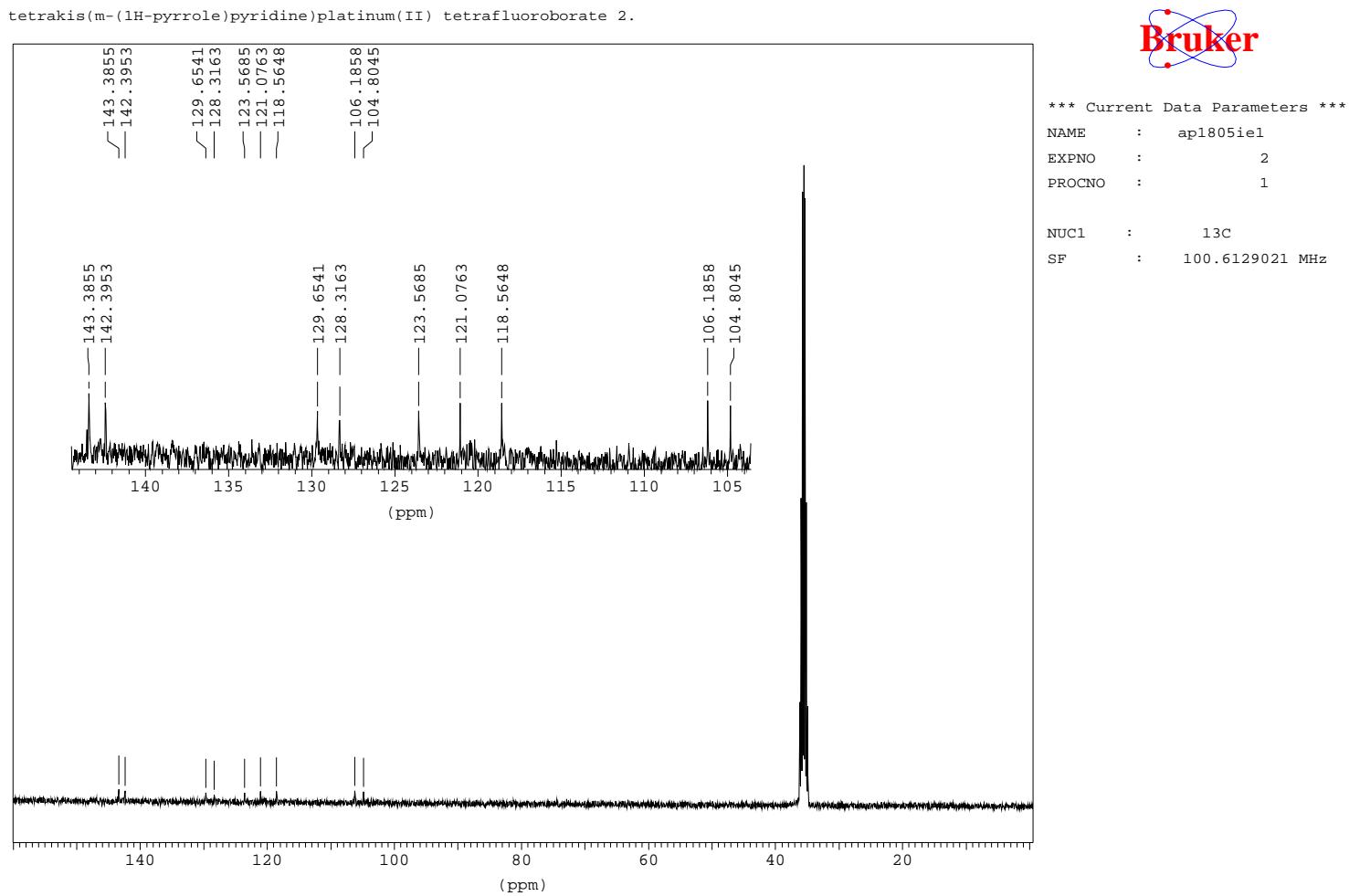


Figure 43 ¹³C NMR spectra of compound 2.

HR Mass spectrum

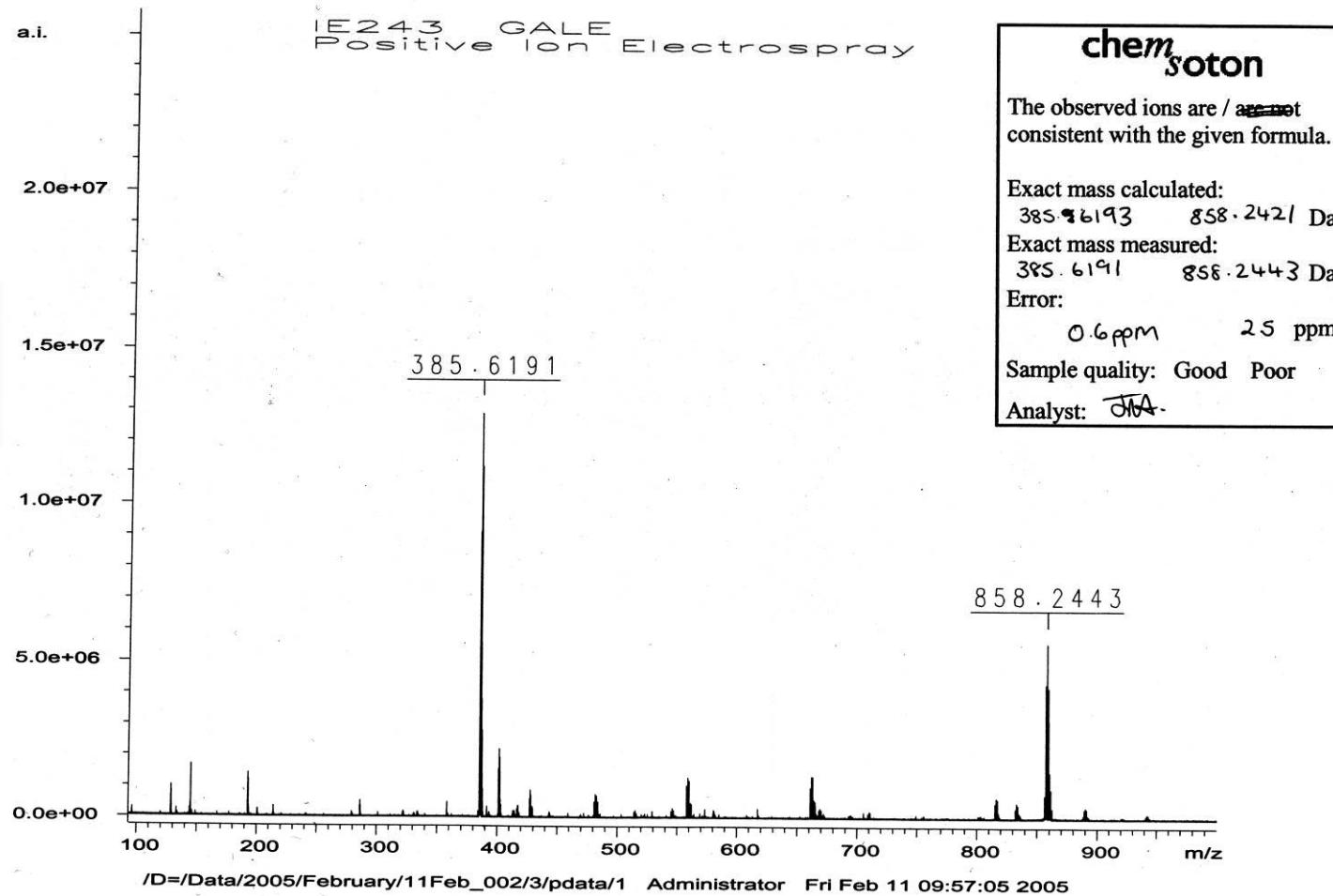


Figure 44 HRES⁺ of compound 2.

Compound 3

^1H NMR

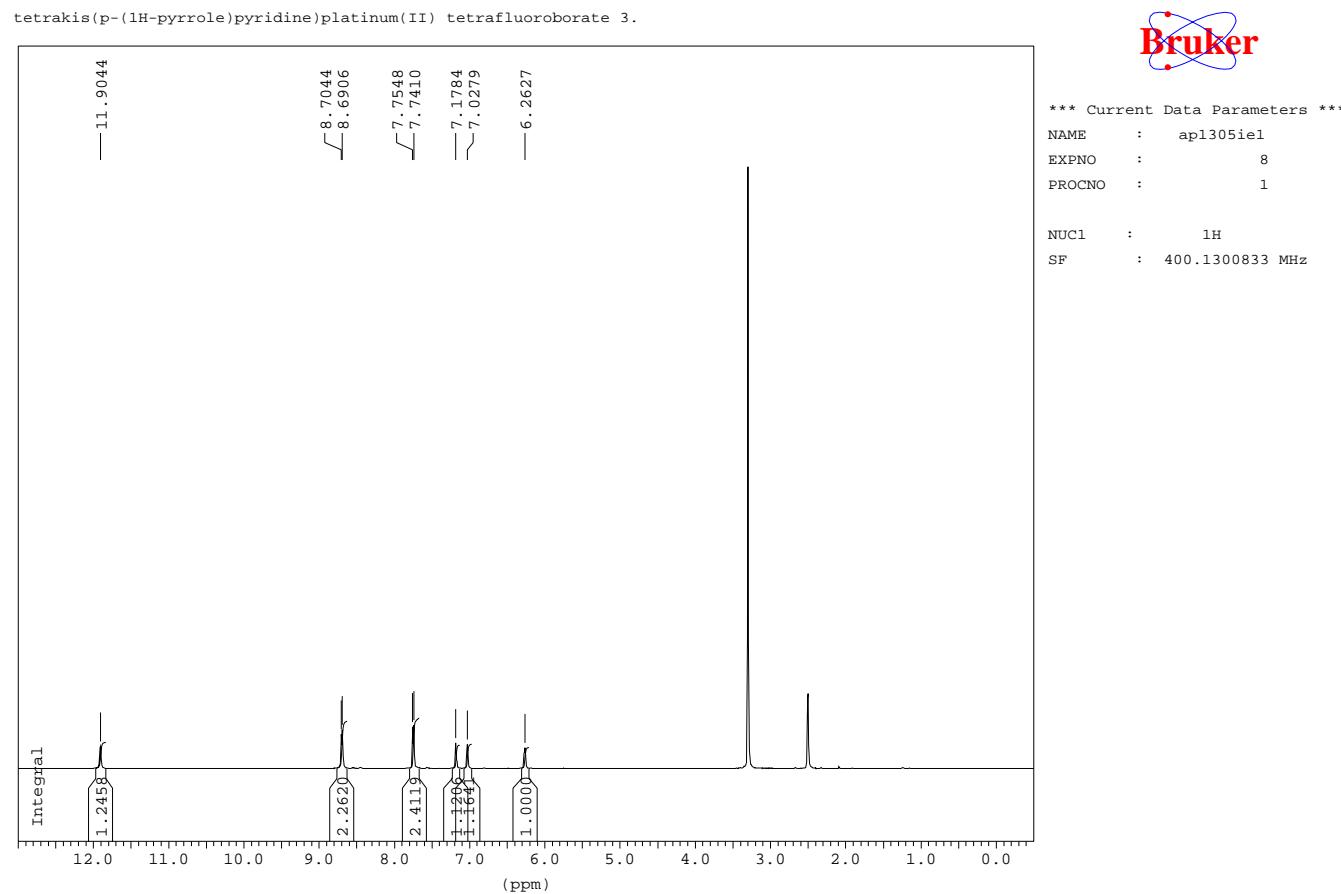


Figure 45 ^1H NMR spectra of compound 3.

¹³C NMR

tetrakis(p-(1H-pyrrole)pyridine)platinum(II) tetrafluoroborate 3.

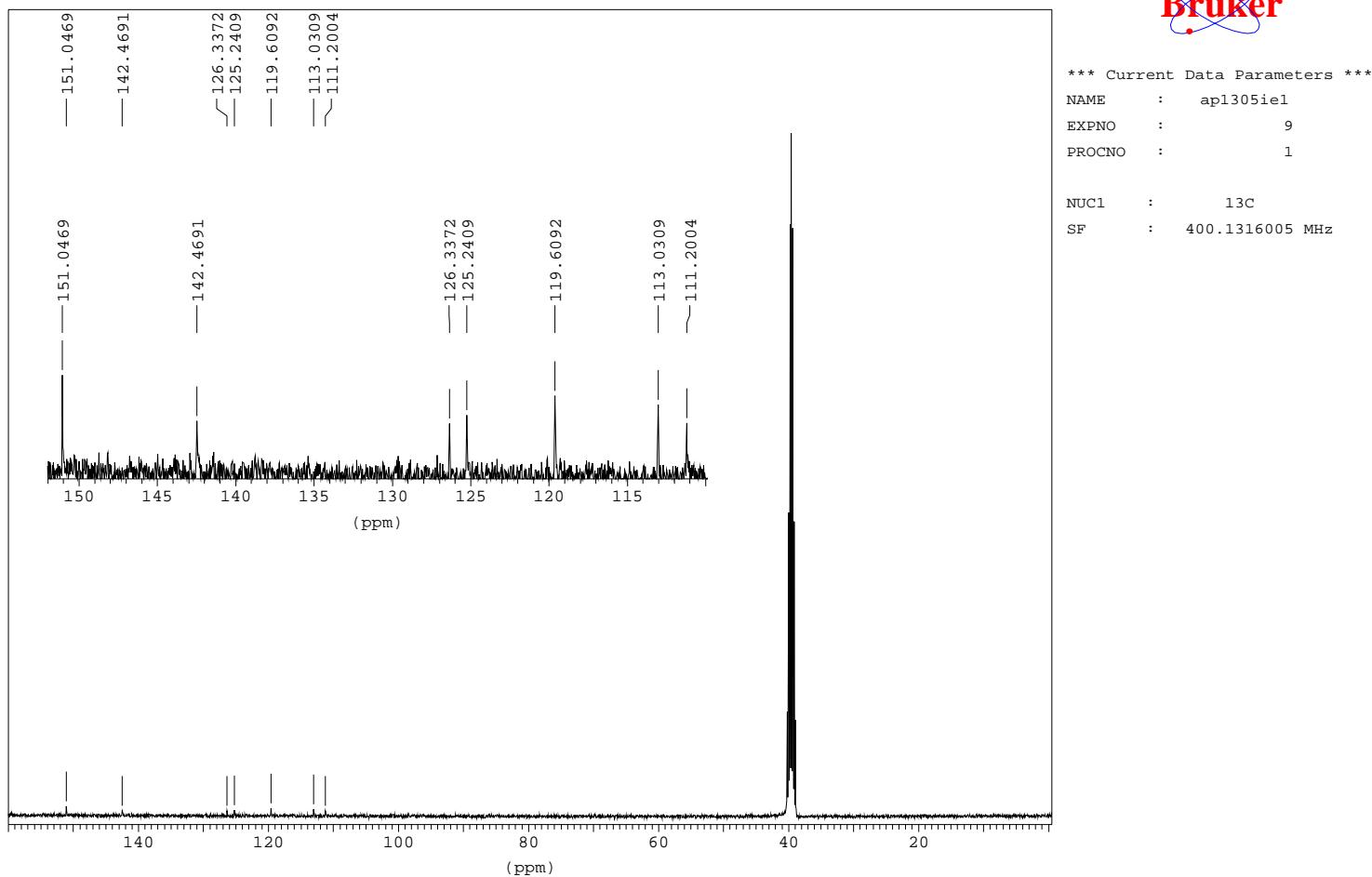


Figure 46 ¹³C NMR spectra of compound 3.

HR Mass spectrum

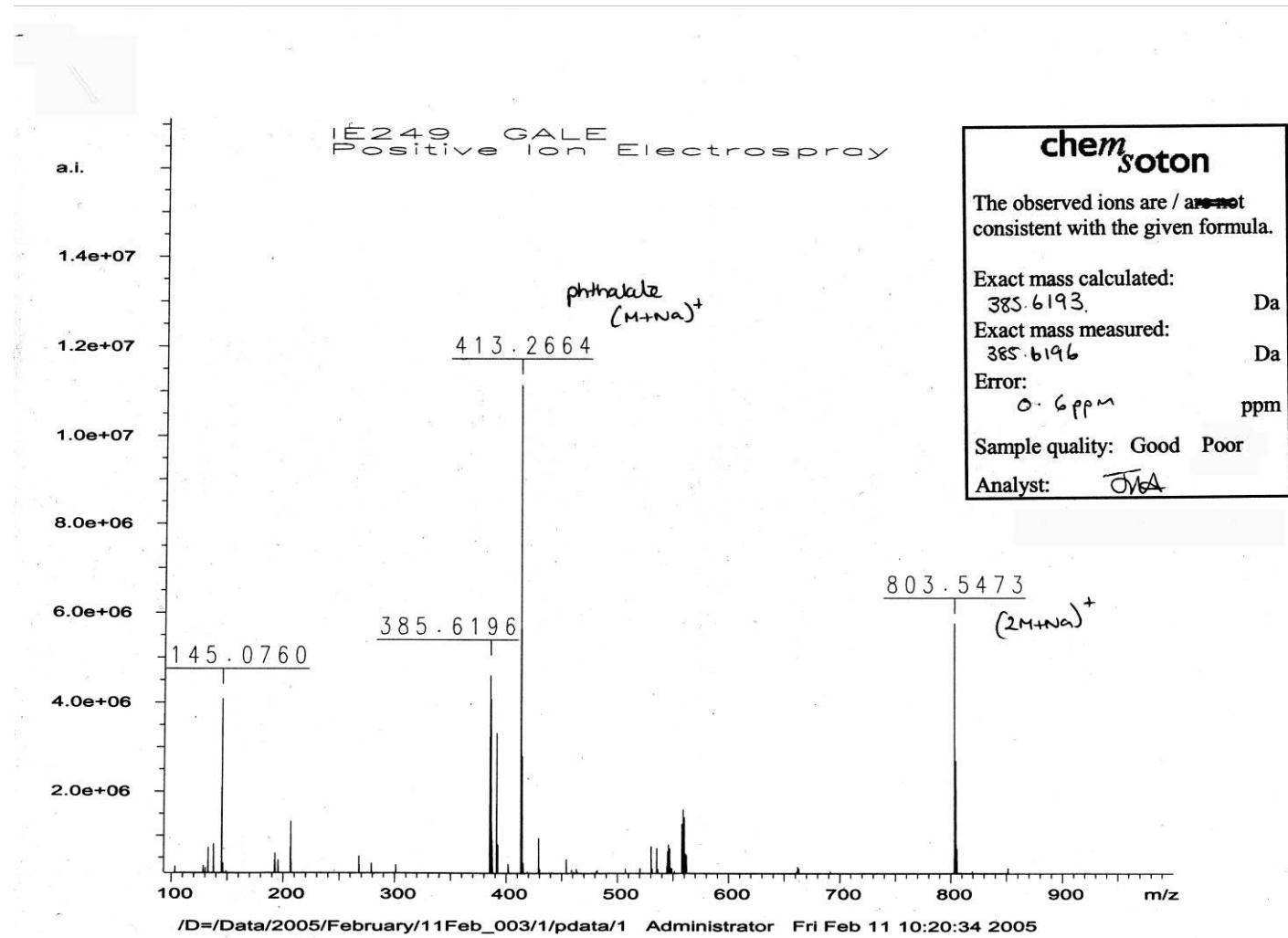


Figure 47 HRES⁺ of compound 3.