

SUPPORTING INFORMATION

Reactivity of the B–H bond in *Tris*(pyrazolyl)hydroborato Zinc Complexes: An Unexpected Example of Zinc Hydride Formation in a Protic Solvent and its Relevance towards Hydrogen Transfer to NAD⁺ Mimics by *Tris*(pyrazolyl)hydroborato Zinc Complexes in Alcoholic Media

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Experimental Details

General Considerations

$[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$,¹ $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}_2$,² 10-methylacridinium perchlorate³ (*caution!*) and 10-methylacridan,⁴ were prepared by literature methods.

Reduction of 10-Methylacridinium Perchlorate by $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ in ROH

$[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ (3 mg, 0.006 mmol) was added to a solution of 10-methylacridinium perchlorate (3 mg, 0.01 mmol) in *ca.* 0.6 mL deuterio-ROH ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$). The mixture was heated at 80°C for 15 hours,⁵ resulting in the formation of 10-methylacridan and 3-*tert*-butyl-5-methylpyrazole, as demonstrated by ^1H NMR spectroscopy. The spectroscopic yield of 10-methylacridan (based on total amount of added $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$) was *ca.* 85%. In the absence of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$, no reaction was observed between 10-methylacridinium perchlorate and ROH under the same conditions. The analogous reaction between deuterium labeled $[\text{DTp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ and 10-methylacridinium perchlorate in CH_3OH was monitored by ^2H NMR spectroscopy, confirming that deuterium was incorporated into the methylene group.

Reduction of 10-Methylacridinium Perchlorate by $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ in THF

A suspension of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}$ (3 mg, 0.006 mmol) and 10-methylacridinium perchlorate (3 mg, 0.01 mmol) in d_8 -THF (*ca.* 0.6 mL) was heated at 80°C for 1 day, resulting in the formation of 10-methylacridan, as demonstrated by ^1H NMR spectroscopy.

Reduction of 10-Methylacridinium Perchlorate by $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Ti}$ in MeOH

$[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{Ti}$ (3 mg, 0.005 mmol) was added to a solution of 10-methylacridinium perchlorate (3 mg, 0.01 mmol) in CD_3OD (*ca.* 0.6 mL). The reaction was monitored by ^1H NMR spectroscopy which demonstrated the presence of 10-methylacridan and 3-*tert*-butyl-5-methylpyrazole upon mixing. The mixture was heated at 80°C for 2.5 hours to complete the reaction forming a *ca.* 1:3 molar ratio of 10-methylacridan and 3-*tert*-butyl-

5-methylpyrazole. The analogous reaction between deuterium labeled $[\text{DTp}^{\text{Bu}^t, \text{Me}}]\text{I}$ and 10-methylacridinium perchlorate in CH_3OH was monitored by ^2H NMR spectroscopy, confirming that deuterium was incorporated into the methylene group.

Reaction of $\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}_2\}[\text{HOB}(\text{C}_6\text{F}_5)_3]$ towards Methanol

(a) A solution of $\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}_2\}[\text{HOB}(\text{C}_6\text{F}_5)_3]$ (ca. 3 mg) in CD_3OD (ca. 0.6 mL) was monitored by ^1H NMR and ^{19}F spectroscopy. After ca. 30 minutes, ^1H NMR spectroscopy demonstrated the presence of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$,⁶ 3-*tert*-butyl-5-methylpyrazole, and an unidentified complex which has a spectrum consistent with $\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnL}\}^+$, where L is possibly MeOH or H_2O . Over a period of hours, small quantities of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ ⁷ were generated as the mixture decomposed. ^1H NMR spectrum of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ (CD_3OD): 1.37 [s, 3($\text{C}(\text{CH}_3)_3$)], 2.39 [s, 3(CH_3)], 4.56 [s, ZnH] 5.83 [s, 3($\text{C}_3\text{N}_2\text{H}$)], HB not observed. ^1H NMR spectrum of $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnF}$ (CD_3OD): 1.35 [s, 3($\text{C}(\text{CH}_3)_3$)], 2.41 [s, 3(CH_3)], 5.91 [d, $J = 0.3$, 3($\text{C}_3\text{N}_2\text{H}$)], HB not observed. ^1H NMR spectrum of $\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnL}\}^+$ (CD_3OD): 1.38 [s, 3($\text{C}(\text{CH}_3)_3$)], 2.40 [s, 3(CH_3)], 5.95 [s, 3($\text{C}_3\text{N}_2\text{H}$)], HB not observed.

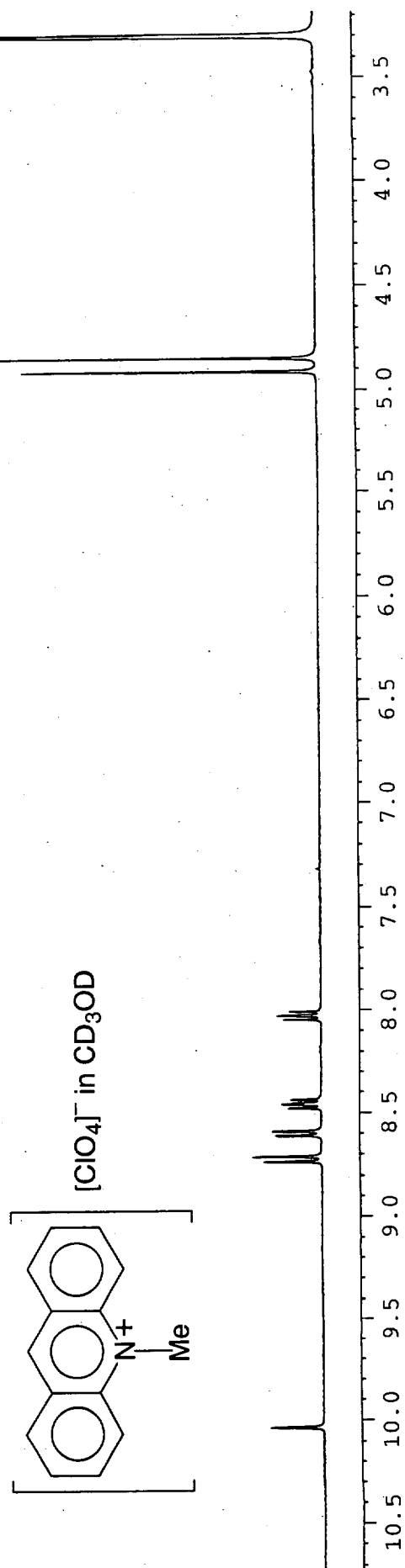
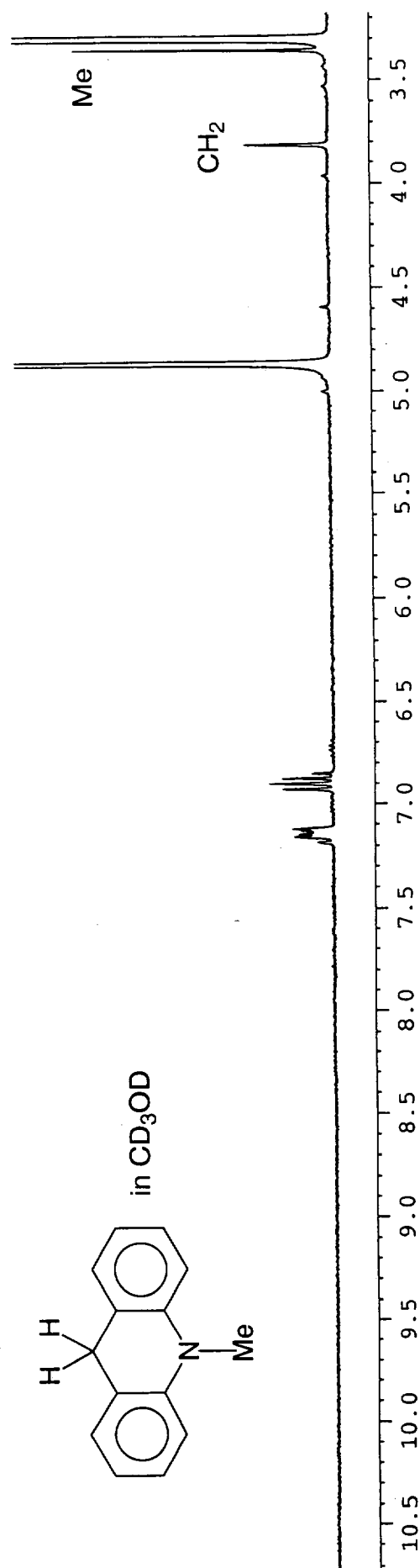
(b) A similar experiment was performed with the deuterium labeled $\{[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnOD}_2\}[\text{DOB}(\text{C}_6\text{F}_5)_3]$ in CD_3OD . Formation of the protio complex $[\text{Tp}^{\text{Bu}^t, \text{Me}}]\text{ZnH}$ was demonstrated by ^1H NMR spectroscopy.

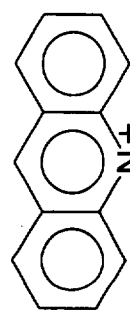
(c) An analogous experiment was performed with the deuterium labeled complex, $\{[\text{DTp}^{\text{Bu}^t, \text{Me}}]\text{ZnOH}_2\}[\text{HOB}(\text{C}_6\text{F}_5)_3]$, in CD_3OD . Formation of the deutero complex $[\text{DTp}^{\text{Bu}^t, \text{Me}}]\text{ZnD}$ was demonstrated by removing the volatile components and obtaining the ^2H NMR spectrum in C_6H_6 .

References

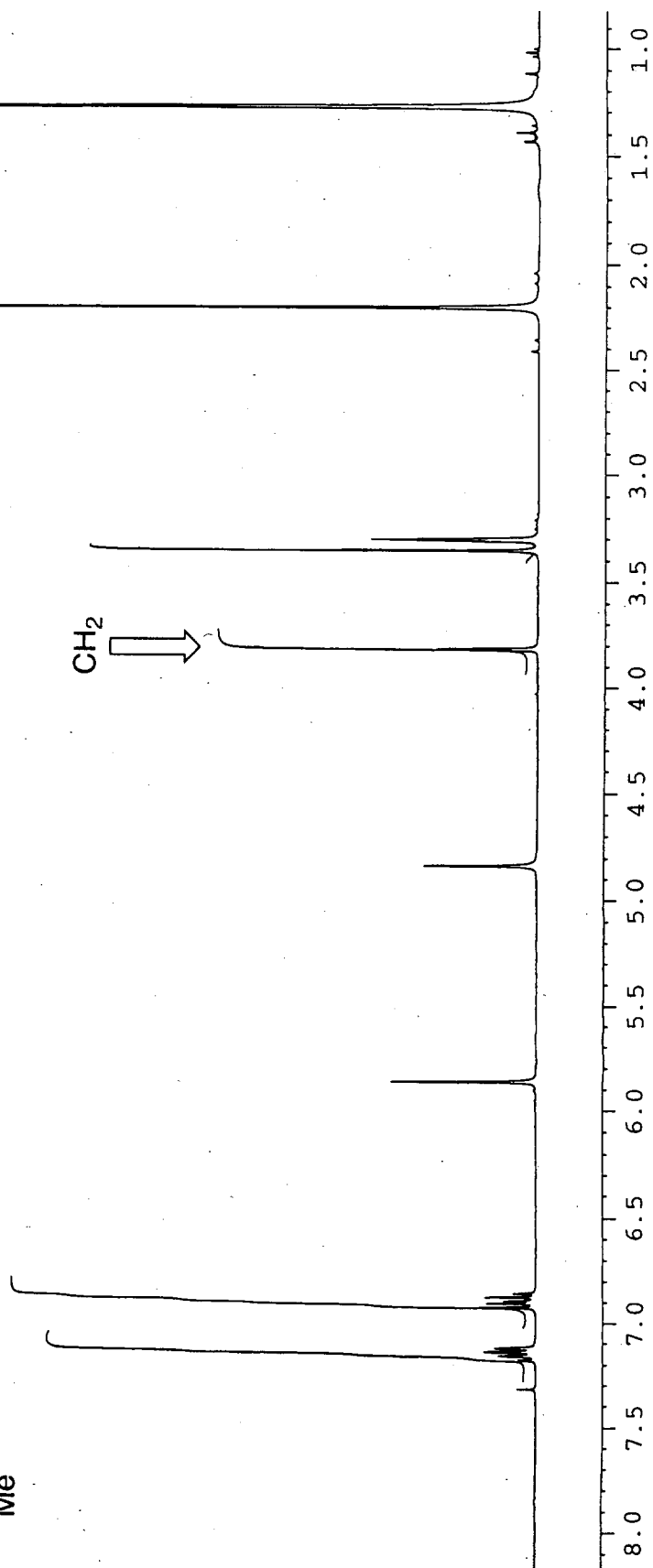
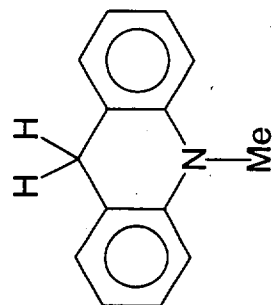
- (1) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690-4697.

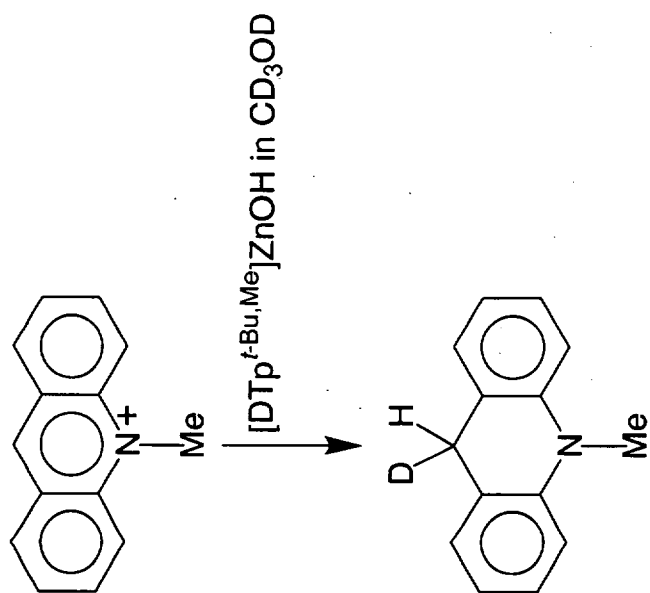
- (2) Bergquist, C.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 6322-6323.
- (3) Fukuzumi, S.; Fujita, M.; Maruta, J.; Chanon, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1597-1602.
- (4) Ostovic, D.; Lee, I. H.; Roberts, R. M. G.; Kreevoy, M. M. *J. Org. Chem.* **1985**, *50*, 4206-4211.
- (5) The initial spectrum at room temperature in CD₃OD indicated the presence of 10-methylacridan and 3-*tert*-butyl-5-methylpyrazole.
- (6) Bergquist, C.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 422-423.
- (7) (a) Kläui, W.; Schilde, U.; Schmidt, M. *Inorg. Chem.* **1997**, *36*, 1598-1601.
(b) The ¹H NMR data that was reported in the literature is incorrect due to an error in the solvent referencing (Kläui, W., personal communication).



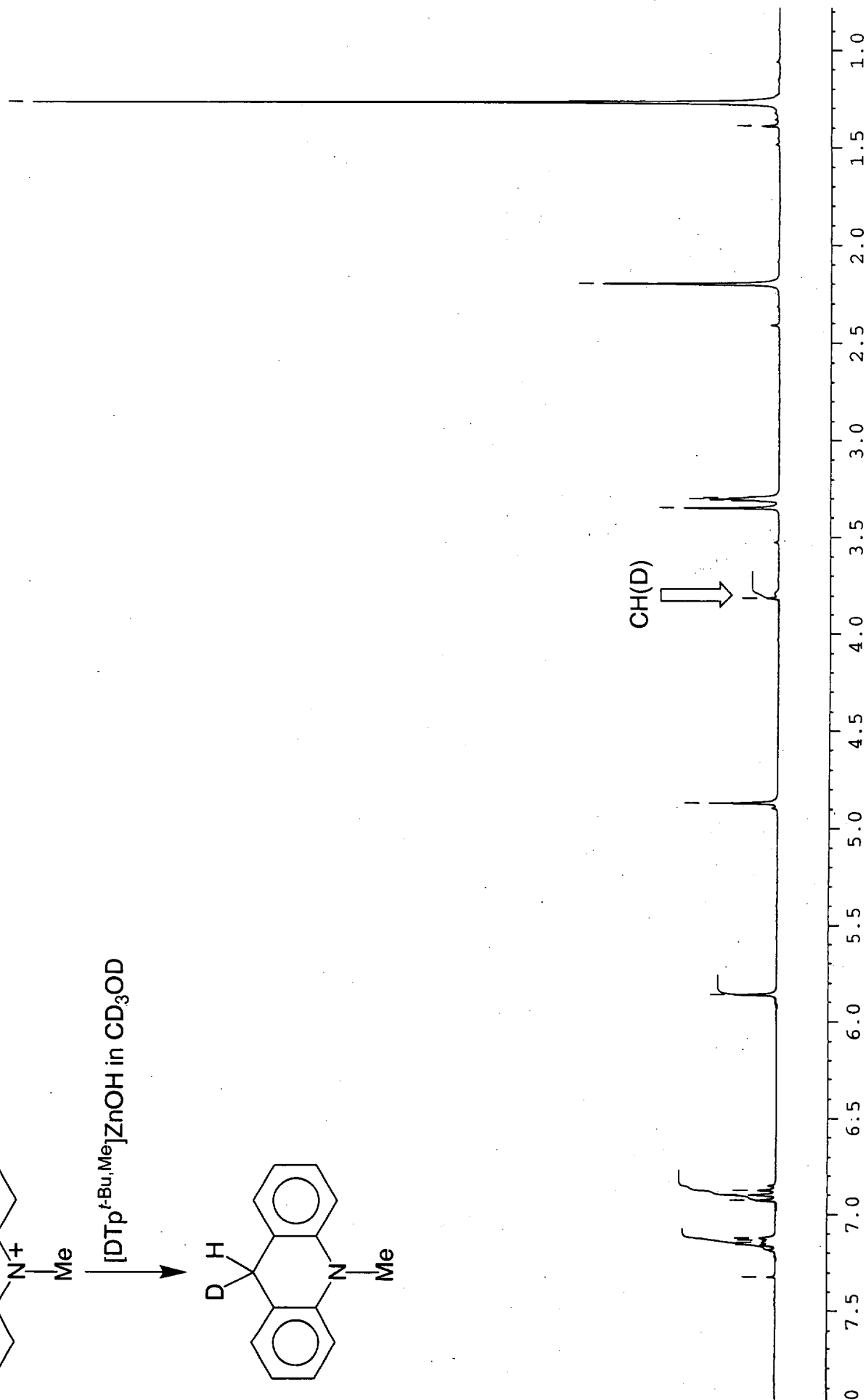
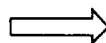


$[\text{Tp}^t\text{Bu,Me}] \text{ZnOH}$ in CD_3OD

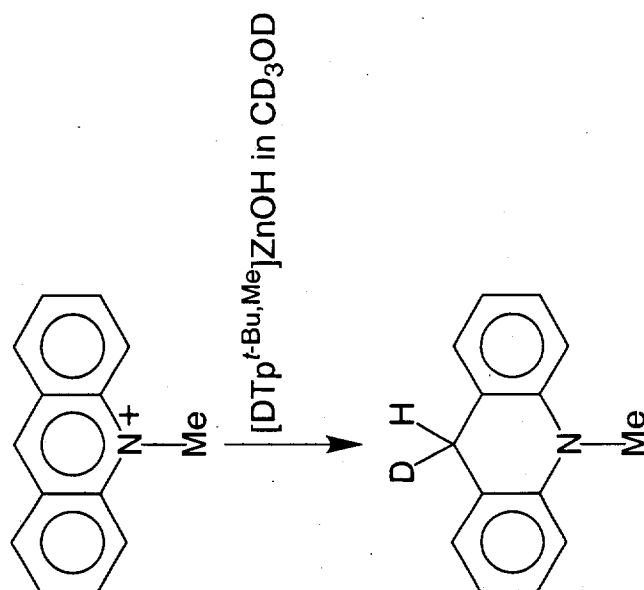
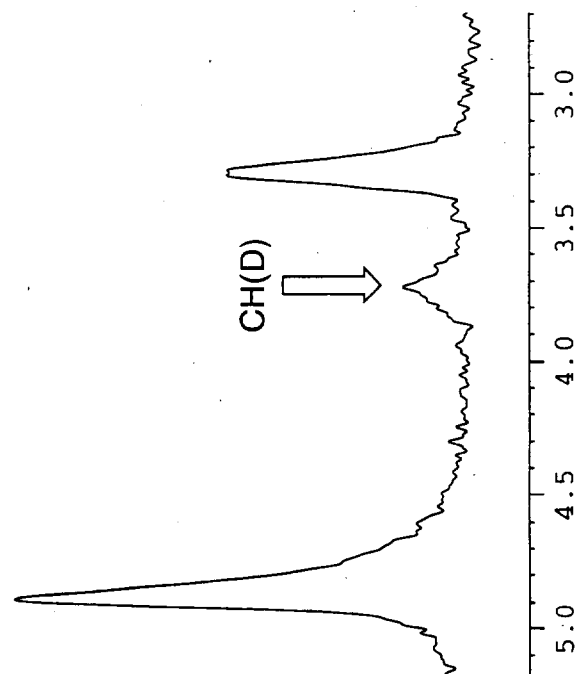




CH(D)



²H NMR Spectrum

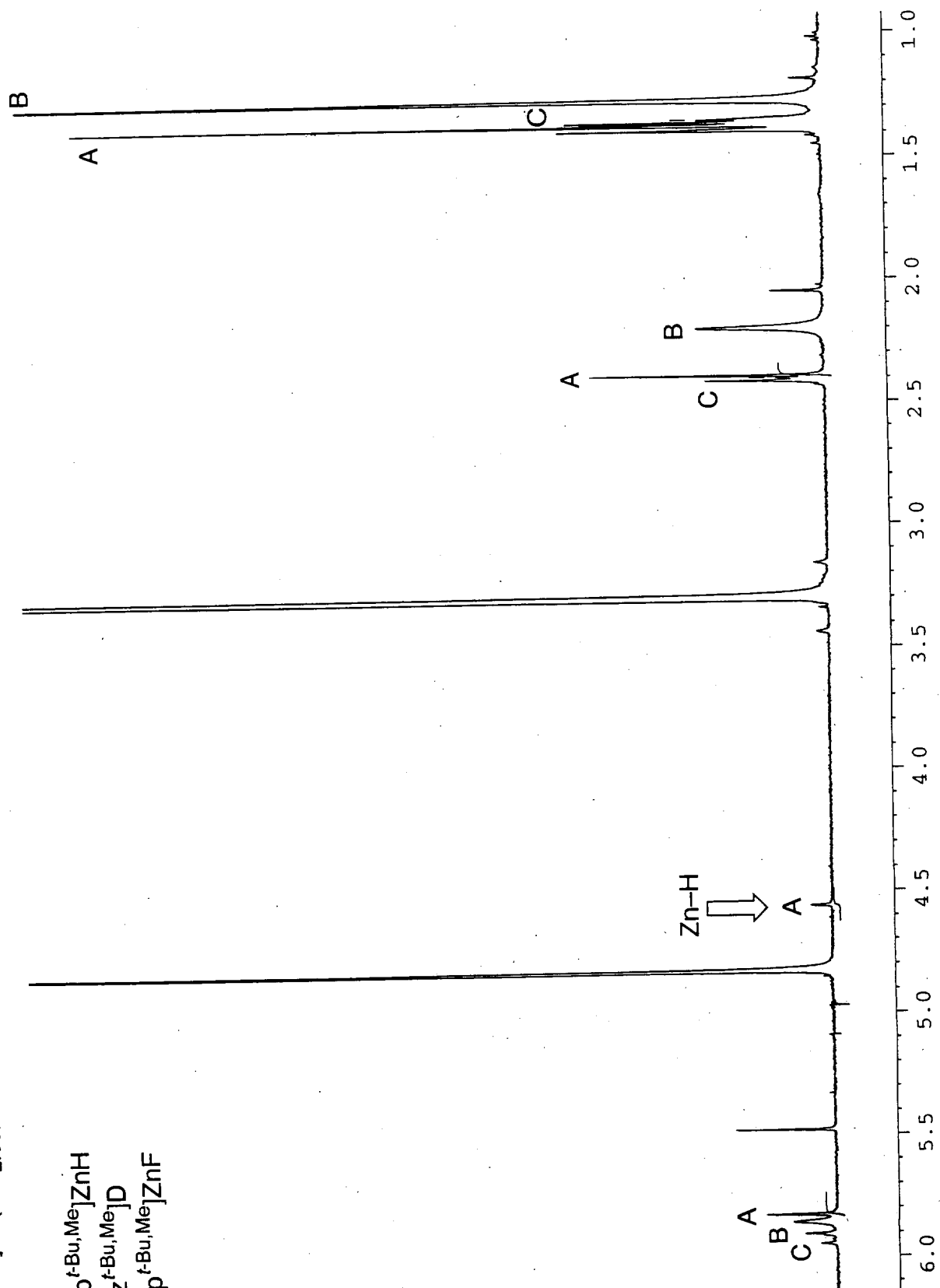




A = $[\text{Tp}^t\text{-Bu,Me}]_2\text{ZnH}$

B = $[\text{pz}^t\text{-Bu,Me}]_2\text{D}$

C = $[\text{Tp}^t\text{-Bu,Me}]_2\text{ZnF}$





2H NMR Spectrum

