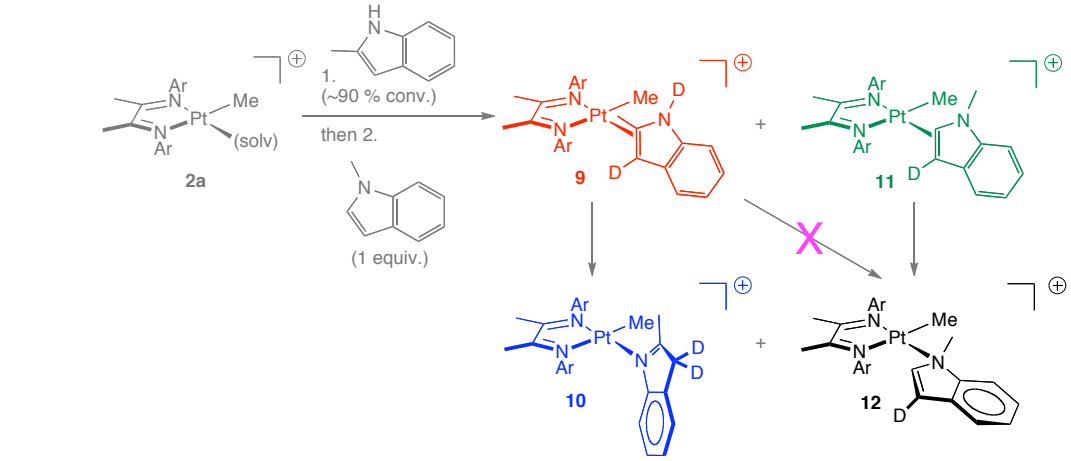
Reactions of Indene and Indoles with Platinum Methyl Cations: Indene C-H Activation, Indole π *vs.* Nitrogen Lone-Pair Coordination

Travis J. Williams, Jay A. Labinger,* and John E. Bercaw*

I. Crossover Experiment between **9** and 1-methylindole.
II. Conversion of **6a** to **8a** at high [H^+].
III. About H/D Exchange and Methane Isotopologs Formed in the Conversion of **3** to **4**.
IV. Selected ^{1}H NMR spectra for new compounds.

I. Crossover Experiment between **9** and 1-methylindole.

A detailed procedure for this experiment is presented in the main text; figure S1 shows kinetic data collected as described.



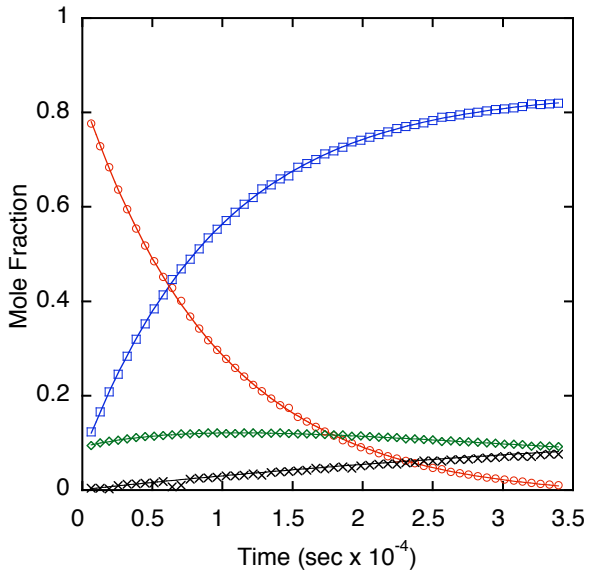


Figure S1. Conversion of **9** to **10** in the presence of 1-methylindole.

II. Conversion of **6a** to **8a** at high [H^+].

A detailed procedure for this experiment is presented in the main text; figure S2 illustrates a sample ^{1}H spectrum (Pt-CH_3 region, 1_10^4 sec after mixing) containing **2a**, **6a**, **8a**, and the intermediate structure postulated to be **7a**.

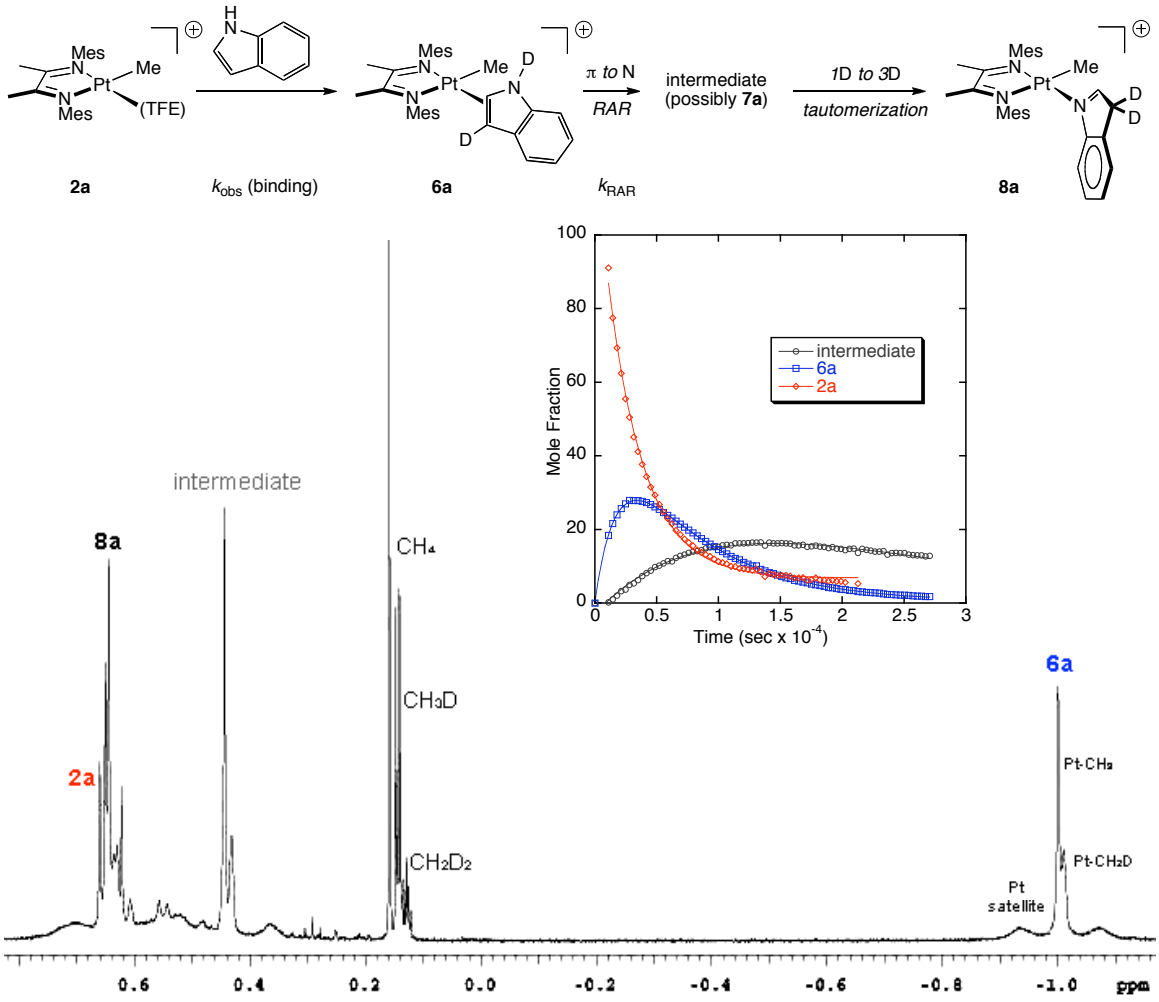
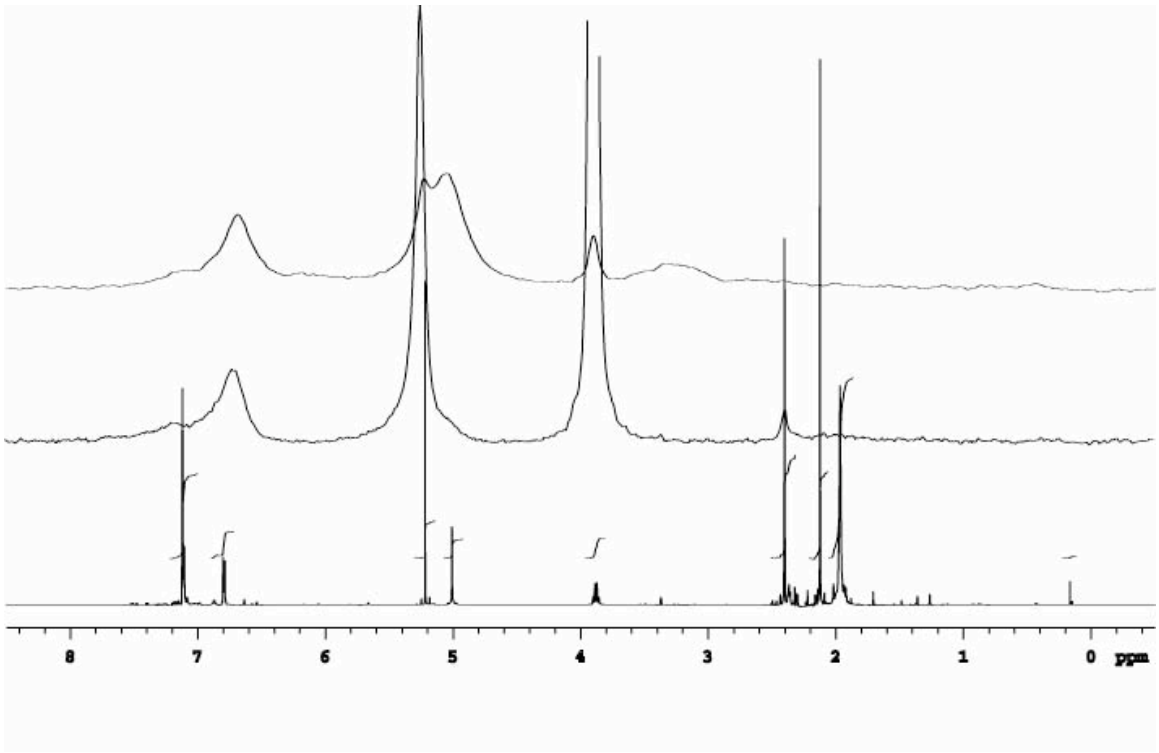


Figure S2. Conversion of **2a** in the presence of 5 equiv. each of BF_3 and indole. Bottom: ^{1}H NMR spectrum (500 MHz, TFE-d_3) for Pt-CH_3 region at t = 1_10^4 sec. Inset: kinetic data for this reaction.

III. About H/D Exchange and Methane Isotopologs Formed in the Conversion of **3** to **4**.

^{2}H NMR spectra of **4a** and **4a**-d_2 were recorded to track ^{2}H incorporation in these compounds as described in the main text. Data are shown in figure S3.

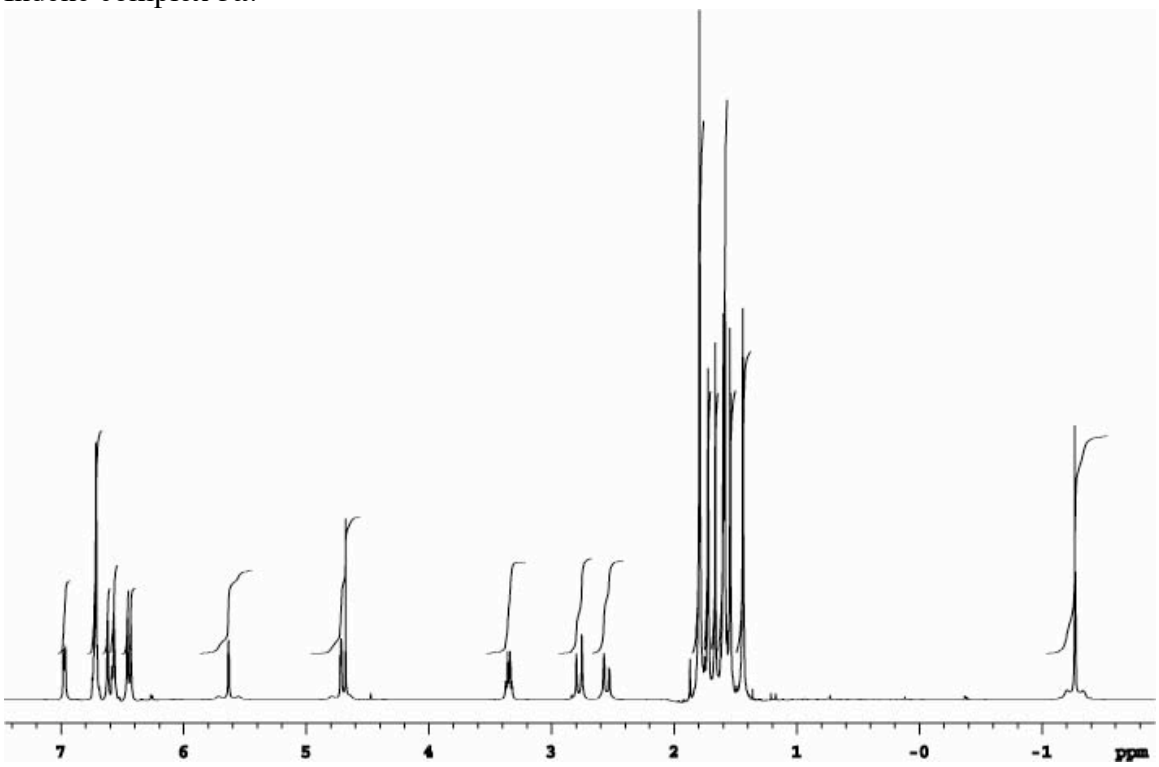
Figure S3. ^{2}H incorporation in the conversion of **3a** to **4a**



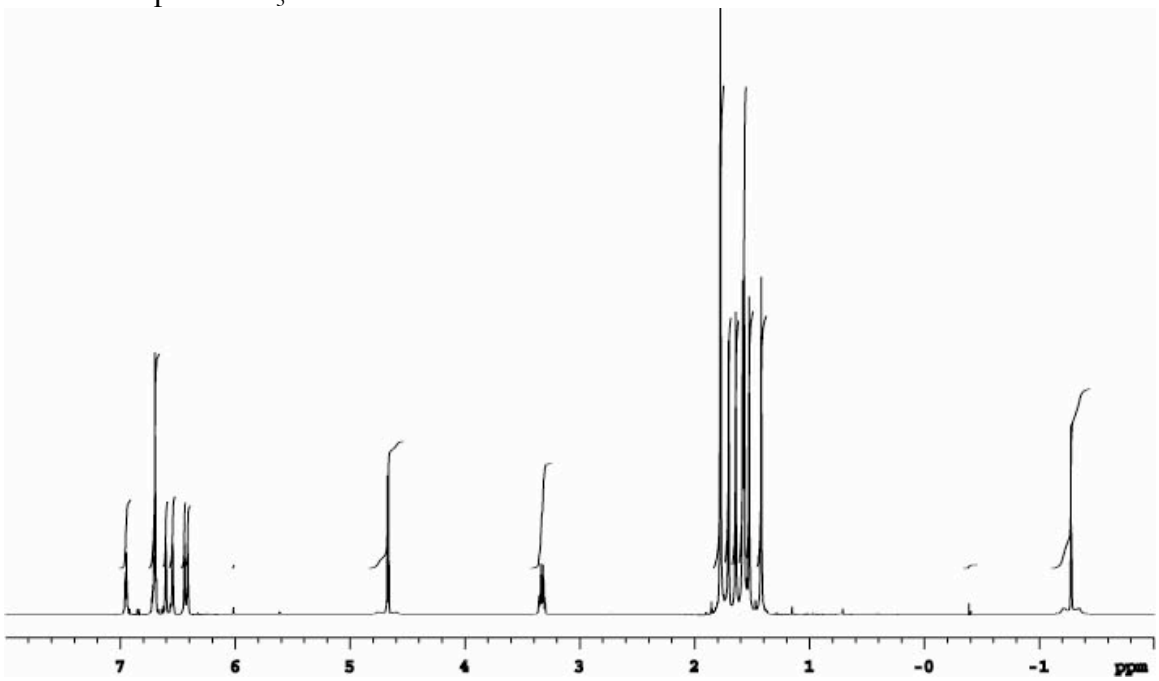
Bottom: ^{1}H spectrum of **4a** (600 MHz). Middle: ^{2}H spectrum of **4a** (76.7 MHz). Solvent has been removed *en vacuo* and replaced with THF-h_3. Top: ^{2}H spectrum of **4a**–d_2 (76.7 MHz). Solvent has been removed *en vacuo* and replaced with THF-h_3 twice. (The broad signal at ~3.3 is a decomposition product that appeared after the second cycle of solvent replacement.)

IV. Selected ^{1}H NMR spectra for new compounds

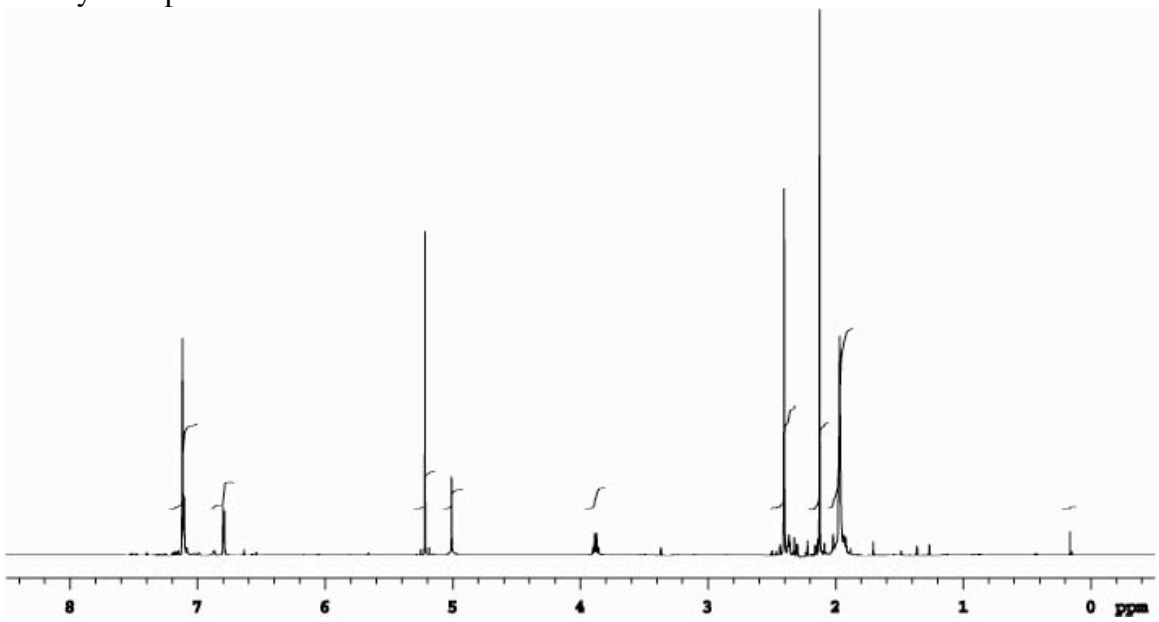
Indene complex **3a**:



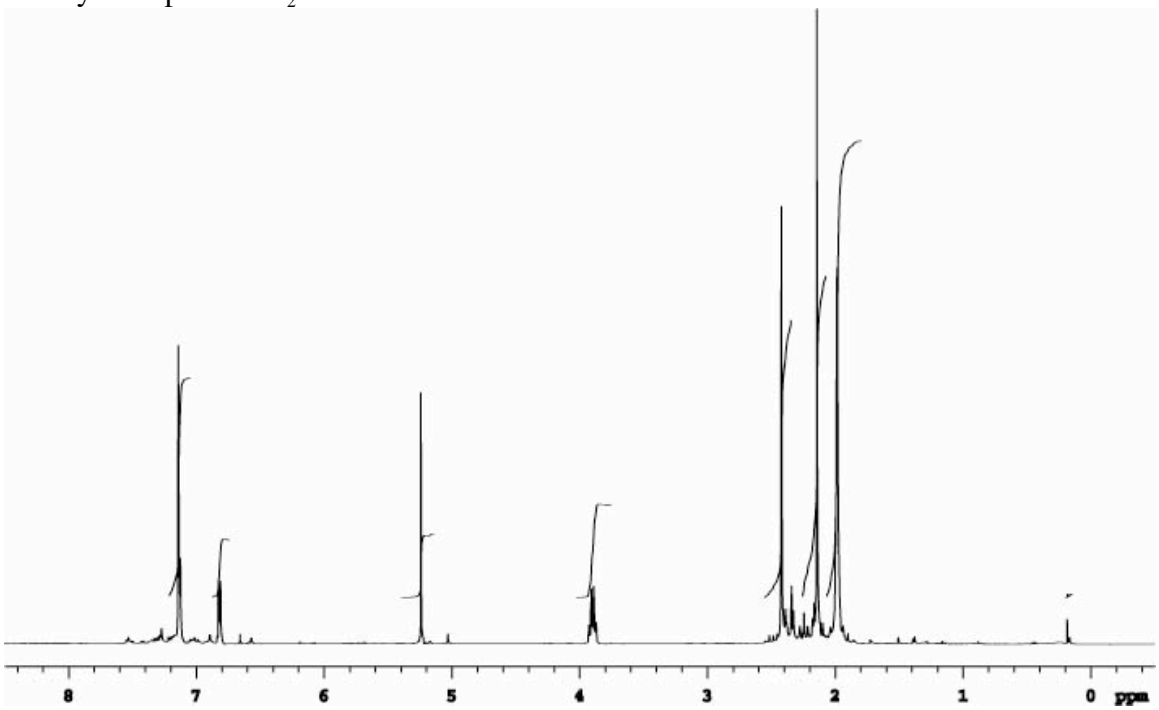
Indene complex **3a**-d_3



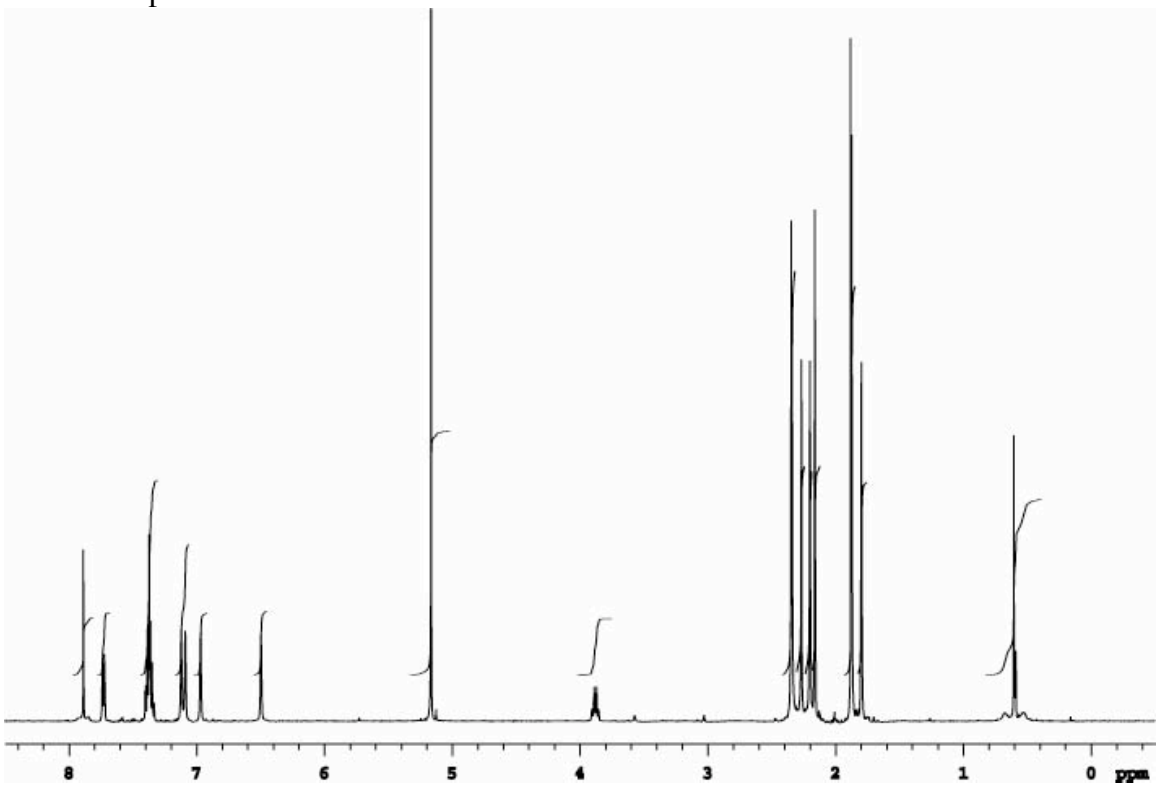
Indenyl complex **4a**:



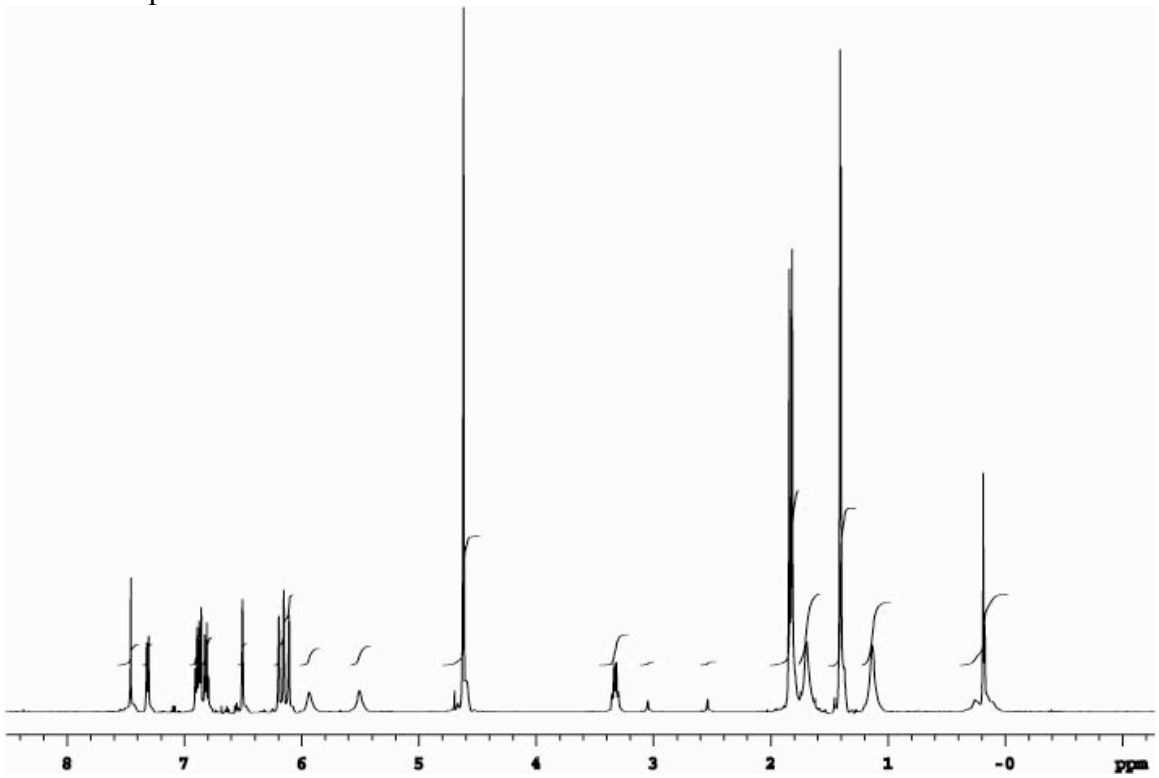
Indenyl complex **4a**-d_2



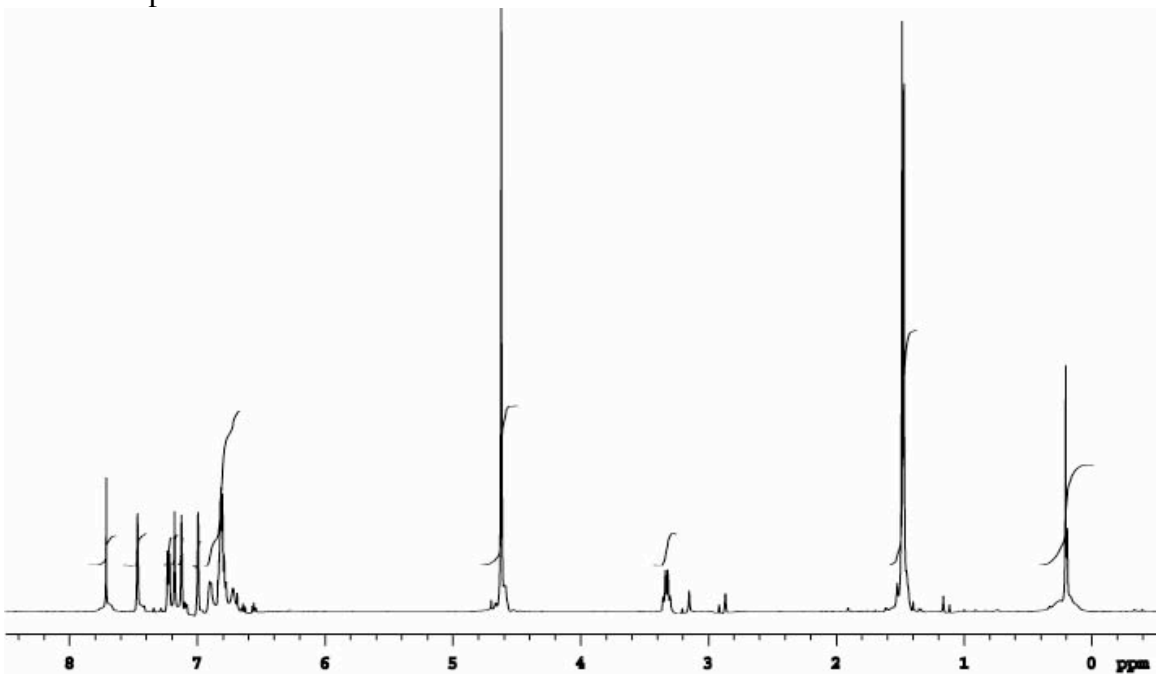
Indole complex **8a**:



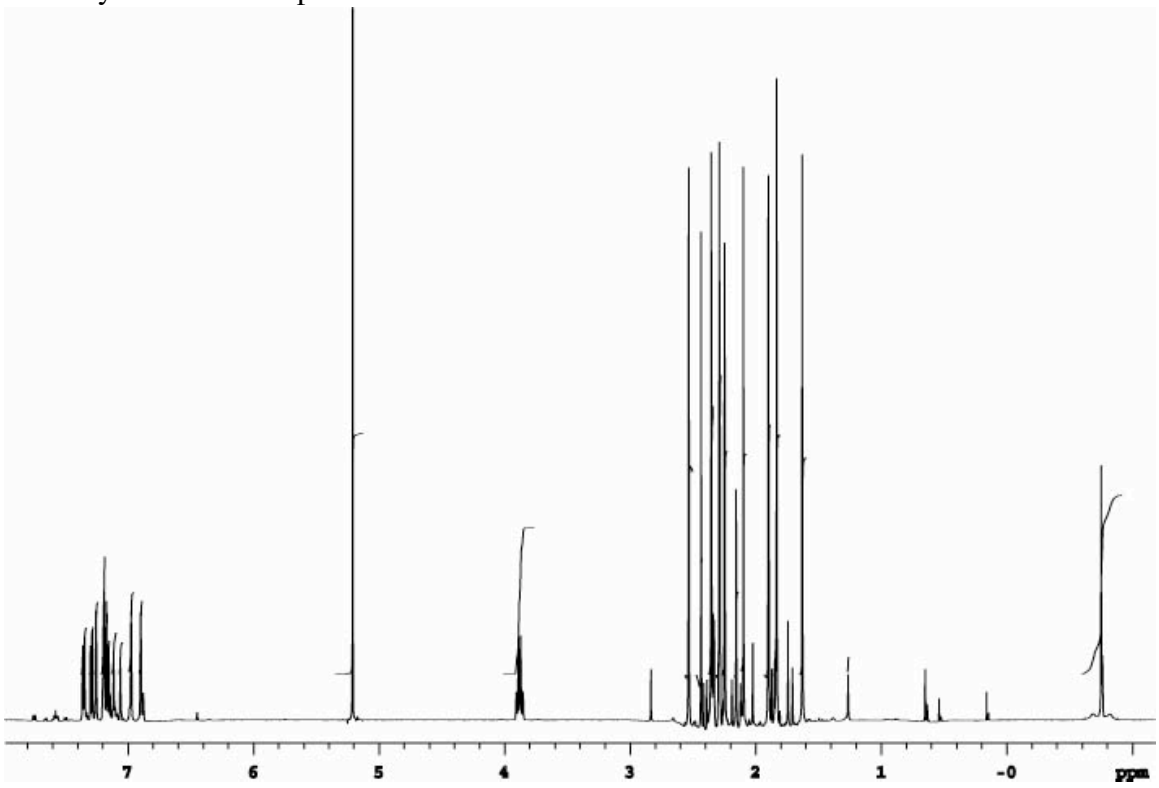
Indole complex **8b**:



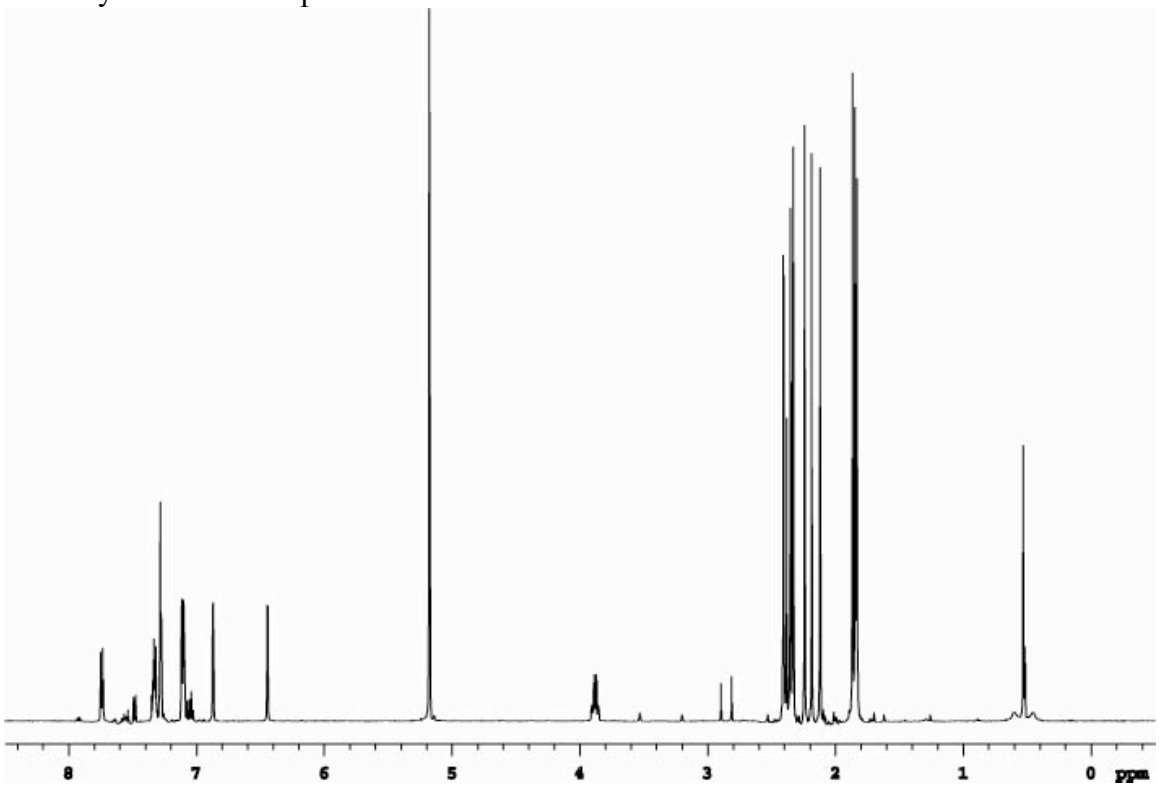
Indole complex **8c**:



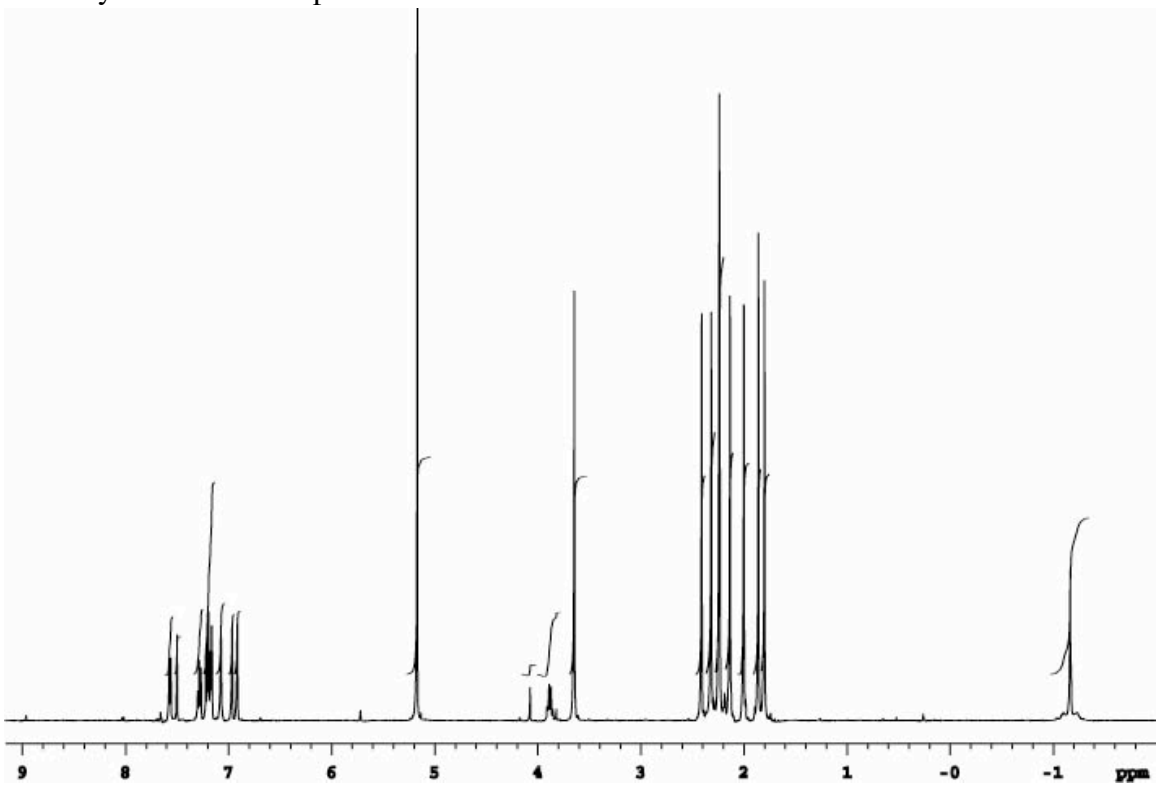
2-Methylindole-π-complex **9**:



2-Methylindole-*N*-complex **10**:



1-Methylindole- π -complex **11**:



1-Methylindole-*N*-complex **12**: