

Supporting information for

Amine-Functionalized Siloxane Oligomer Facilitated Synthesis of Subnanometer Colloidal Au Particles.

Zhen Wang, Evgeny V. Beletskiy, Sungsik Lee, Yuyang Wu, Tiehu Li, Mayfair C. Kung, and Harold H. Kung.

Contents

Fig. S-1. NMR of N-PMHS **IV**

Fig. S-2. NMR of N-SiH-PMHS **V**

Fig. S-3. NMR of Me-SiH-PMHS **VI**

Fig. S-4. NMR of Compound **VIII**

Fig. S-5. NMR of Au(THT)Cl and N-PMHS and N-SiH-PMHS.

Fig. S-6 ^1H NMR of Et₂NH interaction with Au(THT)Cl

Fig. S-7. ^{13}C NMR of $-\text{CH}_2$ and $-\text{CH}_3$ attached to nitrogen of amine.

Fig. S-8 HSQC of Au(THT)Cl and NMR of N-PMHS **IV** with Amine/Au=10

Fig. S-9 HSQC of Au(THT)Cl and NMR of N-PMHS **IV** with Amine/Au=2.5

Fig. S-10 ^1H NMR of Au(THT)Cl and NMR of N-PMHS **IV** with Amine/Au=2.5 with and without addition of triethyl silane.

Fig. S-11 STEM images of Au-Me-SiH-PMHS

Fig. S-12 DLS of samples **a-d**

Fig. S-13 SAXS of sample **a**

Fig. S-14 XANES spectrum of samples **a** and **e** and gold foil.

Fig. S-15 NMR spectrum of the products of catalytic conversion of p-nitrobenzaldehyde catalyzed by sample **a**.

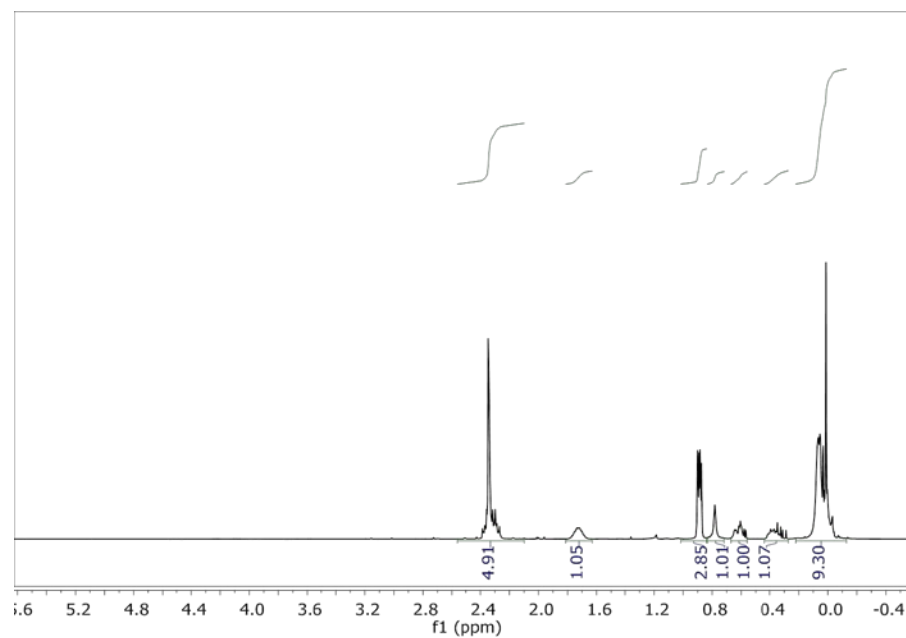


Figure S-1a. ¹H NMR of N-PMHS IV.

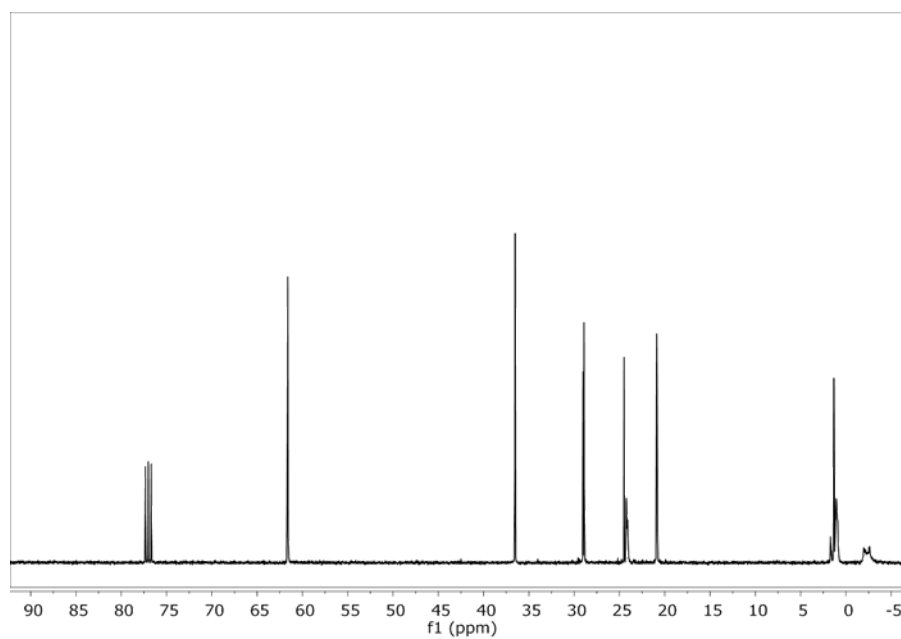


Figure S-1b. ¹³C NMR of N-PMHS IV.

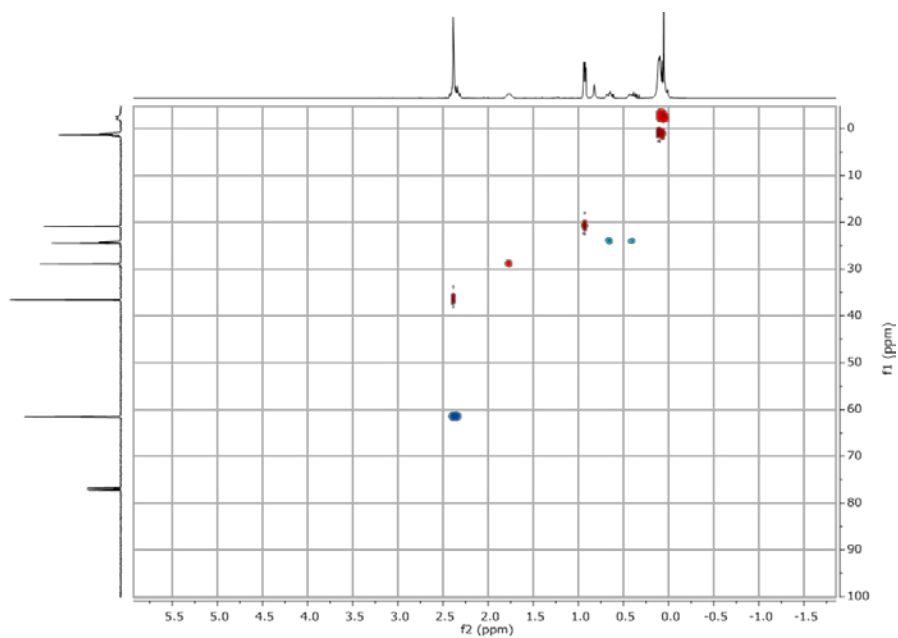


Figure S-1c. HSQCAD of N-PMHS IV.

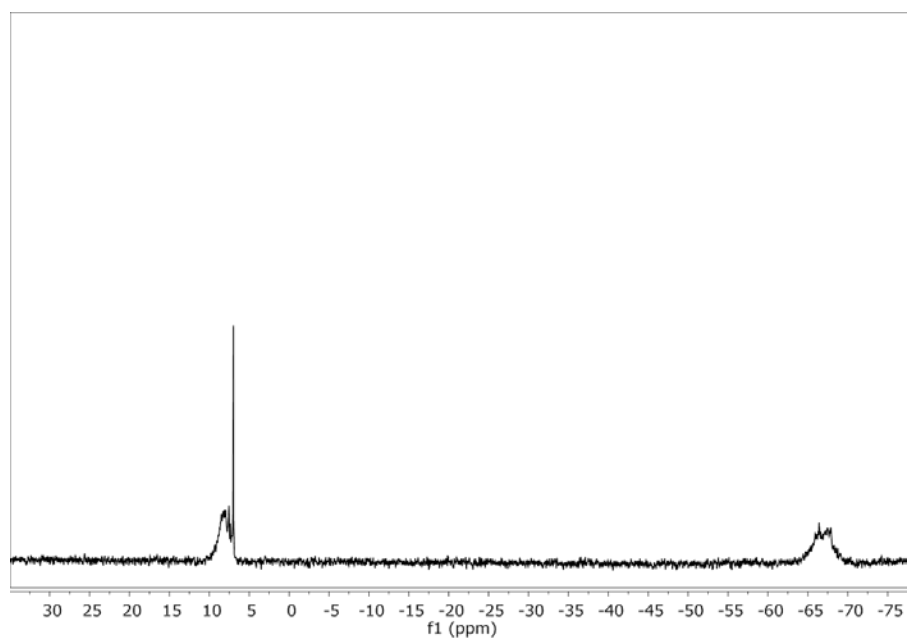


Figure S-1d. ^{29}Si NMR of -PMHS V.

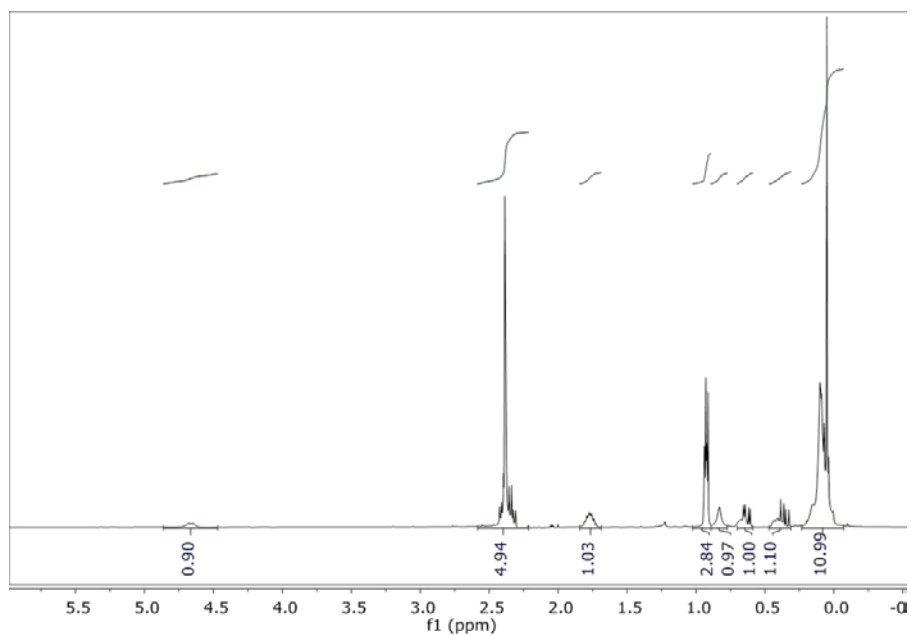


Figure S-2a. ¹H NMR of N-SiH-PMHS V.

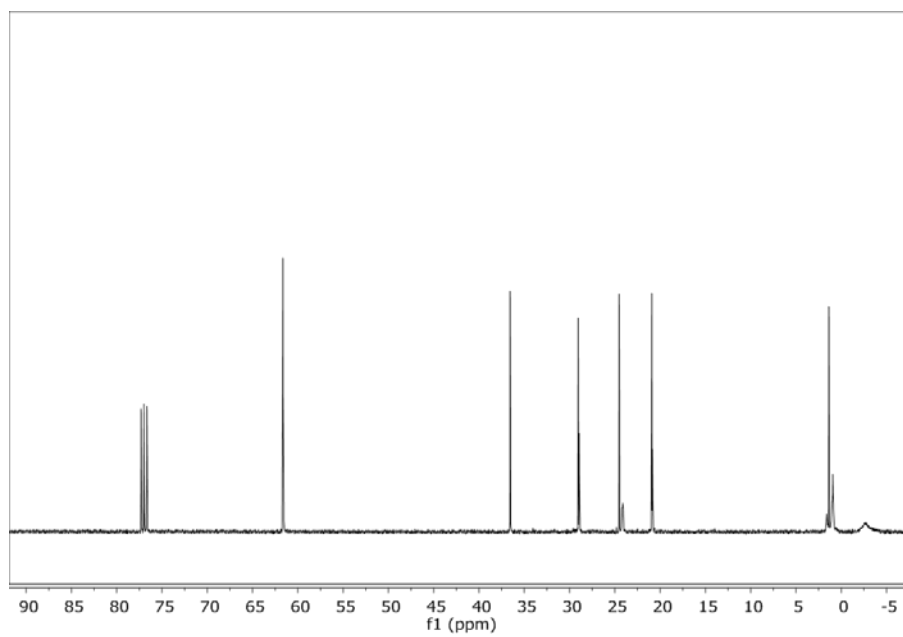


Figure S-2b. ¹³C NMR of N-SiH-PMHS V.

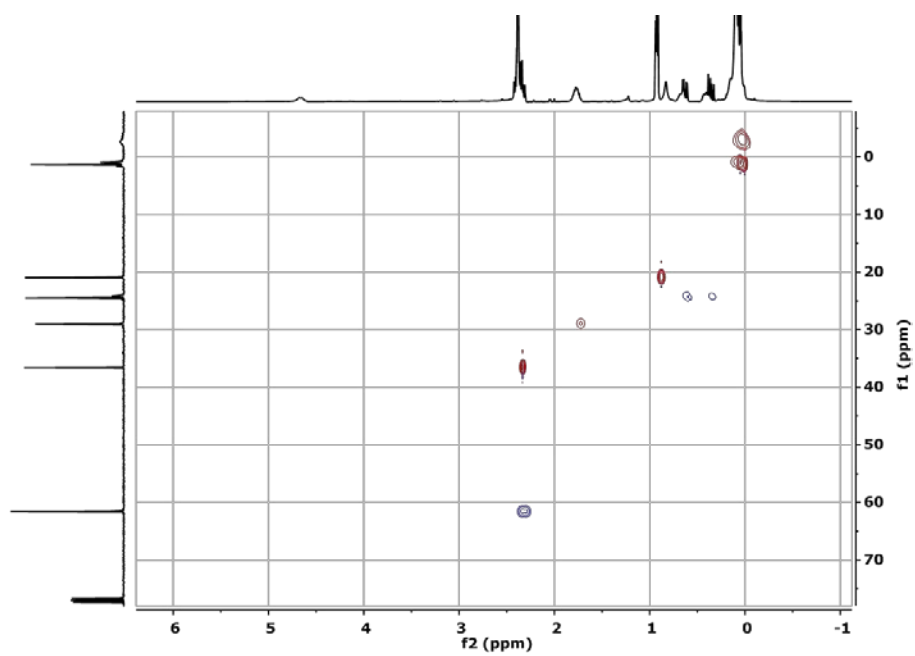


Figure S-2c. HSQCAD of N-SiH-PMHS V.

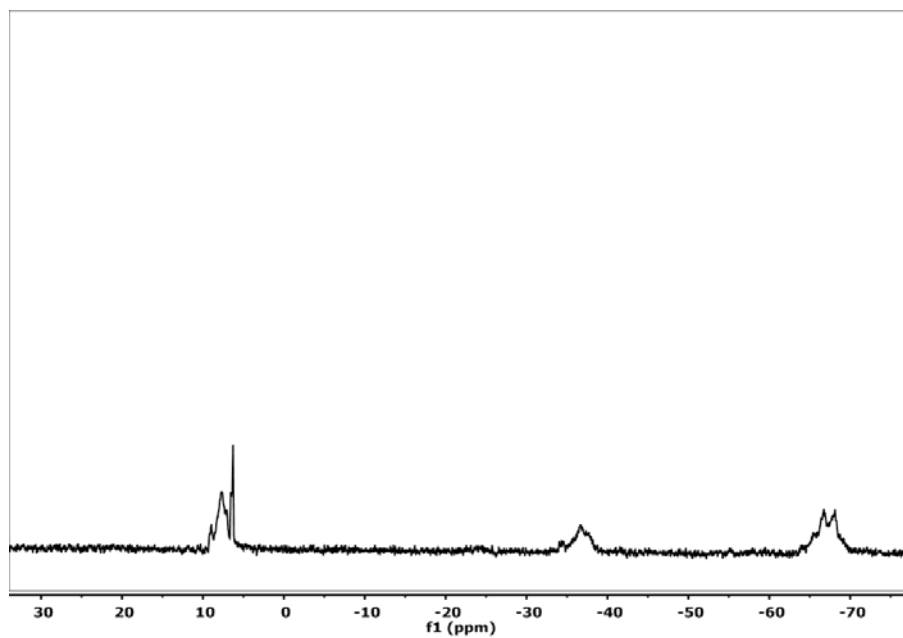


Figure S-2d. ^{29}Si NMR of N-SiH-PMHS V.

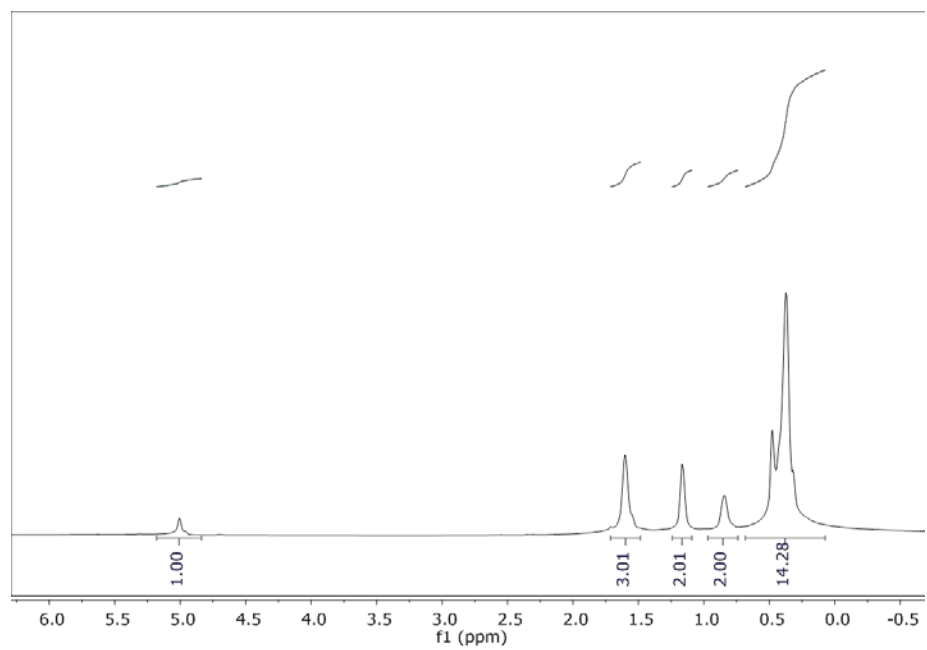


Figure S-3a. ¹H NMR of Me-SiH-PMHS **VI**.

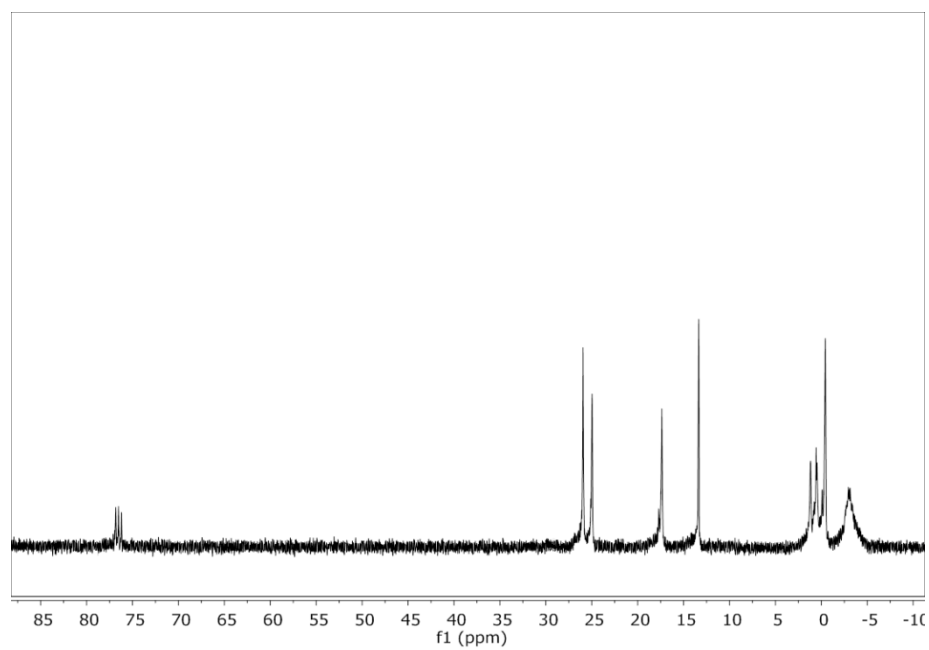


Figure S-3b. ¹³C NMR of Me-SiH-PMHS **VI**.

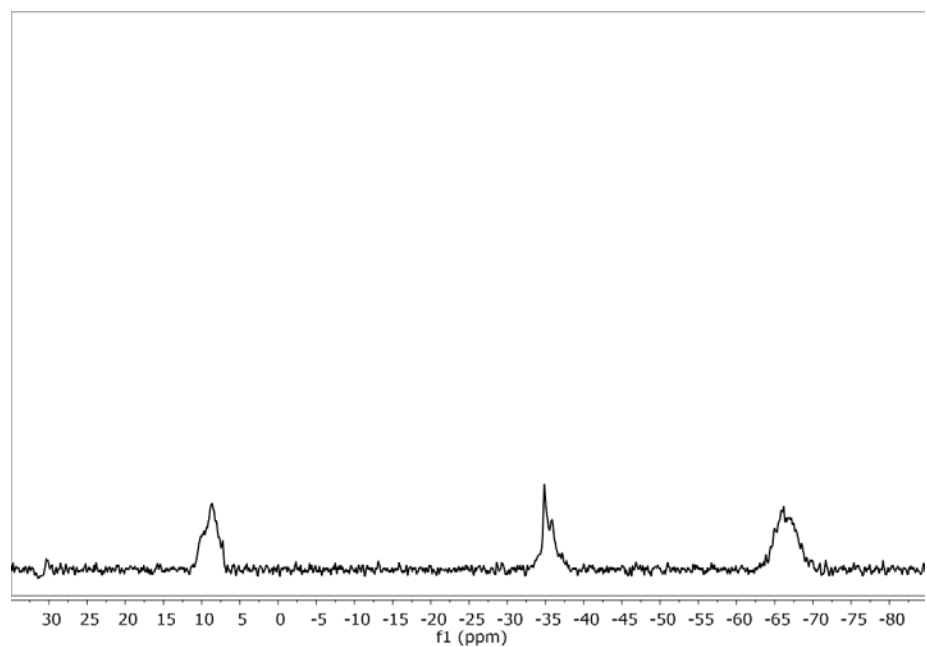


Figure S-3c. ^{29}Si NMR of Me-SiH-PMHS **VI**.

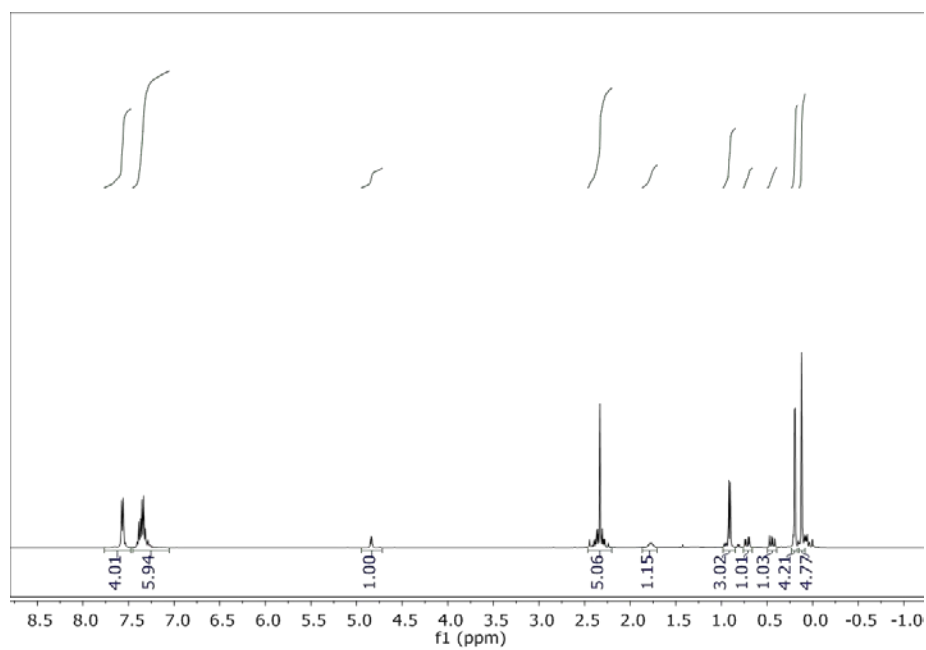


Figure S-4a. ^1H NMR of Compound **VIII**.

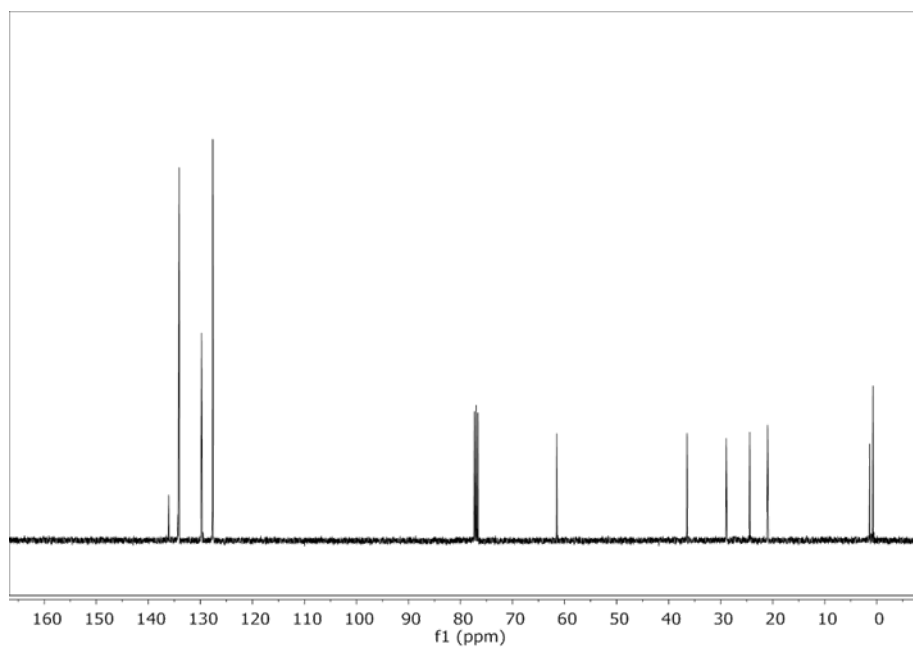


Figure S-4b. ^{13}C NMR of Compound **VIII**.

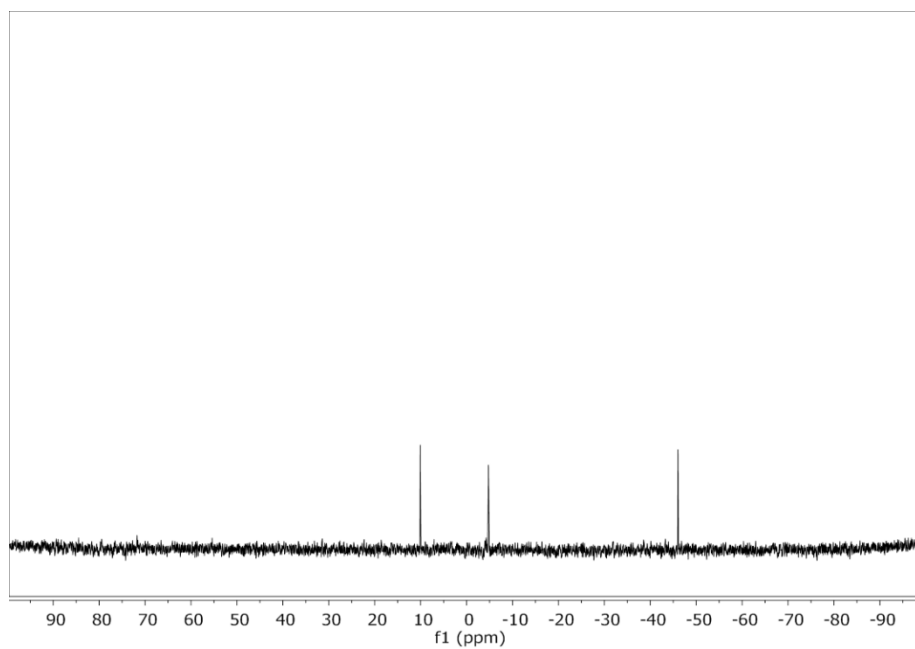


Figure S-4c. ^{29}Si NMR of Compound **VIII**.

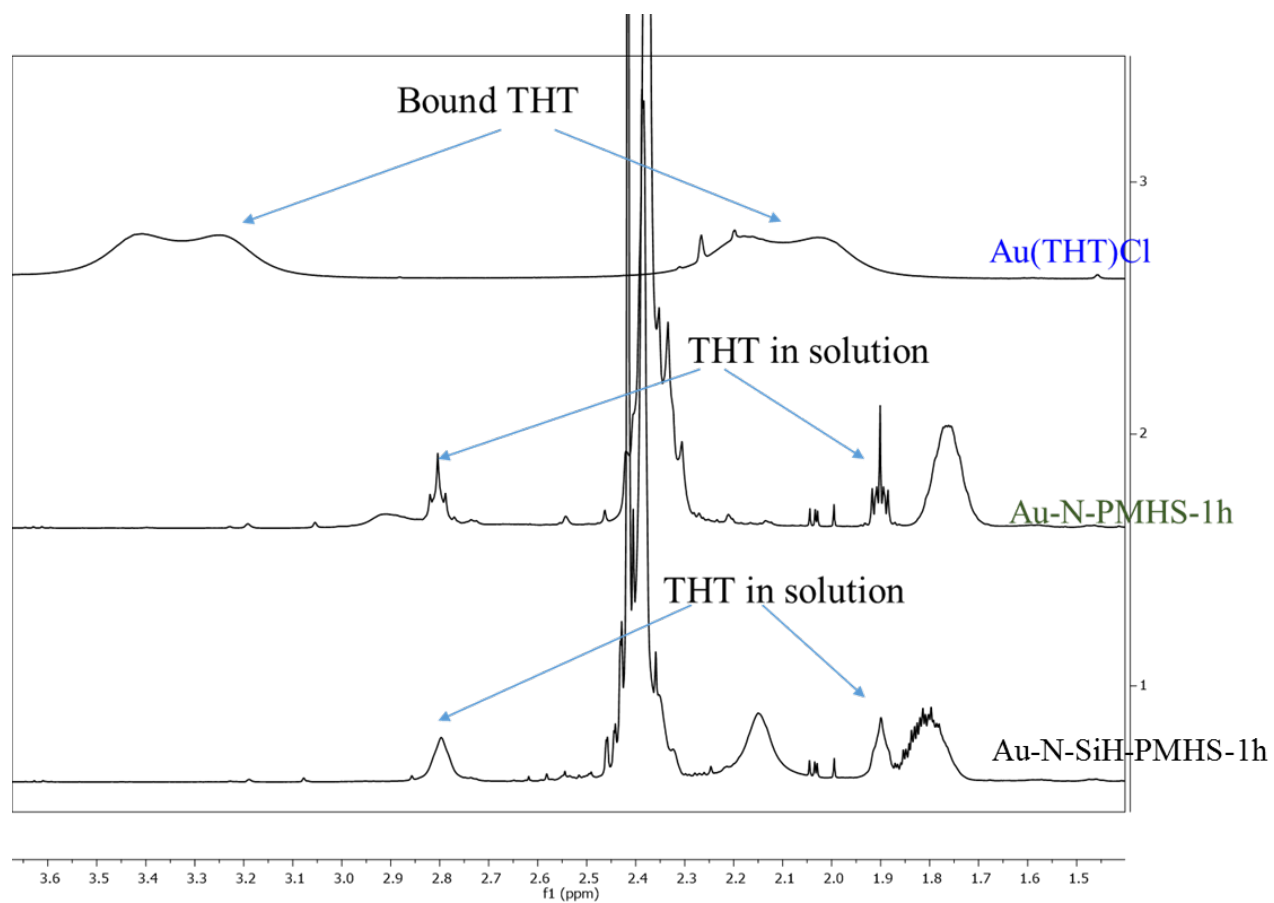


Figure S-5. ^1H NMR showing bound THT in $\text{Au}(\text{THT})\text{Cl}$ and unbound THT 1 h after addition of N-PMHS or N-SiH-PMHS.

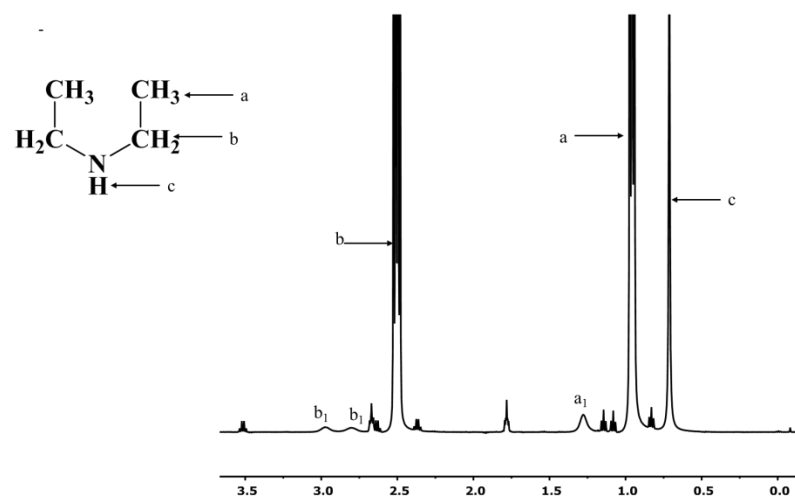


Fig. S-6. ^1H NMR of mixture containing diethylamine and $\text{Au}(\text{THT})\text{Cl}$ at a ratio of diethylamine to $\text{Au}(\text{THT})\text{Cl}$ of 10. Peaks a,b, and c denote resonances of different protons associated with diethylamine in solution. Peaks a1 and b1 are the corresponding protons of diethylamine coordinated to Au. Peak c1 at δ 6.85 ppm is not shown.

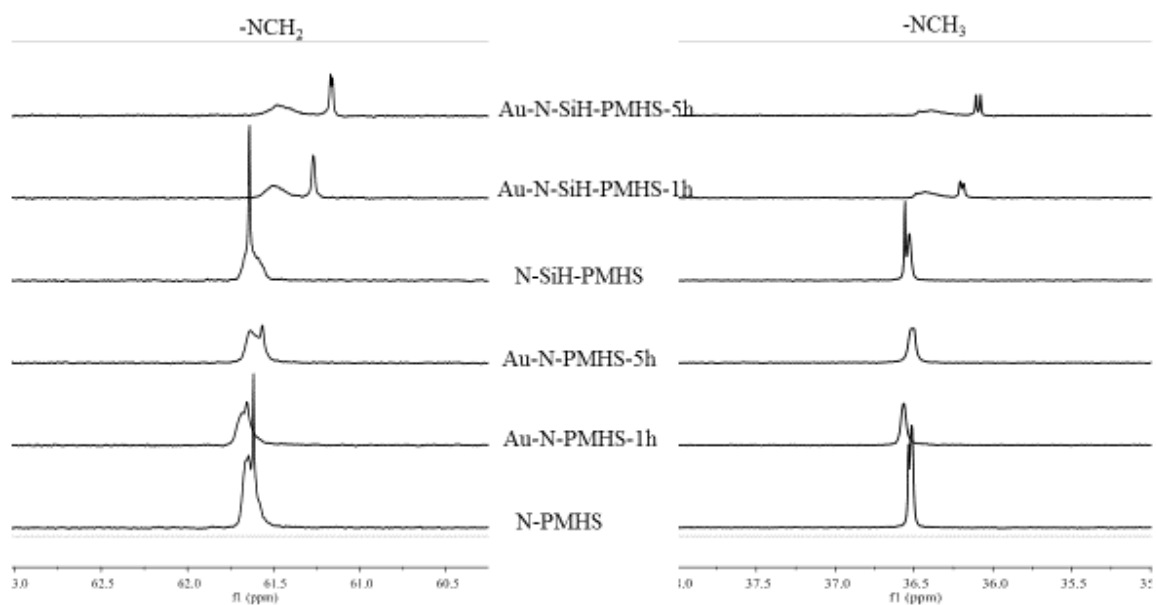


Figure S-7 ^{13}C NMR of CH_3 and CH_2 attached to the nitrogen of amine in various mixtures.

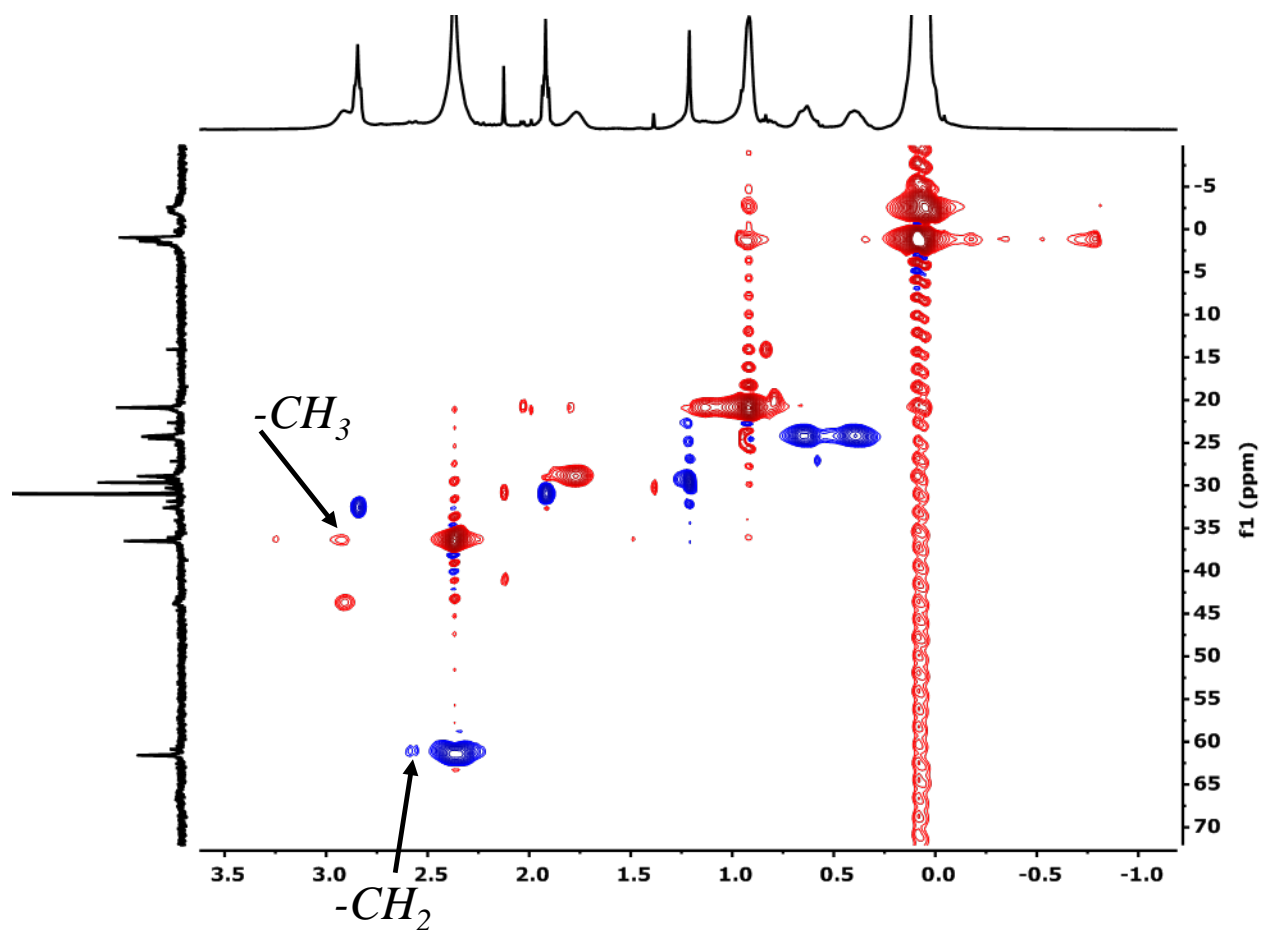


Figure S-8. HSQC of Au-N-PMHS-1h at amine to Au ratio of 10. The broad shoulder at δ 2.9 ppm is assigned to $-CH_3$ attached to N atom of amine coordinated to Au.

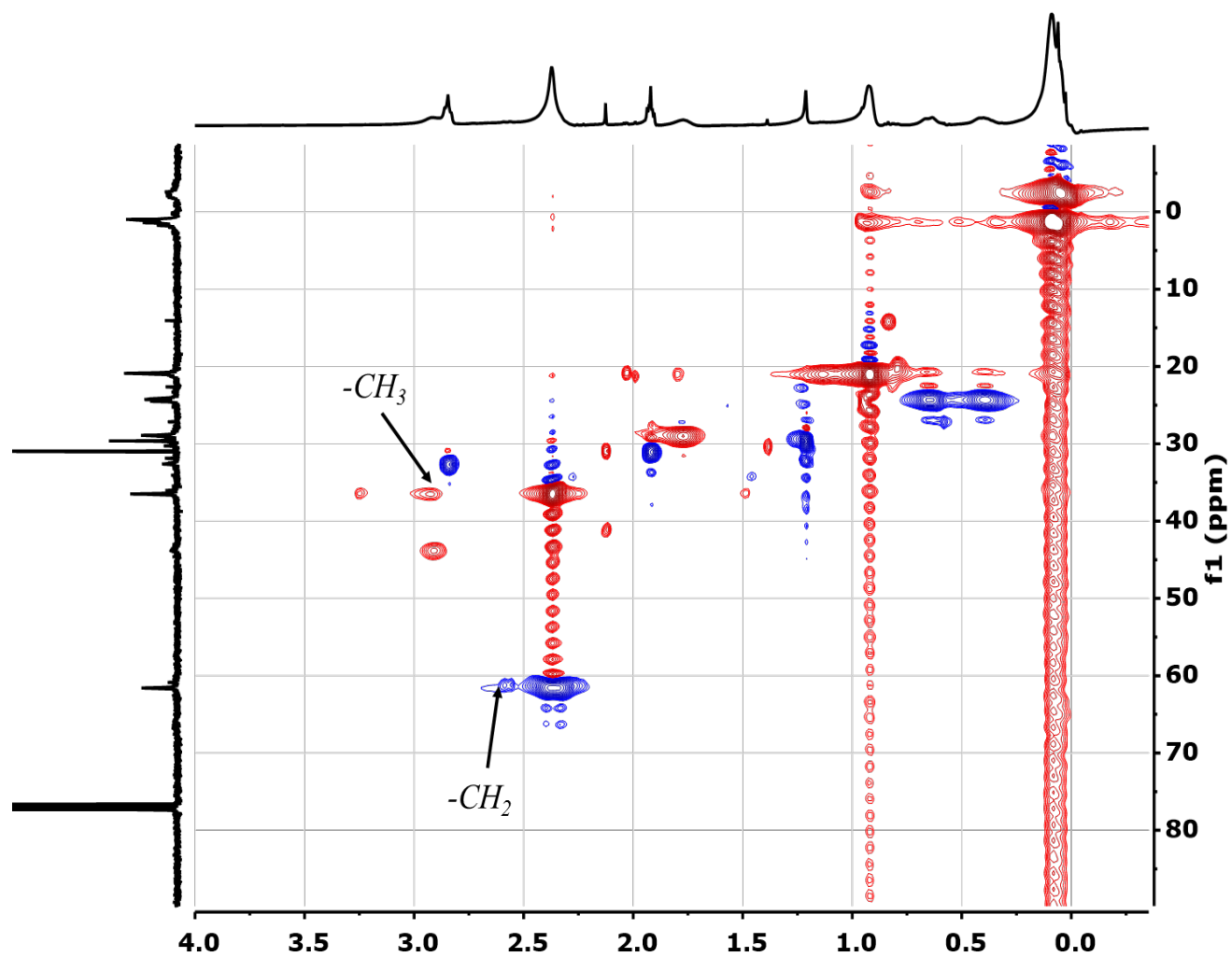


Figure S-9. HSQC of Au-N-PMHS-1h at amine to Au ratio of 2.5

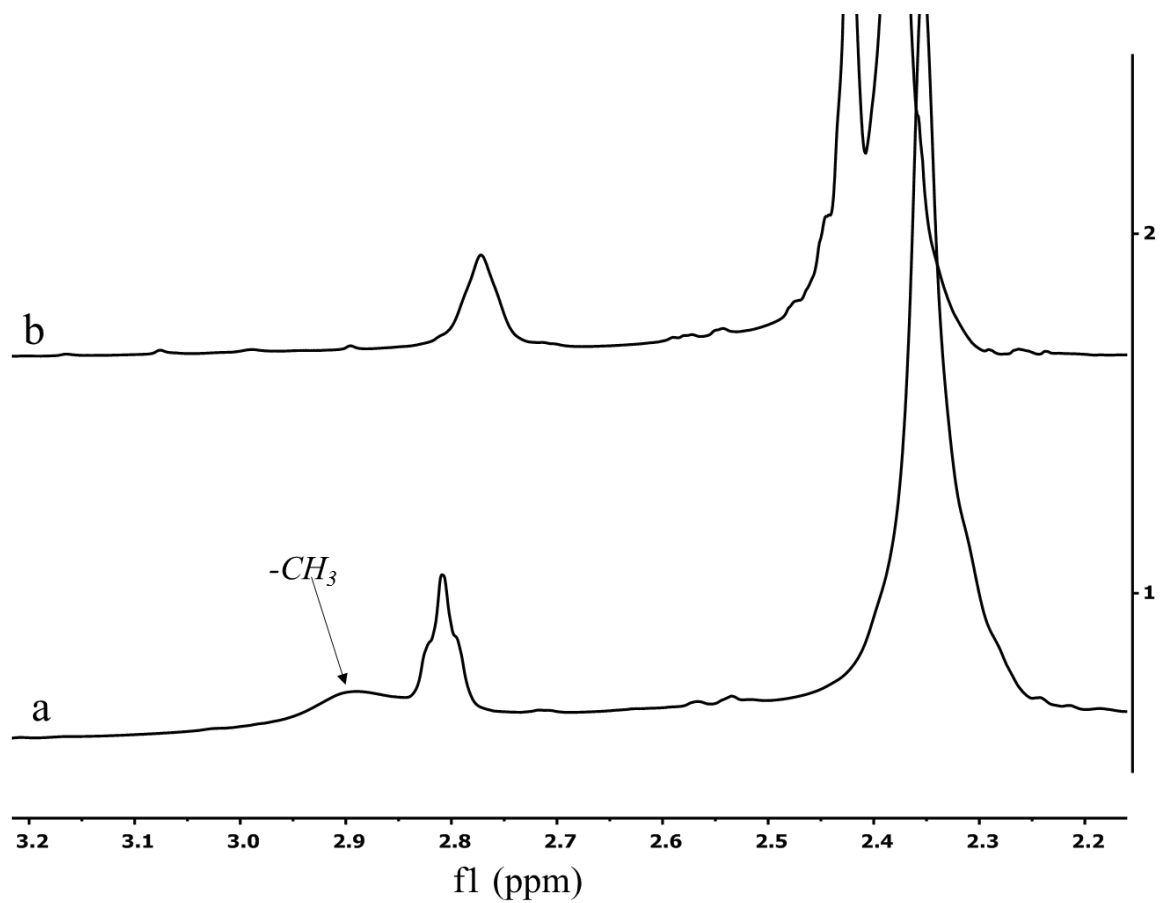


Figure S-10. ^1H spectrum (a) N-PMHS **IV** and $\text{Au}(\text{THT})\text{Cl}$ solution. Amine/Au=2.5 and (b) 10 minutes after addition of Et_3SiH to solution shown in curve a, $\text{Et}_3\text{SiH}/\text{Au}=3$. Spectrum showed that the peaks associated with $-\text{CH}_3$ attached to N atom of amine bound to Au(I) was no longer detectable.

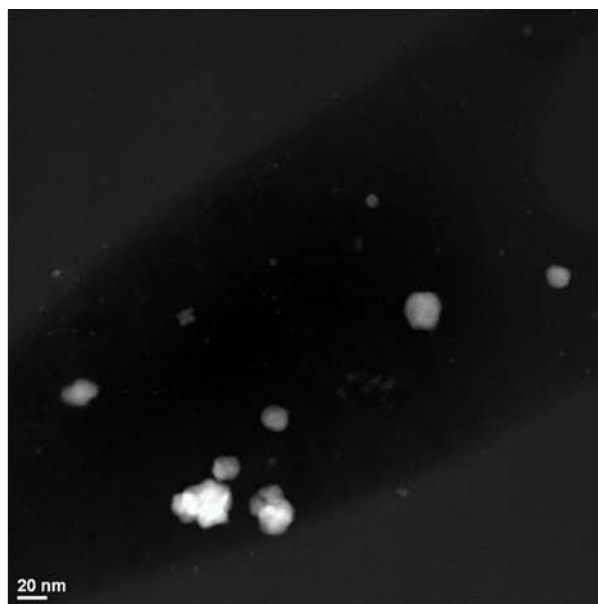
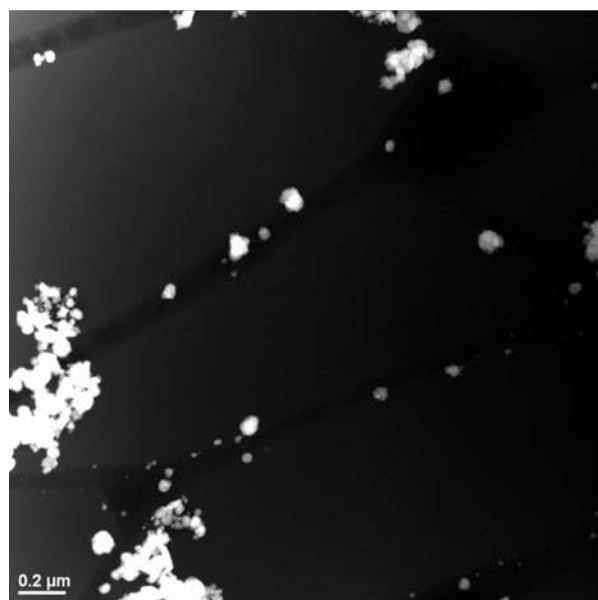


Fig. S-11 STEM images of Au-Me-SiH-PMHS

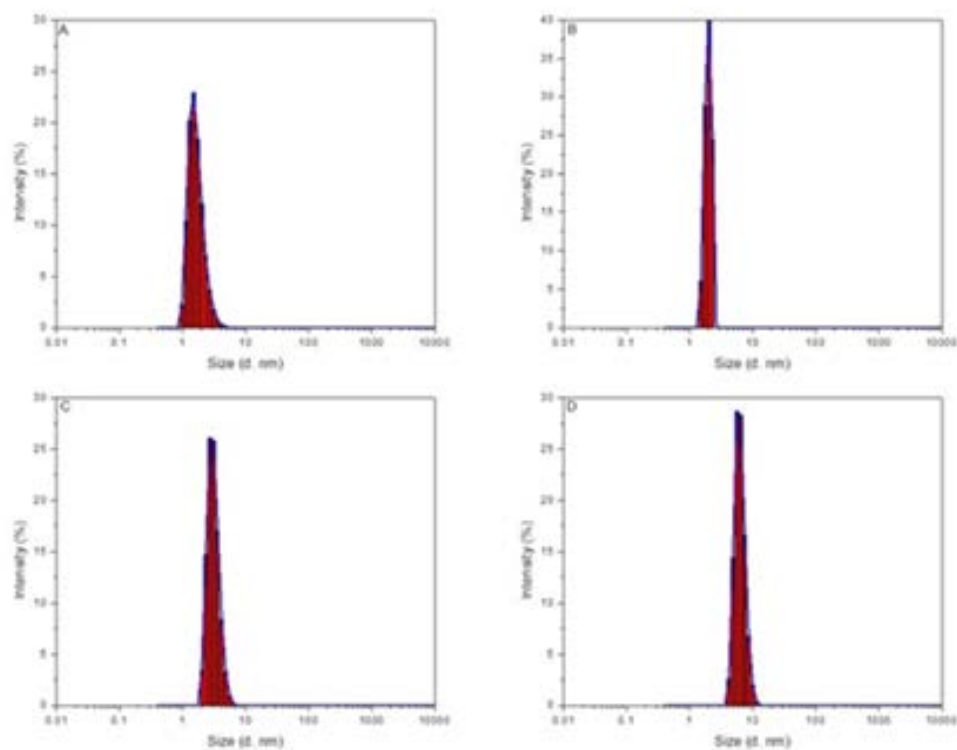


Fig. S-12 Size distribution of gold colloid determined by dynamic light scattering at room temperature for (mean particle size): A. (1.499 nm); B. (2.010 nm); C. (2.696 nm); and D. (5.615 nm). The samples A-D correspond to samples **a-d** listed in Table 1 of the main manuscript. Note that the x-axis is in log scale.

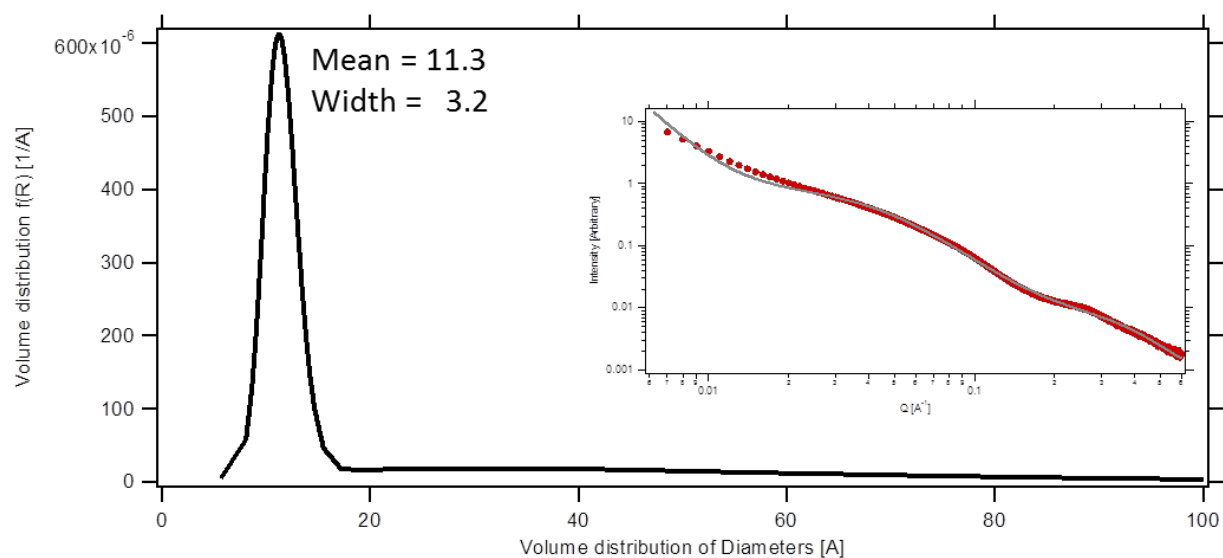


Fig. S-13 Size distribution of gold colloid determined by SAX of sample **a**. inset shows SAXS data and fitted results.

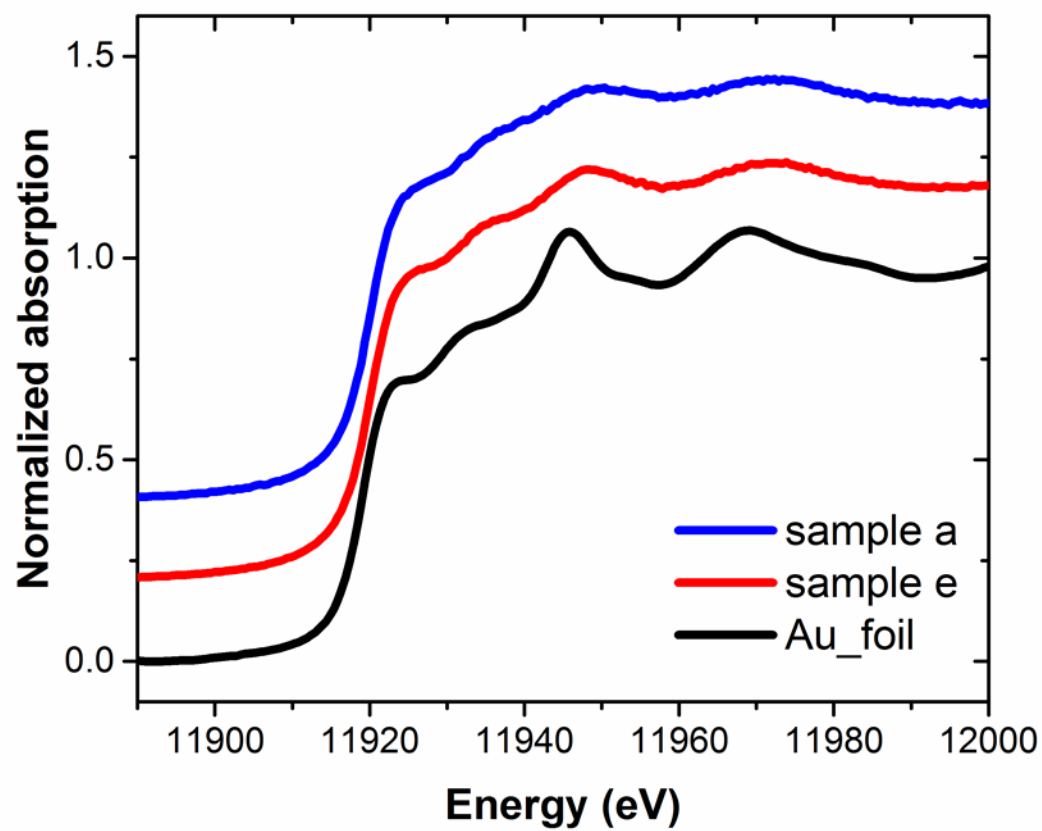


Fig. S-14 XANES spectrum of sample **a**, **e** and gold foil.

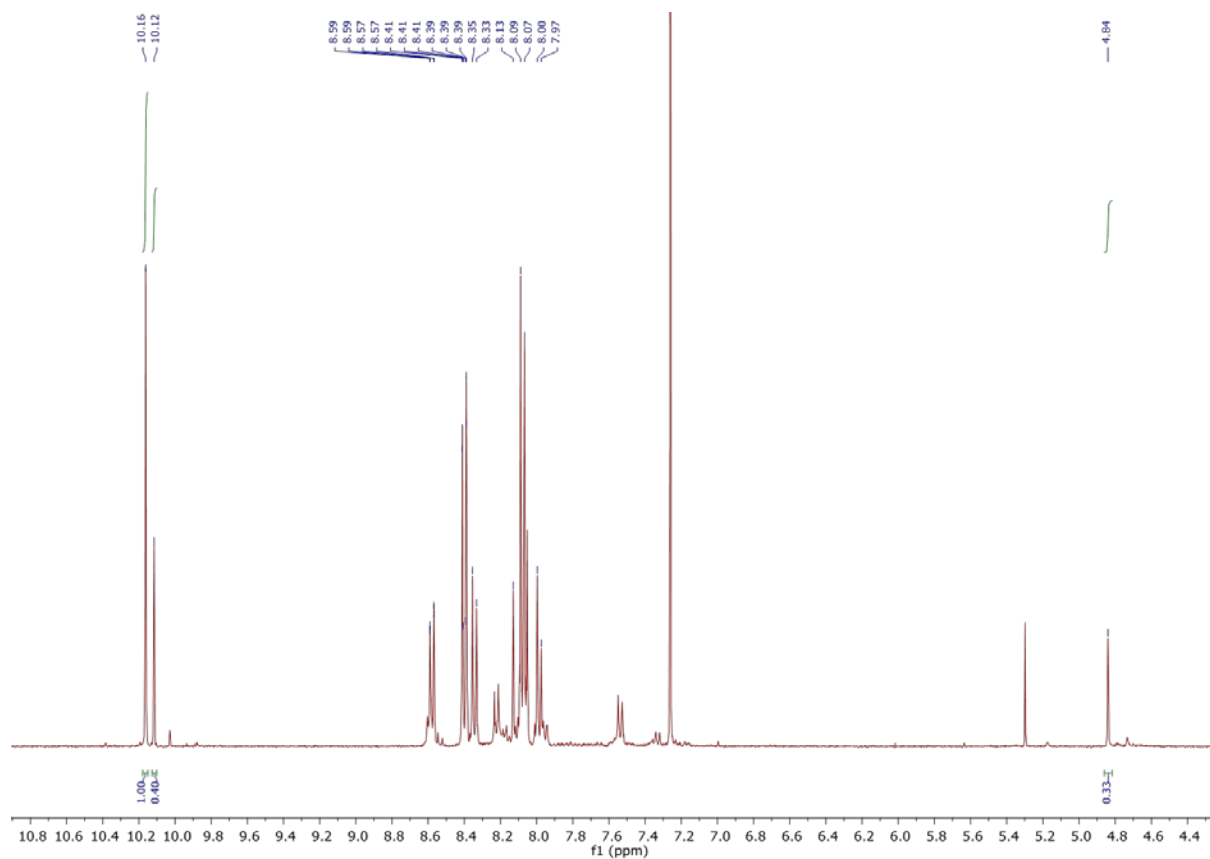


Fig. S-15 NMR spectrum of the products of catalytic conversion of p-nitrobenzaldehyde catalyzed by sample **a**. Calculations were done based on the CHO signal of the starting aldehyde at 10.16 ppm, imine product's CH=N at 10.12 ppm, and the alcohol's CH₂ at 4.84 ppm. Additionally analysis of the aromatic region showed no signs of other products. There is a CH₂Cl₂ peak at 5.3 ppm.