

Supporting Information

A New Chiral N-heterocyclic Carbene Silver(I) Cylinder: Synthesis, Crystal Structure and Catalytic Properties

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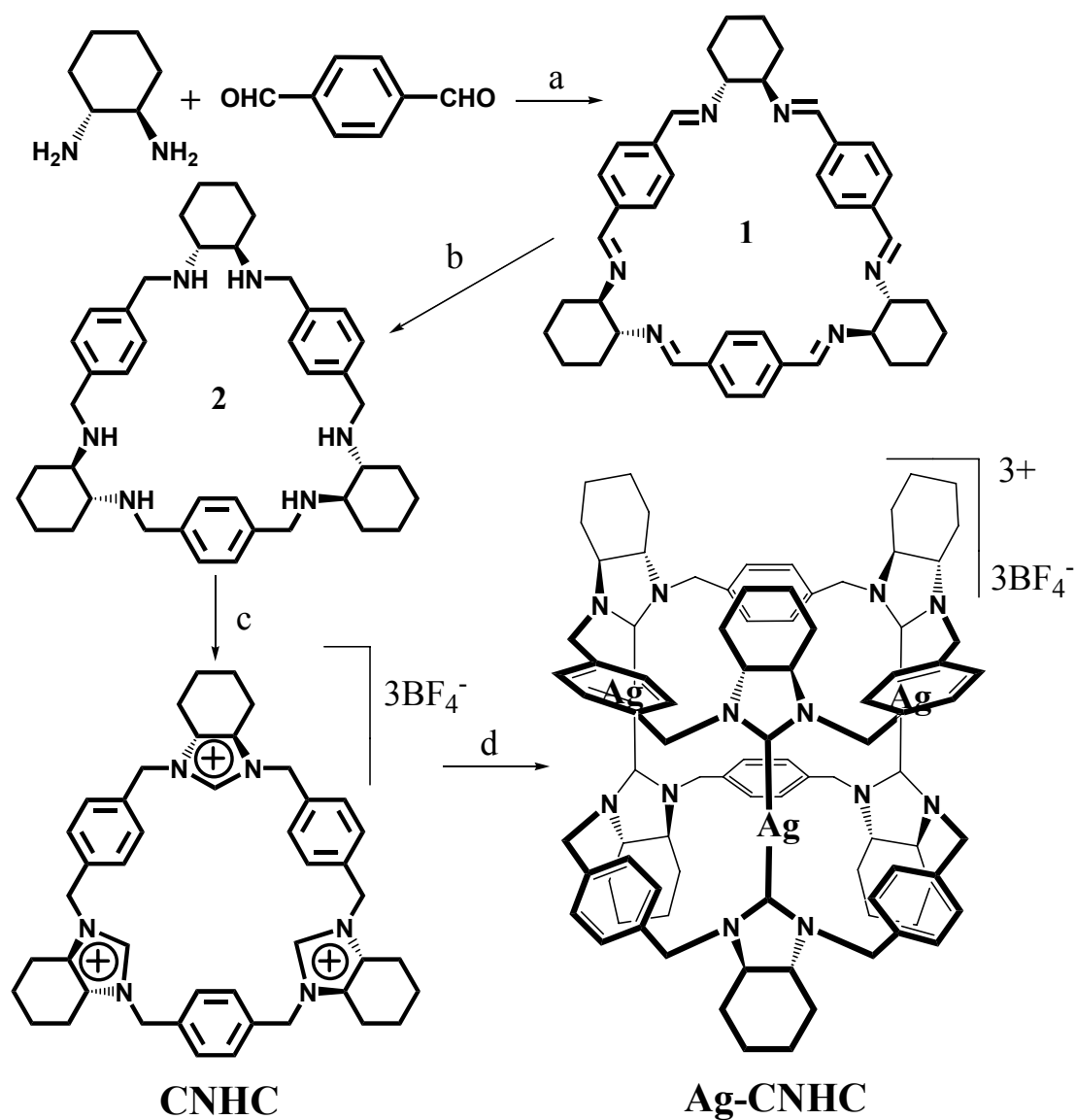
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1. Experimental Section.



Scheme 1 Synthesis of **Ag-CNHC**. Reagents and conditions: (a) (1R, 2R)-(-)-1,2-Diaminocyclohexane, Terephthalaldehyde, CH_3CN , 25°C , 14h, 88%; (b) NaBH_4 , CH_3OH , 0°C , 12h, 65%; (c) Triethylorthoformate, NH_4BF_4 , xylene, 120°C , 4h, 68%; (d) Ag_2O , DMSO, 80°C , 48h, 58%.

Experimental

Materials unless otherwise stated, were obtained from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were measured on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in d^6 -DMSO and CDCl_3 , TMS as internal standard). Mass spectrometric data were obtained on a HP1100LC/MSD mass spectrometry and a LCQ-ToF MS spectrometry and a MALDI micro MXTM spectrometry. The CD spectra was measured on JASCO J-810. HPLC analysis was performed on Agilent 1100 using a ChiralPak AD-H column purchased from Daicel Chemical Industries, Ltd. Products were purified by flash column chromatography on 100-200 mesh silica gel, SiO_2 .

Preparation of CNHC: Compound **2** and **CNHC** were prepared according to the literature (Chem. Commun., 2004, 2206-2207). In a stirring 180 mL dry xylene solution containing **2** (1.3 g, 2 mmol) at 100°C , 2.5 g triethylorthoformate in 30 mL dry xylene were added dropwise. After refluxing for 3 hours, 1.25 g NH_4BF_4 was added. The reaction was carried out at 100°C for another 3 hours, and then heated to 120°C , kept for 1 hour. White powder of crude product was obtained by cooling the solution to room temperature. Colorless crystalline solid **CNHC** was obtained by recrystallization the original powder with water and dried under vacuum, yield 0.82 g. ^1H NMR (d^6 -DMSO, ppm) δ : 9.15 (s, 3H, $\text{H}_{\text{CH-}}$), 7.45 (s, 12H, H_{Ar}), 4.84 (12H, H_{CH_2}), 3.36 (m, 12H, $\text{H}_{\text{cyclohexanyl}}$), 2.03 (d, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 4.0$ Hz), 1.67 (d, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 4.0$ Hz), 1.21 (m, 6H, $\text{H}_{\text{cyclohexanyl}}$), 1.07 (m, 6H, $\text{H}_{\text{cyclohexanyl}}$). ^{13}C NMR (d^6 -DMSO, ppm) δ : 160.30, 133.34, 127.30, 65.77, 47.80, 25.63, 21.92. API-MS m/z : 227.4 [**CNHC**]³⁺, 349.3 [**CNHC**+ H_2O]²⁺, 384.4 [**CNHC**+ BF_4]²⁺, 715.4 [**CNHC**+3 BF_4 +2 H_2O]⁺, 785.4 [**CNHC**+ BF_4 + H_2O]⁺, 855.4 [**CNHC**+2 BF_4]⁺. Single crystals of **CNHC** were prepared by following procedure. Diethyl ether was slowly diffused into the CH_3CN solution of **CNHC** to afford X-ray quality colorless crystals.

Preparation of Ag-CNHC: To a mixture of **CNHC** (0.2 g, 0.215 mmol) and Ag_2O (0.154 g, 0.645 mmol) was added DMSO (30 mL). The mixture was heated at 80°C for 48 hours under the dark and a nitrogen atmosphere. The solution was filtered. The filtrate was diluted with water (200 mL) and the product precipitated. The pure precipitate was collected by filtration as a white

powder in 58% yield. ^1H NMR (d_6 -DMSO, ppm) δ : 7.52 (m, 24H, H_{Ar}), 5.14 (d, 6H, H_{CH_2} , $J = 8.0$ Hz), 4.99 (d, 6H, H_{CH_2} , $J = 8.0$ Hz), 4.47 (d, 6H, H_{CH_2} , $J = 8.0$ Hz), 4.32 (d, 6H, H_{CH_2} , $J = 8.0$ Hz), 3.21 (t, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 14.0$ Hz), 2.84 (t, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 14.0$ Hz), 2.06 (d, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 4.0$ Hz), 1.97 (d, 6H, $\text{H}_{\text{cyclohexanyl}}$, $J = 4.0$ Hz), 1.62 (t, 12H, $\text{H}_{\text{cyclohexanyl}}$, $J = 14.0$ Hz), 1.39 (m, 6H, $\text{H}_{\text{cyclohexanyl}}$), 1.12 (m, 6H, $\text{H}_{\text{cyclohexanyl}}$), 0.89 (m, 12H, $\text{H}_{\text{cyclohexanyl}}$). ^{13}C NMR (d_6 -DMSO, ppm) δ : 210.30, 208.50, 137.51, 134.65, 129.05, 127.96, 69.36, 65.40, 53.86, 51.26, 53.86, 51.26, 28.43, 27.43, 23.88, 23.45, 19.01, 15.63. ESI-MS: 560.51 [Ag-CNHC] $^{3+}$; 884.24 [$\text{Ag-CNHC}+\text{BF}_4$] $^{2+}$. Single crystals of **Ag-CNHC** were prepared by following procedure. Recrystallization from dichloromethane/ether afforded X-ray quality colorless crystals.

General Procedure for the Preparation of Asymmetric Cyanosilylation of Imine Reactions:

To a mixture of Me_3SiCN (1.2 mmol) and imines derivatives (0.5 mmol) was added **Ag-CNHC** (0.01 mmol) and the resulting mixture were stirred at rt for seven days. The reaction was monitored by TLC. Conversion were determined by ^1H -NMR spectra. The e.e. value of the product were determined by HPLC analysis.

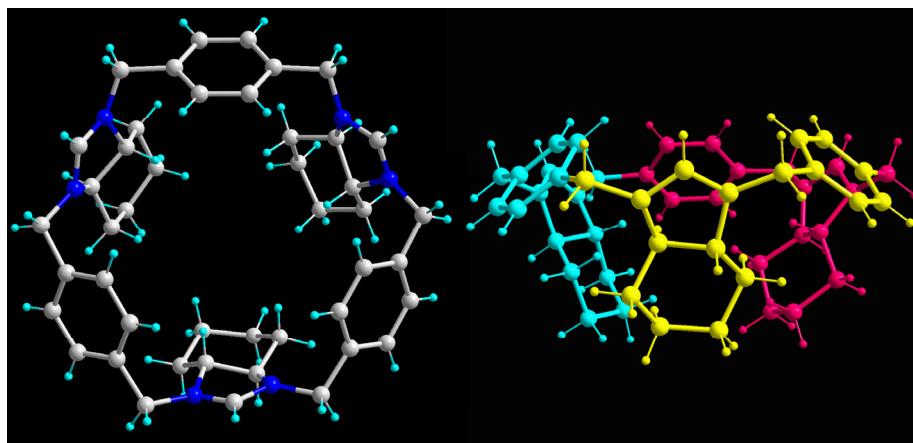
Physical Data of the Asymmetric Cyanosilylation of Imine Products:

2-phenyl-2-(phenylamino)acetonitrile. Purification by column chromatography (gradient elution with CH_2Cl_2) afforded the product as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ : 7.49(m, 2H, H_{Ar}), 7.37(m, 1H, H_{Ar}), 7.31(m, 2H, H_{Ar}), 7.18(t, 2H, H_{Ar}), 7.12(m, 1H, H_{Ar}), 6.78(t, 1H, H_{NH}), 6.65(d, 2H, H_A), 5.31(s, 1H, $\text{H}_{\text{Tert-butyl}}$).

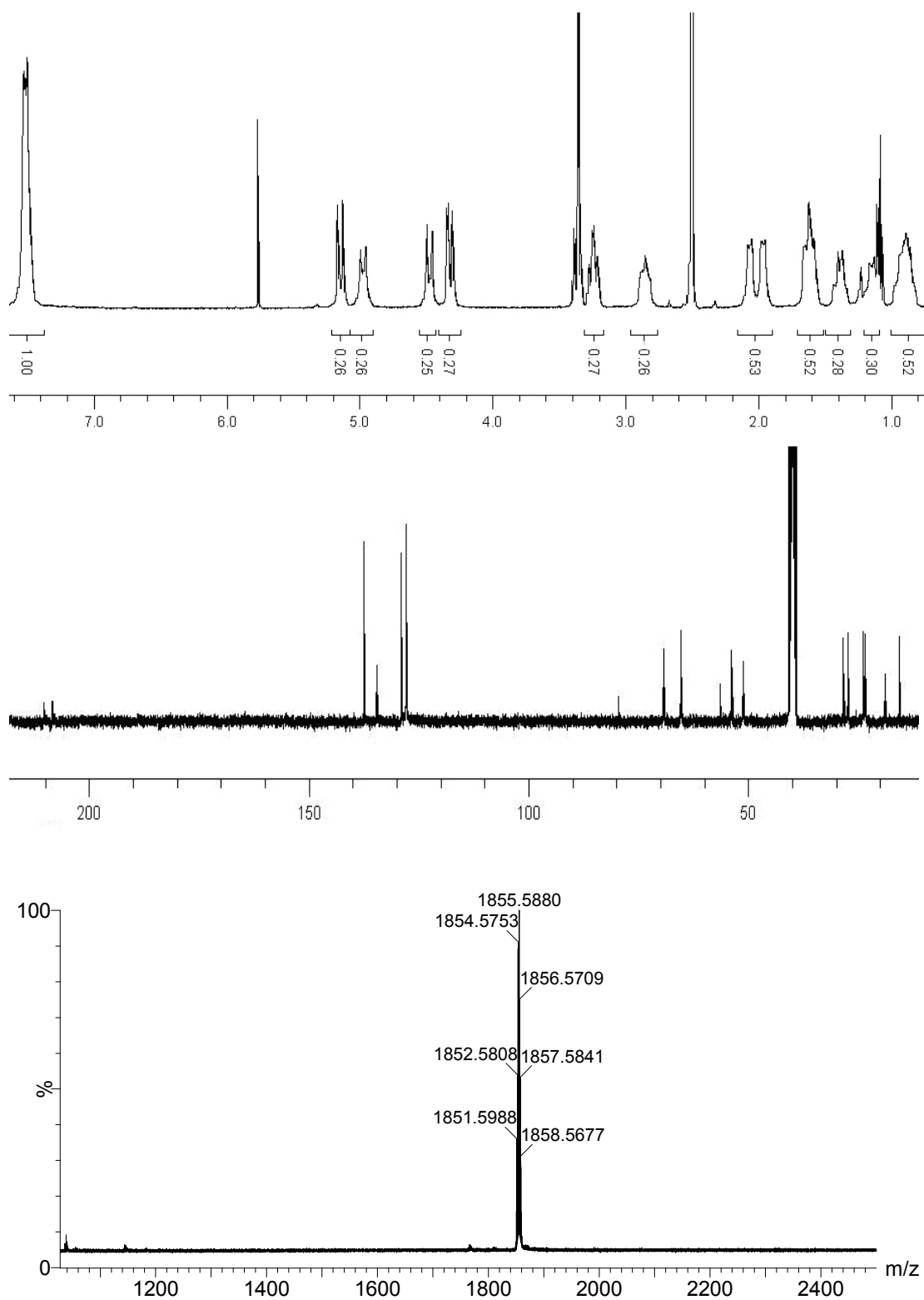
2-(4-(dimethylamino)phenyl)-2-(phenylamino)acetonitrile. Purification by column chromatography (gradient elution with CH_2Cl_2) afforded the product: ^1H NMR (400 MHz, CDCl_3) δ : 7.42(d, 2H, H_{Ar}), 7.28(d, 2H, H_{Ar}), 6.88(t, 1H, H_{Ar}), 6.76(t, 2H, H_{Ar}), 7.12(m, 1H, H_{Ar}), 6.78(t, 2H, H_{Ar}), 5.30(d, 1H, $\text{H}_{\text{Tert-butyl}}$), 3.92(s, 1H, H_{NH}), 2.99(s, 6H, H_{CH_3}).

2-(p-toluidino)-2-phenylacetonitrile. Purification by column chromatography (gradient elution with CH_2Cl_2) afforded the product: ^1H NMR (400 MHz, CDCl_3) δ : 7.60 (d, 2H, H_{Ar}), 7.48 (m, 1H, H_{Ar}), 7.46 (d, 2H, H_{Ar}), 7.09 (d, 2H, H_{Ar}), 6.70 (d, 2H, H_{Ar}), 5.41 (d, 1H, $\text{H}_{\text{Tert-butyl}}$).

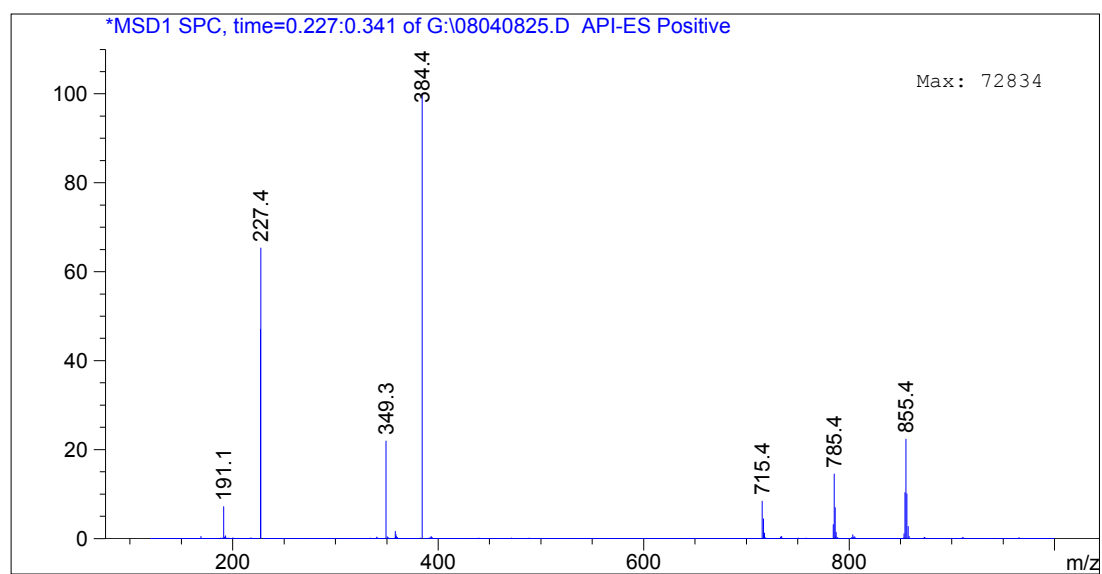
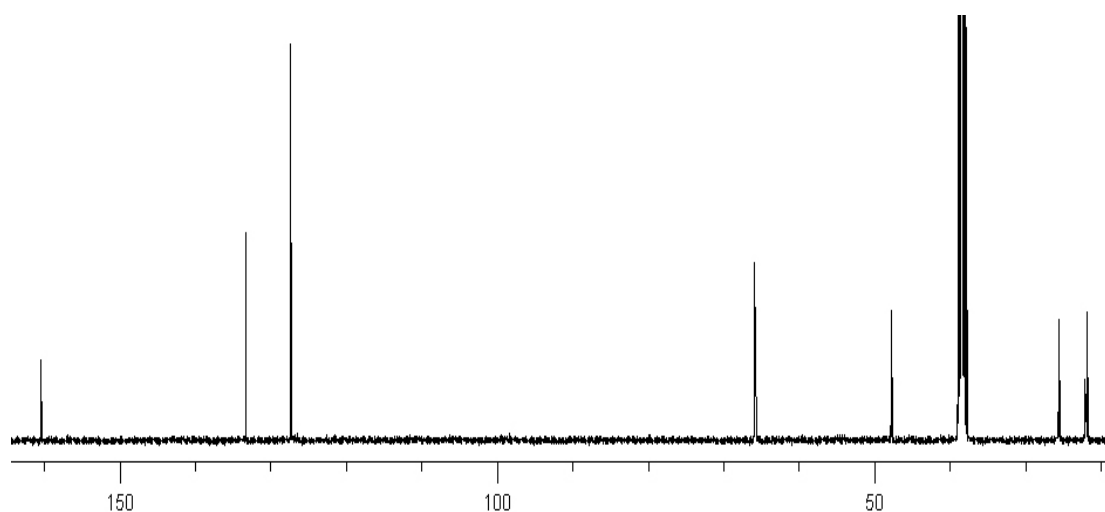
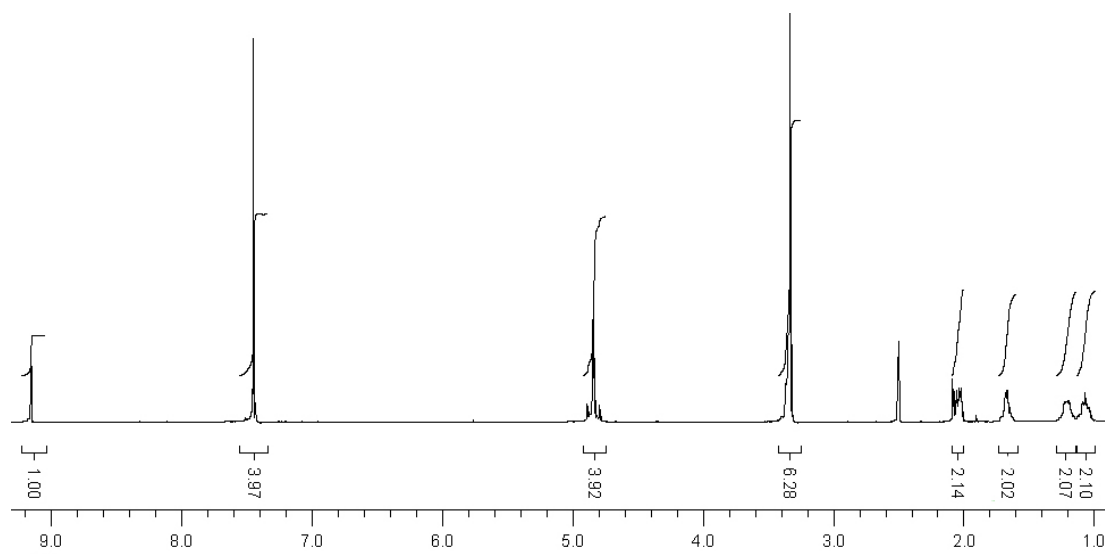
2. Figure S1 Molecular structure of the **CNHC** cation showing the bowl-like cationic character, the anions (BF_4^-) and solvent molecules are omitted for clarify. Selected bond lengths (\AA) and angle ($^\circ$): $\text{N}(1)\text{--C}(8)$ 1.320(5), $\text{N}(2)\text{--C}(8)$ 1.310(5); and $\text{N}(2)\text{--C}(8)\text{--N}(1)$ 113.5(4).



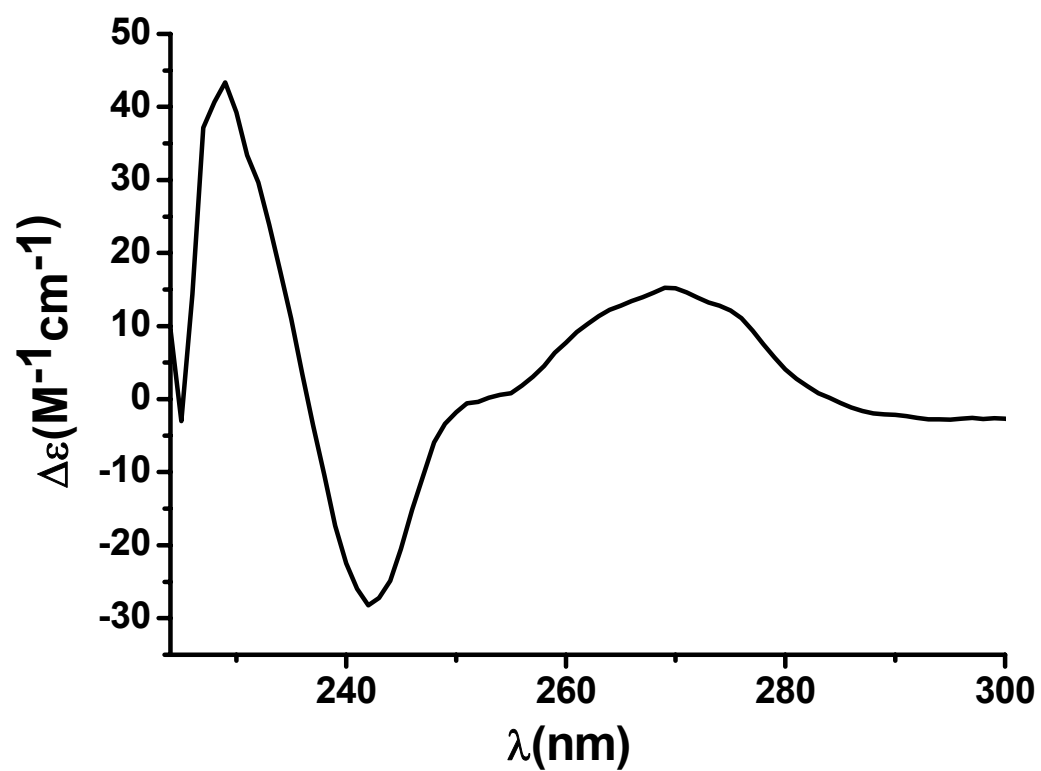
3. Figure S2 ^1H -NMR (top picture) , ^{13}C -NMR (middle picture) and MALDI-TOF (bottom picture) spectra of the **Ag-CNHC** in d^6 -DMSO



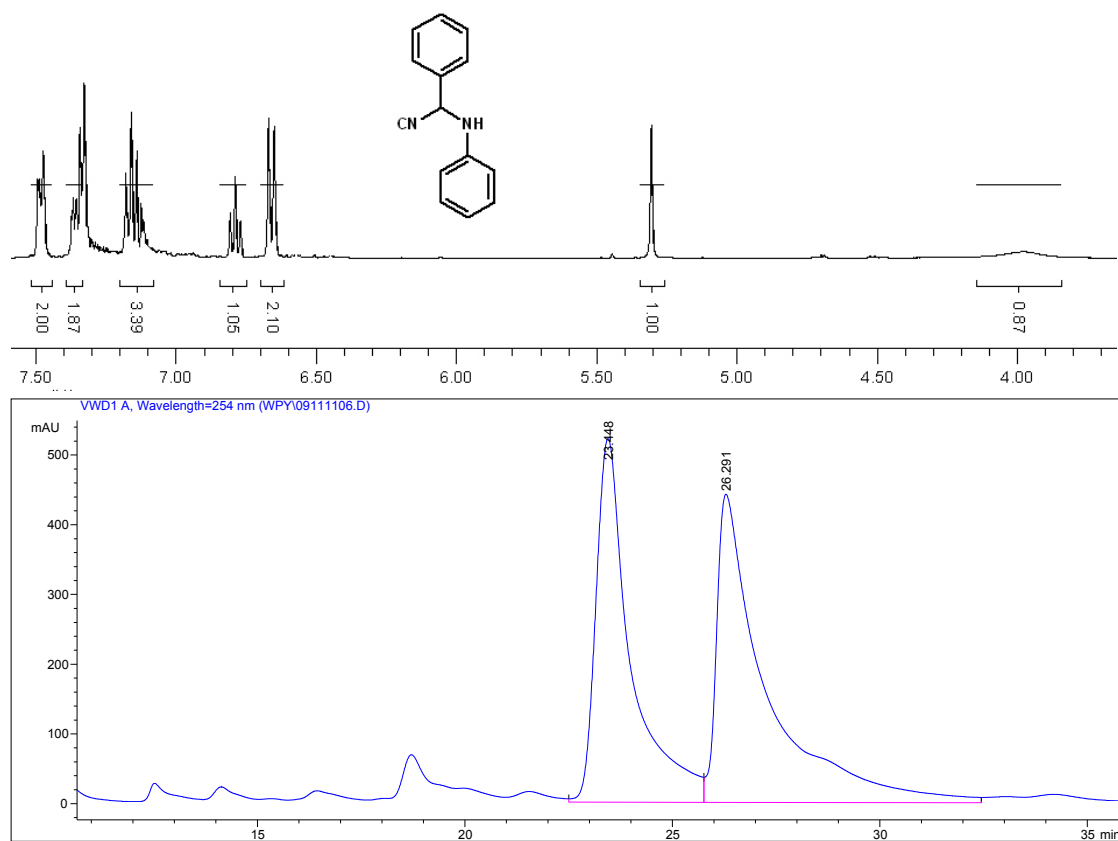
4. Figure S3 $^1\text{H-NMR}$ (top picture), $^{13}\text{C-NMR}$ (middle picture) and ESI-MS spectrum (bottom one) spectra of the **CNHC** in $\text{d}^6\text{-DMSO}$



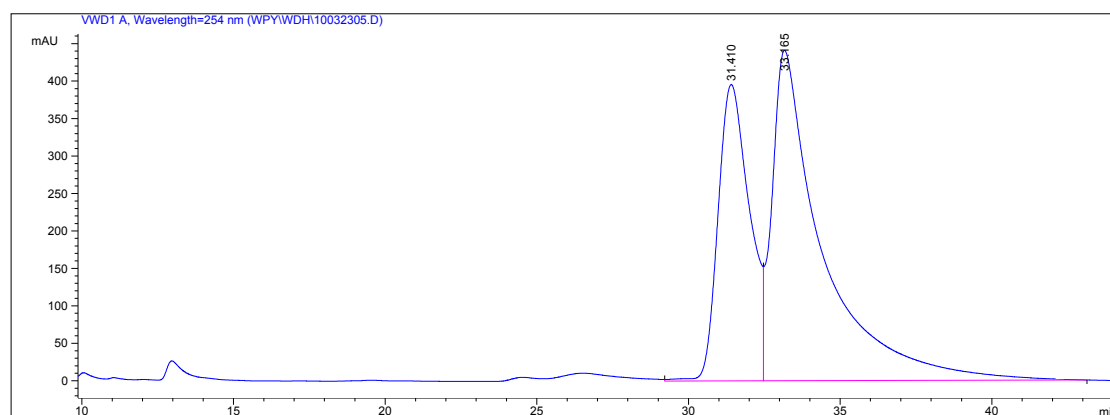
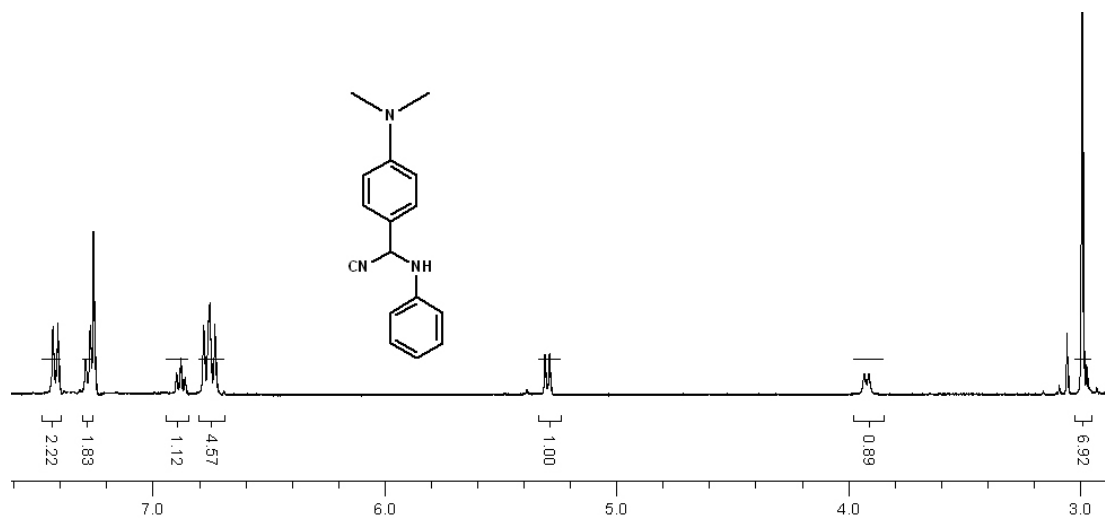
5. Figure S4 CD spectrum of the Ag-CNHC in CH₂Cl₂ solution.



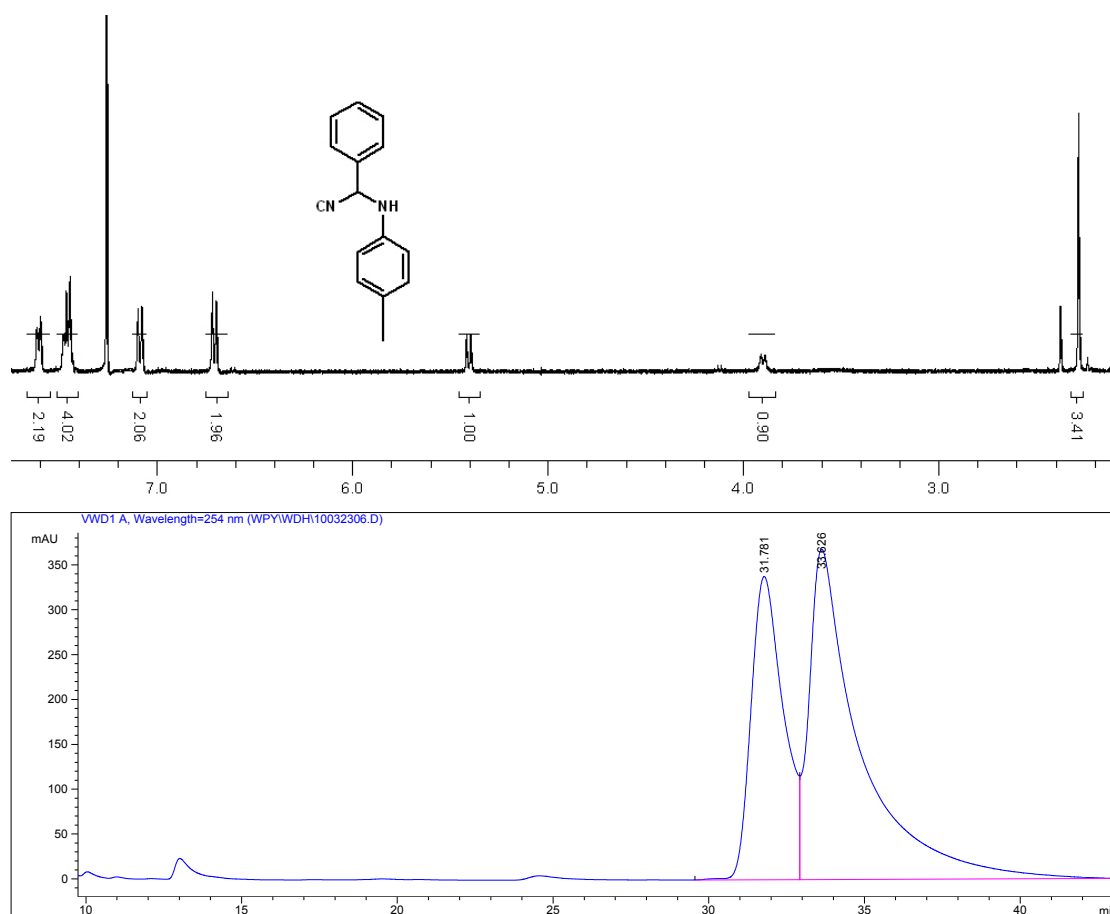
6. Figure S5 ^1H NMR and HPLC analysis for product of the reaction of entry 1



7. Figure S6 ^1H NMR and HPLC analysis for product of the reaction of entry 2



8. Figure S7 ^1H NMR and HPLC analysis for product of the reaction of entry 3



9. Table S1 Control experiments: Me₃SiCN (1.2 mmol) , N-benzylidenebenzenamine (0.5 mmol) and CNHC (0.01 mmol) were stirred at the same condition with the catalytic reactions above.

Ar ₁ CH=NAr ₂	Yield(%)	<i>e.e.</i> (%)
PhCH=NPha	48	10