

**Structure/Catalytic Activity Study of Gold(I)-NHC Complexes, Recyclable and Reusable, in the Hydration of Alkynes in Aqueous Medium**

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**Supplementary Material**

**Table of Contents**

Title page and detailed list of contents of the Supporting Information (SI)	S1
General Method	S2
Synthesis of the Imidazolium Salts	S2
General Procedure for Synthesis of Sulfonated Gold(I)-NHC Complexes [Au(I)-NHC-Cl]	S2
Procedure for Preparation of Weakly Coordinating Anions (Anion Effect)	S3
Procedure for Synthesis of the Complex [(IPr*SO <sub>3</sub> Au) <sup>+</sup> (MeOH)][SbF <sub>6</sub> ] <sup>-</sup> (C6)	S4
General Method for Alkyne Hydration Reactions in water or water:methanol	S4
<sup>1</sup> H and <sup>13</sup> C NMR of (3-Sulfonatepropyl)imidazolium (L5)	S5-S8
<sup>1</sup> H and <sup>13</sup> C NMR of (3-Sulfonatepropyl)imidazol-2-ylidene gold(I) Chloro (C5)	S9-S10
<sup>1</sup> H and <sup>13</sup> C NMR of [1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene Au <sup>+</sup> (CH <sub>3</sub> OH)][SbF <sub>6</sub> ] <sup>-</sup> (C6)	S11-S13
<sup>1</sup> H and <sup>13</sup> C NMR of [1-mesityl-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene Au <sup>+</sup> (CH <sub>3</sub> OH)][SbF <sub>6</sub> ] <sup>-</sup> (C7)	S14-S15

**General Methods.** All reactions were carried out under a dry nitrogen atmosphere by using Schlenk techniques. Deionized water (type II quality) was obtained with a Millipore Elix 10 UV Water Purification System. Organic solvents were dried and distilled under nitrogen and degassed prior to use. Unless otherwise stated, reagents were obtained from commercial sources and used as received. [Au(tht)Cl] was prepared according to reported procedures.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Advance 300 spectrometer. Reaction mixtures were analyzed by gas-liquid chromatography (GLC) with an instrument equipped with a flame-ionization detector and a HP5 capillary column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ).

**Synthesis of the Imidazolium Salts.** All imidazolium salts (**L1-L4**) were prepared according to reported procedures [11b].

*(3-sulfonatepropyl)imidazolium (L5).* White solid (1.323 g, 7.22 mmol, 98%); mp 257-259 °C. Water solubility at 25 °C: 910 g/L;  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  8.65 (s, 1H,  $\text{C}^2\text{Imz}$ ), 7.44 (s, 1H, Imz), 7.36 (s, 1H, Imz), 4.29 (t,  $^3J_{\text{H-H}} = 7.0$ , 2H,  $\text{NCH}_2$ ), 2.81 (t,  $^3J_{\text{H-H}} = 7.5$ , 2H,  $\text{CH}_2\text{S}$ ), 2.22 (q, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  14.22 (s, 1H, NH); 9.11 (s, 1H,  $\text{C}^2\text{Imz}$ ), 7.80 (s, 1H, Imz), 7.68 (s, 1H, Imz), 4.33 (t,  $^3J_{\text{H-H}} = 7.0$ , 2H,  $\text{NCH}_2$ ), 2.40 (t,  $^3J_{\text{H-H}} = 7.5$ , 2H,  $\text{CH}_2\text{S}$ ), 2.11 (q, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  134.7(s, Imz  $\text{C}^2$ ), 121.7 (s, Imz  $\text{C}^5$ ), 119.9 (s, Imz  $\text{C}^4$ ), 47.6 (s,  $\text{NCH}_2$ ), 47.2 (s,  $\text{SCH}_2$ ), 25.1 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  136.0 (s, Imz  $\text{C}^2$ ), 122.6 (s, Imz  $\text{C}^5$ ), 120.3 (s, Imz  $\text{C}^4$ ), 48.1 (s,  $\text{NCH}_2$ ), 47.9 (s,  $\text{SCH}_2$ ), 26.7 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ); Anal. Calcd for  $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_3\text{S}$ : C, 37.88; H, 5.30; N, 14.73; S, 16.85. Found: C, 37.90; H, 5.39; N, 14.65; S, 16.78.

**General Procedure for Synthesis of Sulfonated Gold(I)-NHC Complexes [Au<sup>I</sup>-NHC-Cl].** All complexes (**C1-C5**) were prepared according to reported procedures [11b]. In a 25 mL Schlenk tube was prepared a solution of [Ag<sup>I</sup>-NHC-Cl], from the imidazolium salt (0.60 mmol), silver oxide (0.083 g, 0.36 mmol) and sodium chloride (0.035 g, 0.60 mmol), in MeOH or DMSO (3 mL). [Au(tht)Cl] (0.192 g, 0.60 mmol) was added and the mixture was stirred at room temperature for 4 h. Then, NaCl (0.035 g, 0.60 mmol) was added and the final solution was filtered through a plug of Celite; the solvent was partially removed under vacuum to a remaining volume of 2 mL. The gold complex was then precipitated with dry acetone (20 mL), separated by filtration, washed with dry acetone (3  $\times$  10 mL), and dried under vacuum.

*(3-sulfonatepropyl)imidazol-2-ylidene gold(I) Chloro (C5).* White solid (0.119 g, 0.24 mmol, 80%); mp 153-155 °C. The complex is soluble in methanol, *tert*-butanol and DMSO, partially soluble in *isopropanol*, and insoluble in tetrahydrofuran, diethyl ether and acetone.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):

$\delta$  7.82 (s, 1H, NH), 7.25 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 6.99 (d,  $^3J_{\text{H-H}} = 1.4$ , 1H, Imz), 4.10 (t,  $^3J_{\text{H-H}} = 7.0$ , 2H, NCH<sub>2</sub>), 2.36 (t,  $^3J_{\text{H-H}} = 7.5$ , 2H, CH<sub>2</sub>S), 1.99 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  164.2 (s, Imz C<sup>2</sup>), 123.0 (s, Imz C<sup>5</sup>), 121.7 (s, Imz C<sup>4</sup>), 48.4 (s, NCH<sub>2</sub>), 45.9 (s, SCH<sub>2</sub>), 27.6 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); FT-IR (CsI): 3115 ( $\nu_{\text{NH}}$ ), 3053 ( $\nu_{\text{CH}}$ ); 2931 ( $\nu_{\text{CH}}$ ), 1537, 1516 ( $\nu_{\text{C=C}}$ ), 1455 ( $\nu_{\text{CN}}$ ), 1186 ( $\nu_{\text{S=O}}$ ,  $\nu_{\text{OSO}}$ ) and 1044 ( $\nu_{\text{CN}}$ ) cm<sup>-1</sup>; ESI-MS (negative ion, MeOH):  $m/z$ : 421.02 [M-Na]<sup>-</sup>; Anal. Calcd for C<sub>6</sub>H<sub>9</sub>AuClN<sub>2</sub>NaO<sub>3</sub>S: C, 16.20; H, 2.04; N, 6.30; S, 7.21. Found: C, 16.12; H, 2.01; N, 6.36; S, 7.29.

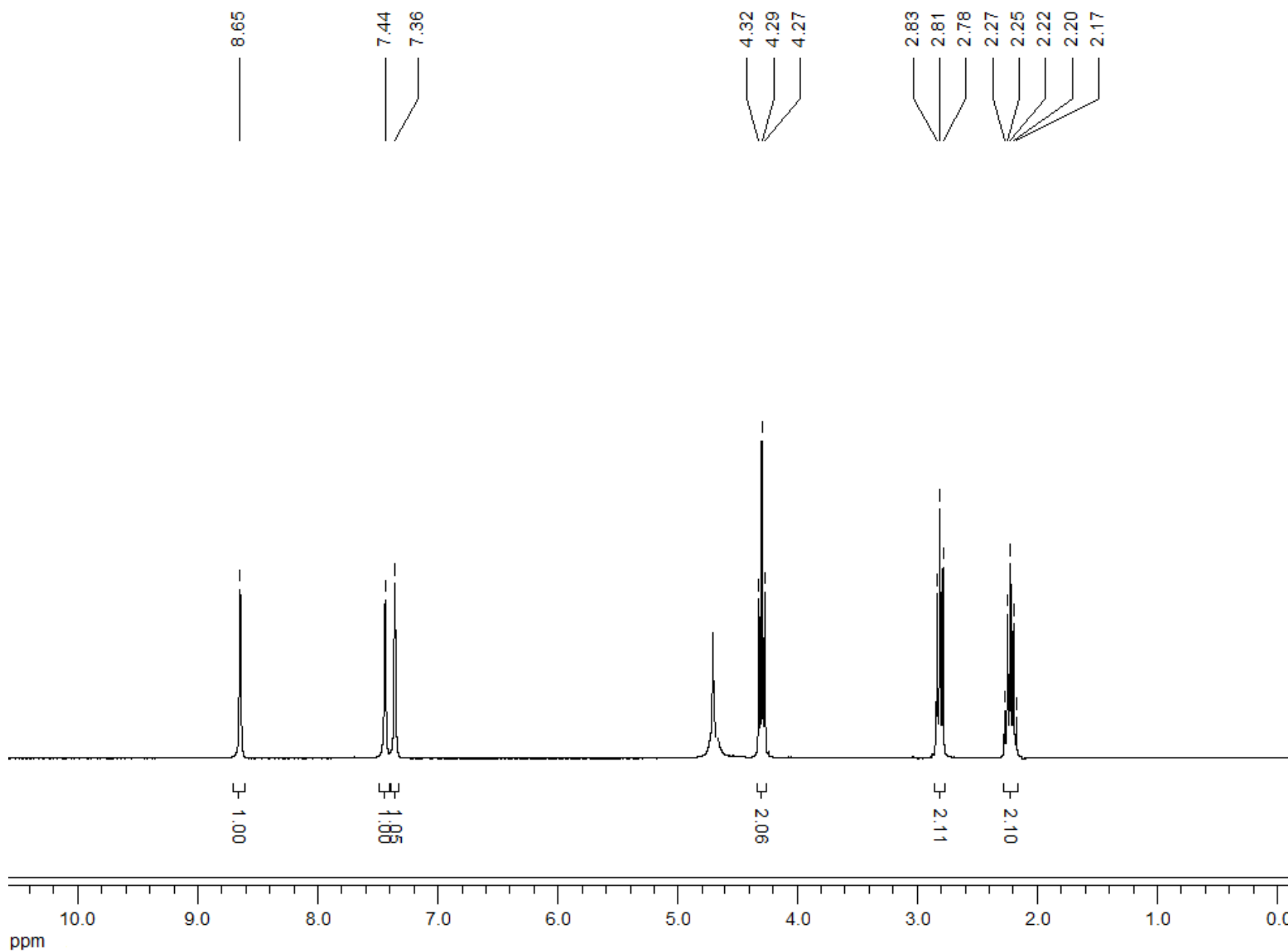
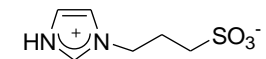
**Procedure for of Weakly Coordinating Anions (Anion effect).** In a Schlenk tube containing a magnetic stirring bar, **C1** (0.004 g, 0.005 mmol) was dissolved in 1.5 mL of methanol and AgX, X= SbF<sub>6</sub>, OTs, SCN (0.005 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. To generate the active species with chloride as anion, activation was carried just heating a solution of **C1** in methanol at 100 °C for 30 minutes.

**Procedure for Synthesis of the Complex [(IPr\*SO<sub>3</sub>Au)<sup>+</sup>(MeOH)][SbF<sub>6</sub>]<sup>-</sup> (C6).** In a Schlenk tube containing a magnetic stirring bar, (IPr\*SO<sub>3</sub>)AuCl (0.100 g, 0.12 mmol) was dissolved in 2 mL of methanol and AgSbF<sub>6</sub> (0.041 g, 0.12 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and filtered through a pad of Celite to give a colorless solution. Complete removal of the solvent under vacuum led to the isolation of a white solid (0.122 mg) in 96% yield. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  7.75 (s, 4H, Ar), 7.65 (s, 2H, Imz), 3.31 (s, 3H, CH<sub>3</sub>), 2.55 (h,  $^3J_{\text{HH}} = 7.0$  Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  8.00 (s, 2H, Imz), 7.59 (s, 4H, Ar), 3.17 (s, 3H, CH<sub>3</sub>), 2.47 (h,  $^3J_{\text{HH}} = 7.0$  Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  160.3 (s, Imz C<sup>2</sup>), 150.4 (s, Ar C<sup>4</sup>), 145.4 (s, Ar C<sup>2</sup>), 134.4 (s, Ar C<sup>1</sup>), 125.4 (s, Ar C<sup>3</sup>), 121.6 (s, Imz C<sup>4,5</sup>), 28.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>).

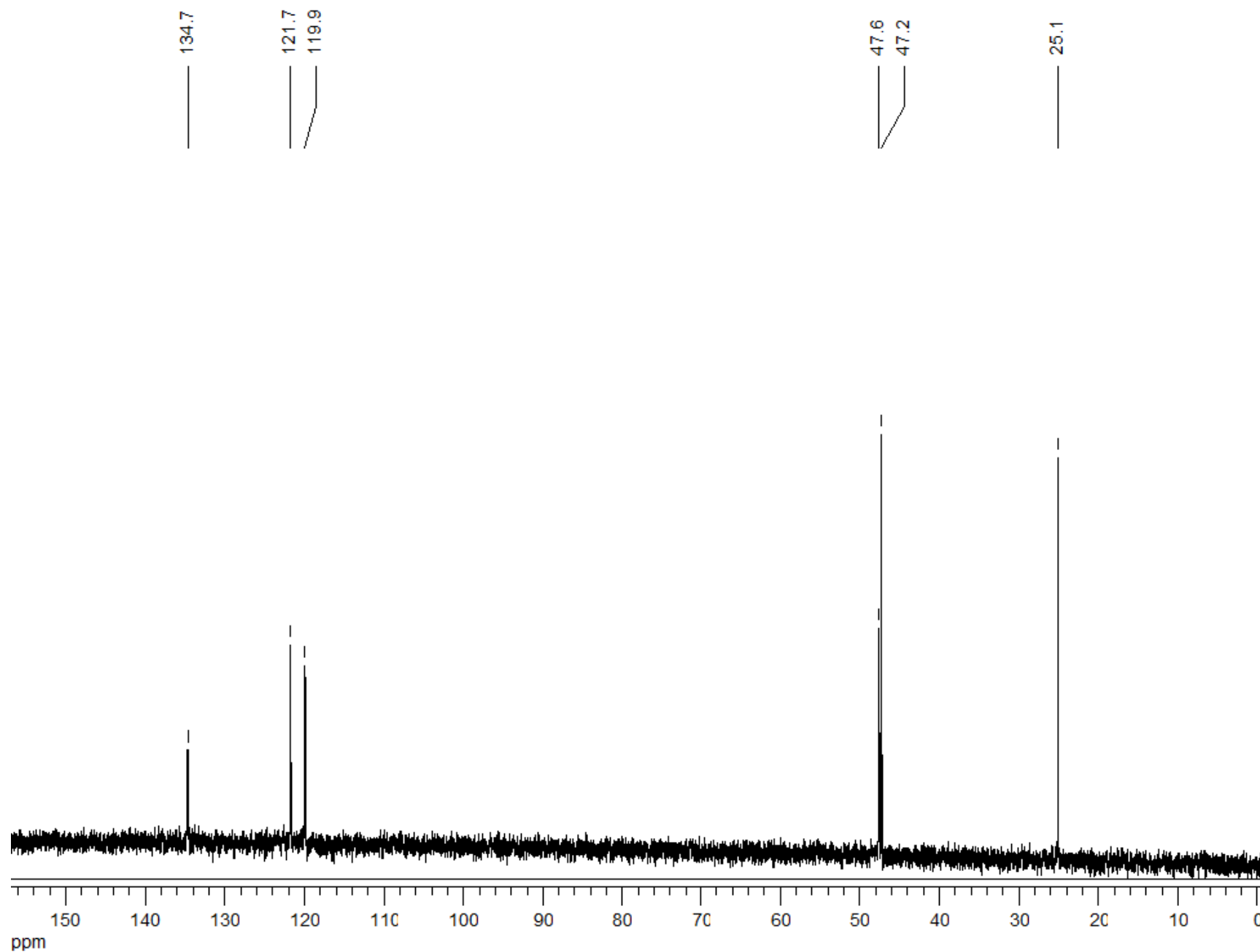
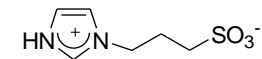
**[(IMesSO<sub>3</sub>Au)<sup>+</sup>(MeOH)][SbF<sub>6</sub>]<sup>-</sup> (C7).** The complex was obtained as a white solid (0.093 mg, 98%) by a similar procedure to that described for complex **C6**. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  7.40 (s, 1H, Imz), 6.92 (s, 1H, Imz), 6.86 (s, 2H, Ar), 4.22 (t,  $^3J_{\text{HH}} = 6.0$  Hz, 2H, NCH<sub>2</sub>), 3.28 (s, 3H, CH<sub>3</sub>), 2.70 (t,  $^3J_{\text{HH}} = 6.0$  Hz, 2H, CH<sub>2</sub>S), 2.11 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.06 (s, 3H, *p*-CH<sub>3</sub>Ar), 1.81 (s, 6H, *o*-CH<sub>3</sub>Ar); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O):  $\delta$  169.3 (s, Imz C<sup>2</sup>), 139.5 (s, Ar C<sup>1</sup>), 135.0 (s, Ar C<sup>2</sup>), 134.8 (s, Ar C<sup>4</sup>), 129.0 (s, Ar C<sup>3</sup>), 123.1 (s, Imz C<sup>4</sup>), 122.2 (s, Imz C<sup>5</sup>), 53.4 (s, NCH<sub>2</sub>), 49.1 (CH<sub>3</sub>), 47.8 (s, CH<sub>2</sub>S), 26.4 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.8 (s, *p*-CH<sub>3</sub>Ar), 16.9 (s, *o*-CH<sub>3</sub>Ar).

**General method for the alkyne hydration reactions in water or water:methanol.** 0.005 mmol of AgX (if required) and 0.005 mmol of catalyst were added to a solution of alkyne (0.5 mmol, 55.5  $\mu$ L) in pure water (3 mL) or in water:methanol (1.5:1.5 mL). The mixture was vigorously stirred at 100 °C or 80 °C (oil bath) in an ampoule tube equipped with a PTFE valve. Reaction time was monitored by GC by taking samples at different times. After allowing to cool down to room temperature, the organic product was extracted with diethyl ether (3  $\times$  5 mL), the combined ethereal layers were dried over MgSO<sub>4</sub>, and the volatiles removed under vacuum to give the desired product. The aqueous phase was reused for several cycles as it was specified in the Results and Discussion Section.

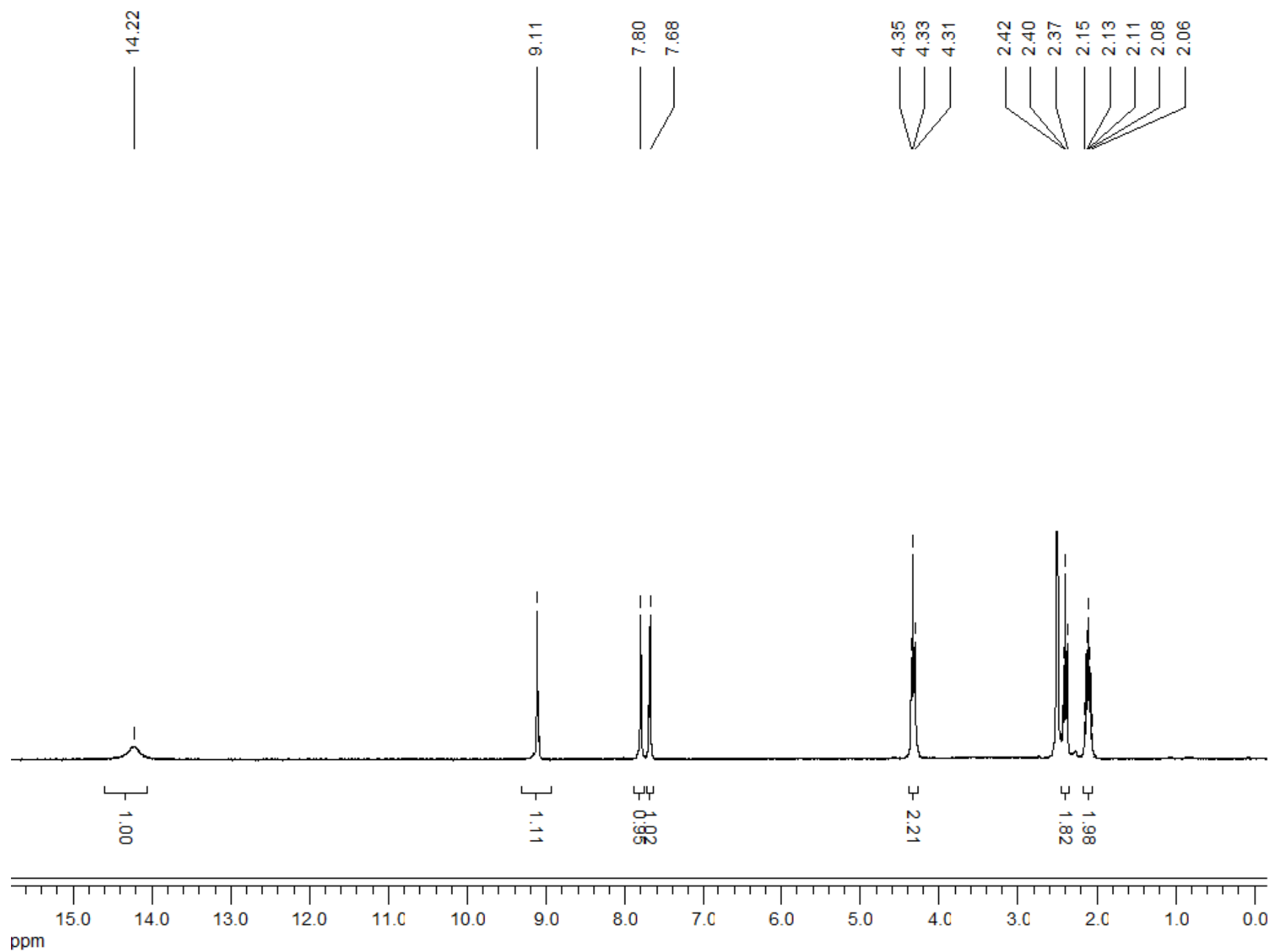
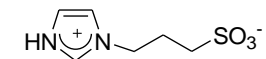
(3-Sulfonatepropyl)imidazolium (L5) ( $^1\text{H}$ -RMN,  $\text{D}_2\text{O}$ )



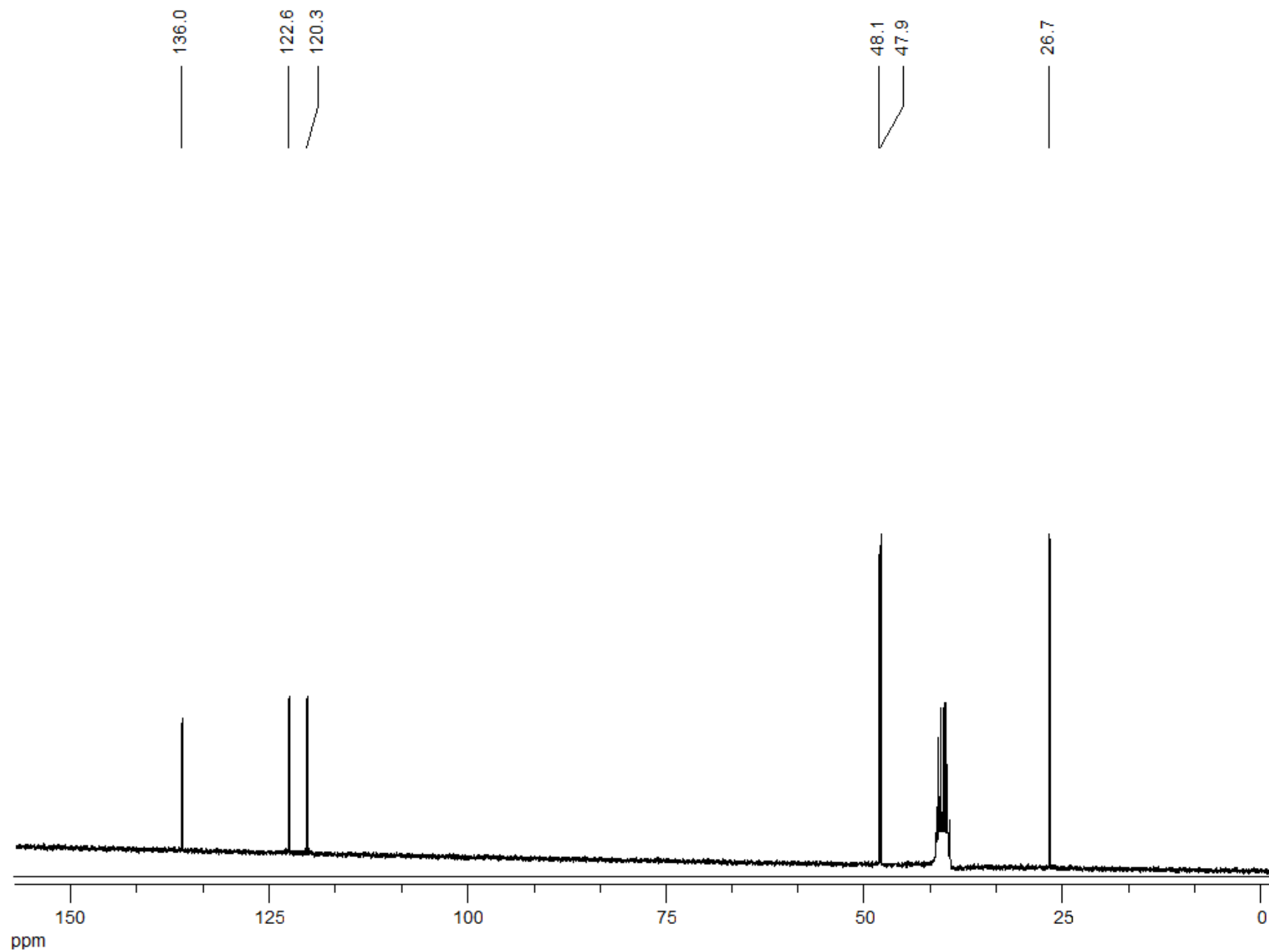
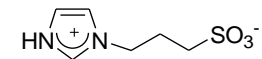
(3-Sulfonatepropyl)imidazolium (L5) ( $^{13}\text{C}$ -RMN,  $\text{D}_2\text{O}$ )



(3-Sulfonatepropyl)imidazolium (L5) ( $^1\text{H}$ -RMN,  $\text{DMSO-d}_6$ )

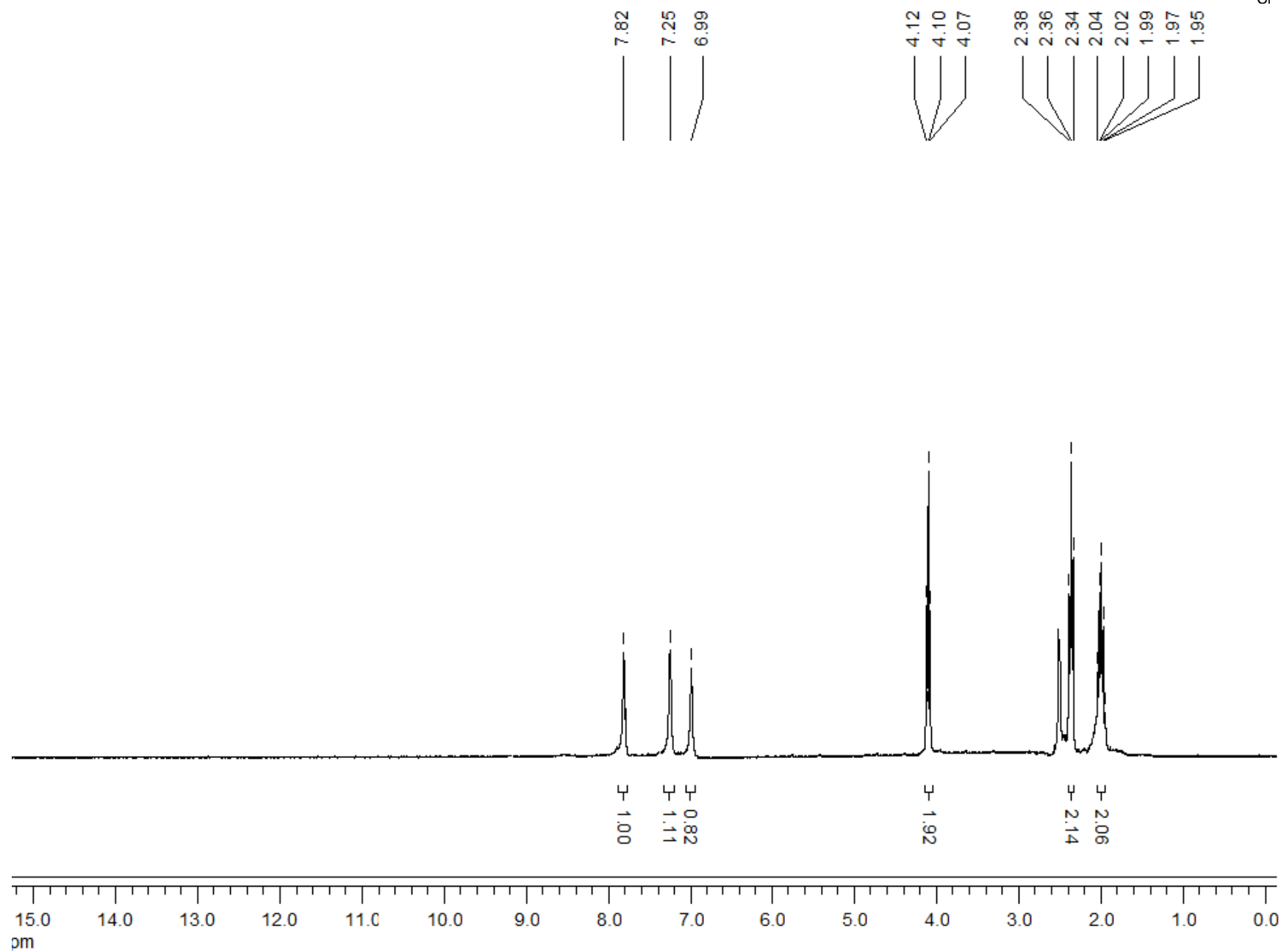
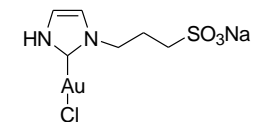


(3-Sulfonatepropyl)imidazolium (L5) ( $^{13}\text{C}$ -RMN, DMSO- $d_6$ )

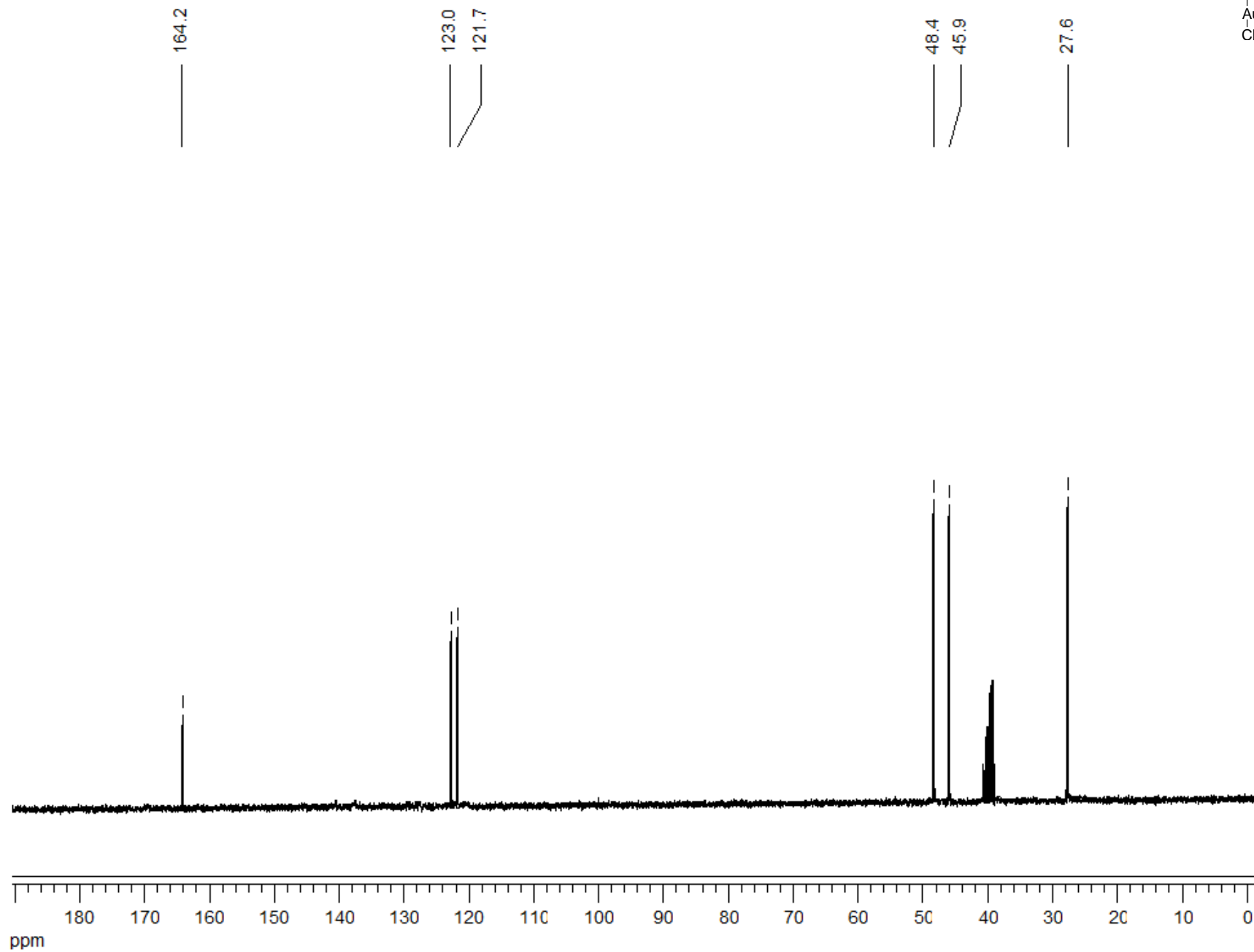
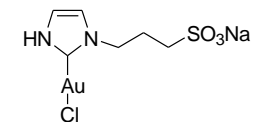




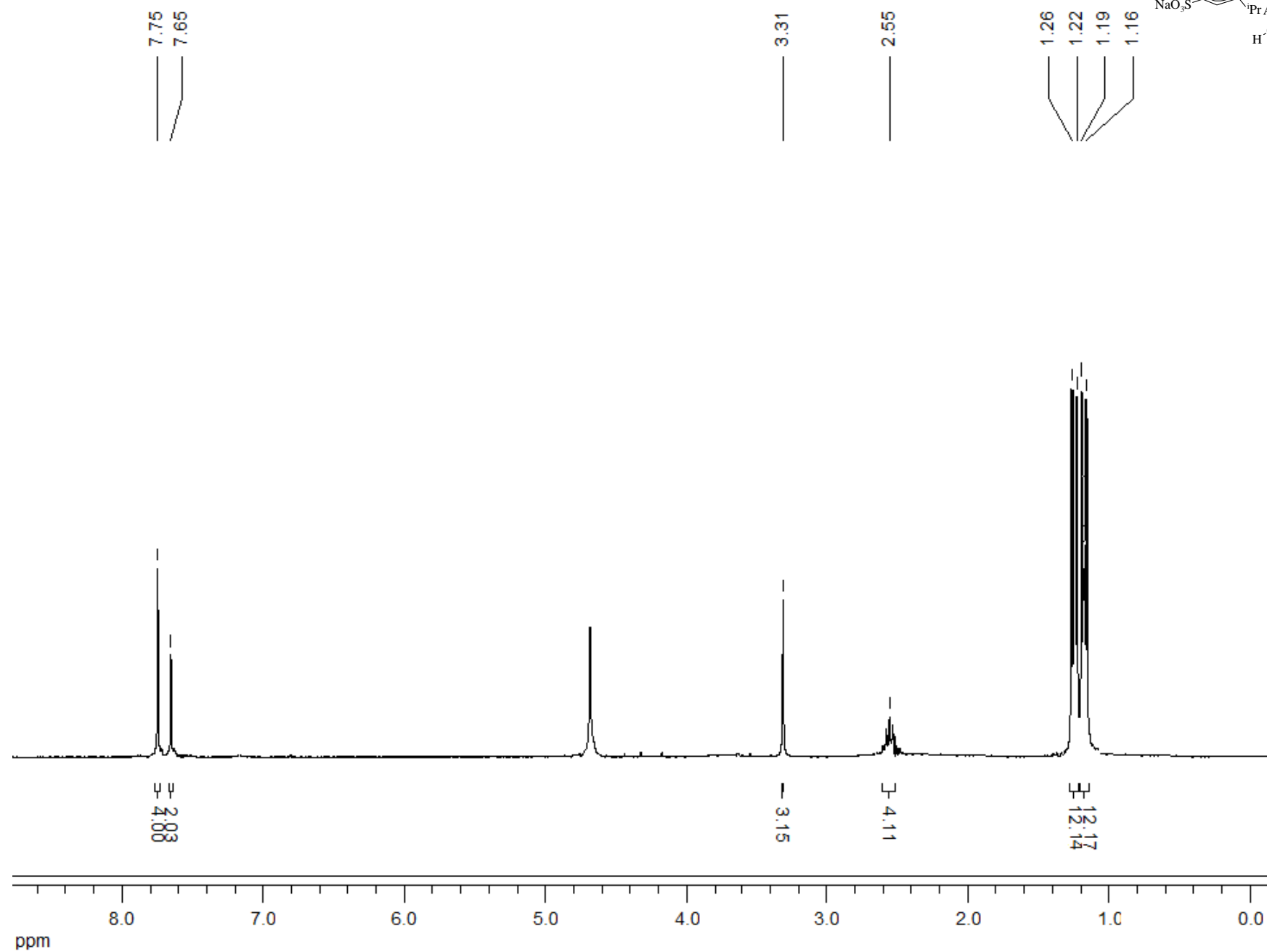
(3-Sulfonatepropyl)imidazol-2-ylidene gold(I) Chloro (C5) ( $^1\text{H}$ -RMN,  $\text{DMSO-d}_6$ )



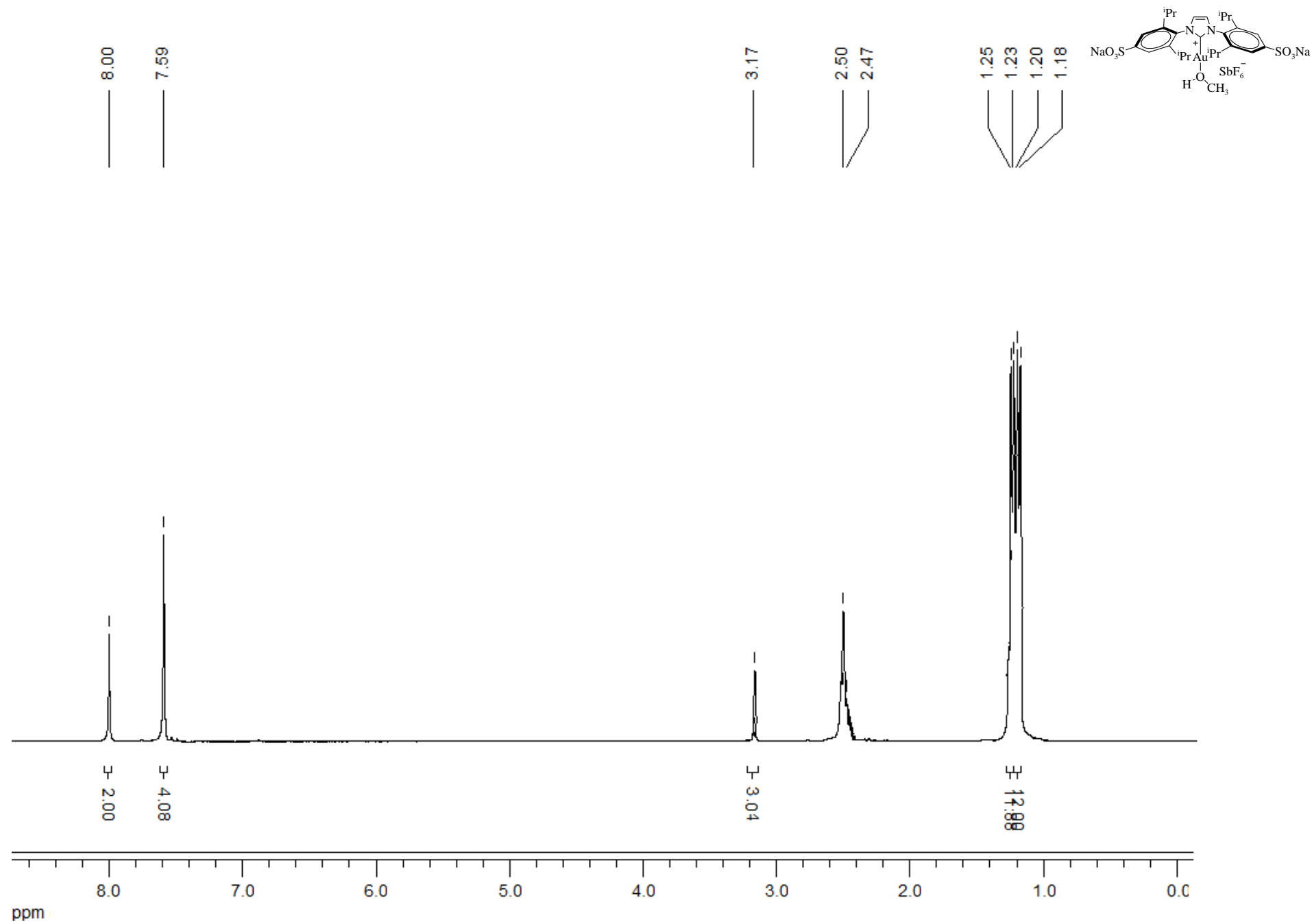
**(3-Sulfonatepropyl)imidazol-2-ylidene gold(I) Chloro (C5)** ( $^{13}\text{C}$ -RMN, DMSO- $d_6$ )



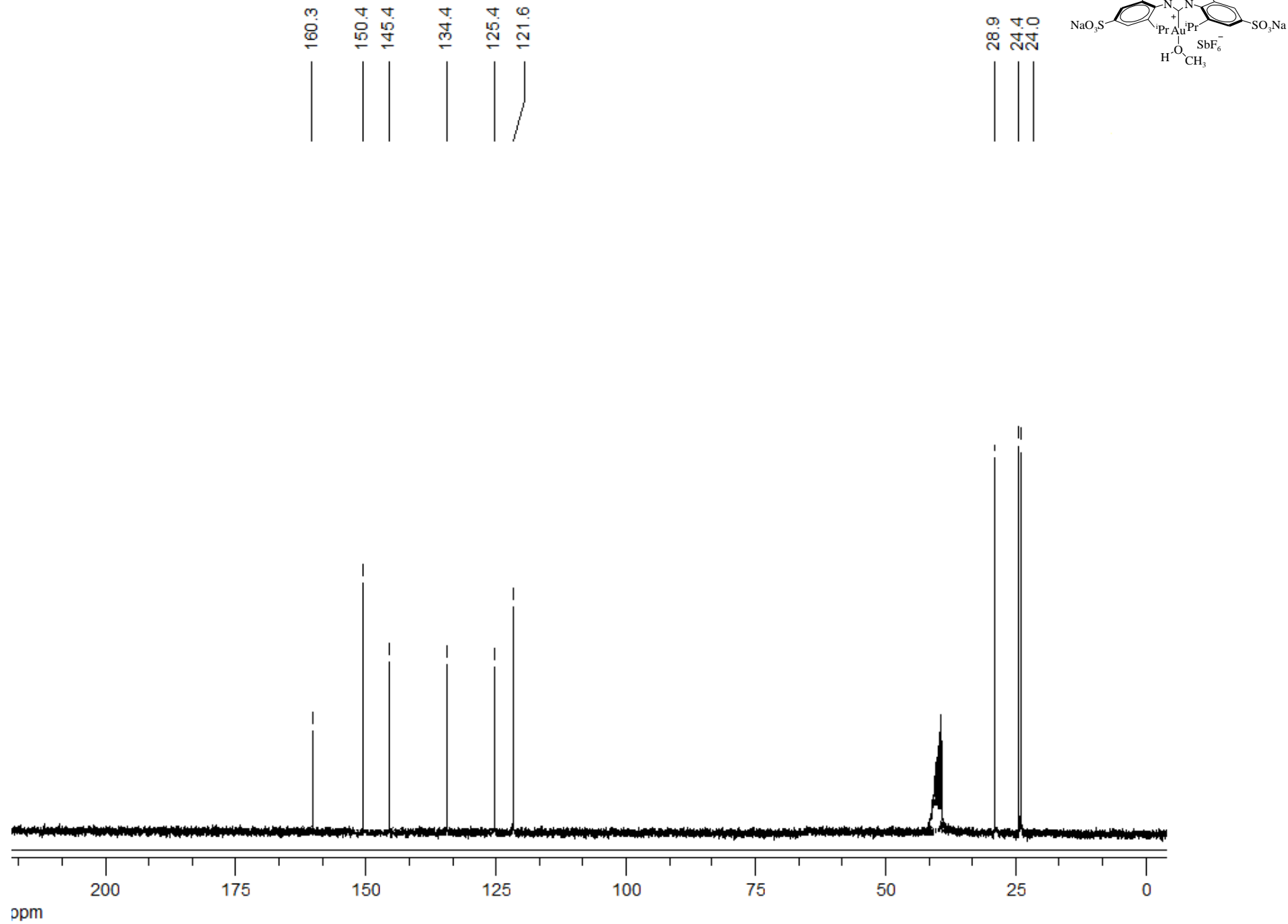
[1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene Au<sup>+</sup>(CH<sub>3</sub>OH)][SbF<sub>6</sub><sup>-</sup>](C6) (<sup>1</sup>H-RMN, D<sub>2</sub>O)



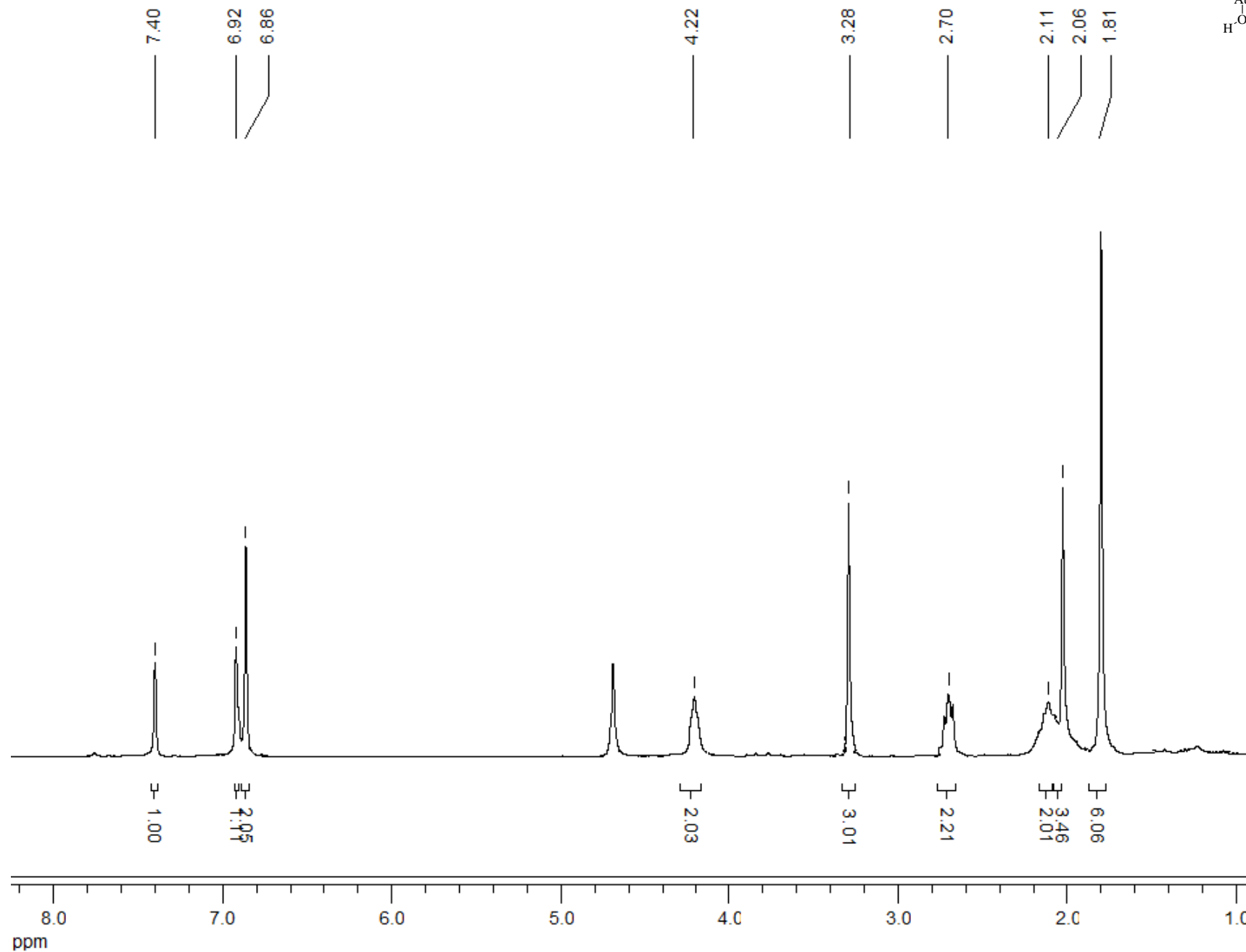
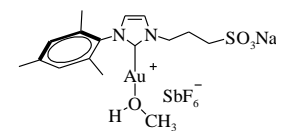
[1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene Au<sup>+</sup>(CH<sub>3</sub>OH)][SbF<sub>6</sub><sup>-</sup>](C6) (<sup>1</sup>H-RMN, DMSO-d<sub>6</sub>)



[1,3-bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene Au<sup>+</sup>(CH<sub>3</sub>OH)][SbF<sub>6</sub><sup>-</sup>](C6) (<sup>13</sup>C-RMN, DMSO-d<sub>6</sub>)



[1-mesityl-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene Au<sup>+</sup>(CH<sub>3</sub>OH)][SbF<sub>6</sub><sup>-</sup>](C7) (<sup>1</sup>H-RMN, D<sub>2</sub>O)



[1-mesityl-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene Au<sup>+</sup>(CH<sub>3</sub>OH)][SbF<sub>6</sub><sup>-</sup>](C7) (<sup>13</sup>C-RMN, D<sub>2</sub>O)

