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# SYNTHESIS, CHARACTERIZATION OF NEW ASYMMETRICALLY IMIDAZOLIUM SALTS WITH THEIR Ag(I) AND Pd(II)-*N*-HETEROCYCLIC CARBENE COMPLEXES

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**Abstract**: New substituted asymmetrically imidazolium salts with Ag(I) and Pd(II) *N*-heterocyclic carbene complexes were synthesized and characterized. In order to produce asymmetrically substituted salts, imidazolium salts have been produced using a variety of substituents, including aliphatic chain and phenyl acetamide chloride **(5,6,7)**. Using the carbene site deprotonation process, silver(I)-NHC complexes **(8,9,10)** were produced from the reaction of asymmetrically substituted imidazolium salts with $Ag_2O$. The appropriate Pd(II)-NHC **(11,12,13)** were then synthesized using the transmetallation process using Ag(I)-complexes. NHC as transfer reagents. The complexes were identified using spectroscopy methods such as $^{1}$H-, $^{13}$C-NMR and FT-IR spectroscopy. The recorded spectra of the prepared complexes and their salts agree with theoretical ones.

## Introduction

For many years, scientists have been fascinated by the structure and behavior of carbenes. Which were thought initially of be material transitory intermediates that were too reactive to be isolated.[1] Enormous advances in the field have enabled to the successfully isolate a large group of stable free

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carbenes.[2–5] Many carbenes and their complexes have found wide practical applications in synthesis, industries[6–9] and medicine.[10,11] Carbenes are neutral compounds characterized by a divalent carbon atom that has only six electrons in its valence shell. The carbene is linked to two atoms by single covalent bonds, and it possesses two nonbonding electrons that determine the geometry and reactivity of the carbenes.[12,13]

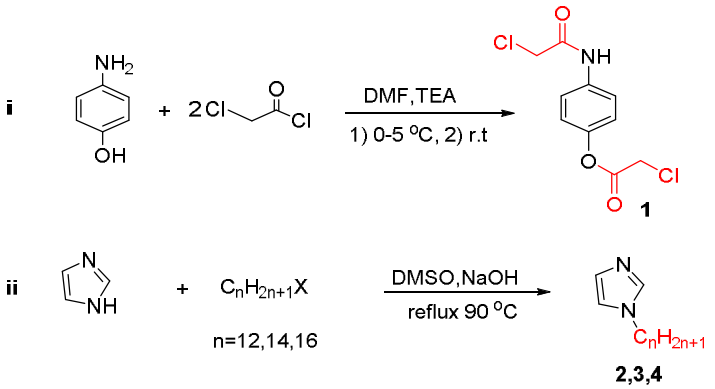
Stable carbenes have attracted a lot of interest from many researchers over the past few decades.[14] A carbon center in singlet carbene compounds carries a single electrons pair in a $sp^2$ hybridization orbital, leaving empty a p orbital. There are also known triplet carbenes the two electrons are each resides in a degenerate p orbital.[15] *N*-Heterocyclic carbenes (NHCs) are a specific form of this class of carbene compounds. In the first not widely applied in chemistry, despite the fact that NHCs had been known since the groundbreaking work of Wanzlick, who observed their dimerization[16] and was able to trap them to form mercury-salt carbene complexes,[17] It took thirty years until the first NHC was isolated. In the following years, while Bertrand and co-workers described in 1988 the stable carbenes, which did not act as a ligand,[18] and the first isolable carbenes were reported 1991 by Arduengo.[19] They have now been use in a broad range of fields, including organocatalysis[8] and organometallic chemistry.[20]

## Results and discussion

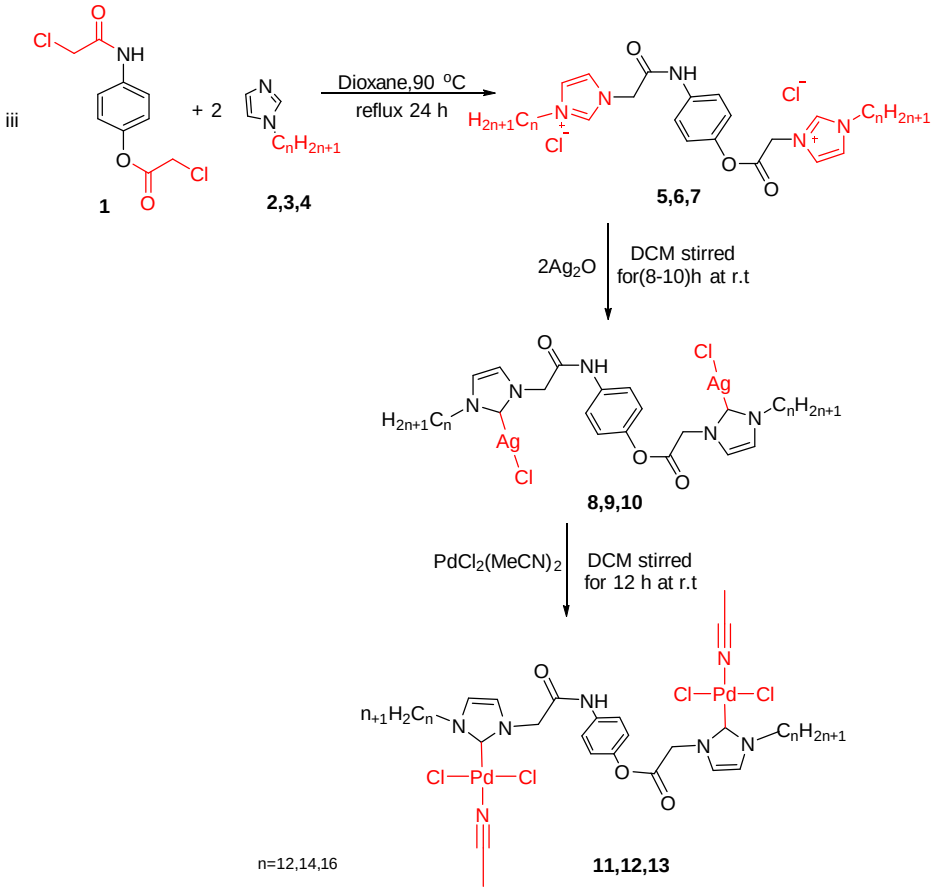
### *NHCs precursors and complexes*

Compound 4-(2-chloroacetamido)phenyl-2-chloroacetate **(1)** (i- in Scheme 1) was prepared, and subsequently used to prepare the compounds **(7, 6 and 5)** after its reaction with the fashioned N-imidazole **(2, 3 and 4)** (ii-in Scheme 1) in 4-dioxane, and refluxing the mixture while being stirred

at (90°C) for 24 hours to prepare the ligands. Moreover (iii-**1** in Scheme 2), it was stable in air and humidity, soluble in certain common solvents including DCM, DMF and DMSO, but insoluble in other solvents including diethyl ether, benzene, and water. Ag(I)-NHC **(8, 9 and 10)** were prepared in accordance with a documented process (iii-**2** in Scheme 2), by reacting silver oxide *in situ* with the corresponding imidazolium salts **(7, 6 and 5)**, respectively. The reaction of $Ag_2O$ with an imidazolium salt in dichloromethane for ten hours at room temperature results in complexes with good yields when processed properly in glassware covered by aluminum foil to block light from them. All reactions produced a dark suspension that was filtered with a celite pad to get rid of extra $Ag_2O$. The solvent was then eliminated at decreased pressure, to give the complexes as dark-brown oil. Palladium **(11, 12 and 13)** complexes were synthesized by using transmetallation method. (iii-**3** in Scheme 2), in which $PdCl_2(CH_3CN)_2$ reacted with Ag(I)-NHC complexes by stirring them in dichloromethane (DCM) for six hours at room temperature. It resulted in the production of new Pd(II)-NHC complexes after appropriate treatment with good yields when processed properly in glassware covered with light-blocking aluminum foil. All reactions produced a dark suspension that was filtered through celite to remove precipitated AgCl. The solvent was then eliminated under reduced pressure, to give the complexes as pale-brown oil. Ag(I)-NHC and Pd(II)-NHC complexes are soluble in some organic solvents, such as acetone, acetonitrile, DCM, DMF and DMSO, but it is insoluble in other solvents including benzene, diethyl ether and water. Synthesis of complexes **(1-13)** is shown in Schemes 1 and 2.




**Scheme 1. (i)** Synthesis of phenyl acetamide chloride **(1)**, **(ii)** *N*-substituted imidazole **(2, 3, 4)**.




**Scheme 2. (iii-1)** 1,3-disubstituted imidazolium salts **(5, 6, 7)** (NHC) precursors, **(iii-2)** their corresponding Ag(I)-NHC **(8, 9, 10)** and **(iii-3)** Pd(II)-NHC **(11, 12, 13)** complexes.

*FT-IR spectroscopy*

When compared ligands (NHCs) and their suitable metal complexes (M-NHCs), the utilization of FT-IR spectra can provide some useful information. All imidazolium salts, as well as their Ag(I) and Pd(II) complexes, had infrared spectra recorded (in Figures 3, 4 and 5). The bands seen in the imidazolium salt between 3233 and 3212 $cm^{-1}$ are caused by N-H stretching. The expansion bands are seen for ($C=O_{ester}$) at 1758–1741 $cm^{-1}$, and ($C=O_{amide}$) at 1684–1673 $cm^{-1}$. A second band, attributed to the C-N stretch, is seen in the 1244–1200 $cm^{-1}$ range. Most of the aforementioned bands are displaced up or down in Ag(I)-NHC and Pd(II)-NHC complexes, and this may be regarded as a preliminary sign of effective complication with Ag and Pd[21] (Table 1).

*NMR spectroscopy*

All NMR spectra for the matching imidazolium salts, Ag(I)-NHC and Pd(II)-NHC complexes were obtained in $d_6$-DMSO, (Figures 8, 9, 10, 13, 14, and 15). The $^1$H-NMR spectra display the expected signals for this group of synthesized complexes. An (N-H) proton specific signal in the range of (10.25 ppm) was observed, in the $^1$H-NMR of imidazolium salts **(5-7)**. In the range of 9.24 - 9.22 ppm, imidazolium H2' significant signals were seen. Multiple peaks of aromatic protons (Ar-H) in the range of 7.83-7.37 ppm were observed. H5'/H4' imidazolium protons, however, showed multiple peaks in the range of 7.41–7.38 ppm (Figure 8). In both Ag(I)-NHC and Pd(II)-NHC complexes **(8-13)**, the $^1$H-NMR spectra showed no H2' signals, which is a specific pattern of imidazolium salts. According to the literature, attributed to the successful coordination with the metals used, (Ar-H) aromatic protons are in the range of 7.83-7.37 ppm. They appeared as

multiple peaks, while the protons of H5'/H4' imidazolium salts appeared in a range of 6.99-6.48 ppm (Figures 9 and 10 and table 2)[22–24]. In $^{13}$C-NMR spectrum, the most significant signals are the one furnished by imidazolium C2' that could be seen at 153.80 ppm (Figure 13), and the distinct signals for carbene carbon-Ag and carbine carbon-Pd that lay at 188.64 ppm for Ag(I)-NHCs and 183.98 ppm for Pd(II)-NHC complexes (Figures 14 and 15 and table 3).

All of these observations are in good agreement with the literature data on the preparation and complexation of imidazolium salts.[25–27]

**Table 1.** FT-IR peaks of compounds.

| Com. | N-H | C-H aromatic | C-H asy-aliph | C-H sy-aliph | C=O ester | C=O amide | C=C | C-N | C≡N |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3268 | 3060 | 2947 | _ | 1761 | 1673 | _ | 1200 | _ |
| 2 | _ | 3057 | 2920 | 2854 | _ | _ | 1563 | 1232 | _ |
| 3 | _ | 3063 | 2919 | 2853 | _ | _ | 1564 | 1233 | _ |
| 4 | _ | 3033 | 2916 | 2850 | _ | _ | 1561 | 1234 | _ |
| 5 | 3237 | 3058 | 2921 | 2853 | 1744 | 1685 | 1554 | 1247 | _ |
| 6 | 3219 | 3052 | 2921 | 2853 | 1745 | 1684 | 1553 | 1244 | _ |
| 7 | 3252 | 3062 | 2918 | 2852 | 1762 | 1688 | 1549 | 1243 | _ |
| 8 | 3208 | 3055 | 2920 | 2853 | 1731 | 1653 | 1558 | 1242 | _ |
| 9 | 3233 | 3065 | 2921 | 2853 | 1758 | 1682 | 1555 | 1233 | _ |
| 10 | 3249 | 3089 | 2918 | 2851 | 1747 | 1690 | 1563 | 1247 | _ |
| 11 | 3237 | 3055 | 2919 | 2853 | 1732 | 1652 | 1566 | 1232 | 2258 |
| 12 | 3212 | 3063 | 2917 | 2852 | 1741 | 1681 | 1558 | 1212 | 2257 |
| 13 | 3246 | 3054 | 2916 | 2851 | 1727 | 1685 | 1557 | 1242 | 2258 |

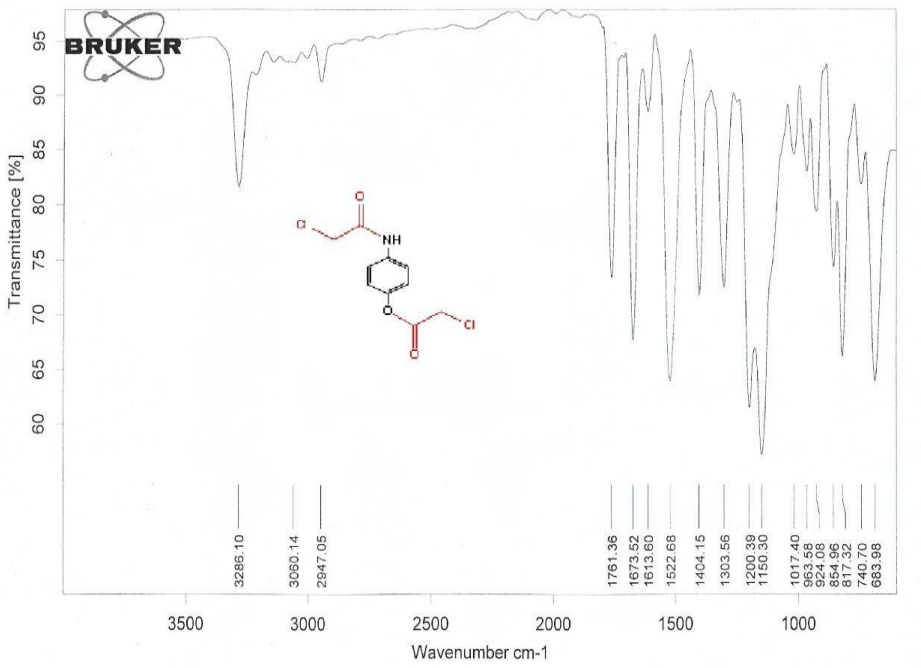



**Figure 1.** FT-IR spectrum of compound **1.**

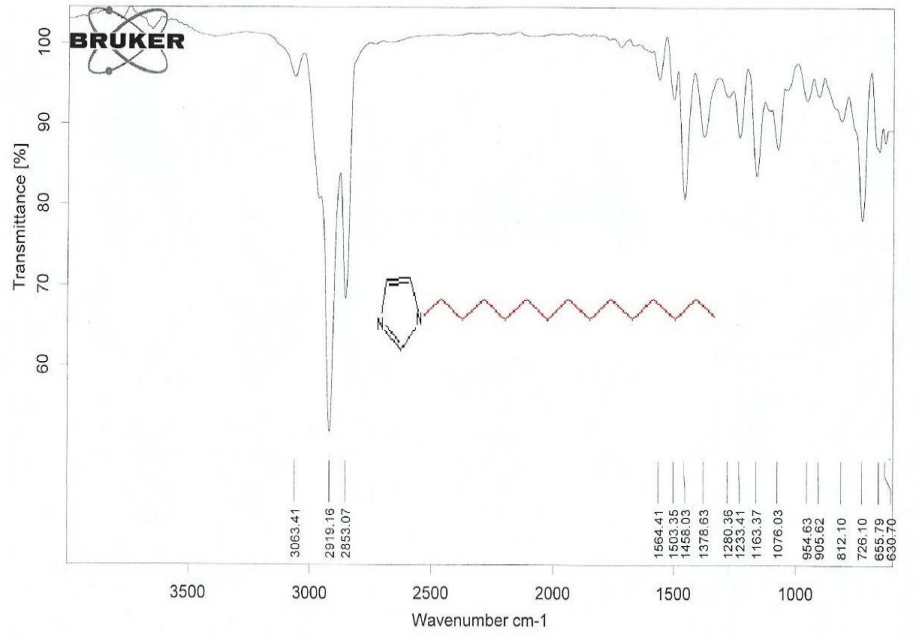



**Figure 2.** FT-IR spectrum of compound **3.**

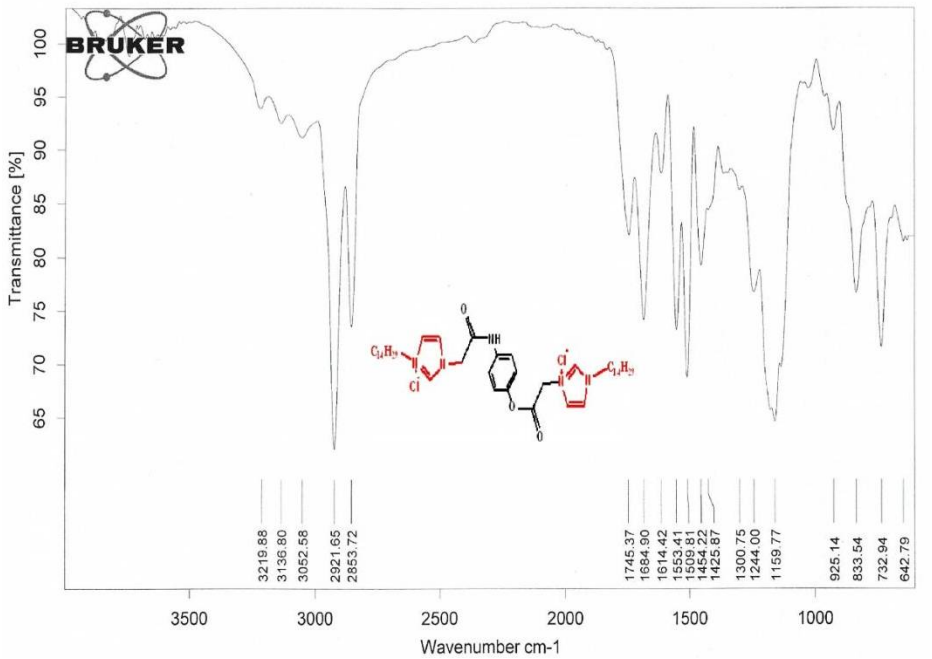



**Figure 3.** FT-IR spectrum of compound **6.**

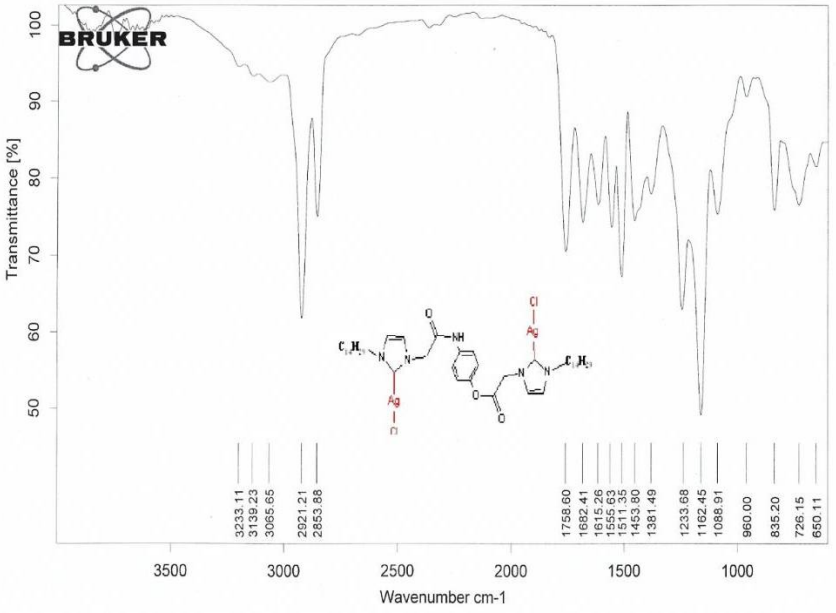



**Figure 4.** FT-IR spectrum of compound **9.**

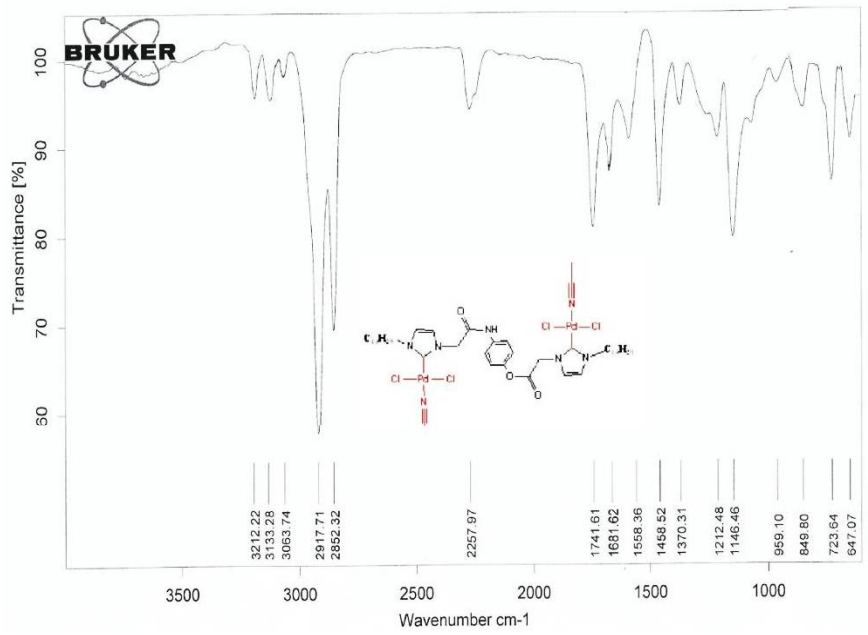



**Figure 5.** FT-IR spectrum of compound **12.**

**Table 2.** $^{1}$H-NMR Chemical shift range of compounds

| Com. | N-H | NCHN | Ar-H | NCH im | N-$CH_2$ | ester-$CH_2$ | amide-$CH_2$ | CN-$CH_3$ | N-$CH_2$-$\underline{CH_2}$ | $CH_2$ alip | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 10.42 | _ | 7.66-7.14 | _ | _ | 4.69 | 4.21 | _ | _ | _ | _ |
| **3** | _ | 7.65 | _ | 7.01-6.75 | 4.27-4.23 | _ | _ | _ | 1.85-1.75 | 1.35-1.17 | 0.99-0.95 |
| **6** | 10.25 | 9.24, 9.22 | 7.83-7.76 | 7.41-7.36 | 5.22-5.16 | 4.28 | 4.22 | _ | 1.81-1.74 | 1.28-1.17 | 0.86-0.83 |
| **9** | 10.18 | _ | 7.82-7.37 | 6.74-6.68 | 4.18-4.15 | 3.93 | 3.91 | _ | 1.82-1.75 | 1.27-1.17 | 0.87-0.84 |
| **12** | 10.23 | _ | 7.83-7.46 | 6.99-6.84 | 4.18-4.14 | 3.93 | 3.92 | 2.09 | 1.81-1.74 | 1.29-1.17 | 0.87-0.83 |

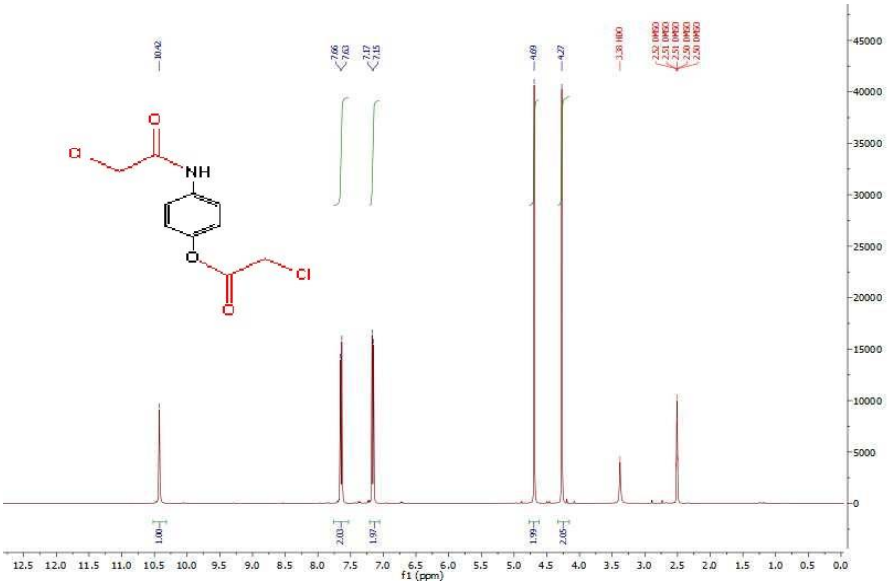



**Figure 6.** $^{1}$H-NMR spectrum of compound **1.**

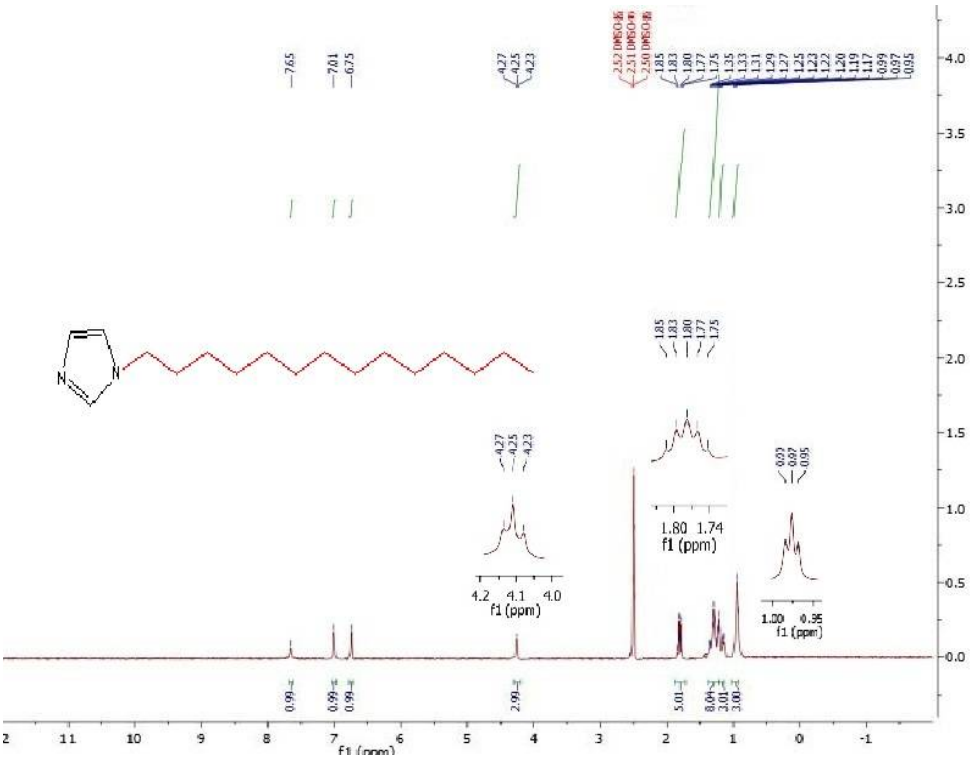



**Figure 7.** $^{1}$H-NMR spectrum of compound **3.**

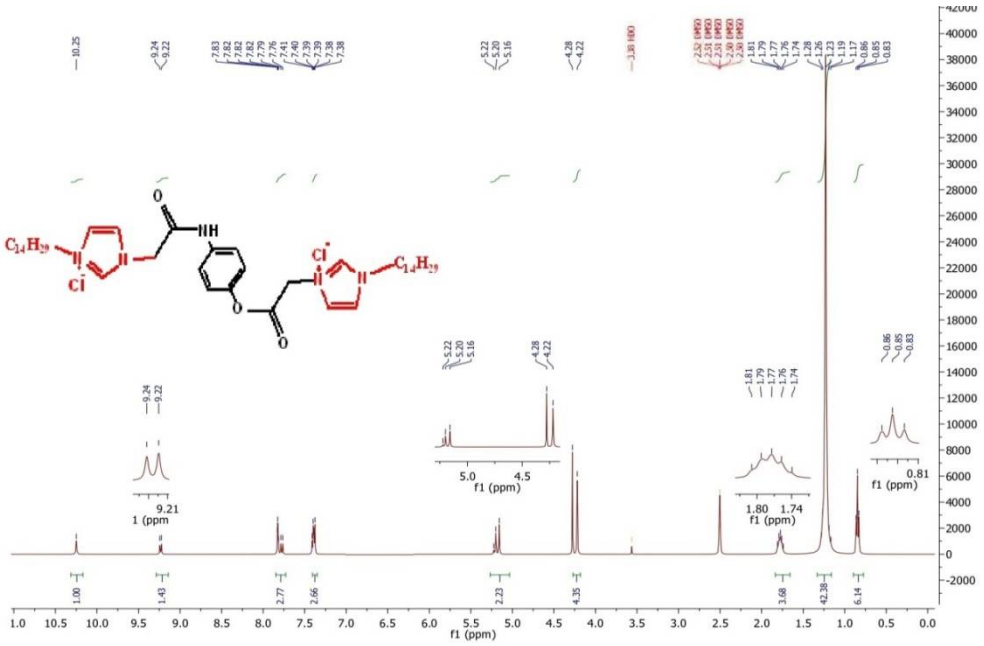


**Figure 8.** $^{1}$H-NMR spectrum of compound **6.**

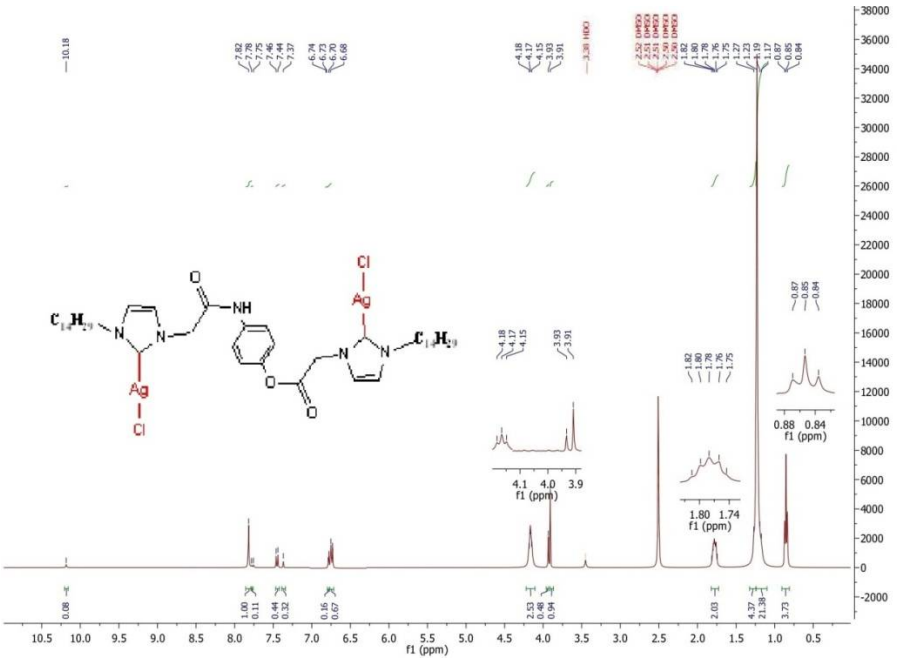


**Figure 9.** $^{1}$H-NMR spectrum of compound **9.**

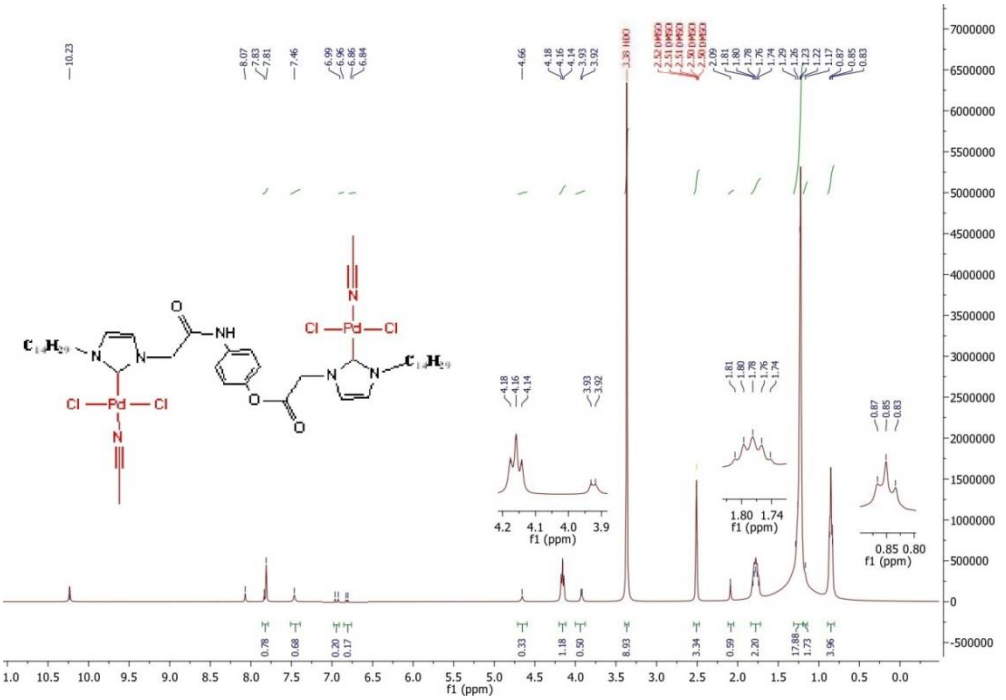



**Figure 10.** $^{1}$H-NMR spectrum of compound **12.**

**Table 3.** $^{13}$C-NMR chemical shift range of compounds.

| Com. | C=O amid | C=O ester | NCHN | Ar-C-O | Ar-C-N | Ar-C | amide-$CH_2$ | ester-$CH_2$ | N-$CH_2$ | $CH_2$ | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 167.01 | 165.17 | _ | 146.37 | 136.95 | 122.35, 120.88 | 43.99 | 41.79 | _ | _ | _ |
| **3** | _ | _ | 138.43 | _ | _ | _ | _ | _ | 47.54 | 31.88-22.03 | 14.05 |
| **6** | 168.60 | 168.18 | 153.80 | 137.18 | 130.15 | 124.06-120.82 | 43.55 | 41.55 | 40.43 | 31.35-22.15 | 14.01 |
| **9** | 174.18 | 170.13 | 183.95 | 136.04 | 130.13 | 122.53-120.84 | 59.55 | 48.86 | 43.55 | 31.35-22.15 | 14.00 |
| **12** | 175.38 | 161.33 | 188.64 | 147.45 | 136.41 | 130.74-122.96 | 51.27 | 49.30 | 42.11 | 31.78-22.58 | 14.43 |

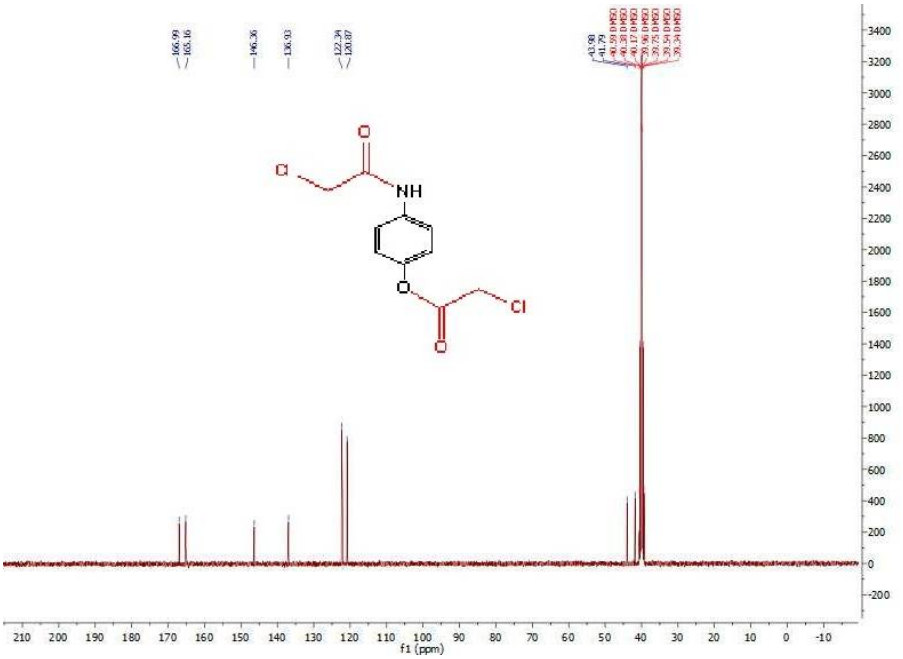



**Figure 11.** $^{13}$C-NMR spectrum of compound **1.**

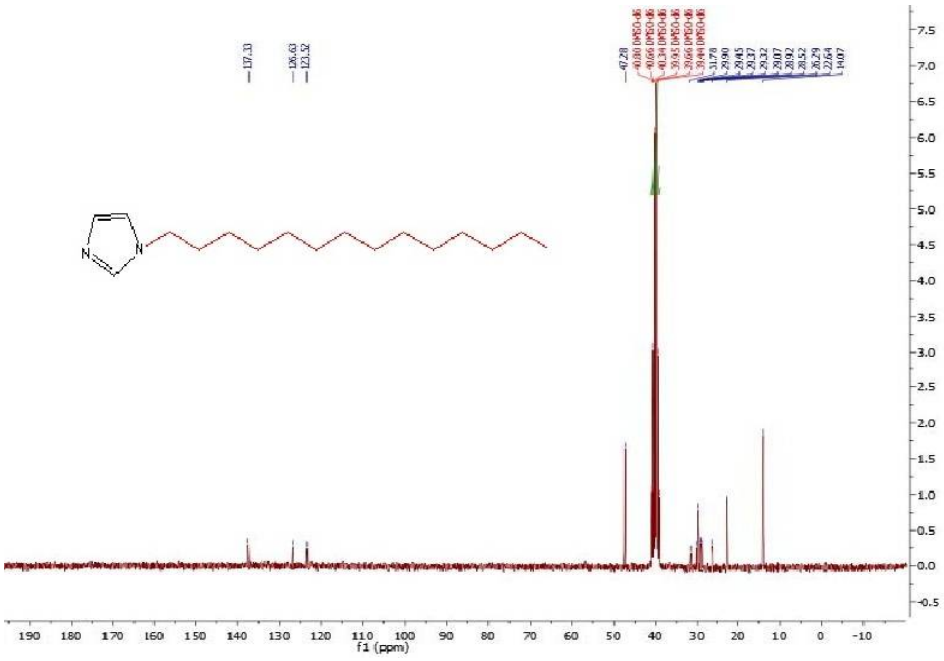



**Figure 12.** $^{13}$C-NMR spectrum of compound **3.**

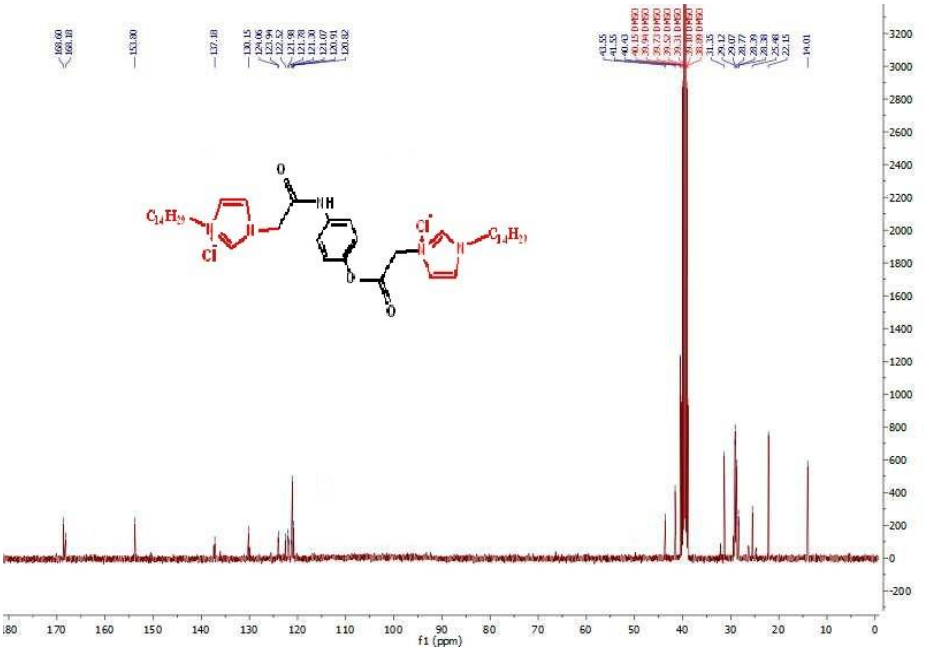



**Figure 13.** $^{13}$C-NMR spectrum of compound **6.**

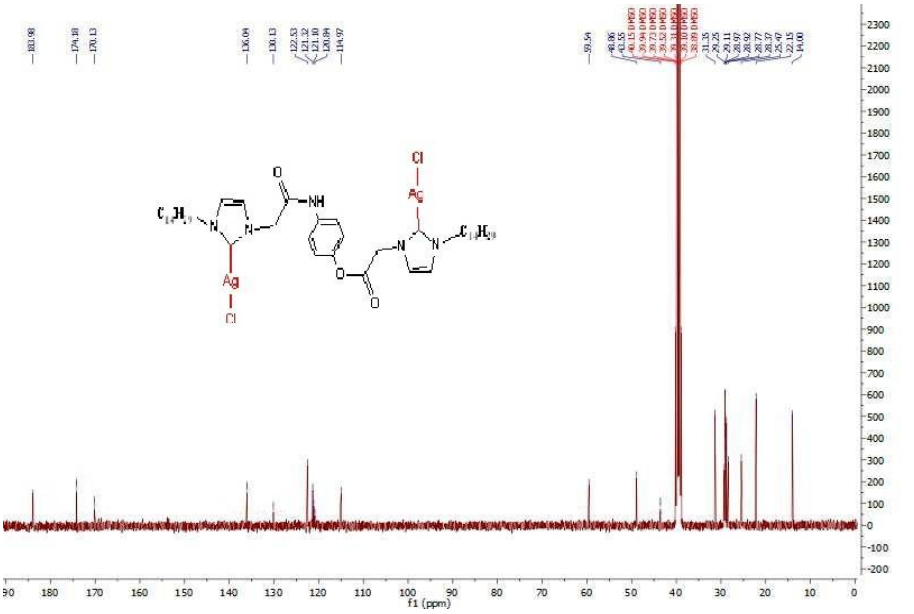



**Figure 14.** $^{13}$C-NMR spectrum of compound **9.**

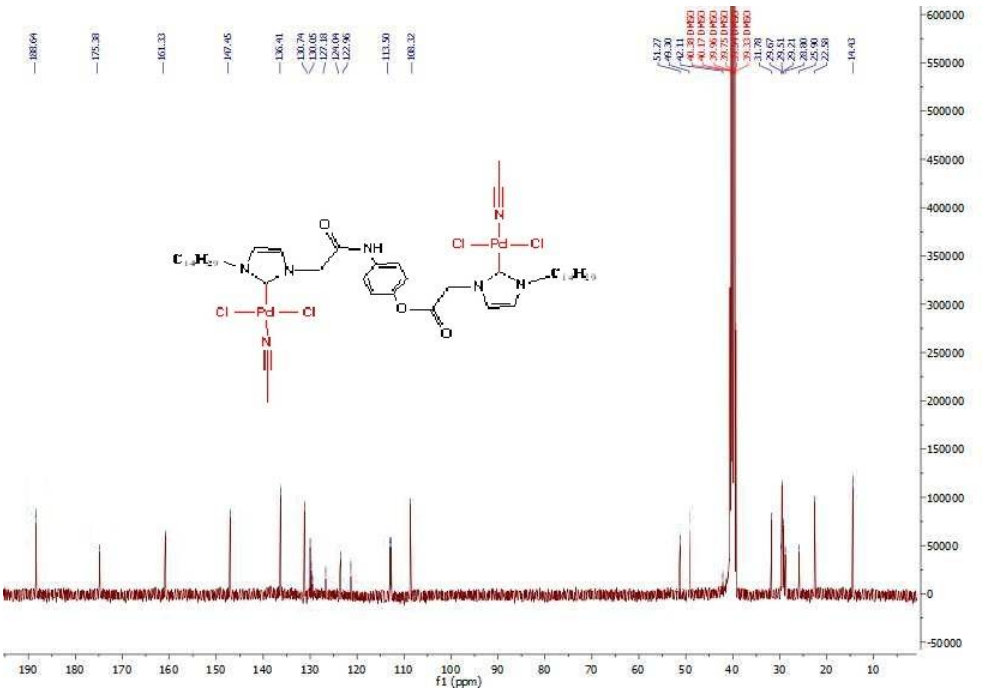



**Figure 15.** $^{13}$C-NMR spectrum of compound **12.**

## Experimental

*Materials and instrumentation*

All chemicals ($Ag_2O$, $PdCl_2(MeCN)_2$, imidazole, aliphatic chain bromide, and *p*-aminophenol) and used solvents were of the highest analytical quality and were not purified before use. Bruker 400 MHz spectrometer was used to record nuclear magnetic resonance (NMR) spectra at room temperature. Chemical shifts (ppm) were compared to signals from the solvent $d_6$-DMSO. FT-IR spectra were acquired with a Bruker FTIR-spectrophotometer in a 4000 to 600 $cm^{-1}$ wavenumber range.

*Procedures*

*Synthesis of 4-(2-chloroacetamido)phenyl 2-chloroacetate (1)*[28]

It was synthesized according with the procedure from the literature[28] using (1.09 g, 10 mmol) of *p*-aminophenol dissolved in DMF (20 mL). Then triethylamine (TEA) (1.5 mL) was added, and the mixture was stirred for

20 minutes, after which chloroacetyl chloride (1:2) (3 g, 20 mmol) was added dropwise at (0–5 °C), and the mixture was stirred for another 30 minutes at room temperature (i- in scheme 1). After completion of the reaction, the reaction mixture was filtered and washed with distilled water, and then recrystallized with absolute ethanol, to give 3.4 g (85 % yield) as a fine pale brown powder (m.p = 257-260°C). FT-IR $cm^{-1}$: 3268 (N-H), 3060 (C-H $_{aromatic}$), 2947 (C-H $_{aliph}$), 1761 (C=O $_{ester}$), 1673 (C=O $_{amide}$), 1200 (C-N). $^{1}$H-NMR (400 MHz, $d_6$-DMSO) δ, ppm: 10.42 (s, H, N-H), 7.66-7.14 (m, 4H, Ar-H), 4.69 (s, 2H, ester-$CH_2$), 4.21 (s, 2H, amide-$CH_2$). $^{13}$C-NMR (100 MHz, $d_6$-DMSO) δ, ppm: 167.01 (C=O $_{amide}$), 165.17 (C=O $_{ester}$), 146.37 (Ar-C-O), 136.95 (Ar-C-N), 122.35, 120.88 (Ar-C), 43.99 (amide-$CH_2$), 41.79 (ester-$CH_2$).

*General procedure for the syntheses of N-substituted imidazole (2, 3, 4)*[29]

Compounds **(2, 3, 4)** were synthesized according with the procedure from the literature[29] using imidazole and NaOH powder were put into a round bottom flask. The mixture of starting materials was mixed with 20 mL of DMSO, and the formed mixture of reactants was stirred at 90 °C for 2 hours. After cooling to 30 °C, 5 g of alkyl bromide was cautiously added dropwise while being stirred continuously. After full alkyl bromide was added at low temperature, the mixture was continue stirred for 1 hour at 40 °C (ii- in scheme 1). Then, 10 mL of crushed ice was poured into the solution, the mixture was left for 1 hour before extraction with distilled water and DCM (3 x 10 mL).

*Preparation of 1-dodecyl-1H-imidazole (2)*

It was obtained according to the above-mentioned general procedure from (1.36 g, 20 mmol) imidazole dissolved in 20 mL of DMSO, (0.8 g,

20 mmol) NaOH powder and (5 g, 20 mmol) of 1-bromododecane. The mixture was added to 10 mL of crushed ice and the mixture was left for 1 hour before extraction was using distilled water and DCM (3 x 10 mL). Then the solvent was removed using a rotary evaporator to obtain the product as a pure yellow oil, 4 g (84 %). FT-IR $cm^{-1}$: 3057 (C-H $_{aromatic}$), 2920 (C-H $_{asy\text{-}aliph}$), 2854 (C-H $_{sy\text{-}aliph}$), 1563 (C=C), 1232 (C-N).

*Preparation of 1-tetradecyl-1H-imidazole (3)*

It was obtained according to the above-mentioned general procedure from (1.2 g, 18 mmol) imidazole dissolved in 20 mL of DMSO, (0.72 g, 18 mmol) NaOH powder and 1-bromotetradecane (5 g, 18 mmol). The mixture was added to 10 mL of crushed ice and the mixture was left for 1 hour before extraction was using distilled water and DCM (3 x 10 mL). Then the solvent is removed using a rotary evaporator to obtain the product as a pure yellow oil, 4.2 g (89 % yield). FT-IR $cm^{-1}$: 3063 (C-H $_{aromatic}$), 2919 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 1564 (C=C), 1233 (C-N). $^{1}$H-NMR δ, ppm: 7.65 (s,H, NCHN), 7.01 (s, 1H, NCH im), 6.75 (s, 1H, CHN im), 4.27-4.23 (t, 2H, N-$CH_2$), 1.85-1.75 (p ,2H, $CH_2$), 1.35-1.17 (m, 18H, $CH_2$), 0.99-0.95 (t, 3H, $CH_3$). $^{13}$C-NMR δ, ppm: 138.43 (NCHN), 126.55 (CH–im), 123.32 (CH–im), 47.54 (N-$CH_2$), 31.88-22.03 ($CH_2$), 14.05 ($CH_3$).

*Preparation of 1-hexadecyl-1H-imidazole (4)*

It was obtained according to the above-mentioned general procedure from (1 g, 16 mmol) imidazole dissolved in 20 mL of DMSO, (0.64 g, 16 mmol) NaOH powder and 1-bromohexadecane (5 g, 16 mmol). The mixture was added to 10 mL of crushed ice and the mixture was left for 1 hour before extraction was using distilled water and DCM (3 x 10 mL).

Then the solvent is removed using a rotary evaporator to obtain the product as a pure yellow oil, 4.9 g (81 % yield). FT-IR $cm^{-1}$: 3033 (C-H $_{aromatic}$), 2916 (C-H $_{asy\text{-}aliph}$), 2850 (C-H $_{sy\text{-}aliph}$), 1561 (C=C), 1234 (C-N).

*General Synthesis of 1,3-disubstiuted imidazolium salts (5, 6, 7)*[30]

Compounds **(5, 6, 7)** were synthesized according with the procedure from the literature[30] using compound **(1)** (1.31 g, 5 mmol) dissolved in 4-dioxane (20 mL), then compounds **(2, 3, 4)** (10 mmol) was added in a (1 : 2) ratio on the compound **(1)**. Then the solution was refluxed for 24 hours at 90°C (iii-1 in scheme 2). After the completion of the reaction the solvent was removed by using a rotary evaporator.

*Preparation of* **1***-dodecyl-3-(2-(4-(2-(1-dodecyl-1H-imidazol-3-ium-3-yl) acetamido) phenoxy)-2-oxoethyl)-1H-imidazol-3-ium (5)*

It was obtained according to the above-mentioned general procedure from compound **(1)** (1.31 g, 5 mmol), 4-dioxane (20 mL), and compound **(2)** (2.36 g, 10 mmol) (1:2). The solution was refluxed for 24 hours at 90°C. After the completion of the reaction the solvent was removed by using a rotary evaporator to get the product as dark-brown oil, 2.8 g (yield 78 %). FT-IR $cm^{-1}$: 3237 (N-H), 3058 (C-H $_{aromatic}$), 2921 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 1744 (C=O $_{ester}$), 1685 (C=O $_{amide}$), 1554 (C=C), 1247 (C-N).

*Preparation of 2-tetradecyl-3-(2-(4-(2-(1-tetradecyl-1H-imidazol-3-ium-3-yl)acetamido) phenoxy)-2-oxoethyl)-1H-imidazol-3-ium (6)*

It was obtained according to the above-mentioned general procedure from compound **(1)** (1.31 g, 5 mmol), 4-dioxane (20 mL), and compound **(3)** (2.64 g, 10 mmol). After the completion of the reaction the solvent was

removed by using a rotary evaporator to get the product as dark-brown oil, 3 g (yield 77 %). FT-IR $cm^{-1}$: 3219 (N-H), 3052 (C-H $_{aromatic}$), 2921 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 1745 (C=O $_{ester}$), 1684 (C=O $_{amide}$), 1553 (C=C), 1244 (C-N). $^{1}$H-NMR δ, ppm: 10.25 (s, H, NH amide), 9.24, 9.22 (s, 2H, NCHN), 7.83-7.76 (m, 4H,Ar-H), 7.41-7.36 (m, 2H, CHN im), 5.22-5.16 (t, 4H, N-$CH_2$), 4.28 (s, 2H, carbonyl-$CH_2$-N), 4.22 (s, 2H, carbonyl-$CH_2$-O), 1.81-1.74 (p, 4H, N-$CH_2$-$\underline{CH_2}$), 1.28-1.17 (m, $CH_2$ chain), 0.86-0.83 (t, 6H, $CH_3$). $^{13}$C-NMR δ, ppm: 168.60 (C=O $_{amide}$), 168.18 (C=O $_{ester}$), 153.80 (NCHN), 137.18 (Ar-C-N), 130.15 (Ar-C-O), 124.06-120.82 (Ar-C), 43.55 (carbonyl-$CH_2$-N), 41.55 (carbonyl-$CH_2$-O), 40.43 (N-$CH_2$), 31.35- 22.15 (-$CH_2$ chain), 14.01 (-$CH_3$ terminal).

*Preparation of* **3***-hexadecyl-3-(2-(4-(2-(1-hexadecyl-1H-imidazol-3-ium-3-yl)acetamido) phenoxy)-2-oxoethyl)-1H-imidazol-3-ium (7)*

Compound **(1)** (1.31 g, 5 mmol) was dissolved in 4-dioxane (20 mL), compound **(4)** (2.92 g, 10 mmol) dissolved in (10 mL) of 4-dioxane then was added, dropwise (1:2) over the compound **(1)**. Then the solution refluxed for 24 hours at 90°C. After the completion of the reaction the solvent was removed by using a rotary evaporator to get the product as dark-brown oil, 3.2 g (yield 80 %). FT-IR $cm^{-1}$: 3252 (N-H), 3062 (C-H $_{aromatic}$), 2918 (C-H $_{asy\text{-}aliph}$), 2852 (C-H $_{sy\text{-}aliph}$), 1762 (C=O $_{ester}$), 1688 (C=O $_{amide}$), 1549 (C=C), 1243 (C-N).

*General synthesis of silver(I)-NHC Complexes (8, 9, 10)*[31]

Compounds **(8, 9, 10)** of silver were synthesized according with the procedure described in the literature[31]**.** Silver oxide ($Ag_2O$) was added to the compounds **(5, 6, 7)** (1 g) dissolved in 20 mL DCM (2 : 1). The mixture stirred for 10 hours at room temperature in glassware covered by aluminum foil

(iii-2 in scheme 2). After that, the black mixture was filtered through celite to removed excess of $Ag_2O$ particles, then the solvent was removed using a rotary evaporator.

*Preparation of compound (8)*

It was obtained according to the above-mentioned general procedure from silver oxide ($Ag_2O$) (0.62 g, 2.72 mmol) and compound **(5)** solution (1 g, 1.36 mmol) dissolved in 20 mL DCM (2:1). The mixture stirred for 10 hours at room temperature in glassware covered by aluminum foil. After that, the black mixture was filtered through celite to removed excess of $Ag_2O$ particles, then the solvent was removed using a rotary evaporator to get the product as dark-brown oil, 1.2 g (75 % yield), FT-IR $cm^{-1}$: 3208 (N-H), 3055 (C-H $_{aromatic}$), 2029 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 1731 (C=O $_{ester}$), 1653 (C=O $_{amide}$), 1558 (C=C), 1242 (C-N).

*Preparation of compound (9)*

It was obtained according to the above-mentioned general procedure from silver oxide ($Ag_2O$) (0.58 g, 2.6 mmol) and compound **(6)** (1 g, 1.3 mmol) dissolved in 20 mL DCM (2 : 1). The mixture was stirred for 10 hours at room temperature in glassware covered by aluminum foil. After that, the black mixture was filtered through celite to removed excess of $Ag_2O$ particles, then the solvent was removed using a rotary evaporator to get the product as dark-brown oil, 1 g (70 % yield), FT-IR $cm^{-1}$: 3233 (N-H), 3065 (C-H $_{aromatic}$), 2921 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 1758 (C=O $_{ester}$), 1682 (C=O $_{amide}$), 1555 (C=C), 1233 (C-N). ). $^1$H-NMR δ, ppm: 10.18 (s, H, NH amide), 7.82-7.37 (m, 4H, Ar-H), 6.74-6.68 (m, 2H, CHN im), 4.18-4.15 (t, 4H, N-$CH_2$), 3.93 (s, 2H, carbonyl-$CH_2$-N), 3.91 (s, 2H, carbonyl-$CH_2$-O), 1.82-1.75 (p, 4H, N-$CH_2$-$\underline{CH_2}$), 1.27-1.17 (m,

$CH_2$ chain), 0.87-0.84 (t, 6H, $CH_3$). $^{13}$C-NMR δ, ppm: 183.95 (NCN), 174.18 (C=O $_{amide}$), 170.13 (C=O $_{ester}$), 136.04 (Ar-C-N), 130.13 (Ar-C-O), 122.53-120.84 (Ar-C), 59.55 (carbonyl-$CH_2$-N), 48.86 (carbonyl-$CH_2$-O), 43.55 (N-$CH_2$), 31.35- 22.15 (-$CH_2$ chain), 14.00 (-$CH_3$ terminal).

*Preparation of compound (10)*

It was obtained according to the above-mentioned general procedure fromsilver oxide ($Ag_2O$) (0.55 g, 2.4 mmol) and compound **(7)** (1 g, 1.2 mmol) dissolved in 20 mL DCM (2:1). The mixture was stirred for 10 hours at room temperature in glassware covered by aluminum foil. After that, the black mixture was filtered by celitte to removed excess of $Ag_2O$ particles, then the solvent was removed using a rotary evaporator to get as a giving the product as dark-brown oil, 1.1 g (67 % yield), FT-IR $cm^{-1}$: 3249 (N-H), 3089 (C-H $_{aromatic}$), 2918 (C-H $_{asy\text{-}aliph}$), 2851 (C-H $_{sy\text{-}aliph}$), 1747 (C=O $_{ester}$), 1690 (C=O $_{amide}$), 1563 (C=C), 1247 (C-N).

*General synthesis of palladium(II)-NHC complexes (11, 12, 13)*[32]

Synthesis of Palladium compounds **(11, 12, 13)** was made according with the procedure in the literature[32]**.** Palladium complex [$PdCl_2(CH_3CN)_2$] was added to complexes **(8, 9, 10)** dissolved in 20 mL DCM. The mixture was stirred for 6 hours at room temperature in glassware covered by aluminum foil (iii-3 in scheme 2). After that, the black mixture was filtered through celite to remove the AgCl particles, then the solvent was removed using a rotary evaporator.

*Preparation of compound (11)*

It was obtained according to the above-mentioned general procedure from palladium complex [$PdCl_2(CH_3CN)_2$] (0.1 g, 0.38 mmol) and complex

**(8)** (0.36 g, 0.38 mmol) dissolved in (10 mL) of DCM. At the end the product was obtained as pale-brown oil, 0.35 g (76 % yield), FT-IR $cm^{-1}$: 3237 (N-H), 3055 (C-H $_{aromatic}$), 2919 (C-H $_{asy\text{-}aliph}$), 2853 (C-H $_{sy\text{-}aliph}$), 2258 (C≡N), 1732 (C=O $_{ester}$), 1652 (C=O $_{amide}$), 1566 (C=C), 1232 (C-N).

*Preparation of compound (12)*

It was obtained according to the above-mentioned general procedure from palladium complex $[PdCl_2(CH_3CN)_2]$ (0.1 g, 0.38 mmol) and complex **(9)** (0.38 g, 0.38 mmol) dissolved in (10 mL) of DCM. At the end the product was obtained as pale-brown oil, 0.34 g (70 % yield), FT-IR $cm^{-1}$: 3212 (N-H), 3063 (C-H $_{aromatic}$), 2917 (C-H $_{asy\text{-}aliph}$), 2852 (C-H $_{sy\text{-}aliph}$), 2257 (C≡N), 1741 (C=O $_{ester}$), 1681 (C=O $_{amide}$), 1558 (C=C), 1212 (C-N) . $^{1}$H-NMR δ, ppm: 10.23 (s, H, NH amide), 7.83-7.46 (m, 4H, Ar-H), 6.99-6.84 (m, 2H, CHN im), 4.18-4.14 (t, 4H, N-$CH_2$), 3.93 (s, 2H, carbonyl-$CH_2$-N), 3.92 (s, 2H, carbonyl-$CH_2$-O), 2.09 (s, 6H, CN-$CH_3$), 1.81-1.74 (p, 4H, N-$CH_2$-$\underline{CH_2}$), 1.29-1.17 (m, $CH_2$ chain), 0.87-0.83 (t, 6H, $CH_3$). $^{13}$C-NMR δ, ppm: 188.64 (NCN), 175.38(C=O $_{amide}$), 161.33 (C=$O_{ester}$), 147.45 (Ar-C-N), 136.41 (Ar-C-O), 130.74-122.96 (Ar-C), 113.50 (C≡N), 51.27 (carbonyl-$CH_2$-N), 49.30 (carbonyl-$CH_2$-O), 42.11 (N-$CH_2$), 31.78- 22.58 (-$CH_2$ chain), 14.43 (-$CH_3$ terminal).

*Preparation of compound (13)*

It was obtained according to the above-mentioned general procedure from palladium complex $[PdCl_2(CH_3CN)_2]$ (0.1 g, 0.38 mmol) and complex **(10)** (0.4 g, 0.38 mmol) dissolved in (10 mL) of DCM. At the end the product was obtained as pale-brown oil, 0.36 g (72 % yield), FT-IR $cm^{-1}$: 3246 (N-H), 3054 (C-H $_{aromatic}$), 2916 (C-H $_{asy\text{-}aliph}$), 2851 (C-H $_{sy\text{-}aliph}$), 2258 (C≡N), 1727 (C=O $_{ester}$), 1685 (C=O $_{amide}$), 1557 (C=C), 1242 (C-N).

## Conclusion

New Ag(I)-NHC and Pd(II)-NHC complexes **(8–13)** were synthesized from asymmetric imidazolium salts **(5–7)** as NHCs ligands. *In situ* reaction of ligands with $Ag_2O$ was gives Ag(I)-NHC complexes. Transmatellation method by reaction of Ag(l)-NHC with $PdCl_2(CH_3CN)_2$ was used to synthesized of Pd(II)-NHC complexes. The results of imidazolium salts isotopes and their complexes are in good agreement with these observations shown, by FT-IR, $^{1}$HNMR and $^{13}$CNMR spectroscopy.

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