

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

Ihab Hamid Mohammed and Mohammed Zghair Ghdhayeb*

*Department of Chemistry, Faculty of Science, University of Kufa, Kufa P.O.
BOX (21), Najaf, Iraq*

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 Ag₂O. 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 ¹H-, ¹³C-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

*Mohammed Ghdhayeb, *e-mail*: ehabhamed20@gmail.com

carbenes.²⁻⁵ Many carbenes and their complexes have found wide practical applications in synthesis, industries⁶⁻⁹ 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}

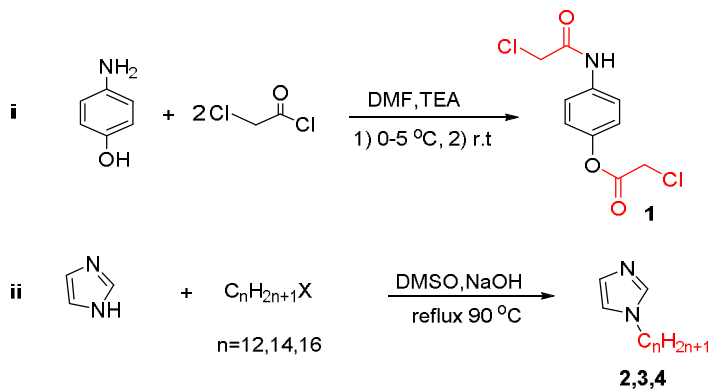
Stable carbenes have attracted a lot of interest from many researchers over the past few decades.¹⁴ A carbon center in singlet carbene compounds carries a single electrons pair in a sp^2 hybridization orbital, leaving empty a p orbital. There are also known triplet carbenes the two electrons are each 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 dimerization¹⁶ 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 organocatalysis⁸ and organometallic chemistry.²⁰

Results and discussion

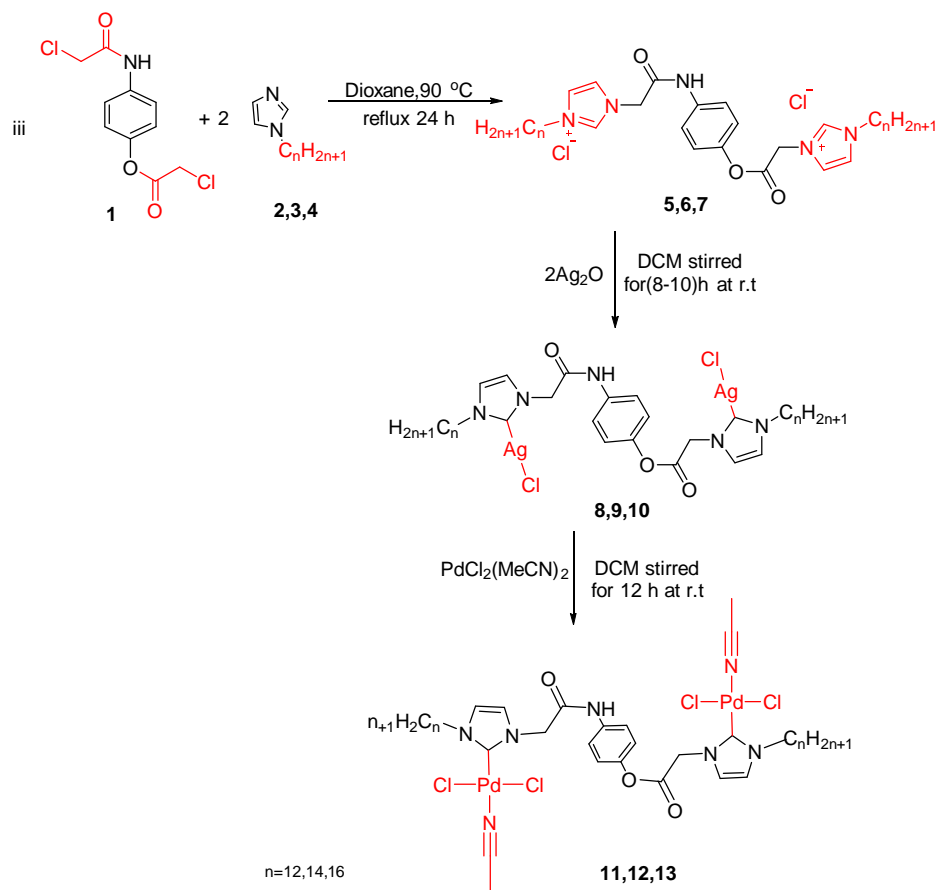
NHCs precursors and complexes

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 Ag₂O 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 Ag₂O. 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 PdCl₂(CH₃CN)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 ($\text{C}=\text{O}_{\text{ester}}$) at 1758–1741 cm^{-1} , and ($\text{C}=\text{O}_{\text{amide}}$) 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 Pd²¹ (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 ¹H-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 ¹H-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 ¹H-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 ¹³C-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 carbene 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

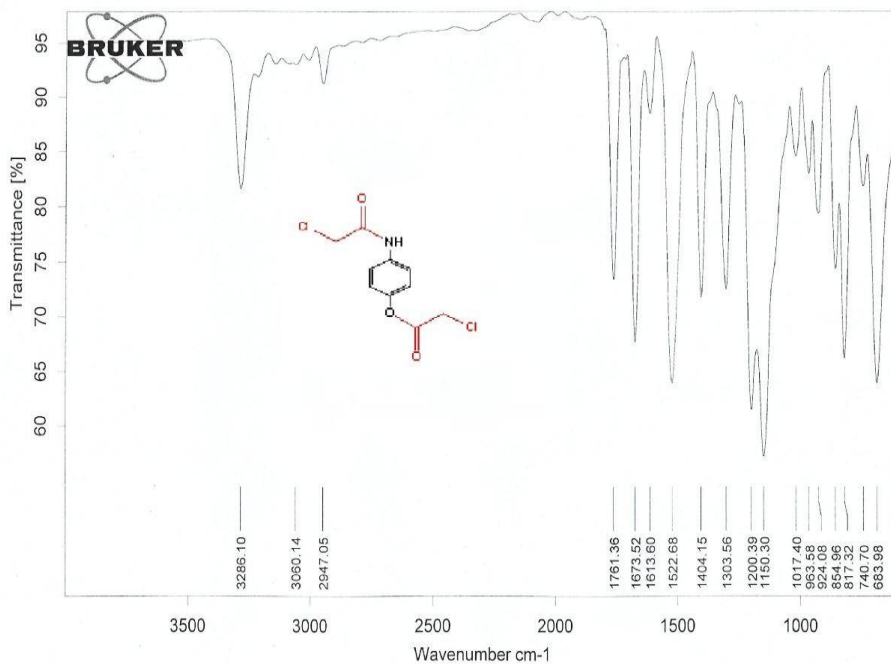


Figure 1. FT-IR spectrum of compound 1.

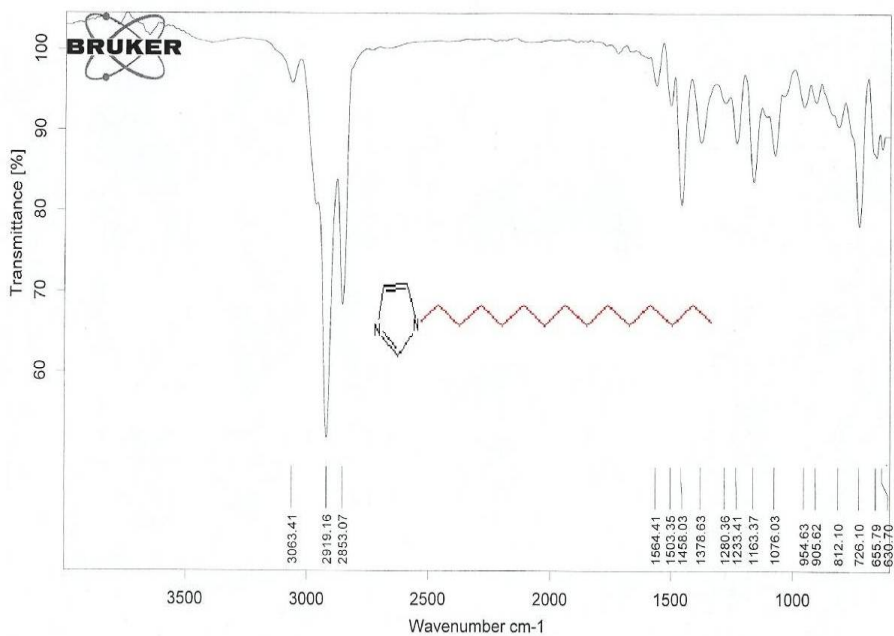


Figure 2. FT-IR spectrum of compound 3.

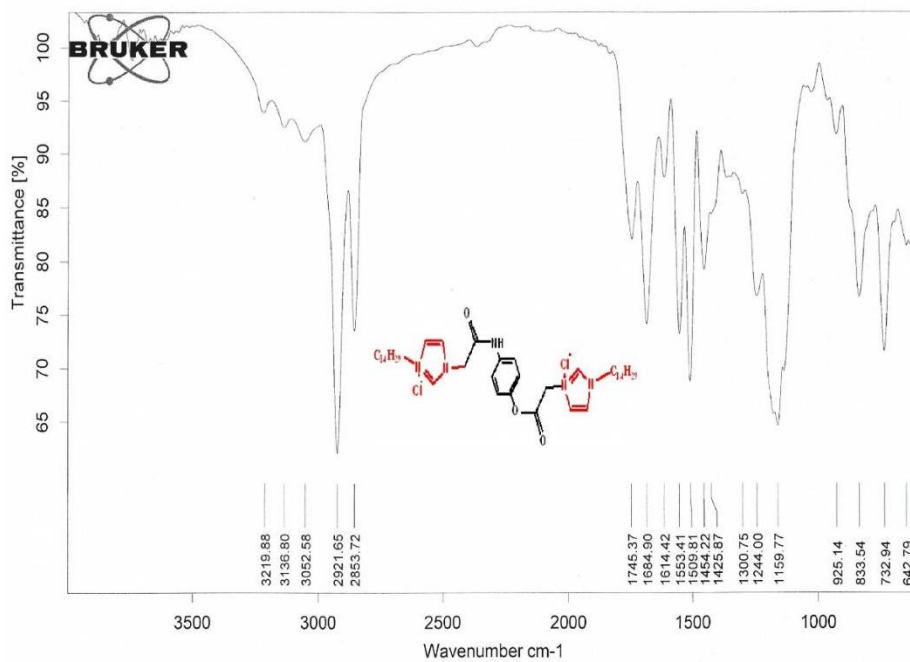


Figure 3. FT-IR spectrum of compound 6.

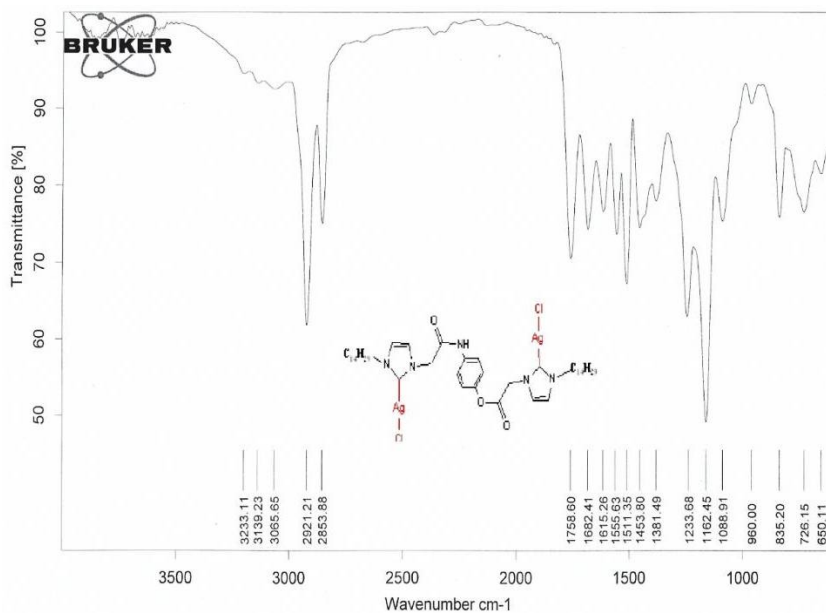


Figure 4. FT-IR spectrum of compound 9.

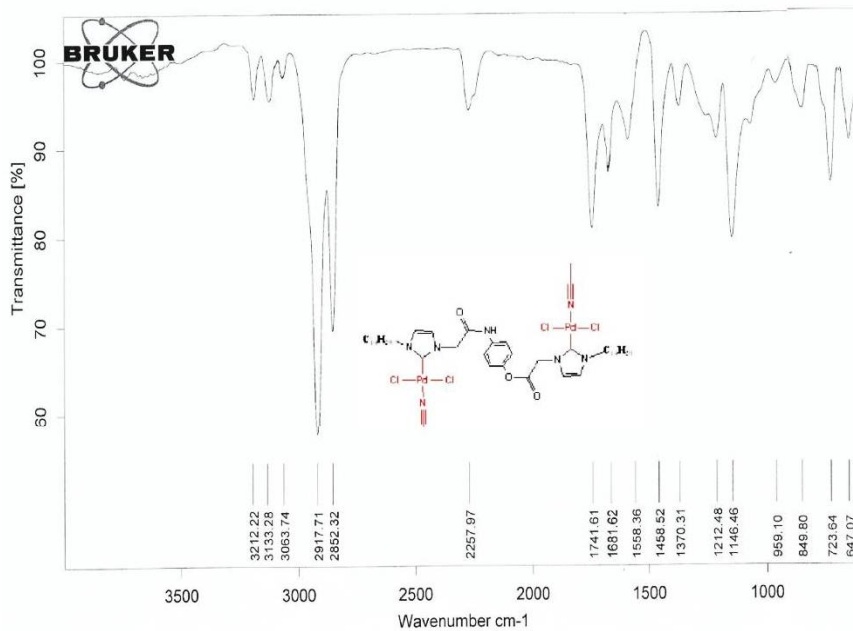


Figure 5. FT-IR spectrum of compound 12.

Table 2. $^1\text{H-NMR}$ 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 - <u>CH₂</u>	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

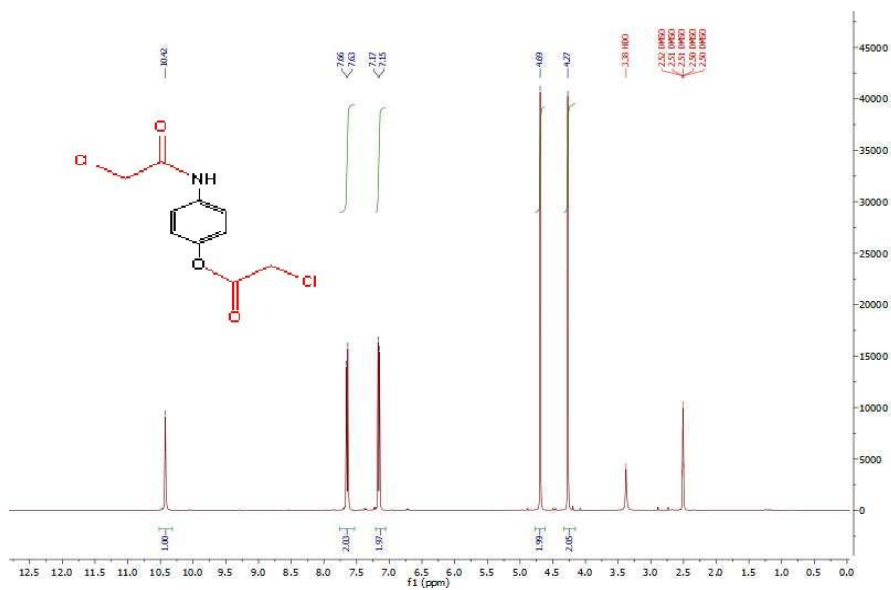


Figure 6. $^1\text{H-NMR}$ spectrum of compound 1.

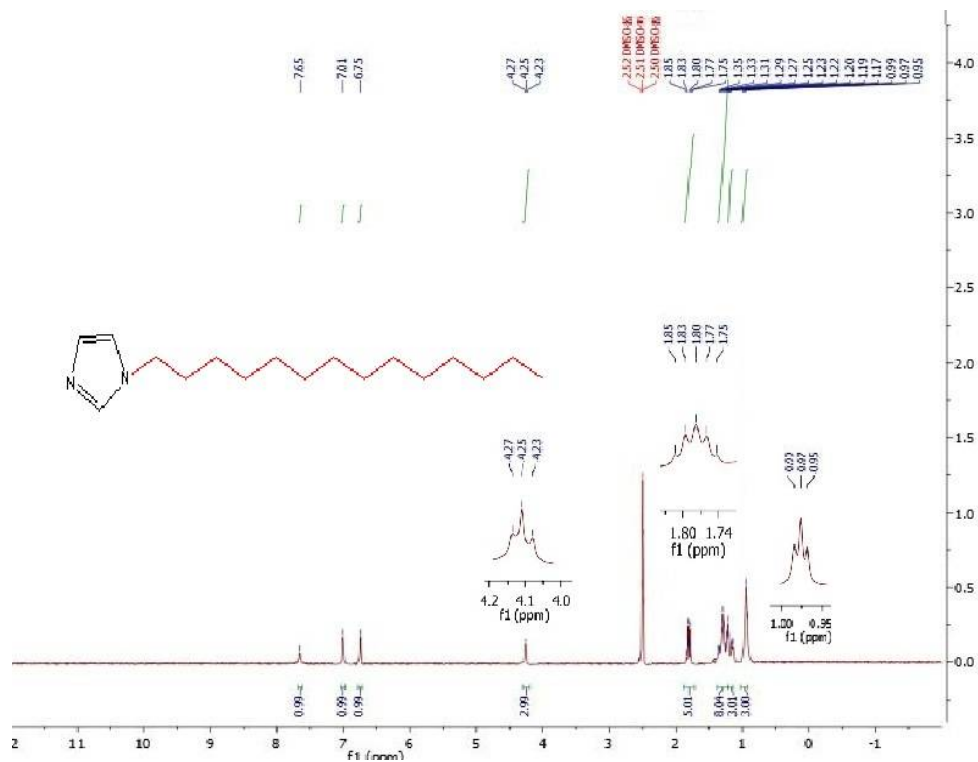


Figure 7. $^1\text{H-NMR}$ spectrum of compound 3.

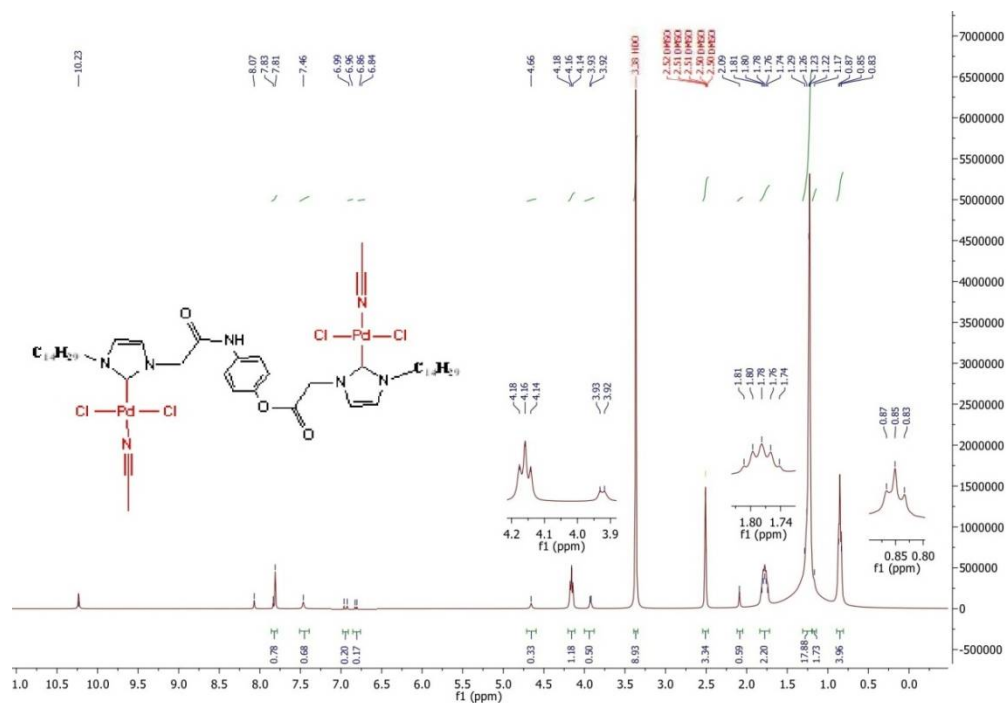


Figure 10. $^1\text{H-NMR}$ spectrum of compound **12**.

Table 3. $^{13}\text{C-NMR}$ 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

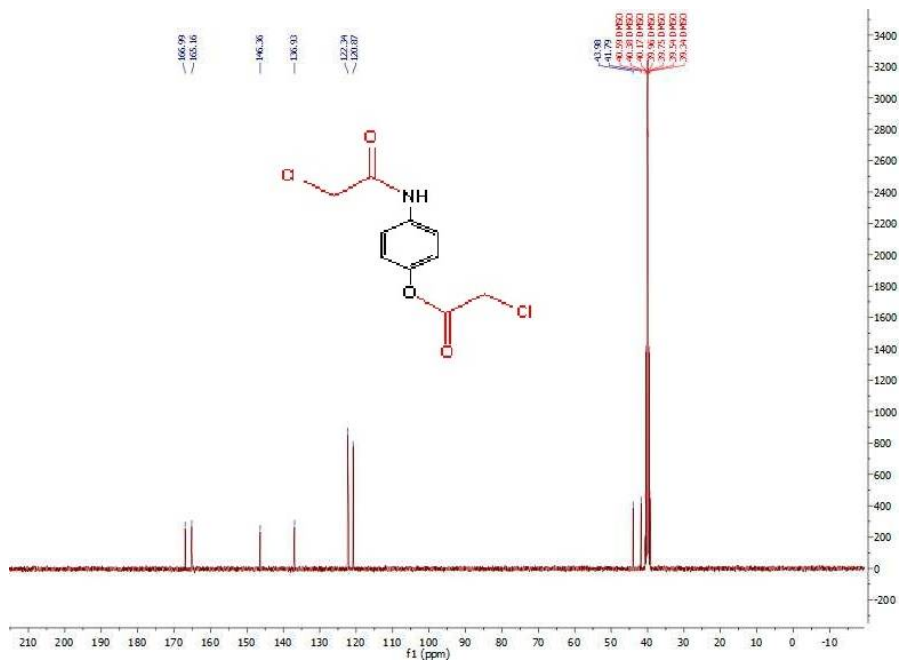


Figure 11. ^{13}C -NMR spectrum of compound 1.

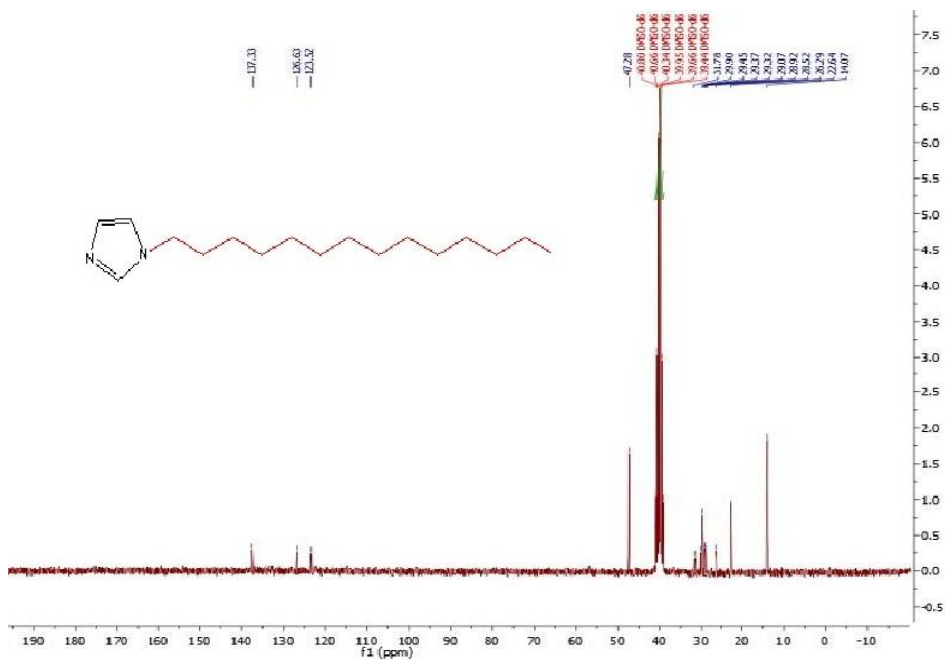


Figure 12. ^{13}C -NMR spectrum of compound 3.

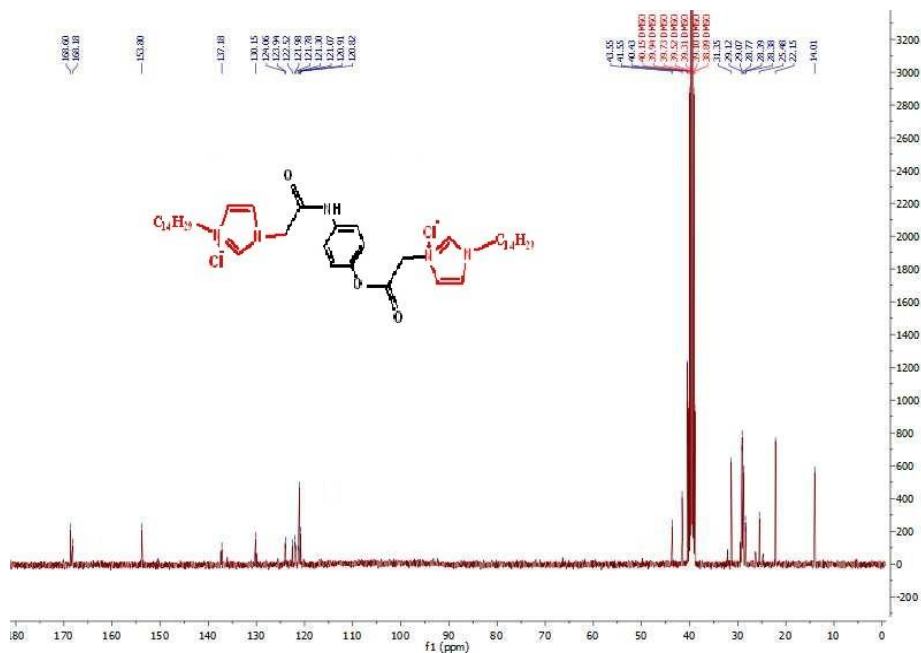


Figure 13. ^{13}C -NMR spectrum of compound 6.

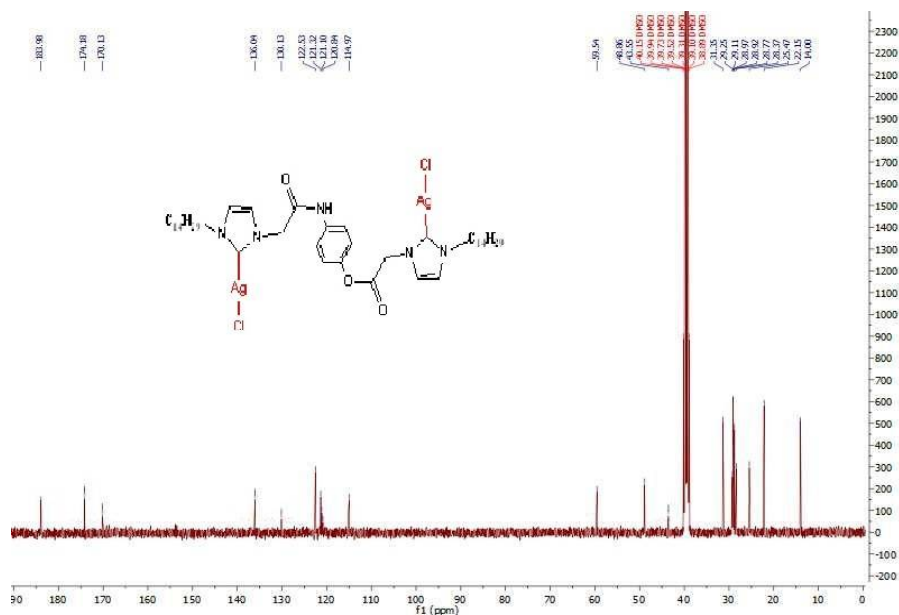


Figure 14. ^{13}C -NMR spectrum of compound 9.

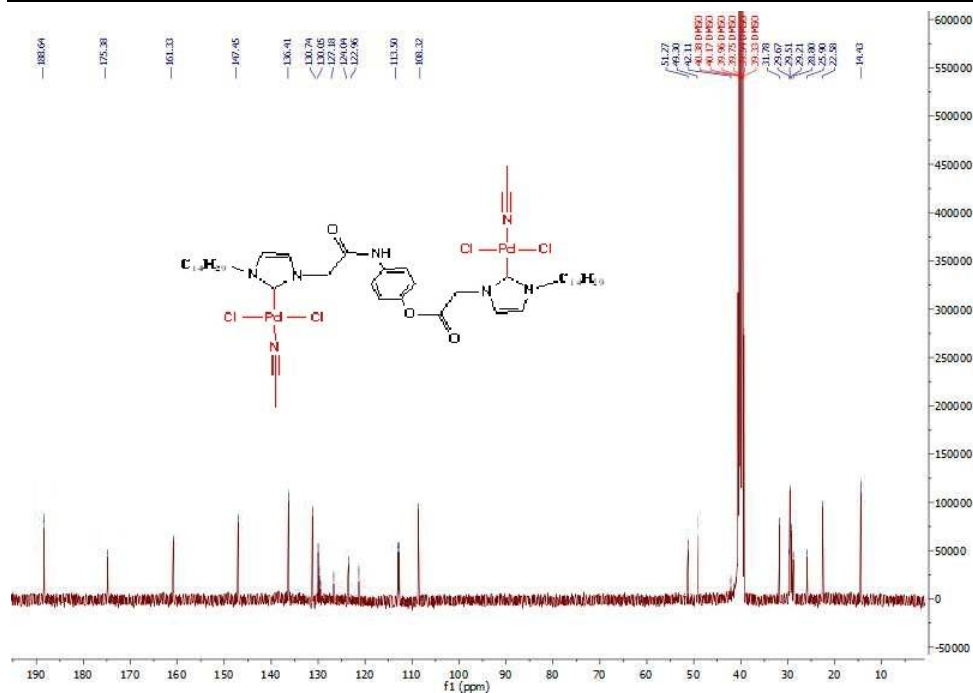


Figure 15. ¹³C-NMR spectrum of compound 12.

Experimental

Materials and instrumentation

All chemicals (Ag_2O , $\text{PdCl}_2(\text{MeCN})_2$, 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 literature²⁸ 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). $^1\text{H-NMR}$ (400 MHz, $\text{d}_6\text{-DMSO}$) 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). $^{13}\text{C-NMR}$ (100 MHz, $\text{d}_6\text{-DMSO}$) 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 literature²⁹ 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-aliph), 2854 (C-H sy-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-aliph), 2853 (C-H sy-aliph), 1564 (C=C), 1233 (C-N). $^1\text{H-NMR}$ 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-CH₂), 1.85-1.75 (p, 2H, CH₂), 1.35-1.17 (m, 18H, CH₂), 0.99-0.95 (t, 3H, CH₃). $^{13}\text{C-NMR}$ δ , ppm: 138.43 (NCHN), 126.55 (CH-im), 123.32 (CH-im), 47.54 (N-CH₂), 31.88-22.03 (CH₂), 14.05 (CH₃).

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-aliph}), 2850 (C-H_{sy-aliph}), 1561 (C=C), 1234 (C-N).

General Synthesis of 1,3-disubstituted imidazolium salts (5, 6, 7)³⁰

Compounds (**5**, **6**, **7**) were synthesized according with the procedure from the literature³⁰ 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-aliph}), 2853 (C-H_{sy-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-aliph), 2853 (C-H sy-aliph), 1745 (C=O ester), 1684 (C=O amide), 1553 (C=C), 1244 (C-N). $^1\text{H-NMR}$ 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-CH₂), 4.28 (s, 2H, carbonyl-CH₂-N), 4.22 (s, 2H, carbonyl-CH₂-O), 1.81-1.74 (p, 4H, N-CH₂-CH₂), 1.28-1.17 (m, CH₂ chain), 0.86-0.83 (t, 6H, CH₃). $^{13}\text{C-NMR}$ 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-CH₂-N), 41.55 (carbonyl-CH₂-O), 40.43 (N-CH₂), 31.35- 22.15 (-CH₂ chain), 14.01 (-CH₃ 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-aliph), 2852 (C-H sy-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 literature³¹. Silver oxide (Ag₂O) 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-aliph), 2853 (C-H sy-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-aliph), 2853 (C-H sy-aliph), 1758 (C=O ester), 1682 (C=O amide), 1555 (C=C), 1233 (C-N).). $^1\text{H-NMR}$ 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 - CH_2), 1.27-1.17 (m,

CH₂ chain), 0.87-0.84 (t, 6H, CH₃). ¹³C-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-CH₂-N), 48.86 (carbonyl-CH₂-O), 43.55 (N-CH₂), 31.35- 22.15 (-CH₂ chain), 14.00 (-CH₃ terminal).

Preparation of compound (10)

It was obtained according to the above-mentioned general procedure from silver oxide (Ag₂O) (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 Ag₂O 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-aliph}), 2851 (C-H_{sy-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 literature³². Palladium complex [PdCl₂(CH₃CN)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 [PdCl₂(CH₃CN)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-aliph), 2853 (C-H sy-aliph), 2258 (C \equiv 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 $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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-aliph), 2852 (C-H sy-aliph), 2257 (C \equiv N), 1741 (C=O ester), 1681 (C=O amide), 1558 (C=C), 1212 (C-N). $^1\text{H-NMR}$ 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 $_2$ -CH $_2$), 1.29-1.17 (m, CH $_2$ chain), 0.87-0.83 (t, 6H, CH $_3$). $^{13}\text{C-NMR}$ 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 \equiv 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 $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (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-aliph), 2851 (C-H sy-aliph), 2258 (C \equiv 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 Ag₂O was gives Ag(I)-NHC complexes. Transmetallation method by reaction of Ag(I)-NHC with PdCl₂(CH₃CN)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, ¹HNMR and ¹³CNMR spectroscopy.

Acknowledgements

Ihab H. Mohammed and Mohammed Z. Ghdayeb thank the Department of Chemistry, Faculty of Science, University of Kufa, for their support.

References

1. Schuster, G. B. Structure and Reactivity of Carbenes Having Aryl Substituents. In *Advances in physical organic chemistry*; Elsevier, **1986**, 22, 311–361.
2. Lakliang, Y.; Mankad, N. P. Heterometallic Cu₂Fe and Zn₂Fe₂ Complexes Derived from [Fe(CO)₄] 2- and Cu/Fe Bifunctional N₂O Activation Reactivity. *Organometallics* **2020**, 39(11), 2043–2046.
3. Capacci, C.; Cesari, C.; Femoni, C.; Iapalucci, M. C.; Mancini, F.; Ruggieri, S.; Zacchini, S. Structural Diversity in Molecular Nickel Phosphide Carbonyl Nanoclusters. *Inorg. Chem.* **2020**, 59(21), 16016–16026.
4. Berti, B.; Bortoluzzi, M.; Cesari, C.; Femoni, C.; Iapalucci, M. C.; Mazzoni, R.; Vacca, F.; Zacchini, S. Thermal Growth of Au–Fe Heterometallic Carbonyl Clusters Containing N-Heterocyclic Carbene and Phosphine Ligands. *Inorg. Chem.* **2020**, 59(4), 2228–2240.
5. Kirmse, W. Stable Singlet Carbenes-Plentiful and Versatile. *Angew. Chemie Int. Ed.* **2004**, 43(14), 1767–1769.
6. Michalak, M.; Kośnik, W. Chiral N-Heterocyclic Carbene Gold Complexes: Synthesis and Applications in Catalysis. *Catalysts* **2019**, 9(11), 890.
7. Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of N-Heterocyclic Carbenes. *Nature* **2014**, 510(7506), 485–496.

8. Enders, D.; Niemeier, O.; Henseler, A. Organocatalysis by N-Heterocyclic Carbenes. *Chem. Rev.* **2007**, *107*(12), 5606–5655.
9. Sinha, A.; Daw, P.; Rahaman, S. M. W.; Saha, B.; Bera, J. K. A RuII–N-Heterocyclic Carbene (NHC) Complex from Metal–Metal Singly Bonded Diruthenium (I) Precursor: Synthesis, Structure and Catalytic Evaluation. *J. Organomet. Chem.* **2011**, *696*(6), 1248–1257.
10. Berti, B.; Bortoluzzi, M.; Cesari, C.; Femoni, C.; Iapalucci, M. C.; Mazzoni, R.; Vacca, F.; Zacchini, S. Synthesis and Characterization of Heterobimetallic Carbonyl Clusters with Direct Au–Fe and Au··· Au Interactions Supported by N-Heterocyclic Carbene and Phosphine Ligands. *Eur. J. Inorg. Chem.* **2019**, *2019*(26), 3084–3093.
11. Oehninger, L.; Rubbiani, R.; Ott, I. N-Heterocyclic Carbene Metal Complexes in Medicinal Chemistry. *Dalt. Trans.* **2013**, *42* (10), 3269–3284.
12. Parkin, G. Impact of the Coordination of Multiple Lewis Acid Functions on the Electronic Structure and *vn* Configuration of a Metal Center. *Dalt. Trans.* **2022**, *51*(2), 411–427.
13. von E. Doering, W.; Knox, L. H. The Reaction of Carbalkoxycarbene with Saturated Hydrocarbons. *J. Am. Chem. Soc.* **1956**, *78* (19), 4947–4950.
14. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, *100*(1), 39–92.
15. Chen, B.; Rogachev, A. Y.; Hrovat, D. A.; Hoffmann, R.; Borden, W. T. How to Make the $\Sigma\pi^2$ Singlet the Ground State of Carbenes. *J. Am. Chem. Soc.* **2013**, *135*(37), 13954–13964.
16. Wanzlick, H.; Schikora, E. Ein Neuer Zugang Zur Carben-Chemie. *Angew. Chemie* **1960**, *72*(14), 494.
17. Schönherr, H.; Wanzlick, H. Chemie Nucleophiler Carbene, XX HX-Abspaltung Aus 1.3-Diphenyl-imidazoliumsalzen. Quecksilbersalz-Carben-Komplexe. *Chem. Ber.* **1970**, *103*(4), 1037–1046.
18. Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. Analogous. Alpha.,. Alpha.'-Bis-Carbenoid, Triply Bonded Species: Synthesis of a Stable. Lambda. 3-Phosphino Carbene-. Lambda. 5-Phosphaacetylene. *J. Am. Chem. Soc.* **1988**, *110*(19), 6463–6466.
19. Arduengo, A. J. I. I. I.; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*(1), 361–363.

20. Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*(8), 3612–3676.
21. Patil, S.; Deally, A.; Gleeson, B.; Müller-Bunz, H.; Paradisi, F.; Tacke, M. Novel Benzyl-Substituted N-Heterocyclic Carbene–Silver Acetate Complexes: Synthesis, Cytotoxicity and Antibacterial Studies. *Metallomics* **2011**, *3*(1), 74–88.
22. Haque, R. A.; Salman, A. W.; Budagumpi, S.; Abdullah, A. A.; Abdul Hameed Al-Mударis, Z. A.; Abdul Majid, A. M. S. Silver (I)-N-heterocyclic Carbene Complexes of Bis-imidazol-2-ylidenes Having Different Aromatic-spacers: Synthesis, Crystal Structure, and in Vitro Antimicrobial and Anticancer Studies. *Appl. Organomet. Chem.* **2013**, *27*(8), 465–473.
23. Ghdayeb, M. Z.; Haque, R. A.; Budagumpi, S.; Ahamed, M. B. K.; Majid, A. M. S. A. Mono-and Bis-N-Heterocyclic Carbene Silver (I) and Palladium (II) Complexes: Synthesis, Characterization, Crystal Structure and in Vitro Anticancer Studies. *Polyhedron* **2017**, *121*, 222–230.
24. Özdemir, İ.; Gürbüz, N.; Doğan, Ö.; Günal, S.; Özdemir, İ. Synthesis and Antimicrobial Activity of Ag (I)-N-heterocyclic Carbene Complexes Derived from Benzimidazol-2-ylidene. *Appl. Organomet. Chem.* **2010**, *24*(11), 758–762.
25. Haque, R. A.; Salman, A. W.; Guan, T. S.; Abdallah, H. H. New N-Heterocyclic Carbene Mercury (II) Complexes: Close Mercury–Arene Interaction. *J. Organomet. Chem.* **2011**, *696*(22), 3507–3512.
26. Haque, R. A.; Ghdayeb, M. Z.; Salman, A. W.; Budagumpi, S.; Ahamed, M. B. K.; Majid, A. M. S. A. Ag (I)-N-Heterocyclic Carbene Complexes of N-Allyl Substituted Imidazol-2-Ylidenes with Ortho-, Meta-and Para-Xylyl Spacers: Synthesis, Crystal Structures and in Vitro Anticancer Studies. *Inorg. Chem. Commun.* **2012**, *22*, 113–119.
27. Paulose, T. A. P.; Wu, S.-C.; Quail, J. W.; Foley, S. R. Synthesis, Characterization and Properties of a Tri (N-Heterocyclic Carbene) Palladium (II) Complex. *Inorg. Chem. Commun.* **2012**, *15*, 37–39.
28. Reddy, T. R. K.; Li, C.; Guo, X.; Fischer, P. M.; Dekker, L. V. Design, Synthesis and SAR Exploration of Tri-Substituted 1, 2, 4-Triazoles as Inhibitors of the Annexin A2–S100A10 Protein Interaction. *Bioorg. Med. Chem.* **2014**, *22*(19), 5378–5391.
29. Mohsen, D. H.; Radhi, A. J.; Shaheed, D. Q.; Abbas, H. K. Synthesis

- New Benzimidazole Derivatives as Antibacterial. *J. Pharm. Negat. Results* **2022**, 893–898.
30. Visbal, R.; Gimeno, M. C. N-Heterocyclic Carbene Metal Complexes: Photoluminescence and Applications. *Chem. Soc. Rev.* **2014**, 43(10), 3551–3574.
31. Nadeem, R. Y.; Yaqoob, M.; Yam, W.; Haque, R. A.; Iqbal, M. A. Synthesis, Characterization and Biological Evaluation of Bis-Benzimidazolium Salts and Their Silver(I)-N-Heterocyclic Carbene Complexes. *Med. Chem. Res.* **2022**, 31(10), 1783–1791.
32. César, V.; Bellemin-Laponnaz, S.; Gade, L. H. Direct Coupling of Oxazolines and N-Heterocyclic Carbenes: A Modular Approach to a New Class of C–N Donor Ligands for Homogeneous Catalysis. *Organometallics* **2002**, 21(24), 5204–5208.