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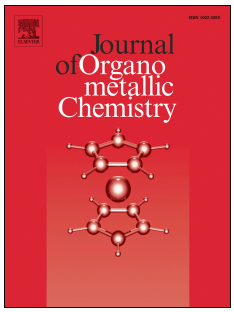

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Ether and coumarin–functionalized (benz)imidazolium salts and their silver(I)–N–heterocyclic carbene complexes: Synthesis, characterization, crystal structures and antimicrobial studies

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Abstract

To explore the impact of different coumarin substituted N–heterocyclic carbene (NHC) ligand backbones on the biological applications of corresponding silver(I) complexes, a series of structurally related ether–functionalized imidazolium (**3–5**) and benzimidazolium (**6–8**) hexafluorophosphate salts bearing 6–methylcoumarin, 6–chlorocoumarin and 5,6–benzannulated coumarin substituents, have been reported. These salts have been employed to react with silver(I) oxide at mild reaction conditions to obtain corresponding ionic, bis–NHC coordinated silver(I) hexafluorophosphate complexes (**9–14**) in excellent yields following *in situ* deprotonation method. Further, the bromide counterparts of the salts have been treated with silver(I) oxide in dichloromethane to afford neutral mono–NHC coordinated bromido silver(I) complexes (**15–20**). Both, azolium salts and their silver(I)–NHC complexes, have been thoroughly characterized by ^{1}H and ^{13}C NMR, ATR–IR and elemental analyses. The structure of a benzannulated coumarin substituted imidazolium hexafluorophosphate salt **5** and a silver complex **12** of benzimidazole–based NHC bearing methylcoumarin substituent have been studied through single crystal X–ray diffraction technique. In the case of complex **12**, the metal center lies at the inversion center adopting linear coordination geometry with *anti*– arrangement of the NHC ligands. Feeble π–π stacking interactions between adjacent coumarin rings have been evident in the extended complex structure along with the hydrogen bonding interactions. In the preliminary antibacterial evaluations, silver complexes displayed promising activity with the MIC values in the range 8–64 µg/mL against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Salmonella typhi*, while azolium salts displayed almost no activity.

Key words: Antibacterial agent; Azolium salt; Benzannulated coumarin; N–heterocyclic carbene; Silver(I)–NHC complex; X–ray diffraction.

1. Introduction

Appropriately substituted azolium salts have been the common precursors of N–heterocyclic carbene (NHC) ligands ever since the first isolation of a stable, free NHC from an imidazolium salt by Arduengo *et al.* in 1991 [1]. NHCs have cherished organometallic chemistry in many aspects and became the pick of ligands for the synthesis of numerous valued chemicals because of their strong σ–donor ability, easy access, inexpensiveness and non–air–sensitive nature [2]. NHCs can efficiently induce desired electronic and steric properties around the metal atoms in the NHC–metal complexes predominantly through functionalization of either the azole backbone or hydrocarbyl/heterocyclic substituents bound to N–atoms. The research for new transition metal–NHC complexes for various applications has mainly been dominated by early and group X metals as efficient catalytic systems [3]. Nevertheless, over the past few years, coinage metal NHC complexes have been proposed for biological applications as antimicrobial and anticancer agents [4]. To date, most applications of transition metal–NHC complexes are concentrated on various types of homogeneous catalysis.

By far the most widespread and efficacious class of biologically relevant coinage metal–NHC complexes that have been studied so far are principally based on silver(I) system. Silver derivatives have been at the focal point with increased attention due to their usually strong antibacterial and anticancer potentials. Recently, Tacke and co–workers reported a series of NHC silver(I) acetate complexes as metal-based drugs against microbial strains and cancer cells [5]. Among others, 1,3-dibenzyl-4,5-diphenylimidazol-2-ylidene) silver(I) acetate displayed some promising antimicrobial and anticancer potentials. Despite the large archive of coinage metal–NHC complexes available, there is a comparatively less number of silver complexes derived from *O*–functionalized NHC ligands that have been explored. The high medicinal values of silver(I) gives concomitantly less toxicity and high cytotoxic activity against normal cells and bacterial strains or cancer cells, respectively. Importantly, the facile functionalization of the NHC ligand scaffold with a biocompatible heterocyclic system such as coumarin [6], employed for these complexes can lead to improved biological applications. In particular, substituted coumarin derivatives have been extensively studied

mainly due to their well–known biological properties [7] ranging from antimicrobial to anticancer potentials which are due to their structural characteristic that lead to the possible establishment of desired interactions with the biomacromolecules. The possible structural modifications particularly at positions 6– and 7– of benzene ring fused to the α–pyrone found able to control their conforming biological applications [8].

The main goal in the development of new bioactive silver complexes bearing coumarin–tethered (benz)imidazole–based NHC ligands is to access a class of derivatives that show appropriate stability under physiological conditions. Conversely, ether functionality has been considered to understand the donor behavior of etherial oxygen to the metal center [9]. In fact, the core azole and coumarin derivatives individually found stable and highly active for biological applications, and it is thought that their combination along with silver would lead to form even better candidates encompassing promising antibacterial potentials. More recently, we reported a series of similar silver complexes of coumarin–tethered NHCs that found stable in solution upon exposing to sunlight for more than a week time [10]. On the other hand, our very recent studies have shown that a similar set of sterically–modulated silver complexes [11] displayed almost comparable antibacterial activities against *E. coli* with that of standard drug, ampicillin. Herein, as a continuation of our work on the biologically active silver complexes, especially those derived from functionalized NHC ligands, we report synthesis, structural characterization and antibacterial potentials of a series of new ether and coumarin substituted (benz)imidazolium salts and their silver(I)–NHC complexes.

2. Results and discussion

2.1. Synthesis of (benz)imidazolium salts and silver(I)–NHC complexes

In comparison with those N,N'–dialkyl imidazole and benzimidazole–based azolium salts as NHC precursors, the silver complexes of *O*–functionalized NHC ligands for biological applications have been reported less frequently. The N,N'–disubstituted (benz)imidazolium salts were synthesized by first preparing their corresponding ethers (**1** and **2**) following base assisted N–alkylation pathway, an aromatic electrophilic substitution reaction between the azole and *n*–bromoalkyl ether. In these reactions, the azoles were treated with excess

potassium hydroxide in dimethyl sulphoxide at elevated temperature and consequent reaction with the bromoalkyl ether resulted in the formation of desired ether substituted azoles, **1** and **2**, in good yields. Subsequently, these ether–substituted azoles were treated with 4–bromomethyl–6–methylcoumarin/4–bromomethyl–6–chlorolcoumarin/4–bromomethyl–5,6–benzocoumarin in 1,4–dioxane at refluxing temperature for 24 h to afford corresponding N–ether–N'–coumarin substituted (benz)imidazolium bromide salts in good yields. Subsequently, the hexafluorophosphate derivatives, **3**–**8**, were then synthesized by following the salt metathesis reactions of the corresponding bromide salts. These salts were prepared by treating water/methanolic (1:9 v/v) solution of potassium hexafluorophosphate with the stirring methanolic solution of bromide salts for 4 h at room temperature as shown in Scheme 1. Completeness of the reactions was monitored by TLC technique. The products were isolated by filtration and washed with fresh cold methanol and water to remove unreacted potassium hexafluorophosphate and characterized by standard spectral and analytical techniques. Both ether–substituted imidazolium and benzimidazolium analogues with non–coordinating anions show significant solubility in polar solvents such as DMSO, DMF, acetonitrile and sparingly soluble in DCM and insoluble in non–polar solvents.

Numerous silver(I) complexes have been reported to display different architectures due to the presence of functionalized NHC ligands at varied reaction conditions. The synthesis of silver(I) complexes with NHC ligands following *in situ* deprotonation of corresponding azolium salts is a well–established method [12]. Especially, azolium salts with non–coordinating anions such as hexafluorophosphate and tetrafluoroborate proved to be suitable candidates due to their exceptional air, moisture and light stability. The title silver(I)–NHC complexes were prepared by *in situ* deprotonation of azolium salts, the most widely used pathway. The ether substituted azolium hexafluorophosphate salts, **3**–**8**, were treated with silver(I) oxide in acetonitrile at 45^{o}C for 24 h under dark; the desired complexes were obtained as off–white, light–sensitive solids in 90–95% isolated yields after recrystallization from acetonitrile/diethyl ether mixtures (Scheme 2). The complexes **9**–**14** were readily soluble in polar organic solvents such as DMSO, DMF, acetonitrile, acetone and sparingly soluble in DCM and insoluble in non–polar organic solvents. These new compounds were fully characterized by ^{1}H and {^{1}H}^{13}C NMR and ATR–IR spectroscopic and elemental

analyses and conductivity studies. The structure of representative complexes, **9** and **12** were unambiguously established following single crystal X–diffraction method.

To investigate the implication of a bromido ligand on the structural and biological characteristics of silver(I) complexes, a set of neutral silver(I) complexes having general molecular formula [NHC–Ag–Br] has been explored. The reactions of the ether substituted (benz)imidazolium bromide salts with silver(I) oxide in dichloromethane for 24 h at room temperature under dark yielded the desired ether–functionalized NHC coordinated silver(I) bromido complexes, **15–20**, as light–sensitive solids depicted in Scheme 3. These complexes were purified by repeated precipitation in methanol using diethyl ether to yield stable beige colored solids in good to moderate yields. Melting points of these complexes found relatively lesser than that of bis–NHC coordinated silver complexes, which could be presumably due to the easier elimination of bromide as hydrogen bromide, while this is not the case with the latter complexes. Like, bis–NHC coordinated complexes, NHC silver(I) bromido complexes are soluble in high polar organic solvents and insoluble in less polar solvents such as diethyl ether and n–pentane. All these bromido–coordinated complexes were fully characterized through classical techniques such as ^{1}H and $\{^{1}H\}^{13}$C NMR and ATR–IR spectroscopy and elemental analysis. Despite various attempts to grow suitable single crystals of these complexes for structure determination through X–ray diffraction technique, all our efforts ended up giving either amorphous solids or multiple crystals that are not suitable for desired analysis.

2.2. Spectral characterization

The formation of the desired coumarin and ether–functionalized (benz)imidazolium salts and their silver(I) mono– and bis–carbene complexes was confirmed by NMR spectroscopy in d_6–DMSO, and the NMR data of complexes together with their carbene precursors are presented in experimental section. For the bis–carbene complexes, the two NHC groups are chemically equivalent as are the coumarin and ether substituents of the azole rings are same. In the ^{1}H NMR spectra of the azolium salts, a characteristic singlet proton resonance peak centered at δ 9.28–9.82 ppm was observed, which is attributed to the resonance of C2 (NC*H*N) proton. Similarly, coumarin methyl, methoxyethyl and C4–coumarin methylene

proton resonances were observed at around δ 2.3, 3.0–4.7 and 6.0 ppm, respectively, and are in well agreement with the NMR data of analogous 4–substituted coumarin and alkoxy derivatives [13]. Further, two sharp singlet peaks were observed at around δ 6.0 and 7.5 ppm in the cases of salts **3**, **4**, **6** and **7**, which have been attributed to the resonances of coumarin C3 and C5 protons, respectively and at δ 6.0 ppm in the cases of salts **5** and **8** for former proton resonances. Coumarin, imidazole and benzimidazole ring aromatic proton resonances have been observed in the range δ 6.0–8.2 ppm, which are in good agreement with the similar azolium analogues reported earlier by us [14] and others [15]. In their ^{13}C NMR spectra, salts displayed a characteristic peak at around δ 137.5–137.7 and 143.6–143.7 ppm for imidazolium and benzimidazolium salts, respectively; ascribed to the resonance of C2 carbon (N*C*HN). Furthermore, three characteristic carbon resonance signals were observed at around δ 148, 152 and 159 ppm assigned to the resonances of coumarin ring carbons nuclei. Finally, two sets of distinguished carbon resonance peaks were observed at around δ 51–71 and 112–145 ppm, ascribed to the resonances of aliphatic methoxyethyl and aromatic carbon nuclei, respectively. Observed ^{13}C NMR spectral data and their corresponding interpretations are in good agreement with the reported azolium analogues, which cannot act as a bidentate chelating NHC ligand [16].

As expected, in the ^{1}H NMR spectra of mono– and bis–carbene silver complexes **9–20**, singlet peaks centered at δ 9.28–9.82 ppm representing their C2 proton (NC*H*N) resonances of azolium salts **3–8** were notably absent. This observation confirmed the successful formation of desired silver complexes through deprotonation of azolium salts. It is worth mentioning that in the corresponding ^{13}C NMR spectra of the complexes, resonances of carbene carbon atom coordinating with silver center were observed at around δ 191.7 and 192.4 ppm for complexes **13** and **14**, respectively; however, in the cases of rest of the complexes, this resonance was not observed, which is due to the bulky nature of NHC ligands. In all the cases, a distinguished carbon resonance peak centered at δ 137.6 and 143.6 ppm for imidazolium and benzimidazolium salts, respectively representing their C2 carbon (N*C*HN) resonance of salts was particularly absent. These two observations collectively confirmed the formation of desired silver complexes. Unsurprisingly, the other proton and carbon resonances are appeared in the complex spectra with no or minor differences with that

of corresponding salts. All the carbon NMR spectral observations and their interpretations are in line with the similar compounds reported earlier [17].

Azolium salts, **3–8**, and their mono– and bis–carbene coordinated silver complexes, **9–20**, were studied for their structure using ATR–IR spectroscopy over the range 600–4000 cm^{-1}. Upon proper examination of the IR spectra of the silver complexes **9–14**, in comparison with those of the free azolium salts, the most significant observation was the appearance of azole stretching vibrations to the lesser energy region. Further, no significant changes were observed in the stretching vibrations of lactonic carbonyl module in all the complexes, indicating its non–involvement in the coordination with the metal center. It is worth mentioning that in several reports such a characteristic observation was attributed to the non–participation of the lactone carbonyl module in complex formation [18]; nevertheless, it has also been reported for numerous 3–/4–substituted coumarin derivatives that the lactone carbonyl was involved in coordination [19], which provides structural diversity to the resulting complexes. It is highly difficult to distinguish mono– and bis–carbene complexes on the basis of their IR spectra. In all the cases, however, sharp high intensity bands without significant change in their position were observed at around 2860, 2935 cm^{-1} and 980 cm^{-1}, ascribed to the stretching vibrations of aliphatic/aromatic C–H and C–O modules, respectively.

2.3. Elemental analyses and molar conductivity studies

In addition, the azolium salts and their mono– and bis–carbene coordinated silver(I) complexes are further characterized by CHN microelemental analyses and the data obtained is in well agreement with the calculated percentages of these elements with an acceptable limit of variation with ±0.4 % in all the cases.

Room–temperature, solution conductivities of the azolium salts and bis–carbene and mono–carbene coordinated silver(I) complexes are provided in the experimental part. These molar conductivity values were determined for compounds **3–20** in dichloromethane at 10^{-3} M concentration. By their nature, these conductivity measurements are influenced by the electrostatic force of attraction between azolium cations and hexafluorophosphate anions. The azolium salts displayed a molar conductivity value in the range 141–170 S cm^2 mol^{-1},

which is well above the observed molar conductivity values reported for non–complex 1:1 electrolytes such as tetraalkylammonium halides/perchlorates [20]. However, molar conductivity values of bis–carbene coordinated silver(I) complexes fall into the range expected for weak 1:1 electrolytes [21], 43–60 S cm^2 mol^{-1} in dichloromethane, which could be presumably due to the strong interactions operating between NHC–silver(I) cations and hexafluorophosphate anions, which is further evidenced by the single crystal X–ray diffraction studies. As expected, mono NHC coordinated silver complexes displayed almost no molar conductivity, and therefore it can be concluded that these complexes are neutral in nature, which further confirms the coordination of bromido ligand with the silver center.

2.4. Single crystal X–ray diffraction studies

To obtain the solid–state bonding and special connectivity information between azolium or bis–NHC silver complex cations and hexafluorophosphate anions, a representative benzannulated imidazolium hexafluorophosphate salt **5** and a benzimidazole complex **12** were structurally elucidated using single crystal X–ray diffraction technique. Suitable X–ray quality crystals of **5** and **12** were obtained through the diffusion of diethyl ether into the acetonitrile solution of **5** and **12**, which allowed us to get insights on the solid–state structure of the compounds.

The crystallographic and refinement data for compounds **5** and **12** are shown in Table 1. The molecular structure of imidazolium salt **5** is depicted in Figure 1. Imperative bond distances and angles for salt **5** are tabulated in Table 2. Salt **5** is a well ordered structure, crystallized in the triclinic space group, *P*–1, having one 5,6–benzannulated coumarin substituted imidazolium cation as well as one hexafluorophosphate anion in the asymmetric unit without any co–crystallized solvent or water molecule. The 5,6–benzannulated coumarin and imidazole rings are almost planar and aromatic with C–C, C–O and C–N bond distances in the range 1.357(2)–1.465(3) Å. The dihedral angle between the planes of these two aromatic systems is 114.3(2)^o, and the ether wingtip is intact with the salt structure, attached to other nitrogen atom of the imidazole ring with a bond angle of 110.9(2)^o for N2–C4–C5 having no disorders. The internal bond angle at imidazole ring C1 and benzannulated coumarin O2 atom are 108.4(2)^o and 122.4(1)^o for N1–C1–N2 and C10–O2–C11, respectively. Further, the

bond distance for exocyclic C10–O3 of coumarin and O1–C6 of ether are 1.213(3) and 1.422(2) Å, respectively. These bond distances and angles are in well agreement with the similar previously reported azolium [22] and substituted coumarin derivatives [23]. In the extended crystal structure of the salt **5**, the imidazolium cations are assembled in a head–to–tail overlapping manner as shown in Figure S1 (Supporting Information), due to which the interactions between the benzannulated coumarin rings of adjacent cations stack along the c–axis. This stacking arrangement of the imidazolium cations lead to the formation of feeble π–π stacking interactions between coumarin rings parallel to the *bc*–plane with the interaction distance of 3.508 Å. Alongside, two predominant intramolecular (OCH3---F2 and C1H---O1) and one intermolecular (C16H---F3) hydrogen bonding interactions have been observed in the crystal structure with the interaction bond distance of 2.947, 2.634 and 2.803 Å, respectively. These hydrogen bonding interactions and many short distance interactions stabilize the salt and in turn formed 3–dimensional networks between imidazolium cations and hexafluorophosphate anions.

On the other hand, complex **12** crystallized in the triclinic space group, *P*–1, with the silver(I) at the inversion center. An asymmetric unit of complex **12** is composed of half a molecule of the complex cation and half a molecule of the hexafluorophosphate anion. The hexafluorophosphate anion displayed positional disorder over two sets, which has been satisfactorily refined. The molecular structure of complex **12** is depicted in Figure 2 with thermal ellipsoids drawn at the 50% probability level. Pertinent bond distances and angles for complex **12** are tabulated in Table 3. The ion pair portrayed in the figure bearing bis–NHC coordinated silver(I) as cationic fragment and the hexafluorophosphate as the counter anionic fragment (not shown). In the complex, silver(I) center adopted a perfectly linear coordination geometry through the bond angle of 180^{o} for C1–Ag1–C1A with an antiparallel eclipsed arrangement of NHC ligands. The bond angle at carbene carbon center in benzimidazole ring, 106.0(2)^{o} for N1–C1–N2, found significantly declined due to the coordination of carbene carbon with the silver center [24], while the bond angle at coumarin heterocyclic oxygen atom, 121.7(7)^{o} for C11–O1–C12, found almost unaffected compared with its structural analogous salt **5**. As foreseen, the two coumaryl substituents projected away from the coordination sphere, and hence the steric repulsion between the two NHC ligands has

been reduced. Interestingly, two types of distinct intermolecular bonding interactions have been observed between Ag1–H19, Ag1–H19A and Ag1–H8, Ag1–H8A with the interaction distances of 2.978 and 3.007 Å, respectively that are slightly higher than that of the sum of the Van Der Walls radii of silver and hydrogen (2.92 Å). Like salt **5**, the dihedral angle between the planes of benzimidazole and coumarin rings in the case of complex **12** is 113.7(2)^{o} for N2–C8–C9 and exocyclic lactonic carbonyl bond distance is 1.208(3) Å. Observed bond angles and bond distances are well comparable with the reported complexes bearing non–coordinating coumarin substituents [25]. Further, the methoxyethyl chain is intact with the structure, making a bond angle of 112.6(2)^{o} for N1–C19–C20 with the azole without any disorder. In the extended crystal structure of the complex (Figure S2, Supporting Information), an intra–cationic hydrogen bonding interaction between ethereal oxygen and ethyl hydrogen atoms (2.603 Å for O3---H19) and two types of prominent interionic hydrogen bonding interactions between methoxy hydrogen and phenyl ring hydrogen atoms with hexafluorophosphate anion have been observed (3.185 Å for C21H---F3 and 2.853 Å for C13H---F1). Further, the benzimidazolium cations aggregate in a staggered orientation, leading to the formation of weak π–π stacking interactions between the benzimidazole rings of adjacent molecules parallel to *b*–axis with an interaction bond distance of 3.695 Å. Together with hydrogen bonding interactions, π–π stacking and other short distance interactions operated in the complex crystal to form the 3–dimensional networks between benzimidazolium cations and hexafluorophosphate anions.

2.4. Antimicrobial studies

The existence of multidrug–resistant bacterial strains of *S. aureus* and *P. aeruginosa* to well–known penicillin and sulfonamide drugs opened an avenue for the metal–based drugs as newer alternatives. Recently, metallocene derivatives of iron and ruthenium were reported for their antibacterial properties by high level of inhibition of $_{DD}$–carboxypeptidase 64–575, a penicillin binding protein through the formation of a covalent acyl−enzyme complex [26]. In this perspective, silver(I) complexes of both functionalized and non–functionalized NHC ligands have been proved as a class of important candidates possessing promising antibacterial and anticancer potentials [27]. These potentials of complexes are majorly

dependent on the nature of the wingtip substitutes of NHC ligands that in turn lead to the formation of diverse structural motifs [5,28]. In the present study, we selected a series of structurally varied analogues of coumarin and ether functionalized (benz)imidazolium salts and corresponding two series of structurally different silver(I) NHC complexes to explore their antibacterial potentials against Gram positive bacterial strains, *S. aureus* (ATCC 29213), *B. subtilis* (ATCC 6633), and Gram negative bacterial strains, *E. coli* (ATCC 25922), *S. typhi* (ATCC 19214) following broth microdilution method using ampicillin as a standard drug.

The MIC (minimum inhibitory concentration) values for both (benz)imidazolium salts (**3–8**) and corresponding bis–carbene (**9–14**) and mono–carbene (**15–20**) coordinated silver(I) complexes are summarized in Table 4. All the microbial experiments were carried out in triplicates and at least any two concurrent results are discussed. The solvent, DMSO, used to prepare the stock solutions of the test samples **9–20** played no role in growth inhibition of the bacterial strains. In line with our previous observations [10,11,14,29], both the types of azolium salts found inactive against all the bacterial strains tested in the working concentration range of 0.5–128 µg/mL. However, bis– and mono–carbene coordinated silver complexes displayed poor antimicrobial activity against Gram positive bacteria, *B. subtilis*, with a MIC value of 128 µg/mL. This observation could be attributed to the poor activity of azolium salts. Meanwhile, former complexes evidenced a promising activity against *S. aureus* with a MIC of 16 µg/mL, while latter complexes displayed an activity with a MIC value in the range 16–128 µg/mL. Nevertheless, the antimicrobial activity of bis–NHC complexes against Gram negative bacteria, *E. coli*, is found significant with a MIC value in the range 8–16 µg/mL, while mono–NHC complexes displayed activity that is two dilutions higher than corresponding bis–NHC complexes. Finally, all the complexes displayed poor antimicrobial activity against *S. typhi* with a MIC value of 128 µg/mL, except complex **14**, which has shown a MIC of 64 µg/mL. Since the antimicrobial data of the complexes is a preliminary study, it is difficult to predict the structure activity relationships.

3. Conclusions

A series of ether and substituted coumarin functionalized (benz)imidazolium bromide and hexafluorophosphate salts and their corresponding ionic bis–carbene coordinated silver(I) hexafluorophosphate and neutral mono–carbene coordinated silver(I) bromido complexes are reported. Salts were prepared in good to excellent yields by successive N–alkylation method using 1–bromo–2–methoxyethane and substituted 4–bromomethyl coumarins as N–alkylating agents with 1H–imidazole or 1H–benzimidazole followed by salt metathesis reaction with KPF_6. Difference in the counterions of the azolium salts and reaction conditions resulted in the formation of two series of carbene coordinated silver complexes. Salts with non–coordinating anion, hexafluorophosphate anion, treated with silver(I) oxide at slightly elevated temperature in acetonitrile afforded ionic bis–carbene coordinated silver(I) complexes with hexafluorophosphate as a counterion, while bromide salts treated with the metal source in dichloromethane at room temperature resulted in the formation of neutral mono–carbene coordinated silver(I) bromido complexes in excellent yields. All salts and complexes were characterized by conventional spectroscopic techniques such as ^{1}H and $\{^{1}H\}^{13}C$ NMR and ATR–IR spectroscopies and CHN microelemental analyses. Furthermore, the structure of a representative benzo–coumarin substituted imidazolium salt and a benzimidazole–based bis–carbene silver(I) hexafluorophosphate complex were unambiguously studied by single crystal X–ray diffraction method. In the preliminary antibacterial studies against two Gram positive and two Gram negative bacterial strains, silver complexes were found active with MIC values in the range 8–64 µg/mL, while all the salts displayed almost no activity against all the bacteria tested.

4. Experimental

4.1. General considerations

All solvents and chemicals used in the present investigation were obtained from commercial sources and used as received unless otherwise indicated. Starting chemicals such as 1H–imidazole, 1H–benzimidazole, 1–bromo–2–methoxyethane, ethyl acetoacetate, bromine, 4–methylphenol, 4–chlorophenol, 2–naphthol, concentrated sulphuric acid, potassium hexafluorophosphate, silver(I) oxide, nutrient agar and nutrient broth were purchased from commercial sources. N–alkylated azoles such as, 1–(2–methoxyethyl)–1H–imidazole (**1**) and

1–(2'–methoxyethyl)–1H–benzimidazole (**2**) [30] and coumarin derivatives such as, 4–bromomethyl–6–methylcoumarin, 4–bromomethyl–6–chlorocoumarin and 4–bromomethyl–5,6–benzocoumarin [31] were synthesized following literature procedures with slight modifications. The preparations of (benz)imidazolium bromide/hexafluorophosphate salts and corresponding mono– and bis–carbene silver(I) complexes were performed without using sophisticated Schlenk technique and dry box. Thin layer chromatography was carried out on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the desired products spots were witnessed with UV light at 254 nm or in an iodine chamber. ^{1}H and ^{13}C NMR spectra of all the new derivatives were collected in d_6–DMSO solvent either on Bruker AVANCE III 400 MHz or Bruker 300 MHz NMR spectrometer. Chemical shifts (δ ppm) are given with solvent peaks as the internal references, and the signals are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The melting points were assessed using a Stuart Scientific (UK) instrument with an accuracy of ±0.3 ^{o}C. CHN microelemental analyses were performed using a Perkin Elmer 2400 Series II CHN/S microanalyzer. Infrared spectra were recorded on a Bruker ECO–ATR spectrophotometer in the range 600–4000 cm^{-1}.

4.2. X–ray crystallography

*For the crystals of salt **5***: The X–ray intensity data were collected at a temperature of 296(2) K on a Bruker Proteum2 CCD diffractometer equipped with an X–ray generator operating at 45 kV and 10 mA, using Cu*K*α radiation of wavelength 1.54178 Å. The structure was solved by direct methods and refined by full–matrix least squares method on F^2 using SHELXS and SHELXL programs, while the geometrical calculations were carried out using the PLATON program. The molecular graphic designs and packing diagrams of salt **5** for publication were performed using OLEX2 and MERCURY software packages.

*For the crystals of complex **12***: The crystal was mounted in turn on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X–ray intensity data were collected with graphite monochromated MoKα radiation (λ = 0.71073 Å) at a temperature of 295(2) K, with ω scan mode. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [32] were applied. All the non–hydrogen atoms were

refined anisotropically using full–matrix, least–squares technique. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent carbon atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom. The Olex2 [33] and SHELXS, SHELXL [34] programs were used for all the calculations. The geometrical calculations were carried out using the PLATON program. The molecular graphic designs and packing diagram for publication were performed using Olex2 and MERCURY software packages.

*4.3. Synthesis of 1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) imidazolium bromide/hexafluorophosphate (**3**)*

A solution of 1–(2–methoxyethyl)–1H–imidazole (**1**) (0.254 g, 2 mmol) in 35 mL of 1,4–dioxane was added drop wise a solution of 4–(bromomethyl)–6–methyl–coumarin (0.506 g, 2 mmol) in 1,4–dioxane and stirred at room temperature for homogenization. The pale yellow mixture was allowed to stir at reflux for 24 h based on TLC analysis. After the stipulated time, the mixture was cooled to room temperature and the off–white solid obtained was filtered and washed with fresh 1,4–dioxane (3 x 5 mL) to yield the corresponding imidazolium bromide salt. Further, to a methanolic solution of so obtained bromide salt was added a methanol–water solution (9:1 v/v) of potassium hexafluorophosphate at room temperature and stirred for 4 h to precipitate the imidazolium hexafluorophosphate salt **3** as an off–white solid through salt metathesis reaction. Crude salt **3** was filtered and washed with fresh methanol and distilled water to remove any unreacted potassium hexafluorophosphate and was purified by repeated precipitation in acetonitrile and diethyl ethyl ether mixture. Yield: 65.2 %; M.P.: 140–141 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 2.49 (3H, s, C*H*$_3$–coumarin), 3.27 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.73–3.70 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.40 (2H, t, J = 8.8 Hz, CH$_3$–O–CH$_2$–C*H*$_2$), 5.81 (2H, s, C*H*$_2$–C4–coumarin), 5.98 (1H, s, C3*H*–coumarin), 7.40 (1H, d, J = 8.4 Hz, C4*H*–imidazole), 7.53 (1H, d, J = 8.6 Hz, C5*H*–imidazole), 7.66–7.60 (1H, m, ArC*H*–coumarin), 7.87–7.81 (2H, m, ArC*H*–coumarin), 9.28 (1H, s, C2*H*–imidazole). ^{13}C{^{1}H} NMR (75 MHz, d_6–DMSO, 298 K): δ 20.3 (*C*H$_3$–coumarin), 48.9 (*C*H$_3$–O–CH$_2$–CH$_2$), 49.0 (CH$_3$–O–*C*H$_2$–CH$_2$), 50.0 (CH$_3$–O–

CH_2–*C*H_2), 69.3 (*C*H_2–C4–coumarin), 123.3, 124.0 (*C*4, *C*5–imidazole), 113.4, 116.6, 123.0, 133.5, 134.1, 149.1, 151.0, 159.4 (Ar*C*–coumarin), 137.5 (*C*2–imidazole). ATR–IR (in cm^{-1}): 2920, ~2860 ν(C–H, aliphatic and aromatic), 1703 ν(C=O, lactonic), 1568 ν(C=N, imidazole), 1118 ν(C–O, coumarin). Anal. Calc. for $C_{17}H_{19}N_2O_3PF_6$: C, 46.0; H, 4.3; N, 6.3. Found: C, 46.3; H, 4.6; N, 6.5. Molar conductance (in CH_2Cl_2, 302 K): 150 S cm^2 mol^{-1}.

*4.4. Synthesis of 1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) imidazolium bromide/hexafluorophosphate (**4**)*

Salt **4** was prepared following the procedure analogous to that of salt **3** with 4–(bromomethyl)–6–chloro–coumarin (0.547 g, 2 mmol) instead of 4–(bromomethyl)–6–methyl–coumarin. Off–white solid; Yield: 67.1 %; M.P.: 162 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 3.26 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.71 (2H, t, *J* = 8.8 Hz, CH_3–O–C*H*$_2$–CH_2), 4.39 (2H, t, *J* = 8.4 Hz, CH_3–O–CH_2–C*H*$_2$), 5.80 (2H, s, C*H*$_2$–C4–coumarin), 6.12 (1H, s, C3*H*–coumarin), 7.55 (1H, d, *J* = 8.7 Hz, C4*H*–imidazole), 7.77 (1H, d, *J* = 8.8 Hz, C5*H*–imidazole), 7.85 (2H, d, *J* = 7.3 Hz, ArC*H*–coumarin), 7.96 (1H, s, ArC*H*–coumarin), 9.26 (1H, s, C2*H*–imidazole). ^{13}C{^{1}H} NMR (75 MHz, d_6–DMSO, 298 K): δ 48.1 (*C*H_3–O–CH_2–CH_2), 49.0 (CH_3–O–*C*H_2–CH_2), 58.0 (CH_3–O–CH_2–*C*H_2), 69.3 (*C*H_2–C4–coumarin), 114.9, 118.9, 122.9, 128.7, 132.3, 148.2, 151.6, 158.8 (Ar*C*–coumarin), 123.4, 123.9 (*C*4, *C*5–imidazole), 137.5 (*C*2–imidazole). ATR–IR (in cm^{-1}): 2912, ~2860 ν(C–H, aliphatic and aromatic), 1720 ν(C=O, lactonic), 1552 ν(C=N, imidazole), 1122 ν(C–O, coumarin). Anal. Calc. for $C_{16}H_{16}N_2O_3ClPF_6$: C, 41.4; H, 3.5; N, 6.0. Found: C, 41.0; H, 3.7; N, 6.1. Molar conductance (in CH_2Cl_2, 302 K): 165 S cm^2 mol^{-1}.

*4.5. Synthesis of 1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) imidazolium bromide/hexafluorophosphate (**5**)*

Salt **5** was prepared following the procedure analogous to that of salt **3** with 4–(bromomethyl)–5,6–benzo–coumarin (0.578 g, 2 mmol) instead of 4–(bromomethyl)–6–methyl–coumarin. Off–white solid; Yield: 83.0 %; M.P.: 160–162 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 3.26 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.70 (2H, t, *J* = 8.6 Hz, CH_3–O–C*H*$_2$–CH_2), 4.43 (2H, t, *J* = 8.8 Hz, CH_3–O–CH_2–C*H*$_2$), 5.82 (1H, s, C*H*$_2$–C4–coumarin), 6.35 (1H, s, C3*H*–coumarin), 7.79–7.64 (3H, m, ArC*H*–imidazole/coumarin), 7.88–7.83 (2H, m,

ArC*H*–coumarin), 8.15 (1H, d, *J* = 8.1 Hz, ArC*H*–coumarin), 8.31 (1H, d, *J* = 9 Hz, ArC*H*–coumarin), 8.37 (1H, d, *J* = 8.7 Hz, ArC*H*–coumarin), 9.25 (1H, s, C2*H*–imidazole). $^{13}C\{^{1}H\}$ NMR (75 MHz, d_6–DMSO, 298 K): δ 49.0 (*C*H_3–O–CH_2–CH_2), 52.4 (CH_3–O–*C*H_2–CH_2), 58.0 (CH_3–O–CH_2–*C*H_2), 69.3 (*C*H_2–C4–Coumarin), 112.5, 117.4, 123.0, 125.9, 128.4, 128.6, 129.9, 130.9, 134.6, 151.7, 154.2, 158.9 (Ar*C*–benzo–coumarin), 123.4, 125.1 (*C*4, *C*5–imidazole), 137.7 (*C*2–imidazole). ATR–IR (in cm^{-1}): 3059, 2965 ν(C–H, aliphatic and aromatic), 1695 ν(C=O, lactonic), 1550 ν(C=N, imidazole), 1097 ν(C–O, coumarin). Anal. Calc. for $C_{20}H_{19}N_2O_3PF_6$: C, 50.0; H, 4.0; N, 5.8. Found: C, 50.5; H, 4.4; N, 6.0. Molar conductance (in CH_2Cl_2, 302 K): 141 S cm^2 mol^{-1}.

*4.6. Synthesis of 1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) benzimidazolium bromide/hexafluorophosphate (**6**)*

Salt **6** was prepared following the procedure analogous to that of salt **3** with 1–(2–methoxyethyl)–1H–benzimidazole (**2**) (0.353 g, 2 mmol) instead of 1–(2–methoxyethyl)–1H–imidazole (**1**). Yellow solid; Yield: 80.7 %; M.P.: 230–232 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 2.44 (3H, s, C*H*$_3$–coumarin), 3.28 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.83 (2H, t, *J* = 8.8 Hz, CH_3–O–C*H*$_2$–CH_2), 4.77–4.73 (2H, m, CH_3–O–CH_2–C*H*$_2$), 5.86 (1H, s, C3*H*–coumarin), 6.19 (2H, s, C*H*$_2$–C4–coumarin), 7.41 (1H, d, *J* = 8.4 Hz, ArC*H*–benzimidazole), 7.56 (1H, d, *J* = 8.4 Hz, ArC*H*–benzimidazole), 7.77–7.69 (3H, m, ArC*H*–benzimidazole/coumarin), 8.04 (1H, d, *J* = 7.8 Hz, ArC*H*–coumarin), 8.18 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin), 9.82 (1H, s, C2*H*–benzimidazole). $^{13}C\{^{1}H\}$ NMR (75 MHz, d_6–DMSO, 298 K) : δ 20.3 (*C*H_3–coumarin), 46.3 (*C*H_3–O–CH_2–CH_2), 46.8 (CH_3–O–*C*H_2–CH_2), 58.1 (CH_3–O–CH_2–*C*H_2), 68.7 (*C*H_2–C4–coumarin), 112.2, 113.6, 114.1, 124.3, 126.9 (Ar*C*–benzimidazole), 116.6, 126.7, 131.0, 131.4, 133.5, 133.9, 148.7, 151.0, 159.4 (Ar*C*–coumarin), 143.6 (*C*2–benzimidazole). ATR–IR (in cm^{-1}): 2962, ~2890 ν(C–H, aliphatic and aromatic), 1705 ν(C=O, lactonic), 1569 ν(C=N, benzimidazole), 1108 ν(C–O, coumarin). Anal. Calc. for $C_{21}H_{21}N_2O_3PF_6$: C, 51.0; H, 4.3; N, 5.7. Found: C, 51.2; H, 4.3; N, 5.8. Molar conductance (in CH_2Cl_2, 302 K): 144 S cm^2 mol^{-1}.

*4.7. Synthesis of 1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) benzimidazolium bromide/hexafluorophosphate (**7**)*

Salt **7** was prepared following the procedure analogous to that of salt **3** with 1–(2–methoxyethyl)–1H–benzimidazole (**2**) (0.353 g, 2 mmol) and 4–(bromomethyl)–6–chloro–coumarin (0.547 g, 2 mmol) instead of 1–(2–methoxyethyl)–1H–imidazole (**1**) and 4–(bromomethyl)–6–methyl–coumarin, respectively. Pale yellow solid; Yield: 98.5 %; M.P.: 236–237 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 3.28 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.85–3.82 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.76–4.73 (2H, m, CH$_3$–O–CH$_2$–C*H*$_2$), 5.98 (1H, s, C3*H*–coumarin), 6.19 (2H, s, C*H*$_2$–C4–coumarin), 7.56 (1H, d, *J* = 9.0 Hz, ArC*H*–benzimidazole) 7.82–7.70 (3H, m, ArC*H*–benzimidazole), 8.07–8.01 (2H, m, ArC*H*–coumarin), 8.18 (1H, d, *J* = 8.1 Hz, ArC*H*–coumarin), 9.80 (1H, s, C2*H*–benzimidazole). ^{13}C{^{1}H} NMR (75 MHz, d_6–DMSO, 298 K): δ 46.2 (*C*H$_3$–O–C*H*$_2$–CH$_2$), 46.8 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.1 (CH$_3$–O–CH$_2$–*C*H$_2$), 68.7 (*C*H$_2$–C4–coumarin), 113.4, 114.1, 118.2, 118.8, 124.3, 126.8 (Ar*C*–benzimidazole), 113.6, 126.9, 128.6, 130.9, 131.5, 132.3, 147.9, 151.6, 158.8 (Ar*C*–coumarin), 143.6 (*C*2–benzimidazole). ATR–IR (in cm^{-1}): ~2930, 2820 ν(C–H, aliphatic and aromatic), 1715 ν(C=O, lactonic), 1562 ν(C=N, benzimidazole), 1103 ν(C–O, coumarin). Anal. Calc. for $C_{20}H_{18}N_2O_3ClPF_6$: C, 46.7; H, 3.5; N, 5.4. Found: C, 46.7; H, 3.5; N, 5.5. Molar conductance (in CH_2Cl_2, 302 K): 165 S cm^2 mol^{-1}.

*4.8. Synthesis of 1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) benzimidazolium bromide/hexafluorophosphate (**8**)*

Salt **8** was prepared following the procedure analogous to that of salt **3** with 1–(2–methoxyethyl)–1H–benzimidazole (**2**) (0.353 g, 2 mmol) and 4–(bromomethyl)–5,6–benzo–coumarin (0.578 g, 2 mmol) instead of 1–(2–methoxyethyl)–1H–imidazole (**1**) and 4–(bromomethyl)–6–methyl–coumarin, respectively. Pale yellow solid; Yield: 87.5 %; M.P.: 254–256 °C. ^{1}H NMR (300 MHz, d_6–DMSO, 298 K): δ 3.26 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.84–3.81 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.78–4.75 (2H, m, CH$_3$–O–CH$_2$–C*H*$_2$), 5.81 (1H, s, C3*H*–coumarin), 6.69 (2H, s, C*H*$_2$–C4–coumarin), 7.80–7.69 (5H, m, ArC*H*–benzimidazole/coumarin), 8.08 (1H, d, *J* = 8.1 Hz, ArC*H*–coumarin), 8.19 (2H, m, ArC*H*–coumarin), 8.34 (1H, d, *J* = 9.0 Hz, ArC*H*–coumarin), 8.52 (1H, d, *J* = 8.7 Hz, ArC*H*–coumarin), 9.76 (1H, s, C2*H*–benzimidazole). ^{13}C{^{1}H} NMR (75 MHz, d_6–DMSO, 298 K): δ 46.3 (*C*H$_3$–O–CH$_2$–CH$_2$), 48.5 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.1 (CH$_3$–O–CH$_2$–*C*H$_2$), 68.7 (*C*H$_2$–

C4–coumarin), 111.7, 112.3, 114.2, 117.5, 125.6, 126.8 (Ar*C*–benzimidazole), 114.0, 125.9, 127.0, 128.5, 128.7, 130.9, 131.0, 131.4, 134.7, 151.2, 154.3, 158.9 (Ar*C*–benzo–coumarin), 143.7 (*C*2–benzimidazole). ATR–IR (in cm^{-1}): ~2930, 2812 ν(C–H, aliphatic and aromatic), 1711 ν(C=O, lactonic), 1556 ν(C=N, benzimidazole), 1102 ν(C–O, coumarin). Anal. Calc. for $C_{24}H_{21}N_2O_3PF_6$: C, 54.4; H, 4.0; N, 5.3. Found: C, 54.5; H, 4.3; N, 5.6. Molar conductance (in CH_2Cl_2, 302 K): 170 S cm^2 mol^{-1}.

*4.9. Synthesis of bis{1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidene}silver(I) hexafluorophosphate complex (**9**)*

A suspension of imidazolium hexafluorophosphate salt **3** (0.445 g, 1 mmol) and silver(I) oxide (0.138 g, 0.6 mmol) in acetonitrile was stirred at 45 °C for 24 h under the exclusion of light (in a round bottom flask wrapped with aluminum foil). After the stipulated time, the reaction mixture was filtered through a bed of cilite and filtrate was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the resulted crude product was washed with methanol (3 x 3 mL) and purified by repeated precipitation in acetonitrile–diethyl ether mixture to afford light sensitive complex **9** as an off–white solid. Yield: 95.0 %; M.P.: 112–114 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 2.31 (3H, s, C*H*$_3$–coumarin), 3.09 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.50 (2H, t, *J* = 8.4 Hz, CH_3–O–C*H*$_2$–CH_2), 4.25 (2H, m, CH_3–O–CH_2–C*H*$_2$), 5.52 (1H, s, C3*H*–coumarin), 5.64 (2H, s, C*H*$_2$–C4–coumarin), 7.24 (1H, d, *J* = 8.4 Hz, C4*H*–imidazole), 7.43 (1H, d, *J* = 8.4 Hz, C5*H*–imidazole), 7.53–7.52 (3H, m, ArC*H*–coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 20.8 (*C*H_3–coumarin), 50.8 (*C*H_3–O–CH_2–CH_2), 51.3 (CH_3–O–*C*H_2–CH_2), 58.4 (CH_3–O–CH_2–*C*H_2), 71.6 (*C*H_2–C4–coumarin), 123.2, 124.3 (*C*4, *C*5–imidazole), 112.5, 116.9, 117.0, 133.7, 134.2, 151.3, 152.2, 159.7 (Ar*C*–coumarin), *C*2–imidazole absent. ATR–IR (in cm^{-1}): 2883, 2930 ν(C–H, aliphatic and aromatic), 1720 ν(C=O, lactonic), 1572 ν(C=N, imidazole), 1113 ν(C–O, coumarin). Anal. Calc. for $C_{34}H_{36}N_4O_6AgPF_6$: C, 48.1; H, 4.3; N, 6.6. Found: C, 48.5; H, 4.3; N, 6.9. Molar conductance (in CH_2Cl_2, 302 K): 58 S cm^2 mol^{-1}.

*4.10. Synthesis of bis{1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidene}silver(I) hexafluorophosphate complex (**10**)*

Complex **10** was prepared following the procedure analogous to that of bis–carbene coordinated silver(I) complex **9** with imidazolium hexafluorophosphate salt **4** (0.464 g, 1 mmol) instead of imidazolium hexafluorophosphate salt **3**. Off–white solid; Yield: 93.0 %; M.P.: 82–84 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.12 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.55 (2H, t, *J* = 8.8 Hz, CH$_3$–O–C*H*$_2$–CH$_2$), 4.28 (2H, t, *J* = 8.8 Hz, CH$_3$–O–CH$_2$–C*H*$_2$), 5.57 (1H, s, C3*H*–coumarin), 5.68 (2H, s, C*H*$_2$–C4–coumarin), 7.41 (1H, d, *J* = 8.4 Hz, C4*H*–imidazole), 7.54–7.49 (2H, m, ArC*H*–imidazole/coumarin), 7.67 (1H, d, *J* = 8.4 Hz, ArC*H*–coumarin), 7.85–7.80 (1H, m, ArC*H*–coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 50.7 (*C*H$_3$–O–CH$_2$–CH$_2$), 51.3 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.5 (CH$_3$–O–CH$_2$–*C*H$_2$), 71.7 (*C*H$_2$–C4–coumarin), 123.5, 124.2 (*C*4, *C*5–imidazole), 113.5, 118.6, 119.2, 123.1, 129.0, 132.7, 151.5, 151.8, 159.1 (Ar*C*–coumarin), *C*2–Imidazole absent. ATR–IR (in cm^{-1}): 2962, ~3020 ν(C–H, aliphatic and aromatic), 1718 ν(C=O, lactonic), 1563 ν(C=N, imidazole), 1093 ν(C–O, coumarin). Anal. Calc. for $C_{32}H_{30}N_4O_6AgCl_2PF_6$: C, 43.2; H, 3.4; N, 6.3. Found: C, 43.0; H, 3.3; N, 6.6. Molar conductance (in CH_2Cl_2, 302 K): 60 S cm^2 mol^{-1}.

*4.11. Synthesis of bis{1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidene}silver(I) hexafluorophosphate complex (**11**)*

Complex **11** was prepared following the procedure analogous to that of bis–carbene coordinated silver(I) complex **9** with imidazolium hexafluorophosphate salt **5** (0.481 g, 1 mmol) instead of imidazolium hexafluorophosphate salt **3**. Off–white solid; Yield: 76.3 %; M.P.: 86–88 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.17 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.63–3.58 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.38–4.34 (2H, m, CH$_3$–O–CH$_2$–C*H*$_2$), 5.32 (1H, s, C3*H*–coumarin), 6.13 (2H, s, C*H*$_2$–C4–coumarin), 7.26 (1H, d, *J* = 8.4 Hz, ArC*H*–imidazole), 7.42–7.34 (3H, m, ArC*H*–imidazole/coumarin), 7.56–7.53 (1H, m, ArC*H*–coumarin), 7.88 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin), 7.99 (1H, d, *J* = 8.8 Hz, ArC*H*–coumarin), 8.18 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 51.3 (*C*H$_3$–O–CH$_2$–CH$_2$), 54.7 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.5 (CH$_3$–O–CH$_2$–*C*H$_2$), 71.7 (*C*H$_2$–C2–coumarin), 123.5, 125.7 (*C*4, *C*5–imidazole), 111.6, 112.5, 117.4, 117.9, 123.1, 128.4, 128.7, 129.9, 131.1, 134.6, 154.2, 154.7, 159.1 (Ar*C*–benzo–coumarin), *C*2–Imidazole absent. ATR–IR (in cm^{-1}): 3015, 2943 ν(C–H, aliphatic and aromatic), 1724

ν(C=O, lactonic), 1548 ν(C=N, imidazole), 1113 ν(C–O, coumarin). Anal. Calc. for $C_{40}H_{36}N_4O_6AgPF_6$: C, 52.1; H, 4.0; N, 6.1. Found: C, 52.5; H, 4.3; N, 5.9. Molar conductance (in CH_2Cl_2, 302 K): 43 S cm^2 mol^{-1}.

*4.12. Synthesis of bis{1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidene}silver(I) hexafluorophosphate complex (**12**)*

Complex **12** was prepared following the procedure analogous to that of bis–carbene coordinated silver(I) complex **9** with benzimidazolium hexafluorophosphate salt **6** (0.495 g, 1 mmol) instead of imidazolium hexafluorophosphate salt **3**. Off–white solid; Yield: 93.3 %; M.P.: 212–214 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 2.38 (3H, s, C*H*$_3$–coumarin), 3.02 (1H, s, C*H*$_3$–O–CH_2–CH_2), 3.55–3.52 (2H, m, CH_3–O–C*H*$_2$–CH_2) 4.67–4.65 (2H, m, CH_3–O–CH_2–C*H*$_2$), 5.35 (1H, s, C3*H*–coumarin), 6.13 (2H, s, C*H*$_2$–C4–coumarin), 7.27 (1H, d, *J* = 8.4 Hz, ArC*H*–benzimidazole), 7.48–7.39 (3H, m, ArC*H*–benzimidazole), 7.72 (2H, d, *J* = 7.6 Hz, ArC*H*–coumarin), 7.77 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 20.9 (*C*H_3–coumarin), 48.5 (*C*H_3–O–CH_2–CH_2), 49.1 (CH_3–O–*C*H_2–CH_2), 58.6 (CH_3–O–CH_2–*C*H_2), 71.0 (*C*H_2–C4–coumarin), 112.5, 116.9, 117.1, 124.7, 124.9 (Ar*C*–benzimidazole), 111.5, 113.0, 124.8, 133.8, 134.0, 134.2, 151.6, 159.6, 159.7 (Ar*C*–coumarin), *C*2–benzimidazole absent. ATR–IR (in cm^{-1}): 2962, ~2865 ν(C–H, aliphatic and aromatic), 1715 ν(C=O, lactonic), 1567 ν(C=N, benzimidazole), 1107 ν(C–O, coumarin). Anal. Calc. for $C_{42}H_{40}N_4O_6AgPF_6$: C, 53.1; H, 4.2; N, 5.9. Found: C, 53.5; H, 4.3; N, 5.6. Molar conductance (in CH_2Cl_2, 302 K): 48 S cm^2 mol^{-1}.

*4.13. Synthesis of bis{1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidene}silver(I) hexafluorophosphate complex (**13**)*

Complex **13** was prepared following the procedure analogous to that of bis–carbene coordinated silver(I) complex **9** with benzimidazolium hexafluorophosphate salt **7** (0.515 g, 1 mmol) instead of imidazolium hexafluorophosphate salt **3**. Off–white solid; Yield: 91.2 %; M.P.: 210–212 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.09 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.66–3.60 (2H, m, CH_3–O–C*H*$_2$–CH_2), 4.69 (2H, t, *J* = 8.8 Hz, CH_3–O–CH_2–C*H*$_2$), 5.37 (1H, s, C3*H*–coumarin), 6.15 (2H, s, C*H*$_2$–C4–coumarin), 7.48–7.36 (3H, m, ArC*H*–benzimidazole), 7.72 (2H, d, *J* = 8.8 Hz, ArC*H*–benzimidazole/coumarin), 7.88 (1H, d, *J* =

8.0 Hz, ArC*H*–coumarin), 8.00 (1H, s, ArC*H*–coumarin). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6–DMSO, 298 K): δ 48.4 (*C*H_3–O–CH_2–CH_2), 49.1 (CH_3–O–*C*H_2–CH_2), 58.7 (CH_3–O–CH_2–*C*H_2), 71.0 (*C*H_2–C4–coumarin), 112.4, 113.1, 118.8, 119.1, 124.7 (Ar*C*–benzimidazole), 112.5, 127.6, 129.0, 132.7, 133.8, 134.1, 151.0, 151.9, 159.0 (Ar*C*–coumarin), 191.7 (*C*2–benzimidazole). ATR–IR (in cm^{-1}): 2969, 2861 ν(C–H, aliphatic and aromatic), 1701 ν(C=O, lactonic), 1522 ν(C=N, benzimidazole), 1107 ν(C–O, coumarin). Anal. Calc. for $C_{40}H_{34}N_4O_6AgCl_2PF_6$: C, 48.5; H, 3.5; N, 5.7. Found: C, 48.3; H, 3.6; N, 5.6. Molar conductance (in CH_2Cl_2, 302 K): 44 S cm^2 mol^{-1}.

*4.14. Synthesis of bis{1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidene}silver(I) hexafluorophosphate complex (**14**)*

Complex **14** was prepared following the procedure analogous to that of bis–carbene coordinated silver(I) complex **9** with benzimidazolium hexafluorophosphate salt **8** (0.531 g, 1 mmol) instead of imidazolium hexafluorophosphate salt **3**. Off–white solid; Yield: 78.7 %; M.P.: 138–140 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.11 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.68–3.62 (2H, m, CH_3–O–C*H*$_2$–CH_2), 4.72–4.67 (2H, m, CH_3–O–CH_2–C*H*$_2$), 5.24 (1H, s, C3*H*–coumarin), 6.54 (2H, s, C*H*$_2$–C4–coumarin), 7.36–7.31 (1H, m, ArC*H*–benzimidazole), 7.47–7.40 (2H, m, ArC*H*–benzimidazole), 7.57–7.52 (2H, m, ArC*H*–benzimidazole/coumarin), 7.64 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin), 7.88 (1H, d, *J* = 8.0 Hz, ArC*H*–coumarin), 8.01 (1H, m, ArC*H*–coumarin), 8.13 (1H, d, *J* = 8.2 Hz, ArC*H*–coumarin). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6–DMSO, 298 K): δ 49.2 (*C*H_3–O–CH_2–CH_2), 52.7 (CH_3–O–*C*H_2–CH_2), 58.7 (CH_3–O–CH_2–*C*H_2), 71.0 (*C*H_2–C4–coumarin), 112.8, 113.0, 117.6, 124.7, 126.0 (Ar*C*–benzimidazole), 111.1, 126.3, 128.6, 129.1, 130.0, 131.3, 131.9, 133.6, 134.1, 134.9, 153.9, 154.5, 159.1 (Ar*C*–benzo–coumarin), 192.4 (*C*2–benzimidazole). ATR–IR (in cm^{-1}): ~2930, 2807 ν(C–H, aliphatic and aromatic), 1724 ν(C=O, lactonic), 1549 ν(C=N, benzimidazole) 1113 ν(C–O, coumarin). Anal. Calc. for $C_{48}H_{40}N_4O_6AgPF_6$: C, 56.4; H, 4.0; N, 5.5. Found: C, 56.5; H, 4.3; N, 5.7. Molar conductance (in CH_2Cl_2, 302 K): 48 S cm^2 mol^{-1}.

*4.15. Synthesis of 1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidenesilver(I) bromide complex (**15**)*

A suspension of imidazolium bromide salt, 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide, (0.380 g, 1 mmol) and silver(I) oxide (0.253 g, 1.1 mmol) in dichloromethane was stirred at room temperature for 24 h under the exclusion of light (in a round bottom flask wrapped with aluminum foil). After the stipulated time, the reaction mixture was filtered through a bed of cilite and filtrate was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the resulted crude product was washed with diethyl ether (3 x 3 mL) and purified by repeated precipitation using acetonitrile–diethyl ether mixture to afford light sensitive complex **15** as a beige colored solid. Yield: 60.2 %; M.P.: 80–82 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 2.35 (3H, s, C*H*$_3$–coumarin), 3.12 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.61 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.28 (2H, t, *J* = 8.8 Hz, CH$_3$–O–CH$_2$–C*H*$_2$), 5.58 (1H, s, C3*H*–coumarin), 5.69 (2H, s, C*H*$_2$–C4–coumarin), 7.22 (1H, d, *J* = 8.2 Hz, C4*H*–imidazole), 7.44 (1H, d, *J* = 8.4 Hz, C5*H*–imidazole), 7.53–7.62 (3H, m, ArC*H*–coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 20.9 (*C*H$_3$–coumarin), 50.5 (*C*H$_3$–O–CH$_2$–CH$_2$), 51.4 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.4 (CH$_3$–O–CH$_2$–*C*H$_2$), 71.5 (*C*H$_2$–C4–coumarin), 123.3, 124.5 (*C*4, *C*5–imidazole), 112.5, 116.4, 117.5, 132.7, 133.2, 151.5, 152.1, 159.9 (Ar*C*–coumarin), *C*2–imidazole absent. ATR–IR (in cm^{-1}): 2922, ~2885 ν(C–H, aliphatic and aromatic), 1711 ν(C=O, lactonic), 1564 ν(C=N, imidazole), 1111 (C–O, coumarin). Anal. Calc. for $C_{17}H_{18}N_2O_3AgBr$: C, 42.0; H, 3.7; N, 5.8. Found: C, 42.4; H, 3.4; N, 5.6. Molar conductance (in CH_2Cl_2, 302 K): 0 S cm^2 mol^{-1}.

*4.16. Synthesis of 1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidenesilver(I) bromide complex (**16**)*

Complex **16** was prepared following the procedure analogous to that of mono–carbene coordinated silver(I) complex **15** with imidazolium bromide salt, 1–(2–methoxyethyl)–3–(6–chlorocoumarin–4–yl)imidazolium bromide, (0.400 g, 1 mmol) instead of 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide. Beige colored solid; Yield: 50.0 %; M.P.: 56–58 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.14 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.58 (2H, t, *J* = 8.6 Hz, CH$_3$–O–C*H*$_2$–CH$_2$), 4.26 (2H, t, *J* = 8.8 Hz, CH$_3$–O–CH$_2$–C*H*$_2$), 5.60 (1H, s, C3*H*–Coumarin), 5.72 (2H, s, C*H*$_2$–C4–Coumarin), 7.43 (1H, d, *J* = 8.4 Hz, C4*H*–Imidazole), 7.56 (2H, d, *J* = 8.4 Hz, C5*H*–Imidazole), 7.69 (2H, d, *J* = 8.2 Hz,

ArC*H*–Coumarin), 7.88–7.82 (1H, m, ArC*H*–Coumarin). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6–DMSO, 298 K): δ 50.3 (*C*H_3–O–CH_2–CH_2), 51.5 (CH_3–O–*C*H_2–CH_2), 58.6 (CH_3–O–CH_2–*C*H_2), 71.7 (*C*H_2–C4–Coumarin), 123.0, 123.6 (*C*4, *C*5–Imidazole), 113.5, 118.7, 119.3, 124.6, 129.1, 132.7, 151.6, 151.8, 159.3 (Ar*C*–Coumarin), *C*2–Imidazole absent. ATR–IR (in cm^{-1}): 2923, ~2880 ν(C–H, aliphatic and aromatic), 1716 ν(C=O, lactonic), 1566 ν(C=N, Imidazole), 1103 (C–O, Coumarin). Anal. Calc. for $C_{16}H_{15}N_2O_3AgClBr$: C, 37.9; H, 3.0; N, 5.5. Found: C, 37.7; H, 3.3; N, 5.7. Molar conductance (in CH_2Cl_2, 302 K): 02 S cm^2 mol^{-1}.

*4.17. Synthesis of 1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) imidazol–2–ylidenesilver(I) bromide complex (**17**)*

Complex **17** was prepared following the procedure analogous to that of mono–carbene coordinated silver(I) complex **15** with imidazolium bromide salt, 1–(2–methoxyethyl)–3–(5,6–benzocoumarin–4–yl)imidazolium bromide, (0.416 g, 1 mmol) instead of 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide. Beige colored solid; Yield: 52.0 %; M.P.: 112–114 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.13 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.64–3.56 (2H, m, CH_3–O–C*H*$_2$–CH_2), 4.39 (2H, d, *J* = 8.8 Hz, CH_3–O–CH_2–C*H*$_2$), 5.33 (1H, s, C3*H*–Coumarin), 6.15 (2H, s, C*H*$_2$–C4–Coumarin), 7.29 (1H, d, *J* = 8.4 Hz, ArC*H*–Imidazole), 7.40–7.33 (3H, m, ArC*H*–Imidazole/Coumarin), 7.58–7.52 (1H, m, ArC*H*–Coumarin), 7.83 (1H, d, *J* = 8.0 Hz, ArC*H*–Coumarin), 8.01 (1H, d, *J* = 8.2 Hz, ArC*H*–Coumarin), 8.18 (1H, m, ArC*H*–Coumarin). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6–DMSO, 298 K): δ 51.4 (*C*H_3–O–CH_2–CH_2), 54.7 (CH_3–O–*C*H_2–CH_2), 58.8 (CH_3–O–CH_2–*C*H_2), 71.6 (*C*H_2–C2–Coumarin), 123.4, 125.7 (*C*4, *C*5–Imidazole), 111.7, 112.7, 117.9, 123.1, 128.5, 128.7, 129.7, 131.4, 134.6, 151.3, 154.7, 159.6 (Ar*C*–Benzo–coumarin), *C*2–Imidazole absent. ATR–IR (in cm^{-1}): 2926, 2866 ν(C–H, aliphatic and aromatic), 1715 ν(C=O, lactonic), 1561 ν(C=N, Imidazole), 1109 (C–O, Coumarin). Anal. Calc. for $C_{20}H_{18}N_2O_3AgBr$: C, 46.0; H, 3.5; N, 5.4. Found: C, 46.3; H, 3.4; N, 5.5. Molar conductance (in CH_2Cl_2, 302 K): 02 S cm^2 mol^{-1}.

*4.18. Synthesis of 1–(2–methoxyethyl)–3–((6–methyl–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidenesilver(I) bromide complex (**18**)*

Complex **18** was prepared following the procedure analogous to that of mono–carbene coordinated silver(I) complex **15** with benzimidazolium bromide salt, 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)benzimidazolium bromide, (0.430 g, 1 mmol) instead of 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide. Beige colored solid; Yield: 58.3 %; M.P.: 90–92 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 2.33 (3H, s, C*H*$_3$–Coumarin), 3.04 (1H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.56 (2H, t, *J* = 8.2 Hz, CH$_3$–O–C*H*$_2$–CH$_2$) 4.69–4.64 (2H, m, CH$_3$–O–CH$_2$–C*H*$_2$), 5.37 (1H, s, C3*H*–Coumarin), 6.18 (2H, s, C*H*$_2$–C4–Coumarin), 7.24 (1H, d, *J* = 8.2 Hz, ArC*H*–Benzimidazole), 7.52–7.47 (3H, m, ArC*H*–Benzimidazole), 7.70 (2H, d, *J* = 8.0 Hz, ArC*H*–Coumarin), 7.79 (1H, d, *J* = 8.0 Hz, ArC*H*–Coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 20.8 (*C*H$_3$–Coumarin), 48.8 (*C*H$_3$–O–CH$_2$–CH$_2$), 49.4 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.6 (CH$_3$–O–CH$_2$–*C*H$_2$), 71.1 (*C*H$_2$–C4–Coumarin), 112.6, 116.9, 117.3, 124.3, 124.4, (Ar*C*–Benzimidazole), 111.5, 113.1, 124.8, 133.7, 134.1, 134.2, 151.5, 159.8, 159.8 (Ar*C*–Coumarin), *C*2–Benzimidazole absent. ATR–IR (in cm^{-1}): 2929, ~2830 ν(C–H, aliphatic and aromatic), 1710 ν(C=O, lactonic), 1564 ν(C=N, Imidazole), 1113 (C–O, Coumarin). Anal. Calc. for $C_{21}H_{20}N_2O_3AgBr$: C, 47.0; H, 3.8; N, 5.2. Found: C, 47.4; H, 4.0; N, 5.4. Molar conductance (in CH_2Cl_2, 302 K): 02 S cm^2 mol^{-1}.

*4.19. Synthesis of 1–(2–methoxyethyl)–3–((6–chloro–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidenesilver(I) bromide complex (**19**)*

Complex **19** was prepared following the procedure analogous to that of mono–carbene coordinated silver(I) complex **15** with benzimidazolium bromide salt, 1–(2–methoxyethyl)–3–(6–chlorocoumarin–4–yl)benzimidazolium bromide, (0.450 g, 1 mmol) instead of 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide. Beige colored solid; Yield: 54.4 %; M.P.: 124–126 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.13 (3H, s, C*H*$_3$–O–CH$_2$–CH$_2$), 3.61–3.57 (2H, m, CH$_3$–O–C*H*$_2$–CH$_2$), 4.72 (2H, t, *J* = 8.6 Hz, CH$_3$–O–CH$_2$–C*H*$_2$), 5.39 (1H, s, C3*H*–Coumarin), 6.16 (2H, s, C*H*$_2$–C4–Coumarin), 7.48–7.42 (3H, m, ArC*H*–Benzimidazole), 7.74 (2H, d, *J* = 8.8 Hz, ArC*H*–Benzimidazole/Coumarin), 7.89 (1H, d, *J* = 8.0 Hz, ArC*H*–Coumarin), 8.02 (1H, s, ArC*H*–Coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 48.5 (*C*H$_3$–O–CH$_2$–CH$_2$), 49.3 (CH$_3$–O–*C*H$_2$–CH$_2$), 58.7 (CH$_3$–

O–CH_2–CH_2), 71.2 (CH_2–C4–Coumarin), 112.4, 113.6, 118.3, 119.1, 124.3 (Ar*C*–Benzimidazole), 112.5, 127.7, 129.2, 131.3, 133.4, 134.1, 151.5, 151.9, 159.6 (Ar*C*–Coumarin), *C*2–Benzimidazole absent. ATR–IR (in cm^{-1}): ~2920, 2869 ν(C–H, aliphatic and aromatic), 1722 ν(C=O, lactonic), 1596 ν(C=N, Imidazole), 1110 (C–O, Coumarin). Anal. Calc. for $C_{20}H_{17}N_2O_3AgBrCl$: C, 43.2; H, 3.1; N, 5.0. Found: C, 43.5; H, 3.2; N, 5.2. Molar conductance (in CH_2Cl_2, 302 K): 0 S cm^2 mol^{-1}.

*4.20. Synthesis of 1–(2–methoxyethyl)–3–((5,6–benzo–2–oxo–2H–chromen–4–yl)methyl) benzimidazol–2–ylidenesilver(I) bromide complex (**20**)*

Complex **20** was prepared following the procedure analogous to that of mono–carbene coordinated silver(I) complex **15** with benzimidazolium bromide salt, 1–(2–methoxyethyl)–3–(5,6–benzocoumarin–4–yl)benzimidazolium bromide, (0.466 g, 1 mmol) instead of 1–(2–methoxyethyl)–3–(6–methylcoumarin–4–yl)imidazolium bromide. Beige colored solid; Yield: 52.3 %; M.P.: 146–148 °C. ^{1}H NMR (400 MHz, d_6–DMSO, 298 K): δ 3.09 (3H, s, C*H*$_3$–O–CH_2–CH_2), 3.66 (2H, t, *J* = 8.2 Hz, CH_3–O–C*H*$_2$–CH_2), 4.77–4.73 (2H, m, CH_3–O–CH_2–C*H*$_2$), 5.27 (1H, s, C3*H*–Coumarin), 6.54 (2H, s, C*H*$_2$–C4–Coumarin), 7.38–7.34 (1H, m, ArC*H*–Benzimidazole), 7.48–7.42 (2H, m, ArC*H*–Benzimidazole), 7.59–7.54 (2H, m, ArC*H*–Benzimidazole/Coumarin), 7.66 (1H, d, *J* = 8.2 Hz, ArC*H*–Coumarin), 7.88 (1H, m, ArC*H*–Coumarin), 8.02 (1H, m, ArC*H*–Coumarin), 8.14 (1H, d, *J* = 8.2 Hz, ArC*H*–Coumarin), 8.41 (1H, m, ArC*H*–Coumarin). ^{13}C{^{1}H} NMR (100 MHz, d_6–DMSO, 298 K): δ 49.5 (*C*H_3–O–CH_2–CH_2), 52.7 (CH_3–O–*C*H_2–CH_2), 58.3 (CH_3–O–CH_2–*C*H_2), 71.1 (*C*H_2–C4–Coumarin), 112.7, 113.0, 117.9, 124.7, 126.3 (Ar*C*–Benzimidazole), 111.3, 126.8, 128.6, 129.3, 131.5, 131.9, 133.8, 134.2, 134.9, 152.4, 154.5, 159.2 (Ar*C*–Benzo–coumarin). ATR–IR (in cm^{-1}): ~2930, 2857 ν(C–H, aliphatic and aromatic), 1719 ν(C=O, lactonic), 1596 ν(C=N, Imidazole), 1112 (C–O, Coumarin). Anal. Calc. for $C_{24}H_{20}N_2O_3AgBr$: C, 50.4; H, 3.5; N, 4.9. Found: C, 50.5; H, 3.5; N, 4.6. Molar conductance (in CH_2Cl_2, 302 K): 02 S cm^2 mol^{-1}.

4.21. Determination of antibacterial potentials of azolium salts and silver complexes

The antibacterial potentials of the prepared azolium hexafluorophosphate salts (**3–8**) and their mono– and bis–carbene silver(I) complexes (**9–20**) in terms of minimum inhibitory

concentrations (MIC) were determined against both the type of bacteria following broth dilution method. The stock solution (256 µg/mL) of the salts and complexes **3–20** was prepared by using dimethylsulphoxide. A loop of the bacterial strain was suspended in autoclaved distilled water and the turbidity of this solution was set to that of 0.5 McFarland standard. The MIC of the salts and complexes was determined by serially diluting the test compounds **3–20** to obtain a concentration range of 1–256 µg/mL which is further diluted by adding 1 mL bacterial suspension to obtain a final concentration range from 0.5–128 µg/mL and a final desired inoculum of 5×10^5 CFU mL^{-1}. The control test tubes contained 10 % DMSO mixture in nutrient broth along with the bacterial suspension. All the test tubes were incubated at 37 ^oC for 16 h. MIC was read as the lowest concentration of the complex that inhibits visible bacterial growth.

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Supplementary material

The crystallographic data for structural analysis have been deposited in the Cambridge Crystallographic Data Center, CCDC 1570022 and 1570021 contain the supplementary crystallographic data for the imidazolium salt **5** and silver complex **12**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal packing diagrams for compounds **5** and **12** are also available as Supporting Information.

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Table 3.1. Crystallographic data and the structure refinement details for the imidazolium salt **5** and benzimidazolium silver–NHC complex **12**.

	5	**12**
Formula	$C_{20}H_{19}F_6N_2O_3P$	$C_{42}H_{40}AgN_4O_6F_6P$
Formula weight	480.34	949.62
Crystal system	triclinic	triclinic
Space group	*P*–1	*P*–1
Unit cell dimensions		
a (Å)	6.9003(3)	8.1369(5)
b (Å)	9.3165(4)	8.8872(5)
c (Å)	16.6234(6)	15.0525(8)
α (°)	103.9680(10)	105.314(5)
β (°)	93.236(2)	100.370(5)
γ (°)	105.611(2)	96.199(5)
V (Å^3)	990.34(7)	1018.74(11)
Z	2	1
Density(calcd) (g/cm^3)	1.611	1.548
Abs. coeff. (mm^{-1})	2.007	6.184
F(000)	492	484
Crystal size (mm)	0.19 x 0.12 x 0.08	0.21 x 0.11 x 0.03
Temperature (K)	296(2)	295(2)
Radiation (Å)	1.54178	0.71073
θ Min, Max (°)	2.76, 64.50	3.420, 29.343
Data set	–8:7, –10:10, –18:19	–10:11, –11:11, –19:18
Tot., Uniq. Data	10397, 290	23009, 437
R (int)	0.0486	0.0762
N_{ref}, N_{par}	3267, 290	4755, 437
R, wR_2, S	0.0387, 0.1082, 1.052	0.0456, 0.1906, 1.087

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Table 3.2. Important bond distances and angles for imidazolium salt **5**.

Module	Bond distance (Å)
N(1)–C(1)	1.331(2)
N(2)–C(1)	1.331(2)
O(2)–C(10)	1.356(2)
O(2)–C(11)	1.370(2)
O(3)–C(10)	1.213(2)
O(1)–C(5)	1.410(2)
O(1)–C(6)	1.422(2)
P(1)–F(1)	1.6027(13)
Module	**Bond angle (°)**
N(1)–C(1)–N(2)	108.37(16)
C(1)–N(1)–C(2)	108.95(15)
C(1)–N(2)–C(3)	108.58(15)
N(1)–C(7)–C(8)	114.27(14)
N(2)–C(4)–C(5)	110.93(16)
C(5)–O(1)–C(6)	113.21(15)
O(3)–C(10)–O(2)	117.35(16)
C(10)–O(2)–C(11)	122.37(14)
F(1)–P(1)–F(2)	89.48(7)
F(1)–P(1)–F(4)	178.37(7)

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Table 3.3. Important bond distances and angles for silver complex **12**.

Module	Bond distance (Å)
Ag(1)–C(1)	2.073(3)
N(1)–C(1)	1.345(3)
N(2)–C(1)	1.359(3)
O(1)–C(12)	1.374(3)
O(1)–C(11)	1.359(4)
O(2)–C(11)	1.208(3)
O(3)–C(20)	1.405(4)
O(3)–C(21)	1.423(3)
P(1)–F(1)	1.580(2)
Module	Bond angle (^{o})
C(1)–Ag(1)–C(1)	180.00(7)
N(1)–C(1)–Ag(1)	130.34(19)
N(2)–C(1)–Ag(1)	123.38(19)
N(1)–C(1)–N(2)	103.5(6)
N(2)–C(8)–C(9)	113.8(2)
N(1)–C(19)–C(20)	112.6(2)
C(20)–O(3)–C(21)	112.0(3)
C(11)–O(1)–C(12)	121.7(2)

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Table 4. Antibacterial activity results measured in terms of minimum inhibitory concentration[a] (in µg/mL) of azolium salts **3–8** and their mono– and bis–carbene silver complexes **9–20** against different bacterial strains.

Sl. No.	Salt/Complex	*Gram +ve*		*Gram –ve*	
		S. aureus	*B. subtilis*	*E. coli*	*S. typhi*
1	**3**	>128	>128	>128	>128
2	**4**	>128	>128	>128	>128
3	**5**	>128	>128	>128	>128
4	**6**	>128	>128	>128	>128
5	**7**	>128	>128	>128	>128
6	**8**	>128	>128	>128	>128
7	**9**	16	128	08	128
8	**10**	16	128	16	128
9	**11**	16	128	16	128
10	**12**	16	128	16	128
11	**12**	16	128	16	128
12	**14**	16	128	16	128
13	**15**	16	128	32	128
14	**16**	32	128	32	64
15	**17**	128	128	64	128
16	**18**	16	128	32	128
17	**19**	32	128	64	128
18	**20**	32	128	64	128
19	Ampicillin	≤0.5	≤0.5	4	≤0.5

[a]: MIC is measured as two concurrent values from three individual analyses.

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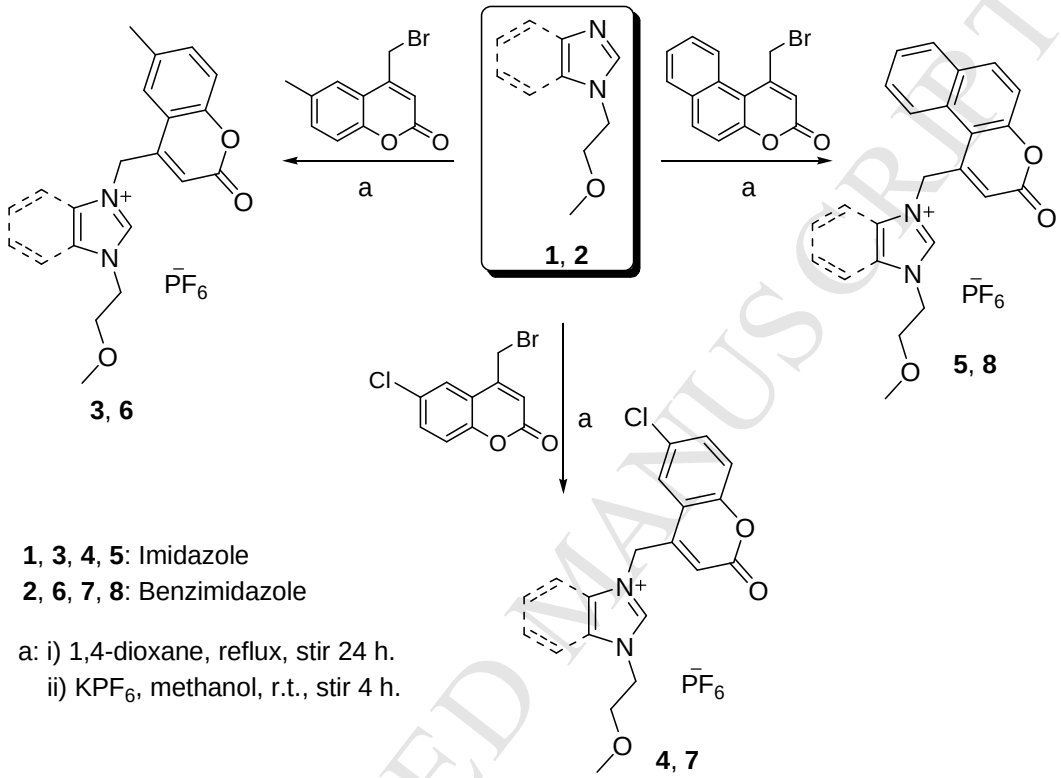
Scheme 1. Synthesis of ether and coumarin substituted (benz)imidazolium hexafluorophosphate salts.



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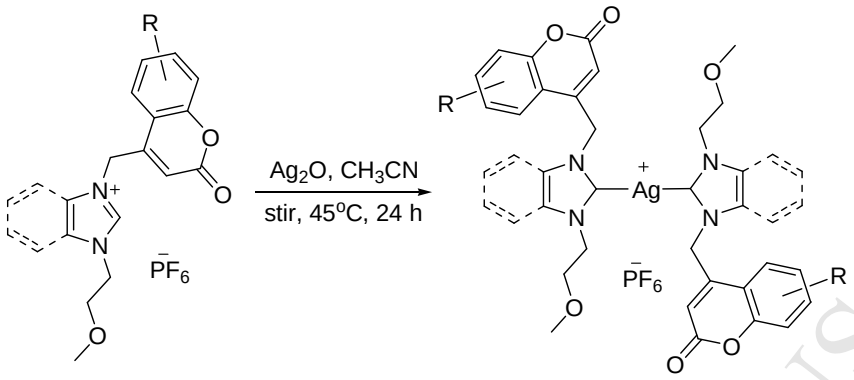
Scheme 2. Synthesis of silver(I) hexafluorophosphate complexes bearing ether and coumarin substituted NHC ligands.



3 - **8** **9** - **14**

	azole	R
3, **9** :	Imidazole	6-Me
4, **10**:	Imidazole	6-Cl
5, **11**:	Imidazole	5,6-benzo
6, **12**:	Benzimi	6-Me
7, **13**:	Benzimi	6-Cl
8, **14**:	Benzimi	5,6-benzo

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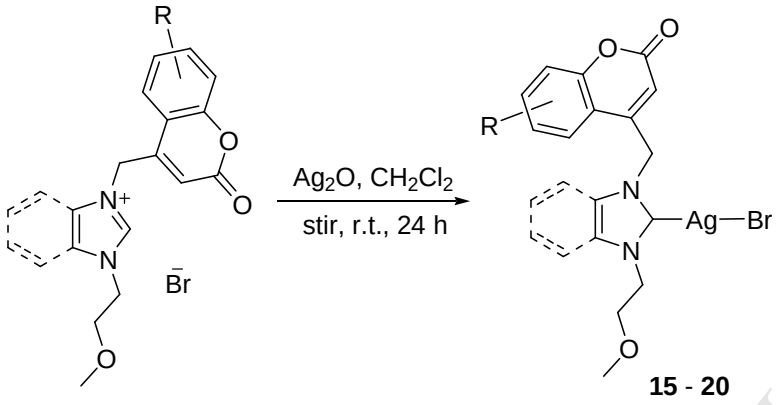
Scheme 3: Synthesis of neutral silver(I) bromido complexes bearing ether and coumarin substituted NHC ligands.



15 - **20**

	azole	R
15 :	Imidazole	6-Me
16 :	Imidazole	6-Cl
17 :	Imidazole	5,6-benzo
18 :	Benzimi	6-Me
19 :	Benzimi	6-Cl
20 :	Benzimi	5,6-benzo

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Figure 1. Molecular structure of imidazolium hexafluorophosphate salt **5**.

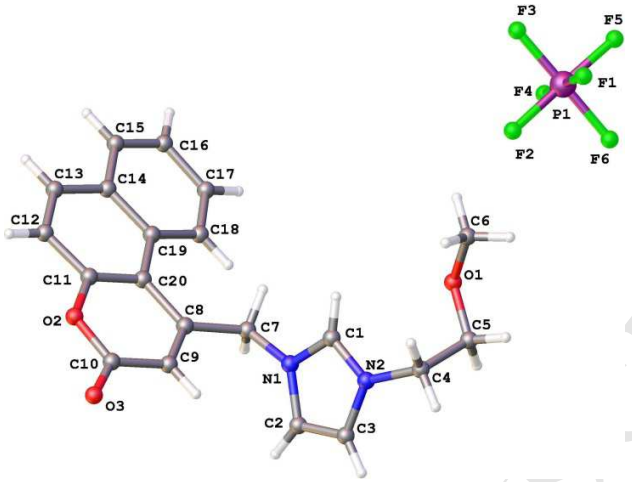

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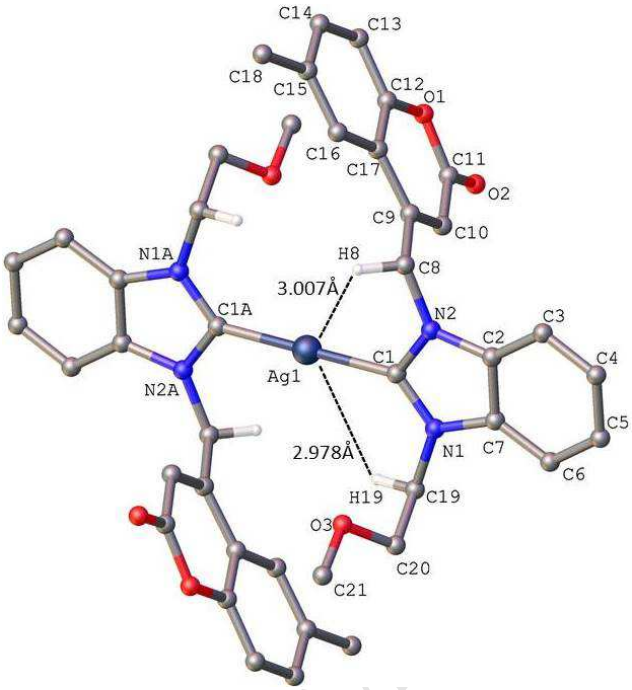
Figure 2. Molecular structure of complex **12**. Hydrogen atoms (except H8, H19, H8A and H19A) and hexafluorophosphate anion have been excluded for clarity.



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Highlights:

- A series of ether and coumarin substituted (benz)imidazolium salts are prepared
- There corresponding bis- and mono-NHC Ag complexes are prepared
- Both the types of compounds are fully characterized
- Compounds are tested for their antimicrobial potentials
- Bis-NHC Ag complexes displayed better activity over their mono-NHC complexes

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