Research Article

Journal of Physical Organic Chemistry

Received: 1 March 2011, Revised: 3 June 2011, Accepted: 5 June 2011 Published online in Wiley Online Library: 20 July 2011

(wileyonlinelibrary.com) DOI: 10.1002/poc.1899

Selectivity in metal ions mediated C–N bond formation reactions of 8-aminoquinoline derivatives

Dipjyoti Kalita[a] and Jubaraj B. Baruah[a]*

Cyclisation reactions via C–N bond formation of 2-bromo-*N*-(quinolin-8-yl)propanamide (I) and 2-bromo-*N*-(quinolin-8-yl)acetamide (II) are facilitated by metal salts such as copper (+2), nickel (+2) perchlorate or nitrate and palladium (+2) acetate. Nickel (+2) perchlorate mediated reaction of I and II resulted in C–N bond formation to give corresponding perchlorate salts of three fused six-membered heterocyclic rings. The copper (+2) mediated reactions are found to be solvent dependent for I, but independent for II. Copper mediated reaction of II gave cyclised product analogous to the one obtained from reaction of II with nickel (+2) perchlorate in methanol or ethanol. But the reaction of I with copper (+2) perchlorate in methanol gave C–N bonded methoxylated cyclised product. This reaction took place in two steps, cyclisation followed by methoxylation. The source of methoxy group is confirmed to be from methanol by deuterium labelling experiments. Whereas similar copper mediated reaction of I in ethanol led to nucleophilic substitution of bromide ion by ethoxide. The structures of the salts of fused heterocyclic compounds were determined and their fluorescence emissions were studied. The large difference in fluorescence emission of compound V formed from copper mediated reaction in ethanol from the compound VI formed from nickel mediated reaction in methanol or ethanol, this feature can be used to distinguish nickel (+2) and copper (+2) ions. The reaction of II with palladium (+2) acetate resulted in the formation of C–N bond to yield the corresponding heterocycle as bromide salt; without anion exchange. Copyright © 2011 John Wiley & Sons, Ltd.
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Keywords: 8-aminoquinoline; anion binding; C–N bond formation; metal mediated synthesis; role of solvent; selective transformations

INTRODUCTION

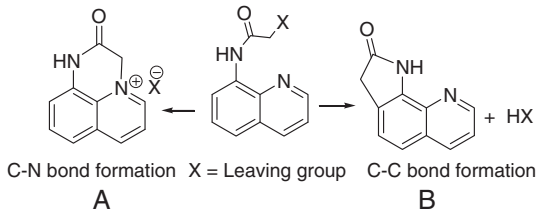
Several naturally occurring drug molecules contain quinoline rings as their constituents.[1–10] Aminoquinoline derivatives are useful in cyclisation reactions for ring expansion[11–19] and for the synthesis of steroids.[20,21] Multiple possibilities exist to obtain cyclised products from intramolecular cyclisation reactions of 8-aminoquinoline derivatives. For example, when an amino group of 8-aminoquinoline is functionalised to an amide group linked to a leaving group, such compounds may lead to the formation of new rings in different ways as shown in Scheme 1. The formation of such products can be controlled by using metal catalysts.[22–25] For example, when N-8-quinoline benzene sulphonamides were cyclised in the presence of a palladium catalyst,[26] this led to heterocyclic compounds through C–C bond formation. Novel heterocyclic compounds through intramolecular C–C bond formation by palladium catalysed reactions were observed from imine derivatives of 8-aminoquinoline.[22] Recently, the coordination effects of amide functionalised 8-aminoquinoline derivatives were used for intramolecular cyclisation within a compound at a remote end.[27] We have also shown that intramolecular cyclisation via aldol condensation leads to interesting heterocyclic products through multiple paths involving both C–N and C–C bond formation reactions.[28] Furthermore, the halo derivatives shown in Scheme 1 can also undergo conventional nucleophilic substitution by nucleophiles such as water, alcohol, amine etc. in the presence of a base and in aprotic solvents.[29,30] Thus, the competitive reactions of cyclisation versus nucleophilic substitution reactions in the presence or absence of metal ions are of interest. Here, we studied the copper (+2) and nickel (+2) ion mediated reactions of 2-bromo-*N*-(quinolin-8-yl) propanamide (**I**) and 2-bromo-*N*-(quinolin-8-yl) acetamide (**II**) and 2-bromo-*N*-(quinolin-5-yl) acetamide (**III**) (Fig. 1) in alcohols and show that the fluorescence emission properties of the products can be useful in differentiating solvents.

RESULTS AND DISCUSSION

In the presence of different metal salts of copper(+2) or nickel (+2) in methanol, 2-bromo-*N*-(quinolin-8-yl) propanamide(**I**) underwent cyclisation reactions through C–N bond formation to give two different products depending on the metal ion used (Scheme 2). Such reactions were also found to be solvent dependent. When copper (+2) salts were used in methanol exclusively methoxylated as well as cyclised product **IV** was

* *Correspondence to: Jubaraj B. Baruah, Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781 039 Assam, India. E-mail: juba@iitg.ernet.in*

a *D. Kalita, J. B. Baruah*
Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781 039 Assam, India



Scheme 1. Two different ways to cyclise in 8-aminoquinoline derivatives

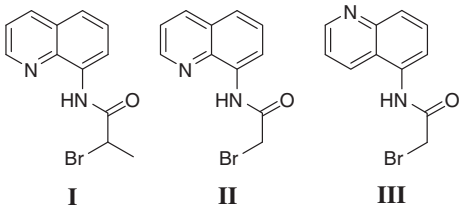
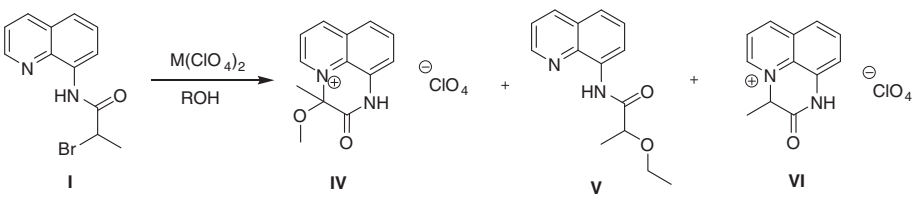


Figure 1. Structure of the substrates

obtained via C–N and C–O bond formation reactions. When the reaction was carried in ethanol with copper (+2) salts, cyclisation of **I** was not observed, but compound **V** was formed by C–O bond formation through nucleophilic substitution. It was also observed that the intramolecular cyclisation reaction of **I** was promoted by nickel (+2) salts and the compound **VI** was formed in both methanol or ethanol. Thus, these reactions are highly sensitive towards both metal ions and solvents. The solution of **I** in methanol or ethanol do not give products alone but presence of stoichiometric amount of copper (+2) or nickel (+2) ions in such solution gave the products within 2 h. The counter anions have roles in these reactions; the anions such as perchlorate and nitrate were found to be suitable over ions like acetate, chloride or bromide. In either case the cyclic product through C–C bond formation as depicted in Scheme 1 was not formed. This is due to the preference of forming a six-membered ring during C–N bond formation over the five-membered ring that would have formed in the case of C–C bond formation. The intramolecular cyclisation reactions leading to heterocyclic rings are very common in organic chemistry[31–34] and preferences of formation of thermodynamically favoured products are well documented. The compound **IV** and **VI** have structural similarities, and the difference between them is a methoxy group. Thus, to show distinction of each product obtained from the reactions of **I**, the ^{1}H-NMR spectra of the products **IV**, **V** and **VI** can be used. Some of the peak positions in ^{1}H-NMR of these compounds can be clearly discerned. For example, the compound **IV** has a signal at 3.5 ppm because of the –OMe group and there is a signal of a methyl group at 1.9 ppm as a singlet. The compound **VI** is devoid of signal from –OMe because of its absence, but it shows a multiplet signal at 5.8 ppm because of the CH next to the methyl group. The methyl group of **VI** has a signal at 1.8 ppm. The compound **V** has characteristic quartet and triplet from the OCH_2CH_3 group (3.4 and 1.0 ppm) and it has a doublet at 1.8 ppm and a quartet at 5.8 ppm from the CH_3 and CH groups. Because nickel (+2) has similar electronic features with palladium (+2), we carried out the reaction of **II** with a stoichiometric amount of palladium (+2) acetate in methanol. It gave the C–N bond product similar to a nickel-mediated reaction but in the form of bromide salt. That is, the reaction led to no anion exchange. The reaction with nickel (+2) acetate in methanol was not effective at room temperature. Thus, the metal has a role in these reactions and anion exchange processes are dependent on the metal ion in consideration.

To look at the role of the solvent, in the intramolecular cyclisation of **I**, we carried out the copper (+2) perchlorate-mediated reaction in a 1:1 mixed solvent of methanol and ethanol. From this reaction only compound **IV** was obtained. To know the source of the incorporated methoxy group in compound **IV**, we carried out the copper (+2) perchlorate-mediated reaction of **I** in deuterated methanol. The cyclic product **IVa** containing the deuterium-labelled methoxy group (Scheme 3) was obtained from this reaction. This shows the methanol-d_4 solvent to be the source of incorporated deuterated methoxy group. The mass spectra of **IV** has *m/e* at 229.09 whereas the mass spectra of **IVa** has *m/e* at 232.09 confirming the latter to have the CD_3O group. Furthermore, when compound **VI** was reacted with copper (+2) perchlorate hexahydrate, in CD_3OD we obtained compound **IVa** (Scheme 3). This proves that in the case of copper (+2) mediated reaction, first, the intramolecular nucleophilic substitution takes place to form a C–N bond, leading to product **VI**, and it further reacted with methanol in the presence of copper (+2) perchlorate to give product **IV**. The $S_{RN}1$ mechanism for coupling of nucleophile is well established in quinoline derivatives.[35] Thus, it may be a methoxy radical that is introduced via a C–H bond cleavage of **VI** to result into the formation of **IV**, where the radical formation is initiated by the copper (+2) ions. Copper (+2) ions are good for radical generation[36] by interconversion to copper (+1). In the case of nickel, such redox couple is absent, thus not leading to the incorporation of the methoxy group. In a nutshell, copper (+2) ion resulted in



% ratio of product IV : V : VI			
M = Cu, R=CH_3 ;	100	0	0
M = Cu, R=CH_3CH_2 ;	0	100	0
M = Ni, R=CH_3CH_2, CH_3 ;	0	0	100

Scheme 2. Synthesis of product **IV**, **V**, **VI**

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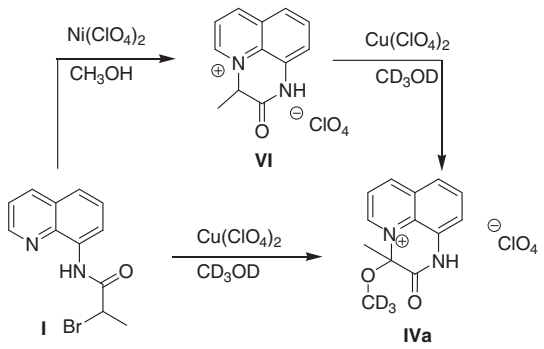


Scheme 3. Formation of deuterium substituted product **IVa**

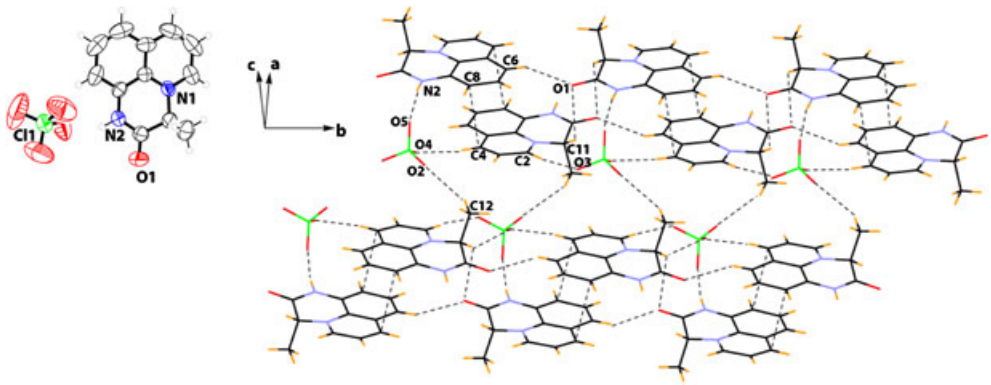
cyclisation followed by methoxy group incorporation to the cyclised product. The conversion of **I** to **IV** was also monitored by UV–Vis spectroscopy (please see supplementary materials). The compound **IV** has absorption at 379 nm, whereas the compound **I** has no absorbance at this wavelength. It was observed that the addition of copper (+2) perchlorate solution to a methanol solution of **I** led to growth of absorption at 379 nm because of the formation of **IV**. From this UV–Vis study, however, we could not monitor the formation of **VI** as an intermediate compound; the compound **VI** has absorption at 395 nm but with comparable extinction coefficient, and no observation of a peak of **VI** in the visible spectra points out that the transformation of **VI** to **IV** is fast. In the case of nickel the formation of **VI** could be seen as this is the end product in that reaction.

The structural chemistry of quinoline derivatives is interesting from molecular recognition[37] and from observation of multiple numbers of symmetry nonequivalent molecules in unit cell.[29] The structure of the compound **VI** is determined by X-ray crystallography and is shown in Fig. 2(a). The compound **VI** crystallises in monoclinic space group *P*2(1)/*n*. Its asymmetric unit comprises of a cation of three fused heterocyclic rings and one perchlorate anion. The molecules are self-assembled and the self-assembly is governed by π–π interactions (C8–C4, 3.370 Å) and C–H···O interactions (C6–H6···O1; C11–H11···O1). These interactions lead to the arrangement of molecules in the form of one-dimensional chain. The perchlorate anions are held between two such one-dimensional chains through C–H···O (C4–H4···H4; C2–H2···O3) and N–H···O (N2–H2A···O5) interactions. The two methyl groups are projected away from each other and the methyl protons are involved in C–H···O interactions (C12–H12A···O2) with the oxygen atoms of perchlorate anions. The self assembly of the compound **VI** is shown in Fig. 2(b).

We also studied the reaction of 2-bromo-*N*-(quinolin-8-yl) acetamide (**II**) with nickel (+2) and copper (+2) salts in methanol as well as in ethanol. In this case irrespective of metal ion, anion or the solvent cyclised product through C–N bond formation was observed (Scheme 4). Depending on the counter anion on the metal salt used, the cyclic amides **VIIa** and **VIIb** were formed. In the case of **II**, when acetone was used as solvent with primary amines along with potassium carbonate, we could replace the bromide ion to form nucleophilic products; however, in the case of the substrate **II** we have not observed nucleophilic substitution of the bromide ion either by ethanol or methanol.

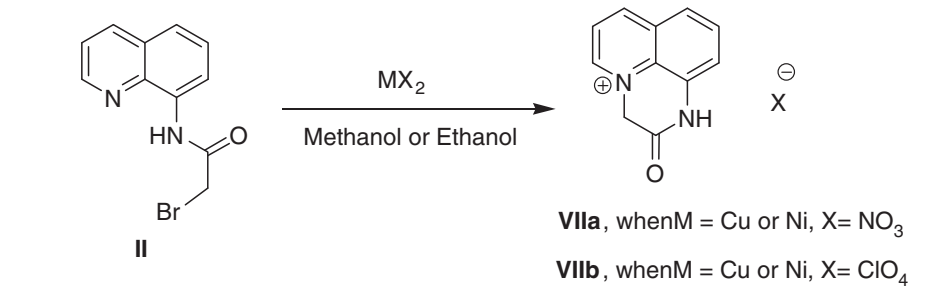
These results suggest that there is an initial coordination of metal ion to the precursor **I** and **II** and as the bromide is abstracted by metal, concomitant C–N bond formation takes place to form a cation of three fused heterocyclic rings. In both cases of copper and nickel ions the substitution is favoured by the coordination effect. This coordination effect is not favourable in the case of the substrate **III**; hence, we did not observe any nucleophilic substitution in **III** under ordinary conditions. The crystal structure of compound **VIIa** (Fig. 3(a)) and **VIIb** (Fig. 4(a)) shows that the same molecule adopts different structures with different anions. Compound **VIIa** crystallises in the monoclinic space group *P*2(1)/*c* whereas the compound **VIIb** crystallises in the orthorhombic space group *Pnma*. Previously, it has been established that in quinoline-based compounds the host molecule adopts a different structural orientation depending on the nature of the guests.[29] Hence, this difference in structural orientation is attributed to the size and structure of the counter anion. In the case of **VIIa** the counter ion is a perchlorate anion that is of tetrahedral shape, and in the case of **VIIb** the counter ion is a nitrate anion that is planar. Here, it is also observed that in compound **VIIa** the whole cationic part of the molecule and the perchlorate anion is present in the asymmetric unit (Fig. 3 (a)), whereas in the case of compound **VIIb** only one-half of the molecule is present in the asymmetric unit (Fig. 4(b)).

The compound **VIIa** forms a one-dimensional chain with a C–H···O interaction (C4–H4···O1), which is further linked by another C–H···O interaction with the perchlorate anion (C8–H8···O2). The two one-dimensional chains are further interlinked by a C–H···O interaction (C2–H2···O1) and a π–π interaction (C6–C6, 3.34 Å). The self assembly formation of compound **VIIa** is shown in Fig. 3(b).

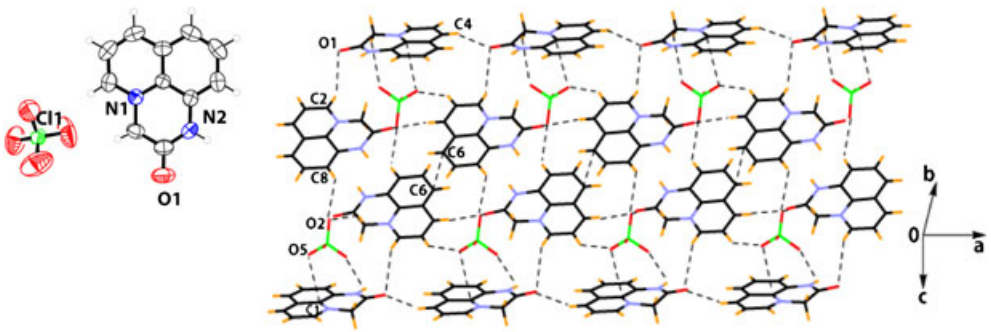


(a) **(b)**

Figure 2. (a) ORTEP diagram of the compound **VI** (Drawn with 50% thermal ellipsoid). (b) Short range interactions in **VI**



Scheme 4. Synthesis of compounds **VIIa** and **VIIb**



(a) (b)

Figure 3. (a) ORTEP diagram of the compound **VIIa** (drawn with 50% thermal ellipsoid). (b) Short range interactions in **VIIa**

The crystal structure of compound **VIIb** shows interesting crystallographic features, the asymmetric unit contains only one-half of the molecule even though the molecule is not symmetric. It is observed that the two nitrogen atoms (N1 and N2) and the two carbon atoms (C2 and C7) are disordered and share a 50% electron density each as shown in Fig. 4(c). The self-assembly of the compound **VIIb** is also governed by a number of weak interactions such as C–H···O (C3–H3···O2; C5–H5···O1) and N–H···O interaction (N2–H···O3). These weak interactions led to the formation of a two-dimensional wave-like structure as shown in Fig. 4(a).

Quinoline-based receptors have been identified to be sensitive to anion binding.[38–42] Thus, we have studied the absorption and emission of these compounds. The compound **I** shows an absorbance maximum at 326 nm whereas the compounds **IV, V** and **VI** show an absorbance maximum at 316 nm. In addition to the peak at 316 nm, the compounds **IV, V** and **VI** show a peak at 379, 369 and 395 nm, respectively. The UV–Vis spectra are shown in Fig. 5(a). All these compounds are fluorescence active except compound **IV**. The emission spectra of compounds **I**, **IV**, **V** and **VI** are much different from each other as shown in Fig. 5(b). Compound **I** shows an emission peak at 398 nm upon excitation at 310 nm (Fig. 5(b)). The fluorescence emission intensity is very weak for compound **IV** (Fig. 5(b)); however, the compound **V** shows an intense emission peak at 375 nm upon excitation at 310 nm (Fig. 5(b)). Unlike the other compounds, **VI** shows an emission peak in a much different region, that is, at 463 nm upon excitation at the same wavelength (Fig. 5 (b)). The large difference in fluorescence emission of **V** and **VI** occurs because of the difference in structures. This point is important as nickel (+2) and copper (+2) ion can be distinguished from the fluorescence emission by using this property. Second, the compound **IV** has a very weak fluorescence than **V** and at a different wavelength; this can indirectly distinguish the two solvents methanol and ethanol.

The compounds **II**, **VIIa** and **VIIb** show absorbance maximum at 316 nm (Fig. 6(a)). In addition to a peak at 316 nm, compound **II** shows an absorbance peak at 373 nm whereas both compound **VIIa** and **VIIb** show absorbance at 386 nm. This shows that there is a 13-nm shift in the absorbance on the formation of cyclised perchlorate or nitrate salt. This also shows that the anion does not cause change in the absorption spectra of these products. All the compounds **II**, **VIIa** and **VIIb** are fluorescence active; similar to the UV spectra the emission spectra of the products (**VIIa** and **VIIb**) are different from the starting material (**II**). Compound **II** shows an emission peak at 497 nm upon excitation at 380 nm, whereas both the compounds **VIIa** and **VIIb** show an emission peak at 510 nm upon excitation at 380 nm. The emission spectra are shown in Fig. 6(b). Thus, the trend in change in fluorescence emission is similar to the absorption spectra, that is, cyclised products have an emission at higher wavelength with enhancement of intensity.

In conclusion, C–N bond formation leading to intramolecular cyclisation reactions of **I** and **II** are facilitated by copper (+2) and nickel (+2) ions. The copper(+2) mediated intramolecular cyclisation reactions are substrate dependent. In the case of **I** the initially formed cyclised product further undergoes C–H activation to give OMe-substituted derivative in methanol. The same reaction in ethanol replaces bromide with ethoxide, without formation of a cyclic product. Nickel(+2) mediated reactions invariably led to the formation of a cyclic product through C–N bond formation. Thus, in the case of copper, multiple mechanisms involving cation and radical are favoured, whereas in the case of nickel it is an ionic mechanism leading to anion exchange.

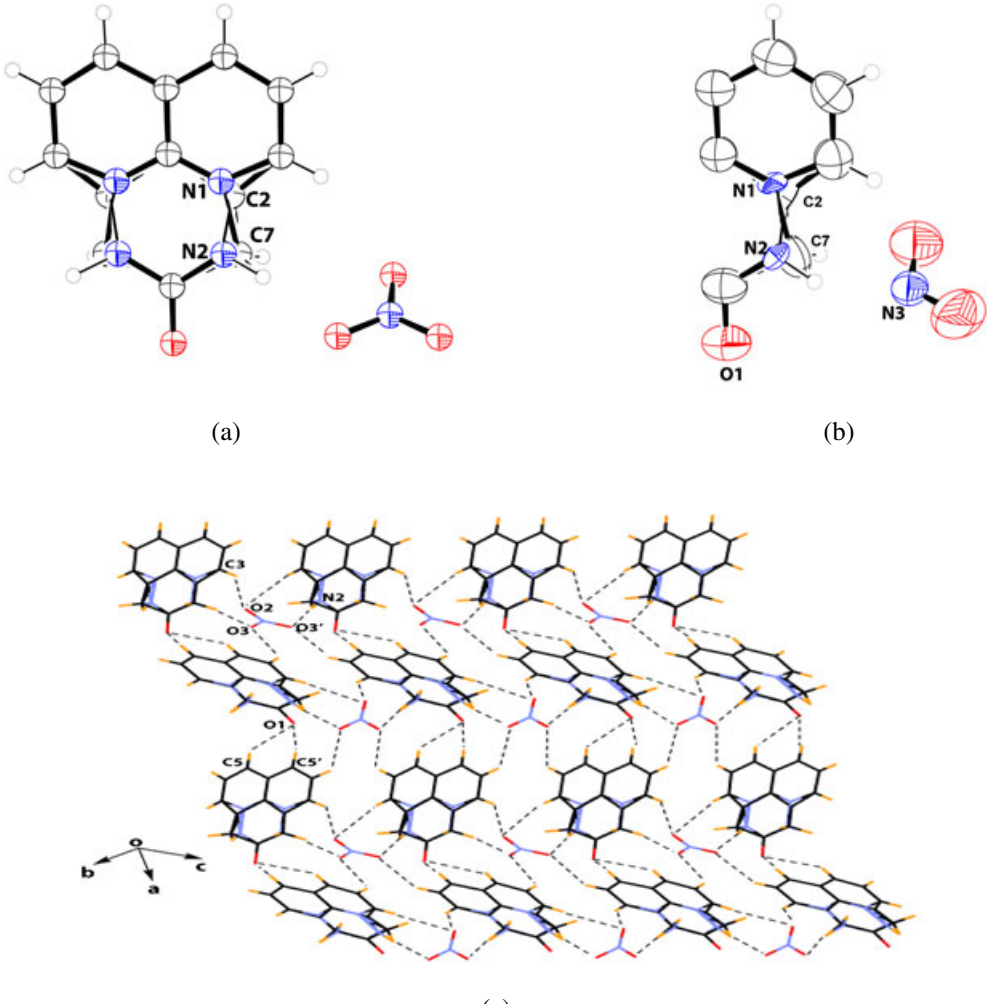


Figure 4. (a) Structure of **VIIb** (C, N atoms are disordered); (b) ORTEP diagram of the asymmetric unit of compound **VIIb** (Drawn with 50% thermal ellipsoid); and (c) short range interactions in **VIIb**

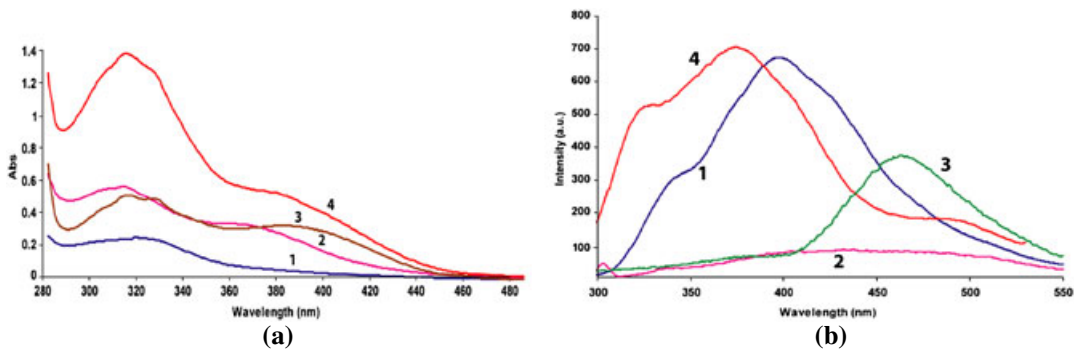
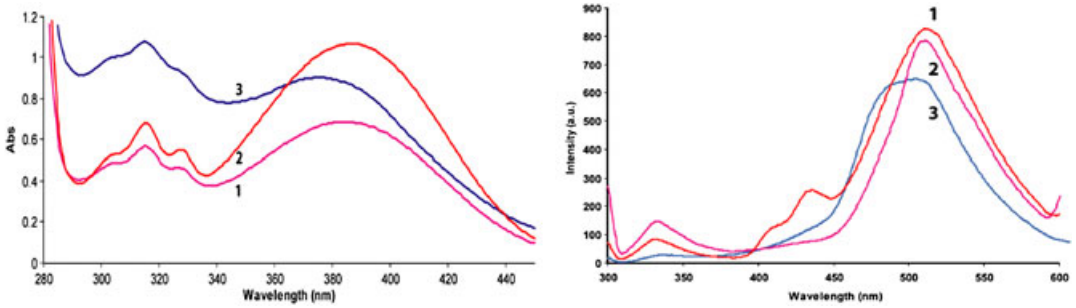


Figure 5. (a) UV–Vis spectra of (1) compound **I**; (2) compound **IV**; (3) compound **VI** and (4) compound **V**; (b) Emission spectra (λ_{ex}=310 nm) of (1) compound **I**; (2) compound **IV**; (3) compound **VI** and (4) compound **V**. (In all cases methanolic solution 6.6×10^{-5} M were used)

Furthermore, the three fused heterocyclic rings described here are fluorescence active. The chemical reactivity differences can be used as a tool to distinguish the solvents as well as metal ions because the fluorescence emission of each product differs. Palladium (+2) acetate causes intramolecular cyclisation of **II** without anion exchange.

EXPERIMENTAL

The compounds **I** and **II** were synthesised by the reported procedure [43]. **Caution**: The perchlorate salts are potentially explosive and should be handled with care in limited amounts. However, no such observations by us in the present experiments in 1 mmol



(a) (b)

Figure 6. (a) UV–Vis spectra of (1) compound **VIIa**, (2) compound **VIIb** and (3) compound **II**. (b) Emission spectra (λ_{ex}=380 nm) of (1) compound **VIIa**, (2) compound **VIIb** and (3) compound **II**. (In all cases methanolic solution 6.6×10^{-5} M were used)

scale were observed. Nevertheless, they should be handled with care and such reactions are to be carried under a fume cupboard.

Synthesis of 2-bromo-*N*-(quinolin-5-yl) acetamide (III)

The compound was synthesised by a procedure similar to **II**; the difference was the use of 5-aminoquinoline in place of 8-aminoquinoline. Yield: 72%. IR (KBr, cm^{-1}): 3446 (bs), 3019 (m), 1689 (s), 1629 (s), 1596 (m), 1560 (m), 1537 (s), 1408 (m), 1369 (s), 1287 (s), 1235 (m), 1116 (w), 912 (w), 813 (s), 695 (m). ^{1}H-NMR (DMSO-d^6, 400 MHz): 11.0 (1H, s); 9.5 (1H, d, J=8.4 Hz); 9.3 (1H, d, J=5.2 Hz); 8.2 (2H, d, J=6.8 Hz); 8.0 (2H, m); 4.3 (2H, s). ^{13}C-NMR (DMSO-d^6, 100 MHz): 29.2, 117.4, 120.8, 123.8, 135.0, 138.1, 143.0, 144.1, 166.6. LC-MS [M+]: calculated for $C_{11}H_9BrN_2O$ 264.9932; found 265.0150.

Synthesis of compound (IV)

2-Bromo-*N*-(quinolin-8-yl) propanamide (**I**) (1 mmol, 0.28 g) was dissolved in methanol (15 ml) and copper (+2) perchlorate hexahydrate (1 mmol, 0.370 g) was added. The solution was then stirred for 30 min in room temperature and kept undisturbed. Brown-coloured crystals of compound **IV** were observed after 4 days. The solution was then filtered and the product was isolated. Yield: 47%. IR (KBr, cm^{-1}): 3433 (bs), 3006 (m), 2934 (w), 2890 (w), 2853 (m), 1704 (s), 1583 (w), 1545 (m), 1495 (w), 1469 (m), 1390 (m), 1275 (w), 1229 (m), 1174 (m), 1143 (s), 1114 (s), 1086 (s), 839 (m), 625 (m). ^{1}H-NMR (DMSO-d^6, 400 MHz): 12.3 (s, 1H); 9.6 (d, 1H, J=5.6 Hz); 9.3 (d, 1H, J=8.0 Hz); 8.3 (d, 1H, J=6.0 Hz); 8.1 (d, 1H, J=8.0 Hz), 7.9 (t, 1H, J=8.0 Hz); 7.6 (d, 1H, J=7.2 Hz); 3.5 (s, 3H); 1.9 (s, 3H). ^{13}C-NMR (DMSO-d^6, 100 MHz): 23.7, 48.8, 63.2, 118.0, 122.8, 123.6, 125.5, 129.9, 130.3, 131.0, 147.0, 147.3, 164.5. LC-MS [M+]: calculated for $C_{13}H_{13}N_2O_2$ 229.0977; found 229.0975. Vis: (Methanol, λ_{max}) 379 nm ($\varepsilon=4.64\times10^3\,M^{-1}\,cm^{-1}$).

Synthesis of compound (V)

Compound **V** was synthesised by a procedure similar to compound **IV**, except that in this case ethanol was used as solvent instead of methanol. Yield: 63%. IR (KBr, cm^{-1}): 3444 (bs), 1627 (s), 1501(m), 1467 (m), 1399 (m), 1121 (w), 1086 (w), 829 (w), 788 (w), 636 (w). ^{1}H-NMR (DMSO-d^6, 400 MHz): 11.8 (s, 1H); 9.5 (d, 1H, J=5.6 Hz); 9.2 (d, 1H, J=8.4 Hz); 8.2 (t, 1H, J=6.0 Hz); 8.0 (d, 1H, J=8.4 Hz); 7.9 (t, 1H, J=7.6 Hz); 7.6 (d, 1H, J=7.6 Hz); 5.8 (q, 1H, J=7.2 Hz); 3.4 (m, 2H); 1.8 (d, 3H, J=7.6 Hz); 1.0 (t, 3H, J=8.8 Hz). ^{13}C-NMR (DMSO-d^6, 100 MHz): 19.1, 24.1, 56.7, 63.5, 118.3, 123.2, 124.1, 125.9, 130.2, 130.7, 131.4, 147.3, 147.7, 164.9. LC-MS [M–1]: calculated for $C_{14}H_{15}N_2O_2$ 243.1134; found 243.1302. Vis: (Methanol, λ_{max}) 369 nm ($\varepsilon=8.45\times10^3\,M^{-1}\,cm^{-1}$).

Synthesis of compound (VI)

2-Bromo-*N*-(quinolin-8-yl) propanamide (**I**) (1 mmol, 0.28 g) was dissolved in methanol (15 ml) and nickel (+2) perchlorate hexahydrate (1 mmol, 0.365 g) was added. The solution was stirred for 40 min at room temperature and kept undisturbed. Brown-coloured crystals of compound **VI** were observed after 3 days. The solution was then filtered to isolate the product. Yield: 71%. IR (KBr, cm^{-1}): 3424 (bs), 3043 (m), 2903 (w), 1694 (s), 1607 (w), 1587 (w), 1542 (m), 1492 (w), 1422 (m), 1392(m), 1365 (m), 1241 (w), 1140 (s), 1116 (s), 1078 (s), 835 (m), 760 (w), 624 (m). ^{1}H-NMR (DMSO-d^6, 400 MHz): 11.8 (s, 1H); 9.5 (s, 1H); 9.2 (d, 1H, J=7.6 Hz); 8.2 (d, 1H, J=5.2 Hz); 8.0(m, 2H); 7.5 (d, 1H, J=6.8 Hz); 5.8 (m, 1H); 1.8 (s, 3H). ^{13}C-NMR (DMSO-d^6, 100 MHz): 24.1, 63.5, 118.3, 123.1, 124.0, 125.9, 130.2, 130.6, 131.4, 147.3, 147.6, 164.9. LC-MS [M+]: calculated for $C_{12}H_{11}N_2O$ 199.08 found 199.03. Vis: (Methanol, λ_{max}) 395 nm ($\varepsilon=4.72\times10^3\,M^{-1}\,cm^{-1}$).

Synthesis of compound (VIIa)

2-Bromo-*N*-(quinolin-8-yl) acetamide (**II**) (1 mmol, 0.26 g) was dissolved in methanol (15 ml) and copper (+2) nitrate tetrahydrate trihydrate (1 mmol, 0.24 g) was added. The solution was stirred for 30 min at room temperature and kept undisturbed. Brown-coloured crystals of compound **VIIa** were observed after 3 days. A similar reaction performed with nickel (+2) nitrate resulted in compound **VIIa**. Yield: 72%. IR (KBr, cm^{-1}): 3434 (bm), 3043 (m), 3013 (m), 2929 (m), 2852 (w), 1698 (s), 1584 (m), 1543 (m), 1491 (w), 1384 (s), 1239 (w), 1154 (w), 1130 (w), 839 (m), 795 (w), 754 (w), 526 (w). ^{1}H-NMR (DMSO-d^6, 400 MHz) : 11.8 (s, 1H); 9.2 (d, 1H, J=6.0 Hz); 9.1 (d, 1H, J=8.4 Hz); 8.2 (t, 1H, J=6.0 Hz); 7.9 (m, 2H); 7.5 (d, 1H, J=7.2 Hz); 5.6 (s, 2H). ^{13}C-NMR (DMSO-s^6, 100 MHz): 56.2, 118.1, 122.8, 123.5, 126.7, 130.0, 131.4, 147.2, 147.7, 161.6. LC-MS [M^+]: calculated for $C_{11}H_9N_2O$ 185.0715; found 185.0626. Vis: (Methanol, λ_{max}) 386 nm ($\varepsilon=1.02\times10^4\,M^{-1}\,cm^{-1}$).

Synthesis of compound (VIIb)

A similar synthetic procedure to **VIIa** was used for the synthesis of compound **VIIb**, the only difference is that in this case copper (+2) perchlorate hexahydrate was used instead of copper (+2) nitrate trihydrate. The reaction was also performed with nickel (+2) perchlorate; resulted in compound **VIIb**. Yield: 74%. IR (KBr,

cm^{-1}): 3433 (bm), 3013 (m), 2928 (m), 2852 (m), 1698 (s), 1607 (w), 1584 (m), 1543 (s), 1428 (m), 1417 (m), 1385 (s), 1298 (w), 1240 (m), 1144 (s), 1115 (s), 1079 (s), 909 (w), 838 (m), 754 (m), 624 (m). Vis: (methanol, λ_{max}) 386 nm ($\varepsilon = 1.60 \times 10^3 M^{-1} cm^{-1}$).

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