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Palladium-catalysed reactions of 8-hydroxy- and 8-benzyloxy-5,7-diiodoquinoline under aminocarbonylation conditions

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ABSTRACT

Various 5-carboxamido-7-iodo-8-benzyloxyquinolines were synthesised via selective aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline in the presence of 'in situ' generated palladium(0) catalysts. Under similar conditions (50 °C, 80 bar CO), 5,7-bis(*N*-*tert*-butyl-glyoxylamido)-8-hydroxyquinoline was obtained using *tert*-butylamine as *N*-nucleophile. The unprotected 5,7-diiodo-8-hydroxyquinoline underwent dehydroiodination resulting in 8-hydroxyquinoline as the major product.

1. Introduction

The introduction of a carboxamide moiety into a skeleton of practical importance, via simple homogeneous catalytic methods, is of high interest.[1,2] There are a number of applications both for the synthesis of simple building blocks and for the functionalization of biologically important skeletons.[3,4]

The aminocarbonylation of aryl- and enol-triflates leading to aryl and unsaturated carboxamides, respectively, has been carried out.[5] Recently, iodoarenes and iodoalkenes, the corresponding synthetic analogues of aryl triflates, have found important applications as substrates in carbonylation reactions.

Palladium-catalysed cross-coupling reactions of iodoquinoline derivatives with alkynes have been carried out in order to synthesise tri-substituted pyrroloquinolines[6] and 4-substituted quinolines.[7] Recently, we published carbonylation reactions of 5-chloro-7-iodo-quinoline derivatives.[8] The improvement of alternative synthetic methods for alkoxyquinoline derivatives is of great interest due to their potential biological activity as PDE4 inhibitors[9] as well as for the preparation of electroluminescent materials for organic LEDs.[10] As for our parent model compound, 5,7-diiodoquinoline-8-ol, it was used as a ligand for the spectrophotometric determination of yttrium[11] and erbium[12] in a ternary ion-association complex. 3,6-Diiodoquinoline served as a coupling partner to 1,4-diethynyl-benzene derivative in palladium-catalysed reaction providing a novel copolymer.[13]

Accordingly, due to the importance of diiodoquinolines, the facile, selective, high-yielding palladium-catalysed aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline with various *N*-nucleophiles, as well as the dehydroiodination of its 8-hydroxy analogue are described in the present paper.

2. Results and discussion

2.1. Aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline (1)

5,7-Diiodo-8-benzyloxyquinoline (**1**), prepared from 5,7-iodo-8-hydroxyquinoline (**4**) with benzyl bromide,[14] was reacted with various amines and carbon monoxide in the presence of 'in situ' palladium(0) catalysts (Scheme 1). The formation of highly active, low-ligated palladium(0) complexes from the palladium(II) precursors, such as $Pd(OAc)_2$ used in our systems, was proved by cyclic voltammetry and NMR measurements.[15,16] The aminocarbonylation under high pressure (80 bar) was unexpectedly regioselective at position-5 resulting in **2a** and **2b** by using secondary amines, such as morpholine (**a**) and piperidine (**b**), respectively (Table 1, entries 1

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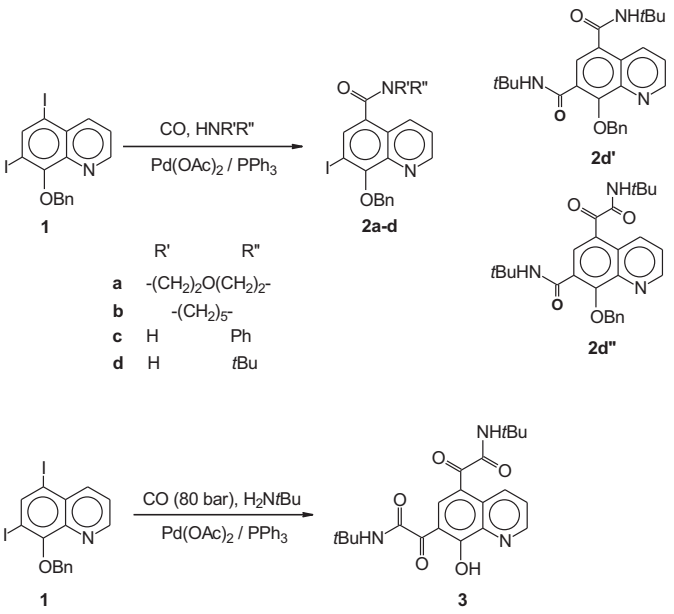
and 2). Carrying out the reaction under the same carbon monoxide pressure even 5-(*N*-phenylcarboxamide) derivative (**2c**) could be isolated by using aniline (entry 3). Arylamines of low basicity have shown low reactivity in aminocarbonylation of both iodoarene and iodoalkene type substrates.[17,18] When the reaction was carried out by using one of the most reactive primary amines, *tert*-butylamine (**d**), much lower carbon monoxide pressure proved to be sufficient to yield the same type of carboxamide, **2d** (entry 4).



Scheme 1. Aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline (**1**).

Table 1
Aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline (**1**) with various amines[a]

Entry	Amine	Amine/ substrate ratio	*R.* time [h]	*p*(CO) [bar]	Product (isolated yield)[b] [%]
1	**a**	3/1	25	80	**2a** (87)
2	**b**	3/1	25	80	**2b** (86)
3	**c**	4/1	70	80	**2c** (81)
4	**d**	6/1	70	1	**2d** (76)
5	**d**	6/1	58	20	**2d′** (40); **2d″** (8)
6	**d**	6/1	70	80	**3** (47)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3; 1 mmol substrate; 10 mL DMF; 0.5 mL Et_3N; 50 °C; practically full conversions (>98%) were obtained in all cases.
[b] Isolated yields are based on the amount of the starting material (**1**).

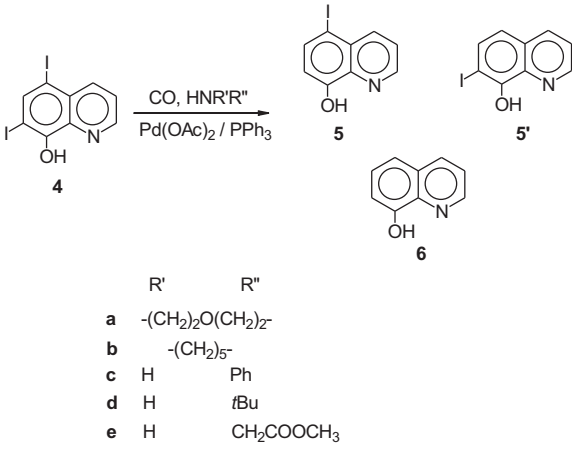
It is worth noting that the aminocarbonylation proceeds with high regioselectivity leading to 5-carboxamido derivatives, i.e., the 7-iodoaryl functionality remained untouched. The characterization of the products was carried out by detailed NMR measurements including 2D NMR techniques (HMBC, HSQC). Even the practically unchanged chemical shift of the sharp singlet in ^{1}H NMR, assigned to the methylene protons (at ca. 5.5 ppm), suggests that carbonylation occurred in position-5 in case of the monocarbonylated products **2a**–**d**. When carbonylation took place in position-7 as well (**2d′** and **2d″**) the above signal has a downfield shift of 0.1 and 0.2 ppm, respectively.

The expected 5,7-dicarboxamide can be obtained with 40% isolated yield only with *tert*-butylamine (**d**) as *N*-nucleophile under optimized reaction conditions (58 h, 20 bar CO) (entry 5). Under these reaction conditions the corresponding carboxamide–ketocarboxamide derivative (**2d″**) resulting from double carbonyl insertion in position-5 was isolated as minor product (8%). It is worth noting that the aminocarbonylation of simple iodoarenes, such as iodobenzene or 2-iodonaphthalene provided a mixture of the corresponding carboxamides and 2-ketocarboxamides with the prevailing formation of the latter product under similar reaction conditions.[19]

However, the use of *tert*-butylamine (**d**) for aminocarbonylation under high carbon monoxide pressure resulted in the formation of 5,7-bis(*tert*-butyl-glyoxylamido)-8-hydroxyquinoline (**3**) as a major product (entry 6). The expected 5,7-bis(*tert*-butyl-glyoxylamido)-8-benzyloxyquinoline (**3′**) was formed as a minor product only (<6%) and was detected by NMR spectroscopy as a minor component of a mixture formed with **3**. The most interesting feature of the latter reaction is the almost complete deprotection of the 8-benzyloxy functionality while double carbonylation occurred at both iodoarene functionalities.

2.2. Palladium-catalysed dehydroiodination of 5,7-diiodo-8-hydroxyquinoline

5,7-Diiodo-8-hydroxyquinoline (**4**) was subjected to aminocarbonylation as its 8-protected derivative, **1** under similar reaction conditions (60 bar CO, 50 °C) (Scheme 2). Unexpectedly, no carboxamide or ketocarboxamide derivatives were formed. 8-Hydroxyquinoline (**6**), the 'fully dehydroiodinated' derivative of **4**, was formed as the major or exclusive product in all cases (vide infra).



Scheme 2. Dehydroiodination of 5,7-diiodo-8-hydroxyquinoline (**4**) under carbonylation conditions.

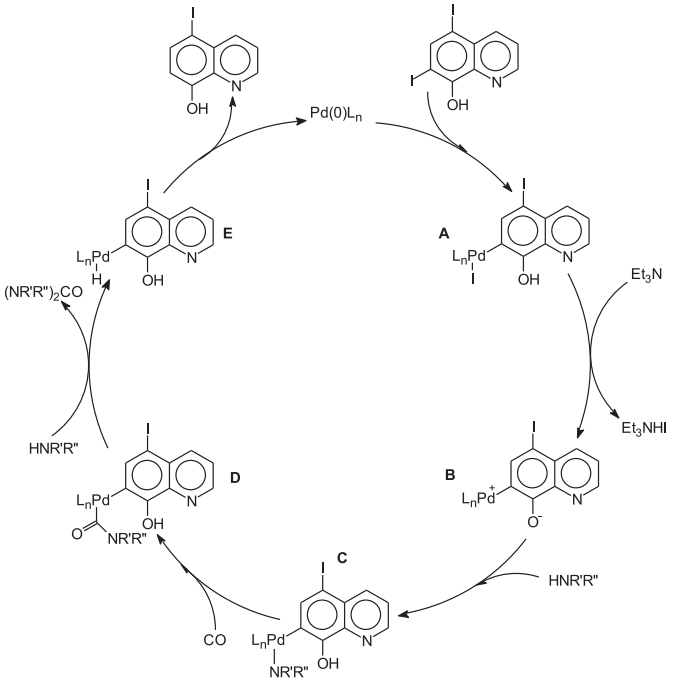
The application of high-pressure conditions led to the exclusive formation of **6** by using both secondary (**a** and **b**) and primary (**c** and **d**) amines (Table 2, entries 1,2 and entries 4,5, respectively). The only exception among the used amines is methyl glycinate (**e**) (entry 9). In this peculiar case the monoiodo-8-hydroxyquinoline isomers (**5** and **5′**), due to monodehydroiodination, were also formed. The latter products were obtained as major ones at a ratio of 60/40 when atmospheric carbon monoxide pressure and **d** were used (entry 8). The syntheses of the iodo-8-hydroxyquinolines (**5** and **5′**) were published before.[20,21] It has to be added that the above reaction is always accompanied by the direct carbonylation of the amine resulting in the corresponding urea-type compound ($(R'R''N)_2CO$) (see also Scheme 3) or in the oxalylamide-type compounds ($(R'R''N)_2(CO)_2$), the latter one detected in traces only by GC/MS.

It has to be added that an oxidative addition followed by dehydroiodination might be operative. The following simplified reaction mechanism, including the involvement of the phenolic OH group, is suggested for dehydroiodination. A plausible mechanism for the dehydroiodination process is depicted in Scheme 3. The oxidative addition of the substrate (**4**) on low-ligated Pd(0) species,

Table 2
Dehydroiodination of 5,7-diiodo-8-hydroxyquinoline (**4**) with various amines under aminocarbonylation conditions[a]

Entry	Amine	Amine/substrate ratio	*R.* time [h]	*p*(CO) [bar]	Product distribution [b] [%]	Isolated yield[c] [%]
1	**a**	3/1	24	70	**6** (100)	**6** (81)
2	**b**	3/1	24	70	**6** (100)	**6** (83)
3	**b**	3/1	20	1	**5** (39); **5′** (61)[f]	n.d.[e]
4	**c**	4/1	70	70	**6** (100)	**6** (77)
5	**d**	6/1	70	80	**6** (100)	**6** (74)
6	**d**	6/1	48	40	**6** (100)	n.d.[e]
7	**d**	6/1	24	10	**6** (100)	n.d.[e]
8	**d**	6/1	70	1	**5** (60); **5′** (40)	**5** (45)
9	**e**[d]	3/1	24	70	**6** (60); **5** (30); **5′** (10)	**6** (51)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3; 1 mmol substrate; 10 mL DMF; 0.5 mL Et_3N; 50 °C; practically full conversions (>98%) were obtained (unless otherwise stated).
[b] Determined by GC/MS.
[c] Isolated yields are based on the amount of the starting material (**4**).
[d] Compound **e** was used as hydrochloride salt.
[e] Not determined.
[f] Conversion 32%.



Scheme 3. A proposed mechanism for dehydroiodination of **4**.

formed in situ from the Pd(II) precursor, resulted in the iodo-aryl-palladium(II) species (**A**). Its dehydroiodination by triethylamine leads to **B**, which activates the primary or secondary amine by forming the aryl–amido complex (**C**). The coordination of carbon monoxide as a terminal carbonyl (not indicated on the Scheme) and its insertion into the Pd–N bond resulted in the formation of the corresponding carbamoyl-palladium(II) complex (**D**). The carbamoyl species reacts with the 'second' primary or secondary amine forming the urea-type product (carbonylation of the amine) and the aryl-hydrido-species (**E**). The reductive elimination provides the dehydroiodination product and the palladium(0) species in the product-forming step. Consequently, the hydrogen necessary to formal dehydroiodination stems from the amine.

3. Conclusions

5-Carboxamido-7-iodo-8-benzyloxyquinolines were synthesised in high-yielding palladium-catalysed aminocarbonylation of 5,7-diiodo-8-benzyloxyquinoline. The iodoarene functionality of the target carboxamides is suitable for further functionalization. Furthermore, the control of CO pressure allowed the formation of the bis-carboxamide or the carboxamide–ketocarboxamide derivative using the most reactive *tert*-butylamine. Unexpectedly, either complete or partial dehydroiodination of 5,7-diiodo-8-hydroxyquinoline took place leading to 8-hydroxyquinoline or iodo-8-hydroxyquinoline isomers, respectively, in the presence of most primary and secondary amines under homogeneous carbonylation conditions.

4. Experimental

4.1. General procedures

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts δ are reported in parts per million relative to $CHCl_3$ (7.26 and 77.00 ppm for ^1H and ^{13}C, respectively). Elemental analyses were measured on a 1108 Carlo Erba apparatus. Samples of the dehydrogenation reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1. The MALDI-TOF spectra of the isolated carboxamides were obtained on an Autoflex II TOF/TOF spectrometer (Bruker Daltonics) in positive ion modes, using 2,5-dihydroxybenzoic acid (DHB) as matrix.

5,7-Diiodo-8-benzyloxyquinoline was synthesised according to the benzylation of 5,7-dibromo-8-hydroxyquinoline as described previously.[14] 5,7-iodo-8-hydroxyquinoline, as well as the amines were purchased from Aldrich and were used without any further purification. Solvents were dried and purified by generally used procedures.

The syntheses of the dehydroiodination products (**5**[20] and **5′**[21]) were published and the analytical data are in good agreement with those obtained in the present study. The missing analytical data of these known compounds are also presented below.

4.2. Aminocarbonylation reaction at high-pressure

In a typical reaction 5.6 mg (0.025 mmol) of $Pd(OAc)_2$ and 13.1 mg (0.05 mmol) of PPh_3 together with 1 mmol of substrate (**1**) were placed into a 100 mL autoclave equipped with a magnetic stirring bar. The atmosphere was changed to argon and all the solid substances were dissolved in 10 mL of DMF, then 0.5 mL of triethylamine and 0.6 mL (6 mmol) *tert*-butylamine (**d**) (or 3 mmol of **a**, **b**; 4 mmol of **c**) were added. The atmosphere was changed to carbon monoxide, the autoclave was pressurized by carbon monoxide to the given pressure and the reaction mixture was kept at 50 °C for the given reaction time. The solvent was evaporated to dryness and the residue dissolved in chloroform. It was washed three times with

water and brine. The organic phase was dried over Na_2SO_4 and evaporated. The carboxamides were isolated via column chromatography by using chloroform/ethyl acetate mixtures as eluents (for exact ratios see analytical characterization below).

4.3. Analytical and spectroscopic data of compounds

*4.3.1. 5-(N,N-(Penta-3′-oxa-1′,5′-diyl)carboxamido)-7-iodo-8-benzyloxyquinoline (**2a**).* ^{1}H NMR ($CDCl_3$) δ: 8.96 (d, J=3.7 Hz, 1H, H-2); 8.20 (d, J=8.3 Hz, 1H, H-4); 7.82 (s, 1H, H-6); 7.67 (d, J=7.3 Hz, 2H, Ph); 7.31–7.55 (m, 4H, Ph+H-3); 5.51 (s, 2H, OCH_2); 3.75–3.99 (m, 4H, $O(CH_2)_2$); 3.43–3.70 (m, 2H, NCH_2); 3.19–3.35 (m, 2H, NCH_2). ^{13}C NMR ($CDCl_3$) δ: 166.9; 157.1; 150.5; 142.6; 137.2; 134.2; 133.8; 132.3; 129.1 (double intensity); 128.5 (double intensity); 128.4; 127.1; 122.6; 91.2; 76.8; 67.2 (double intensity); 48.1; 42.7. IR (KBr, (cm^{-1})): 1628 (CON). MS m/z: 474 (M^+), 347 (M^+–I). Anal. Calcd for $C_{21}H_{19}N_2O_3I$ (474.30): C, 53.18; H, 4.04; N, 5.91; found: C, 53.41; H, 4.29; N, 5.64; R_f (50% EtOAc/$CHCl_3$) 0.41; mp 120–121 °C. Yellow solid. Yield: 410 mg (87%).

*4.3.2. 5-(N,N-(Penta-1′,5′-diyl)carboxamido)-7-iodo-8-benzyloxyquinoline (**2b**).* ^{1}H NMR ($CDCl_3$) δ: 8.96 (d, J=3.8 Hz, 1H, H-2); 8.19 (d, J=8.0 Hz, 1H, H-4); 7.80 (s, 1H, H-6); 7.66 (d, J=7.3 Hz, 2H, Ph); 7.51 (dd, J=3.8, 8.0 Hz, 1H, H-3); 7.31–7.40 (m, 3H, Ph); 5.49 (s, 2H, OCH_2); 3.75–3.90 (m, 2H, $(NCH_2)_2$); 3.17 (br s, 2H, NCH_2); 1.35–1.80 (m, 6H, $(CH_2)_3$). ^{13}C NMR ($CDCl_3$) δ: 166.7; 156.3; 150.4; 142.6; 137.3; 134.1; 133.6; 131.9; 129.0 (double intensity); 128.5 (double intensity); 128.3; 127.1; 122.4; 91.4; 76.8; 48.8; 43.2; 27.0; 26.0; 24.7. IR (KBr, (cm^{-1})): 1630 (CON). MS m/z: 472 (M^+), 345 (M^+–I). Anal. Calcd for $C_{22}H_{21}N_2O_2I$ (472.33): C, 55.94; H, 4.48; N, 5.93; found: C, 55.71; H, 4.59; N, 5.66; R_f (40% EtOAc/$CHCl_3$) 0.69. Highly viscous yellow oil. Yield: 405 mg (86%).

*4.3.3. 5-(N-Phenylcarboxamido)-7-iodo-8-benzyloxyquinoline (**2c**).* ^{1}H NMR ($CDCl_3$) δ: 8.96 (d, J=3.4 Hz, 1H, H-2); 8.75 (d, J=8.2 Hz, 1H, H-4); 8.08 (s, 1H, H-6); 7.90 (br s, 1H, NH); 7.60–7.68 (m, 4H, Ph); 7.49 (dd, J=3.4, 8.2 Hz, 1H, H-3); 7.28–7.40 (m, 6H, Ph); 5.54 (s, 2H, OCH_2). ^{13}C NMR ($CDCl_3$) δ: 164.9; 157.8; 150.4; 142.6; 137.9; 137.1; 135.1; 134.9; 131.2; 129.4 (double intensity); 129.0 (double intensity); 128.5 (double intensity); 128.4; 127.8; 125.2; 122.8; 121.1; 120.4; 90.4; 76.9. IR (KBr, (cm^{-1})): 3270 (NH); 1644 (CON). MS m/z: 480 (M^+), 353 (M^+–I). Anal. Calcd for $C_{23}H_{17}N_2O_2I$ (480.30): C, 57.52; H, 3.57; N, 5.83; found: C, 57.40; H, 3.69; N, 5.70; R_f (10% EtOAc/$CHCl_3$) 0.55; mp 178–179 °C. Pale yellow solid. Yield: 390 mg (81%).

*4.3.4. 5-(N-tert-Butylcarboxamido)-7-iodo-8-benzyloxyquinoline (**2d**).* ^{1}H NMR ($CDCl_3$) δ: 8.95 (d, J=3.9 Hz, 1H, H-2); 8.69 (d, J=8.4 Hz, 1H, H-4); 7.94 (s, 1H, H-6); 7.66 (d, J=7.3 Hz, 2H, Ph); 7.51 (dd, J=3.9, 8.4 Hz, 1H, H-3); 7.32–7.40 (m, 3H, Ph); 5.80 (br s, 1H, NH); 5.53 (s, 2H, OCH_2); 1.52 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 166.5; 157.1; 150.2; 142.6; 137.2; 134.9; 134.4; 132.7; 129.0 (double intensity); 128.5 (double intensity); 128.4; 127.7; 122.5; 90.5; 76.7; 52.6; 29.1. IR (KBr, (cm^{-1})): 3307 (NH); 1634 (CON). MS m/z: 460 (M^+), 333 (M^+–I). Anal. Calcd for $C_{21}H_{21}N_2O_2I$ (460.31): C, 54.80; H, 4.60; N, 6.09; found: C, 54.61; H, 4.69; N, 5.84; R_f (10% EtOAc/$CHCl_3$) 0.59; mp 125–126 °C. Dark green crystals. Yield: 350 mg (76%).

*4.3.5. 5,7-Bis(N-tert-butylcarboxamido)-8-benzyloxyquinoline (**2d′**).* ^{1}H NMR ($CDCl_3$) δ: 9.02 (d, J=4.0 Hz, 1H, H-2); 8.91 (d, J=8.0 Hz, 1H, H-4); 8.40 (s, 1H, H-6); 8.19 (br s, 1H, NH); 7.52 (d, J=5.8 Hz, 2H, Ph), 7.52–7.56 (m, 1H, H-3); 7.39–7.41 (m, 3H, Ph); 6.06 (br s, 1H, NH); 5.61 (s, 2H, OCH_2); 1.52 (s, 9H, $C(CH_3)_3$); 1.23 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 167.2; 163.4; 155.3; 149.9; 142.7; 136.3; 135.0; 130.5; 129.3; 129.2 (double intensity); 129.0; 128.8 (double intensity); 126.1; 124.3; 123.0; 79.0; 52.2; 51.3; 28.8; 28.4. IR (KBr, (cm^{-1})): 3375 (NH); 1639 and 1659 (CON). FABMS: 434.2445 (M+H) (calcd 434.2444). Anal. Calcd for $C_{26}H_{31}N_3O_3$ (433.55): C, 72.03; H, 7.21; N, 9.69; found: C, 71.77; H, 7.40; N, 9.45; R_f (15% EtOAc/CH_2Cl_2) 0.68; mp 59–61 °C. Pale yellow solid. Yield: 172 mg (40%).

*4.3.6. 7-(N-tert-Butylcarboxamido)-5-(N-tert-butylglyoxylamido)-8-benzyloxyquinoline (**2d″**).* ^{1}H NMR ($CDCl_3$) δ: 8.97 (d, J=2.0 Hz, 1H, H-2); 8.80 (d, J=8.0 Hz, 1H, H-4); 7.69 (s, 1H, H-6); 7.50 (d, J=7.1 Hz, 2H, Ph), 7.54 (dd, J=5.0 and 3.4 Hz, 1H, H-3); 7.31–7.38 (m, 3H, Ph); 6.01 (br s, 1H, NH); 6.42 (br s, 1H, NH); 5.75 (s, 2H, OCH_2); 1.51 (s, 9H, $C(CH_3)_3$); 1.34 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 193.0; 167.0; 161.4; 157.2; 149.8; 142.3; 137.5; 134.8; 130.8; 130.0; 128.3 and 128.2 (double intensity); 128.0; 126.5; 124.7; 123.3; 77.6; 52.3; 51.7; 28.8; 28.3. IR (KBr, (cm^{-1})): 3278 (NH); 1658 and 1640 (CON). FABMS: 462.2398 (M+H) (calcd 462.2393); R_f (15% EtOAc/CH_2Cl_2) 0.50; mp 64–66 °C. Green solid. Yield: 37 mg (8%).

*4.3.7. 5,7-Bis(N-tert-butyl-glyoxylamido)-8-hydroxyquinoline (**3**).* ^{1}H NMR ($CDCl_3$) δ: 9.42 (s, 1H, H-6); 9.22 (d, J=2.8 Hz, 1H, H-2); 8.69 (br s, 1H, H-4); 8.20 (br s, 1H, OH); 7.58 (dd, 1H, H-3); 6.71 (br s, 1H, NH); 6.66 (br s, 1H, NH); 1.50 (s, 18H, 2×$C(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ: 189.8; 189.7; 163.7; 163.4; 155.3; 148.0; 142.3; 138.6; 135.0; 130.1; 126.3; 115.1; 107.9; 52.1; 52.0; 28.7. IR (KBr, (cm^{-1})): 3307 (NH); 1677 (CON); 1628 (CON). MS m/z: 421 (M^+–H+Na), 299 (M^+–CONH^{t}Bu). Anal. Calcd for $C_{21}H_{25}N_3O_5$ (399.45): C, 63.15; H, 6.31; N, 10.52; found: C, 63.31; H, 6.42; N, 10.30; R_f (20% EtOAc/$CHCl_3$) 0.44; mp 104–105 °C. Yellow solid. Yield: 188 mg (47%).

*4.3.8. 5-Iodo-8-hydroxy-quinoline (**5**).* ^{1}H NMR ($CDCl_3$) δ: 8.75 (d, J=2.4 Hz, 1H, H-2); 8.10 (d, J=8.2 Hz, 1H, H-4); 7.75 (d, J=8.4 Hz, 1H, H-7); 7.45 (dd, J=4, 8.4 Hz, 1H, H-3); 7.09 (d, J=8.4 Hz, 1H, H-6), 6.95 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 153.2, 148.7, 137.7, 136.5, 136.4, 128.3, 122.5, 119.4, 90.8. MS m/z: 271/100 (M^+), 243/7, 144/6, 116/33. Anal. Calcd for C_9H_6ION (271.06): C, 39.88; H, 2.23; N, 5.17; found: C, 39.75; H, 2.47; N, 4.88. Highly viscous yellow oil. Yield: 122 mg (45%).

*4.3.9. 7-Iodo-8-hydroxyquinoline (**5′**).* Compound 5′ (isolated as a 70/30 mixture of **5**/**5′**): MS m/z: 271/100 (M^+), 243/10, 144/5, 116/30.

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