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Quinoline and Phenanthroline Preparation Starting From Glycerol via Improved Microwave-Assisted Modified Skraup Reaction

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Hanen Saggadi,^{a,b} Denis Luart,^a Nicolas Thiebault,^a Isabelle Polaert,^b Lionel Estel,^b and C. Len^{a,*}

Efficient “green” modified Skraup reaction in neat water was developed using inexpensive, abundant and environmentally-friendly glycerol under microwave irradiation conditions. Starting from aniline derivatives, various quinolines were obtained in 10-66% yields. The use of nitroaniline led to the corresponding phenanthrolines in 15-52% yields, respectively.

Introduction

Quinoline and phenanthroline derivatives represent an important class of nitrogen heterocyclic compounds. The first one, quinoline, is an industrial chemical used as colorants and as a solvent for the resins and terpenes. Quinoline is also a building block for the preparation of a wide range of value-added products used in various industries such as food, pharmaceuticals and cosmetics. The carbon atom structure of the quinoline derivatives is generally obtained by various conventional reactions such as Skraup reaction,¹ Doebner-Miller reaction,² Friedlander reaction,³ Pfitzinger reaction,⁴ Conrad-Limpach reaction,⁵ and Combes reaction⁶ depending of the substitution of the target compound. For the synthesis of the 5-, 6-, 7- and 8-substituted quinolines having three hydrogen atoms in position 2, 3 and 4, the Skraup reaction is the best one. This procedure has the advantage of a simple experimental procedure and the use of glycerol as major by-product of the biodiesel industry. Starting from glycerol (**1**) and analogues of aniline in presence of a strong acid and various oxidants in refluxing solvent, the corresponding quinoline derivatives were obtained with a medium yield.⁷ Obviously, the use of glycerol does not allow the obtention of substituted quinoline in position 2, 3 and 4 of the aromatic ring. The second one, phenanthroline, is also attractive building block that is commonly used for catalytic reactions and chemical architectures. Specially, 1,10-phenanthrolines are important bidentate nitrogen

donating ligands in coordination chemistry.⁸⁻¹⁰ Most often their synthesis is similar to those described for the quinoline.

In parallel with the academic and industrial applications, organic chemists have a growing interests for green chemistry and try to contribute partially or totally to the development of new alternative technologies, such as catalysis from renewable resources, the atom economy, the less dangerous chemical synthesis, the use of safer solvents, the auxiliaries and the use of alternative technologies such as microwave irradiation.¹¹⁻¹³ This latter technique is a practical alternative to conventional heating and allows often shorten reaction times and get a better selectivity. In this regards, microwave activation has been developed for the “green” synthesis of different heterocyclic compounds such nucleoside analogues¹⁴⁻¹⁷ and 6-hydroxyquinoline by our group.¹⁸ To the best of our knowledge, only one paper described the Skraup reaction under microwave activation but the authors used toxic oxidant as As₂O₅.¹⁹ In order to provide a more general protocol for the synthesis of quinoline and phenanthroline analogues according to the principles of green chemistry and sustainable development, modified Skraup reaction under microwave activation was examined and toxic reagents were removed.

Results and discussion

In the first set of experiments, the most toxic and poisonous reagents like arsenic oxide and nitrobenzene were removed and water was added as green solvent changing the temperature and the activation compared with the conventional Skraup reaction. In this regards, the reaction of glycerol (**1**) (3 equiv) with aniline (**2**) (1 equiv) in presence of sulfuric acid (1 equiv) was carried out as a model reaction in sole water at 200 °C under microwave irradiations (Table 1). The mixture was irradiated with a power high enough to reach the predicted temperature with a heating ramp of 36 °C.min⁻¹, then 200 °C for 10 minutes (total time 15 minutes). In our hands, the

target quinoline (**3**) was obtained in 8% yield with a low conversion of aniline (14%) (Table 1, entry 1). Increasing the catalyst loading to 300 mol% H_2SO_4 gave compound **3** in 44% yield with a total conversion of aniline **2** (Table 1, entry 2). Using “green” solvent-free conditions, heterocycle **3** in presence of different amounts of H_2SO_4 (100 mol% and 300 mol%) was obtained in 19% and 43% yields, respectively (Table 1, entries 3 and 4). It was notable that the “green” solvent-free conditions in presence of 300 mol% of H_2SO_4 gave similar yields (43% vs 44%) but extraction protocol was more difficult when the Skraup reaction was runned without water as solvent (Table 1, entries 2 and 4). Moreover, the scale-up protocol using continuous flow procedure could be not appropriated without addition of water as solvent. Microwave activation protocol was modified to have a heating ramp of $6\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, then $200\text{ }^\circ\text{C}$ for 10 minutes. This longer reaction time (total time 40 minutes) afforded similar yields than those obtained with the first heating ramp protocol (total time 15 minutes) except for the Skraup reaction in presence of 300 mol% of H_2SO_4 in absence of solvent. In this case, the use of water as solvent gave higher yield (43% vs 21%) (Table 1, entry 4). It was notable that the yield of heterocycle **3** did not excess 5% using the above conditions under conventional heating activation.

Table 1 Variation of acidic concentration for the modified Skraup reaction starting from glycerol (**1**) and aniline under microwave irradiations

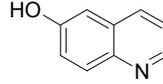
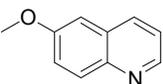
| Entry | H_2SO_4 (mol%) | H_2O (mL) | Conversion of 2 (%) | Yield of 3 (%) ^a |
|-------|--------------------------------|---------------------------|-----------------------------------|------------------------------------|
| 1 | 100 | 10 | 14 ^b (31) ^c | 8 ^b (10) ^c |
| 2 | 300 | 10 | 100 ^{b,c} | 44 ^b (38) ^c |
| 3 | 100 | 0 | 100 ^{b,c} | 19 ^b (18) ^c |
| 4 | 300 | 0 | 100 ^{b,c} | 43 ^b (21) ^c |

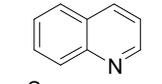
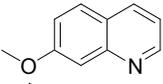
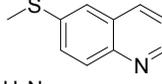
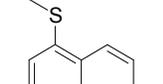
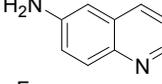
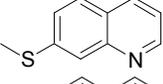
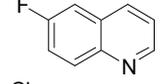
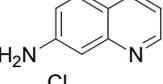
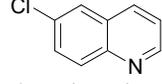
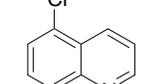
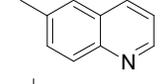
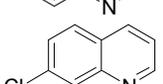
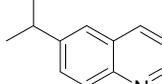
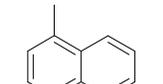
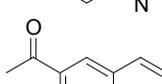
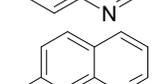
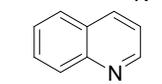
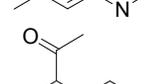
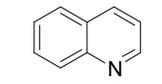
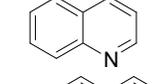
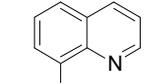
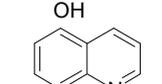
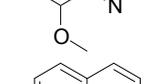
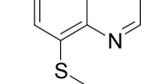
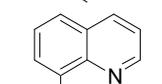
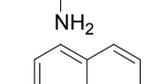
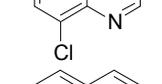
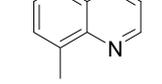
^a The yield was calculated from HPLC analysis with a calibration curve. ^b Reaction conditions: **1** (30 mmol), **2** (10 mmol), H_2SO_4 , water, 15 min under microwave activation (heating ramp = $36\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ then $200\text{ }^\circ\text{C}$ for 10 min). ^c Reaction conditions: **1** (30 mmol), **2** (10 mmol), H_2SO_4 , water, 40 min under microwave activation (heating ramp = $6\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ then $200\text{ }^\circ\text{C}$ for 10 min).

In search of a more efficient catalyst, the next step consisted of examining different acids such as FeCl_3 , $\text{H}_2\text{SO}_4/\text{FeCl}_3$, $\text{FeCl}_3/\text{AcOH}$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{H}_2\text{SO}_4/\text{Fe}_2(\text{SO}_4)_3$ and by varying their concentration (from 1.0 equiv to 5 equiv) using the experimental conditions described above (Table 1, entry 2). Even though all the acid or mixture of acids promoted the formation of quinoline (**3**), none of these acids was as good as H_2SO_4 (3 equiv). Lowering the temperature from $200\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ decreased the yield of the target compound **3**. Less than $200\text{ }^\circ\text{C}$, the formation of acrolein as intermediate from glycerol (**1**) was not efficient and did not permit the formation of the target heterocycle **3** in good yield. Considering the yield obtained at $200\text{ }^\circ\text{C}$, this temperature was chosen. With our optimized reaction conditions in hand (Table 1, entry 2), a range of aniline derivatives having different electronic and steric demands in

the Skraup synthesis was screened. All the reactions were performed using glycerol (**1**, 30 mmol, 3 equiv), aniline derivative (10 mmol, 1 equiv), H_2SO_4 (300 mol%) in water (10 mL) at $200\text{ }^\circ\text{C}$ during a total reaction time of 15 minutes (Table 2). Considering aniline derivatives with electron donating group in the para position (Table 2, entries 1-9), the Skraup adducts **4-11** were obtained most often in 18-66% yields. Starting from 4-hydroxyaniline, 6-hydroxyquinoline (**4**) was prepared in good yield (66%). This result was better than this obtained using our previous protocol¹⁸ (66% vs 27%). It was notable that, for the specifically production of 6-hydroxyquinoline (**4**), the use of nitrobenzene permitted to furnish selectively the hydroxyl derivative **4** in better yield (77%) via modified Skraup reaction and Bamberger rearrangement.¹⁸ The thiomethyl group afforded medium yield (28%) (Table 2, entry 4) while the thiol function conducted only to the quinoline **3** in low yield (Table 2, entry 3). The presence of sulfur atom was not appropriated for our optimized acidic conditions probably due to the instability of the group. Starting from 4-aminoaniline, our optimized conditions gave selectively the 6-aminoquinoline (**7**) in 18% yield (Table 2, entry 5). In our hands, the double Skraup reaction affording the resultant phenanthrolines was not observed. 4-Fluoro-, 4-chloro-, and 4-methylanilines furnished lower yields than those obtained from 4-hydroxyaniline (46-50% vs 66%) while 4-isopropyl analogue gave similar yield (63%) (Table 2, entry 9). As expected, the electron-withdrawing groups conducted to the quinoline derivatives in low yield. Starting from 4-acetylaniline, the corresponding quinoline derivative **12** was obtained in 18% yield (Table 2, entry 10) whereas 4-aminobenzoic acid and 4-cyanoaniline did not afford the corresponding 6-substituted quinolines but only the quinoline **3** (table 2, entries 11 and 12). The sterically demanding 2-substituted aniline proved to be difficult substrates for the Skraup reaction. Electron donating groups in the ortho position (Table 2, entries 13-15, 17 and 18) furnished the quinoline derivatives **13-15**, **17** and **18** in 25-48% yields. The 1,2-diaminobenzene gave the 8-aminoquinoline (**16**) in poor yield (10%) compared with the hydroxyl analogue **13** (10% vs 34%). In contrast with the 4-substituted anilines, the presence of a methyl group gave better yield than the hydroxyl one. The methylketone derivative afforded the corresponding analogue **19** in 19% yield (Table 2, entry 19). This result was similar with this obtained starting from the 4-acetylaniline.

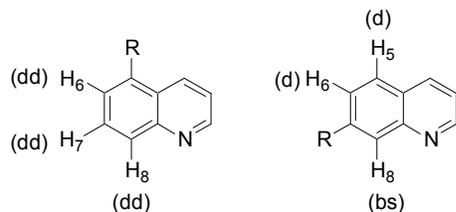
Table 2 Variation of the nature of aniline derivatives for the modified Skraup reaction starting from glycerol (**1**) in water under microwave irradiations^a

| Entry | R | Compounds | Yield (%) |
|-------|--------------------|--|-----------|
| 1 | 4-OH | 4  | 66 |
| 2 | 4-OCH ₃ | 5  | 36 |

| | | | | | | | | | |
|----|-------------------------------------|----|---|----|----|---------------------|----|--|----|
| 3 | 4-SH | 3 |  | nd | 21 | 3-OCH ₃ | 21 |  | 29 |
| 4 | 4-SCH ₃ | 6 |  | 28 | 22 | 3-SCH ₃ | 22 |  | 10 |
| 5 | 4-NH ₂ | 7 |  | 18 | | | 23 |  | 32 |
| 6 | 4-F | 8 |  | 50 | 23 | 3-NH ₂ | 24 |  | 16 |
| 7 | 4-Cl | 9 |  | 46 | | | 25 |  | 9 |
| 8 | 4-CH ₃ | 10 |  | 49 | 24 | 3-Cl | 26 |  | 21 |
| 9 | 4-CH(CH ₃) ₂ | 11 |  | 63 | | | 27 |  | 17 |
| 10 | 4-COCH ₃ | 12 |  | 18 | 25 | 3-CH ₃ | 28 |  | 32 |
| 11 | 4-COOH | 3 |  | nd | | | 29 |  | 5 |
| 12 | 4-CN | 3 |  | nd | 26 | 3-COCH ₃ | 30 |  | 10 |
| 13 | 2-OH | 13 |  | 34 | | | | | |
| 14 | 2-OCH ₃ | 14 |  | 44 | | | | | |
| 15 | 2-SCH ₃ | 15 |  | 39 | | | | | |
| 16 | 2-NH ₂ | 16 |  | 10 | | | | | |
| 17 | Cl | 17 |  | 25 | | | | | |
| 18 | 2-CH ₃ | 18 |  | 48 | | | | | |
| 19 | 2-COCH ₃ | 19 |  | 19 | | | | | |
| 20 | 3-OH | 20 |  | 25 | | | | | |

^a Reaction conditions: **1** (30 mmol), **2** (10 mmol), H₂SO₄ (30 mmol), water (10 mL), 15 min under microwave activation (heating ramp = 36 °C.min⁻¹ then 200 °C for 10 min).

Starting from aniline derivatives with electron donating group in the meta position (Table 2, entries 20-26), the Skraup reaction furnished selectively the 7-substituted quinolines **20**, **21** and **24** or a mixture of two regioisomers: 5-substituted quinolines and 7-substituted quinolines **22-23**, **25-26**, **27-28** and **29-30** in a different ratio. Each regioisomer was purified by flash chromatography. In the optimized conditions, the electron donating hydroxyl, methoxy and amino groups furnished selectively the corresponding 7-branched quinolines **20**, **21** and **24** in 25%, 29% and 16% yields, respectively. In contrast, the use of thiomethyl, chloro, methyl and acetyl groups afforded a mixture of the two regioisomers **22-23**, **25-26** and **27-28** in 42%, 30% and 49%, respectively. As expected, the use of 3-acetylaniline afforded a mixture of the two regioisomers **29** and **30** in low yield (15%) (Table 2, entry 26). The structural determination of the regioisomers was realized by NMR experiments. The NMR spectroscopy of the 7-substituted quinoline derivatives showed a broad singlet for the C(8)H and two doublets for the C(5)H and C(6)H while for the 5-substituted quinoline no singlet was observed and three multiplets (dd) for the C(6)H, C(7)H and C(8)H were present (Fig. 1).



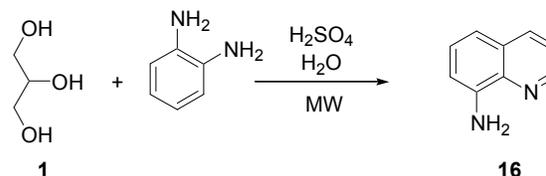
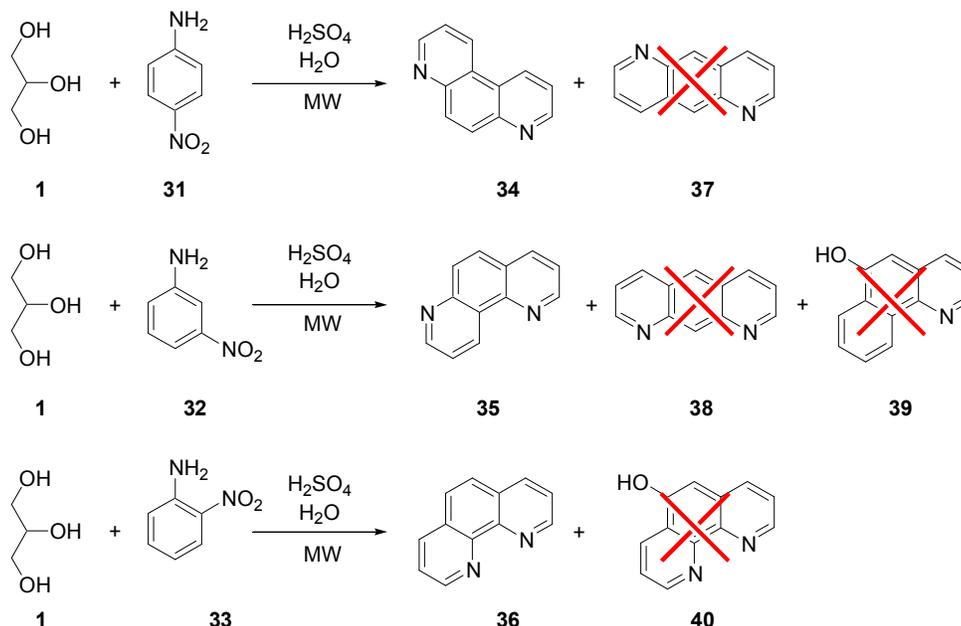
5-substituted quinoline 7-substituted quinoline

Fig.1 Structure of 5- and 7-substituted quinoline.

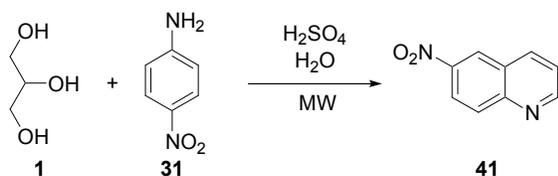
Using our optimized conditions, the diaminobenzene derivatives led only to the corresponding aminoquinolines in low yield (Table 2, entries 5, 16 and 23). Starting from 1,2-diaminobenzene, an increased glycerol content (4 equiv vs 3 equiv) led only to the formation of the corresponding 8-aminoquinoline (**16**) without formation of 1,10-phenanthroline (Scheme 1).

Starting from nitroaryl derivative, quinoline analogue was prepared in high yield.¹⁵ Using similar protocol (glycerol (**1**, 40 mmol, 4 equiv), aniline derivative (10 mmol, 1 equiv), H₂SO₄ (300

mol%) in water (10 mL) at 200 °C during a total reaction time of 15 minutes), the nitro analogues **31-33** afforded selectively the corresponding phenanthroline derivatives **34-36** in 52%, 27% and 15%, respectively (Scheme 2). In our hands, the potent regioisomers **37** and **38** were not detected as well as the alcohols **39** and **40** obtained *via* a Bamberger rearrangement.

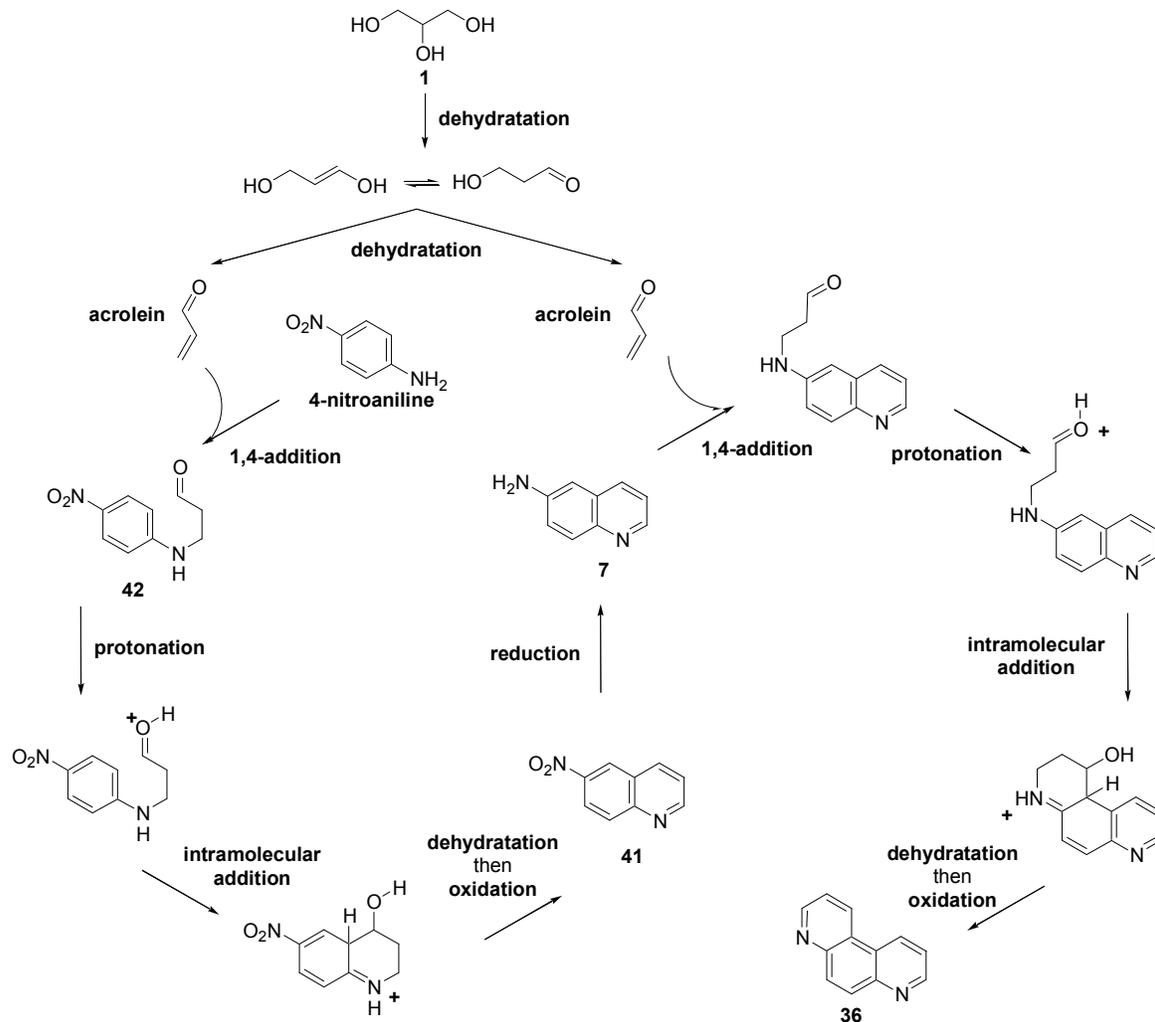
**Scheme 1** Reaction conditions: **1** (40 mmol), 1,2-diaminobenzene (10 mmol), H₂SO₄ (30 mmol), water (10 mL), 15 min under microwave activation (heating ramp = 36 °C.min⁻¹ then 200 °C for 10 min).**Scheme 2** Reaction conditions: **1** (40 mmol), nitroaniline (10 mmol), H₂SO₄ (30 mmol), water (10 mL), 15 min under microwave activation (heating ramp = 36 °C.min⁻¹ then 200 °C for 10 min).

It was notable that when a lower concentration of glycerol (**1**) (1 equiv vs 4 equiv) was used, the nitro derivative **41** was prepared selectively in 46% yield (Scheme 3).

**Scheme 3** Reaction conditions: **1** (10 mmol), 4-nitroaniline (10 mmol), H₂SO₄ (30 mmol), water (10 mL), 15 min under microwave activation (heating ramp = 36 °C.min⁻¹ then 200 °C for 10 min).

The selective synthesis of nitro analogue **41** showed that the first cyclization was realized with the amino group and then reduction of the nitro group to the amino one permitted to furnish the second Skraup reaction. In this regards, the main plausible mechanism was proposed (Scheme 4). The formation of acrolein from glycerol (**1**) by double dehydration in acidic conditions is a known mechanism. The regioselective 1,4-addition of 4-nitroaniline to acrolein afforded the corresponding aldehyde **42**. After protonation of aldehyde **42**, the dehydrative ring closure obtained in two steps by intramolecular addition and dehydration was followed by oxidation of the aromatic ring conducted to the 6-nitroquinoline (**41**). The nitro compound **41** was reduced to the corresponding amino derivatives **7** which was the starting material for a second Skraup reaction. Compound **7** furnished in “one pot five steps” using similar mechanism the target 4,7-phenanthroline (**36**).

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Scheme 4 Plausible mechanism for the synthesis of phenanthroline derivative **36**.

Conclusions

In summary, the classical Skraup reaction was modified to obtain different 5-, 6-, 7- and 8-substituted quinolines from aniline derivatives. From the view point of green chemistry, the toxic reagents like arsenic(V) oxide was removed, water was used as green solvent and alternative microwave irradiations were developed. Our optimized simple and efficient protocol permitted to prepare quinoline in 44% yield. 5-, 6-, 7- and 8-substituted quinolines with substituents with various steric and electronic demands were obtained selectively in medium to good yield. When the meta-substituted anilines were used, regioselectivity was observed for the 7-hydroxy, 7-methoxy and 7-amino analogues in

25%, 29% and 16%. The 4,7-, 1,7- and 1,10-phenanthrolines were obtained regioselectively starting from the 4-, 3- and 2-nitroanilines in 52%, 27% and 15%. This latest reaction furnished one efficient domino reaction with a “one pot eleven steps” using only glycerol, nitroaniline, sulphuric acid and water *via* a double modified Skraup reaction.

Experimental Section

All products were purchased either from Acros or Sigma Aldrich depending on their availability and were used without further purification. All solvents were purchased from Carlo Erba. Reactions were monitored by TLC (Kieselgel 60F254 MERCK aluminium sheet) with detection by UV light or potassium permanganate acidic solution. Column chromatography was performed on silica gel 40-

60 μm . Flash column chromatography was performed on an automatic Grace apparatus, using silica gel cartridges. The qualitative and quantitative analysis of the reactants and products was performed on a HPLC Shimadzu system in reversed phase using a C18 column and PDA detector. Products were identified by a comparison with authentic samples. Microwave experiments were conducted in a commercial microwave reactor especially designed for synthetic chemistry. Monowave300 (Anton Paar, Austria) is a mono-mode cavity with a microwave power delivery system ranging from 0 to 850 W. The temperatures of the reactions were mainly monitored via contactless infrared pyrometer, which was calibrated in control experiments with a fiber-optic contact thermometer. Described reaction time corresponds to 15 min (heating ramp = 36 $^{\circ}\text{C}\cdot\text{min}^{-1}$ then 200 $^{\circ}\text{C}$ for 10 min) or 40 min (heating ramp = 6 $^{\circ}\text{C}\cdot\text{min}^{-1}$ then 200 $^{\circ}\text{C}$ for 10 min). Sealed vessels and magnetic stir bar inside the vessel were used. Temperature and power profiles were monitored in both cases through the software provided by the manufacturer. NMR spectra of products were recorded on a Bruker instrument operating at 400.17 MHz for proton, 100.63 MHz for carbon and 376.49 MHz for fluor using CDCl_3 (D, 99.5%) and $\text{DMSO}-d_6$ (D, 99.8%) as solvent. GC/MS (EI) analysis was recorded on a Agilent 5975 Series MSD apparatus using a HP5-MS (30 m x 250 μm x 0.25 μm) column. Melting points are recorded on a Stuart SMP 10 and are uncorrected.

General procedure for the preparation of the quinoline derivatives 3-30

A 30 mL sealed vessel was charged with aniline derivative (10 mmol), glycerol (1, 30 mmol, 3.0 eq), H_2SO_4 (30 mmol, 3 eq) in water (10 mL). The mixture was irradiated with a power high enough to reach the predicted temperature with a heating ramp of 36 $^{\circ}\text{C}\cdot\text{min}^{-1}$, then 200 $^{\circ}\text{C}$ for 10 min. After cooling at room temperature, pH was adjusted at 8-9 by addition of NaOH and the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude residue was purified by column chromatograph (cyclohexane/EtOAc) on silica gel yielding the corresponding quinoline.

General procedure for the preparation of the phenanthroline derivatives 34-36

A 30 mL sealed vessel was charged with aniline derivative (10 mmol), glycerol (1, 40 mmol, 4.0 eq), H_2SO_4 (30 mmol, 3 eq) in water (10 mL). The mixture was irradiated with a power high enough to reach the predicted temperature with a heating ramp of 36 $^{\circ}\text{C}\cdot\text{min}^{-1}$, then 200 $^{\circ}\text{C}$ for 10 min. After cooling at room temperature, pH was adjusted at 8-9 by addition of NaOH and the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude residue was purified by column chromatograph (cyclohexane/EtOAc) on silica gel yielding the corresponding phenanthroline.

6-Hydroxyquinoline (4)²⁰

mp = 197 $^{\circ}\text{C}$

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.01 (br s, 1H, HO), 8.65 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.13 (d, $J_{3,4} = 8$ Hz, 1H, H-4), 7.86 (d, $J_{7,8} = 9.2$ Hz, 1H, H-8), 7.38 (dd, 1H, H-3), 7.31 (dd, $J_{7,5} = 2.4$ Hz, 1H, H-7), 7.14 (d, 1H, H-5).

^{13}C NMR (100 MHz, $\text{dmsO}-d_6$) δ 155.3, 147.0, 142.9, 134.0, 130.3, 129.2, 121.8, 121.3, 108.2.

6-Methoxyquinoline (5)²¹

^1H NMR (400 MHz, CDCl_3) δ 8.76 (dd, $J_{2,3} = 4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.04 (d, $J_{3,4} = 8$ Hz, 1H, H-4), 7.99 (d, $J_{7,8} = 9.2$ Hz, 1H, H-8), 7.36 (dd, $J_{7,5} = 2.4$ Hz, 1H, H-7), 7.34 (dd, 1H, H-3), 7.06 (d, 1H, H-5), 3.92 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 147.9, 144.4, 134.8, 130.8, 129.3, 122.3, 121.3, 105.1, 55.5.

6-Thiomethylquinoline (6)²²

mp = 41 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 8.82 (dd, $J_{2,3} = 4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.03 (d, $J_{3,4} = 8.4$ Hz, 1H, H-4), 7.98 (d, $J_{7,8} = 9.2$ Hz, 1H, H-8), 7.58 (dd, $J_{7,5} = 2.4$ Hz, 1H, H-7), 7.52 (d, 1H, H-5), 7.06 (dd, 1H, H-3), 2.58 (s, 3H, SCH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 146.4, 137.5, 134.7, 129.5, 128.9, 128.7, 122.3, 121.6, 15.6.

6-Aminoquinoline (7)²³

mp = 110 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 8.65 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 7.91 (d, $J_{7,8} = 8.8$ Hz, 1H, H-8), 7.90 (dd, $J_{3,4} = 8.4$ Hz, 1H, H-4), 7.26 (dd, 1H, H-3), 7.15 (dd, $J_{7,5} = 2.4$ Hz, 1H, H-7), 6.89 (d, 1H, H-5), 3.96 (br s, 2H, NH_2).

^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 144.6, 143.1, 133.9, 130.3, 129.8, 121.7, 121.3, 107.3.

6-Fluoroquinoline (8)²⁴

^1H NMR (400 MHz, CDCl_3) δ 8.87 (d, $J_{2,3} = 4$ Hz, 1H, H-2), 8.10-8.07 (m, 2H, H-4, H-8), 7.47 (dd, $J_{7,8} = 8.8$ Hz, $J_{7,5} = 2.4$ Hz, 1H, H-7), 7.42-7.37 (m, 2H, H-3, H-5).

^{13}C NMR (100 MHz, CDCl_3) δ 160.3 ($J = 246.7$ Hz), 149.6 ($J = 2.6$ Hz), 145.3, 135.3 ($J = 5.4$ Hz), 131.9 ($J = 9.1$ Hz), 128.82 ($J = 9.9$ Hz), 121.7, 119.7 ($J = 25.6$ Hz), 110.6 ($J = 21.4$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -113.3.

6-Chloroquinoline (9)²⁵

mp = 38 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 8.90 (dd, $J_{2,3} = 4.0$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.07 (dd, $J_{3,4} = 8.4$ Hz, 1H, H-4), 8.04 (d, $J_{7,8} = 8.8$ Hz, 1H, H-8), 7.80 (d, $J_{5,7} = 2.4$ Hz, 1H, H-5), 7.65 (dd, 1H, H-7), 7.42 (dd, 1H, H-3).

^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 146.6, 135.1, 132.3, 131.1, 130.4, 128.8, 126.4, 121.9.

6-Methylquinoline (10)²⁶

^1H NMR (400 MHz, CDCl_3) δ 8.84 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.06 (d, $J_{3,4} = 8.0$ Hz, 1H, H-4), 7.99 (d, $J_{7,8} = 8.4$ Hz, 1H, H-8), 7.57-7.53 (m, 2H, H-5, H-7), 7.35 (dd, 1H, H-3), 2.53 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 146.8, 136.4, 135.4, 131.7, 129.0, 128.3, 126.5, 121.0, 21.5.

6-Isopropylquinoline (11)²⁷

^1H NMR (400 MHz, CDCl_3) δ 8.835 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.05 (d, $J_{3,4} = 8.0$ Hz, 1H, H-4), 8.03 (d, $J_{7,8} = 8.8$ Hz, 1H, H-8), 7.60 (dd, $J_{7,5} = 2.0$ Hz, 1H, H-7), 7.57 (d, 1H, H-5), 7.31 (dd, 1H, H-3), 3.06 (m, 1H, CH), 1.33 (s, 3H, CH_3), 1.31 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 149.5, 147.1, 147.0, 135.5, 129.2, 129.1, 128.2, 123.7, 120.9, 33.9, 23.7.

6-Acetylquinoline (12)²⁸

mp = 72 $^{\circ}\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 9.01 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.45 (d, $J_{5,7} = 1.6$ Hz, 1H, H-5), 8.29-8.25 (m, 2H, H-4, H-

7), 8.16 (d, $J_{7-8} = 8.8$ Hz, 1H, H-8), 7.35 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-3), 2.74 (s, 3H, CH₃).
¹³C NMR (100 MHz, CDCl₃) δ 197.4, 152.6, 150.1, 137.5, 134.9, 130.0, 129.8, 127.7, 127.4, 121.9, 26.8.

8-Hydroxyquinoline (13)²⁹

mp = 71 °C

¹H NMR (400 MHz, CDCl₃) δ 8.78 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.15 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.48-7.41 (m, 2H, H-3, H-6), 7.33 (d, $J_{3-4} = 8.4$ Hz, 1H, H-5), 7.20 (dd, $J_{5-7} = 1.2$ Hz, $J_{6-7} = 7.6$ Hz, 1H, H-7).

¹³C NMR (100 MHz, CDCl₃) δ 152.2, 147.9, 138.2, 136.1, 128.5, 127.7, 121.8, 117.8, 110.1.

8-Methoxyquinoline (14)³⁰

¹H NMR (400 MHz, CDCl₃) δ 8.93 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.13 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.47 (t, $J_{5-6} = J_{6-7} = 8.0$ Hz, 1H, H-6), 7.43 (dd, 1H, H-3), 7.39 (dd, $J_{5-7} = 1.2$ Hz, 1H, H-5), 7.06 (dd, 1H, H-7), 4.09 (s, 3H, OCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 155.1, 149.0, 139.7, 136.3, 129.3, 126.9, 121.7, 119.5, 107.7, 56.0.

8-Thiomethylquinoline (15)³¹

mp = 76 °C

¹H NMR (400 MHz, CDCl₃) δ 8.94 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.14 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.58 (d, $J_{5-6} = 7.6$ Hz, 1H, H-5), 7.50 (t, $J_{6-7} = 7.6$ Hz, 1H, H-6), 7.44 (dd, 1H, H-3), 7.40 (d, 1H, H-7), 2.56 (s, 3H, SCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 149.1, 145.3, 139.9, 136.3, 128.1, 126.6, 123.5, 122.8, 121.7, 14.3.

8-Aminoquinoline (16)³²

mp = 63 °C

¹H NMR (400 MHz, CDCl₃) δ 8.77 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.06 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.36 (dd, 1H, H-3), 7.34 (t, $J_{5-6} = J_{6-7} = 7.6$ Hz, 1H, H-6), 7.15 (dd, $J_{5-7} = 0.8$ Hz, 1H, H-5), 6.93 (dd, 1H, H-7), 5.00 (br s, 2H, NH₂).

¹³C NMR (100 MHz, CDCl₃) δ 147.4, 143.9, 138.4, 135.9, 128.8, 127.3, 121.3, 115.9, 109.9.

8-Chloroquinoline (17)³³

¹H NMR (400 MHz, CDCl₃) δ 9.01 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.14 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.80 (dd, $J_{5-7} = 1.2$ Hz, $J_{5-6} = 7.6$ Hz, 1H, H-5, H-7), 7.71 (dd, $J_{6-7} = 7.6$ Hz, 1H, H-5, H-7), 7.45-7.41 (m, 2H, H-3, H-6).

¹³C NMR (100 MHz, CDCl₃) δ 150.9, 144.3, 136.4, 133.4, 129.5, 129.4, 126.9, 126.4, 121.8.

8-Methylquinoline (18)³⁴

¹H NMR (400 MHz, CDCl₃) δ 8.95 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.13 (dd, $J_{3-4} = 8.0$ Hz, 1H, H-4), 7.66 (d, $J_{5-6} = 8.0$ Hz, 1H, H-5), 7.57 (d, $J_{6-7} = 8.0$ Hz, 1H, H-7), 7.43 (t, 1H, H-6), 7.39 (dd, 1H, H-3), 2.83 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 149.2, 147.3, 137.0, 136.3, 129.6, 128.2, 126.3, 125.8, 120.8, 18.1.

8-Acetylquinoline (19)²⁸

mp = 39 °C

¹H NMR (400 MHz, CDCl₃) δ 8.97 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.19 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.93 (d, $J_{5-6} = J_{6-7} = 8.0$ Hz, 2H, H-5, H-7), 7.57 (t, 1H, H-6), 7.44 (dd, 1H, H-3), 2.94 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 203.9, 150.4, 145.5, 136.7, 136.2, 131.2, 129.2, 128.2, 126.0, 121.4, 32.7.

7-Hydroxyquinoline (20)³⁵

mp = 244 °C

¹H NMR (400 MHz, dms_o-d₆) δ 10.16 (br s, 1H, HO), 8.73 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 2.0$ Hz, 1H, H-2), 8.19 (dd, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.80 (d, $J_{5-6} = 9.0$ Hz, 1H, H-5), 7.27 (dd, 1H, H-3), 7.24 (dd, $J_{6-8} = 2.4$ Hz, 1H, H-8), 7.16 (dd, 1H, H-6).

¹³C NMR (100 MHz, dms_o-d₆) δ 158.4, 150.3, 149.4, 135.5, 129.2, 122.1, 119.1, 118.3, 109.8.

7-Methoxyquinoline (21)³⁶

¹H NMR (400 MHz, CDCl₃) δ 8.83 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.09 (d, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.70 (d, $J_{5-6} = 8.8$ Hz, 1H, H-5), 7.44 (d, $J_{6-8} = 2.4$ Hz, 1H, H-8), 7.27 (dd, 1H, H-3), 7.21 (dd, 1H, H-6), 3.95 (s, 3H, OCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 160.9, 149.8, 149.2, 136.4, 128.8, 123.6, 120.1, 118.9, 106.6, 55.6.

5-Thiomethylquinoline (22)²²

mp = 76 °C

¹H NMR (400 MHz, CDCl₃) δ 8.92 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.59 (d, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.92 (d, $J_{7-8} = 8.4$ Hz, 1H, H-8), 7.64 (t, $J_{6-7} = 8.4$ Hz, 1H, H-7), 7.44-7.41 (m, 2H, H-3, H-6), 2.57 (s, 3H, SCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 150.5, 148.3, 136.3, 132.6, 129.2, 127.0, 126.9, 124.1, 120.8, 16.3.

7-Thiomethylquinoline (23)³¹

¹H NMR (400 MHz, CDCl₃) δ 8.85 (dd, $J_{2-3} = 4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.07 (d, $J_{3-4} = 8.0$ Hz, 1H, H-4), 7.79 (d, $J_{6-8} = 1.2$ Hz, 1H, H-8), 7.67 (d, $J_{5-6} = 8.8$ Hz, 1H, H-5), 7.39 (dd, 1H, H-6), 7.31 (dd, 1H, H-3), 2.60 (s, 3H, SCH₃).

¹³C NMR (100 MHz, CDCl₃) δ 150.7, 148.7, 141.3, 135.8, 127.6, 125.9, 125.8, 122.9, 120.2, 15.0.

7-Aminoquinoline (24)³⁷

mp = 89 °C

¹H NMR (400 MHz, CDCl₃) δ 8.73 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 7.95 (d, $J_{3-4} = 8.4$ Hz, 1H, H-4), 7.59 (d, $J_{5-6} = 8.4$ Hz, 1H, H-5), 7.20 (d, $J_{6-8} = 2.0$ Hz, 1H, H-8), 7.12 (dd, 1H, H-3), 6.96 (dd, 1H, H-6), 4.13 (br s, 2H, NH₂).

¹³C NMR (100 MHz, CDCl₃) δ 150.6, 149.9, 147.6, 1356, 128.9, 122.2, 118.6, 117.7, 109.2.

5-Chloroquinoline (25)³⁸

¹H NMR (400 MHz, CDCl₃) δ 8.96 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.58 (d, $J_{3-4} = 8.4$ Hz, 1H, H-4), 8.04 (t, $J_{7-8} = J_{7-8} = 5.2$ Hz, 1H, H-7), 7.63 (d, 2H, H-6, H-8), 7.50 (dd, 1H, H-3).

¹³C NMR (100 MHz, CDCl₃) δ 150.9, 148.8, 135.2, 131.2, 129.1, 128.6, 126.5, 126.3, 121.8.

7-Chloroquinoline (26)³⁹

¹H NMR (400 MHz, CDCl₃) δ 8.92 (dd, $J_{2-3} = 4.4$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.14 (d, $J_{3-4} = 8.0$ Hz, 1H, H-4), 8.11 (d, $J_{6-8} = 1.6$ Hz, 1H, H-8), 7.76 (d, $J_{5-6} = 8.8$ Hz, 1H, H-6), 7.51 (d, 1H, H-5), 7.40 (dd, 1H, H-3).

¹³C NMR (100 MHz, CDCl₃) δ 151.3, 148.5, 135.8, 132.8, 128.9, 128.4, 127.6, 126.6, 121.2.

5-Methylquinoline (27)⁴⁰

¹H NMR (400 MHz, CDCl₃) δ 8.90 (dd, $J_{2-3} = 4.0$ Hz, $J_{2-4} = 1.6$ Hz, 1H, H-2), 8.29 (dd, $J_{3-4} = 8.8$ Hz, 1H, H-4), 7.96 (d, $J_{7-8} = 8.4$ Hz, 1H, H-8), 7.58 (t, $J_{6-7} = 8.4$ Hz, 1H, H-7), 7.39 (dd, 1H, H-3), 7.37-7.34 (m, 1H, H-6), 2.66 (s, 3H, CH₃).

^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 148.4, 134.5, 132.4, 129.0, 127.6, 127.5, 126.2, 120.6, 18.5.

7-Methylquinoline (28)³⁶

mp = 70 °C

^1H NMR (400 MHz, CDCl_3) δ 8.85 (dd, $J_{2,3} = 4.0$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.07 (dd, $J_{3,4} = 8.4$ Hz, 1H, H-4), 7.79 (d, $J_{6,8} = 0.8$ Hz, 1H, H-8), 7.68 (d, $J_{5,6} = 8.4$ Hz, 1H, H-5), 7.37-7.34 (m, 1H, H-6), 7.30 (dd, 1H, H-3), 2.55 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 148.3, 139.6, 135.6, 128.7, 128.2, 127.3, 126.9, 120.2, 21.8.

5-Acetylquinoline (29)⁴¹

^1H NMR (400 MHz, CDCl_3) δ 9.19 (d, $J_{3,4} = 8.8$ Hz, 1H, H-4), 8.93 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.25 (d, $J_{6,7} = 8.8$ Hz, 1H, H-6), 8.04 (d, $J_{7,8} = 8.0$ Hz, 1H, H-8), 7.72 (dd, 1H, H-7), 7.49 (dd, 1H, H-3), 2.74 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 200.5, 150.7, 148.3, 134.7, 134.6, 129.6, 127.8, 125.9, 122.8, 29.5.

7-Acetylquinoline (30)

^1H NMR (400 MHz, CDCl_3) δ 8.98 (dd, $J_{2,3} = 4.0$ Hz, $J_{2,4} = 1.2$ Hz, 1H, H-2), 8.66 (s, 1H, H-8), 8.17 (d, $J_{5,6} = 8.8$ Hz, 1H, H-6), 8.09 (dd, $J_{3,4} = 8.4$ Hz, 1H, H-4), 7.85 (d, 1H, H-5), 7.48 (dd, 1H, H-3), 2.73 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 151.3, 147.7, 137.4, 135.8, 131.4, 130.7, 128.2, 124.3, 122.9, 26.7.

4,7-Phénanthroline (34)⁴²

mp = 175 °C

^1H NMR (400 MHz, dmsO-d_6) δ 9.27 (dd, $J_{2,4} = 1.6$ Hz, $J_{3,4} = 8.4$ Hz, 1H, H-4), 9.02 (dd, $J_{2,3} = 4.4$ Hz, 1H, H-2), 8.18 (s, 1H, H-5), 7.76 (dd, 1H, H-3).

^{13}C NMR (100 MHz, dmsO-d_6) δ 150.6, 146.9, 131.7, 131.6, 124.6, 122.3.

1,7-Phenanthroline (35)⁴³

mp = 81 °C

^1H NMR (400 MHz, CDCl_3) δ 9.31 (dd, $J_{3,4} = 8.0$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-4), 8.86 (dd, $J_{2,3} = 4.4$ Hz, 1H, H-2/H-8), 8.79 (dd, $J_{7,8} = 4.4$ Hz, $J_{6,8} = 1.6$ Hz, 1H, H-2/H-8), 7.92 (dd, $J_{6,7} = 8.0$ Hz, 1H, H-6), 7.85 (d, $J_{9,10} = 9.0$ Hz, 1H, H-10), 7.64 (d, 1H, H-9), 7.42 (dd, 1H, H-3/H-7), 7.31 (dd, 1H, H-3/H-7).

^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 148.9, 145.3, 135.4, 132.2, 128.6, 128.5, 126.4, 125.6, 121.9, 121.5.

1,10-Phenanthroline (36)⁴⁴

mp = 115 °C

^1H NMR (400 MHz, CDCl_3) δ 9.13 (dd, $J_{2,3} = 4.4$ Hz, $J_{2,4} = 1.6$ Hz, 1H, H-2), 8.24 (d, $J_{3,4} = 8.0$ Hz, 1H, H-4), 7.79 (s, 1H, H-5), 7.62 (dd, 1H, H-3),

^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 146.1, 136.0, 128.6, 126.5, 123.1.

6-Nitroquinoline (41)⁴⁵

mp = 152 °C

^1H NMR (400 MHz, CDCl_3) δ 9.10 (dd, $J_{3,4} = 8.4$ Hz, $J_{2,4} = 1.2$ Hz, 1H, H-4), 8.80 (d, $J_{5,7} = 2.4$ Hz, 1H, H-5), 8.49 (dd, $J_{7,8} = 9.2$ Hz, 1H, H-7), 8.36 (d, $J_{3,4} = 8.4$ Hz, 1H, H-4), 8.25 (dd, 1H, H-8), 7.58 (d, 1H, H-3).

^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 150.2, 145.6, 137.8, 131.4, 127.0, 124.6, 123.0, 122.9.

Notes and references

^a Transformations Intégrées de la Matière Renouvelable, EA 4297, UTC-ESCOM, Centre de Recherche de Royallieu, BP 20529, F-60200 Compiègne, France. Fax: +33(0)344971591; Tel: +33(0)344238828; E-mail: christophe.len@utc.fr

^b Laboratoire de Sécurité des Procédés Chimiques – EA 4704 INSA Rouen, Avenue de l'Université, F-76801 Saint-Etienne-du-Rouvray cedex, France

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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Graphical abstract

