# Synthesis of 5-Substituted Quinolin-8-ols

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A new preparative procedure for 5-aryl- or 5-decylquinolin-8-ols was developed. The key step of the procedure is the cross coupling of 8-benzyloxy-5-bromoquinoline with arylboronic acid or 9-decyl-9-borabicyclo[3.3.1]nonane (Suzuki reaction). Deprotection of the benzyloxy group was accomplished successfully by Pd/C catalyzed hydrogen transfer from cyclohexa-1,4-diene.

In the course of our investigation on axial chirality in metal chelates, 4- or 5-aryl-substituted quinolin-8-ols were required. If the aryl groups with bulky substituents on the quinoline ring have sufficient rotational barrier around the pivot bond, as in 5-arylquinolin-8-ols shown in the Scheme, this series of ligands is very fruitful for the development of a new entry to axial chirality using quinolin-8-ol chelates. Furthermore, considering the applicability of the ligands in analytical sciences, electronic devices and pharmaceuticals, the ligands are promising and important in various fields of science. Classically, 5-arylquinolin-8-ol was prepared via Skraup synthesis from 2-amino-4-arylphenol and acrolein or its equivalent.<sup>2</sup> If the required aryl groups are able to be introduced to the desired position of quinolin-8-ol directly, the synthetic route is much more advantageous. We found that a halide group on the quinoline ring could be substituted with carbon nucleophiles successfully. The aryl group of arylboronic acid (Suzuki reaction<sup>3</sup>) and the carbon anion of an active methylene carbon<sup>4</sup> are effective as the nucleophiles.

Here, we wish to report a new preparative method for 5arylquinolin-8-ol as outlined in the scheme. The key step in this procedure is the substitution reaction of 8-benzyloxy-5-haloquinoline with an aryl group. The substitution reaction was found to be efficient and chemoselective as observed previously, in general, for the Suzuki reaction. Deprotection of the benzyloxy group was accomplished by catalytic hydrogen transfer from cyclohexa-1.4-diene. The hydroxy group of quinolin-8-ol (1) was benzylated with benzyl chloride in the usual manner.<sup>5</sup> Chlorination or bromination of 8-benzyloxyquinoline (2) was accomplished with the corresponding N-halosuccinimide<sup>6a</sup> and iodination with  $I_2$ -iodic acid<sup>6b</sup> to give the 5-bromo- or 5-iodoquinoline derivatives 3a and 3b, respectively. Arylboronic acids 4a and 4e-f were commercially available and **4b-d** were prepared by the reaction of aryllithium with isopropyl borate at  $-(60-70)^{\circ}$ C. 9-Decyl-9-BBN (4g) was obtained from the reaction of 9-BBN and dec-1ene, and was used for the coupling reaction directly. First of all, reaction conditions were examined qualitatively using phenylboronic acid as shown in Table 1. Entries 2 and 3 showed that Pd(PPh<sub>3</sub>)<sub>4</sub> was a better catalyst than Pd(dppp)Cl<sub>2</sub> and entries 1, 2, and 4 showed that bromide was the best of the three halides employed. The chloride was inactive in our experiments.

The reactions of arylboronic acids under typical Suzuki reaction conditions gave chemospecifically the biaryl

OH

OBn

$$A = Af$$
 $A = Af$ 
 $A = A$ 

 $4a-f = RB(OH)_2$ ; 4g = 9-BBN-9-BBN

4-6	R	4-6	R
a b c d	Ph 1-naphthyl 2-methyl-1-naphthyl 2-methoxy-1-naphthyl	e f g	$3-NO_2C_6H_4$ $3-NH_2C_6H_4$ decyl

Scheme

Table 1. Examination of the Reaction Conditions using Phenylboronic Acid

Entry	X	Catalyst	Yield (%)
1	Cl	Pd(PPh <sub>3</sub> ) <sub>4</sub>	_
2	Br	$Pd(PPh_3)_4$	85
3	Br	Pd(dppp)Cl <sub>2</sub>	42
4	I	$Pd(PPh_3)_4$	72

Table 2. Results of Coupling Reaction

Entry	RB(OH) <sub>2</sub> <b>4</b>	Equiv	Product 5	Yield (%)	mp (°C)
1	a	1.1	a	85	125-126
2	b	1.1	b	75	148 - 150
3	c	1.1	c	65	129 - 130
4	d	1.1	d	47	148 - 149
5	d	1.25	d	65	
6	e	1.1	e	67	160 - 161
7	f	1.1	f	65	171 - 172
8	g	1.1	g	21	58 - 59
9	g	2.2	g	64	

compounds in moderate yields, except that of 4-carboxyphenylboronic acid as shown in Table 2. The results showed that the reaction was rather insensitive to steric hindrance. In the case of the alkyl group only 5-decyl1426 Papers SYNTHESIS

quinoline derivative **5g** could be obtained using 9-decyl-9-BBN (**4g**) instead of decylboronic acid. Although a detailed mechanism is not yet known, the aryl nucleophile generated from arylboronic acid will attack the C-5 carbon of a quinoline ring.

Normal hydrogenolysis using  $H_2$  and Pd/C gave one crystalline product ( $M^+ = 225$ ) in the case of 5c. The compound was contaminated with paramagnetic species and could not be purified. Since the compound did not show a C-O stretching vibration in its IR spectrum, we assumed that it must be overreduced material.

Catalytic transfer hydrogenation (CTH) using cyclohexa-1,4-diene and Pd/C catalyst in absolute ethanol<sup>7</sup> was successful. In Table 3 are listed the results on a 0.5 mmol scale. Reaction conditions of the CTH procedure were examined with attention to stoichiometry and reaction time. Hydrogenolysis of **5a-g** gave 5-aryl- and 5-decyl-quinolin-8-ols **6**. Runs 1-4 gave 5-substituted quinolin-8-ols in relatively good yields. Although the yields were low to moderate, deprotection was accomplished chemoselectively.

Table 3. Hydrogenolyses of 5

Run	5	Cyclohexa- 1,4-diene (Equiv)	Pd/C (% wt/wt)	Product 6	Yield (%)	mp (°C)
1	a	3	30	a	79	87-89
2	b	3	100	b	51	180 - 181
3	c	5	70	c	71	187 - 188
4	d	3	30	d	78	154-156
5	e	3	90	e	20	189-190
6	f	3	80	f	47	145-146
7	g	3	80	g	41	63-64

In conclusion, the procedure reported here represents a new synthetic approach to 5-substituted quinolin-8-ols. The procedure is advantageous over tedious classic procedures such as Skraup quinoline syntheses.

All the melting points are uncorrected. IR spectra were recorded on a Hitachi 295 spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a JEOL GSX-400 spectrometer at 400 MHz and 100 MHz, respectively. Mass spectra were recorded on a JEOL JMS-DX300 spectrometer operating at 300 mA. Elemental analyses were performed at the Ibaraki University Instrumental Analysis Center with a YANACO MT-5 CHN Corder.

# 5-Aryl- or 5-Decyl-8-benzyloxyquinolines 5; General Procedure:

A mixture of 3 (2 mmol), 4 (2.2 mmol), benzene (20 mL), EtOH (4 mL), and 2 M aq Na<sub>2</sub>CO<sub>3</sub> (24 mL) was degassed under an Ar atmosphere. To the mixture was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 mmol) and the mixture was refluxed under Ar for 24 h. The crude product extracted with benzene was recrystallized from EtOH except for 5d. In the case of 5d, the crude product was purified by column chromatography. In the case of 5g, 9-decyl-9-BBN (2.2 equiv) prepared from 9-BBN dimer and dec-1-ene was used as the borane reagent.

 $8\hbox{-}\textit{Benzyloxy-5-phenylquinoline (5\,a)}:$ 

 $C_{22}H_{17}NO$  calcd C 84.89 H 5.50 N 4.50 (311.39) found 85.08 5.74 4.39

IR (KBr): v = 3030 (C–H st), 1571, 1463, 1307, 1089 (C–O–C st), 815, 787, 771 cm<sup>-1</sup>.

MS: m/z (%) = 311 (M<sup>+</sup>, 58), 235 (M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub> + 1, 90), 220 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 37), 91 (C<sub>7</sub>H<sub>7</sub>, 100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 5.49 (2 H, s, O–C $H_2$ C<sub>6</sub>H<sub>5</sub>), 7.07 (1 H, d, J = 7.6 Hz), 7.25–7.51 (10 H, m), 7.54 (2 H, d, J = 7.2 Hz), 8.21 (1 H, dd, J = 2.0, 8.4 Hz), 8.99 (1 H, dd, J = 1.6, 4.0 Hz).

 $^{13}\mathrm{C}$  NMR (TMS/CDCl<sub>3</sub>):  $\delta=70.7$  (O– $C\mathrm{H}_2$ –Ph), 109.3, 121.44, 127.02, 127.1, 127.7, 127.8, 128.4, 128.6, 130.1, 132.0, 132.1, 134.2, 137.0, 139.3, 149.1, 153.7.

8-Benzyloxy-5-(1-naphthyl)quinoline (5b):

C<sub>26</sub>H<sub>19</sub>NO calcd C 86.40 H 5.30 N 3.88 (361.45) found 86.61 5.45 3.97

IR (KBr):  $\nu = 3045$  (C–H st), 2855, 1616, 1498, 1308, 1223, 1093 (C–O–C st), 791, 731 cm<sup>-1</sup>.

MS: m/z (%) = 362 (M<sup>+</sup>, 55), 284 (19, M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>), 271 (10, M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 235 (90, M<sup>+</sup> - C<sub>10</sub>H<sub>7</sub> + 1), 222 (100), 91 (C<sub>7</sub>H<sub>7</sub>, 82).

 $^1\mathrm{H}$  NMR (TMS/CDCl<sub>3</sub>):  $\delta=5.49$  (2 H, s, O—C $H_2$ C<sub>6</sub>H<sub>5</sub>), 7.14 (1 H, d, J=8.0 Hz), 7.13–7.48 (10 H, m), 7.54–7.60 (2 H, m), 7.67 (1 H, dd, J=2.0, 8.4 Hz), 7.93 (2 H, d, J=8.4 Hz), 8.97 (1 H, dd, J=2.0, 4.0 Hz).

 $^{13}\text{C NMR} \ (\text{TMS/CDCl}_3): \ \delta = 70.9 \ (\text{C-O-}C\text{H}_2\text{C}_6\text{H}_5), \ 109.3, \\ 121.5, 125.4, 125.9, 128.1, 128.2, 128.3, 128.7, 129.0, 130.5, 133.0, \\ 133.6, 134.8, 137.0, 140.3, 149.3, 154.1.$ 

8-Benzyloxy-5-(2-methyl-1-naphthyl)quinoline (5c):

C<sub>27</sub>H<sub>21</sub>NO calcd C 86.37 H 5.64 N 3.88 (375.48) found 86.61 5.45 3.97

IR (KBr):  $\nu = 3035$  (C–H st), 1571, 1308, 1225, 1159, 1126, 1097 (C–O–C st), 1030, 791, 731 cm $^{-1}$ .

MS: m/z (%) = 375 (M<sup>+</sup>, 75), 268 (M<sup>+</sup> – OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 6), 235 (M<sup>+</sup> – C<sub>10</sub>H<sub>6</sub>CH<sub>3</sub> + 1, 52), 91 (C<sub>7</sub>H<sub>7</sub>, 100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 2.08 (3 H, s, CH<sub>3</sub>), 5.23 (2 H, s, O–C $H_2$ C<sub>6</sub>H<sub>5</sub>), 7.11–7.34 (5 H, m), 7.35–7.50 (6 H, m), 7.61 (2 H, d, J = 7.2 Hz), 7.86 (2 H, dd, J = 2.8, 8.0 Hz), 8.97 (1 H, dd, J = 2.0, 4.0 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>): δ = 20.6 (CH<sub>3</sub>), 70.9 (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 109.6, 121.7, 124.9, 126.0, 126.1, 127.3, 127.8, 128.8, 129.5, 132.0, 133.7, 134.3, 134.6, 135.0, 137.1, 140.6, 149.3, 153.9.

8-Benzyloxy-5-(2-methoxy-1-naphthyl)quinoline (5d):

C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub> calcd C 82.34 H 5.41 N 3.58 (391.48) found 82.78 5.56 3.64

IR (KBr): v = 3030 (C–H st), 1501, 1263, 1128, 1098 (C–O–C st, C–OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 1072 (C–O–C st, C–OCH<sub>3</sub>), 816, 791, 732 cm<sup>-1</sup>. MS: m/z (%) = 391 (M<sup>+</sup>, 96), 314 (M<sup>+</sup>–C<sub>6</sub>H<sub>5</sub>, 15), 285 (M<sup>+</sup>–OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>+1, 30), 270 [M<sup>+</sup>–(OCH<sub>3</sub>+CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)+1, 13], 149 (100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 3.72 (3 H, s, CH<sub>3</sub>), 5.50 (2 H, s, OC $H_2$ C<sub>6</sub>H<sub>5</sub>), 7.15–7.24 (4 H, m), 7.29–7.33 (3 H, m), 7.37–7.41 (3 H, m), 7.58–7.60 (3 H, m), 7.84 (1 H, d, J = 8.4 Hz), 7.95 (1 H, d, J = 8.8 Hz), 8.95 (1 H, dd, J = 2.0, 4.0 Hz).

 $^{13}\mathrm{C\,NMR}$  (TMS/CDCl<sub>3</sub>):  $\delta=56.5$  (OCH<sub>3</sub>), 70.8 (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 109.4, 113.6, 121.4, 121.5, 123.6, 125.2, 126.4, 126.5, 127.2, 127.7, 127.8, 128.6, 128.8, 129.0, 129.1, 129.7, 134.4, 134.5, 137.1, 140.6, 149.1, 153.9, 154.8.

8-Benzyloxy-5-(3-nitrophenyl)quinoline (5e):

C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> calcd C 74.14 H 4.53 N 7.86 (356.39) found 74.42 4.60 7.87

IR (KBr):  $\nu = 3032$ , 1527 (NO<sub>2</sub> st as), 1348 (NO<sub>2</sub> st sy), 790, 745, 696 cm<sup>-1</sup>.

MS: m/z (%) = 356 (M<sup>+</sup>, 17), 279 (M<sup>+</sup>-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 5), 250 (M<sup>+</sup>-OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>+1, 9), 91 (C<sub>7</sub>H<sub>7</sub>, 100).

 $^{1}\mathrm{H}$  NMR (TMS/CDCl<sub>3</sub>):  $\delta=5.51$  (2 H, s, OC $H_{2}$ C<sub>6</sub>H<sub>5</sub>), 7.11 (2 H, d, J=8.0 Hz), 7.30–7.46 (5 H, m), 7.55 (2 H, d, J=8.8 Hz), 7.65 (1 H, t, J=8.0 Hz), 7.73–7.76 (1 H, m), 8.10 (1 H, dd, J=2.0, 8.4 Hz), 8.26–8.29 (2 H, m), 9.03 (1 H, dd, J=2.0, 7.6 Hz).

<sup>13</sup>CNMR (TMS/CDCl<sub>3</sub>):  $\delta = 70.8$  (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 109.3, 122.1,

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122.2, 124.8, 127.1, 127.3, 127.8, 128.0, 128.7, 129.4, 129.6, 133.3, 136.1, 136.6, 140.5, 141.1, 148.4, 149.5, 154.6.

5-(3-Aminophenyl)-8-benzyloxyquinoline (5f):

C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O calcd C 80.95 H 5.56 N 8.58 (326.41) found 80.73 5.66 8.37

IR (KBr):  $\nu = 3442$ , 3312, 3200 (N-H st), 3060, 3022 (C-H st), 1597, 1505, 1469, 1381, 1306, 1089 (C-O-C st), 786, 728, 695 cm<sup>-1</sup>.

MS: m/z (%) = 326 (M<sup>+</sup>, 8), 236 (100), 235 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>).

<sup>1</sup>HNMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 3.74 (2 H, s, NH<sub>2</sub>), 5.32 (2 H, s, OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.70–6.73 (2 H, m), 6.78 (1 H, dd, J = 0.6, 6.4 Hz), 7.05 (1 H, d, J = 8.0 Hz), 7.21–7.39 (6 H, m), 7.54 (2 H, d, J = 7.6 Hz), 8.27 (1 H, dd, J = 1.2, 8.4 Hz), 8.97 (1 H, dd, J = 1.2, 4.0 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 71.0 (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 109.6, 114.3, 117.1, 120.9, 121.7, 127.0, 127.4, 128.1, 128.9, 129.6, 133.1, 134.8, 137.3, 140.7, 140.78, 146.7, 149.4, 153.9.

## 8-Benzyloxy-5-decylquinoline (5g):

 $C_{26}H_{33}NO$  calcd C 83.15 H 8.86 N 3.73 (375.56) found 83.11 8.58 3.43

IR (KBr): v = 2918, 2849 (aliph C-H st), 1370, 1092 (C-O-C st), 787, 742, 697 cm<sup>-1</sup>.

MS: m/z (%) = 375 (M<sup>+</sup>, 43), 298 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 23), 248 (M<sup>+</sup> - C<sub>9</sub>H<sub>19</sub>, 26), 234 (M<sup>+</sup> - C<sub>10</sub>H<sub>21</sub>, 7), 91 (C<sub>7</sub>H<sub>7</sub>, 100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta = 0.88$  (3 H, t, J = 2.8 Hz, CH<sub>3</sub>), 1.26–1.38 (14 H, m), 2.93 (2 H, t, J = 4.0 Hz, CH<sub>2</sub>–C<sub>9</sub>H<sub>19</sub>), 5.43 (2 H, s, OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.94 (1 H, d, J = 8.0 Hz), 7.18 (1 H, d, J = 8.0 Hz), 7.29–7.38 (3 H, m), 7.45 (1 H, dd, J = 4.0, 8.8 Hz), 7.51 (2 H, d, J = 6.8 Hz), 8.31 (1 H, dd, J = 1.6, 7.6 Hz), 8.97 (1 H, dd, J = 2.4, 4.8 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 14.1 (CH<sub>3</sub>), 22.7, 29.3, 29.5, 29.6, 31.0, 31.9, 70.7 (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 109.5, 121.1, 125.8, 127.1, 127.7, 127.9, 128.6, 131.0, 132.3, 137.2, 140.9, 148.7, 152.7.

#### Hydrogenolysis of 5a-g; General Procedure:

A mixture of 5 (0.5 mmol), Pd/C (54 mg) and cyclohexa-1,4-diene (0.12 g) in abs EtOH (5 mL) was refluxed under Ar for 1 h. The mixture was filtered and EtOH was evaporated. The residue was recrystallized from EtOH or MeOH.

## 5-Phenylquinolin-8-ol (6a):

 $C_{15}H_{11}NO$  calcd C 81.43 H 5.01 N 6.33 (221.26) found 81.70 5.19 6.33

IR (KBr): v = 3312 (OH st), 1513, 1471, 1414, 790, 762, 706 cm<sup>-1</sup>. MS: m/z (%) = 221 (M<sup>+</sup>, 100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 7.24 (1 H, d, J = 8.0 Hz), 7.39–7.51 (7 H, m), 8.28 (1 H, dd, J = 1.6, 8.4 Hz), 8.80 (1 H, dd, J = 1.6, 4.0 Hz).

 $^{13}\text{C NMR}$  (TMS/CDCl<sub>3</sub>):  $\delta = 109.5,\ 121.8,\ 126.7,\ 127.2,\ 128.3,\ 128.5,\ 130.1,\ 130.9,\ 134.7,\ 138.3,\ 139.4,\ 147.7,\ 151.6.$ 

5-(1-Naphthyl)quinolin-8-ol (6b):

C<sub>19</sub>H<sub>13</sub>NO calcd C 84.11 H 4.83 N 5.16 (271.32) found 84.97 4.95 5.21

IR (KBr): v = 3339 (OH st), 3042, 1503, 1474, 1389, 1269, 790, 775, 719 cm<sup>-1</sup>.

MS: m/z (%) = 271 (M<sup>+</sup>, 100).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 7.19–7.26 (3 H, m), 7.34 (1 H, d, J = 8.0 Hz), 7.38–7.43 (3 H, m), 7.51 (1 H, dd, J = 7.2, 8.0 Hz), 7.65 (1 H, dd, J = 1.6, 8.4 Hz), 7.88 (2 H, d, J = 8.4 Hz), 8.71 (1 H, dd, J = 2.0, 4.4 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 109.4, 121.8, 125.9, 126.1, 126.3, 128.0, 128.1, 128.3, 128.4, 128.9, 129.3, 133.1, 133.6, 135.1, 136.9, 138.1, 147.8, 151.8.

5-(2-methyl-1-naphthyl)quinolin-8-ol (6c):

 $C_{20}H_{15}NO$  calcd C 84.18 H 5.30 N 4.91 (285.35) found 84.53 5.48 4.63 IR (KBr):  $\nu = 3048, 1500, 1267, 784, 746 \text{ cm}^{-1}$ .

MS: m/z (%) = 285 (M<sup>+</sup>, 100), 270 (M<sup>+</sup> – CH<sub>3</sub>, 15), 143 (C<sub>9</sub>H<sub>6</sub>NO, 4), 142 (C<sub>11</sub>H<sub>9</sub>, 3).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 2.11 (3 H, s, CH<sub>3</sub>), 7.16 (2 H, d, J = 8.4 Hz), 7.21–7.25 (2 H, m), 7.31–7.46 (3 H, m), 7.49–7.53 (2 H, m), 7.85–7.88 (2 H, m), 8.78 (1 H, dd, J = 1.6, 8.4 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>): δ = 20.6 (CH<sub>3</sub>), 109.8, 121.9, 124.9, 127.7, 128.8, 127.8, 128.6, 129.3, 132.0, 133.8, 134.4, 134.6, 135.1, 138.5, 147.8, 151.7.

## 5-(2-Methoxy-1-naphthyl)quinolin-8-ol (6d):

 $\begin{array}{cccccccccc} C_{20}H_{15}NO_2 & calcd & C & 79.71 & H & 5.02 & N & 4.65 \\ (301.35) & found & 79.64 & 5.16 & 4.56 \end{array}$ 

IR (KBr): v = 2930, 1501, 1267, 1071 (C-O-C st), 812, 795, 749 cm<sup>-1</sup>.

MS: m/z (%) = 301 (M<sup>+</sup>, 100), 286 (M<sup>+</sup> – CH<sub>3</sub>, 34).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 3.75 (3 H, s, OCH<sub>3</sub>), 7.21–7.35 (3 H, m), 7.40–7.43 (2 H, m), 7.65 (1 H, dd, J = 1.6, 8.8 Hz), 7.86 (1 H, d, J = 8.0 Hz), 7.97 (1 H, d, J = 8.8 Hz), 8.76 (1 H, dd, J = 1.6, 4.0 Hz).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 56.6 (OCH<sub>3</sub>), 109.7, 113.5, 121.6, 123.6, 124.6, 125.2, 125.5, 127.9, 128.1, 129.1, 129.7, 130.0, 134.5, 135.0, 138.5, 147.6, 151.7, 154.9.

#### 5-(3-Nitrophenyl)quinolin-8-ol (6e):

 $\begin{array}{ccccc} C_{15}H_{10}N_2O_3 & calcd & C & 67.66 & H & 3.79 & N & 10.52 \\ (266.27) & found & 67.79 & 3.68 & 10.39 \end{array}$ 

IR (KBr): v = 3028, 3088, 1530 (NO  $_2$  st as), 1351 (NO  $_2$  st sy), 737, 713, 693 cm  $^{-1}$ .

MS: m/z (%) = 266 (M<sup>+</sup>, 100), 220 (M<sup>+</sup> – NO<sub>2</sub>, 39).

 $^{1}{\rm H}$  NMR (TMS/CDCl<sub>3</sub>):  $\delta=7.19$  (1 H, d, J=7.6 Hz, quinoline C-7), 7.38–7.41 (2 H, m), 7.60 (1 H, t, J=8.0 Hz), 7.72 (1 H, dt, J=1.2,~7.6 Hz), 8.10 (1 H, dd, J=1.6,~8.8 Hz), 8.19–8.22 (2 H, m), 8.25 (1 H, t, J=2.0 Hz), 8.77 (1 H, t, J=1.2,~4.0 Hz, quinoline C-2 H).

 $^{13}\text{C NMR}$  (TMS/CDCl<sub>3</sub>):  $\delta = 109.5$  (quinoline C-7), 122.2, 122.4, 124.8, 126.3, 128.0, 128.9, 129.5, 133.7, 136.1, 138.3, 141.1, 148.0, 148.4, 152.6.

# 5-(3-Aminophenyl)quinolin-8-ol (6f):

C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O calcd C 76.25 H 5.12 N 11.86 (236.28) found 76.29 5.36 11.77

IR (KBr): v = 3404, 3302, 3208, 3022, 1503, 791, 710 cm<sup>-1</sup>.

MS: m/z (%) = 237 (M<sup>+</sup> +1, 100), 211 (M<sup>+</sup> – NH, 6).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta = 6.71-6.74$  (2 H, m), 6.80-6.82 (1 H, m), 7.18-7.26 (2 H, m), 7.36-7.41 (2 H, m), 8.31 (1 H, dd, J = 1.6, 8.8 Hz, quinoline C-4 H), 8.76 (1 H, dd, J = 1.2, 4.0 Hz, quinoline C-2 H).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>): δ = 109.4 (quinoline C-7), 113.9, 116.7, 120.6, 121.6, 126.7, 127.9, 129.3, 131.1, 134.9, 138.2, 140.5, 146.5, 147.6, 151.5 (quinoline C-8).

#### 5-Decylquinolin-8-ol (6g):

C<sub>19</sub>H<sub>27</sub>NO calcd C 79.95 H 9.53 N 4.90 (285.44) found 79.84 9.34 4.84

IR (KBr):  $v = 3312, 2915, 2846, 1510, 786, 666 \text{ cm}^{-1}$ .

MS: m/z (%) = 285 (M<sup>+</sup>, 100), 256 (M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>, 4), 242 (4), 228 (4), 214 (4), 200 (4), 186 (7), 172 (34), 158 (100), 144 (M<sup>+</sup> - C<sub>10</sub>H<sub>21</sub>, 5).

<sup>1</sup>H NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 0.79 (3 H, t, J = 7.2 Hz,  $CH_3$ –CH<sub>2</sub>), 1.72–1.31 (14 H, m), 1.58 (2 H, quin, J = 7.6 Hz,  $C_8H_{17}$ –CH<sub>2</sub>–CH<sub>2</sub>), 2.86 (2 H, t, J = 8.0 Hz,  $C_9H_{19}$ –CH<sub>2</sub>), 7.01 (1 H, d, J = 7.6 Hz, quinoline C-7 H), 7.18 (1 H, d, J = 8.0 Hz, quinoline C-6 H), 7.36 (1 H, dd, J = 4.0, 4.4 Hz, quinoline C-3 H), 8.24 (1 H, dd, J = 1.6, 8.0 Hz, quinoline C-2 H), 8.68 (1 H, dd, J = 1.2, 4.4 Hz, quinoline C-4 H).

<sup>13</sup>C NMR (TMS/CDCl<sub>3</sub>):  $\delta$  = 14.4 ( $CH_3$ - $CH_2$ ), 23.0 ( $CH_3$ - $CH_2$ ), 29.5, 29.6, 29.8, 29.9, 31.5, 32.1, 32.2, 84.8 ( $C_9H_{19}$ - $CH_2$ ), 109.6 (quinoline C-7), 121.6 (quinoline C-3), 127.3, 129.7, 133.1, 133.4, 139.0, 147.5 (quinoline C-8), 150.7 (quinoline C-2).

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- (1) (a) Nakano, Y.; Sato, S. Inorg. Chem. 1982, 21, 1315.
  (b) Nakano, Y.; Yoshikawa, Y.; Kondo, H. J. Am. Chem. Soc. 1986, 108, 7630.
- (2) Manske, R.H.F.; Kulka, M. Org. React. 1953, 7, 80.
- (3) (a) Suzuki, A. J. Chem. Soc., Chem. Commun. 1979, 866.
  (b) Miyaura, N.; Yanagi, T.; Suzuki, A. Synth. Commun. 1981,
- (4) The detailed results will be published at a later date.
- (5) Chin-Hsien, W.; Xiang-Te, L.; Xiao-Hun, C. Synthesis 1982,
- (6) (a) Gershon, H.; McNeil, M.W. J. Org. Chem. 1972, 37, 4078.
- (b) Suzuki, H.; Tamura, Y. Nippon Kagaku Zassi 1971, 92, 1021. Felix, A.M.; Heimer, E.P.; Lambros, T.J.; Tzougraki, C.; Meienhofer, J. J. Org. Chem. 1978, 43, 4194.