Silver Phosphotungstate: A Novel and Recyclable Heteropoly Acid for Friedländer Quinoline Synthesis

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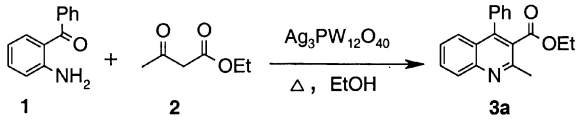
Abstract: *o*-Aminoaryl ketones undergo smooth condensation with α-methylene ketones on the surface of silver heteropoly acid ($Ag_3PW_{12}O_{40}$) under mild reaction conditions to afford the corresponding polysubstituted quinolines in excellent yields with high selectivity. The catalyst can be recovered by simple filtration and can be recycled in subsequent reactions.

Keywords: heteropoly acids, *o*-aminoaryl ketones, α-methylene ketones, quinolines

Quinoline nucleus is a back-bone of many natural products and pharmacologically significant compounds displaying a broad range of biological activity.[1] Many functionalized quinolines are widely used as antimalarial, anti-inflammatory agents, antiasthmatic, antibacterial, antihypertensive and tyrokinase PDGF-RTK inhibiting agents.[2,3] In addition to the medicinal importance, polyquinolines derived from quinolines, are found to undergo hierarchical self-assembly into a variety of nano- and mesostructures with enhanced electronic and photonic functions.[4] Consequently, various methods such as Skraup, Doebner–von Miller, Friedlander and Combes methods have been developed for the preparation of quinoline derivatives.[5,6] Among them, Friedländer annulation is of the most simple and straightforward approaches for the synthesis of polysubstituted quinolines.[6b] Friedländer reactions are generally carried out either by refluxing an aqueous or alcoholic solution of reactants in the presence of base or by heating a mixture of the reactants at high temperatures ranging from 150–220 °C in the absence of catalyst.[7] Under thermal or base catalysis conditions, *o*-aminobenzophenone fails to react with simple ketones such as cyclohexanone, deoxybenzoin and β-keto esters.[8] Subsequent work showed that acid catalysts are more effective than base catalysts for the Friedländer annulation.[8] Acid catalysts such as hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid and phosphoric acids have been widely used for this conversion.[7a,9] However, many of these classical methods require high temperatures, prolonged reaction times and drastic conditions and the yields reported are far from satisfactory due to the occurrence of several side reactions. Therefore, new catalytic systems are being continuously explored in search of improved efficiencies and cost effectiveness.[10] Since quinoline derivatives are increasingly useful and important in drugs and pharmaceuticals, the development of simple, convenient and environmentally benign approaches are desirable.

In recent years, the use of solid acids as heterogeneous catalysts has received considerable interest in different areas of organic synthesis.[11] Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process economically viable. In many cases, heterogeneous catalysts can be recovered with only minor change in activity and selectivity so that they can be conveniently used in continuous flow reactions. Among various heterogeneous catalysts, heteropoly acids are most attractive, because of their reusability, flexibility in modifying the acid strength, ease of handling, environmental compatibility, nontoxicity and experimental simplicity.[12] However, there are no examples of the use of silver salt of heteropoly acid for the preparation of quinolines. The use of heteropoly acid as a recyclable catalyst makes the process convenient, economic and environmentally benign.

In view of the emerging importance of the use of heterogeneous solid acids as reusable catalysts in organic synthesis, we wish to disclose a simple and efficient procedure for the polysubstituted quinolines using heteropoly acid as a catalyst. Accordingly, treatment of 2-aminobenzophenone (**1**) with ethyl acetoacetate (**2**) in the presence of silver salt of heteropoly acid ($Ag_3PW_{12}O_{40}$)[13] resulted in the formation of ethyl 2-methyl-4-phenyl-3-quinolinecarboxylate (**3a**) in 92% yield (Scheme 1).



1 2 3a

Scheme 1

Similarly, various ketones such as acetyl acetone, butan-2-one and acetophenone reacted smoothly with 2-aminobenzophenone to give the corresponding substituted quinolines. In most cases, the products were isolated by simple filtration. The crude products were purified either by recrystallization from a mixture of diethyl ether/*n*-hexane or by silica gel column chromatography. Interestingly, cyclic ketones such as cyclopentanone and cyclohexanone also underwent smooth condensation with

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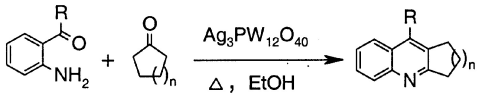


Scheme 2

2-aminoaryl ketones to afford respective tricyclic quinolines (Scheme 2).

This method is equally effective for both cyclic and acyclic ketones (Table 1). Various substituted 2-aminoaryl ketones such as 2-aminoacetophenone, 2-aminobenzophenone, 2-amino-5-chlorobenzophenone and 2-amino-5-chloro-2′-chlorobenzophenone reacted smoothly with α-methylene ketones to produce a range of quinoline derivatives. As solvent, ethanol appears to be superior giving the best results. The products were characterized by ^{1}H, ^{13}C NMR, IR and mass spectroscopic data and also by comparison with authentic samples.[7a] This method is very useful for the preparation of quinolines from both 2-aminoacetophenone and 2-aminobenzophenone. The efficacy of other solid acids such as K10 clay, SiO_2, and H-ZSM-5 was studied for this reaction and the results are presented in Table 2. Among these catalysts, silver salt of 12-tungustophosphoric acid ($Ag_3PW_{12}O_{40}$) was found to be superior in terms of conversion and reaction rates. However, in the absence of heteropoly acid, the reaction did not proceed even after long reaction times (8–12 h). The heteropoly acid ($Ag_3PW_{12}O_{40}$) provides an ease separation of the catalyst and the product. The catalyst was easily separated by simple filtration and reused after activation with gradual decrease in activity. For instance, the reaction of 2-aminobenzophenone and acetyl acetone afforded the corresponding 3-acetyl-2-methyl-4-phenylquinoline in 89%, 86%, 82%, and 80% yields over four cycles. Furthermore, this method is clean and free from side reactions such as self-condensation of ketones, which was normally observed under basic conditions. Unlike reported methods, present protocol does not require either strong acids such as conc. HCl, conc. H_2SO_4, *p*-TSA and H_3PO_4 or high temperature (190–250 °C) conditions to produce quinoline derivatives. Thus, this procedure provides an easy access to the preparation of substituted quinolines with a wide range of substitution patterns. This method offers several advantages such as high conversions, short reaction times, cleaner reaction profiles and simple experimental and workup procedures. The scope and generality of this process is illustrated with respect to various 2-aminoaryl ketones and α-methylene ketones and the results are summarized in Table 1.

Table 1 $Ag_3PW_{12}O_{40}$-Catalyzed Friedlander Synthesis of Quinolines

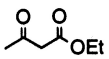
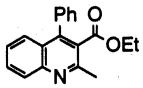
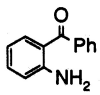
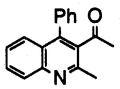
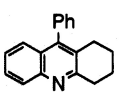
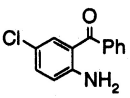
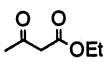
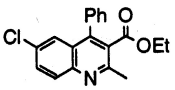
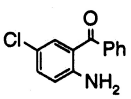
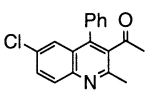
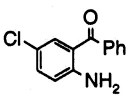
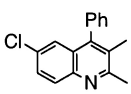
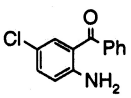
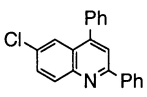
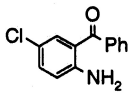
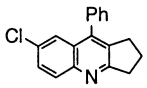
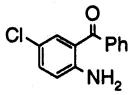
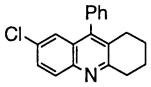
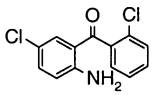
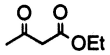
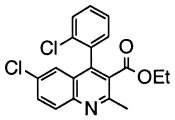
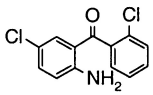
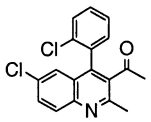
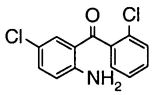
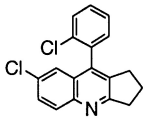
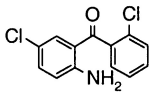
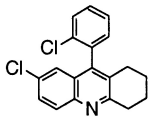
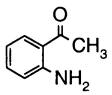
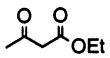
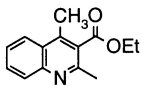
Entry	2-Aminoketone **1**	Ketone **2**	Quinoline[a] **3**	Time (h)	Yield[b] (%)
a				3.0	92
b				4.5	89
c				3.5	87
d				3.0	90
e				6.0	81
f				4.5	83
g				5.0	80

Table 1 $Ag_3PW_{12}O_{40}$-Catalyzed Friedlander Synthesis of Quinolines (continued)

Entry	2-Aminoketone **1**	Ketone **2**	Quinoline[a] **3**	Time (h)	Yield[b] (%)
h				4.0	87
i				3.5	89
j				5.5	82
k				4.5	86
l				4.0	83
m				5.5	80
n				3.5	85

[a] All products were characterized by ^1H NMR, ^{13}C NMR, IR and mass spectroscopy.
[b] Isolated and unoptimized yields.

Table 2 Comparative Study of Various Solid Acids in the Synthesis of Ethyl 2-Methyl-4-phenyl-3-quinoline Carboxylate (**3a**)

Entry	Catalyst	Quinoline	Time (h)	Yield[a] (%)
1	HZSM-5	**3a**	3.0	65
		3a	6.0	80
2	KSF-Clay	**3a**	3.0	60
		3a	6.0	75
3	Conc. H_2SO_4	**3a**	3.0	80
		3a	6.0	85
4	$Ag_3PW_{12}O_{40}$	**3a**	3.0	92

[a] Isolated and unoptimized yields.

In summary, we have described a mild and efficient protocol for the synthesis of quinolines and polycyclic quinolines via Friedländer condensation of 2-aminoaryl ketones with α-methylene ketones using heteropoly acid as a recyclable heterogeneous catalyst. The simple experimental procedure combined with ease of recovery and reuse of this novel catalyst make this method quite simple, more convenient and environmentally benign for the synthesis of highly functionalized quinolines.

Melting points were recorded on Büchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^1H and ^{13}C NMR spectra were recorded on Gemini-200 and Varian Unity-500 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. TLC was monitored on 0.25 mm precoated silica gel plates (60F-254). All commercially available reagent grade chemicals were purchased from Aldrich Chemical Company and used as received without further purification unless otherwise stated. All the solvents distilled, dried and stored under N_2 prior to use.

Polysubstituted Quinolines; General Procedure

A mixture of *o*-aminobenzophenone (1 mmol), ketone (1.5 mmol), and $Ag_3PW_{12}O_{40}$ (0.2 mmol) in EtOH (10 mL) was stirred at reflux temperature for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and washed with EtOAc (2 × 10 mL). The combined organic extracts were concentrated in vacuo and the resulting product was directly charged on small silica gel column and eluted with a mixture of EtOAc–*n*-hexane (2:8) to afford pure trisubstituted quinoline.

The recovered catalyst was washed with MeOH and activated at 120 °C for 3–4 h prior to reuse.

Ethyl 2-Methyl-4-phenylquinoline-3-carboxylate (3a)
Pale yellow solid; mp 97 °C.

IR (KBr): 3062, 2981, 2932, 1728, 1568, 1487, 1444, 1402, 1296, 1229, 1066, 768 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 6.9 Hz, 2 H), 2.78 (s, 3 H), 4.00–4.05 (q, *J* = 6.9 Hz, 2 H), 7.30–7.55 (m, 7 H), 7.65–7.70 (m, 2 H), 8.05 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (proton decoupled, 50 MHz, $CDCl_3$): δ = 13.5, 23.5, 60.7, 96.0, 125.0, 126.0, 126.2, 127.9, 128.1, 129.0, 129.3, 129.7, 135.9, 145.7, 147.7, 154.2, 167.8.

EI-MS: *m*/*z* (%) = 291 (M^+, 80), 247 (100), 218 (46), 177 (21), 178 (10), 75 (25), 43 (25).

1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3b)
Pale yellow solid; mp 113 °C.

IR (KBr): 3062, 2961, 1699, 1567, 1439, 1393, 1214, 764, 706 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 3 H), 2.68 (s, 3 H), 7.35–7.50 (m, 6 H), 7.60 (d, *J* = 7.9 Hz, 1 H), 7.68–7.70 (t, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 23.7, 31.8, 125.0, 126.0, 126.4, 128.6, 128.8, 129.9, 134.7, 135.1, 143.8, 147.4, 153.4.

EI-MS: *m*/*z* (%) = 261 (M^+, 50), 246 (100), 218 (50), 178 (9), 176 (22), 75 (20), 43 (35).

9-Phenyl-1,2,3,4-tetrahydroacridine (3c)
Pale yellow solid; mp 137 °C.

IR (KBr): 3060, 2935, 2862, 1571, 1487, 1443, 1219, 764, 703 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.75–1.85 (m, 2 H), 1.95–2.00 (m, 2 H), 2.60 (t, *J* = 6.7 Hz, 2 H), 3.18 (t, *J* = 7.0 Hz, 2 H), 7.20–7.30 (m, 4 H), 7.40–7.60 (m, 4 H), 7.98 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 50 MHz, $CDCl_3$): δ = 22.9, 23.1, 27.9, 34.0, 96.1, 125.1, 125.5, 126.5, 127.5, 127.8, 128.0, 128.4, 128.6, 129.1, 137.3, 146.0, 146.4, 158.5.

EI-MS: *m*/*z* (%) = 259 (M^+, 100), 230 (12), 183 (9).

Ethyl 6-Chloro-2-methyl-4-phenylquinoline-3-carboxylate (3d)
Pale yellow solid; mp 99 °C.

IR (KBr): 3065, 2984, 1725, 1605, 1225, 908, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.95 (t, *J* = 6.9 Hz, 3 H), 2.74 (s, 3 H), 4.00–4.06 (q, *J* = 6.9 Hz, 2 H), 7.30–7.34 (m, 2 H), 7.48–7.51 (m, 4 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 13.4, 23.6, 61.2, 125.0, 125.8, 128.4, 128.7, 129.1, 130.4, 131.0, 132.2, 135.1, 145.2, 146.0, 154.2, 168.0.

EI-MS: *m*/*z* (%) = 325 (M^+, 77), 280 (100), 252 (35), 217 (37), 189 (10), 176 (38), 149 (53), 123 (13), 109 (20), 88 (20), 71 (20), 57 (33).

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (3e)
Pale yellow solid; mp 151 °C.

IR (KBr): 3026, 2960, 1700, 1605, 1565, 1481, 908, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.68 (s, 3 H), 7.30–7.40 (m, 2 H), 7.50–7.60 (m, 4 H), 7.65 (d, *J* = 7.6 Hz, 4 H), 8.00 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 23.5, 31.6, 124.8, 125.8, 128.7, 129.0, 129.7, 130.8, 132.2, 134.5, 135.3, 142.8, 145.8, 153.7, 204.7.

EI-MS: *m*/*z* (%) = 295 (M^+, 39), 281 (100), 252 (27), 217 (27), 176 (12), 43 (41).

6-Chloro-2,3-dimethyl-4-phenylquinoline (3f)
Pale yellow solid; mp 117 °C.

IR (KBr): 3062, 2955, 1605, 1482, 1215, 754 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 2.72 (s, 3 H), 7.20–7.24 (m, 3 H), 7.48–7.52 (m, 4 H), 7.92 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 16.7, 24.4, 124.8, 127.7, 128.0, 128.7, 128.9, 129.2, 130.2, 131.2, 136.7, 144.5, 145.5, 159.0.

EI-MS: *m*/*z* (%) = 267 (M^+, 100), 232 (25), 189 (12).

6-Chloro-2,4-diphenylquinoline (3g)
Pale yellow solid; mp 129 °C.

IR (KBr): 3058, 1684, 1482, 910, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.45 (m, 3 H), 7.55–7.70 (m, 9 H), 7.94 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 120.1, 124.4, 126.5, 127.5, 128.6, 129.4, 130.3, 131.6, 132.7, 137.6, 139.0, 147.2, 148.4, 157.2.

EI-MS: *m*/*z* (%) = 316 (M^+, 30), 288 (100), 125 (10), 89 (10), 77 (45).

7-Chloro-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3h)
Pale yellow solid; mp 95 °C.

IR (KBr): 3062, 2958, 1605, 1485, 827, 714 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.18–2.28 (m, 2 H), 2.98 (s, *J* = 7.0 Hz, 2 H), 3.28 (t, *J* = 7.2 Hz, 2 H), 7.35 (m, 2 H), 7.50–7.60 (m, 5 H), 8.24 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 23.2, 30.2, 35.0, 124.2, 126.8, 128.2, 128.7, 129.1, 130.2, 131.2, 134.3, 135.7, 141.8, 146.2, 167.6.

EI-MS: *m*/*z* (%) = 279 (M^+, 80), 244 (100), 202 (20), 167 (20), 121 (50), 114 (17), 94 (10), 75 (15), 63 (5).

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3i)
Pale yellow solid; mp 162 °C.

IR (KBr): 3061, 2945, 1604, 1570, 1482, 1215, 704 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.75–1.80 (m, 2 H), 1.95–2.00 (m, 2 H), 2.58 (t, *J* = 6.7 Hz, 2 H), 3.15 (t, *J* = 7.0 Hz, 2 H), 7.18–7.22 (m, 3 H), 7.45–7.55 (m, 4 H), 7.90 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 23.1, 28.2, 34.4, 124.5, 127.5, 128.2, 128.8, 129.1, 129.3, 129.5, 130.3, 131.3, 136.7, 144.8, 145.7, 159.5.

EI-MS: *m*/*z* (%) = 293 (M^+, 100), 258 (41), 242 (12), 230 (20), 176 (5), 150 (12), 89 (7), 77 (45).

Ethyl 6-Chloro-4-(2-chlorophenyl)-2-methyl-3-quinolinecarboxylate (3j)
Pale yellow solid; mp 110 °C.

IR (KBr): 3062, 2981, 1727, 1573, 1471, 1390, 1222, 1077, 759 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.90–0.98 (t, *J* = 7.0 Hz, 3 H), 2.78 (s, 3 H), 4.00–4.10 (q, *J* = 7.0 Hz, 2 H), 7.20–7.65 (m, 6 H), 8.00 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 23.1, 28.2, 34.4, 124.5, 127.5, 128.2, 128.8, 129.1, 129.3, 129.5, 130.3, 131.3, 136.7, 144.8, 145.7, 159.5.

EI-MS: *m*/*z* (%) = 361 (M^+, 80), 315 (100), 287 (37), 252 (39), 217 (30), 76 (9), 43 (35).

1-[6-Chloro-4-(2-chlorophenyl)-2-methyl-3-quinolyl]-1-ethanone (3k)
Pale yellow solid; mp 104 °C.

IR (KBr): 2925, 1702, 1568, 1471, 1386, 1202, 1055, 768 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 2.68 (s, 3 H), 7.20–7.25 (m, 2 H), 7.40–7.50 (m, 2 H), 7.55–7.65 (m, 2 H), 8.00 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 50 MHz, $CDCl_3$): δ = 23.8, 30.4, 124.5, 125.4, 127.3, 128.7, 130.0, 130.6, 130.8, 131.1, 132.0, 132.5, 132.8, 133.4, 140.4, 145.6, 154.0, 167.6.

EI-MS: *m*/*z* (%) = 331 (M^+, 70), 293 (100), 286 (43), 251 (28), 216 (9), 75 (7), 43 (37).

7-Chloro-9-(2-chlorophenyl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3l)
Pale yellow solid; mp 141 °C.

IR (KBr): 3058, 2961, 1608, 1477, 1386, 1212, 954, 756 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.10–2.30 (m, 2 H), 2.70–3.00 (m, 2 H), 3.20–3.30 (m, 2 H), 7.20–7.30 (m, 2 H), 7.40–7.50 (m, 2 H), 7.55–7.65 (m, 2 H), 8.00 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (proton decoupled, 50 MHz, $CDCl_3$): δ = 23.0, 29.9, 34.9, 124.0, 126.8, 127.0, 129.1, 129.8, 130.0, 130.4, 130.7, 131.5, 133.1, 134.9, 135.5, 139.2, 146.2, 167.8.

EI-MS: *m*/*z* (%) = 313 (25) M^+, 279 (30), 261 (7), 122 (30), 97 (16), 75 (100), 43 (15).

7-Chloro-9-(2-chlorophenyl)-1,2,3,4-tetrahydroacridine (3m)
Pale yellow solid; mp 153 °C.

IR (KBr): 3060, 2962, 1615, 1478, 1390, 1225, 1067, 758 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78–1.84 (m, 2 H), 1.95–2.02 (m, 2 H), 2.45–2.55 (m, 2 H), 3.10–3.20 (m, 2 H), 7.05 (m, 1 H), 7.15–7.20 (m, 1 H), 7.40–7.45 (m, 2 H), 7.50–7.60 (m, 2 H), 7.94 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 21.8, 26.6, 28.8, 33.2, 125.9, 126.5, 127.5, 128.6, 129.0, 129.2, 129.3, 130.7, 129.8, 132.2, 134.3, 138.2, 149.1, 158.8.

EI-MS: *m*/*z* (%) = 329 (M^+, 98), 292 (100), 265 (22), 256 (15), 230 (27), 201 (8), 154 (10), 127 (12), 111 (9), 71 (30), 57 (52), 43 (60).

Ethyl 2,4-Dimethylquinoline-3-carboxylate (3n)
Pale yellow oil.

IR (KBr): 3068, 2930, 2872, 1723, 1615, 1587, 1212, 1082, 758 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 6.9 Hz, 3 H), 2.98 (s, 3 H), 3.10 (s, 3 H), 4.75–4.80 (q, *J* = 6.9 Hz, 2 H), 7.85–8.05 (m, 3 H), 8.40 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (proton decoupled, 75 MHz, $CDCl_3$): δ = 14.0, 15.4, 23.5, 61.2, 123.7, 125.7, 126.0, 127.9, 129.3, 129.8, 141.1, 147.0, 154.1, 168.8.

EI-MS: *m*/*z* (%) = 229 (M^+, 100), 186 (70), 158 (20), 125 (12).

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