Copper-Catalyzed One-Pot Synthesis of Substituted Benzimidazo[1,2-*a*]quinolines

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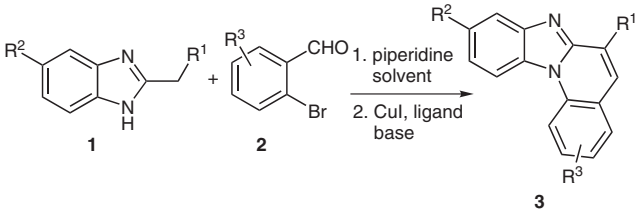
Abstract: A one-pot procedure for the synthesis of substituted benzimidazo[1,2-*a*]quinolines from the corresponding benzimidazoles and 2-bromobenzaldehydes has been developed. The titled products were prepared through Knoevenagel condensation and copper-catalyzed intramolecular Ullmann-type coupling in moderate to good yields.

Key words: Knoevenagel condensation, copper catalyst, Ullmann coupling, quinoline synthesis, cascade process

Substituted benzimidazoles and their azino-fused derivatives show a wide range of biological activity such as antiviral, anticancer, antibacterial, antifungal, DNA intercalator, etc.[1]

Unsubstituted benzimidazo[1,2-*a*]quinoline was first prepared in 1938 by Morgan and Stewart via classical condensation from 2-aminoquinoline and picric acid.[2] Substituted benzimidazo[1,2-*a*]quinolines have been synthesized by photochemical dehydrocyclization and dehydrohalogenation cyclization of acyclic benzimidazolyl-substituted acrylonitriles[3] and by palladium-catalyzed intramolecular Buchwald–Hartwig amination of 2-(2-bromoanilino)quinolines.[4]

Recently, aza-fused polycyclic quinolines were synthesized by Cai et al. via a copper-catalyzed cascade process. Cai's method could be applied to a wide range of 2-halogenated arylaldehydes to yield the corresponding products.[5] Herein we wish to report a novel one-pot synthesis of substituted benzimidazo[1,2-*a*]quinolines that firstly uses the Knoevenagel condensation[6] of the corresponding 2-bromobenzaldehydes and substituted benzimidazoles, followed by copper-catalyzed intramolecular Ullmann-type coupling reaction (Scheme 1).[7] Reaction conditions such as base, ligand, solvent, and temperature were carefully investigated. The results obtained show different substrate scope and substituent effects compared with those from the group of Cai.



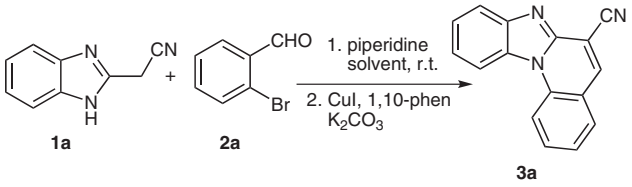
Scheme 1 One-pot synthesis of benzimidazo[1,2-*a*]quinolines

Initially, benzimidazole-2-acetonitrile (**1a**) and 2-bromobenzaldehyde (**2a**) were chosen as model substrates. Since the condensation in the first step proceeded easily in the presence of a catalytic amount of piperidine, we focused our efforts on the coupling reaction (Table 1). Using copper(I) iodide (0.1 equiv) as the catalyst and 1,10-phenanthroline (0.2 equiv) as the ligand and with potassium carbonate (2 equiv) as the base in refluxing tetrahydrofuran for five hours (entry 1) gave **3a** in 48% isolated yield. Varying the solvent (entries 2–6) showed that dioxane was the best and it was used in the next step of the optimization process.

We then evaluated the ligands and bases in the model reaction. The results shown in Table 2, entries 1–4, show that 1,10-phenanthroline is the better ligand for this C–N coupling reaction. The yield did not increase when the reaction temperature and time were increased (entry 5). The bases were also investigated and it was found that the yield with cesium carbonate was comparable to that with potassium carbonate, while potassium phosphate was less satisfactory (entries 4, 6, and 7).

The optimized reaction conditions for the formation of **3a** were applied to a wide range of substrates and the results

Table 1 Optimization of the Solvent[a]



Entry	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	THF	reflux	8	48
2	MeCN	reflux	8	56
3	toluene	90	12	trace
4	dioxane	90	8	84
5	DMSO	90	12	trace
6	DMF	90	8	20

[a] Reaction conditions: 1. **1a** (0.5 mmol), **2a** (0.6 mmol), piperidine (0.1 mmol), solvent (2 mL), r.t., 3 h; 2. CuI (0.05 mmol), 1,10-phenanthroline (0.1 mmol), K_2CO_3 (1 mmol), 90 °C, 5–7 h.
[b] Isolated yield based on **1a**.

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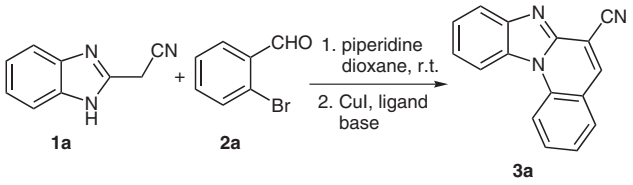
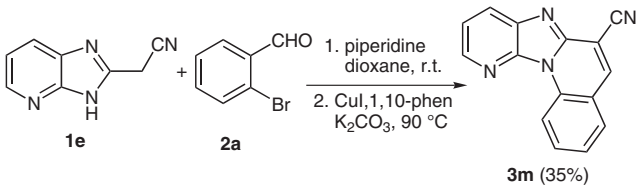
Table 2 Optimization of the Ligand and Base[a]

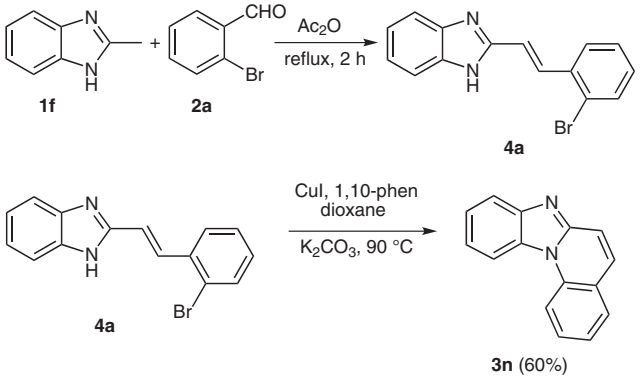


Entry	Ligand[b]	Base	Time (h)	Yield[c] (%)
1	A	K_2CO_3	8	27
2	B	K_2CO_3	8	20
3	C	K_2CO_3	8	trace
4	D	K_2CO_3	8	84
5	D	K_2CO_3	12	84[d]
6	D	K_3PO_4	8	79
7	D	Cs_2CO_3	8	83

[a] Reaction conditions: 1. **1a** (0.5 mmol), **2a** (0.6 mmol), piperidine (0.1 mmol), dioxane (2 mL), r.t., 3 h; 2. CuI (0.05 mmol), ligand (0.1 mmol), base (1 mmol), 90 °C, 5–7 h.
[b] Ligands: A, L-proline; B, *N*-methylglycine; C, *N*,*N*-dimethylglycine; D, 1,10-phenanthroline.
[c] Isolated yield based on **1a**.
[d] The intramolecular coupling reaction was performed at reflux.



Scheme 2 One-pot synthesis of **3m**



Scheme 3 Synthesis of unsubstituted benzimidazo[1,2-*a*]quinoline (**3n**)

are summarized in Table 3. 2-Bromobenzaldehydes **2a**–**e** reacted well with benzimidazole-2-acetonitriles **1a**–**c** to give the corresponding products **3a**–**h** in moderate to good yields (entries 1–8), however, the reactions of 2-bromobenzaldehydes **2a**,**b**,**e**,**f** with ethyl 2-benzimidazolylacetate **1d** afforded the desired products **3i**–**l** in relatively low yields (entries 9–12). To our delight, 5-methylbenzimidazole-2-acetonitrile (**1b**) gave **3f** in excellent yield, although it was an isomeric mixture as identified by ^1H and ^{13}C NMR (entry 6). A similar result was obtained in the reaction of **1b** with **2b**, which was probably caused by isomerization of the benzimidazole ring in the intermediate (entry 8). Among the benzaldehydes screened, the yields with substrates containing an electron-withdrawing group are generally higher than those with an electron-donating group.

The above results promoted us to examine the reaction of imidazo[4,5-*b*]pyridine-2-acetonitrile (**1e**) with 2-bromobenzaldehyde (**2a**) (Scheme 2). As expected, the reaction proceeded smoothly to give **3m** in 35% yield.

After carrying out the cascade process for the synthesis of substituted benzimidazo[1,2-*a*]quinolines **3a**–**l**, we wondered whether this strategy could be extended to the synthesis of unsubstituted benzimidazo[1,2-*a*]quinoline (**3n**). However, this one-pot method failed to afford product **3n** due to the limitations of the Knoevenagel condensation. To our delight, unsubstituted benzimidazo[1,2-*a*]quinoline (**3n**) was obtained from intramolecular coupling of pre-synthesized 2-(2-bromostyryl)benzimidazole (**4a**) in 60% yield (Scheme 3).[8]

In order to improve the yield of **3n**, further optimization was investigated including solvent, ligand, and temperature. The results (Table 4) show that the intramolecular C–N coupling reaction proceeded smoothly at relative low temperatures (76 °C) in acetonitrile under CuI/L-proline catalysis to afford the desired product **3n** in excellent yield (90%).

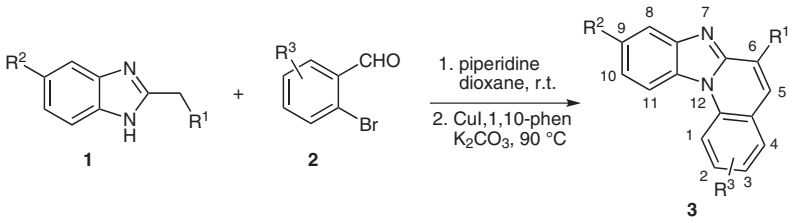
In conclusion, we have developed a one-pot, efficient, general, and practical cascade process for the synthesis of benzimidazo[1,2-*a*]quinoline derivatives in moderate to good yields. Benzimidazole-2-acetonitriles with electron-withdrawing group or electron-donating group all afforded the corresponding products in good yields. Catalyzed by copper, unsubstituted benzimidazo[1,2-*a*]quinoline was obtained by intramolecular Ullmann-type coupling in excellent yield. These results are different from those of Cai. Further studies on the practical applications of these compounds is underway in our laboratory.

All reactions were carried out in the Schlenk tubes under N_2 atmosphere and solvents were purified and dried by standard procedures. Reactions were followed by TLC using SILG/UV 254 silica gel plates, which were visualized via a UV fluorescent lamp. Melting points were obtained using micro melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectrums were obtained on a Bruker 500 MHz instrument. LR-MS and HRMS were obtained by using EI and ESI ionizations.

Copper-Catalyzed One-Pot Synthesis of Substituted Benzimidazo[1,2-*a*]quinolines 3; General Procedure

To a soln of substituted benzimidazole **1** (0.5 mmol) and 2-bromobenzaldehyde **2** (0.6 mmol) in dioxane (2 mL) in a Schlenk tube was added piperidine (0.1 mmol) using a syringe. The mixture was stirred at r.t. for 3 h under N_2 and then CuI (0.05 mmol), 1,10-phenanthroline (0.1 mmol), and K_2CO_3 (1 mmol) were added successively to the soln under N_2. The mixture was heated at 90 °C for the appropriate time until TLC monitoring indicated no further im-

Table 3 One-Pot Synthesis of Substituted Benzimidazo[1,2-*a*]quinolines[a]



Entry	Substrates					Product		Yield[b] (%)
	1	R^1	R^2	**2**	R^3	**3**	R^3	
1	**1a**	CN	H	**2a**	H	**3a**	H	84
2	**1a**	CN	H	**2b**	5-OMe	**3b**	3-OMe	75
3	**1a**	CN	H	**2c**	4-Me	**3c**	2-Me	68
4	**1a**	CN	H	**2d**	5-OH	**3d**	3-OH	43
5	**1a**	CN	H	**2e**	5-Cl	**3e**	3-Cl	79
6	**1b**	CN	Me	**2a**	H	**3f**[c]	H	88
7	**1c**	CN	Cl	**2a**	H	**3g**	H	81
8	**1b**	CN	Me	**2b**	5-OMe	**3h**[c]	3-OMe	72
9	**1d**	CO_2Et	H	**2a**	H	**3i**	H	40
10	**1d**	CO_2Et	H	**2f**	4-Cl	**3j**	2-Cl	45
11	**1d**	CO_2Et	H	**2b**	5-OMe	**3k**	3-OMe	20
12	**1d**	CO_2Et	H	**2e**	5-Cl	**3l**	3-Cl	37

[a] Conditions: 1. **1** (0.5 mmol), **2** (0.6 mmol), piperidine (0.1 mmol), dioxane (2 mL), r.t., 3 h; 2. CuI (0.05 mmol), 1,10-phenanthroline (0.1 mmol), K_2CO_3 (1 mmol), 90 °C, 5–7 h.
[b] Isolated yield based on benzimidazole.
[c] The product is a mixture of isomers.

provement in the conversion. The mixture was washed with CH_2Cl_2 (3 × 15 mL) and filtered using a funnel. The filtrate was dried (anhyd Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–EtOAc, 30:1).

Benzimidazo[1,2-*a*]quinoline-6-carbonitrile (3a)
Yellow solid; mp 254 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 9.0 Hz, 1 H), 8.41 (d, *J* = 8.0 Hz, 1 H), 8.21 (s, 1 H), 8.19–8.16 (m, 1 H), 7.96–7.93 (m, 2 H), 7.65–7.57 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.6, 144.5, 138.8, 136.5, 133.0, 130.9, 130.8, 125.4, 125.1, 124.0, 121.5, 121.4, 115.5, 114.9, 114.0, 103.1.

MS (EI): *m*/*z* = 243 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_9N_3$: 243.0796; found: 243.0800.

3-Methoxybenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3b)
Yellow solid; mp 250 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.64–8.56 (m, 3 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.60–7.50 (m, 3 H), 7.48–7.44 (m, 1 H), 3.89 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 155.8, 143.9, 143.6, 139.9, 130.3, 130.2, 124.9, 123.4, 122.4, 121.6, 120.2, 117.2, 115.4, 114.5, 112.6, 101.5, 55.7.

MS (EI): *m*/*z* = 273 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{17}H_{11}N_3O$: 273.0902; found: 273.0909.

2-Methylbenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3c)
Yellow solid; mp 270 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.85 (d, *J* = 8.0 Hz, 1 H), 8.78 (s, 1 H), 8.64 (s, 1 H), 8.06–8.01 (m, 2 H), 7.65–7.57 (m, 2 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 2.71 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 145.1, 144.6, 143.8, 140.4, 136.0, 131.0, 130.5, 126.5, 125.0, 123.4, 120.1, 119.0, 115.5, 115.4, 115.1, 99.9, 21.8.

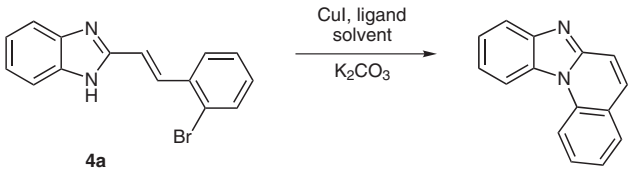
MS (EI): *m*/*z* = 257 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{17}H_{11}N_3$: 257.0953; found: 257.0961.

3-Hydroxybenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3d)
Yellow solid; mp >300 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.23 (s, 1 H), 8.72–8.64 (m, 3 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.60–7.54 (m, 2 H), 7.47–7.44 (m, 2 H).

Table 4 Optimization of the Conditions for the Synthesis of Unsubstituted Benzimidazo[1,2-*a*]quinoline[a]



Entry	Solvent	Ligand[b]	Temp (°C)	Yield[c] (%)
1	dioxane	D	90	60
2	dioxane	E	90	86
3	dioxane	A	90	74
4	DMSO	A	90	56
5	THF	A	reflux	45
6	MeCN	A	76	90
7	MeCN	E	76	73
8	MeCN	D	76	59

[a] Conditions: **4a** (0.5 mmol), CuI (0.05 mmol), ligand (0.1 mmol), K_2CO_3 (1 mmol), solvent (2 mL), 8 h.
[b] Ligand: A, L-proline; D, 1,10-phenanthroline; E, *N*,*N*-dimethylethylenediamine.
[c] Isolated yield based on **4a**.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 154.4, 144.0, 143.6, 140.3, 130.3, 129.2, 124.8, 123.3, 122.6, 122.2, 120.2, 117.3, 115.6, 114.8, 114.5, 101.3.

MS (EI): *m*/*z* = 259 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{16}H_9N_3O$: 259.0746; found: 259.0766.

3-Chlorobenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3e)
Yellow solid; mp 263 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.76 (d, *J* = 9.0 Hz, 1 H), 8.67 (s, 1 H), 8.61 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 2.5 Hz, 1 H), 8.01–7.99 (m, 1 H), 7.92 (q, *J* = 9.0 Hz, 1 H), 7.63–7.55 (m, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 144.2, 143.7, 139.4, 134.4, 132.9, 130.4, 129.8, 129.0, 125.3, 124.0, 122.6, 120.4, 117.9, 115.1, 114.7, 102.6.

MS (EI): *m*/*z* = 277 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{16}H_8ClN_3$: 277.0407; found: 277.0412.

9/10-Methylbenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3f)
Yellow solid; mp 183 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.67–8.65 (m, 2 H), 8.45 (d, *J* = 8.5 Hz, 0.5 H), 8.39 (s, 0.5 H), 8.09–8.05 (m, 1 H), 7.95–7.90 (m, 1 H), 7.81 (d, *J* = 8.5 Hz, 0.5 H), 7.70 (s, 0.5 H), 7.62–7.58 (m, 1 H), 7.38–7.30 (m, 1 H), 2.52 (s, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 144.1, 143.9, 143.7, 141.7, 139.9, 139.7, 135.5, 135.4, 134.4, 133.3, 133.3, 133.2, 130.9, 130.8, 130.4, 128.3, 126.4, 124.9, 124.8, 121.0, 120.9, 119.6, 119.5, 115.7, 115.5, 115.4, 114.2, 114.0, 101.1, 101.0, 21.57, 21.14.

MS (EI): *m*/*z* = 257 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{17}H_{11}N_3$: 257.0953; found: 257.0964.

9-Chlorobenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3g)
Yellow solid; mp 290 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.86–8.83 (m, 3 H), 8.15 (d, *J* = 7.5 Hz, 1 H), 8.03–7.98 (m, 2 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.66–7.63 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 145.2, 142.4, 141.1, 135.4, 133.8, 131.2, 130.9, 128.0, 125.5, 125.4, 121.3, 121.2, 116.3, 115.1, 114.5, 101.2.

MS (EI): *m*/*z* = 277 $[M]^+$.

HRMS (EI): *m*/*z* [M] for $C_{16}H_8ClN_3$: 277.0407; found: 277.0414.

3-Methoxy-9/10-methylbenzimidazo[1,2-*a*]quinoline-6-carbonitrile (3h)
Yellow solid; mp 182 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35–8.30 (m, 1 H), 8.05 (d, *J* = 8.5 Hz, 0.5 H), 7.97–7.93 (m, 2 H), 7.83 (s, 0.5 H), 7.41–7.36 (m, 1.5 H), 7.31–7.26 (m, 0.5 H), 7.19–7.17 (m, 1 H), 3.95 (s, 3 H), 2.64 (s, 1.5 H), 2.57 (s, 1.5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 144.7, 144.1, 143.7, 142.4, 137.7, 137.5, 135.2, 133.9, 130.8, 130.8, 130.7, 128.7, 126.9, 125.3, 122.3, 122.2, 121.4, 121.2, 120.8, 120.7, 116.5, 116.5, 115.0, 114.9, 113.4, 113.0, 111.7, 111.6, 103.3, 103.1, 55.8, 22.3, 21.7.

MS (EI): *m*/*z* = 287 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{18}H_{13}N_3O$: 287.1059; found: 287.1074.

Ethyl Benzimidazo[1,2-*a*]quinoline-6-carboxylate (3i)
Green solid; mp 119 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.5 Hz, 1 H), 8.43 (s, 1 H), 8.39 (d, *J* = 8.5 Hz, 1 H), 8.18 (q, *J* = 8.0 Hz, 1 H), 7.94 (q, *J* = 8.0 Hz, 1 H), 7.86–7.82 (m, 1 H), 7.58–7.49 (m, 3 H), 4.58 (q, *J* = 7.0 Hz, 2 H), 1.51 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 145.2, 145.0, 136.8, 135.5, 131.9, 131.0, 130.5, 124.7, 124.5, 123.2, 121.8, 121.7, 120.1, 115.2, 113.7, 61.8, 14.4.

MS (EI): *m*/*z* = 290 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{18}H_{14}N_2O_2$: 290.1055; found: 290.1068.

Ethyl 2-Chlorobenzimidazo[1,2-*a*]quinoline-6-carboxylate (3j)
Yellow solid; mp 129 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 1.0 Hz, 1 H), 8.40 (s, 1 H), 8.35–8.33 (m, 1 H), 8.20 (d, *J* = 7.5 Hz, 1 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 7.61–7.54 (m, 2 H), 7.51 (q, *J* = 8.5 Hz, 1 H), 4.58 (q, *J* = 7.0 Hz, 2 H), 1.51 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6, 144.9, 138.2, 137.1, 134.7, 131.9, 130.2, 125.1, 125.1, 123.7, 121.8, 120.2, 115.4, 113.5, 62.0, 14.4.

MS (EI): *m*/*z* = 324 $[M]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ for $C_{18}H_{13}ClN_2O_2$: 325.0744 found: 325.0735.

Ethyl 3-Methoxybenzimidazo[1,2-*a*]quinoline-6-carboxylate (3k)
Yellow solid; mp 110 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 9.0 Hz, 1 H), 8.35 (s, 1 H), 8.32 (d, *J* = 8.5 Hz, 1 H), 8.17 (d, *J* = 8.0 Hz, 1 H), 7.56–7.52 (m, 1 H), 7.51–7.47 (m, 1 H), 7.40 (q, *J* = 9.0 Hz, 1 H), 7.31 (d, *J* = 3 Hz, 1 H), 4.57 (q, *J* = 7.0 Hz, 2 H), 3.94 (s, 1 H), 1.51 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 156.0, 144.7, 135.1, 131.2, 130.3, 124.5, 123.0, 122.8, 121.6, 120.5, 120.4, 116.4, 113.4, 112.1, 61.8, 55.7, 14.4.

MS (EI): *m*/*z* = 320 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{19}H_{16}N_2O_3$: 320.1161; found: 320.1177.

Ethyl 3-Chlorobenzimidazo[1,2-*a*]quinoline-6-carboxylate (3l)
Yellow solid; mp 130 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 9.0 Hz, 1 H), 8.29 (s, 1 H), 8.27 (d, *J* = 8.5 Hz, 1 H), 8.17 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 2.5 Hz, 1 H), 7.75 (q, *J* = 9.0 Hz, 1 H), 7.58–7.54 (m, 1 H), 7.52–7.48 (m, 1 H), 4.57 (q, *J* = 7.0 Hz, 2 H), 1.50 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.5, 144.9, 144.7, 135.0, 133.9, 131.7, 130.3, 129.9, 129.9, 124.9, 123.6, 123.0, 121.9, 121.4, 116.4, 113.5, 62.0, 14.3.

MS (EI): *m*/*z* = 324 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{18}H_{13}ClN_2O_2$: 324.0666; found: 324.0689.

Pyrido[3′,2′:4,5]imidazo[1,2-*a*]quinoline-6-carbonitrile (3m)
Yellow solid; mp 218 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 8.5 Hz, 1 H), 8.69 (q, *J* = 4.5 Hz, 1 H), 8.41 (q, *J* = 8.0 Hz, 1 H), 8.28 (s, 1 H), 7.98–7.90 (m, 2 H), 7.63–7.56 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.6, 144.7, 144.3, 140.4, 136.7, 135.9, 133.7, 129.9, 128.6, 125.8, 121.1, 120.9, 118.1, 114.6, 102.9.

MS (EI): *m*/*z* = 244 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{15}H_8N_4$: 244.0749; found: 244.0760.

Benzimidazo[1,2-*a*]quinoline-6-carbonitrile (3n)
White solid; mp 160 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 16.5 Hz, 1 H), 7.68–7.65 (m, 2 H), 7.52 (q, *J* = 7.5 Hz, 1 H), 7.46 (q, *J* = 8.0 Hz, 1 H), 7.28–7.25 (m, 2 H), 7.22–7.16 (m, 2 H), 7.09–7.05 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.8, 139.0, 135.5, 133.6, 133.2, 130.0, 127.7, 126.9, 124.5, 123.2, 119.8, 115.2.

MS (EI): *m*/*z* = 218 $[M]^+$.

HRMS (EI): *m*/*z* $[M]^+$ for $C_{15}H_{10}N_2$: 218.0844; found: 218.0849.

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