One-Pot Synthesis of 9*H*-Indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines, 1*H*-Dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines and 1*H*-Imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines: Three New Heterocyclic Systems

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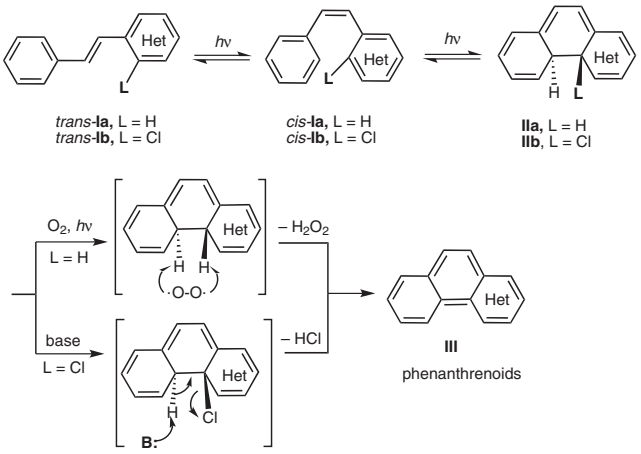
Abstract: An efficient synthesis of three new kinds of heterocyclic systems, 9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines, 1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines and 1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines, has been achieved by the photochemical oxidative dehydrogenation and subsequent photocyclization and dehydrochlorination of 5-(2-chloro-1*H*-indol-3-yl)-, 5-(5-chloro-1*H*-pyrazol-4-yl)- and 5-(5-chloro-1*H*-imidazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles in the presence of pyridine in acetone.

Key words: photodehydrogenation, photocyclization, 9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines, 1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines, 1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines

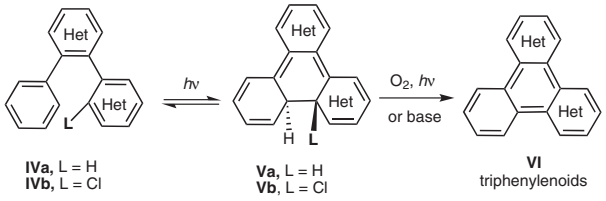
The oxidative photocyclization of stilbene is the most useful and versatile method for the synthesis of phenanthrene.[1] In this reaction, the unstable intermediate 4a,4b-dihydrophenanthrene (**IIa**) could be produced by a photochemically allowed, conrotatory cyclization of *cis*-stilbene (**Ia**) and then aromatized in situ by an oxidant, leading to phenanthrene (**III**) (Scheme 1). This reaction is equally useful for the synthesis of the heterocyclic analogues of phenanthrene, the so-called 'phenanthrenoids'.[1e,2] The use of stilbene containing a good leaving group at one of the *ortho* positions of the aryl ring (e.g., **Ib**) allows the operation of an interesting variant of the oxidative photocyclization of stilbenes for the synthesis of phenanthrene. For example, the irradiation of stilbene **Ib** leads to a dihydrophenanthrene **IIb** that can be aromatized by the action of a base (Scheme 1).[1,3]

As an expansion of the photocyclization of 'stilbenoids', the photocyclization of terphenyl analogues (i.e., **IVa** and **IVb**) supplies an easy entry for the construction of useful polycyclic compounds similar to triphenylene (**VI**) (Scheme 2),[1] for example, alkaloids such as arcyriacyanin A,[4a] cryptopleurine,[4b] granulatimide,[4c] rebeccamycin[4d] and staurosporinone,[4e] and other biological active molecules.[5]

Recently, we reported the synthesis of indolo[3,2-*c*]quinolin-6-ones and pyrazolo[4,3-*c*]quinolin-4-ones by the dechlorinative photocyclization of *N*-aryl-2-chloro-1*H*-indole-3-carboxamides and *N*-aryl-5-chloro-1*H*-pyrazole-4-carboxamides.[6] In this paper, we wish to report a one-pot synthesis of three new kinds of polycyclic compounds, 9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines **2a–d**, 1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines **4a–d** and 1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines **6a**,**b**, by the photochemical oxidative dehydrogenation and subsequent photocyclization of 5-(2-chloro-1*H*-indol-3-yl)-, 5-(5-chloro-1*H*-pyrazol-4-yl)- and 5-(5-chloro-1*H*-imidazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles (Schemes 3–5). These three kinds of polycyclic compounds represent three new heterocyclic systems, all of them containing a pyrazolo[1,5-*a*]quinoline structural unit. The pyrazolo[1,5-*a*]quinoline unit has been found to possess some interesting biological activities, for example, compounds with such units are antibacterial agents[7a] and DNA gyrase inhibitors.[7b]



Scheme 1 Photocyclization of stilbene analogues



Scheme 2 Photocyclization of terphenyl analogues

In the initial study, we tried to synthesize 2,9-dimethyl-9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinoline (**2a**) by two successive photooxidation reactions of **1a**: photooxidative dehydrogenation of the 4,5-dihydropyrazole ring and pho-

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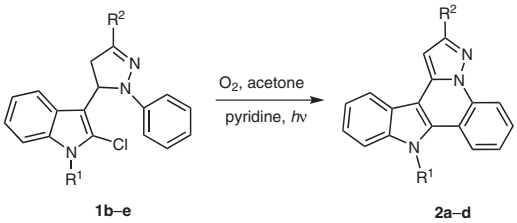
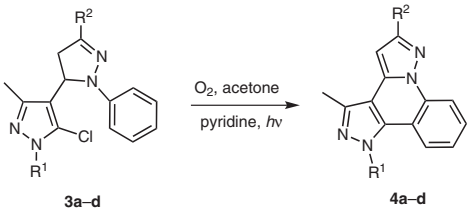
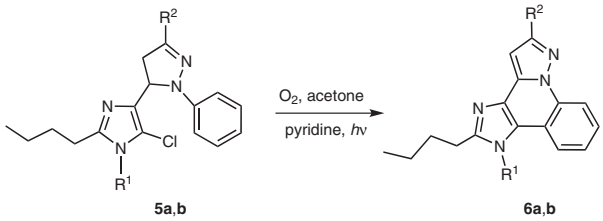


Scheme 3 Photoreaction of 5-(2-chloro-1*H*-indol-3-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles **1b–e**



Scheme 4 Photoreaction of 5-(5-chloro-1*H*-pyrazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles **3a–d**



Scheme 5 Photoreaction of 5-(5-chloro-1*H*-imidazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles **5a**,**b**

tooxidative 6π-electrocyclization with three different oxidants under an irradiation of λ > 300 nm (Scheme 6). We found, however, only photooxidative aromatization of the 4,5-dihydropyrazole ring took place to give **1aa**; no cyclization product **2a** could be detected.

Then, another reactant **1b** with a chloro substituent at the 2-position of the indole ring was prepared and subjected to the photoreaction in the presence of both air and a base such as pyridine under an irradiation of λ > 300 nm at room temperature. We found that the desired cyclization product **2a** could be obtained in excellent yield; also, the intermediate product **1ba** could be separated after one hour of irradiation and it could be smoothly transformed into the cyclization product **2a** after longer irradiation (Scheme 7).

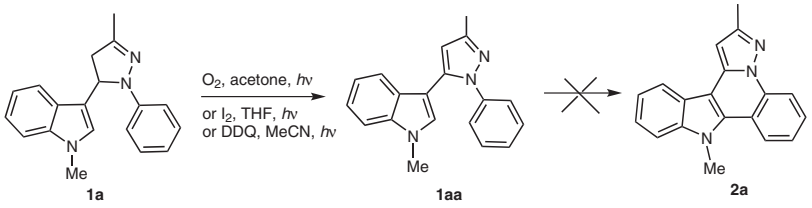
This photocyclization reaction of **1b** could also proceed in other solvents with the addition of pyridine, for example in dichloromethane or acetonitrile (Table 1), but the yield of **2a** was higher in acetone, probably because of the sensitization effect of acetone. Therefore, acetone was selected as the solvent in all subsequent photooxidative dehydrogenation and photocyclization reactions. No great difference was observed for the photoreaction of **1b** under air versus oxygen.

Table 1 Photocyclization of **1b** in Different Solvents[a]

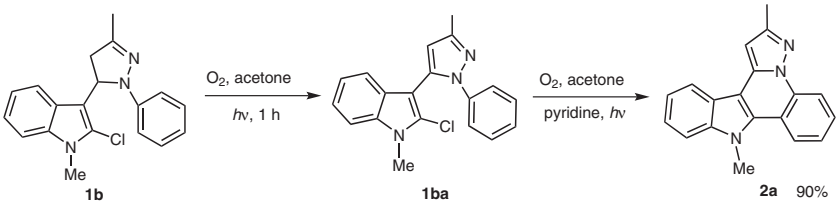
Entry	Solvent	Time (h)	Conversion[b] (%)	Yield[c] (%)
1	CH_2Cl_2	5	72	60
2	MeCN	5	61	45
3	acetone	3	95	90

[a] The solutions were irradiated with Pyrex-filtered light (>300 nm) from a 500 W medium-pressure Hg lamp at room temperature.
[b] Conversions are based on **1b**.
[c] Isolated yields.

Encouraged by these results, three kinds of substrates **1b–e**, **3a–d** and **5a**,**b** were prepared and their photoreactions were investigated under similar conditions (Schemes 3–5). In general, each substrate afforded the corresponding cyclization product, the 9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines **2a–d**, 1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines **4a–d** and 1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines **6a**,**b**, as the sole product in high yield after irradiation for 3–30 hours (Table 2). All products were fully identified by ^{1}H and ^{13}C NMR spectroscopy and HRMS.[7]



Scheme 6 Photoreaction of 5-(1*H*-indol-3-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole **1a**



Scheme 7 Photoreaction of 5-(2-chloro-1*H*-indol-3-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole **1b**

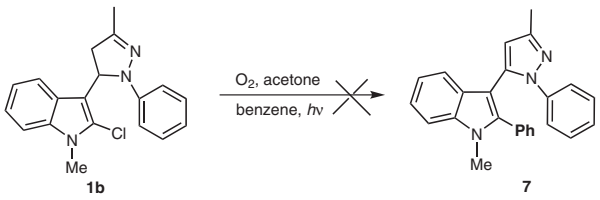
Table 2 Photocyclization of 5-(2-Chloro-1*H*-indol-3-yl)-, 5-(5-Chloro-1*H*-pyrazol-4-yl)- and 5-(5-Chloro-1*H*-imidazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles[a]

Entry	Substrate	R^1	R^2	Time (h)	Conv.[b] (%)	Product	Yield[c] (%)	Mp (°C)
1	**1b**	Me	Me	3	95	**2a**	90	206–207
2	**1c**	Me	Ph	5	95	**2b**	85	200–203
3	**1d**	Ph	Me	4	98	**2c**	95	143–145
4	**1e**	Ph	Ph	6	98	**2d**	96	174–176
5	**3a**	H	Me	24	92	**4a**	90	208–211
6	**3b**	H	Ph	30	87	**4b**	85	263–264
7	**3c**	Ph	Me	16	95	**4c**	80	191–193
8	**3d**	Ph	Ph	24	90	**4d**	72	197–198
9	**5a**	H	Me	12	95	**6a**	80	dense oil
10	**5b**	H	Ph	20	88	**6b**	60	dense oil

[a] Solutions were irradiated with Pyrex-filtered light (> 300 nm) from a 500 W medium-pressure Hg lamp at r.t..
[b] Based on the amount of substrate used.
[c] Isolated yields.

It can be observed from Table 2 that the type of chloro-substituted heterocyclic unit, 5-(2-chloro-1*H*-indol-3-yl), 5-(5-chloro-1*H*-pyrazol-4-yl) or 5-(5-chloro-1*H*-imidazol-4-yl), has a great effect on the photocyclization reactions. Comparatively, the photoreaction efficiency of the substrates **1b–e** containing the 5-(2-chloro-1*H*-indol-3-yl) unit is much higher than that of those substrates containing the 5-(5-chloro-1*H*-pyrazol-4-yl) or 5-(5-chloro-1*H*-imidazol-4-yl) unit. The substituent R^2 in substrates **1b–e**, **3a–d** and **5a**,**b** also has some effect on the photoreaction efficiency; the substrates with R^2 = Me react faster and the yields of the corresponding products are higher than those with R^2 = Ph.

In our previous work,[6] we found that *N*-aryl-2-chloro-1*H*-indole-3-carboxamides could couple with the solvent benzene under irradiation; thus, a radical mechanism was proposed to explain the dechlorinative photocyclization. In contrast, we found that the irradiation of **1b** in benzene only gives the cyclization product **2a**; no solvent-incorporated product, the 5-(2-phenyl-1*H*-indol-3-yl)-1-phenyl-1*H*-pyrazole **7**, was detected (Scheme 8).

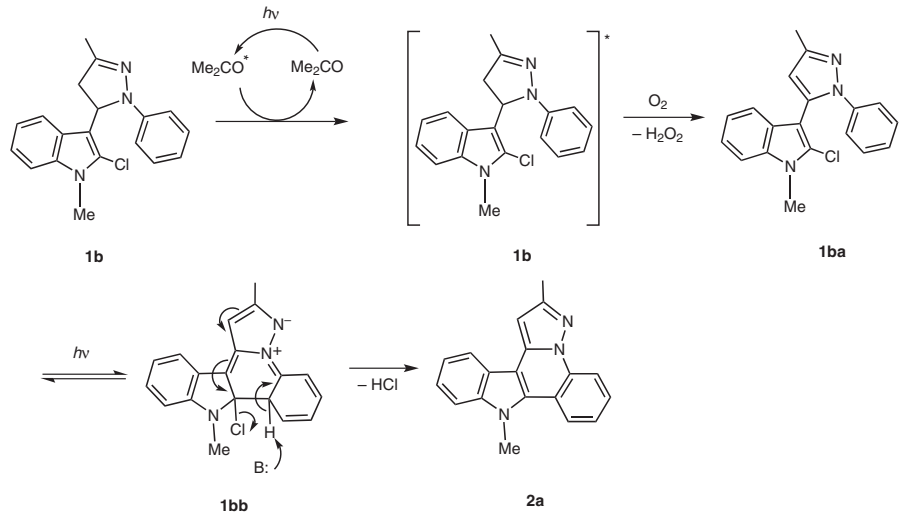


Scheme 8 Photoreaction of 5-(2-chloro-1*H*-indol-3-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole **1b** in benzene

In other words, no C–Cl bond fission takes place in the photoreaction of **1b**. It could be supposed that the photocyclization of intermediate **1ba** is just a 6π-electrocyclization reaction and that pyridine helps the dehydrochlorination; however, from the comparison of the photoreactions of **1a** and **1b** (Schemes 6 and 7), it seems that the presence of a chloro substituent in the substrate is necessary for aromatization of the intermediate of a 6π-electrocyclization reaction. According to these results, a mechanism for the formation of **2a** is proposed as follows (Scheme 9): oxidative dehydrogenation of **1b** gives the intermediate product **1ba**; the subsequent 6π-electrocyclization reaction of **1ba** gives the unstable cyclization intermediate **1bb** which undergoes dehydrochlorination with the help of pyridine to afford the product **2a**.

In summary, an efficient one-pot synthesis of three kinds of new heterocyclic compounds, 9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinolines, 1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinolines and 1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinolines, has been achieved by the photochemical oxidative dehydrogenation and subsequent photocyclization and dehydrochlorination of 5-(2-chloro-1*H*-indol-3-yl)-, 5-(5-chloro-1*H*-pyrazol-4-yl)- and 5-(5-chloro-1*H*-imidazol-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazoles in the presence of pyridine in acetone.

All reagents were purchased from commercial suppliers and used without further purification. All solvents were dried and redistilled before use. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was performed with silica gel GF_{254} plates, and the products were visualized by UV detection. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker AM-400 or a Bruker DRX-300 NMR spectrometer. HRMS data were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI.



Scheme 9 Proposed mechanism for the formation of **2a**

1-Methyl-3-(3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-indole (1a)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.083 (s, 3 H, CH_3), 2.844 (q, *J* = 1.7 Hz, 1 H), 3.441 (q, *J* = 1.7 Hz, 1 H), 3.689 (s, 3 H, NCH_3), 5.285 (q, *J* = 1.7 Hz, 1 H), 6.727 (q, *J* = 4.5 Hz, 1 H), 6.917 (s, 1 H), 7.046 (d, *J* = 7.5 Hz, 2 H, 2 CH), 7.051–7.063 (m, 3 H), 7.231 (d, *J* = 5.1 Hz, 1 H), 7.303 (d, *J* = 8.1 Hz, 1 H), 7.587 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.11 (CH_3), 32.76 (NCH_3), 46.58 (CH_2), 57.92 (CH), 109.52 (CH), 113.26 (CH), 115.87 (CH), 118.40 (CH), 119.03 (CH), 121.85 (CH), 125.55 (C), 126.29 (CH), 128.76 (CH), 137.51 (C), 146.57 (C), 149.52 (C).

1-Methyl-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-1*H*-indole (1aa)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.417 (s, 3 H, CH_3), 3.685 (s, 3 H, NCH_3), 6.409 (s, 1 H), 6.687 (s, 1 H), 7.112 (t, *J* = 4.5 Hz, 1 H), 7.216–7.372 (m, 5 H), 7.400 (d, *J* = 7.2 Hz, 2 H), 7.840 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.64 (CH_3), 31.69 (NCH_3), 32.87 (CH), 53.67 (CH), 105.14 (C), 107.06 (CH), 109.34 (CH), 119.98 (CH), 120.06 (CH), 122.12 (CH), 125.08 (CH), 126.36 (CH), 126.95 (CH), 128.06 (CH), 128.69 (CH), 136.53 (C), 137.66 (C), 140.56 (C), 149.43 (C).

2-Chloro-1-methyl-3-(3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-indole (1b)

Yellow solid; mp 129–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.016 (s, 3 H, CH_3), 2.901 (d, *J* = 1.8 Hz, 1 H), 3.354 (m, *J* = 1.8 Hz, 1 H), 3.724 (s, 3 H, NCH_3), 5.343 (d, *J* = 1.3 Hz, 1 H), 6.676 (t, *J* = 7.2 Hz, 1 H), 6.979–7.119 (m, 5 H), 7.180 (t, *J* = 7.6 Hz, 1 H), 7.273 (d, *J* = 6.0 Hz, 1 H), 7.508 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.79 (CH_3), 29.84 (NCH_3), 45.23 (CH_2), 57.00 (CH), 109.29 (CH), 111.10 (C), 113.00 (CH), 118.50 (CH), 119.18 (C), 120.24 (CH), 122.20 (CH), 123.15 (C), 124.28 (CH), 128.81 (CH), 136.15 (C), 146.36 (C), 148.78 (C).

2-Chloro-1-methyl-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-1*H*-indole (1ba)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.442 (s, 3 H, CH_3), 3.703 (s, 3 H, NCH_3), 6.379 (s, 1 H), 7.179–7.327 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.03 (CH_3), 30.23 (NCH_3), 103.18 (C), 109.43 (CH), 109.56 (CH), 109.60 (CH), 119.33 (CH), 121.01 (CH), 122.65 (CH), 123.80 (CH), 125.57 (C), 126.23 (C), 126.69 (C), 128.88 (CH), 135.27 (C), 135.79 (C), 140.87 (CH), 149.74 (C).

2,9-Dimethyl-9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinoline (2a); Typical Procedure for the Photochemical Reactions

To acetone (50 mL) in a reaction flask was added **1b** (162 mg, 0.5 mmol); then, pyridine (0.1 mL) was added after dissolution of the solid. The resulting colorless solution was irradiated with a 500 W medium-pressure Hg lamp with stirring at r.t. for 3 h. After completion of the reaction, as monitored by TLC, the solvent was removed under reduced pressure and the product was separated by silica gel column chromatography [hexane–acetone, 10:1 (v/v)] to afford **2a**. The solid was further purified by recrystallization (EtOH) to give pure **2a**.

Yield: 128 mg (90%); colorless needles; mp 206–207 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.602 (s, 3 H, CH_3), 4.135 (s, 3 H, NCH_3), 6.603 (s, 1 H), 7.010 (t, *J* = 7.6 Hz, 1 H), 7.120–7.320 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.53 (CH_3), 33.71 (NCH_3), 96.35 (CH), 106.80 (C), 109.52 (CH), 115.46 (C), 117.10 (CH), 120.45 (CH), 120.79 (CH), 122.03 (C), 122.80 (CH), 123.79 (CH), 124.33 (CH), 128.02 (CH), 131.35 (C), 134.10 (C), 136.00 (C), 140.09 (C), 151.74 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}N_3$: 286.1339; found: 286.1341.

9-Methyl-2-phenyl-9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinoline (2b)

Yield: 147 mg (85%); colorless needles; mp 200–203 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.837 (s, 3 H, NCH_3), 6.846 (s, 1 H), 7.195–7.523 (m, 8 H), 7.802 (d, *J* = 7.6 Hz, 1 H), 8.026 (d, *J* = 8 Hz, 1 H), 8.82 (d, *J* = 7.2 Hz, 2 H), 8.635 (d, *J* = 4.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.68 (NCH_3), 33.08 (CH), 93.03 (CH), 106.31 (C), 109.13 (CH), 115.32 (C), 117.01 (CH), 120.03 (CH), 120.37 (CH), 121.53 (C), 122.27 (CH), 123.72 (CH), 123.91 (CH), 126.40 (CH), 127.48 (CH), 128.08 (CH), 130.68 (C), 133.66 (C), 133.72 (C), 135.88 (C), 139.56 (C), 152.79 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{18}N_3$: 348.1495; found: 348.1499.

2-Methyl-9-phenyl-9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinoline (2c)
Yield: 165 mg (95%); pale yellow powder; mp 143–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.637 (s, 3 H, CH_3), 6.787 (s, 1 H), 7.058 (t, *J* = 8 Hz, 1 H), 7.139 (d, *J* = 7.2 Hz, 1 H), 7.322–7.393 (m, 3 H), 7.487–7.510 (m, 3 H), 7.637–7.644 (m, 3 H), 8.089 (t, *J* = 7.6 Hz, 1 H), 8.676 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5 (CH_3), 29.85 (CH), 96.75 (CH), 107.71 (C), 110.90 (CH), 114.79 (C), 116.80 (CH), 120.31 (CH), 121.52 (CH), 122.38 (C), 123.10 (CH), 123.44 (CH), 124.69 (CH), 128.09 (CH), 129.19 (CH), 130.40 (CH), 131.54 (C), 134.27 (C), 135.98 (C), 139.06 (C), 141.62 (C), 151.79 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{18}N_3$: 348.1495; found: 348.1497.

2,9-Diphenyl-9*H*-indolo[3,2-*c*]pyrazolo[1,5-*a*]quinoline (2d)
Yield: 197 mg (96%); pale yellow powder; mp 174–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.123 (t, *J* = 8 Hz, 1 H), 7.178 (d, *J* = 8 Hz, 1 H), 7.233 (d, *J* = 8.2 Hz, 1 H), 7.316 (s, 1 H), 7.371–7.456 (m, 3 H), 7.513–7.595 (m, 5 H), 7.675 (d, *J* = 2.4 Hz, 3 H), 8.204 (t, *J* = 7.2 Hz, 3 H), 8.872 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 94.05 (CH), 107.91 (C), 111.06 (CH), 115.31 (CH), 117.35 (CH), 120.44 (CH), 121.70 (C), 122.45 (CH), 123.16 (CH), 123.98 (CH), 124.89 (CH), 126.72 (CH), 128.24 (CH), 128.47 (CH), 128.93 (CH), 129.18 (CH), 129.59 (CH), 130.51 (CH), 131.64 (C), 133.90 (C), 134.49 (C), 136.52 (C), 139.08 (C), 141.74 (C), 153.58 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{20}N_3$: 410.1652; found: 410.1648.

3,5-Dimethyl-1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinoline (4a)
Yield: 106 mg (90%); colorless needles; mp 208–211 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.540 (s, 3 H, CH_3), 2.655 (s, 3 H, CH_3), 6.450 (s, 1 H), 7.395 (t, *J* = 7.2 Hz, 1 H), 7.607 (t, *J* = 7.2 Hz, 1 H), 8.111 (d, *J* = 7.6 Hz, 1 H), 8.490 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.99 (CH_3), 29.63 (CH_3), 97.51 (C), 116.08 (CH), 119.23 (C), 122.91 (CH), 123.60 (C), 124.65 (CH), 128.63 (C), 133.13 (C), 134.52 (CH), 150.60 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}N_4$: 237.1135; found: 237.1137.

3-Methyl-5-phenyl-1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinoline (4b)
Yield: 126 mg (85%); colorless needles; mp 263–264 °C.

^{1}H NMR (400 MHz, DMSO–$CDCl_3$): δ = 3.188 (s, 3 H, CH_3), 6.906 (s, 1 H), 7.234–7.410 (m, 4 H), 7.535–7.971 (m, 1 H), 7.980 (t, *J* = 7.6 Hz, 2 H), 8.222 (d, *J* = 7.2 Hz, 1 H), 8.529 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.93 (CH_3), 93.61 (C), 107.71 (C), 115.95 (2 CH), 122.41 (C), 124.12 (C), 125.52 (4 CH), 127.65 (C), 128.09 (3 CH), 129.26 (C), 132.72 (CH), 135.07 (C), 151.93 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{15}N_4$: 299.1291; found: 299.1289.

3,5-Dimethyl-1-phenyl-1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinoline (4c)
Yield: 124 mg (80%); white powder; mp 191–193 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.577 (s, 3 H, CH_3), 2.702 (s, 3 H, CH_3), 6.547 (s, 1 H), 7.123 (t, *J* = 7.5 Hz, 1 H), 7.343 (d, *J* = 7.8 Hz, 1 H), 7.535–7.598 (m, 6 H), 8.581 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.14 (CH_3), 14.21 (CH_3), 97.18 (CH), 113.02 (C), 116.85 (CH), 122.98 (CH), 123.67 (CH), 127.13 (CH), 129.11 (CH), 129.43 (CH), 129.72 (CH), 133.98 (C), 134.16 (C), 134.51 (C), 140.86 (C), 143.87 (C), 151.51 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{17}N_4$: 313.1448; found: 313.1452.

3-Methyl-1,5-diphenyl-1*H*-dipyrazolo[1,5-*a*:4′,3′-*c*]quinoline (4d)
Yield: 134 mg (72%); colorless needles; mp 197–198 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.735 (d, *J* = 1.2 Hz, 3 H, CH_3), 6.984 (s, 1 H), 7.108 (t, *J* = 3.8 Hz, 1 H), 7.318–7.412 (m, 3 H), 7.49 (q, *J* = 7.6 Hz, 2 H), 7.544–7.582 (m, 5 H), 8.090 (d, *J* = 8 Hz, 2 H), 8.725 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.33 (CH_3), 94.42 (CH), 94.48 (C), 110.71 (C), 113.49 (CH), 117.38 (CH), 123.02 (CH), 124.20 (C), 126.47 (CH), 127.25 (CH), 128.47 (CH), 128.83 (CH), 129.23 (CH), 129.57 (CH), 133.40 (CH), 134.31 (C), 135.04 (C), 140.91 (CH), 144.03 (C), 153.28 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{19}N_4$: 375.1604; found: 375.1613.

2-Butyl-5-methyl-1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinoline (6a)
Yield: 111 mg (80%); yellow dense oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.794 (t, *J* = 4.8 Hz, 3 H, CH_3), 1.127–1.280 (m, 2 H, CH_2), 1.679–1.755 (m, 2 H, CH_2), 2.467 (s, 3 H, CH_3), 2.925 (t, *J* = 7.6 Hz, 2 H, CH_2), 6.504 (s, 1 H), 7.286 (t, *J* = 8 Hz, 1 H), 7.457–7.499 (m, 1 H), 8.210 (d, *J* = 8 Hz, 1 H), 8.572 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.66 (CH_3), 14.32 (CH_3), 22.49 (CH_2), 29.03 (CH_2), 30.96 (CH_2), 96.25 (CH), 116.45 (CH, C), 122.29 (CH, C), 124.68 (CH, C), 127.52 (C), 132.71 (CH, C), 151.51 (C), 154.05 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}N_4$: 279.1604; found: 279.1606.

2-Butyl-5-phenyl-1*H*-imidazo[4,5-*c*]pyrazolo[1,5-*a*]quinoline (6b)
Yield: 102 mg (60%); yellow dense oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.768 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.848–0.887 (m, 2 H, CH_2), 1.734–1.800 (m, 2 H, CH_2), 2.922 (t, *J* = 8 Hz, 2 H, CH_2), 7.011 (s, 1 H), 7.308–7.426 (m, 5 H), 7.550 (t, *J* = 8 Hz, 1 H), 7.978 (d, *J* = 7.6 Hz, 2 H), 8.130 (d, *J* = 8 Hz, 1 H), 8.747 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.79 (CH_3), 22.56 (CH_2), 29.04 (CH_2), 30.98 (CH_2), 93.36 (CH), 116.98 (CH, C), 122.00 (C), 124.89 (2 CH, C), 124.95 (C), 126.54 (CH), 127.44 (CH), 128.47 (CH), 128.87 (2 CH), 132.87 (CH, C), 133.50 (C), 153.15 (C), 153.76 (C).

ESI-HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}N_4$: 341.1761; found: 341.1763.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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