Short and Simple Method of Synthesis of Some Pyrrolo[3,2-*b*]quinoline Derivatives from Easily Available Nitrobenzene Derivatives

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Abstract: The Vilsmeier–Hack condensation of *ortho*-cyanomethylated nitroarenes with *N*-methylpyrrolidone, followed by cyclization promoted by *O*,*N*-bistrimethylsilylacetamide and DBU in DMF led directly to pyrrolo[3,2-*b*]quinoline derivatives.

Key words: indoles, cyclization, fused-ring systems, heterocycles, annulation

In our studies on synthesis of polycyclic nitrogen heterocycles from easily available, cheap, diversely substituted nitroarenes, we explore reactions which involve bases and Lewis acids, working in tandem in the crucial step of the reaction, forming a new nitrogen ring.

The ring is built on the existing nitrogen atom of the nitro group, and employs a chain connected to the *ortho* position of the arene. The latter can be a side chain existing in the substrate, or can be formed in the addition reaction of appropriate nucleophile to the nitroarene, with formation of σ^H adduct in the *ortho* position. Thus, two ways of the reaction course can be formulated, and are depicted in Scheme 1.

Path a consists of the reactions of carbanions and other nucleophiles of allylic/benzylic character, with nitroaromatic compounds, leading to the σ^H adducts, which undergo transformation to the corresponding nitrosoarenes, formally as a result of base-induced elimination of water, which can be assisted by proton or Lewis acids. The intermediates undergo cyclization to the annulated heterocyclic systems such as substituted quinoline,[1,2] 1-hydroxyindole,[2,3] acridine[4] or more complex polycyclic heterocyclic structures.[5]

Path b, on the other hand, involves transformation of benzylic-type anions, generated from nitroarenes possessing an unsaturated side chain in the *ortho* position. The negative charge of the anion, which in fact is generated by abstraction of the γ hydrogen, is strongly delocalized and stabilized by electron-withdrawing group (EWG). While cyclization of such anions can be performed with the use of a base in protic media, it often leads nonselectively to five-, and six-membered-ring formation.[6,7] In the base/Lewis acid systems, such as Et_3N–Me_3SiCl, the quinoline derivatives are formed exclusively in high yields.[7]

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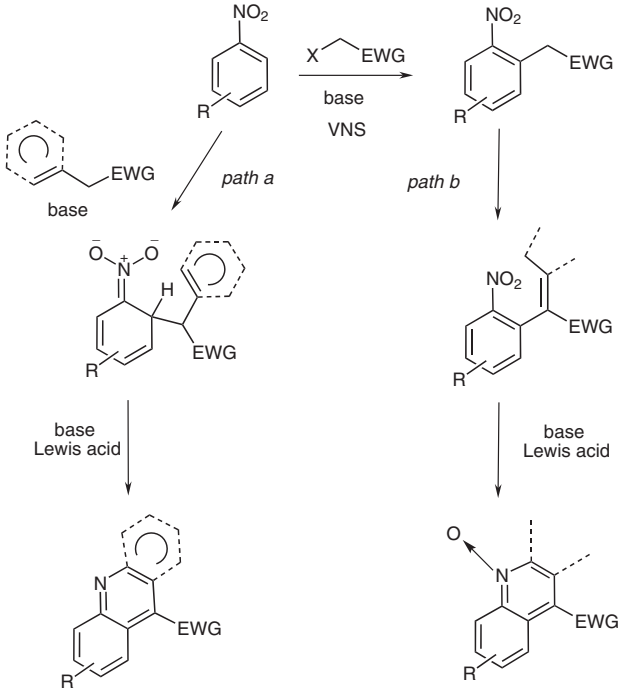
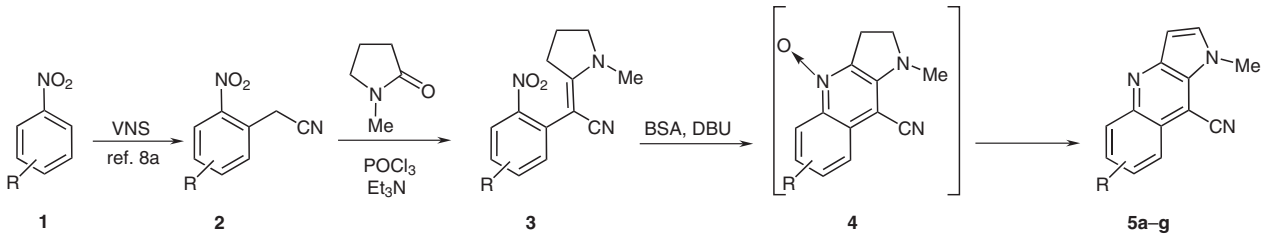
Although condensed benzo-heterocycles are very often synthesized by means of various condensations of nitroarenes, when a functionalized carbon substituent in the *ortho* position is present, preparation of required starting nitroarenes is not always an easy task, or they are not stable compounds. On the contrary, the first method (path a in Scheme 1) does not need synthesis of any *ortho* substituted derivative of the nitroarene, while the synthesis of starting materials for the second approach, can be often accomplished easily via vicarious nucleophilic substitution of hydrogen (VNS)[8] usually followed by appropriate modification of the introduced side chain.[6,7]



Scheme 1

In this communication we present the results of attempted application of the second method mentioned above, for a short synthesis of some pyrrolo[3,2-*b*]quinoline derivatives. While many heterocycles containing the 4-azaindole core, e.g. tetracyclic analogues such as cryptolepine and its derivatives,[9] have been reported to show a wide range of biological activities, pyrrolo[3,2-*b*]quinolines are less studied, and their pharmacological potential has not been disclosed yet. Only a small number of them have been obtained, and methods of their synthesis are rather



Scheme 2 Synthesis of pyrrolo[3,2-*b*]quinolines from nitroarenes

limited. The most popular approach consists of building of a pyrrole ring on the 2-methyl-3-aminoquinolines by cyclocondensation with triethyl orthoformate,[10a] Vilsmeier reagent,[10b] and other reagents.[10c] Similarly, reductive cyclization of 3-nitroquinoline possessing *N*,*N*-dimethylaminovinyl group in position 2 leads to formation of the pyrrole ring.[10d] Another approach involves base-catalyzed Friedlander reaction for construction of the pyridine ring in the reaction of 3-pyrrolidone derivatives with *ortho*-aminobenzaldehydes or their acetals, which produces 2,3-dihydro derivatives of pyrrolo[3,2-*b*]quinoline.[11] Similar, but more convenient route, omitting *ortho*-aminoaldehydes, employs functionalized 3-pyrrolidone derivatives.[12] An interesting two-step method, starting from *ortho*-nitrobenzaldehyde derivatives comprises their condensation with pyrrole, followed by reductive cyclization, involving the nitro group and one of the two pyrrole groups, promoted by $SnCl_2 \cdot 2H_2O$ in refluxing methanol.[13a] As a result, the method is limited to pyrrolo[3,2-*b*]quinolines bearing additional 2-pyrrole substituent at C-9 position. Earlier attempts of similar cyclizations were much less effective.[13b] Condensation of 2-amino-5-phenyl-3*H*-1,4-benzodiazepines with 1,3-dicarbonyl compounds is a method in which both nitrogen rings are formed in the annulation process.[14]

The starting materials for the described syntheses are not easily available, and reaction conditions are usually harsh, which excludes synthesis of compounds with labile substituents.

Many more methods are available for the synthesis of 4-azaindoles[15] which, however, have not found applications in synthesis of their benzo analogues, especially pyrrolo[3,2-*b*]quinolines.

The three steps in simple route presented in this paper, lead to the derivatives of 1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline, substituted, in the carbocyclic ring, and with suitable for further functionalization carbonitrile group at C-9 position.

The whole synthesis started from substituted nitroarenes **1** with at least one *ortho* position available for nucleophilic attack (Scheme 2). They were converted into cyanomethyl derivatives **2** by reaction with 4-chlorophenoxyacetonitrile in the presence of potassium *tert*-butoxide, according to the well-known vicarious nucleophilic substitution (VNS) scheme.[8] Incorporation of the *N*-methylpyrrolidone as a nitrogen-containing five-membered-ring building block via Vilsmeier–Haack-type reaction has also been precedented in one of our paper.[16] The crucial step is a cyclization of **3** to **4**. It was based on previously described reactions of some 2-propylidene derivatives of **2**, which under particular conditions led to the appropriate quinoline *N*-oxides.[6,7] Unfortunately, none of the earlier examined conditions, including the more successful NaOH–MeOH[6] and Me_3SiCl–Et_3N–DMF[7] systems, worked in this case.

However, a more powerful system, composed of *O*,*N*-bistrimethylsilylacetamide (BSA) and DBU in DMF was found effective, when applied for prolonged time at room temperature, or elevated temperature. We found this system efficient in some cyclizations of σ^H adducts, according to the path a in Scheme 1.[1b,2,5] Under such conditions, the expected primary product **4** was not observed in the reaction mixture, instead, the deoxygenation–aromatization of **4** took place spontaneously, furnishing the target pyrrolo[3,2-*b*]quinoline derivative **5**.

The examples collected in Table 1 show, that while the yields of this cyclization–disproportionation step vary strongly with diversely substituted substrates, in several cases they can be of practical value. Analysis of the results indicates a disfavoring effect of electron-rich substituents, and those located at position *ortho* to the nitro group.

In cases, when such unfavorable conditions are not met, the presented approach seems to offer one of the simplest and most convenient methods of synthesis of pyrrolo[3,2-*b*]quinoline derivatives from easily available nitroarenes.

Table 1 Two-Step Synthesis of Pyrrolo[3,2-*b*]quinolines **5** from *ortho*-Cyanomethylated Nitroarenes **2**[17,18]

Entry	**5**	R	**3** from **2**	**5** from **3**		
			Yield (%)[a]	Temp	Time (days)	Yield (%)[a]
1	**a**	7-Cl	63	r.t.	1	59
2	**b**	7-Br	44	r.t.	1	59
3	**c**	7-F	47	r.t.	1	51
4	**d**	7-MeO	69	r.t.	14	27
5	**e**	7-SPh	54[b]	r.t.	2	45
6	**f**	5,7-Cl_2	29	50 °C	7	24
7	**g**	5-MeO-7-Cl	85	80 °C	14	25

[a] Isolated yield.
[b] 3-Cyano-5-phenylthio[2,1]benzisoxazole (14%) was also isolated.

Contrary to another reported method, also involving intramolecular cyclization of the nitro group with five-membered nitrogen ring,[13a] it does not require reductive conditions, and thus seems to be more promising for sensitive substituents.

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(17) **General Procedure for the Synthesis of 5 from 2**: The cyanomethylated nitroarene **2** (2 mmol) dissolved in anhyd *N*-methylpyrrolidone (10 mL) was cooled to 0 °C and Et_3N (3 mL) was added followed by slow addition of $POCl_3$ (0.5 mL). The cooling bath was then removed, and the reaction mixture was stirred for 30 min at r.t. The mixture was treated with diluted, cold, aq NaCl (200 mL) and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with brine and dried with Na_2SO_4. The solvent was evaporated and the residue was chromatographed on SiO_2 using hexane–EtOAc mixture as an eluent. The obtained **3** (0.5 mmol) was dissolved in anhyd DMF (3 mL). BSA (2.5 mmol, 0.6 mL) and DBU (2.5 mmol, 0.38 mL) were added subsequently. The reaction mixture was stirred for the time, and at the temperature specified in Table 1, then it was poured into diluted aq NaCl solution (50 mL), and extracted with EtOAc (3 × 30 mL). The extracts were combined, washed with brine, dried over Na_2SO_4, and the solvent was evaporated. The residue was chromatographed on SiO_2 using hexane–EtOAc mixture as an eluent.
(18) Analytical data for the products: **(2*E*,*Z*)-(5-Chloro-2-nitrophenyl)(1-methylpyrrolidin-2-ylidene)acetonitrile (3a)**: red crystals; mp 112–115 °C. Two isomers, M (major)/N (minor) = 1.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85–1.92 (m, 2 H, N), 2.00–2.10 (m, 2 H, M), 2.37 (t, *J* = 7.7 Hz, 2 H, N), 2.47 (s, 3 H, M), 3.06 (t, *J* = 7.7 Hz, 2 H, M), 3.38 (s, 3 H, N), 3.50–3.58 (m, 2 H, M + 2 H, N), 7.34–7.38 (m, 1 H, M + 1 H, N), 7.44 (d, *J* = 2.0 Hz, 1 H, M), 7.46 (d, *J* = 2.0 Hz, 1 H, N), 7.82 (d, *J* = 8.7 Hz, 1 H, N), 7.88 (d, *J* = 8.7 Hz, 1 H, M). MS (EI, 70 eV): *m*/*z* (%) = 277 (21), 137 (100). HRMS (EI): *m*/*z* calcd for $C_{13}H_{12}N_3O_2{}^{35}Cl$: 277.0618; found: 277.0615. **(2*E*,*Z*)-(5-Bromo-2-nitrophenyl)(1-methyl-pyrrolidin-2-ylidene)acetonitrile (3b)**: red crystals; mp 105–107 °C (EtOH). Two isomers, M (major)/N (minor) = 1.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85–1.92 (m, 2 H, N), 2.00–2.10 (m, 2 H, M), 2.37 (t, *J* = 7.6 Hz, 2 H, N), 2.47 (s, 3 H, M), 3.06 (t, *J* = 7.8 Hz, 2 H, M), 3.38 (s, 3 H, N), 3.50–3.58 (m, 2 H, M + 2 H, N), 7.34–7.38 (m, 1 H, M + 1 H, N), 7.44 (d, *J* = 2.0 Hz, 1 H, M), 7.46 (d, *J* = 2.0 Hz, 1 H, N), 7.82 (d, *J* = 8.7 Hz, 1 H, N), 7.88 (d, *J* = 8.7 Hz, 1 H, M). MS (EI, 70 eV): *m*/*z* (%) = 323 (10), 321 (10), 137 (100). HRMS (EI): *m*/*z* calcd for $C_{13}H_{12}N_3O_2{}^{79}Br$: 321.0113; found: 321.0118. **(2*E*,*Z*)-(5-Fluoro-2-nitrophenyl)(1-methylpyrrolidin-2-ylidene)acetonitrile (3c)**: orange crystals; mp 120–121 °C (hexane–EtOAc). Two isomers, M (major)/N (minor) = 1.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.84–1.92 (m, 2 H, N), 2.00–2.11 (m, 2 H, M), 2.38 (t, *J* = 7.7 Hz, 2 H, N), 2.47 (s, 3 H, M), 3.06 (t, *J* = 7.8 Hz, 2 H, M), 3.39 (s, 3 H, N), 3.50–3.58 (m, 2 H, M + 2 H, N), 7.05–7.10 (m, 1 H, M + 1 H, N), 7.12–7.17 (m, 1 H, M + 1 H, N), 7.92 (dd, *J* = 8.8, 5.3 Hz, 1 H, N), 7.99 (dd, *J* = 8.9, 5.3 Hz, 1 H, M). MS (EI, 70 eV): *m*/*z* (%) = 261 (11), 137 (100). HRMS (EI): *m*/*z* calcd for $C_{13}H_{12}N_3O_2F$: 261.0914; found: 261.0925. **(2*E*,*Z*)-(5-Methoxy-2-nitrophenyl)(1-methylpyrrolidin-2-ylidene)acetonitrile (3d)**:[16] red crystals; mp 89–92 °C. Two isomers, M (major)/N (minor) = 2. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.82–1.88 (m, 2 H, N), 2.00–2.09 (m, 2 H, M), 2.34 (t, *J* = 7.7 Hz, 2 H, N), 2.44 (s, 3 H, M), 3.06 (t, *J* = 7.7 Hz, 2 H, M), 3.44–3.65 (m, 2 H, M + 2 H, N), 3.88 (s, 3 H, N), 3.89 (s, 3 H, M), 3.99 (s, 3 H, N), 6.86–6.90 (m, 2 H, M + 2 H, N), 7.97 (d, *J* = 9.0 Hz, 1 H, N), 8.02 (d, *J* = 9.0 Hz, 1 H, M). MS (EI, 70 eV): *m*/*z* (%) = 274 (14), 137 (100). Anal. Calcd for $C_{14}H_{15}N_3O_3$: C, 61.53; H, 5.53; N, 15.38. Found: C, 61.59; H, 5.46; N, 15.22. **(2*E*,*Z*)-(1-Methylpyrrolidin-2-ylidene)[2-nitro-5-(phenylthio)phenyl]acetonitrile (3e)**: red crystals; mp 147–151 °C (hexane–EtOAc). Two isomers, M (major)/N (minor) = 1.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.80–1.88 (m, 2 H, N), 1.95–2.10 (m, 2 H, M), 2.30 (t, *J* = 7.6 Hz, 2 H, N), 2.42 (s, 3 H, M), 3.00–3.05 (m, 2 H, M), 3.36 (s, 3 H, N), 3.46–3.56 (m, 2 H, M + 2 H, N), 6.99–7.06 (m, 1 H, M + 1 H, N), 7.15 (d, *J* = 2.0 Hz, 1 H, M), 7.17 (d, *J* = 1.9 Hz, 1 H, N), 7.42–7.47 (m, 3 H, M + 3 H, N), 7.50–7.55 (m, 2 H, M + 2 H, N), 7.76 (d, *J* = 8.6 Hz, 1 H, N), 7.82 (d, *J* = 8.6 Hz, 1 H, M). MS (EI, 70 eV): *m*/*z* (%) = 351 (38), 252 (76), 223 (54), 137 (100). HRMS (EI): *m*/*z* calcd for $C_{19}H_{17}N_3SO_2$: 351.1041; found: 351.1050. **(2*E*,*Z*)-(3,5-Dichloro-2-nitrophenyl)(1-methylpyrrolidin-2-ylidene)acetonitrile (3f)**: pale yellow crystals; mp 163–167 °C (hexane–EtOAc).

Two isomers, M/N = 1. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85–1.92 (m, 2 H, N), 1.98–2.06 (m, 2 H, M), 2.43 (t, *J* = 7.8 Hz, 2 H, M or N), 2.56 (s, 3 H, M or N), 2.96–3.02 (m, 2 H, M or N), 3.33 (s, 3 H, M or N), 3.48–3.55 (m, 2 H, M + 2 H, N), 7.33 (d, *J* = 2.1 Hz, 1 H, M or N), 7.33 (d, *J* = 2.0 Hz, 1 H, M or N), 7.45 (d, *J* = 2.0 Hz, 1 H, M or N), 7.46 (d, *J* = 2.1 Hz, 1 H, M or N). MS (EI, 70 eV): *m*/*z* (%) = 311 (9), 137 (100). HRMS (EI): *m*/*z* calcd for $C_{13}H_{11}N_3O_2{}^{35}Cl_2$: 311.0228; found: 311.0222. **(2*E*,*Z*)-(5-Chloro-3-methoxy-2-nitrophenyl)(1-methylpyrrolidin-2-ylidene)-acetonitrile (3g)**: yellow crystals; mp 146–149 °C (EtOH). Two isomers, M (major)/ N (minor) = 1.2. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.82–1.90 (m, 2 H, N), 1.96–2.04 (m, 2 H, M), 2.44 (t, *J* = 7.8 Hz, 2 H, N), 2.57 (s, 3 H, M), 2.95–3.01 (m, 2 H, M), 3.32 (s, 3 H, N), 3.46–3.54 (m, 2 H, M + 2 H, N), 6.96–7.00 (m, 2 H, M + 2 H, N). MS (EI, 70 eV): *m*/*z* (%) = 307 (24), 137 (100). **7-Chloro-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5a)**: yellow crystals; mp 198–201 °C. ^{1}H NMR (500 MHz, THF-d_8): δ = 4.19 (s, 3 H), 6.79 (d, *J* = 3.5 Hz, 1 H), 7.65 (dd, *J* = 9.1, 2.3 Hz, 1 H), 7.86 (d, *J* = 3.5 Hz, 1 H), 8.14 (d, *J* = 9.1 Hz, 1 H), 8.19 (d, *J* = 2.3 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 34.8, 94.5, 103.4, 115.5, 123.4, 124.8, 128.8, 129.7, 132.8, 133.2, 142.4, 143.3, 152.6. MS (EI, 70 eV): *m*/*z* (%) = 241 (100), 240 (31), 179 (5). HRMS (EI): *m*/*z* calcd for $C_{13}H_8N_3{}^{35}Cl$: 241.0407; found: 241.0410. **7-Bromo-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5b)**: yellow crystals; mp 209–211 °C. ^{1}H NMR (500 MHz, THF-d_8): δ = 4.20 (s, 3 H), 6.80 (d, *J* = 3.5 Hz, 1 H), 7.78 (dd, *J* = 8.9, 2.2 Hz, 1 H), 7.88 (d, *J* = 3.5 Hz, 1 H), 8.07 (d, *J* = 8.9 Hz, 1 H), 8.36 (d, *J* = 2.2 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 33.8, 93.4, 102.4, 114.5, 120.4, 124.3, 125.7, 128.6, 130.4, 131.8, 141.6, 142.4, 151.6. MS (EI, 70 eV): *m*/*z* (%) = 287 (88), 285 (100), 205 (10), 179 (9). HRMS (EI): *m*/*z* calcd for $C_{13}H_8N_3{}^{79}Br$: 284.9902; found: 284.9911. **7-Fluoro-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5c)**: pale green crystals; mp 182–185 °C (hexane–EtOAc). ^{1}H NMR (500 MHz, THF-d_8): δ = 4.18 (s, 3 H), 6.79 (d, *J* = 3.5 Hz, 1 H), 7.53 (ddd, *J* = 9.3, 8.1, 2.8 Hz, 1 H), 7.83 (d, *J* = 3.5 Hz, 1 H), 7.84 (ddd, *J* = 9.7, 2.8, 0.5 Hz, 1 H), 8.19 (ddd, *J* = 9.3, 5.7, 0.5 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 34.8, 94.7 (d, $J_{C\text{-}F}$ = 5.9 Hz), 103.4, 107.8 (d, $J_{C\text{-}F}$ = 24.5 Hz), 115.7, 118.4 (d, $J_{C\text{-}F}$ = 26.4 Hz), 125.1 (d, $J_{C\text{-}F}$ = 10.2 Hz), 129.7, 133.8 (d, $J_{C\text{-}F}$ = 9.3 Hz), 141.6 (d, $J_{C\text{-}F}$ = 1.0 Hz), 142.1, 151.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 161.8 (d, $J_{C\text{-}F}$ = 247.8 Hz). MS (EI, 70 eV): *m*/*z* (%) = 225 (100), 197 (15), 183 (10), 171 (6). HRMS (EI): *m*/*z* calcd for $C_{13}H_8N_3F$: 225.0702; found: 225.0709. **7-Methoxy-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5d)**: yellow crystals; mp 217–218 °C (EtOAc). ^{1}H NMR (400 MHz, THF-d_8): δ = 3.99 (s, 3 H), 4.16 (s, 3 H), 6.73 (d, *J* = 3.5 Hz, 1 H), 7.32 (dd, *J* = 9.3, 2.8 Hz, 1 H), 7.45 (d, *J* = 2.8 Hz, 1 H), 7.69 (d, *J* = 3.5 Hz, 1 H), 8.03 (dd, *J* = 9.3, 0.3 Hz, 1 H). ^{13}C NMR (100 MHz, THF-d_8): δ = 34.7, 55.9, 93.8, 101.8, 103.3, 116.3, 121.5, 125.9, 129.5, 132.6, 139.8, 141.4, 150.0, 159.6. MS (EI, 70 eV): *m*/*z* (%) = 237 (100), 222 (39), 194 (69). HRMS (EI): *m*/*z* calcd for $C_{14}H_{11}N_3O$: 237.0902; found: 237.0896. **1-Methyl-7-(phenylthio)-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5e)**: yellow crystals; mp 186–188 °C (EtOAc). ^{1}H NMR (500 MHz, THF-d_8): δ = 4.16 (s, 3 H), 6.76 (d, *J* = 3.5 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.46–7.49 (m, 2 H), 7.50 (dd, *J* = 9.0, 2.0 Hz, 1 H), 7.81 (*J* = 3.5 Hz, 1 H), 8.05 (*J* = 9.0, 0.5 Hz, 1 H), 8.11 (*J* = 2.0, 0.5 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 33.8, 93.5, 102.3, 114.6, 123.6, 123.7, 127.8, 128.6, 128.7, 129.4, 130.8, 132.1, 134.2, 135.7, 140.8, 142.9, 151.1. MS (EI, 70 eV): *m*/*z* (%) = 315 (100), 299 (12), 194 (8). HRMS (EI): *m*/*z* calcd for $C_{19}H_{13}N_3S$: 315.0830; found: 315.0837. **5,7-Dichloro-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5f)**: pale brown crystals; mp 252 °C (dec.). ^{1}H NMR (500 MHz, THF-d_8): δ = 4.22 (s, 3 H), 6.91 (d, *J* = 3.5 Hz, 1 H), 7.90 (d, *J* = 2.2 Hz, 1 H), 7.96 (d, *J* = 3.5 Hz, 1 H), 8.17 (d, *J* = 2.2 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 34.8, 95.3, 103.8, 115.3, 122.8, 125.6, 128.8, 130.0, 132.2, 136.4, 139.4, 143.5, 152.7. MS (EI, 70 eV): *m*/*z* (%) = 277 (70), 275 (100). HRMS (EI): *m*/*z* calcd for $C_{13}H_7N_3{}^{35}Cl_2$: 275.0017; found: 275.0025. **7-Chloro-5-methoxy-1-methyl-1*H*-pyrrolo[3,2-*b*]quinoline-9-carbonitrile (5g)**: pale brown crystals; mp >250 °C. ^{1}H NMR (500 MHz, THF-d_8): δ = 4.06 (s, 3 H), 4.19 (s, 3 H), 6.82 (d, *J* = 3.5 Hz, 1 H), 7.08 (d, *J* = 2.0 Hz, 1 H), 7.75 (d, *J* = 2.0 Hz, 1 H), 7.83 (d, *J* = 3.5 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ = 34.7, 56.6, 94.2, 103.9, 107.8, 114.9, 115.8, 125.7, 129.7, 133.7, 136.0, 141.6, 150.9, 158.4. MS (EI, 70 eV): *m*/*z* (%) = 271 (95), 242 (100), 236 (35), 206 (11). HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}N_3O{}^{35}Cl$: 271.0512; found: 271.0519.