A convenient synthesis of 2-substituted [1,2,4]triazolo- [1,5-\(a\)]quinolines and [1,2,4]triazolo[5,1-\(a\)]isoquinolines

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Abstract
Upon reaction with aqueous potassium hydroxide and aliphatic and aromatic aldehydes 2 the salts 1,2-diaminoquinolinium tosylate 4 and 1,2-diaminoisoquinolinium tosylate 9 were converted into the corresponding 2-substituted [1,2,4]triazolo[1,5-\(a\)]quinolines 8 and [1,2,4]triazolo[5,1-\(a\)]isoquinolines 13, respectively. The formation of the final products requires aerial oxidation.

Key words: Fused [1,2,4]triazoles, 1,2-diaminoquinolinium tosylate, 1,2-diaminoisoquinolinium tosylate, 1-amino-2-iminoquinoline, 2-amino-1-iminoisoquinoline, hydrazone, ring-chain tautomerism, aerial oxidation

Introduction
We have recently reported\(^1\) that 1,2-diaminopyridinium tosylate 1 readily reacts with aldehydes 2 furnishing 2-substituted triazolo[5,1-\(a\)]pyridines 3 in moderate to good yields (Scheme 1).

Scheme 1

In continuation of this study, and pursuing our continuous interest in the synthesis of polycyclic heteroaromatic compounds we decided to explore if this straightforward ring formation procedure can be extended. In this paper we describe a successful application of this
synthetic strategy to prepare 2-substituted angularly fused benzo homologues of 3, i.e. the title ring systems 8 and 13 (Scheme 2).

Various synthetic approaches to the tricyclic system of structures 8 and 13 have been reported in the literature. The pyridine and triazole rings of [1,2,4]triazolo[1,5-a]quinolines 8 have been prepared by ring closure and cycloaddition reactions: The construction of the pyridine ring by formation of bond 5-C/5a-C bond has been reported in a patent.2 The triazole ring has resulted from the formation of bonds 1-N/10-N, 3 2-C/3-N, 4 and 3-N/3a-C. 5 In the course of the [3+2] cycloaddition reaction of 1H-[1,2]benzodiazepine with benzonitrile oxide the bonds 1-N/2-C and 3-N/3a-C were formed in one step affording 8e. 6 Both heterocyclic moieties of 8 were obtained in an obviously geared double condensation reaction forming bonds 3a-C/10-N and 4-C/5-C, 7 and by the intramolecular cycloaddition reaction of an in situ generated nitrile imine functionality with a nitrile group providing the 3a-C/10-N and 2-C/3-N bonds. 8 The isomeric [1,2,4]triazolo[5,1-a]isoquinolines 13 have been accessed by building up the triazole moiety by either ring closure or [3+2] cycloaddition reactions. The formation of bonds 3-N/4-N, 9 1-N/10b-C, 5,10,11 and 2-C/3-N12 has been reported. In a [3+2] cycloaddition reaction of azomethine imines (in situ generated by deprotonation of 2-aminoisoquinolines) with nitriles bonds 1-N/10b-C and 2-C/3-N have been formed concomitantly.13-16 Some of these compounds, in particular, 2-aryl-substituted [1,2,4]triazolo[5,1-a]isoquinolines 13 have received considerable attention because of biological activities; e.g. 13e or 13 (R = 4-ClC₆H₄, Lotrifien) are nonhormonal antifertility agents.17, 18

Results and Discussion

Here we report the formation of the tricyclic structures 8 and 13 in the course of the condensation reaction of 1,2-diaminoquinoline 5 or -isoquinoline 10 with an aldehyde forming two bonds 1-N/2-C and 2-C/3-N of the triazole ring. The starting compounds of this reaction, 1,2-diaminoquinolinium tosylate 419 and 1,2-diaminoisoquinolinium tosylate 919 are readily available from 2-aminoquinoline and 1-aminoisoquinoline by direct N-amination procedure using O-tosylhydroxylamine20 according to our previously published procedure. 21 When a solution of the tosylates 4 or 9 in methanol is mixed with an aliphatic or aromatic aldehyde 2 and treated with aqueous potassium hydroxide at room temperature the respective 2-substituted fused [1,2,4]triazoles 8 and 13 are obtained within a few hours (Scheme 2). In some cases the crystalline products 8 and 13 precipitate from the reaction mixture and are collected by filtration (Method A). Alternatively, the products are isolated upon extraction from the reaction mixture with dichloromethane (Method B). The yields of the tricyclic products 8 (69-95%) and 13 (57-86%) are generally very good. It is interesting to note that these yields are significantly higher than those found for the bicyclic ring system 3. 1 The higher conversion rates may be due to the enhanced stability of the imino-amino bases 5 and 10 which – in contrast to the quite unstable conjugate base formed from 1 – have been isolated as stable crystalline compounds.
The reaction proceeds via the in situ generation of the free bases 1-amino-2-iminoquinoline 5 and 2-amino-1-iminoisoquinoline 10, respectively. This has been proved by separate experiments with these compounds reacting with benzaldehyde 2c and affording the fused [1,2,4]triazoles 8c and 13c, respectively. Thus the free base 5 or 10 reacts with aldehydes 2 to give the condensation products 6 and 11, respectively. These hydrazones 6 and 11 are presumed to coexist in an equilibrium with ring chain tautomers, the corresponding dihydrotriazole derivatives 7 and 12 which, in turn, upon dehydrogenation induced by air oxidation yield the final heteroaromatic products 8 and 13, respectively. Oxygen from air is required for this oxidation step. This has been proved by carrying out the reaction of 2-amino-1-iminoisoquinoline 10 with benzaldehyde 2c under exclusion of air. After 6 h no product 2-phenyl[1,2,4]triazolo[5,1-α]isoquinoline 13c could be detected. When this reaction mixture was stirred and exposed to air the product 13c was isolated in virtually the same yield as following Procedure A.

Scheme 2

The structures of products 8 and 13 were confirmed by 1H and 13C NMR spectra. The assignment of the significant signals is according to a two-dimensional NMR study on
[1,2,4]triazolo[1,5-f]phenanthridines, a tetracyclic system that has embedded both tricyclic structures 8 and 13. The 1H NMR spectra of the quinoline derivatives 8 exhibit the doublet signal of 9-H at lowest field (δ 8.40–8.62). The isoquinoline derivatives 13 show the AB system of 5-H and 6-H at of δ 7.11–7.33 and δ 8.22–8.38, respectively; the signal of 10-H appears in the range of δ 8.53–8.74. On the basis of the NMR data established for [1,2,4]triazolo[1,5-f]phenanthridines most of the significant 13C NMR data of compounds 8 and 13 have been assigned.

Further investigation on the application of this triazole ring closure strategy is in progress and is currently extended to 2,3-diaminoisoquinolines 14 (Scheme 2) aiming at the preparation of linearly fused [1,2,4]triazolo[1,5-b]isoquinolines.

**Experimental Section**

**General Procedures.** Melting points were determined with a Büchi apparatus. IR spectra were recorded with a Nicolet 205 FT spectrometer, NMR spectra were recorded on a Varian VXR-200 (200 MHz 1H NMR) spectrometer, and mass spectra were measured with a MS-902 instrument (70 eV).

**1,2-Diaminoquinolinium tosylate (4).** To a stirred solution of quinolin-2-ylamine (0.5 g, 3.5 mmol) in dichloromethane (5 mL) was added a solution of O-tosylhydroxylamine (0.7 g, 3.9 mmol) in dichloromethane (5 mL) at rt. Within a few minutes a precipitate began to separate. The product was filtered off and recrystallized from methanol to give colorless crystals 4 (0.984 g, 85%); mp 219–222 °C. IR (KBr): 3310, 3240, 3180, 1670, 1640, 1600, 1520, 1500, 1450, 1230, 1170, 1120, 1030, 1100, 820, 760, 680 cm⁻¹; 1H NMR (DMSO-d₆): δ 2.27 (s, 3H, CH₃), 6.4 (s, 2H, NH₂), 7.07, 7.12 (AA', 2H, 3,5-H C₆H₄), 7.16 (d, J = 9.4 Hz, 1H, 3-H), 7.45, 7.49 (XX', 2H, 2,6-H C₆H₄), 7.52 (dd, J = 7.6, 8.0 Hz, 1H, 6-H), 7.87 (dd, J = 7.6, 8.4 Hz, 1H, 7-H), 8.04 (d, J = 8.4 Hz, 1H, 8-H), 8.30 (d, J = 9.4 Hz, 1H, 4-H), 9.15 (br s, 2H, NH₂). 13C NMR (DMSO-d₆): δ 20.97, 113.88, 115.99, 121.94, 125.34, 125.65, 128.25, 129.45, 132.70, 137.87, 139.58, 141.24, 155.73. Anal. Calcd. for C₁₇H₁₇N₃O₃S (331.40): C, 57.99; H, 5.17; N, 12.68. Found: C, 57.69; H, 5.05; N, 12.46.

**1,2-Diaminoisoquinolinium tosylate (9).** Applying the same protocol as described before to isoquinolin-1-ylamine (0.5 g, 3.5 mmol) afforded colorless crystals 9 (1.008 g, 87%); mp 218–220 °C (methanol). IR (KBr): 3300, 3240, 3180, 1670, 1640, 1600, 1510, 1480, 1230, 1170, 1120, 1020, 1000, 800, 670 cm⁻¹; 1H NMR (DMSO-d₆): δ 2.25 (s, 3H, CH₃), 6.8 (s, 2H, NH₂), 7.07, 7.12 (AA’, 2H, 3,5-H C₆H₄), 7.1–7.9 (m, 4H, 5,6,7,8-H), 7.45, 7.49 (XX’, 2H, 2,6-H C₆H₄), 8.55 (d, J = 6.4 Hz, 1H, 3-H), 9.25 (br s, 2H, NH₂). 13C NMR (DMSO-d₆): δ 20.76, 110.90, 117.81, 125.46, 125.58, 127.62, 128.07, 128.76, 134.13, 134.45, 134.86, 137.71, 145.53, 154.00. Anal. Calcd. for C₁₇H₁₇N₃O₃S (331.40): C, 57.99; H, 5.17; N, 12.68. Found: C, 57.65; H, 5.13; N, 12.57.
General procedures For the Synthesis of Triazoles 8 and 13.

Procedure A. An aqueous solution (14 mL) of potassium hydroxyde (2.8 g, 50 mmol) was added to a solution of 1,2-diamoquinolinium tosylate (4) or 1,2-diaminoisoquinolinium tosylate (9) (1.66 g, 5 mmol) and aldehyde 2 (7 mmol) in methanol (50 mL). Upon stirring the reaction solution in an open flask at rt for 3-5 min a precipitate appeared. After 1 h the precipitate formed was filtered off and washed with methanol (5 mL). This procedure was repeated in 1 h intervals until no more precipitate was formed and the filtrate remained as a clear solution. The combined crop of solid material was washed with water and dried in a desiccator. Recrystallization from an appropriate solvent provided the pure crystalline products 8 and 13, respectively.

Procedure B. The reaction mixture of the 1,2-diamoquinolinium tosylate (4) or 1,2-diaminoisoquinolinium tosylate 9 (1.66 g, 5 mmol), the aldehyde 2 (20 mmol) in methanol (50 mL) and an aqueous solution (14 mL) of potassium hydroxyde (2.8 g, 50 mmol) was stirred in an opened flask at rt for 6 h. The reaction solution was then poured into water (100 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed until neutral and dried over sodium sulfate. The residue after evaporation of the solvent was purified by column chromatography on silica gel with diethyl ether. Removal of the eluent solvent from the appropriate fractions furnished the solid product on cooling or on standing. Recrystallization from petroleum ether or n-hexane gave the pure product.

2-Methyl[1,2,4]triazolo[1,5-a]quinoline (8a). Procedure B. Colorless crystals, 0.78 g (85%); mp 77 °C (n-hexane). IR (KBr,): 1618 (s), 1561, 1537, 1490, 1486, 1453, 1306 (s), 826, 759, 753 cm⁻¹; ¹H NMR (CDCl₃): δ 2.67 (s, 3H, CH₃), 7.44–7.84 (m, 5H, 4,5,6,7,8-H), 8.41 (d, J = 8.4 Hz, 1H, 9-H); ¹³C NMR (CDCl₃): δ 14.4 (CH₃), 114.4 (CH), 115.6 (CH), 122.8 (5a-C), 125.1 (CH), 128.5 (CH), 129.9 (CH), 130.2 (CH), 133.4 (9a-C), 149.4 (3a-C), 162.8 (2-C). Anal. Calcd. for C₁₁H₉N₃ (183.21): C, 72.11; H, 4.95; N, 22.94. Found: C, 72.38; H, 4.97; N, 22.30.

2-Propyl[1,2,4]triazolo[1,5-a]quinoline (8b). Procedure B. Colorless crystals (0.91 g, 86%); mp 47 °C (n-hexane). IR (KBr): 2962, 1617 (s), 1538, 1483, 1330, 1312, 815 (s), 760 cm⁻¹; ¹H NMR (CDCl₃): δ 1.07 (t, J = 7.4 Hz, 3H, CH₃), 1.96 (qt, J = 7.4 Hz, 2H, CH₂CH₃), 2.97 (t, J = 7.4 Hz, 2H, 2-CCH₂), 7.36–7.77 (m, 5H, 4,5,6,7,8-H), 8.40 (d, J = 8.4 Hz, 1H, 9-H); ¹³C NMR (CDCl₃): δ 13.8 (CH₃), 21.7 (CH₂CH₃), 30.6 (2-CH₂), 114.4 (CH), 115.5 (CH), 122.7 (5a-C), 124.9 (CH), 128.3 (CH), 129.7 (CH), 129.9 (CH), 133.3 (9a-C), 149.1 (3a-C), 166.3 (2-C). Anal. Calcd. for C₁₃H₁₃N₃ (211.26): C, 73.91; H, 6.20; N, 19.89. Found: C, 74.47; H, 6.37; N, 19.76.

2-Phenyl[1,2,4]triazolo[1,5-a]quinoline (8c). Procedure A. Colorless crystals (1.09 g, 89%); mp 142 °C (ethanol/water 4:1; lit. mp 137–139 °C). IR (KBr): 1620, 1561, 1544, 1459, 1453 (s), 1441, 1333, 834, 767, 750, 718, 717, 699, 686 cm⁻¹; ¹H NMR (CDCl₃): δ 7.36–7.77 (m, 5H, 4,5,6,7,8-H), 8.36 (dd, J = 8.2, 2.0 Hz, 2H, 1-H C₆H₅), 8.57 (dd, J = 8.4, 0.6 Hz, 1H, 9-H); ¹³C NMR (CDCl₃): δ 114.8 (CH), 116.0 (CH), 123.1 (5a-C), 125.5 (CH), 127.1 (2-C or 3,5-C C₆H₅), 128.6 (3C, 1-C, 2-C or 3,5-C C₆H₅), 129.8 (CH), 130.1 (CH), 130.7 (CH), 130.9 (4-C C₆H₅), 133.7 (9a-C), 149.8 (3a-C), 163.2 (2-C). Anal. Calcd. for C₁₆H₁₁N₃ (245.28): C, 78.35; H, 4.52; N, 17.13. Found: C, 78.25; H, 4.62; N, 17.03. Following Procedure A and using 1-amino-2-
iminoquinoline (5)\textsuperscript{22} (0.80 g, 5 mmol) and water (11 mL, instead of an aqueous potassium hydroxide solution) afforded after 6 h \textsuperscript{8c} (0.90 g, 73%).

2-(4-Methylphenyl)[1,2,4]triazolo[1,5-\textit{a}]quinoline (8d). Procedure A. Colorless crystals, 1.02 g (78%); mp 191 °C (ethanol). IR (KBr): \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textsuperscript{13}C NMR (CDCl\textsubscript{3}): Anal. Calcd. for C\textsubscript{17}H\textsubscript{13}N\textsubscript{3} (259.31): C, 78.74; H, 5.05; N, 16.20. Found: C, 78.54; H, 5.09; N, 16.13.

2-(4-Methoxyphenyl)[1,2,4]triazolo[1,5-\textit{a}]quinoline (8e). Procedure A. Colorless crystals, 0.96 g (69%); mp 146 °C (ethanol/water 3:1). IR (KBr): \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textsuperscript{13}C NMR (CDCl\textsubscript{3}): Anal. Calcd. for C\textsubscript{17}H\textsubscript{13}N\textsubscript{3}O (275.30): C, 74.17; H, 4.76; N, 15.26. Found: C, 74.13; H, 4.59; N, 15.18.

2-(4-Nitrophenyl)[1,2,4]triazolo[1,5-\textit{a}]quinoline (8f). Procedure A. Yellowish needles, 1.38 g (95%); mp 279 °C (DMF). IR (KBr): \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textsuperscript{13}C NMR (CDCl\textsubscript{3}): Anal. Calcd. for C\textsubscript{16}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2} (290.28): C, 66.32; H, 3.34; N, 19.11.

2-Styryl[1,2,4]triazolo[1,5-\textit{a}]quinoline (8g). Procedure A. Yellowish needles, 1.11 g (81%); mp 175 °C (ethanol). IR (KBr): \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textsuperscript{13}C NMR (CDCl\textsubscript{3}): Anal. Calcd. for C\textsubscript{18}H\textsubscript{13}N\textsubscript{3} (271.32): C, 79.66; H, 4.69; N, 15.40.

2-Methyl[1,2,4]triazolo[5,1-\textit{a}]isoquinoline (13a).\textsuperscript{27, 28} Procedure B. Colorless crystals, 0.52 g (57%); mp 84 °C (n-hexane; lit.\textsuperscript{27} mp 88–89 °C; lit.\textsuperscript{28} mp 86.5–88 °C). IR (KBr): 1639, 1524 (s), 1490, 1474, 1461, 1445, 1311, 963, 832, 754 (s), 687 cm\textsuperscript{-1}. IR (KBr): 1639, 1524 (s), 1490, 1474, 1461, 1445, 1311, 963, 832, 754 (s), 687 cm\textsuperscript{-1}. IR (KBr): 1639, 1524 (s), 1490, 1474, 1461, 1445, 1311, 963, 832, 754 (s), 687 cm\textsuperscript{-1}.
(86%); mp 58 °C (petroleum ether). IR (KBr): 2936, 1638, 1530, 1527, 1471, 1434, 1373, 1285, 800 (s), 752, 706 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.06 (t, \(J = 7.4\) Hz, 3H, CH\(_3\)), 1.95 (qt, \(J = 7.4\) Hz, 2H, 2\(\text{CH}_{2}\)), 2.96 (t, \(J = 7.4\) Hz, 2H, 2\(\text{CH}_{2}\)), 7.11 (d, \(J = 7.4\) Hz, 1H, 6-H), 7.60–7.75 (m, 3H, 7,8,9-H), 8.22 (d, \(J = 7.2\) Hz, 1H, 5-H), 8.55–8.60 (m, 1H, 9-H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 13.8 (CH\(_3\)), 21.8 (CH\(_{2}\)), 30.6 (2-CH\(_{2}\)), 113.1 (CH), 121.7 (6a-C), 123.9 (CH), 124.1 (CH), 126.8 (CH), 128.0 (CH), 129.4 (CH), 131.0 (10a-C), 149.4 (10b-C), 166.0 (2-C). Anal. Calcd. for C\(_{13}\)H\(_{13}\)N\(_3\) (211.26): C, 73.91; H, 6.20; N, 19.89. Found: C, 74.53; H, 6.22; N, 19.77.

2-Phenyl[1,2,4]triazolo[5,1-a]isoquinoline (13c).\(^{27}\) Procedure A. Colorless needles, 1.03 g (84%); mp 160 °C (ethanol/water 4:1; lit. 27 mp 157–158 °C). IR (KBr): 1638, 1518, 1461, 1450, 1440, 1421, 1364, 1355, 1250, 1126, 816, 749, 719 (s), 685 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.17 (d, \(J = 7.2\) Hz, 1H, 6-H), 7.41–7.78 (m, 6H, 7,8,9-H and 3,4,5-H C\(_6\)H\(_5\)), 8.30 (d, \(J = 7.8\) Hz, 1H, 5-H), 8.34 (dd, \(J = 7.8\) Hz, 1.8 Hz, 2H, 2,6-H C\(_6\)H\(_5\)), 8.65–8.70 (m, 1H, 10-H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 113.8 (CH), 122.2 (6a-C), 124.3 (CH), 124.5 (CH), 127.1 (3C), 128.3 (CH), 128.6 (2C), 129.7 (CH), 129.8 (CH), 131.0 (1-C C\(_6\)H\(_5\)), 131.2 (10a-C), 150.1 (10b-C), 163.2 (2-C). Anal. Calcd. for C\(_{16}\)H\(_{11}\)N\(_3\) (245.28): C, 78.35; H, 4.52; N, 17.13. Found: C, 79.44; H, 4.53; N, 17.22. Following Procedure A and using 1-amino-2-iminoquinoline (10)\(^{23}\) (0.80 g, 5 mmol; instead of the tosylate 8) and water (11 mL; instead of an aqueous potassium hydroxide solution) after 6 h afforded 13c (0.98 g, 80%). When this reaction was carried out under exclusion of air in a closed reaction flask no product precipitated after 6 h. After opening the flask and continued stirring 13c precipitated within 2 h and was isolated by filtration (0.97 g, 79%).

2-(4-Methylphenyl)[1,2,4]triazolo[5,1-a]isoquinoline (13d).\(^{27}\) Procedure A. Colorless crystals, 1.11 g (85%); mp 204 °C (ethanol/water 4:1). IR (KBr): 1637, 1517, 1457 (s), 1436, 1346, 1251, 1181, 1125, 898, 826, 819, 742 (s), 708 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.42 (s, 3H, CH\(_3\)), 7.18 (d, \(J = 7.4\) Hz, 1H, 6-H), 7.29, 7.33 (AA’, 2H, 3,5-H C\(_6\)H\(_4\)), 7.62–7.80 (m, 3H, 7,8,9-H), 8.21, 8.25 (XX’, 2H, 2,6-H C\(_6\)H\(_4\)), 8.31 (d, \(J = 7.4\) Hz, 1H, 5-H), 8.66–8.71 (m, 1H, 10-H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 21.4 (CH\(_3\)), 113.7 (CH), 122.2 (6-C), 124.3 (CH), 124.5 (CH), 127.1 (3,5-C C\(_6\)H\(_4\), CH), 128.3 (CH), 129.4 (2,6-C C\(_6\)H\(_4\)), 129.7 (CH), 131.3 (10a-C), 139.8 (4-C C\(_6\)H\(_4\)), 150.1 (10b-C), 163.4 (2-C). Anal. Calcd. for C\(_{17}\)H\(_{13}\)N\(_3\) (259.31): C, 78.74; H, 5.05; N, 16.20. Found: C, 78.94; H, 4.96; N, 16.14.

2-(4-Methoxyphenyl)[1,2,4]triazolo[5,1-a]isoquinoline (13e).\(^{27}\) Procedure A. Colorless crystals, 0.99 g (72%); mp 162 °C (ethanol/water 4:1). IR (KBr): 1613, 1519, 1457 (s), 1438, 1410, 1363, 1346, 1251, 1181, 1125, 898, 826, 819, 742 (s), 708 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 3.85 (s, 3H, CH\(_3\O)) 6.99, 7.04 (AA’, 2H, 3,5-H C\(_6\)H\(_4\)), 7.14 (d, \(J = 7.4\) Hz, 1H, 6-H), 7.62–7.76 (m, 2H, 7-H, 8- or 9-H), 7.70–7.77 (m, 1H, 8-or 9-H), 8.24, 8.29 (XX’, 2H, 2,6-H C\(_6\)H\(_4\)), 8.27 (d, \(J = 7.2\) Hz, 1H, 5-H), 8.63–8.68 (m, 1H, 10-H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 55.2 (CH\(_3\O)), 113.5 (CH), 114.0 (3,5-C C\(_6\)H\(_4\)), 122.1 (6-C), 123.6 (1-C C\(_6\)H\(_4\)), 124.3 (CH), 124.4 (CH), 127.1 (CH), 128.1 (CH), 128.5 (2,6-C, C\(_6\)H\(_4\)), 129.6 (CH), 131.2 (10a-C), 150.0 (10b-C), 160.9 (4-C C\(_6\)H\(_4\)), 163.1 (2-C). Anal. Calcd. for C\(_{17}\)H\(_{13}\)N\(_3\)O (275.30): C, 74.17; H, 4.76; N, 15.26. Found: C, 74.33; H, 4.62; N, 15.26.

2-(4-Nitrophenyl)[1,2,4]triazolo[5,1-a]isoquinoline (13f).\(^{27}\) Procedure A. Yellowish crystals, 1.20 g (83%); mp 282 °C (DMF). IR (KBr): 1639, 1604, 1527 (s), 1519 (s), 1456, 1440, 1368,
1341 (s), 1307, 862, 854, 800, 755, 723 (s) cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 7.33 (d, $J = 7.4$ Hz, 1H, 6-H), 7.75–7.20 (m, 2H, 7-H, 8- or 9-H), 7.84–7.91 (m, 1H, 8- or 9-H), 8.34, 8.37 (AA’, 2H, 3,5-H C$_6$H$_5$), 8.38 (d, $J = 7.2$ Hz, 1H, 5-H), 8.51, 8.55 (BB’, 2H, 2,6-H C$_6$H$_5$), 8.69–8.74 (m, 1H, 10-H); MS (EI) $m/z$ (%): 290 (100, M$^+$), 244 (33, M –NO$_2$), 128 (19, C$_9$H$_6$N). Anal. Calcd. for C$_{16}$H$_{10}$N$_4$O$_2$ (290.28): C, 66.20; H, 3.47; N, 19.30. Found: C, 66.84; H, 3.38; N, 19.21.

2-Styryl[1,2,4]triazolo[5,1-a]isoquinoline (13g). Procedure A. Yellowish crystals, 1.14 g (84%); mp 156 °C (ethanol/water 4:1). IR (KBr): 1524, 1500, 1461, 1437, 1373, 982, 970, 792 (s), 783, 759, 754, 695 (s), 686 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 7.15 (d, $J = 7.2$ Hz, 1H, 6-H), 7.27 (d, $J = 16.4$ Hz, 1H, =C=CH$_2$), 7.26–7.43 (m, 3H, H arom), 7.60–7.78 (m, 5H, H arom), 7.89 (d, $J = 16.4$ Hz, 1H, 2-CH=), 8.24 (d, $J = 7.2$ Hz, 1H, 5-H), 8.61-8.66 (m, 1H, 10-H); $^{13}$C NMR (CDCl$_3$): $\delta$ 113.8 (CH), 117.7 (CH), 121.9 (6a-C), 124.3 (CH), 124.2, 127.1 (2CH$_{Ph}$), 127.1 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH$_{Ph}$), 129.8 (CH), 131.3 (10a-C), 135.7 (CH), 136.3 (C$_{Ph}$), 149.8 (10b-C), 162.6 (2-C). Anal. Calcd. for C$_{18}$H$_{13}$N$_3$ (271.32): C, 79.68; H, 4.83; N, 15.49. Found: C, 80.33; H, 4.82; N, 15.52.

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