Oxidative Heterocyclization of 2-Alkynylbenzaldehydes with 1,2-Phenylenediamine

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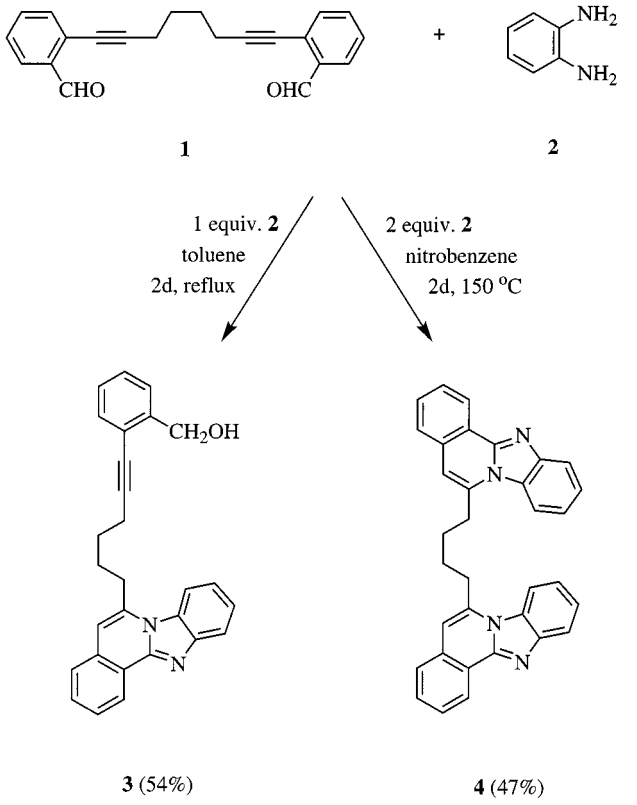
Upon condensation of *ortho*-phenylenediamine (**2**) with *ortho*-alkynylbenzaldehydes in nitrobenzene, oxidative cyclizations are observed, which result in benzimidazo[2,1-*a*]isoquinolines **(8)** or isoindolo[2,1-*a*]quinoxalines **(9)** depending on the influence of additional substituents at the alkyne.

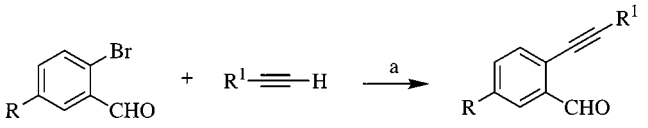
Introduction

Aryl-substituted carbonyl compounds with an alkynyl group in the *ortho*-position, and their imino derivatives, are prone to undergo cyclization reactions, especially when aromatic intermediates or products are formed thereby.[1] Recently, we described a rearrangement reaction based on such an initial cyclization of a bis(alkynyl)benzil.[2] In the case of the condensation reaction of the bis(aldehyde) **1** with one equivalent of *ortho*-phenylene diamine (**2**) we originally intended to test the feasibility of the formation of a macrocyclic bis(imine) and were surprised to find the benzimidazo[2,1-*a*]isoquinoline **(3)** as the main product (Scheme 1): obviously a disproportionation had taken place, with the oxidation of one aldehyde carbon atom, presumably after the condensation with **2**, and the reduction of the other one to give a hydroxymethyl group.[3] This result suggests that an external oxidizing agent should enhance the formation of the benzimidazoisoquinoline moiety and, indeed, with two equivalents of **2** and with nitrobenzene[4] as the solvent we could isolate **4** as the product of a twofold oxidative heterocyclization. In this article we report on the scope and limitations and present a mechanistic interpretation of this type of heterocyclization.

The formation of the benzimidazo[2,1-*a*]isoquinoline moiety is not without precedent: Sun and LaVoie[1b] described a related annulation reaction of a functionalized benzimidazole, but catalyzed by palladium acetate. In order to test the scope and limitations of our oxidative heterocyclization we synthesized the 2-alkynylbenzaldehydes **7** as model compounds by a Sonogashira coupling reaction.[5] Starting from the 2-bromobenzaldehydes **5** and various terminal alkynes **6** moderate to good yields were obtained (Scheme 2), accept for 2-ethynylpyridine **(6c)**. In this case the yield dropped below 20%, but nevertheless gave sufficient material for our purposes.



Scheme 1. Condensation of phenylenediamine **2** with bis(aldehyde) **1** under neutral and under oxidative conditions



5.1: R = H	**6a**: R^1 = *n*-butyl	**7.1a** (47%)
	6b: R^1 = phenyl	**7.1b** (88%)
	6c: R^1 = 2-pyridyl	**7.1c** (19%)
	6d: R^1 = 2-furyl	**7.1d** (54%)
	6e: R^1 = 2-(5-methylfuryl)	**7.1e** (61%)
	6f: R^1 = 2,4-dimethoxyphenyl	**7.1f** (55%)
5.2: R = OH	**6b**: R^1 = phenyl	**7.2b** (26%)

Scheme 2. Reaction conditions: a. 1 mol-% $Pd(OAc)_2$, 2 mol-% PPh_3, 1.4–2 mol-% CuI (none in case of **7.2b**), Et_3N, Ar, 80 °C, 10 h

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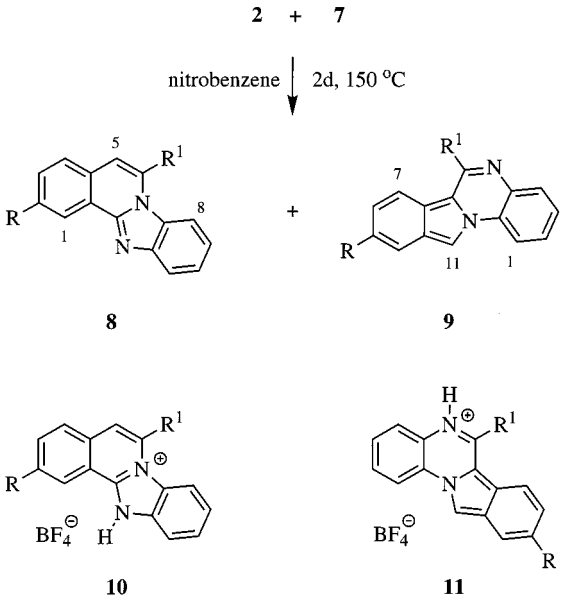
The oxidative cyclization of the functionalized aldehydes **7** with *ortho*-phenylene diamine (**2**) in nitrobenzene led, as expected, to the formation of the benzimidazo[2,1-*a*]isoquinolines **8** in up to 88% yield (Scheme 3, Table 1). In the ^{1}H NMR spectra of **8** and of the corresponding HBF_4 salts **10** the signal of the "bay region" proton 1-H is shifted to relatively low field at 8.9 ppm; only in the case of **8.2b**, with the additional hydroxyl-substituent in the 2-position, is the signal of 1-H seen at 8.06 ppm. For those benzimidazoisoquinolines **8** and **10** with an aryl-substituent in the 6-position the signal of 8-H is found at remarkably high field between 6.39 and 6.66 ppm. This can be explained by an anisotropic up-field shift of about 1.5 ppm relative to the butyl-substituted derivative **8.1a** and indicates a perpendicular conformation of the aryl-substituent. This special geometry was confirmed by the X-ray structure of **10.1b** (Figure 1, a).[6]



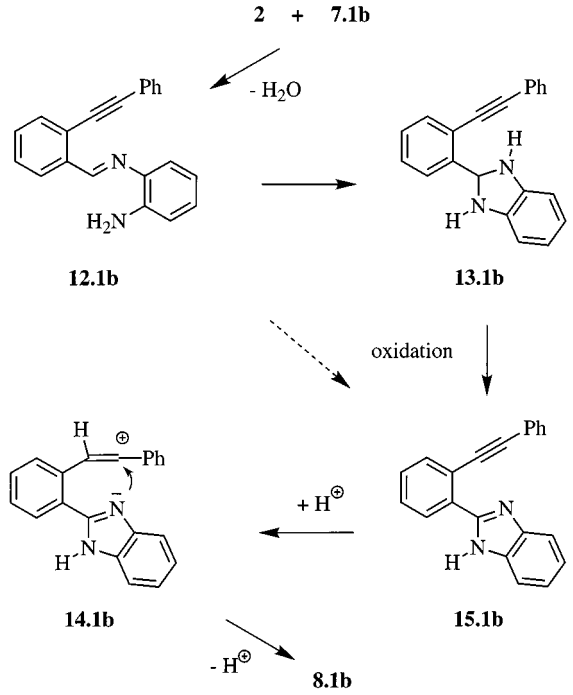
Scheme 3. Oxidative cyclization of functionalized benzaldehydes **7** with *ortho*-phenylene diamine (**2**) and corresponding HBF_4 salts of the cyclization products

Table 1. Yields and product ratio of benzimidazo[2,1-*a*]isoquinolines **8** and isoindolo[2,1-*a*]quinoxalines **9** (product ratio based on ^{1}H NMR spectrum of the crude product)

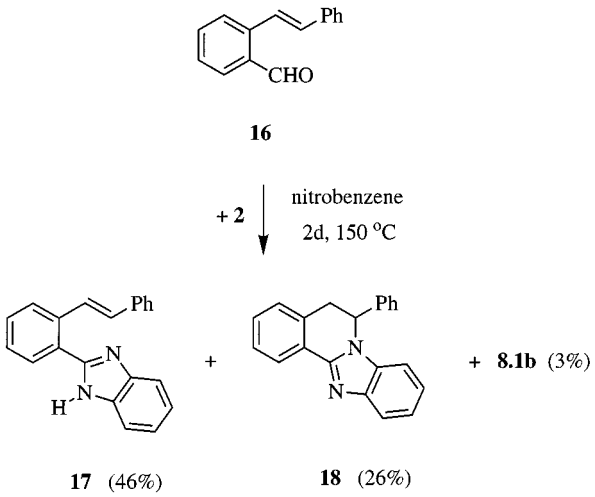
Entry	R	R^1	Products	Yield [%]	Ratio
1	H	*n*-butyl	**8.1a/9.1a**	46	100:0
2	H	phenyl	**8.1b/9.1b**	83	100:0
3	H	2-pyridyl	**8.1c/9.1c**	38	100:0
4	H	2-furyl	**8.1d/9.1d**	44	7:93
5	H	2-(5-methylfuryl)	**8.1e/9.1e**	55	9:91
6	H	2,4-dimethoxyphenyl	**8.1f/9.1f**	64	100:0
7	OH	phenyl	**8.2b/9.2b**	88	100:0

Exclusively in cases where **7** had a furyl substituent connected to the alkyne, the isoindolo[2,1-*a*]quinoxalines **9** became the main products of the heterocyclization (Table 1, entries 4 and 5). Since these hetarenes are rather sensitive they were characterized as their HBF_4 salts **11**. From **11.1e** with a methylfuryl substituent we obtained single crystals suitable for an X-ray structure analysis,[6] which revealed that, in contrast to **10.1b**, the aryl substituent prefers an almost coplanar confirmation in the solid state (Figure 1, b). The same seems to be true for the preferred conformation in solution: in the ^{1}H NMR spectrum of **11.1e** the signal of H-7 is observed at 8.33 ppm which is in agreement with an anisotropic down-field shift of the neighbouring aryl-group.

Our mechanistic considerations for the formation of the benzimidazoisoquinolines **8** are exemplified with the phenyl derivative **8.1b** (Scheme 4). We assume that the benzimidazole **15.1b** is formed as a key intermediate either directly during oxidation of the Schiff base **12.1b** or by oxidation of the *N*,*N*-acetal **13.1b**. The oxidation with nitrobenzene should take place via radical cations as described in the



Scheme 4. Proposed mechanistic pathway to benzimidazo[2,1-*a*]isoquinoline **8.1b**



Scheme 5. Products of the oxidative cyclization of functionalized stilbene **16** with *ortho*-phenylenediamine (**2**)

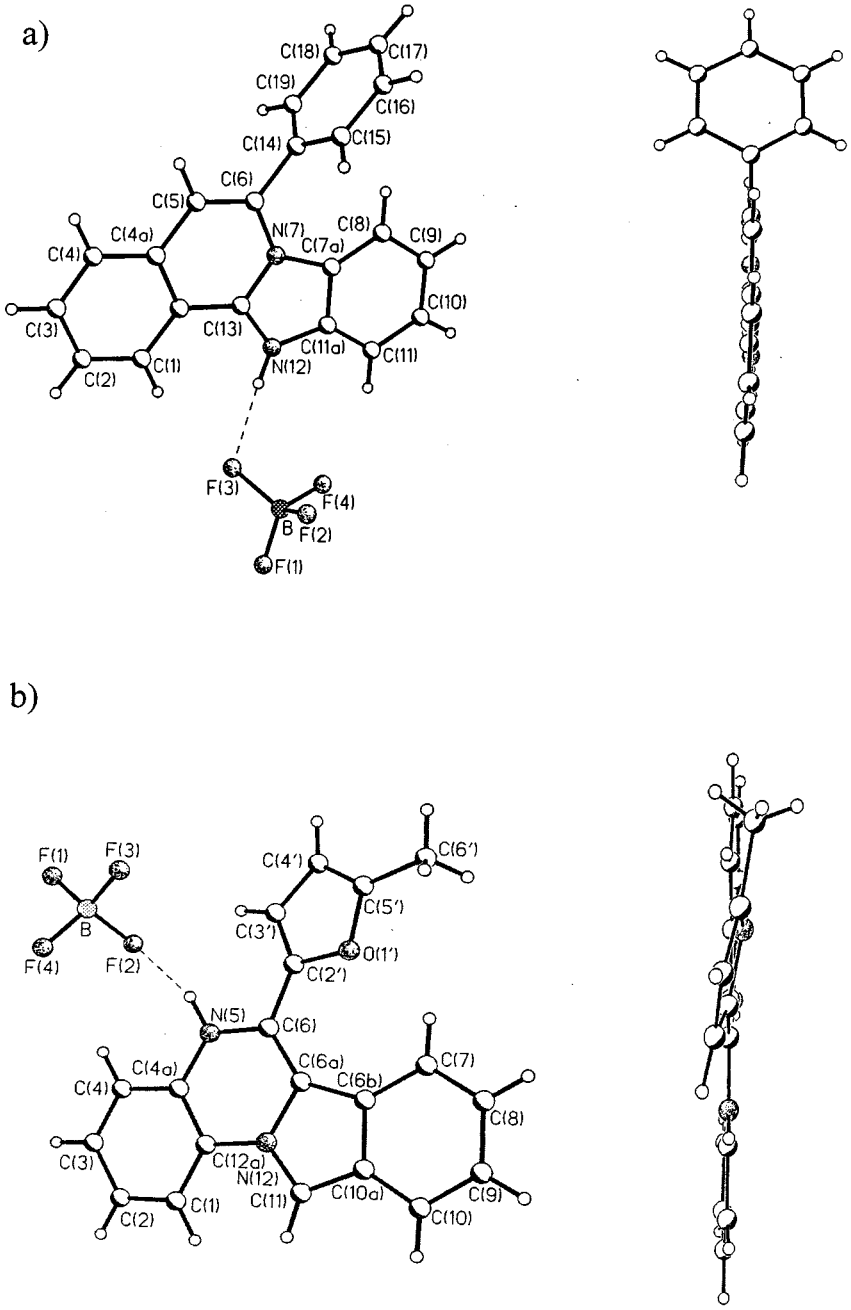
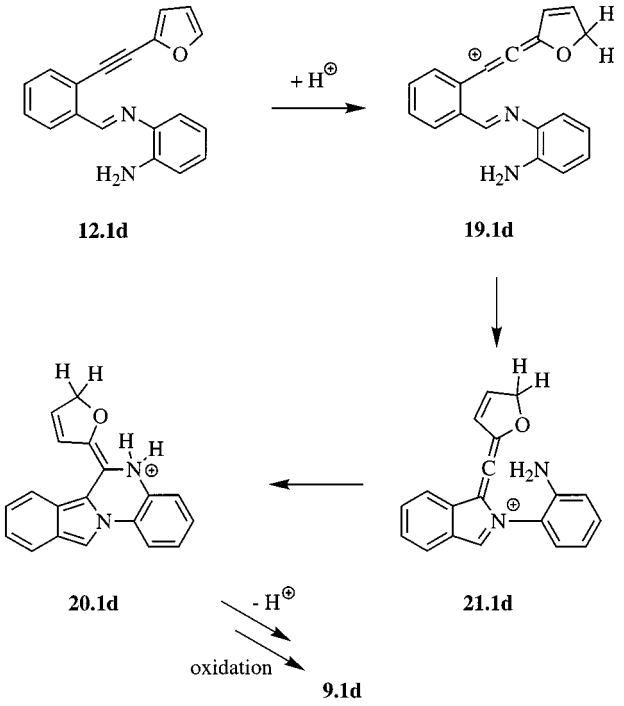


Figure 1. Perspective views of the X-ray structures of a) **10.1b** and b) **11.1e**

literature.[4] Presumably the final cyclization is initialized by protonation of the alkyne to give the vinylic cation **14.1b**. This mechanistic scheme is further supported by the result of the related oxidative condensation of the stilbene derivative **16** with **2** (Scheme 5). In this case we could isolate both the imidazole **17** and its annulation product **18**; the latter is slowly oxidized under the reaction conditions to give the final product **8.1b**.

In order to explain the formation of isoindoloquinoxalines **9** it is important to ascertain that the unique behaviour of the furyl-substituted starting materials **7.1d** and **7.1e** is not due to their influence as electron-rich +M-substituents with the similar electron-rich 2,4-dimethoxyphenyl substituent no quinoxaline is observed (Table 1, entry 6). Therefore we assume that, in the case of the furyl-substituted starting materials **7.1d** and **7.1e**, the cyclization at the alkyne is initiated by protonation of the furan ring rather than by protonation of the alkyne itself (Scheme 6). The first cyclization of the cationic intermediate **19.1d** leads to the formation of the isoindole moiety; **21.1d** is then activated for a second cyclization to give **20.1d**. The subsequent deprotonation and oxidation is a reasonable pathway to the observed product **9.1d**.

In summary, we have developed a domino process to benzimidazo[2,1-*a*]isoquinolines **(8)** and, in special cases, to isoindolo[2,1-*a*]quinoxalines **(9)**, thus proving once more



Scheme 6. Proposed mechanistic pathway to isoindolo[2,1-*a*]quinoxaline **9.1d**

the feasibility of annelation reactions of *ortho*-functionalized arylalkynes.

Experimental Section

General: m.p. (uncorrected): Reichert Thermovar. – IR: Perkin–Elmer 983. – UV: Perkin–Elmer 554. – NMR: Bruker DRX 500, Bruker WM 300; ^{1}H NMR spectra (500 MHz or 300 MHz) were recorded in $CDCl_3$ (unless otherwise stated) with TMS as the internal standard; ^{13}C NMR spectra (125.8 MHz or 75.5 MHz) were recorded in $CDCl_3$ which was also used as the internal standard (unless otherwise stated). – MS: MAT 311A (70 eV). – For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV254" from Macherey–Nagel were used. 2-Ethynylpyridine (**6c**) was bought from Lancaster and used without further purification.

2-Alkynylbenzaldehydes 1 and 7. – General Procedure: A mixture of the terminal alkyne (20 mmol), a small excess of 2-bromobenzaldehyde (**5**), CuI (76 mg, 0.40 mmol), palladium acetate (45 mg, 0.20 mmol) and triphenylphosphane (105 mg, 0.400 mmol) in triethylamine (40 mL) was heated at 80 °C for 10 h under argon in a screw-capped tube (deviations from the usual amounts of reagents are mentioned below for special cases). After filtration through silica with methyl *tert*-butyl ether the solvent was distilled off and the residue fractionated by flash chromatography.

Bis(aldehyde) 1: From 1,7-octadiyne (2.1 g, 20 mmol) and 2-bromobenzaldehyde (**5.1**; 8.0 g, 5.0 mL, 43 mmol) and double the amount of all reagents and solvents in the general procedure, since the alkyne is bifunctional in this case. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 2:1): R_f = 0.60, 0.39, 0.00. The fraction with R_f = 0.39 was isolated by flash chromatography, crystallized from petroleum ether/methyl *tert*-butyl ether (1:1) and dried in vacuo (0.1 mbar, 50 °C) to give **1** (2.07 g, 33%) as colourless crystals, m.p. 76–77 °C. – IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1} (w), 2839 (w), 2753 (w), 1693 (s), 1594 (m), 1473 (m), 1461 (w), 1447 (w), 1424 (w), 1392 (w), 1340 (w), 1275 (w), 1247 (w), 1190 (m), 825 (w), 766 (m), 638 (w). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 232 nm (4.84), 258 (4.32), 265 (4.25, sh), 317 (3.79). – ^{1}H NMR (500 MHz): δ = 1.85 ("quint", "*J*" = 3.0 Hz, 4 H), 2.58 ("quint", "*J*" = 2.8 Hz, 4 H), 7.37–7.41 (m, 2 H), 7.51–7.53 (m, 4 H), 7.88 ("dt", "*J*" = 7.5, 0.8 Hz, 2 H), 10.54 ("t", "*J*" = 0.7 Hz, 2 H). – ^{13}C NMR (126 MHz): δ = 19.3 (t), 27.7 (t), 76.9 (s), 97.2 (s), 127.1 (d), 127.7 (s), 128.1 (d), 133.4 (d), 133.8 (d), 136.0 (s), 192.1 (d). – MS (70 eV); *m/z* (%): 314 (6) [M$^+$], 313 (10) [M$^+$ – 1], 296 (12), 285 (51), 283 (23), 269 (22), 268 (33), 267 (27), 258 (27), 257 (52), 229 (30), 228 (22), 215 (37), 144 (21), 129 (24), 128 (43), 116 (21), 115 (100), 89 (27). – $C_{22}H_{18}O_2$ (314.4): calcd. C 84.05, H 5.77; found C 84.09, H 5.74.

2-(1-Hexyn-1-yl)benzaldehyde (7.1a): From 1-hexyne (**6a**) (1.52 g, 20 mmol) and 2-bromobenzaldehyde (**5.1**; 4.0 g, 2.5 mL, 21.5 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 9:1): R_f = 0.63, 0.50, 0.42. The fraction with R_f = 0.50 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1a** (1.75 g, 47%) as a brownish oil. The NMR spectra were in agreement with reported data.[7] – ^{1}H NMR (500 MHz): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 1.50 ("q", "*J*" = 7.5 Hz, 2 H), 1.63 (m, 2 H), 2.49 (t, *J* = 7.1 Hz, 2 H), 7.36–7.40 (m, 1 H), 7.49–7.54 (m, 2 H), 7.89 (ddd, *J* = 7.8, 1.4, 0.8 Hz, 1 H), 10.54 (d, *J* = 0.8 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 13.6 (q), 19.3 (t), 22.1 (t), 30.6 (t), 76.3 (s), 98.2 (s), 126.9 (d), 127.9 (d), 128.0 (s), 133.3 (d), 133.7 (d), 136.0 (s), 192.3 (d).

2-(Phenylethynyl)benzaldehyde (7.1b): From ethynylbenzene (**6b**; 2.04 g, 20 mmol) and 2-bromobenzaldehyde (**5.1**; 4.0 g, 2.5 mL, 21.5 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.69, 0.56, 0.38. The fraction with R_f = 0.56 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1b** (3.61 g, 88%) as a brownish oil. The NMR spectra were in agreement with reported data.[7] – ^{1}H NMR (500 MHz): δ = 7.37–7.40 (m, 3 H), 7.44 ("dd", "*J*" = 8.1, 7.6 Hz, 1 H), 7.55–7.57 (m, 2 H), 7.58 (dd, *J* = 6.1, 1.4 Hz, 1 H), 7.64 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1 H), 7.95 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1 H), 10.66 (d, *J* = 0.8 Hz, 1 H).

2-(2-Pyridylethynyl)benzaldehyde (7.1c): From 2-ethynylpyridine (**6c**; 0.50 g, 4.9 mmol) and 2-bromobenzaldehyde (**5.1**; 0.90 g, 0.56 mL, 4.9 mmol). A quarter of the amount of reagents from the general procedure was used. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.73, 0.28, 0.09. The fraction with R_f = 0.28 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1c** (0.19 g, 19%) as a slightly yellow solid with m.p. 43–44 °C. – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (w), 3004 (w), 2839 (w), 2749 (w), 2221 (w), 1696 (vs), 1592 (s), 1580 (s), 1559 (m), 1478 (s), 1461 (s), 1427 (m), 1281 (w), 1267 (m), 1194 (m), 1152 (w), 989 (w), 819 (m), 778 (s), 765 (s), 739 (w), 639 (m), 630 (w). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 206 nm (4.41), 226 (4.37), 246 (4.47), 270 (4.21), 278 (4.21), 286 (4.30), 294 (4.34), 318 (4.08). – ^{1}H NMR (500 MHz): δ = 7.30 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1 H), 7.49 ("td", "*J*" = 7.5, 0.9 Hz, 1 H), 7.57–7.59 (m, 1 H), 7.60 ("td", "*J*" = 7.5, 1.5 Hz, 1 H), 7.70–7.74 (m, 2 H), 7.96 (ddd, *J* = 7.8, 1.5, 0.6 Hz, 1 H), 8.65 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1 H), 10.66 (d, *J* = 0.8 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 84.4 (s), 95.0 (s), 123.4 (d), 125.6 (s), 127.4 (d), 127.5 (d), 129.4 (d), 133.7 (d), 133.8 (d), 136.2 (s), 136.3 (d), 142.6 (s), 150.3 (d), 191.3 (d). – MS (70 eV); *m/z* (%): 207 (21) [M$^+$], 180 (15), 179 (100) [M$^+$ – CO], 178 (44), 152 (13), 151 (13), 76 (11). – $C_{14}H_9NO$ (207.2): calcd. C 81.14, H 4.38, N 6.76; found C 80.96, H 4.36, N 6.70.

2-(2-Furylethynyl)benzaldehyde (7.1d): From 2-ethynylfuran[8] (**6d**; 0.92 g, 10 mmol) and 2-bromobenzaldehyde (**5.1**; 1.9 g, 1.2 mL,

10 mmol). Half of the amount of reagents from the general procedure was used. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.56, 0.33, 0.20. The fraction with R_f = 0.33 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1d** (1.05 g, 54%) as brownish needles with m.p. 30–31 °C. – IR (KBr): $\tilde{\nu}$ = 3151 cm^{-1} (w), 3065 (w), 2844 (w), 2746 (w), 2206 (w), 1696 (s), 1594 (m), 1489 (w), 1467 (m), 1286 (w), 1265 (m), 1194 (m), 1170 (w), 1014 (m), 931 (m), 833 (w), 799 (w), 761 (s), 643 (m), 609 (m). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 212 nm (4.20), 226 (4.17), 253 (4.40, sh), 257 (4.41), 292 (4.14), 300 (4.25), 335 (4.01). – ^{1}H NMR (500 MHz): δ = 6.47 (dd, *J* = 3.5, 1.9 Hz, 1 H, 4′-H), 6.76 (dd, *J* = 3.5, 0.7 Hz, 1 H, 3′-H), 7.45–7.49 (m, 1 H), 7.48 (dd, *J* = 1.9, 0.7 Hz, 1 H, 5′-H), 7.59 ("td", "*J*" = 7.5, 1.4 Hz, 1 H), 7.64 (ddd, *J* = 7.7, 1.3, 0.6 Hz, 1 H), 7.95 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 1 H), 10.57 (d, *J* = 0.8 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 86.2 (s), 89.2 (s), 111.3 (d), 116.6 (d), 125.8 (s), 127.5 (d), 129.0 (d), 133.0 (d), 133.8 (d), 135.7 (s), 136.4 (s), 144.5 (d), 191.3 (d). – MS (70 eV); *m*/*z* (%): 197 (14) [M^+ + 1], 196 (100) [M^+], 168 (22) [M^+ – CO], 140 (31), 139 (80), 114 (10), 113 (9), 63 (10). – $C_{13}H_8O_2$ (196.2): calcd. C 79.57, H 4.11; found C 79.58, H 4.15.

2-[(5-Methyl-2-furyl)-ethynyl]benzaldehyde (7.1e): From 2-ethynyl-5-methylfuran[9] (**6e**; 0.96 g, 9.0 mmol) and 2-bromobenzaldehyde (**5.1**; 1.7 g, 1.1 mL, 9.2 mmol). Half of the amount of reagents from the general procedure was used. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 15:1): R_f = 0.50, 0.40, 0.33, 0.20. The fraction with R_f = 0.33 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1e** (1.15 g, 61%) as a brownish solid. Recrystallization from petroleum ether/methyl *tert*-butyl ether 15:1 gave colourless crystals with m.p. 70–71 °C. – IR (KBr): $\tilde{\nu}$ = 3125 cm^{-1} (w), 2926 (w), 2842 (w), 2754 (w), 2198 (m), 1692 (s), 1596 (m), 1564 (w), 1533 (m), 1469 (m), 1448 (w), 1394 (w), 1311 (w), 1292 (w), 1266 (m), 1196 (s), 1023 (m), 834 (w), 797 (m), 763 (s), 642 (w). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 215 nm (4.23), 227 (4.21, sh), 260 (4.34), 298 (4.08, sh), 306 (4.16), 344 (3.98). – ^{1}H NMR (500 MHz): δ = 2.35 (t, *J* = 0.5 Hz, 3 H), 6.05 ("dq", "*J*" = 3.3, 1.0 Hz, 1 H), 6.65 (dd, *J* = 3.3, 0.4 Hz, 1 H), 7.43 ("td", "*J*" = 7.9, 1.3, 0.9 Hz, 1 H), 7.56 ("td", "*J*" = 7.5, 1.4 Hz, 1 H), 7.60 ("dt", "*J*" = 7.8, 0.8 Hz, 1 H), 7.93 ("dt", "*J*" = 7.9, 0.7 Hz, 1 H), 10.56 (d, *J* = 0.8 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 13.9 (q), 86.8 (s), 89.0 (s), 107.6 (d), 118.0 (d), 126.2 (s), 127.3 (d), 128.7 (d), 132.7 (d), 133.8 (d), 134.5 (s), 135.5 (s), 154.8 (s), 191.4 (d). – MS (70 eV); *m*/*z* (%): 211 (23) [M^+ + 1], 210 (100) [M^+], 209 (19) [M^+ – 1], 181 (26), 168 (14), 167 (24), 153 (24), 152 (16), 139 (27), 43 (26). – $C_{21}H_{14}N_2$ (210.2): calcd. C 79.98, H 4.79; found C 79.83, H 4.76.

2-(2,4-Dimethoxyphenylethynyl)benzaldehyde (7.1f): From 1,3-dimethoxy-4-ethynylbenzene[10] (**6e**; 0.31 g, 1.9 mmol) and 2-bromobenzaldehyde (**5.1**; 0.71 g, 3.8 mmol). A quarter of the amount of reagents from the general procedure was used. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.57, 0.41, 0.32, 0.13. The fraction with R_f = 0.32 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1f** (0.28 g, 55%) as yellow needles with m.p. 93–95 °C. – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (w), 2840 (w), 2211 (m), 1691 (s), 1608 (s), 1593 (s), 1568 (m), 1507 (m), 1467 (m), 1437 (w), 1323 (w), 1302 (m), 1288 (m), 1268 (m), 1253 (w), 1212 (s), 1165 (m), 1119 (w), 1033 (m), 762 (w). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 203 nm (4.59), 220 (4.52), 258 (4.47), 288 (4.27), 304 (4.26, sh), 312 (4.35), 348 (4.18). – ^{1}H NMR (500 MHz): δ = 3.84 (s, 3 H), 3.91 (s, 3 H), 6.48 (d, *J* = 2.4 Hz, 1 H, 3′-H), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1 H, 5′-H), 7.40 ("tt", "*J*" = 7.6, 0.9 Hz, 1 H), 7.44 (d, *J* = 8.5 Hz, 1 H, 6′-H), 7.56 ("td", "*J*" = 7.5, 1.5 Hz, 1 H), 7.62 (ddd, *J* = 7.8, 1.2, 0.5 Hz, 1 H), 7.93 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1 H), 10.73 (d, *J* = 0.8 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 55.5 (q), 55.9 (q), 87.9 (s), 93.4 (s), 98.4 (d), 104.2 (s), 105.0 (d), 126.9 (d), 127.9 (s), 128.0 (d), 132.7 (d), 133.7 (d), 134.2 (d), 135.7 (s), 161.8 (s), 161.9 (s), 192.7 (d). – MS (70 eV); *m*/*z* (%): 267 (19) [M^+ + 1], 266 (100) [M^+], 251 (14), 249 (9), 238 (9), 237 (25) [M^+ – CHO], 223 (19), 221 (12), 180 (9), 165 (22), 152 (22). – $C_{17}H_{14}O_3$ (266.3): calcd. C 76.68, H 5.30; found C 76.52, H 5.30.

5-Hydroxy-2-(phenylethynyl)benzaldehyde (7.2b): From ethynylbenzene (**6b**; 2.0 g, 10 mmol) and 5-hydroxy-2-bromobenzaldehyde (**5.2**; 0.71 g, 3.8 mmol). Half the amount of reagents from the general procedure was used. TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.92, 0.86, 0.25, 0.22, 0.14. The fraction with R_f = 0.22 was isolated by flash chromatography and dried in vacuo (10 mbar, 50 °C) to give **7.1f** (575 mg, 26%) as a colourless solid, according to the NMR spectra pure enough for further transformations. – ^{1}H NMR (500 MHz): δ = 7.12 (dd, *J* = 8.4, 2.8 Hz, 1 H, 4-H), 7.37–7.38 (m, 3 H), 7.44 (dd, *J* = 2.7, 0.3 Hz, 1 H, 6-H), 7.53–7.55 (m, 2 H), 7.55 (dd, *J* = 8.4, 0.4 Hz, 1 H, 3 H), 10.58 (s, 1 H). – ^{13}C NMR (126 MHz): δ = 84.8 (s), 94.8 (s), 113.1 (d), 119.6 (s), 122.0 (d), 122.7 (s), 128.5 (d, 2C), 128.8 (d), 131.6 (d, 2C), 135.0 (d), 137.2 (s), 156.4 (s), 192.1 (d).

Redox Reaction of Bis(benzaldehyde) 1 With *ortho*-Phenylenediamine (2): A solution of bis(benzaldehyde) **1** (500 mg, 1.59 mmol) and diamine **2** (172 mg, 1.59 mmol) in 50 mL of toluene was refluxed at the Dean-Stark trap for 7 d. The crude product was recrystallized from dichloromethane/*n*-pentane to give 330 mg (54%) of **3** as a colourless solid with m.p. 193–197 °C. – IR (KBr): $\tilde{\nu}$ = 3197 cm^{-1} (m, br), 3057 (m), 2942 (m), 2861 (m), 1642 (w), 1527 (s), 1477 (w), 1452 (s), 1370 (w), 1337 (m), 1294 (w), 1283 (w), 1235 (w), 1052 (m), 1020 (w), 834 (w), 767 (s), 754 (s), 735 (s). – UV/Vis (dichloromethane): λ_{max} (lg ε) = 240 nm (4.45), 256 (4.37), 269 (4.44), 279 (4.53), 313 (3.81), 339 (3.71), 357 (3.66). – ^{1}H NMR (500 MHz): δ = 1.92 ("quint", "*J*" = 7.3 Hz, 2 H), 2.15 ("quint", "*J*" = 7.7 Hz, 2 H), 2.22 (s, br, 1 H, –O*H*), 2.60 (t, *J* = 6.9 Hz, 2 H), 3.40 (t, *J* = 7.5 Hz, 2 H), 4.72 (s, 2 H), 6.84 (s, 1 H, 5-H), 7.20 ("td", "*J*" = 7.6, 1.3 Hz, 1 H), 7.29 ("td", "*J*" = 7.7, 1.4 Hz, 1 H), 7.33 ("tt", "*J*" = 8.5, 1.3 Hz, 2 H), 7.40 (ddd, *J* = 7.6, 1.3, 0.6 Hz, 1 H), 7.48 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H), 7.60–7.67 (m, 3 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 8.03 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 8.81–8.83 (m, 1 H). – ^{13}C NMR (126 MHz): δ = 19.5 (t), 26.6 (t), 28.2 (t), 33.1 (t), 64.0 (t), 79.0 (s), 94.3 (s), 110.0 (d), 114.1 (d), 120.1 (d), 121.8 (s), 212.9 (d), 122.4 (s), 124.3 (d), 125.1 (d), 126.0 (d), 127.2 (d), 127.4 (d, 2C), 128.2 (d), 130.1 (d), 130.7 (s), 131.6 (s), 132.3 (d), 138.4 (s), 142.4 (s), 144.3 (s), 148.7 (s). – MS (70 eV); *m*/*z* (%): 405 (17) [M^+ + 1], 404 (57) [M^+], 259 (20), 246 (24), 245 (100), 243 (15), 232 (46), 231 (17), 202 (9), 44 (10). – $C_{28}H_{24}N_2O$ (404.5): calcd. C 83.14, H 5.98, N 6.93; found C 82.90, H 5.95, N 6.92.

Oxidative Cyclization Reactions of 2-Alkynylbenzaldehydes with *ortho*-Phenylene Diamine (2). – General Procedure: A solution of 100–500 mg of 2-alkynylbenzaldehyde **1** or **7** and 1–2 equivalents of *ortho*-phenylenediamine (**2**) in 50 mL of nitrobenzene was heated at 150 °C for 2 d. The solvent was then removed by distillation in vacuo and the residue fractionated by flash chromatography.

1,4-Bis(6-benzimidazo[2,1-*a*]isoquinolinyl)butane (4): From bis(benzaldehyde) **1** (500 mg, 1.59 mmol) and *ortho*-phenylenediamine (**2**; 344 mg, 3.18 mmol). TLC of the crude product (silica, petroleum ether/acetic acid ethyl ester 1:1): R_f = 0.79, 0.51, 0.45. The fraction with R_f = 0.45 was isolated by flash chromatography and dried in

vacuo (0.1 mbar, 50 °C) to give **4** (363 mg, 47%) as a yellow solid which starts decomposing above 280 °C. – IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (w), 2937 (w), 2865 (w), 1642 (m), 1607 (w), 1558 (w), 1526 (s), 1473 (w), 1452 (s), 1432 (m), 1401 (w), 1333 (m), 1293 (w), 1275 (w), 1237 (w), 1180 (w), 822 (w), 751 (m), 733 (s). – UV/Vis (dichloromethane): λ_{max} (lg ε) = 236 nm (4.74), 269 (4.92), 279 (5.01), 309 (4.22), 339 (4.14), 357 (4.10). – ^{1}H NMR (500 MHz): δ = 2.20 (s, br, 4 H), 3.40 (s, br, 4 H), 6.77 (s, 2 H), 7.34 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 2 H), 7.51 (ddd, *J* = 8.1, 7.2, 0.9 Hz, 2 H), 7.61–7.64 (m, 6 H), 7.94 (d, *J* = 8.4 Hz, 2 H), 8.05 (d, *J* = 7.8 Hz, 2 H), 8.82–8.84 (m, 2 H). – ^{13}C NMR (126 MHz): δ = 27.0 (t), 33.4 (t), 110.3 (d), 113.9 (d), 120.3 (d), 122.0 (d), 122.5 (s), 124.3 (d), 125.1 (d), 126.0 (d), 127.5 (d), 130.1 (d), 130.6 (s), 131.5 (s), 138.0 (s), 144.4 (s), 148.7 (s). – MS (70 eV); *m*/*z* (%):491 (24) [M^+ + 1], 490 (60) [M^+], 258 (13), 257 (15), 246 (23), 245 (100), 243 (20), 232 (17), 231 (27), 230 (11), 44 (32). – $C_{34}H_{26}N_4$ (490.6): calcd. C 83.24, H 5.34, N 11.42; found C 82.23, H 5.27, N 11.15; calcd. including 1.5 weight-% dichloromethane C 82.20, H 5.29, N 11.25. – HRMS: calcd. 490.21576; found 490.21633.

6-*n*-Butylbenzimidazo[2,1-*a*]isoquinoline (8.1a): From 2-alkynylbenzaldehyde **7.1a** (0.50 g, 2.7 mmol) and *ortho*-phenylenediamine (**2**; 0.29 g, 2.7 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.81, 0.65, 0.43. The fraction with R_f = 0.43 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give **8.1a** (337 mg, 46%) as bright yellow needles with m.p. 133–135 °C.[11] – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} (w), 2954 (m), 2934 (m), 2869 (w), 1641 (w), 1524 (s), 1466 (w), 1451 (s), 1430 (m), 1328 (w), 1275 (w), 1178 (w), 830 (m), 755 (m), 736 (s). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 203 nm (4.92, sh), 234 (4.75, sh), 258 (4.63), 267 (4.75), 277 (4.85), 324 (4.50), 356 (3.87). – ^{1}H NMR (500 MHz): δ = 1.03 (t, *J* = 7.4 Hz, 3 H, 4′-H), 1.59 ("hex", "*J*" = 7.4 Hz, 2 H, 3′-H), 1.88 ("quint", "*J*" = 7.7 Hz, 2 H, 2′-H), 3.28 (t, *J* = 7.4 Hz, 2 H, 1′-H), 6.75 (d, *J* = 0.6 Hz, 1 H, 5-H), 7.36 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1 H, 9-H), 7.49 (ddd, *J* = 8.2, 7.1, 1.0 Hz, 1 H, 10-H), 7.58–7.64 (m, 3 H, 2-H, 3-H, 4-H), 7.96 ("dt", "*J*" = 8.5, 0.8 Hz, 1 H, 8-H), 8.04 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H, 11-H), 8.80–8.83 (m, 1 H, 1-H). – NOE difference experiment; spin saturation at δ = 6.75 (5-H): δ = 1.03 (+0.4%, 4′-H), 1.59 (+0.8%, 3′-H), 1.88 (+4.6%, 2′-H), 3.28 (+3.5%, 1′-H) 7.58–7.64 (+10.0%, 4-H). – ^{13}C NMR (126 MHz): δ = 14.0 (q, C-4′), 22.4 (t, C-3′), 29.4 (t, C-2′), 33.1 (t, C-1′), 109.6 (d, C-5), 114.2 (d, C-8), 120.0 (d, C-11), 121.73 (d, C-9), 122.28 (s), 124.12 (d, C-10), 124.98 (d, C-1), 125.90 (d), 127.13 (d), 129.9 (d), 130.7 (s), 131.7 (s), 139.0 (s), 144.3 (s), 148.6 (s). – MS (70 eV); *m*/*z* (%): 275 (20) [M^+ + 1], 274 (90) [M^+], 245 (7), 243 (8), 233 (17), 232 (100), 231 (54), 230 (16), 229 (15). – $C_{19}H_{18}N_2$ (274.4): calcd. C 83.18, H 6.61, N 10.21; found C 83.01, H 6.66, N 10.19.

6-Phenylbenzimidazo[2,1-*a*]isoquinoline (8.1b) and Its HBF_4 Salt 10.1b: From 2-alkynylbenzaldehyde **7.1b** (0.50 g, 2.4 mmol) and *ortho*-phenylenediamine (**2**; 0.26 g, 2.4 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.61, 0.39, 0.30, 0.27, 0.15. The fraction with R_f = 0.27 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give **8.1b** (592 mg, 83%) as bright yellow needles with m.p. 185–187 °C.[11] – IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1} (w), 3022 (w), 1640 (w), 1527 (m), 1493 (w), 1449 (s), 1394 (w), 1332 (m), 1311 (m), 1276 (m), 1235 (m), 1160 (w), 835 (m), 766 (m), 760 (m), 748 (s), 738 (s). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 203 nm (4.77, sh), 230 (4.66), 260 (4.53, sh), 270 (4.64, sh), 283 (4.76), 322 (4.24), 354 (3.86). – ^{1}H NMR (500 MHz): δ = 6.49 (d, *J* = 8.5 Hz, 1 H, 8-H), 6.91 (s, 1 H, 5 H), 7.00 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1 H, 9-H), 7.39 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H, 10 H), 7.60–7.61 (m, 4 H, Ph-H), 7.61–7.65 (m, 1 H, Ph-H), 7.68–7.70 (m, 2 H), 7.70–7.74 (m, 1 H), 7.99 (d, *J* = 8.2 Hz, 1 H, 11-H), 8.89 (dd, *J* = 6.0, 3.4 Hz, 1 H, 1-H). – ^{13}C NMR (126 MHz): δ = 112.6 (d, C-5), 114.1 (d, C-8), 119.7 (d, C-11), 121.3 (d, C-9), 122.9 (s), 124.2 (d, C-10), 125.1 (d, C-1), 126.7 127.91 (d), 129.0 (d, 2C), 129.4 (d, 2C), 129.9 (d), 130.1 (d), 130.7 (s), 131.6 (s), 134.7 (s), 137.5 (s), 144.3 (s), 148.3 (s). – MS (70 eV); *m*/*z* (%): 295 (23) [M^+ + 1], 294 (100) [M^+], 293 (59), 292 (28), 147 (10) [M^{2+}], 147 (21), 146 (13). – $C_{21}H_{14}N_2$ (294.4): calcd. C 88.69, H 4.79, N 9.52; found C 85.50, H 4.82, N 9.52.

The HBF_4 salt **10.1b** was formed by adding a few drops of tetrafluoroboric acid–diethyl ether complex to an analytical sample of **8.1b** in dichloromethane. The grey precipitate was filtered off and recrystallized from methanol/diethyl ether to give colourless crystals of **10.1b** which started to decompose at 200 °C (complete melting at 265 °C) and were suitable for X-ray structure analysis. – UV/Vis (methanol): λ_{max} (lg ε) = 230 nm (4.55), 272 (4.60, sh), 280 (4.71), 311 (4.00), 320 (3.96, sh), 335 (3.92), 352 (3.81). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.44 (d, *J* = 8.6 Hz, 1 H, 8-H), 7.32 (ddd, *J* = 8.5, 7.4, 1.0 Hz, 1 H), 7.67 ("td", "*J*" = 7.5, 0.6 Hz, 1 H), 7.73–7.82 (m, 6 H), 8.00–8.04 (m, 2 H), 8.07 ("td", "*J*" = 7.7, 1.1 Hz, 1 H), 8.21 (d, *J* = 7.7 Hz), 8.82 (d, *J* = 8.0 Hz, 1 H, 1-H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 114.9 (d), 115.2 (d), 116.6 (d), 117.0 (s), 124.1 (d), 124.6 (d), 127.5 (d), 128.0 (d), 128.5 (s), 129.4 (d, 2C), 129.6 (d, 2C), 129.7 (d), 130.9 (d), 132.7 (s), 133.0 (s), 133.2 (s, br), 133.6 (d), 136.7 (s), 143.8 (s).

Crystal Structure Determination of 10.1b: Siemens P4RA four-circle diffractometer, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, rotating anode generator, scintillation counter, 150 K, empirical absorption corrections, SHELXL97 programs, direct methods, least-squares refinements on F^2, one scaling factor, one isotropic extinction parameter. *Crystal data*: monoclinic, space group $P2_1/n$, *a* = 8.559(1), *b* = 12.955(2), *c* = 15.546(3) Å, β = 94.22(1)°, *V* = 1719.1 Å^3, *Z* = 4, $\rho_{calcd.}$ = 1.477 gcm^{-3}, μ(Mo-K_α) = 0.117 mm^{-1}, transmission range 0.981–0.966, crystal dimensions ca. 0.56·0.19·0.17 mm, ω-scan, $2\Theta_{max}$ = 54°, 3993 independent reflections, *R* (R_w) = 0.0368 (0.0884) for 3745 observed reflections [$I > 2\sigma(I)$], 264 variables, all heavy atoms anisotropic, H atoms at idealised positions.

6-(2-Pyridyl)-benzimidazo[2,1-*a*]isoquinoline (8.1c) and its HBF_4 Salt: From 2-alkynylbenzaldehyde **7.1c** (0.19 g, 0.93 mmol) and *ortho*-phenylenediamine (**2**; 0.10 g, 0.93 mmol). TLC of the crude product (silica, petroleum ether/acetic acid ethyl ester 1:1): R_f = 0.76, 0.61, 0.53, 0.39. The fraction with R_f = 0.39 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give **8.1c** (103 mg, 38%) as a slightly impure yellow oil. – ^{1}H NMR (500 MHz): δ = 6.40 ("dt", "*J*" = 8.4, 0.9 Hz, 1 H, 8-H), 7.03 (dd, *J* = 7.1, 1.1 Hz, 1 H), 7.04 (s, 1 H, 5-H), 7.39 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1 H), 7.56 (ddd, *J* = 7.7, 4.9, 1.2 Hz, 1 H), 7.66–7.77 (m, 3 H), 7.70 ("dt", "*J*" = 7.7, 1.0 Hz, 1 H), 7.96 (dd, *J* = 7.7, 1.8 Hz, 1 H), 7.99 ("dt", "*J*" = 7.9, 0.9 Hz, 1 H), 8.86 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1 H), 8.87–8.89 (m, 1 H).

Since the free base **8.1c** was difficult to purify, the complete characterisation was done with its HBF_4 salt. Upon treatment of a solution of **8.1c** in dichloromethane with tetrafluoroboric acid–diethyl ether complex the salt **10.1c**·HBF_4 precipitated; obviously, **8.1c** was protonated twice, at N-12 and at the pyridine nitrogen. Recrystallization from methanol/methyl *tert*-butyl ether gave analytically pure **10.1c**·HBF_4 as yellow crystals which started to decompose at 148 °C (complete melting at 272 °C). – IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1} (m), 2900 (m), 1626 (s), 1564 (m), 1539 (m), 1486 (w), 1462 (m), 1296 (w), 1255 (w), 1240 (w), 1174 (w), 1082 (vs), 1056 (vs), 1014

(s), 962 (w), 776 (s), 751 (vs), 695 (m), 609 (m), 522 (w). – UV/Vis (methanol): λ_{max} (lg ε) = 230 nm (4.39), 273 (4.40), 314 (3.95), 334 (3.97), 350 (3.96), 377 (3.63, sh). – ^{1}H NMR (500 MHz, [D$_6$]DMSO/CDCl$_3$ 1:1): δ = 6.47 ("dd", "*J*" = 7.9, 0.7 Hz, 1 H), 7.31 (ddd, *J* = 8.5, 7.3, 1.2 Hz, 1 H), 7.67 (ddd, *J* = 8.3, 7.3, 1.0 Hz, 1 H), 7.71 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1 H), 7.83 (s, 1 H, 5-H), 7.91 ("dt", "*J*" = 7.7, 1.0 Hz, 1 H), 7.94 ("dt", "*J*" = 8.2, 0.9 Hz, 1 H), 7.99 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1 H), 8.05 ("td", "*J*" = 7.2, 1.2 Hz, 1 H), 8.13 (dd, *J* = 7.7, 1.8 Hz, 1 H), 8.17 (d, *J* = 7.9 Hz, 1 H), 8.82 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1 H), 8.84 ("d", "*J*" = 8.1 Hz, 1 H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO/CDCl$_3$ 1:1): δ = 112.8 (d), 114.7 (d), 115.3 (s), 117.4 (d), 123.6 (d), 123.6 (d), 123.9 (d), 124.7 (d), 126.6 (s), 127.0 (d), 127.2 (d), 129.3 (d), 130.4 (s), 131.7 (s), 133.0 (d), 134.0 (s), 137.2 (d), 141.8 (s), 148.7 (d), 149.2 (s). – MS (70 eV); *m*/*z* (%): 296 (24) [M$^+$ + 1], 295 (94) [M$^+$], 294 (100) [M$^+$ – 1], 293 (25) [M$^+$ – 2], 147.8 (15) [M^{2+}], 147.2 (18) [M^{2+} – 1], 146.8 (7) [M^{2+} – 2], 49/48 (17)/(4) [BF$_2^+$]. – $C_{20}H_{13}N_3$·2(HBF$_4$) (471.0): calcd. C 51.01, H 3.21, N 8.92; found C 51.12, H 3.25, N 9.02.

6-(2-Furyl)-benzimidazo[2,1-*a*]isoquinoline (8.1d), 6-(2-Furyl)-isoindolo[2,1-*a*]quinoxaline (9.1d) and Their HBF$_4$ Salts 10.1d and 11.1d: From 2-alkynylbenzaldehyde **7.1d** (0.50 g, 2.6 mmol) and *ortho*-phenylenediamine (**2**; 0.28 g, 2.6 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 3:1): R_f = 0.62, 0.40, 0.29, 0.22, 0.12. A combined fraction with R_f = 0.40 and 0.29 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give a 1:14.1 mixture of **8.1d** and **9.1d** (321 mg, 44%) as a brown oil.

8.1d: ^{1}H NMR (500 MHz): δ = 6.53 ("dt", "*J*" = 8.4, 0.9 Hz, 1 H, 8-H), 6.73 (dd, *J* = 3.4, 1.9 Hz, 1 H, 4′-H), 6.84 (dd, *J* = 3.3, 0.8 Hz, 1 H, 3′-H), 7.16 (s, 1 H, 5-H), 7.19 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H), 7.45 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1 H), 7.68–7.77 (m, 4 H), 8.00 (d, *J* = 8.1 Hz, 1 H, 11-H), 8.88 ("d", "*J*" = 7.7 Hz, 1 H, 1-H).

9.1d: ^{1}H NMR (500 MHz): δ = 6.73 (dd, *J* = 3.4, 1.8 Hz, 1 H, 4′-H), 7.23 (d, *J* = 3.4 Hz, 1 H, 3′-H), 7.29 (ddd, *J* = 8.6, 6.6, 0.9 Hz, 1 H, 8-H), 7.38 ("dd", "*J*" = 7.9, 7.0 Hz, 1 H, 9-H), 7.57 (m, 2 H), 7.79 ("t", "*J*" = 0.9 Hz, 1 H, 5′-H), 7.87 (d, *J* = 8.4 Hz, 1 H, 10-H), 8.07 (d, *J* = 7.9 Hz, 1 H, 7-H), 8.07–8.11 (m, 2 H), 8.50 (s, 1 H, 11-H). – ^{13}C NMR (126 MHz): δ = 107.9 (d), 111.9 (d), 112.5 (d), 114.9 (d), 116.4 (s), 119.3 (d), 121.3 (d), 121.4 (s), 123.4 (d), 124.5 (d), 125.7 (s), 127.1 (d), 127.1 (d), 127.3 (s), 130.1 (d), 137.4 (s), 143.6 (d), 144.2 (s), 151.7 (s).

Since the free bases **8.1d** and **9.1d** were difficult to separate and to purify the complete characterisation was done with their HBF$_4$ salts. Upon treatment of a solution of **8.1d** and **9.1d** in dichloromethane with tetrafluoroboric acid–diethyl ether complex, the precipitate was recrystallized from dichloromethane/petroleum ether in several fractions to give analytically pure yellow crystals of **11.1d** which started to decompose at 185 °C (complete melting at 255–260 °C).[11] – IR (KBr): $\tilde{\nu}$ = 3279 cm^{-1} (m), 3218 (w), 3131 (m), 1618 (s), 1601 (m), 1551 (w), 1526 (w), 1510 (m), 1471 (w), 1453 (m), 1429 (m), 1397 (w), 1383 (w), 1330 (s), 1237 (w), 1116 (m), 1083 (vs), 1056 (vs), 1030 (vs), 901 (w), 822 (w), 801 (w), 767 (s), 745 (m). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 205 nm (4.48), 230 (4.52), 255 (4.54), 276 (4.39), 287 (4.35), 314 (4.27, sh), 324 (4.34), 364 (4.00, sh), 380 (4.11), 414 (4.05). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.09 (dd, *J* = 3.5, 1.8 Hz, 1 H), 7.63–7.66 (m, 2 H), 7.72 (d, *J* = 3.5 Hz, 1 H), 7.80–7.83 (m, 2 H), 8.02–8.04 (m, 1 H), 8.06–8.08 (m, 1 H), 8.15–8.17 (m, 1 H), 8.41 (d, *J* = 1.5 Hz, 1 H), 8.65–8.67 (m, 1 H), 9.79 (s, 1 H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 113.4 (d), 115.1 (s), 117.2 (d), 118.7 (d), 120.7 (d), 121.6 (d), 122.0 (d), 122.4 (d), 124.1 (s), 126.1 (s), 127.0 (d), 127.9 (s), 128.3 (d), 128.6 (d), 128.7 (s), 129.6 (d), 135.6 (s), 143.2 (s), 148.0 (d). – MS (70 eV); *m*/*z* (%): 285 (21) [M$^+$ + 1], 284 (100) [M$^+$], 283 (24), 255 (17), 128 (10), 127.5 (6), 127.0 (9). – $C_{19}H_{12}N_2O$·HBF$_4$ (372.1): calcd. C 61.33, H 3.52, N 7.53; found C 61.23, H 3.67, N 7.61.

An analytically pure sample of **10.1d**·0.5(HBF$_4$) was obtained from the combined filtrates of the recrystallization procedure by the following steps: 1. treating the combined filtrates with aqueous NaOH solution to give a mixture of the bases, this time enriched with **8.1d**; 2. flash chromatography for further enrichment of **8.1d**; 3. formation of the HBF$_4$ salt and crystallization from methanol/diethyl ether to give **10.1d**·0.5(HBF$_4$) as slightly yellow crystals which started to decompose at 170 °C (complete melting at 256 °C).[11] – IR (KBr): $\tilde{\nu}$ = 3145 cm^{-1} (w), 1654 (w), 1619 (w), 1590 (w), 1553 (s), 1493 (m), 1464 (m), 1084 (vs), 973 (m), 919 (w), 894 (w), 761 (s), 749 (s). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 222 nm (4.35), 232 (4.31, sh), 284 (4.54), 314 (3.84), 332 (3.77), 348 (3.60). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.46 (d, *J* = 8.4 Hz, 1 H, 8-H), 6.96 (dd, *J* = 3.4, 1.9 Hz, 1 H, 4′-H), 7.18 (d, *J* = 3.3 Hz, 1 H, 3′-H), 7.44 ("t", "*J*" = 7.7 Hz, 1 H, 9 H), 7.66 ("t", "*J*" = 7.5 Hz, 1 H, 10-H), 7.90 (s, 1 H, 5-H), 7.97 (dd, *J* = 7.3, 1.5 Hz, 1 H, 2-H), 7.99 (dd, *J* = 7.5, 1.7 Hz, 1 H, 3-H), 8.02 (d, *J* = 8.2 Hz, 1 H, 11-H), 8.17–8.19 (m, 2 H, 4-H, 5′ H), 8.79 (dd, *J* = 7.7, 1.6 Hz, 1 H, 1-H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 112.5 (d, C-4′), 113.5 (d, C-8), 113.9 (d, C-3′), 116.6 (d), 117.9 (d, C-5), 119.8 (s), 123.8, (d, C-9), 124.7 (d, C-1), 125.8 (s), 126.5 (d, C-10), 128.2 (d), 128.6 (s), 130.1 (d), 131.7 (s), 132.5 (d), 144.8 (s), 145.1 (d). – MS (70 eV); *m*/*z* (%):285 (20) [M$^+$ + 1], 284 (100) [M$^+$], 283 (31) [M$^+$ – 1], 255 (20), 128 (11), 49 (6). – $C_{19}H_{12}N_2O$·1.5(HBF$_4$) (416.0): calcd. C 55.48, H 3.30, N 6.81; found C 55.64, H 3.34, N 6.74

6-(5-Methyl-2-furyl)isoindolo[2,1-*a*]quinoxaline (9.1e) and Its HBF$_4$ Salt 11.1e: From 2-alkynylbenzaldehyde **7.1e** (0.16 g, 0.74 mmol) and *ortho*-phenylenediamine (**2**; 80 mg, 0.74 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 1:1): R_f = 0.62, 0.56, 0.35. According to the ^{1}H NMR spectrum of the crude product and based on the diagnostic signal at δ = 8.9 (m, 1 H, 1-H) the ratio of **8.1e**/**9.1e** was determined to be 9:91. The fraction with R_f = 0.35 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give **9.1e** (110 mg, 50%) as a slightly impure oily solid. – ^{1}H NMR (500 MHz): δ = 2.54 (t, *J* = 0.5 Hz, 3 H), 6.31 (m, 1 H), 7.13 (d, *J* = 0.8 Hz, 1 H), 7.30 ("td", "*J*" = 6.4, 1.1 Hz, 1 H), 7.36–7.39 (m, 1 H), 7.55–7.57 (m, 2 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 8.08–8.11 (m, 2 H), 8.23 (dd, *J* = 8.7, 0.8 Hz, 1 H), 8.52 (s, 1 H, 11-H). – ^{13}C NMR (126 MHz): δ = 14.1 (q), 107.9 (d), 108.2 (d), 114.1 (d), 114.9 (d), 116.2 (s), 119.4 (d), 121.5 (s), 121.5 (d), 123.3 (d), 124.5 (d), 125.7 (s), 126.9 (d), 127.1 (d), 127.3 (s), 129.9 (d), 137.4 (s), 144.5 (s), 149.8 (s), 154.1 (s).

Since the free base **9.1e** was difficult to obtain with analytical purity the complete characterisation was done with its HBF$_4$ salt **11.1e**. Upon treatment of a sample of **9.1e** in dichloromethane with tetrafluoroboric acid–diethyl ether complex, the precipitate was recrystallized from dichloromethane/petroleum ether to give analytically pure brown crystals of **11.1e** which started to decompose at 180 °C (complete melting at 255 °C) and were suitable for an X-ray structure analysis.[11] – IR (KBr): $\tilde{\nu}$ = 3085 cm^{-1} (w), 1626 (m), 1598 (m), 1561 (s), 1522 (m), 1507 (s), 1472 (w), 1451 (s), 1426 (m), 1373 (s), 1331 (m), 1320 (w), 1124 (vs), 1084 (vs), 802 (w), 756 (s), 533 (w). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 231 nm (4.45), 249 (4.42), 276 (4.30), 286 (4.23), 328 (4.25), 367 (4.01, sh), 382 (4.11), 415 (3.99, sh). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.60 (s, 3 H, –C*H*$_3$), 6.72 (d, *J* = 2.9 Hz, 1 H, 4′ H), 7.66 (m, 2 H), 7.79 ("dd",

"*J*" = 6.1, 3.4 Hz, 2 H), 7.82 (d, *J* = 3.4 Hz, 1 H), 8.17 (d, *J* = 7.9 Hz, 1 H), 8.26 ("dd", "*J*" = 6.3, 3.2 Hz, 1 H), 8.30 (d, *J* = 8.3 Hz, 1 H), 8.67 ("dd", "*J*" = 6.2, 3.3 Hz, 1 H), 9.80 (s, 1 H, 11-H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO/CDCl$_3$ 1:1): δ = 13.7 (q), 109.8 (d, C-4′), 114.4 (s), 116.8 (d, C-1), 120.5 (d), 120.6 (d, C-4), 120.7 (d, C-7), 121.9 (d, C-10), 123.0 (d, C-11), 123.5 (s), 126.7 (s), 126.9 (d), 127.0 (s), 128.2 (d), 128.5 (d), 128.9 (s), 129.3 (d), 134.6 (s), 140.7 (s), 158.3 (s). – MS (70 eV); *m*/*z* (%): 299 (42) [M$^+$ + 1], 298 (100) [M$^+$], 297 (36) [M$^+$ – 1], 283 (8) [M$^+$ – CH$_3$], 255 (12), 149.5 (3) [(M + 1)$^{2+}$], 149.0 (14) [M^{2+}], 49 (9) [BF$_2^+$]. – C$_{20}$H$_{14}$N$_2$O·HBF$_4$ (386.2).

Crystal Structure Determination of 11.1e: *Crystal Data:* triclinic, space group $P\bar{1}$, *a* = 7.870(3), *b* = 10.955(3), *c* = 11.129(4) Å, *α* = 65.36(2), *β* = 77.17(2), *γ* = 80.28(2) °, *V* = 847.2 Å^3, *Z* = 2, $\rho_{calcd.}$ = 1.514 gcm^{-3}, μ(Mo-K_α) = 0.124 mm^{-1}, transmission range 0.973–0.893, crystal dimensions ca. 0.65·0.22·0.19 mm, ω-scan, $2\Theta_{max}$ = 54°, 3975 independent reflections, *R* (*R*$_w$) = 0.0659 (0.1740) for 3699 observed reflections [$I > 2\sigma(I)$], 254 variables, all heavy atoms anisotropic, H atoms at idealised positions.

6-(2,4-Dimethoxyphenyl)-benzimidazo[2,1-*a*]isoquinoline (8.1f): From 2-alkynylbenzaldehyde **7.1f** (0.10 g, 0.38 mmol) and *ortho*-phenylenediamine (**2**; 41 mg, 0.38 mmol). TLC of the crude product (silica, petroleum ether/methyl *tert*-butyl ether 1:1): R_f = 0.53, 0.41, 0.31, 0.21, 0.03. The fraction with R_f = 0.21 was isolated by flash chromatography and dried in vacuo (0.1 mbar, 50 °C) to give **8.1f** (86 mg, 64%) as bright yellow crystals which started to decompose at 185 °C (complete melting at 195 °C). – IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1} (w), 3004 (w), 2937 (w), 2839 (w), 1641 (m), 1609 (s), 1578 (m), 1526 (m), 1502 (s), 1450 (s), 1416 (w), 1308 (m), 1279 (m), 1262 (w), 1234 (w), 1210 (s), 1164 (s), 1130 (w), 1037 (m), 841 (w), 756 (m), 743 (m). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 199 nm (4.69), 222 (4.52), 261 (4.34, sh), 272 (4.52, sh), 284 (4.66), 314 (3.92, sh), 337 (3.86), 355 (3.72). – ^{1}H NMR (500 MHz): δ = 3.56 (s, 3 H), 3.96 (s, 3 H), 6.64 (d, *J* = 2.3 Hz, 1 H, 3′-H), 6.66 (d, *J* = 8.5 Hz, 1 H, 8-H), 6.69 (dd, *J* = 8.3, 2.3 Hz, 1 H, 5′-H), 6.90 (s, 1 H, 5-H), 7.04 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1 H), 7.38 (dd, *J* = 8.1, 1.0 Hz, 1 H), 7.39 (d, *J* = 8.3 Hz, 1 H, 6′-H), 7.66–7.67 (m, 2 H), 7.71–7.73 (m, 1 H), 7.98 (dd, *J* = 8.2, 0.6 Hz, 1 H), 8.88–8.90 (m, 1 H, 1-H). – ^{13}C NMR (126 MHz): δ = 55.6 (q), 55.6 (q), 98.9 (d), 104.6 (d), 113.0 (d), 113.3 (d), 116.7 (s), 119.5 (d), 121.4 (d), 123.0 (s), 123.9 (d), 125.1 (d), 126.6 (d), 127.6 (d), 129.9 (d), 131.2 (s), 131.8 (s), 131.9 (d), 134.9 (s), 144.0 (s), 148.2 (s), 159.3 (s), 162.6 (s). – MS (70 eV); *m*/*z* (%): 355 (27) [M$^+$ + 1], 354 (100) [M$^+$], 353 (11) [M$^+$ – 1], 339 (11), 324 (7), 267 (9), 177 (5), 140 (7). – C$_{23}$H$_{18}$N$_2$O$_2$ (294.4): calcd. C 77.95, H 5.12, N 7.81; found C 77.77, H 5.12, N 7.90.

2-Hydroxy-6-phenyl-benzimidazo[2,1-*a*]isoquinoline (8.2b): From 2-alkynylbenzaldehyde **7.2b** (234 mg, 1.05 mmol) and *ortho*-phenylenediamine (**2**; 114 mg, 1.05 mmol). The crude product was recrystallized from dichloromethane by adding a layer of petroleum ether. After filtration and drying in vacuo (0.1 mbar, 50 °C) **8.2b** (289 mg, 88%) was obtained as slightly coloured crystals which started to decompose at 290 °C. – IR (KBr): $\tilde{\nu}$ = 3437 cm^{-1} (w), 3059 (w), 2898 (w), 2733 (w), 2692 (w), 2606 (w), 1613 (m), 1597 (m), 1527 (m), 1494 (m), 1452 (s), 1379 (w), 1349 (s), 1269 (m), 1256 (s), 1232 (m), 855 (w), 766 (w), 739 (m), 699 (w). – UV/Vis (methanol): λ_{max} (lg ε) = 199 nm (4.69), 222 (4.52), 261 (4.34, sh), 272 (4.52, sh), 284 (4.66), 314 (3.92, sh), 337 (3.86), 355 (3.72). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.39 (d, *J* = 8.4 Hz, 1 H), 6.86 (s, 1 H, 5 H), 6.90 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1 H), 7.18 (dd, *J* = 8.5, 2.6 Hz, 1 H, 3-H), 7.27 (ddd, *J* = 8.2, 7.1, 1.0 Hz, 1 H), 7.55–7.59 (m, 5 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.79 (d, *J* = 8.2 Hz, 1 H), 8.06 (d, *J* = 2.5 Hz, 1 H, 1-H), 9.88 (s, br, 1 H, O*H*). – ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 108.3 (d), 112.0 (d), 113.6 (d), 118.9 (d), 119.8 (d), 120.4 (d), 123.3 (d), 123.7 (s), 123.9 (s), 128.1 (d), 128.5 (d, 2C), 129.0 (d, 2C), 129.2 (d), 130.1 (s), 133.7 (s), 134.2 (s), 143.6 (s), 147.2 (s), 157.1 (s). – MS (70 eV); *m*/*z* (%): 311 (23) [M$^+$ + 1], 310 (100) [M$^+$], 309 (31) [M$^+$ – 1], 280 (9), 155.1 (6), [M^{2+}], 154.6 (7) [M^{2+} – 1], 140 (10). – C$_{21}$H$_{14}$N$_2$ (310.4): calcd. C 81.27, H 4.55, N 9.03; found C 81.04, H 4.50, N 9.02.

Oxidative Cyclization of 2′-Formyl-*trans*-stilbene (16) with *ortho*-Phenylenediamine (2): A solution of 2′-formyl-*trans*-stilbene (**16**; 500 mg, 2.40 mmol) and *ortho*-phenylenediamine (**2**; 260 mg, 2.40 mmol) in nitrobenzene (50 mL) was heated at 150 °C for 2 d after which time the solvent was removed in vacuo. The residue was fractionated by flash chromatography; TLC (silica, petroleum ether/methyl *tert*-butyl ether 1:1): R_f = 0.63, 0.48, 0.35–0.32. First fraction benzimidazoisoquinoline **8.1b** (22 mg, 3%; R_f = 0.48). The second fraction with R_f = 0.35–0.32 was crystallized from dichloromethane/petroleum ether to give benzimidazole **17** (327 mg, 46%; R_f = 0.35) as a colourless solid which starts to decompose at 185 °C (complete melting at 215 °C). – IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (m), 3023 (m), 2922 (m), 2878 (m), 2791 (m), 2729 (m), 2683 (m), 1618 (w), 1598 (w), 1539 (w), 1491 (m), 1444 (s), 1417 (m), 1316 (w), 1270 (m), 1220 (w), 968 (m), 954 (m), 750 (vs), 742 (s), 693 (m). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 203 nm (4.78), 283 (4.55), 310 (4.44), 433 (2.07). – ^{1}H NMR (500 MHz, [D$_6$]DMSO, somewhat broad signals): δ = 7.21–7.28 (m, 3 H), 7.29 (d, *J* = 16.7 Hz, 1 H), 7.37 ("t", "*J*" = 7.7 Hz, 2 H), 7.48 ("td", "*J*" = 7.5, 0.9 Hz, 1 H), 7.51–7.56 (m, 4 H), 7.74 (d, *J* = 7.5 Hz, 1 H), 7.80 (dd, *J* = 7.7, 1.0 Hz, 1 H), 7.98 (d, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 16.4 Hz, 1 H). – ^{1}H NMR (500 MHz, [D$_6$]DMSO + 1 drop of CF$_3$COOH, sharp signals): δ = 7.26 ("t", "*J*" = 7.3 Hz, 1 H), 7.33 ("t", "*J*"[1]= 7.6 Hz, 2 H), 7.39 (d, *J* = 12.8 Hz, 1 H), 7.55 (d, *J* = 7.5 Hz, 2 H), 7.59 (dd, *J* = 6.1, 3.3 Hz, 2 H), 7.74 ("t", "*J*" = 7.5 Hz, 1 H), 7.83 (dd, *J* = 7.7, 1.1 Hz, 1 H), 7.86 (dd, *J* = 6.1, 3.1 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 1 H). – ^{13}C NMR (126 MHz, [D$_6$]DMSO + 1 drop of CF$_3$COOH): δ = 114.7 (d, 2C), 122.6 (s), 124.6 (d), 126.5 (d, 2C), 127.2 (d), 127.6 (d, 2C), 128.4 (d), 128.8 (d), 129.1 (d, 2C), 132.1 (d), 132.3 (s, 2C), 133.3 (d), 133.8 (d), 137.1 (s), 137.1 (s), 149.4 (s). – MS (70 eV); *m*/*z* (%): 297 (4) [M$^+$ + 1], 296 (20) [M$^+$], 295 (9), 220 (17), 219 (100), 218 (11), 147 (4).

The filtrate of the crystallization process was concentrated and the residue purified again by flash chromatography to give slightly impure 5,6-dihydro-6-phenylbenzimidazo[2,1-*a*]isoquinoline (**18**; 183 mg, 26%; R_f = 0.32). – ^{1}H NMR (500 MHz): δ = 3.36 (dd, *J* = 15.9, 3.6 Hz, 1 H, 5-H$_a$), 3.80 (dd, *J* = 15.9, 6.8 Hz, 1 H, 5-H$_b$), 5.77 (dd, *J* = 6.8, 3.7 Hz, 1 H, 6-H$_a$), 6.96–6.98 (m, 2 H), 7.00 ("dt", "*J*" = 8.2, 0.9 Hz, 1 H), 7.14 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1 H), 7.18 (d, *J* = 7.5 Hz, 1 H), 7.20 7.22 (m, 3 H), 7.25 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1 H), 7.34 ("td", "*J*" = 7.5, 1.4 Hz, 1 H), 7.40 ("t", "*J*" = 7.5 Hz, 1 H), 7.84 ("dt", "*J*" = 8.1, 0.9 Hz, 1 H), 8.36 (dd, *J* = 7.7, 1.0 Hz, 1 H).

Because of the difficult purification of the free base, compound **18** was fully characterized as its HBF$_4$ salt **18**·HBF$_4$: slightly green needles which start to decompose at 175 °C (complete melting at 234–237 °C). – IR (KBr): $\tilde{\nu}$ = 3172 cm^{-1} (w), 1626 (w), 1613 (w), 1584 (w), 1570 (w), 1515 (w), 1493 (w), 1463 (m), 1421 (w), 1332 (w), 1184 (w), 1158 (m), 1083 (s), 970 (m), 754 (s), 725 (w), 707 (w). – UV/Vis (methanol): λ_{max} (lg ε) = 243 nm (4.31), 250 (4.25), 285 (4.27, sh), 295 (4.36), 308 (4.48), 322 (4.44). – ^{1}H NMR (500 MHz): δ = 3.59 (dd, *J* = 16.6, 2.8 Hz, 1 H, 5-H$_a$), 4.01 (dd, *J* = 16.5, 7.3 Hz, 1 H, 5-H$_b$), 6.47 (dd, *J* = 7.2, 2.8 Hz, 1 H, 6-H$_a$), 7.10–7.11 (m, 2 H), 7.27–7.30 (m, 3 H), 7.50–7.53 (m, 2 H), 7.58–

7.68 (m, 4 H), 7.94 (d, J = 8.2 Hz, 1 H), 8.26 (dd, J = 7.4, 1.3 Hz, 1 H). – ^{13}C NMR (126 MHz): δ = 34.7 (t, C-5), 54.8 (d, C-6), 112.3 (d), 115.1 (d), 120.1 (s), 125.9 (d), 125.9 (d, 2C), 126.1 (d), 126.3 (d), 128.2 (d), 128.5 (d), 129.0 (d, 2C), 129.6 (d), 131.3 (s), 132.6 (s, br), 134.0 (d), 134.7 (s), 137.6 (s), 146.1 (s). – MS (70 eV); *m/z* (%): 297 (23) [M^+ + 1], 296 (100) [M^+], 295 (11), 220 (17) 219 (96), 218 (15), 148 (6), 77 (5). – $C_{21}H_{16}N_2 \cdot HBF_4$ (384.2): calcd. C 65.60, H 4.46, N 7.29; found C 65.30, H 4.50, N 7.25.

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