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Ring contraction of 1,3-diphenylbenzo[1,2,4]triazinyl radicals to 1,2-diphenylbenzimidazoles

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Abstract

Reductive ring contraction of 1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yls (Blatter's radicals) using zinc powder (2 equiv.) in acetic acid heated to *ca.* 118 °C gives 1,2-diphenylbenzimidazoles in high yield. 1,3-Diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one and the zwitterionic tetraphenylhexaazaanthracene (TPHA) also undergo reductive ring contractions to give 1,2-diphenylbenzimidaz-6-ol and 1,2,6,7-tetraphenyl-1,7-dihydrobenzo[1,2-*d*:4,5-*d*′]diimidazole, respectively. By using less zinc, the incomplete reduction of TPHA gave the stable organic radical 1,3,7,8-tetraphenyl-4,8-dihydro-1*H*-imidazo[4,5-*g*][1,2,4]benzotriazin-1-yl. Imidazolo-, oxazolo- and thiazolo-fused 1,2,4-benzotriazinyls all undergo zinc mediated ring contractions to give imidazolo-, oxazolo- and thiazolo-fused benzimidazoles in excellent yields.

1. Introduction

1,2,4-Benzotriazinyls are stable organic radicals (*e.g.*, Blatter's radical **1**),[1] which display a range of magnetic behaviours,[1f,2] and were the inspiration behind the preparation of the unusual zwitterionic biscyanine tetraphenylhexaazaanthracene **2** (TPHA).[3] While Blatter radical **1a** (R = H) is essentially stable in its crystalline form, it can be oxidized on treatment with either MnO_2 or $KMnO_4$ to the useful heterocyclic scaffold, 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**3**),[1d,2d] which readily undergoes regiospecific addition of nucleophiles at C-6 and of electrophiles at C-8.[4] The benzotriazinone **3** also participates in a range of cyclisation reactions that led to extension of the acene core, which included the formation of new zwitterions (*e.g.*, the quinoxalino fused **4**),[5] the preparation of alkaloid-like tetraazafluoranthenones **5**,[6] and π extended azole fused benzotriazinyls **6**-**8**.[1a,1b] Furthermore, analogues of the benzotriazinone **3**, including the triazafluoranthenone **5**, inhibited the formation of amyloid fibres and inhibited AChE and BChE.[7] Interestingly, the 7-trifluoromethyl substituted analogue of Blatter's radical **1e** (R = F_3C) was stable to oxidation[2d] and along with other Blatter radicals mediated the polymersiation of styrene.[8] The synthesis and chemistry of 1,2,4-triazines and their benzo derivatives have been extensively reviewed,[9] while recent reviews on stable organic radicals and their potential application in organic electronics have also appeared.[10]

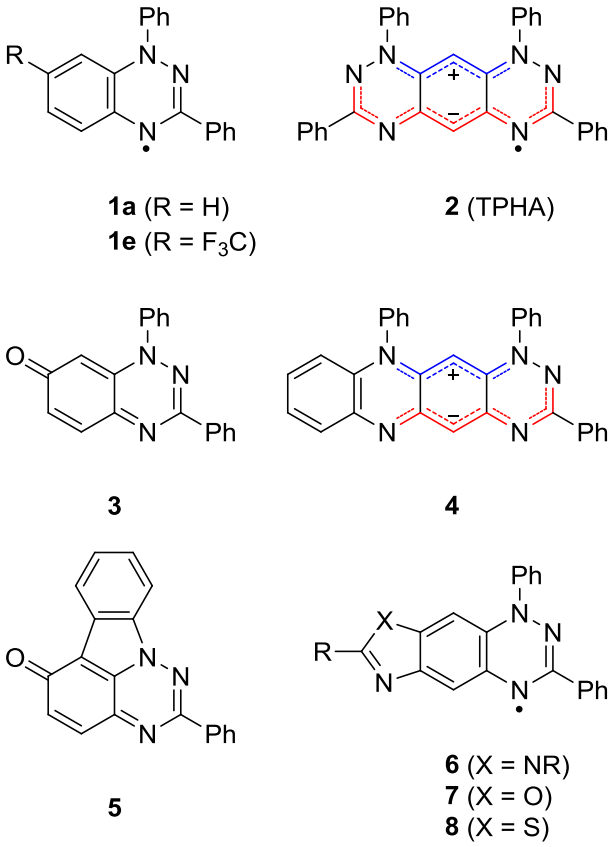
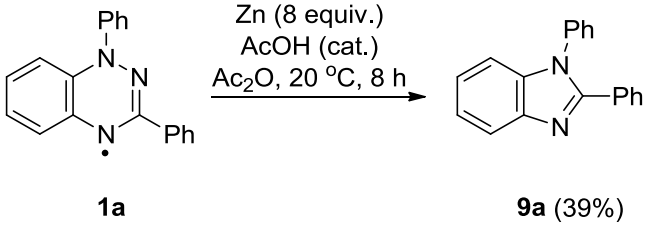


Figure 1 Structures of important 1,2,4-benzotriazines **1-8**.

As a continuation of our studies on 1,2,4-benzotriazines, we became interested in the reductive ring contraction of Blatter's radical **1a** reported by Barton *et al.*: Treatment of Blatter's radical **1a** with Zn powder (8 equiv.) and a catalytic amount of acetic acid in acetic anhydride at *ca.* 20 °C for 8 h gave 1,2-diphenylbenzimidazole (**9a**) in 39% yield (Scheme 1).[11]



Scheme 1 Barton's reductive ring contraction conditions.

The acid catalyzed zinc mediated reduction of various 1,2-diaza heteroarenes has been extensively used to effect ring contractions: 1,2,4,5-Tetrazines,[12] cinnolines,[13] phthalazines[14] and pyridazines[15] treated with zinc powder in acetic acid afford 1,2,4-triazoles, indoles, isoindoles, and pyrroles, respectively. A number of reports have also appeared on monocyclic 1,2,4-triazines which give imidazoles on chemical or electrochemical reduction,[15,16] and mixtures of pyrazoles and imidazoles on photolysis.

In light of these reductive ring contractions we reinvestigated the metal mediated reductive ring contraction of benzotriazinyl radicals and identified optimum conditions for their nearly quantitative conversion into benzimidazoles.

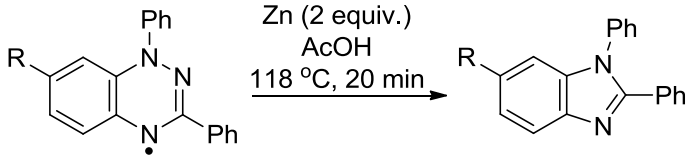
2. Results and discussion

The reductive ring contraction of Blatter's radical **1a** in alkanoic acids was optimized with respect to the metal [In (IP 5.78 eV), Sn (7.34 eV), Ni (7.63 eV), Cu (7.72 eV), Fe (7.87 eV) and Zn (9.39 eV)],[17] alkanoic acid (HCO_2H pK_a 3.77, AcOH pK_a 4.79 and F_3CCO_2H pK_a 0.23)[17] and reaction temperature (rt *vs* reflux). Initially, the effect of the alkanoic acid was investigated in the absence of any metal reducing agent: Blatter's radical **1a** in neat HCO_2H (bp 101 ^oC), AcOH (bp 118 ^oC), or F_3CCO_2H (bp 72 ^oC) at *ca.* 20 ^oC for 72 h was recovered unchanged, while in these solvents when heated at their respective boiling points the radical **1a** slowly (*ca.* 30 h) degraded only in AcOH. The various metals screened were In, Sn, Ni, Cu, Fe and Zn. In general, the benzotriazinyl **1a** in all (three) alkanoic acids in the presence of every metal screened was reduced to the *leuco* form (the benzotriazine) at rt after *ca.* 12 h or immediately at *ca*. 118 ^oC, which on alkali work-up gave back the radical. The radical **1a** in formic or

acetic acids (24 h at *ca*. 118 ^{o}C) with either In or Sn powder (2 equiv.) followed by an alkali work up led to a nearly quantitative recovery of the radical. With Ni, Cu and Fe the reactivity of the radical **1a** was dependant on the alkanoic acid used: The use of either Ni, Cu or Fe powder (2 equiv.) in AcOH heated at reflux gave in all cases the benzimidazole **9a** in 55, 95 and 53% yields, respectively but these metals failed to give any benzimidazole in formic acid heated at reflux. When Zn powder (2 equiv.) was used in AcOH heated to *ca.* 118 ^{o}C, the benzotriazinyl **1a** was rapidly (20 min) converted into the benzimidazole **9a**, while in formic acid heated to *ca.* 100 ^{o}C the conversion was slow (22 h) and the benzimidazole was isolated in a lower yield (74%). Interestingly, increasing the equivalents of Zn powder (from 2 to 4 equiv.) shortened the reaction time without a drop in yield. While the use of less than 2 equiv. of Zn (1 or 1.5 equiv.) led to long reaction times (*ca.* 30 h), a drop in product yield and complex reaction mixtures.

The optimized conditions for the zinc powder mediated reductive ring contraction [*i.e.*, Zn (2 equiv.), AcOH heated to *ca.* 118 ^{o}C] worked equally well for chloro, bromo, trifluoromethyl, phenyl and fur-2-yl C-7 substituted benzotriazinyl analogues. However, some protodeiodination was observed with the 7-iodo-substituted analogue **1d** which gave a mixture of 6-iodo-1,2-diphenylbenzimidazole (**9d**) and 1,2-diphenylbenzimidazole (**9a**). Fortunately, both compounds could be separated by silica chromatography or even by fractional recrystallisation of the crude product (Table 1).

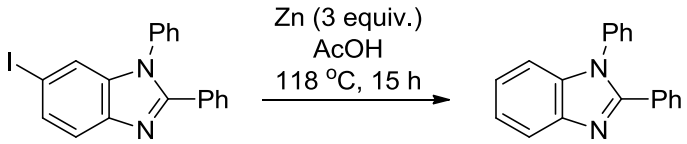
Table 1 Reductive ring contraction of 7-substituted benzotriazinyls **1a-g** into benzimidazoles **9a-g**.



1a-g **9a-g**

R	Yields **9** (%)
H	**9a** (95)
Cl	**9b** (98)
Br	**9c** (97)
I	**9d** (60) + **9a** (10)
F_3C	**9e** (96)
Ph	**9f** (99)
Fur-2-yl	**9g** (95)

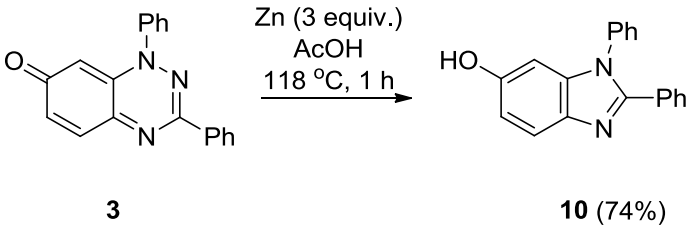
Iodoarenes are known to undergo protodeiodination in the presence of Zn powder and AcOH.[18] Not surprisingly, treating a pure sample of 6-iodo-1,2-diphenylbenz-imidazole (**9d**) with Zn (3 equiv.) in AcOH at *ca.* 118 °C for 15 h gave the diphenylbenzimidazole **9a** in 97% yield (Scheme 2).



9d **9a** (97%)

Scheme 2 Zinc mediated protodeiodination of the 6-iodobenzimidazole **9d**.

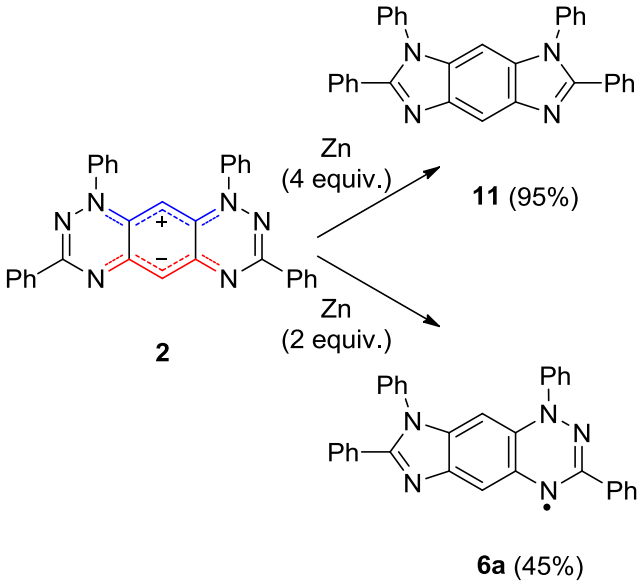
Interestingly, the reductive ring contraction also worked with 1,3-diphenylbenzo[*e*]-[1,2,4]triazin-7(1*H*)-one (**3**) but needed at least 3 equivalents of Zn powder to drive the reaction to completion and afford 1,2-diphenylbenzimidaz-6-ol (**10**)[19] in 74% yield (Scheme 3).



3 **10** (74%)

Scheme 3 Reductive ring contraction of the 1,2,4-benzotriazinone **3**.

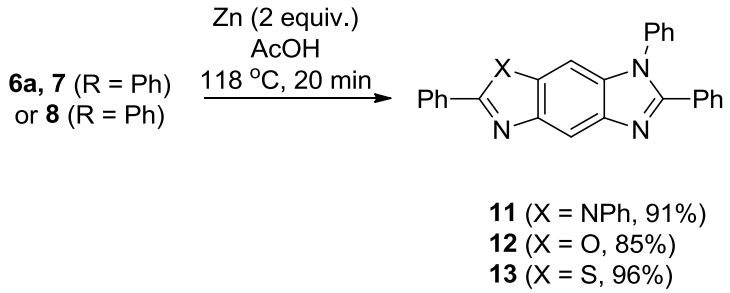
Furthermore, the zwitterionic tetraphenylhexaazaanthracene **2** (TPHA) when treated with Zn (4 equiv.) in AcOH (1 ml) for 1 h gave the anticipated 1,2,6,7-tetraphenyl-1,7-dihydro-benzo[1,2-*d*:4,5-*d'*]diimidazole (**11**)[20] in 95% yield (Scheme 4).



Scheme 4 Reductive ring contraction of TPHA **2** using 2 or 4 equivalents of zinc powder.

However, when only 2 equivalents of zinc were used the reaction could not be driven to completion and the diimidazole **11** was obtained in only 22% yield together with the unusual imidazolo fused radical **6a** in 45% yield: Radical **6a** has been recently synthesized independently by our team starting from the benzotriazinone **3**.[1a] The radical **6a** and its oxazolo- and thiazolo-fused analogues **7** (R = Ph)[1a] and **8** (R = Ph)[1b]

can be reduced with Zn (2 equiv.) in AcOH to the expected imidazolo-, oxazolo- and thiazolo-fused benzimidazoles **11** (X = NPh), **12** (X = O) and **13** (X = S) in excellent yields (Scheme 5).

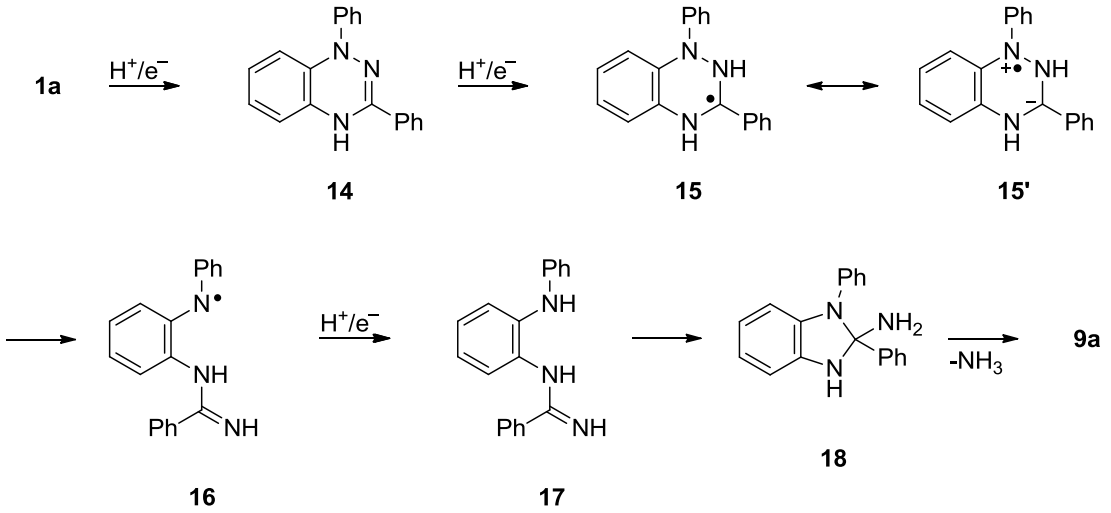


11 (X = NPh, 91%)
12 (X = O, 85%)
13 (X = S, 96%)

Scheme 5 Reductive ring contraction of imidazolo-, oxazolo- and thiazolo-fused benzotriazinyl radicals **6a**, **7** (R = Ph) and **8** (R = Ph).

Mechanistic Rationale for Ring Contraction

The zinc mediated ring contraction of various 1,2-diaza heteroazines is assumed to take place *via* reductive cleavage of the N-N bond followed by recyclization with loss of ammonia.[21] At least two equivalents of Zn powder were needed to consume the starting benzotriazinyl radical **1a** and this is slightly above the theoretical amount needed based on the electron transfer mechanism outlined below which requires the transfer of three electrons (Scheme 6).

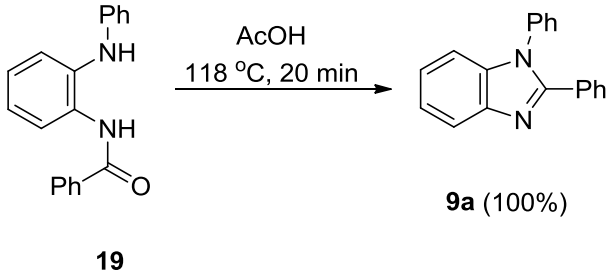


Scheme 6 Tentative mechanism for reductive ring contraction of benzotriazinyls.

The first reduction, affords the *leuco* form benzotriazine **14**, which when protonated in AcOH then undergoes a second reduction to afford the radical intermediate **15**, that is tentatively stabilized by several resonance charge separated forms such as **15'**. Radical **15** then undergoes a ring opening to give an intermediate similar to **16** that is reduced to *N*-[2-(phenylamino)phenyl]benzimidamide (**17**). Intramolecular cyclisation affords the 2,3-dihydrobenzimidazole **18** that eliminates ammonia to give the observed 1,2-diphenylbenzimidazole **9a**.

While variations of this tentative mechanism can be readily proposed, there is sufficient evidence for the chemical[22] and electrochemical[23] reduction of 1,2,4-triazines to support the proposed mechanism as far as triazinyl **14**. Furthermore, while to the best of our knowledge examples of the final cyclisation step (**17** to **9a**) have been limited to *N*-(2-aminophenyl)imidamides[24] and 1-(2-aminophenyl)guanidines,[25] we note that the more closely related cyclisation of *N*-[2-(anilino)aryl]benzamides in hot AcOH are known to give 1,2-diarylbenzimidazoles[26] in high yield. In our hands

heating a pure sample of *N*-[2-(phenylamino)phenyl]benzamide (**19**)[20] in neat AcOH for 20 min gave 1,2-diphenylbenzimidazole (**9a**) in 100% yield (Scheme 7).



19 **9a** (100%)

Scheme 7 Cyclodehydration of *N*-[2-(phenylamino)phenyl]benzamide (**19**).

3. Conclusions

To conclude, treatment of benzotriazinyl radicals with reducing metals (Zn, Cu, Fe and Ni) in alkanoic acids can lead to a reductive ring contraction to afford the *N*-phenylbenzimidazoles. The optimum reaction conditions that give nearly quantitative yields for the conversion are: Zn powder (2 equiv.), in AcOH heated to reflux for 20 min. Indium or tin which are milder reductants in hot alkanoic acids fail to reduce the radical beyond its *leuco* form, which identifies them as prospective mild and selective agents for modification of substituted benzotriazinyl radicals. While this method for the synthesis of simple benzimidazoles may not compare favourably with the many known procedures, it does nevertheless, provide an unusual route to heterole (imidazolo, oxazolo and thiazolo) fused benzimidazoles that are considerably more challenging to access.

4. Experimental Section

4.1. General methods

Anhydrous Na_2SO_4 was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography[27] was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting and decomposition points were determined using either a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus or a TA Instruments DSC Q1000 with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 ^{o}C/min. Solvents used for recrystallisation are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation 'inf'. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike Miracle Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a BrukerAvance 300 machine (at 300 and 75 MHz, respectively) or on a Bruker 500 MHz instrument (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GC/MS with direct inlet probe. 1,3-Diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1a**),[1d] 7-chloro-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1b**),[1d] 7-bromo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1c**),[1d] 7-iodo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1d**),[1d] 1,3-diphenyl-7-(trifluoromethyl)-1,4-di-

hydro-benzo[*e*][1,2,4]triazin-4-yl (**1e**),[1d] 1,3,7-triphenyl-1,4-dihydrobenzo[*e*][1,2,4]-triazin-4-yl (**1f**),[1c] 7-(fur-2-yl)-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1g**),[1c] the tetraphenylhexaazaanthracene **2** (TPHA),[3a] 1,3-diphenylbenzo[*e*][1,2,4]-triazin-7(1*H*)-one (**3**)[1d] and *N*-[2-(phenylamino)phenyl]benzamide (**19**)[20] were prepared using literature procedures.

4.2. Reaction of benzotriazines with Zn powder (2 equiv.) in hot AcOH.

4.2.1. 1,2-Diphenylbenzimidazole (**9a**) (Typical Procedure).

A stirred mixture of 1,4-dihydro-1,3-diphenylbenzo[*e*][1,2,4]triazin-4-yl (**1a**) (50 mg, 0.176 mmol) and Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) was heated at *ca.* 118 °C for 20 min. The reaction mixture was then allowed to cool to *ca.* 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried, filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution with DCM removed minor non polar side products and further elution (Et_2O/*n*-hexane, 1:1) gave the title compound **9a** as colourless needles (45 mg, 95%), mp 109-110 °C (from *n*-hexane), (lit.,[11] 110-111 °C), R_f (Et_2O/*n*-hexane, 1:1) 0.32; ν_{max}/cm^{-1} 3063w, 3051w and 3011w (Ar CH), 1611w, 1595w, 1584w, 1526w, 1491m, 1476m, 1456m, 1445m, 1383s, 1329w, 1306w, 1279w, 1261w, 1204w, 1194w, 1182w, 1173w, 1150w, 1117w, 1109w, 1076w, 1028w, 1011w, 997w, 976w, 932w, 907w, 849w, 833w, 781m, 764s; δ_H(500 MHz, $CDCl_3$) 7.89 (1H, d, *J* 8.0, Ar *H*), 7.57 (2H, d, *J* 7.3, Ar *H*), 7.53-7.45 (3H, m, Ar *H*), 7.38-7.24 (8H, m, Ar *H*); δ_C(75 MHz, DMSO-d_6) 151.8 (s), 142.5 (s), 137.0 (s), 136.4 (s), 130.0 (d), 129.8 (s), 129.5 (d), 129.1 (d), 128.8 (d), 128.3 (d), 127.5 (d), 123.3 (d),

122.7 (d), 119.4 (d), 110.4 (d); *m/z* (EI) 270 (M^+, 75%), 269 (100), 166 (5), 139 (6), 135 (6), 77 (22), 63 (5), 51 (16); identical to an authentic sample.

4.2.2. 6-Chloro-1,2-diphenylbenzimidazole (**9b**).

Similar treatment of 7-chloro-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1b**) (56 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 ^oC for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9b** as colourless needles (53 mg, 98%), mp (DSC) onset: 132.9 ^oC, peak max: 134.3 ^oC (from *n*-hexane), R_f (Et_2O/*n*-hexane, 1:1) 0.37; (found: C, 75.04; H, 4.22; N, 9.10. $C_{19}H_{13}ClN_2$ requires C, 74.88; H, 4.30; N, 9.19%); λ_{max}(DCM)/nm 233 (log ε 3.42), 302 (3.38); ν_{max}/cm^{-1} 3063w (Ar CH), 1611w, 1597w, 1499s, 1474m, 1460m, 1447m, 1435m, 1377m, 1331m, 1312w, 1302w, 1288w, 1273m, 1246w, 1202w, 1179w, 1157w, 1109w, 1074w, 1057m, 1028w, 988w, 978w, 937w, 922w, 854m, 841m, 824m, 812s, 775s; δ_H(300 MHz, $CDCl_3$) 7.79 (1H, d, *J* 9.0, Ar *H*), 7.58-7.48 (5H, m, Ar *H*), 7.40-7.27 (6H, m, Ar *H*), 7.23 (1H, d, *J* 2.1, Ar *H*); δ_C(75 MHz, $CDCl_3$) 153.1 (s), 141.5 (s), 137.7 (s), 136.4 (s), 130.0 (d), 129.7 (d), 129.4 (s), 129.3 (d), 129.0 (s), 128.9 (d), 128.3 (d), 127.2 (d), 123.6 (d), 120.6 (d), 110.5 (d); *m/z* (EI) 306 (M^++2, 32%), 304 (M^+, 100), 268 (41), 166 (5), 164 (6), 152 (4), 139 (7), 135 (13), 77 (33), 63 (7), 51 (17).

4.2.3. 6-Bromo-1,2-diphenylbenzimidazole (**9c**).

Similar treatment of 7-bromo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1c**) (64 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 ^oC for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9c** as colourless needles (59 mg, 97%), mp (DSC) onset: 154.4 ^oC, peak

max: 156.0 °C (from *n*-hexane), R_f (Et_2O/*n*-hexane, 1:1) 0.37; (found: C, 65.42; H, 3.68; N, 8.16. $C_{19}H_{13}BrN_2$ requires C, 65.35; H, 3.75; N, 8.02%); λ_{max}(DCM)/nm 234 (log ε 3.47), 302 (3.43); ν_{max}/cm^{-1} 3049w (Ar CH), 1603w, 1593w, 1501m, 1476w, 1456m, 1445m, 1435w, 1373m, 1329m, 1312w, 1290w, 1275m, 1206w, 1182w, 1157w, 1123w, 1111w, 1072w, 1047w, 1030w, 1005w, 993w, 976w, 930w, 922w, 907w, 854w, 839m, 806s, 775s, 762m; δ_H(300 MHz, $CDCl_3$) 7.75 (1H, d, *J* 8.5, Ar *H*), 7.59-7.48 (5H, m, Ar *H*), 7.44 (1H, dd, *J* 8.6, 1.8, Ar *H*), 7.40-7.28 (6H, m, Ar *H*); δ_C(75 MHz, $CDCl_3$) 153.0 (s), 141.9 (s), 138.2 (s), 136.4 (s), 130.0 (d), 129.7 (d), 129.4 (s), 129.3 (d), 128.9 (d), 128.3 (d), 127.2 (d), 126.2 (d), 121.0 (d), 116.4 (s), 113.4 (d); *m/z* (EI) 350 (M^++2, 95%), 348 (M^+, 100), 268 (73), 242 (3), 192 (3), 164 (9), 139 (12), 135 (38), 121 (3), 115 (3), 105 (3), 89 (4), 77 (46), 63 (15), 51 (20).

4.2.4. 6-Iodo-1,2-diphenylbenzimidazole (**9d**).

Similar treatment of 7-iodo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1d**) (72 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 °C for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9d** as colourless needles (43 mg, 61%), mp (DSC) onset: 185.7 °C, peak max: 186.5 °C (from *n*-hexane), R_f (Et_2O/*n*-hexane, 1:1) 0.37; (found: C, 57.69; H, 3.24; N, 7.20. $C_{19}H_{13}IN_2$ requires C, 57.59; H, 3.31; N, 7.07%); λ_{max}(DCM)/nm 232 (log ε 3.57), 306 (3.51); ν_{max}/cm^{-1} 3063w and 3048w (Ar CH), 1591w, 1501s, 1474m, 1454m, 1445m, 1431m, 1383m, 1373m, 1325m, 1312w, 1290w, 1277m, 1250w, 1204w, 1180w, 1173w, 1157w, 1124w, 1111w, 1072w, 1042w, 1030w, 1005w, 993w, 974w, 928w, 920m, 905w, 854m, 843w, 806s, 775s, 762s; δ_H(300 MHz, $CDCl_3$) 7.66-7.59 (2H, m, Ar *H*), 7.59-7.55 (2H, m, Ar *H*), 7.55-7.47 (4H, m, Ar *H*), 7.40-7.27 (5H, m, Ar *H*); δ_C(75 MHz, $CDCl_3$) 152.7 (s), 142.5 (s), 138.7 (s), 136.4 (s), 131.9 (d),

130.0 (d), 129.7 (d), 129.4 (d), 129.3 (s), 128.9 (d), 128.3 (d), 127.3 (d), 121.5 (d), 119.4 (d), 86.7 (s); *m/z* (EI) 396 (M^+, 100%), 268 (44), 166 (10), 140 (8), 139 (9), 135 (21), 77 (38), 63 (18), 51 (13). Further elution (Et_2O/*n*-hexane, 1:1) gave the starting 1,2-diphenylbenzimidazole (**9a**) as colourless needles (5 mg, 10%), mp 109-110 °C (from *n*-hexane), (lit.,[11] 110-111 °C); R_f (Et_2O/*n*-hexane, 1:1) 0.32; δ_H(500 MHz, $CDCl_3$) 7.89 (1H, d, *J* 8.0, Ar *H*), 7.57 (2H, d, *J* 7.3, Ar *H*), 7.53-7.45 (3H, m, Ar *H*), 7.38-7.24 (8H, m, Ar *H*); identical to that described above.

4.2.5. 1,2-Diphenyl-6-(trifluoromethyl)benzimidazole (**9e**).

Similar treatment of 1,3-diphenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]-triazin-4-yl (**1e**) (62 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 °C for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9e** as colourless prisms (57 mg, 96%), mp (DSC) onset: 144.8 °C, peak max: 146.0 °C (from *n*-hexane), R_f (Et_2O/*n*-hexane, 1:1) 0.38; (found: C, 71.12; H, 3.80; N, 8.20. $C_{20}H_{13}F_3N_2$ requires C, 71.00; H, 3.87; N, 8.28%); λ_{max}(DCM)/nm 234 (log ε 3.47), 276 inf (3.34), 293 (3.39); ν_{max}/cm^{-1} 3067w, 3048w and 3032w (Ar CH), 1628w, 1597w, 1522w, 1499m, 1472w, 1454w, 1443w, 1387w, 1331s, 1317m, 1279m, 1250m, 1202w, 1165m, 1153m, 1132m, 1115s, 1076w, 1053m, 1028w, 980w, 947w, 926w, 914w, 874m, 841m, 781m, 762m; δ_H(300 MHz, $CDCl_3$) 7.96 (1H, d, *J* 8.5, Ar *H*), 7.63-7.52 (6H, m, Ar *H*), 7.51-7.49 (1H, m, Ar *H*), 7.43-7.29 (5H, m, Ar *H*); δ_C(75 MHz, $CDCl_3$) 154.8 (s), 145.1 (s), 136.7 (s), 136.3 (s), 130.2 (d), 130.0 (d), 129.5 (d), 129.2 (s), 129.1 (d), 128.4 (d), 127.3 (d), 125.4 (q, $^2J_{FC}$ 32.4, *C*CF_3), 124.8 (q, $^1J_{FC}$ 272.0, C*C*F_3), 120.2 (d), 119.9 (q, $^3J_{FC}$ 3.5, Ar *C*H), 108.2 (q, $^3J_{FC}$ 4.2, Ar *C*H); *m/z* (EI) 338 (M^+, 65%), 337 (100), 319 (3), 317 (5), 268 (19), 159 (4), 139 (3), 77 (16), 51 (11).

4.2.6. 1,2,6-Triphenylbenzimidazole (**9f**).

Similar treatment of 1,3,7-triphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1f**) (63 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 °C for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9f** as beige needles (60 mg, 99%), mp (DSC) onset: 209.0 °C, peak max: 209.8 °C (from cyclohexane), R_f (Et_2O/*n*-hexane, 1:1) 0.20; (found: C, 86.74; H, 4.89; N, 8.36. $C_{25}H_{18}N_2$ requires C, 86.68; H, 5.24; N, 8.09%); λ_{max}(DCM)/nm 232 (log ε 3.52), 244 (3.54), 311 (3.55); ν_{max}/cm^{-1} 3065w and 3034w (Ar CH), 1618w, 1595m, 1570w, 1501m, 1470m, 1454m, 1445m, 1431m, 1385m, 1342w, 1329w, 1310w, 1285w, 1240w, 1192w, 1179w, 1153w, 1111w, 1074m, 1038w, 1028w, 1016w, 999w, 989w, 972w, 937w, 922w, 914w, 866m, 847w, 837w, 818m, 775s, 768s, 758m; δ_H(300 MHz, $CDCl_3$) 7.94 (1H, d, *J* 8.5, Ar *H*), 7.64-7.56 (5H, m, Ar *H*), 7.55-7.47 (3H, m, Ar *H*), 7.46-7.28 (9H, m, Ar *H*); δ_C(75 MHz, $CDCl_3$) one CH signal missing 152.9 (s), 142.5 (s), 141.7 (s), 137.8 (s), 137.1 (s), 136.9 (s), 129.92 (d), 129.88 (s), 129.5 (d), 129.4 (d), 128.7 (d), 128.6 (d), 128.3 (d), 127.4 (d), 127.0 (d), 122.9 (d), 119.9 (d), 108.9 (d); *m/z* (EI) 346 (M^+, 100%), 268 (3), 241 (5), 178 (4), 173 (8), 165 (4), 151 (3), 139 (7), 121 (4), 77 (11), 51 (8).

4.2.7. 6-(Fur-2-yl)-1,2-diphenylbenzimidazole (**9g**).

Similar treatment of 7-(fur-2-yl)-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1g**) (62 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at *ca.* 118 °C for 20 min gave on chromatography (Et_2O/*n*-hexane, 1:1) the *title compound* **9g** as beige needles (56 mg, 95%), mp (DSC) onset: 183.6 °C, peak max: 185.6 °C (from cyclohexane), R_f (Et_2O/*n*-hexane, 1:1) 0.20; (found: C, 82.20; H, 4.86; N, 8.20. $C_{23}H_{16}N_2O$ requires C, 82.12; H, 4.79; N, 8.33%); λ_{max}(DCM)/nm 232 (log ε

3.48), 251 (3.42), 307 inf (3.42), 326 (3.55), 330 (3.55); ν_{max}/cm^{-1} 3067w and 3053w (Ar CH), 1618w, 1595w, 1582w, 1501m, 1470w, 1456m, 1437w, 1391m, 1337m, 1306w, 1296w, 1285m, 1238w, 1217w, 1180w, 1159w, 1150w, 1128w, 1111w, 1074w, 1030w, 1011m, 993w, 978w, 972w, 951w, 922w, 891m, 883w, 864m, 841w, 812m, 793m, 773s; δ_H(300 MHz, $CDCl_3$) 7.87 (1H, d, *J* 8.5, Ar *H*), 7.67 (1H, dd, *J* 8.5, 1.5, Ar *H*), 7.59-7.52 (6H, m, Ar *H*), 7.46-7.42 (1H, m, Ar *H*), 7.40-7.27 (5H, m, Ar *H*), 6.63 (1H, d, *J* 3.4, Ar *H*), 6.47 (1H, dd, *J* 3.4, 1.7, Ar *H*); δ_C(75 MHz, $CDCl_3$) 154.4 (s), 153.0 (s), 142.5 (s), 141.7 (d), 137.6 (s), 136.8 (s), 129.9 (d), 129.8 (s), 129.5 (d), 129.3 (d), 128.7 (d), 128.3 (d), 127.4 (d), 126.6 (s), 120.0 (d), 119.8 (d), 111.7 (d), 105.5 (d), 104.6 (d); *m/z* (EI) 336 (M^+, 100%), 335 (59), 307 (11), 305 (11), 204 (8), 168 (6), 153 (13), 140 (6), 102 (5), 77 (11), 51 (6).

4.2.8. 1,2-Diphenylbenzimidaz-6-ol **(10).**

A stirred mixture of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one (**3**) (53 mg, 0.176 mmol) and Zn powder (34.5 mg, 0.527 mmol) in glacial AcOH (1 ml) was heated at *ca.* 118 °C for 1 h. The reaction mixture was allowed to cool to *ca.* 20 °C, diluted with DCM (50 ml), washed with sat. Na_2CO_3 (2 × 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (20 ml) and column chromatographed (neutral Al_2O_3). Elution with (Et_2O) removed minor non polar side products and further elution (EtOH) gave the title compound **10** as beige needles (56 mg, 95%), mp (DSC) onset: 212.4 °C, peak max: 218.5 °C (from cyclohexane), (lit.,[19] 223 °C), R_f (Et_2O) 0.59; λ_{max}(DCM)/nm 230 (log ε 3.32), 256 inf (3.13), 308 (3.31); ν_{max}/cm^{-1} 3061w, 3049w and 3042w (Ar CH), 1620m, 1595m, 1560w, 1524w, 1501m, 1483s, 1474s, 1454m, 1385s, 1337m, 1312w, 1287m, 1250s, 1211m, 1175s, 1113m, 1074m, 1030w, 1003w, 984w, 968w, 920w, 908w, 887w, 876w, 853m, 831s, 810s, 775s,

764s; δ_H(300 MHz, DMSO-d_6) 9.39 (1H, s, O*H*), 7.61-7.50 (4H, m, Ar *H*), 7.48-7.43 (2H, m, Ar *H*), 7.41-7.27 (5H, m, Ar *H*), 6.78 (1H, dd, *J* 8.7, 2.3, Ar *H*), 6.51 (1H, d, *J* 2.1, Ar *H*); δ_C(75 MHz, DMSO-d_6) 154.6 (s), 150.3 (s), 138.0 (s), 136.8 (s), 136.0 (s), 130.1 (s), 130.0 (d), 129.1 (d), 128.8 (d), 128.7 (d), 128.3 (d), 127.4 (d), 119.9 (d), 112.6 (d), 95.4 (d); *m/z* (EI) 286 (M^+, 94%), 285 (100), 266 (3), 255 (6), 178 (6), 165 (3), 154 (11), 143 (6), 134 (3), 127 (10), 115 (3), 104 (4), 84 (6), 77 (28), 69 (12), 63 (8), 56 (39), 51 (25); identical to an authentic sample.

*4.2.9. 1,2,6,7-Tetraphenyl-1,7-dihydrobenzo[1,2-*d*:4,5-*d*']diimidazole (**11**).*

A stirred mixture of tetraphenylhexaazaanthracene **2** (TPHA) (86 mg, 0.176 mmol) and Zn powder (46 mg, 0.703 mmol) in glacial AcOH (1 ml) was heated at *ca.* 118 °C for 20 min. The reaction mixture was allowed to cool to *ca.* 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (5 ml), adsorbed onto silica and chromatographed (Et_2O) to remove all non-polar minor side products. Further elution (THF) gave the title compound **11** as colourless needles (77 mg, 95%), mp (DSC) onset: 281.6 °C, peak max: 282.5 °C (from EtOH), (lit.,[20] 283-285 °C), R_f (Et_2O) 0.18; (found: C, 83.22; H, 4.67; N, 12.01. $C_{32}H_{22}N_4$ requires C, 83.09; H, 4.79; N, 12.11%); λ_{max}(DCM)/nm 231 (log ε 3.56), 278 (3.59), 327 inf (3.70), 337 (3.74); ν_{max}/cm^{-1} 3063w and 3036w, (Ar CH), 2970w, 1632w, 1597m, 1522w, 1497s, 1476m, 1452w, 1445w, 1427s, 1398s, 1360m, 1327m, 1310m, 1283m, 1207m, 1177m, 1150w, 1113w, 1094w, 1076m, 1051m, 1026m, 1003w, 980w, 966w, 920w, 897m, 880w, 864w, 851m, 824m, 806w, 772s, 754m; δ_H(300 MHz, $CDCl_3$) 8.36 (1H, s, Ar *H*), 7.61-7.54 (4H, m, Ar *H*), 7.52-7.40 (6H, m, Ar *H*), 7.39-7.27 (10H, m, Ar *H*), 6.96 (1H, s, Ar *H*); δ_C(75 MHz, $CDCl_3$) 153.1 (s), 140.6 (s), 137.2 (s), 135.7 (s), 129.93 (s),

129.87 (d), 129.32 (d), 129.27 (d), 128.4 (d), 128.2 (d), 127.4 (d), 109.1 (d), 90.0 (d); *m/z* (EI) 462 (M^+, 100%), 461 (52), 384 (5), 357 (7), 231 (17), 179 (5), 165 (3), 152 (3), 128 (5), 77 (9).

4.3. Reduction of tetraphenylhexaazaanthracene 2 (TPHA) using Zn (2 equiv.).

*4.3.1. 1,3,7,8-Tetraphenyl-4,8-dihydro-1*H*-imidazo*[4,5-g][1,2,4]*benzotriazin-1-yl* (**6**).

To a stirred mixture of the tetraphenylhexaazaanthracene **2** (TPHA) (86.0 mg, 0.176 mmol) in glacial AcOH (1 ml) at *ca.* 20 °C was added Zn powder (23.0 mg, 0.352 mmol). The reaction mixture was then heated at *ca.* 118 °C for 20 min, then allowed to cool to *ca.* 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (5 ml) and chromatographed on basic Al_2O_3 (DCM) to give unreacted starting material **2** as purple prisms (20 mg, 23%), mp 376 °C (from PhMe), (lit.,[3a] 376 °C), identical to an authentic sample. Further elution (DCM) gave the title compound **6** as dark brown needles (38 mg, 45%), mp (DSC) onset: 300.8 °C, peak max: 306.1 °C (decomp.) (from PhH) (lit.,[1a] mp (DSC) onset: 300.8 °C, peak max: 306.1 °C (decomp.), R_f (Et_2O) 0.64; (found: C, 80.52; H, 4.56; N, 14.82. $C_{32}H_{22}N_5$ requires C, 80.65; H, 4.65; N, 14.70%); λ_{max}(DCM)/nm 291 (log ε 3.61), 330 inf (3.02), 419 (3.35), 465 inf (2.63), 540 (2.50), 624 inf (2.16); ν_{max}/cm^{-1} 3061w and 3044w (Ar CH), 2972w, 2918w, 1595w, 1503w, 1489w, 1470m, 1452w, 1435m, 1402m, 1389m, 1350w, 1317w, 1296w, 1287w, 1267w, 1236w, 1200w, 1179w, 1159w, 1096s, 1065w, 1024w, 984w,

972w, 934s, 897s, 854m, 831w, 777m, 770w, 762m; *m/z* (EI) 476 (M^+, 100%), 373 (7), 371 (6), 267 (13), 238 (18), 180 (6), 164 (3), 140 (3), 103 (3), 77 (22), 51 (5); identical to an authentic sample. Further elution (THF) gave 1,2,6,7-tetraphenyl-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]diimidazole (**11**) as colourless needles (18 mg, 22%), mp (DSC) onset: 281.6 °C, peak max: 282.5 °C (from EtOH), (lit.,[20] 283-285 °C), identical to that described above.

4.4. Reduction of imidazolo-, oxazolo- and thiazolo-fused benzotriazinyls 6-8

*4.4.1. 1,2,6,7-Tetraphenyl-1,7-dihydrobenzo[1,2-*d*:4,5-*d*']diimidazole (**11**).*

A stirred mixture of 1,3,7,8-tetraphenyl-4,8-dihydro-1*H*-imidazo[4,5-*g*][1,2,4]benzotriazin-1-yl (**6**) (84 mg, 0.176 mmol) and Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) was heated at *ca.* 118 °C for 20 min. The reaction mixture was allowed to cool to *ca.* 20 °C, diluted with DCM (20 ml), washed with sat. Na_2CO_3 (2 × 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (1 ml) and chromatographed on silica (*t*-BuOMe/*n*-hexane, 1:1) to give the title compound **11** as colourless needles (74 mg, 91%), mp (DSC) onset: 281.6 °C, peak max: 282.5 °C (from EtOH), (lit.,[20] 283-285 °C), R_f (Et_2O) 0.18; δ_H(300 MHz, $CDCl_3$) 8.36 (1H, s, Ar *H*), 7.61-7.54 (4H, m, Ar *H*), 7.52-7.40 (6H, m, Ar *H*), 7.39-7.27 (10H, m, Ar *H*), 6.96 (1H, s, Ar *H*); *m/z* (EI) 462 (M^+, 100%), 461 (52), 384 (5), 357 (7), 231 (17), 179 (5), 165 (3), 152 (3), 128 (5), 77 (9); identical to that described above.

*4.4.2. 2,6,7-Triphenyl-7*H*-imidazo[4,5-*f*]benzoxazole (**12**).*

Similar treatment of 1,3,7-triphenyl-1,4-dihydro[1,3]oxazolo[4,5-*g*][1,2,4]benzotriazin-4-yl (**7**) (71 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial

AcOH (1 ml) gave the *title compound* **12** as beige needles (58 mg, 85%), mp (DSC) onset: 236.7 °C, peak max: 237.7 °C (from cyclohexane), (found: C, 80.70; H, 4.60; N, 10.75. $C_{26}H_{17}N_3O$ requires C, 80.60; H, 4.42; N, 10.85%); R_f (*t*-BuOMe) 0.63; λ_{max}(DCM)/nm 231 (log ε 3.47), 270 (3.54), 334 (3.74); ν_{max}/cm^{-1} 3044w (Ar CH), 1630w, 1597w, 1585w, 1560m, 1516w, 1501s, 1489m, 1477m, 1458w, 1447w, 1425s, 1387m, 1364s, 1333w, 1323w, 1310w, 1292m, 1283w, 1211w, 1198w, 1179w, 1153s, 1142w, 1097w, 1074w, 1057s, 1026w, 1001w, 970w, 939w, 926m, 920w, 887m, 862w, 845m, 839m, 831m, 800w, 772s, 737m, 729w; δ_H(500 MHz; $CDCl_3$) 8.32-8.21 (3H, m, Ar *H*), 7.62 (2H, d, *J* 7.3, Ar *H*), 7.59-7.50 (6H, m, Ar *H*), 7.43-7.36 (4H, m, Ar *H*), 7.36-7.30 (2H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) one *C*H peak missing, 163.0 (s), 153.3 (s), 148.4 (s), 140.8 (s), 139.2 (s), 136.9 (s), 136.1 (s), 131.3 (d), 130.0 (d), 129.63 (s), 129.57 (d), 129.3 (d), 128.9 (d), 128.8 (d), 128.3 (d), 127.4 (d), 127.2 (s), 109.5 (d), 91.8 (d); MALDI-TOF (*m/z*): 389 (MH^++1, 9%), 388 (MH^+, 51), 387 (M^+, 100), 169 (1), 93 (12).

*4.4.3. 2,6,7-Triphenyl-7*H*-imidazo[4,5-*f*]benzothiazole (**13**).*

Similar treatment of 1,3,7-triphenyl-1,4-dihydro[1,3]thiazolo[4,5-*g*][1,2,4]benzotriazin-4-yl (**8**) (73 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) gave the *title compound* **13** as beige needles (68 mg, 96%), mp (DSC) onset: 245.1 °C, peak max: 245.6 °C (from cyclohexane), (found: C, 77.21; H, 4.39; N, 10.32. $C_{26}H_{17}N_3S$ requires C, 77.39; H, 4.25; N, 10.41%); R_f (*t*-BuOMe) 0.65; λ_{max}(DCM)/nm 234 (log ε 3.55), 286 (3.76), 341 (3.70); ν_{max}/cm^{-1} 3049w (Ar CH), 1595w, 1558w, 1518w, 1504m, 1487m, 1476s, 1443w, 1423s, 1373s, 1337s, 1308w, 1290w, 1283w, 1252w, 1194w, 1184w, 1152w, 1074w, 1028w, 972w, 953m, 920w, 885w, 853s, 843w, 775m, 766s; δ_H(500 MHz; $CDCl_3$) 8.58 (1H, s, Ar *H*), 8.15-8.08

(2H, m, Ar *H*), 7.70 (1H, s, Ar *H*), 7.63 (2H, d, *J* 7.3, Ar *H*), 7.59-7.48 (6H, m, Ar *H*), 7.42-7.36 (3H, m, Ar *H*), 7.36-7.31 (2H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) one *C*H peak missing, 166.7 (s), 154.0 (s), 151.2 (s), 142.8 (s), 136.84 (s), 136.75 (s), 133.7 (s), 131.7 (s), 130.8 (d), 130.1 (d), 129.8 (d), 129.51 (d), 129.46 (s), 129.0 (d), 128.9 (d), 128.4 (d), 127.5 (d), 113.3 (d), 102.0 (d); MALDI-TOF (*m/z*): 406 (MH^++2, 2%), 405 (MH^++1, 11), 404 (MH^+, 34), 403 (M^+, 100), 402 (M^+-1, 4), 284 (1).

4.5. Conversion of 6-iodo-1,2-diphenylbenzimidazole (9d) to 1,2-diphenyl-benzimidazole (9a)

A stirred mixture of 6-iodo-1,2-diphenylbenzimidazole (**9d**) (35 mg, 0.088 mmol) and Zn powder (17 mg, 0.264 mmol) in glacial AcOH (0.5 ml) was heated at *ca.* 118 °C for 15 h. The reaction mixture was then allowed to cool to *ca.* 20 °C, diluted with DCM (20 ml), washed with 1 M NaOH (2 × 20 ml), dried (Na_2SO_4), filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution with DCM removed minor non polar side products and further elution (Et_2O/*n*-hexane, 1:1) gave the title compound **9a** as colourless needles (23 mg, 97%), mp 109-110 °C (from *n*-hexane), (lit.,[11] 110-111 °C), R_f (Et_2O/*n*-hexane, 1:1) 0.32; δ_H(500 MHz, $CDCl_3$) 7.89 (1H, d, *J* 8.0, Ar *H*), 7.57 (2H, d, *J* 7.3, Ar *H*), 7.53-7.45 (3H, m, Ar *H*), 7.38-7.24 (8H, m, Ar *H*); identical to that described above.

4.6. Conversion of *N*-[2-(phenylamino)phenyl]benzamide (19) to 1,2-diphenyl-benzimidazole (9a)

A stirred mixture of *N*-[2-(phenylamino)phenyl]benzamide (**19**) (51 mg, 0.176 mmol) in glacial AcOH (1 ml) was heated at *ca.* 118 ^{o}C for 20 min. The reaction mixture was then allowed to cool to *ca.* 20 ^{o}C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried (Na_2SO_4), filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution (Et_2O/*n*-hexane, 1:1) gave the title compound **9a** as colourless needles (47 mg, 100%), mp 109-110 ^{o}C (from *n*-hexane), (lit.,[11] 110-111 ^{o}C), R_f (Et_2O/*n*-hexane, 1:1) 0.32; δ_H(500 MHz, $CDCl_3$) 7.89 (1H, d, *J* 8.0, Ar *H*), 7.57 (2H, d, *J* 7.3, Ar *H*), 7.53-7.45 (3H, m, Ar *H*), 7.38-7.24 (8H, m, Ar *H*); identical to that described above.

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Supporting Information Available ^{1}H and ^{13}C NMR spectral data for all new compounds. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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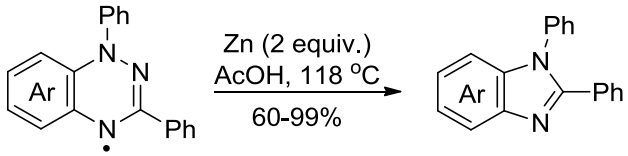
Graphical Abstract



Ar = substituted and fused arenes

Caption

Optimized conditions for the reductive ring contraction of benzotriazinyl radicals and related analogues afford benzimidazoles in near quantitative yields.