Synthesis of novel twisted heterocyclic analogues of *s*-indacenes

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Abstract

A series of novel compounds as candidates for OLED applications were synthesized by cyclization reactions of neighbouring rings in dipyrazolo[3,4-*b*:4',3'-*e*]pyridines **8-12**. The desymmetrization of these molecules leading to **14** can be performed using both KOH/isoquinoline or palladium catalysts. The resulting structures contain a helical arrangement of four different rings.

Keywords: Aza-*s*-indacenes, helicenes, synthetic methods, organic diodes

Introduction

In our previous reports we successfuly used KOH/(iso)quinoline system for the production of 6-aryl-6*H*-5,6,7-triazadibenzo[*f*,*h*]naphtho[3,2,1-*cd*]azulenes **3** originating from 4-(2-halophenyl)-1*H*-pyrazolo[3,4-*b*]quinolines **2** (Figure 1).[1]

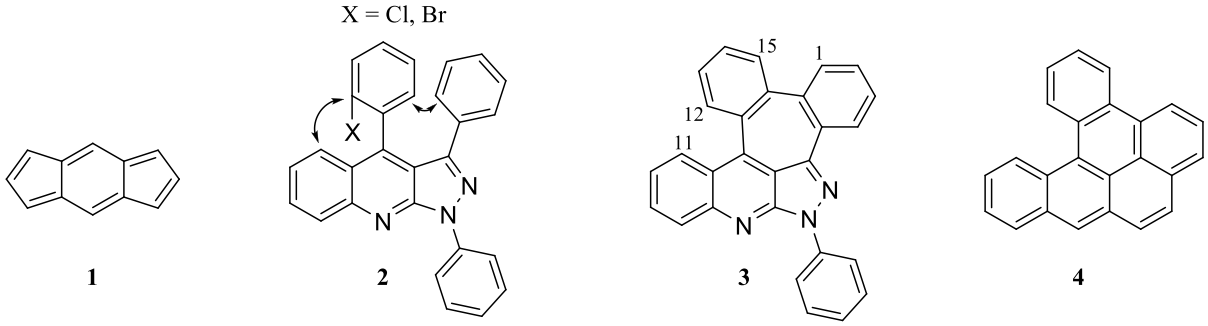
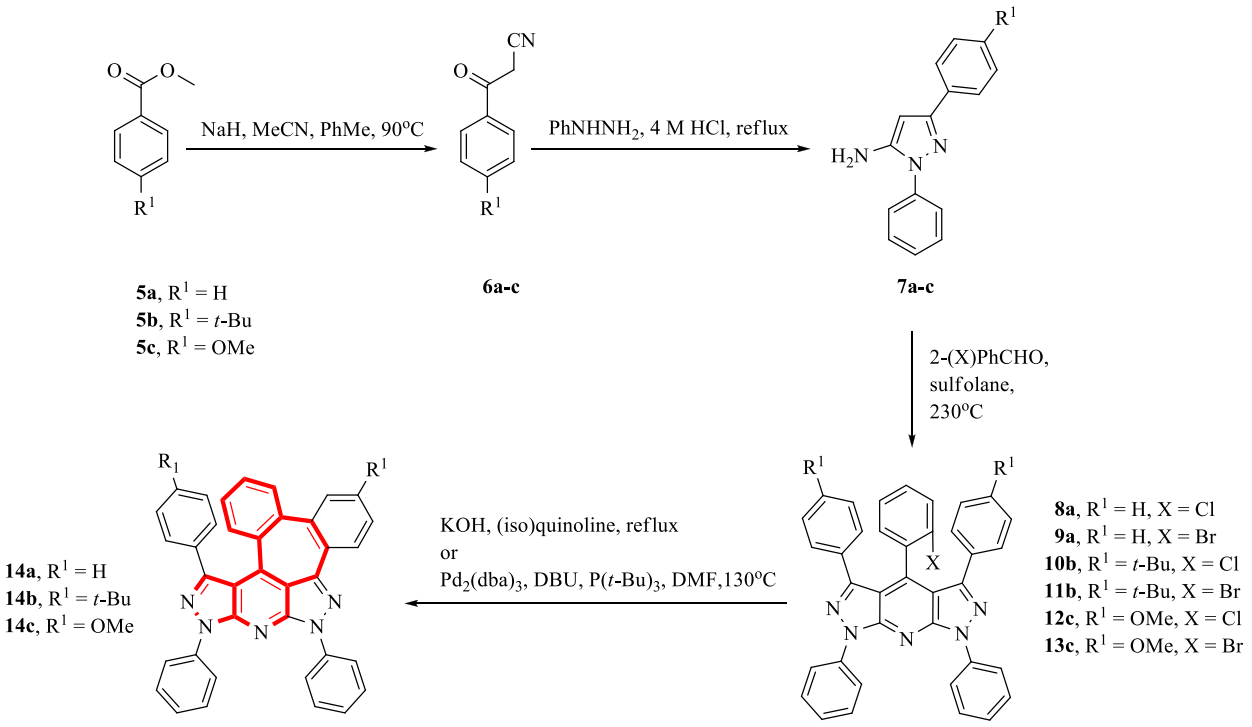


Figure 1. 1 *s*-indacene; **2** 4-(2-halophenyl)-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline; **3** 6-phenyl-6*H*-5,6,7-triazadibenzo[*f*,*h*]naphtho[3,2,1-*cd*]azulene, with atomic numbering; **4** dibenzo[*a*,*l*]pyrene.

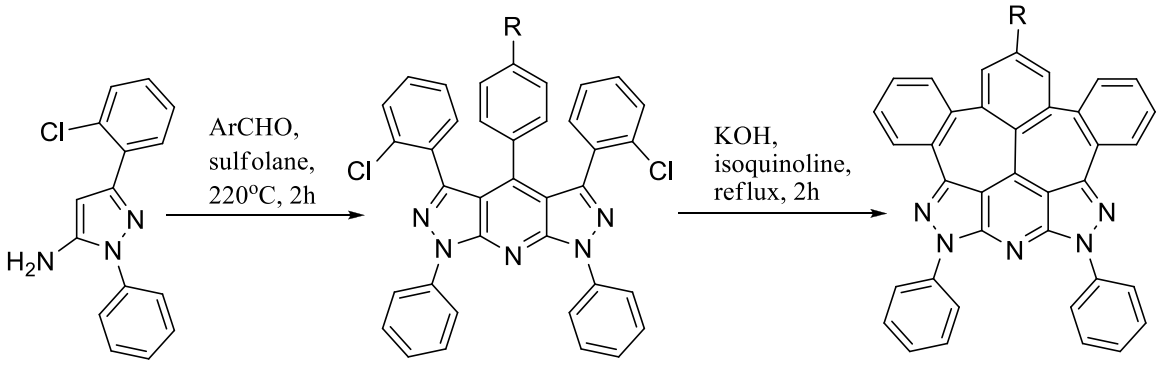
These new dyes are characterized by the presence of a seven-membered ring adjoining aromatic moieties and may be of interest for luminescent or electroluminescent applications. Similar arrangements of rings can be found in a variety of biologically active compounds,[2a] novel nucleosides,[2b] carbon nanotubes as so called Stone-Wales defects,[3] or in recently synthesized dimeric triazadibenzo[*cd*,*g*]azulenes.[4] These angularly arranged rings in **3** impose helicity on the molecules and should prevent to some extent their aggregation in the bulk thus extending the lifetime of a potential organic light-emitting diode (OLED). This distortion, reminiscent of that encountered in either dibenzo[*a*,*l*]pyrene[5] DB[*a*,*l*]P **4**, or benzo[*c*]phenanthrene ([4]helicene),[6] is the result of strongly interacting protons at the positions 1,15 and 11,12 in **3**, respectively. Recently, 3,12-dimethoxy-7,8-dicyano[5]helicene was evaluated as a novel emissive material for organic light-emitting diodes.[7] In this communication, we report a new series of dyes, modified aza *s*-indacenes **14**, derived from 4-(2-halophenyl)-1,3,5,7-tetraaryl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridines **8-12**. Dipyrazolopyridine derivatives have recently been extensively tested as promising blue emitters in OLEDs.[8] The emission maxima of newly designed dyes are shifted to a longer wavelength.

Results and Discussion



Scheme 1

Pyrazolo[3,4-*b*]quinoline **2** (PQ) has two possible sites for cyclization (Figure 1). In the case of (iso)quinoline/KOH this preference is meaningless: always a seven-membered ring is formed.[1] Palladium-assisted ring closure is not so obvious: in some cases there are negligible amounts of seven-membered isomers formed apart from the main five-membered ring products.[1a] This holds true if the substituent at the 6-position of the PQ skeleton is not bulky enough, or secondary amine. These precautions were kept in mind when we turned our attention to 1,3,4,5,7-pentaphenyl-1,7-dihydrodipyrazolo[3,4-*b*:4',3'-*e*]pyridines. These interesting aza analogues of *s*-indacene **1** have a plane of symmetry, thus they are devoid of the aforementioned obstacles. Therefore, it was tempting to use our procedure to create the novel annulated systems **14**, 1,3,5-triphenyl-2,3,4,5,6-pentaazadibenzo[4,5:6,7]cyclohepta[1,2,3-*cd*]*s*-indacenes, abbreviated as TPPACI. The aforementioned bispyrazolo[3,4-*b*:4',3'-*e*]pyridines can be obtained in several steps (4, 3 or 2) starting from commercially available aromatic carboxylic acids, methyl benzoates **5** or aroylacetonitriles **6** (Scheme 1). Finally, these by treatment with phenylhydrazine in boiling 4 M hydrochloric acid, gave aminopyrazoles **7**. The reaction of these with 2-halobenzaldehydes in sulfolane delivered precursors **8-13**. However the conversion from **7** to **8-13** did not always go in the same way. Condensation of **7c** (R^1 = OMe) with 2-bromobenzaldehyde yielded the expected product **13c** only in a trace amount (TLC). After replacement of the aldehyde with its chloro analogue we obtained **12c** in 21% yield after column purification. Reaction of pyrazole **7a** with 2-halobenzaldehydes delivered **8a** and **9a**, in 35% and 32% yields respectively, which did not require chromatographic isolation. The preparation of both *tert*-butylated analogues of bispyrazolopiridines **10-11b** did not encounter any problems either, although chromatographic purification was performed to afford the pure products. The rationale to prepare bromo derivatives was to attempt a ring closure under palladium catalysis to avoid drastic conditions. First to afford TPPACI we cyclized (KOH, isoquinoline, method A) our intermediates **8-12** as in previous reports.[1] We observed that bromo-analogues reacted faster (1 hour). For chloro derivatives, 2 hours were required to complete the conversion. Generally, reaction times were shorter, because the 2-halophenyl moiety has two neighboring phenyls to be attacked, compared to one in 4-(2-halophenyl)-1*H*-pyrazolo[3,4-*b*]quinolines **2**.[1] Palladium-assisted cyclization performed (method B) on **9a** and **11b** delivered the targets after 5 hours in good yields. The progress of reaction could be easily monitored by TLC: intensely blue emitting spots of **9a** and **11b** were converted to less polar TPPACI of yellow emission. Compound **14b** was more soluble than **14a** and **14c**. It also had a high melting point (Table 1).



15 **16a, R = H** **16b, R = *t*-Bu** **17a, R = H** **17b, R = *t*-Bu**

Scheme 2

The above results encouraged us to try a double cyclization to obtain **17a** (Scheme 2). The first attempt was not satisfactory, because the target compound was extremely insoluble in all common organic solvents (mp > 350 °C). It could only be dissolved in boiling DMAC, DMSO or 1-methyl-2-pyrrolidinone. Taking into account the solubility studies performed on TPPACI we introduced a tertiary butyl to make the compound **17b** amenable for further treatment. Indeed, this moiety improved the solubility substantially and we were able to record both ^{1}H and ^{13}C NMR spectra. It also had a high melting point (339–341 °C). The absorption (λ_{abs}) and luminescence (λ_{fl}) data of the annulated compounds are summarized in Table 1. One can observe a slight bathochromic shift in the peak maximum of absorbance in going from **14a** to **14c**, and a 'jump' of 70 nm for completely cyclized **17b**. A similar effect was also found for the emission peak maximum. The quantum yields decreased from 0.50 for **14a** to 0.32 for **14c**. These data are in the range of already reported values.[8d] The smaller quantum yield of yellow-orange fluorescence **17b** falls within the range of red emitting benzo[*a*]aceanthrylene derivatives.[9]

Table 1. Preparation of TPPACI and **17b** from bispyrazolo[3,4-*b*;4',3'-*e*]pyridines **8-12,16b** and photophysical properties of investigated compounds in cyclohexane (see Experimental Section).

Entry	Method, Yield (%)		TPPACI	λ_{abs} [nm]	λ_{fl} [nm]	Φ_{fl}	Mp (°C)
	A	B					
8a	83	-	**14a**	440	520	0.50	282-284
9a	99	92					
10b	60	-	**14b**	444	525	0.45	320-322
11b	51	74					
12c	85	-	**14c**	452	547	0.32	291-293
16b	81	-	**17b**	459, 487, 522	576	0.08	339-341

Conclusions

In summary, a new and general synthesis of heterocyclic indacenes was developed using two methods: a classical approach based on KOH/isoquinoline and, using milder conditions, employing $Pd_2(dba)_3$/P(*t*-Bu)$_3$ catalytic systems. We also obtained a trisubstituted octacyclic azarene **17b**, which could possibly be used as a fluorescent core[10] to generate novel and interesting dendrimers. Further studies are in due course to expand the scope of the present method (palladium cyclization of chlorinated analogues of bispyrazolo[3,4-*b*;4',3'-*e*]pyridines), and to use the products for further conversion as well as for LED purposes.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Mercury-Vx 300 MHz Varian operating at 300 and 75MHz, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Melting points were measured on a Melt-Temp II instrument. The purity of the compounds obtained was checked by TLC. Methyl benzoates **5** were commercially available or were synthesized by heating the corresponding acids at reflux with MeOH in the presence of concentrated sulfuric acid. 3-Oxonitriles **6** were produced by reaction of the esters with acetonitrile in the presence of 60% suspension of sodium hydride in toluene.[11] Aminopyrazoles **7** and **15** were prepared following the method described in the literature.[12] Finally, bispyrazolopyridines **8-12** and **16a,b** were obtained via reported methods.[13] Absorption (λ_{abs}) and emission (λ_{abs}) measurements were carried out using a scanning spectrophotometer UV-VIS 2101 (Shimadzu) and a conventional fluorescence spectrometer supplied with the cooled photomultiplier EMI 955 8B, respectively. Emission quantum yields (Φ_{fl}) were measured using quinine sulfate in 0.05M H_2SO_4 solution as an actinometer. Both the optical absorption and fluorescence spectra were measured at room temperature in cyclohexane with the molar concentration of the dyes being about 10^{-5} M in each case.

4-(2-Chlorophenyl)-1,3,5,7-tetraphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (8a). Yield 2.02 g (35%); light yellow solid; mp = 251–253 °C; R_f = 0.55 (toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.79 (td, 1H, *J* = 7.5, 1.2 Hz), 6.88−6.94 (m, 2H), 6.99−7.05 (m, 5H), 7.11−7.18 (m, 6H), 7.34 (t, 2H, *J* = 7.5 Hz), 7.58 (t, 4H, *J* = 7.5 Hz), 8.55 (d, 4H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 112.68, 120.81, 125.66, 125.76, 127.35, 127.77, 128.82, 128.99, 129.07, 129.87, 131.19, 132.25, 133.04, 133.24, 138.24, 139.60, 147.82, 150.59; Anal. Calcd. for $C_{37}H_{24}ClN_5$: C, 77.41; H, 4.21; N,12.20; found: C, 77.21; H, 4.44; N, 12.11.

4-(2-Bromophenyl)-1,3,5,7-tetraphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (9a). Yield 991 mg (32%); yellow solid; mp = 242–243 °C; R_f = 0.34 (toluene/PE, 1:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.82–6.96 (m, 3H), 7.00–7.05 (m, 4H), 7.11–7.18 (m, 7H), 7.34 (t, 2H, *J* =

7.5 Hz), 7.58 (t, 4H, *J* = 7.5 Hz), 8.55 (d, 4H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 112.55, 120.79, 123.35, 125.65, 126.31, 127.32, 127.75, 128.99, 129.18, 129.89, 131.25, 132.00, 132.26, 134.98, 139.61, 139.75, 147.81, 150.61; Anal. Calcd. for $C_{37}H_{24}BrN_5$: C, 71.85; H, 3.91; N,11.32; found: C, 72.01; H, 4.06; N, 11.49.

3,5-Bis-(4-*tert*-butylphenyl)-4-(2-chlorophenyl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (10b). Yield 976 mg (34%); light yellow solid; mp = 274–277 °C; R_f = 0.48 (toluene/PE, 1:1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (s, 18H, *t*-Bu), 6.71 (td, 1H, *J* = 7.5, 1.5 Hz), 6.82 (td, 2H, *J* = 9.0, 1.5 Hz), 6.93 (ddd, 1H, *J* = 9.0, 7.2, 1.8 Hz), 7.02 (d, 4H, *J* = 8.7 Hz), 7.07 (d, 4H, *J* = 8.7 Hz), 7.33 (t, 2H, *J* = 7.5 Hz), 7.57 (t, 4H, *J* = 7.5 Hz), 8.56 (d, 4H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.17, 34.42, 112.85, 120.69, 124.21, 125.49, 128.58, 128.76, 128.96, 129.14, 129.35, 131.19, 133.00, 133.23, 138.30, 139.74, 147.94, 150.61, 150.67; Anal. Calcd. for $C_{45}H_{40}ClN_5$: C, 78.76; H, 5.87; N, 10.20; found: C, 78.60; H, 6.04; N, 10.01.

4-(2-Bromophenyl)-3,5-bis-(4-*tert*-butylphenyl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (11b). Yield 2.16 g (29%); light yellow solid; mp = 270–272 °C; R_f = 0.62 (toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (s, 18H, *t*-Bu), 6.74–6.87 (m, 3H), 7.00–7.04 (m, 5H), 7.06 (d, 4H, *J* = 8.7 Hz), 7.33 (t, 2H, *J* = 7.5 Hz), 7.57 (t, 4H, *J* = 7.5 Hz), 8.57 (d, 4H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.16, 34.41, 112.70, 120.64, 123.27, 123.35, 124.17, 125.47, 126.04, 128.85, 128.95, 129.12, 129.36, 131.23, 131.74, 134.91, 139.73, 139.80, 147.93, 150.62; Anal. Calcd. for $C_{45}H_{40}BrN_5$: C, 73.96; H, 5.52; N, 9.58; found: C, 73.61; H, 5.72; N, 9.69.

4-(2-Chlorophenyl)-3,5-bis-(4-methoxyphenyl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (12c). Yield 1.48 g (21%); deep yellow solid; mp = 247–249 °C; R_f = 0.24 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.73 (s, 6H, OMe), 6.55 (d, 4H, *J* = 9.0 Hz), 6.82–6.91 (m, 2H), 6.97–7.09 (m, 6H), 7.33 (t, 2H, *J* = 7.5 Hz), 7.56 (t, 4H, *J* = 7.5 Hz), 8.53 (d, 4H, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.23, 112.60, 112.92, 114.53, 120.71, 124.77, 125.50, 125.84, 128.94, 129.76, 130.26, 131.29, 133.19, 133.29, 138.22, 139.64, 147.56, 150.56, 159.264; Anal. Calcd. for $C_{39}H_{28}ClN_5O_2$: C, 73.87; H, 4.45; N, 11.04; found: C, 74.07; H, 4.62; N, 10.91.

General procedure for the preparation of the TPPACIs (method A)

9a (500 mg, 0.808 mmol), powdered KOH (1.5 g, 27 mmol) and isoquinoline (10 mL) were heated at reflux for 1 hour. After cooling water (50 mL) was added. The mixture was extracted with toluene (2 x 50 mL). Organic phase was washed with 4 M HCl (2 x 25 mL) and finally with saturated aqueous NaCl solution. After drying (Na_2SO_4) the solvent was removed to dryness and the yellow residue was dissolved in $CHCl_3$. The product was precipitated by a slow addition of MeOH. For **8a** the same amounts of reagents were used, however the mixture was heated at reflux for 2 hours.

3,5-Dihydro-1,3,5-triphenyl-2,3,4,5,6-pentaazadibenzo[4,5:6,7]cyclohepta[1,2,3-*cd*]*s*-indacene (14a). Yield 430 mg (99%) from **9a** and 390 mg (83%) from **8a**; yellow solid; mp = 282–284 °C; R_f = 0.47 (toluene/PE); (*note:* about 7 mg of **14a** can be dissolved in 0.87 mL of $CDCl_3$ at room

temperature); ^{1}H NMR ($CDCl_3$, 300 MHz) δ ; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 6.83 (ddd, 1H, *J* = 8.1, 7.2, 1.2 Hz), 7.25 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.28−7.38 (m, 6H), 7.50−7.61 (m, 6H), 7.65−7.71 (m, 3H), 7.88−7.94 (m, 1H), 8.38−8.45 (m, 1H), 8.52 (d, 2H, *J* = 8.7 Hz), 8.56 (d, 2H, *J* = 8.7 Hz); Anal. Calcd. for $C_{37}H_{23}N_5$: C, 82.66; H, 4.31; N, 13.03; found: C, 82.35; H, 4.41; N, 13.03.

9-(*tert*-Butyl)-1-[4-(*tert*-butyl)phenyl]-3,5-dihydro-3,5-diphenyl-2,3,4,5,6-pentaazadibenzo [4,5:6,7]cyclohepta[1,2,3-*cd*]*s*-indacene (14b). Yield 227 mg (51%) from **11b** and 284 mg (60%) from **10b**; deep yellow solid after column purification; mp = 320–322 °C; R_f = 0.82 (toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu), 6.72 (ddd, 1H, *J* = 7.9, 7.2,1.2 Hz), 7.16 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.23–7.34 (m, 5H), 7.51–7.59 (m, 7H), 7.62 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.87 (d, 1H, *J* = 2.1 Hz), 8.32 (d, 1H, *J* = 8.1 Hz), 8.52 (d, 2H, *J* = 8.7 Hz), 8.53 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.31, 31.32, 34.66, 34.96, 109.21, 119.47, 120.24, 121.08, 124.98, 125.25, 125.56, 126.08, 126.33, 127.35, 128.88, 128.90, 128.94, 129.10, 129.57, 130.47, 130.54, 132.74, 134.15, 136.03, 137.45, 139.77, 139.94, 140.32, 140.74, 144.48, 147.01, 150.55, 151.45, 151.88, 152.93; Anal. Calcd. for $C_{45}H_{39}N_5$: C, 83.17; H, 6.05; N, 10.78; found: C, 82.98; H, 6.00; N, 10.65.

3,5-Dihydro-9-methoxy-1-(4-methoxyphenyl)-3,5-diphenyl-2,3,4,5,6-pentaazadibenzo [4,5:6,7]cyclohepta[1,2,3-*cd*]*s*-indacene (14c). Yield 403 mg (85%) from **12c**; yellow solid, no column required; mp = 291–293 °C; R_f = 0.39 ($CHCl_3$); (*note:* about 5 mg of **14c** can be dissolved in 0.87 mL of $CDCl_3$ at room temperature); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.82 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.84 (d, 2H, *J* = 9.0 Hz), 6.89 (ddd, 1H, *J* = 8.1,7.2, 1.2 Hz), 7.12 (dd, 1H, *J* = 8.7, 2.7 Hz), 7.28−7.37 (m, 4H), 7.42 (d, 1H, *J* = 2.7 Hz), 7.54−7.63 (m, 6H), 7.74 (dd, 1H, *J* = 8.1, 1.2 Hz), 8.35 (d, 1H, *J* = 8.7 Hz), 8.52 (d, 2H, *J* = 8.7 Hz), 8.56 (d, 2H, *J* = 8.7 Hz); Anal. Calcd. for $C_{39}H_{27}N_5O_2$: C, 78.38; H, 4.55; N, 11.72; found: C, 78.15; H, 4.68; N, 11.68.

Palladium-assisted cyclization of (9a) and (11b) (method B)

9a (100 mg, 0.162 mmol), $Pd_2(dba)_3$ (30 mg, 0.032 mmol, 20% mol) and DBU (0.25 mL) were dissolved in dry DMF (10 mL). The mixture was purged with argon for 10 min. Next P(*t*-Bu)$_3$ (0.13 mL, 1M in toluene) was added in one portion, which was heated at 130 °C for 5 hours. After cooling, water was added and the yellow solid that precipitated was extracted with toluene. After drying and concentration, the oily residue was passed through a short column packed with alumina. **14a**, yield: 80 mg (92%). For **14b**: **11b** (150 mg, 0.205 mmol), $Pd_2(dba)_3$ (37.5 mg, 0.041 mmol, 20% mol), DBU (0.25 mL), P(*t*-Bu)$_3$ (0.16 mL, 1M in toluene) and DMF (10 mL). Yield 98 mg (74%).

Preparation of doubly annulated aza s-indacenes

The precursors **16a** and **16b** were prepared as for **8-12**.

3,5-Bis(2-chlorophenyl)-1,4,7-triphenyl-1,7-dihydrodipyrazolo[3,4-*b*:4',3'-*e*]pyridine (16a). Yield 1.18 g (26%); colorless solid; mp = 264–266 °C; R_f = 0.59 (toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.64 (t, 2H, *J* = 7.2 Hz), 6.83–6.89 (m, 3H), 7.02–7.13 (m, 6H), 7.19–7.24 (m, 2H),

7.34 (t, 2H, *J* = 7.5 Hz), 7.58 (t, 4H, *J* = 7.5 Hz), 8.53 (d, 4H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 113.37, 120.90, 125.72, 125.95, 126.02, 127.72, 128.89, 128.99, 129.54, 129.62, 131.03, 131.64, 132.40, 134.15, 139.58, 142.50, 145.02, 150.42; Anal. Calcd. for $C_{37}H_{23}Cl_2N_5$: C, 73.03; H, 3.81; N, 11.51; found: C, 72.95; H, 3.91; N, 11.60.

4-(4-*tert*-Butylphenyl)-3,5-bis-(2-chlorophenyl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-*b*;4',3'-*e*]pyridine (16b). Yield 1.84 g (28%); colorless solid; mp = 297–300 °C; R_f = 0.59 (toluene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (s, 9H, *t*-Bu), 6.62 (d, 2H, *J* = 8.7 Hz), 6.70 (d, 2H, *J* = 8.1 Hz), 6.97−7.08 (m, 6H), 7.16 (dd, 2H, *J* = 6.6 Hz), 7.34 (t, 2H, *J* = 7.2 Hz), 7.58 (t, 4H, *J* = 8.7 Hz), 8.54 (d, 4H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.01, 34.19, 113.48, 120.85, 122.76, 125.65, 125.89, 127.95, 128.80, 128.97, 129.12, 129.38, 131.70, 132.39, 134.16, 139.64, 142.83, 145.12, 150.44, 150.51; Anal. Calcd. for $C_{41}H_{31}Cl_2N_5$: C, 74.09; H, 4.70; N, 10.54; found: C, 74.21; H, 4.65; N, 10.50.

11-*tert*-Butyl-2,4-diphenyl-2,4-dihydro-1,2,3,4,5-pentaazatribenzo[3,4:5,6:7,8]heptaleno [2,1,10,9-*cdef*]*s*-indacene (17b). 16b (500 mg, 0.753 mmol), KOH (2.53 g, 45 mmol) and isoquinoline (10 mL) were heated at reflux for 2 hours. After cooling, water (50 mL) was added, followed by toluene (50 mL). The inorganic phase was discarded, and isoquinoline was extracted with 4 M HCl. The organic phase was washed with saturated aqueous NaCl (50 mL) and dried (K_2CO_3). After evaporation, the solid residue was dissolved in toluene and passed through a short column packed with alumina. After evaporation of the volatiles the red crystals were dissolved in chloroform and MeOH was added dropwise with stirring. The red amorphous solid was filtered off. Yield 359 mg (81%); R_f = 0.76 (toluene); mp = 339–341 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (s, 9H, *t*-Bu), 7.20–7.23 (m, 2H), 7.30 (t, 2H, *J* = 7.2 Hz), 7.42–7.49 (m, 4H), 7.53 (t, 4H, *J* = 7.2 Hz), 7.55 (s, 2H), 8.31–8.34 (m, 2H), 8.45 (d, 4H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.94, 34.76, 113.21, 120.76, 125.48, 126.21, 128.59, 128.88, 129.10, 130.94, 131.03, 132.85, 134.44, 137.33, 139.71, 140.07, 142.43, 144.84, 152.44, 153.26; Anal. Calcd. for $C_{41}H_{29}N_5$: C, 83.22; H, 4.94; N, 11.84; found: C, 83.42; H, 4.83; N, 11.80.

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