*Heteroacenes*

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# Derivatives of Octaethynylphenazine and Hexaethynylquinoxaline**

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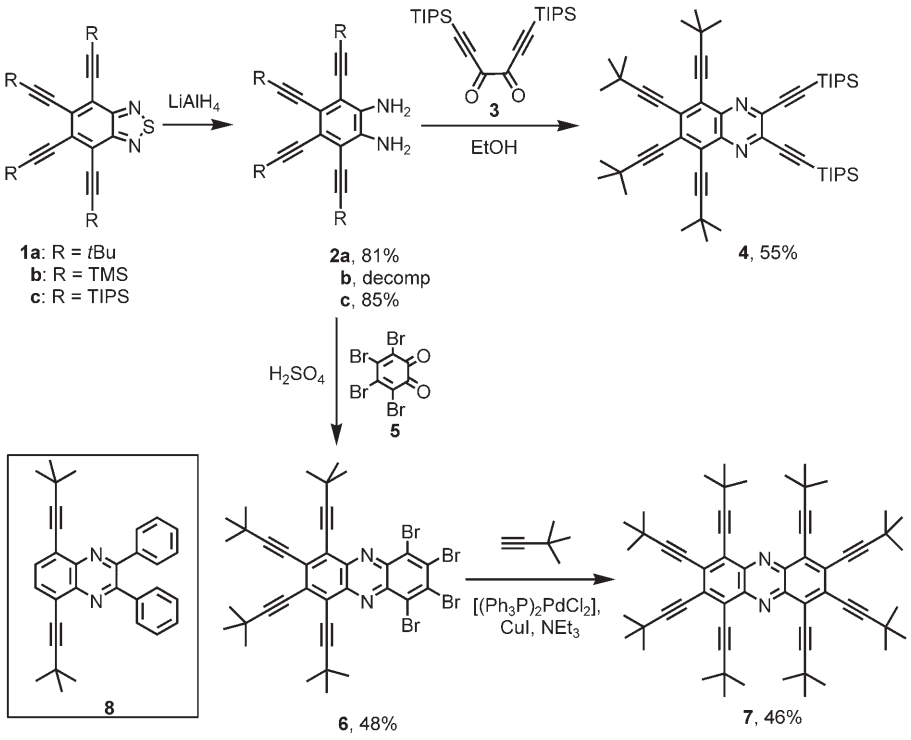
In 1986, hexaethynylbenzene, the first peralkynylated π perimeter, was obtained by Vollhardt and co-workers.[1] Since then, peralkynylated cyclobutadiene complexes, cymantrenes, ferrocenes, cylcopentadienyl radicals, thiophenes, and extended systems derived from tetraethynylethylenes and hexaethynylbenzenes have been reported.[2–7] Peralkynylated N-heterocycles are scarce, and only recently peralkynylpyrazinophorphyrazine and triethynyltriazine were reported.[8,9] Dialkynylated pentacenes, hexacenes, and heptacenes play a significant role in materials science and are fairly easily accessible.[10] Peralkynylated acenes as a class, however, are entirely unknown; the peri interactions in acenes would result in steric crowding of the alkynes and their all-too-close spacing would lead to Bergman-type reactions. If the peri interactions could be removed in naphthalene, anthracene, or the larger acenes, peralkynylation should be possible: Hexaethynylquinoxaline and octaethynylphenazine are attractive synthetic targets that might show promise as n-type semiconductors and as unusual sensory platforms for metal cations.[11] Herein, we report the synthesis of the first representatives of the heteroacenes, namely, hexaethynylquinoxaline and octaethynylphenazine.

Tetraethynylbenzothiadiazoles **1a–c** are easily available by Pd-catalyzed alkynylation of tetrabromobenzothiadiazole.[12] The attempted reduction of **1b** with $LiAlH_4$ led to decomposition of the starting material without the formation of an isolable product, probably through desilylation and concomitant polymerization (Scheme 1). Desulfurization of the sterically more shielded derivatives **1a** and **1c** with $LiAlH_4$ furnished spectroscopically pure **2a** and **2c** after aqueous workup. Both products are stable under ambient conditions for a day or so, after which they decompose (observed as darkening), presumably by oxidation of the amine groups. To secure the structure of **2a**, we attempted to crystallize it from dichloromethane; microcrystalline powders formed. Upon crystallization from hexafluorobenzene, a suitable single-crystalline specimen was obtained.[13]




***Scheme 1.*** Synthesis of hexaethynylquinoxaline (**4**), octaethynylphenazine (**7**), and the quinoxaline **8**. TMS = trimethylsilyl; TIPS = triisopropylsilyl.

Figure 1 shows a ball-and-stick representation of **2a**. A weak F···H hydrogen bond (2.36 Å) is apparent between an amine group of **2a** and a fluorine substituent of the hexafluorobenzene. The electron-poor hexafluorobenzene and the electron-rich diamine **2a** lie on top of each other, as would be expected from the electrostatic potentials of these

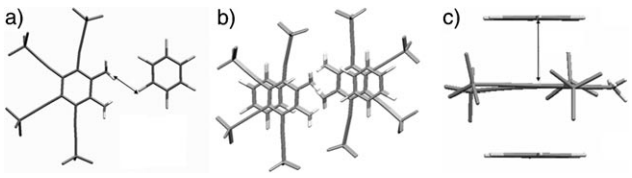



***Figure 1.*** Stick representation of the complex **2a**·$C_6F_6$. a) NH···F hydrogen bond indicated by arrow (2.36(3) Å, 152°). b) Stacking of the molecules, viewed along the crystallographic *a* axis. c) The distance between $C_6F_6$ and **2a** in the stacks, as indicated by the arrow, is 3.29 Å (view shown along the crystallographic *b* axis).[13]

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molecules.[14] A tightly packed, π–π-stacked structure results; compound **2a** is the first reported tetraalkynylated phenylenediamine and, as such, is valuable for the construction of other structures.

Upon treatment of **2a** with dione **3** in ethanol with molecular sieves, the hexaethynylquinoxaline derivative **4** formed in 55% yield.[11] If **2a** was treated with the commercially available quinone **5**, the tetrabromide **6** was isolated (Scheme 1). Pd-catalyzed coupling of **6** to an excess of 3,3-dimethylbutyne gave the octaethynylphenazine representative **7** as a stable, orange, crystalline solid. While spectral data indicated the presence of a peralkynylated phenazine, the attractive topology of **7** was confirmed by single-crystal X-ray structural analysis (Figure 2).[15] The bond lengths and bond angles for **7** are in excellent agreement with the expected values.[1,5,7]

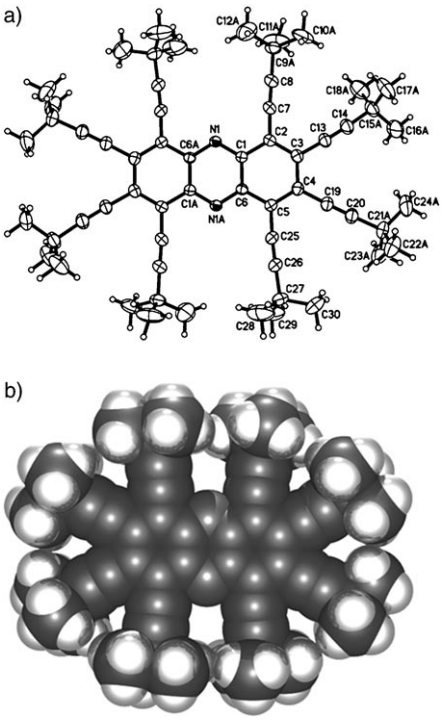


***Figure 2.*** a) ORTEP drawing of **7** at the 50% probability level. b) Space-filling view of **7**. The phenazine nucleus can carry eight alkyne units, as the pyrazine ring creates a void that accommodates the substituents and forms an internal pocket.

Figure 3 shows the packing of **7** in the solid state. The molecules are arranged in tilted stacks that are 0.97-nm apart along the *b* axis in a classic herringbone arrangement. Close π–π contacts are not observed due to the bulky *tert*-butyl groups that encase the aromatic faces of **7**.

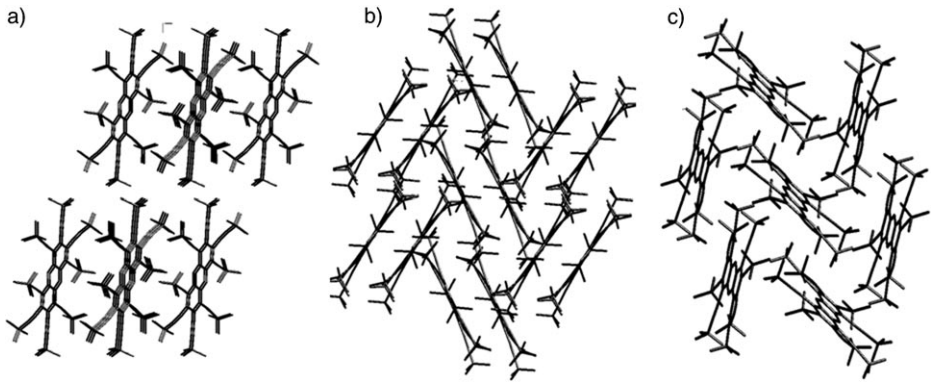


***Figure 3.*** Packing of **7** in the solid state. a, b) View along the *b* and *a* axes, respectively. The stacking distance is 0.97 nm. c) View along the approximate diagonal of *a* and *c* axes. The herringbone pattern is visible in (b) and (c).

Upon going from **4** to **7**, significant red shifts in both the absorption and emission spectra were recorded (Figure 4) which result from the extension of the π system. While the

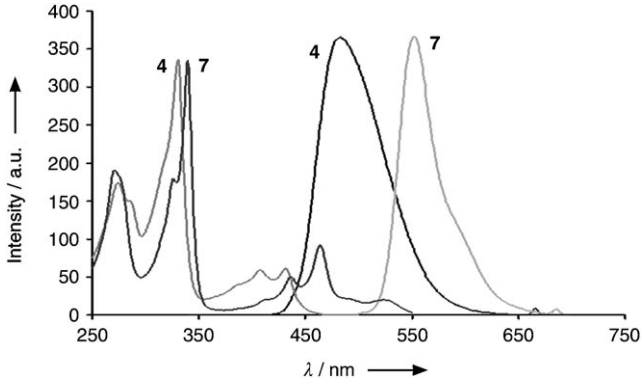


***Figure 4.*** Absorption (left) and emission spectra (right) of **4** ($\lambda_{max}$ = 434 nm [2.85 eV], $\lambda_{em}$ = 485 nm) and **7** ($\lambda_{max}$ = 527 nm [2.35 eV], $\lambda_{em}$ = 554 nm) in chloroform.

emission spectra of **4** and **7** are unstructured, their absorption spectra feature a similar fine structure as those of anthracene or phenazine; compounds **4** and **7** are obviously "true" acenes, despite their alkyne decoration.[16] When comparing the UV/Vis spectrum of **7** ($\lambda_{max}$ = 527 nm) to that of phenazine ($\lambda_{max}$ = 363 nm), a red shift of 162 nm in the absorption is noted. To estimate the band gap and the position of the frontier orbitals of **7**, an ab initio quantum chemical calculation (B3LYP, 6-31G**) was performed (*tert*-butyl groups omitted; HOMO: −5.80 eV; LUMO: −3.19 eV; gap: 2.61 eV). To compare the band gap and position of the frontier orbitals, we also performed quantum chemical calculations (B3LYP, 6-31G**) on anthracene (HOMO: −5.24 eV; LUMO: −1.65 eV; gap: 3.59 eV) and phenazine (HOMO: −6.09 eV; LUMO: −2.43 eV; gap: 3.66 eV). The introduction of the nitrogen atoms into the frame of the acenes lowers the energy of the HOMO and LUMO, but does not significantly decrease the band gap. Alkyne decoration, however, leads to a decrease in the band gap. The calculations

  

agree well with the absorption data and reflect the gross electronic differences between phenazine and **7**.

The crystal structure of **7** reveals a rigid binding pocket generated by the alkyne groups and the phenazine nitrogen atom. The three π-basic sites should allow the complexation of metal cations. Phenazine itself forms coordination polymers with copper and silver.[17] Exposure of **4** and of **7** to silver triflate led to a bathochromic shift in their absorption spectra and to quenching of their emission. The shift is larger in **7** than in **4**. Upon exposure to $Cu^{I}$ or $Cu^{II}$, no chromic changes occurred but slight quenching was observed for both peralkynyls with $Cu^{II}$ triflate. Surprised by the lack of binding to copper ions, we treated **4** and **7** with a series of metal salts (see Figure 5 and Table 1). While alkali and alkaline-earth metals generally do not lead to spectral shifts, $Ba^{2+}$ did cause a shift in the absorption spectrum of **7**. $Ag^{+}$, $As^{3+}$, and $Hg^{2+}$ ions, as well as trifluoroacetic acid generated chromic responses in **4** and **7**, while indium and tin triflates induced a bathochromic shift in **7**. According to the shape of the spectra of **7**, $In^{3+}$, $Ba^{2+}$, and $Sn^{2+}$ ions can be grouped together as they elicit the same response from **7**, while $Ag^{+}$, $As^{3+}$, and $Hg^{2+}$ ions and proton acids show spectral responses that are different from each other and from those of the first group (Table 1). The presence of the second alkynylated fused benzene unit in **7** as compared to **4** seems to significantly increase the binding of the pyrazine motif to metal cations. Changes in emission are much less pronounced, suggesting that **4** and **7** bind less strongly to metal cations in their excited states.

To understand the relationship between molecular structure and metal binding, we performed a titration of **4**, **7**, and **8** with AgOTf and $Hg(OTf)_2$. However, attempts to obtain the binding constants for association of **4**, **7**, and **8** to $Hg(OTf)_2$ were inconclusive; multiple coordination equilibria are present, and various combinations of proposed simple metal-to-ligand stoichiometries did not lead to a reasonable fit of the experimental data to any assumed model using the program SPECFIT.[18]

From the results of titrations with AgOTf, compounds **4** and **7** first form 1:1 and then 2:1 metal–ligand complexes, with $\log\beta_1 = 4.5$ ($\pm 0.2$) and $\log\beta_2 = 8.8$ ($\pm 0.1$) for **4**, and $\log\beta_1 = 6.5$ ($\pm 0.3$) and $\log\beta_2 = 12.8$ ($\pm 0.2$) for **7**. The presence of the two alkynylated phenyl arms aligned parallel in structure **7** increases the binding to silver by a factor of 100, as compared to the quinoxaline **4**. A similar effect is apparent for the binding of the second silver ion, which is, in both cases, only slightly less strongly coordinated than the first one, suggesting that the additional positive charge does not significantly affect the binding properties of the second pocket. We have investigated the binding of AgOTf to **8** and found that nonlinear least-squares fitting with the program SPECFIT[18] leads to a different complexation behavior. The spectral data are best interpreted by a 1:2 and a 1:4 ligand-to-metal complex stoichiometry with $\log\beta_2 =$

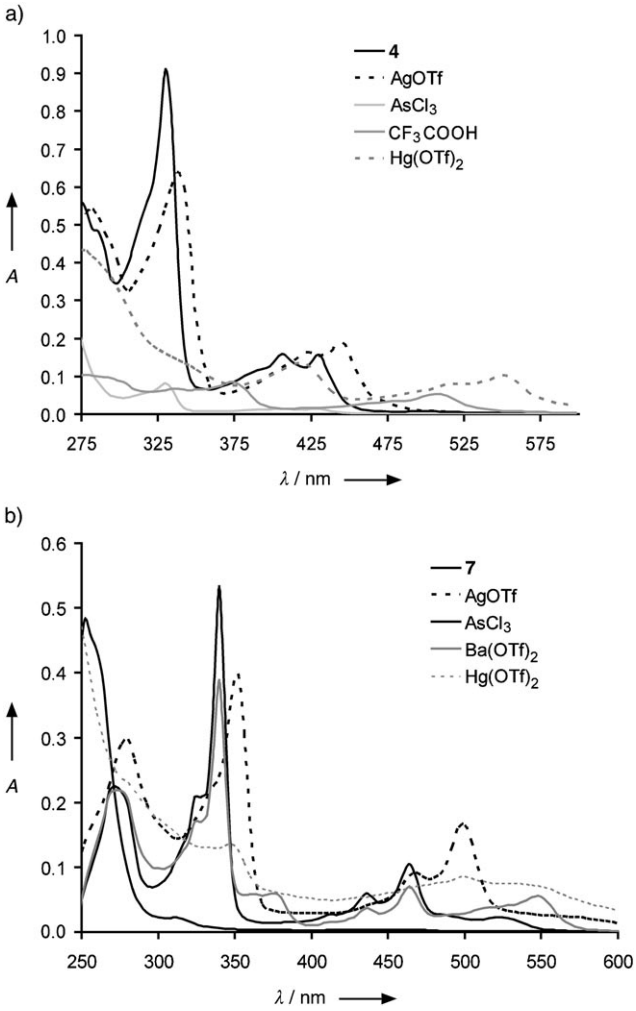


***Figure 5.*** Absorption spectra of a) **4** and b) **7** in the presence of representative metal cations. OTf = $CF_3SO_3^-$.

***Table 1:*** Absorption ($\lambda_{max}$) and emission ($\lambda_{em}$) data for the interaction of **4** and **7** with metal ions.[a]

| | **4** | | **7** | |
|---|---|---|---|---|
| | $\lambda_{max}$ [nm] | $\lambda_{em}$ [nm] | $\lambda_{max}$ [nm] | $\lambda_{em}$ [nm] |
| no metal | 331, 409, 432 | 482 | 340, 464, 523 sh | 553 |
| $CF_3CO_2H$ | 376, 509 | quenched | 376, 510, 548 | quenched |
| AgOTf | 340, 420, 446 | 514 vw | 351, 467, 500 | quenched |
| $AsCl_3$ | 331, 407, 446 vw | quenched | 314, 466, 550 vw | quenched |
| $Ba(OTf)_2$ | no change | no change | 340, 377, 464, 548 | 553[b] |
| $Ca(OTf)_2$, $CdCl_2$, Cu(OTf), CuI, $Eu(OTf)_3$, KOTf, LiOTf, $Mg(OTf)_2$, Na(OTf), $Pb(NO_3)_2$, Tl(OTf), $Zn(OTf)_2$ | no change | no change[c] | no change | no change[c] |
| $Hg(OTf)_2$ | 278, 418, 552 | quenched | 348, 449, 543 br | 567 w |
| $In(OTf)_3$ | no change | no change | 340, 376, 464, 548 | 546 w |
| $Sn(OTf)_2$ | no change | no change | 340, 376, 464, 548 | quenched |

[a] sh = shoulder; w = weak; vw = very weak; br = broad. [b] Decreased intensity. [c] Slight quenching with $Cu(OTf)_2$.

  

13.0 (±0.3) and $\log\beta_4 = 22.1$ (±0.3). Not unexpectedly, the presence of the phenyl groups increases the interaction with the silver cations and leads to this somewhat exotic complexation behavior.

The underlying structural principle of alkyne-framed N-heterocycles will be exploited in the future to construct a more general class of rigid receptors **7** by coupling differentiated functional alkynes to **6**. Those starting alkynes would carry auxiliary binding sites and/or modulate the electronic properties of the system to investigate the interaction of these ligands with metal cations in water and in organic solvents.[18]

In conclusion, we have described a facile synthetic approach that yields peralkynylated quinoxalines and phenazines. Both **4** and **7**, which are the first reported peralkynylated heteroacenes, show attractive and quite selective metal-binding properties that will be harnessed in the future. Derivatives of this class of fluorescent molecules might find use as organic n-type semiconductors.

## Experimental Section

**2**: Dry THF (150 mL) was added to a flame-dried 250-mL Schlenk flask charged with **1**, then $LiAlH_4$ (4 equiv) was added to the mixture under a stream of nitrogen over a period of 30 min, and stirring was continued for 4 h. Analytically pure **2** was obtained after aqueous workup.

**2a**: Prepared from **1a** (1.00 g, 2.18 mmol). Red solid (0.760 g, 81 %); m.p.: 167 °C (decomp); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.34$ (bs, 4H), 1.42 (s, 18H), 1.40 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 136.89$, 119.38, 112.01, 108.50, 102.97, 77.37, 75.46, 31.25, 31.02, 28.76, 28.52 ppm.

**2c**: Prepared from **1c** (1.00 g, 1.16 mmol). Red solid (0.706 g, 73 %); m.p.: 185 °C (decomp); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 3.22$ (bs, 4H), 1.17–1.13 ppm (m, 84H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 136.45$, 118.97, 112.69, 104.47, 102.25, 101.48, 96.35, 19.14, 12.16, 11.42 ppm.

**4**: Molecular sieves, **2a** (0.204 g, 0.476 mmol), **3** (0.209 g, 0.500 mmol), and toluene (10 mL) were heated at 80 °C for 4 h. Removal of the solvent and chromatography of the residue (3:1 hexanes/$CH_2Cl_2$) furnished **4** (0.315 g, 55 %); m.p.: 194–196 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.43$ (s, 18H), 1.37 (s, 18H) 1.18 ppm (s, 42H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 141.53$, 140.38, 130.29, 126.08, 112.48, 108.94, 104.26, 99.52, 78.46, 75.23, 33.58, 29.16, 18.75, 11.89 ppm; IR (KBr): $\nu = 2966$, 2945, 2866, 2222, 1539, 1462, 1411, 1313 cm$^{-1}$; MS (70 eV): $m/z$ (%): 811 (100) [$M^+$], 726 (60), 645 (5); HR-MS: $m/z$ calcd for $C_{54}H_{78}N_2Si_2$: 810.57036; found: 810.56716.

**7**: **2a** (0.274 g, 0.639 mmol), **5** (0.273 g, 0.645 mmol), ethanol (10 mL), and a drop of $H_2SO_4$ were heated at reflux for 14 h. Filtration followed by crystallization from $CH_3OH/CH_2Cl_2$ yielded **6** (0.250 g, 48 %); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (s, 18H), 1.37 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$): $\delta = 143.87$, 139.54, 132.67, 131.29, 127.99, 126.09, 113.08, 112.62, 79.46, 75.09, 32.63, 31.15, 28.35, 28.00 ppm. Triethylamine (7 mL), **6** (0.424 g, 0.519 mmol), $[(PPh_3)_2PdCl_2]$ (5 mol %), CuI (5 mol %), and 3,3-dimethylbutyne (5 equiv) were stirred at 120 °C for 18 h in a sealed flask. Aqueous workup and column chromatography (4:1 hexanes/$CH_2Cl_2$) furnished **7** (0.196 g, 46 %); m.p.: 248 °C (decomp.); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.46$ (s, 36H), 1.32 ppm (s, 36H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 141.82$, 130.27, 124.71, 111.36, 110.00, 77.46, 75.92, 31.92, 30.84, 28.56, 28.31 ppm; IR (KBr): $\nu =$ 2966, 2923, 2862, 2214, 1728, 1712, 1695, 1548, 1452, 1440, 1390, 1361, 1261 cm$^{-1}$; MS (70 eV): $m/z$ (%): 820 (100) [$M^+$]; HR-MS: $m/z$ calcd for $C_{60}H_{72}N_2$: 820.56955; found: 820.56726.

**8**: A mixture of 3,6-bis(3,3-dimethylbut-1-ynyl)benzene-1,2-diamine (1.70 g, 6.33 mmol), molecular sieves (1.0 g),and 1,2-diphenylethane-1,2-dione (2.00 g, 9.51 mmol) in dry toluene (50 mL) was heated at reflux for 18 h. Workup and column chromatography (silica gel, 1:1 hexane/$CH_2Cl_2$) afforded **8** (1.77 g, 63 %); m.p.: 232–234 °C; IR (KBr): $\nu = 3055$, 2966, 2922, 2895, 2864, 2216, 1560, 1466, 1337, 1242, 1097, 841, 700 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$–7.72 (m, 6H), 7.38–7.31 (m, 6H), 1.45 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 152.27$, 140.93, 138.94, 132.40, 130.21, 129.04, 128.03, 123.33, 106.84, 75.98, 31.02, 28.52 ppm; HR-MS (70 eV): $m/z$ calcd for $C_{32}H_{30}N_2$ [$M^+$]: 442.24090; found: 442.24153.

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[13] Crystallographic data for **2a**: yellow blocks, crystal dimensions $0.44 \times 0.36 \times 0.30\ mm^3$, space group $P2_1/c$ (no. 14, monoclinic), $a = 6.671(3)$ Å, $b = 26.982(9)$ Å, $c = 20.034(7)$ Å, $\beta = 92.721(15)°$, $V = 2751.0(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.134\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.087\ mm^{-1}$. Data were measured on a Bruker SMART APEX diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 150(1) K, and the structure was solved by direct methods. Of 3309 reflections collected, 2503 were unique reflections ($R_{int} = 0.1251$); data/restraints/parameters 2503/6/422; final $R$ indices [$I > 2\sigma(I)$]: $R_1 = 0.0758$, $wR_2 = 0.1881$; $R$ indices (all data): $R_1 = 0.0891$, $wR_2 = 0.2025$; largest diff. peak and hole: 0.329 and $-0.241$ e Å$^{-3}$.
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[15] Crystallographic data for **7**: irregular orange-red crystals, crystal dimensions $0.52 \times 0.40 \times 0.22\ mm^3$, space group $P2_1/c$ (no. 14, monoclinic), $a = 19.4214(9)$ Å, $b = 9.9650(5)$ Å, $c = 15.4061(7)$ Å, $\beta = 112.6820(10)°$, $V = 2751.0(2)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 0.991\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.056\ mm^{-1}$. Data were measured on a Bruker SMART APEX diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 293(1) K, and the structure was solved by direct methods. Three of the four crystallographically inequivalent *tert*-butyl groups are rotationally disordered. Of 18417 reflections collected, 3950 were unique ($R_{int} = 0.0338$); data/restraints/parameters 3950/19/370; final $R$ indices [$I > 2\sigma(I)$]: $R_1 = 0.0518$, $wR_2 = 0.1420$; $R$ indices (all data): $R_1 = 0.0636$, $wR_2 = 0.1536$; largest diff. peak and hole: 0.195 and $-0.185$ e Å$^{-3}$. CCDC-275052 (**2a**) and -275053 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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