# Fulvadienes Derived from Fluorenes and Their Oxidation to Spirodiazatetracenes

Gunther Buehrdel,[a] Rainer Beckert,*[a] Helmar Görls[b]

[a] Institute of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany
Fax +49(3641)948212; E-mail: C6bera@uni-jena.de

[b] Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena, Lessingstr. 8, 07743 Jena, Germany

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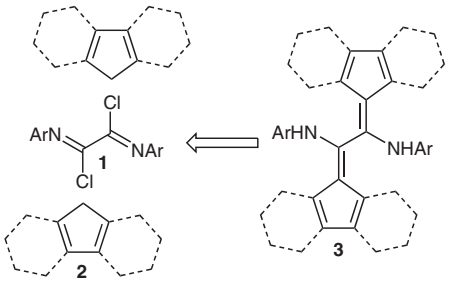
**Abstract:** Based on the acylation reaction of fluorenyl anions with the bis(imidoyl) chlorides of oxalic acid, a short and efficient synthesis for a series of novel bis(arylamino) fulvadienes was developed. The products were isolated as red colored and crystalline compounds in good yields. Their structures were determined by elemental analysis, MS, NMR, and additionally by X-ray crystal structural analysis. Monoimidoyl chlorides showed the same reactivity. Enamines were isolated in good yields as products. The bis(arylamino) fulvadienes can be transformed by an oxidation-ring annulation sequence into diazatetracene derivatives. These to date unknown bis-spiro derivatives of diazatetracene are well soluble in common solvents and display green fluorescence in solution.

**Key words:** amines, oxidation, radical reaction, fulvadienes, bis(imidoyl) chlorides

Among fulvalenes, their heteroanalogues derivatives, such as tetrathia- and tetraazafulvalenes, are mainly of considerable interest to material sciences. These cross-conjugated, π-electron systems display a multi-step redox activity, which can be used in widespread applications. Their vinylogous derivatives, which can be regarded as fulvadienes are not only of theoretical interest, but are also capable of forming polycylic hydrocarbons via electrocyclization processes.[1]

As a continuation of our studies on cross-conjugated systems, amino substructures should be integrated into fulvadienes. A promising synthetic pathway to compounds of type **3** based on our previous experience should consist of the acylation reaction of cyclopentadienyl anions with bis(arylimidoyl) chlorides **1** (Scheme 1). During the last decade, we demonstrated that the latter derivatives are excellent (and selective) bis-electrophiles that can be employed as $C_2$-building blocks for heterocyclic as well as for carbocyclic compounds.[2] It has been observed in many cases during the acylation of substrates with **1** that a very fast prototropic shift takes place, forming enamino substructures. Our aim was, therefore, to develop a short and efficient route to diarylamino fulvadienes **3** exploiting this acylation-prototropism cascade. We first studied the reaction of **1** with fluorenyl anions from **2**. They are easily available due to the high acidity of fluorene and, in addition, the products are unable to undergo subsequent electrocyclization processes.




**Scheme 1** Retrosynthetic approach for diaminofulvadienes

Fluorene **2a** reacted readily with bis-electrophile **1a** under quite mild conditions (THF in the presence of *t*-BuOK at –78 °C), forming a red crystalline product in good yield. Elemental analysis and MS data confirmed the presence of a 2:1 acylation product **3a**. Evidence for the symmetry in this novel diarylaminofulvadiene **3a** (Scheme 2) was provided by single sets of signals in its $^1$H and $^{13}$C NMR spectra. The NH protons of derivative **3a** showed resonance at δ = 6.19.

Employing the same procedure, the bis(imidoyl) chlorides **1b–e**, as well as 2-bromofluorene (**2b**) and 2,7-dibromofluorene (**2c**) were integrated into this reaction. The products **3b–g** were obtained in good yields as crystalline compounds, which showed similar chemical properties to **3a**. It must be noted that derivatives **3e**,**f** were isolated as inseparable mixtures of *E*/*Z*-isomers originating from the asymmetry of 2-bromofluorene (**2b**). Therefore, these mixtures display a complex set of signals in their $^1$H and $^{13}$C NMR spectra.

Further structural details were obtained from single crystal X-ray analyses of **3a** and **3d**, hence the derivatives **3** have a 1,2-difluorenylidene-1,2-diarylaminoethane structure. The result of these analyses showed that **3a** and **3d** are monomers in the solid state. Figure 1 displays the solid state structures of **3a** and **3d**. The bond lengths and angles were within the expected range; only the bonds between N1–C1/N2–C2 (1.38 Å) were somewhat shortened. Because of the bulky fluorene moiety, the C=C bond is twisted by around 16°, and the torsion angle for **3a** between N2–C2–C3–C15 is –17.3(2)°; N1–C1–C16–C18 for **3d** is –16.4(3)°. As a result of the steric demand of the fluorenyl and arylamino groups, the central C–C bond

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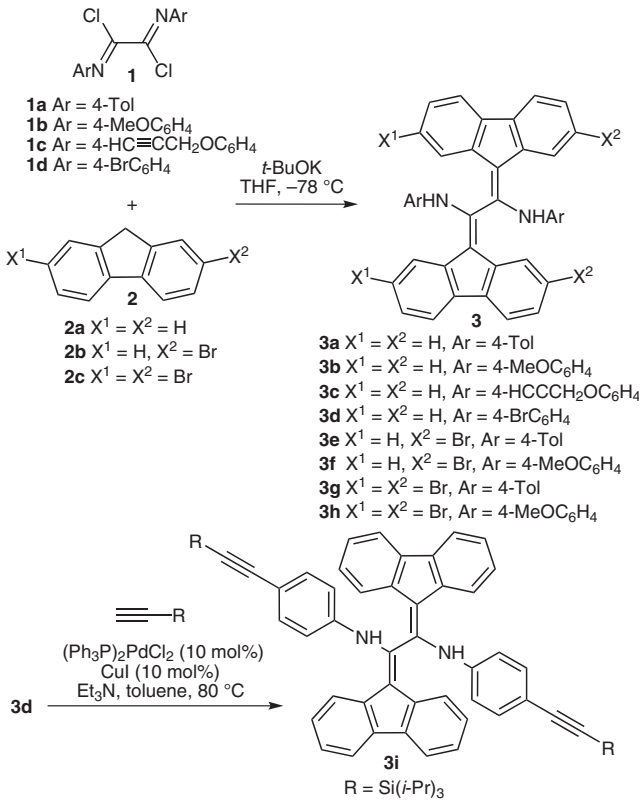


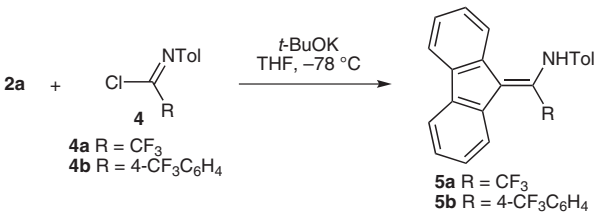

**Scheme 2** Synthesis of 1,2-difluorenylidene-1,2-diarylaminoethanes **3** and modification by Sonogashira cross-coupling reaction

(C1–C2) is twisted by around 57°, and the torsion angle for **3a** between C16–C1–C2–C3 is –56.9(2)°. The staggered arrangement of the substituents on the C–C bond (C1–C2) leads to a propeller-like structure.

The bromo-substituted derivatives offer the preconditions for subsequent modifications, as exemplified here for the Sonogashira cross-coupling method. The red bis-acetylene **3i** was isolated in a high yield upon treatment of **3d** with (triisopropylsilyl)acetylene under standard Sonogashira conditions (Scheme 2).

As a result of two donor–acceptor chromophores, in combination with torsion of the double bonds in the molecule, compounds **3** formed dark red solutions; **3a**, for example, absorbed in $CHCl_3$ at $\lambda_{max}$ = 450 nm, (log ε = 4.2).

Finally, we tested the synthetic concept on monofunctional imidoyl chlorides. The reaction of the imidoyl chlorides **4a**,**b** with fluorene (**2a**), under the same mild conditions, resulted in the yellow products **5a**,**b** (Scheme 3). Elemental analyses and MS data confirmed the presence of 1:1 acylation products **5**. The enamine substructure was proven by characteristic signals for the NH protons at δ = 6.09 (**5a**) and δ = 6.77 (**5b**) in the $^1$H NMR spectra.




**Scheme 3** Reaction of fluorene with monoimidoyl chlorides

The formation of yellow by-products **6** was observed by TLC even during the recrystallization of derivatives **3** under aerobic conditions. Based on electrochemical measurements, we suggest that these new products originated from oxidative transformation processes of **3**. Thus, the cyclovoltammogram of compound **3a** revealed two irreversible oxidation peaks. Employing square wave measurements on derivative **3a**, two peaks at 1.133 and at 1.709 V can be ascribed to two different electron transfer steps.

We tested several oxidants for the oxidation of **3b**. Using lead(IV) acetate in the presence of potassium carbonate, the formation of a yellow side product **6b** displaying green fluorescence ($\lambda_{Em}$ = 512 nm) was observed. However, due to the formation of several by-products, this product was only isolated in a low yield. Better results

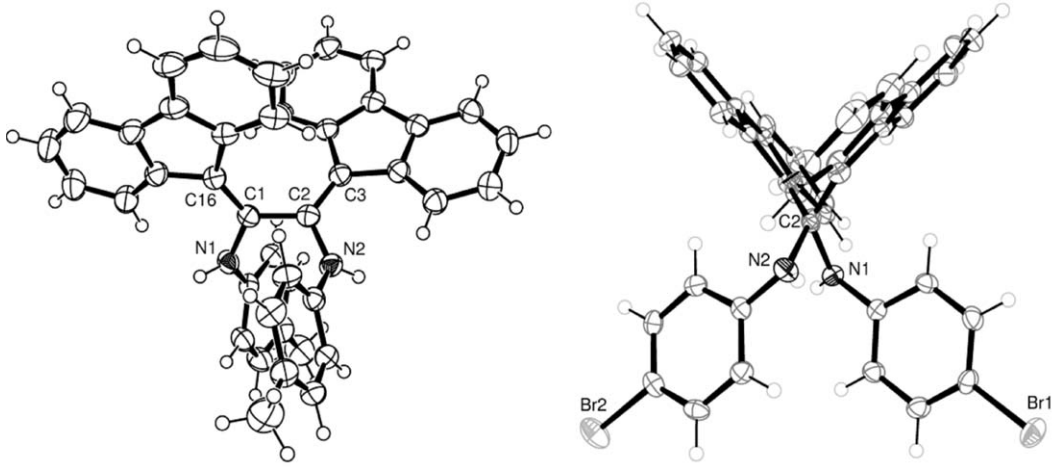
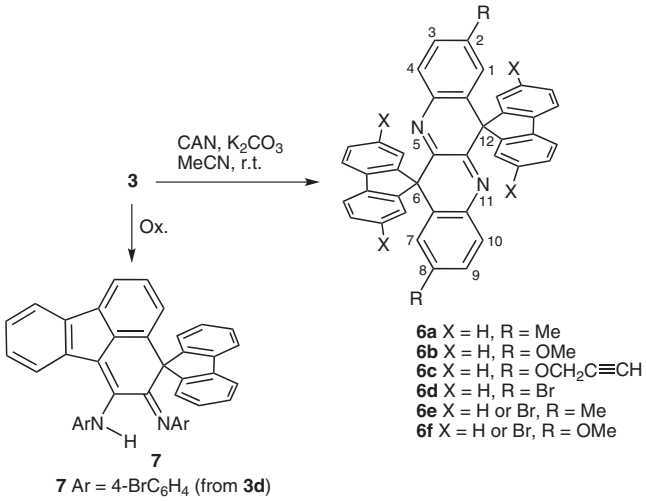



**Figure 1** ORTEP plot (50% probability ellipsoids) of the solid state molecular structure (X-ray analysis) of derivative **3a** (left side) and **3d** (right side, view along the central C1–C2 bond), selected bond lengths in Å for **3a**: N1–C1 1.387(2), N2–C2 1.386(2), C1–C2 1.493(3), C2–C3 1.363(3), C1–C16 1.364(3)

were obtained by using ceric ammonium nitrate (CAN)/potassium carbonate. We succeeded in isolating this yellow colored and green fluorescent product **6b** by column chromatography in a satisfactory yield. The MS data indicated, in this case, the loss of four hydrogen atoms. Evidence for the structure of bis(spirofluorene)dihydrodiazanaphthacene derivative **6b** (Scheme 4) was mainly provided by the $^1$H and $^{13}$C NMR spectra. Instead of the characteristic signals for a 4-methoxy-substituted phenyl substructure, the typical signals for a AMX spin system of a 1,2,4-trisubstituted benzene were detected in the $^1$H NMR spectra, a doublet at δ = 7.11 ($^3J$ = 8 Hz), a double doublet δ = 6.72 ($^3J$ = 8 Hz, $^4J$ = 2.8 Hz), and a doublet at δ = 5.70 ($^4J$ = 2.8 Hz) were observed. Only the simple set of signals for a 1,2-disubstituted benzene were observed for the fluorenyl moiety. In the $^{13}$C NMR spectra, the characteristic resonance of a spiro carbon at δ = 61.3 was detected. A resonance at 60.8 ppm in the $^{13}$C NMR was measured for the spiro carbon of bis(spirofluorene)dihydronaphthacene.[3]




**Scheme 4** Oxidative transformation of **3**

A single crystal X-ray analysis of **6b** confirmed the molecular structure of a bis-spiro annulated diazanaphthacene (Figure 2). The result of this analysis showed that **6b** is a monomer in the solid state in which the bond lengths and angles lie in the expected range.

The molecule exhibits a 'twisted-saddle' conformation, whereby the fluorenyl moieties are each folded to the same side of the tetracene framework by about 15°. Moreover, the two spiro connected fluorenyl substructures, which are orthogonal to their attached six-membered rings, are bent slightly in the opposite direction from the dihydronaphthacene framework.

The other fulvadienes of type **3** could successfully be involved into this oxidative reaction cascade (Scheme 4), whereby the bromofluorenyl substituted derivatives **6e**,**f** could be isolated in higher yields. Compounds **6e** and **6f** were isolated as inseparable mixture of two isomers, which displayed a complex set of signals in their $^1$H and

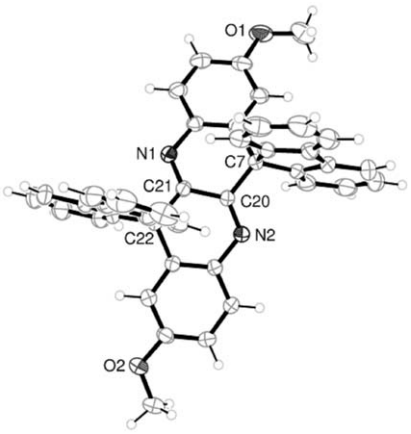



**Figure 2** ORTEP plot (50% probability ellipsoids) of the solid state molecular structure (X-ray analysis) of derivative **6b**, selected bond lengths in Å: N1–C21 1.287(3), N2–C20 1.281(3), C7–C20 1.527(3), C20–C21 1.484(3), C21–C22 1.517(4)

$^{13}$C NMR spectra. All new synthesized bis(spirofluorene)diazatetracenes **6a**–**h** display a green fluorescence in solution, whereby the emission maxima and the quantum yields were influenced by the substituents R [**6b**: $\lambda_{max}$ = 402 nm, (log ε = 4.1), $\lambda_{Em}$ = 512 nm, Φ = 0.1).

As a side product of the oxidation of **3d**, compound **7** was isolated, in traces, as yellow crystals after column chromatography. The MS data indicated, in this case, the loss of only two hydrogen atoms. In the $^1$H NMR, a singlet for the NH proton at δ = 8.00 was observed; in the $^{13}$C NMR spectra of **7**, the signal for a spiro carbon was detected at δ = 61.3. A single crystal X-ray analysis of **7** displays the structure of this side product as a spirofluoranthene derivative (Scheme 4) (Figure 3).

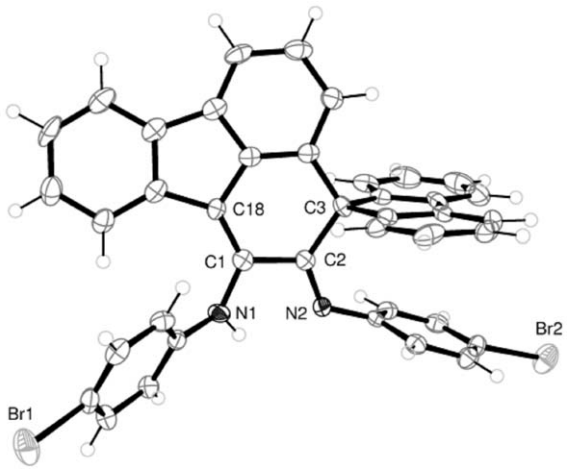
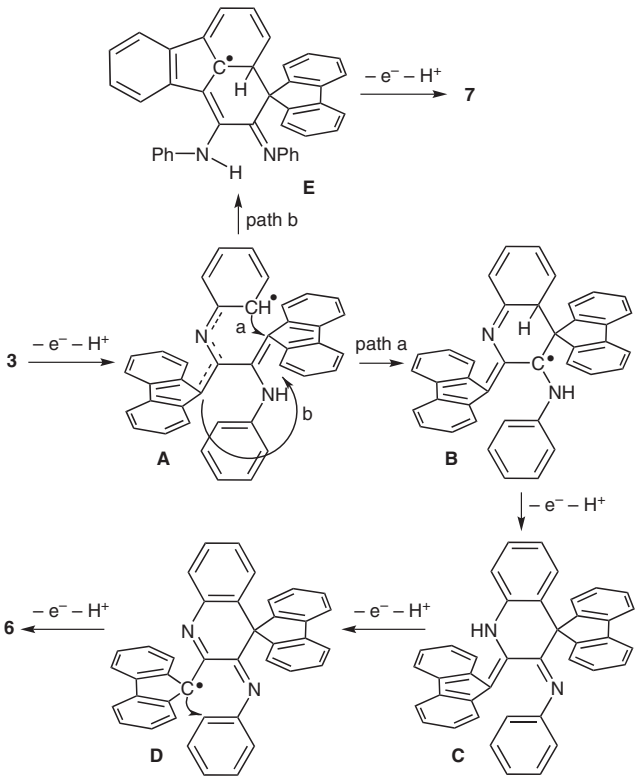



**Figure 3** ORTEP plot (50% probability ellipsoids) of the solid state molecular structure (X-ray analysis) of derivative **7**, selected bond lengths in Å: N1–C1 1.381(4), N2–C2 1.270(4), C1–C2 1.513(4), C2–C3 1.556(4), C1–C18 1.364(4)

Based on recent results, we postulate the following mechanism (Scheme 5) for the formation of the diazanaphthacenes of type **6**. Firstly, oxidation/deprotonation takes




**Scheme 5** Proposed mechanism for the formation of **6** and **7**

place under the intermediate formation of the radical **A** derived from a secondary amine. Radical **A** is able to intramolecularly attack the adjacent double bond on the C-9 fluorene carbon to give **B** (path a). A proton allyl shift, followed by oxidation, results in the intermediate **C**. A second two-electron oxidation reaction is then leading (via **D**) to the main product **6**. On the other hand, the fluoranthene derivative **7** also originates from radical **A** (path b), which in this case attacks the adjacent fluorenyl-ring on C-1 to give **E** and finally **7**.

This mechanism where aminyl radicals/radical cations are the key intermediates is supported by experimental facts. Generally, anilines can easily be oxidized and the thus formed amine radical cations tend to deprotonate quickly.[4] The aryl-substituted aminyl radicals are relatively stable and under suitable conditions they undergo substitution reactions.[5]

We have recently found that heterocycles, which possess vicinal arylamino-arylimino substructures gave derivatives of quinoxaline under oxidative conditions; quantum chemical calculations suggest a mechanism where aminyl radicals are the key intermediates.[6]

In conclusion a short and efficient synthesis for a series of novel bis(arylamino) fulvadienes **3** was developed based on the acylation reaction of fluorenyl anions with bis(imidoyl) chlorides **1**. The products **3** were isolated as red crystalline compounds in good yields. Their structure was determined by elemental analysis, MS, NMR and additionally, by X-ray crystal structural analysis. Monoimidoyl chlorides such as **4a**,**b** showed the same reactivity; as products the enamines **5a**,**b** were isolated as yellow crystals in good yields.

The fulvadienes **3** can be transformed by an oxidation–annulation sequence into dibenzonaphthyridine derivatives **6**. These to date unknown bis-spiro derivatives of diazatetracene are well soluble in common solvents and display green fluorescence in solution.

The reagents described in the following section were purchased from commercial sources and were used directly unless otherwise stated in the text. All solvents were of reagent grade and dried according to common practice and were distilled prior to use. The bis(aryloxaldiimidoyl) chlorides **1** were synthesized according to literature.[2a] Reactions were monitored by TLC, carried out on 0.2 mm Merck silica gel plates (60 $F_{254}$). The $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker Avance 250 and 400 spectrometers, shifts are relative to the signals of the solvent. Melting points were measured with a Galen III apparatus (Boëtius system) or with the Kofler apparatus and are uncorrected. Electrochemical measurements were carried out in $CH_2Cl_2$ with a Metrohm 663 VA Stand using platinum electrodes (reference electrode SCE) and tetrabutylammonium hexafluorophosphate as conductive salt.

### 1,2-Difluorenylidene-1,2-diarylaminoethanes 3 and Fluorenylidene(4-tolylamino)methanes (5); General Procedure

A solution of the corresponding fluorene **2** (12 mmol) in anhyd THF (60 mL) was cooled down to –30 °C and *t*-BuOK (2.7 g, 24 mmol) was added. To the solution, the corresponding bis(arylimidoyl) chloride **1** (6 mmol) or the corresponding arylimidoyl chloride **4** (12 mmol) was added. The deep red reaction mixture was stirred at –30 °C for 15 min. The mixture was acidified by the addition of HCl to pH 5–6. The mixture was diluted with $H_2O$ (500 mL) and the red (for **5** yellow) precipitate was collected by filtration, washed with $H_2O$ and after drying, it was purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane). Recrystallization from $CHCl_3$–*n*-heptane gave **3** as red crystals and **5** as yellow crystals.

### 1,2-Bis(4-tolylamino)-1,2-difluorenylideneethane (3a)

Yield: 82%; red crystals; mp 280–281 °C.

$^1H$ NMR (250 MHz, $CDCl_3$): δ = 8.21 (m, 2 H, Ar-H), 7.83 (m, 4 H, Ar-H), 7.70 (m, 2 H, Ar-H), 7.34 (m, 4 H, Ar-H), 7.10 (m, 2 H, Ar-H), 6.91 (m, 6 H, Ar-H), 6.60 (m, 4 H, Tol-H), 6.19 (s, 2 H, NH), 2.23 (s, 6 H, Tol-H).

$^{13}C$ NMR (63 MHz, $CDCl_3$): δ = 139.1, 138.21, 138.18, 137.9, 137.2, 136.5, 131.8, 129.5, 126.9, 126.8, 126.6, 125.6, 123.9, 123.0, 122.9, 119.9, 119.3, 118.8, 20.7.

MS (EI): *m*/*z* (%) = 564 (10, [$M^+$]), 282 (100, [$M/2^+$]), 165 (80, [$C_{13}H_9^+$]).

UV/Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 311 (4.3), 359 (4.4), 450 nm (4.2).

Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 89.01; H, 5.90; N, 4.93.

### 1,2-Bis(4-methoxyphenylamino)-1,2-difluorenylideneethane (3b)

Yield: 79%; red crystals; mp 305–307 °C.

$^1H$ NMR (250 MHz, DMSO-$d_6$): δ = 8.91 (s, 2 H, NH), 8.00–6.70 (m, 20 H, CH), 6.62 (d, *J* = 8 Hz, 4 H, CH), 3.59 (s, 6 H, $OCH_3$).

$^{13}C$ NMR (63 MHz, DMSO-$d_6$): δ = 155.0, 139.9, 138.7, 137.3, 137.6, 137.2, 135.8, 135.3, 126.8, 126.2, 125.6, 124.6, 123.9, 122.3, 120.8, 119.8, 119.7, 114.1, 55.5.

MS (EI): *m*/*z* (%) = 596 (10, [$M^+$]), 595 (20), 431 (10), 298 (100, [$M/2^+$]), 165 (60).

Anal. Calcd for $C_{42}H_{32}N_2O_2$: C, 84.54; H, 5.41; N, 4.69. Found: C, 84.33; H, 5.53; N, 4.23.

**1,2-Bis[4-(propargyloxy)phenylamino]-1,2-difluorenylidene-ethane (3c)**

Yield: 73%; red crystals; mp 320 °C (dec.).

$^1$H NMR (250 MHz, acetone-$d_6$): δ = 8.20–7.70 (m, 8 H, CH), 7.33–7.26 (m, 4 H, CH), 7.03–7.01 (m, 2 H, CH), 6.95 (d, $J$ = 8 Hz, 4 H, CH), 6.90–6.77 (m, 2 H, CH), 6.70 (d, $J$ = 8 Hz, 4 H, CH), 4.63 (d, $J$ = 2.4 Hz, 4 H, $OCH_2$), 3.02 (t, $J$ = 2.4 Hz, 2 H, CºCH).

$^{13}$C NMR (63 MHz, acetone-$d_6$): δ = 153.4, 138.5, 138.4, 138.1, 137.8, 137.4, 135.5, 126.4, 125.9, 125.7, 124.8, 123.5, 122.5, 121.4, 120.6, 119.3, 119.2, 115.0, 79.1, 75.8, 55.8 ($OCH_2$).

MS (EI): $m/z$ (%) = 644 (2, [M$^+$]), 606 (1, [M – $C_3H_3^+$], 458 (1), 322 (20, [M/2$^+$]), 181 (100).

Anal. Calcd for $C_{46}H_{32}N_2O_2$: C, 85.69; H, 5.00; N, 4.34. Found: C, 85.47; H, 4.84; N, 4.06.

**1,2-Bis(4-bromophenylamino)-1,2-difluorenylidene-ethane (3d)**

Yield: 86%; red crystals; mp 264–266 °C.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 8.1–6.8 (m, 20 H, CH), 6.56 (d, $J$ = 8 Hz, 4 H, CH), 6.10 (s, 2 H, NH).

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 140.0, 139.4, 138.8, 137.4, 136.8, 134.4, 132.0, 127.4, 127.1, 126.5, 124.4, 123.5, 123.0, 120.1, 119.7, 119.6, 114.7.

MS (EI): $m/z$ (%) = 696/694/692 (20/40/20, [M$^+$]), 524/522/520 (20/40/20), 348/346 (90/100, [M/2$^+$]), 267 (60), 165 (60).

Anal. Calcd for $C_{40}H_{26}Br_2N_2$: C, 69.18; H, 3.77; N, 4.03. Found: C; 68.84, H 3.58; N, 3.86.

**1,2-Bis(2-bromofluorenylidene)-1,2-bis(4-tolylamino)ethane (3e)**

Yield: 81%; red crystals; mp 270 °C (dec.).

$^1$H NMR (250 MHz, $CDCl_3$): δ = 8.20–7.90 (m, 2 H, CH), 7.90–6.10 (m, 22 H, 20 CH + 2 NH), 2.26 (s, 6 H, $CH_3$).

MS (DEI): $m/z$ (%) = 724/722/720 (20/40/20, [M$^+$]), 479/477 (20/40, [M – $C_{13}H_8Br^+$]), 362/360 (15/20, [M/2$^+$]), 260/258 (60/50), 91 (100).

Anal. Calcd for $C_{42}H_{30}Br_2N_2$: C, 69.82; H, 4.19; N, 3.88. Found: C 69.53; H, 4.01; N, 3.77.

**1,2-Bis(2-bromofluorenylidene)-1,2-bis(4-methoxyphenylamino)ethane (3f)**

Yield: 87%; red crystals; mp 295 °C (dec.).

$^1$H NMR (250 MHz, $CDCl_3$): δ = 8.20–7.90 (m, 2 H, CH), 7.90–7.60 (m, 5 H, CH), 7.60–7.30 (m, 4 H, CH), 7.10–6.90 (m, 3 H, CH), 6.66 (m, 8 H, CH), 6.50–6.10 (m, 2 H, NH), 3.73 (s, 6 H, $OCH_3$).

MS (DEI): $m/z$ (%) = 756/754/752 (15/30/15, [M$^+$]), 511/509 (15/20, [M – $C_{13}H_8Br^+$]), 378/376 (40/60, [M/2$^+$]), 260/258 (90/100), 151 (60).

Anal. Calcd for $C_{42}H_{30}Br_2N_2O_2$: C, 66.86; H, 4.01; N, 3.71. Found: C, 66.43; H, 3.88; N, 3.51.

**1,2-Bis(2,7-dibromofluorenylidene)-1,2-bis(4-tolylamino)ethane (3g)**

Yield: 85%; red crystals; mp ≥ 350 °C (dec.).

$^1$H NMR (250 MHz, acetone-$d_6$): δ = 8.80 (s, 2 H, NH), 8.06 (s, 2 H, CH), 7.80–7.70 (m, 6 H, CH), 7.64 (dd, $^3J$ = 8 Hz, $^4J$ = 1.7 Hz, 2 H, CH), 7.14 (dd, $^3J$ = 8 Hz, $^4J$ = 1.7 Hz, 2 H, CH), 7.0–6.8 (m, 8 H, Tol-H), 2.19 (s, 6 H, Tol-H).

$^{13}$C NMR (63 MHz, acetone-$d_6$): δ = 140.5, 140.0, 138.7, 138.4, 135.6, 135.4, 132.6, 129.2, 128.4, 127.6, 126.1, 125.3, 121.1, 121.0, 120.2, 119.8, 119.4, 19.9.

MS (ESI negative, MeOH–acetone): $m/z$ (%) = 883/881/879/877/875 (30/70/100/70/20, [M – H$^-$]).

Anal. Calcd for $C_{42}H_{28}Br_4N_2$: C, 57.31; H, 3.21; N, 3.18. Found: C, 57.03; H, 3.05; N, 2.92.

**1,2-Bis(2,7-dibromofluorenylidene)-1,2-bis(4-methoxyphenylamino)ethane (3h)**

Yield: 82%; red crystals; mp 273–276 °C.

IR (ATR): 3064, 3006, 2921, 2838, 1602, 1574, 1479, 1446, 1430, 1279, 1257, 1223, 1205, 1157, 1121, 1030, 993 cm$^{-1}$.

$^1$H NMR (250 MHz, acetone-$d_6$): δ = 8.10 (s, 2 H, NH), 7.81–7.65 (m, 6 H, CH), 7.44 (dd, $^3J$ = 8 Hz, $^4J$ = 1.7 Hz, 2 H, CH), 7.16 (dd, $^3J$ = 8 Hz, $^4J$ = 1.7 Hz, 2 H, CH), 6.91 (d, $^3J$ = 8 Hz, 4 H, Ar-H), 6.71 (d, $^3J$ = 8 Hz, 4 H, Ar-H), 3.69 (s, 6 H, $OCH_3$).

$^{13}$C NMR (63 MHz, acetone-$d_6$): δ = 156.3, 141.0, 140.0, 138.7, 135.4, 135.1, 133.7, 128.2, 127.3, 125.8, 125.1, 121.3, 121.1, 121.0, 120.2, 119.8, 117.8, 114.0, 54.8.

MS (DEI): $m/z$ (%) = 914/912/910 (25/30/25, [M$^+$]), 589 (25), 338 (60), 300 (60), 149 (60), 123 (100).

UV/Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 304 (4.5), 364 (4.3), 454 nm (4.2).

Anal. Calcd for $C_{42}H_{28}Br_4N_2O_2$: C, 55.30; H, 3.09; N, 3.07. Found: C, 54.90; H, 3.00; N, 2.95.

**Fluorenylidene(4-tolylamino)trifluoromethylmethane (5a)**

Yield: 71%; yellow solid; mp 82–86 °C.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 8.00–7.90 (m, 1 H, CH), 7.70–7.60 (m, 2 H, CH), 7.50–7.20 (m, 4 H, CH), 7.10–7.00 (m, 1 H, CH), 6.98 (d, $J$ = 8 Hz, 2 H, CH), 6.74 (d, $J$ = 8 Hz, 2 H, CH), 6.09 (s, 1 H, NH), 2.24 (s, 3 H, $CH_3$).

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 140.8, 140.0, 139.9, 136.1, 134.9, 131.2, 130.0, 129.2 (q, $J$ = 2 Hz), 128.6, 128.5, 127.6, 127.4, 126.5, 125.5 (q, $J$ = 14 Hz), 124.9, 122.7 (q, $J$ = 270 Hz), 119.6, 119.4, 115.9, 20.7.

MS (EI): $m/z$ (%) = 351 (60, [M$^+$]), 267 (30), 186 (80), 165 (80), 91 (100).

Anal. Calcd for $C_{22}H_{16}F_3N$: C, 78.67; H, 4.72; N, 3.28. Found: C, 78.21; H, 4.63; N, 3.19.

**Fluorenylidene(4-tolylamino)(4-trifluoromethylphenyl)methane (5b)**

Yield: 64%; yellow crystals; mp 155–157 °C.

IR (ATR): 3393, 3334, 3062, 2925, 2863, 1713, 1650, 1650, 1601, 1578, 1514, 1447, 1321, 1300, 1162, 1119, 1105, 1064, 1017 cm$^{-1}$.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 7.90–7.70 (m, 7 H, CH), 7.40–7.20 (m, 3 H, CH), 7.00–6.90 (m, 3 H, CH), 6.77 (s, 1 H, NH), 6.70–6.50 (m, 3 H, CH), 2.26 (s, 3 H, $CH_3$).

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 142.0, 139.8, 138.5, 138.4, 138.3, 138.1, 137.8, 132.0 (q, $J$ = 32 Hz, $CCF_3$), 131.7, 129.8, 126.8, 126.1, 125.9, 125.8, 125.7 (q, $J$ = 4 Hz), 125.4, 124.2 (q, $J$ = 270 Hz, $CF_3$), 122.4, 122.2, 119.9, 119.5, 119.1, 118.3, 20.8.

MS (DEI): $m/z$ (%) = 427 (100, [M$^+$]), 411 (20), 262 (20), 91 (20).

UV/Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 295 (3.9), 416 nm (3.9).

Anal. Calcd for $C_{42}H_{20}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 89.01; H, 5.90; N, 4.93.

**Sonogashira Cross-Coupling Reaction with 3d; 1,2-Difluorenylidene-1,2-(4-triisopropylsilylethynylphenylamino)ethane (3i)**

To a suspension of **3d** (1.40 g, 2 mmol), $(Ph_3P)_2PdCl_2$ (73 mg, 0.1 mmol), $Ph_3P$ (55 mg, 0.2 mmol), and CuI (20 mg, 0.1 mmol) in degassed toluene (20 mL) were added (triisopropylsilyl)acetylene (550 mg, 3 mmol) and $Et_3N$ (5 mL, 36 mmol). The mixture was stirred at 80 °C for 4 h under argon. The mixture was filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane); yield: 1.52 g (85%); red crystals; mp 320 °C (dec.).

$^1$H NMR (250 MHz, $CDCl_3$): δ = 8.00–6.80 (m, 20 H, CH), 6.63 (d, *J* = 8 Hz, 4 H, CH), 6.11 (s, 2 H, NH), 1.18–1.01 [m, 42 H, 6 × $CH(CH_3)_2$].

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 141.0, 139.5, 138.9, 137.3, 137.2, 136.9, 134.4, 133.0, 129.1, 127.5, 127.1, 126.6, 124.3, 123.6, 123.1, 119.6, 117.6, 116.9, 107.1, 89.7, 18.6, 11.3.

MS (FAB in NBA): *m*/*z* (%) = 897 (20, [M + H$^+$]), 896 (20, [M$^+$]), 732 (40), 448 (100, [M/2$^+$]).

Anal. Calcd for $C_{62}H_{68}N_2Si_2$: C, 82.98; H, 7.64; N, 3.12. Found: C, 82.51; H, 7.83; N, 3.01.

**6,6,12,12-Bis[spiro(fluorenyl)]-5,11-diaza-6,12-dihydrotetracenes 6; General Procedure**

A mixture of the corresponding 1,2-difluorenylidene-1,2-diarylaminoethanes **3** (2 mmol), $K_2CO_3$ (1.4 g, 10 mmol), and CAN (2.5 g, 4–5 mmol) in MeCN (50 mL) was stirred at r.t. until no starting material **3** could be detected (TLC, ca. 0.5 h). Most of the solvent was removed in vacuo and the residue was added to $H_2O$ (100 mL). The crude product was extracted with $CHCl_3$ (2 × 50 mL), the insoluble solid was filtered off, and washed with MeOH (10 mL). The organic layers were combined and dried ($Na_2SO_4$). After removing the solvent in vacuo, the product was purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane). Recrystallization from $CHCl_3$–*n*-heptane gave **6** as yellow crystals.

**6,6,12,12-Bis[spiro(fluorenyl)]-2,8-dimethyl-5,11-diaza-6,12-dihydrotetracene (6a)**

Yield: 45%; yellow crystals; mp 315 °C (dec.).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8 Hz, 4 H, CH), 7.43 (m, 4 H, CH), 7.21 (d, *J* = 8 Hz, 2 H, CH), 7.15 (m, 4 H, CH), 7.01 (d, *J* = 8 Hz, 4 H, CH), 6.92 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.5 Hz, 2 H, CH), 6.26 (d, $^4J$ = 1.5 Hz, 2 H, CH), 2,04 (s, 6 H, $CH_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 157.9, 148.1, 140.8, 140.4, 138.8, 133.7, 129.9, 128.7, 127.9, 127.7, 126.6, 126.0, 120.3, 61.3 (spiro-C), 21.2

MS (DEI): *m*/*z* (%) = 560 (100, [M$^+$]), 545 (25), 280 (20, [M/2$^+$]), 83 (30).

Emission ($CHCl_3$): $\lambda_{max}$ = 480 nm.

Anal. Calcd for $C_{42}H_{28}N_2$: C, 89.97; H, 5.03; N, 5.00. Found: C, 89.60; H, 4.71; N, 4.73.

**6,6,12,12-Bis[spiro(fluorenyl)]-2,8-dimethoxy-5,11-diaza-6,12-dihydrotetracene (6b)**

Yield: 50%; yellow crystals; mp 241–244 °C.

IR (ATR): 3064, 3006, 2921, 2838, 1602, 1574, 1479, 1446, 1430, 1279, 1257, 1223, 1205, 1121, 1030, 736 cm$^{-1}$.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8 Hz, 4 H, CH), 7.40 (m, 4 H, CH), 7.24 (d, *J* = 8 Hz, 2 H, CH), 7.13 (m, 4 H, CH), 7.00 (m, 4 H, CH), 6.60 (dd, $^3J$ = 8 Hz, $^4J$ = 2.8 Hz, 2 H, CH), 5.98 (d, $^4J$ = 2.8 Hz, 2 H, CH), 3.52 (s, 6 H, $OCH_3$).

$^1$H NMR (250 MHz, DMSO-$d_6$): δ = 7.99 (d, *J* = 8 Hz, 4 H, CH), 7.45 (m, 4 H, CH), 7.15 (m, 4 H, CH), 7.11 (d, *J* = 8 Hz, 2 H, CH), 6.92 (m, 4 H, CH), 6.72 (dd, $^3J$ = 8 Hz, $^4J$ = 2.8 Hz, 2 H, CH), 5.70 (d, $^4J$ = 2.8 Hz, 2 H, CH), 3.47 (s, 6 H, $OCH_3$).

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 159.4, 156.1, 148.0, 140.7, 136.8, 135.9, 131.3, 127.9, 127.7, 125.9, 120.3, 112.2, 112.0, 61.3 (spiro-C), 55.1 ($OCH_3$).

MS (EI): *m*/*z* (%) = 592 (100, [M$^+$]), 577 (20), 431 (10), 83 (80).

UV/Vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 307 (3.9), 402 nm (4.1).

Emission ($CHCl_3$): $\lambda_{max}$ = 512 nm.

Anal. Calcd for $C_{42}H_{28}N_2O_2$: C, 85.11; H, 4.76; N, 4.73. Found: C, 84.88; H, 4.51; N, 4.49.

**6,6,12,12-Bis[spiro(fluorenyl)]-2,8-di(propargyloxy)-5,11-diaza-6,12-dihydrotetracene (6c)**

Yield: 37%; yellow crystals; mp 310 °C (dec.).

$^1$H NMR (250 MHz, acetone-$d_6$): δ = 7.94 (d, *J* = 8 Hz, 4 H, CH), 7.60–7.15 (m, 10 H, CH), 7.00 (m, 4 H, CH), 6.81 (dd, $^3J$ = 8 Hz, $^4J$ = 2.8 Hz, 2 H, CH), 5.99 (d, $^4J$ = 2.8 Hz, 2 H, CH), 4.51 (d, $^4J$ = 2.4 Hz, 4 H, $OCH_2$), 2.92 (t, $^4J$ = 2.4 Hz, 2 H, CºCH).

$^{13}$C NMR (63 MHz, acetone-$d_6$): δ = 157.7, 155.9, 149.0, 140.9, 137.0, 135.8, 130.9, 128.2, 127.8, 125.5, 120.4, 113.4, 113.0, 78.1, 76.4, 61.1 (spiro-C), 55.4 ($OCH_2$).

MS (DEI): *m*/*z* (%) = 640 (50, [M$^+$]), 601 (80, [M – $C_3H_3^+$]), 533 (40), 180 (100).

Anal. Calcd for $C_{46}H_{28}N_2O_2$: C, 86.23; H, 4.40; N, 4.37. Found: C, 85.89; H, 4.25; N, 4.22.

**6,6,12,12-Bis[spiro(fluorenyl)]-2,8-dibromo-5,11-diaza-6,12-dihydrotetracene (6d)**

Yield: 31%; yellow crystals; mp 390 °C (dec.).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8 Hz, 4 H, CH), 7.45 (m, 4 H, CH), 7.25 (d, $^4J$ = 2.1 Hz, 2 H, CH), 7.19–7.08 (m, 8 H, CH), 6.95 (d, $^3J$ = 8 Hz, 2 H, CH), 6.58 (d, $^4J$ = 2.1 Hz, 2 H, CH).

$^{13}$C NMR (400 MHz, $CDCl_3$): δ = 158.4, 146.9, 140.8, 135.9, 132.7, 131.6, 131.3, 129.1, 128.4, 127.9, 125.8, 120.6, 61.0 (spiro-C).

MS (DEI): *m*/*z* (%) = 692/690/688 (50/80/55, [M$^+$]), 611/609 (60/80, [M – HBr$^+$]), 528 (10, [M –2 HBr$^+$]), 305 (35), 264 (100).

Emission ($CHCl_3$): $\lambda_{max}$ = 482 nm.

Anal. Calcd for $C_{40}H_{22}Br_2N_2$: C, 69.59; H, 3.21; N, 4.06. Found: C, 69.24; H, 3.03; N, 3.89.

**6,6,12,12-Bis[spiro(2-bromofluorenyl)]-2,8-dimethyl-5,11-diaza-6,12-dihydrotetracene (6e)**

Yield: 61%; yellow crystals; mp 325–326 °C.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 7.82 (m, 2 H, CH), 7.68 (m, 2 H, CH), 7.56–7.42 (m, 4 H, CH), 7.24 (m, 4 H, CH), 7.09–6.94 (m, 6 H, CH), 6.24 (m, 2 H, CH), 2.06 (s, 6 H, $CH_3$).

$^{13}$C NMR (63 MHz, $CDCl_3$): δ = 157.1–120.5, 61.3/61.2 (spiro-C), 21.4.

MS (DEI): *m*/*z* (%) = 720/718/716 (40/60/40, [M$^+$]), 639/637 (20/20, [M – Br]), 360/358 (45/40, [M/2$^+$]), 319 (30), 311 (40), 264 (100).

Emission ($CHCl_3$): $\lambda_{max}$ = 481 nm.

Anal. Calcd for $C_{42}H_{26}Br_2N_2$: C, 70.21; H, 3.65; N, 3.90. Found: C, 69.81; H, 3.42; N, 3.58.

**6,6,12,12-Bis[spiro(2-bromofluorenyl)]-2,8-dimethoxy-5,11-diaza-6,12-dihydrotetracene (6f)**

Yield: 65%; yellow crystals; mp 292–293 °C.

$^1$H NMR (250 MHz, $CDCl_3$): δ = 7.80 (m, 2 H, CH), 7.70 (m, 2 H, CH), 7.53 (m, 2 H, CH), 7.44 (m, 2 H, CH), 7.31–7.17 (m, 4 H, CH),

7.12–7.00 (m, 4 H, CH), 6.65 (m, 2 H, CH), 5.98 (m, 2 H, CH), 3.56 (s, 6 H, $OCH_3$).

$^{13}C$ NMR (63 MHz, $CDCl_3$): δ = 159.7–112.2, 61.3/61.2 (spiro-C), 55.2.

MS (DEI): *m/z* (%) = 752/750/748 (60/100/60, [$M^+$]), 376/374 (30/30, [$M/2^+$]).

Emission ($CHCl_3$): $\lambda_{max}$ = 516 nm.

Anal. Calcd for $C_{42}H_{26}Br_2N_2O_2$: C, 67.22; H, 3.49; N, 3.73. Found: C, 66.92; H, 3.29; N, 3.41.

**5-(4-Bromophenylimino)-6-(4-bromophenylamino)-4,4-spiro(fluorenyl)-4,5-dihydrofluoranthene (7)**

The side product **7** was isolated during the purification of **6d** by column chromatography on silica gel ($CHCl_3$–*n*-heptane) in traces. Recrystallization from $CHCl_3$–*n*-heptane gave **7** as yellow crystals, mp 340 °C (dec.).

$^1H$ NMR (200 MHz, $CDCl_3$): δ = 8.00 (s, 1 H, NH), 7.80–6.60 (m, 20 H, CH), 6.00–5.30 (m, 3 H, CH).

$^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 149.3, 146.8, 142.0, 141.1, 141.0, 136.1, 134.6, 134.4, 134.3, 131.9, 130.9, 130.5, 129.3, 128.5, 128.1, 127.6, 126.8, 126.4, 124.3, 123.4, 123.1, 121.3, 120.8, 120.6, 120.4, 119.9, 118.1, 114.1, 113.8, 61.3 (spiro-C).

MS (ESI in MeOH–$CHCl_3$): *m/z* (%) = 695/693/691 (60/90/60, [M + $H^+$]), 587 (100), 559 (90), 413 (80).

**Crystal Structure Determination of 3a, 3d, 6b, and 7**

The intensity data for the compound was collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-$K_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[7] The structure was solved by direct methods (SHELXS),[8] and refined by full-matrix least squares techniques against $Fo^2$ (SHELXL-97).[9] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[4] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

**Crystal Data for 3a**[10]

Empirical formula: $C_{42}H_{32}N_2$; red prism, size 0.05 × 0.05 × 0.05 $mm^3$, monoclinic, space group $P2_1/n$, unit cell dimensions $a$ = 10.1879(5), $b$ = 18.9116(6), $c$ = 16.3908(7) Å, β = 90.076(3)°, $V$ = 3158.0(2) $Å^3$, $T$ = –90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.188 $gcm^{-3}$, μ(Mo-$K_\alpha$) = 0.69 $cm^{-1}$, $F$(000) = 1192, 21347 reflections in $h$(–13/11), $k$(–24/24), $l$(–21/18), measured in the range 2.15° ≤ Θ ≤ 27.49°, completeness $\Theta_{max}$ = 99.6%, 7208 independent reflections, $R_{int}$ = 0.0679, 4237 reflections with $F_o > 4\rho(F_o)$, 407 parameters, 0 restraints, $R1_{obs}$ = 0.0581, $wR2_{obs}$ = 0.1190, $R1_{all}$ = 0.1196, $wR2_{all}$ = 0.1449, GOOF = 1.023, largest difference peak and hole: 0.242/0.232 e $Å^{-3}$.

**Crystal Data for 3d**[10]

Empirical formula: $C_{40}H_{26}Br_2N_2$ 2($CHCl_3$); red prism, size 0.07 × 0.07 × 0.05 $mm^3$, monoclinic, space group $P2_1/n$, $a$ = 15.0246(4), $b$ = 9.8644(2), $c$ = 26.7844(6) Å, β = 103.9510(10)°, $V$ = 3852.58(16) $Å^3$, $T$ = –90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.609 $gcm^{-3}$, μ(Mo-$K_\alpha$) = 25.55 $cm^{-1}$, $F$(000) = 1864, 26153 reflections in $h$(–19/18), $k$(–12/12), $l$(–32/34), measured in the range 2.21° ≤ Θ ≤ 27.45°, completeness $\Theta_{max}$ = 99.8%, 8793 independent reflections, $R_{int}$ = 0.0669, 5553 reflections with $F_o > 4\rho(F_o)$, 469 parameters, 0 restraints, $R1_{obs}$ = 0.0506, $wR2_{obs}$ = 0.0949, $R1_{all}$ = 0.1024, $wR2_{all}$ = 0.1095, GOOF = 1.012, largest difference peak and hole: 1.486/–0.985 e $Å^{-3}$.

**Crystal Data for 6b**[10]

Empirical formula: $C_{42}H_{28}N_2O_2$ 0.4($CHCl_3$), yellow prism, size 0.06 × 0.06 × 0.05 $mm^3$, monoclinic, space group $P2_1/c$, $a$ = 13.5730(4), $b$ = 17.3936(6), $c$ = 16.016(3) Å, β = 106.146(2)°, $V$ = 3632.0(7) $Å^3$, $T$ = –90 °C, $Z$ = 4, $\rho_{calcd}$ = 1.171 $gcm^{-3}$, μ(Mo-$K_\alpha$) = 1.57 $cm^{-1}$, $F$(000) = 1333, 24011 reflections in $h$(–16/17), $k$(–22/21), $l$(–20/17), measured in the range 4.14° ≤ Θ ≤ 27.49°, completeness $\Theta_{max}$ = 98.5%, 8213 independent reflections, $R_{int}$ = 0.0475, 5444 reflections with $F_o > 4\rho(F_o)$, 447 parameters, 0 restraints, $R1_{obs}$ = 0.0881, $wR2_{obs}$ = 0.2574, $R1_{all}$ = 0.1270, $wR2_{all}$ = 0.2971, GOOF = 1.037, largest difference peak and hole: 1.340/–0.357 e $Å^{-3}$.

**Crystal Data for 7**[10]

Empirical formula:$C_{40}H_{24}Br_2N_2$; yellow-orange prism, size 0.05 × 0.04 × 0.04 $mm^3$, monoclinic, space group $P2_1/n$, $a$ = 9.2484(3), $b$ = 25.9276(9), $c$ = 13.2181(4) Å, β = 107.635(2)°, $V$ = 3020.60(17) $Å^3$, $T$ = –140 °C, $Z$ = 4, $\rho_{calcd}$ = 1.523 $gcm^{-3}$, μ(Mo-$K_\alpha$) = 27.17 $cm^{-1}$, $F$(000) = 1392, 18354 reflections in $h$(–11/10), $k$(–33/31), $l$(–17/17), measured in the range 2.51° ≤ Θ ≤ 27.48°, completeness $\Theta_{max}$ = 99.3%, 6865 independent reflections, $R_{int}$ = 0.0775, 3736 reflections with $F_o > 4\sigma(F_o)$, 397 parameters, 0 restraints, $R1_{obs}$ = 0.0472, $wR2_{obs}$ = 0.0813, $R1_{all}$ = 0.1252, $wR2_{all}$ = 0.0980, GOOF = 0.943, largest difference peak and hole: 0.472/–0.588 e $Å^{-3}$.

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(10) (10)CCDC-762471 (**3a**), CCDC-762472 (**3d**), CCDC-762473 (**6b**), and CCDC-762474 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; or deposit@ccdc.cam.ac.uk].