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3,4-Dihydro-3*H*-pyrrol-2-imines as Conformationally Restrained 1,3-Diazabutadienes: Synthesis, Structural Properties and Protonation[‡]

Simon Janich,[a] Roland Fröhlich,[a] Andrea Wilken,[a] Jan von Zamory,[a] Atsushi Wakamiya,[b] Shigehiro Yamaguchi,[b] and Ernst-Ulrich Würthwein*[a]

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5-Aryl-3,3,4,4-tetramethyl-3,4-dihydro-3*H*-pyrrol-2-imines, conformationally restrained 1,3-diazabuta-1,3-diene derivatives, were easily prepared by treating aryllithium species with 2,2,3,3-tetramethylsuccinonitrile (**1**). Trapping the reaction intermediate with chlorotrimethylsilane gave *N*-silylated compounds **2a**–**e**, whereas aqueous workup gave N-H derivatives **3a**,**b**. Pyrenyl-substituted compound **3b** was characterised by X-ray diffraction studies, revealing the presence of both intermolecular aromatic face-to-face contacts and the formation of homodimers by twofold H-bonding. *N*-Silylated derivatives **2a**–**d** were used successfully as nucleophilic components in palladium-catalysed C–N bond-forming reactions to obtain *N*-arylated compounds **5b**–**h**,**j**,**k**,**m** and **7a**–**d**. The UV spectra of compounds **5** and **7** exhibit long wavelength absorptions up to 462 nm for **7d**, thus indicating extended π–π* conjugation. Dihydropyrrolimine-based compounds with larger conjugated aryl substituents in the 5-position react with Brønsted and Lewis acids displaying a significant colour change that could be used to estimate the pK_b of **3a** to a value of –4.5. Derivatives **2c**,**e** and **3a**,**b**, which are not *N*-arylated, are fluorescent with a Stokes shift of 107 nm (6034 cm^{-1}) for **3a**.

Introduction

1,3-Diazabuta-1,3-dienes can be regarded as nitrogen-rich analogues of buta-1,3-dienes. They contain an amidine subunit, thus forming a backbone of alternating C–N double and single bonds. Unlike the 1,3-butadienes, 1,3-diazabuta-1,3-dienes as other oligonitriles[1,2] have a low energetic barrier for rotations about the central C–N single bond, which leads to high structural flexibility.[3,4,5] In addition, they prefer a three-dimensionally twisted structure due to n–π interactions between the lone pairs at the nitrogen atoms and the neighbouring double bonds. Thus, in contrast to polyenes, no continuous conjugation along the molecule backbone is observed.

Recently, we reported on the synthesis of oligonitrile derivatives with conformationally restrained (5-imino-4,5-dihydro-3*H*-pyrrol-2-yl)amine subunits as planarised 1,3,5-triazapenta-1,3-diene moieties.[12] Unlike their open-chained counterparts, the N–C–N–C–N backbone is fixed in a W shape conformation, thus leading to π–π* conjugation of the two consecutive C–N double bonds. This results in properties that differ considerably from the open-chained oligonitriles, such as absorptions in the UV/Vis spectra at longer wavelengths, indicating the presence of larger chromophores due to the extended conjugation. Replacing the terminal amino group with an aryl moiety leads to conformationally restrained 1,3-diazabuta-1,3-diene derivatives that can form extended conjugated systems spreading over both the aromatic part and the heteropolyene chain. As a result of the asymmetric substitution of the dihydropyrrole subunit, these building blocks have a distinct dipole moment pointing roughly in the direction of the exocyclic imino moiety. Exploiting this feature by choosing an electron-donating group for the 5-position and attaching an electron-poor moiety at the imino nitrogen atom could give rise to interesting optical properties by an intramolecular charge transfer along the molecule backbone (Figure 1).

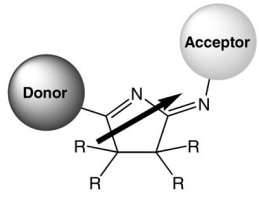

Figure 1. Schematic presentation of the donor–acceptor substituted 1,3-diazabuta-1,3-diene system with the dipole vector.

For the synthesis of conformationally restrained 1,3-diazabuta-1,3-diene derivatives, we employed a anionic cyclisation reaction that is known for the synthesis of heterocyclic

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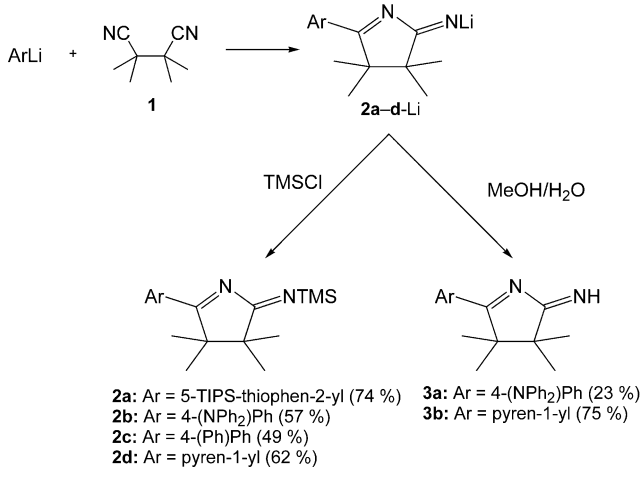
[a] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität,
Corrensstraße 40, 48149 Münster, Germany
Fax: +49-251-83-39772
E-mail: wurthwe@uni-muenster.de
[b] Department of Chemistry, Graduate School of Science, Nagoya University,
Nagoya 464-8602, Japan

compounds from 1,2- or 1,3-dinitriles. Linstead and Elvidge described the preparation of succinimidine by heating succinonitrile with a methanol solution of ammonia under pressure.[6] Scheffold and his coworkers synthesised dihydropyrrolimine derivatives by treating nucleophilic methyl species with tetramethylsuccinonitrile.[7] The same reaction mechanism can be found in polymer science, such as intramolecular anionic cyclisations in polyacrylonitriles[8,9] or the synthesis of polynitriles from succinonitrile and fumaronitrile, as studied by Wöhrle.[10,11]

In this report, we describe the synthesis of conformationally restrained 1,3-diazabuta-1,3-dienes and their use as nucleophilic components in palladium-catalysed C–N bond-formation reactions. Furthermore, we report on the optical and structural properties of these compounds as studied by UV/Vis and fluorescence spectroscopy and by X-ray diffraction.

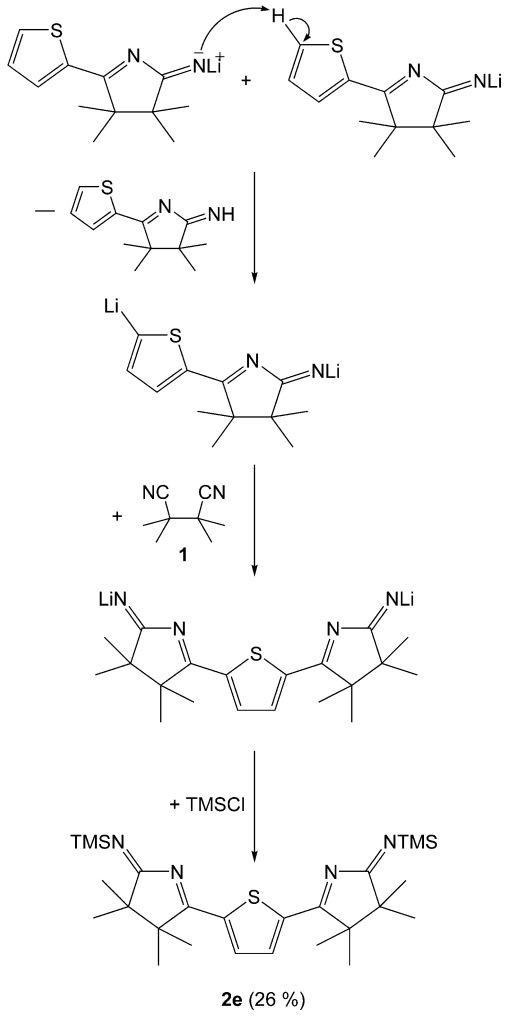
Results and Discussion

The procedure for the synthesis of the *N*-silylated 5-aryldihydropyrrol-2-imines was adapted from the protocol used by Marihart, Greving et al. to synthesise conformationally restrained 1,3,5-triazapenta-1,3-diene building blocks for oligonitriles,[12]which in turn is based on a procedure published by Wöhrle.[11] The employed 2,2,3,3-tetramethylsuccinonitrile (**1**) is easily available by controlled decomposition of azoisobutyronitrile (AIBN).[13] This tetramethyl-substituted dinitrile is nonenolisable, which is advantageous for the reactions reported here. The synthesis starts with the transformation of an aryl bromide into the nucleophilic aryllithium compound by a metal–halogen exchange with *n*-butyllithium at –78 °C. To this, a solution of a slight excess of dinitrile **1** is added. After warming to 0 °C and stirring for 30 min, the solution is cooled to –78 °C again, and the lithiated intermediate is trapped by adding chlorotrimethylsilane to give *N*-silylated compounds **2**. Aqueous workup instead of quenching with TMSCl results in unprotected compounds **3** (Scheme 1).



Scheme 1.

Reactions with 2-bromothiophene as starting material give the unusual bis-dihydropyrrolimine **2e** as the main product. It appears that the proton in the 5-position of the thiophene is acidic enough to be abstracted by the basic lithiated intermediate, thus creating a second nucleophilic site that reacts with another equivalent of dinitrile **1** (Scheme 2).



Scheme 2.

Compounds **2** and **3** were completely characterised by spectroscopic methods. Bis-dihydropyrrolimine **2e** exhibits clear indications in the ^{1}H NMR spectrum of two isomeric forms in a 5:1 ratio, probably conformers regarding the orientation of the dihydropyrrole moieties relative to the central thiophene unit and to each other. Pyrenyl-substituted derivative **3b** could also be characterised in the solid state by X-ray structure determination. The packing structure of this compound is governed by face-to-face aromatic interactions between the pyrenyl groups that are 3.456 Å apart and by NH···N interactions between the terminal imino moieties and the dihydropyrrole nitrogen atoms forming a homodimeric structure with two equivalent H-bonds. However, these interactions do not seem to be very strong, as the N–N distances are 3.320 Å with N–H distances of 2.428 Å

(Figure 2). Our earlier examples of such homodimers displayed N–N distances from 2.919 to 2.988 Å.[12] The pyrenyl moiety is significantly tilted relative to the dihydropyrrole ring, as illustrated by the torsion angle C_{1a}–C_{ipso}–C–N (70.35°).

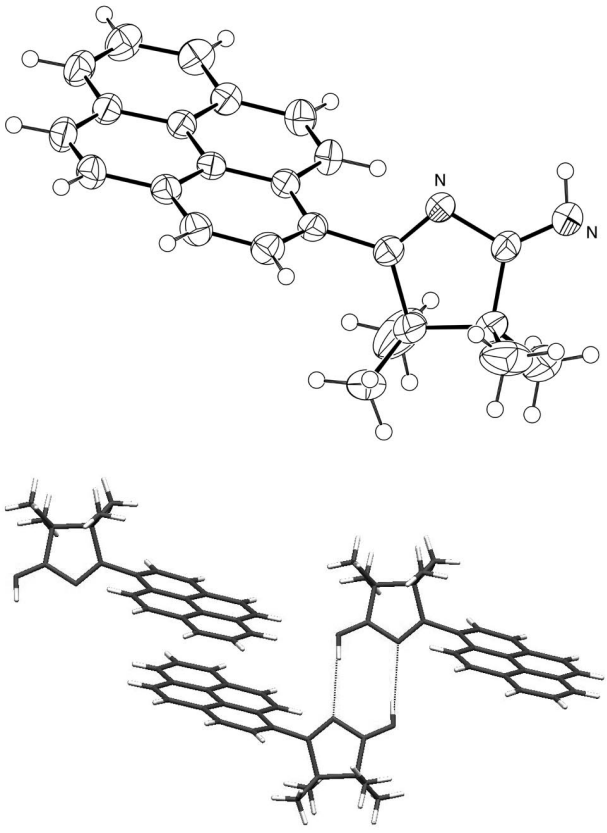
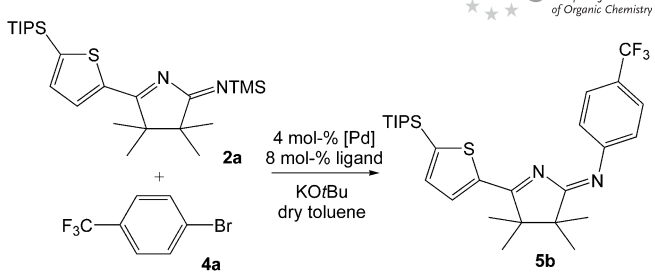


Figure 2. Molecular structure of **3b** in the crystalline state as obtained by X-ray diffraction. Top: single molecule (PLATON plot[14]); bottom: ensemble of three molecules exhibiting face-to-face aromatic interactions on the left-hand side and long NH···N interactions between the middle and the right-hand molecule (MERCURY plot [15]).

In order to obtain dihydropyrrolimines bearing an additional aryl substituent at the imine moiety, *N*-silylated compounds **2** were employed as nucleophiles in a Buchwald–Hartwig-type palladium-catalysed cross-coupling reaction with aryl halides **4**.[16–21] The most suitable catalyst system and reaction conditions were determined by a series of test reactions with dihydropyrrolimine **2a** as the nucleophile and 1-bromo-4-(trifluoromethyl)benzene (**4a**) as the electrophilic component (Scheme 3, Table 1).

Because the employed palladium source hardly affected the outcome of the reaction, a catalyst system consisting of the cheaper and less-sensitive palladium(II)acetate and *rac*-BINAP was chosen for the following syntheses of a variety of *N*-arylated dihydropyrrolimines **5** (Scheme 4, Table 2).

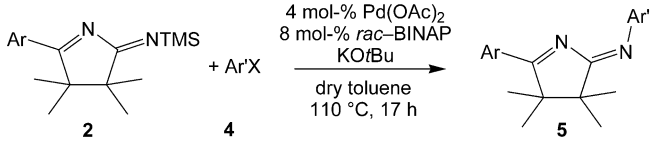
The employed *N*-silylated dihydropyrrolimine barely affected the outcome of the reaction, and only bis-dihydropyrrolimine **2e** did not react. A possible reason for this could be deactivation of the catalyst by the compound. Both electron-rich and electron-poor aryl halides and even



Scheme 3.

Table 1. Screening of catalysts and reaction conditions for the reaction of **2a** with **4a** to give **5b**.

Entry	Pd source	Ligand	Conditions	Yield [%]
1	$Pd_2(dba)_3$	P(*o*-Tol)$_3$	90 °C, 17 h	0
2	$Pd_2(dba)_3$	P(*t*Bu)$_3$	90 °C, 17 h	3
3	$Pd_2(dba)_3$	*S*-Phos[19,20]	90 °C, 17 h	43
4	$Pd_2(dba)_3$	*rac*-BINAP	90 °C, 17 h	57
5	$Pd(OAc)_2$	*rac*-BINAP	90 °C, 4 h	43
6	$Pd(OAc)_2$	*rac*-BINAP	r.t., 17 h	8



Scheme 4.

Table 2. Substitution pattern of compounds **2**, **4** and **5** and yields of *N*-arylated-5-aryldihydropyrrol-2-imines **5**.

5	2	Ar	4	Ar′	X	Yield [%]
a	**e**	Thiophen-2,5-diyl	**a**	4-(CF_3)Ph	Br	0
b	**a**	5-TIPS-thiophen-2-yl	**a**	4-(CF_3)Ph	Br	57
c	**c**	4-(Ph)Ph	**a**	4-(CF_3)Ph	Br	62
d	**d**	Pyren-1-yl	**a**	4-(CF_3)Ph	Br	65
e	**b**	4-(NPh_2)Ph	**a**	4-(CF_3)Ph	Br	67
f	**b**	4-(NPh_2)Ph	**b**	4-BrPh	I	72
g	**b**	4-(NPh_2)Ph	**c**	2-BrPh	I	73
h	**b**	4-(NPh_2)Ph	**d**	2,4,6-(CH_3)Ph	Br	36
i	**b**	4-(NPh_2)Ph	**e**	2,6-(*i*Pr)Ph	I	0
j	**b**	4-(NPh_2)Ph	**f**	4-(Ph)Ph	Br	52
k	**b**	4-(NPh_2)Ph	**g**	4-(NPh_2)Ph	Br	25
l	**b**	4-(NPh_2)Ph	**h**	Pyridin-2-yl	Br	0
m	**b**	4-(NPh_2)Ph	**i**	Pyridin-3-yl	Br	16
n	**b**	4-(NPh_2)Ph	**j**	Pyrimidin-2-yl	Br	0
o[a]	**b**	4-(NPh_2)Ph	**k**	(*N*-Boc)-pyrrol-2-yl	Br	0
p[b]	**b**	4-(NPh_2)Ph	**l**	5-Phenyl-(*N*-Boc)-pyrrol-2-yl	Br	0
q[a]	**b**	4-(NPh_2)Ph	**m**	3,4,5-Triphenyl-(*N*-Boc)-pyrrol-2-yl	Br	0

[a] K_3PO_4 as base. [b] Cs_2CO_3 as base.

slightly sterically hindered electrophiles like 2-bromomesitylene (**4d**) and 1-bromo-2-iodobenzene (**4c**) could be used without problems in this reaction. In contrast, more sterically hindered aryl halides like 2,6-diisopropyl bromobenzene (**4e**) and the *N*-Boc-protected 2-bromo-3,4,5-triphenylpyrrole **4m** did not react at all under the employed conditions. Reactions with 2-azaaryl halides like 2-bromo-

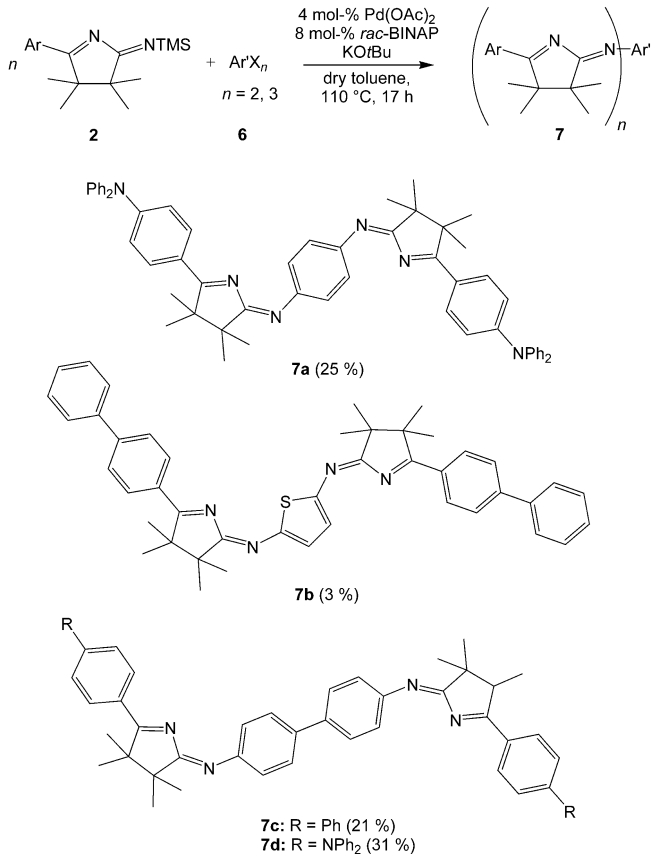
pyridine (**4h**), 2-bromopyrimidine (**4j**) and the less-hindered 2-bromopyrrole derivatives (**4k**,**l**) always gave complex mixtures of products that showed no trace of the desired products.

By using the same conditions as above, the synthesis of several branched *N*-arylated dihydropyrrolimines (**7**) based on symmetric aryl di- or trihalides (**6**) was attempted (Table 3, Scheme 5).

Table 3. Substitution pattern of compounds **2**, **6** and **7** and yields of branched *N*-arylated-5-aryldihydropyrrol-2-imines **7**.

7	2	Ar	6	Ar′X_n	Yield [%]
a	**b**	4-(NPh_2)Ph	**a**	1,4-diiodobenzene	25
b	**c**	4-(Ph)Ph	**b**	2,5-dibromothiophene	3
c	**c**	4-(Ph)Ph	**c**	4,4′-dibromobiphenyl	21
d	**b**	4-(NPh_2)Ph	**c**	4,4′-dibromobiphenyl	31
e	**b**	4-(NPh_2)Ph	**d**	2,7-dibromofluorene	0[a]
f	**c**	4-(Ph)Ph	**e**	1,3,5-tribromobenzene	0[b]
g	**b**	4-(NPh_2)Ph	**e**	1,3,5-tribromobenzene	0[b]

[a] Only monosubstituted product. [b] Only mono- and disubstituted products.



Scheme 5.

The lower yields obtained throughout are likely to be a result of an increase in the electron density in the electrophile after the attachment of the first strongly electron-donating dihydropyrrole moiety, resulting in deactivation of the aryl halide towards further coupling reactions. In the case of 2,7-dibromofluorene **6d**, which is already electron rich by itself, this deactivation is sufficient to prevent a second substitution to produce **7e** completely. A threefold coupling reaction at 1,3,5-tribromobenzene **6e** to give compounds like **7f**,**g** is probably prevented by the substantial steric demand of the dihydropyrrolimino substituents.

Obtained compounds **5** and **7** were completely characterised by spectroscopic methods, compounds **5b** and **5k** additionally by X-ray structure analysis. Both compounds share common characteristics in the solid state: the aryl moiety in the 5-position of the dihydropyrrole ring is nearly coplanar to the dihydropyrrole ring itself, the iminic double bond is *Z* configured and the aryl substituent at the imine nitrogen atom is twisted out of plane (Figure 3). This is illustrated by the corresponding dihedral angles along the S–C–C–N–C–N–C_{ipso}–C_{ortho} backbone of **5b** (–18.66, 177.16, 167.58, –3.63 and –64.12°) and the dihedral angles along the C_{ortho}–C_{ipso}–C–N–C–N–C_{ipso}–C_{ortho} backbone of **5k** (from the 5-aryl substituent to the aryl moiety at the imine nitrogen; –9.61, 177.57, 164.32, 7.18 and 34.99°).

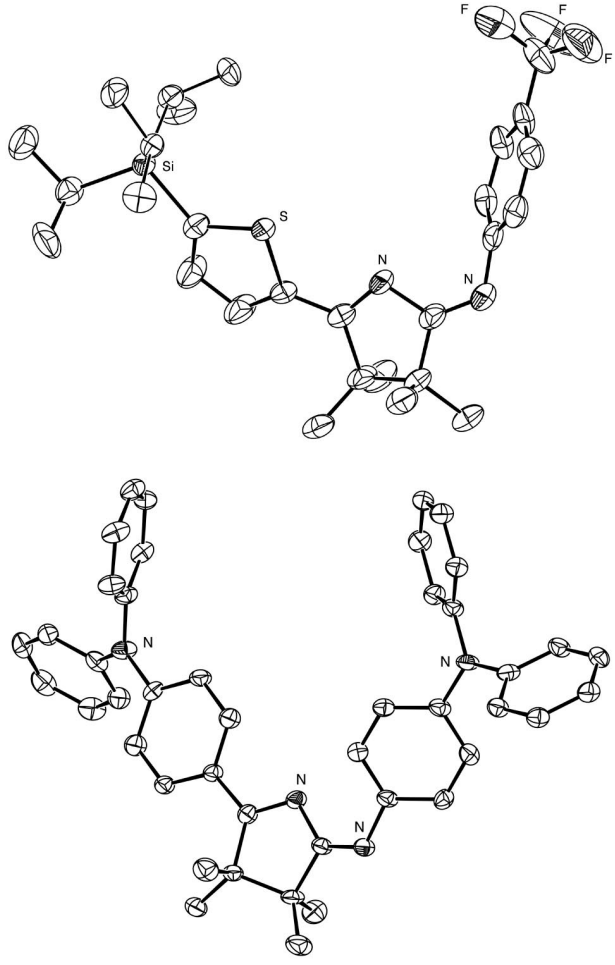
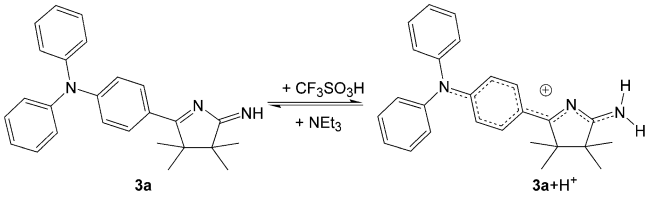


Figure 3. Molecular structures of **5b** (top) and **5k** (bottom) in the crystalline state as obtained by X-ray diffraction (PLATON plots,[14] hydrogen atoms omitted for clarity).

The UV/Vis spectra show clear indications of extended π–π* conjugation of the aryl substituents in the 5-position and the dihydropyrrole moiety. The longest wavelength absorptions range from 374 to 462 nm for **5b** and **7d**, respec-

tively, depending on the size and electronic properties of the aryl substituents and the overall extent of the conjugated system, resulting in intense yellow to red hues. In the case of derivatives of **5** and **7** with larger aryl groups in the 5-position, such as pyrenyl or 4-(*N*,*N*-diphenylamino)phenyl moieties, the compounds show a significant colour change upon treatment with Brønsted or Lewis acids (Scheme 6, Figure 4). Figure 4 shows the colour change in a THF solution of **3a** upon addition of trifluoromethanesulfonic acid and a corresponding series of UV/Vis spectra recorded with increasing amounts of the acid. Quantitative evaluation of these spectra allows the pK_B value of the protonation reaction to be determined as roughly –4.5, thus underlining the basicity of the dihydropyrrolimines. The colour change is fully reversible by addition of a base, such as triethylamine. A crystal structure of a hydro iodide of a related 5-amino-dihydropyrrolimine obtained by Marihart[12] shows protonation at the exocyclic imino nitrogen atom. In the case of a 5-aryldihydropyrrolimine, this could lead to structure **3**+H$^+$, in which the positive charge is delocalised along the whole backbone of the molecule, and which bears similarities to the well-known cyanine dyes. This interpretation is well supported by quantum chemical DFT calculations [B3LYP/6-311+G(2d,p)],[22] which give a HOMO/LUMO gap of 3.56 (**3a**) and 3.37 eV (**3b**) for the nonprotonated species, but a much smaller gap of 2.75 eV (**3a**+H$^+$) and 2.53 eV (**3b**+H$^+$) for the *N*-protonated forms.

Compounds **3a** and **3b** and their *N*-silylated derivatives **2c** and **2e** are fluorescent under irradiation with UV light. In the fluorescence spectrum of **3a**, a single emission band with a maximum at 478 nm is visible (Figure 5, top). The Stokes shift is 6034 cm^{-1} (107 nm). The absorption spectrum of pyrenyl-substituted compound **3b** is very much similar to the corresponding spectrum of pyrene.[23] The emission spectrum, in contrast, differs significantly: Whereas the less-intense and sharp bands at 383 and 397 nm can be contributed to emissions of the pyrene moiety, the strong band with a maximum at 432 nm and a shoulder at roughly 450 nm seem to be the result of the influence of the DHPI substituent (Figure 5, bottom). The Stokes shift between the last sharp absorption band and the first emission band – both associated to the pyrene moiety – is 3049 cm^{-1} (40 nm). In the *N*-arylated derivatives of these compounds the excitation necessary for fluorescence appears to be relaxed on nonradiative pathways, probably by rotation of the highly flexible aryl moiety at the imino function.



Scheme 6.

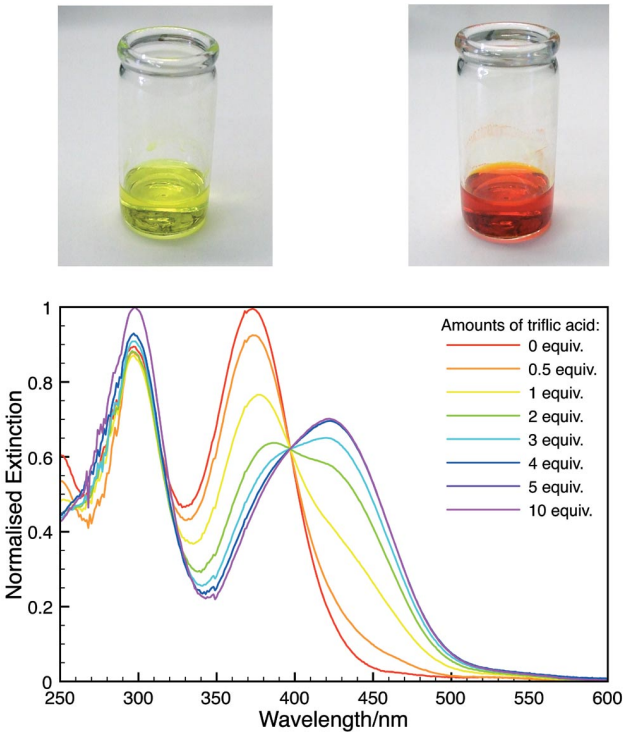


Figure 4. Colour change in a THF solution of **3a** upon addition of trifluoromethanesulfonic acid.

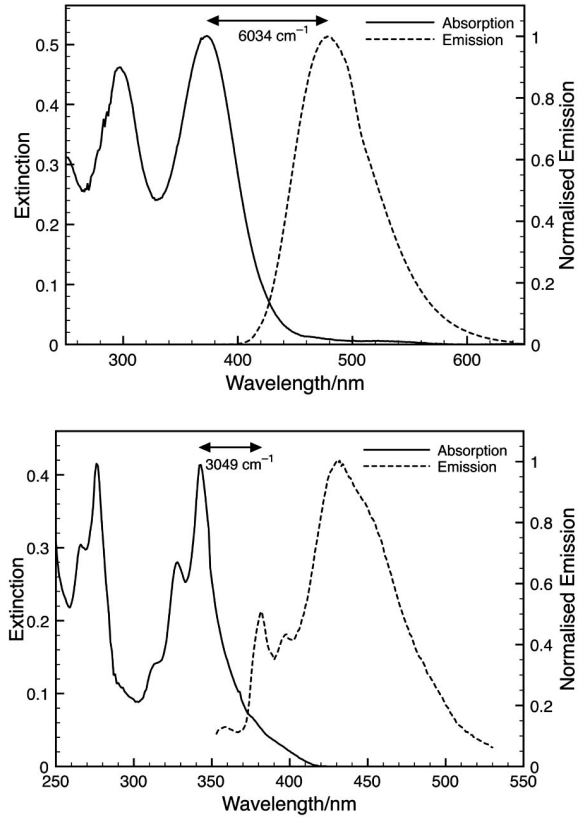


Figure 5. Absorption and emission spectra of **3a** (top) and **3b** (bottom) (fluorescence spectra: THF, $c = 10^{-6}$ M).

Conclusions

We have described the synthesis of 5-aryl-3,4-dihydropyrrol-2-imines by reaction of aryllithium species with 2,2,3,3-tetramethylsuccinonitrile **1**. Trapping lithiated intermediate **2**-Li with chlorotrimethylsilane yields *N*-silylated compounds **2a**–**e**, whereas aqueous workup gives unprotected derivatives **3a**,**b**. *N*-Silylated compounds **2** were employed as nucleophiles in palladium-catalysed cross-coupling reactions to obtain *N*-arylated compounds **5** and the corresponding bis-armed derivatives **7**. Conformation and configuration in the solid state were determined by X-ray diffraction studies of **3b**, **5b** and **5k**.

The optical properties of the obtained products with the longest wavelength absorptions of up to 462 nm for branched compound **7d** are regarded as clear indications of π–π* conjugation between the aryl groups and the planarised azapolyene substructure. Derivatives with large conjugated aryl substituents in the 5-position react to Brønsted and Lewis acids with a substantial colour change. Derivatives that are not *N*-arylated, **2c**,**e** and **3a**,**b**, in addition show intense fluorescence with Stokes shifts of 6034 and 3049 cm^{-1} for **3a** and **3b**, respectively.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC. ^1H NMR: Bruker WM 300 (300.13 MHz), JEOL AL-400 (399.65 MHz), Bruker AMX 400 (400.13 MHz), Varian INOVA 500 (499.8 MHz) and Varian Unity 600 (599.86 MHz); internal reference tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), JEOL AL-400 (100.40 MHz), Bruker AMX 400 (100.61 MHz), Varian INOVA 500 (125.7 MHz) and Varian Unity 600 (150.84 MHz); internal reference solvent. MS-ESI-EM: Bruker MicroTOF. UV/Vis: Shimadzu UV-3150, Varian Cary 1 Bio. Fluorescence: Aminco-Bowman Series 2. CHN elemental analysis: Elementar Vario El III. Melting points are uncorrected. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum–syringe technique) in glassware that had been thoroughly dried by repeated heating under an atmosphere of argon and subsequent evacuation. Column chromatography: Silica gel Merck 60 (0.040–0.063 mm). TLC: Merck silica gel plates (silica gel 60 F254); detection with UV light.

General Procedure for the Synthesis of Compounds 2a–e: The aryl halide (10.0 mmol) was dissolved in anhydrous THF (10.0 mL) in a Schlenk flask that had been dried and then flushed with argon. The solution was cooled down to –78 °C and *n*-butyllithium (1.6 M in *n*-hexane, 6.9 mL, 11.0 mmol) was added. After stirring for 1 h at –78 °C, 2,2,3,3-tetramethylsuccinonitrile (**1**; 1.50 g, 11.0 mmol) dissolved in anhydrous THF (10.0 mL) was slowly added. The reaction mixture was stirred at –78 °C for 30 min, warmed to 0 °C and stirred for an additional 30 min. Then the solution was cooled down to –78 °C again and chlorotrimethylsilane (1.20 g, 1.4 mL, 11.0 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The crude product was obtained by removing the solvent under vacuum and subsequently purified by Kugelrohr distillation.

3,3,4,4-Tetramethyl-5-[5-(triisopropylsilyl)thiophen-2-yl]-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imine (2a): From 2-bromo-5-(triisopropylsilyl)thiophene (1.60 g, 5.0 mmol), of *n*-butyllithium (3.13 mL, 5.0 mmol), **1** (0.68 g, 5.0 mmol) and chlorotrimethylsilane (0.7 mL, 0.60 g, 5.5 mmol). Yield: 1.66 g (3.7 mmol, 74%), yellow oil, b.p. 156 °C (0.08 Torr). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.26 (s, 9 H, $SiCH_3$), 1.05 (s, 6 H, CH_3), 1.12 (d, ^3J = 7.5 Hz, 18 H, *i*PrCH_3), 1.31 (s, 6 H), 7.28 (d, ^3J = 3.7 Hz, 2 H), 7.83 (d, ^3J = 3.7 Hz, 2 H, $CH_{thioph.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 1.4 ($SiCH_3$), 2.1, 11.9 (SiCH), 18.7 [$SiCH(CH_3)_2$], 22.9, 23.7 (CH_3), 50.1, 52.6 ($C_{quat.}$), 125.2, 132.1, 136.4 ($C_{arom.}$), 149.0 (C_{ipso}), 183.4, 184.8 (C=N) ppm. IR: $\tilde{\nu}$ = 2965 (m), 2945 (m), 2893 (w), 2866 (m), 2361 (w), 2342 (w), 1693 (s), 1543 (vs), 1506 (m), 1499 (m), 1460 (m), 1425 (w), 1391 (w), 1375 (w), 1368 (m), 1327 (w), 1281 (w), 1265 (w), 1242 (s), 1200 (w), 1161 (w), 1146 (w), 1090 (m), 1074 (m), 1016 (m), 999 (m), 980 (m), 907 (m), 881 (vs), 837 (s), 829 (vs), 804 (m), 762 (m), 750 (m), 727 (w), 710 (w), 685 (s), 656 (vs), 642 (vs), 633 (vs), 606 (m), 596 (m), 584 (m), 565 (s) cm^{-1}. MS-ESI-EM: calcd. for $[M - TMS + H]^+$ 377.2441; found 377.2436. $C_{24}H_{44}N_2SSi_2$ (448.86): calcd. C 64.22, H 9.88, N 6.24; found C 64.01, H 9.86, N 6.27.

***N*-Phenyl-*N*-{4-[3,3,4,4-tetramethyl-5-(trimethylsilylimino)-4,5-dihydro-3*H*-pyrrol-2-yl]phenyl}benzenamine (2b):** From of 4-bromo-*N*,*N*-diphenylbenzenamine (3.24 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol), **1** (1.50 g, 11.0 mmol) and chlorotrimethylsilane (1.4 mL, 1.20 g, 11.0 mmol). Yield: 2.60 g (5.7 mmol, 57%), bright yellow glasslike solid, b.p. 221 °C (2.8×10^{-2} mbar). ^1H NMR (399.65 MHz, $CDCl_3$): δ = 0.25 (s, 9 H, $SiCH_3$), 1.04 (s, 6 H, CH_3), 1.28 (s, 6 H), 7.02 (d, ^3J = 8.8 Hz, 2 H), 7.10–7.18 (m, 7 H), 7.30–7.34 (m, 4 H), 7.91 (d, ^3J = 8.8 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.40 MHz, $CDCl_3$): δ = 1.4 ($SiCH_3$), 22.7, 23.7 (CH_3), 50.7, 52.6 ($C_{quat.}$), 120.4, 124.5, 125.9, 129.7, 130.9 ($C_{arom.}$), 146.7, 151.0 (C_{ipso}), 184.0, 190.0 (C=N) ppm. IR: $\tilde{\nu}$ = 3061 (w), 3038 (w), 2970 (w), 2930 (w), 2361 (w), 2340 (vw), 1663 (m), 1609 (w), 1587 (s), 1564 (m), 1524 (m), 1508 (s), 1489 (s), 1450 (w), 1422 (m), 1395 (m), 1379 (w), 1369 (w), 1325 (s), 1294 (s), 1285 (s), 1271 (s), 1248 (m), 1219 (m), 1192 (m), 1182 (m), 1161 (w), 1144 (m), 1123 (m), 1096 (m), 1074 (m), 1028 (w), 968 (w), 889 (s), 833 (s), 748 (s), 718 (w), 694 (vs), 664 (w), 637 (w), 621 (m), 569 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M - TMS + H]^+$ 382.2278; found 382.2278. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}\,cm^{-1}$) = 371 (26954, 24000), 296 (33783, 19600) nm.

5-Biphenyl-3,3,4,4-tetramethyl-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imine (2c): From 4-bromobiphenyl (2.33 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mol), **1** (1.50 g, 11.0 mmol) and chlorotrimethylsilane (1.4 mL, 1.20 g, 11.0 mmol). Yield: 1.79 g (4.9 mmol, 49%), yellow solid, b.p. 156 °C (2.5×10^{-2} mbar). ^1H NMR (300.14 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiCH_3$), 1.00 (s, 6 H, CH_3), 1.23 (s, 6 H, CH_3), 7.31–7.42 (m, 2 H), 7.55–7.61 (m, 5 H), 8.00 (d, ^3J = 8.4 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 1.4 ($SiCH_3$), 22.7 (CH_3), 23.4 (CH_3), 50.6 ($C_{quat.}$), 52.9 ($C_{quat.}$), 127.2, 127.2, 127.3, 128.1, 129.0, 129.7, 129.9 ($C_{arom.}$), 132.9, 140.2, 144.1 (C_{ipso}), 183.3, 190.8 (C=N) ppm. IR: $\tilde{\nu}$ = 3032 (vw), 2974 (m), 2926 (w), 2903 (w), 2872 (vw), 2361 (vw), 2326 (vw), 1707 (s), 1672 (w), 1607 (w), 1566 (m), 1533 (s), 1487 (w), 1472 (w), 1460 (w), 1447 (w), 1404 (w), 1391 (m), 1377 (w), 1369 (w), 1358 (w), 1314 (m), 1302 (m), 1285 (w), 1267 (m), 1238 (m), 1196 (w), 1165 (w), 1144 (m), 1123 (w), 1084 (s), 1040 (w), 1024 (w), 1009 (m), 997 (w), 926 (w), 895 (s), 847 (s), 826 (vs), 770 (s), 750 (m), 737 (vs), 714 (m), 694 (s), 658 (w), 635 (w), 627 (w), 604 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M - TMS + H]^+$ calcd. 291.1856; found 291.1851.

3,3,4,4-Tetramethyl-5-(pyren-1-yl)-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imine (2d): From 1-bromopyrene (385 mg, 1.4 mmol), *n*-butyllithium (0.94 mL, 1.4 mmol), **1** (205 mg, 1.5 mmol) and chlorotrimethylsilane (0.2 mL, 164 mg, 1.5 mmol). Yield: 357 mg

(0.9 mmol, 62%), yellow crystalline solid, b.p. 211 °C (1.9×10^{-2} mbar). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.44 (s, 9 H, $SiCH_3$), 1.23 (s, 6 H, CH_3), 1.38 (s, 6 H, CH_3), 7.99–8.26 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 2.1 ($SiCH_3$), 22.7 (CH_3), 23.4 (CH_3), 48.6 ($C_{quat.}$), 54.7 ($C_{quat.}$), 128.5, 128.6, 128.7, 129.0, 129.3, 129.4, 129.9 ($C_{arom.}$), 131.8 (C_{ipso}), 186.4, 192.3 (C=N) ppm. IR: $\tilde{\nu}$ = 3211 (w), 3038 (w), 2967 (m), 2897 (w), 2868 (w), 2361 (w), 2344 (w), 1717 (w), 1686 (m), 1676 (m), 1653 (w), 1599 (w), 1572 (s), 1539 (w), 1508 (w), 1497 (w), 1489 (w), 1476 (w), 1458 (m), 1445 (w), 1418 (w), 1391 (m), 1375 (w), 1366 (m), 1327 (m), 1304 (w), 1265 (m), 1244 (m), 1221 (w), 1196 (w), 1180 (w), 1167 (w), 1159 (w), 1152 (w), 1138 (w), 1124 (w), 1109 (m), 1086 (s), 1051 (m), 1009 (w), 959 (w), 930 (w), 885 (s), 843 (vs), 833 (vs), 772 (m), 756 (s), 746 (m), 735 (m), 721 (m), 708 (s), 691 (m), 681 (m), 664 (w), 640 (m), 617 (w), 606 (w), 588 (w), 579 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M - TMS + H]^+$ 339.1851; found 339.1851.

3,3,4,4-Tetramethyl-5-{5-[3,3,4,4-tetramethyl-5-(trimethylsilylimino)-4,5-dihydro-3*H*-pyrrol-2-yl]thiophen-2-yl}-*N*-(trimethylsilyl)-3,4-dihydropyrrol-2-imine (2e): From 2-bromothiophene (1.81 g, 7.5 mmol), *n*-butyllithium (9.4 mL, 15.0 mmol), **1** (2.04 g, 15 mmol) and chlorotrimethylsilane (1.9 mL, 1.63 g, 15 mmol). Yield: 0.96 g (1.6 mmol, 26%), yellow solid, b.p. 196 °C (0.12 Torr). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.25 (s, 18 H, $SiCH_3$), 1.05 (s, 10 H), 1.18 (s, 2 H), 1.30 (s, 10 H), 1.34 (s, 2 H, CH_3), 7.23 (s, 1.5 H), 7.77 (s, 0.5 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 1.3 ($SiCH_3$), 22.7 (CH_3), 23.4 (CH_3), 50.3 ($C_{quat.}$), 52.6 ($C_{quat.}$), 131.6 ($C_{arom.}$), 143.3 (C_{ipso}), 182.4, 184.5 (C=N) ppm. IR: $\tilde{\nu}$ = 3262 (w), 3215 (w), 2976 (m), 2932 (w), 2872 (w), 2361 (w), 2342 (w), 1693 (w), 1665 (s), 1641 (w), 1541 (vs), 1516 (m), 1474 (m), 1462 (m), 1447 (m), 1395 (m), 1379 (m), 1369 (m), 1342 (m), 1317 (vs), 1277 (w), 1248 (m), 1225 (m), 1200 (m), 1144 (s), 1123 (m), 1078 (m), 1049 (s), 1018 (w), 968 (m), 957 (m), 937 (m), 918 (m), 903 (m), 885 (m), 839 (m), 820 (s), 812 (s), 764 (m), 754 (w), 739 (m), 708 (m), 692 (w), 667 (w), 656 (w), 642 (w), 617 (w), 596 (w), 579 (w), 571 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M - TMS + H]^+$ 357.2107; found 357.2103.

General Procedure for the Synthesis of Compounds 3: The aryl halide (10.0 mmol) was dissolved in anhydrous THF (10 mL) in a Schlenk flask that had been dried and then flushed with argon. The solution was cooled down to –78 °C and *n*-butyllithium (1.6 M in *n*-hexane, 7.8 mL, 11.0 mmol) was added. After stirring for 1 h at –78 °C, 2,2,3,3-tetramethylsuccinonitrile (**1**; 1.50 g, 11.0 mmol) dissolved in anhydrous THF (10 mL) was slowly added. The reaction mixture was stirred at –78 °C for 30 min, warmed to room temperature and stirred for an additional 2 h. Then, methanol (20 mL) and water (20 mL) were added. The organic layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were then dried with magnesium sulfate, before the solvents were removed in vacuo. The obtained crude product was purified by column chromatography (pentane/ethyl acetate, 2:1 + 5% triethylamine).

***N*-[4-(5-Imino-3,3,4,4-tetramethyl-4,5-dihydro-3*H*-pyrrol-2-yl)-phenyl]-*N*-phenylbenzenamine (3a):** From 4-bromo-*N*,*N*-diphenylbenzenamine (3.24 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol) and **1** (1.50 g 11.0 mmol). Yield: 0.89 g (2.3 mmol, 23%), yellow resin, m.p. 104 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.14 (s, 6 H, CH_3), 1.31 (s, 6 H), 7.02 (d, ^3J = 9.0 Hz, 2 H), 7.10–7.17 (m, 7 H), 7.28–7.34 (m, 4 H), 7.86 (d, ^3J = 8.4 Hz, 2 H, $CH_{arom.}$), 8.56 (br. s, 1 H, NH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.7, 23.4 (CH_3), 54.1, 60.5 ($C_{quat.}$), 120.3, 124.6, 125.3, 125.9, 129.7, 130.7 ($C_{arom.}$), 146.6, 151.4 (C_{ipso}) ppm. IR: $\tilde{\nu}$ = 3063 (w), 3036 (w), 2968 (w), 2926 (w), 2868 (w), 2361 (w), 1666 (m), 1639 (m), 1587 (s), 1566 (m), 1530 (m), 1487 (s), 1450 (m), 1393 (m), 1377 (m), 1368 (m), 1325 (s), 1314 (s), 1277 (s), 1221 (m), 1192 (m), 1179 (m), 1142 (m), 1117 (m), 1074 (m), 1051 (m), 1030 (m), 997 (w), 961 (m), 920 (w), 891 (m), 839 (m), 797 (w), 752 (s), 694 (vs), 669 (m), 637 (m), 623 (m), 563 (m), 554 (m), 532 (m), 523 (s), 517 (s), 511 (s) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 382.2278; found 382.2295. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, M^{-1}cm^{-1}) = 371 (26954, 17800), 297 (33670, 14200) nm. Fluorescence (THF, $c = 10^{-6}$ M): λ ($\tilde{\nu}$, cm^{-1}) = 478 (20921) nm.

3,3,4,4-Tetramethyl-5-(pyren-1-yl)-3,4-dihydropyrrol-2-imine (3b): From 1-bromopyrene (1.00 g, 3.6 mmol), *n*-butyllithium (2.40 mL, 4.0 mmol) and **1** (0.53 g, 4.0 mmol). Yield: 0.58 g (2.7 mmol, 75%), yellow crystalline solid, m.p. 193 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.21 (s, 6 H, CH_3), 1.38 (s, 6 H, CH_3), 7.97–8.25 (m, 9 H, $CH_{arom.}$), 9.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.5 (CH_3), 23.2 (CH_3), 47.3 ($C_{quat.}$), 57.2 ($C_{quat.}$), 123.7, 124.4, 124.4, 124.7, 125.6, 125.9, 126.4, 127.1, 128.4, 128.7, 129.2 ($C_{arom.}$), 130.6, 131.1, 132.1 (C_{ipso}), 187.3, 195.1 (C=N) ppm. IR: $\tilde{\nu}$ = 3211 (w), 3042 (w), 2967 (m), 2922 (m), 2868 (w), 2851 (w), 1674 (m), 1578 (s), 1560 (m), 1539 (m), 1506 (w), 1487 (w), 1476 (m), 1458 (m), 1437 (w), 1393 (m), 1377 (m), 1368 (m), 1325 (s), 1290 (w), 1273 (m), 1244 (m), 1219 (m), 1192 (m), 1180 (w), 1157 (w), 1138 (w), 1107 (m), 1076 (m), 1049 (m), 957 (m), 926 (m), 847 (vs), 835 (s), 822 (m), 808 (s), 799 (m), 772 (m), 760 (m), 721 (m), 708 (m), 681 (m), 660 (w), 644 (m), 577 (m), 536 (m), 509 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 339.1851; found 339.1848. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, M^{-1}cm^{-1}) = 343 (29155, 72300), 328 (30488, 49000), 314 (sh.; 31847, 24700), 276 (36232, 72600), 266 (37594, 53300) nm. Fluorescence (THF, $c = 10^{-6}$ M): λ ($\tilde{\nu}$, cm^{-1}) = 383 (26110), 397 (25189), 432 (23148), 450 (sh., 22222) nm.

X-ray Crystal Structure Analysis of 3b:[24,25] Formula $C_{24}H_{22}N_2$, M = 338.44, colourless crystal 0.25 × 0.15 × 0.10 mm, a = 8.9136(4) Å, b = 9.6706(4) Å, c = 20.9122(9) Å, β = 94.607(3)°, V = 1797.80(13) Å^3, $\rho_{calcd.}$ = 1.251 g cm^{-3}, μ = 0.561 mm^{-1}, empirical absorption correction ($0.873 \leq T \leq 0.946$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 14250 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3169 independent (R_{int} = 0.046) and 2776 observed reflections [$I \geq 2\sigma(I)$], 244 refined parameters, R = 0.051, wR^2 = 0.140, max. (min.) residual electron density 0.41 (–0.26) e Å^{-3}, hydrogen atom at N2 from difference fourier map, others calculated and refined as riding atoms.

General Procedure for the Palladium-Catalysed Cross-Coupling Reactions with *N*-Silylated Dihydropyrrolimines: In a dried and argon-flushed Schlenk tube, palladium acetate (9.0 mg, 4 mol-%), *rac*-BINAP (49.8 mg, 8 mol-%), potassium *tert*-butoxide (145.9 mg, 1.3 equiv.), aryl halide **4** or **6** (10 mmol) and *N*-silylated dihydropyrrolimine **2** (1.1 equiv. per coupling site) were dissolved in dried toluene (5 mL). The reaction mixture was heated at reflux for 6 h before being diluted with *n*-pentane (10 mL) and filtered through Celite, which was washed with more *n*-pentane (30 mL). The solvent was removed under vacuum, and the crude product was purified by column chromatography.

***N*-{3,3,4,4-Tetramethyl-5-[5-(triisopropylsilyl)thiophen-2-yl]-3,4-dihydropyrrol-2-ylidene}-4-(trifluoromethyl)benzenamine (5b):** From **4a** (112.5 mg, 0.5 mmol) and **2a** (246.9 mg, 0.6 mmol). Purification by column chromatography (hexane/ethyl acetate, 4:1). Yield: 156.0 mg (0.3 mmol, 57%), yellow crystalline solid, m.p. 124 °C. ^{1}H NMR (399.65 MHz, $CDCl_3$): δ = 1.09 (d, ^3J = 7.4 Hz, 18 H, *i*PrCH$_3$), 1.24 (s, 1 H, CH_3), 1.35 (sept., ^3J = 7.3 Hz, 3 H, *i*PrCH),

1.41 (s, 6 H, CH_3), 7.18 (d, ^3J = 8.4 Hz, 2 H), 7.28 (d, ^3J = 3.8 Hz, 2 H), 7.55 (d, ^3J = 8.3 Hz, 2 H), 7.87 (d, ^3J = 3.7 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 11.9 (SiCH), 18.6 [$SiCH(CH_3)_2$], 23.0, 23.8 (CH_3), 50.0, 53.6 ($C_{quat.}$), 123.3, 125.4, 125.5, 125.6, 133.2, 136.6 ($C_{arom.}$), 142.0, 145.3, 152.8 (C_{ipso}), 178.2, 187.9 (C=N) ppm. IR: $\tilde{\nu}$ = 2968 (w), 2945 (m), 2891 (w), 2868 (w), 2841 (w), 1676 (m), 1611 (m), 1580 (w), 1533 (s), 1503 (m), 1474 (m), 1460 (m), 1425 (w), 1393 (w), 1377 (w), 1369 (w), 1323 (vs), 1287 (m), 1252 (w), 1229 (m), 1175 (w), 1157 (s), 1113 (vs), 1103 (vs), 1063 (vs), 1015 (m), 997 (s), 980 (m), 959 (w), 939 (w), 932 (w), 899 (m), 883 (m), 849 (m), 802 (s), 748 (w), 714 (w), 685 (m), 664 (m), 648 (s), 604 (m), 594 (w), 581 (m), 569 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 521.2628; found 521.2615. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 380 (sh.; 26315, 4700), 332 (30166, 12900) nm. $C_{28}H_{39}F_3N_2SSi$ (520.77): calcd. C 64.58, H 7.55, N 5.38; found C 64.35, H 7.47, N 5.16.

X-ray Crystal Structure Analysis of 5b:[24,26] Formula $C_{28}H_{39}F_3N_2SSi$, M = 520.76, yellow crystal 0.15 × 0.15 × 0.15 mm, a = 10.984(3) Å, b = 22.860(5) Å, c = 12.422(3) Å, β = 113.556(1)°, V = 2859.3(11) $Å^3$, $\rho_{calcd.}$ = 1.210 $g cm^{-3}$, μ = 0.193 mm^{-1}, empirical absorption correction ($0.9716 \leq T \leq 0.9809$), Z = 4, monoclinic, space group $P2_1/a$ (No. 14), λ = 0.71073 Å, T = 123(2) K, ω scans, 19210 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.60 $Å^{-1}$, 5030 independent (R_{int} = 0.063) and 4057 observed reflections [$I \geq 2\sigma(I)$], 386 refined parameters, R = 0.079, wR^2 = 0.180, max. (min.) residual electron density 0.59 (–0.40) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

***N*-(5-Biphenyl)-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene-4-(trifluoromethyl)benzenamine (5c):** From **4a** (225.0 mg, 1.0 mmol) and **2c** (398.8 mg, 1.1 mmol). Purification by column chromatography (pentane/ethyl acetate, 2:1 + 5% triethylamine). Yield: 269 mg (0.6 mmol, 62%), yellow solid, m.p. 182 °C. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.27 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 7.17 (d, ^3J = 8.0 Hz, 2 H), 7.34–7.42 (m, 4 H), 7.56–7.67 (m, 6 H), 8.02 (d, ^3J = 8.8 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.8, 23.4 (CH_3), 50.2, 53.9 ($C_{quat.}$), 122.7, 125.5, 125.5, 127.2, 127.2, 128.2, 129.1, 130.0, 132.2 ($C_{arom.}$), 139.9, 144.8 (C_{ipso}), 177.9, 194.3 (C=N) ppm. IR: $\tilde{\nu}$ = 3028 (vw), 2988 (w), 2934 (vw), 2874 (vw), 2361 (w), 2338 (w), 1738 (w), 1717 (w), 1659 (m), 1609 (m), 1578 (w), 1560 (m), 1520 (s), 1485 (w), 1476 (m), 1460 (w), 1447 (w), 1406 (w), 1398 (w), 1381 (m), 1371 (m), 1323 (vs), 1310 (s), 1285 (m), 1246 (w), 1231 (m), 1190 (w), 1173 (s), 1163 (s), 1146 (m), 1119 (vs), 1099 (vs), 1063 (vs), 1007 (m), 980 (w), 955 (w), 930 (w), 914 (w), 876 (w), 851 (s), 839 (m), 810 (m), 785 (w), 772 (m), 756 (m), 745 (s), 698 (s), 671 (m), 660 (w), 642 (w), 635 (w), 604 (m), 594 (m), 563 (m), 554 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 435.2043; found 435.2052. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 374 (sh.; 26738, 15100), 312 (32051, 45800) nm. $C_{27}H_{25}F_3N_2$ (434.50): calcd. C 74.64, H 5.80, N 6.45; found C 74.53, H 5.89, N 6.24.

***N*-[3,3,4,4-Tetramethyl-5-(pyren-1-yl)-3,4-dihydropyrrol-2-ylidene]-4-(trifluoromethyl)benzenamine (5d):** From **4a** (126.3 mg, 0.6 mmol) and **2d** (298.0 mg, 0.6 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1). Yield: 179.0 mg (0.4 mmol, 65%), bright yellow crystalline solid, m.p. 190 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.30 (s, 6 H, CH_3), 1.46 (s, 6 H, CH_3), 7.20 (d, ^3J = 8.2 Hz, 2 H), 7.54 (d, ^3J = 8.2 Hz, 2 H), 7.96–8.23 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.8, 23.5 (CH_3), 48.9, 56.8 ($C_{quat.}$), 122.3, 123.8, 125.0 (q, CF_3), 125.8, 125.9, 125.9, 126.1, 126.5, 127.2, 128.6, 129.0, 129.5, 130.7, 131.3, 132.4 ($C_{arom.}$), 152.8, 152.8 (C_{ipso}), 178.1, 198.2 (C=N) ppm. IR: $\tilde{\nu}$ = 3048 (vw), 2968 (w), 2932 (w), 2913 (vw), 2872 (vw), 1670 (m), 1609 (m), 1582 (w), 1562 (m), 1547 (m), 1522 (m), 1506 (m), 1487 (w), 1474 (w), 1458 (w), 1447 (w), 1395 (m), 1381 (m), 1369 (w), 1319 (vs), 1275 (m), 1240 (w), 1229 (m), 1200 (w), 1157 (s), 1140 (m), 1115 (vs), 1103 (vs), 1063 (vs), 1013 (m), 961 (w), 926 (w), 907 (w), 870 (m), 847 (vs), 835 (s), 820 (m), 800 (s), 760 (m), 727 (m), 708 (m), 694 (w), 681 (w), 656 (w), 621 (w), 613 (w), 590 (m), 567 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 483.2048; found 483.2041. $C_{31}H_{25}F_3N_2$ (482.54): calcd. C 77.16, H 5.22, N 5.81; found C 77.06, H 5.13, N 5.68.

***N*-{5-[4-(Diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}-4-(trifluoromethyl)benzenamine (5e):** From **4a** (112.5 mg, 0.5 mmol) and **2b** (249.5 mg, 0.6 mmol). Purification by column chromatography (hexane/ethyl acetate, 4:1). Yield: 197.0 mg (0.4 mmol, 67%), yellow crystalline solid, m.p. 131 °C. ^1H NMR (399.65 MHz, $CDCl_3$): δ = 1.22 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3), 6.96 (d, ^3J = 8.9 Hz, 2 H), 7.11–7.15 (m, 9 H), 7.29–7.33 (m, 4 H), 7.52 (d, ^3J = 8.3 Hz, 2 H), 7.84 (d, ^3J = 9.0 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.40 MHz, $CDCl_3$): δ = 22.9, 23.7 (CH_3), 50.3, 53.5 ($C_{quat.}$), 119.9, 123.0, 124.8, 125.5 (q, CF_3), 126.1, 129.7, 131.3 ($C_{arom.}$), 146.5, 151.7 (C_{ipso}), 178.5, 193.3 (C=N) ppm. IR: $\tilde{\nu}$ = 3067 (vw), 2972 (vw), 2928 (vw), 2868 (vw), 2359 (vw), 2330 (vw), 1666 (m), 1657 (m), 1609 (m), 1589 (s), 1557 (m), 1512 (m), 1487 (s), 1452 (m), 1427 (m), 1395 (m), 1377 (vw), 1369 (vw), 1344 (m), 1319 (vs), 1283 (s), 1263 (m), 1248 (m), 1227 (m), 1194 (s), 1175 (m), 1161 (m), 1153 (m), 1134 (s), 1113 (vs), 1101 (vs), 1080 (m), 1063 (vs), 1026 (m), 1013 (m), 989 (vw), 982 (vw), 966 (vw), 955 (vw), 932 (vw), 880 (m), 851 (s), 831 (m), 808 (s), 783 (m), 756 (s), 698 (vs), 662 (m), 642 (m), 619 (m), 604 (vw), 594 (m), 557 (vw) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 526.2465; found 526.2463. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 395 (25349, 24100), 292 (34305, 13400) nm. $C_{33}H_{30}F_3N_3$ (525.61): calcd. C 75.41, H 5.75, N 7.99; found C 75.48, H 5.88, N 8.01.

4-Bromo-*N*-{5-[4-(diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}benzenamine (5f): From **4b** (424.5 mg, 1.5 mmol) and **2b** (748.6 mg, 1.7 mmol). Purification by column chromatography (hexane/ethyl acetate, 4:1). Yield: 587 mg (1.1 mmol, 72%), yellow crystalline solid, m.p. 152 °C. ^1H NMR (399.65 MHz, $CDCl_3$): δ = 1.20 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 6.97 (d, ^3J = 9.0 Hz, 2 H), 7.00 (d, ^3J = 8.6 Hz, 2 H) 7.11–7.16 (m, 6 H), 7.29–7.33 (m, 4 H), 7.37 (d, ^3J = 8.7 Hz, 2 H), 7.84 (d, ^3J = 9.0 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.40 MHz, $CDCl_3$): δ = 22.8, 23.7 (CH_3), 50.3, 53.4 ($C_{quat.}$), 116.7, 120.1, 124.8, 125.1, 125.6, 129.7, 131.2, 131.2 ($C_{arom.}$), 146.6, 149.0, 151.6 (C_{ipso}), 177.8, 192.7 (C=N) ppm. IR: $\tilde{\nu}$ = 3059 (w), 3036 (w), 2982 (w), 2930 (w), 2870 (w), 2357 (w), 2330 (vw), 1651 (m), 1609 (m), 1587 (s), 1560 (m), 1516 (m), 1503 (s), 1479 (vs), 1450 (m), 1422 (m), 1395 (m), 1373 (w), 1360 (w), 1314 (s), 1292 (s), 1279 (s), 1221 (m), 1190 (s), 1182 (s), 1171 (m), 1140 (s), 1117 (s), 1072 (s), 1026 (m), 1009 (m), 980 (w), 955 (w), 937 (w), 924 (m), 891 (w), 868 (w), 843 (s), 816 (m), 804 (m), 781 (w), 754 (s), 745 (m), 725 (w), 692 (vs), 673 (m), 660 (m), 648 (m), 633 (m), 623 (m), 615 (m), 600 (w), 586 (w), 561 (s) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 538.1681; found 538.1674. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 393 (25445, 29500), 292 (34247, 16400) nm. $C_{32}H_{30}BrN_3$ (536.50): calcd. C 71.64, H 5.64, N 7.83; found C 71.84, H 5.38, N 7.51.

2-Bromo-*N*-{5-[4-(diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}benzenamine (5g): From **4c** (282.9 mg, 1.0 mmol) and **2b** (498.0 mg, 1.1 mmol). Purification by column chromatography (hexane/ethyl acetate, 4:1). Yield: 391 mg (0.7 mmol, 73%), yellow solid, m.p. 125 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.27 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3), 6.87 (ddd, ^3J = 8.4 Hz, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1 H), 6.93 (d, ^3J

= 9.0 Hz, 2 H), 6.99 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1 H) 7.10–7.13 (m, 6 H), 7.19 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1 H) 7.25–7.31 (m, 5 H), 7.51 (dd, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 1 H), 7.80 (d, ^3J = 9.0 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.9, 23.7 (CH3), 50.1, 53.7 ($C_{quat.}$), 116.4, 120.1, 123.0, 124.1, 124.6, 125.6, 125.9, 127.4, 129.6, 129.7, 131.2, 132.4 ($C_{arom.}$), 146.5, 149.2, 151.4 (C_{ipso}), 178.4, 193.1 (C=N) ppm. IR: $\tilde{\nu}$ = 3059 (w), 2970 (w), 2928 (w), 2866 (w), 2359 (w), 2340 (vw), 2328 (vw), 1736 (w), 1668 (m), 1611 (m), 1589 (s), 1560 (m), 1503 (s), 1487 (vs), 1460 (s), 1425 (s), 1393 (m), 1377 (w), 1368 (m), 1341 (m), 1312 (s), 1302 (s), 1285 (s), 1221 (m), 1196 (s), 1184 (s), 1136 (s), 1115 (s), 1076 (m), 1042 (m), 1026 (m), 1003 (m), 991 (w), 976 (w), 962 (w), 928 (m), 901 (w), 876 (w), 839 (m), 824 (m), 814 (m), 781 (w), 760 (s), 746 (vs), 727 (m), 696 (vs), 675 (m), 665 (m), 652 (m), 640 (m), 627 (m), 617 (m), 604 (w), 586 (w), 575 (w), 563 (w), 554 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 538.1681; found 538.1670. $C_{32}H_{30}BrN_3$ (536.50): calcd. C 71.64, H 5.64, N 7.83; found C 72.01, H 5.76, N 7.48.

***N*-{5-[4-(Diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}-2,4,6-trimethylbenzenamine (5h):** From **4d** (199.1 mg, 1.0 mmol) and **2b** (498.0 mg, 1.1 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1). Yield: 182 mg (0.4 mmol, 36%), yellow-orange glass-like solid, m.p. 77 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.26 (s, 6 H, CH3), 1.34 (s, 6 H, CH_3), 2.04 (s, 6 H, *o*-CH_3), 2.23 (s, 3 H, *p*-CH_3), 6.79 (s, 2 H), 6.92 (d, ^3J = 9.0 Hz, 2 H), 7.07–7.12 (m, 6 H), 7.25–7.30 (m, 4 H), 7.74 (d, ^3J = 9.0 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 18.5, 20.9 (mesitylen-CH_3), 23.0, 23.6 (CH_3), 49.8, 53.4 ($C_{quat.}$), 120.3, 124.5, 125.8, 127.1, 128.2, 129.7, 131.0, 131.3 ($C_{arom.}$), 145.6, 146.7, 151.2 (C_{ipso}), 176.1, 192.1 (C=N) ppm. IR: $\tilde{\nu}$ = 2968 (w), 2911 (w), 2866 (w), 2361 (w), 2342 (w), 2326 (w), 1676 (m), 1609 (w), 1587 (s), 1560 (m), 1520 (m), 1504 (s), 1487 (vs), 1450 (m), 1422 (m), 1393 (m), 1369 (w), 1333 (m), 1310 (s), 1296 (s), 1279 (vs), 1219 (m), 1192 (m), 1182 (m), 1153 (m), 1142 (s), 1117 (s), 1076 (w), 1030 (w), 1011 (w), 980 (w), 961 (w), 924 (w), 899 (w), 847 (m), 752 (s), 733 (w), 716 (w), 694 (vs), 667 (w), 654 (w), 637 (w), 621 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 500.3060; found 500.3060. $C_{35}H_{37}N_3$ (499.69): calcd. C 84.13, H 7.46, N 8.41; found C 84.42, H 7.62, N 8.16.

***N*-{5-[4-(Diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}-4-phenylbenzenamine (5j):** From **4f** (116.6 mg, 0.5 mmol) and **2b** (249.5 mg, 0.6 mmol). Purification by column chromatography (hexane/ethyl acetate, 4:1). Yield: 152 mg (0.3 mmol, 52%), yellow-brown glass-like solid, m.p. 89 °C. ^1H NMR (399.65 MHz, $CDCl_3$): δ = 1.22 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 6.95 (d, ^3J = 8.9 Hz, 2 H), 7.07–7.13 (m, 7 H), 7.20–7.29 (m, 8 H), 7.29–7.33 (m, 4 H), 7.37 (t, ^3J = 7.6 Hz, 2 H), 7.52 (d, ^3J = 8.4 Hz, 2 H), 7.58 (d, ^3J = 7.2 Hz, 2 H), 7.85 (d, ^3J = 8.9 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.40 MHz, $CDCl_3$): δ = 22.8, 23.6 (CH_3), 50.3, 53.2 ($C_{quat.}$), 120.1, 123.8, 124.6, 125.7, 125.9, 126.0,126.7, 127.0, 127.7, 128.1, 128.7, 129.7, 131.1, ($C_{arom.}$), 136.4, 141.4, 146.5, 149.1, 151.3 (C_{ipso}), 177.3, 192.2 (C=N) ppm. IR: $\tilde{\nu}$ = 3057 (w), 3030 (w), 2970 (w), 2926 (w), 2868 (vw), 1665 (w), 1587 (s), 1564 (m), 1481 (s), 1450 (m), 1422 (m), 1393 (m), 1377 (w), 1369 (w), 1310 (s), 1296 (s), 1277 (s), 1227 (m), 1192 (m), 1182 (m), 1140 (m), 1117 (s), 1076 (m), 1028 (w), 1007 (w), 926 (w), 872 (w), 845 (m), 810 (m), 754 (s), 731 (m), 716 (w), 694 (vs), 669 (m), 640 (w), 617 (m), 592 (w), 561 (w) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 534.2904; found 534.2886. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 390 (25641, 27300), 291 (34364, 28043) nm. $C_{38}H_{35}N_3$ (533.70): calcd. C 85.52, H 6.61, N 7.87; found C 85.15, H 6.55, N 7.61.

***N*^{1}-{5-[4-(Diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}-*N*^{4},*N*^{4}-diphenylbenzene-1,4-diamine (5k):** From **4g** (162.1 mg, 0.5 mmol) and **2b** (249.5 mg, 0.6 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1) and recrystallisation from dichloromethane. The compound crystallises with one molecule of dichloromethane. Yield: 107 mg (0.1 mmol, 25%), red-orange glass-like solid, m.p. 103 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.20 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3), 6.93–7.22 (m, 22 H), 7.29–7.33 (m, 4 H), 7.88 (d, ^3J = 8.8 Hz, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.8, 23.6 (CH_3), 50.5, 53.1 ($C_{quat.}$), 120.2, 122.1, 123.7, 124.6, 125.1, 125.8, 126.0, 129.7, 131.1 ($C_{arom.}$), 143.8, 145.0, 146.6, 148.2, 151.3 (C_{ipso}), 176.4, 191.9 (C=N) ppm. IR: $\tilde{\nu}$ = 3061 (w), 3038 (w), 2967 (w), 2926 (w), 2868 (vw), 2363 (vw), 2342 (vw), 2326 (vw), 1653 (w), 1585 (s), 1560 (w), 1487 (vs), 1450 (m), 1422 (m), 1393 (m), 1369 (w), 1335 (m), 1312 (s), 1271 (s), 1225 (m), 1194 (m), 1182 (m), 1169 (m), 1142 (m), 1117 (s), 1076 (m), 1028 (w), 1011 (w), 1001 (w), 955 (w), 924 (w), 903 (w), 895 (w), 870 (w), 843 (m), 816 (m), 808 (m), 752 (s), 729 (s), 692 (vs), 671 (m), 644 (w), 637 (m), 621 (m), 615 (m), 594 (w), 557 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 625.3326; found 625.3331. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, $M^{-1}cm^{-1}$) = 386 (25907, 15300), 297 (33670, 20100) nm. $C_{44}H_{40}N_4$ (624.82): calcd. for $C_{44}H_{40}N_4 \cdot CH_2Cl_2$ C 76.15, H 5.96, N 7.89; found C 76.29, H 5.78, N 7.67.

X-ray Crystal Structure Analysis of 5k:[24,25] Formula $C_{45}H_{42}Cl_2N_4$, M = 709.73, yellow crystal 0.10 × 0.10 × 0.10 mm, a = 9.974(8) Å, b = 13.488(10) Å, c = 14.836(12) Å, α = 103.34(2)°, β = 98.17(2)°, γ = 92.92(1)°, V = 1915(2) Å^3, $\rho_{calcd.}$ = 1.231 gcm^{-3}, μ = 0.207 mm^{-1}, empirical absorption correction ($0.9697 \leq T \leq 0.9796$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 123(2) K, ω scans, 12802 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.60 Å^{-1}, 6624 independent (R_{int} = 0.045) and 4395 observed reflections [$I \geq 2\sigma(I)$], 464 refined parameters, R = 0.090, wR^2 = 0.254, max. (min.) residual electron density 0.67 (–0.78) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

***N*-{5-[4-(Diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}pyridin-3-amine (5m):** From **4i** (158.0 mg, 1.0 mmol) and **2b** (498.0 mg, 1.1 mmol). Purification by column chromatography (pentane/ethyl acetate, 2:1 + 5% triethylamine). Yield: 77 mg (0.2 mmol, 16%), orange crystalline solid, m.p. 181 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.22 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3), 6.96 (d, ^3J = 8.7 Hz, 2 H), 7.07–7.13 (m, 7 H), 7.14 (d, ^3J = 8.7 Hz, 6 H), 7.20 (dd, ^3J = 4.8 Hz, ^3J = 8.1 Hz, 1 H), 7.28–7.33 (m, 4 H), 7.48 (dt, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1 H), 7.86 (d, ^3J = 9.0 Hz, 2 H), 8.28 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1 H), 8.41 (d, ^3J = 2.1 Hz, 1 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.9, 23.7 (CH_3), 50.4, 53.5 ($C_{quat.}$), 119.9, 123.0, 124.8, 125.2, 126.0, 129.7, 130.3, 131.3 ($C_{arom.}$), 144.7, 145.2, 145.9, 146.4 151.6 (C_{ipso}), 179.2, 193.2 (C=N) ppm. IR: $\tilde{\nu}$ = 3061 (w), 3038 (w), 2982 (w), 2928 (w), 2872 (w), 1647 (m), 1609 (w), 1587 (s), 1568 (w), 1558 (m), 1485 (s), 1450 (m), 1422 (m), 1412 (m), 1395 (m), 1371 (w), 1314 (s), 1296 (m), 1279 (s), 1271 (s), 1225 (m), 1192 (m), 1182 (s), 1155 (w), 1142 (m), 1117 (s), 1074 (m), 1028 (m), 1018 (m), 1003 (w), 978 (w), 959 (w), 943 (w), 928 (m), 893 (w), 864 (w), 841 (m), 831 (m), 799 (m), 781 (w), 754 (s), 745 (s), 725 (w), 712 (m), 692 (vs), 671 (m), 662 (m), 644 (m), 633 (m), 615 (m), 586 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 459.2543; found 459.2545. $C_{44}H_{40}N_4$ (624.82): calcd. for $C_{31}H_{30}N_4$ C 81.19, H 6.59, N 12.22; found C 80.59, H 6.59, N 12.04.

***N*^{1},*N*^{4}-Bis{5-[4-(diphenylamino)phenyl]-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene}benzene-1,4-diamine (7a):** From **6a** (165.0 mg, 0.5 mmol) and **2b** (498.0 mg, 1.1 mmol). Purification by column

chromatography (pentane/ethyl acetate, 2:1 + 5% triethylamine). Yield: 107 mg (0.1 mmol, 25%), orange solid, m.p. 129 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.19 (s, 12 H, CH_3), 1.34 (s, 12 H, CH_3), 6.96 (d, ^3J = 9.0 Hz, 4 H), 7.06–7.15 (m, 14 H), 7.25–7.31 (m, 10 H), 7.85 (d, ^3J = 9.0 Hz, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.8, 23.5 (CH_3), 50.34, 53.0 ($C_{quat.}$), 120.3, 123.5, 124.5, 125.8, 126.1, 129.6, 131.0 ($C_{arom.}$), 145.7, 146.6, 151.0 (C_{ipso}), 176.2, 191.2 (C=N) ppm. IR: $\tilde{\nu}$ = 3059 (w), 3036 (w), 2970 (w), 2926 (w), 2868 (w), 2359 (w), 2336 (w), 1736 (w), 1719 (w), 1684 (w), 1663 (w), 1653 (m), 1609 (w), 1587 (s), 1560 (m), 1506 (s), 1487 (vs), 1450 (m), 1420 (m), 1393 (m), 1369 (m), 1312 (s), 1279 (s), 1227 (m), 1219 (m), 1192 (m), 1182 (m), 1140 (s), 1115 (s), 1074 (m), 1028 (m), 1013 (w), 1003 (w), 980 (w), 961 (w), 926 (w), 897 (w), 839 (m), 752 (s), 694 (vs), 669 (m), 638 (m), 617 (m), 586 (w), 571 (m), 565 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 837.4639; found 837.4651.

***N*,*N*′-Bis(5-biphenyl-4-yl-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-yl-idene)thiophene-2,5-diamine (7b):** From **6b** (241.9 mg, 1.00 mmol) and **2c** (797.7 mg, 2.2 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1). Yield: 35 mg (0.05 mmol, 5%), deep red crystalline solid, m.p. 229 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.22 (s, 12 H, CH_3), 1.39 (s, 12 H, CH_3), 7.05 (s, 2 H, $CH_{thioph.}$), 7.23–7.27 (m, 5 H), 7.33–7.35 (m, 4 H), 7.43 (d, ^3J = 8.4 Hz, 5 H), 8.26 (d, ^3J = 8.4 Hz, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.9, 23.7 (CH_3), 50.3, 53.9 ($C_{quat.}$), 124.2, 127.1, 127.3, 128.9, 130.6, 132.8 ($C_{arom.}$), 139.8, 144.4, 150.5 (C_{ipso}), 172.3, 190.2 (C=N) ppm. IR: $\tilde{\nu}$ = 3057 (w), 3030 (w), 2965 (m), 2920 (m), 2851 (m), 2361 (m), 2342 (w), 1734 (m), 1719 (w), 1701 (w), 1684 (w), 1647 (m), 1636 (w), 1605 (w), 1560 (m), 1539 (w), 1520 (m), 1506 (s), 1487 (m), 1474 (m), 1464 (m), 1456 (m), 1447 (m), 1437 (m), 1404 (m), 1395 (m), 1369 (m), 1362 (m), 1312 (m), 1300 (m), 1279 (m), 1233 (m), 1217 (m), 1184 (m), 1142 (m), 1117 (s), 1074 (m), 1040 (m), 1026 (m), 1020 (m), 1007 (m), 997 (m), 976 (m), 959 (w), 926 (w), 860 (m), 849 (m), 829 (m), 800 (s), 770 (s), 745 (s), 737 (s), 723 (m), 694 (vs), 669 (m), 648 (m), 627 (m), 611 (w), 588 (w), 571 (m), 561 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 661.3359; found 661.3362. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, M^{-1}cm^{-1}) = 462 (21645, 5000), 321 (31152, 20100), 303 (sh.; 33003, 19000) nm.

***N*^{4},*N*$^{4'}$-Bis(5-biphenyl-4-yl-3,3,4,4-tetramethyl-3,4-dihydropyrrol-2-ylidene)biphenyl-4,4′-diamine (7c):** From **6c** (203.0 mg, 0.5 mmol) and **2c** (406.7 mg, 1.1 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1). Yield: 40 mg (0.1 mmol, 21%), orange-brown solid, m.p. 236 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.26 (s, 12 H, CH_3), 1.40 (s, 12 H, CH_3), 7.22 (d, ^3J = 8.0 Hz, 4 H), 7.34–7.40 (m, 4 H), 7.44–7.47 (m, 7 H), 7.57–7.65 (m, 12 H), 8.04 (d, ^3J = 8.0 Hz, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.9, 23.4 (CH_3), 50.4, 53.8 ($C_{quat.}$), 123.6, 126.8, 127.2, 127.3, 128.2, 129.1, 130.1 ($C_{arom.}$), 132.7, 136.9, 144.5, 148.3 (C_{ipso}), 176.7, 193.0 (C=N) ppm. IR: $\tilde{\nu}$ = 3030 (w), 2922 (s), 2853 (m), 1738 (m), 1665 (m), 1605 (m), 1564 (m), 1528 (s), 1487 (s), 1476 (s), 1449 (m), 1404 (m), 1393 (m), 1377 (m), 1369 (m), 1341 (w), 1315 (m), 1304 (m), 1279 (m), 1260 (m), 1242 (m), 1229 (m), 1206 (m), 1186 (m), 1175 (m), 1140 (m), 1117 (s), 1076 (m), 1042 (m), 1024 (m), 1007 (m), 980 (w), 957 (w), 926 (w), 910 (w), 866 (m), 841 (s), 816 (m), 797 (s), 770 (s), 750 (s), 735 (vs), 719 (m), 694 (s), 665 (w), 656 (w), 642 (w), 606 (w), 579 (w), 571 (w), 555 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + H]^+$ 731.4108; found 731.4057. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, M^{-1}cm^{-1}) = 384 (26042, 8400), 297 (33670, 34900) nm.

Diphenyl[4-(3,3,4,4-tetramethyl-5-phenylimino-4,5-dihydro-3*H*-pyrrol-2-yl)phenyl]amine (7d): From **6c** (203.0 mg, 0.5 mmol) and **2b** (498.0 mg, 1.1 mmol). Purification by column chromatography (pentane/ethyl acetate, 4:1). The compound crystallises with one molecule of ethyl acetate. Yield: 151 mg (0.2 mmol, 31%), glassy orange solid, m.p. 249 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.22 (s, 12 H, CH_3), 1.36 (s, 12 H, CH_3), 6.97 (d, ^3J = 8.8 Hz, 4 H), 7.08–7.15 (m, 14 H), 7.20 (d, ^3J = 8.4 Hz, 4 H), 7.27–7.31 (m, 9 H), 7.53 (d, ^3J = 8.4 Hz, 4 H), 7.87 (d, ^3J = 8.8 Hz, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.8, 23.6 (CH_3), 50.3, 53.2 ($C_{quat.}$), 120.2, 123.7, 124.6, 125.9, 126.7, 129.7, 131.1 ($C_{arom.}$), 136.7, 146.6, 148.5, 151.3 (C_{ipso}), 177.0, 192.0 (C=N) ppm. IR: $\tilde{\nu}$ = 3059 (w), 3036 (w), 2970 (w), 2926 (w), 2868 (w), 2361 (w), 2342 (w), 1736 (w), 1719 (w), 1699 (w), 1666 (m), 1609 (m), 1587 (s), 1560 (m), 1503 (s), 1485 (vs), 1422 (m), 1393 (m), 1369 (m), 1335 (m), 1312 (s), 1298 (s), 1279 (s), 1221 (m), 1192 (s), 1182 (m), 1140 (s), 1128 (s), 1117 (s), 1074 (m), 1026 (m), 1003 (m), 980 (w), 959 (w), 926 (w), 899 (w), 870 (w), 839 (m), 797 (m), 781 (m), 752 (s), 721 (w), 694 (vs), 669 (m), 660 (m), 640 (m), 617 (m), 588 (w), 571 (m) cm^{-1}. MS-ESI-EM: calcd. for $[M + 2H]^{2+}$ 457.2512; found 457.2535. UV/Vis (THF): λ ($\tilde{\nu}$, cm^{-1}; ε, M^{-1}cm^{-1}) = 388 (25773, 31400), 296 (33784, 37400) nm. $C_{64}H_{60}N_6$ (913.22): calcd. for $C_{64}H_{60}N_6 \cdot C_4H_8O_2$ C 81.57, H 6.85, N 8.39; found C 81.73, H 6.54, N 8.13.

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[26] Intensity data for **5b** and **5k** were collected at 123 K with a Rigaku Single Crystal CCD X-ray Diffractometer Saturn 7 with MicroMax 7 with Mo-K_α radiation (λ = 0.71070 Å) and graphite monochromator. The structure was solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares on F^2 (SHELXL-97).

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