Diels–Alder reactions of 3,6-disubstituted 1,2,4,5-tetrazines. Synthesis and X-ray crystal structures of diazafluoranthene derivatives†

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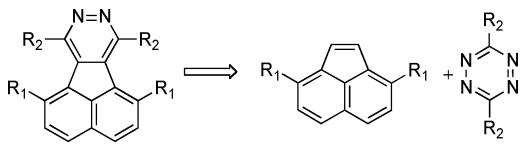
The synthesis of a series of 3,6-disubstituted-1,2,4,5-tetrazines has been effected using an inverse electron demand [2 + 4] cycloaddition strategy. The crystal structures of 18 members of this series of diazafluoranthenes are reported. Stereochemical analysis shows that diazafluoranthenes, substituted across the bay region, are helically-twisted strained aromatic molecules. The dihedral angle between pyridazyl *vs* naphthyl rings ranges from 0.5° to 20.9°, and follows the degree of steric congestion in the bay region. The crystal structures are compared to computational structures determined using density functional theory, with the M06-2X/cc-pVDZ method.

Introduction

The use of 3,6-disubstituted 1,2,4,5-tetrazines as heterodienes in [2 + 4] cycloadditions has found widespread use in many fields of organic chemistry, ranging from mechanistic investigation to natural product synthesis.[1] Introduction of electron-withdrawing groups at the 3 and 6 positions of the tetrazine accelerate, while electron-donating groups retard this reaction.[2] In this work, we investigate the use of the Carboni–Lindsey[3] reaction between 3,6-disubstituted 1,2,4,5-tetrazines and acenaphthylene or 3,8-dimethylacenaphthylene (Scheme 1) to form diazafluoranthenes.

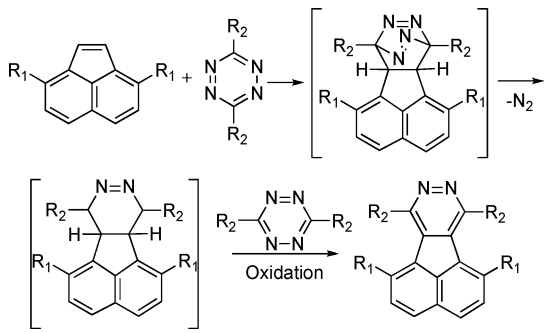


Scheme 1 Retrosynthesis of diazafluoranthene derivatives.

Synthesis

The use of acenaphthylene as an active dienophile in the inverse electron demand cycloaddition reaction is well known.[4,5] In contrast, such chemistry with the sterically encumbered 3,8-dimethylacenaphthylene[6] is to our knowledge unknown, but would lead to 3,4,9,10-tetrasubstituted-diazafluoranthenes. Analogous to the synthesis of corannulene, where tetrasubstituted-fluoranthenes act as synthetic precursors, tetrasubstituted-diazafluoranthenes are attractive targets as intermediates to diazacorannulene.[5b]

Starting materials have been taken in a 1:2 ratio of acenaphthalene:tetrazine; the second molecule of diene serves as an oxidizing agent for the initially formed dihydro intermediate of 8,9-diazafluoranthene (Scheme 2). This moderate-to-good yielding method gave a series of diazafluoranthenes, of which **4a** and **10a** were previously reported[5,7] (Table 1).



Scheme 2 Cycloaddition mechanism.

Reactions were often carried out in an autoclave (180 °C, 600 psi) using *p*-xylene as a solvent; however in favorable cases they proceeded at reflux in mesitylene, chlorobenzene, dichloroethane or dichloromethane. Increase of the electron-withdrawing character of the substituent on the 1,2,4,5-tetrazines (*e.g.* pyridyl, 3,5-dimethyl-1*H*-pyrazol-1-yl, CO_2Me *etc.*) increased the reactivity of the diene, which allowed the use of milder reaction conditions or shorter times.

Steric and electronic effects influence the reactivity of the dienophile. Higher yields were generally obtained by use of the sterically unencumbered acenaphthylene as a dienophile. The sterically hindered but electronically favored 3,8-dimethylacenaphthylene remained a competent dienophile and provided good yields of the desired products.

To probe the acenaphthalene reactivity further, 3,8-dibromoacenaphthylene was prepared (Scheme 3) Use of **3**, which is sterically hindered and electronically disfavored, gave no reaction, even under more drastic conditions; the reaction was carried out at the melting point of the educts or in an autoclave at 10 kbar, but no product was detected.

To test the steric and electronic factors, a comparison experiment was run using **3** *vs.* 5,6-dichloroacenaphthylene (**16**) as the

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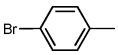
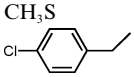
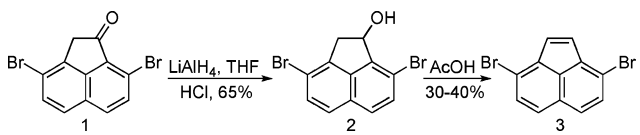
Table 1 Diazafluoranthene derivatives

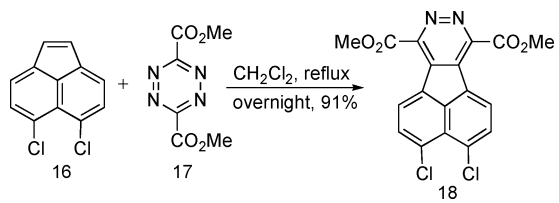
R_2	Entry (R_1 = H)	Conditions	Time	Yield %	Entry (R_1 = Me)	Conditions	Time	Yield %
Ph	**4a**	CH_2Cl_2, reflux	5 d	58%	**4b**	*p*-xylene, autoclave, 180 °C	3 d	27%
	**5a**	chlorobenzene, reflux	2 d	75%	**5b**	*p*-xylene, autoclave, 180 °C	2 d	60%
	**6a**	mesitylene, reflux	1 d	50%	**6b**	*p*-xylene, autoclave, 180 °C	2 d	38%
	**7a**	CH_2Cl_2, reflux	3 d	78%	**7b**	mesitylene, reflux	1 d	85%
	**8a**	DCE, reflux	4 d	39%	**8b**	*p*-xylene, autoclave, 180 °C	3 d	59%
	**9a**	chlorobenzene, reflux	2 d	73%	**9b**	chlorobenzene, reflux	1.5 d	47%
	**10a**	chlorobenzene, reflux	12 h	60–70%				
CO_2Me	**11a**	*p*-xylene, autoclave, 180 °C	12 h	80–95%	**11b**	CH_2Cl_2, reflux	1 d	70%
$CONH_2$	**12a**[a,b]	DMSO, 100 °C	12 h	50%	**12b**	DMSO, 120 °C	1 h	95%
CH_3	**13a**	*p*-xylene, autoclave, 180 °C	2 d	70–80%	**13b**	*p*-xylene, autoclave, 180 °C	3 d	70%
CH_3S	**14a**	*p*-xylene, reflux	1 d	75%	**14b**	mesitylene, reflux	2 d	20%
	**15a**	*p*-xylene, autoclave, 180 °C	2.5 d	30–50%				

[a] Compound **12a** was obtained as a mixture with 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxamide. The yield of **12a** was determined from the integral intensity ratio in the ^{1}H-NMR spectrum. [b] A cognate of **12a**, **12a′**, was prepared using 4,7-di-*tert*-butylacenaphthylene as a dienophile. Conditions: DMSO, 120 °C, 1 h, 95%.



Scheme 3 Formation of 3,8-dibromoacenaphthylene.

dienophile. In **16** the halo groups are situated *para* to the ace-bridge and therefore should not sterically encumber the reactive site. The strong role of steric hindrance becomes clear upon contemplation of the fact that dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate and **16** react in dichloromethane to form dimethyl 3,4-dichloro-8,9-diaza-fluoranthene-7,10-dicarboxylate in 91% yield (Scheme 4). However, a mixture of 1,2,4,5-tetrazine-3,6-dicarboxylate and **3** does not react even in *p*-xylene in autoclave at 180 °C and 600 Psi.



Scheme 4 Synthesis of dimethyl 3,4-dichloro-8,9-diazafluoranthene-7,10-dicarboxylate.

Structure

Molecular distortion provides insight to molecular strain. The introduction of substituents in the *peri* and *bay* regions can cause steric overcrowding, and splaying or twisting distortions in the molecule become evident (Fig. 1).[8] *Peri*-substituted naphthalenes, and 4,5-disubstituted phenanthrenes manifest each of these distortion modes as a function of steric bulk of the substituents. The classic examples of bulky substitution (*tert*-butyl, trimethyl-X, aryl *etc.*) in the *peri* positions of a naphthalene ring,[9] show a deflection of the *peri* groups from each other and an out-of-plane C_2 symmetric twisting.[9–12] In the case of phenyl substituted naphthalenes, steric effects force the phenyl groups into a splayed-stacked geometry.[13,14]

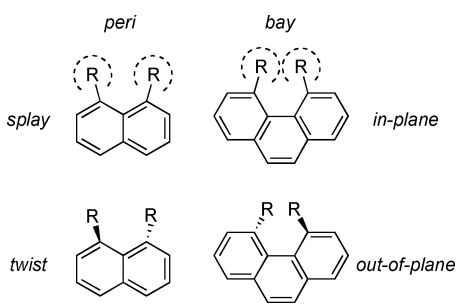
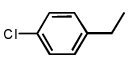


Fig. 1 *Peri* and *bay* regions and molecular distortions.

Table 2 Dihedral angle and bay region measurements

Compd	R_2	Dihedral angle $R_1 = H$ exptl [calcd][b]	Dihedral angle $R_1 = CH_3$ exptl [calcd]	∑ Bay angles[a] $R_1 = H$ exptl [calcd]	∑ Bay angles[a] $R_1 = CH_3$ exptl [calcd]
4	Ph	6.5(2) [7.6]	14.2(1) [20.2]	517.2(4) [516.3]	522.9(3) [520.7]
5		7.4(2) 8.7(3) 15.9(3) [4.5] 12.0(3)	20.9(3) [18.5]	519.1(4), 509.7(4) 517.9(3), 510.0(3) 512.5(5), 517.3(4) [516.0] 520.0(4), 511.9(3)	518.0(4) [521.8]
7		5.0(1) [3.6]	— [17.5]	513.3(2), 519.5(2) [515.3]	— [519.95]
8		13.6(2) [9.3]	17.0(2) [21.3]	515.5(3) [516.7]	521.6(4) [520.4]
9		— [6.0]	13.3 (5) [20.7]	— [520.7]	523(1), 525(1) [521.2]
10		3.8(2) [3.4]	— [23.9]	517.8(3) [515.1]	— [525.3]
11	CO_2Me	1.0(2) 4.4(2) [1.4]	10.4(2) [12.9]	515.8(3), 515.4(3) 516.2(3), 516.8(4) [515.6]	521.6(4) [518.5]
12[c]	$CONH_2$	2.4(4) 6.7(4) [0]	— [16.1]	515.9(5), 514.2(5) 516.6(5), 515.8(5) [516.6]	— [520.0]
13	CH_3	2.2(3) [0]	0.6(2) [15.6]	513.5(3), 512.4(5) [514.1]	524.2(4), 524.9(4) [521.4]
14	CH_3S	3.0(2) [0]	17.9(2) [15.6]	509.9(3) [511.8]	517.7(4), 521.2(3) [520.3]
15		5.3(2) [—]	— —	513.8(4), 513.7(3)	—
Avg[d]		5.8 [3.6]	13.5 [18.2]	515.0 [515.8]	521.8 [520.9]

[a] Sum of α, β, γ, and δ (see Fig. 3). [b] M06-2X/cc-pVDZ. [c] X-ray data come from **12a′**. [d] Diazafluoranthene ref. calcd ∑α, β, γ, and δ = 514.3°.

Newman[15] speculated that the structure of 4,5-dimethylphenanthrene would show displacement of the methyl groups out of the mean plane of the aromatic system due to steric clashing. This assumption was supported by X-ray crystal structures, in which aromatic systems such as 4,5-dimethylphenanthrene demonstrate a helical twist.[16]

In fluoranthenes there are bay-like regions on two sides of the molecule. Symmetrical substitution can lead to two kinds of symmetrical out-of-plane distortions, C_2-twists and C_s-folds (Fig. 2). The X-ray structure of 1,6,7,10-tetramethylfluoranthene shows a C_2-geometry with a twist of approximately 16°, presumably due to the steric repulsion between methyl groups.[17] The C_2-twist and C_s-fold options for molecular distortion were evaluated computationally, and the twist was favored by 1–2 kcal/mol. A similar preference for twist distortions are expected for the analogous diazafluoranthene derivatives.

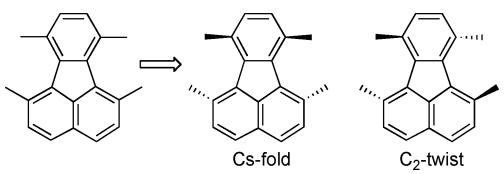


Fig. 2 Folding and twisting distortion modes of fluoranthene.

The crystal structures of **3**, **4(a/b)**, **5(a/b)**, **7a**, **8(a/b)**, **9b**, **10a**, **11(a/b)**, **12a′**, **13(a/b)**, **14(a/b)**, and **15(a/b)** have been determined, 18 structures in all. From the crystallographic data obtained, the dihedral angle between the best-planes-of-fit through atoms C7/N/N/C10 of the pyridazyl ring and atoms C2/C3/C4/C5 of the naphthyl ring was determined. In addition, the bay region bond angles α, β, γ, and δ for each side of the molecule were measured and summed (Fig. 3). The same parameters were determined from coordinates obtained by quantum mechanical computations (Table 2).

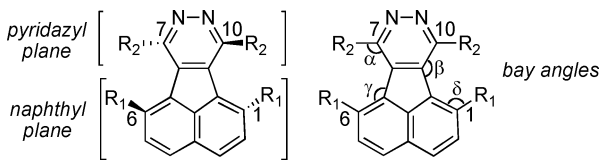


Fig. 3 Distortion parameters for diazafluoranthenes: left) pyridazyl/naphthyl dihedral; right) bay angles α, β, γ, δ.

A reasonable reference compound is the parent diazafluoranthene ($R_1 = R_2 = H$). Here the molecule is flat (dihedral angle = 0°) and the sum of bay angles is calculated to be 514.3°. On average, replacement of R_2 by a carbon atom based functional group (not tertiary) yields a molecule with slight twist (exptl 5.8° calcd [3.6°]) and essentially no splaying as judged by the sum of the bay

angles (exptl 515.0° calcd [515.8°]). The same R_2 substitution when R_1=Me leads to a more substantial twist (exptl 13.5° calcd [18.2°]) and some evidence for splaying (exptl 521.8° calcd [520.9°]). It would appear that the out-of-plane twisting is a softer distortion mode than the in-plane splaying mode. At higher twisting angles the mode becomes stiffer and the splaying mode sets in to accommodate the steric encroaching of substituents across the bay region.

An exception to this steric bulk model is 1,6,7,10-tetramethyl-8,9-diazafluoranthene (**13b**) for which the crystallographic model exhibits a greater twist of the molecule for the dimethyl compound **13a** (R_1 = H; 2.2(3)°) than for **13b** (R_1 = Me; 0.6(2)°). Although the experimental diffraction data for **13b** models well as a planar form, the H···H distances between adjacent methyl groups range from 2.04–2.16 Å, and some of the methyl C-atoms have quite elongated atomic displacement ellipsoids perpendicular to the molecular plane. Computations on **13b** predict a twist angle of 15.6° and, as mentioned above, computation and X-ray structures of the hydrocarbon analog, tetramethylfluoranthene, display twists between 15–20°. Thus, the X-ray structure of **13b** must either reflect an unresolved disorder or a substantial packing effect on the molecular conformation. A packing effect would arise from a trade of higher strain energy as a planar form in return for better packing energy. Computations on the planar form predict only a 1.2 kcal/mol difference from the twisted ground state. Such an energy would be within the bounds of packing effects.

Conclusion

In this work, two series of substituted 8,9-diazafluoranthenes were synthesized using an inverse electron demand Diels–Alder reaction strategy. Increase of the electron-withdrawing demand of the substituent in *s*-tetrazines increases the yield of desired products. Steric hindrance in the *ortho* positions of the dienophile can be tolerated if the substituents are methyl groups. X-Ray crystallographic structure analysis has been carried out on eighteen derivatives and compared with theoretical calculations. The structure of these molecules show a helical twist due to steric interactions across the bay region. The dihedral and sum of bay region angles correlate with the degree of bay region steric congestion.

Chemical abstract nomenclature

7,10-Diphenylacenaphtho[1,2-*d*]pyridazine (**4a**), 1,6-dimethyl-7,10-diphenylacenaphtho[1,2-*d*]pyridazine (**4b**), 2,2′-acenaphtho-[1,2-*d*]pyridazine-7,10-diyldiphenol (**5a**), 2,2′-(1,6-dimethylacenaphtho[1,2-*d*]pyridazine-7,10-diyl)diphenol (**5b**), 7,10-bis(4-bromophenyl)acenaphtho[1,2-*d*]pyridazine (**6a**), 7,10-bis(4-bromophenyl)-1,6-dimethylacenaphtho[1,2-*d*]pyridazine (**6b**), 7,10-bis(3,5-dimethyl-1*H*-pyrazol-1-yl) acenaphtho[1,2-*d*]pyridazine (**7a**), 7,10-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,6-dimethylacenaphtho[1,2-*d*]pyridazine (**7b**), 7,10-di(thiophen-2-yl)acenaphtho-[1,2-*d*]pyridazine (**8a**), 1,6-dimethyl-7,10-di(thiophen-2-yl)acenaphtho[1,2-*d*]pyridazine (**8b**), 7,10-di(furan-2-yl)acenaphtho-[1,2-*d*]pyridazine (**9a**), 7,10-di(furan-2-yl)-1,6-dimethylacenaphtho[1,2-*d*]pyridazine (**9b**), 7,10-di(pyridin-2-yl)acenaphtho[1,2-*d*]pyridazine (**10a**), dimethyl acenaphtho[1,2-*d*]pyridazine-7,10-dicarboxylate (**11a**), dimethyl 1,6-dimethylacenaphtho[1,2-*d*]pyridazine-7,10-dicarboxylate (**11b**), acenaphtho[1,2-*d*]pyridazine-7,10-dicarboxamide (**12a**), 2,5-di-*tert*-butylacenaphtho[1,2-*d*]pyridazine-7,10-dicarboxamide (**12b**), 7,10-dimethylacenaphtho[1,2-*d*]pyridazine (**13a**), 1,6,7,10-tetramethylacenaphtho[1,2-*d*]pyridazine (**13b**), 7,10-bis(methylsulfanyl) acenaphtho[1,2-*d*]-pyridazine (**14a**), 1,6-dimethyl-7,10-bis(methylsulfanyl)acenaphtho[1,2-*d*]pyridazine (**14b**), 7,10-bis(4-chlorobenzyl)acenaphtho-[1,2-*d*]pyridazine (**15a**).

Computational methods

The conformational analyses of the molecules described in this study were carried out with the Gaussian 03[18] software package, using density functional methods. In particular, the M06-2X[19] functional together with Dunning's correlation consistent basis set, cc-pVDZ,[20] a [3s2p1d] was employed. Full geometry optimizations were performed and uniquely characterized *via* second derivative (Hessian) analysis to determine the number of imaginary frequencies (0 = minima; 1 = transition state). Analysis of dihedral and bay region angles was carried out using QMView[21] and PLATON.[22]

Experimental

General information

All reactions were carried out under nitrogen (except for compound **3**). Solvents were used as purchased (p.a. grade) without further purification. 3,6-Disubstituted-1,2,4,5-tetrazines were synthesized according literature procedures. Commercially available acenaphthylene was also used as purchased without further purification. Melting points were determined using a heating microscope from Cristoffel Labor- and Betriebstechnik and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Compounds were measured as KBr pellets. Absorption bands are given in wavenumbers (cm^{-1}), and the intensities are characterized as follows: *s* = strong (0–33% transmission), *m* = medium (34–66% transmission), *w* = weak (67–100% transmission). ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker ARX 300 (75 MHz), Bruker Avance 400 (400 MHz), Bruker Avance 500 (500 MHz), Bruker DRX-500 (500 MHz) and Bruker DRX-600 (600 MHz) spectrometers, with the solvent as the internal standard. Data are reported as follows: chemical shift in ppm, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *dd* = doublet of doublets, *dt* = doublet of triplet, *etc.*), coupling constant ^{n}J in Hz, integration and interpretation. The atom numbering used for compounds **5a** and **10a** is shown in Fig. 4. Mass spectra (MS) were obtained from Finnigan MAT95 instrument. Analytical thin layer chromatography (TLC) was performed with Macherey-Nagel POLYGRAM SIL N-HR/UV_{254} and POLYGRAM ALOX

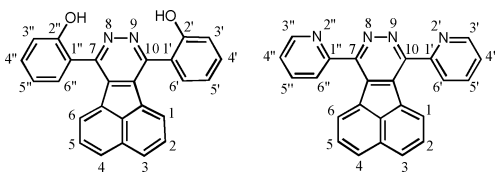


Fig. 4 Atom numbering of diazafluoranthene derivatives.

N/UV_{254}, visualization by an ultraviolet (UV) lamp ($\lambda = 254$ nm and $\lambda = 366$ nm). Column chromatography was carried out on silica gel (Merck 60 0.040–0.063 mm) or deactivated (5% water) aluminium oxide (Sigma-Aldrich type 507C, 150 mesh).

3,8-Dibromo-1-acenaphthenol (2). To a dry three-necked 100 mL round-bottom flask, equipped with a condenser, N_2 inlet and a stir bar, dry THF (28 mL) and 3,8-dibromo-1-acenaphthenone (1.6 g, 4.9 mmol) were added. The mixture was cooled in an acetone/ice bath and $LiAlH_4$ (0.28 g, 7.3 mmol) was added in small portions with stirring. After stirring at rt overnight and 24 h at reflux, the mixture was hydrolyzed (28 mL of 1 N HCl was added dropwise) with ice cooling, concentrated to about one-half its volume, extracted with CH_2Cl_2 (3×50 mL) and dried with $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane) to yield a white solid (1.1 g, 65%). mp 129 °C; IR (KBr): 3377*s* (br. OH), 3083*w*, 3038*w*, 2925*w*, 2667*w*, 1898*w*, 1607*m*, 1581*m*,1479*s*, 1443*w*, 1405*m*, 1346*w*, 1287*m*, 1272*m*,1227*w*, 1217*m*, 1189*m*, 1168*w*, 1115*m*, 1103*m*, 1084*s*, 1025*s*, 996*w*, 976*m*, 898*s*, 868*w*, 837*s*, 824*s*, 779*m*, 682*w*, 605*w*, 574*w*, 527*m*, 493*w*; ^{1}H-NMR (500 MHz, $CDCl_3$), δ 7.6 (d, 1H, $^3J = 8.5$ Hz), 7.56 (d, 1H, $^3J = 3.5$ Hz), 7.54 (d, 1H, $^3J = 4.0$ Hz), 7.51 (d, 1H, $^3J = 9.0$ Hz), 5.7 (ddd, 1H, $^3J = 2.1$, $^3J = 4.0$, $^3J = 7.0$ Hz), 3.7 (dd, 1H, $^3J = 7.1$, $^2J = 18.4$ Hz), 3.3 (dd, 1H, $^3J = 2.1$, $^2J = 18.4$ Hz), 2.6 (d, 1H, OH, $^3J = 4.0$ Hz); ^{13}C-NMR (500 MHz, $CDCl_3$) δ 144.7, 141.8, 139.2, 131.9, 131.6, 129.0, 127.4, 125.3, 116.2, 115.7, 74.0, 42.0; MS (EI) *m*/*z* (%): 328 (M^+, 79), 310 (22), 247 (42), 230 (27), 168 (100), 150 (22), 139 (69%).

3,8-Dibromoacenaphthylene (3). 3,8-Dibromo-1-acenaphthenol (0.50 g, 1.5 mmol) was stirred at reflux in acetic acid (32 mL) for 3 d. The mixture was diluted with water (30 mL), extracted with CH_2Cl_2 and dried with $MgSO_4$. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane) to yield a yellow solid (0.21 g, 44%). mp 103 °C; IR (KBr): 2922*w*, 2852*w*, 1886*w*, 1814*w*, 1632*w*, 1601*s*, 1472*w*, 1462*m*, 1439*m*, 1420*m*, 1409*m*, 1356*w*, 1301*w*, 1261*w*, 1196*w*, 1149*m*, 1124*w*, 1106*w*, 1078*s*, 954*w*, 899*m*, 871*s*, 823*s*, 723*s*, 707*m*, 523*m*, 507*w*, 494*w*; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.6 (d, 1H, $^3J = 9.0$ Hz), 7.5 (d, 1H, $^3J = 8.5$ Hz), 7.1 (s, 1H); ^{3}C-NMR (500 MHz, $CDCl_3$) δ 140.3, 131.8, 130.7, 129.3, 129.2, 125.9, 121.2; MS (EI) *m*/*z* (%): 310 (M^+, 100), 308 ($M^+ - 2$, 52), 229 (29), 150 (71), 75 (33%).

7,10-Diphenyl-8,9-diazafluoranthene (4a). A mixture of 3,6-diphenyl-1,2,4,5-tetrazine (0.310 g, 1.32 mmol) and acenaphthylene (0.10 g, 0.66 mmol) in CH_2Cl_2 (10 mL) was stirred at reflux for 5 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane, hexane/acetone 1:5) to yield a yellow solid (0.18 g, 58%). mp 312 °C (dec); IR (KBr): 3057*s*, 3035*m*, 3010*m*, 2863*w*, 2239*w*, 1962*w*, 1904*w*, 1602*w*, 1580*w*, 1552*m*, 1534*m*, 1485*m*, 1440*m*, 1419*s*, 1382*s*, 1355*m*, 1342*m*, 1312*m*, 1231*m*, 1177*m*, 1158*m*, 1121*m*, 1087*s*, 1072*s*, 1016*m*, 1001*m*, 986*m*, 928*m*, 919*w*, 857*w*, 829*s*, 783*s*, 769*s*, 750*s*, 730*w*, 705*s*, 674*m*, 640*m*, 622*m*, 610*m*, 566*w*, 530*w*, 520*m*, 495*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.04 (d, $^3J = 8.1$ Hz, 1H), 7.97–8.0 (m, 2H, Ph), 7.8 (d, 1H, $^3J = 7.2$ Hz), 7.6–7.7 (m, 3H, Ph), 7.6 (dd, 1H, $^3J = 7.2$, 8.1 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.1, 137.1, 134.0, 132.6, 131.8, 130.3, 129.8, 129.6, 128.6, 128,1, 126,6; MS (EI) *m*/*z* (%): 356 (M^+, 100), 326 (57), 163 (28%).

1,6-Dimethyl-7,10-diphenyl-8,9-diazafluoranthene (4b). A mixture of 3,6-diphenyl-1,2,4,5-tetrazine (0.050 g, 0.28 mmol) and 2,7-dimethylacenaphthylene (0.13 g, 0.56 mmol) in *p*-xylene (5 mL) was stirred at 180 °C in an autoclave (600 Psi) for 3 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/acetone 5:1→1:5) to yield a yellow solid (0.03 g, 27%). mp 335 °C (dec); IR (KBr): 3056*m*, 3025*m*, 3006*m*, 2924*m*, 2241*w*, 1971*w*, 1944*w*, 1879*w*, 1769*w*, 1611*m*, 1570*w*, 1530*w*, 1501*m*, 1487*s*, 1444*s*, 1408*s*, 1379*s*, 1354*m*, 1335*s*, 1304*w*, 1258*w*, 1205*m*, 1173*w*, 1161*m*, 1110*m*, 1091*s*, 1072*m*, 1059*s*, 1028*m*, 1013*m*, 985*w*, 950*w*, 916*m*, 848*s*, 800*m*, 775*m*, 757*s*, 696*s*, 679*m*, 640*w*, 599*w*, 541*m*, 532*m*, 484*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.9 (d, 1H, $^3J = 8.4$ Hz), 7.78–7.81 (m, 2H, Ph), 7.52–7.53 (m, 3H, Ph), 7.4 (d, 1H, $^3J = 8.4$ Hz), 1.95 (s, 3H, CH_3); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 155.8, 140.9, 139.2, 135.8, 133.5, 132.4, 130.7, 130.3, 130.2, 129.5, 129.2, 127.1, 23.1; MS (EI) *m*/*z* (%): 384 (M^+, 100), 356 (40), 341 (24%).

7,10-Bis(2-hydroxyphenyl)-8,9-diazafluoranthene (5a). A mixture of 3,6-bis(2-hydroxyphenyl)-1,2,4,5-tetrazine (0.18 g, 0.68 mmol) and acenaphthylene (0.050 g, 0.33 mmol) in chlorobenzene (10 mL) was stirred at reflux for 2 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/acetone 7:1) to yield a yellow solid (0.1 g, 75%). mp 233 °C (dec); IR (KBr): 3065*m* (br., OH), 1940*w*, 1740*w*, 1618*s*, 1580*s*, 1517*m*, 1487*s*, 1463*m*, 1449*m*, 1416*s*, 1379*s*, 1355*s*, 1298*s*, 1253*s*, 1236*m*, 1213*m*, 1178*m*, 1125*w*, 1088*m*, 1038*m*, 953*w*, 838*w*, 825*s*, 778*s*, 764*s*, 725*m*, 665*m*, 615*w*, 599*w*, 574*w*, 503*w*, 486*w*, 464*w*, 451*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.9 (s, br., 1H, OH), 8.3 (d, 1H, $^3J = 7.5$ Hz), 8.1 (d, 1H, $^3J = 8.1$ Hz), 8.05 (dd, 1H, $^4J = 1.8$, $^3J = 7.8$ Hz, H-C (6′, 6″)), 7.7 (dd, 2H, $^3J = 7.5$, 8.1 Hz), 7.5 (ddd, 1H, $^4J = 1.5$, $^3J = 7.2$, 8.4 Hz, H-C (4′, 4″)), 7.3 (dd, 1H, $^4J = 1.2$, $^3J = 8.4$ Hz, H-C (3′, 3″)), 7.1 (td, 1H, $^4J = 1.2$, $^3J = 7.5$ Hz, H-C (5′, 5″)); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 157.3, 155.9, 135.4, 132.6, 132.2, 131.9, 131.5, 130.9, 130.2, 128.4, 127.5, 119.6, 119.5, 118.7; MS (EI) *m*/*z* (%): 388 (M^+, 100%).

7,10-Bis(2-hydroxyphenyl)-1,6-dimethyl-8,9-diazafluoranthene (5b). A mixture of 3,6-bis(2-hydroxyphenyl)-1,2,4,5-tetrazine (0.15 g, 0.56 mmol) and 2,7-dimethylacenaphthylene (0.050 g, 0.28 mmol) in *p*-xylene (5 mL) was stirred at 180 °C in an autoclave (600 Psi) for 2 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate 10:1→5:1) to yield a yellow solid (0.12 g, 60%). mp 333 °C (dec); IR (KBr): 3523*m* and 3281*m* (br., OH), 3049*m*, 2961*m*, 2922*m*, 2852*m*, 1728*w*, 1700*w*, 1614*s*, 1576*s*, 1517*m*, 1485*s*, 1460*s*, 1413*s*, 1375*s*, 1341*s*, 1293*s*, 1236*s*, 1209*s*, 1178*s*, 1153*s*, 1091*s*, 1061*s*, 1036*s*, 951*w*, 849*m*, 837*s*, 897*m*, 787*s*, 748*s*, 701*w*, 666*w*, 657*m*, 605*m*, 533*m*, 501*w*, 440*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.5 (s, br., 1H, OH), 8.0 (d, 1H, $^3J = 8.4$ Hz), 7.5 (d, 1H, $^3J = 8.1$ Hz), 7.37–7.42 (m, 2H), 7.2 (d, 1H, $^3J = 7.8$ Hz), 6.9 (t, 1H, $^3J = 7.5$ Hz), 2.2 (s, 3H); ^{13}C-NMR δ 156,2, 154.6, 139.9, 137.0, 133.1, 132.1, 131.6, 130.7, 130.6, 130.0, 126.7, 122.9, 120.2, 118.4, 23.7; MS (EI) *m*/*z* (%): 416 (M^+, 34), 399 (100%).

7,10-Bis(4-bromophenyl)-8,9-diazafluoranthene (6a). A mixture of 3,6-bis(4-bromophenyl)-1,2,4,5-tetrazine (0.10 g, 0.66 mmol) and acenaphthylene (0.10 g, 1.32 mmol) in mesitylene

(10 mL) was stirred at reflux for 1 d. The reaction was cooled to the room temperature, the yellow precipitate was filtered, stirred for 1.5 h in CH_2Cl_2 to dissolve the rest of the starting materials, filtered off, and dried *in vacuo*, yielding (0,17 g 50%) of a yellow solid. mp 356 °C; IR (KBr): 3056*m*, 3010*m*, 2229*w*, 1924*w*, 1862*w*, 1590*s*, 1527*w*, 1479*s*, 1457*w*, 1435*w*, 1419*s*, 1396*s*, 1378*s*, 1353*m*, 1334*s*, 1297*m*, 1233*m*, 1178*w*, 1117*m*, 1103*m*, 1086*s*, 1071*s*, 1009*s*, 985*m*, 948*m*, 835*s*, 812*m*, 784*s*, 746*m*, 728*s*, 674*m*, 651*m*, 631*w*, 590*w*, 568*w*, 527*s*, 514*m*, 503*w*, 461*m*, 451*m*, 415*w*; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.1 (d, 1H, ^3J = 8.0 Hz), 7.87–7.89 (m, 3H), 7.79–7.81 (m, 2H), 7.6 (dd, 1H, ^3J = 8.4, 8.4 Hz); ^{13}C-NMR (600 MHz, $CDCl_3$), 155,5, 136.4, 134.1, 132.5, 132.3, 132.0, 131.2, 131.0, 130,2, 128.5, 126.8, 124.4; MS (EI) *m*/*z* (%): 514 (M^+, 100), 486 (18), 405 (18), 326 (73), 243 (M^{2+},13), 163, (41), 149, (10%).

7,10-Bis(4-bromophenyl)-1,6-dimethyl-8,9-diazafluoranthene (6b). A mixture of 2,7-dimethylacenaphthylene (0.050 g, 0.28 mmol) and 3,6-bis(4-bromophenyl)-1,2,4,5-tetrazine (0.22 g, 0.56 mmol) in *p*-xylene (5 mL) was stirred in an autoclave (600 Psi) at 180 °C for 2 d. The solvent was evaporated, the residue was washed thoroughly with acetone and dried *in vacuo* to yield a light yellow solid (0.05 g, 33%). mp 310 °C (dec); IR (KBr): 3055*w*, 2995*w*, 2956*w*, 2916*w*, 2236*w*, 1970*w*, 1899*w*, 1638*m*, 1608*m*, 1595*s*, 1563*m*, 1503 1479*s*, 1446*s*, 1412*s*, 1391*s*, 1374*s*, 1347*m*, 1331*s*, 1318*m*, 1293*w*, 1206*m*, 1183*m*, 1154*s*, 1108*s*, 1066*s*, 1030*m*, 1007*s*, 854*s*, 834*s*, 811*m*, 795*m*, 740*m*, 726*m*, 678*m*, 626*m*, 546*m*, 534*m*, 445*m*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.9 (d, 1H, ^3J = 8.1 Hz), 7.68 (s, 4H, 4-bromophenyl), 7.4 (d, 1H, ^3J = 8.1 Hz), 2.0 (s, 3H, CH_3); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 154.8, 139.7, 139.2, 135.8, 133.5, 132.5, 132.4, 131.8, 130.5, 130.3, 127.1, 124.1, 23.63; MS (EI) *m*/*z* (%): 542 (M^+, 100), 514 (42), 420 (46), 353 (26), 276 (22), 169 (M $^{2+}$ (43%)).

7,10-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-8,9-diazafluoranthene (7a). A mixture of 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine (0.18 g, 0.66 mmol) and acenaphthylene (0.050 g, 0.33 mmol) in dichloromethane (10 mL) was stirred at reflux for 3 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 5:1) to yield a light yellow solid (0.1 g, 78%). mp 203 °C (dec); IR (KBr): 3055*w*, 2978*w*, 2921*m*, 2856*w*, 1560*s*, 1537*m*, 1488*w*, 1466*m*, 1439*m*, 1419*s*, 1284*w*, 1264*w*, 1231*w*, 1184*w*, 1146*w*, 1091*m*, 1043*m*, 1022*m*, 988*w*, 968*m*, 823*m*, 770*s*, 760*s*, 746*m*, 698*w*, 676*w*, 632*w*, 571*w*, 502*w*; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.1 (d, 1H, ^3J = 8.0 Hz), 8.0 (d, 1H, ^3J = 7.0 Hz), 7.7 (dd, 1H, ^3J = 7.7, 7,7 Hz), 6.2 (s, 1H, pyrazol), 2.5 (s, 1H, CH_3), 2.4 (s, 1H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.8, 150.6, 142.1, 134.3, 131.9, 131.2, 130.5, 129.5, 129.1, 128.5, 108,0, 13.6, 12.1; MS (EI) *m*/*z* (%): 392 (M^+, 74), 391 ($M^+ - 1$, 100), 393 ($M^+ + 1$, 19%).

7,10-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,6-dimethyl-8,9-diazafluoranthene (7b). A mixture of 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine (0.15 g, 0.56 mmol) and 2,7-dimethylacenaphthylene (0.050 g, 0.28 mmol) in mesitylene (8 mL) was stirred at reflux for 1 d. The mixture was cooled to the room temperature, the precipitate was filtered, washed thoroughly with acetone and dried *in vacuo* to yield a yellow solid (0.1 g 85%). mp 350 °C; IR (KBr): 3014*w*, 2961*w*, 2925*m*, 2860*w*, 1614*w*, 1554*s*, 1505*s*, 1462*s*, 1414*s*, 1398*s*, 1375*s*, 1348*m*, 1274*w*, 1202*m*, 1195*m*, 1157*w*, 1139*w*, 1102*s*, 1071*m*, 1034*m*, 1023*m*, 977*w*, 859*s*, 811*w*, 798*m*, 788*s*, 773*m*, 743*m*, 693*w*, 655*w*, 615*w*, 606*w*, 540*w*, 506*w*, 438*w*; ^{1}H-NMR (400 MHz, CD_2Cl_2), 8.0 (d, 1H, ^3J = 8.4 Hz), 7.5 (d, 1H, ^3J = 8.4 Hz), 6.2 (s, 1H, pyrazol), 6.2 (s, 1H, pyrazol), 2.5 (s, 1H, CH_3), 2.3 (s, 1H, CH_3), 2.1 (s, 1H, CH_3); ^{13}C-NMR (500 MHz, nitrobenzene-d_5, 140 °C), 150.9, 150.3, 142,9, 141.6, 135.1, 133.9, 131.9, 130.7, 128.0, 126.8, 107.7, 19,4, 12.7, 11.0; (600 MHz, CD_2Cl_2), 150.6, 150.6, 142.8, 141.7, 135.3, 133.2, 132.2, 131.2, 127.7, 126.7, 107.8, 19.7, 13.4, 11.7; MS (EI) *m*/*z* (%): 420 (M^+, 11), 405 (100), 195 (7%).

7,10-Di(thiophen-2-yl)-8,9-diazafluoranthene (8a). A mixture of 3,6-di(thiophen-2-yl)-1,2,4,5-tetrazine (0.32 g, 1.32 mmol) and acenaphthylene (0.10 g, 0.66 mmol) in 1,2-dichloroethane (10 mL) was stirred at reflux for 4 d. The yellow precipitate was filtered, washed thoroughly with methanol and dried *in vacuo*, yielding (0.095 g, 39%). mp 220 °C (dec); IR (KBr): 3102*s* (br.), 3058*s*, 2582*m* (br.), 1811*w*, 1695*w*, 1630*m*, 1607*m*, 1579*m*, 1554*m*, 1506*w*, 1485*m*, 1458*m*, 1418*s*, 1379*s*, 1333*s*, 1311*s*, 1221*m*, 1187*m*, 1111*s*, 990*w*, 928*w*, 852*s*, 826*s*, 785*m*, 775*s*, 741*m*, 698*s*, 669*w*, 618*s*, 518*w*, 501*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.3 (d, 1H, ^3J = 7.2 Hz), 8.1 (d, 1H, ^3J = 8.1 Hz), 7.9 (d, 1H, ^3J = 3.0 Hz), 7.66–7.71 (m, 2H), 7.3 (dd, 1H, ^3J = 4.8, 4.8 Hz); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 150.9, 139.8, 134.1, 132.7, 132.1, 131.4, 130.5, 129.5, 129.3, 128.8, 127.9, 127,1; MS (EI) *m*/*z* (%): 368 (M^+, 100), 340 (62), 295 (24), 248 (14), 170 (11%).

7,10-Di(thiophen-2-yl)-1,6-dimethyl-8,9-diazafluoranthene (8b). A mixture of 2,7-dimethylacenaphthylene (0.05 g, 0.28 mmol) and 3,6-di(thiophen-2-yl)-1,2,4,5-tetrazine (0.14 g, 0.56 mmol) in *p*-xylene (5 mL) was stirred at 180 °C in an autoclave (600 Psi) for 3 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate 5:1, hexane/acetone 5:1) to yield a yellow solid (0.065 g, 59%). mp 260 °C (dec); IR (KBr): 3107*w*, 3022*w*, 3004*w*, 2913*w*, 2250*w*, 1788*w*, 1612*m*, 1573*w*, 1550*w*, 1498*m*, 1443*m*, 1404*s*, 1375*s*, 1332*s*, 1315*m*, 1220*w*, 1202*m*, 1174*w*, 1155*w*, 1094*m*, 1055*m*, 1039*m*, 987*w*, 974*w*, 900*w*, 853*s*, 832*m*, 798*w*, 769*m*, 693*s*, 637*w*, 606*w*, 541*w*; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.9 (d, 1H, ^3J = 8.4 Hz), 7.5 (dd, 1H, ^4J = 1.2, ^3J = 5.2 Hz), 7.4 (d, 1H, ^3J = 8.4 Hz), 7.3 (dd, 1H, ^4J = 0.8, ^3J = 3.2 Hz), 7.2 (dd, 1H, ^3J = 3.6, 5.2 Hz), 2.2 (s, 3H, CH_3); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 149.9, 141.8, 139.6, 136.2, 132.4, 130.4, 130.3, 129.8, 128.7, 127.7, 127.0, 23.3; MS (EI) *m*/*z* (%): 396 (M^+, 100), 368 (41), 353 (40), 319 (18%).

7,10-Di(furan-2-yl)-8,9-diazafluoranthene (9a). A mixture of acenaphthylene (0.05 g, 0.33 mmol) and 3,6-di(furan-2-yl)-1,2,4,5-tetrazine (0.14 g, 0.66 mmol) in chlorobenzene (10 mL) was stirred at reflux for 2 d. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, hexane). *Note: evaporation of solvent should be carried out below 30 °C (decomposition of product).* Yield (0.08 g, 73%) of a yellow solid. mp 150 °C; IR (KBr): 3138*w*, 3059*w*, 2924*m*, 2853*w*, 1599*m*, 1529*w*, 1490*m*, 1476*s*, 1421*s*, 1398*s*, 1323*s*, 1217*m*, 1181*w*, 1161*m*, 1129*s*, 1104*w*, 1071*w*, 1055*m*, 1012*s*, 888*s*, 827*s*, 810*s*, 773*s*, 728*s*, 628*w*, 592*m*; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.8 (d, 1H, ^3J = 7.2 Hz), 8.3 (d, 1H, ^3J = 8.4 Hz), 8.1 (dd, 1H, ^4J = 0.6, ^3J = 1.6 Hz, furyl), 7.9 (dd, 1H, ^3J = 7.8, 7.8. Hz), 7.5 (dd, 1H, ^4J = 1.2, ^3J = 3.6 Hz, furyl), 6.9 (dd, 1H, ^3J = 1.6, 3.2 Hz, furyl); ^{13}C-NMR (400 MHz, acetone-d_6) δ 152.0, 145.9, 144,4, 132, 131.82, 131.8,

130.8, 130.0, 128.6, 128.3, 112.4, 112,2; MS (EI) *m/z* (%): 336 (M^+, 100), 308 (21), 279 (80), 250 (51%).

7,10-Di(furan-2-yl)-1,6-dimethyl-8,9-diazafluoranthene (9b). A mixture of 2,7-dimethylacenaphthylene (0.050 g, 0.28 mmol) and 3,6-di(furan-2-yl)-1,2,4,5-tetrazine (0.12 g, 0.56 mmol) in chlorobenzene (10 ml) was stirred at reflux for 1.5 days. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, hexane). *Note: evaporation of solvent should be carried out below 30 °C (decomposition of product).* Yield (0.047 g, 47%) of a yellow solid. mp 170 °C (dec); IR (KBr): 3105*m*, 3062*m*, 3026*m*, 3008*m*, 2972*m*, 2933*m*, 2879*w*, 2247*w*, 1979*w*, 1954*w*, 1741*w*, 1608*s*, 1573*m*, 1523*w*, 1503*m*, 1479*m*, 1450*s*, 1410*s*, 1380*s*, 1335*s*, 1256*w*, 1218*m*, 1208*s*, 1159*s*, 1110*w*, 1095*s*, 1070*s*, 1037*m*, 1012*s*, 908*s*, 885*m*, 856*s*, 827*m*, 799*w*, 780*m*, 736*s*, 727*s*, 666*w*, 596*s*, 543*m*, 468*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.9 (d, 1H, ^3J = 8.1 Hz), 7.6 (dd, 1H, ^4J = 0.9, ^3J = 1.8 Hz, furyl), 7.4 (d, 1H, ^3J = 8.1 Hz), 7.2 (dd, 1H, ^4J = 0.9, ^3J = 3.3 Hz, furyl), 6.7 (dd, 1H, ^3J = 1.8, ^3J = 3.3 Hz, furyl), 2.3 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 152.4, 146.7, 143.7, 141.1, 139.4, 135.3, 131.5, 129.8, 129.3, 126.5, 112.4, 111.2, 19.8; MS (EI) *m/z* (%): 364 (M^+, 100), 336 (25), 307 (32), 293 (17), 263 (24%).

7,10-Di(pyridin-2-yl)-8,9-diazafluoranthene (10a). A mixture of acenaphthylene (0.50 g, 3.3 mmol) and 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (1.55 g, 6.6 mmol) in chlorobenzene (25 mL) was stirred at reflux overnight. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 15:1–5:1) to yield a yellow solid (0.8 g, 68%). mp 305 °C (dec); IR (KBr): 3091*m*, 3057*m*, 3011*m*, 2937*w*, 2255*w*, 1951*w*, 1896*w*, 1847*w*, 1586*s*, 1569*s*, 1548*m*, 1533*m*, 1476*m*, 1429*s*, 1419*s*, 1381*s*, 1356*m*, 1342*s*, 1294*m*, 1244*m*, 1232*m*, 1150*m*, 1109*m*, 1090*s*, 1045*m*, 1001*m*, 991*s*, 961*m*, 827*s*, 802*s*, 784*s*, 774*s*, 751*s*, 674*m*, 649*m*, 630*m*, 617*m*, 608*m*, 568*w*, 533*w*, 521*w*, 448*w*, 404*m*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.9 (ddd, 2H, ^3J = 4.8, ^4J = 1.8, ^5J = 0.9 Hz, H-C (6′, 6″)), 8.4 (d, 2H, ^3J = 7.2 Hz), 8.36 (dt, 2H, ^3J = 7.8, ^4J = 0.9 Hz, H-C (3′, 3″)), 8.1 (d, ^3J = 8.1 Hz, 2H), 8.0 (td, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-C (5′, 5″)), 7.7 (dd, 2H, ^3J = 7.5, ^3J = 8.1 Hz), 7.6 (ddd, 2H, ^3J = 7.5, ^3J = 4.8, ^4J = 1.2 Hz, H-C (4′, 4″)); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 157.0, 155.7, 149.3, 137.8, 135.8, 133.0, 132.9, 131.1, 130.2, 129.5, 128.6, 125.6, 124.9; MS (EI) *m/z* (%): 358 (M^+, 100), 357 (M^+ −1, 84), 329 (33), 280 (22%).

Dimethyl 8,9-diazafluoranthene-7,10-dicarboxylate (11a). A mixture of acenaphthylene (0.10 g, 0.66 mmol) and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (0.260 g, 1.32 mmol) in chlorobenzene (10 mL) was stirred at reflux overnight. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate 10:1→5:1, ethyl acetate) to yield a yellow solid (0.17 g, 80%). mp 215 °C; IR (KBr): 3125*w*, 3103*w*, 3051*m*, 3008*m*, 2949*m*, 2845*m*, 1976*w*, 1885*w*, 1775*w*, 1726*s* (C=O), 1601*m*, 1523*w*, 1488*w*, 1458*w*, 1434*s*, 1421*s*, 1367*m*, 1336*s*, 1277*s*, 1235*s*, 1217*s*, 1187*m*, 1146*s*, 1090*m*, 1042*s*, 996*m*, 970*m*, 935*m*, 835*s*, 789*s*, 776*s*, 753*m*, 626*m*, 570*w*, 505*w*, 450*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.7 (d, 1H, ^3J = 7.5 Hz), 8.0 (d, 1H, ^3J = 8.1 Hz), 7.7 (dd, 1H, ^3J = 7.8, 7.8 Hz), 4.2 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 165.6, 147.5, 136.1, 132.3, 131.7, 130.2, 129.3, 128.4, 53.3, 29.6; MS (EI) *m/z* (%): 320 (M^+, 14), 262 (33), 203 (100%).

Dimethyl 1,6-dimethyl-8,9-diazafluoranthene-7,10-dicarboxylate (11b). A mixture of 2,7-dimethylacenaphthylene (0.050 g, 0.28 mmol) and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (0.11 g, 0.56 mmol) in dichloromethane (10 mL) was stirred at reflux for 1 d. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, hexane/ethyl acetate 10:1→ hexane/acetone 3:2), to yield a yellow solid (0.07 g, 70%). mp 225 °C; IR (KBr): 3007*w*, 2949*m*, 2258*w*, 1987*w*, 1960*w*, 1724*s* (C=O), 1614*m*, 1577*m*, 1503*m*, 1449*m*, 1434*s*, 1412*s*, 1375*s*, 1344*s*, 1282*s*, 1209*s*, 1193*m*, 1161*s*, 1045*s*, 961*w*, 857*s*, 834*m*, 815*m*, 800*w*, 753*m*, 675*w*, 638*w*, 603*w*, 542*w*, 535*w*, 425*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.0 (d, 1H, ^3J = 8.1 Hz), 7.5 (d, 1H, ^3J = 8.1 Hz), 4.2 (s, 3H, CH_3), 2.7 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 167.2, 149.9, 140. 3, 133.6, 133.0, 131.9, 131.6, 127.6, 126.6, 53.5, 22.4; MS (EI) *m/z* (%): 349 (M^+ + 1, 20), 348 (M^+, 99), 333 (100), 290 (70), 231 (54), 202 (28%).

8,9-Diazafluoranthene-7,10-dicarboxamide (12a). A mixture of acenaphthylene (0.10 g, 0.66 mmol) and 1,2,4,5-tetrazine-3,6-dicarboxamide (0.22 g, 1.32 mmol) in DMSO (10 mL) was heated to 120 °C for 1 h. After 20 min of stirring the mixture turned yellow, then light brown. The reaction was stirred at 100 °C for an additional 10 h, and cooled to room temperature. The orange precipitate was filtered off, washed with methanol and dried *in vacuo.* The ^{1}H-NMR (DMSO-d_6) spectrum has shown mixture of dimethyl-8,9-diazafluoranthene-7,10-dicarboxamide and 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxamide. Both compounds are soluble only in DMSO at 100 °C. Attempts to separate the desired product from tetrazine derivatives using column chromatography or crystallization methods was unsuccessful.

2,5-Di-*tert*-butyl-8,9-diazafluoranthene-7,10-dicarboxamide (12b). A mixture of 3,6-di-*tert*-butylacenaphthylene (0.20 g, 0.76 mmol) and 1,2,4,5-tetrazine-3,6-dicarboxamide (0.250 g, 1.52 mmol) in DMSO was stirred at 120 °C for 1 h. After 10 min stirring the mixture became clear. The reaction was stirred an additional 10 h at 100 °C. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, acetone/methanol 5:1) to yield a light yellow solid (0.29 g, 95%). mp 325 °C (dec); IR (KBr): 3299*s* (br), 2961*s*, 2870*m*, 1676*s* (br), 1651*s*, 1596*s* (br), 1478*s*, 1441*s*, 1396*s*, 1370*s*, 1309*s*, 1258*m*, 1231*s*, 1213*m*, 1179*m*, 1149*m*, 1121*m*, 1102*m*, 1050*m*, 1024*w*, 931*w*, 899*m*, 828*w*, 802*m*, 752*m*, 636*m*, 585*m* (br), 535*m*; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.2 (s, 1H), 8.7 (s, 1H, NH_2), 8.3 (s, 1H), 8.2 (s, 1H, NH_2); ^{13}C-NMR (75 MHz, DMSO-d_6) δ 167.0, 151.6, 150.5, 135.4, 129.6, 129.3, 129.1, 128.7, 127.3, 35.6, 31.4; MS (EI) *m/z* (%): 402 (M^+, 11), 387 (100), 299 (10%).

7,10-Dimethyl-8,9-diazafluoranthene (13a). A mixture of 3,6-dimethyl-1,2,4,5-tetrazine (0.070 g, 0.658 mmol) and acenaphthylene (0.05 g, 0.329 mmol) in *p*-xylene (5 mL) was stirred at 180 °C in an autoclave (600 Psi) for 2 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/acetone 5:1) to yield a yellow solid (0.4 g, 88%). mp 290 °C; IR (KBr): 3054*m*, 2922*m*, 2853*m*, 2178*w*, 1928*w*, 1727*w*, 1598*w*, 1564*m*, 1549*m*, 1483*m*, 1423*s*, 1397*s*, 1367*m*, 1290*w*, 1251*m*, 1222*m*, 1183*s*, 1139*m*, 1093*m*, 1074*m*, 1030*m*, 826*s*, 775*s*, 749*m*, 632*m*, 565*w*, 551*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 1H, ^3J = 7.2 Hz) 8.0 (d, 1H, ^3J = 8.4 Hz), 7.7 (dd, 1H, ^3J = 7.4, 8.1 Hz); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 153.9, 134.1, 134.0, 131.6,

130.3, 130.2, 128.9, 126.5, 21.4; MS (EI) *m/z* (%): 232 (M^+, 100), 203 (58), 189 (15), 101 (16%).

1,6,7,10-Tetramethyl-8,9-diazafluoranthene (13b). A mixture of 3,6-dimethyl-1,2,4,5-tetrazine (0.120 g, 1.12 mmol) and 2,7-dimethylacenaphthylene (0.1 g, 0.56 mmol) in *p*-xylene (5 mL) was stirred at 180 °C in an autoclave (600 Psi) for 3 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ester 5:1, hexane/acetone 3:2) to yield a yellow solid (0.1 g, 70%). mp 210 °C (dec); IR (KBr): 3061*m*, 3037*m*, 3021*m*, 3004*m*, 2926*m*, 2858*m*, 2270*w*, 1978*w*, 1609*s*, 1565*w*, 1531*w*, 1503*s*, 1456*s*, 1431*s*, 1409*s*, 1387*s*, 1375*s*, 1333*m*, 1244*w*, 1227*w*, 1197*s*, 1176*w*, 1158*m*, 1138*w*, 1086*m*, 1051*m*, 1032*m*, 846*s*, 827*w*, 798*s*, 774*m*, 636*w*, 535*m*, 463*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.9 (d, 1H, ^3J = 8.1 Hz), 7.5 (d, 1H, ^3J = 8.4 MHz), 3.2 (s, 3H, CH_3), 3.0 (s, 3H, CH_3); ^{13}C-NMR (400 MHz, $CDCl_3$), 152.1, 137.6, 136.1, 133.3, 132.8, 131.5, 130.3, 127.4; MS (EI) *m/z* (%): 260 (M^+, 100), 217 (32), 202 (36%).

7,10-Bis(methylthio)-8,9-diazafluoranthene (14a). A mixture of acenaphthylene (0.050 g, 0.33 mmol) and 3,6-bis(methylthio)-1,2,4,5-tetrazine (0.11 g, 0.66 mmol) in *p*-xylene (10 ml) was stirred at reflux for 1 day. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, hexane/ethyl acetate 20:1 → 10:1) to yield a yellow solid (0.07 g, 75%). mp 165 °C; IR (KBr): 2923*s*, 2853*s*, 1727*m*, 1590*m*, 1529*w*, 1491*s*, 1413*s*, 1346*m*, 1282*s*, 1165*m*, 1141*m*, 1074*s*, 1040*s*, 983*m*, 828*s*, 796*m*, 776*s*, 695*w*, 570*w*; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.5 (d, 1H, ^3J = 7.2 Hz), 8.1 (d, 1H, ^3J = 8.1 Hz), 7.8 (dd, 1H, ^3J = 7.2, 7.2 Hz), 3.0 (s, 3H, CH_3); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.3, 132.1, 131.9, 130.2, 130.0, 129.1, 128.2, 127.8, 12.9; MS (EI) *m/z* (%): 296 (M^+, 100), 249 (21), 238 (52), 203 (24), 119 (37%).

1,6-Dimethyl-7,10-bis(methylthio)-8,9-diazafluoranthene (14b). A mixture of 2,7-dimethylacenaphthylene (0.10 g, 0.56 mmol) and 3,6-bis(methylthio)-1,2,4,5-tetrazine (0.20 g, 0.11 mmol) in mesitylene (10 mL) was stirred at reflux for 2 d. The solvent was evaporated, the residue was purified by column chromatography (aluminium oxide, hexane → hexane/ethyl acetate 10:1) to yield a yellow solid (0.037 g, 20%). mp 165 °C (dec); IR (KBr): 2955*s*, 2920*s*, 2853*s*, 1717*w*, 1612*m*, 1505 *m*, 1488*m*, 1460*s*, 1444*s*, 1411*s*, 1370*s*, 1334*m*, 1304*m*, 1278*s*, 1212*s*, 1185*s*, 1158*m*, 1084*m*, 1033*s*, 981*s*, 899*w*, 846*s*, 806*m*, 794*s*, 778*m*, 725*w*, 632*m*, 612*m*, 536*m*; ^{1}H-NMR (400 MHz, $CDCl_3$), 7.9 (d, 1H, ^3J = 8.0 Hz), 7.5 (d, 1H, ^3J = 8.0 Hz), 3.2 (s, 3H, CH_3), 2.8 (s, 3H, CH_3); ^{13}C-NMR (400 MHz, $CDCl_3$), 153.0, 139.0, 134.2, 132.5, 132.2, 130.4, 130.1, 126.7, 26.5, 15.2; MS (EI) *m/z* (%): 324 (M^+, 30), 309 (100), 265 (24), 231 (18%).

7,10-Bis(4-chlorobenzyl)-8,9-diazafluoranthene (15a). A mixture of acenaphthylene (0.050 g, 0.33 mmol) and 3,6-bis(4-chlorobenzyl)-1,2,4,5-tetrazine (0.22 g, 0.66 mmol) in *p*-xylene was stirred in an autoclave at 180 °C (600 Psi) for 2.5 d. The solvent was evaporated, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate 5:1, hexane/acetone 1:5) to yield a beige solid (0.082 g, 55%). mp 255 °C; IR (KBr): 3045*m*, 3010*m*, 2928*w*, 2205*w*, 1898*w*, 1595*w*, 1562*w*, 1540*m*, 1490*s*, 1460*m*, 1420*s*, 1381*s*, 1356*m*, 1320*w*, 1268*w*, 1225*w*, 1192*m*, 1143*m*, 1103*s*, 1089*s*, 1052*s*, 1015*s*, 990*w*, 955*w*, 926*w*, 860*m*, 828*s*, 796*s*, 779*s*, 722*m*, 684*w*, 628*w*, 609*w*, 589*w*, 562*w*, 553*m*, 500*m*, 482*m*, 411*w*; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.4 (d, 1H, ^3J = 7.2 Hz), 8.2 (d, 1H, ^3J = 8.4 Hz), 7.8 (dd, ^3J = 7.2, 7.2 Hz), 7.4 (d, ^3J = 8.4 Hz), 7.3 (d, ^3J = 8.8 Hz), 4.9 (s, 2H, CH_2); ^{13}C-NMR (400 MHz, CD_2Cl_2) δ 155.9, 137.2, 135.0, 133.3, 132.8, 132.0, 130.7, 130.63, 130.61, 130.46, 129.14, 129.12, 129.0, 127.1, 40.3; MS (EI) *m/z* (%): 451 (M^+ − 2, 100), 453 (M^+, 77), 416 (11), 276 (8%).

Dimethyl 3,4-dichloro-8,9-diazafluoranthene-7,10-dicarboxylate (18). A mixture of 5,6-dichloroacenaphthylene (0.10 g, 0.45 mmol) and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (0.18 g, 0.9 mmol) was refluxed in CH_2Cl_2 overnight. The solvent was evaporated the residue was washed thoroughly with methanol and dried *in vacuo.* Yield 0.16 g (91%) of a yellow solid. mp 233 °C; IR (KBr): 3119*w*, 3075*w*, 3007*w*, 2956*w*, 1933*w*, 1732*s* (C=O), 1589*w*, 1567*s*, 1437*s*, 1413*s*, 1377*s*, 1339*m*, 1324*m*, 1284*s*, 1201*s*, 1149*s*, 1101*m*, 1088*s*, 1055*s*, 964*m*, 946*w*, 863*w*, 845*s*, 819*m*, 802*m*, 781*m*, 661*w*, 578*w*, 554*w*, 513*w*; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.9 (d, 1H, ^3J = 7.5 Hz), 7.9 (d, 1H, ^3J = 8.0 Hz), 4.2 (s, 3H, CH_3); ^{13}C-NMR (500 MHz, $CDCl_3$) δ 165.8, 147.7, 137.1, 135.8, 135.6, 132.6, 131.4, 129.6, 125.3, 53.9; MS (EI) *m/z* (%): 388 (M^+, 14), 330 (41), 271 (100), 237 (8%).

Crystal data

All X-ray crystal structure determination measurements were made on a *Nonius KappaCCD* area-detector diffractometer[23] using graphite monochromated Mo *K*α radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler.

Compound 3. (Obtained from CH_2Cl_2): $C_{12}H_6Br_2$, M = 309.99, space group: $P2_1/c$ (monoclinic), a = 7.8327(2) Å, b = 19.1058(4) Å, c = 6.8699(2) Å, β = 105.770(1)°, V = 989.39(4) Å^3, Z = 4, μ(Mo *K*α) = 8.167 mm^{-1}, Dx = 2.081 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 22044 measured reflections, 2893 independent reflections, 2315 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97,[24] 128 parameters, $R(F)$ [$I>2\sigma(I)$ reflections] = 0.0402, $wR(F^2)$ [all data] = 0.1004, goodness of fit = 1.086, $\Delta\rho_{max}$ = 0.89 e Å^{-3}.

Compound 4a. (Obtained from acetone): $C_{26}H_{16}N_2$, M = 356.43, space group: $C2/c$ (monoclinic), a = 22.513(2) Å, b = 9.9474(8) Å, c = 7.9414(6) Å, β = 103.717(5)°, V =1727.7(2) Å^3, Z = 4, μ(Mo *K*α) = 0.0806 mm^{-1}, Dx = 1.370 g cm^{-3}, $2\theta_{(max)}$ = 50°, T = 160 K, 10175 measured reflections, 1531 independent reflections, 996 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 129 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0524, $wR(F^2)$ [all data] = 0.1445, goodness of fit = 1.047, $\Delta\rho_{max}$ = 0.37 e Å^{-3}. The molecule possesses crystallographic C_2 symmetry.

Compound 4b. (Obtained from CH_2Cl_2): $C_{28}H_{20}N_2$, M = 384.48, space group: $C2/c$ (monoclinic), a = 21.7712(6) Å, b = 9.9895(3) Å, c = 9.2316(3) Å, β = 104.664(2)°, V =1942.3(1) Å^3, Z = 4, μ(Mo *K*α) = 0.0769 mm^{-1}, Dx = 1.315 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 29059 measured reflections, 2827 independent reflections, 2042 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 138 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0609, $wR(F^2)$ [all data] = 0.1688, goodness of fit = 1.033, $\Delta\rho_{max}$ = 0.41 e Å^{-3}. The molecule has crystallographic C_2 symmetry.

Compound 5a·0.25CH_2Cl_2. (Obtained from CH_2Cl_2): $C_{26.25}H_{16.50}Cl_{0.50}N_2O_2$, M = 409.66, space group: Pn (monoclinic), a = 7.4781(1) Å, b = 22.6399(3) Å, c = 23.8830(3) Å, β = 97.0449(7)°, V =4012.95(9) Å^3, Z = 8, μ(Mo *K*α) = 0.150 mm^{-1},

Dx = 1.356 g cm^{-3}, $2\theta_{(max)}$ = 55°, T = 160 K, 86266 measured reflections, 17993 independent reflections, 14245 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 1132 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0563, $wR(F^2)$ [all data] = 0.1380, goodness of fit = 1.074, $\Delta\rho_{max}$ = 0.45 e Å^{-3}. The asymmetric unit contains four molecules of the polycyclic compound and one molecule of CH_2Cl_2. The atomic coordinates of the model were tested carefully for a relationship from a higher symmetry space group using the program *PLATON*,[22] but none could be found.

Compound 5b·2CHCl$_3$. (Obtained from $CHCl_3$): $C_{30}H_{22}Cl_6N_2O_2$, M = 655.23, space group: $C2/c$ (monoclinic), a = 14.6105(4) Å, b = 18.4987(4) Å, c = 11.5185(3) Å, β = 110.070(1)°, V = 2924.1(1) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.619 mm^{-1}, Dx = 1.488 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 38403 measured reflections, 4282 independent reflections, 2786 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 188 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0563, $wR(F^2)$ [all data] = 0.1608, goodness of fit = 1.033, $\Delta\rho_{max}$ = 0.51 e Å^{-3}. The asymmetric unit contains one half of the polycyclic molecule, which sits across a C_2 axis, plus one molecule of $CHCl_3$.

Compound 7a. (Obtained from acetone): $C_{24}H_{20}N_6$, M = 392.46, space group: $P2_1/n$ (monoclinic), a = 11.4681(2) Å, b = 8.0005(1) Å, c = 20.8185(4) Å, β = 94.471(1)°, V = 1904.30(5) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.0853 mm^{-1}, Dx = 1.369 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 52686 measured reflections, 5570 independent reflections, 4014 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 276 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0509, $wR(F^2)$ [all data] = 0.1330, goodness of fit = 1.040, $\Delta\rho_{max}$ = 0.33 e Å^{-3}.

Compound 8a. (Obtained from CH_2Cl_2): $C_{22}H_{12}N_2S_2$, M = 368.47, space group: $Pbcn$ (orthorhombic), a = 21.4777(6) Å, b = 10.0334(3) Å, c = 7.5250(3) Å, V = 1621.60(9) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.336 mm^{-1}, Dx = 1.509 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 24334 measured reflections, 2364 independent reflections, 1861 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 119 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0503, $wR(F^2)$ [all data] = 0.1365, goodness of fit = 1.039, $\Delta\rho_{max}$ = 0.42 e Å^{-3}. The molecule possesses crystallographic C_2 symmetry about an axis through the middle of the N–N bond and the centre of the molecule.

Compound 8b. (Obtained from CH_2Cl_2): $C_{24}H_{16}N_2S_2$, M = 396.52, space group: $C2/c$ (monoclinic), a = 8.8710(2) Å, b = 10.0494(2) Å, c = 21.2597(5) Å, β = 102.122(2)°, V = 1853.00(7) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.300 mm^{-1}, Dx = 1.421 g cm^{-3}, $2\theta_{(max)}$ = 55°, T = 160 K, 16306 measured reflections, 2108 independent reflections, 1655 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 166 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0552, $wR(F^2)$ [all data] = 0.1484, goodness of fit = 1.088, $\Delta\rho_{max}$ = 0.34 e Å^{-3}. The molecule has crystallographic C_2 symmetry. The heterocyclic five-membered ring is disordered through an approximately 180° rotation of the ring about its bond to the polycyclic system. Two sets of overlapping positions were defined for the unsubstituted atoms of the heterocyclic five-membered ring and the site occupation factor of the major conformation of these groups refined to 0.767(3). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while neighbouring atoms within and between each conformation of the disordered ring were restrained to have similar atomic displacement parameters.

Compound 9b. (Obtained from acetone): $C_{24}H_{16}N_2O_2$, M = 364.40, space group: $P2_1/c$ (monoclinic), a = 8.3569(5) Å, b = 9.9526(6) Å, c = 21.8278(9) Å, β = 100.864(4)°, V = 1782.9(2) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.0875 mm^{-1}, Dx = 1.357 g cm^{-3}, $2\theta_{(max)}$ = 50°, T = 160 K, 21964 measured reflections, 3189 independent reflections, 1544 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 257 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0565, $wR(F^2)$ [all data] = 0.1775, goodness of fit = 1.046, $\Delta\rho_{max}$ = 0.18 e Å^{-3}. The crystals are twinned by a two-fold rotation about [201]. The twin volume fraction of the major twin component is 0.247(2). There is some suggestion that the structure should belong to a higher symmetry space group ($C2/c$), however, attempts to refine the structure in this higher symmetry space group gave inferior results and many systematic absence violations. The current model refuses to converge with the displacement parameters of the two central C atoms, C(4) and C(14), "hunting" around some mean value. It is thought that this is a consequence of matrix correlations brought about by the pseudo-symmetry.

Compound 10a. (Obtained from CH_2Cl_2): $C_{24}H_{14}N_4$, M = 358.40, space group: $Pbcn$ (orthorhombic), a = 21.4230(5) Å, b = 10.0153(3) Å, c = 7.9227(3) Å, V = 1699.88(9) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.0854 mm^{-1}, Dx = 1.400 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 39180 measured reflections, 2479 independent reflections, 1785 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 128 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0698, $wR(F^2)$ [all data] = 0.1879, goodness of fit = 1.062, $\Delta\rho_{max}$ = 0.53 e Å^{-3}. The molecule possesses crystallographic C_2 symmetry about an axis through the middle of the N–N bond and the centre of the molecule.

Compound 11a. (Obtained from hexane/acetone): $C_{18}H_{12}N_2O_4$, M = 320.30, space group: $P2_1$ (monoclinic), a = 9.9472(2) Å, b = 13.2994(2) Å, c = 11.5775(2) Å, β = 114.6580(8)°, V = 1391.95(4) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.110 mm^{-1}, Dx = 1.528 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 39027 measured reflections, 4226 independent reflections, 3767 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 438 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0434, $wR(F^2)$ [all data] = 0.1187, goodness of fit = 1.085, $\Delta\rho_{max}$ = 0.46 e Å^{-3}. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program *PLATON*, but none could be found.

Compound 11b. (Obtained from CH_2Cl_2): $C_{20}H_{16}N_2O_4$, M = 348.36, space group: $C222_1$ (orthorhombic), a = 8.3958(2) Å, b = 9.9699(2) Å, c = 19.624(5) Å, V = 1391.95(4) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.0995 mm^{-1}, Dx = 1.408 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 12353 measured reflections, 1086 independent reflections, 1000 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 122 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0448, $wR(F^2)$ [all data] = 0.1135, goodness of fit = 1.161, $\Delta\rho_{max}$ = 0.23 e Å^{-3}. The molecule exhibits crystallographic C_2 symmetry.

Compound 12a′·0.5CH$_3$OH. (Obtained from MeOH): $C_{24.5}H_{28}N_4O_{2.5}$, M = 418.51, space group: $P2/c$ (monoclinic), a = 15.7180(7) Å, b = 13.3493(6) Å, c = 23.922(1) Å, β = 92.478(2)°,

V = 5014.7(4) Å^3, Z = 8, μ(Mo $K\alpha$) = 0.0732 mm^{-1}, Dx = 1.109 g cm^{-3}, $2\theta_{(max)} = 50°$, T = 160 K, 49418 measured reflections, 8767 independent reflections, 5315 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 553 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0.0933, $wR(F^2)$ [all data] = 0.2758, goodness of fit = 1.053, $\Delta\rho_{max}$ = 0.44 e Å^{-3}. The asymmetric unit contains two molecules of the polycyclic compound and one disordered molecule of MeOH. Attempts to model the solvent molecule were unsuccessful. Therefore the *SQUEEZE*[25] routine of the program *PLATON* was employed. This procedure, which allows the disordered solvent molecule to be omitted entirely from the subsequent refinement model, gave improved refinement results and there were no significant peaks of residual electron density to be found in the voids of the structure. When the solvent molecule is omitted from the model, each unit cell contains two cavities of 566 Å^3. The electron count in each cavity was calculated to be approximately 34 e. As the crystals grew from a MeOH solution, it is assumed the cavities contain MeOH molecules. Allowing for two molecules of MeOH per cavity yields 36 e and this estimate was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient and $F(000)$. As a consequence, the ratio of polycyclic molecules to solvent molecules is 2:1.

Compound 13a. (Obtained from $CDCl_3$): $C_{16}H_{12}N_2$, M = 232.28, space group: $C2/c$ (monoclinic), a = 15.681(1) Å, b = 10.8157(9) Å, c = 15.085(1) Å, β = 118.174(4)°, V = 2255.3(3) Å^3, Z = 8, μ(Mo $K\alpha$) = 0.0818 mm^{-1}, Dx = 1.368 g cm^{-3}, $2\theta_{(max)}$ = 50°, T = 160 K, 16289 measured reflections, 1999 independent reflections, 1251 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 165 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0608, $wR(F^2)$ [all data] = 0.1785, goodness of fit = 1.015, $\Delta\rho_{max}$ = 0.27 e Å^{-3}.

Compound 13b·0.5CH$_3$CN. (Obtained from hexane/acetonitrile): $C_{19}H_{17.5}N_{2.5}$, M = 280.86, space group: *Fddd* (orthorhombic), a = 13.9453(4) Å, b = 25.7283(5) Å, c = 31.5668(7) Å, V = 11325.8(5) Å^3, Z = 32, μ(Mo $K\alpha$) = 0.0786 mm^{-1}, Dx = 1.318 g cm^{-3}, $2\theta_{(max)}$ = 50°, T = 260 K, 36810 measured reflections, 2505 independent reflections, 1612 with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 214 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0559, $wR(F^2)$ [all data] = 0.1748, goodness of fit = 1.014, $\Delta\rho_{max}$ = 0.23 e Å^{-3}. The unit cell contains eight cavities of 105 Å^3 that are occupied by highly disordered solvent molecules. The *SQUEEZE* routine of the *PLATON* program did not produce any improvement in the refinement results, so was not employed, but the electron count per unit cell of 431 e is roughly consistent with two MeCN molecules per cavity, or 0.5 MeCN molecules per polycyclic molecule in the structure. A logical arrangement of atoms in the cavities could not be defined, so the detected residual electron density peaks were assigned arbitrarily to partial occupancy C-atoms and this approximation led to acceptable refinement results for the organic molecule of interest.

Compound 14a. (Obtained from CH_2Cl_2): $C_{16}H_{12}N_2S_2$, M = 296.40, space group: $P2_1/m$ (monoclinic), a = 5.2259(1) Å, b = 18.3970(5), c = 7.1404(2) Å, β = 109.441(2)°, V = 647.33(3) Å^3, Z = 2, μ(Mo $K\alpha$) = 0.400 mm^{-1}, Dx = 1.521 g cm^{-3}, $2\theta_{(max)}$ = 55°, T = 160 K, 14381 measured reflections, 1538 independent reflections, 1273 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 95 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0420, $wR(F^2)$ [all data] = 0.1104, goodness of fit = 1.054, $\Delta\rho_{max}$ = 0.40 e Å^{-3}. The molecule possesses crystallographic mirror symmetry about a plane perpendicular to the molecular plane

Compound 14b. (Obtained from CH_2Cl_2): $C_{18}H_{16}N_2S_2$, M = 324.46, space group: $P\bar{1}$ (triclinic), a = 7.5950(1) Å, b = 10.1858(2) Å, c = 10.5743(2) Å, α = 105.965(1)°, β = 105.306(1)°, γ = 95.0213(9)°, V = 747.20(2) Å^3, Z = 2, μ(Mo $K\alpha$) = 0.353 mm^{-1}, Dx = 1.442 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 21179 measured reflections, 4352 independent reflections, 3454 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 203 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0563, $wR(F^2)$ [all data] = 0.1515, goodness of fit = 1.037, $\Delta\rho_{max}$ = 0.58 e Å^{-3}.

Compound 15a. (Obtained from CH_2Cl_2): $C_{28}H_{18}Cl_2N_2$, M = 453.37, space group: $P\bar{1}$ (triclinic), a = 9.5615(2) Å, b = 9.9958(3) Å, c = 12.9420(3) Å, α = 85.621(1)°, β = 72.671(1)°, γ = 62.302(1)°, V = 1042.65(5) Å^3, Z = 2, μ(Mo $K\alpha$) = 0.331 mm^{-1}, Dx = 1.444 g cm^{-3}, $2\theta_{(max)}$ = 60°, T = 160 K, 26889 measured reflections, 6052 independent reflections, 4975 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 289 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0742, $wR(F^2)$ [all data] = 0.2015, goodness of fit = 1.085, $\Delta\rho_{max}$ = 0.80 e Å^{-3}.

References

1 J. Sauer, *Khim. Geterotsikl. Soedin.*, 1995, **25**, 1307; D. Boger and S. Sakya, *J. Org. Chem.*, 1988, **53**, 1415; S. Sakya, K. Groskopf and D. Boger, *Tetrahedron Lett.*, 1997, **38**, 3805.
2 D. Boger, *Tetrahedron*, 1983, **39**, 2868.
3 R. Carboni and R. Lindsey, *J. Am. Chem. Soc.*, 1959, **81**, 4342.
4 (*a*) A. Schönberg and N. Latif, *J. Chem. Soc.*, 1952, 446; (*b*) H. Tucker, *J. Chem. Soc.*, 1958, 1462; (*c*) D. Morrison, *J. Org. Chem.*, 1960, **25**, 1665.
5 (*a*) For a previous synthesis of **4a**, see: T. Sasaki, K. Kanematsu and T. Hiramatsu, *J. Chem. Soc., Perkin Trans. 1*, 1974, **11**, 1213; (*b*) For synthesis of the related bromophenyl derivative, see: V. M. Tsefrikas, S. Arns, P. M. Merner, C. C. Warford, B. L. Merner, L. T. Scott and G. Bodwell, *J. Org. Lett.*, 2006, **8**, 5195.
6 (*a*) G. Wittig, H. Reppe and T. Eicher, *Liebings Ann. Chem.*, 1961, **643**, 47; (*b*) P. Belliard and E. Marechal, *Bull. Chem. Soc. France*, 1972, **11**, 4255.
7 For a previous synthesis of **10a**, see: (*a*) A. Pozharskii, V. Ozeryanskii and N. Vistorobskii, *Russ. Chem. Bull.*, 2003, **52**, 218; (*b*) M. Ghedini, F. Neve and M. Bruno, *Inorg. Chim. Acta*, 1988, **143**, 89.
8 (*a*) S. Kashino, D. Zacharias, R. Peck, J. Glusker, T. Bhatt and M. Coombs, *Cancer Res.*, 1986, **46**, 1817; (*b*) L. Weis, A. Rummel, S. Masten, J. Trosko and B. Upham, *Env. Health Persp.*, 1998, **106**, 17; (*c*) K. Troche, S. Braga, V. Coluci and D. Galvao, *Int. J. Quantum Chem.*, 2005, **103**, 718; (*d*) K. Prout, A. Smith, G. Daub, D. Zacharias and J. Glusker, *Carcinogenesis*, 1992, **13**, 1775.
9 F. Cozzi, U. Sjöstrand and K. Mislow, *J. Organomet. Chem.*, 1979, **174**, C1.
10 (*a*) J. Blount, F. Cozzi, J. Damewood, L. Iroff, U. Sjöstrand and K. Mislow, *J. Am. Chem. Soc.*, 1980, **102**, 99; (*b*) C. Wolf and B. Ghebremariam, *Tetrahedron: Asymmetry*, 2002, **13**, 1153; (*c*) C. Wolf and B. Ghebremariam, *Synthesis*, 2002, **6**, 749; (*d*) F. Imashiro, K. Takegoshi, A. Saika, Z. Taira and Y. Asahi, *J. Am. Chem. Soc.*, 1985, **107**, 2341.
11 (*a*) R. Franck and E. Leser, *J. Am. Chem. Soc*, 1969, **91**, 1577; (*b*) F. Franck and E. Leser, *J. Org. Chem.*, 1970, **35**, 3932; (*c*) J. Anderson, R. Franck and W. Mandella, *J. Am. Chem. Soc.*, 1972, **94**, 4608; (*d*) J. Handal, J. White, R. Franck, Y. Yuh and N. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 3345; (*e*) J. White, R. Franck, Y. Yuh and N. Allinger, *J. Am. Chem. Soc.*, 1979, **101**, 5654.

12 D. Seyferth and S. Vick, *J. Organomet. Chem.*, 1977, **141**, 173.
13 (*a*) R. Clough and J. Roberts, *J. Am. Chem. Soc.*, 1976, **98**, 1018; (*b*) P. Evrard, P. Piret and M. van Meerssche, *Acta Crystallogr., Sect. B*, 1972, **28**, 497; (*c*) R. Ogilvie, Ph.D. Thesis, Massachusetts Institute of Technology, 1971; (*d*) R. Clough, W. Marsh and J. Roberts, *J. Org. Chem.*, 1976, **41**, 3603.
14 F. Cozzi, M. Cinquini, R. Annunziata, T. Dwyer and J. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 5729.
15 M. Newman, *J. Am. Chem. Soc.*, 1940, **62**, 2295.
16 (*a*) R. Armstrong, H. Ammon and J. Darnow, *J. Am. Chem. Soc.*, 1987, **109**, 2077; (*b*) M. Newman and A. Hussey, *J. Am. Chem. Soc.*, 1947, **69**, 3023; (*c*) A. Kitaigorodsky and V. Dashevsky;, *Tetrahedron*, 1968, **24**, 5917.
17 A. Borchardt, K. Hardcastle, P. Gantzel and J. Siegel, *Tetrahedron Lett.*, 1993, **34**, 273.
18 *Gaussian 03, Revision A.6*, Gaussian, Inc., Wallingford, CA, 1998.
19 Y. Zhao and D. Truhlar, *Theor. Chem. Acccts.*, 2008, **120**, 215.
20 T. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007.
21 K. Baldridge and J. Greenberg, *Mol. Graphics*, 1995, **13**, 63.
22 A. Spek, *PLATON, Program for the Analysis of Molecular Geometry*, University of Utrecht, The Netherlands, 2007.
23 R. Hooft, *Kappa CCD Collect Software*, Nonius BV, Delft, The Netherlands, 1999.
24 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.
25 P. von der Sluis and A. Spek, *Acta Crystallogr.*, 1990, **A46**, 194.

