



Supporting Information

for

Knoevenagel condensation of 4,5- and 1,8-diazafluorenes

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Analytical data, protonation data, thin-layer chromatography data, X-ray data, spectra of synthesized compounds

1. Analytical data

9-(3-Nitrobenzylidene)-9H-4,5-diazafluorene (3a).

Yields: 20.4 mg, 38% (method A1); 7.5 mg, 14% (method B1), 15.1 mg, 18% (method B2); mp 208.1–209.9 °C; δ_{H} (CDCl₃, 500.13 MHz): 8.76 (d, $J = 3.3$ Hz, 1H), 8.67 (d, $J = 3.3$ Hz, 1H), 8.43 (s, 1H), 8.31 (d, $J = 7.5$ Hz, 1H), 8.12 (d, $J = 7.5$ Hz, 1H), 7.92 (d, $J = 7.2$ Hz, 1H), 7.74 (s, 1H), 7.72–7.67 (m, 2H), 7.37 (dd, $^1J = 7.5$ Hz, $^2J = 4.9$ Hz, 1H), 7.10 (dd, $^1J = 7.5$ Hz, $^2J = 4.9$ Hz, 1H); δ_{C} (CDCl₃, 125.76 MHz): 158.7, 156.8, 151.1, 151.1, 148.6, 137.5, 135.4, 133.4, 133.2, 131.2, 130.6, 130.1, 128.0, 127.8, 124.2, 123.7, 123.3, 122.8; HRMS found: $[\text{M}]^{+\cdot}$ 301.0847, C₁₈H₁₁N₃O₂ requires $[\text{M}]^{+\cdot}$ 301.0846; Elem. Analysis. Found: C, 71.68; H, 3.75; N, 13.72% for C₁₈H₁₁N₃O₂, requires: C, 71.75; H, 3.68; N, 13.95%.

9-(4-Bromobenzylidene)-9H-4,5-diazafluorene (3b).

Yields: 50.2 mg, 84% (method A1); 16.7 mg, 28% (method B1); 16.7 mg, 28% (method B2); mp 209.2–210.4 °C; δ_{H} (CDCl₃, 500.13 MHz): 8.73 (d, $J = 3.9$ Hz, 1H), 8.66 (d, $J = 3.6$ Hz, 1H), 8.09 (d, $J = 7.2$ Hz, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 7.68 (s, 1H), 7.62 (d, $J = 7.9$ Hz, 2H), 7.44 (d, $J = 7.9$ Hz, 2H), 7.34 (dd, $^1J = 3.9$ Hz, $^2J = 7.2$ Hz, 1H), 7.11 (dd, $^1J = 3.6$ Hz, $^2J = 7.2$ Hz, 1H); δ_{C} (CDCl₃, 125.76 MHz): 158.4, 156.5, 150.7, 134.7, 133.7, 132.1, 131.5, 131.4, 131.0, 129.9, 127.8, 123.3, 123.1, 122.6; HRMS found: $[\text{M}]^{+\cdot}$ 334.0099, C₁₈H₁₁N₂Br requires $[\text{M}]^{+\cdot}$ 334.0100; Elem. Analysis. Found: C, 64.52; H, 3.34; Br, 23.92; N, 8.22% for C₁₈H₁₁N₂Br, requires: C, 64.50; H, 3.31; Br, 23.84; N, 8.36%.

9-Benzylidene-9H-4,5-diazafluorene (3c).

Yields: 20.6 mg, 45% (method A1), 15.5 mg, 34% (method B2); mp 155.8–158.1 °C; δ_{H} (CDCl₃, 500.13 MHz): 8.74 (d, $J = 2.9$ Hz, 1H), 8.65 (d, $J = 2.8$ Hz, 1H), 8.12 (d, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 7.7$ Hz, 1H), 7.80 (s, 1H), 7.57 (d, $J = 6.8$ Hz, 2H), 7.51–7.48 (m, 2H), 7.46 (d, $J = 7.1$ Hz, 1H), 7.35 (dd, $^1J = 2.9$ Hz, $^2J = 7.8$ Hz, 1H), 7.09 (dd, $^1J = 2.8$ Hz, $^2J = 7.7$ Hz, 1H); δ_{C} (CDCl₃, 125.76 MHz): 158.3, 156.4, 150.5, 135.8, 133.9, 131.5, 131.5, 131.3, 130.9, 129.4, 129.0, 128.9, 127.7, 123.1, 122.6; the NMR spectrum corresponds to that described in [1]; HRMS found: $[\text{M}-1]^{+\cdot}$ 255.0916, C₁₈H₁₁N₂ requires $[\text{M}-1]^{+\cdot}$ 255.0917; Elem. Analysis. Found: C, 84.12; H, 4.94; N, 10.94% for C₁₈H₁₂N₂, requires: C, 84.35; H, 4.72; N, 10.93%.

9-(4-Methoxybenzylidene)-9H-4,5-diazafluorene (3d).

Yields: 34.2 mg, 67% (method A1); 14.8 mg, 29% (method B2); mp 235.5–237.3 °C; δ_{H} (CDCl₃, 300.13 MHz): 8.71 (dd, $^1J = 1.2$ Hz, $^2J = 4.9$ Hz, 1H), 8.65 (dd, $^1J = 1.2$ Hz, $^2J = 4.9$ Hz, 1H), 8.08 (dd, $^1J = 1.2$ Hz, $^2J = 7.8$ Hz, 1H), 8.03 (dd, $^1J = 1.2$ Hz, $^2J = 8.1$ Hz, 1H), 7.73 (s, 1H), 7.53 (d, $J =$

8.6 Hz, 2H), 7.32 (dd, $^1J = 4.9$ Hz, $^2J = 7.8$ Hz, 1H), 7.11 (dd, $^1J = 4.9$ Hz, $^2J = 8.1$ Hz, 1H), 7.01 (d, $J = 8.6$ Hz, 2H), 3.89 (s, 3H); δ_C (CDCl₃, 75.47 MHz): 160.3, 158.1, 156.1, 150.2, 150.1, 134.1, 131.6, 131.3, 131.2, 129.6, 128.0, 127.5, 122.9, 122.5, 114.3, 55.5; HRMS found: $[M]^+$ 286.1103, C₁₉H₁₄N₂O requires $[M]^+$ 286.1101; Elem. Analysis. Found: C, 80.02; H, 4.91; N, 9.71% for C₁₉H₁₄N₂O, requires: C, 79.70; H, 4.93; N, 9.78%.

9-(3-Nitrobenzylidene)-9H-1,8-diazafluorene (4a).

Yields: 36.0 mg, 67% (method A2, ethanol); 26.9 mg, 50% (method A2, toluene); 25.3 mg, 47% (method B1); 15.1 mg, 28% (method B2); mp 184.7–186.0 °C; δ_H (CDCl₃, 500.13 MHz): 10.03 (s, 1H), 8.70–8.67 (m, 2H), 8.59 (d, $J = 4.3$ Hz, 1H), 8.28 (s, 1H), 8.26 (d, $J = 8.8$ Hz, 1H), 8.04 (d, $J = 7.3$ Hz, 1H), 7.98 (d, $J = 7.3$ Hz, 1H), 7.64 (dd, $^1J = 7.8$ Hz, $^2J = 7.8$ Hz, 1H), 7.35–7.31 (m, 2H); δ_C (CDCl₃, 125.76 MHz): 157.0, 155.0, 148.8, 148.4, 138.7, 136.7, 134.9, 132.8, 132.3, 130.3, 129.2, 128.0, 127.9, 124.4, 123.3; HRMS found: $[M-1]^{++}$ 300.0767, C₁₈H₁₀N₃O₂ requires $[M-1]^{++}$ 300.0768; Elem. Analysis. Found: 71.72; H, 3.64; N, 13.89% for C₁₈H₁₁N₃O₂, requires: C, 71.75; H, 3.68; N, 13.95%.

9-(4-Bromobenzylidene)-9H-1,8-diazafluorene (4b).

Yields: 35.9 mg, 60% (method A2, ethanol); 16.2 mg, 27% (method A2, toluene); 19.1 mg, 32% (method B1); 26.8 mg, 45% (method B2); mp 162.3–163.6 °C; δ_H (CDCl₃, 500.13 MHz): 8.64 (d, $J = 4.3$ Hz, 1H), 8.60 (d, $J = 8.2$ Hz, 2H), 8.56 (d, $J = 4.3$ Hz, 1H), 8.25 (s, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.98 (d, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 2H), 7.32–7.28 (m, 2H); δ_C (CDCl₃, 125.76 MHz): 157.5, 155.4, 148.7, 148.2, 134.8, 134.4, 134.2, 132.9, 132.4, 131.6, 129.8, 127.7, 127.6, 124.9, 122.7, 122.6; HRMS found: $[M-1]^{++}$ 333.0016, C₁₈H₁₀N₂Br requires $[M-1]^{++}$ 333.0022; Elem. Analysis. Found: 64.57; H, 3.35; Br, 23.96; N, 8.12% for C₁₈H₁₀N₂Br, requires: C, 64.50; H, 3.31; Br, 23.84; N, 8.36%.

9-Benzylidene-9H-1,8-diazafluorene (4c).

Yields: 38.9 mg, 85% (method A2, ethanol); 18.7 mg, 41% (method A2, toluene); 26.1 mg, 57% (method B2); mp 112.1–113.9 °C; δ_H (CDCl₃, 400.13 MHz): 8.72 (d, $J = 7.5$ Hz, 2H), 8.67 (d, $J = 4.1$ Hz, 1H), 8.60 (d, $J = 4.2$ Hz, 1H), 8.36 (s, 1H), 8.04 (d, $J = 7.5$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.54–7.50 (m, 2H), 7.47–7.43 (m, 1H), 7.32–7.28 (m, 1H); δ_C (CDCl₃, 75.47 MHz): 157.7, 155.6, 148.6, 148.3, 136.0, 135.2, 133.3, 132.2, 130.4, 129.7, 128.4, 127.7, 127.6, 122.6, 122.5; HRMS found: $[M-1]^{++}$ 255.0913, C₁₉H₁₁N₂ requires $[M-1]^{++}$ 255.0917; Elem. Analysis. Found: C, 84.42; H, 4.79; N, 10.79% for C₁₈H₁₂N₂, requires: C, 84.35; H, 4.72; N, 10.93%.

9-(4-Methoxybenzylidene)-9H-1,8-diazafluorene (4d).

Yields: 19.9 mg, 39% (method A2, ethanol); 26.6 mg, 52% (method A2, toluene); 13.8 mg, 27% (method B2); mp 155.9 °C with subsequent decomposition; δ_{H} (CDCl₃, 300.13 MHz): 8.83 (d, $J = 8.8$ Hz, 2H), 8.69 (d, $J = 4.8$ Hz, 1H), 8.59 (d, $J = 4.8$ Hz, 1H), 8.33 (s, 1H), 8.06 (dd, $^1J = 0.9$ Hz, $^2J = 7.6$ Hz, 1H), 8.00 (dd, $^1J = 0.9$ Hz, $^2J = 7.7$ Hz, 1H), 7.32–7.28 (m, 2H), 7.05 (d, $J = 8.8$ Hz, 2H), 3.91 (s, 3H); δ_{C} (CDCl₃, 125.76 MHz): 161.5, 157.9, 155.6, 148.4, 148.0, 136.0, 135.7, 131.7, 129.7, 129.1, 128.3, 127.6, 127.6, 122.0, 121.9, 114.0, 55.5; HRMS found: $[\text{M}-1]^+$ 285.1023, C₁₉H₁₃O₁N₂ requires $[\text{M}-1]^+$ 285.1022; Elem. Analysis. Found: C, 79.81; H, 4.89; N, 9.69% for C₁₉H₁₄N₂O, requires: C, 79.70; H, 4.93; N, 9.78%.

9-(Di(pyridin-2-yl)methylene)-9H-4,5-diazafluorene (4,5-DPDAF).

Yield: 32.2 mg, 54% (method A2, toluene); mp 252.9–255.1 °C; δ_{H} (CDCl₃, 500.13 MHz): 8.77 (d, $J = 3.4$ Hz, 2H), 8.60 (d, $J = 3.4$ Hz, 2H), 7.82 (dd, $^1J = 7.3$ Hz, $^2J = 7.3$ Hz, 2H), 7.57 (d, $J = 7.3$ Hz, 2H), 7.41 (dd, $^1J = 4.9$ Hz, $^2J = 7.3$ Hz, 2H), 6.97 (dd, $^1J = 4.9$ Hz, $^2J = 7.3$ Hz, 2H), 7.57 (d, $J = 7.3$ Hz, 2H); δ_{C} (CDCl₃, 125.76 MHz): 158.2, 158.0, 150.5, 144.6, 137.3, 132.6, 132.0, 131.8, 125.5, 123.8, 122.6; HRMS found: $[\text{M}-1]^+$ 333.1138, C₂₂H₁₃N₄ requires $[\text{M}-1]^+$ 333.1135; Elem. Analysis. Found: C, 79.25; H, 4.18; N, 16.57% for C₂₂H₁₄N₄, requires: C, 79.02; H, 4.22; N, 16.76%.

9-(Di(pyridin-2-yl)methylene)-9H-1,8-diazafluorene (1,8-DPDAF).

Yield: 20.3 mg, 34% (method A2, toluene); mp 189.4 °C with subsequent decomposition; δ_{H} ((CD₃)₂CO, 500.13 MHz): 8.53 (ddd, $^1J = 4.9$ Hz, $^2J = 1.7$ Hz, $^3J = 0.9$ Hz, 2H), 8.19 (dd, $^1J = 7.7$ Hz, $^2J = 1.7$ Hz, 2H), 8.16 (dd, $^1J = 4.8$ Hz, $^2J = 1.5$ Hz, 2H), 7.75 (ddd, $^1J = 7.7$ Hz, $^2J = 7.7$ Hz, $^3J = 1.8$ Hz, 2H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.30 (ddd, $^1J = 7.5$ Hz, $^2J = 5.0$ Hz, $^3J = 1.2$ Hz, 2H), 7.27 (dd, $^1J = 7.7$ Hz, $^2J = 4.9$ Hz, 2H); δ_{C} ((CD₃)₂CO, 125.76 MHz): 159.9, 157.1, 149.6, 148.8, 135.7, 133.6, 133.6, 132.4, 128.5, 127.3, 123.8, 123.2; HRMS found: $[\text{M}-1]^+$ 333.1133, C₂₂H₁₃N₄ requires $[\text{M}-1]^+$ 333.1135; Elem. Analysis. Found: C, 79.15; H, 4.25; N, 16.60% for C₂₂H₁₄N₄, requires: C, 79.02; H, 4.22; N, 16.76%.

3. Evaluation of stability of compounds 3b and 4b in acetic acid.

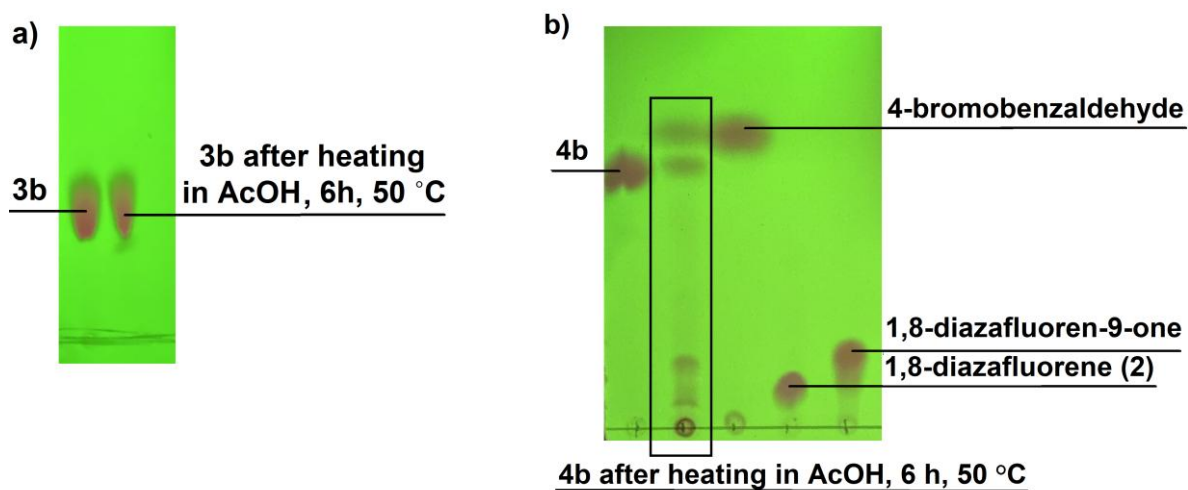
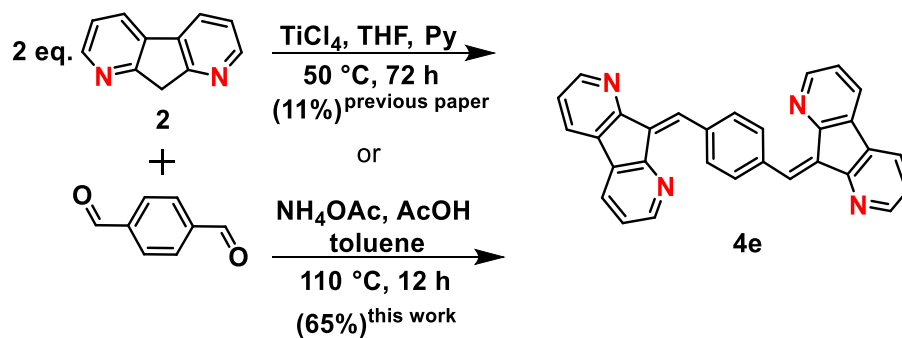


Figure S3: TLC data on compounds **3b** (a) and **4b** (b) after heating at 50 °C in AcOH.



Scheme S1: Condensation approaches of **2** with terephthalaldehyde. Reaction yields are given in parenthesis.

4. X-ray data

Supplementary Note S1: X-ray structure of 1,8-DPDAF

1,8-DPDAF crystallizes as colorless plates. The conformation of the pyridine fragments is non-planar relative to the diazafluorene fragment due to sterical repulsion of pyridine moieties: $\varphi_1 = 68.1(4)^\circ$ ($N_3-C_{13}-C_{12}-C_{10}$) and $\varphi_2 = 83.0(4)^\circ$ ($N_4-C_{18}-C_{12}-C_{10}$) (Figure S4a). Molecules are packed into stacks along the *a*-axis due to π -stacking interactions between diazafluorenes and hydrogen bonds with water molecule (Figure S4b). The structure also has lattice channels of approximately 984 \AA^3 with removed disordered water molecules (Figure S4c).

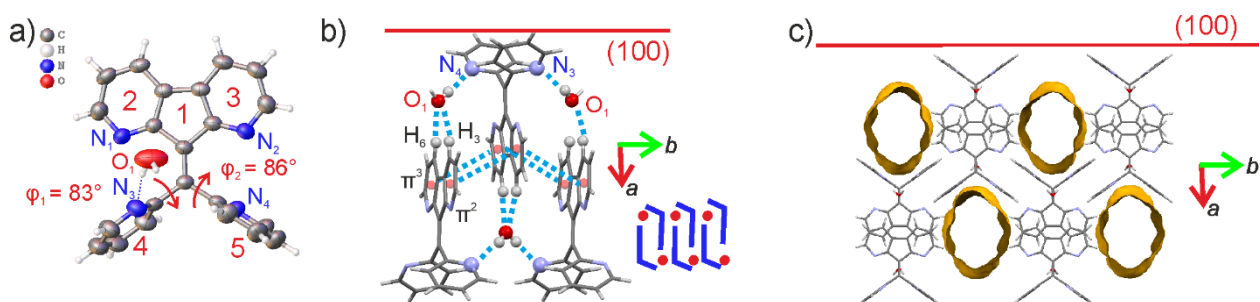


Figure S4: Molecular structure, atom and cycle numbering of 1,8-DPDAF with anisotropic displacement ellipsoids drawn at a 50% probability level (a); crystal structure fragment with π -stacking of 1,8-DPDAF (b). Lattice channels of approximately 405 \AA^3 as mapped by the contact yellow surface of a probe with a radius of 1.2 \AA . Dashed blue lines represent noncovalent interactions. The arrows indicate the orientation of crystallographic axes. Red line shows the (001) plane. The schematic packing motif is shown in blue, water molecules are shown as red dots.

Table S1: Crystal data, data collection, and structure refinement parameters for 4,5-DPDAF, Zn-4,5-DPDAF and 1,8- DPDAF.

	4,5-DPDAF	Zn-4,5-DPDAF	1,8-DPDAF
Chemical formula	C ₂₂ H ₁₄ N ₄	C ₄₄ H ₂₈ Cl ₂ N ₈ Zn ₂ ·2(ZnCl ₃ H ₂ O)·1.5(O)	C ₂₂ H ₁₄ N ₄ ·H ₂ O·1[H ₂ O]
M_r	334.37	1273.85	370.40
Crystal system, space group	monoclinic, <i>C2/c</i>	orthorhombic, <i>Pbam</i>	orthorhombic, <i>Pbca</i>
a, b, c (Å)	13.7111 (8), 10.5932 (6), 23.4823 (15)	15.659 (6), 12.596 (4), 13.175 (5)	19.9962 (14), 7.1401 (7), 29.647 (2)
β (°)	105.598 (7)	90	90
V (Å ³)	3285.1 (4)	2598.7 (16)	4232.9 (6)
Z/Z'	8/1	2/0.5	2/1
D_{calcd} (g cm ⁻³)	1.352	1.628	1.162
Solvent mask in 1 void per unit cell			984 Å ³ (136 e)
No. of measured and independent reflections	16194, 2971, 2441	7194, 2290, 1449	49107, 3856, 2659
R_{int}	0.031	0.081	0.102
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.097, 1.03	0.099, 0.288, 1.13	0.075, 0.204, 1.05
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.12, -0.18	2.28, -1.28	0.23, -0.20

Table S2: Noncovalent interactions for 4,5-DPDAF, Zn-4,5-DPDAF and 1,8-DPDAF.

	Interactions	Cg–Cg, Å	D_{pln} , Å	π – π , °	
4,5-DPDAF	$\pi^1 \cdots \pi^2$	3.5029(9)	3.4840(6)	1.17(7)	
	$\pi^1 \cdots \pi^3$	3.5424(9)	3.4135(6)	1.15(7)	
	$\pi^2 \cdots \pi^2$	3.9452(9)	3.4765(6)	0.00(7)	
	$\pi^3 \cdots \pi^3$	3.6234(9)	3.3987(6)	0.00(7)	
	$\pi^4 \cdots \pi^4$	3.7687(9)	3.5831(6)	17.40(7)	
		H \cdots Cg (Å)	D_{pln} (Å)	C–H \cdots Cg (°)	
		C ₁₆ –H \cdots π^5	3.09	3.08	134
		C ₃ –H \cdots π^4 (intra)	2.82	2.55	145
		C ₇ –H \cdots π^5 (intra)	2.92	2.60	146
		H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (°)	
	C ₁₄ –H \cdots N ₁	2.52	3.393(2)	157	
	C ₁₉ –H \cdots N ₂	2.72	3.475(2)	139	
Zn-4,5-DPDAF		Cg–Cg, Å	D_{pln} , Å	π – π , °	
		$\pi^1 \cdots \pi^1$	3.447(6)	3.411(5)	0.0(6)
		$\pi^1 \cdots \pi^2$	3.949(6)	3.406(5)	2.3(5)
		$\pi^2 \cdots \pi^2$	3.553(6)	3.41	3.414(4)
		$\pi^2 \cdots \pi^3$	4.37	4.08	39
		H/Cl \cdots Cg (Å)	D_{pln} (Å)	C–H/Cl \cdots Cg (°)	
		C ₁ –H \cdots π^2	3.09	2.99	109
		C ₉ –H \cdots π^3 (intra)	2.98	2.53	139
		Zn ₁ –Cl ₁ \cdots π^1	3.737(7)	3.291	100.64(18)
		Cl \cdots O (Å)	Zn–Cl \cdots O (°)	Cl \cdots O–Zn (°)	
	Cl ₂ \cdots O ₁	3.20	113	125	
1,8-DPDAF		Cg–Cg, Å	D_{pln} , Å	π – π , °	
		$\pi^2 \cdots \pi^2$	4.0132(15)	3.4140(10)	6.19(12)
		$\pi^3 \cdots \pi^3$	4.0391(15)	3.3892(10)	7.14(12)
		H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (°)	
		O ₁ –H _{1a} \cdots N ₄	2.09	2.941(4)	179
		O ₁ –H _{1b} \cdots N ₃	2.16	2.970(4)	160
		C ₃ –H \cdots O ₁	2.58	3.476(4)	162
	C ₆ –H \cdots O ₁	2.62	3.512(4)	161	

Cg is the aromatic ring center; D_{pln} is the nearest distance between H-atom and aromatic ring plane.

Atom labels are corresponding to the label scheme in Figure 2 and Figure S4.

5. Spectroscopy data

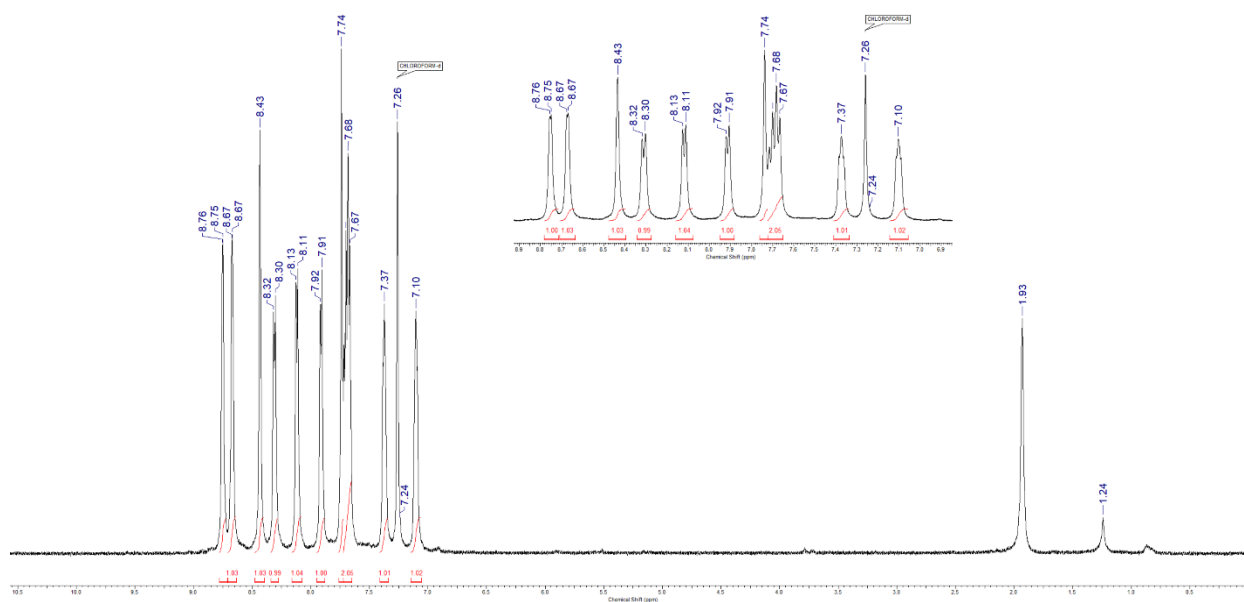


Figure S5: ¹H NMR spectrum of 9-(3-nitrobenzylidene)-9H-4,5-diazafluorene (**3a**) in CDCl₃.

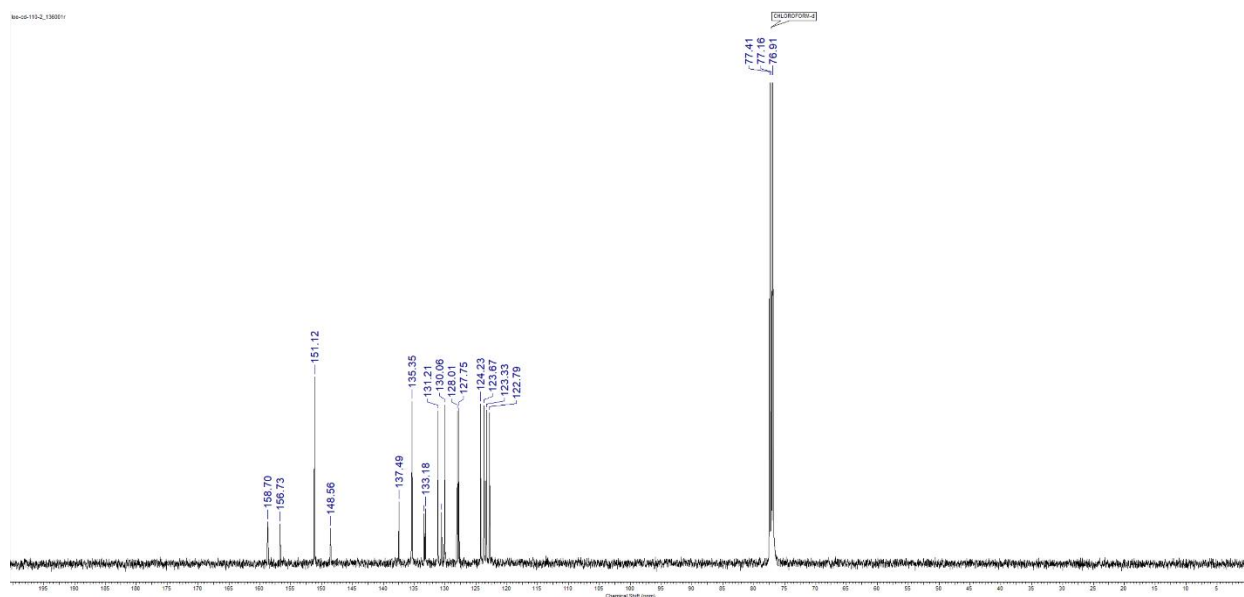


Figure S6: ¹³C NMR spectrum of 9-(3-nitrobenzylidene)-9H-4,5-diazafluorene (**3a**) in CDCl₃.

cd-110m #5 RT: 0.22 AV: 1 NL: 1.85E6
T: + c EI Full ms [32.50-330.50]

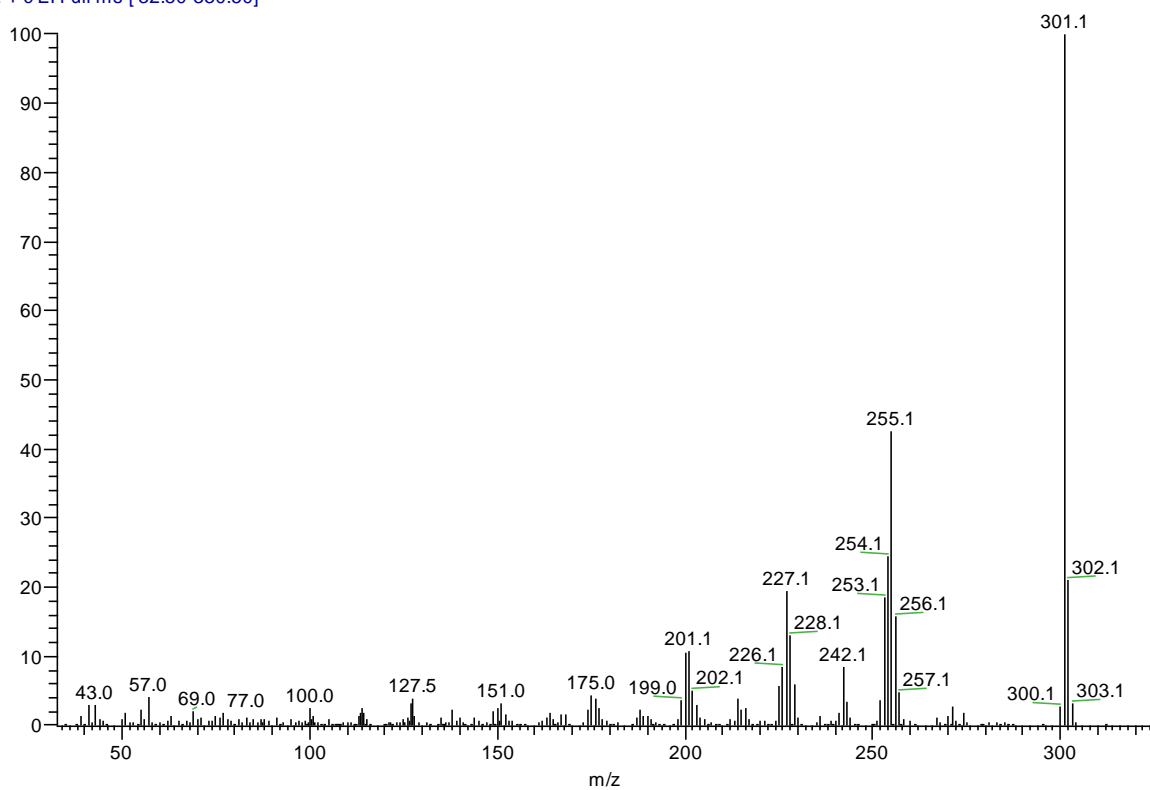


Figure S7: HRMS overview spectrum of 9-(3-nitrobenzylidene)-9H-4,5-diazafluorene (**3a**) ($T_{\text{source}} = 70\text{ }^{\circ}\text{C}$, $T_{\text{probe}} = 200\text{ }^{\circ}\text{C}$).

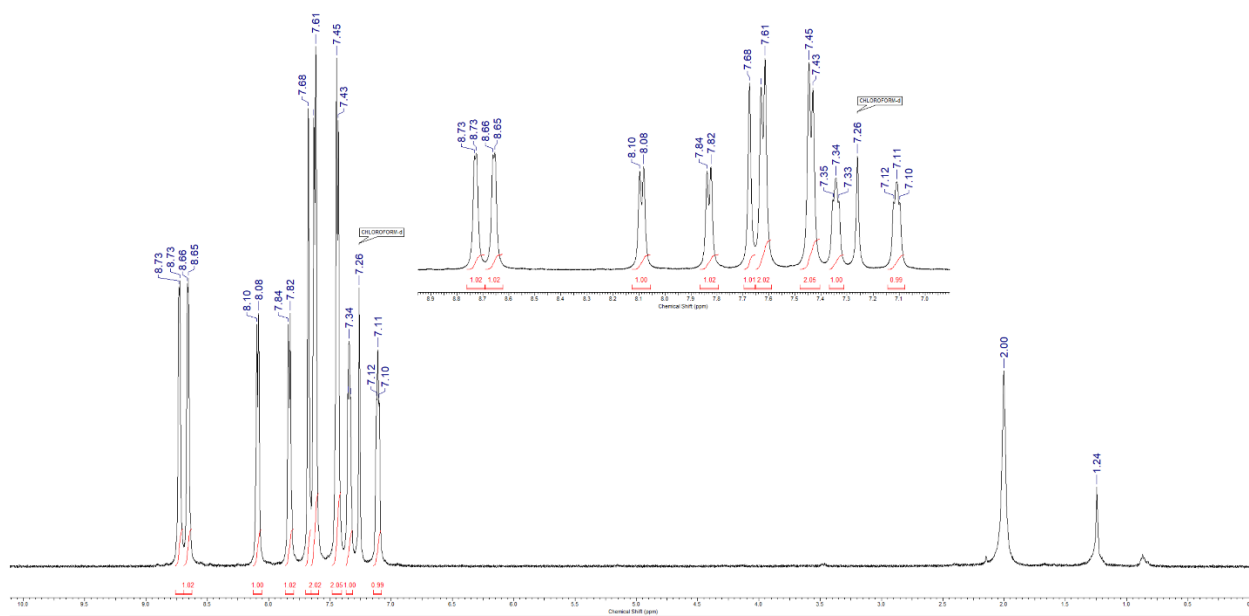


Figure S8: ^1H NMR spectrum of 9-(4-bromobenzylidene)-9H-4,5-diazafluorene (**3b**) in CDCl_3 .

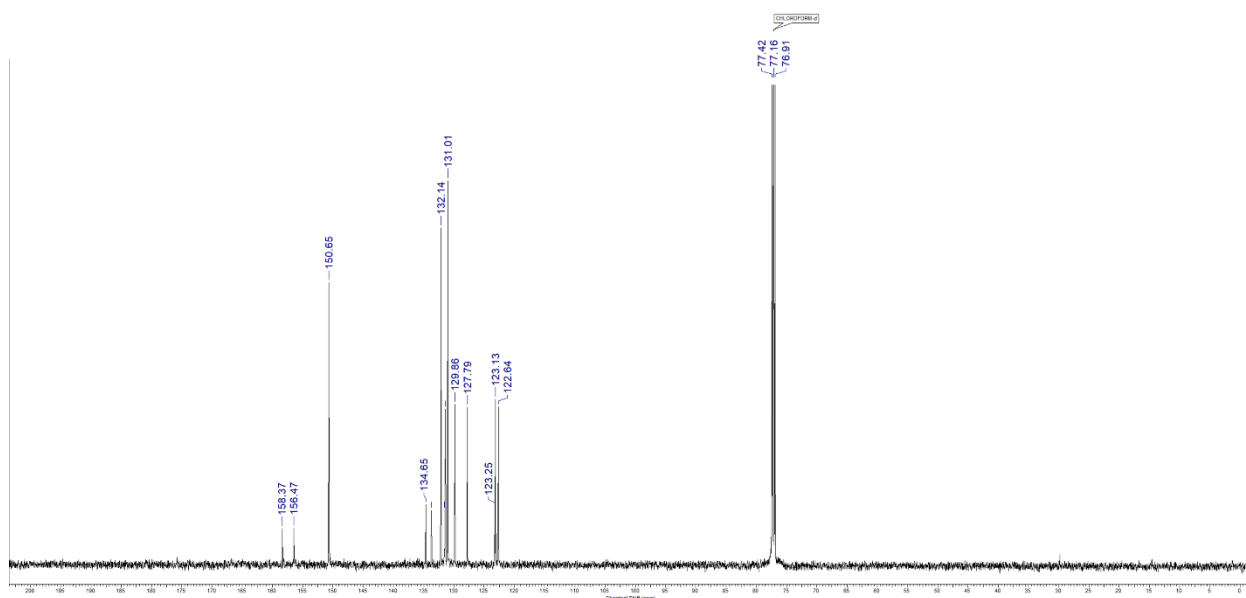


Figure S9: ^{13}C NMR spectrum of 9-(4-bromobenzylidene)-9H-4,5-diazafluorene (**3b**) in CDCl_3 .

cd-55m #17 RT: 0.95 AV: 1 NL: 1.02E7
T: + c EI Full ms [32.50-370.50]

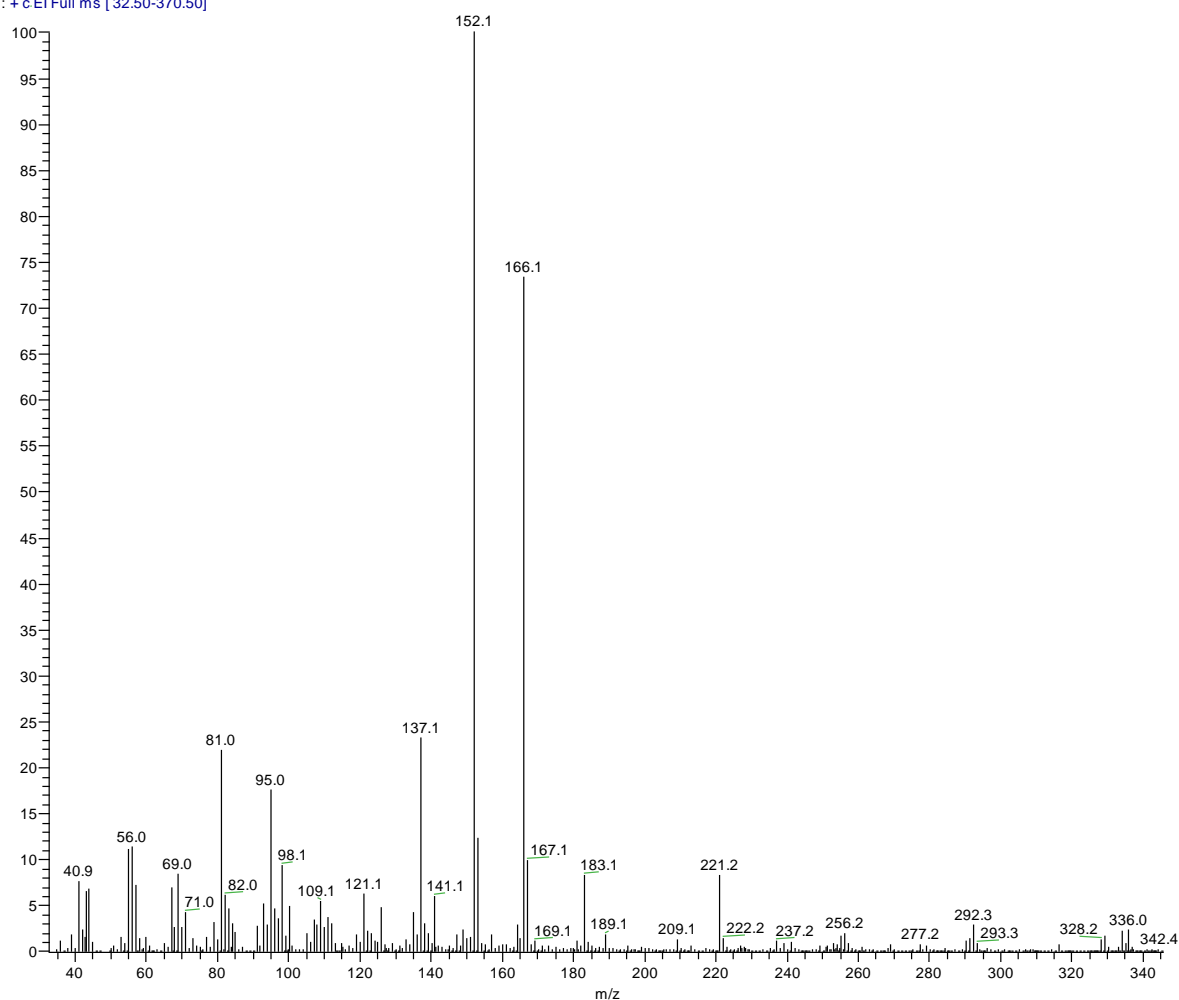


Figure S10: HRMS overview spectrum of 9-(4-bromobenzylidene)-9H-4,5-diazafluorene (**3b**) ($T_{\text{source}} = 75\text{ }^\circ\text{C}$, $T_{\text{probe}} = 160\text{ }^\circ\text{C}$).

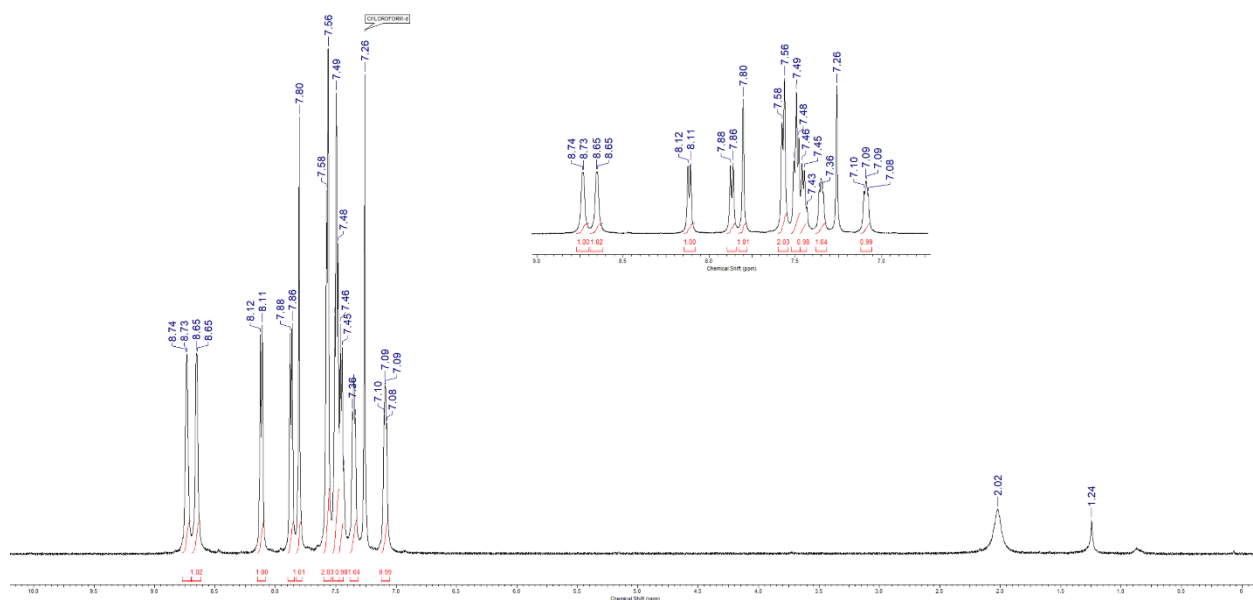


Figure S11: ¹H NMR spectrum of 9-benzylidene-9H-4,5-diazafluorene (**3c**) in CDCl₃.

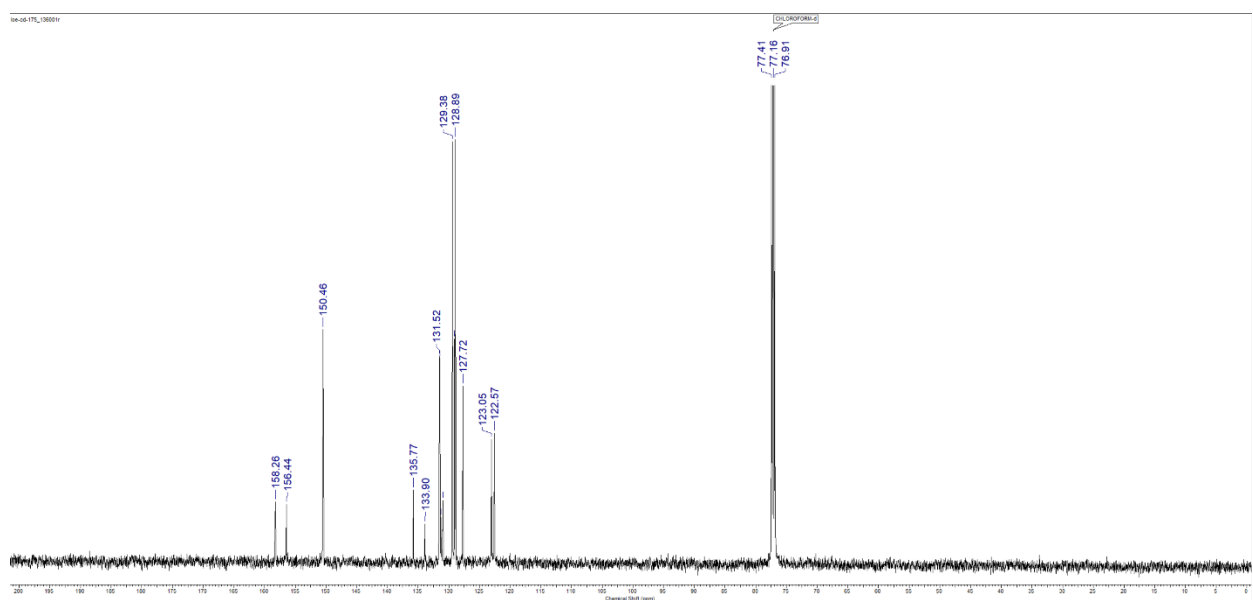


Figure S12: ¹³C NMR spectrum of 9-benzylidene-9H-4,5-diazafluorene (**3c**) in CDCl₃.

cd-175m #3 RT: 0.14 AV: 1 NL: 1.69E6
T: + c EI Full ms [14.50-290.50]

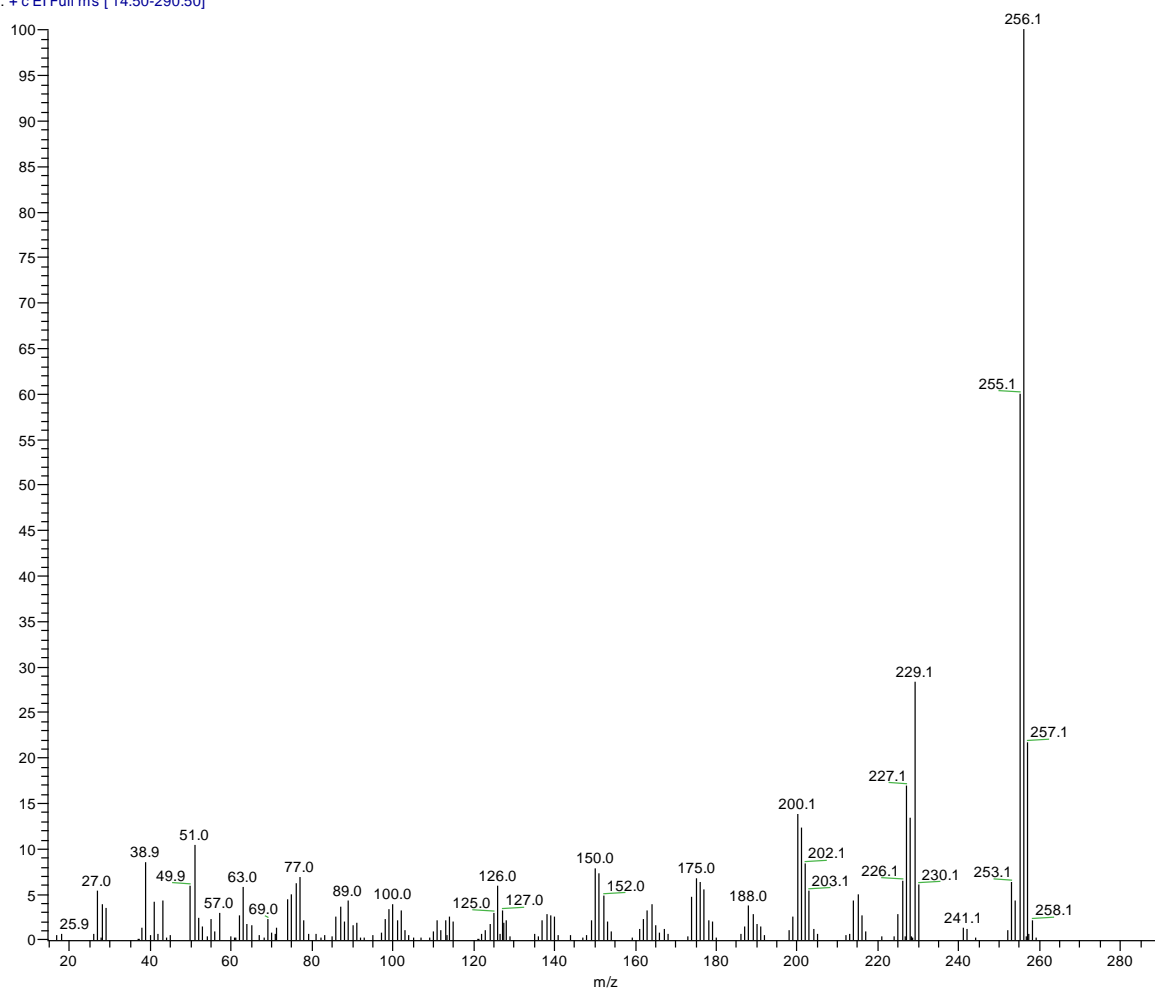


Figure S13: HRMS overview spectrum of 9-benzylidene-9H-4,5-diazafluorene (**3c**) ($T_{\text{source}} = 50\text{ }^{\circ}\text{C}$, $T_{\text{probe}} = 220\text{ }^{\circ}\text{C}$).

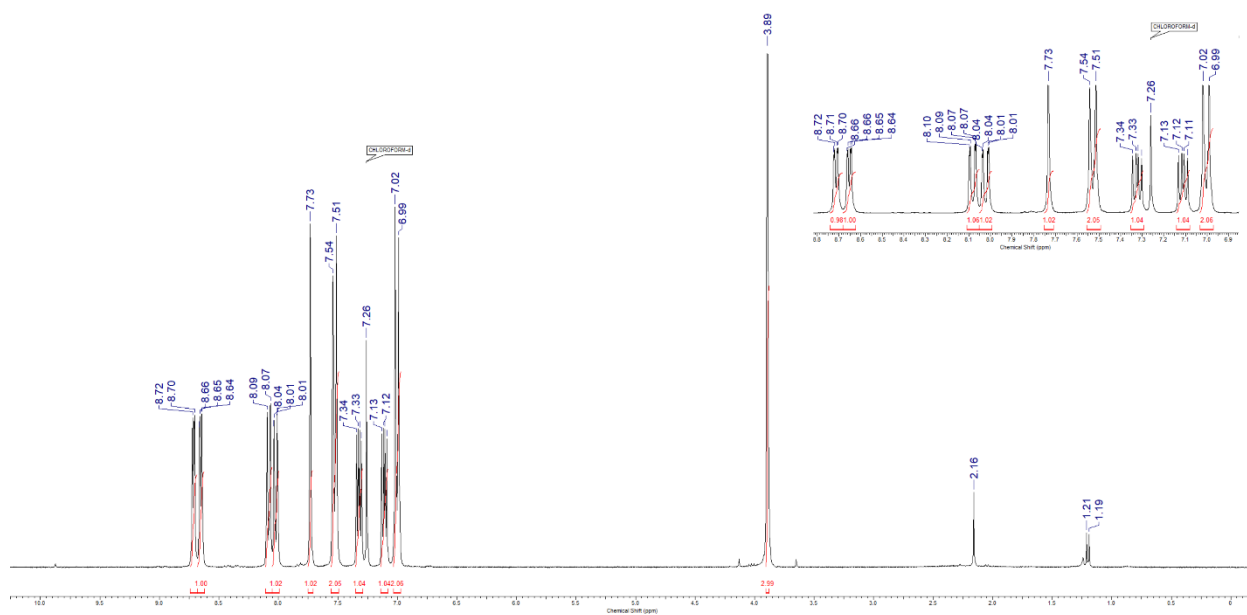


Figure S14: ^1H NMR spectrum of 9-(4-methoxybenzylidene)-9H-4,5-diazafluorene (**3d**) in CDCl_3 .

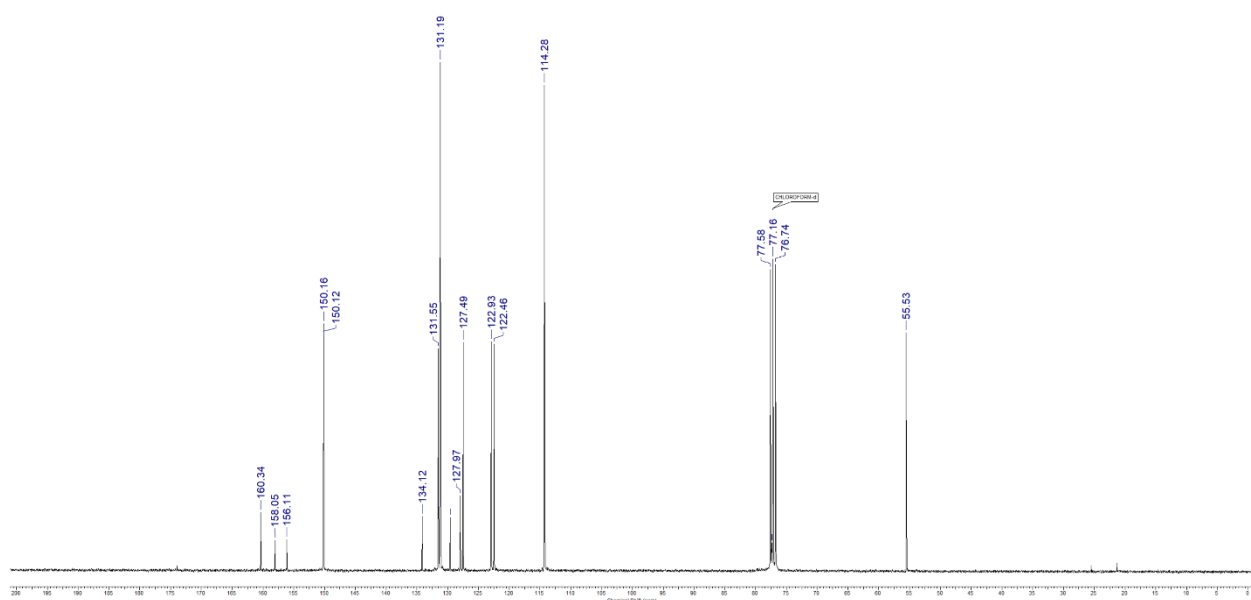


Figure S15: ^{13}C NMR spectrum of 9-(4-methoxybenzylidene)-9H-4,5-diazafluorene (**3d**) in CDCl_3 .

cd-87m #19 RT: 0.97 AV: 1 NL: 1.15E6
T: + c EI Full ms [32.50-320.50]

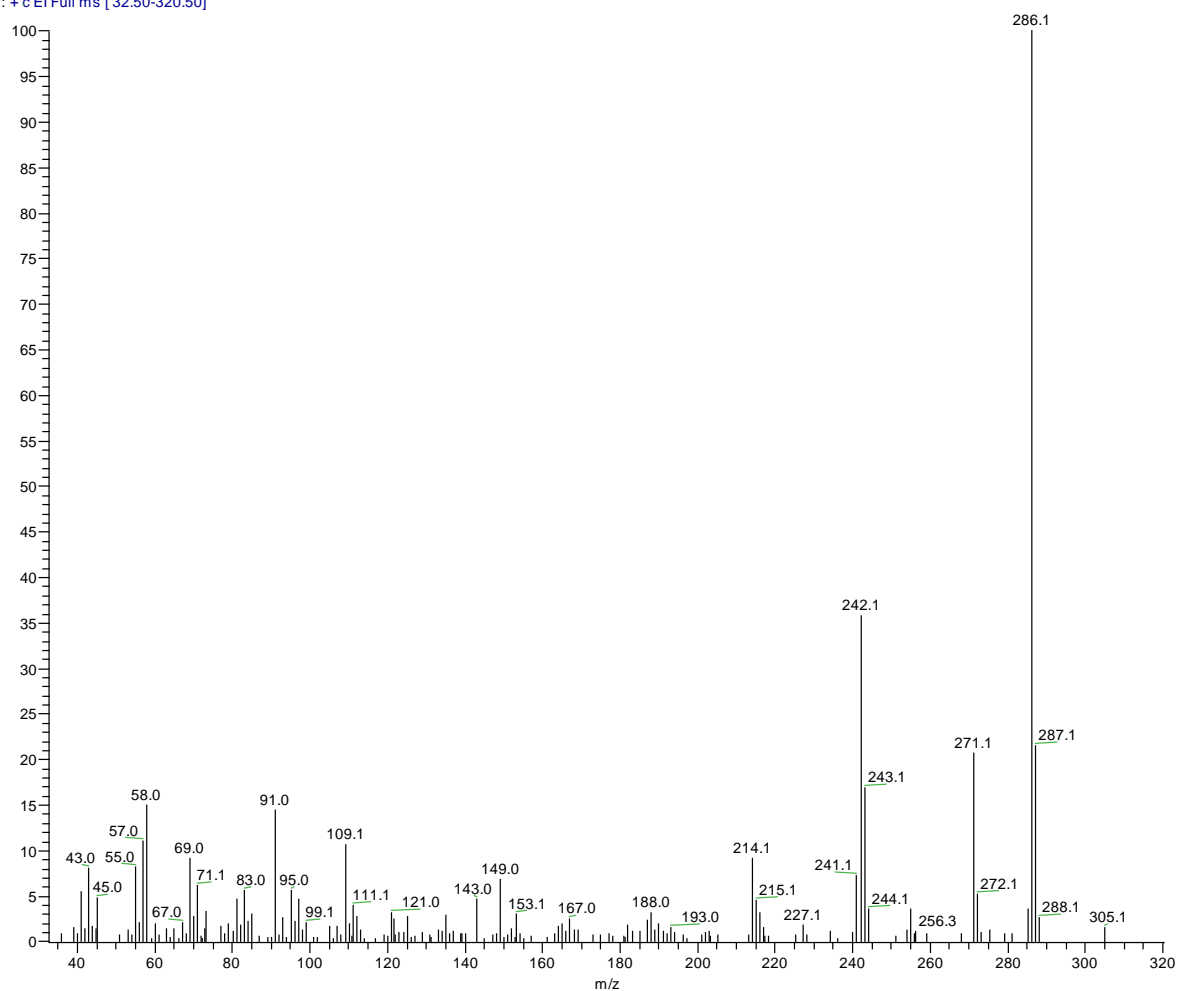


Figure S16: HRMS overview spectrum of 9-(4-methoxybenzylidene)-9H-4,5-diazafluorene (**3d**) ($T_{\text{source}} = 95\text{ }^\circ\text{C}$, $T_{\text{probe}} = 200\text{ }^\circ\text{C}$).

cd-165m #8 RT: 0.40 AV: 1 NL: 1.57E7
T: + cEI Full ms [32.50-330.50]

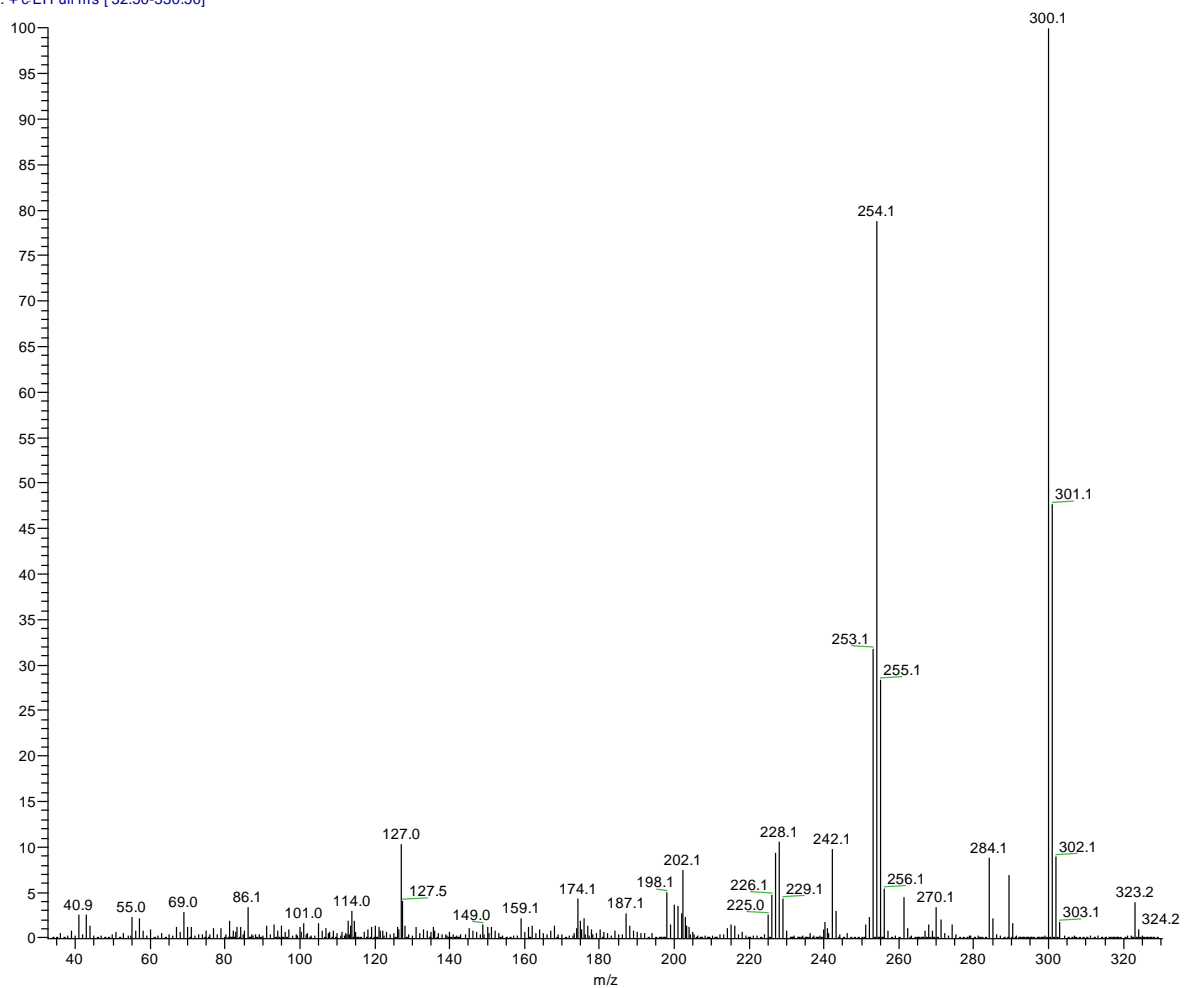


Figure S19: HRMS overview spectrum of 9-(3-nitrobenzylidene)-9H-1,8-diazafluorene (**4a**) ($T_{\text{source}} = 70\text{ }^{\circ}\text{C}$).

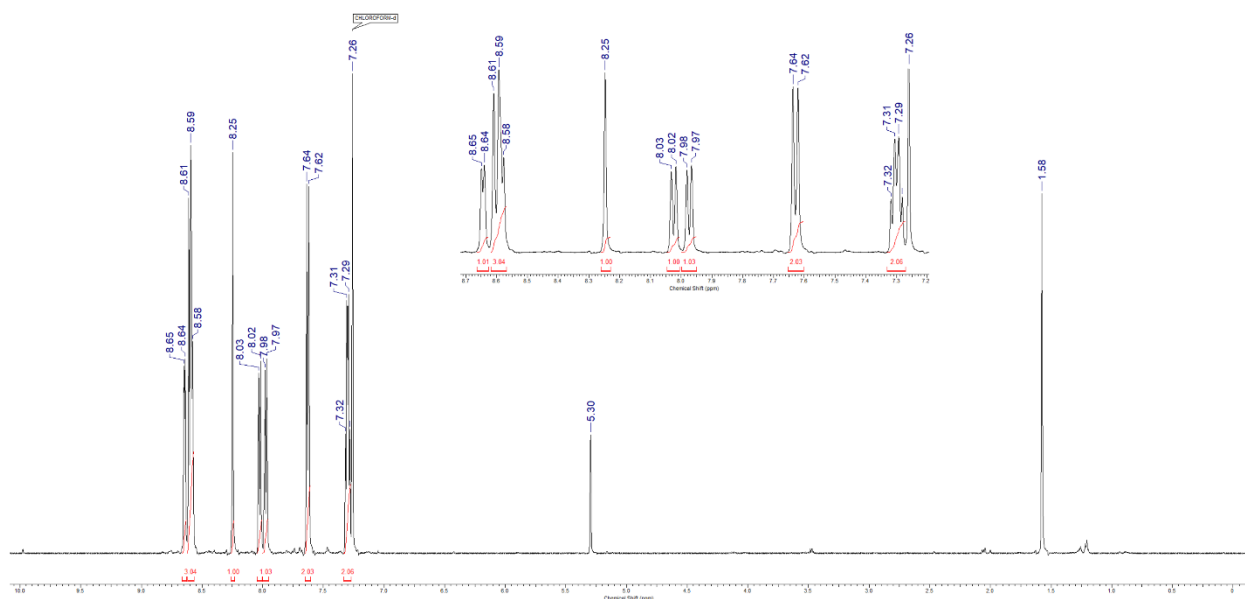


Figure S20: ^1H NMR spectrum of 9-(4-bromobenzylidene)-9H-1,8-diazafluorene (**4b**) in CDCl_3 .

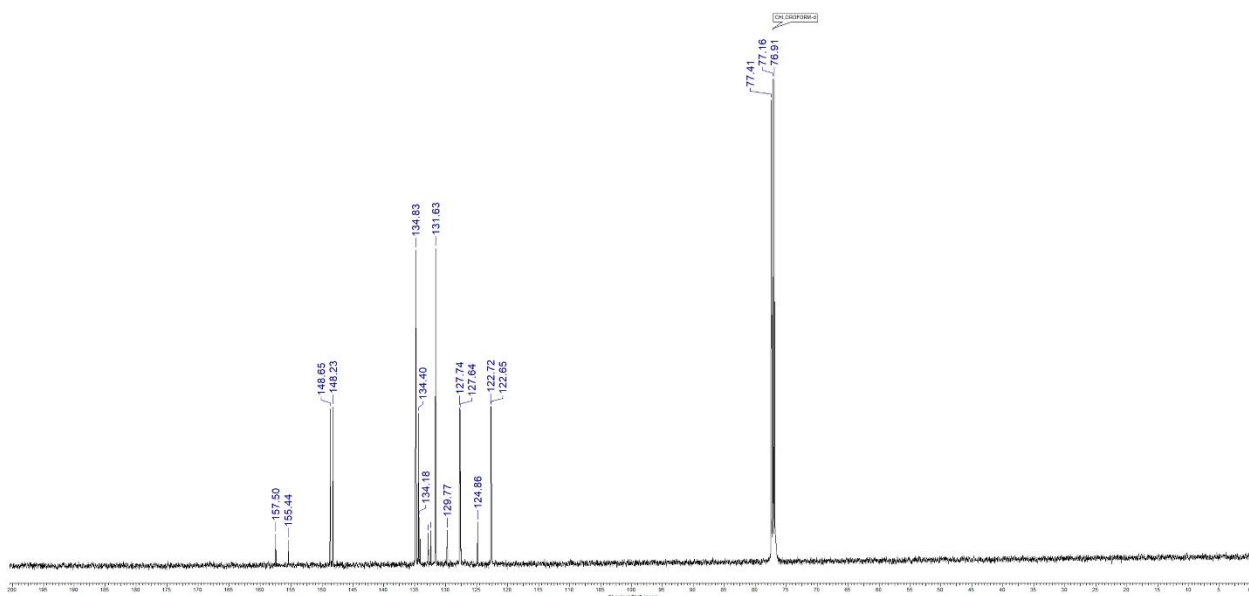


Figure S21: ^{13}C NMR spectrum of 9-(4-bromobenzylidene)-9H-1,8-diazafluorene (**4b**) in CDCl_3 .

cd-53m #5 RT: 0.30 AV: 1 NL: 2.93E5
T: + c EI Full ms [14.50-360.50]

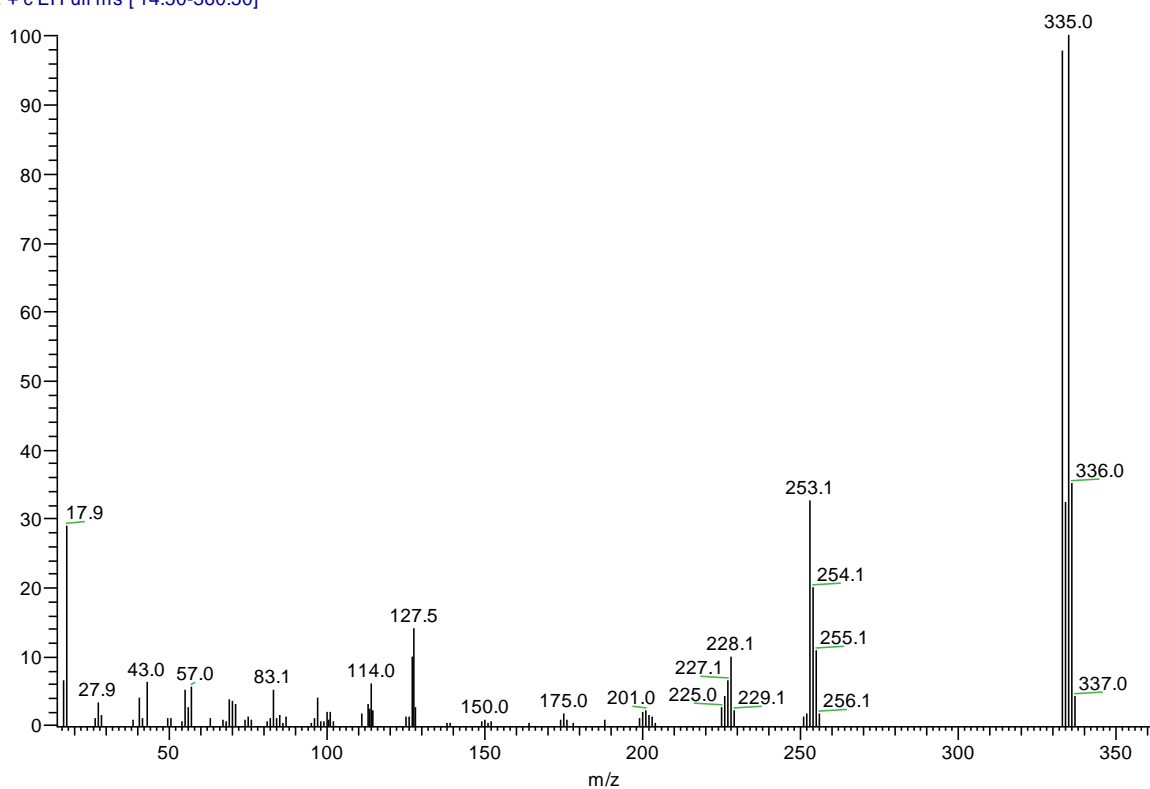


Figure S22: HRMS overview spectrum of 9-(4-bromobenzylidene)-9H-1,8-diazafluorene (**4b**) ($T_{\text{source}} = 105\text{ }^\circ\text{C}$).

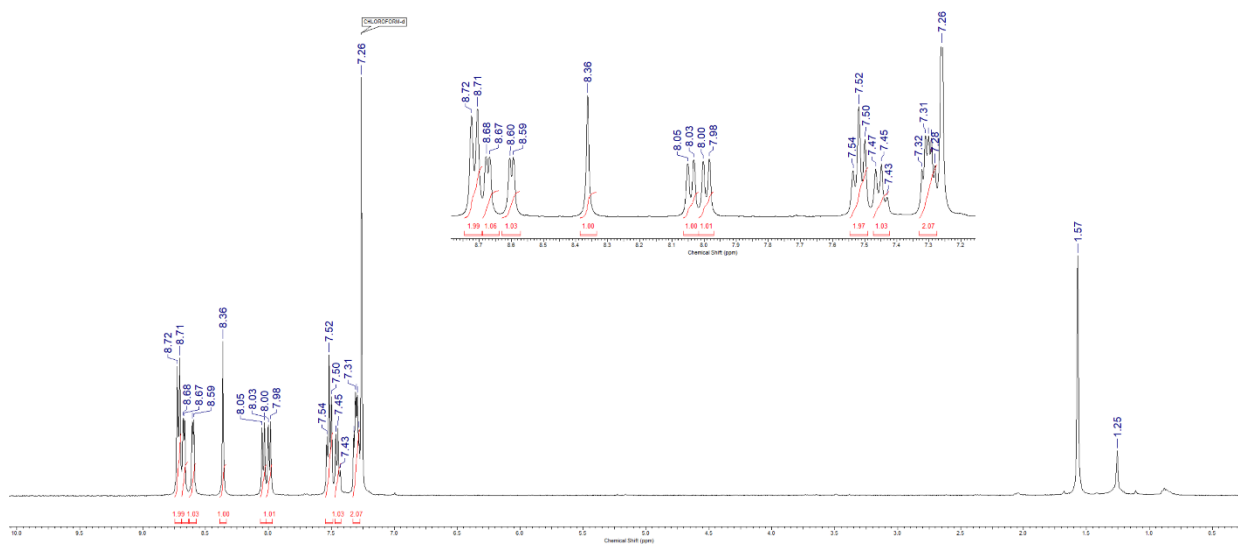


Figure S23: ^1H NMR spectrum of 9-benzylidene-9H-1,8-diazafluorene (**4c**) in CDCl_3 .

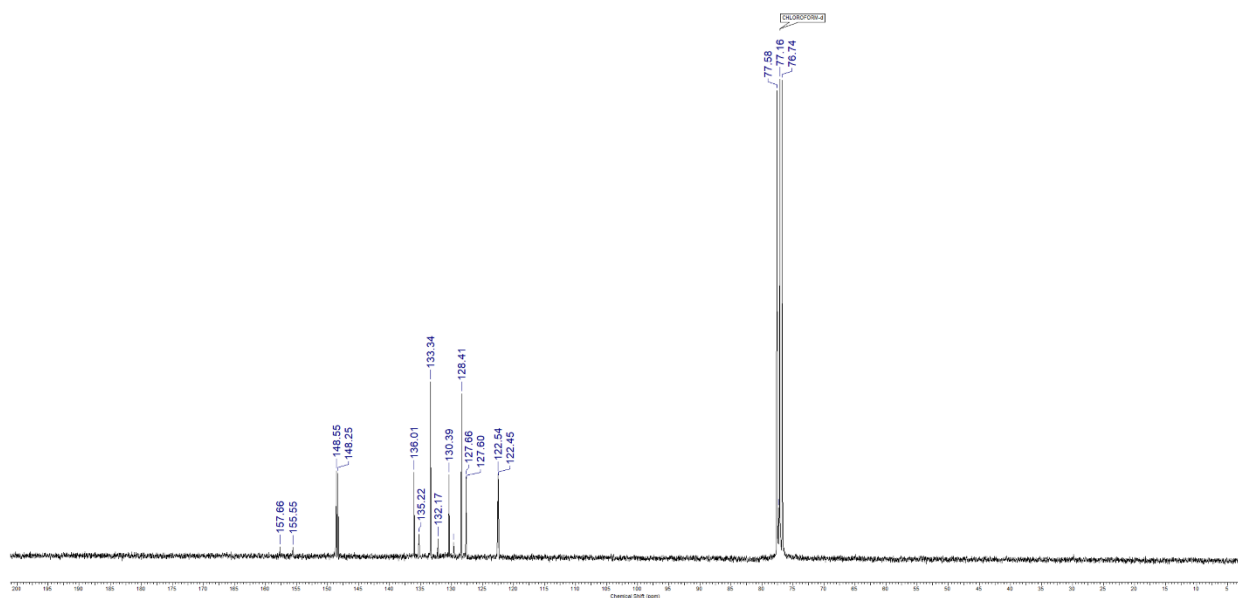


Figure S24: ^{13}C NMR spectrum of 9-benzylidene-9H-1,8-diazafluorene (**4c**) in CDCl_3 .

cd-176m #2 RT: 0.07 AV: 1 NL: 3.73E6
T: + c EI Full ms [14.50-300.50]

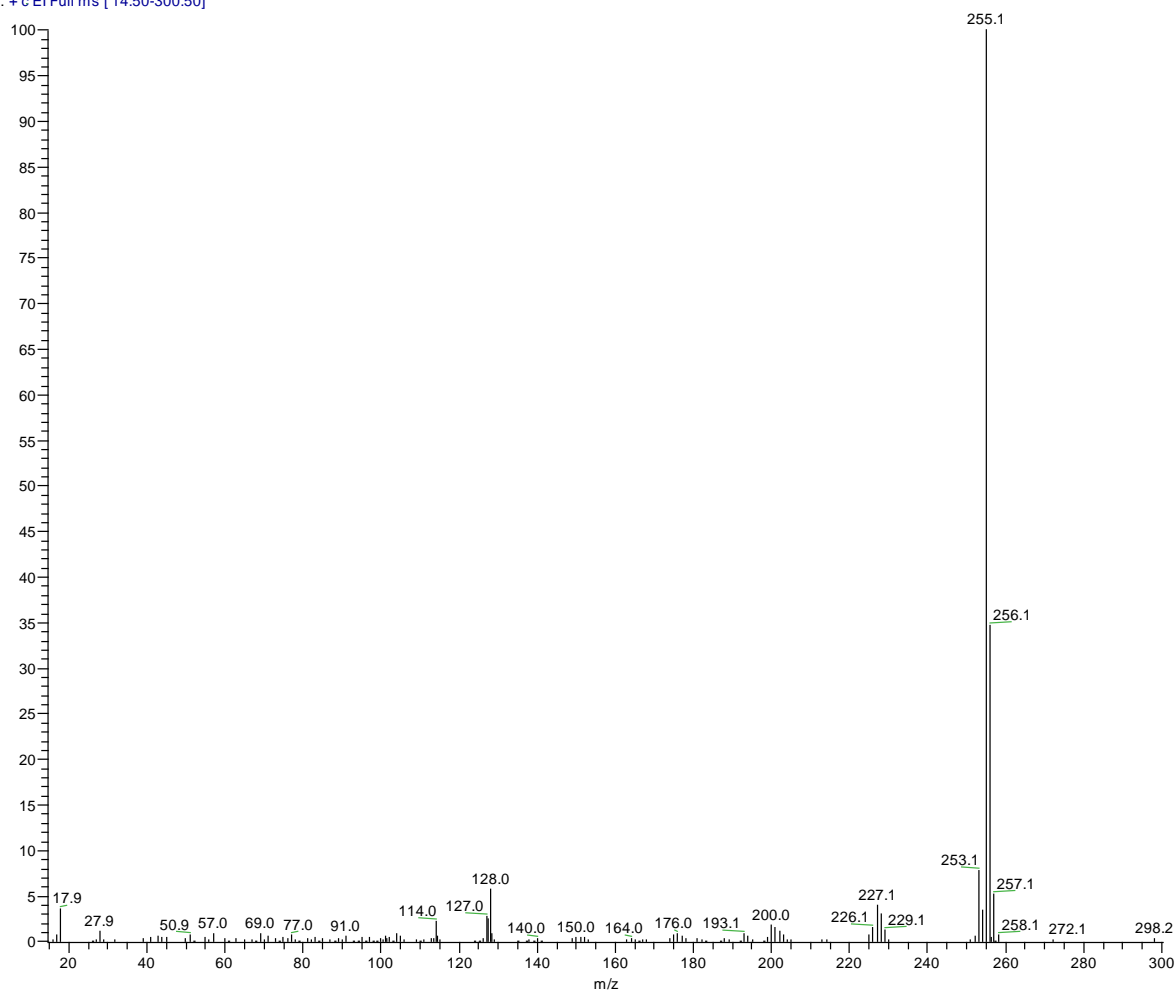


Figure S25: HRMS overview spectrum of 9-benzylidene-9H-1,8-diazafluorene (**4c**) ($T_{\text{source}} = 50\text{ }^{\circ}\text{C}$, $T_{\text{probe}} = 200\text{ }^{\circ}\text{C}$).

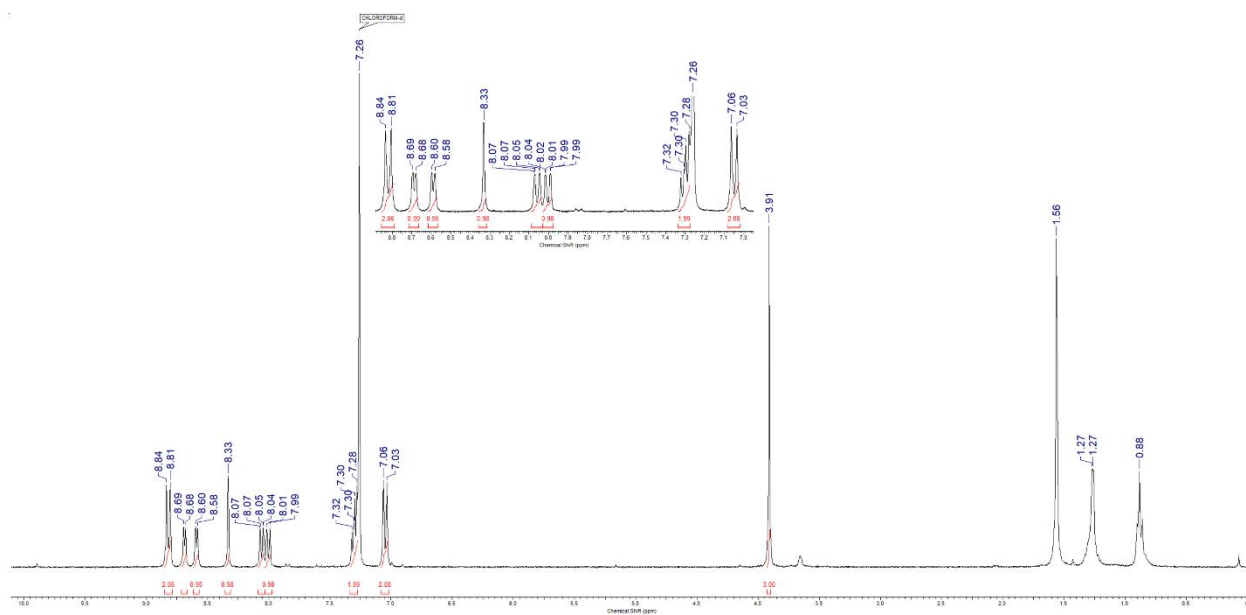


Figure S26: ^1H NMR spectrum of 9-(4-methoxybenzylidene)-9H-1,8-diazafluorene (**4d**) in CDCl_3 .

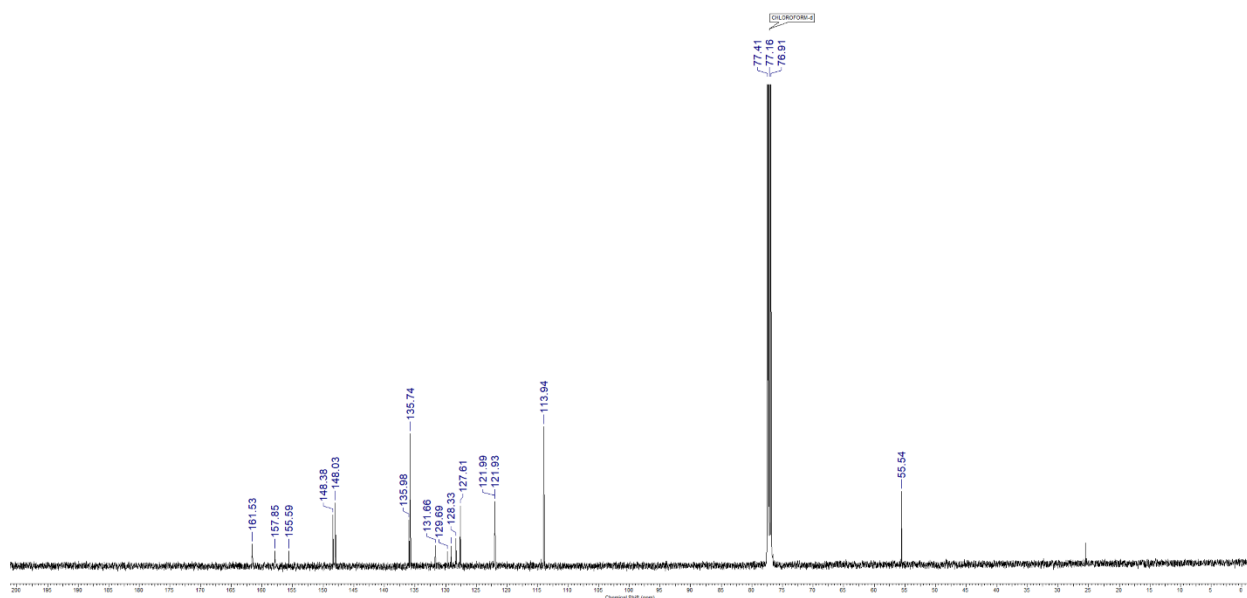


Figure S27: ^{13}C NMR spectrum of 9-(4-methoxybenzylidene)-9H-1,8-diazafluorene (**4d**) in CDCl_3 .

cd-170m #3 RT: 0.15 AV: 1 NL: 1.09E7
T: + c EI Full ms [14.50-320.50]

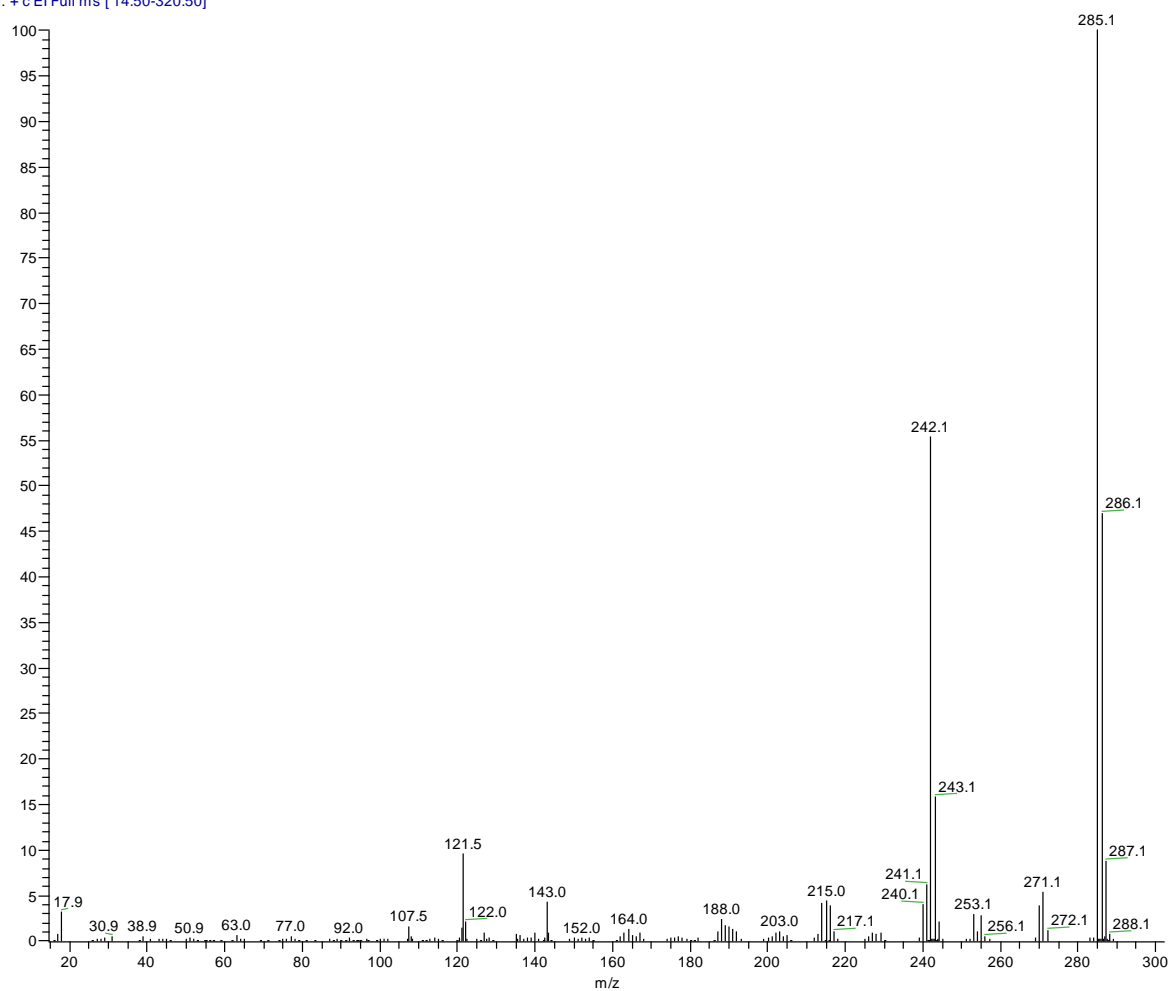


Figure S28: HRMS overview spectrum of 9-(4-methoxybenzylidene)-9H-1,8-diazafluorene (**4d**) ($T_{\text{source}} = 60\text{ }^\circ\text{C}$, $T_{\text{probe}} = 200\text{ }^\circ\text{C}$).

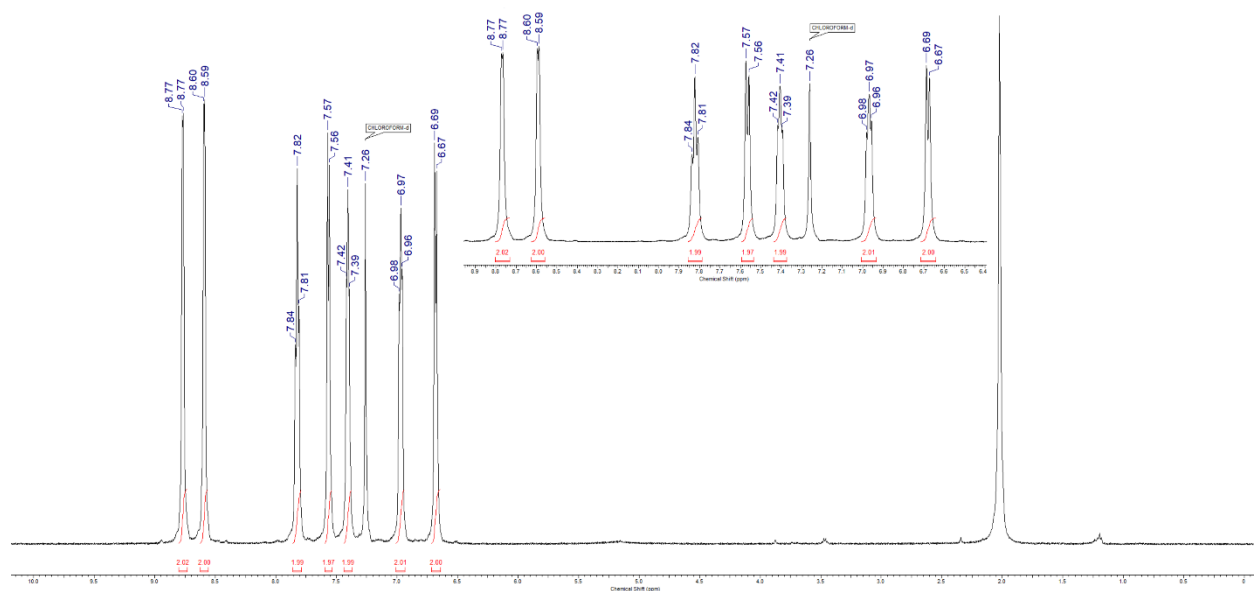


Figure S29: ^1H NMR spectrum of 9-(di(pyridin-2-yl)methylene)-9*H*-4,5-diazafluorene (4,5-DPDAF) in CDCl_3 .

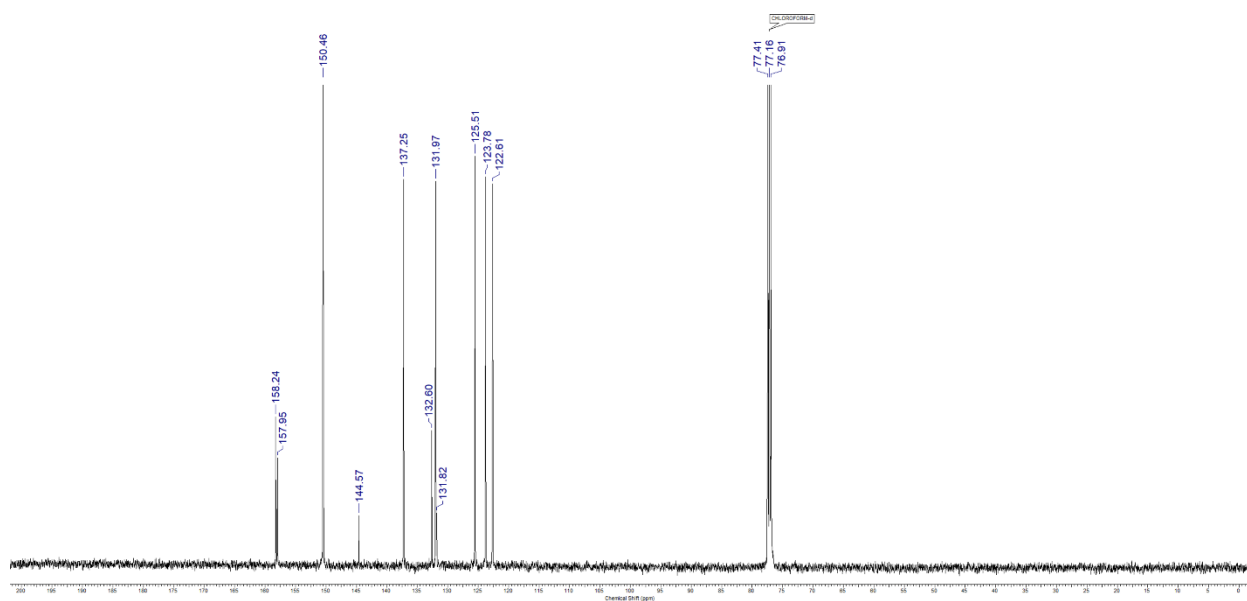


Figure S30: ^{13}C NMR spectrum of 9-(di(pyridin-2-yl)methylene)-9*H*-4,5-diazafluorene (4,5-DPDAF) in CDCl_3 .

cd-168m #2 RT: 0.06 AV: 1 NL: 4.05E6
T: + c EI Full ms [32.50-380.50]

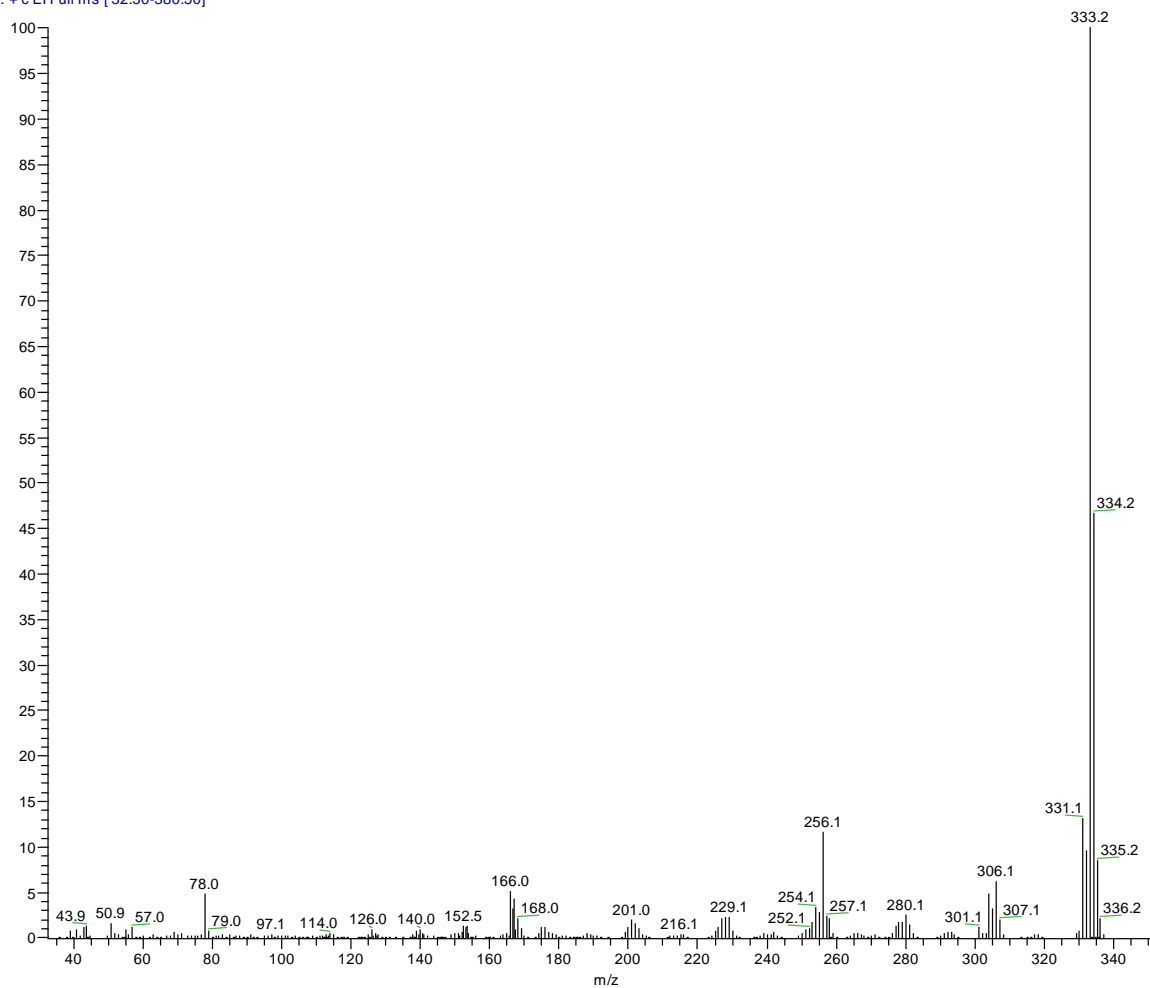


Figure S31: HRMS overview spectrum of 9-(di(pyridin-2-yl)methylene)-9H-4,5-diazafluorene (4,5-DPDAF) ($T_{\text{source}} = 70\text{ }^{\circ}\text{C}$, $T_{\text{probe}} = 200\text{ }^{\circ}\text{C}$).

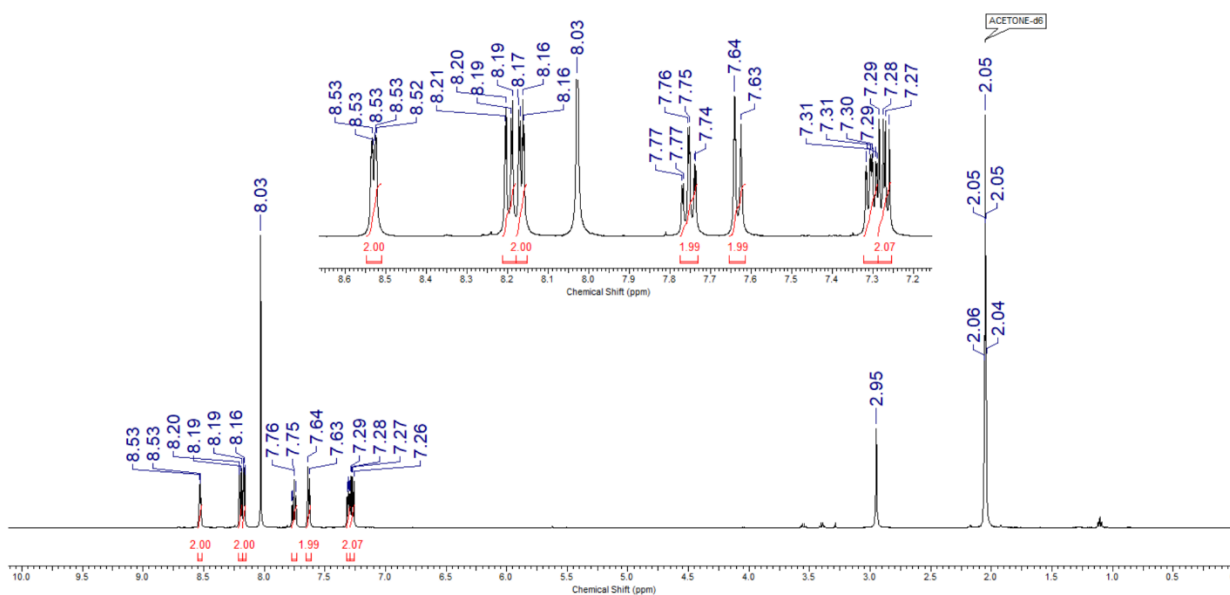


Figure S32: ^1H NMR spectrum of 9-(di(pyridin-2-yl)methylene)-9H-1,8-diazafluorene (1,8-DPDAF) in CDCl_3 .

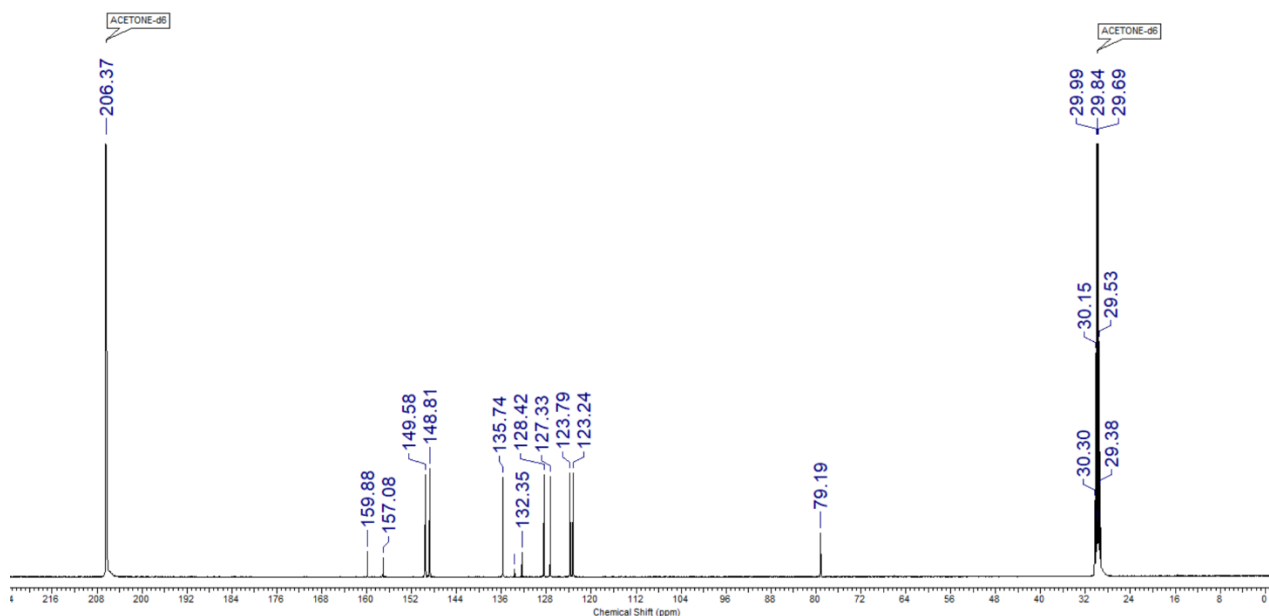


Figure S33: ^{13}C NMR spectrum of 9-(di(pyridin-2-yl)methylene)-9H-1,8-diazafluorene (1,8-DPDAF) in CDCl_3 .

cd-177m_pm #3 RT: 0.11 AV: 1 NL: 2.62E5
T: + c EI Full ms [32.50-344.50]

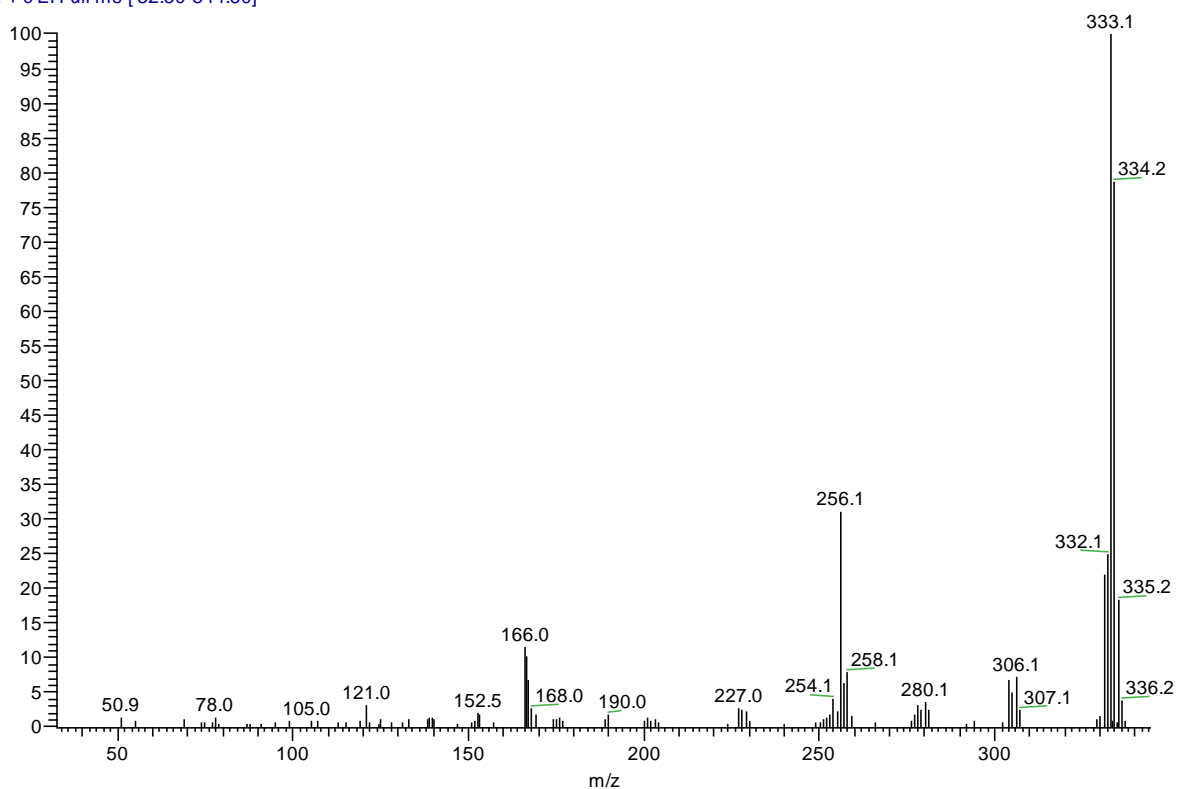


Figure S34: HRMS overview spectrum of 9-(di(pyridin-2-yl)methylene)-9H-1,8-diazafluorene (1,8-DPDAF) ($T_{\text{source}} = 85\text{ }^\circ\text{C}$, $T_{\text{probe}} = 200\text{ }^\circ\text{C}$).

Reference

- 1) Plater, M. J.; Kemp, S.; Lattmann, E. *J. Chem. Soc., Perkin Trans. 1* **2000**, 6, 971–979.