New *p*-aminophenol based dendritic melamines. Iterative synthesis, structure and electrochemical characterisation

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SUPPORTING INFORMATION (SI)

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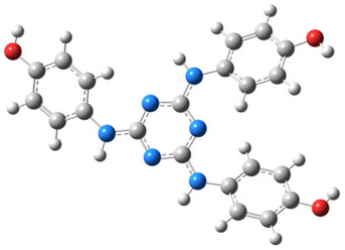
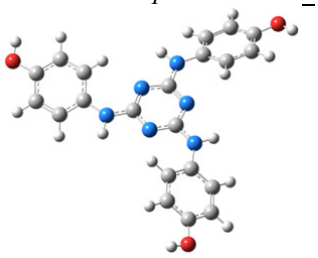
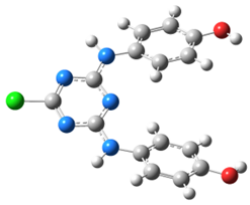
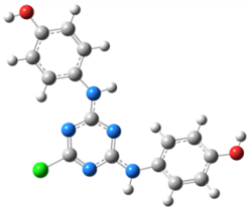
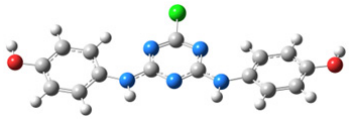
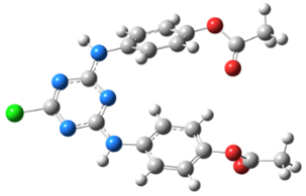
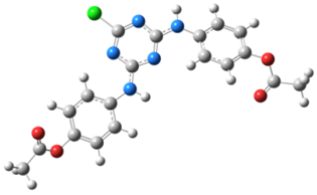
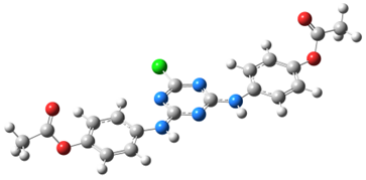
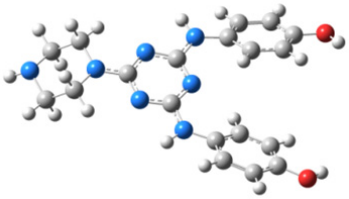
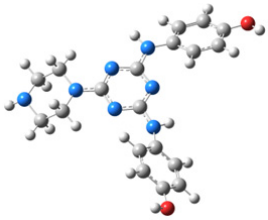
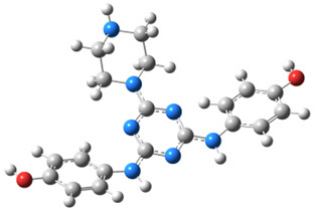
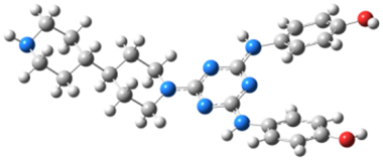
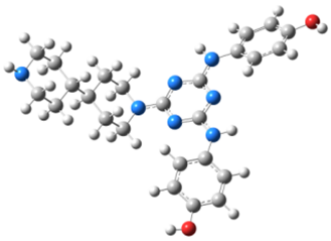
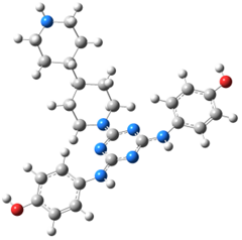
Table SI-1. Relative conformational electronic energies ΔE_{conf} (kJ/mol) of rotamers of (G-0) dendron **1a**[a]; the *asymmetric* conformation total electronic energies were taken as the reference values.

1a *Asymmetric*	**1a** *Propeller*
	
0.000 (Gas phase)	+4.013 (Gas phase)
0.000 (DMSO)	+1.245 (DMSO)

[a]The full geometry optimization have been carried out at the DFT level of theory considering the M06-2X [13] exchange-correlation functional together with the def2-TZVP [14] basis set in the presence of solvent environment implemented in the Gaussian 09 [15] program package. The solvent effects have been taken into account via the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [16] considering the DMSO (ε=46.826) as the solvent environment.

Table SI-2. Relative conformational electronic energies ΔE_{conf} (kJ/mol) of *anti-anti*, *anti-syn* and *syn-syn* rotamers of (G-0) dendrons **1b**, **2**, **3a** and **3b**[a]. The *anti-anti* conformation total electronic energies were taken as the reference values.

anti-anti	*syn-anti*	*syn-syn*
		
1b 0.000 (Gas phase) 0.000 (DMSO)	**1b** +4.371 (Gas phase) +3.087 (DMSO)	**1b** +5.308 (Gas phase) +4.562 (DMSO)
		
2 0.000 (Gas phase) 0.000 (DMSO)	**2** +6.094 (Gas phase) +4.333 (DMSO)	**2** +7.613 (Gas phase) +6.240 (DMSO)
		
3a 0.000 (Gas phase) 0.000 (DMSO)	**3a** +3.343 (Gas phase) -0.684 (DMSO)	**3a** +2.279 (Gas phase) -1.643 (DMSO)
		
3b 0.000 (Gas phase) 0.000 (DMSO)	**3b** +2.805 (Gas phase) -0.682 (DMSO)	**3b** +1.929 (Gas phase) -2.124 (DMSO)

[a]The full geometry optimization have been carried out at the DFT level of theory considering the M06-2X [13] exchange-correlation functional together with the def2-TZVP [14] basis set in the presence of solvent environment implemented in the Gaussian 09 [15] program package. The solvent effects have been taken into account via the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [16] considering the DMSO (ε=46.826) as the solvent environment

Preparation of compound 1a

Under inert atmosphere and with vigorous stirring, to a cooled (0-5 °C) butanone (18 mL) solution containing cyanuric chloride (1.100 g, 5.96 mmol), *p*-aminophenol (2.150 g, 19.72 mmol) was added portionwise during 30 min. After 30 min., a water (9 mL) solution containing anhyd. sodium acetate (1.617 g, 19.72 mmol) was injected dropwise at 5-9 °C. The reaction mixture was kept at this temperature for 30 min. and then heated at reflux for 3 h (TLC monitoring, eluent ligroin/acetone 1:1 v/v). After cooling at room temperature, the reaction mixture was poured on ice (150 g) and the resulted suspension was filtered off and well washed with cooled water. The crude product (about 2.300 g) was purified by crystallisation from boiling water (24 mL) to afford compound **1a** (2.181 g) as pure analytical sample.

2,4,6-Tris[(4-hydroxy)phenylamino]-s-triazine (**1a**). Light-pink powder (Lit.[3] white powder). Yield 91% (Lit.[3] 89%). Mp 289.3-289.8 °C (Lit. [1a] 301 °C). R_f (50% Ligroin/Acetone) = 0.51. Anal. calcd. for $C_{21}H_{18}N_6O_3$: C, 62.68; H, 4.51; N, 20.88%. Found: C, 62.49; H, 4.77; N, 21.08%. IR (KBr) ν_{max} 3387 (m), 1619 (w), 1585 (m), 1554 (m), 1515 (s), 1504 (s), 1427 (m), 1352 (w), 1234 (m), 836 (w), 804 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 6.66 (6H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.47 (6H, br s, H-2, -6, Ph), 8.74 (3H, br s, NH), 9.06 (3H, br s, OH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ_H 6.69 (6H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5), 7.46 (6H, d, $^3J_{H,H}$=8.5 Hz, H-2, -6), 8.37 (3H, s, NH), 8.74 (3H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=152 μm^2/s. ^{13}C J_{mod}-NMR (100 MHz, DMSO-d_6, 298 K) δ_C 114.8 (C-3, -5, Ph), 122.4 (C-2, -6, Ph), 131.6 (C-1, Ph), 152.6 (C-4, Ph), 164.1 (*s*-triazine) ppm. HRMS (ESI) (relative intensity) *m*/*z*: 403.1517 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{21}H_{19}N_6O_3$, 403.1519.

Preparation of compound 1b

Under inert atmosphere and with vigorous stirring, to a cooled (0-5 °C) suspension of cyanuric chloride (3.688 g, 20.00 mmol) in acetone (5 mL), *p*-aminophenol (4.365 g, 40.00 mmol) suspended in acetone (100 mL) was added portionwise during 2 h. Then, a water solution (48 mL) containing $NaHCO_3$ (3.360 g, 40.00 mmol) was injected dropwise at 5-9 °C. The reaction mixture was heated at 45 °C for 3h, then let to stir at room temperature for additional 15 h (TLC monitoring, eluent hexane/acetone 1:1 v/v) and finally evaporated under reduced pressure to the complete removal of acetone. The resulted aqueous suspension was filtered off with well washing with cooled water to provide compound **1b** as crude product. This was crystallised from boiling ethanol (24 mL) to give compound **1b** (4.804 g) as pure analytical sample.

2-Chloro-4,6-bis[(4-hydroxy)phenylamino]-s-triazine (**1b**). White powder (Lit. [4b, 4c] black crystals). Yield 73% (Lit. [4b, 4c] 67%). Mp 343.7-344.1 °C (Lit. [4b, 4c] 251-252 °C). R_f (50% Hexane/Acetone) = 0.50. Anal. calcd. for $C_{15}H_{12}ClN_5O_2$: C, 54.64; H, 3.67; N, 21.24%. Found: C, 54.69; H, 3.97; N, 20.98%. IR (KBr) ν_{max} 3384 (m), 3297 (m), 1618 (m), 1590 (s), 1551 (s), 1515 (s), 1454 (m), 1441 (m), 1383 (m), 1265 (m), 1217 (m), 991 (m), 824 (m), 789 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 6.68 and 6.72 (4H, 2×d, $^3J_{H,H}$=8.0 Hz and $^3J_{H,H}$=7.5 Hz respectively, H-3, -5, Ph), 7.35 and 7.52 (4H, d and br s respectively, $^3J_{H,H}$=8.0 Hz, H-2, -6, Ph), 9.27 (2H, s, OH), 9.70, 9.83 and 9.91 (2H, 2× brs and s respectively, NH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ_H 6.71 (4H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.38 (4H, d, $^3J_{H,H}$=9.0 Hz, H-2, -6, Ph), 8.91 (2H, br s, OH), 9.46 (2H, br s, NH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=218 μm^2/s. ^{13}C J_{mod}-NMR (100 MHz, DMSO-d_6, 298 K) δ_C 114.9 and 115.1 (C-3, -5, Ph), 122.5, 123.1 and 123.4 (C-2, -6, Ph), 129.8 and 130.3 (C-1, Ph), 153.8 (C-4, Ph), 163.8 and 164.1 (C-4, -6, *s*-triazine), 167.8 and 168.3 (C-2, *s*-triazine) ppm. HRMS (ESI) (relative intensity) *m*/*z*: 330.0755 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{15}H_{13}ClN_5O_2$, 330.0758.

Preparation of compound 2

At room temperature and with vigorous stirring, in an anhyd. THF (23 mL) solution containing compound **1b** (1.000 g, 3.03 mmol), anhyd. K_2CO_3 (0.418 g, 3.03 mmol) was suspended. Acetic anhydride (0.640 ml, 0.690 g, 6.77 mmol) was injected dropwise and the reaction mixture was let to stir at room temperature for 4 h then heated at reflux for 10 h (TLC monitoring, eluent ligroin/acetone 2:1 v/v). The reaction mixture was evaporated to dryness under reduced pressure and the residual solid was taken with water (10 mL). The resulted suspension was filtered off and well washed with water to the complete removal of minerals. The dried crude product was crystallised from boiling isopropanol (5 mL) to yield compound **2** (1.126 g) as pure analytical sample.

2-Chloro-4,6-bis[(4-acetyloxy)phenylamino]-s-triazine (**2**). White powder. Yield 90%. Mp 250.1-250.5 °C. R_f (66% Ligroin/Acetone) = 0.53. Anal. calcd. for $C_{19}H_{16}ClN_5O_4$: C, 55.15; H, 3.90; N, 16.92%. Found: C, 55.26; H, 3.69; N, 17.28%. IR (KBr) ν_{max} 3327 (m), 1731 (s), 1611 (m), 1565 (s), 1541 (m), 1524 (m), 1503 (m), 1413 (s), 1369 (m), 1236 (s), 1191 (s), 1017 (w), 985 (w), 942 (w), 919 (w), 836 (m), 796 (w), 737 (w),

653 (w), 598 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 2.26 (6H, s, CH_3), 7.09 (4H, d, $^3J_{H,H}$=8.0 Hz, H-3, -5, Ph), 7.62 and 7.78 (4H, 2×br s, H-2, -6, Ph), 10.18 and 10.34 (2H, 2×br s, NH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 353 K) δ_H 2.26 (6H, s, CH_3), 7.08 (4H, dd, $^3J_{H,H}$=7.0 Hz, $^4J_{H,H}$=2.0 Hz, H-3, -5, Ph), 7.65 (4H, d, $^3J_{H,H}$=8.5 Hz, H-2, -6, Ph), 9.97 (2H, br s, NH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D= 230 $\mu m^2/s$. ^{13}C DEPT-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 25.3 (CH_3), 126.1, 126.4 and 126.6 (C-2, -3, -5, -6, Ph), 140.3 and 140.5 (C-4, Ph), 150.8 (C-1, Ph), 167.9 (C-4, -6, *s*-triazine), 168.4 (C-2, *s*-triazine), 172.5, 172.9 and 173.8 (C=O) ppm. HRMS (ESI) (relative intensity) *m*/*z*: 414.0966 (65) $[M+H]^+$, 369.3843 (100) $[M-CO_2]^+$, 341.3530 (30) $[M-CO_2-CO]^+$; $[M+H]^+$ calcd for $C_{19}H_{17}ClN_5O_4$, 414.0969; $[M-CO_2]^+$ calcd. for $C_{18}H_{16}ClN_5O_2$, 369.0993; $[M-CO_2-CO]^+$ calcd. for $C_{17}H_{16}ClN_5O$, 341.1043.

Preparation of compound 3a

At room temperature and with vigorous stirring, in an anhyd. THF (60 mL) solution containing anhyd. piperazine (2.090 g, 24.28 mmol), anhyd. K_2CO_3 (0.838 g, 6.07 mmol) was suspended. To this suspension, compound **1b** (2.000 g, 6.07 mmol) was added as five equal portions every 3-4 hrs. After each portion, TLC monitoring indicated the complete consumption of **1b** (eluent hexane/acetone 1:1 v/v) and formation of **3a** as a single major spot (eluent EtOH : aq. NH_3 25% 9:1 v/v). After that, the reaction mixture was evaporated under reduced pressure to dryness. The residual crude solid was taken with water (28 mL), filtered off and well washed with water to the complete removal of minerals and excess of piperazine. The crude product was twice crystallised from boiling EtOH (3 and 6 mL respectively) to afford compound **3a** (1.956 g) as pure analytical sample.

2-(Piperazin-1-yl)-4,6-bis[(4-hydroxy)phenylamino]-s-triazine (**3a**). Beige powder (Lit. [4c] dark black crystals). Yield 85% (83% if column chromatography on silica gel is used, eluent eluent EtOH : aq. NH_3 25% 9:1 v/v) (Lit.[4c] 82%). Mp 276.8-278.7 °C (Lit. [4c] 287-289 °C). R_f (90% EtOH/aq. NH_3 25%) = 0.60. Anal. calcd. for $C_{19}H_{21}N_7O_2$: C, 60.15; H, 5.58; N, 25.84%. Found: C, 59.96; H, 5.66; N, 25.93%. IR (KBr) ν_{max} 3419 (w), 3287 (w), 3200 (w), 1635 (w), 1592 (m), 1557 (m), 1515 (s), 1441 (s), 1420 (s), 1246 (m), 1214 (m), 1017 (w), 830 (m), 802 (m) cm^{-1}. ^1H and 2D-^1H,^{15}N-HMBC-NMR (500 MHz, DMSO-d_6, 298 K) δ_H 2.69 (4H, t, $^3J_{H,H}$=4.8 Hz, H-3, -5, Pip), 3.63 (4H, t, $^3J_{H,H}$=4.3 Hz, H-2, -6, Pip), 6.65 (4H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.43 (4H, br d, $^3J_{H,H}$=4.5 Hz, H-2, -6, Ph), 8.71 (2H, br s, NH), 9.01 (2H, s, OH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ_H 2.73 (4H, t, $^3J_{H,H}$=5.0 Hz, H-3, -5, Pip), 3.65 (4H, t, $^3J_{H,H}$=5.0 Hz, H-2, -6, Pip), 6.67 (4H, ddd, $^3J_{H,H}$=9.5 Hz, $^4J_{H,H}$=2.8 Hz, $^5J_{H,H}$=2.8 Hz, H-3, -5, Ph), 7.42 (4H, ddd, $^3J_{H,H}$=9.5 Hz, $^4J_{H,H}$=2.8 Hz, $^5J_{H,H}$= 2.8 Hz, H-2, -6, Ph), 8.34 (2H, s, NH), 8.68 (2H, s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=152 $\mu m^2/s$. ^{13}C DEPT- and 2D-^1H,^{13}C-HSQC-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 44.5 (C-2, -6, Pip), 46.0 (C-3, -5, Pip), 115.2 (C-3, -5, Ph), 122.4 (C-2, -6, Ph), 132.2 (C-1, Ph), 152.9 (C-4, Ph), 164.5 (C-2, *s*-triazine), 165.0 (C-4, -6, *s*-triazine) ppm. HRMS (APCI) (relative intensity) *m*/*z*: 380.1836 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{19}H_{22}N_7O_2$, 380.1835.

Preparation of compound 4a

At room temperature and with vigorous stirring, in an anhyd. 1,4-dioxane (10 mL) solution containing compound **1b** (0.660 g. 2.00 mmol) and anhyd. piperazine (0.172 g, 2.00 mmol), anhyd. K_2CO_3 (0.276 g, 2.00 mmol) was suspended. The reaction mixture was refluxed for 8 h (TLC monitoring, eluent EtOH/aq. NH_3 25% 9:1 v/v) and then evaporated to dryness under reduced pressure. The residual solid was taken with water (13 mL), filtered off and well washed with water to the complete removal of minerals. After drying, the crude material was separated by column chromatography on silica gel (see above) providing compound **4a** as the first fraction (0.558 g, 83% partial conversion of **1b**), pure analytical sample. Next elution provided compound **3a** (0.129 g, 17% partial conversion of **1b**) as pure analytical sample.

1,4-Bis{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-piperazine (**4a**). Beige powder. Yield 83%. Mp 304 (dec.) °C. R_f (90% EtOH/aq. NH_3 25%) = 0.84. Anal. calcd. for $C_{34}H_{32}N_{12}O_4$: C, 60.71; H, 4.79; N, 24.99%. Found: C, 61.05; H, 5.01; N, 24.93%. IR (KBr) ν_{max} 3412 (m), 3250 (m), 1628 (m), 1568 (m), 1488 (s), 1429 (m), 1352 (w), 1260 (m), 1215 (m), 1005 (w), 835 (w), 802 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 3.79 (8H, s, Pip), 6.67 (8H, d, $^3J_{H,H}$=8.0 Hz, H-3, -5, Ph), 7.46 (8H, br s, H-2, -6, Ph), 8.81 (4H, br s, NH), 9.04 (4H, s, OH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ_H 3.81 (8H, s, Pip), 6.69 (8H, dd, $^3J_{H,H}$=7.0 Hz, $^4J_{H,H}$=2.0 Hz, H-3, -5, Ph), 7.44 (8H, dd, $^3J_{H,H}$=7.0 Hz, $^4J_{H,H}$=2.3 Hz, H-2, -6, Ph), 8.41 (4H, s, NH), 8.69 (4H, s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D= 137 $\mu m^2/s$. ^{13}C J_{mod}-NMR (100 MHz, DMSO-d_6, 298 K) δ_C 42.7 (Pip), 114.8 (C-3, -5, Ph), 122.0 (C-2, -6, Ph), 131.7 (C-1, Ph), 152.5 (C-4, Ph), 164.1 (C-2, *s*-triazine), 164.7 (C-4, -6, *s*-triazine) ppm. HRMS (APCI) (relative intensity) *m*/*z*: 673.2740 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{34}H_{33}N_{12}O_4$, 673.2748.

Preparation of compound 3b

At room temperature and with vigorous stirring, in an anhyd. THF (150 mL) solution containing freshly obtained 4,4'-bipiperidine (3.920 g, 23.28 mmol) from its dihydrochloride, anhyd. K_2CO_3 (0.805 g, 5.82 mmol) was suspended. To this suspension, compound **1b** (1.920 g, 5.82 mmoli) was added as six equal portions every 3-4 hrs. After each portion, TLC monitoring indicated the complete consumption of **1b** (eluent hexane/acetone 1:1 v/v) and formation of **3b** as a single major spot (eluent EtOH/aq. NH_3 25% 3:1 v/v). After that, the reaction mixture was stirred for additional 18 h (to the complete consumption of traces of **1b**) and then evaporated to dryness under reduced pressure. The residual solid was taken with boiling water (100 mL), filtered off and well washed with hot water. The crude dried product was stirred with an aq. HCl 18% (15 mL) solution and the resulted suspension was heated at 55 °C then cooled at 0 °C and filtered off. At room temperature, the dried clorohydrate (3.110 g) was taken with water (35 mL) then made alkaline with anhyd. K_2CO_3 (0.870 g, pH = 9). The resulted suspension was filtered off and well washed with water to neutrality. The dried solid was twice crystallised from boiling ethanol (10 mL) to provide compound **3b** (2.309 g) as pure analytical sample. *Recovery of excess of 4,4'-bipiperidine*: the first aqueous filtrate (about 150 mL) was evaporated to dryness under reduced pressure and taken with THF (100 mL) with vigorous stirring. KOH (2.45 g, 43.75 mmol) as distilled water (2.5 mL) solution was added and the resulted emulsion was stirred, at room temperature, for 3 h. The clear THF layer was decanted and the solid residue was extracted three times with THF (50 mL). The combined THF solution was dried over anh. Na_2SO_4, filtered off and evaporated to dryness under reduced pressure to provide the recovered 4,4'-bipiperidine (2.35 g, 80% yield of recovering) free base as a white yellowish solid. CARE! Store the product under dry inert atmosphere to avoid the carbonation of this diamine!

2-(4,4'-Bipiperidin-1-yl)-4,6-bis[(4-hydroxy)phenylamino]-s-triazine (**3b**). Beige powder. Yield 86 % (45% if column chromatography on silica gel was used, eluent EtOH/aq. NH_3 25% 3:1 v/v). Mp 225-228 °C. R_f (75% EtOH/ aq. NH_3 25%) = 0.49. Anal. calcd. for $C_{25}H_{31}N_7O_2$: C, 65.06; H, 6.77; N, 21.24%. Found: C, 64.97; H, 7.02; N, 21.43%. IR (KBr) ν_{max} 3390 (m), 3250 (m), 2942 (m), 2847 (m), 1619 (m), 1587 (m), 1569 (m), 1514 (s), 1491 (s), 1437 (s), 1418 (m), 1362 (m), 1262 (m), 1217 (m), 995 (w), 833 (m), 805 (m) cm^{-1}. ^1H and 2D-$^1H,^1H$-COSY-NMR (500 MHz, DMSO-d_6, 298 K) δ_H 1.03-1.09 (4H, m, H-3, -3', -5, -5'-ax, Bipip), 1.12-1.16 (1H, m, H-4'-ax, Bipip), 1.27-1.33 (1H, m, H-4-ax, Bipip), 1.60 (2H, d, $^2J_{H,H}$=12.0 Hz, H-3', -5'-eq, Bipip), 1.71 (2H, d, $^2J_{H,H}$=11.5 Hz, H-3, -5-eq, Bipip), 2.41 (2H, dd app. t, $^2J_{H,H}$=11.5 Hz, H-2', -6'-ax, Bipip), 2.72 (2H, dd app. t, $^2J_{H,H}$=12.0 Hz, H-2, -6-ax, Bipip), 2.95 (2H, d, $^2J_{H,H}$=11.5 Hz, H-2', -6'-eq, Bipip), 4.70 (2H, br d, $J_{H,H}$=9.0 Hz, H-2, -6-eq, Bipip), 6.65 (4H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.44 (4H, br d, $^3J_{H,H}$=1.0 Hz, H-2, -6, Ph), 8.72 (2H, br s, NH), 9.02 (2H, s, OH) ppm; ^1H, 2D-$^1H,^1H$-COSY-, 2D-$^1H,^{15}N$-HSQC- and -HMBC-NMR (500 MHz, DMSO-d_6, 363 K) δ_H 1.09-1.13 (4H, m, H-3, -3', -5, -5'-ax, Bipip), 1.15-1.21 (1H, m, H-4'-ax, Bipip), 1.32-1.35 (1H, m, H-4-ax, Bipip), 1.61 (2H, dd, $^2J_{H,H}$=12.0 Hz, $^3J_{H,H}$=1.0 Hz, H-3', -5'-eq, Bipip), 1.71 (2H, dd, $^2J_{H,H}$=11.0 Hz, $^3J_{H,H}$=2.0 Hz, H-3, -5-eq, Bipip), 2.45 (2H, ddd app. td, $^2J_{H,H}$=11.8 Hz, $^3J_{H,H}$=1.5 Hz, H-2', -6'-ax, Bipip), 2.77 (2H, ddd app. td, $^2J_{H,H}$=13.0 Hz, $^3J_{H,H}$=2.2 Hz, H-2, -6-ax, Bipip), 2.97 (2H, d, $^2J_{H,H}$=12.5 Hz, H-2', -6'-eq, Bipip), 4.67 (2H, d, $^2J_{H,H}$=13.0 Hz, H-2, -6-eq, Bipip), 6.67 (4H, dd, $^3J_{H,H}$=6.8 Hz, $^4J_{H,H}$=2.3 Hz, H-3, -5, Ph), 7.43 (4H, dd, $^3J_{H,H}$=6.5 Hz, $^4J_{H,H}$=2.0 Hz, H-2, -6, Ph), 8.33 (2H, s, NH), 8.66 (2H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=131 $\mu m^2/s$. ^{13}C DEPT-, 2D-$^1H,^{13}C$-HSQC- and -HMBC-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 29.3 (C-3, -5, Bipip), 30.3 (C-3', -5', Bipip), 41.3 (C-4', Bipip), 41.8 (C-4, Bipip), 43.6 (C-2, -6, Bipip), 46.8 (C-2', -6', Bipip), 115.2 (C-3, -5, Ph), 122.3 (C-2, -6, Ph), 132.3 (C-1, Ph), 152.8 (C-4, Ph), 164.6 (C-2, *s*-triazine), 164.7 (C-4, -6, *s*-triazine) ppm. HRMS (APCI) (relative intensity) *m*/*z*: 462.2613 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{25}H_{32}N_7O_2$, 462.2617

Preparation of compound 4b

At room temperature and with vigorous stirring, in an anhyd. 1,4-dioxane (5 mL) solution containing compounds **1b** (0.143 g, 0.43 mmol) and **3b** (0.200 g, 0.43 mmol), anhyd. K_2CO_3 (0.060 g, 0.43 mmol) was suspended. The reaction mixture was refluxed for 13 h (TLC monitoring, eluent $CHCl_3$/EtOH 5:1 v/v) then evaporated to dryness under reduced pressure. The residual solid was taken with water (5 mL), filtered off and well washed with water to the complete removal of minerals. After drying, the crude product was purified by twice crystallisations from boiling ethanol (2 mL) to yield compound **4b** (0.210 g) as pure analytical sample.

1,1'-Bis{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-4,4'-bipiperidine (**4b**). Beige powder. Yield 64%. Mp 232-234 °C. R_f (83% $CHCl_3$/EtOH) = 0.53. Anal. calcd. for $C_{40}H_{42}N_{12}O_4$: C, 63.65; H, 5.61; N, 22.27%. Found: C, 63.77; H, 5.52; N, 22.44%. IR (KBr) ν_{max} 3411 (m), 2940 (w), 2850 (w), 1580 (m), 1547 (m),

1512 (s), 1494 (s), 1430 (m), 1363 (w), 1215 (m), 833 (w), 801 (w) cm^{-1}. ^1H and 2D-^1H,^1H-COSY, -NOESY-NMR (500 MHz, DMSO-d_6, 298 K) δ_H 1.10 (4H, dd, $^2J_{H,H}$=21.5 Hz, $J_{H,H}$=11.5 Hz, H-3, -3', -5, -5'-ax, Bipip), 1.37 (2H, dd app. t, $^2J_{H,H}$=10.0 Hz, H-4, -4'-ax, Bipip), 1.74 (4H, d, $^2J_{H,H}$=11.0 Hz, H-3, -3', -5, -5'-eq, Bipip), 2.73 (4H, dd app. t, $^2J_{H,H}$=12.5 Hz, H-2, -2', -6, -6'-ax, Bipip), 4.71 (4H, br d, $^2J_{H,H}$=7.5 Hz, H-2, -2', -6, -6'-eq, Bipip), 6.65 (8H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.44 (8H, br s, H-2, -6, Ph), 8.72 (4H, br s, NH), 9.01 (4H, s, OH) ppm; ^1H NMR (500 MHz, DMSO-d_6, 353 K) δ_H 1.17 (4H, dd, $^2J_{H,H}$=20.8 Hz, $^2J_{H,H}$=11.3 Hz, H-3, -3', -5, -5'-ax, Bipip), 1.41 (2H, dd app. t, $^2J_{H,H}$=9.8 Hz, H-4, -4'-ax, Bipip), 1.75 (4H, d, $^2J_{H,H}$= 12.5 Hz, H-3, -3', -5, -5'-eq, Bipip), 2.78 (4H, dd app. t, $^2J_{H,H}$=11.8 Hz, H-2, -2', -6, -6'-ax, Bipip), 4.69 (4H, d, $^2J_{H,H}$=13.0 Hz, H-2, -2', -6, -6'-eq, Bipip), 6.67 (8H, d, $^3J_{H,H}$=9.0 Hz, H-3, -5, Ph), 7.43 (8H, d, $^3J_{H,H}$=9.0 Hz, H-2, -6, Ph), 8.36 (4H, s, NH), 8.70 (4H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=125 $\mu m^2/s$. ^{13}C DEPT-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 29.3 (C-3, -3', -5, -5', Bipip), 41.3 (C-4, -4', Bipip), 43.6 (C-2, -2', -6, -6', Bipip), 115.2 (C-3, -5, Ph), 122.3 (C-2, -6, Ph), 132.3 (C-1, Ph), 152.8 (C-4, Ph), 164.6 (C-2, *s*-triazine), 164.7 (C-4, -6, *s*-triazine) ppm. HRMS (ESI) (relative intensity) *m/z*: 755.3539 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{40}H_{43}N_{12}O_4$, 755.3530.

Preparation of compound 5a

At -15 °C and with vigorous stirring, in an anhyd. THF (80 mL) solution containing cyanuric chloride (0.486 g, 2.64 mmol), anhyd. K_2CO_3 (0.364 g, 2.64 mmol) was suspended. To this suspension, compound **3a** (1.000 g, 2.64 mmol) was added as four equal portions every 5-6 h. After each period, TLC monitoring (eluent EtOH : aq. NH_3 25% 9:1 v/v) still indicated traces of the starting material, **3a**. Therefore, the reaction mixture was let to reach the room temperature when a second molar equiv. of reagents was added portionwise, anhyd. K_2CO_3 (0.364 g, 2.64 mmol) and **3a** (1.000 g, 2.64 mmol) as four equal portions every 5-6 h. Since TLC monitoring of the consumption of **3a** still indicated its presence in traces, the reaction mixture was evaporated to dryness under reduced pressure. Anhyd. 1,4-dioxane (80 mL) was added in the reaction mixture which was then refluxed for 36 h. After this period, TLC monitoring (eluent $CHCl_3$/EtOH 5:1 v/v) revealed formation of compound **5a** as a major spot. The reaction mixture was evaporated to dryness under reduced pressure and taken with water (45 mL) in order to remove, after filtration, all minerals. The crude product was next purified by crystallisation from boiling ethanol (10 mL) then by recrystallization from $CHCl_3$/EtOH 5:1 v/v (24 mL) to give compound **5a** (2.065 g) as pure analytical sample.

2-Chloro-4,6-bis-{{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-piperazin-4-yl}-s-triazine (**5a**). Beige powder. Yield 90 %. Mp 274 (dec.) °C. R_f (83% $CHCl_3$/EtOH) = 0.46. Anal. calcd. for $C_{41}H_{40}ClN_{17}O_4$: C, 56.58; H, 4.63; N, 27.36%. Found: C, 56.37; H, 4.81; N, 27.39%. IR (KBr) ν_{max} 3387 (m), 2961 (w), 1620 (m), 1568 (s), 1514 (s), 1486 (s), 1431 (s), 1359 (m), 1297 (w), 1262 (m), 1218 (m), 1098 (w), 1003 (w), 970 (w), 832 (m), 799 (m) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 3.80 (8H, t, $^3J_{H,H}$=6.3 Hz, H-2, -6, Pip), 3.84 (8H, t, $^3J_{H,H}$=5.5 Hz, H-3, -5, Pip), 6.68 (8H, d, $^3J_{H,H}$=7.0 Hz, H-3, -5, Ph), 7.46 (8H, br s, H-2, -6, Ph), 8.83 (4H, br s, NH), 9.04 (4H, s, OH) ppm; ^1H and 2D-^1H,^{15}N-HMBC-NMR (500 MHz, DMSO-d_6, 363 K) δ_H 3.82 (16H, s, Pip), 6.69 (8H, d, $^3J_{H,H}$=8.0 Hz, H-3, -5, Ph), 7.44 (8H, d, $^3J_{H,H}$=8.0 Hz, H-2, -6, Ph), 8.54 (4H, s, NH), 8.79 (4H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=90 $\mu m^2/s$. ^{13}C DEPT-, 2D-^1H,^{13}C-HSQC- and -HMBC-NMR (125 MHz, DMSO-d_6, 363 K) δ_C 42.6 (C-2, -6, Pip), 43.1 (C-3, -5, Pip), 115.0 (C-3, -5, Ph), 122.4 (C-2, -6, Ph), 131.7 (C-1, Ph), 152.9 (C-4, Ph), 164.2 (C-2, *s*-triazine T-0), 164.4 (C-4, -6, *s*-triazine T-0), 165.0 (C-4, -6, *s*-triazine T-1), 168.9 (C-2, *s*-triazine T-1) ppm. HRMS (ESI) (relative intensity) *m/z*: 870.3259 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{41}H_{41}ClN_{17}O_4$, 870.3216.

Preparation of compound 5b

At -15 °C and with vigorous stirring, in an anhyd. THF (35 mL) solution containing cyanuric chloride (0.200 g, 1.08 mmol), anhyd. K_2CO_3 (0.150 g, 1.08 mmol) was suspended. To this suspension, compound **3b** (0.500 g, 1.08 mmol) was added and the reaction mixture was stirred at -15 °C for 6 h then let to reach the room temperature for additional 16 h. After this period, TLC monitoring (eluent EtOH : aq. NH_3 25% 3:1 v/v) indicated the complete consumption of **3b**. A second molar equiv. of reagents was added, anhyd. K_2CO_3 (0.150 g, 1.08 mmol) and **3b** (0.500 g, 1.08 mmol). Since after 24 h at room temperature, TLC monitoring (see above) of the consumption of **3b** still indicated its presence, the reaction mixture was evaporated to dryness under reduced pressure and THF was replaced by anhyd. 1,4-dioxane (35 mL). After 36 h of reflux, TLC monitoring (eluent $CHCl_3$/EtOH 5:1 v/v) revealed formation of compound **5b** as a major spot. The reaction mixture was evaporated to dryness under reduced pressure and taken with water (22 mL) in order to remove, after filtration, all minerals. The crude product was next purified by crystallisation from boiling

ethanol (5 mL) then by recrystallization from $CHCl_3$/EtOH 5:1 v/v (9 mL) to give compound **5b** (0.960 g) as pure analytical sample.

2-Chloro-4,6-bis-{{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-4,4'-bipiperidin-1-yl}-s-triazine (**5b**). Beige powder. Yield 86% (47% if column chromatography on silica gel was used, eluent $CHCl_3$/EtOH 5:1 v/v). Mp 257 (dec.) °C. R_f (83% $CHCl_3$/EtOH) = 0.49. Anal. calcd. for $C_{53}H_{60}ClN_{17}O_4$: C, 61.53; H, 5.85; N, 23.01%. Found: C, 61.67; H, 5.98; N, 22.85%. IR (KBr) ν_{max} 3444 (m), 2920 (w), 2848 (w), 1612 (m), 1586 (m), 1567 (m), 1508 (s), 1433 (m), 1361 (m), 1300 (w), 1235 (m), 987 (w), 831 (m), 803 (m) cm^{-1}. ^1H and 2D-^1H,^1H-COSY-NMR (500 MHz, DMSO-d_6, 298 K) δ_H 1.05-1.09 (8H, m, H-3, -3', -5, -5'-ax, Bipip), 1.36 (4H, br s, H-4, -4'-ax, Bipip), 1.72 (8H, d, $^2J_{H,H}$=12.0 Hz, H-3, -3', -5, -5'-eq, Bipip), 2.68-2.80 (8H, m, H-2, -2', -6, -6'-ax, Bipip), 4.54 and 4.61 (4H, d, $^2J_{H,H}$=12.0 Hz, H-2, -6-eq, Bipip), 4.69 (4H, br d, $^2J_{H,H}$=5.5 Hz, H-2', -6'-eq, Bipip), 6.65 (8H, d, $^2J_{H,H}$=9.0 Hz, H-3, -5, Ph), 7.44 (8H, br s, H-2, -6, Ph), 8.72 (4H, br s, NH), 9.01 (4H, s, OH) ppm; ^1H and 2D-^1H,^{15}N-HMBC-NMR (500 MHz, DMSO-d_6, 353 K) δ_H 1.12-1.16 (8H, m, H-3, -3', -5, -5'-ax, Bipip), 1.41 (4H, br s, H-4, -4'-ax, Bipip), 1.72-1.78 (8H, m, H-3, -3', -5, -5'-eq, Bipip), 2.76-2.86 (8H, m, H-2, -2', -6, -6'-ax, Bipip), 4.57 (4H, d, $^2J_{H,H}$=12.5 Hz, H-2, -6-eq, Bipip), 4.67 (4H, d, $^2J_{H,H}$=12.5 Hz, H-2', -6'-eq, Bipip), 6.67 (8H, d, $^3J_{H,H}$=9.0 Hz, H-3, -5, Ph), 7.43 (8H, d, $^3J_{H,H}$=8.5 Hz, H-2, -6, Ph), 8.32 (4H, s, NH), 8.66 (4H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=72 μm^2/s. ^{13}C QC-, DEPT-, 2D-^1H,^{13}C-HSQC- and -HMBC-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 29.3 (8C, C-3, -3', -5, -5', Bipip), 40.9 and 41.1 (4C, C-4, -4', Bipip), 43.6 (4C, C-2', -6', Bipip), 43.9 (4C, C-2, -6, Bipip), 115.2 (8C, C-3, -5, Ph), 122.3 (8C, C-2, -6, Ph), 132.3 (4C, C-1, Ph), 152.8 (4C, C-4, Ph), 163.9 (2C, C-2, *s*-triazine T-0), 164.6 (4C, C-4, -6, *s*-triazine T-0), 164.7 (2C, C-4, -6, *s*-triazine T-1), 169.2 (1C, C-2, *s*-triazine T-1) ppm. HRMS (APCI) (relative intensity) *m*/*z*: 1034.6765 (7) $[M+H]^+$. $[M+H]^+$ calcd for $C_{53}H_{61}ClN_{17}O_4$, 1034.4781.

Preparation of compound 6

At room temperature and with vigorous stirring, in an anhyd. THF (160 mL) solution containing anhyd. piperazine (0.772 g, 8.96 mmol), anhyd. K_2CO_3 (0.310 g, 2.24 mmol) was suspended. To this suspension, compound **5a** (1.950 g, 2.24 mmol) was added as five equal portions every 4-6 hrs. After each portion, TLC monitoring indicated the complete consumption of **5a** (eluent $CHCl_3$/EtOH 5:1 v/v) and formation of **6** as a single major spot (eluent EtOH : aq. NH_3 25% 9:1 v/v). After that, the reaction mixture was brought at reflux for additional 12 h and then evaporated to dryness under reduced pressure. The residual crude solid was taken with boiling water (40 mL), filtered off and well washed with hot water (30 mL) to the complete removal of minerals and excess of piperazine. The crude product was twice crystallised from boiling EtOH (8 and 6 mL respectively) to afford compound **6** (1.812 g) as pure analytical sample.

2-(Piperazin-1-yl)-4,6-bis-{{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-piperazin-4-yl}-s-triazine (**6**). Beige powder. Yield 88% (55% if column chromatography on silica gel was used, eluent EtOH : aq. NH_3 25% 9:1 v/v). Mp 242 (dec.) °C. R_f (90% EtOH/aq. NH_3 25%) = 0.56. Anal. calcd. for $C_{45}H_{49}N_{19}O_4$: C, 58.75; H, 5.37; N, 28.93%. Found: C, 59.11; H, 5.31; N, 28.98%. IR (KBr) ν_{max} 3409 (w), 2850 (w), 1548 (m), 1499 (s), 1430 (s), 1355 (m), 1257 (m), 1215 (m), 1001 (m), 801 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 2.93 (4H, br s, H-3, -5, Pip-1), 3.77 (20H, br s; 16H, Pip-0; 4H, H-2, -6, Pip-1), 6.68 (8H, d, $^3J_{H,H}$=8.0 Hz, H-3, -5, Ph), 7.45 (8H, br s, H-2, -6, Ph), 8.78 (4H, br s, NH), 9.04 (4H, s, OH) ppm; ^1H and 2D-^1H,^{15}N-HMBC-NMR (500 MHz, DMSO-d_6, 363 K) δ_H 2.95 (4H, t, $^3J_{H,H}$=5.0 Hz, H-3, -5, Pip-1), 3.78 (16H, s, Pip-0), 3.80 (4H, s, H-2, -6, Pip-1), 6.69 (8H, d, $^3J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.44 (8H, d, $^3J_{H,H}$=8.5 Hz, H-2, -6, Ph), 8.47 (4H, br s, NH), 8.78 (4H, br s, OH) ppm. 2D-^1H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=82 μm^2/s. ^{13}C DEPT-, 2D-^1H,^{13}C-HSQC- and -HMBC-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 41.8 (C-2, -6, Pip-1), 43.1 and 43.2 (Pip-0), 44.2 (C-3, -5, Pip-1), 115.3 (C-3, -5, Ph), 122.6 (C-2, -6, Ph), 132.2 (C-1, Ph), 153.0 (C-4, Ph), 164.6 (C-2, *s*-triazine T-1), 165.2 (C-4, -6, *s*-triazine T-1), 165.25 (C-2, *s*-triazine T-0), 165.32 (C-4, -6, *s*-triazine T-0) ppm. HRMS (APCI) (relative intensity) *m*/*z*: 920.4267 (100) $[M+H]^+$. $[M+H]^+$ calcd for $C_{45}H_{50}N_{19}O_4$, 920.4293.

Preparation of compound 7

Under inert atmosphere and room temperature, in an anhyd. 1,4-dioxane (7.5 mL) solution containing cyanuric chloride (0.018 g, 0.10 mmol) and compound **6** (0.300 g, 0.33 mmol), anhyd. K_2CO_3 (0.045 g, 0.33 mmol) was suspended with vigorous stirring. The reaction mixture was stirred for 24 h then was brought to reflux for additional 48 h. Finally, the resulted suspension was evaporated to dryness under reduced pressure and taken with water (7.5 mL). After filtering off and well washing with water to remove all minerals, the

crude dried product was twice crystallised from boiling ethanol (3 and 6 mL respectively) to afford pure compound **7** (0.240 g) as pure analytical sample.

2,4,6-Tris-{{4,6-bis-{{4,6-bis[(4-hydroxy)phenylamino]-s-triazin-2-yl}-piperazin-4-yl}-s-triazin-2-yl}-piperazin-4-yl}-s-triazine (**7**). Brownish powder. Yield 85%. Mp 292 (dec.) ^{o}C. Anal. calcd. for $C_{138}H_{144}N_{60}O_{12}$: C, 58.46; H, 5.12; N, 29.64%. Found: C, 58.71; H, 4.93; N, 29.88%. IR (KBr) ν_{max} 3441 (m), 2851 (w), 1618 (m), 1546 (s), 1496 (s), 1429 (s), 1354 (m), 1257 (m), 1215 (m), 1166 (w), 998 (m), 833 (w), 801 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ_H 3.79 (72H, br s, Pip-0, -1), 6.68 (24H, br s, H-3, -5, Ph), 7.45 (24H, br s, H-2, -6, Ph), 8.79 (12H, br s, NH), 9.05 (12H, s, OH) ppm; ^{1}H NMR (500 MHz, DMSO-d_6, 363 K) δ_H 3.81 (72H, s, Pip-0, -1), 6.70 (24H, d, $^{3}J_{H,H}$=8.5 Hz, H-3, -5, Ph), 7.44 (24H, d, $^{3}J_{H,H}$=9.0 Hz, H-2, -6, Ph), 8.39 (12H, br s, NH), 8.70 (12H, br s, OH) ppm. 2D-^{1}H-DOSY-NMR (500 MHz, 5 mM in DMSO-d_6, 298 K) D=70 μm^2/s. ^{13}C QC- and DEPT-NMR (125 MHz, DMSO-d_6, 298 K) δ_C 43.1 (36C, Pip-0, -1), 115.3 (24C, C-3, -5, Ph), 122.5 (24C, C-2, -6, Ph), 132.2 (12C, C-1, Ph), 153.0 (12C, C-4, Ph), 164.5 (12C, C-2, -4, -6, *s*-triazine T-1, -2), 165.2 (8C; 6C, C-2, *s*-triazine T-0; 2C, C-4, -6, *s*-triazine T-0), 165.3 (10C, C-4, -6, *s*-triazine T-0) ppm. HRMS (ESI) (relative intensity) *m*/*z*: 2833.2556 (73) [M]$^{+}$. [M]$^{+}$ calcd for $C_{138}H_{144}N_{60}O_{12}$, 2833.2502.

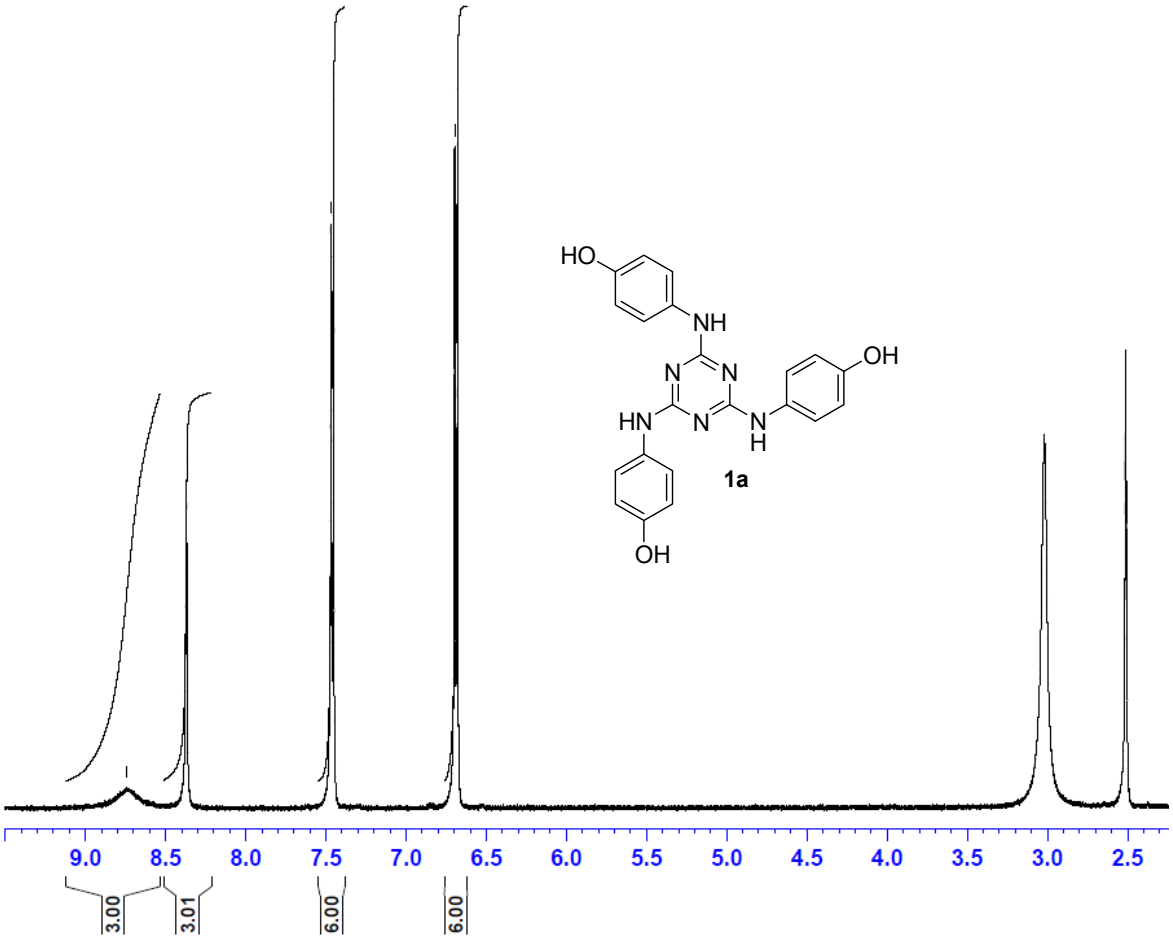


Figure SI-1. ^{1}H NMR spectrum of compound **1a** (500 MHz, DMSO-d_6, 363 K)

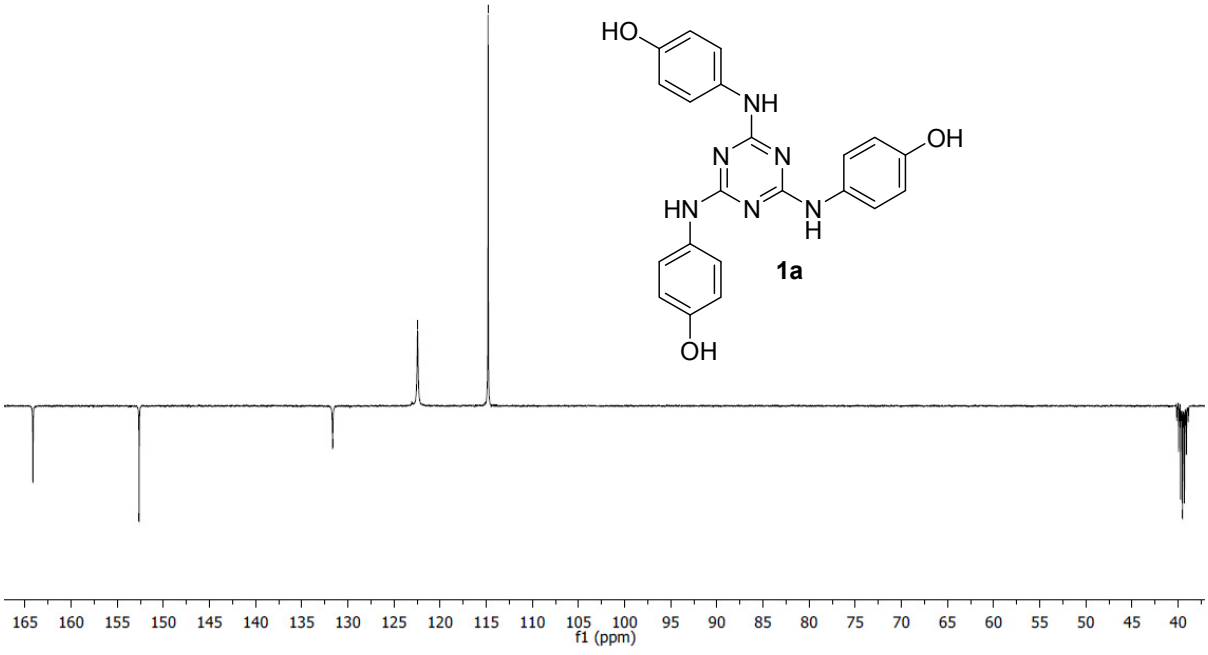


Figure SI-2. ^{13}C J_{mod}-NMR spectrum of compound **1a** (100 MHz, DMSO-d_6, 298 K)

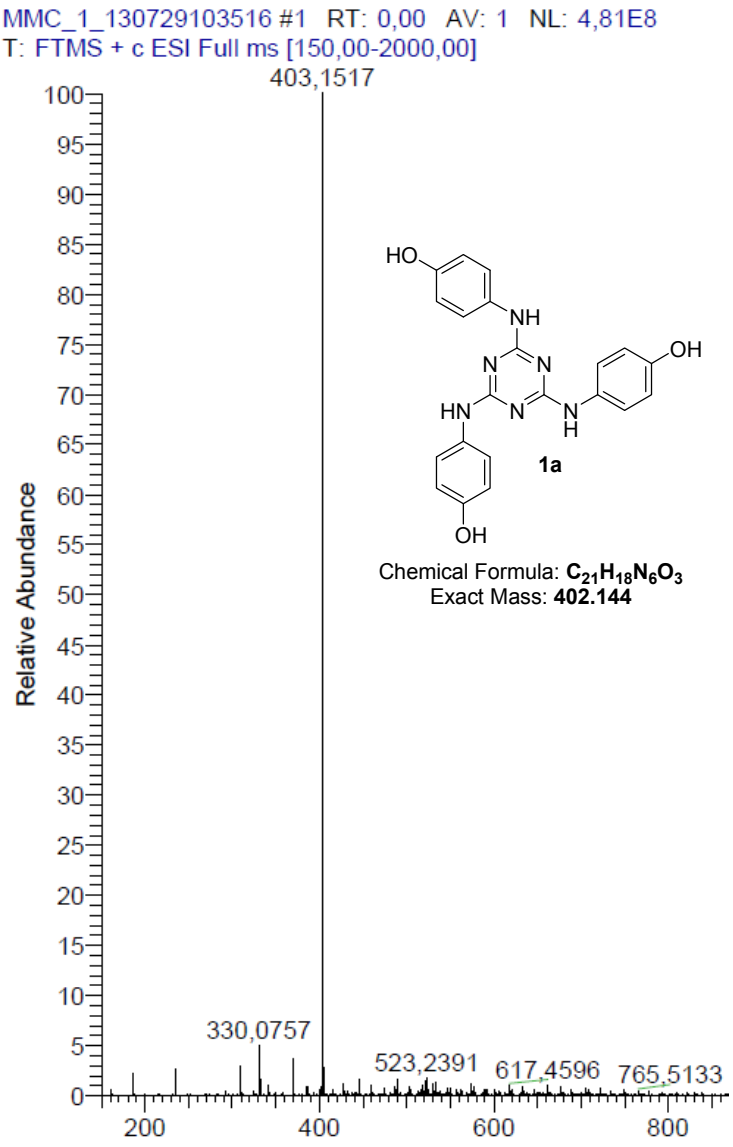


Figure SI-3. Mass spectrum of compound **1a** [HRMS (ESI)]

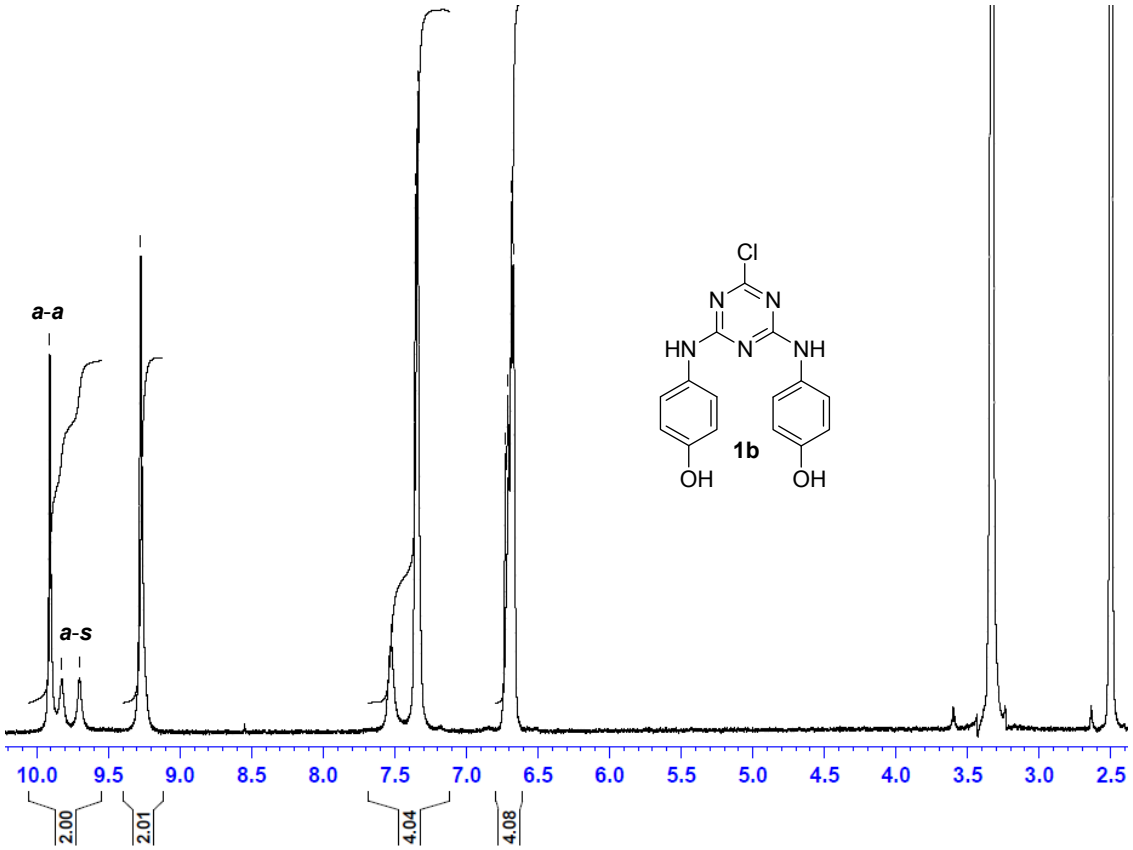


Figure SI-4. ^{1}H NMR spectrum of compound **1b** (500 MHz, DMSO-d_6, 298 K)

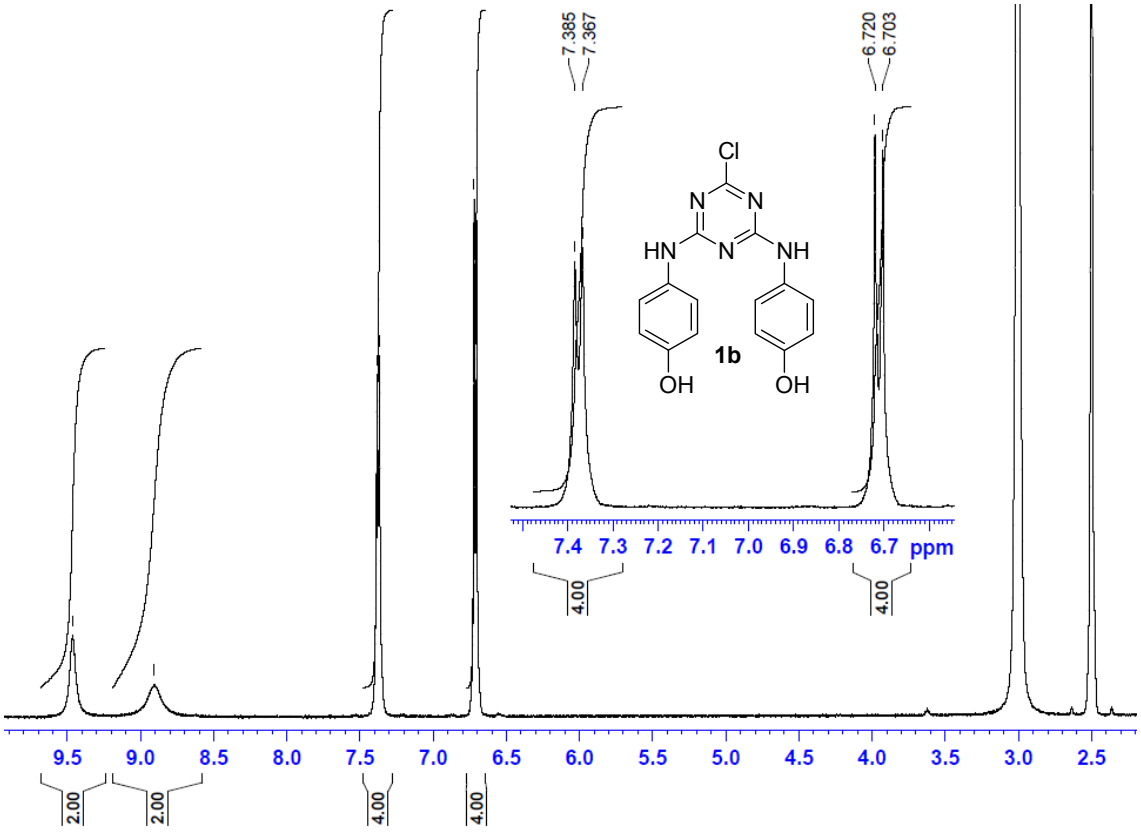


Figure SI-5. ^{1}H NMR spectrum of compound **1b** (500 MHz, DMSO-d_6, 363 K)

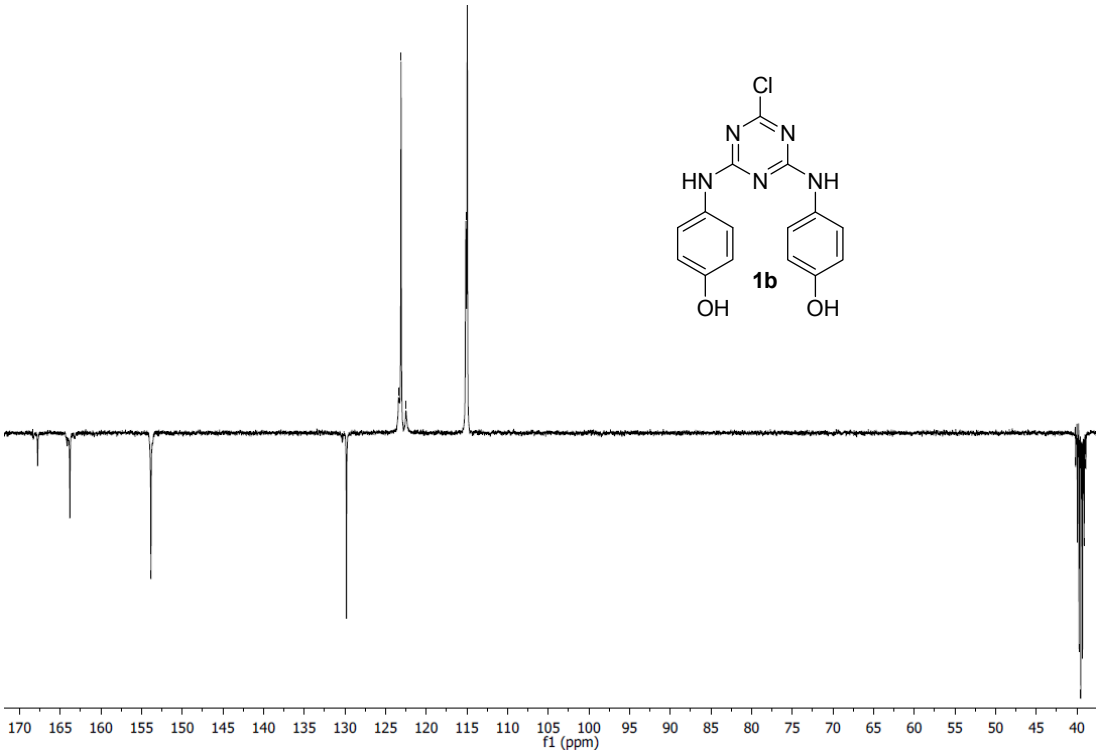


Figure SI-6. ^{13}C J_{mod}-NMR spectrum of compound **1b** (100 MHz, DMSO-d_6, 298 K)

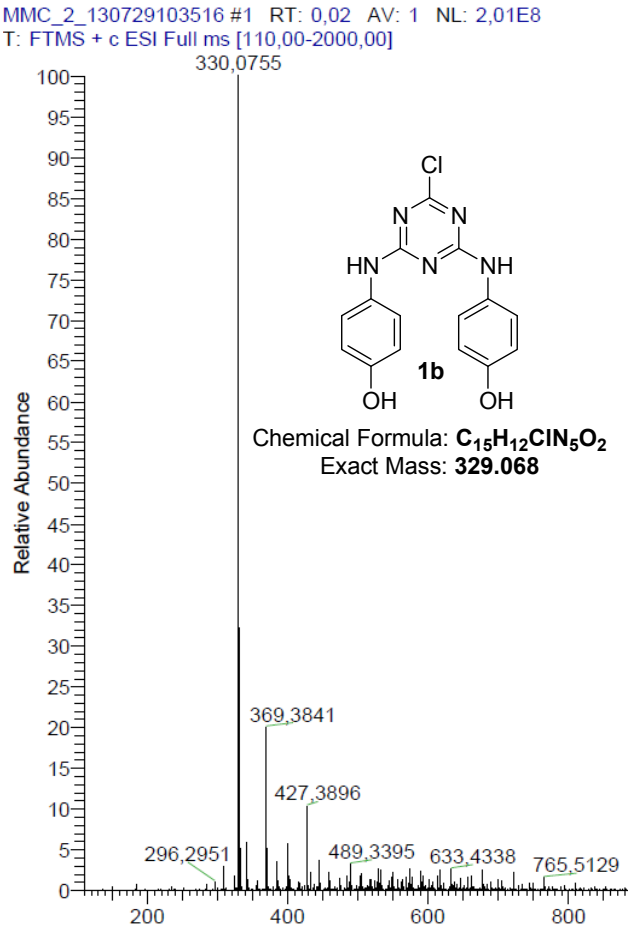


Figure SI-7. Mass spectrum of compound **1b** [HRMS (ESI)]

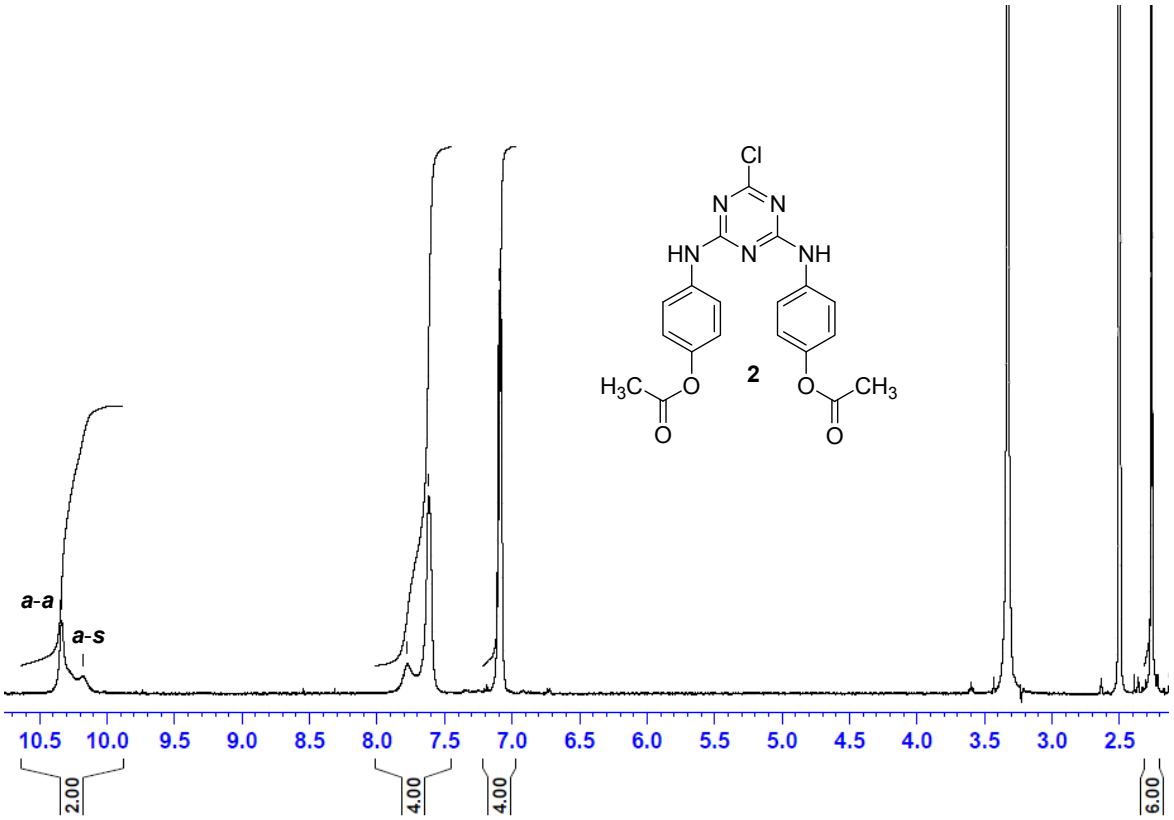


Figure SI-8. ^{1}H NMR spectrum of compound **2** (500 MHz, DMSO-d_6, 298 K)

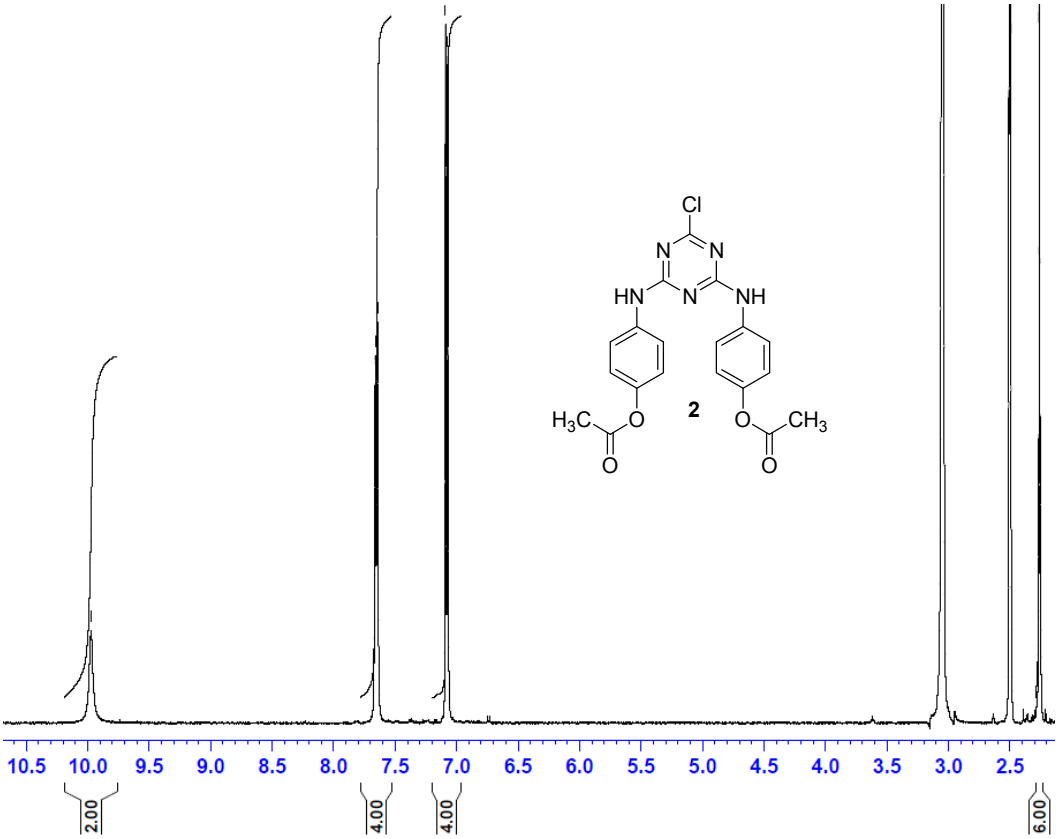


Figure SI-9. ^{1}H NMR spectrum of compound **2** (500 MHz, DMSO-d_6, 353 K)

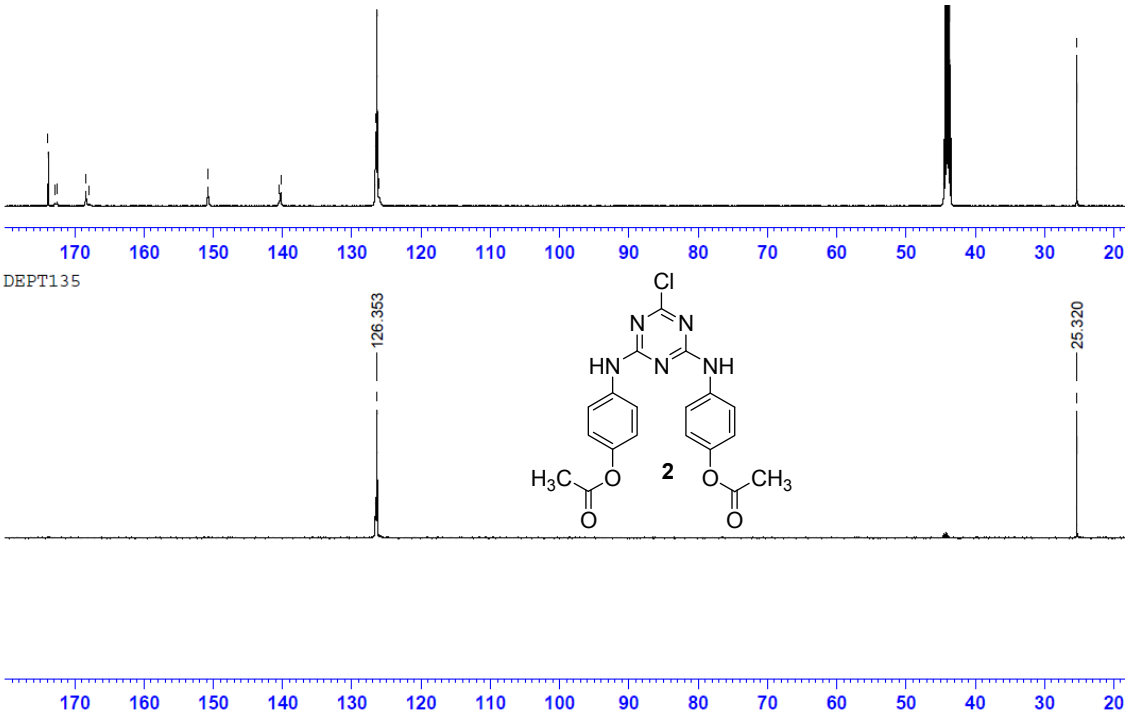


Figure SI-10. ^{13}C DEPT-NMR spectrum of compound **2** (125 MHz, DMSO-d_6, 298 K)

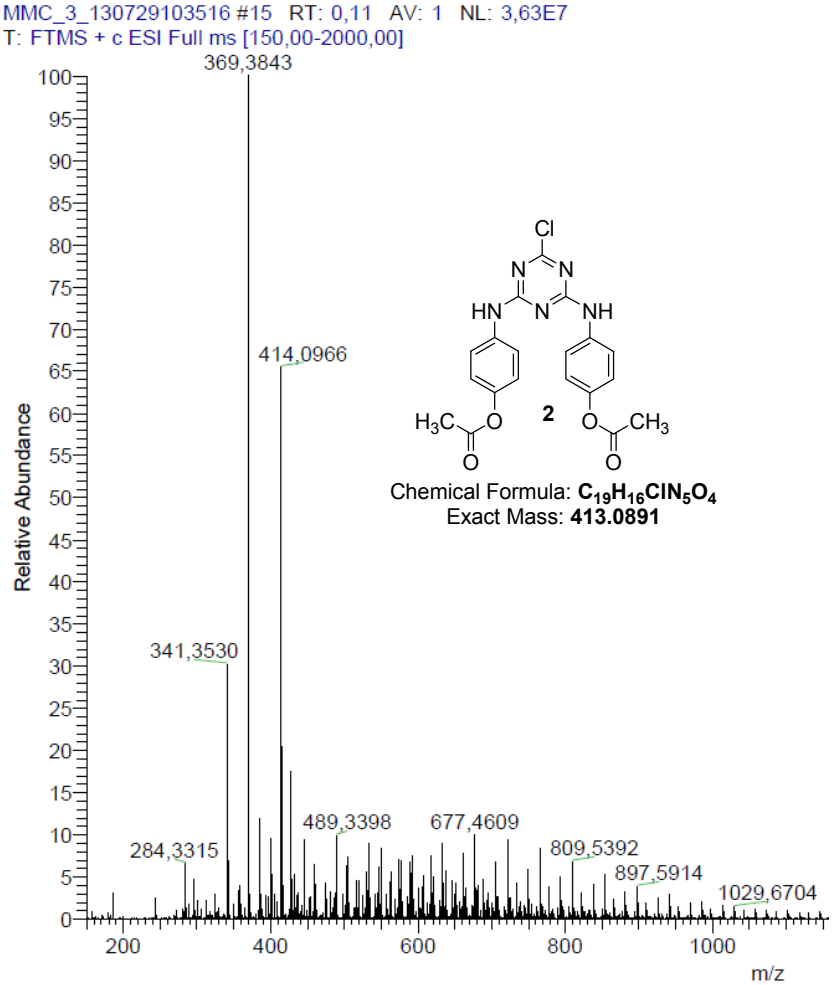


Figure SI-11. Mass spectrum of compound **2** [HRMS (ESI)]

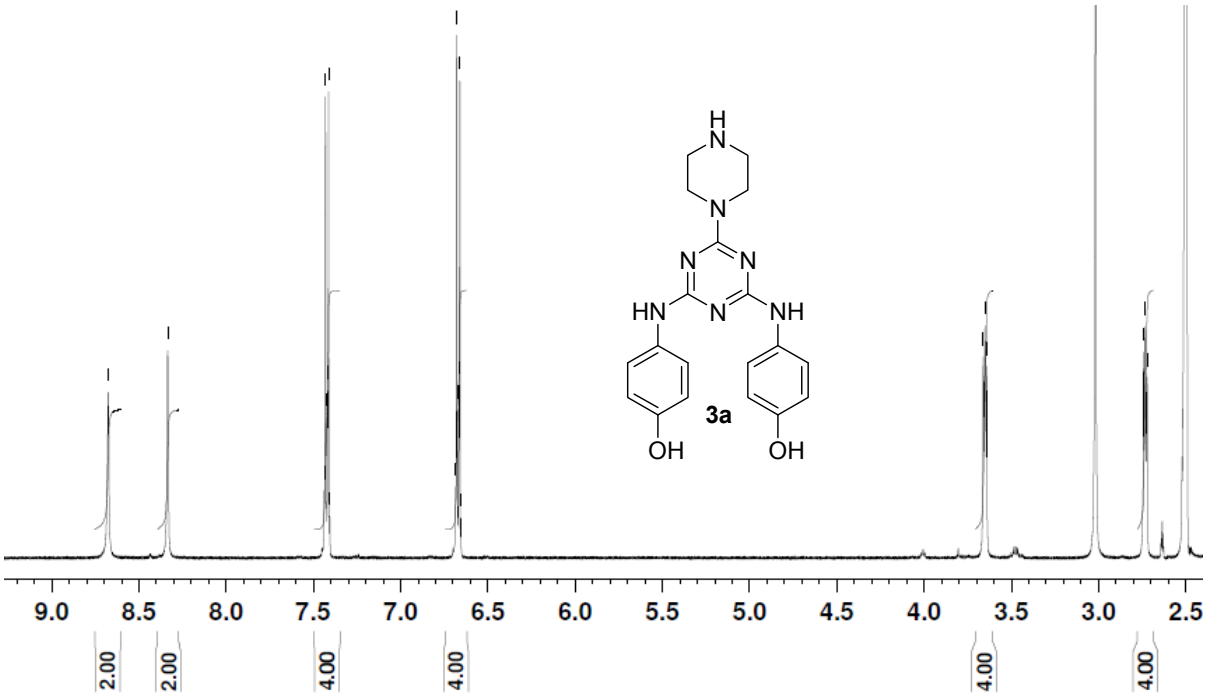


Figure SI-12. ^{1}H NMR spectrum of compound **3a** (500 MHz, DMSO-d_6, 363 K)

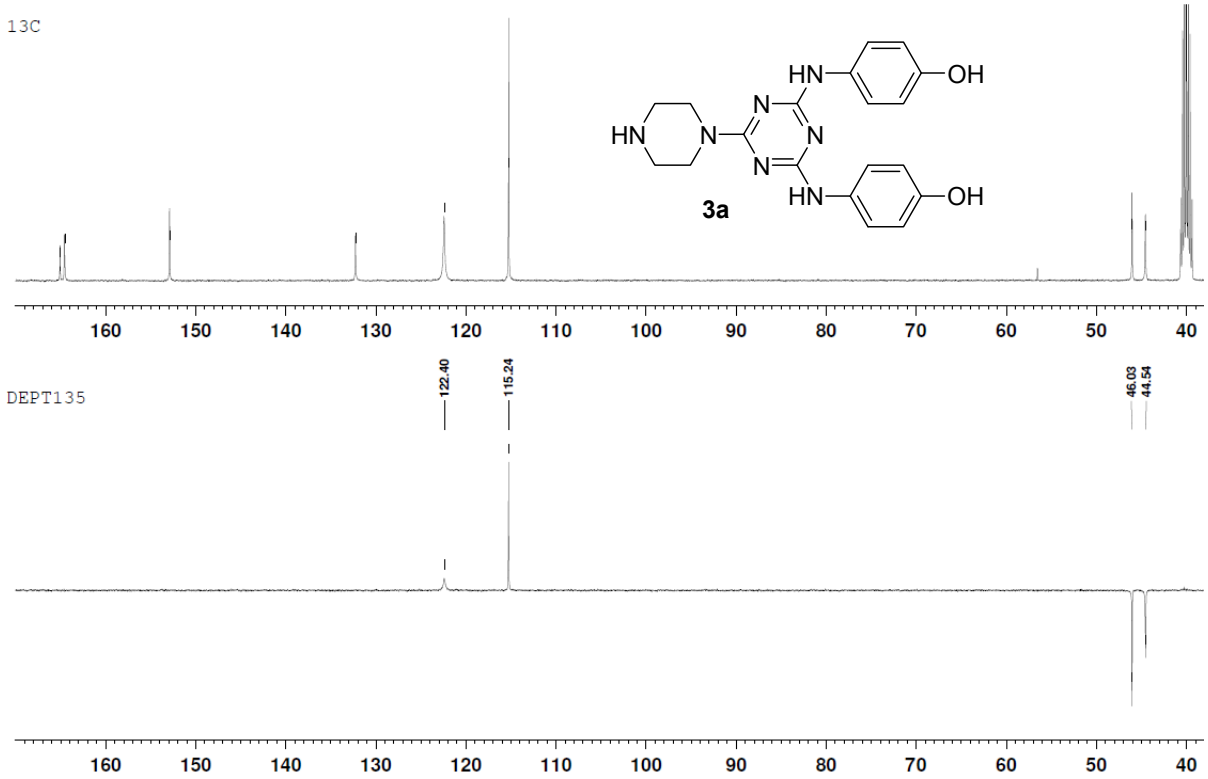


Figure SI-13. ^{13}C DEPT-NMR spectrum of compound **3a** (125 MHz, DMSO-d_6, 298 K)

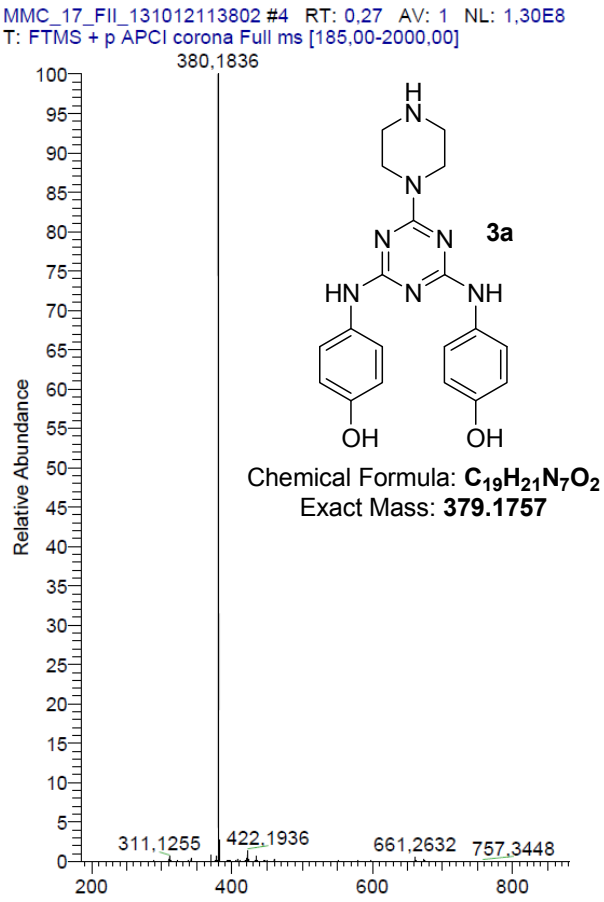


Figure SI-14. Mass spectrum of compound **3a** [HRMS (APCI)]

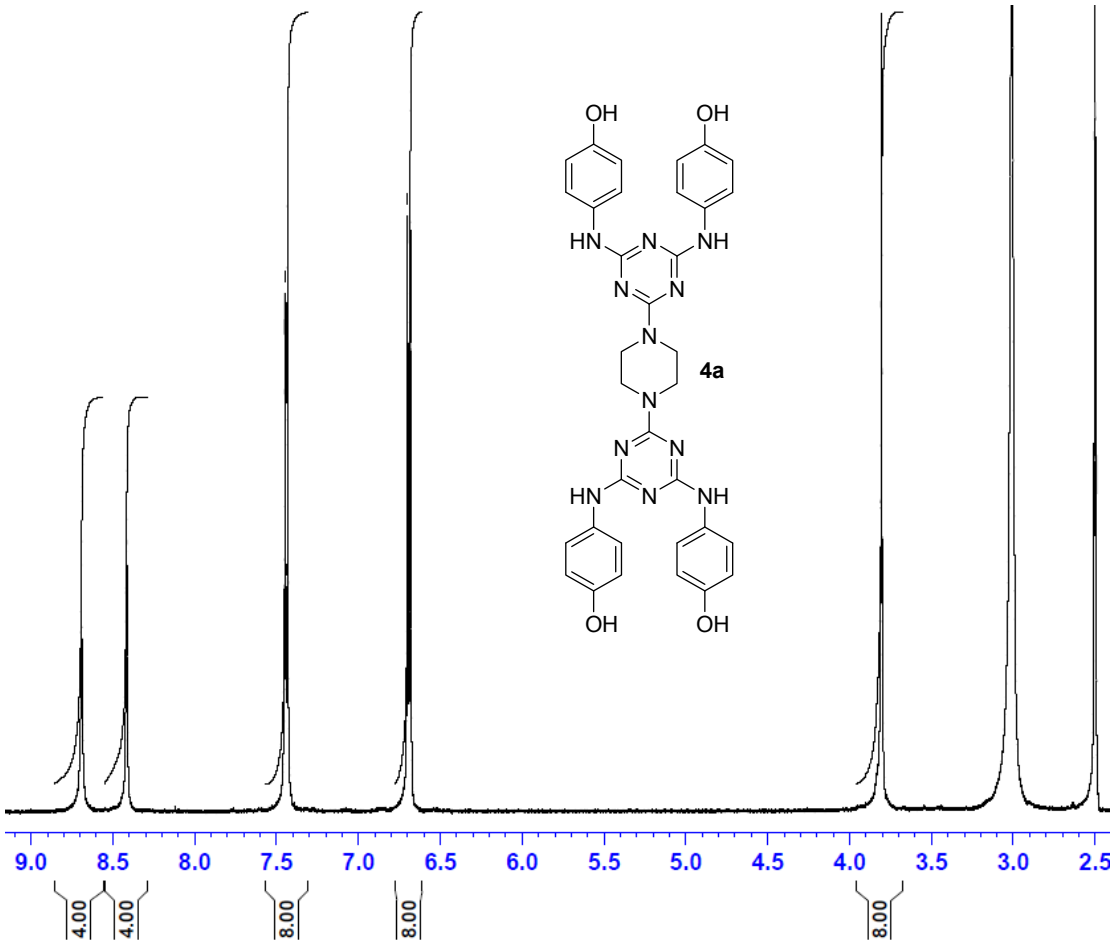


Figure SI-15. ^{1}H NMR spectrum of compound **4a** (500 MHz, DMSO-d_6, 363 K)

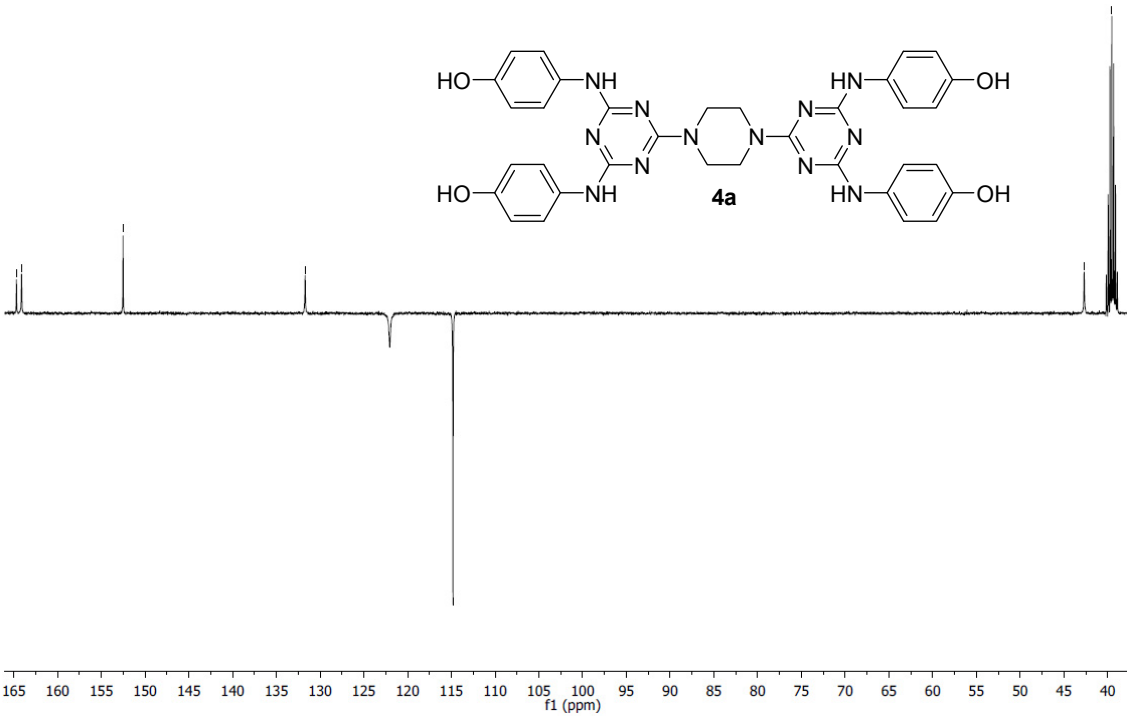


Figure SI-16. ^{13}C J_{mod}-NMR spectrum of compound **4a** (100 MHz, DMSO-d_6, 298 K)

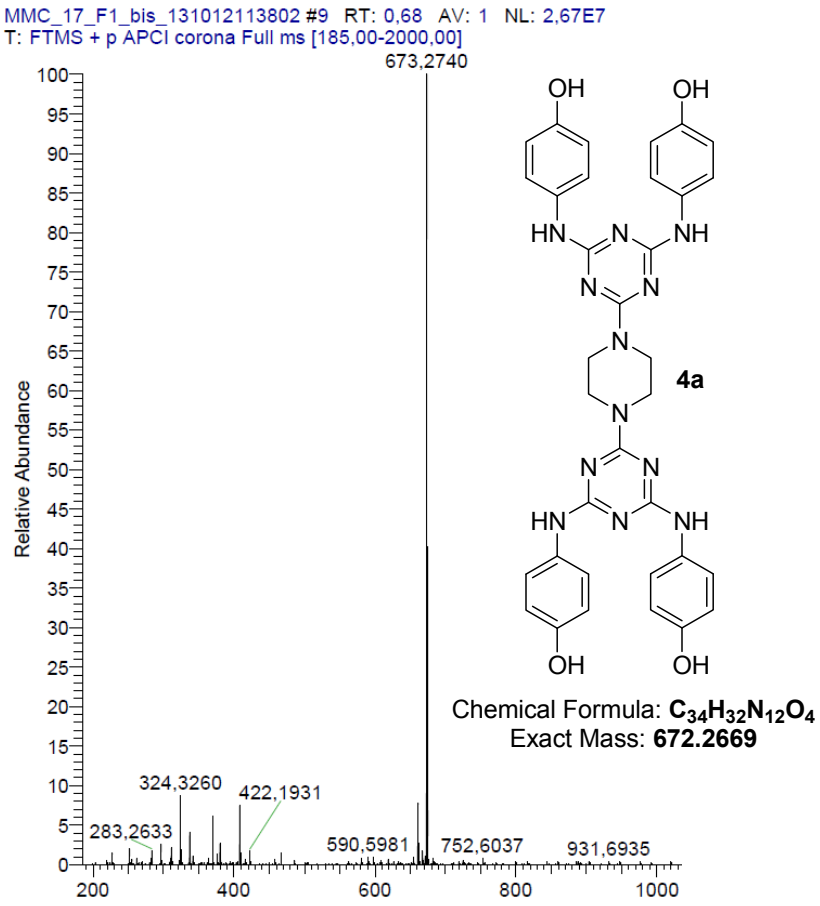


Figure SI-17. Mass spectrum of compound **4a** [HRMS (APCI)]

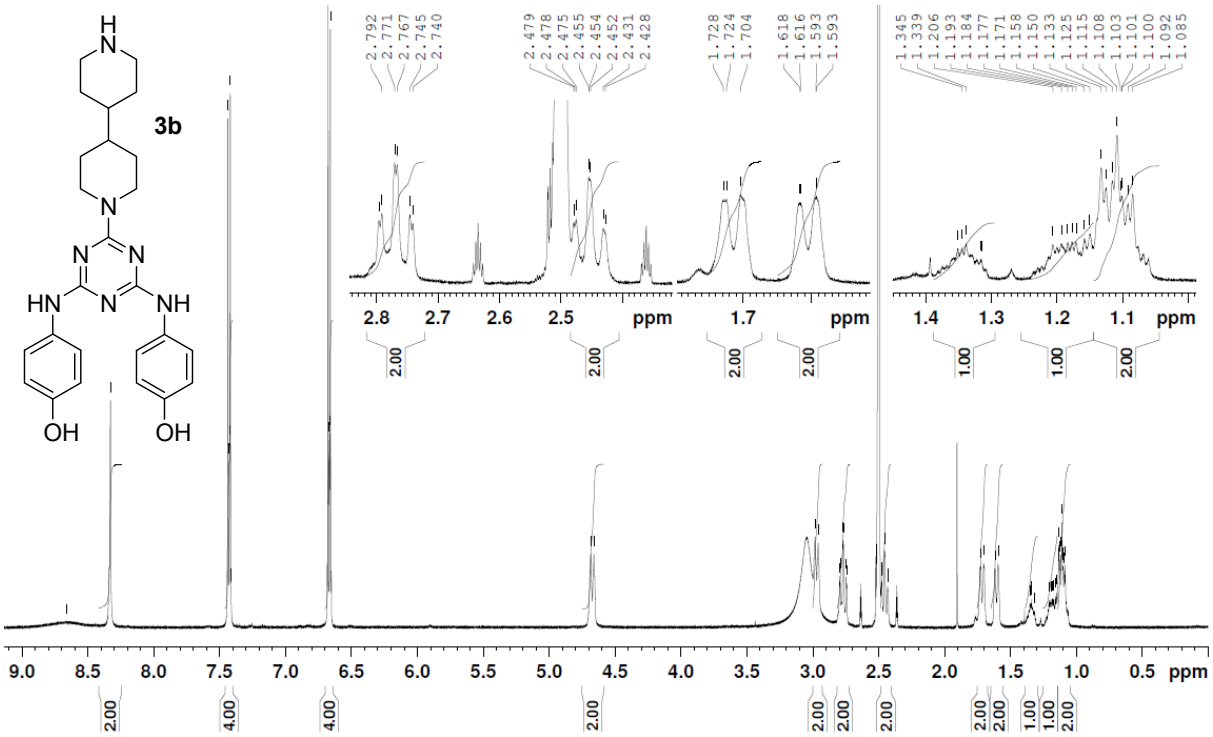


Figure SI-18. ^{1}H NMR spectrum of compound **3b** (500 MHz, DMSO-d_6, 363 K)

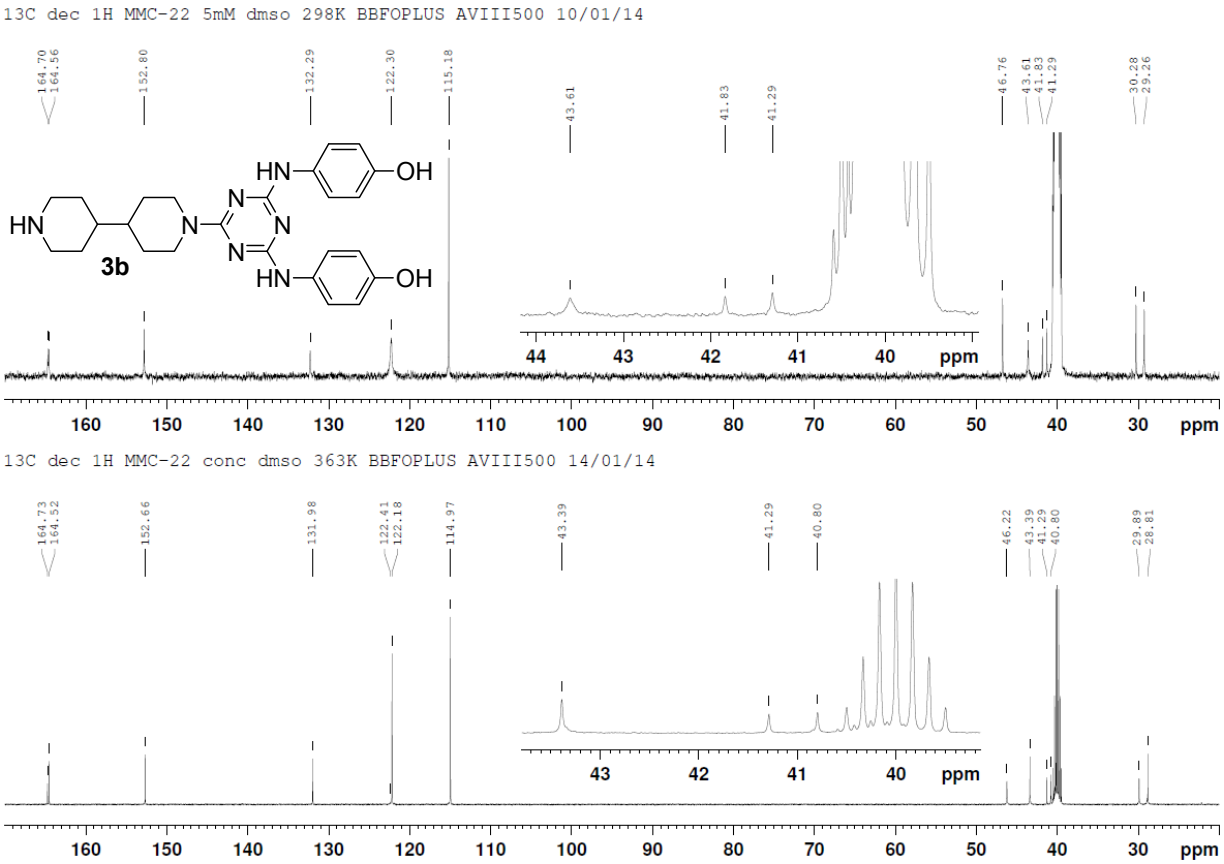


Figure SI-19. ^{13}C NMR spectrum of compound **3b** (125 MHz, DMSO-d_6, 298 K, 363 K)

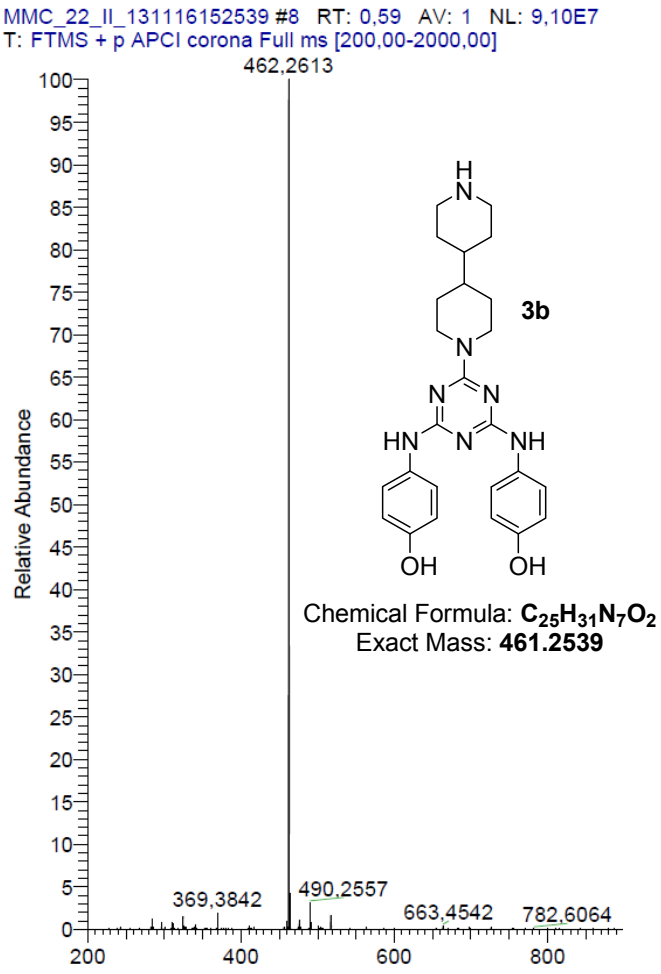


Figure SI-20. Mass spectrum of compound **3b** [HRMS (APCI)]

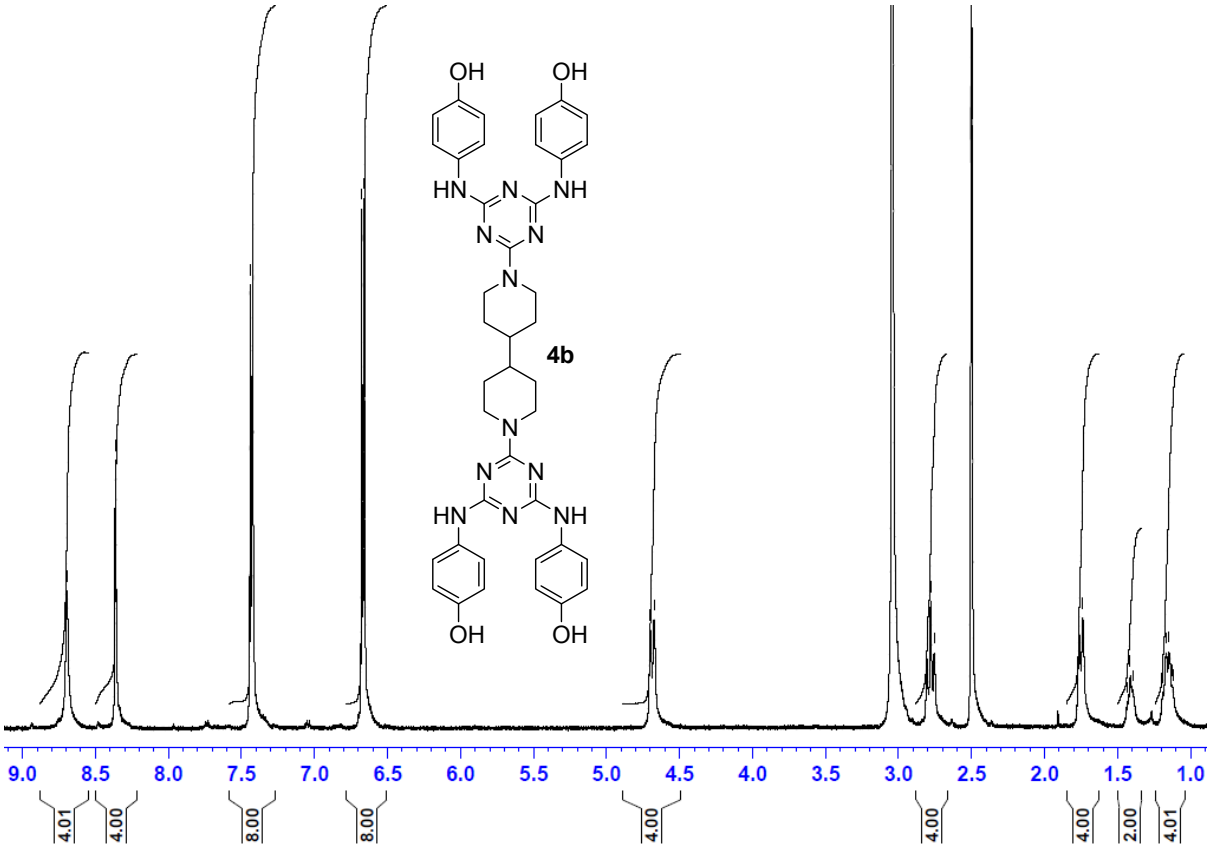


Figure SI-21. ^{1}H NMR spectrum of compound **4b** (500 MHz, DMSO-d_6, 353 K)

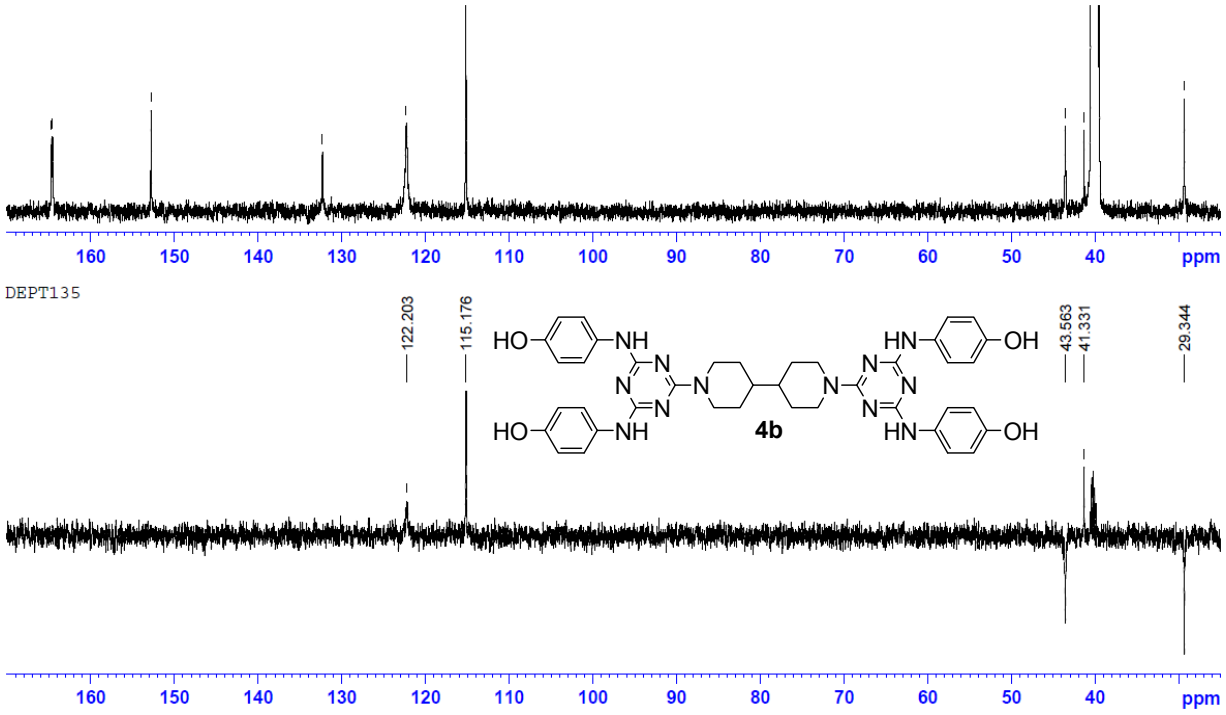


Figure SI-22. ^{13}C DEPT-NMR spectrum of compound **4b** (125 MHz, DMSO-d_6, 298 K)

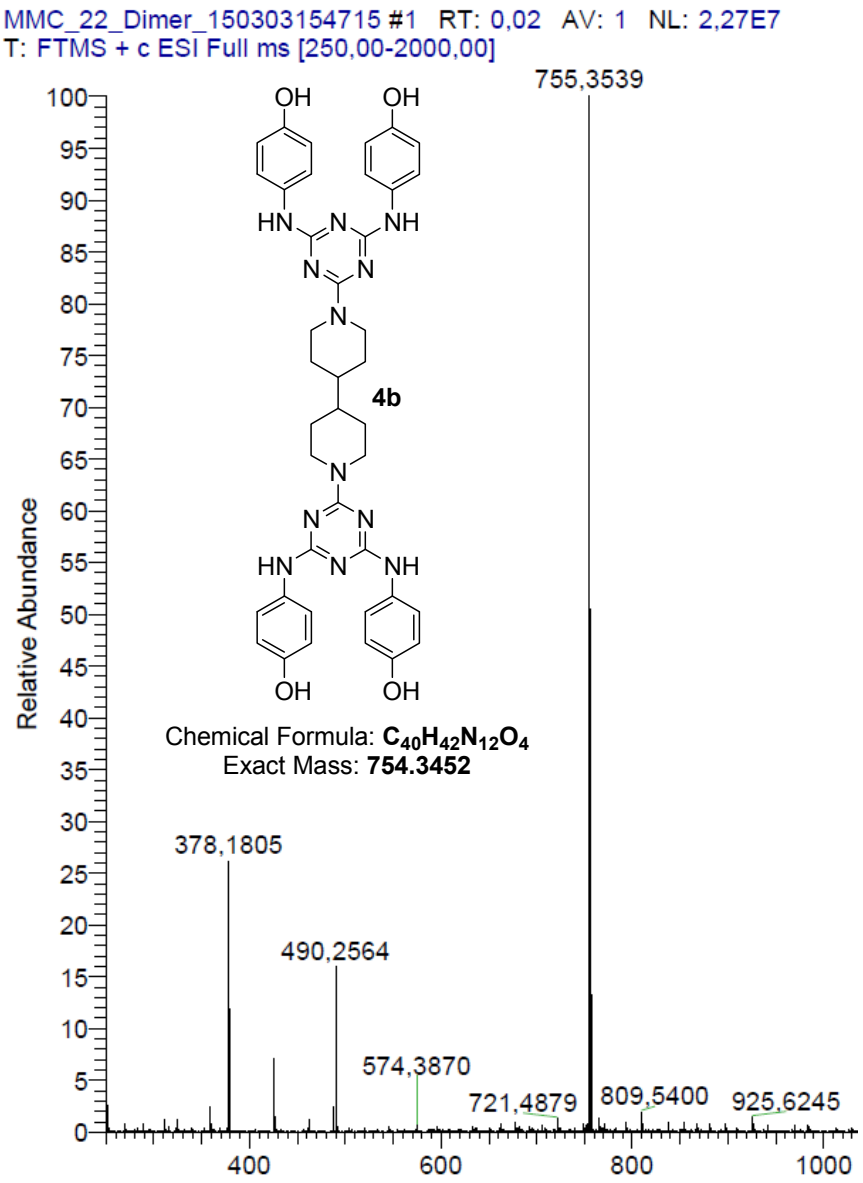


Figure SI-23. Mass spectrum of compound **4b** [HRMS (ESI)]

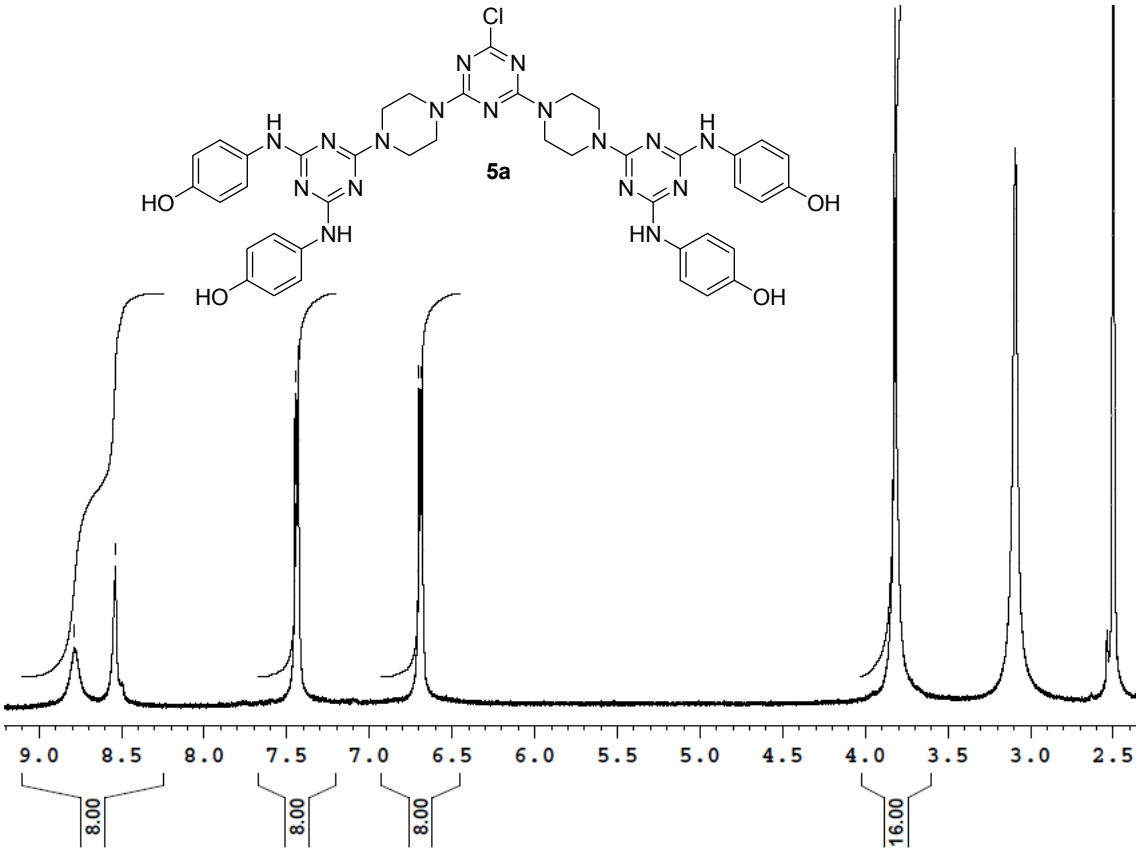


Figure SI-24. ^{1}H NMR spectrum of compound **5a** (500 MHz, DMSO-d_6, 363 K)

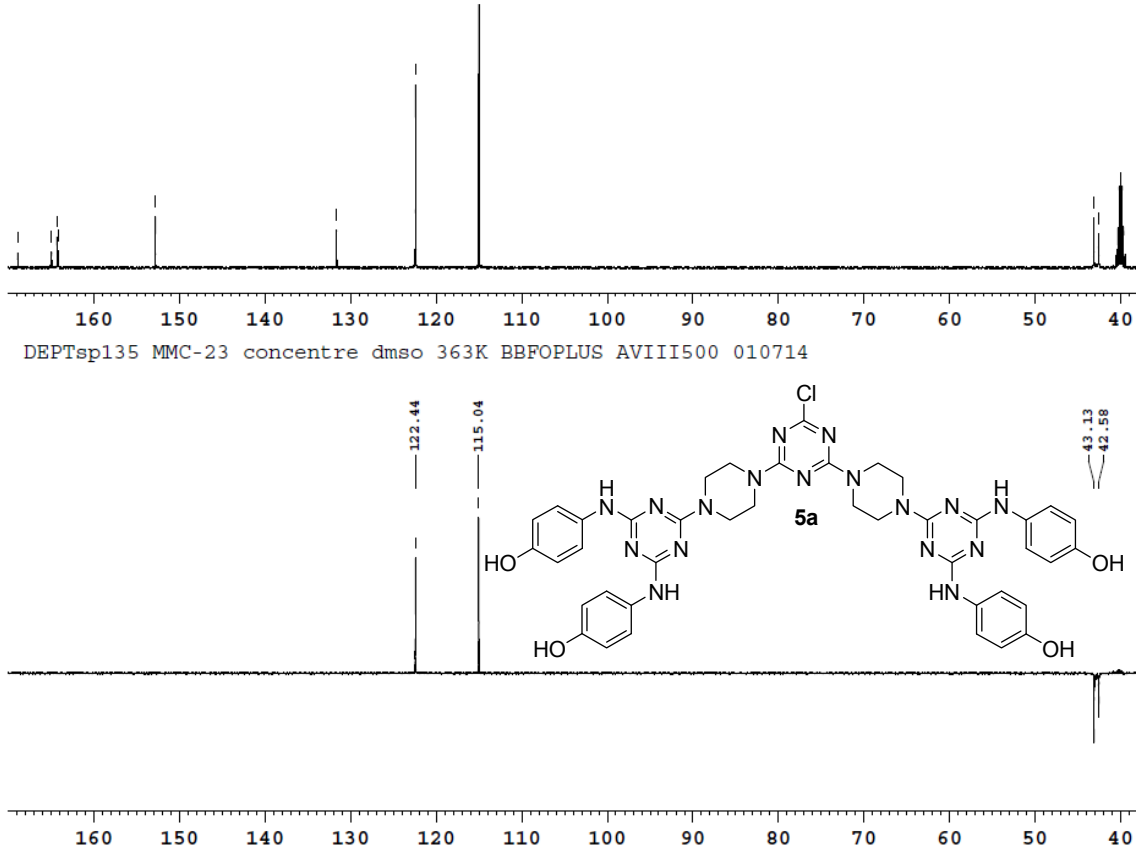


Figure SI-25. ^{13}C DEPT-NMR spectrum of compound **5a** (125 MHz, DMSO-d_6, 363 K)

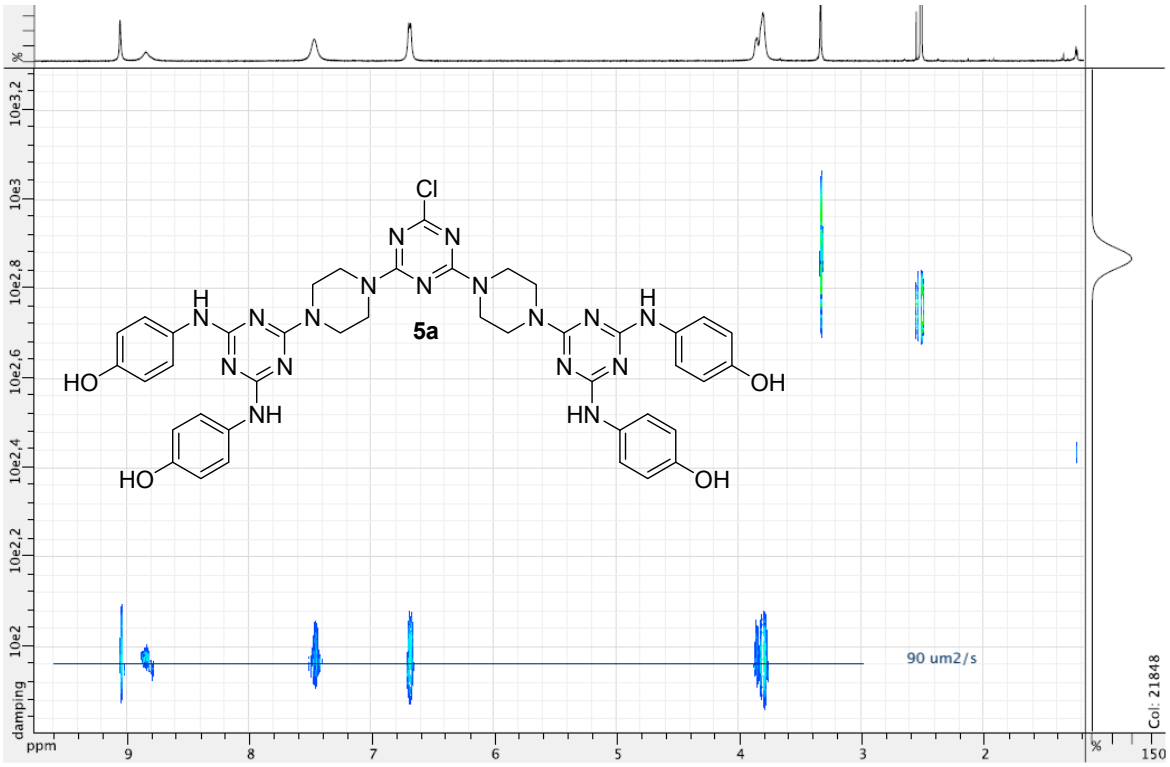


Figure SI-26. 2D-^{1}H-DOSY-NMR spectrum of compound **5a** (500 MHz, 5 mM in DMSO-d_6, 298 K)

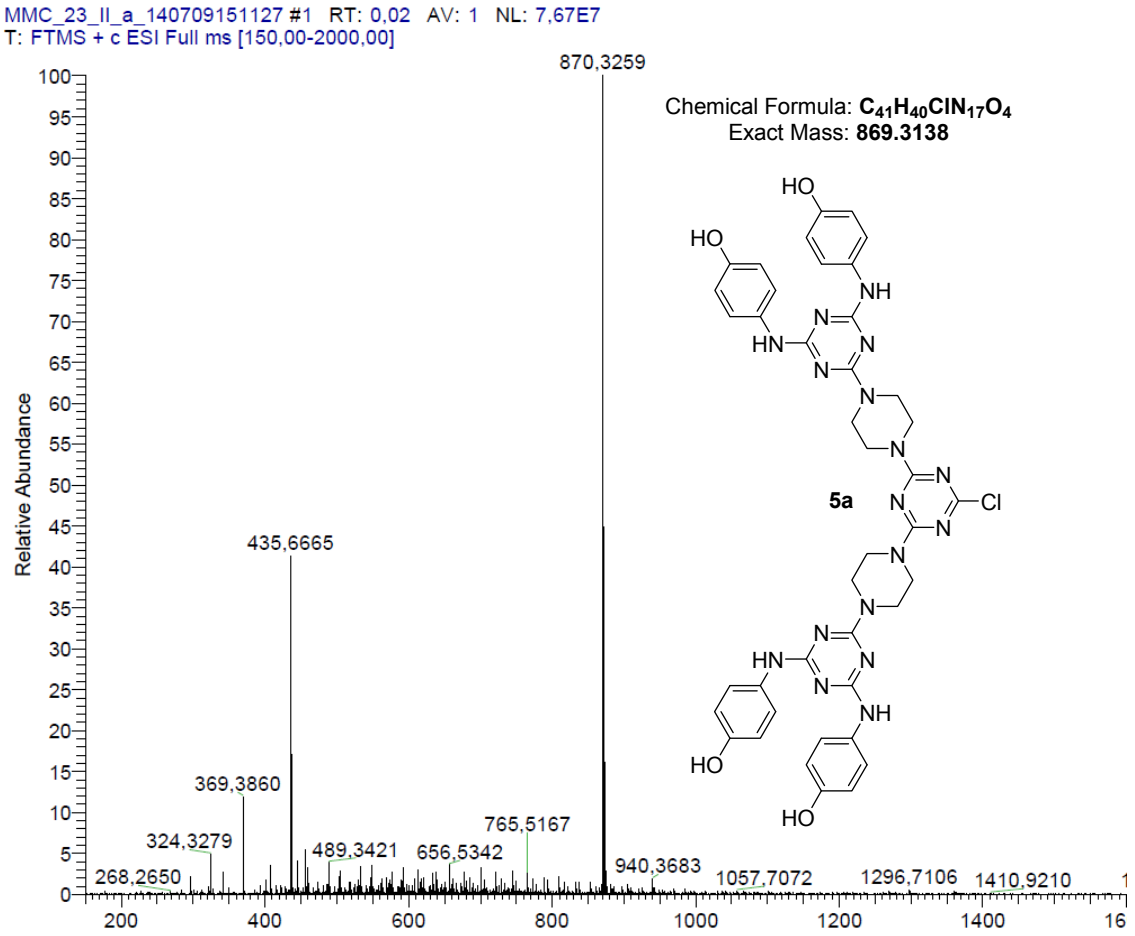


Figure SI-27. Mass spectrum of compound **5a** [HRMS (ESI)]

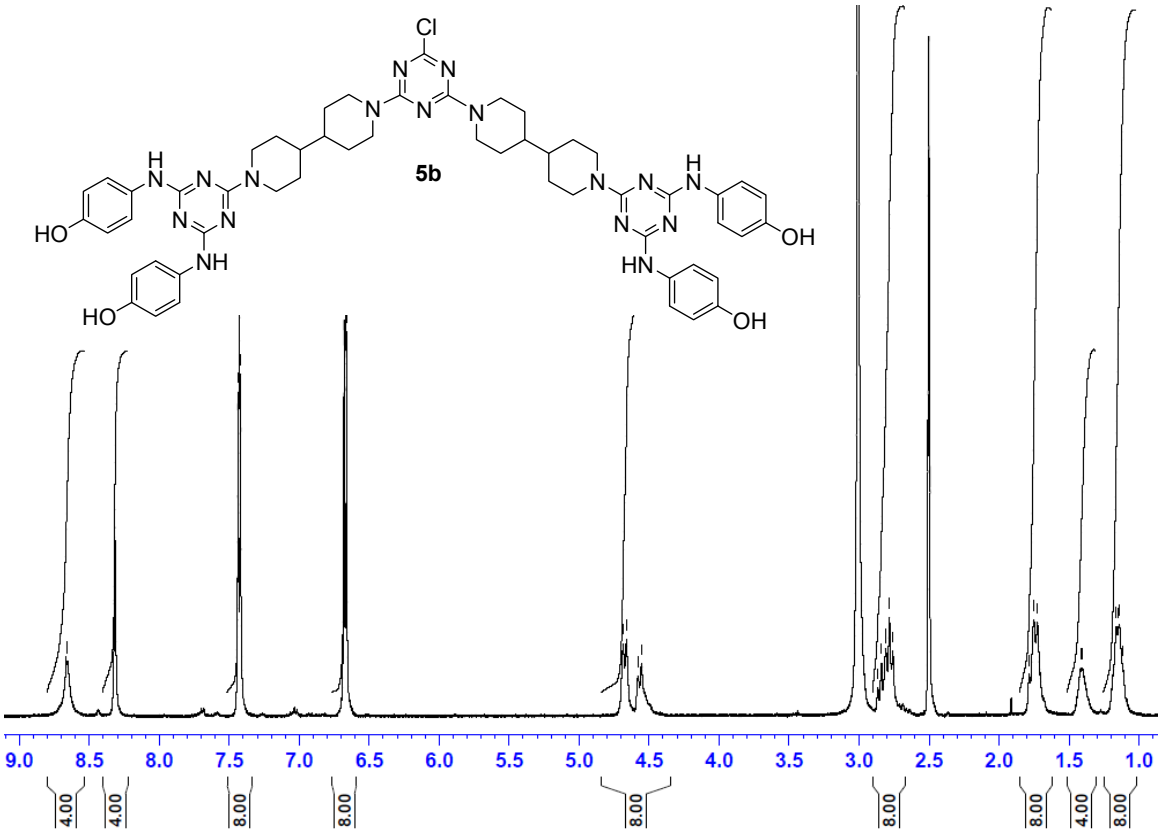


Figure SI-28. ^{1}H NMR spectrum of compound **5b** (500 MHz, DMSO-d_6, 353 K)

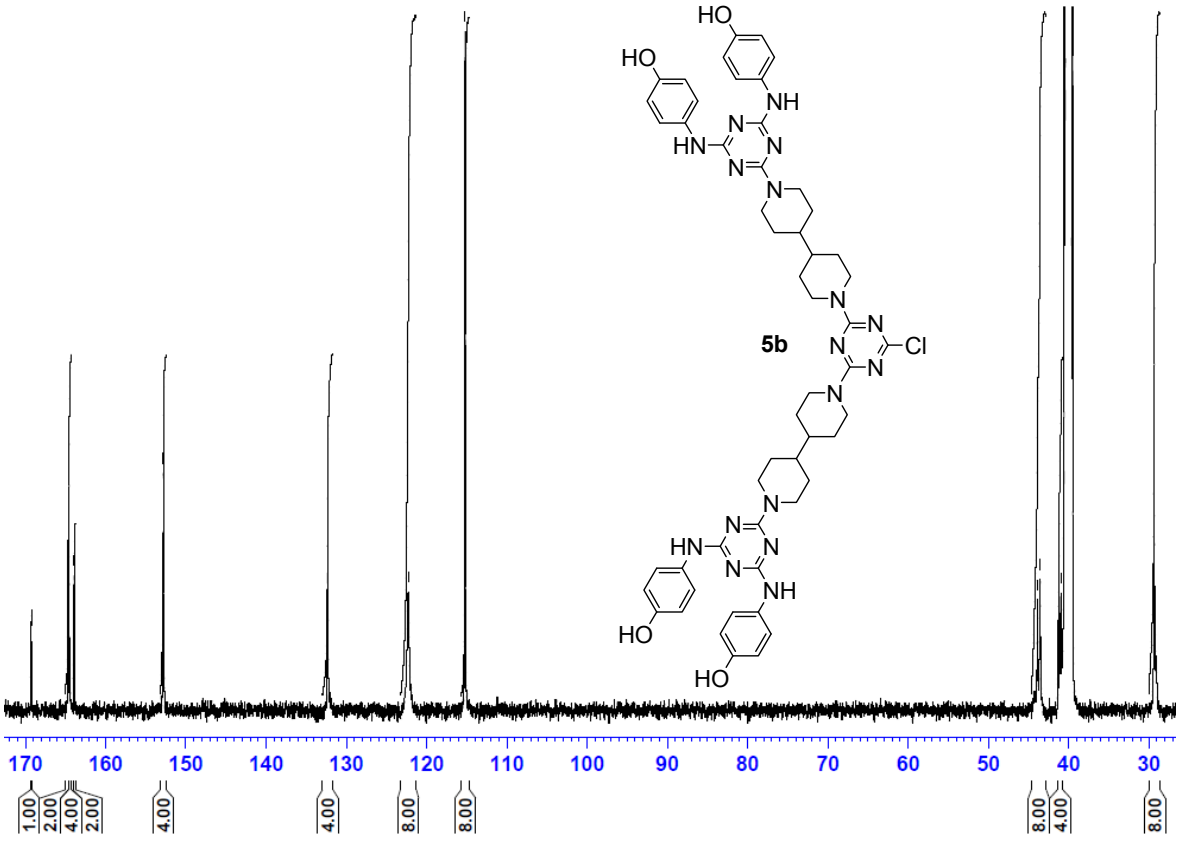


Figure SI-29. ^{13}C QC-NMR spectrum of compound **5b** (125 MHz, DMSO-d_6, 298 K)

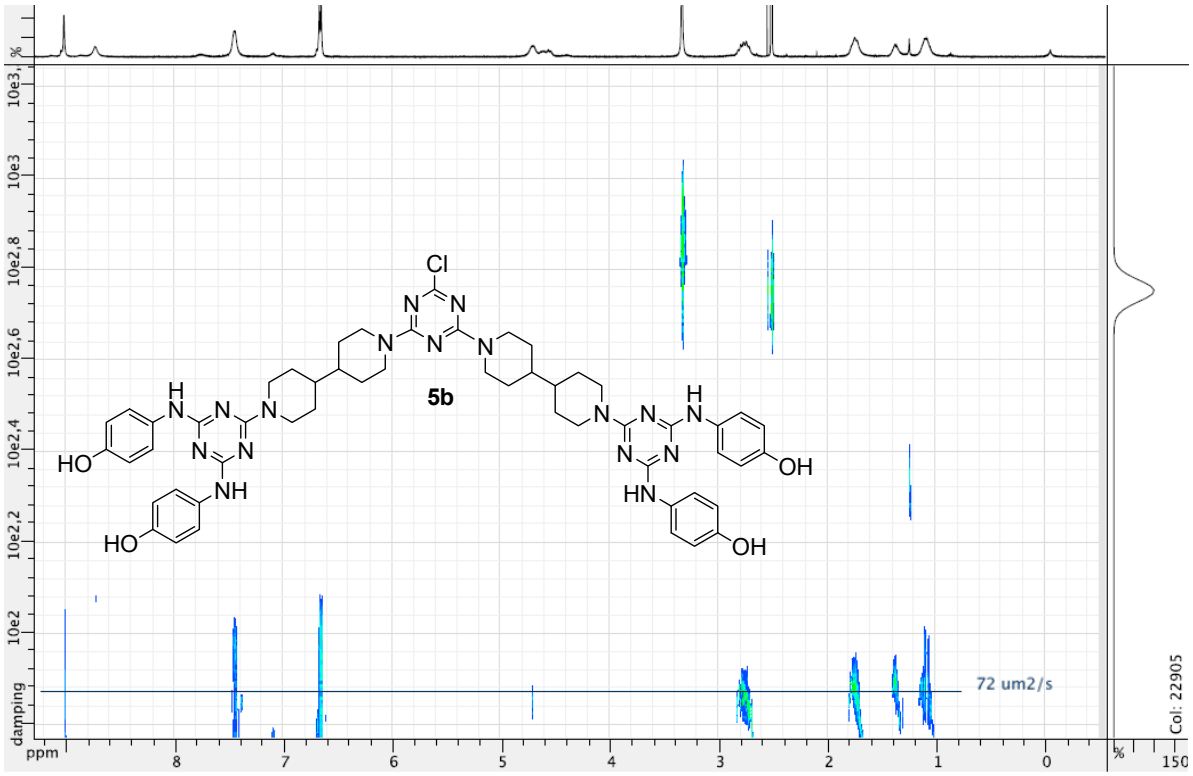


Figure SI-30. 2D-^{1}H-DOSY-NMR spectrum of compound **5b** (500 MHz, 5 mM in DMSO-d_6, 298 K)

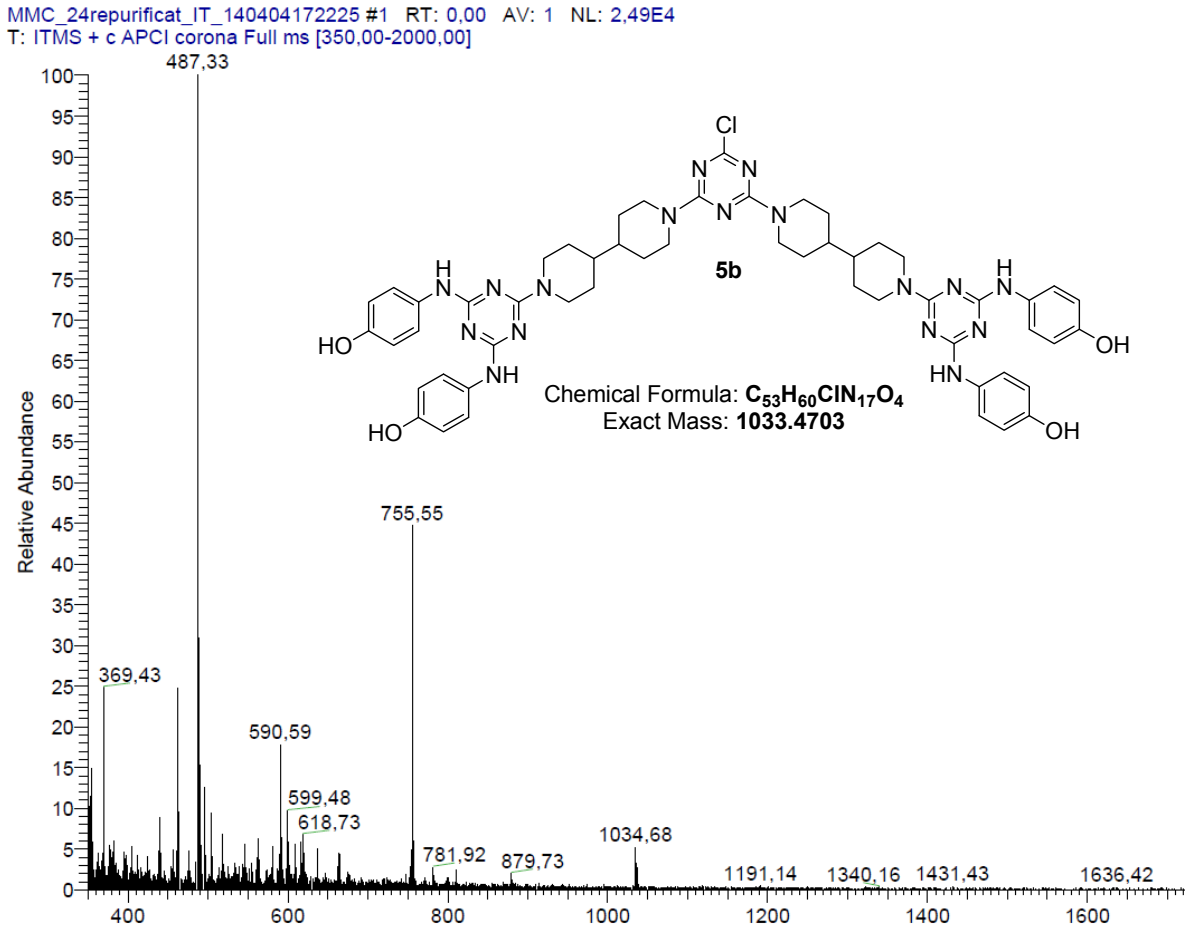


Figure SI-31. Mass spectrum of compound **5b** [HRMS (APCI)]

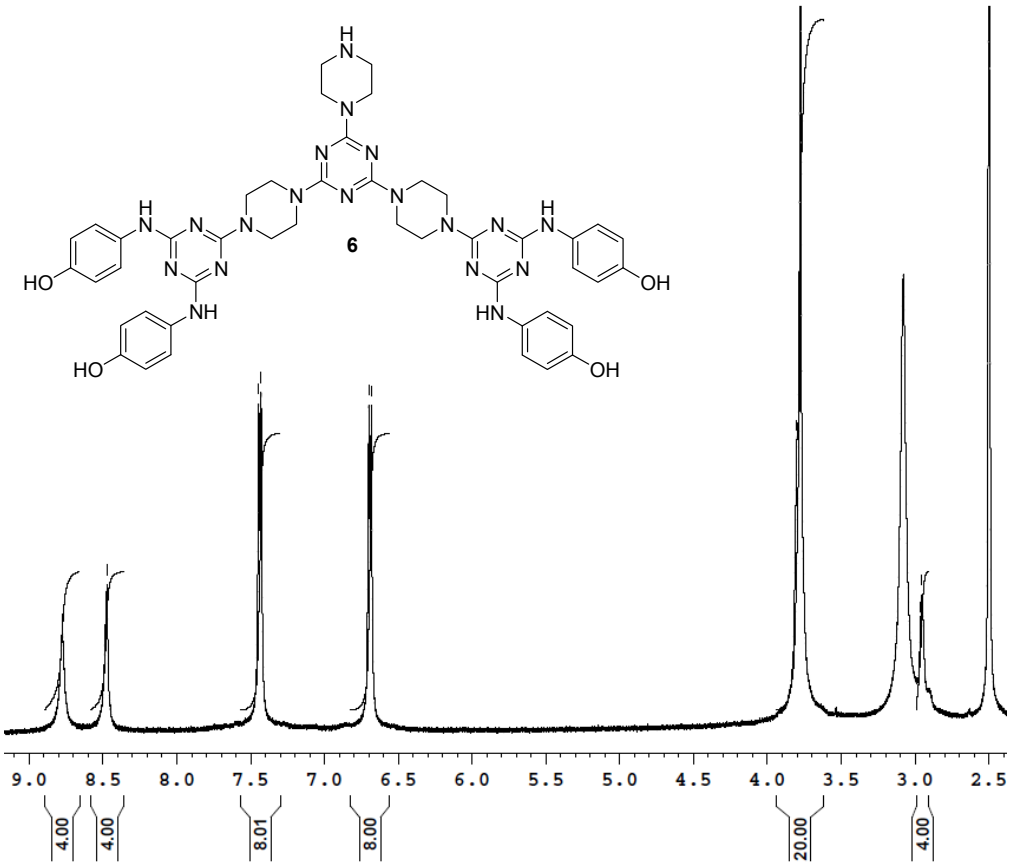


Figure SI-32. ^{1}H NMR spectrum of compound **6** (500 MHz, DMSO-d_6, 363 K)

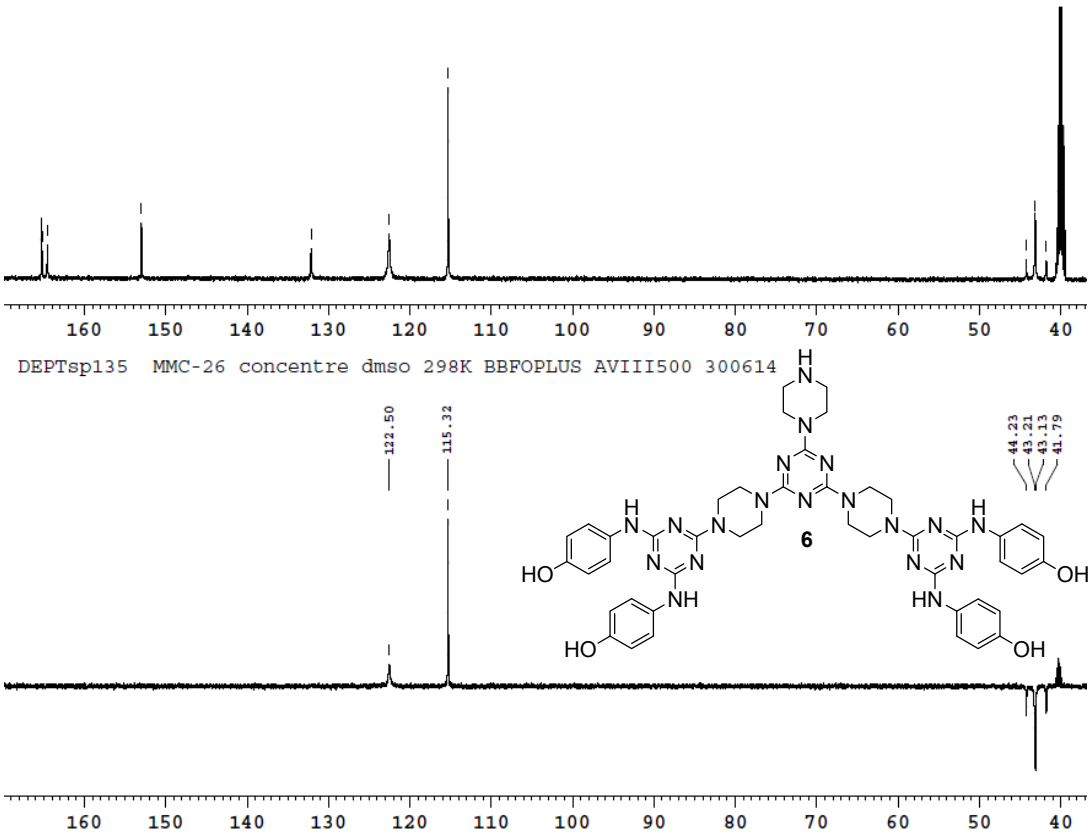


Figure SI-33. ^{13}C NMR-DEPT spectrum of compound **6** (125 MHz, DMSO-d_6, 298 K)

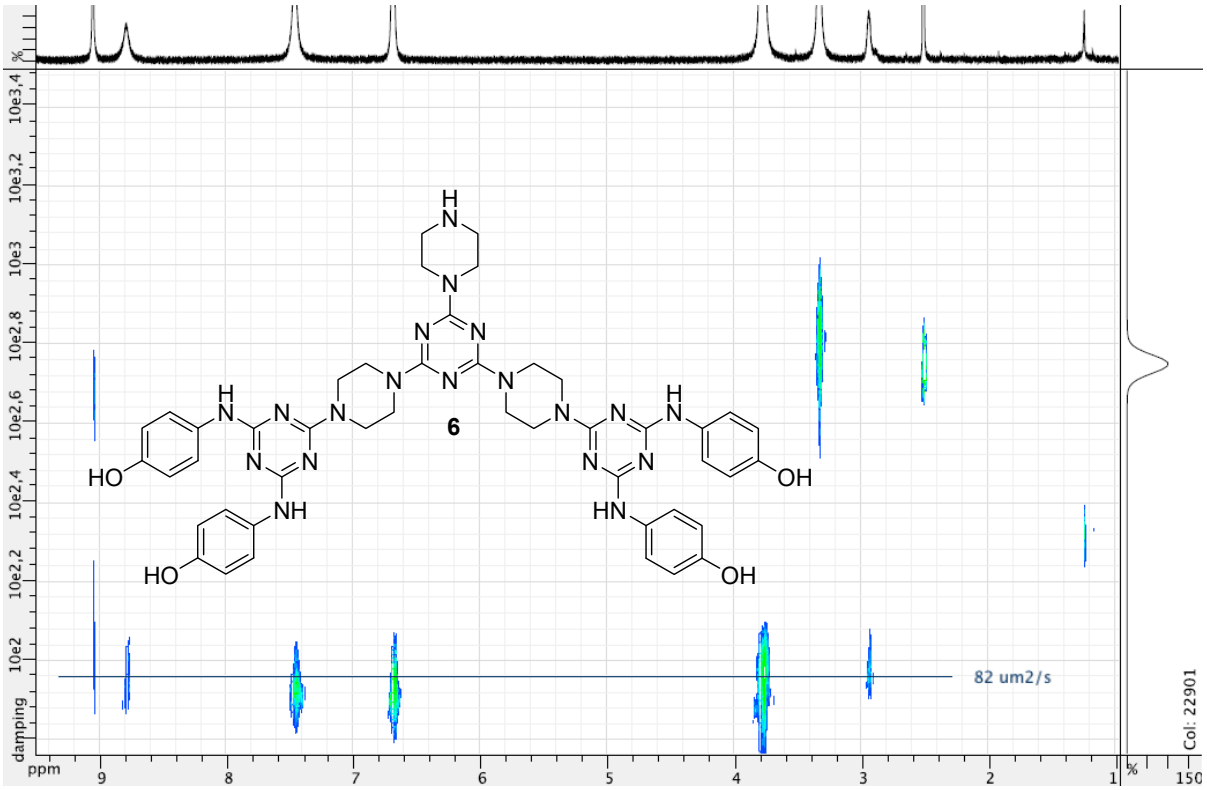


Figure SI-34. 2D-^{1}H-DOSY-NMR spectrum of compound **6** (500 MHz, 5 mM in DMSO-d_6, 298 K)

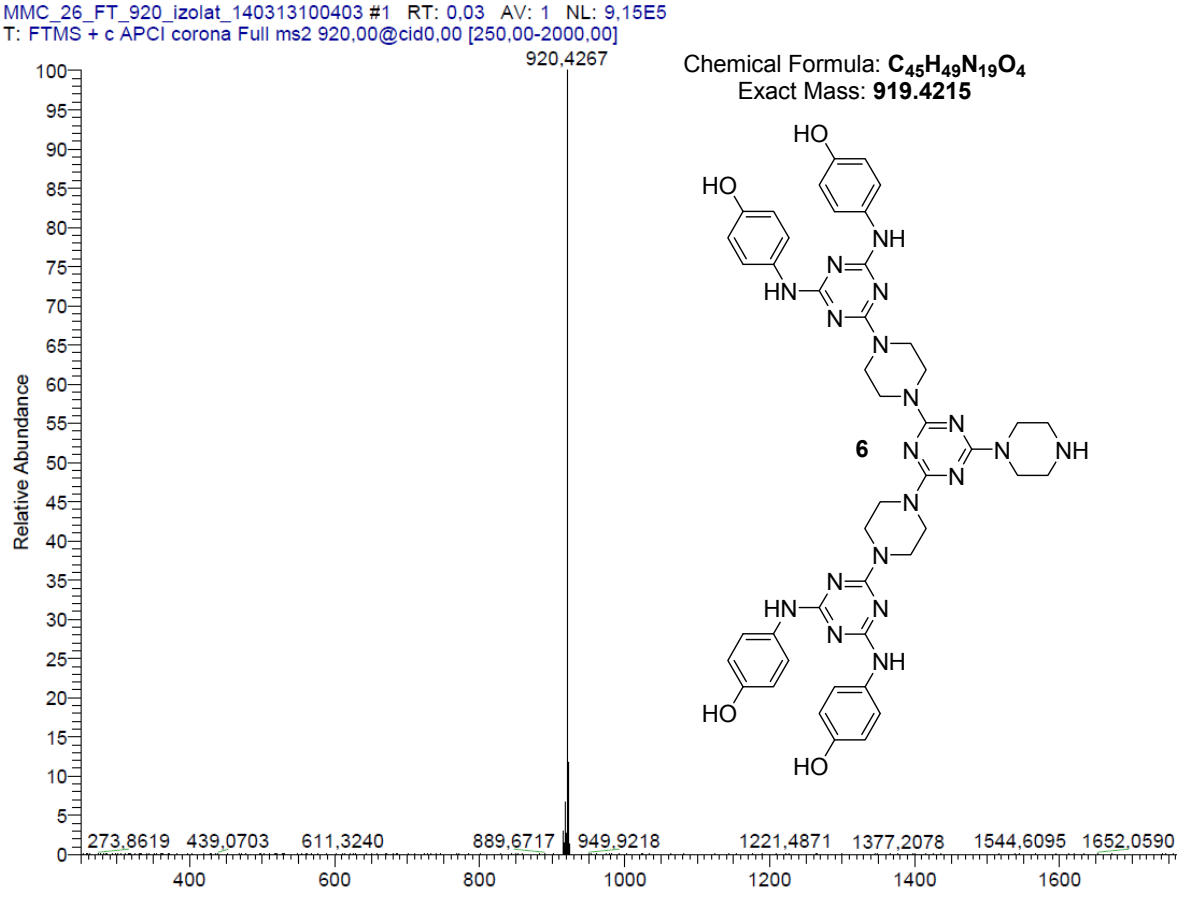


Figure SI-35. Mass spectrum of compound **6** [HRMS (APCI)]

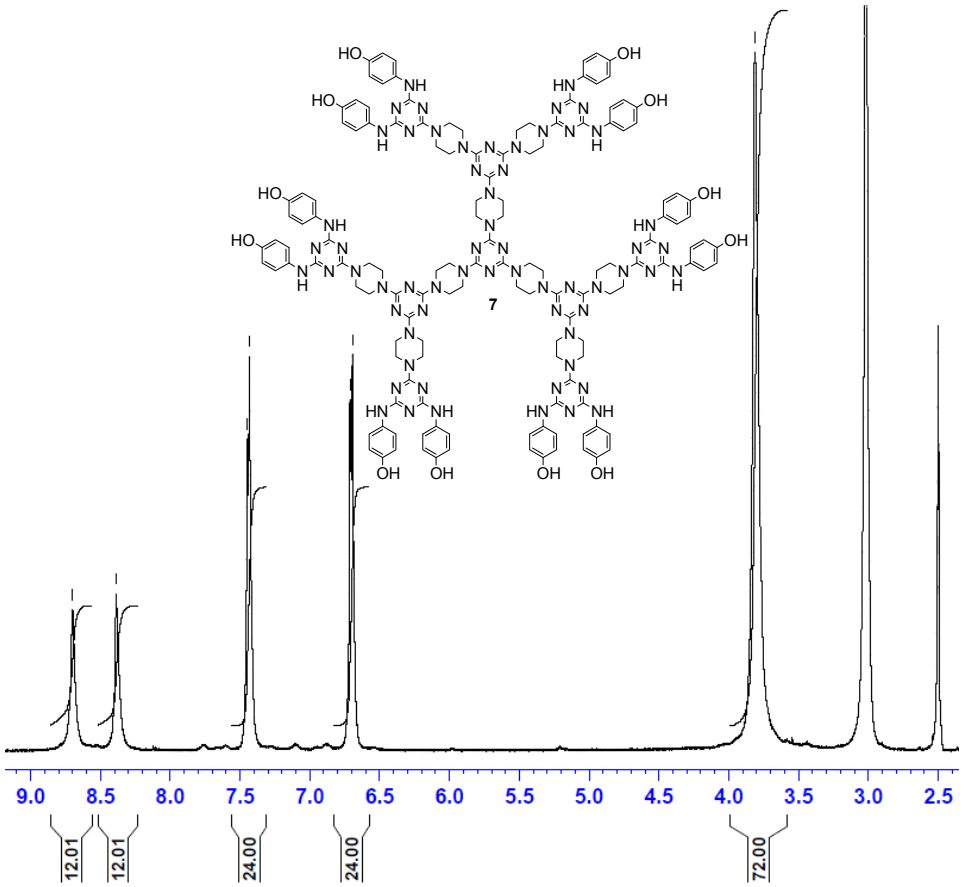


Figure SI-36. ^{1}H NMR spectrum of compound **7** (500 MHz, DMSO-d_6, 363 K)

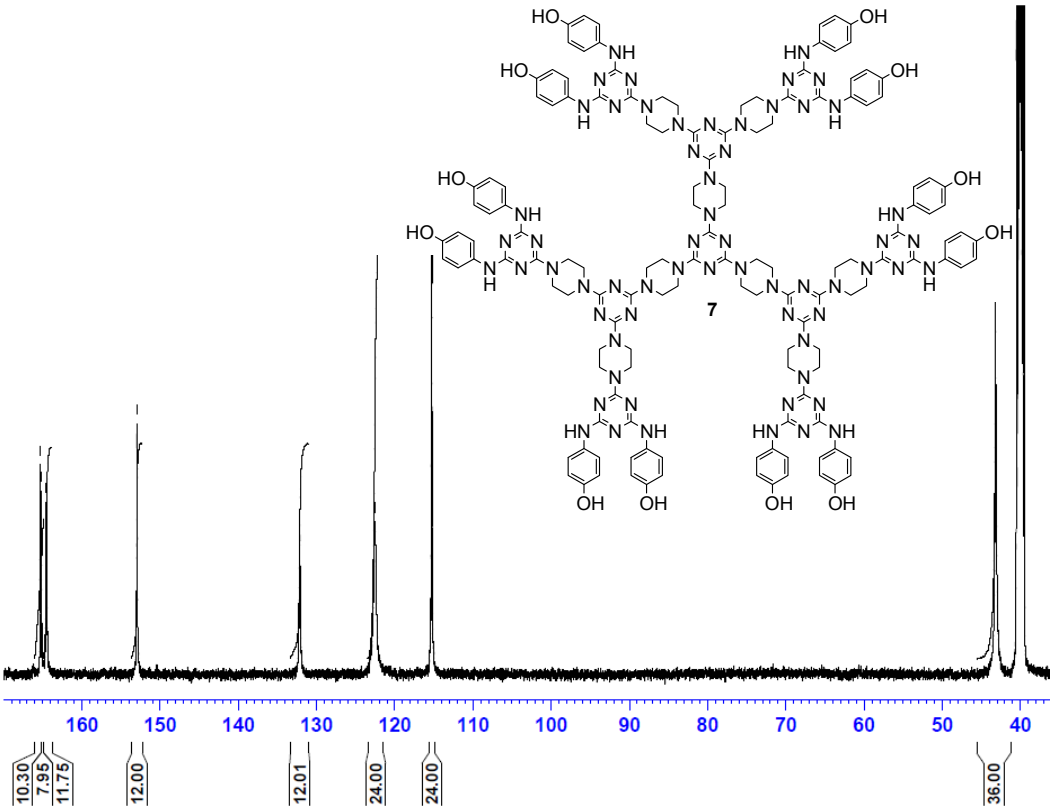


Figure SI-37. ^{13}C QC-NMR spectrum of compound **7** (125 MHz, DMSO-d_6, 298 K)

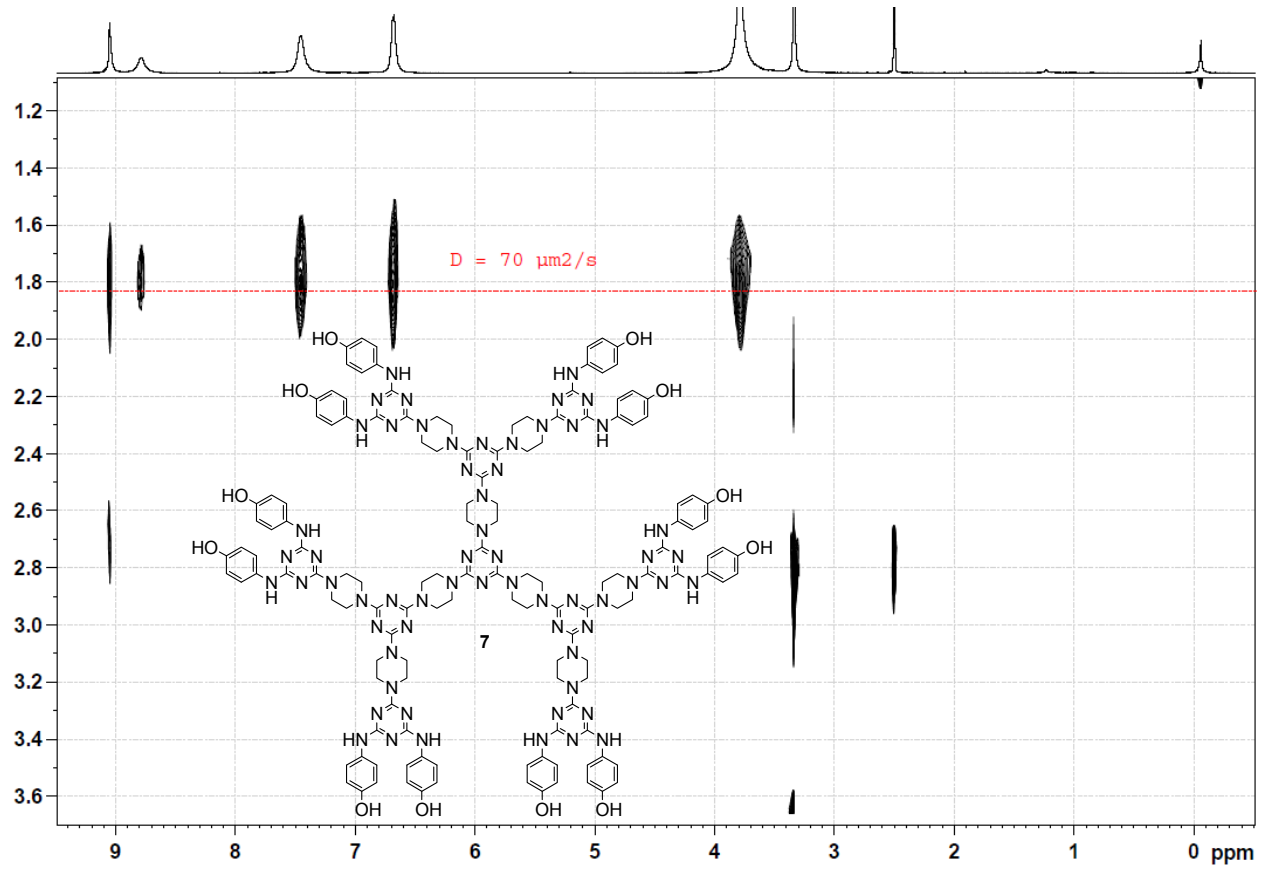


Figure SI-38. 2D-^{1}H-DOSY-NMR spectrum of compound **7** (500 MHz, 5 mM in DMSO-d_6, 298 K)

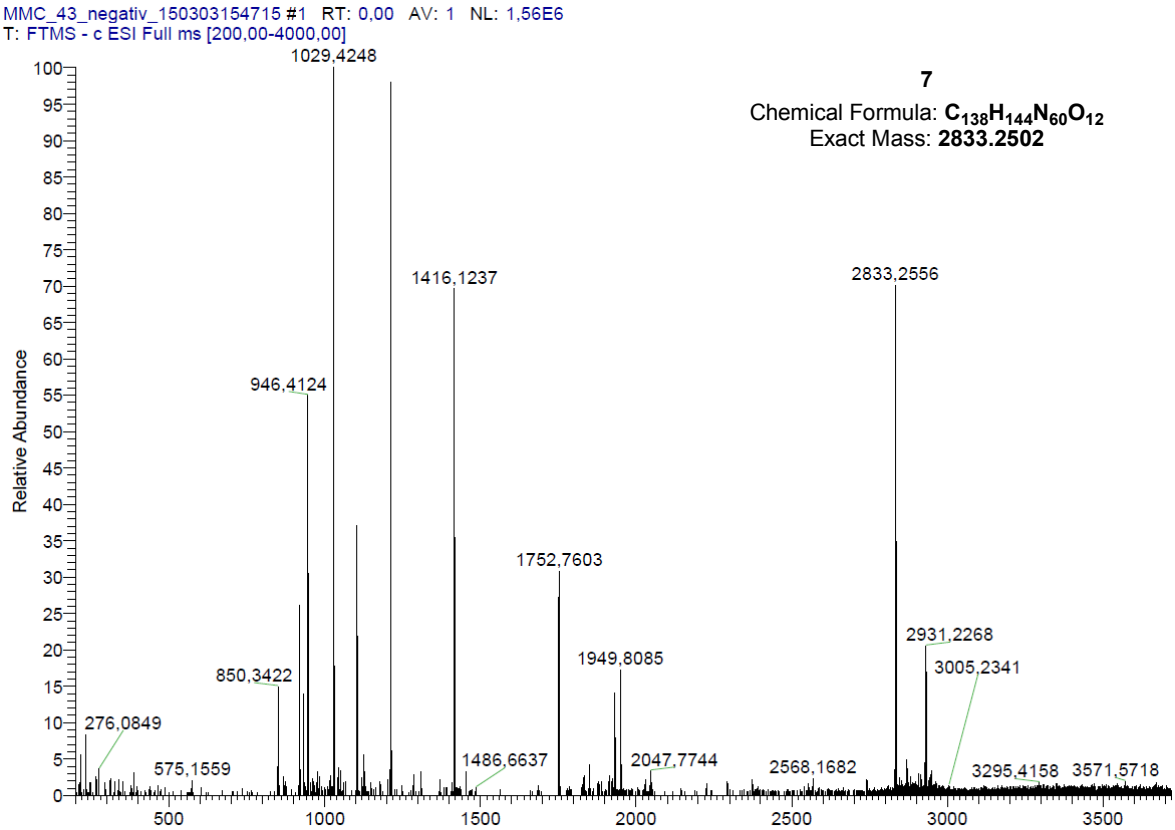


Figure SI-39. Mass spectrum of compound **7** [HRMS (ESI)]