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One ring to rule them all: effect of aryl substitution on glass-forming ability in mexylaminotriazine molecular glasses

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ABSTRACT

Mexylaminotriazines are an exciting new class of small molecules capable of forming glassy phases (molecular glasses) that have shown outstanding glass-forming properties and resistance to crystallization. The effect of the structure of the 'headgroup' at the 2-position of the triazine ring on glass-forming properties has been studied, but the role of the arylamino substituents is unclear, though it has been shown that one of the aryl groups can be substituted with other aryl groups without loss of glass-forming ability. Herein, a library of mexylaminotriazine derivatives with various arylamino and cycloalkylamino groups has been synthesized and characterized. It was found that glass-forming ability is tolerant to a wide range of substituents, with all the compounds reported being capable of forming glassy phases, and only one compound crystallizing upon heating. On the other hand, the structure of the ancillary group has a profound impact on the glass transition temperatures (T_g) of the compounds, with values ranging from 52 to 131 °C having been obtained. Several trends between substitution pattern and T_g were observed.

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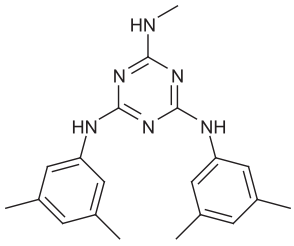
1. Introduction

Molecular glasses, or amorphous molecular materials, are an exciting class of compounds that possess the ability to form glassy phases, as opposed to crystals, in a fashion similar to polymers.[1] However, being small, monodisperse species, molecular glasses prove easier to purify, characterize and process, and show high homogeneity from one sample to another. Those advantages are counterbalanced by faster crystallization kinetics due to the higher mobility of molecules. This highly undesirable property translates into often needing to use special processing (including cooling at very high rates, freeze-drying, and spray-drying) to access the glassy state in the first place, and the propensity of glasses to revert to their thermodynamically favored crystalline forms upon heating or prolonged standing.[2] Nevertheless, molecular glasses have been successfully used so far for opto-electronic devices,[3] nano-lithography,[4] and amorphous drug formulations.[5]

Some empirical guidelines have been established for the design of novel molecular glasses. For example, molecules with globular, irregular shapes tend to pack poorly and irregularly, thereby increasing their propensity to form glasses. Multiple conformations, chirality, and the absence of strong and directional interactions between molecules also enhance this tendency.[6] However, the design of molecular glasses still relies heavily on trial and error, and the relationship between the molecular structure of a compound and its glass-forming ability and glass transition temperature (T_g) are still as elusive as the molecular mechanism of the glass transition itself.[7]



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Mexylaminotriazines, as exemplified by molecular glass **1**,[8] have proven to be a fascinating class of molecular glasses for several reasons, some of which are counterintuitive when considering the 'classic' guidelines of molecular glass design. Firstly, they possess higher symmetry than most previously reported molecular glasses.

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Second, they can engage in directional self-assembly by hydrogen bonding, which has been observed in the glassy state.[9] Because of this enhanced rigidity akin to polymer networks, some derivatives have shown extreme resistance to crystallization, which is extremely appealing for eventual practical applications. Finally, subtle structural modifications can translate into large changes in T_g or loss of glass-forming ability altogether, making mexylaminotriazines an attractive model class of compounds to study how macroscopic properties of the bulk material are related to the structure of individual molecules.

The role of the 'headgroup' at the 2-position of the triazine ring in glass formation, T_g,[10] and rheological properties,[11] has been studied by both experiment and atomistic simulation.[12] However, while it is known that one of the mexylamino groups can be substituted for other arylamino groups (as demonstrated in a spectacular fashion with a tetraphenylporphyrin core substituted with four mexylaminotriazine groups) without loss of glass-forming ability,[13] the effect of aryl group structure on T_g and glass-forming ability is yet poorly understood. The impact of substituting both mexylamino groups on glass formation is also mostly unknown, though it has been shown that phenyl- or tolylamino groups fail to induce glass formation.

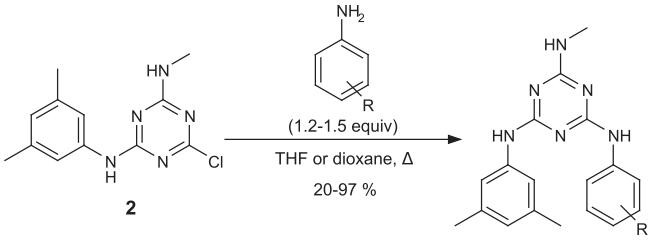
Herein, a simple and efficient procedure has been used to synthesize a library of mexylaminotriazine derivatives bearing various arylamino or cycloalkylamino groups to study the relationship between aryl group structure and glass formation and T_g. All mexylaminotriazine derivatives have proven to be capable of glass formation with T_g ranging between 52 and 131 °C, and only the 2,4,6-trimethylphenyl-substituted derivative recrystallized when heated under standard conditions.

2. Results and discussion

2.1. Synthesis

In order to easily generate a library of analogues with various aryl groups, a divergent approach from a common precursor was used. A methylamino group was used as headgroup, for both synthetic reasons and because of the high T_g and resistance to crystallization it induces. Precursor 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine **2** was thus synthesized in two steps from cyanuric chloride by sequential substitution of two chloro groups by methylamine and 3,5-dimethylaniline (Scheme 1).[8,10] The amines can be introduced in any order, though higher overall yields are obtained when starting with 3,5-dimethylaniline.

The third chloro group of precursor **2** can then be substituted with a wide range of anilines by heating both reagents (with a slight excess of amine) in THF (Scheme 2). A list of substituents



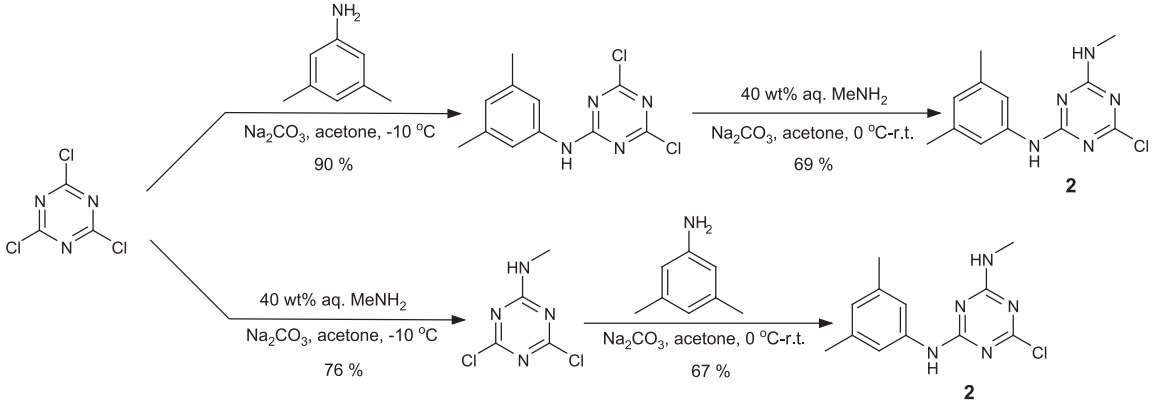
Scheme 2.

introduced can be found in Table 1. The addition of a base proved unnecessary for the reaction (with rare exceptions), and in most cases even hindered the reaction. It is thought that the HCl generated is quenched by the product itself (the p*K*a of protonated melamine is 5.66)[14] or can somehow activate precursor **2**. The excess of aniline can then conveniently be removed via acidic aqueous extraction, leaving behind the desired compound, typically in high yield. Ortho-substituted anilines react more slowly than their

Table 1
Substituents and T_g values for compounds **3**–**49**. T_g values were measured by DSC at a heating rate of 5 °C/min and averaged over at least two heating runs. The value for compound **1** is included for reference

Compound	R	T_g (°C)	Compound	R	T_g (°C)
1	3,5-$Me_2C_6H_3$	94	**26**	4-(OMe)C_6H_4	64
3	Ph	73	**27**	3,5-$(OMe)_2C_6H_3$	68
4	2-MeC_6H_4	61	**28**	3,4,5-$(OMe)_3C_6H_2$	82
5	3-MeC_6H_4	64	**29**	4-$(CHCHCO_2Et)C_6H_4$	71
6	4-MeC_6H_4	70	**30**	3-$(CH_2OH)C_6H_4$	69
7	2,4-$Me_2C_6H_3$	63	**31**	4-$(CH_2CH_2OH)C_6H_4$	73
8	2,5-$Me_2C_6H_3$	71	**32**	3-$(CH_2Br)C_6H_4$	62
9	2,6-$Me_2C_6H_3$	84	**33**	1-Naphthyl	83
10	3,4-$Me_2C_6H_3$	72	**34**	4-$NH_2C_6H_4$	102
11	2,4,6-$Me_3C_6H_2$	79[a]	**35**	4-$N_3C_6H_4$	52
12	2-FC_6H_4	55	**36**	3-$(CN)C_6H_4$	80
13	3-FC_6H_4	62	**37**	3-$(CONH_2)C_6H_4$	104
14	4-FC_6H_4	64	**38**	3-$(CHO)C_6H_4$	59
15	2-ClC_6H_4	53	**39**	3-$(CO_2H)C_6H_4$	131
16	3-ClC_6H_4	74	**40**	3-$(CO_2Me)C_6H_4$	74
17	4-ClC_6H_4	68	**41**	3-$(NO_2)C_6H_4$	82
18	3,5-$Cl_2C_6H_3$	84	**42**	Cyclohexyl	74
19	3-BrC_6H_4	78	**43**	1-Adamantyl	93
20	4-BrC_6H_4	69	**44**	1,3-C_6H_4	120
21	3-IC_6H_4	84	**45**	1,4-C_6H_4	124
22	4-IC_6H_4	72	**46**	4,4′-Biphenyl	125
23	3-$(OH)C_6H_4$	86	**47**	4,4′-Diphenylmethane	126
24	4-$(OH)C_6H_4$	95	**48**	4,4′-Azobenzene	131
25	4-$(SH)C_6H_4$	84	**49**	4,4′-Diphenyl disulfide	119

[a] T_c 151 °C, T_{dec} 253 °C.



Scheme 1.

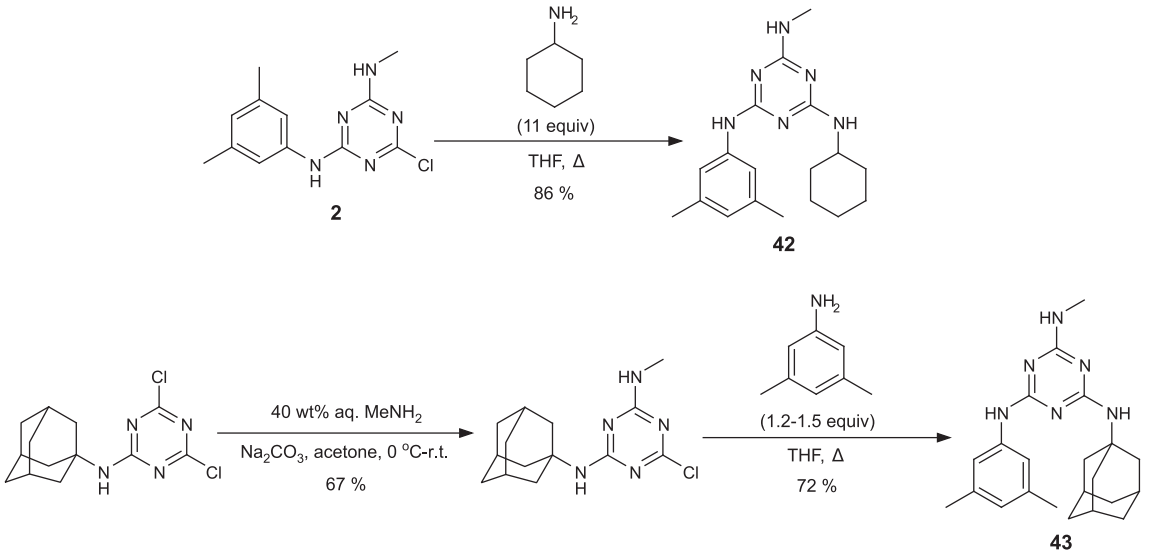
meta- or para-isomers, but the reaction can be driven to completion by carrying out the reaction in dioxane instead of THF and using a longer reaction time. On the other hand, anilines bearing strongly deactivating substituents in ortho or para completely failed to react, owing to the decreased nucleophilicity of the amino group. The meta isomers, however, reacted normally. It would be possible in principle to synthesize those isomers by reacting the deactivated aniline with cyanuric chloride in the first step, thus requiring several synthetic steps and more complex purification procedures. Since their meta counterparts are easier to synthesize and purify, they were omitted for practical reasons.

Compound **2** can also be reacted with alkylamines, as exemplified by cyclohexylamine (Scheme 3), but a large excess of amine was necessary for the reaction to be complete. For bulkier 1-aminoadamantane, the direct reaction with precursor **2** was not successful and the bulky amine had to be introduced on cyanuric chloride in the first step,[15] followed by methylamine and 3,5-dimethylaniline (Scheme 3).

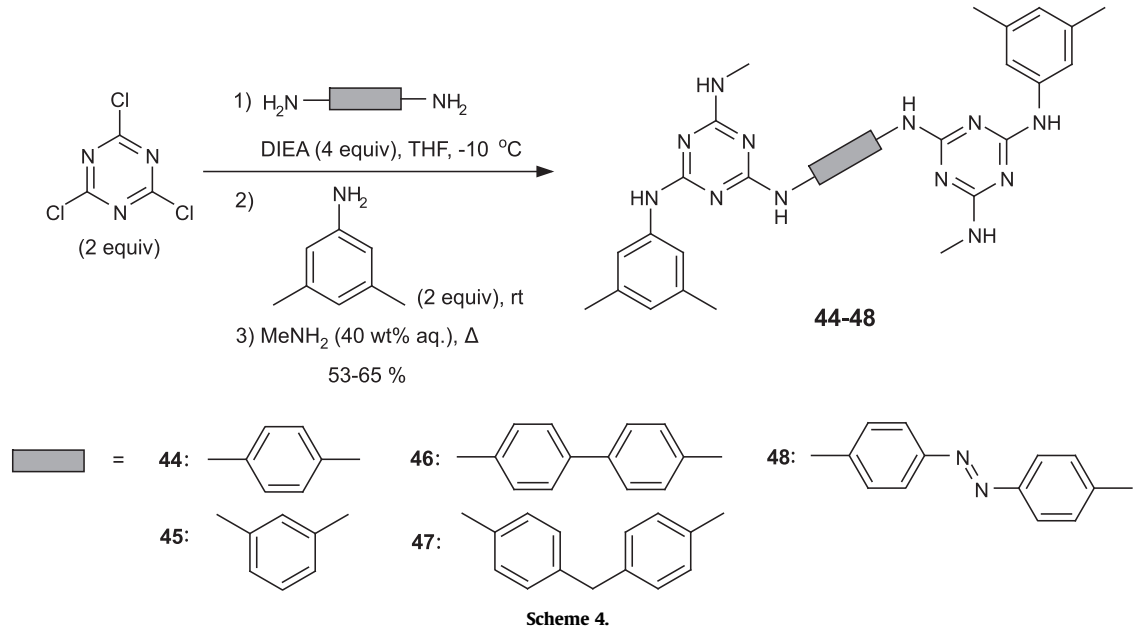
Aromatic diamines can be substituted with two mexylaminotriazine groups in a one-pot sequential series of substitutions on cyanuric chloride similar to the one used for tetraphenylporphyrin (Scheme 4),[13] to give the products in 53–65% yield after purification on a short silica pad.

Some compounds bear functional groups that can be further transformed. The hydroxymethyl group of compound **30** can be converted to a bromomethyl substituent with PBr_3 to give benzylic bromide **31**.[16] Amino-substituted compound **34** can be converted to the corresponding azide **35** by diazotization followed by reaction with NaN_3.[17] The cyano group of compound **36** can be hydrolyzed to give amide **37**,[18] while carboxylic acid **39** can be esterified, as exemplified with methyl ester **40**. Finally, thiol **25** can be oxidized to the corresponding disulfide with $K_3Fe(CN)_6$ (Scheme 5).[19]

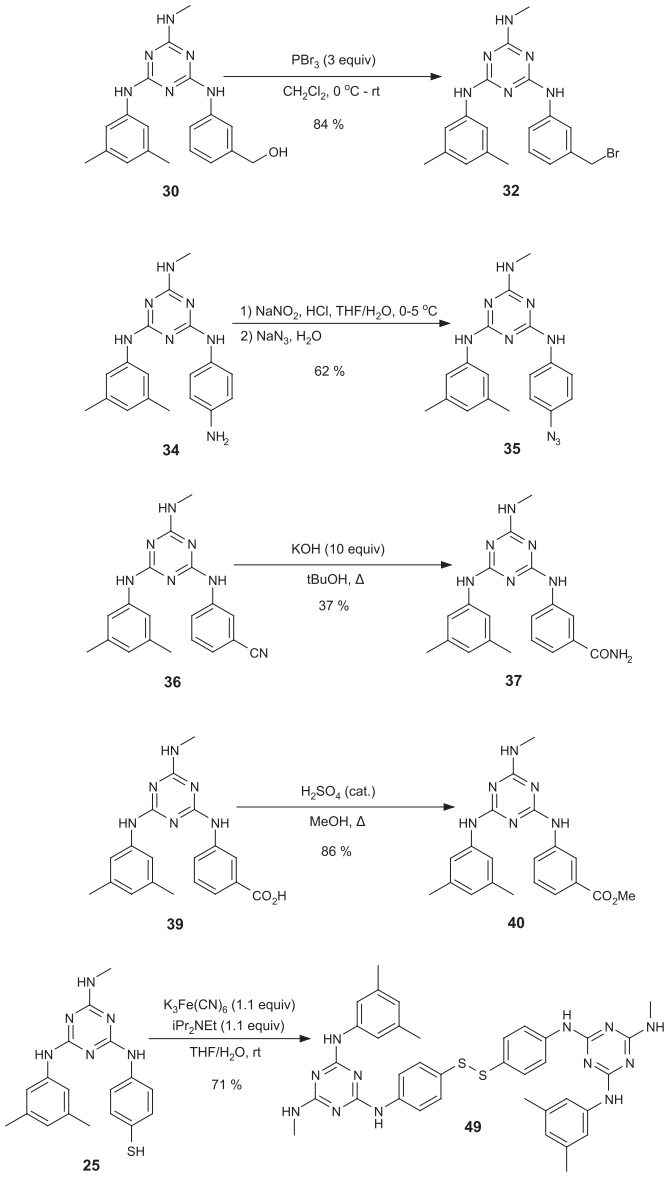
While in most cases the excess reagents or reaction by-products could be removed without the need for further purification (recrystallization, chromatography, etc.), the compounds tend to be difficult to completely rid of solvents. THF, and dioxane



Scheme 3.



Scheme 4.

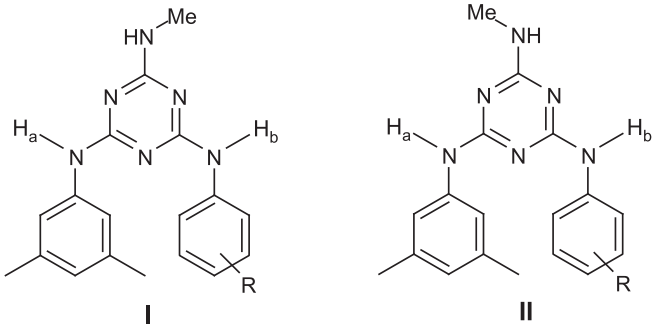


Scheme 5.

to an even greater degree, tend to stay trapped within the glassy materials, and the only way to obtain analytically pure samples is to melt them under vacuum, thereby releasing all volatiles.

2.2. NMR spectroscopy

The NH–triazine bond is strongly conjugated, especially with alkylamino substituents,[20] causing two conformers (**I** and **II**) to exist for the methylamino substituent of mexylaminotriazine glasses **3**–**49** (Scheme 6), the interconversion of which is slower than the NMR experiment time at ambient temperature. For this reason, broad peaks and split signals are common in the ^{1}H NMR spectra of all compounds described herein. For example, the ^{1}H NMR spectrum of compound **2** in DMSO-d_6 shows two sets of N–H signals integrating for 0.7H and 0.3H, respectively. Furthermore, the mexyl protons ortho to the NH group show a broad doublet, and the methylamino group shows two doublets for the CH_3 protons. When the spectrum is recorded at 90 °C, all signals coalesce into a single signal for each set of equivalent protons. In $CDCl_3$ this effect is weaker, but not all compounds are soluble enough in $CDCl_3$ to acquire suitable spectra (in particular precursor **2** and compounds with highly polar groups), the ArN–H peaks often overlap with other aromatic signals, and the solvent peak overlaps with the mexyl ortho signal. Therefore, DMSO was used for all compounds for ease of comparison.



Scheme 6.

For mexylaminotriazine derivatives **3**–**49**, some common observations can be made. Because of the headgroup being static at ambient temperature, the two ArN–H peaks are in two distinct chemical environments and each give two broad singlets, each integrating for roughly 0.5H. Aromatic protons ortho to the amino groups give broad signals. For the ortho protons of the mexylamino group, which are also located in the vicinity of the triazine ring, a broad doublet is observed around 7.4 ppm.

Ortho protons from ortho- and para-substituted anilines give a broad singlet, while for meta-substituted anilines, the proton located between the two substituents gives a broad doublet, the distance between peaks increasing with substituent size. This trend is demonstrated in Fig. 1 with 3-halophenyl derivatives **13**, **16**, **19**, and **21**. The distance between the peaks decreases progressively with increasing temperature and they eventually coalesce into a single peak with proper splitting above 60 °C, as shown in Fig. 2 with 3-methylcarboxy derivative **40**. It should be noted that this behavior is also observed for the ArN–H signals and other ortho aromatic peaks (Fig. 2). Other compounds of the series behave similarly. 2,6-Disubstituted aryl groups, in which rotation of the bulky aryl groups is also hindered, give spectra that are even more difficult to analyze at room temperature, as some signals are split into uneven peaks while some others are split into three; the ^{1}H spectra must be recorded above 60 °C for these compounds to draw any information.

While ^{13}C NMR spectra tend to show less splitting behavior, peak splitting still occurs in some compounds. In the ^{13}C spectrum of compound **2** recorded at ambient temperature, virtually every peak is doubled. For compounds with ortho-substituted aryl groups, both triazine carbon atoms bearing the arylamino substituents tend to be split into two. Increasing the temperature causes the peaks to coalesce, as shown in Fig. 3 with 2-fluorophenyl derivative **12**.

2.3. Thermal analysis

Typically, most compounds reported herein do not show any signs of decomposition below 250 °C. A few notable exceptions to this trend are bromomethyl derivative **32** and azide **35**. The T_g of compounds **3**–**49** were determined by differential scanning calorimetry (DSC), using a heating and cooling rate of 5 °C/min (results are compiled in Table 1). This heating rate is slow enough to allow monitoring the presence or absence of undesirable crystallization upon heating. It was found that, as expected, all compounds **3**–**49**

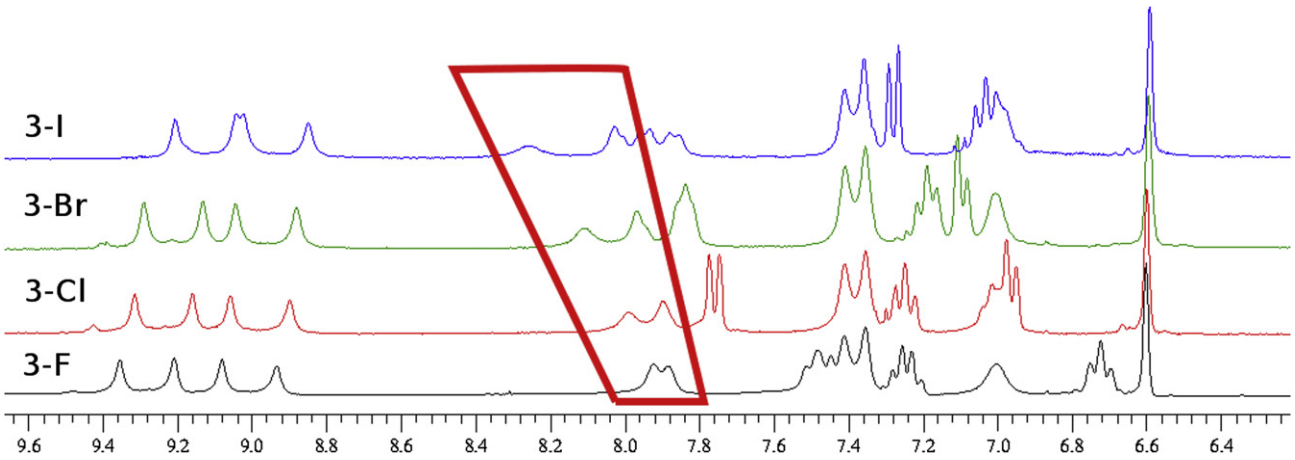


Fig. 1. Aromatic region of the ^{1}H NMR spectra recorded at 298 K of 3-halophenyl derivatives **13** (3-F), **16** (3-Cl), **19** (3-Br), and **21** (3-I). The signals for the proton in the 2-position of the ring are delimited by the red box.

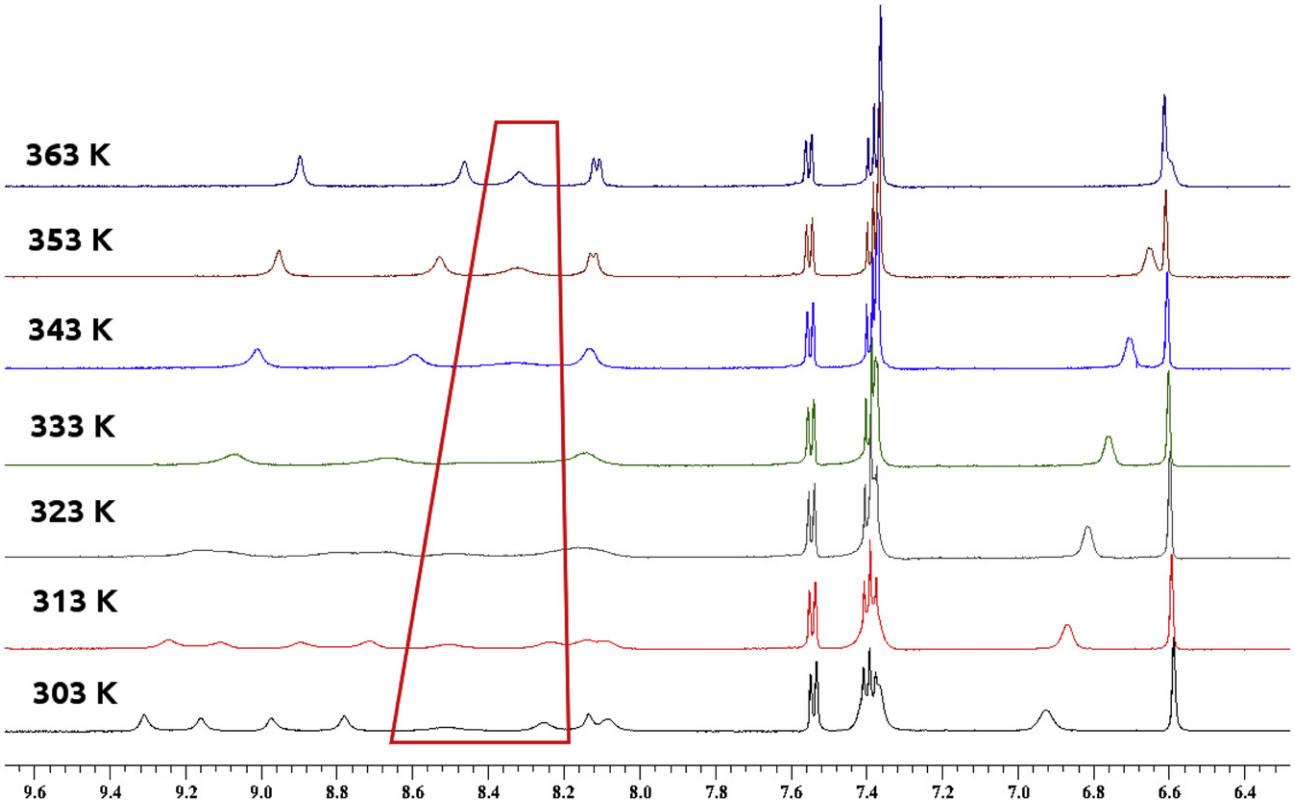


Fig. 2. Aromatic region of the ^{1}H NMR spectra of methyl ester **40**, taken at various temperatures from 303 K to 363 K. The signals for the proton in the 2-position of the ring are delimited by the red box.

exhibit reversible T_g ranging from 52 °C to 131 °C (a thermogram of compound **40** is shown in Fig. 4a). Among all compounds studied, only 2,4,6-trimethylphenyl derivative **11** showed crystallization under the conditions used, with a T_c of 151 °C (Fig. 4b). Its melting temperature T_m could not be determined as the compound decomposes before reaching the melting point. All other glass-forming derivatives failed to show any crystallization under the conditions used, thereby demonstrating that one of the mexyl groups can be substituted with a wide range of substituted aryl or cycloalkyl groups without loss of glass-forming ability showed by parent compound **1**. It is believed that compound **11** possesses a higher propensity to crystallize because of the steric bulk caused by its methyl groups in both ortho positions that limits its conformational freedom; however closely related 2,6-dimethylphenyl homologue **9** did not show any signs of crystallization, even with heating rates as slow as 1 °C/min. These results highlight the fact that while the 3,5-dimethyl substitution pattern has been shown to frustrate crystallization, this phenomenon is not due to steric bulk alone, as in this case the bulkier 2,4,6-trimethylphenyl group rather favors crystallization. It should also be noted that chlorotriazine precursors 2-methylamino-4-mexylamino-6-chloro-1,3,5-triazine (**2**) and 2-(1-adamantylamino)-4-methylamino-6-chloro-1,3,5-triazine do not form glasses upon cooling from the melt under the conditions used, and readily crystallize from solution upon

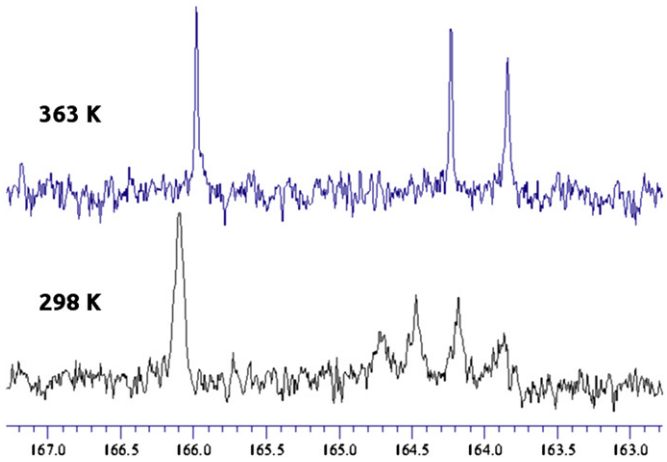


Fig. 3. Triazine region of the ^{13}C NMR spectra of 2-fluorophenyl derivative **12**, taken at 298 K and 363 K.

evaporation of the solvent. Some structure–property relationships can be extracted from the correlations between substitution pattern and T_g:

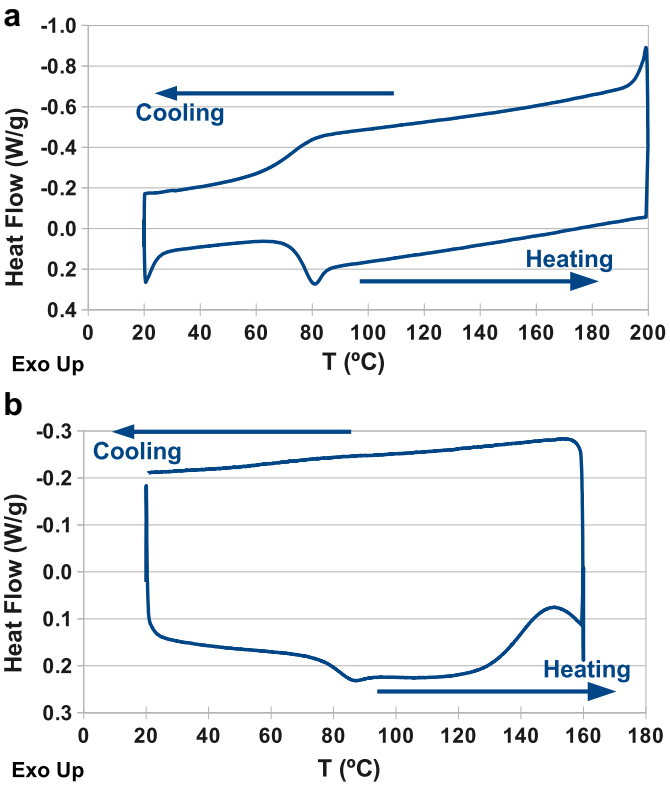


Fig. 4. (a) Representative DSC scan of glass **40**, recorded at a heating/cooling rate of 5 °C/min. Note the absence of crystallization. (b) DSC scan of glass **11**, recorded at a heating/cooling rate of 5 °C/min.

1) Monosubstituted aryl groups typically show higher T_g in the order ortho<meta<para. Arguably, the para isomers possess higher symmetry, while substituents in ortho positions possibly hinder hydrogen bonding. One notable exception to this trend is halo substituents, with the exception of fluorine, where meta isomers show higher T_g.
2) Substituting one mexyl group by another dimethylphenyl group always leads to T_g values lower than that of bis(3,5-dimethylphenyl) isomer **1**, due to lower symmetry. While the 2,5- and 3,4-isomers, which both possess one methyl group in a meta position, show similar T_g values, the 2,4-isomer possesses a lower T_g, while the bulkier 2,6-isomer undergoes glass transition at a higher temperature.
3) Because compounds **3**–**43** possess lower symmetry than parent compound **1**, most compounds show lower T_g, which follows previous observations for molecular glasses. However, compounds with groups capable of participating in bidirectional hydrogen bonding (OH, NH_2, $CONH_2$, CO_2H) show T_g values close to, or higher to that of compound **1** (notable exceptions to this trend are more flexible alkyl alcohols **30** and **31**). In particular, the T_g for carboxylic acid **39** is 131 °C, the highest among the compounds reported within. In comparison, even closely related amide **37** shows a much lower T_g of 104 °C. This could be due to the presence of zwitterionic species that form reversibly within the glass, as the triaminotriazine moiety is basic enough to deprotonate the carboxylic acid group, although not quantitatively.[14]
4) Bis(mexylaminotriazine) derivatives **44**–**49** synthesized from various aromatic diamines show higher T_g values than those for compounds with a single triazine function. T_g values for compounds **44**–**49** span a relatively narrow range, however (between 119 and 131 °C). The presence of two triazine moieties, each capable of engaging in hydrogen bonding, overshadows the effect of the structure of the core diamine group, leading to more uniform T_g.
5) The substituent can be an alkyl ring without loss of glass-forming ability, as evidenced with cyclohexyl- and adamantyl-substituted derivatives **42** and **43**. Compound **42** shows a T_g value similar to that of its phenyl analogue **3**, while the T_g of bulkier adamantyl derivative **43** (93 °C) is similar to that of parent compound **1**.

3. Conclusion

A library of mexylaminotriazine derivatives has been generated, with high yields in most cases, using a simple synthetic procedure starting from a common precursor, 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine. It has been demonstrated that one of the arylamino groups can be readily substituted with a wide range of arylamines or cycloalkylamines without loss of glass-forming ability. Of all the compounds synthesized and characterized herein, only the 2,4,6-trimethylphenyl-substituted derivative showed signs of crystallization upon heating at a rate of 5 °C/min. The T_g of the compounds reported herein varied from 52 to 131 °C. While most of the compounds show T_g values lower than that of their symmetrically substituted parent compound, the presence of functional groups that can participate in further hydrogen bonding can result in T_g that are equal or higher. Bis(mexylaminotriazine) derivatives can be synthesized from aryldiamines, and also show glass-forming ability, with no crystallization observed upon heating and T_g values somewhat higher, though less dependent on aryldiamine structure, than their monotriazine counterparts.

4. Experimental section

4.1. General

4,6-Dichloro-2-methylamino-1,3,5-triazine,[21] 4,6-dichloro-2-mexylamino-1,3,5-triazine,[22] 4,6-dichloro-2-(1-adamantylamino)-1,3,5-triazine,[15] 4,4′-diaminoazobenzene,[23] 4-aminothiophenol,[24] 3-aminobenzyl alcohol,[25] and 3-aminobenzaldehyde diethyl acetal[26] were synthesized by literature procedures. All other reagents were purchased from commercial sources and used without further purification. All reactions were performed under ambient

atmosphere. SiliaFlash P60 grade silica gel and TLC plates were purchased from SiliCycle. NMR spectra were recorded on a Bruker Avance 400 MHz, a Bruker Avance 500 MHz, or a Varian Mercury 300 MHz spectrometer at 298 K unless otherwise noted. FTIR spectra were either recorded on a Perkin Elmer Spectrum GX spectrometer as thin films deposited from CH_2Cl_2 solution on KBr windows, or on a Tensor 27 FT-IR spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled HgCdTe detector and a MIRacle (Pike Technologies) silicon attenuated total reflection (ATR) accessory as films directly cast on the ATR crystal from CH_2Cl_2 solution. Decomposition analyses of molecular glasses were obtained using a TGA 2950 thermogravimetric analyzer (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere. T_g, T_c and T_m were recorded by DSC with a TA Instruments Q100, Q1000, or Q2000 calorimeter calibrated with indium using a heating/cooling rate of 5 °C/min from 20 °C to 200 °C, unless otherwise noted. T_g were reported after an initial cycle of heating and cooling at 5 °C/min, and as the average of the values observed in heating.

4.2. Synthesis

*4.2.1. Synthesis of 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine (**2**) (Method 1).* 2-Methylamino-4,6-dichloro-1,3,5-triazine (18.9 g, 105 mmol) was dissolved in acetone (150 mL) in a round-bottomed flask equipped with a magnetic stirrer. The flask was placed in an ice bath to keep temperature inside the flask under 5 °C, then a solution of 3,5-dimethylaniline (13.2 mL, 12.8 g, 105 mmol) in acetone (50 mL) was added dropwise to the mixture. The ice bath was removed once the addition was complete, then the mixture was stirred at room temperature for an additional 30 min, at which point the mixture was poured in H_2O (500 mL), and stirring was continued for 20 min until precipitation was completed. The precipitate was collected by filtration, then the crude product was triturated in hot toluene, filtered and allowed to dry completely to afford 19.2 g pure title compound (72.8 mmol, 69%); T_m 231 °C; FTIR (CH_2Cl_2/KBr) 3264, 3196, 3123, 3007, 2914, 2848, 1634, 1615, 1587, 1542, 1453, 1391, 1373, 1276, 1239, 1157, 1125, 1059, 986, 880, 836, 800, 723, 682, 634 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ 9.92, 9.75 (s, s, 1H), 8.02, 7.92 (s, s, 1H), 7.40, 7.34 (s, s, 2H), 6.65 (s, 1H), 2.85, 2.80 (s, d, ^3J=4.6 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 9.44 (br s, 1H), 7.57 (br s, 1H), 7.35 (s, 2H), 6.68 (s, 1H), 2.86 (s, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.3, 167.6, 165.9, 165.8, 163.6, 163.1, 138.8, 138.7, 137.37, 137.35, 124.4, 124.3, 117.9, 117.8, 27.3, 27.2, 21.11, 21.08 ppm; HRMS (ESI, MH^+) calcd for $C_{12}H_{15}N_5Cl$ *m/e*: 264.1015, found: 264.1029. Anal. Calcd for $C_{12}H_{14}N_5Cl$: C, 54.60; H, 5.31; N, 26.54. Found: C, 26.46, C, 54.66, H, 5.32.

*4.2.2. Synthesis of 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine (**2**) (Method 2).* 2-Mexylamino-4,6-dichloro-1,3,5-triazine (24.3 g, 90.4 mmol) was dissolved in acetone (150 mL) in a round-bottomed flask equipped with a magnetic stirrer, then Na_2CO_3 (9.58 g, 90.4 mmol) was added. The flask was placed in an ice bath to keep temperature inside the flask under 5 °C, then a solution of methylamine (7.06 mL, 40 wt % aqueous, 90.4 mmol) in acetone (50 mL) was added dropwise to the mixture. The ice bath was removed once the addition was complete, then the mixture was stirred at room temperature for an additional 30 min, at which point the mixture was poured in H_2O (500 mL), and stirring was continued for 20 min until precipitation was completed. The precipitate was collected by filtration, then the crude product was triturated in hot toluene, filtered and allowed to dry completely to afford 15.9 g pure title compound (60.2 mmol, 67%) with spectroscopic properties in accordance with the product obtained by Method 1.

4.2.3. Synthesis of 2-mexylamino-4-methylamino-6-arylamino-1,3,5-triazine derivatives (Method A). In a typical reaction procedure, 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine (1.0 mmol) and a substituted aniline (1.2 mmol) were dissolved in THF (10 mL) in a 40 mL tube. The tubes were placed in a Büchi Syncore Parallel Reactor equipped with a water-jacketed cooling element, then the reaction mixtures were refluxed overnight while shaking at a rate of 200 rpm. After allowing to cool down at ambient temperature, 1 M aqueous HCl and CH_2Cl_2 were added to the reaction mixture, then both layers were separated. The organic layer was extracted with aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the solvent was thoroughly evaporated under reduced pressure to give the title compounds as glassy solids in acceptable purity.

4.2.4. Synthesis of 2-mexylamino-4-methylamino-6-arylamino-1,3,5-triazine derivatives (Method B). In a typical reaction procedure, 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine (1.0 mmol) and a substituted aniline (1.2 mmol) were dissolved in THF (10 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser, then the reaction mixture was refluxed overnight under constant stirring. After allowing to cool down at ambient temperature, a workup similar to the one used in Method A was used to isolate and purify the product: 1 M aqueous HCl and CH_2Cl_2 were added to the reaction mixture, then both layers were separated. The organic layer was extracted with aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the solvent was thoroughly evaporated under reduced pressure to give the title compounds.

4.2.5. Synthesis of 2-mexylamino-4-methylamino-6-arylamino-1,3,5-triazine derivatives (Method C). The derivatives were synthesized by a procedure similar to Method B, but the reaction was performed in dioxane (5 mL/mmol) instead of THF and the mixture was refluxed for 3 days.

*4.2.6. Synthesis of 2-mexylamino-4-methylamino-6-(phenylamino)-1,3,5-triazine (**3**).* The compound was synthesized using Method A. Yield: 94%; T_g 73 °C; FTIR (CH_2Cl_2/KBr) 3408, 3282, 3195, 3030, 2951, 2918, 2865, 1616, 1581, 1554, 1514, 1497, 1442, 1430, 1398, 1360, 1321, 1299, 1263, 1253, 1235, 1182, 1160, 1121, 1083, 1033, 997, 973, 957, 888, 872, 841, 808, 752, 736, 690 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.13 (br s, 0.5H), 9.00 (br s, 1H), 8.85 (br s, 0.5H), 7.79 (br m, 2H), 7.40 (br d, 2H), 7.25 (t, ^3J=7.6 Hz, 2H), 6.94 (t, ^3J=7.6 Hz, 1H), 6.90 (br s, 1H), 6.59 (s, 1H), 2.84 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.61 (br s, 1H), 8.46 (br s, 1H), 7.75 (d, ^3J=8.6 Hz, 2H), 7.37 (s, 2H), 7.25 (t, ^3J=7.6 Hz, 2H), 6.96 (t, ^3J=7.3 Hz, 1H), 6.62 (s, 1H), 6.52 (br s, 1H), 2.88 (d, ^3J=4.8 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.9, 140.3, 140.0, 137.1, 128.2, 123.1, 121.4, 119.8, 117.7, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{21}N_6$ *m/e*: 321.1828, found: 321.1821.

*4.2.7. Synthesis of 2-mexylamino-4-methylamino-6-(2-methylphenylamino)-1,3,5-triazine (**4**).* The compound was synthesized using Method C. Yield: 81%; T_g 61 °C; FTIR (CH_2Cl_2/KBr) 3406, 3277, 3020, 2954, 2918, 2857, 1606, 1575, 1558, 1539, 1517, 1506, 1440, 1398, 1360, 1321, 1299, 1254, 1184, 1117, 1083, 1039, 886, 871, 838, 809, 737, 688, 654, 611 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.90 (br s, 0.5H), 8.74 (br s, 0.5H), 8.44 (br s, 0.5H), 8.27 (br s, 0.5H), 7.45 (br m, 1H), 7.33 (br d, 2H), 7.21 (d, ^3J=7.0 Hz, 1H), 7.17 (d, ^3J=7.6 Hz, 1H), 7.07 (t, ^3J=7.6 Hz, 1H), 6.80 (s, 1H), 6.50 (s, 1H), 2.82 (d, 3J=4.7 Hz, 3H), 2.24 (s, 3H), 2.14 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.39 (br s, 1H), 7.89 (br s, 1H), 7.52 (d, ^3J=7.6 Hz, 1H), 7.30 (s, 2H), 7.20 (d, ^3J=7.3 Hz, 1H), 7.16 (t, ^3J=7.6 Hz, 1H), 7.05 (t,

^3J=7.6 Hz, 1H), 6.54 (s, 1H), 6.43 (br s, 1H), 2.84 (d, ^3J=4.8 Hz, 3H), 2.25 (s, 3H), 2.17 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.0, 164.8, 164.2, 164.0, 140.3, 137.6, 136.9, 133.0, 130.1, 126.3, 125.7, 124.5, 122.7, 117.0, 27.2, 21.1, 18.1 ppm; HRMS (ESI, MH$^+$) calcd for $C_{19}H_{23}N_6$ *m*/*e*: 335.1984, found: 335.1985.

*4.2.8. Synthesis of 2-mexylamino-4-methylamino-6-(3-methylphenylamino)-1,3,5-triazine (**5**).* The compound was synthesized using Method A. Yield: 78%; T_g 64 °C; FTIR (CH_2Cl_2/KBr) 3405, 3277, 3170, 3024, 2947, 2918, 2861, 1610, 1580, 1556, 1513, 1487, 1426, 1398, 1357, 1319, 1299, 1243, 1178, 1166, 1085, 1036, 840, 808, 775, 736, 688 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.03 (br s, 0.5H), 8.97 (br s, 0.5H), 8.88 (br s, 0.5H), 8.81 (br s, 0.5H), 7.66 (d, ^3J=8.2 Hz, 1H), 7.54 (br d, 1H), 7.40 (br d, 2H), 7.12 (t, ^3J=7.6 Hz, 1H), 6.89 (br s, 1H), 6.76 (d, ^3J=7.6 Hz, 1H), 6.58 (s, 1H), 2.84 (d, ^3J=4.1 Hz, 3H), 2.26 (s, 3H), 2.22 (s, 6H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.57 (br s, 1H), 8.49 (br s, 1H), 7.60 (d, ^3J=8.1 Hz, 1H), 7.52 (s, 1H), 7.37 (s, 2H), 7.12 (t, ^3J=7.8 Hz, 1H), 6.78 (d, ^3J=7.3 Hz, 1H), 6.61 (s, 1H), 6.57 (br s, 1H), 2.87 (d, ^3J=4.8 Hz, 3H), 2.28 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.8, 140.2, 140.0, 137.3, 137.0, 128.0, 123.1, 122.2, 120.3, 117.7, 117.0, 27.2, 21.1, 21.2 ppm; HRMS (ESI, MH$^+$) calcd for $C_{19}H_{23}N_6$ *m*/*e*: 335.1984, found: 335.1964.

*4.2.9. Synthesis of 2-mexylamino-4-methylamino-6-(4-methylphenylamino)-1,3,5-triazine (**6**).* The compound was synthesized using Method A. Yield: 70%; T_g 70 °C; FTIR (CH_2Cl_2/KBr) 3408, 3278, 3175, 3025, 2947, 2919, 2865, 1610, 1574, 1555, 1513, 1502, 1422, 1403, 1359, 1321, 1299, 1235, 1182, 1084, 1037, 839, 808, 737, 686 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.01 (br s, 0.5H), 8.94 (br s, 0.5H), 8.85 (br s, 0.5H), 8.79 (br s, 0.5H), 7.64 (br s, 2H), 7.39 (br d, 2H), 7.05 (d, ^3J=8.2 Hz, 2H), 6.84 (br s, 1H), 6.58 (s, 1H), 2.83 (d, ^3J=4.7 Hz, 3H), 2.24 (s, 3H), 2.22 (s, 6H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.51 (br s, 1H), 8.43 (br s, 1H), 7.61 (d, ^3J=8.3 Hz, 2H), 7.37 (s, 2H), 7.06 (d, ^3J=8.3 Hz, 2H), 6.60 (s, 1H), 6.49 (br s, 1H), 2.87 (d, ^3J=4.8 Hz, 3H), 2.27 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.9, 140.1, 137.7, 137.0, 130.3, 128.6, 123.1, 120.0, 117.6, 27.2, 21.1, 20.3 ppm; HRMS (ESI, MH$^+$) calcd for $C_{19}H_{23}N_6$ *m*/*e*: 335.1984, found: 335.1965.

*4.2.10. Synthesis of 2-mexylamino-4-methylamino-6-(2,4-dimethylphenylamino)-1,3,5-triazine (**7**).* The compound was synthesized using Method C. Yield: 96%; T_g 63 °C; FTIR (ATR/CH_2Cl_2) 3395, 3275, 3195, 2949, 2917, 2731, 2267, 1572, 1505, 1435, 1399, 1360, 1322, 1300, 1264, 1221, 1186, 1143, 1125, 1084, 1037, 957, 871, 840, 810, 736, 720, 689, 652, 634, 617 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.84 (br s, 0.5H), 8.69 (br s, 0.5H), 8.39 (br s, 0.5H), 8.21 (br s, 0.5H), 7.28 (br d, 2H), 7.24 (br s, 1H), 7.02 (s, 1H), 6.97 (d, ^3J=7.6 Hz, 1H), 6.75 (br s, 1H), 6.48 (s, 1H), 2.79 (d, ^3J=4.1 Hz, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 2.12 (s, 6H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.34 (br s, 1H), 7.84 (br s, 1H), 7.32 (d, ^3J=7.8 Hz, 1H), 7.29 (s, 2H), 7.02 (s, 1H), 6.97 (d, ^3J=8.0 Hz, 1H), 6.53 (s, 1H), 6.38 (br s, 1H), 2.83 (d, ^3J=4.5 Hz, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 2.16 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.0, 164.1, 140.3, 136.8, 134.9, 133.7, 133.3, 130.6, 126.7, 126.3, 122.6, 116.9, 27.1, 21.0, 20.4, 18.0 ppm; HRMS (ESI, MH$^+$) calcd for $C_{20}H_{25}N_6$ *m*/*e*: 349.2141, found: 349.2149.

*4.2.11. Synthesis of 2-mexylamino-4-methylamino-6-(2,5-dimethylphenylamino)-1,3,5-triazine (**8**).* The compound was synthesized using Method C. Yield: 59%; T_g 71 °C; FTIR (CH_2Cl_2/KBr) 3403, 3273, 3165, 3019, 2965, 2949, 2919, 2863, 1581, 1556, 1516, 1494, 1441, 1411, 1399, 1358, 1321, 1299, 1293, 1261, 1187, 1122, 1037, 996, 877, 840, 809, 737, 690, 668 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.89 (br s, 0.5H), 8.74 (br s, 0.5H), 8.41 (br s, 0.5H), 8.25 (br s, 0.5H), 7.33 (br d, 2H), 7.22 (br d, 1H), 7.09 (d, ^3J=7.6 Hz, 1H), 6.89 (d, ^3J=8.2 Hz, 1H), 6.80 (br s, 1H), 6.50 (s, 1H), 2.82 (d, ^3J=4.1 Hz, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 2.13 (s, 6H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.36 (br s, 1H), 7.83 (br s, 1H), 7.30 (s, 3H), 7.08 (d, ^3J=7.6 Hz, 1H), 6.88 (d, ^3J=8.1 Hz, 1H), 6.53 (s, 1H), 6.42 (br s, 1H), 2.83 (d, ^3J=4.8 Hz, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 2.16 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.1, 164.9, 164.2, 164.0, 140.4, 137.4, 136.9, 134.6, 130.2, 129.9, 127.1, 125.4, 122.7, 117.0, 27.2, 21.1, 20.6, 17.7 ppm; HRMS (ESI, MH$^+$) calcd for $C_{20}H_{25}N_6$ *m*/*e*: 349.2141, found: 349.2124.

*4.2.12. Synthesis of 2-mexylamino-4-methylamino-6-(2,6-dimethylphenylamino)-1,3,5-triazine (**9**).* The compound was synthesized using Method C. Yield: 94%; T_g 84 °C; FTIR (ATR/CH_2Cl_2) 3402, 3276, 3192, 3019, 2950, 2918, 2860, 1570, 1504, 1436, 1398, 1323, 1301, 1264, 1219, 1186, 1166, 1141, 1098, 1036, 919, 888, 840, 811, 769, 739, 690, 649 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.34 (br s, 1H), 7.91 (br s, 1H), 7.24 (br s, 2H), 7.07 (m, 3H), 6.49 (s, 1H), 6.37 (br s, 1H), 2.81 (d, ^3J=4.7 Hz, 3H), 2.20 (s, 6H), 2.12 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.2, 164.2, 140.4, 136.7, 136.4, 135.9, 127.5, 125.8, 122.4, 116.5, 27.1, 21.1, 18.3 ppm; HRMS (ESI, MH$^+$) calcd for $C_{20}H_{25}N_6$ *m*/*e*: 349.2141, found: 349.2150.

*4.2.13. Synthesis of 2-mexylamino-4-methylamino-6-(3,4-dimethylphenylamino)-1,3,5-triazine (**10**).* The compound was synthesized using Method A. Yield: 72%; T_g 72 °C; FTIR (CH_2Cl_2/KBr) 3409, 3280, 3021, 2962, 2942, 2919, 2862, 1611, 1581, 1570, 1558, 1506, 1423, 1358, 1320, 1299, 1261, 1243, 1209, 1186, 1086, 1035, 1021, 997, 865, 839, 809, 736, 689 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.93 (br s, 1H), 8.77 (br s, 1H), 7.53 (d, ^3J=7.6 Hz, 1H), 7.40 (br d, 2H), 6.99 (d, ^3J=8.2 Hz, 1H), 6.84 (br s, 1H), 6.57 (s, 1H), 2.84 (d, ^3J=4.7 Hz, 3H), 2.21 (s, 6H), 2.17 (s, 3H), 2.15 (s, 3H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.41 (br s, 2H), 7.48 (d, ^3J=8.1 Hz, 1H), 7.46 (s, 1H), 7.36 (s, 2H), 7.00 (d, ^3J=8.1 Hz, 1H), 6.60 (s, 1H), 6.49 (br s, 1H), 2.87 (d, ^3J=4.8 Hz, 3H), 2.24 (s, 6H), 2.20 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 164.1, 163.9, 140.1, 137.9, 137.0, 135.7, 129.2, 123.1, 121.3, 117.6, 2.2, 21.1, 19.6, 18.6 ppm; HRMS (ESI, MH$^+$) calcd for $C_{20}H_{25}N_6$ *m*/*e*: 349.2141, found: 349.2126. Anal. Calcd for $C_{20}H_{24}N_6$: C, 68.94; H, 6.94; N, 24.12. Found: C, 69.02, H, 7.14; N, 23.79.

*4.2.14. Synthesis of 2-mexylamino-4-methylamino-6-(2,4,6-trimethylphenylamino)-1,3,5-triazine (**11**).* The compound was synthesized using Method C. Yield: 91%; T_g 79 °C, T_c 151 °C, T_{dec} 253 °C; FTIR (ATR/CH_2Cl_2) 3402, 3274, 3010, 2949, 2917, 2862, 1569, 1516, 1504, 1436, 1398, 1323, 1300, 1250, 1229, 1187, 1036, 1013, 839, 810, 738, 688, 649 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.26 (s, 1H), 7.76 (s, 1H), 7.23 (s, 2H), 6.88 (s, 2H), 6.48 (s, 1H), 6.29 (s, 1H), 2.81 (d, ^3J=4.5 Hz, 3H), 2.25 (s, 3H), 2.15 (s, 6H), 2.12 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.3, 164.1, 140.4, 136.7, 135.5, 134.5, 133.8, 128.1, 122.3, 116.5, 27.1, 20.9, 20.4, 18.2 ppm; HRMS (ESI, MH$^+$) calcd for $C_{21}H_{27}N_6$ *m*/*e*: 363.2297, found: 363.2281.

*4.2.15. Synthesis of 2-mexylamino-4-methylamino-6-(2-fluorophenylamino)-1,3,5-triazine (**12**).* The compound was synthesized using Method A. Yield: 72%; T_g 55 °C; FTIR (CH_2Cl_2/KBr) 3425, 3279, 3185, 3021, 2949, 2919, 2875, 1623, 1595, 1577, 1561, 1513, 1503, 1480, 1451, 1399, 1360, 1321, 1300, 1287, 1246, 1185, 1103, 1032, 840, 809, 748, 687 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.98 (br s, 0.5H), 8.82 (br s, 0.5H), 8.61 (br s, 0.5H), 8.44 (br s, 0.5H), 7.75 (br s, 2H), 7.33 (br d, 2H), 7.21 (m, 1H), 7.15 (m, 2H), 6.91 (br s, 1H), 6.53 (s, 1H), 2.80 (br d, 3H), 2.16 (s, 6H) ppm; ^{1}H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.54 (br s, 1H), 8.01 (br s, 1H), 7.89 (dt, ^3J=7.3 Hz, ^4J=1.7 Hz, 1H), 7.32 (s, 2H), 7.19 (m, 1H), 7.13 (m, 2H), 6.60 (br s, 1H), 6.58 (s, 1H), 2.85 (d, ^3J=4.9 Hz, 3H), 2.20 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 165.3, 165.0, 164.7, 164.4, 157.4, 154.1 (J_{C-F}=243 Hz), 140.6, 137.5, 127.7, 127.6, 127.0, 125.4, 124.4, 123.5,

117.9, 116.0, 115.7, 27.7, 21.6 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}FN_6$ *m/e*: 339.1733, found: 339.1715.

*4.2.16. Synthesis of 2-mexylamino-4-methylamino-6-(3-fluorophenylamino)-1,3,5-triazine (**13**).* The compound was synthesized using Method A. Yield: 85%; T_g 62 °C; FTIR (CH_2Cl_2/KBr) 3411, 3279, 3183, 3129, 3021, 2951, 2919, 2870, 1613, 1584, 1554, 1508, 1487, 1435, 1399, 1361, 1319, 1301, 1276, 1263, 1243, 1187, 1177, 1145, 1087, 1072, 1035, 1001, 965, 936, 861, 843, 808, 772, 737, 702, 681 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.35 (br s, 0.5H), 9.21 (br s, 0.5H), 9.08 (br s, 0.5H), 8.93 (br s, 0.5H), 7.90 (br d, 1H), 7.48 (t, ^3J=9.4 Hz, 1H), 7.38 (br d, 2H), 7.24 (q, ^3J=7.0 Hz, 1H), 7.00 (br s, 1H), 6.72 (t, ^3J=8.2 Hz, 1H), 6.60 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.89 (br s, 1H), 8.57 (br s, 1H), 7.81 (d, ^3J=12.3 Hz, 1H), 7.50 (d, ^3J=8.3 Hz, 1H), 7.36 (s, 2H), 7.24 (q, ^3J=7.3 Hz, 1H), 6.71 (dt, ^3J=8.3 Hz, ^4J=2.5 Hz, 1H), 6.65 (br s, 1H), 6.63 (s, 1H), 2.88 (d, ^3J=4.5 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.0, 163.8, 163.8, 160.6 (J_{C-F}=239 Hz), 142.4, 142.2, 139.9, 137.1, 129.7, 129.5, 123.3, 117.9, 115.1, 107.6, 107.3, 106.3, 106.0, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}FN_6$ *m/e*: 339.1733, found: 339.1743. Anal. Calcd for $C_{18}H_{19}FN_6$: C, 63.79; H, 5.66; N, 24.46. Found: C, 64.10; H, 5.60; N, 24.65.

*4.2.17. Synthesis of 2-mexylamino-4-methylamino-6-(4-fluorophenylamino)-1,3,5-triazine (**14**).* The compound was synthesized using Method A. Yield: 20%; T_g 64 °C; FTIR (CH_2Cl_2/KBr) 3408, 3277, 3178, 3044, 2953, 2919, 2870, 1611, 1582, 1553, 1505, 1440, 1423, 1403, 1360, 1320, 1299, 1263, 1213, 1185, 1155, 1085, 1037, 1012, 834, 809, 781, 737, 688, 667 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.16 (br s, 0.5H), 9.01 (br s, 1H), 8.84 (br s, 0.5H), 7.78 (br s, 2H), 7.38 (br d, 2H), 7.07 (t, ^3J=8.8 Hz, 2H), 6.91 (br s, 1H), 6.58 (s, 1H), 2.83 (d, ^3J=4.7 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.68 (br s, 1H), 8.47 (br s, 1H), 7.75 (dd, ^3J=9.1 Hz, J_{C-F}=5.0 Hz, 2H), 7.35 (s, 2H), 7.04 (t, ^3J=9.1 Hz, 2H), 6.61 (s, 1H), 6.54 (br s, 1H), 2.87 (d, ^3J=4.8 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 164.1, 163.8, 158.8, 155.6 (J_{C-F}=238 Hz), 140.0, 137.1, 136.7, 123.2, 121.5, 117.7, 114.8, 114.6, 27.3, 21.2 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}FN_6$ *m/e*: 339.1733, found: 339.1734. Anal. Calcd for $C_{18}H_{19}FN_6$: C, 63.89; H, 5.66; N, 24.84. Found: C, 63.91; H, 5.73; N, 24.48.

*4.2.18. Synthesis of 2-mexylamino-4-methylamino-6-(2-chlorophenylamino)-1,3,5-triazine (**15**).* The compound was synthesized using Method C. Yield: 91%; T_g 53 °C; FTIR (ATR/CH_2Cl_2) 3408, 3279, 3179, 3068, 3015, 2948, 2916, 2867, 1582, 1558, 1502, 1465, 1433, 1401, 1358, 1321, 1300, 1265, 1229, 1184, 1168, 1161, 1132, 1089, 1055, 1034, 939, 885, 841, 809, 747, 690, 655 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.03 (br s, 0.5H), 8.86 (br s, 0.5H), 8.25 (br s, 0.5H), 8.10 (br s, 0.5H), 7.93 (br s, 1H), 7.49 (d, ^3J=8.2 Hz, 1H), 7.32 (m, 3H), 7.14 (t, ^3J=7.6 Hz, 1H), 6.99 (br s, 1H), 6.54 (s, 1H), 2.82 (d, ^3J=4.1 Hz, 3H), 2.16 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.64 (br s, 1H), 8.10 (dd, ^3J=7.9 Hz, ^4J=1.5 Hz, 1H), 7.77 (br s, 1H), 7.46 (dd, ^3J=7.9 Hz, ^4J=1.5 Hz, 1H), 7.32 (s, 2H), 7.30 (dd, ^3J=8.1 Hz, ^4J=1.3 Hz, 1H), 7.11 (dt, ^3J=7.3 Hz, ^4J=1.5 Hz, 1H), 6.70 (br s, 1H), 6.59 (s, 1H), 2.86 (d, ^3J=4.7 Hz, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.1, 164.5, 164.1, 163.8, 139.9, 136.9, 136.0, 129.1, 127.2, 126.7, 126.1, 124.9, 123.0, 117.3, 27.1, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}ClN_6$ *m/e*: 355.1438, found: 355.1435.

*4.2.19. Synthesis of 2-mexylamino-4-methylamino-6-(3-chlorophenylamino)-1,3,5-triazine (**16**).* The compound was synthesized using Method A. Yield: 89%; T_g 74 °C; FTIR (ATR/CH_2Cl_2) 3405, 3274, 3175, 3018, 2951, 2918, 2872, 1572, 1504, 1477, 1425, 1359, 1320, 1301, 1263, 1240, 1184, 1167, 1148, 1096, 1077, 1037, 997, 976, 904, 884, 842, 810, 774, 738, 694, 683 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.32 (br s, 0.5H), 9.16 (br s, 0.5H), 9.06 (br s, 0.5H), 8.90 (br s, 0.5H), 7.95 (br d, 1H), 7.76 (d, ^3J=8.2 Hz, 1H), 7.39 (br d, 2H), 7.25 (t, ^3J=8.2 Hz, 1H), 7.02 (br s, 1H), 6.96 (d, ^3J=8.2 Hz, 1H), 6.60 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.88 (br s, 1H), 8.57 (br s, 1H), 7.90 (s, 1H), 7.74 (dd, ^3J=8.3 Hz, ^4J=2.1 Hz, 1H), 7.36 (s, 2H), 7.24 (t, ^3J=8.1 Hz, 1H), 6.96 (dd, ^3J=7.9 Hz, ^4J=1.9 Hz, 1H), 6.67 (br s, 1H), 6.62 (s, 1H), 2.88 (d, ^3J=4.9 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 164.0, 163.7, 141.9, 139.8, 137.1, 132.7, 129.7, 123.3, 120.8, 118.8, 117.8, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}ClN_6$ *m/e*: 355.1438, found: 355.1442.

*4.2.20. Synthesis of 2-mexylamino-4-methylamino-6-(4-chlorophenylamino)-1,3,5-triazine (**17**).* The compound was synthesized using Method A. Yield: 66%; T_g 68 °C; FTIR (CH_2Cl_2/KBr) 3409, 3281, 3198, 3032, 2952, 2918, 2860, 1607, 1573, 1556, 1513, 1502, 1490, 1415, 1401, 1360, 1321, 1300, 1285, 1238, 1184, 1090, 1035, 1012, 976, 958, 940, 887, 827, 810, 738, 692 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.27 (br s, 0.5H), 9.12 (br s, 0.5H), 9.02 (br s, 0.5H), 8.87 (br s, 0.5H), 7.83 (br s, 2H), 7.38 (br d, 2H), 7.27 (d, ^3J=8.2 Hz, 2H), 6.95 (br s, 1H), 6.59 (s, 1H), 2.84 (d, ^3J=4.1 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.83 (br s, 1H), 8.53 (br s, 1H), 7.80 (d, ^3J=8.8 Hz, 2H), 7.36 (s, 2H), 7.26 (d, ^3J=8.8 Hz, 2H), 6.63 (s, 1H), 6.61 (br s, 1H), 2.88 (d, ^3J=4.5 Hz, 3H), 2.26 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.0, 164.1, 163.8, 139.9, 139.4, 137.1, 128.0, 124.9, 123.3, 121.2, 117.7, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}ClN_6$ (*m/e*): 355.1438, found: 355.1436.

*4.2.21. Synthesis of 2-mexylamino-4-methylamino-6-(3,5-dichlorophenylamino)-1,3,5-triazine (**18**).* The compound was synthesized using Method C. Yield: 98%; T_g 84 °C; FTIR (ATR/CH_2Cl_2) 3408, 3277, 3174, 3115, 3016, 2951, 2914, 2872, 2843, 1596, 1505, 1418, 1359, 1320, 1302, 1263, 1227, 1184, 1114, 1088, 1037, 993, 951, 928, 840, 819, 738, 701, 672 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.45 (br s, 0.5H), 9.30 (br s, 0.5H), 9.10 (br s, 0.5H), 8.93 (br s, 0.5H), 7.93 (br d, 2H), 7.37 (br d, 2H), 7.08 (br s, 1H), 7.06 (s, 1H), 6.61 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 9.07 (br s, 1H), 8.64 (br s, 1H), 7.89 (d, ^4J=1.7 Hz, 2H), 7.34 (s, 2H), 7.02 (t, ^4J=1.9 Hz, 1H), 6.78 (br s, 1H), 6.64 (s, 1H), 2.88 (d, ^3J=4.7 Hz, 3H), 2.26 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 163.9, 163.6, 142.9, 139.6, 137.1, 133.6, 123.5, 120.0, 118.0, 117.2, 27.1, 21.1 ppm; HRMS (ESI) calcd for $C_{18}H_{19}Cl_2N_6$ *m/e*: 389.1043, found: 389.1053.

*4.2.22. Synthesis of 2-mexylamino-4-methylamino-6-(3-bromophenylamino)-1,3,5-triazine (**19**).* The compound was synthesized using Method A. Yield: 91%; T_g 78 °C; FTIR (ATR/CH_2Cl_2) 3403, 3273, 3175, 3022, 2950, 2917, 2869, 1570, 1503, 1474, 1423, 1360, 1320, 1301, 1262, 1233, 1184, 1168, 1090, 1069, 1036, 994, 881, 842, 809, 772, 683 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.29 (br s, 0.5H), 9.13 (br s, 0.5H), 9.04 (br s, 0.5H), 8.88 (br s, 0.5H), 8.04 (br d, 1H), 7.84 (br s, 1H), 7.38 (br d, 2H), 7.19 (t, ^3J=8.2 Hz, 1H), 7.09 (d, ^3J=8.2 Hz, 1H), 7.01 (br s, 1H), 6.59 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.88 (br s, 1H), 8.57 (br s, 1H), 8.01 (s, 1H), 7.81 (dd, ^3J=8.1 Hz, ^4J=1.9 Hz, 1H), 7.36 (s, 2H), 7.18 (t, ^3J=8.1 Hz, 1H), 7.10 (dd, ^3J=8.1 Hz, ^4J=1.9 Hz, 1H), 6.68 (br s, 1H), 6.63 (s, 1H), 2.88 (s, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.7, 142.1, 139.8, 137.1, 130.1, 123.8, 123.3, 121.7, 121.3, 118.3, 117.8, 27.2, 21.1 ppm; HRMS (ESI) calcd for $C_{18}H_{20}BrN_6$ (*m/e*): 399.0927, found: 399.0932. Anal. Calcd for $C18H_{19}BrN_6$: C, 54.14; H, 4.80; N, 21.05. Found: C, 54.11; H, 4.71; N, 20.74.

*4.2.23. Synthesis of 2-mexylamino-4-methylamino-6-(4-bromophenylamino)-1,3,5-triazine (**20**).* The compound was synthesized

using Method B. Yield: 93%; T_g 69 °C; FTIR (CH_2Cl_2/KBr) 3406, 3274, 3180, 3108, 3020, 2920, 2852, 1599, 1572, 1507, 1489, 1417, 1398, 1360, 1321, 1301, 1285, 1237, 1179, 1073, 1008, 841, 824, 809, 690 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.28 (br s, 0.5H), 9.14 (br s, 0.5H), 9.04 (br s, 0.5H), 8.88 (br s, 0.5H), 7.78 (br s, 2H), 7.41 (s, 2H), 7.38 (br s, 2H), 6.96 (br s, 1H), 6.59 (s, 1H), 2.84 (d, ^3J=4.1 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.83 (br s, 1H), 8.54 (br s, 1H), 7.75 (d, ^3J=9.1 Hz, 2H), 7.38 (d, ^3J=9.1 Hz, 2H), 7.36 (s, 2H), 6.62 (s, 1H), 6.61 (br s, 1H), 2.88 (d, ^3J=4.8 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 164.6, 164.3, 140.4, 140.3, 137.6, 131.4, 123.8, 122.1, 118.3, 113.3, 27.7, 21.6 ppm; HRMS (EI) calcd for $C_{18}H_{19}BrN_6$ (*m*/*e*): 396.0855, found: 396.0846. Anal. Calcd for $C_{18}H_{19}BrN_6$: C, 54.14; H, 4.80; N, 21.05. Found: C, 53.97; H, 4.65; N, 20.71.

*4.2.24. Synthesis of 2-mexylamino-4-methylamino-6-(3-iodophenylamino)-1,3,5-triazine (**21**).* The compound was synthesized using Method A. Yield: 94%; T_g 84 °C; FTIR (ATR/CH_2Cl_2) 3405, 3274, 3170, 3061, 3019, 2950, 2916, 2867, 1594, 1566, 1502, 1470, 1421, 1360, 1321, 1301, 1232, 1184, 1168, 1086, 1063, 1036, 992, 874, 842, 809, 772, 742, 682, 658 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.21 (br s, 0.5H), 9.03 (br d, 1H), 8.85 (br s, 0.5H), 8.26, 8.03 (br d, 1H), 7.91 (br dd, 1H), 7.38 (br d, 2H), 7.28 (d, ^3J=7.6 Hz, 1H), 7.03 (t, ^3J=8.2 Hz, 1H), 7.01 (br s, 1H), 6.59 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.81 (br s, 1H), 8.56 (br s, 1H), 8.14 (s, 1H), 7.86 (d, ^3J=8.1 Hz, 1H), 7.35 (s, 2H), 7.29 (d, ^3J=8.3 Hz, 1H), 7.03 (t, ^3J=7.9 Hz, 1H), 6.68 (br s, 1H), 6.62 (s, 1H), 2.88 (s, 1H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 163.9, 163.8, 141.9, 139.8, 137.0, 130.1, 129.7, 127.7, 127.5, 123.2, 118.8, 117.7, 94.2, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}IN_6$ (*m*/*e*): 447.0794, found: 447.0795.

*4.2.25. Synthesis of 2-mexylamino-4-methylamino-6-(4-iodophenylamino)-1,3,5-triazine (**22**).* The compound was synthesized using Method A. Yield: 51%; T_g 72 °C; FTIR (CH_2Cl_2/KBr) 3406, 3276, 3178, 3102, 3024, 2951, 2918, 2863, 1597, 1568, 1511, 1501, 1485, 1456, 1425, 1415, 1396, 1360, 1321, 1302, 1283, 1236, 1181, 1168, 1116, 1086, 1062, 1036, 1004, 976, 957, 939, 888, 841, 821, 809, 737, 703, 688 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.25 (br s, 0.5H), 9.10 (br s, 0.5H), 9.02 (br s, 0.5H), 8.87 (br s, 0.5H), 7.64 (br s, 2H), 7.55 (d, ^3J=8.2 Hz, 2H), 7.38 (br d, 2H), 6.95 (br s, 1H), 6.59 (s, 1H), 2.84 (d, ^3J=4.1 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.81 (br s, 1H), 8.53 (br s, 1H), 7.62 (d, ^3J=8.8 Hz, 2H), 7.55 (d, ^3J=8.8 Hz, 2H), 7.36 (s, 2H), 6.63 (s, 1H), 6.61 (br s, 1H), 2.88 (d, ^3J=4.5 Hz, 3H), 2.26 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.0, 164.0, 163.7, 140.3, 139.9, 137.1, 136.7, 123.3, 122.1, 117.7, 84.3, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}IN_6$ (*m*/*e*): 447.0794, found: 447.0782. Anal. Calcd for $C_{18}H_{19}IN_6$: C, 48.44; H, 4.29; N, 18.83. Found: C, 48.13; H, 4.16; N, 18.49.

*4.2.26. Synthesis of 2-mexylamino-4-methylamino-6-(3-hydroxyphenylamino)-1,3,5-triazine (**23**).* The compound was synthesized using Method A. Yield: 62%; T_g 86 °C; FTIR (ATR/CH_2Cl_2) 3404, 3283, 3024, 2950, 2914, 2865, 1579, 1558, 1514, 1433, 1401, 1362, 1319, 1264, 1248, 1189, 1157, 1091, 1037, 999, 971, 937, 842, 808, 772, 737, 701, 686 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.18 (s, 1H), 8.94 (br d, 1H), 8.82 (br s, 0.5H), 8.76 (br s, 0.5H), 7.41 (br d, 2H), 7.30 (d, ^3J=8.2 Hz, 1H), 7.19, 7.09 (br d, 1H), 7.02 (t, ^3J=8.2 Hz, 1H), 6.83 (br s, 1H), 6.57 (s, 1H), 6.38 (dd, ^3J=7.6 Hz, 4J=2.3 Hz, 1H), 2.84 (d, ^3J=4.7 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.85 (s, 1H), 8.51 (br s, 1H), 8.43 (br s, 1H), 7.38 (s, 2H), 7.24 (dd, ^3J=7.9 Hz, ^4J=1.9 Hz, 1H), 7.15 (s, 1H), 7.02 (t, ^3J=8.1 Hz, 1H), 6.60 (s, 1H), 6.52 (br s, 1H), 6.41 (dd, ^3J=7.9 Hz, ^4J=2.4 Hz, 1H), 2.87 (d, ^3J=4.7 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.8, 157.2, 141.2, 140.0, 137.0, 128.7, 123.0, 117.5, 111.0, 108.8, 107.1, 27.2, 21.1 ppm; HRMS (ESI) calcd for $C_{18}H_{21}N_6O$ *m*/*e*: 337.1771, found: 337.1777.

*4.2.27. Synthesis of 2-mexylamino-4-methylamino-6-(4-hydroxyphenylamino)-1,3,5-triazine (**24**).* The compound was synthesized using Method B. Yield: 96%; T_g 95 °C; FTIR (CH_2Cl_2/KBr) 3446, 3418, 3055, 2987, 1575, 1559, 1510, 1423, 1353, 1266, 1182, 1170, 1093, 1037, 984, 896, 839, 810 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.01 (s, 1H), 8.87 (br s, 0.5H), 8.80 (br s, 0.5H), 8.71 (br s, 0.5H), 8.62 (br s, 0.5H), 7.45 (br s, 2H), 7.35 (br d, ^3J=10.5 Hz, 2H), 6.71 (br s, 1H), 6.65 (d, ^3J=8.8 Hz, 2H), 6.54 (s, 1H), 2.79 (d, ^3J=4.7 Hz, 3H), 2.19 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.71 (br s, 1H), 8.47 (br s, 1H), 8.42 (br s, 1H), 7.45 (d, ^3J=8.8 Hz, 2H), 7.35 (s, 2H), 6.69 (d, ^3J=9.1 Hz, 2H), 6.60 (s, 1H), 6.51 (br s, 1H), 2.86 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 164.4, 152.9, 140.7, 137.5, 132.1, 123.4, 122.6, 118.0, 115.2, 27.7, 21.7 ppm; HRMS (EI) calcd for $C_{18}H_{20}N_6O$ (*m*/*e*): 336.1699, found: 336.1689.

*4.2.28. Synthesis of 2-mexylamino-4-methylamino-6-(4-mercaptophenylamino)-1,3,5-triazine (**25**).* The compound was synthesized using Method B. Yield: 95%; T_g 84 °C; FTIR (CH_2Cl_2/KBr) 3448, 3416, 3283, 3054, 2987, 1575, 1556, 1496, 1423, 1400, 1355, 1323, 1266, 1183, 896, 841, 810, 705 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.09 (br s, 0.5H), 8.96 (br s, 1H), 8.81 (br s, 0.5H), 7.66 (br s, 2H), 7.35 (br d, ^3J=15.2 Hz, 2H), 7.15 (d, ^3J=8.2 Hz, 2H), 6.87 (br s, 1H), 6.57 (s, 1H), 5.15 (br s, 1H), 2.81 (d, ^3J=4.1 Hz, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 164.7, 140.6, 138.7, 137.7, 129.9, 123.8, 123.3, 121.3, 118.4, 27.9, 21.7 ppm; HRMS (EI) calcd for $C_{18}H_{20}N_6S$ (*m*/*e*): 352.1470, found: 352.1477. **Caution: the compound slowly oxidizes to the corresponding disulfide in DMSO, NMR spectra must be recorded on freshly prepared samples.

*4.2.29. Synthesis of 2-mexylamino-4-methylamino-6-(4-methoxyphenylamino)-1,3,5-triazine (**26**).* The compound was synthesized using Method A. Yield: 68%; T_g 64 °C; FTIR (CH_2Cl_2/KBr) 3402, 3277, 3001, 2952, 2868, 2834, 1614, 1573, 1504, 1452, 1422, 1399, 1360, 1321, 1300, 1244, 1231, 1179, 1115, 1084, 1035, 828, 808, 737, 686, 667 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.93 (br s, 1H), 8.77 (br s, 1H), 7.61 (br s, 2H), 7.37 (br d, 2H), 6.82 (d, ^3J=8.8 Hz, 2H), 6.80 (br s, 1H), 6.54 (s, 1H), 3.70 (s, 3H), 2.81 (d, ^3J=4.7 Hz, 3H), 2.19 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.48 (br s, 1H), 8.42 (br s, 1H), 7.61 (d, ^3J=8.8 Hz, 2H), 7.37 (s, 2H), 6.85 (d, ^3J=9.1 Hz, 2H), 6.60 (s, 1H), 6.47 (br s, 1H), 3.75 (s, 3H), 2.87 (d, ^3J=4.8 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.9, 154.3, 140.1, 137.0, 133.2, 123.0, 121.7, 117.5, 113.5, 55.0, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{19}H_{23}N_6O$ *m*/*e*: 351.1933, found: 351.1910.

*4.2.30. Synthesis of 2-mexylamino-4-methylamino-6-(3,5-dimethoxyphenylamino)-1,3,5-triazine (**27**).* The compound was synthesized using Method A. Yield: 77%; T_g 68 °C; FTIR (CH_2Cl_2/KBr) 3398, 3281, 3142, 3001, 2955, 2937, 2838, 1594, 1557, 1516, 1480, 1455, 1424, 1397, 1360, 1318, 1250, 1202, 1175, 1154, 1091, 1064, 839, 809, 686 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.04 (br s, 0.5H), 8.96 (br s, 0.5H), 8.89 (br s, 0.5H), 8.79 (br s, 0.5H), 7.40 (br d, 2H), 7.07 (br d, 2H), 6.94 (br s, 1H), 6.58 (s, 1H), 6.11 (t, ^4J=2.0 Hz, 1H), 3.69 (s, 6H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.58 (br s, 1H), 8.45 (br s, 1H), 7.38 (s, 2H), 7.06 (d, ^4J=2.3 Hz, 2H), 6.62 (s, 1H), 6.59 (br s, 1H), 6.14 (t, ^4J=2.3 Hz, 1H), 3.73 (s, 6H), 2.89 (d, ^3J=4.8 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.9, 160.2, 141.9, 140.0, 137.2, 123.2, 117.7, 98.3, 93.5, 54.9, 27.3, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{20}H_{25}N_6O_2$ *m*/*e*: 381.2039, found: 381.2046.

*4.2.31. Synthesis of 2-mexylamino-4-methylamino-6-(3,4,5-trimethoxyphenylamino)-1,3,5-triazine (**28**).* The compound was

synthesized using Method A. Yield: 75%; T_g 82 °C; FTIR (CH_2Cl_2/KBr) 3370, 3282, 3132, 2998, 2954, 2938, 2839, 1587, 1555, 1520, 1502, 1453, 1421, 1398, 1359, 1320, 1300, 1231, 1202, 1185, 1127, 1090, 1005, 837, 809, 735, 684 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.99 (br s, 0.5H), 8.93 (br s, 0.5H), 8.84 (br s, 0.5H), 8.77 (br s, 0.5H), 7.42 (br d, 2H), 7.16 (br d, 2H), 6.95 (br s, 1H), 6.57 (s, 1H), 3.72 (s, 6H), 3.61 (s, 3H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.21 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.49 (br s, 1H), 8.38 (br s, 1H), 7.37 (s, 2H), 7.15 (s, 2H), 6.61 (s, 1H), 6.56 (br s, 1H), 3.76 (s, 6H), 3.67 (s, 3H), 2.89 (d, ^3J=4.8 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.0, 163.8, 152.4, 140.1, 137.1, 136.3, 132.3, 123.1, 117.6, 97.9, 60.0, 55.5, 27.3, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{21}H_{27}N_6O_3$ *m*/*e*: 411.2145, found: 411.2132.

*4.2.32. Synthesis of 2-mexylamino-4-methylamino-6-[4-(2-ethoxycarbonylvinyl)-phenylamino]-1,3,5-triazine (**29**).* The compound was synthesized using Method A. Yield: 97%; T_g 70 °C; FTIR (CH_2Cl_2/KBr) 3402, 3283, 3188, 3106, 2980, 2948, 2919, 2871, 1701, 1606, 1575, 1504, 1417, 1363, 1325, 1304, 1265, 1237, 1207, 1178, 1037, 982, 883, 835, 809, 739 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.42 (br s, 0.5H), 9.28 (br s, 0.5H), 9.07 (br s, 0.5H), 8.93 (br s, 0.5H), 7.89 (br s, 2H), 7.60 (d, ^3J=8.2 Hz, 2H), 7.60 (d, $^3J_{trans}$=15.8 Hz, 1H), 7.40 (br s, 2H), 7.01 (br s, 1H), 6.61 (s, 1H), 6.48 (d, $^3J_{trans}$=15.8 Hz, 1H), 4.18 (q, ^3J=7.0 Hz, 2H), 2.85 (d, ^3J=4.1 Hz, 3H), 2.24 (s, 6H), 1.25 (t, ^3J=7.0 Hz, 3H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.94 (br s, 1H), 8.55 (br s, 1H), 7.86 (d, ^3J=8.3 Hz, 2H), 7.59 (d, $^3J_{trans}$=16.1 Hz, 1H), 7.54 (d, ^3J=8.3 Hz, 2H), 7.37 (s, 2H), 6.64 (s, 1H), 6.64 (br s, 1H), 6.40 (d, $^3J_{trans}$=15.9 Hz, 1H), 4.21 (q, ^3J=7.1 Hz, 2H), 2.89 (d. ^3J=4.3 Hz, 3H), 2.26 (s, 6H), 1.28 (t, ^3J=7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 166.0, 164.0, 163.7, 144.4, 142.8, 139.9, 137.1, 128.9, 126.9, 123.3, 119.3, 117.8, 115.0, 59.7, 27.3, 21.1, 14.2 ppm; HRMS (ESI, MH^+) calcd for $C_{23}H_{27}N_6O_2$ (*m*/*e*): 419.2195, found: 419.2177.

*4.2.33. Synthesis of 2-mexylamino-4-methylamino-6-[3-(hydroxymethyl)phenylamino]-1,3,5-triazine (**30**).* 2-Mexylamino-4-methylamino-6-chloro-1,3,5-triazine (2.59 g, 9.82 mmol) and 3-aminobenzoic acid (1.45 g, 11.8 mmol) were added in THF (50 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. The mixture was refluxed for 3 h, at which point a precipitate had formed. The precipitate was collected by filtration and washed with CH_2Cl_2, resuspended in MeOH, then AcOEt and aqueous $NaHCO_3$ were added and the mixture was shaken in an extraction funnel. Both layers were separated, the aqueous layer was extracted with a second portion of AcOEt, then the combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under vacuum to yield 2.60 g of the title compound (7.42 mmol, 76%): T_g 69 °C; FTIR (CH_2Cl_2/KBr) 3401, 3376, 3286, 3021, 2943, 2921, 2869, 1611, 1583, 1565, 1553, 1527, 1514, 1487, 1461, 1434, 1400, 1362, 1321, 1301, 1262, 1245, 1188, 1177, 1166, 1083, 1037, 1012, 998, 973, 956, 890, 842, 808, 784, 736, 693, 650 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.01 (br s, 0.5H), 8.97 (br s, 1H), 8.80 (br s, 0.5H), 7.77 (t, ^3J=7.6 Hz, 1H), 7.56 (br s, 1H), 7.40 (br d, 2H), 7.20 (t, ^3J=7.6 Hz, 1H), 6.92 (d, ^3J=7.6 Hz, 1H), 6.89 (br s, 1H), 6.58 (s, 1H), 5.13 (t, ^3J=5.9 Hz, 1H), 4.46 (d, ^3J=5.9 Hz), 2.85 (d, ^3J=4.7 Hz, 3H), 2.22 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.1, 164.1, 163.9, 142.6, 140.1, 137.1, 127.9, 123.1, 119.7, 118.3, 118.1, 117.6, 63.1, 27.2, 21.1 ppm; HRMS (EI) calcd for $C_{19}H_{22}N_6O$ (*m*/*e*): 350.1855, found: 350.1848.

*4.2.34. Synthesis of 2-mexylamino-4-methylamino-6-[4-(hydroxyethyl)phenylamino]-1,3,5-triazine (**31**).* The title compound was prepared by a procedure similar to the one used for 3-hydroxymethyl derivative **30**. Yield: 79%; T_g 73 °C; FTIR (ATR/CH_2Cl_2) 3557, 3387, 3286, 3202, 3025, 2946, 2913, 2875, 2842, 1574, 1506, 1421, 1361, 1323, 1301, 1237, 1184, 1043, 839, 809, 735, 688 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.03 (br s, 0.5H), 8.95 (br s, 0.5H), 8.88 (br s, 0.5H), 8.80 (br s, 0.5H), 7.65 (br s, 2H), 7.40 (br d, 2H), 7.10 (d, ^3J=8.2 Hz, 2H), 6.83 (br s, 1H), 6.58 (s, 1H), 4.61 (t, ^3J=5.3 Hz, 1H), 3.57 (q, ^3J=5.3 Hz, 2H), 2.84 (d, ^3J=4.7 Hz, 3H), 2.67 (t, ^3J=7.0 Hz, 2H), 2.23 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.55 (br s, 1H), 8.46 (br s, 1H), 7.62 (d, ^3J=8.5 Hz, 2H), 7.37 (s, 2H), 7.10 (d, ^3J=8.3 Hz, 2H), 6.60 (s, 1H), 6.50 (br s, 1H), 4.24 (br s, 1H), 3.63 (t, ^3J=7.1 Hz, 2H), 2.87 (d, ^3J=4.9 Hz, 3H), 2.70 (t, ^3J=7.1 Hz, 2H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.9, 140.0, 138.1, 137.0, 132.5, 128.6, 123.0, 120.0, 117.6, 62.4, 38.4, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{20}H_{25}N_6O$ *m*/*e*: 365.2084, found: 365.2088.

*4.2.35. Synthesis of 2-mexylamino-4-methylamino-6-[3-(bromomethyl)phenylamino]-1,3,5-triazine (**32**).* 2-Mexylamino-4-methylamino-6-(3-hydroxymethylphenylamino)-1,3,5-triazine (0.350 g, 1.00 mmol) was dissolved in dry CH_2Cl_2 (2 mL) in a dry round-bottomed flask equipped with a magnetic stirrer. The solution was cooled down to 0 °C, and PBr_3 (0.282 mL, 0.81 g, 3.00 mmol) was added dropwise under inert atmosphere. Once the addition was complete, the mixture was stirred under inert atmosphere at ambient temperature for 18 h. A precipitate started forming after 2–3 h. The mixture was poured into aqueous $NaHCO_3$, THF, and CH_2Cl_2 were added, then after stirring for 20 min to ensure that the mixture was completely neutralized, the remaining precipitate was removed by filtration and both layers were separated. The aqueous layer was extracted with CH_2Cl_2, then the combined organic extracts were extracted with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under reduced pressure to yield 0.348 g of the title compound (0.840 mmol, 84%): T_g 62 °C, T_{dec} 131 °C; FTIR (CH_2Cl_2/KBr) 3399, 3275, 3171, 3137, 3023, 2955, 2921, 2866, 1611, 1583, 1564, 1554, 1515, 1488, 1463, 1432, 1398, 1361, 1320, 1301, 1262, 1245, 1214, 1188, 1168, 1145, 1125, 1084, 1037, 998, 971, 933, 886, 842, 810, 786, 766, 738, 693 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.23 (br s, 0.5H), 9.09 (br s, 0.5H), 9.02 (br s, 0.5H), 8.85 (br s, 0.5H), 7.95 (br s, 1H), 7.82 (br m, 1H), 7.41 (br d, 2H), 7.24 (t, ^3J=7.6 Hz, 1H), 7.02 (d, ^3J=7.6 Hz, 1H), 7.01 (br s, 1H), 6.59 (s, 1H), 4.64 (s, 2H), 2.87 (d, ^3J=4.1 Hz, 3H), 2.23 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.9, 164.0, 163.7, 140.6, 139.9, 137.9, 137.1, 128.5, 123.2, 122.2, 120.4, 119.7, 117.7, 34.9, 27.2, 21.1 ppm; HRMS (EI) calcd for $C_{19}H_{21}BrN_6$ (*m*/*e*): 412.1011, found: 412.1003.

*4.2.36. Synthesis of 2-mexylamino-4-methylamino-6-(1-naphthylamino)-1,3,5-triazine (**33**).* The compound was synthesized using Method B. Yield: 87%; T_g 83 °C; FTIR (ATR/CH_2Cl_2) 3408, 3273, 3169, 3050, 3013, 2948, 2917, 2872, 1581, 1558, 1518, 1495, 1436, 1395, 1358, 1322, 1301, 1275, 1247, 1186, 1160, 1143, 1103, 1016, 885, 840, 809, 791, 771, 735, 687 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.13 (br s, 0.5H), 8.92 (br d, 1H), 8.72 (br s, 0.5H), 8.04 (br s, 1H), 7.93 (m, 1H), 7.77 (d, ^3J=7.6 Hz, 1H), 7.63 (br m, 1H), 7.52 (m, 4H), 7.24 (br d, 2H), 6.82 (br s, 1H), 6.47 (s, 1H), 2.82 (d, ^3J=4.7 Hz, 3H), 2.08 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.60 (br s, 1H), 8.41 (br s, 1H), 8.05 (m, 1H), 7.91 (m, 1H), 7.74 (d, ^3J=8.3 Hz, 1H), 7.71 (d, ^3J=7.3 Hz, 1H), 7.50 (m, 3H), 7.23 (s, 2H), 6.50 (s, 1H), 6.48 (br s, 1H), 2.84 (d, ^3J=4.7 Hz, 3H), 2.11 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 165.9, 165.7, 164.2, 163.9, 140.1, 136.8, 135.0, 133.8, 129.6, 129.3, 127.8, 125.7, 125.5, 125.5, 124.9, 123.4, 122.7, 117.0, 27.2, 21.0 ppm; HRMS (ESI, MH^+) calcd for $C_{22}H_{23}N_6$ *m*/*e*: 371.1979, found: 371.1988. Anal. Calcd for $C_{22}H_{22}N_6$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.08; H, 5.98; N, 22.40.

*4.2.37. Synthesis of 2-mexylamino-4-methylamino-6-(4-aminophenylamino)-1,3,5-triazine (**34**).* 2-Mexylamino-4-methylamino-6-chloro-1,3,5-triazine (25.0 g, 94.9 mmol), 1,4-phenylenediamine

(15.4 g, 142 mmol), and triethylamine (19.8 mL, 14.4 g, 142 mmol) were dissolved in THF (250 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser, then the mixture was refluxed for 16 h. After allowing the mixture to cool down to room temperature, 1 M aqueous HCl was added, then NaOH was added until the solution was basic (pH 12), upon which a precipitate formed. The precipitate was collected by filtration, then abundantly washed with hot water and thoroughly dried under vacuum to yield 24.6 g of the title compound in acceptable purity (73.4 mmol, 77%): T_g 102 °C; FTIR (CH_2Cl_2/KBr) 3402, 3279, 3200, 3024, 2945, 2914, 1572, 1505, 1430, 1399, 1362, 1300, 1264, 1236, 1185, 1037, 838, 809, 777, 689 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 8.82 (br s, 0.5H), 8.66 (br s, 1H), 8.46 (br s, 0.5H), 7.33 (br m, 4H), 6.67 (br s, 1H), 6.55 (s, 1H), 6.49 (d, ^3J=8.2 Hz, 2H), 4.76 (s, 2H), 2.80 (d, ^3J=4.7 Hz, 2H), 2.21 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 8.31 (br s, 1H), 8.13 (br s, 1H), 7.37 (s, 2H), 7.32 (d, ^3J=8.8 Hz, 2H), 6.58 (s, 1H), 6.55 (d, ^3J=8.8 Hz, 2H), 6.35 (br s, 1H), 4.49 (br s, 2H), 2.86 (d, ^3J=4.8 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 164.6, 144.3, 140.8, 137.5, 129.7, 123.3, 123.0, 117.9, 114.3, 27.7, 21.7 ppm; HRMS (EI) calcd for $C_{18}H_{21}N_7$ (*m*/*e*): 335.1858, found: 335.1847.

*4.2.38. Synthesis of 2-mexylamino-4-methylamino-6-(4-azidophenylamino)-1,3,5-triazine (**35**).* Mexylamino-4-methylamino-6-(4-aminophenylamino)-1,3,5-triazine (0.335 g, 1.00 mmol) was dissolved in THF (5 mL) in a round-bottomed flask equipped with a magnetic stirrer. 10% aqueous HCl (5 mL) was added, then the flask was placed in an ice bath, and a solution of sodium nitrite (0.0690 g, 1.00 mmol) in H_2O (1 mL) was added dropwise. The mixture was stirred at 0–5 °C for 30 min. A solution of sodium azide (0.0980 g, 1.50 mmol) in H_2O (1 mL) was then added dropwise, then the mixture was stirred for 1 h while allowing to warm up to ambient temperature. AcOEt and H_2O were added, both layers were shaken vigorously, then the remaining precipitate was removed by filtration and washed with AcOEt, and both layers were separated. The organic layer was extracted with aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under reduced pressure (at no higher than 60 °C) to yield 0.224 g of the title compound (0.620 mmol, 62%): T_g 52 °C; FTIR (CH_2Cl_2/KBr) 3450, 3418, 3055, 2987, 2121, 1575, 1556, 1504, 1422, 1355, 1265, 1182, 988, 896, 835, 810, 706 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.22 (br s, 0.5H), 9.08 (br s, 0.5H), 9.00 (br s, 0.5H), 8.84 (br s, 0.5H), 7.83 (br s, 2H), 7.38 (br d, 2H), 6.99 (d, ^3J=8.8 Hz, 2H), 6.92 (br s, 1H), 6.59 (s, 1H), 2.83 (d, ^3J=4.1 Hz, 3H), 2.22 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.0, 164.0, 163.8, 139.4, 137.7, 137.0, 131.9, 123.1, 121.2, 118.9, 117.7, 27.2, 21.1 ppm; HRMS (EI) calcd for $C_{18}H_{19}N_9$ (*m*/*e*): 361.1763, found: 361.1776. **Caution: the compound may detonate if overheated.

*4.2.39. Synthesis of 2-mexylamino-4-methylamino-6-(3-cyanophenylamino)-1,3,5-triazine (**36**).* The compound was synthesized using Method B. Yield: 92%; T_g 80 °C; FTIR (ATR/CH_2Cl_2) 3385, 3279, 3193, 3016, 2950, 2912, 2842, 2230, 1578, 1557, 1512, 1476, 1426, 1360, 1321, 1302, 1288, 1243, 1185, 1085, 1037, 1000, 885, 842, 810, 789, 737, 682 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.48 (br s, 0.5H), 9.33 (br s, 0.5H), 9.11 (br s, 0.5H), 8.97 (br s, 0.5H), 8.33 (s, 1H), 8.04 (br dd, 1H), 7.37 (m, 4H), 7.09 (br s, 1H), 6.61 (s, 1H), 2.86 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 9.05 (br s, 1H), 8.64 (br s, 1H), 8.24 (t, ^4J=1.9 Hz, 1H), 8.05 (dd, ^3J=8.3 Hz, ^4J=1.9 Hz, 1H), 7.43 (t, ^3J=8.1 Hz, 1H), 7.35 (s, 2H), 7.33 (dt, ^3J=7.7 Hz, ^4J=1.3 Hz, 1H), 6.74 (br s, 1H), 6.63 (s, 1H), 2.88 (d, ^3J=4.7 Hz, 3H), 2.26 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.1, 163.6, 141.4, 139.8, 137.1, 129.5, 124.6, 123.9, 123.4, 121.9, 119.0, 117.9, 111.2, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{19}H_{20}N_7$ *m*/*e*: 346.1775, found: 346.1780.

*4.2.40. Synthesis of 2-mexylamino-4-methylamino-6-(3-carboxamidophenylamino)-1,3,5-triazine (**37**).* To a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser were added potassium hydroxide (0.561 g, 10.0 mmol) and *tert*-butanol (20 mL). The mixture was slightly heated until the solid had completely dissolved. 2-Mexylamino-4-methylamino-6-(3-cyanophenylamino)-1,3,5-triazine (0.345 g, 1.00 mmol) was added, and the mixture was refluxed for 18 h. After the mixture had cooled down to ambient temperature, CH_2Cl_2 and 1 M aqueous HCl was added, and both layers were separated. The organic layer was extracted with $NaHCO_3$, dried over Na_2SO_4, filtered, and the solvent was thoroughly evaporated under vacuum to yield 0.133 g of the title compound (0.366 mmol, 37%). T_g 104 °C; FTIR (ATR/CH_2Cl_2) 3287, 3209, 3021, 2653, 2920, 2870, 1667, 1580, 1557, 1517, 1488, 1428, 1398, 1322, 1302, 1238, 1184, 1091, 1036, 998, 886, 842, 810, 757, 686 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.23 (br s, 0.5H), 9.07 (br s, 0.5H), 9.00 (br s, 0.5H), 8.83 (br s, 0.5H), 8.18, 8.00 (br d, 1H), 8.00 (s, 1H), 7.83 (s, 1H), 7.45 (d, ^3J=7.6 Hz, 1H), 7.40 (br d, 2H), 7.32 (t, ^3J=7.6 Hz, 2H), 6.95 (br s, 1H), 6.57 (s, 1H), 2.85 (d, ^3J=4.7 Hz, 3H), 2.21 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.76 (br s, 1H), 8.51 (br s, 1H), 8.10 (s, 1H), 7.97 (dd, ^3J=8.1 Hz, ^4J=2.1 Hz, 1H), 7.45 (dt, ^3J=7.7 Hz, ^4J=1.7 Hz, 1H), 7.37 (s, 2H), 7.31 (t, ^3J=7.9 Hz, 1H), 7.21 (br s, 1H), 6.62 (br s, 1H), 6.60 (s, 1H), 2.88 (d, ^3J=4.9 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.1, 166.0, 164.1, 163.8, 140.2, 140.0, 137.0, 134.7, 128.0, 123.1, 122.9, 120.5, 119.5, 117.5, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{19}H_{22}N_7O$ *m*/*e*: 364.1880, found: 364.1887.

*4.2.41. Synthesis of 2-mexylamino-4-methylamino-6-(3-formylphenylamino)-1,3,5-triazine (**38**).* To a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser were added 2-mexylamino-4-methylamino-6-chloro-1,3,5-triazine (6.03 g, 22.9 mmol) and 3-aminobenzaldehyde diethyl acetal (5.36 g, 27.4 mmol) in THF (125 mL), then the mixture was refluxed for 18 h, at which point 1 M aqueous HCl (25 mL) was added and the refluxed was continued for 1 h. CH_2Cl_2 and 1 M aqueous HCl were added, and both layers were separated. The organic layer was extracted with H_2O and aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under vacuum to yield 6.13 g of the title compound in acceptable purity (17.6 mmol, 77%). T_g 59 °C; FTIR (CH_2Cl_2/KBr) 3405, 3281, 3201, 3124, 3050, 3022, 2960, 2921, 2857, 2730, 1697, 1613, 1580, 1566, 1556, 1526, 1507, 1483, 1429, 1396, 1360, 1320, 1301, 1263, 1244, 1187, 1176, 1157, 1088, 1036, 998, 975, 958, 886, 843, 809, 792, 737, 702, 684 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.93 (s, 1H), 9.43 (br s, 0.5H), 9.28 (br s, 0.5H), 9.05 (br s, 0.5H), 8.87 (br s, 0.5H), 8.44, 8.28 (br d, 1H), 8.14 (br d, 1H), 7.49 (br s, 2H), 7.37 (br d, 2H), 7.03 (br s, 1H), 6.59 (s, 1H), 2.85 (d, ^3J=4.1 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 9.97 (s, 1H), 8.98 (br s, 1H), 8.52 (br s, 1H), 8.32 (s, 1H), 8.11 (d, ^3J=7.3 Hz, 1H), 7.49 (m, 2H), 7.37 (s, 2H), 6.65 (br s, 1H), 6.63 (s, 1H), 2.90 (d, ^3J=4.0 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 193.1, 166.0, 164.1, 163.8, 141.2, 139.9, 137.1, 136.5, 129.1, 125.4, 123.3, 122.4, 122.0, 120.8, 120.4, 117.8, 27.2, 21.1 ppm; HRMS (EI) calcd for $C_{19}H_{20}N_6O$ (*m*/*e*): 348.1699, found: 348.1693.

*4.2.42. Synthesis of 2-mexylamino-4-methylamino-6-(3-carboxyphenylamino)-1,3,5-triazine (**39**).* 2-Mexylamino-4-methylamino-6-chloro-1,3,5-triazine (1.06 g, 3.94 mmol) and 3-aminobenzoic acid (0.811 g, 5.92 mmol) were added in THF (50 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. The mixture was refluxed for 18 h, then once the mixture had cooled down to room temperature the precipitate

was collected by filtration and abundantly washed with THF, water, and acetone. The crude product was resuspended in H_2O, $NaHCO_3$ (1.68 g, 20.0 mmol) was added, then glacial AcOH was added with stirring until the pH of the solution was 4–5. The precipitate was collected by filtration, washed with water, and dried overnight in an oven to yield 1.17 g of the title compound (3.21 mmol, 81%): T_g 131 °C, T_m 263 °C; FTIR (CH_2Cl_2/KBr) 3356, 3275, 3098, 3011, 2951, 2918, 2850, 1690, 1668, 1614, 1574, 1519, 1428, 1385, 1343, 1299, 1260, 1237, 1166, 1077, 1019, 998, 936, 908, 882, 839, 806, 776, 756, 705, 684 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 9.31 (br s, 0.5H), 9.16 (br s, 0.5H), 9.01 (br s, 0.5H), 8.83 (br s, 0.5H), 8.30 (m, 1H), 8.08 (m, 1H), 7.53 (d, ^3J=7.6 Hz, 1H), 7.39 (s, 2H), 7.37 (t, ^3J=8.2 Hz, 1H), 6.94 (br s, 1H), 6.58 (s, 1H), 2.85 (br s, 3H), 2.21 (s, 6H) ppm; ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 9.42 (br s, 1H), 9.12 (br s, 1H), 8.19 (s, 1H), 8.05 (d, ^3J=8.1 Hz, 1H), 7.62 (d, ^3J=7.6 Hz, 1H), 7.40 (t, ^3J=8.1 Hz, 1H), 7.32 (s, 2H), 6.68 (s, 1H), 2.92 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.5, 166.1, 164.2, 164.0, 140.6, 140.0, 137.2, 131.1, 128.5, 124.4, 123.3, 122.4, 121.0, 117.7, 27.3, 21.1 ppm; HRMS (EI) calcd for $C_{19}H_{20}N_6O_2$ (m/e): 364.1648, found: 364.1639.

*4.2.43. Synthesis of 2-mexylamino-4-methylamino-6-(3-carboxyphenylamino)-1,3,5-triazine methyl ester (**40**).* In a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser, 2-mexylamino-4-methylamino-6-(3-carboxyphenylamino)-1,3,5-triazine (0.364 g, 1.00 mmol) was added to methanol (20 mL). Concentrated sulfuric acid (0.1 mL) was added, then the mixture was refluxed for 18 h. Aqueous $NaHCO_3$ and CH_2Cl_2 were added, and both layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic washings were dried over Na_2SO_4, filtered, and the volatiles were thoroughly evaporated under vacuum to yield 0.326 g of the title compound (0.861 mmol, 86%). T_g 74 °C; FTIR (ATR/CH_2Cl_2) 3401, 3279, 3200, 3133, 3016, 2950, 2917, 2870, 2844, 1724, 1581, 1557, 1514, 1488, 1427, 1399, 1361, 1301, 1290, 1250, 1228, 1185, 1168, 1108, 1083, 1037, 999, 897, 842, 809, 755, 685 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.37 (br s, 0.5H), 9.22 (br s, 0.5H), 9.04 (br s, 0.5H), 8.85 (br s, 0.5H), 8.53, 8.28 (br d, 1H), 8.09 (m, 1H), 7.55 (d, ^3J=7.6 Hz, 1H), 7.40 (m, 3H), 6.99 (br s, 1H), 6.58 (s, 1H), 3.82 (s, 3H), 2.87 (br s, 3H), 2.21 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.46 (br s, 1H), 8.32 (br s, 1H), 8.11 (d, ^3J=8.1 Hz, 1H), 7.55 (d, ^3J=7.7 Hz, 1H), 7.38 (t, ^3J=7.9 Hz, 1H), 7.36 (s, 2H), 6.61 (s, 1H), 6.60 (br s, 1H), 3.85 (s, 3H), 2.90 (d, ^3J=4.7 Hz, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.3, 166.0, 164.1, 163.8, 140.7, 139.9, 137.0, 129.8, 128.6, 124.5, 124.1, 123.2, 122.0, 120.4, 117.7, 51.9, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{20}H_{23}N_6O_2$ m/e: 379.1877, found: 379.1884.

*4.2.44. Synthesis of 2-mexylamino-4-methylamino-6-(3-nitrophenylamino)-1,3,5-triazine (**41**).* The compound was synthesized using Method C. Yield: 86%; T_g 82 °C; FTIR (ATR/CH_2Cl_2) 3405, 3280, 3194, 3127, 3014, 2949, 2919, 1581, 1557, 1527, 1511, 1480, 1428, 1400, 1348, 1301, 1239, 1184, 1086, 1037, 998, 886, 842, 831, 809, 736, 675 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.64 (br s, 0.5H), 9.49 (br s, 0.5H), 9.11 (br s, 0.5H), 8.92 (br s, 1H), 8.55 (br s, 0.5H), 8.35, 8.21 (br dd, 1H), 7.78 (d, ^3J=8.2 Hz, 1H), 7.53 (t, ^3J=8.2 Hz, 1H), 7.38 (br d, 2H), 7.09 (br s, 1H), 6.60 (s, 1H), 2.87 (d, ^3J=4.1 Hz, 3H), 2.22 (s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 9.20 (br s, 1H), 8.70 (br s, 1H), 8.54 (br s, 1H), 8.23 (d, ^3J=8.3 Hz, 1H), 7.75 (dd, ^3J=8.1 Hz, ^4J=2.1 Hz, 1H), 7.51 (t, ^3J=8.1 Hz, 1H), 7.35 (s, 2H), 6.71 (br s, 1H), 6.63 (s, 1H), 2.91 (d, ^3J=4.9 Hz, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 164.1, 163.7, 147.9, 141.7, 139.8, 137.1, 129.5, 125.3, 123.4, 117.8, 115.6, 113.6, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{20}N_7O_2$ m/e: 366.1673, found: 366.1680.

*4.2.45. Synthesis of 2-mexylamino-4-methylamino-6-(cyclohexylamino)-1,3,5-triazine (**42**).* The compound was synthesized using Method B, but 1.00 mL cyclohexylamine (11.6 mmol, 11.6 equiv) was used. Yield: 86%; T_g 74 °C; FTIR (ATR/CH_2Cl_2) 3405, 3394, 3274, 3203, 3016, 2929, 2853, 1567, 1515, 1435, 1396, 1365, 1325, 1298, 1260, 1189, 1176, 1147, 1127, 1114, 1036, 890, 840, 811, 737, 688, 650 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.81 (br s, 0.5H), 8.67 (br s, 0.5H), 7.43 (s, 2H), 6.77 (br s, 0.5H), 6.57 (br s, 0.5H), 6.52 (s, 1H), 6.48 (br s, 1H), 3.75 (br s, 1H), 2.77 (br s, 3H), 2.21 (s, 6H), 1.88 (br d, 2H), 1.71 (br d, 2H), 1.60 (d, J=11.7 Hz, 1H), 1.24 (m, 4H), 1.12 (m, 1H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.24 (br s, 1H), 7.39 (s, 2H), 6.56(s, 1H), 6.22 (br s, 1H), 6.14 (br s, 1H), 3.78 (m, 1H), 2.80 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H), 1.91 (m, 2H), 1.74 (m, 2H), 1.60 (d, ^3J=13.0 Hz, 1H), 1.29 (m, 4H), 1.18 (m, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 164.8, 163.9, 140.6, 136.8, 122.5, 117.0, 48.8, 32.7, 27.1, 25.3, 25.1, 21.2 ppm; HRMS (ESI, MH^+) calcd for $C_{18}H_{27}N_6$ m/e: 327.2292, found: 327.2297.

*4.2.46. Synthesis of 2-mexylamino-4-methylamino-6-(adamantylamino)-1,3,5-triazine (**43**).* To a solution of 2-(1-adamantyl)amino-4,6-dichloro-1,3,5-triazine (5.73 g, 19.2 mmol) in acetone (50 mL) in a round-bottomed flask equipped with a magnetic stirrer was added Na_2CO_3 (2.03 g, 19.2 mmol). The flask was placed in an ice bath to keep temperature inside the flask under 5 °C, then a solution of methylamine (1.49 mL, 40 wt % aqueous, 19.2 mmol) in acetone (25 mL) was added dropwise to the mixture. The ice bath was removed once the addition was complete, then the mixture was stirred at room temperature for an additional 30 min, at which point the mixture was poured in H_2O (500 mL), and stirring was continued for 20 min until precipitation was completed. The precipitate was collected by filtration, then the crude product was recrystallized from toluene, filtered and allowed to dry completely to afford 3.77 g 2-(1-adamantyl)amino-4-methylamino-6-chloro-1,3,5-triazine (12.8 mmol, 67%). T_{dec} 224 °C; FTIR (ATR/CH_2Cl_2) 3417, 3269, 3211, 3130, 2906, 2850, 1621, 1573, 1542, 1504, 1454, 1424, 1390, 1361, 1344, 1308, 1294, 1282, 1258, 1234, 1190, 1165, 1121, 1095, 1033, 976, 946, 935, 899, 877, 851, 804, 779, 737, 703, 657, 633, 612 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 7.25 (br s, 1H), 6.86 (br s, 1H), 2.80 (d, ^3J=4.7 Hz, 3H), 2.08 (s, 6H), 2.05 (s, 3H), 1.66 (s, 6H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6, 363 K) δ 167.0, 165.2, 164.3, 50.9, 40.4, 35.6, 28.5, 26.6 ppm; HRMS (ESI, MH^+) calcd for $C_{14}H_{21}ClN_5$ m/e: 316.1299, found: 316.1304.

Intermediate 2-(1-adamantyl)amino-4-methylamino-6-chloro-1,3,5-triazine (0.223 g, 0.759 mmol), and 3,5-dimethylaniline (0.114 mL, 0.110 g, 0.911 mmol) were dissolved in THF (10 mL) in a round-bottomed flask equipped with a magnetic stirrer and a water-jacketed condenser. The mixture was refluxed for 18 h, then allowed to cool down to room temperature. 1 M aqueous HCl and CH_2Cl_2 were added, and both layers were separated. The organic layer was extracted with aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and the solvent was thoroughly evaporated under vacuum to yield 0.208 g of compound **43** (0.550 mmol, 72%). T_g 93 °C; FTIR (ATR/CH_2Cl_2) 3408, 3275, 3200, 3013, 2906, 2849, 1589, 1556, 1515, 1435, 1396, 1359, 1308, 1263, 1244, 1192, 1141, 1100, 1037, 979, 935, 883, 840, 812, 739, 689, 622, 607 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.62, 8.46 (br d, 1H), 7.32 (br s, 2H), 6.54 (s, 1H), 6.54 (br s, 1H), 6.10, 5.92 (br d, 1H), 2.77 (d, ^3J=4.1 Hz, 3H), 2.20 (s, 6H), 2.05 (br s, 6H), 2.01 (br s, 3H), 1.62 (br s, 6H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.19 (br s, 1H), 7.29 (s, 2H), 6.58 (s, 1H), 6.24 (br s, 1H), 5.57 (br s, 1H), 2.81 (d, ^3J=4.7 Hz, 3H), 2.23 (s, 6H), 2.09 (s, 6H), 2.05 (s, 3H), 1.67 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.6, 165.0, 163.6, 140.2, 136.8, 122.8, 117.5, 50.3, 41.2, 35.9, 28.9, 27.1, 21.0 ppm; HRMS (ESI, MH^+) calcd for $C_{22}H_{31}N_6$ m/e: 379.2605, found: 379.2606.

*4.2.47. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-1,4-diaminobenzene (**44**).* To a solution of cyanuric

chloride (3.41 g, 18.5 mmol) in acetone (50 mL) in a round-bottomed flask equipped with a magnetic stirrer held at −10 °C in an acetone/ice bath was slowly added a solution of 1,4-phenylenediamine (1.00 g, 9.25 mmol) in acetone (20 mL). When the addition was complete, *N*,*N*-diisopropylethylamine (6.45 mL, 4.78 g, 37.0 mmol) was added, and the mixture was stirred for 2 h at −10 °C. At that point, a solution of 3,5-dimethylaniline (2.31 mL, 2.24 g, 18.5 mmol) in acetone (10 mL) was slowly added, the ice bath was removed, then the mixture was stirred at room temperature. When the reaction was complete (2 h; the reaction can be followed by TLC by the appearance of a spot at R_f 0.85 (AcOEt/Hexanes 1:1)), aqueous methylamine (25 mL, 40 wt %) was added, the flask was fitted with a water-jacketed condenser and the mixture was refluxed for 18 h. The volatiles were evaporated in vacuo, and AcOEt and H_2O were added to the residue. Both layers were separated, the organic layer was recovered, hexanes was added and the precipitate was collected by filtration and washed with hexanes. The crude product was purified on a short silica pad using acetone/CH_2Cl_2 (1:1) as eluent to give 3.23 g compound **44** (5.74 mmol, 62%); T_g 124 °C; IR (KBr) 3421 (br), 3279 (br), 3019, 2957, 2926, 2860, 1609, 1567, 1494, 1453, 1425, 1404, 1262, 1217, 1182, 1089, 1051, 943, 877, 825, 808, 769, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.73 (s, 2H), 8.50 (s, 2H), 7.82 (d, ^3J=8.9 Hz, 4H), 7.51 (d, ^3J=8.7 Hz, 4H), 7.39 (s, 4H), 6.62 (s, 2H), 6.55 (q, ^3J=4.2 Hz, 2H), 2.89 (d, ^3J=5.0 Hz, 6H), 2.26 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 164.1, 163.9, 140.1, 139.3, 137.1, 133.1, 125.9, 123.2, 120.2, 117.8, 27.3, 21.2; HRMS (ESI, MH^+) calcd for $C_{36}H_{39}N_{12}$ *m*/*e*: 639.3415, found: 639.3410.

Compounds **45**–**48** were prepared by the same procedure as **44** starting from the respective aromatic diamines. For less reactive amines, the reaction with 3,5-dimethylaniline can proceed more slowly, in which case the mixture can be gently heated at 30–35 °C. In any case, the progress of the reaction can be monitored by TLC by the appearance of the desired product and consumption of 3,5-dimethylaniline.

*4.2.48. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-1,3-diaminobenzene (**45**).* Yield: 65%; T_g 120 °C; IR (KBr) 3414 (br), 3279 (br), 3019, 2957, 2926, 2860, 1577, 1557, 1525, 1494, 1453, 1404, 1262, 1220, 1182, 1085, 1051, 877, 829, 808, 773, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.51 (s, 2H), 8.40 (s, 2H), 7.62 (s, 4H), 7.36 (s, 4H), 6.59 (s, 2H), 6.46 (q, ^3J=5.0 Hz, 2H), 2.87 (d, ^3J=4.3 Hz, 6H), 2.24 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 164.1, 163.9, 140.1, 137.1, 134.5, 123.1, 120.1, 117.6, 27.3, 21.2; HRMS (ESI, MH^+) calcd for $C_{30}H_{35}N_{12}$ *m*/*e*: 563.3102, found: 563.3110.

*4.2.49. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-4,4′-diaminobiphenyl (**46**).* Yield: 53%; T_g 126 °C; IR (KBr) 3428 (br), 3279 (br), 3019, 2957, 2926, 2860, 1605, 1584, 1560, 1494, 1453, 1435, 1404, 1262, 1217, 1186, 1161, 1082, 1054, 877, 846, 825, 811, 770, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.42 (s, 4H), 8.01 (t, ^4J=1.8 Hz, 1H), 7.45 (dd, ^3J=8.1 Hz, ^4J=2.0 Hz, 2H), 7.38 (s, 4H), 7.13 (t, ^3J=8.1 Hz, 1H), 6.60 (s, 2H), 6.51 (q, ^3J=4.9 Hz, 2H), 2.87 (d, ^3J=4.8 Hz, 6H), 2.24 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 164.2, 163.9, 140.2, 140.1, 137.1, 128.0, 123.1, 117.4, 114.0, 112.4, 27.3, 21.2; HRMS (ESI, MH^+) calcd for $C_{30}H_{35}N_{12}$ *m*/*e*: 563.3102, found: 563.3100.

*4.2.50. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-4,4′-diaminodiphenylmethane (**47**).* Yield: 61%; T_g 125 °C; IR (KBr) 3425 (br), 3279 (br), 3019, 2957, 2926, 2856, 1609, 1577, 1557, 1494, 1453, 1404, 1262, 1217, 1182, 1158, 1144, 1085, 1051, 1019, 874, 846, 825, 773, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 363 K) δ 8.55 (s, 2H), 8.42 (s, 2H), 7.64 (d, ^3J=8.3 Hz, 4H), 7.35 (s, 4H), 7.09 (d, ^3J=8.1 Hz, 4H), 6.58 (s, 2H), 6.49 (q, ^3J=4.8 Hz, 2H), 3.85 (s, 2H), 2.86 (d, ^3J=4.4 Hz, 6H), 2.22 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 164.2, 163.9, 140.1, 138.1, 137.1, 134.8, 128.4, 123.1, 120.2, 117.6, 39.9, 27.3, 21.2; HRMS (ESI, MH^+) calcd for $C_{37}H_{41}N_{12}$ *m*/*e*: 653.3571, found: 653.3530.

*4.2.51. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-4,4′-diaminoazobenzene (**48**).* Yield: 55%; T_g 131 °C; IR (KBr) 3439 (br), 3303 (br), 3019, 2957, 2926, 2860, 1609, 1577, 1557, 1494, 1453, 1435, 1404, 1304, 1262, 1210, 1155, 1089, 1078, 1051, 877, 825, 687 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ 9.53 (s, 1H), 9.41 (s, 1H), 9.09 (s, 1H), 8.93 (s, 1H), 8.05 (br s, 4H), 7.80 (d, ^3J=8.0 Hz, 4H), 7.45 (s, 2H), 7.40 (s, 2H), 7.03 (s, 2H), 6.61 (s, 2H), 2.89 (d, ^3J=4.7 Hz, 6H), 2.25 (s, 12H); (400 MHz, DMSO-d_6, 363 K) δ 9.03 (s, 2H), 8.54 (s, 2H), 8.01 (d, ^3J=8.8 Hz, 4H), 7.79 (d, ^3J=8.8 Hz, 4H), 7.39 (s, 4H), 6.64 (s, 2H), 6.64 (s, 2H), 2.92 (d, ^3J=4.2 Hz, 6H), 2.27 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 164.2, 163.9, 146.6, 143.2, 139.9, 137.2, 123.4, 122.9, 119.6, 117.9, 27.3, 21.2; HRMS (ESI, MH^+) calcd for $C_{36}H_{39}N_{14}$ *m*/*e*: 677.3477, found: 677.3483.

*4.2.52. Synthesis of N,N′-bis[2-mexylamino-4-methylamino-1,3,5-triazin-6-yl]-4,4′-diaminodiphenyl disulfide (**49**).* Potassium ferricyanide (0.362 g, 1.10 mmol) was dissolved in water (10 mL) in a round-bottomed flask equipped with a magnetic stirrer, then a solution of thiol **25** (0.352 g, 1.00 mmol) and *N*,*N*-diisopropylethylamine (0.192 mL, 0.142 g, 1.10 mmol) in THF (10 mL) were added and the mixture was stirred for 18 h at room temperature. CH_2Cl_2 was added, both layers were separated, and hexanes were added to the organic layer until a precipitate stopped forming. The precipitate was collected by filtration, washed with hexanes and dried to give 0.248 g compound **49** in acceptable purity (0.354 mmol, 71%); T_g 119 °C; FTIR (ATR/CH_2Cl_2) 3431, 3278, 3187, 3017, 2949, 2917, 2871, 1579, 1559, 1511, 1481, 1450, 1400, 1362, 1322, 1302, 1288, 1247, 1186, 1105, 1083, 1034, 933, 841, 809, 750, 687, 656 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 9.34 (br s, 1H), 9.20 (br s, 1H), 9.04 (br s, 1H), 8.89 (br s, 1H), 7.84 (br s, 4H), 7.38 (m, 8H), 6.95 (br s, 2H), 6.57 (s, 2H), 2.84 (d, ^3J=4.7 Hz, 6H), 2.20 (s, 12H) ppm; ^1H NMR (500 MHz, DMSO-d_6, 363 K) δ 8.89 (br s, 2H), 8.56 (br s, 2H), 7.81 (d, ^3J=8.8 Hz, 4H), 7.37 (d, ^3J=8.8 Hz, 4H), 7.34 (s, 4H), 6.63 (br s, 2H), 6.60 (s, 2H), 2.87 (d, ^3J=4.7 Hz, 6H), 2.23 (s, 12H) ppm ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.0, 164.0, 163.7, 140.8, 139.8, 137.0, 130.2, 127.5, 123.3, 120.1, 117.8, 27.2, 21.1 ppm; HRMS (ESI, MH^+) calcd for $C_{36}H_{39}N_{12}S_2$ *m*/*e*: 703.2857, found: 703.2873.

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Supplementary data

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