

## Supporting Information available

### Copper-catalyzed ambient-temperature decarboxylative annulation of isatins with amidine hydrochlorides: a facile access to 2-(1,3,5-triazin-2-yl)aniline derivatives

Feng-Cheng Jia,<sup>\*a</sup> Cheng Xu,<sup>b</sup> Yu-Wei Wang,<sup>a</sup> Zhi-Peng Chen,<sup>a</sup> Yun-Feng Chen<sup>a</sup> and An-Xin Wu<sup>\*b</sup>

---

<sup>a</sup>School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, China.

E-mail: fengcheng-jia@wit.edu.cn.

<sup>b</sup>Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China.

E-mail: chwuax@mail.ccnu.edu.cn.

Table of Contents	Pages
1. General.....	S2
2. General procedure for the synthesis of <b>3</b> .....	S2
3. Optimization of the Reaction Conditions.....	S2
4. Crystallographic data and molecular structure of <b>3jf</b> .....	S3
5. Spectral data of compound <b>3aa-3ka</b> , <b>3ab-3jf</b> .....	S4-S10
6. Appendix: spectral copies of <sup>1</sup> H NMR, and <sup>13</sup> C NMR .....	S11-S32

---

## 1. General

All isatins (**1a-1k**), amidine hydrochlorides (**2a-2h**) and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in  $\text{cm}^{-1}$ .  $^1\text{H}$  spectra were recorded in  $\text{CDCl}_3$  on a Varian Mercury 600 MHz spectrometers.  $^{13}\text{C}$  spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  on 150 MHz or 100 MHz NMR spectrometers. Chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an Apex-Ultra MS equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected.

## 2. General procedure for the synthesis of 3 (3aa as an example)

A sealed tube was charged with isatin **1a** (44.1 mg, 0.3 mmol), amidine hydrochlorides **2a** (140.9 mg, 0.9 mmol), CuI (5.7 mg, 0.03 mmol) and  $\text{K}_3\text{PO}_4$  (509.5 mg, 2.4 mmol) at room temperature, and then solvent DMSO (3 mL) was added. The resulting mixture was stirred at 25 °C in a sealed vessel under air after 24 hours, then added 50mL water to the mixture, extracted with  $\text{CH}_2\text{Cl}_2$  3 times ( $3 \times 50$  mL). The extract was washed with 30% NaCl solution (V/V), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether /dichloromethane = 20:1) to yield the desired product **3aa** as a yellow solid (58% yield).

## 3. Optimization of the Reaction Conditions

Table 1. Optimization of the Reaction Conditions<sup>a</sup>

entry	catalyst	base	solvent	B equiv	base equiv	temp ( °C)	yield <sup>b</sup> (%)
1	CuI	$\text{Et}_3\text{N}$	DMSO	3	8	25	30
2	CuI	DBU	DMSO	3	8	25	50
3	CuI	DABCO	DMSO	3	8	25	26
4	CuI	$\text{K}_2\text{HPO}_4$	DMSO	3	8	25	trace
5	CuI	$\text{KH}_2\text{PO}_4$	DMSO	3	8	25	trace
6	CuI	$\text{K}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	DMSO	3	8	25	10
7	CuI	$\text{K}_3\text{PO}_4$	DMSO	2.5	8	25	60
8	CuI	$\text{K}_3\text{PO}_4$	DMSO	2.2	8	25	54
9	CuI	$\text{K}_3\text{PO}_4$	DMSO	2	8	25	44
10	CuI	$\text{K}_3\text{PO}_4$	DMSO	3	6	25	55
11	CuI	$\text{K}_3\text{PO}_4$	DMSO	3	4	25	43

<sup>a</sup>Reactions conditions: **1a** (0.3 mmol), **2a**, CuI (10% mmol) and base were heated in 3 mL solvent in a sealed vessel under air for 24 h. <sup>b</sup>Isolated yield.

## 4. Molecular Structure and Crystallographic Data

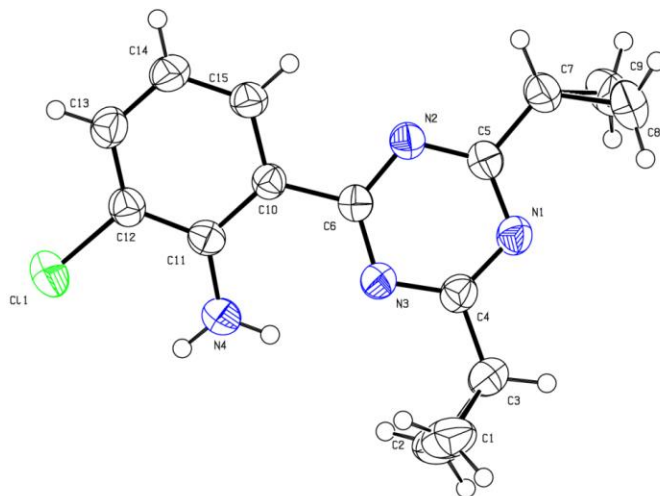
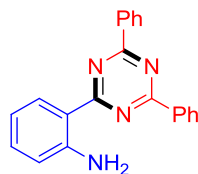


Figure S1 X-ray crystal structure of **3jf**.

Table S1. Crystal data and structure refinement for compound **3jf** (CCDC: 1834221)

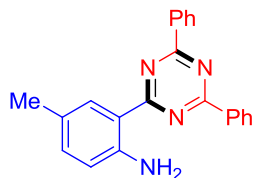
Bond precision:	C-C = 0.0030 Å	Wavelength=0.71073	
Cell:	a=10.585 (2)	b=8.8309 (18)	c=15.039 (3)
	alpha=90	beta=96.741 (3)	gamma=90
Temperature:	273 K		
	Calculated	Reported	
Volume	1396.1 (5)	1396.1 (5)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C15 H15 Cl N4	?	
Sum formula	C15 H15 Cl N4	C15 H15 Cl N4	
Mr	286.76	286.76	
Dx, g cm <sup>-3</sup>	1.364	1.364	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.269	0.269	
F000	600.0	600.0	
F000'	600.75		
h, k, lmax	15, 13, 22	15, 12, 21	
Nref	4896	4318	
Tmin, Tmax	0.943, 0.953	0.864, 0.864	
Tmin'	0.943		
Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864			
AbsCorr = MULTI-SCAN			
Data completeness=	0.882	Theta (max)= 32.150	
R(reflections)=	0.0582 ( 3138)	wR2(reflections)= 0.2028 ( 4318)	
S =	1.005	Npar= 181	

## 5. Spectral data of compound 3aa-3ka, 3ab-3jk.



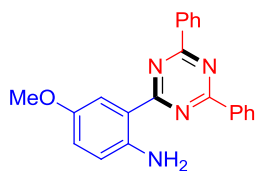
### 2-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3aa):

yellow solid; mp 195-197 °C; IR (KBr): 3362, 3255, 1615, 1588, 1523, 1443, 1364, 1248, 1024 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 8.63 (d, *J* = 7.8 Hz, 1H), 8.58 (d, *J* = 7.2 Hz, 4H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 4H), 7.52 (br, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.71 (t, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 172.2, 169.8, 151.6, 135.6, 133.8, 132.8, 130.9, 129.0, 128.4, 117.2, 115.3, 114.5; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>17</sub>N<sub>4</sub>: 325.1448; found: 325.1449.



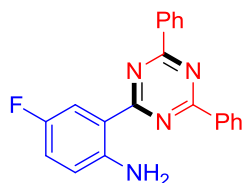
### 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-4-methylaniline (3ba):

yellow solid; mp 190-192 °C; IR (KBr): 3355, 3265, 1625, 1588, 1523, 1442, 1370, 1296, 1244, 1171, 1138, 1022 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.65 (d, *J* = 7.2 Hz, 4H), 8.54 (s, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 4H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.41 (br, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.7, 170.6, 148.1, 136.3, 134.8, 132.4, 130.9, 128.8, 128.6, 126.0, 117.5, 116.7, 20.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>19</sub>N<sub>4</sub>: 339.1604; found: 339.1606.



### 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-4-methoxyaniline (3ca):

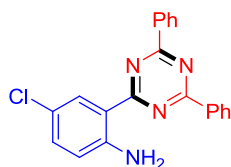
yellow solid, mp 167-169 °C; IR (KBr): 3353, 1590, 1523, 1445, 1371, 1242, 1139, 1029 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.64 (d, *J* = 7.2 Hz, 4H), 8.30 (s, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 6.29 (br, 2H), 3.89 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.4, 170.6, 151.1, 145.0, 136.2, 132.4, 128.8, 128.6, 122.4, 118.9, 117.0, 113.6, 55.9; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>19</sub>N<sub>4</sub>O: 355.1553; found: 355.1555.



### 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-4-fluoroaniline (3da):

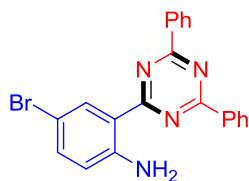
yellow solid; mp 223-225 °C; IR (KBr): 3346, 1587, 1520, 1445, 1370, 1350, 1243, 1210, 1147, 1122, 1021 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.63 (d, *J* = 7.8 Hz,

4H), 8.48-8.42 (m, 1H), 7.61 (t,  $J = 7.2$  Hz, 2H), 7.56 (t,  $J = 7.2$  Hz, 4H), 7.10-7.04 (m, 1H), 6.74-6.68 (m, 1H), 6.43 (br, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.8, 170.7, 155.6, 154.0, 146.8, 136.0, 132.6, 128.8, 128.7, 121.4, 121.3, 118.5, 118.4, 117.0, 116.2, 116.0$ ; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{FN}_4$ : 343.1354; found: 343.1353.



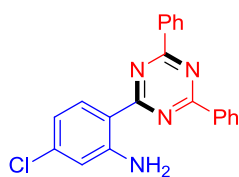
**4-chloro-2-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3ea):**

yellow solid; mp 201-203 °C; IR (KBr): 3337, 1615, 1587, 1520, 1443, 1370, 1350, 1237, 1143, 1022  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.73$ -8.69 (m, 1H), 8.62 (d,  $J = 7.2$  Hz, 4H), 7.61 (t,  $J = 7.2$  Hz, 2H), 7.56 (t,  $J = 7.8$  Hz, 4H), 7.25-7.22 (m, 1H), 6.70 (d,  $J = 9.0$  Hz, 1H), 6.59 (s, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.7, 170.8, 148.9, 136.0, 133.4, 132.6, 130.4, 128.8, 128.7, 121.4, 118.7, 117.6$ ; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{ClN}_4$ : 359.1058; found: 359.1056.



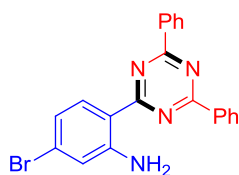
**4-bromo-2-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3fa):**

yellow solid; mp 194-196 °C; IR (KBr): 3340, 1587, 1521, 1443, 1368, 1347, 1242, 1142, 1023  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.83$ -8.79 (m, 1H), 8.59 (d,  $J = 7.2$  Hz, 4H), 7.59 (t,  $J = 7.2$  Hz, 2H), 7.54 (t,  $J = 7.8$  Hz, 4H), 7.36-7.31 (m, 1H), 6.69-6.46 (m, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.5, 170.7, 149.2, 136.0, 135.9, 133.3, 132.6, 128.8, 128.7, 119.0, 118.1, 108.3$ ; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{BrN}_4$ : 403.0533; found: 403.0555.



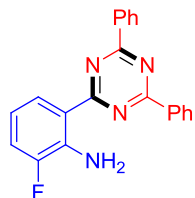
**5-chloro-2-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3ga):**

yellow solid; mp 200-202 °C; IR (KBr): 3377, 3268, 1591, 1525, 1354, 1242, 1173, 1065, 1024  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.69$  (d,  $J = 8.4$  Hz, 1H), 8.60 (d,  $J = 7.2$  Hz, 4H), 7.60 (t,  $J = 7.2$  Hz, 2H), 7.55 (t,  $J = 7.8$  Hz, 4H), 6.78-6.71 (m, 2H), 6.66 (br, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.9, 170.6, 151.0, 139.4, 136.0, 132.8, 132.5, 128.8, 128.7, 117.2, 116.4, 115.2$ ; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{ClN}_4$ : 359.1058; found: 359.1057.



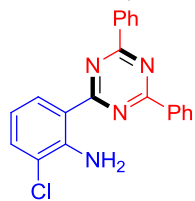
**5-bromo-2-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3ha):**

yellow solid; mp 213-215 °C; IR (KBr): 3459, 3294, 1614, 1584, 1525, 1444, 1354, 1326, 1248, 1176, 1064, 1022 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.66-8.55 (m, 5H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H), 6.94-6.88 (m, 2H), 6.65 (br, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.0, 170.7, 151.1, 136.1, 132.8, 132.5, 128.8, 128.7, 128.2, 120.1, 119.5, 115.6; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>BrN<sub>4</sub>: 403.0553; found: 403.0552.



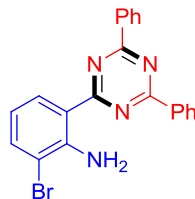
**2-(4,6-diphenyl-1,3,5-triazin-2-yl)-6-fluoroaniline (3ia):**

yellow solid; 208 °C decomposed; IR (KBr): 3460, 3306, 1631, 1592, 1525, 1468, 1445, 1364, 1274, 1246, 1204, 1065, 1025 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.62 (d, *J* = 7.2 Hz, 4H), 8.53 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 4H), 7.17-7.11 (m, 1H), 6.80-6.30 (m, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.2, 170.7, 152.7, 151.1, 139.5, 139.4, 136.0, 132.5, 128.8, 128.7, 126.4, 118.5, 117.9, 117.8, 115.1, 115.0; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>FN<sub>4</sub>: 343.1354; found: 343.1358.



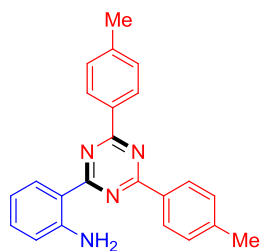
**2-chloro-6-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3ja):**

yellow solid; mp 210-212 °C; IR (KBr): 3468, 3282, 1617, 1585, 1520, 1443, 1360, 1321, 1279, 1244, 1074, 1024 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.70 (d, *J* = 7.2 Hz, 1H), 8.61 (d, *J* = 7.2 Hz, 4H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 4H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.24-6.68 (br, 2H), 6.72 (t, *J* = 7.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.1, 170.6, 146.4, 136.0, 133.2, 132.6, 130.1, 128.8, 128.7, 120.5, 117.8, 116.1; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>ClN<sub>4</sub>: 359.1058; found: 359.1062.



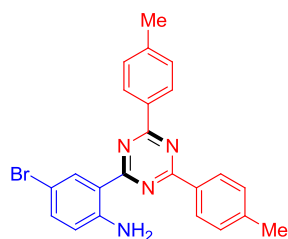
**2-bromo-6-(4,6-diphenyl-1,3,5-triazin-2-yl)aniline (3ja):**

yellow solid; 213 °C decomposed; IR (KBr): 3458, 3272, 1608, 1521, 1442, 1360, 1317, 1279, 1245, 1051, 1024 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.78-8.72 (m, 1H), 8.61 (d, *J* = 7.2 Hz, 4H), 7.63-7.57 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 4H), 7.24-6.90 (br, 2H), 6.67 (t, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 171.9, 170.7, 147.3, 136.7, 135.9, 132.6, 131.0, 128.8, 128.7, 117.9, 116.8, 111.3; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>BrN<sub>4</sub>: 403.0553; found: 403.0545.



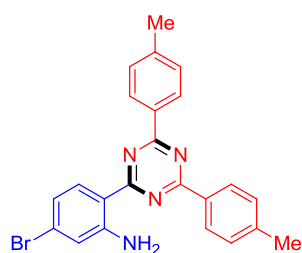
**2-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)aniline (3ab):**

yellow solid; mp 214-216 °C; IR (KBr): 3461, 3295, 1613, 1583, 1515, 1360, 1251, 1177, 1139, 1018 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.76 (d, *J* = 7.8 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.71-6.11 (br, 2H), 2.45 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.5, 170.5, 150.2, 142.9, 133.6, 133.4, 131.4, 129.4, 128.8, 117.3, 117.1, 116.9, 21.7; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>21</sub>N<sub>4</sub>: 353.1761; found: 353.1761.



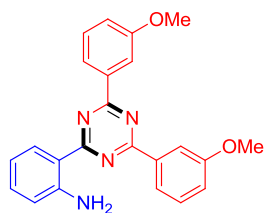
**4-bromo-2-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)aniline (3fb):**

yellow solid; mp 255-257 °C; IR (KBr): 3382, 3282, 1607, 1581, 1516, 1401, 1372, 1348, 1241, 1144, 1112, 1018 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.86-8.83 (m, 1H), 8.51 (d, *J* = 7.8 Hz, 4H), 7.40-7.33 (m, 5H), 6.67 (d, *J* = 9.0 Hz, 1H), 2.47 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 171.4, 170.6, 149.0, 143.2, 135.9, 133.3, 129.5, 128.8, 119.0, 118.5, 108.4, 21.7; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>BrN<sub>4</sub>: 431.0866; found: 431.0869.



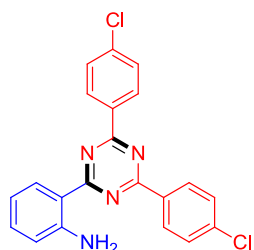
**5-bromo-2-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)aniline (3hb):**

yellow solid; 265 °C decomposed; IR (KBr): 3455, 3285, 1605, 1581, 1515, 1407, 1355, 1246, 1179, 1067, 1018 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.61 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 7.8 Hz, 4H), 7.35 (d, *J* = 7.8 Hz, 4H), 6.94 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 171.9, 170.6, 150.9, 143.1, 133.4, 132.8, 129.4, 128.8, 127.9, 120.1, 119.5, 116.0, 21.7; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>BrN<sub>4</sub>: 431.0866; found: 431.0868.



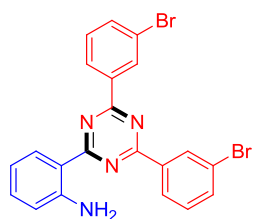
**2-(4,6-bis(3-methoxyphenyl)-1,3,5-triazin-2-yl)aniline (3ac):**

yellow solid; mp 135-137 °C; IR (KBr): 3459, 3314, 1612, 1585, 1531, 1453, 1371, 1352, 1281, 1256, 1227, 1160, 1039 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.75 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 2H), 8.18 (s, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.73-6.16 (br, 2H), 3.94 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.6, 170.4, 159.9, 150.2, 137.7, 133.6, 131.4, 129.7, 121.3, 118.2, 117.4, 117.0, 116.8, 113.8, 55.4; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>21</sub>N<sub>4</sub>O<sub>2</sub>: 385.1659; found: 385.1661.



**2-(4,6-bis(4-chlorophenyl)-1,3,5-triazin-2-yl)aniline (3ad):**

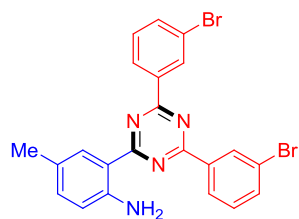
yellow solid, mp 246-248 °C; IR (KBr): 3482, 3305, 1616, 1583, 1518, 1400, 1357, 1307, 1251, 1167, 1090, 1011 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 8.55 (d, *J* = 7.2 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 4H), 7.65 (d, *J* = 8.4 Hz, 4H), 7.43 (s, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.68 (t, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 172.2, 168.9, 151.6, 137.7, 134.2, 133.9, 130.8, 130.1, 129.0, 117.2, 115.3, 114.2; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>4</sub>: 393.0668; found: 393.0670.



**2-(4,6-bis(3-bromophenyl)-1,3,5-triazin-2-yl)aniline (3ae):**

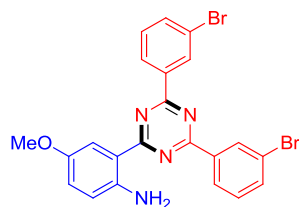
yellow solid; mp 183-185 °C; IR (KBr): 3364, 3274, 1614, 1524, 1354, 1307, 1247, 1141, 1065 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.64-8.57 (m, 3H), 8.44 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.57-6.27 (br, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 172.6, 169.2, 150.4, 137.9, 135.3, 134.0, 131.6, 131.4, 130.1, 127.3, 122.9, 117.3, 116.9, 116.0; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>4</sub>: 480.9658; found: 480.9662.



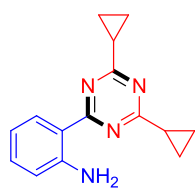


**2-(4,6-bis(3-bromophenyl)-1,3,5-triazin-2-yl)-4-methylaniline (3be):**

yellow solid; mp 166-168 °C; IR (KBr): 3457, 3347, 1626, 1524, 1359, 1245, 1063  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.71 (s, 2H), 8.53 (d,  $J$  = 7.8 Hz, 2H), 8.45 (s, 1H), 7.72 (d,  $J$  = 7.8 Hz, 2H), 7.43 (t,  $J$  = 7.8 Hz, 2H), 7.16 (d,  $J$  = 7.8 Hz, 1H), 6.69 (d,  $J$  = 8.4 Hz, 1H), 6.60-5.99 (br, 2H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.9, 169.5, 148.3, 138.1, 135.4, 135.3, 131.7, 130.9, 130.2, 127.4, 126.1, 122.9, 117.6, 116.1, 20.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{17}\text{Br}_2\text{N}_4$ : 496.9814; found: 496.9794.

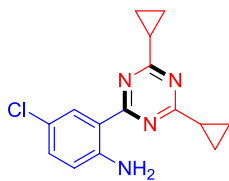


**2-(4,6-bis(3-bromophenyl)-1,3,5-triazin-2-yl)-4-methoxyaniline (3ce):** yellow solid; mp 187-189 °C; IR (KBr): 3376, 1632, 1523, 1362, 1332, 1242, 1139, 1035  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.65 (s, 2H), 8.47 (d,  $J$  = 7.8 Hz, 2H), 8.17-8.10 (m, 1H), 7.70 (d,  $J$  = 8.4 Hz, 2H), 7.40 (t,  $J$  = 7.8 Hz, 2H), 7.02-6.96 (m, 1H), 6.70 (d,  $J$  = 9.0 Hz, 1H), 6.48-5.59 (br, 2H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.4, 169.4, 151.1, 145.0, 137.9, 135.4, 131.6, 130.2, 127.3, 122.9, 122.8, 119.0, 116.4, 113.4, 55.8; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{17}\text{Br}_2\text{N}_4\text{O}$ : 510.9764; found: 510.9756.



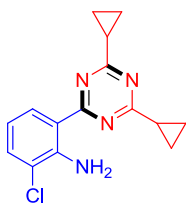
**2-(4,6-dicyclopropyl-1,3,5-triazin-2-yl)aniline (3af):**

yellow solid; mp 52-54 °C; IR (KBr): 3448, 3321, 1616, 1585, 1522, 1446, 1380, 1302, 1248, 1162, 1058, 1021  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.47 (d,  $J$  = 8.4 Hz, 1H), 7.24 (t,  $J$  = 7.8 Hz, 1H), 6.72 (t,  $J$  = 7.8 Hz, 1H), 6.68 (d,  $J$  = 7.8 Hz, 1H), 6.61-5.97 (br, 2H), 2.15-2.10 (m, 2H), 1.26-1.22 (m, 4H), 1.13-1.09 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 178.6, 170.9, 150.1, 133.2, 131.1, 117.1, 116.6, 116.3, 17.9, 11.4; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_4$ : 253.1448; found: 253.1449.



**4-chloro-2-(4,6-dicyclopropyl-1,3,5-triazin-2-yl)aniline (3ef):**

yellow solid; mp 133-135 °C; IR (KBr): 3490, 3286, 1612, 1583, 1527, 1446, 1399, 1376, 1299, 1280, 1160, 1052, 1031  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.44 (s, 1H), 7.19-7.15 (m, 1H), 6.62 (d,  $J$  = 9.0 Hz, 1H), 6.41 (br, 2H), 2.16-2.09 (m, 2H), 1.28-1.21 (m, 4H), 1.16-1.09 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 178.8, 169.8, 148.7, 133.0, 130.1, 121.2, 118.5, 117.2, 18.0, 11.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{ClN}_4$ : 287.1058; found: 287.1060.



**2-chloro-6-(4,6-dicyclopropyl-1,3,5-triazin-2-yl)aniline (3jf):**

yellow solid; mp 111-113 °C; IR (KBr): 3454, 3289, 1606, 1580, 1524, 1446, 1400, 1373, 1314, 1237, 1123, 1054  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.44 (d,  $J$  = 7.8 Hz, 1H), 7.39 (d,  $J$  = 7.8 Hz, 1H), 6.99 (br, 2H), 6.66 (t,  $J$  = 7.8 Hz, 1H), 2.18-2.09 (m, 2H), 1.27-1.21 (m, 4H), 1.16-1.08 (m, 4H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 178.8, 170.4, 146.2, 132.9, 129.9, 120.4, 117.4, 115.9, 18.0, 11.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{ClN}_4$ : 287.1058; found: 287.1059.

## 6. Appendix: spectral copies of $^1\text{H}$ NMR, and $^{13}\text{C}$ NMR

