Supporting Information for

The Preparation of N-Containing Functionalized Porous Organic Polymers for Selective Synthesis of C3-Alkylated Indoles and Triazine Derivatives

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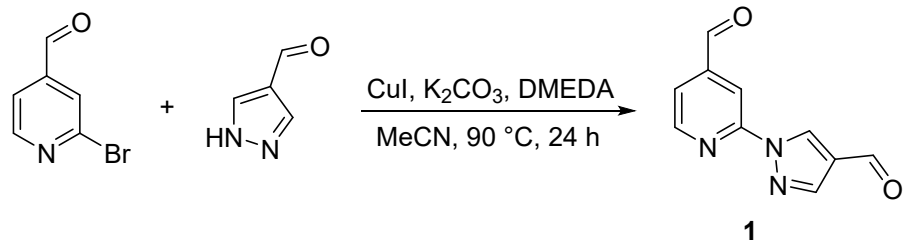
Contents

1. General Methods and Materials

All chemicals were provided from Energy Chemical, TCI India, Sigma-Aldrich, and used without further purification. All reactions were performed under argon, oxygen or air atmosphere in oven-dried reaction flask or Schlenk techniques. The desired products were confirmed by ^{1}H-NMR, ^{13}C-NMR spectra in chloroform-d ($CDCl_3$) or (DMSO-d_6) with tetramethylsilane (TMS) as internal reference, ^{1}H-NMR, ^{13}C-NMR spectra were recorded at 400 MHz or 101 MHz on Bruker Advance III HD 400 MHz spectrometer. For thin layer chromatography (TLC) analysis were used, Visualization was performed by UV light (254 nm). Flash column chromatography was carried out on 230-430 mesh silica gel. IR spectra were recorded by Fourier infrared spectrometer (NICOLET 6700). High resolution mass spectra (HRMS) were recorded on LTQ-FTUHRA mass spectrometer. SEM image and EDX spectra was performed on a HITACHI S-4800 field-emission scanning electron microscope. XPS data were recorded with electron energy analyzer (Thermo ESCALAB 250XI).

2. Preparation of Ru@Py-POP

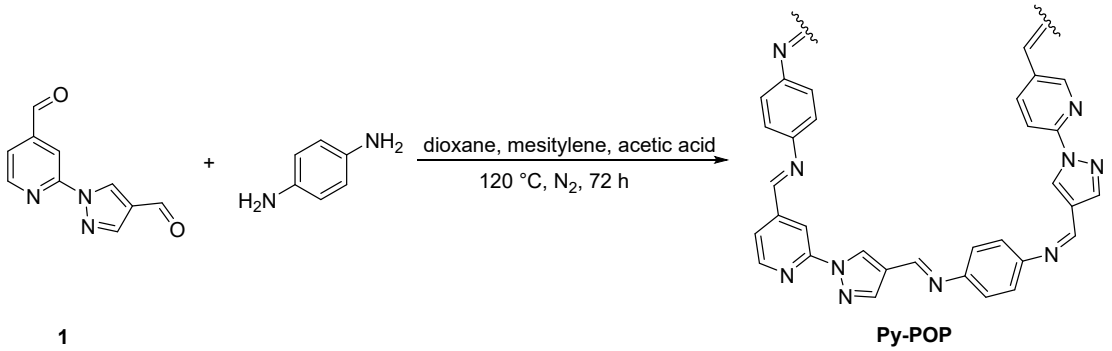
2.1 Procedure for synthesis of monomer 1



1

To 100 mL reaction flask was added 2-bromoisonicotinaldehyde (10 mmol), 1H-pyrazole-4-carbaldehyde (15 mmol), CuI (1.5 mmol), K_2CO_3 (20 mmol), DMEDA (4.5 mmol), MeCN (15 mL). The mixture was stirred at 90 ^{o}C for 24 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product, and the crude product was purified by flash column chromatography on silica gel to obtained the product **1** (White solid, 50% yield).

2.2 Procedure for synthesis of Py-POP



1 Py-POP

Py-POP was synthesized according to literature[1]. Under N_2 atmosphere, **1** (1.006 g), 1,4-diaminobenzene (811 mg), solvent (dioxane: mesitylene: acetic acid=5:5:1, 15 mL) were added into a 50 mL reaction tube and the resulting mixture stirred at 120 °C for 72 h. The reaction mixture cooled to room temperature and solid washed with dichloromethane, acetone and tetrahydrofuran in centrifugation for several times to afforded product Py-POP.

2.3 Procedure for synthesis of Ru@Py-POP

Under N_2 atmosphere, Py-POP (1.0 g), $Ru_2(p\text{-cym})_2Cl_4$ (61 mg, 0.10 mmol) and dry methanol (8 mL) were added into a 50 mL Schlenk tube, and the resulting mixture was stirred at 65 °C for 24 h. After the reaction mixture was cooled to room temperature, and solid washed with ethanol in centrifugation for several times to afforded product Ru@Py-POP.

3. Characterization of Py-POP and catalyst Ru@Py-POP

Fig.S1 showed TG patterns of Py-POP and Ru@Py-POP.

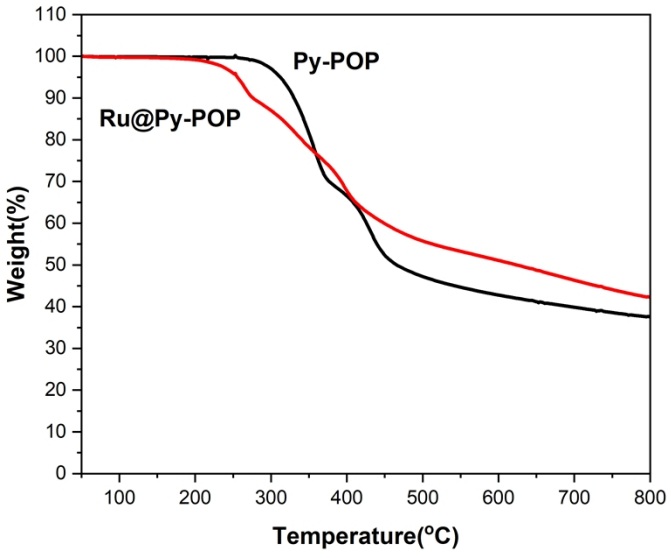


Fig. S1. TG patterns of Py-POP and Ru@Py-POP

Fig.S2 showed PXRD patterns of Py-POP and Ru@Py-POP

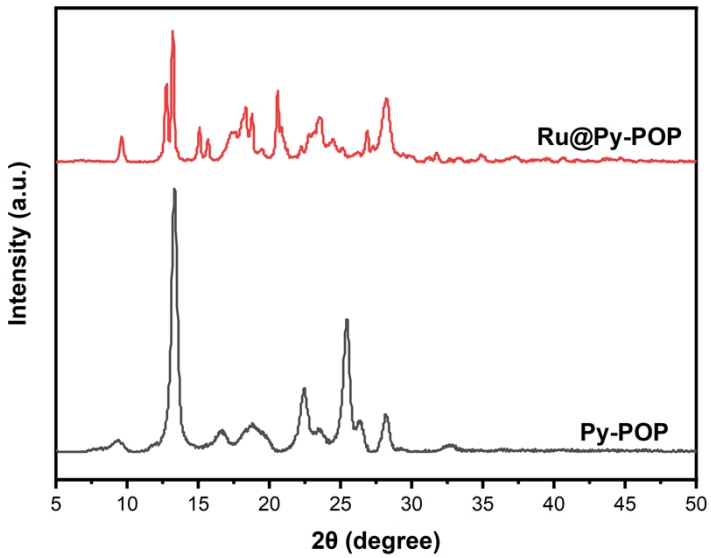


Fig S2. PXRD patterns of Py-POP and Ru@Py-POP

Fig.S3 showed SEM and TEM images of Ru@Py-POP after five runs.

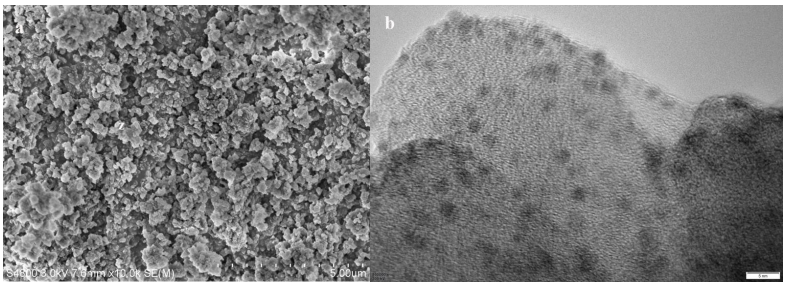


Fig.S3. (a) SEM images of Ru@Py-POP after five runs, (b) TEM images of Ru@Py-POP after five runs

Fig.S4 showed SEM EDS image of Ru@Py-POP (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Ru, (f) Cl, which revealed ruthenium species was supported on Py-POP successfully.

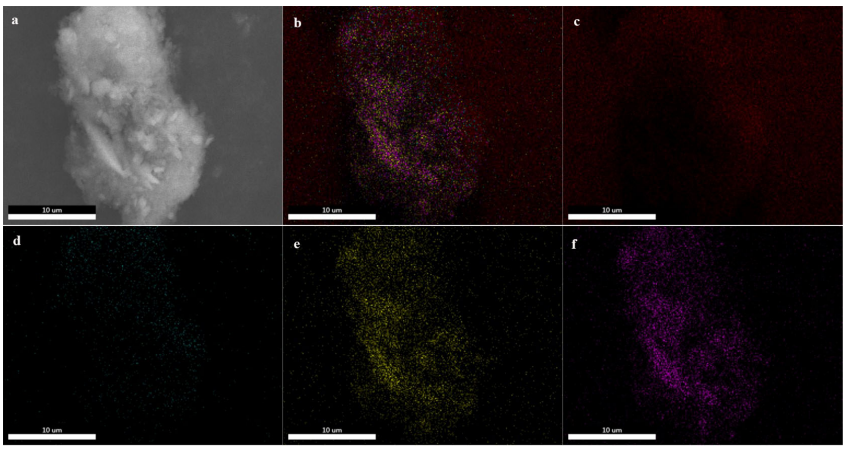
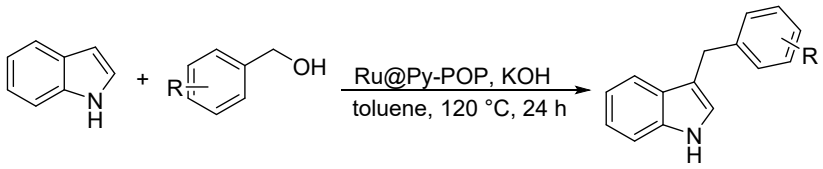


Fig.S4. SEM EDS image of Ru@Py-POP (a), (b), and corresponding elemental mapping images of (c) C, (d) N, (e) Ru, (f) Cl.

Table S1. Quantitative elemental composition of C, Cl, N and Ru from the Ru@Py-POP XPS data

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area(N) TPP-2M	Atomic %
C1s	294.98	284.62	275.18	142715.19	1.9	356395.26	4996.94	82.88
Cl2p	209.98	197.5	190.18	10814.14	1.25	23233.41	112.59	1.87
N1s	409.98	399.51	392.18	38627.24	2.2	95968.72	867.01	14.38
Ru3p	495.98	462.53	448.18	6198.83	2.35	43831.12	52.37	0.87

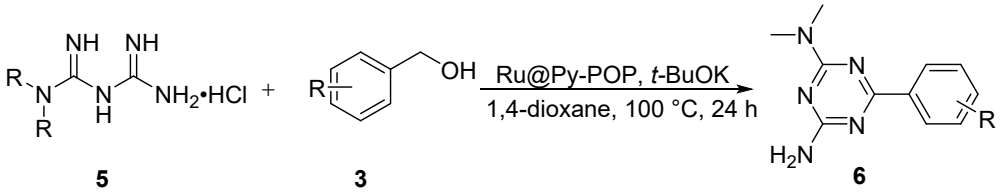
4. General procedure for 4



2 **3** **4**

Under N_2 atmosphere, **2** (1.0 mmol), **3** (2.2 mmol), KOH (0.7 equiv.), Ru@Py-POP (20 mg) and toluene (2.0 mL) were added into a 25 mL Schlenk tube. The mixture was stirred at 120 °C for 24 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product, and the crude product was purified by flash column chromatography on silica gel to obtained the product **4**.

5. General procedure for 6

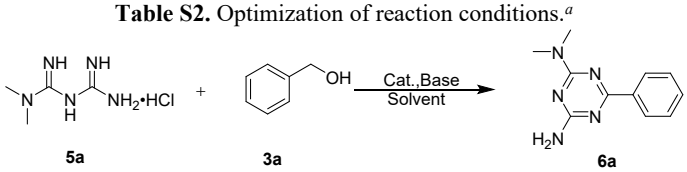


5 **3** **6**

Under O_2 atmosphere, **5** (1.0 mmol), **3** (1.1 mmol), *t*-BuOK (2.0 equiv.), Ru@Py-POP (20 mg) and 1,4-dioxane (2.0 mL) were added into a 25 mL Schlenk tube. The mixture was stirred at 100 °C for 24 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate three times. The organic phases were dried over anhydrous $MgSO_4$ and concentrated by removing the solvent under vacuum to give a crude product, and the crude product was purified by flash column chromatography on silica gel to obtained the product **6**.

Table S2 showed Optimization of reaction conditions.

Table S2. Optimization of reaction conditions.[a]

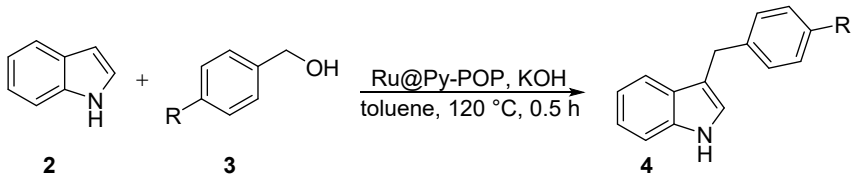


5a **3a** **6a**

Entry	Catalyst	Solvent	Base	Yield [%][b]
1[c]	Ru@Py-POP	toluene	KOH	63
2	Ru@Py-POP	H_2O	*t*-BuOK	24
3	Ru@Py-POP	DMF	*t*-BuOK	34
4	Ru@Py-POP	THF	*t*-BuOK	40
5	Ru@Py-POP	toluene	*t*-BuOK	65
6	Ru@Py-POP	nitrobenzene	*t*-BuOK	55
7	Ru@Py-POP	1,4-dioxane	*t*-BuOK	75
8	-	1,4-dioxane	*t*-BuOK	<5
9	Ru@Py-POP	1,4-dioxane	KOH	67
10	Ru@Py-POP	1,4-dioxane	K_2CO_3	34
11	Ru@Py-POP	1,4-dioxane	CsOH	65
12	Ru@Py-POP	1,4-dioxane	$NaHCO_3$	48
13[d]	Ru@Py-POP	1,4-dioxane	*t*-BuOK	59
14[e]	Ru@Py-POP	1,4-dioxane	*t*-BuOK	77
15[f]	Ru@Py-POP	1,4-dioxane	*t*-BuOK	64
16[g]	Ru@Py-POP	1,4-dioxane	*t*-BuOK	78
17[h]	**Ru@Py-POP**	**1,4-dioxane**	***t*-BuOK**	**88**

[a] Reagents and conditions: **5a** (1.0 mmol), **3a** (1.1 mmol), base (2.0 mmol), Ru@Py-POP (20 mg), 100 ℃. [b] Yields of isolated product. [c] **3a** (2.2 mmol), KOH (0.7 mmol), 120 ℃, toluene (2 mL). [d] 80 ℃. [e] 120 ℃. [f] 12 h. [g] 36 h. [h] O_2.

6. Hammett plot equation



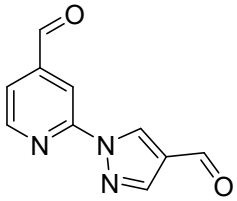
2 **3** **4**

Experimental procedure: Under N_2 atmosphere, **2** (1.0 mmol), **3** (2.2 mmol), KOH (0.7 equiv.), Ru@Py-POP (20 mg) and toluene (2.0 mL) were added into a 25 mL Schlenk tube. The mixture was stirred at 120 °C for 0.5 h. The water mixture was extracted with ethyl acetate three times, and the yield of product **4** was determined by GC.

R	OMe	Me	H	F	CF_3
Yield	22%	17%	14%	9%	6%

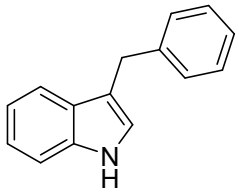
7. Analytical data of the obtained compounds

(1) 2-(4-formyl-1H-pyrazol-1-yl)isonicotinaldehyde (1).



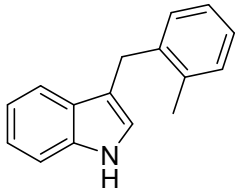
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (d, *J* = 0.6 Hz, 1H), 10.01 (s, 1H), 9.10 (d, *J* = 0.7 Hz, 1H), 8.68 (dt, *J* = 4.9, 0.7 Hz, 1H), 8.43 (dd, *J* = 1.4, 0.8 Hz, 1H), 8.20 (d, *J* = 0.7 Hz, 1H), 7.70 (dd, *J* = 4.9, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.32, 184.16, 152.02, 150.01, 144.67, 142.13, 131.30, 125.94, 120.55, 112.98. HRMS Calculated for $C_{10}H_8N_3O_2$ $[M+H]^+$ 202.0617, found 202.0618.

(2) 3-benzyl-1H-indole (4a)[2].



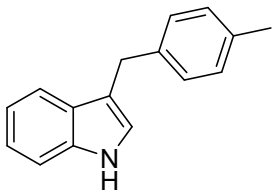
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.50 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30 – 7.22 (m, 5H), 7.19 – 7.13 (m, 2H), 7.06 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.80 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.09 (d, *J* = 1.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.33, 136.52, 128.80, 128.44, 127.55, 125.99, 122.45, 122.12, 119.45, 119.24, 115.85, 111.18, 31.68.

(3) 3-(2-methylbenzyl)-1H-indole (4b)[2].



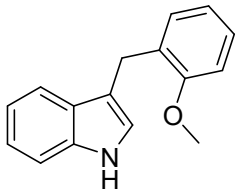
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.54 (dq, *J* = 7.9, 1.0 Hz, 1H), 7.26 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.20 – 7.11 (m, 4H), 7.11 – 7.06 (m, 2H), 6.60 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.03 (d, *J* = 1.1 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.22, 136.58, 136.53, 130.25, 129.53, 127.64, 126.30, 126.07, 122.53, 122.12, 119.43, 119.15, 115.20, 111.21, 29.35, 19.61.

(4) 3-(4-methylbenzyl)-1H-indole (4c)[3].



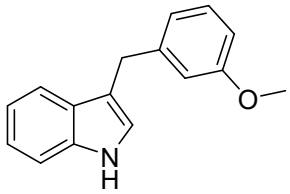
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.12 (m, 3H), 7.05 (dd, *J* = 8.0, 6.7 Hz, 3H), 6.80 – 6.75 (m, 1H), 4.04 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.28, 136.54, 135.40, 129.15, 128.69, 127.58, 122.40, 122.09, 119.43, 119.27, 116.11, 111.18, 31.26, 21.14.

(5) 3-(2-methoxybenzyl)-1H-indole (4d)[4].



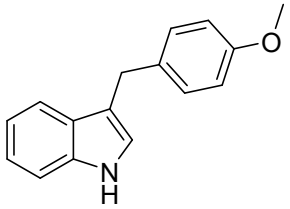
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.28 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.08 (tdd, *J* = 8.0, 7.1, 1.4 Hz, 2H), 6.88 – 6.79 (m, 3H), 4.09 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.36, 136.42, 129.99, 129.76, 127.77, 127.12, 122.54, 121.89, 120.50, 119.33, 119.27, 115.24, 111.08, 110.30, 55.44, 25.21.

(6) 3-(3-methoxybenzyl)-1H-indole (4e)[5].



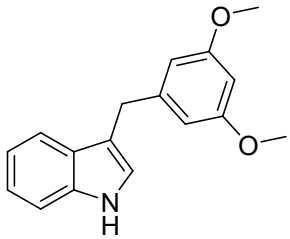
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.51 (ddd, *J* = 7.9, 2.6, 1.6 Hz, 1H), 7.24 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.05 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.78 (dt, *J* = 2.2, 1.0 Hz, 1H), 6.75 – 6.69 (m, 1H), 4.05 (s, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.77, 143.09, 136.53, 129.42, 127.55, 122.53, 122.11, 121.34, 119.45, 119.21, 115.56, 114.69, 111.29, 111.23, 55.23, 31.74.

(7) 3-(4-methoxybenzyl)-1H-indole (4f)[4].



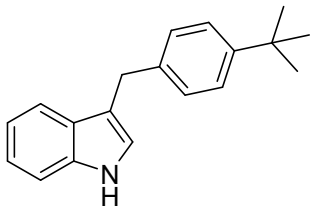
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.49 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.23 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.18 – 7.12 (m, 3H), 7.05 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.81 – 6.74 (m, 3H), 4.02 – 4.00 (m, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.92, 136.59, 133.51, 129.73, 127.53, 122.41, 122.09, 119.41, 119.27, 116.25, 113.90, 111.23, 55.37, 30.82.

(8) 3-(3,5-dimethoxybenzyl)-1H-indole (4g)[5].



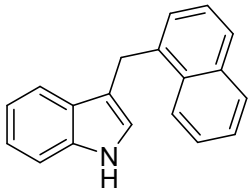
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.24 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.05 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.81 (dt, *J* = 2.2, 1.0 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 2H), 6.31 (t, *J* = 2.3 Hz, 1H), 4.02 (s, 2H), 3.69 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.86, 143.90, 136.52, 127.53, 122.54, 122.08, 119.44, 119.16, 115.33, 111.22, 107.06, 97.97, 55.33, 31.97.

(9) 3-(4-(tert-butyl)benzyl)-1H-indole (4h)[5].



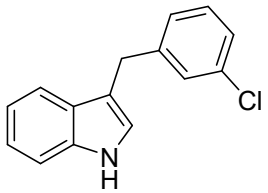
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.54 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.4 Hz, 3H), 7.21 – 7.14 (m, 3H), 7.07 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.83 (dd, *J* = 2.2, 1.1 Hz, 1H), 4.06 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72, 138.28, 136.50, 128.38, 127.63, 125.31, 122.40, 122.07, 119.39, 119.27, 116.03, 111.15, 34.44, 31.53, 31.07.

(10) 3-(naphthalen-1-ylmethyl)-1H-indole (4i)[6].



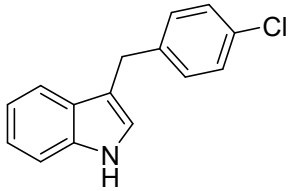
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.86 – 7.82 (m, 1H), 7.72 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.68 (s, 1H), 7.61 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.43 (qd, *J* = 7.2, 1.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.27 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.18 (ddd, *J* = 8.1, 5.9, 1.3 Hz, 1H), 7.10 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.56 (dd, *J* = 2.4, 1.2 Hz, 1H), 4.51 (d, *J* = 1.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.88, 136.42, 133.97, 132.27, 128.69, 127.54, 126.94, 126.72, 125.87, 125.74, 125.57, 124.47, 122.88, 122.14, 119.48, 119.10, 115.43, 111.20, 29.01.

(11) 3-(3-chlorobenzyl)-1H-indole (4j)[2].



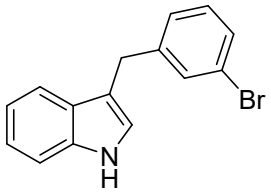
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.47 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.24 (s, 1H), 7.22 – 7.16 (m, 1H), 7.14 (tq, *J* = 3.3, 1.7 Hz, 3H), 7.07 (td, *J* = 7.5, 7.0, 1.1 Hz, 1H), 6.85 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.43, 136.50, 134.17, 129.64, 128.82, 127.33, 126.94, 126.20, 122.55, 122.26, 119.59, 119.08, 114.92, 111.25, 31.35.

(12) 3-(4-chlorobenzyl)-1H-indole (4k)[2].



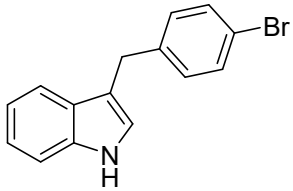
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.49 – 7.42 (m, 1H), 7.30 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.15 (d, *J* = 1.1 Hz, 1H), 7.07 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.84 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.76, 136.52, 131.65, 130.08, 128.48, 127.33, 122.45, 122.25, 119.55, 119.11, 115.28, 111.23, 31.05.

(13) 3-(3-bromobenzyl)-1H-indole (4l).



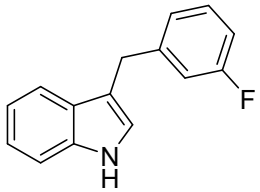
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.38 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.31 (t, *J* = 1.9 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.08 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 2H), 7.02 – 6.95 (m, 2H), 6.72 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.78, 136.50, 131.76, 130.01, 129.15, 127.44, 127.33, 122.60, 122.54, 122.28, 119.62, 119.09, 114.89, 111.30, 31.35. HRMS Calculated for $C_{15}H_{13}BrN$ $[M+H]^+$ 286.0231, found 286.0232.

(14) 3-(4-bromobenzyl)-1H-indole (4m)[7]**.**



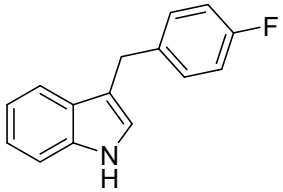
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.45 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.21 – 7.11 (m, 3H), 7.07 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.86 (dt, *J* = 2.2, 1.0 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.26, 136.50, 131.41, 130.47, 127.30, 122.43, 122.24, 119.68, 119.54, 119.09, 115.17, 111.21, 31.10.

(15) 3-(3-fluorobenzyl)-1H-indole (4n)[2].



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.19 (qd, *J* = 7.8, 5.3 Hz, 2H), 7.10 – 7.02 (m, 2H), 6.94 (dt, *J* = 10.2, 2.1 Hz, 1H), 6.90 – 6.79 (m, 2H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.06 (d, *J* = 245.1 Hz), 143.99 (d, *J* = 7.0 Hz), 136.51, 129.74 (d, *J* = 8.4 Hz), 127.36, 124.34 (d, *J* = 2.7 Hz), 122.50, 122.23, 119.55, 119.10, 115.56 (d, *J* = 21.2 Hz), 114.99, 112.84 (d, *J* = 21.2 Hz), 111.22, 31.40 (d, *J* = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.76.

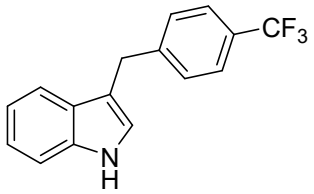
(16) 3-(4-fluorobenzyl)-1H-indole (4o)[2].



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.47 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.35 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.07 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.98 – 6.88 (m, 3H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56, 160.14, 136.81 (d, *J* = 3.2 Hz), 136.51, 130.00 (d, *J* = 7.9 Hz),

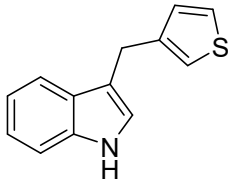
127.33, 122.31, 122.18, 119.28 (d, J = 36.4 Hz), 115.72, 115.05 (d, J = 21.2 Hz), 111.15, 30.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.78.

(17) 3-(4-(trifluoromethyl)benzyl)-1H-indole (4p)[2].



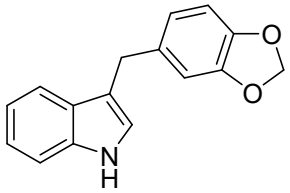
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.48 (dd, J = 17.6, 8.0 Hz, 3H), 7.39 – 7.31 (m, 3H), 7.21 – 7.17 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 2.3 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.43, 136.51, 128.95, 128.30 (q, J = 32.3 Hz), 127.27, 125.30 (q, J = 3.8 Hz), 123.10, 122.52, 122.33, 119.62, 119.01, 114.72, 111.26. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18.

(18) 3-(thiophen-3-ylmethyl)-1H-indole (4q)[8].



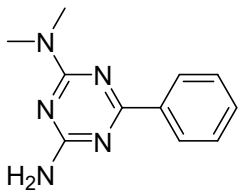
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.29 (dt, J = 8.1, 1.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.08 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.88 – 6.83 (m, 1H), 4.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 136.48, 128.66, 127.44, 125.38, 122.23, 122.13, 120.95, 119.45, 119.18, 115.41, 111.20, 26.33.

(19) 3-(benzo[d][1,3]dioxol-5-ylmethyl)-1H-indole (4r)[5].



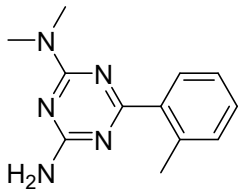
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.50 (dd, J = 7.9, 1.1 Hz, 1H), 7.31 (dt, J = 8.2, 1.0 Hz, 1H), 7.17 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.07 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.77 – 6.69 (m, 3H), 5.87 (s, 2H), 4.01 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.63, 145.72, 136.52, 135.20, 127.40, 122.30, 122.11, 121.42, 119.42, 119.19, 115.96, 111.14, 109.28, 108.10, 100.79, 31.36.

(20) N^2,N^2-dimethyl-6-phenyl-1,3,5-triazine-2,4-diamine (6a)[9].



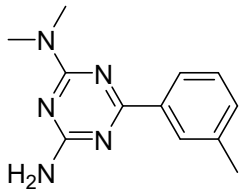
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.4 Hz, 2H), 7.45 (dd, J = 11.5, 6.9 Hz, 3H), 5.41 (s, 2H), 3.28 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.94, 167.40, 165.97, 137.27, 131.34, 128.35, 128.30, 36.26.

(21) N^2,N^2-dimethyl-6-(o-tolyl)-1,3,5-triazine-2,4-diamine (6b)[9].



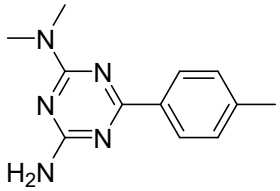
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.23 (t, *J* = 7.7 Hz, 2H), 5.46 (s, 2H), 3.20 (s, 3H), 3.13 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.02, 166.93, 165.57, 137.77, 137.30, 131.27, 129.69, 129.61, 125.78, 36.48, 36.26, 21.26.

(22) N^2,N^2-dimethyl-6-(m-tolyl)-1,3,5-triazine-2,4-diamine (6c)[9].



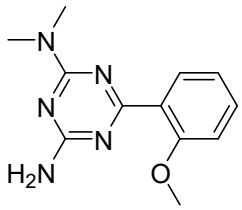
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.35 – 7.27 (m, 2H), 5.23 (s, 2H), 3.29 (s, 3H), 3.16 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.04, 167.28, 165.93, 137.79, 137.13, 132.04, 128.78, 128.13, 125.47, 36.22, 21.48.

(23) N^2,N^2-dimethyl-6-(p-tolyl)-1,3,5-triazine-2,4-diamine (6d)[9].



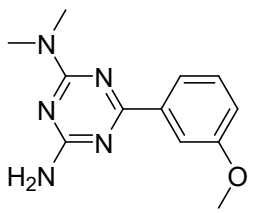
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.9 Hz, 1H), 8.25 (d, *J* = 1.9 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 5.24 (s, 2H), 3.28 (s, 3H), 3.16 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.78, 167.22, 165.90, 141.58, 134.37, 128.95, 128.26, 36.21, 21.56.

(24) 6-(2-methoxyphenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6e)[9].



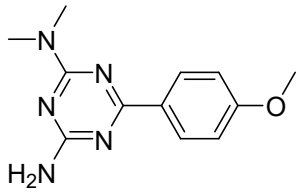
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.36 (ddd, *J* = 8.9, 7.4, 1.9 Hz, 1H), 7.02 – 6.95 (m, 2H), 5.24 (s, 2H), 3.85 (s, 3H), 3.20 (s, 3H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.49, 166.63, 165.72, 157.72, 131.07, 131.02, 128.11, 120.65, 112.24, 56.19, 36.47.

(25) 6-(3-methoxyphenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6f)[9].



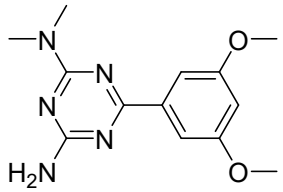
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.83 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 5.16 (s, 2H), 3.89 (s, 3H), 3.28 (s, 3H), 3.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.40, 166.93, 165.81, 159.63, 138.40, 129.22, 120.83, 117.68, 113.02, 55.39, 36.23.

(26) 6-(4-methoxyphenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6g)[9].



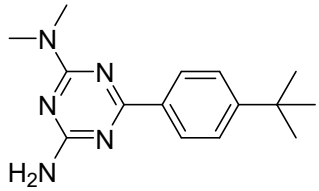
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 2H), 3.85 (s, 3H), 3.27 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.42, 167.21, 165.90, 162.39, 130.10, 129.67, 113.57, 55.45, 36.29.

(27) 6-(3,5-dimethoxyphenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6h)[9].



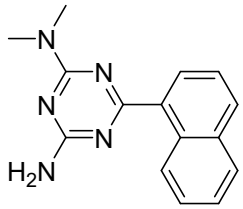
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.4 Hz, 2H), 6.58 (t, *J* = 2.4 Hz, 1H), 5.31 (d, *J* = 22.0 Hz, 2H), 3.84 (s, 6H), 3.26 (s, 3H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60, 167.31, 165.91, 160.71, 139.43, 106.06, 104.02, 55.58, 36.39, 36.24.

(28) 6-(4-(tert-butyl)phenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6i)[10].



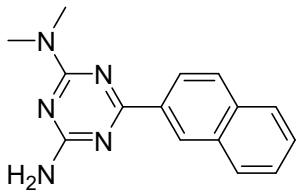
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.70 (s, 2H), 3.25 (s, 3H), 3.13 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.84, 167.39, 165.87, 154.57, 134.51, 128.11, 125.18, 36.24, 34.90, 31.28.

(29) N^2,N^2-dimethyl-6-(naphthalen-1-yl)-1,3,5-triazine-2,4-diamine (6j).



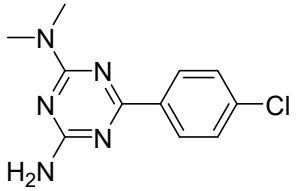
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 – 8.90 (m, 1H), 8.46 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.88 (dd, *J* = 11.2, 8.3 Hz, 2H), 7.56 – 7.48 (m, 2H), 5.21 (s, 2H), 3.36 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.44, 166.80, 165.59, 135.60, 134.05, 130.97, 130.56, 128.34, 128.25, 126.39, 126.23, 125.77, 125.08, 36.25. HRMS Calculated for $C_{15}H_{16}N_5$ $[M+H]^+$ 266.1406, found 266.1405.

(30) N^2,N^2-dimethyl-6-(naphthalen-2-yl)-1,3,5-triazine-2,4-diamine (6k)[9].



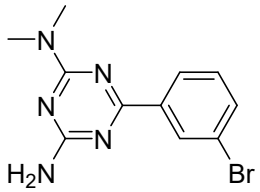
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.71 (m, 1H), 8.00 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.49 (ddd, *J* = 6.9, 4.4, 1.8 Hz, 2H), 5.43 (s, 2H), 3.23 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.49, 166.81, 165.61, 135.60, 134.06, 130.98, 130.57, 128.34, 128.26, 126.39, 126.23, 125.75, 125.07, 36.42.

(31) 6-(4-chlorophenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6l)[9].



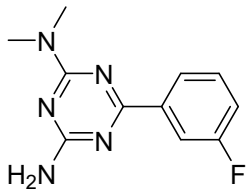
White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 – 8.27 (m, 2H), 7.59 – 7.48 (m, 2H), 6.90 (s, 2H), 3.19 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.83, 167.48, 165.90, 136.48, 136.36, 129.95, 128.69, 36.14.

(32) 6-(3-bromophenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6m) [9].



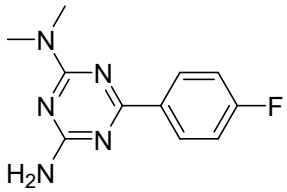
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (t, *J* = 1.8 Hz, 1H), 8.28 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.58 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 5.26 (s, 2H), 3.27 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.57, 167.22, 165.84, 139.36, 134.19, 131.39, 129.84, 126.92, 122.54, 36.47, 36.27.

(33) 6-(3-fluorophenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6n)[9].



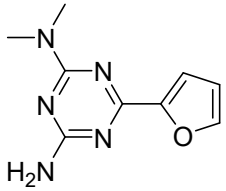
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 7.8, 1.3 Hz, 1H), 8.04 (ddd, *J* = 10.3, 2.8, 1.5 Hz, 1H), 7.37 (td, *J* = 8.0, 5.8 Hz, 1H), 7.15 (tdd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 5.48 (s, 2H), 3.26 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.81 (d, *J* = 3.1 Hz), 167.37, 165.86, 162.96 (d, *J* = 244.6 Hz), 139.79 (d, *J* = 7.6 Hz), 129.73 (d, *J* = 7.8 Hz), 123.95 (d, *J* = 2.8 Hz), 118.14 (d, *J* = 21.3 Hz), 115.19 (d, *J* = 23.0 Hz), 36.34 (d, *J* = 16.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.41.

(34) 6-(4-fluorophenyl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6o)[9].



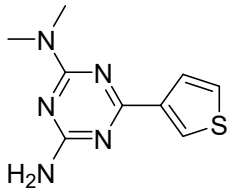
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.32 (m, 2H), 7.14 – 7.03 (m, 2H), 5.29 (s, 2H), 3.26 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92, 167.29, 165.89, 163.84, 133.34 (d, *J* = 2.9 Hz), 130.55 (d, *J* = 8.7 Hz), 115.20 (d, *J* = 21.7 Hz), 36.31 (d, *J* = 14.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.30.

(35) 6-(furan-2-yl)-N^2,N^2-dimethyl-1,3,5-triazine-2,4-diamine (6p) [10].



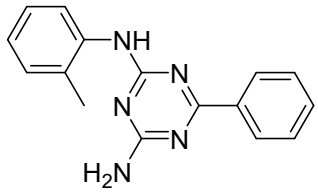
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.27 – 7.24 (m, 1H), 6.48 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.65 (s, 2H), 3.20 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.94, 165.53, 163.40, 151.74, 145.08, 114.36, 111.97, 36.28.

(36) N^2,N^2-dimethyl-6-(thiophen-3-yl)-1,3,5-triazine-2,4-diamine (6q)[9].



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 3.1, 1.2 Hz, 1H), 7.79 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.30 (dd, *J* = 5.1, 3.1 Hz, 1H), 5.17 (s, 2H), 3.24 (s, 3H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.45, 167.17, 165.88, 141.27, 129.05, 127.55, 125.65, 36.27.

(37) 6-phenyl-N^2-(o-tolyl)-1,3,5-triazine-2,4-diamine (6r)[9].



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.24 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.42 – 7.30 (m, 3H), 7.17 (ddd, *J* = 7.8, 3.8, 1.3 Hz, 2H), 7.07 (td, *J* = 7.4, 1.3 Hz, 1H), 5.83 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.08, 167.57, 165.48, 136.54, 136.24, 131.64, 131.46, 130.63, 128.40, 128.36, 126.51, 125.30, 124.78, 18.11.

8. Reference

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