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Solvent-free preparation of tris-pyrazolyl-1,3,5-triazines

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Abstract—Tris-pyrazolyl-1,3,5-triazines have been prepared by cyclotrimerization of aromatic nitriles in solvent-free conditions. The interesting structures of these compounds make them candidates for application in coordination chemistry and crystal engineering.

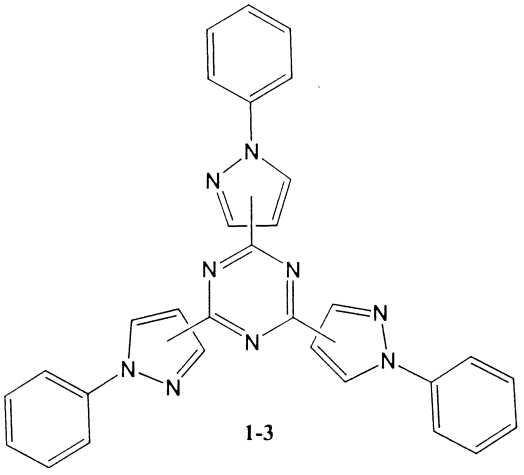
1. Introduction

1,3,5-Triazines substituted with pyridine rings have traditionally found application in analytical chemistry as complexation agents[1] and their quaternary salts in electrochemistry as multi-step redox systems.[2] In the last years, there is a growing interest in these compounds. Due to their characteristic C_3-symmetry, these ligands have been used as templates in the synthesis of supramolecular porphyrin systems,[3–5] and in multidimensional crystal engineering involving metal complexes[6] that, in some cases, produce nanometer sized oligonuclear co-ordination compounds.[7–11]

We have recently described the synthesis of tris(pyrazol-1-yl)1,3,5-triazine, its complexation with palladium and the dynamic behaviour of these complexes.[12] Complexation involved the loss of a pyrazole unit due to the stability of the dinuclear complex, the good leaving ability of the pyrazole and the lability of the triazine carbon–pyrazole nitrogen bond.

In order to obtain more stable ligands, in which the pyrazole and triazine units are attached by carbon–carbon bonds and, at the same time, to have ligands suitable for multidimensional crystal engineering involving metal complexes, we have synthesized tris-pyrazolyl-1,3,5-triazines in which pyrazole and triazine are directly attached through carbon–carbon bonds or separated by a benzene ring (Fig. 1).

Synthesis of aryl substituted 1,3,5-triazines have been performed by cyclotrimerization of nitriles catalysed by



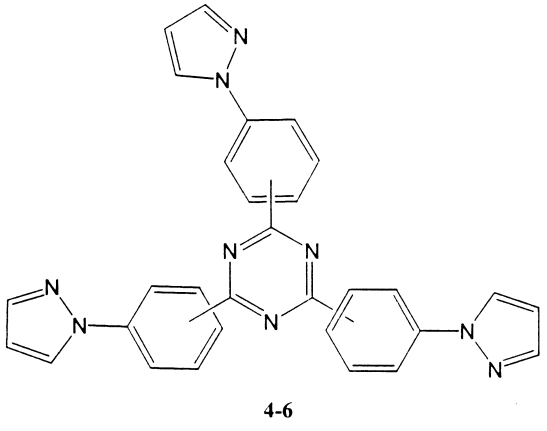


Figure 1. 1, 3-substituted; **2**, 4-substituted; **3**, 5-substituted;**4**, *ortho*-substituted; **5**, *meta*-substituted; **6**, *para*-substituted.

Keywords: solvent-free; triazines; cyclotrimerization.
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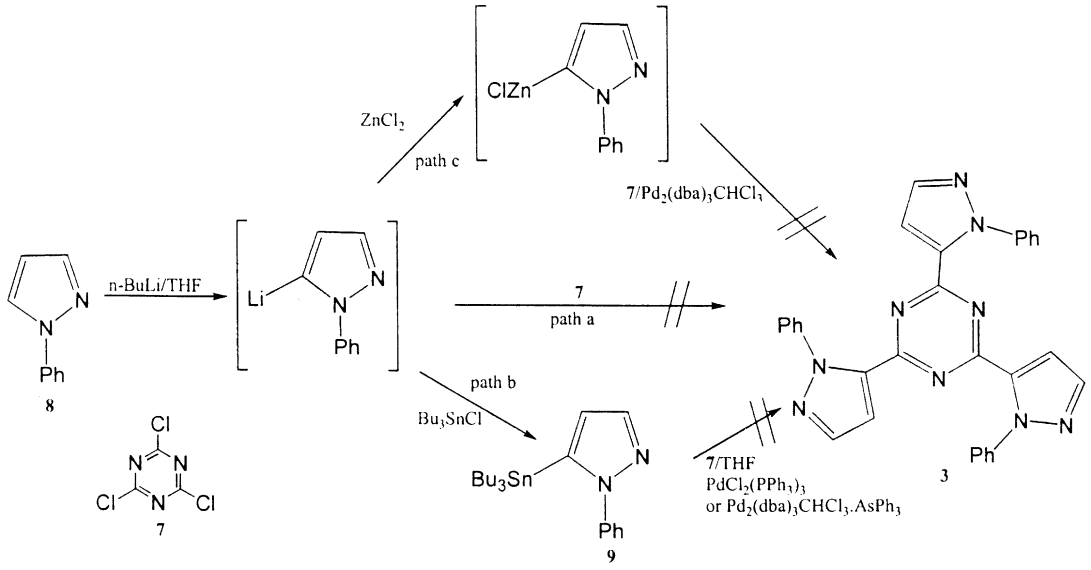


Scheme 1.

acids, bases[13–16] or activated magnesium,[17] cyclization of iminoester and imino chlorides,[15,18] or oxidation of aromatic aldehydes or diimines with Fremy's salt.[19]

An alternative procedure implies the deprotonation of a heterocyclic ring followed by reaction with 2,4,6-trichloro-1,3,5-triazine. In this way tris-thenyl-1,3,5-triazines with NLO properties[20] and 4,6-dichloro-2-pyrazol-5-yl-1,3,5-triazines[21] have been prepared. Finally, 2-(alk-1′-ynyl)-4,6-dimethoxy-1,3,5-triazines have been prepared by palladium catalysed cross-coupling of terminal alkynes and 2-chloro-4,6-dimethoxy-1,3,5-triazine.[22]

2. Results and discussion

The preparation of tris-pyrazolyl-1,3,5-triazines **1**–**6** was planned by the three methods described in the introduction, deprotonation followed by reaction with 2,4,6-trichloro-1,3,5-triazine **7**, palladium catalysed cross-coupling between stannyl substituted pyrazoles and **7**, and cyclotrimerization of aromatic nitriles. The choice of a given methodology depended on the availability of the starting material and the structure of the final product.

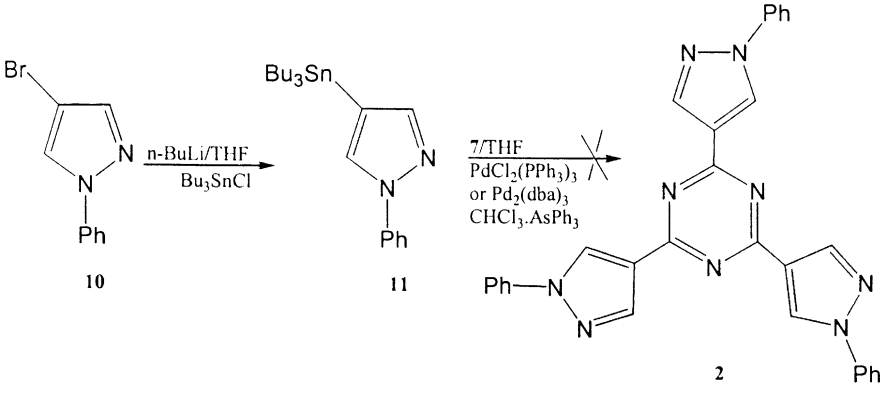
2.1. Deprotonation followed by reaction with 2,4,6-trichloro-1,3,5-triazine

Deprotonation of pyrazole derivatives occurs in position 5. In consequence, synthesis of the 5-substituted triazine **3** was attempted by deprotonation of 1-phenylpyrazole with n-butyllithium by a modification of Tupper's procedure in order to get the triple substitution (Scheme 1, path a);[21] however product **3** was never obtained by this procedure and decomposition of the starting material took place.

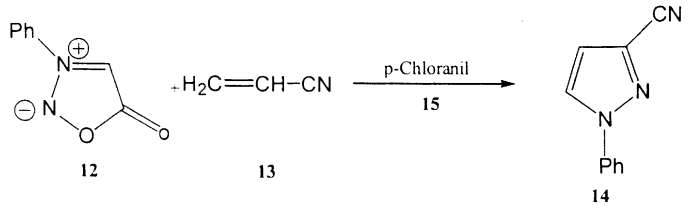
2.2. Palladium catalysed cross-coupling

Synthesis of triazines **2** and **3** was also attempted by palladium catalysed cross-coupling of the corresponding 4- and 5-tributylstannyl derivatives **11** and **9**, respectively.[23–26] In these reactions, we obtained complex mixtures in which the disubstituted products predominated (Scheme 1, path b and Scheme 2).

It has been reported that Negishi cross-couplings using zinc derivatives is the best method for the introduction of aryl or heteroaryl groups into the pyrazole ring.[23–27] In



Scheme 2.



Scheme 3.

consequence we used this procedure for the preparation of compound **3**, starting with the lithium derivative and transmetallation by addition of zinc chloride to obtain the zinc derivative. However, palladium catalysed cross coupling with 2,4,6-trichloro-1,3,5-triazine **7** failed to give the desired product (Scheme 1, path c).

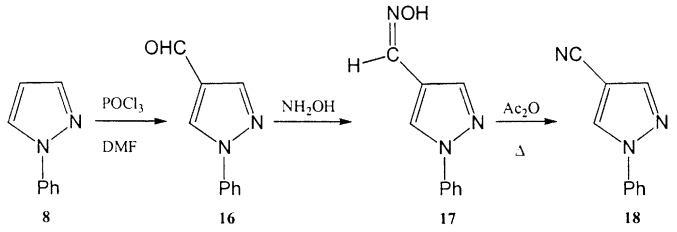
2.2.1. Cyclotrimerization of aromatic nitriles. Finally, we decided to test the preparation of the triazine ring by cyclotrimerization of nitriles. The advantage of this methodology is that only one procedure could be used for the preparation of all the triazine derivatives **1**–**6**. However, this method requires the synthesis of the appropriate aromatic nitrile. The necessary pyrazolyl nitriles have been prepared by two different methods. The synthesis of 3-cyano-1-phenylpyrazole was carried out by cycloaddition of *N*-phenylsydnone **12** with acrylonitrile **13** (Scheme 3).[28]

The synthesis of 4-cyano-1-phenylpyrazole **18** was performed starting from 1-phenylpyrazole **15** in a three step synthesis by Vilsmeier formylation to give **16**, followed by formation of the oxime **17** and dehydration to the cyano group (Scheme 4).[29]

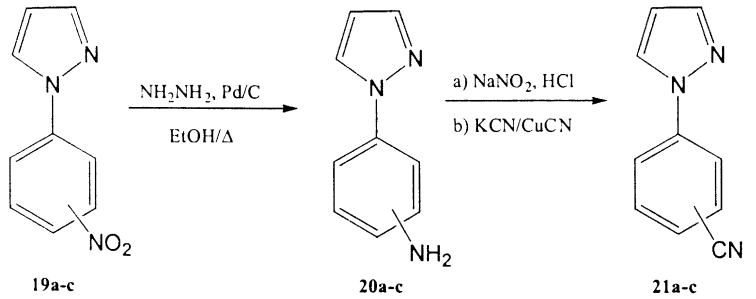
The synthesis of the phenyl substituted nitriles has been carried out following a common procedure, starting from the appropriate nitrophenylpyrazole **19**, then reduction with hydrazine to the amine **20**, and formation of the diazonium salt followed by substitution in situ with cyanide anion (Scheme 5).[30]

Trimerization of aromatic nitriles requires harsh reaction conditions, high temperatures, long reaction times and pressure.[13–17] In order to obtain the desired 1,3,5-triazines in milder reaction conditions we performed the cyclotrimerization of cyanopyrazoles **14**, **18**, **21a**–**c** in the absence of solvent using yttrium trifluromethanesulfonate as catalyst (Schemes 6 and 7). Reactions were performed by heating a mixture of the appropriate cyanopyrazole with piperidine and yttrium trifluromethanesulfonate at 200°C in a closed vessel.

In solvent-free conditions, an enhancement in kinetics can result from increasing concentrations of reactants, and also the decrease in the molecular dynamics can induce a particular selectivity, together with a simplification of the experimental procedures. Solvent-free techniques represent a clean, economical and safe procedure which can lead to substantial benefits.[31] It has been reported that lanthanide ions catalyse the cyclotrimerization of nitriles and reaction can be performed in milder conditions than with other acid or basic catalysts;[13] in our case, it was the yttrium salt that

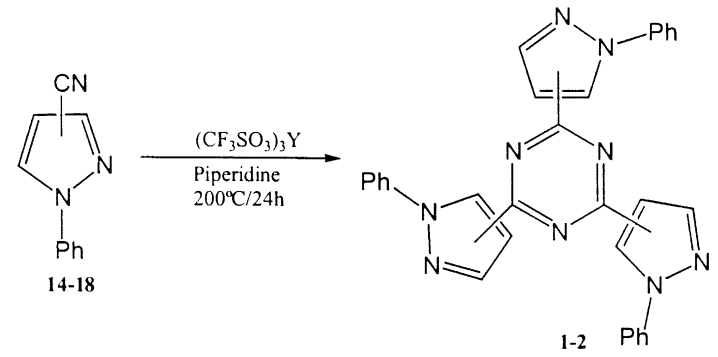


Scheme 4.



a, *ortho*-substituted
b, *meta*-substituted
c, *para*-substituted

Scheme 5.



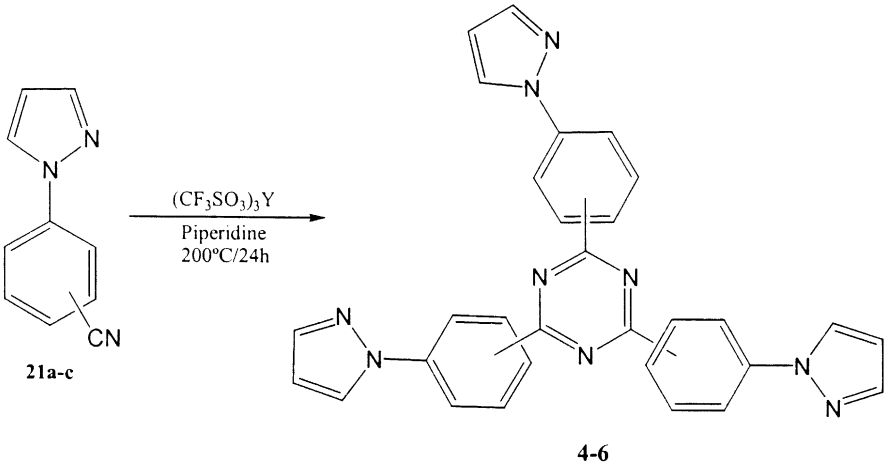
14, 3-Cyano
18, 4-Cyano

Scheme 6.

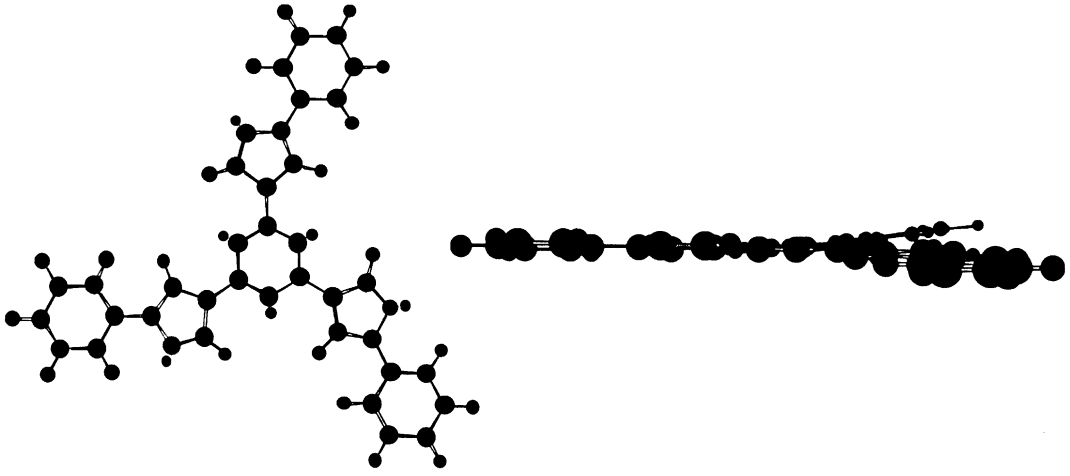
was the best catalyst although the reaction still required high temperatures and pressures. The reaction is very sensitive to steric hindrance, for instance compound **4** was obtained in very low yield and was hardly detectable.

3. Structural determination

The ^{1}H- and ^{13}C-NMR spectra of the pyrazolyltriazines are collected in Tables 1 and 2 together with the NMR spectra of the starting cyanopyrazoles for comparison.



Scheme 7.



Scheme 8. Structure of compound **2** determined by molecular mechanics calculations.

Table 1. ^{1}H-NMR chemical shifts of pyrazolyltriazines **1–6** and cyanopyrazoles **14, 18, 21a–c** (δ ppm, J Hz, solvent $CDCl_3$)

		H-3	H-4	H-5	H-2′	H-3′	H-4′	H-5′	H-6′
1	δ	—	7.58 (d)	8.1 (d)	7.92 (dd)	7.53 (dd)	7.38 (tt)	7.53 (dd)	7.92 (dd)
	J		2.7		8.7, 1.3	8.7, 7.4	7.4, 1.3	8.7, 7.4	8.7, 1.3
14	δ	—	6.86 (d)	7.98 (d)	7.69 (d)	7.51 (dd)	7.4 (tt)	7.51 (dd)	7.69 (dd)
	J		2.6	2.6	8.1	8.1, 7.3	7.3	8.1, 7.3	7.3
2	δ	8.57 (s)	—	8.85 (s)	7.85 (dd)	7.54 (dd)	7.39 (tt)	7.54 (dd)	7.85 (dd)
	J				8.6, 1.1	8.6, 7.3	7.3, 1.1	8.6, 7.3	8.6, 1.1
18	δ	8 (d)	—	8.31 (d)	7.68 (dd)	7.52 (dd)	7.42 (tt)	7.52 (dd)	7.68 (dd)
	J	0.5		0.5	8.3, 1.5	8.3, 7.3	7.3, 1.5	8.3, 7.3	8.3, 1.5
21a	δ	7.6–7.8	6.55 (t)	8.14 (d)	—	7.6–7.8	7.7 (td)	7.43 (td)	7.6–7.8
	J	(m)	2.4	2.7		(m)	8, 1.5	7.8, 1.2	(m)
5	δ	7.82 (d)	6.56 (dd)	8.13 (d)	9.03 (t)	—	8.71 (dd)	7.68 (dd)	8.01 (d)
	J	1.5	2.4, 1.5	2.4	1.7		7.8, 1.7	7.8, 8.1	8.1, 1.7
21b	δ	7.76 (d)	6.53 (dd)	7.9–8	8.03 (t)	—	7.52–7.6	7.52–7.6	7.9–8
	J	1.7	1.9, 1.7	(m)	1.2		(m)	(m)	(m)
6	δ	7.82 (d)	6.56 (dd)	8.09 (d)	7.94 (d)	8.88 (d)	—	8.88 (d)	7.94 (d)
	J	1.7	2.4, 1.7	2.4	8.8	8.8		8.8	8.8
21c	δ	7.78 (d)	6.54 (dd)	8 (d)	7.85	7.75	—	7.75	7.85
	J	1.8	2.4, 1.8	2.4	8.8	8.8		8.8	8.8

Table 2. ^{13}C-NMR chemical shifts of pyrazolyltriazines **1–6** and cyanopyrazoles **14, 18, 21a–c** (δ ppm, solvent $CDCl_3$)

	C-3	C-4	C-5	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	CN or triazine
1	150.68	110.66	128.49	139.92	119.93	129.48	127.38	—	—	167.99
14	139.02	112.79	128.15		119.89	129.7	128.26	—	—	113.83
2	142.04	123.38	129.15	139.69	119.62	129.60	127.39	—	—	167.70
18	143.18	94.34	131.76	138.73	119.89	129.76	128.29	—	—	113.02
21a	141.98	108.65	126.58	140.54	122.13	113.58	129.54	130.35	122.82	116.95
5	141.30	107.84	126.90	148.22	119.18	140.63	129.77	137.11	123.46	171.12
21b	141.98	108.65	126.58	140.54	122.13	113.58	129.54	130.35	122.82	117.96
6	143.18	108.34	126.85	143.18	118.64	130.42	133.85	—	—	170.72
21c	142.33	108.95	126.74	142.87	118.85	133.57	118.31	—	—	118.39

The ^{1}H-NMR spectra of the triazines show a strong deshielding (0.54–1.13 ppm) of the protons situated close to the triazine ring, H-4 (+0.78) in **1**, H-3 (+0.57) and H-5 (+0.54) in **2**, H-2′ and H-6′ (+1.00) in **5** and H-3′ and H-5′ (+1.13) in **6**. This strong effect can be related to the anisotropy of the triazine ring but also to a weak C-H…N interaction due to the proximity of the nitrogen lone pair.[32–33] The magnitude of this effect is closely related to the C-H…N distances determined by molecular mechanics calculations (averaged values, 2.42 for **1**, 2.44 for **2**, 2.10 for **5** and 2.19 Å for **6**)[34] and the calculated dihedral angle between triazine and pyrazole rings (see below) (Scheme 8).

The ^{13}C-NMR spectra of the triazines show a strong deshielding of the carbon attached to the triazine in relation to the cyanopyrazoles (11.66–29.04). The triazine carbon shows a signal at 171 ppm if the triazine is attached to the phenyl group and at 167 ppm when the triazine is attached to the π-excedent pyrazole ring.

The differences, $\delta_{Cmeta}-\delta_{Cortho}$ and $\delta_{Hortho}-\delta_{Hmeta}$, indicate extensive conjugation between the phenyl and pyrazole rings in compounds **1** and **2**.[35] This effect is in good agreement with the calculated dihedral angles between pyrazole and phenyl rings (see below).

Molecular mechanics calculations show that tris-pyrazolyl-1,3,5-triazines **1–6** are non completely planar structures but exhibit a small helicity as deduced by the dihedral angle between triazine and pyrazole rings (averaged values 26.9° for **1**, 27.8° for **2**, 28.6° for **5** and 28.5° for **6**) and the dihedral angle between pyrazole and phenyl rings (averaged values, 27.4° for **1**, 28.1° for **2**, 28.0° for **5** and 27.9° for **6**). As an example, the structure of compound **2** is represented in Scheme 8.

In conclusion, cyclotrimerization of pyrazolylcarbonitriles in solvent-free conditions produces pyrazolyl substituted 1,3,5-triazines with interesting structures which can be used in coordination chemistry and crystal engineering. Their coordination properties and crystal structures of these and related compounds are the subject of our current research interest.

4. Experimental

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Unity 300 spectrometer with TMS as an internal standard. The IR spectra were obtained with FTIR Nicolet-550. Column flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh). The aminopyrazoles were distilled with a Kugelrohr apparatus.

4.1. General procedure for the syntheses of 1-(nitrophenyl)pyrazoles

A solution of malonaldehyde bisdimethylacetal (8.23 mL, 50 mmol), the appropriate nitrophenylhydrazine hydrate (9.48 g, 50 mmol) and ethanol (50 mL) were refluxed for the time indicated. The cold solution was neutralized with

a saturated solution of sodium carbonate. Evaporation of solvent yielded the products **19a**–**19c**.

4.1.1. 1-(2-Nitrophenyl)pyrazole (19a). *o*-Nitrophenylhydrazine (7.65 g, 50 mmol) in ethanol plus some drops of sulfuric acid until acid p*H*. The mixture was refluxed 4 h. Yield 7.4 g (77%), mp 87–88°C (ethanol). Lit. mp 88–89°C;[36] IR (KBr) 1536, 1523, 1394, 1366 cm^{-1} (ν_{NO2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 6.51 (dd, J=2.5 Hz and J=1.8 Hz, 1H, pyrazole-H_4), 7.48–7.71 (m, 3H, Ar-H), 7.72 (d, J=2.5 Hz, 1H, pyrazole-H_5), 7.75 (d, J=1.7 Hz, 1H, pyrazole-H_3), 7.88 (dd, J=8.1 Hz and J=1.5 Hz, 1H, Ar-H_3).

4.1.2. 1-(3-Nitrophenyl)pyrazole (19b). From *m*-nitrophenylhydrazine. The mixture was refluxed 1 h. Yield 8 g (84%), mp 96–98°C (ethanol). Lit. mp 94–95°C;[36] IR (KBr) 1532, 1392, 1349, 1316 cm^{-1} (ν_{NO2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 6.55 (t, J=2.16 Hz, 1H, pyrazole-H_4), 7.65 (t, J=8.1 Hz, 1H, Ar-H_5), 7.78 (d, J=1.6 Hz, 1H, pyrazole-H_3), 8.03 (d, J=2.6 Hz, 1H, pyrazole-H_5), 8.12 (td, J=8.0 Hz and J=2.1 Hz, 2H, Ar-H_4 and H_6), 8.57 (t, J=2.2 Hz, 1H, Ar-H_2).

4.1.3. 1-(4-Nitrophenyl)pyrazole (19c). From *p*-nitrophenylhydrazine The mixture was refluxed 1 h. Yield 8 g (84%), mp 176–177°C (ethanol). Lit. mp 169–170°C;[29] IR (KBr) 1596, 1516, 1392, 1334 cm^{-1} (ν_{NO2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 6.57 (t, J=2.0 Hz, 1H, pyrazole-H_4), 7.80 (d, J=1.5 Hz, 1H, pyrazole-H_3), 8,04 (d, J=2.6 Hz, 1H, pyrazole-H_5), 7.90 (AA′BB′ system, J=9.2 Hz, 2H, Ar-H_2 and Ar-H_6), 8.35 (AA′BB′ system, J=9.2 Hz, 2H, Ar-H_3 and Ar-H_5).

4.2. General procedure for the reduction of nitropyrazoles to aminopyrazoles.

Prepared following a procedure similar to that described in Ref. 30. Palladium-carbon catalyst (10%) was added portionwise during 5–10 min to a hot solution of the appropriate nitropyrazole (5.6 g, 30 mmol) in ethanol (50 mL) containing hydrazine hydrate (7.5 mL, 150 mmol). The mixture was heated under reflux for 1 h. The hot solution was filtered through a Whatman paper to remove Pd, the solution was filtered through silica gel (10 g) and the solvent was evaporated. The amino derivatives **20a**–**20c** were used without further purification.

4.2.1. 1-(2-Aminophenyl)pyrazole (20a). Yield 4.4 g (93%), bp 140°C (ball-to-ball)/0.5 mmHg. Lit. mp: 49°C.[37] IR (KBr) 3450, 3346, 1620 cm^{-1} (ν_{NH2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 4.62 (s, 2H, NH_2), 6.44 (t, J=2.4 Hz, 1H, pyrazole-H_4), 6.71–6.86 (m, 2H, Ar-H_3 and H_5), 7.1–7.2 (m, 2H, Ar-H_4 and H_6), 7.71 (d, J=2.4 Hz, 1H, pyrazole-H_5), 7.74 (d, J=1.5 Hz, 1H, pyrazole-H_3). ^{13}C NMR ($CDCl_3$) δ 106.35 (pyrazole-C_4), 117.24 (Ar-C_3), 118.02 (Ar-C_5), 126.47 (Ar-C_1), 124.11 (Ar-C_6), 128.46 (Ar-C_4), 129.83 (pyrazole-C_5), 140.48 (pyrazole-C_3), 141.03 (Ar-C_2).

4.2.2. 1-(3-Aminophenyl)pyrazole (20b). Yield 3.2 g (68%), bp 150°C (ball-to-ball)/0.5 mmHg. IR (KBr) 3346, 3221, 1608 cm^{-1} (ν_{NH2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 3.82 (s, 2H, NH_2), 6.43 (t, J=2.4 Hz, 1H, pyrazole-H_4), 6.59 (dm, J=8.0 Hz, 1H, Ar-H_4), 7.0 (dm, J=8.0 Hz, 1H, Ar-H_6), 7.09 (t, J=2.2 Hz, 1H, Ar-H_2), 7.2 (t, J=7.8 Hz, 1H, Ar-H_5), 7.69 (d, J=1.7 Hz, 1H, pyrazole-H_3), 7.88 (d, J=2.4 Hz, 1H, pyrazole-H_5). ^{13}C NMR ($CDCl_3$) δ 106.01 (Ar-C_2), 107.28 (pyrazole-C_4), 108.91 (Ar-C_6), 113.04 (Ar-C_4), 126.75 (pyrazole-C_5), 130.14 (Ar-C_5), 140.74 (pyrazole-C_3), 141.15 (Ar-C_1), 147.54 (Ar-C_3).

4.2.3. 1-(4-Aminophenyl)pyrazole (20c). Yield 3.4 g (71%), mp 47–48°C. Lit. mp 42–44°C.[38] IR (KBr) 3297, 3196, 1525 cm^{-1} (ν_{NH2} and ν_{Ar}). ^1H NMR ($CDCl_3$) δ 3.72 (s, 2H, NH_2), 6.41 (t, J=2.1 Hz, 1H, pyrazole-H_4), 7.67 (d, J=1.7 Hz, 1H, pyrazole-H_3), 7.78 (d, J=2.3 Hz, 1H, pyrazole-H_5), 6.75 (AA′BB′ system, J=8.5 Hz, 4H, Ar-H_3 and Ar-H_5), 7.45 (AA′BB′ system, J=8.5 Hz, 4H, Ar-H_2 and Ar-H_6). ^{13}C NMR ($CDCl_3$) δ 106.76 (pyrazole-C_4), 115.43 (Ar-C_3 and C_5), 121.07 (Ar-C_2 and C_6), 126.63 (pyrazole-C_5), 140.20 (pyrazole-C_3), 145.13 (Ar-C_4).

4.3. Synthesis of cyanopyrazoles

4.3.1. 1-Phenyl-3-cyanopyrazole (14). Prepared according to the procedure described in Ref. 28. Yield (13.1 g, 81%), mp 60–62°C. IR (KBr) 2241, 1600, 1508 cm^{-1} (ν_{CN} and ν_{Ar}).

4.3.2. 1-Phenyl-4-cyanopyrazole (18). Prepared according to the procedure described in Ref. 29. Yield (1.1 g, 42%), mp 97–99°C. IR (KBr) 2240, 1551, 1501 cm^{-1} (ν_{CN} and ν_{Ar}).

4.4. General procedure for the syntheses of 1-(cyanophenyl)pyrazoles

The amine (0.75 g, 5 mmol) was dissolved in water (7 mL) containing hydrochloric acid (1.56 g, 15 mmol), and the solution was cooled in ice. The temperature was maintained at 0–5°C and a saturated aqueous solution of sodium nitrite (0.41 g, 6 mmol) was added portionwise, after allowing 15 min. for reaction, until the mixture show an excess of nitrous acid on testing with a starch-iodide paper. The solution of the diazonium salt was neutralized with sodium carbonate maintaining a constant stirring and was added to an aqueous solution (25 mL) of copper (I) cyanide (0.45 g, 5 mmol) potassium cyanide (0.97 g, 15 mmol) in excess and heated at 80°C. Then the mixture was heated at 60°C during 20 min with constant stirring. The solution was filtered and the filtrate was extracted with diethyl ether (3×25 mL). The combined extracts were dried with anhydrous magnesium sulfate. Evaporation of the solvent yielded the cyanoderivatives.

4.4.1. 1-(2-Cyanophenyl)pyrazole (21a). The product was purified by distillation under reduced pressure using a Kugelrohr apparatus. Yield (0.53 g, 63%), bp 125°C (oven temperature)/0.5 mmHg. IR (neat) 2227, 1600, 1522 cm^{-1} (ν_{CN} and ν_{Ar}). Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.83. Found: C, 71.07; H, 4.28; N, 24.81.

4.4.2. 1-(3-Cyanophenyl)pyrazole (21b). The product was purified by column chromatography on silica gel (hexane/ethyl acetate 8:2). Yield (0.54 g, 64%), mp 53–55°C. IR (KBr) 2228, 1586, 1522 cm^{-1} (ν_{CN} and ν_{Ar}). Anal. Calcd

for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.83. Found: C, 70.76; H, 4.23; N, 24.95.

4.4.3. 1-(4-Cyanophenyl)pyrazole (21c). The product was purified by column chromatography on silica gel (hexane/ethyl acetate 8:2). Yield (0.73 g, 87%), mp 87–89°C. IR (KBr) 2226, 1610, 1528 cm^{-1} (ν_{CN} and ν_{Ar}). Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.83. Found: C, 70.87; H, 4.01; N, 25.01.

4.5. General procedure for the synthesis of 1,3,5-triazines

A mixture of the appropriate nitrile (0,85 g, 5 mmol), anhydrous piperidine (0,5 mL, 5 mmol) and yttrium trifluoromethanesulfonate (0,04 g, 0,05 mmol) under argon atmosphere was placed into a closed Pyrex flask[39] and introduced in a stainless block. The mixture was stirred at 200°C for 24 h and the reaction mixture was allowed to cool to room temperature. Extracting with the appropriate solvent afforded the pure products.

4.5.1. 2,4,6-Tris-(1-phenylpyrazol-3-yl)-1,3,5-triazine (1). The crude mixture was washed with ethanol and filtered to obtain the pure triazine (0,56 g, 66%), mp 140–142°C. MS (EI) *m/z* 507.2465 (M). IR (KBr) 1540, 1503, 1373 cm^{-1} ($\nu_{C=C}$ and $\nu_{C=N}$).

4.5.2. 2,4,6-Tris-(1-phenylpyrazol-4-yl)-1,3,5-triazine (2). The crude mixture was washed with ethanol, dimethylformamide and diethyl ether and filtered to have the pure triazine (0,26 g, 30%), mp>262°C. MS (EI) *m/z* 507.2630 (M). IR (KBr) 1567, 1528, 1500 cm^{-1} ($\nu_{C=C}$ and $\nu_{C=N}$).

4.5.3. 2,4,6-Tris-[3-(pyrazol-1-yl)phenyl]-1,3,5-triazine (5). The crude mixture was washed with ethanol and diethyl ether and filtered to obtain the pure triazine (0,22 g, 26%), mp 241–244°C. MS (EI) *m/z* 507.2398 (M). IR (KBr) 1529, 1393, 1369 cm^{-1} ($\nu_{C=C}$ and $\nu_{C=N}$).

4.5.4. 2,4,6-Tris-[4-(pyrazol-1-yl)phenyl]-1,3,5-triazine (6). The crude mixture was washed with ethanol and diethyl ether and filtered to obtain the pure triazine (0,06 g, 7%), mp>260°C. MS (EI) *m/z* 507.2402 (M). IR (KBr) 1520, 1392, 1372 cm^{-1} ($\nu_{C=C}$ and $\nu_{C=N}$).

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