A Novel Synthesis of 3-Aryl-2,6-dicyano-5-methylanilines via Reaction between Nitrostyrenes and Malononitrile

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Received 12 October 2009; revised 13 January 2010

Abstract: A novel and simple synthesis of 3-aryl-2,6-dicyano-5-methylanilines is described. Reactions between nitrostyrenes and excess malononitrile in the presence of sodium carbonate in 80% ethanol proceeded at room temperature to afford the aromatic products in good yields. A mechanism for the formation of the products is proposed.

Key words: 2,6-dicyanoanilines, nitrostyrenes, aromatics, regioselective, cyclizations

The development of novel reactions and useful reagents which enable the formation of carbon–carbon bonds, and particularly the construction of ring systems, is a key part of contemporary organic synthesis.

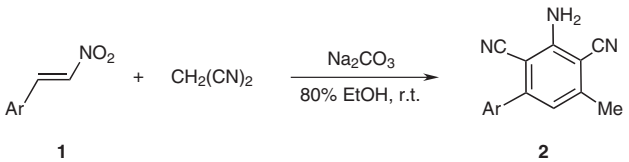
Polysubstituted benzenes are very useful compounds in organic chemistry, natural product chemistry, analytical chemistry and materials science. The regioselective preparation of these compounds is a challenging problem in organic synthesis.[1] Classical methods for the synthesis of substituted aromatics are based on aromatic substitution reactions which introduce a substituent to an existing arene. The most common procedures based on this approach involve electrophilic[2] or nucleophilic[3] substitution, catalyzed coupling reactions[4] and metalation–functionalization reactions.[5] However, these methods frequently suffer from disadvantages including multi-step reaction sequences, low yields, and serious regiochemical ambiguity originating from the activating, deactivating and directing effects of the substituents. On the other hand, modern approaches entail the regioselective construction of the aromatic skeleton starting from acyclic precursors in which the substitution pattern of the final product is dictated by the structures and functional groups of the precursors.[6]

Multi-functionalized benzenes possessing electron-donor and/or acceptor substituents such as 2,6-dicyanoanilines are of considerable interest. They are key constituents of a large number of bioactive natural and synthetic compounds,[7] and are useful as versatile precursors for asymmetric syntheses,[8] and as important substrates for nonlinear optical materials[9] and molecular electronic devices.[10]

SYNTHESIS 2010, No. 9, pp 1526–1530
Advanced online publication: 26.03.2010
DOI: 10.1055/s-0029-1218717; Art ID: T20009SS

2,6-Dicyanoanilines are typically prepared from (arylidene)malononitriles and (1-arylethylidene)malononitriles in the presence of a base.[11] Other synthetic routes include: reaction of malononitrile and α,β-unsaturated ketones,[12] one-pot tandem reaction of (alkylidene)malononitriles with nitroolefins in the presence of a base,[13] reaction of ynones and malononitrile,[14] reaction of α-methylene ketones or enamino ketones with malononitrile,[15] ring-transformation of functionalized 2*H*-pyran-2-ones with malononitrile,[16] the three-component reaction of aldehydes, ketones and malononitrile under solvent-free conditions[17] or microwave irradiation,[18] and reaction between (arylidene)malononitriles, dialkyl acetylenedicarboxylates and malononitrile catalyzed by 1-methylimidazole.[6]

Due to the interesting chemistry of 2,6-dicyanoanilines the development of synthetic methods which enable easy access to these useful compounds is desirable. As part of our studies on the development of efficient and straightforward methods for the preparation of organic compounds from readily available building blocks,[19] we report herein a simple synthesis of 3-aryl-2,6-dicyano-5-methylanilines. Thus, a mixture of nitrostyrenes **1a–l** and an excess of malononitrile, in the presence of sodium carbonate in 80% ethanol, underwent a novel reaction at room temperature to afford the corresponding 3-aryl-2,6-dicyano-5-methylanilines **2a–l** in good yields (Scheme 1, Table 1).



1 2

Scheme 1 Synthesis of 3-aryl-2,6-dicyano-5-methylanilines **2a–l**

The products **2a–l** were characterized on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. The mass spectrum of **2b** displayed the molecular ion peak at *m*/*z* 247, which was consistent with the structure of the adduct. The IR spectrum showed absorptions at 3469, 3361, 3232 and 2212 cm^{-1} indicating the presence of primary amine and nitrile functional groups. The ^{1}H NMR spectrum of **2b** exhibited three sharp singlets due to two methyl groups (δ = 2.42 and δ = 2.53) and an aromatic hydrogen (δ = 6.70). A fairly broad

signal (δ = 5.24) for the amine group and two doublets (δ = 7.29 and 7.43, J = 8.0 Hz) for the *para*-substituted aryl group were observed. In the ^{13}C NMR spectrum of **2b**, the two methyl groups resonated at δ = 21.3 and 21.4, and the signals for the two nitrile carbons were evident at δ = 93.8 and 96.2. In addition, three methines and seven quaternary carbons, all in the aromatic region, were in agreement with the proposed structure.

Table 1 Synthesis of 3-Aryl-2,6-dicyano-5-methylanilines **2a–l**

Product	Ar	Mp °C (Lit.)	Yield (%)[a]
2a	Ph	191 (188–190)[18]	85
2b	4-MeC_6H_4	222 (220)[20]	77
2c	4-$MeOC_6H_4$	196 (190)[20]	82
2d	2-naphthyl	275 (dec.)	84
2e	4-FC_6H_4	242–244 (241–243)[17b]	83
2f	3-$MeOC_6H_4$	201	75
2g	3-ClC_6H_4	240	80
2h	3,4-$(MeO)_2C_6H_3$	226 (224–225)[17b]	71
2i	4-ClC_6H_4	238 (236–240)[17b]	86
2j	3-MeC_6H_4	130	89
2k	3-FC_6H_4	203–204	79
2l	4-BrC_6H_4	260 (250–252)[17b]	88

[a] Yield of isolated product.

Single-crystal X-ray analysis of nitrile **2a** confirmed unambiguously the structures of the products. An ORTEP diagram of **2a** is shown in Figure 1.[21]

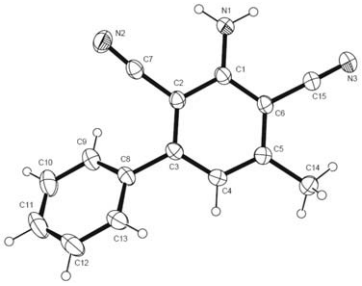


Figure 1 ORTEP representation of the molecular structure of **2a**

The formation of the 3-aryl-2,6-dicyano-5-methylaniline scaffold probably involves a complex multi-step sequence of reactions. A possible mechanism is proposed in Scheme 2. The first step may involve Michael addition of malononitrile to the nitrostyrene **1** in the presence of the base with formation of 1:1 adduct **3**, which may undergo elimination of hydrogen cyanide to form α,β-unsaturated nitrile **4**. Michael addition of a second molecule of malononitrile to intermediate **4** leads to adduct **5**, which may undergo successive addition of two further molecules of malononitrile to the nitrile triple bonds to form the 1:4 adduct **7** by way of imine **6**. Elimination of nitromethane followed by a proton shift would yield 1-azatriene intermediate **8**. Intramolecular nucleophilic attack of the methylene nitrile anion on the imine moiety would produce highly substituted cyclohexadiene intermediate **9**. Three successive 4-*exo*-dig cyclizations via nucleophilic addition of the amine group to the adjacent nitriles and subsequent ring-opening of the spirocyclic intermediates may form bicyclic **14** by way of intermediates **10**–**13**. This may undergo ring-opening and elimination of a molecule of tricyanoamine to afford 3-aryl-2,6-dicyano-5-methylaniline **2**. A fairly similar reaction pathway has been proposed for the reaction between ynones and malononitrile affording the corresponding 2,6-dicyanoanilines.[14]

When the reaction was performed using a nitrostyrene prepared from nitroethane instead of nitromethane, the same 3-aryl-2,6-dicyano-5-methylaniline was obtained, but in lower yield, indicating that the nitroalkane moiety is eliminated during the reaction. Thus the methyl group on the aromatic ring does not originate from the nitrostyrene component.

In summary, we have developed a novel and simple method for the synthesis of potentially interesting 3-aryl-2,6-dicyano-5-methylanilines. Good yields of the products, relatively short reaction times, a straightforward purification process, the use of cheap, readily available starting materials and mild reaction conditions are the main advantages of this method. The synthesis of such unsymmetric, highly substituted benzene derivatives has not been achieved by transition-metal-catalyzed reactions.

All chemicals were obtained from Merck (Germany), and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were obtained using a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-500 Avance (at 500.1 MHz and 125.8 MHz) and Bruker DPX-250 (at 250.1 MHz and 62.9 MHz) spectrometers using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. Mass spectra were recorded on an Agilent Technologies (HP) 5973 mass spectrometer operating at an ionization potential of 20 eV. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer.

3-Aryl-2,6-dicyano-5-methylanilines 2; General procedure

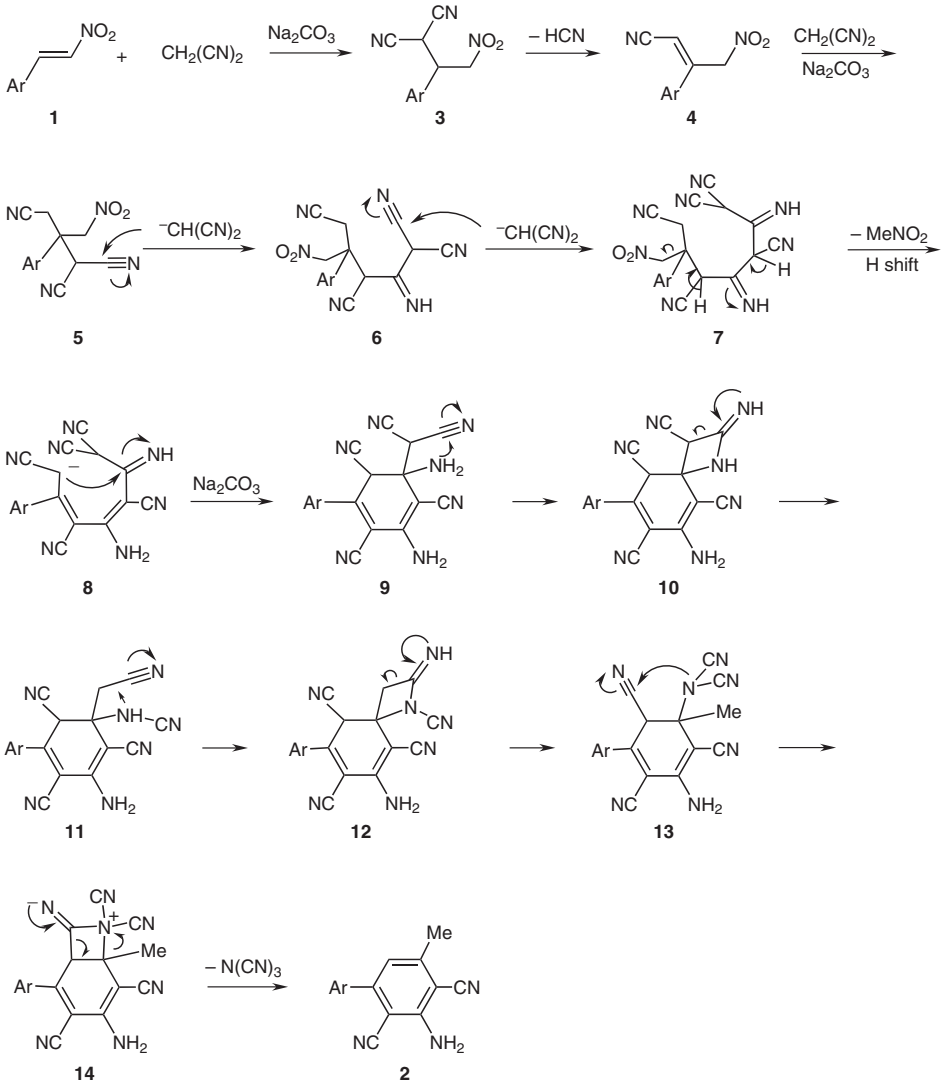
A mixture of the appropriate nitrostyrene (1 mmol), malononitrile (297 mg, 4.5 mmol) and Na_2CO_3 (3 mmol) in 80% EtOH (4 mL) was stirred at r.t. for 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction the resulting white precipitate was removed by filtration and washed with H_2O (2 × 5 mL) and then with cold 96% EtOH (2 × 5 mL). The crude product was purified by recrystallization from EtOAc.

2,6-Dicyano-5-methyl-3-phenylaniline (2a)

Yield: 0.198 g (85%); colorless crystals.

IR (KBr): 3469, 3346 and 3236 (NH), 2225 (CN), 1643, 1583, 1469, 1286, 858, 771, 696 cm^{-1}.

^1H NMR (500.1 MHz, DMSO-d_6): δ = 2.43 (s, 3 H, CH_3), 6.66 (br s, 2 H, NH_2), 6.72 (s, 1 H, CH), 7.49–7.51 (m, 5 H, 5 × CH).



Scheme 2 A possible mechanism for the formation of products **2**

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.8 (CH_3), 92.7 and 95.7 (2 × CN), 115.4 and 116.0 (2 × C), 119.0, 128.3, 128.6 and 129.2 (4 × CH), 137.6, 148.1, 149.5 and 153.3 (4 × C).

MS (EI): *m*/*z* (%) = 233 (100) [M$^+$], 205 (50), 191 (10), 168 (14), 151 (16), 117 (8), 76 (10).

Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.34; H, 4.81; N, 17.85.

2,6-Dicyano-3-(4-methylphenyl)-5-methylaniline (2b)
Yield: 0.190 g (77%); colorless crystals.

IR (KBr): 3469, 3361 and 3232 (NH), 2212 (CN), 1635, 1587, 1553, 1515, 1442, 1286, 1118, 873, 816 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.42 and 2.53 (2 × s, 6 H, 2 × CH_3), 5.24 (br s, 2 H, NH_2), 6.70 (s, 1 H, CH), 7.29 (d, *J* = 8.0 Hz, 2 H, 2 × CH), 7.43 (d, *J* = 8.0 Hz, 2 H, 2 × CH).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.3 and 21.4 (2 × CH_3), 93.8 and 96.2 (2 × CN), 115.4 and 116.1 (2 × C), 120.2, 128.2 and 129.6 (3 × CH), 134.6, 139.7, 147.6, 150.0 and 152.6 (5 × C).

MS (EI): *m*/*z* (%) = 247 (100) [M$^+$], 232 (25), 219 (20), 205 (20), 182 (5), 177 (8), 149 (7), 91 (4).

Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.58; H, 5.37; N, 16.83.

2,6-Dicyano-3-(4-methoxyphenyl)-5-methylaniline (2c)
Yield: 0.216 g (82%); colorless crystals.

IR (KBr): 3465, 3344 and 3244 (NH), 2224 (CN), 1643, 1612, 1582, 1520, 1470, 1443, 1302, 1261, 1186, 1033, 824 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.53 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 5.21 (br s, 2 H, NH_2), 6.69 (s, 1 H, CH), 7.01 (d, *J* = 8.6 Hz, 2 H, 2 × CH), 7.49 (d, *J* = 8.6 Hz, 2 H, 2 × CH).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.4 (CH_3), 55.4 (OCH_3), 93.7 and 96.1 (2 × CN), 114.3 (CH), 115.4 and 116.3 (2 × C), 120.2 and 129.7 (2 × CH), 129.8, 147.5, 149.7, 152.6 and 160.8 (5 × C).

MS (EI): *m*/*z* (%) = 263 (100) [M$^+$], 248 (16), 220 (23), 193 (24), 166 (10), 132 (8).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.77; H, 5.12; N, 15.90.

2,6-Dicyano-5-methyl-3-(2-naphthyl)aniline (2d)
Yield: 0.238 g (84%); colorless crystals.

IR (KBr): 3470, 3357 and 3238 (NH), 2222 (CN), 1639, 1607, 1584, 1470, 1279 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.47 (s, 3 H, CH_3), 6.70 (br s, 2 H, NH_2), 6.87 (s, 1 H, CH), 7.59–7.61 (m, 2 H, 2 × CH), 7.65 (dd, *J* = 8.7 Hz, 2.2 Hz, 1 H, CH), 7.99–8.02 (m, 2 H, 2 × CH), 8.05 (d, *J* = 8.9 Hz, 1 H, CH), 8.11 (s, 1 H, CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.9 (CH_3), 92.9 and 95.7 (2 × CN), 115.4 and 116.1 (2 × C), 119.3, 125.8, 126.7, 127.0, 127.6, 127.8, 128.1 and 128.3 (8 × CH), 132.5, 132.8, 135.0, 148.1, 149.5 and 153.4 (6 × C).

MS (EI): *m*/*z* (%) = 283 (100) [M$^+$], 267 (35), 255 (22), 167 (20), 149 (50), 141 (29), 127 (8).

Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.54; H, 4.62; N, 14.83. Found: C, 80.42; H, 4.81; N, 14.58.

2,6-Dicyano-3-(4-fluorophenyl)-5-methylaniline (2e)
Yield: 0.209 g (83%); pale yellow crystals.

IR (KBr): 3473, 3354 and 3236 (NH), 2224 (CN), 1641, 1610, 1583, 1562, 1518, 1473, 1446, 1256, 1252, 1167, 833 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.43 (s, 3 H, CH_3), 6.67 (br s, 2 H, NH_2), 6.73 (s, 1 H, CH), 7.35 (dd, $^3J_{FH}$ = 8.8 Hz, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH), 7.59 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{FH}$ = 5.5 Hz, 2 H, 2 × CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.8 (CH_3), 92.7 and 95.8 (2 × CN), 115.3 (C), 115.5 (d, $^2J_{FC}$ = 21.8 Hz, CH), 115.9 (C), 119.0 (CH), 130.6 (d, $^3J_{FC}$ = 8.6 Hz, CH), 133.9 (d, $^4J_{FC}$ = 2.4 Hz, C), 148.1, 148.4 and 153.3 (3 × C), 162.6 (d, $^1J_{FC}$ = 246.8 Hz, C–F).

MS (EI): *m*/*z* (%) = 251 (100) [M$^+$], 236 (8), 223 (30), 186 (10), 167 (13), 158 (6), 149 (40), 109 (9).

Anal. Calcd for $C_{15}H_{10}FN_3$: C, 71.70; H, 4.01; N, 16.72. Found: C, 71.79; H, 3.89; N, 16.66.

2,6-Dicyano-3-(3-methoxyphenyl)-5-methylaniline (2f)
Yield: 0.197 g (75%); colorless crystals.

IR (KBr): 3472, 3356 and 3238 (NH), 2222 (CN), 1641, 1602, 1587, 1474, 1417, 1261, 1234, 1165, 1042, 862, 787, 704 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.43 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.64 (br s, 2 H, NH_2), 6.75 (s, 1 H, CH), 7.04–7.09 (m, 3 H, 3 × CH), 7.41 (t, *J* = 7.8 Hz, 1 H, CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.8 (CH_3), 55.2 (OCH_3), 92.7 and 95.7 (2 × CN), 113.8 and 114.8 (2 × CH), 115.3 and 116.0 (2 × C), 119.0, 120.5 and 129.7 (3 × CH), 138.9, 148.0, 149.3, 153.3 and 159.1 (5 × C).

MS (EI): *m*/*z* (%) = 263 (100) [M$^+$], 248 (26), 234 (68), 220 (23), 205 (29), 193 (36), 178 (15), 166 (25), 140 (23), 132 (27).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.81; H, 5.04; N, 15.83.

3-(3-Chlorophenyl)-2,6-dicyano-5-methylaniline (2g)
Yield: 0.214 g (80%); colorless crystals.

IR (KBr): 3464, 3356 and 3240 (NH), 2232 (CN), 1645, 1585, 1545, 1404, 1290, 1244, 1095, 854, 800, 710 cm^{-1}.

^{1}H NMR (250.1 MHz, DMSO-d_6): δ = 2.45 (s, 3 H, CH_3), 6.77 (br s, 2 H, NH_2), 6.79 (s, 1 H, CH), 7.48–7.61 (m, 4 H, 4 × CH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.8 (CH_3), 92.6 and 96.1 (2 × CN), 115.3 and 115.8 (2 × C), 118.9, 127.1, 128.1, 129.0 and 130.4 (5 × CH), 133.2, 139.5, 147.8, 148.3 and 153.3 (5 × C).

MS (EI): *m*/*z* (%) = 269 (31) [M$^+$, ^{37}Cl], 267 (100) [M$^+$, ^{35}Cl], 239 (17), 232 (22), 217 (17), 205 (36), 177 (21), 151 (16), 102 (17), 89 (17), 75 (22).

Anal. Calcd for $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.76; N, 15.70. Found: C, 67.50; H, 3.82; N, 15.52.

2,6-Dicyano-3-(3,4-dimethoxyphenyl)-5-methylaniline (2h)
Yield: 0.208 g (71%); colorless crystals.

IR (KBr): 3485 and 3379 (NH), 2235 (CN), 1632, 1583, 1524, 1479, 1407, 1267, 1230, 1148, 1045, 847, 800 cm^{-1}.

^{1}H NMR (250.1 MHz, DMSO-d_6): δ = 2.44 (s, 3 H, CH_3), 3.81 and 3.82 (2 × s, 6 H, 2 × OCH_3), 6.64 (br s, 2 H, NH_2), 6.78 (s, 1 H, CH), 7.10–7.11 (m, 2 H, 2 × CH), 7.14 (s, 1 H, CH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.8 (CH_3), 55.5 and 55.6 (2 × OCH_3), 92.4 and 95.0 (2 × CN), 111.5 and 112.0 (2 × CH), 115.5 and 116.3 (2 × C), 118.8 and 121.0 (2 × CH), 129.7, 147.8, 148.4, 149.3, 149.6 and 153.4 (6 × C).

MS (EI): *m*/*z* (%) = 293 (100) [M$^+$], 278 (20), 250 (59), 207 (26), 151 (32), 69 (33), 57 (34).

Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.60; H, 5.19; N, 14.17.

3-(4-Chlorophenyl)-2,6-dicyano-5-methylaniline (2i)
Yield: 0.230 g (86%); colorless crystals.

IR (KBr): 3465, 3352 and 3244 (NH), 2212 (CN), 1645, 1578, 1553, 1497, 1470, 1445, 1379, 1286, 1090, 1012, 822 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.43 (s, 3 H, CH_3), 6.71 (br s, 2 H, NH_2), 6.73 (s, 1 H, CH), 7.54 (d, *J* = 8.5 Hz, 2 H, 2 × CH), 7.57 (d, *J* = 8.5 Hz, 2 H, 2 × CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.9 (CH_3), 92.6 and 96.0 (2 × CN), 115.3 and 115.9 (2 × C), 118.9, 128.6 and 130.2 (3 × CH), 134.2, 136.4, 148.2, 148.3 and 153.3 (5 × C).

MS (EI): *m*/*z* (%) = 269 (24) [M$^+$, ^{37}Cl], 267 (100) [M$^+$, ^{35}Cl], 252 (3), 239 (15), 232 (19), 217 (15), 205 (38), 177 (18), 149 (20), 102 (8), 75 (9).

Anal. Calcd for $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.76; N, 15.70. Found: C, 67.44; H, 3.67; N, 15.55.

2,6-Dicyano-5-methyl-3-(3-methylphenyl)aniline (2j)
Yield: 0.220 g (89%); colorless crystals.

IR (KBr): 3424, 3352 and 3238 (NH), 2214 (CN), 1637, 1587, 1558, 1445, 1288, 1030, 864, 775, 702 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.36 and 2.43 (2 × s, 6 H, 2 × CH_3), 6.63 (br s, 2 H, NH_2), 6.72 (s, 1 H, CH), 7.29 (d, *J* = 7.7 Hz, 1 H, CH), 7.31 (d, *J* = 8.1 Hz, 1 H, CH), 7.32 (s, 1 H, CH), 7.38 (t, *J* = 7.5 Hz, 1 H, CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.8 and 20.9 (2 × CH_3), 92.7 and 95.6 (2 × CN), 115.4 and 116.1 (2 × C), 119.0, 125.4, 128.5, 128.8 and 129.8 (5 × CH), 137.6, 137.9, 148.0, 149.7 and 153.4 (5 × C).

MS (EI): *m*/*z* (%) = 247 (100) [M$^+$], 232 (25), 219 (22), 205 (21), 190 (4), 177 (5), 165 (4), 123 (5), 109 (5), 96 (6).

Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.65; H, 5.43; N, 16.86.

2,6-Dicyano-3-(3-fluorophenyl)-5-methylaniline (2k)
Yield: 0.198 g (79%); colorless crystals.

IR (KBr): 3472, 3330 and 3237 (NH), 2224 (CN), 1643, 1614, 1581, 1542, 1469, 1421, 1290, 1249, 1139, 858, 750, 706 cm^{-1}.

^{1}H NMR (250.1 MHz, DMSO-d_6): δ = 2.45 (s, 3 H, CH_3), 6.76 (br s, 2 H, NH_2), 6.78 (s, 1 H, CH), 7.31–7.43 (m, 3 H, 3 × CH), 7.57 (dt, $^3J_{HH}$ = 8.3 Hz, $^4J_{FH}$ = 6.5 Hz, 1 H, CH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 20.3 (CH_3), 92.1 and 95.5 (2 × CN), 114.7 (C), 114.8 (d, $^2J_{FC}$ = 22.7 Hz, CH), 115.3 (C), 115.5 (d, $^2J_{FC}$ = 21.9 Hz, CH), 118.4 (CH), 124.1 (d, $^4J_{FC}$ = 2.8 Hz, CH), 130.1 (d, $^3J_{FC}$ = 8.5 Hz, CH), 139.2 (d, $^3J_{FC}$ = 8.1 Hz, C), 147.4 (d,

$^4J_{FC}$ = 2.0 Hz, C), 147.8 and 152.7 (2 × C), 161.3 (d, $^1J_{FC}$ = 244.6 Hz, C–F).

MS (EI): *m*/*z* (%) = 251 (36) [M$^+$], 206 (67), 155 (91), 125 (19), 75 (20), 43 (100).

Anal. Calcd for $C_{15}H_{10}FN_3$: C, 71.70; H, 4.01; N, 16.72. Found: C, 71.61; H, 4.19; N, 16.68.

3-(4-Bromophenyl)-2,6-dicyano-5-methylaniline (2l)
Yield: 0.275 g (88%); colorless crystals.

IR (KBr): 3450, 3358 and 3244 (NH), 2212 (CN), 1645, 1556, 1501, 1497, 1470, 1445, 1394, 1290, 1080, 1012, 820 cm^{-1}.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 2.42 (s, 3 H, CH_3), 6.72 (br s, 3 H, CH and NH_2), 7.47 (d, *J* = 8.0 Hz, 2 H, 2 × CH), 7.70 (d, *J* = 8.0 Hz, 2 H, 2 × CH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 20.9 (CH_3), 92.5 and 96.0 (2 × CN), 115.4 and 115.9 (2 × C), 118.8 (CH), 122.9 (C), 130.5 and 131.6 (2 × CH), 136.8, 148.2, 148.3 and 153.4 (4 × C).

MS (EI): *m*/*z* (%) = 313 (100) [M$^+$, ^{81}Br], 311 (87) [M$^+$, ^{79}Br], 232 (21), 217 (21), 205 (40), 177 (16), 151 (13), 116 (13), 102 (11), 89 (11), 75 (12).

Anal. Calcd for $C_{15}H_{10}BrN_3$: C, 57.71; H, 3.23; N, 13.46. Found: C, 57.81; H, 3.36; N, 13.30.

Acknowledgment

This research project (6102036/1/02) was supported by the Research Council of the University of Tehran.

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(21) Selected X-ray crystallographic data for compound **2a**: $C_{15}H_{11}N_3$, monoclinic, space group = $P2_1/c$, *a* = 3.9096(5) Å, *b* = 21.267(3) Å, *c* = 14.7077(19) Å, *β* = 95.388(2)°, *V* = 1217.50(4) Å^3, *T* = 295(2) K, *Z* = 4, D_{calcd} = 1.27 g·cm^{-3}, μ (Mo-Kα) = 0.078 mm^{-1}, 1579 observed reflections, final *R*1 = 0.058, *wR*2 = 0.150 and for all data *R*1 = 0.085, *wR*2 = 0.163. Crystallographic data for compound **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 734566. Copies of these data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.