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Synthesis of Di- and Triamino-1,1':3',1''-terphenyls from Arylethylidene- and Arylidenemalonodinitriles

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Abstract

A three-step synthesis of several di- or triamino-*m*-terphenyls **19** - **23** from 3- or 4-nitrobenzylidene-malonodinitriles **1** and 1-[3- or 4-nitro(or amino)phenyl]ethylidenemalonodinitriles **2** is reported. Gewald's method was applied for a one-pot preparation from **1** and **2** of 5'-amino[1,1':3',1''-terphenyl]-4',6'-dicarbonitriles **5** - **15** which bear the nitro or amino/nitro groups on the side rings of the terphenyl system. An attempt to optimize yields of the terphenyls **5** - **15** by selective introduction of the nitro or amino functions on the phenyl groups of starting dinitriles **1** and **2** was carried out. Compounds **5** - **13** were smoothly reduced with tin and hydrochloric acid to afford 5'-amino[1,1':3',1''-terphenyl]-4',6'-dicarbonitriles **14** - **18** having only the amino groups on the side benzene rings. The terphenyls **14** - **18** were denitrilated to yield di- or triamino-1,1':3',1''-terphenyls **19** - **23**. The decyanation reaction was carried out by heating **14** - **18** for 4 h at 220 °C in a pressure vessel (~2.5 MPa) with ethanolic sodium hydroxide solution.

Keywords: polyaryls; polyamines; amino nitriles

Introduction

Amino-*m*-terphenyls are potentially very useful construction units for a variety of applications in organic chemistry, polymer chemistry, and in research related to environmental protection. The amino functions of di- or triamino-1,1':3',1''-terphenyls **19** - **23** (Scheme 1) can be easily exchanged for a number of other substituents and groups, including the isocyanate function. However, a survey of the chemical literature has revealed that there are only few methods of limited scope that are useful for the synthesis of polyamino-*m*-terphenyls.

In this report we wish to outline a three-step synthetic approach which allows the preparation of amino-*m*-terphenyls **19** - **23** in a simple and convenient manner. These potentially useful compounds are synthesized from easily accessible precursors, i.e., benzylidenemalonodinitriles **1** and 1-(phenyl)ethylidenemalonodinitriles **2**. Our general synthetic strategy depicted in Scheme 1 takes advantage of a little-exploited reaction,

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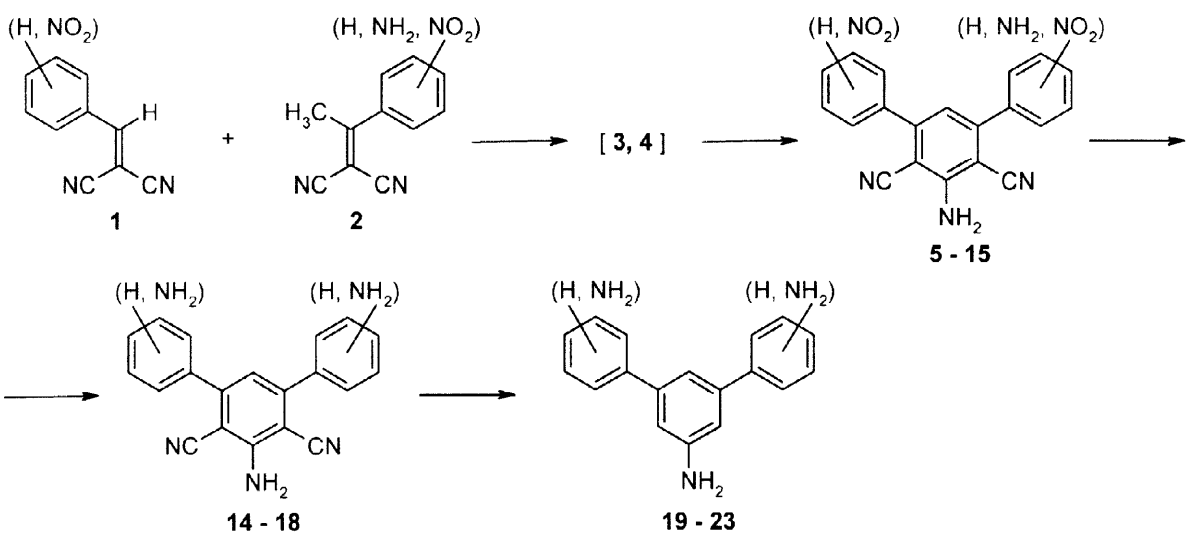
reported for the first time by Gewald and Schill [1]. They had observed that the reaction of a benzylidenemalonodinitrile with 1-(phenyl)ethylidenemalonodinitriles affords, in a single synthetic step, the so called 3,5-diphenyl-2,6-dicyanoanilines. In an approach reported by these authors, the middle ring of the *m*-terphenyl system was thus constructed in a one-pot reaction. Furthermore, two nitrile groups and the amino function introduced in the course of the synthesis on the newly formed middle aromatic ring, are potentially susceptible to further reactions. Such transformation may include the removal of the nitrile functions or the exchange of the amino group for other substituents. Our earlier investigations have revealed that the single nitrile group on an aromatic systems, in the *ortho* or neighbouring positions with respect to the amino functions, is easily removed in a one-pot reaction. This decyanation reaction involves hydrolysis, under pressure, of the nitrile group and the decarboxylation of the resulting aminocarboxylic or *o*-aminocarboxylic anions [2,3]. We have found that aromatic amines obtained through this denitrilation process are not substantially decomposed and the yields of the decyanation reaction leading to aromatic amines are high or very high [4,5]. The observation that the amino group on an aromatic system can resist such severe conditions, as heating under high pressure in alkaline solutions, has encouraged us to investigate decyanation of several *m*-terphenyls **14** - **18**. All these compounds have at least one unprotected amino group in other positions than in the vicinity of the nitrile function. In connection with the above considerations, a new, short and simple route to polyamino-1,1':3',1"-terphenyls **19** - **23** was envisioned.



Scheme 1
General Synthesis of Di- and Triamino-1,1':3',1"-terphenyls **19** - **23** from Benzylidenemalonodinitriles **1** and 1-(Aryl)-ethylidenemalonodinitriles **2**

There are few reported synthetic strategies for the preparation of polyamino-*m*-terphenyls. The nitration of the parent hydrocarbon with fuming nitric acid affords a trinitro compound, which is then reduced to give 4,4',4"-triamino-1,1':3',1"-terphenyl [6]. The benzidine rearrangement seems to give rise to 4,6'-diamino-1,1':3',1"-terphenyl [7]. However, this old preparation of little synthetic value has not been reinvestigated in recent decades. Nearly all other methods

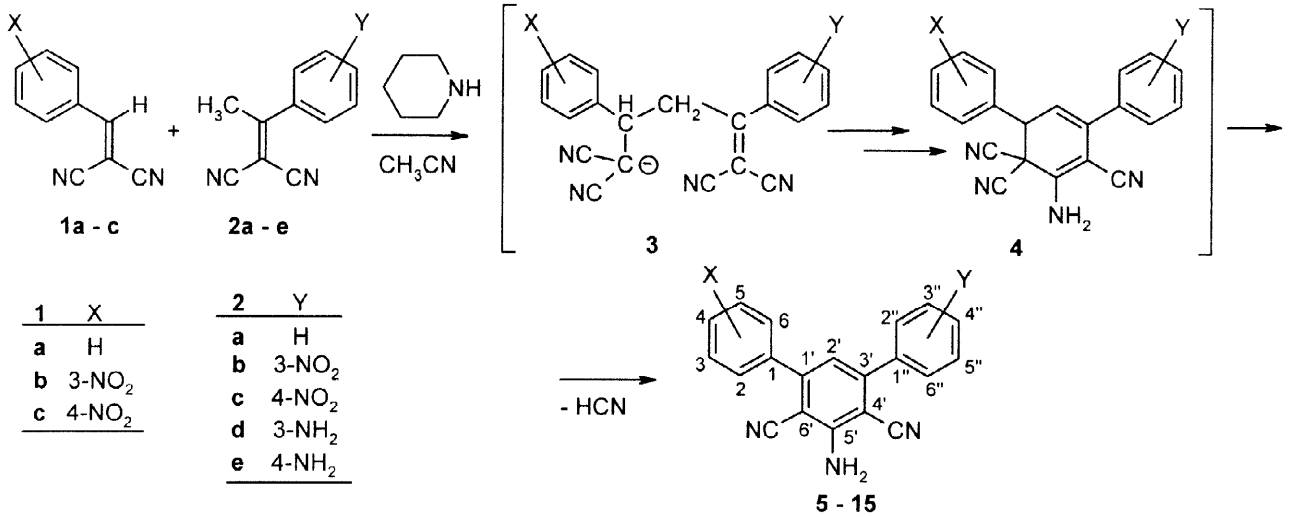
employ the following approach: to a *meta* dihalogenobenzene, or its derivatives, are attached two functionalized phenyl groups. The formation of the new phenyl-phenyl bonds to the central ring of the *m*-terphenyl system has been carried out in the Ullmann [8,9], or more recently, in the Suzuki reaction [10]. Thus, 4,5',4"-triamino-1,1':3',1"-terphenyl (**23**) has presumably been prepared in a complex synthesis involving the anomalous Ullmann reaction. Unfortunately, even the basic physical data for this triaminoterphenyl have not been reported [8]. Di- or triamino-1,1':3',1"-terphenyls have been used as starting compounds for the synthesis of a variety of charge transporting agents [11,12], charge generating agents [13,14], photoreceptors [15,16], or polymers [11,17] - just to mention selected examples. These areas of application of polyamino-*m*-terphenyls are covered by the extensive, recent patent literature. All di- and triamino-*m*-terphenyls **19 - 23** reported herein are new compounds.

Results and Discussion

In redesigning the Gewald reaction to suit the new synthesis of polyamino-*m*-terphenyls, we have turned our attention to nitrobenzylidenemalonodinitriles (**1b**, **1c**) and nitro- or amino-substituted ethylidenemalonodinitriles **2b-e** (Scheme 2). The first step in the Gewald synthesis is the Michael addition of an anion, generated from a molecule of ethylidenemalonodinitrile **2**, to the benzylidenemalonodinitrile **1**. The addition is followed by the Thorpe cyclization of the Michael product **3** to the cyclohexadiene system **4**. Finally, the elimination of hydrogen cyanide from **4** on heating in acetonitrile, affords the substituted 5'-amino[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **5 - 15**. All these compounds have the amino or the nitro groups as substituents on the side rings of the *m*-terphenyl system. We assumed that the introduction of the nitro group on the phenyl system of the investigated benzylidenemalonodinitriles **1** or/and ylidenemalonodinitriles **2**, should enhance reactivity of these dinitriles in the Michael step of the reaction sequence leading to the terphenyls **5 - 9**. It was hoped that the increased reactivity of **1** and/or **2** in the addition step should, in turn, increase the overall yield of **5 - 9** (Table 1). However, no substantial differences in yields of dinitroterphenyls **7**, **8**, and **9**, have been noticed, as compared with the yield of amino-nitro-terphenyls **10**, **11**, and **13**, respectively. It is somewhat surprising that the terphenyls having the amino and nitro groups on the side rings (**10 - 13**) were obtained in slightly better yields than the terphenyls **7 - 9** carrying two nitro groups on the side rings. Thus, the expectation that the introduction of the nitro groups in both ylidenemalonodinitriles **1** and **2** would result in a substantial increase in yields of the terphenyls **7 - 9** were not confirmed by our experiments.

The reaction of **1a** with aminophenylethylidenemalonodinitriles **2d** or **2e** gave terphenyls **14** or **15** in poor yields: 32% and 29%, respectively (Table 1, entries 13 and 14). Presumably an anion generated from **2d** or **2e** acts as a weak nucleophile in the addition step to the molecule of the ylidenedinitrile **1a**. On the other hand, the introduction of the nitro group on the phenyl ring in **1**, as in the case of **1b** and **1c**, caused a nearly two-fold increase in the yields of their reaction with **2d** or **2e** (Table 1, entry 9: **10** - 84%; entry 10: **11** - 53%; entry 11: **12** - 50%;

entry 12: **13** - 52%). Apparently, the ability of **1b** or **1c** to accept a nucleophile generated from **2d** or **2e**, is high enough to overcome the diminished reactivity of aminophenylethylidenemalonodinitriles.



1	X
a	H
b	3-NO_2
c	4-NO_2

2	Y
a	H
b	3-NO_2
c	4-NO_2
d	3-NH_2
e	4-NH_2

Scheme 2
Synthesis of Substituted 5'-Amino[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **5** - **15** from Ylidenemalonodinitriles **1** and **2**

Table 1
Preparation of Nitro- and/or Amino-substituted [1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **5** - **15** from **1a** or Nitrobenzylidenemalonodinitriles **1** and from **2a** or 1-(Amino- or Nitrophenyl)ethylidenemalonodinitriles **2**

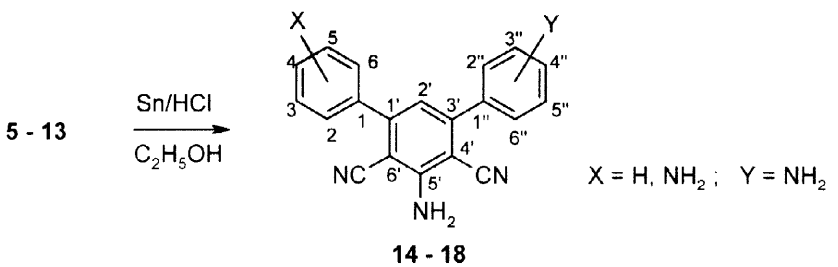
Entry	Substrates	Product	X	Y	Yield (%)
1	**1a** and **2b**	**5**	H	3"-NO_2[a]	59
2	**1b** and **2a**	**5**	3-NO_2	H[a]	66
3	**1a** and **2c**	**6**	H	4"-NO_2[b]	77
4	**1c** and **2a**	**6**	4-NO_2	H[b]	76
5	**1b** and **2b**	**7**	3-NO_2	3"-NO_2	63
6	**1b** and **2c**	**8**	3-NO_2	4"-NO_2	63
7	**1c** and **2b**	**8**	4-NO_2	3"-NO_2	47
8	**1c** and **2c**	**9**	4-NO_2	4"-NO_2	44
9	**1b** and **2d**	**10**	3-NO_2	3"-NH_2	84
10	**1b** and **2e**	**11**	3-NO_2	4"-NH_2	53
11	**1c** and **2d**	**12**	4-NO_2	3"-NH_2	50
12	**1c** and **2e**	**13**	4-NO_2	4"-NH_2	52
13	**1a** and **2d**	**14**	H	3"-NH_2[c]	32
14	**1a** and **2e**	**15**	H	4"-NH_2[d]	29

[a] For compound **5** 3"-NO_2 ≡ 3-NO_2.
[b] For compound **6** 4"-NO_2 ≡ 4-NO_2.
[c] For compound **14** 3"-NH_2 ≡ 3-NH_2.
[d] For compound **15** 4"-NH_2 ≡ 4-NH_2.

Nitro- or aminophenylethylidenemalonodinitriles **2b** - **e** were synthesized through the condensation of corresponding nitro- or aminoacetophenones with malonodinitrile in the presence of ammonium acetate and acetic acid. Unfortunately, **2b** and **2c** were obtained as thick oils which crystallized very slowly at 0 °C in the course of 2 - 3 weeks. The crystallization was more rapid after seeding the oily products with previously obtained

authentic crystals of **2b** or **2c**. In contrast with these difficulties, and with an earlier preparation of **2d** in a very poor yield (14%) [18], the condensation of 3'- or 4'-aminoacetophenone with malonodinitrile went smoothly, giving **2d** or **2e** in satisfactory yields. To introduce three amino groups on the terphenyl system, as in **21** - **23** (Table 3), the intermediate compounds **7** - **13** should have two nitro- (**7** - **9**) or amino- and nitro groups (**10** - **13**, Table 2) on the side rings. Since the synthesis of starting ylidenedinitriles **2d** or **2e** is less complicated than **2b** or **2c**, for a larger-scale preparation of triaminoterphenyls **21** - **23** the route leading from **2d** or **2e**, *via* amino-nitroterphenyls **10** - **13**, seemed more convenient.

The nitro group of ylidenemalonodinitriles **1** and **2** perform an essential role in the first step of the synthetic sequence which leads to the terphenyls **5** - **13**. The presence of the nitro groups in **1** and/or **2** considerably facilitated the formation of the central ring of the terphenyls **5** - **13** and had a substantial influence on their yields (Table 1). The nitro groups of compounds **5** - **13** are also precursors of the amino groups of the target aminoterphenyls **21** - **23**. After performing their task in the first stages of the synthetic sequence, the nitro groups of **5** - **13** were reduced to give the amino functions. This reduction was necessary since the next transformation involves heating of **14** - **18** in strong alkaline solutions (Table 3). The reduction of nitro terphenyls **5** - **13** was carried out in a standard manner using tin and ethanol-hydrochloric acid solutions (Scheme 3). Under these conditions, the reduction of dinitroterphenyls **5** - **9** was as smooth and efficient as the reduction of amino-nitroterphenyls **10** - **13** (Scheme 3, Table 2).



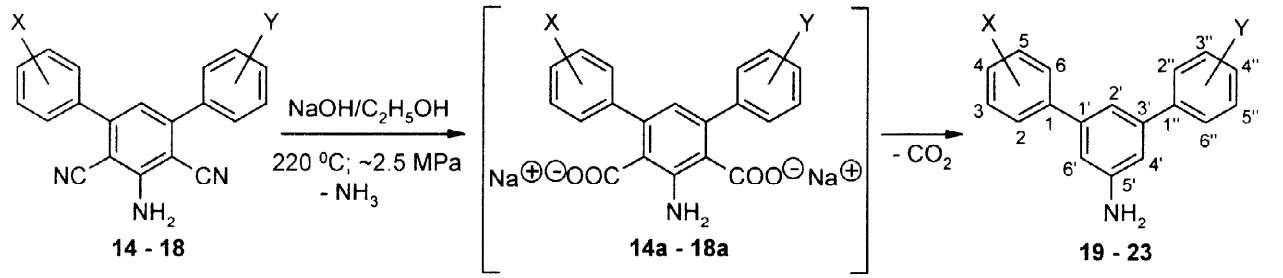
Scheme 3
Preparation of Di- or Triamino[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **14** - **18**

Table 2
The Reduction of Nitro-substituted 5'-Amino-[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **5** - **13** with Tin and Hydrochloric Acid

Entry	Substrate	X	Y	Product	X	Y	Yield (%)
1	**5**	H	3"-NO_2[a]	**14**	H	3"-NH_2[b]	87
2	**6**	H	4"-NO_2[c]	**15**	H	4"-NH_2[d]	95
3	**7**	3-NO_2	3"-NO_2	**16**	3-NH_2	3"-NH_2	91
4	**10**	3-NO_2	3"-NH_2	**16**	3-NH_2	3"-NH_2	93
5	**8**	3-NO_2	4"-NO_2	**17**	3-NH_2	4"-NH_2	95
6	**11**	3-NO_2	4"-NH_2	**17**	3-NH_2	4"-NH_2	88
7	**12**	4-NO_2	3"-NH_2	**17**	4-NH_2	3"-NH_2	92
8	**9**	4-NO_2	4"-NO_2	**18**	4-NH_2	4"-NH_2	90
9	**13**	4-NO_2	4"-NH_2	**18**	4-NH_2	4"-NH_2	86

[a] For compound **5** 3"-NO_2 ≡ 3-NO_2.
[b] For compound **14** 3"-NH_2 ≡ 3-NH_2.
[c] For compound **6** 4"-NO_2 ≡ 4-NO_2.
[d] For compound **15** 4"-NH_2 = 4-NH_2.

Di- or triamino-[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles (**14 - 18**) were then subjected to the final, denitrilation reaction. This reaction involves heating in a pressure vessel at ~220 °C for several hours of the fine powdered terphenyls **14 - 18** with an excess of sodium hydroxide dissolved in ethanol. Under such conditions, the two nitrile groups of **14 - 18** were removed to afford di- or triaminoterphenyls **19 - 23** in moderate yield. As expected, the unprotected amino groups on the terphenyl system were not substantially affected by the severe conditions of the denitrilation reaction.



Scheme 4
Denitrilation of Di- and Triamino[1,1':3',1"-terphenyl]-4',6'-dicarbonitriles **14 - 18**

Table 3
Synthesis of Di- and Triamino-1,1':3',1"-terphenyls **19 - 23**

Entry	Substrate	Product	X	Y	Yield (%)	m.p. (°C)
1	**14**	**19**	H	3"-NH_2[a]	69	62-63
2	**15**	**20**	H	4"-NH_2[b]	79	69-70
3	**16**	**21**	3-NH_2	3"-NH_2[a]	68	89-91
4	**17**	**22**	3-NH_2	4"-NH_2	36	96-98
5	**18**	**23**	4-NH_2	4"-NH_2	49	191-192

[a] For compound **19** 3"-NH_2 ≡ 3-NH_2.
[b] For compound **20** 4"-NH_2 ≡ 4-NH_2.

At this point it seems appropriate to mention that simple and efficient Gewald synthesis of 1-amino-3,5-diarylbenzene-2,6-dicarbonitriles [1] has remained for a very long time without practical use in organic synthesis. Its synthetic potential has been totally unexploited and has stayed dormant. This has presumably been due to a very low reactivity of sterically hindered nitrile groups of the Gewald's amino-3,5-diarylbenzenedicarbonitriles [19]. These compounds are unaffected under a variety of hydrolytic conditions. It is presumed that heating of compounds **14 - 18** with ethanolic sodium hydroxide solution at pressure of ~ 2.5 MPa and at temp. above 200 °C, may cause the conversion of the nitrile groups to anions of corresponding carboxylic acids **14a - 18a** (Scheme 4). These dianions seem to be unstable at temperatures 220 - 230 °C and easily decarboxylate to amines **19 - 23**. It is difficult to establish whether both dicarboxylic acid anions (**14a - 18a**) decarboxylate simultaneously or in a sequential process. Thus, the nature of the decarboxylation reaction remains unclear.

Amines **19 - 23** are obtained as solids which have proved difficult to purify by several routine methods such as crystallization or sublimation under reduced pressure. When sublimed, they form very thick oils which solidify into glass-like solids of an undefined or of a very

broad melting points. Attempts to recrystallize amino-terphenyls **19 - 23** from a variety of alcohols and other solvents often result in formation of syrup-like solutions. These properties are presumably associated with the specific nature of investigated amines. All obtained compounds have a characteristic substitution pattern, i.e. in **19 - 23** at least one amino group is in the *meta* position with respect to other phenyl groups. The synthesized amines resemble *meta*-aminobiphenyls, which also form very thick oils. Furthermore, a hypothesis concerning the existence of stable non-planar conformers for *m*-terphenyl has also been put forward [20,21].

Amines **19 - 23** are stable during storage. They behave as relatively strong bases and easily form hydrochlorides which dissolve well in water.

Conclusions

The regioselectivity of introducing the amino functions on the *m*-terphenyl system *via* the reaction sequence presented here (Scheme 1), has some limitations. The Gewald reaction obviously allows the introduction of the amino group on the middle ring of synthesized terphenyls, exclusively in the 5' position. The amino functions on the side rings can be placed in the following position: 3 or 4 for the diamino-*m*-terphenyls **19** or **20**, and in (3,3"), (3,4") or (4,4") positions for the triamino-terphenyls **21**, **22**, and **23**, respectively (Table 3). The substitution pattern of amino-terphenyls **19 - 23** is thus closely connected with the mode of substitution of starting ylidenemalonodinitriles **1** and **2**, and their ability to undergo the transformation in the Gewald reaction. Unfortunately, *o*-nitrobenzylidenemalonodinitrile and 1-(2-nitrophenyl)ethylidenemalonodinitrile have failed, presumably due to sterical reasons, to undergo the Gewald reaction. Hence, we have not been able to introduce the amino functions in the 2 or both 2 and 2" positions of the *m*-terphenyl system. Therefore, the synthesis of certain triamino-*m*-terphenyls which would have at least one amino group in the 2 or 2" position, has not been feasible by the approach presented herein.

Experimental Section

Melting points were determined on a Mel-Temp II melting point apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Brucker IFS 48 spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were taken at 500 MHz and 125 MHz respectively with a Brucker AMX 500 spectrometer using $CDCl_3$ or DMSO-d_6 as solvents and TMS as an internal standard. High resolution mass spectra (HRMS) were obtained on a FINNIGAN MAT 95S spectrometer. Accurate masses are reported for the molecular ion (M^+). Elementar analyses were performed by the Regional Laboratory of Physical and Chemical Analyses, Kraków.

Synthesis of starting ylidenemalonodinitriles.

Benzylidenemalonodinitrile (**1a**) [22], 3-nitrobenzylidenemalonodinitrile (**1b**) [22], 4-nitrobenzylidenemalonodinitrile (**1c**) [23], and 1-phenylethylidenemalonodinitrile (**2a**) [24] were obtained according to procedures reported in the literature.

*1-(3- or 4-Nitrophenyl)ethylidenemalonodinitriles (**2b**) and (**2c**); General Procedure:*

In a flask fitted with Dean-Stark water separator was placed glacial AcOH (2.4 g, 0.04 mol) and ammonium acetate (1.5 g, 0.02 mol). The flask was gently heated to dissolve ammonium acetate. A solution of 3'- or 4'-nitroacetophenone (8.3 g, 0.05 mol) in benzene (40 ml) and malonodinitrile (3.3 g, 0.05 mol) were added. The solution was heated to vigorous reflux during 4 h, washed with water (3×40 ml), and dried over anhydrous magnesium sulfate. Benzene was removed under reduced pressure to give thick, brown oil. The oil was dissolved in hot ethanol (40 ml), chilled to room temperature and seeded with authentic crystals of **2b** or **2c**. The precipitate was filtered off and recrystallized from ethanol. It was found that, unless seeded, crude oily **2b** or **2c** crystallized with difficulty when kept at 0°C for 2 or 3 weeks. In some experiments cooling of the ethanol solutions of crude oily **2b** or **2c** to -78°C was also helpful to induce the crystallization.

*1-(3-Nitrophenyl)ethylidenemalonodinitrile (**2b**) [25]:*
light brown cubic crystals; yield 7.1 g (67 %); m.p. 102 - 103°C (lit. [25] m.p. 145 °C, no spectral data); ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 3H), 7.76 (dd, 1H, *J*= 8.1, 7.9 Hz), 7.91 (d, 1H, *J*= 7.9 Hz), 8.38 (s, 1H), 8.42 (d, 1H, *J*= 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 24.3, 87.5, 111.7, 111.8, 122.3, 126.4, 130.6, 132.9, 137.3, 148.5, 172.4; IR (KBr) 3086, 2929, 2226, 1600, 1586, 1530, 1360, 854, 758, 702 cm^{-1}. Anal. Calcd for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 62.08; H, 3.26; N, 19.76.

*1-(4-Nitrophenyl)ethylidenemalonodinitrile (**2c**) [24]:*
light brown cubic crystals; yield 7.5 g (70 %); m.p. 153 °C (lit. [24] m.p. 154 °C); ^{1}H NMR ($CDCl_3$) δ 2.70 (s, 3H), 7.71 (d, 2H, *J*= 8.7 Hz), 8.37 (d, 2H, *J*= 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 24.4, 87.6, 111.6, 111.7, 124.3 (2C), 128.4 (2C), 141.6, 149.5, 172.8; IR (KBr) 3111, 2939, 2232, 1600, 1580, 1523, 1354, 858, 758, 701 cm^{-1}.

*1-(3- or 4-Aminophenyl)ethylidenemalonodinitriles (**2d**) and (**2e**); General Procedure:*

A mixture of 3'- or 4'-aminoacetophenone (13.5 g, 100 mmol), malonodinitrile (6.9 g, 105 mmol), ammonium acetate (2.5 g, 32 mmol), glacial AcOH (2.5 g, 42 mmol), and benzene (30 ml) was magnetically stirred and heated for 3 h with continuous removal of water in a water separator. Usually, shortly after the beginning of heating (~ 15 min) yellow crystalls of the condensation product start to separate from the hot reaction solution. The mixture was

chilled to 10°C, the solid ylidenemalonodinitrile was filtered off and washed with cold ethanol to afford **2d** or **2e** as yellow needles.

*1-(3-Aminophenyl)ethylidenemalonodinitrile (**2d**):*
yield 15.5 g (85%); m.p. 166 - 167°C; ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3H), 3.88 (s, 2H), 6.79 (s, 1H), 6.82 (d, 1H, *J*= 8.0 Hz), 6.88 (d, 1H, *J*= 7.8 Hz), 7.26 (dd, 1H, *J*= 8.0, 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 24.2, 84.2, 112.8, 113.0 (2C), 117.2, 118.6, 130.1, 136.9, 146.9, 175.9; IR (KBr) 3463, 3369, 3230, 2226, 1624 cm^{-1}. Anal. Calcd for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 71.98; H, 4.84; N, 23.06.

*1-(4-Aminophenyl)ethylidenemalonodinitrile (**2e**) [18]:*
yield 16.1 g (88%); m.p. 205 - 206 °C (lit. [18] m.p. 185 °C); ^{1}H NMR ($(CD_3)_2SO$) δ 2.52 (s, 3H), 6.47 (s, 2H), 6.64 (d, 2H, *J*= 8.8 Hz), 7.60 (d, 2H, *J*= 8.8 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 22.8, 73.7, 112.8 (2C), 115.3, 115.7, 121.3, 131.0 (2C), 154.3, 173.5; IR (KBr) 3456, 3362, 3237, 2214, 1643 cm^{-1}.

*Synthesis of Nitro- and/or Amino-substituted 5'-Amino[1,1':3',1''-terphenyl]-4',6'-dicarbonitriles **5** - **15**; General Procedure:*

To a magnetically stirred solution of arylidenemalonodinitrile **1** (15 mmol) and 1-aryl-ethylidenemalonodinitrile **2** (15 mmol) in acetonitrile (25 ml) was slowly added piperidine (0.5 ml). The solution darkened, warmed up, and the solid Thorpe product **4** usually precipitated. The mixture was then heated and stirred under gentle reflux for 1 - 2 h to complete the elimination of hydrogen cyanide from **4**. The solid terphenyls **5** - **15** were filtered off and recrystallized (Table 1).

*5'-Amino-3-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**5**):*
colourless rods from CH_3CN, m.p. 234 - 236 °C ; ^{1}H NMR ($(CD_3)_2SO$) δ 6.93 (s, 1H), 6.99 (s, 2H, N*H*$_2$), 7.51-7.57 (m, 3H), 7.65-7.68 (m, 2H), 7.84 (dd, 1H, *J*= 8.2, 7.8 Hz), 8.13 (d, 1H, *J*= 7.8 Hz), 8.37 (d, 1H, *J*= 8.2 Hz), 8.49 (s, 1H); ^{13}C NMR ($(CD_3)_2SO$) δ 94.1, 94.9, 115.8, 115.9, 118.6, 123.5, 124.2, 128.6 (2C), 128.7 (2C), 129.6, 130.3, 135.4, 137.3, 138.8, 147.4, 147.8, 150.2, 154.1; IR (KBr) 3475, 3369, 3243, 2208, 1636, 1522, 1338 cm^{-1}. Anal. Calcd for $C_{20}H_{12}N_4O_2$: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.39; H, 3.61; N, 16.41.

*5'-Amino-4-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**6**):*
yellow needles from CH_3NO_2, m.p. 241 - 242 °C, (lit. [26] m.p. 244 - 246 °C); ^{1}H NMR ($(CD_3)_2SO$) δ 6.88 (s, 1H), 7.01 (s, 2H, N*H*$_2$), 7.51-7.57 (m, 3H), 7.65-7.68 (m, 2H), 7.95 (d, 2H, *J*= 8.6 Hz), 8.37 (d, 2H, *J*= 8.6 Hz); ^{13}C NMR could not be obtained due to low solubility of **6** in most NMR solvents; IR (KBr) 3456, 3356, 3243, 2214, 1661, 1513, 1347 cm^{-1}. Anal. Calcd for $C_{20}H_{12}N_4O_2$: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.42; H, 3.58; N, 16.34.

5'-Amino-3,3''-dinitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (7):
pale yellow amorphous solid (after sublimation), m.p. 256 - 257 °C, insoluble in common solvents; ^{1}H NMR and ^{13}C NMR could not be obtained; IR (KBr) 3469, 3349, 3243, 2220, 1649, 1530, 1347 cm^{-1}. Anal. Calcd for $C_{20}H_{11}N_5O_4$: C, 62.34; H, 2.88; N, 18.17. Found: C, 61.99; H, 2.92; N, 18.15.

5'-Amino-3,4''-dinitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (8):
light yellow amorphous solid from CH_3NO_2, m.p. 306 - 307 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 7.02 (s, 1H), 7.14 (s, 2H, NH_2), 7.85 (dd, 1H, *J*= 8.2, 7.9 Hz), 7.96 (d, 2H, *J*= 8.8 Hz), 8.14 (d, 1H, *J*= 7.9 Hz), 8.37-8.40 (m, 3H), 8.51 (s, 1H); ^{13}C NMR could not be obtained due to insufficient solubility of **8** in most NMR solvents; IR (KBr) 3444, 3349, 3249, 2214, 1655, 1520, 1349 cm^{-1}. Anal. Calcd for $C_{20}H_{11}N_5O_4$: C, 62.34; H, 2.88; N, 18.17. Found: C, 62.09; H, 2.78; N, 18.25.

5'-Amino-4,4''-dinitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (9):
yellow needles from CH_3NO_2, m.p. 352 - 353 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 6.96 (s, 1H), 7.15 (s, 2H, NH_2), 7.95 (d, 4H, *J*= 8.8 Hz), 8.38 (d, 4H, *J*= 8.8 Hz); ^{13}C NMR could not be obtained due to insufficient solubility of **9** in most NMR solvents; IR (KBr) 3475, 3369, 3237, 2214, 1642, 1523, 1352 cm^{-1}. Anal. Calcd for $C_{20}H_{11}N_5O_4$: C, 62.34; H, 2.88; N, 18.17. Found: C, 62.09; H, 2.88; N, 17.90.

3,5'-Diamino-3''-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (10):
pale yellow plates from CH_3NO_2, m.p. 270 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.35 (s, 2H, NH_2), 6.69 (d, 1H, *J*= 7.8 Hz), 6.74 (d, 1H, *J*= 7.4 Hz), 6.77 (s, 1H), 6.84 (s, 1H), 6.92 (s, 2H, NH_2), 7.16 (dd, 1H, *J*= 7.8, 7.4 Hz), 7.84 (dd, 1H, *J*= 7.8, 7.5 Hz), 8.11 (d, 1H, *J*= 7.5 Hz), 8.37 (d, 1H, *J*= 7.8 Hz), 8.45 (s, 1H); ^{13}C NMR ($(CD_3)_2SO$) δ 93.7, 94.8, 113.5, 114.9, 115.75, 115.85, 115.88, 118.4, 123.4, 124.1, 129.2, 130.4, 135.3, 138.0, 138.9, 147.2, 147.8, 149.0, 151.2, 154.1; IR (KBr) 3425, 3356, 3224, 2214, 1643, 1530, 1359 cm^{-1}. Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.40; H, 3.60; N, 19.43.

4,5'-Diamino-3''-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (11):
small yellow rods from CH_3NO_2, m.p. 281 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.65 (s, 2H, NH_2), 6.65 (d, 2H, *J*= 8.4 Hz), 6.77 (s, 2H, NH_2), 6.82 (s, 1H), 7.38 (d, 2H, *J*= 8.4 Hz), 7.81 (dd, 1H, *J*= 7.8, 7.6 Hz), 8.08 (d, 1H, *J*= 7.6 Hz), 8.34 (d, 1H, *J*= 7.8 Hz), 8.43 (s, 1H); ^{13}C NMR ($(CD_3)_2SO$) δ 92.1, 93.7, 113.4 (2C), 116.4, 113.6, 118.0, 123.3, 123.6, 123.9, 129.8 (2C), 130.3, 135.2, 139.2, 146.8, 147.8, 150.6, 150.7, 154.3; IR (KBr) 3431, 3349, 3224, 2208, 1649, 1532, 1350 cm^{-1}. Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.36; H, 3.75; N, 19.70.

3,5'-Diamino-4''-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (12):
yellow amorphous solid (after sublimation), m.p. 308 - 309 °C; ^{1}H NMR and ^{13}C NMR spectra of **12** could not be obtained due to insufficient solubility; IR (KBr) 3419, 3343, 3161, 2214,

1668, 1513, 1347 cm^{-1}. Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.28; H, 3.74; N, 19.60.

*4,5'-Diamino-4''-nitro[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**13**):*
orange needles from CH_3NO_2, m.p. 286 - 287 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.65 (s, 2H, N*H*$_2$), 6.65 (d, 2H, *J*= 8.5 Hz), 6.77 (s, 2H, N*H*$_2$), 6.78 (s, 1H), 7.37 (d, 2H, *J*= 8.5 Hz), 7.89 (d, 2H, *J*= 8.7 Hz), 8.34 (d, 2H, *J*= 8.7 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 94.9, 93.8, 113.4 (2C), 116.0, 116.5, 117.8 (2C), 123.6 (2C), 129.8 (2C), 130.1 (2C), 144.1, 147.0, 147.8, 150.6, 150.7, 154.3; IR (KBr) 3425, 3349, 3205, 2208, 1655, 1523, 1347 cm^{-1}. Anal. Calcd for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71. Found: C, 67.39; H, 3.75; N, 19.79.

*3,5'-Diamino[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**14**):*
colourless needles from CH_3NO_2, m.p. 243 - 244 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.31 (s, 2H, N*H*$_2$), 6.60-6.76 (m, 4H), 6.77 (s, 2H, N*H*$_2$), 7.13 (s, 1H), 7.45-7.68 (m, 5H); ^{13}C NMR ($(CD_3)_2SO$) δ 93.7, 93.9, 113.5, 114.8, 115.7, 116.0, 116.1, 118.3, 128.4 (2C), 128.7 (2C), 129.2, 129.4, 137.5, 138.1, 148.9, 149.6, 150.8, 154.1; IR (KBr) 3425, 3393, 3349, 3218, 2208, 1655 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.09; H, 4.63; N, 18.36.

*4,5'-Diamino[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**15**):*
pale yellow needles from CH_3NO_2, m.p. 321 - 322 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.64 (s, 2H, N*H*$_2$), 6.66-6.70 (m, 3H), 6.71 (s, 2H, N*H*$_2$), 7.37 (d, 2H, *J*= 8.2 Hz), 7.49-7.61 (m, 5H); ^{13}C NMR ($(CD_3)_2SO$) δ 92.2, 92.9, 113.5 (2C), 116.4, 116.8, 117.9, 123.9, 128.5 (2C), 128.7 (2C), 129.3, 129.7 (2C), 137.8, 149.4, 150.5 (2C), 154.4; IR (KBr) 3431, 3356, 3218, 2208, 1643 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.07; H, 4.60; N, 18.13.

*The Reduction of Nitro-substituted 5'-Amino[1,1':3',1''-terphenyl]-4',6''-dicarbonitriles **5** - **13**; General Procedure:*

A vigorously stirred mixture of the terphenyl **5** - **13** (4 mmol), tin powder (2.5 g), and ethanol (30 ml) was heated to 80 °C and conc. hydrochloric acid (18 ml) was slowly added during 2 h. After approximately one third of the acid had been added, the suspension of the nitro-terphenyl usually dissolved and the mixture became clear for a few minutes, then a fine precipitate began to separate. After additional 1 h of heating and stirring, the chilled mixture was poured into stirred, 20% sodium hydroxide solution. The terphenyls **14** - **18** were filtered off, washed with water, and recrystallized from nitromethane (Table 2). For compounds **14** and **15** obtained from nitroterphenyls **5** and **6**, respectively, physical and spectral data were identical with the data of **14** and **15** synthesized directly from aminophenyl-ethylidenemalonodinitriles (Table 1, entry 13 and 14).

*3,3'',5'-Triamino[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**16**):*
pale yellow needles from DMF - H_2O, m.p. 284 - 285 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.32 (s, 4H, 2×NH_2), 6.65 (s, 1H), 6.70 (d, 2H, *J*= 7.8 Hz), 6.71 (s, 2H), 6.72 (d, 2H, *J*= 7.4 Hz), 6.76 (s, 2H, NH_2), 7.15 (dd, 2H, *J*= 7.8, 7.4 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 93.5 (2C), 113.4 (2C), 114.8 (2C), 115.6 (2C), 116.1 (2C), 118.0 (2C), 129.1 (2C), 138.2 (2C), 148.9 (2C), 150.6 (2C), 154.0; IR (KBr) 3469, 3375, 3331, 3224, 2214, 1630 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_5$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.48; H, 4.69; N, 21.63.

*3,4'',5'-Triamino[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**17**):*
pale yellow needles from DMF - H_2O, m.p. 322 - 323 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.28 (s, 2H, NH_2), 5.60 (s, 2H, NH_2), 6.57 (s, 2H, NH_2), 6.63 (s, 1H), 6.64 (d, 2H, *J*= 8.5 Hz), 6.65 (d, 2H, *J*= 7.8 Hz), 6.68 (d, 2H, *J*= 7.8 Hz), 6.72 (s, 1H), 7.12 (t, 1H, *J*= 7.8 Hz), 7.33 (d, 2H, *J*= 8.5 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 92.1, 92.6, 113.5 (2C), 114.6, 115.6, 116.3, 116.8, 117.6, 124.0, 129.1, 129.6 (2C), 138.5, 148.9, 150.2, 150.3, 150.4, 154.3, 162.3; IR (KBr) 3437, 3349, 3218, 2208, 1643 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_5$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.57; H, 4.71; N, 21.29.

*4,4'',5'-Triamino[1,1':3',1''-terphenyl]-4',6'-dicarbonitrile (**18**):*
yellow amorphous solid from DMF - H_2O, m.p. 395 - 396 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.57 (s, 4H, 2×NH_2), 6.46 (s, 2H, NH_2), 6.63 (s, 1H), 6.64 (d, 4H, *J*= 8.4 Hz), 7.32 (d, 4H, *J*= 8.4 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 91.3 (2C), 113.4 (4C), 117.0 (2C), 117.3, 124.3 (2C), 129.5 (4C), 150.0 (2C), 150.2 (2C), 154.6; IR (KBr) 3431, 3356, 3218, 2208, 1649 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_5$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.43; H, 4.67; N, 21.46.

*Elimination of Nitrile Groups from the Terphenyls **14** - **18**. General Procedure for the synthesis of Amines **19** - **23**:*

Di- or triaminodicyanoterphenyl **14** - **18** (6 mmol) was suspended in a solution of sodium hydroxide (3.0 g, 75 mmol) in ethanol (100 ml). The mixture was heated at 220 °C for 4 h, without stirring, in a 250 ml autoclave (~2.5 MPa). On opening of the autoclave a strong odour of ammonia was noticeable. Ethanol was evaporated under reduced pressure and the residue was mixed with water to dissolve inorganic salts and the excess of sodium hydroxide. The mixture was cooled in ice-water for 2 h and the precipitated crude amine was filtered off and washed thoroughly with water. Dry amine was dissolved in 10 % hydrochloric acid (5 ml) and the brown solution was filtered, cooled in an ice bath, and neutralized by the slow addition of aqueous ammonia. White precipitate was filtered off and washed with water. The amines **19** - **23** obtained in this manner were suitable for most synthetic purposes. An analytical sample was further purified by dissolving of a di- or triaminoterphenyl in a small amount of methanol and converting it again into a hydrochloride by the addition of conc. hydrochloric acid. The hydrochloride solution was cooled to 0 °C for 3 - 4 h, the precipitate was filtered off and dissolved in a small amount of water. The hydrochloride was converted into free amine with

conc. aqueous ammonia. The precipitated amine was filtered off, washed with water and dried under vacuum over silica gel. Some di- or triaminoterpenyls **19 - 23** can be recrystallized from a mixture of methanol-water. Others crystallize with difficulty or separate from such solutions as glassy solids of undefined melting points. The purified amines can be stored at room temp. and in darkness for several months, while their hydrochlorides slowly decompose on storage.

*[1,1':3',1''-Terphenyl]-3,5'-diamine (**19**):*
yield 69 %, colourless needles from methanol - H_2O, m.p. 62 - 63 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.28 (br.s., 4H, 2×NH_2), 6.57 (d, 1H, *J*= 7.1 Hz), 6.79 (d, 1H, *J*= 7.1 Hz), 6.80 (s, 1H), 6.82 (s, 1H), 6.88 (s, 1H), 6.96 (s, 1H), 7.09 (t, 1H, *J*= 7.1 Hz), 7.33 (t, 1H, *J*= 6.8 Hz), 7.44 (t, 2H, *J*= 6.8 Hz), 7.61 (d, 2H, *J*= 6.8 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 111.3, 111.5, 112.3, 113.1, 113.2, 114.5, 126.6 (2C), 127.2, 128.8 (2C), 129.2, 141.2, 141.4, 141.7, 142.5, 148.8, 149.3; IR (KBr) 3425, 3349, 3212, 3029, 1617, 1592, 1580, 1411, 852, 764, 695 cm^{-1}; HRMS calcd for $C_{18}H_{16}N_2$ (M^+) 260.1313, found 260.1321.

*[1,1':3',1''-Terphenyl]-4,5'-diamine (**20**):*
yield 79 %, colourless amorphous solid (after sublimation), m.p. 69 - 70 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.28 (br.s., 4H, 2×NH_2), 6.68 (d, 2H, *J*= 8.0 Hz), 6.76 (s, 1H), 6.80 (s, 1H), 6.96 (s, 1H), 7.33 (t, 1H, *J*= 6.8 Hz), 7.37 (d, 2H, *J*= 8.0 Hz), 7.43 (t, 2H, *J*= 6.8 Hz), 7.62 (d, 2H, *J*= 6.8 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 110.3, 110.6, 112.5, 114.3 (2C), 126.6 (2C), 127.07, 127.14 (2C), 128.5, 128.7 (2C), 141.35, 141.37, 142.0, 148.0, 149.2; IR (KBr) 3431, 3343, 3205, 3029, 1609, 1592, 1575, 1511, 827, 764, 695 cm^{-1}; HRMS calcd for $C_{18}H_{16}N_2$ (M^+) 260.1313, found 260.1320.

*[1,1':3',1''-Terphenyl]-3,3'',5'-triamine (**21**):*
yield 68 %, colourless needles from methanol - H_2O, m.p. 89 - 91 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.19 (br.s., 6H, 3×NH_2), 6.55 (d, 2H, *J*= 7.7 Hz), 6.74 (s, 2H), 6.75 (d, 2H, *J*= 7.7 Hz), 6.83 (s, 2H), 6.88 (s, 1H), 7.08 (t, 2H, *J*= 7.7 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 111.1 (2C), 112.2 (2C), 113.0 (2C), 113.1, 114.3 (2C), 129.2 (2C), 141.9 (2C), 142.2 (2C), 148.9 (2C), 149.2; IR (KBr) 3419, 3349, 3212, 3036, 1610, 1592, 1580, 1492, 1411, 852, 783, 695 cm^{-1}; HRMS calcd for $C_{18}H_{17}N_3$ (M^+) 275.1422, found 275.1424.

*[1,1':3',1''-Terphenyl]-3,4'',5'-triamine (**22**):*
yield 36 %, colourless amorphous solid from methanol - H_2O, m.p. 96 - 98 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.21 (br.s., 6H, 3×NH_2), 6.55 (d, 1H, *J*= 7.5 Hz), 6.64 (d, 2H, *J*= 8.4 Hz), 6.66 (s, 1H), 6.72 (s, 1H), 6.75 (d, 1H, *J*= 7.5 Hz), 6.84 (s, 1H), 6.86 (s, 1H), 7.07 (dd, 1H, *J*= 7.7, 7.5 Hz), 7.31 (d, 2H, *J*= 8.4 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 110.2, 110.3, 112.3, 112.4, 113.0, 114.2 (2C), 114.5, 127.0 (2C), 128.6, 129.1, 141.7, 142.0, 142.2, 148.0, 148.7, 149.0; IR (KBr) 3429, 3345, 3209, 3031, 1617, 1592, 1580, 1517, 1404, 1287, 827, 785, 693 cm^{-1}; HRMS calcd for $C_{18}H_{17}N_3$ (M^+) 275.1422, found 275.1419.

[1,1':3',1''-Terphenyl]-4,4'',5'-triamine (23):
yield 49 %, small colourless rods from methanol - H_2O, m.p. 191 - 192 °C; ^{1}H NMR ($(CD_3)_2SO$) δ 5.13 (br.s., 6H, 3×NH_2), 6.62 (s, 2H), 6.63 (d, 4H, *J*= 8.2 Hz), 6.83 (s, 1H), 7.31 (d, 4H, *J*= 8.2 Hz); ^{13}C NMR ($(CD_3)_2SO$) δ 109.2 (2C), 111.5, 114.1 (4C), 127.0 (4C), 128.7 (2H), 141.7 (2C), 148.0 (2C), 149.0; IR (KBr) 3449, 3356, 3209, 3021, 1617, 1590, 1517, 1467, 1283, 1182, 827, 698 cm^{-1}; HRMS calcd for $C_{18}H_{17}N_3$ (M^+) 275.1422, found 275.1419.

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