

## Synthesis of 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles via dimerisation of phthalonitrile radical anion in liquid ammonia

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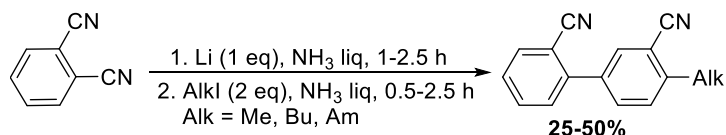
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### Abstract

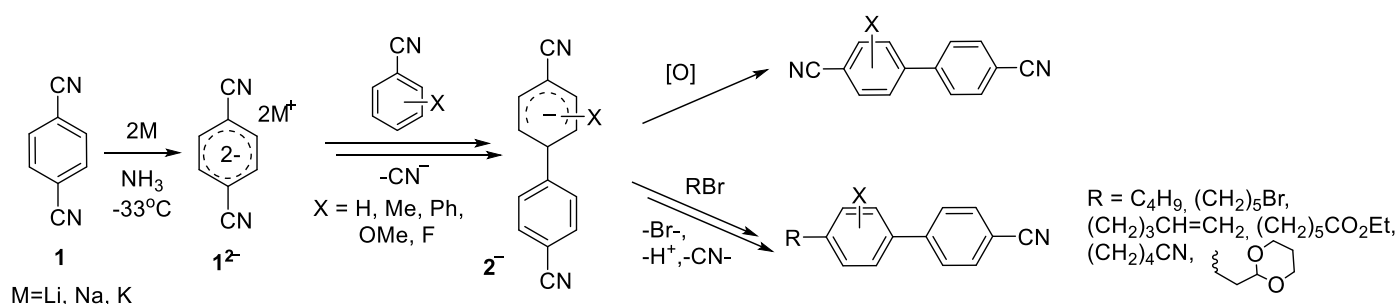
Single-electron reduction of phthalonitrile by metallic lithium in liquid ammonia resulted in a radical anion salt that underwent dimerisation yielding a long-lived intermediate, the 1,2-dicyano-4-(2-cyanophenyl)cyclohexa-2,5-dienyl anion. Alkylation of this anion with primary alkyl iodides resulted in a convenient one-pot synthesis of 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles.



**Keywords:** Phthalonitrile; radical anions; dimerisation; reductive alkylation; biphenyl-2,3'-dicarbonitriles

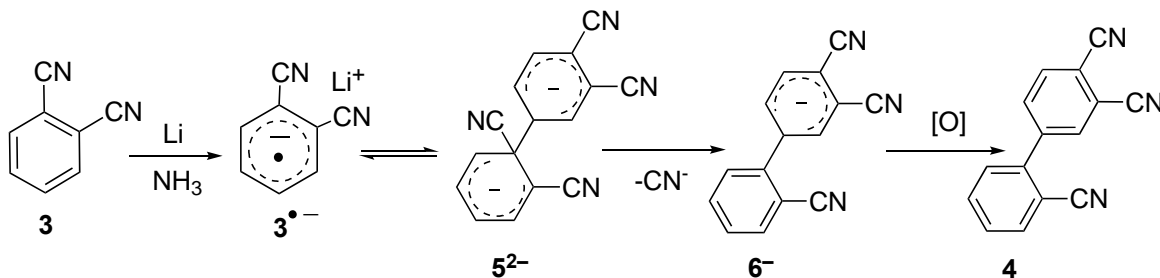
## Introduction

Biphenyls, containing a cyano group and an alkyl moiety, are considered privileged structures: precursors of new materials<sup>1-7</sup> and bioactive substances.<sup>8</sup> This stimulates the development of new, short and economical approaches to such compounds. Earlier, we demonstrated that the anionic forms – easily generated in preparative quantities by the reduction of cyanoarenes with alkali metals in liquid ammonia – are effective reagents for biaryl cross-coupling. In particular, treating the terephthalonitrile dianion (**1<sup>2-</sup>**) with neutral aromatic nitriles produces long-lived intermediates: 1-cyano-4-(4-cyanophenyl)cyclohexa-2,5-dienyl anions (**2<sup>-</sup>**; Scheme 1).<sup>9</sup> Variation of the neutral aromatic substrate and/or the type of further treatment of intermediate **2<sup>-</sup>** (oxidation or alkylation) provides a one-pot synthesis of dicyanobiphenyls,<sup>10</sup> -terphenyls<sup>11</sup> and their alkylated derivatives<sup>12</sup> in good yields (30–90%).



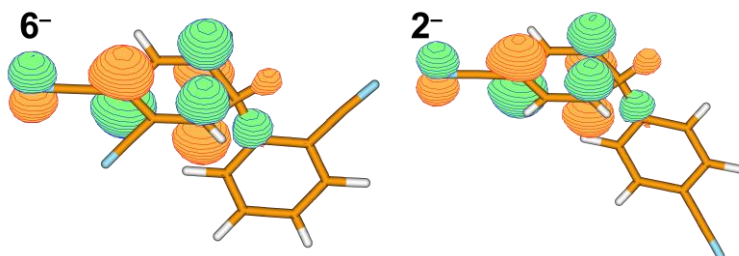
**Scheme 1.** Cross-coupling of terephthalonitrile dianion **1<sup>2-</sup>** with a neutral cyanoarene, affording cyanobiarenes.

Another synthetically fruitful biaryl coupling has been found for alkali salts of the phthalonitrile radical anion (**3<sup>•-</sup>**) in liquid ammonia, which, after simply holding the reaction mixture and further exposure to ambient air, transforms into 2,3',4'-tricyanobiphenyl (**4**), hard to prepare by other methods.<sup>13</sup> The yield of **4** depends on the nature of the counterion in the **3<sup>•-</sup>** salt, its concentration and exposure time. Optimal conditions involve stirring a 0.2–0.3 M solution of the **3<sup>•-</sup>** lithium salt in liquid ammonia for 1–2 hours at –33 °C and result in a mixture containing desired product **4** (yield 45–58%) and starting phthalonitrile **3**. The suggested reaction scheme<sup>13</sup> includes ‘head-to-tail’ dimerisation of **3<sup>•-</sup>**, yielding a dianion (**5<sup>2-</sup>**), the fast decyanation of which gives a monoanion (**6<sup>-</sup>**) presumably as a long-lived intermediate, and its further oxidation with air oxygen into tricyanobiphenyl **4** (Scheme 2).



**Scheme 2.** Dimerisation of phthalonitrile radical anion lithium salt **3<sup>•-</sup>** leading to tricyanobiphenyl **4**.

With a convenient approach to tricyanobiphenyl **4** available, we have used it as a universal precursor of previously inaccessible zinc complexes of aryl-substituted phthalocyanines.<sup>14</sup> Also, the azo-derivative of **4** ((*E*)-4-[[4-(dibutylamino)phenyl]diazenyl]-[1,1'-biphenyl]-2,3',4'-tricarbonitrile) demonstrated liquid crystalline properties and unusual phase transitions under X-ray irradiation<sup>15</sup> and thus was considered to be a promising precursor of nonlinear optical materials.<sup>16</sup> It is reasonable to suppose that the synthetic potential of radical anion **3**<sup>•-</sup> can be expanded further by involving dimer intermediate **6**<sup>-</sup> in the alkylation, if it should prove as long-lived as anion **2**<sup>-</sup>. The similarity in electronic structure (Figure 1) allows the supposition that anion **6**<sup>-</sup> would provide alkylated products similar to those from **2**<sup>-</sup>.

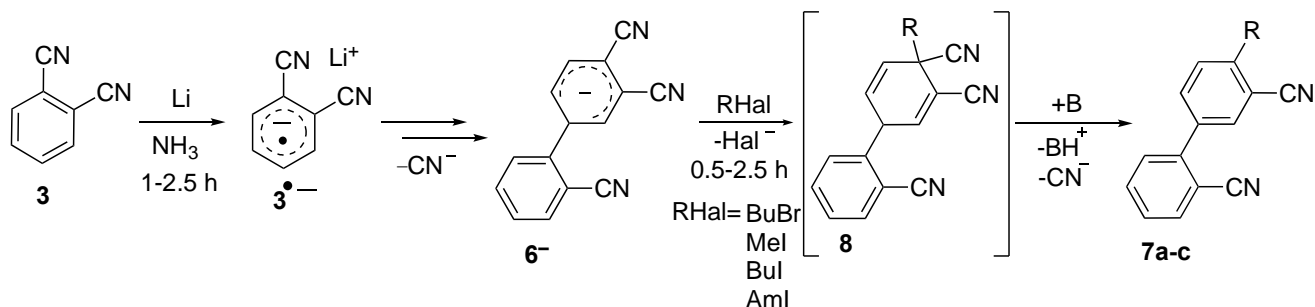


**Figure 1.** HOMO view of anions **6**<sup>-</sup> and **2**<sup>-</sup> (DFT B3LYP/6-31+G(d), GAMESS US;<sup>17</sup> Molden<sup>18,19</sup>).

Thus, the aim of the present work was to study the reactivity of anion **6**<sup>-</sup> toward alkyl halides. In the case of success, one-pot synthesis of 4'-alkyl-2,3'-dicyanobiphenyls, hard to reach by other methods, will be suggested. Moreover, biaryl coupling based on the anionic forms of aromatic nitriles will be expanded, allowing researchers to purposefully select an anionic form and an alkylating reagent for one-pot syntheses of alkylated cyanobiphenyls with a given number and positions of cyano groups and a desired alkyl moiety.

## Results and Discussion

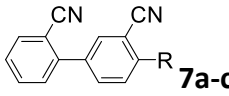
Anion **6**<sup>-</sup> was generated by the addition of metallic lithium to phthalonitrile **3** in liquid ammonia with subsequent stirring of the reaction mixture for 1–2.5 hours. Next, addition of an excess of an alkyl halide (BuBr, BuI, Aml or MeI) followed by stirring of the reaction mixture for 0.5–2.5 hours under the same conditions provided the desired 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles (**7**) in all cases (Scheme 3, Table 1). Along with these compounds, tricyanobiphenyl **4**, starting phthalonitrile **3** and the products of **3**<sup>•-</sup> alkylation were also detected.<sup>13,20,21</sup> Alkyldicyanobiphenyls **7** were easily isolated via preparative thin layer chromatography.



**Scheme 3.** One-pot synthesis of 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles **7**.

The results confirm that anion **6<sup>-</sup>** is long-lived and able to be alkylated at the low temperature of liquid ammonia. The yield of alkylcyanobiphenyls **7** depends mostly on the nature of the halogen atom in the alkyl halide and is significantly higher when bromine is replaced by iodine. The reactions with alkyl iodides provided yields of **7** comparable to those of tricyanobiphenyl **4**, which were obtained earlier under optimised conditions.<sup>13</sup> The addition of KI<sup>22</sup> slightly increased the yield of **7a** in the reaction of **6<sup>-</sup>** with butyl bromide (entries 1 and 2 in Table 1).

**Table 1.** The interaction of **6<sup>-</sup>** lithium salt<sup>a</sup> with primary alkyl halides in liquid ammonia

Entry	Alkyl halide, mmol	Reaction time, min		NMR yield, mol.%, <sup>b</sup> (isolated yield, <sup>c</sup> mol.%)
		Before alkylation	After RHal added	 <b>7a-c</b>
1	BuBr, 15.0	60	40	<b>7a</b> 11
2 <sup>d</sup>	BuBr 15.0	150	55	<b>7a</b> 18
3	BuI 15.0	60	150	<b>7a</b> 51 ( <b>45</b> )
4	BuI 11.3	150	30	<b>7a</b> 54
5	AuI 11.3	150	150	<b>7b</b> 50 ( <b>34</b> )
6 <sup>e</sup>	MeI 11.3	105	85	<b>7c</b> 30 ( <b>11</b> )
7 <sup>e</sup>	MeI 29.7	150	60	<b>7c</b> 39 ( <b>25</b> )

<sup>a</sup> **6<sup>-</sup>** generation: phthalonitrile **3** (7.5 mmol), Li (7.4 mmol), liquid NH<sub>3</sub> (30–40 ml), –33 °C. <sup>b</sup> Calculated as mean values of no less than two runs. Deviation does not exceed 5%. <sup>c</sup> Preparative TLC. <sup>d</sup> KI (7.5 mmol) additive. <sup>e</sup> The reaction mixtures also contained two dicyanobiphenyls of unidentified structure (~5%, M<sup>+</sup> = 204).

The structure of **7a–c**, together with the absence of other alkylated cyanobiphenyls, indicates highly selective alkylation at position 1 of anion **6<sup>-</sup>** thereby initially generating dihydro-derivatives (**8**), which are prone to fast dehydrocyanation under basic reaction conditions, thus forming final products **7** (Scheme 3). The high reaction regioselectivity revealed here – and the increase in the yields of products after switching from an alkyl bromide to iodide – define anion **6<sup>-</sup>** as a nucleophile reacting with alkyl halides via the S<sub>N</sub>2 mechanism. Thus, **6<sup>-</sup>** behaves like all the previously studied cyclohexadienyl anions of cyanoarenes **2<sup>3</sup>** which generally undergo heterolytic alkylation at the *ipso*-position (toward the cyano group) bearing the maximum of electronic density (a HOMO view of anions **2<sup>-</sup>** and **6<sup>-</sup>** is presented in Figure 1). This statement, at first glance, is not consistent with the observed decrease of the product yield when we go from BuI and AuI to MeI. The most probable reason is the faster solvolysis of MeI in comparison with other alkyl iodides. The resulting methylammonium salt protonates **6<sup>-</sup>**, competing with MeI, and causes the emergence of small amounts of dicyanobiphenyls together with **7c** (Entries 6, 7 in the table). The high selectivity of anion **6<sup>-</sup>** alkylation rules out the assumption of the electron transfer as the main pathway of the reaction under study. Comparatively low yields of **7** in the case of butyl bromide suggest that anion **6<sup>-</sup>** is less reactive than anions like **2<sup>-</sup>** (intermediates of cross-coupling of dianion **1<sup>2-</sup>** with neutral cyanoarenes), which under the same conditions afford alkylcyanobiphenyls with yields from good to high (Scheme 1). Obviously, such a decrease in **6<sup>-</sup>** reactivity is due to the additional electron-withdrawing cyano group in the cyclohexadienyl fragment of **6<sup>-</sup>**.

## Conclusions

We report a new economical one-pot synthesis of 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles **7**, showing promise as precursors of liquid crystalline composites for electrooptical devices<sup>24-27</sup> and drugs for agriculture.<sup>28</sup> Before the present work, compounds with a similar arrangement of cyano groups and alkyl moiety in the biphenyl scaffold were unknown. Close structural analogues of **7** are commonly obtained via transition metal-catalysed cross-coupling,<sup>8,29,30</sup> which requires reagents and catalytic systems much less available than phthalonitrile, lithium and alkyl iodide. Liquid ammonia, which is necessary as a solvent, is recyclable<sup>31</sup> and is regarded nowadays as a solvent suitable for green chemistry processes.<sup>32,33</sup>

## Experimental Section

**General.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on a Bruker Avance-III 500 instrument (at 500.03 MHz and 125.73 MHz, respectively) in *d*<sub>6</sub>-acetone, chemical shifts ( $\delta$ ) of <sup>1</sup>H and <sup>13</sup>C are in ppm relative to TMS using the solvent signals as the internal standard ( $\delta_{\text{H}} = 2.05$  ppm,  $\delta_{\text{C}} = 29.8$  and 206.3 ppm for *d*<sub>6</sub>-acetone). Signal assignment and structure justification were carried out on the basis of 2D COSY, HSQC and HMBC data. IR spectra were recorded on a Vector-22 instrument for neat samples or pelleted with KBr (0.25%). The GC-MS analysis was performed on a Hewlett-Packard G1081A instrument. The precise molecular ion weights were determined on a DFS instrument.

The relative energies and HOMOs of the anionic intermediates **2**<sup>-</sup> and **6**<sup>-</sup> were calculated with DFT B3LYP/6-31+G(d) level of theory. Both structures correspond to the local minima at the potential energy surface according to the analysis of normal vibrations. All the calculations were made with the GAMESS US package.<sup>17</sup> The HOMOs view was obtained with the MOLDEN utility.<sup>18,19</sup>

Liquid ammonia was purified just before use by dissolving in it metallic sodium, followed by distillation into a reaction vessel, cooled to -78 °C. Metallic lithium was freed from oxide film under dry hexane. Commercial phthalonitrile was purified by sublimation. Methyl iodide (Alfa Aesar) used without further purification. Commercially available butyl bromide, butyl iodide and pentyl iodide were passed through a layer of silica prior to use. Diethyl ether and hexane were distilled before use.

### Synthesis of 4'-alkyl-[1,1'-biphenyl]-2,3'-dicarbonitriles **7**: general procedure

Metallic lithium (0.052 g, 7.4 mmol) was added to a stirred suspension of phthalonitrile **3** (0.960 g, 7.50 mmol) in liquid ammonia (30–40 mL) at -33 °C under an atmosphere of ammonia. The dark-brown solution thus obtained of radical anion lithium salt **3**<sup>•-</sup> after stirring for 1-2.5 h transformed into a black-brown thin dispersion. Alkyl halide (1.5-4.0 eq to **3**) was added dropwise, and the stirring was continued for 0.5-2 h, resulting in a change of the initial dispersion colour to red-brown. Then, Et<sub>2</sub>O (30 mL) was added, the reaction mixture was allowed into contact with air and the stirring was continued until the ammonia evaporated completely and rt reached. Water (*ca.* 30 mL) was poured onto the residue to dissolve inorganic salts, insoluble tricyanobiphenyl **4** was filtered off, washed with water (2 × 10 mL), Et<sub>2</sub>O (2 × 10 mL) and dried to constant mass. The products from the water fraction were extracted with Et<sub>2</sub>O (3 × 25 mL). The combined organic extract was washed successively with water until pH 7 and brine, and dried with MgSO<sub>4</sub>. The crude residue obtained after Et<sub>2</sub>O evaporation was analysed by <sup>1</sup>H NMR spectroscopy and GC-MS. The pure products **7** were isolated by preparative TLC on glass plates with a fixed layer of silica gel (60 PF254 with

addition of gypsum, Merck), eluent – hexane/Et<sub>2</sub>O mixture (10 vol% of Et<sub>2</sub>O). The separation was controlled visually under UV irradiation. Fractions containing **7** were eluted with Et<sub>2</sub>O.

**4'-Butyl-[1,1'-biphenyl]-2,3'-dicarbonitrile (7a)**. Colorless oil (433 mg, 45%, entry 3 in Table 1). <sup>1</sup>H NMR (500.03 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 7.95 (d, *J* 2.0 Hz, H<sup>2'</sup>, 1H), 7.92 (ddd, *J* 7.8, 1.3, 0.5 Hz, H<sup>3</sup>, 1H), 7.86 (dd, *J* 8.0, 2.0 Hz, H<sup>6'</sup>, 1H), 7.82 (td, *J* 7.7, 7.7, 1.3 Hz, H<sup>5</sup>, 1H), 7.70 (ddd, *J* 7.9, 1.2, 0.5 Hz, H<sup>6</sup>, 1H), 7.65 (d, *J* 8.0 Hz, H<sup>5'</sup>, 1H), 7.64 (td, *J* 7.6, 7.6, 1.2 Hz, H<sup>4</sup>, 1H), 2.94 (t, *J* 7.8 Hz, CH<sub>2</sub><sup>1''</sup>, 2H), 1.76–1.70 (m, CH<sub>2</sub><sup>2''</sup>, 2H), 1.48–1.42 (m, CH<sub>2</sub><sup>3''</sup>, 2H), 0.98 (t, *J* 7.3 Hz, CH<sub>3</sub><sup>4''</sup>, 3H). <sup>13</sup>C NMR (125.73 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 147.8 (1C, C<sup>4'</sup>), 143.7 (C<sup>1</sup>, 1C), 137.9 (C<sup>1'</sup>, 1C), 134.7 (C<sup>3</sup>, 1C), 134.3 (C<sup>6'</sup>, 1C), 134.2 (C<sup>5</sup>, 1C), 133.7 (C<sup>2'</sup>, 1C), 131.1(1) (C<sup>5'</sup> or C<sup>6</sup>, 1C), 131.0(5) (C<sup>6</sup> or C<sup>5'</sup>, 1C), 129.6 (C<sup>4</sup>, 1C), 118.8 (C<sup>2</sup>–CN, 1C), 118.2 (C<sup>3'</sup>–CN, 1C), 113.6 (C<sup>3'</sup>, 1C), 112.1 (C<sup>2</sup>, 1C), 34.6 (C<sup>1''</sup>, 1C), 33.7 (C<sup>2''</sup>, 1C), 23.0 (C<sup>3''</sup>, 1C), 14.1 (C<sup>4''</sup>, 1C). IR (neat)  $\nu_{\max}$  (cm<sup>-1</sup>): 2226 (CN). MS (EI, 70 eV), *m/z* (I<sub>rel.</sub>, %): 260 (44.7) [M<sup>+</sup>], 259 (12.8), 245 (43.8), 232 (15.9), 231 (12.8), 219 (15.2), 218 (100.0), 217 (59.5), 190 (30.8). HRMS (*m/z*): M<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>, 260.1308; found, 260.1303.

**4'-Pentyl-[1,1'-biphenyl]-2,3'-dicarbonitrile (7b)**. Colorless oil (345 mg, 34%, entry 5 in Table 1). <sup>1</sup>H NMR (500.03 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 7.95 (d, *J* 1.9 Hz, H<sup>2'</sup>, 1H), 7.92 (ddd, *J* 7.8, 1.4, 0.6 Hz, H<sup>3</sup>, 1H), 7.86 (dd, *J* 8.0, 2.0 Hz, H<sup>6'</sup>, 1H), 7.82 (ddd, *J* 7.9, 7.6, 1.4 Hz, H<sup>5</sup>, 1H), 7.70 (ddd, *J* 7.9, 1.2, 0.6 Hz, H<sup>6</sup>, 1H), 7.65 (d, *J* = 8.0 Hz, H<sup>5'</sup>, 1H), 7.64 (td, *J* 7.6, 7.6, 1.2 Hz, H<sup>4</sup>, 1H), 2.93 (t, *J* 7.9 Hz, CH<sub>2</sub><sup>1''</sup>, 2H), 1.77–1.73 (m, CH<sub>2</sub><sup>2''</sup>, 2H), 1.46–1.37 (m, CH<sub>2</sub><sup>3''</sup>, CH<sup>4''</sup>, 4H), 0.93 (t, *J* 7.0 Hz, CH<sub>3</sub><sup>5''</sup>, 3H). <sup>13</sup>C NMR (125.73 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 147.8 (C<sup>4'</sup>, 1C), 143.8 (C<sup>1</sup>, 1C), 137.9 (C<sup>1'</sup>, 1C), 134.7 (C<sup>3</sup>, 1C), 134.3 (C<sup>5</sup>, 1C), 134.2 (C<sup>6'</sup>, 1C), 133.7 (C<sup>2'</sup>, 1C), 131.1 (C<sup>6</sup> or C<sup>5'</sup>, 1C), 131.0 (C<sup>5'</sup> or C<sup>6</sup>, 1C), 129.6 (C<sup>4</sup>, 1C), 118.8 (C<sup>2</sup>–CN, 1C), 118.1 (C<sup>3'</sup>–CN, 1C), 113.7 (C<sup>3'</sup>, 1C), 112.1 (C<sup>2</sup>, 1C), 34.8 (C<sup>1''</sup>, 1C), 32.2 (C<sup>3''</sup>, 1C), 31.2 (C<sup>2''</sup>, 1C), 23.1 (C<sup>4''</sup>, 1C), 14.2 (C<sup>5''</sup>, 1C). IR (neat)  $\nu_{\max}$  (cm<sup>-1</sup>): 2226 (CN). MS (EI, 70 eV), *m/z* (I<sub>rel.</sub>, %): 274 (35.6) [M<sup>+</sup>], 259 (16.4), 246 (43.7), 245 (38.9), 232 (15.0), 231 (25.8), 219 (16.4), 218 (100.0), 217 (49.9), 190 (32.1). HRMS (*m/z*): M<sup>+</sup> calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>, 274.1465; found 274.1457.

**4'-Methyl-[1,1'-biphenyl]-2,3'-dicarbonitrile (7c)**. White solid (203 mg, 25%, entry 7 in Table 1), mp 123.4 °C. <sup>1</sup>H NMR (500.03 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 7.93 (d, *J* 2.0 Hz, H<sup>2'</sup>, 1H), 7.91 (ddd, *J* 7.8, 1.3, 0.5 Hz, H<sup>3</sup>, 1H), 7.83–7.80 (m, H<sup>5</sup> and H<sup>6'</sup>, 2H), 7.68 (ddd, *J* 7.9, 1.2, 0.6 Hz, H<sup>6</sup>, 1H), 7.64 (td, *J* 7.7, 7.7, 1.2 Hz, H<sup>4</sup>, 1H), 7.67 (dm, *J* 8.0 Hz, H<sup>5'</sup>, 1H), 2.61 (br.s, CH<sub>3</sub>, 3H). <sup>13</sup>C NMR (125.73 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, δ): 143.8 (C<sup>4'</sup>, 1C), 143.1 (C<sup>1</sup>, 1C), 137.8 (C<sup>1'</sup>, 1C), 134.7 (C<sup>3</sup>, 1C), 134.2 (C<sup>6'</sup>, 1C), 134.1 (C<sup>5</sup>, 1C), 133.4 (C<sup>2'</sup>, 1C), 131.7 (C<sup>5'</sup>, 1C), 131.1 (C<sup>6</sup>, 1C), 129.6 (C<sup>4</sup>, 1C), 118.8 (C<sup>2</sup>–CN, 1C), 118.1 (C<sup>3'</sup>–CN, 1C), 114.1 (C<sup>3'</sup>, 1C), 112.1 (C<sup>2</sup>, 1C), 20.2 (C<sup>1''</sup>, 1C). IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 2226 (CN). MS (EI, 70 eV), *m/z* (I<sub>rel.</sub>, %): 219 (17.0), 218 (100.0) [M<sup>+</sup>], 217 (26.0), 204 (7.9), 191 (7.6), 190 (24.9), 164 (6.3). HRMS (*m/z*): M<sup>+</sup> calcd for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>, 218.0839; found 218.0843.

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## Supplementary Material

Supplementary material contains copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra of the synthesized compounds and optimized geometries of anionic intermediates  $2^-$  and  $6^-$ .

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