



Reaction of bromopentafluorobenzene and pentafluorophenyllithium with α -lithiated arylacetonitriles

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Abstract

Bromopentafluorobenzene and pentafluorophenyllithium react with α -lithiated arylacetonitriles in ether to give α -aryl-2,3,5,6-tetrafluorophenylacetonitriles, respectively. However, the reaction of bromopentafluorobenzene with α -lithiated arylacetonitriles in ether/THF affords *trans*-1,2-dicyanostilbenes. Mechanisms for the formation of the various products are proposed.

Keywords: Bromopentafluorobenzene; Pentafluorophenyllithium; \(\alpha \)-Lithiated arylacetonitriles; NMR spectroscopy; IR spectroscopy

1. Introduction

We recently found that the reaction of pentachlorophenyllithium with α -lithioarylacetonitriles at -70 °C to room temperature gave none of the expected benzyne products, α tetrachloroarylated nitriles, but rather α -aryl-2,3,5,6-tetrachlorophenylacetonitriles [1]. The condensation of the two reactants was proposed to proceed through a four-centered transition state. Similar treatment of hexachlorobenzene and α -lithioarylacetonitriles afforded α -aryl-2,3,4,5,6-pentachlorophenylacetonitriles, presumably by the usual nucleophilic aromatic substitution pathway. However, bromopentachlorobenzene reacted with α -lithioarylacetonitriles to give trans-1,2-dicyanostilbenes. The trans-stilbenes were thought to arise by a base-mediated dimerization of α -chloroarylacetonitriles, produced by lithium-chlorine exchange between bromopentachlorobenzene and the α -lithioarylacetonitriles. We have extended these studies to the reaction of bromopentafluorobenzene (1) and pentafluorophenyllithium (2) with α -lithiated arylacetonitriles 4 and report the results herein.

2. Results and discussion

We first studied the reaction of pentafluorophenyllithium (2) with α -lithioarylacetonitriles 4a-i. As shown in Scheme

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1, ether solutions of 2 and ether slurries of 4a-i (prepared at -70 °C by treating bromopentafluorobenzene (1) and arylacetonitriles 3a-i, respectively, with n-butyllithium) were mixed at -70 °C, and the resulting solutions warmed to room temperature. After proton-quench and usual work-up, the α -

Scheme 1

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$$F = \begin{cases} F & 1.4 \\ F & 2.-70^{\circ}\text{C} - \text{rt} \end{cases}$$

$$1 \text{ and } 4a-i \\ \text{in } Et_2O \end{cases}$$

$$1 \text{ in } Et_2O$$

$$4a-c, e, g \text{ in } THF \end{cases}$$

$$1 \text{ and } 4a-i \\ \text{Surple of } F = \begin{cases} F & F \\ F & F \end{cases}$$

$$1 \text{ and } 4a-i \\ \text{Surple of } F = \begin{cases} F & F \\ F & F \end{cases}$$

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$$1 \text{ and } 4a-i \\ \text{Surple of } F = \begin{cases} F & F \\ F & F \end{cases}$$

$$1 \text{ and } F = \begin{cases} F & F \\ F & F \end{cases}$$

$$1 \text{ and } F = \begin{cases} F & F \\ F & F \end{cases}$$

Table 1 Nitriles (7, 9) and trans-stilbenes (10) prepared

| Entry | Solvent a | Halo-arene | α-Lithio-nitrile | Nitrile product yield (%) | trans stilbenes yield (%) |
|-------|-----------|------------|------------------|---------------------------------|---------------------------------|
| 1 | A | 2 | 4a | 7a, 59 | |
| 2 | Α | 2 | 4b | 7b , 67 | |
| 3 | Α | 2 | 4c | 7c, 66 | |
| 4 | Α | 2 | 4d | 7d, 62 | |
| 5 | Α | 2 | 4e | 7e , 57 | |
| 6 | Α | 2 | 4f | 7f, 62 | |
| 7 | Α | 2 | 4g | 7g , 67 | |
| 8 | Α | 2 | 4h | 7h , 67 | |
| 9 | Α | 2 | 4i | 7i, 75 | |
| 10 | B (A) | 1 | 4a | 9a, 38 | (10a, 46) |
| 11 | B (A) | 1 | 4b | 9b, 51 | (10b, 27) |
| 12 | B (A) | 1 | 4c | 9c, 52 | (10c, 53) |
| 13 | B (A) | 1 | 4d | 9d, 58 | ,, |
| 14 | B (A) | 1 | 4e | 9e, 54 | (10e, 33) |
| 15 | B (A) | 1 | 4f | 9f, 56 | (,, |
| 16 | B (A) | 1 | 4g | 9g, 49 | (10g, 22) |
| 17 | B (A) | 1 | 4h | 9h, 53 | (= - 6) ==) |
| 18 | B (A) | 1 | 4i | 9i, 56 | |

a Solvent A = ether, solvent B = 1:1 ether: THF

aryl-2,3,5,6-tetrafluorophenylacetonitriles 7a-i were supplied in 57%-75% yield (see Table 1). In addition, a small amount (5%-10%) of pentafluorobenzene (8) was obtained. When these reactions were run in THF solvent the yields of 7 (<25%) were considerably reduced. The IR, ¹H NMR and ¹³C NMR spectral data for 7a-i, which are reported under Experimental details, are consistent with the proposed structures. The structure of α -(3',4'-dimethoxyphenyl)-2,3,5,6-tetrafluorophenylacetonitrile (7d) was further confirmed by X-ray crystallography [2]. Careful examination of the reaction mixtures revealed the absence of arynic products, α -aryl-

2,3,4,5-tetrafluorophenylacetonitriles 6, which would have been formed by the reaction of 4a-i and tetrafluorobenzyne (5). Thus pentafluorophenyllithium, like pentachlorophenyllithium, resists arynic generation in the presence of α -lithiated arylacetonitriles.

Bromopentafluorobenzene (1) was then treated with α -lithiated arylacetonitriles $4\mathbf{a}$ —i in ether under the same conditions as those used in the reaction of 2 and 4, and gave α -aryl-4-bromo-2,3,5,6-tetrafluorophenylacetonitriles $9\mathbf{a}$ —i in 38%–58% yield [Eq. (1)]. However, as shown in Eq. (2), 1 reacted with arylacetonitriles $4\mathbf{a}$ —c, e, g in THF, to afford the corresponding trans-1,2-dicyanostilbenes $10\mathbf{a}$ —c, e, g in 20%–50% yield along with varying amounts (20%–45%) of pentafluorobenzene (11). The IR, 1 H NMR and 13 C NMR spectral data for $9\mathbf{a}$ —i and $10\mathbf{a}$ —c, e, g were consistent with proposed structures. In addition, the structures of α -(3'-tolyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (9h) and 1,2-dicyano-1,2-di-(4'-methoxyphenyl) ethylene ($10\mathbf{c}$) were also confirmed by X-ray crystallography [3].

The mechanism for the reaction of bromopentafluorobenzene with nitrile anions 4 most likely proceeds through a typical nucleophilic aromatic pathway as shown in Scheme 2, since attack occurs preferentially at the 4-fluorine atom and the resulting Meisenheimer complex (11a-i) would be expected to be particularly stabilized by the inductive effect of the six halogen atoms [4]. In support of this mechanism, chloropentafluorobenzene when treated with α -lithiophenylacetonitrile (4a) gave the expected substitution product, i.e. α -phenyl-4-chloro-2,3,5,6-tetrafluorophenylacetonitrile. It is possible that the reaction of pentafluorophenyllithium (2) with 4a-j in ether proceeds through a similar nucleophilic aromatic substitution pathway. However the Meisenheimer complex would be expected to be destabilized by the excess negative charge at the 1-lithio site, and thus a higher reaction temperature might be necessary for such a pathway. A more likely pathway for the condensation of 2 and 4a-i involves a four-centered transition state such as 12a-i shown in Scheme 3. Subsequent proton-quench of the resulting adduct 13a-i would then afford the products 7a-i.

Finally, as shown in Scheme 4, when the reaction of 1 and 4a-c, e, g is carried out in the more polar solvent THF com-

Scheme 3.

pared to ether, the reactants most likely undergo bromolithium exchange to yield pentafluorophenyllithium (2) and α -bromoarylacetonitriles 14a, c, e, g. Under the basic conditions of the reaction, these α -bromonitriles dimerize to 1,2dicyanostilbenes 10a, c, e, g in a manner similar to that proposed previously by Makosza et al. [5].

In conclusion, we have shown that α -arylacetonitriles 4 react with pentafluorophenyllithium (2) and bromopentafluorobenzene (1) in Et₂O to yield novel α -aryl-2,3,5,6-tetrafluoro- (7) and α -aryl-4-bromo-2,3,5,6-tetrafluorophenylacetonitriles (9), respectively. However, when the reactions are run in THF, trans-1,2-dicyanostilbenes 10 are produced from the reaction of 1 and 4.

3. Experimental details

3.1. General data

All reactions were carried out under a dry, oxygen-free nitrogen atmosphere and the glassware was heated at 125 °C in an oven overnight prior to use. Tetrahydrofuran (THF) and diethyl ether solvents were passed through a column containing neutral alumina and then refluxed in the presence of sodium benzophenone ketyl until a permanent blue color was achieved. The arylacetonitrile, bromopentafluorobenzene, tetrahydrofuran (THF), ethyl ether and "BuLi were obtained from Aldrich, and were distilled or recrystallized prior to use. Melting points were taken on an electrochemical apparatus and are uncorrected. FT-IR spectra were obtained on a Nicolet Magna-IR spectrometer 550 with samples dissolved in chloroform, while NMR spectra of CDCl₃ solutions were recorded on a Brucker, WMSY 200 MHz spectrometer and ¹H chemical shifts are related to TMS as internal standard. The elemental analyses were performed by the SMU Chemistry Analytical Services.

3.2. General procedure for the reaction of pentafluorophenyllithium (2) with α -lithioarylacetonitriles (4) yielding α-aryl-2,3,5,6-tetrafluorophenylacetonitriles 7

To a stirred solution of bromopentafluorobenzene (1, 2.82) g, 10 mmol) and 40 ml of ether (or THF) at -70 °C was added 10 mmol of n-butyllithium (4 ml of a 2.5 M soln.) dropwise. Stirring was continued at -70 °C until a clear, yellow solution was obtained, indicating the conversion of 1 to pentafluorophenyllithium (2). In a separate flask, the α lithiated nitrile (4, 11 mmol) was prepared by adding nbutyllithium (11 mmol, 4.4 ml of a 2.5 M soln.) to the appropriate nitrile (3, 11 mmol in 40 ml of ether) at -70°C, followed by additional stirring (at least 2 h) until the preparation of 2 in the other flask was complete. The resulting ether slurry of 4 was then cannulated into the pentafluorophenyllithium (2) solution, which immediately turned bright red with the color intensifying as the reaction mixture was stirred an additional 2 h at -70 °C and then warmed to room temperature. After stirring for 12 h at room temperature, saturated NH₄Cl (50 ml) was added, the solution was rotoconcentrated and the residue extracted several times with CH₂Cl₂. The CH₂Cl₂ extracts were combined, washed with

Scheme 4.

water and dried (Na₂SO₄). The solvent was rotoevaporated and the crude mixture separated by chromatography using Merck Silica gel 60 (230–400 mesh) [eluant: hexanes to obtained 1,2,4,5-tetrachlorobenzene (8) followed by 19:1 hexanes/acetone to afford the nitrile 7]. The isolated yields of 7 are shown in Table 1, whereas the m.p. elemental analyses and spectral data for 7 are given below.

α-Phenyl-2,3,5,6-tetrafluorophenylacetonitrile (**7a**): colorless solid, m.p. 82–83 °C. IR (CHCl₃) (cm⁻¹): 2245 (CN). ¹H NMR (CHCl₃) δ: 5.56 (s, 1H,); 7.01–7.11 (m, 1H); 7.31–7.42 (m, 5H) ppm. Analysis: Calc. for $C_{14}H_7NF_4$: C, 63.40; H, 2.66; N, 5.28%. Found: C, 63.67; H, 2.60; N, 5.34%

 α -(3'-Methoxyphenyl)-2,3,5,6-tetrafluorophenylacetonitrile (**7b**): colorless solid, m.p. 76–77 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ: 3.79 (s, 3H); 5.51 (s, 1H); 6.96 (s, 1H); 6.96–7.01 (m, 2H); 7.07–7.08 (m, 1H); 7.24–7.28 (m, 1H) ppm. ¹³C NMR (CHCl₃) δ: 39.48; 55.40; 113.11; 116.06; 118.83; 119.47; 130.10; 131.47; 132.88; 133.05; 133.26; 134.50; 160.03 ppm. Analysis: Calc. for C₁₃H₉NF₄: C, 61.02; H, 3.07; N, 4.74%. Found: C, 61.14; H, 3.04; N, 4.85%.

 α -(4'-Methoxyphenyl)-2,3,5,6-tetrafluorophenylacetonitrile (7c): colorless solid, m.p. 76–77 °C. IR (CHCl₃) (cm⁻¹): 2248 (CN). ¹H NMR (CHCl₃) δ : 3.79 (s, 3H); 5.50 (s, 1H); 6.86 (d, J=5.8 Hz, 2H); 7.37 (d, J=5.8 Hz, 2H); 7.02–7.12 (m, 1H) ppm. Analysis: Calc. for C₁₅H₉NOF₄: C, 61.02; H, 3.07; N, 4.74%. Found: C, 61.11; H, 3.02: N, 4.94%.

 α -(3',4'-Dimethoxyphenyl)-2,3,5,6-tetrafluorophenylacetonitrile (**7d**): colorless solid, m.p. 112–113 °C. IR (CHCl₃) (cm⁻¹): 2245 (CN). ¹H NMR (CHCl₃) δ: 3.80 (s, 3H); 3.87 (s, 3H); 6.27 (s, 1H); 6.77 (s, 1H); 6.78 (d, J=5.0 Hz, 1H); 6.87 (d, J=5.0Hz, 1H); 7.67 (s, 1H) ppm. Analysis: Calc. for C₁₆H₁₁NO₂F₄: C, 59.08; H, 3.41; N, 3.41%. Found: C, 59.05; H, 3.40; N, 3.44%.

 α -(3',4'-Methylenedioxy) phenyl-2,3,5,6-tetrafluorophenylacetonitrile (7e): colorless solid, m.p. 82–83 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 5.46 (s, 1H); 6.22 (s, 2H); 6.78 (s, 1H); 6.90 (d, J = 4 Hz, 1H); 6.96 (d, J = 4 Hz, 1H); 7.00–7.13 (m, 1H) ppm. Analysis: Calc. for C₁₅H₇N₂F₄: C, 58.26; H, 2.28; N, 4.53%. Found: C, 58.21; H, 2.18; N, 4.60.

 α - (1'- Naphthyl) -2,3,5,6- tetrafluorophenylacetonitrile (7f): colorless solid, m.p. 132–134 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 6.17 (s, 1H); 7.02–7.17 (m, 1H); 7.44–7.53 (m, 3H); 7.85–7.95 (m, 4H) ppm. Analysis: Calc. for C₁₈H₉NF₄: C, 70.80; H, 2.67; N, 4.13%. Found: C, 70.97; H, 2.61; N, 4.16%.

 α -(2'-Thienyl)-2,3,5,6-tetrafluorophenylacetonitrile (7g): viscous oil. IR (CHCl₃) (cm⁻¹): 2256 (CN). ¹H NMR (CHCl₃) δ : 5.72 (s, 1H); 6.91–7.01 (m, 1H); 7.10–7.31 (m, 3H) ppm. Analysis: Calc. for C₁₂H₅NSF₄: C, 53.14; H, 1.86; N, 5.16%. Found: C, 52.97; H, 1.87; N, 5.23%.

 α -(3'-Tolyl)-2,3,5,6-tetrafluorophenylacetonitrile (7h): viscous oil. IR (CHCl₃) (cm⁻¹): 2247 (CN). ¹H NMR

(CHCl₃) δ : 2.35 (s, 3H); 5.51 (s, 1H); 7.00–7.45 (m, 5H) ppm. Analysis: Calc. for C₁₅H₁₀F₄: C, 64.52; H, 3.25; N, 5.02%. Found: C, 64.38; H, 3.19; N, 5.12%.

 α -(4'-Tolyl)-2,3,5,6-tetrafluorophenylacetonitrile (7i): colorless solid, m.p. 120–121 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 2.30 (s, 3H); 5.50 (s, 1H); 7.03–7.08 (m, 1H); 7.18 (d, J=8 Hz, 2H); 7.31 (d, J=8 Hz, 2H) ppm. Analysis: Calc. for C₁₅H₆N₅: C, 64.52; H, 3.25; N, 5.02%. Found: C, 64.39; H, 3.29; N, 5.18%.

3.3. General procedure for the reaction of bromopentafluorobenzene (1) and α -lithioaryl-acetonitriles 4 in Et₂O to give α -aryl-4-bromo-2,3,5,6-tetrafluorophenylacetonitriles 9

An ether suspension of the lithiated nitrile 4 (11 mmol), prepared in the same manner as described in the general procedure for the reaction of 2, was cannulated into an ether solution of 1 at -70 °C. The resulting suspension was allowed to warm to room temperature during which time the suspension gradually dissolved to give a deep red solution. A bright scarlet precipitate gradually formed as the solution was stirred overnight. The mixture was then worked-up in the same manner as described for the reaction of 2 and 4. The isolated yields of 9 are shown in Table 1, whereas their m.p., elemental analyses and spectra data are given below.

α-Phenyl-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (9a): colorless solid, m.p. 106–107 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ: 5.55 (s, 1H); 7.35–7.46 (m, 5H) ppm. Analysis: Calc. for $C_{14}H_6NCl_5$: C, 46.01; H, 1.65; N, 3.83%. Found: C, 46.20; H, 1.59; N, 3.98%.

 α - (3'-Methoxyphenyl) - 4-bromo - 2,3,5,6-tetrafluorophenylacetonitrile (**9b**): colorless solid, m.p. 81–82 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 3.79 (s, 3H); 5.50 (s, 1H); 6.85–7.3 (m, 4H) ppm. Analysis: Calc. for C₁₅H₈NCl₅: C, 45.55; H, 2.04; N, 3.54%. Found: C, 45.67; H, 2.08; N, 3.50%.

 α -(4'-Methoxyphenyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9c**): colorless solid, m.p. 80–81 °C. IR (CHCl₃) (cm⁻¹): 2248 (CN). ¹H NMR (CHCl₃) δ : 3.79 (s, 3H); 6.28 (s, 1H); 6.86 (d, J=5.8 Hz, 2H); 7.23 (d, J=5.8 Hz, 2H); 7.67 (s, 1H) ppm. Analysis: Calc. for C₁₅H₈NOCl₅: C, 45.55; H, 2.04; N, 3.54%. Found: C, 45.61; H, 2.01; N, 3.59%.

 α -(3',4'-Dimethoxyphenyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9d**): colorless solid, m.p. 92–93 °C. IR (CHCl₃) (cm⁻¹): 2249 (CN). ¹H NMR (CHCl₃) δ : 3.84 (s, 6H); 6.27 (s, 1H); 6.77 (s, 1H); 6.78 (d, J=5.0 Hz, 1H); 6.87 (d, J=5.0 Hz, 1H); 7.67 (s, 1H) ppm. Analysis: Calc. for C₁₆H₁₀O₂Cl₅: C, 46.93; H, 2.46; N, 3.42%. Found: C, 46.95; H, 2.36; N, 3.47%.

 α -(3',4'-Methylenedioxyphenyl)-4-bromo-2,3,5,6-tetra-fluorophenylacetonitrile (**9e**): colorless solid, m.p. 110 °C. IR (CHCl₃) (cm⁻¹): 2249 (CN). ¹H NMR (CHCl₃) δ : 5.95 (s, 2H); 6.22 (s, 1H); 6.74 (s, 1H); 6.79 (s, 2H); 7.67 (s,

1H) ppm. Analysis: Calc. for C₁₅H₆NO₂Cl₅: C, 44.00; H, 1.48; N, 3.42%. Found: C, 44.13; H, 1.42; N, 3.48%.

 α -(1'-Naphthyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9f**): colorless solid, m.p. 138–139 °C. IR (CHCl₃) (cm⁻¹): 2250 (CN). ¹H NMR (CHCl₃) δ: 6.72 (s, 1H); 7.45 (d, J = 5.1 Hz, 2H); 7.50–7.62 (m, 2H), 7.82–7.9 (m, 3H); 7.74 (s, 1H) ppm. 13 C NMR (CHCl₃) δ: 38.54; 116.31; 122.12; 124.94; 125.79; 126.26; 127.16; 127.37; 129.38; 130.12; 130.15; 131.64; 133.43; 133.77; 134.07; 135.05 ppm. Analysis: Calc. for C₁₈H₈NCl₅: C, 52.03; H, 1.94; N, 3.37%. Found: C, 52.18; H, 1.99; N, 3.45%.

 α -(2'-Thienyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9g**): colorless solid: m.p. 94–95 °C, IR (CHCl₃) (cm⁻¹): 2247 (CN). ¹H NMR (CHCl₃) δ : 6.40 (s, 1H); 6.98 (d, J=5.4 Hz, 1H); 6.98 (d, J=5.1 Hz, 1H); 7.3 (dd, J=5.1, 5.4 Hz, 1H); 7.67 (s, 1H) ppm. ¹³C NMR (CHCl₃) δ : 35.47; 114.82; 125.62; 126.43; 126.73; 131.08; 132.45; 132.66; 132.92; 134.59 ppm. Analysis: Calc. for C₁₂H₄NSCl₅: C, 38.80; H, 1.09; N, 3.77%. Found: C, 38.91; H, 1.12; N, 3.71%.

 α -(3'-Tolyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9h**): colorless solid, m.p. 104–105 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 2.34 (s, 3H); 6.30 (s, 1H); 7.11 (s, 1H); 7.14–7.24 (m, 3H); 7.68 (s, 1H) ppm. Analysis: Calc. for C₁₅H₈NCl₃: C, 47.47; H, 2.12; N, 3.69%. Found: C, 52.39; H, 2.60; N, 4.18%.

 α -(4'-Tolyl)-4-bromo-2,3,5,6-tetrafluorophenylacetonitrile (**9i**): colorless solid, m.p. 112–113 °C. IR (CHCl₃) (cm⁻¹): 2246 (CN). ¹H NMR (CHCl₃) δ : 2.34 (s, 3H); 6.30 (s, 1H); 7.19 (s, 4H); 7.67 (s, 1H) ppm. Analysis: Calc. for C₁₅H₈NCl₅: C, 47.47; H, 2.12; N, 3.69%. Found: C, 47.39; H, 2.10; N, 3.76%.

3.4. General procedure for the reaction of bromopentafluorobenzene (1) and α -lithioaryl-acetonitriles 4 in THF/ether to give 1,2-dicyano-1,2-diarylethylenes 10

A THF solution (40 ml) of lithiated nitrile 4 (11 mmol), prepared in the same manner as described in the general procedure for the reaction of 2 with 4, was cannulated into an ether solution of 1 at -70 °C. The resulting solution was allowed to warm to room temperature during which time the suspension gradually dissolved to give a deep red solution. The mixture was then worked-up in the same manner described for the reaction of 2 and 4 with the exception that a 6:1 hexane/acetone solution was required to remove the stilbenes 10 from the chromatographic column. The isolated yields of 10 are shown in Table 1, whereas their m.p., elemental analyses and spectral data are given below.

1,2-Dicyano-1,2-diphenylethylene (**10a**): colorless solid, m.p. 161–162 °C (lit. value [5]: 160 °C). ¹³C NMR (CHCl₃) &: 116.61; 125.58; 128.65; 129.25; 131.64; 131.98 ppm.

1,2-Dicyano-1,2-di-(3'-methoxyphenyl) ethylene (**10b**): colorless solid, m.p. 212–213 °C. ¹H NMR (CHCl₃) δ : 3.86 (s, 6H); 7.24–7.33 (m, 6H); 7.39 (s, 2H) ppm. Analysis: Calc. for C₁₈H₁₄N₂O: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.92; H, 5.18; N, 10.17%.

1,2-Dicyano-1,2-di-(4'-methoxyphenyl) ethylene (10c): colorless solid, m.p. 191–192 °C. ¹H NMR (CHCl₃) δ : 3.86 (s, 6H); 6.99 (d, J = 8.8 Hz, 4H); 7.78 (d, J = 8.8 Hz, 4H) ppm. 13 C NMR (CHCl₃) δ : 55.53; 114.56; 117.25; 122.68; 124.60; 130.40; 161.99 ppm. Analysis: Calc. for C₁₈H₁₄N₂O: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.71; H, 5.11; N, 10.26%.

1,2-Dicyano-1,2-di-(3',4'-methylenedioxyphenyl) ethylene (**10e**): colorless solid, m.p. 226–228 °C. ¹H NMR (CHCl₃) δ : 6.06 (s, 4H); 6.90 (d, J = 6.9 Hz, 2H); 7.26 (bs, 2H); 7.26–7.34 (m, 2H) ppm. Analysis: Calc. for C₁₈H₁₀O₄: C, 67.93; H, 3.17; N, 8.80%. Found: C, 67.79; H, 3.15; N, 8.83%.

1,2-Dicyano-1,2-di-(3'-thienyl) ethylene (10g): colorless solid, m.p. 128.5–129.0 °C. ¹H NMR (CHCl₃) δ : 7.13 (dd, J=5.1, 3.0 Hz, 2H); 7.73 (dd, J=5.1, 1.6 Hz, 2H); 8.06 (dd, J=3.0, 1.6 Hz, 2H) ppm. Analysis: Calc. for $C_{12}H_6N_2S_2$: C, 59.48; H, 2.50; N, 11.56%. Found: C, 59.60; H, 2.55; N, 11.63%.

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