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Reaction of bromopentafluorobenzene and pentafluorophenyllithium with α-lithiated arylacetonitriles

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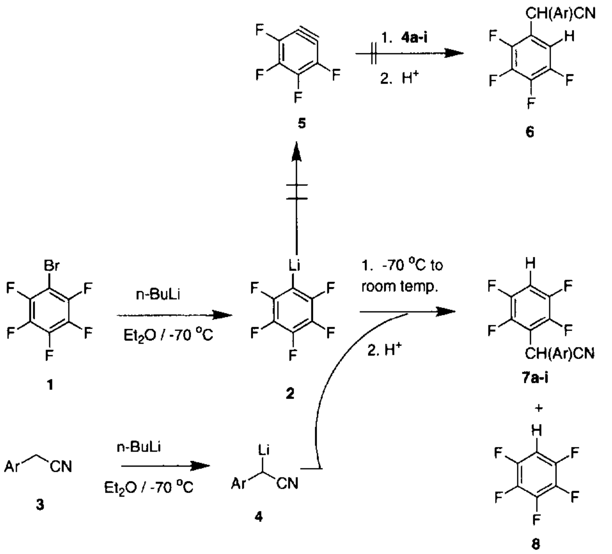
Abstract

Bromopentafluorobenzene and pentafluorophenyllithium react with α-lithiated arylacetonitriles in ether to give α-aryl-2,3,5,6-tetrafluorophenylacetonitriles and α-aryl-4-bromo-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; α-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.



a. Ar = C_6H_5
b. Ar = 3-MeO-C_6H_4
c. Ar = 4-MeO-C_6H_4
d. Ar = 3,4-$(MeO)_2C_6H_3$
e. Ar = 3,4-$(OCH_2O$-C_6H_3
f. Ar = 1-naphthyl
g. Ar = 2-thienyl
h. Ar = 3-Me-C_6H_4
i. Ar = 4-Me-C_6H_4

Scheme 1.

2. Results and discussion

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

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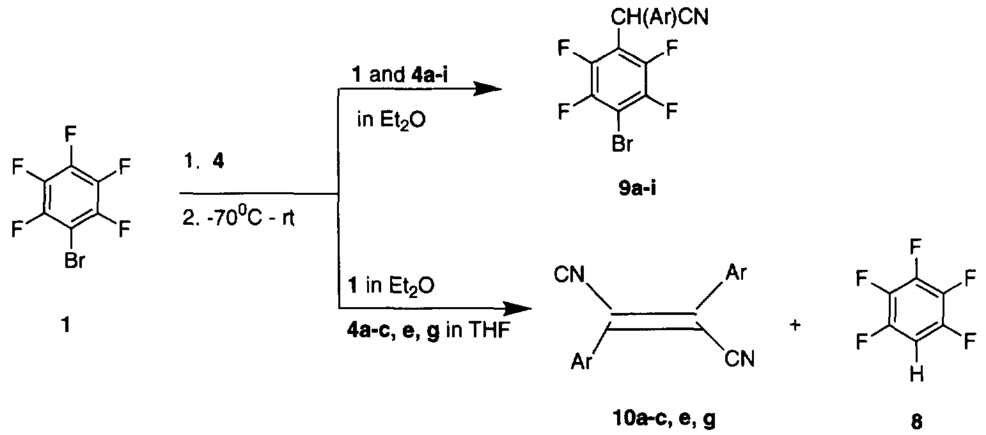


1 9a-i 10a-c, e, g 8

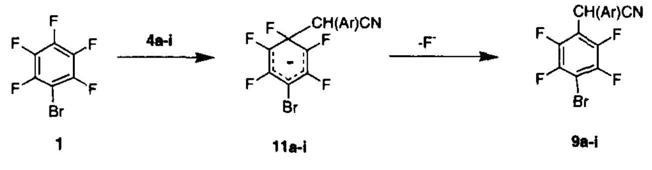
(1)

(2)

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	A	2	**4b**	**7b**, 67	
3	A	2	**4c**	**7c**, 66	
4	A	2	**4d**	**7d**, 62	
5	A	2	**4e**	**7e**, 57	
6	A	2	**4f**	**7f**, 62	
7	A	2	**4g**	**7g**, 67	
8	A	2	**4h**	**7h**, 67	
9	A	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	
18	B (A)	1	**4i**	**9i**, 56	

[a] Solvent A = ether, solvent B = 1:1 ether:THF.



1 11a-i 9a-i

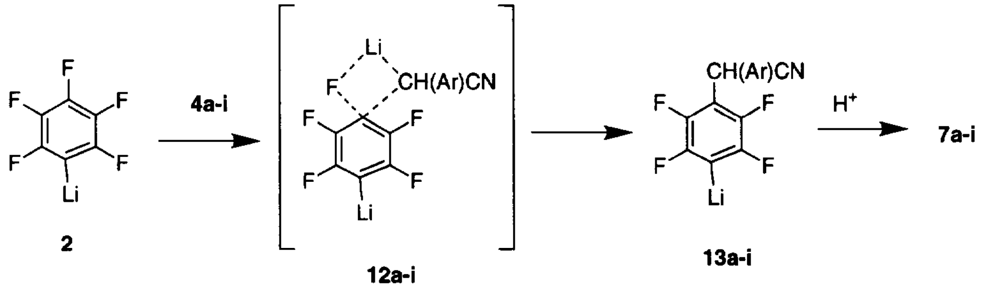
Scheme 2.

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, ^{1}H NMR and ^{13}C 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 **4a–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 **9a–i** in 38%–58% yield [Eq. (1)]. However, as shown in Eq. (2), **1** reacted with arylacetonitriles **4a–c**, **e**, **g** in THF, to afford the corresponding *trans*-1,2-dicyanostilbenes **10a–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 **9a–i** and **10a–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 (**10c**) 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 bromo–lithium exchange to yield pentafluorophenyllithium (**2**) and α-bromoarylacetonitriles **14a**, **c**, **e**, **g**. Under the basic conditions of the reaction, these α-bromonitriles dimerize to 1,2-dicyanostilbenes **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 Et_2O 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**.

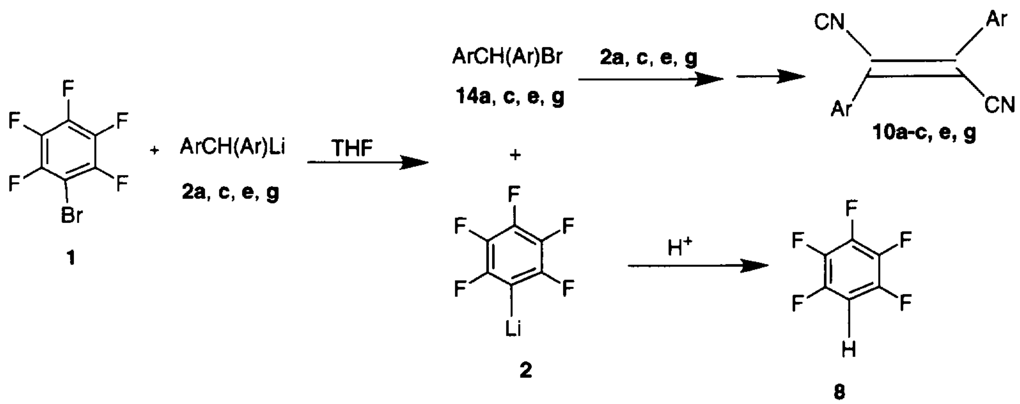
3. Experimental details

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 ^{n}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 $CDCl_3$ solutions were recorded on a Brucker, WMSY 200 MHz spectrometer and ^{1}H 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 n-butyllithium (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 NH_4Cl (50 ml) was added, the solution was rotoconcentrated and the residue extracted several times with CH_2Cl_2. The CH_2Cl_2 extracts were combined, washed with



Scheme 4.

water and dried (Na_2SO_4). 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 ($CHCl_3$) (cm^{-1}): 2245 (CN). ^1H NMR ($CHCl_3$) 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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. ^{13}C NMR ($CHCl_3$) 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 $C_{13}H_9NF_4$: 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 ($CHCl_3$) (cm^{-1}): 2248 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_9NOF_4$: 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 ($CHCl_3$) (cm^{-1}): 2245 (CN). ^1H NMR ($CHCl_3$) 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 $C_{16}H_{11}NO_2F_4$: 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_7N_2F_4$: 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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 $C_{18}H_9NF_4$: 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 ($CHCl_3$) (cm^{-1}): 2256 (CN). ^1H NMR ($CHCl_3$) δ: 5.72 (s, 1H); 6.91–7.01 (m, 1H); 7.10–7.31 (m, 3H) ppm. Analysis: Calc. for $C_{12}H_5NSF_4$: 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 ($CHCl_3$) (cm^{-1}): 2247 (CN). ^1H NMR ($CHCl_3$) δ: 2.35 (s, 3H); 5.51 (s, 1H); 7.00–7.45 (m, 5H) ppm. Analysis: Calc. for $C_{15}H_{10}F_4$: 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_6N_5$: 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 Et_2O 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) δ: 3.79 (s, 3H); 5.50 (s, 1H); 6.85–7.3 (m, 4H) ppm. Analysis: Calc. for $C_{15}H_8NCl_5$: 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 ($CHCl_3$) (cm^{-1}): 2248 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_8NOCl_5$: 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 ($CHCl_3$) (cm^{-1}): 2249 (CN). ^1H NMR ($CHCl_3$) 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 $C_{16}H_{10}O_2Cl_5$: 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-tetrafluorophenylacetonitrile (**9e**): colorless solid, m.p. 110 °C. IR ($CHCl_3$) (cm^{-1}): 2249 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_6NO_2Cl_5$: 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 ($CHCl_3$) (cm^{-1}): 2250 (CN). ^1H NMR ($CHCl_3$) 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 ($CHCl_3$) 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 $C_{18}H_8NCl_5$: 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 ($CHCl_3$) (cm^{-1}): 2247 (CN). ^1H NMR ($CHCl_3$) 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. ^{13}C NMR ($CHCl_3$) 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 $C_{12}H_4NSCl_5$: 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) 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 $C_{15}H_8NCl_3$: 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 ($CHCl_3$) (cm^{-1}): 2246 (CN). ^1H NMR ($CHCl_3$) δ: 2.34 (s, 3H); 6.30 (s, 1H); 7.19 (s, 4H); 7.67 (s, 1H) ppm. Analysis: Calc. for $C_{15}H_8NCl_5$: 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). ^{13}C NMR ($CHCl_3$) δ: 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 ($CHCl_3$) δ: 3.86 (s, 6H); 7.24–7.33 (m, 6H); 7.39 (s, 2H) ppm. Analysis: Calc. for $C_{18}H_{14}N_2O$: 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 ($CHCl_3$) 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 ($CHCl_3$) δ: 55.53; 114.56; 117.25; 122.68; 124.60; 130.40; 161.99 ppm. Analysis: Calc. for $C_{18}H_{14}N_2O$: 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 ($CHCl_3$) 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 $C_{18}H_{10}O_4$: 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 ($CHCl_3$) 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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