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# $N^1$-(5-Fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine

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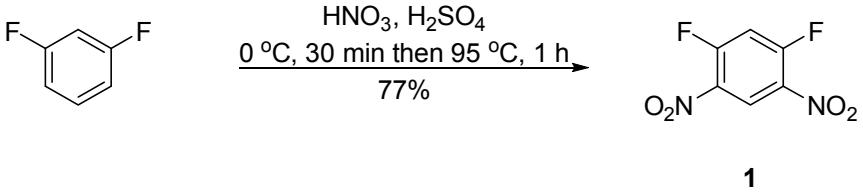
**Abstract:** Treating 1,5-difluoro-2,4-dinitrobenzene (**1**) with $N^1$-phenyl-5-(trifluoromethyl)benzene-1,2-diamine (**4**) and *N*,*N*-diisopropylethylamine in EtOH at *ca.* 0 °C for 4 h affords a mixture of $N^1$-(5-ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**5**) (38%) and $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) (51%) that can be separated by chromatography. Repeating the reaction in dichloromethane led to the sole formation of $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) in 96% yield.

**Keywords:** nucleophilic aromatic substitution; 1,5-difluoro-2,4-dinitrobenzene; benzenediamines; diarylamines; halonitrobenzenes

## 1. Introduction

1,5-Difluoro-2,4-dinitrobenzene (**1**), which can be prepared by direct nitration of 1,3-difluoro-benzene in high (77%) yield (Scheme 1) [1], is a commercially available dihalodinitroarene that is synthetically useful owing to its high reactivity towards nucleophilic aromatic substitution. The easily controlled step-wise displacement of each fluoride provides products that can be further modified via reduction of the 2,4-dinitro groups.




**1**

**Scheme 1.** Preparation of 1,5-difluoro-2,4-dinitrobenzene (**1**) from 1,3-difluorobenzene [1].

1,5-Difluoro-2,4-dinitrobenzene (**1**) has been used to prepare several biologically active fused heterocycles, such as phenazinimines [2], 1,5-benzodiazepin-2-ones [3], benzo[1,4]oxazin-3-ones [4], benzo[1,4]thiazin-3-ones [5], and indoles [6], as well as provide interesting oligo(arylamines) that show interesting H-bonding and $\pi$–$\pi$ interactions in both solution and the solid state [7–9]. Furthermore, owing to its electron deficient arene core, difluorodinitrobenzene **1** forms 1:1 and 1:2 complexes with benzenediamine and benzidine donors [10] and solid charge transfer complexes with hydroxyl aryl Schiff bases [11]. 1,5-Difluoro-2,4-dinitrobenzene (**1**) can also be used to enable the chromatographic resolution of chiral secondary alcohols [12]. More recently, difluorodinitrobenzene **1** has been extensively used as a monomer unit to prepare unusual azamacrocycles via cyclooligomerisation chemistry [13–19].

Our interest in difluorodinitrobenzene **1** stems from its use as a starting point in the synthesis of biscyanine azaacenes such as the hexaazaanthracene **2** [20,21] and the tetraazapentacene **3** [22–25] (Figure 1) that followed a modification of Nietzki's classical preparation of tetraazapentacene from 1,2-diaminobenzenes and the considerably less reactive 1,5-dichloro-2,4-dinitrobenzene [26].

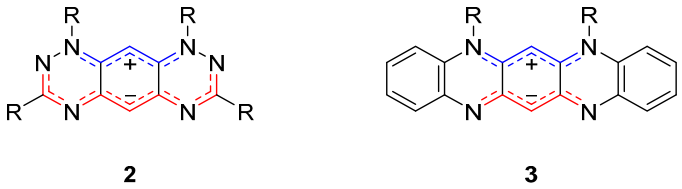


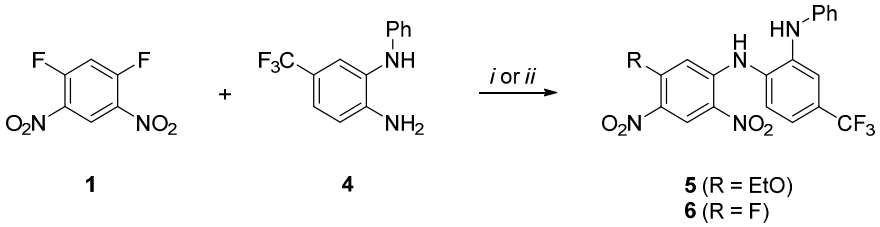

**Figure 1.** General structure of biscyanines **2** and **3** prepared from difluorodinitrobenzene **1** [20–25].

A key initial step in preparing asymmetrically-substituted biscyanine tetraazaacene analogues [23] is the selective displacement of one fluorine by $N^1$-aryl/alkyl 1,2-benzenediamines and this is typically achieved at 0–20 °C in solvents such as EtOH or MeOH in the presence of either triethylamine or pyridine (1 equiv) or additional $N^1$-aryl/alkyl 1,2-benzenediamine (1 equiv). Herein, we report the synthesis of $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) (Scheme 2) using two different sets of reaction conditions: (i) the first, using EtOH as solvent that led to mixtures and only a moderate yield of the desired target and (ii) the second, using dichloromethane (DCM) as solvent which gave the target in near quantitative yield.

## 2. Results and Discussion

The target, $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**), was needed as a starting point for the synthesis of asymmetrically substituted biscyanine tetraazaacenes. Initially, we followed a known protocol [23] that required access to readily available 1,5-difluoro-2,4-dinitrobenzene (**1**) and $N^1$-phenyl-5-(trifluoromethyl)benzene-1,2-diamine (**4**) [27].

As such, we treated a solution of 1,5-difluoro-2,4-dinitrobenzene (**1**) in EtOH at *ca.* 0 °C with $N^1$-phenyl-5-(trifluoromethyl)benzene-1,2-diamine (**4**) and then with *N*,*N*-diisopropylethylamine (1.1 equiv) (Conditions (i), Scheme 2). Disappointingly, after 4 h, we obtained a mixture of $N^1$-(5-ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**5**) (38%) and the desired $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) (51%) which required chromatographic separation (*n*-hexane/DCM) (Scheme 2).




**Scheme 2.** Synthetic scheme for the preparation of $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) and side product $N^1$-(5-ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**5**). *Reaction conditions*: (i) $^i$Pr$_2$NEt (1.1 equiv), EtOH, 0 °C, 4 h, 38% (**5**), 51% (**6**); and (ii) $^i$Pr$_2$NEt (1.1 equiv), DCM, 0 °C, 30 min, 96% (**6**).

The structural identity of both compounds was supported by mass spectrometry, UV–vis, IR, and NMR spectroscopy (see Supplementary Materials) and by elemental analysis. Presumably, the formation of the undesired ethoxy-substituted side product **5** was attributed to the presence of the *para*-trifluoromethyl (*p*-F$_3$C) group. The powerful inductively electron withdrawing *p*-F$_3$C group

can deactivate the primary amine of the 1,2-benzenediamine **4** towards nucleophilic attack enabling a competitive displacement of fluoride by the ethoxide that must originate from the abundant EtOH used as the reaction solvent.

Considering this, we switched the solvent from EtOH to various non-nucleophilic aprotic solvents (1,4-dioxane, tetrahydrofuran, DCM, dimethylformamide, and dimethylacetamide). Gratifyingly, repeating the reaction in DCM at *ca*. 0 °C led to completion of the reaction (by thin-layer chromatography (TLC)) within 30 min to afford only the desired $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) in 96% yield, enabling its chromatography free isolation.

## 3. Materials and Methods

### *3.1. General Methods*

All chemicals were commercially available except those whose synthesis is described. Reactions were protected from moisture with $CaCl_2$ drying tubes. All volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass-backed TLC plates (Merck Kieselgel 60 $F_{254}$, Darmstadt, Germany). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography [28] was used throughout for all non-TLC scale chromatographic separations and employed Merck Silica Gel 60 (less than 0.063 mm). Melting and decomposition points were determined using a PolyTherm-A, Wagner & Munz, Kofler hot-stage microscope apparatus (Wagner and Munz, Munich, Germany). The solvents used for recrystallization are indicated after the respective melting points. UV–vis spectra were obtained using a Perkin-Elmer Lambda-25 UV–vis spectrophotometer (Perkin-Elmer, Waltham, MA, USA) and inflections are identified by the abbreviation 'inf'. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) with a Pike Miracle Ge ATR accessory (Pike Miracle, Madison, WI, USA) and strong, medium and weak peaks are represented by s, m, and w, respectively. $^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker Avance 500 machine (at 500 and 125 MHz, respectively) (Bruker, Billerica, MA, USA). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. APT (Advance Proton Test) NMR studies identified carbon multiplicities, which are indicated by (s), (d), (t), and (q) notations. MALDI-TOF (matrix assisted laser desorption/ionization-time of flight) mass spectra (+ve mode) were conducted on a Bruker Autoflex III Smartbeam instrument (Bruker, Billerica, MA, USA). Elemental analyses were run by the London Metropolitan University Elemental Analysis Service. $N^1$-Phenyl-5-(trifluoromethyl)-benzene-1,2-diamine (**4**) was synthesized according to a literature procedure [27].

### *3.2. Method A: $N^1$-(5-Ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine* (**5**) *and $N^1$-(5-Fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine* (**6**)

To a stirred solution of 1,5-difluoro-2,4-dinitrobenzene (**1**) (204 mg, 1.0 mmol) in EtOH (5 mL) at *ca*. 20 °C, was added in several portions over a period of 30 min $N^1$-phenyl-5-(trifluoro-methyl)benzene-1,2-diamine (**4**) (252 mg, 1.0 mmol). A crystalline orange precipitate formed within 30 min, at which time and while keeping the temperature at *ca*. 0 °C, was added *N*,*N*-diisopropylethylamine (192 µL, 1.1 mmol). The mixture was slowly left to warm to at *ca*. 20 °C. Upon completion (by TLC, 4 h), the orange precipitate was filtered and chromatographed (*n*-hexane/DCM, 50:50) to give $N^1$-(5-ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl- 4-(trifluoromethyl)benzene-1,2-diamine (**5**) (178 mg, 38%) as orange needles, m.p. (hot-stage) 174.1–176.7 °C (from EtOH); $R_f$ 0.44 (*n*-hexane/DCM, 50:50); found: C, 54.63; H, 3.76; N, 12.57. $C_{21}H_{17}F_3N_4O_5$ requires C, 54.55; H, 3.71; N, 12.12%; $\lambda_{max}$ (DCM)/nm 284 (log ε 4.66), 360 inf (4.20); $\nu_{max}$/cm$^{-1}$ 3391 m and 3347 m (N–H), 1626 m, 1609 m, 1593 m, 1568 s, 1535 m, 1518 w, 1497 m, 1481 w, 1443 m, 1410 s, 1339 s, 1327 m, 1292 s, 1279 s, 1250 m, 1225 m, 1179 m, 1159 m, 1126 s, 1074 m, 1030 w, 939 m, 905 w, 878 m, 825 w, 814 m, 777 w, 766 w, 750 m, 740 m, 721 w;

$\delta_H$ (500 MHz, $CDCl_3$) 9.66 (1H, s, NH), 9.02 (1H, s), 7.58 (1H, d, *J* 1.5), 7.38 (1H, d, *J* 8.0), 7.35 (2H, dd, *J* 7.8, 7.8), 7.22 (1H, dd, *J* 8.5, 1.5), 7.12 (1H, dd, *J* 7.5, 7.5), 7.08 (2H, d, *J* 8.0), 6.27 (1H, s), 5.89 (1H, s), 3.97 (2H, q, *J* 7.0, $OCH_2$), 1.43 (3H, t, *J* 7.0, $CH_3$); $\delta_C$ (125 MHz, $CDCl_3$) 158.4 (s), 147.0 (s), 140.8 (s), 140.1 (s), 131.0 (q, $^2J_{CF}$ 32.6), 130.6 (s), 129.8 (d), 127.7 (d), 127.4 (s), 127.2 (d), 125.5 (s), 123.9 (d), 123.6 (q, $^1J_{CF}$ 271.1, $CF_3$), 120.5 (d), 117.2 (q, $^3J_{CF}$ 3.6), 113.1 (q, $^3J_{CF}$ 3.6), 97.7 (d), 66.3 (t, $OCH_2$), 14.0 (q, $CH_3$); *m/z* (MALDI-TOF) 462 ($M^+$, 20%), 445 (100), 444 (53), 415 (47). Further elution (*n*-hexane/DCM, 40:60) gave $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**) (222 mg, 51%) as red cubes, m.p. (hot-stage): 185.4–188.6 °C (from toluene); $R_f$ 0.38 (*n*-hexane/DCM, 50:50); found: C, 52.35; H, 2.81; N, 12.86. $C_{19}H_{12}F_4N_4O_4$ requires C, 52.30; H, 2.77; N, 12.84%; $\lambda_{max}$(DCM)/nm 248 (log $\varepsilon$ 4.40), 300 (4.54), 358 (4.33), 403 (4.14); $\nu_{max}/cm^{-1}$ 3399 m and 3321 m (N–H), 3061 w (aryl C–H), 1632 s, 1595 s, 1537 m, 1530 m, 1508 s, 1499 s, 1443 m, 1418 m, 1369 m, 1331 s, 1300 s, 1275 s, 1254 m, 1221 m, 1180 m, 1128 s, 1117 s, 1072 m, 1055 m, 1030 w, 941 m, 918 w, 883 w, 845 m, 827 m, 773 w, 760 m, 743 s, 727 m, 708 m; $\delta_H$ (500 MHz, $CDCl_3$) 9.61 (1H, s, NH), 9.14 (1H, d, *J* 8.0), 7.53 (1H, s), 7.38 (1H, d, *J* 8.0), 7.34 (2H, dd, *J* 8.0, 8.0), 7.25 (1H, d, *J* 7.5, overlap with $CDCl_3$), 7.12 (1H, dd, *J* 7.5, 7.5), 7.05 (2H, d, *J* 8.0), 6.67 (1H, d, $J_{HF}$ 13.0), 5.83 (1H, s); $\delta_C$ (125 MHz, $CDCl_3$) one C (s) resonance missing, 159.8 (d, $^1J_{CF}$ 270.9, *C*F), 147.7 (d, $^2J_{CF}$ 12.5), 140.9 (s), 140.0 (s), 131.7 (q, $^2J_{CF}$ 32.5), 129.8 (d), 128.5 (s), 127.9 (d), 127.5 (d), 126.9 (s), 124.3 (d), 123.5 (q, $^1J_{CF}$ 271.3, $CF_3$), 121.0 (d), 117.6 (q, $^3J_{CF}$ 3.6), 113.9 (q, $^3J_{CF}$ 3.6), 103.7 (d, $^2J_{CF}$ 27.5); *m/z* (MALDI-TOF) 437 ($MH^+$, 41%), 436 ($M^+$, 100).

### *3.3. Method B: $N^1$-(5-Fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine* (**6**)

To a stirred solution of 1,5-difluoro-2,4-dinitrobenzene (**1**) (204 mg, 1.0 mmol) in DCM (5 mL) at *ca*. 0 °C, was added in one portion $N^1$-phenyl-5-(trifluoromethyl)benzene-1,2-diamine (**4**) (252 mg, 1.0 mmol), followed by addition of *N*,*N*-diisopropylethylamine (192 μL, 1.1 mmol). The reaction mixture was allowed to warm to *ca*. 20 °C (over 30 min), after which time the reaction was complete (by TLC). The solvent was evaporated in vacuo to afford an orange-red residue that was recrystallized to afford the title compound **6** as red cubes (418 mg, 96%); identical to that described above.

**Supplementary Materials:** The following are available online: www.mdpi.com/1422-8599/2017/4/M967. $^1H$ and $^{13}C$ NMR spectra of $N^1$-(5-ethoxy-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**5**) and $N^1$-(5-fluoro-2,4-dinitrophenyl)-$N^2$-phenyl-4-(trifluoromethyl)benzene-1,2-diamine (**6**).

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**Author Contributions:** P.A. Koutentis conceived the experiments; G.A. Zissimou designed and performed the experiments, analyzed the data, and wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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