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Synthesis of N^1-(3,5-Bis(trifluoromethyl)benzyl)benzene-1,2-diamine and *N*,*N*-Bis(2-nitrophenyl)-3,5-bis(trifluoromethyl)aniline

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Abstract: A monosubstituted benzene-1,2-diamine building block, N^1-(3,5-bis(trifluoromethyl)benzyl) benzene-1,2-diamine, was prepared in two steps from commercially available 3,5-bis(trifluoromethyl) benzylamine and 1-fluoro-2-nitrobenzene, while the use of 3,5-bis(trifluoromethyl)aniline as the starting amine gave a triarylamine, *N*,*N*-bis(2-nitrophenyl)-3,5-bis(trifluoromethyl)aniline. The structures of the newly synthesized compounds were fully characterized.

Keywords: 2-fluoronitrobenzene; nucleophilic aromatic substitution; aromatic nitro group reduction

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1. Introduction

The synthesis of diaminobenzene derivatives is widely known. Substituted diaminobenzenes have found innumerable applications. They are important starting materials for the formation of arylbenzimidazoles, benzotriazolium salts, and biologically active compounds, among others. Substituted diaminobenzenes are used as starting materials for the preparation of arylbenzimidazole-based organic light-emitting diodes [1–3]. Benzotriazolium salts prepared by reaction of substituted benzenediamines with *tert*-butyl nitrite followed by treatment with trimethyloxonium tetrafluoroborate are used as a Lewis acid catalyst in the Nazarov reaction [4]. Dihydrotetraazaanthracenes have been prepared by cyclization of *N*-substituted *orto*-phenylenediamines as new materials for use in organic electronic devices [5]. 1,2-Disubstituted benzimidazoles based on substituted diaminobenzenes have been tested for their cytotoxicity against cancer cells [6,7]. Benzene-1,2-diamine derivatives have been tested as donors for double hydrogen bond donors in non-covalent organocatalysts [8]. Triphenylamine-based diamines are important and versatile monomers for the synthesis of aromatic polyamides with different properties [9–15].

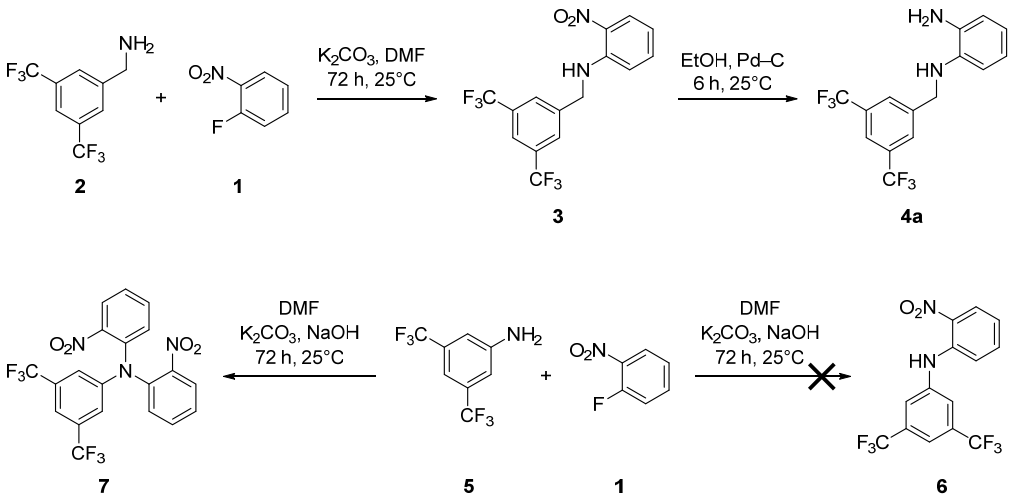
Recently, we reported the synthesis and catalytic activity of (*S*)-quininamine-based organocatalysts bearing benzene-1,2-diamine as hydrogen bond donors. Benzene-1,2-diamine-based organocatalysts were prepared in a three-step synthesis from (*S*)-quininamine and 1-fluoro-2-nitrobenzene. Most of the synthesized catalysts possessed an amino group functionalized with methylenemalonitrile [8]. The same three-step methodology was used to attempt to prepare a camphor-derived analogue. Unfortunately, undesirable camphor-derived benzo[*d*]imidazole was obtained [16]. Attempts to introduce the 3,5-bis(trifluoromethyl)benzyl group and the 3,5-bis(trifluoromethyl)phenyl group on the primary amino group were unsuccessful [16]. Therefore, an alternative approach to access benzene-1,2-diamine camphor derivatives of type **9** with 3,5-bis(trifluoromethyl)benzyl group and/or 3,5-bis(trifluoromethyl)phenyl group was developed starting from N^1-(3,5-bis(trifluoromethyl)benzyl)benzene-1,2-diamine (**4a**) or N^1-(3,5-bis(trifluoromethyl)phenyl) benzene-1,2-diamine (**4b**) and 10-pyrrolidinecamphor **8** [17] by reductive amination.

In this work, we present the synthesis of N^1-(3,5-bis(trifluoromethyl)benzyl)benzene-1,2-diamine (**4a**) and *N*,*N*-bis(2-nitrophenyl)-3,5-bis(trifluoromethyl)aniline (**7**), as well

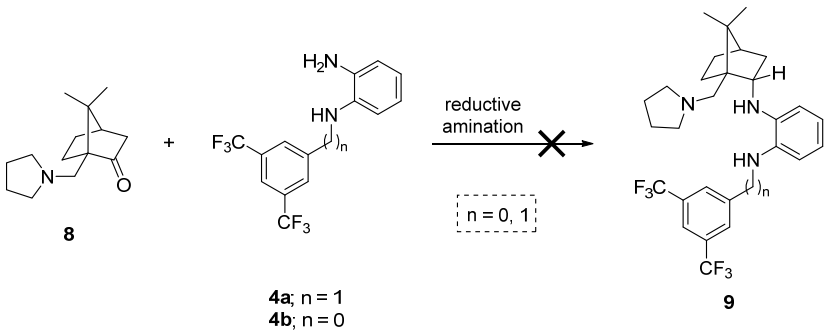
as an experiment on the reductive amination of 10-pyrrolidinecamphor **8** with N^1-(3,5-bis(trifluoromethyl)benzyl)benzene-1,2-diamine (**4a**).

2. Results and Discussion

N^1-(3,5-Bis(trifluoromethyl)benzyl)benzene-1,2-diamine (**4a**) was prepared in two steps from commercially available 3,5-bis(trifluoromethyl)benzylamine (**2**) and 1-fluoro-2-nitrobenzene (**1**) (Scheme 1). In the first step, nucleophilic aromatic substitution gave the *N*-substituted nitroaniline **3** at a 98% yield. Subsequent catalytic hydrogenation of **3** afforded the desired diamine **4a** at a 97% yield. The product **4a** was clean enough for further synthesis and was not subjected to additional purification. If necessary, the diamine **4a** can be easily purified by column chromatography using a mixture of EtOAc/petroleum ether in a 1:2 ratio on silica gel 60 as a stationary phase. In contrast, the preparation of N^1-(3,5-bis(trifluoromethyl)phenyl)benzene-1,2-diamine (**4b**) [4,18] from 3,5-bis(trifluoromethyl)aniline (**5**) and 1-fluoro-2-nitrobenzene (**1**) did not afford the corresponding nitroaniline **6**. Instead, the double nucleophilic aromatic substitution product **7** was isolated at a 20% yield. Finally, attempts to prepare the desired benzene-1,2-diamine camphor derivative **9** from diamine **4a** and 10-pyrrolidinecamphor **8** [17] by reductive amination with $NaBH_3CN$ failed (Scheme 2) [19].



Scheme 1. Synthesis of benzenediamine **4a** and a double nucleophilic aromatic substitution product **7**.



Scheme 2. Attempted synthesis of camphor-derived noncovalent bifunctional organocatalysts of type **9**.

The structures of compounds **3**, **4a**, and **7** were confirmed by spectroscopic methods (^{1}H- and ^{13}C-NMR, DEPT 135, 2D-NMR, IR, and high-resolution mass spectrometry) (Supplementary Materials). The structures of compounds **3** and **7** were additionally confirmed by single-crystal X-ray diffraction analysis (Figures 1 and 2).

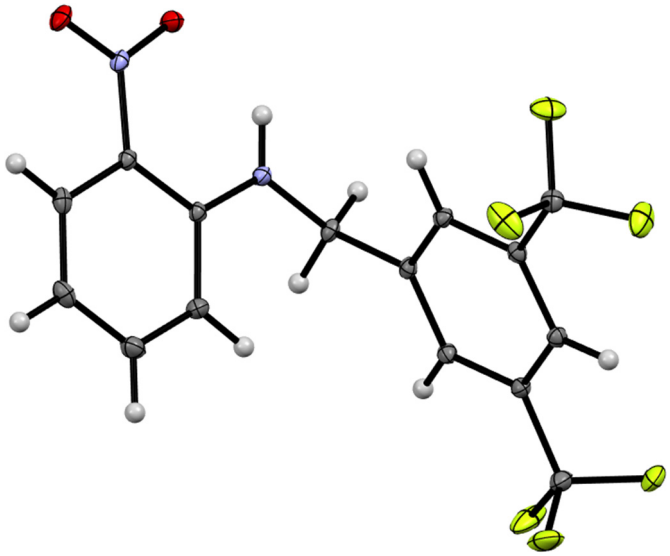


Figure 1. Molecular structure of product **3**. Thermal ellipsoids are shown at 50% probability.

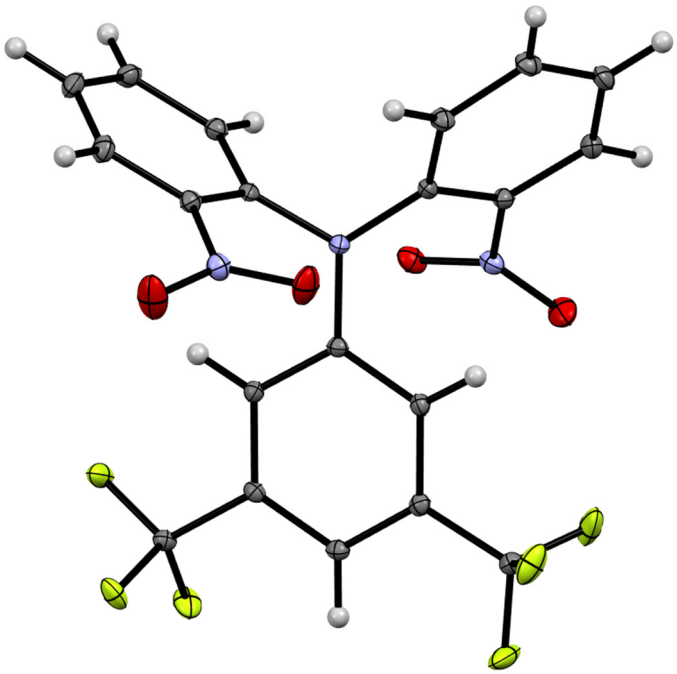


Figure 2. Molecular structure of product **7**. Thermal ellipsoids are shown at 50% probability.

In summary, compounds **3**, **4a**, and **7** have been prepared and fully characterized and are now available to the scientific community.

3. Materials and Methods

Solvents for extractions and chromatography were of technical grade and were distilled prior to use. Extracts were dried over technical grade anhydrous Na_2SO_4. Melting points were determined on a Kofler micro hot stage and on SRS OptiMelt MPA100—Automated Melting Point System (Stanford Research Systems, Sunnyvale, CA, USA). The NMR spectra were obtained on a Bruker UltraShield 500 plus (Bruker, Billerica, MA, USA) at 500 MHz for ^{1}H and 126 MHz for ^{13}C nucleus, using $CDCl_3$ with TMS as the internal standard, as solvents. Mass spectra were recorded on an Agilent 6224 Accurate Mass TOF LC/MS (Agilent Technologies, Santa Clara, CA, USA), IR spectra on a Perkin–Elmer Spectrum BX FTIR spectrophotometer (PerkinElmer, Waltham, MA, USA). Column chro-

matography (CC) was performed on silica gel (Silica gel 60, particle size: 0.035–0.070 mm (Sigma-Aldrich, St. Louis, MI, USA)). All the commercially available chemicals used were purchased from Sigma-Aldrich (St. Louis, MI, USA). Catalytic hydrogenation was performed on a Parr Pressure Reaction Hydrogenation Apparatus (Moline, IL, USA).

*3.1. Synthesis of N-(3,5-Bis(trifluoromethyl)benzyl)-2-nitroaniline (**3**)*

A mixture of (3,5-bis(trifluoromethyl)phenyl)methanamine (**2**) (10 mmol, 2.43 g), 1-fluoro-2-nitrobenzene (**1**) (10 mmol, 1.05 mL), and K_2CO_3 (10 mmol, 1.38 g), in anhydrous DMF (20 mL) was stirred at 25 °C for 72 h. The reaction mixture was diluted with H_2O (40 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, and the volatile components were evaporated in vacuo. Yield: 3.93 g (10.8 mmol, 98%) of yellow solid; mp = 111.0–112.0 °C. EI-HRMS: m/z = 365.0729 (MH^+); $C_{15}H_{11}F_6N_2O_2$ requires: m/z = 365.0725 (MH^+); ν_{max} 3399, 1619, 1572, 1511, 1451, 1433, 1417, 1367, 1348, 1330, 1283, 1247, 1229, 1161, 1140, 1116, 1093, 1039, 988, 926, 907, 884, 859, 844, 742, 707, 683 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 4.84 (*d*, *J* = 6.4, 2H), 6.71 (*ddd*, *J* = 1.2, 6.9, 8.3, 1H), 6.94 (*dd*, *J* = 1.2, 8.7, 1H), 7.47 (*ddd*, *J* = 1.6, 6.8, 8.6, 1H), 8.00 (*s*, 1H), 8.10 (*dd*, *J* = 1.6, 8.6, 1H), 8.13 (*s*, 2H), 8.82 (*t*, *J* = 6.5, 1H, NH). ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 44.79, 114.59, 115.87, 120.89 (*p*, *J* = 3.8), 123.36 (*q*, *J* = 272.9), 126.40, 127.92 (*q*, *J* = 4.0), 130.32 (*q*, *J* = 32.8), 131.80, 136.51, 142.79, 144.34.

*3.2. Synthesis of N^1-(3,5-Bis(trifluoromethyl)benzyl)benzene-1,2-diamine (**4a**)*

A mixture of *N*-(3,5-bis(trifluoromethyl)benzyl)-2-nitroaniline (**3**) (10.8 mmol, 3.93 g) and Pd–C (ω = 10%, 100 mg) in EtOH (50 mL) was shaken in a Paar shaker hydrogenation apparatus in H_2 atmosphere (4 bar) at 25 °C for 6 h. The reaction mixture was filtrated through a plague of Celite® to remove Pd–C, and the volatile components were evaporated in vacuo. The product **4a** was clean enough for further synthesis and was not additionally purified. If needed, the product can easily be purified by column chromatography (Silica Gel 60; EtOAc/petroleum ether = 1:2). The oily product turned dark, even though it was stored under Argon. Yield: 3.50 g (10.5 mmol, 97%) of brownish oil. EI-HRMS: m/z = 335.0979 (MH^+); $C_{15}H_{13}F_6N_2$ requires: m/z = 335.0983 (MH^+); ν_{max} 3337, 1621, 1507, 1454, 1377, 1351, 1314, 1274, 1167, 1120, 996, 884, 844, 741, 704, 681 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 4.51 (*d*, *J* = 5.1 Hz, 2H), 4.61 (*s*, 2H), 5.36 (*t*, *J* = 7.1 Hz, 1H), 6.34 (*dd*, *J* = 7.2, 2.0 Hz, 1H), 6.40–6.49 (*m*, 2H), 6.60 (*dd*, *J* = 7.0, 2.1 Hz, 1H), 7.94 (*s*, 1H), 8.08 (*s*, 2H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 46.00, 110.55, 114.47, 117.46, 117.63, 120.22–120.39 (*m*), 123.46 (*q*, *J* = 272.7 Hz), 127.89 (*d*, *J* = 3.8 Hz), 130.08 (*q*, *J* = 32.6 Hz), 134.85, 135.55, 144.65.

*3.3. Synthesis of N,N-Bis(2-nitrophenyl)-3,5-bis(trifluoromethyl)aniline (**7**)*

A mixture of 3,5-bis(trifluoromethyl)aniline (**5**) (5 mmol, 777 µL), 1-fluoro-2-nitrobenzene (**1**) (5 mmol, 525 µL), K_2CO_3 (5 mmol, 691 mg), and NaOH (7 mmol, 280 mg) in anhydrous DMF (10 mL) was stirred at 25 °C for 72 h. The reaction mixture was diluted with H_2O (30 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered, next the volatile components were evaporated in vacuo. The residue was purified by column chromatography (Silica Gel 60; EtOAc/petroleum ether = 1:10). Fractions containing the product **7** were combined, and the volatile components were evaporated in vacuo. Yield: 482 mg (1.02 mmol, 20%) of yellowish solid; mp = 142–147 °C. EI-HRMS: m/z = 472.0726 (MH^+); $C_{20}H_{12}F_6N_3O_4$ requires: m/z = 472.0732 (MH^+); ν_{max} 3341, 3098, 1598, 1578, 1525, 1478, 1466, 1381, 1353, 1338, 1279, 1267, 1166, 1120, 1045, 1000, 986, 961, 932, 903, 878, 848, 837, 776, 757, 744, 722, 702, 682, 633 cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 7.20 (*s*, 2H), 7.50 (*dd*, *J* = 8.2, 1.3 Hz, 2H), 7.60 (*ddd*, *J* = 8.4, 7.5, 1.3 Hz, 2H), 7.71 (*s*, 1H), 7.82 (*td*, *J* = 7.8, 1.6 Hz, 2H), 8.09 (*dd*, *J* = 8.2, 1.5 Hz, 2H). ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 115.23–116.46 (*m*), 118.69, 122.71 (*q*, *J* = 272.9 Hz), 126.28, 127.87, 129.97, 131.59 (*q*, *J* = 33.1 Hz), 135.34, 136.65, 144.85, 147.05.

3.4. X-ray Crystallography

Single-crystal X-ray diffraction data were collected on an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using monochromated Cu-Kα radiation (λ = 1.54184 Å) at 150 K. The data were processed using CrysAlis PRO [20]. Using Olex2.1.2. [21], the structures were solved by direct methods implemented in SHELXS [22] or SHELXT [23] and refined by a full-matrix least-squares procedure based on F2 with SHELXT-2014/7 [24]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and were refined using a riding model. The drawings and the analysis of the bond lengths, angles, and intermolecular interactions were carried out using Mercury [25] and Platon [26]. Structural and other crystallographic details on data collection and refinement for compounds **3** and **7** were deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC Deposition Numbers 2287121 and 2284800, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 29 August 2023) or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

Supplementary Materials: The following are available online: Synthesis and characterization data; Copies of ^{1}H- and ^{13}C-NMR spectra; Copies of 2D spectra; Copies of HRMS reports; Copies of IR spectra; Structure determination by X-ray diffraction analysis.

Author Contributions: Conceptualization, L.C., U.G., J.S. and B.Š.; methodology, L.C. and U.G.; software, L.C., H.B., U.G., J.S. and B.Š.; validation, L.C., H.B., U.G., J.S., F.P. and B.Š.; formal analysis, U.G., H.B. and L.C.; investigation, L.C. and U.G.; resources, L.C., U.G. and J.S.; data curation, L.C., H.B., U.G., J.S. and B.Š.; writing—original draft preparation, L.C., U.G., J.S. and B.Š.; writing—review and editing, L.C., U.G., J.S., F.P. and B.Š.; visualization, L.C., H.B., U.G., B.Š. and J.S.; supervision, U.G.; project administration, U.G. and J.S.; funding acquisition, U.G. and J.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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