

Efficient Synthesis of 2,2'-Dicarbazole-1,1'-Biphenyl - Prospective Host Material for PHOLEDs

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Abstract: 2,2'-Dicarbazole-1,1'-diphenyl (2,2'-CBP) is a prospective host material for phosphorescent light emitting diodes (PHOLED)s. The synthesis of 2,2'-CBP is limited by the availability of starting materials. We wish to report an efficient protocol for the synthesis of 2,2'-CBP with overall yield about 90% starting from o-nitrobenzoic acid. Thus, Pd catalyzed homocoupling of o-nitrobenzoic acid affords 2,2'-dinitro-1,1'-diphenyl (2,2'-DNNDP) in 95% yield. Pd catalyzed reduction of 2,2'-DNNDP and the following double arylation of 2,2'-diaminodiphenyl with 2,2'-dibromo-1,1'-diphenyl (which can be obtained from 2,2'-diamino-1,1'-diphenyl in 70-76% yield) affords the final product in 95% yield with overall yield after 3 steps of 90 %.

Keywords: 2,2'-CBP, Pd coupling, PHOLEDs

Introduction

During last decades the efficiencies of organic light-emitting devices (OLEDs) have advanced rapidly because of the development of efficient phosphorescent guest molecules containing transition metals that can harvest both electrogenerated singlet and triplet excitons for emission [1]. Due to the simultaneous light generation from both triplet and singlet excitons the internal quantum efficiency of such devices can reach nearly 100% [2]. In these phosphorescent OLEDs (PHOLEDs), a host with a triplet energy (E_T) level higher than that of the dopant is necessary to prevent quenching of the dopant emission by energy transfer from the dopant to the host. Typically, 4,4'-N,N'-dicarbazole-1,1'-biphenyl (CBP), is widely used as host material for PHOLED applications [3]. In the search for other high triplet energy molecules, various strategies can be utilized. For example, Tokito et al. reported that introduction of two methyl groups into biphenyl unit of 4,4'-CBP (by replacing of biphenyl by 2,2'-dimethylbiphenyl)

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provided the larger triplet energy host than CBP ($E_T = 2.79$ eV) [4] due to disrupting the planarity of the molecule. On the other hands symmetrical CBPs, for example 2,2'- or 3,3'-CBP maintain the most beneficial properties of CBPs such as charge transport and thermal stability, or film-forming properties, but would possess the increased triplet energy, due to the lack of planarity and reduced effective conjugation. Based on this criteria, our target molecule 2,2'-dicarbazole-1,1'-biphenyl looked the most promising candidate for PHOLED applications. Here, we wish to report the yield effective synthesis of 2,2'-CBP.

Methods

General Information

Anhydrous DMSO, DMF and toluene were prepared according to known procedures. Pd(CF₃CO₂)₂ (Pd(TFA)₂, Pd₂(dba)₃ and Ag₂CO₃ were freshly prepared. 2,2'-Dibromobiphenyl and all other reagents were purchased from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel, particle size 40-60 μm, using flash techniques. Analytical thin layer chromatography was performed on pre-coated aluminum-backed silica gel F254 plates with visualization under UV light. Melting points were obtained using a hot-stage apparatus and are uncorrected.

2,2'-Dinitrobiphenyl (1) [5].

In general the slightly modified procedure of I. Larrosa et al. [5] utilized as follows. Under argon a suspension of 2-nitrobenzoic acid (0.083 g, 0.5 mmol), freshly prepared Ag₂CO₃ (0.138 g, 0.5 mmol) and freshly prepared Pd(TFA)₂ (0.012 g, 0.036 mmol) in 9.5 mL freshly distilled dry DMF and freshly distilled dry DMSO 0.5 mL was stirred at 120 °C for 24 h in a small pressure vessel. The reaction mixture was cooled down to room temperature, diluted with EtOAc (10 mL) and filtered through a plug of celite. The filtrate was washed with a saturated solution of NaHCO₃ (3 × 40 mL), brine (3 × 30 mL) and evaporated to dryness *in vacuo*. The residue was purified by column chromatography using 5% acetone in hexanes to afford the desired product (0.058 g, 95%) as an yellow-white needles. ¹H NMR (CDCl₃, 297K) δ 8.23 (d, 2H, J = 8.4 Hz), 7.72 – 7.68 (m, 2H), 7.63 – 7.59 (m, 2H), 7.31 (d, 2H, J = 7.6 Hz); ¹³C NMR (CDCl₃, 297K) δ 147.1, 134.3, 133.4, 131.0, 129.0, 124.8.

2,2'-Diaminobiphenyl (2).

2,2'-Dinitrobiphenyl (0.116 g, 0.420 mmol) and 10 percent Pd/C (0.017 g) were combined with 50 mL of EtOAc in a small hydrogenation vessel. The vessel was pressurized to 40-42 psi H₂ for 6 h. The suspension was filtered through a plug of celite. Evaporation *in vacuo* followed by drying for 12 hrs *in vacuo* afforded the desired product as an light orange powder. ¹H NMR (CDCl₃, 297K): δ 7.19 (td, 2H, J=7.4, 1.5 Hz). 7.12 (dd, 2H, J=8.0, 1.5 Hz), 6.85 (td, 2H, J=7.4,

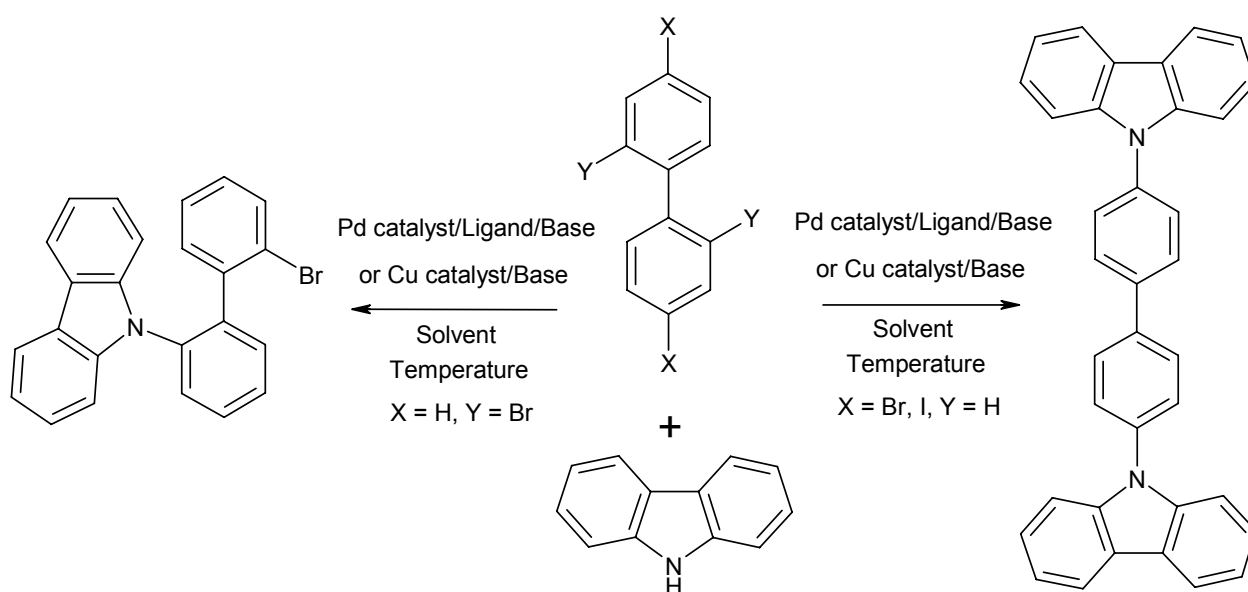
1.2 Hz), 6.80 (dd, 2H, J=8.0, 1.2 Hz), 3.75 (b.s., 4H); ^{13}C NMR (CDCl_3 , 297K): δ 144.2, 131.1, 128.8, 124.6, 118.7, 115.6.

2,2'-Dicarbazole-1,1'-Biphenyl (3) [6].

Slightly modified procedure of K. Nozaki et al. [5] utilized as follows. Under argon to a solution of tri(*tert*-butyl)phosphine (0.020 g, 0.10 mmol) in dry freshly distilled toluene (3.0 mL) was added a mixture of 2,2'-dibromobiphenyl (0.137 g, 0.60 mmol), 2,2'-diaminobiphenyl (0.046 g, 0.25 mmol), sodium *tert*-butoxide (0.115 g, 1.20 mmol) and $[\text{Pd}_2(\text{dba})_3]$ (0.023 g, 0.025 mmol). After the heating at 80 °C for 24 h the reaction mixture was evaporated to dryness *in vacuo* together with small amount of silica-gel and placed on a column and the following column chromatography using 5% acetone in hexanes afforded the product (0.115 g, 95% (total yield after 3 steps is 90 %)) as colorless needles. All the analytical data for **3** were the same as in [6].

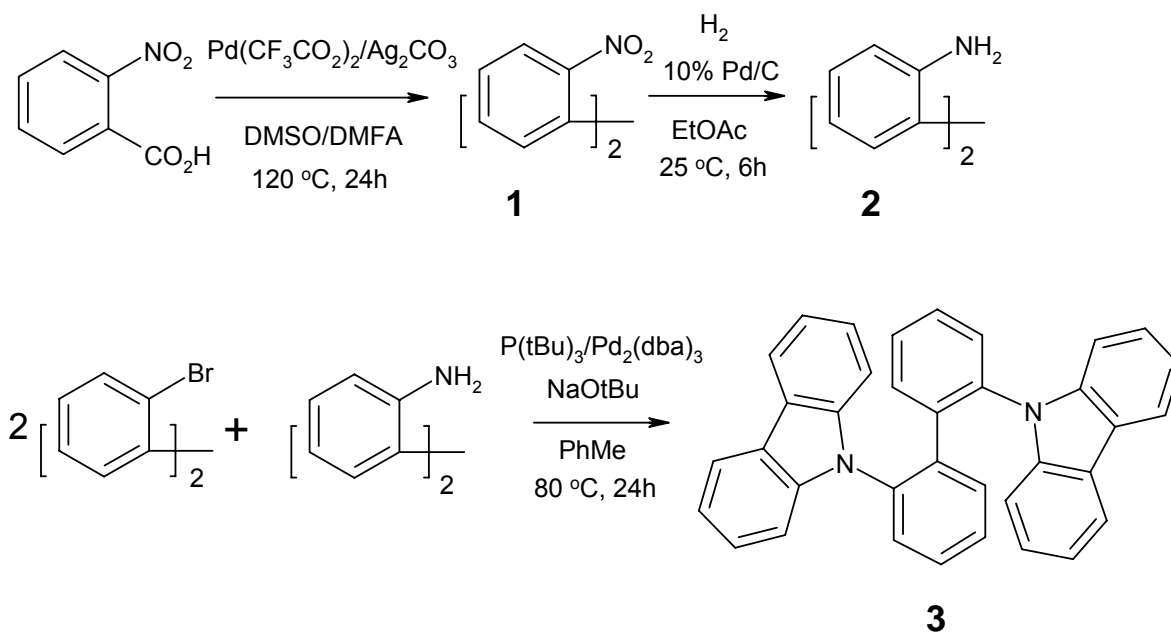
Results and discussion

There are two main strategies for the preparation of isomeric CBPs. Typically, 4,4'-CBP is prepared from biphenyl halides and carbazole by Pd catalyzed Buchwald-Hartwig amination or copper catalyzed Ullman reactions with yields 60-80% (Scheme 1) [7]. The availability of these methods is limited by the availability of biphenyl halides and possible steric hindrances during the amination of more bulky halides. For instance, 2,2'-dibromobiphenyl in Ullman or Buchwald conditions afforded only partially aminated product 2-carbazolyl-2'-bromobiphenyl [6]. As an alternative strategy, sterically crowded CBPs can be prepared by double N-arylation of various diaminobiphenyls in yields exceeding 90%. The major drawback of this method for the synthesis of 2,2'-CBP is the availability of 2,2'-diaminobiphenyl as a starting material.



Scheme 1

Our synthetic strategy was targeted to use more available reagents for preparing of 2,2'-diaminobiphenyl and 2,2'-CBP in high yield. Based on recent studies we choose the decarboxylative homocoupling of (hetero)aromatic carboxylic acids reported by I. Larossa et al [5] for obtaining of 2,2-dinitrobiphenyl **1** as a key precursor. Thus, heating of 2-nitrobenzoic acid with freshly prepared Ag_2CO_3 and $\text{Pd}(\text{TFA})_2$ in dry DMF-DMSO (20:1) mixture for 24 hours afforded **1** in isolated yield of 95% (Scheme 2). The following hydrogenation of **1** over 10% Pd on charcoal in pressure vessel results in 2,2'-diamino-1,1'-biphenyl **2** in 100% yield.



Scheme 2

As a final step, double N-arylation of **2** with 2,2'-dibromobiphenyl in toluene with $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3/\text{NaOtBu}$ afforded the desired 2,2'-dicarbazole-1,1'-biphenyl **3** in 95 % yield. And the total yield of **3** based on 2-nitrobenzoic acid exceeds 90%.

It worth to be mentioned, that compound **3** as a prospective PHOLED host material have demonstrated a very promising photophysical properties.

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Conclusion

In conclusion we have developed a very effective synthetic strategy for the synthesis of 2,2-dicarbazole-1,1'-biphenyl. This methodology can be utilized for the synthesis of other symmetrical CBPs.

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