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Solid-State C−N Cross-Coupling Reactions with Carbazoles as Nitrogen Nucleophiles Using Mechanochemistry

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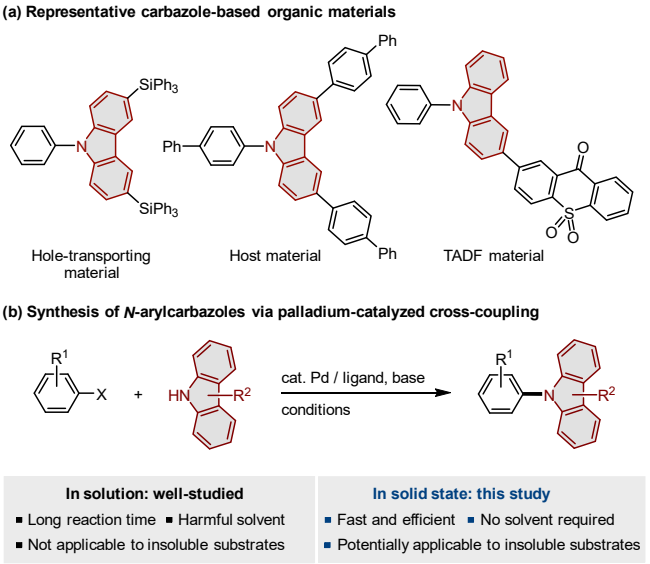
Abstract: The palladium-catalyzed solid-state C−N cross-coupling of carbazoles with aryl halides via a high-temperature ball-milling technique has been reported. This reaction allows simple, fast, and efficient synthesis of *N*-arylcarbazole derivatives in good to excellent yields without the use of large amounts of organic solvents in air. Importantly, the developed solid-state coupling approach enables the cross-coupling of poorly soluble aryl halides with large polyaromatic structures that are barely reactive under conventional solution-based conditions.

N-Arylcarbazole derivatives have attracted considerable attention for their applications in organic solar cells, organic light-emitting diodes (OLEDs), and luminescent materials owing to their high thermal stability, hole transporting properties, and photoconductivity (Scheme 1a).[1] Therefore, the development of efficient synthetic methods for these compounds is of great importance for the discovery of novel organic materials. To date, many useful procedures for the *N*-arylation of carbazoles have been reported.[2-5] Among them, the palladium-catalyzed cross-coupling of aryl halides with amine nucleophiles (Buchwald−Hartwig amination) has been widely employed in the synthesis of *N*-arylcarbazole derivatives (Scheme 1b).[3,6] However, these reactions usually require long reaction times and significant amounts of dry and degassed organic solvents, limiting the practical utility of these methods. In addition, the application of conventional solution-based approaches to poorly soluble aryl halides with large polyaromatic structures is limited, despite the fact that many cutting-edge organic functional materials often contain large π-conjugated core structures.[1,7] Therefore, the development of solvent-independent solid-state *N*-arylation of carbazoles would provide an efficient, practical, and sustainable method for accessing a wide range of *N*-arylcarbazole derivatives and new carbazole-based organic materials that cannot be prepared by another approach (Scheme 1b). Despite the potential benefits, solid-state cross-coupling of carbazoles has not yet been reported.

Recently, ball-milling techniques have been applied to solvent-free palladium-catalyzed C−N bond-forming coupling reactions.[8-11] The first report of ball-milling in solvent-free mechanochemical C−N coupling reactions catalyzed by $Pd(OAc)_2$/XPhos, presented by Su and co-workers in 2018,[9] was soon followed by a robust mechanochemical C−N coupling catalyzed by Pd-PEPPSI-iPENT reported by Browne et al.[10] However, these protocols mainly focus on liquid substrates that serve as both reactants and solvents. In 2019, our group developed the first general solid-state C−N coupling reaction using the $Pd(OAc)_2$/*t*-Bu_3P/1,5-cod catalytic system under ball-milling conditions[11] that allows a wide range of solid diarylamine nucleophiles to form triarylamine derivatives in high yields. However, carbazole derivatives acting as nitrogen nucleophiles did not form the corresponding *N*-arylated products under the previously reported mechanochemical conditions.[11] This is probably because carbazoles can strongly coordinate to any off-cycle palladium species during the reaction and, thus, inhibit the catalyst.[6a,b] Because the solvent-free solid-state reactions proceed under extremely high concentrations, the interaction between reactants and catalysts is much stronger than in a solution.[12] Therefore, the catalyst deactivation pathway would be more favorable in the solid-state reaction, explaining the observed low reactivity of carbazole derivatives under solvent-free ball-milling conditions.



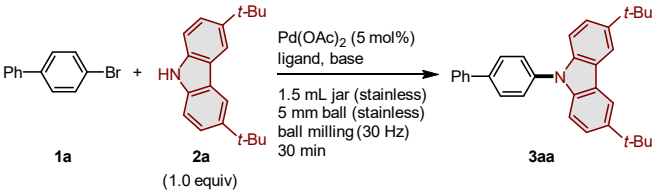
Scheme 1. Representative carbazole-based organic materials and their synthesis via cross-coupling with carbazoles as nitrogen nucleophiles. TADF, thermally activated delayed fluorescence.

We recently reported a broadly applicable solid-state palladium-catalyzed Suzuki-Miyaura cross-coupling reaction, achieved with a high-temperature ball-milling technique using a heat gun,[13] which is faster than the conventional room temperature ball-milling reactions. Inspired by this success, we envisioned that the high-temperature ball-milling conditions would allow the dissociation of carbazoles from off-cycle palladium species, enabling an efficient solid-state coupling. Here, we report the first general solid-state C−N cross-coupling procedure for the synthesis of a wide range of *N*-arylcarbazoles in good to excellent

yields using carbazoles as nitrogen nucleophiles (Scheme 1b). This reaction is very fast and is characterized by a broad substrate scope. Moreover, we demonstrated that *N*-arylation of carbazoles with poorly soluble aryl halides bearing large polyaromatic structures, which are barely reactive under conventional solution-based conditions, can be carried out under the solid-state conditions presented herein.

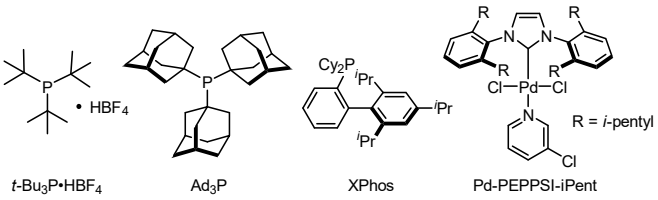
All mechanochemical reactions were conducted in a Retsch MM400 mill (stainless-steel milling jar; 30 Hz; stainless-steel balls). First, we investigated the coupling reaction between 4-bromo-1,1'-biphenyl (**1a**) and 3,6-di-*tert*-butyl-9*H*-carbazole (**2a**) (Table 1). Our previously reported solid-state conditions using the $Pd(OAc)_2$/*t*-Bu_3P/1,5-cod catalytic system at room temperature did not yield the desired product (<1%, entry 1). To accelerate the solid-state cross-coupling with **2a**, we carried out the reaction at a higher temperature. In particular, we used a commercially available temperature-controllable heat gun, which was placed directly above the ball-milling jar (see the Supporting Information for details).[13] The desired product (**3aa**) was obtained using a heat gun preset to 150 °C (2%, entry 2). The internal temperature of reaction mixture (80 °C) was assessed by thermography immediately after opening the milling jar (see the Supporting Information for details). The yield of **3aa** was significantly improved when the internal temperature increased to 125 °C (80%, entry 3) and when the 1,5-cod, a dispersant and stabilizer for the palladium-based catalyst,[11,14] which is not essential under high-temperature ball-milling conditions, was omitted (93%, entry 4). Replacement of *t*-Bu_3P with its air-stable precursor, tri-*tert*-butylphosphonium tetrafluoroborate (*t*-$Bu_3P{\cdot}HBF_4$), lowered the reaction yield (41%, entry 5). The process was improved by an increase in the amount of *t*-$Bu_3P{\cdot}HBF_4$ and replacement of Na(O-*t*-Bu) with NaOH, providing **3aa** in an excellent yield (97%, entry 6). Further increase in the NaOH amount resulted in a quantitative yield of **3aa** (>99%, entry 7). Since NaOH is hygroscopic, the glove box was used when NaOH was added to the ball-milling jar to obtain scientifically accurate results. We confirmed that the reaction also proceeded smoothly to give **3aa** in a quantitative yield even when NaOH was added to the jar in air (see the Supporting Information for details). Notably, **3aa** was not obtained when the reaction was carried out at room temperature under the optimized conditions (<1%, entry 8), suggesting that the high temperature is necessary. The appearance of the solid-state reaction mixture changed depending on the applied conditions (Figure 1): the ball milling at room temperature (entry 8) produced a pale pink solid (Figure 1b), while a black waxy solid (Figure 1c) was obtained after ball milling at 125 °C (entry 7). The change in ligand from *t*-Bu_3P to a more electron-donating Ad_3P[15] lowered the yield of **3aa** (87%, entry 9), while the use of XPhos, which is the optimal ligand under the conditions reported by Su et al., provided **3aa** in high yield (91%, entry 10).[9] On the other hand, the reaction with Pd-PEPPSI-iPent, which is the optimal palladium-based catalyst under the conditions reported by Browne et al., resulted in a poor yield of **3aa** (15%, entry 11).[10] Under the optimized conditions (entry 7), we found that the amount of the palladium catalyst can be reduced to 1 mol %, and **3aa** was obtained in a quantitative yield (see the Supporting Information for details).

Table 1. Optimization study.[a,b]



1a **2a** (1.0 equiv) **3aa**

Entry	Ligand (mol%)	Base (equiv)	Additive (0.20 µL/mg)	Internal temp. (°C)	Yield (%)[b]
1	*t*-Bu_3P (5 mol%)	Na(O-*t*-Bu) (1.5 equiv)	1.5-cod	30 °C	<1
2	*t*-Bu_3P (5 mol%)	Na(O-*t*-Bu) (1.5 equiv)	1.5-cod	80 °C	2
3	*t*-Bu_3P (5 mol%)	Na(O-*t*-Bu) (1.5 equiv)	1.5-cod	125 °C	80
4	*t*-Bu_3P (5 mol%)	Na(O-*t*-Bu) (1.5 equiv)	none	125 °C	93
5	*t*-$Bu_3P{\cdot}HBF_4$ (5 mol%)	Na(O-*t*-Bu) (1.5 equiv)	none	125 °C	41
6	*t*-$Bu_3P{\cdot}HBF_4$ (10 mol%)	NaOH (1.5 equiv)	none	125 °C	97
7	*t*-$Bu_3P{\cdot}HBF_4$ (10 mol%)	NaOH (4.0 equiv)	none	125 °C	>99
8	*t*-$Bu_3P{\cdot}HBF_4$ (10 mol%)	NaOH (4.0 equiv)	none	30 °C	<1
9	Ad_3P (10 mol %)	NaOH (4.0 equiv)	none	125 °C	87
10	XPhos (10 mol%)	NaOH (4.0 equiv)	none	125 °C	91
11	Pd-PEPPSI-iPent (5 mol %)	NaOH (4.0 equiv)	none	125 °C	15



t-$Bu_3P{\bullet}HBF_4$ Ad_3P XPhos Pd-PEPPSI-iPent

[a] Conditions: **1a** (0.30 mmol), **2a** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol, 5 mol%), ligand, base, and liquid additive in a stainless-steel milling jar (1.5 mL) with a stainless-steel ball (5 mm). [b] Determined by ^{1}H NMR analysis of the crude reaction mixture with an internal standard.

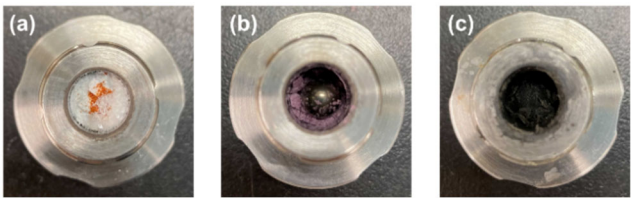
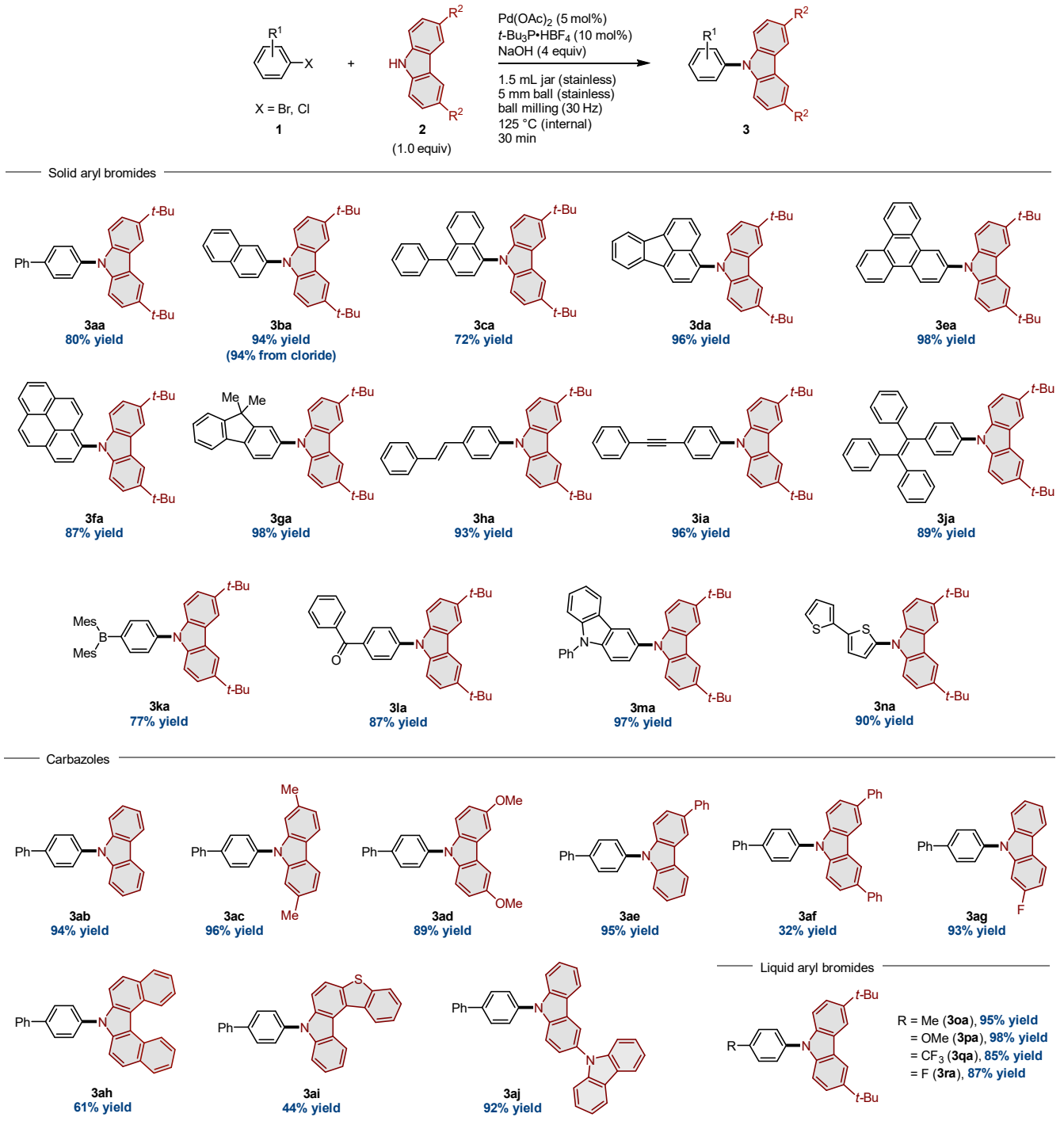


Figure 1. Reaction mixture (a) before ball milling, (b) after ball milling at 30 °C (entry 9, Table 1, <1% yield of **3aa**), and (c) after ball milling at 125 °C (entry 8, Table 1, >99% yield of **3aa**).

With the optimized conditions in hand, we explored the substrate scope of aryl bromides for the solid-state C−N cross-coupling with carbazole derivatives (Table 2), and found that the reaction is applicable to a wide range of substrates and allows a rapid synthesis of various *N*-arylcarbazoles with polycyclic aromatic cores. For example, aryl halides containing naphthalene, acenaphthene, triphenylene, pyrene, and fluorene efficiently formed the corresponding *N*-arylcarbazoles (**3aa**−**3ga**) in good to excellent yields (72−98%). *N*-arylcarbazoles carrying stilbene (**3ha**), internal alkyne (**3ia**), and tetraphenyl ethylene (**3ja**) moieties were synthesized in excellent yields (89−96%) under the optimized conditions. Dimesitylboryl-substituted *N*-arylcarbazole (**3ka**), which is widely known as a donor-acceptor-type charge-transfer luminescent material,[16] can also be prepared via this solid-state cross-coupling reaction in a good yield (77%). Ketone-, carbazole-, and dithiophene-containing *N*-arylcarbazoles (**3la**–**3na**) were obtained in high yields (87, 97, and 90%, respectively). This method is also applicable to solid aryl chlorides, such as 2-chloronaphthalene (**1b'**), which formed **3ba** in excellent yield (94%).

Table 2. Substrate scope.[a,b]

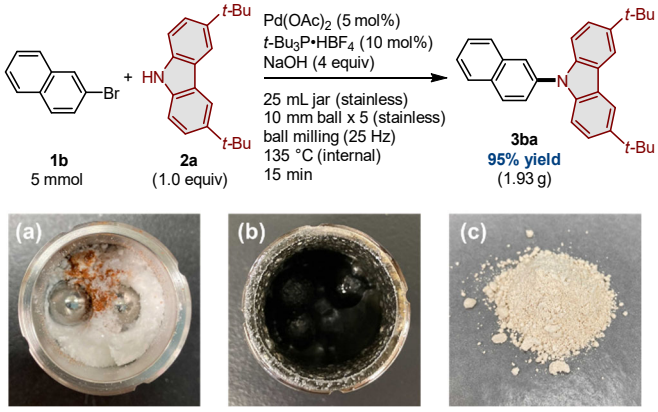


[a] Conditions: **1** (0.30 mmol), **2** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol, 5 mol%), *t*-$Bu_3P{\cdot}HBF_4$ (0.015 mmol, 5 mol%), NaOH (1.2 mmol, 4 equiv) in a stainless-steel milling jar (1.5 mL) with a stainless-steel ball (5 mm). [b] Isolated yields.

Subsequently, we focused on the scope of carbazole nucleophiles (Table 2). The reaction of unsubstituted carbazole (**2b**) provided the corresponding coupling product **3ab** in excellent yield (94%). Carbazoles bearing methyl-, methoxy-, phenyl-, and fluoro-substituents (**2c**–**2g**) also reacted under the applied solid-state conditions to afford the corresponding products (**3ac**–**3ag**) in moderate to high yield (32−96%). Furthermore, the reactions of π-extended carbazoles (**2h** and **2i**) and 3,9'-bicarbazole (**2j**) provided the desired products (**3ah**–**3aj**) in moderate to high yield (44−92%).

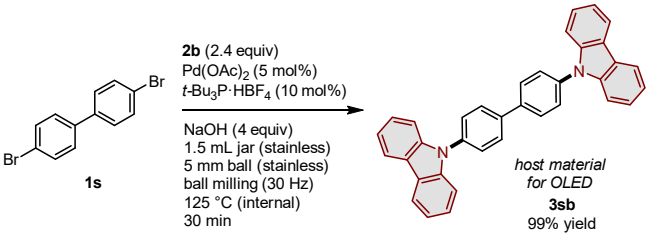
The developed mechanochemical protocol is also applicable to liquid aryl bromides (Table 2). The reactions between aryl bromides bearing electron-donating and electron-withdrawing groups and **2a** proceeded smoothly to afford the corresponding products (**3oa**–**3ra**) in high yields (85–98%).

The gram-scale synthesis of *N*-arylcarbazoles under solvent-free mechanochemical conditions was performed to demonstrate the practical utility of this solid-state protocol (Scheme 2). The solid-state cross-coupling of 2-bromonaphthalene (**1b**) with **2a** was carried out on a 5 mmol scale in a stainless-steel ball-milling jar (25 mL) with five stainless-steel balls (diameter: 10 mm) using a heat gun preset to 250 °C, ensuring an internal reaction temperature of 135 °C (Scheme 2a). The reaction reached completion within 15 min, when the reaction mixture appeared as a black waxy solid (Scheme 2b). Simple re-precipitation from CH_2Cl_2/MeOH gave **3ba** in excellent yield (95%, 1.93 g, Scheme 2c). This result clearly shows the potential utility of the present solid-state protocol for a large-scale synthesis of *N*-arylcarbazole derivatives.



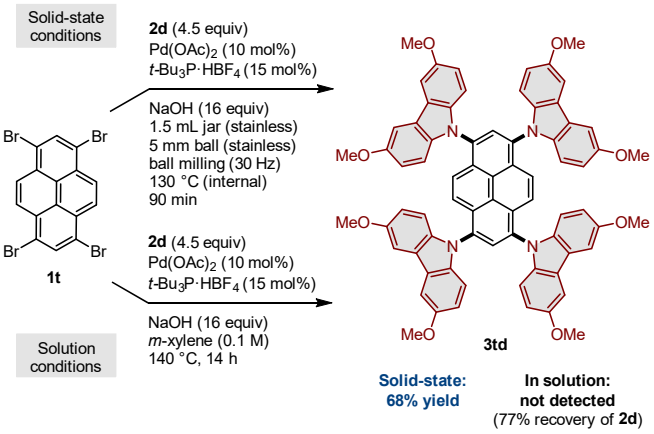
Scheme 2. Solid-state cross-coupling on a gram scale using 25 mL stainless-steel jar with five stainless-steel balls (diameter: 10 mm). Reaction mixture (a) before ball milling, (b) after ball milling. (c) Isolated product **3ba**.

To demonstrate the applicability of the developed solid-state conditions to the synthesis of carbazole-based organic materials, we synthesized host materials for efficient organic light-emitting diodes (Scheme 3). Under the optimized solid-state conditions, the reaction of 4,4'-dibromo-1,1'-biphenyl (**1s**) and **2b** afforded 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (**3sb**)[17] in excellent yield (99%). This result suggests the great potential of this solid-state *N*-arylation of carbazoles to efficiently prepare materials-science-oriented carbazole derivatives in an environmentally friendly manner.



Scheme 3. Synthesis of a host material for organic light-emitting diodes via solid-state coupling.

We found that the solid-state *N*-arylation of carbazoles is particularly useful for poorly soluble aryl halides (Scheme 4). The 1,3,6,8-tetrabromopyrene (**1t**) is poorly soluble in common organic solvents and exhibits lower solubility in toluene ($3.9 \cdot 10^{-4}$ M at 23 °C) than fullerene ($4.8 \cdot 10^{-3}$ M at 23 °C), which is one of the most iconic poorly soluble molecules.[18] In fact, the reaction between **1t** and **2d** in solution (140 °C for 14 h) did not result in product formation, and 77% of **2d** was recovered. Although we applied a variety of solution-based conditions using different bases, solvents, and temperatures, the reactions did not yield the desired product **3td** (see the Supporting Information for details). Notably, our solid-state cross-coupling protocol enabled the synthesis of **3td** in a good yield (68%). The molecular structure of **3td** was confirmed by single-crystal X-ray diffraction (Figure 2). This is the first reported synthesis of tetra-carbazole substituted pyrene derivative. Given that pyrene derivatives having four diarylamine substituents have been extensively studied as potential hole-transporting materials (HTMs) for perovskite-based solar cells,[19] **3td** could become a promising candidate for high-performance HTMs. Our results suggest that the present solid-state coupling strategy would allow access to novel carbazole-based organic materials from poorly soluble substrates that are incompatible with solution-based protocols.[1]



Scheme 4. Reactions of poorly soluble 1,3,6,8-tetrabromopyrene (**1t**) with dimethoxy-substituted carbazole **2td**.

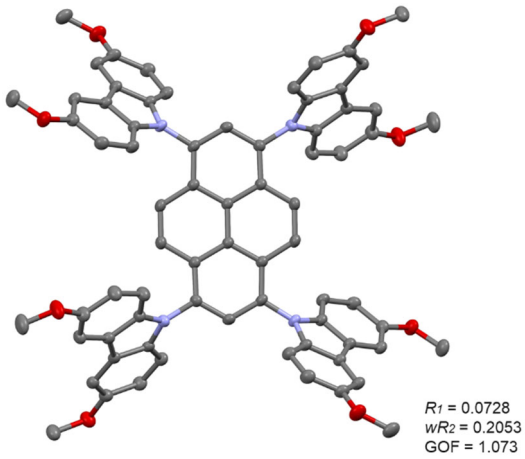


Figure 2. X-ray crystal structure of **3td** with thermal ellipsoids at 50% probability; all hydrogen atoms are omitted for clarity (color code: grey = carbon; purple = nitrogen; red = oxygen).

In summary, we developed a mechanochemical procedure for solid-state C−N cross-coupling with carbazoles as nitrogen nucleophiles to afford *N*-arylcarbazoles with polycyclic aromatic structures. This reaction is fast and can be carried out on a gram-scale in air without the need for large amounts of dry and degassed organic solvents. In addition to these practical benefits, the method allows cross-coupling between carbazoles and poorly soluble aryl halides that are practically unreactive in solution. The present study thus illustrates the outstanding potential of the solid-state coupling approach for the discovery of novel carbazole-based organic materials.

Acknowledgements

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Keywords: ball mills • mechanochemistry • carbazole • cross-coupling • solid-state reaction

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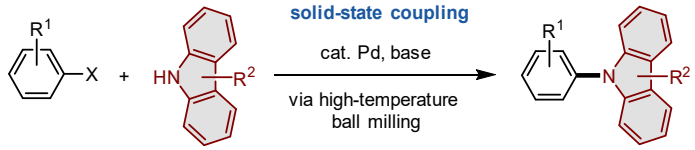

Herein, we report fast and efficient solid-state palladium-catalyzed C–N cross-coupling reactions with carbazoles as nitrogen nucleophiles via a high-temperature ball-milling technique. This solid-state protocol enables the synthesis of novel *N*-arylcarbazole derivatives from poorly soluble aryl halides with large polyaromatic structures that are inaccessible under conventional solution-based conditions.