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

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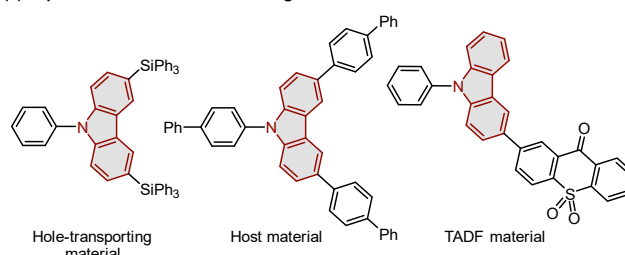
**Abstract:** The palladium-catalyzed solid-state C–N cross-coupling of carbazoles with aryl halides via a high-temperature ball-milling technique has been reported. This reaction allows simple, fast, and efficient synthesis of *N*-arylcarbazole derivatives in good to excellent yields without the use 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).<sup>[1]</sup> 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.<sup>[2–5]</sup> 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).<sup>[3,6]</sup> 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  $\pi$ -conjugated core structures.<sup>[1,7]</sup> 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.

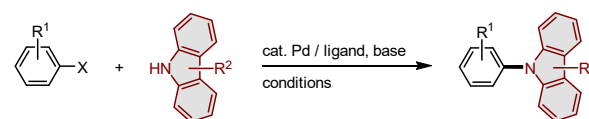
Recently, ball-milling techniques have been applied to solvent-free palladium-catalyzed C–N bond-forming coupling reactions.<sup>[8–11]</sup> The first report of ball-milling in solvent-free mechanochemical C–N coupling reactions catalyzed by Pd(OAc)<sub>2</sub>/XPhos, presented by Su and co-workers in 2018,<sup>[9]</sup> was soon followed by a robust mechanochemical C–N coupling catalyzed by Pd-PEPPSI-iPENT reported by Browne et al.<sup>[10]</sup> 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)<sub>2</sub>/*t*-Bu<sub>3</sub>P/1,5-cod catalytic system under ball-

milling conditions<sup>[11]</sup> 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.<sup>[11]</sup> This is probably because carbazoles can strongly coordinate to any off-cycle palladium species during the reaction and, thus, inhibit the catalyst.<sup>[6a,b]</sup> 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.<sup>[12]</sup> 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.

## (a) Representative carbazole-based organic materials



## (b) Synthesis of *N*-arylcarbazoles via palladium-catalyzed cross-coupling



### In solution: well-studied

- Long reaction time
- Harmful solvent
- Not applicable to insoluble substrates

### In solid state: this study

- Fast and efficient
- No solvent required
- Potentially applicable to insoluble substrates

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

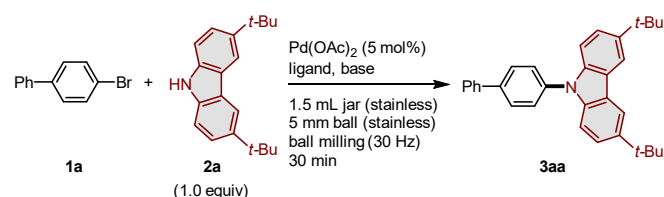
We recently reported a broadly applicable solid-state palladium-catalyzed Suzuki–Miyaura cross-coupling reaction, achieved with a high-temperature ball-milling technique using a heat gun,<sup>[13]</sup> which is faster than the conventional room temperature ball-milling reactions. Inspired by this success, 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

## COMMUNICATION

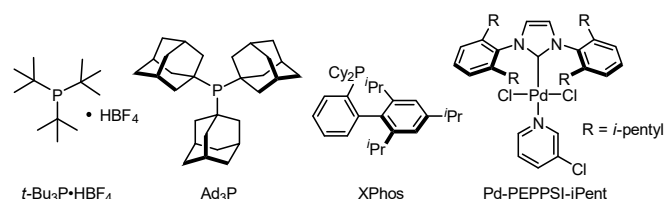
yields using carbazoles as nitrogen nucleophiles (Scheme 1b). This reaction is very fast and is characterized by a broad substrate scope. Moreover, we demonstrated that *N*-arylation of carbazoles with poorly soluble aryl halides bearing large polyaromatic structures, which are barely reactive under 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)<sub>2</sub>/*t*-Bu<sub>3</sub>P/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).<sup>[13]</sup> 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,<sup>[11,14]</sup> which is not essential under high-temperature ball-milling conditions, was omitted (93%, entry 4). Replacement of *t*-Bu<sub>3</sub>P with its air-stable precursor, tri-*tert*-butylphosphonium tetrafluoroborate (*t*-Bu<sub>3</sub>P·HBF<sub>4</sub>), lowered the reaction yield (41%, entry 5). The process was improved by an increase in the amount of *t*-Bu<sub>3</sub>P·HBF<sub>4</sub> 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<sub>3</sub>P to a more electron-donating Ad<sub>3</sub>P<sup>[15]</sup> 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).<sup>[9]</sup> On the other hand, the reaction with Pd-PEPPSI-*i*Pent, 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).<sup>[10]</sup> 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).

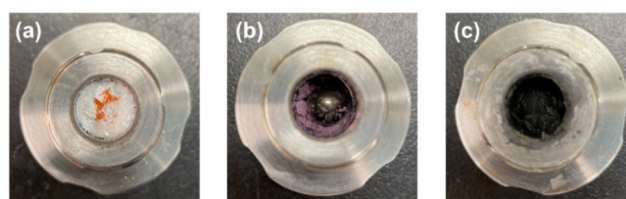
**Table 1.** Optimization study.<sup>[a,b]</sup>



Entry	Ligand (mol%)	Base (equiv)	Additive (0.20 μL/mg)	Internal temp. (°C)	Yield (%) <sup>[b]</sup>
1	<i>t</i> -Bu <sub>3</sub> P (5 mol%)	Na(O- <i>t</i> -Bu) (1.5 equiv)	1,5-cod	30 °C	<1
2	<i>t</i> -Bu <sub>3</sub> P (5 mol%)	Na(O- <i>t</i> -Bu) (1.5 equiv)	1,5-cod	80 °C	2
3	<i>t</i> -Bu <sub>3</sub> P (5 mol%)	Na(O- <i>t</i> -Bu) (1.5 equiv)	1,5-cod	125 °C	80
4	<i>t</i> -Bu <sub>3</sub> P (5 mol%)	Na(O- <i>t</i> -Bu) (1.5 equiv)	none	125 °C	93
5	<i>t</i> -Bu <sub>3</sub> P·HBF <sub>4</sub> (5 mol%)	Na(O- <i>t</i> -Bu) (1.5 equiv)	none	125 °C	41
6	<i>t</i> -Bu <sub>3</sub> P·HBF <sub>4</sub> (10 mol%)	NaOH (1.5 equiv)	none	125 °C	97
7	<i>t</i> -Bu <sub>3</sub> P·HBF <sub>4</sub> (10 mol%)	NaOH (4.0 equiv)	none	125 °C	>99
8	<i>t</i> -Bu <sub>3</sub> P·HBF <sub>4</sub> (10 mol%)	NaOH (4.0 equiv)	none	30 °C	<1
9	Ad <sub>3</sub> P (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- <i>i</i> Pent (5 mol %)	NaOH (4.0 equiv)	none	125 °C	15



[a] Conditions: **1a** (0.30 mmol), **2a** (0.30 mmol), Pd(OAc)<sub>2</sub> (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 <sup>1</sup>H NMR analysis of the crude reaction mixture with an internal standard.



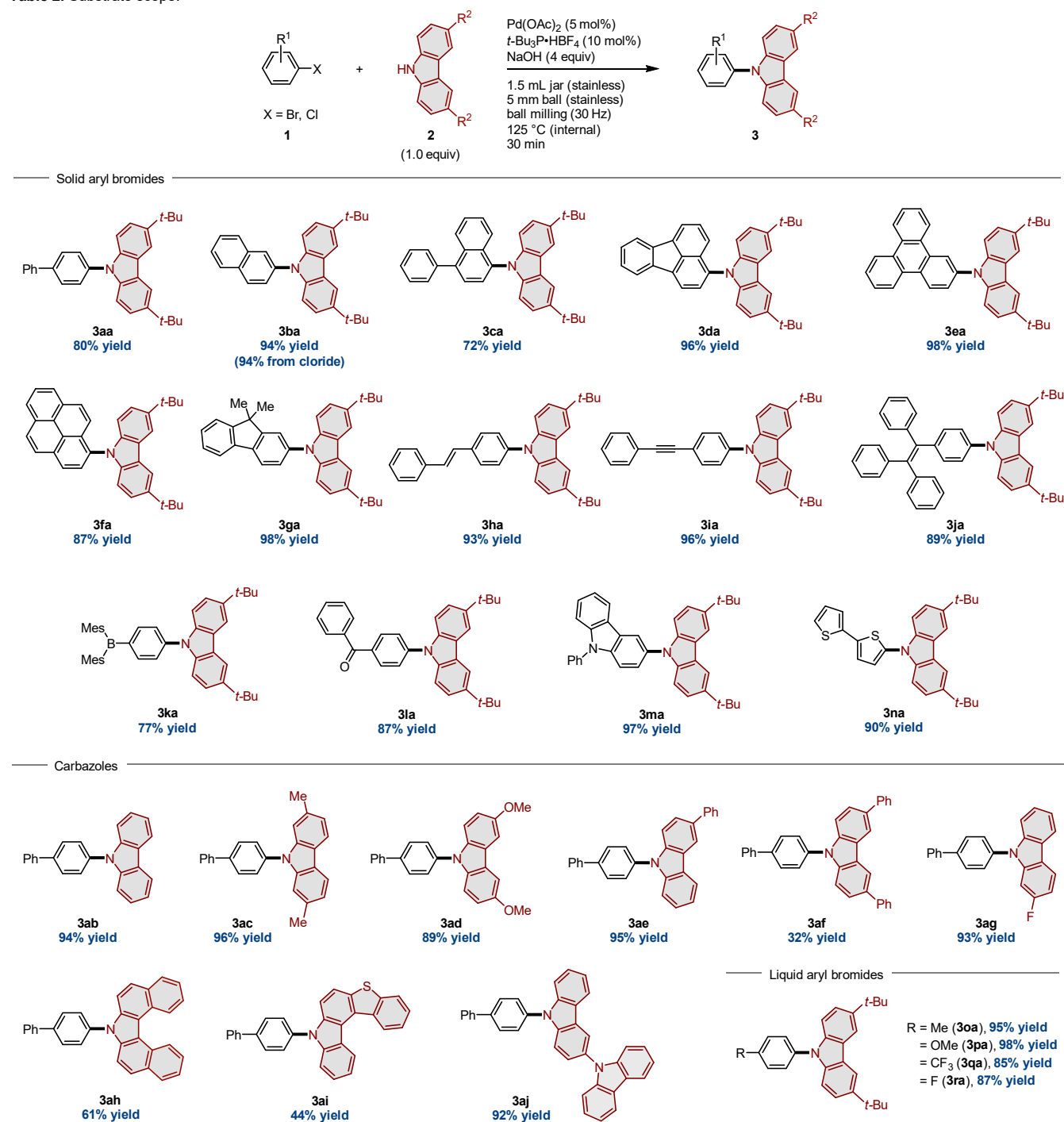
**Figure 1.** Reaction mixture (a) before ball milling, (b) after ball milling at 30 °C (entry 9, Table 1, <1% yield of **3aa**), and (c) after ball milling at 125 °C (entry 8, Table 1, >99% yield of **3aa**).

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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,<sup>[16]</sup> 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.<sup>[a,b]</sup>



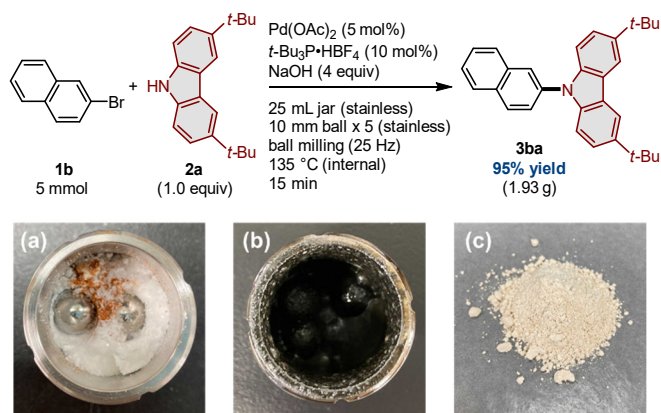
[a] Conditions: **1** (0.30 mmol), **2** (0.30 mmol),  $\text{Pd}(\text{OAc})_2$  (0.015 mmol, 5 mol%),  $t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$  (0.015 mmol, 5 mol%), NaOH (1.2 mmol, 4 equiv) in a stainless-steel milling jar (1.5 mL) with a stainless-steel ball (5 mm). [b] Isolated yields.

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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  $\pi$ -extended carbazoles (**2h** and **2i**) and 3,9'-bicarbazole (**2j**) provided the desired products (**3ah–3aj**) in moderate to high yield (44–92%).

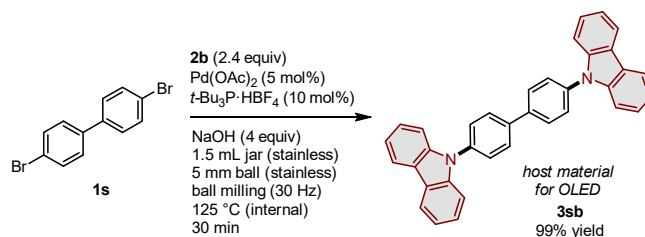
The developed mechanochemical protocol is also applicable to liquid aryl bromides (Table 2). The reactions between aryl bromides bearing electron-donating and electron-withdrawing groups and **2a** proceeded smoothly to afford the corresponding products (**30a–30r**) in high yields (85–98%).

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 reprecipitation from CH<sub>2</sub>Cl<sub>2</sub>/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.



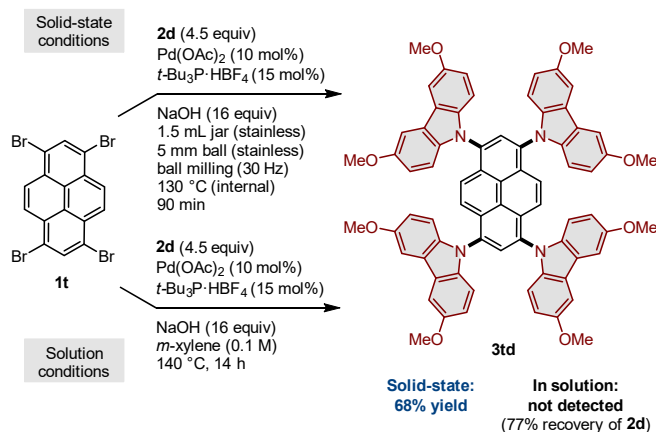
**Scheme 2.** Solid-state cross-coupling on a gram scale using 25 mL stainless-steel jar with five stainless-steel balls (diameter: 10 mm). Reaction mixture (a) before ball milling, (b) after ball milling, (c) isolated product **3ba**.

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**)<sup>[17]</sup> 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.



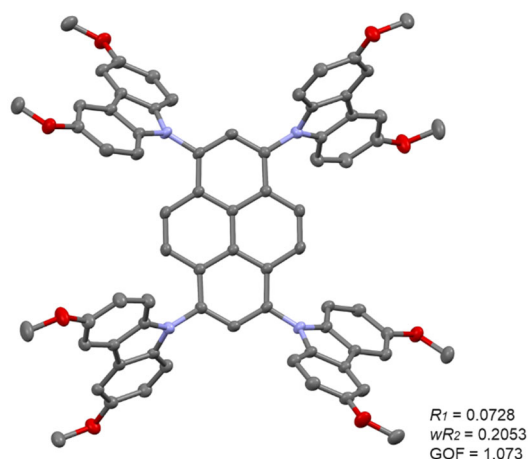
**Scheme 3.** Synthesis of a host material for organic light-emitting diodes via solid-state coupling.

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.<sup>[18]</sup> 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,<sup>[19]</sup> **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.<sup>[1]</sup>



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





**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.

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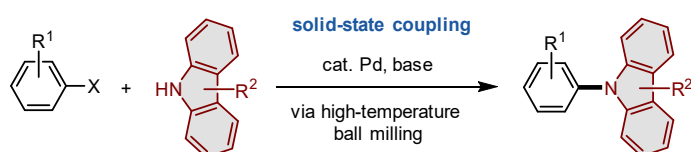
This work was financially supported by the Japan Society for the Promotion of Science (JSPS) via KAKENHI grants 18H03907, 17H06370, 20H04795, and 21H01926; by the JST via CREST grant JPMJCR19R1; FOREST grant JPMJFR2011; and by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI), MEXT, Japan. We thank Nippon Chemical Industrial Co., Ltd. for the generous donation of the Buchwald ligands. We also thank Mitsubishi Chemical Corporation for their cooperation and helpful discussions.

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

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## Entry for the Table of Contents



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.