Solid-state nickel(0)-mediated Yamamoto coupling enabled by mechanochemistry

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Herein, we report the first solid-state protocol for nickel(0)-mediated Yamamoto coupling reactions using ball milling. A variety of aryl halides reacted efficiently in the presence of bis(cyclooctadiene)nickel(0) [Ni(cod)$_2$] and 4,4'-di-*tert*-butyl-2,2'-bipyridyl under solid-state mechanochemical conditions, affording the corresponding biaryls in high yields. Considering that potentially harmful and high-boiling organic solvents are not required, the present study provides a more convenient, environmentally friendly, and sustainable alternative to conventional solution-based Yamamoto coupling. Solid-state Yamamoto coupling polymerization and the development of a catalytic variant are also described.

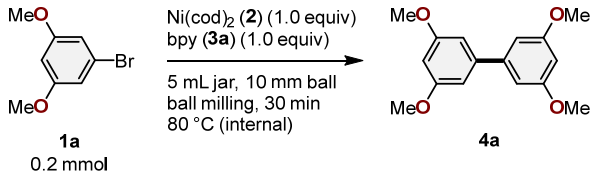
Keywords: Ball milling, Mechanochemistry, Solid-state, Yamamoto coupling

Nickel(0)-mediated homocoupling reactions of aryl halides, termed Yamamoto coupling, have been recognized as one of the most reliable, versatile, and powerful methods for biaryl synthesis.[1] In particular, the utility of this homocoupling has been well-demonstrated by the efficient synthesis of structurally complex, conjugated organic materials.[2] In a recent study, Itami, Segawa et al. used Yamamoto coupling in key steps to synthesize of a series of carbon nanobelts.[2c,2d] In addition to the preparation of such small aromatic molecules, Yamamoto coupling polymerization has also been an efficient method for the preparation of various conjugated liner polymers and microporous polymer networks.[3] Despite the widespread use of Yamamoto coupling in material sciences, the requirement of significant amounts of potentially harmful and high-boiling organic solvents that are difficult to remove [e.g. *N*,*N*-dimethylformamide (DMF)] represent a significant drawback from an environmental perspective and practical utility.[1-3]

Over the past decade, organic synthesis has greatly benefited from mechanochemistry using ball milling.[4,5] This technique allows organic reactions to be carried out under solvent-less solid-state conditions, and higher efficiency can often be achieved compared to analogous transformations in solution.[4,5] These benefits of mechanochemical solid-state conditions have also been noted in transition-metal-catalyzed or -mediated coupling reactions.[6,7] Given our recent success in applying solid-state mechanochemical cross-coupling chemistry to many issues associated with conventional solution-based conditions,[5] we envisioned that this mechanochemical strategy could be applied to the Yamamoto coupling of aryl halides. The development of a solvent-free solid-state Yamamoto coupling protocol represents a convenient, environmentally friendly, and sustainable alternative to conventional solution-based methods.

Initially, we conducted an optimization study on the solid-state Yamamoto coupling between 1-bromo-3,5-dimethoxybenzene (**1a**) (0.2 mmol) and bis(cyclooctadiene)nickel(0) [Ni(cod)$_2$] (**2**) (1.0 equiv) in the presence of 2,2-bipyridyl (bpy) (**3a**) (1.0 equiv) (Table 1). The reactions were conducted in a Retch MM400 ball mill in a stainless-steel milling jar (5 mL) using one stainless-steel ball (diameter: 10 mm). We used a commercially available temperature-controllable heat gun placed directly above the ball-milling jar to control the reaction temperature.[8] Reactions were performed using a heat gun with a preset temperature of 160 °C, and the internal temperature of the reaction mixture (80 °C) was assessed by thermography immediately after opening the milling jar (see the Supporting Information for details). Given that **2** is highly sensitive to air,[9] nine chemicals were added to the jar in an argon-filled glovebox. After closing the jar tightly, it was removed from the glovebox and placed in the MM400 ball mill. The mechanochemical reaction conducted at 30 Hz for 10 min provided the desired product **4a** in 56% yield (Entry 1). Prolonging the reaction time (30 min) did not improve the yield (Entry 2, 54%). Decreasing the frequency (25 and 20 Hz) afforded better yields (Entries 3 and 4; 58% and 71% yields, respectively). The reaction at 20 Hz for 10 min provided a slightly lower yield than that obtained after 30 min (Entry 5, 68% yield).

Table 1. Optimization of the mechanochemical parameters[a]

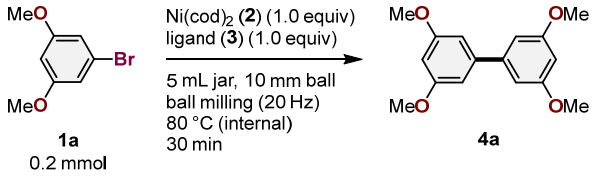


Entry	Frequency (Hz)	Time	Yield (%)[b]
1	30	10	56
2	30	30	54
3	25	30	58
4	20	30	71
5	20	10	68

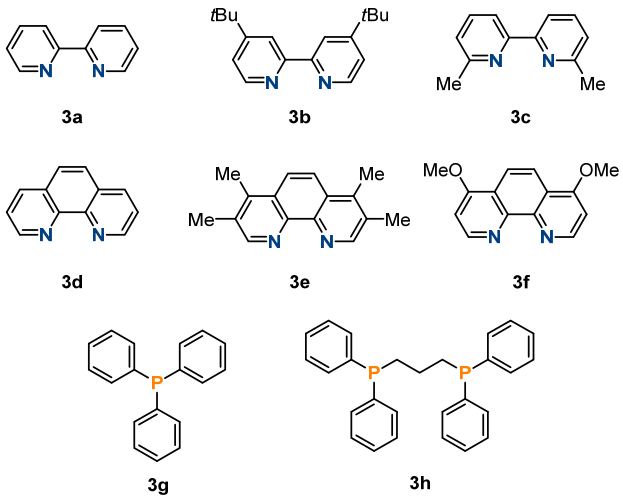
[a]Conditions: **1a** (0.20 mmol), **2** (0.20 mmol), and bpy (**3a**) (0.20 mmol) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using an internal standard.

Next, the effect of the ligand on solid-state Yamamoto coupling was investigated (Table 2). The use of di-*tert*-butyl-2,2'-bipyridyl (dtbpy) (**3b**) instead of **3a** afforded the desired product **4a** in excellent yield (Entry 2, 86%). The sterically hindered 6,6'-dimethyl-2,2'-bipyridine (**3c**) also showed high efficiency, but the yield was lower than that of **3b** (Entry 3, 80%). The reactions using 1,10-phenanthroline-type ligands (**3d**–**3f**) proceeded to give **4a** in moderate yields (Entries 4–6, 46–58% yields). The use of phosphine ligands such as triphenylphosphine (**3g**) and 1,3-bis(diphenylphosphino)propane (**3h**) afforded the desired product **4a** in moderate yields (Entries 7 and 8; 43% and 65% yields, respectively). In the absence of a ligand, the reaction did not result in the formation of any product (Entry 9).

Table 2. Screening of ligands[a]



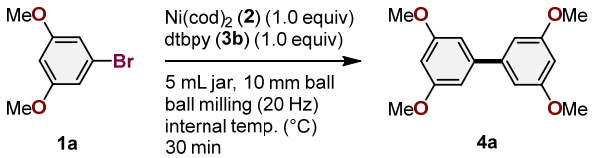
Entry	Ligand (**3**)	Yield (%)[b]
1	**3a**	71
2	**3b**	86
3	**3c**	80
4	**3d**	48
5	**3e**	58
6	**3f**	46
7	**3g**	43
8	**3h**	65
9	none	0



[a]Conditions: **1a** (0.20 mmol), **2** (0.20 mmol), ligand (**3**) (0.20 mmol) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using an internal standard.

Finally, we investigated the effects of reaction temperature and scale on this reaction (Table 3). Increasing the reaction temperature from 80 to 120 °C, improved the yield of **4a** (Entry 2, 91%). While the reaction on a 0.5 mmol scale afforded **4a** in a lower yield than that of a 0.2 mmol scale (Entry 3, 80%), the use of 1.2 equivalents of **2** and **3b** provided the best result (Entry 4, 93%).

Table 3. Effects of temperature and scale[a]



Entry	Scale of **1a**	Internal temp (°C)	Yield (%)[b]
1	0.2 mmol	80	86
2	0.2 mmol	120	91
3	0.5 mmol	120	80
4[c]	0.5 mmol	120	93 (93)

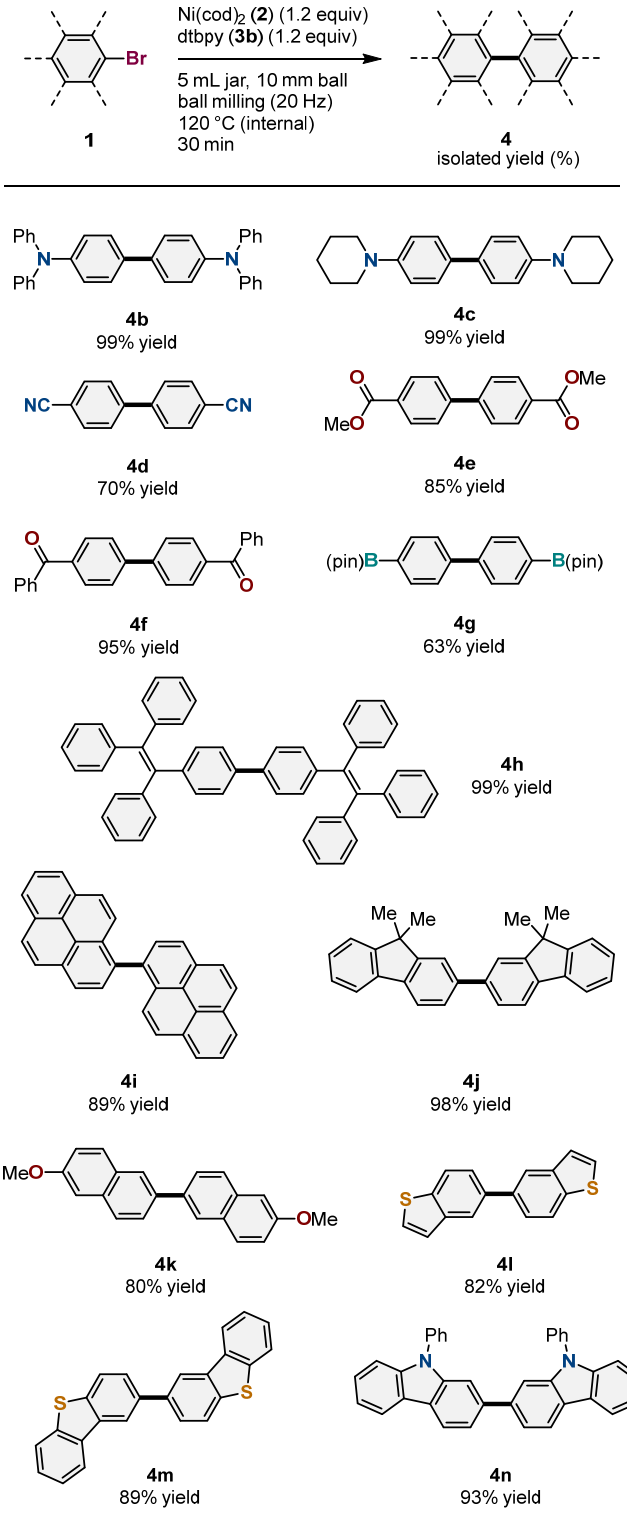
[a]Conditions: **1a** (0.20 mmol), **2** (0.20 mmol), and ligand (**3**) (0.20 mmol) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). [b]Determined by ^{1}H NMR analysis of the crude reaction mixture using an internal standard. Isolated yields are given in parenthesis. [c]1.2 equivalents of **2** and 1.2 equivalents of **3b** were used.

With the optimized conditions in hand, the substrate scope was investigated (Table 4). Substrates containing electron-donating and electron-withdrawing groups (**1b**–**1f**) reacted smoothly to afford the desired homocoupling products (**4b**–**4f**) in good to excellent yields (70–99%). A pinacol boronic ester group [B(pin)], a synthetically useful functional group, was tolerated under the optimized mechanochemical conditions (**4g**, 63% yield). This method enables the rapid synthesis of polycyclic aromatic molecules (**4h**–**4k**). Furthermore, heteroaromatic substrates such as benzothiophene, dibenzothiophene, and carbazole also underwent the mechanochemical solid-state Yamamoto coupling to afford the corresponding products (**4l**–**4n**) in high yields (82–93%).

Subsequently, we performed reactions with different aryl halides (Scheme 1). This method was applicable to aryl iodide (**1o**) and chloride (**1p**) to deliver the desired product **4e** in high yields (81% and 87% yields, respectively).

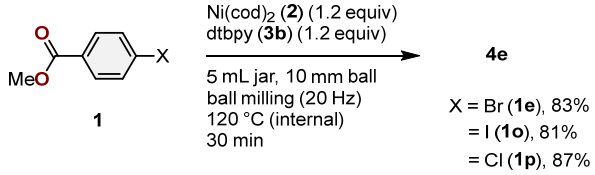
To demonstrate the practical utility of this protocol, a gram-scale reaction was investigated (Scheme 2). A 10 mL jar and two balls (diameter: 10 mm) were used for the gram-scale reaction of **1b** (4.2 mmol), and the desired product **4b** was obtained in quantitative yield (99%, 1.026 g) without any yield loss during the scale-up process.

Table 4. Substrate scope[a]



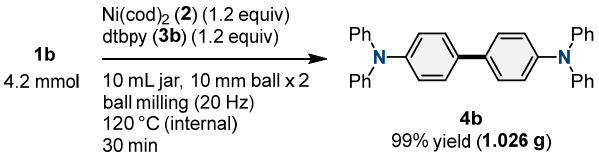
[a]Conditions: **1** (0.5 mmol), **2** (0.6 mmol), and dtbpy (**3b**) (0.6 mmol) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). Isolated yields are shown.

Scheme 1. Reactions using different halides[a]



[a]Conditions: **1** (0.5 mmol), **2** (0.6 mmol), dtbpy (**3b**) (0.6 mmol) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). ^{1}H NMR yields are shown.

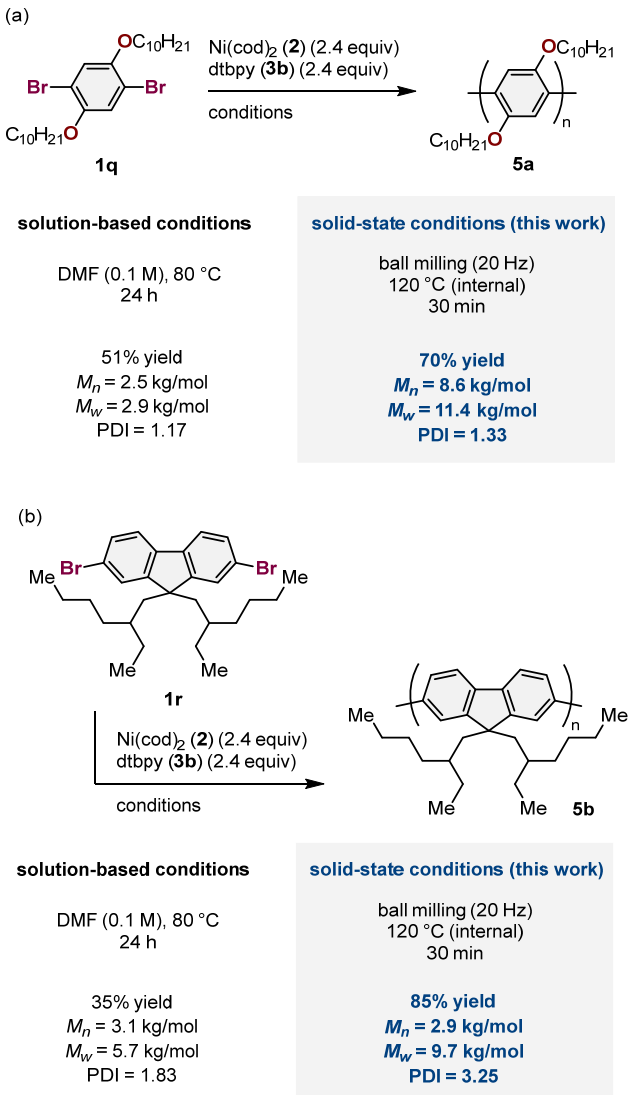
Scheme 2. Gram-scale solid-state Yamamoto coupling reaction[a]



[a]Conditions: **1b** (3.4 mmol), **2** (4.1 mmol), and dtbpy (**3b**) (4.1 mmol) in a stainless-steel jar (5 mL) with two stainless-steel balls (10 mm). Isolated yields are shown.

Yamamoto homocoupling polymerization is one of the most powerful tools to synthesize conjugated polymers.[3] Considering that the solid-state Yamamoto polymerization using mechanochemistry could provide an eco-friendly solvent-free protocol for the preparation of functional polymers,[10] the solid-state polymerization of 1,4-dibromo-2,5-bis(decyloxy)benzene (**1q**) for the preparation of poly(*para*-phenylene) derivative (**5a**), which is one of the core structures of organic electric materials,[11] was attempted (Scheme 3a). Under solution-based conditions using DMF for 24 h, the desired polymer **5a** was obtained [number-average molecular weight (M_n) = 2.5 kg/mol; weight average molecular weight (M_w) = 2.9 kg/mol; polydispersity index (PDI) = 1.17)]. Both the M_n and M_w increased under the developed mechanochemical conditions (M_n = 8.6 kg/mol; M_w = 11.4 kg/mol; PDI = 1.33). This result suggests that the solid-state conditions allow the preparation of longer conjugated polymers with better efficiency than those of solution-based conditions.[12] This is probably because polymer growth ends with low solubility could be efficiently involved in polymerization under solid-state conditions.[12] The solid-state Yamamoto coupling polymerization of fluorene derivative **1r** also afforded a higher molecular-weight polymer **5b** (M_n = 2.9 kg/mol; M_w = 9.7 kg/mol; PDI = 3.25) than that obtained under solution-based conditions (M_n = 3.1 kg/mol; M_w = 5.7 kg/mol; PDI = 1.83) (Scheme 3b). Although the details are still unknown, the larger PDI of the solid-state polymerization is probably due to homocoupling between long polymer growth ends with low solubility, producing very large polymers under solid-state conditions. Such coupling is unlikely to occur in solution but may have proceeded only under solid conditions.

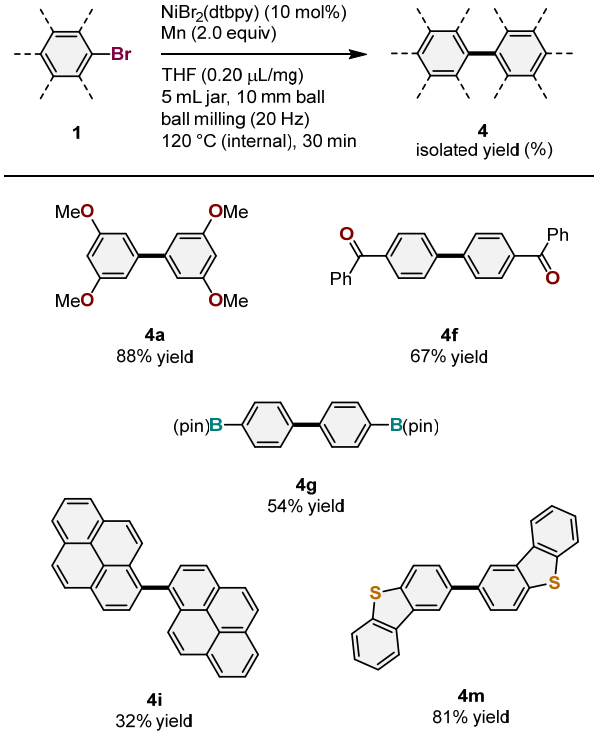
Scheme 3. Solid-state Yamamoto coupling polymerization[a]



[a]See the Supporting Information for the details of these conditions.

Encouraged by the successful development of the solid-state Yamamoto coupling protocol using a stoichiometric amount of nickel, we investigated nickel-catalyzed solid-state Yamamoto coupling using a stoichiometric reductant. Based on the previously reported nickel-catalyzed reductive coupling under solution-based conditions,[1e,1h,1i,13] manganese metal was used as the reductant under mechanochemical conditions. After the optimization study (see the Supporting Information for details), the reaction of aryl bromides (**1a**, **1f**, **1g**, **1i**, and **1m**) using $NiBr_2$(dtbpy) (10 mol%), manganese metal (2.0 equiv), and THF as a liquid-assisted-grinding additive[1] afforded the desired products (**4a**, **4f**, **4g**, **4i**, and **4m**) in moderate-to-good yields (32−88%) (Table 5). However, lower yields were obtained compared with the stoichiometric conditions in all attempted cases.

Table 5. Development of solid-state catalytic Yamamoto coupling under mechanochemical conditions[a]



[a]Conditions: **1** (0.5 mmol), $NiBr_2$(dtbpy) (0.05 mmol), Mn (1.0 mmol), and THF (0.20 μL/mg) in a stainless-steel jar (5 mL) with a stainless-steel ball (10 mm). The isolated yields are shown.

In summary, we developed the first solid-state mechanochemical protocol for nickel(0)-mediated Yamamoto coupling to give biaryls in good yields. The newly developed conditions do not require potentially harmful and high-boiling organic solvents and can be applied to various aryl halides bearing both electron-donating and electron-withdrawing groups, thus providing a practical and sustainable method to complement conventional solution-based conditions. The first solid-state Yamamoto coupling polymerization and development of a catalytic variant were also achieved.

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Supporting Information is available at http://dx.doi.org/10.1246/cl.******.

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