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Graphical Abstract

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Homocoupling Reactions of Terminal Alkynes and Arylboronic Compounds Catalyzed by *in situ* Formed $Al(OH)_3$-Supported Palladium Nanoparticles

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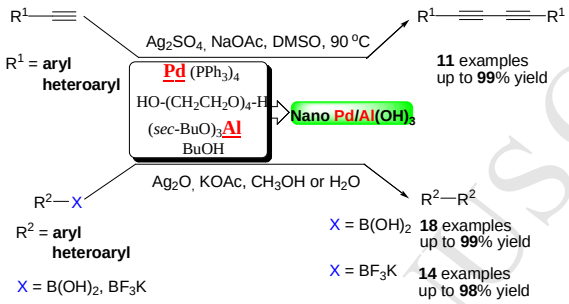

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ABSTRACT

Palladium nanoparticles supported on newly generated $Al(OH)_3$ was found to be a highly efficient catalyst in oxidative homo-couplings of (Het)aryl alkynes, (Het)arylboronic acids and potassium (Het)aryltrifluoroborates, respectively. Moderate to excellent yields of symmetrical 1,3-dieyes and biaryls were obtained under mild conditions.

1. Introduction

Considering the importance of environmental protection, it is very valuable and necessary to carry out chemical reactions under benign conditions using recyclable catalysts.[1] These catalysts are usually immobilized on a solid, and green support for easy separation and reuse.[2] Moreover, it has been demonstrated that support properties, which include the material itself and the structure, play an important role in the catalyst's performance and catalytic activities.[3] Therefore, the development of better catalyst supports is necessary to enhance the activity of the catalyst. On the other hand, nano-transition-metal catalyzed organic reactions have received much attention recently because of their extremely small size and large surface-to-volume ratio.[4] It is essential to choose suitable support materials with optimized structures to immobilize nano-material for specific chemical reactions.

1,3-Diyne derivatives are a prevalent and important class of intermediates with diverse applications in organic chemistry and functional materials, such as for the synthesis of natural products, pharmaceuticals, *p*-conjugated acetylenic polymers, and carbon-rich materials.[5] Transition-metal-catalyzed oxidative homo-coupling of terminal alkynes provides an easy and efficient access to such compounds.[6] A number of catalyst systems have been explored for this reaction, including palladium,[7] nickel,[8] copper,[9] cobalt,[10] gold,[11] and silver.[12] Among them, the pd-catalyzed Glaser-type coupling reactions represent one of the most promising methods for the synthesis of 1,3-diynes and have been broadly used to access 1,3-diynes.[13] Despite these advances, significant challenges still remain, owing to the difficulty of catalyst recovery. While the coupling with homogeneous catalyst can be accomplished with good results, efforts to develop efficient heterogeneous catalyst to facilitate the coupling have been met with relatively less success.[14] It is still necessary to develop highly efficient and environmentally friendly methods using nano-catalyst for the synthesis of broadly defined 1,3-diynes via a Glaser coupling pathway.

Given the prevalence of symmetric biaryls in medicinally relevant, natural, bioactive compounds and material sciences, it would be desirable to develop more highly efficient and greener methods using suitable compounds as partners via homo-coupling for the construction of such compounds. Although there have been several reports on the palladium-catalyzed homo-coupling of arylboronic acids,[15] the reports via nano-palladium-catalyzed approach are still rare.[16] Furthermore, palladium-catalyzed homo-coupling of potassium aryltrifluoroborates has been met with limited success.[17] Additionally, to the best of our knowledge, there is only one example that nano-palladium was utilized as a catalyst.[18]

Herein we report our efforts in nano-catalyst development (See Scheme 1) for such coupling reactions. With the $Al(OH)_3$-supported nano-pd catalyst,[19] Glaser-type coupling can be realized with high yields and the homocoupling of potassium (Het)aryltrifluoroborates could smoothly be finished with modest to excellent yields. At the same time, we also describe the application of this catalyst in the homo-coupling of arylboronic acids.

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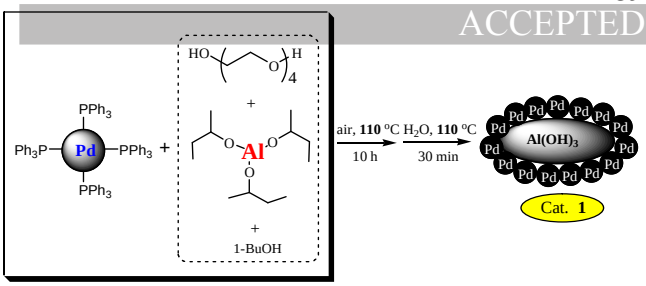


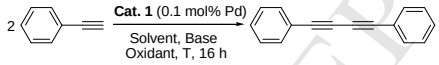
Scheme 1. Preparation of Pd nanoparticles catalyst **1**.

2. Results and discussion

We commenced the optimization studies with phenylacetylene (**1a**) as a model substrate using different solvents and bases with a series of silver salts as oxidant in the presence of the nanoparticles pd catalyst **1** (Table 1). First, a series of solvents, such as CH_3CN, toluene, DMSO, DMF, NMP, and Dioxane were screened. DMSO was proven to be the most effective solvent, while the others were not as effective (Table 1, entries 1−6). The investigation of bases revealed that 1 equiv. of NaOAc exhibited superior results compared to NaOH, CsF, DIPEA, and KOAc (Table 1, entry 3 *vs.* 7−10). Increasing the amount of the NaOAc (2 equiv.) led to the lower yield (Table 1, entry 11). Next we studied the reaction by varying the reaction temperature. Unfortunately, the reaction was not significantly improved and the increasing reaction temperature to 90 °C led to 55% yield (Table 1, entries 12−14). Subsequently, our attention was focused on oxidants. Ag_2SO_4 was found to be the oxidant of choice giving the highest yield (Table 1, entry 20), whereas I_2, Ag_2O, $AgNO_3$, AgBr and $AgBF_4$ afforded the desired product in 48−71% yields (Table 1, entries 15−19). Excitedly, 99% yield was obtained when 30 mol% Ag_2SO_4 was adopted (Table 1, entry 22). Additionally, no reaction occurred in the absence of a palladium catalyst or in the presence of $Al(OH)_3$ served as a catalyst, and 44% and 58% yields were obtained when $Pd(Ph_3P)_4$ or $Pd/Al(OH)_3$ that was prepared by co-precipitation was utilized as a catalyst. These all indicated that this nano-pd catalyst is essential for this reaction (Table 1, entries 23−26).

Table 1

Optimization for the palladium-catalyzed homo-coupling reaction of phenylacetylene[a]



1a **2a**

Entry	Solvent	Base (equiv.)	T (°C)	Oxidant (mol%)	Yield (%)[b]
1	CH_3CN	NaOAc (1)	50	—	3
2	toluene	NaOAc (1)	50	—	trace
3	DMSO	NaOAc (1)	50	—	39
4	DMF	NaOAc (1)	50	—	17
5	NMP	NaOAc (1)	50	—	11
6	Dioxane	NaOAc (1)	50	—	9
7	DMSO	NaOH (1)	50	—	trace
8	DMSO	CsF (1)	50	—	14
9	DMSO	DIPEA (1)	50	—	29
10	DMSO	KOAc (1)	50	—	27
11	DMSO	NaOAc (2)	50	—	30
12	DMSO	NaOAc (1)	70	—	44
13	DMSO	NaOAc (1)	90	—	55
14	DMSO	NaOAc (1)	120	—	42
15	DMSO	NaOAc (1)	90	I_2 (10)	61
16	DMSO	NaOAc (1)	90	Ag_2O (10)	61
17	DMSO	NaOAc (1)	90	$AgNO_3$ (10)	48
18	DMSO	NaOAc (1)	90	AgBr (10)	54
19	DMSO	NaOAc (1)	90	$AgBF_4$ (10)	71
20	DMSO	NaOAc (1)	90	Ag_2SO_4 (10)	77
21	DMSO	NaOAc (1)	90	Ag_2SO_4 (20)	81
22	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	99
23[c]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	trace
24[d]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	44
25[e]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	trace
26[f]	DMSO	NaOAc (1)	90	Ag_2SO_4 (30)	58

[a] Reaction conditions: **1a** (0.2 mmol), nano-Pd catalyst (0.1 mol% pd), solvent (1 mL), time (16 h).

[b] Isolated yield.

[c] Without nano-Pd catalyst.

[d] 0.1 mol% $Pd(Ph_3P)_4$ was used as a catalyst.

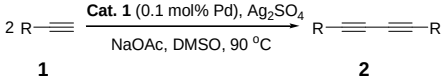
[e] 0.1 mol% $Al(OH)_3$ served as a catalyst.

f 0.1 mol% $Pd/Al(OH)_3$ which was prepared by co-precipitation was utilized as a catalyst.

With the optimized reaction conditions in hand, we examined the scope of the functionalized phenylacetylene in order to establish the generality of the protocol. This transformation proved to be a general method for the preparation of various functional groups substituted symmetrical 1,3-dieyes. Phenylacetylene with electron-donating or electron-withdrawing groups on aryl rings, such as methyl, amino, and fluoro all gave the corresponding symmetrical 1,3-dieyes in good to excellent yields, thus implying that the electronic nature of the substrates has little influence on the yield (Table 2, entries 1−8). At the same time, the steric hindrance did not obviously affect the reaction yields and catalytic activity (Table 2, entry 2 *vs.* 3−4 and entry 5 *vs.* 6−7). The desired symmetrical 1,3-dieyes were obtained in moderate to good yields when heteroaryl alkynes were employed as the substrates (Table 2, entries 9-11).

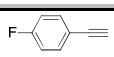
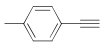
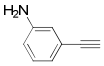
Table 2

Nano-Pd catalyzed homocoupling of terminal alkynes[a]



1 **2**

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1		16	**2a**	99
2		9	**2b**	97
3		9	**2c**	95

4		9	**2d**	99
5		12	**2e**	97
6		11	**2f**	99
7		8	**2g**	99
8		9	**2h**	85
9		16	**2i**	85
10		16	**2j**	86
11		48	**2k**	50

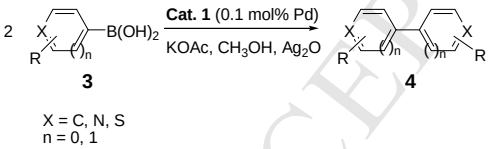
[a] Reaction conditions: **1** (0.2 mmol), nano-Pd (0.1 mol% Pd), NaOAc (0.2 mmol), DMSO (1 mL), Ag_2SO_4 (30 mol%), temperature (90 °C).

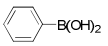
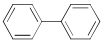
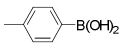
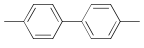
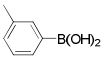
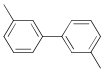
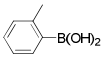
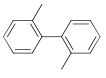
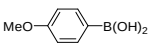
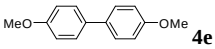
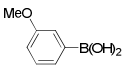
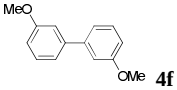
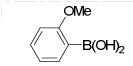
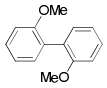
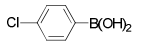
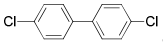
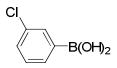
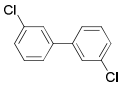
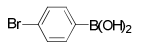
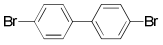
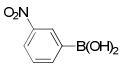
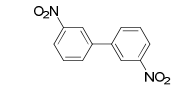
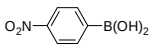
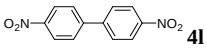
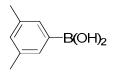
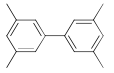
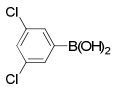
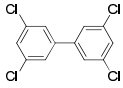
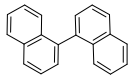
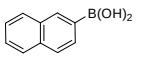
[b] Isolated yield.

To demonstrate the generality of this nanoparticles palladium catalyst, we set out to explore its reaction reactivity in the homo-coupling of arylboronic acids. Various arylboronic acids as coupling partners were next examined under the optimized reaction conditions established (Table 3).[20] Both the electronic effect of substituents and steric hindrance had influence on yields. The substrates possessing an electron-donating group showed the better results than those having a strong electron-withdrawing group (Table 2, entries 2−7 *vs.* 11 and 12). Among the substrates, *o*-substituted arylboronic acids, which are sterically hindered, gave somewhat lower yields (Table 2, entry 4 *vs.* 2, 3 and 7 *vs.* 5, 6). Both 3,5-dimethyl- and 3,5-Cl-substitution were well tolerated giving the good yields, respectively (Table 3, entries 13 and 14). Naphthylboronic acids were also suitable substrates for this process, furnishing the desired products in high yields (Table 3, entries 15 and 16). In addition, 67% and 78% yields were obtained when 2-thiopheneboronic acid and 4-pyridylboronic acid were employed as substrates, respectively (Table 3, entries 17 and 18).

Table 3

Palladium-catalyzed homocoupling of arylboronic acids[a]



Entry	$ArB(OH)_2$	Product	t (h)	Yield (%)[b]
1		 **4a**	15	>99
2		 **4b**	15	>99
3		 **4c**	15	>99
4[c]		 **4d**	20	93
5		 **4e**	20	95
6		 **4f**	15	>99
7[c]		 **4g**	20	88
8		 **4h**	15	>99
9		 **4i**	15	>99
10		 **4j**	18	91
11[d]		 **4k**	24	74
12		 **4l**	24	82
13		 **4m**	15	99
14		 **4n**	20	89
15		 **4o**	15	90
16		**4p**	15	95
17[d]		**4q**	36	67
18[d]		**4r**	36	78

[a] Reaction conditions: arylboronic acid (0.2 mmol), nano-Pd catalyst (0.1 mol% Pd), KOAc (0.2 mmol), CH_3OH (0.8 mL), Ag_2O (45 mol%), 40 °C.

[b] Isolated yield.

[c] temperature (60 °C).

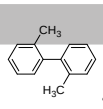
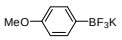
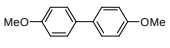
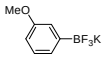
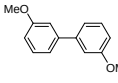
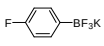
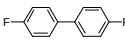
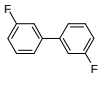
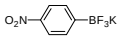
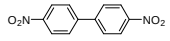
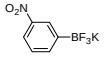
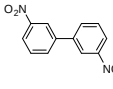
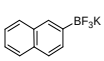
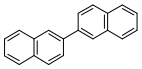
[d] 0.15 mol% Pd catalyst was used.

Subsequently, the scope of potassium aryltrifluoroborates were also investigated using H_2O as solvent.[21] It was found that the examined substrates gave modest to excellent yields which was similar or somewhat lower than the corresponding arylboronic acids provided (Table 4). And both the electronic effect of substituents and steric hindrance had similar influence on yields.

Table 4

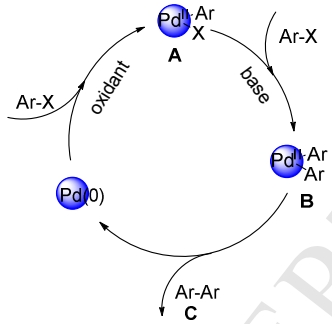
Substrate scope of palladium-catalyzed homocoupling of potassium aryltrifluoroborate[a]

Entry	$ArBF_3K$	Product	T (°C)	t (h)	Yield (%)[b]
1		**4a**	50	16	98
2		**4b**	50	16	90
3		**4c**	50	20	87

4		 **4d**	60	40	82
5		 **4e**	70	28	91
6		 **4f**	70	36	86
7		 **4g**	80	40	81
8		 **4s**	60	24	84
9		 **4t**	60	24	73
10		 **4l**	80	40	82
11		 **4k**	80	48	67
12		 **4p**	60	20	91
13		 **4q**	70	48	42
14		 **4r**	70	48	65

[a] Reaction conditions: potassium aryltrifluoroborate (0.2 mmol), nano-Pd catalyst (0.1 mol% Pd), KOAc (19.6 mg, 1.0 equiv.), H_2O (0.8 mL), Ag_2O (50 mol%), 50 °C.

[b] Isolated yield.



Scheme 2. Proposed cyclic mechanism.

According to the reported literatures,[22] a possible mechanism is proposed for the $Al(OH)_3$-supported nano-Pd catalyzed homo-coupling reactions of aromatic compounds (See Scheme 2). Initially, the oxidative addition of aryl reagents to Pd/$Al(OH)_3$ takes place which leads to the formation of an organopalladium intermediate **A**. Then the organic moiety of another aryl reagent is transferred to the same nano-palladium atom in the presence of the base resulting in the formation of intermediate **B**. Finally, a very quick reductive elimination may be finuished to give the desired homo-coupling product **C** and the Pd(II) is reduced back to Pd(0).

3. Conclusion

In conclusion, we have successfully developed three facile and efficient protocols for newly generated $Al(OH)_3$ supported nano-Pd catalyzed oxidative homo-coupling of terminal alkynes to 1,3-diynes, and oxidative homo-coupling of arylboronic acids and potassium aryltrifluoroborates to symmetrical biaryls, respectively. These three reactions proved to be tolerant to a variety of functional groups with good yields.

4. Experimental section

4.1. General methods

Unless otherwise indicated, all reagents were purchased from commercial sources and used without further purification. And deuterated solvents were purchased from Aldrich. Refinement of the mixed system through column chromatography which was performed on silica gel (200-300 mesh) with petroleum ether (solvent A)/ethyl acetate (solvent B) gradients as elution. In addition, all yields were referred to isolated yields (average of two runs) of compounds unless otherwise specified. The known compounds were partly characterized by melting points (for solid samples), ^{1}H NMR, and compared to authentic samples or the literature data. Melting points were measured with a RD-II digital melting point apparatus and were uncorrected. ^{1}H NMR data were acquired at 300 K on a Bruker Advance 600 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent $CDCl_3$ resonance as the internal standard ($CDCl_3$ = 7.26). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. On the other hand, the unknown compounds were characterized by ^{13}C NMR and HR-MS as well. The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.04 ppm). High-resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI).

4.2. Typical experimental procedure for homocoupling of alkynes

A mixture of alkyne **1** (0.2 mmol), nano-Pd (0.1 mol% Pd), Ag_2SO_4 (30 mol%), NaOAc (1 equiv), and DMSO (1 mL) was stirred at 90 °C until complete consumption of starting material as judged by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford the product **2** (petroleum ether or petroleum ether/ethyl acetate).

*4.2.1 1,4-Diphenylbuta-1,3-diyne (**2a**).* White solid; R_f = 0.5 (Petroleum ether); M.p. = 86-88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (t, J = 1.7 Hz, 1H), 7.33-7.36 (m, 3H), 7.36 (t, J = 1.5 Hz, 1H), 7.37-7.39 (m, 1H), 7.52-7.54 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.53, 129.24, 128.47, 121.80, 81.58, 73.93 ppm.

*4.2.2 1,4-Bis(2-fluorophenyl)buta-1,3-diyne (**2b**).* Colourless oil; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.08-7.13 (m, 4H), 7.34-7.37 (m, 2H), 7.52 (td, J = 1.5, 7.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.32, 131.19, 124.17, 115.82, 115.61, 110.54, 78.41, 75.88 ppm.

*4.2.3 1,4-Bis(3-fluorophenyl)buta-1,3-diyne (**2c**).* Yellow solid; M.p. = 120-122 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05-7.13 (m, 2H), 7.20-7.23 (m, 2H), 7.30-7.32 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.20, 128.50, 123.43, 119.13, 117.03, 116.82, 80.62, 74.42 ppm.

*4.2.4 1,4-Bis(4-fluorophenyl)buta-1,3-diyne (**2d**).*White solid; M.p. = 193-194 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.03 (t, J = 8.7 Hz, 4H), 7.50-7.52 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.59, 124.50, 116.03, 115.81, 80.43, 73.54 ppm.

*4.2.5 1,4-Bis(4-methylphenyl)buta-1,3-diyne (**2e**).* White solid; M.p. = 28-29 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.49 (s, 6H), 7.13-7.17 (m, 2H), 7.20-7.28 (m, 4H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ =141.66, 132.93, 129.59,129.12, 125.67, 121.73, 81.15, 77.52, 20.77 ppm.

*4.2.6 1,4-Bis(3-methylphenyl)buta-1,3-diyne (**2f**).* White solid; M.p. = 68-70 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 6H), 7.16-7.19 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.32-7.33 (m, 1H), 7.34-7.35 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.19, 133.00, 130.14, 129.63, 128.34, 121.65, 81.63, 73.65, 21.23 ppm.

*4.2.7 1,4-Bis(4-methylphenyl)buta-1,3-diyne (**2g**).* White solid; M.p. = 182-183 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.36 (s, 6H), 7.13 (d, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 8.1 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.52, 132.41, 129.24, 118.80, 81.57, 73.47, 21.65 ppm.

*4.2.8 1,4-Bis(3-aminophenyl)buta-1,3-diyne (**2h**).* White solid; M.p. = 124-125 °C; R_f = 0.3 (Petroleum ether/Ethyl acetate = 2/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.70 (s, 4H), 6.68 (ddd, *J* = 0.9, 2.4, 8.1 Hz, 2H), 6.82 (t, *J* = 2.1 Hz, 2H), 6.92-6.94 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$); δ 146.34, 129.40, 122.96, 122.46, 118.41, 116.29, 81.68, 73.40 ppm; HRMS (ESI): Calcd for $C_{16}H_{12}N_2$+H 233.1079, found 233.1084.

*4.2.9 1,4-Bis(2-thienyl)-1,3-butadiyne (**2i**).* White solid; M.p. = 92-93 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.00 (dd, *J* = 3.7, 5.1 Hz, 2H), 7.32 (dd, *J* = 1.1, 5.2 Hz, 2H), 7.34 (dd, *J* = 1.1, 3.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.44, 128.95, 127.25, 121.93, 77.79, 76.67 ppm; HRMS (ESI): Calcd for $C_{12}H_6S_2$+H 214.9989, found 214. 9992.

*4.2.10 1,4-Bis(3-thienyl)-1,3-butadiyne (**2j**).* White solid; M.p. = 110 °C; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.17 (dd, *J* = 1.1, 5.0 Hz, 2H), 7.28 (dd, *J* = 3.0, 5.0 Hz, 2H), 7.58 (dd, *J* = 1.1, 3.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.28, 130.19, 125.64, 120.90, 76.60, 73.55 ppm; HRMS (ESI): Calcd for $C_{12}H_6S_2$+H 214.9989, found 214. 9991.

*4.2.11 1,4-Di(pyridin-2-yl)buta-1,3-diyne (**2k**).* Brown solid; M.p. = 118-120 °C; R_f = 0.3 (Petroleum ether/Ethyl acetate = 2/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (ddd, *J* = 1.1, 4.9, 6.0 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.69 (td, *J* = 1.7, 7.7 Hz, 2H), 8.63 (d, *J* = 4.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.39, 141.86, 136.23, 128.42, 123.82, 80.91, 73.16 ppm; HRMS (ESI): Calcd for $C_{14}H_8N_2$+H 205.0766, found 205.0760.

4.3.Typical experimental procedure for homocoupling of arylboronicacids

A mixture of arylboronic acid **3** (0.2 mmol), nano-Pd (0.1 mol% Pd), Ag_2O (45 mol%), KOAc (1 equiv), and CH_3OH (0.8 mL) was stirred at 40 °C until complete consumption of starting material as judged by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford the corresponding homocoupling product **4** (petroleum ether or petroleum ether/ethylacetate).

*4.3.1 Biphenyl (**4a**).* White solid, M.p. = 68-70 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62–7.64 (m, 4H), 7.46–7.48 (m, 4H), 7.36–7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.31, 128.83, 127.32, 127.24 ppm.

*4.3.2 4,4'-Dimethylbiphenyl (**4b**).* White solid, M.p. = 118-119 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 4.8, 1.2 Hz, 4H), 7.22 (d, *J* = 7.6 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.37, 136.76, 129.52, 126.89, 21.16 ppm.

*4.3.3 3,3'-Dimethylbiphenyl (**4c**).* Colorless liquid, R_f = 0.6 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 6H), 7.14 (d, *J* = 11.4 Hz, 2H), 7.29 (t, *J* = 10.8 Hz, 2H), 7.37 (d, *J* = 13.8 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.30, 137.21, 127.56, 126.94, 126.86, 123.24, 20.50 ppm.

*4.3.4 2,2'-Dimethylbiphenyl (**4d**).* Colorless liquid, R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.04 (s, 6H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.19-7.22 (m, 2H), 7.24-7.25 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.63, 135.84, 129.84, 129.32, 127.18, 125.57, 19.87 ppm.

*4.3.5 4,4'-Bianisole (**4e**).* White solid; M.p. = 178-180 °C; R_f = 0.3 (Petroleum ether/Ethyl acetate = 50/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.83 (s, 6H), 6.96 (dt, *J* = 3.0, 8.8 Hz, 4 H), 7.48 (dt, *J* = 3.0, 8.7 Hz, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.70, 133.49, 127.75, 114.18, 55.36 ppm.

*4.3.6 3,3'-Bianisole (**4f**).* Colorless oil; R_f = 0.3 (Petroleum ether/Ethyl acetate = 50/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.86 (s, 6H), 6.90 (dd, *J* = 2.5, 8.2 Hz, 2H), 7.10-7.13 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.91, 142.66, 129.75, 119.73, 112.97, 112.83, 55.33 ppm.

*4.3.7 2,2'-Bianisole (**4g**).* White solid; M.p. = 155-156 °C; R_f = 0.3 (Petroleum ether/Ethyl acetate = 50/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.77 (s, 6H), 6.98 (dd, *J* = 0.8, 8.3 Hz, 2H), 7.01 (td, *J* = 1.1, 7.4 Hz, 2H), 7.25 (dd, *J* = 1.8, 7.4 Hz, 2H), 7.33 (ddd, *J* = 1.8, 7.5, 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.06, 131.50, 128.65, 127.84, 120.38, 111.12, 55.73 ppm.

*4.3.8 4,4'-Dichlorobiphenyl (**4h**).* White solid; M.p. = 146-147 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.39-7.42 (m, 4H), 7.46-7.48 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.43, 133.76, 129.06, 128.23 ppm.

*4.3.9 3,3'-Dichlorobiphenyl (**4i**).* Colorless oil; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.33 (t, *J* = 1.8 Hz, 1H), 7.35 (dd, *J* = 1.5, 1.9 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 1.6 Hz, 1H), 7.44 (t, *J* = 1.5 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.59, 133.79, 129.11, 126.86, 126.24, 124.24 ppm.

*4.3.10 4,4'-Dibromobiphenyl (**4j**).* White solid; M.p. = 164-166 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.40-7.42 (m, 4H), 7.55-7.57 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.92, 132.04, 128.53, 121.97 ppm.

*4.3.11 3,3'-Dinitrobiphenyl (**4k**).* White solid; M.p. = 201-202°C; R_f = 0.2 (Petroleum ether/Ethyl acetate = 50/1 v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ =7.71 (t, *J* = 8.0 Hz, 2H), 7.98 (ddd, *J* = 1.0, 1.8, 7.7 Hz, 2H), 8.31 (ddd, *J* = 1.0, 2.2, 8.2 Hz, 2H), 8.50 (t, *J* = 2.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.89, 140.34, 133.08, 130.31, 123.32, 122.12 ppm.

*4.3.12 4,4'-Dinitrobiphenyl (**4l**).* Yiellow solid; M.p. = 238-239 °C; R_f = 0.2 (Petroleum ether/Ethyl acetate = 10/1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.80 (d, *J* = 8.8 Hz, 4H), 8.37 (d, *J* = 8.8 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.64, 138.77, 129.18, 127.40 ppm.

*4.3.13 3,3',5,5'-Tetramethylbiphenyl (**4m**).* Colorless oil; R_f = 0.5 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 2.37 (d, *J* = 0.5 Hz, 12H), 6.96-6.98 (m, 2H), 7.18-7.19 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.52, 138.15, 128.78, 125.17, 21.46 ppm.

*4.3.14 3,3',5,5'-Tetrachlorobiphenyl (**4n**).* White solid; M.p. = 169-170 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): *δ* = 7.39 (t, *J* = 1.9 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 4H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.38, 134.64, 127.35, 124.58 ppm.

*4.3.15 1,1´-Binaphthyl (**4o**).* White solid; M.p. = 156-157 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26-7.29 (m, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.44-7.50 (m, 4H), 7.58 (t, J = 7.0 Hz, 2H), 7.95 (dd, J = 5.6, 8.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.48, 133.54, 132.87, 128.17, 127.91, 127.85, 126.58, 126.00, 125.83, 125.40 ppm.

*4.3.16 2,2´-Binaphthyl (**4p**).* White solid; M.p. = 156-157 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48-7.53 (m, 4H), 7.87 (d, J = 1.9 Hz, 2H), 7.89 (d, J = 1.8 Hz, 2H), 7.93 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 1.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.69, 128.55, 128.26, 127.70, 126.38, 126.14, 126.03, 125.76 ppm.

*4.3.17 3,3'-Bithiophenyl (**4q**).*White solid; M.p. = 126-127 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32-7.36 (m, 4H), 7.37-7.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.26, 126.38, 126.11, 119.81 ppm; HRMS (ESI): Calcd for $C_8H_6S_2$+H 166.9989, found 166.9985.

*4.3.18 4,4'-Bipyridyl (**4r**).* White solid; M.p. = 111-112 °C; R_f = 0.3 (Petroleum ether/Ethyl acetate = 2/1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, J = 1.6, 4.5 Hz, 4H), 8.76 (d, J = 5.7 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.63, 145.50, 121.40 ppm; HR-MS (ESI): Calcd for $C_{10}H_8N_2$+H 157.0766, found 157.0755.

4.4.Typical experimental procedure for homocoupling of potassium aryltrifluoroborates

A mixture of potassium aryltrifluoroborate **5** (0.2 mmol), nano-Pd (0.1 mol% Pd), Ag_2O (45 mol%), KOAc (1 equiv), and H_2O (0.8 mL) was stirred at specified temperature until complete consumption of starting material as determined by TLC. After the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford the corresponding homocoupling product **4** (petroleum ether or petroleum ether/ethylacetate).

*4.4.1 4,4'-Difluorobiphenyl (**4s**).* White solid; M.p. = 88-91 °C; R_f = 0.6 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08-7.15 (m, 4H), 7.45-7.51 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.63, 128.55, 115.80, 115.59 ppm.

*4.4.2 3,3'-Difluorobiphenyl (**4t**).* Colorless oil; R_f = 0.6 (Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (tdd, J = 1.0, 2.6, 8.4 Hz, 2H), 7.25 (t, J = 1.8 Hz, 1H), 7.28 (t, J = 2.3 Hz, 1H), 7.34 (t, J = 1.4 Hz, 1H), 7.36 (t, J = 1.4 Hz, 1H), 7.38-7.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.44 (d, J = 8.5 Hz) 122.76 (d, J = 2.8 Hz) 114.77, 114.56, 114.16, 113.94 ppm; HR-MS (ESI): Calcd for $C_{12}H_8F_2$+H 191.0672, found 191.0675.

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20. Reaction conditions: arylboronic acid (0.2 mmol), nano-Pd catalyst (0.1 mol% Pd), KOAc (0.2 mmol), CH_3OH (0.8 mL), Ag_2O (45 mol%), 40 °C.
21. Reaction conditions: potassium aryltrifluoroborate (0.2 mmol), nano-Pd catalyst (0.1 mol% Pd), KOAc (19.6 mg, 1.0 equiv.), H_2O (0.8 mL), Ag_2O (50 mol%), 50–80 °C.
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