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# Palladium nanoparticle catalyzed *aryl-amine* coupling reaction: High performance of aryl and pyridyl chlorides as the coupling partner

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**General Considerations:** Solvents were distilled from appropriate drying agent prior to use. Commercially available reagents were used without further purification unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE<sup>III</sup>-400 spectrometer.<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were registered in CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in  $\delta$  units (ppm). All coupling constants (*J*) are reported in hertz (Hz).

# Table: S1. Optimization of Reaction condition<sup>a</sup>

$O_2N$ + HN		Catalyst		2 <sup>N</sup>		
	1a	2d	Solvent, Base,	remp.	3ad	
Entry	Catalyst (wt%)	Solvent	Base	T ( <sup>0</sup> C)	Time	Yield (%) <sup>b</sup>
1	Pd-CN(10)	NMP	K <sub>2</sub> CO <sub>3</sub>	100	18	87
2	Pd-CN(10)	NMP	Cs <sub>2</sub> CO <sub>3</sub>	100	12	62
3	Pd-CN(10)	NMP	KOAc	100	12	70
4	Pd-CN(10)	NMP	K <sub>3</sub> PO <sub>4</sub>	100	12	94
5	Pd-CN(10)	NMP	KO <sup>t</sup> Bu	100	16	65
6	Pd-CN(10)	NMP	Et <sub>3</sub> N	100	16	27
7	Pd-CN(10)	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	100	12	95
8	Pd-CN(10)	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	95
9	Pd-CN(5)	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	95
10	Pd-CN(3)	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	88
11	$Pd(OAc)_2(5)^c$	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	64
12	$Pd(PPh_3)_4(5)^c$	NMP	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	72
13	Pd-CN(5)	THF	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	32
14	Pd-CN(5)	DMF	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	32
15	Pd-CN(5)	DMAc	CF <sub>3</sub> SO <sub>3</sub> Li	80	12	32

(a) Reaction conditions: 1-chloro-4-nitrobenzene (158mg, 1.0 mmol), piperidine (85 mg, 1.0 mmol), Base (1.5 mmol), Pd-CN catalyst (5mg) and solvent (2 mL). (b) Isolated yields. (c) mol%

Reference number	Condition used in reference	Aryl halide used	Reported Compound(s)	Yield (%) in the reference	Yield (%) in the present report
1	2-pyridinyl b- ketone ligands 20 m01%, CuI 10 mol%, 2 equiv. Cs <sub>2</sub> CO <sub>3</sub> , rt, DMF	Iodide	Зас	95	93
2	Allylnickel Chloride/N- Heterocyclic Carbene complex (2.5 mol%), NaO <sup>t</sup> But, rt, THF	Chloride	<b>3</b> bc	99	92
			3bd	99	94
			3bb	62	91
3	Pd(OAc) <sub>2</sub> ,( x mol%), Bicyclic Triaminophosphine Ligand (2x mol%), NaO <sup>t</sup> But, 80 <sup>o</sup> C, Toluene.	Bromide	3bb	88	91
4	(IPr)Pd(acac)Cl (1 mol%), KO <sup>t</sup> But,	Chloride	3bd	95	94
	100 C, DIVIE.		300	00	71

 Table: S2. Yield comparison of present work with few earlier reported works.

# **Characterization of coupling products:**

*N*.*N*-diethyl-4-nitroaniline(3aa):<sup>5</sup> Pale yellow solid, (yield:146 mg, 75%). Synthesized following

the general procedure from 1-chloro-4-nitrobenzene1a (158 mg, 1.0 mmol)  $O_2N$ 

and diethylamine2a (73 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.20-1.21(m, 6H), 3.42-3.45 (m, 4H), 6.54-6.57 (m, 2H), 8.06-8.09 (m, 2H);<sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>): δ 12.4 (2C), 44.9 (2C), 109.8 (2C), 126.5 (2C), 136.3, 152.2.



**N.N-dibutyl-4-nitroaniline(3ab)**:<sup>6</sup> Pale vellow liquid, (vield: 220 mg, 88%). Synthesized following the general procedure from 1-chloro-4-nitrobenzene1a (158 mg, 1.0 mmol) anddibutylamine2b (129 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.94-0.97(m, 6H),1.33-1.39 (m, 4H), 1.56-1.58 (m, 4H) 3.32-3.36 (m, 4H), 6.52 (d, J=9.6 Hz, 2H), 8.06 (d, J=9.2 Hz, 2H);  ${}^{13}C$ 

NMR (100 MHz, CDCl<sub>3</sub>): δ 13.8 (2C), 20.2 (2C), 29.2 (2C), 51.0 (2C), 109.9 (2C), 126.4 (2C), 136.2, 152.6.

1-(4-nitrophenyl)pyrrolidine(3ac):<sup>5</sup> Pale yellow liquid, (yield:179 mg, 93%). Synthesized following the general procedure from 1-chloro-4-nitrobenzenela (158 mg,

 $O_2N$ 

1.0 mmol) andpyrrolidine2c(71 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.01-2.04 (m, 4H), 3.32-3.36 (m, 4H), 6.39 (d, *J*= 9.2 Hz, 2H),

8.03 (d, J= 9.2 Hz, 2H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.3 (2C), 47.8 (2C), 110.3 (2C), 126.1 (2C), 136.4, 151.7.

1-(4-nitrophenyl)piperidine(3ad):<sup>5</sup> Pale yellow liquid, (yield: 196 mg, 95%). Synthesized following the general procedure from 1-chloro-4-nitrobenzene1a (158 mg, 1.0 mmol) and piperidine2d (85 mg, 1.0 mmol). <sup>1</sup>H NMR (400 MHz, O<sub>2</sub>N CDCl<sub>3</sub>): 1.64 (brs, 6H), 3.39 (brs, 4H), 6.73 (d, J= 9.2 Hz, 2H), 8.03 (d,

J=9.2 Hz, 2H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  24.1, 25.2 (2C), 48.3 (2C), 112.2 (2C), 126.0 (2C), 137.3, 154.8.

*N*,*N*-diethylpyridin-2-amine(3ba):<sup>7</sup> Colorless liquid, (yield: 125 mg, 83%). Synthesized following the general procedure from 2-chloropyridine1b (114 mg, 1.0 mmol) anddiethylamine2a (73 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.15 (t, J= 7.2 Hz, 6H), 3.39 (q, J= 7.1 Hz, 4H), 6.41-6.46 (m, 2H), 7.37 (t, J= 7.8 Hz, 1H) 8.12 (d, J= 4.4 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 12.9, 42.4 (2C), 105.5, 110.7, 136.9, 148.1,

157.5.

*N*,*N*-dibutylpyridin-2-amine(3bb):<sup>8</sup> Colorless liquid, (yield: 187 mg, 91%). Synthesized



following the general procedure from 2-chloropyridine1b (114 mg, 1.0 mmol) and dibutylamine2b (129 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.93 (t, J= 7.4 Hz, 6H), 1.30-1.36 (m, 4H), 1.52-1.57 (m, 4H), 3.40 (t, J= 7.6 Hz, 4H), 6.38-6.44 (m, 2H), 7.33-7.38 (m, 1H), 8.10-8.11 (m, 1H); <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>): § 14.0 (2C), 20.3 (2C), 29.8 (2C), 48.4 (2C), 105.5, 110.6, 136.8, 148.0, 157.9.

**2-(pyrrolidin-1-yl)pyridine(3bc)**:<sup>9</sup> Colorless liquid, (yield: 136 mg, 92%). Synthesized following the general procedure from 2-chloropyridine1b (114 mg, 1.0 mmol) and pyrrolidine2c (71 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.78 (brs, 4H), 3.23 (brs, 4H), 6.12 (d, J= 8.8 Hz, 1H), 6.30-6.31 (m, 1H), 7.10-7.20 (m, 1H),

7.98 (d, J= 4.8 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  25.0 (2C), 46.1 (2C), 105.9, 110.5, 136.3, 147.6, 156.8.

2-(piperidin-1-yl)pyridine (3bd):9 Colorless liquid, (yield: 152 mg, 94%). Synthesized following the general procedure from 2-chloropyridine1b (114 mg, 1.0 mmol) and piperidine2d (85 mg, 1.0 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.54 (brs, 6H), 3.43 (brs, 4H), 6.44-6.47 (m, 1H), 6.53 (d, J= 8.8 Hz, 1H), 7.30-7.35 (m, 1H),

8.09-8.10 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.5, 25.2 (2C), 46.0 (2C), 106.7, 112.1, 136.9, 147.6, 159.4.

N,N-diethyl-3-nitropyridin-2-amine(3ca):<sup>10</sup> Colorless liquid, (yield: 154 mg, 79%). Synthesized following the general procedure from 2-chloro-3-nitropyridine1c (158 mg, 1.0 NO<sub>2</sub> mmol) and diethylamine2a (73 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.16-1.21 (m, 6H), 3.40-3.45 (m, 4H), 6.59-6.64 (m, 1H), 7.98-8.02 (m, 1H), 8.25-8.28 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 12.5 (2C), 44.0 (2C), 111.8, 132.6, 135.1,

151.3, 152.1.



*N*,*N*-dibutyl-3-nitropyridin-2-amine(3cb):<sup>11</sup> Colorless liquid, (yield: 208 mg, 83%). Synthesized following the general procedure from 2-chloro-3nitropyridine1c (158 mg, 1.0 mmol) and dibutylamine2b (129 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.85-0.87 (m, 6H), 1.23-1.27 (m, 4H), 1.53-1.57 (m, 4H), 3.33-3.36 (m, 4H), 6.60-6.63 (m, 1H), 8.01-8.03 (m, 1H), 8.26-8.27 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.8 (2C), 20.0 (2C), 29.5 (2C), 49.5 (2C), 111.8, 132.7, 135.2, 151.3, 152.8.

3-nitro-2-(pyrrolidin-1-yl)pyridine(3cc):<sup>12</sup> Colorless liquid, (yield: 172 mg, 89%). Synthesized following the general procedure from 2-chloro-3-nitropyridine1c (158 mg, 1.0 NO<sub>2</sub> mmol) and pyrrolidine2c (71 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.94-1.97 (m, 4H), 3.35-3.38 (m, 4H), 6.60-6.63 (m, 1H), 8.03-8.05 (m, 1H), 8.29-8.30 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.4 (2C), 49.4 (2C), 110.9, 131.7,

134.8, 150.3, 151.8.

3-nitro-2-(piperidin-1-yl)pyridine (3cd):<sup>12</sup> Colorless liquid, (yield: 180 mg, 87%). Synthesized



following the general procedure from 2-chloro-3-nitropyridine1c (158 mg, 1.0 mmol) and piperidine 2d (85 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.66 (brs, 6H), 3.73 (m, 4H), 6.63-6.67 (m, 1H), 8.06-8.09 (m, 1H), 8.27-8.28 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.2, 25.7 (2C), 49.2 (2C), 112.5, 132.7,

135.6, 151.7, 153.2.

5-chloro-N,N-diethylpyridin-2-amine(3da): Colorless liquid, (yield: 145 mg, 79%). Synthesized following the general procedure from 2,5-dichloropyridine1d (148 mg, 1.0 mmol) and diethylamine2a (73 mg, 1.0 mmol).<sup>1</sup>H NMR (400 CI MHz, CDCl<sub>3</sub>): 1.40 (t, J= 7.0Hz, 6H), 3.44-3.47 (m, 4H), 6.36 (d, J= 8.8Hz, 1H), 7.60-7.62 (m, 1H), 8.03 (s, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 12.8 (2C), 42.7 (2C), 106.1, 125.1, 136.7, 138.4, 148.4.

*N*,*N*-dibutyl-5-chloropyridin-2-amine(3db): Colorless liquid, mg, 95%). (yield: 228 Synthesized following the general procedure from 2.5dichloropyridine1d (148 mg, 1.0 mmol) anddibutylamine2b (129 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.92-0.95 (m, 6H), 1.31-1.34 (m, 4H), 1.52-1.56 (m, 4H), 3.45-3.40 (m, 4H), 6.32-6.38 (m, 1H), 7.28-

7.32 (m, 1H), 8.01-8.04 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 14.0 (2C), 20.3 (2C), 29.7 (2C), 48.7 (2C), 106.2, 117.5, 136.5, 146.3, 156.3.



5-chloro-2-(pyrrolidin-1-yl)pyridine(3dc): Colorless liquid, (yield: 178 mg, 98%). Synthesized following the general procedure 2,5-dichloropyridine1d (148 mg, 1.0 mmol) and pyrrolidine2c (71 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.93 (brs, 4H), 3.33 (brs, 4H), 6.19 (d, J= 9.2 Hz, 1H), 7.27 (dd, J= 8.8, 2.4 Hz, 1H),

8.04 (d, J= 2.4 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.5, 25.3 (2C), 46.3 (2C), 107.6, 118.9, 136.8, 146.0, 157.8.

5-chloro-2-(piperidin-1-yl)pyridine(3dd): Colorless liquid, (yield: 192 mg, 98%). Synthesized following the general procedure 2,5-dichloropyridine1d (148 mg, 1.0 mmol) and piperidine2d (85 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.58 (brs, 6H), 3.44-3.45 (brs, 4H), 6.51 (d, J= 8.8 Hz, 1H), 7.27 (dd, J= 8.8,

2.4 Hz, 1H), 8.03 (d, J= 2.4Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  25.4 (2C), 46.7 (2C), 106.9, 117.9, 136.4, 146.2, 155.5.

N,N-diethyl-4-nitropyridin-2-amine(3ea): Colorless liquid, (yield: 157 mg, 90%). Synthesized following the general procedure from 2-chloro-4-nitropyridine1e (159 mg, 1.0 mmol) and diethylamine2a (73 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.19 (t, J= 7.2 Hz,6H), 3.53-3.55 (m, 4H), 7.09-7.10 (m, 2H), 8.28-8.30 (m, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 12.7 (2C), 42.9 (2C), 97.9, 102.8, 150.4,

155.6, 158.7.

 $O_2N$ 

N,N-dibutyl-4-nitropyridin-2-amine(3eb): Colorless liquid, (yield: 231 mg, 92%). Synthesized following the general procedure from 2-chloro-4-nitropyridine1e (159 mg,  $O_2N$ 1.0 mmol) and dibutylamine2b (129 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.92 (t, J= 7.4 Hz, 6H), 1.28-1.34 (m, 4H), 1.49-1.53 (m, 4H), 3.19-3.23 (m, 4H), 6.31 (dd, J=6.0, 2.0 Hz, 1H), 6.37 (d, J= 2.4 Hz, 1H), 7.87 (d,*J*= 6.0 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.8 (2C), 20.1 (2C), 28.9 (2C), 50.1 (2C), 105.0, 105.6, 149.1, 152.3, 154.4.

4-nitro-2-(pyrrolidin-1-yl)pyridine(3ec):<sup>13</sup> Colorless liquid, (yield: 185 mg, 96%). Synthesized following the general procedure from 2-chloro-4-nitropyridine1e (159 mg, 1.0 mmol) and pyrrolidine2c (71 mg, 1.0 mmol).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.93 (t, J= 6.6 Hz, 4H), 3.16-3.19 (m, 4H), 6.18 (dd, J= 5.8, 2.0 Hz, 1H), 6.23 (s, 1H), 7.81 (d, J= 6.0 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 25.0 (2C), 46.9 (2C), 105.2, 106.1, 148.5, 151.6, 153.2.

**4-nitro-2-(piperidin-1-yl)pyridine(3ed**):<sup>14</sup> Colorless liquid, (yield: 201 mg, 97%). Synthesized following the general procedure from 2-chloro-4-nitropyridine1e (159 mg, 1.0 mmol) and piperidine2d (85 mg, 1.0 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.50-1.52 (m, 6H), 3.19-3.21 (m, 4H), 6.42 (dd, *J*= 6.2, 2.2 Hz, 1H), 6.49 (d,*J*= 2.0 Hz, 1H), 7.83 (d, *J*= 6.0 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ

23.9, 24.7 (2C), 47.0 (2C), 106.5, 106.9, 149.1, 152.3, 156.2.

# **References:**

- 1. D. Wang, K. Ding, Chem. Commun, 2009, 1891-1893.
- 2. M. J. Iglesias, A. Prieto, M. C. Nicasio, Adv. Synth. Catal., 2010, 352, 1949-1954.
- 3. S. Urgaonkar, J-H Xu, J. G. Verkade, J. Org. Chem., 2003, 68, 8416-8423.
- 4. N. Marion, E. C. Ecarnot, O. Navarro, D. Amoroso, A. Bell, S. P. Nolan, J. Org. Chem., 2006, 71, 3816-3821.
- 5. R. B. N Baig, R. S. Varma, RSC Advances, 2014, 4, 6568-6572.
- 6. J. P. Stambuli, R. Kuwano, J. F. Hartwig, Angew. Chem. Int. Ed. 2002, 41, 4746-4748.
- 7. M. Balkenhohl, C. François, D. S. Roman, P. Quinio, P. Knochel, Org. Lett., 2017, 19, 536-539.
- 8. M. J. Iglesias, A. Prieto, M. C. Nicasioa, Adv. Synth. Catal. 2010, 352, 1949-1954.
- 9. G. Manolikakes, A. Gavryushin, P. Knochel, J. Org. Chem, 2008, 73, 1429-34.
- 10. J. M. Bakke, H. Svensen, Tetrahedron Lett., 2001, 42, 4393-4395.
- 11. T. B. Nguyen, L. Ermolenko, A. Al-Mourabit, Green Chem., 2016, 18, 2966-2970.
- 12. M. M. V. Ramana, M. R. Sharma, J. Chem. Pharm. Res., 2013, 5, 122-133.
- 13. T. Ikemura, E. Ohshima, K. Horikoshi, S. Ohtsuka, K. Mori, H. Kusaka, PCT Int. Appl., 2006137421, 28 December, 2006.
- 14. J. Hood, S. Kumar KC, D. M. Wallace, G. K. Mittapalli, B. J. Hofilena, C. C. Mak, V. Bollu, B. Eastman, PCT Int. Appl., 2015143380, 24 Sep2015.

General procedures for the preparation of Pd-CN: In a typical experiment, 10 g of urea was kept in a covered crucible at 80 °C under ambient pressure for 12h. After that the dried urea was put in a Muffle Furnace for 4h at 550 °C. Lemon yellow colored solid mass obtained was washed repeatedly with distilled water to remove any unwanted bi-product such as ammonia form the sample surface. Resulted solid was dried at 80°C for 24 h under vacuum. The dried solid support was collected for palladium immobilization on it. Each 0.5 g of the solid carbon nitride was dispersed in 10 mL of water in 3 separate 25 mL of round bottom flux. 0.1 M of K<sub>2</sub>PdCl<sub>4</sub> (1.40 mL, 2.34 mL and 4.68 mL) was added drop wise (3 wt%, 5 wt% and 10 wt% loading of Pd). After that, 5 mL of 1×10<sup>-3</sup> M NaBH<sub>4</sub> solution was added to each flux drop wise for the reduction of palladium salt. At the end, the material was filtered, washed with water and dried. The resultant material was characterized using different microscopic and spectroscopic techniques and used as catalyst for the amination of aryl chloride. Transmission electron microscopy (TEM) studies were carried out at an accelerated voltage of 200 kV using a Philips CM200 TEM equipped with a LaB6 source and the sample specimens were prepared by sonicating the dried sample for the period of 2h in aqueous medium and 2µL of the dispersed solution was deposited onto a lacey carbon coated copper grid.

**General procedure for amination reaction:** To a 25 mL round bottom flask fitted with a magnetic stirrer, aryl or pyridyl chloride (1 mmol) aryl di-alkyl amine (1.0 mmol), CF<sub>3</sub>SO<sub>3</sub>Li (234 mg, 1.5 mmol), and 5.0 mg of Pd-CN (5.0 wt% of Pd) catalyst were added in NMP (2 mL). The reaction mixture was allowed to reflux under stirring condition at 80°C for 12 h. Once reaction mixture cooled down to room temperature, diluted with distilled water (20 mL) and was extracted with EtOAc (3 ×20 mL). The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. Organic solvent was removed under reduced pressure. Resulted gummy mass was subjected to column chromatography over silica gel using n-hexane and an increasing proportion of ethyl acetate as eluent to obtain the purified final product.

The palladium leaching, into the reaction mixture, was analyzed with ICP-MS. For this purpose, filtrate was collected during the aryl-amine coupling reaction (reaction temperature: 80 °C), the solvent was evaporated, and the residue was dissolved in HNO<sub>3</sub>. The analysis of the sample with ICP-MS showed that the Pd concentration in the filtrate was less than the detection limit (i.e., 0.1  $\mu$ g/L). The same result was obtained when the complete reaction mixture of the aryl-amine coupling reaction was analyzed as above.





Scheme S1: A proposed catalytic cycle for the aryl-amine bond formation reaction.



Figure S2. <sup>13</sup>C NMR spectrum of 3aain CDCl<sub>3</sub>



Figure S3. <sup>1</sup>H NMR spectrum of 3ab in CDCl<sub>3</sub>



Figure S4. <sup>13</sup>C NMR spectrum of **3ab** in CDCl<sub>3</sub>



Figure S6. <sup>13</sup>C NMR spectrum of **3ac** in CDCl<sub>3</sub>



Figure S7. <sup>1</sup>H NMR spectrum of 3ad in CDCl<sub>3</sub>



Figure S8. <sup>13</sup>C NMR spectrum of 3ad in CDCl<sub>3</sub>



Figure S9. <sup>1</sup>H NMR spectrum of 3bain CDCl<sub>3</sub>



Figure S10. <sup>13</sup>C NMR spectrum of 3bain CDCl<sub>3</sub>



Figure S11. <sup>1</sup>H NMR spectrum of 3bb in CDCl<sub>3</sub>



Figure S12. <sup>13</sup>C NMR spectrum of 3bb in CDCl<sub>3</sub>



Figure S13. <sup>1</sup>H NMR spectrum of 3bc in CDCl<sub>3</sub>



Figure S14. <sup>13</sup>C NMR spectrum of **3bc** in CDCl<sub>3</sub>



Figure S16. <sup>13</sup>C NMR spectrum of 3bd in CDCl<sub>3</sub>



Figure S17. <sup>1</sup>H NMR spectrum of 3ca in CDCl<sub>3</sub>



Figure S18. <sup>13</sup>C NMR spectrum of 3ca in CDCl<sub>3</sub>



Figure S20. <sup>13</sup>C NMR spectrum of 3cb in CDCl<sub>3</sub>



Figure S22. <sup>13</sup>C NMR spectrum of 3cc in CDCl<sub>3</sub>





Figure S24. <sup>13</sup>C NMR spectrum of 3cd in CDCl<sub>3</sub>

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

10 ppm

![](_page_22_Figure_0.jpeg)

Figure S27. <sup>1</sup>H NMR spectrum of 3dbin CDCl<sub>3</sub>

![](_page_22_Figure_2.jpeg)

Figure S28. <sup>13</sup>C NMR spectrum of 3db in CDCl<sub>3</sub>

![](_page_23_Figure_0.jpeg)

Figure S29. <sup>1</sup>H NMR spectrum of 3dc in CDCl<sub>3</sub>

![](_page_23_Figure_2.jpeg)

Figure S30. <sup>13</sup>C NMR spectrum of 3dc in CDCl<sub>3</sub>

![](_page_24_Figure_0.jpeg)

Figure S31. <sup>1</sup>H NMR spectrum of 3dd in CDCl<sub>3</sub>

![](_page_24_Figure_2.jpeg)

Figure S32. <sup>13</sup>C NMR spectrum of 3dd in CDCl<sub>3</sub>

![](_page_25_Figure_0.jpeg)

Figure S33. <sup>1</sup>H NMR spectrum of 3ea in CDCl<sub>3</sub>

![](_page_25_Figure_2.jpeg)

Figure S34. <sup>13</sup>C NMR spectrum of 3ea in CDCl<sub>3</sub>

![](_page_26_Figure_0.jpeg)

Figure S35. <sup>1</sup>H NMR spectrum of 3eb in CDCl<sub>3</sub>

![](_page_26_Figure_2.jpeg)

Figure S36. <sup>13</sup>C NMR spectrum of 3eb in CDCl<sub>3</sub>

![](_page_27_Figure_0.jpeg)

Figure S37. <sup>1</sup>H NMR spectrum of 3ec in CDCl<sub>3</sub>

![](_page_27_Figure_2.jpeg)

Figure S38. <sup>13</sup>C NMR spectrum of 3ec in CDCl<sub>3</sub>

![](_page_28_Figure_0.jpeg)

Figure S40. <sup>13</sup>C NMR spectrum of 3ec in CDCl<sub>3</sub>