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A comparison of homogeneous and heterogeneous copper catalyzed arylation of amines

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General.

Commercially available compounds (iodobenzene, 2-iodopyridine, *n*-octylamine **1a**, copper(I) iodide, copper nanoparticles (25, 40 and 60 nm) ligands **L1-L6**, cesium carbonate, anhydrous DMSO) were used as purchased. DMSO and DMF were distilled over dried molecular sieves, dichloromethane was distilled over CaH_2. Adamantane-containing amines **1b-h** were synthesized as described [S1-S6]. ^{1}H NMR spectra were registered with Bruker Avance 400 spectrometer in $CDCl_3$.

Experimental.

Copper-catalyzed arylation of amines **1a-h**.

Homogeneous version. A vial equipped with a magnetic stirrer was charged with iodobenzene (0.625 mmol, 128 mg) or 2-iodopyridine (0.625 mmol, 128 mg), CuI (10 mol%, 0.05 mmol, 9.5 mg), the corresponding ligand (20 mol%), DMSO (1 ml), amine **1a-h** (0.5 mmol) and Cs_2CO_3 (0.625 mmol, 204 mg). The reaction was stirred at 110 ^{o}C for 24 h After cooling to ambient temperature, CH_2Cl_2 (1 ml) was added, the suspension was filtered, the residue was washed with CH_2Cl_2 (1 ml), the combined organic phases were washed with distilled water (20 ml), dried over molecular sieves and evaporated *in vacuo*.

Heterogeneous version. Essentially the same as described above, but instead of CuI copper nanoparticles of size 25 nm were employed (3.2 mg, 10 mol%). In order to carry out amination with 5 mol% CuNPs the same amount of copper nanoparticles was used, and all other components and solvent were taken twofold. ^{1}H NMR spectra of compounds **2a, 2b-h**, **3a** and **3b-f** are in good agreement with those reported [S7-S10].

Experiments on recycling nanocatalyst.

A vial equipped with a magnetic stirrer was charged with iodobenzene (1 mmol, 204 mg), CuNPs 25 nm (20 mol%, 0.2 mmol, 12.8 mg), 2-isobutyrylcyclohexanone **L1** (20 mol%, 0.2 mmol, 34 mg), DMSO (2 ml), amine **1a** (1 mmol, 129 mg) and Cs_2CO_3 (1.25 mmol, 408 mg).

The mixture was stirred at 110°C for 6 h, after cooling down to ambient temperature the residue was filtered using paper filter, washed with additional 2 ml DMSO, the paper filter with resting CuNPs was finely torn and transferred into a new vial which was charged, as indicated previously, with iodobenzene, ligand **L1**, DMSO, amine and Cs_2CO_3. In the next run the workup of the reaction mixture was essentially the same.

Table S1. Amination of iodobenzene and 2-iodopyridine in the presence of CuI. Reaction conditions: 0.5 mmol amine, 0.625 mmol (Het)ArI, 1 ml DMSO, 10-20 mol% CuI, 20-40 mol% ligand, 110°C, 24 h.

Entry	Amine	(Het)ArI	CuI (mol%)	Ligand (mol%)	Product, yield
1	**1a**	PhI	10	**L1** (20)	**2a**, 69%
2	**1b**	PhI	10	**L1** (20)	**2b**, 69%
3	**1b**	PhI	20	**L1** (40)	**2b**, 76%
4	**1b**	PhI	10	**L2** (20)	**2b**, 33%
5	**1b**	PhI	10	**L3** (20)	**2b**, 21%
6	**1b**	PhI	10	**L4** (20)	**2b**, 5%
7	**1b**	PhI	10	**L5** (20)	**2b**, 5%
8	**1b**	PhI	10	**L6** (20)	**2b**, 2%
9	**1c**	PhI	10	**L1** (20)	**2c**, 72%
10	**1d**	PhI	10	**L1** (20)	**2d**, 60%
11	**1e**	PhI	10	**L1** (20)	**2e**, 67%
12	**1f**	PhI	10	**L1** (20)	**2f**, 68%
13	**1g**	PhI	20	**L1** (40)	**2g**, 62%
14	**1h**	PhI	20	**L1** (40)	**2h**, 31%
15	**1a**	2-IPy	20	**L1** (40)	**3a**, 66%
16	**1b**	2-IPy	10	**L1** (20)	**3b**, 73%
17	**1b**	2-IPy	20	**L1** (40)	**3b**, 77%
18	**1c**	2-IPy	10	**L1** (20)	**3c**, 34%
19	**1c**	2-IPy	20	**L1** (40)	**3c**, 62%
20	**1d**	2-IPy	10	**L1** (20)	**3d**, 45%
21	**1d**	2-IPy	20	**L1** (40)	**3d**, 71%
22	**1e**	2-IPy	10	**L1** (20)	**3e**, 70%
23	**1f**	2-IPy	10	**L1** (20)	**3f**, 54%

Table S2. Amination of iodobenzene and 2-iodopyridine in the presence of CuNPs. Reaction conditions: 0.5 mmol amine, 0.625 mmol (Het)ArI, 1 ml DMSO, 5-10 mol% CuNPs, 5-20 mol% ligand, 110°C, 24 h.

Entry	Amine	(Het)ArI	CuNPs (mol%)	Ligand (mol%)	Product, yield
1	**1a**	PhI	25 nm (10)	**L1** (20)	**2a**, 66%
2	**1a**	PhI	25 nm (20)	**L1** (40)	**2a**, 74%
3	**1a**	PhI	40 nm (10)	**L1** (20)	**2a**, 52%
4	**1a**	PhI	60 nm (10)	**L1** (20)	**2a**, 45%
5	**1a**	PhI	25 nm (5)	**L1** (10)	**2a**, 81%
6	**1a**	PhI	25 nm (5)	**L1** (5)	**2a**, 89%
7	**1a**	PhI	25 nm (10)	**L3** (20)	**2a**, 80%
8	**1a**	PhI	25 nm (10)	**L3** (10)	**2a**, 86%
9	**1a**	PhI	25 nm (5)	**L3** (5)	**2a**, 32%
10	**1a**	2-IPy	25 nm (10)	**L1** (20)	**3a**, 64%
11	**1a**	2-IPy	25 nm (10)	**L1** (10)	**3a**, 68%
12	**1a**	2-IPy	25 nm (10)	**L3** (20)	**3a**, 77%
13	**1a**	2-IPy	25 nm (10)	**L4** (20)	**3a**, 75%
14	**1a**	2-IPy	25 nm (10)	**L3** (10)	**3a**, 82%
15	**1a**	2-IPy	25 nm (5)	**L3** (5)	**3a**, 61%
16	**1b**	PhI	25 nm (10)	–	**2b**, 1%
17	**1b**	PhI	40 nm (10)	–	**2b**, <1%
18	**1b**	PhI	25 nm (10)	**L1** (20)	**2b**, 80%
19	**1b**	PhI	25 nm (10)	**L1** (10)	**2b**, 88%
20	**1b**	PhI	25 nm (5)	**L1** (5)	**2b**, 86%
21	**1b**	PhI	25 nm (10)	**L3** (20)	**2b**, 70%
22	**1b**	PhI	25 nm (10)	**L3** (10)	**2b**, 77%
23	**1b**	PhI	25 nm (5)	**L3** (5)	**2b**, 27%
24	**1b**	PhI	25 nm (10)	**L4** (20)	**2b**, 58%
25	**1b**	PhI	25 nm (10)	**L4** (10)	**2b**, 57%
26	**1b**	2-IPy	25 nm (10)	**L1** (10)	**3b**, 69%
27	**1b**	2-IPy	25 nm (10)	**L3** (10)	**3b**, 46%
28	**1c**	PhI	25 nm (5)	**L1** (5)	**2c**, 86%
29	**1c**	2-IPy	25 nm (10)	**L1** (10)	**3c**, 48%
30	**1c**	2-IPy	25 nm (10)	**L3** (10)	**3c**, 64%
31	**1d**	PhI	25 nm (5)	**L1** (5)	**2d**, 85%
32	**1d**	2-IPy	25 nm (10)	**L1** (10)	**3d**, 43%
33	**1d**	2-IPy	25 nm (10)	**L3** (10)	**3d**, 71%
34	**1e**	PhI	25 nm (5)	**L1** (5)	**2e**, 86%
35	**1e**	2-IPy	25 nm (10)	**L1** (10)	**3e**, 64%
36	**1e**	2-IPy	25 nm (10)	**L3** (10)	**3e**, 76%
37	**1f**	PhI	25 nm (5)	**L1** (5)	**2f**, 85%
38	**1f**	2-IPy	25 nm (10)	**L1** (10)	**3f**, 62%
39	**1f**	2-IPy	25 nm (10)	**L3** (10)	**3f**, 54%

References

S1. B. Gopalan, A. Thomas and D. M. Shah, PCT Int. Appl. WO 2006090244 (2006); *Chem. Abstr.*, 2006, **145**, 292604.

S2. I. A. Novakov, I. A. Kulev, S. S. Radchenko, K. A. Birznieks, E. I. Boreko, G. V. Vladyko and L. V. Korobchenko, *Pharm. Chem. J.*, 1987, **21**, 287.

S3. Yu. V. Popov, V. M. Mokhov and N. A. Tankabekyan, *Russ. J. Appl. Chem.*, 2013, **86**, 404.

S4. S. S. Novikov, A. P. Khardin, S. S. Radchenko, I. A. Novakov, B. S. Orlinson, V. F. Blinov, V. I. Gorelov and V. P. Zamakh, Pat. USSR 682507 (1978); *Chem. Abstr.*, 1979, **91**, P193887e.

S5. I. A. Novakov, B. S. Orlinson, E. N. Savelyev, E. A. Potaenkova and A. K. Shilin, Patent RF RU 2495020 C1 (2013).

S6. A. D. Averin, E. R. Ranyuk, S. L. Golub, A. K. Buryak, E. N. Savelyev, B. S. Orlinson, I. A. Novakov and I. P. Beletskaya, *Synthesis*, **2007**, 2215.

S7. H. Zeng, D. Cao, Z. Qiu and C.-J. Li, *Angew. Chem. Int. Ed.*, 2018, **57**, 3752.

S8. S. P. Panchenko, A. S. Abel, A. D. Averin, O. A. Maloshitskaya, E. N. Savelyev, B. S. Orlinson, I. A. Novakov and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2017, **53**, 1497.

S9. T. Harada, Y. Ueda, T. Iwai and M. Sawamura, *Chem. Commun.*, 2018, **54**, 1718.

S10. A. S. Abel, A. D. Averin, M. V. Anokhin, O. A. Maloshitskaya, G. M. Butov, E. N. Savelyev, B. S. Orlinson, I. A. Novakov and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2015, **51**, 301.