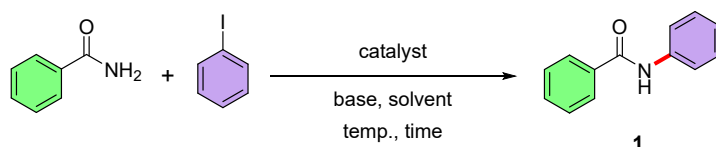


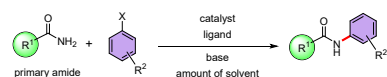
Table S1



Entry	Catalyst	Base	Solvent	Temp.(°C)	Time	Yield(%) ^b
1	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	86
2	Co(acac) ₂ /CuI	Cs ₂ CO ₃	DMF	110	24h	45
3	Co(acac) ₂ /CuI	Cs ₂ CO ₃	DMSO	110	24h	76
4	Co(acac) ₂ /CuI	Cs ₂ CO ₃	THF	90	24h	72
5	Co(acac) ₂ /CuI	Cs ₂ CO ₃	PEG-600	110	24h	70
6	Co(acac) ₂ /CuI	Cs ₂ CO ₃	toluene	110	24h	31
7	Co(acac) ₂ /CuI	Cs ₂ CO ₃	PhCl	110	24h	55
8	Co(acac) ₂ /CuI	Cs ₂ CO ₃	H ₂ O	110	24h	40
9	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP+H ₂ O	110	24h	60
10	Co(acac) ₂ /CuI	Cs ₂ CO ₃	—	110	24h	80
11 ^c	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	88
12 ^c	Co(OAc) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	67
13 ^c	CoBr ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	43
14 ^c	CoI ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	51
15 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	24h	90
16 ^c	Co(acac) ₂ /CuI	Na ₂ CO ₃	NMP	110	24h	70
17 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	90	24h	58
18 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	60	24h	0
19 ^c	Co(acac) ₂ /-	K ₂ CO ₃	NMP	110	24h	0
20 ^c	-/CuI	K ₂ CO ₃	NMP	110	24h	11
21 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMPH	110	15h	91
22 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	12h	81
23 ^{c,d}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	90
24^{c,e}	Co(acac)₂/CuI	K₂CO₃	NMP	110	15h	93
25 ^{c,f}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	74
26 ^{c,g}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	87
27 ^{c,h}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	81
28 ^{c,i}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMPH	110	15h	72
29 ^{c,j}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	93

^a Reaction conditions: amide (0.5 mmol), aryl halide (0.5 mmol), Co-catalyst (10 mol%), CuI (10 mol%), base (0.75 mmol), solvent (1 mL) under argon atmosphere. ^b Isolated yields. ^cNMP was used 100 μ L for 1.0 mmol scale of reaction. ^d Reaction was carried out under nitrogen atmosphere. ^e Reaction was carried out in open air. ^fCo(acac)₂ (5 mol%) and CuI (5 mol%) were used. ^gCo(acac)₂ (5 mol%) and CuI (10 mol%) were used. ^hCo(acac)₂ (10 mol%) and CuI (5 mol%) were used. ⁱamide (0.75 mmol), aryl halide (0.5 mmol) were used. ^jamide (0.5 mmol), aryl halide (0.75 mmol) were used.

Table S2a.



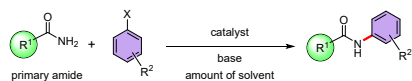
Entry	R ¹	X	Catalyst	Ligand	Base	Amount of solvent for 1.0 mmol scale of reaction	Yield (%)	Mechanistic study	Mechanistic cycle	Reusability of catalyst	Substrate scope	Gram-scale synthesis	Conventional work-up required	Ref
1	R ¹ = Ph * Aliphatic * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	CoCl ₂ ·6H ₂ O (20 mol%)	DMEDA	K ₃ PO ₄ ·H ₂ O	0.7 mL	24-28	No	not provided	No	2	No	Yes	14a
2	R ¹ = Aryl * Aliphatic * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	Co(C ₂ O ₄) ₂ ·2H ₂ O (10-20 mol%)	DMEDA	Cs ₂ CO ₃	0.2 mL	18-92	No	Co(II)/Co(IV)	No	29	No	Yes	14b
3	R ¹ = Aliphatic * Aryl * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	Co(C ₂ O ₄) ₂ ·2H ₂ O (20 mol%)	DMEDA	Cs ₂ CO ₃	0.2 mL	trace-75	No	not provided	No	16	No	Yes	14c
4	R ¹ = C ₃ H ₇ * Aryl * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	Co(acac) ₂ (10 mol%) Cul (10 mol%)	—	Cs ₂ CO ₃	4.0 mL	82 (for R ² = 4-Cl) 90 (for R ² = 1-naphthyl)	No	Co(I)/Co(III)	No	2	No	Yes	13e
5	R ¹ = Aliphatic, Aryl, Heteroaryl	X = Br, I, Cl Aryl and Heteroaryl halides	Co(acac) ₂ (10 mol%) Cul (10 mol%)	—	K ₂ CO ₃	0.1 mL or Solvent-free	43-94 (for X = I, Br) 10-80 (for X = Cl)	Yes	Co(0)/Co(II)	Yes	51	Yes	No	Our Work

"*" indicates "not applicable", which are significant disadvantages with respect to our present method.

Red colour indicates significant disadvantage with respect to our present method.

Blue colour indicates minor disadvantage with respect to our present method.

Table S2b.



Entry	R ¹	X	Catalyst	Base	Amount of solvent for 1.0 mmol scale of reaction	Yield (%)	Mechanistic study	Mechanistic cycle	Reusability of catalyst	Substrate scope	Gram-scale synthesis	Conventional work-up required	Ref
1	R ¹ = CH ₃ , Aryl, heteroaryl	X = I * X = Br, Cl * Heteroaryl	Cul	K ₃ PO ₄ or, CsF	0.4 mL	39-97	No	not provided	No	5	Yes	Yes	8a
2	R ¹ = Pentyl, Ph * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	CuO NPs	Cs ₂ CO ₃	0.8 mL	25-88	No	provided but not mentioned the oxidation state of Cu species either in the text or in the catalytic cycle	Yes	6	No	Yes	8b
3	R ¹ = CH ₃ , Pentyl, Ph * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	Cu ₂ O NPs	KOH	0.7 mL	70-80	No	provided but not mentioned the oxidation state of Cu species either in the text or in the catalytic cycle	Yes	9	No	Yes	8c
4	R ¹ = 4-BrPh, Ph * Aliphatic * Heteroaryl	X = I * X = Br, Cl * Heteroaryl	Cu/Al ₂ O ₃	KOH	2.0 mL	78-81	No	not provided	Yes	2	No	Yes	8e
5	R ¹ = CH ₃ , Ph * Heteroaryl	X = I, Br * X = Cl * Heteroaryl	Pre-prepared biogenic CuONP	K ₂ CO ₃	3.0 mL	85-96	Yes	provided but no redox process shown at the Cu center	Yes	13	No	Yes	7j
6	R ¹ = Ph * Aliphatic * Heteroaryl	X = Br (only bromobenzene) * X = Cl * Heteroaryl	Cul	K ₃ PO ₄	0.5 mL	49	No	not provided	No	1	No	Yes	8g
7	R ¹ = Aliphatic, Aryl, Heteroaryl	X = Br, I, Cl Aryl and Heteroaryl halides	Co(acac) ₂ /Cul	K ₂ CO ₃	0.1 mL or Solvent-free	43-94 (for X = I, Br) 10-80 (for X = Cl)	Yes	Co(0)/Co(II)	Yes	51	Yes	No	Our Work

"*" indicates "not applicable", which are significant disadvantages with respect to our present method.

Red colour indicates significant disadvantage with respect to our present method.

Blue colour indicates minor disadvantage with respect to our present method.