Efficient Copper-Catalyzed Coupling of 2-Haloacetanilides with Phosphine Oxides and Phosphites under Mild Conditions

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Abstract: We have developed a highly efficient method for the copper-catalyzed coupling of 2-haloacetanilides with phosphine oxides and phosphites in the presence of a catalytic amount of copper(I) iodide and *N*-methylpyrrolidine-2-carboxamide under mild conditions (45–55 °C); the P-arylation products were synthesized in good to excellent yields in short times using 2-bromotrifluoroacetanilides and 2-iodotrifluoroacetanilides as the starting materials. This represents the lowest reaction temperatures for copper-catalyzed P-arylation thus far.

Key words: Ullmann reaction, P-arylation, *ortho* effect, copper catalysis, N,N-ligand

Many efficient arylphosphine ligands with diverse structures have been developed and utilized extensively in both academic research and industry.[1] Aryl- and vinylphosphonic acid moieties are key functionalities in many biologically active compounds,[2] and flame retardants.[3] Although many approaches to these compounds have been reported, the direct coupling of aryl halides with P–H bonds is the most straightforward strategy and palladium-catalyzed P-arylation reactions are popular.[4] Recently, several examples involving copper-catalyzed P-arylations have been reported by us[5a,b] and other groups,[5c–f] but only aryl iodides are good substrates; aryl bromides show weak reactivity. In addition, the copper-catalyzed coupling usually requires aggressive reagents or rather harsh conditions, such as higher heating temperatures (more than 100 °C) and long reaction times (>10 h). Since *o*-aminoarylphosphines[6] and *o*-aminoarylphosphonates[7] have been used as the ligands for asymmetric synthesis and biological active molecules, respectively, it is highly desired to develop more convenient and economic synthetic routes. Herein, we report a mild and highly efficient method for the copper-catalyzed P-arylation of phosphine oxides and phosphites catalyzed by copper(I) iodide/*N*-methylpyrrolidine-2-carboxamide.

The *ortho*-$NHCOCF_3$ in 2-halotrifluoroacetanilides could promote copper-catalyzed Ullmann-type biaryl formation and the enantioselective arylation of 2-methylacetoacetates in the presence of suitable ligands under mild conditions[8] and avoid the formation of benzoxazoles at higher temperature,[9] hence we initially transformed 2-haloanilines into 2-halotrifluoroacetanilides. We also optimized the catalysis conditions, including copper source, ligand, base, solvent, and amount of catalyst and ligand, in order to achieve good coupling yields of aryl halides with organophosphorus compounds containing P–H (Table 1).

Several ligands, *N*,*N*′-dimethylethylenediamine (**A**, Table 1, entry 1),[10] amino acids **B**–**E** (Table 1, entries 2–5),[11] *rac*-BINOL **F** (Table 1, entry 6),[12] *N*-methylpyrrolidine-2-carboxamide (**G**, Table 1, entry 7),[13] were tested with 2-bromotrifluoroacetanilide and diphenylphosphine oxide used as model substrates. The results showed that *N*-methylpyrrolidine-2-carboxamide (**G**) exhibited the best activity. We also studied the effect of solvents (cf. Table 1, entries 7, 9–11); 1,4-dioxane and *N*,*N*-dimethylformamide provided better yields, but toluene was a poor solvent. The base also influenced the reaction rate; cesium carbonate gave the highest yield (Table 1, entry 7), by comparison sodium carbonate (Table 1, entry 12), potassium phosphate (Table 1, entry 13), and potassium carbonate (Table 1, entry 14) provided lower yields. The copper sources were also investigated (cf. Table 1, entries 7, 15–18) and the results show that copper(I) iodide was the best catalyst. The reaction yield improved as increasing amounts of copper(I) iodide and *N*-methylpyrrolidine-2-carboxamide (**G**) were used. The coupling yield greatly decreased (<35%) when the *ortho*-$NHCOCF_3$ in 2-halotrifluoroacetanilides was replace with an *ortho*-NHCOMe group. After optimization of the ligand, solvent, base, and catalyst, the cross-coupling reactions were carried out under our standard conditions, 30 mol% copper(I) iodide as the catalyst, 100 mol% *N*-methylpyrrolidine-2-carboxamide as the ligand relative to the aryl halide, anhydrous 1,4-dioxane as the solvent, and 1.5 equivalents of cesium carbonate as the base.

As shown in Table 2, aryl bromides and iodides **1** (X = Br or I) gave the products **3** in good to excellent yields and aryl iodides displayed slightly higher activity than aryl bromides. The aryl chloride **1** (X = Cl) was a weak substrate, but it also provided a moderate yield (50%) of **3a** when the reaction temperature was raised to 110 °C (Table 2, entry 3). Phosphites were better substrates than phosphine oxides. The addition of electron-donating groups to the 2-halotrifluoroacetanilides improved P-ary-

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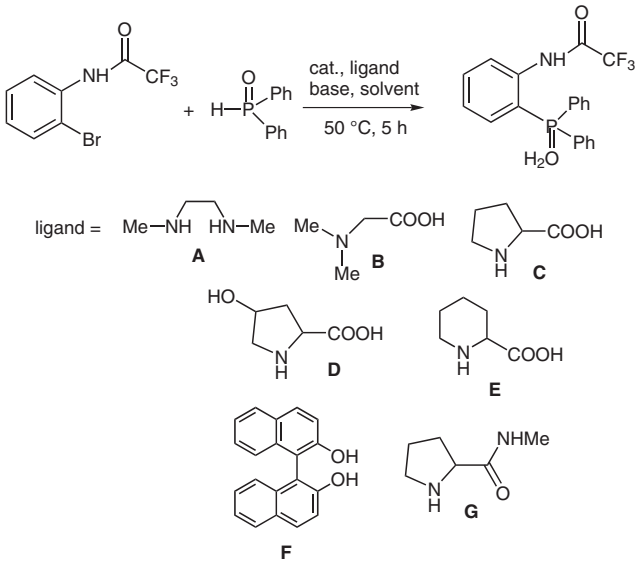
Table 1 Copper-Catalyzed P-Arylation; Optimization of the Catalytic Conditions[a]



Entry	Catalyst	Ligand	Base	Solvent	Yield[b] (%)
1	CuI	**A**	Cs_2CO_3	1,4-dioxane	23
2	CuI	**B**	Cs_2CO_3	1,4-dioxane	21
3	CuI	**C**	Cs_2CO_3	1,4-dioxane	54
4	CuI	**D**	Cs_2CO_3	1,4-dioxane	61
5	CuI	**E**	Cs_2CO_3	1,4-dioxane	56
6	CuI	**F**	Cs_2CO_3	1,4-dioxane	37
7	CuI	**G**	Cs_2CO_3	1,4-dioxane	78
8	CuI	–	Cs_2CO_3	1,4-dioxane	0[c]
9	CuI	**G**	Cs_2CO_3	DMSO	68
10	CuI	**G**	Cs_2CO_3	DMF	72
11	CuI	**G**	Cs_2CO_3	toluene	0
12	CuI	**G**	Na_2CO_3	1,4-dioxane	35
13	CuI	**G**	K_3PO_4	1,4-dioxane	49
14	CuI	**G**	K_2CO_3	1,4-dioxane	46
15	$CuSO_4$	**G**	Cs_2CO_3	1,4-dioxane	0
16	$Cu(OAc)_2$	**G**	Cs_2CO_3	1,4-dioxane	0
17	$CuCl_2$	**G**	Cs_2CO_3	1,4-dioxane	35
18	CuBr	**G**	Cs_2CO_3	1,4-dioxane	65

[a] Reagents and conditions: 2-bromotrifluoroacetanilide (1.0 mmol), Ph_2PHO (1.5 mmol), catalyst (0.3 mmol), ligand (1 mmol), base (1.5 mmol), solvent (2 mL) under N_2.
[b] Isolated yield.
[c] In the absence of ligand.

lation of the substrates and inhibited the formation of the reduced products (debromination); completion of P-arylation needed longer times for aryl halides containing electron-withdrawing groups. We also investigated the *ortho* effect of halotrifluoroacetanilides, the reactions selectively occurred at the *ortho* site for 2,4-dibromotrifluoroacetanilide (Table 2, entries 8, 9). We attempted the coupling of 3-bromotrifluoroacetanilide or 4-bromotrifluoroacetanilide with diphenylphosphine oxide at 50 °C under our standard conditions, however, only trace amounts of P-arylation products were observed. Reaction of 2,4-dibromotrifluoroacetanilide with diphenylphosphine oxide (Table 2, entry 8) or diisopropyl phosphite (Table 2, entry 9) provided the monosubstituted products **3d** and **3e**. These results show that the *ortho*-$NHCOCF_3$ group in 2-halotrifluoroacetanilides could promote P-arylation.

In summary, we have developed a highly efficient method for the synthesis of [2-(trifluoroacetamido)aryl]phosphine oxides and 2-(trifluoroacetamido)arylphosphonates using inexpensive copper(I) iodide/*N*-methylpyrrolidine-2-carboxamide as the catalyst. Various substituted 2-halotrifluoroacetanilides were used as the substrate and the coupling reactions were complete in short times under mild conditions (45–55 °C). This method is of wide application for the synthesis of diverse *o*-aminoarylphosphine oxides, *o*-aminoarylphosphines, and *o*-aminoarylphosphonates.

All reactions were carried out under an N_2 atmosphere. DMF was dried over CaH_2 and freshly distilled before use. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard (^1H NMR: TMS δ = 0.00, $CDCl_3$ δ = 7.24; ^{13}C NMR: $CDCl_3$ δ = 77.0).

Synthesis of (*S*)-*N*-Methylpyrrolidine-2-carboxamide

(*S*)-*N*-Methylpyrrolidine-2-carboxamide was prepared according to the reported procedure.[13]

Synthesis of 3a–j; General Procedure

A flask was charged with CuI (57 mg, 0.3 mmol), *N*-methylpyrrolidine-2-carboxamide (128 mg, 1 mmol), Cs_2CO_3 (489 mg, 1.5 mmol), halotrifluoroacetanilide (1 mmol), phosphine oxide or phosphite (1.5 mmol), and 1,4-dioxane (2 mL). The flask was sealed and the mixture was allowed to stir under N_2 at the indicated temperature and time (Tables 1 and 2). When the coupling reaction was complete (TLC), the mixture was diluted with EtOAc, the soln was filtered, and the inorganic salts were removed. The solvent of the filtrate was removed with the aid of a rotary evaporator and the residue was purified by flash column chromatography (silica gel, PE–EtOAc, 10:1 to 2:1) to provide the desired product.

Diphenyl[2-(trifluoroacetamido)phenyl]phosphine Oxide (3a)

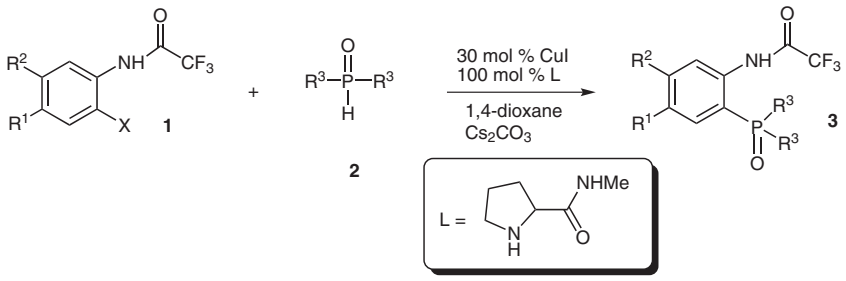
White solid; yield: 80% (X = I); 78% (X = Br); 50% (X = Cl); mp 120–121 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 12.64 (s, 1 H), 8.55–8.58 (m, 1 H), 7.47–7.65 (m, 11 H), 7.08–7.21 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.4 (q, *J* = 37.2 Hz), 142.2, 133.7, 133.1, 132.9, 132.2, 132.0, 131.5, 130.1, 129.0, 124.8, 124.6, 122.3, 117.8 (m).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 38.01.

Table 2 *N*-Methylpyrrolidine-2-carboxamide-Promoted Copper-Catalyzed Coupling of Aryl Halides with Organophosphorus Compounds Containing P–H[a]



Entry	R^1	R^2	R^3	X	Temp (°C)/ Time (h)	Product	Yield[b] (%)
1	H	H	Ph	Br	50/5	**3a**	78
2	H	H	Ph	I	50/4	**3a**	80
3	H	H	Ph	Cl	110/10	**3a**	50
4	H	H	O*i*-Pr	Br	45/4	**3b**	93
5	H	H	O*i*-Pr	I	45/1.5	**3b**	92
6	H	H	OBu	Br	45/2	**3c**	90
7	H	H	OBu	I	45/1.5	**3c**	91
8	Br	H	Ph	Br	50/6	**3d**	84
9	Br	H	O*i*-Pr	Br	45/3	**3e**	72
10	Me	H	Ph	Br	50/10	**3f**	78
11	Me	H	OBu	Br	45/3.5	**3g**	91
12	Me	H	O*i*-Pr	Br	45/4.5	**3h**	92
13	H	NO_2	OBu	Br	55/48	**3i**	56
14	H	NO_2	O*i*-Pr	Br	50/10	**3j**	87

[a] Reagents and conditions: aryl halide (1.0 mmol), phosphine oxide or phosphite (1.5 mmol), CuI (0.3 mmol), ligand **G** (1 mmol), Cs_2CO_3 (1.5 mmol), 1,4-dioxane (2 mL) under N_2.
[b] Isolated yield.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{16}F_3NO_2P$: 390.0871; found: 390.0875.

Diisopropyl 2-(Trifluoroacetamido)phenylphosphonate (3b)
White oil; yield: 92% (X = I); 93% (X = Br).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.96 (s, 1 H), 8.54 (t, *J* = 7.50 Hz, 1 H), 7.53–7.63 (m, 2 H), 7.23 (t, *J* = 1.38 Hz, 1 H), 4.62–4.67 (m, 2 H), 1.36 (d, *J* = 6.18 Hz, 6 H), 1.25 (d, *J* = 6.18 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3 (q, *J* = 37.3 Hz), 139.9, 139.8, 132.9, 129.2, 121.1, 120.9, 119.6 (m), 72.3, 23.9.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 15.08.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{20}F_3NO_4P$: 354.1082; found: 354.1089.

Dibutyl 2-(Trifluoroacetamido)phenylphosphonate (3c)
Colorless oil; yield: 91% (X = I); 90% (X = Br).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.91 (s, 1 H), 8.56 (t, *J* = 6.51 Hz, 1 H), 7.57–7.65 (m, 2 H), 7.24–7.26 (m, 1 H), 3.83–4.12 (m, 4 H), 1.53–1.72 (m, 4 H), 1.28–1.38(m, 4 H), 0.88 (t, *J* = 7.56 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6 (q, *J* = 36.8 Hz), 140.3, 134.3, 132.7, 129.2, 121.2, 120.9, 118.7 (m), 66.7, 32.3, 18.6, 13.5.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 19.30.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{24}F_3NO_4P$: 382.1395; found: 382.1393.

[5-Bromo-2-(trifluoroacetamido)phenyl]diphenylphosphine Oxide (3d)
White solid; yield: 84%; mp 125–127 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45–8.48 (m, 1 H), 7.52–7.67 (m, 11 H), 7.13–7.21 (dd, *J* = 7.21 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5 (q, *J* = 38.0 Hz), 141.1, 136.5, 135.2, 135.1, 135.0, 133.3, 132.3, 132.2, 132.0, 130.6, 129.3, 129.2, 124.0 (m).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.57.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}BrF_3NO_2P$: 467.9976; found: 467.9982.

Diisopropyl 5-Bromo-2-(trifluoroacetamido)phenylphosphonate (3e)
Colorless oil; yield: 72%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.85 (s, 1 H), 8.42–8.45 (m, 1 H), 7.64–7.74 (m, 2 H), 4.68–4.71 (m, 2 H), 1.38 (d, *J* = 6.18 Hz, 6 H), 1.23 (d, *J* = 6.18 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.2 (q, *J* = 38.2 Hz), 138.6, 136.8, 135.3, 135.2, 122.6, 122.3, 118.1 (m), 72.9, 23.8.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.80.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}BrF_3NO_4P$: 432.0187; found: 432.0186.

[5-Methyl-2-(trifluoroacetamido)phenyl]diphenylphosphine Oxide (3f)
Colorless oil; yield: 78%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41–8.44 (m, 1 H), 7.43–7.67 (m, 11 H), 6.91 (d, *J* = 6.78 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.2 (q, *J* = 37.2 Hz), 134.3, 133.1, 132.9, 132.8, 132.4, 132.2, 132.0, 131.6, 129.0, 122.3, 122.2, 118.3 (m), 21.1.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.90.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}F_3NO_2P$: 404.1027; found: 404.1029.

Dibutyl 5-Methyl-2-(trifluoroacetamido)phenylphosphonate (3g)
Colorless oil; yield: 91%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.77 (s, 1 H), 8.42 (t, *J* = 7.52 Hz, 1 H), 7.37–7.42 (m, 2 H), 3.97–4.11 (m, 4 H), 2.35 (s, 3 H), 1.54–1.75 (m, 4 H), 1.29–1.41 (m, 4 H), 0.87 (t, *J* = 7.56 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.2 (q, *J* = 37.4 Hz), 135.1, 134.9, 132.8, 132.7, 121.2, 121.0, 116.6 (m), 66.7, 32.3, 20.8, 18.6, 13.4.

^{31}P NMR (121 MHz, $CDCl_3$) δ = 19.52.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{26}F_3NO_4P$: 396.1552; found: 396.1558.

Diisopropyl 5-Methyl-2-(trifluoroacetamido)phenylphosphonate (3h)
Colorless oil; yield: 92%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.80 (s, 1 H), 8.39 (t, *J* = 7.56 Hz, 1 H), 7.34–7.43 (m, 2 H), 4.62–4.67 (m, 2 H), 2.29 (s, 3 H), 1.37 (d, *J* = 6.18 Hz, 6 H), 1.20 (d, *J* = 6.18 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.1 (q, *J* = 37.2 Hz), 134.6, 133.0, 132.9, 121.2, 120.9, 118.2 (m), 72.2, 23.9, 23.6.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 17.51.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{22}F_3NO_4P$: 368.1239; found: 368.1246.

Dibutyl 4-Nitro-2-(trifluoroacetamido)phenylphosphonate (3i)
Yellow oil; yield: 56%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.54 (m, 3 H), 3.87–4.05 (m, 4 H), 1.58–1.63 (m, 4 H), 1.31–1.37 (m, 4 H), 0.81–0.87 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1 (q, *J* = 37.3 Hz), 134.7, 134.6, 118.2 (m), 115.1, 110.5, 110.3, 110.2, 66.4, 32.3, 18.7, 13.5.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.65.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{23}F_3N_2O_6P$: 427.1246; found: 427.1244.

Diisopropyl 4-Nitro-2-(trifluoroacetamido)phenylphosphonate (3j)
Red oil: yield: 87%.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.57 (m, 3 H), 4.46–4.66 (m, 2 H), 1.34 (d, *J* = 6.18 Hz, 6 H), 1.20 (d, *J* = 6.18 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7 (q, *J* = 37.3 Hz), 134.9, 134.6, 116.9 (m), 110.5, 110.4, 110.3, 110.2, 71.7, 24.0.

^{31}P NMR (121 MHz, $CDCl_3$): δ = 16.38.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}F_3N_2O_6P$: 399.0933; found: 399.0937.

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