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Rapid synthesis of an electron-deficient *t*-BuPHOX ligand: cross-coupling of aryl bromides with secondary phosphine oxides

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ABSTRACT

Herein an efficient and direct copper-catalyzed coupling of oxazoline-containing aryl bromides with electron-deficient secondary phosphine oxides is reported. The resulting tertiary phosphine oxides can be reduced to prepare a range of PHOX ligands. The presented strategy is a useful alternative to known methods for constructing PHOX derivatives.

Phosphinooxazoline (PHOX) ligands have found broad applications in transition metal catalysis.[1] Developed by Pfaltz,[2] Helmchen,[3] and Williams,[4] PHOX ligands have become a preeminent class of P,N-ligands,[5] with *t*-BuPHOX (**L1**, Scheme 1) representing a most prominent example.[6] We have recently demonstrated the utility of *t*-BuPHOX in palladium-catalyzed enantioselective decarboxylative alkylation[7] and protonation[8] reactions. We, however, became aware of examples where *t*-BuPHOX provided only moderate results with respect to yields and enantioselectivities, and designed an electronically-modified version of this ligand, *p*-$(CF_3)_3$-*t*-BuPHOX (**L2**). In some cases, the electron-withdrawing trifluoromethyl groups affected the reactivity of the corresponding transition metal complex, leading to significantly shorter reaction times and enhanced selectivities. For example, we were able to achieve 99% yield and 87% ee in our palladium-catalyzed, enantioselective allylic alkylation reaction of allyl enol carbonate **1** within only 10 min at 25 °C with the use of (*S*)-**L2**, while the use of (*S*)-**L1** required 120 min reaction time to give 96% yield and 88% ee.[9] Further, this ligand was successfully applied in the catalytic asymmetric total synthesis of (+)-elatol where the key allylic alkylation of chloroallyl enol carbonate **2** was performed with (*R*)-**L2**, resulting in 82% yield of product in 87% ee, compared to only −81% ee and a poor 23% yield with the use of (*S*)-**L1**.[10] Moreover, we recently published a palladium-catalyzed, enantioselective enolate alkylation cascade, which provides products with up to 99% enantiomeric excess,[11] where (*S*)-*p*-$(CF_3)_3$-*t*-BuPHOX was far superior to (*S*)-*t*-BuPHOX for the alkylation of β-keto ester **3**.

Previously, we published a convenient and scalable synthesis for *t*-BuPHOX,[12] using an Ullmann-type coupling developed by Buchwald.[13] While this approach proved useful for the coupling of aryl halides and secondary phosphines, most substituted secondary phosphines are not commercially available. Similarly, substituted secondary phosphines (e.g., bis(4-(trifluoromethyl)phenyl)phosphine) are difficult to prepare in the required purity due to their propensity to oxidize upon exposure to air.[14] Although the preparation of synthetically challenging PHOX variants was possible using our previously described conditions, a more efficient and higher yielding protocol was desired. Therefore a synthetic strategy for the synthesis of *p*-$(CF_3)_3$-*t*-BuPHOX (**L2**) that avoids phosphine intermediates was needed. We envisioned a preparative route toward this electron-deficient PHOX ligand in which an oxazoline-containing aryl bromide is joined directly with a secondary phosphine oxide.[15,16] Herein, we demonstrate a copper-catalyzed coupling of aryl halides to secondary phosphine oxides for the synthesis of electron-deficient PHOX ligands.

Oxazoline-containing aryl bromide **4** and secondary phosphine oxide **5** can be readily synthesized on multi-gram scale (Scheme 2). Aryl bromide **4** was prepared using modified conditions from a published route,[10] requiring only one purification by flash chromatography. The treatment of (*S*)-*t*-leucinol with acid chloride **6**[7] in the presence of sodium carbonate provided amide **7** in 93% yield.[17] Subsequent mesylation of the free hydroxyl of **7**, followed by in situ mesylate displacement results in the formation of oxazoline **4** in 99% yield.[18] Bis(4-(trifluoromethyl)phenyl)phosphine oxide **5**[19] is produced in 80% yield by careful exposure of 4-(trifluoromethyl)phenylmagnesium bromide **8**, synthesized via the Leazer method,[20] to diethyl phosphite.[21] Unlike the related secondary phosphine, phosphine oxide **5** can be purified by column chromatography and is stable to air at room temperature for several months.

Our modification to Buchwald's copper iodide-catalyzed conditions for the coupling of secondary phosphines with aryl bromides[9,12] was tested for the coupling of secondary phosphine oxide **5** with oxazolinyl aryl bromide **4** (Table 1, entries 1 and 2). Gratifyingly, when a catalytic amount of CuI (12.5 mol %) was used in combination with *N*,*N*′-dimethylethylenediamine as ligand and

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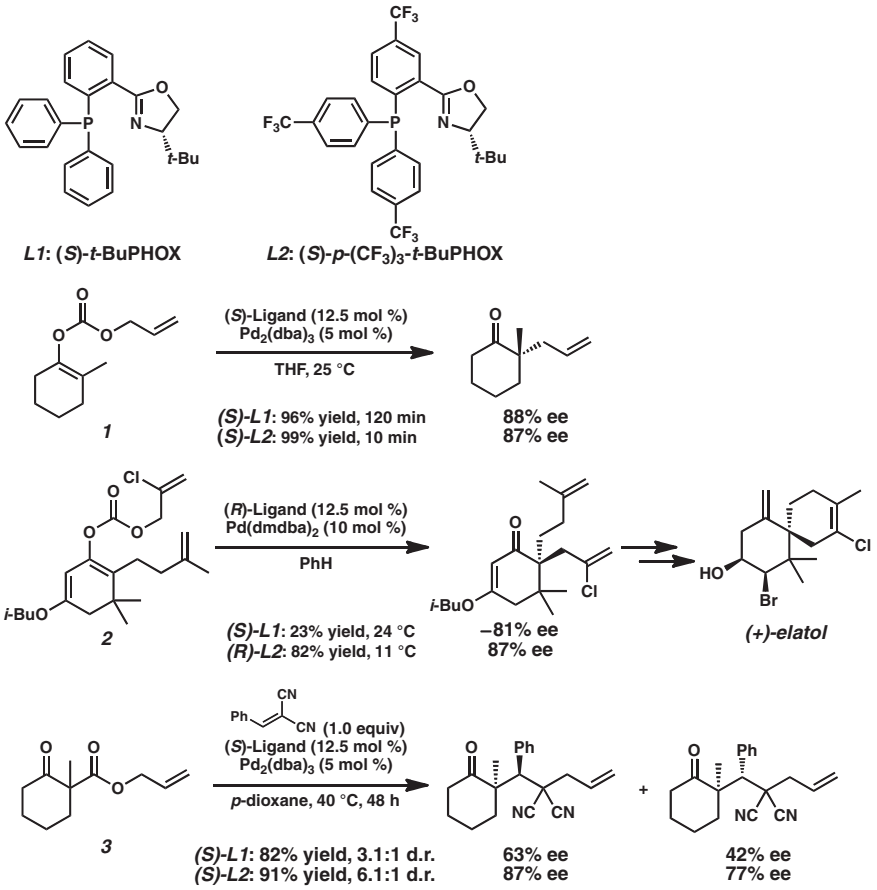
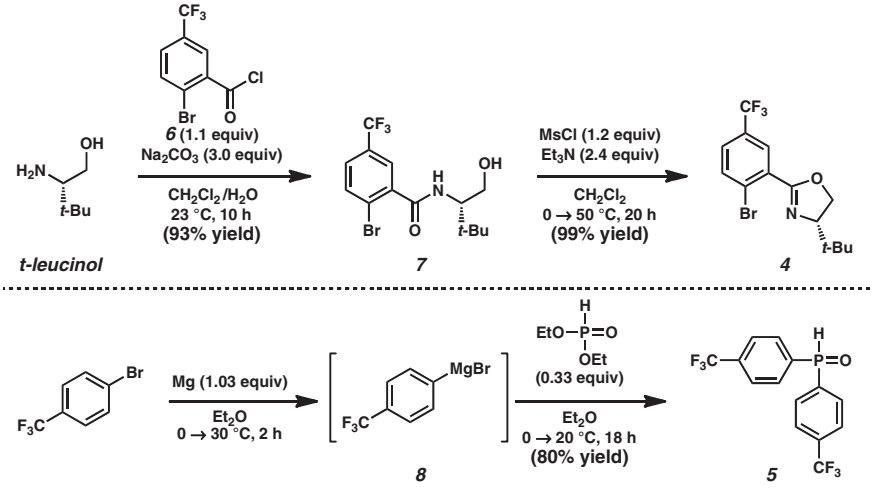


Scheme 1. PHOX ligands and their use in synthesis and methodology development.

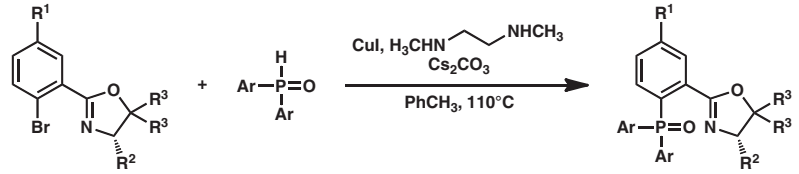
Cs_2CO_3 as base, secondary phosphine oxide **5** could be successfully coupled with aryl bromide **4** to produce **9** in 57% yield (entry 1). Reaction times could be reduced, and product yields improved to 65% with the use of a stoichiometric amount of CuI at a higher reaction concentration (entry 2).[22] To our satisfaction, secondary phosphine oxide **5** could be coupled with other aryl bromides **10**–**12** in moderate to good yields using catalytic amounts of CuI (entries 3–5). Similarly, bis(3,5-bis(trifluoromethyl)phenyl)phosphine oxide (**13**) could be coupled with oxazoline-containing aryl bromides using catalytic loadings of CuI (entries 6 and 7).

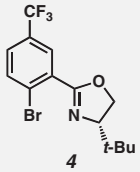
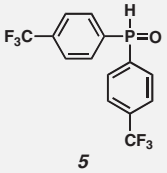
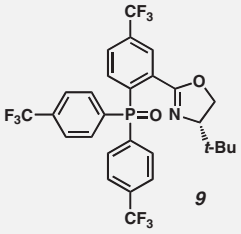
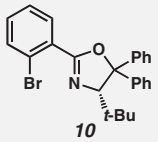
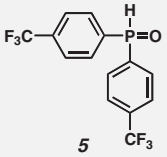
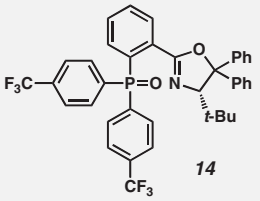
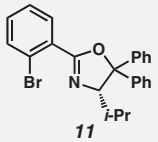
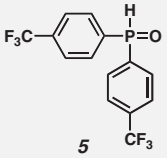
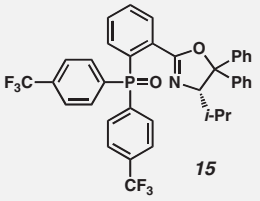
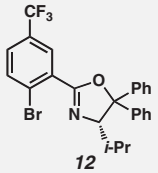
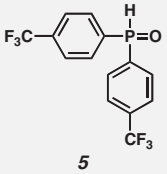
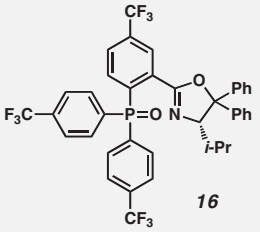
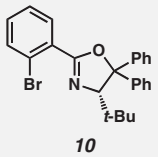
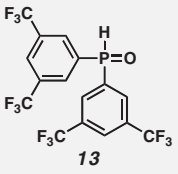
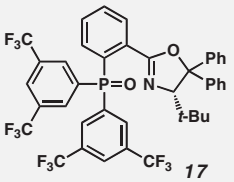
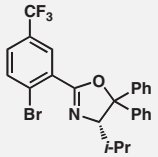
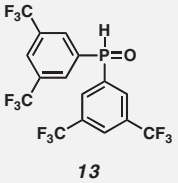
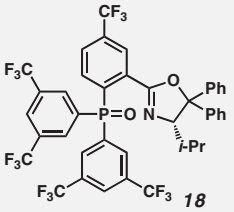
The resulting triarylphosphine oxides **9** and **14**–**18** can be smoothly purified by column chromatography and reduced to the corresponding PHOX ligands via silane reduction.[23] For example, reduction of **9** to the desired *p*-$(CF_3)_3$-*t*-BuPHOX ligand was accomplished with neat diphenylsilane, yielding **L2** in 86% isolated yield (Scheme 3).[24]



Scheme 2. Synthesis of oxazoline-containing aryl bromide **4** and secondary phosphine oxide **5**.

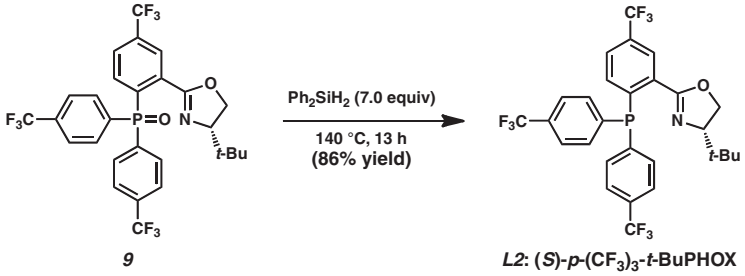
Table 1
Copper-catalyzed coupling of aryl bromides with secondary phosphine oxides[a]



Entry	Aryl bromide	Secondary phosphine oxide	Product	Yield[b] (%)
1	 **4**	 **5**	 **9**	57
2[c]				65
3	 **10**	 **5**	 **14**	85
4	 **11**	 **5**	 **15**	62
5	 **12**	 **5**	 **16**	55
6	 **10**	 **13**	 **17**	46
7	 **12**	 **13**	 **18**	36

[a] Reactions were performed with aryl bromide (1.0 equiv), secondary phosphine oxide (1.3 equiv), CuI (12.5 mol %), *N*,*N*′-dimethylethylenediamine (87.5% mol %), and Cs_2CO_3 (3.7 equiv) in $PhCH_3$ (0.1 m) at 110 °C for 38–42 h.
[b] Yield of isolated product.
[c] Reaction was performed with 1.0 equiv of CuI and 3.0 equiv of *N*,*N*′-dimethylethylenediamine in $PhCH_3$ (0.25 M) for 15 h.

In conclusion, we have developed a rapid synthesis of *p*-$(CF_3)_3$-*t*-BuPHOX (**L2**) that results in an overall 51% yield starting from (*S*)-*t*-leucine under relatively mild conditions in four linear steps. The route utilizes a copper iodide-catalyzed coupling of oxazoline-containing aryl bromide **4** to secondary phosphine oxide **5**, followed by a silane-mediated reduction of the resulting triarylphosphine



Scheme 3. Reduction of **9** to afford (*S*)-*p*-$(CF_3)_3$-*t*-BuPHOX.

oxide, to prepare the phosphinooxazoline core structure. We believe that the copper-catalyzed coupling of aryl bromides to secondary phosphine oxides provides a convenient alternative to the coupling of air-sensitive secondary phosphines for the preparation of tertiary phosphines.

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17. *(S)-2-Bromo-N-(1-hydroxy-3,3-dimethylbutan-2-yl)-5-(trifluoromethyl)benzamide* (**7**): To a 250 mL, round-bottomed flask charged with a magnetic stirring bar and (*S*)-*t*-leucinol (2.10 g, 17.9 mmol, 1.0 equiv) was added methylene chloride (60 mL). To the mixture was added a solution of sodium carbonate (5.70 g, 53.8 mmol, 3.0 equiv) in water (45 mL). The biphasic mixture is vigorously stirred at 23 °C. To the mixture was added 2-bromo-5-(trifluoromethyl)benzoyl chloride **6**[9] (5.66 g, 19.7 mmol, 1.1 equiv) dropwise over 15 min. The reaction mixture was vigorously stirred at 23 °C for 10 h. The layers were separated, and the aqueous layer was extracted with methylene chloride (4 × 50 mL). The combined organic layers were stirred with a 1 N potassium hydroxide solution in methanol (10 mL) for 30 min, then acidified to neutral pH with 1 N hydrochloric acid (~8 mL). To the mixture was added water (15 mL), and the layers were separated. The aqueous layer was extracted with methylene chloride (4 × 20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. The resulting residue **7** (6.10 g, 16.6 mmol, 93% yield) was found to be pure by ^{1}H NMR, and used without further purification. Analytical data matched literature values for the corresponding (*R*)-enantiomer.[10]
18. *(S)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-4-tert-butyl-4,5-dihydrooxazole* (**4**): To a flame-dried, 250 mL three-necked flask charged with a magnetic stirring bar and *(S)*-2-bromo-*N*-(1-hydroxy-3,3-dimethylbutan-2-yl)-5-(trifluorome thyl)benzamide **7** (6.10 g, 16.6 mmol, 1.0 equiv) were added methylene chloride (86 mL) and freshly distilled triethylamine (5.60 mL, 40.0 mmol, 2.4 equiv). The solution was cooled to 0 °C in an ice bath, and methanesulfonyl chloride (1.50 mL, 19.4 mmol, 1.2 equiv) was added dropwise over 3 min. A reflux condenser was attached to the flask, and the reaction mixture was heated to 50 °C with stirring for 20 h. The crude reaction mixture was allowed to cool to ambient temperature, and an aqueous saturated sodium bicarbonate solution (30 mL) was added with vigorous stirring for 5 min. The layers were separated, and the aqueous phase was extracted with methylene chloride (3 × 20 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated. The resulting residue was subjected to silica gel chromatography, and eluted with hexanes/ethyl acetate (9:1 → 6:1) to afford **4** (5.76 g, 16.4 mmol, 99% yield) as a colorless oil. Analytical data matched literature values.[9]
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21. *Bis(4-(trifluoromethyl)phenyl)phosphine oxide* (**5**): To a flame-dried, 50 mL flask charged with magnesium metal (607 mg, 25.0 mmol, 3.1 equiv) was added diethyl ether (12 mL). The mixture was cooled to 0 °C and 4-bromobenzotrifluoride (3.38 mL, 24.2 mmol, 3.0 equiv) was added dropwise over 25 min, during which the mixture changed from colorless to yellow to black. A reflux condenser was attached to the flask, and the mixture was allowed to warm to 23 °C over 20 min, and then heated to 30 °C for 90 min. The Grignard solution was transferred via cannula to a flame-dried, 25 mL flask to remove excess magnesium metal. The resulting Grignard solution was cooled to 0 °C, and diethyl phosphite (1.04 mL, 8.05 mmol, 1.0 equiv) was added dropwise over 5 min. The reaction mixture was allowed to slowly warm to 23 °C with stirring over 18 h. The reaction mixture was cooled to 0 °C and treated with 2 m aqueous hydrochloric acid (10 mL). The mixture was allowed to warm to ambient temperature and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over sodium sulfate and concentrated. The resulting residue was subjected to silica gel chromatography, and eluted with hexane/ethyl acetate (1:1 → 1:9), to give **5** (2.18 g, 6.46 mmol, 80% yield) as a pale yellow solid. Mp: 67–69 °C (lit. 65–67 °C); R_f = 0.29 (hexane/ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J_{HP} = 492 Hz, 1H), 7.83–7.90 (m, 4H), 7.78–7.82 (m, 4H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 17.80 (J_{PH} = 490 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.35; FTIR (neat film, NaCl) 3482, 3042, 2341, 1401, 1325, 1171, 1128, 1103, 1062, 1018, 942, 832, 711 cm^{-1}; HRMS (FAB, Pos) *m*/*z* calcd for $C_{14}H_{10}OPF_6$ $[M+H]^+$: 339.0373, found 339.0387.

22. *(S)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphoryl)-5-(trifluoromethyl)phenyl)-4-tert-butyl-4,5-dihydro-oxazole* (**9**): To a 50 mL Schlenk flask charged with a magnetic stirring bar, CuI (976 mg, 5.12 mmol, 1.0 equiv), and bis(4-(trifluoromethyl)phenyl)phosphine oxide **5** (2.25 g, 6.66 mmol, 1.3 equiv) was added toluene (15 mL) under an Ar atmosphere. To the mixture was added *N*,*N*′-dimethylethylenediamine (1.65 mL, 15.4 mmol, 3.0 equiv) and the resulting mixture was stirred for 20 min. To the mixture were then added (*S*)-2-(2-bromo-5-(trifluoromethyl)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole **4** (1.79 g, 5.12 mmol, 1.0 equiv), Cs_2CO_3 (6.18 g, 19.0 mmol, 3.7 equiv), and 5 mL toluene. The Schlenk flask was sealed and the reaction mixture was heated to 110 °C with stirring for 15 h. The crude reaction mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. ^{1}H NMR of the mixture showed ~70% conversion into the desired product with formation of ~30% of debrominated **4**. The concentrated reaction mixture was subjected to silica gel chromatography, and eluted with hexanes/ethyl acetate (3:1 → 1:1) to provide **9** (1.97 g, 3.33 mmol, 65% yield) as white crystals. Mp: 159–161 °C; R_f = 0.60 (hexane/ethyl acetate, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 7.80–8.03 (m, 4H), 7.72 (s, 1H), 7.70–7.78 (m, 5H), 3.89 (dd, *J* = 17.1, 8.7 Hz, 1H), 3.86 (dd, *J* = 18.9, 8.7 Hz, 1H), 3.38 (app t, *J* = 9.6 Hz, 1H), 0.71 (s, 9H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 27.96; ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.26, −63.26, −63.42; FTIR (neat film, NaCl) 3435, 2105, 1644, 1479, 1399, 1323, 1173, 1131, 1062 cm^{-1}; HRMS: HRMS (FAB, Pos) *m*/*z* calcd for $C_{28}H_{24}O_2PNF_9$ $[M+H]^+$: 608.1401, found 608.1414; $[\alpha]_D^{25}$ = −56.3 (*c* 1.03, CH_2Cl_2).
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24. *(S)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)-5-(trifluoromethyl)phenyl)-4-tert-butyl-4,5-dihydrooxazole*, (**L2**): To a flame-dried 50 mL Schlenk tube charged with a magnetic stirring bar and (*S*)-2-(2-(bis(4-(trifluoromethyl) phenyl)phosphoryl)-5-(trifluoromethyl)phenyl)-4-*tert*-butyl-4,5-dihydro-oxazole **9** (2.02 g, 3.33 mmol, 1.0 equiv) under an Ar atmosphere was added diphenylsilane (4.30 mL, 23.3 mmol, 7.0 equiv). The Schlenk tube was sealed and the clear solution was heated to 140 °C with stirring for 13 h. The crude reaction mixture was allowed to cool to ambient temperature, then subjected directly to silica gel chromatography, and eluted with hexanes and methylene chloride (3:1), to provide ligand **L2** as a colorless, semi-crystalline oil. Crystallization was induced with pentane (4 mL) at −20 °C to yield **L2** (1.69 g, 2.86 mmol, 86% yield) as colorless crystals. Analytical data matched literature values.[9,10]