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Exploration of Aryllithium-Derived Copper Reagents for Quaternary-Stereogenic-Center-Forming Allylic Substitution of γ,γ-Disubstituted Secondary Allylic Picolinates

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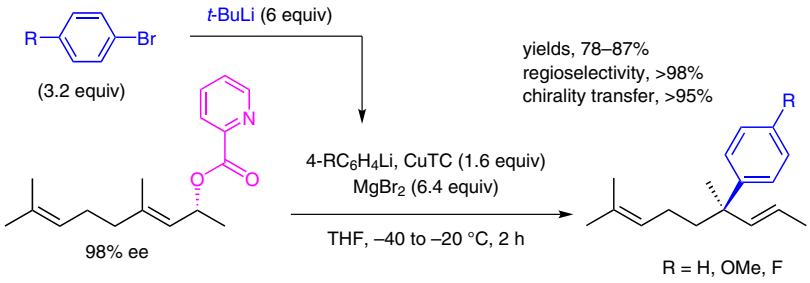

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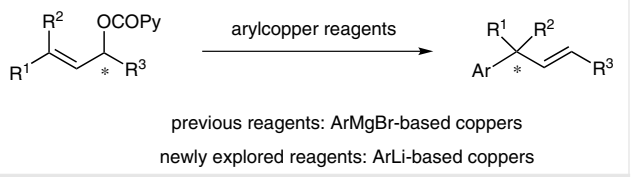
Abstract The allylic substitution of γ,γ-disubstituted secondary allylic picolinates (esters of 2-PyCO$_2$H) with aryllithium-based copper reagents was carried out in order to construct quaternary carbons. Initially, 2-methyl-7-phenylhept-2-en-4-yl picolinate was reacted with phenyl copper reagents derived from phenyllithium with Cu(acac)$_2$, Cu(OMe)$_2$, CuBr·Me$_2$S, and CuCN in 1–3:1 ratios in the presence of excess magnesium bromide. Although the S_N2' product with a quaternary carbon was formed, the regioselectivity was 90% at most. Instead, phenyllithium/copper(I) thiophene-2-carboxylate/magnesium bromide (Ph/Cu = 1.5–2:1, Mg/Li = >1) was found to produce >98% regioselectivity and sufficient reactivity. This system was successful with eight aryllithium based copper reagents possessing sterically congested, electron-donating, or electron-withdrawing substituents. The *anti* stereochemical course was established by using an enantiomerically enriched geranaldehyde-derived picolinate.

Key words allylic substitution, aryl lithium, *anti* S_N2', copper reagents, picolinate, quaternary carbon

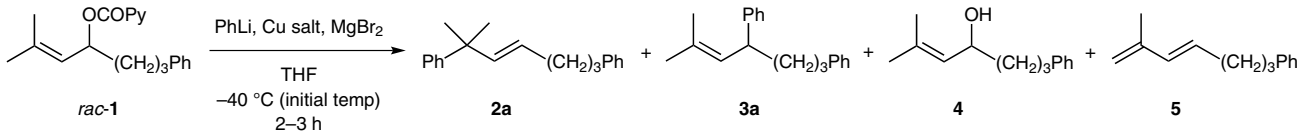
The development of methods for the construction of quaternary stereogenic centers is an important subject in organic synthesis as many biologically active compounds consist of quaternary stereogenic center(s). To date a variety of reactions have been explored for this purpose and summarized in recent reviews.[1] The 1,4-addition of organometallics to enones, alkylation of enolates, and Diels–Alder reactions are among the most efficient methods. Allylic substitution of primary and secondary allylic substrates using copper catalysts and copper reagents is another possibility. Notably, several efficient methods for the substitution have been developed.[2–4] The carbon framework and array of functional groups on the products differ from those derived in the aforementioned reactions, and thus advantageous in target-oriented organic syntheses. As for allylic substitutions of secondary allylic derivatives,[3,4] our substitution using allylic picolinates is applicable to aryl copper reagents derived from arylmagnesium bromide and Cu(acac)$_2$, producing quaternary carbons stereo- and regioselectively (Scheme 1),[4] whereas other protocols[3,4] proceed with alkyl reagents with the exception of a few cases.[2i,5] Use of aryl reagents for substitution of primary allylic substrates is rare.[5] In order to expand the potential of the method using secondary allylic picolinates, we studied allylic substitution with aryllithium-based copper reagents. The results are presented herein.



Scheme 1 Construction of a quaternary carbon by allylic substitution

Phenylation of racemic picolinate **1** with phenyllithium-based copper reagents was examined under conditions delineated in Table 1, in which magnesium bromide (4 equiv) was added to activate the picolinoxy group in accord with our observation.[6] On the basis of the previous use of the copper reagents derived from arylmagnesium bromide and Cu(acac)$_2$,[4b,7] a phenyl copper reagent derived from commercial phenyllithium and Cu(acac)$_2$ (2:1) in the presence of excess magnesium bromide was investigated and was found to afford a mixture of unidentified products (Table 1, entry 1). On the other hand, a 3:1 reagent mixture produced a mixture of **2a**, regioisomer **3a**, alcohol **4**, diene **5**, and the unreacted picolinate **1** (Table 1, entry 2), which indicated a somewhat low regioselectivity (rs) of **2a**/**3a** (89:11 calculated from 45:4), low product selectivity, and low reactivity. The *trans* stereochemistry of **2a** was deter-

Table 1 Exploration of Reagents



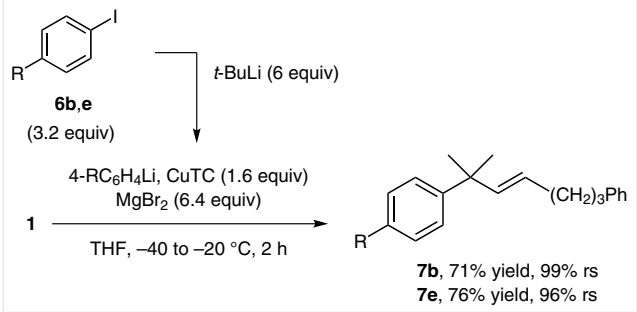
Entry	PhLi (equiv)	Cu salt (equiv)	Ph/Cu	$MgBr_2$ (equiv)	Temp (°C)	Time (h)	Ratio of **2a**/**3a**/**4**/**5**/**1**[a]	Yield (%)[b]
1	3	$Cu(acac)_2$ (1.5)	2:1	4	–40 to –10	3	mixture[c]	n.d.
2	3	$Cu(acac)_2$ (1.1)	3:1	4	–40 to –10	3	45:4:21:10:21	n.d.
3	3	$CuBr·SMe_2$ (3)	1:1	4	–40 to –10	3	82:18:0:0:0	n.d.
4	3	$CuBr·SMe_2$ (2)	1.5:1	4	–40 to 0	2	90:10:0:0:0	n.d.
5	3	$CuBr·SMe_2$ (1.5)	2:1	4	–40 to 0	2	81:18:0:1:0	n.d.
6	3	$Cu(OMe)_2$ (1.5)	2:1	4	–40 to –20	3	77:3:8:2:10	n.d.
7	3	$Cu(OMe)_2$ (1.1)	3:1	4	–40 to –20	3	0:0:12:4:84	n.d.
8	3	CuCN (2)	1.5:1	4	–40 to –20	3	83:16:1:0:0	n.d.
9	2	CuTC (2)	1:1	3	–40 to –20	2	mixture[c]	n.d.
10	3	CuTC (2)	1.5:1	4	–40 to –20	2	99:1:0:0:0	n.d.
11	3	CuTC (1.6)	2:1	4	–40 to –20	2	97:1:2:0:0	n.d.
12	3	CuTC (1.6)	2:1	3.2	–40 to –10	2	96:2:2:0:0	88[d]
13	3	CuTC (1.6)	2:1	2	–40 to –20	2	46:3:6:0:44	n.d.

[a] Determined by ^{1}H NMR integration ratios of the following protons: **2a**: δ = 5.44 (dt, 1 H), 5.64 (d, 1 H) ppm; **3a**: δ = 5.26 (d, 1 H) ppm; **4**: δ = 5.15 (dm, 1 H) ppm; **5**: δ = 4.87 (s, 2 H), 6.15 (d, 1 H) ppm; **1**: δ = 5.29 (d, 1 H), 5.80–5.89 (m, 1 H) ppm.
[b] n.d. = not determined.
[c] A mixture of unidentified products.
[d] Isolated yield.

mined using the coupling constant between the olefinic protons (J = 15.6 Hz). No *cis* isomer was formed as analyzed by ^{1}H NMR spectroscopy.

Next, we evaluated $CuBr·Me_2S$-based copper reagents comprised of phenyllithium and $CuBr·Me_2S$ in 1:1, 1.5:1, and 2:1 ratios. The reaction proceeded to completion and was irrespective of the phenyl/copper ratios. The regioselectivity, however, remained unimproved (Table 1, entries 3–5). After unsuccessful attempts using other copper sources (Table 1, entries 6–8), we were pleased to find that highly regioselective reagents could be derived from phenyllithium and CuTC (TC: thiophene-2-carboxylate)[8] in 1.5:1 and 2:1 ratios (Table 1, entries 10 and 11), whereas a 1:1 ratio gave a complex mixture of products (Table 1, entry 9). Finally, the quantity of magnesium bromide was examined as in entries 12 and 13 (Table 1) to find that 3.2 equivalents of magnesium bromide were as effective as 4 equivalents and afforded **2a** in 88% isolated yield, whereas 2 equivalents resulted in an incomplete reaction. These results suggested that a >1:1 ratio of Mg^{2+}/Li^+ was required for efficient reactivity.

The procedure used in entry 12 of Table 1 with the phenyl reagent, which was prepared by mixing phenyllithium and Cu(TC) (method A), was applied with 4-MeC_6H_4Li- and 4-$MeOC_6H_4Li$-based copper reagents, which were derived by the halogen–lithium exchange of the corresponding iodides **6b** and **6e** with *t*-BuLi[9] followed by reaction with CuTC (method B; suffixes **b** and **e** indicate the Me and MeO groups in Table 2). As delineated in Scheme 2, both copper reagents reacted with **1** in a highly regioselective fashion to produce *trans* olefins **7b** and **7e** in good yields.



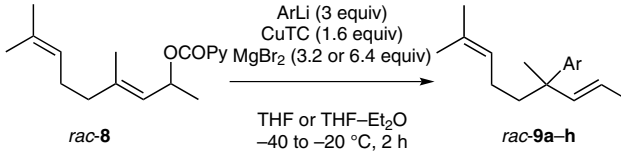
Scheme 2 Allylic substitution of **1** with 4-RC_6H_4Li-derived copper reagents; for **b**, R = Me; **e**, R = MeO

Next, the aforementioned protocol was applied with racemic picolinate *rac*-**8**. This substrate was synthesized by esterification of *rac*-**11**, which was prepared from geraniol (**10**) stereoselectively (see Scheme 3). Lithium reagents (ArLi) were obtained from a commercial source or were prepared by halogen–lithium exchange and direct lithiation,[10] and they were subsequently converted into copper reagents

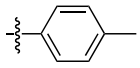
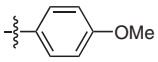
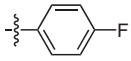
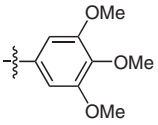
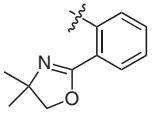
as indicated in the footnote of Table 2 (methods A–C). Substitution with the phenyl copper reagent prepared via method A took place smoothly to afford *rac*-**9a** with high regioselectivity and product selectivity in 92% yield (Table 2, entry 1). The phenylcopper reagent prepared via bromine–lithium exchange (method B) showed a similar efficiency to that produced in entry 1 (Table 2, entry 2). These results indicated that lithium bromide produced in situ by the exchange did not affect the efficiency of the reaction. Another successful example of a copper reagent prepared via method B is delineated in entry 3 (Table 2). A high efficiency was also observed with 3- and 2-MeC_6H_4 reagents, which gave *rac*-**9c** and *rac*-**9d**, respectively (Table 2, entries 4 and 5). Notably, the Me group in the *ortho* position of the phenyl ring did not affect the efficiency of the reaction. The 4-$MeOC_6H_4$ reagent afforded *rac*-**9e** as well (Table 2, entry 6). The effects of electron-withdrawing or electron-donating groups on the phenyl ring were examined using 4-FC_6H_4 and 3,4,5-$(MeO)_3C_6H_2$ reagents as shown in entries 7 and 8 (Table 2). Both reagents were highly reactive and efficiently delivered the Ar groups in the S_N2' fashion. An oxazoline-containing aryl copper reagent was prepared via *ortho* lithiation (method C) and was subsequently subjected to the substitution. Although we were concerned that the steric congestion of the oxazoline substituent at the *ortho* position would affect the reaction, the reaction proceeded completely and regioselectively to afford *rac*-**9h** in 71% yield. The oxazoline group is a synthetic equivalent to an ester.[11] An additional note is that no production of the *cis* olefin isomer was detected in all cases by ^1H NMR spectroscopy (see NMR spectra in the Supporting Information).

Next, stereochemistry of the substitution reaction was investigated using picolinate (*R*)-**8**, which was prepared by the method shown in Scheme 3. Since the previous synthesis of alcohol (*R*)-**11** via CBS reduction of the corresponding ketone suffered from somewhat low enantiomeric purity (82% ee),[4b] kinetic resolution of racemic alcohol *rac*-**11** was carried out according to the literature procedure[12] using the Sharpless asymmetric epoxidation[13] to afford 97% ee of (*R*)-**11**,[14] which produced picolinate (*R*)-**8** upon esterification with $PyCO_2H$. Substitution with the phenylcopper reagent, prepared again using the bromine–lithium exchange, afforded (*R*)-**9a** with 95% ee as determined by chiral HPLC analysis; therefore a high chirality transfer (97% CT[15]) was achieved (Table 3, entry 1). Furthermore, the retention time on chiral HPLC definitely indicated the same absolute configuration as that obtained by the allylic substitution of (*R*)-**8** with the phenylcopper reagent derived from phenylmagnesium bromide and $Cu(acac)_2$. Similarly, the 4-$MeOC_6H_4$ copper reagent derived from 4-$MeOC_6H_4Br$ via bromine–lithium exchange furnished (*R*)-**9e** with 98% CT (Table 3, entry 2). The absolute configuration of the product was determined by specific rotation analysis {$[\alpha]_D$} of the aldehyde

Table 2 Substitution of *rac*-**8** with Aryllithium/Magnesium Bromide

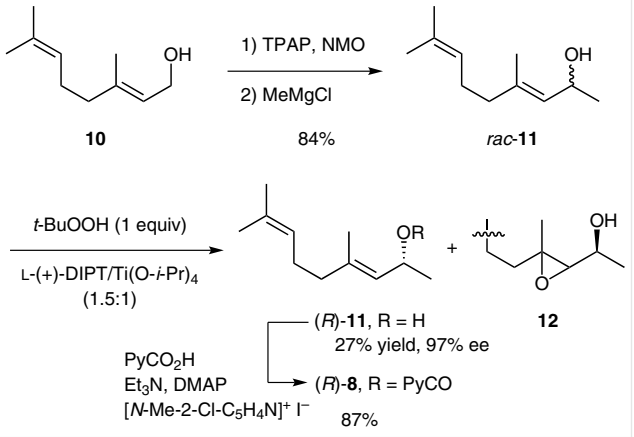


rac-**8** *rac*-**9a–h**

Entry	Ar	Method[a]	Product **9**[b]	Yield (%)	rs (%)
1	Ph	A	*rac*-**9a**	92	98
2	Ph	B	*rac*-**9a**	89	99
3		B	*rac*-**9b**	89	96
4		B	*rac*-**9c**	92	99
5		B	*rac*-**9d**	92	99
6		B[c]	*rac*-**9e**	93	99
7		B	*rac*-**9f**	84	99
8		B	*rac*-**9g**	94	99
9		C	*rac*-**9h**	71	99

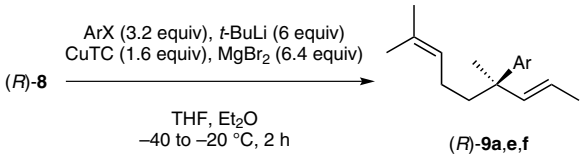
[a] Method A: PhLi (3 equiv), CuTC (1.6 equiv), $MgBr_2$ (3.2 equiv). Method B: ArX (X = Br, I: 3.2 equiv), *t*-BuLi (6 equiv), CuTC (1.6 equiv), $MgBr_2$ (6.4 equiv). Method C: ArH (3.2 equiv), *n*-BuLi (3 equiv), CuTC (1.6 equiv), $MgBr_2$ (3.2 equiv).
[b] The *trans* stereochemistry of *rac*-**9a**–**h** was determined using the coupling constant between the olefinic protons (*J* = 15.6–15.8 Hz).
[c] The use of 4-$MeOC_6H_4Li$ derived from 4-$MeOC_6H_4I$ and *t*-BuLi gave a similar result except for the chirality transfer (see Table 3).

[$OHC(CH_2)_2CMe(4\text{-}MeOC_6H_4)CHO$], which was derived from (*R*)-**9e** by ozonolysis.[16] Surprisingly, a somewhat lower CT was observed in the substitution with the 4-$MeOC_6H_4$ copper reagent, which was derived from 4-$MeOC_6H_4I$ via the iodine–lithium exchange (Table 3, entry 3 and footnote f). Lithium iodide, which is generated in situ, is likely to cause partial racemization by enhancing the leaving power of the $PyCO_2$–$MgBr_2$ complex. With these results in mind, the bromine–lithium exchange was applied to 4-FC_6H_4Br to prepare the 4-FC_6H_4 copper reagent, which produced (*R*)-**9f** with high enantiomeric purity upon allylic substitution (Table 3, entry 4).



Scheme 3 Synthesis of (*R*)-**8**

Table 3 Chirality Transfer of the Substitution Reaction Using (*R*)-**8**[a]



Entry	ArX	Product **9**[b]	Yield (%)	ee (%)[c]	CT (%)[d]
1	PhBr	(*R*)-**9a**	85	95	97
2	4-MeOC$_6$H$_4$Br	(*R*)-**9e**	87	96	98
3	4-MeOC$_6$H$_4$I	(*R*)-**9e**	91	87	89[e]
4	4-FC$_6$H$_4$Br	(*R*)-**9f**[f]	78	>95[g]	>95[g]

[a] Prepared from alcohol (*R*)-**11** of 98% ee; see ref 14.
[b] 97–99% regioselectivity.
[c] The ee was determined by chiral HPLC.
[d] CT: chirality transfer.
[e] A repeated reaction with a similar reaction scale [ca. 50 mg of (*R*)-**8**] afforded (*R*)-**9e** with 91% CT in 93% yield.
[f] Absolute configuration was determined by comparison with (*R*)-**9e**.
[g] Baseline separation was not attained on six chiral HPLC columns (see the Supporting Information).

In summary, aryl copper reagents derived from aryllithium and copper(I) thiophene-2-carboxylate were developed for the allylic substitution of γ,γ-disubstituted secondary allylic picolinates to afford quaternary stereogenic carbons. Aryllithium reagents prepared by bromine–lithium exchange and *ortho* lithiation were examined and were found to result in high efficiency in terms of reactivity and regio- and stereoselectivity. Fairly large substituents in the *ortho* position marginally affected the reioselectivity and reactivity of the reaction. Furthermore, the *anti*-S_N2' pathway of the reaction was established.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560907.

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(5) Substitution of secondary allylic 4-$Ph_2PC_6H_4$ esters with PhMgBr produces mixture of regioisomers (ref. 3b and 3d), whereas that of primary allylic phosphates with $ArAlEt_2$ proceeds with high regioselectivity and with somewhat low enantioselectivity (ref. 2j). Pd-catalyzed substitution of allylic acetates and $PhB(OH)_2$ gives S_N2' products. However, stereoselectivity was not studied: Ohmiya, H.; Makida, Y.; Li, D.; Tanabe, M.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 879.

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(14) The kinetic resolution was repeated several times and the alcohol with 98% ee was used for the next reaction.

(15) Defined as (% ee of product)·100/[% ee of (*R*)-**8**].

(16) (a) Ozonolysis of (*R*)-**9e** derived from (*R*)-**8** (87% ee) gave the aldehyde with $[\alpha]_D^{22}$ +23 (*c* 1.03, $CHCl_3$); *cf.* $[\alpha]_D^{20}$ –65.2 (*c* 1.45, $CHCl_3$).[16b] The lower value is attributed to contamination of unidentified compound (s) that was eluted with the aldehyde during chromatography. (b) Kita, Y.; Furukawa, A.; Futamura, J.; Ueda, K.; Sawama, Y.; Hamamoto, H.; Fujioka, H. *J. Org. Chem.* **2001**, *66*, 8779.