Communication

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Copper Catalyzed sp^3 C-H Etherification with Acyl Protected Phenols

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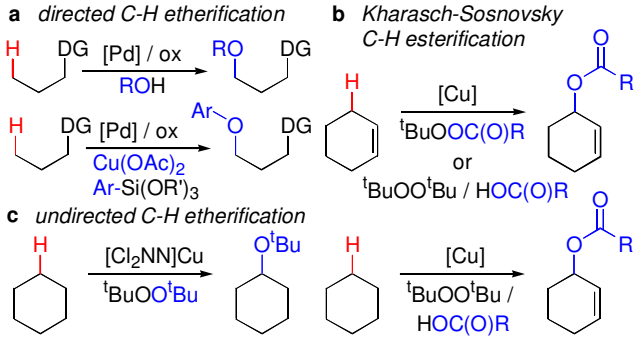
Supporting Information Placeholder

ABSTRACT: A variety of acyl-protected phenols AcOAr participate in sp^3 C-H etherification of substrates R-H to give alkyl aryl ethers R-OAr employing ^{t}BuOO^{t}Bu as oxidant with copper(I) β-diketiminato catalysts [Cu^I]. While 1°, 2°, and 3° C-H bonds may be functionalized, selectivity studies reveal a preference for the construction of hindered, 3° C-OAr bonds. Mechanistic studies indicate that β-diketiminato copper(II) phenolates [Cu^{II}]-OAr play a key role in this C-O bond forming reaction, formed via transesterification of AcOAr with [Cu^{II}]-O^{t}Bu intermediates generated upon reaction of [Cu^I] with ^{t}BuOO^{t}Bu.

Alkyl aryl ether linkages R-OAr are ubiquitous in natural and synthetic substances, particularly in bioactive molecules targeted as pharmaceuticals.[1] While the Williamson ether synthesis represents a classic approach involving phenols and alkyl halides, it often suffers from elimination, especially when targeting hindered carbon centers. The Mitsunobu reaction partially addresses this limitation through the coupling of alkyl and aryl alcohols, but generates significant waste with phosphine and diazocarboxylate co-reagents.[2] Metal catalyzed approaches employ alkyl alcohols in the Buchwald-Hartwig coupling with aryl halides[1,3] or the Chan-Lam coupling with aryl boronic acids[4] or aryltrifluoroborates.[5] In a metal-free protocol, hindered aryl alkyl ethers Ar-OR may be prepared from diaryliodonium salts [Ar$_2$I]X and alkyl alcohols HOR.[6]

While methods exist to directly oxidatively convert sp^2 C-H bonds to aryl ethers C-OR via alcohols and phenols HOR,[7] the corresponding etherification of sp^3 C-H bonds have progressed much more slowly.[7a] Directing groups, often based on pyridyl- or quinolinyl-substituted amides, allow for the installation of dialkyl ether linkages at sp^3 C-H sites with alkyl alcohols under Pd catalysis (Scheme 1a).[7e,8] The related formation of alkyl aryl ethers R-OAr requires the separate incorporation of the O and Ar groups through Cu(OAc)$_2$ and ArSi(OR)$_3$ reagents, respectively.[9] On the other hand, the copper catalyzed Kharasch-Sosnovsky reaction[10] has been long known to convert sp^3 C-H bonds (especially allylic) to esters via peroxyesters ^{t}BuOOC(O)R (Scheme 1b).[11] More recent variations allow the use of carboxylic acids HOC(O)R

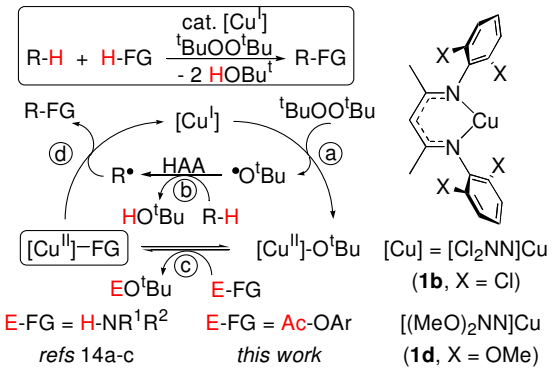
Scheme 1. Catalytic C-H Etherification and Esterification.



with the mild oxidant ^{t}BuOO^{t}Bu. Interestingly, many saturated C-H substrates such as cyclohexane undergo tandem dehydrogenation to give to allylic esters.[12] Demonstrating that related protocols could lead to undirected C-H etherification, we reported that the β-diketiminato catalyst [Cl$_2$NN]Cu (**1b**) provides the hindered dialkyl ether Cy-O^{t}Bu in good yield from cyclohexane and ^{t}BuOO^{t}Bu (Scheme 1c).[13]

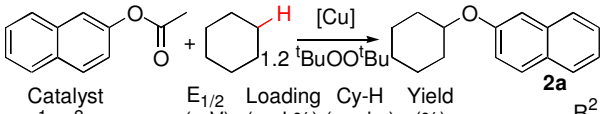
Mechanistic studies of related C-H amination protocols catalyzed by [Cl$_2$NN]Cu that employ alkyl and aryl amines along with ^{t}BuOO^{t}Bu as oxidant provide a conceptual platform to develop new classes of C-H functionalization reactions.[13-14] ^{t}BuOO^{t}Bu reacts swiftly with [Cl$_2$NN]Cu to give [Cu^{II}]-O^{t}Bu and the *t*-butoxy radical (Scheme 2a)[13] that readily reacts via H-atom abstraction with sp^3 C-H bonds in substrates R-H to generate the C-based radical R• (Scheme 2b).[15] Acid-base exchange

Scheme 2. Catalytic C-H Amination with H-NR^{1}R^2 and C-H Etherification with AcOAr.

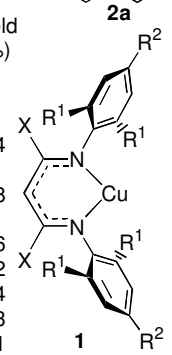


between [Cu^{II}]-O^{t}Bu and H-NR^{1}R^2 forms copper(II) amides [Cu^{II}]-NR^{1}R^2 (Scheme 2c) capable of efficient capture of organic radicals R• to form a new C-N bond in R-NR^{1}R^2 (Scheme 2d).[14c] Coupled with pioneering studies by Kochi who demonstrated that many copper(II) species containing anions X (X = O_2CR, Cl, Br, I, SCN, N_3, CN) are capable of capturing radicals R• to give new R-X species,[16] we anticipated that this mechanistic scheme could be applied to other functional groups in complexes [Cu^{II}]-FG.[14c] Unfortunately, this protocol did not deliver alkyl aryl ethers R-OAr upon substitution of HOAr for amines using cyclohexane as the C-H substrate.

Table 1. Copper catalyzed C-H etherification of cylclohexane with 2-napthyl acetate.



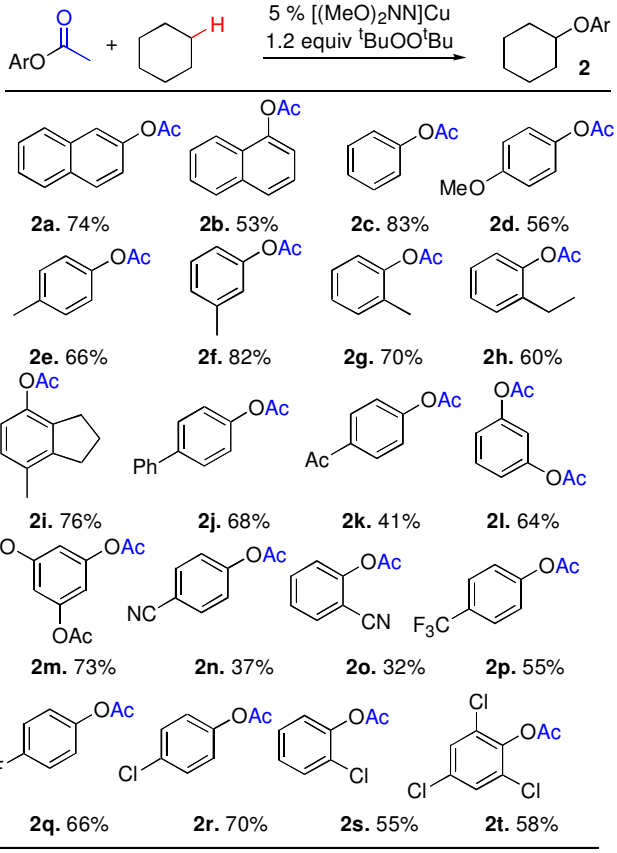
Catalyst (R^1, R^2, X)		$E_{1/2}$ (mV)	Loading (mol %)	Cy-H (equiv.)	Yield (%)
[Cl_2NN$_{F6}$]Cu (Cl, H, CF_3)	**1a**	+220	20	10	0
[Cl_2NN]Cu (Cl, H, CH_3)	**1b**	-140	20	10	44
[Me_3NN]Cu (Me, Me, CH_3)	**1c**	-390	20	10	68
[$(MeO)_2$NN]Cu (OMe, H, CH_3)	**1d**	-480	20	10	76
			10	10	72
general conditions:			5	10	74
90 °C, neat, 24 h			20	50	83
(oxidation potentials			20	20	81
vs. Fc^+/Fc in MeCN)			20	1	trace



We turned our attention to acyl protected phenols AcOAr that would not potentially suffer from the relatively acidic (pKa = 7 - 11)[17] and weak O-H bond (BDE ~ 85 - 93 kcal/mol)[18] present in phenols. Gratifyingly, [Cl_2NN]Cu catalyzes the C-H etherification of cyclohexane (10 equiv.) with 2-napthyl acetate in 44% yield employing ^{t}BuOO^{t}Bu (1.2 equiv.) as oxidant (Table 1). Screening a small set of copper(I) β-diketiminato complexes revealed that increasing the electron-richness of the β-diketiminate supporting ligand increases the C-H etherification yield (Table 1 and S1). Under the same conditions, the [Me_3NN]Cu (**1c**) and [$(MeO)_2$NN]Cu (**1d**) catalysts provided a 68% and 76% yield, respectively, while the electron-poor catalyst [Cl_2NN_{F6}]Cu gave no product. Since further attempts at optimization of this reaction with [$(MeO)_2$NN]Cu led only to marginal increases in yield (e.g. 83% with 50 equiv. cyclohexane), we opted to examine the phenol and C-H substrate scope of this new protocol employing 10 equiv. cyclohexane with 5 mol% [$(MeO)_2$NN]Cu.

A wide range of acyl protected phenols participate in the C-H etherification of cyclohexane (Table 2). Commercially available aryl acetates derived from both electron-neutral (**2a** - **2c**) as well as electron-rich (**2d** - **2i**) arenols afforded good to excellent yields (63 - 82%) while those containing electron-withdrawing groups (**2k** - **2t**) occassionally provided somewhat lower yields (32 - 73%). Noteworthy is the absence of any functionalization of benzylic C-H bonds present in aryl acetates (**2e** - **2i**).

Table 2. Copper catalyzed etherification of cyclohexane with acyl protected phenols ArOAc.

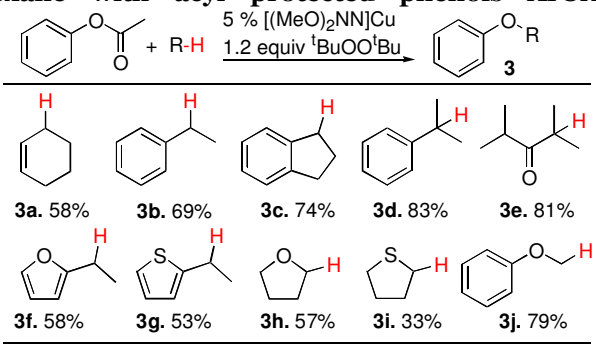


Conditions: 10 equiv. cyclohexane, neat, 90 °C, 24 h

Substrates containing multiple aryl acetate functionalities (**2l** and **2m**) undergo single C-H functionalization under these conditions.

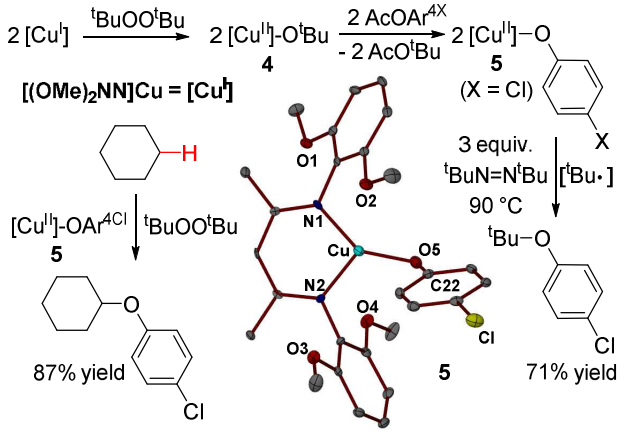
A range of 2° and 3° sp^3 C-H bonds undergo C-H etherification with AcOPh (Table 3). Cyclohexene, ethylbenzene, and indane (**3a** - **3c**) gave slightly lower yields (58% - 74%) than cyclohexane (**2c**: 83%). Cumene (**3d**) and diisopropyl ketone (**3e**) undergo efficient, selective C-H functionalization at their 3° C-H bonds (83 and 81% yield, respectively). The 2° benzylic C-H bonds in 2-ethylfuran (**3f**) and 2-ethylthiofuran also participate in C-H etherification. Saturated heterocycles (**3h** and **3i**) undergo functionalization at the heteroatom α-C-H bond similar to anisole (**3j**).

Table 3. Copper catalyzed etherification of cyclohexane with acyl protected phenols ArOAc.



Conditions: 20 equiv. R-H, neat, 90 °C, 24 h

Scheme 3. Transesterification at [Cu^{II}]-O^{t}Bu gives [Cu^{II}]-OAr active in C-H etherification via radical capture.

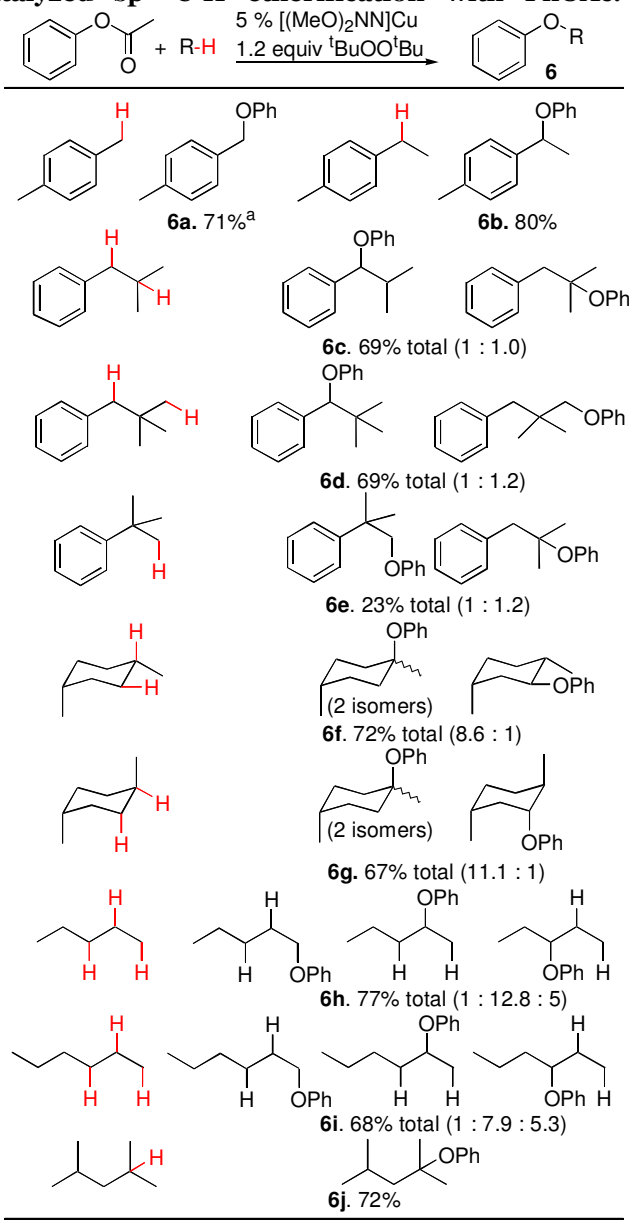


In analogy to copper(II) anilides [Cu^{II}]-NHAr that serve as intermediates that capture sp^3 C-based radicals R• in C-H amination (Scheme 2d),[14c] we anticipated the intermediacy of closely related β-diketiminato copper(II) phenolates [Cu^{II}]-OAr.[19] Reaction of [(MeO)$_2$NN]Cu(η^2-toluene) with ^{t}BuOO^{t}Bu quantitatively generates [(MeO)$_2$NN]Cu-O^{t}Bu (**4**) (Schemes 2a, 3) via UV-vis spectroscopy and may be isolated from pentane as purple crystals in 69% yield. Reaction of **4** with an excess of 4-chlorophenyl acetate provides the corresponding copper(II) phenolate [(MeO)$_2$NN]Cu-OAr^{4Cl} (**5**) in 54% isolated yield as dark brown crystals. X-ray analysis reveals the trigonal [(MeO)$_2$NN]Cu-OAr^{4Cl} (**5**) that features a short Cu-O bond (1.837(3) Å) with the OAr ring roughly perpendicular to the β-diketiminato backbone (Scheme 3). There is a slight distortion, however, to allow for gentle contact with one the β-diketiminato methoxy groups (Cu···O2 = 2.840 Å). To gain insight into the formation of [Cu^{II}]-OAr intermediates (Scheme 2c), we kinetically monitored the transesterification of AcOAr^{4Cl} with [Cu^{II}]-O^{t}Bu that proceeds cleanly with activation parameters $\Delta H^{\ddagger}$ = 9.7(8) kcal/mol and $\Delta S^{\ddagger}$ = -34(2) e.u ($k_{60°C}$ = 1.1 × 10^{-1} M^{-1}s^{-1}). Moreover, electron-rich phenolates react more swiftly with [Cu^{II}]-O^{t}Bu as revealed by a Hammett plot with a modest range of *p*-substituted acyl phenolates (X = Me, H, F, Ac) that gives ρ = -0.51(5) against σ$^+$ (Figure S18).

Importantly, these copper(II) phenolates [Cu^{II}]-OAr efficiently react with radicals R• generated by H-atom abstraction of C-H substrates R-H (Scheme 2d). Heating [(MeO)$_2$NN]Cu-OAr^{4Cl} (**5**) with ^{t}BuOO^{t}Bu and 20 equiv. cyclohexane generates the C-H functionalized product Cy-OAr^{4Cl} in 87% yield, presumably via the intermediacy of Cy• radicals.[13,14c] Using UV-vis spectroscopy to follow the C-H etherification of ethylbenzene with AcOAr^{4Cl} and ^{t}BuOO^{t}Bu catalyzed by **1d**, we observe initial formation of [Cu^{II}]-O^{t}Bu (**4**) followed by the persistent presence of [Cu^{II}]-OAr^{4Cl} (**5**) which gradually decays (Scheme S10; Figures S19-S20). Moreover, reaction of [Cu^{II}]-OAr^{4Cl} (**5**) with 3 equiv. ^{t}BuN=N^{t}Bu at 90 °C provides ^{t}BuOAr^{4Cl} in 71% yield through capture of ^{t}Bu• radicals generated by thermal decomposition of this azoalkane.[20]

A brief survey of regioselective preferences in sp^3 C-H etherification with PhOAc reveals that 2° and especially 3° C-H sites undergo functionalization in the presence of

Table 4. Exploration of regiochemistry in copper catalyzed sp^3 C-H etherification with PhOAc.



Conditions: 20 equiv. R-H, neat, 90 °C, 24 h.
[a]10 equiv. R-H, 1.4 equiv. ^{t}BuOO^{t}Bu

1° C-H bonds (Table 4). Nonetheless, the 1° benzylic substrate p-xylene undergoes etherification (entry **6a**) although toluene does not. Etherification of 4-ethyltoluene (entry **6b**) illustrates preferential functionalization at 2° over 1° benzylic positions. Isobutylbenzene (entry **6c**) gave a 1:1.0 mixture of 2° and 3° products while neopentylbenzene (entry **6d**) gave a nearly equimolar ratio of 2° and 1° products (1: 1.2).

Indeed, unactivated 1° C-H bonds undergo H-atom abstraction (HAA) as illustrated by the use of *t*-butylbenzene (entry **6e**). The mixture of 1° and 3° products obtained, however, suggests that the 1° radical intermediate PhC(CH$_3$)$_2$CH$_2$• derived from HAA of sp^3 C-H bond undergoes facile rearrangement to the 3° radical PhCCH$_2$CMe$_2$• as first reported by Kharasch.[21] In support of a common 3° radical intermediate, *cis*- and *trans*-1,4-dimethylcyclohexane give the same predominant 3° C-H

etherification product (entries **6f** and **6g**); competing 2° C-H functionalization that provides slightly different product mixtures in good combined yields (72 and 67%, respectively). The observation of three isomers each for C-H etherification of n-pentane and n-hexane indicates competitive H-atom abstraction at the C-1, C-2, and C-3 sites (entries **6h** and **6i**), with a mild preference the C-2 position. Nonetheless, 2,4-dimethylpentane exclusively gives the 3° alkyl aryl ether (entry **6j**). Curiously, the 1°, 2°, and 3° C-H bonds of this alkane undergo H-atom abstraction with ^{t}BuO• radical in a 24 : 9 : 67 ratio at 60 °C in neat substrate based on trapping studies with TEMPO•.[22] We do not observe 1° C-H functionalization adjacent to 3° sites as reported in C-H amidation with $PhC(O)NH_2$ by a $[(phen)Cu]^+$ / ^{t}BuOO^{t}Bu system.[23] Thus, our catalyst system may promote alkyl radical isomerization to deliver the most hindered 3° ether product derived from the most stable 3° alkyl radical.

This simple copper catalyzed protocol provides 1°, 2°, and 3° alkyl aryl ethers R-OAr from a wide range of commercially available, acyl protected phenols AcOAr and sp^3 C-H bonds in substrates R-H. In analogy to C-H amination with ^{t}BuOO^{t}Bu via [Cu^{II}]-NHR intermediates, simple mechanistic studies support H-atom abstraction of R-H by the ^{t}BuO• radical to give R• that is captured by copper(II) phenolates [Cu^{II}]-OAr generated by transesterification of [Cu^{II}]-O^{t}Bu intermediates with AcOAr. Besides directly converting C-H to C-OAr bonds, this radical based C-H functionalization protocol offers opportunities for the preparation of hindered 3° alkyl aryl ethers R-OAr.[6] Studies are underway to extend this methodology for undirected C-H etherification to unprotected alkyl alcohols HOR' to give dialkyl ethers R-OR'.[24]

ASSOCIATED CONTENT

Supporting Information. Experimental and characterization details (PDF) as well as X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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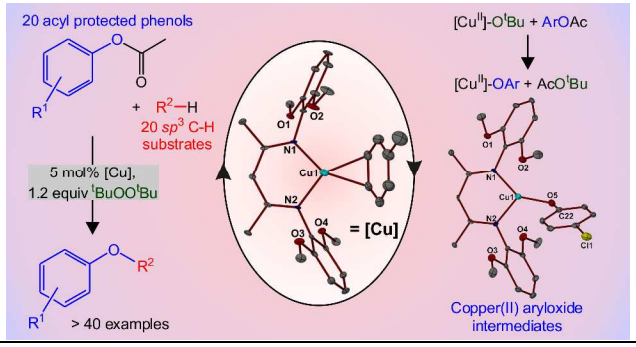
REFERENCES

(1) Maligres, P. E.; Li, J.; Krska, S. W.; Schreier, J. D.; Raheem, I. T. *Angew. Chem. Int. Ed.* **2012**, *51*, 9071-9074.
(2) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. P. *Chem. Rev.* **2009**, *109*, 2551-2651.
(3) (a) Enthaler, S.; Company, A. *Chem. Soc. Rev.* **2011**, *40*, 4912-4924. (b) Wu, X.; Fors, B. P.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 9943-9947. (c) Altman, R. A.; Shafir, A.; Choi, A.; Lichtor, P. A.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 284-286. (d) Wolter, M.; Nordmann, G.; Job, G. E.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 973-976. (e) Parrish, C. A.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 2498-2500. (f) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 10718-10719.
(4) (a) Qiao, J. X.; Lam, P. Y. S. In *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine, and Materials*; 2nd ed.; Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2011, p 315-361. (b) Ley, S. V.; Thomas, A. W. *Angew. Chem. Int. Ed.* **2003**, *42*, 5400-5449.
(5) (a) El Khatib, M.; Molander, G. A. *Org. Lett.* **2014**, *16*, 4944-4947. (b) Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, *5*, 1381-1384.
(6) Lindstedt, E.; Stridfeldt, E.; Olofsson, B. *Org. Lett.* **2016**, *18*, 4234-4237.
(7) (a) Liu, B.; Shi, B.-F. *Tett. Lett.* **2015**, *56*, 15-22. (b) Bhadra, S.; Matheis, C.; Katayev, D.; Gooßen, L. J. *Angew. Chem. Int. Ed.* **2013**, *52*, 9279-9283. (c) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem. Int. Ed.* **2011**, *50*, 11062-11087. (d) Roane, J.; Daugulis, O. *Org. Lett.* **2013**, *15*, 5842-5845. (e) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300-2301.
(8) (a) Zong, Y.; Rao, Y. *Org. Lett.* **2014**, *16*, 5278-5281. (b) Shan, G.; Yang, X.; Zong, Y.; Rao, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 13606-13610. (c) Chen, F.-J.; Zhao, S.; Hu, F.; Chen, K.; Zhang, Q.; Zhang, S.-Q.; Shi, B.-F. *Chem. Sci.* **2013**, *4*, 4187-4192. (d) Zhang, S.-Y.; He, G.; Zhao, Y.; Wright, K.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2012**, *134*, 7313-7316. (e) Frindy , S.; El Kadib, A.; Lahcini, M.; Primo, A.; García, H. *ChemistrySelect* **2016**, *1*, 157-162.
(9) Zhang, J.; Chen, H.; Wang, B.; Liu, Z.; Zhang, Y. *Org. Lett.* **2015**, *17*, 2768-2771.
(10) (a) Kharasch, M. S.; Sosnovsky, G. *J. Am. Chem. Soc.* **1958**, *80*, 756. (b) Kharasch, M. S.; Sosnovsky, G. *J. Am. Chem. Soc.* **1959**, *81*, 5819-5824.
(11) (a) Andrus, M. B.; Lashley, J. C. *Tetrahedron* **2002**, *58*, 845-866. (b) Rawlingson, D. J.; Sosnovsky, G. *Synthesis* **1972**, 1-28. (c) Beckwith, A. L. J.; Zavitsas, A. A. *J. Am. Chem. Soc.* **1986**, *108*, 8230-8234.
(12) (a) Tran, B. L.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 17292-17301. (b) Wang, C.-Y.; Song, R.-J.; Wei, W.-T.; Fan, J.-H.; Li, J.-H. *Chem. Commun.* **2015**, *51*, 2361-2363.
(13) Gephart, R. T.; McMullin, C. L.; Sapiezynski, N. G.; Jang, E. S.; Aguila, M. J. B.; Cundari, T. R.; Warren, T. H. *J. Am. Chem. Soc.* **2012**, *134*, 17350-17353.
(14) (a) Wiese, S.; Badiei, Y. M.; Gephart, R. T.; Mossin, S.; Varonka, M. S.; Melzer, M. M.; Meyer, K.; Cundari, T. R.; Warren, T. H. *Angew. Chem. Int. Ed.* **2010**, *49*, 8850-8855. (b) Gephart, R. T.; Huang, D. L.; Aguila, M. J. B.; Schmidt, G.; Shahu, A.; Warren, T. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 6488-6492. (c) Jang, E. S.; McMullin, C. L.; Käß, M.; Meyer, K.; Cundari, T. R.; Warren, T. H. *J. Am. Chem. Soc.* **2014**, *136*, 10930-10940.
(15) Finn, M.; Friedline, R.; Suleman, N. K.; Wohl, C. J.; Tanko, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 7578-7584.
(16) (a) Kochi, J. K.; Subramanian, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 1508-1514. (b) Kochi, J. K.; Jenkins, C. L. *J. Org. Chem.* **1971**, *36*, 3095-3102. (c) Kochi, K. K.; Jenkins, C. L. *J. Org. Chem.* **1971**, *36*, 3103-3111. (d) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 856-865.
(17) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421-6427.
(18) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press, Boca Raton, FL, 2002.
(19) Jazdzewski, B. A.; Holland, P. L.; Pink, M.; Victor G. Young, J.; Spencer, D. J. E.; Tolman, W. B. *Inorg. Chem.* **2001**, *40*, 6097-6107.
(20) Engle, P. S. *Chem. Rev.* **1980**, *80*, 99-150.
(21) (a) Urry, W. H.; Kharasch, M. S. *J. Am. Chem. Soc.* **1944**, *66*, 1438-1440. (b) Lindsay, D. A.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 7087-7093.
(22) Dokolas, P.; Loffler, S. M.; Solomon, D. H. *Aust. J. Chem.* **1998**, *51*, 1113-1120.
(23) Tran, B. L.; Li, B.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *134*, 2555-2563.
(24) Warren, T. H.; Sapiezynski, N. G. Catalytic C-H Bond Activation. US Patent 9,416,080, August 16, 2016.


20 acyl protected phenols
+ R2—H
20 sp3 C-H substrates
5 mol% [Cu],
1.2 equiv tBuOOtBu
> 40 examples
= [Cu]
[CuII]-OtBu + ArOAc
[CuII]-OAr + AcOtBu
Copper(II) aryloxide intermediates