Supporting Information for

Cu-Catalyzed Generation of Alkyl Radicals from Alkylsilyl Peroxides and Subsequent C(sp³)-C(sp²) Cross-Coupling with Arylboronic Acids

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2. Further Optimization of Reaction Conditions

Table S1.

Ph O-OSi 1a (1.5 equi	(HO) ₂ B + Me ₃ F iv) 2a (1.0 equiv)	Cul (5 mol%) L1 (5 mol%) K ₂ CO ₃ (1.0 equiv) THF (0.2 M) r.t., 6 h	Ph 3a
Entry	Deviation from above	NMR yield of 3a (%)	
1	 	96 (95 ^a)	
2	NiCl ₂	N.R.	
3	NiCl ₂ (PPh ₃) ₂ , w/o L1	N.R.	
4	Ni(OAc) ₂ •4H ₂ O	N.R.	
5	FeCl ₂	N.R.	
6	FeSO ₄ •7H ₂ O	N.R.	⊆N N L1 (bpy)
7	Fe(acac) ₃	N.R.	
8	NiCl ₂ , FeCl ₂ , L1 (10 mol%)	N.R.	
9	Entry 8, 60 °C	N.R.	
10	Na ₂ CO ₃	91	
11	Cs ₂ CO ₃	85	
12	K ₃ PO ₄	>99	

Internal Standard = 1,1,2,2-Tetrachloroethane.

^alsolated yield based on 2a.

2. ¹H NMR and ¹³C{¹H} NMR Spectra

¹H NMR spectrum of **1i** (500 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR spectrum of 1i (125 MHz, CDCl_3)



¹H NMR spectrum of **1k** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **1k** (125 MHz, CDCl₃)



¹H NMR spectrum of **3a** (500 MHz, CDCl₃)



 $^{13}C{^{1}H}$ NMR spectrum of **3a** (125 MHz, CDCl₃)



¹H NMR spectrum of **3b** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3b** (125 MHz, CDCl₃)



¹H NMR spectrum of **3c** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3c** (125 MHz, CDCl₃)



¹H NMR spectrum of **3d** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3d** (125 MHz, CDCl₃)



¹H NMR spectrum of **3e** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3e** (125 MHz, CDCl₃)



¹H NMR spectrum of **3f** (500 MHz, CDCl₃)



¹H NMR spectrum of **3g** (500 MHz, CDCl₃)



¹H NMR spectrum of **3h'** (500 MHz, CDCl₃)



¹H NMR spectrum of **3i** (500 MHz, CDCl₃)



¹H NMR spectrum of **3j** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3j** (125 MHz, CDCl₃)



¹H NMR spectrum of **3k** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3k** (125 MHz, CDCl₃)



¹H NMR spectrum of **3l** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3l** (125 MHz, CDCl₃)



¹H NMR spectrum of **3m** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3m** (125 MHz, CDCl₃)



¹H NMR spectrum of **3n** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3n** (125 MHz, CDCl₃)



¹H NMR spectrum of **30** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **30** (125 MHz, CDCl₃)



¹H NMR spectrum of **3p** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3p** (125 MHz, CDCl₃)



¹H NMR spectrum of **3q** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3q** (125 MHz, CDCl₃)



¹H NMR spectrum of **3r** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3r** (125 MHz, CDCl₃)



¹H NMR spectrum of **3s** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3s** (125 MHz, CDCl₃)



¹H NMR spectrum of **3t** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3t** (125 MHz, CDCl₃)



¹H NMR spectrum of **3u** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3u** (125 MHz, CDCl₃)



¹H NMR spectrum of **3v** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3v** (125 MHz, CDCl₃)



¹H NMR spectrum of **3w** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3w** (125 MHz, CDCl₃)



¹H NMR spectrum of **3x** (500 MHz, CDCl₃)



¹³C{¹H} NMR spectrum of **3x** (125 MHz, CDCl₃)



¹H NMR spectrum of **3y** (500 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR spectrum of 3y (125 MHz, CDCl₃)



¹H NMR spectrum of **3z** (500 MHz, CDCl₃)



 $^{13}C\{^1H\}$ NMR spectrum of 3z (125 MHz, CDCl₃)



¹H NMR spectrum of **4b** (500 MHz, CDCl₃)



¹H NMR spectrum of **4d** (500 MHz, CDCl₃)





 $^{13}C\{^{1}H\}$ NMR spectrum of 4d (125 MHz, CDCl₃)