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Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b03294 • Publication Date (Web): 15 Jan 2020

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Cu-Catalyzed Generation of Alkyl Radicals from Alkylsilyl Peroxides and Subsequent C(sp^3)–C(sp^2) Cross-Coupling with Arylboronic Acids

Shunya Sakurai,[†] Saori Tsuzuki,[†] Ryu Sakamoto,[†] and Keiji Maruoka*[†‡§]

[†] Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

[‡] Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo, Kyoto 606-8501, Japan

[§] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

ABSTRACT: This article describes a novel and practical method for the Cu-catalyzed C(sp^3)–C(sp^2) cross-coupling of alkylsilyl peroxides with arylboronic acids. The reductive cleavage of the O–O bond of alkylsilyl peroxides and the desired cross-coupling reactions to afford alkyl-substituted aromatic rings proceed smoothly at room temperature promoted by simple Cu-based catalysts and do not require activation by visible-light. The results of mechanistic investigations support a radical-mediated C(sp^3)–C(sp^2) bond formation via β-scission of the alkoxy radicals generated from the alkylsilyl peroxides.

The transition-metal-catalyzed formation of carbon-carbon bonds is one of the most important reactions in organic synthesis.[1] Among these, Suzuki-Miyaura cross-coupling (SMC) reactions represent some of the most powerful and reliable coupling reactions, especially in academic and industrial pharmaceutical research,[2] which generally provide C(sp^2)–C(sp^2)-coupled products. Although Pd-catalyzed SMC reactions have been extensively studied and are now well-established, further efforts have recently been dedicated to catalysts based on other metals such as Ni[3], Cu[4], Fe[5] as these are more cost-effective and abundant than Pd catalysts. When considering these factors, catalysts based on Cu seem to be the most suitable among this group for SMC reactions. However, the number of papers published on Cu-catalyzed SMC reactions,[4] especially C(sp^3)–C(sp^2)-coupling reactions, is low compared to those on Pd- or Ni-catalyzed SMC reactions. In this context, we considered that the development of reliable Cu-catalyzed C(sp^3)–C(sp^2) SMC reactions would be highly desirable.[6]

The reaction pattern of Cu-catalyzed cross-coupling reactions can be divided into two major categories according to the pathways they follow: (a) A non-radical catalysis, and (b) a radical catalysis[4j,7] (Figure 1). The non-radical catalysis, along which conventional Pd-catalyzed SMC reactions proceed, consists of the following steps: (i) Oxidative addition of the C–X bond to Cu^n to afford C–Cu^{n+2}–X, (ii) transmetalation between C–Cu^{n+2}–X and an organoboronic species to form a C–Cu^{n+2}–C intermediate, and (iii) reductive elimination from this intermediate to give the desired C–C-coupled product under concomitant regeneration of the Cu^n catalyst (Figure 1a). On the other hand, the radical catalysis includes the following steps: (iv) Single-electron-transfer (SET) from Cu^n to the C–X bond to generate a carbon radical and Cu^{n+1} species followed by (v) a metal-radical coupling (Figure 1b). So far, various examples of Cu-catalyzed cross-coupling reactions that proceed via the

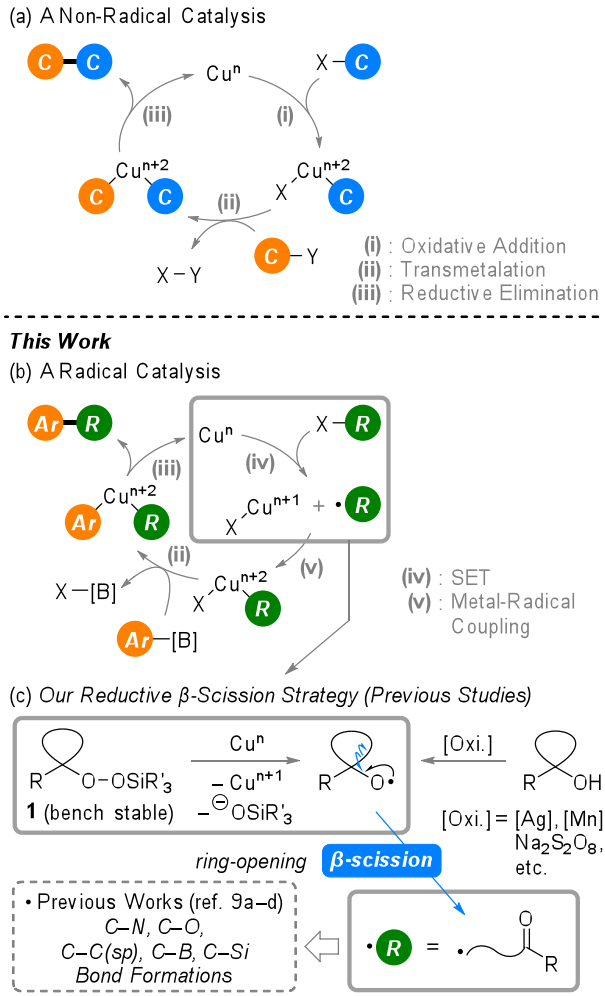
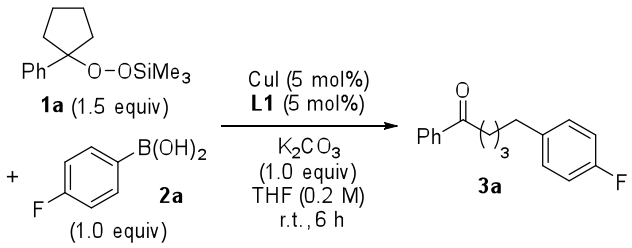


Figure 1. (a) A Non-Radical Catalysis. (b) A Radical Catalysis. (This Work) (c) Our Previous Studies.

non-radical catalysis have been reported,[4h] but radical-mediated coupling reactions in the absence of visible light[7] remain scarce, as the Cu catalyst can be expected to play two different roles:[4j] (i) Single-electron donor to generate radical species without activation by visible-light,[8] and (ii) mediator in the cross-coupling step to form a new C–C bond. Therefore, we sought to design novel highly practical Cu-catalyzed SMC reactions that proceed under mild conditions via a radical process.

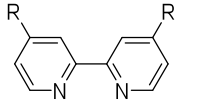
In order to generate C(sp^3)-radicals, β-scission of alkoxy radicals, which are usually generated from alkanols under strongly oxidative conditions, has emerged as one of the most reliable methods.[9] However, the strong oxidants employed may limit the choice of solvent and/or the functional-group tolerance. On the other hand, we have recently reported the successful generation of alkyl radicals from alkylsilyl peroxides **1** under mildly reductive conditions (reductive β-scission strategy) by using Cu catalysts, and its applications to C(sp^3)–N, C(sp^3)–O, C(sp^3)–C(sp), C(sp^3)–B and C(sp^3)–Si bond formations (Figure 1c).[10a–d] Alkylsilyl peroxides were synthesized from corresponding alcohols or olefins,[11] bench stable and easily handled. In the present study, we hypothesized that our reductive β-scission strategy could also be applicable to radical-mediated C(sp^3)–C(sp^2) cross-coupling reactions, i.e., novel Cu-catalyzed SMC reactions that employ arylboronic acids.

Table 1. Optimizing the Reaction Conditions for the Cu-Catalyzed Coupling of 1a and 2a.[a]

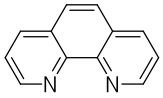


Entry	Reaction Conditions	Yield of **3a** (%)[b]
1	w/o CuI and **L**	0
2	w/o **L**	12
3	**L1**	96 (95)[c], [91][d]
4	**L2**	57
5	**L3**	61
6	**L4**	89
7	IMesCuCl	15
8	$Cu(acac)_2$	0
9	**1a** (1.0 eq.)	63
10	Ar-B(neop) (**2a'**)	48
11	w/o K_2CO_3	0
12	Toluene	0
13[e]	other metal catalysts	0

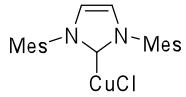
[a]Reactions were carried out in the presence of **1a** (0.3 mmol), **2a** (0.2 mmol), metal catalyst (5 mol%), **L** (5 mol%) and K_2CO_3 (0.2 mmol) in THF (1.0 mL) for 6 h under an atmosphere of argon. [b]The yield of **3a** was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c]Isolated yield is given in parentheses. [d]Isolated yield on the gram-scale reaction in the brackets. [e]See Supporting Information for details.



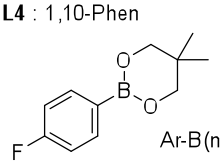
L1 : R = H (bpy)
L2 : R = *t*Bu (dtbbpy)
L3 : R = CF_3 (dCF_3bpy)



L4 : 1,10-Phen



IMesCuCl



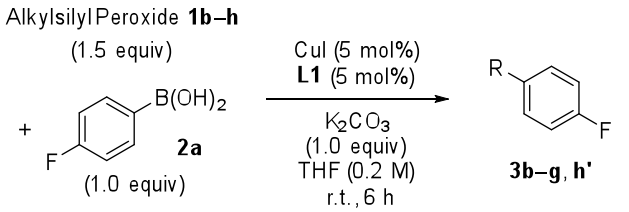
Ar-B(neop) (**2a'**)

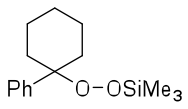
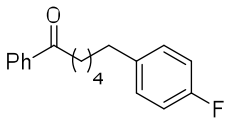
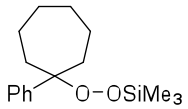
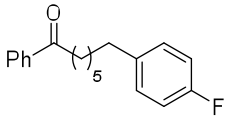
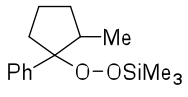
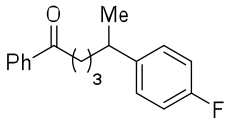
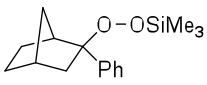
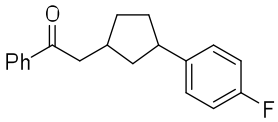
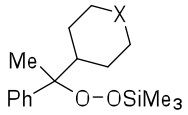
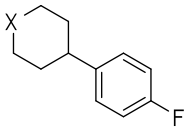
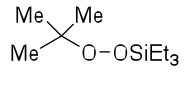
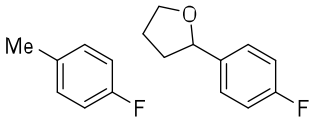
To test our hypothesis, we optimized the conditions of the Cu-catalyzed reaction between cyclic alkylsilyl peroxide **1a**, (4-fluorophenyl)boronic acid (**2a**) and K_2CO_3 (Table 1). Firstly, we confirmed the necessity of the presence of a Cu catalyst in this reaction, and found that CuI promoted the cleavage of the O–O bond of alkylsilyl peroxide **1a** to afford the desired product **3a** in 12% yield at room temperature (entries 1 and 2). Secondly, we investigated potentially effective ligands for this coupling reaction and discovered that bipyridine (**L1**) furnished **3a** in excellent yield (95%; entry 3). This method was applicable to the gram-scale reaction, and **3a** was obtained in 91% yield. Using electron-rich (**L2**; entry 4) or -poor bipyridine derivatives (**L3**; entry 5) afforded **3a** in 57% and 61% yield, respectively, while 1,10-phenanthroline (**L4**; entry 6) furnished **3a** in 89% yield. We also tested a *N*-heterocyclic carbene (NHC)-ligated Cu complex (IMesCuCl) as the catalyst, but the yield of **3a** decreased to 15% (entry 7). Additionally, the Cu^{II} salt $Cu(acac)_2$ was not suitable as a catalyst (entry 8). When reducing the amount of **1a** or using arylboronic ester **2a'** instead of **2a**, **3a** was obtained in moderate yield (entries 9 and 10). The reaction did not proceed without K_2CO_3 (entry 11), and toluene, which is generally considered a good solvent for SMC reactions,[2i,3e,4d] was not effective in this reaction (entry 12). Other metal catalysts such as Ni[3] or Fe[5] salts did not promote this reaction (entry 13, see the Supporting Information for details).

With the optimized reaction conditions in hand, we subsequently examined the scope of this reaction with respect to alkylsilyl peroxide substrates **1** (Table 2). The use of six- and seven-membered cycloalkylsilyl peroxides **1b–c** furnished the corresponding products **3b–c** in acceptable yields. Methyl-substituted five-membered cycloalkylsilyl peroxide **1d** and bicycloalkylsilyl peroxide **1e**, the latter of which is derived from the corresponding norbornene derivative, furnished the desired products **3d–e** in high yields with high regioselectivities. Additionally, the selective transfer of secondary alkyl groups such as the cyclohexyl or tetrahydropyranyl moiety from **1f** and **1g** were also possible, and **3f** and **3g** were obtained in excellent yields. When alkylsilyl peroxide **1h** was used as a methylating agent, the desired product **3h** was not detected, and only 2-(4-fluorophenyl)tetrahydrofuran **3h'** was obtained in moderate yield.[12] We considered this result would indicate that the phenyl-moiety on alkylsilyl peroxides effectively promoted β-scission step because thermodynamically more stable aromatic ketones were formed than aliphatic ketones, and tested its effect as shown in Scheme 1. As expected, a desired product **4a** was obtained in better yield when using **1i** than **1j** in the reaction with **2b**.

We then examined the scope with respect to arylboronic acids **2c–t** in the reactions with alkylsilyl peroxide **1a** (Table 3). The reactions using phenylboronic acid and 2-naphthylboronic acid afforded the corresponding products **3i–j** in 80% and 55% yield, respectively. Subsequently, we tested

Table 2. Scope with Respect to Alkylsilyl Peroxides 1.[a]



Alkylsilyl Peroxides **1**	Products **3**
 **1b**	 **3b**, 36%
 **1c**	 **3c**, 66%
 **1d**	 **3d**, 85%
 **1e** (single structure)	 **3e**, 91% (dr = 1:1)
 **1f** (X = CH_2) **1g** (X = O)	 **3f**, 93% **3g**, 96%
 **1h** (2.0 equiv)	 **3h**, 0% **3h'**, 35%

[a]Unless otherwise specified, reactions were carried out in the presence of **1** (0.3 mmol), **2a** (0.2 mmol), CuI (5 mol%), **L1** (5 mol%) and K_2CO_3 (0.2 mmol) in THF (1.0 mL) for 6 h under an atmosphere of argon.

Scheme 1. Effect on Ph-Group on Alkylsilyl Peroxide

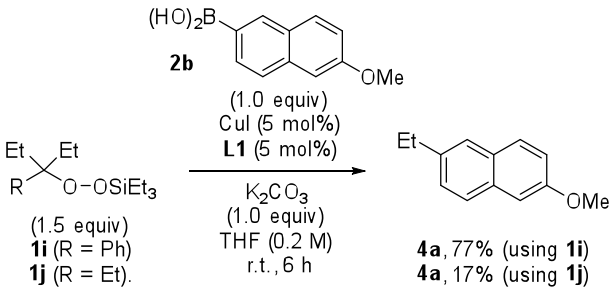
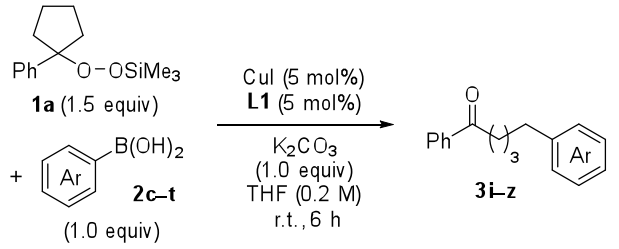
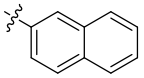
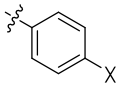


Table 3. Scope with Respect to Arylboronic Acids 2.[a]

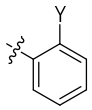


 **3i**, 80%

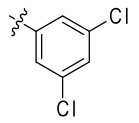
 **3j**, 55%

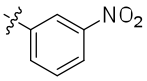


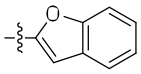
X = Me	**3k**, 76%
X = OMe	**3l**, 75%
X = OPh	**3m**, 50%
X = SMe	**3n**, 74%
X = Br	**3o**, 82%
X = CO_2Me	**3p**, 79%
X = CF_3	**3q**, 94%
X = OCF_3	**3r**, 78%

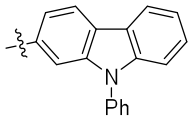


Y = Me	**3u**, 91%
X = OMe	**3v**, 41%
X = F	**3w**, 95%
X = CF_3	**3x**, 70%

 **3s**, 93%

 **3t**, 53%

 **3y**, 79%

 **3z**, 85%

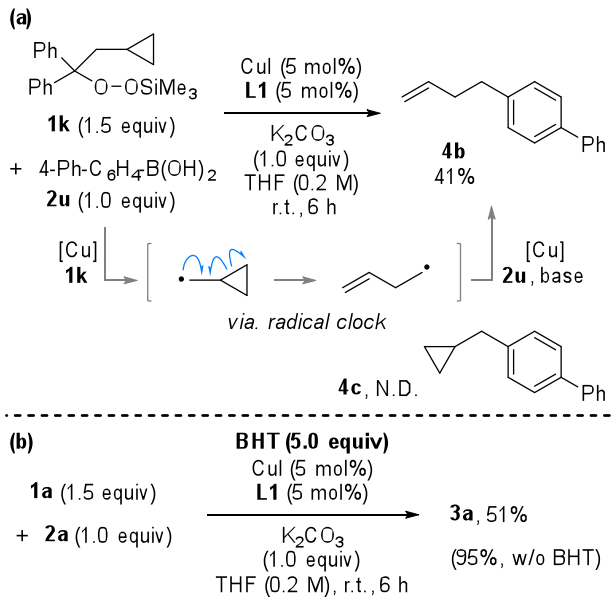
[a]The reactions were carried out in the presence of **1a** (0.3 mmol), **2** (0.2 mmol), CuI (5 mol%), **L1** (5 mol%) and K_2CO_3 (0.2 mmol) in THF (1.0 mL) for 6 h under an atmosphere of argon.

para-substituted arylboronic acid derivatives, and a variety of aryl groups that contain electron-donating or electron-withdrawing substituents successfully furnished the corresponding products **3k–r** in moderate to excellent yields (50–94%). *Meta*- and *ortho*-substituted arylboronic acids were also applicable to this reaction, which afforded **3s–x** in good to high yields (41–95%). Moreover, heteroaromatic boronic acids furnished **3y–z** in 79% and 85% yield, respectively.

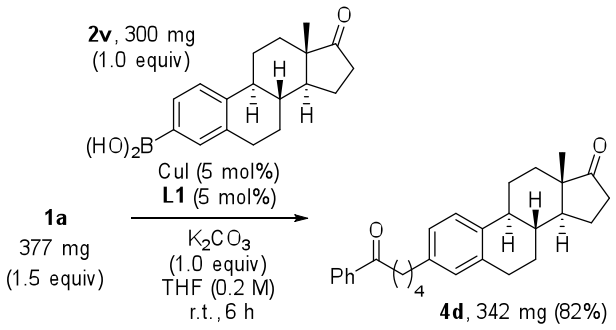
In order to better understand the underlying reaction mechanism and to confirm the radical process of this reaction, a control experiment was carried out (Scheme 2). For that purpose, we synthesized the new alkylsilyl peroxide **1k**, whichcontains a cyclopropylmethyl moiety, and used it for the reaction with **2u**. As expected, the radical clock reaction proceeded smoothly and the desired coupling product **4b** was obtained in 41% yield, while the formation of **4c** was not detected (Scheme 2a). And also, the addition of BHT (2,6-*tert*-butyl-*p*-cresol) as a radical-inhibitor under standard conditions inhibited the reaction between **1a** and **2a** (Scheme 2b).

Furthermore, the synthetic utility of this approach was demonstrated by the reaction of alkylsilyl peroxide **1a** with estrone-derived 3-deoxyestrone-3-boronic acid (**2v**) which afforded the desired $C(sp^2)$–$C(sp^3)$-coupling product **4d** in 82% yield (Scheme 3).

Scheme 2. Control Experiments



Scheme 3. Application using an Estrone Derivative



In conclusion, we have developed a Cu-catalyzed C(sp^3)–C(sp^2) cross-coupling reaction of alkylsilyl peroxides with arylboronic acids that proceeds via a radical process. At room temperature, the reaction smoothly affords alkyl-substituted aromatic rings. Further investigations into the applications of such a reductive β-scission strategy to alkylsilyl peroxides for the formation of carbon–carbon or carbon–heteroatom bonds, and applications to enantioselective reactions are currently progress in our laboratory.

EXPERIMENTAL SECTION

General Information. ^{1}H-NMR spectra were measured on JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, dt = doublet-triplet, dq = doublet-quartet, td = triplet-doublet, m = multiplet, app = apparent), coupling constants (Hz), and assignment. ^{13}C-NMR spectra were measured on JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling (^{13}C{^{1}H}). Chemical shifts were reported in ppm from the residual solvent as an internal standard (77.16 ppm). High-resolution mass spectra (HRMS) were performed on Thermo Exactive plus (ESI, quadrupole) spectrometer or Bruker micrOTOF II (APCI) spectrometer. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (Merck, TLC Silica-gel 60 F_{254}) were used. The products were purified by flash column chromatography (Kanto Chemical Co., Inc., Silica-gel 60 N, spherical, neutral, 40-50 μm) or preparative thin layer chromatography silica-gel (Merck, PLC Silica-gel 60 F_{254}. 0.5 mm). Commercially available reagents and solvents were purchased from FUJIFILM Wako, Sigma-Aldrich, TCI, and used as received. Alkylsilyl peroxides **1** were prepared according to the literate procedures.[10a–d]

Triethyl((3-phenylpentan-3-yl)peroxy)silane (1i). Synthesized from 3-phenylpentan-3-ol on 50 mmol scale. Colorless oil. 4.08 g, 28% over 2 steps. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32-7.28 (4H, m), 7.22-7.19 (1H, m), 2.02 (2H, td, J = 14.3, 7.1 Hz), 1.83 (2H, td, J = 14.3, 7.1 Hz), 1.01-0.98 (9H, m), 0.75-0.70 (12H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 143.2, 127.8, 126.4, 126.2, 88.5, 29.2, 8.00, 7.00, 4.00; **HRMS (ESI)** Calcd. for $C_{17}H_{30}O_2NaSi$: m/z 317.1907 ([M + Na]$^+$), Found: m/z 317.1906 ([M + Na]$^+$); **IR (neat)** 2956, 1458, 867, 728 cm^{-1}.

((2-Cyclopropyl-1,1-diphenylethyl)peroxy)trimethylsilane (1k). Synthesized from 2-cyclopropyl-1,1-diphenylethan-1-ol on 30 mmol scale. Colorless oil. 4.62 g, 47% over 2 steps. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33-7.31 (4H, m), 7.28-7.25 (4H, m), 7.24-7.20 (2H, m), 2.35 (2H, d, J = 6.5 Hz), 0.66-0.58 (1H, m), 0.26-0.22 (2H, m), 0.08 (9H, s), -0.12 (2H, td, J = 5.2, 4.3 Hz); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 144.4, 127.8, 127.5, 126.9, 89.3, 41.5, 6.2, 4.8, -1.1; **HRMS (ESI)** Calcd. for $C_{20}H_{26}O_2NaSi$: m/z 349.1594 ([M + Na]$^+$), Found: m/z 349.1593 ([M + Na]$^+$); **IR (neat)** 2959, 1249, 841, 695 cm^{-1}.

General Procedure for Cu-Catalyzed C(sp^3)–C(sp^2) Cross-Coupling of Alkylsilyl Peroxides 1 with Arylboronic Acids 2. To a solution of CuI (1.9 mg, 0.01 mmol, 5 mol%), 2,2'-bipyridine (**L1**, 1.6 mg, 0.01 mmol, 5 mol%), arylboronic acid **2** (0.2 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was added alkylsilyl peroxide **1** (0.3 mmol, 1.5 equiv). After being stirred at room temperature for 6 h under argon atmosphere, the reaction mixture was passed through a short silica-gel / Na_2SO_4 plug to remove inorganic salts, eluting with a solution of EtOAc / hexane (1 / 3). The obtained solution was concentrated and the residue was purified by flash column chromatography on silica-gel (EtOAc / hexane = 1 / 8) to afford following products. [Gram-scale reaction was carried out on 5.0 mmol scale, using **1a** (1.25 g, 7.5 mmol) and **2a** (0.7 g, 5.0 mmol). The product **3a** was obtained in 91% yield (1.17 g).]

5-(4-Fluorophenyl)-1-phenylpentan-1-one (3a). Colorless oil. 48.7 mg, 95%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95-7.93 (2H, m), 7.57-7.54 (1H, m), 7.47-7.44 (2H, m), 7.14-7.12 (2H, m), 6.98-6.94 (2H, m), 2.99 (2H, t, J = 7.2 Hz), 2.64 (2H, t, J = 7.5 Hz), 1.81-1.75 (2H, m), 1.72-1.66 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, C-F coupling)** δ 200.2, 161.3 (d, J_{C-F} = 243.2 Hz), 137.9 (d, J_{C-F} = 2.4 Hz), 137.1, 133.0, 129.8 (d, J_{C-F} = 7.2 Hz), 128.7, 128.1, 115.1 (d, J_{C-F} = 20.3 Hz), 38.4, 35.1, 31.3, 23.9; **HRMS (ESI)** Calcd. for $C_{17}H_{18}OF$: m/z 257.1336 ([M + H]$^+$), Found: m/z 257.1336 ([M + H]$^+$); **IR (neat)** 2934, 1683, 1508, 1219 cm^{-1}.

6-(4-Fluorophenyl)-1-phenylhexan-1-one (3b). White solid. 19.5 mg, 36%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96-7.94

(2H, m), 7.56 (1H, app t, J = 7.5 Hz), 7.47-7.44 (2H, m), 7.11 (2H, app dd, J = 8.6, 5.5 Hz), 6.95 (2H, app t, J = 8.8 Hz), 2.96 (2H, t, J = 7.4 Hz), 2.60 (2H, t, J = 7.8 Hz), 1.80-1.74 (2H, m), 1.68-1.62 (2H, m), 1.44-1.38 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, C-F coupling)** δ 200.5, 161.3 (d, $J_{C\text{-}F}$ = 242.0 Hz), 138.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 137.2, 133.1, 129.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.7, 128.2, 115.1 (d, $J_{C\text{-}F}$ = 20.3 Hz), 38.6, 35.1, 31.6, 29.0, 24.2; **HRMS (ESI)** Calcd. for $C_{18}H_{19}OFNa$: *m/z* 293.1312 ([M + Na]$^+$), Found: *m/z* 293.1313 ([M + Na]$^+$); **IR (neat)** 2931, 1684, 1508, 1219 cm^{-1}.

7-(4-Fluorophenyl)-1-phenylheptan-1-one (3c). Colorless oil. 37.5 mg, 66%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96-7.93 (2H, m), 7.57-7.54 (1H, m), 7.47-7.44 (2H, m), 7.11 (2H, app dq, J = 11.9, 2.8 Hz), 6.97-6.92 (2H, m), 2.96 (2H, t, J = 7.4 Hz), 2.57 (2H, t, J = 7.7 Hz), 1.77-1.71 (2H, m), 1.64-1.57 (2H, m), 1.44-1.33 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, C-F coupling)** δ 200.6, 161.3 (d, $J_{C\text{-}F}$ = 243.2 Hz), 138.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 137.2, 133.1, 129.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.7, 128.2, 115.1 (d, $J_{C\text{-}F}$ = 21.5 Hz), 38.7, 35.2, 31.6, 29.3, 29.1, 24.4; **HRMS (ESI)** Calcd. for $C_{19}H_{22}OF$: *m/z* 285.1649 ([M + H]$^+$), Found: *m/z* 285.1650 ([M + H]$^+$); **IR (neat)** 2930, 1684, 1508, 1219 cm^{-1}.

5-(4-Fluorophenyl)-1-phenylhexan-1-one (3d). White solid. 46.0 mg, 85%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91-7.90 (2H, m), 7.55 (1H, app t, J = 7.5 Hz), 7.47-7.43 (2H, m), 7.15-7.12 (2H, m), 6.97 (2H, app t, J = 8.6 Hz), 2.94-2.90 (2H, m), 2.73 (1H, m), 1.71-1.57 (4H, m), 1.24 (3H, d, J = 7.1 Hz); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, C-F coupling)** δ 200.3, 161.3 (d, $J_{C\text{-}F}$ = 243.2 Hz), 143.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 137.1, 133.1, 128.7, 128.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.1, 115.2 (d, $J_{C\text{-}F}$ = 20.3 Hz), 39.4, 38.6, 38.1, 22.6, 22.5; **HRMS (ESI)** Calcd. for $C_{18}H_{19}OFNa$: *m/z* 293.1312 ([M + Na]$^+$), Found: *m/z* 293.1313 ([M + Na]$^+$); **IR (neat)** 2958, 1683, 1508, 1221 cm^{-1}.

2-(3-(4-Fluorophenyl)cyclopentyl)-1-phenylethan-1-one (3e). Colorless oil. 51.4 mg, 91%. A 1:1 diastereomeric mixture. **^{1}H NMR (500 MHz, $CDCl_3$, 1:1 diastereomeric mixture)** δ 7.98-7.96 (4H, m), 7.58-7.55 (2H, m), 7.49-7.45 (4H, m), 7.19-7.16 (4H, m), 6.96 (4H, app t, J = 8.6 Hz), 3.19-3.03 (6H, m), 2.77-2.71 (1H, m), 2.62 (1H, dt, J = 17.5, 6.9 Hz), 2.35-2.30 (1H, m), 2.16-2.04 (4H, m), 1.99-1.93 (1H, m), 1.83-1.77 (1H, m), 1.72-1.59 (2H, m), 1.53-1.45 (1H, m), 1.41-1.26 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, C-F coupling, 1:1 diastereomeric mixture)** δ 200.1 (2C), 161.3 (d, $J_{C\text{-}F}$ = 243.2 Hz), 161.2 (d, $J_{C\text{-}F}$ = 243.2 Hz), 141.8 (d, $J_{C\text{-}F}$ = 68.0 Hz), 141.8 (d, $J_{C\text{-}F}$ = 68.0 Hz), 137.3 (2C), 137.2, 133.1 (2C), 128.7 (2C), 128.4 (d, $J_{C\text{-}F}$ = 7.2 Hz), 128.4 (d, $J_{C\text{-}F}$ = 7.2 Hz), 128.2 (2C), 115.0 (d, $J_{C\text{-}F}$ = 20.3 Hz), 45.5, 45.1, 45.0, 43.8, 42.3, 40.5, 35.9, 35.3, 35.1, 33.5, 33.4, 32.0; **HRMS (ESI)** Calcd. for $C_{19}H_{19}OFNa$: *m/z* 305.1312 ([M + Na]$^+$), Found: *m/z* 305.1311 ([M + Na]$^+$); **IR (neat)** 2945, 1683, 1509, 1219 cm^{-1}.

1-Cyclohexyl-4-fluorobenzene (3f). Purified by flash column chromatography on silica-gel (hexane). White solid. 33.2 mg, 93%. Spectral data matched those reported in the literature.[13]

4-(4-Fluorophenyl)tetrahydro-2*H*-pyran (3g). Colorless oil. 34.6 mg, 96%. Spectral data matched those reported in the literature.[14]

2-(4-Fluorophenyl)tetrahydrofuran (3h'). Colorless oil. 11.6 mg, 35%. Spectral data matched those reported in the literature.[15]

1,5-Diphenylpentan-1-one (3i). Colorless oil. 38.1 mg, 80%. Spectral data matched those reported in the literature.[16]

5-(Naphthalen-2-yl)-1-phenylpentan-1-one (3j). Colorless oil. 31.7 mg, 55%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95-7.93 (2H, m), 7.83-7.75 (3H, m), 7.62 (1H, app s), 7.56-7.55 (1H, m), 7.47-7.39 (4H, m), 7.34 (1H, app dd, J = 8.4, 1.8 Hz), 3.01 (2H, t, J = 6.8 Hz), 2.84 (2H, t, J = 6.9 Hz), 1.86-1.80 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.4, 139.9, 137.1, 133.7, 133.0, 132.1, 128.7, 128.1, 128.0, 127.7, 127.5, 127.4, 126.49, 126.0, 125.2, 38.5, 36.1, 31.1, 24.1; **HRMS (ESI)** Calcd. for $C_{21}H_{20}ONa$: *m/z* 311.1406 ([M + Na]$^+$), Found: *m/z* 311.1407 ([M + Na]$^+$); **IR (neat)** 2934, 1683, 1222, 748 cm^{-1}.

1-Phenyl-5-(*p*-tolyl)pentan-1-one (3k). White solid. 38.4 mg, 76%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (2H, app d, J = 7.1 Hz), 7.54 (1H, app d, J = 7.4 Hz), 7.45 (2H, app t, J = 7.7 Hz), 7.08 (4H, app s), 2.98 (2H, t, J = 7.2 Hz), 2.63 (2H, t, J = 7.7 Hz), 2.31 (3H, s), 1.78 (2H, m), 1.71-1.68 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.5, 139.3, 137.2, 135.3, 133.1, 129.1, 128.7, 128.4, 128.2, 38.6, 35.5, 31.4, 24.1, 21.1; **HRMS (ESI)** Calcd. for $C_{18}H_{20}ONa$: *m/z* 275.1406 ([M + Na]$^+$), Found: *m/z* 275.1407 ([M + Na]$^+$); **IR (neat)** 2945, 1683, 1509, 1219 cm^{-1}.

5-(4-Methoxyphenyl)-1-phenylpentan-1-one (3l). White solid. 40.3 mg, 75%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95-7.93 (2H, m), 7.57-7.53 (1H, m), 7.47-7.44 (2H, m), 7.10 (2H, app d, J = 8.8 Hz), 6.82 (2H, app dd, J = 6.7, 2.1 Hz), 3.78 (3H, s), 2.98 (2H, t, J = 7.4 Hz), 2.61 (2H, t, J = 7.5 Hz), 1.81-1.75 (2H, m), 1.71-1.65 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.5, 157.8, 137.2, 134.5, 133.0, 129.4, 128.7, 128.2, 113.9, 55.4, 38.5, 35.0, 31.5, 24.1; **HRMS (ESI)** Calcd. for $C_{18}H_{20}O_2Na$: *m/z* 291.1356 ([M + Na]$^+$), Found: *m/z* 291.1356 ([M + Na]$^+$); **IR (neat)** 2925, 1734, 1683, 732 cm^{-1}.

5-(4-Phenoxyphenyl)-1-phenylpentan-1-one (3m). Colorless oil. 33.0 mg, 50%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96-7.94 (2H, m), 7.57-7.54 (1H, m), 7.47-7.44 (2H, m), 7.33-7.29 (2H, m), 7.14 (2H, app dd, J = 8.9, 2.4 Hz), 7.09-7.05 (1H, m), 6.99-6.97 (2H, m), 6.93 (2H, app dt, J = 9.1, 2.4 Hz), 3.00 (2H, t, J = 7.2 Hz), 2.65 (2H, t, J = 7.5 Hz), 1.84-1.78 (2H, m), 1.74-1.69 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.4, 157.8, 155.2, 137.4, 137.2, 133.1, 129.8, 129.7, 128.7, 128.2, 123.0, 119.2, 118.6, 38.5, 35.2, 31.3, 24.1; **HRMS (ESI)** Calcd. for $C_{23}H_{22}O_2Na$: *m/z* 353.1512 ([M + Na]$^+$), Found: *m/z* 353.1515 ([M + Na]$^+$); **IR (neat)** 2933, 1685, 1488, 1233, cm^{-1}.

5-(4-(Methylthio)phenyl)-1-phenylpentan-1-one (3n). Colorless oil. 42.1 mg, 74%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95-7.93 (2H, m), 7.57-7.54 (1H, m), 7.47-7.44 (2H, m), 7.20-7.18 (2H, m), 7.11 (2H, app d, J = 8.5 Hz), 2.98 (2H, t, J = 7.1 Hz), 2.63 (2H, t, J = 7.5 Hz), 2.46 (3H, s), 1.82-1.76 (2H, m), 1.72-1.66 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.5, 139.6, 137.1, 135.3, 133.1, 129.1, 128.7, 128.2, 127.3, 38.5, 35.4, 31.2, 24.0, 16.5; **HRMS (ESI)** Calcd. for $C_{18}H_{20}ONaS$: *m/z* 307.1127 ([M + Na]$^+$), Found: *m/z* 307.1129 ([M + Na]$^+$); **IR (neat)** 2921, 1683, 1457, 690 cm^{-1}.

5-(4-Bromophenyl)-1-phenylpentan-1-one (3o). Colorless oil. 52.0 mg, 82%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (2H, app dd, J = 7.8, 0.7 Hz), 7.57-7.54 (1H, m), 7.46 (2H, app t, J = 7.7 Hz), 7.39 (2H, app d, J = 8.2 Hz), 7.06 (2H, app d, J = 8.5 Hz), 2.98 (2H, t, J = 7.2 Hz), 2.62 (2H, t, J = 7.5 Hz), 1.81-1.75 (2H, m), 1.72-1.66 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 200.2, 141.3, 137.1, 133.1, 131.5, 130.3, 128.7, 128.1, 119.6, 38.4, 35.3, 31.0, 23.9; **HRMS (ESI)**

Calcd. for $C_{17}H_{17}OBrNa$: *m/z* 339.0355 ([M + Na]$^+$), Found: *m/z* 339.0358 ([M + Na]$^+$); **IR (neat)** 2933, 1683, 1488, 690 cm^{-1}.

Methyl 4-(5-Oxo-5-phenylpentyl)benzoate (3p). White solid. 46.8 mg, 79%. Product **3o** was purified by flash column chromatography on silica-gel (EtOAc / hexane = 1 / 6). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95-7.93 (4H, m), 7.56 (1H, app t, J = 7.4 Hz), 7.47-7.44 (2H, m), 7.25-7.24 (2H, m), 3.90 (3H, s), 3.00 (2H, t, J = 7.1 Hz), 2.72 (2H, t, J = 7.5 Hz), 1.83-1.70 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.2, 167.2, 147.9, 137.1, 133.1, 129.8, 128.7, 128.6, 128.2, 127.9, 52.1, 38.4, 36.0, 30.9, 24.0; **HRMS (ESI)** Calcd. for $C_{19}H_{20}O_3Na$: *m/z* 319.1305 ([M + Na]$^+$), Found: *m/z* 319.1307 ([M + Na]$^+$); **IR (neat)** 1717, 1684, 1280, 730 cm^{-1}.

1-Phenyl-5-(4-(trifluoromethyl)phenyl)pentan-1-one (3q). Colorless oil. 57.6 mg, 94%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95-7.93 (2H, m), 7.57-7.52 (3H, m), 7.47-7.44 (2H, m), 7.29 (2H, app d, J = 7.9 Hz), 3.00 (2H, t, J = 6.9 Hz), 2.73 (2H, t, J = 7.4 Hz), 1.83-1.70 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, C-F coupling)** δ 200.2, 146.5, 137.1, 133.1, 128.8, 128.7, 128.4, 128.1, 125.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.5 (app d, $J_{C\text{-}F}$ = 270.6 Hz), 38.4, 35.8, 30.9, 23.9; **HRMS (ESI)** Calcd. for $C_{18}H_{17}OF_3Na$: *m/z* 329.1124 ([M + Na]$^+$), Found: *m/z* 329.1127 ([M + Na]$^+$); **IR (neat)** 1684, 1324, 1120, 1067 cm^{-1}.

1-Phenyl-5-(4-(trifluoromethoxy)phenyl)pentan-1-one (3r). Colorless oil. 50.3 mg, 78%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95-7.93 (2H, m), 7.57-7.54 (1H, m), 7.47-7.44 (2H, m), 7.20-7.18 (2H, m), 7.12 (2H, app d, J = 8.2 Hz), 2.99 (2H, t, J = 7.2 Hz), 2.67 (2H, t, J = 7.7 Hz), 1.83-1.77 (2H, m), 1.74-1.68 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.2, 147.5 (2C), 141.1, 137.1, 133.1, 129.7, 128.7, 128.2, 121.0, 38.4, 35.3, 31.1, 23.9; **HRMS (ESI)** Calcd. for $C_{18}H_{17}O_2F_3Na$: *m/z* 345.1073 ([M + Na]$^+$), Found: *m/z* 345.1075 ([M + Na]$^+$); **IR (neat)** 1684, 1255, 1218, 1156 cm^{-1}.

5-(3,5-Dichlorophenyl)-1-phenylpentan-1-one (3s). Colorless oil. 57.1 mg, 93%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.96-7.94 (2H, m), 7.58-7.55 (1H, m), 7.48-7.45 (2H, m), 7.18 (1H, app t, J = 2.0 Hz), 7.07 (2H, app d, J = 2.0 Hz), 3.00 (2H, t, J = 7.1 Hz), 2.63 (2H, t, J = 7.7 Hz), 1.79 (2H, m), 1.73-1.67 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.1, 145.7, 137.0, 134.8, 133.2, 128.7, 128.1, 127.1, 126.2, 38.3, 35.4, 30.7, 23.8; **HRMS (ESI)** Calcd. for $C_{17}H_{16}OCl_2Na$: *m/z* 329.0470 ([M + Na]$^+$), Found: *m/z* 329.0472 ([M + Na]$^+$); **IR (neat)** 1684, 1565, 1217, 796 cm^{-1}.

5-(3-Nitrophenyl)-1-phenylpentan-1-one (3t). Yellow oil. 30.0 mg, 53%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.06-8.04 (2H, m), 7.96-7.94 (2H, m), 7.58-7.55 (1H, m), 7.51 (1H, app t, J = 8.4 Hz), 7.48-7.42 (3H, m), 3.02 (2H, t, J = 6.8 Hz), 2.79 (2H, t, J = 7.4 Hz), 1.85-1.74 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.0, 148.5, 144.3, 137.0, 134.9, 133.2, 129.3, 128.8, 128.1, 123.3, 121.2, 38.3, 35.6, 30.8, 23.8; **HRMS (ESI)** Calcd. for $C_{17}H_{17}O_3NNa$: *m/z* 306.1101 ([M + Na]$^+$), Found: *m/z* 306.1103 ([M + Na]$^+$); **IR (neat)** 1734, 1521, 1350, 1217 cm^{-1}.

1-Phenyl-5-(*o*-tolyl)pentan-1-one (3u). Colorless oil. 45.9 mg, 91%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95 (2H, app dd, J = 8.4, 1.3 Hz), 7.57-7.54 (1H, m), 7.46 (2H, app t, J = 7.7 Hz), 7.15-7.08 (4H, m), 3.01 (2H, t, J = 7.2 Hz), 2.66 (2H, t, J = 7.9 Hz), 2.31 (3H, s), 1.87-1.81 (2H, m), 1.70-1.64 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.4, 140.5, 137.2, 135.9, 133.0, 130.2, 128.9, 128.7, 128.1, 126.0, 126.0, 38.5, 33.3, 30.0, 24.4, 19.4; **HRMS (ESI)** Calcd. for $C_{18}H_{20}ONa$: *m/z* 275.1406 ([M + Na]$^+$), Found: *m/z* 275.1405 ([M + Na]$^+$); **IR (neat)** 1734, 1684, 1217, 740 cm^{-1}.

5-(2-Methoxyphenyl)-1-phenylpentan-1-one (3v). White solid. 22.0 mg, 41%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.96-7.94 (2H, m), 7.55 (1H, app t, J = 7.4 Hz), 7.45 (2H, app t, J = 7.5 Hz), 7.17 (1H, app t, J = 7.8 Hz), 7.14 (1H, app d, J = 7.7 Hz), 6.87 (1H, app t, J = 7.4 Hz), 6.84 (1H, app d, J = 7.9 Hz), 3.81 (3H, s), 3.00 (2H, t, J = 7.4 Hz), 2.67 (2H, t, J = 7.7 Hz), 1.83-1.77 (2H, m), 1.71-1.65 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.8, 157.6, 137.3, 133.0, 130.8, 129.9, 128.7, 128.2, 127.1, 120.5, 110.4, 55.4, 38.6, 30.1, 29.7, 24.4; **HRMS (ESI)** Calcd. for $C_{18}H_{20}O_2Na$: *m/z* 291.1356 ([M + Na]$^+$), Found: *m/z* 291.1356 ([M + Na]$^+$); **IR (neat)** 1734, 1684, 1363, 1240 cm^{-1}.

5-(2-Fluorophenyl)-1-phenylpentan-1-one (3w). Colorless oil. 48.7 mg, 95%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.95 (2H, app d, J = 7.9 Hz), 7.55 (1H, app t, J = 7.4 Hz), 7.46 (2H, app t, J = 7.7 Hz), 7.20-7.14 (2H, m), 7.05 (1H, app t, J = 7.2 Hz), 7.01-6.98 (1H, m), 3.00 (2H, t, J = 7.2 Hz), 2.70 (2H, t, J = 7.4 Hz), 1.84-1.78 (2H, m), 1.75-1.69 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, C-F coupling)** δ 200.3, 161.2 (d, $J_{C\text{-}F}$ = 244.4 Hz), 137.1, 133.0, 130.7 (d, $J_{C\text{-}F}$ = 4.8 Hz), 129.1 (d, $J_{C\text{-}F}$ = 15.5 Hz), 128.7, 128.1, 127.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 22.7 Hz), 38.4, 29.9, 28.9, 24.0; **HRMS (ESI)** Calcd. for $C_{17}H_{17}OFNa$: *m/z* 279.1156 ([M + Na]$^+$), Found: *m/z* 279.1158 ([M + Na]$^+$); **IR (neat)** 1684, 1490, 1227, 754 cm^{-1}.

1-Phenyl-5-(2-(trifluoromethyl)phenyl)pentan-1-one (3x). Colorless oil. 42.9 mg, 70%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.96 (2H, app dd, J = 8.4, 1.3 Hz), 7.61 (1H, app d, J = 7.9 Hz), 7.57-7.54 (1H, m), 7.48-7.44 (3H, m), 7.34 (1H, app d, J = 7.7 Hz), 7.28 (1H, app t, J = 7.7 Hz), 3.02 (2H, t, J = 7.1 Hz), 2.84 (2H, t, J = 7.9 Hz), 1.89-1.83 (2H, m), 1.76-1.69 (2H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, C-F coupling)** δ 200.2, 141.2, 137.2, 133.1, 131.8, 131.1, 128.7, 128.5 (app d, $J_{C\text{-}F}$ = 29.8 Hz), 128.2, 126.0 (q, $J_{C\text{-}F}$ = 7.2 Hz), 126.0, 38.4, 32.6, 31.4, 24.3, one peak was not detected due to C-F coupling; **HRMS (ESI)** Calcd. for $C_{18}H_{17}OF_3Na$: *m/z* 329.1124 ([M + Na]$^+$), Found: *m/z* 329.1126 ([M + Na]$^+$); **IR (neat)** 1684, 1331, 1113, 768 cm^{-1}.

5-(Benzofuran-2-yl)-1-phenylpentan-1-one (3y). Colorless oil. 44.0 mg, 79%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.96-7.94 (2H, m), 7.55 (1H, app t, J = 7.5 Hz), 7.48-7.44 (3H, m), 7.40 (1H, app d, J = 7.7 Hz), 7.21-7.15 (2H, m), 6.41 (1H, s), 3.03 (2H, t, J = 6.8 Hz), 2.84 (2H, t, J = 6.5 Hz), 1.88-1.85 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.1, 159.1, 154.8, 137.1, 133.1, 129.1, 128.7, 128.2, 123.3, 122.5, 120.4, 110.8, 102.2, 38.3, 28.5, 27.5, 23.9; **HRMS (ESI)** Calcd. for $C_{19}H_{18}O_2Na$: *m/z* 301.1199 ([M + Na]$^+$), Found: *m/z* 301.1200 ([M + Na]$^+$); **IR (neat)** 1734, 1684, 1455, 730 cm^{-1}.

1-Phenyl-5-(9-phenyl-9*H*-carbazol-2-yl)butan-1-one (3z). Colorless oil. 66.2 mg, 85%. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.09 (1H, app d, J = 7.7 Hz), 8.03 (1H, app d, J = 7.9 Hz), 7.93-7.91 (2H, m), 7.61 (2H, app t, J = 7.9 Hz), 7.57-7.52 (3H, m), 7.45 (3H, app dt, J = 20.9, 7.7 Hz), 7.37-7.36 (2H, m), 7.26-7.24 (1H, m), 7.20 (1H, app s), 7.13 (1H, app d, J = 7.9 Hz), 2.98 (2H, t, J = 7.1 Hz), 2.80 (2H, t, J = 7.4 Hz), 1.84-1.73 (4H, m); **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 200.4, 141.4, 141.1, 140.9, 137.9, 137.2, 133.0, 130.0, 128.7, 128.2, 127.5, 127.3, 125.5, 123.5, 121.5, 120.9, 120.2, 120.1, 119.9, 109.8, 109.4, 38.5, 36.7, 31.8, 24.2; **HRMS (APCI)** Calcd. for

$C_{29}H_{25}ON$: *m/z* 404.2009 ([M + H]$^+$), Found: *m/z* 404.1999 ([M + H]$^+$); **IR (neat)** 1734, 1684, 1458, 1232 cm^{-1}.

Control Experiments. Radical Clock Experiment: To a solution of CuI (1.9 mg, 0.01 mmol, 5 mol%), 2,2'-bipyridine (**L1**, 1.6 mg, 0.01 mmol, 5 mol%), [1,1'-biphenyl]-4-ylboronic acid (**2u**) (39.6 mg, 0.2 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was added alkylsilyl peroxide **1k** (98.0 mg, 0.3 mmol, 1.5 equiv). After being stirred at room temperature for 6 h under argon atmosphere, the reaction mixture was passed through a short silica-gel / Na_2SO_4 plug to remove inorganic salts, eluting with hexane. The obtained solution was concentrated and the residue was purified by flash column chromatography on silica-gel (hexane) to afford 4-(but-3-en-1-yl)-1,1'-biphenyl (**4b**) as a colorless oil (17.0 mg, 41%. Spectral data macthed those reported in the literature.[17]) without any detection of 4-(cyclopropylmethyl)-1,1'-biphenyl (**4c**). **Reaction with BHT:** To a solution of CuI (1.9 mg, 0.01 mmol, 5 mol%), 2,2'-bipyridine (**L1**, 1.6 mg, 0.01 mmol, 5 mol%), arylboronic acid **2a** (0.2 mmol, 1.0 equiv), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 equiv) and BHT (2,6-*tert*-butyl-*p*-cresol, 220 mg, 1.0 mmol, 5.0 equiv) in anhydrous THF (1.0 mL) was added alkylsilyl peroxide **1a** (0.3 mmol, 1.5 equiv). After being stirred at room temperature for 6 h under argon atmosphere, the reaction mixture was passed through a short silica-gel / Na_2SO_4 plug to remove inorganic salts, eluting with a solution of EtOAc / hexane (1 / 3). The obtained solution was concentrated and the yield of **3a** was determined by ^{1}H-NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

Application using Estrone Derivative. 3-Deoxyestrne-3-boronic acid (**2v**) was prepared from estrone, followed by reported literatures.[18] To a solution of CuI (9.5 mg, 0.05 mmol, 5 mol%), 2,2'-bipyridine (**L1**, 8.0 mg, 0.05 mmol, 5 mol%), **2t** (300 mg, 1.0 mmol, 1.0 equiv) and K_2CO_3 (138 mg, 1.0 mmol, 1.0 equiv) in anhydrous THF (5.0 mL) was added alkylsilyl peroxide **1a** (376 mg, 1.5 mmol, 1.5 equiv). After being stirred at room temperature for 6 h under argon atmosphere, the reaction mixture was passed through a short silica-gel / Na_2SO_4 plug to remove inorganic salts, eluting with a solution of EtOAc / hexane (1 / 3). The obtained solution was concentrated and the residue was purified by flash column chromatography on silica-gel (EtOAc / hexane = 1 / 5) to afford a desired product **4d** as a white solid (342 mg, 82%).

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(5-oxo-5-phenylpentyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4d). White solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95-7.94 (2H, m), 7.57-7.54 (1H, m), 7.46 (2H, app t, J = 7.7 Hz), 7.20 (1H, d, J = 7.9 Hz), 6.98 (1H, d, J = 7.9 Hz), 6.93 (1H, app s), 2.99 (2H, t, J = 7.4 Hz), 2.88 (2H, m), 2.61 (2H, t, J = 7.7 Hz), 2.50 (1H, m), 2.44-2.40 (1H, m), 2.28 (1H, m), 2.18-2.10 (1H, m), 2.08-1.99 (2H, m), 1.97-1.93 (1H, m), 1.83-1.77 (2H, m), 1.73-1.67 (2H, m), 1.65-1.59 (2H, m), 1.55-1.41 (4H, m), 0.90 (3H, s); **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 221.1, 200.4, 139.8, 137.2, 137.1, 136.4, 133.0, 129.1, 128.6, 128.1, 125.9, 125.4, 50.6, 48.1, 44.4, 38.5, 38.3, 36.0, 35.3, 31.7, 31.2, 29.5, 26.7, 25.8, 24.1, 21.7, 13.9; **HRMS (ESI)** Calcd. for $C_{29}H_{34}O_2Na$: *m/z* 437.2451 ([M + Na]$^+$), Found: *m/z* 437.2452 ([M + Na]$^+$); **IR (neat)** 2929, 1735, 1684, 1217 cm^{-1}.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Further reaction optimizations and ^{1}H and ^{13}C{^{1}H} NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: maruoka.keiji.4w@kyoto-u.ac.jp (K. Maruoka).

ORCID

Syunya Sakurai: 0000-0003-1331-2794
Keiji Maruoka: 0000-0002-0044-6411

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support via JSPS KAKENHI Grant Number JP26220803 and JP17H06450 (Hybrid Catalysis). S.S. thanks for a Grant-in-Aid for JSPS Fellowship for Young Scientists.

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