Nickel catalyzed Synthesis of Silanes from Silyl Ketones

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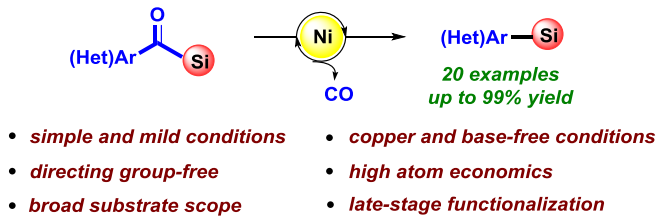
Supporting Information Placeholder

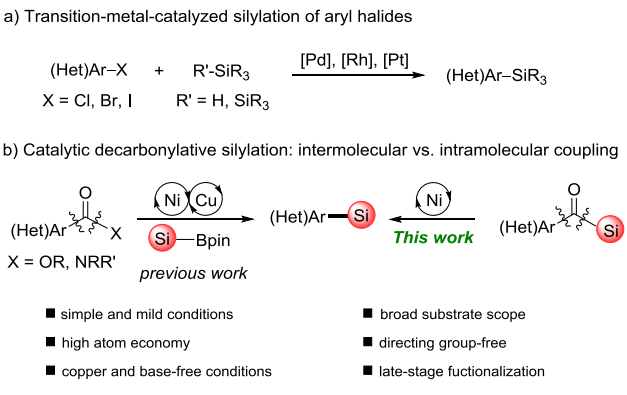


ABSTRACT: An unprecedented nickel-catalyzed decarbonylative silylation via CO extrusion intramolecular recombination fragment coupling of unstrained and non-directing group-assisted silyl ketones is described. The inexpensive and readily available catalyst performs under mild reaction conditions and enables the synthesis of structurally diverse arylsilanes, including heterocyclic and natural product derivatives.

Transition-metal-catalyzed cross-coupling reactions have been established as a powerful and straightforward approach for creating C–C or C–heteroatom bonds which are common in modern organic synthesis.[1] In this context, over the past few years, the transition-metal-catalyzed decarbonylative cross-coupling of naturally abundant carboxylic acid derivatives with numerous nucleophiles has attracted increasing attention, as it avoids classical electrophilic coupling partners such as organohalides.[2] Moreover, intramolecular decarbonylative coupling reactions emerged as a more efficient and higher atom-economic strategy due to the absence of nucleophiles and bases.[3] In this case, the general mechanism consists of oxidative addition by the transition-metal complex to the C(acyl)–C(alpha) or C(acyl)–heteroatom bond, subsequent decarbonylation and reductive elimination. Regarding this approach, transition-metal-mediated decarbonylative intramolecular couplings of aldehydes, ketones and other carboxylic acid derivatives have been extensively studied under various conditions, leading to C-C[3,4] and C-heteroatom[5-11] bond constructions. However, to the best of our knowledge, C–Si bond formation derived from acylsilanes has not been explored previously.

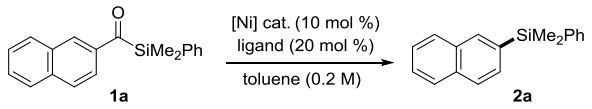
Organosilicons have been used as key building blocks for natural product synthesis, drug development and material sciences.[12] Arylsilanes are traditionally synthesized by the addition of Grignard or organolithium reagents to chlorosilanes or cyclosiloxanes.[13] Subsequently, reactions of aryl halides with disilanes or hydrosilanes as coupling reagents have evolved based on transition-metal catalysis (Scheme 1a).[14] Furthermore, recently, our group successfully developed the nickel/copper-catalyzed decarbonylative silylation of esters and amides in the presence of silylboranes (Scheme 1b, left).[15] However, this process requires the preformation of the phenol ester or amide and provides as a stoichiometric byproduct the phenol or imide respectively. Hence, a procedure which would start from the acylsilane instead of the activated ester or amide would only provide CO as a traceless byproduct. We herein report the first nickel-catalyzed intramolecular decarbonylation for the transformation of silyl ketones into arylsilanes (Scheme 1b, right).

Scheme 1. Transition-metal-catalyzed silylation reactions.



Our primary investigation in this study focused on the reaction of (dimethyl(phenyl)silyl)(naphthalen-2-yl)methanone (**1a**) with $Ni(cod)_2$, in the presence of different phosphine ligands (Table 1, entries 1–5). P^nBu_3 was found as the most effective ligand which provided the decarbonylative product **2a** in 60% NMR yield. The yield increased to 72% when the reaction was conducted for 36 h (entry 6). Additives such as Mn, and Zn were able to slightly improve the yield to 64% and 71%, respectively (entries 8 and 9, see also the Supporting Information). Subsequently, we evaluated the *in situ* generation of nickel(0) species from nickel(II) complexes in the presence of a strong reductant, however, unsatisfactory results were obtained (entries 11–12). In 1,4-dioxane as solvent the yield dropped to 24% (entry 14). The effect of temperature was investigated and 150 °C was found to be optimal, the desired product **2a** being obtained in high yield after isolation (83%, entry 15). Furthermore, control experiments indicated that $Ni(cod)_2$ and P^nBu_3 are required for this process (entries 7 and 13).

Table 1. Optimization of the reaction conditions.[a]

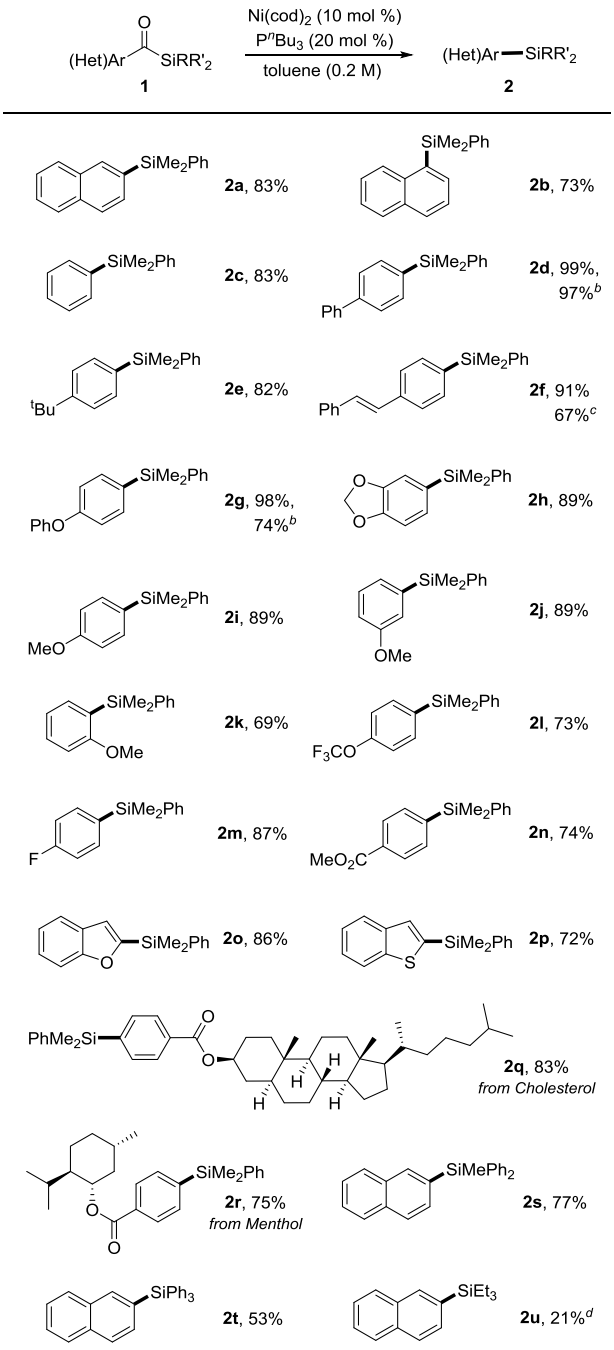


entry	[Ni] Cat.	ligand	additive	yield (%)
1[b]	$Ni(cod)_2$	dcype	–	21
2[b]	$Ni(cod)_2$	dppe	–	26
3	$Ni(cod)_2$	PCy_3	–	trace
4	$Ni(cod)_2$	PPh_3	–	41
5	$Ni(cod)_2$	P^nBu_3	–	60
6[c]	$Ni(cod)_2$	P^nBu_3	–	72
7	$Ni(cod)_2$	-	–	0
8	$Ni(cod)_2$	P^nBu_3	Mn	64
9	$Ni(cod)_2$	P^nBu_3	Zn	71
10[c]	$Ni(cod)_2$	P^nBu_3	Zn	80
11[c]	$Ni(acac)_2$	P^nBu_3	Zn	0
12[c]	$Ni(OAc)_2{\cdot}4H_2O$	P^nBu_3	Zn	21
13[c]	–	P^nBu_3	Zn	0
14[c,d]	$Ni(cod)_2$	P^nBu_3	Zn	24
15[c,e]	**$Ni(cod)_2$**	**P^nBu_3**	**Zn**	**86(83)[f]**
16[c,g]	$Ni(cod)_2$	P^nBu_3	Zn	70

[a]Reaction conditions: **1a** (0.20 mmol), $Ni(cod)_2$ (10 mol %, 0.02 mmol), ligand (20 mol %, 0.04 mmol), toluene (1 mL), 160 °C, 16 h, yield determined by ^1H NMR spectroscopy using $1,3,5\text{-}(OMe)_3C_6H_3$ as an internal standard. [b]Ligand (10 mol %, 0.02 mmol). [c]Running for 36 h. [d]Using 1,4-dioxane. [e]At 150 °C. [f]Yield after column chromatography. [g]At 140 °C.

With the optimized reaction conditions in hand, the substrate scope of the nickel-catalyzed intramolecular decarbonylative silylation of acylsilanes was investigated. Silyl ketones **1a-c** lacking substituents on the aromatic ring, were smoothly converted into the corresponding products **2a-c** in good to high yields. Next, the effect of different electron-donating and electron-withdrawing substituents in the *para*-position of the phenyl ring was investigated. Various functional groups were tolerated under the optimal conditions affording the corresponding products **2d**–**2i** and **2l**–**2n** in good to high yields.

Scheme 2. Substrate scope with respect to aryl and silyl substitution.[a]



[a]Reaction conditions: **1** (0.20 mmol), $Ni(cod)_2$ (10 mol %, 0.02 mmol), P^nBu_3 (20 mol %, 0.04 mmol), Zn (2.0 equiv), toluene (1 mL), 150 °C, 36 h, yield after isolation. [b]Without Zn. [c]reaction on 1 mmol scale, 48 h. [d]NMR yield.

Substituents in the *meta* and *ortho* position were also tolerated, and the products **2j** and **2k** were obtained in satisfactory yields. Furthermore, heterocyclic silyl ketones **1o** and **1p** were con-

verted into the decarbonylated products **2o** and **2p** in gratifying yields. Due to the chemoselectivity of the decarbonylation reaction, applicable specifically to the silyl ketone functional group (**1n**), these conditions allowed the late-stage functionalization of cholesterol and menthol derivatives **1q** and **1r** in high yields. Additionally, the scope of different silyl groups was evaluated and the expected products **2s** and **2t** were isolated in good to moderate yields (Scheme 2 bottom). Under identical reaction conditions, naphthalen-2-yl(triethylsilyl)-methanone (**1u**) was tested, however, the analogous product **2u** was obtained in lower yield.

To investigate the influence of the steric properties of the silicon residue further, we conducted a series of parallel reactions with substrates **1a**, **1s**, and **1t** and noticed that the sterically encumbered substrate **1t**, bearing three phenyl rings on the silicon atom exhibited the slowest rate, most probably due to the weak coordinating ability to the nickel complex (Figure 1, see also the Supporting Information).

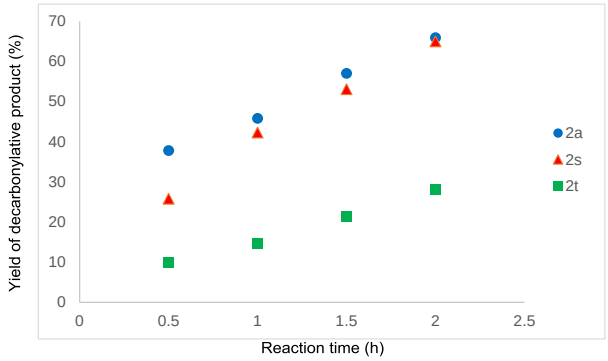
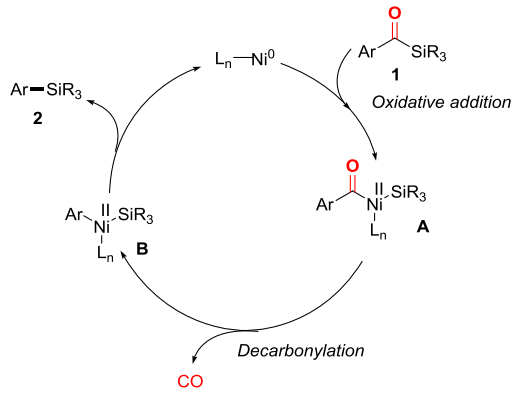


Figure 1. Initial reactions with substrates bearing different substituents on the α-silicon atom.

Based on our results, a plausible catalytic pathway is illustrated in Scheme 3. The insertion of nickel(0) species into Si–C(=O) bond favors the formation of acylnickel(II) intermediate **A**,[16] which can undergo decarbonylation to generate arylnickel(II) silane species **B**. Lastly, reductive elimination of **B** leads to arylsilane product, along with the regenerated nickel(0) species, which is then able to reenter the catalytic cycle.

Scheme 3. Proposed catalytic cycle.



In summary, we describe a new nickel-catalyzed intramolecular decarbonylative silylation of silyl ketones. The method is attractive as it makes use of an inexpensive catalytic system and avoids the use of exogenous bases, strained or directing group-containing substrates or activated esters and amides and generates CO as the only byproduct. The protocol tolerates various functional groups, including heterocycles and natural product derivatives and affords products in good yields. Given the efficiency of this approach, it is anticipated that it will find consideration in expanding the field of strong σ-bond activation via nickel catalysis.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, spectral data for all compounds, and copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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REFERENCES

(1) Recent reviews on transition-metal-catalyzed cross-coupling reactions, see: (a) de Meijere, A.; Diederich, F. in *Metal-Catalyzed Cross-Coupling Reactions*, *Vol. 1*, Wiley-VCH, Weinheim, 2004. (b) Li, H.; Shi, Z.-J. in *Homogeneous Catalysis for Unreactive Bond Activation*, John Wiley & Sons Ltd., Chichester, U.K., 2014, pp. 575. (c) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. C. *Science* **2016**, *352*, 1304-1308. (d) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. *Acc. Chem. Res.* **2016**, *49*, 1429-1439. (e) Qi, X.; Li, Y.; Bai, R.; Lan, Y. *Acc. Chem. Res.* **2017**, *50*, 2799-2808. (f) Feng, Z.; Xiao, Y.-L.; Zhang, X. *Acc. Chem. Res.* **2018**, *51*, 2264-2278. (g) Shi, S.; Nolan, S. P.; Szostak, M. *Acc. Chem. Res.* **2018**, *51*, 2589-2599. (h) Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *Chem. Rev.* **2015**, *115*, 9587-9652. (i) Xia, Y.; Qiu, D.; Wang, J. *Chem. Rev.* **2017**, *117*, 13810-13889. (j) Kaga, A.; Chiba, S. *ACS Catal.* **2017**, *7*, 4697-4706. (k) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486-1495. (l) Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270-5298. (m) Johnson, J. B.; Rovis, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 840-871. (n) Rudolph, A.; Lautens, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 2656-2670.

(2) Reviews on decarbonylative cross-couplings, see: (a) Guo, L.; Rueping, M. *Acc. Chem. Res.* **2018**, *51*, 1185-1195. (b) Takise, R.; Muto, K.; Yamaguchi, J. *Chem. Soc. Rev.* **2017**, *46*, 5864-5888. (c) Guo, L.; Rueping, M. *Chem. Eur. J.* **2018**, *24*, 7794-7809.

(3) (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540-541. (b) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285-8290.

(4) (a) Masuda, Y.; Hasegawa, M.; Yamashita, M.; Nozaki, K.; Ishida, N.; Murakami, M. *J. Am. Chem. Soc.* **2013**, *135*, 7142-7145. (b) Morioka, T.; Nishizawa, A.; Furukawa, T.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2017**, *139*, 1416-1419. (c) Zhao, T.-T.; Xu, W.-H.; Zheng, Z.-J.; Xu, P.-F.; Wei, H. *J. Am. Chem. Soc.* **2018**, *140*, 586-589. (d) Lei, Z.-Q.; Li, H.; Li, Y.; Zhang, X.-S.; Chen, K.; Wang, X.; Sun, J.; Shi, Z.-J. *Angew. Chem. Int. Ed.* **2012**, *51*, 2690-2694. (e) Somerville, R. J.; Martin, R. *Angew. Chem. Int. Ed.* **2017**, *56*, 6708-6710. (f) Whittaker, R. E.; Dong, G. *Org. Lett.* **2015**, *17*, 5504-5507. (g) Dermenci, A.; Whittaker, R. E.; Gao, Y.; Cruz, F. A.; Yu, Z.-X.; Dong, G. *Chem. Sci.* **2015**, *6*, 3201-3210. (h) Dermenci, A.; Whittaker, R. E.; Dong, G. *Org. Lett.* **2013**, *15*, 2242-2245.

(5) (a) Tsuji, J.; Ohno, K. *Tetrahedron Lett*. **1965**, *6*, 3969-3971. (b) Ding, K.; Xu, S.; Alotaibi, R.; Paudel, K.; Reinheimer, E. W.; Weatherly, J. *J. Org. Chem.* **2017**, *82*, 4924-4929. (c) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206-5215.

(6) Malapit, C. A.; Ichiishi, N.; Sanford, M. S. *Org. Lett.* **2017**, *19*, 4142-4145.

(7) Liu, X.; Yue, H.; Jia, J.; Guo, L.; Rueping, M. *Chem. Eur. J.* **2017**, *23*, 11771-11775.

(8) Takise, R.; Isshiki, R.; Muto, K.; Itami, K.; Yamaguchi, J. *J. Am. Chem. Soc.* **2017**, *139*, 3340-3343.

(9) (a) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett*. **1987**, *28*, 6321-6324. (b) Ichiishi, N.; Malapit, C. A.; Woźniak, Ł.; Sanford, M. S. *Org. Lett.* **2018**, *20*, 44-47. (c) Kato, T.; Kuniyasu, H.; Kajiura, T.; Minami, Y.; Ohtaka, A.; Kinomoto, M.; Terao, J.; Kurosawa, H.; Kambe, N. *Chem. Commun.* **2006**, 868-870. (d) Liu, C.; Szostak, M. *Chem. Commun.* **2018**, *54*, 2130-2133. (e) Zheng, Z.-J.; Jiang, C.; Shao, P.-C.; Liu, W.-F.; Zhao, T.-T.; Xu, P.-F.; Wei, H. *Chem. Commun.* **2019**, 55, 1907-1910. (f) Lee, S.-C.; Liao, H.-H.; Chatupheeraphat, A.; Rueping, M. *Chem. Eur. J.* **2018**, *24*, 3608-3612. (g) Ishitobi, K.; Isshiki, R.; Asahara, K. K.; Lim, C.; Muto, K.; Yamaguchi, J. *Chem. Lett.* **2018**, *47*, 756-759.

(10) (a) Chatupheeraphat, A.; Liao, H.-H.; Lee, S.-C.; Rueping, M. *Org. Lett.* **2017**, *19*, 4255-4258. (b) Murahashi, S.-I.; Naota, T.; Nakajima, N. *J. Org. Chem.* **1986**, *51*, 898-901.

(11) Yu, R.; Chen, X.; Martin, S. F.; Wang, Z. *Org. Lett.* **2017**, *19*, 1808-1811.

(12) For reviews on organosilicon compounds, see: (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175-292. (b) Brook, M. in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000. (c) Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835-846. (d) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374-2390. (e) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893-4901. (f) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946-8975. (g) Denmark, S. E.; Liu, J. H.-C. *Angew. Chem. Int. Ed.* **2010**, *49*, 2978-2986. (h) Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631-651.

(13) (a) Denmark, S. E.; Neuville, L. *Org. Lett.* **2000**, *2*, 3221-3224. (b) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565-568. (c) Luliński, S.; Serwatowski, J. *J. Org. Chem.* **2003**, *68*, 9384-9388. (d) Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305-8314.

(14) (a) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895-1896. (b) Chen, L.; Huang, J.-B.; Xu, Z.; Zheng, Z.-J.; Yang, K.-F.; Cui, Y.-M.; Caoa, J.; Xu, L.-W. *RSC Adv.* **2016**, *6*, 67113-67117. (c) Iizuka, M.; Kondo, Y. *Eur. J. Org. Chem.* **2008**, 1161-1163. (d) Yamanoi, Y. *J. Org. Chem.* **2005**, *70*, 9607-9609. (e) Yamanoi, Y.; Nishihara, H. *J. Org. Chem.* **2008**, *73*, 6671-6678. (f) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483-3486. (g) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2006**, *8*, 931-934. (h) McNeill, E.; Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 3785-3788. (i) Xu, Z.; Xu, J.-Z.; Zhang, J.; Zheng, Z.-J.; Cao, J.; Cui, Y.-M.; Xu, L.-W. *Chem. Asian J.* **2017**, *12*, 1749-1757.

(15) (a) Guo, L.; Chatupheeraphat, A.; Rueping, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 11810-11813. (b) Lee, S.-C.; Guo, L.; Yue, H.; Liao, H.-H.; Rueping, M. *Synlett* **2017**, *28*, 2594-2598.

(16) Selected examples on C(sp^3)–Si bond activation via transition metals, see: (a) Meng, T.; Ouyang, K.; Xi, Z. *RSC Adv*. **2013**, *3*, 14273-14276. (b) Yang, Q.; Liu, L.; Chi, Y.; Hao, W.; Zhang, W.-X.; Xi, Z. *Org. Chem. Front*. **2018**, *5*, 860-863. (c) Yu, Z.; Zhang, T.; Bai, R.; Lan, Y. *Catal. Sci. Technol*. **2019**, *9*, 646-651. (d) Ishida, N.; Ikemoto, W.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 5912-5915. (e) Onoe, M.; Baba, K.; Kim, Y.; Kita, Y.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2012**, *134*, 19477-19488. (f) Yu, Z.; Lan, Y. *J. Org. Chem*. **2013**, *78*, 11501-11507. (g) Zhang, Q.-W.; An, K.; He, W. *Angew. Chem. Int. Ed.* **2014**, *53*, 5667-5671. (h) Zhang, Q.-W.; An, K.; Liu, L.-C.; Guo, S.; Jiang, C.; Guo, H.; He, W. *Angew. Chem. Int. Ed.* **2016**, *55*, 6319-6323.