Catalyst-free carbosilylation of alkenes using silyl boronates and organic fluorides via selective C-F bond activation

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A regioselective carbosilylation of alkenes has emerged as a powerful strategy to access molecules with functionalized silylated alkanes, by incorporating silyl and carbon groups across an alkene double bond. However, to the best of our knowledge, organic fluorides have never been used in this protocol. Here we disclose the catalyst-free carbosilylation of alkenes using silyl boronates and organic fluorides mediated by t-BuOK. The main feature of this transformation is the selective activation of the C-F bond of an organic fluoride by the silyl boronate without undergoing potential side-reactions involving C-O, C-Cl, heteroaryl-CH, and even CF3 groups. Various silylated alkanes with tertiary or quaternary carbon centers that have aromatic, hetero-aromatic, and/or aliphatic groups at the β-position are synthesized in a single step from substituted or non-substituted aryl alkenes. An intramolecular variant of this carbosilylation is also achieved via the reaction of a fluoroarene with a ω-alkenyl side chain and a silyl boronate.
The use of two independent reactants for the transition-metal-catalyzed difunctionalization of alkenes has emerged as a powerful strategy to access molecules with multiple functional groups, by incorporating two new functional groups across an alkene double bond. One of the two coupling partners commonly used in this context are activated halogenated arenes or alkanes, or an equivalent thereof (Ar-X or Alkyl-X; X = e.g., I, Br, Cl, OTf, or OMs). Reactions using these molecules generally proceed via oxidative addition and/or radical processes. In contrast, fluorinated compounds such as aryl or alkyl fluorides have not yet been used as a counterpart for the difunctionalization of alkenes due to the high bond-dissociation energy of the carbon–fluorine (C–F) bond (Fig. 1a).

In recent years, a variety of organofluorine compounds has become ubiquitous due to the rapid establishment of technologies for their synthesis. There are more than 340 registered fluoro-pharmaceuticals with complex structures and more than 425 registered fluoro-agrochemicals. It has been estimated that there are more than 8,800,000 commercially available fluoroo-organic synthesis, electronics, photonics, and drug discovery. Despite previous successes in the hydrolysis of aryl and alkyl fluorides in the presence of silyl boronates via C–F bond cleavage under mild conditions both with or without Ti catalysts, we decided to undertake a much more challenging research topic: the difunctionalization of alkenes with aryl or alkyl fluorides in the presence of silyl boronates via C–F bond cleavage (Fig. 1b).

Herein, we disclose a protocol consisting of the catalyst-free defluorinative carbosilylation of alkenes with silyl boronates and fluorinated compounds with an inert C(sp²)-F bond (Table 1). A wide variety of aryl fluorides and alkyl fluorides are smoothly incorporated into the alkenes via the cleavage of a C–F bond in the presence of silyl boronates to provide β-functionalized silyl alkynes in good to excellent yield, without any help of transition-metal catalysis nor photoredox system. The alkene, aryl fluoride, and alkyl fluoride substrate scope tolerated by this reaction is extensive. Unsubstituted styrene derivatives as well as substituted aryl aralkyl aryl heteroaryl, and/or alkyl units at the β-carbon of the silyl alkynes. The reaction proceeds with high regio- and chemoselectivity. Aryl and conjugated alkenes are reactive, whereas non-aryl alkenes are entirely unreactive. The potentially cleavable C-O bond of ethers, C-Cl bond, and the C(sp²)-H bond of heteroaromatic compounds are well-tolerated. Most significantly, the C(sp²)-F bond of the trifluoromethyl (CF₃) group remains intact. An intramolecular carbosilylation via the cleavage and coupling of a C–F bond was also achieved. Three-component coupling reactions involving drug derivatives that contain a fluoride moiety were also demonstrated to prove the utility of this transformation in the drug discovery process. The reaction should proceed through a cascade radical process initiated by single-electron transfer, which was supported by the experimental studies.

**Results and discussion**

Optimization of the reaction conditions. We first investigated the reaction of 4-fluorobiphenyl (1a) with styrene (3a) in the presence of the silyl boronate Et₃SiBpin and a variety of catalysts (Table 1, also see Supplementary Tables S1–S5 for more details).
Using the conditions described in our earlier report on the defluorosilylation of aryl fluorides, we were able to obtain the expected biphenyl-phenylethyl-triethylsilane 4aa in 99% yield, which is similar to that obtained in entry 5, within 2.5 h without eroding the reaction efficiency (entry 6). Replacement of KOtBu with NaOtBu revealed that the Ni catalyst is not necessary; we continued the substrate scope under Ni-free conditions. Fluoro-indole (1f) was also efficiently converted into arylsilylation product 4fa (63%), whereas 4-methyl-substituted aryl fluoride 1g provided a higher yield (4qa: 85%). The excellent chemoselectivity profile of this process is nicely illustrated by the tolerance of the reaction conditions toward functional groups such as ethers (-O-: 1h, 1i, and 1j), CF₃ groups (1k and 1l), or Cl groups (1m), all of which could potentially be cleaved with the C–F bond activation. The desired products 4 were obtained in the following yields: 4ha: 75%, 4ia: 73%, 4ja: 69%, 4ka: 50%, 4la: 53%, 4ma: 70%. It was most surprising to find that the CF₃ groups of 1k and 1l remained intact. We next repeated the same substrate scope by the best reaction conditions in the presence of Ni(COD)₂ (entry 6, Table 1). Although the yield products 4aa–4na were somewhat improved, the differences were not so significant, as shown in Fig. 2.

Encouraged by the fact that the transformation fundamentally does not require Ni catalyst, we continued the substrate scope under catalyst-free conditions (entry 11, Table 1). Next, we focused on the hetero-aromatic fluorides 1n–1u. The nitrogen-containing hetero-aromatic fluorides 1n–1t were successfully coupled with 3a in the presence of Et₃SiBpin in good to high yield; a 1H-indole derivative (4na: 57%), 1H-pyrole derivative (4oa: 32%), and a number of pyridine derivatives (4pa: 80%; 4qa: 68%; 4ra: 74%; 4sa: 88%) were well-tolerated under the optimized conditions. Fluoro-indole (1t) and fluoro-benzofuran (1u), despite having several reactive aryl C(sp²)–H bonds, also participated well in this transformation, selectively furnishing carbosilylation products 4ta (85%) and 4ua (49%) via C–F bond cleavage, without the anticipated C–H activation–silylation reaction of the hetero-aromatic moiety. Notably, other silyl boronates such as PhMe₂SiBPin, Pr₂SiBPin, and BuMe₂SiBPin, could also be used in this transformation instead of Et₃SiBpin. The corresponding silylated products 4aa', 4aa'', and 4aa''' were obtained from fluoroarene 1a and styrene (3a) in 47%, 88%, and 94% yields, respectively.

Next, we set out to evaluate the scope of the alkene component (3) of the reaction. A range of aryl alkenes were efficiently converted into the corresponding arylation products 4 in high yield; for example, biphenyl products (4aa: 91%; 4ba: 87%; 4ca: 42%), 1-naphthyl product (4da: 87%), and 4-(naphthalen-1-yl)phenyl (4ea: 90%) were all obtained using this methodology. Simple fluoroazobenzene

### Table 1 Optimization of the reaction conditions.

| Entry | Ni(COD)₂ (mol%) | Et₃SiBpin | Base (equiv) | Cyclohexane/THF | Yield (%) |
|-------|----------------|-----------|-------------|----------------|-----------|
| 1     | 10             | 1.5       | KOtBu (2.5) | 1/2            | 32        |
| 2     | 10             | 1.5       | KOtBu (3.5) | 1/2            | 38        |
| 3     | 10             | 1.5       | KOtBu (4)   | 1/2            | 52        |
| 4     | 10             | 2         | KOtBu (4)   | 1/2            | 81        |
| 5     | 10             | 2         | KOtBu (4)   | 8/1            | 98 (95)   |
| 6     | 1              | 2         | KOtBu (4)   | 8/1            | 99 (94)   |
| 7     | 1              | 2         | NaOtBu (4)  | 8/1            | 15        |
| 8     | 1              | 2         | 0           | 8/1            | 0         |
| 9     | 1              | 2         | LiOtBu, KOMe or KHMDS (4) | 8/1 | 0 |
| 10    | 1              | 2         | KOtBu (4)   | 8/1            | 45        |
| 11    | 0              | 2         | KOtBu (4)   | 8/1            | 94 (91)   |

*Unless otherwise noted, the reaction was carried out using 1a (0.1 mmol), 3a (0.2 mmol), Et₃SiBpin, Ni(COD)₂, and a base in cyclohexane/THF (0.75 mL) at rt for 2.5 h. Yields were determined by 1H NMR and 19F NMR analysis of the crude reaction mixture using 3-fluoropyridine as the internal standard. 5.0 equiv of 3a was used.

**Substrate scope.** With the optimized reaction conditions (Table 1, entries 6 and 11), we investigated the scope of the Ni-catalyzed or catalyst-free carbosilylation of the alkenes 3 with fluoroarenes 1 and Et₃SiBpin (Fig. 2). First, the scope of the aromatic fluorides was examined under catalyst-free conditions (entry 11, Table 1). A wide range of fluoroarenes that bear π-extended building blocks were efficiently converted into the corresponding defluorosilylation arylation products (4) in good to high yield. For example, biphenyl products (4aa: 91%; 4ba: 87%; 4ca: 42%), a 1-naphthyl product (4da: 87%), and 4-(naphthalen-1-yl)phenyl (4ea: 90%) were all obtained using this methodology. Simple fluoroazobenzene
Fig. 2 Carbosilylation of alkenes with silyl boronates and aryl/alkyl fluorides. a, b. a. The reaction was carried using 1 or 2 (0.2 mmol), 3 (2.0 equiv.), Et3SiBpin, Me3PhSiBpin, 3Pr3SiBpin or tBuMe2SiBpin (2.0 equiv.), and KOtBu (4.0 equiv.) in cyclohexane/THF (1.5 mL, 8/1, v/v) at room temperature. b. Isolated yield is shown. c. The reaction was carried out in the presence of Ni(COD)2 (1.0 mol%). d. 0.4 mmol of 1 was used.
(3f, 3g), dioxole (3h), and MeS (3i) groups were all, even the highly sterically hindered ortho-MeO-styrene 3g, well-tolerated as substrates and furnished the desired products 4 in good to excellent yield (4ac: 81%; 4ad: 67%; 4ae: 79%; 4af: 81%; 4ag: 75%; 4ah: 59%; 4ai: 91%). It is important to note that this three-component coupling reaction tolerated any combination of the coupling components. A wide variety of substituted or non-substituted fluoroarenes 1, aryl alkenes 3, and silyl boronates R₃SiBpin furnished the desired silylated alkanes 4 in good to high yield (4cg: 46%; 4ci: 33%; 4lc: 70%; 4mc: 84%; 4vi: 65%; 4ab: 92%). We also investigated the reaction of substituted styrene derivatives with a quaternary carbon center at the β-position of the silyl moiety. For example, α,α-diphenylethylene 3j, α-methylstyrene 3k, and (4-methoxybut-1-en-2-yl)benzene 3l reacted with fluoroarenes 1 under the standard reaction conditions to give the corresponding products 4 (4aj: 71%; 4ak: 51%; 4fk: 73%; 4mk: 69%). Furthermore, we attempted the defluorinating alkylsilylation of alkenes using alkyl fluoro-rides with an inert C(sp³)–F bond under the same reaction conditions. Primary alkyl fluoro-rides 2a–2h efficiently reacted regioselectively with styrenes (3a, 3c, 3i) to afford the corresponding alkylsilylation products in up to 94% yield (5aa: 94%; 5ba: 89%; 5ca: 85%; 5da: 91%; 5ei: 76%; 5fi: 86%; 5gi: 40%; 5hc: 83%). Notably, the trilluromethoxy (CF₃O) moiety of 2d remained intact to provide 5da. Secondary alkyl fluoro-rides 2i and 2j also furnished the desired defluorinating alkylsilylation products 5ia and 5ja in 36% and 52% yield, respectively. The reaction using alkyl fluoro-rides was also carried out in the presence of Ni(COD)₂ catalyst (1 mol%) under the best conditions (entry 6, Table 1). We obtained almost the same results (72–95%) as the yields without Ni catalyst. Thus, the defluorinating carboxylation does not require Ni catalysis independent of the case of aryl or alkyl fluoro-ride.

To highlight the synthetic utility of this three-component defluorinating carboxylation reaction, we examined the functionalization of several drug derivatives with fluoroarene moieties (Fig. 3). (±)-α-Tocopherol derivative 1w successfully underwent carboxylation to afford (±)-α-tocopherol derivative 4wa in 43% yield (Fig. 3a). (-)-Menthol-derived fluoro-benzene 1x proceeded well under identical conditions to give carboxylation product 4xa in 55% yield (Fig. 3b). Steroid derivatives 4ya and 4am were synthesized in 53% and 79% yield via (1) the defluorination of fluoro-incorporated estrone derivative 1y or (2) the defluorination of 1a with alkene- incorporated estrone derivative 3m (Fig. 3c, d). Moreover, the liquid crystalline material 1z was also successfully functionalized using this transformation with 3i to give 4zi in 41% yield (Fig. 3e).

Furthermore, we examined both the chemoselectivity and site-selectivity of the alkenyl moiety (Fig. 4). (E)-Buta-1,3-dien-1-
Ylbenzene (3n) was site-selectively converted into the 1,4-type arylsilylation product 4an in 41% yield with an E/Z ratio of 1.1/1 (determined by 1H nuclear magnetic resonance (NMR) analysis), whereas no 1,2-adduct was observed (Fig. 4a). Conversely, phenoprene 3o preferably furnished 4ao (65%), a compound with a quaternary carbon center, under the standard reaction conditions via the 1,2-arylsilylation process and not the 1,4-process (Fig. 4b). When we examined the reaction of 1-(but-3-en-1-yl)-2-fluorobenzene (6a) with 3a in the presence of Et3SiBpin, only the three-component condensation product 7aa was obtained in 51% yield, whereas the intramolecular product was not detected (Fig. 4c). For the reaction of 6-fluorohex-1-ene (2k) and 10-fluorodec-1-ene (2l) having a terminal olefin moiety with styrenes 3a and 3i, the three-component condensation products 5ka and 5li were obtained in 93% and 70% yields, respectively, whereas the intramolecular products were not detected (Fig. 4d, e). In contrast, an intramolecular carbosilylation was achieved via the reaction of styrene-substituted fluoroarene 6b–6d with Et3SiBpin under identical conditions to furnish 8b–8d, molecules with a quaternary carbon center, in 81–95% yield (Fig. 4f–h). The five-component condensation was observed for the reaction of difunctionalized 1,8-difluorooctane (2m) with styrene 3c and Et3SiBpin to provide 5mc in 88% yield (Fig. 4i). It should be noted that, under the applied conditions, bromo-, and iodo-substituted arenes 9, 10 afforded a mixture of two-component condensation products of silylated 11 and borylated 12 compounds, whereas the targeted three-component product 4aa was not detected (Fig. 4j). We also attempted the reaction of alkyl chloride 13 instead of alkyl fluoride 3a under the same conditions. Although the three-component product 5aa was obtained by alkyl fluoride 3a, the two-component product, triethyl[phenethyl]silane (14), made from 3a and Et3SiBpin, was obtained in 22% yield without incorporation of alkyl chloride 13 (Fig. 4k). Alkyl bromide and iodide were also not converted into 5aa under identical conditions (Supplementary Fig. 5). Encouraged by the results, we attempted the chemoselective activation of the alkyl C–F bond over the alkyl C–Cl bond by the competitive reaction between 2a and 13. Interestingly, the alkyl fluoride 2a was consumed to 5aa (95%), whereas the alkyl chloride 13 was recovered (90%, Fig. 4l), more details in Supplementary Figs. 6–8). These behaviors show

Fig. 4 Chemo- and site-selective coupling reactions. a Selective 1,4-type addition carbosilylation of 1,3-diene 3n. b Selective 1,2-carbosilylation of 1,3-diene 3o. c–e Selective three-component carbosilylation of styrenes (3a or 3i) in the presence of an aliphatic alkene moiety in aryl fluoride 6a or alkyl fluorides 2k or 2l. f–h Intramolecular carbosilylation of 6b–d to provide cyclized silylated products 8b–d. i Five-component carbosilylation of styrene 3c with 1,8-difluorooctane (2m). j Comparisons of aryl halides (1a, 9, and 10) for the carbosilylation. k Comparisons of alkyl halides (2a and 13) for the carbosilylation. l The competitive reaction between 2a and 13.
the advantage of fluorine in our reaction system compared to commonly used halogens both in aromatic and aliphatic cases.

Mechanistic study. Based on this consideration and on the results obtained so far, a radical pathway seems to be a viable hypothesis. To gain an insight into the reaction mechanism, some experiments were undertaken. First, the transformation of 1a with 3a to 4aa under the best conditions was significantly inhibited by the addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Fig. 5a). These results strongly suggested the reaction involves radical species. We also attempted the same reaction in the presence of Ni catalyst. The same results were obtained. We next examined the radical clock experiment with the substrate containing a cyclopropyl moiety at the α-position of the styrene derivative 3p (Fig. 5b). The silylated ring-opening product 15 was obtained as a major product in 55% yield and most of the aryl derivative 6e was recovered. On the other hand, the expected three-component product was not clearly observed, the trace of the desired material was detected only by gas chromatography–mass spectrometry (GCMS). The results are also in good agreement with the radical-mediated reaction mechanism, as the potential cyclopropyl carbinyl radical is known to be spontaneously rearrange to allycarbiny radical. Furthermore, the substrate 6e having both fluorourene and styrene moieties was transformed into the silylcyclopropyl compound 16 in 76% yield (Fig. 5c), which also supports the radical pathway. The treatment of 2k with Et3SiBPin in the absence of styrenes 3 predominately gave a silylalkene 17 in 73% yield via C–F bond activation, whereas the transformation was completely inhibited by the addition of TEMPO independent of the existence of Ni catalyst (Fig. 5d). Thus, the generation of radical species does not require the reaction with styrenes 3.

Based on both the experiments’ results here and in previous reports,44,67–74 we propose a single-electron transfer/radical-mediated carboxylation reaction mechanism triggered by the known ability of KOtBu to serve as a single-electron reductant75,76 (Fig. 5e). First, Et3SiBPin reacts with a molecule of KOtBu to form an intermediate A. The formation of A has previously been confirmed by the Avasare group based on density functional theory calculations77. We also confirmed the intermediate A by the 11B-NMR and 29Si-NMR study (Supplementary Figs. 12–15)78. Next, a single-electron transfer process would start by the additional amount of KOtBu as a trigger75,76. Namely, a single electron is transferred from t-butoxy anion (–OtBu) to the silicon atom of intermediate A to furnish a triethysilyl radical ‘SiEt3 via a cleavage of the Si–B bond. The t-butoxy radical ‘OtBu is also generated, which would be captured by the borate anion B. The mechanisms for the cleavage of Si–B bonds are various; the radical-mediated Si–B bond cleavage76–80 should be highly acceptable due to the experimental results using ‘BuOK75,76. The generated triethysilyl radical ‘SiEt3 reacts with styrene 3a to give a radical adduct C. The radical cascade process should happen between the radical species C, aryl 1 or alkyl fluorides 2, t-butoxy radical ‘OtBu, and borate anion B in the transition state TS-I, where the C–F bond of aryl 1 or alkyl fluorides 2 is activated by the approach of K+. The boron atom in B would also participate in activation of the C–F bond. Finally, the C–C bond formation is completed under concomitant generation of stable D [BPin(OtBu)2]K (Supplementary Fig. 14)78 and KF to furnish the desired three-component adduct 4 or 5. The generation of benzyl radical species C was supported by the cyclopropyl experiments (Fig. 5b, c). It should be noted that through the experiments, we observed side products such as Et3Si–SiEt3 and double styrene adducts 18. These formations can be explained by the dimerization of triethysilyl radical ‘SiEt3 and the overreaction of benzyl radical C with styrene 3a.

In conclusion, we have developed a carboxylation of alkenes that uses silyl boronates and organic fluorides, and that proceeds via the activation of an inert C–F bond without a catalyst. This reaction should be initiated by the radical cleavage of Si–B bond via a single-electron transfer from ‘BuOK. A variety of β-functionalized silyl compounds can be synthesized efficiently and rapidly in good to excellent yield under very mild conditions at room temperature. The most significant feature of this protocol is its broad substrate scope. This highly efficient protocol accepts a variety of fluorides, including aryl and alkyl fluorides, and even...
transforms sterically demanding secondary alkyl fluorides. A broad range of aryl alkenes, such as styrene derivatives and α-substituted aryl alkenes, are also tolerated by this method. Silyl boronates were identified as viable substrates. Moreover, the chemico- and site-selectivity displayed in this reaction are remarkable. Aryl alkenes selectively react in the presence of non-aryl alkenes and an intramolecular carbofunctionalization was achieved with substrates that possess both fluoroarene and aryl alkene moieties. The tolerance of the reaction toward different functional groups is also significant. Substrates with ether, CF₃, and hetero-aromatic moieties react smoothly without the detection of C–O cleavage, C–F bond activation, or C–H activation; only the inert C–F bonds of the fluoroarenes and fluoroalkanes are activated. Notably, this method also allows for the synthesis of silyl compounds with a quaternary carbon center at the β-position. The 1,4-type addition carbofunctionalization of 1,3-dienes was also achieved. Given the high number of fluorinated compounds that are commercially available, including structurally complex pharmaceuticals, agrochemicals, and functional materials, this protocol widens the potential utility of organosilicon compounds in organic synthesis, the structural design of lead drug compounds, and functional materials.

Finally, the limitations of the method should be mentioned. The conjugated diene is acceptable but electron-deficient acrylates and acrylamides are not suitable. Internal styrenes such as cis-stilbene and trans-β-methylstilbene did not react (Supplementary Figs. 1 and 2). The chemoselective activation of aromatic C–F bonds over aromatic C–Br and C–I bonds is difficult, whereas the only aromatic fluoride was transformed into the desired three-component product (Supplementary Figs. 3 and 4).

Methods

General procedure for the defluorinative carbofunctionalization of alkenes 3 using RuSiBpin and aryl fluorides 1 or alkyl fluorides 2:

1. A N₂-filled glovebox to a flame-dried screw-capped test tube were added organic fluorides 1 or 2 (0.20 mmol, 1.0 equiv), silyl boronates RuSiBpin (0.4 mmol, 2.0 equiv), alkenes 3 (0.40 mmol, 2.0 equiv), KOtBu (90 mg, 0.8 mmol, 4.0 equiv), and cyclohexene/THF (1.5 mL, v/v) sequentially. The tube was then sealed and removed from the glovebox. The mixture was stirred at room temperature for 2.5 h. To the reaction tube was added hexane (5 mL) and then it was subjected to filter through a short silica pad, washed with Et₂O, and concentrated under vacuum, followed by 3-fluoroalkanes were activated. Notably, this method also allows for component product (Supplementary Figs. 3 and 4).

References

1. Dhungana, R. K. & Giri, R. Transition metal-catalyzed dicarbofunctionalization of unactivated olefins. Chem. Rev. 18, 1314–1340 (2018).
2. Derosa, J. et al. Recent developments in nickel-catalyzed intermolecular dicarbofunctionalization of alkenes. Chem. Sci. 11, 4287–4296 (2020).
3. Yin, G. Y., Mu, X. & Liu, G. S. Palladium(II)-catalyzed oxidative dicarbofunctionalization of alkenes: bond forming at a high-valent palladium center. Acc. Chem. Res. 49, 2413–2423 (2016).
4. McDonald, R. I., Liu, G. & Stahl, S. S. Palladium(II)-catalyzed alkene functionalization via nucleopalladation: stereochemical pathways and enantioselective catalytic applications. Chem. Rev. 111, 2981–3019 (2019).
5. Li, Z. L. et al. Recent advances in copper-catalysed radical-involved asymmetric 1,2-functionalization of alkenes. Chem. Soc. Rev. 49, 32–48 (2020).
6. Jiang, H. & Studer, A. Intramolecular radical carboamination of alkenes. Chem. Soc. Rev. 49, 1790–1811 (2020).
39. Welle, A. et al. Copper-catalysed domino silylative aldol reaction leading to stereosecontrolled chiral quartenary carbons. *Chem. Eur. J.* 16, 10980–10983 (2010).

40. Obora, Y., Tsuji, Y. & Kawamura, T. Palladium-catalyzed decarbonylative coupling of acid chlorides, organodisilanes, and 1,3-dienes. *J. Am. Chem. Soc.* 115, 10414–10415 (1993).

41. Obora, Y., Tsuji, Y. & Kawamura, T. 1,4-Carbosilylation of 1,3-dienes via palladium catalyzed three-component coupling reaction. *J. Am. Chem. Soc.* 117, 9814–9821 (1995).

42. Liu, Z. et al. Palladium(0)-catalyzed directed syn-1,2-carboration and -silylation: alkene scope, applications in dearromatization, and stereocontrol by a chiral auxiliary. *Angew. Chem. Int. Ed.* 58, 17068–17073 (2019).

43. Peng, H. et al. Radical 1,2-aryl migration in α,α-diaryl allylic alcohols toward β-silyl ketones. *Org. Biomol. Chem.* 13, 10299–10302 (2015).

44. Zhang, L., Liu, D. & Liu, Z. Q. A free radical cascade silylarylation of activated alkenes: highly selective activation of the Si–H/C–H bonds. *Org. Lett.* 17, 2534–2537 (2015).

45. Yang, Y. et al. Iron-catalyzed intramolecular 1,2-difunctionalization of styrenes and conjugated alkenes with silanes and nucleophiles. *Angew. Chem. Int. Ed.* 56, 7916–7919 (2017).

46. Hou, J. et al. Visible-light-mediated metal-free difunctionalization of alkenes with CO₂ and silanes or C(sp³)–H/C–H bonds. *ACS Catal.* 9, 835–846 (2022).

47. Nakao, Y. & Hiyama, T. Silicon-based cross-coupling reaction: an important bond related to catalysis. *Org. Biomol. Chem.* 13, 17222–17224 (2018).

48. Sun, D. et al. Highly efficient blue-light-emitting glass-forming molecules based on tetraarylamethylene/silane and fluorene: synthesis and thermal, optical, and electrochemical properties. *Chem. Mater.* 17, 443–445 (2005).

49. Ponomarenko, S. A. & Kirchmeyer, S. Conjugated organosilicon materials for organic electronics and photonics. *Silicon Polym.* 235, 33–110 (2010).

50. Prasad, A. K. & Wilson, S. O. Organosilicon molecules with medicinal applications. *J. Med. Chem.* 56, 388–405 (2013).

51. Obligacion, J. V. & Chirik, P. J. Earth-abundant transition metal catalysts for alkene hydrosilylation and hydrosilylation. *Nat. Rev. Chem.* 2, 15–18 (2014).

52. Du, X. Y. & Huang, Z. Advances in base-metal-catalyzed alkene hydrosilylation. *ACS Catal.* 7, 1227–1243 (2017).

53. Cui, B. et al. Difluorosilylation of fluoroarenes and fluoroalcohols. *Nat. Commun.* 9, 4393 (2018).

54. Wang, J., Ogawa, Y. & Shibata, N. Selective synthesis of spirobienzines, alkyl chloride, and monofluoroalcohols from unactivated gem-difluoroalcohols controlled by aluminum-based Lewis acids. *Sci. Rep.* 9, 19113 (2019).

55. Wang, J., Ogawa, Y. & Shibata, N. Activation of saturated fluorocarbons to synthesize spirobienzines, monofluoroalcohols, and indane derivatives. *iScience* 17, 132–143 (2019).

56. Tanaka, J. et al. Asymmetric desymmetrization via metal-free C–F bond activation: synthesis of 3,5-diaryl-5-fluoromethylazol-2-ones with quaternary carbon centers. *Angew. Chem. Int. Ed.* 55, 9432–9436 (2016).

57. Yu, D. G., Li, B. J. & Shi, Z. J. Exploration of new C–O electrophiles in cross-coupling reactions. *Adv. Synth. Catal.* 43, 1486–1495 (2010).

58. MacQueen, P. M. et al. Exploiting ancillary ligation to enable nickel-catalyzed C–O cross-couplings of aryl electrophiles with aliphatic alcohols. *J. Am. Chem. Soc.* 140, 5023–5027 (2018).

59. Toutov, A. A. et al. Silylation of C–H bonds in aromatic heterocycles by an earth-abundant metal catalyst. *Nature* 518, 80–84 (2015).

60. Gu, Y. T. et al. A mild and direct site-selective sp2 C–H silylation of (poly) azines. *J. Am. Chem. Soc.* 141, 127–132 (2019).

61. Yuan, X. et al. Photocatalytic radical defluoroalkylation of unactivated alkenes via distal heteroaryl ipso-migration. *Commun. Chem.* 3, 98 (2020).

62. Li, Z. X. et al. Radical addition enables 1,2-aryl migration from a vinyl-substituted all-carbon quaternary center. *Angew. Chem. Int. Ed.* 60, 186–190 (2021).

63. Jenkins, I. D. & Krenke, E. H. Mechanistic aspects of hydroisolation/potassium tert-butoxide (HSiR₃/KO₂Bu)-mediated reactions. *ACS Omega* 5, 7053–7058 (2020).

64. Alberti, A. & Pedulli, G. F. Addition reactions of silyl radicals to unsaturated compounds. *Rev. Chem. Intermed.* 8, 207–246 (1987).