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Regioselective lithiation/retro-Brook rearrangement via direct deprotonation

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ABSTRACT

A regioselective lithiation/retro-Brook rearrangement via direct deprotonation was developed. Varieties of benzyl silanes and vinyl silanes are obtained effectively up to 93% yields.

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1. Introduction

Functionalized organosilanes are attractive and potentially useful reagents in organic chemistry.[1] Vinyl silanes have potential synthetic utility in silicon-based cross-couplings, providing an efficient protocol for accessing the configurationally pure multi-substituted olefins.[2] Desilylation of benzyl silanes is useful to generate radicals or cationic species, providing a versatile route to electrophilic synthetic equivalents.[3] In general, the silanes were prepared by several protocols: (1) direct installation of the silane unit through metal–lithium or halogen–lithium exchange[4] and trapping with a silicon electrophile, (2) addition reaction of silicon reagents, such as silylcuprate reagent with allenes or acetylenes, etc. One of the powerful methods to prepare the functionally diverse organic silanes is the utilization of the retro-Brook rearrangement, which means trialkylsilyl group shift from the oxygen atom to a carbanion terminus.[5] The required carbanion terminus was rarely obtained by direct deprotonation with organolithium bases,[6–9] although this method is the most direct way to prepare carbanion termini, which has been well developed in the pioneering work of Witting and Gilman.[7] In recent years, several *ortho*, *lateral*, and vinyl lithiation have been reported.[9] These results prompted us to investigate its potential in retro-Brook rearrangement. Herein we report a regioselective lithiation/retro-Brook rearrangement via direct deprotonation.

2. Results and discussions

To verify our hypothesis, *tert*-butyldimethyl(*o*-tolyloxy)silane was chosen as a model substrate. Various strong bases, such as *n*-BuLi, *s*-BuLi, *t*-BuLi, and LDA were utilized to promote this proposed transformation. When LDA was used, the lateral lithiation did happen, giving the desired 1,4-retro-Brook rearrangement product.[10] Further optimization showed that the product 2-((*tert*-butyldimethylsilyl)methyl)phenol could be obtained in 93% yield when 4 equiv of LDA was used in THF from −78 °C to rt and reflux for 24 h.

Having the optimized reaction conditions in hand, the scope and limitation of the substrates were examined and the results were shown in Table 1. When aryloxylsilanes containing *ortho*-, *meta*-, and *para*-alkyl substituents were tested under the standard condition, it was observed that the retro-Brook rearrangement proceeded smoothly to afford the desired products in high yields (entries 1–4).[11] In the case of substrates with different alkyl chains, the desired products were also obtained in satisfied yields, which were slightly lower compared with 1a, presumably due to the steric hindrance of their alkyl chains (entries 5–8). Treatment of substrate **9a** (1-methylnaphthalen-2-yloxy)-(*tert*-butyl)dimethylsilane gave the corresponding product **9b** in 89% yield, while treatment of *tert*-butyldimethyl((2-methylnaphthalen-1-yl)oxy)silane didn't work under the standard condition.

Interestingly, treatment of substrates **10a** and **11a** with the standard condition afforded a same *trans*-vinyl silane **10b**, which formation was rationed in Scheme 1.[8,12] Deprotonation of **10a** or **11a**, the same compound A would be produced, followed the retro-Brook

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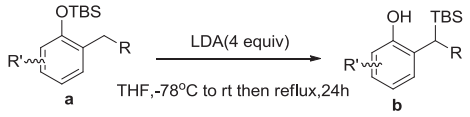
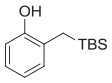
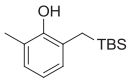
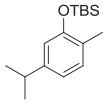
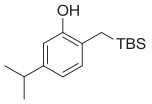
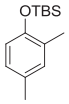
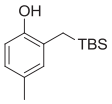
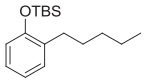
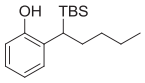
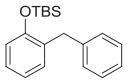
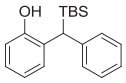
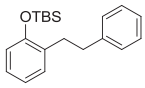
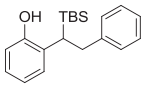
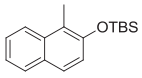
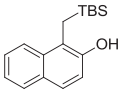
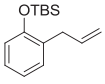
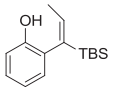
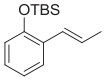
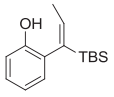
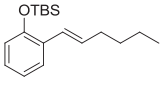
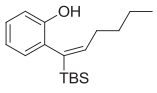
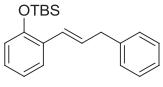
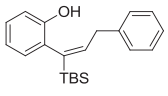
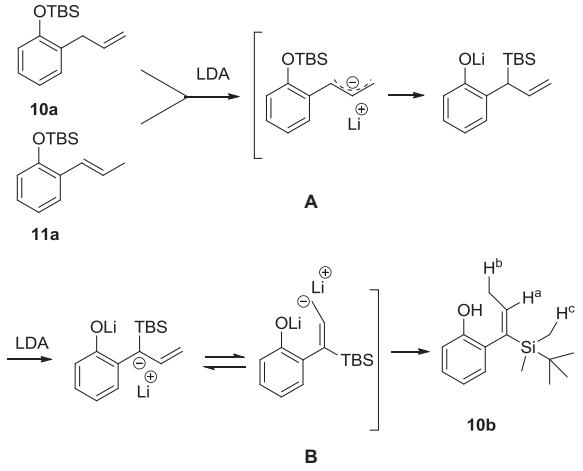
Table 1
Lithiation/retro-Brook rearrangement of substrates



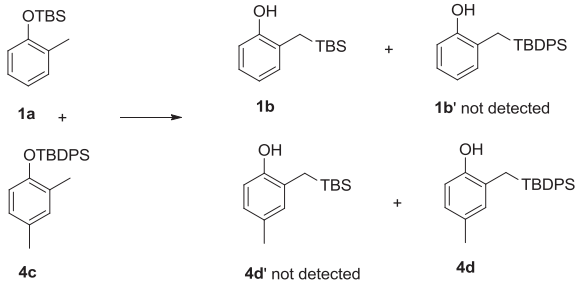
Entry	Substrate	Product	Yield (%)
1	 **1a**	 **1b**	93
2	 **2a**	 **2b**	91
3	 **3a**	 **3b**	90
4	 **4a**	 **4b**	91
5	 **5a**	 **5b**	83
6	 **6a**	 **6b**	78
7	 **7a**	 **7b**	61
8	 **8a**	 **8b**	82
9	 **9a**	 **9b**	89
10	 **10a**	 **10b**	73
11	 **11a**	 **10b**	61
12	 **12a**	 **12b**	53
13	 **13a**	 **13b**	57

rearrangement and deprotonation, compound B would be obtained, which was stabilized by lithium-ion. Another factor in the formation of *trans*-vinyl silane would be that **10b** was thermodynamically stable. Some *trans*-vinyl silanes were obtained in moderate yields (entries 10–13).

Cross reaction tests were done with substrates **1a** and **4c** (see Scheme 2). The reactions proceeded successfully. There were only



Scheme 1. Plausible mechanism about lithiation/retro-Brook rearrangement of substrates **10a** and **11a**.

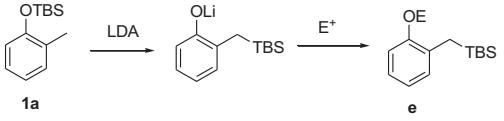


Scheme 2. Cross reaction tests of retro-Brook rearrangement.

products **1b** and **4d** observed and neither of cross-migration products **1b′** and **4d′** were detected. It was suggested that the kind of retro-Brook rearrangement herein is intramolecular.

Based on the concept of anion relay chemistry (ARC),[13] a lithiation/retro-Brook rearrangement/electrophile trapping reaction sequence was also developed. A variety of electrophiles were used to provide the corresponding protected benzyl silanes **1e**–**5e** with good to moderate yields in all cases (Table 2).

Table 2
Lithiation/retro-Brook rearrangement/electrophile trapping reaction of **1a**



Entry	Electrophile	E	Product	Yield (%)
1	TESCl	TES	**1e**	71
2	MOMCl	MOM	**2e**	67
3	Allyl bromide	Allyl	**3e**	63
4	Epoxide propyl chlorine	Epoxide propyl	**4e**	59
5	MeI	Me	**5e**	70

3. Conclusion

In summary, a regioselective lithiation/retro-Brook rearrangement via direct deprotonation has been developed. Many useful benzyl silanes and *trans*-vinyl silanes can be prepared directly. Further investigation and application of the methodology are under way in our lab.

4. Experimental

4.1. General

All commercially available reagents were used without further purification unless otherwise noted. Solvents were purified and dried by standard methods prior to use. Column chromatography was generally performed on silica gel (200–300 mesh). Melting points were determined with a digital Koffer apparatus and were uncorrected. The ^{1}H and ^{13}C NMR data were recorded on a *Mercury Plus*-300 MHz spectrometer or *Bruker* AM-400 MHz instrument using $CDCl_3$ as solvent at room temperature. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 for ^{1}H NMR and 77.0 for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained on a *Bruker Daltonics* APEXII47e FT-ICR mass spectrometer.

4.2. General procedure for lithiation/retro-Brook rearrangement of 1a

A solution of silane **1a** (1 mmol) in anhydrous THF (10 mL) was cooled to −78 °C under Ar. LDA (4 mmol, 2 M) was added at −78 °C slowly under stirring. The mixture was allowed to warm up to room temperature slowly, then heated to reflux and refluxed for 24 h and monitored by TLC. When the starting material was consumed, the resulting mixture was cooled to room temperature and quenched with NH_4Cl. The layers were separated and the aqueous layer was extracted with ethyl acetate (three times). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. Concentration under reduced pressure gave a residue, which was purified by flash column chromatography to afford the product **1b**.

*4.2.1. 2-((tert-Butyldimethylsilyl)methyl)phenol (**1b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, J=11.5, 4.4 Hz, 2H), 6.89–6.78 (m, 1H), 6.73 (d, J=7.8 Hz, 1H), 4.57 (s, 1H), 2.09 (s, 2H), 0.96 (s, 9H), −0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 130.2, 126.9, 125.1, 120.6, 114.9, 26.5, 16.9, 15.7, −6.3; IR (KBr) 3533, 3448, 2953, 2929, 2856, 1588, 1499, 1455, 1361, 1249, 1159, 934, 831, 750, 699 cm^{-1}; HRMS (ESIMS) calcd for $C_{13}H_{26}NOSi^+$ $[M+NH_4]^+$240.1778, found 240.1772.

*4.2.2. 2-((tert-Butyldimethylsilyl)methyl)-6-methylphenol (**2b**).* Colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.01–6.96 (m, 2H), 6.86 (t, J=7.5 Hz, 1H), 4.65 (s, 1H), 2.34 (s, 3H), 2.22 (s, 2H), 1.10 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 127.9, 126.9, 126.2, 122.5, 120.1, 26.5, 17.8, 16.0, 15.8, −6.3; IR (KBr) 3574, 2929, 2856, 1591, 1467, 1251, 1192, 1161, 1071, 920, 832, 744, 699 cm^{-1}; HRMS (ESIMS) calcd for $C_{14}H_{28}NOSi^+$ $[M+NH_4]^+$ 254.1935, found 254.1937.

*4.2.3. 2-((tert-Butyldimethylsilyl)methyl)-5-isopropylphenol (**3b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J=7.6 Hz, 1H), 6.72 (d, J=7.6 Hz, 1H), 6.63 (s, 1H), 4.71 (m, 1H), 2.84 (m, 1H), 2.08 (s, 2H), 1.26 (dd, J=0.8, 6.8 Hz, 6H), 0.99 (t, J=1.6 Hz, 9H), −0.03 (t, J=1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 146.3, 129.9, 123.8, 118.7, 113.1, 33.5, 26.5, 24.0, 16.8, 15.2, −6.3; IR (KBr) 3396, 2929, 2858, 1593, 1470, 1384, 1266, 1218, 1096, 919, 838, 774 cm^{-1}; HRMS (ESIMS) calcd for $C_{16}H_{32}NOSi^+$ $[M+NH_4]^+$282.2248, found 282.2246.

*4.2.4. 2-((tert-Butyldimethylsilyl)methyl)-4-methylphenol (**4b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, J=10.6 Hz, 2H), 6.62 (d, J=7.9 Hz, 1H), 4.44 (s, 1H), 2.25 (s, 3H), 2.05 (s, 2H), 0.96 (s, 9H), −0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 130.8, 129. 7, 126.6, 125.5, 114.8, 26.5, 20.6, 16.9, 15.6, −6.3; IR (KBr) 3443, 2952, 2929, 2857, 1715, 1605, 1507, 1466, 1255, 1166, 828, 747, 698 cm^{-1}; HRMS (ESIMS) calcd for $C_{14}H_{28}NOSi^+$ $[M+NH_4]^+$ 254.1935, found 254.1935.

*4.2.5. 8-(tert-Butyldimethylsilyl)-5,6,7,8-tetrahydronaphthalen-1-ol (**5b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, J=7.6 Hz, 1H), 6.71 (d, J=7.5 Hz, 1H), 6.54 (d, J=7.8 Hz, 1H), 4.75–4.61 (m, 1H), 2.07 (s, 1H), 2.01–1.89 (m, 2H), 1.67 (d, J=6.4 Hz, 1H), 1.05–1.01 (m, 9H), 0.09 (d, J=1.1 Hz, 3H), −0.15 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 138.8, 127.7, 124.1, 121.3, 111.8, 29.1, 27.3, 24.3, 21.7, 19.1, 18.1, −4.8, −5.6; IR (KBr) 3518, 2932, 2856, 1581, 1463, 1251, 1157, 1075, 1014, 828, 769, 679 cm^{-1}; HRMS (ESIMS) calcd for $C_{16}H_{30}NOSi^+$ $[M+NH_4]^+$ 280.2091, found 280.2085.

*4.2.6. 2-(1-(tert-Butyldimethylsilyl)hexyl)phenol (**6b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J=7.7 Hz, 1H), 6.99 (dd, J=10.6, 4.5 Hz, 1H), 6.92–6.86 (m, 1H), 6.72 (d, J=7.9 Hz, 1H), 4.76 (s, 1H), 2.68–2.57 (m, 1H), 1.79 (s, 2H), 1.25 (m, 6H), 0.91 (s, 9H), 0.86 (t, J=6.4 Hz, 3H), 0.07 (s, 3H), −0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 131.0, 127.0, 124.9, 120.7, 114.9, 31.7, 29.2, 27.1, 25.8, 22.6, 22.5, 17.6, 14.1, −6.8, −7.2; IR (KBr) 3400, 2956, 2929, 2857, 1658, 1581, 1465, 1427, 1363, 1251, 1178, 1082, 945, 832, 748 cm^{-1}; HRMS (ESIMS) calcd for $C_{18}H_{36}NOSi^+$ $[M+NH_4]^+$ 310.2561, found 310.2565.

*4.2.7. 2-((tert-Butyldimethylsilyl)(phenyl)methyl)phenol (**7b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J=7.6, 1.3 Hz, 1H), 7.41 (d, J=7.3 Hz, 2H), 7.28 (dd, J=9.3, 5.9 Hz, 2H), 7.16 (t, J=7.3 Hz, 1H), 7.04 (td, J=7.8, 1.6 Hz, 1H), 6.92 (td, J=7.5, 1.0 Hz, 1H), 6.74 (dd, J=7.9, 1.0 Hz, 1H), 5.39 (d, J=15.8 Hz, 1H), 4.24 (s, 1H), 0.86 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.3, 130.5, 130.2, 129.3, 128.2, 126.2, 125.0, 120.4, 115.5, 33.4, 27.2, 17.8, −5.3, −5.9; IR (KBr) 3428, 2928, 2856, 1598, 1490, 1453, 1256, 1080, 917, 836, 751, 700 cm^{-1}; HRMS (ESIMS) calcd for $C_{19}H_{30}NOSi^+$ $[M+NH_4]^+$ 316.2091, found 316.2093.

*4.2.8. 2-(1-(tert-Butyldimethylsilyl)-2-phenylethyl)phenol (**8b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 1H), 7.14 (dd, J=7.8, 6.5 Hz, 3H), 7.11–7.06 (m, 1H), 7.03 (d, J=7.2 Hz, 2H), 6.92 (td, J=7.7, 1.6 Hz, 1H), 6.86 (dd, J=14.5, 4.1 Hz, 1H), 6.59 (d, J=8.9 Hz, 1H), 4.37 (d, J=18.3 Hz, 1H), 3.31–2.94 (m, 3H), 0.94 (s, 9H), 0.19 (s, 3H), −0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 142.6, 130.2, 128.4, 128.2, 127.9, 125.5, 125.3, 120.8, 115.1, 32.5, 27.1, 25.9, 17.7, −6.6, −6.9; IR (KBr) V_{max} cm^{-1}: 3535, 3525, 2953, 2929, 2856, 1595, 1496, 1453, 1362, 1249, 1165, 1089, 828, 752, 699; HRMS (ESIMS) calcd for $C_{20}H_{32}NOSi^+$ $[M+NH_4]^+$330.2248, found 330.2240.

*4.2.9. 1-((tert-Butyldimethylsilyl)methyl)naphthalen-2-ol (**9b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J=8.0, 3.5 Hz, 1H), 7.88–7.80 (m, 1H), 7.63–7.58 (m, 1H), 7.56–7.49 (m, 1H), 7.43–7.37 (m, 1H), 7.09 (dd, J=8.7, 1.6 Hz, 1H), 5.27 (s, 1H), 2.63 (d, J=3.4 Hz, 2H), 1.14 (dd, J=3.1, 2.3 Hz, 9H), −0.04 (dd, J=3.5, 2.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 133.1, 129.4, 128.5, 125.5, 123.8, 122.8, 119.2, 117.4, 26.6, 17.1, 10.7, −5.5; IR (KBr) 3546, 3428, 2952, 2928, 2856, 1624, 1600, 1513, 1467, 1353, 1259, 1150, 934, 829, 806, 745 cm^{-1}; HRMS (ESIMS) calcd for $C_{17}H_{28}NOSi^+$ $[M+NH_4]^+$ 290.1935, found 290.1931.

*4.2.10. (E)-2-(1-(tert-Butyldimethylsilyl)prop-1-en-1-yl)phenol (**10b**).* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.11 (m, 1H), 6.97–6.88 (m, 3H), 6.48 (q, J=6.5 Hz, 1H), 5.00 (d, J=2.5 Hz, 1H), 1.63 (d, J=6.5 Hz, 3H), 0.87 (d, J=1.3 Hz, 9H), 0.15 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.1, 138.1, 128.4, 127.9, 127.5, 120.1, 114.6, 26.9, 17.4, 16.4, −4.8, −5.7; IR (KBr) 3532, 2955, 2930, 2856,

1595, 1577, 1481, 1460, 1338, 1248, 1205, 1034, 901, 829, 754 cm^{-1}; HRMS (ESIMS) calcd for $C_{15}H_{23}OSi^-$ $[M-H]^-$ 247.1525, found 247.1525.

*4.2.11. (E)-2-(1-(tert-Butyldimethylsilyl)hex-1-en-1-yl)phenol (**12b**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (ddd, J=12.5, 6.3, 3.6 Hz, 1H), 6.94–6.86 (m, 3H), 6.35 (t, J=6.9 Hz, 1H), 4.97 (s, 1H), 1.93 (ddd, J=14.7, 7.0, 3.4 Hz, 2H), 1.46–1.35 (m, 2H), 1.10 (t, J=6.8 Hz, 2H), 0.88 (s, 9H), 0.85 (d, J=7.4 Hz, 3H), 0.14 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 149.1, 137.0, 128.5, 128.3, 127.4, 120.0, 114.5, 32.5, 26.9, 25.9, 22.2, 17.4, 13.7, −4.7, −5.7; IR (KBr) 3532, 2957, 2930, 2858, 1581, 1482, 1459, 1338, 1251, 1204, 1170, 1035, 922, 832, 754, 664 cm^{-1}; HRMS (ESIMS) calcd for $C_{18}H_{29}OSi^-$ $[M-H]^-$ 289.1995, found 289.1993.

*4.2.12. (E)-2-(1-(tert-Butyldimethylsilyl)-3-phenylprop-1-en-1-yl) phenol (**13b**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J=13.8, 6.2 Hz, 2H), 7.25–7.11 (m, 4H), 7.00–6.86 (m, 3H), 6.49 (dd, J=14.2, 6.8 Hz, 1H), 5.01 (s, 1H), 3.30 (qd, J=15.5, 7.0 Hz, 2H), 0.89 (s, 9H), 0.16 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 146.6, 143.1, 139.7, 137.7, 128.5, 128.4, 127.9, 127.7, 126.1, 120.2, 114.8, 36.8, 26.9, 17.5, −4.8, −5.8. HRMS (ESIMS) calcd for $C_{21}H_{27}OSi^-$ $[M-H]^-$ 323.1837, found 323.1841.

4.3. General procedure for lithiation/retro-Brook rearrangement/electrophile trapping reaction of 1a

A solution of silane **1a** (1 mmol) in anhydrous THF (10 mL) was cooled to −78 °C under Ar. LDA (4 mmol, 2 M) was added at −78 °C slowly under stirring. The mixture was allowed to warm up to room temperature slowly, then heated to reflux and refluxed for 24 h. The resulting mixture was cooled to room temperature and then an excess of the corresponding electrophile was added. The mixture was stirred another 12 h and quenched with NH_4Cl. The layers were separated and the aqueous layer was extracted with ethyl acetate (three times). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. Concentration under reduced pressure gave a residue, which was purified by flash column chromatography to afford the product **e**.

*4.3.1. tert-Butyldimethyl(2-((triethylsilyl)oxy)benzyl)silane (**1e**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, J=5.2 Hz, 1H), 6.95 (d, J=7.6 Hz, 1H), 6.83 (t, J=7.3 Hz, 1H), 6.77 (d, J=7.9 Hz, 1H), 2.11 (s, 2H), 1.03 (t, J=7.9 Hz, 9H), 0.96 (s, 9H), 0.81 (q, J=7.9 Hz, 6H), −0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 131.2, 129.9, 124.7, 120.6, 117.8, 26.6, 16.86, 16.0, 6.8, 5.4, −6.4; IR (KBr) 2955, 2880, 1580, 1489, 1465, 1413, 1362, 1256, 921, 833, 747 cm^{-1}; HRMS (ESIMS) calcd for $C_{19}H_{40}NOSi_2^+$ $[M+NH_4]^+$354.2643, found 354.2645.

*4.3.2. tert-Butyl(2-(methoxymethoxy)benzyl)dimethylsilane (**2e**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.03 (m, 3H), 6.93 (t, J=7.1 Hz, 1H), 5.21 (s, 2H), 3.54 (d, J=1.6 Hz, 3H), 2.19 (s, 2H), 1.06–0.98 (m, 9H), −0.02 to −0.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 130.0, 129.7, 125.0, 121.4, 113.7, 94.7, 56.0, 26.5, 16.0, −6.2; IR (KBr) 2952, 2930, 2856, 1585, 1491, 1466, 1235, 1158, 1077, 1009, 924, 838, 751 cm^{-1}; HRMS (ESIMS) calcd for $C_{15}H_{30}NO_2Si^+$ $[M+NH_4]^+$284.2040, found 284.2044.

*4.3.3. (2-(Allyloxy)benzyl)(tert-butyl)dimethylsilane (**3e**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.10–6.97 (m, 2H), 6.93–6.77 (m, 2H), 6.17–6.00 (m, 1H), 5.45 (dd, J=17.3, 1.3 Hz, 1H), 5.28 (dt, J=9.2, 4.6 Hz, 1H), 4.51 (d, J=5.1 Hz, 2H), 2.16 (s, 2H), 0.95 (s, 9H), −0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 133.7, 129.6, 124.8, 120.3, 116.8, 110.9, 68.4, 26.5, 16.9, 15.9, −6.4; IR (KBr) 3402, 2927, 2855, 1700, 1640, 1461, 1408, 1243, 1090, 1024, 996, 916, 829, 806, 749 cm^{-1}; HRMS (ESIMS) calcd for $C_{16}H_{30}NOSi^+$ $[M+NH_4]^+$ 280.2091, found 280.2095.

*4.3.4. tert-Butyldimethyl(2-(oxiran-2-ylmethoxy)benzyl)silane (**4e**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.11–7.01 (m, 2H), 6.88 (t, J=7.4 Hz, 1H), 6.79 (d, J=8.1 Hz, 1H), 4.22–4.15 (m, 1H), 3.96 (dd, J=10.9, 5.6 Hz, 1H), 3.43–3.35 (m, 1H), 2.96–2.89 (m, 1H), 2.77 (dd, J=5.0, 2.6 Hz, 1H), 2.18 (s, 2H), 0.98 (s, 9H), −0.09 (d, J=3.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 129.7, 124.9, 120.8, 110.8, 68.6, 50.2, 44.6, 26.5, 16.9, 15.9, −6.4; IR (KBr) 2928, 2856, 1591, 1492, 1454, 1242, 1159, 1048, 918, 830, 748 cm^{-1}; HRMS (ESIMS) calcd for $C_{16}H_{30}NO_2Si^+$ $[M+NH_4]^+$ 296.2040, found 296.2047.

*4.3.5. tert-Butyl(2-methoxybenzyl)dimethylsilane(**5e**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14–7.09 (m, 1H), 7.04 (dd, J=4.9, 2.3 Hz, 1H), 6.92–6.81 (m, 2H), 3.83 (d, J=2.3 Hz, 3H), 2.17 (d, J=3.5 Hz, 2H), 0.99 (d, J=4.1 Hz, 9H), −0.08 (d, J=4.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 129.5, 129.5, 124.9, 120.2, 109.7, 54.8, 26.5, 16.9, 16.1, −6.3; IR (KBr) 2928, 2856, 1593, 1492, 1469, 1240, 1178, 1082, 1051, 839, 748, 698 cm^{-1}; HRMS (ESIMS) calcd for $C_{15}H_{30}NOSi^+$ $[M+NH_4]^+$ 268.2091, found 268.2091.

*4.3.6. 2-((tert-Butyldiphenylsilyl)methyl)-4-methylphenol (**4d**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.61 (d, J=1.6, 4H), 7.45–7.42 (m, 2H), 7.38–7.35 (m, 4H), 6.72–6.69 (dd, J=8.2, 2.0 Hz, 1H), 6.56–6.55 (d, J=1.6 Hz, 1H), 6.51–6.49 (d, J=8 Hz, 1H), 4.24 (s, 1H), 2.73 (s, 2H), 2.07 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 136.3, 134.6, 131.5, 129.5, 129.2, 127.4, 125.9, 125.5, 115.4, 27.8, 20.4, 18.6, 14.0; HRMS (ESIMS) calcd for $C_{24}H_{32}NOSi^+$ $[M+NH_4]^+$ 378.2248, found 378.2244.

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Supplementary data

NMR spectra (^1H and ^{13}C) for all products. This material is available free of charge. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.11.024.

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