Nickel(II)-Catalyzed Reductive Silylation of Alkenyl Methyl Ethers for the Synthesis of Alkyl Silanes

(Supporting Information)

Xiaodong Qiu,* Li Zhou, Haoran Wang, Lingyi Lu, Yong Ling and Yanan Zhang*

School of Pharmacy, Nantong University, Nantong 226001, China

Email: qiuxiaodong@ntu.edu.cn; yznj00@outlook.com

CONTENTS

1. General Information.	2
2. General Procedure for Synthesis of Alkenyl Methyl Ethers	2
3. Experimental Procedure for the Synthesis of Compound 9	7
4. General Procedure for Reductive Silylation of Alkenyl Methy	71
Ethers	8
5. Experimental Procedure for Mechanistic Studies	19
6. Isolation of Quantification of Disiloxane	25
7. References	25
8. Spectral data	27

1. General Information.

Unless otherwise noted, all reactions were performed under an nitrogen atmosphere using flame-dried glassware. Toluene and THF were distilled over Na. 1,4-dioxane was purchased as anhydrous solvent and used directly. All new compounds were fully characterized. NMR-spectra were recorded on Bruker AV-300, ARX-400 MHz or a ARX-600 Associated. ¹H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26), methanol (δ 3.30), or DMSO (δ 2.50) if collected in CDCl₃, CD₃OD, or DMSO-d⁶. ¹³C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.0) methanol (δ 49.0) or DMSO (δ 39.5) if collected in CDCl₃ (the carbon attached to B was not observed), CD₃OD, DMSO-d⁶. ¹H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doubletof doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doubletof quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25 mL Schlenk tubes with Teflon screw caps under nitrogen. B₂Pin₂ was vacuumized under room temperature for 12 h before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Compounds 1a-1e, 1g-1h, 1j, 1l-1o, 1q, 1s and 5l,¹ 1i, 1r and 5h,² 1k,³ 1t,⁴ 1v,⁵ 1w,⁶ 1x,⁷ 5b,⁸ 5f,⁹ 7a, 7b,¹⁰ and 7e¹¹ were prepared according to litriture reports.

2. General Procedure for Synthesis of Alkenyl Methyl Ethers

$$R-CHO + MeO PPh_{3} \xrightarrow{t-BuOK} R \xrightarrow{CI} OMe$$

$$THF, 0 °C - rt$$

$$1, 5 or 7$$

$$E/Z$$

To a flame dried flask was added (methoxymethyl)triphenylphosphonium chloride (6.0 mmol, 2.06 g) and *t*-BuOK (6.5 mmol, 0.73 g), the flask was vacuumed and refilled with nitrogen three times and put under the ice bath. 15 mL anhydrous THF was added and the mixture was stirred for 30 min. After that, the solution of aldehyde (5.0 mmol) in THF (5 mL) was added dropwise into the reaction mixture, then the reaction was stirred under room temperature overnight. The reaction was monitored by TLC. After the aldehyde was dispeared, 30 mL water was added and stirred for another 5 min. The aqueous phase

was extracted by ethyl acetate and the combined organic phase was dried over anhydrous sodium sulfate. The mixture was then filtered and the solvent was removed under reduced pressure. Further purification through flash chromatography using petroleum ether and ethyl acetate as the eluent provided the alkenyl methyl ether products as a mixture with both E and Z isomers.

2-(4-(2-Methoxyvinyl)phenyl)pyridine (1f)



Compound **1f** was prepared from 4-(pyridin-2-yl)benzaldehyde in 91% yield as a pale yellow solid (962 mg). The spectral data were given for the mixture of both (*E*)-**1f** and (*Z*)-**1f** (E:Z = 54:46). ¹H NMR (400 MHz, CDCl₃) δ 8.75 – 8.60 (m, 1.81H), 8.01 – 7.86 (m, 3.66H), 7.79 –

7.62 (m, 5.35H), 7.39 – 7.29 (m, 1.94H), 7.24 – 7.09 (m, 2.77H), 6.20 (d, J = 7.0 Hz, 0.87H), 5.86 (d, J = 13.0 Hz, 1H), 5.28 (d, J = 7.1 Hz, 0.86H), 3.82 (s, 2.59H), 3.72 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.3, 157.1, 149.58, 149.57, 149.4, 148.6, 137.2, 136.7, 136.65, 136.61, 136.56, 136.4, 128.5, 127.1, 126.6, 125.3, 121.8, 121.7, 120.2, 120.1, 105.2, 104.6, 60.8, 56.6. HRMS m/z (ESI) calcd for C₁₄H₁₄NO (M + H)⁺ 212.1070, found 212.1068.

4-(2-Methoxyvinyl)-*N*,*N*-dimethylbenzamide (1p)

OMe



Compound **1p** was prepared from 4-formyl-*N*,*N*-dimethylbenzamide in 88% yield as a white solid (900 mg). The spectral data were given for the mixture of both (*E*)-**1p** and (*Z*)-**1p** (*E*:*Z* = 59:41). ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.54 (m, 1.42H),

7.38 – 7.30 (m, 3.46H), 7.27 – 7.20 (m, 1.99H), 7.09 (d, J = 13.0 Hz, 0.99H), 6.19 (d, J = 7.0 Hz, 0.69H), 5.80 (d, J = 13.0 Hz, 1H), 5.23 (d, J = 7.0 Hz, 0.69H), 3.80 (s, 2.05H), 3.70 (s, 3H), 3.16 – 2.94 (m, 11.10H). ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 171.6, 149.8, 148.9, 137.9, 137.3, 133.2, 133.1, 127.8, 127.7, 127.2, 124.7, 105.0, 104.4, 60.8, 56.6, 39.6, 35.4. HRMS m/z (ESI) calcd for C₁₂H₁₆NO₂ (M + H)⁺ 206.1176, found 206.1178.

9-(2-Methoxyvinyl)anthracene (1u)



E/Z

Compound 1u was prepared from anthracene-9-carbaldehyde in 84% yield as a yellow solid (979 mg). The spectral data were given for the mixture of both (*E*)-

1u and (*Z*)-**1u** (*E*:*Z* = 56:44). ¹H NMR (400 MHz, CDCl₃) δ 8.46 – 8.36 (m, 3.79H), 8.31 – 8.24 (m, 1.52H), 8.06 – 7.98 (m, 3.52H), 7.56 – 7.45 (m, 7.13H), 6.79 (d, *J* = 13.1 Hz, 0.98H), 6.60 (d, *J* = 6.9 Hz, 0.77H), 6.44 (d, *J* = 13.0 Hz, 1H), 6.02 (d, *J* = 6.9 Hz, 0.77H), 3.95 (s, 3H), 3.64 (s, 2.31H). ¹³C NMR (101 MHz, CDCl₃) δ 152.8, 148.5, 131.5, 131.4, 130.5, 130.1, 129.6, 129.4, 128.6, 128.5, 126.7, 126.2, 126.1, 125.7, 125.1, 125.01, 124.99, 124.9, 101.3, 98.9, 59.9, 56.5. HRMS m/z (ESI) calcd for C₁₇H₁₅O (M + H)⁺ 235.1117, found 235.1115.

2-(2-Methoxyvinyl)furan (5a)



Compound **5a** was prepared from furan-2-carbaldehyde in 74% yield as a colorless oil (455 mg). The spectral data were given for the mixture of both (*E*)-**5a** and (*Z*)-**5a** (*E*:*Z* = 63:37). Due to the low boil point of compound **5a**, the NMR spectrum contained some petroleum ether signals and it had no effect to the

reaction. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 1.5 Hz, 0.58H), 7.25 (d, *J* = 1.6 Hz, 0.95H), 7.08 (d, *J* = 12.9 Hz, 1.02H), 6.49 (d, *J* = 3.3 Hz, 0.58H), 6.39 (dd, *J* = 3.4, 1.9 Hz, 0.59H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 0.98H), 6.08 (d, *J* = 6.8 Hz, 0.59H), 6.01 (d, *J* = 3.2 Hz, 0.97H), 5.67 (d, *J* = 12.9 Hz, 1H), 5.36 (d, *J* = 6.8 Hz, 0.59H), 3.80 (s, 1.80H), 3.66 (s, 3.07H). ¹³C NMR (101 MHz, CDCl₃) δ 151.6, 150.9, 148.8, 146.2, 140.1, 139.9, 111.3, 111.0, 107.7, 104.0, 96.1, 95.4, 60.7, 56.5. HRMS m/z (ESI) calcd for C₇H₉O₂ (M + H)⁺ 125.0597, found 125.0597.

2-(2-Methoxyvinyl)-6-methylpyridine (5c)



136.5, 119.9, 116.8, 105.2, 56.7, 24.5. HRMS m/z (ESI) calcd for $C_9H_{12}NO (M + H)^+$ 150.0913, found 150.0912.

2-(2-Methoxyvinyl)-1-methyl-1H-imidazole (5d)

OMe

5d E/Z Compound **5d** was prepared from 1-methyl-1*H*-imidazole-2-carbaldehyde in 77% yield as a colorless oil (530 mg). The spectral data were given for the mixture

of both (*E*)-**5d** and (*Z*)-**5d** (*E*:*Z* = 51:49). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (s, 0.95H), 7.49 (s, 0.93H), 7.37 (s, 0.97H), 7.19 (s, 0.99H), 6.79 (d, *J* = 13.0 Hz, 0.98H), 5.98 (d, *J* = 6.4 Hz, 0.96H), 5.57 (d, *J* = 13.0 Hz, 1H), 5.16 (d, *J* = 6.4 Hz, 0.96H), 3.84 (s, 2.92H), 3.82 (s, 3.01H), 3.73 (s, 2.93H), 3.59 (s, 3.08H). ¹³C NMR (101 MHz, CDCl₃) δ 147.3, 145.3, 138.5, 136.1, 128.7, 126.1, 117.6, 116.6, 96.2, 94.7, 60.0, 56.2, 38.7, 38.6. HRMS m/z (ESI) calcd for C₇H₁₁N₂O (M + H)⁺ 139.0866, found 139.0864.

5-(2-Methoxyvinyl)pyrimidine (5e)

Compound **5e** was prepared from pyrimidine-5-carbaldehyde in 92% yield as a colorless oil (628 mg). The spectral data were given for the mixture of both (*E*)-**5e** *E/Z* **5e** and (*Z*)-**5e** (*E*:*Z* = 61:39). ¹H NMR (400 MHz, CDCl₃) δ 8.98 – 8.92 (m, 1.59H), 8.87 (s, 1.26H), 8.59 (s, 1.94H), 7.12 (d, *J* = 13.1 Hz, 1H), 6.35 (d, *J* = 6.8 Hz, 0.65H), 5.65 (d, *J* = 13.1 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 0.65H), 3.84 (s, 1.94H), 3.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.8, 155.4, 155.3, 152.8, 151.4, 151.3, 130.5, 130.2, 98.5, 97.8, 61.1, 56.8. HRMS m/z (ESI) calcd for C₇H₉N₂O (M + H)⁺ 137.0709, found 137.0708.

2-(2-Methoxyvinyl)quinoline (5g)



Compound **5g** was prepared from quinoline-2-carbaldehyde in 82% yield as a colorless oil (759 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.92 (m, 2H), 7.72 – 7.66 (m, 2H), 7.63 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.40 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 6.08 (d, J = 12.9

Hz, 1H), 3.77 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.0, 154.3, 148.0, 136.0, 129.4, 128.4, 127.4, 126.5, 125.1, 118.5, 105.9, 56.8. HRMS m/z (ESI) calcd for C₁₂H₁₂NO (M + H)⁺ 186.0913, found 186.0911.

4-(2-Methoxyvinyl)-1*H*-indole (5i)



Compound **5i** was prepared from 1*H*-indole-4-carbaldehyde in 73% yield as a pale yellow solid (634 mg). The spectral data were given for the mixture of both (*E*)-**5i** and (*Z*)-**5i** (*E*:*Z* = 43:57). ¹H NMR (400 MHz, CDCl₃) δ 8.25 – 7.95 (m, 1.64H), 7.77 (dd, *J* = 6.4, 1.9 Hz, 0.97H), 7.25 – 7.11 (m, 5.61H), 7.07 (d, *J* = 7.2 Hz, 0.76H), 6.70 – 6.62 (m, 1.74H), 6.30 (d, *J* = 7.0 Hz, 1H), 6.21 (d, *J* = 12.9 Hz, 0.76H), 5.70 (d, *J* = 7.0 Hz,

1H), 3.83 (s, 3H), 3.78 (s, 2.31H). ¹³C NMR (101 MHz, CDCl₃) & 149.3, 148.0, 136.0, 135.7, 128.5, 127.6, 126.3, 125.5, 123.8, 123.4, 122.24, 122.17, 119.5, 115.8, 108.8, 108.7, 103.5, 102.7, 101.1, 101.0, 60.6, 56.5. HRMS m/z (ESI) calcd for $C_{11}H_{12}NO (M + H)^+$ 174.0913, found 174.0911.

7-(2-Methoxyvinyl)-1*H*-indole (5j)

ÒMe **5j** E/Z

Compound 5j was prepared from 1*H*-indole-7-carbaldehyde in 66% yield as a pale yellow solid (570 mg). The spectral data were given for the mixture of both (E)-5j and (Z)-5j (E:Z = 34:66). ¹H NMR (400 MHz, CDCl₃) δ 9.54 (brs, 0.96H), 8.15 (brs, 0.46H), 7.58 - 7.51 (m, 0.93H), 7.51 - 7.45 (m, 0.48H), 7.21 (t, J = 2.8 Hz, 1.13H), 7.15 (t, J = 2.8 Hz, 1.13H) 2.8 Hz, 0.50H), 7.11 – 7.00 (m, 3.43H), 6.54 (dd, J = 3.1, 2.2 Hz, 1.47H), 6.06 (d, J = 7.3 Hz, 1H), 6.00 (d, J = 12.8 Hz, 0.51H), 5.46 (d, J = 7.3 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 1.52H). ¹³C

119.69, 119.5, 119.0, 118.9, 118.6, 105.0, 103.1, 102.3, 100.6, 60.6, 56.7. HRMS m/z (ESI) calcd for $C_{11}H_{12}NO (M + H)^+$ 174.0913, found 174.0911.

NMR (101 MHz, CDCl₃) & 149.7, 144.4, 133.6, 133.1, 128.3, 127.9, 124.0, 123.6, 123.1, 120.1, 119.74,

3-(2-Methoxyvinyl)-1-methyl-1*H*-pyrrolo[2,3-b]pyridine (5k)



Compound 5k was prepared from 1-methyl-1H-pyrrolo[2,3-b]pyridine-3carbaldehyde in 85% yield as a yellow solid (796 mg). The spectral data were given for the mixture of both (E)-5k and (Z)-5k (E:Z = 47:53). ¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.29 (m, 1.79H), 7.98 – 7.92 (m, 1.89H), 7.60 (s, 0.85H), 7.11 - 6.99 (m, 3.72H), 6.16 (d, J = 6.5 Hz, 1H), 5.92 (d, J = 13.0 Hz, 0.89H),

5.50 (dd, *J* = 6.5, 0.6 Hz, 1H), 3.87 (s, 2.95H), 3.84 (s, 2.65H), 3.82 (s, 3.03H), 3.70 (s, 2.67H). ¹³C NMR (101 MHz, CDCl₃) & 148.1, 147.4, 147.0, 145.3, 143.0, 142.8, 128.2, 127.8, 127.1, 125.1, 119.3, 118.4, 115.2, 115.1, 109.5, 108.5, 97.3, 96.4, 60.3, 56.4, 31.1, 31.0. HRMS m/z (ESI) calcd for $C_{11}H_{13}N_2O$ (M + H)⁺ 189.1022, found 189.1021.

tert-Butyl 4-(methoxymethylene)piperidine-1-carboxylate (7c)



Compound 7c was prepared from tert-butyl 4-oxopiperidine-1-carboxylate in 85% yield as a colorless oil (966 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.82 (s, 1H), 3.53 (s, 3H), 3.34 (d, J = 5.2 Hz, 4H), 2.21 (brs, 2H), 2.02 – 1.90 (m,

2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) & 154.7, 140.5, 113.5, 79.3, 59.3, 46.0, 44.0, 29.5, 28.4,

25.1. HRMS m/z (ESI) calcd for $C_{12}H_{21}NNaO_3$ (M + Na)⁺ 250.1414, found 250.1412.

1-benzyl-4-(methoxymethylene)piperidine (7d)



3. Experimental Procedure for the Synthesis of Compound 9



Compound **9'** was synthesized according to the literature report.¹² To a flame dried 50 mL Schlenk tube were added acetophenone (2.0 mmol, 240 mg), TsNHNH₂ (2.0 mmol, 372 mg), TBAI (0.4 mmol, 147.6 mg), TBHP (70 wt.-% in H₂O, 12.0 mmol), and the mixture was stirred in MeOH (8 mL) at room temperature for 16 h. Then the reaction mixture was diluted with diethyl ether (40 mL), washed with saturated Na₂S₂O₃, then dried with anhydrous Na₂SO₄, and filtered. Then solvent was removed under vacuum, and the crude product was purified by flash chromatography with silica gel by gradient elution with ethyl acetate in petroleum ether to obtain the corresponding product **9'** (242 mg, 81%).

To a flame dried flask was added (methoxymethyl)triphenylphosphonium chloride (1.62 mmol, 901 mg) and t-BuOK (1.78 mmol, 200 mg), the flask was vacuumed and refilled with nitrogen three times and put under the ice bath. 5 mL anhydrous THF was added and the mixture was stirred for 30 min. After that, the solution of **9**' (1.62 mmol, 242 mg) in THF (2 mL) was added dropwise into the reaction mixture, then the reaction was stirred under room temperature overnight. The reaction was monitored by TLC. After the aldehyde was dispeared, 10 mL water was added and stirred for another 5 min. The aqueous phase was extracted by ethyl acetate and the combined organic phase was dried over anhydrous sodium sulfate. The mixture was then filtered and the solvent was removed under reduced pressure.

Further purification through flash chromatography using petroleum ether and ethyl acetate as the eluent provided the alkenyl methyl ether product **9** (235 mg, 83%) as a mixture with both *E* and *Z* isomers. The spectral data were given for the mixture of both (*E*)-**9** and (*Z*)-**9** (*E*:*Z* = 57:43). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.9 Hz, 1.47H), 7.43 – 7.26 (m, 5.60H), 7.24 – 7.16 (m, 1.73H), 6.55 (s, 1H), 6.36 (s, 0.74H), 4.39 (s, 2.06H), 4.14 (s, 1.53H), 3.80 – 3.71 (m, 5.32H), 3.38 – 3.30 (m, 5.35H). ¹³C NMR (101 MHz, CDCl₃) δ 148.9, 148.9, 138.4, 136.1, 128.4, 128.0, 127.7, 126.3, 126.2, 125.5, 115.5, 112.5, 73.9, 66.7, 60.6, 60.3, 57.5, 57.0. HRMS m/z (ESI) calcd for C₁₁H₁₄NaO₂ (M + H)⁺ 201.0886, found 21.0885.

4. General Procedure for Reductive Silylation of Alkenyl Methyl Ethers



To a flame dried 25 mL Schlenk tube were added Ni(acac)₂ (0.03 mmol, 7.7 mg), IMes·HCl (0.03 mmol, 10.2 mg) and Zn (0.06 mmol, 3.9 mg) and K₃PO₄ (0.45 mmol, 95.4 mg). The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (1.5 mL). Substrates **1**, **5**, **or 7** (0.3 mmol), **2** (0.6 mmol, 145.2 mg) and HSiEt₃ (0.9 mmol, 104.4 mg) were also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, the reaction was stirred under 110 °C in the heating module for 24-48 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether and ethyl acetate as the eluent to afford the pure alkyl silane product.

Triethyl(phenethyl)silane (3a)

Substrate 1a (0.3 mmol, 40.2 mg) reacted with 2 for 24 h affording 3a as a colorless oil (50.3 mg, 76%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.25 (m, 3H), 7.24 – 7.13 (m, 2H), 2.65 – 2.56 (m, 2H), 0.95 (t, J = 7.9 Hz, 9H), 0.92 – 0.85 (m, 2H), 0.55 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 145.6, 128.3, 127.7, 125.4, 30.0, 13.6, 7.4, 3.2. HRMS m/z (ESI) calcd for C₁₄H₂₅Si (M + H)⁺ 221.1720, found 221.1726. The spectra data are consistent with reports in the literature.¹³

Triethyl(4-methylphenethyl)silane (3b)



Substrate 1b (0.3 mmol, 44.4 mg) reacted with 2 for 48 h affording 3b SiEt₃ as a colorless oil (51.3 mg, 73%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (s, 4H), 2.64 – 2.54 (m, 2H), 2.34 (s, 3H), 0.98 (t, J =7.9 Hz, 9H), 0.92 - 0.85 (m, 2H), 0.57 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 142.6, 134.8, 128.9, 127.5, 29.5, 21.0, 13.8, 7.5, 3.2. HRMS m/z (ESI) calcd for $C_{15}H_{27}Si$ (M + H)⁺ 235.1877, found 235.1875. The spectra data are consistent with reports in the literature.¹³

Triethyl(3-methylphenethyl)silane (3c)



(4-(tert-Butyl)phenethyl)triethylsilane (3d)



Substrate 1d (0.3 mmol, 57.0 mg) reacted with 2 for 24 h affording 3d as a colorless oil (71.1 mg, 86%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 2.66 – 2.57 (m, 2H), 1.34 (s, 9H), 0.99 (t, J = 8.0 Hz, 9H), 0.95 - 0.88 (m, 2H), 0.59 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 142.5, 127.3, 125.1, 34.3, 31.4, 29.4, 13.5, 7.5, 3.3. HRMS m/z (ESI)

calcd for $C_{18}H_{33}Si (M + H)^+ 277.2346$, found 277.2344.

(2-([1,1'-Biphenyl]-4-yl)ethyl)triethylsilane (3e)



Substrate 1e (0.3 mmol, 63.0 mg) reacted with 2 for 24 h affording 3e as a colorless oil (82.5 mg, 93%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.47 – 7.41 (m, 2H),

7.37 – 7.27 (m, 3H), 2.72 – 2.63 (m, 2H), 1.04 – 0.91 (m, 11H), 0.60 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 141.2, 138.4, 128.7, 128.1, 127.04, 126.97, 126.9, 29.7, 13.6, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{20}H_{29}Si (M + H)^+ 297.2033$, found 297.2029.

2-(4-(2-(Triethylsilyl)ethyl)phenyl)pyridine (3f)



Substrate **1f** (0.3 mmol, 63.3 mg) reacted with **2** for 24 h affording **3f** as a colorless oil (75.9 mg, 85%). Eluent: petroleum ether : ethyl acetate = $50 : 1. {}^{1}$ H NMR (400 MHz, CDCl₃) δ 8.68 (dt, *J* = 4.8, 1.4 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H),

7.19 (ddd, J = 5.6, 4.8, 2.8 Hz, 1H), 2.72 – 2.63 (m, 2H), 1.03 – 0.88 (m, 11H), 0.58 (q, J = 7.9 Hz, 6H).
¹³C NMR (101 MHz, CDCl₃) δ 157.5, 149.5, 146.6, 136.7, 136.6, 128.1, 126.8, 121.7, 120.2, 29.8, 13.5,
7.4, 3.2. HRMS m/z (ESI) calcd for C₁₉H₂₈NSi (M + H)⁺ 298.1986, found 298.1983.

Triethyl(4-methoxyphenethyl)silane (3g)



(3,5-Dimethylphenethyl)triethylsilane (3h)



(3,4-Dimethoxyphenethyl)triethylsilane (3i)



Substrate **1i** (0.3 mmol, 58.2 mg) reacted with **2** for 24 h affording **3i** as a colorless oil (68.8 mg, 82%). Eluent: petroleum ether : ethyl acetate = 50 : 1. ¹H NMR (400 MHz, CDCl₃) δ 6.82 – 6.71 (m, 3H), 3.89 (s, 3H),

3.86 (s, 3H), 2.62 – 2.52 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.92 – 0.82 (m, 2H), 0.55 (q, *J* = 7.9 Hz, 6H).
¹³C NMR (101 MHz, CDCl₃) δ 148.7, 146.9, 138.3, 119.2, 111.14, 111.06, 55.9, 55.8, 29.6, 13.7, 7.5,
3.2. HRMS m/z (ESI) calcd for C₁₆H₂₉O₂Si (M + H)⁺ 281.1931, found 281.1930.

(3,5-Dimethoxyphenethyl)triethylsilane (3j)



Triethyl(3,4,5-trimethoxyphenethyl)silane (3k)



(2-(2,3-Dihydrobenzofuran-5-yl)ethyl)triethylsilane (31)



Substrate **11** (0.3 mmol, 52.8 mg) reacted with **2** for 48 h affording **31** as a colorless oil (55.1 mg, 70%). Eluent: petroleum ether : ethyl acetate = 100 : 1. ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H),

6.70 (d, J = 8.0 Hz, 1H), 4.54 (t, J = 8.6 Hz, 2H), 3.18 (t, J = 8.6 Hz, 2H), 2.58 – 2.50 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.90 – 0.79 (m,2H), 0.55 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 157.9, 137.8, 126.9, 126.8, 124.1, 108.8, 71.1, 29.8, 29.4, 14.2, 7.5, 3.3. HRMS m/z (ESI) calcd for C₁₆H₂₇OSi (M + H)⁺ 263.1826, found 263.1830.

Triethyl(4-fluorophenethyl)silane (3m)



H)⁺ 239.1626, found 239.1632. The spectra data are consistent with reports in the literature.¹³

Triethyl(4-(trifluoromethyl)phenethyl)silane (3n)

Substrate 1n (0.3 mmol, 60.6 mg) reacted with 2 for 24 h affording 3n SiEt₃ as a colorless oil (69.0 mg, 80%). Eluent: petroleum ether. ¹H NMR (400 CF 3n MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.72 – 2.62 (m, 2H), 0.97 (t, J = 7.9 Hz, 9H), 0.92 - 0.84 (m, 2H), 0.57 (q, J = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 149.7 (d, J = 1.3 Hz), 128.0, 127.8 (q, J = 32.2 Hz), 125.2 (q, J = 3.8 Hz), 124.4 (q, J = 271.6 Hz), 30.0, 13.5, 7.4, 3.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.2. HRMS m/z (ESI) calcd for $C_{15}H_{24}F_3Si (M + H)^+ 289.1594$, found 289.1582.

Methyl 4-(2-(triethylsilyl)ethyl)benzoate (30)



N,N-dimethyl-4-(2-(triethylsilyl)ethyl)benzamide (3p)



Substrate 1p (0.3 mmol, 61.5 mg) reacted with 2 for 24 h affording **3p** as a colorless oil (61.5 mg, 70%). Eluent: petroleum ether : ethyl acetate = 20 : 1. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.1 Hz,

2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.09 (s, 3H), 2.99 (s, 3H), 2.66 – 2.57 (m, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.90 - 0.83 (m, 2H), 0.55 (q, J = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 171.8, 147.2, 133.4, 127.6, 127.2, 39.6, 35.4, 29.9, 13.5, 7.4, 3.2. HRMS m/z (ESI) calcd for $C_{17}H_{30}NOSi$ (M + H)⁺ 292.2091, found 292.2088.

Triethyl(2-methylphenethyl)silane (3q)

Substrate 1q (0.3 mmol, 44.4 mg) reacted with 2 for 48 h affording 3q as a SiEt₃ colorless oil (33.1 mg, 47%). Eluent: petroleum ether. ¹H NMR (400 MHz, Me 12 3q

 $CDCl_3$) δ 7.19 – 7.03 (m, 4H), 2.62 – 2.52 (m, 2H), 2.29 (s, 3H), 0.97 (t, J = 7.9 Hz, 9H), 0.86 – 0.77 (m, 2H), 0.58 (q, J = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 143.7, 135.2, 130.1, 127.9, 126.0, 125.6, 27.4, 19.1, 12.5, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{15}H_{27}Si$ (M + H)⁺ 235.1877, found 235.1876.

N,N-diethyl-3-methoxy-4-(2-(triethylsilyl)ethyl)aniline (3r)

Substrate 1r (0.3 mmol, 70.5 mg) reacted with 2 for 24 h affording 3r SiEt₃ as a colorless oil (68.5 mg, 71%). Eluent: petroleum ether : ethyl acetate Et₂N OMe 3r = 20 : 1. ¹H NMR (400 MHz, CDCl₃) δ 7.02 (d, J = 7.9 Hz, 1H), 6.34 – 6.24 (m, 2H), 3.84 (s, 3H), 3.36 (q, J = 7.0 Hz, 4H), 2.62 – 2.46 (m, 2H), 1.19 (t, J = 7.1 Hz, 6H), 1.00 (t, J = 7.9 Hz, 9H), 0.90 - 0.81 (m, 2H), 0.59 (q, J = 7.9 Hz, 6H).¹³C NMR (101 MHz, CDCl₃) δ 158.0, 147.4, 129.1, 121.6, 104.4, 96.2, 55.1, 44.6, 23.2, 12.6, 12.1, 7.4, 3.3. HRMS m/z (ESI) calcd for $C_{19}H_{36}NOSi (M + H)^+ 322.2561$, found 322.2558.

Triethyl(2-(naphthalen-2-yl)ethyl)silane (3s)



SiEt₃ a colorless oil (72.8 mg, 90%). Eluent: petroleum ether. ¹H NMR (400 3s MHz, CDCl₃) δ 7.86 – 7.75 (m, 3H), 7.66 (s, 1H), 7.51 – 7.35 (m, 3H), 2.86 - 2.76 (m, 2H), 1.08 - 0.96 (m, 11H), 0.62 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 133.7, 131.9, 127.8, 127.6, 127.4, 127.0, 125.8, 125.2, 124.9, 30.2, 13.5, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{18}H_{27}Si (M + H)^+ 271.1877$, found 271.1882. The spectra data are consistent with reports in the literature.¹³

Substrate 1s (0.3 mmol, 55.2 mg) reacted with 2 for 24 h affording 3s as

Triethyl(2-(naphthalen-1-yl)ethyl)silane (3t)



Substrate 1t (0.3 mmol, 55.2 mg) reacted with 2 for 24 h affording 3t as a colorless oil (69.0 mg, 85%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.45 – 7.34 (m, 2H), 3.13 – 3.04 (m, 2H), 1.07 – 0.98 (m, 11H), 0.65 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 133.9, 131.5, 128.8, 126.2, 125.7, 125.6,

125.3, 124.7, 123.6, 27.2, 13.2, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{18}H_{27}Si (M + H)^+ 271.1877$, found 271.1872.

(2-(Anthracen-9-yl)ethyl)triethylsilane (3u)



14.2, 7.7, 3.3. HRMS m/z (ESI) calcd for $C_{22}H_{29}Si (M + H)^+$ 321.2033, found 321.2029.

(2,2-Diphenylethyl)triethylsilane (3v)

Substrate 1v (0.3 mmol, 63.0 mg) reacted with 2 for 48 h affording 3v as a colorless Ph SiEt₃ oil (44.4 mg, 50%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.20 (m, 8H), 7.17 – 7.10 (m, 2H), 4.06 (t, J = 7.9 Hz, 1H), 1.41 (d, J = 7.9 Hz, 3H), 0.82 (t, J = 7.9 Hz, 9H), 0.33 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 147.3, 128.3, 127.5, 125.9, 47.1, 19.0, 7.3, 3.4. HRMS m/z (ESI) calcd for C₂₀H₂₈NaSi (M + Na)⁺ 319.1852, found 319.1852. The spectra data are consistent with reports in the literature.¹⁴

Triethyl(1-phenylpropan-2-yl)silane (3w)

Substrate 1w (0.3 mmol, 44.4 mg) reacted with 2 for 48 h affording 3w as a colorless oil (42.6 mg, 61%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 2.89 (dd, *J* = 13.7, 3.4 Hz, 1H), 2.25 (dd, *J* = 13.7, 11.9 Hz, 1H), 1.16 – 1.04 (m, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.84 (d, *J* = 7.4 Hz, 3H), 0.60 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 128.8, 128.0, 125.5, 38.2, 19.2, 13.8, 7.7, 2.2. HRMS m/z (ESI) calcd for C₁₅H₂₇Si (M + H)⁺ 235.1877, found 235.1887.

1,4-Bis(2-(triethylsilyl)ethyl)benzene (3x)



4H), 0.99 (t, J = 8.0 Hz, 18H), 0.94 – 0.85 (m, 4H), 0.58 (q, J = 8.0 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 142.7, 127.6, 29.5, 13.7, 7.5, 3.3. HRMS m/z (ESI) calcd for C₂₂H₄₃Si₂ (M + H)⁺ 363.2898, found 363.2893.

Triethyl(2-(furan-2-yl)ethyl)silane (6a)

Substrate **5a** (0.3 mmol, 37.2 mg) reacted with **2** for 48 h affording **6a** as a colorless oil (40.4 mg, 64%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃)
$$\delta$$
 7.29 (d, $J = 1.0$ Hz, 1H), 6.27 (dd, $J = 3.1, 1.9$ Hz, 1H), 5.98 (dd, $J = 3.1, 1.0$ Hz, 1H), 2.67 – 2.57 (m, 2H), 1.01 – 0.85 (m, 11H), 0.53 (q, $J = 7.9$ Hz, 6H). ¹³C NMR (101 MHz, CDCl₃)

 δ 158.7, 140.5, 110.1, 103.7, 22.3, 9.5, 7.4, 3.1. HRMS m/z (ESI) calcd for C₁₂H₂₃OSi (M + H)⁺ 211.1513, found 211.1510.

(2-(Benzofuran-2-yl)ethyl)triethylsilane (6b)



a colorless oil (29.0 mg, 37%). Eluent: petroleum ether. ¹H NMR (400 MHz, SiEt₃ CDCl₃) δ 7.50 – 7.45 (m, 1H), 7.42 – 7.38 (m, 1H), 7.22 – 7.13 (m, 2H), 6b 6.38 (d, J = 1.0 Hz, 1H), 2.81 - 2.72 (m, 2H), 1.05 - 0.91 (m, 11H), 0.57 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.0, 154.6, 129.0, 123.0, 122.3, 120.1, 110.6, 100.8, 22.9, 9.4, 7.4, 3.1. HRMS m/z (ESI) calcd for $C_{16}H_{25}OSi (M + H)^+$ 261.1669, found 261.1670.

Substrate 5b (0.3 mmol, 52.2 mg) reacted with 2 for 48 h affording 6b as

2-Methyl-6-(2-(triethylsilyl)ethyl)pyridine (6c)

Substrate 5c (0.3 mmol, 44.7 mg) reacted with 2 for 24 h affording 6c as a SiEt₃ colorless oil (50.7 mg, 72%). Eluent: petroleum ether : ethyl acetate = 50 : 1. ¹H Мe 6c NMR (400 MHz, CDCl₃) δ 7.46 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 2.80 - 2.71 (m, 2H), 2.51 (s, 3H), 1.00 - 0.89 (m, 11H), 0.54 (q, J = 7.9 Hz, 6H).¹³C NMR (101 MHz, CDCl₃) δ 164.1, 157.4, 136.5, 120.2, 118.4, 32.6, 24.5, 11.7, 7.4, 3.2. HRMS m/z (ESI) calcd for $C_{14}H_{26}NSi (M + H)^+ 236.1829$, found 236.1827.

1-Methyl-2-(2-(triethylsilyl)ethyl)-1H-imidazole (6d)

Substrate **5d** (0.3 mmol, 41.4 mg) reacted with **2** for 24 h affording **6d** as a colorless oil (41.9 mg, 62%). Eluent: petroleum ether : ethyl acetate = 5 : 1. ¹H MMR (400 MHz, CDCl₃)
$$\delta$$
 7.31 (s, 1H), 7.13 (s, 1H), 3.84 (s, 3H), 2.50 – 2.41 (m, 2H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.87 – 0.77 (m, 2H), 0.53 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 138.1, 127.6, 125.3, 38.7, 18.4, 13.0, 7.4, 3.2. HRMS m/z (ESI) calcd for C₁₂H₂₅N₂Si (M + H)⁺ 225.1782, found 225.1778.

5-(2-(Triethylsilyl)ethyl)pyrimidine (6e)



3-(2-(Triethylsilyl)ethyl)quinoline (6f)



2-(2-(Triethylsilyl)ethyl)quinoline (6g)

Substrate 5g (0.3 mmol, 55.5 mg) reacted with 2 for 24 h affording 6g as a colorless oil (62.8 mg, 77%). Eluent: petroleum ether : ethyl acetate = 6g 50 : 1. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 8.3, 5.3 Hz, 2H), 7.76 (dd, J = 8.1, 1.4 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.46 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 3.02 – 2.92 (m, 2H), 1.11 – 1.02 (m, 2H), 0.98 (t, J = 7.9 Hz, 9H), 0.60 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 147.8, 136.3, 129.2, 128.7, 127.4, 126.6, 125.5, 120.7, 33.5, 12.0, 7.4, 3.2. HRMS m/z (ESI) calcd for C₁₇H₂₆NSi (M + H)⁺ 272.1829, found 272.1826. The spectra data are consistent with reports in the literature.¹⁵

1-Methyl-3-(2-(triethylsilyl)ethyl)-1*H*-indole (6h)



Substrate **5h** (0.3 mmol, 56.1 mg) reacted with **2** for 24 h affording **6h** as a colorless oil (62.4 mg, 76%). Eluent: petroleum ether : ethyl acetate = 100 : 1. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 14.8 Hz, 1H), 6.85 (s, 1H), 3.75 (s, 3H), 2.80 – 2.70 (m, 2H), 1.05 – 0.94 (m, 11H), 0.60 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 127.5, 125.3, 121.4, 119.0, 118.7, 118.4, 109.1, 32.5, 19.2, 12.2, 7.5, 3.3. HRMS m/z (ESI) calcd for C₁₇H₂₈NSi (M + H)⁺ 274.1986, found 274.1982.

4-(2-(Triethylsilyl)ethyl)-1H-indole (6i)



Substrate **5i** (0.3 mmol, 51.9 mg) reacted with **2** for 48 h affording **6i** as a colorless oil (49.1 mg, 63%). Eluent: petroleum ether : ethyl acetate = 50 : 1. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (brs, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.17 – 7.10 (m, 1H), 6.97 (d, *J* = 7.1 Hz, 1H), 6.59 (ddd, *J* = 3.2, 2.1, 1.0 Hz, 1H), 2.95 – 2.86 (m, 2H), 1.08 – 0.94 (m, 11H), 0.61 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 138.0,

135.7, 126.6, 123.4, 122.2, 118.0, 108.6, 100.9, 27.5, 12.8, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{16}H_{26}NSi$ (M + H)⁺ 260.1829, found 260.1825.

7-(2-(Triethylsilyl)ethyl)-1H-indole (6j)

Substrate **5j** (0.3 mmol, 51.9 mg) reacted with **2** for 48 h affording **6j** as a colorless oil (61.9 mg, 76%). Eluent: petroleum ether : ethyl acetate = 50 : 1. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (brs, 1H), 7.50 (dd, *J* = 6.6, 2.4 Hz, 1H), 7.22 (t, *J* = 2.8 Hz, 1H), 7.12 – SiEt₃ **6j** 7.04 (m, 2H), 6.58 (dd, *J* = 3.2, 2.0 Hz, 1H), 2.90 – 2.80 (m, 2H), 1.10 – 0.90 (m, 11H), 0.61 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 134.4, 127.62, 127.60, 123.6, 120.3, 120.0, 118.4, 103.1, 25.2, 11.2, 7.5, 3.3. HRMS m/z (ESI) calcd for C₁₆H₂₆NSi (M + H)⁺ 260.1829, found 260.1827.

1-Methyl-3-(2-(triethylsilyl)ethyl)-1*H*-pyrrolo[2,3-b]pyridine (6k)



Substrate **5k** (0.3 mmol, 56.4 mg) reacted with **2** for 24 h affording **6k** as a colorless oil (68.5 mg, 83%). Eluent: petroleum ether : ethyl acetate = $20 : 1. {}^{1}$ H NMR (400 MHz, CDCl₃) δ 8.31 (dd, J = 4.7, 1.5 Hz, 1H), 7.87 (dd, J = 7.8, 1.6 Hz, 1H), 7.02 (dd, J = 7.8, 4.7 Hz, 1H), 6.96 (d, J = 1.2 Hz, 1H), 3.83 (s, 3H), 2.77 – 2.68 (m, 3H), 1.02 – 0.92 (m, 11H), 0.58 (q, J = 7.9 Hz, 6H). 13 C NMR

(101 MHz, CDCl₃) δ 148.1, 142.6, 126.9, 125.2, 119.9, 117.0, 114.5, 30.9, 19.3, 12.0, 7.5, 3.2. HRMS m/z (ESI) calcd for C₁₆H₂₇N₂Si (M + H)⁺ 275.1938, found 275.1935.

9-Ethyl-3-(2-(triethylsilyl)ethyl)-9H-carbazole (6l)



Substrate 51 (0.3 mmol, 75.3mg) reacted with 2 for 24 h affording 61 as SiEt₃ a colorless oil (85.7 mg, 85%). Eluent: petroleum ether : ethyl acetate = 50 : 1. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 7.48 - 7.31 (m, 4H), 7.20 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 4.36 (q, J = 7.2Hz, 2H), 2.86 – 2.77 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.16 – 0.94 (m, 11H), 0.60 (q, J = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 138.3, 136.2, 125.7, 125.3, 122.9, 122.8, 120.3, 118.9, 118.4, 108.3, 108.1, 37.5, 30.0, 14.6, 13.8, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{22}H_{32}NSi$ $(M + H)^+$ 338.2299, found 338.2293.

Triethyl(4-phenylbutyl)silane (8a)

Substrate 7a (0.3 mmol, 48.6 mg) reacted with 2 for 48 h affording 8a as a SiEt₃ Ph' 8a colorless oil (47.8 mg, 64%). Eluent: petroleum ether. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 2.66 – 2.54 (m, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.41 – 1.29 (m, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.59 - 0.44 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 128.4, 128.2, 125.5, 35.70, 35.65, 23.6, 11.2, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{16}H_{29}Si$ (M + H)⁺ 249.2033, found 249.2038. The spectra data are consistent with reports in the literature.¹⁶

(2-Cyclohexylethyl)triethylsilane (8b)



0.42 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 41.0, 33.1, 31.3, 26.9, 26.5, 8.1, 7.5, 3.3. HRMS m/z (ESI) calcd for $C_{14}H_{31}Si (M + H)^+ 227.2190$, found 227.2196. The spectra data are consistent with reports in the literature.¹⁷

tert-Butyl 4-((triethylsilyl)methyl)piperidine-1-carboxylate (8c)



Substrate 7c (0.3 mmol, 37.8 mg) reacted with 2 for 48 h affording 8c as a colorless oil (45.2 mg, 48%). Eluent: petroleum ether : ethyl acetate = 40 : 1. ¹H NMR (400 MHz, CDCl₃) δ 4.02 (brs, 2H), 2.66 (t, J = 12.5 Hz, 2H),

1.70 - 1.55 (m, 3H), 1.45 (s, 9H), 1.18 - 1.04 (m, 2H), 0.92 (t, J = 7.9 Hz, 9H), 0.62 - 0.42 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 79.1, 44.2, 35.6, 32.5, 28.5, 19.3, 7.5, 4.1. HRMS m/z (ESI) calcd for C₁₇H₃₅NNaO₂Si (M + H)⁺ 336.2329, found 336.2325.

1-Benzyl-4-((triethylsilyl)methyl)piperidine (8d)



5. Experimental Procedure for Mechanistic Studies



To a flame dried 25 mL Schlenk tube were added Ni(acac)₂ (0.03 mmol, 7.7 mg), IMes·HCl (0.03 mmol, 10.2 mg) and Zn (0.06 mmol, 3.9 mg) and K₃PO₄ (0.45 mmol, 95.4 mg). The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (1.5 mL). Substrates **7e** (0.3 mmol, 44.4 mg), **2** (0.6 mmol, 145.2 mg) and HSiEt₃ (0.9 mmol, 104.4 mg) were also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, the reaction was stirred under 110 °C in the heating module for 48 h. Then the mixture was cooled to room temperature and was tested by GC-MS. After that, the solvent was removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether and ethyl acetate as the eluent to afford **8e** as a colorless oil (47.2 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.23 – 7.12 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.67 – 1.56 (m, 2H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.61 – 0.53 (m, 2H), 0.49 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 142.8, 128.4, 128.2, 125.6, 40.2, 26.1, 11.3, 7.4, 3.3. HRMS m/z (ESI) calcd for C₁₆H₂₉Si (M + H)⁺ 249.2033, found 249.2038. The spectra data are consistent with reports in the literature.¹⁸



main products detected by GC-MS

To a flame dried 25 mL Schlenk tube were added Ni(acac)₂ (0.03 mmol, 7.7 mg), IMes·HCl (0.03 mmol, 10.2 mg) and Zn (0.06 mmol, 3.9 mg) and K₃PO₄ (0.45 mmol, 95.4 mg). The tube was vacuumed and refilled with nitrogen three times followed by the addition of anhydrous toluene (1.5 mL). Substrates **9** (0.3 mmol, 53.4 mg), **2** (0.6 mmol, 145.2 mg) and HSiEt₃ (0.9 mmol, 104.4 mg) were also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, the reaction was stirred under 110 °C in the heating module for 48 h. Then the mixture was cooled to room temperature and was tested by GC-MS. A little amount of main products **10** and **11** was detected as a result (**10** was synthesized through another reported method¹⁹ and was tested by GC-MS to confirm that our product had exactly the correct structure). Due to the low yield of **10** and **11**, as well as the complexity of the reaction, we didn't go for additional purification.



GC-spectrum of the reaction above (without any further purification)





MS-spectrum of compound 10





MS-spectrum of compound 11





MS-spectrum of E/Z mixture 11'

6. Isolation of Quantification of Disiloxane





mmol, 10.2 mg) and Zn (0.06 mmol, 3.9 mg) and K_3PO_4 (0.45 mmol, 95.4 mg). The tube was vacuumed and refilled with nitrogen three times followed by the addition of new distilled toluene (1.5 mL). HSiEt₃ (0.3 mmol, 34.8 mg) and H₂O (0.15 mmol, 2.7 mg) were also added with a syringe under nitrogen atmosphere and the plug is screwed. After that, the reaction was stirred under 110 °C in the heating module for 12 h. Then the mixture was cooled to room temperature, the solvents were removed under reduced pressure and the crude product was purified through flash chromatography with petroleum ether as the eluent. Disiloxane was isolated as a colorless oil in 53% yield (19.8 mg).

7. References

- (1) Qiu, X.; L, Y.; Zhou, L.; Chen, P.; Li, F.; Zhang, Y.; Ling, Y. Org. Lett. 2020, 22, 6424.
- (2) Hostier, T.; Neouchy, Z.; Ferey, V.; Pardo, D. G.; Cossy, J. Org. Lett. 2018, 20, 1815.
- (3) Balti, M.; Efrit, M. L.; Leadbeater, N. E. Tetrahedron Lett. 2016, 57, 1804.
- (4) Gentili, P. and et. al. Chem. Eur. J. 2018, 24, 7683.
- (5) Jena, T. K.; Khan, F. A. J. Org. Chem. 2019, 84, 14270.
- (6) Cuthbertson, J.; Wilden, J. D. Tetrahedron 2015, 71, 4385.
- (7) Campa, C.; Sanchez-Ferrando, F.; Tristan-Polo, M. Nouv. J. Chim. 1985, 7, 493.
- (8) Kondo, M.; Kochi, T.; Kakiuchi, F. J. Am. Chem. Soc. 2011, 133, 32.
- (9) Brindisi, M. and et. al. Eur. J. Med. Chem. 2019, 162, 290.
- (10) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. J. Am. Chem. Soc. 2015, 137, 1400.
- (11) Zhu, Q.; Luo, Y.; Guo, Y.; Zhang, Y.; Tao, Y. J. Org. Chem. 2021, 86, 5463.
- (12) Yu, H.; Xu, Y.; Fang, Y.; Dong, R. Eur. J. Org. Chem. 2016, 5257.
- (13) Dong, J.; Yuan, X.-A.; Yan, Z.; Mu, L.; Ma, J.; Zhu, C.; Xie, J. Nat. Chem. 2021, 13, 182.
- (14) Balasubramaniam, S.; Kumar, S.; Andrews, A. P.; Varghese, B.; Jemmis, E. D.; Venugopal, A. Eur.
- J. Inorg. Chem. 2019, 28, 3265.
- (15) Li, W.; Huang, X.; You, J. Org. Lett. 2016, 18, 666.
- (16) Cui, B.; Jia, S.; Tokunaga, E.; Shibata, N. Nat. Commun. 2018, 9, 4393.
- (17) Nii, S.; Terao, J.; Kambe, N. J. Org. Chem. 2004, 69, 573.
- (18) Roy, A.; Bonetti, V.; Wang, G.; Wu, Q.; Klare, H. F. T.; Oestreich, M. Org. Lett. 2020, 22, 1213.
- (19) Andrews, R. J.; Chitnis, S. S.; Stephan, D. W. Chem. Commun. 2019, 55, 5599.

8. Spectral data



























































































































10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)












































































































