

Supporting Information

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Supporting Information

Sc(OTf)₃-Mediated Silylation of OH Funtional Group on Solid Surface: A Catalytic Grafting Method Operation at Room Temperature

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1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column Chromatography were monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60 F-254) using UV light as a visualizing agent and *p*-anisaldehyde solution, and heat as developing agent. Gas chromatographic analyses were performed on a Donam DS 6200 instrument with FID detector and a Hewlett Packard HP-5 capillary column. Low-resolution mass spectra were measured on a Hewlett Packard HP G1800A GCD system equipped with a Hewlett Packard HP-5 capillary column. ¹H NMR and ¹³C NMR were recorded on a Bruker Advance/DPX 250 (250 MHz ¹H, 62.9MHz ¹³C) and a Bruker Advance II/DPX 400 (400 MHz ¹H, 100 MHz ¹³C) spectrometers with chemical shifts reported relative to residual deuterated solvent peaks. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. ¹H NMR spectra were referenced to tetramethylsilane (δ 0.00 ppm) as an internal standard and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). ¹³C NMR spectra were referenced to the residual CDCl₃ (§ 77.26 ppm). High Resolution Mass spectra and Elementary Analyses were provided by the Organic Chemistry Research Center, Sogang University, and ¹³C CP-MAS NMR spectra (spin rate= 7 kHz) were provided by the National Instrumentation Center for Environmental Management (NICEM). Contact angles were provided by DSA10, Kruss in Technology Innovation Center for Electronic Materials (TICEM). Cyclic voltammetric measurements were performed using a EG&G Potentiostat/Galvanostat Model 263A. X-ray photoelectron spectroscopy (XPS) spectra were provided by ESCALAB250 in Busan Center, KBSI.

2. Materials

Reagent grade chemicals (allyl chloride, chlorodimethylsilane, dichloromethylsilane, 3-chloropropyltrichlorosilane, 3-chloro-2-methylpropene, magnesium turning, 3-chloropropyltriethoxysilane (**2e**), phenylacetylene, ethynylferrocene), NMR solvents (CDCl₃, CD₃CN, C₆D₆) were purchased from Aldrich Chemical Company and used as received without further purification unless otherwise stated. Chloroplatinic acid hexahydrate was purchased from STREM Chemicals. Sc(OTf)₃ (**3**) was purchased from Lancaster. Amorphous silica (40-63 μ m, 480-540 m²/g) throughout the overall experiments was purchased from Merck, and silica ball (10 μ m, 300 m²/g) was purchased from RS Tech. MCF-5F¹ and SBA-15 were synthesized by reported procedure. Dabsyl chloride was purchased from Pierce. Acetonitrile and THF were distilled by reported procedure prior to use.

3. Experimental

Scheme S1. Detection of the liberated isobutene by *in-situ* ¹H NMR.



For detecting the liberated isobutene, following *in-situ* ¹H NMR experiment was carried out. The reaction of **1** and **2b** under 2 mol% of **3** in C_6D_6 solvent was proceeded in NMR tube, and the changes of ¹H NMR signals were recorded every 15 minutes. The resulting NMR spectra are depicted in Figure S1.

Characterization Data for 2b: ¹H NMR(250 MHz, CDCl₃) δ 4.60-4.48(d, J= 30.4 Hz, 2H), 3.53-3.48(t, J= 7.0 Hz, 2H), 1.80-1.72(m, 2H), 1.71(s, 3H), 1.56(s, 2H), 0.67-0.60(m, 2H), 0.09(s, 6H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.6, 108.7, 48.2, 27.8, 27.2, 25.5, 13.3, -2.9; IR spectrum (neat) 3083, 2960, 2919, 1644, 1450, 1250, 1168, 1004, 876, 743 cm⁻¹; Anal. Calcd for C₉H₁₉ClSi: C, 56.66; H, 10.04; found: C, 56.60; H, 10.21

¹ Schmidt-Winkel, P.; Lukens, W. W., Jr.; Yang, P.; Margolese, D. I.; Lettow, J. S.; Ying, J. Y.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 686-696.



Figure S1. Time profile of ¹H NMR spectral changes of 2b in the presence of 3 (a) before the addition of 3 (b) 15 min after the addition of 3. (c) after 30 min. The peaks marked with letters m and i correspond to proton of the methallyl group and isobutene, respectively.

Scheme S2. Isomerization of 2p during the reaction with or without 1 in the presence of Sc(OTf)₃.



Reaction of **2p** with **1** in the presence of $Sc(OTf)_3$ (**3**) gave the unexpected ¹³C CP-MAS NMR signals at around 142 ppm and 110 ppm as shown in Figure S2-(b). Same observation was obtained by solution ¹³C NMR experiment when the reaction of **2p** under **3** was carried out in CD₃CN without **1** (new peaks at 142.2 and 110.18 ppm were also appeared (Figure S2-(a)). We speculated that some isomerization process of methallyl groups in **2p** by **3** might be responsible for the new peaks, though the exact reason is not clear at the present stage.



Figure S2. ¹³C NMR of **2p** after the reaction with **3a** in the absence of **1** (a) and the ¹³C CP-MAS NMR spectrum of **4p** (derived from **2p** and **1** in the presence of **3**) (b). The peaks marked with letters m and iso. correspond to carbon atom of the original methallyl group and isomerized methallyl group, respectively.

Characterization Data for 2p: ¹H NMR(250 MHz, CDCl₃) δ 4.67-4.56(d, J= 27.0 Hz, 6H), 3.26-3.20(t, J= 7.0 Hz, 2H), 1.78(s, 9H), 1.77-1.60(m, 2H), 1.66(s, 6H), 0.72-0.66(m, 2H); ¹³C NMR(62.9 MHz, CDCl₃) δ 149.9, 110.0, 54.7, 25.7, 24.2, 23.7, 10.5; IR spectrum (neat) 3395, 3076, 2968, 2921, 2098, 1639, 1447, 1281, 1166, 1050, 865 cm⁻¹; Anal. Calcd for C₁₅H₂₇N₃Si: C, 64.93; H, 9.81; N, 15.14; found: C, 64.94; H, 9.82; N, 14.96.

Representative Procedure of Catalytic Immobilization Reaction (equation 1): $Sc(OTf)_3$ (**3**, 73.8 mg (3 mol%)) and amorphous silica gel (**1**, 1.0 g) was added in 5 ml pressure cap vial. 3-Azidopropyldimethallylmethylsilane (**2a**, 1.2 g (5 mmol)) and acetonitrile (3 ml) was added and the reaction mixture was stirred at room temperature for 1 hour. During the reaction, the evolution of gas-bubbles (isobutene) was observed. After the reaction, the mixture was filtered and washed by methanol and dichloromethane using cellulose thimble, and extracted by a Soxhlet apparatus with ethanol for 12 h, and dried under reduced pressure for 12 hours gave 1.11 g of the grafted silica. Loading rate for **4a**: C, 6.4210; N, 6.0990; H, 1.7218. (loading rate of **4a**

= 1.34 mmol of 2a / 1g of sample 4a)

Preparation of 3-chloropropyldimethallylmethylsilane(2c)

10 % wt. H₂PtCl₆·xH₂O in 2-propanol (0.2 ml) and dichloromethylsilane (26 ml) was added in a 2-necked round-bottom flask, and the mixture was stirred until it became homogeneous. Diethyl ether (10 ml) was added into the reaction vessel and the reaction temperature was raised to 40 °C by an oil-bath. After dropwise addition of allyl chloride (20 ml), the mixture was stirred for 12 hours at 60 °C. After the reaction, all volatiles were evaporated. The crude product (3-chloropropyldichloromethylsilane: ¹H NMR (250 MHz, CDCl₃) δ 3.61-3.55 (d, *J* = 6.5 Hz, 4H), 2.05-1.93 (m, 2H), 1.32-1.23 (m, 2H), 0.8(s, 3H)) was used in the next step without further purification. The crude 3-chloropropyldichloromethylsilane was added dropwisely into excess methallyl magnesium chloride solution in THF and the reaction mixture was stirred for 4 hours. After the reaction, saturated aqueous NH₄Cl added, and it was extracted with diethyl ether (3 times). The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-hexane; R_f 0.6) to give **2c** (27 g, yield: 50 %).

¹H NMR(250 MHz, CDCl₃) δ 4.63-4.51(d, J= 30.7 Hz, 4H), 3.53-3.47(t, J= 13.9 Hz, 2H), 1.86-1.76(m, 2H), 1.73(s, 6H), 1.60(s, 4H), 0.73-0.68(m, 2H), 0.09(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.3, 109.3, 48.1, 27.7, 25.8, 25.66, 11.9, -4.2; IR spectrum (neat) 3083, 2966, 2914, 1644, 1450, 1748, 1378, 1280, 1168, 871, 840 cm⁻¹; Anal. Calcd for C₁₂H₂₃ClSi: C, 62.43; H, 10.04; found: C, 62.48; H, 9.93

Preparation of 3-chloropropyltrimethallylsilane(2d)

3-Chloropropyltrichlorosilane (5.0 g, 24 mmol) was added under anhydrous condition, and distilled THF (20 ml) was added. Excess methallylmagnesium chloride solution in THF was added dropwisely. After the reaction, saturated aqueous NH₄Cl solution and diethyl ether were added and this solution was rinsed by saturated NaCl solution. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, R_f = 0.67) to give **2d** (6.3 g, yield: 97 %).

¹H NMR (250 MHz, CDCl₃) δ 4.67-4.48 (d, J= 27.5 Hz, 6H), 3.52-3.47 (t, J= 6.9 Hz, 2H), 1.87-1.80 (m, 2H), 1.75 (s, 9H), 1.56 (s, 6H), 0.78-0.72 (m, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ 149.9, 110.0, 54.7, 25.7, 24.2, 23.7, 10.5; IR spectrum (neat) 3072, 2925, 2864, 2721, 2663, 1747, 1635, 1462, 1374, 1150, 877, 719 cm⁻¹; Anal. Calcd for C₁₅H₂₇ClSi: C, 66.50; H, 10.05; found: C, 66.47; H, 10.30.

Preparation of 3-azidopropyldimethallylmethylsilane(2a)

3-Chloropropyldimethallylsilane (**2c**, 6.4 g (27.6 mmol)) and sodium azide(3.75 g, 55.2 mmol) was added into 100 ml round bottom flask in DMF and stirred at 80 °C for 4 hours. After the reaction, saturated NH₄Cl aqueous solution was added, and diethyl ether and aqueous layer was extracted with diethyl ether for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, R_f = 0.6) to give **2a** (5.3 g, yield: 81 %).

¹H NMR(250 MHz, CDCl₃) δ 4.64-4.51(d, J= 28.5 Hz, 4H), 3.26-3.21(t, J= 7.0 Hz, 2H), 1.78(s, 6H), 1.77-1.60(m, 2H), 1.58(s, 4H), 0.66-0.60(m, 2H), 0.07(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.3, 109.3, 54.7, 25.8, 25.6, 23.8, 11.4, -4.2; IR spectrum (neat) 3079, 2971, 2922, 2876, 2102, 1748, 1636, 1459, 1378, 1282, 1255, 1170, 873, 846 cm⁻¹; Anal. Calcd for $C_{12}H_{23}N_3Si$: C, 60.71; H, 9.76; N, 17.70 found C, 60.68; H, 9.72; N, 16.78.

Preparation of 3-aminopropyldimethallylmethylsilane(2e)

3-Azidopropyldimethallylmethylsilane (**2a**, 4.0 g (16.9 mmol)) was added in THF (25 ml). Then, triphenylphosphine (4.9 g, 18.6 mmol) and distilled water (457 mg, 25.4 mmol) were added, and the mixture was stirred during 4 hours at room temperature. After the reaction, residual solvent was evaporated and 3.0 g (75 %) of **2e** was obtained after column chromatography (dichloromethane:methanol = 9:1; $R_f 0.2$)

¹H NMR(400 MHz, CDCl₃) δ 4.61-4.50(d, J= 27.3 Hz, 4H), 2.70-2.64(t, J= 7.0 Hz, 2H), 1.72(s, 6H), 1.58(s, 4H), 1.50-1.43(m, 2H), 0.61-0.54(m, 2H), 0.06(s, 3H) ¹³C NMR(100 MHz, CDCl₃) δ 143.5, 108.9, 45.7, 28.2, 25.7, 25.5, 11.1, -4.3; MS(EI, 70 eV) m/z(relative intensity) 210(M-1, 0.02), 156(4), 101(16), 100(100), 98(28); IR spectrum (neat) 3374, 3076, 3048, 2966, 2925, 2876, 2308, 1634, 1437, 1417, 1372, 1262, 1164, 1033, 972, 878, 743 cm⁻¹

Preparation of 3-cyanopropyldimethallylmethylsilane(2f)

3-Chloropropyldimethallylsilane (**2c**, 4.25 g (18.4 mmol)) and sodium cyanide (1.8 g, 36.8 mmol) was added into DMF in 100 mL round bottom flask and the mixture was stirred at 120 °C for 4 h. After reaction, saturated NH₄Cl aqueous solution and diethyl ether were added, and aqueous layer was extracted with diethyl ether for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, R_f =

0.4) to give **2f** (3.5 g, yield: 85 %).

¹H NMR(250 MHz, CDCl₃) δ 4.64-4.51(d, J= 31.4 Hz, 4H), 2.38-2.33(t, J= 7.0 Hz, 2H), 1.73(s, 6H), 1.74-1.69(m, 2H), 1.59(s, 4H), 0.79-0.71(m, 2H), 0.08(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.0, 119.9, 109.5, 25.8, 25.6, 21.1, 20.8, 14.0, -4.2; IR spectrum (CHCl₃) 3074, 2956, 2931, 2906, 2877, 2245, 1639, 1444, 1425, 1366, 1275, 1251, 1166, 1040, 1000, 978, 869, 738 cm⁻¹; Anal. Calcd for C₁₂H₂₃NSi: C, 70.52; H, 10.47; N, 6.33 found C, 70.46; H, 10.55; N, 6.42.

Preparation of 3-formylpropyldimethallylmethylsilane(2g)

3-Cyanopropyldimethallylsilane (**2f**, 2.6 g (11.8 mmol)) was added in dichloromethane. The reaction vessel was cooled to -78 °C, and 1.0 M DIBAL-H in dichloromethane (13.9 ml) was slowly added. Then reaction temperature was raised to -40 °C and stirred for 1 hour. After the reaction, silica gel and water were added, and the mixture was stirred for 1 hour at 0 °C. The collected organic layer was dried with anhydrous MgSO₄ and K₂CO₃, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, R_f = 0.4) to give **2f** (1.56 g, yield: 60 %).

¹H NMR(400 MHz, CDCl₃) δ 9.76-9.75(t, J=1.8 Hz, 1H), 4.61-4.50(t, J= 28.5 Hz, 4H), 2.48-2.44(td, J_{ab}= 7.15Hz, J_{bc}= 1.75Hz, 2H), 1.72(s, 6H), 1.70-1.65(m, 2H), 1.59(s, 4H), 0.63-0.59(m, 2H), 0.07(s, 3H); ¹³C NMR(100 MHz, CDCl₃) δ 143.4, 109.2, 47.7, 25.8, 25.6, 17.0, 14.1, -4.2; IR spectrum (neat) 3428, 3071, 2964, 2935, 2913, 2882, 2812, 2713, 1725, 1634, 1447, 1410, 1369, 1278, 1249, 1165, 1126, 1054, 1031, 1000, 973, 872, 839 cm⁻¹; MS(EI, 70 eV) m/z(relative intensity) 210(M-1, 0.02), 156(4), 101(16), 100(100), 98(28); Anal. Calcd for C₁₃H₂₄OSi: C, 69.58; H, 10.78; found C, 69.62; H, 10.72.

Preparation of 3-acetoxypropyldimethallylmethylsilane(2h)

3-Chloropropyldimethallylsilane (**2c**, 3.0 g (13.0 mmol)) and sodium acetate (2.1 g, 26.0 mmol) were added into DMF (30 ml) in 100 ml round bottom flask, and the mixture was stirred at 120 °C for 12 hours. After the reaction, saturated NH₄Cl aqueous solution and diethyl ether were added, and aqueous layer was extracted with diethyl ether for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, $R_f = 0.34$) to give **2h** (2.5 g, yield: 75 %).

¹H NMR(250 MHz, CDCl₃) δ 4.62-4.50(d, J= 29.0 Hz, 4H), 4.03-3.98(t, J= 7 Hz, 2H), 2.05(s, 3H), 1.73(s, 6H), 1.68-1.59(m, 2H), 1.59(s, 4H), 0.63-0.56(m, 2H), 0.07(s, 3H);

¹³C NMR(62.9 MHz, CDCl₃) δ 171.3, 143.3, 109.2, 67.2, 25.7, 25.5, 23,2, 21.2, 10.0, -4.3; IR spectrum (neat) 3081, 2962, 2906, 2890, 1738, 1636, 1442, 1363, 1233, 1169, 1053, 872, 843, 741 cm⁻¹; Anal. Calcd for $C_{12}H_{23}N_3Si$: C, 66.09; H, 10.30; found C, 66.08; H, 10.33.

Preparation of 3-hydroxypropyldimethallylmethylsilane (2i)

3-Acetoxypropyldimethallylmethylsilane (**2h**, 1.5 g (5.9 mmol)) was added in diethyl ether (10 ml). LiAlH₄ (300 mg, 0.0079 mol) was added carefully, and the mixture was stirred for 2 hours. After the reaction, H₂O (10 ml) was added carefully, and the aqueous layer was extracted with diethyl ether for 2 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 5:1, Rf = 0.34) to give **2i** (1.0 g, yield: 75 %). ¹H NMR(250 MHz, CDCl₃) δ 4.62-4.51(d, J= 28.7 Hz, 4H), 3.61-3.56(t, J= 6.4 Hz, 2H), 1.79(s, 6H), 1.72-1.52(m, 2H), 1.62(s, 4H), 0.62-0.55(m, 2H), 0.07(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.5, 109.1, 65.9, 27.2, 25.8, 25.6, 9.8, -4.2; IR spectrum (neat) 3381, 3074, 2957, 2929, 2910, 2878, 1635, 1439, 1411, 1375, 1276, 1251, 1159, 1057, 1010, 976, 869, 836 cm⁻¹; Anal. Calcd for C₁₂H₂₄OSi: C, 67.86; H, 11.39; found C, 67.82; H, 11.50.

Preparation of 3-(4-Phenyl-[1,2,3]triazolyl)propyldimethallylmethylsilane(2j)

Phenylacetylene (940 mg, 9.2 mmol) was added into the mixture of H₂O and THF (40 mL, v/v = 1:1) in 100 mL round-bottom flask. After addition of CuSO₄·5H₂O (230 mg, 0.92 mmol) and sodium ascorbate (357 mg, 18.4 mmol), 3azidopropyldimethallylmethylsilane (2a, 2.4 g (10.1 mmol)) was added dropwisely. The reaction mixture was stirred at room temperature for 12 hours. After the reaction, the reaction mixture was washed with water, and organic layer was separated. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 5:1, Rf = 0. 4) to give 2j (3.1 g, yield: 95 %).

¹H NMR(250 MHz, CDCl₃) δ 7.84-7.81(d, J= 8.0 Hz, 2H), 7.75(s, 1H), 7.44-7.30(m, 3H) 4.61-4.48(d, J= 32.8 Hz, 4H), 4.36-4.30(t, J= 7.1 Hz, 2H), 1.98-1.91(m, 2H), 1.68(s, 6H), 1.57(s, 4H), 0.63-0.56(m, 2H), 0.07(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 147.7, 142.9, 130.9, 128.9, 128.1, 125.7, 119.7, 109.3, 53.3, 25.6, 25.4, 25.3, 11.0, -4.3; IR spectrum (neat) 3131, 3072, 2967, 2938, 2915, 2882, 1634, 1608, 1484, 1462, 1446, 1435, 1368, 1278, 1252, 1221, 1185, 1164, 1075, 1047, 972, 869, 837, 762, 738, 693 cm⁻¹; HR-MS(TOF) calcd for C₂₀H₂₉N₃Si(M+Na⁺) 362.2028 found 362.2026. Anal.

Calcd for C₂₀H₂₉N₃Si: C, 70.74; H, 8.61; N, 12.38; found C, 69.95; H, 8.48; N, 12.31.

Preparation of 3-(4-Ferrocenyl-[1,2,3]triazolyl)propyldimethallylmethylsilane(2k)

2k was synthesized by the same procedure of **2j** but ethynylferrocene (657 mg, 3.1 mmol) was used instead of phenylacetylene. Yield (1.29 g, 92 %).

¹H NMR(250 MHz, CDCl₃) δ 7.43(s, 1H), 4.73-4.71(t, J= 2.0 Hz, 4H), 4.63-4.49(d, J= 32 Hz, 4H), 4.35-4.29(m, 2H), 4.3(s, 2H) 4.1(s, 5H), 2.01-1.90(m, 2H), 1.71(s, 6H), 1.72-1.52(m, 2H), 1.59(s, 4H), 0.63-0.56(m, 2H), 0.09(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 146.8, 143.1, 119.0, 109.4, 69.9, 69.0, 67.0, 53.4, 25.7, 25.6, 25.3, 11.2, -4.2; IR spectrum (neat) 3076, 3050, 2968, 2940, 2912, 2884, 1634, 1588, 1439, 1372, 1264, 1165, 1106, 1047, 999, 876, 836, 819, 739, 703 cm⁻¹; Anal. Calcd for C₂₄H₃₃FeN₃Si: C, 64.42; H, 7.43; N, 9.39; found C, 64.74; H, 7.34; N, 9.51.

Preparation of DABS-aminopropane.(5) [Regis. No. 72720-17-3]

Dabsyl chloride (653 mg, 2 mmol)) was added in acetonitrile (20 ml). Triethylamine (0.4 ml) and propylamine (70 μ l) were added and the reaction mixture was stirred at room temperature for 12 hours. After the reaction, water (20 ml) was added, and the mixture was extracted with dichloromethane for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-hexane:ethyl acetate= 1:1 R_f 0.5) to give **5** (634 mg, yield: 91 %).

¹H NMR(250 MHz, CDCl₃) δ 7.98-7.88 (m, 6H), 6.77-6.74(d, J= 9.2 Hz, 2H), 4.61-4.56(t, J= 6.2 Hz, 1H), 3.12(s, 6H), 3.0-2.91(q, J= 6.7 Hz, 2H), 1.54-1.45(m, 2H), 0.90-0.84(m, 3H).

Preparation of DABS-aminopropyldimethallylmethylsilane.(2m)

Dabsyl chloride (500 mg, 1.55 mmol) was added in 10 ml of acetonitrile. Triethylamine (203 mg, 2.0 mmol) and 3-aminopropyldimethallylmethylsilane (**2e**, 425 mg (2.0 mmol)) were added and stirred at room temperature for 12 hours. After the reaction, saturated NaHCO₃ was added, and the mixture was extracted by dichloromethane for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-hexane:ethyl acetate= 1:1 Rf 0.5) to give **2m** (640 mg, yield: 83 %).

¹H NMR(400 MHz, CDCl₃) δ 7.96-7.88 (d, J= 12.0 Hz, 6H), 6.77-6.74(d, J= 9.1 Hz, 2H), 4.58-4.45(d, J= 32.2 Hz, 4H), 4.58-4.55(t, J= 6.2 Hz, 1H), 3.11(s, 6H), 3.0-2.91(q, J= 6.7 Hz, 2H)1.67(s, 6H), 1.53(s, 4H), 1.56-1.46(m, 2H), 0.54-0.47(m, 2H), 0.00(s, A) = 0.000(s), 0.00(s), 0.00(s),

3H), ¹³C NMR(100 MHz, CDCl₃) δ 155.9, 153.3, 143.8, 143.2, 139.7, 128.3, 126.0, 122.8, 111.7, 109.3, 46.6, 40.5, 25.8, 25.6, 24.5, 11.2, -4.2. IR spectrum (CH₂Cl₂) 3368, 3280, 3048, 2960, 2930, 2908, 2303, 1631, 1602, 1519, 1442, 1422, 1365, 1331, 1313, 1264, 1165, 1135, 1090, 875, 840, 825, 737, 701 cm⁻¹; HR-MS(TOF) calcd for C₂₆H₃₈N₄O₂SSi(M+Na⁺) 521.2382 found 521.2383. Anal. Calcd for C₂₆H₃₈N₄O₂SSi : C, 62.61; H, 7.68; N, 11.23; found: C, 63.06; H, 7.72; N, 11.18.

in Table 2 (entry 1~8) and scheme 3 (entry 9)					
entry	R		C (%)	N (%)	H (%)
1	N ₃ (4a)		6.6758	6.1756	1.8088
2	NH_2 (4e)		8.9024	1.9181	1.9006
3	CN (4f)		9.1011	1.9964	1.8296
4	СНО (4g)		10.3513	0.1930	2.1794
5	OCOCH ₃ (4h)		10.5342	-	2.0374
6	OH (4i)		8.7382	-	1.9852
7	∽ _N ∕∕⊳∕X	$\begin{array}{c} X = Ph \\ (4j) \end{array}$	8.4852	2.2715	1.3446
8	N=N	$\begin{array}{c} X = Fc \\ (4k) \end{array}$	6.3411	1.2578	1.1443
9	Dabsyl(4m)		3.8778	0.8568	0.9961

Elementary Analysis of 4c and 4m from experiments

Preparation of Octadecyldimethallylmethylsilane(2n)

10 % wt. H₂PtCl₆·*x*H₂O in 2-propanol (0.2 ml) and dichloromethylsilane (9 ml) was added in a 2-necked round-bottom flask, and the mixture was stirred until it became homogeneous. Diethyl ether (15 ml) was added into the reaction vessel and the reaction temperature was raised to 40 °C by an oil-bath. After dropwise addition of 1-octadecene (28 ml), the mixture was stirred for 12 hours at 60 °C. After the reaction, were eliminated by distillation. The crude product (Octadecyldichloromethylsilane) was used in the next step without further purification. The crude octadecyldichloromethylsilane was added drop-wise into excess methallyl magnesium chloride solution in THF and the reaction mixture was stirred for 4 hours. After the reaction, saturated aqueous NH₄Cl added, and it was extracted with diethyl ether (3 times). The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-hexane; R_f 0.8) to give **2c** (9.5 g, yield: 27 %).

¹H NMR(250 MHz, CDCl₃) δ 4.51(d, J= 26 Hz, 4H), 1.68(s, 6H), 1.61(s, 4H), 1.30(s, 36H), 0.85(t, J= 6.3 Hz, 4H), 0.57(m, 2H), 0.01(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.8, 108.9, 34.0, 32.2, 30.0, 29.9, 29.6, 26.0, 25.7, 24.0, 23.0, 14.4, 14.3, -4.2; IR spectrum (neat) 3067, 2844, 2719, 1747, 1635, 1465, 1412, 1371, 1278, 1251, 1163,

1122, 1033, 997, 972, 870, 839, 820, 741, 719 cm⁻¹; Anal. Calcd for C₂₇H₅₄Si: C, 79.72; H, 13.38; found C, 79.65; H, 13.26.

Preparation of 11-azidoundecenyldimethallylmethylsilane

11-Chloropropyldimethallylsilane (5.5 g, 16.7 mmol) and sodium azide(2.18 g, 33.5 mmol) was added into 100 ml round bottom flask in DMF and stirred at 80 °C for 4 hours. After the reaction, saturated NH₄Cl aqueous solution was added, and aqueous layer was extracted with diethyl ether for 3 times. The collected organic layer was dried with anhydrous MgSO₄, and it was filtered through Celite pad and purified by column chromatography (*n*-Hexane:ethyl acetate = 10:1, $R_f = 0.6$) to give 11-azidoundecenyldimethallylmethylsilane (4.3 g, yield: 77 %).

¹H NMR(250 MHz, CDCl₃) δ 4.51(d, J= 27.3 Hz, 4H), 3.22(t, J= 6.9 Hz, 2H), 1.68(s, 6H), 1.58(m, 6H), 1.24(s, 18H), 0.54(t, J= 7.8 Hz, 2H), 0.01(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.7, 108.9, 51.7, 33.9, 30.0, 29.8, 29.5, 29.4, 29.1, 26.9, 25.9, 25.6, 23.9, 14.3, -4.3; IR spectrum (neat) 3072, 2921, 2851, 2094, 1636, 1454, 1373, 1279, 1250, 1166, 998, 971, 868, 839, 722 cm⁻¹; Anal. Calcd for C₂₀H₃₉N₃Si: C, 68.71; H, 11.24; N, 12.02 found C, 68.60; H, 12.15; N, 12.15.

Preparation of 11-(4-Ferrocenyl-[1,2,3]triazolyl)undecenyldimethallylmethylsilane (20)

20 was synthesized by the same procedure of **2j** but ethynylferrocene (1g, 5.24 mmol) and 11-azidoundecenyldimethallylmethylsilane(1.8g, 4.76mmol) were used instead of phenylacetylene and **2a**. Yield (2.65 g, 99 %).

¹H NMR(250 MHz, CDCl₃) δ 7.44(s, 1H), 4.17(t, J= 1.8 Hz, 2H), 4.54(d, J= 26.8 Hz, 4H), 4.35(t, J= 7.3 Hz, 2H), 4.29(t, J= 1.8 Hz, 2H) 4.10(s, 5H), 1.92(t, J= 6.5 Hz, 2H), 1.79(s, 6H), 1.57(s, 4H), 1.29(m, 20H), 0.56(t, J= 7.5 Hz, 2H), 0.09(s, 3H); ¹³C NMR(62.9 MHz, CDCl₃) δ 143.8, 118.8, 108.8, 69.7, 68.8, 66.8, 50.5, 33.9, 30.5, 30.0, 29.5, 29.2, 26.7, 25.9, 25.6, 23.9, 14.3, -4.2; IR spectrum (neat) 3049, 2982, 2922, 2851, 2683, 2304, 1632, 1588, 1438, 1419, 1369, 1264, 1217, 1163, 1099, 1045, 999, 876, 837, 738, 701 cm⁻¹; HR-MS(TOF) calcd for C₃₂H₄₉N₃FeSi(M+Na⁺) 582.6713 found 582.2949. Anal. Calcd for C₂₄H₃₃FeN₃Si: C, 68.67; H, 8.82; N, 7.51; found C, 68.65; H, 8.93; N, 7.68.

Glass slide (Microscope Slide) preparation and Contact Angle (in Figure 2a)

Glass slide was treated by Piranha solution ($H_2SO_4 : H_2O_2 = 7 : 3, 10 \text{ mL}$) for 1 hour. The reaction of octadecyldimethallylmethylsilane (**2n**) and glass slide in the presence of 3 mol% of **3** in acetonitrile solvent during 1 hour. After the reaction, modified glass slide was washed with methanol and water. The contact angles of glass slide after treatment of Piranha solution and surface-modified glass slide (**4n**) were measured as 35° and 96° , respectively.

Electrode Preparation and Cyclic Voltammetry (in Figure 2b)

ITO glass was treated by Piranha solution ($H_2SO_4 : H_2O_2 = 7 : 3, 10 \text{ mL}$) for 1 hour. 11-(4-Ferrocenyl-[1,2,3]triazolyl)undecenyldimethallylmethylsilane (**2o**) was reacted with ITO glass in the presence of 2 or 10 mol% of **3** in acetonitrile solvent for 12 hours. After the reaction, resulting ITO glass **4o** was washed with methylene chloride, water and methanol. Ferrocene-impregnated ITO glass (**4o**), a platinum wire and a standard Ag/AgCl (saturated KCl) electrode were used as a working, counter and reference electrode, respectively. The electrodes were immersed into the phosphate buffer (pH 7.0). The XPS spectra of resulting electrodes are shown below.

Dabsyl-Immobilized Glass (Microscope Slide) Preparation and XPS Spectra

Glass slide was treated by Piranha solution ($H_2SO_4 : H_2O_2 = 7 : 3, 10 \text{ mL}$) for 1 hour. The reaction of DABS-aminopropyldimethallylmethylsilane (**2m**) and glass slide in the presence of 2 or 10 mol% of **3** in acetonitrile solvent during 12 hour. After the reaction, modified glass slide was washed with methanol, water and acetone. The XPS spectra of resulting samples are shown below.

XPS spectra of Dabsyl-immobilized microscope slide and Ferrocene- immobilized ITO glass (40)

Figure S3. XPS spectra of Dabsyl-immobilized microscope slide and Ferroceneimmobilized ITO glass (40)



Dabsyl-immobilized microscope slide



Ferrocene-immobilized ITO glass

(a) XPS spectra of Dabsyl-immobilized microscope slide by the reactions in the presence of 10 mol% of 3



(b) XPS spectra of Dabsyl-immobilized microscope slide by the reactions in the presence of $2 \mod 0$ of 3





(c) XPS spectra of Fc-immobilized ITO glass (40) by the reaction of 10 mol% of 3

(d) XPS spectra of Fc-immobilized ITO glass (40) by the reaction of 2 mol% of 3

