Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

$CpFe(CO)_2$ anion-catalyzed highly efficient hydrosilylation of ketones and aldehydes

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Contents

1. Experimental Section

General Considerations.

All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data were recorded on Bruker Mercury Plus 300, 400 and 600 MHz NMR spectrometers. Chemical shifts are referenced against external Me_4Si for ^{1}H, ^{13}C and ^{29}Si NMR. $K[CpFe(CO)_2]$ (**1**K) and $[NEt_4][CpFe(CO)_2]$ (**1**NEt_4) were synthesized according to the published procedure.[S1, S2]

General procedure for hydrosilylation of corbonyl compounds catalyzed by 1NEt_4. In the glovebox, 10 μl of **1**NEt_4 (0.05M in THF) was added in a Schlenk tube eqquiped with a stir bar, then remove the THF under vacuum condition. 1 mmol of substrate and 0.34 or 0.5 mmol of $PhSiH_3$ was added to the Schlenk tube sequentially. The reaction was stirred for 10 – 30 min, then exposed to air to stop the reaction. The conversions were determined by ^{1}H NMR spectroscopy at ambient temperature. The pure products were isolated by filtered through a Celite pad to remove the catalyst and then evacuating the volatiles under vacuum.

Scaled-up reaction of hydrosilylation of acetophenone catalyzed by 1NEt_4. In a argon atmosphere, 15 mg of **1**NEt_4 (0.05 mmol) and of 12.0 g of acetophenone (100 mmol) was added in a Schlenk tube eqquiped with a stir bar, and the mixture was cooled to 0 °C, then 3.7 g of $PhSiH_3$ (0.34 mmol) was slowly added to the Schlenk tube. The reaction was stirred for 10 min, then exposed to air to stop the reaction. The conversions were determined by ^{1}H NMR spectroscopy at ambient temperature.

Charcaterization of the hydrosilylation Products

$PhSi(OCH(Me)Ph)_3$ (3a)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H, Ar-*H*), 7.40 (d, J = 7.4 Hz, 2H, Ar-*H*), 7.34 – 7.18 (m, 16H, Ar-*H*), 5.11 – 4.96 (m, 3H, OC*H*(CH_3)), 1.43 (dd, J = 10.1, 6.4 Hz, 5H, (OCH(CH_3)), 1.33 (dd, J = 8.8, 6.4 Hz, 5H, (OCH(CH_3)). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.94, 128.05 (d, J = 6.4 Hz), 127.62, 126.85 (d, J = 8.4 Hz), 125.36 (d, J = 5.3 Hz), 77.32, 77.00, 76.68, 71.12, 26.49 (d, J = 10.1 Hz).

$PhSi(OCH(Me)(p\text{-}OMeC_6H_4))_3$ (3b)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.27 (m, 6H, Ar-*H*), 7.23 – 7.08 (m, 5H, Ar-*H*), 6.88 – 6.74 (m, 6H, Ar-*H*), 5.03 – 4.87 (m, 3H, (OC*H*(CH_3)), 3.84 – 3.75 (m, 9H, OCH_3), 1.60 – 1.28 (m, 9H, (OCH(CH_3)). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.67, 137.55, 137.43, 134.93, 134.18, 133.34, 130.45, 127.82, 126.76, 126.71, 126.64, 113.57, 113.50, 77.00, 71.51, 55.23, 55.19, 26.33, 26.20.

$PhSi(OCH(Me)(p\text{-}CNC_6H_4))_3$ (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.17 (m, 17H, Ar-*H*), 5.03 (s, 3H, (OC*H*(CH_3)), 1.42 (dd, J = 38.4, 27.8 Hz, 9H, (OCH(CH_3)). ^{13}C NMR (101 MHz, $CDCl_3$): 150.29, 134.56, 134.31, 133.93, 128.09, 125.81, 125.79, 118.63, 111.04 (*C*N), 70.78, 26.33. ^{29}Si NMR (79 MHz, $CDCl_3$): δ -60.77. HRMS (ESI), m/z calcd. for $C_{33}H_{29}N_3O_3Si$ $(M+Na)^+$ 566.1876, found: 566.1875. Elemental analysis (%) calcd for $C_{33}H_{29}N_3O_3Si$: C, 72.90; H, 5.38; N, 7.73; O, 8.83; Found: C, 72.79; H, 5.45; N, 7.75; O, 8.67.

$PhSi(OCH(Me)(p\text{-}BrC_6H_4))_3$. (3d) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 21.3, 7.6 Hz, 1H, Ar-*H*), 7.51 (d, J = 6.8 Hz, 1H, Ar-*H*), 7.45 – 7.29 (m, 9H, Ar-*H*), 7.09 (dd, J = 16.7, 8.4 Hz, 3H, Ar-*H*), 7.00 (t, J = 8.9 Hz, 3H, Ar-*H*), 4.94 (ddd, J = 19.1, 11.0, 6.4 Hz, 3H, C*H*), 1.47 – 1.39 (m, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): 144.15, 135.80, 134.05, 131.24, 130.75, 127.97, 127.05, 120.86, 71.30, 26.28. ^{29}Si NMR (79 MHz, $CDCl_3$): δ -60.28. HRMS (ESI), m/z calcd. for $C_{30}H_{29}Br_3O_3Si$ $(M+Na)^+$ 724.9334, found: 724.9515. Elemental analysis (%) calcd for $C_{30}H_{29}Br_3O_3Si$: C, 51.08; H, 4.14; O, 6.80; Found: C, 51.28; H, 4.30; O, 6.66.

PhSi(OCH(Me)(*p*-COOMeC$_6$H$_4$))$_3$ (3e). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.7 Hz, 5H, Ar-*H*), 7.47 – 7.45 (m, 2H, Ar-*H*), 7.33 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.27 – 7.10 (m, 6H, Ar-*H*), 4.84 (m, 3H, C*H*), 3.80 (s, 9H, COO*Me*), 1.34 – 1.22 (m, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.92(*C*OOCH$_3$), 150.51 (d, *J* = 4.5 Hz), 150.39 (d, *J* = 3.6 Hz), 134.72, 129.73, 129.55 (d, *J* = 2.2 Hz), 129.46, 127.85. 125.22, 125.08 (d, *J* = 3.4 Hz), 70.83, 51.97(COO*C*H$_3$), 26.31 (d, *J* = 11.3 Hz). ^{29}Si NMR (79 MHz, $CDCl_3$): δ -60.04. HRMS (ESI), m/z calcd. for $C_{36}H_{38}O_9Si$ $(M+Na)^+$ 665.2183, found: 665.2180. Elemental analysis (%) calcd for $C_{36}H_{38}O_9Si$: C, 67.27; H, 5.96; O, 22.40; Found: C, 67.41; H, 5.75; O, 22.23.

PhSi(OCH(Me)(*m*-ClC$_6$H$_4$))$_3$ (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.61 – 7.12 (m, 17H, Ar-*H*), 5.01 – 4.90 (m, *J* = 19.4 Hz, 3H, (OC*H*(CH$_3$)), 1.39 – 1.55 (m, *J* = 31.1, 29.4 Hz, 9H, (OCH(CH_3)) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ147.43, 134.78, 134.10, 130.61, 129.50, 128.87, 127.19, 125.50, 123.41, 70.75, 26.44. ^{29}Si NMR (79 MHz, $CDCl_3$): δ -60.23. HRMS (ESI), m/z calcd. for $C_{30}H_{29}Cl_3O_3Si$ $(M+Na)^+$ 593.0849, found: 593.0848. Elemental analysis (%) calcd for $C_{30}H_{29}Cl_3O_3Si$: C, 63.00; H, 5.11; O, 8.39; Found: C, 63.24; H, 5.21; O, 8.63.

PhSi(OCH(CF$_3$)Ph)$_3$ (3g)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.29 (m, 17H, Ar-*H*), 7.21 – 7.17 (m, 3H, Ar-*H*), 5.24 – 4.99 (m, 3H, OC*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.86 (d, *J* = 3.6 Hz), 133.59 (d, *J* = 3.8 Hz), 133.44 (d, *J* = 5.0 Hz), 131.67 (d, *J* = 4.8 Hz), 129.63 (d, *J* = 0.9 Hz), 129.54 (d, *J* = 1.7 Hz), 128.45 (t, *J* = 4.2 Hz), 127.69 (dd, *J* = 11.0, 6.3 Hz), 125.09 (d, *J* = 5.7 Hz), 122.28 (d, *J* = 6.0 Hz), 73.84 (q, *J* = 33.0 Hz).

PhSi(OCH$_2$C$_6$H$_5$)$_3$ (3h)[S4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.7 Hz, 2H, Ar-*H*), 7.38 (dd, *J* = 9.3, 5.5 Hz, 4H, Ar-*H*), 7.34 – 7.28 (m, 14H, Ar-*H*), 4.86 (s, 6H, CH_2).

PhSi(OCH$_2$(*p*-NMe$_2$C$_6$H$_4$))$_3$ (3i). ^{1}H NMR (400 MHz, $CDCl_3$)：δ 7.60 – 7.59 (m, 2H，Ar-*H*), 7.30 – 7.25 (m, 3H，Ar-*H*), 7.11 – 7.09 (m, 6H，Ar-*H*), 6.60 – 6.58 (m, 6H，Ar-*H*), 4.65 (s, 6H, CH_2), 2.82 (s, 18H, N(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ150.00, 135.06, 134.23, 130.21, 128.50, 128.34, 127.68, 112.45, 64.88(CH_2), 40.66 (N(*C*H$_3$)$_2$). ^{29}Si NMR (79 MHz, C_6D_6): δ -56.96. HRMS (ESI), m/z calcd. for $C_{33}H_{41}N_3O_3Si$ $(M+Na)^+$ 578.2809, found: 578.2810. Elemental analysis (%) calcd for $C_{33}H_{41}N_3O_3Si$: C, 71.31; H, 7.44; N, 7.56; O, 8.64; Found: C, 71.69; H, 7.35; N, 7.75; O, 8.76.

PhSi(OCH$_2$(*p*-CCHC$_6$H$_4$))$_3$ (3j). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 6.2 Hz, 2H, Ar-*H*), 7.50 (d, *J* = 7.8 Hz, 6H, Ar-*H*), 7.29 (s, 3H, Ar-*H*), 7.10 (s, 6H, Ar-*H*), 4.73 (s, 6H, CH_2), 2.82 (s, 3H, CC*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.54, 140.50, 134.52, 132.20, 130.78, 127.97, 126.63, 126.15, 121.16, 83.45(*C*CH), 77.20(C*C*H), 64.62(*C*H$_2$). ^{29}Si NMR (79 MHz, C_6D_6): δ -56.29. HRMS (ESI), m/z calcd. for $C_{33}H_{26}O_3Si$ $(M+Na)^+$ 521.1549, found: 521.1548. Elemental analysis (%) calcd for $C_{33}H_{26}O_3Si$: C, 79.49; H, 5.26; O, 9.63; Found: C, 79.13; H, 5.32; O, 9.81.

PhSiH(OCy)$_2$ (4k)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.72 (m, 2H, Ar-*H*), 7.46 – 7.26 (m, 3H, Ar-*H*), 5.08 (s, 1H, Si*H*), 3.97 – 3.92 (m, 2H, OC*H*), 1.92 (m, 4H, CH_2), 1.78 – 1.77 (m, 4H, CH_2), 1.56 – 1.55 (m, 4H, CH_2), 1.25 – 1.21 (m, 6H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.72, 134.01, 130.17, 127.71, 71.91, 35.42, 25.56, 23.98.

PhSiH(OCH(Me)(*n*hexyl))$_2$ (4l). ^{1}H NMR (400 MHz，$CDCl_3$) δ 7.66 (d, *J* = 6.5 Hz, 2H, Ar-*H*), 7.39 (d, *J* = 6.8 Hz, 3H, Ar-*H*), 4.99 (s, 1H, Si*H*), 4.04 (d, *J* = 5.7 Hz, 2H (OC*H*(CH$_3$)), 1.55 (s, 2H), 1.40 (s, 4H), 1.32 – 1.18 (m, 20H), 0.87 (s, 6H) ppm. ^{13}C NMR (101 MHz，$CDCl_3$)：δ134.06, 130.27, 127.78, 70.19, 69.91 (d，*J* = 3.6 Hz), 39.37, 29.29, 22.63, 14.07. ^{29}Si NMR (79 MHz, C_6D_6): δ -60.11. HRMS (ESI), m/z calcd. for $C_{22}H_{40}O_2Si$ $(M+Na)^+$ 387.2690, found: 387.2688. Elemental analysis (%) calcd for $C_{22}H_{40}O_2Si$: C, 72.47; H, 11.06; O, 8.78; Found: C, 72.64; H, 11.09; O, 8.63.

PhSiH(OCH(*i*Pr)$_2$)$_2$ (4m)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.44 – 7.40 (m, 3H, Ar-*H*), 5.08 (s, 1H, Si*H*), 3.66 – 3.61 (m, 2H, OC*H*), 1.83 – 1.76 (m, 2H, (C*H*(CH$_3$)$_2$)), 1.59 – 1.49 (m, 5H, (CH(CH_3)$_2$)), 0.97 – 0.86(m, 21H, (CH(CH_3)$_2$)) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.79, 134.03, 130.14, 127.72, 80.07 (s), 79.88 (d, *J* = 2.3 Hz), 32.64 (d, *J* = 4.5 Hz), 26.48 (d, *J* = 7.4 Hz), 18.94, 17.37 (d, *J* = 5.4 Hz), 10.20 (d, *J* = 6.5 Hz).

PhSiH(OCH(Me)*t*Bu)$_2$ (4n)[S5]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 5.0 Hz, 2H,Ar-*H*), 7.39 (d, *J* = 7.4 Hz, 3H,Ar-*H*), 4.99 (s, 1H,Si*H*), 3.72 (m, 2H, (OC*H*(CH_3)), 1.12 – 1.17 (m, 6H, (OCH(C*H*$_3$)), 0.88 (s, 18H, tBu-*H*) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ:134.70, 134.08, 130.16, 127.76, 77.87, 35.47 (d, *J* = 4.7 Hz), 25.78, 18.24 (dd, *J* = 16.9, 6.9 Hz). HRMS (ESI), m/z calcd. for $C_{18}H_{32}O_2Si$ $(M+Na)^+$ 331.2064, found: 331.2063.

PhSiH(OCH(Me)(1-butenyl))$_2$ (4o). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.41 (dt, *J* = 13.9, 6.8 Hz, 3H, Ar-*H*), 5.76 – 5.83 (m, 2H, (C*H*=CH_2)), 4.99 – 5.08 (m, 3H, (CH=C*H*$_2$)), Si*H*), 4.95 (dd, *J* = 12.3, 5.8 Hz, 2H, (CH=C*H*$_2$)), 4.16 – 4.00 (m, 2H, (OC*H*(CH_3))), 2.07 – 2.18 (m, 4H，(C*H*$_2$CH=CH_2)), 1.72 – 1.64 (m, 2H, (OCH(C*H*$_2$)), 1.74 – 1.49 (m, 2H, (OCH(C*H*$_2$)), 1.33 – 1.08 (m, 6H, (OCH(C*H*$_3$)) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.51, 133.29, 127.66, 114.77, 114.53 (d, J = 45.3 Hz), 77.39, 77.07, 76.75, 67.66, 38.51, 38.27, 30.16, 29.79, 23.37 (d, J = 15.7 Hz). ^{29}Si NMR (79 MHz, C_6D_6): δ -59.04. HRMS (ESI), m/z calcd. for $C_{18}H_{28}O_2Si$ $(M+Na)^+$ 327.1751, found: 327.1752. Elemental analysis (%) calcd for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27; O, 10.51; Found: C, 70.88; H, 9.38; O, 10.78.

PhSiH(OCH$_2$Cy)$_2$ (4p)[S4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 6.4 Hz, 2H, Ar-*H*), 7.45 – 7.38 (m, *3*H, Ar-*H*), 4.91(s, 1H, Si*H*), 3.60 (d, *J* = 6.4 Hz, 4H, C*H*$_2$), 1.80 – 1.71 (m, 10H, C*H*$_2$), 1.57 – 1.52 (m, 2H, C*H*), 1.26 – 1.14 (m, 6H, C*H*$_2$), 0.98 – 0.89 (m, 4H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ135.78, 134.07, 130.42, 127.84, 69.28, 40.18, 29.60, 26.59, 25.82.

PhSiH(OCH$_2$*t*Bu)$_2$ (4q)[S6]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.8, 1.4 Hz, 2H, Ar-*H*), 7.47 – 7.37 (m, 3H, Ar-*H*), 4.92 (s, 1H, Si*H*), 3.46 (s, 4H, C*H*$_2$), 0.92 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ135.85, 134.18, 130.44, 128.00 (d, *J* = 25.3 Hz), 73.84, 26.52 (d, *J* = 55.5 Hz). HRMS (ESI), m/z calcd. for $C_{16}H_{28}O_2Si$ $(M+Na)^+$ 303.1756, found: 303.1762.

PhSiH(OCH(*p*-MeC$_6$H$_4$)$_2$)$_2$ (4r)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$)： δ 7.44 (m, 2H, Ar-*H*), 7.29 (m, 1H, Ar-*H*), 7.22 (m, 2H, Ar-*H*), 7.07 – 7.01 (m, 8H, Ar-*H*), 6.94 (m, 8H, Ar-*H*), 5.68 (s, 2H, C*H*), 4.91 (s, 1H, Si*H*), 2.19 (s, 12H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ140.86 (d, *J* = 8.2 Hz), 136.43 (d, *J* = 19.8 Hz), 134.70, 132.70, 130.26, 128.64 (d, *J* = 10.6 Hz), 127.56, 126.25 (d, *J* = 22.3 Hz), 76.50, 20.88. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -31.09 (d, J = 246.9 Hz). HRMS (ESI), m/z calcd. for $C_{36}H_{36}O_2Si$ $(M+Na)^+$ 551.2382, found: 551.2434.

PhSiH(OCH(Me)thiophene)$_2$ (4s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H, Ar-*H*), 7.46 (d, *J* = 18.4 Hz, 3H, Ar-*H*), 7.26(m, 2H, thiophene-*H*), 6.95 (d, *J* = 21.9 Hz, 4H, thiophene-*H*), 5.37 (m, 2H, (OC*H*(CH_3)), 5.10 (s, 1H, Si*H*), 1.70 – 1.55 (m, 6H, (OCH(C*H*$_3$)) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.83, 135.82, 134.66, 130.52 (d, *J* = 28.3 Hz), 127.80 (d, *J* = 18.9 Hz), 126.29, 123.80, 122.84, 67.97 (d, *J* = 8.6 Hz), 26.32. ^{29}Si NMR (79 MHz, $CDCl_3$): δ -59.63. HRMS (ESI), m/z calcd. for $C_{18}H_{20}O_2S_2Si$ $(M+Na)^+$ 383.0572, found: 383.0570. Elemental analysis (%) calcd for $C_{18}H_{20}O_2S_2Si$: C, 59.96; H, 5.59; O, 8.87; Found: C, 59.78; H, 5.33; O, 8.68.

2. NMR spectra

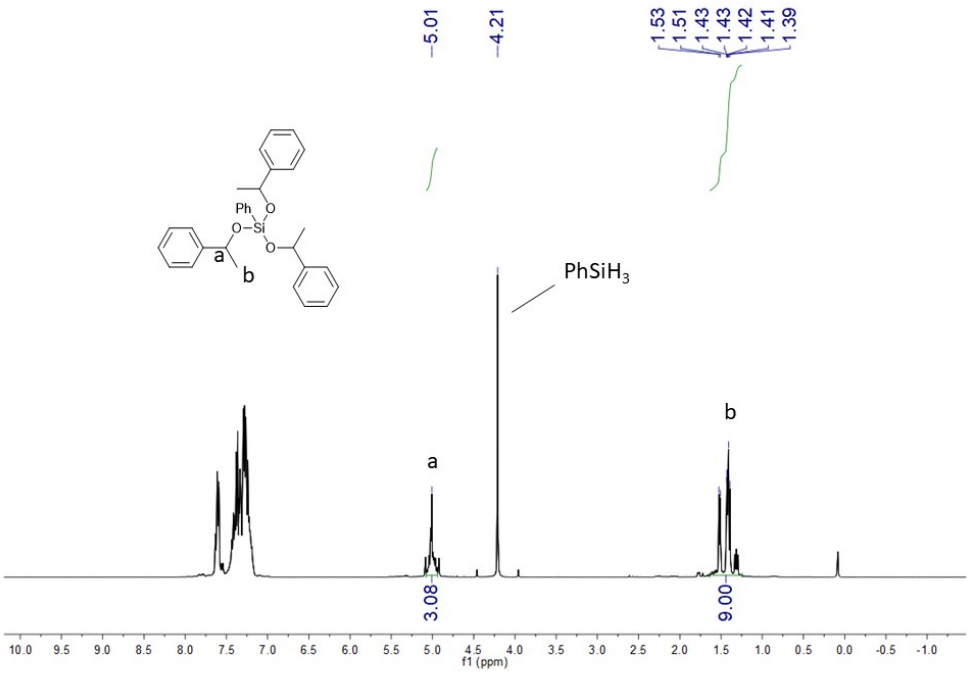

Figure S1. ^{1}H NMR spectrum of 2a react with $PhSiH_3$ (400MHz, $CDCl_3$).

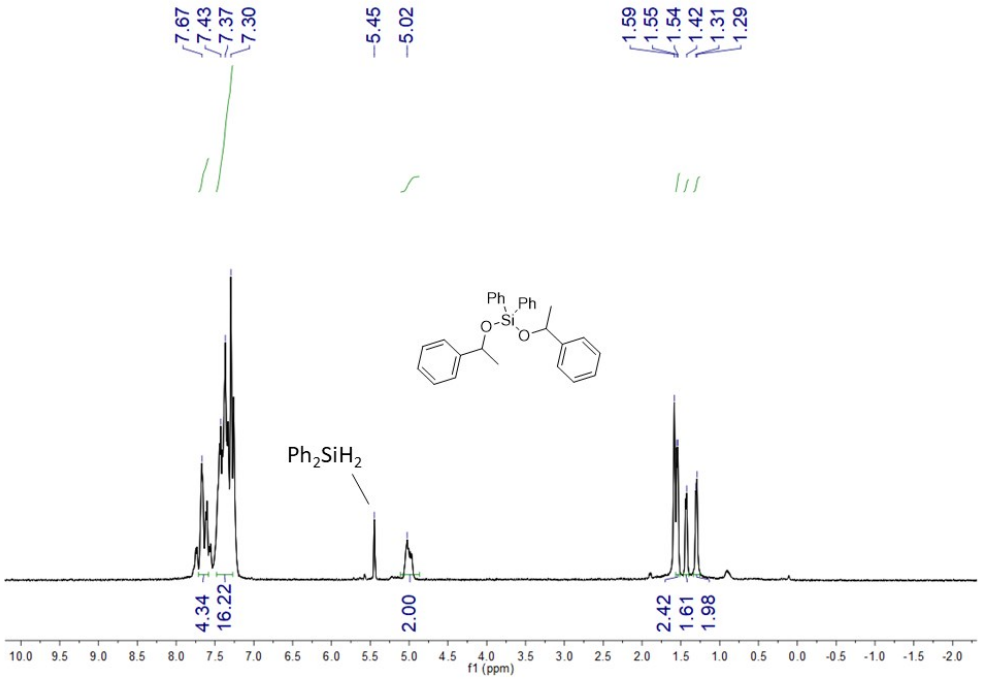

Figure S2. ^{1}H NMR spectrum of 2a react with Ph_2SiH_2 (400MHz, $CDCl_3$).

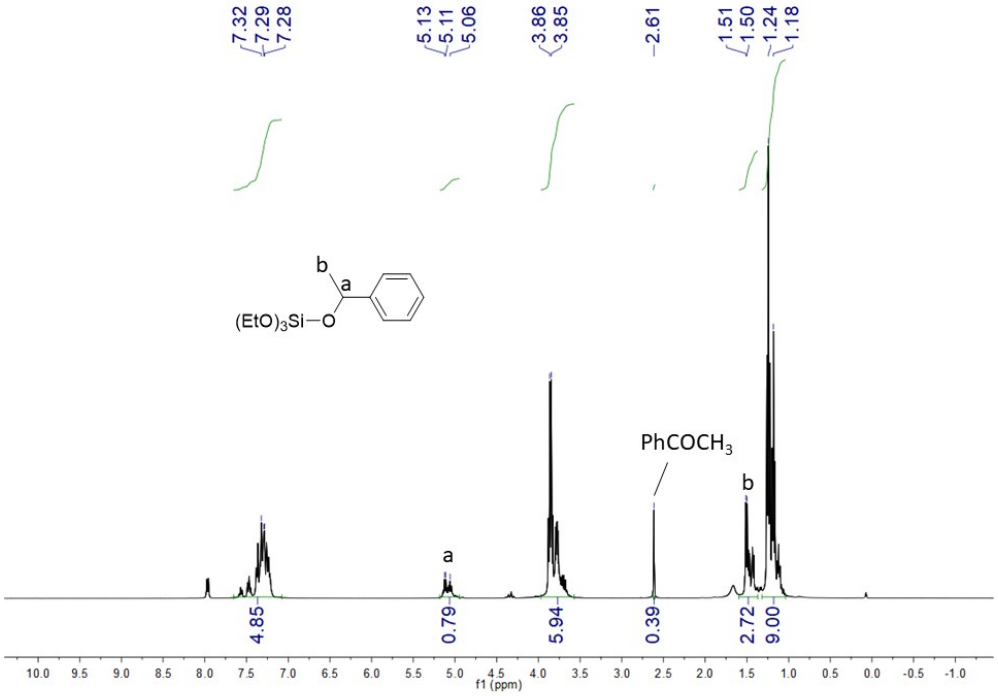

Figure S3. ^{1}H NMR spectrum of 2a react with $(EtO)_3SiH$ (400MHz, $CDCl_3$).

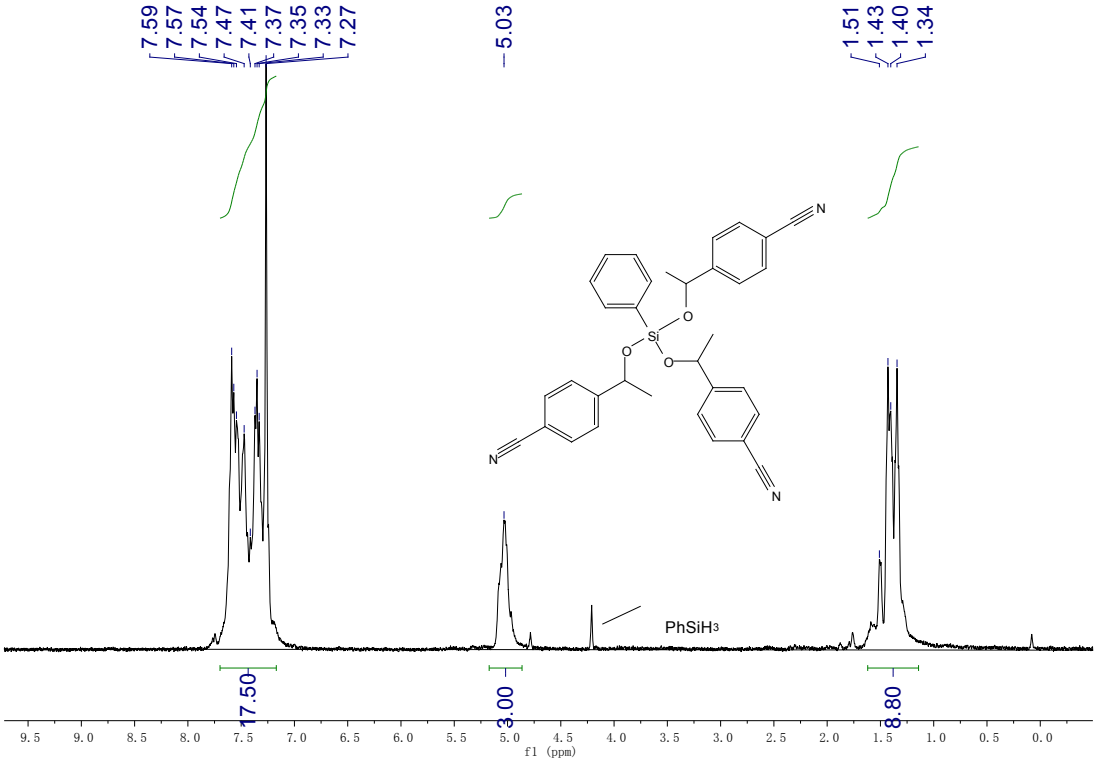

Figure S4. ^{1}H NMR spectrum of 3c (400MHz, $CDCl_3$).

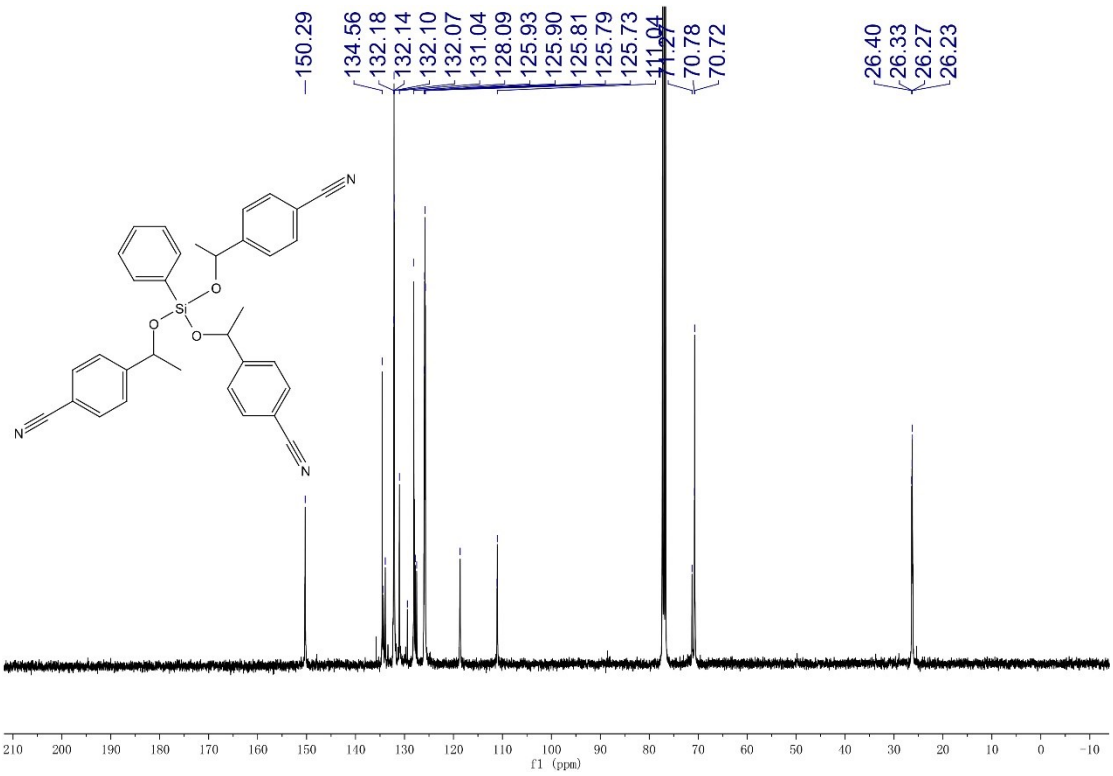

Figure S5. ^{13}C NMR spectrum of 3c (101 MHz, $CDCl_3$).

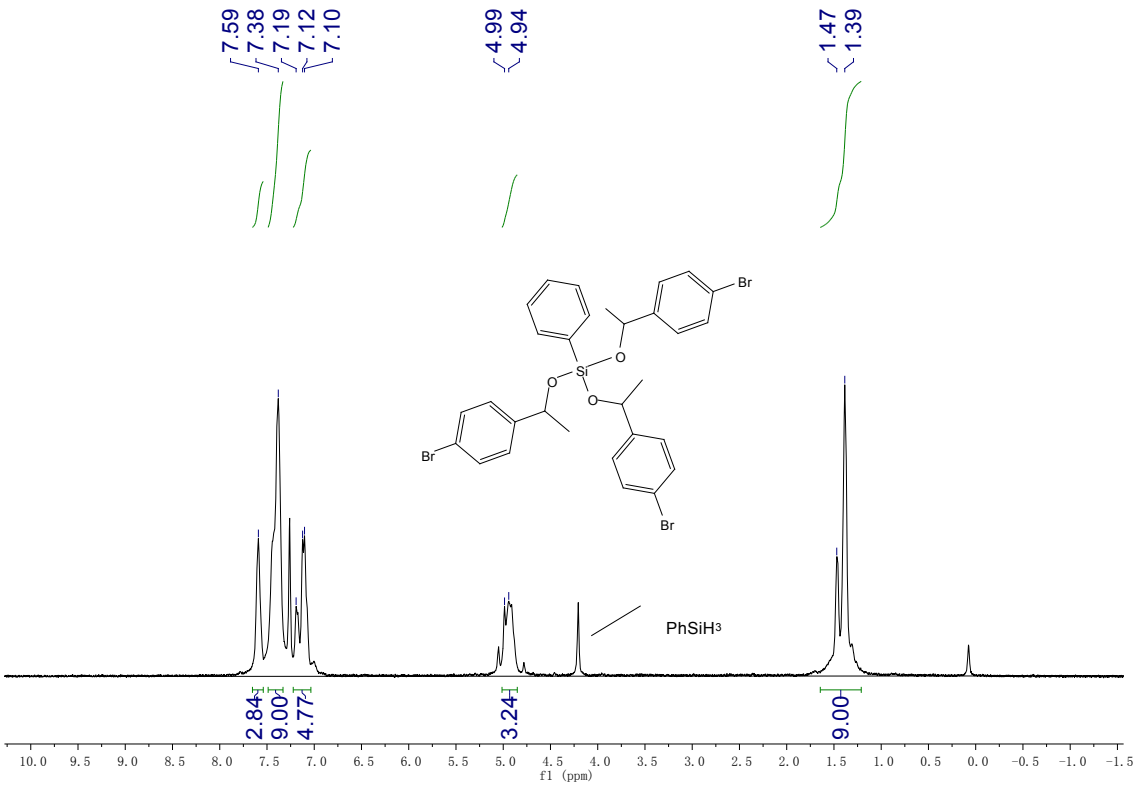

Figure S6. ^{1}H NMR spectrum of 3d (400MHz, $CDCl_3$).

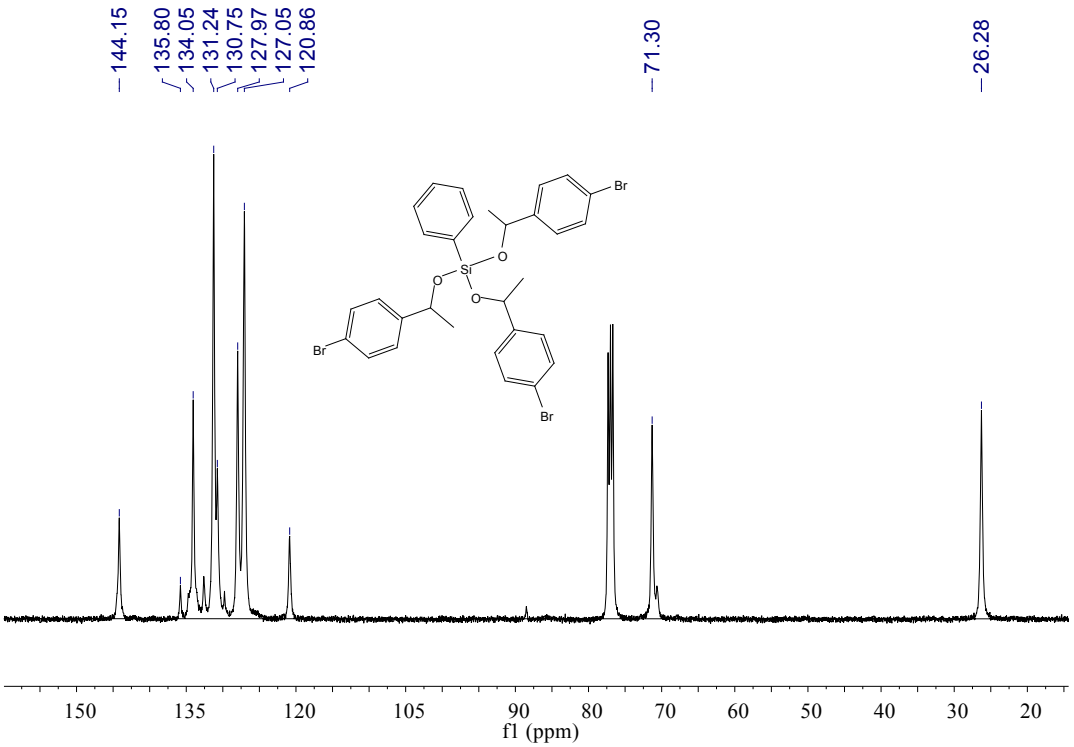

Figure S7. ^{13}C NMR spectrum of 3d (101 MHz, $CDCl_3$).

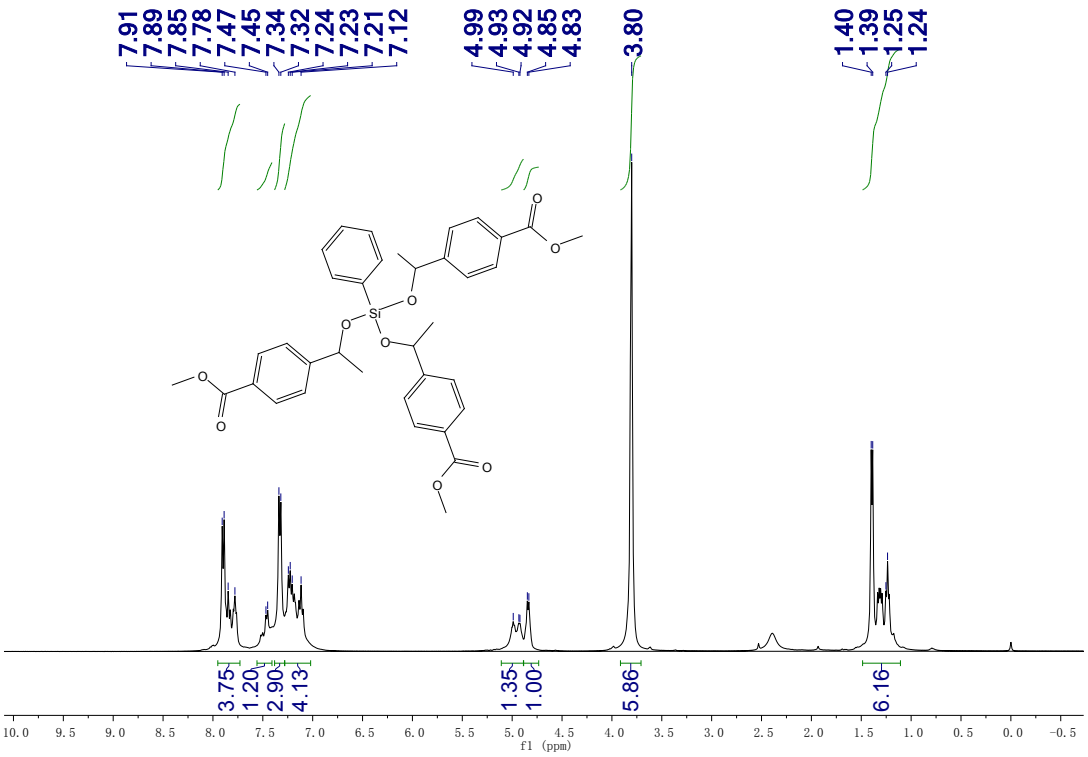

Figure S8. ^{1}H NMR spectrum of 3e (400MHz, $CDCl_3$).

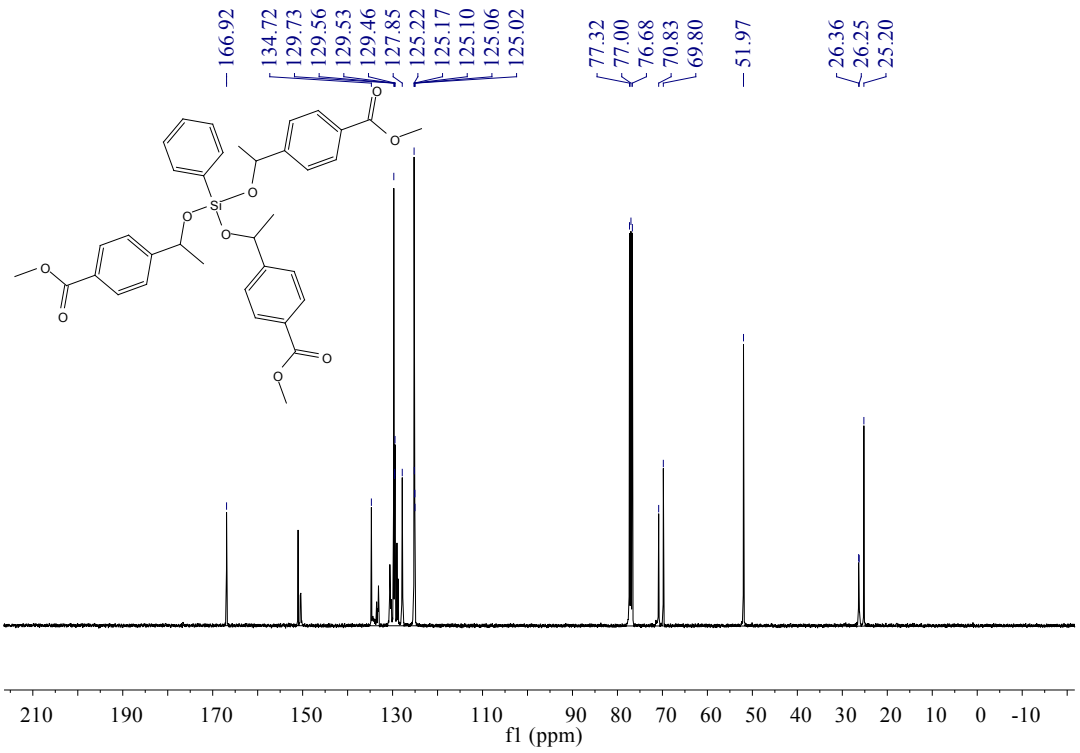

Figure S9. ^{13}C NMR spectrum of 3e (101 MHz, $CDCl_3$).

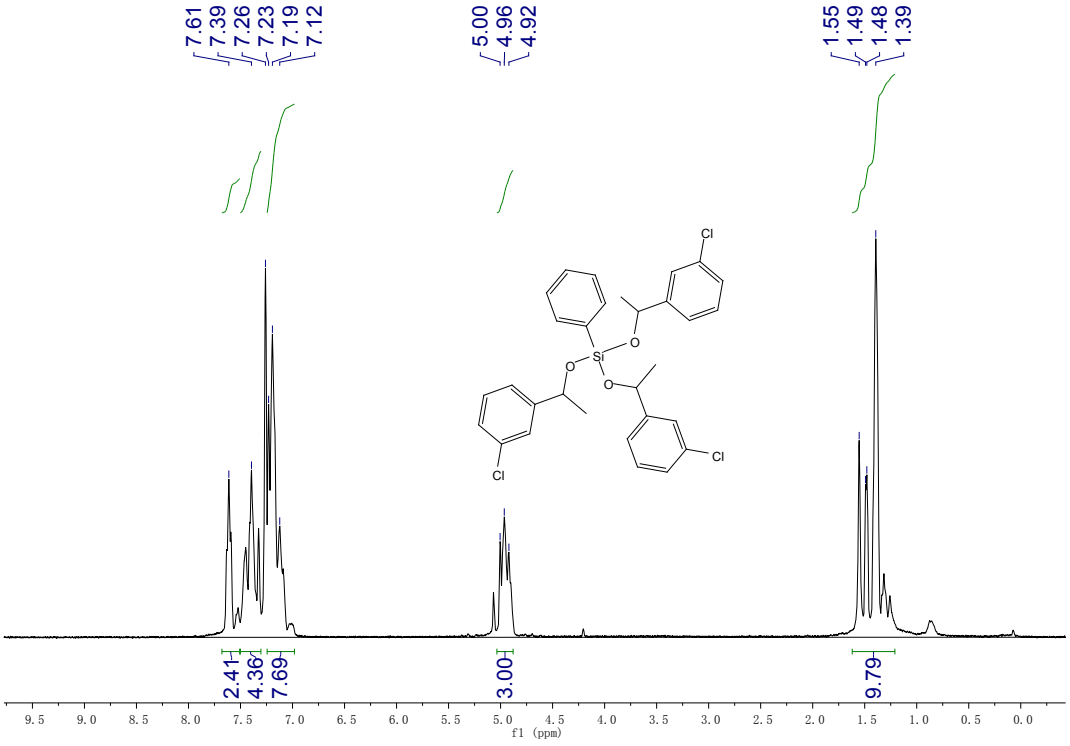

Figure S10. ^{1}H NMR spectrum of 3f (400MHz, $CDCl_3$).

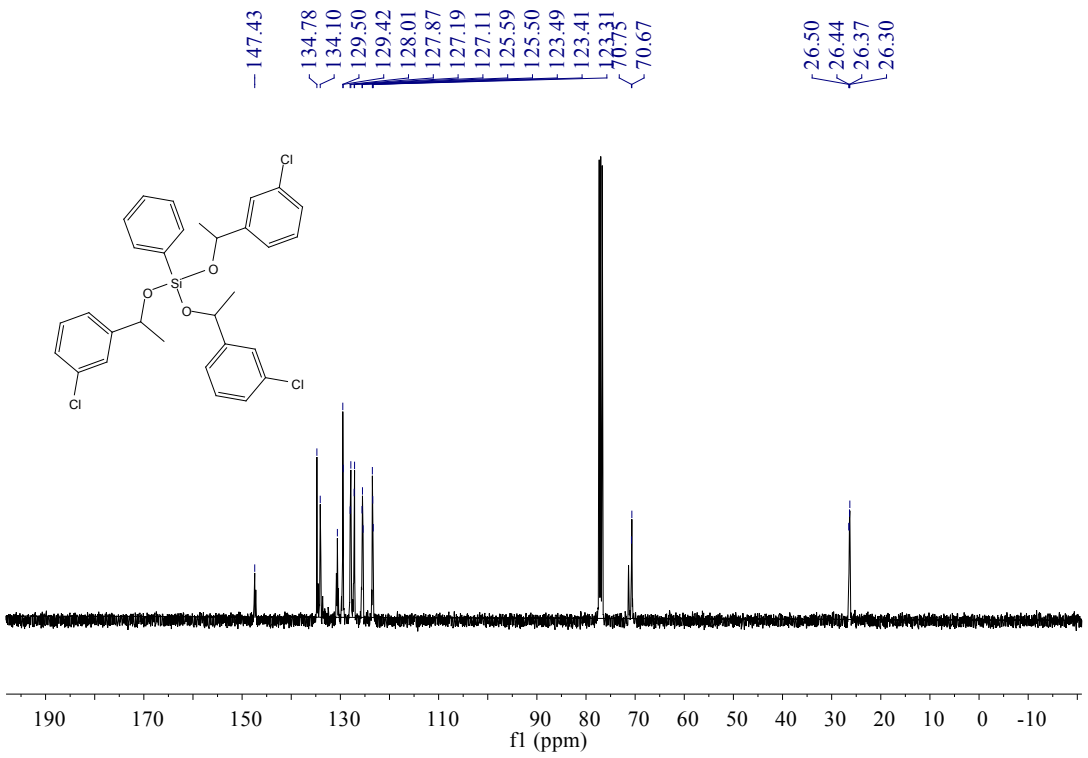

Figure S11. ^{13}C NMR spectrum of 3f (101 MHz, $CDCl_3$).

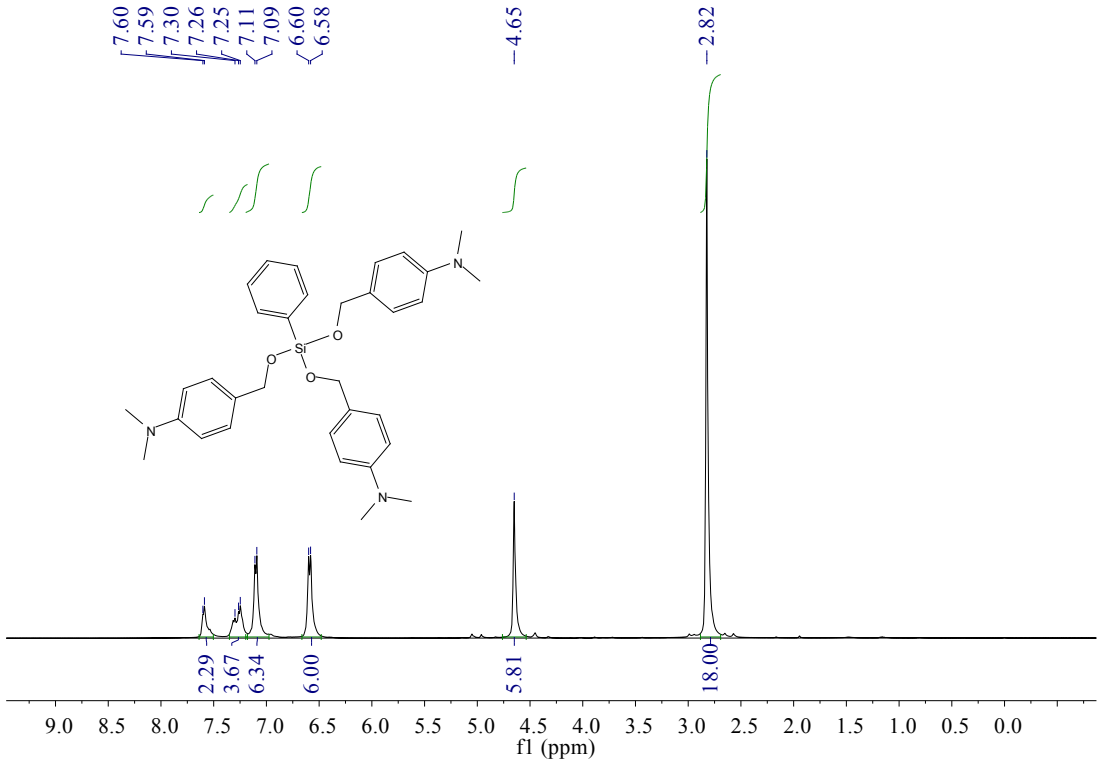

Figure S12. ^{1}H NMR spectrum of 3i (400MHz, $CDCl_3$).

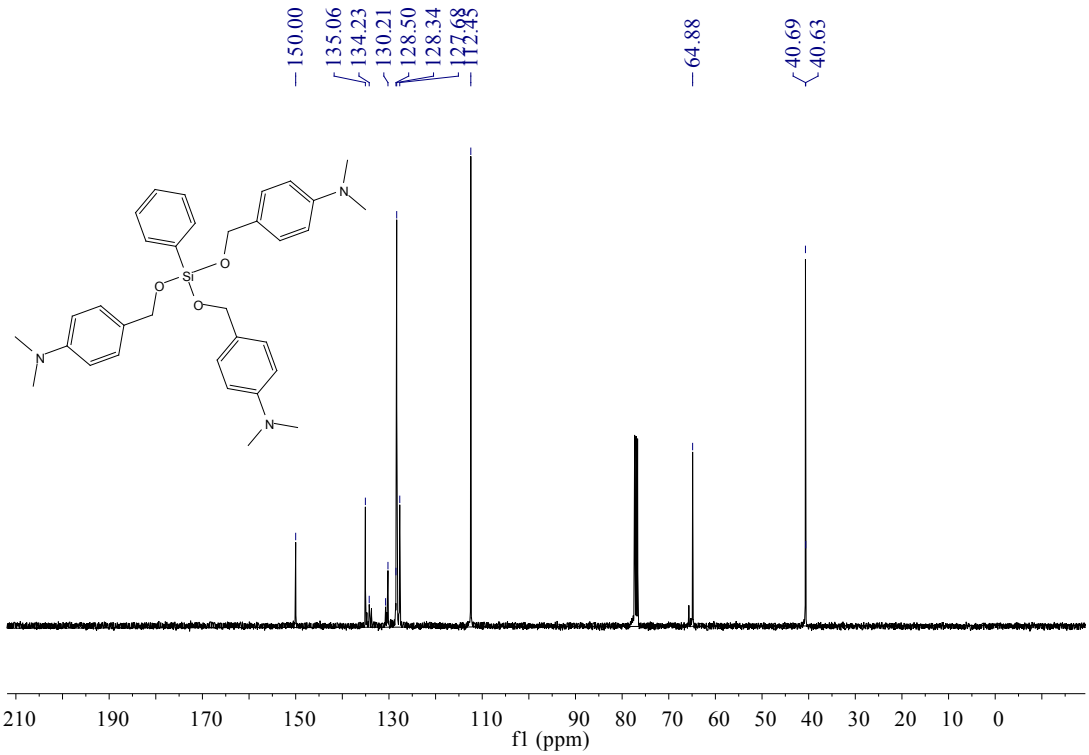

Figure S13. ^{13}C NMR spectrum of 3i (101 MHz, $CDCl_3$).

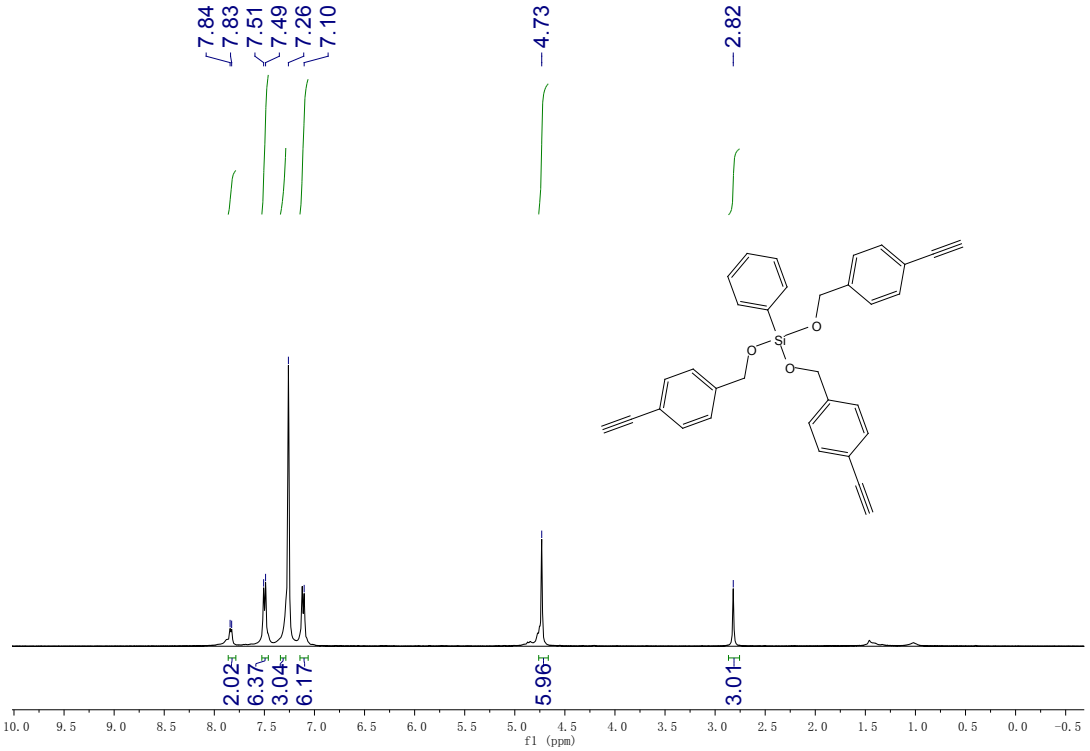

Figure S14. ^{1}H NMR spectrum of 3j (400MHz, $CDCl_3$).

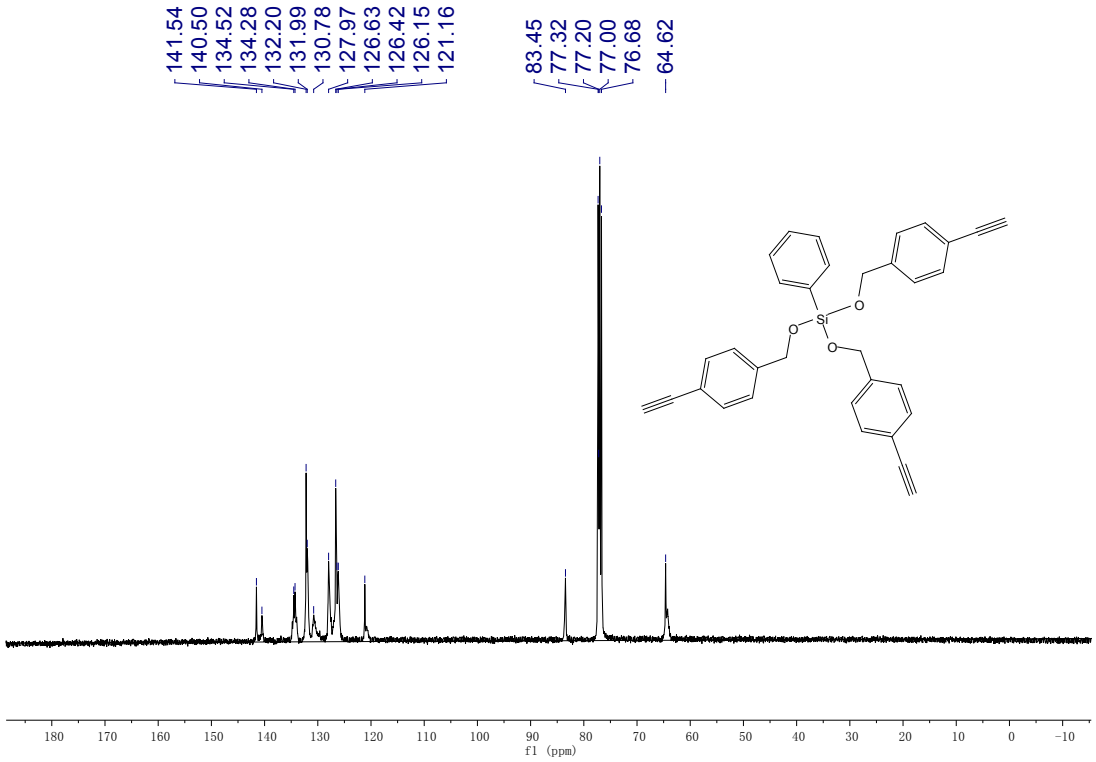

Figure S15. ^{13}C NMR spectrum of 3j (101 MHz, $CDCl_3$).

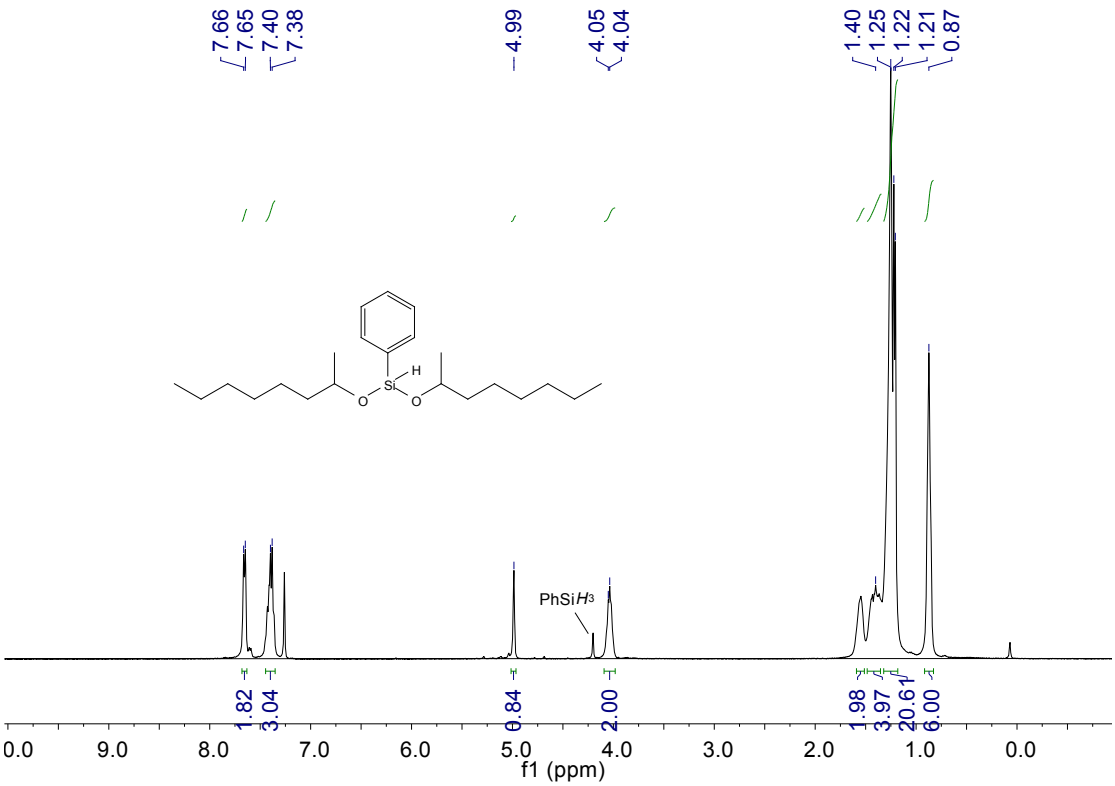

Figure S16. ^{1}H NMR spectrum of 4l (400MHz, $CDCl_3$).

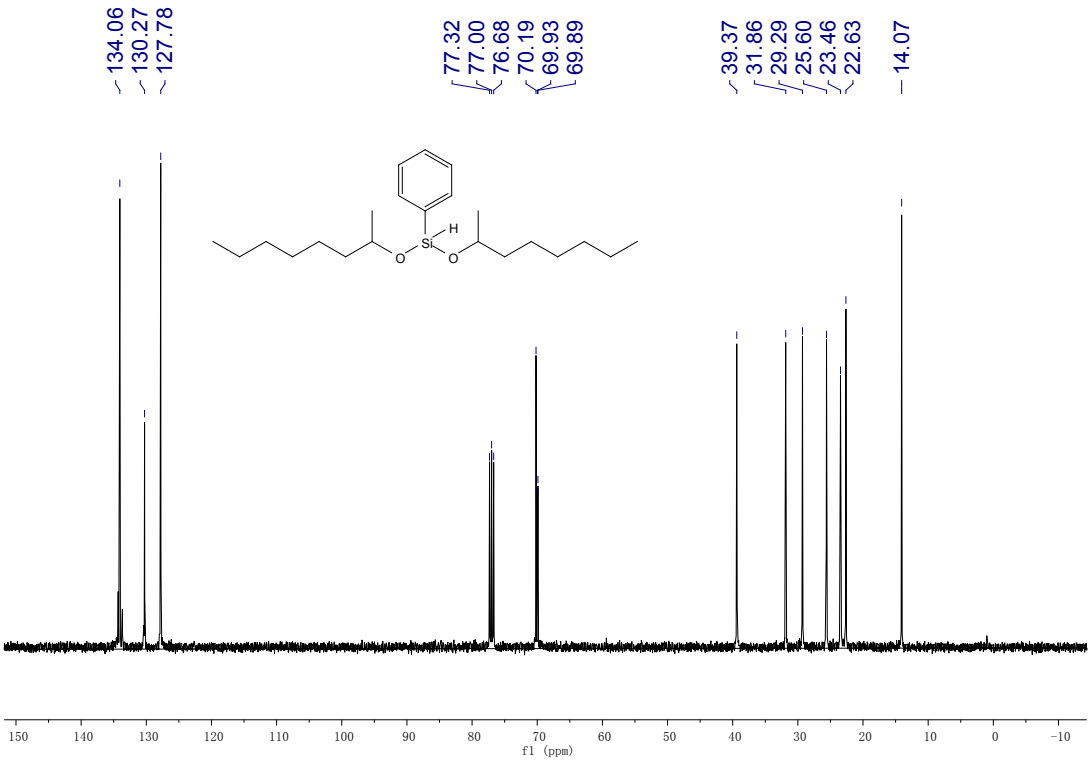

Figure S17. ^{13}C NMR spectrum of 4l (101 MHz, $CDCl_3$).

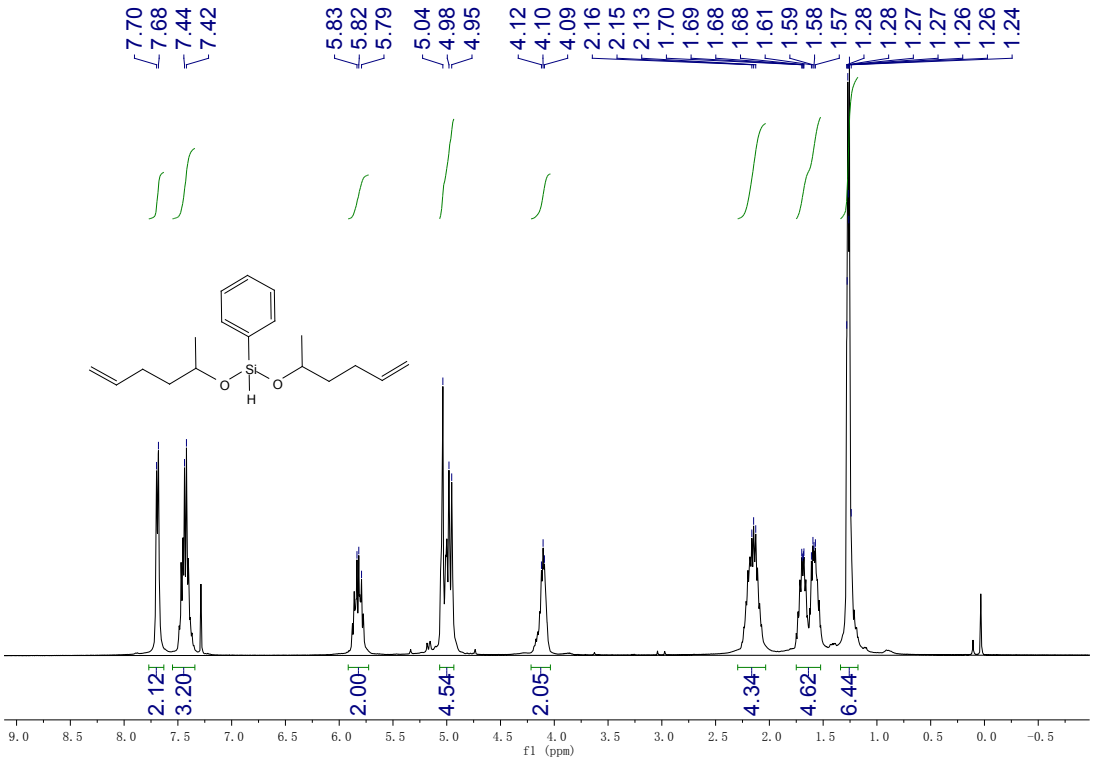

Figure S18. ^{1}H NMR spectrum of 4o (400MHz, $CDCl_3$).

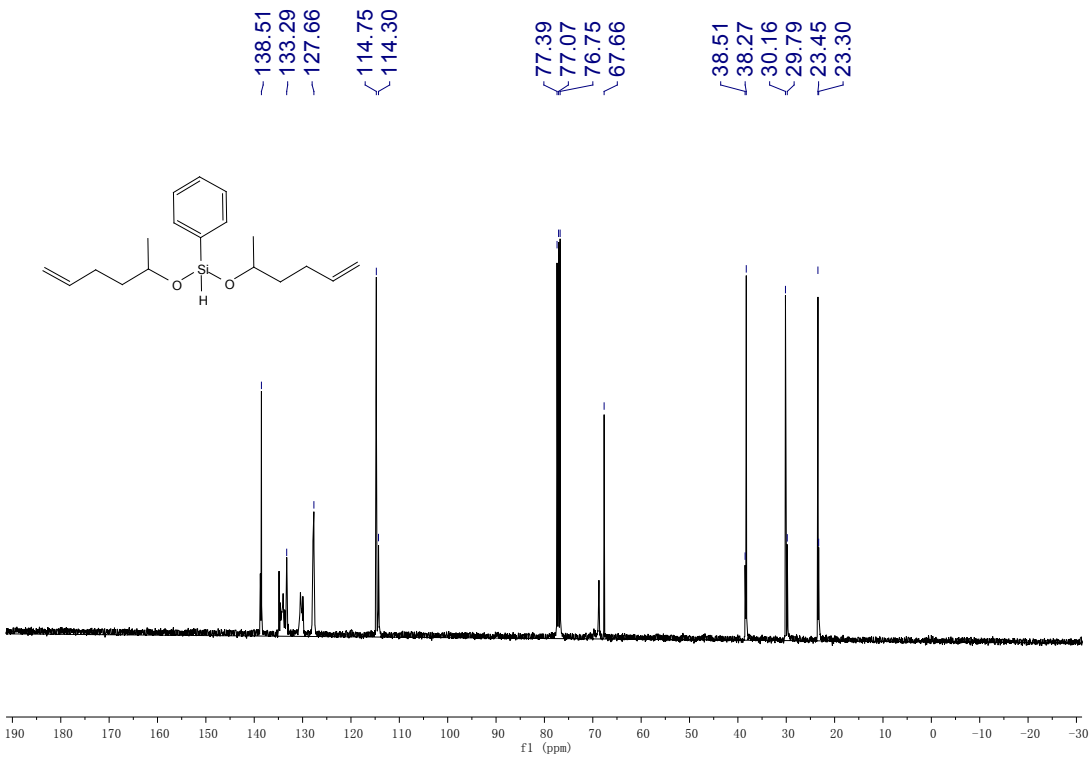

Figure S19. ^{13}C NMR spectrum of 4o (101 MHz, $CDCl_3$).

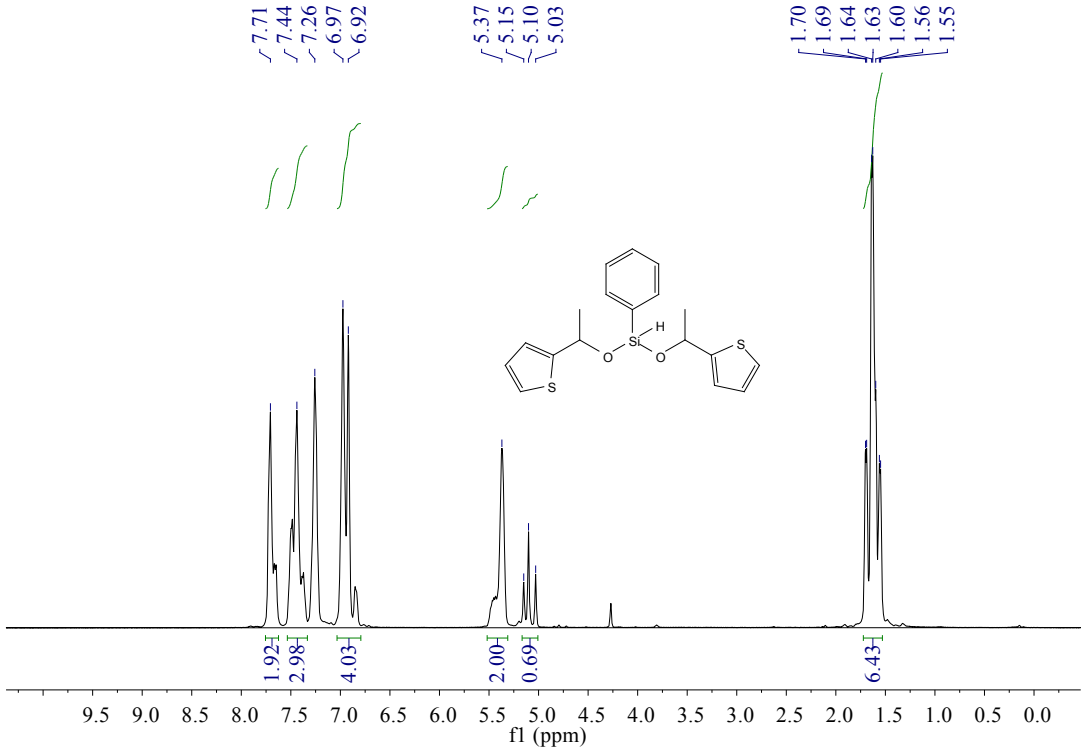

Figure S20. ^{1}H NMR spectrum of 4s (400MHz, $CDCl_3$).

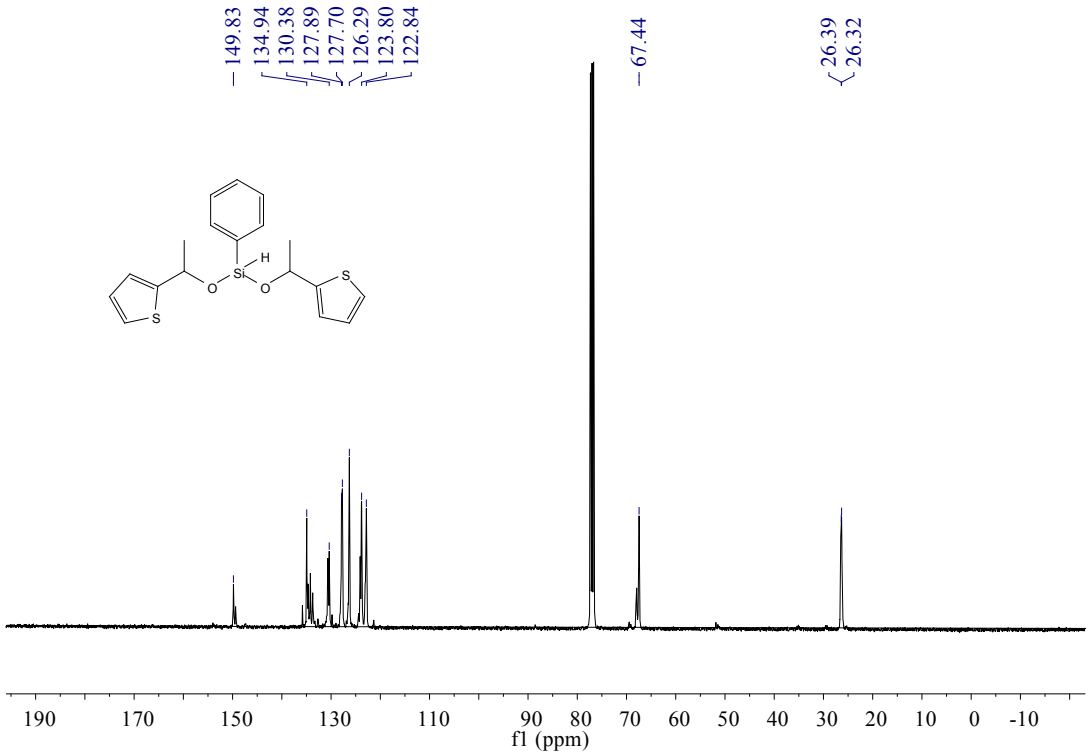

Figure S21. ^{13}C NMR spectrum of 4o (101 MHz, $CDCl_3$).

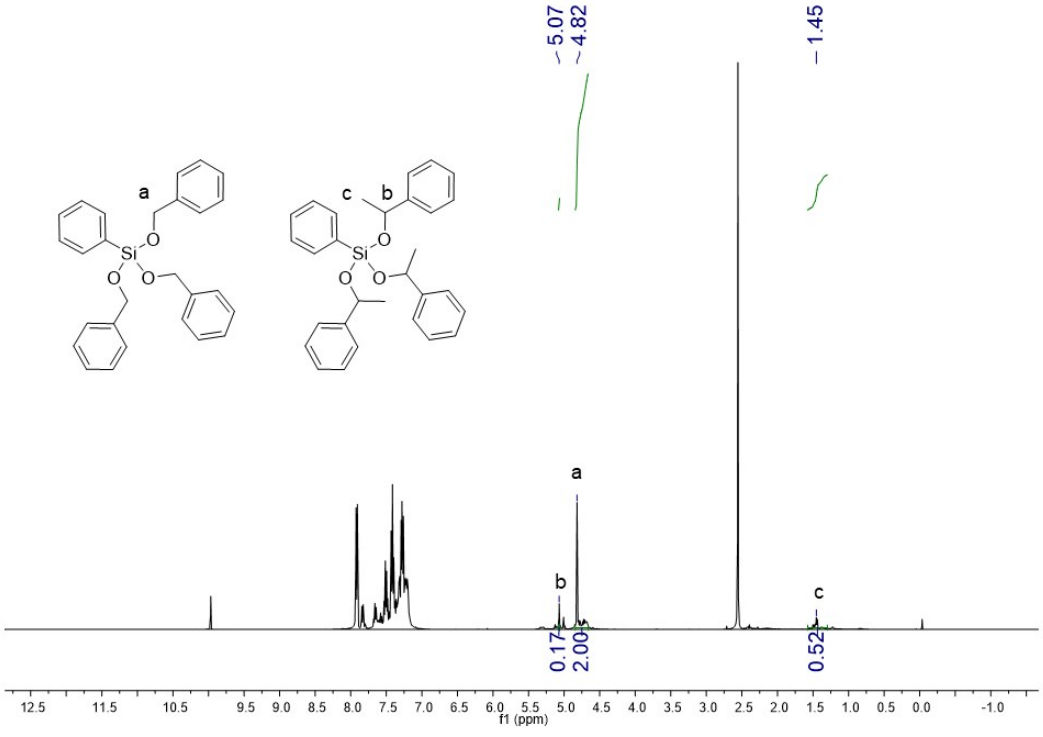

Figure S22. ^{1}H NMR spectrum of intermolecular chemoselective reaction (101 MHz, $CDCl_3$).

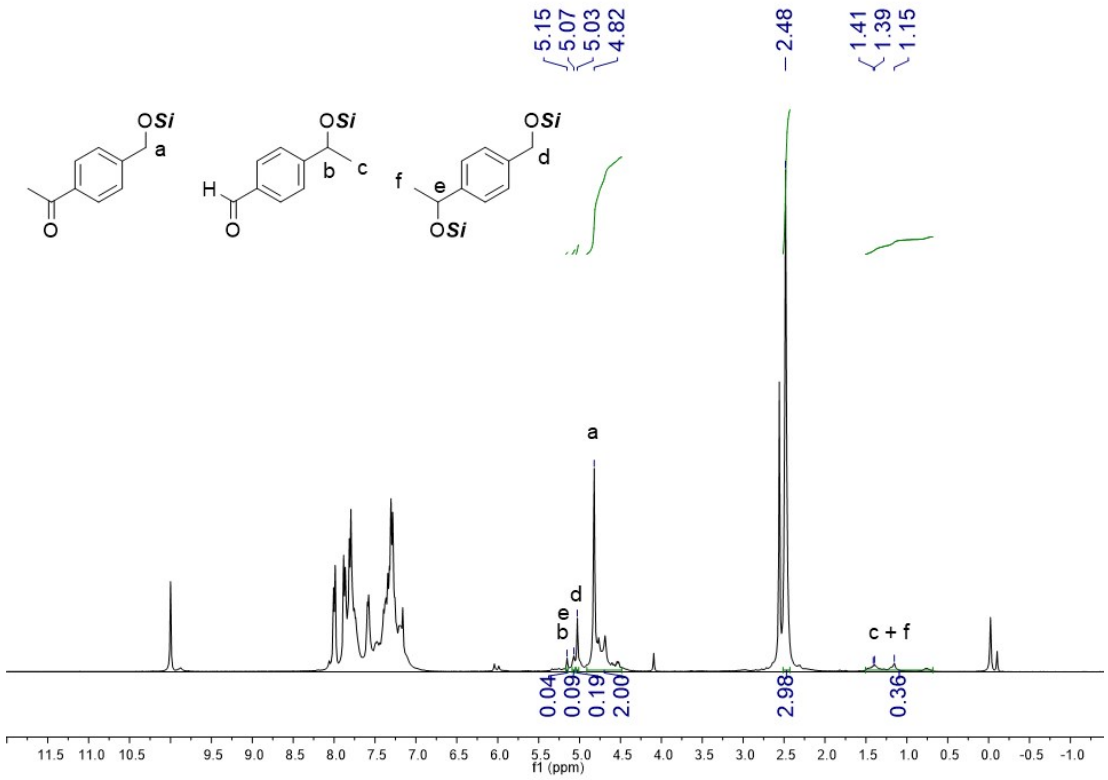

Figure S23. ^{1}H NMR spectrum of intramolecular chemoselective reaction (101 MHz, $CDCl_3$).

3. References

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