Supporting Information

Nickel(0)-Catalyzed Ring-Opening Reaction of Silacyclobutanes with 1,3-Dienes to Access Allylsilane

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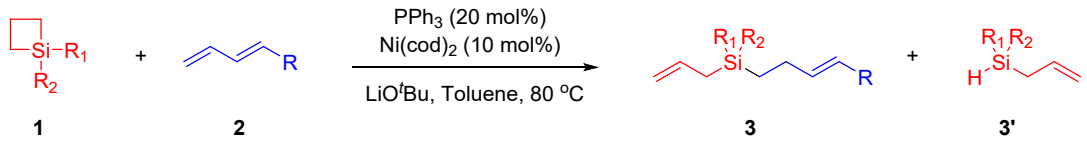
Content

1. General Information

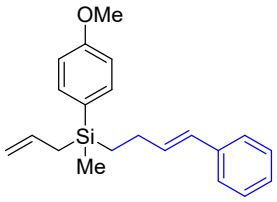
All reactions were carried out under an atmosphere of argon in sealed tube with magnetic stirring. ^{1}H NMR spectra, ^{19}F NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Substituted silacyclobutanes[1] (SCBs) and 1,3-Dienes[2] were known compounds and synthesized according to reported methods.

2. General Procedure for the Synthesis of Products 3



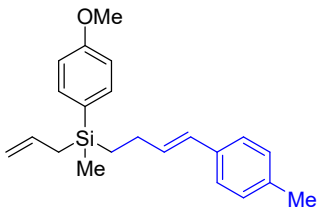
To a 10 mL sealed tube equipped with a stir bar was added $Ni(cod)_2$ (10 mol%), PPh_3 (20 mol%), LiO^tBu (1.0 equiv), substituted SCBs **1** (0.3 mmol, 1.0 equiv), 1,3-dienes **2** (0.45 mmol, 1.5 equiv). The flask was evacuated and refilled with nitrogen. Then 3 mL toluene was added to the tube under nitrogen atmosphere, and stirred at 80 °C for 12-24 h. After the reaction was completed (monitored by TLC), the filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **3**.

2.1 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-phenylbut-3-en-1-yl)silane (**3aa**)



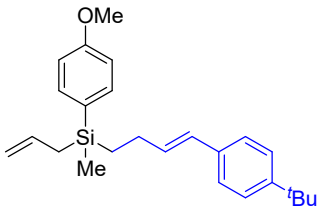
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3aa** as yellow oil (89.0 mg, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.5 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.16 (m, 1H), 6.91 (d, J = 8.5 Hz, 2H), 6.36 – 6.29 (m, 1H), 6.21 (m, 1H), 5.78 (m, 1H), 4.93 – 4.78 (m, 2H), 3.79 (s, 3H), 2.23 (m, 2H), 1.79 (d, J = 8.1, 1.2 Hz, 2H), 1.03 – 0.88 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 137.8, 135.3, 134.6, 133.3, 128.5, 128.4, 128.1, 126.7, 125.9, 113.6, 113.5, 54.9, 27.1, 22.4, 13.6, -5.3. HRMS (EI) calculated for $[C_{21}H_{26}OSi]^+$: 322.1753, found: 322.1748.

2.2 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(p-tolyl)but-3-en-1-yl)silane (**3ab**)



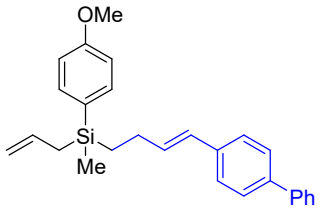
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ab** as colorless oil (81.6 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.93 – 6.88 (m, 2H), 6.29 (d, J = 15.6 Hz, 1H), 6.16 (m, 1H), 5.85 – 5.71 (m, 1H), 4.94 – 4.75 (m, 2H), 3.79 (s, 3H), 2.30 (s, 3H), 2.22 (dd, J = 11.1, 5.6 Hz, 2H), 1.79 (d, J = 8.1 Hz, 2H), 0.96 (td, J = 8.1, 2.2 Hz, 2H), 0.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 136.4, 135.3, 135.1, 134.6, 132.3, 129.1, 128.4, 128.1, 125.8, 113.6, 113.5, 54.9, 27.1, 22.4, 21.1, 13.7, -5.2. HRMS (ESI) calculated for $[M+Na]^+ = [C_{22}H_{28}NaOSi]^+$: 359.1802 found: 359.1798.

2.3 (*E*)-allyl(4-(4-(tert-butyl)phenyl)but-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3ac**)



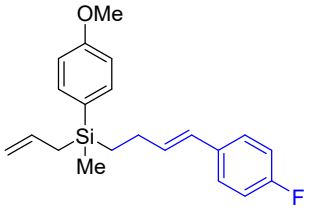
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ac** as colorless oil (86.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.17 (m, 1H), 5.86 – 5.71 (m, 1H), 4.93 – 4.80 (m, 2H), 3.79 (s, 3H), 2.27 – 2.17 (m, 2H), 1.79 (m, 2H), 1.30 (s, 9H), 1.02 – 0.90 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 149.7, 135.3, 135.1, 134.6, 132.5, 128.2, 128.1, 125.6, 125.3, 113.6, 113.5, 54.9, 31.3, 27.2, 22.4, 13.7, -5.2. HRMS (ESI) calculated for $[M+Na]^+ = [C_{25}H_{34}NaOSi]^+$: 401.2271 found: 401.2273.

2.4 (*E*)-(4-([1,1'-biphenyl]-4-yl)but-3-en-1-yl)(allyl)(4-methoxyphenyl)(methyl)silane (**3ad**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ad** as yellow oil (108.9 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 6.24 (m, 1H), 5.79 (m, 1H), 4.93 – 4.81 (m, 2H), 3.76 (s, 3H), 2.29 – 2.19 (m, 2H), 1.80 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.03 – 0.91 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 140.8, 139.4, 136.9, 135.3, 134.5, 133.5, 128.7, 128.1, 127.1, 126.8, 126.3, 113.6, 113.5, 54.9, 27.2, 22.3, 13.6, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{27}H_{30}NaOSi]^+$: 421.1958 found: 421.1962.

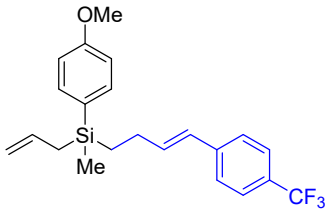
2.5 (*E*)-allyl(4-(4-fluorophenyl)but-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3ae**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ae** as yellow oil (94.1 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.22 (m, 2H), 6.99 – 6.87 (m, 4H), 6.27 (d, *J* = 15.8 Hz, 1H), 6.11 (m, 1H), 5.88 – 5.68 (m, 1H), 4.94 – 4.79 (m, 2H), 3.79 (s, 3H), 2.21 (dd, *J* = 10.6, 6.0 Hz, 2H), 1.79 (d, *J* = 8.1 Hz, 2H), 0.99 – 0.92 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 160.6, 160.5, 135.3, 134.5, 134.0 (d, *J* = 3.1 Hz), 133.1 (d, *J* = 2.2 Hz), 128.0, 127.3 (d, *J* = 5.2 Hz), 127.2, 115.3, 115.1, 113.6, 113.5, 77.3, 77.0, 76.7, 54.9, 27.1, 22.3, 13.6, -5.3.

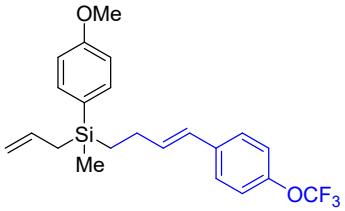
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.83. HRMS (EI) calculated for $[C_{21}H_{25}FOSi]^+$: 340.1659, found: 340.1657.

2.6 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)silane (**3af**)



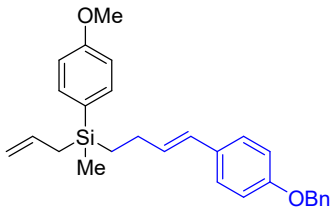
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3af** as yellow oil (91.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.37 (m, 4H), 7.29 – 7.22 (m, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.71 (dt, *J* = 15.6, 2.3 Hz, 1H), 6.18 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.79 (m, 1H), 4.93 – 4.82 (m, 2H), 3.80 (s, 3H), 2.27 (m, 2H), 1.80 (dt, *J* = 8.0, 1.2 Hz, 2H), 1.04 – 0.93 (m, 2H), 0.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 137.6, 135.3, 134.5, 131.6, 128.0, 127.1, 126.4, 125.6 (t, *J* = 5.8 Hz), 124.6 (d, *J* = 2.2 Hz), 113.6 (d, *J* = 6.5 Hz), 55.0, 27.5, 22.3, 13.5, -5.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.6. HRMS (EI) calculated for $[C_{22}H_{25}F_3OSi]^+$: 390.1627, found: 390.1626.

2.7 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(4-(trifluoromethoxy)phenyl)but-3-en-1-yl)silane (**3ag**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ag** as yellow oil (104.8 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.29 – 7.23 (m, 2H), 7.10 (m, 2H), 6.94 – 6.88 (m, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.18 (m, 1.9 Hz, 1H), 5.87 – 5.71 (m, 1H), 4.93 – 4.82 (m, 2H), 3.79 (s, 3H), 2.28 – 2.18 (m, 2H), 1.80 (d, *J* = 8.1 Hz, 2H), 0.96 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 147.9, 136.7, 135.3, 134.5 (d, *J* = 2.1 Hz), 127.1, 127.0, 121.0, 113.6, 113.6, 54.9, 27.1, 22.3, 13.6, -5.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.84. HRMS (EI) calculated for $[C_{22}H_{25}F_3O_2Si]^+$: 406.1576, found: 406.1569.

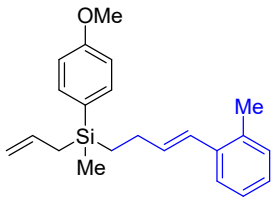
2.8 (*E*)-allyl(4-(4-(benzyloxy)phenyl)but-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3ah**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the product **3ah** as yellow oil (108.7 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.88 (dd, *J* = 10.8, 8.3 Hz, 4H), 6.25 (d, *J* = 15.7 Hz, 1H), 6.06 (m, 1H), 5.78 (m, 1H), 5.00

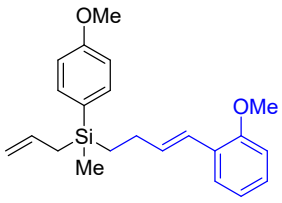
(s, 2H), 4.92 – 4.81 (m, 2H), 3.76 (s, 3H), 2.25 – 2.15 (m, 2H), 1.78 (d, J = 8.1 Hz, 2H), 1.01 – 0.90 (m, 2H), 0.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 157.8, 137.0, 135.3, 134.5, 131.3, 130.9, 128.5, 127.8, 127.4, 126.9, 114.8, 113.5, 113.4, 69.9, 54.9, 27.1, 22.3, 13.7, -5.3. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{28}H_{32}NaO_2Si]^+$: 451.2064 found: 451.2064.

2.9 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(o-tolyl)but-3-en-1-yl)silane (**3ai**)



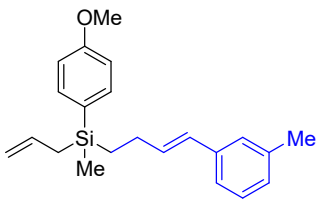
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ai** as colorless oil (94.2 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.32 (m, 1H), 7.18 – 7.03 (m, 3H), 6.94 – 6.86 (m, 2H), 6.51 (dt, J = 15.6, 1.6 Hz, 1H), 6.08 (dt, J = 15.6, 6.6 Hz, 1H), 5.79 (m, 1H), 4.93 – 4.81 (m, 2H), 3.78 (s, 3H), 2.29 (s, 3H), 2.25 (m, 2H), 1.80 (m, 2H), 1.03 – 0.92 (m, 2H), 0.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 136.9, 135.3, 134.8, 134.6, 134.5, 130.1, 128.1, 126.7, 126.3, 125.9, 125.4, 113.6, 113.5, 54.9, 27.5, 22.4, 19.8, 13.8, -5.2. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{22}H_{28}NaOSi]^+$: 359.1802 found: 359.1799.

2.10 (*E*)-allyl(4-methoxyphenyl)(4-(2-methoxyphenyl)but-3-en-1-yl)(methyl)silane (**3aj**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the product **3aj** as yellow oil (84.7 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.22 – 7.09 (m, 1H), 6.93 – 6.84 (m, 3H), 6.81 (d, J = 8.2 Hz, 1H), 6.72 – 6.62 (m, 1H), 6.21 (m, 1H), 5.86 – 5.71 (m, 1H), 4.92 – 4.81 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.31 – 2.20 (m, 2H), 1.79 (d, J = 8.1 Hz, 2H), 1.03 – 0.93 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 156.2, 135.3, 134.6, 134.0, 128.2, 127.7, 126.9, 126.3, 123.1, 120.6, 113.5, 113.4, 110.7, 55.3, 54.9, 27.6, 22.4, 13.7, -5.3. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{22}H_{28}NaO_2S]^+$: 375.1751 found: 375.1756.

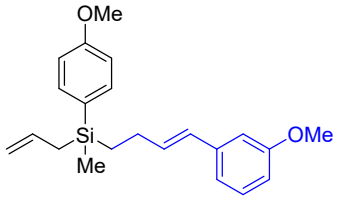
2.11 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(m-tolyl)but-3-en-1-yl)silane (**3ak**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ak** as colorless oil (93.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.5 Hz, 2H), 7.22 – 7.11 (m, 1H), 7.08

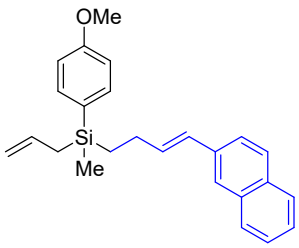
(m, 2H), 6.98 (m, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.29 (d, J = 15.7 Hz, 1H), 6.19 (dt, J = 15.7, 6.3 Hz, 1H), 5.78 (m, 1H), 4.91 – 4.82 (m, 2H), 3.78 (s, 3H), 2.30 (s, 3H), 2.27 – 2.18 (m, 2H), 1.79 (d, J = 8.1 Hz, 2H), 1.02 – 0.90 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.9, 137.8, 135.3, 134.6, 133.1, 128.6, 128.3, 128.1, 127.5, 126.6, 123.0, 113.6, 113.5, 54.9, 27.1, 22.4, 21.4, 13.6, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{22}H_{28}NaOSi]^+$: 359.1802 found: 359.1806.

2.12 (*E*)-allyl(4-methoxyphenyl)(4-(3-methoxyphenyl)but-3-en-1-yl)(methyl)silane (**3al**)



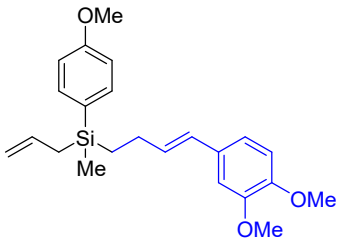
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the product **3al** as yellow oil (90.4 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 6.89 (m, 3H), 6.84 – 6.81 (m, 1H), 6.72 (dd, J = 8.2, 2.5 Hz, 1H), 6.29 (d, J = 15.9 Hz, 1H), 6.25 – 6.16 (m, 1H), 5.86 – 5.71 (m, 1H), 4.92 – 4.81 (m, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 2.22 (dt, J = 11.2, 6.7 Hz, 2H), 1.79 (d, J = 8.1 Hz, 2H), 1.02 – 0.92 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 159.7, 139.3, 135.3, 134.5, 133.6, 129.3, 128.4, 128.0, 118.6, 113.6, 113.5, 112.3, 111.2, 55.0, 54.9, 27.1, 22.3, 13.5, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{22}H_{28}NaO_2Si]^+$: 375.1751 found: 375.1751.

2.13 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(naphthalen-2-yl)but-3-en-1-yl)silane (**3am**)



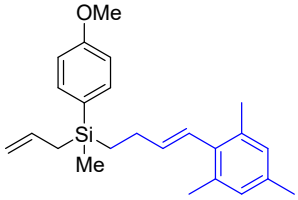
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3am** as yellow oil (83.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 1H), 7.80 (dd, J = 6.9, 2.7 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.49 – 7.43 (m, 5H), 7.43 – 7.34 (m, 1H), 7.05 (d, J = 15.4 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.23 (dt, J = 15.4, 6.6 Hz, 1H), 5.81 (m, 1H), 4.96 – 4.83 (m, 2H), 3.77 (s, 3H), 2.40 – 2.29 (m, 2H), 1.82 (d, J = 8.1 Hz, 2H), 1.10 – 0.95 (m, 2H), 0.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 136.6, 135.6, 135.3, 134.6, 133.6, 131.1, 128.4, 128.0, 127.1, 125.7, 125.6, 125.5, 123.9, 123.4, 113.6, 113.5, 54.9, 27.6, 22.4, 13.7, -5.2. HRMS (EI) calculated for $[C_{25}H_{28}OSi]^+$: 372.1909, found: 372.1904.

2.14 (*E*)-allyl(4-(3,4-dimethoxyphenyl)but-2-en-1-yl)(4-methoxyphenyl)(methyl) silane (**3an**)



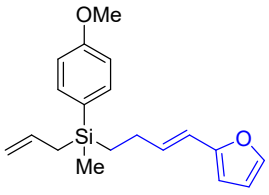
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 30:1) to afford the product **3an** as yellow oil (106.3 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.26 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.08 (dt, *J* = 15.7, 6.5 Hz, 1H), 5.79 (m, 1H), 4.93 – 4.80 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 2.27 – 2.18 (m, 2H), 1.83 – 1.74 (m, 2H), 1.03 – 0.93 (m, 2H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 148.9, 148.1, 135.2, 134.5, 131.3, 130.9, 128.1, 128.0, 118.7, 113.5, 113.4, 111.1, 108.4, 55.8, 55.6, 54.8, 27.0, 22.3, 13.6, -5.4. HRMS (ESI) calculated for $[M+Na]^+ = [C_{23}H_{30}NaO_3Si]^+$: 405.1856 found: 405.1848.

2.15 (*E*)-allyl(4-mesitylbut-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3ao**)



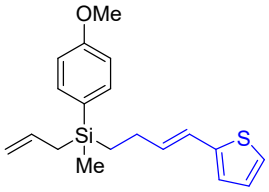
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ao** as colorless oil (93.0 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.83 (s, 2H), 6.24 (d, *J* = 16.0 Hz, 1H), 5.79 (m, 1H), 5.67 (dt, *J* = 16.0, 6.5 Hz, 1H), 4.96 – 4.81 (m, 2H), 3.79 (s, 3H), 2.24 (m, 11H), 1.81 (dt, *J* = 8.0, 1.2 Hz, 2H), 1.02 – 0.92 (m, 2H), 0.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 137.9, 135.8, 135.5, 135.3, 134.6, 134.5, 128.4, 128.1, 125.7, 113.6, 113.5, 54.9, 27.6, 22.3, 20.9, 14.1, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{24}H_{32}NaOSi]^+$: 387.2115 found: 387.2118.

2.16 (*E*)-allyl(4-(furan-2-yl)but-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3ap**)



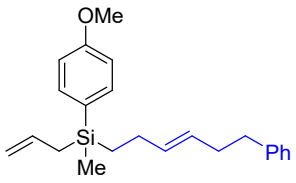
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ap** as yellow oil (69.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.31 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.25 – 6.14 (m, 2H), 6.09 (d, *J* = 3.3 Hz, 1H), 5.77 (m, 1H), 4.91 – 4.81 (m, 2H), 3.79 (s, 3H), 2.26 – 2.14 (m, 2H), 1.78 (dt, *J* = 7.9, 1.2 Hz, 2H), 0.99 – 0.90 (m, 2H), 0.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 153.3, 141.1, 135.3, 134.5, 132.4, 127.9, 117.3, 113.6, 113.5, 111.0, 105.9, 54.9, 26.8, 22.3, 13.4, -5.3. HRMS (EI) calculated for $[C_{19}H_{24}O_2Si]^+$: 312.1546, found: 312.1538.

2.17 (*E*)-allyl(4-methoxyphenyl)(methyl)(4-(thiophen-2-yl)but-3-en-1-yl)silane (**3aq**)



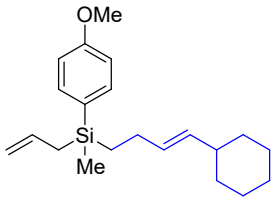
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3aq** as yellow oil (58.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 5.1 Hz, 1H), 6.95 – 6.89 (m, 3H), 6.83 (d, *J* = 3.5 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.08 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.78 (m, 1H), 4.92 – 4.81 (m, 2H), 3.81 (s, 3H), 2.19 (m, 2H), 1.83 – 1.76 (m, 2H), 1.03 – 0.90 (m, 2H), 0.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 143.1, 135.3, 134.5, 133.4, 128.0, 127.2, 124.1, 123.0, 121.9, 113.6, 113.5, 55.0, 26.9, 22.3, 13.5, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{19}H_{24}NaOSSi]^+$: 351.1209 found: 351.1209.

2.18 (*E*)-allyl(4-methoxyphenyl)(methyl)(6-phenylhex-3-en-1-yl)silane (**3ar**)



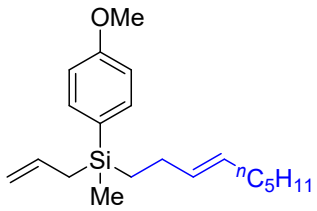
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ar** as colorless oil (66.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.26 (m, 2H), 7.15 (m, 3H), 6.96 – 6.85 (m, 2H), 5.76 (m, 1H), 5.42 (m, 2H), 4.92 – 4.79 (m, 2H), 3.78 (s, 3H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.31 – 2.21 (m, 2H), 2.01 (dt, *J* = 9.9, 5.8 Hz, 2H), 1.75 (d, *J* = 8.1 Hz, 2H), 0.84 (m, 2H), 0.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 142.1, 135.3, 134.7, 133.4, 128.4, 128.2, 128.1, 125.6, 113.5, 113.3, 54.9, 36.0, 34.3, 26.6, 22.4, 13.8, -5.3. HRMS (ESI) calculated for $[M+Na]^+ = [C_{23}H_{30}NaOSi]^+$: 373.1958 found: 373.1961.

2.19 (*E*)-allyl(4-cyclohexylbut-3-en-1-yl)(4-methoxyphenyl)(methyl)silane (**3as**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3as** as yellow oil (78.4 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 6.93 – 6.85 (m, 2H), 5.76 (m, 1H), 5.45 – 5.25 (m, 2H), 4.91 – 4.78 (m, 2H), 3.79 (s, 3H), 2.01 (m, 2H), 1.90 – 1.80 (m, 1H), 1.76 (d, *J* = 8.1 Hz, 2H), 1.72 – 1.55 (m, 4H), 1.31 – 1.08 (m, 4H), 1.08 – 0.93 (m, 2H), 0.91 – 0.80 (m, 2H), 0.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 135.3, 135.1, 134.7, 130.0, 128.4, 113.5, 113.3, 54.9, 40.5, 33.2, 26.7, 26.2, 26.1, 22.5, 13.9, -5.2. HRMS (EI) calculated for $[C_{21}H_{32}OSi]^+$: 328.2222, found: 328.2214.

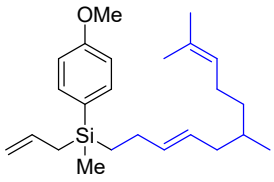
2.20 (*E*)-allyl(4-methoxyphenyl)(methyl)(non-3-en-1-yl)silane (**3at**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3at** as

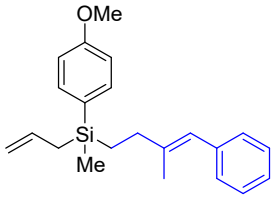
colorless oil (78.8 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.76 (m, 1H), 5.47 – 5.31 (m, 2H), 4.91 – 4.78 (m, 2H), 3.80 (s, 3H), 2.07 – 1.88 (m, 4H), 1.80 – 1.71 (m, 2H), 1.36 – 1.20 (m, 6H), 0.92 – 0.80 (m, 5H), 0.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 135.3, 134.7, 132.6, 129.1, 128.4, 113.5, 113.3, 54.9, 32.4, 31.4, 29.3, 26.6, 22.5, 22.4, 14.1, 13.9, -5.2. HRMS (EI) calculated for $[C_{20}H_{32}OSi]^+$: 316.2222, found: 316.2210.

2.21 (*E*)-allyl(6,10-dimethylundeca-3,9-dien-1-yl)(4-methoxyphenyl)(methyl)silane (**3au**)



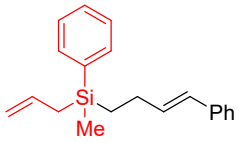
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3au** as colorless oil (80.8 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 6.93 – 6.87 (m, 2H), 5.83 – 5.70 (m, 1H), 5.39 (m, 2H), 5.13 – 5.06 (m, 1H), 4.91 – 4.79 (m, 2H), 3.79 (s, 3H), 2.00 (m, 5H), 1.81 – 1.74 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.51 – 1.26 (m, 2H), 1.19 – 1.04 (m, 1H), 0.93 – 0.79 (m, 5H), 0.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 135.3, 134.7, 134.0, 130.9, 128.3, 127.4, 125.0, 113.5, 113.3, 54.9, 39.9, 36.6, 32.8, 26.7, 25.7, 25.6, 22.4, 19.4, 17.6, 14.0, -5.2. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{24}H_{38}NaOSi]^+$: 393.2584 found: 393.2582.

2.22 (*E*)-allyl(4-methoxyphenyl)(methyl)(3-methyl-4-phenylbut-3-en-1-yl)silane (**3av**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3av** as yellow oil (36.3 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.29 (m, 2H), 7.23 – 7.14 (m, 3H), 6.92 (m, 2H), 6.25 (s, 1H), 5.92 – 5.70 (m, 1H), 4.95 – 4.80 (m, 2H), 3.81 (s, 1H), 2.26 – 2.11 (m, 2H), 1.83 (s, 1H), 1.82 – 1.79 (m, 1H), 1.07 – 0.97 (m, 2H), 0.30 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 141.2, 138.7, 135.3, 134.6, 128.8, 128.0, 125.7, 123.6, 113.6, 113.5, 55.0, 34.6, 22.3, 17.6, 12.4, -5.3. HRMS (EI) calculated for $[C_{22}H_{28}OSi]^+$: 336.1909, found: 336.1902.

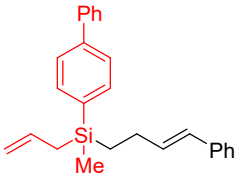
2.23 (*E*)-allyl(methyl)(phenyl)(4-phenylbut-3-en-1-yl)silane (**3ba**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ba** as colorless oil (79.0 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.35 (m, 4H), 7.31 – 7.22 (m,

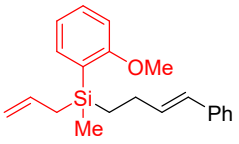
4H), 6.36 – 6.28 (m, 1H), 6.21 (m, 1H), 5.86 – 5.72 (m, 1H), 4.92 – 4.82 (m, 2H), 2.27 – 2.15 (m, 2H), 1.85 – 1.78 (m, 2H), 0.99 (m, 2H), 0.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 137.3, 134.4, 133.9, 133.2, 129.1, 128.6, 128.4, 127.8, 126.7, 125.9, 113.6, 27.1, 22.1, 13.4, -5.4. HRMS (EI) calculated for $[C_{20}H_{24}Si]^+$: 292.1647, found: 292.1642.

2.24 (*E*)-[1,1'-biphenyl]-4-yl(allyl)(methyl)(4-phenylbut-3-en-1-yl)silane (**3ca**)



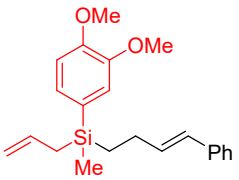
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ca** as yellow oil (99.5 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 – 7.6 (m, 6H), 7.4 (m, 2H), 7.4 – 7.2 (m, 5H), 7.2 – 7.1 (m, 1H), 6.3 (dd, *J* = 15.9, 3.6 Hz, 1H), 6.2 (m, 1H), 5.9 – 5.7 (m, 1H), 5.0 – 4.8 (m, 2H), 2.3 (m, 2H), 1.8 (dd, *J* = 8.3, 3.6 Hz, 2H), 1.0 (td, *J* = 8.4, 3.7 Hz, 2H), 0.3 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 141.0, 137.8, 136.1, 134.4, 134.3, 133.2, 128.7, 128.6, 128.4, 127.4, 127.1, 126.7, 126.5, 125.9, 113.7, 27.1, 22.1, 13.5, -5.4. HRMS (EI) calculated for $[C_{26}H_{28}Si]^+$: 368.1960, found: 368.1963.

2.25 (*E*)-allyl(2-methoxyphenyl)(methyl)(4-phenylbut-3-en-1-yl)silane (**3da**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3da** as yellow oil (62.9 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.21 (m, 4H), 7.20 – 7.12 (m, 1H), 6.94 (td, *J* = 7.4, 2.2 Hz, 1H), 6.81 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.35 – 6.17 (m, 2H), 5.89 – 5.71 (m, 1H), 4.94 – 4.77 (m, 2H), 3.78 (s, 3H), 2.21 (m, 2H), 1.88 (m, 2H), 1.08 – 0.96 (m, 2H), 0.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 138.0, 135.6, 135.3, 133.8, 131.0, 128.4, 128.3, 126.6, 125.9, 125.1, 120.5, 113.0, 109.5, 54.9, 27.4, 22.1, 13.5, -5.0. HRMS (EI) calculated for $[C_{21}H_{26}OSi]^+$: 322.1753, found: 322.1750.

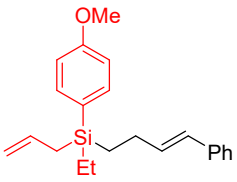
2.26 (*E*)-allyl(3,4-dimethoxyphenyl)(methyl)(4-phenylbut-3-en-1-yl)silane (**3ea**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the product **3ea** as yellow oil (96.3 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.0 Hz, 4H), 7.16 (t, *J* = 6.6 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.6, 6.4 Hz, 1H), 5.89 – 5.72 (m, 1H), 4.96 – 4.82 (m, 2H), 3.86 (s, 6H), 2.25 (dt, *J* = 11.1, 6.7 Hz, 2H), 1.81 (d, *J* = 8.0 Hz, 2H), 1.02 – 0.94 (m, 2H), 0.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.5, 137.7, 134.5, 133.1, 128.6, 128.5, 128.4, 127.0, 126.7, 125.8, 116.2, 113.5,

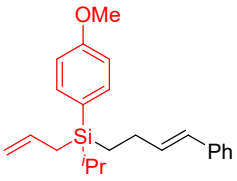
110.9, 55.8, 55.6, 27.1, 22.3, 13.6, -5.2. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{22}H_{28}NaO_2S]^+$: 375.1751 found: 375.1752.

2.27 (*E*)-allyl(ethyl)(4-methoxyphenyl)(4-phenylbut-3-en-1-yl)silane (**3fa**)



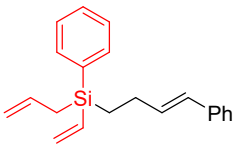
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3fa** as colorless oil (75.0 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.32 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 6.91 (m, 2H), 6.33 (dd, *J* = 16.1, 2.6 Hz, 1H), 6.28 – 6.17 (m, 1H), 5.88 – 5.73 (m, 1H), 4.96 – 4.83 (m, 2H), 3.78 (s, 3H), 2.24 (m, 2H), 1.84 (d, *J* = 8.1 Hz, 2H), 0.99 (m, 5H), 0.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.8, 135.6, 134.6, 133.4, 128.5, 128.4, 127.0, 126.7, 125.9, 113.6, 113.5, 54.9, 27.1, 20.2, 11.7, 7.3, 3.9. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{22}H_{28}NaOSi]^+$: 359.1802 found: 359.1810.

2.28 (*E*)-allyl(isopropyl)(4-methoxyphenyl)(4-phenylbut-3-en-1-yl)silane (**3ga**)



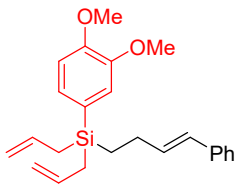
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the product **3ga** as colorless oil (77.8 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.17 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.7, 6.2 Hz, 1H), 5.93 – 5.78 (m, 1H), 5.00 – 4.84 (m, 2H), 3.79 (s, 3H), 2.26 (dt, *J* = 11.6, 6.7 Hz, 2H), 1.90 (d, *J* = 8.0 Hz, 2H), 1.12 (dt, *J* = 13.7, 7.0 Hz, 1H), 1.00 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.8, 135.9, 134.8, 133.5, 128.4, 128.3, 126.7, 126.0, 125.9, 113.7, 113.5, 54.9, 27.1, 18.7, 17.8, 12.1, 10.4. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{23}H_{30}NaOSi]^+$: 373.1958 found: 373.1960.

2.29 (*E*)-allyl(phenyl)(4-phenylbut-3-en-1-yl)(vinyl)silane (**3ha**)



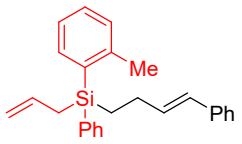
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ha** as colorless oil (84.0 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.22 (m, 4H), 7.16 (dd, *J* = 9.2, 5.2 Hz, 1H), 6.37 – 6.13 (m, 4H), 5.87 – 5.73 (m, 2H), 4.98 – 4.84 (m, 2H), 2.32 – 2.22 (m, 2H), 1.93 (d, *J* = 8.0 Hz, 2H), 1.14 – 1.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.4, 134.8, 134.6, 134.5, 134.0, 133.1, 129.3, 128.7, 128.4, 127.8, 126.7, 125.9, 114.2, 27.0, 20.5, 11.8. HRMS (EI) calculated for $[C_{21}H_{24}Si]^+$: 304.1647, found: 304.1642.

2.30 (*E*)-diallyl(3,4-dimethoxyphenyl)(4-phenylbut-3-en-1-yl)silane (**3ia**)



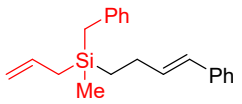
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ia** as colorless oil (97.4 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 4H), 7.16 (t, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.00 (s, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.4 Hz, 1H), 5.90 – 5.75 (m, 2H), 5.00 – 4.85 (m, 4H), 3.86 (s, 3H), 3.86 (s, 3H), 2.27 (m, 2H), 1.87 (d, *J* = 8.1 Hz, 4H), 1.08 – 0.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 148.5, 137.6, 134.1, 133.0, 128.6, 128.4, 127.4, 126.8, 126.7, 125.8, 116.5, 114.0, 110.9, 55.8, 55.5, 26.9, 20.2, 11.8. HRMS (ESI) calculated for $[M+Na]^+ = [C_{24}H_{30}NaO_2Si]^+$: 401.1907 found: 401.1898.

2.31 (*E*)-allyl(phenyl)(4-phenylbut-3-en-1-yl)(o-tolyl)silane (**3ja**)



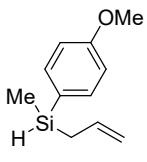
Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ja** as colorless oil (66.3 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.46 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.26 (d, *J* = 2.0 Hz, 2H), 7.23 – 7.13 (m, 4H), 6.34 – 6.17 (m, 2H), 5.74 (m, 1H), 4.97 – 4.83 (m, 2H), 2.29 – 2.16 (m, 7H), 1.41 – 1.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 137.8, 136.4, 135.9, 134.5, 134.1, 133.5, 133.1, 130.1, 129.8, 129.2, 128.7, 128.4, 127.9, 126.8, 125.9, 125.0, 114.4, 27.1, 23.2, 20.8, 12.0. HRMS (ESI) calculated for $[M+Na]^+ = [C_{26}H_{28}NaSi]^+$: 391.1852 found: 391.1855.

2.32 (*E*)-allyl(benzyl)(methyl)(4-phenylbut-3-en-1-yl)silane (**3ka**)



Prepared according to general procedure. The crude product was purified by column chromatography (petroleum ether) to afford the product **3ka** as colorless oil (82.8 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.38 – 7.32 (m, 3H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 2H), 6.51 – 6.44 (m, 1H), 6.36 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.91 (m, 1H), 5.07 – 4.99 (m, 2H), 2.41 – 2.26 (m, 4H), 1.76 – 1.64 (m, 2H), 0.93 – 0.83 (m, 2H), 0.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.8, 134.5, 133.3, 128.6, 128.5, 128.3, 128.2, 126.8, 125.9, 124.1, 113.5, 27.0, 23.7, 21.4, 12.7, -5.5. HRMS (EI) calculated for $[C_{21}H_{26}Si]^+$: 306.1804, found: 306.1794.

2.33 allyl(4-methoxyphenyl)(methyl)silane (**3aa'**)

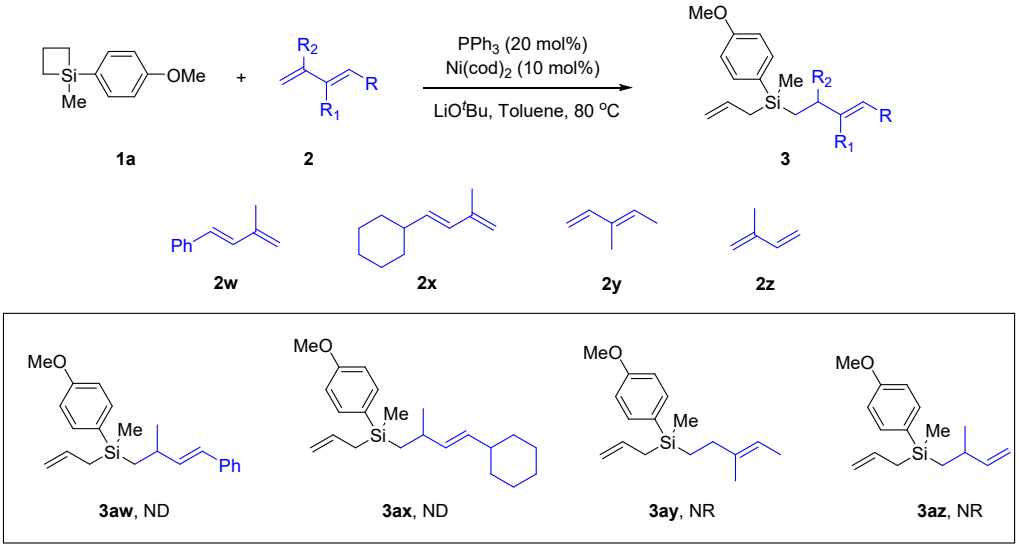


The crude product was purified by column chromatography (petroleum ether) to afford the by-product **3aa'** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.40 (m, 2H), 6.89 (m, 2H), 5.85 – 5.68 (m, 1H), 4.93 – 4.80 (m, 2H), 3.81 (s, 3H), 1.92 – 1.69 (m, 2H), 0.31 (m, 3H), .0.0.3-0.07

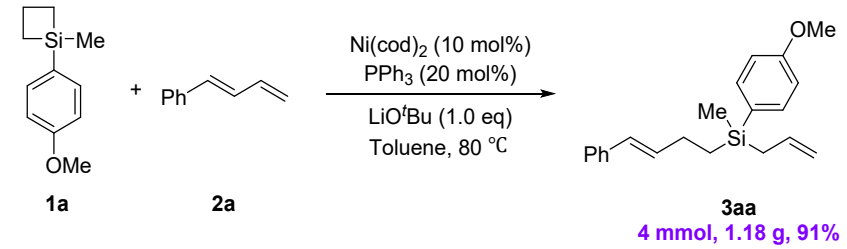
(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 134.9, 133.9, 114.0, 113.4, 55.0, 25.5, -1.4.

Unsuccessful substrates:

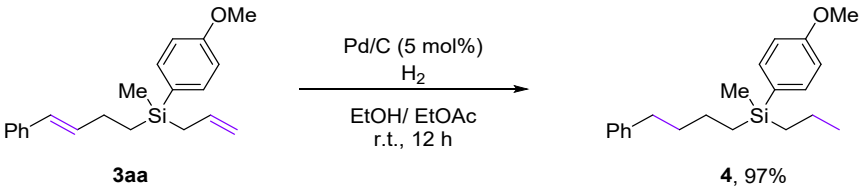
We have tried various disubstituted and simple dienes, but none of them have obtained satisfactory results, only **2v** could obtain the corresponding product **3av** with low yield of 36%.



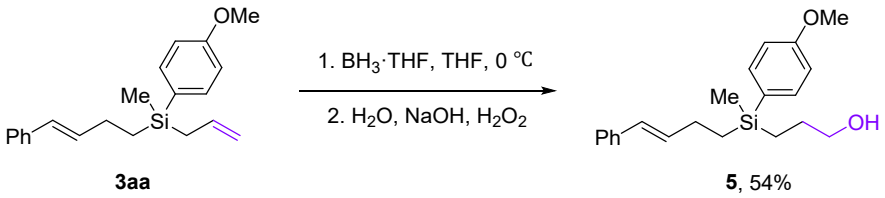
3. Gram-scale synthesis and synthetic applications



To a 100 mL sealed tube equipped with a stir bar was added $Ni(cod)_2$ (0.4 mmol, 10 mol%), PPh_3 (0.8 mmol, 20 mol%), LiO^tBu (4 mmol, 1.0 equiv), **1a** (4 mmol, 1.0 equiv), **2a** (6 mmol, 1.5 equiv). The flask was evacuated and refilled with nitrogen. Then 40 mL toluene was added to the tube under nitrogen atmosphere, and stirred at 80 °C for 48 h. After the reaction was completed (monitored by TLC), the filtrate was evaporated to dryness under reduced pressure and the crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200:1 to 50:1) to afford the desired product **3aa** (1.18 g, 91% yield).

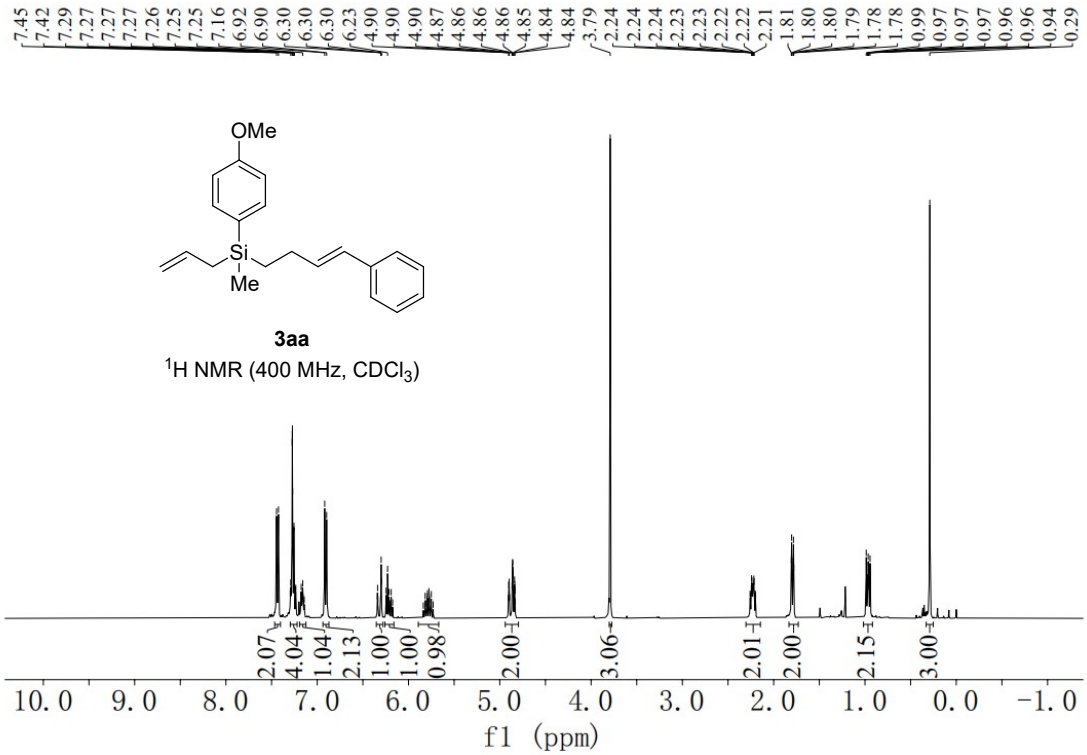


To a solution of **3aa** (77.9 mg, 0.2 mmol, 1.0 equiv) in 1.5 mL of an EtOH/EtOAc mixture (3: 2) was added 10% Pd/C (10.6 mg, 10 μmol) under a H_2 atmosphere. After being stirred at room temperature for 12 h, the reaction mixture was filtered through silica gel and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to give **4** (64.5 mg, 97% yield) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.17 – 7.09 (m, 3H), 6.89 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H), 2.63 – 2.52 (m, 2H), 1.68 – 1.56 (m, 2H), 1.41 – 1.28 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H), 0.81 – 0.68 (m, 4H), 0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 142.8, 135.2, 129.5, 128.3, 128.2, 125.5, 113.5, 54.9, 35.5, 35.4, 23.6, 18.4, 17.4, 17.1, 14.2, -4.9. HRMS (ESI) calculated for $[M+Na]^+ = [C_{21}H_{30}NaOSi]^+$: 349.1958 found: 349.1952.



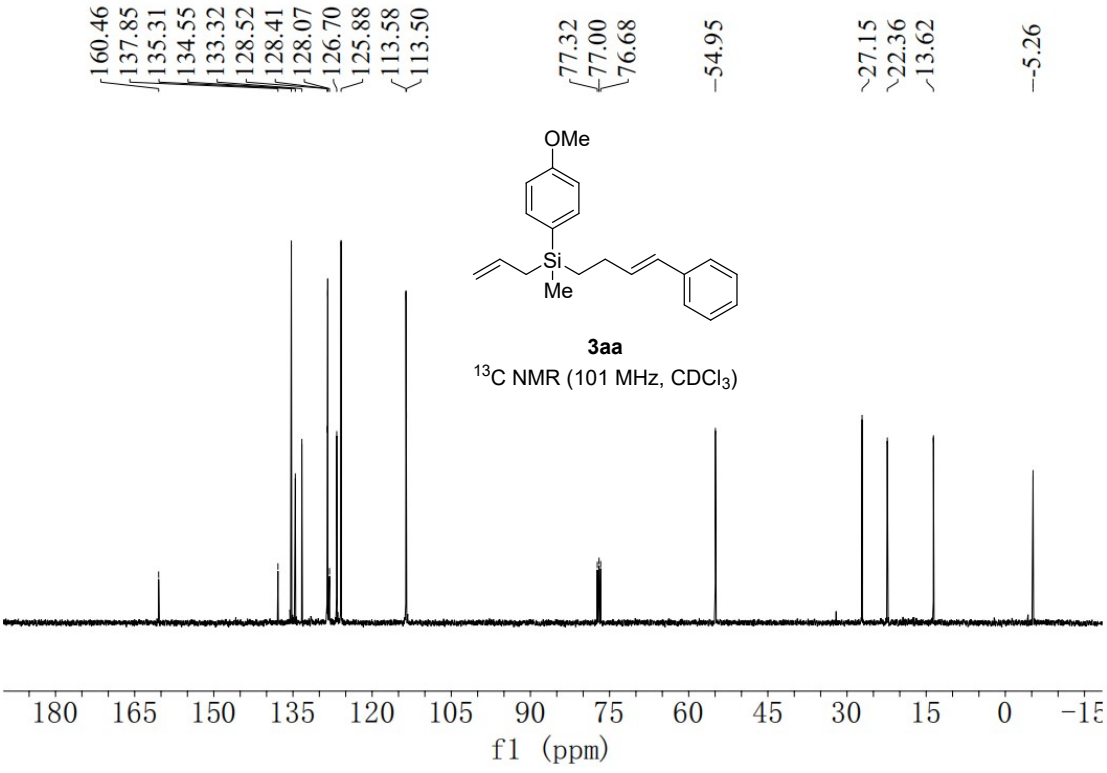
An oven-dried 10 mL sealed tube equipped with a stir bar was charged with **3aa** (96.8 mg, 0.3 mmol) and THF (1 mL). The solution was then cooled to 0 °C. BH_3·THF (132 μL, 0.132 mmol, 0.44 equiv) was added dropwise. The mixture was allowed to stir at 0 ℃ for 1 h. Then deionized water (30 μL), NaOH (0.3 mL, 2.5 M aqueous solution, 0.75 mmol, 2.5 equiv.), and H_2O_2 (90 μL, 30% aqueous solution, 0.75 mmol, 2.5 equiv.) were added dropwise to the system sequentially. The mixture was allowed to stir for 4 h at room temperature afterwards. Once complete, the reaction was quenched with water and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified via silica gel chromatography (petroleum ether/ethyl acetate = 10:1), and **5** was obtained in 54% yield (55.2 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.17 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.33 (dt, *J* = 15.8, 1.2 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.3 Hz, 1H), 3.81 (s, 3H), 3.57 (t, *J* = 6.7 Hz, 2H), 2.29 – 2.17 (m, 2H), 1.58 (m, 2H), 1.29 (dd, *J* = 18.6, 12.1 Hz, 1H), 1.02 – 0.93 (m, 2H), 0.84 – 0.73 (m, 2H), 0.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.8, 135.2, 133.4, 128.5, 128.4, 126.7, 125.9, 113.6, 65.7, 55.0, 27.2, 27.1, 14.0, 10.1, -5.0. HRMS (ESI) calculated for $[M+Na]^+$ = $[C_{21}H_{28}NaO_2Si]^+$: 363.1751 found: 363.1757.

4. Copies of NMR Spectra



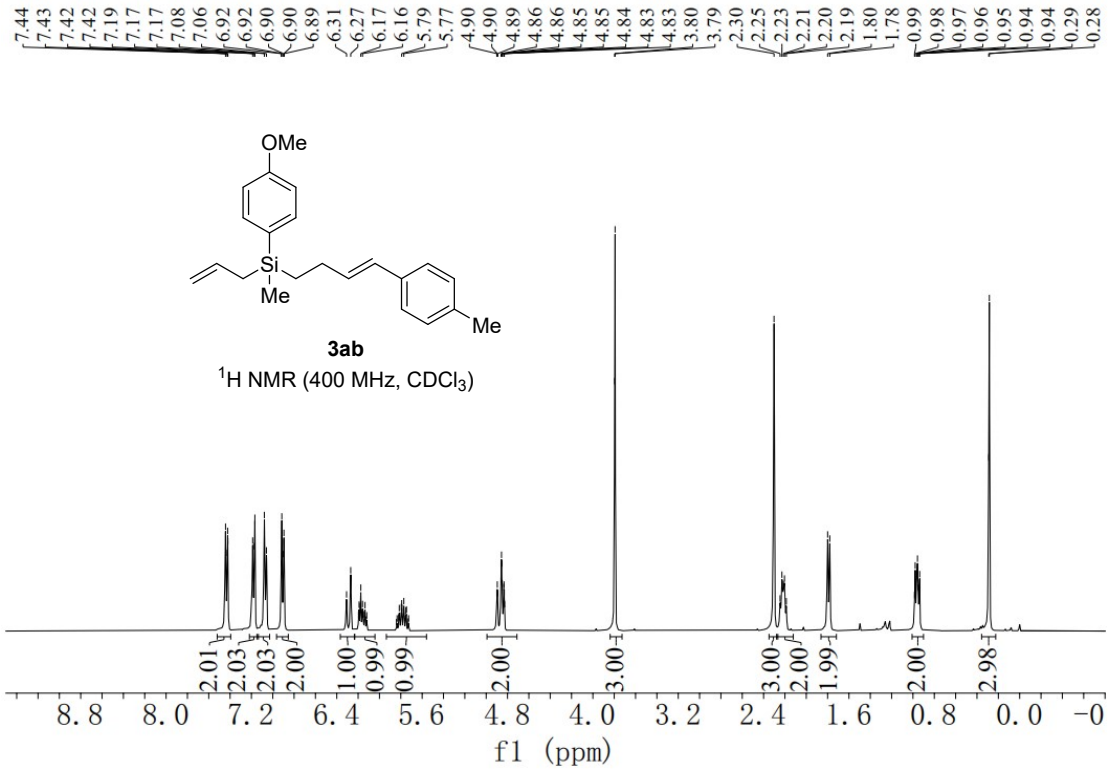
3aa

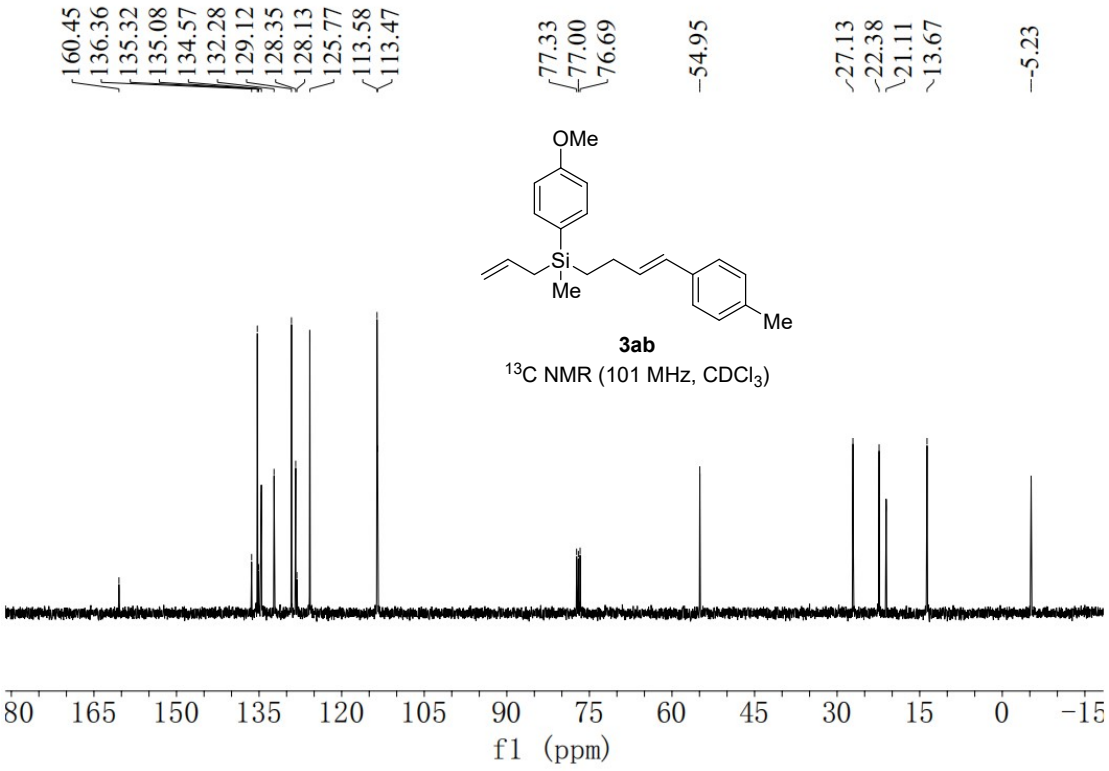
^{1}H NMR (400 MHz, $CDCl_3$)

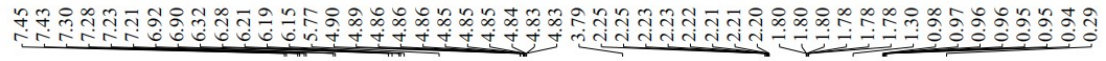


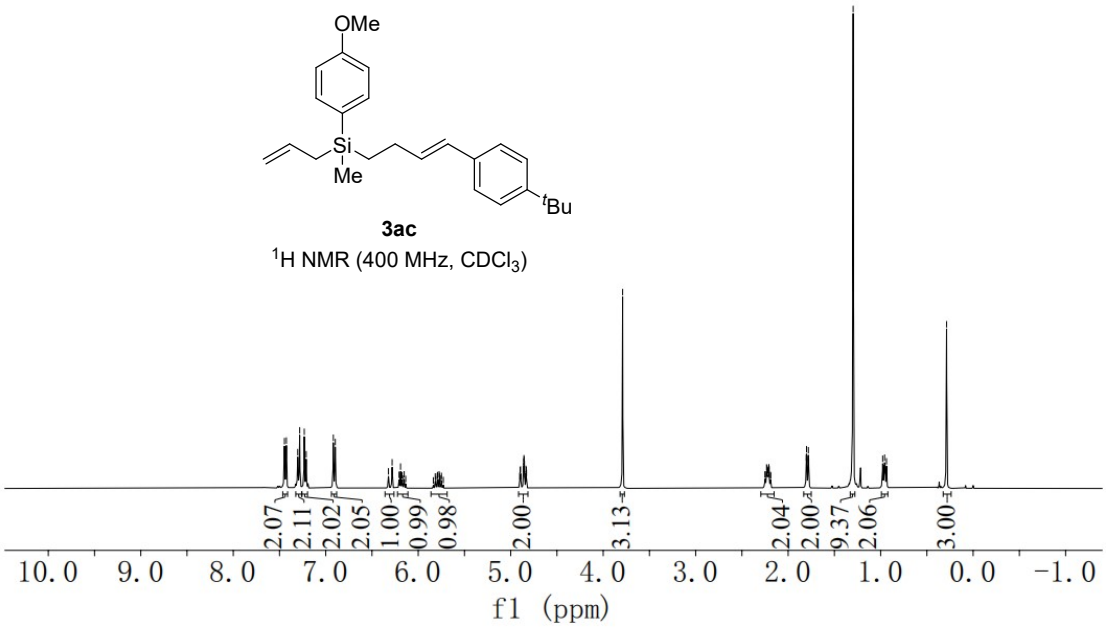
3aa

^{13}C NMR (101 MHz, $CDCl_3$)


7.44
7.43
7.42
7.42
7.19
7.17
7.17
7.08
7.06
6.92
6.92
6.90
6.90
6.89
6.31
6.27
6.17
6.16
5.79
5.77
4.90
4.90
4.89
4.86
4.86
4.85
4.85
4.84
4.83
4.83
3.80
3.79
2.30
2.25
2.23
2.21
2.20
2.19
1.80
1.78
0.99
0.98
0.97
0.96
0.95
0.94
0.94
0.29
0.28
OMe
Si
Me
Me
3ab
1H NMR (400 MHz, CDCl3)
2.01
2.03
2.03
2.00
1.00
0.99
0.99
2.00
3.00
3.00
2.00
1.99
2.00
2.98
8.8
8.0
7.2
6.4
5.6
4.8
4.0
3.2
2.4
1.6
0.8
0.0
−0
f1 (ppm)

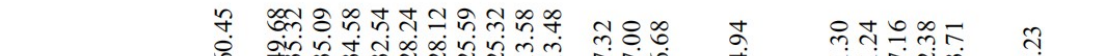

160.45
136.36
135.32
135.08
134.57
132.28
129.12
128.35
128.13
125.77
113.58
113.47
77.33
77.00
76.69
54.95
27.13
22.38
21.11
13.67
-5.23
OMe
Si
Me
Me
3ab
13C NMR (101 MHz, CDCl3)
80
165
150
135
120
105
90
75
60
45
30
15
0
−15
f1 (ppm)

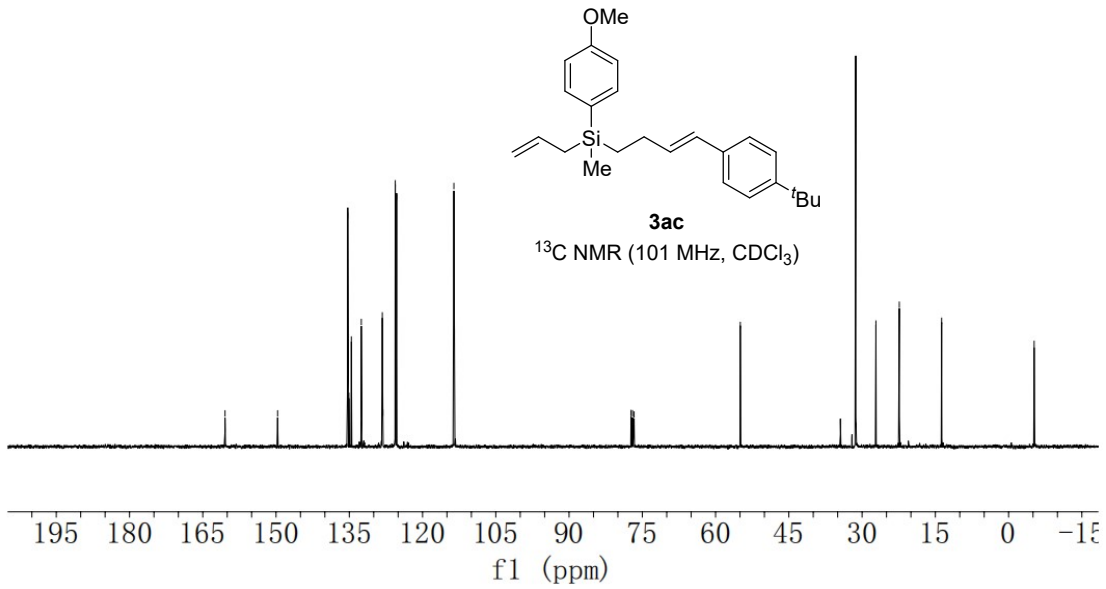




3ac

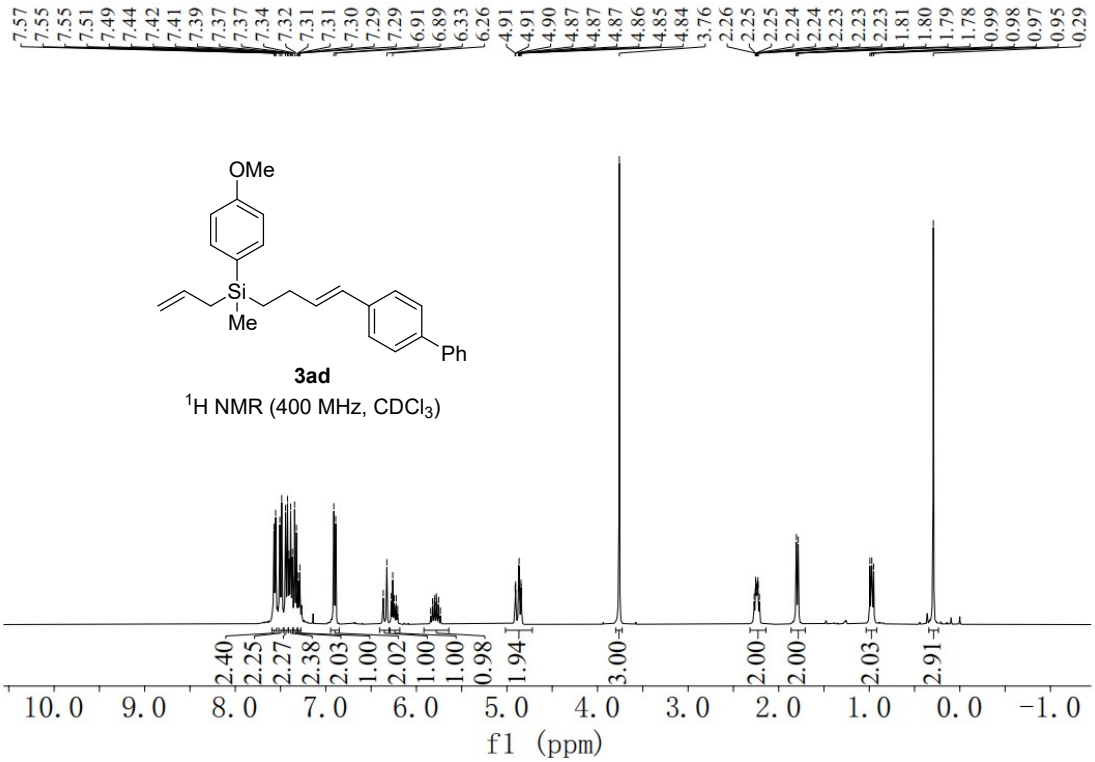
^{1}H NMR (400 MHz, $CDCl_3$)

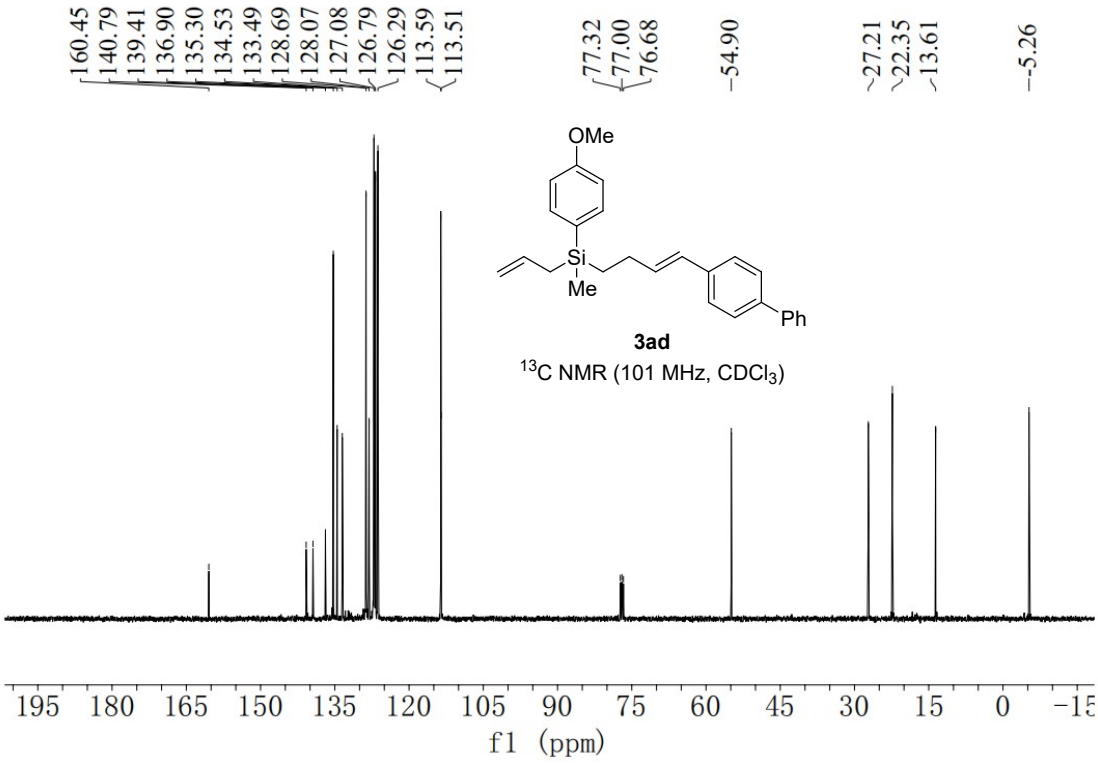


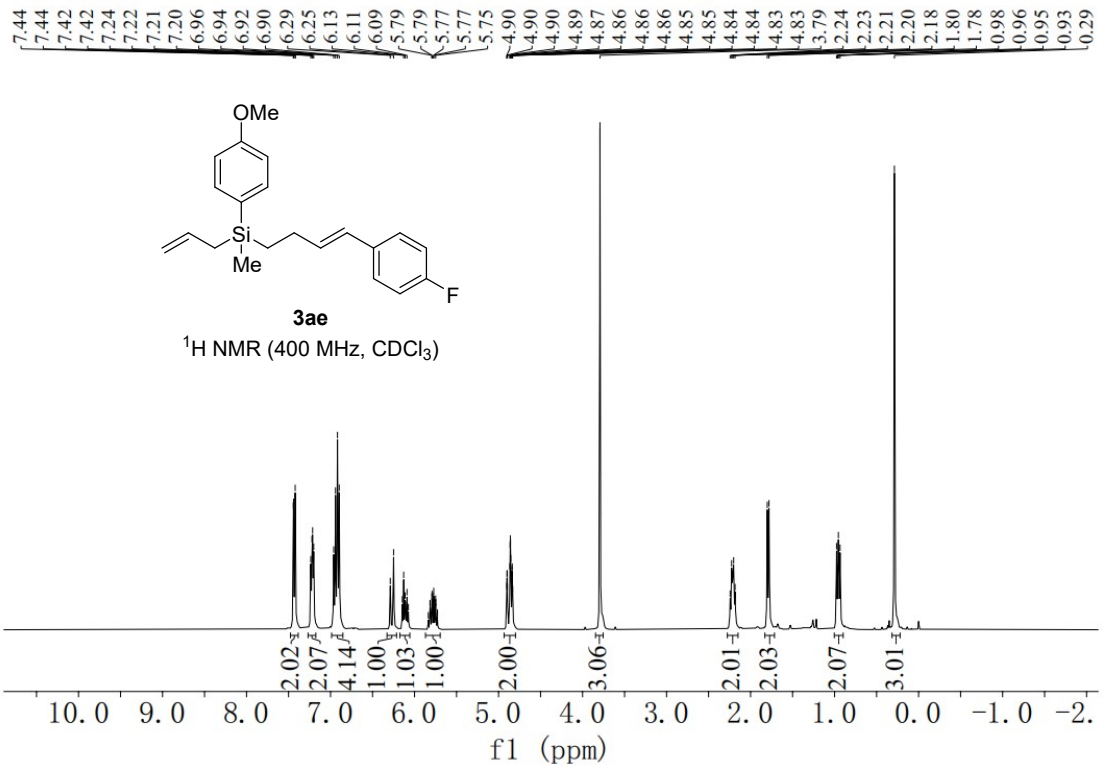


3ac

^{13}C NMR (101 MHz, $CDCl_3$)

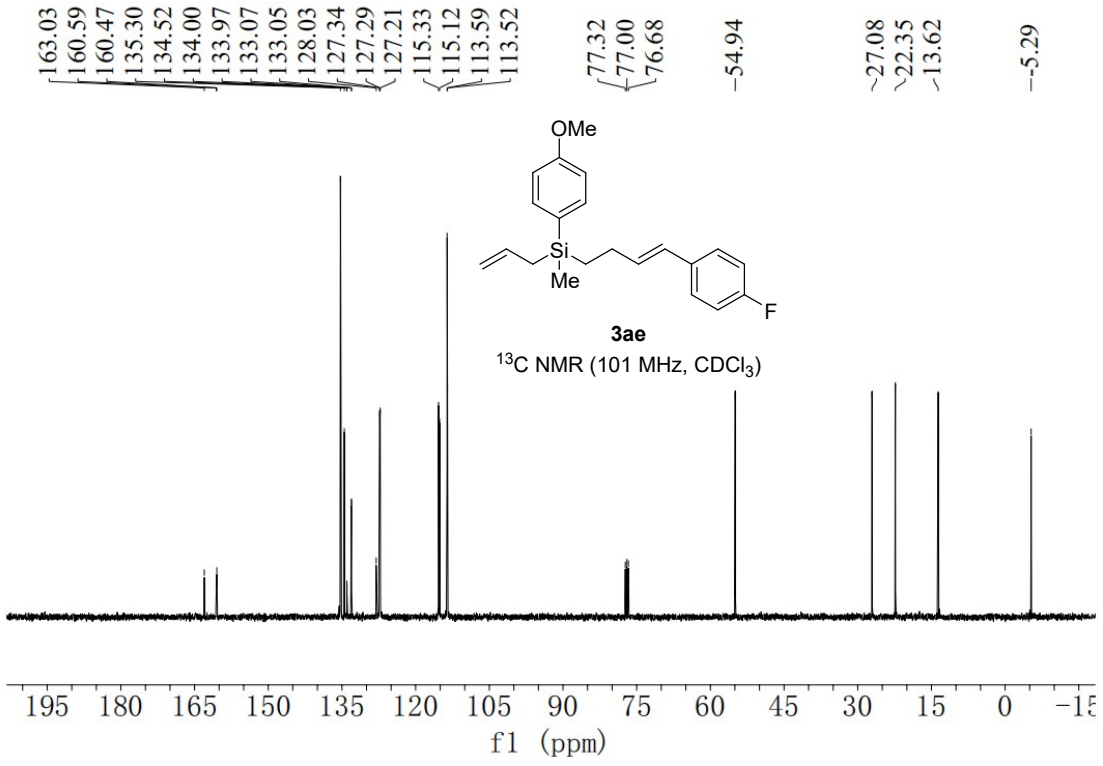

OMe
Si
Me
Ph
3ad
1H NMR (400 MHz, CDCl3)
f1 (ppm)


OMe
Si
Me
Ph
3ad
13C NMR (101 MHz, CDCl3)
f1 (ppm)



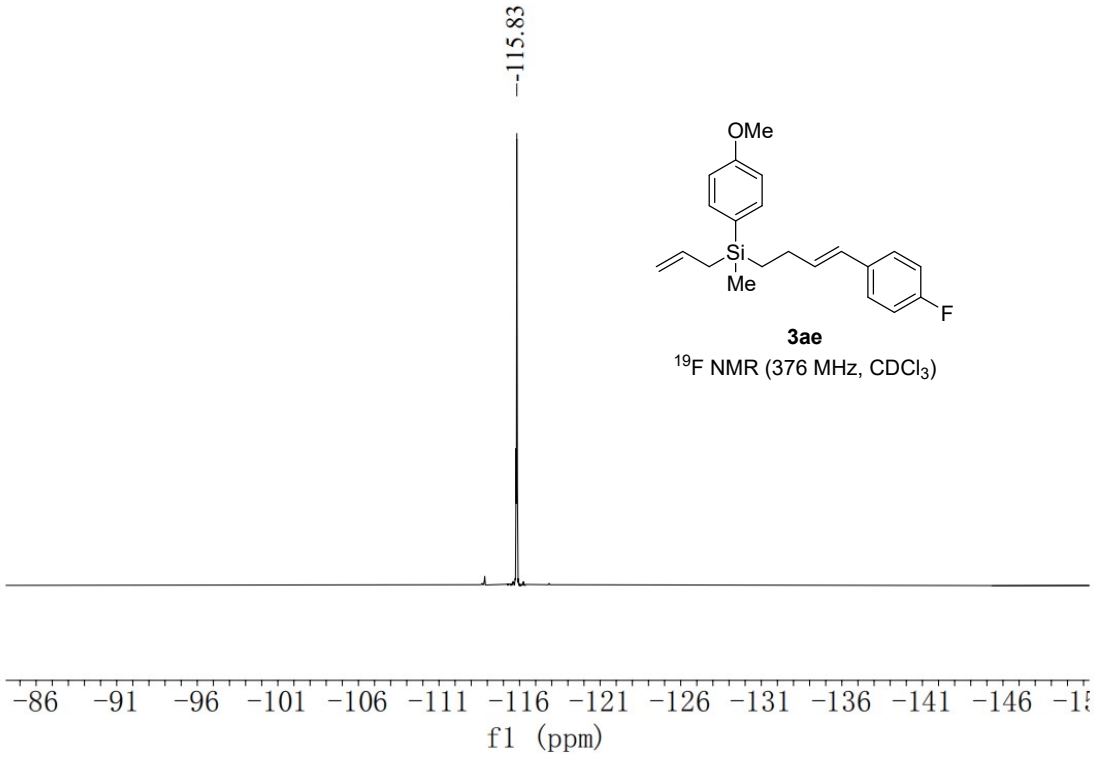
3ae

^{1}H NMR (400 MHz, $CDCl_3$)



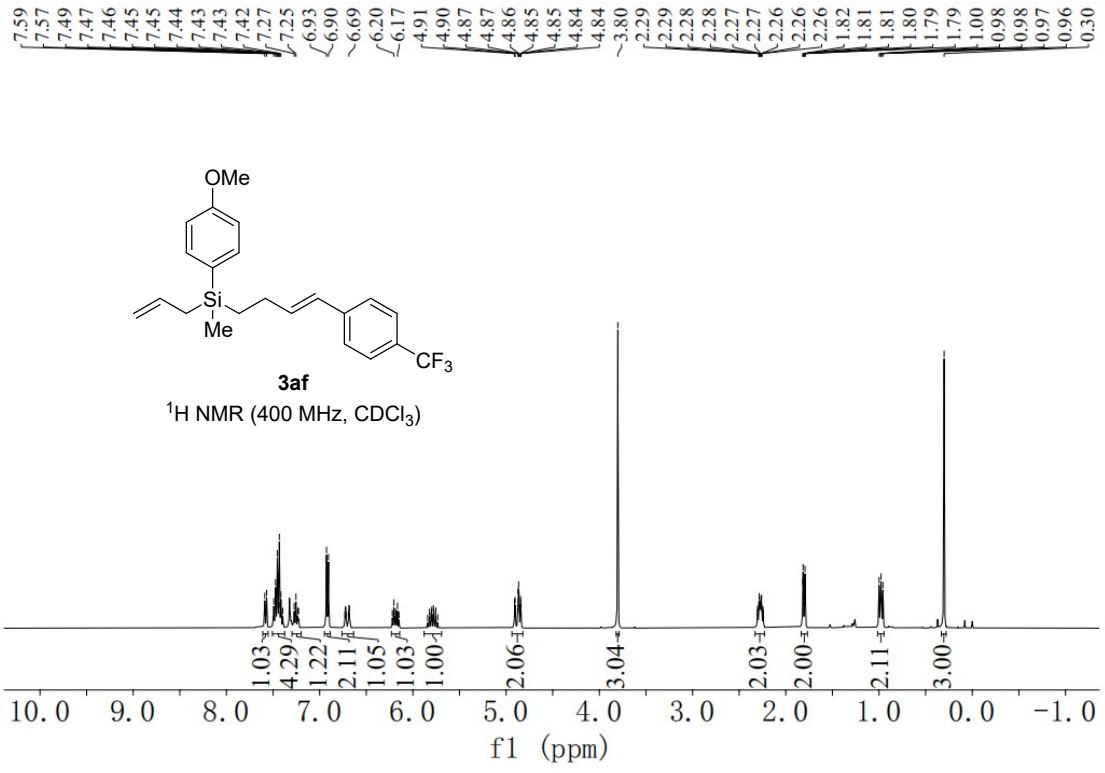
3ae

^{13}C NMR (101 MHz, $CDCl_3$)



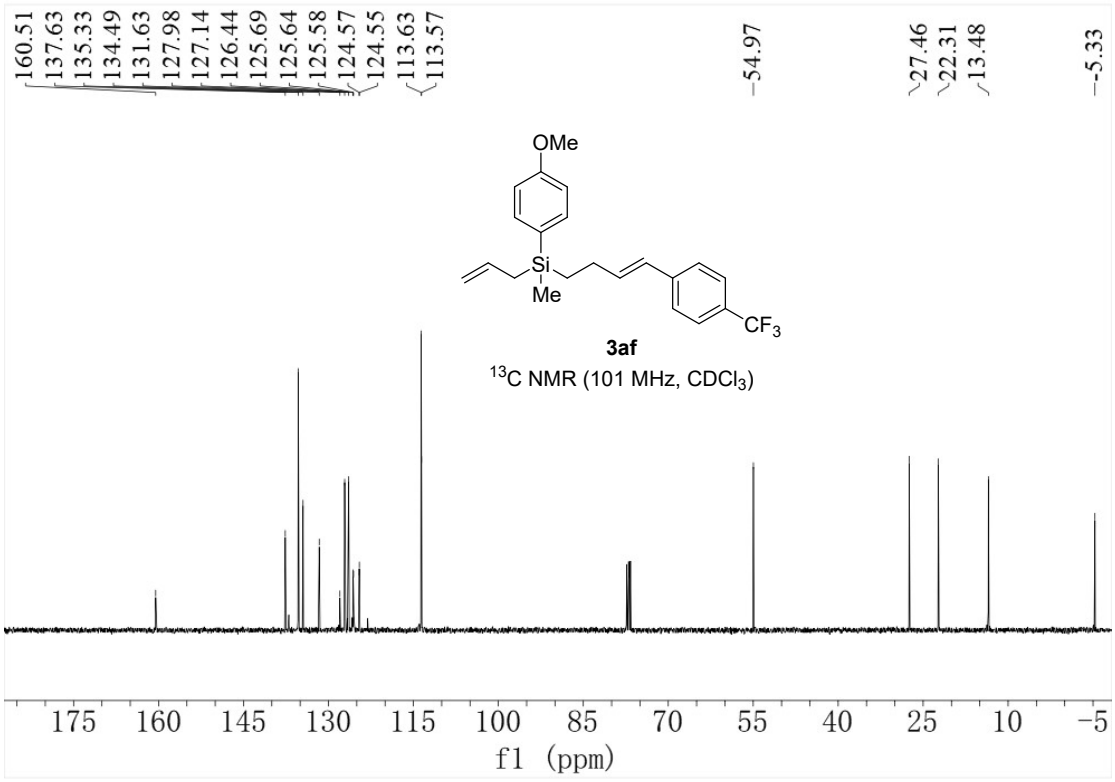
3ae

^{19}F NMR (376 MHz, $CDCl_3$)



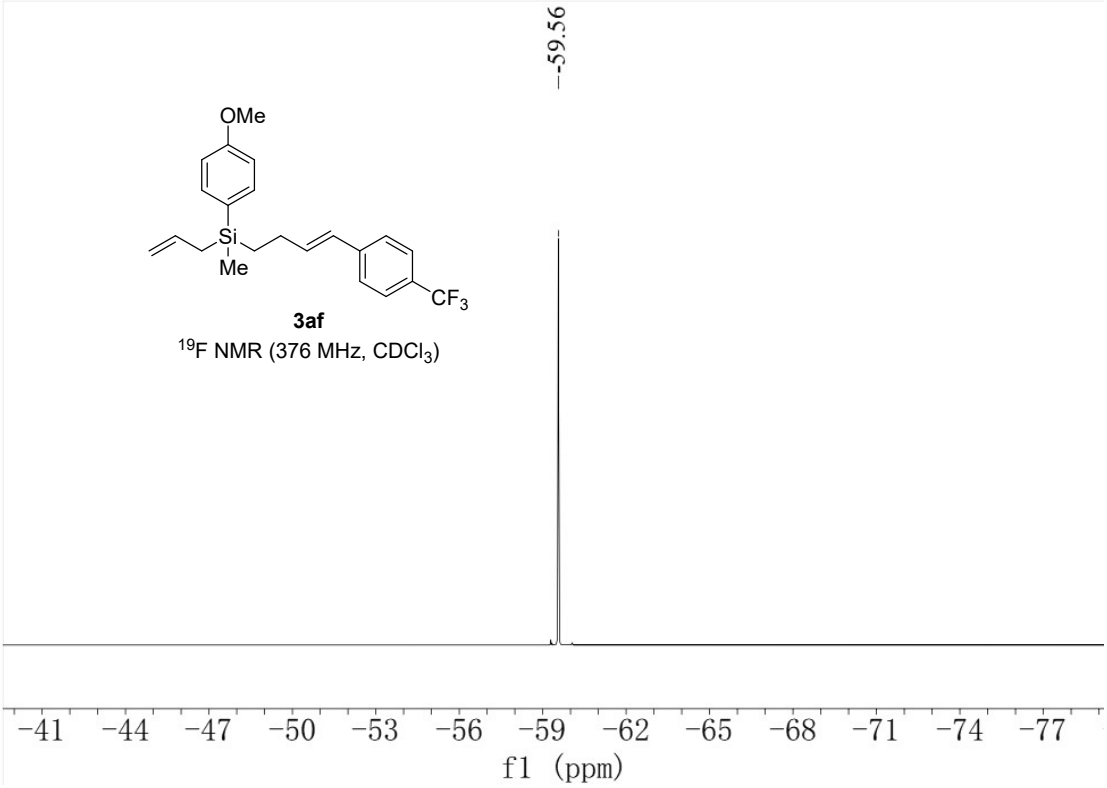
3af

^{1}H NMR (400 MHz, $CDCl_3$)



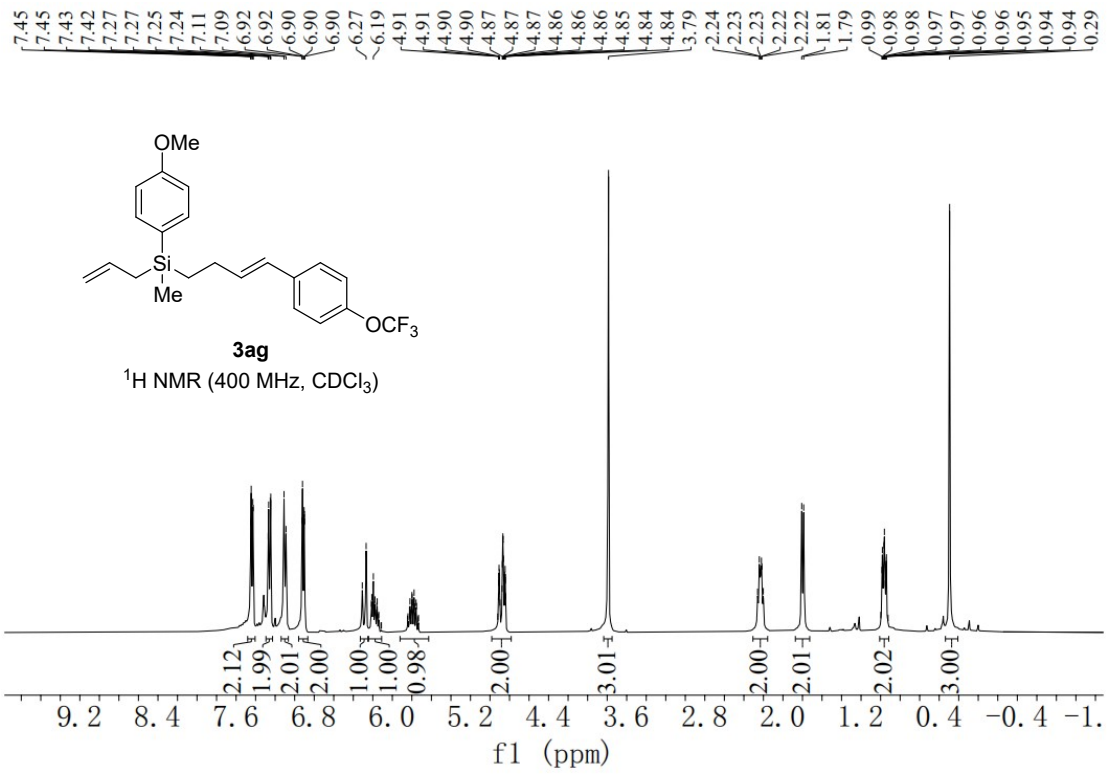
3af

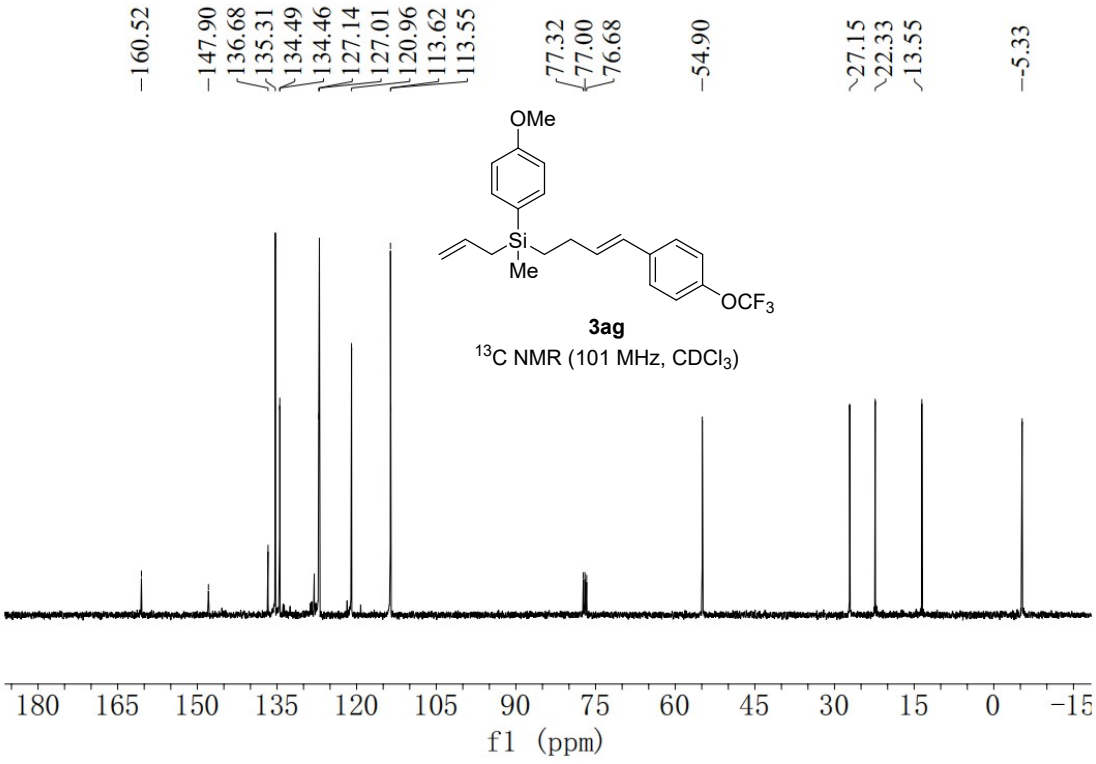
^{13}C NMR (101 MHz, $CDCl_3$)

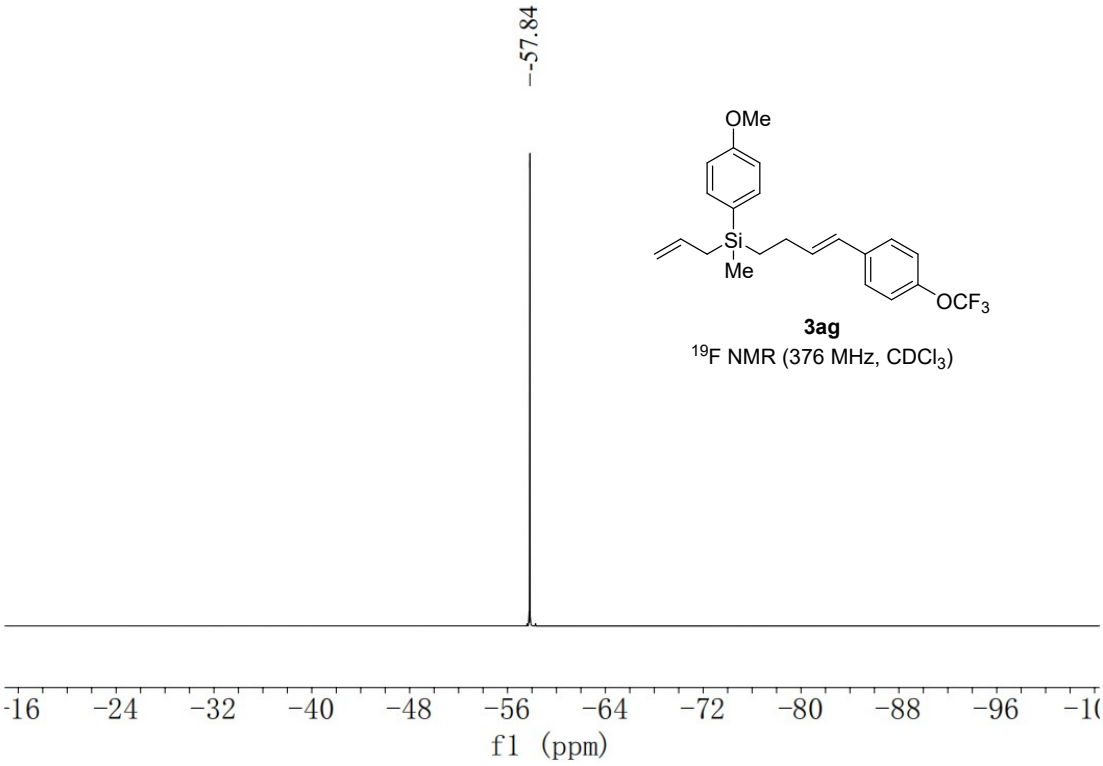


3af

^{19}F NMR (376 MHz, $CDCl_3$)

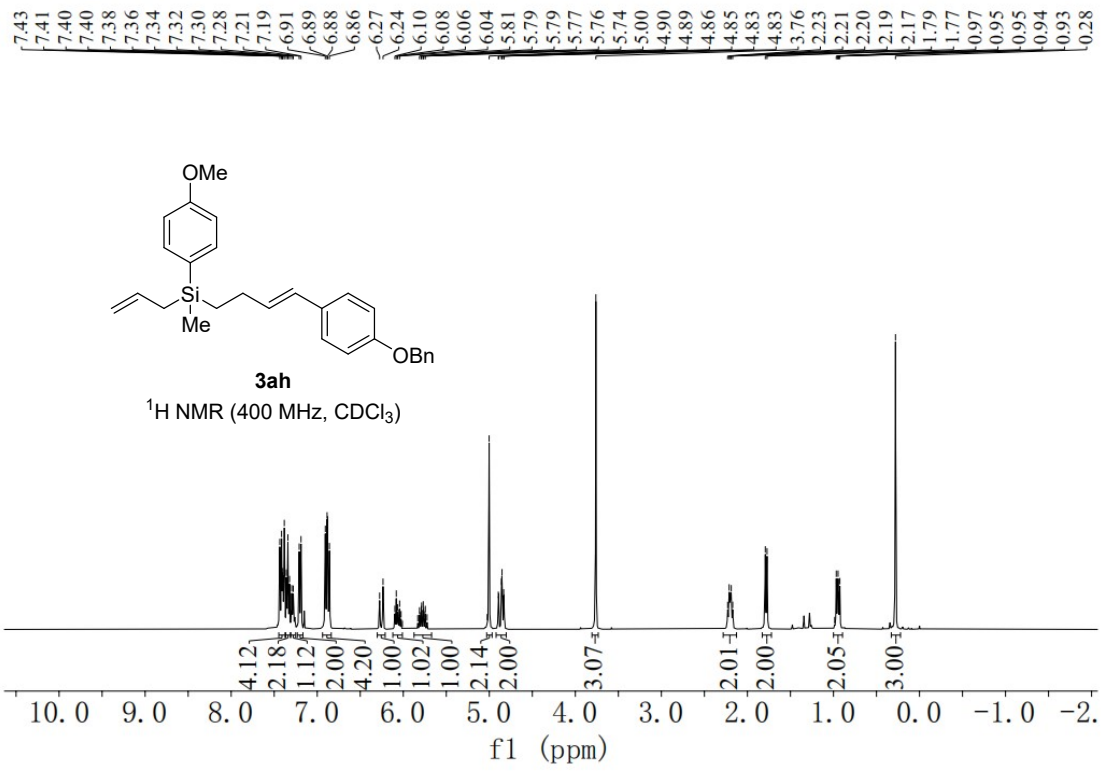

7.45 7.45 7.43 7.42 7.27 7.27 7.25 7.24 7.11 7.09 6.92 6.92 6.90 6.90 6.90 6.27 6.19 4.91 4.91 4.90 4.90 4.87 4.87 4.87 4.86 4.86 4.86 4.85 4.84 4.84 3.79 2.24 2.23 2.23 2.22 2.22 1.81 1.79 0.99 0.98 0.98 0.97 0.97 0.96 0.96 0.95 0.94 0.94 0.29
OMe
Si
Me
OCF3
3ag
1H NMR (400 MHz, CDCl3)
2.12 1.99 2.01 2.00 1.00 1.00 0.98 2.00 3.01 2.00 2.01 2.02 3.00
9.2 8.4 7.6 6.8 6.0 5.2 4.4 3.6 2.8 2.0 1.2 0.4 −0.4 −1.
f1 (ppm)


160.52 147.90 136.68 135.31 134.49 134.46 127.14 127.01 120.96 113.62 113.55 77.32 77.00 76.68 54.90 27.15 22.33 13.55 −5.33
OMe
Si
Me
OCF3
3ag
13C NMR (101 MHz, CDCl3)
180 165 150 135 120 105 90 75 60 45 30 15 0 −15
f1 (ppm)



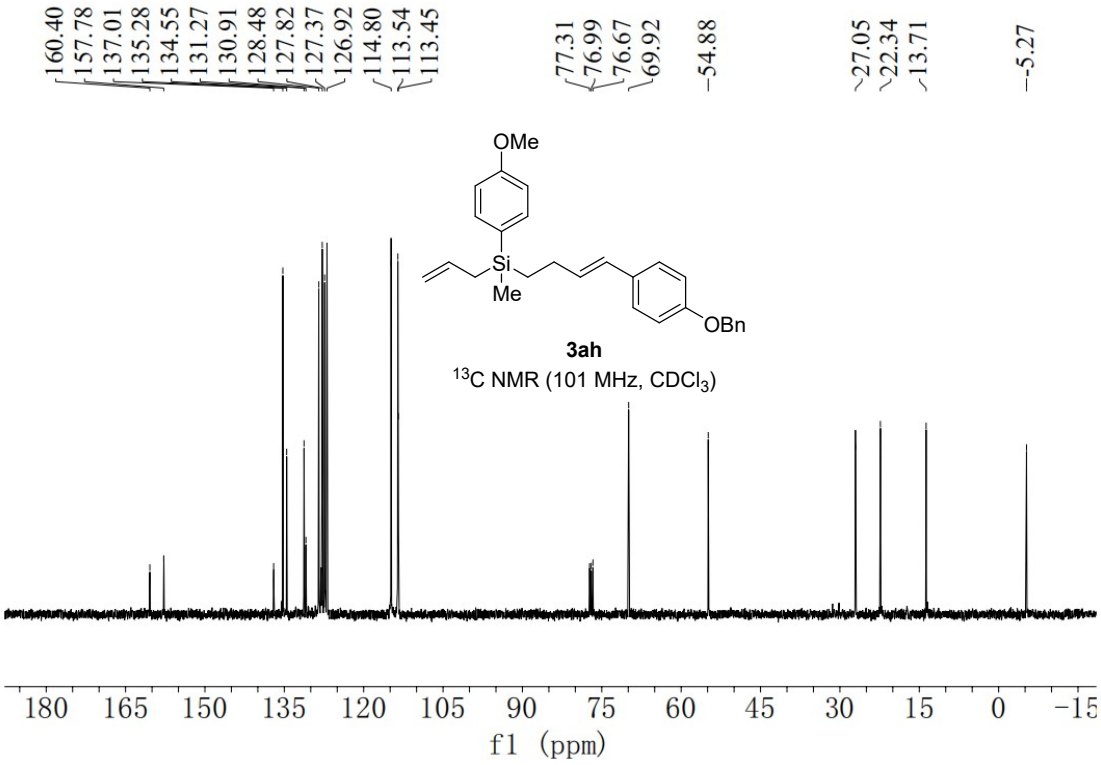
3ag

^{19}F NMR (376 MHz, $CDCl_3$)



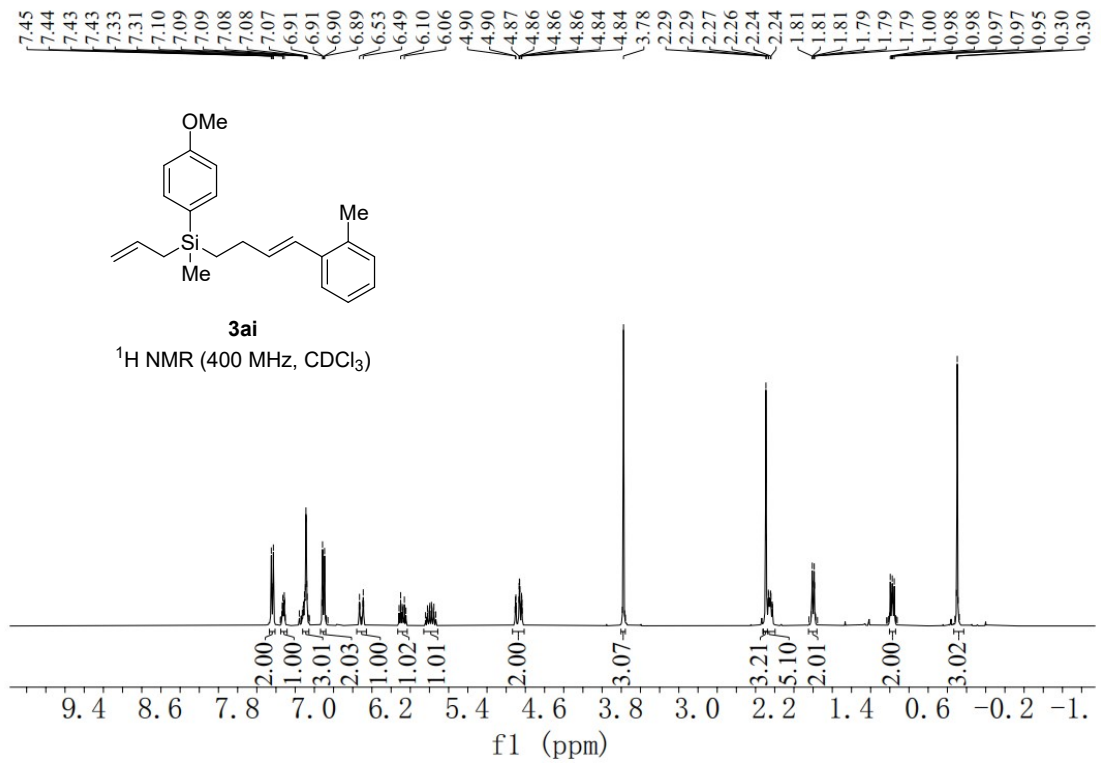
3ah

^{1}H NMR (400 MHz, $CDCl_3$)



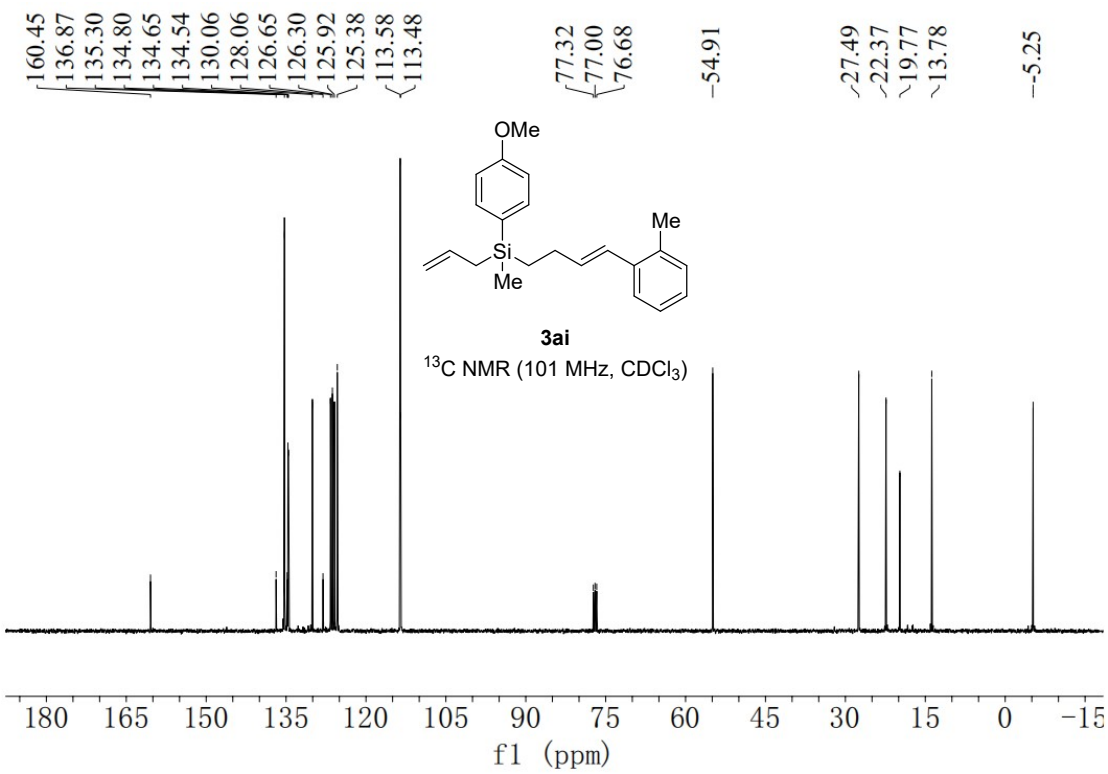
3ah

^{13}C NMR (101 MHz, $CDCl_3$)



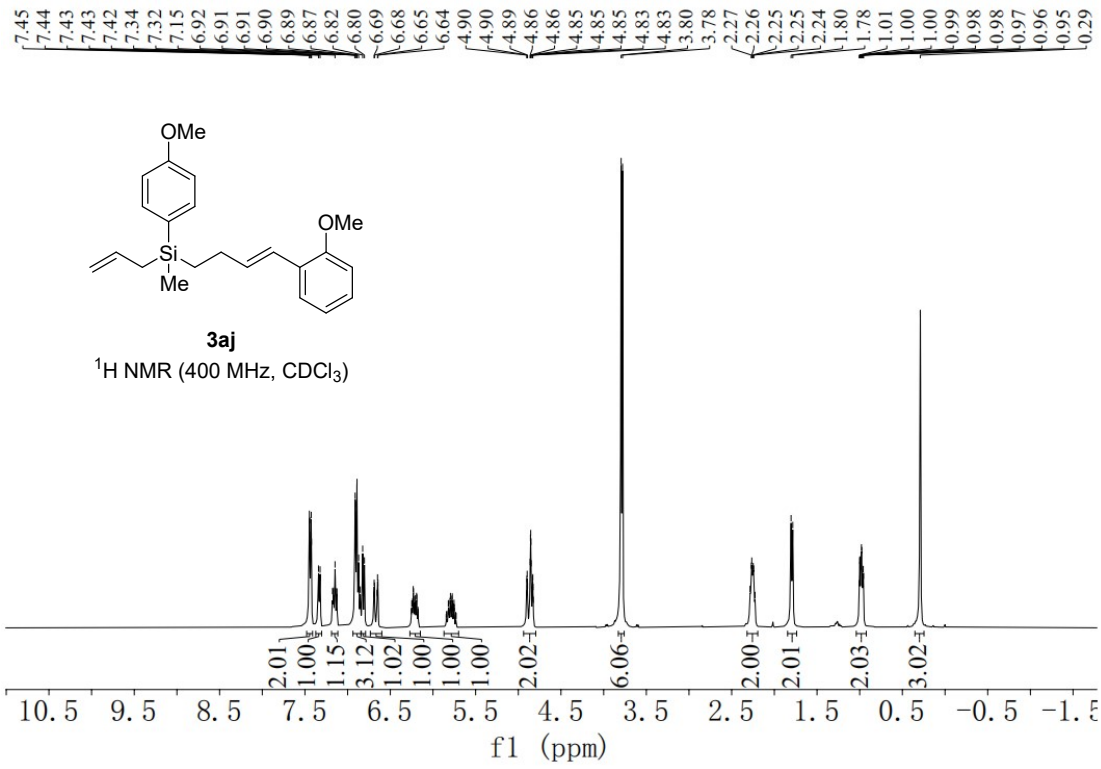
3ai

^{1}H NMR (400 MHz, $CDCl_3$)



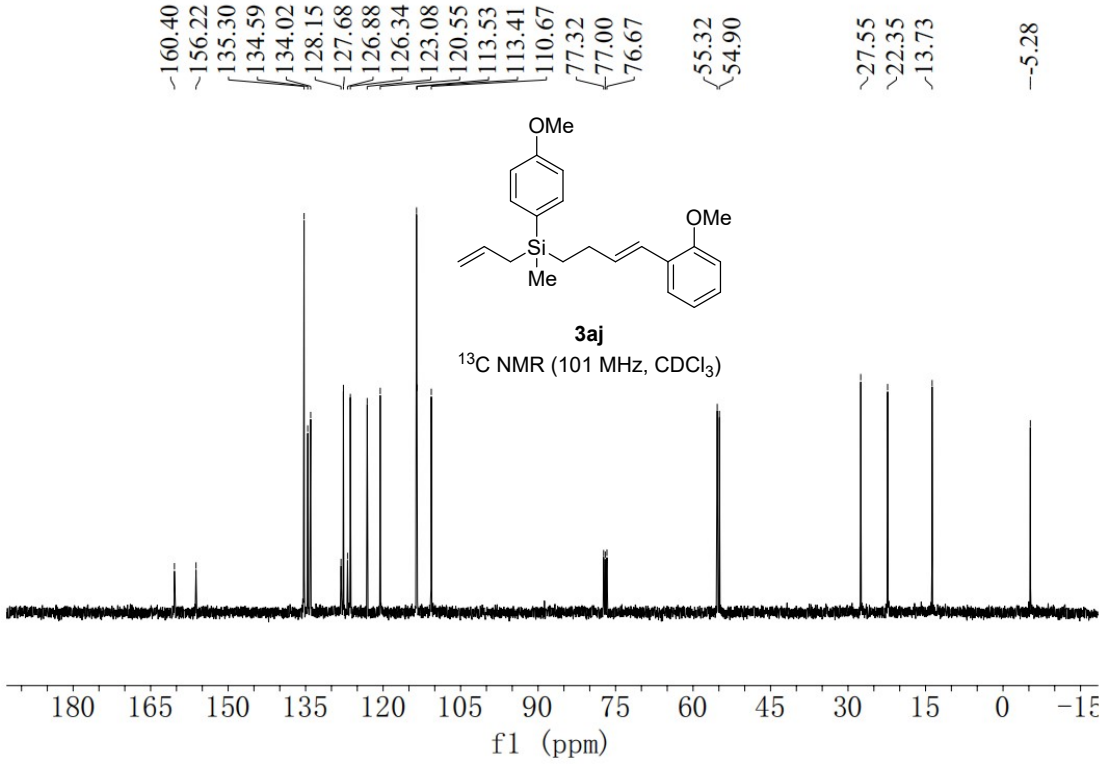
3ai

^{13}C NMR (101 MHz, $CDCl_3$)



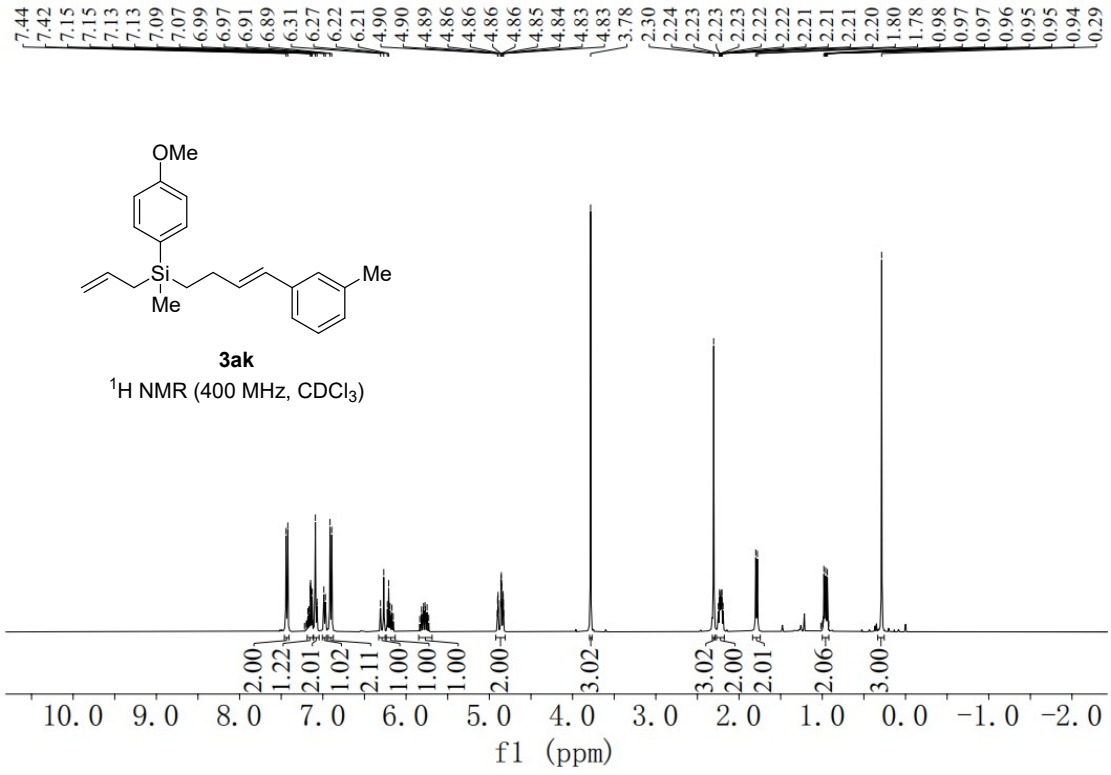
3aj

^{1}H NMR (400 MHz, $CDCl_3$)



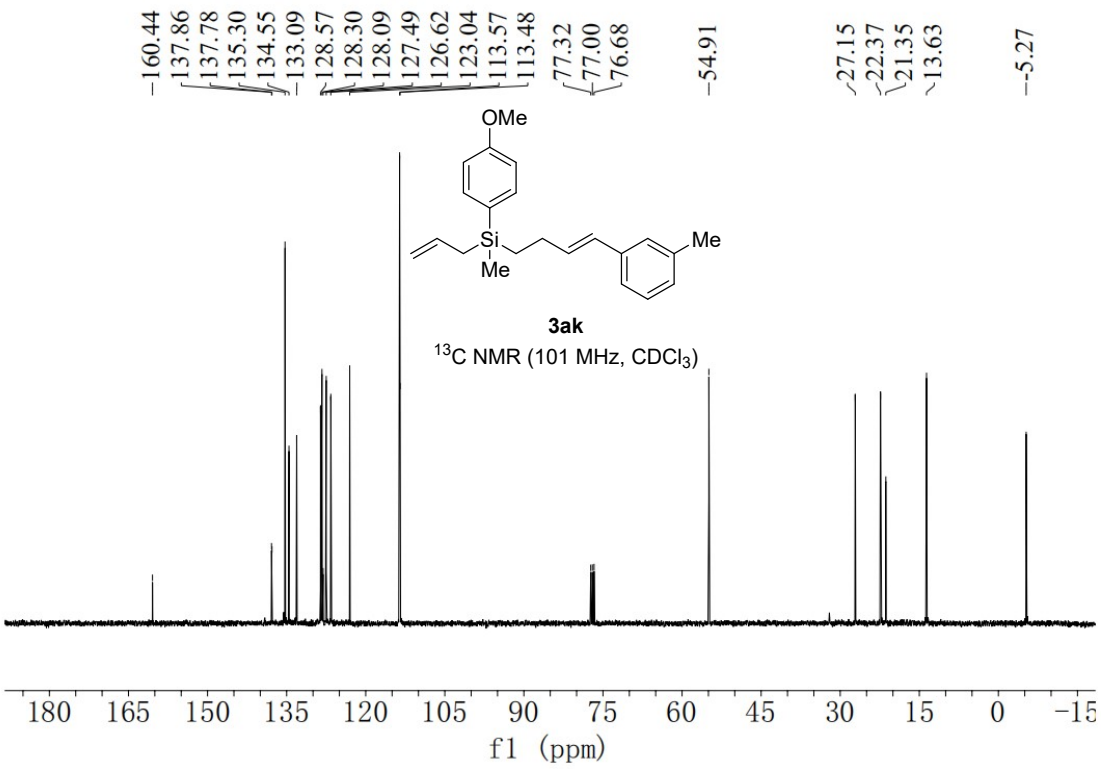
3aj

^{13}C NMR (101 MHz, $CDCl_3$)



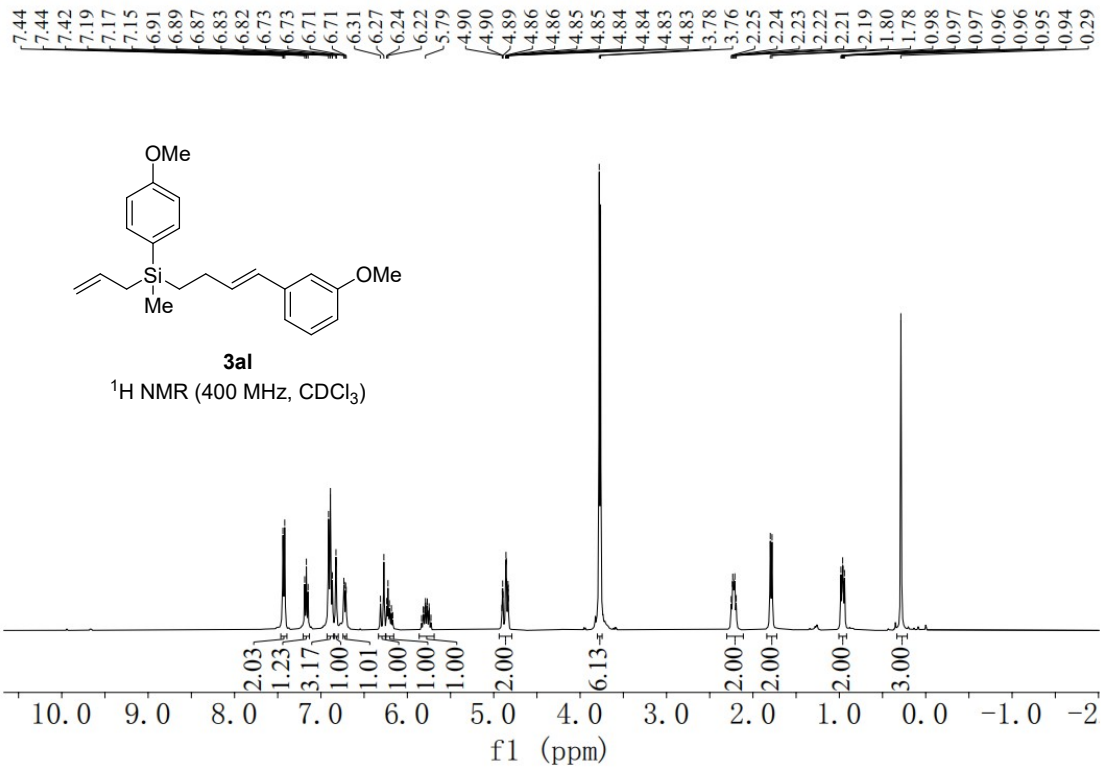
3ak

^{1}H NMR (400 MHz, $CDCl_3$)



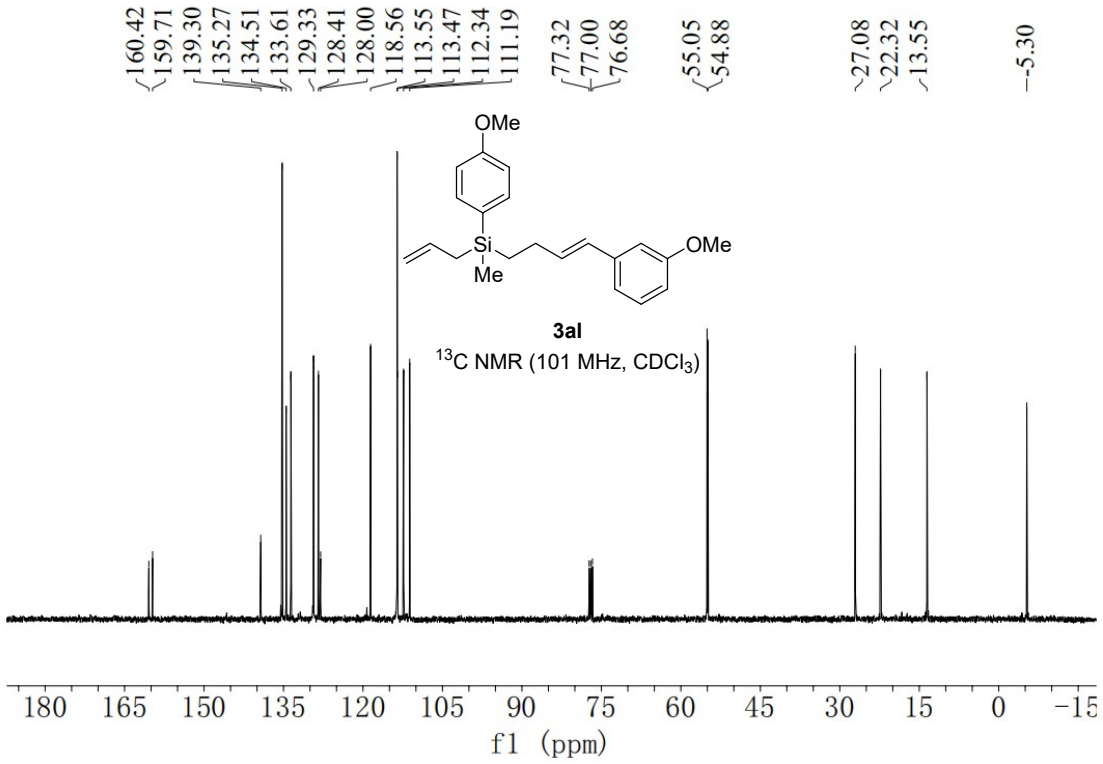
3ak

^{13}C NMR (101 MHz, $CDCl_3$)



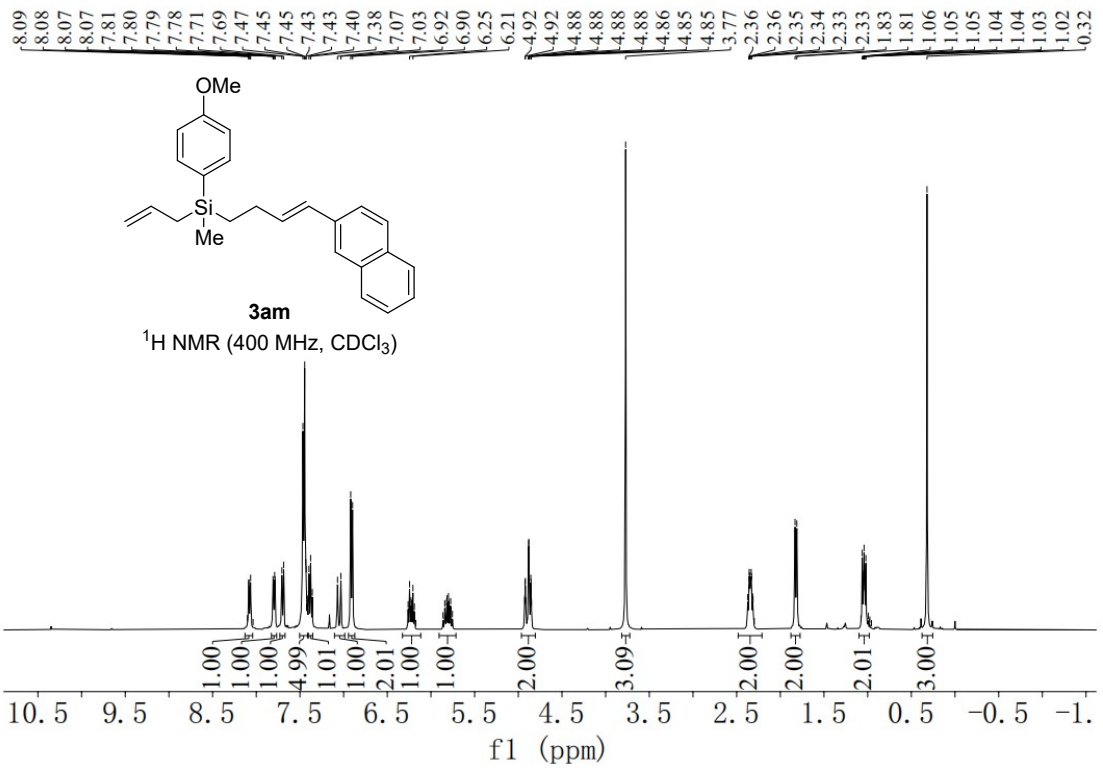
3al

^{1}H NMR (400 MHz, $CDCl_3$)



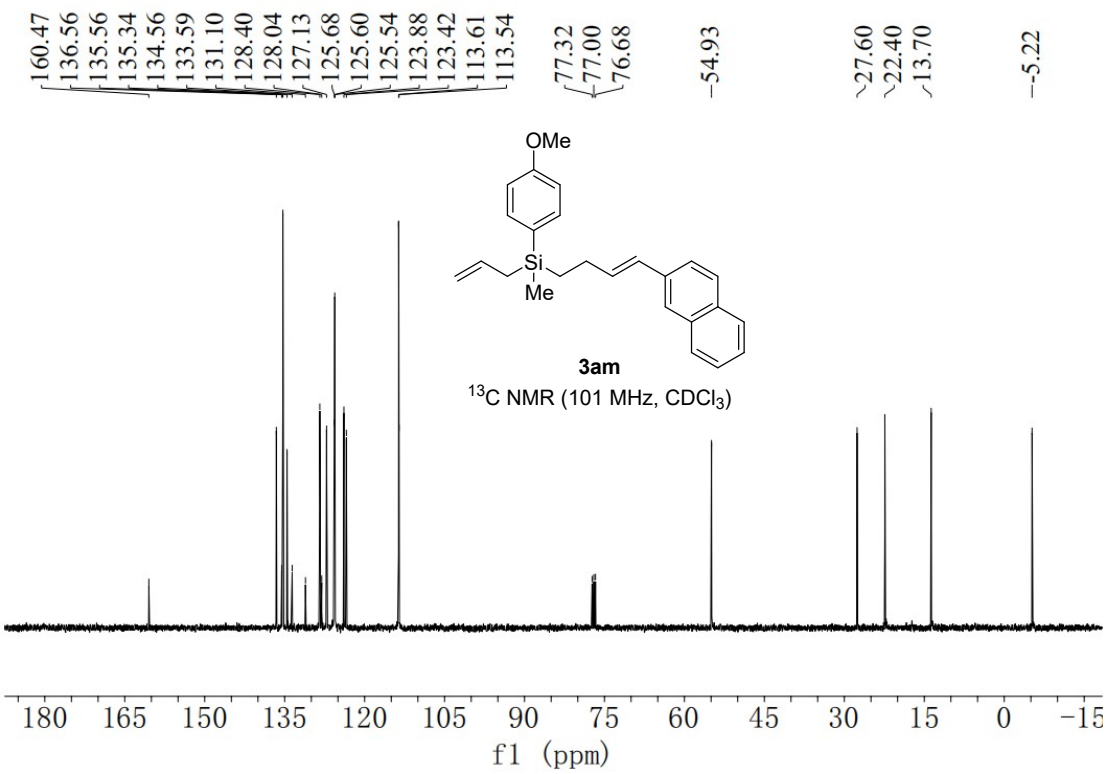
3al

^{13}C NMR (101 MHz, $CDCl_3$)



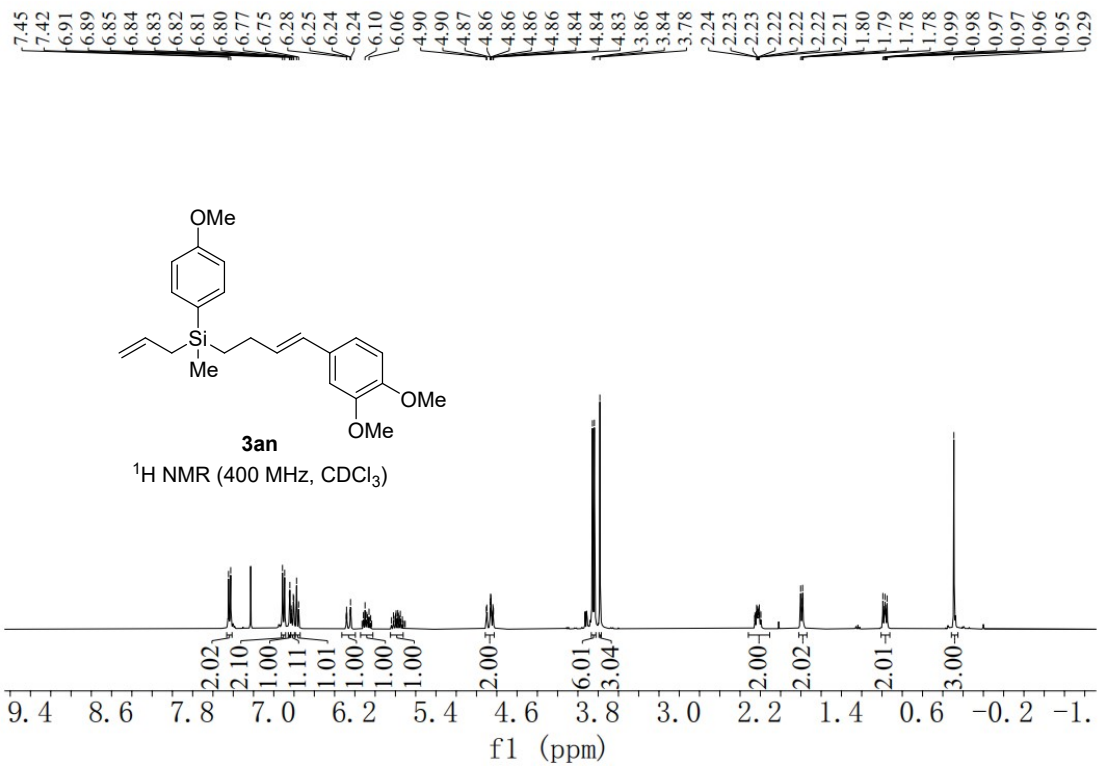
3am

^{1}H NMR (400 MHz, $CDCl_3$)



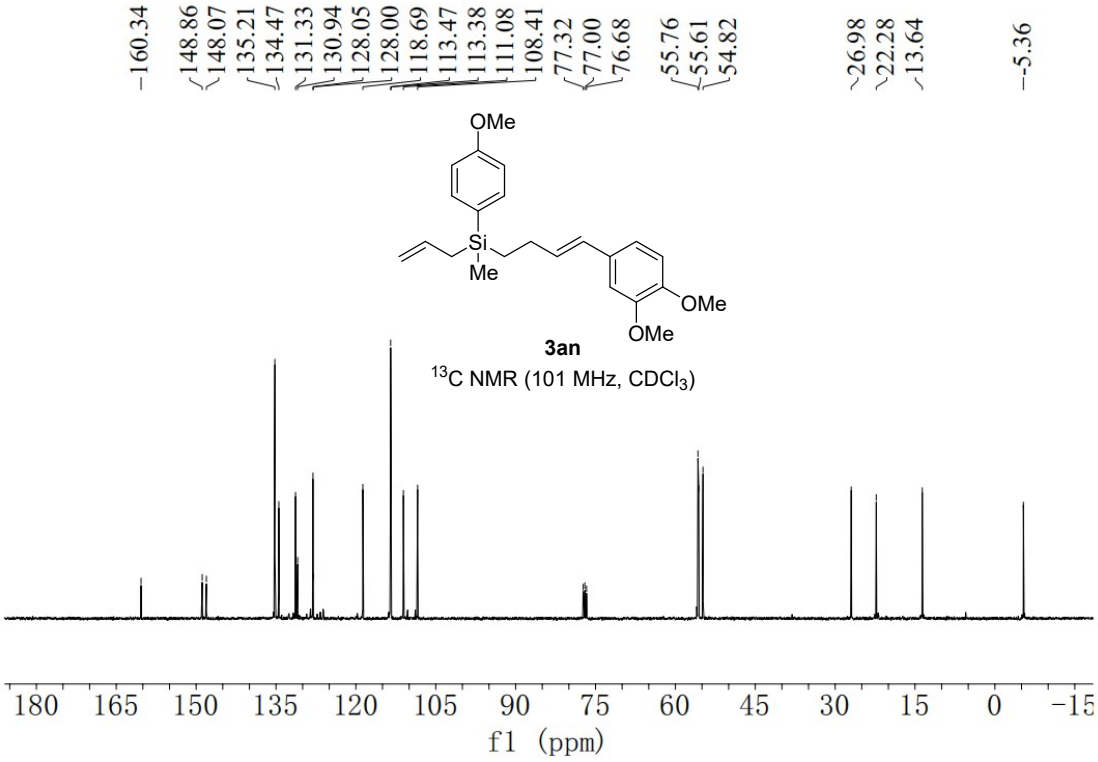
3am

^{13}C NMR (101 MHz, $CDCl_3$)



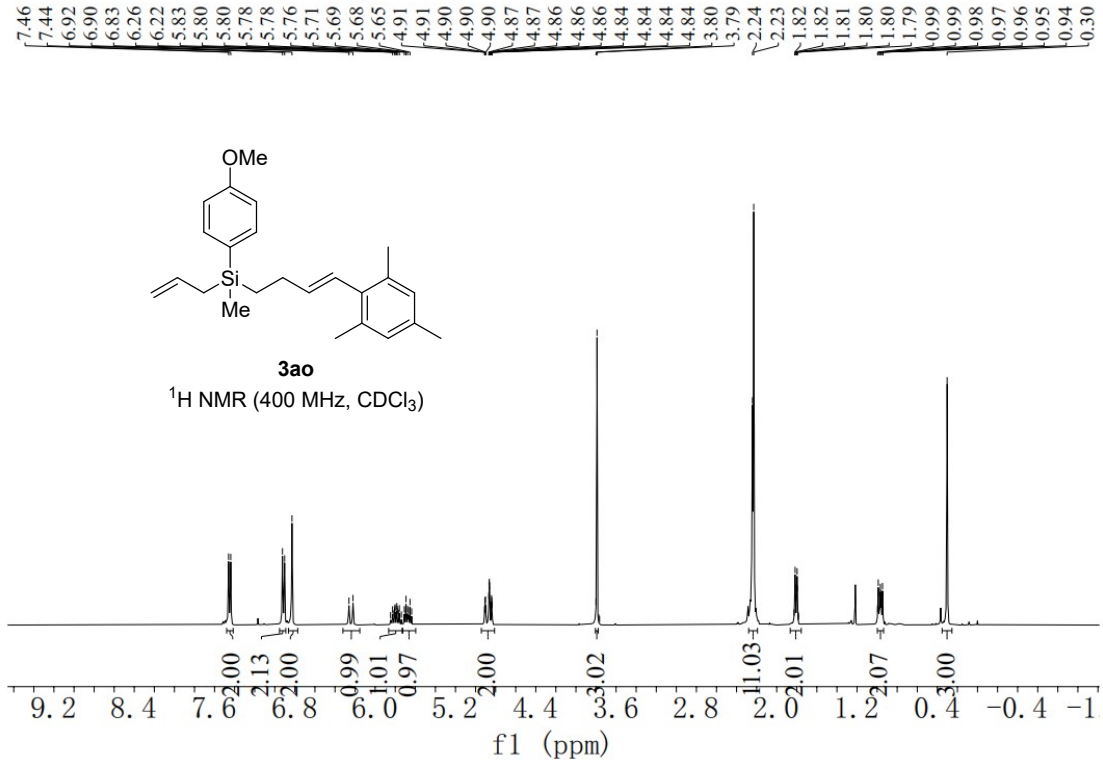
3an

^{1}H NMR (400 MHz, $CDCl_3$)



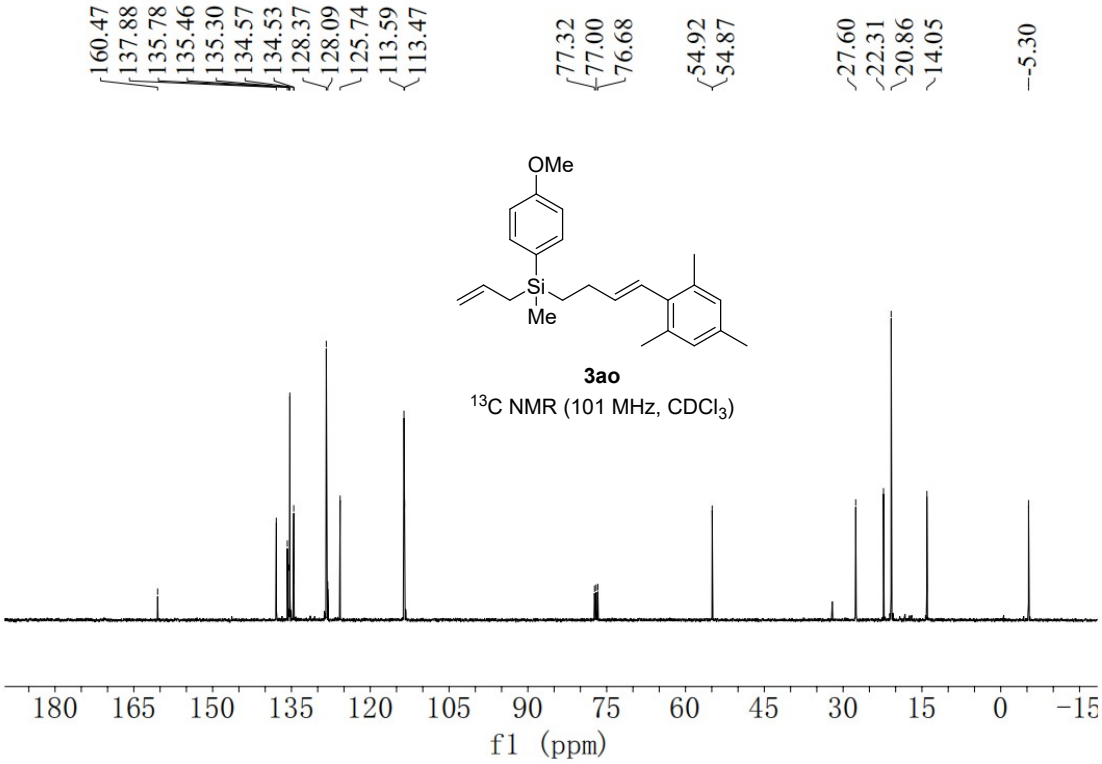
3an

^{13}C NMR (101 MHz, $CDCl_3$)



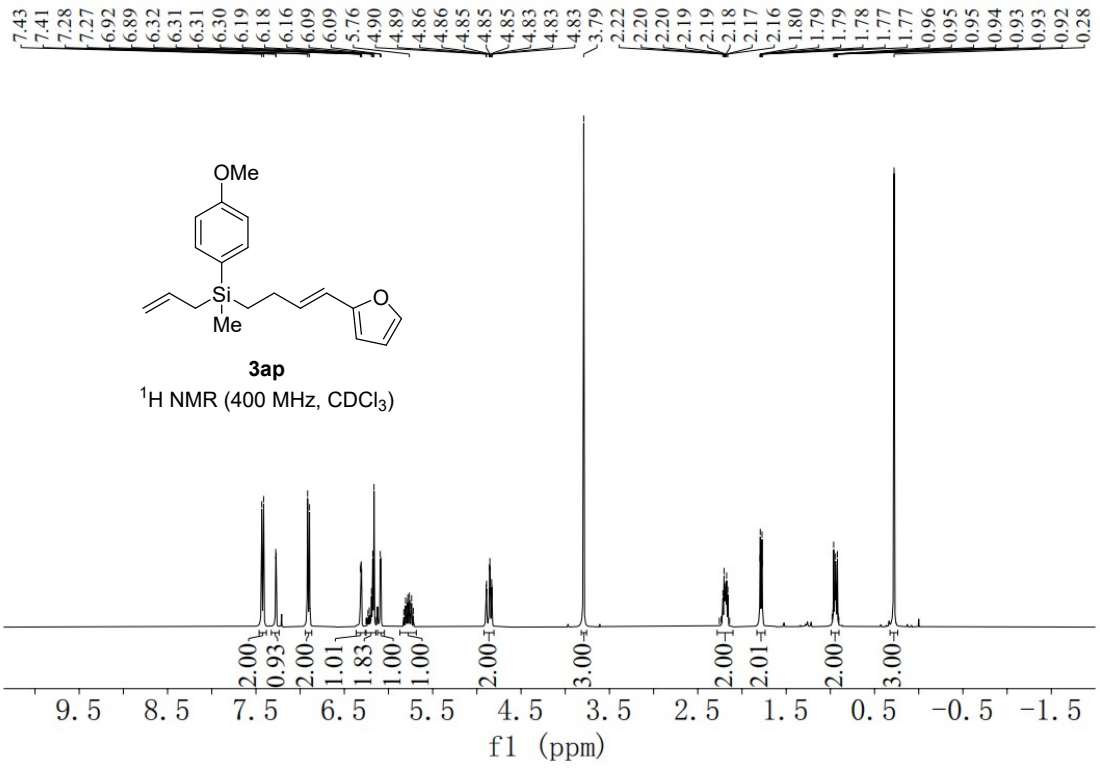
3ao

^{1}H NMR (400 MHz, $CDCl_3$)



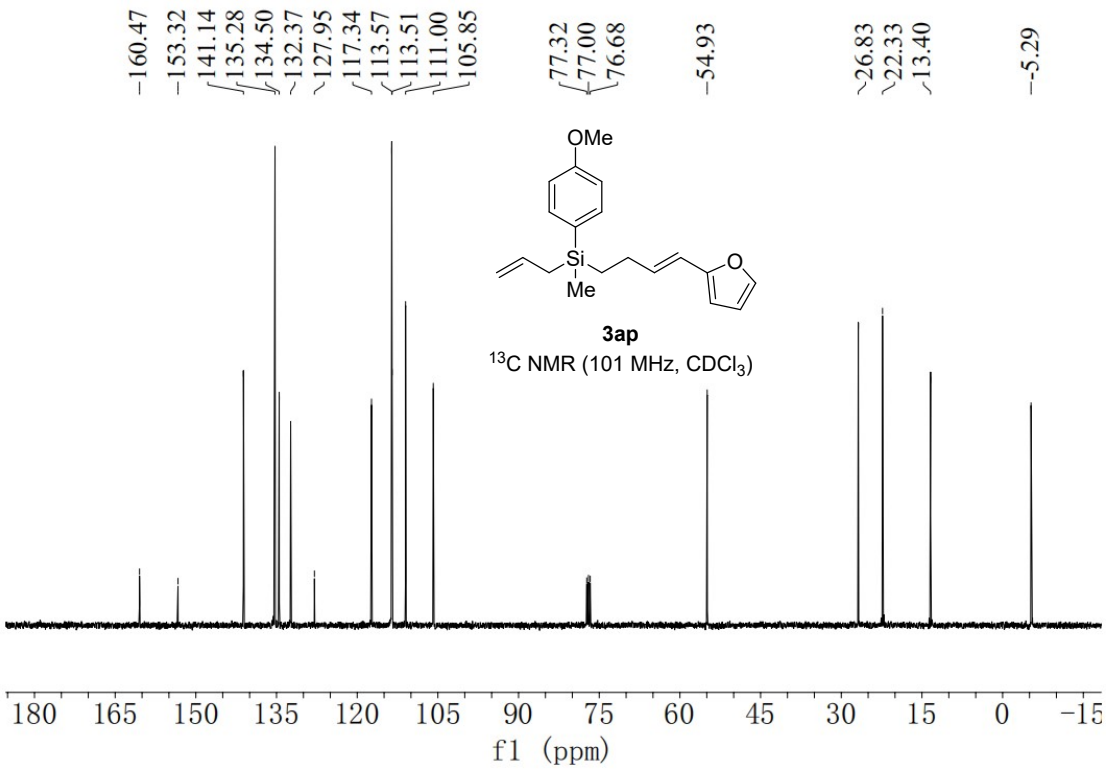
3ao

^{13}C NMR (101 MHz, $CDCl_3$)



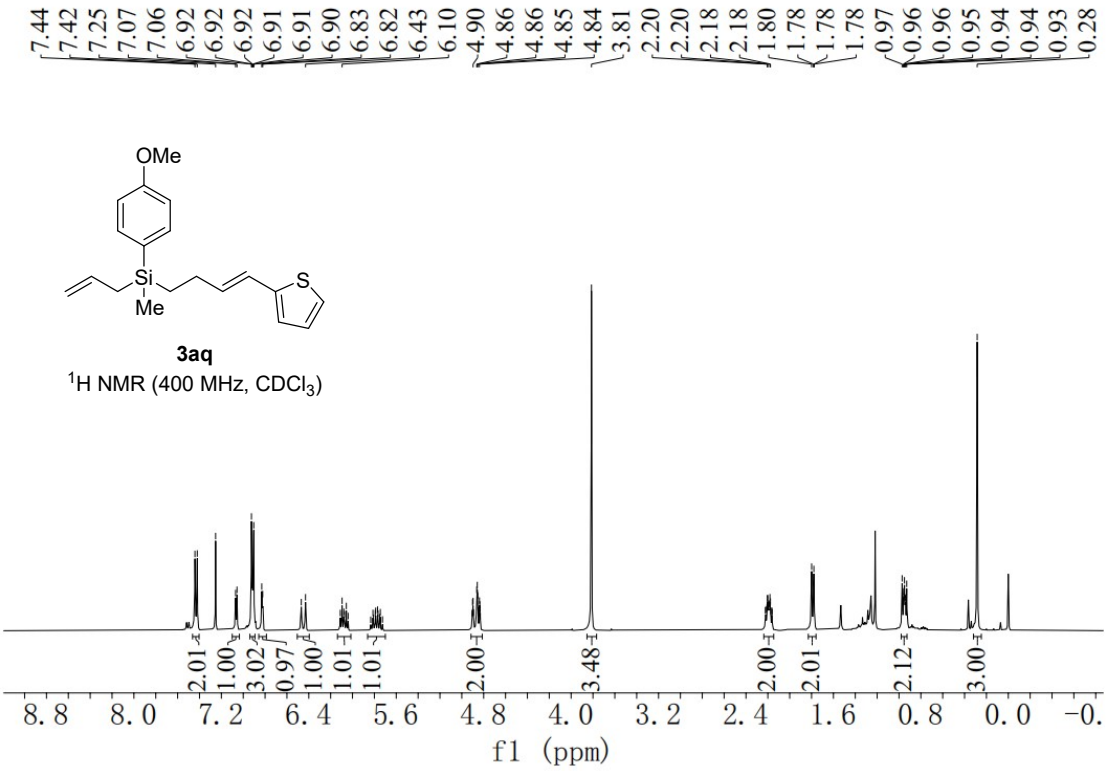
3ap

^{1}H NMR (400 MHz, $CDCl_3$)



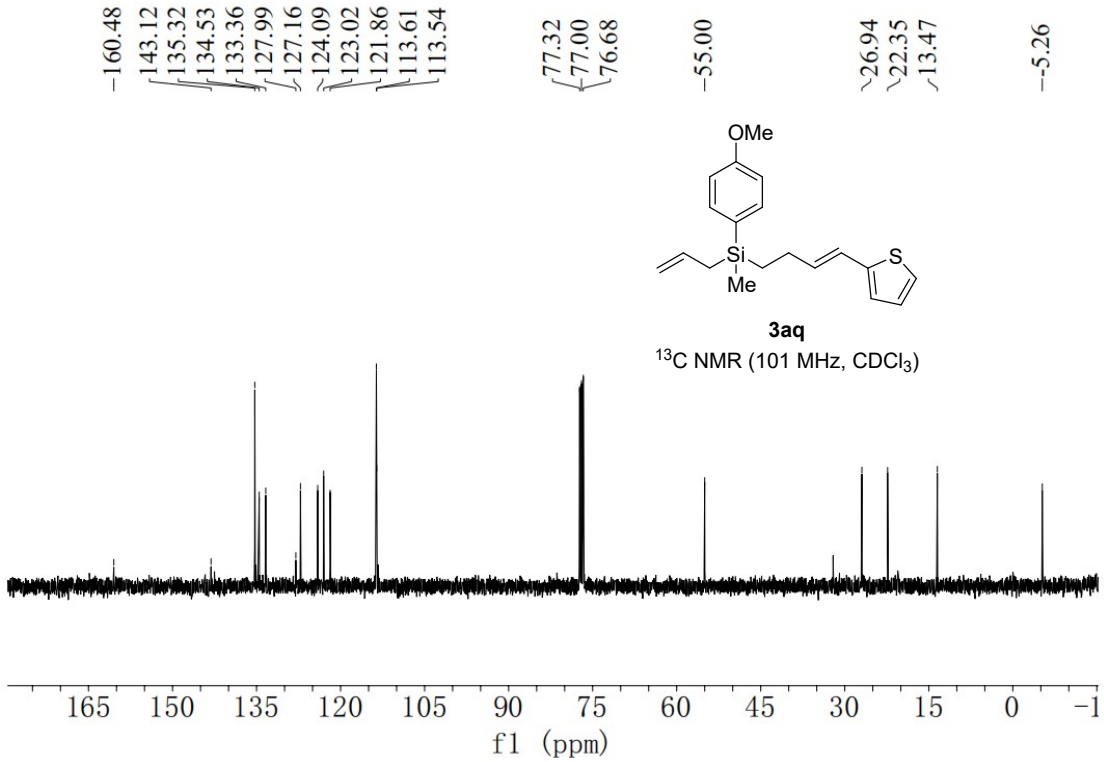
3ap

^{13}C NMR (101 MHz, $CDCl_3$)



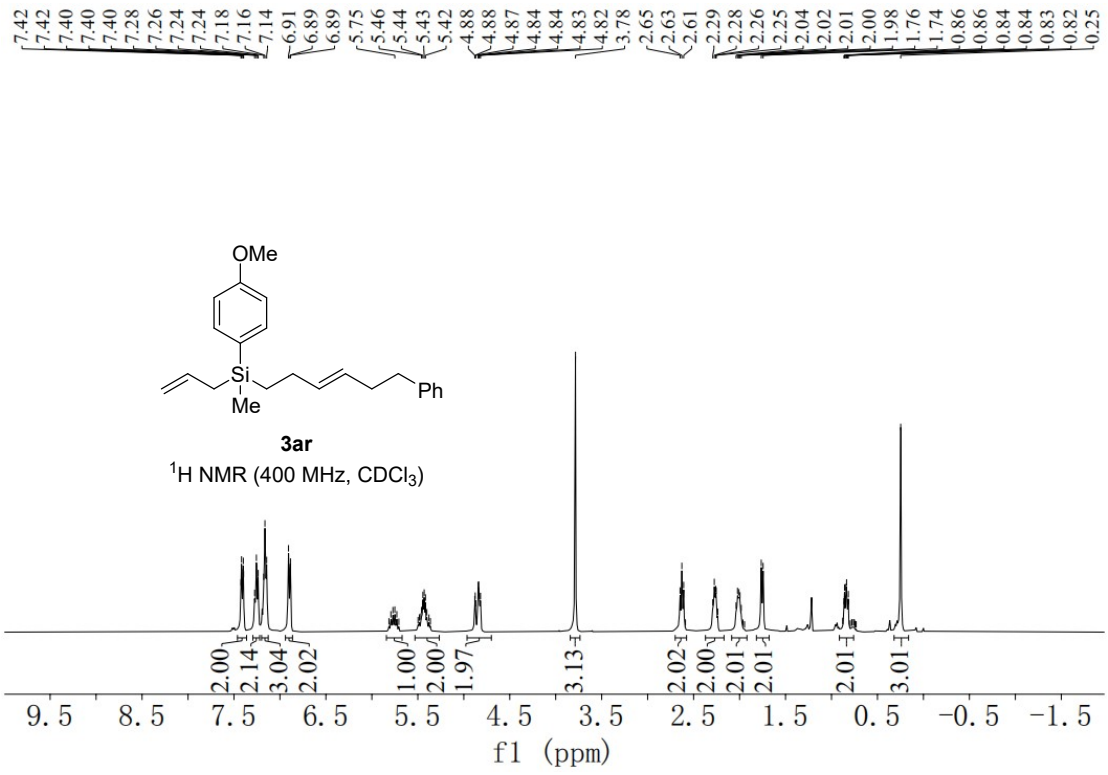
3aq

^{1}H NMR (400 MHz, $CDCl_3$)



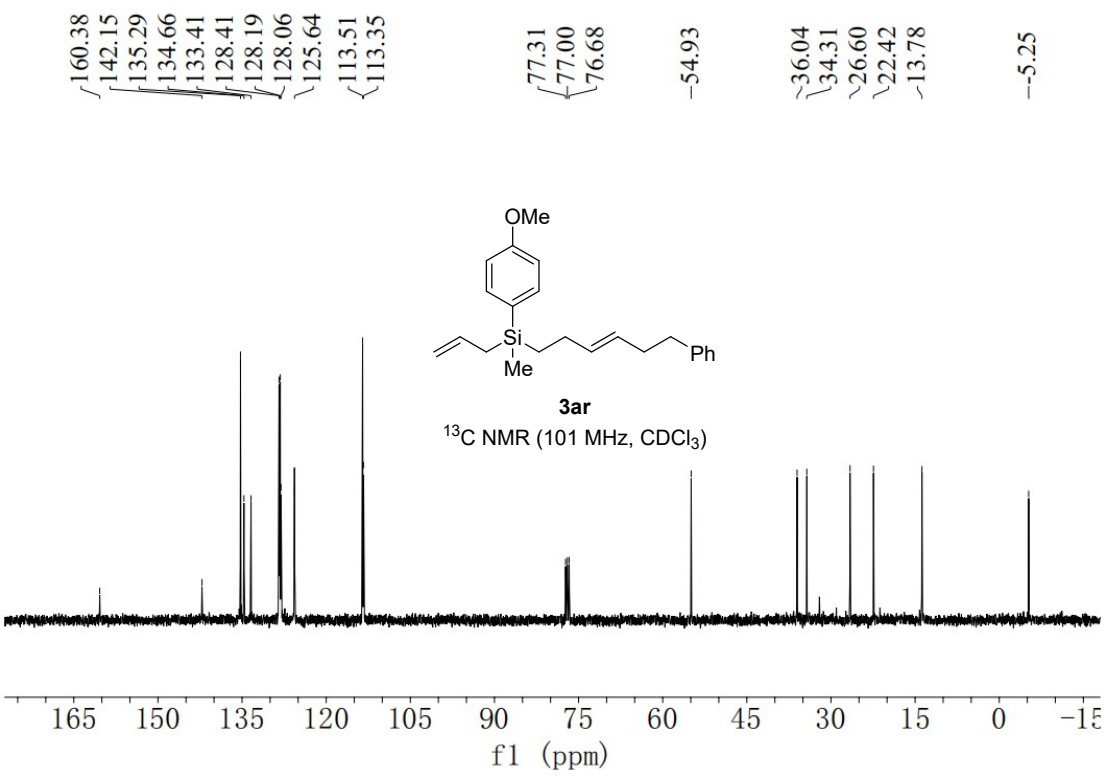
3aq

^{13}C NMR (101 MHz, $CDCl_3$)



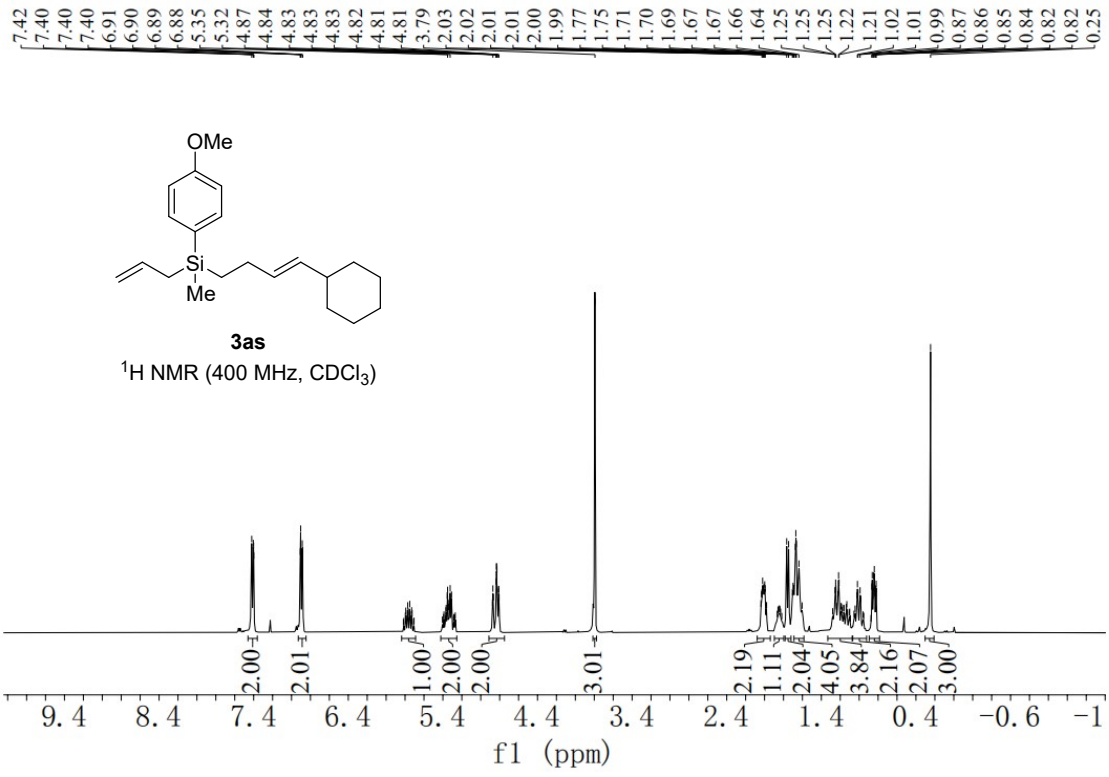
3ar

^{1}H NMR (400 MHz, $CDCl_3$)



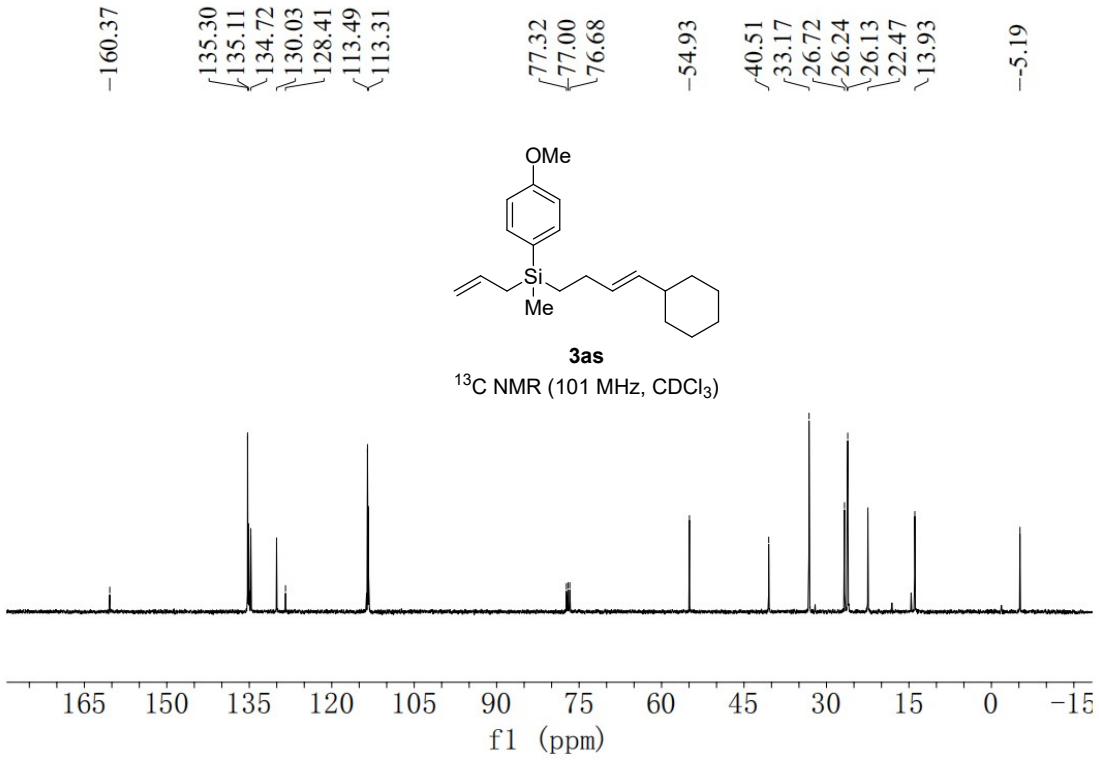
3ar

^{13}C NMR (101 MHz, $CDCl_3$)



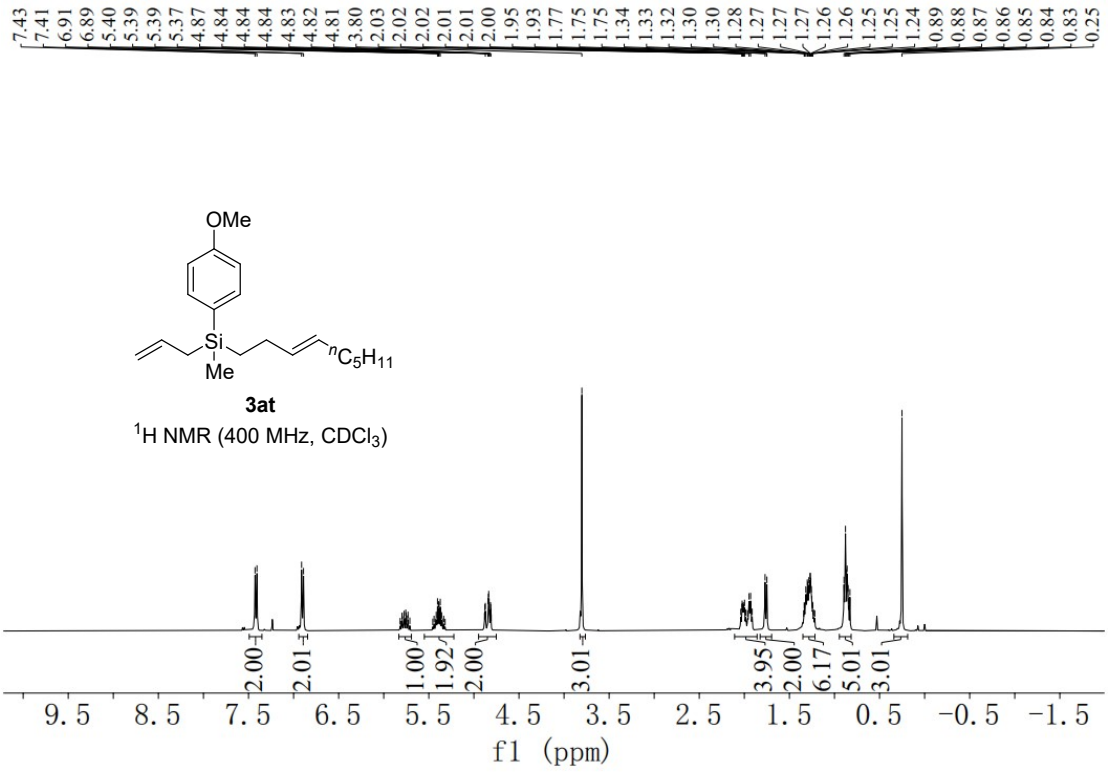
3as

^{1}H NMR (400 MHz, $CDCl_3$)



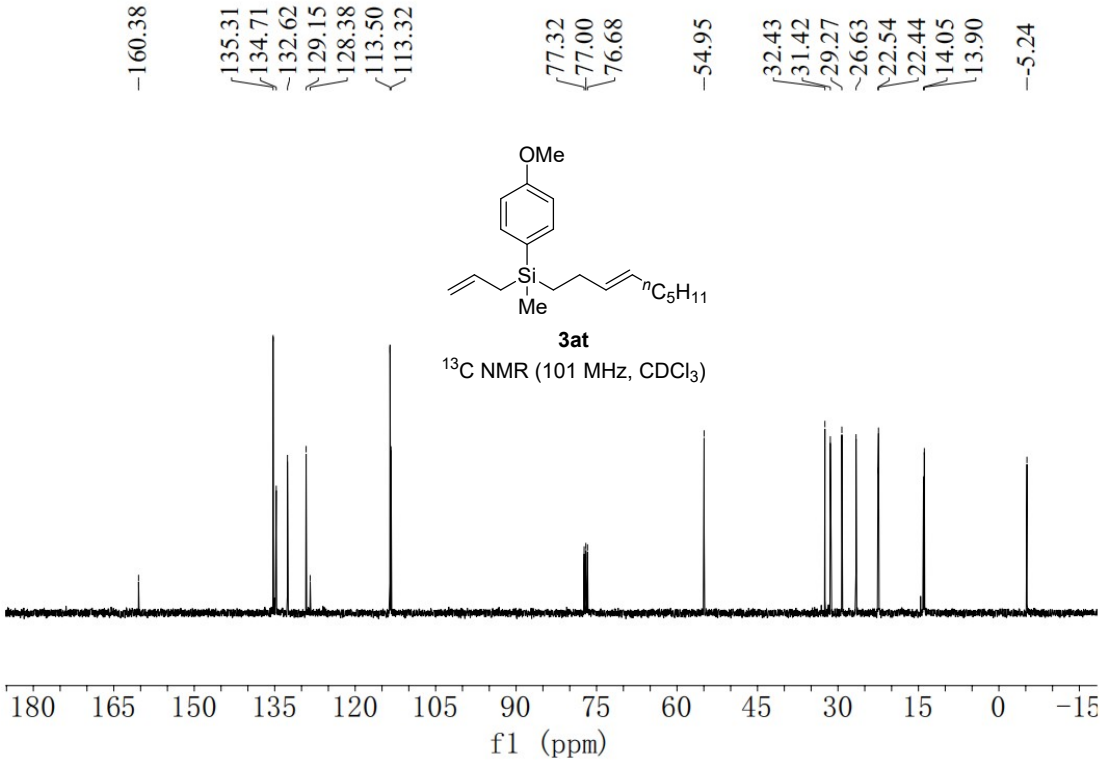
3as

^{13}C NMR (101 MHz, $CDCl_3$)



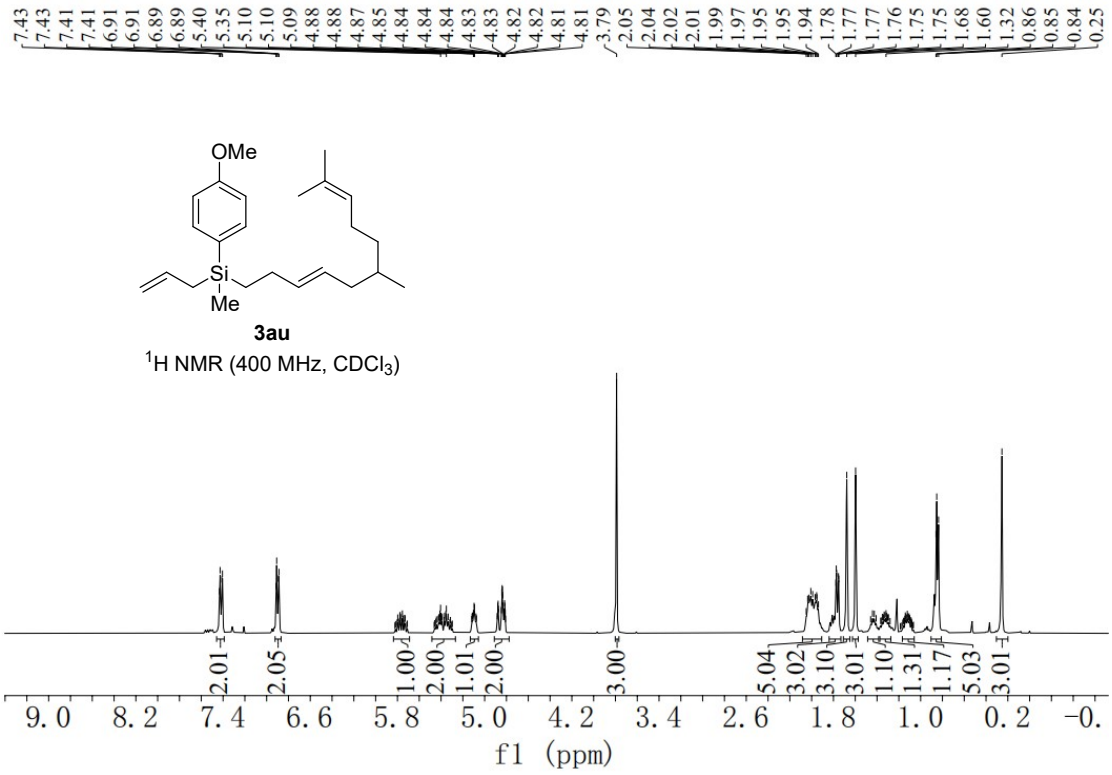
3at

^{1}H NMR (400 MHz, $CDCl_3$)



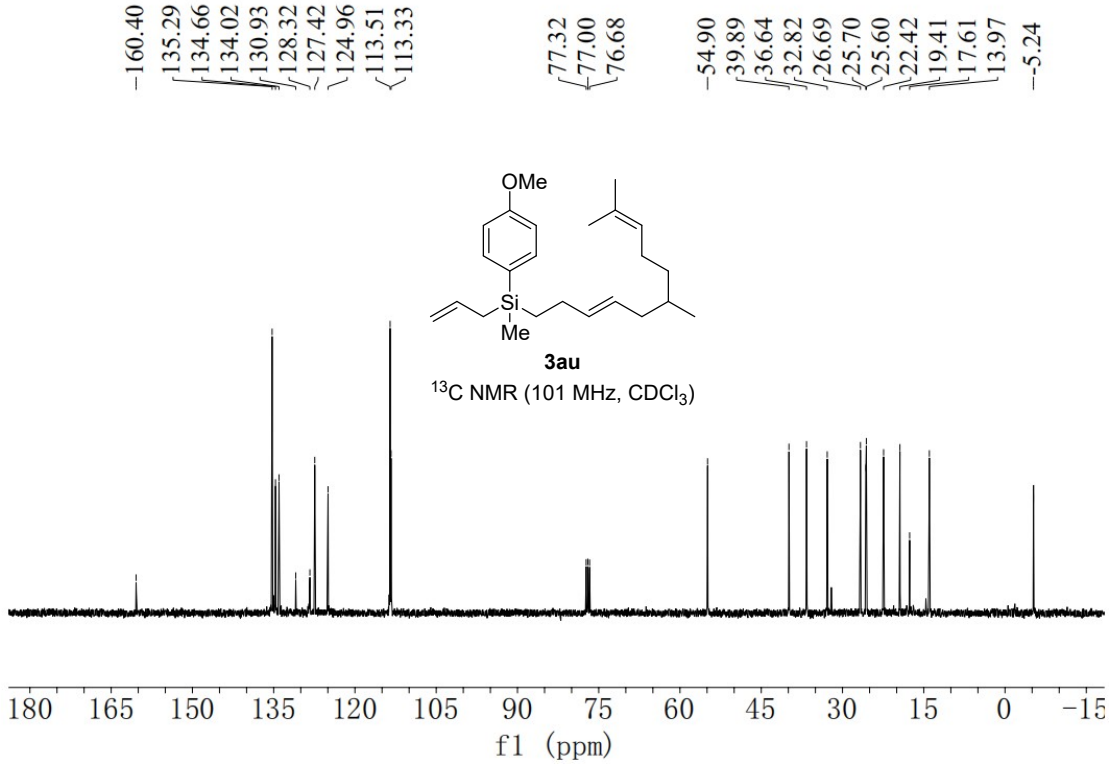
3at

^{13}C NMR (101 MHz, $CDCl_3$)



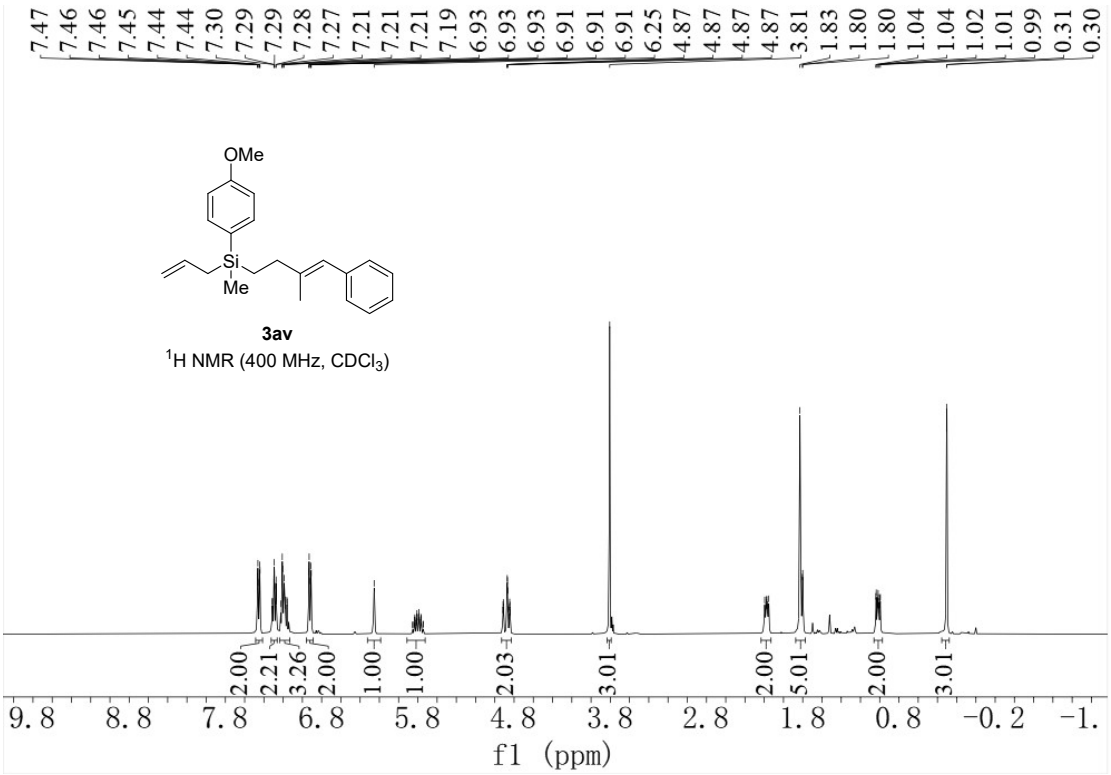
3au

^{1}H NMR (400 MHz, $CDCl_3$)



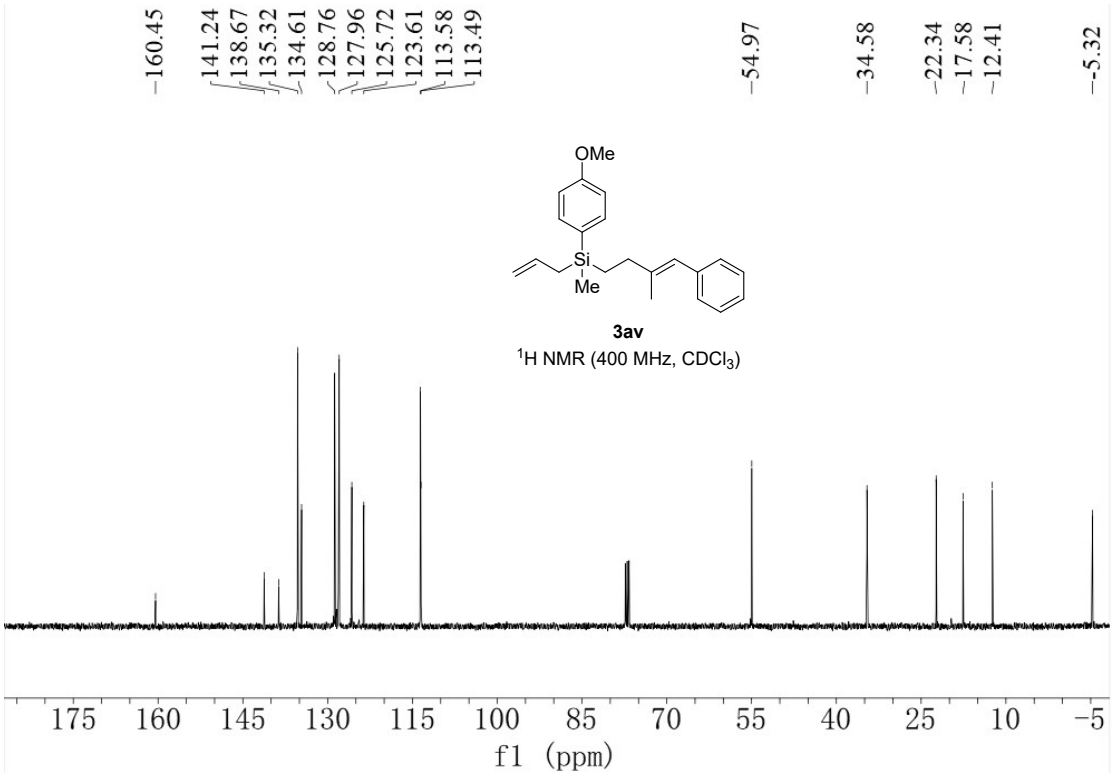
3au

^{13}C NMR (101 MHz, $CDCl_3$)



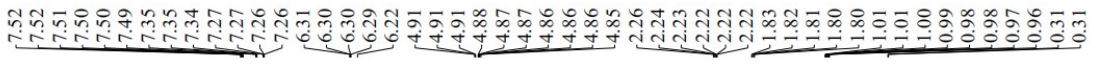
3av

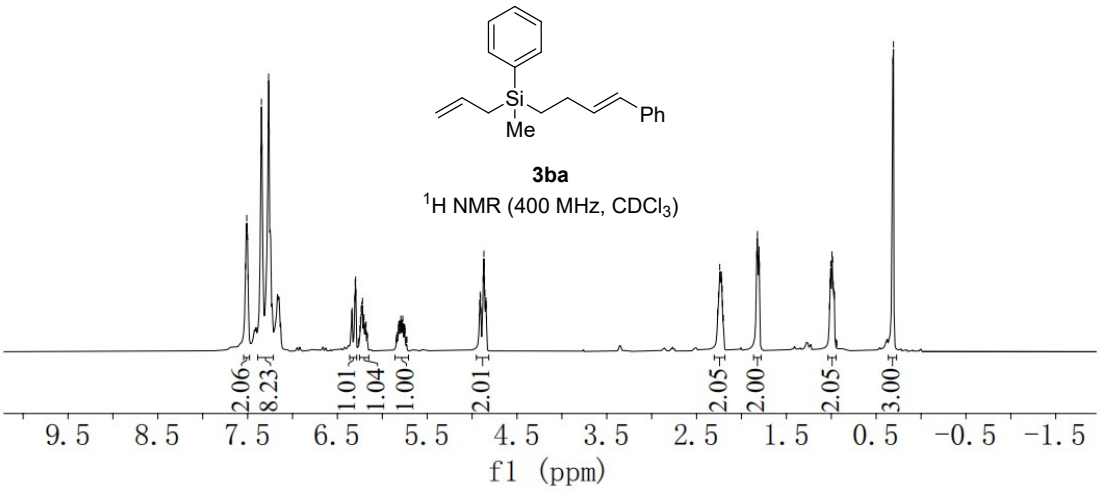
^{1}H NMR (400 MHz, $CDCl_3$)



3av

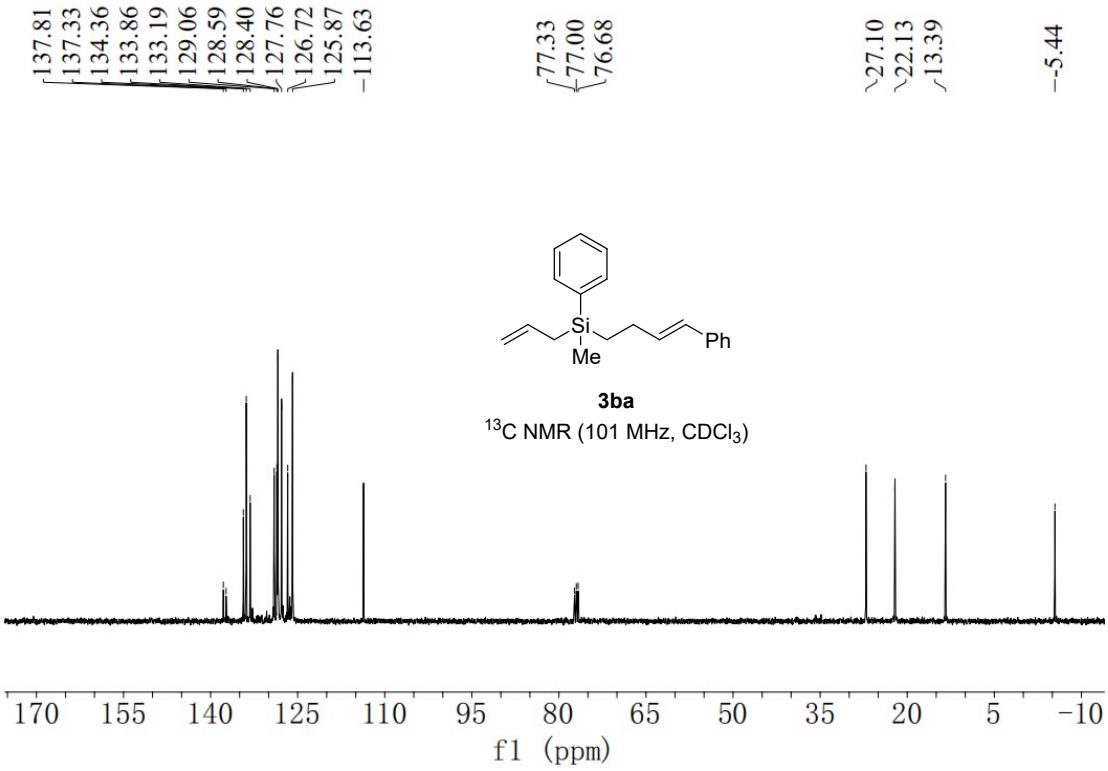
^{1}H NMR (400 MHz, $CDCl_3$)





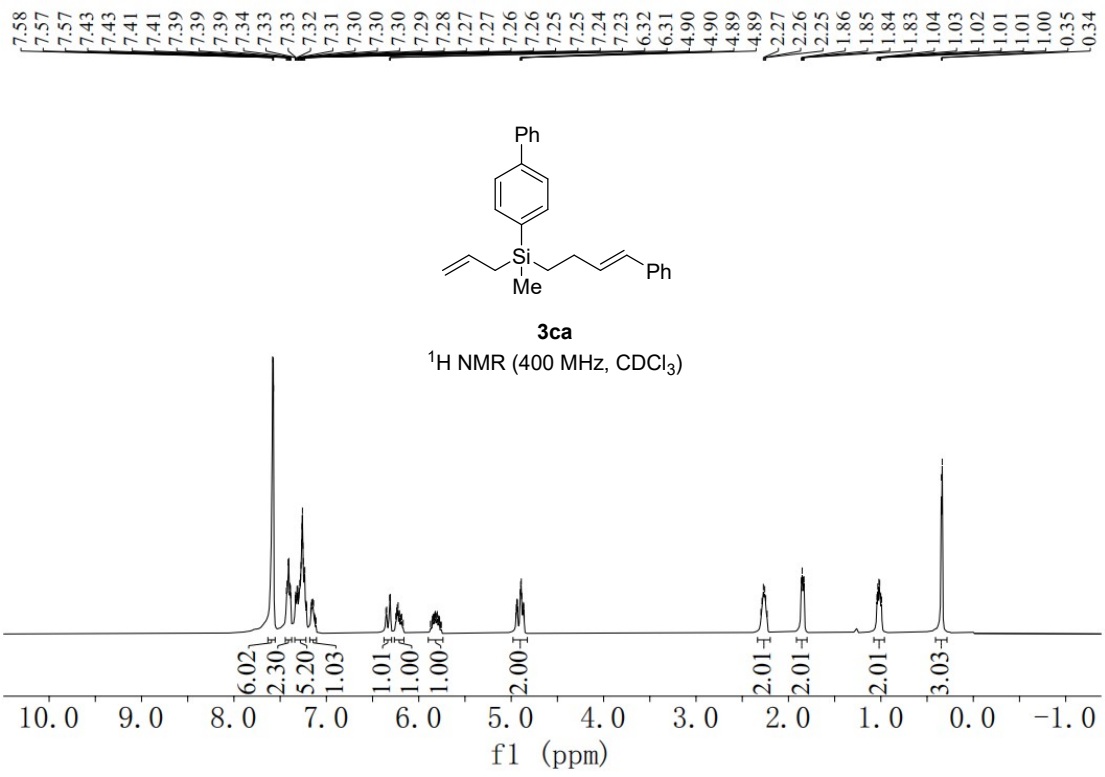
3ba

^{1}H NMR (400 MHz, $CDCl_3$)



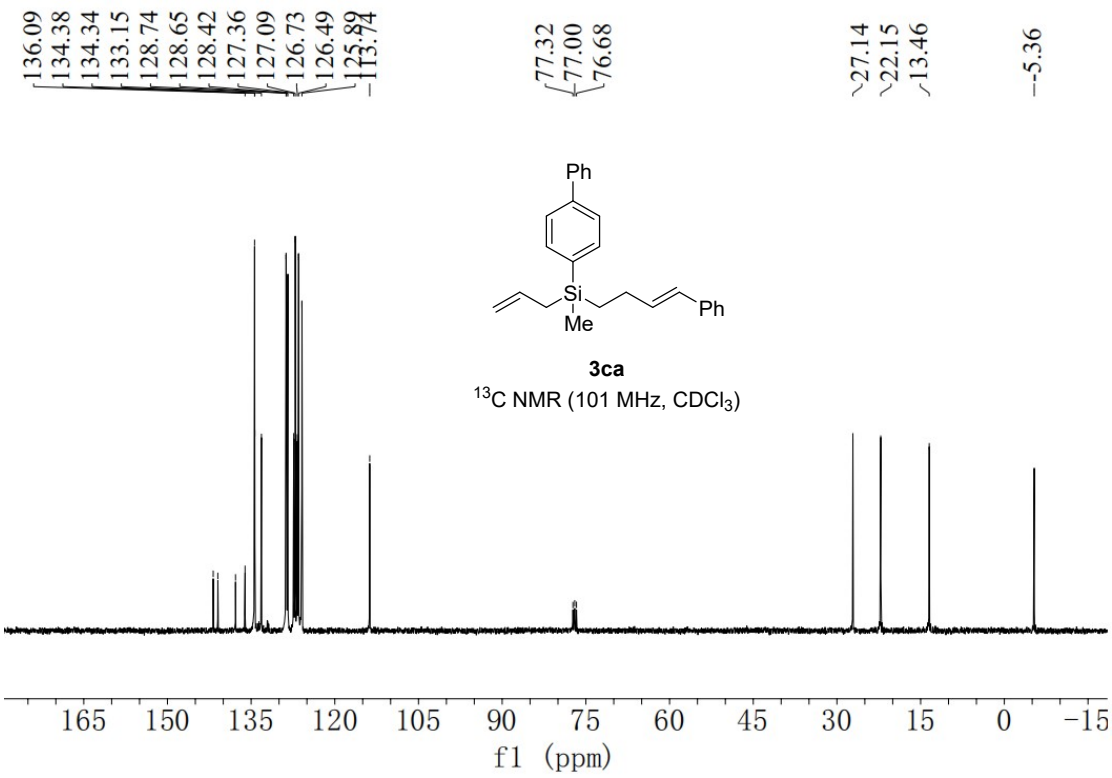
3ba

^{13}C NMR (101 MHz, $CDCl_3$)



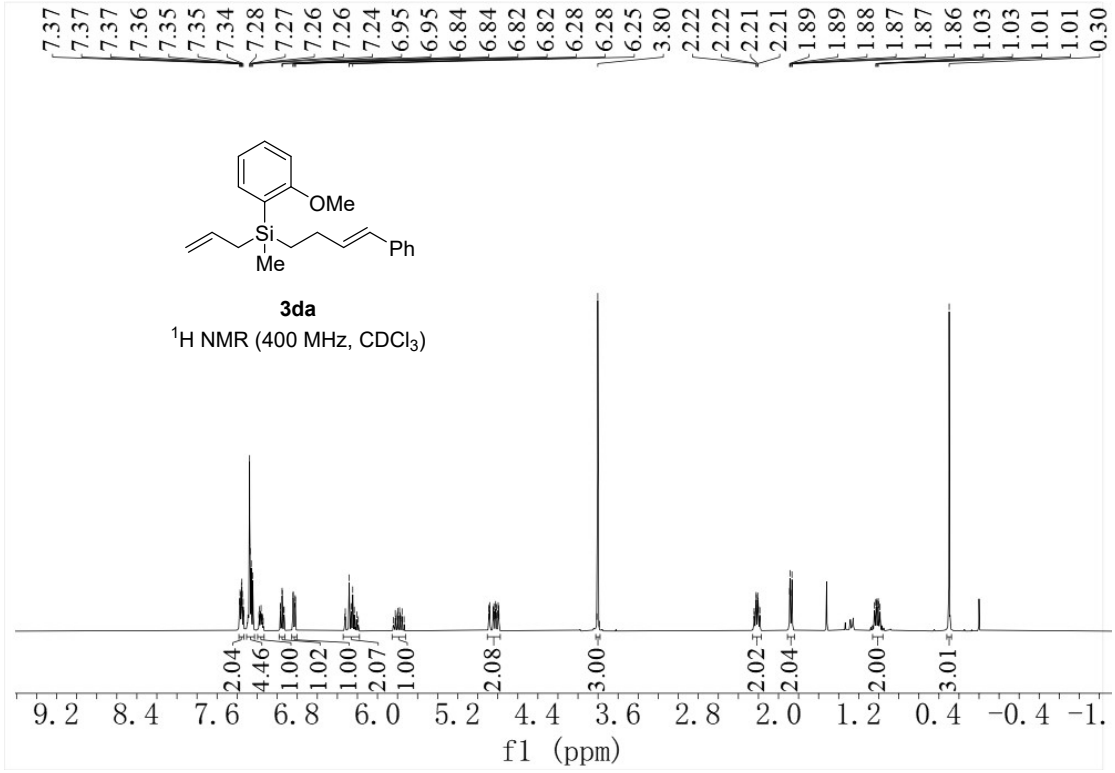
3ca

^{1}H NMR (400 MHz, $CDCl_3$)



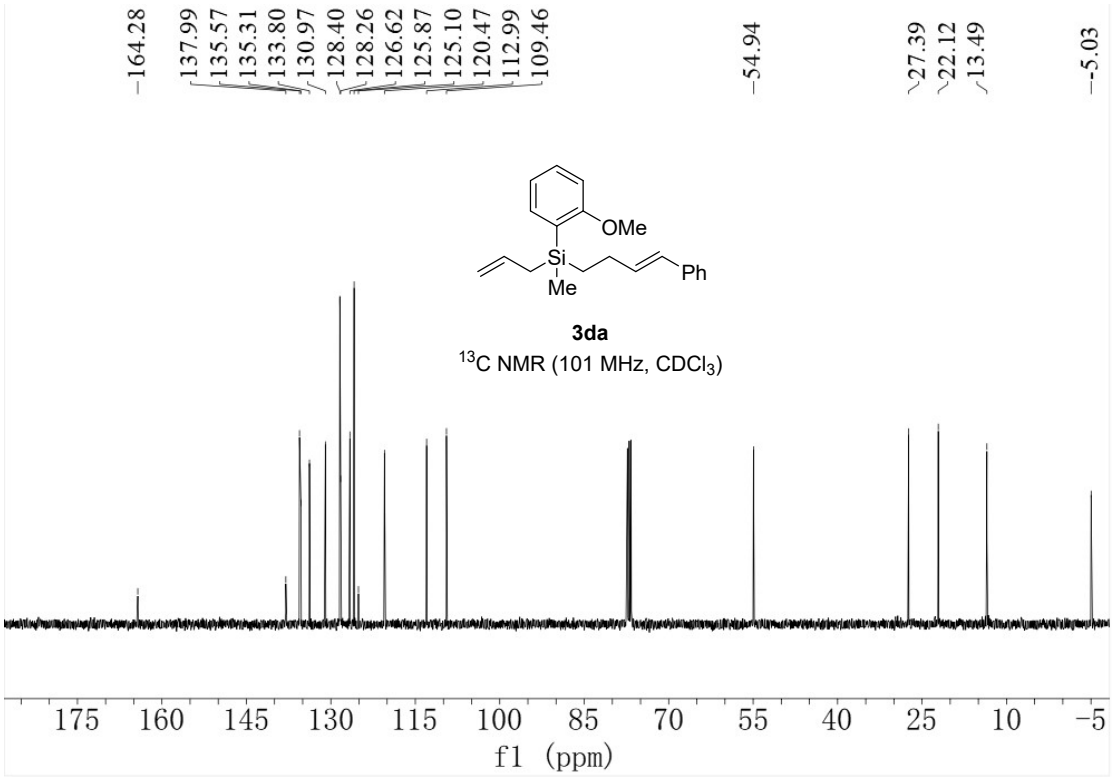
3ca

^{13}C NMR (101 MHz, $CDCl_3$)



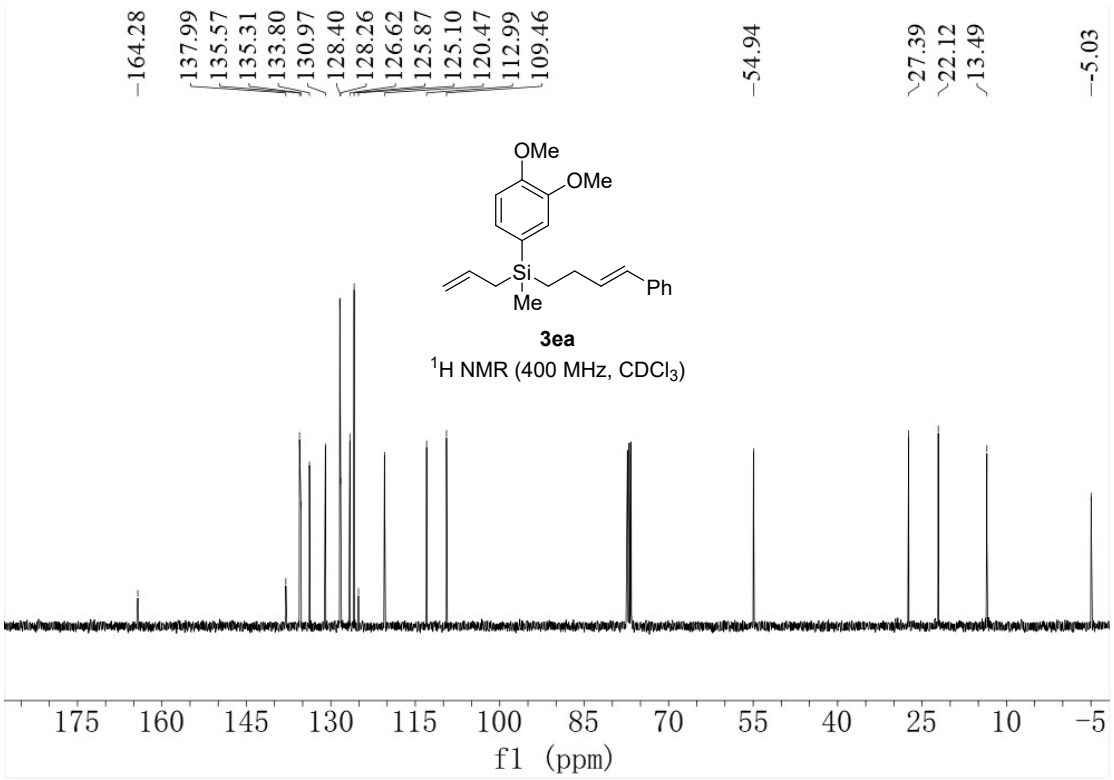
3da

^{1}H NMR (400 MHz, $CDCl_3$)



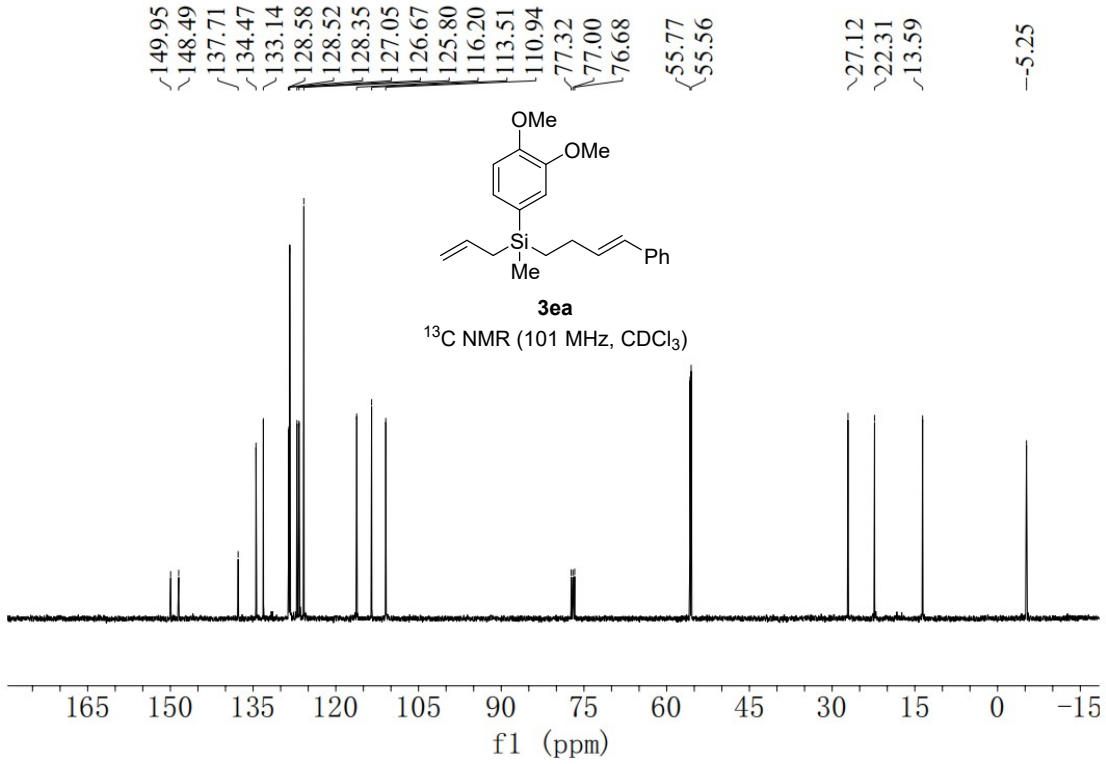
3da

^{13}C NMR (101 MHz, $CDCl_3$)



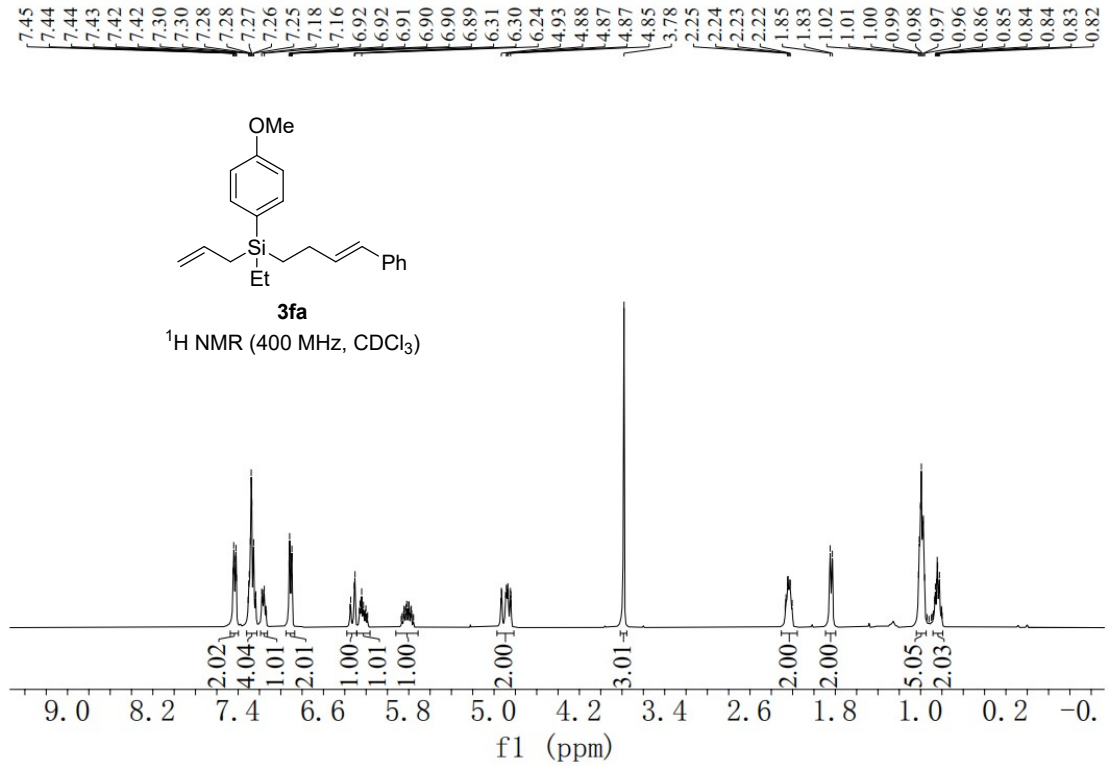
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



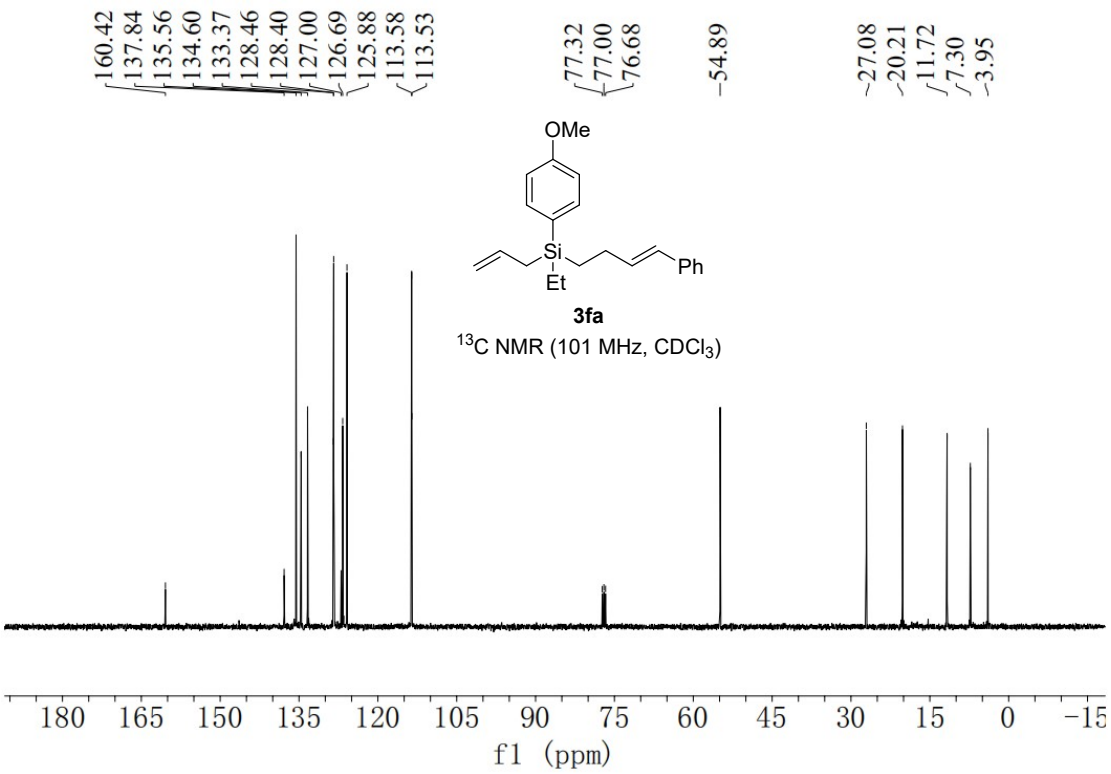
3ea

^{13}C NMR (101 MHz, $CDCl_3$)



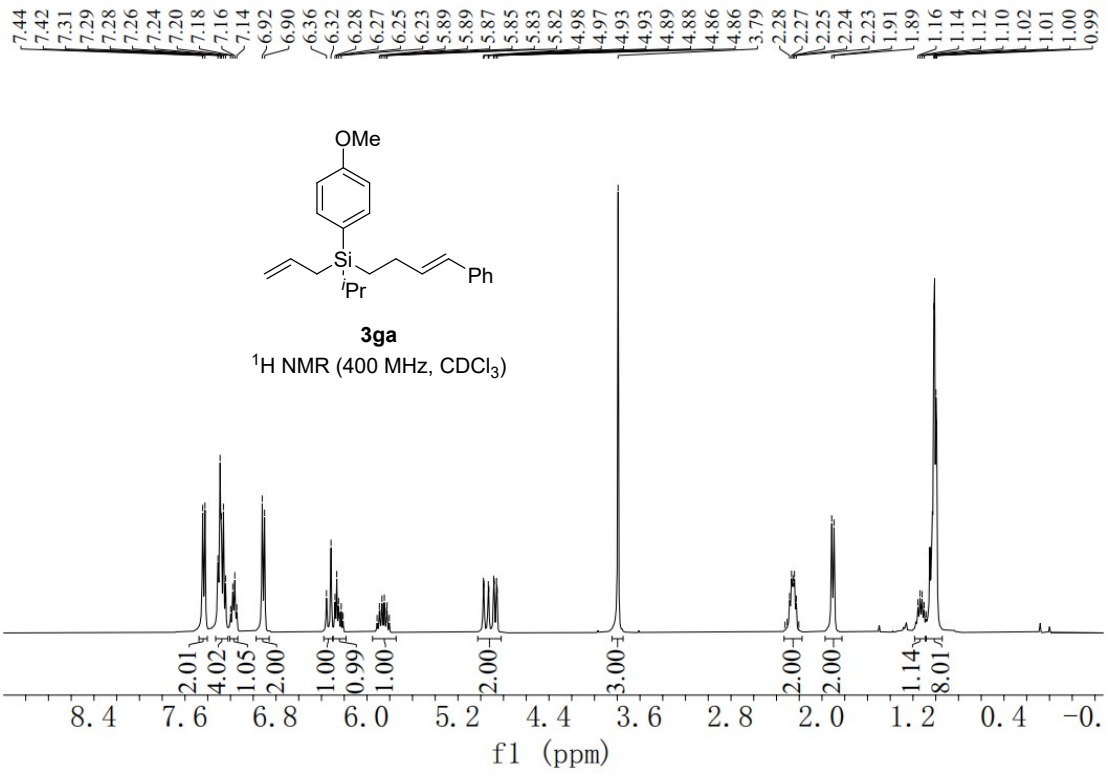
3fa

^{1}H NMR (400 MHz, $CDCl_3$)



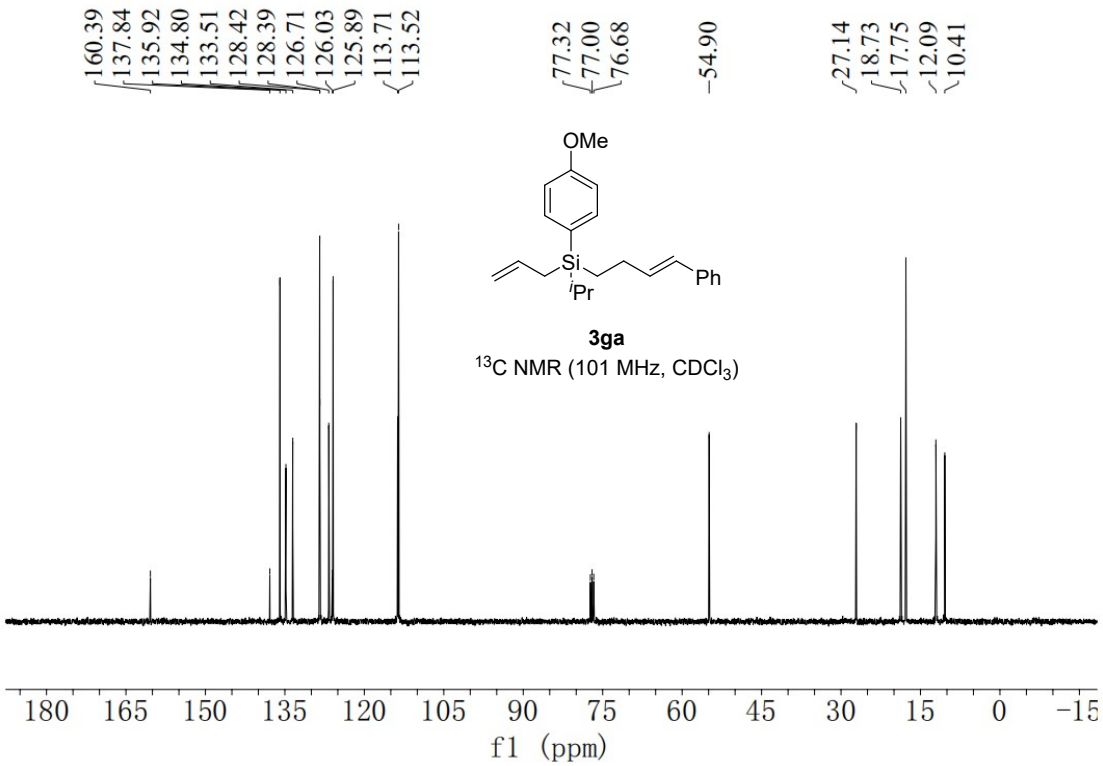
3fa

^{13}C NMR (101 MHz, $CDCl_3$)



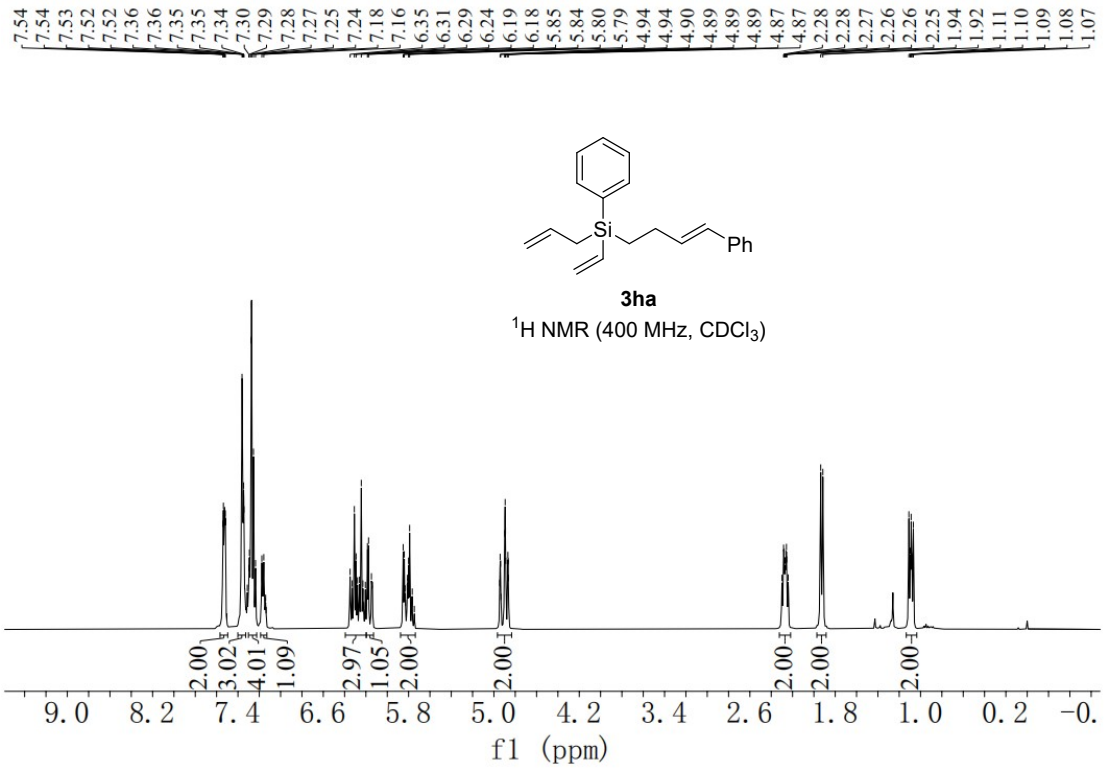
3ga

^{1}H NMR (400 MHz, $CDCl_3$)



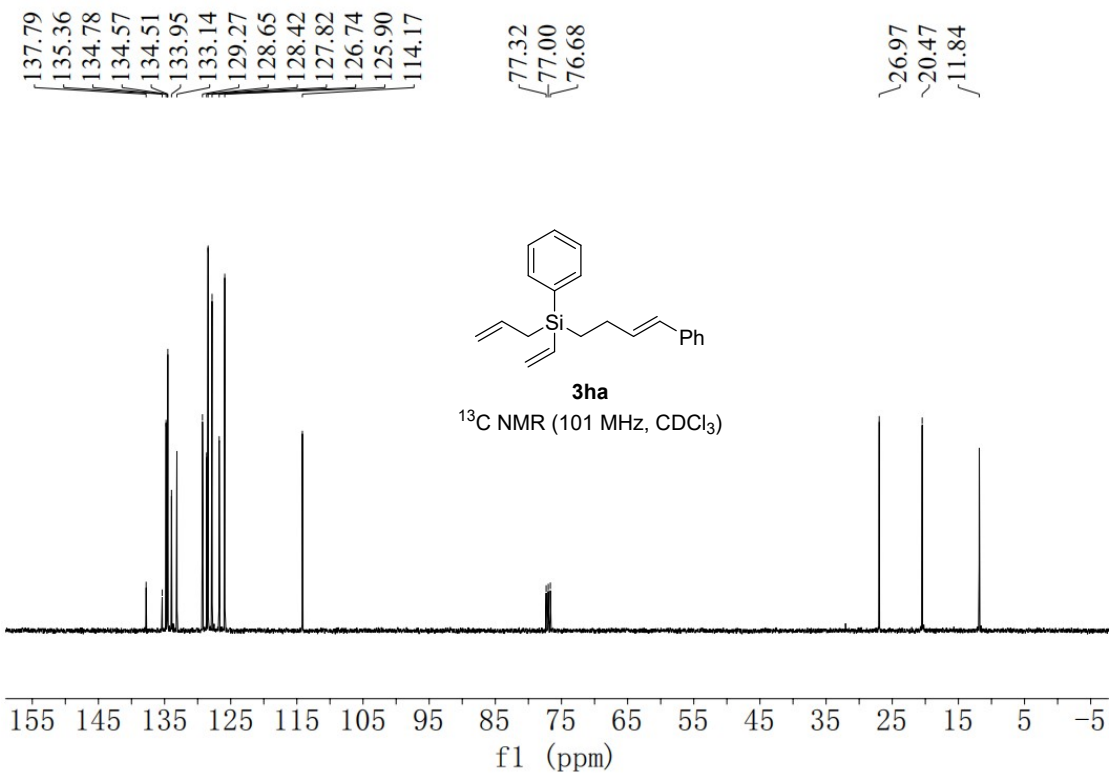
3ga

^{13}C NMR (101 MHz, $CDCl_3$)



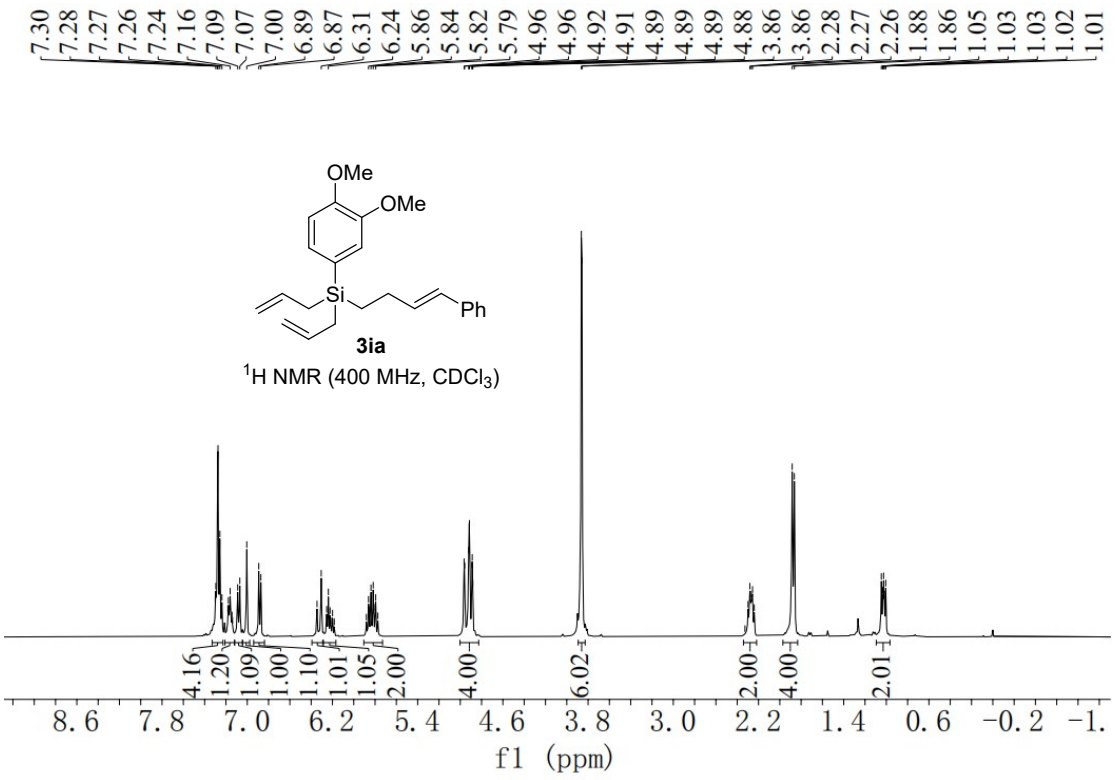
3ha

^{1}H NMR (400 MHz, $CDCl_3$)



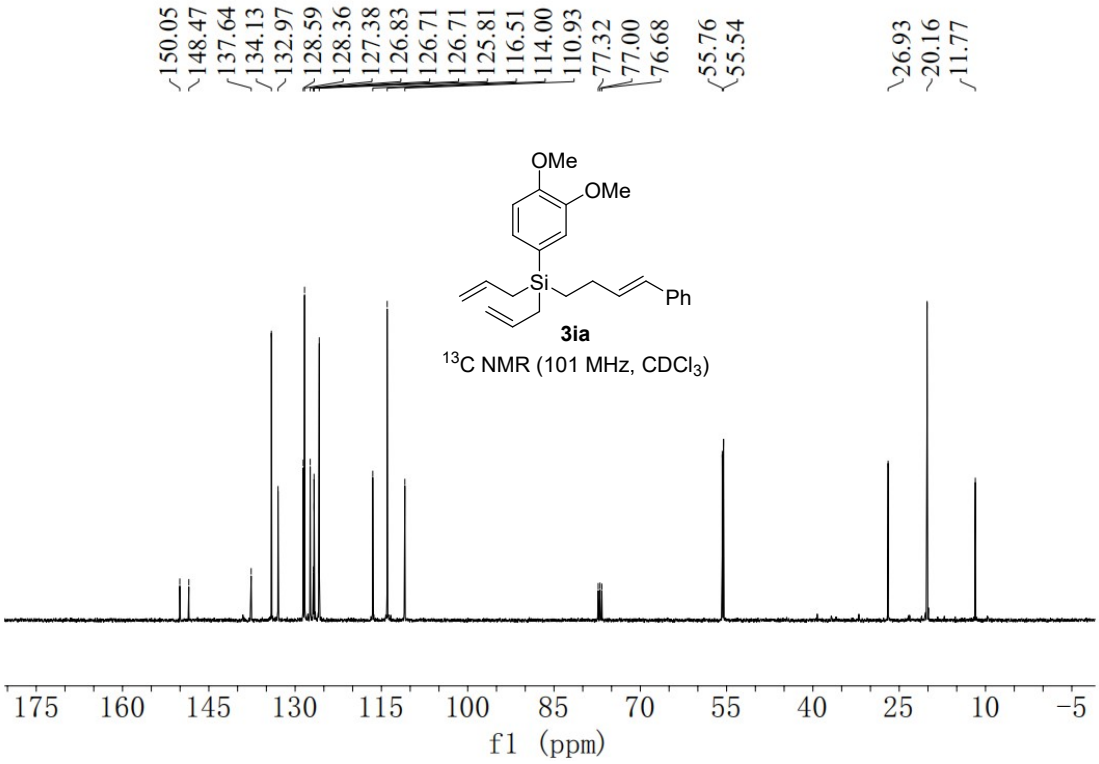
3ha

^{13}C NMR (101 MHz, $CDCl_3$)



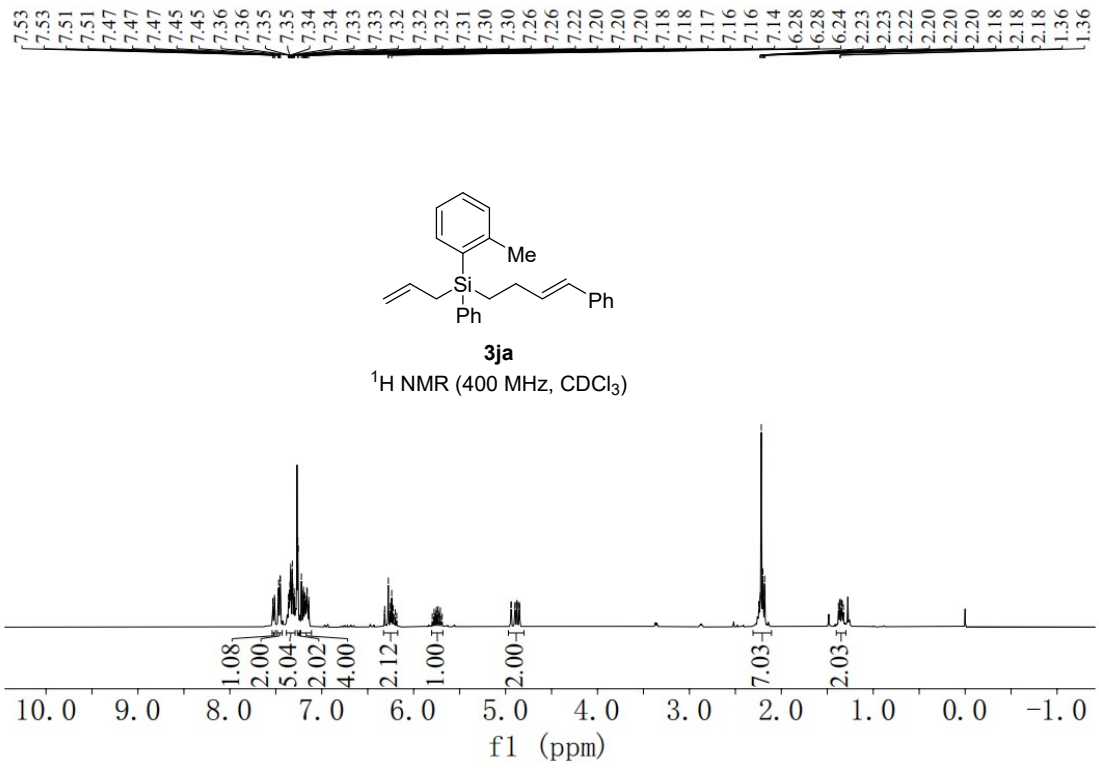
3ia

^{1}H NMR (400 MHz, $CDCl_3$)



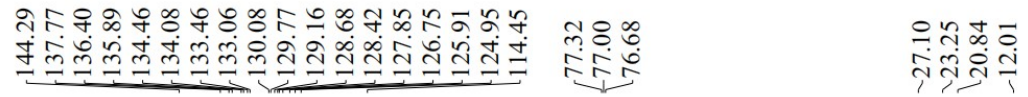
3ia

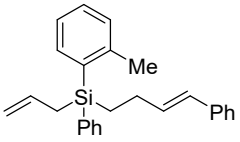
^{13}C NMR (101 MHz, $CDCl_3$)



3ja

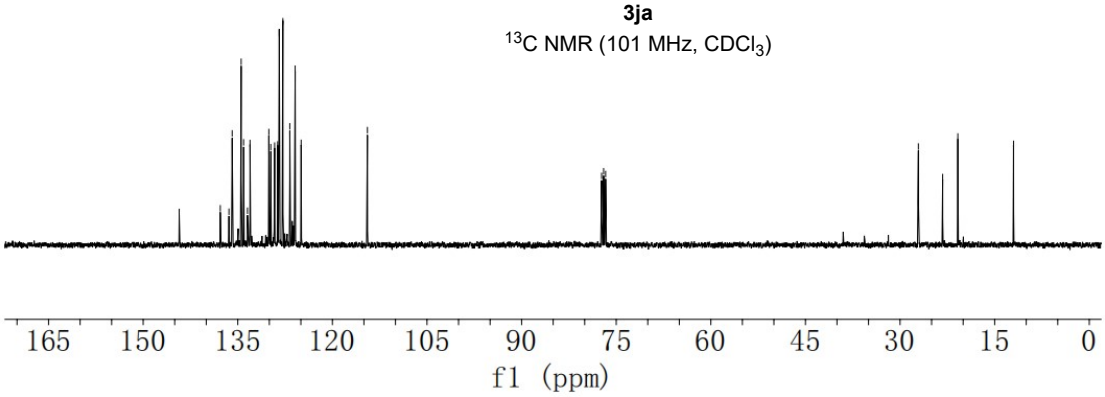
^{1}H NMR (400 MHz, $CDCl_3$)

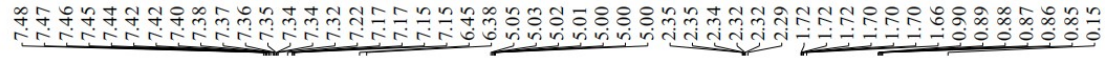


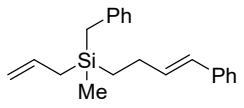


3ja

^{13}C NMR (101 MHz, $CDCl_3$)

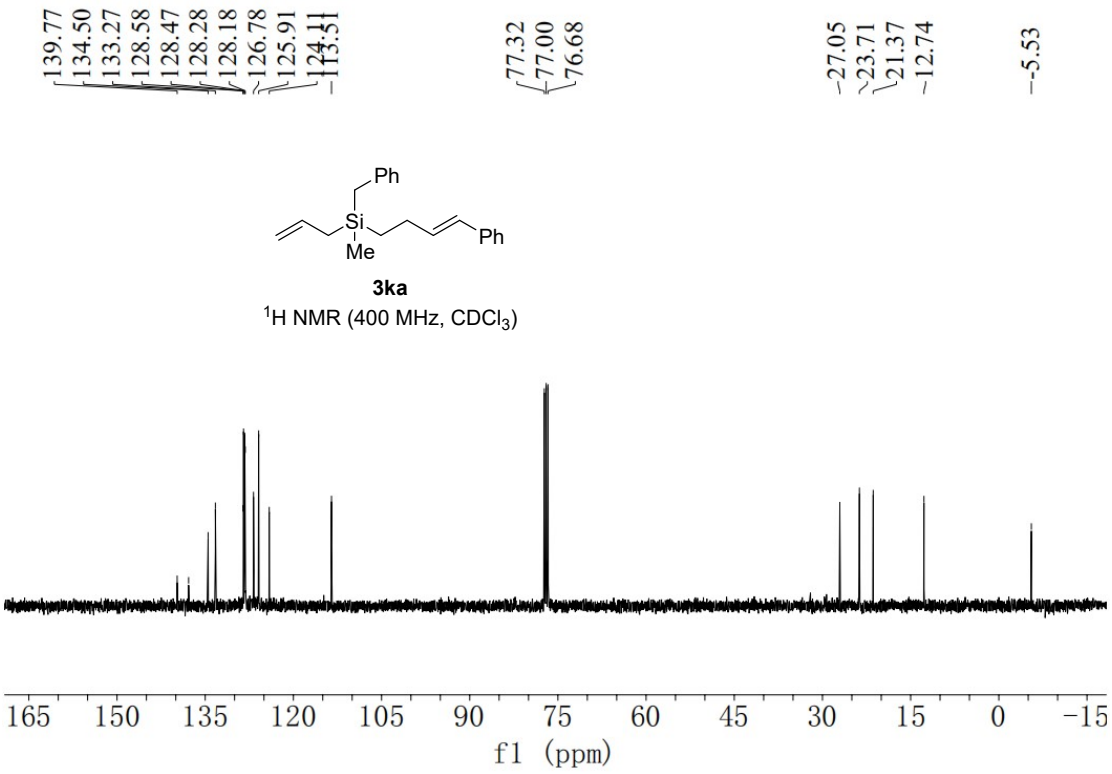






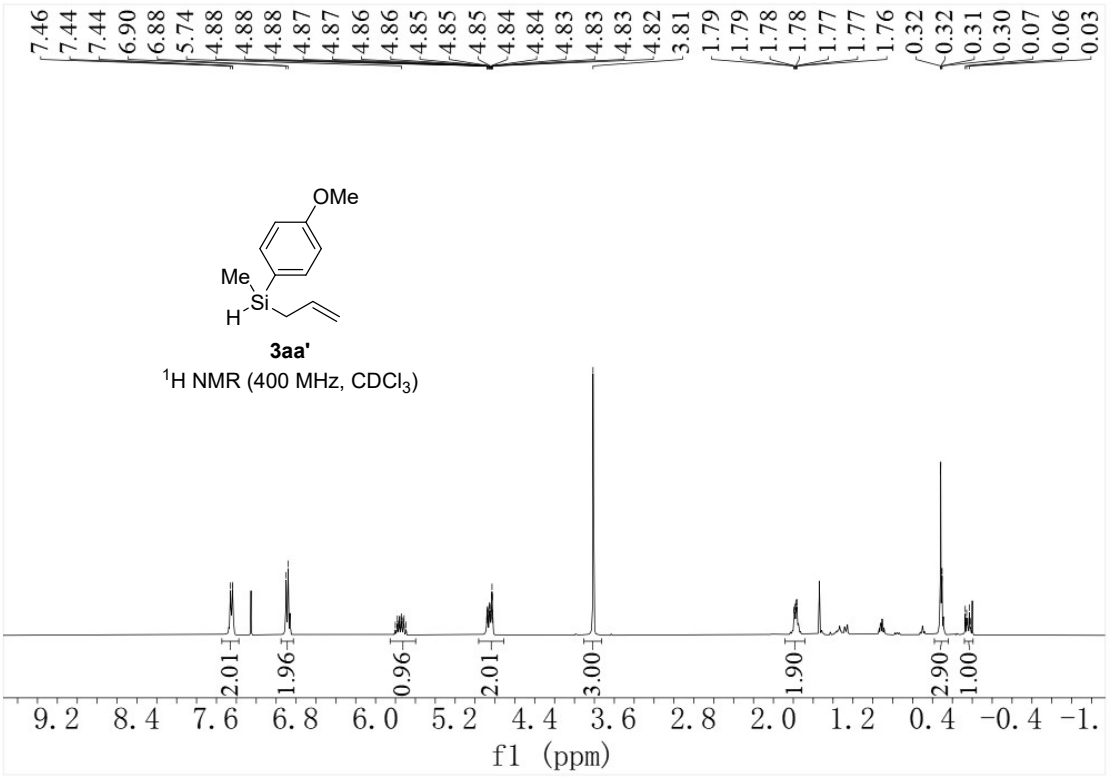
3ka

^{13}C NMR (101 MHz, $CDCl_3$)



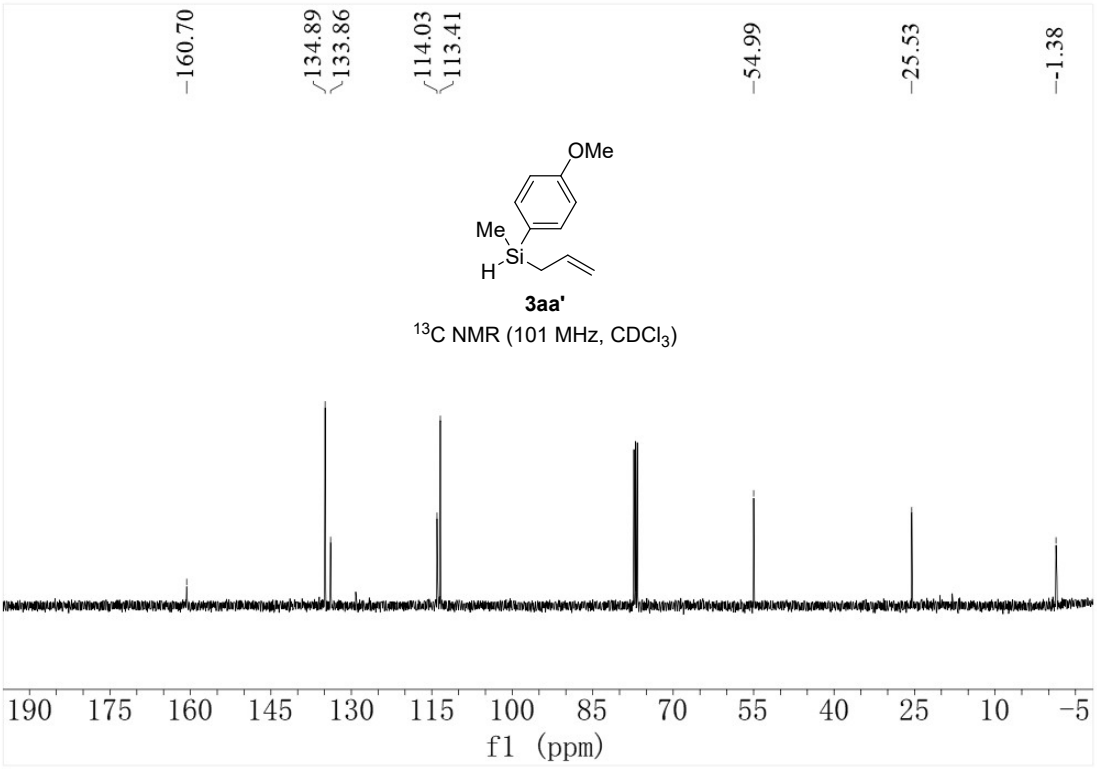
3ka

^{1}H NMR (400 MHz, $CDCl_3$)



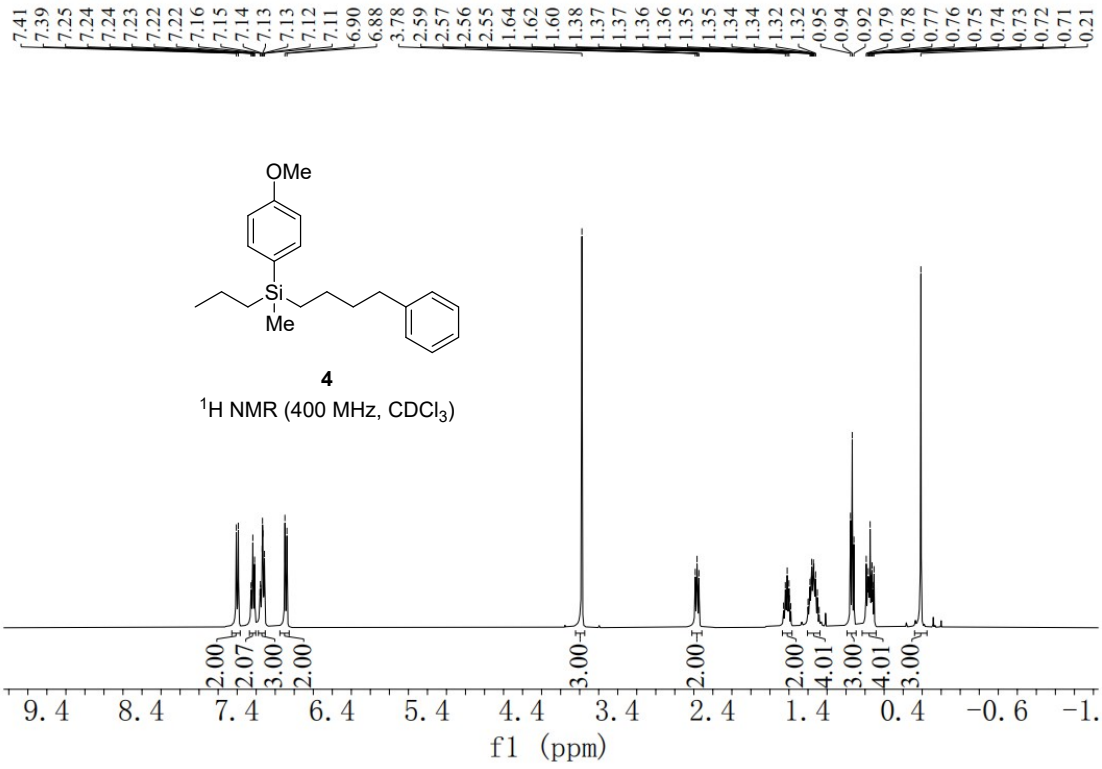
3aa'

^{1}H NMR (400 MHz, $CDCl_3$)



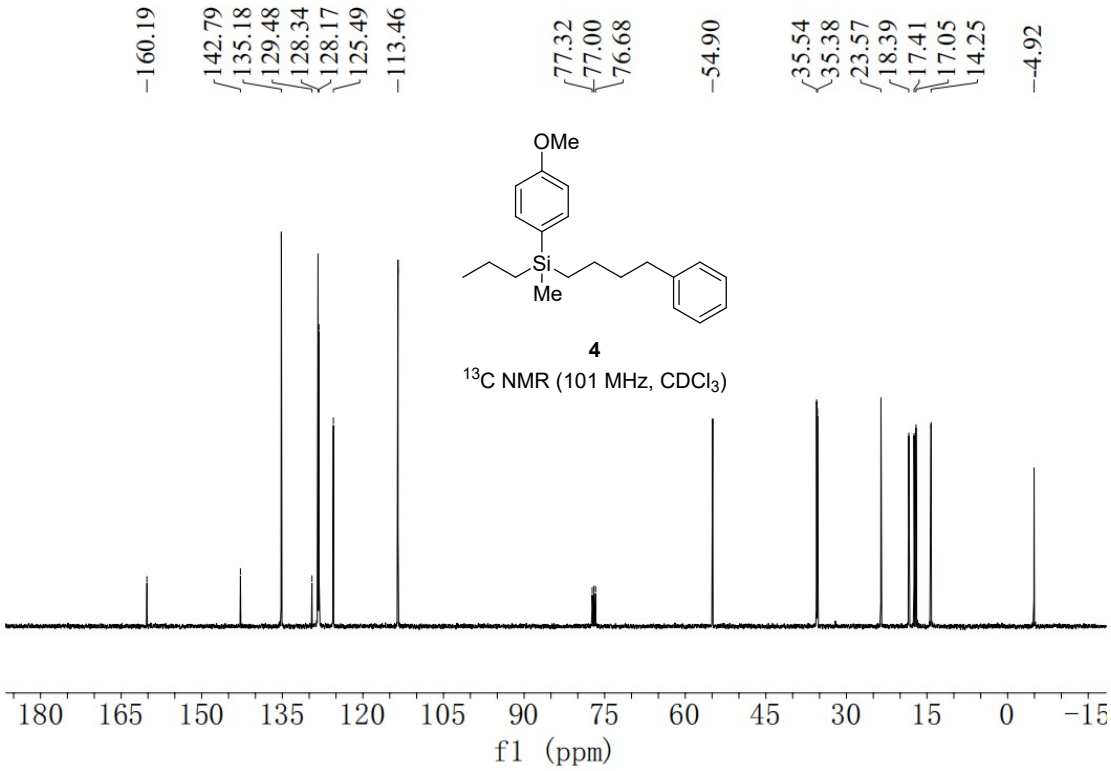
3aa'

^{13}C NMR (101 MHz, $CDCl_3$)



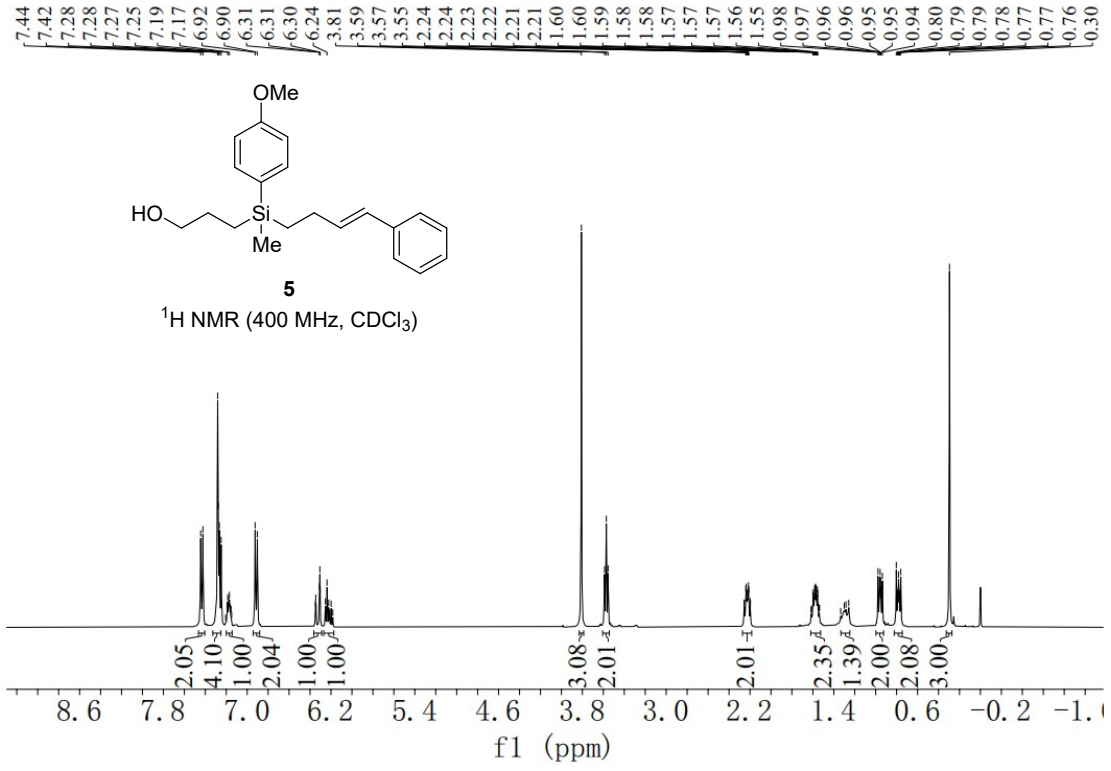
4

^{1}H NMR (400 MHz, $CDCl_3$)



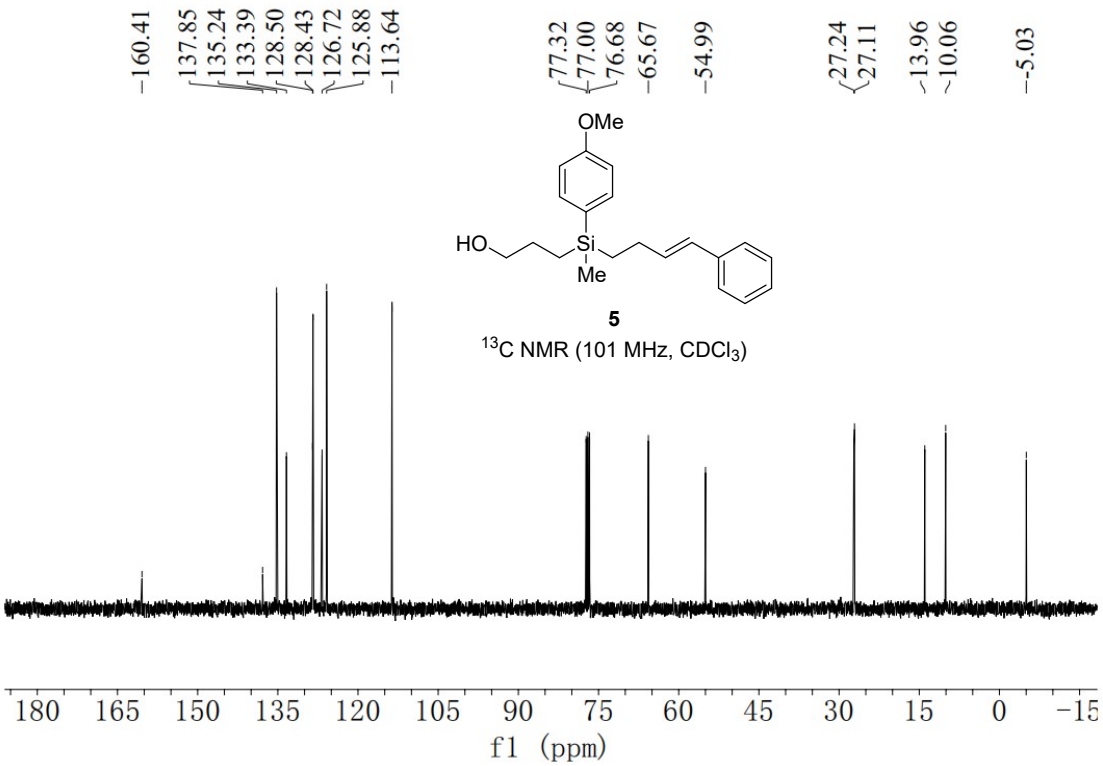
4

^{13}C NMR (101 MHz, $CDCl_3$)



5

^{1}H NMR (400 MHz, $CDCl_3$)



References:

[1] (a) H. Chen, Y. Chen, X. Tang, S. Liu, R. Wang, T. Hu, L. Gao and Z. Song. Rhodium-Catalyzed Reaction of Silacyclobutanes with Unactivated Alkynes to Afford Silacyclohexenes, *Angew. Chem. Int. Ed.* 2019, **58**, 4695-4699; (b) T. He, B. Li, L. Liu, W. Ma and W. He. Rhodium-Catalyzed Intermolecular Silylation of Csp−H by Silacyclobutanes, *Chem. Eur. J.,* 2021, **27,** 5648-5652.

[2] (a) K. P. S. Cheung, D. Kurandina, T. Yata and V. Gevorgyan. Photoinduced Palladium-Catalyzed Carbofunctionalization of Conjugated Dienes Proceeding via Radical-Polar Crossover Scenario: 1,2-Aminoalkylation and Beyond, *J. Am. Chem. Soc.,* 2020, **142**, 9932-9937; (b) N. J. Adamson, E. Hull and S. J. Malcolmson. Enantioselective Intermolecular Addition of Aliphatic Amines to Acyclic Dienes with a Pd-PHOX Catalyst, *J. Am. Chem. Soc.,* 2017, **139**, 7180-7183.