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Visible-Light-Induced Decarboxylation/Defluorosilylation Protocol for Synthesis of gem-Difluoroalkenes

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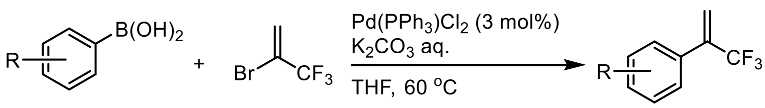
1.General Information

Reagents were purchased from commercial sources and were used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on an Agilent DD2 400 MHz spectrometer and Bruker ARX-500 MHz. ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker ARX-126 MHz. ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker ARX-471 MHz. The chemical shifts in ^{1}H NMR spectra were recorded relative to $CDCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.0). High-resolution mass spectrometry (HRMS) data were conducted at Bruker Dalton MAXIS. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography as performed over silica gel (200-300 mesh). Blue LED (5 W, λmax = 450-465 nm) purchased from GeAo chemical was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature (about 30 °C).

Photograph of the Photocatalytic reactor used for reactions conducted under blue LED irradiation.

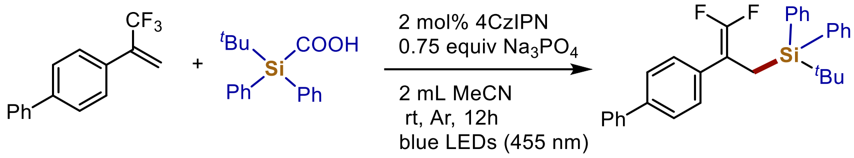
2. General Procedure for Synthesis of Starting Materials



According to literature reports. [1] A Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv, 3 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 0.09 mmol, 63.2 mg). The vessel was evacuated and filled with argon (three times), and then aqueous K_2CO_3 (2.0 M, 6 mL) and THF (9 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (2.0 equiv, 6.0 mmol, 0.63 mL), the solution was stirred at 60 °C with heating mantle for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE/EA). The spectral data is consistent with the literature data.[1]

3. Mechanistic Studies

Radical trapping experiments

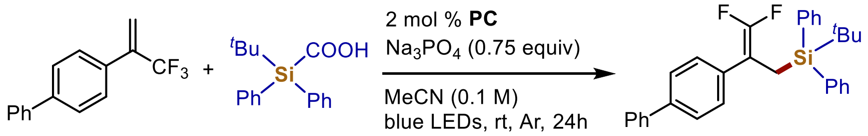


1a 0.2 mmol **2a** 0.24 mmol **3aa**

radical inhibitor	yield of **3aa**
1.0 equiv TEMPO	0%
1.0 equiv BHT	0%

To a 10 mL glass vial was added 4CzIPN (3.2 mg, 0.004 mmol, 2 mol %), α-trifluoromethyl arylalkene **1a** (0.2 mmol, 1.0 equiv), organosilicic acid **2a** (0.24 mmol, 1.2 equiv), Na_3PO_4 (0.15 mmol), radical inhibitor (TEMPO or BHT) (1.0 equiv) and MeCN (2 mL) under Ar at room temperature. The mixture was then stirred rapidly and irradiated with a 40 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with DCM, dried over Na_2SO_4, and concentrated in vacuo. The reaction mixture was detected by GC-MS and crude NMR. The reaction was totally suppressed by the addition of a radical scavenger, which suggests that the involvement of radical intermediates is likely during the reaction.

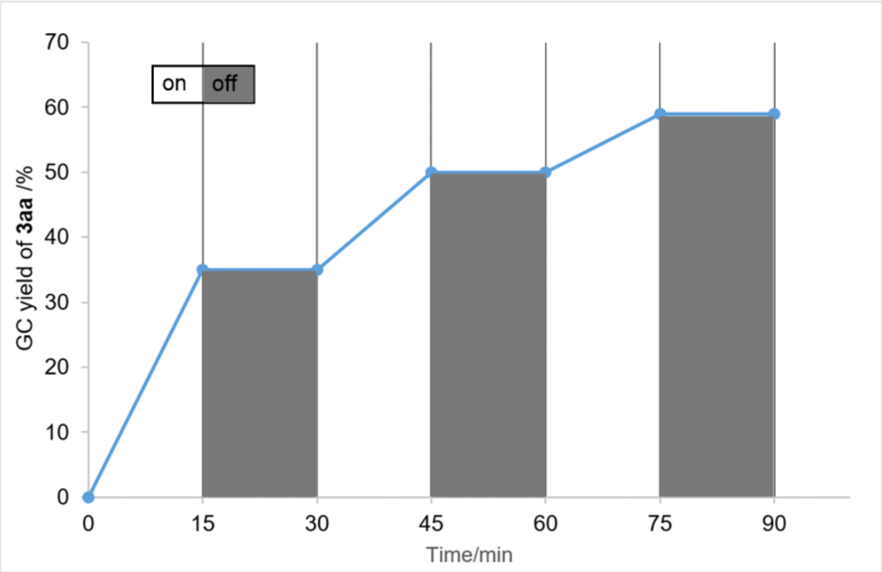
Light/dark experiment



1,1.0 equiv **2**,1.2 equiv **3**

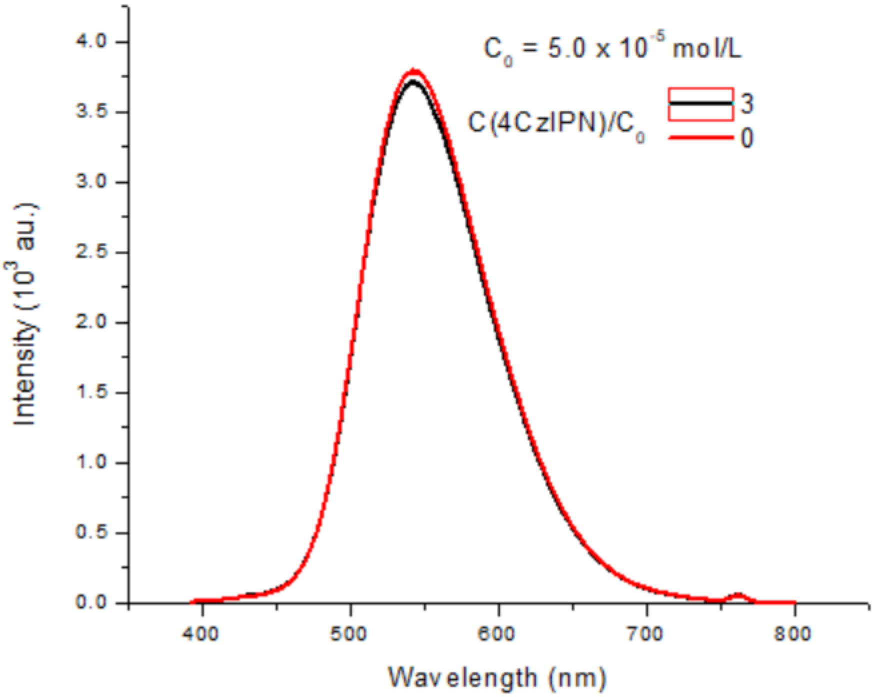
To a 10 mL schlenk tube were charged with 4 CzIPN (3.2 mg, 0.004 mmol, 2 mol %), **1** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), base (0.15 mmol), MeCN (2 mL), rt, Ar atmosphere. The mixtures were then stirred rapidly and irradiated with a 5 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 15 min, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 15 min. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 15 min of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 15 min. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 15 min, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 15 min, then, a vial was removed for analysis and the Blue LED was turned back on to irradiate the remaining two reaction mixtures.

After 15 min, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 15 min, and then it was analyzed. The yield was determined by GC spectroscopy using dodecane as an internal standard.



Emission quenching experiments

The solution of 4CzIPN in CH_3CN was excited at 378 nm. CH_3CN was degassed with a stream of argon for 30 min. First, the emission spectrum of a 5.0×10^{-5} mol/L solution of 4CzIPN in CH_3CN was collected. Then, 3.0 equiv of silacarboxylic acid **2a** was added to the measured solution and the emission spectrum of the sample was collected.



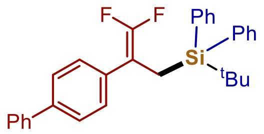
4. Experimental Procedures and Product Characterization

4.1 General procedure for the decarboxylation/defluorosilylation protocol

To a 10 mL glass vial was added 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), α-trifluoromethyl arylalkene **1** (0.2 mmol, 1.0 equiv), organosilicic acid **2** (0.24 mmol, 1.2 equiv), Na_3PO_4 (0.15 mmol), and MeCN (2 mL) under Ar at room temperature. The mixture was then stirred rapidly and irradiated with a 40 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with DCM, dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

4.2 Product characterization

(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)(tert-butyl)diphenylsilane（3aa）



3aa

According to the *general procedure*.

Yellow oil (79.60 mg, 85%)

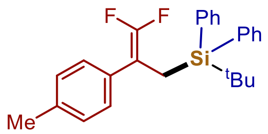
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 7.42 – 7.40 (m, 2H), 7.36 – 7.33 (m, 6H), 7.27 – 7.21 (m, 3H), 7.16 –7.11 (m, 6H), 6.89 – 6.87 (m, 2H), 2.32 (t, *J* = 2.5 Hz, 2H), 0.97 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 151.3 (dd, J_{C-F} = 286.0, 288.5 Hz), 139.8, 138.5, 135.0, 132.7, 132.4, 132.3, 127.9, 127.9, 127.8 (t, J_{C-F} = 2.5 Hz), 126.2, 126.1, 125.91, 125.48, 88.9 (dd, J_{C-F} = 16.4, 22.7 Hz), 26.6, 17.3, 10.6.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.80 (d, *J* = 47.1 Hz), -94.07 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{31}H_{30}F_2Si((M + Na)^+$ 491.1977,found 491.1970.

***tert*-butyl(3,3-difluoro-2-(p-tolyl)allyl)diphenylsilane (3ba)**



3ba

According to the *general procedure*.

Yellow oil (75.0 mg, 92%)

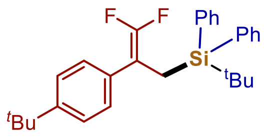
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.43 (dd, *J* = 1.6, 8.0 Hz, 4H), 7.35 – 7.30 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 4H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 2.36 (t, *J* = 2.4 Hz, 2H), 2.24 (s, 3H), 1.04 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.2 (dd, J_{C-F} = 284.8, 287.3 Hz), 136.5, 136.1, 133.9, 128.9, 128.6, 128.4 (t, J_{C-F} = 2.5 Hz), 127.9, 127.2, 89.9 (dd, J_{C-F} = 15.1, 21.4 Hz), 27.7, 21.1, 18.3, 11.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.40 (d, *J* = 47.1 Hz), -94.93 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{26}H_{28}F_2Si$ $(M + Na)^+$ 429.1821, found 429.1854.

***tert*-butyl(2-(4-(tert-butyl)phenyl)-3,3-difluoroallyl)diphenylsilane (3ca)**



3ca

According to the *general procedure*.

Yellow oil (78.1 mg, 81%).

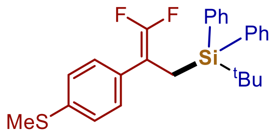
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 – 7.43 (dd, *J*= 1.2, 8.0 Hz, 4H), 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 4H), 7.11 – 7.06 (dd, *J* = 2.0, 6.4 Hz, 2H), 6.90 (dd, *J* = 1.6, 8.8 Hz, 2H), 2.40 (t, *J* = 2.4 Hz, 2H), 1.29 (s, 9H), 1.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 152.2 (dd, $J_{C\text{-}F}$ = 284.8, 287.3 Hz), 149.6, 136.1, 133.9, 131.4 (dd, $J_{C\text{-}F}$ = 2.5, 5.0 Hz), 129.0, 128.2 (t, $J_{C\text{-}F}$ = 2.5 Hz), 127.2, 124.8, 89.9 (dd, $J_{C\text{-}F}$ = 15.1, 21.4 Hz), 34.4, 31.3, 27.7, 18.4, 11.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) = -91.46 (d, *J* = 51.8 Hz), -94.70 (d, *J* = 51.8 Hz).

HRMS m/z (ESI): calcd for $C_{29}H_{34}F_2Si$ $(M + Na)^+$ 471.2290, found 471.2296.

***tert*-butyl(3,3-difluoro-2-(4-(methylthio)phenyl)allyl)diphenylsilane (3da)**



3da

According to the *general procedure*.

Yellow oil (61.7 mg, 70%)

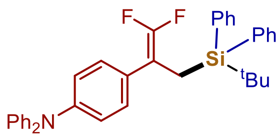
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 (d, *J* = 7.6 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 5H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.36 (t, *J* = 2.4 Hz, 2H), 1.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 152.3 (dd, $J_{C\text{-}F}$ = 286.0, 288.5 Hz), 136.9, 136.0, 133.8, 131.3 (dd, $J_{C\text{-}F}$ = 2.5, 5.0 Hz), 129.0, 128.9 (t, $J_{C\text{-}F}$ = 3.2 Hz), 127.3, 126.2, 89.7 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 27.7, 18.4, 15.9, 11.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) = -90.88 (d, *J* = 47.1 Hz), -94.26 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{26}H_{28}F_2SSi$ $(M + Na)^+$ 461.1541, found 461.1570.

4-(3-(*tert*-butyldiphenylsilyl)-1,1-difluoroprop-1-en-2-yl)-N,N-diphenylaniline(3ea)



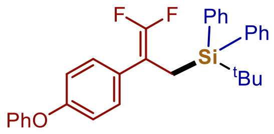
3ea

According to the *general procedure*.

Yellow oil (72.2 mg, 64%)

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.51 (dd, J = 1.6, 6.4 Hz, 4H), 7.43 – 7.33 (m, 2H), 7.32 – 7.27 (t, J = 7.6 Hz, 5H), 7.24 (d, J = 4.8 Hz, 3H), 7.04 – 7.00 (m, 6H), 6.81 (dd, J = 8.8, 16.4 Hz, 4H), 2.38 (t, J = 2.4 Hz, 2H), 1.07 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.3 (dd, J_{C-F} = 284.8, 287.3 Hz), 147.6, 146.4, 136.2, 135.4, 133.9, 129.4 (t, J_{C-F} = 2.5 Hz), 129.2, 129.1, 127.3, 124.2, 123.3, 122.7, 89.7 (dd, J_{C-F} = 16.4, 22.7 Hz), 27.7, 18.4, 11.4.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.13 (d, J = 47.1 Hz), -94.49 (d, J = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{37}H_{35}F_2NSi$ $(M + Na)^+$ 582.2399, found 582.2450.

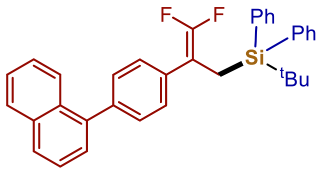
***tert*-butyl(3,3-difluoro-2-(4-phenoxyphenyl)allyl)diphenylsilane (3fa)**



3fa

According to the *general procedure*.
Yellow oil (74.9 mg, 77%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.48 (d, J = 6.8 Hz, 4H), 7.39 – 7.33 (m, 4H), 7.29 (d, J = 7.6 Hz, 3H), 7.25 (s, 1H), 7.12(t, J = 7.6 Hz ,1H), 6.95 (d, J = 8.4 Hz, 2H), 6.89(d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 2.39 (t, J = 2.4 Hz, 2H), 1.07 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 157.2, 155.9, 152.3 (dd, J_{C-F} = 284.8, 287.3 Hz), 136.1, 135.4, 133.8, 130.0 (t, J_{C-F} = 3.2 Hz), 129.7, 129.1, 127.3, 123.2, 118.8, 118.3, 89.6 (dd, J_{C-F} = 16.4, 22.7 Hz), 27.7, 18.4, 11.7.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.27 (d, J = 47.1 Hz), -94.60 (d, J = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{31}H_{30}F_2OSi$ $(M + Na)^+$ 507.1926, found 507.1966.

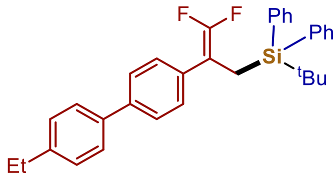
***tert*-butyl(3,3-difluoro-2-(4-(naphthalen-1-yl)phenyl)allyl)diphenylsilane （3ga）**



3ga

According to the *general procedure*.
Yellow oil (72.4 mg, 70%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.94 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.59 – 7.46 (m, 7H), 7.38 (t, J = 6.8 Hz, 3H), 7.35 – 7.26 (t, J = 6.0 Hz, 4H), 7.23 (d, J = 7.2 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.51 (s, 2H), 1.14 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.4 (dd, J_{C-F} = 284.8, 287.3 Hz), 139.9, 139.2, 136.2, 134.8, 133.8, 133.5 (dd, J_{C-F} = 2.5, 5.0 Hz), 131.5, 129.5, 129.1, 128.5 (t, J_{C-F} = 3.2 Hz), 128.3, 127.6, 127.3, 126.8, 126.2, 125.9, 125.8, 125.4, 90.0 (dd, J_{C-F} = 15.1, 21.4 Hz), 27.7, 18.4, 11.6.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.69 (d, J = 47.1 Hz), -94.00 (d, J = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{35}H_{32}F_2Si$ $(M + Na)^+$ 541.2134, found 541.2178.

tert-butyl(2-(4'-ethyl-[1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)diphenylsilane (3ha)



3ha

According to the *general procedure*.

Yellow oil (70.2 mg, 71%)

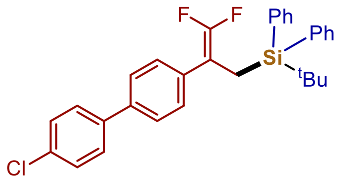
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.51 – 7.43 (m, 6H), 7.39 – 7.26 (m, 5H), 7.29 – 7.20 (m, 5H), 7.00 (dd, *J* = 8.4, 1.2 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.45 (t, *J* = 2.4 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H), 1.10 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.4 (dd, $J_{C\text{-}F}$ = 284.8, 287.3 Hz), 143.4, 139.6, 138.3, 136.1, 133.8, 133.2 (dd, $J_{C\text{-}F}$ = 2.5, 5.0 Hz), 129.0, 128.9 (t, $J_{C\text{-}F}$ = 3.2 Hz), 128.3, 127.3, 126.9, 126.4, 90.0 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 28.6, 27.7, 18.4, 15.6, 11.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.81 (d, *J* = 47.1 Hz), -94.07 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{33}H_{34}F_2Si$ $(M + Na)^+$ 519.2290, found 519.2324.

tert-butyl(2-(4'-chloro-[1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)diphenylsilane (3ia)



3ia

According to the *general procedure*.

Yellow oil (70.5 mg, 70%).

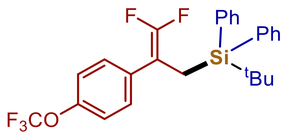
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.49 – 7.40 (m, 8H), 7.36 – 7.30 (m, 2H), 7.28 – 7.17 (m, 6H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 2H), 1.09 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.3 (dd, $J_{C\text{-}F}$ = 286.0, 288.5 Hz), 139.3, 138.3, 136.1, 133.82 (t, $J_{C\text{-}F}$ = 2.5 Hz), 133.77, 133.3, 129.03 (t, $J_{C\text{-}F}$ = 2.5 Hz), 128.97, 128.91, 128.2, 127.3, 126.4, 89.9 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 27.7, 18.4, 11.6.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.57 (d, *J* = 47.1 Hz), -93.83 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{31}H_{29}ClF_2Si$ $(M + Na)^+$ 525.1587, found 525.1603.

tert-butyl(3,3-difluoro-2-(4-(trifluoromethoxy)phenyl)allyl)diphenylsilane (3ja)



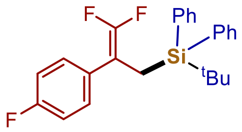
3ja

According to the *general procedure*.

Yellow oil (88.9 mg, 90%)

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.44 – 7.40 (m, 4H), 7.36 – 7.31 (m, 2H), 7.27 – 7.18 (m, 4H), 6.94 – 6.82 (m, 4H), 2.38 (t, J = 2.4 Hz, 2H), 1.07 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.3 (dd, $J_{C\text{-}F}$ = 286.0, 287.3 Hz), 147.8 (d, $J_{C\text{-}F}$ = 1.3 Hz), 136.0, 134.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 133.5, 133.2 (dd, $J_{C\text{-}F}$ = 2.5, 5.0 Hz), 129.9 (t, $J_{C\text{-}F}$ = 3.2 Hz), 129.2, 127.4, 120.3, 89.4 (dd, $J_{C\text{-}F}$ = 15.1, 22.7 Hz), 27.6, 18.4, 11.6.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -57.77, -90.58 (d, J = 47.1 Hz), -93.73 (d, J = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{26}H_{25}F_5OSi$ $(M + Na)^+$ 499.1487, found 499.1470.

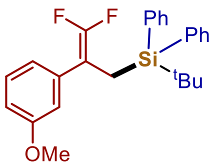
***tert*-butyl(3,3-difluoro-2-(4-fluorophenyl)allyl)diphenylsilane (3ka)**



3ka

According to the *general procedure*.
Yellow oil (47.3 mg, 58%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.40 (d, J = 8.4 Hz, 4H), 7.31 (t, J = 6.8 Hz, 2H), 7.21 (t, J = 8.0 Hz, 5H), 6.86 – 6.77 (t, J = 8.8 Hz, 2H), 6.69 (t, J = 8.8 Hz, 2H), 2.33 (t, J = 2.4 Hz, 2H), 1.03 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 162.5, 160.6, 152.2 (dd, $J_{C\text{-}F}$ = 284.8, 286.0 Hz), 136.0, 133.6, 130.2 (td, $J_{C\text{-}F}$ = 3.2, 8.8 Hz), 129.1, 127.3, 114.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 89.4 (dd, $J_{C\text{-}F}$ = 16.4 ,22.7 Hz), 27.6, 18.3, 11.7.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.29 (d, J = 47.1 Hz), -94.56 (d, J = 47.1 Hz), -115.46.
HRMS m/z (ESI): calcd for $C_{25}H_{25}F_3Si$ $(M + Na)^+$ 433.1570, found 433.1617.

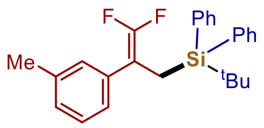
***tert*-butyl(3,3-difluoro-2-(3-methoxyphenyl)allyl)diphenylsilane (3la)**



3la

According to the *general procedure*.
Yellow oil (78.8 mg, 93%)
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (dd, J = 1.5, 8.0 Hz, 4H), 7.40 -7.37 (m, 2H), 7.30 (t, J = 7.5 Hz, 4H), 7.05 (t, J = 8.0 Hz, 1H), 6.69 – 6.63 (m, 2H), 6.46 (s, 1H), 3.66 (s, 3H), 2.43 (t, J = 2.5 Hz, 2H), 1.11 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 159.1, 152.3 (dd, $J_{C\text{-}F}$ = 286.0, 288.5 Hz), 136.1, 134.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 133.8, 129.1, 128.9, 127.3, 121.1 (t, $J_{C\text{-}F}$ = 2.5 Hz), 114.2 (t, $J_{C\text{-}F}$ = 3.2 Hz), 112.9, 90.2 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 55.0, 27.7, 18.4, 11.6.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.86 (d, J = 47.1 Hz), -93.81 (d, J = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{26}H_{28}F_2OSi$ $(M + Na)^+$ 445.1770, found 445.1805.

***tert*-butyl(3,3-difluoro-2-(m-tolyl)allyl)diphenylsilane (3ma)**



3ma

According to the *general procedure*.

Yellow oil (69.0 mg, 85%).

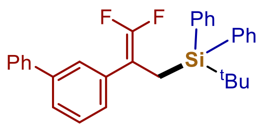
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.46 – 7.43 (m, 4H), 7.36 – 7.31 (m, 2H), 7.27 – 7.22 (m, 4H), 6.98 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.2 Hz, 1H), 6.65 (s, 1H), 2.38 (t, J = 2.4 Hz, 2H), 2.13 (s, 3H), 1.06 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.4 (dd, $J_{C\text{-}F}$ = 286.0, 287.3 Hz), 137.4, 136.2, 134.0, 130.4, 129.5 (t, $J_{C\text{-}F}$ = 3.2 Hz), 129.1, 128.0, 127.8, 127.7, 127.3, 125.7 (t, $J_{C\text{-}F}$ = 3.2 Hz), 90.3 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 27.7, 21.3, 18.4, 11.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.21 (d, J = 47.1 Hz), -94.36 (d, J = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{26}H_{28}F_2Si$ $(M + Na)^+$ 429.1821, found 429.1838.

(2-([1,1'-biphenyl]-3-yl)-3,3-difluoroallyl)(*tert*-butyl)diphenylsilane （3na）



3na

According to the *general procedure*.

Yellow oil (75.8 mg, 81%)

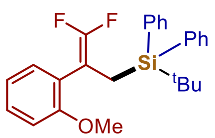
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.51 (dd, J = 1.2, 8.0 Hz, 4H), 7.50 – 7.35 (m, 5H), 7.38 – 7.29 (m, 3H), 7.26 (t, J = 7.6 Hz, 4H), 7.18 (t, J = 8.0 Hz, 2H), 6.98 (d, J = 7.2 Hz, 1H), 2.49 (t, J = 2.4 Hz, 2H), 1.12 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.4 (dd, $J_{C\text{-}F}$ = 286.0, 287.3 Hz), 141.0 (d, $J_{C\text{-}F}$ = 18.9 Hz), 136.1, 135.0 (t, $J_{C\text{-}F}$ = 4.4 Hz), 133.7, 129.1, 128.6, 128.4, 127.6 (t, $J_{C\text{-}F}$ = 3.2 Hz), 127.5 (t, $J_{C\text{-}F}$ = 3.2 Hz), 127.3, 127.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 125.8, 90.2 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 27.7, 18.4, 11.7.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.89 (d, J = 47.1 Hz), -93.98 (d, J = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{31}H_{30}F_2Si$ $(M + Na)^+$ 491.1977, found 491.2008.

***tert*-butyl(3,3-difluoro-2-(2-methoxyphenyl)allyl)diphenylsilane (3oa)**



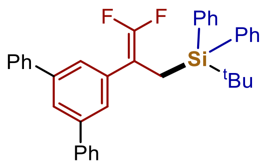
3oa

According to the *general procedure*.

Yellow oil (71.8 mg, 85%)

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.44 (d, *J* = 7.2 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 4H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.59 (dd, *J* = 17.6, 8.0 Hz, 2H), 6.39 (s, 1H), 3.60 (s, 3H), 2.36 (t, *J* = 2.4 Hz, 2H), 1.04 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 159.0, 152.3 (dd, J_{C-F} = 284.8, 287.3 Hz), 136.1, 135.9 (dd, J_{C-F} = 2.5, 5.0 Hz), 133.8, 129.0, 128.8, 127.3, 121.1 (t, J_{C-F} = 3.2 Hz), 114.1 (t, J_{C-F} = 3.2 Hz), 112.9, 90.1 (dd, J_{C-F} = 16.4, 22.7 Hz), 55.0, 27.6, 18.3, 11.6.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.90 (d, *J* = 47.1 Hz), -93.86 (d, *J* = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{26}H_{28}F_2OSi$ $(M + Na)^+$ 445.1770, found 445.1788.

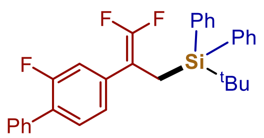
(2-([1,1':3',1''-terphenyl]-5'-yl)-3,3-difluoroallyl)(*tert*-butyl)diphenylsilane（3pa）



3pa

According to the *general procedure*.
Yellow oil (77.9 mg, 72%).
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.54 – 7.51 (m, 5H), 7.46 (d, *J* = 4.4 Hz, 8H), 7.42 – 7.37 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 4H), 7.15 (t, *J* = 1.2 Hz, 2H), 2.53 (t, *J* = 2.4 Hz, 2H), 1.14 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.5 (dd, J_{C-F} = 284.8, 287.3 Hz), 141.5, 141.0, 136.1, 135.5 (dd, J_{C-F} = 3.8, 5.0 Hz), 133.7, 129.2, 128.7, 127.3 (t, J_{C-F} = 5.0 Hz), 126.6 (t, J_{C-F} = 2.5 Hz), 125.0, 90.3 (dd, J_{C-F} = 16.4, 22.7 Hz), 27.7, 18.5, 11.7.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.90 (d, *J* = 47.1 Hz), -93.44 (d, *J* = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{37}H_{34}F_2Si$ $(M + Na)^+$ 567.2290, found 567.2296.

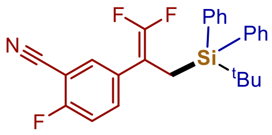
***tert*-butyl(3,3-difluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)allyl)diphenylsilane (3qa)**



3qa

According to the *general procedure*.
Yellow oil (82.5 mg, 85%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.53 – 7.44 (m, 9H), 7.41 – 7.34 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 3H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 12.0 Hz, 1H), 2.44 (t, *J* = 2.4 Hz, 2H), 1.13 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 160.0, 158.0, 152.5 (dd, J_{C-F} = 286.0, 288.5 Hz), 136.1, 135.9, 135.6, 133.6, 130.0 (d, J_{C-F} =3.8Hz), 129.2, 128.9 (d, J_{C-F} = 3.8Hz), 128.5, 127.7, 127.4, 124.5 (dd, J_{C-F} = 3.8, 6.3 Hz), 116.3 (td, J_{C-F} = 3.2, 23.9 Hz), 89.5 (dd, J_{C-F} = 15.1, 22.7 Hz), 27.7, 18.4, 11.4.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -89.88 (d, *J* = 47.1 Hz), -92.68 (d, *J* = 47.1 Hz), -118.68.
HRMS m/z (ESI): calcd for $C_{31}H_{29}F_3Si$ $(M + Na)^+$ 509.1883, found 509.1932.

5-(3-(*tert*-butyldiphenylsilyl)-1,1-difluoroprop-1-en-2-yl)-2-fluorobenzonitrile (3ra)



3ra

According to the *general procedure*.

Yellow oil (80.4 mg, 92%).

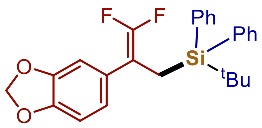
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.45 – 7.36 (m, 6H), 7.27 (t, *J* = 7.2 Hz, 4H), 7.10 – 7.05 (m, 1H), 6.95 – 6.91 (m, 1H), 6.81 (t, *J* = 8.8 Hz, 1H), 2.36 (t, *J* = 2.4 Hz, 2H), 1.07 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 161.5(d, $J_{C\text{-}F}$ = 259.6 Hz), 152.5 (dd, $J_{C\text{-}F}$ = 287.3, 288.5 Hz), 135.9, 135.0 (dt, $J_{C\text{-}F}$ = 8.8, 2.5 Hz), 133.6 (t, $J_{C\text{-}F}$ = 3.2 Hz), 133.2, 129.5, 127.6, 115.8 (d, $J_{C\text{-}F}$ = 20.2 Hz), 113.5, 101.0 (d, $J_{C\text{-}F}$ = 16.4 Hz), 88.6 (dd, $J_{C\text{-}F}$ = 15.1, 23.9 Hz), 27.6, 18.4, 11.3.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -89.62 (d, *J* = 42.4 Hz), -92.54 (d, *J* = 47.1 Hz), -108.99.

HRMS m/z (ESI): calcd for $C_{26}H_{24}F_3NSi$ $(M + Na)^+$ 458.1522, found 458.1534.

(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)(*tert*-butyl)diphenylsilane (3sa)



3sa

According to the *general procedure*.

Yellow oil (62.5 mg, 72%)

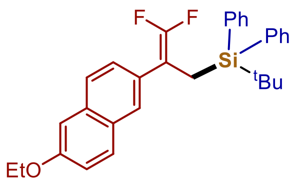
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.44 – 7.41 (m, 4H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 4H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.39 – 6.35 (m, 1H), 6.29 (t, *J* = 1.2 Hz, 1H), 5.83 (s, 2H), 2.30 (t, *J* = 2.4 Hz, 2H), 1.03 (s, 9H).

^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.3 (dd, $J_{C\text{-}F}$ = 284.8, 287.3 Hz), 147.0, 146.4, 136.0, 133.9, 129.0, 127.3, 122.2 (t, $J_{C\text{-}F}$ = 2.5 Hz), 109.2 (t, $J_{C\text{-}F}$ = 3.2 Hz), 107.7, 100.8, 89.9 (dd, $J_{C\text{-}F}$ = 16.4, 22.7 Hz), 27.7, 18.4, 12.0.

^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -91.82 (d, *J* = 47.1 Hz), -94.53 (d, *J* = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{26}H_{26}F_2O_2Si$ $(M + Na)^+$ 459.1562, found 459.1606.

***tert*-butyl(2-(6-ethoxynaphthalen-2-yl)-3,3-difluoroallyl)diphenylsilane (3ta)**



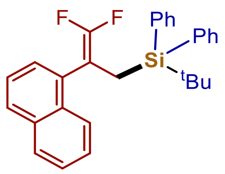
3ta

According to the *general procedure*.

Yellow oil (74.4 mg, 76%).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.45 – 7.41 (m, 6H), 7.23 – 7.27 (m, 2H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 4H), 7.08 – 7.00 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 2.4 Hz, 2H), 1.49 (t, *J* = 6.8 Hz, 3H), 1.06 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 157.0, 152.5 (dd, $J_{C\text{-}F}$ = 286.0, 288.5 Hz), 136.1, 133.9, 133.5, 129.4, 129.0, 128.4, 128.0, 127.7 (t, $J_{C\text{-}F}$ = 3.2 Hz), 127.2, 126.8 (t, $J_{C\text{-}F}$ = 3.2 Hz), 126.3, 118.9, 106.2, 90.3 (dd, $J_{C\text{-}F}$ = 15.1, 21.4 Hz), 63.5, 27.7, 18.4, 14.9, 11.7.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.84 (d, *J* = 47.1 Hz), -94.45 (d, *J* = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{31}H_{32}F_2OSi$ $(M + Na)^+$ 509.2083, found 509.2099.

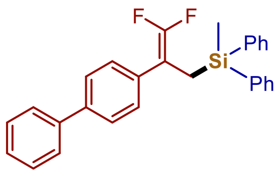
***tert*-butyl(3,3-difluoro-2-(naphthalen-1-yl)allyl)diphenylsilane (3ua)**



3ua

According to the *general procedure*.
Yellow oil (68.8 mg, 78%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.74 (dd, *J* = 7.6, 12.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.21 (m, 10H), 7.13 – 7.02 (m, 3H), 6.74 (d, *J* = 7.2 Hz, 1H), 2.63 (d, *J* = 14.4 Hz, 1H), 2.50 (d, *J* = 14.8 Hz, 1H), 1.00 (s, 9H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.4 (dd, $J_{C\text{-}F}$ = 283.5, 287.3 Hz), 135.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 133.7, 133.5, 133.3, 131.9 (dd, $J_{C\text{-}F}$ = 1.3, 5.0 Hz), 131.4 (dd, $J_{C\text{-}F}$ = 1.3, 5.0 Hz), 129.0 (d, $J_{C\text{-}F}$ = 31.5 Hz), 128.4, 128.1, 127.7 (dd, $J_{C\text{-}F}$ = 1.3, 3.8 Hz), 127.2 (d, $J_{C\text{-}F}$ = 29.0 Hz), 126.0, 125.5, 125.0 (d, $J_{C\text{-}F}$ = 13.9 Hz), 88.1 (dd, $J_{C\text{-}F}$ = 20.2, 22.7 Hz), 27.6, 18.4, 12.5.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.80 (d, *J* = 47.1 Hz), -92.25 (d, *J* = 47.1 Hz)
HRMS m/z (ESI): calcd for $C_{29}H_{28}F_2Si$ $(M + Na)^+$ 465.1821,found 465.1845.

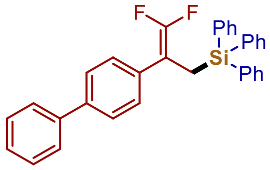
(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)(methyl)diphenylsilane (3ab)



3ab

According to the *general procedure*.
Yellow oil (73.7 mg, 85%)
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (q, *J* = 7.6 Hz, 8H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.33 (d, *J* = 7.6 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.36 (t, *J* = 2.4 Hz, 2H), 0.45 (s, 3H).
^{13}C NMR (126 MHz, CDCl$_3$) δ (ppm) = 152.8 (dd, $J_{C\text{-}F}$ = 286.0, 289.8 Hz), 140.7, 139.8, 136.1, 134.4, 134.1, 133.7 (t, $J_{C\text{-}F}$ = 3.8 Hz), 129.4, 128.8 (d, $J_{C\text{-}F}$ = 5.0 Hz), 127.8, 127.4, 127.0, 126.8, 89.5 (dd, $J_{C\text{-}F}$ = 15.1, 22.7 Hz), 15.3, -4.2.
^{19}F NMR (471 MHz, CDCl$_3$) δ (ppm) = -90.74 (d, *J* = 47.1 Hz), -93.45 (d, *J* = 47.1 Hz).
HRMS m/z (ESI): calcd for $C_{28}H_{24}F_2Si$ $(M + Na)^+$ 449.1508, found 449.1549.

(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)triphenylsilane (3ac)



3ac

According to the *general procedure*.

Yellow oil (57.2 mg, 59%)

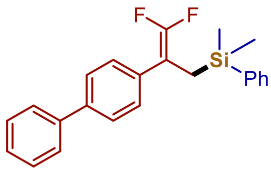
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.51 (d, J = 7.2 Hz, 2H), 7.46 – 7.29 (m, 13H), 7.32 – 7.22 (m, 7H), 7.06 (d, J = 8.4 Hz, 2H), 2.63 (t, J = 2.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 152.7 (dd, J_{C-F} = 286.0, 288.5 Hz), 140.8, 139.8, 135.7, 134.0, 133.5 (t, J_{C-F} = 3.8 Hz), 129.5, 128.9 (t, J_{C-F} = 3.2 Hz), 128.8, 127.8, 127.3, 127.0, 126.8, 89.4 (dd, J_{C-F} = 16.4, 22.7 Hz), 14.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) = -90.02 (d, J = 47.1 Hz), -93.39 (d, J = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{33}H_{26}F_2Si$ $(M + Na)^+$ 511.1664, found 511.1684.

(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)dimethyl(phenyl)silane (3ad)



3ad

According to the *general procedure*.

Yellow oil (36.8 mg, 50%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 4H), 7.41 – 7.27 (m, 6H), 2.03 (t, J = 2.4 Hz, 2H), 0.22 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 152.9 (dd, J_{C-F} = 286.0, 289.8 Hz), 140.7, 139.9, 138.2, 133.9 (t, J_{C-F} = 4.4 Hz), 133.5, 129.1, 128.8, 128.7 (t, J_{C-F} = 3.2 Hz), 127.8, 127.4, 127.0, 126.9, 89.8 (dd, J_{C-F} = 15.1, 23.9 Hz), 16.5, -2.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) = -91.06 (d, J = 47.1 Hz), -93.67 (d, J = 47.1 Hz).

HRMS m/z (ESI): calcd for $C_{23}H_{22}F_2Si$ $(M + Na)^+$ 387.1351, found 387.1380.

References

[1] P. Xia, Z. Ye, Y. Hu, D. Song, Xiang H, H. Yang. *Org. Lett.* 2019, **21**, 2658.

5.Spectra of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

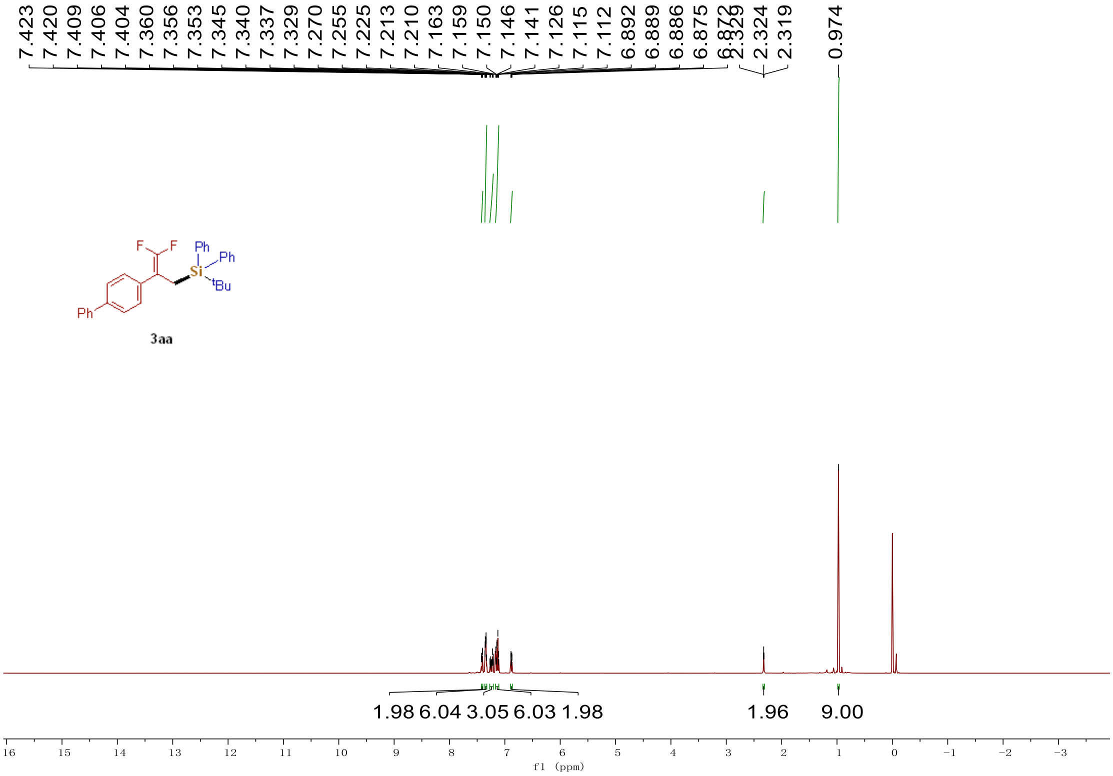


Figure S1. ^{1}H NMR spectra (500 MHz) of **3aa** in $CDCl_3$.

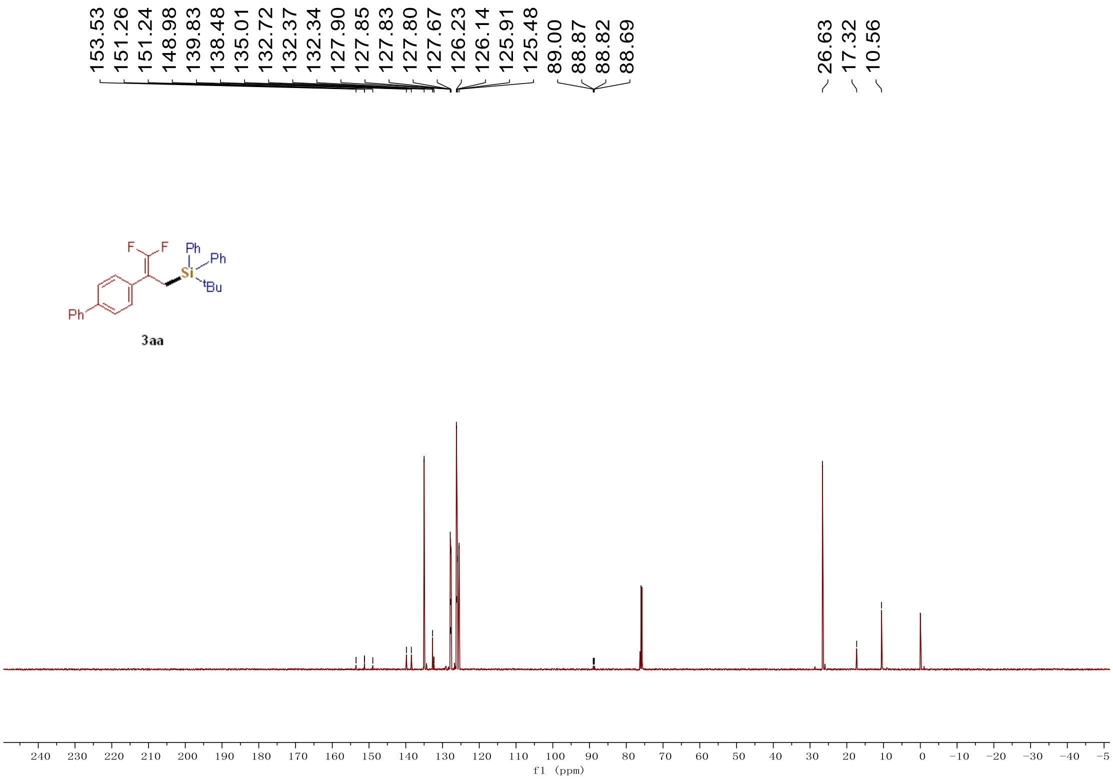


Figure S2. ^{13}C NMR spectra (126 MHz) of **3aa** in $CDCl_3$.

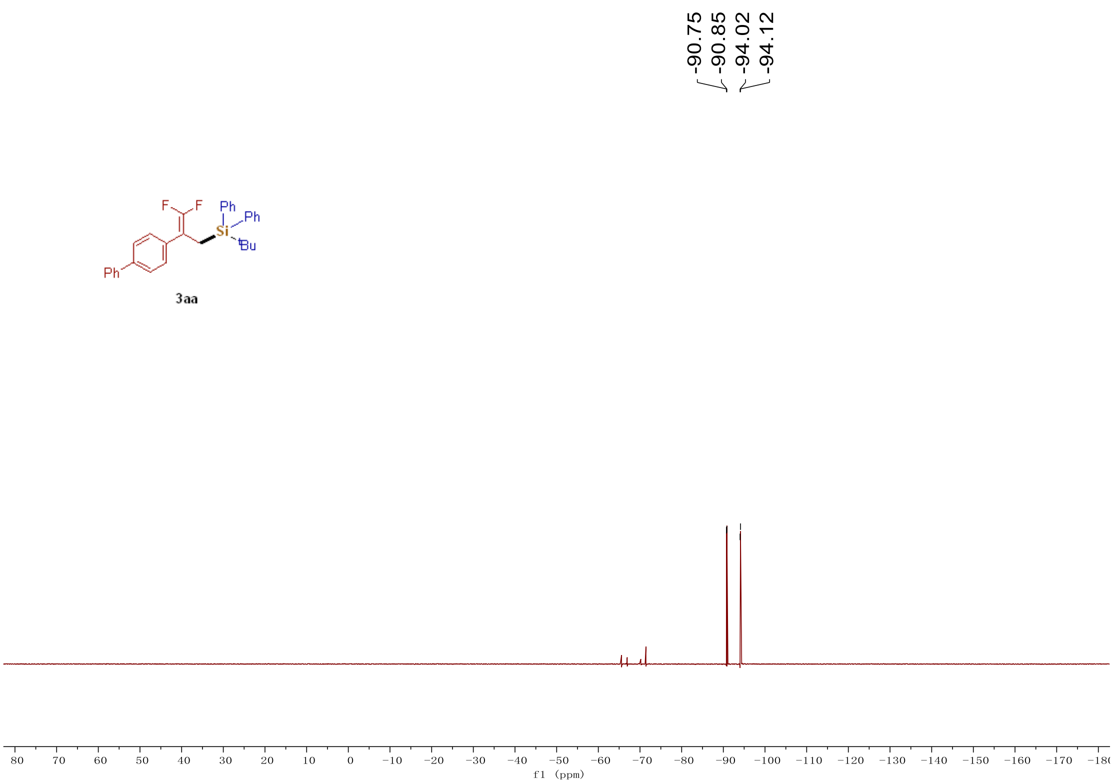


Figure S3. ^{19}F NMR spectra (471 MHz) of **3aa** in $CDCl_3$.

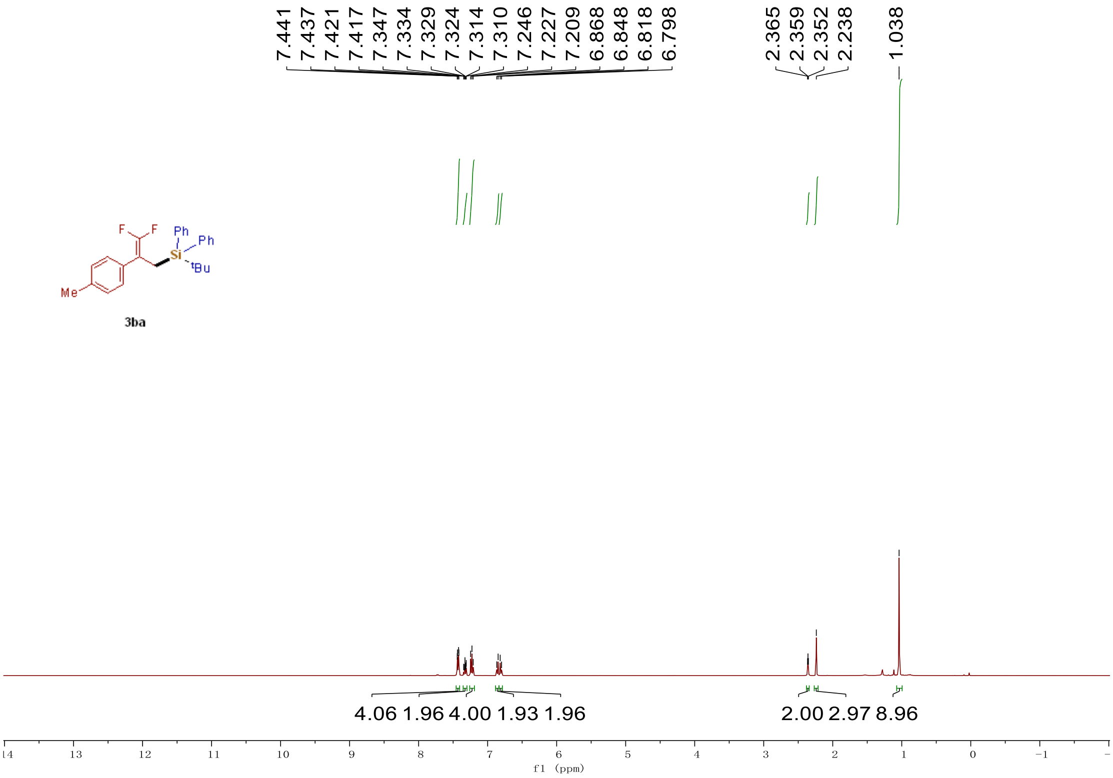


Figure S4. ^{1}H NMR spectra (400 MHz) of **3ba** in $CDCl_3$.

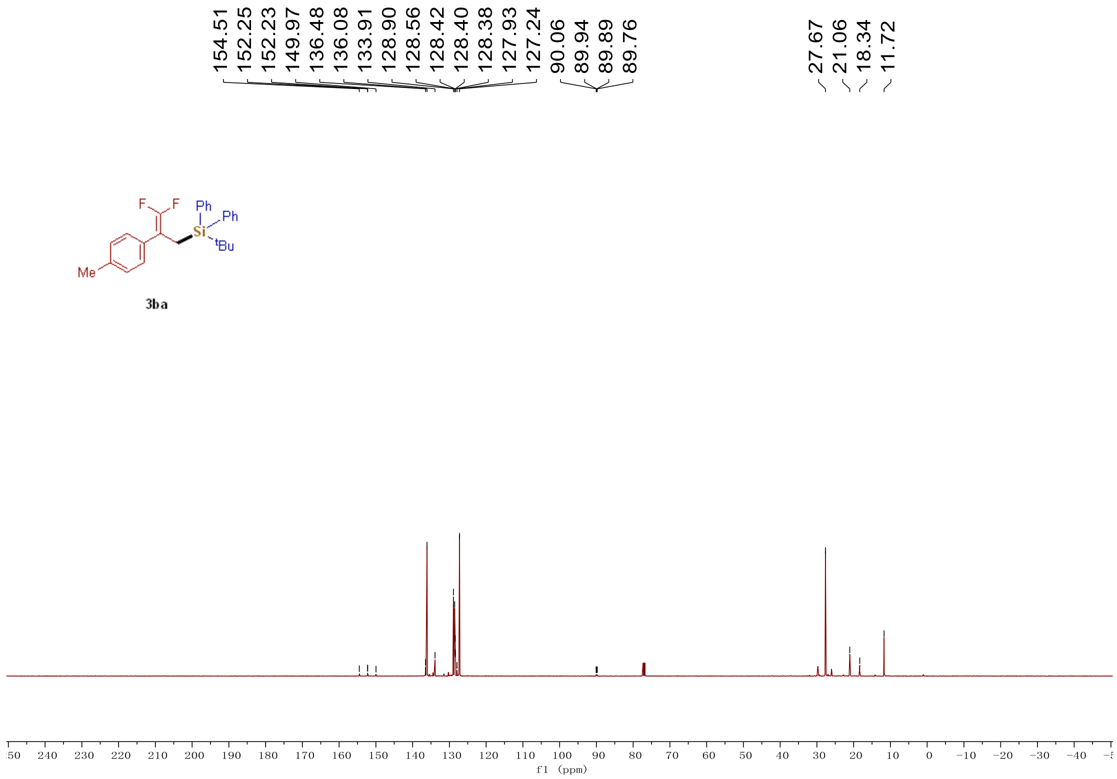


Figure S5. ^{13}C NMR spectra (126 MHz) of **3ba** in $CDCl_3$.

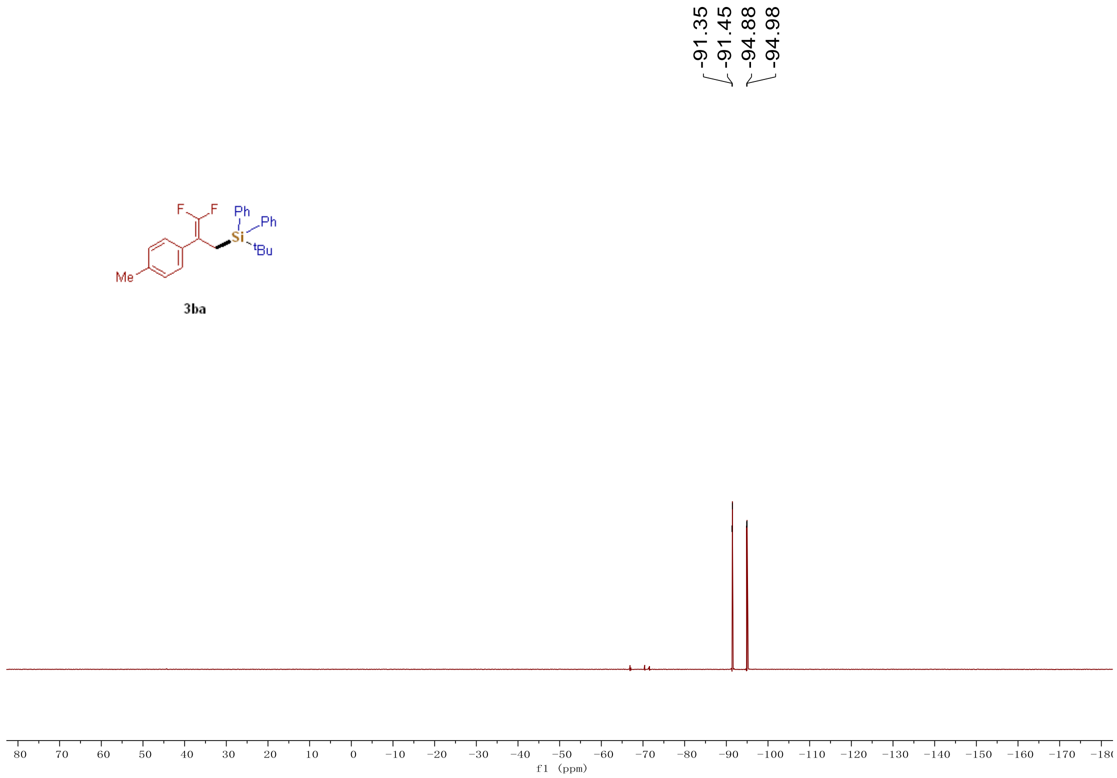


Figure S6. ^{19}F NMR spectra (471 MHz) of **3ba** in $CDCl_3$.

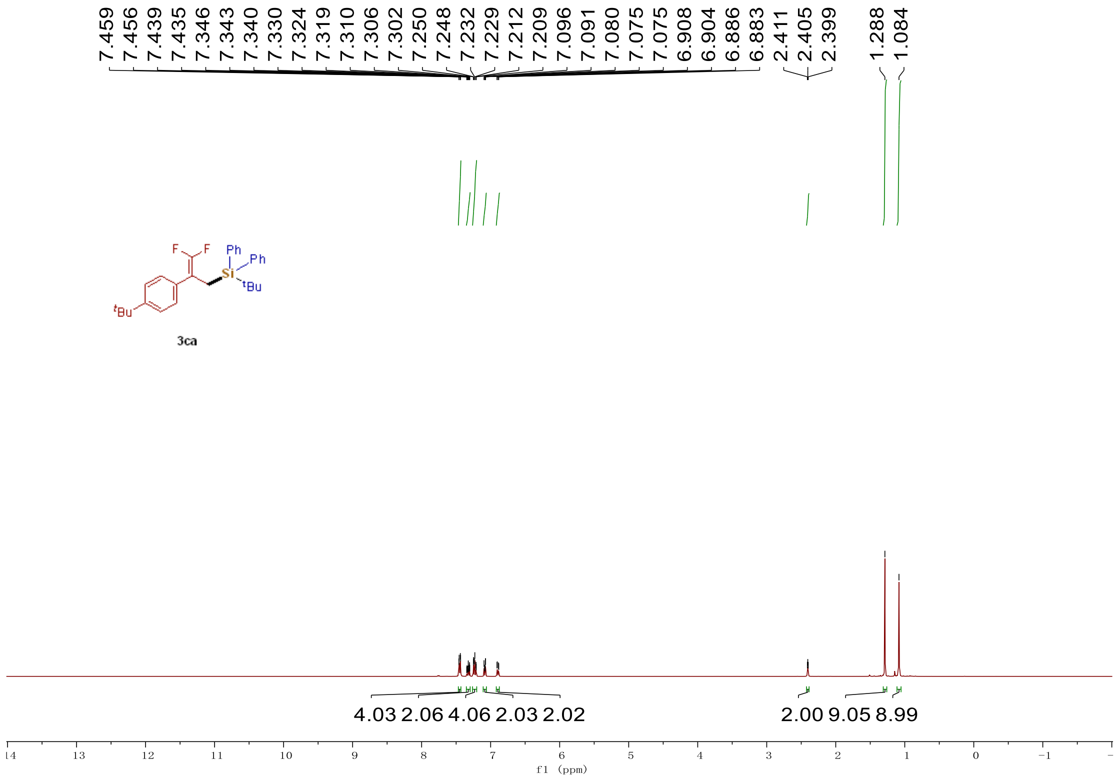


Figure S7. ^{1}H NMR spectra (400 MHz) of **3ca** in $CDCl_3$.

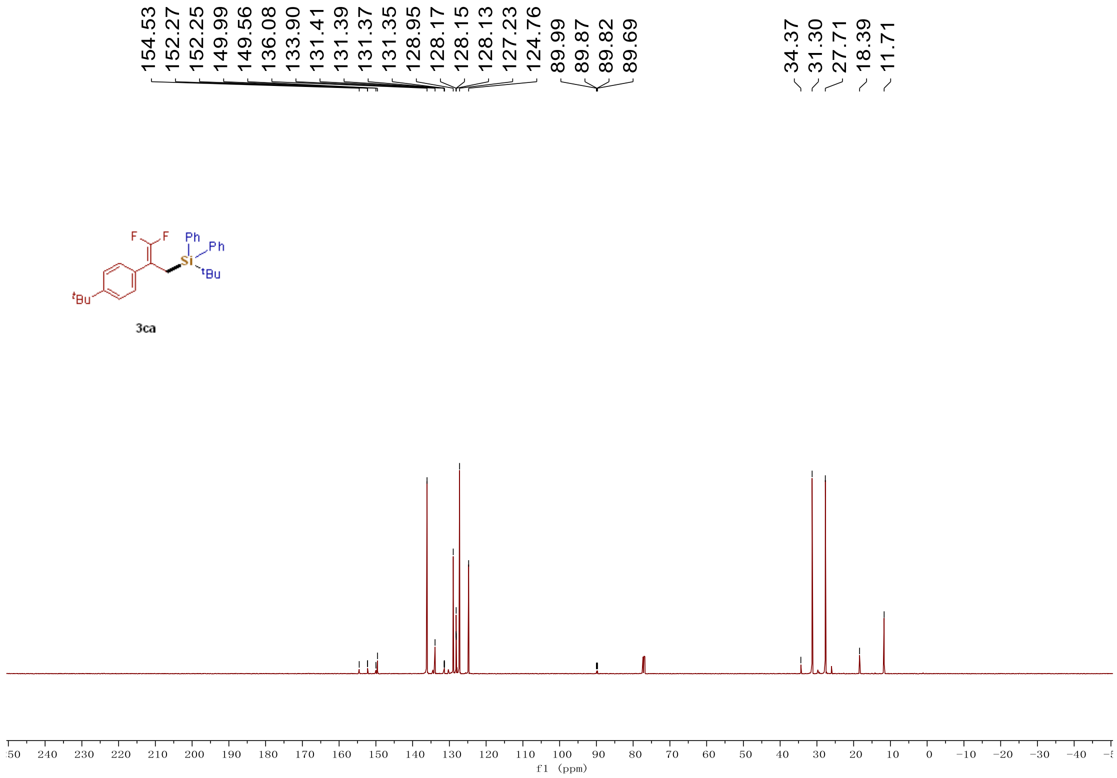


Figure S8. ^{13}C NMR spectra (126 MHz) of **3ca** in $CDCl_3$.

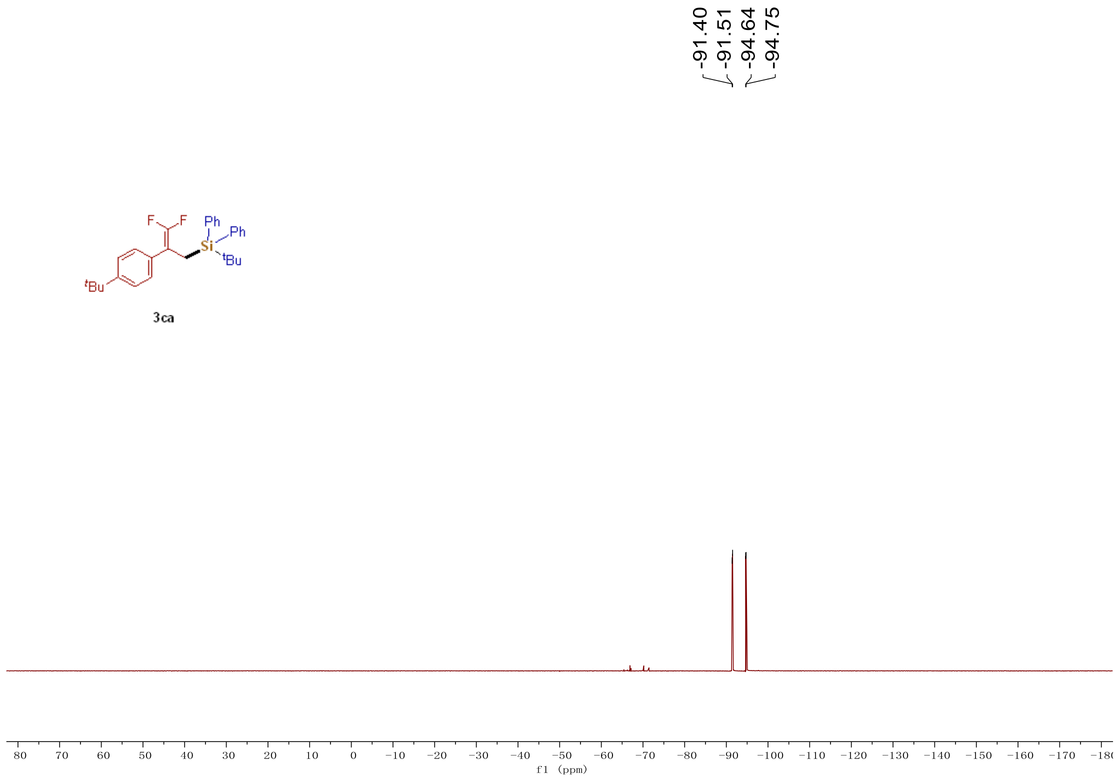


Figure S9. ^{19}F NMR spectra (471 MHz) of **3ca** in $CDCl_3$.

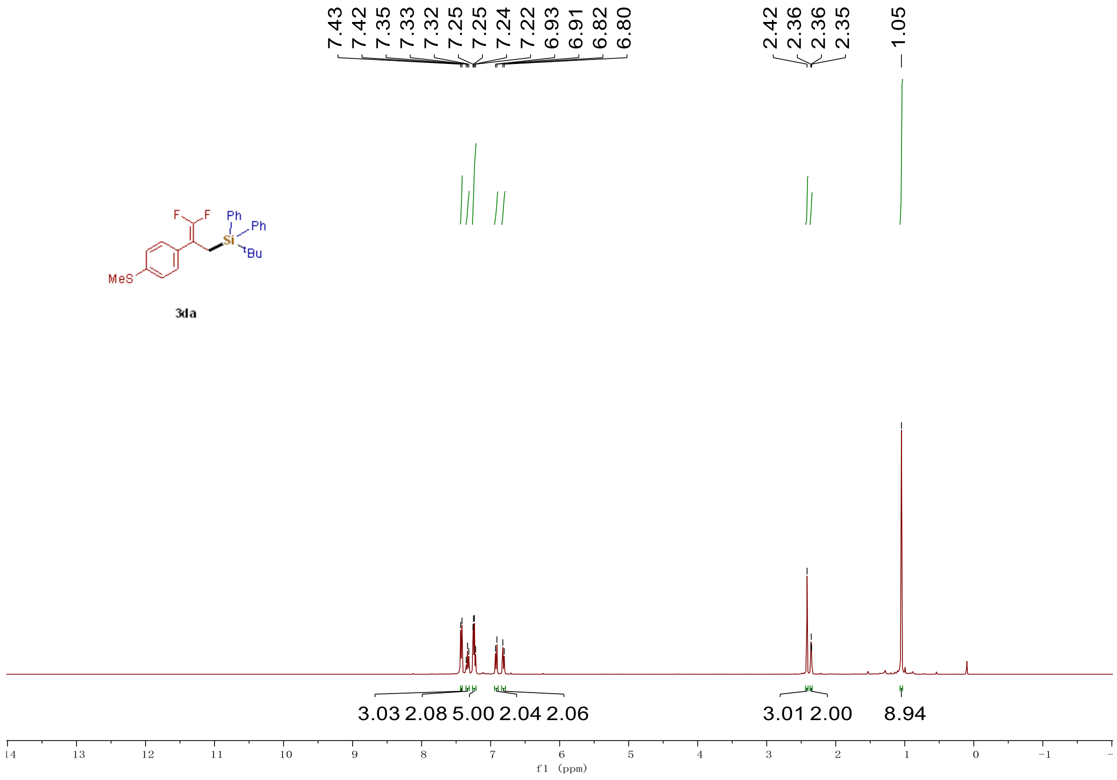


Figure S10. ^{1}H NMR spectra (400 MHz) of **3da** in $CDCl_3$.

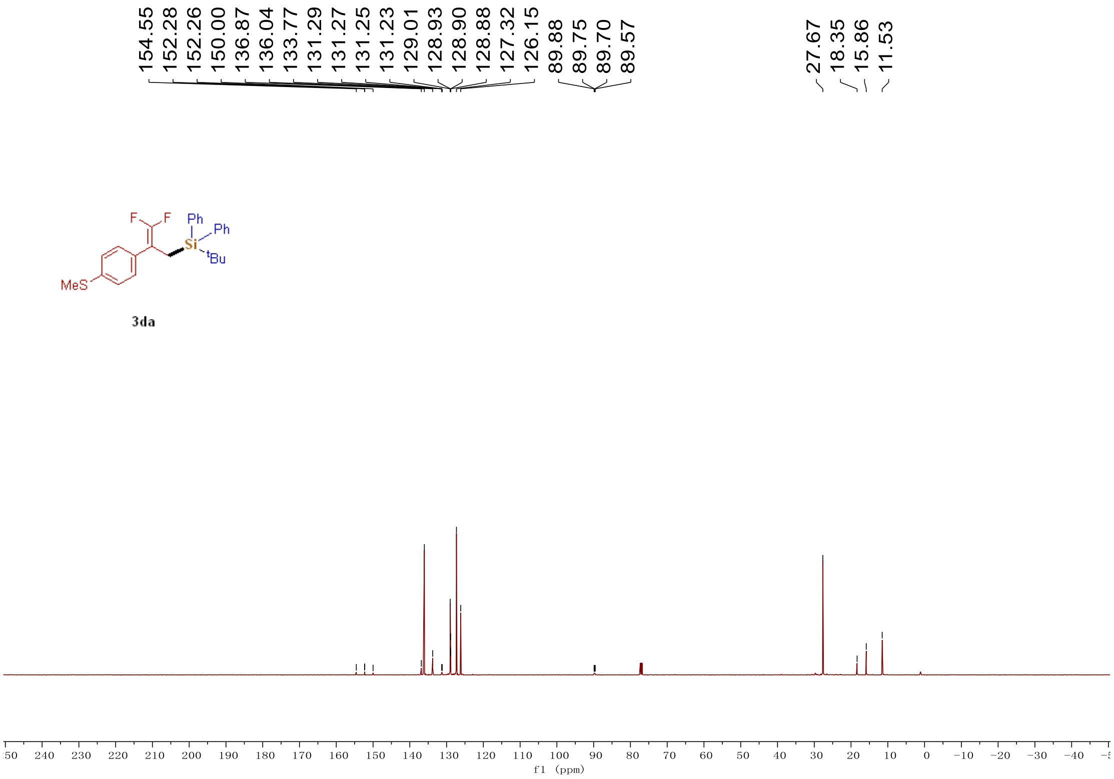


Figure S11. ^{13}C NMR spectra (126 MHz) of **3da** in $CDCl_3$.

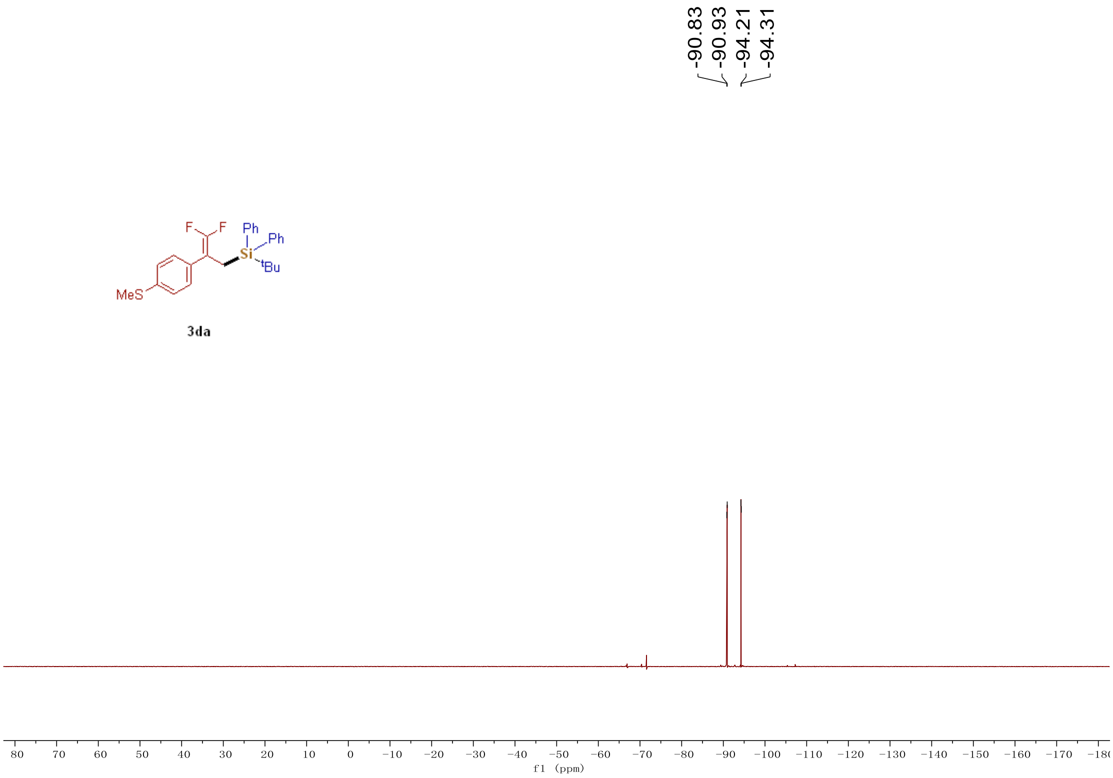


Figure S12. ^{19}F NMR spectra (471 MHz) of **3da** in $CDCl_3$.

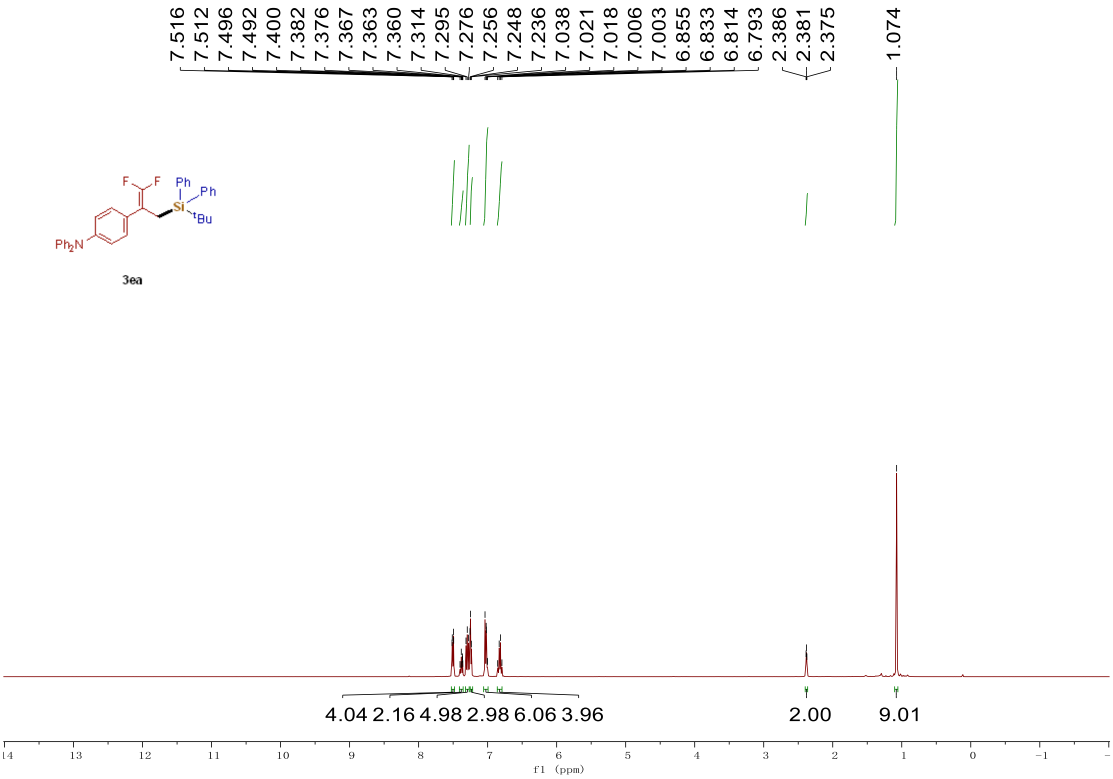


Figure S13. ^{1}H NMR spectra (400 MHz) of **3ea** in $CDCl_3$.

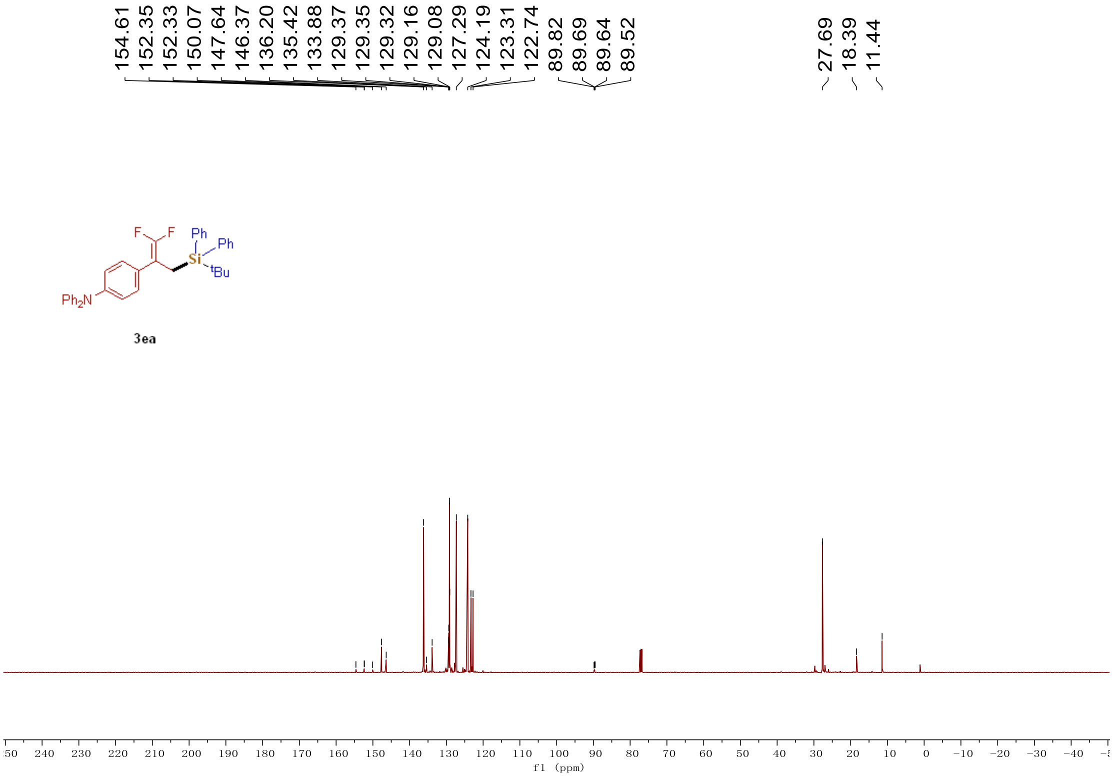


Figure S14. ^{13}C NMR spectra (126 MHz) of **3ea** in $CDCl_3$.

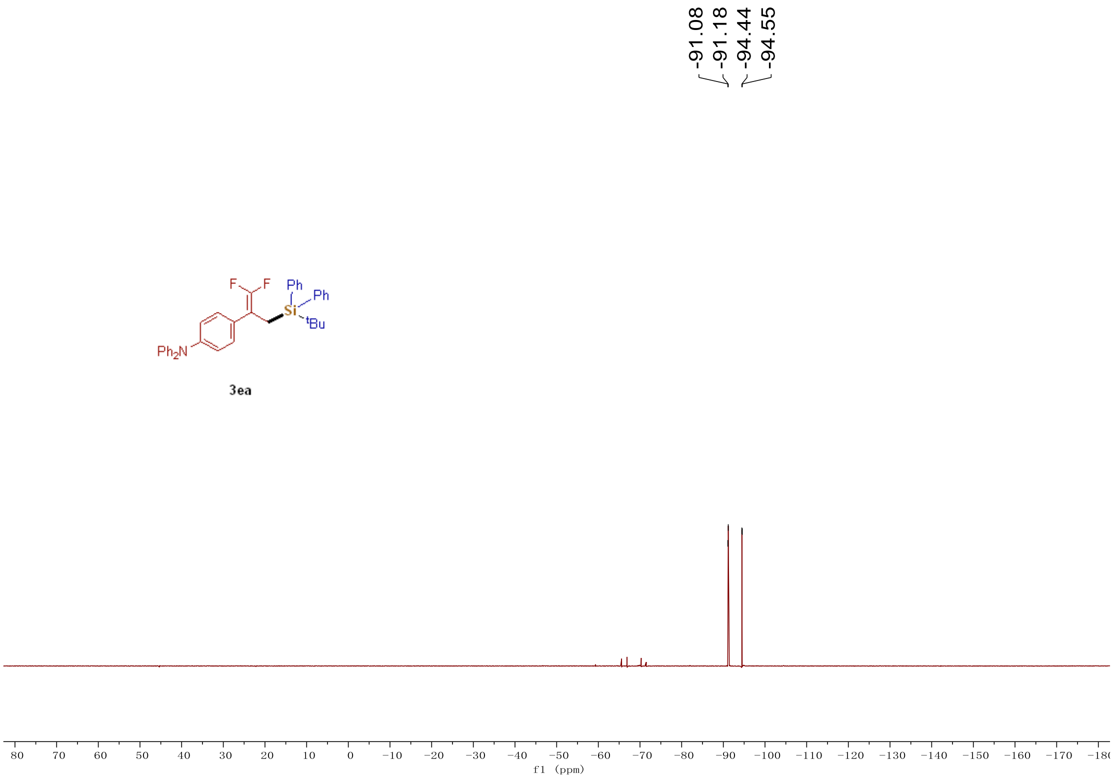


Figure S15. ^{19}F NMR spectra (471 MHz) of **3ea** in $CDCl_3$.

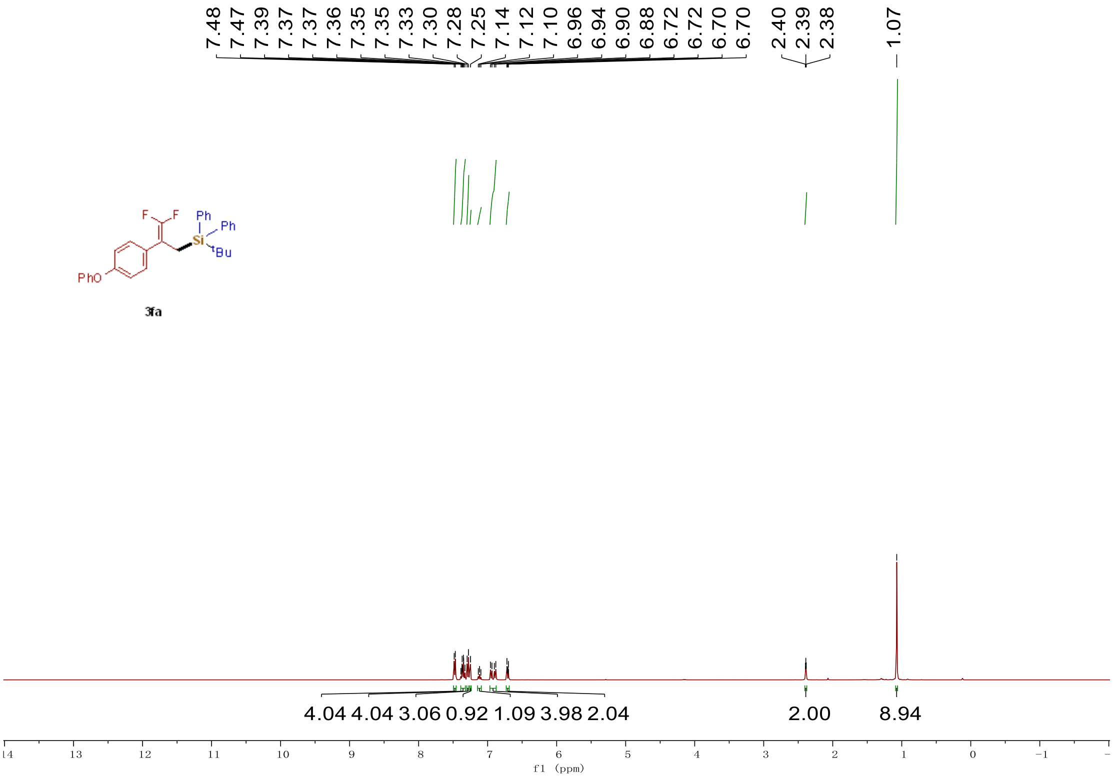


Figure S16. ^{1}H NMR spectra (400 MHz) of **3fa** in $CDCl_3$.

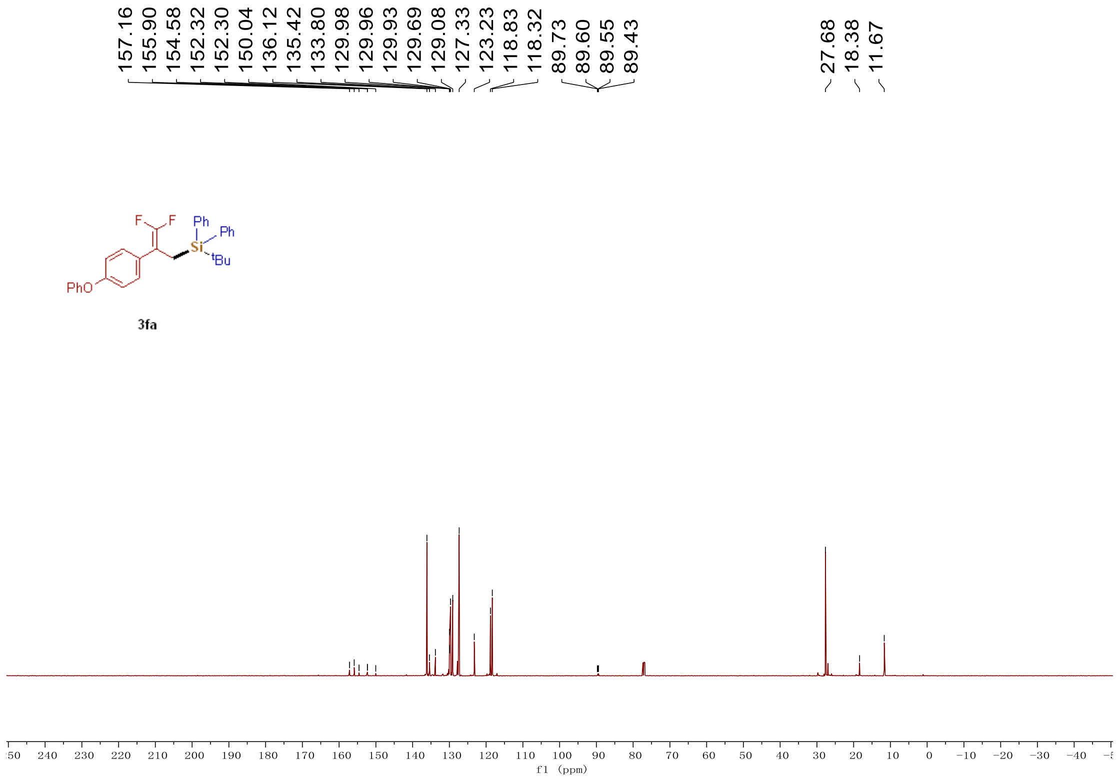


Figure S17. ^{13}C NMR spectra (126 MHz) of **3fa** in $CDCl_3$.

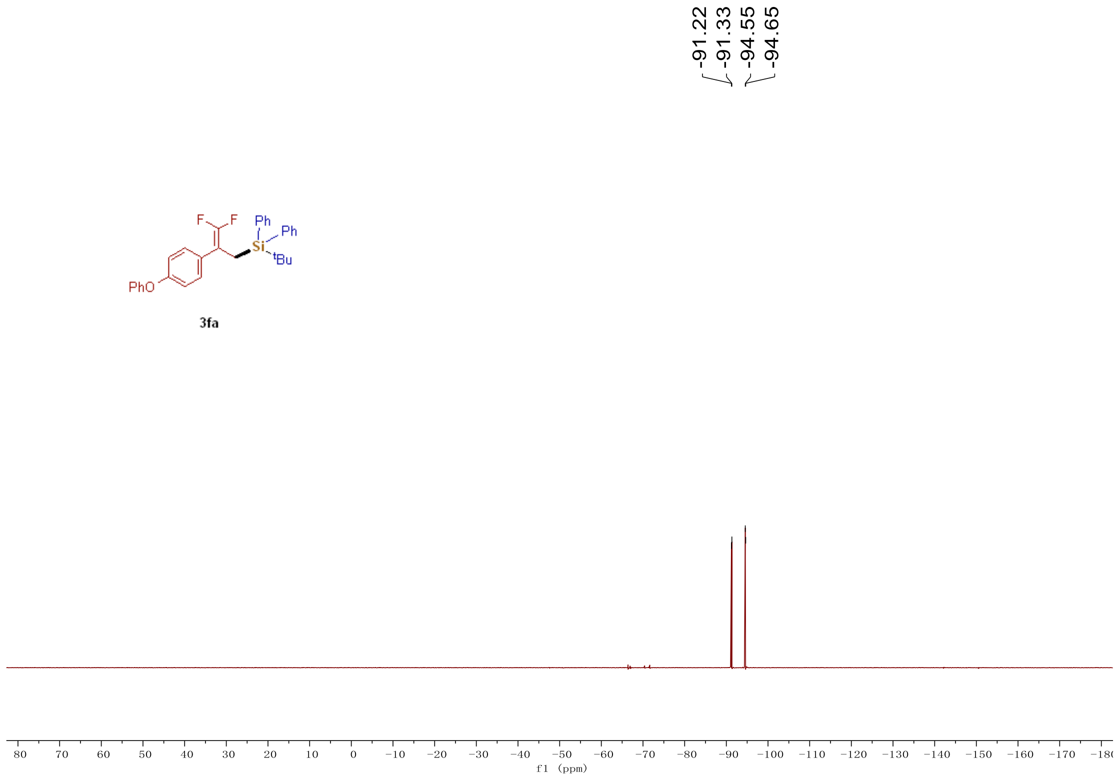


Figure S18. ^{19}F NMR spectra (471 MHz) of **3fa** in $CDCl_3$.

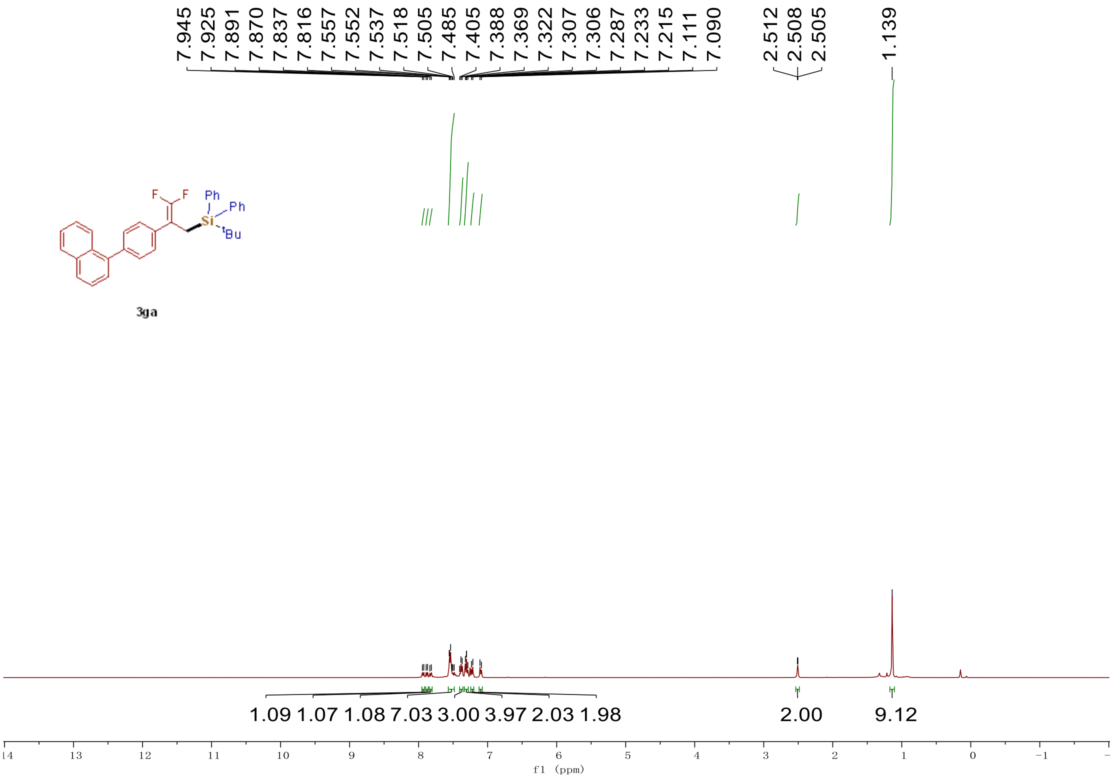


Figure S19. ^{1}H NMR spectra (400 MHz) of **3ga** in $CDCl_3$.

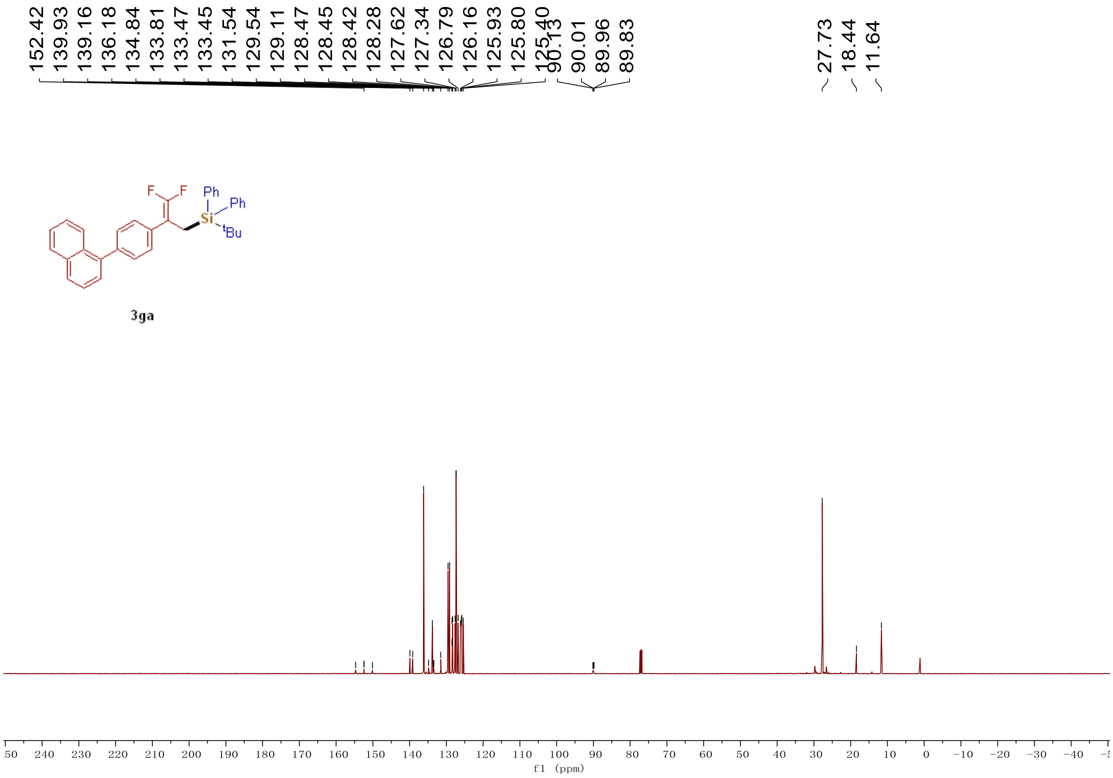


Figure S20. ^{13}C NMR spectra (126 MHz) of **3ga** in $CDCl_3$.

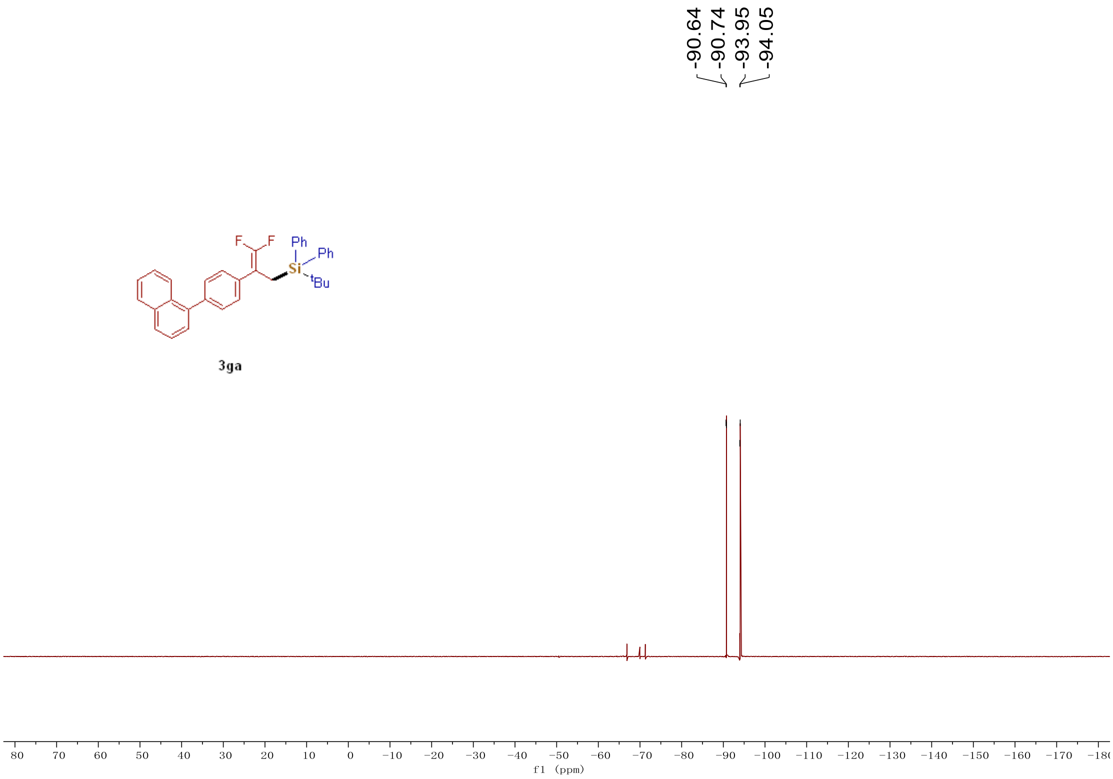


Figure S21. ^{19}F NMR spectra (471 MHz) of **3ga** in $CDCl_3$.

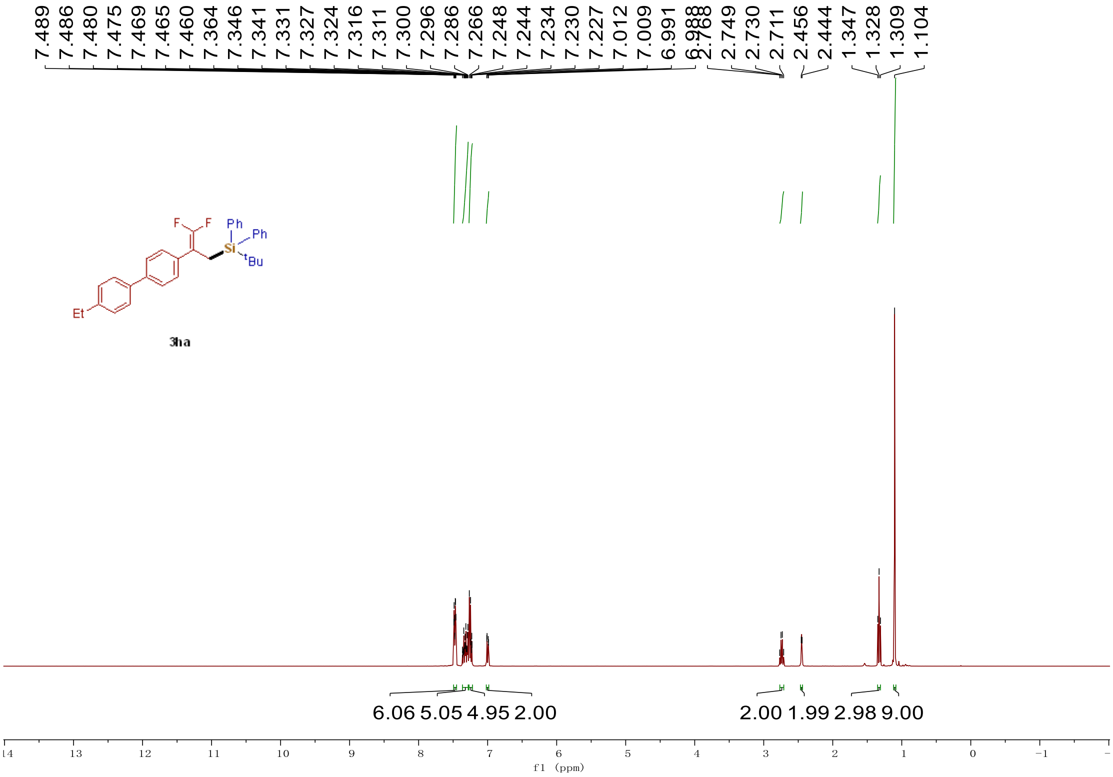


Figure S22. ^{1}H NMR spectra (400 MHz) of **3ha** in $CDCl_3$.

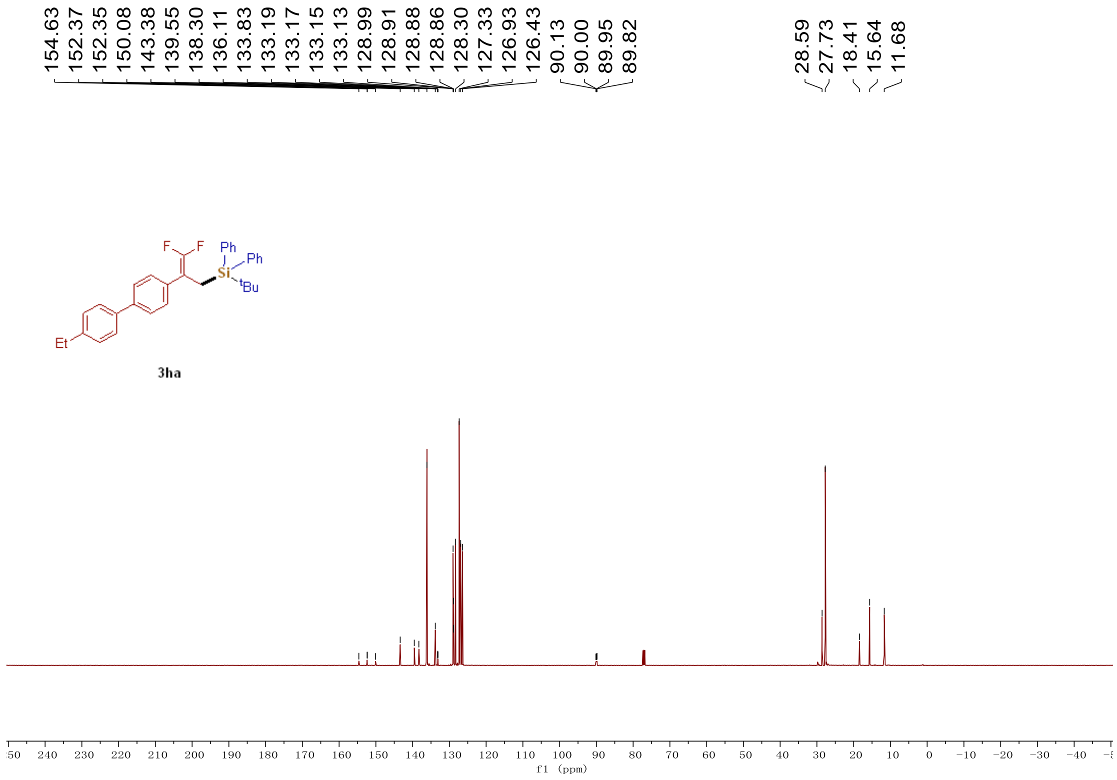


Figure S23. ^{13}C NMR spectra (126 MHz) of **3ha** in $CDCl_3$.

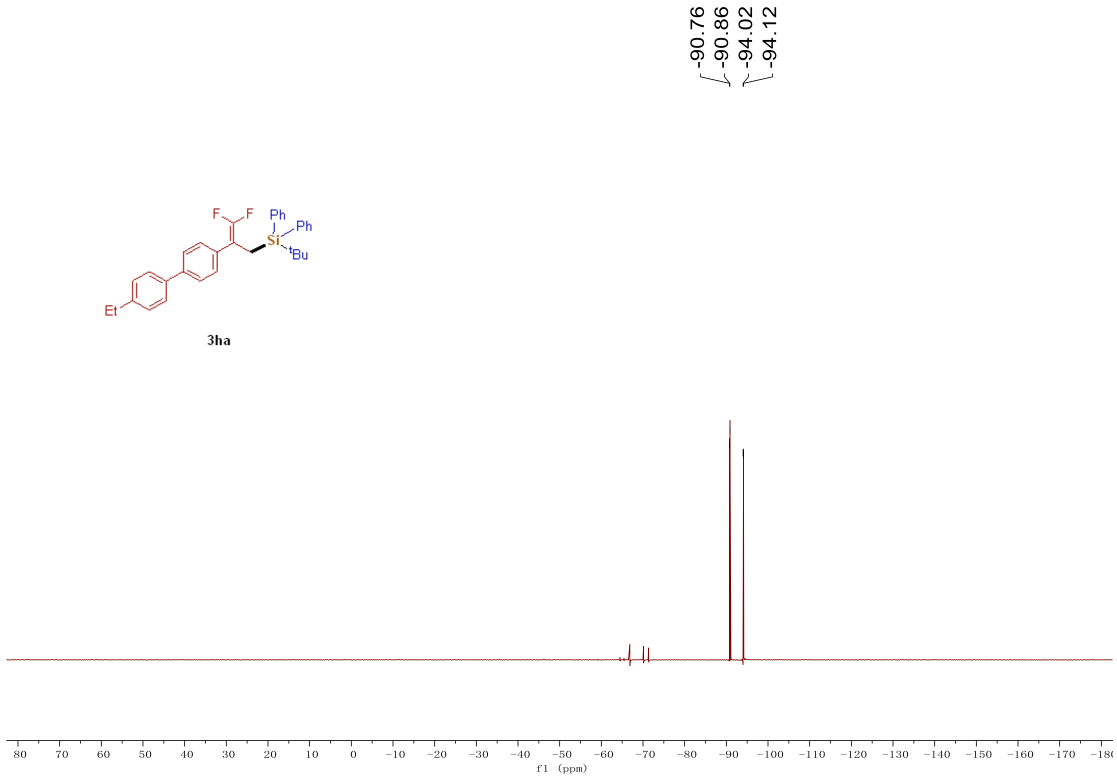


Figure S24. ^{19}F NMR spectra (471 MHz) of **3ha** in $CDCl_3$.

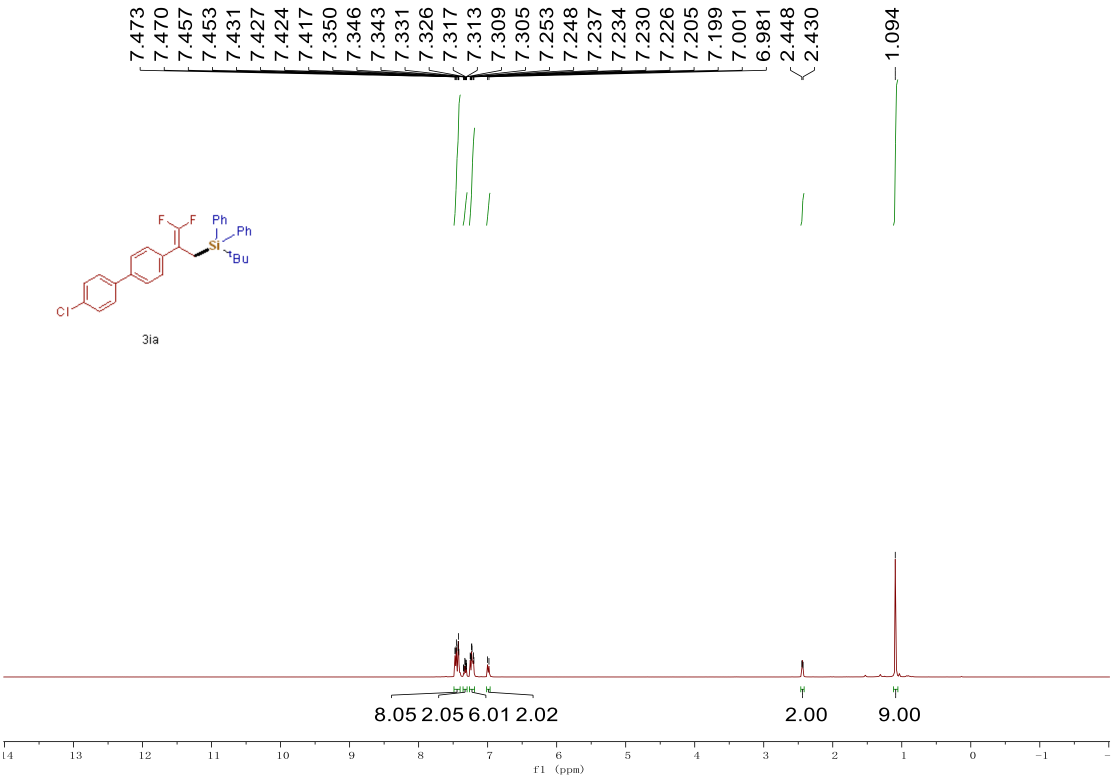


Figure S25. ^{1}H NMR spectra (400 MHz) of **3ia** in $CDCl_3$.

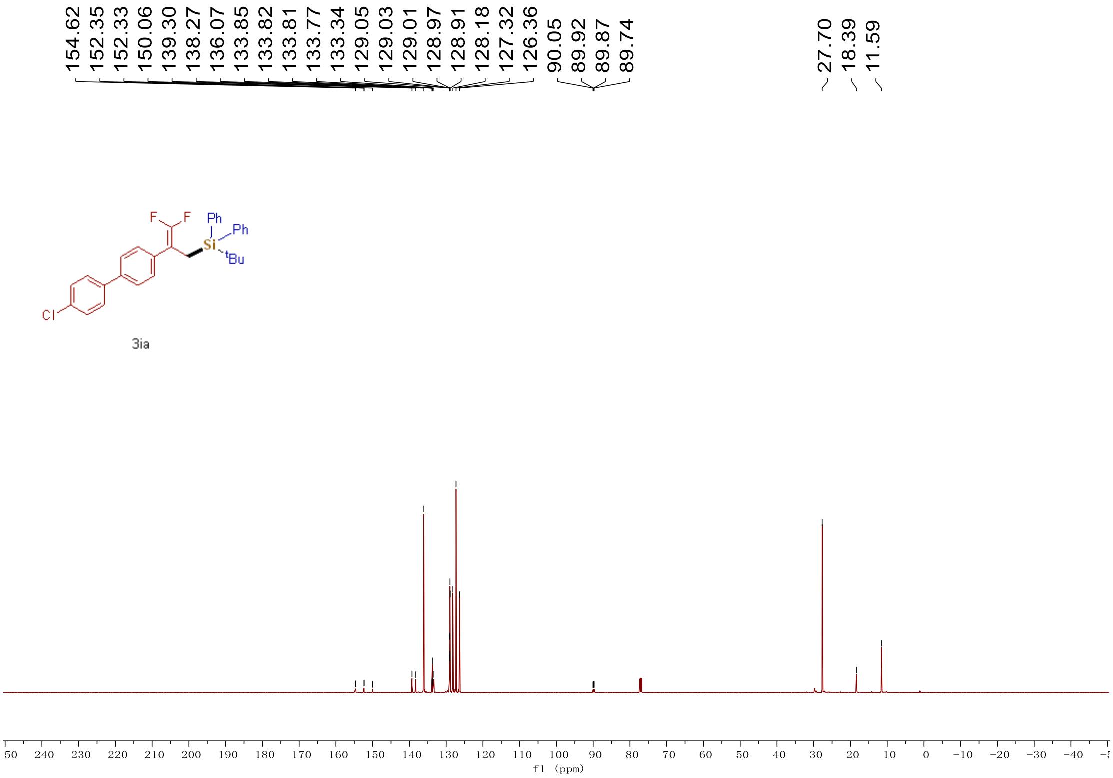


Figure S26. ^{13}C NMR spectra (126 MHz) of **3ia** in $CDCl_3$.

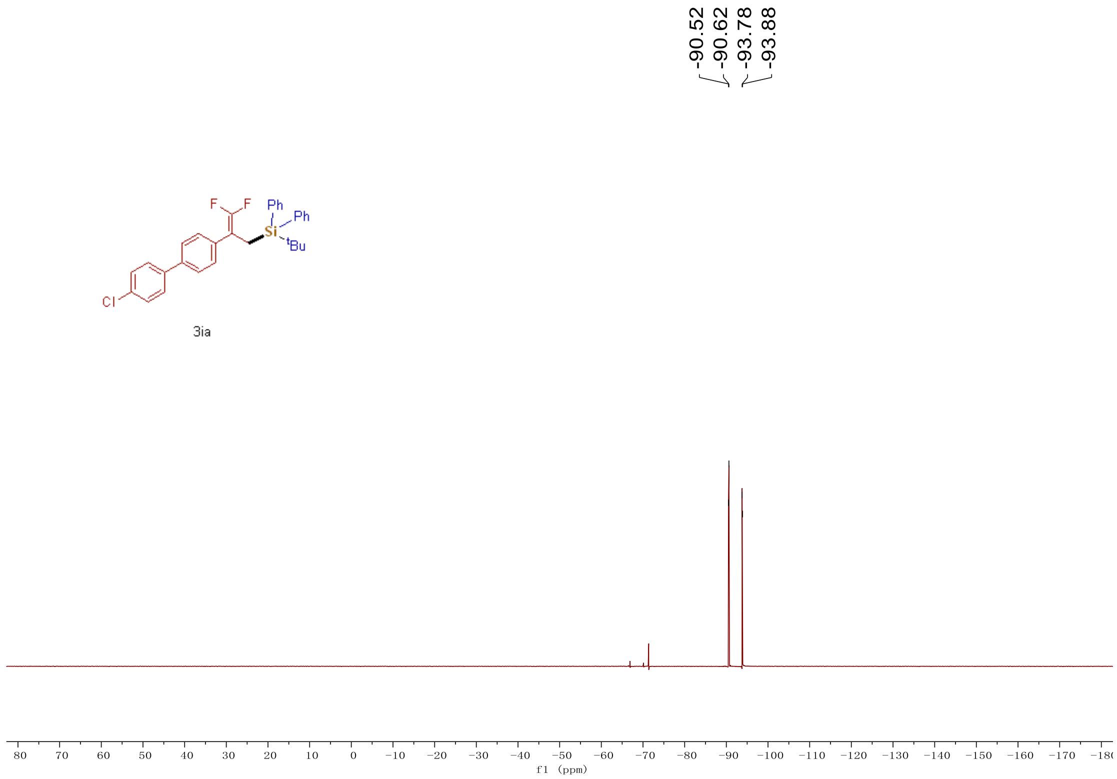


Figure S27. ^{19}F NMR spectra (471 MHz) of **3ia** in $CDCl_3$.

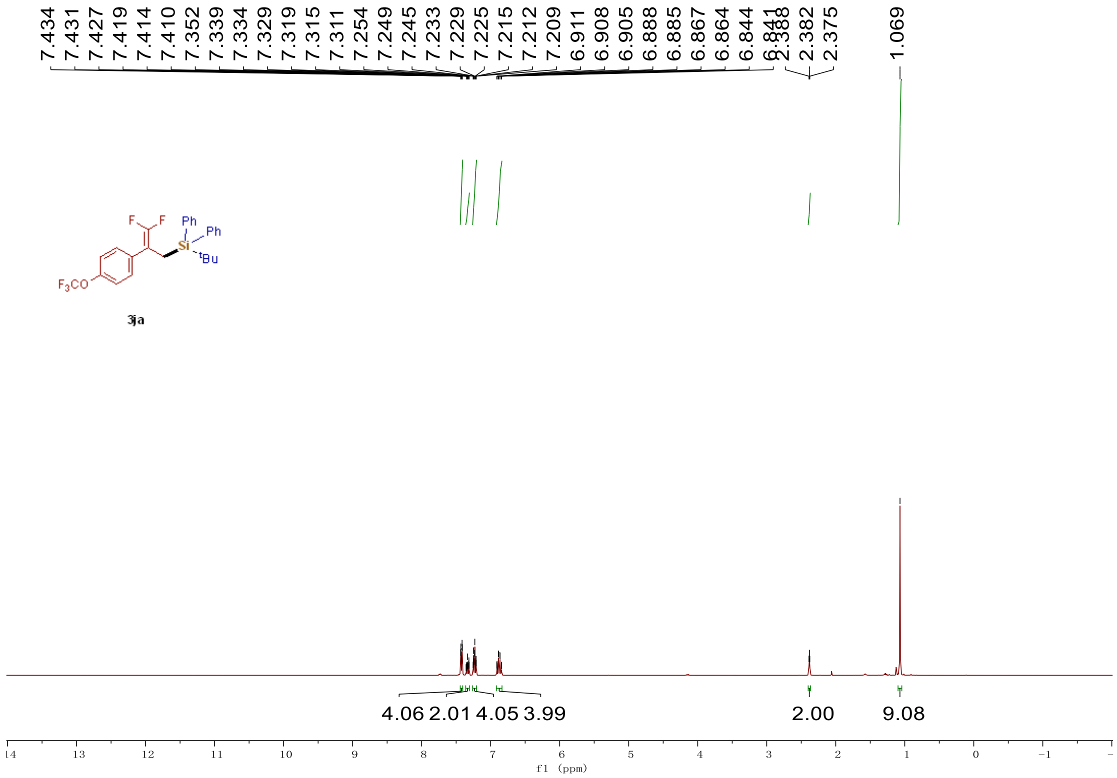


Figure S28. ^{1}H NMR spectra (400 MHz) of **3ja** in $CDCl_3$.

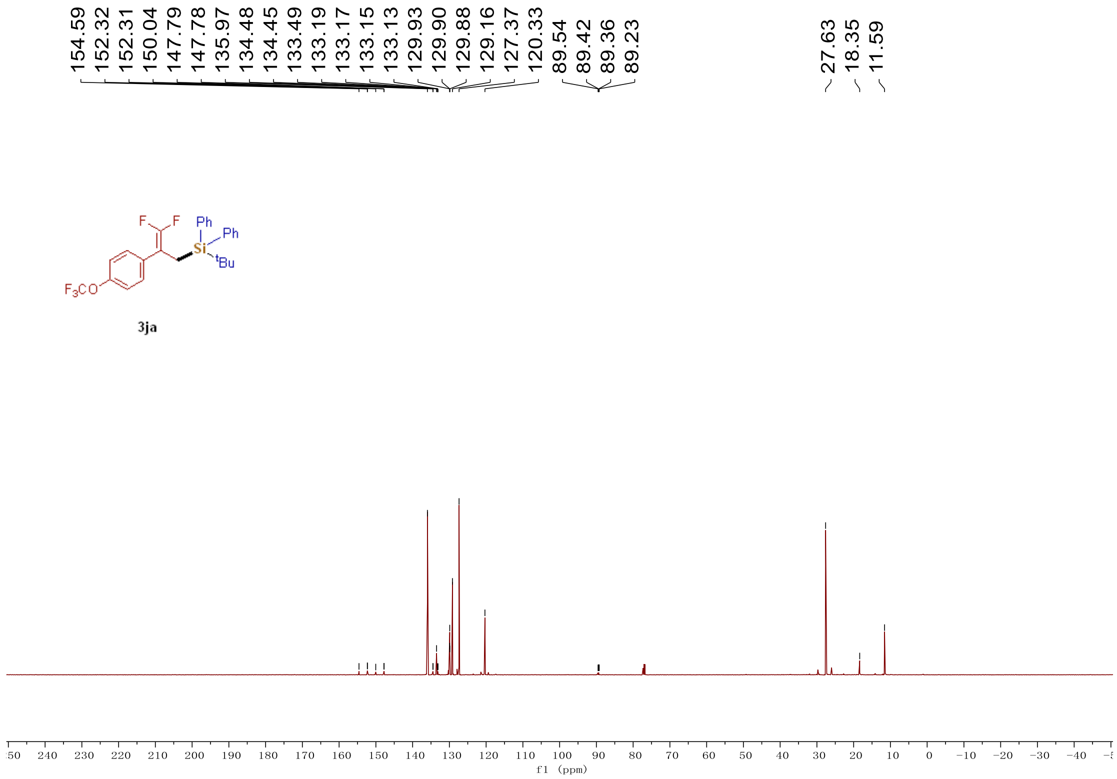


Figure S29. ^{13}C NMR spectra (126 MHz) of **3ja** in $CDCl_3$.

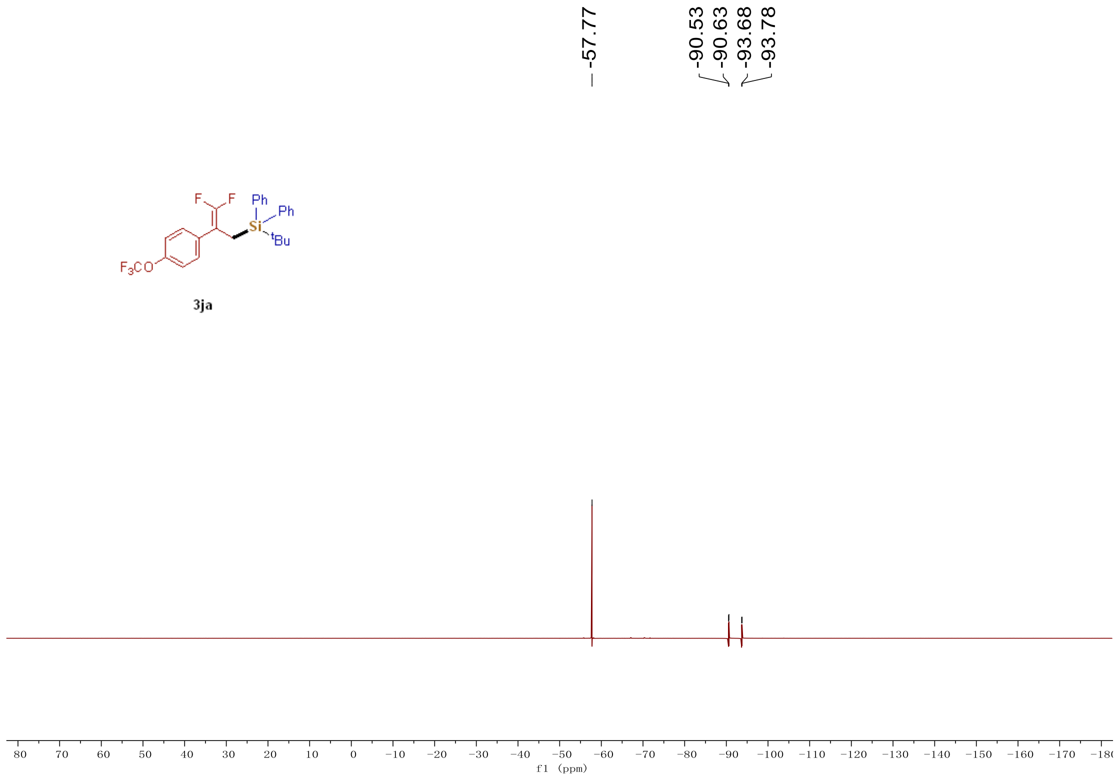


Figure S30. ^{19}F NMR spectra (471 MHz) of **3ja** in $CDCl_3$.

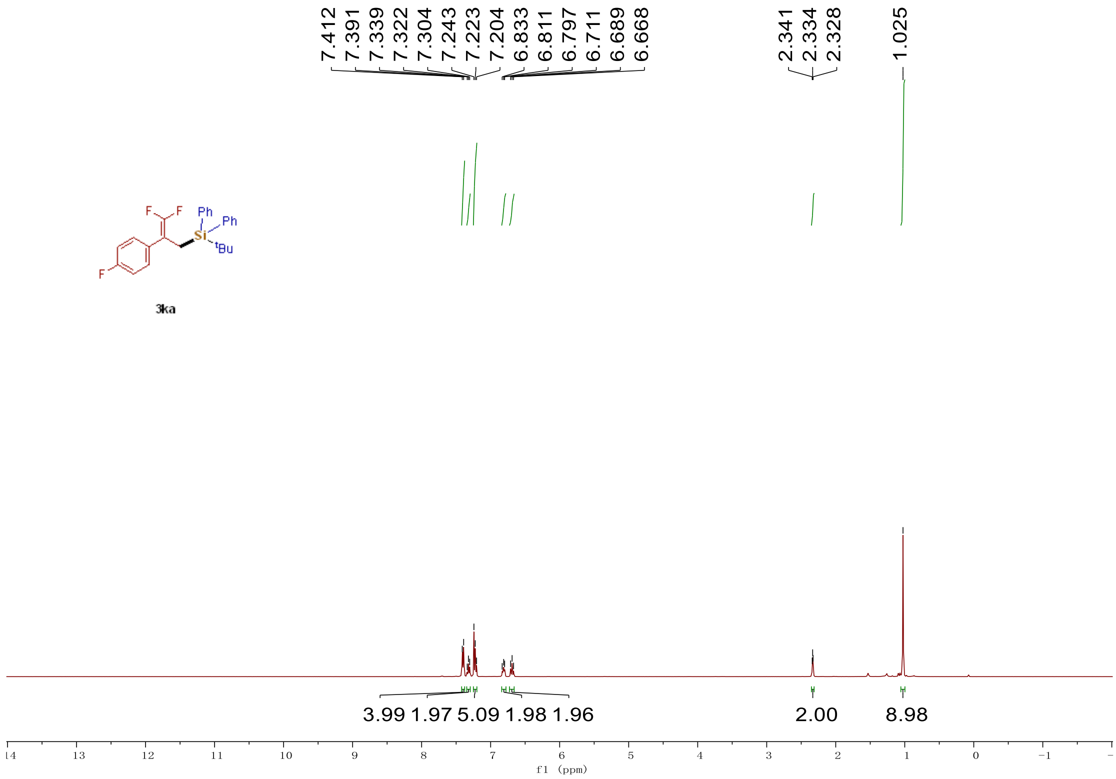


Figure S31. ^{1}H NMR spectra (400 MHz) of **3ka** in $CDCl_3$.

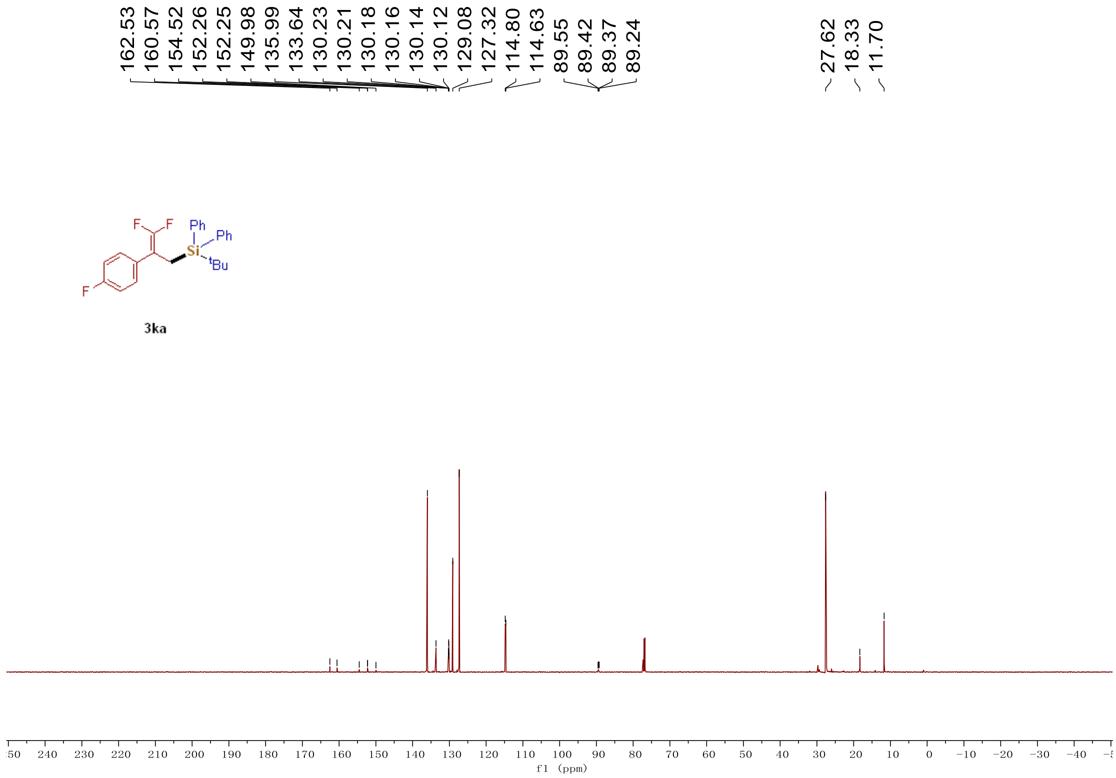


Figure S32. ^{13}C NMR spectra (126 MHz) of **3ka** in $CDCl_3$.

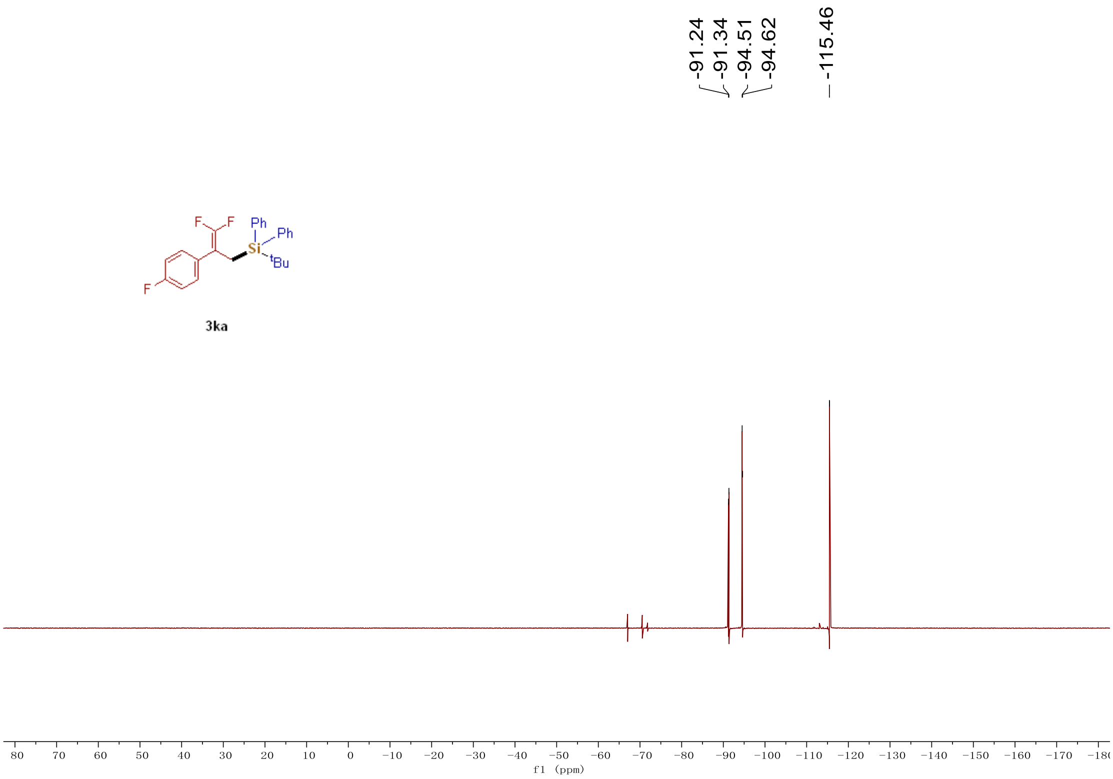


Figure S33. ^{19}F NMR spectra (471 MHz) of **3ka** in $CDCl_3$.

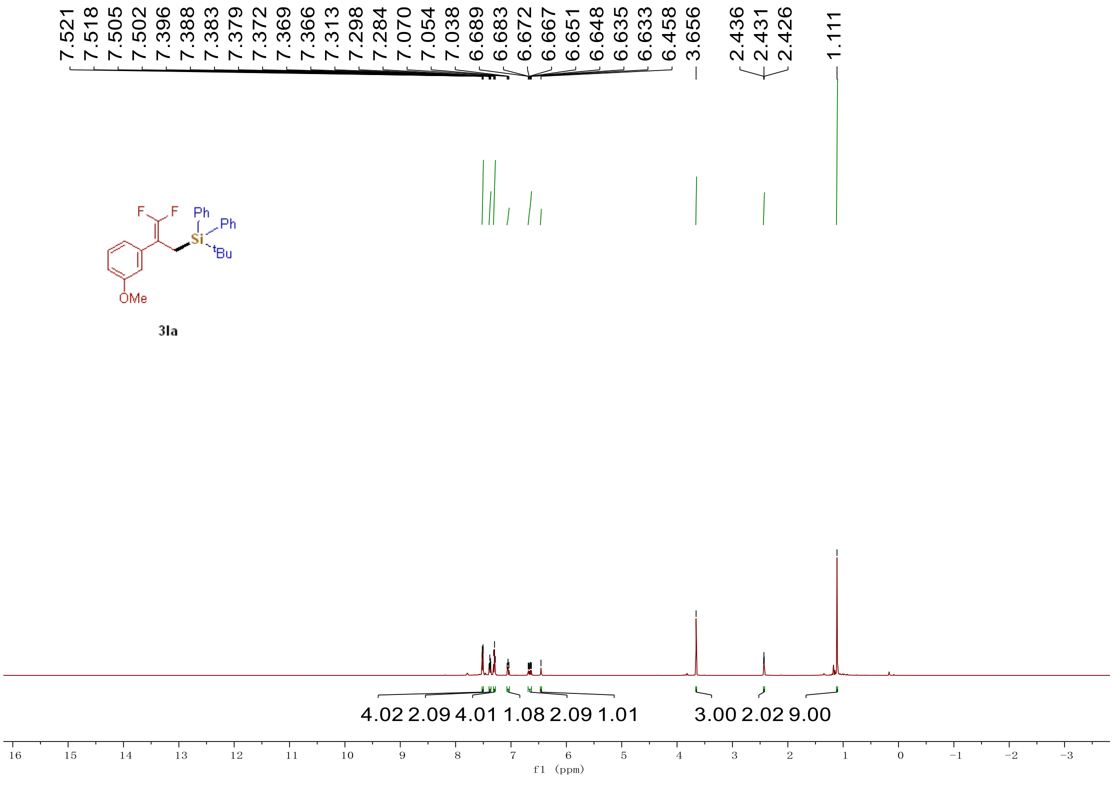


Figure S34. ^{1}H NMR spectra (500 MHz) of **3la** in $CDCl_3$.

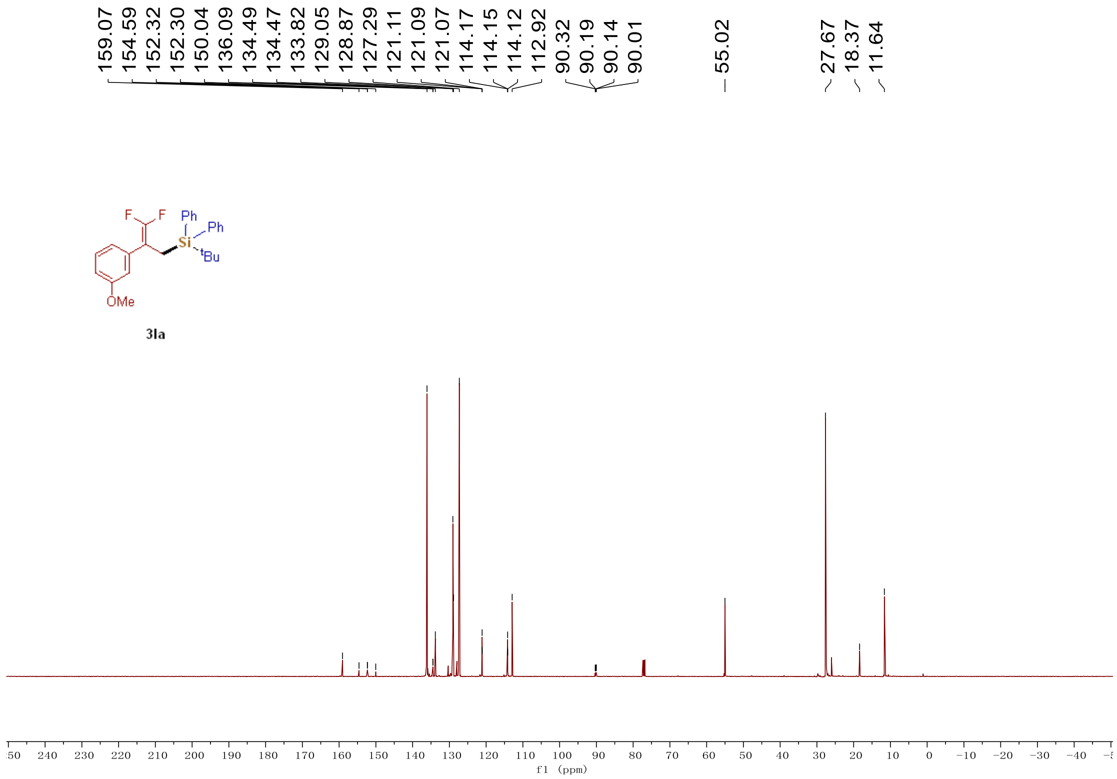


Figure S35. ^{13}C NMR spectra (126 MHz) of **3la** in $CDCl_3$.

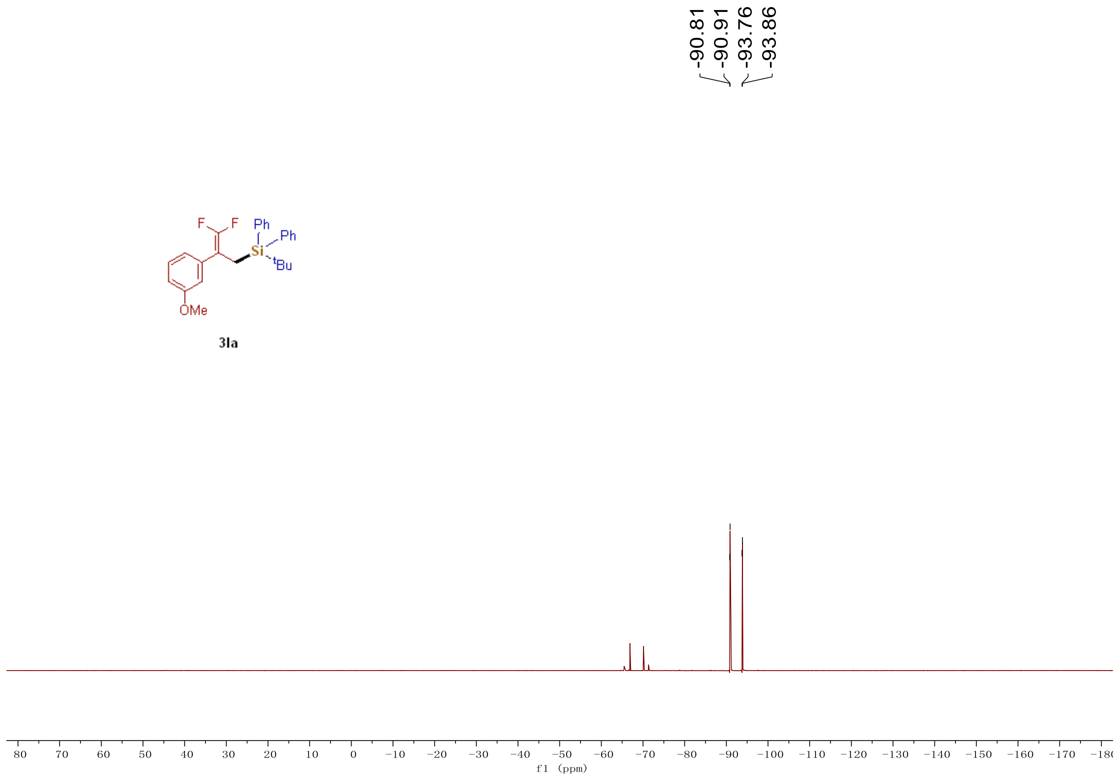


Figure S36. ^{19}F NMR spectra (471 MHz) of **3la** in $CDCl_3$.

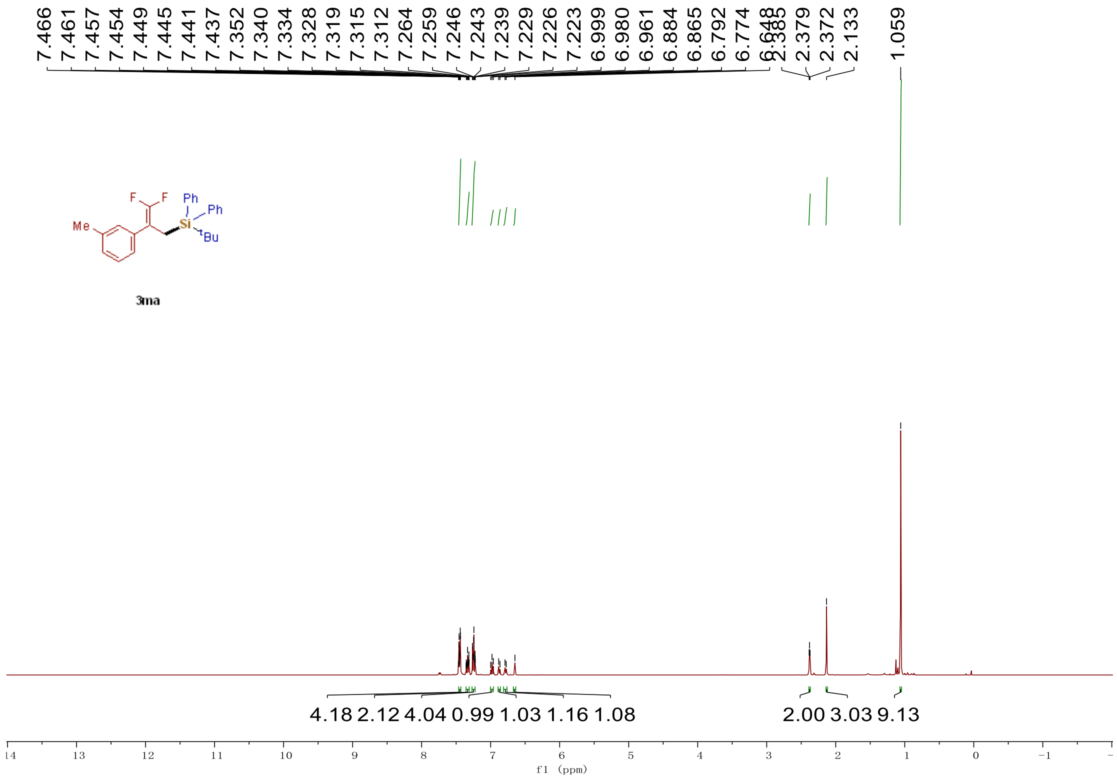


Figure S37. ^{1}H NMR spectra (400 MHz) of **3ma** in $CDCl_3$.

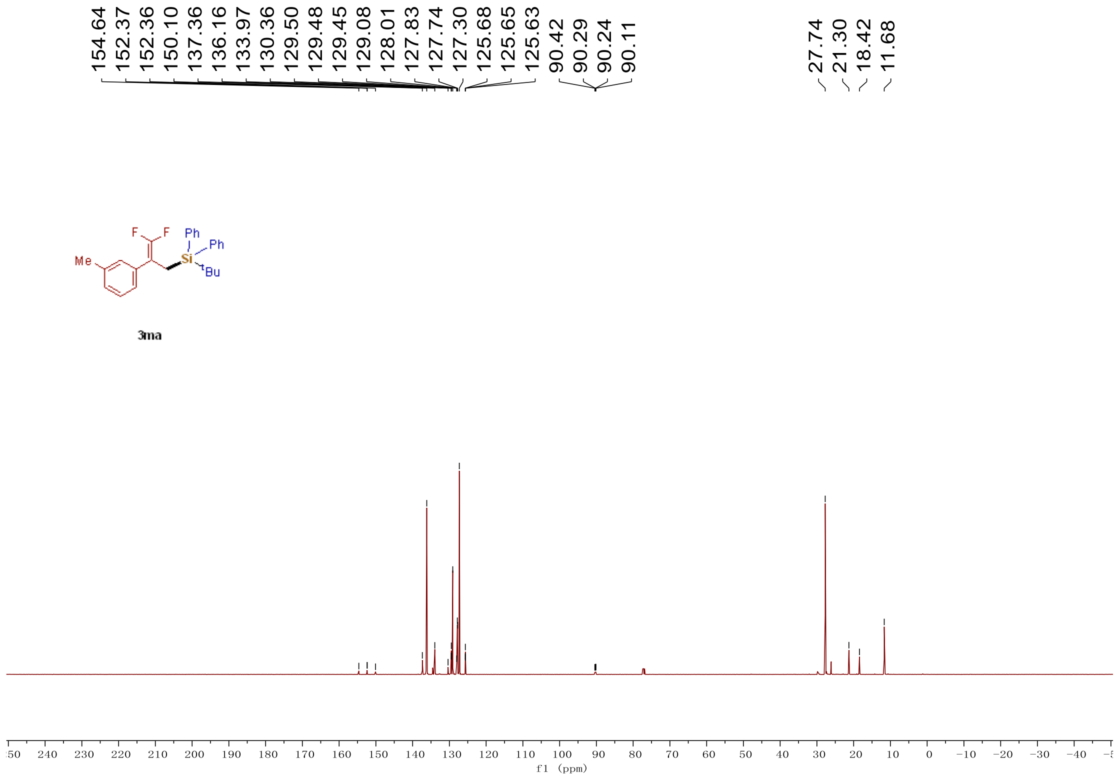


Figure S38. ^{13}C NMR spectra (126 MHz) of **3ma** in $CDCl_3$.

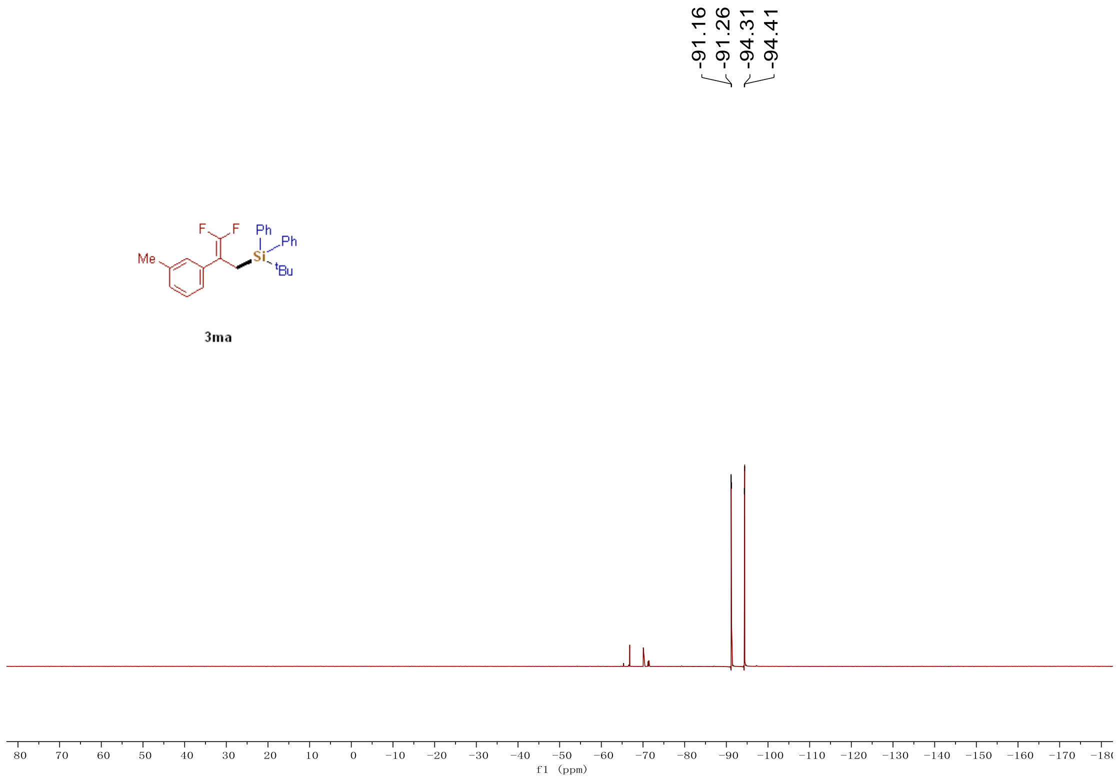


Figure S39. ^{19}F NMR spectra (471 MHz) of **3ma** in $CDCl_3$.

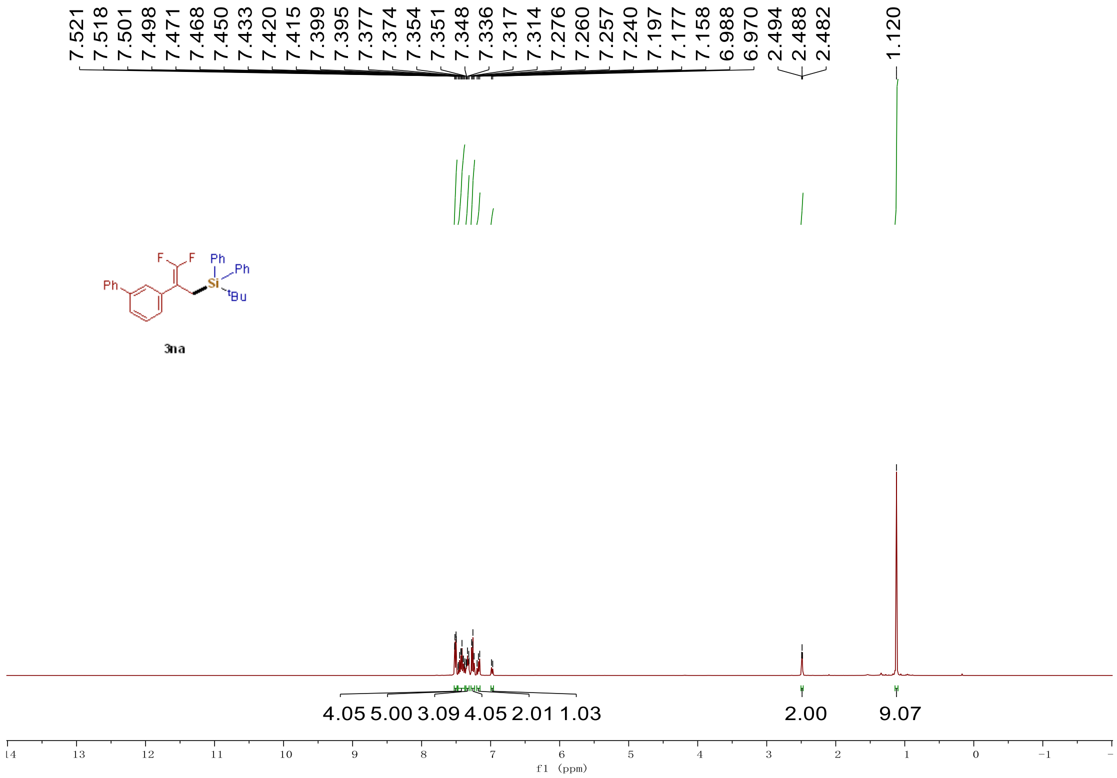


Figure S40. ^{1}H NMR spectra (400 MHz) of **3na** in $CDCl_3$.

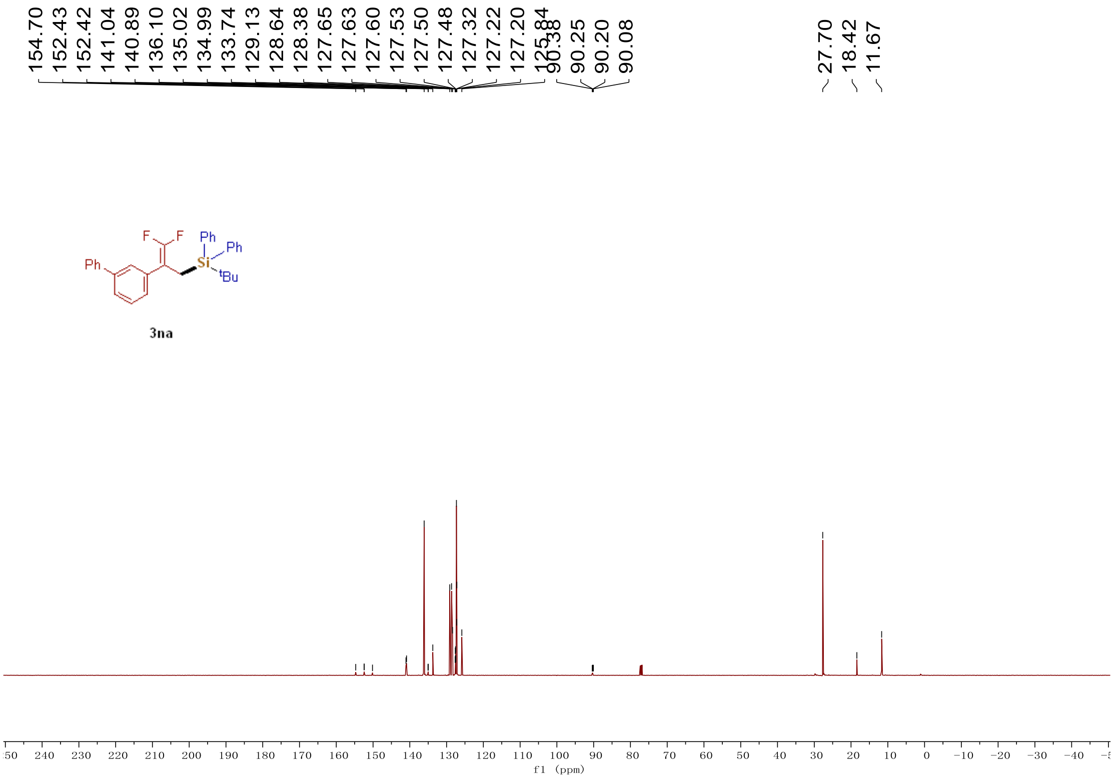


Figure S41. ^{13}C NMR spectra (126 MHz) of **3na** in $CDCl_3$.

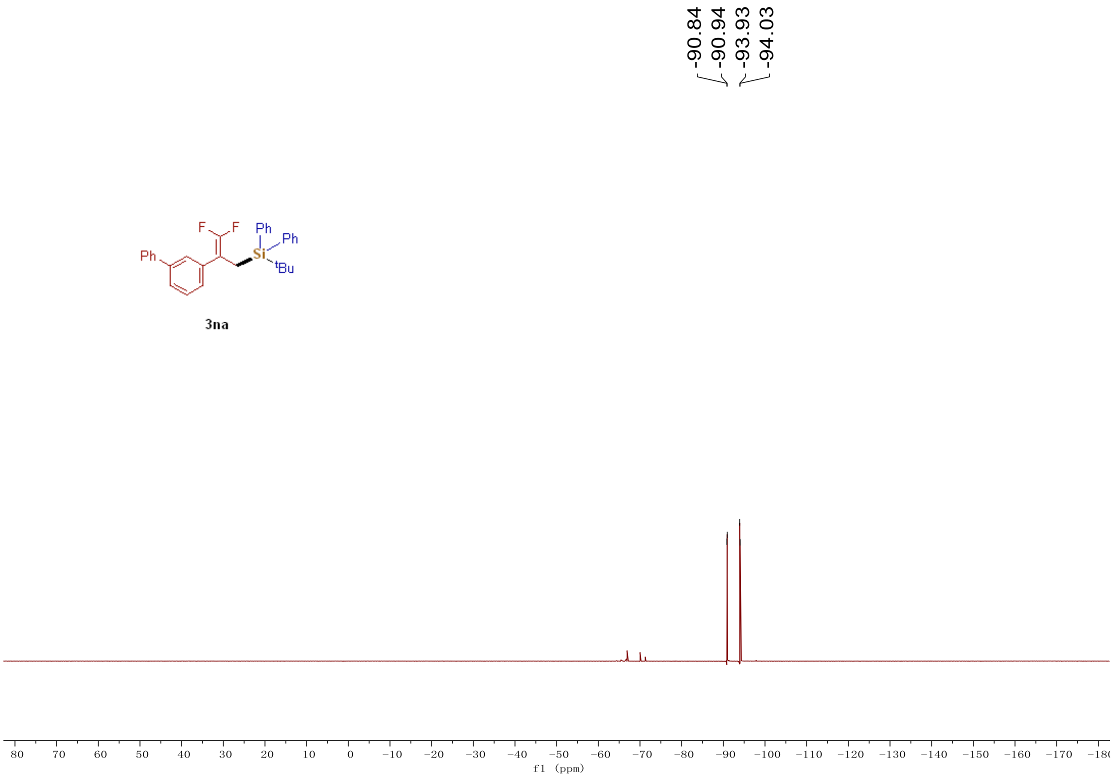


Figure S42. ^{19}F NMR spectra (471 MHz) of **3na** in $CDCl_3$.

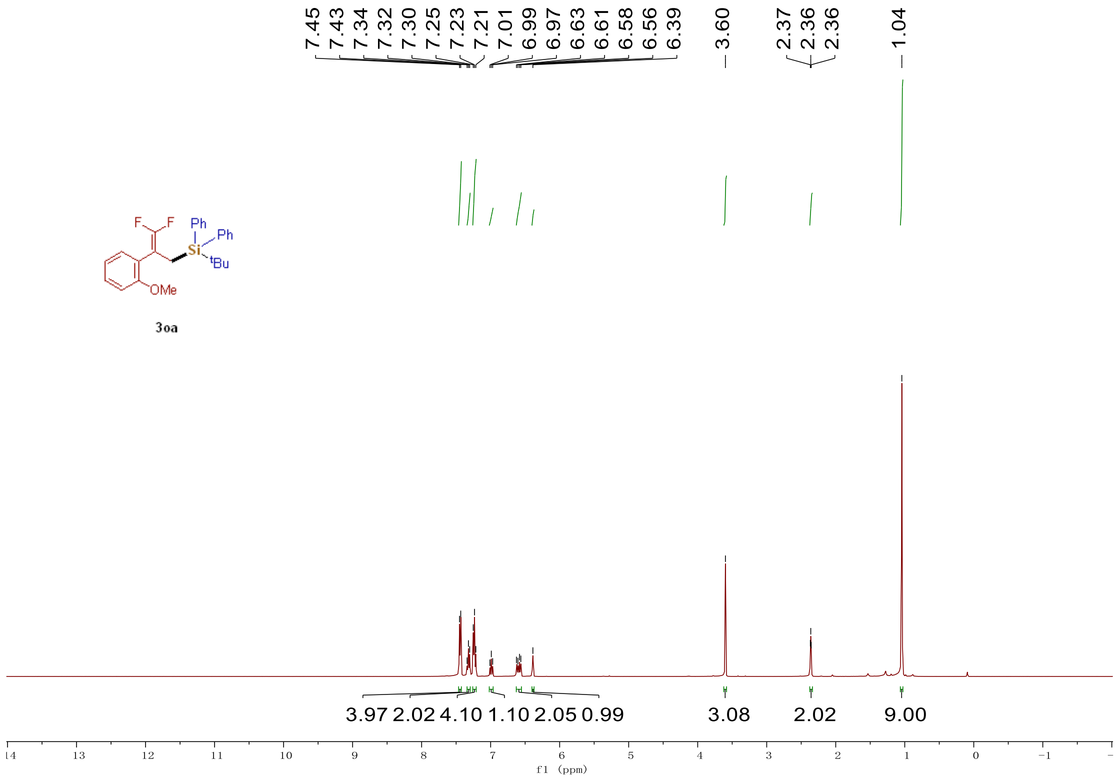


Figure S43. ^{1}H NMR spectra (400 MHz) of **3oa** in $CDCl_3$.

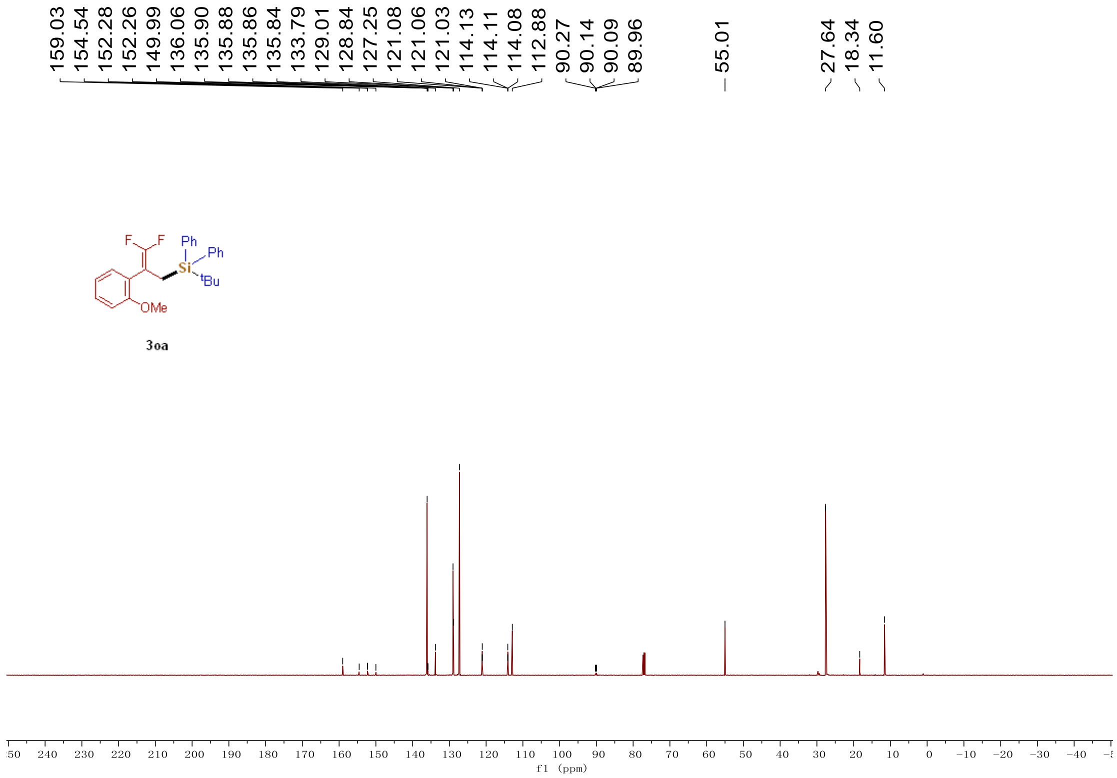


Figure S44. ^{13}C NMR spectra (126 MHz) of **3oa** in $CDCl_3$.

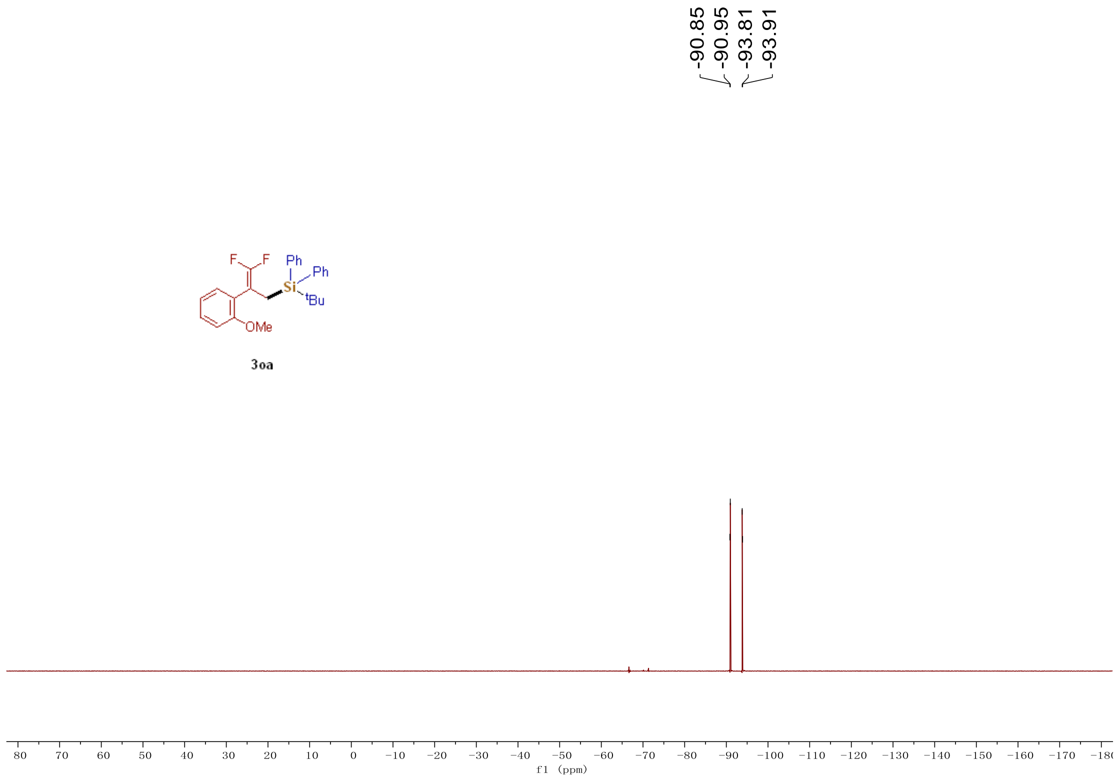


Figure S45. ^{19}F NMR spectra (471 MHz) of **3oa** in $CDCl_3$.

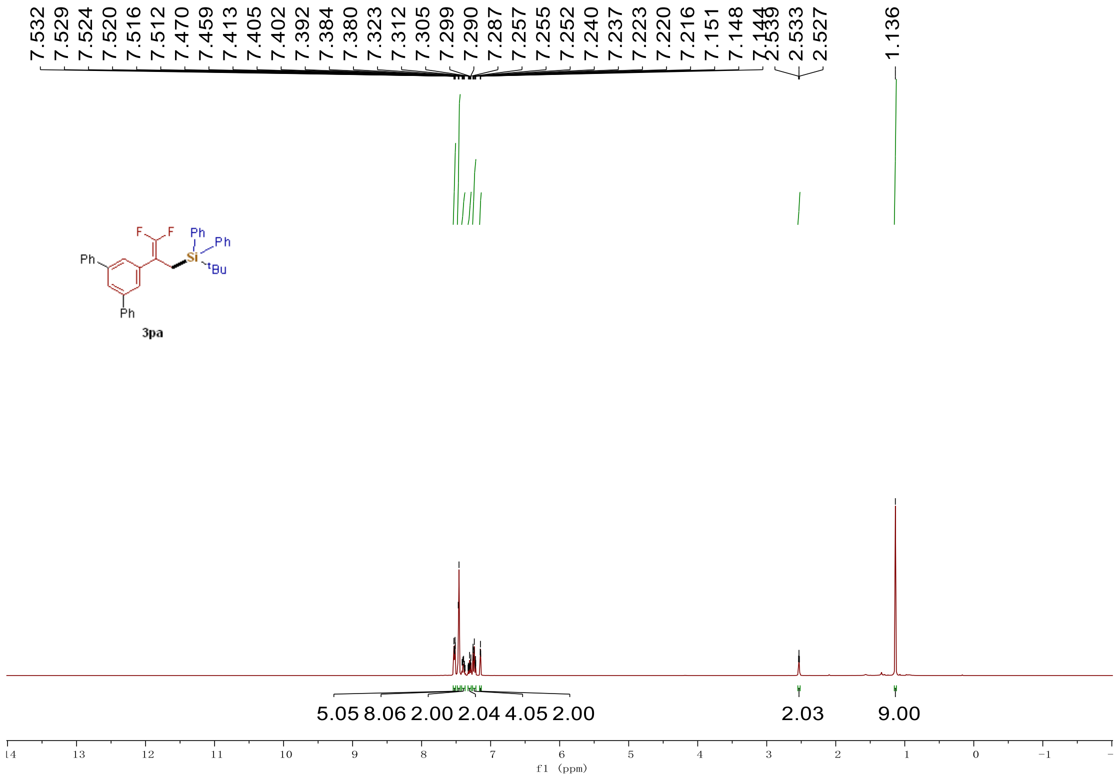


Figure S46. ^{1}H NMR spectra (400 MHz) of **3pa** in $CDCl_3$.

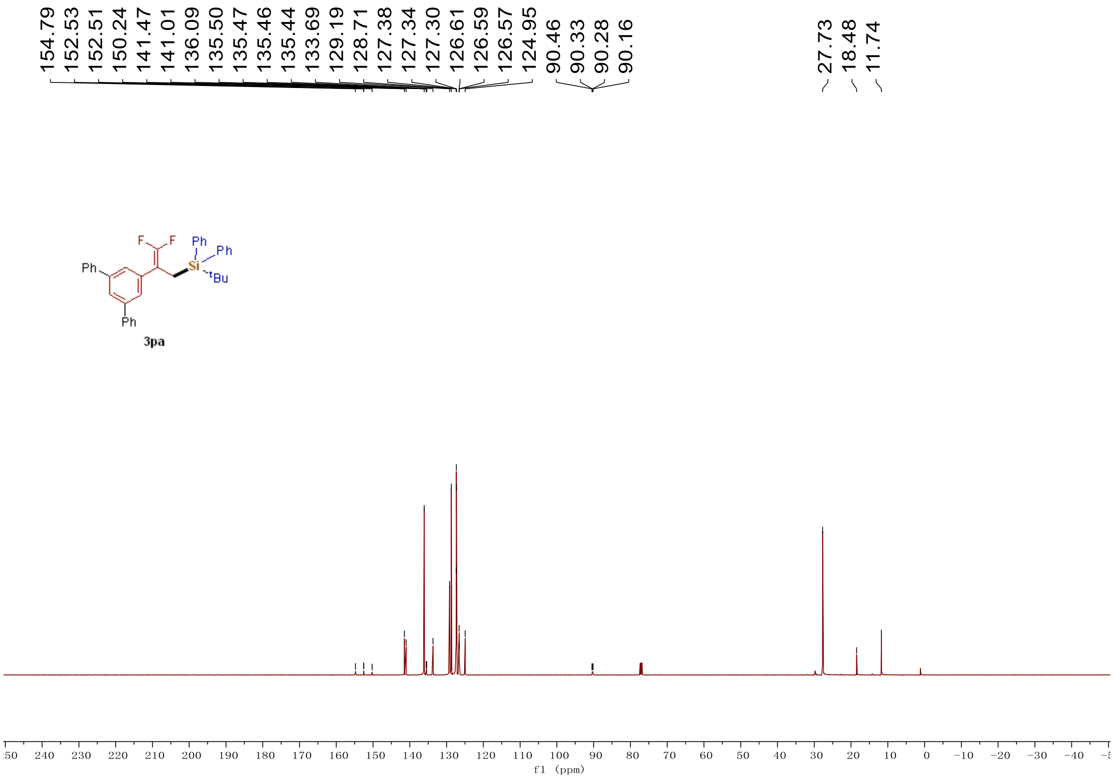


Figure S47. ^{13}C NMR spectra (126 MHz) of **3pa** in $CDCl_3$.

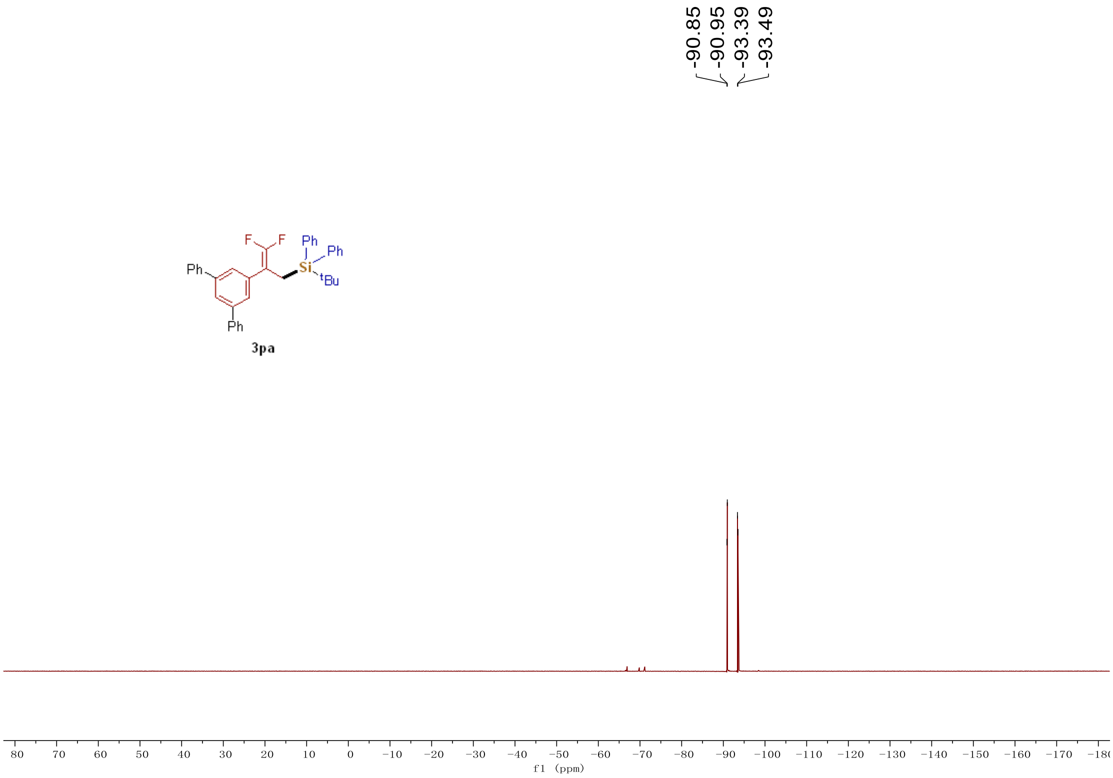


Figure S48. ^{19}F NMR spectra (471 MHz) of **3pa** in $CDCl_3$.

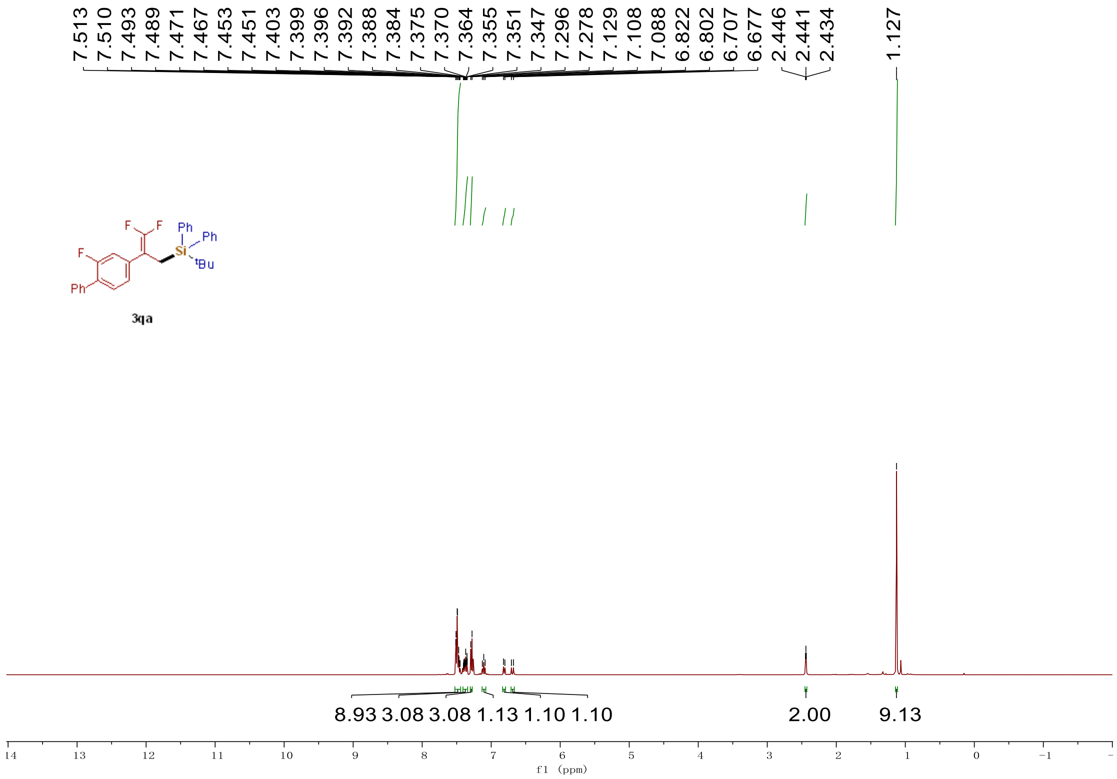


Figure S49. ^{1}H NMR spectra (400 MHz) of **3qa** in $CDCl_3$.

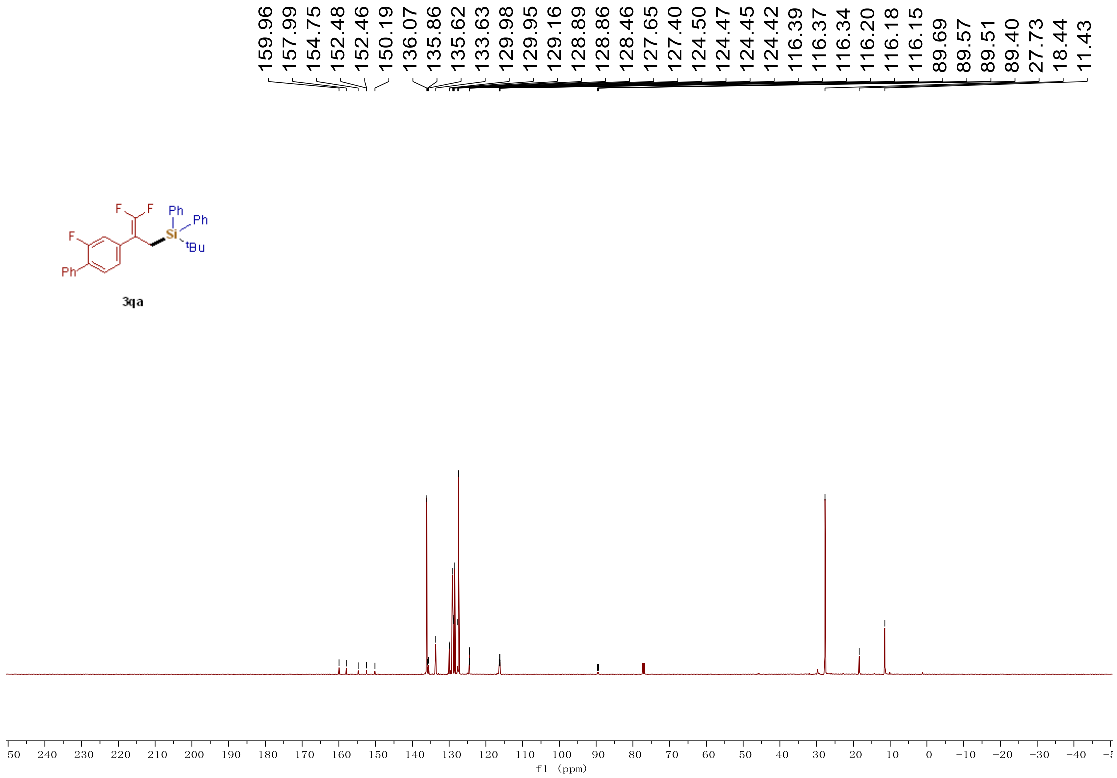


Figure S50. ^{13}C NMR spectra (126 MHz) of **3qa** in $CDCl_3$.

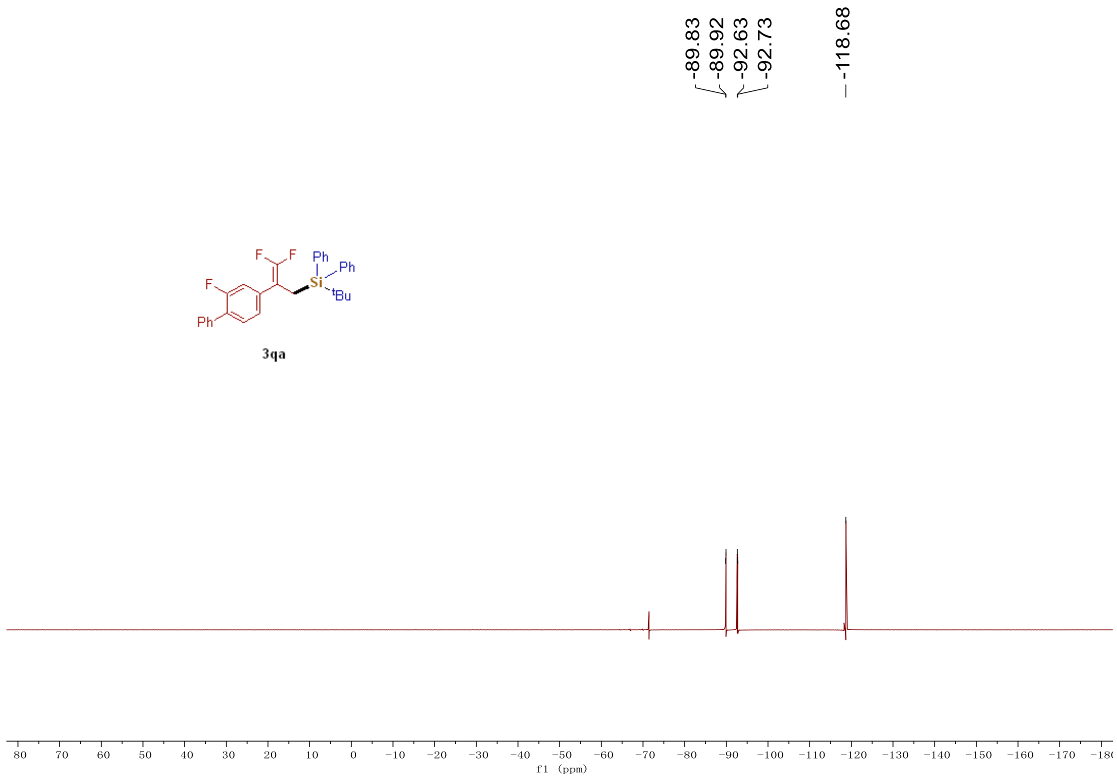


Figure S51. ^{19}F NMR spectra (471 MHz) of **3qa** in $CDCl_3$.

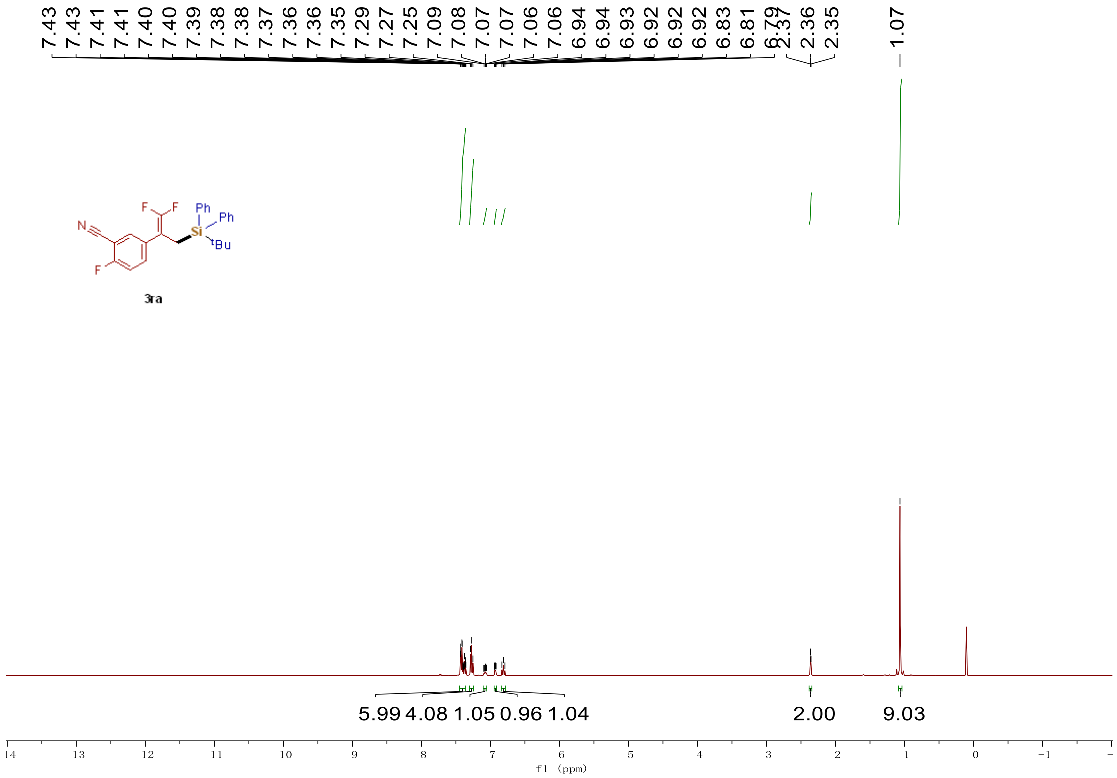


Figure S52. ^{1}H NMR spectra (400 MHz) of **3ra** in $CDCl_3$.

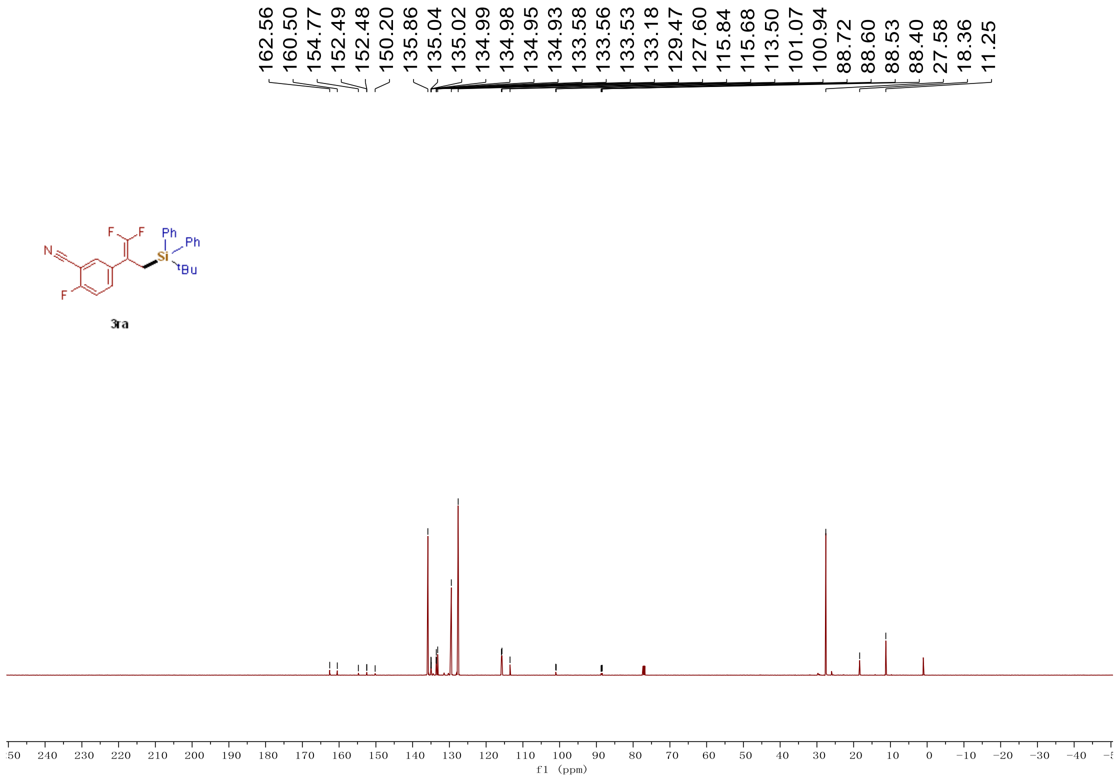


Figure S53. ^{13}C NMR spectra (126 MHz) of **3ra** in $CDCl_3$.

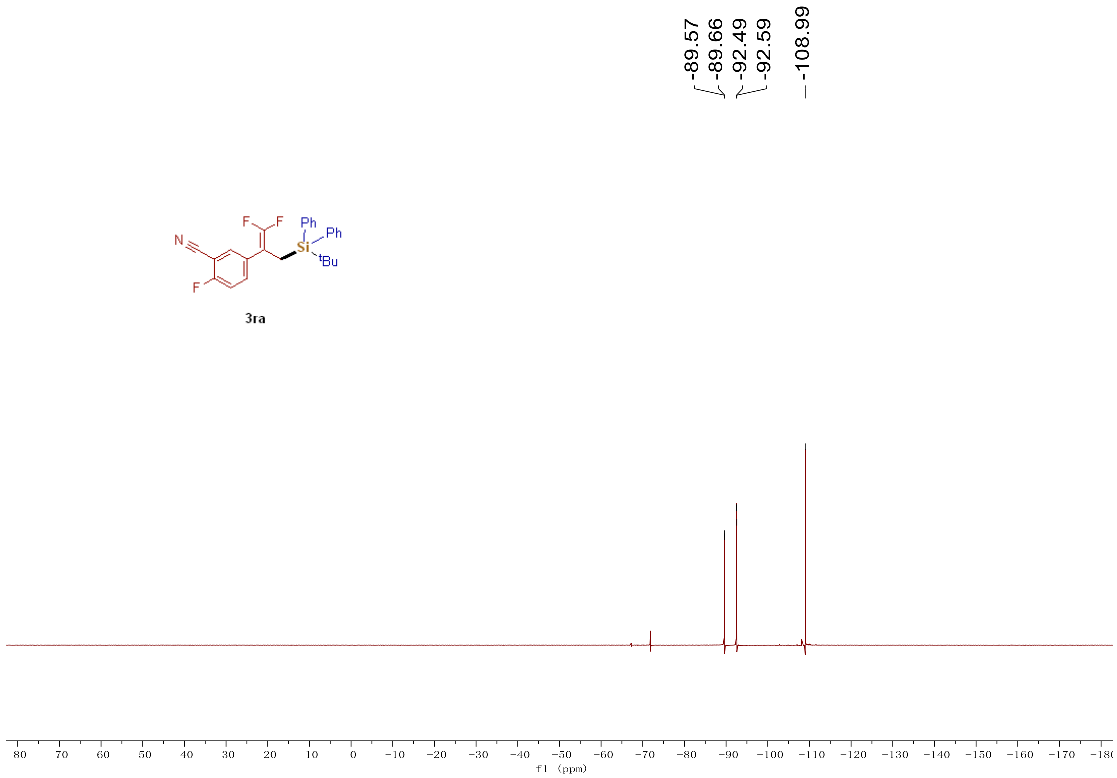


Figure S54. ^{19}F NMR spectra (471 MHz) of **3ra** in $CDCl_3$.

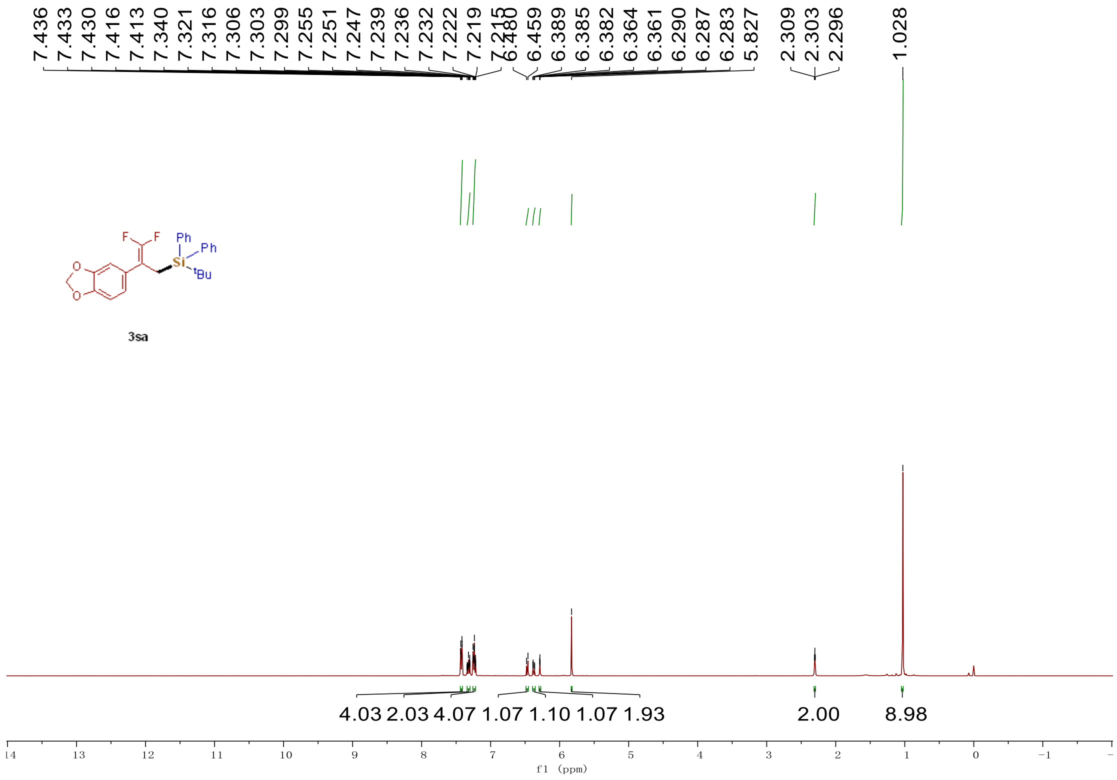


Figure S55. ^{1}H NMR spectra (400 MHz) of **3sa** in $CDCl_3$.

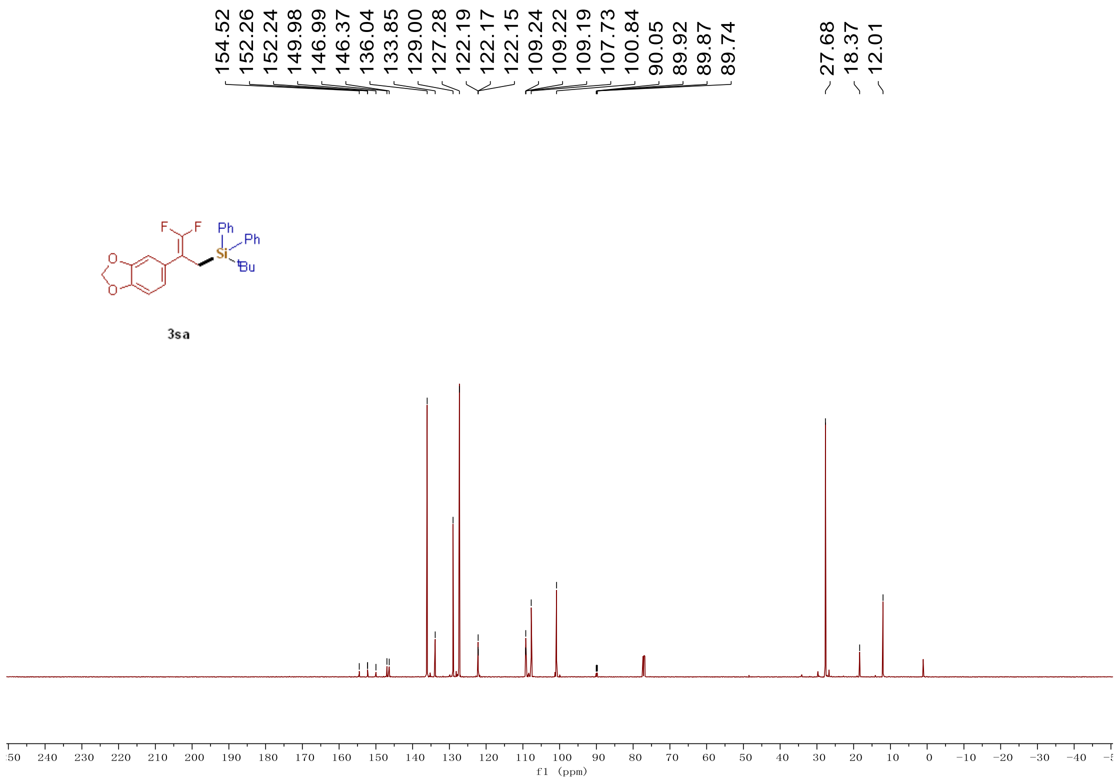


Figure S56. ^{13}C NMR spectra (126 MHz) of **3sa** in $CDCl_3$.

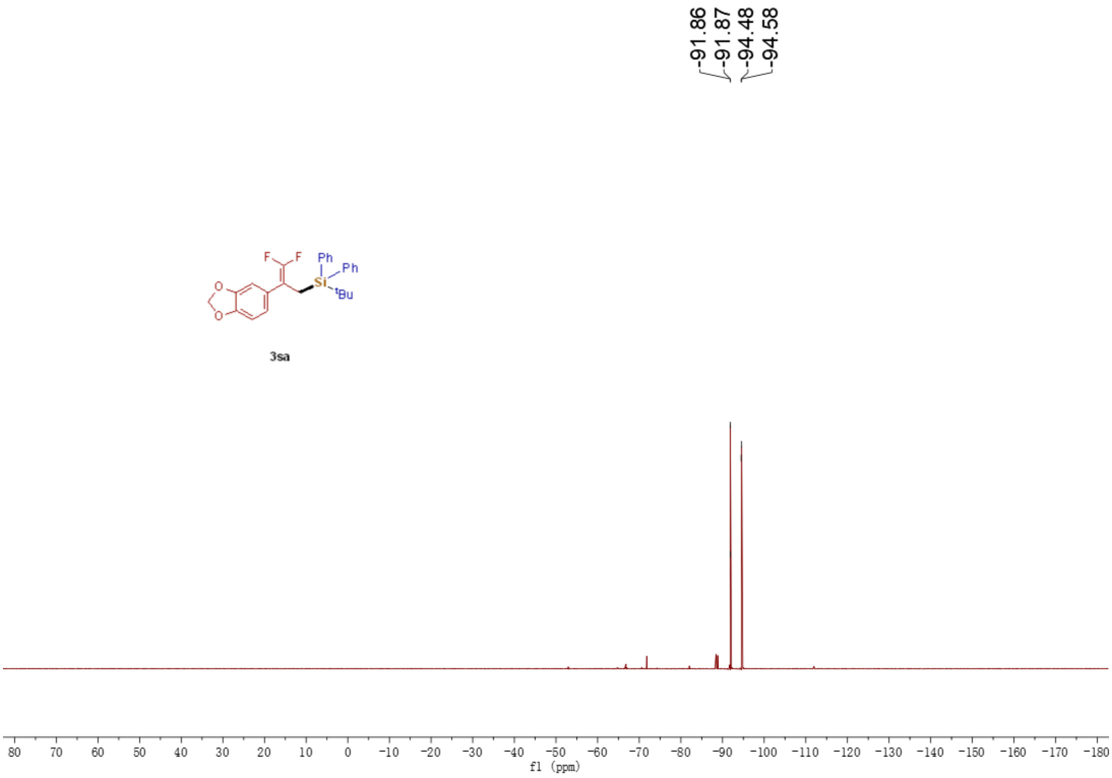


Figure S57. ^{19}F NMR spectra (471 MHz) of **3sa** in $CDCl_3$.

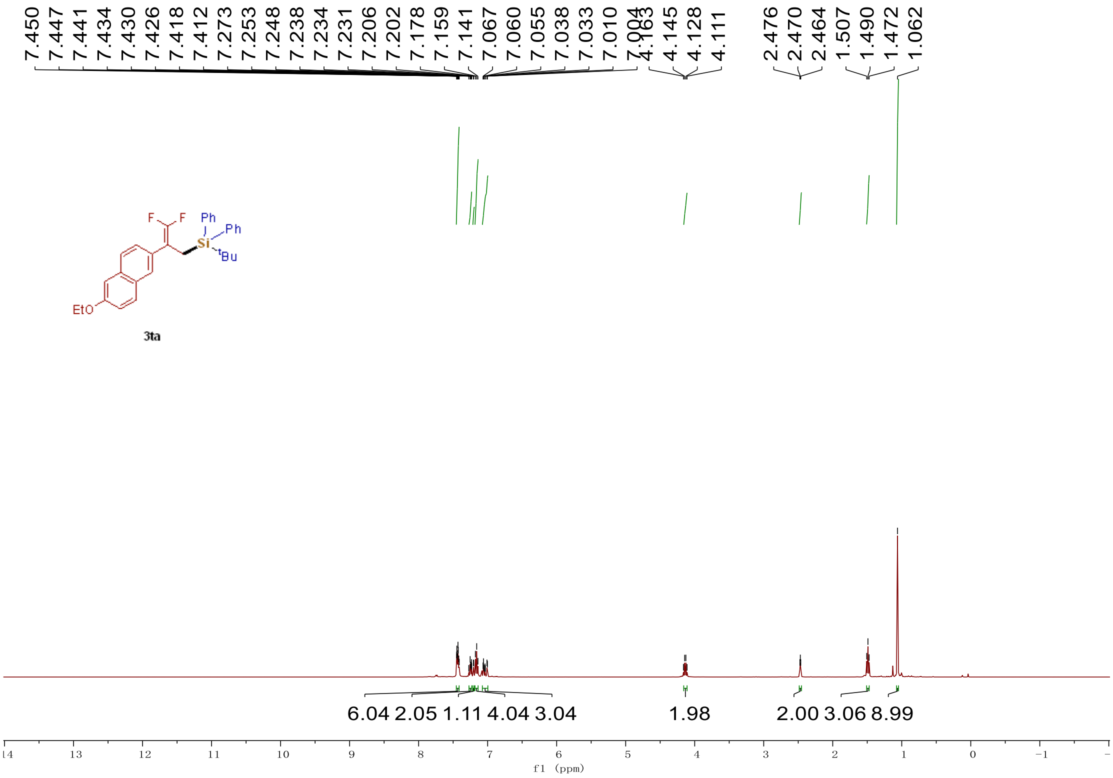


Figure S58. ^{1}H NMR spectra (400 MHz) of **3ta** in $CDCl_3$.

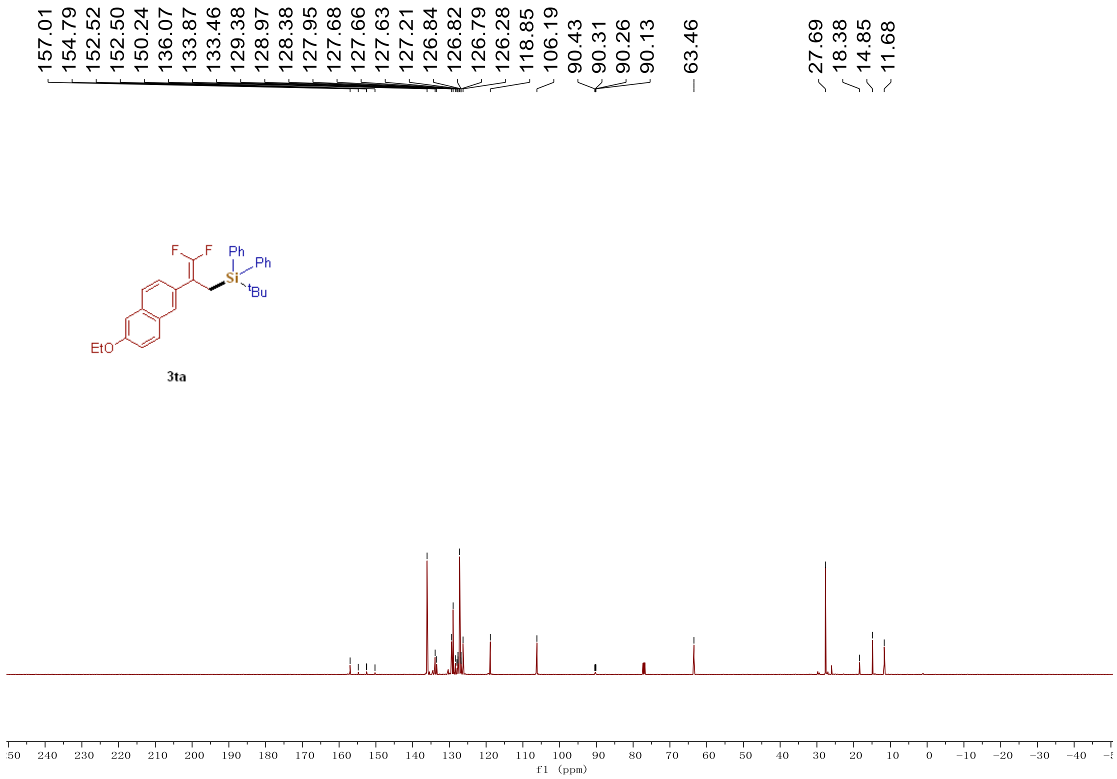


Figure S59. ^{13}C NMR spectra (126 MHz) of **3ta** in $CDCl_3$.

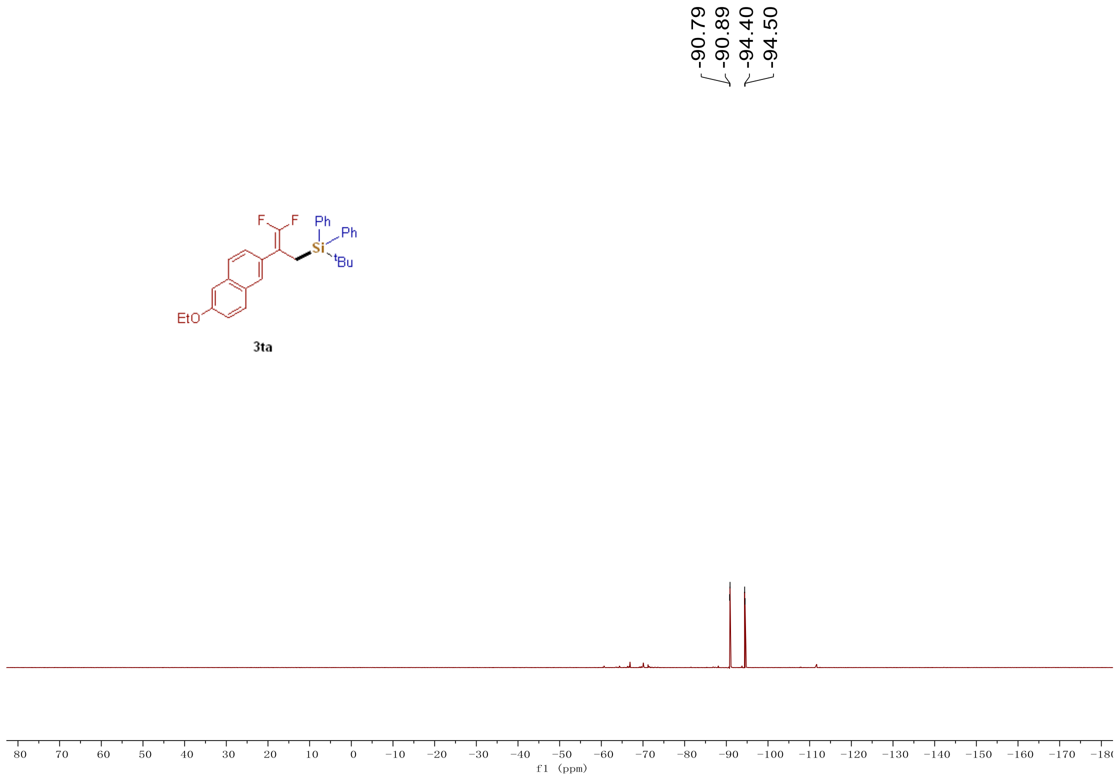


Figure S60. ^{19}F NMR spectra (471 MHz) of **3ta** in $CDCl_3$.

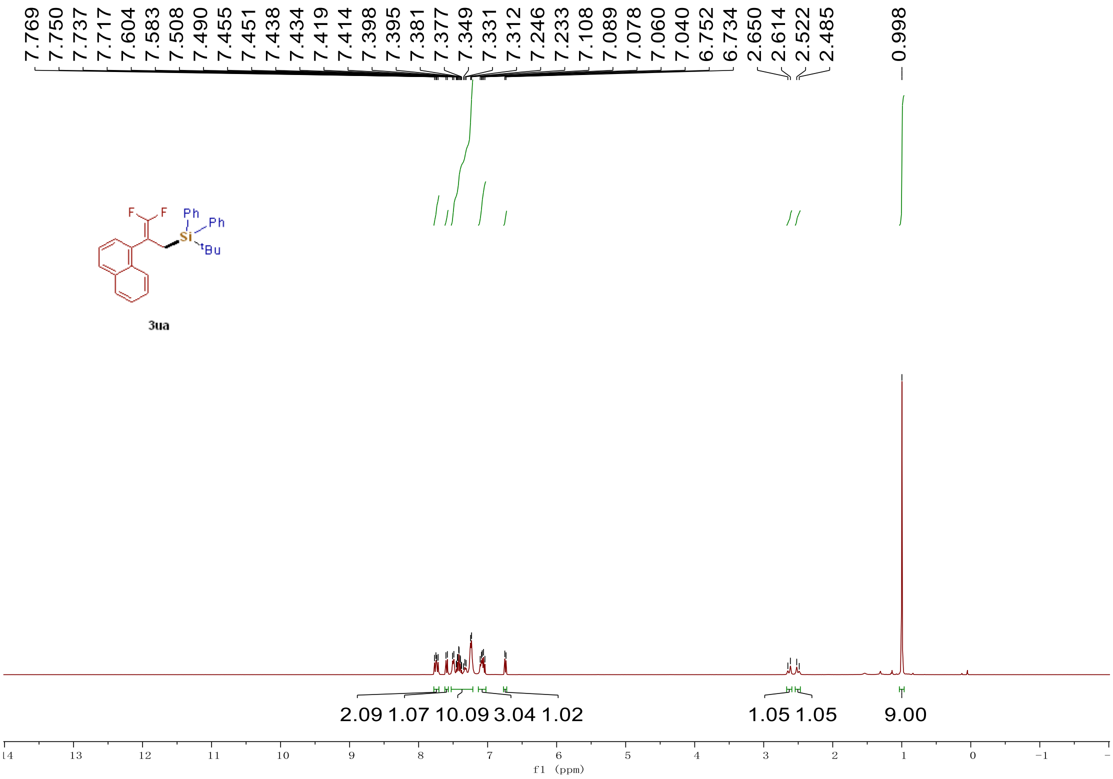


Figure S61. ^{1}H NMR spectra (400 MHz) of **3ua** in $CDCl_3$.

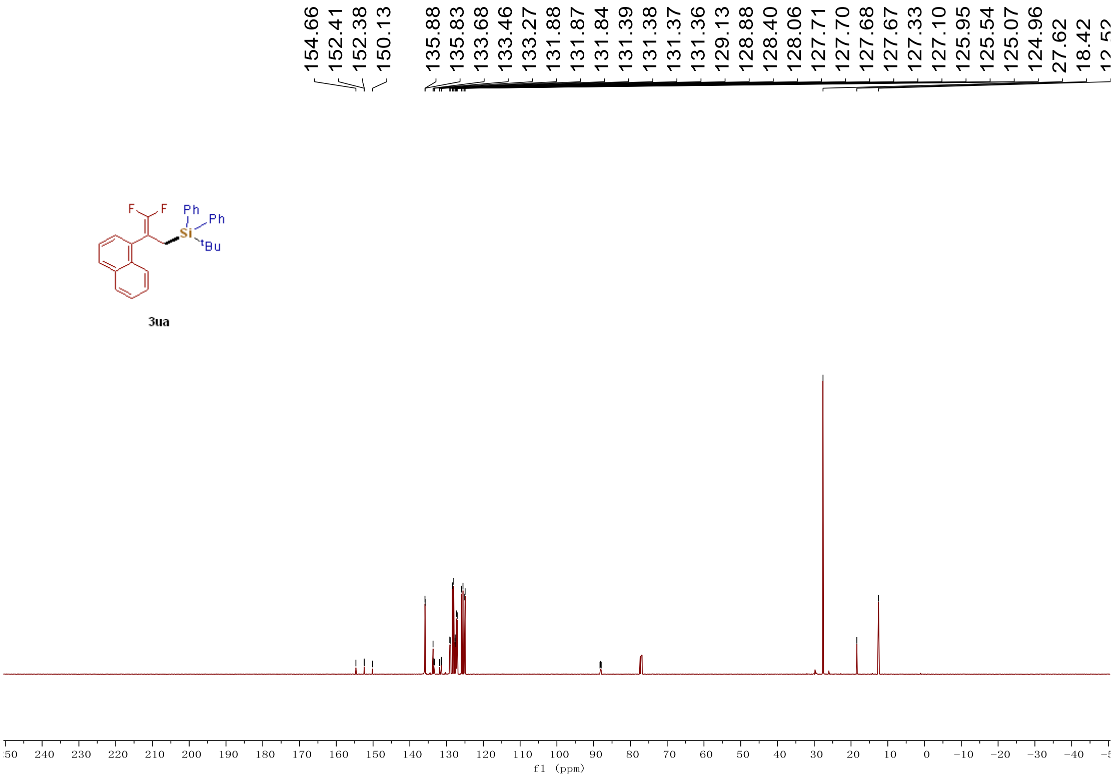


Figure S62. ^{13}C NMR spectra (126 MHz) of **3ua** in $CDCl_3$.

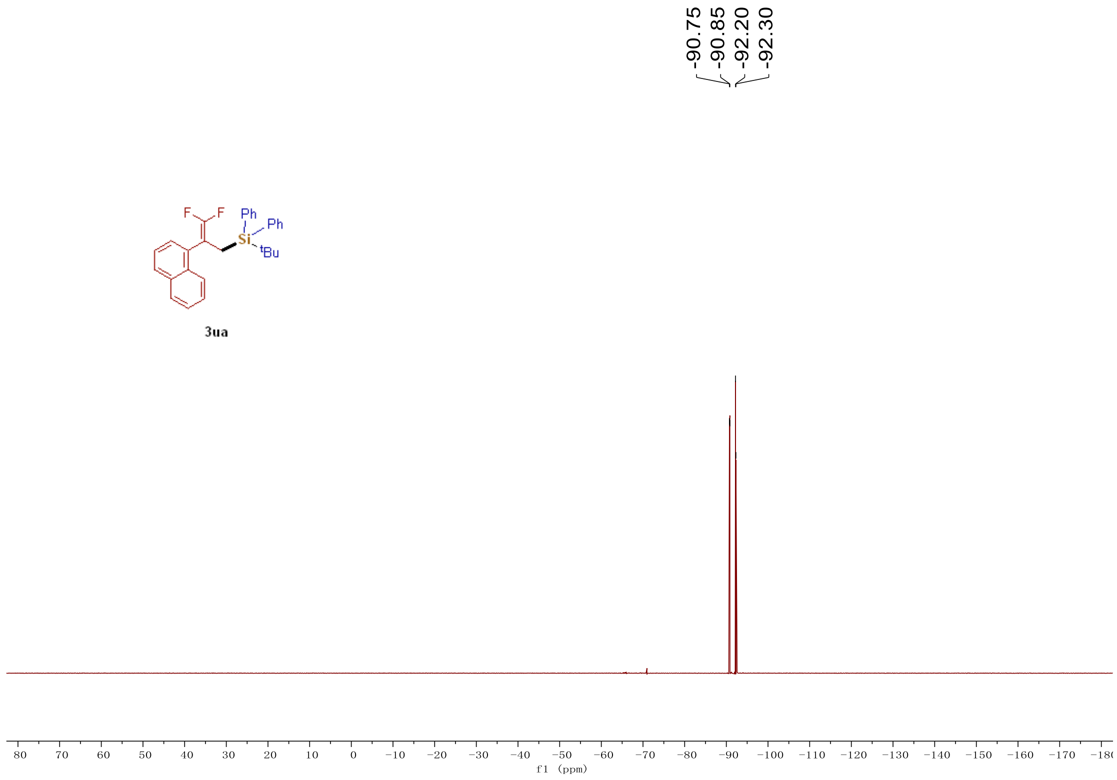


Figure S63. ^{19}F NMR spectra (471 MHz) of **3ua** in $CDCl_3$.

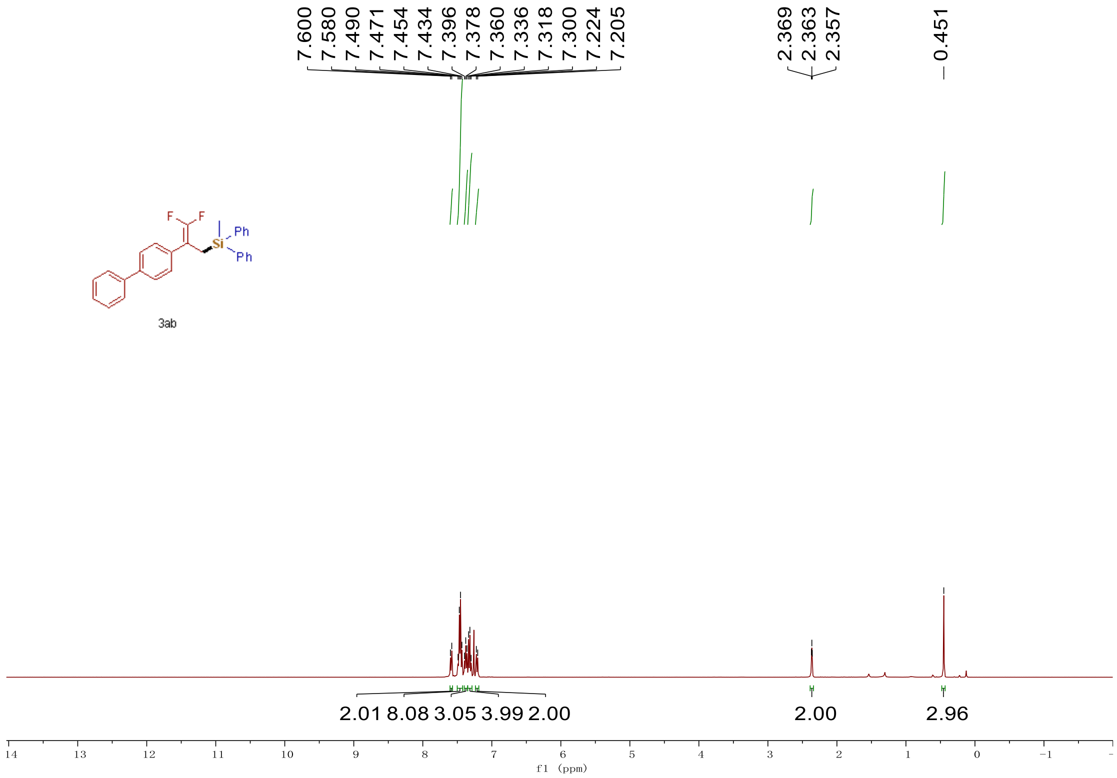


Figure S64. ^{1}H NMR spectra (400 MHz) of **3ab** in $CDCl_3$.

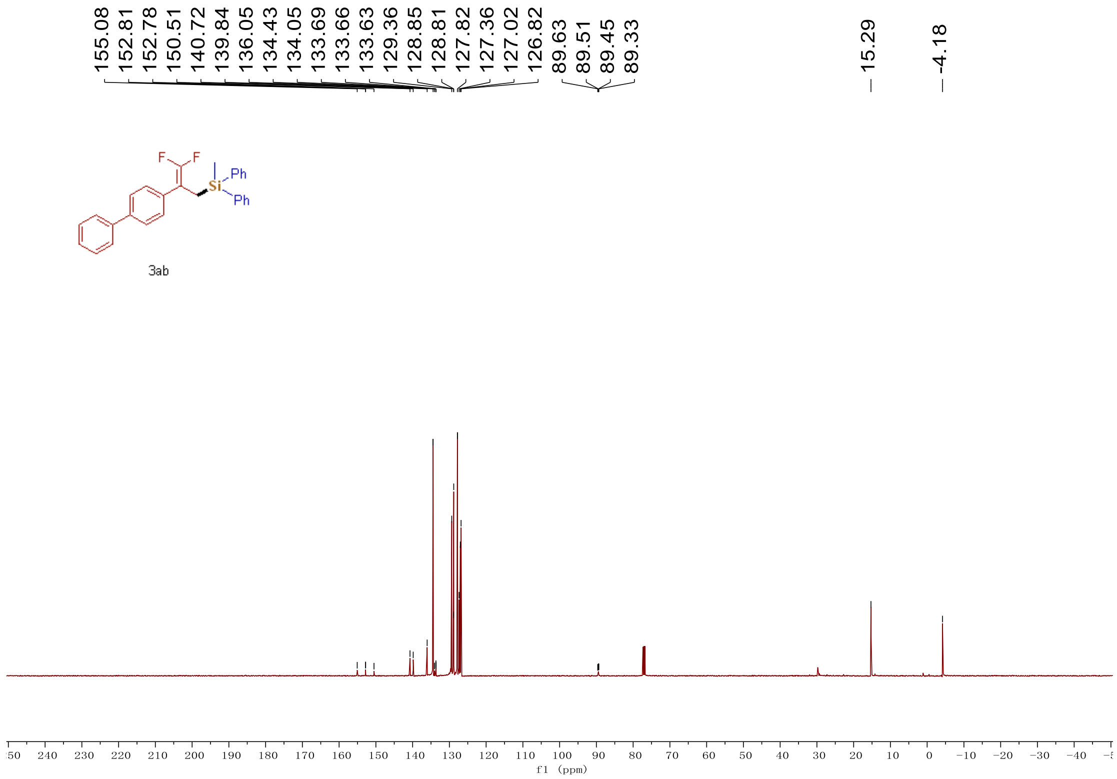


Figure S65. ^{13}C NMR spectra (126 MHz) of **3ab** in $CDCl_3$.

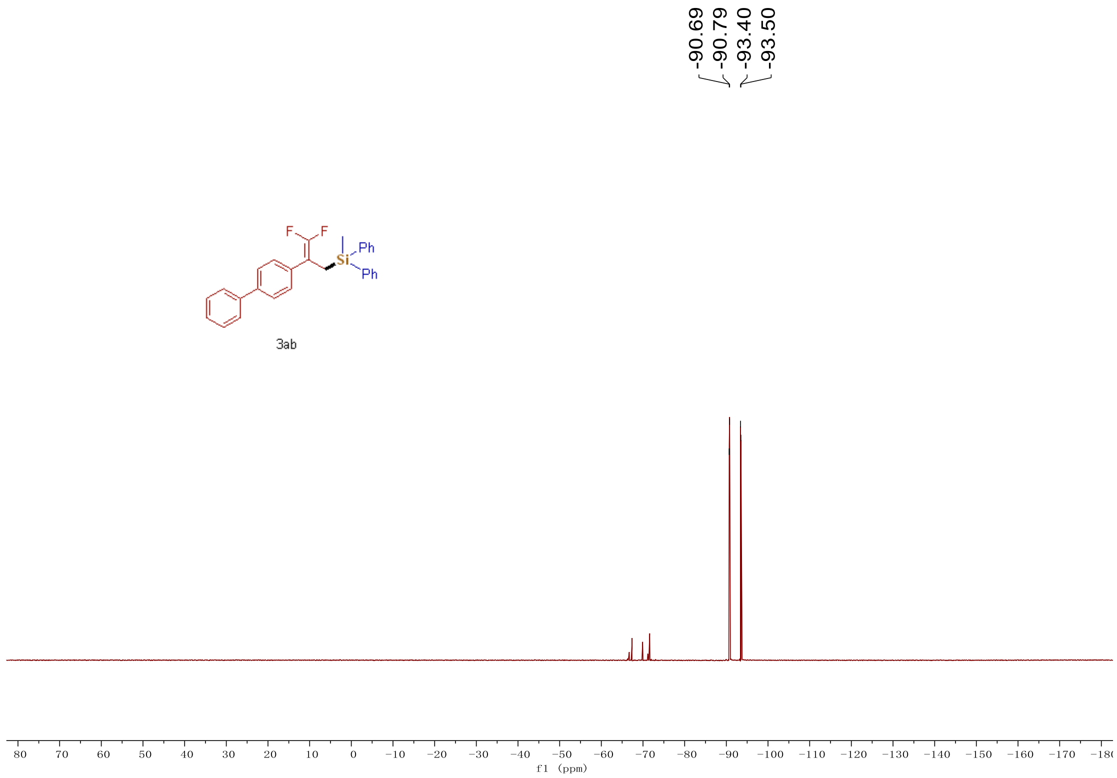


Figure S66. ^{19}F NMR spectra (471 MHz) of **3ab** in $CDCl_3$.

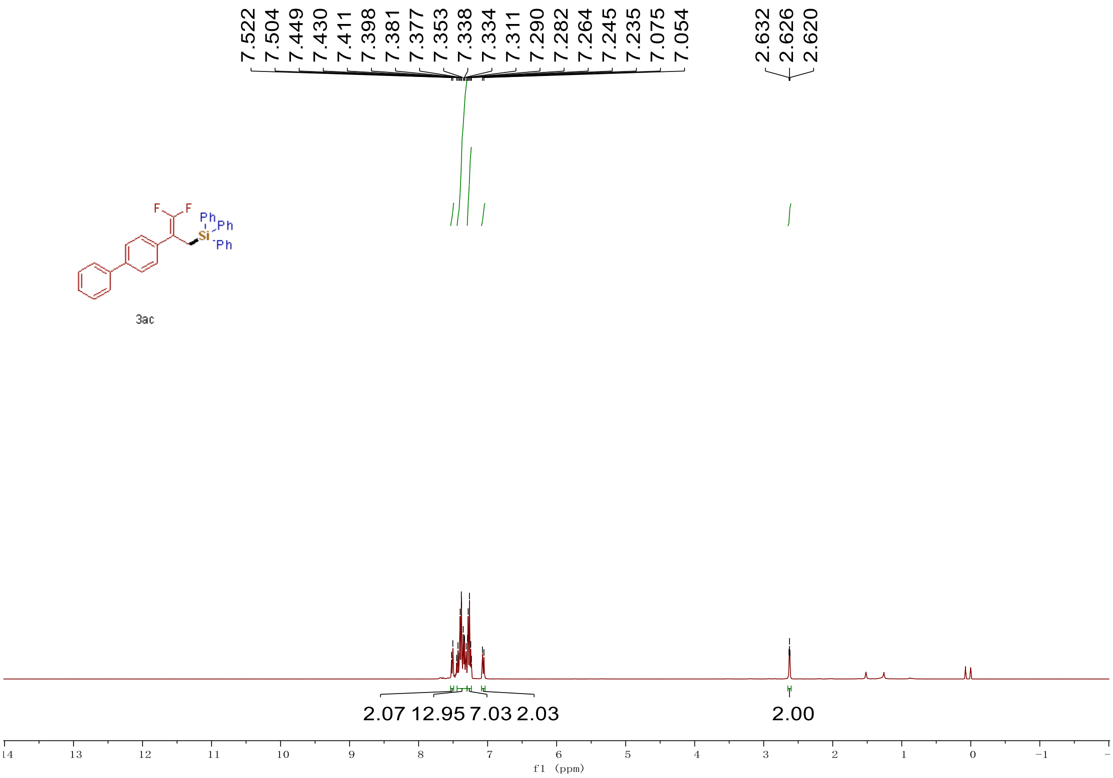


Figure S67. ^{1}H NMR spectra (400 MHz) of **3ac** in $CDCl_3$.

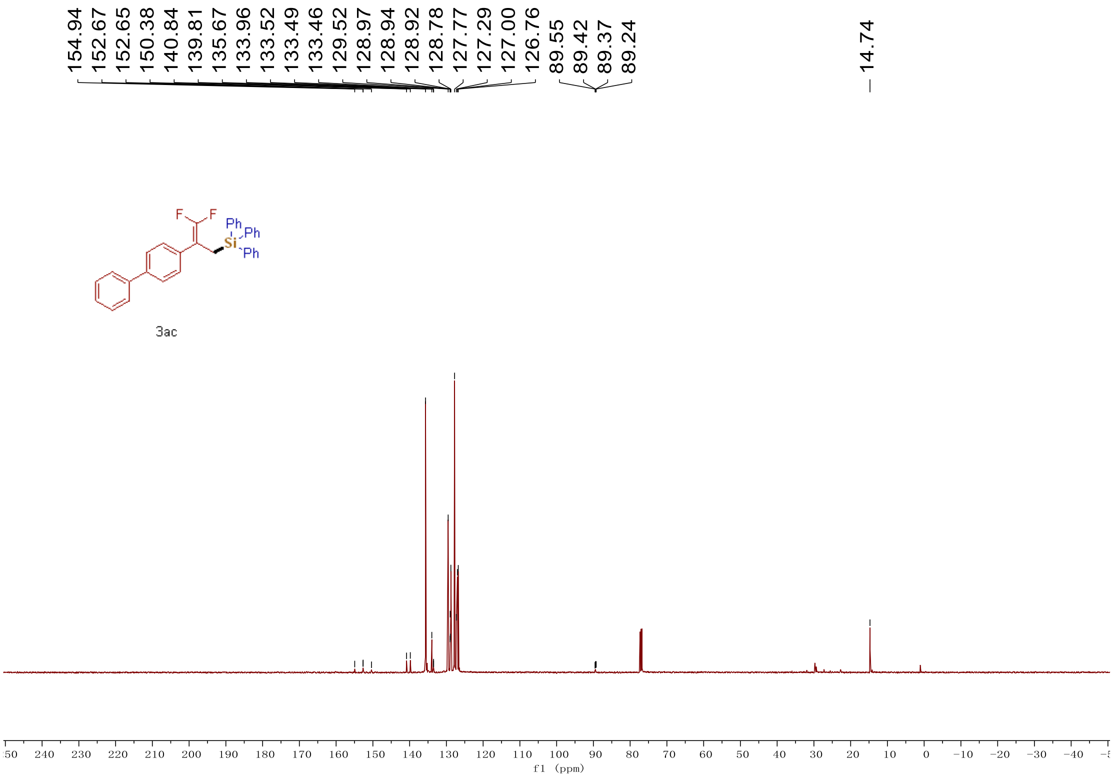


Figure S68. ^{13}C NMR spectra (126 MHz) of **3ac** in $CDCl_3$.

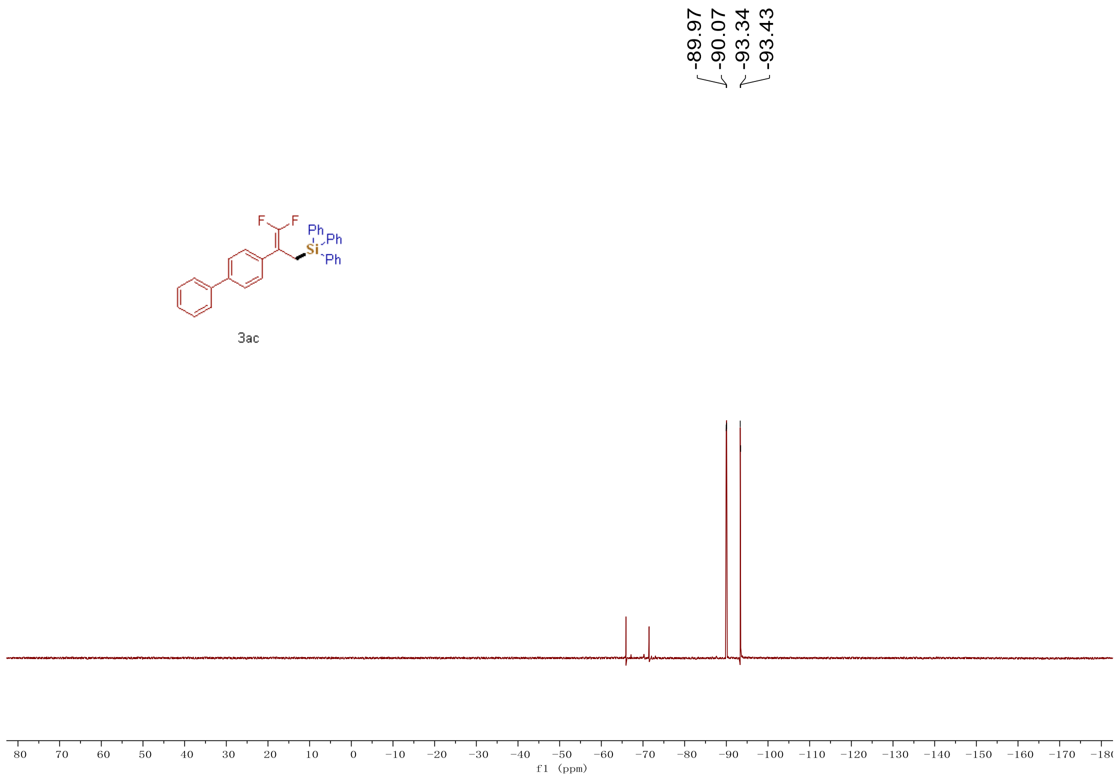


Figure S69. ^{19}F NMR spectra (471 MHz) of **3ac** in $CDCl_3$.

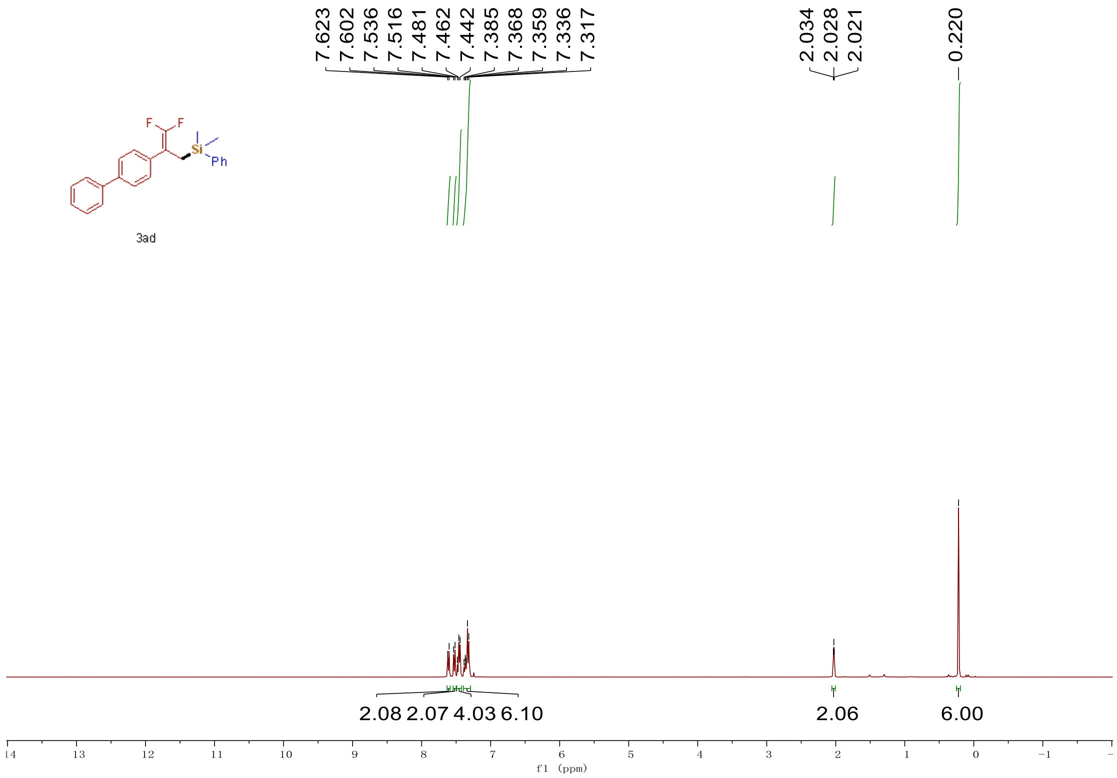


Figure S70. ^{1}H NMR spectra (400 MHz) of **3ad** in $CDCl_3$.

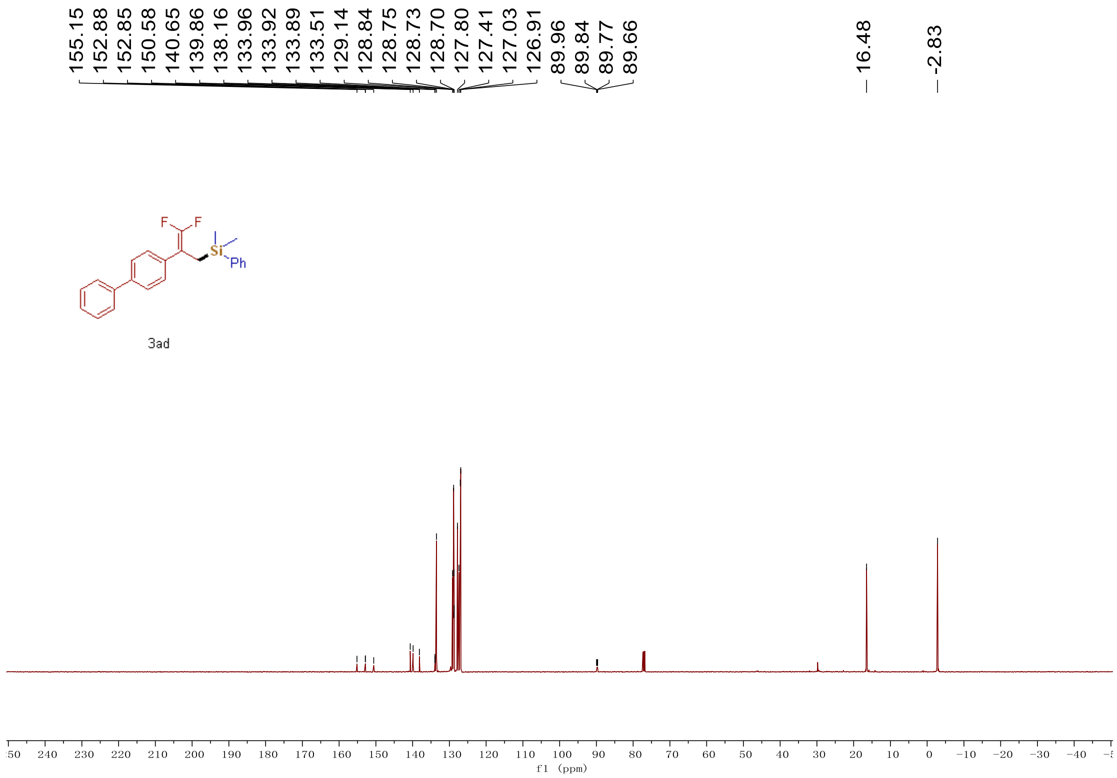


Figure S71. ^{13}C NMR spectra (126 MHz) of **3ad** in $CDCl_3$.

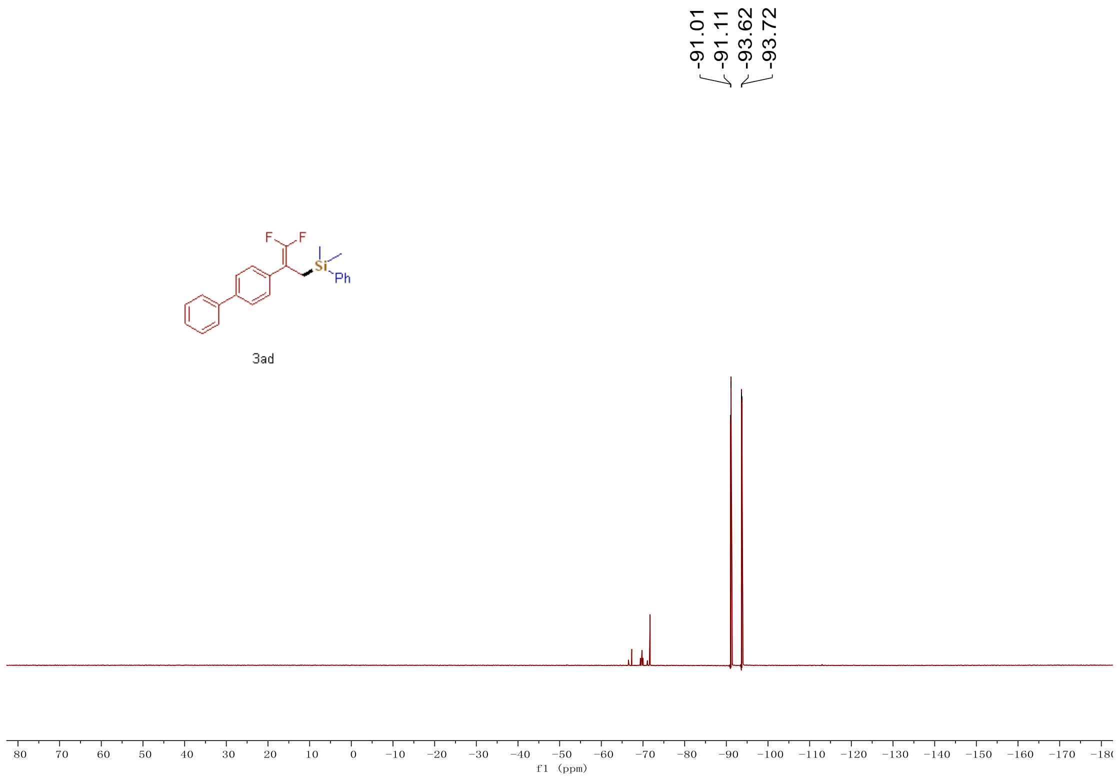


Figure S72. ^{19}F NMR spectra (471 MHz) of **3ad** in $CDCl_3$.