Electronic Supplementary Material (ESI) for ChemComm.

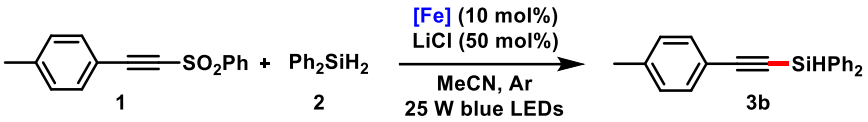
Supporting Information

1. General Information

Unless otherwise noted, Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). UV-Vis spectra was obtained on a UV-VIS-NIR spectrophotometer (SHIMADZU UV-3600). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LEDs (25 W, 440 - 445 nm) purchased from JIADENG (LS) were used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature。

2. Reaction Optimizationa

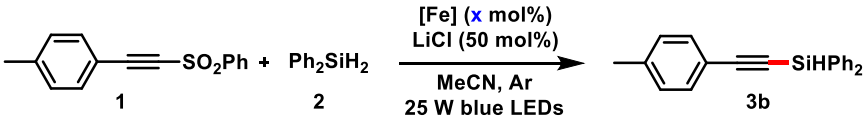
Table S1: Screening of the of iron catalyst[a]



Entry	Iron catalyst	Yield[b](%)
1	$Fe(acac)_3$	0
2	$FeCl_3$	79
3	$FeCl_2$	0
4	$Fe(acac)_2$	0

[a] Standard reaction conditions: **1** (0.3 mmol, 1.0 equiv.), **2** (2.4 mmol, 8.0 equiv.), iron catalyst (10 mol%), LiCl (50 mol%), MeCN (1 mL), 440 nm blue LEDs, room temperature (RT), Ar, 24 h. [b] Isolated yields are provided.

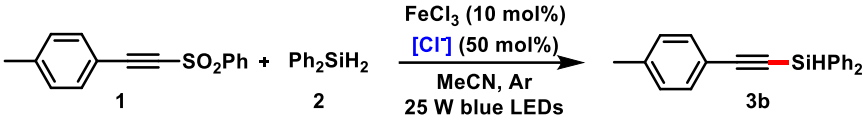
Table S2: Screening of the amount of iron catalyst[a]



Entry	Amount of iron catalyst	Yield[b](%)
1	5 mol%	40
2	10 mol%	79
3	20 mol%	75
4	30 mol%	65

[a] Standard reaction conditions: **1** (0.3 mmol, 1.0 equiv.), **2** (2.4 mmol, 8.0 equiv.), $FeCl_3$ (x mol%), LiCl (50 mol%), MeCN (1 mL), 440 nm blue LEDs, room temperature (RT), Ar, 24 h. [b] Isolated yields are provided.

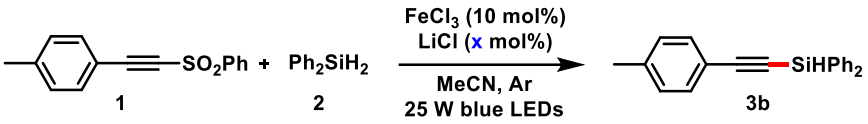
Table S3: Screening of the chlorine ion source[a]



Entry	Chlorine ion source	Yield[b](%)
1	KCl	45
2	LiCl	79
3	nBu$_4$NCl	20
4	NaCl	40

[a] Standard reaction conditions: **1** (0.3 mmol, 1.0 equiv.), **2** (2.4 mmol, 8.0 equiv.), $FeCl_3$ (10 mol%), Cl^- source (50 mol%), MeCN (1 mL), 440 nm blue LEDs, room temperature (RT), Ar, 24 h. [b] Isolated yields are provided.

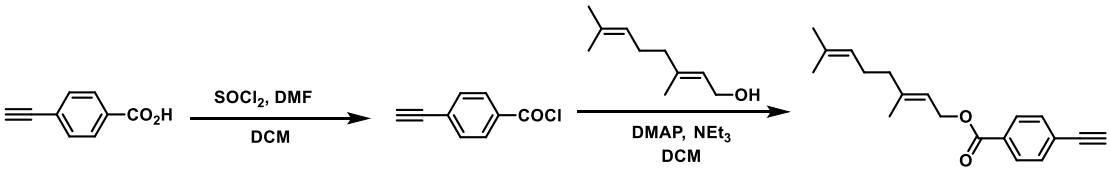
Table S4: Screening of the amount of LiCl[a]



Entry	Amount of LiCl	Yield[b](%)
1	0 mol%	30
2	20 mol%	55
3	50 mol%	79
4	100 mol%	60

[a] Standard reaction conditions: **1** (0.3 mmol, 1.0 equiv.), **2** (2.4 mmol, 8.0 equiv.), $FeCl_3$ (10 mol%), LiCl (x mol%), MeCN (1 mL), 440 nm blue LEDs, room temperature (RT), Ar, 24 h. [b] Isolated yields are provided.

3. General Synthesis of substrates[1, 2]

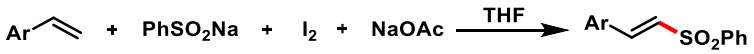


0°C, to a suspension of 4-ethynyl-benzoic acid (1.5 g, 10.0 mmol, 1.0 equiv.) and DMF (35 μL, 0.5 mmol, 0.05 equiv.) in DCM (20 mL) was added $SOCl_2$ (0.9 mL, 6.0 mmol, 1.2 equiv.) in 10 min. The mixture was degassed by Ar and reacted at room temperature overnight until the acid was completely dissolved. The mixture was concentrated in *vacuo* and without further purification to go through next step.

0°C, to a suspension of Geraniol (1.0 equiv), DMAP (0.2 equiv) and Et_3N (1.5 equiv.) in DCM (20 mL) was added benzoyl chloride (1.0 equiv.). The mixture was degassed by Ar and reacted at room temperature overnight. The mixture was quenched by saturated $NaHCO_3$ and extracted with DCM. The combined organic phases were washed with H_2O (20 mL), brine (20 mL), dried with $NaSO_4$, then filtered and concentrated in *vacuo*. The crude product was purified by flash column

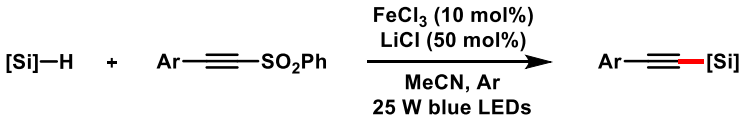
chromatography.

To a suspension of benzenesulfinic acid sodium salt (1.64 g, 10.0 mmol, 2.0 equiv.) in THF (25 mL) was added Alkynes (5.0 mmol, 1.0 equiv.) followed by iodine (0.2 g, 2.5 mmol, 0.5 equiv.), TBHP (15 mmol, 3.0 equiv). The mixture was stirred for 16 h at room temperature before the excess iodine quenched with 10% aq. sodium thiosulfate. The product extracted into EA (3 x 20 mL). The combined organic phases were washed with H_2O (20 mL), brine (20 mL), dried with $NaSO_4$, then filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography. The spectral data is consistent with the literature data.



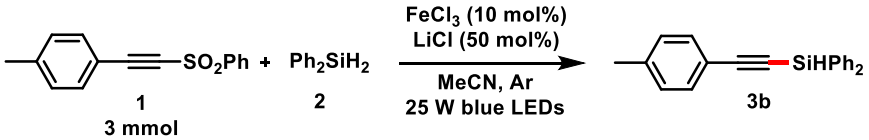
To a suspension of benzenesulfinic acid sodium salt (2.46 g, 15.0 mmol, 3.0 equiv.) and NaOAc (0.62 g, 7.5 mmol, 1.5 equiv.) in MeCN (20 mL) was added olefin (5.0 mmol, 1.00equiv.) followed by iodine (1.9 g, 7.5 mmol, 1.5 equiv.). The mixture was heated to reflux for 1 h before being allowed to cool and the excess iodine quenched with 10% aq. sodium thiosulfate. The product extracted into EA (3 x 20 mL). The combined organic phases were washed with H_2O (20 mL), brine (20 mL), dried with $NaSO_4$, then filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography. The spectral data is consistent with the literature data.

4. General Procedure for Photoredox Reactions



An oven-dried 10 mL tube equipped with a magnetic stirring bar was charged with a ethynyl phenyl sulfones (0.3 mmol, 1.0 equiv.), a hydrosilane (2.4 mmol, 8.0 equiv.), $FeCl_3$ (5 mg, 10 mol%), LiCl (6.4 mg, 50 mol%), and MeCN (1 mL). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle, and the tube was then sealed with PTFE cap. The mixture was then stirred rapidly under irradiation with 25 W blue LEDs (440–445 nm, placed approximately 2 cm from the tube) at room temperature for 24 h. The reaction mixture was concentrated in *vacuo* to remove the MeCN, and the residue was purified by flash chromatography on silica gel with elution by petroleum ether to afford the desired product.

5. Gram-scale Reaction

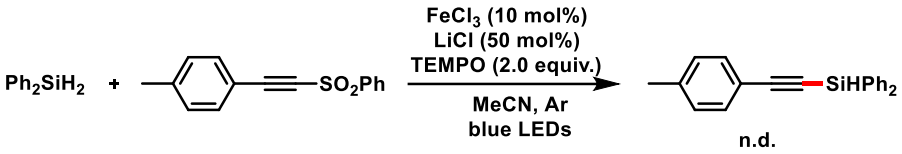


An oven-dried 100 mL three-neck Schlenk flask with magnetic stirring bar was charged with ethynyl phenyl sulfones (768 mg, 3 mmol, 1.0 equiv.), the diphenylsilanes (4.4 mL, 24 mmol, 8.0

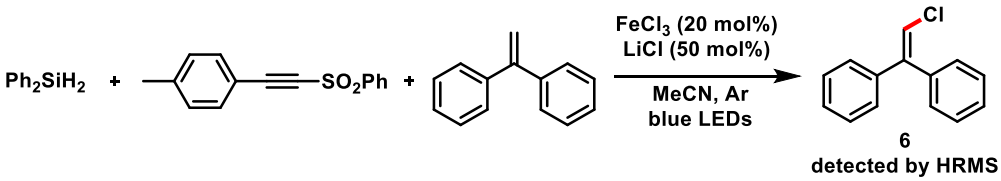
equiv.), $FeCl_3$ (50 mg, 10 mol%), LiCl (64 mg, 50%) and MeCN (10 mL). The reaction mixture was degassed by bubbling with Ar. The mixture was then stirred rapidly and irradiated with 25 W Blue LEDs at room temperature for 72 h. The reaction mixture was concentrated in *vacuo* to remove the MeCN. The mixture was diluted with DCM (50 mL) then concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel using the solvent system to afford the desired product (petroleum ether).

6. Mechanistic Studies

6.1 Radical trapping experiments

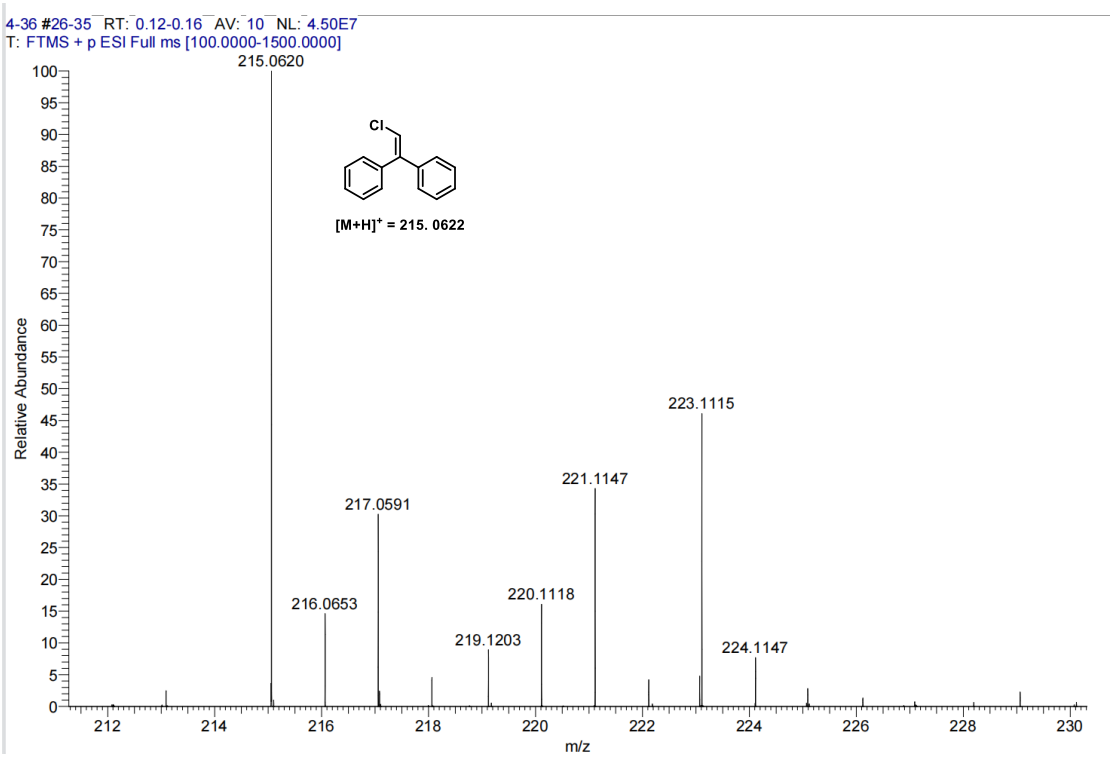


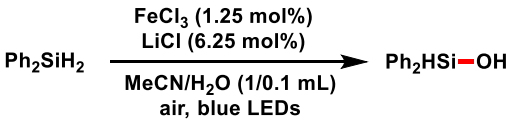
An oven-dried 10 mL tube equipped with a magnetic stirring bar was charged with ethynyl phenyl sulfones (77 mg, 0.3 mmol, 1.0 equiv.), diphenylsilane (440 μL, 2.4 mmol, 8.0 equiv.), $FeCl_3$ (5 mg, 10 mol%), LiCl (6.4 mg, 50 mol%), TEMPO (93.6 mg, 0.6 mmol, 2.0 equiv.) and MeCN (1 mL). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with 25 W Blue LEDs (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction was suppressed.



An oven-dried 10 mL tube equipped with a magnetic stirring bar was charged with ethynyl phenyl sulfones (77 mg, 0.3 mmol, 1.0 equiv.), diphenylsilane (440 μL, 2.4 mmol, 8.0 equiv.), $FeCl_3$ (5 mg, 10 mol%), LiCl (6.4 mg, 50 mol%), 1,1'-(1,2-ethenediyl) dibenzene (0.18 mL, 0.6 mmol, 2.0 equiv.) and MeCN (1 mL). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with 25 W Blue LEDs (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction was suppressed. The radical trapping product **6** can be observed by HRMS (positive mode ESI).

Figure S1. HRMS of product 6.



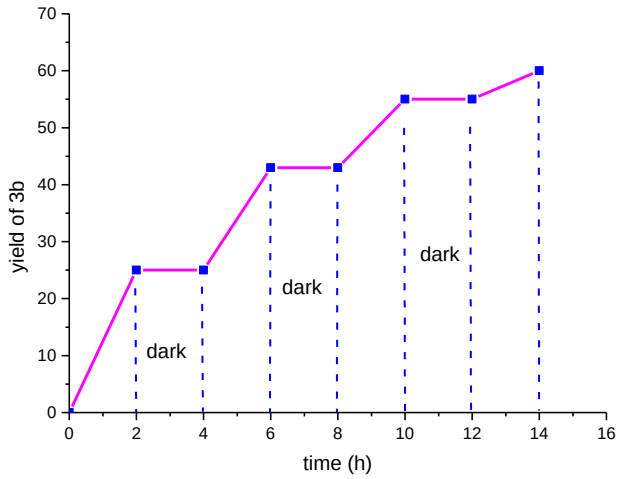


An oven-dried 10 mL tube equipped with a magnetic stirring bar was charged with Diphenylsilanes (56 μL, 0.3 mmol, 1.0 equiv.), $FeCl_3$ (0.6 mg, 1.25 mol%), LiCl (0.8 mg, 6.25%) and MeCN (1 mL). The vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with 25 W Blue LEDs (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the MeCN. The mixture was diluted with DCM (10 mL) then concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel using the solvent system to afford the desired product (petroleum ether/ethyl acetate = 20/1).

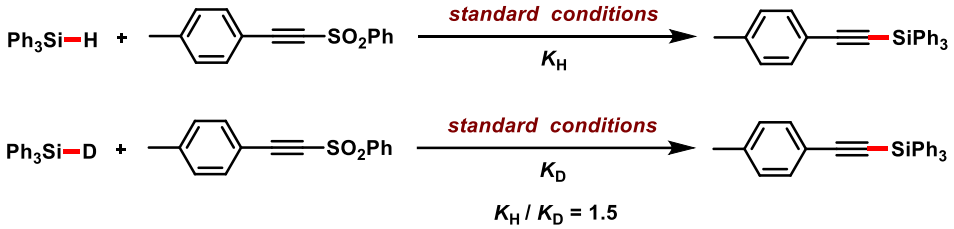
6.2 Light/dark experiment

Seven standard reaction mixtures in 10 mL glass vials were charged with ethynyl phenyl sulfones (77 mg, 0.3 mmol, 1.0 equiv.), diphenylsilane (440 μL, 2.4 mmol, 8.0 equiv.), $FeCl_3$ (5 mg, 10 mol%), LiCl (6.4 mg, 50 mol%) and MeCN (1 mL). The reaction mixtures were degassed by bubbling with Ar for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with 25 W Blue LEDs (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LEDs were turned off, and one vial was removed from the irradiation setup for analysis. The remaining six vials was stirred in the absence of light for an additional 2 h. Then, one tube was removed for analysis, and the Blue LEDs were turned back on to irradiate the remaining five reaction mixtures. After an additional 2 h of irradiation, the Blue LEDs were turned off, and one vial was removed for analysis. The remaining

four vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LEDs were turned back on to irradiate the remaining three reaction mixtures. After 2 h, the Blue LEDs were turned off, and one vial was removed for analysis. The remaining two vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LEDs were turned back on to irradiate the remaining one reaction mixtures. After 2 h, it was analyzed. The yield was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.



6.3 Parallel kinetic isotope effect experiment



Triphenylsilanes(2.4 mmol, 8.0 equiv.) or [D]-triphenylsilanes(2.4 mmol, 8.0 equiv.), ethynyl phenyl sulfones (0.3 mmol, 1.0 equiv.), $FeCl_3$ (5 mg, 10 mol%), LiCl (6.4 mg, 50%) and MeCN (1 mL) were placed in two separated tube charged with a stirring bar. The reaction mixture was degassed by bubbling with Ar. The mixture was then stirred rapidly and irradiated with 25 W Blue LEDs at room temperature for 4 h. The reaction mixture was concentrated in *vacuo* to remove the MeCN. The mixture was diluted with DCM (50 mL) then concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel using the solvent system to afford the desired product (petroleum ether). (27% and 18%). The ratio is determined to be 1.5, indicating that Si−H bond cleavage might not be the kinetically rate-determining step in this reaction.

6.4 UV-Vis experiment

Figure S2. Absorbance spectrum of iron(III) species in MeCN.

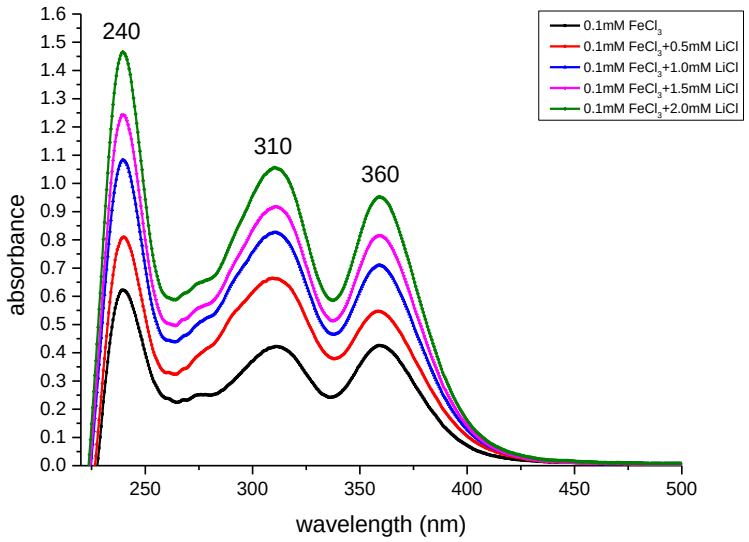
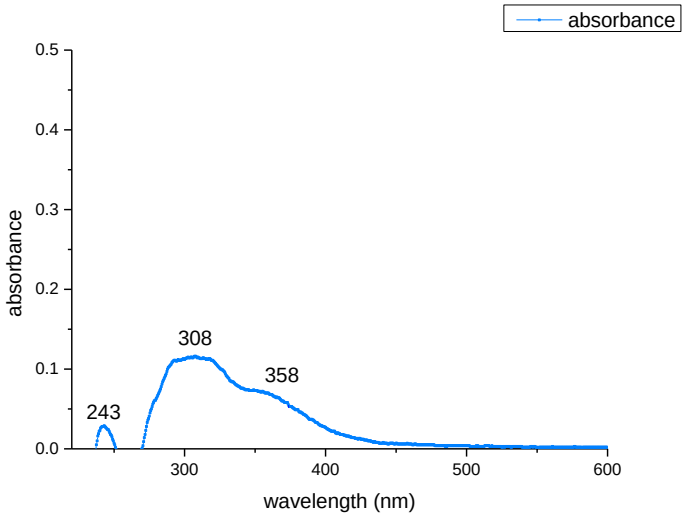
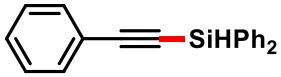


Figure S3. Absorbance spectrum of 100 μM $FeCl_3$ and 250 μM solution of LiCl in MeCN after irradiation for 24 h.



7. Characterization Data for Photoredox Products

diphenyl(phenylethynyl)silane 3a

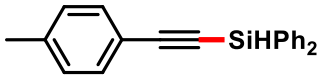


On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3a** as a colorless oil (63.9 mg, 75% yield).

R*f* = 0.7 (Petroleum ether);

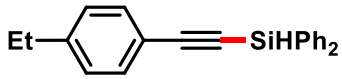
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 6.1 Hz, 4H), 7.57 – 7.52 (m, 2H), 7.46 – 7.38 (m, 6H), 7.35 – 7.29 (m, 3H), 5.31 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 134.4, 132.3, 130.2, 129.2, 128.4, 128.2, 122.5, 109.6, 87.2.
HRMS (ESI): Calcd for $C_{20}H_{16}SiNa$ $[M+Na]^+$: 307.0913; found: 307.0915

diphenyl(p-tolylethynyl)silane 3b



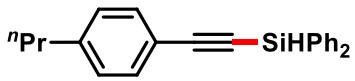
On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3b** as a white solid (70.8 mg, 79% yield).
M. p. = 66℃–67℃;
R*f* = 0.7 (Petroleum ether);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 4H), 7.47 – 7.39 (m, 8H), 7.14 (d, J = 7.2 Hz, 2H), 5.30 (s, 1H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 135.2, 132.3, 132.1, 130.1, 129.0, 128.1, 119.4, 109.9, 86.3, 21.6.
HRMS (ESI): Calcd for $C_{21}H_{18}SiNa$ $[M+Na]^+$: 321.1070; found: 321.1073

((4-ethylphenyl)ethynyl)diphenylsilane 3c



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3c** as a yellow oil (62.7 mg, 67% yield).
R*f* = 0.7 (Petroleum ether);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 4H), 7.47 (d, J = 8.2 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.15 (d, J = 8.2 Hz, 2H), 5.30 (s, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 135.2, 132.3, 132.2, 130.1, 128.1, 127.9, 119.7, 109.9, 86.3, 28.9, 15.3.
HRMS (ESI): Calcd for $C_{22}H_{20}SiNa$ $[M+Na]^+$: 335.1226; found: 335.1227

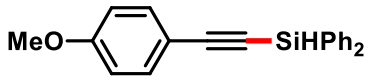
diphenyl((4-propylphenyl)ethynyl)silane 3d



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3d** as a colorless oil (62.6 mg, 64% yield).
R*f* = 0.7 (Petroleum ether);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.4 Hz, 4H), 7.47 (d, J = 7.8 Hz, 2H), 7.43 – 7.37 (m, 6H), 7.14 (d, J = 7.0 Hz, 2H), 5.30 (s, 1H), 2.58 (t, J = 7.6 Hz, 2H), 1.63 (dt, J = 14.9, 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 135.2, 132.3, 132.1, 130.1, 128.5, 128.1, 119.7, 109.9, 86.3, 38.0, 24.3, 13.7.

HRMS (ESI): Calcd for $C_{23}H_{22}SiNa$ $[M+Na]^+$: 349.1383; found: 349.1378

((4-methoxyphenyl)ethynyl)diphenylsilane 3e



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3e** as a colorless oil (69.7 mg, 74% yield).

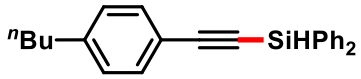
R*f* = 0.5 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 4H), 7.49 (d, J = 8.8 Hz, 2H), 7.42 – 7.38 (m, 6H), 6.84 (d, J = 8.8 Hz, 2H), 5.29 (s, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 135.2, 133.8, 132.4, 130.1, 128.1, 114.6, 113.9, 109.8, 85.5, 55.3.

HRMS (ESI): Calcd for $C_{21}H_{18}OSiNa$ $[M+Na]^+$: 337.1019; found: 337.1014

((4-butylphenyl)ethynyl)diphenylsilane 3f



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3f** as a colorless oil (63.2 mg, 62% yield).

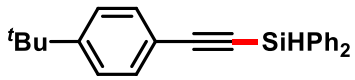
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 4H), 7.46 (d, J = 8.0 Hz, 2H), 7.43 – 7.36 (m, 6H), 7.13 (d, J = 8.0 Hz, 2H), 5.30 (s, 1H), 2.60 (t, J = 7.7 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.38 – 1.29 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 135.2, 132.3, 132.2, 130.1, 128.4, 128.1, 119.6, 110.0, 86.3, 35.7, 33.3, 22.3, 13.9.

HRMS (ESI): Calcd for $C_{24}H_{24}SiNa$ $[M+Na]^+$: 363.1539; found: 363.1535

((4-(tert-butyl)phenyl)ethynyl)diphenylsilane 3g



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3g** as a colorless oil (66.3 mg, 65% yield).

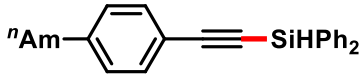
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 4H), 7.52 – 7.47 (m, 2H), 7.42 – 7.38 (m, 6H), 7.36 – 7.33 (m, 2H), 5.30 (s, 1H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 135.2, 132.4, 132.0, 130.1, 128.1, 125.3, 119.5, 109.9, 86.3, 34.9, 31.1.

HRMS (ESI): Calcd for $C_{24}H_{24}SiNa$ $[M+Na]^+$: 363.1539; found: 363.1538

((4-pentylphenyl)ethynyl)diphenylsilane 3h



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3h** as a colorless oil (64.8 mg, 61% yield).

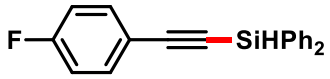
R*f* = 0.7 (Petroleum ethe);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 4H), 7.46 (d, J = 8.0 Hz, 2H), 7.43 – 7.35 (m, 6H), 7.13 (d, J = 8.0 Hz, 2H), 5.30 (s, 1H), 2.59 (t, 2H), 1.60 (dd, J = 14.7, 7.5 Hz, 2H), 1.35 – 1.26 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 135.2, 132.4, 132.2, 130.1, 128.4, 128.1, 119.6, 110.0, 86.3, 35.9, 31.4, 30.9, 22.5, 14.0.

HRMS (ESI): Calcd for $C_{25}H_{26}SiNa$ $[M+Na]^+$: 377.1696; found: 377.1694

((4-fluorophenyl)ethynyl)diphenylsilane 3i



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3i** as a colorless oil (57.1 mg, 63% yield).

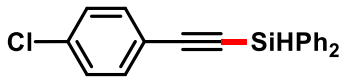
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 4H), 7.53 (dd, J = 8.6, 5.5 Hz, 2H), 7.44 – 7.39 (m, 6H), 7.02 (t, J = 8.6 Hz, 2H), 5.29 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 249 Hz), 135.2, 134.3 (d, J = 8 Hz), 132.0, 130.2, 128.2, 118.6, 115.7 (d, J = 22 Hz), 108.3, 87.0.

HRMS (EI): Calcd for $C_{20}H_{15}FSi$ $[M]^+$: 302.0927; found: 302.0920

((4-chlorophenyl)ethynyl)diphenylsilane 3j



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3j** as a colorless oil (57.2 mg, 60% yield).

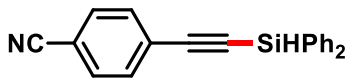
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 4H), 7.49 – 7.46 (m, 2H), 7.44 – 7.39 (m, 6H), 7.32 – 7.29 (m, 2H), 5.29 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 135.2, 133.4, 131.8, 130.2, 128.7, 128.2, 120.9, 108.1, 88.4.

HRMS (EI): Calcd for $C_{20}H_{15}ClSi$ $[M]^+$: 318.0632; found: 318.0622

4-((diphenylsilyl)ethynyl)benzonitrile 3k



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3k** as a colorless oil (51.9 mg, 56% yield).

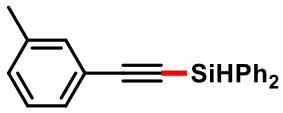
R*f* = 0.5 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 4H), 7.62 (s, 4H), 7.45 – 7.40 (m, 6H), 5.31 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.3, 132.7, 132.0, 131.3, 130.4, 128.3, 127.2, 112.5, 107.0, 92.6.

HRMS (EI): Calcd for $C_{21}H_{15}NSi$ $[M]^+$: 309.0974; found: 309.0967

diphenyl(m-tolylethynyl)silane 3l



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3l** as a colorless oil (68.8 mg, 77% yield).

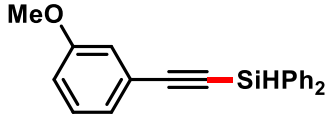
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 4H), 7.44 – 7.37 (m, 8H), 7.24 – 7.20 (m, 1H), 7.16 (d, J = 7.6 Hz, 1H), 5.30 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 135.8, 135.2, 132.8, 132.2, 130.1, 129.3, 128.2, 122.3, 109.8, 100.0, 86.7, 21.2.

HRMS (ESI): Calcd for $C_{21}H_{18}SiNa$ $[M+Na]^+$: 321.1070; found: 321.1066

((3-methoxyphenyl)ethynyl)diphenylsilane 3m



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3m** as a colorless oil (62.2 mg, 66% yield).

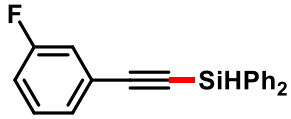
R*f* = 0.6 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.5, 1.5 Hz, 4H), 7.43 – 7.39 (m, 6H), 7.23 – 7.20 (m, 1H), 7.16 (d, 1H), 7.07 (s, 1H), 6.91 (dd, J = 8.2, 1.8 Hz, 1H), 5.30 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 135.2, 132.1, 130.2, 129.4, 128.2, 124.8, 123.4, 116.8, 116.0, 109.4, 87.0, 55.3.

HRMS (ESI): Calcd for $C_{21}H_{18}OSiNa$ $[M+Na]^+$: 337.1019; found: 337.1017

((3-fluorophenyl)ethynyl)diphenylsilane 3n



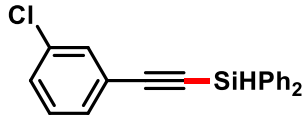
On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3n** as a colorless oil (48.9 mg, 54% yield).

R*f* = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 4H), 7.45 – 7.39 (m, 7H), 7.34 – 7.30 (m, 1H), 7.27 – 7.22 (m, 1H), 7.09 – 7.02 (m, 1H), 5.30 (s, 1H).

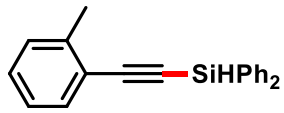
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 250 Hz), 135.2, 131.8, 130.3, 130.0 (d, J = 9 Hz), 128.2, 128.1(d, J = 3 Hz), 124.3, 119.0 (d, J = 23 Hz), 116.6 (d, J = 21 Hz), 107.9, 88.5.
HRMS (EI): Calcd for $C_{20}H_{15}FSi$ $[M]^+$: 302.0927; found: 302.0921

((3-chlorophenyl)ethynyl)diphenylsilane 3o



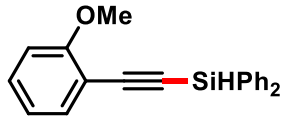
On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3o** as a colorless oil (55.3 mg, 58% yield).
R*f* = 0.7 (Petroleum ether);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 4H), 7.54 (s, 1H), 7.44 – 7.39 (m, 7H), 7.34 (d, J = 8.4 Hz, 1H), 7.25 (t, J = 3.9 Hz, 1H), 5.29 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 132.0, 131.7, 130.3, 130.2, 129.5, 129.4, 128.2, 128.1, 124.2, 107.6, 88.8.
HRMS (EI): Calcd for $C_{20}H_{15}ClSi$ $[M]^+$: 318.0632; found: 318.0626

diphenyl(o-tolylethynyl)silane 3p



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3p** as a colorless oil (70.6 mg, 79% yield).
R*f* = 0.6 (Petroleum ether);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 4H), 7.52 (d, J = 7.6 Hz, 1H), 7.44 – 7.36 (m, 6H), 7.26 – 7.19 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 5.33 (s, 1H), 2.49 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 135.2, 132.6, 132.4, 130.1, 129.5, 129.2, 128.2, 125.6, 122.3, 108.6, 91.0, 20.9.
HRMS (EI): Calcd for $C_{21}H_{18}Si$ $[M]^+$: 298.1178; found: 298.1170

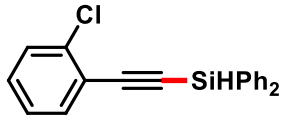
((2-methoxyphenyl)ethynyl)diphenylsilane 3q



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3q** as a colorless oil (66.5 mg, 75% yield).
R*f* = 0.5 (Petroleum ether /EtOAc = 20:1);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.5, 1.7 Hz, 4H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.41 – 7.38 (m, 6H), 7.34 – 7.30 (m, 1H), 6.91 – 6.85 (m, 2H), 5.33 (s, 1H), 3.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 135.3, 134.1, 132.5, 130.7, 130.0, 128.1, 120.4, 111.8, 110.7, 106.1, 91.3, 55.8.

HRMS (ESI): Calcd for $C_{21}H_{18}OSiNa$ $[M+Na]^+$: 337.1019; found: 337.1015

((2-chlorophenyl)ethynyl)diphenylsilane 3r



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3r** as a colorless oil (53.4 mg, 56% yield).

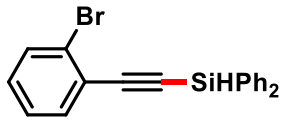
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.4 Hz, 4H), 7.59 – 7.55 (m, 1H), 7.44 – 7.38 (m, 7H), 7.30 – 7.25 (m, 1H), 7.24 – 7.19 (m, 1H), 5.33 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.3, 134.3, 133.9, 131.9, 130.2, 129.3, 128.2, 126.4, 122.5, 105.6, 93.0.

HRMS (ESI): Calcd for $C_{20}H_{15}ClSiNa$ $[M+Na]^+$: 341.0524; found: 341.0521

((2-bromophenyl)ethynyl)diphenylsilane 3s



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3s** as a colorless oil (56.5 mg, 52% yield).

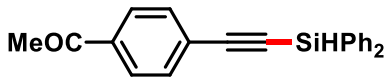
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 4H), 7.58 – 7.54 (m, 2H), 7.43 – 7.38 (m, 6H), 7.26 – 7.17 (m, 2H), 5.33 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 134.3, 134.1, 132.5, 131.9, 130.2, 128.2, 127.0, 126.0, 124.7, 107.2, 92.4.

HRMS (ESI): Calcd for $C_{20}H_{15}BrSiNa$ $[M+Na]^+$: 385.0019; found: 385.0013

1-(4-((diphenylsilyl)ethynyl)phenyl)ethan-1-one 3t



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3t** as a colorless oil (57.7 mg, 59% yield).

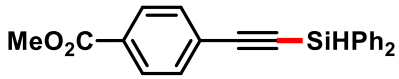
R*f* = 0.2 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 6.7 Hz, 4H), 7.63 (d, J = 8.2 Hz, 2H), 7.49 – 7.38 (m, 6H), 5.32 (s, 1H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 136.9, 135.2, 132.4, 131.6, 130.3, 128.2, 128.2, 127.2, 108.2, 91.0, 26.7.

HRMS (ESI): Calcd for $C_{22}H_{19}OSiNa$ $[M+H]^+$: 327.1200; found: 327.1194

methyl 4-((diphenylsilyl)ethynyl)benzoate 3u



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3u** as a white solid (59.5 mg, 58% yield).

M. p. = 47℃–48℃;

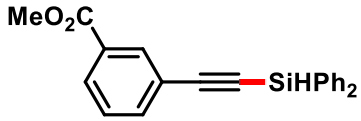
R*f* = 0.4 (Petroleum ether /EtOAc = 30:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 7.0 Hz, 4H), 7.61 (d, J = 8.2 Hz, 2H), 7.46 – 7.41 (m, 6H), 5.31 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 135.2, 132.1, 131.6, 130.3, 129.9, 129.4, 128.2, 127.0, 108.2, 90.6, 52.3.

HRMS (ESI): Calcd for $C_{22}H_{19}O_2Si$ $[M+H]^+$: 343.1149; found: 343.1148

methyl 3-((diphenylsilyl)ethynyl)benzoate 3v



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3v** as a colorless oil (65.7 mg, 64% yield).

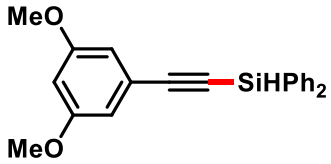
R*f* = 0.4 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.04 – 8.01 (m, 1H), 7.73 – 7.71 (m, 4H), 7.45 – 7.41 (m, 8H), 5.31 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 136.3, 135.2, 134.3, 133.3, 131.8, 130.2, 130.1, 128.5, 128.2, 122.9, 108.1, 88.5, 52.3.

HRMS (ESI): Calcd for $C_{22}H_{18}O_2SiNa$ $[M+Na]^+$: 365.0968; found: 365.0962

((3,5-dimethoxyphenyl)ethynyl)diphenylsilane 3w



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3w** as a colorless oil (55.7 mg, 54% yield).

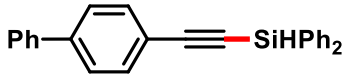
R*f* = 0.5 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 4H), 7.37 – 7.32 (m, 6H), 6.63 (d, J = 2.2 Hz, 2H), 6.41 (t, J = 2.2 Hz, 1H), 5.22 (s, 1H), 3.71 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 134.5, 134.2, 133.2, 131.0, 129.1, 127.1, 127.0, 108.9, 101.7, 54.4.

HRMS (ESI): Calcd for $C_{22}H_{21}O_2Si$ $[M+H]^+$: 345.1305; found: 345.1300

([1,1'-biphenyl]-4-ylethynyl)diphenylsilane 3x



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3x** as a white solid (74.5 mg, 69% yield).

M. p. = 60℃–61℃;

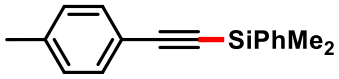
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.2 Hz, 4H), 7.62 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 8.0 Hz, 4H), 7.46 – 7.38 (m, 9H), 5.33 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.2, 135.3, 134.3, 132.7, 132.2, 130.2, 128.9, 128.2, 127.8, 127.0, 121.3, 109.5, 87.9.

HRMS (EI): Calcd for $C_{26}H_{20}Si$ $[M]^+$: 360.1334; found: 360.1324

dimethyl(phenyl)(p-tolylethynyl)silane 3y



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3y** as a colorless oil (54.0 mg, 72% yield).

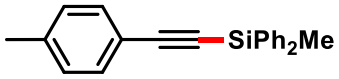
R*f* = 0.6 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.6 Hz, 2H), 7.39 (s, 5H), 7.11 (d, J = 7.1 Hz, 2H), 2.34 (s, 3H), 0.48 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.3, 133.8, 132.1, 129.5, 129.1, 128.0, 119.9, 107.1, 91.2, 21.6, -0.6.

HRMS (ESI): Calcd for $C_{17}H_{18}SiNa$ $[M+Na]^+$: 273.1070; found: 273.1064

methyldiphenyl(p-tolylethynyl)silane 3z



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3z** as a colorless oil (65.5 mg, 70% yield).

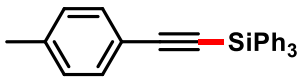
R*f* = 0.4 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.4 Hz, 4H), 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 6H), 7.10 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 135.6, 134.7, 132.2, 129.7, 129.1, 128.0, 119.9, 108.7, 89.5, 21.6, -1.7.

HRMS (ESI): Calcd for $C_{22}H_{21}Si$ $[M+H]^+$: 313.1407; found: 313.1403

triphenyl(p-tolylethynyl)silane 3aa



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3aa** as a

colorless oil (84.1 mg, 75% yield).

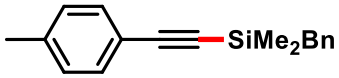
R*f* = 0.4 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 6H), 7.47 (d, J = 8.0 Hz, 2H), 7.41 – 7.35 (m, 9H), 7.11 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 135.7, 133.8, 132.2, 130.0, 129.1, 128.1, 119.7, 110.0, 88.3, 21.7.

HRMS (ESI): Calcd for $C_{27}H_{22}SiNa$ $[M+Na]^+$: 397.1383; found: 397.1378

benzyldimethyl(p-tolylethynyl)silane 3ab



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3ab** as a colorless oil (45.2 mg, 57% yield).

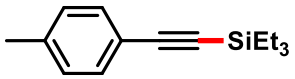
R*f* = 0.5 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.24 (d, J = 4.8 Hz, 2H), 7.12 (s, 5H), 2.34 (s, 3H), 2.27 (s, 2H), 0.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.9, 131.9, 129.1, 128.5, 128.2, 124.4, 120.0, 106.7, 91.8, 26.5, 21.6, -1.9.

HRMS (ESI): Calcd for $C_{18}H_{21}Si$ $[M+H]^+$: 265.1407; found: 265.1402

triethyl(p-tolylethynyl)silane 3ac



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3ac** as a colorless oil (42.8 mg, 62% yield).

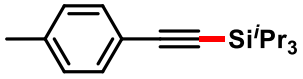
R*f* = 0.8 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H), 1.04 (t, J = 7.9 Hz, 9H), 0.67 (d, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.9, 128.9, 120.2, 106.6, 90.6, 21.5, 7.5, 4.4.

HRMS (EI): Calcd for $C_{15}H_{22}Si$ $[M]^+$: 230.1491; found: 230.1481

triisopropyl(p-tolylethynyl)silane 3ad



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3ad** as a colorless oil (32.7 mg, 40% yield).

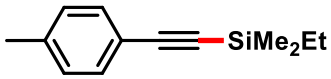
R*f* = 0.8 (Petroleum ethe);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 2.34 (s, 3H), 1.57 (s, 3H), 1.12 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 131.9, 128.9, 120.5, 107.3, 89.5, 21.5, 18.6, 11.3.

HRMS (EI): Calcd for $C_{18}H_{28}Si$ $[M]^+$: 272.1960; found: 272.1955

diethyl(methyl)(p-tolylethynyl)silane 3ae



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3ae** as a colorless oil (34.4 mg, 53% yield).

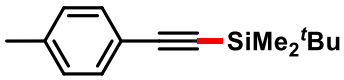
R*f* = 0.8 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H), 1.04 (t, J = 7.9 Hz, 3H), 0.66 (q, J = 7.9 Hz, 2H), 0.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 132.0, 129.0, 120.2, 105.8, 92.5, 21.6, 8.3, 7.5, -2.0.

HRMS (EI): Calcd for $C_{14}H_{20}Si$ $[M]^+$: 216.1334; found: 216. 1328

***tert*-butyldimethyl(p-tolylethynyl)silane 3af**



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3af** as a colorless oil (40.0 mg, 58% yield).

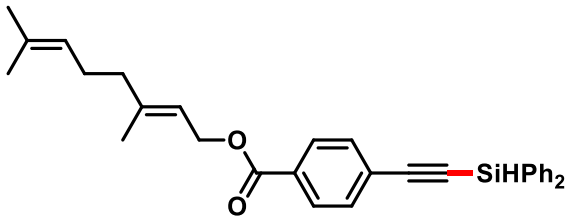
R*f* = 0.8 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H), 1.10 (s, 9H), 0.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.9, 128.9, 120.2, 106.0, 91.5, 26.1, 21.5, 16.7, -4.5.

HRMS (ESI): Calcd for $C_{15}H_{23}Si$ $[M+H]^+$: 231.1564; found: 231.1559

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-((diphenylsilyl)ethynyl)benzoate 3ag



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **3ag** as a colorless oil (62.7 mg, 45% yield).

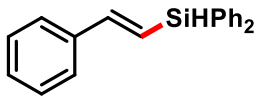
R*f* = 0.6 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 2H), 7.75 – 7.69 (m, 4H), 7.60 (d, J = 8.5 Hz, 2H), 7.48 – 7.38 (m, 6H), 5.46 (dd, J = 7.1, 6.0 Hz, 1H), 5.31 (s, 1H), 5.09 (dd, J = 7.3, 6.1 Hz, 1H), 4.84 (d, J = 7.1 Hz, 2H), 2.15 – 2.06 (m, 4H), 1.76 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 142.6, 135.2, 132.1, 131.9, 131.7, 130.7, 130.3, 129.5, 128.2, 126.8, 123.7, 118.2, 108.3, 90.5, 62.1, 39.5, 26.3, 25.7, 17.7, 16.6.

HRMS (ESI): Calcd for $C_{31}H_{33}O_2Si$ $[M+H]^+$: 465.2244; found: 465.2242

(*E*)-diphenyl(styryl)silane 4a



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4a** as a colorless oil (55.8 mg, 65% yield).

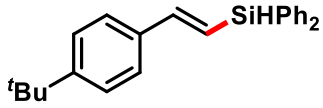
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 4H), 7.48 – 7.45 (m, 2H), 7.43 – 7.36 (m, 6H), 7.34 – 7.27 (m, 3H), 7.09 (d, J = 19.0 Hz, 1H), 6.71 (dd, J = 19.0, 3.2 Hz, 1H), 5.25 (d, J = 3.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 137.8, 135.5, 133.6, 129.8, 128.6, 128.6, 128.1, 126.7, 121.5.

HRMS (EI): Calcd for $C_{20}H_{18}Si$ $[M]^+$: 286.1178; found: 286.1168

(*E*)-(4-(tert-butyl)styryl)diphenylsilane 4b



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4b** as a colorless oil (53.4 mg, 52% yield).

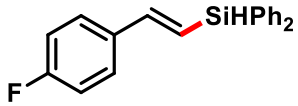
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.44 – 7.36 (m, 10H), 7.07 (d, J = 19.0 Hz, 1H), 6.66 (dd, J = 19.0, 3.2 Hz, 1H), 5.24 (d, J = 3.2 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 148.9, 135.5, 135.1, 133.7, 129.7, 128.0, 126.5, 125.5, 120.3, 34.7, 31.2.

HRMS (ESI): Calcd for $C_{24}H_{26}SiNa$ $[M+Na]^+$: 365.1696; found: 365.1690

(*E*)-(4-fluorostyryl)diphenylsilane 4c



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4c** as a colorless oil (59.3 mg, 65% yield).

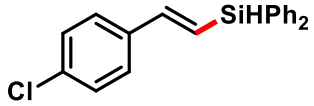
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 4H), 7.46 – 7.36 (m, 8H), 7.05 – 6.99 (m, 3H), 6.61 (dd, J = 19.0, 3.1 Hz, 1H), 5.24 (d, J = 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J = 247 Hz), 147.7, 135.5, 134.1 (d, J = 3 Hz), 133.5, 129.8, 128.4 (d, J = 8 Hz), 128.1, 121.3, 115.5 (d, J = 22 Hz).

HRMS (EI): Calcd for $C_{20}H_{17}FSi$ $[M]^+$: 304.1084; found: 304.1073

(*E*)-(4-chlorostyryl)diphenylsilane 4d



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4d** as a colorless oil (59.5 mg, 62% yield).

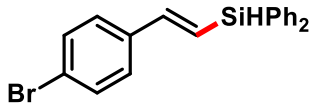
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 4H), 7.44 – 7.36 (m, 8H), 7.29 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 19.0 Hz, 1H), 6.68 (dd, J = 19.0, 3.1 Hz, 1H), 5.23 (d, J = 2.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 136.3, 135.5, 134.3, 133.3, 129.9, 128.7, 128.1, 127.9, 122.5.

HRMS (EI): Calcd for $C_{20}H_{17}ClSi$ $[M]^+$: 320.0788; found: 320.0777

(*E*)-(4-bromostyryl)diphenylsilane 4e



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4e** as a colorless oil (54.6 mg, 50% yield).

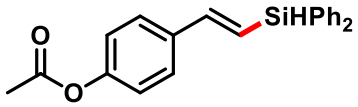
R*f* = 0.7 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.5 Hz, 4H), 7.46 – 7.36 (m, 8H), 7.30 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 19.0 Hz, 1H), 6.70 (dd, J = 19.0, 3.0 Hz, 1H), 5.23 (d, J = 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 136.7, 135.5, 133.3, 131.7, 129.9, 128.2, 128.1, 122.7, 122.6.

HRMS (EI): Calcd for $C_{20}H_{17}BrSi$ $[M]^+$: 364.0283; found: 364.0272

(*E*)-4-(2-(diphenylsilyl)vinyl)phenyl acetate 4f



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **4f** as a white solid (59.9 mg, 58% yield).

M. p. = 71℃–72℃;

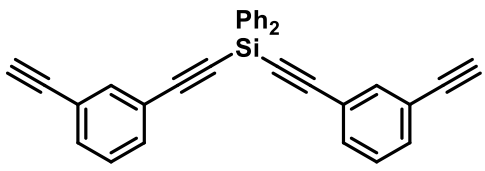
R*f* = 0.4 (Petroleum ether /EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.47 (d, J = 8.6 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.09 – 7.02 (m, 3H), 6.66 (dd, J = 19.0, 3.2 Hz, 1H), 5.24 (d, J = 3.2 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 150.8, 147.9, 135.6, 135.5, 133.4, 129.8, 128.1, 127.7, 121.9, 121.7, 21.1.

HRMS (ESI): Calcd for $C_{22}H_{20}O_2SiNa$ $[M+Na]^+$: 367.1125; found: 367.1121

bis((3-ethynylphenyl)ethynyl)diphenylsilane 5a



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was

purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **5b** as a colorless oil (45.4 mg, 35% yield).

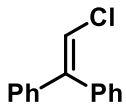
R*f* = 0.3 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 22.4 Hz, 4H), 7.42 (d, J = 8.0 Hz, 6H), 7.34 – 7.28 (m, 4H), 6.99 (d, J = 16.3 Hz, 2H), 6.37 (d, J = 16.2 Hz, 2H), 3.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 136.4, 135.0, 132.2, 131.8, 129.9, 128.8, 126.7, 123.6, 122.5, 108.9, 89.2, 82.7, 77.8.

HRMS (EI): Calcd for $C_{32}H_{20}Si$ $[M]^+$: 432.1334; found: 432.1330

(2-chloroethene-1,1-diyl)dibenzene 6



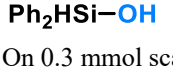
On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, petroleum ether) to give **6** as a colorless oil (5.8 mg, 9% yield).

R*f* = 0.6 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 5H), 7.22 – 7.15 (m, 5H), 6.78 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.7, 128.2, 128.1, 127.7, 127.3, 126.0.

diphenylsilanol 7



On 0.3 mmol scale. Photoredox was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 5% EtOAc in petroleum ether) to give **7** as a colorless oil (19.2 mg, 32% yield).

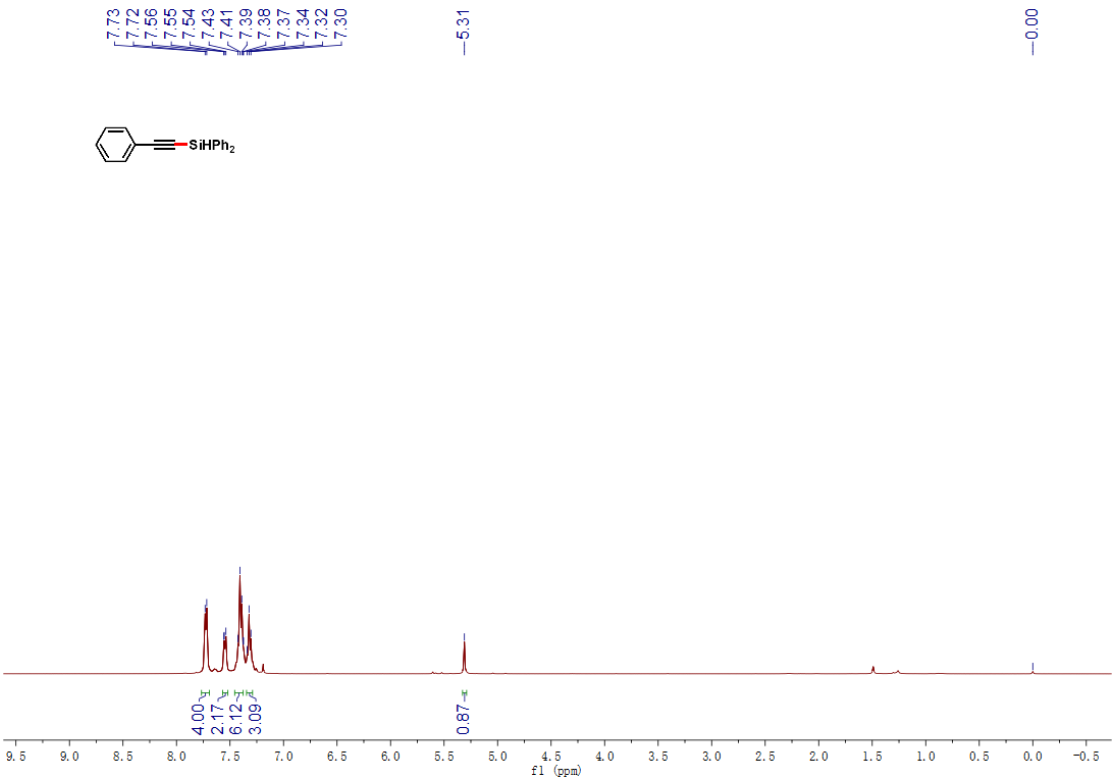
R*f* = 0.4 (Petroleum ether /EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.43-7.33 (m, 6H), 5.65 (s, 1H), 2.89 (s, 1H).

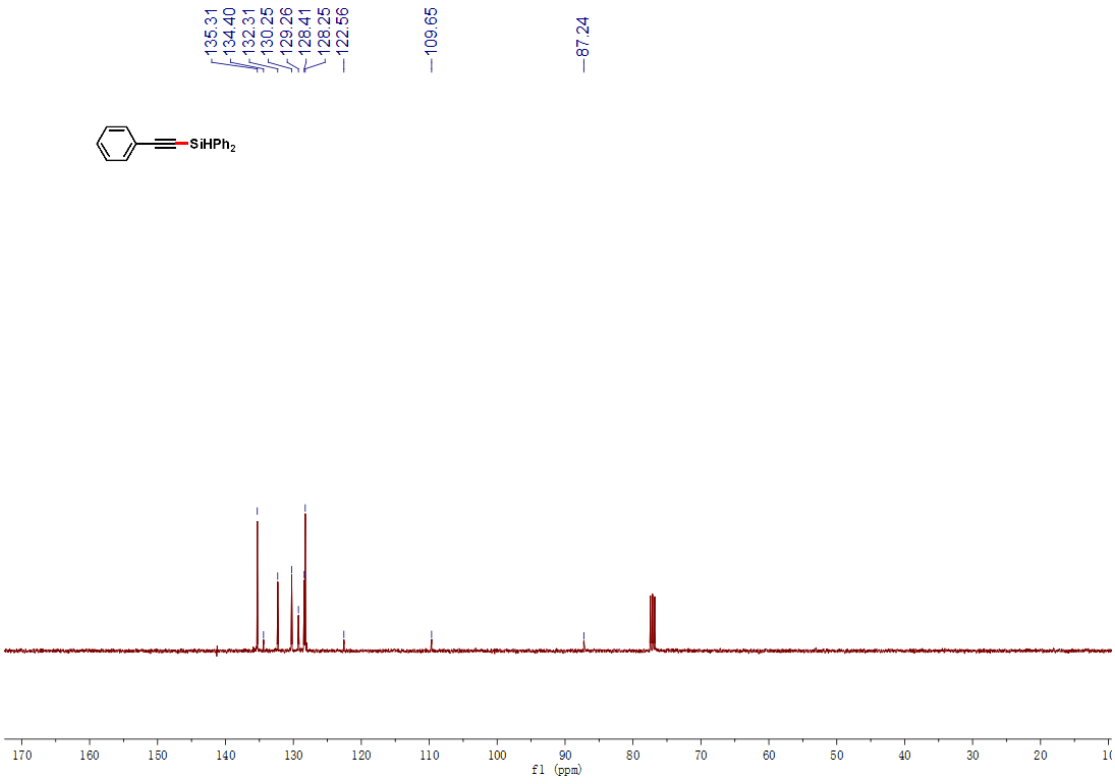
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 130.3, 128.0, 127.8.

8. Spectra of prepared compounds

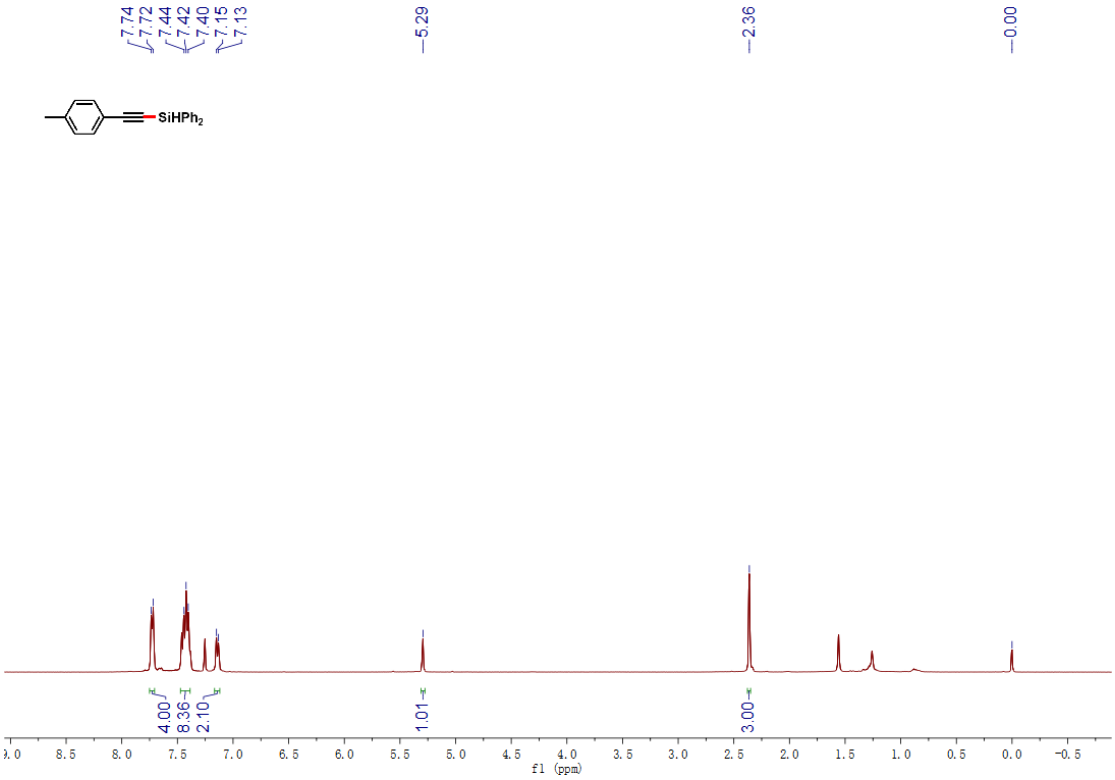
^{1}H NMR spectrum of compound **3a**



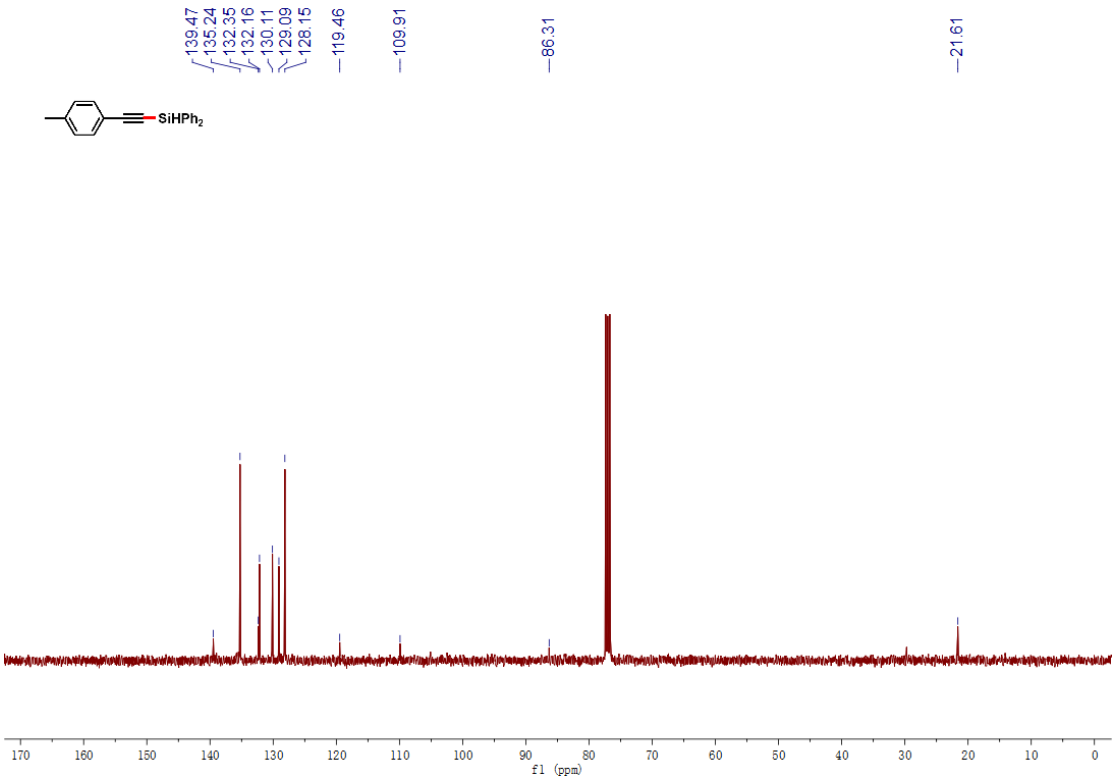
^{13}C NMR spectrum of compound **3a**



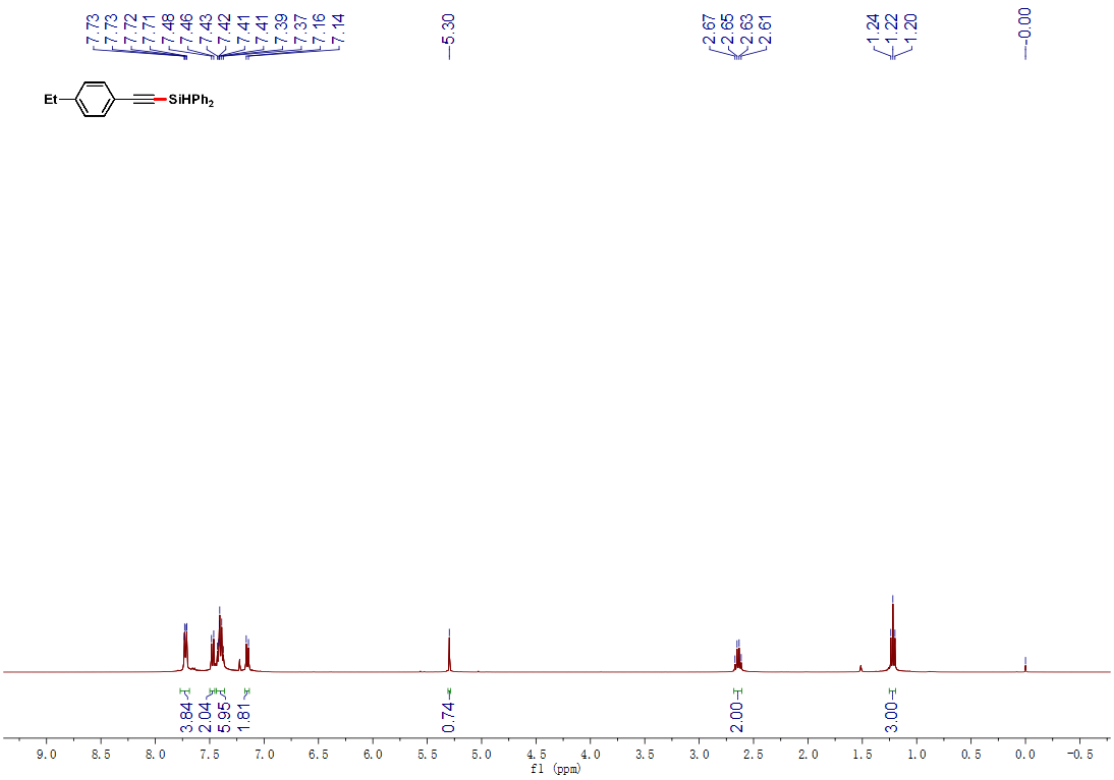
^{1}H NMR spectrum of compound **3b**



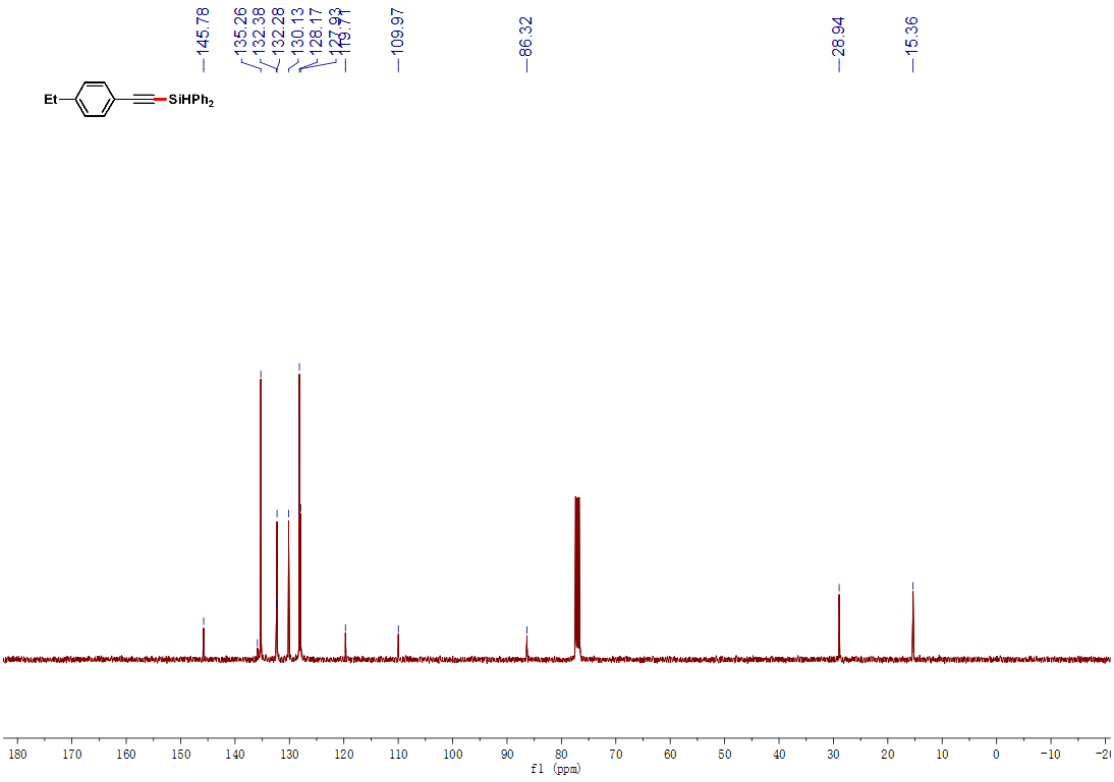
^{13}C NMR spectrum of compound **3b**



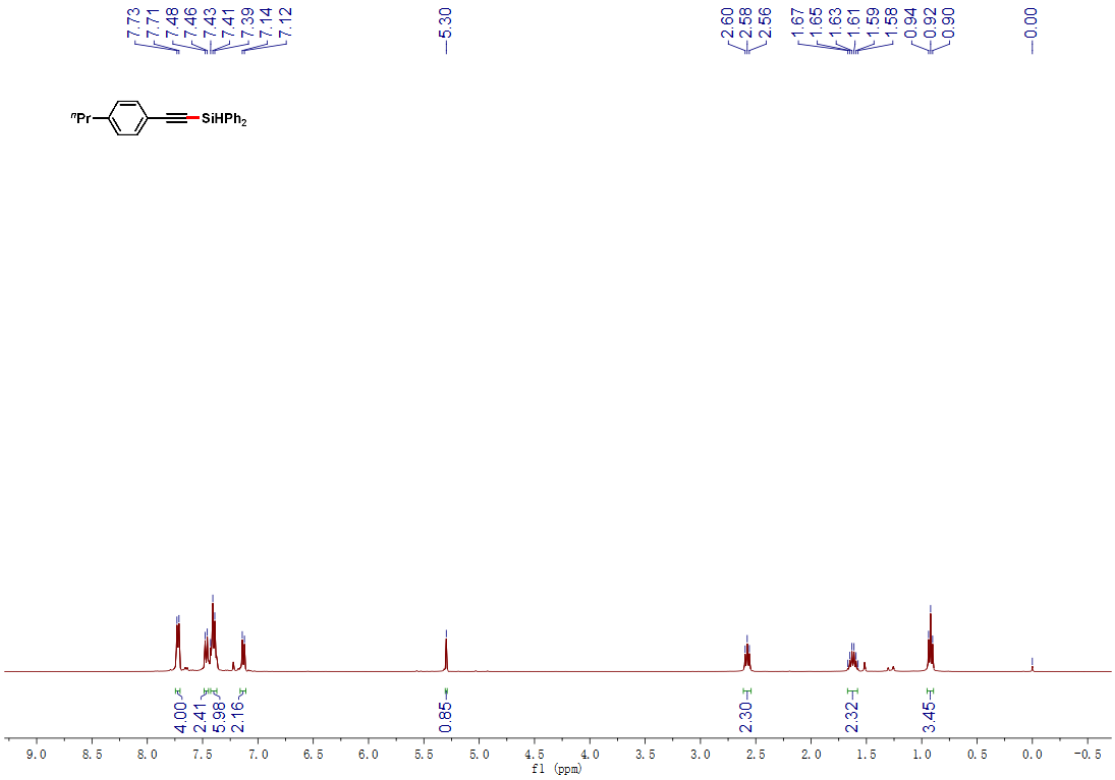
^{1}H NMR spectrum of compound **3c**



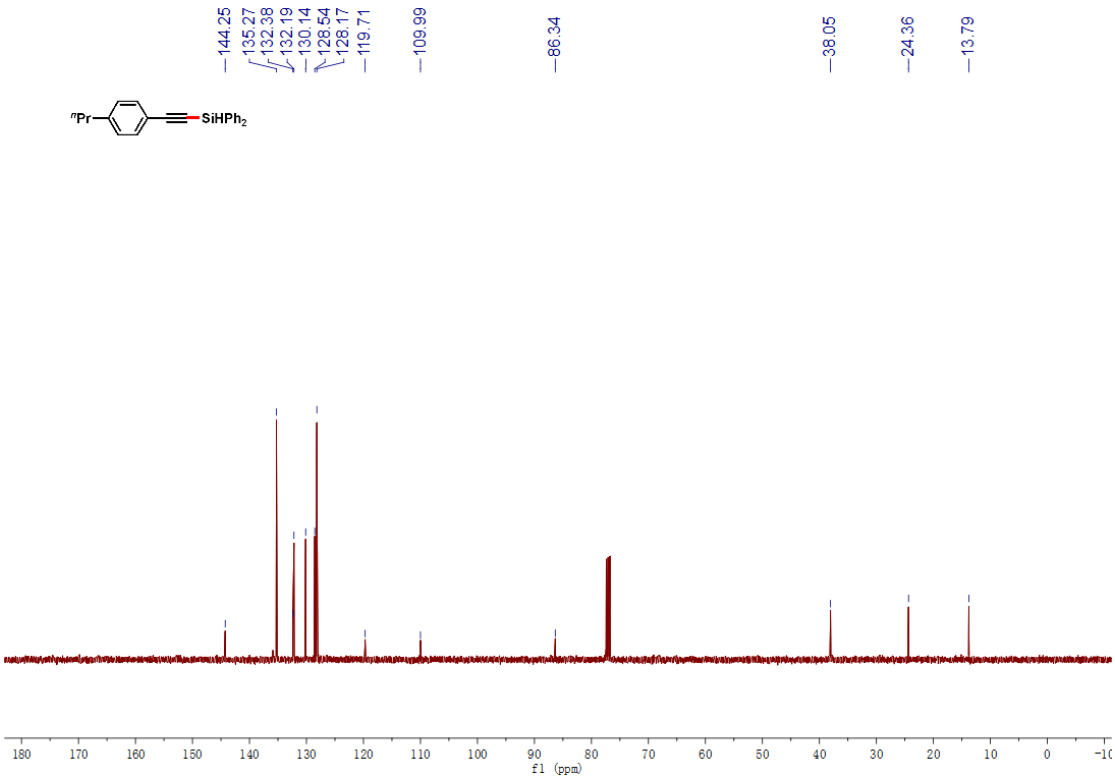
^{13}C NMR spectrum of compound **3c**



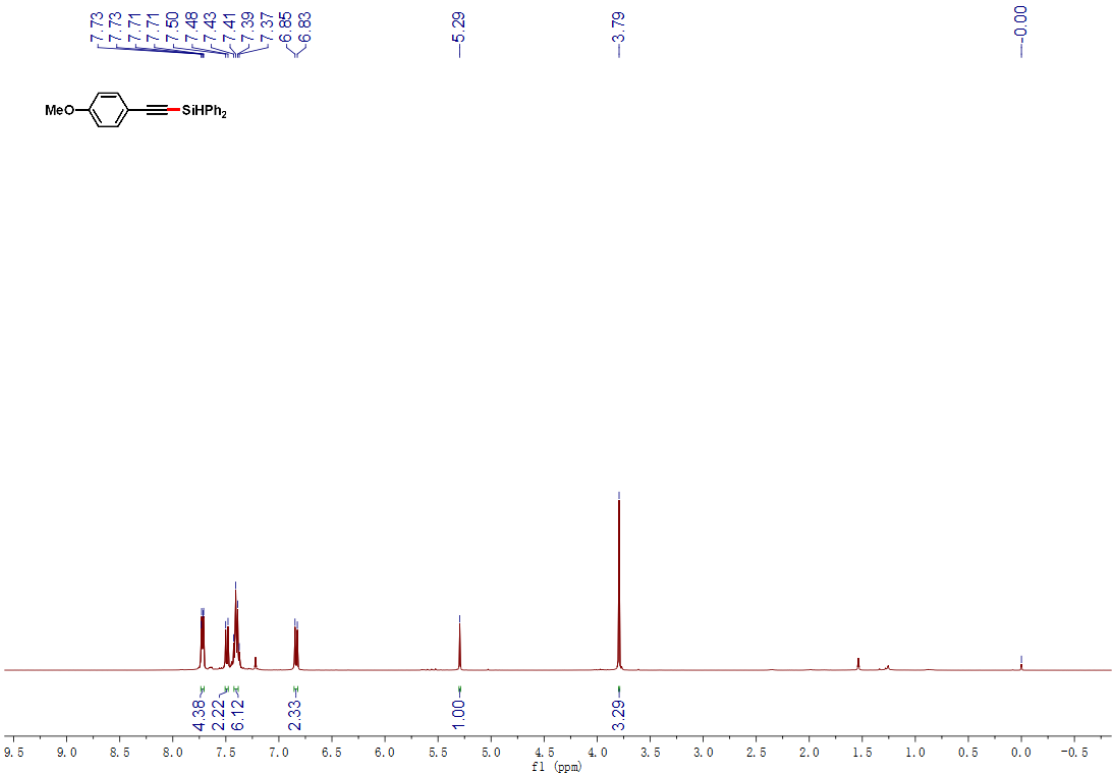
^{1}H NMR spectrum of compound **3d**



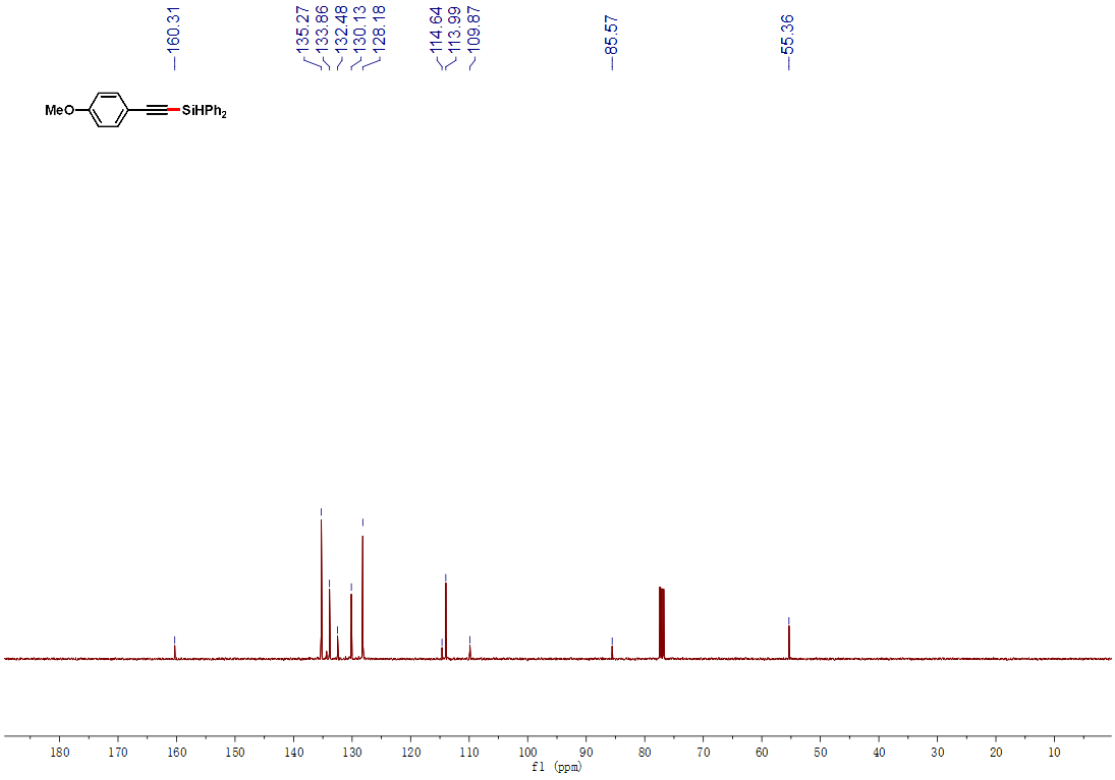
^{13}C NMR spectrum of compound **3d**



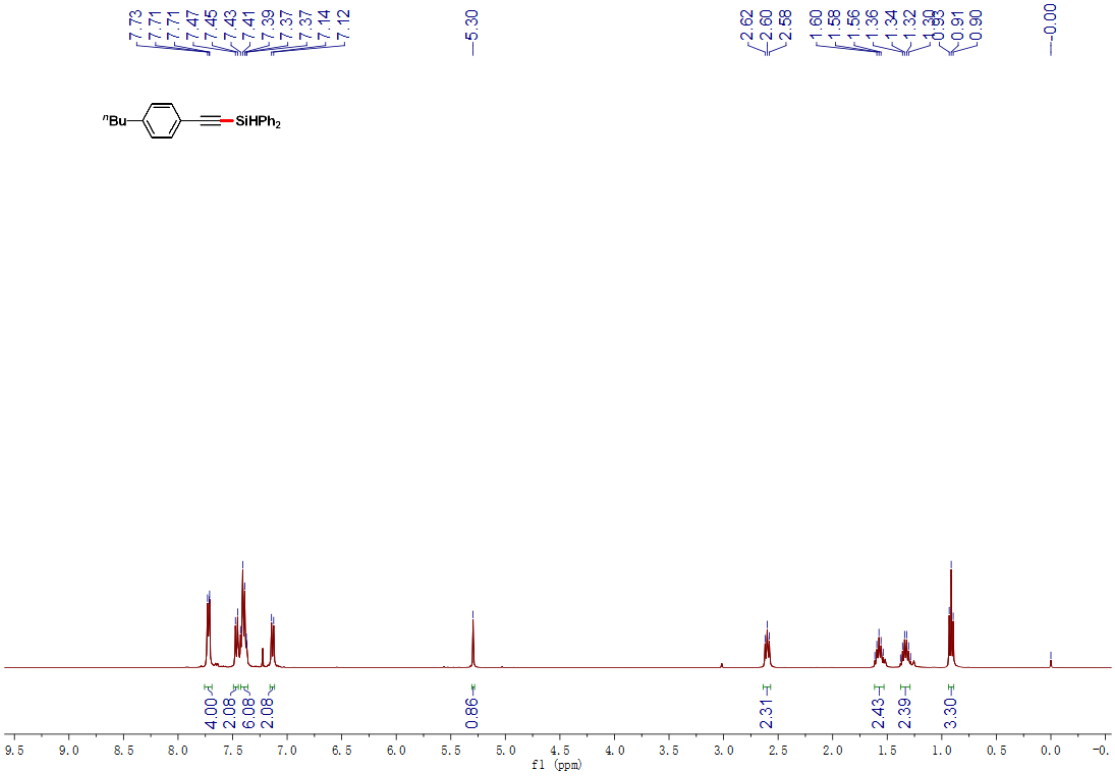
^{1}H NMR spectrum of compound **3e**



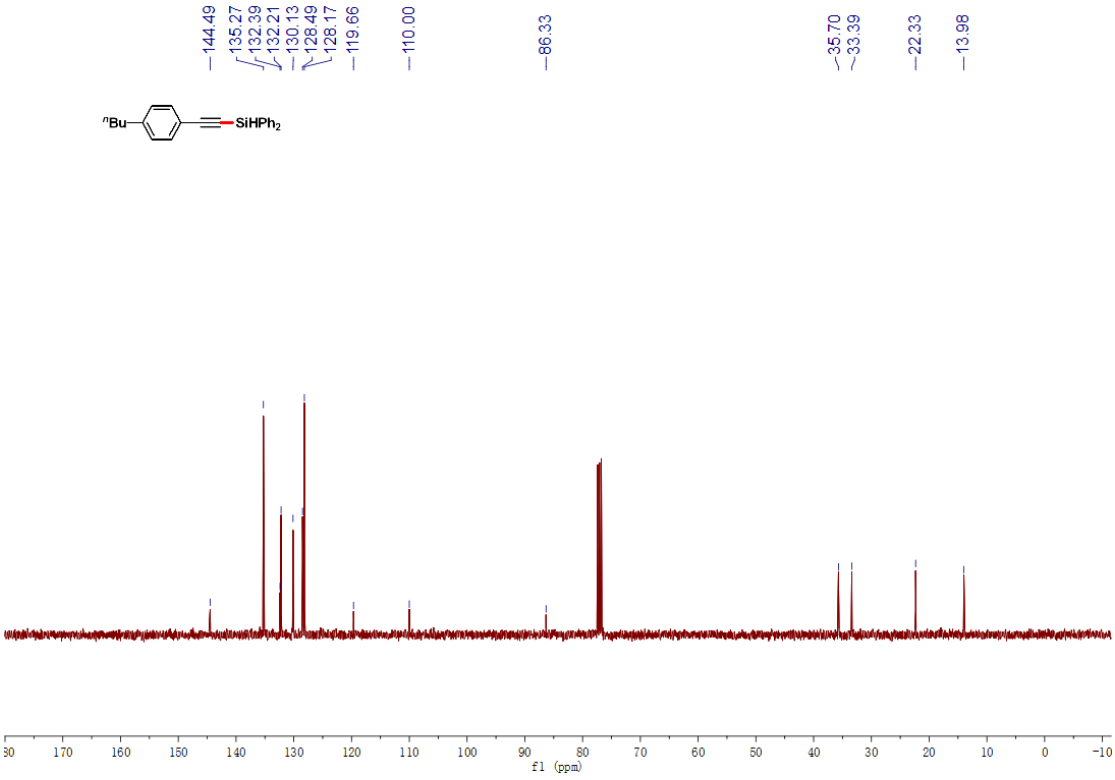
^{13}C NMR spectrum of compound **3e**



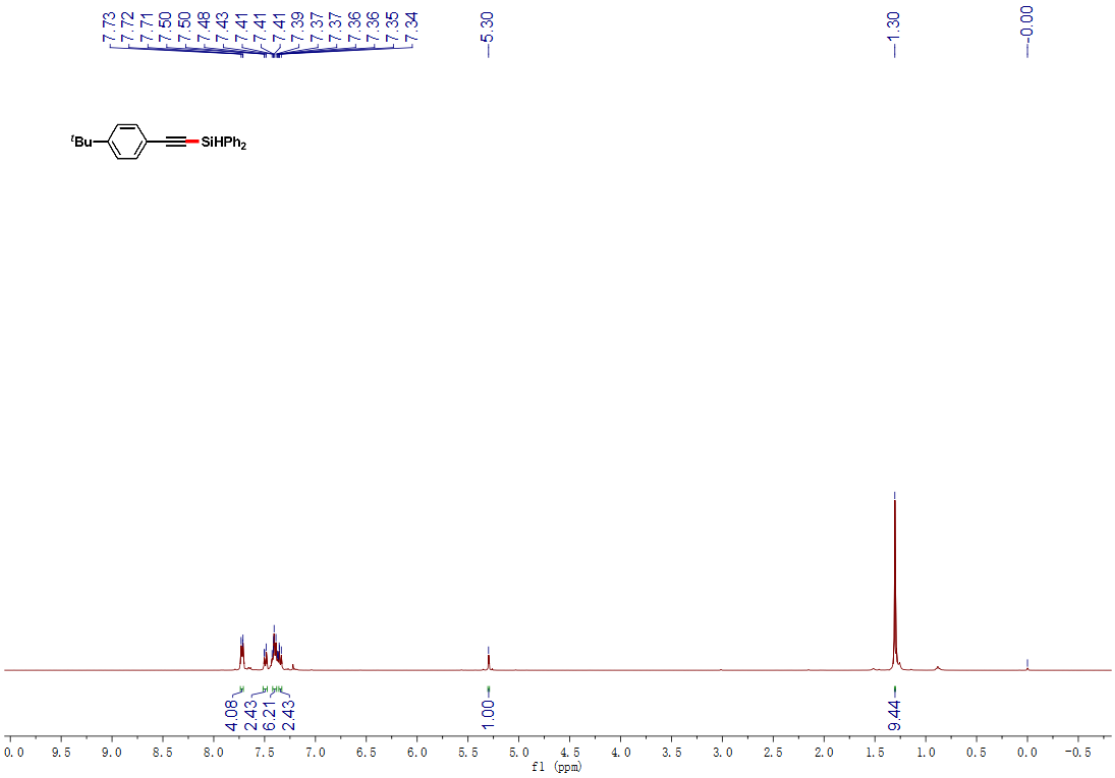
^{1}H NMR spectrum of compound **3f**



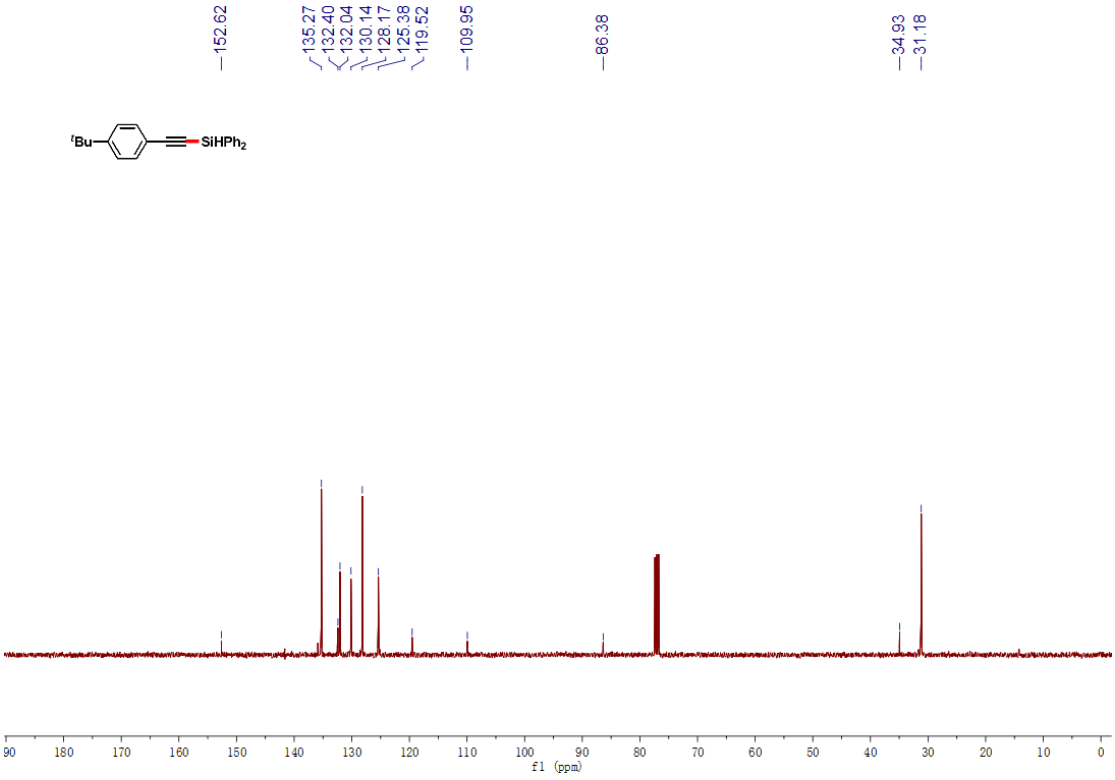
^{13}C NMR spectrum of compound **3f**



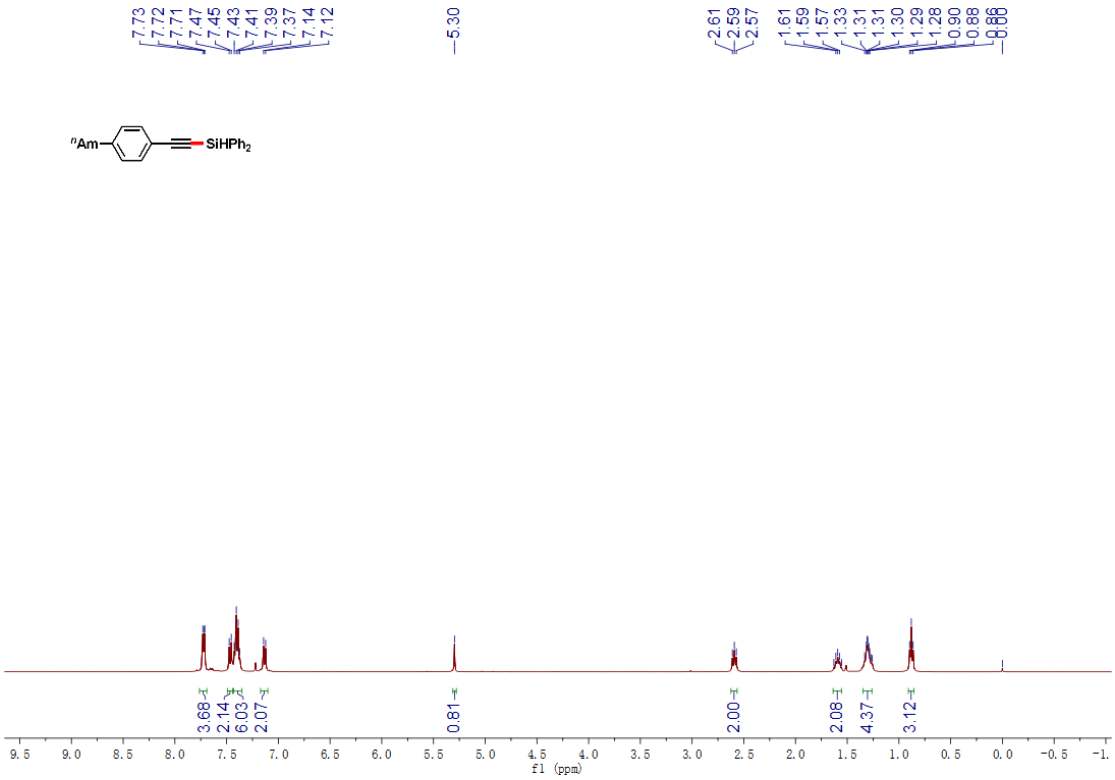
^{1}H NMR spectrum of compound **3g**



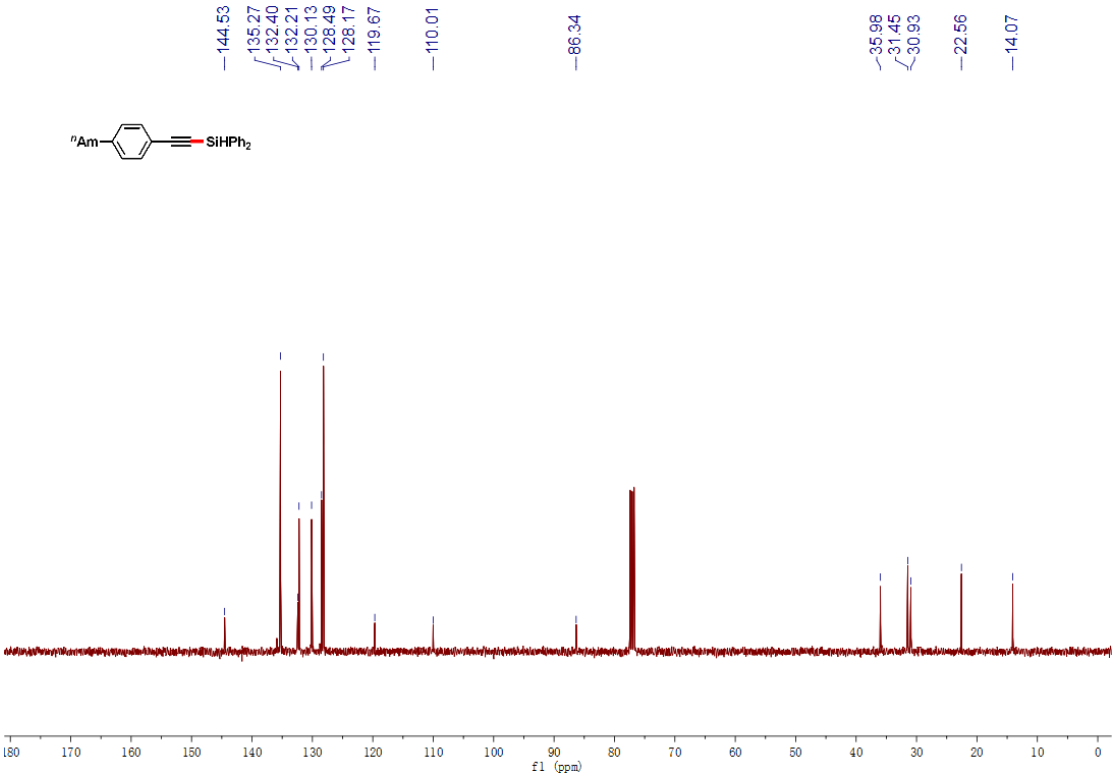
^{13}C NMR spectrum of compound **3g**



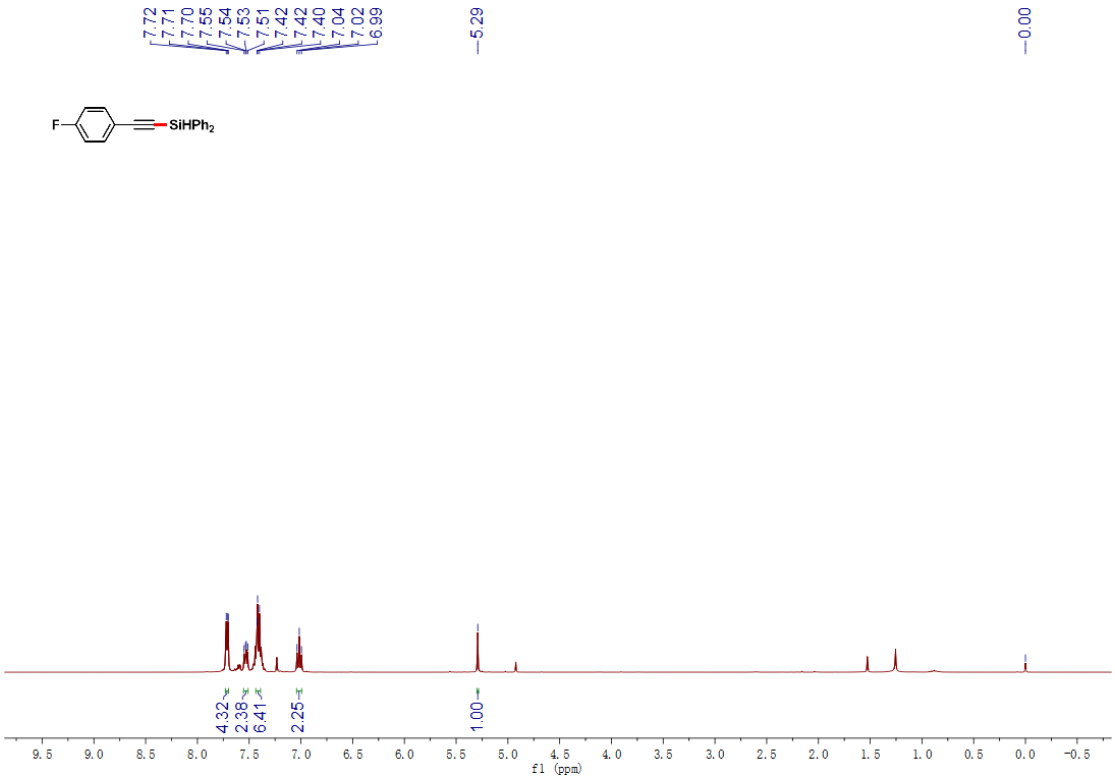
^{1}H NMR spectrum of compound **3h**



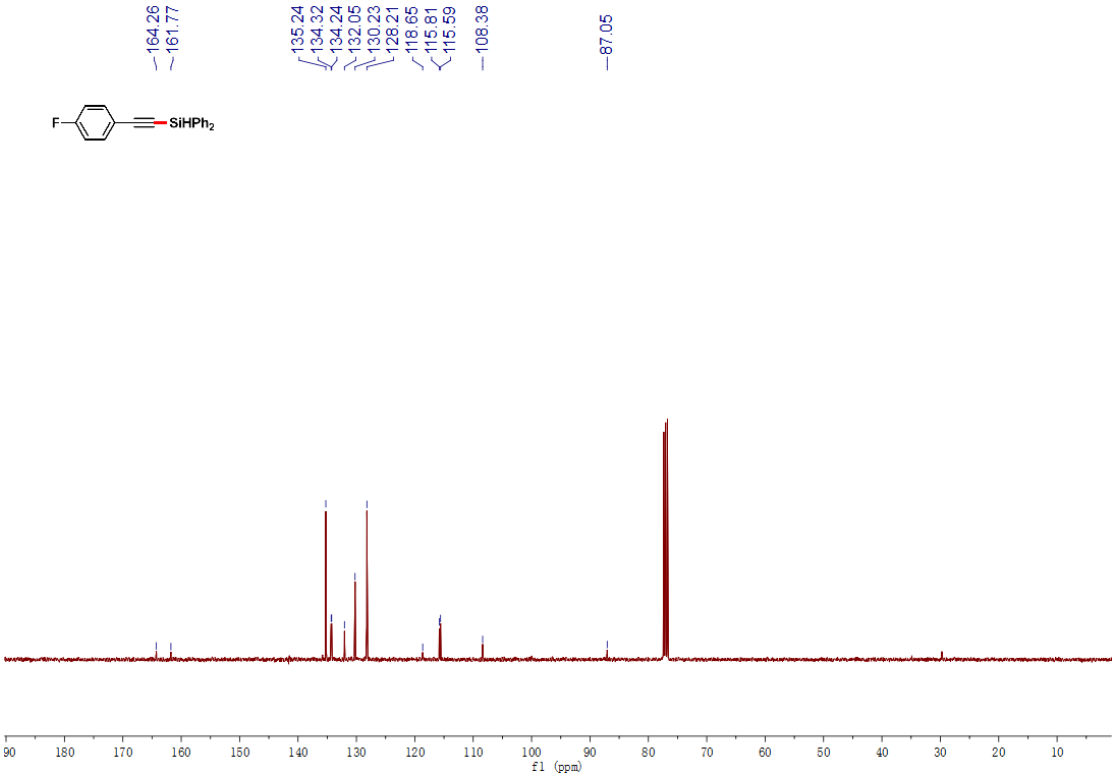
^{13}C NMR spectrum of compound **3h**



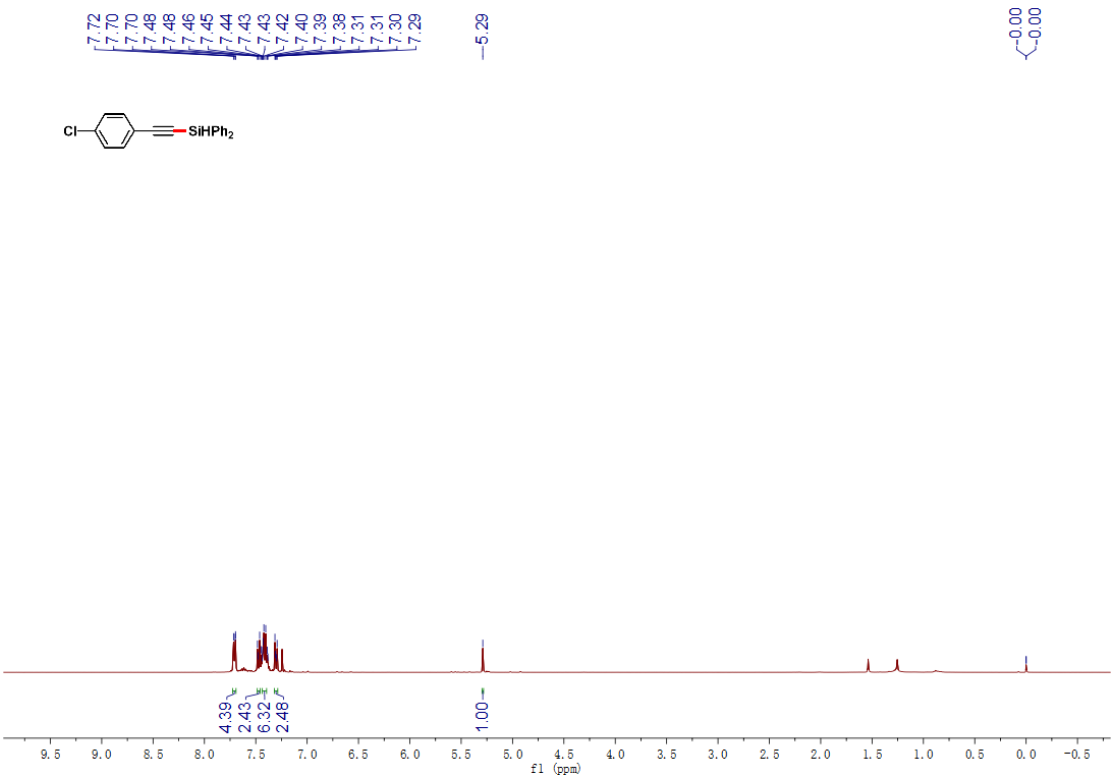
^{1}H NMR spectrum of compound **3i**



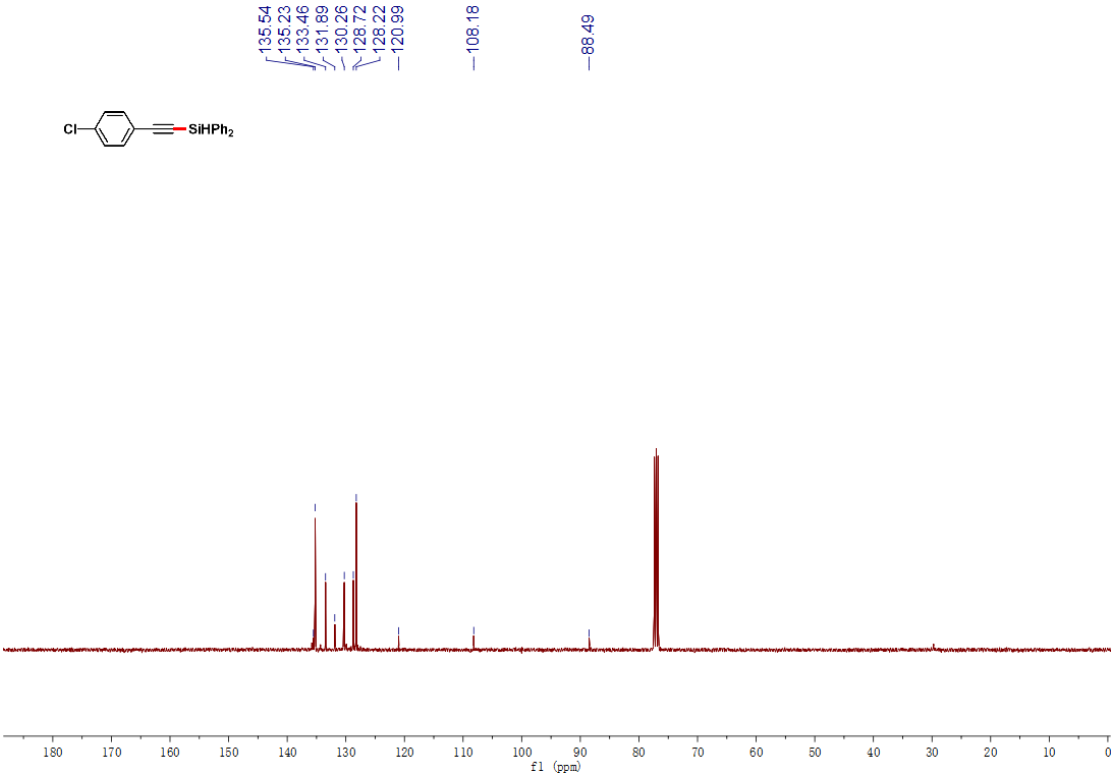
^{13}C NMR spectrum of compound **3i**



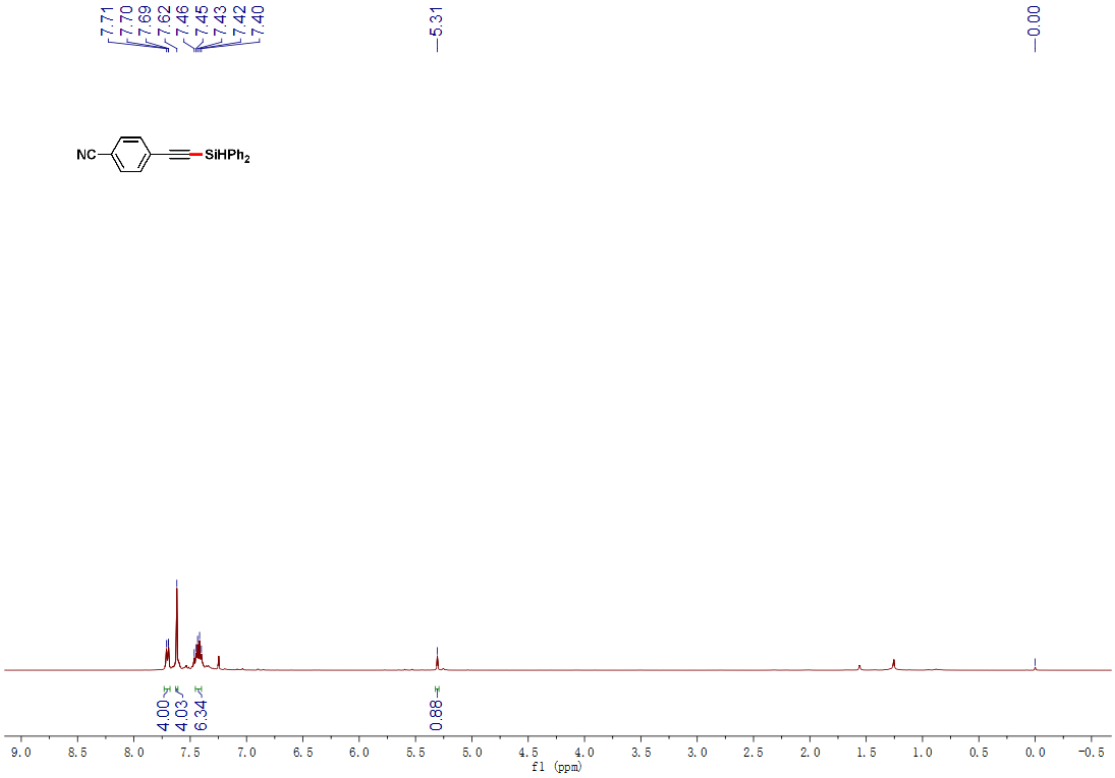
^{1}H NMR spectrum of compound **3j**



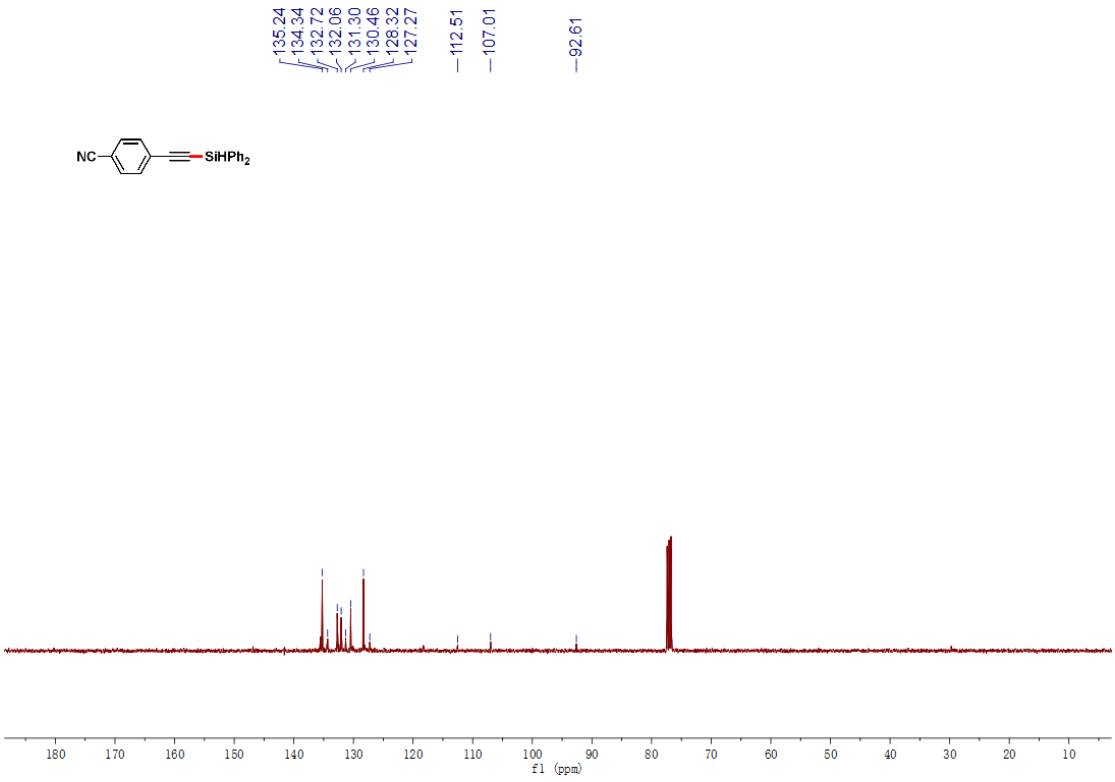
^{13}C NMR spectrum of compound **3j**



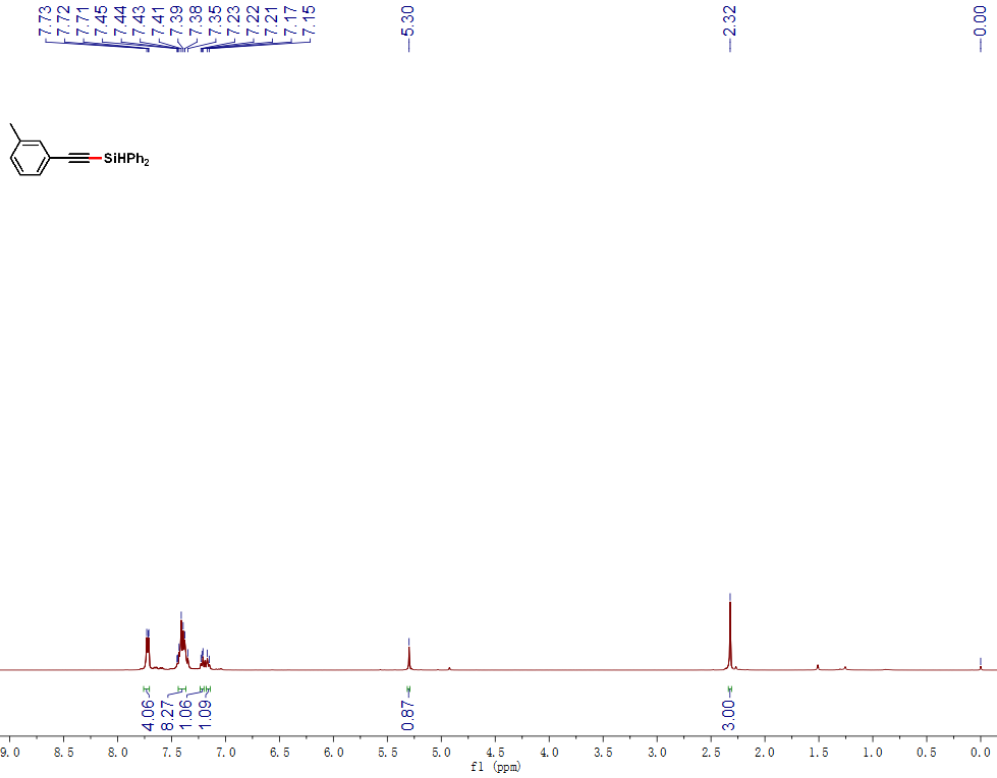
^{1}H NMR spectrum of compound **3k**



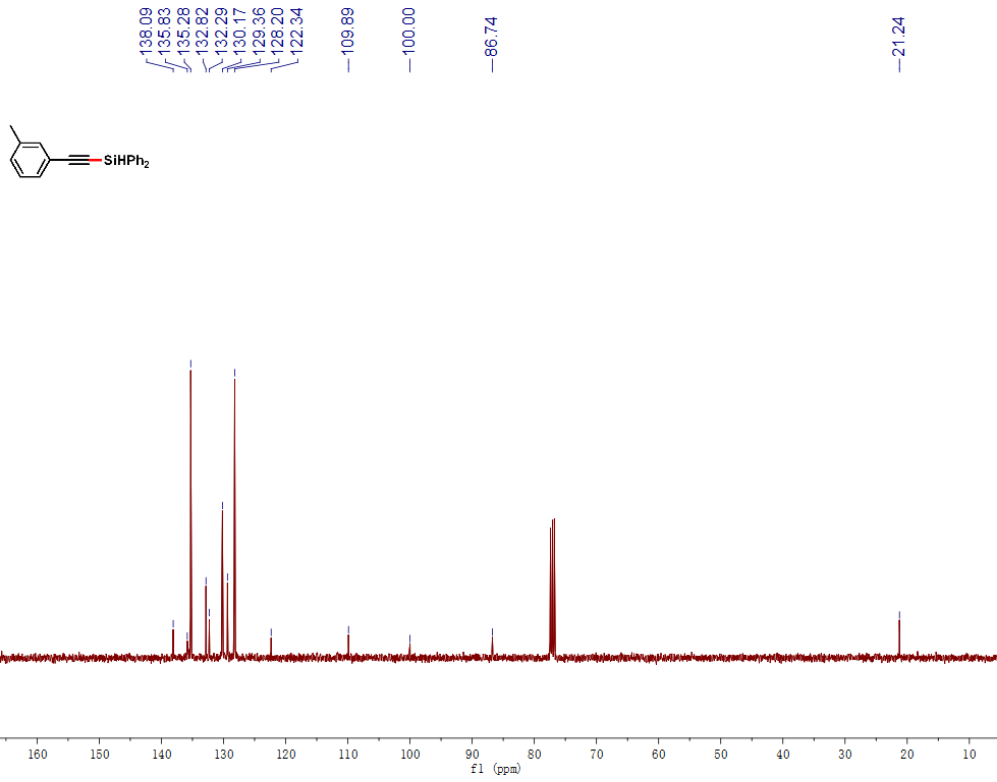
^{13}C NMR spectrum of compound **3k**



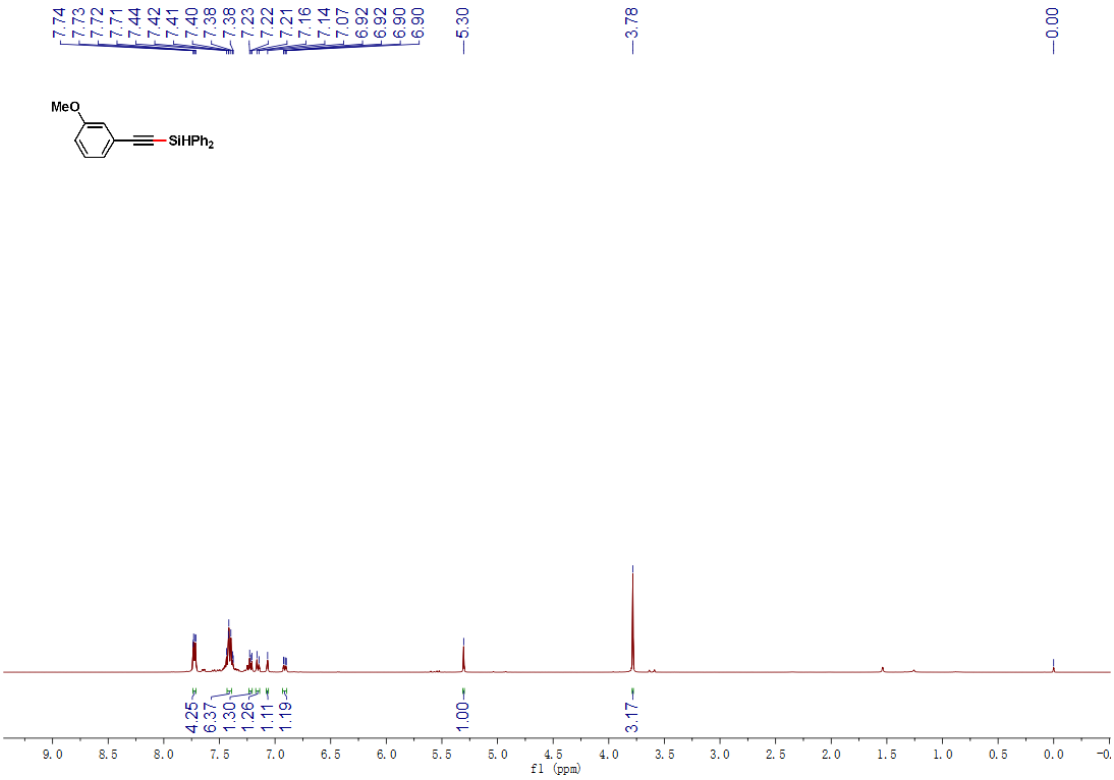
^{1}H NMR spectrum of compound **3l**



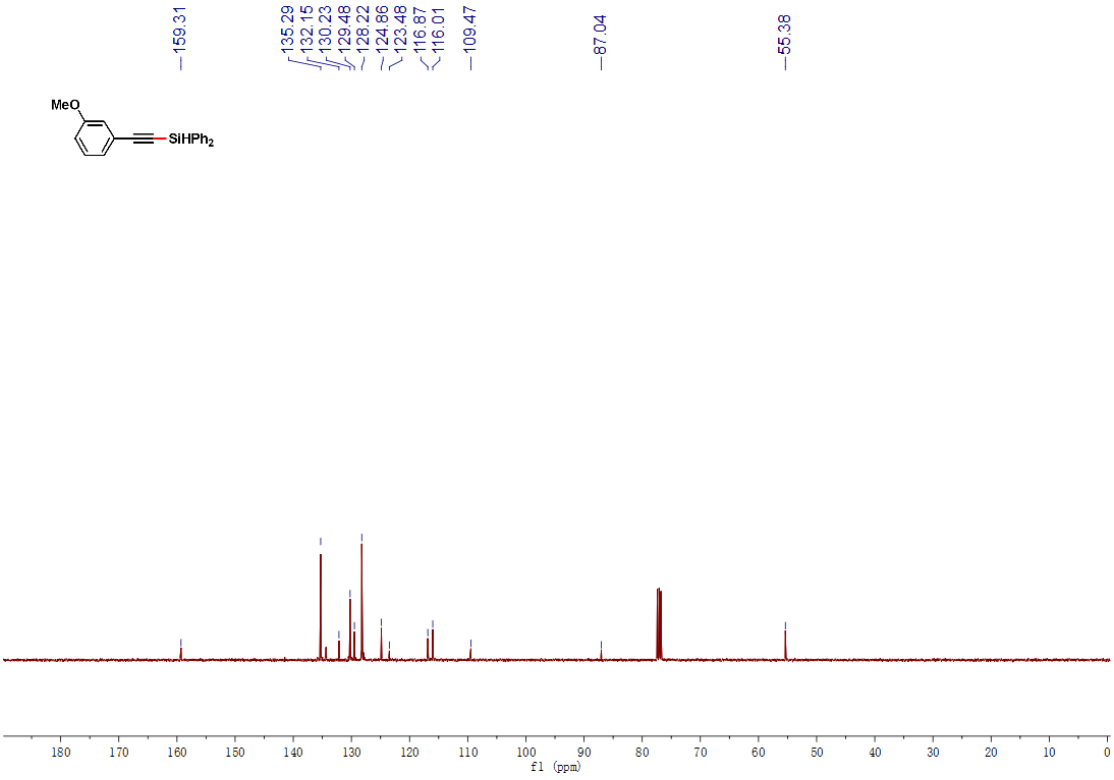
^{13}C NMR spectrum of compound **3l**



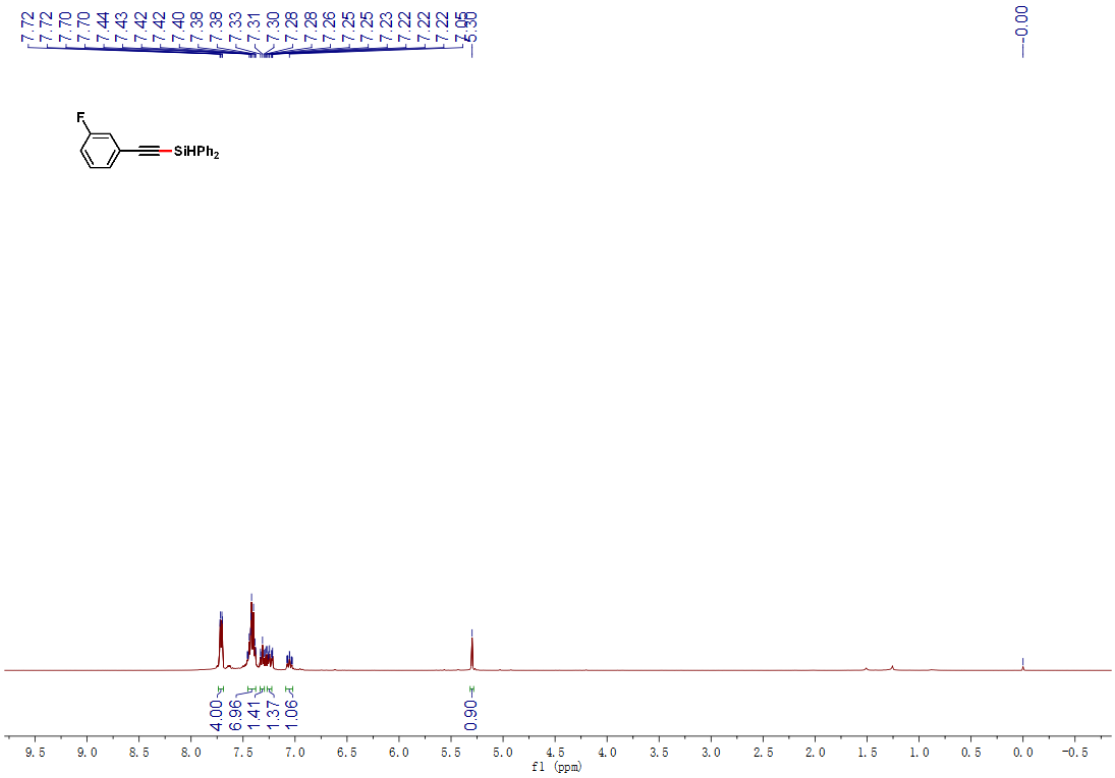
^{1}H NMR spectrum of compound **3m**



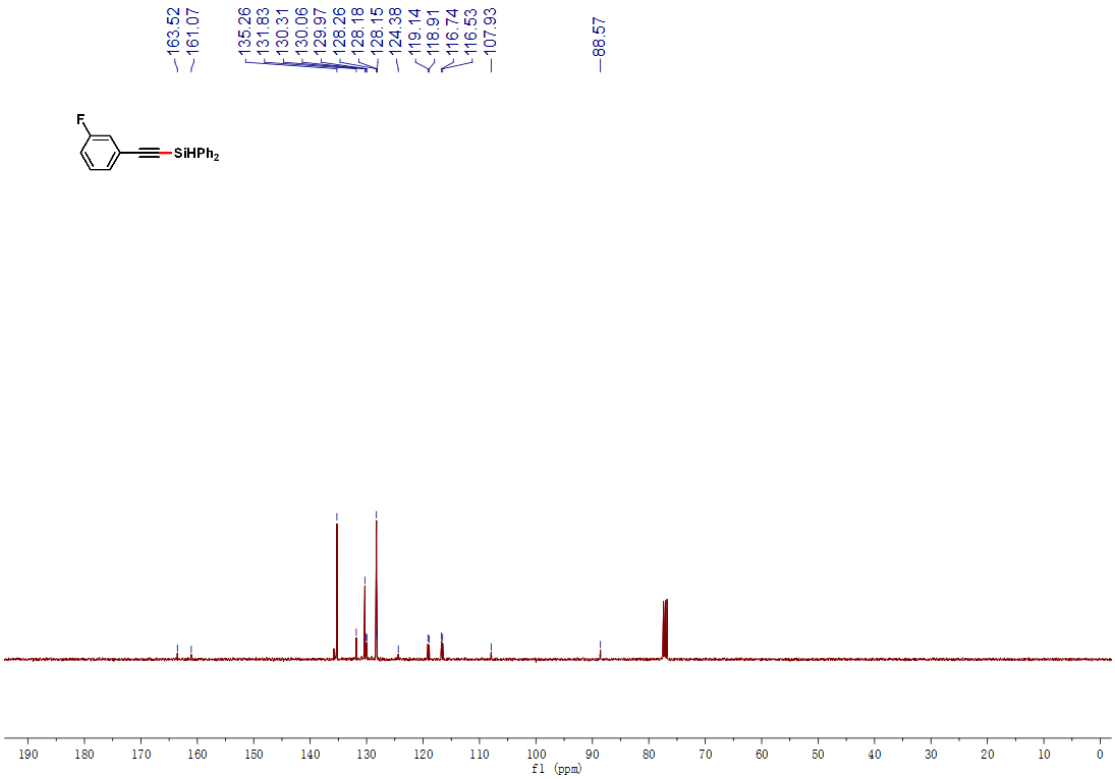
^{13}C NMR spectrum of compound **3m**



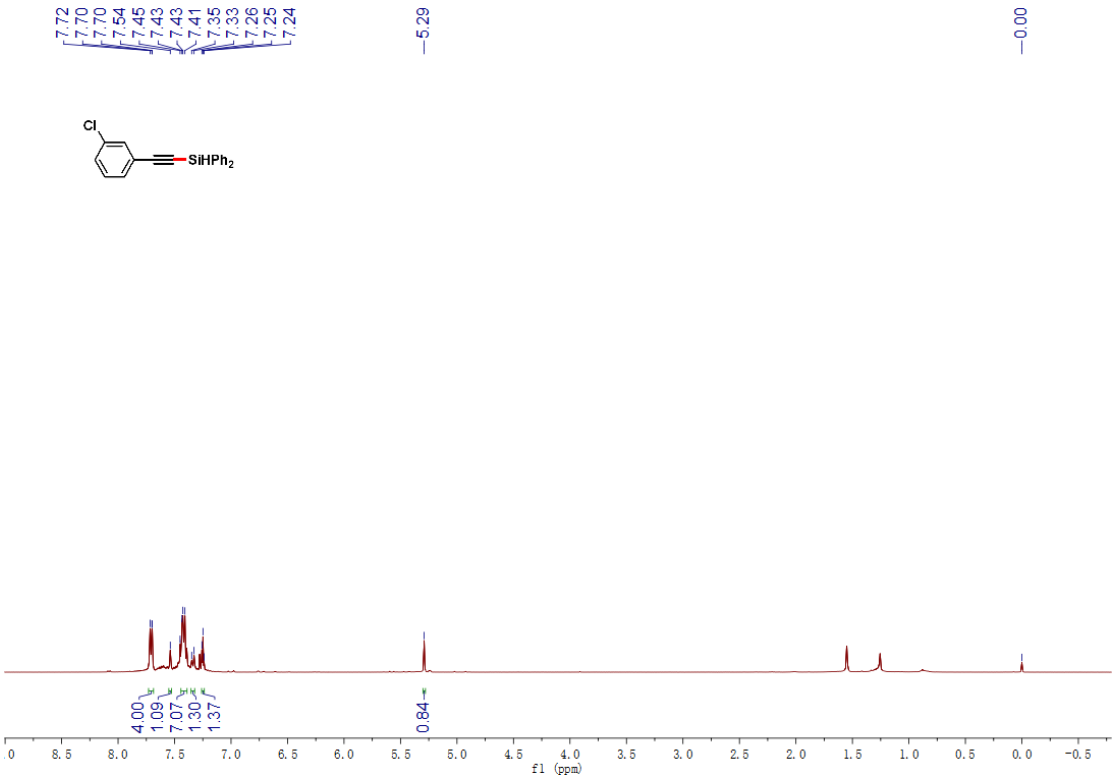
^{1}H NMR spectrum of compound **3n**



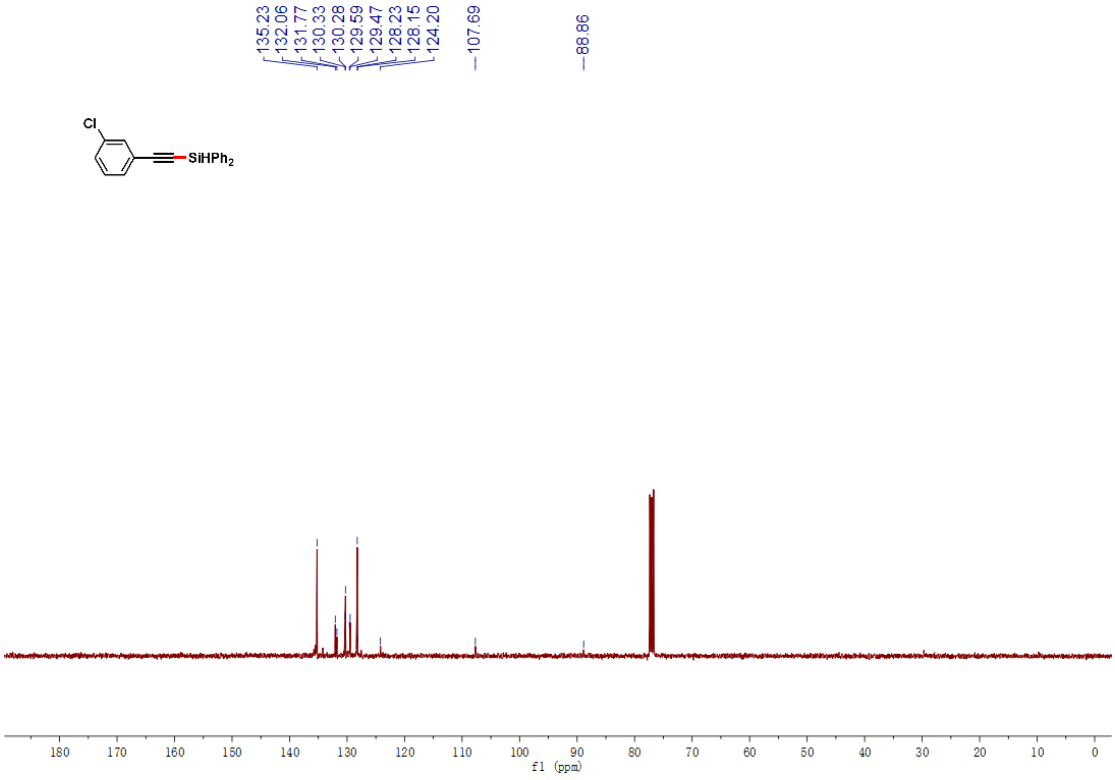
^{13}C NMR spectrum of compound **3n**



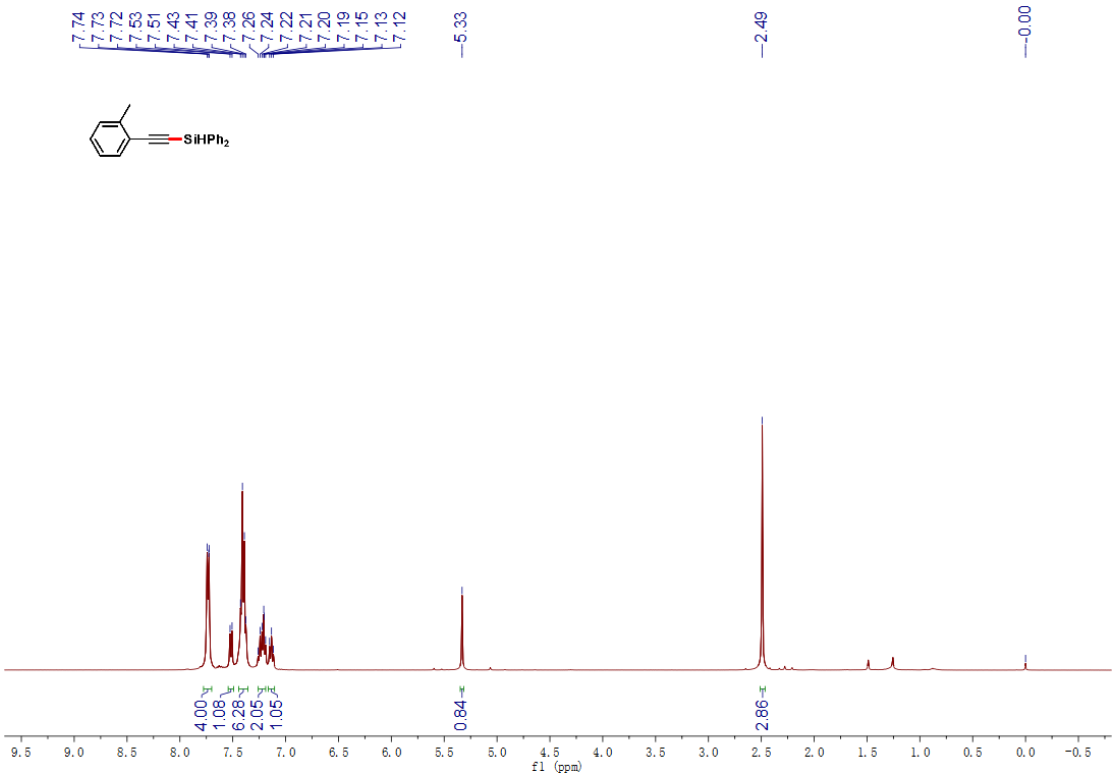
^{1}H NMR spectrum of compound **3o**



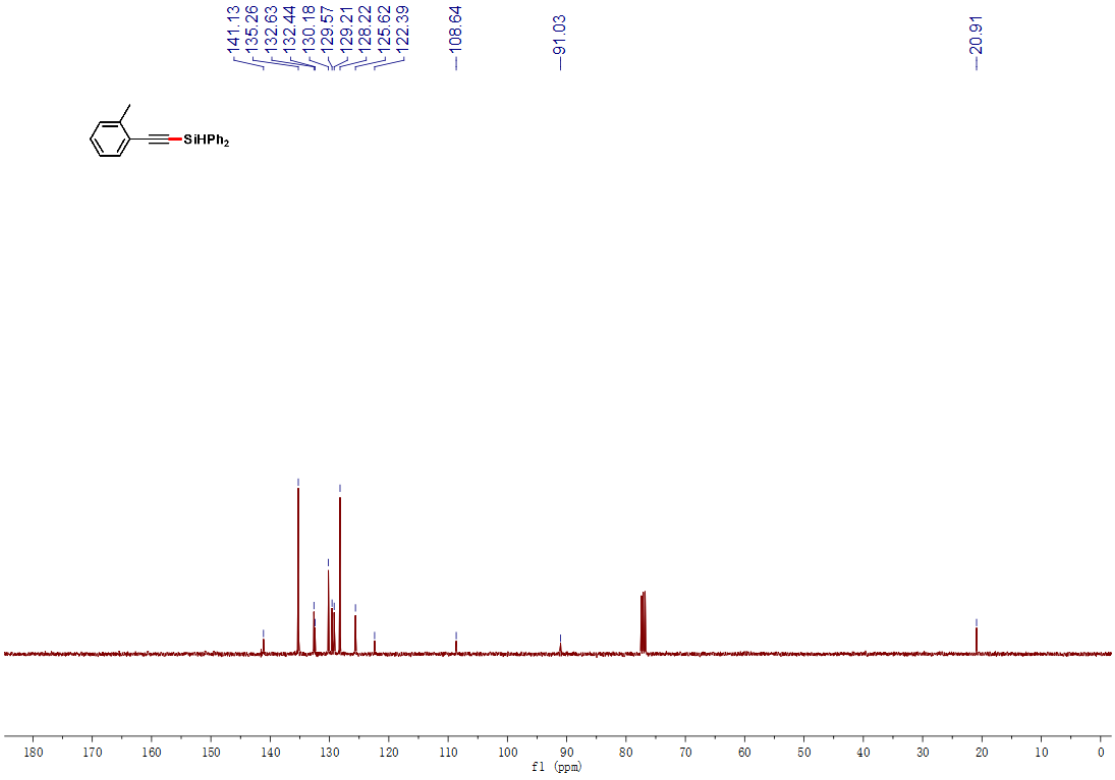
^{13}C NMR spectrum of compound **3o**



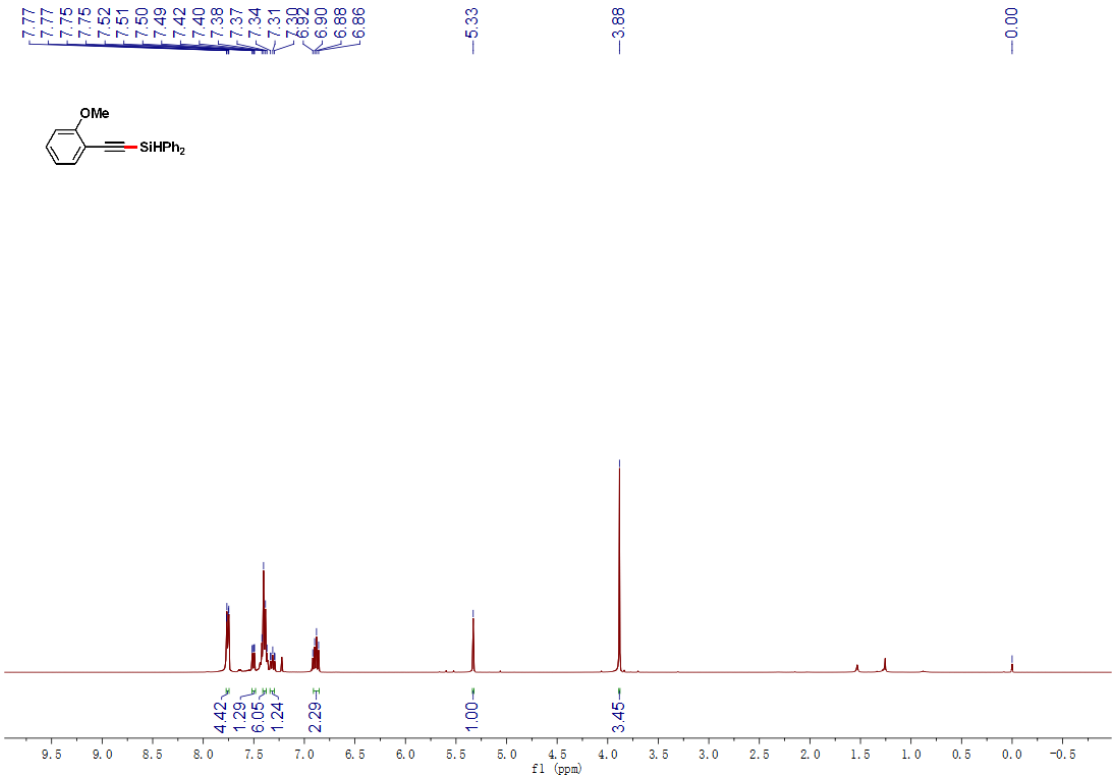
^{1}H NMR spectrum of compound **3p**



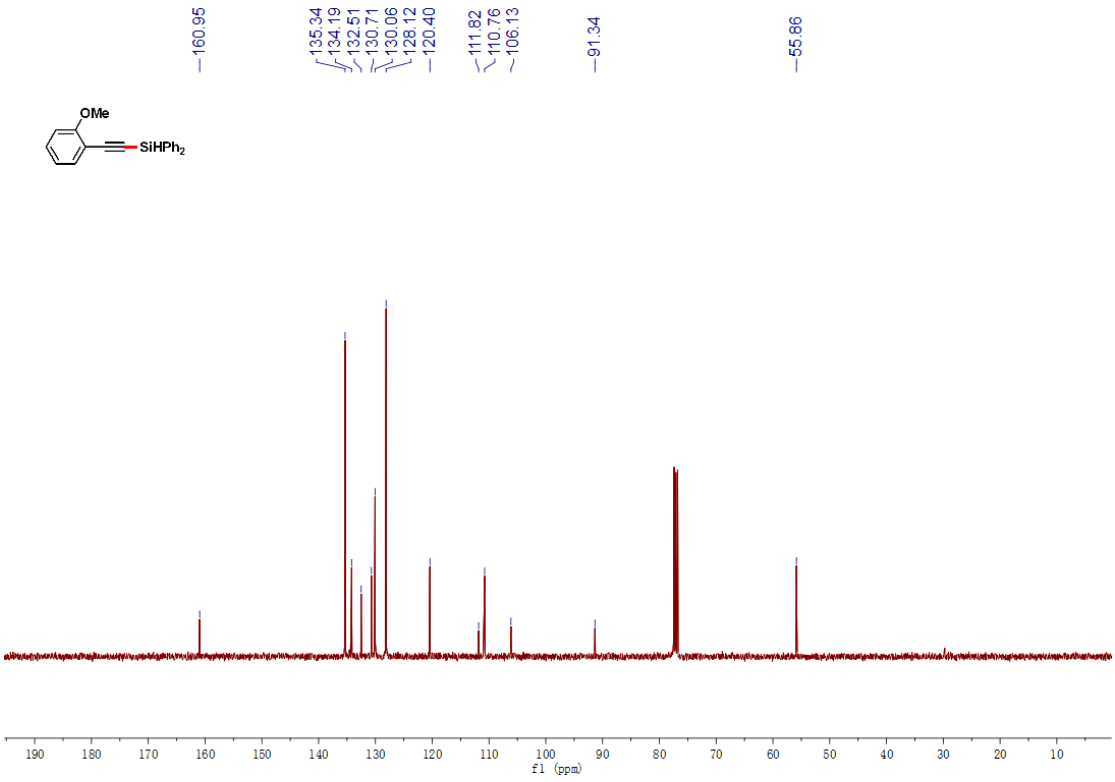
^{13}C NMR spectrum of compound **3p**



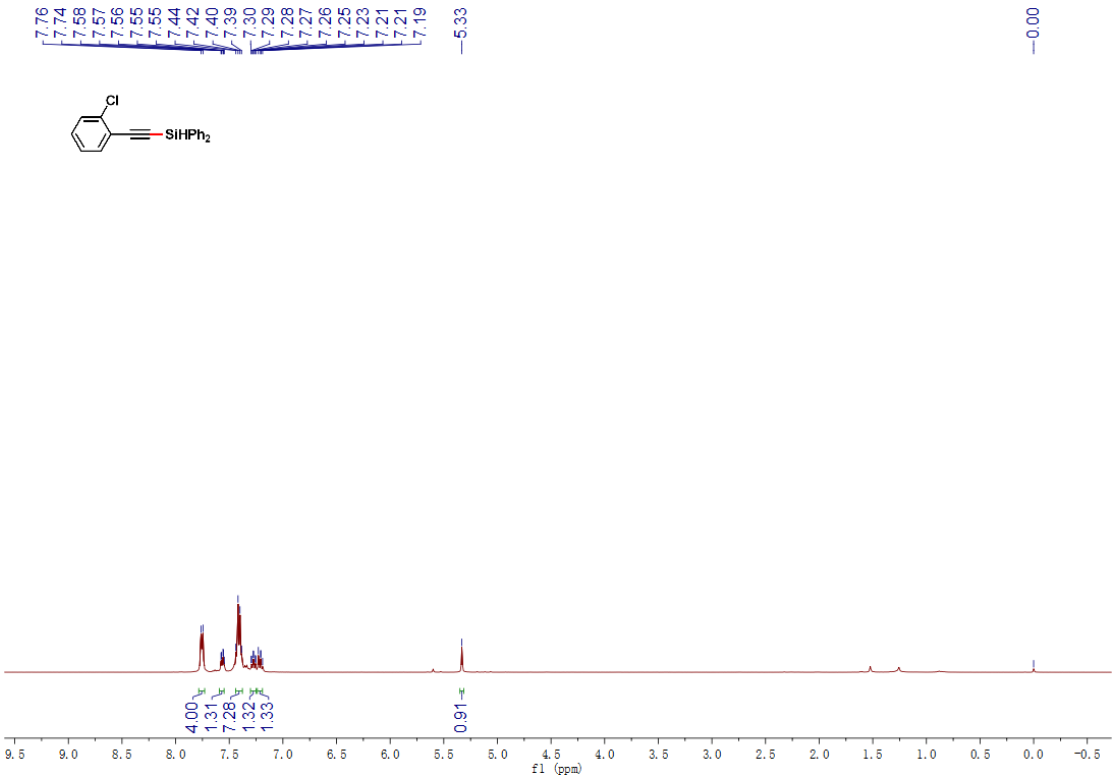
^{1}H NMR spectrum of compound **3q**



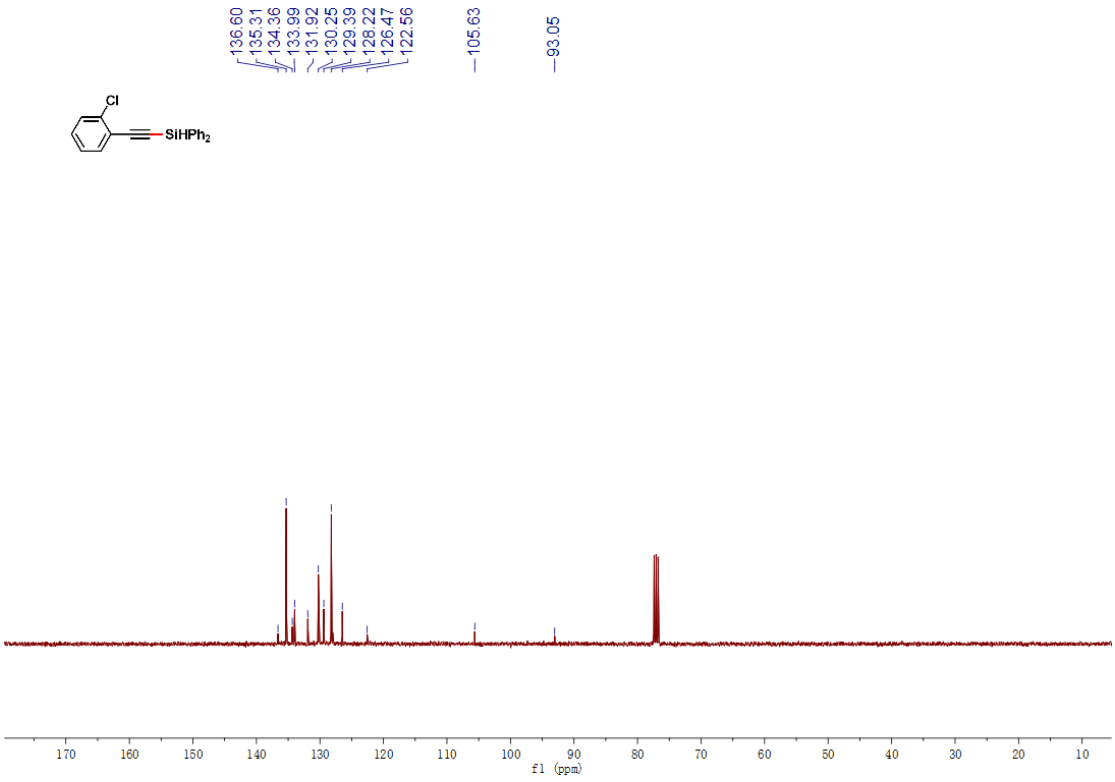
^{13}C NMR spectrum of compound **3q**



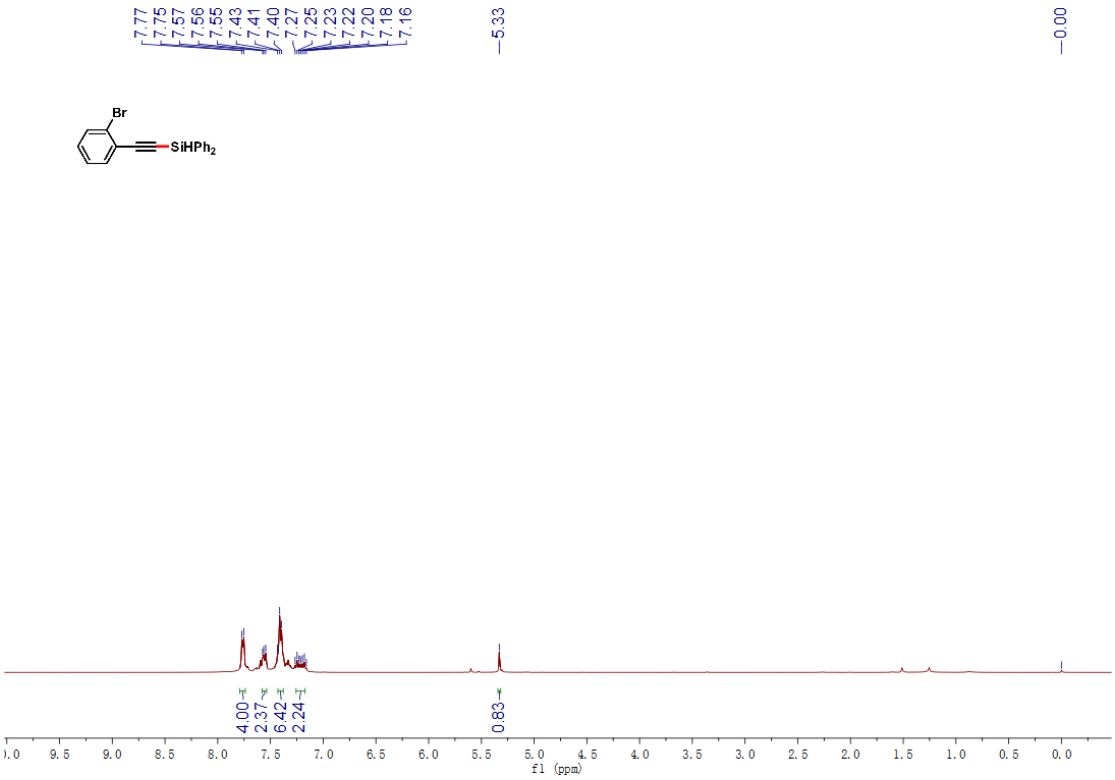
^{1}H NMR spectrum of compound **3r**



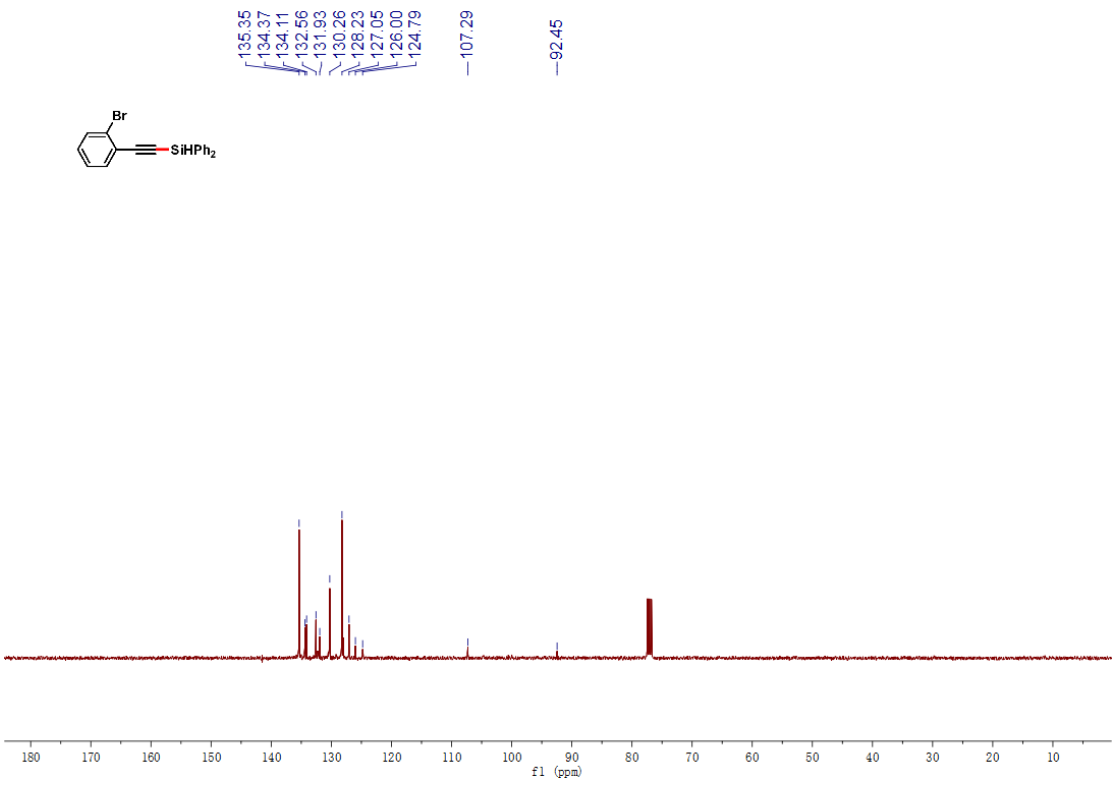
^{13}C NMR spectrum of compound **3r**



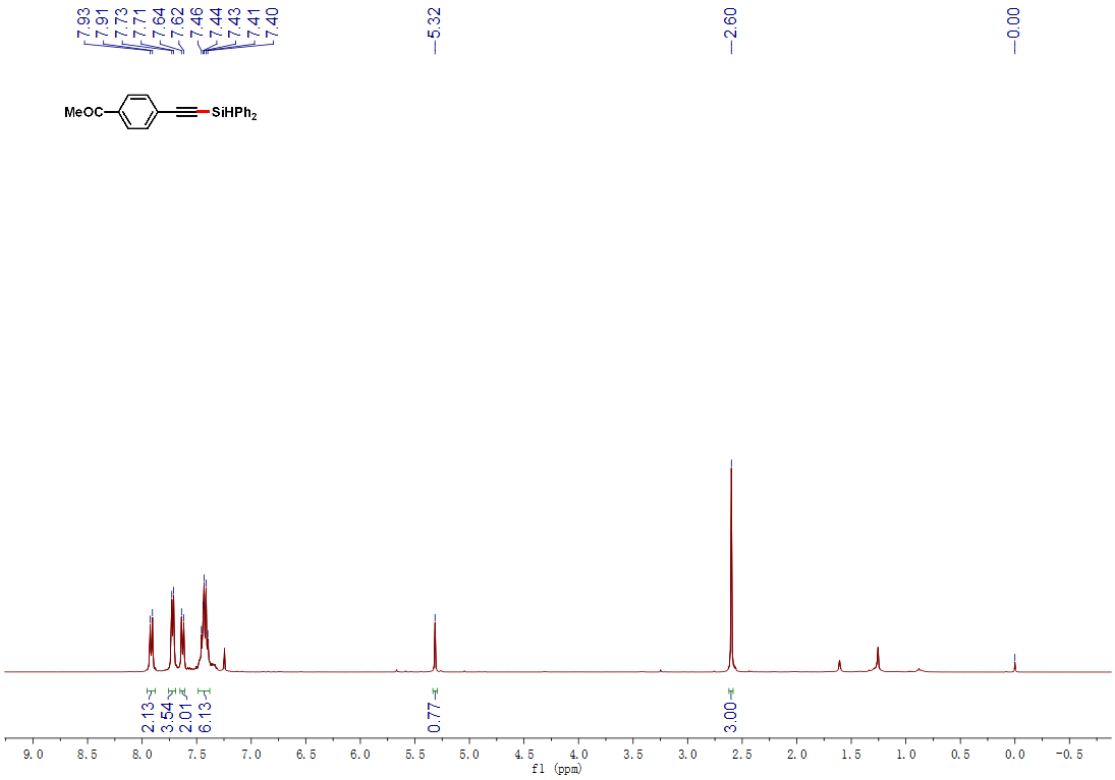
^{1}H NMR spectrum of compound **3s**



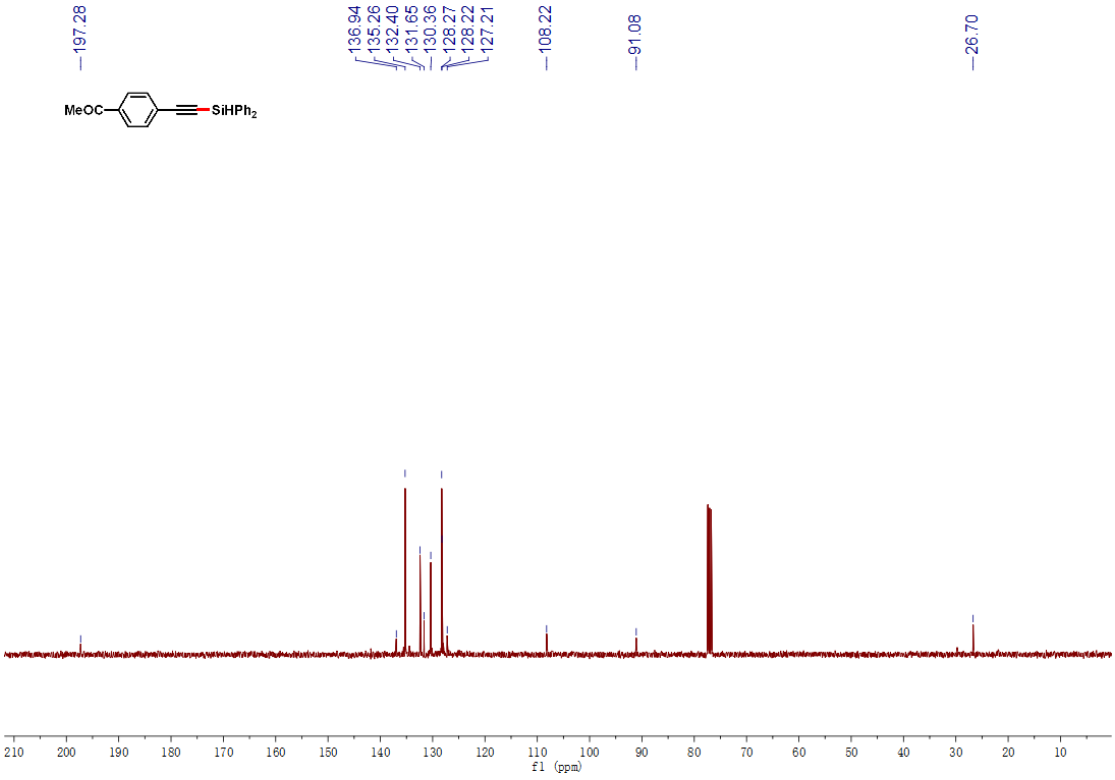
^{13}C NMR spectrum of compound **3s**



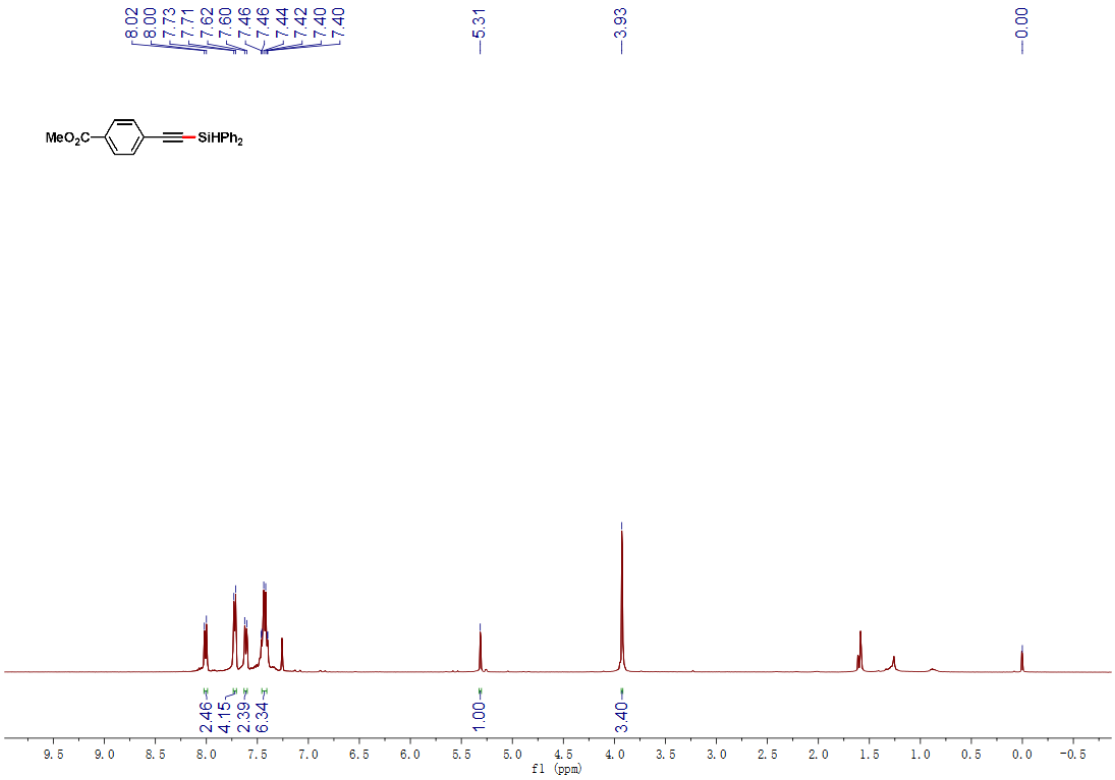
^{1}H NMR spectrum of compound **3t**



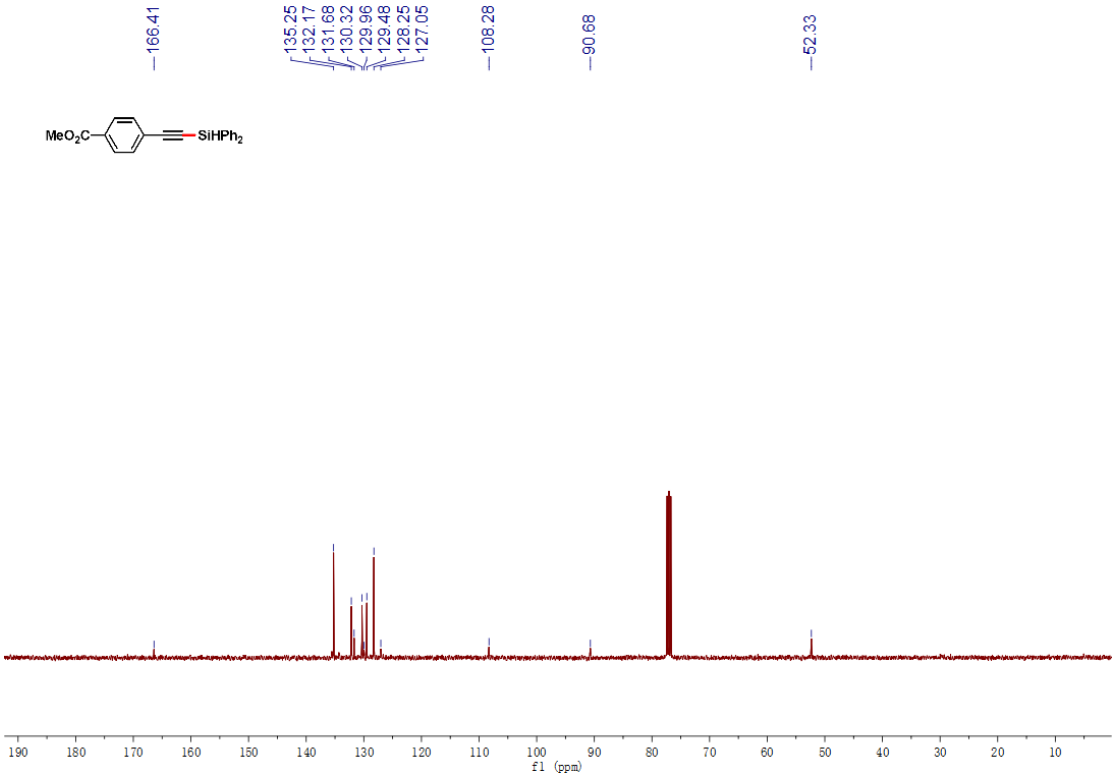
^{13}C NMR spectrum of compound **3t**



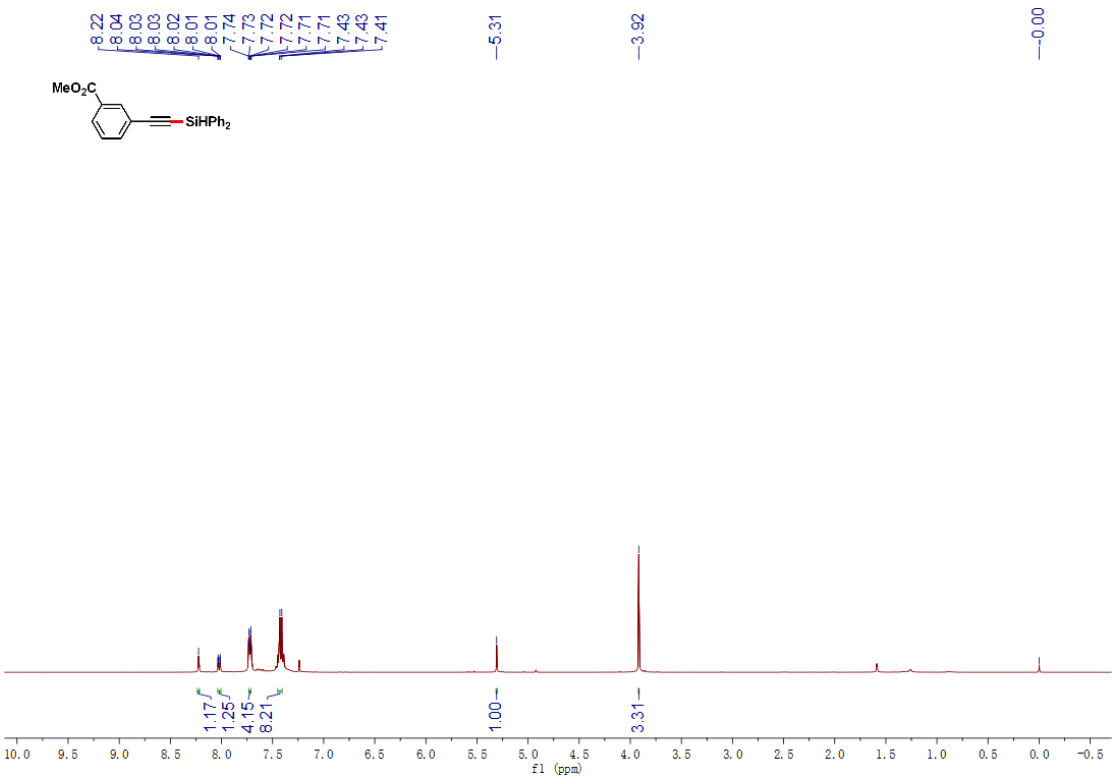
^{1}H NMR spectrum of compound **3u**



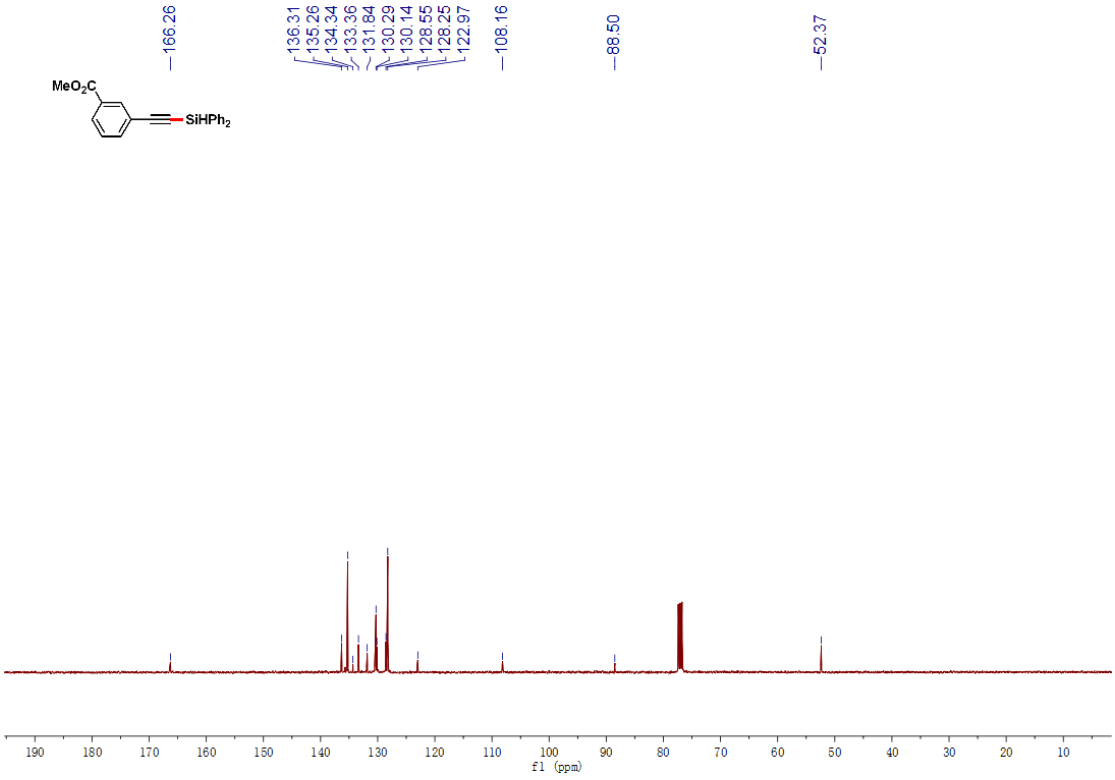
^{13}C NMR spectrum of compound **3u**



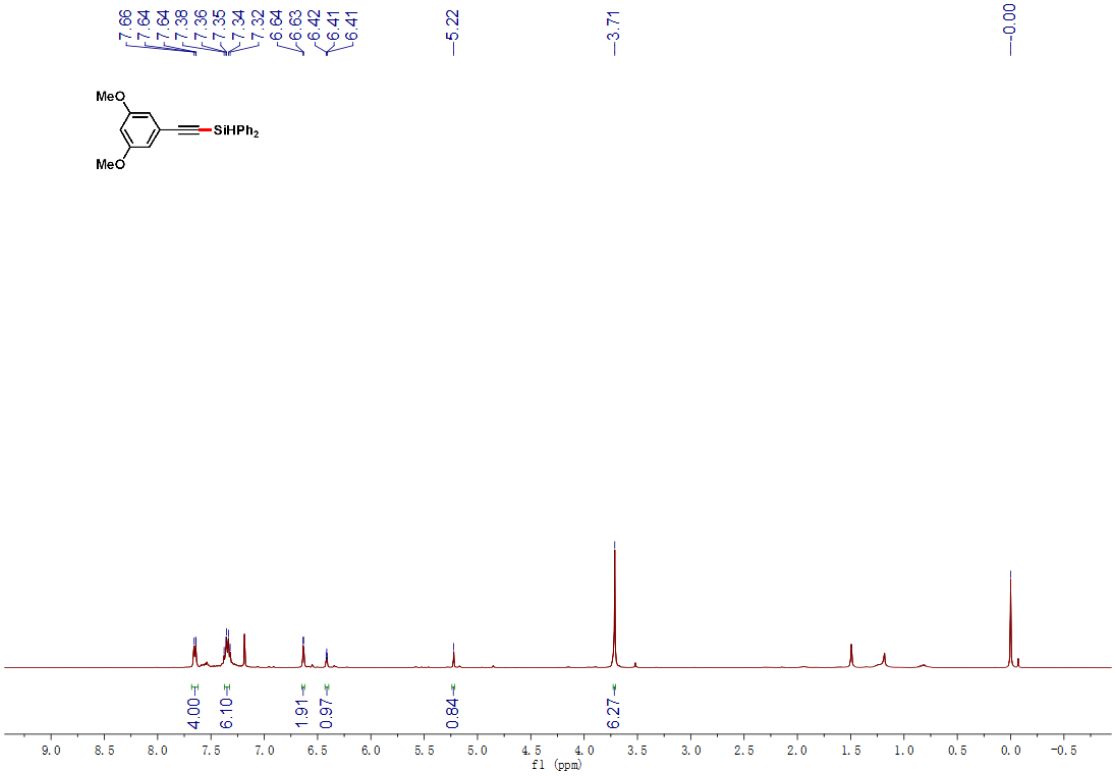
^{1}H NMR spectrum of compound **3v**



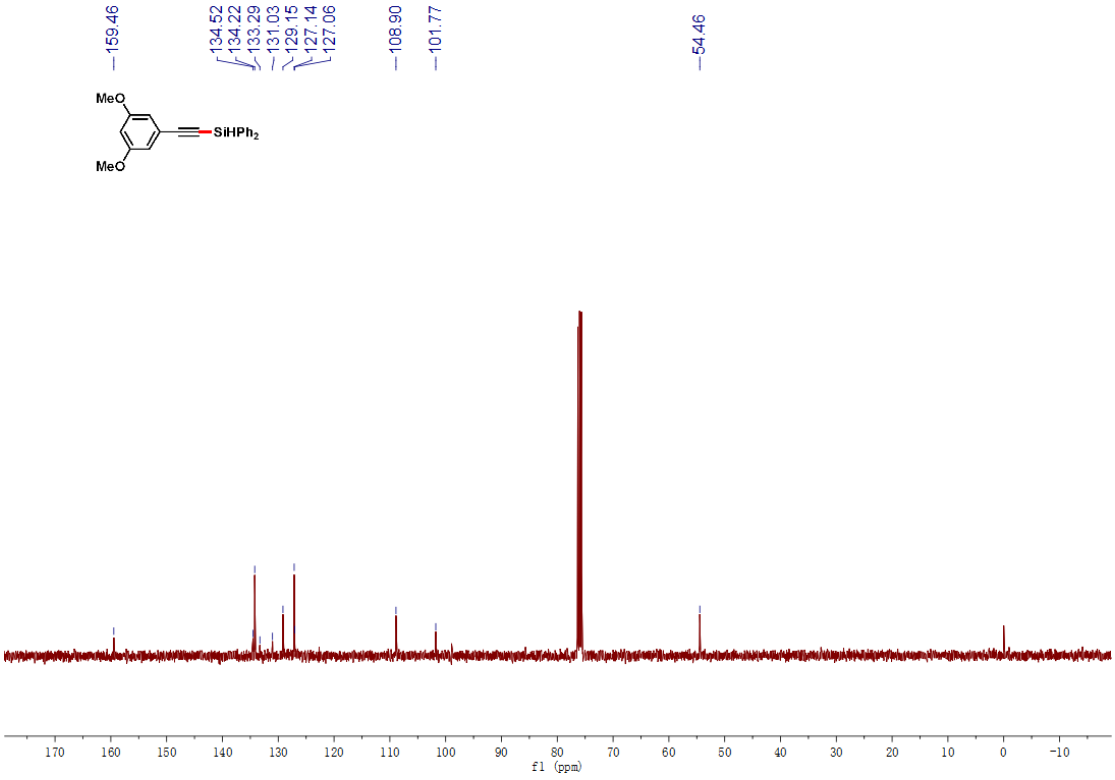
^{13}C NMR spectrum of compound **3v**



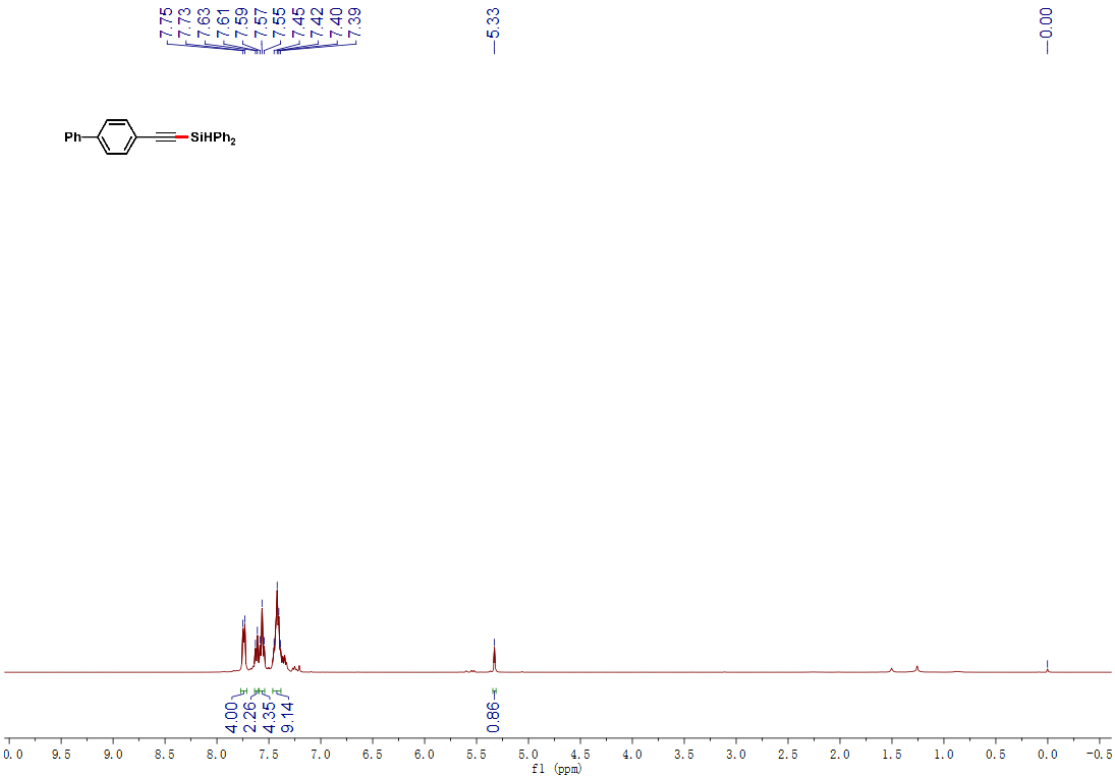
^{1}H NMR spectrum of compound **3w**



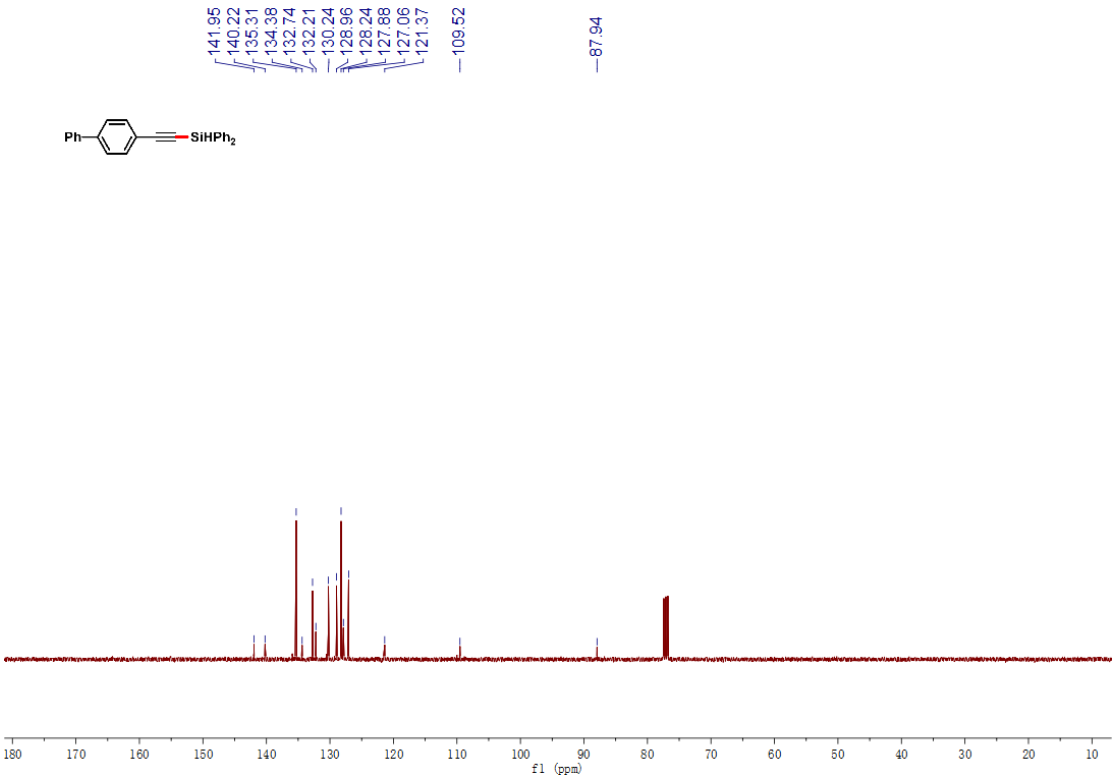
^{13}C NMR spectrum of compound **3w**



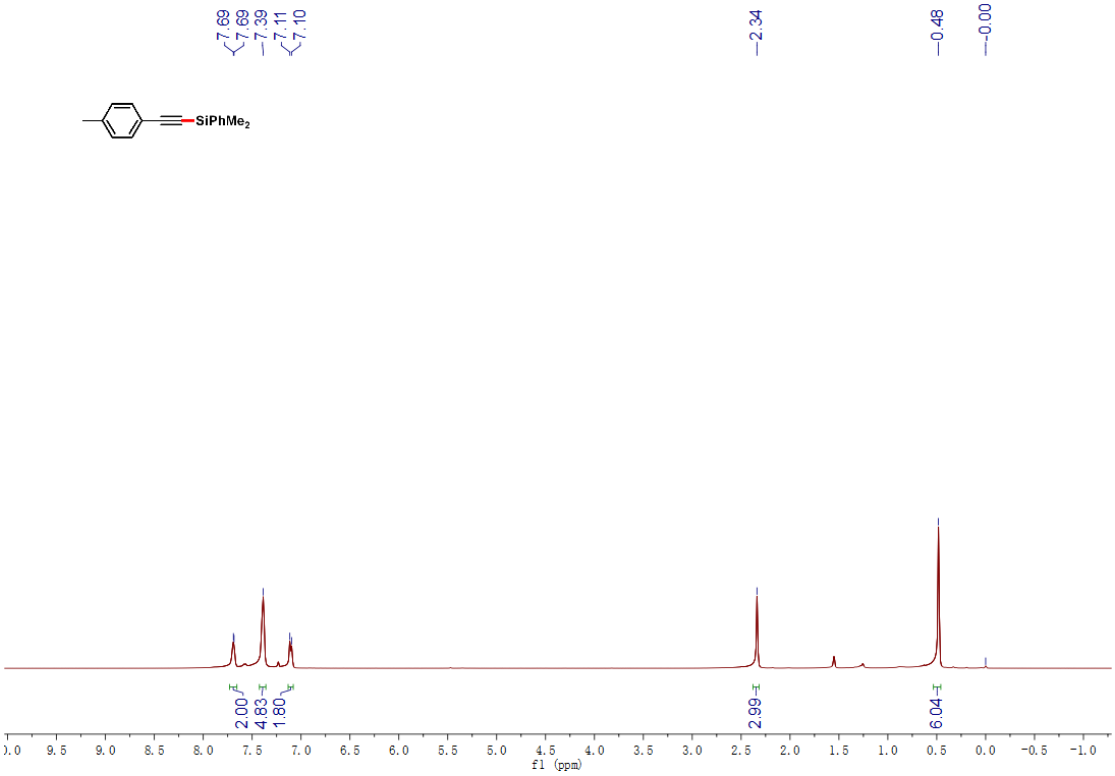
^{1}H NMR spectrum of compound **3x**



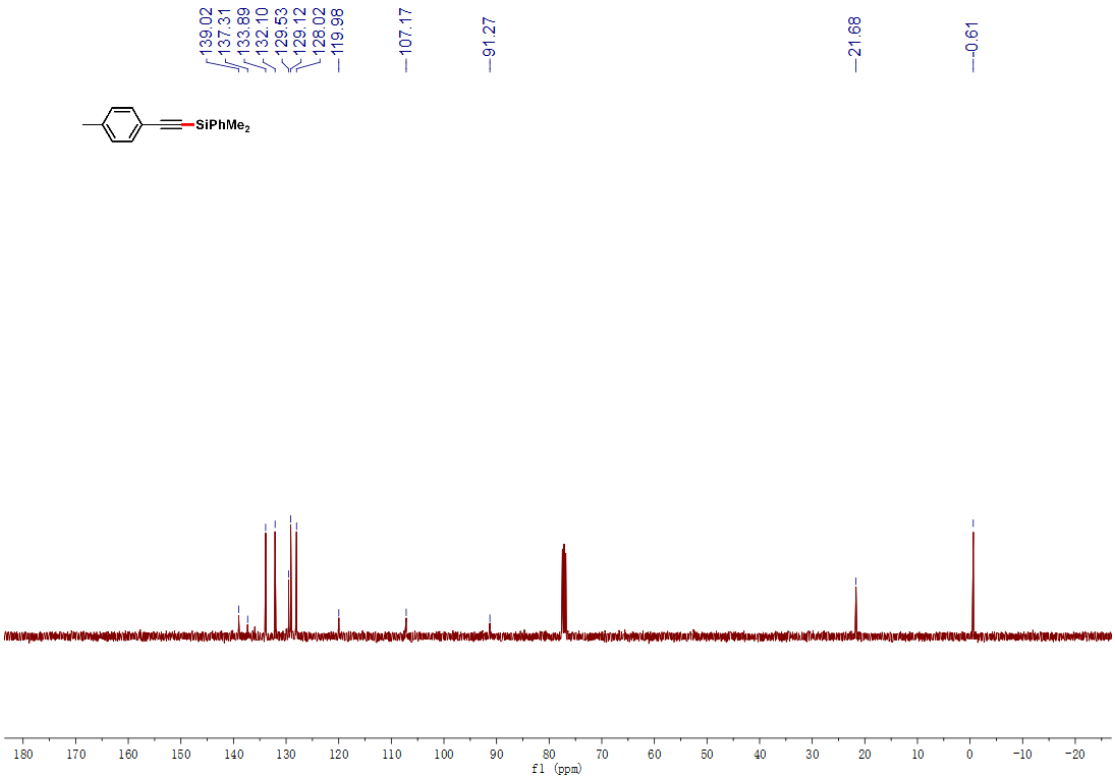
^{13}C NMR spectrum of compound **3x**



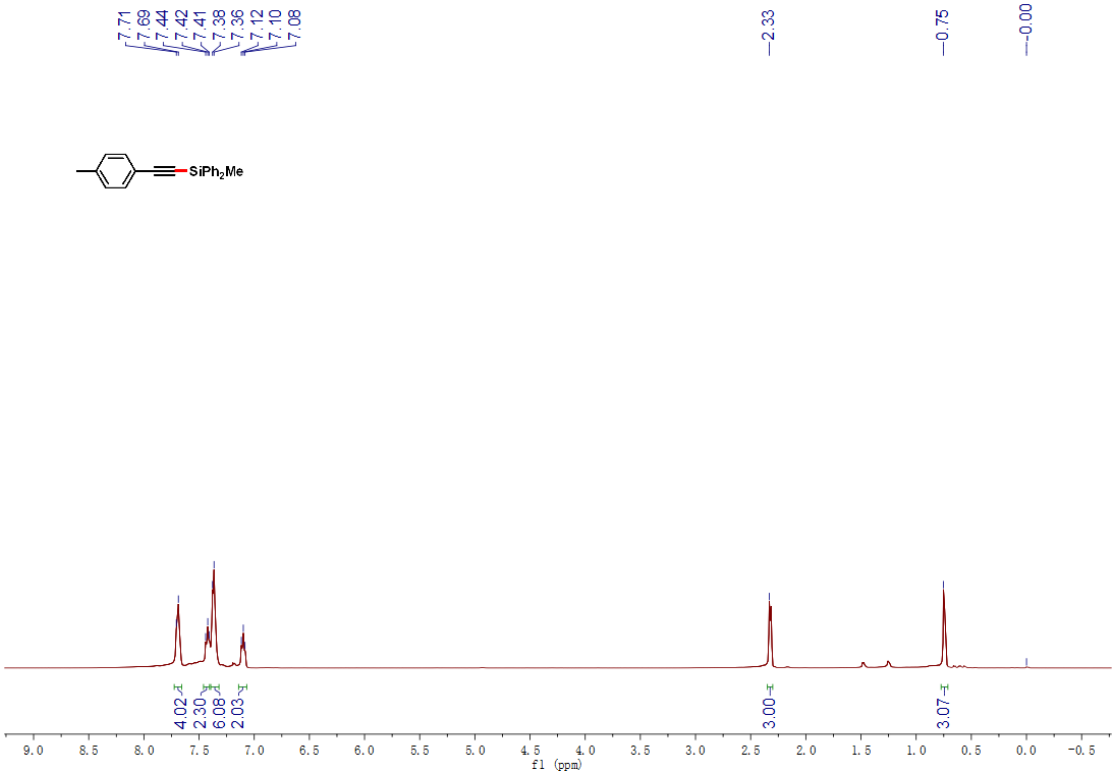
^{1}H NMR spectrum of compound **3y**



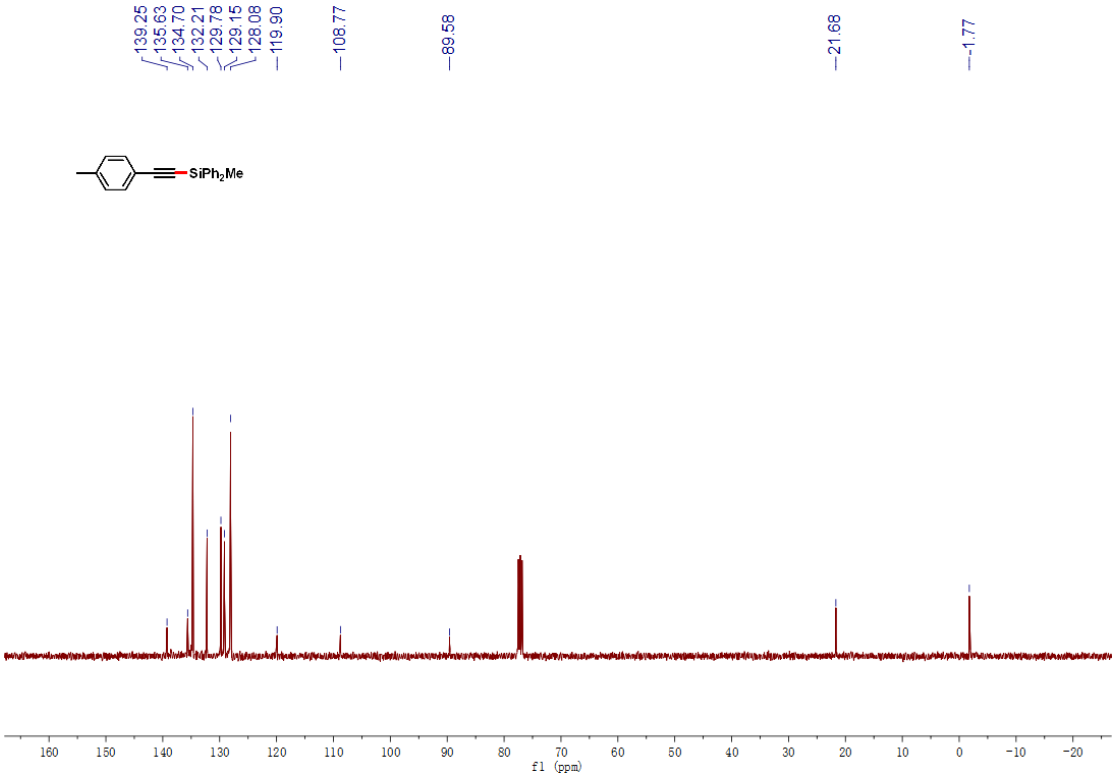
^{13}C NMR spectrum of compound **3y**



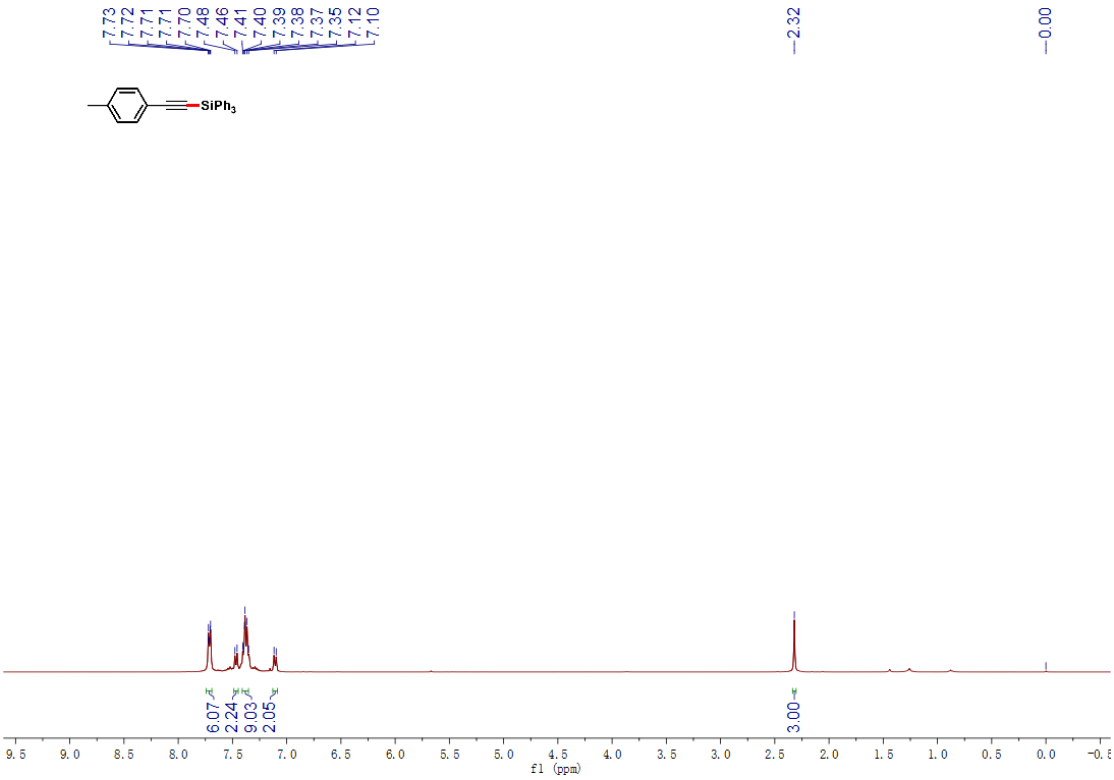
^{1}H NMR spectrum of compound **3z**



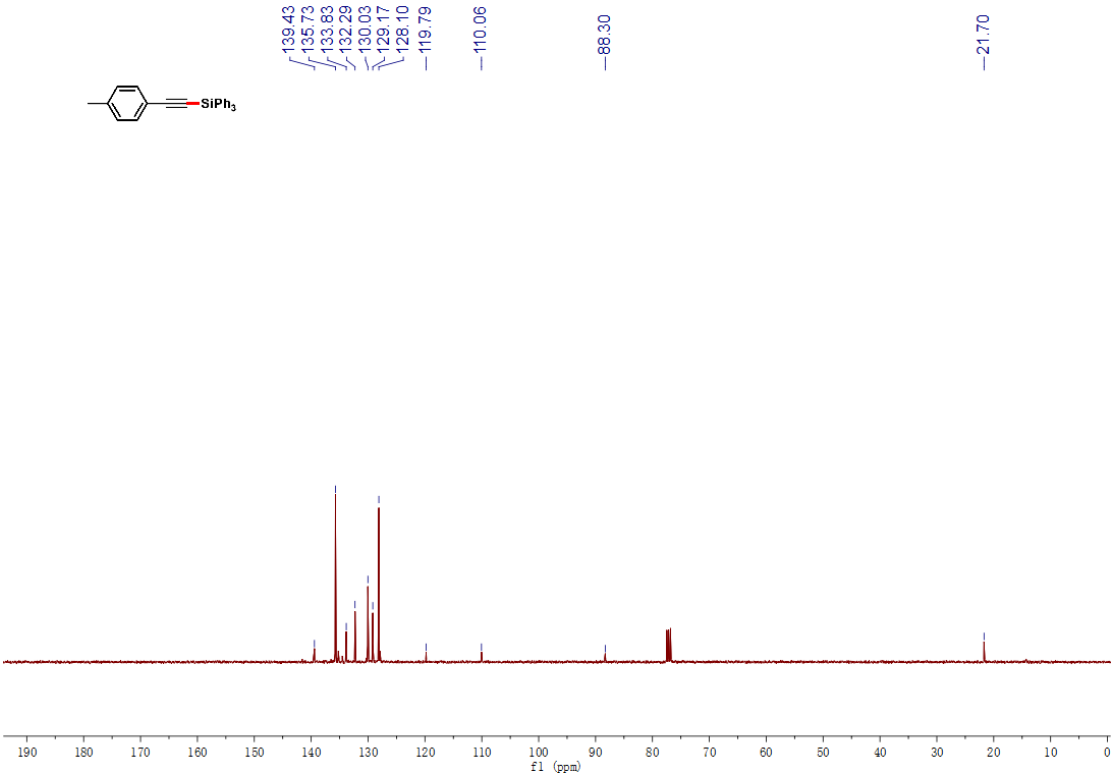
^{13}C NMR spectrum of compound **3z**



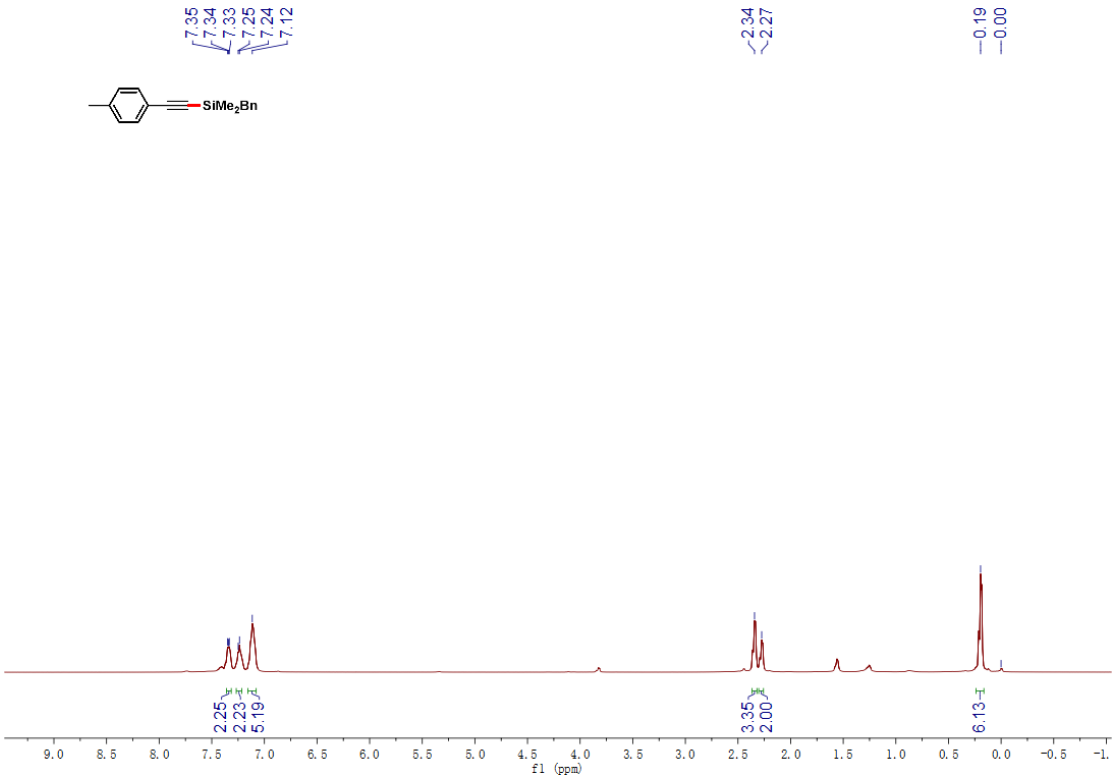
^{1}H NMR spectrum of compound **3aa**



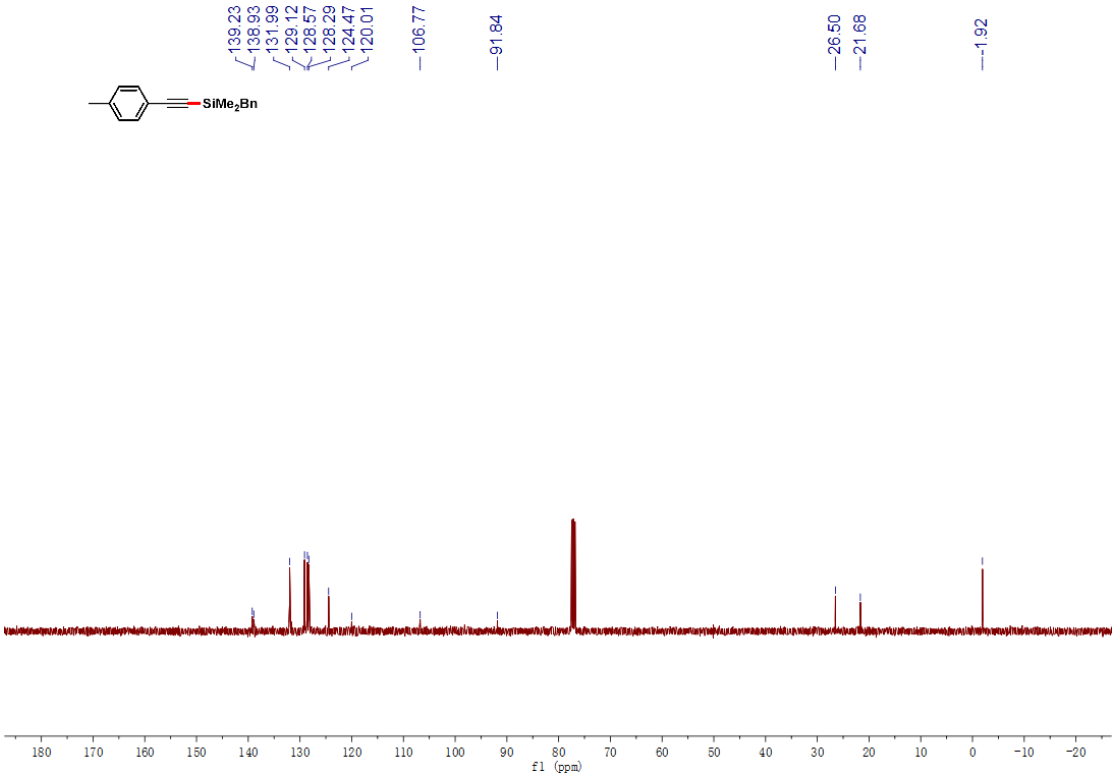
^{13}C NMR spectrum of compound **3aa**



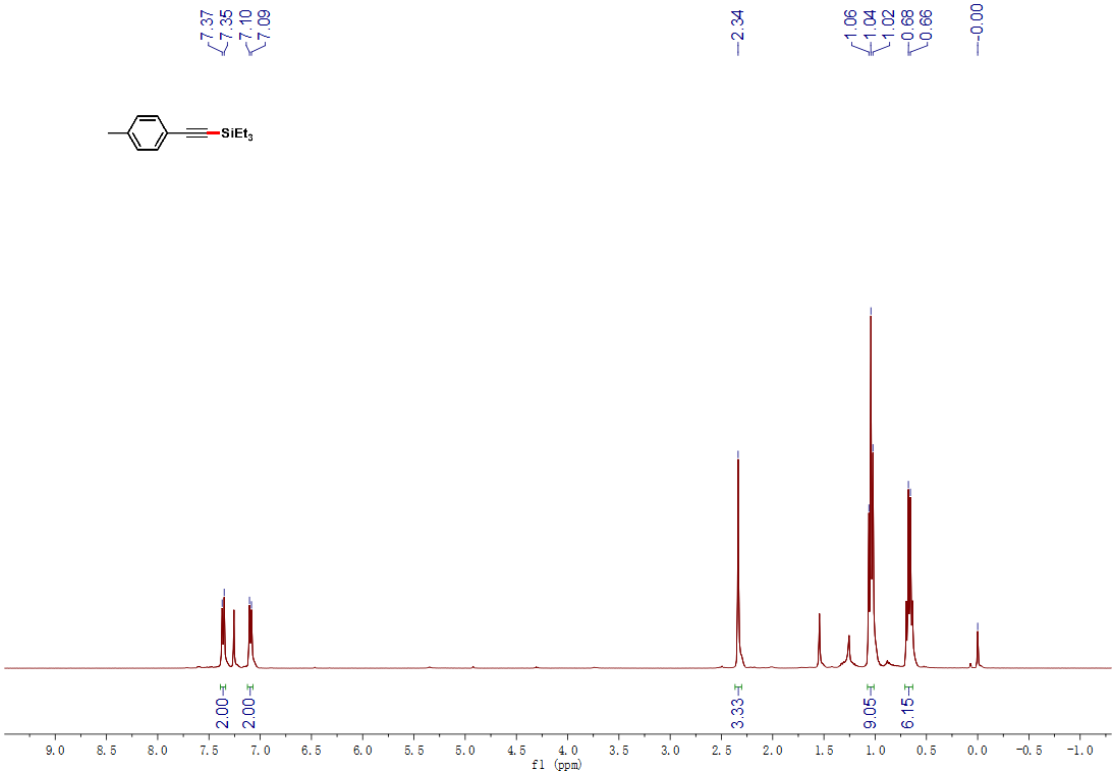
^{1}H NMR spectrum of compound **3ab**



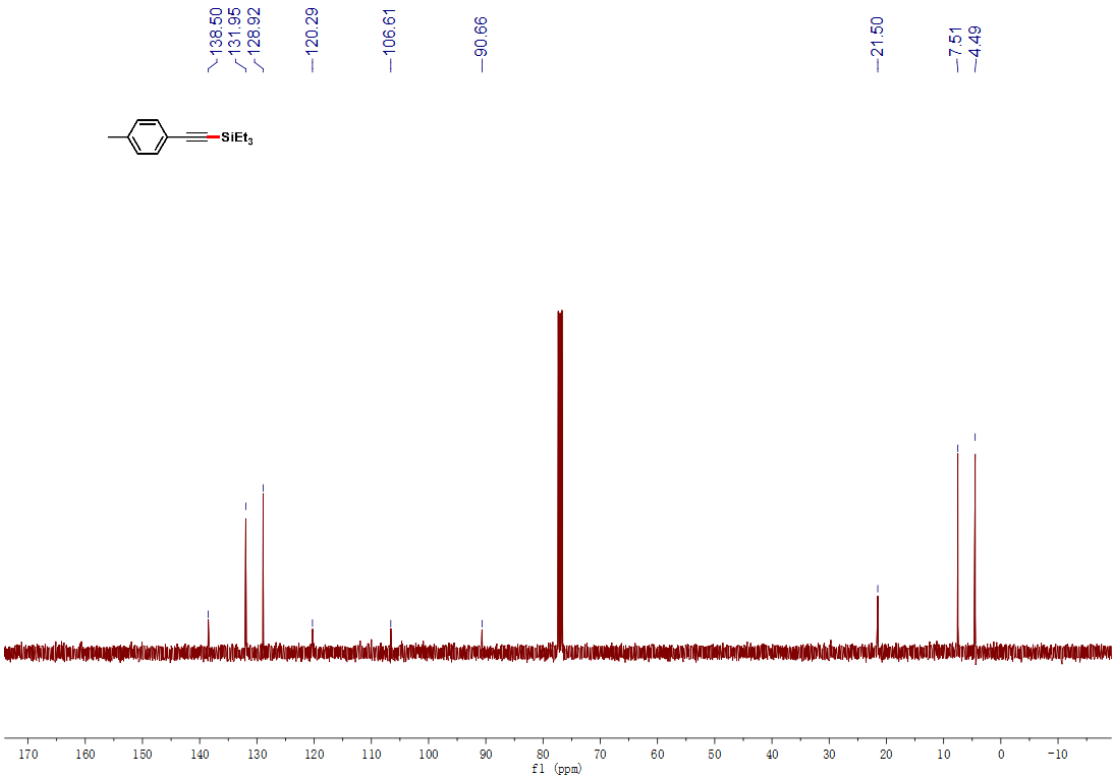
^{13}C NMR spectrum of compound **3ab**



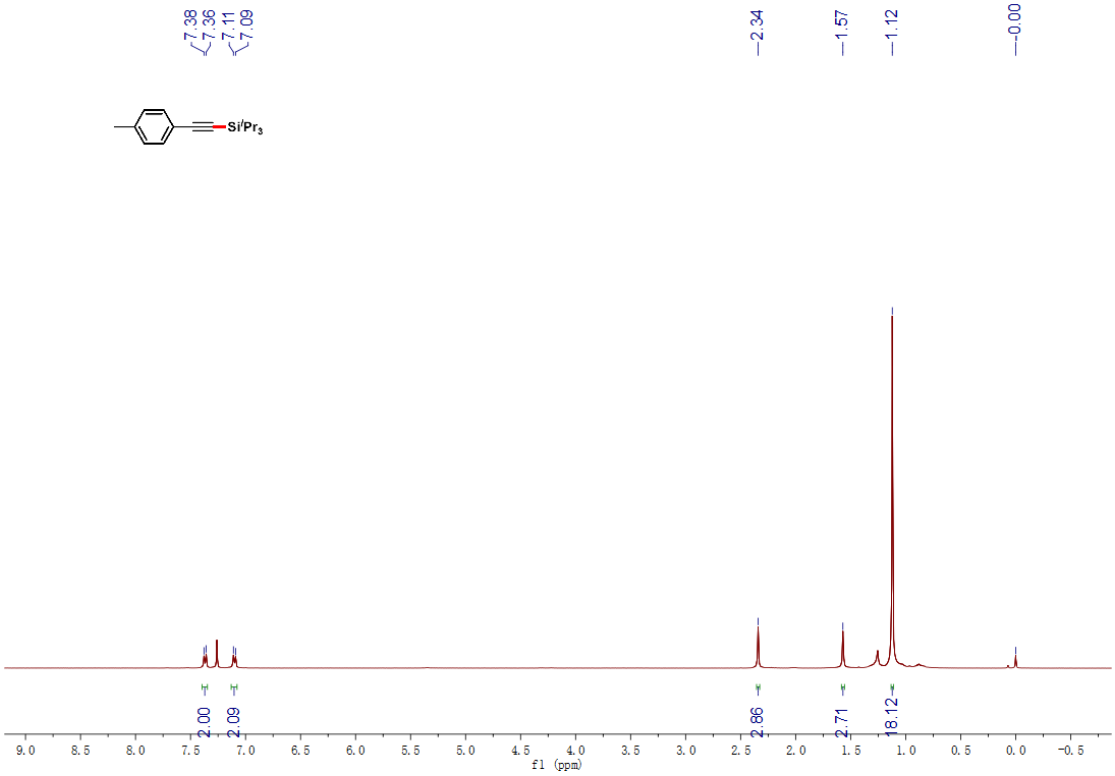
^{1}H NMR spectrum of compound **3ac**



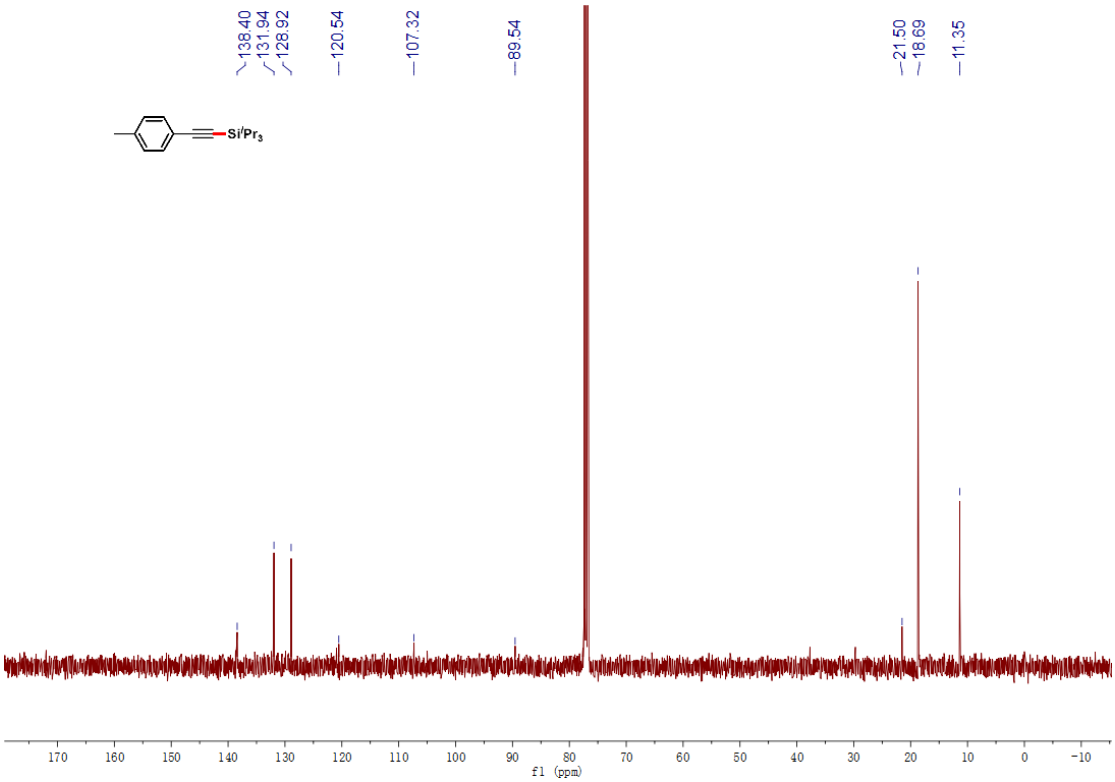
^{13}C NMR spectrum of compound **3ac**



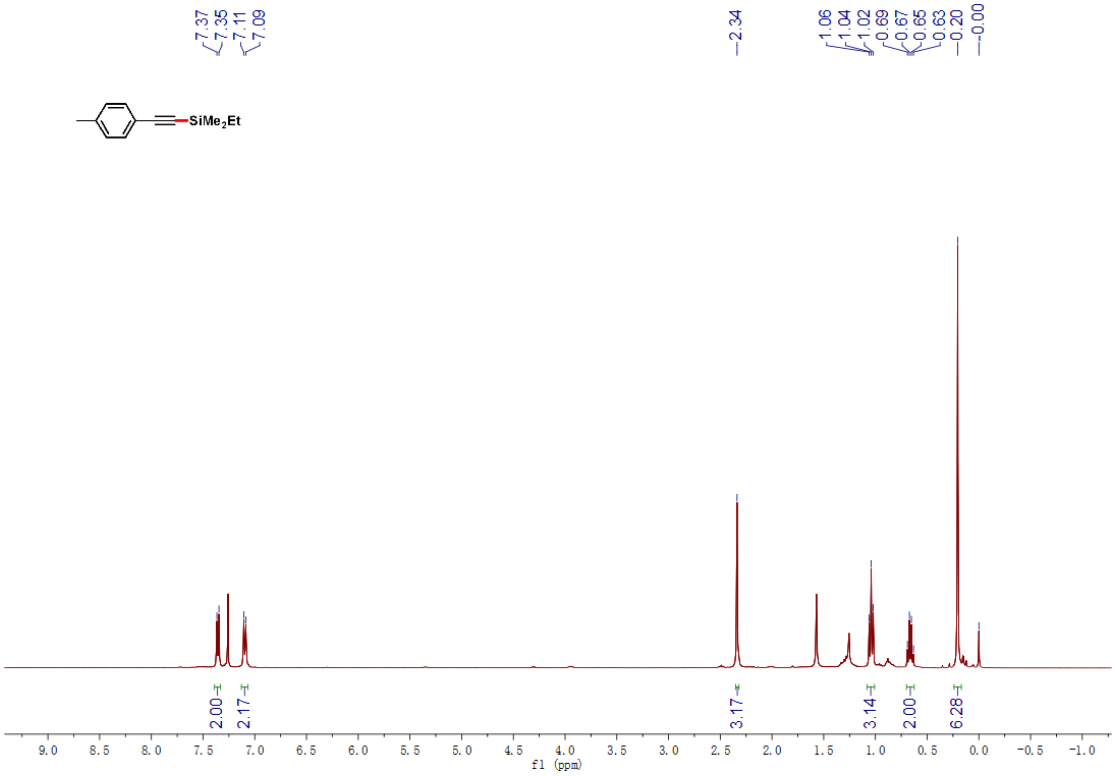
^{1}H NMR spectrum of compound **3ad**



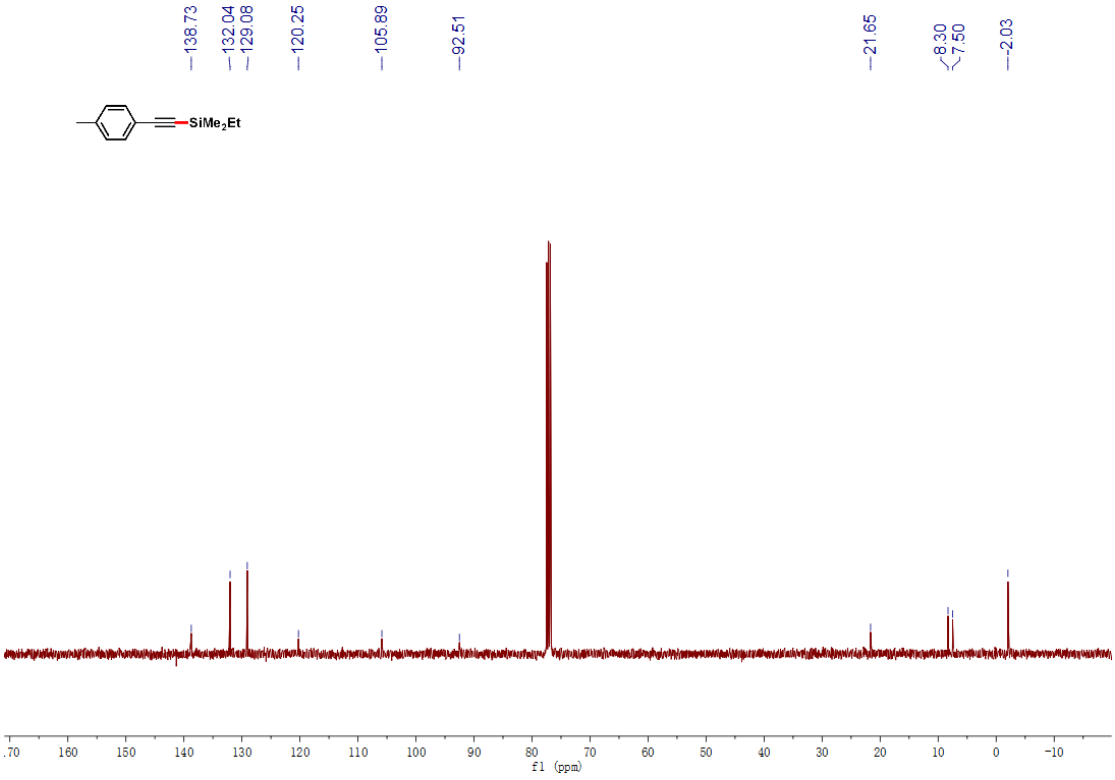
^{13}C NMR spectrum of compound **3ad**



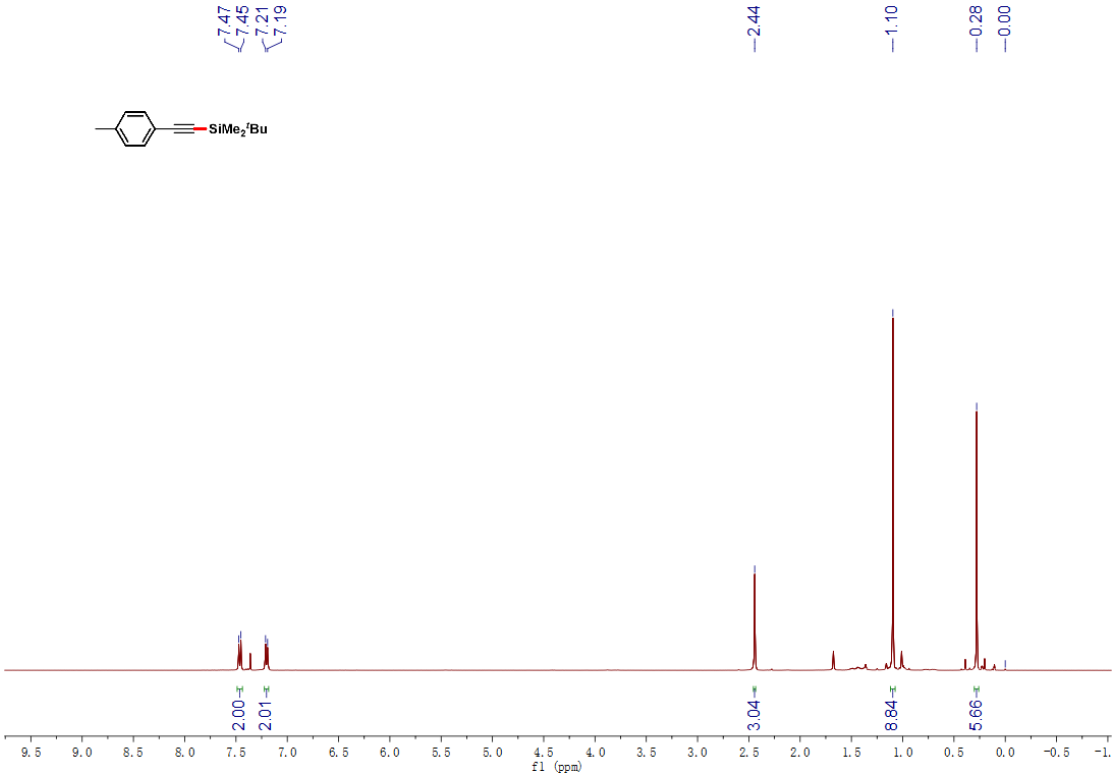
^{1}H NMR spectrum of compound **3ae**



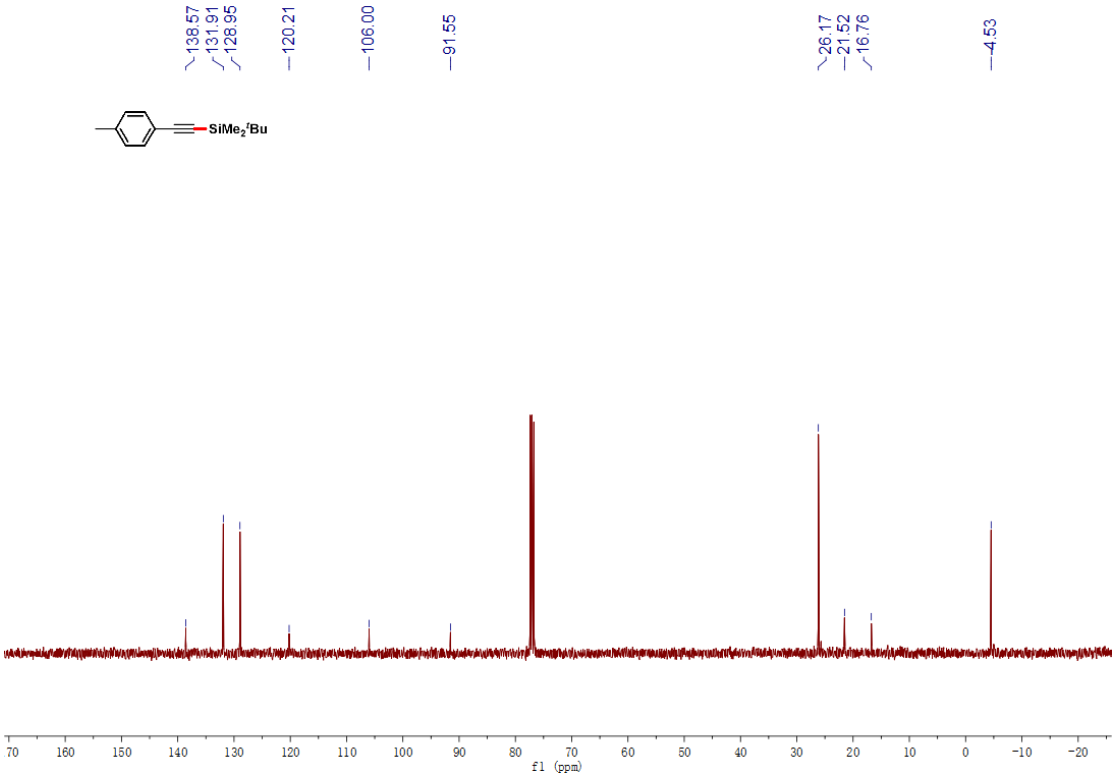
^{13}C NMR spectrum of compound **3ae**



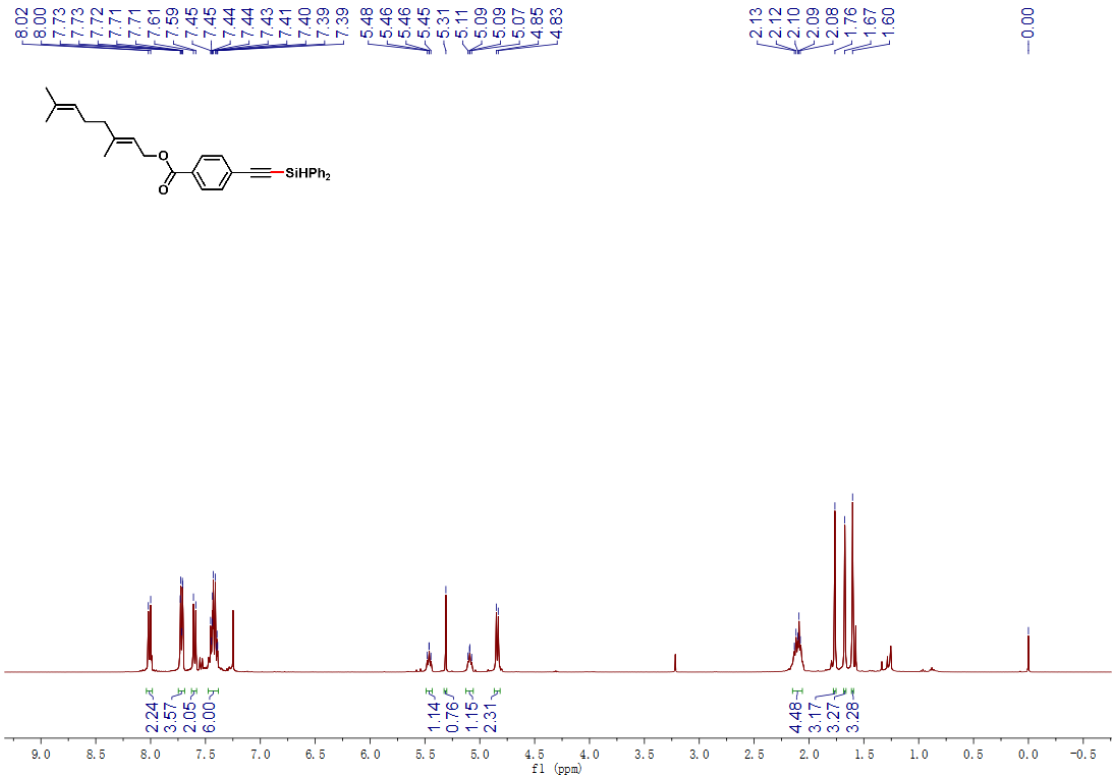
^{1}H NMR spectrum of compound **3af**



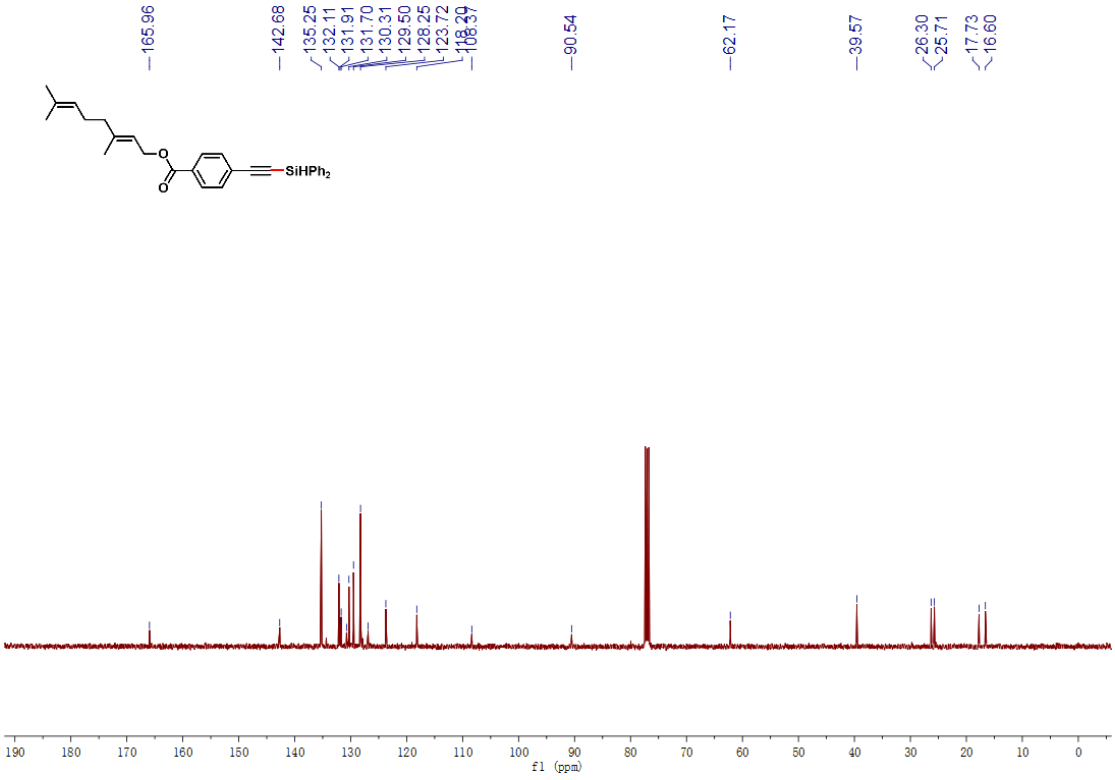
^{13}C NMR spectrum of compound **3af**



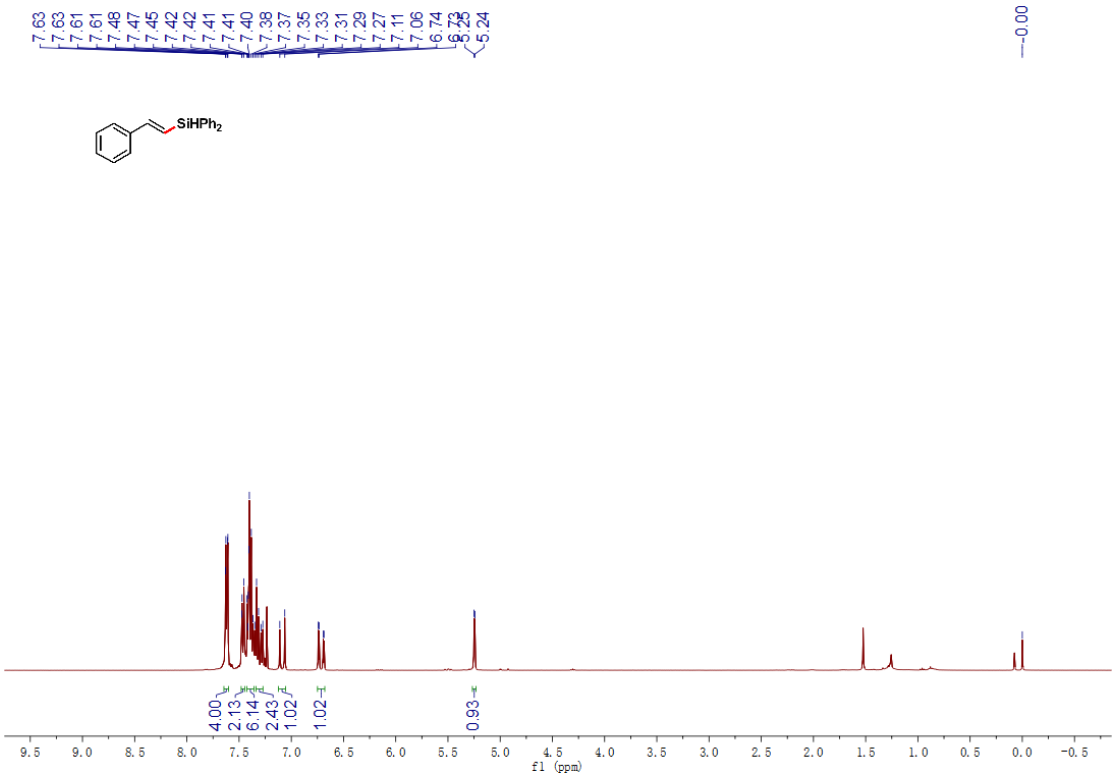
^{1}H NMR spectrum of compound **3ag**



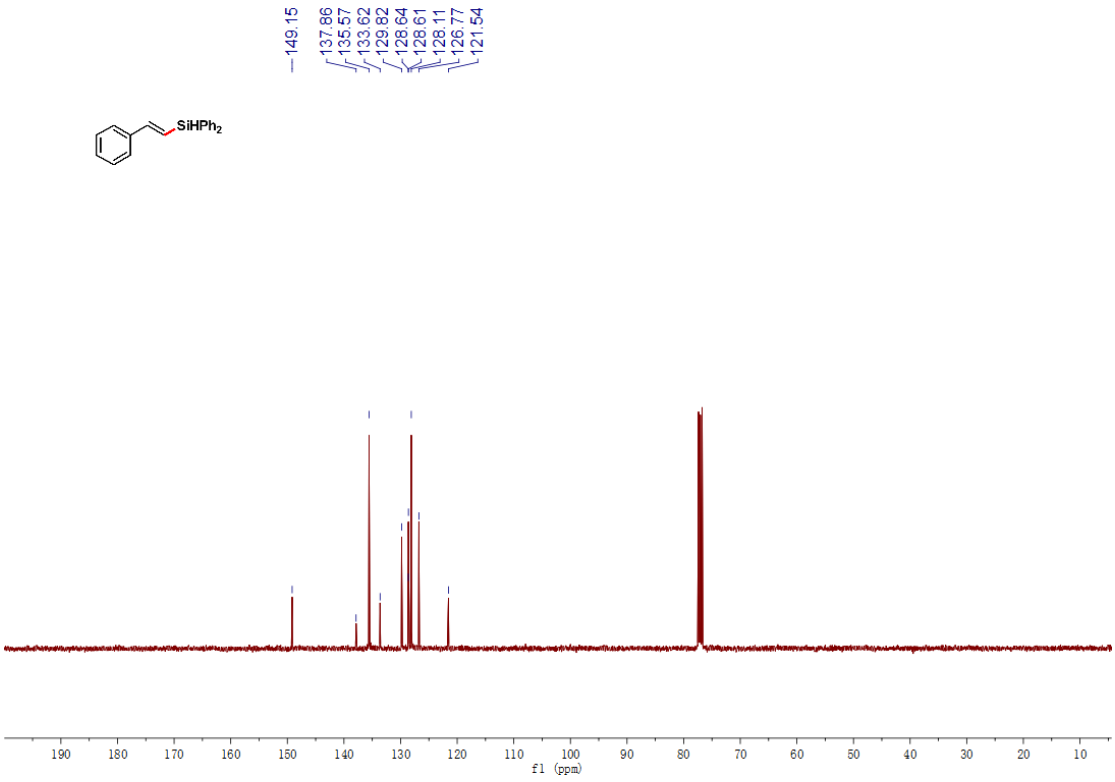
^{13}C NMR spectrum of compound **3ag**



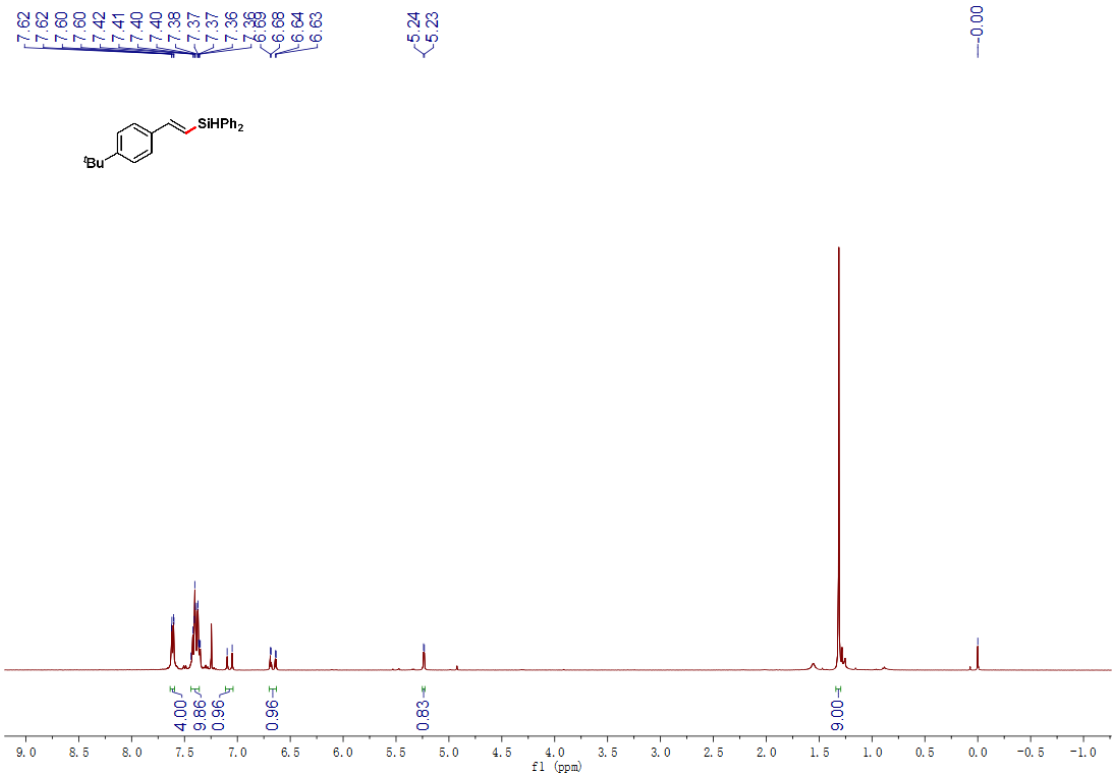
^{1}H NMR spectrum of compound **4a**



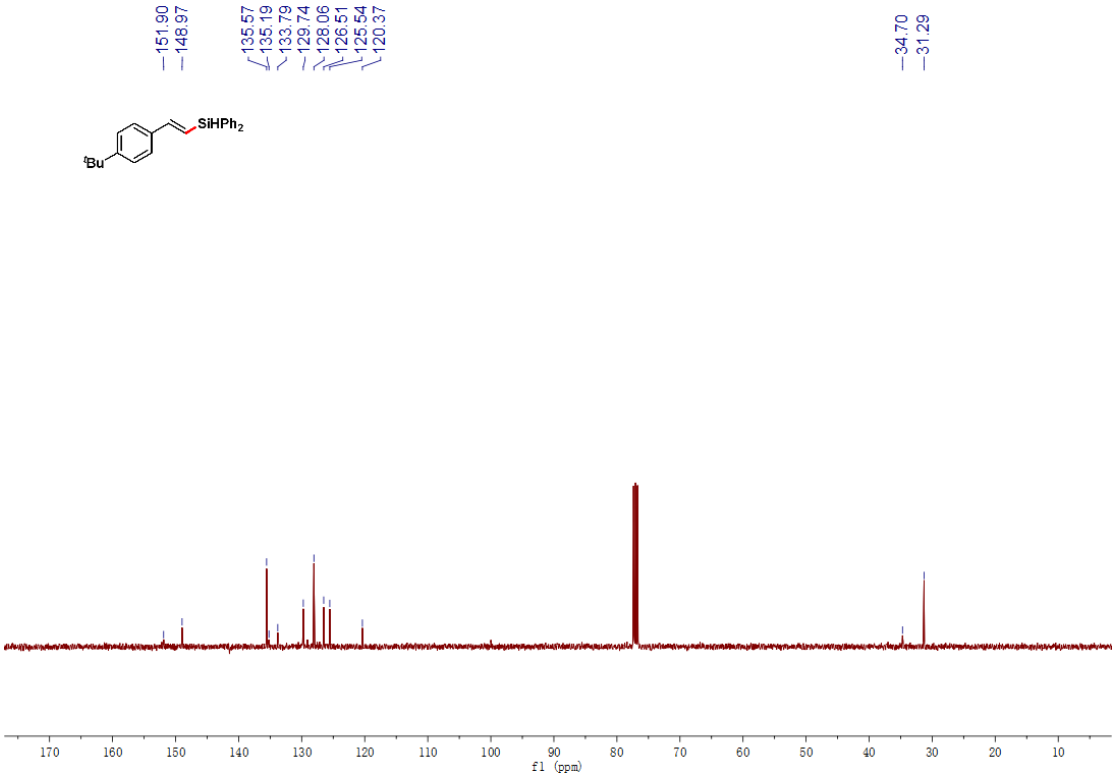
^{13}C NMR spectrum of compound **4a**



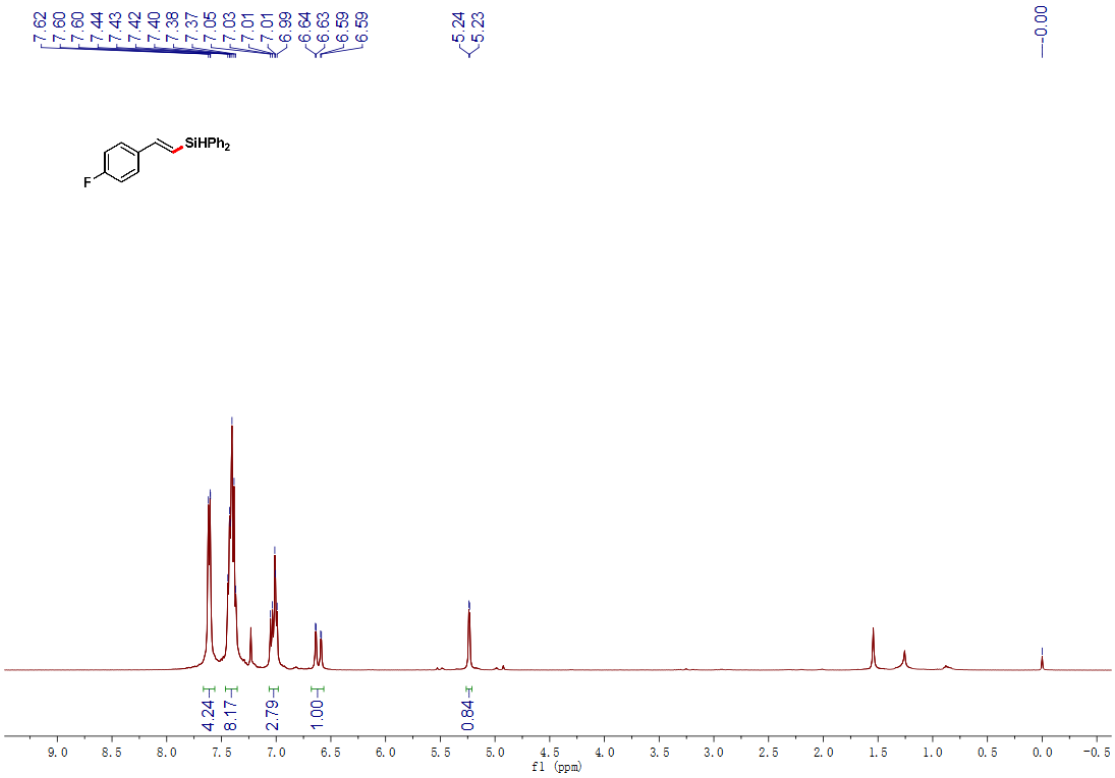
^{1}H NMR spectrum of compound **4b**



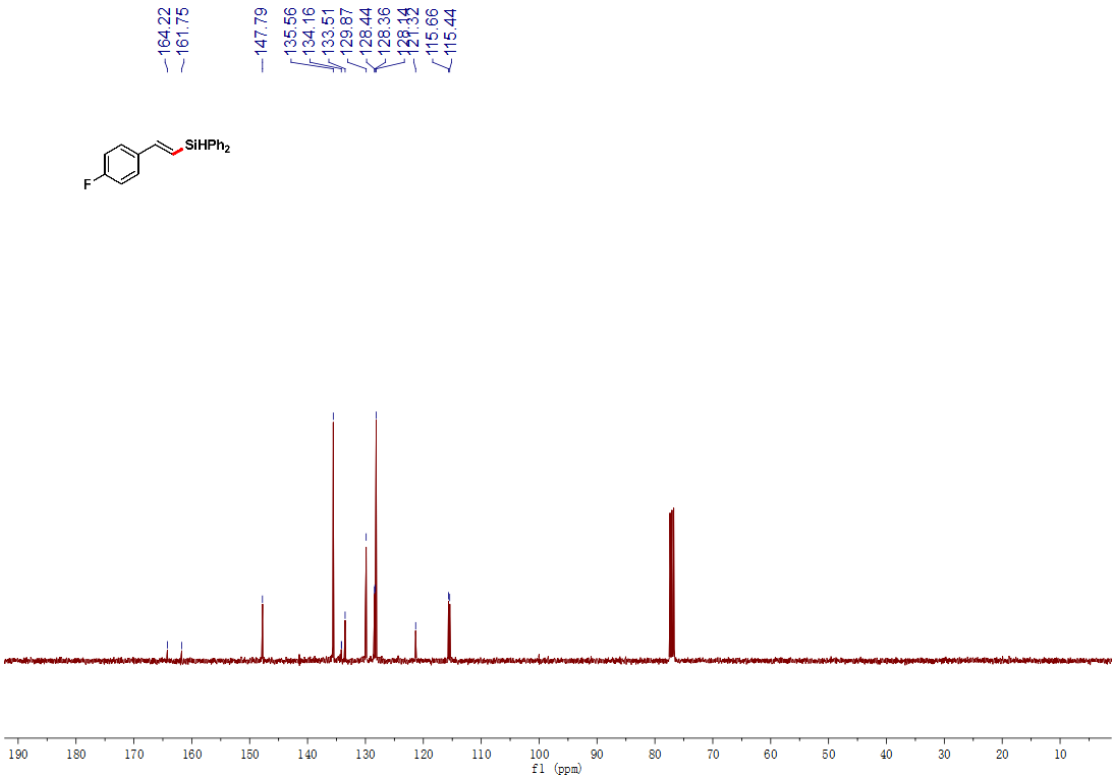
^{13}C NMR spectrum of compound **4b**



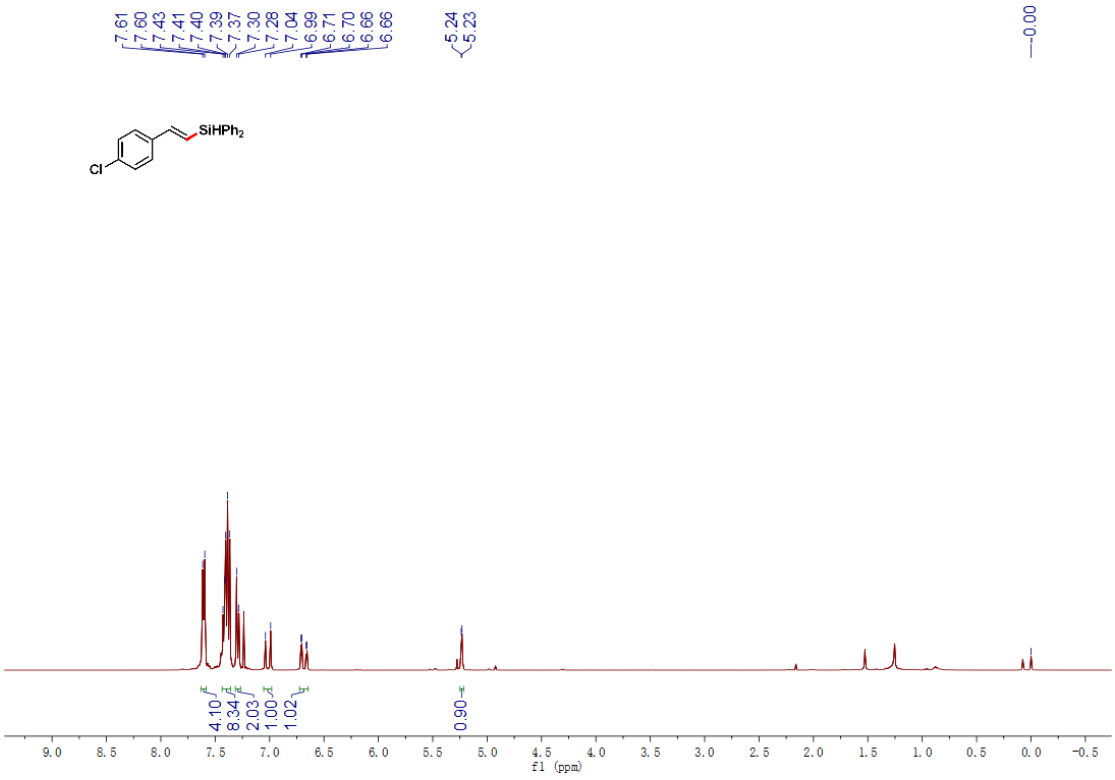
^{1}H NMR spectrum of compound **4c**



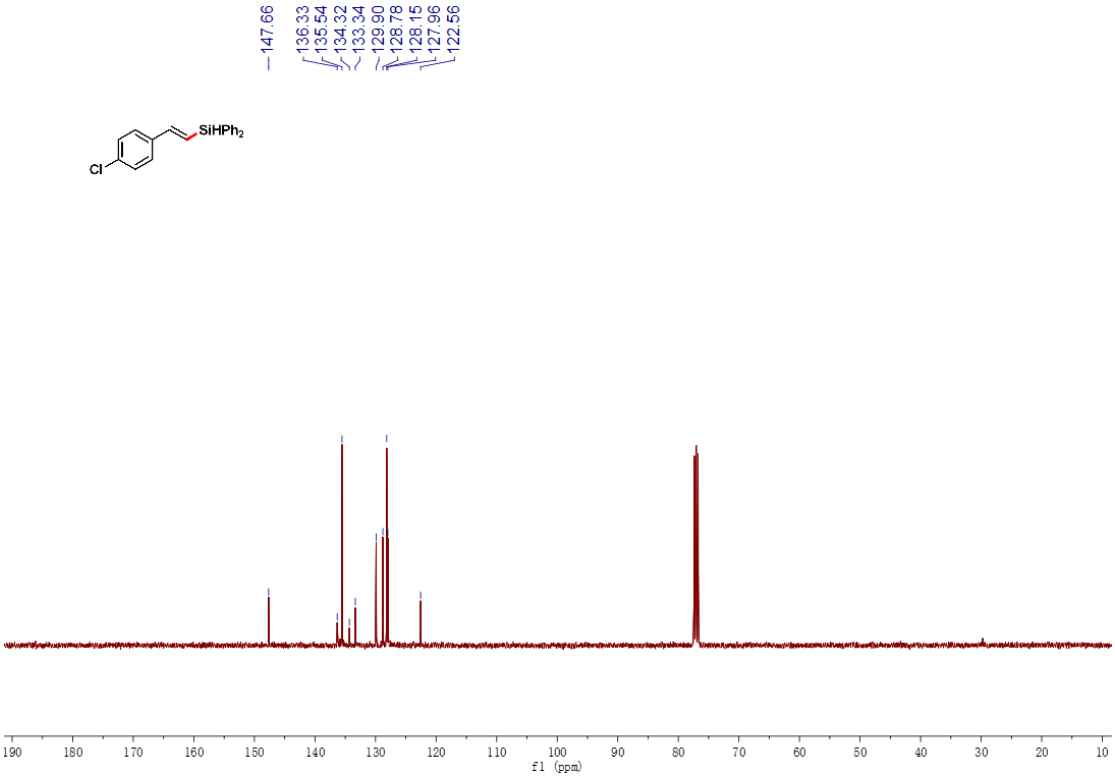
^{13}C NMR spectrum of compound **4c**



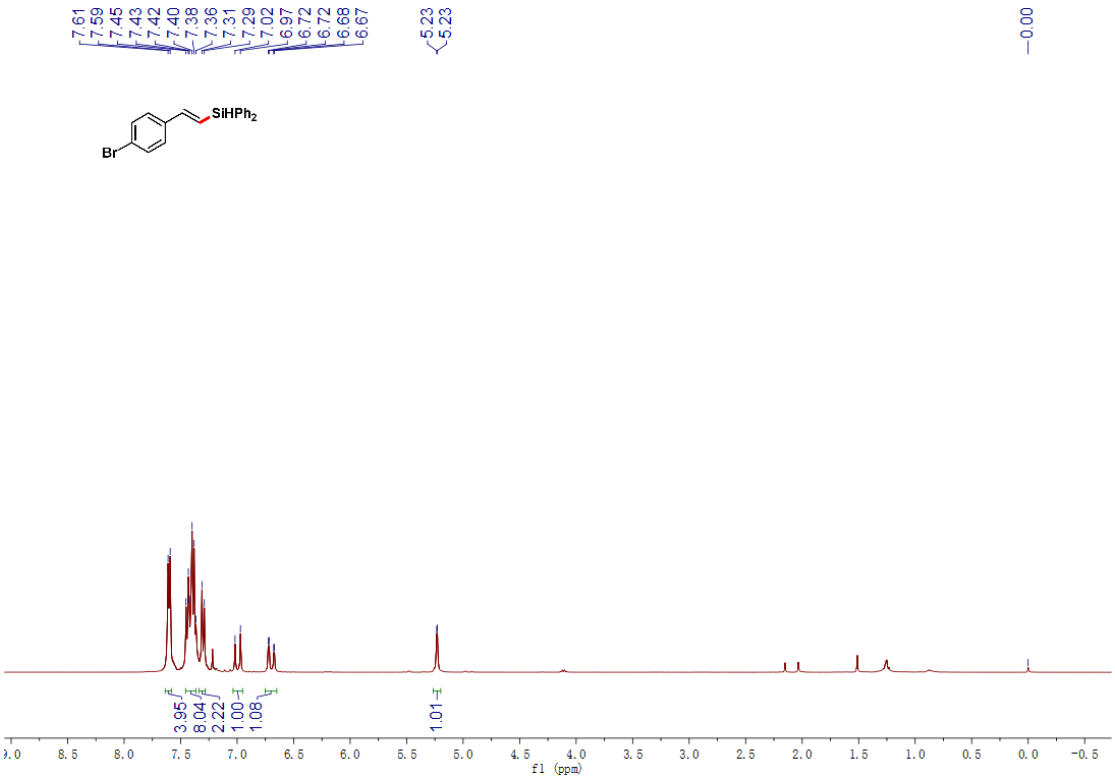
^{1}H NMR spectrum of compound **4d**



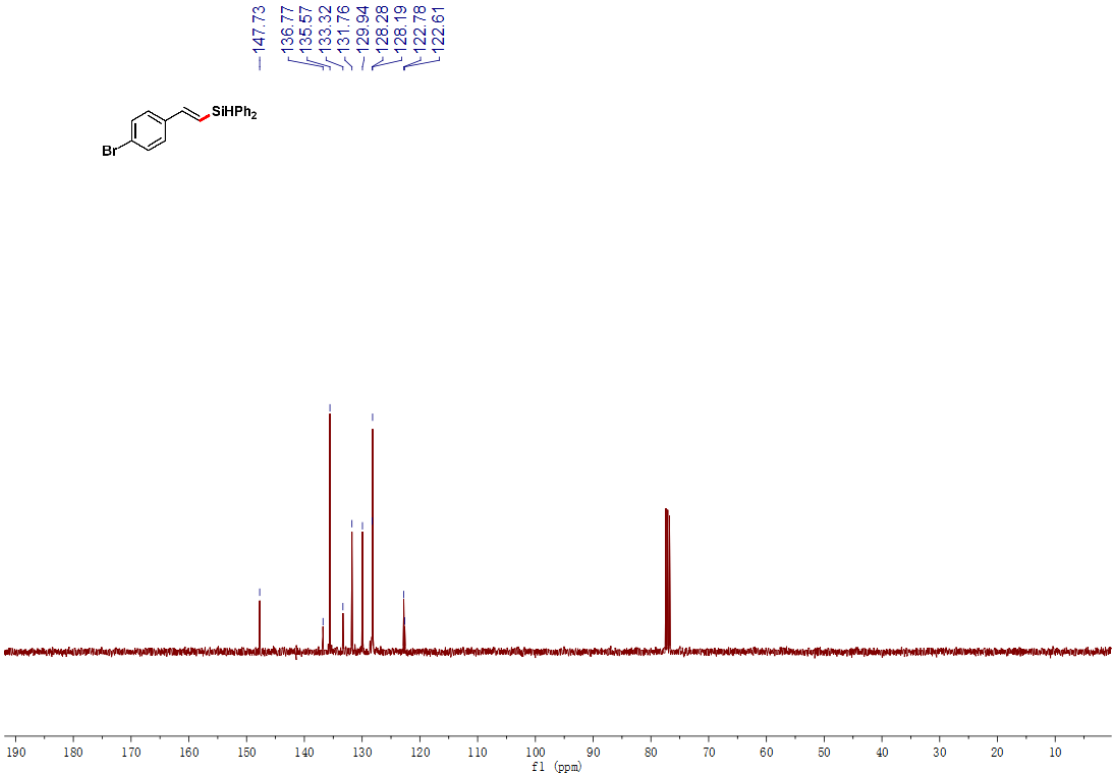
^{13}C NMR spectrum of compound **4d**



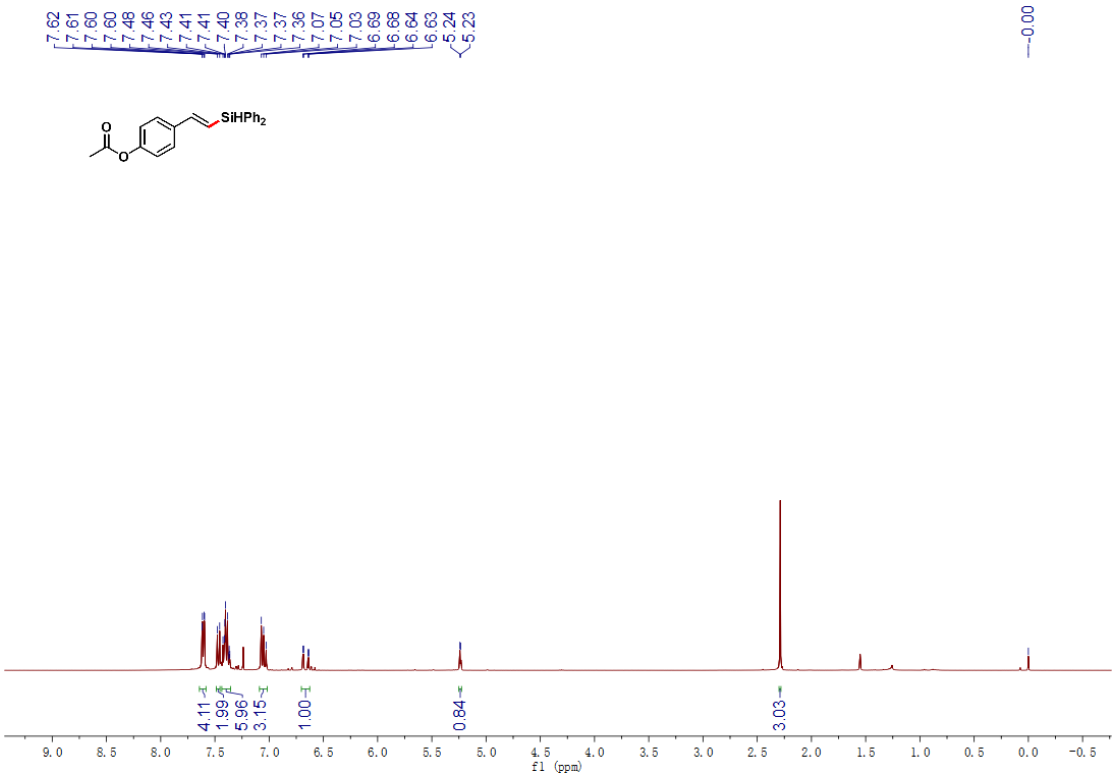
^{1}H NMR spectrum of compound **4e**



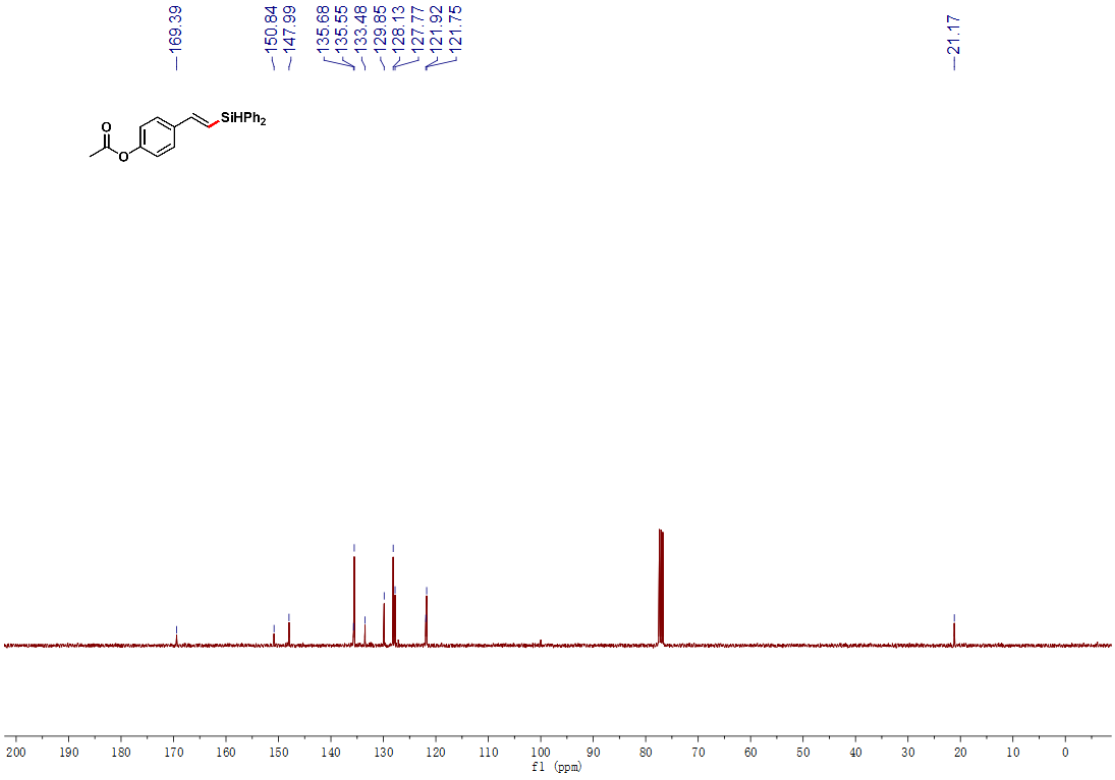
^{13}C NMR spectrum of compound **4e**



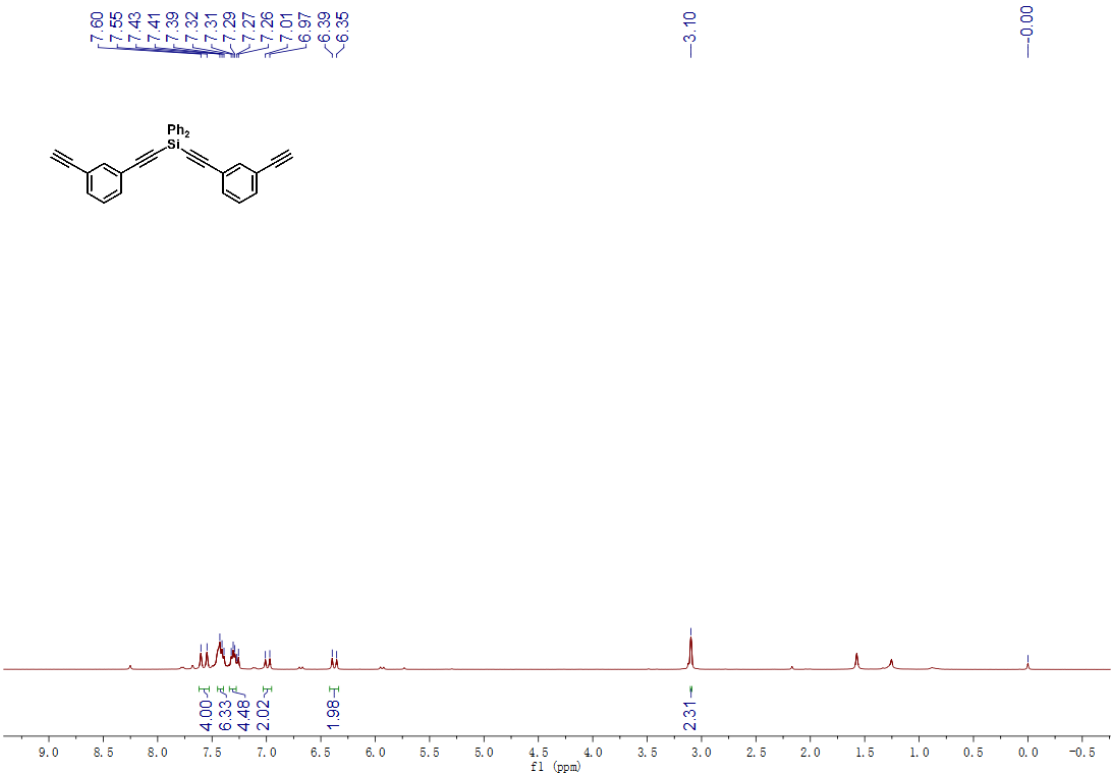
^{1}H NMR spectrum of compound **4f**



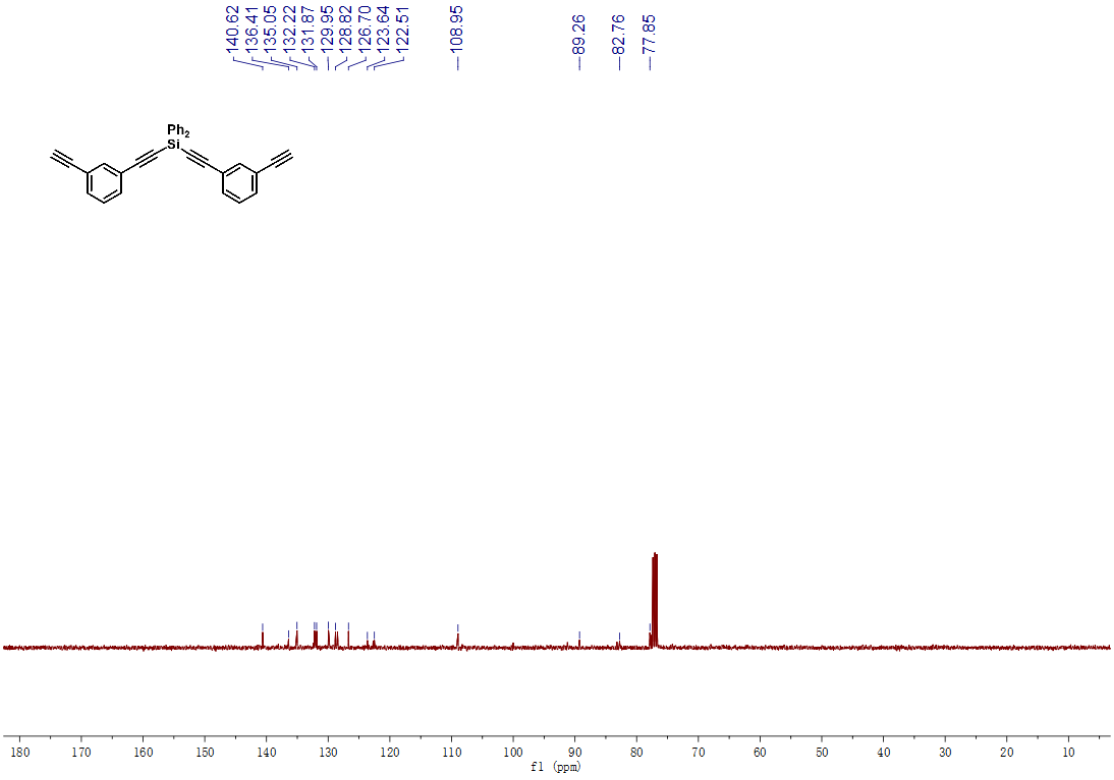
^{13}C NMR spectrum of compound **4f**



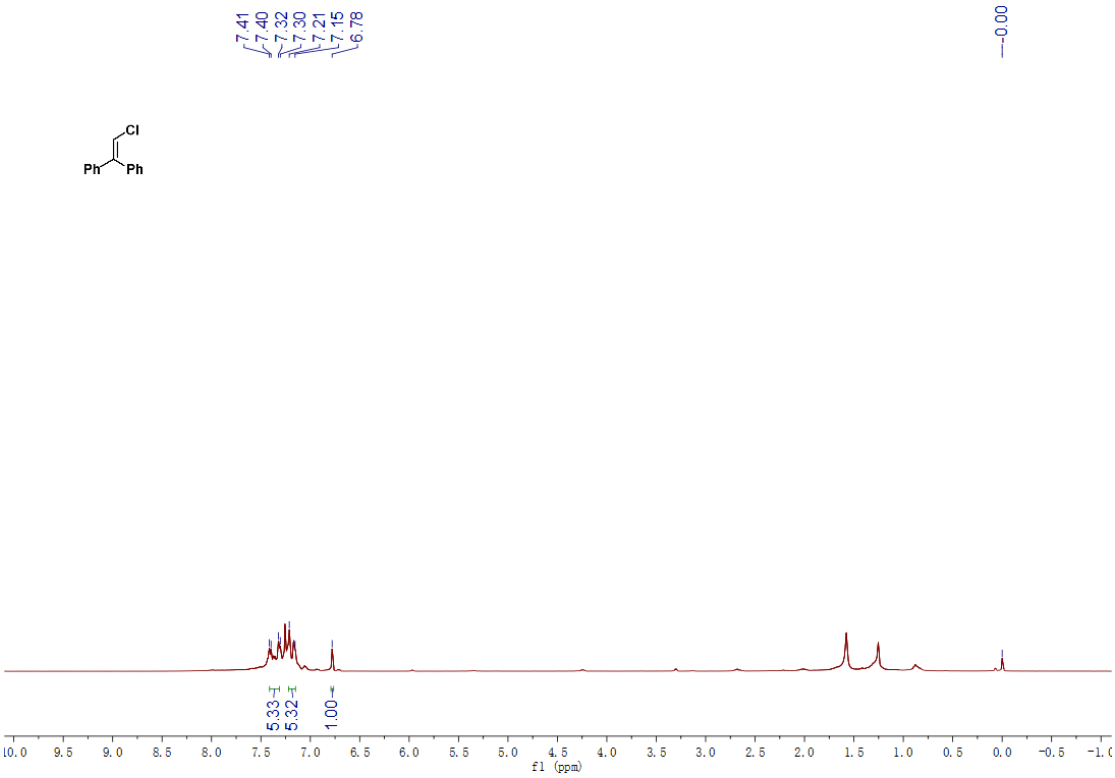
^{1}H NMR spectrum of compound **5a**



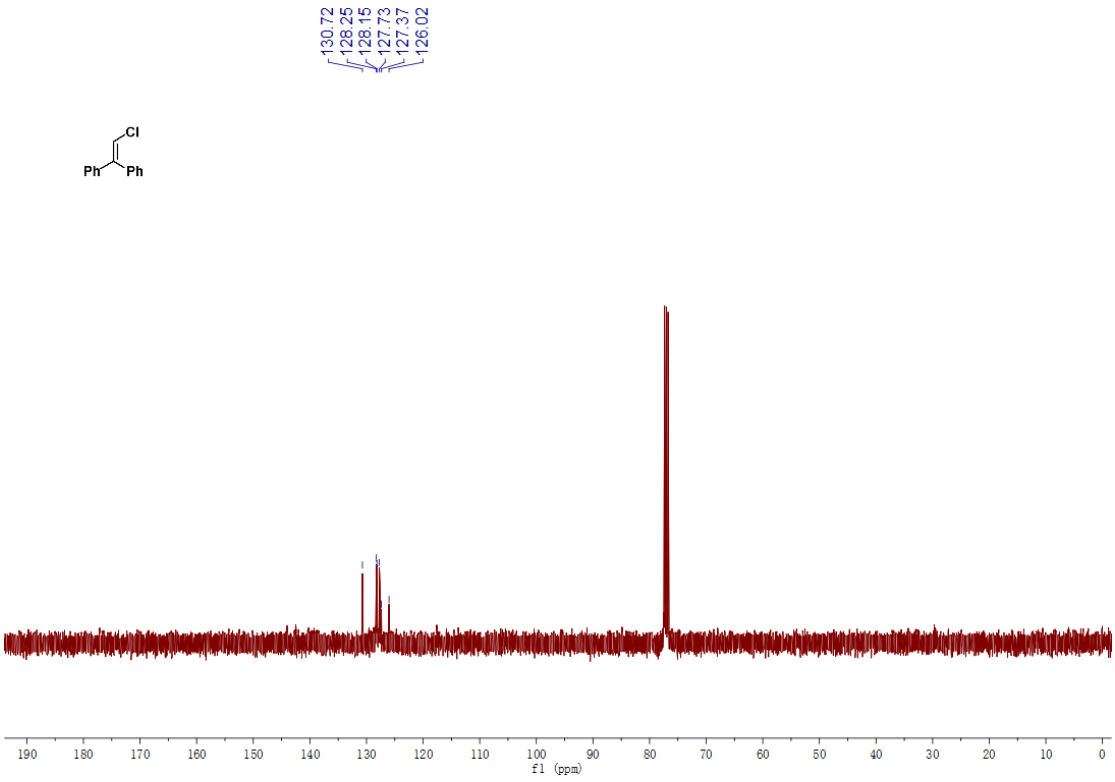
^{13}C NMR spectrum of compound **5a**



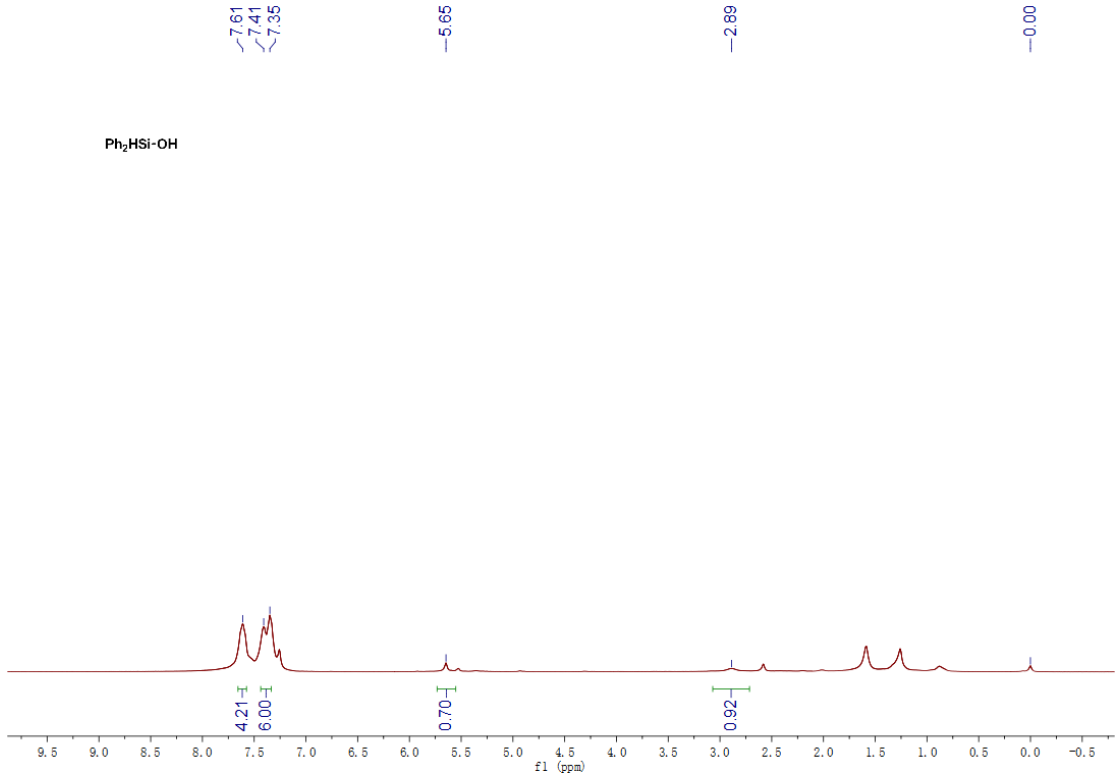
^{1}H NMR spectrum of compound **6**



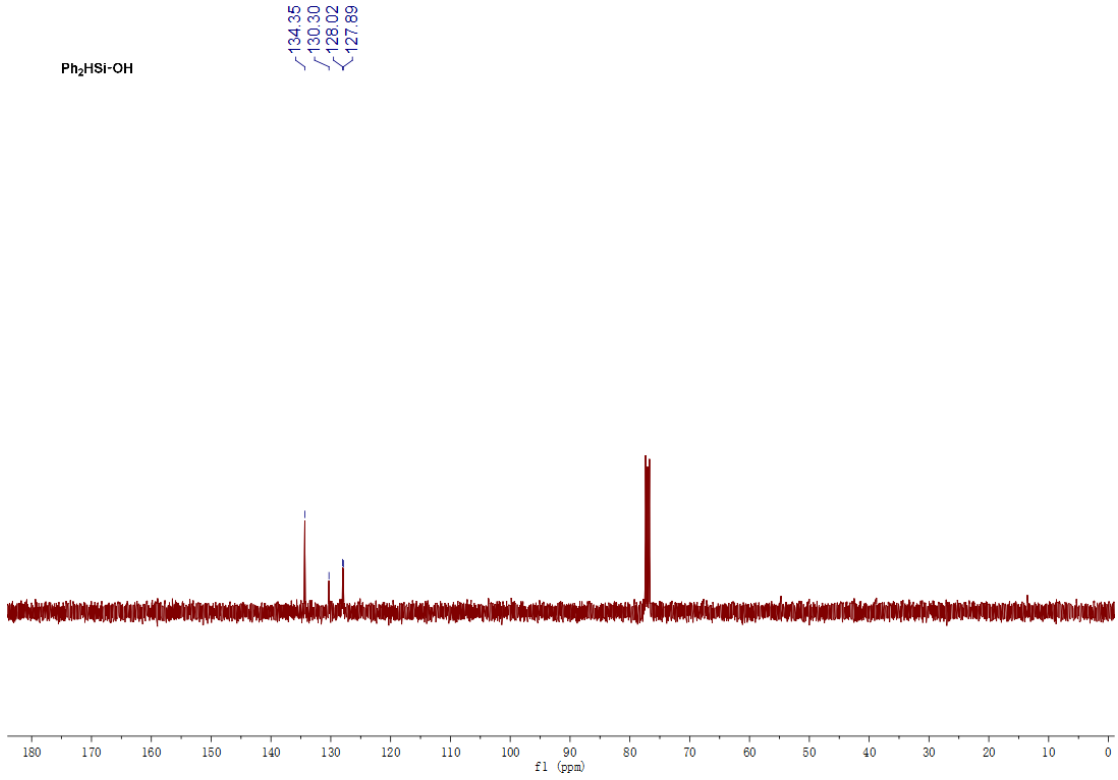
^{13}C NMR spectrum of compound **6**



^{1}H NMR spectrum of compound **7**



^{13}C NMR spectrum of compound **7**



9. Reference

[1] Noble, A. MacMillan, D. W. C. *J. Am. Chem. Soc.,* 2014, **136**, 11602

[2] Jin, W. W.; Wu, M. C.; Xiong, Z. M. Zhu, G. G. *Chem. Commun.*, 2018, **54**, 7924