Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalytic C(sp)-Si Cross-coupling Silylation of Alkynyl bromides with Hydrosilanes by Palladium Catalysis

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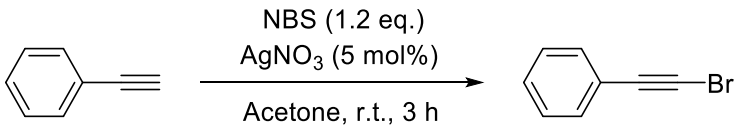
1. General information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Dichloromethane (DCM), toluene, were freshly distilled from CaH_2, Ether (Et_2O), tetrahydrofuran (THF) and 1, 4-dioxane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). ^{1}H, ^{13}C ,^{19}F, NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$ or CD_2Cl_2. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Agilent 1260 infinity using a chiralcel phenomenex column.

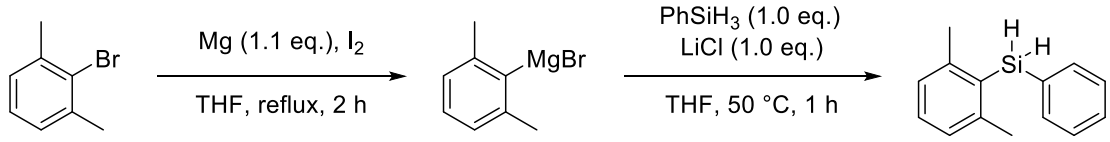
2. Substrates synthesis

2.1 Synthesis of alkynyl bromides



General procedure for the synthesis of alkynyl bromides (**1a-1aa, 1ac-1ae**): $AgNO_3$ (0.17 g, 5 mol%) was added to a solution of phenylacetylene (2.58 mL, 20 mmol, 1.0 equiv.) in acetone (50 mL). Then NBS (4.27 g, 24 mmol, 1.2 equiv.) was added in portion. The mixture was stirred for 3 h at room temperature, and then concentrated in vacuo. The residue was dissolved in PE or DCM and filtered through a short column of silica gel. Solvent was removed in vacuo to afford bromoalkyne (3.58 g, 99% yield). Bromoalkynes (**1a-1aa, 1ac-1ae**) were also obtained as above procedures. Substrates (**1ab**) was prepared using the literature procedure.[1]

2.2 Synthesis of (2,6-dimethylphenyl)(phenyl)silane



The preparation of (2,6-dimethylphenyl)(phenyl)silane was according to literature procedure.[2]To a dried 2-neck round bottom flask equipped with a water-cooled condenser was added magnesium turnings (534.8 mg, 22.0 mmol, 1.1 equiv.), and three pieces of iodine partials, and THF (20 mL) under argon. 2-bromo-1,3-dimethylbenzene (3.7 g, 20.0 mmol, 1.0 equiv.) was added slowly over the course of 15 min to the refluxing mixture of THF and magnesium turnings. Following that, the mixture was refluxed for an additional hour. The resulting Grignard reagent was cooled to 25 ˚C for the following procedure. To a suspension of LiCl (847.8 mg, 20.0 mmol, 1.0 equiv.) in 20.0 mL of THF was added the Grignard reagent, followed by the addition of phenylsilane (2.2 g, 20.0 mmol, 1.0 equiv.), at room temperature under argon. After the reaction mixture was stirred in an oil bath maintained at 50 °C for 6 h, the reaction was quenched by the addition of an aqueous solution of NH_4Cl (10.0 mL) at room temperature. The resulting mixture was filtered through Celite and washed with Et_2O (20 mL x 3). The organic phase was dried over Na_2SO_4 and concentrated in vacuum to give the crude product, which was purified by chromatography on silica gel eluting with hexane to afford the title compound (3.4 g, 80 %) as colorless oil. Other hydrosilanes were also obtained as above procedures or obtained from commercial suppliers and used without further purification.

3. Synthesis of chiral ligands L36

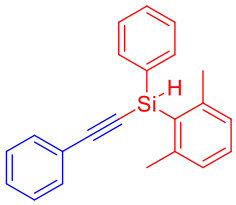
Chiral ligands **L36** was according to literature procedure.[3-4]

4. General procedure for Pd-catalyzed of Si-C coupling of alkynyl bromides with hydrosilanes.

A vial was charged with LiBr (34.74 mg, 0.4 mmol, 2.0 equiv.), $PdBr_2$ (1.33 mg, 2.5 mol%), Xantphos (5.78 mg, 5 mol%) and evacuated under high vacuum and backfilled with N_2. Alkynyl bromide (36.4 mg, 0.2 mmol, 1.0 equiv.), hydrosilane (127 mg, 0.6 mmol, 3.0 equiv.), Et_3N (60 mg, 0.6 mmol, 3.0 equiv.), 1,4-dioxane (2

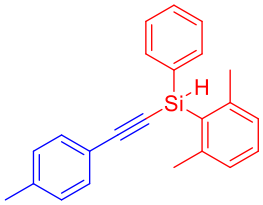
mL) was next added. The mixture was stirred at 60 ℃ for 48 hours. The crude product was purified by silica gel chromatography (petroleum et) to provide the desired product.

5. Spectral Data of Products



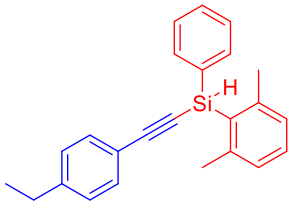
(2,6-dimethylphenyl)(phenyl)(phenylethynyl)silane(3a):

Yellow oil (48 mg, 78% yield), purified by column chromatography (SiO2, PE). 1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2 H), 7.46 – 7.41 (m, 2 H), 7.31 – 7.20 (m, 6 H), 7.13 – 7.17 (m, 1 H), 6.95 (d, *J* = 8 Hz, 2 H), 5.56 (s, 1 H), 2.45 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.49, 134.89, 132.68, 132.17, 130.54, 129.93, 129.33, 129.13, 128.43, 128.26, 127.94, 122.86, 109.02, 88.26, 24.39. HRMS (APCI) m/z: [M+H]+ calculated for $C_{22}H_{21}Si$:313.1407 , found: 313.1398.



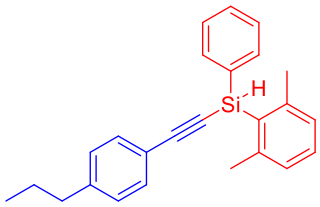
(2,6-dimethylphenyl)(phenyl)(p-tolylethynyl)silane(3b):

Yellow oil (40 mg, 61% yield), purified by column chromatography (SiO2, PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2 H), 7.36 – 7.25 (m, 5 H), 7.13 – 7.17 (m, 1H), 7.03 (d, *J* = 8 Hz, 2 H), 6.95 (d, *J* = 8 Hz, 2 H), 5.56 (s, 1 H), 2.45 (s, 6 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.48, 139.37, 134.89, 132.84, 132.08, 130.47, 129.87, 129.49, 129.18, 128.22, 127.92, 119.82, 109.34, 87.38, 24.38, 21.68. HRMS (APCI) m/z: [M+H]+ calculated for $C_{23}H_{23}Si$: 327.1564, found: 327.1505.



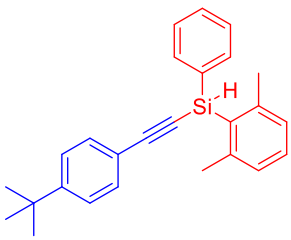
(2,6-dimethylphenyl)((4-ethylphenyl)ethynyl)(phenyl)silane(3c):

Yellow oil (43 mg, 63% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 7.61 – 7.56 (m, 2 H), 7.38 – 7.34 (m, 2 H), 7.30 – 7.24 (m, 3 H), 7.14 (t, J = 8 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 4 Hz, 2 H), 5.56 (s, 1 H), 2.54 (q, J = 8 Hz, 2 H), 2.45 (s, 6 H), 1.12 (t, J = 8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.67, 145.50, 134.90, 132.87, 132.19, 130.48, 129.87, 139.51, 128.23, 128.01, 127.92, 120.07, 109.38, 87.38, 29.01, 24.39, 15.46. HRMS (APCI) m/z: [M+H]+ calculated for $C_{24}H_{25}Si$: 341.172, found: 341.1719.



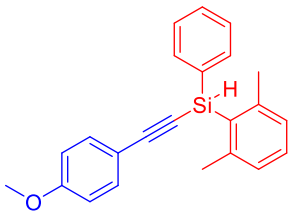
(2,6-dimethylphenyl)(phenyl)((4-propylphenyl)ethynyl)silane(3d):

Yellow oil (46 mg, 66% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) 7.68 – 7.49 (m, 2 H), 7.40 – 7.33 (m, 2 H), 7.34 – 7.22 (m, 3 H), 7.18 – 7.13 (m, 1 H), 7.04 (d, J = 8 Hz, 2 H), 6.95 (d, J = 8 Hz, 2 H), 5.56 (s, 1 H), 2.50 (t, J = 8 Hz, 2 H), 2.46 (s, 6 H), 1.59 – 1.48 (m, 2 H), 0.84 (t, J = 8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.51, 144.16, 134.90, 132.85, 132.10, 130.47, 129.88, 129.50, 128.62, 128.23, 127.91, 120.07, 109.37, 87.36, 38.12, 24.48, 24.42, 13.89. HRMS (APCI) m/z: [M+H]+ calculated for $C_{25}H_{27}Si$: 355.1877, found: 355.1889.



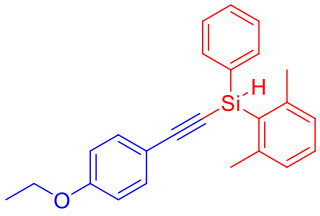
((4-(tert-butyl)phenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3e):

Yellow oil (39 mg, 53% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2 H), 7.41 – 7.37 (m, 2 H), 7.32 – 7.25 (m, 5 H), 7.19 – 7.14 (m, 1 H), 6.96 (d, *J* = 8 Hz, 2 H), 5.56 (s, 1 H), 2.46 (s, 6 H), 1.23 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.48, 145.51, 134.90, 132.84, 131.94, 130.48, 129.87, 129.50, 128.22, 127.91, 125.46, 119.86, 109.31, 87.39, 34.98, 31.25, 24.41. HRMS (APCI) m/z: [M+H]+ calculated for $C_{26}H_{29}Si$: 369.2033, found: 369.1993.



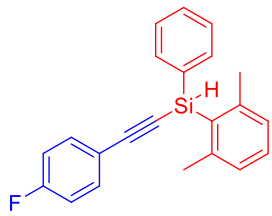
(2,6-dimethylphenyl)((4-methoxyphenyl)ethynyl)(phenyl)silane(3f):

Yellow oil (45 mg, 66% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2 H), 7.41 – 7.37 (m, 2 H), 7.33 – 7.26 (m, 3 H), 7.18 – 7.14 (m, 1 H), 6.96 (d, *J* = 8 Hz, 2 H), 6.76 (d, *J* = 8 Hz, 2 H), 5.56 (s, 1 H), 3.72 (s, 3 H), 2.46 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.25, 145.47, 134.88, 133.73, 132.96, 130.45, 129.84, 129.60, 128.21, 127.91, 114.99, 114.04, 109.24, 86.54, 55.39, 24.38. HRMS (APCI) m/z: [M+H]+ calculated for $C_{23}H_{23}OSi$: 343.1513, found: 343.1592.



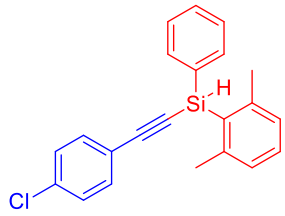
(2,6-dimethylphenyl)((4-ethoxyphenyl)ethynyl)(phenyl)silane(3g):

Yellow oil (38 mg, 53% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2 H), 7.39 – 7.35 (m, 2 H), 7.31 – 7.25 (m, 3 H), 7.17 – 7.13 (m, 1 H), 6.95 (d, *J* = 8 Hz, 2 H), 6.74 (d, *J* = 8 Hz, 2 H), 5.55 (s, 1 H), 3.94 (q, *J* = 8 Hz, 2 H), 2.45 (s, 6 H), 1.32 (t, *J* = 8 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl3) δ 158.48, 144.31, 133.72, 132.56, 131.81, 129.27, 128.66, 128.45, 127.04, 126.73, 113.60, 113.34, 108.16, 85.24, 62.46, 23.22, 13.67. HRMS (APCI) m/z: [M+H]+ calculated for C24H25OSi: 357.1669, found: 357.1600.



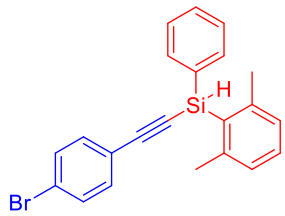
(2,6-dimethylphenyl)((4-fluorophenyl)ethynyl)(phenyl)silane(3h):

Yellow oil (33 mg, 50% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2 H), 7.46 – 7.40 (m, 2 H), 7.34 – 7.26 (m, 3 H), 7.19 – 7.15 (m, 1 H), 6.99 – 6.91 (m, 4 H), 5.55 (s, 1 H), 2.45 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.00 (d, J = 249 Hz), 145.48, 134.87, 134.22, 134.14, 132.54, 130.29 (d, J = 61 Hz), 129.21, 128.29, 127.97, 119.00 (d, J = 4 Hz), 115.78 (d, J = 22 Hz), 107.83, 88.10, 24.39. ^{19}F NMR (500 MHz, $CDCl_3$) δ -109.17. HRMS (APCI) m/z: [M+H]+ calculated for $C_{22}H_{20}FSi$: 331.1313, found: 331.1311.



((4-chlorophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3i):

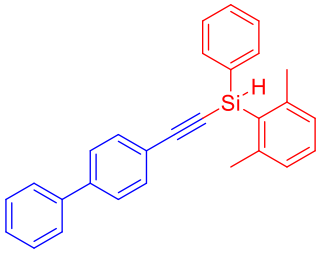
Yellow oil (46 mg, 67% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.59 (m, 2 H), 7.36 (d, J = 8 Hz, 2 H), 7.33 – 7.26 (m, 3 H), 7.23 – 7.12 (m, 3 H), 6.96 (d, J = 8 Hz, 2 H), 5.55 (s, 1 H), 2.45 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.48, 135.21, 134.86, 133.39, 132.35, 130.62, 130.01, 129.05, 128.80, 128.30, 128.23, 127.97, 121.30, 107.62, 89.53, 24.41. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{20}ClSi$: 347.1017, found: 347.0992.



((4-bromophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3j):

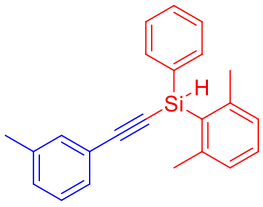
Yellow oil (62 mg, 79% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 2 H), 7.40 – 7.21 (m, 7 H), 7.10 – 7.17 (m,

1 H), 6.95 (d, J = 8 Hz, 2 H), 5.54 (s, 1 H), 2.44 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.44, 134.83, 133.53, 132.30, 131.70, 130.61, 130.00, 129.00, 128.28, 128.25, 127.95, 123.49, 121.73, 107.64, 89.77, 24.38. HRMS (APCI) m/z: $[M+H]^+$calculated for $C_{22}H_{20}BrSi$: 391.0512, found: 391.0499.



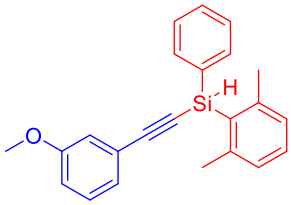
([1,1'-biphenyl]-4-ylethynyl)(2,6-dimethylphenyl)(phenyl)silane(3k):

Yellow solid (60.5 mg, 78% yield), purified by column chromatography (SiO_2, PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2 H), 7.50 – 7.43 (m, 7 H), 7.34 – 7.21 (m, 7 H), 7.16 – 7.12 (m, 1 H), 6.95 (d, J = 8 Hz, 2 H), 5.58 (s, 1 H), 2.46 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.51, 141.84, 140.28, 134.91, 132.68, 132.62, 130.55, 129.94, 129.34, 129.00, 128.28, 127.96, 127.89, 127.16, 127.10, 121.71, 108.93, 89.00, 24.42. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{28}H_{25}Si$: 389.1720, found: 389.1782.



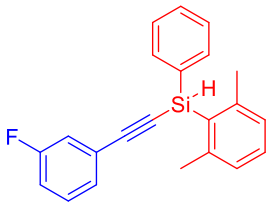
(2,6-dimethylphenyl)(phenyl)(m-tolylethynyl)silane(3l):

Yellow oil (37 mg, 59% yield), purified by column chromatography (SiO_2, PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2 H), 7.32 – 7.25 (m, 5 H), 7.18 – 7.06 (m, 3 H), 6.96 (d, J = 8 Hz, 2 H), 5.56 (s, 1 H), 2.46 (s, 6 H), 2.24 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.50, 138.15, 134.90, 132.78, 132.71, 130.50, 130.04, 129.90, 129.42, 129.27, 128.34, 128.24, 127.93, 122.68, 109.28, 87.79, 24.40, 21.32. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}Si$: 327.1564, found: 327.1583.



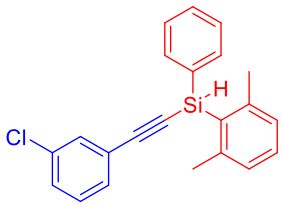
(2,6-dimethylphenyl)((3-methoxyphenyl)ethynyl)(phenyl)silane(3m):

Yellow oil (49mg, 72% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2 H), 7.33 – 7.25 (m, 1 H), 7.18 – 7.12 (m, 2 H), 7.06 – 7.04 (m, 1 H), 6.97 – 6.95 (m, 3 H), 6.83 – 6.80 (m, 1 H), 5.56 (s, 1 H), 3.70 (s, 3 H), 2.46 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.38, 145.49, 134.89, 132.61, 130.55, 129.94, 129.54, 129.29, 128.26, 127.95, 124.73, 123.82, 116.82, 115.83, 108.88, 88.08, 55.38, 24.39. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}OSi$: 343.1513, found: 343.1524.



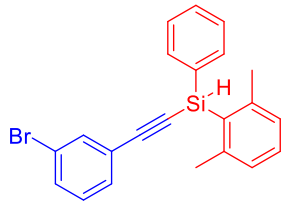
(2,6-dimethylphenyl)((3-fluorophenyl)ethynyl)(phenyl)silane(3n):

Yellow oil (37 mg, 56% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8 Hz, 2 H), 7.32 – 7.26 (m, 3 H), 7.18 – 7.12 (m, 2 H), 7.06 – 7.04 (m, 1 H), 6.97 – 6.95 (m, 3 H), 6.83 – 6.80 (m, 1 H), 5.56 (s, 1 H), 3.70 (s, 3 H), 2.46 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.41 (d, J = 244.4 Hz), 145.53, 134.91, 132.34, 130.68, 130.15, 130.07, 129.03, 128.35, 128.10 (d, J = 3 Hz), 128.02, 124.70 (d, J = 9.4 Hz), 118.96 (d, J = 22.8 Hz), 116.58 (d, J = 20.5 Hz), 107.38, 89.68, 24.42. ^{19}F NMR (500 MHz, $CDCl_3$) δ -112.62. HRMS (APCI) m/z: $[M+H]^+$calculated for $C_{22}H_{20}FSi$: 331.1313, found: 331.1339.



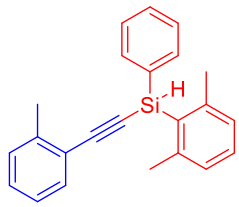
((3-chlorophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3o):

Yellow oil (32 mg, 46% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2 H), 7.44 – 7.43 (m, 1 H), 7.33 – 7.23 (m, 5 H), 7.19 – 7.15 (m, 2 H), 6.97 (d, *J* = 8 Hz, 2 H), 5.55 (s, 1 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.52, 134.88, 134.31, 132.29, 132.00, 130.66, 130.29, 130.05, 129.71, 129.44, 128.98, 128.33, 127.99, 124.56, 107.17, 89.98, 24.41. HRMS (APCI) m/z: $[M+H]^+$calculated for $C_{22}H_{20}ClSi$: 347.1017, found: 347.0997.



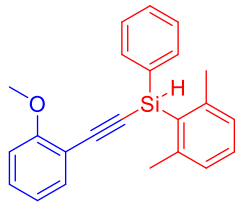
((3-bromophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3p):

Yellow oil (47 mg, 60% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 2 H), 7.33 (m, 5 H), 7.22 – 7.07 (m, 3 H), 6.96 (d, *J* = 8 Hz, 2 H), 5.55 (s, 1 H), 2.44 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.50, 134.87, 132.30, 130.71, 130.66, 130.05, 129.91, 128.95, 128.32, 127.98, 127.94, 124.82, 122.25, 107.02, 90.10, 24.41. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{20}BrSi$: 391.0508, found: 391.0512.



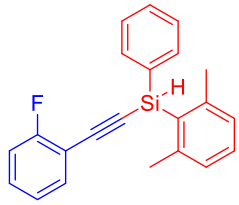
(2,6-dimethylphenyl)(phenyl)(o-tolylethynyl)silane(3q):

Yellow oil (44 mg, 67% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2 H), 7.42 – 7.40 (m, 1H), 7.32 – 7.25 (m, 3 H), 7.17 – 7.09 (m, 3 H), 7.06-7.02 (m, 1 H), 6.95 (d, *J* = 8 Hz, 2 H), 5.59 (s, 1 H), 2.46 (s, 6 H), 2.40 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.46, 141.02, 134.88, 132.90, 132.62, 130.50, 129.88, 129.61, 129.47, 129.11, 128.25, 127.93, 125.67, 122.71, 108.08, 92.04, 24.41, 20.97. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}Si$: 327.1564, found: 327.1508.



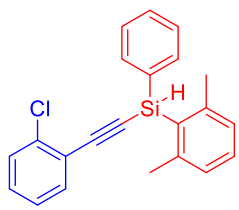
(2,6-dimethylphenyl)((2-methoxyphenyl)ethynyl)(phenyl)silane(3r):

Yellow oil (53 mg, 78% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2 H), 7.40 – 7.38 (m, 1 H), 7.30 – 7.19 (m, 4 H), 7.16 – 7.11 (m, 1 H), 6.94 (d, *J* = 8 Hz, 2 H), 6.82 – 6.75 (m, 2 H), 5.59 (s, 1 H), 3.77 (s, 3 H), 2.47 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.84, 144.38, 133.83, 132.89, 131.83, 129.43, 129.24, 128.62, 128.45, 127.00, 126.70, 119.28, 111.01, 109.62, 104.39, 91.23, 54.66, 23.20. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}OSi$: 343.1513, found: 343.1567.



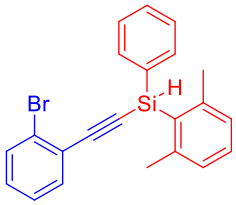
(2,6-dimethylphenyl)((2-fluorophenyl)ethynyl)(phenyl)silane(3s):

Yellow oil (31 mg, 47% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2 H), 7.44 – 7.40 (m, 1 H), 7.32 – 7.22 (m, 4 H), 7.18 – 7.14 (m, 1 H), 7.03 – 6.95 (m, 4 H), 5.58 (s, 1 H), 2.47 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.44 (d, *J* = 250.4 Hz), 145.58, 134.93, 134.00, 132.35, 130.88 (d, *J* = 8 Hz), 130.61, 129.99, 129.05, 128.29, 127.95, 124.06 (d, *J* = 3.8 Hz), 115.72 (d, *J* = 20.6 Hz), 111.60 (d, *J* = 15.4 Hz), 101.96, 94.25 (d, *J* = 3 Hz), 24.38. ^{19}F NMR (500 MHz, $CDCl_3$) δ -108.89. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{20}FSi$: 331.1313, found: 331.1337.



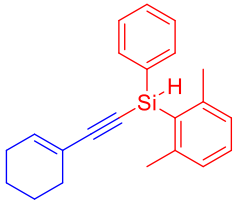
((2-chlorophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3t):

Yellow oil (36 mg, 52% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 2 H), 7.48 – 7.45 (m, 1 H), 7.33 – 7.28 (m, 4 H), 7.18 – 7.12 (m, 3 H), 6.96 (d, *J* = 8 Hz, 2 H), 5.59 (s, 1 H), 2.48 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.58, 136.59, 134.97, 134.00, 132.39, 130.61, 130.08, 129.97, 129.46, 129.07, 128.28, 127.93, 126.55, 122.87, 105.12, 94.10, 24.43. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{20}ClSi$: 347.1017, found: 347.1053.



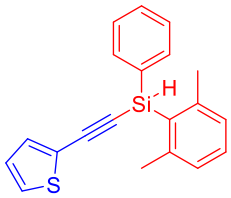
((2-bromophenyl)ethynyl)(2,6-dimethylphenyl)(phenyl)silane(3u):

Yellow oil (48.5 mg, 62% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2 H), 7.51 – 7.45 (m, 2 H), 7.32 – 7.26 (m, 3 H), 7.19 – 7.13 (m, 2 H), 7.12 – 7.07 (m, 1 H), 6.96 (d, *J* = 7.6 Hz, 2 H), 5.59 (s, 1 H), 2.48 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.56, 134.98, 134.13, 132.60, 132.36, 130.61, 130.20, 129.97, 129.04, 128.26, 127.91, 127.11, 125.91, 125.06, 106.73, 93.42, 24.47. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{20}BrSi$: 391.0512, found: 391.0506.



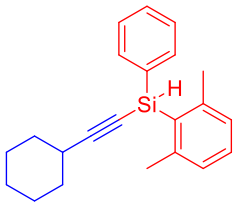
(cyclohex-1-en-1-ylethynyl)(2,6-dimethylphenyl)(phenyl)silane(3v):

Yellow oil (27 mg, 43% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2 H), 7.31 – 7.23 (m, 3 H), 7.17 – 7.11 (m, 1 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.21-6.19 (m, 1 H), 5.48 (s, 1 H), 2.41 (s, 6 H), 2.14 – 1.97 (m, 4 H), 1.59 – 1.47 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.43, 137.43, 134.84, 133.17, 130.35, 129.79, 129.74, 128.15, 127.85, 120.87, 111.35, 84.81, 28.88, 25.82, 24.35, 22.26, 21.49. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{25}Si$:317.1720, found: 317.1723.



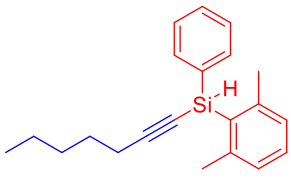
(2,6-dimethylphenyl)(phenyl)(thiophen-2-ylethynyl)silane(3w):

Yellow oil (46 mg, 72% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2 H), 7.33 – 7.28 (m, 3 H), 7.24 – 7.22 (m, 1 H), 7.20 – 7.15 (m, 2 H), 6.97 (d, *J* = 8 Hz, 2 H), 6.90-6.88 (m, 1 H), 5.56 (s, 1 H), 2.45 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.35, 133.74, 132.24, 131.20, 129.43, 128.83, 127.92, 127.12, 126.96, 126.79, 125.94, 121.74, 100.35, 91.73, 23.24. HRMS (APCI) m/z: [M+H]+ calculated for $C_{20}H_{19}SSi$: 319.0971, found: 319.0941.



(cyclohexylethynyl)(2,6-dimethylphenyl)(phenyl)silane(3x):

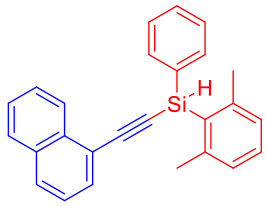
Yellow oil (19 mg, 30% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2 H), 7.30-7.24 (m, 3 H), 7.16 – 7.12 (m, 1 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 5.41 (s, 1 H), 2.41 (s, 6 H), 1.80 – 1.61 (m, 4 H), 1.49 – 1.41 (m, 4 H), 1.26-1.22 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.41, 134.81, 133.52, 130.27, 130.08, 129.65, 128.11, 127.83, 116.21, 77.88, 32.44, 32.42, 30.42, 25.96, 24.90, 24.32. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{27}Si$: 319.1877, found: 319.1895.



(2,6-dimethylphenyl)(hept-1-yn-1-yl)(phenyl)silane(3y):

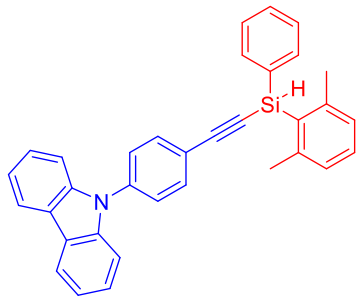
Yellow oil (20 mg, 32% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 2 H), 7.31 – 7.25 (m, 3 H), 7.17 – 7.13 (m,

1 H), 6.94 (d, *J* = 8 Hz, 2 H), 5.41 (s, 1 H), 2.41 (s, 6 H), 2.27 – 2.23 (m, 2 H), 1.51 – 1.48 (m, 2 H), 1.34 – 1.25 (m, 4 H), 0.83 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.40, 134.81, 133.41, 130.31, 129.96, 129.69, 128.12, 127.85, 112.27, 78.29, 31.21, 28.22, 24.31, 22.30, 20.29, 14.11. HRMS (APCI) m/z: [M+H]+ calculated for $C_{21}H_{27}Si$: 307.1877, found: 307.1860.



(2,6-dimethylphenyl)(naphthalen-1-ylethynyl)(phenyl)silane(3z):

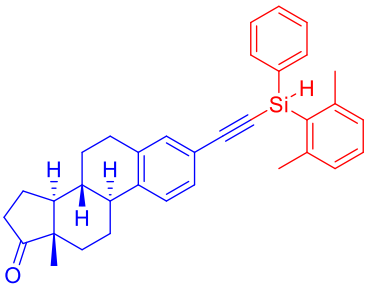
Yellow oil (53 mg, 73% yield), purified by column chromatography (SiO_2, PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 12 Hz, 2 H), 7.95 (d, *J* = 8 Hz, 2 H), 7.92 – 7.89 (m, 3 H), 7.71 – 7.60 (m, 3 H), 7.55 – 7.51 (m, 3 H), 7.41 – 7.38 (m, 1 H), 7.20 (d, *J* = 7.7 Hz, 2 H), 5.93 (s, 1 H), 2.75 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.51, 134.94, 133.57, 133.16, 132.74, 131.49, 130.59, 129.98, 129.63, 129.34, 128.45, 128.33, 127.99, 127.19, 126.64, 126.24, 120.47, 107.19, 93.34, 24.51. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{27}Si$: 363.1564, found: 363.1556.



(4-(((2,6-dimethylphenyl)(phenyl)silyl)ethynyl)phenyl)-9H-carbazole(3aa):

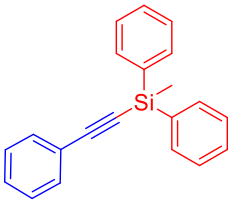
Yellow oil (48 mg, 50% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2 H), 7.67 – 7.61 (m, 4 H), 7.46 – 7.44 (m, 2 H), 7.34 – 7.30 (m, 7 H), 7.22 – 7.16 (m, 3 H), 6.98 (d, *J* = 8 Hz, 2 H), 5.61 (s, 1 H), 2.49 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.36, 139.35, 137.20, 133.74, 132.56, 131.32, 129.46, 128.85, 127.99, 127.15, 126.82, 125.68, 125.62, 125.04, 122.53, 120.53, 119.33, 119.25, 108.63, 106.93, 88.34, 23.28. HRMS (APCI) m/z:

[M+H]$^+$ calculated for $C_{34}H_{28}NSi$: 478.1986, found: 478.2001.



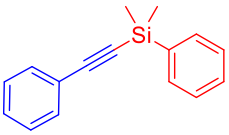
(8R,9S,13S,14S)-3-(((2,6-dimethylphenyl)(phenyl)silyl)ethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(3ab):

Yellow oil (68 mg, 70% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2 H), 7.29 – 7.27 (m, 3 H), 7.23 – 7.17 (m, 2 H), 7.15 – 7.11 (m, 2 H), 6.94 (d, *J* = 8 Hz, 2 H), 5.54 (s, 1 H), 2.79 – 2.75 (m, 2 H), 2.44 (s, 6 H), 2.40 – 2.35 (m, 1 H), 2.31 – 2.14 (m, 2 H), 2.05 – 1.84 (m, 4 H), 1.50 – 1.26 (m, 6 H), 0.79 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.25, 140.07, 135.58, 133.68, 131.59, 131.42, 129.31, 128.70, 128.28, 128.25, 127.04, 126.74, 124.34, 118.95, 108.12, 86.24, 49.31, 46.80, 43.35, 36.76, 34.74, 30.42, 27.98, 25.18, 24.46, 23.22, 20.48, 12.73. HRMS (APCI) m/z: [M+H]+ calculated for C34H37OSi: 489.2608, found: 489.2636.



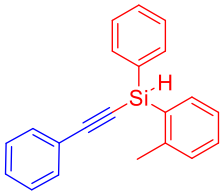
methyldiphenyl(phenylethynyl)silane(3ac):

Yellow oil (49 mg, 77% yield), purified by column chromatography (SiO_2, PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 4 H), 7.45 – 7.42 (m, 2 H), 7.29 – 7.25 (m, 6 H), 7.21 – 7.18 (m, 3 H), 0.66 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.43, 134.69, 132.28, 129.83, 129.03, 128.39, 128.10, 122.91, 108.46, 90.44, -1.82. HRMS (APCI) m/z: [M+H]$^+$ calculated for $C_{21}H_{19}Si$: 299.1251, found: 299.1240.



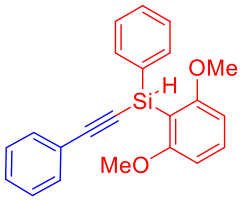
dimethyl(phenyl)(phenylethynyl)silane(3ad):

Yellow oil (43 mg, 42% yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2 H), 7.41 – 7.39 (m, 2 H), 7.30 – 7.28 (m, 3 H), 7.21 – 7.18 (m, 3 H), 0.40 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.13, 133.88, 132.18, 129.58, 128.83, 128.36, 128.05, 123.06, 106.93, 92.14, -0.66. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{16}H_{17}Si$: 237.1094, found: 237.1005.



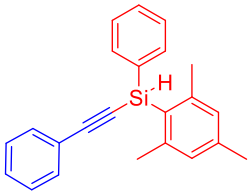
phenyl(phenylethynyl)(o-tolyl)silane(3ae):

Yellow oil (15 mg, 25 % yield), purified by column chromatography (SiO_2, PE). 1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 3 H), 7.55 – 7.53 (m, 2 H), 7.43 – 7.30 (m, 7 H), 7.24 – 7.19 (m, 2 H), 5.37 (s, 1 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.68, 136.79, 135.33, 132.28, 131.01, 130.78, 130.14, 129.86, 129.22, 128.44, 128.28, 125.44, 122.74, 109.64, 87.60, 22.75. HRMS (APCI) m/z: [M+H]+ calculated for $C_{21}H_{19}Si$: 299.1251, found: 299.1249.



(2,6-dimethoxyphenyl)(phenyl)(phenylethynyl)silane(3af):

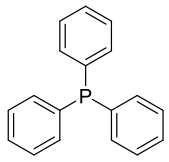
Yellow oil (60.2 mg, 88 % yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 2 H), 7.42 – 7.39 (m, 2 H), 7.25 – 7.23 (m, 4 H), 7.19 – 7.16 (m, 3 H), 6.41 (d, J = 8 Hz, 2 H), 5.36 (s, 1 H), 3.64 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.45, 133.92, 132.70, 132.07, 131.01, 128.29, 127.52, 127.13 , 126.60, 122.26, 106.81, 105.48, 102.99, 88.28, 54.66. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{22}H_{21}Si$: 345.1305, found: 345.1314.



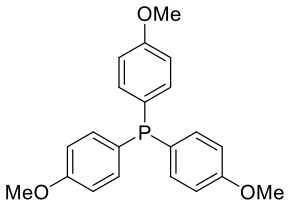
mesityl(phenyl)(phenylethynyl)silane(3ag):

Yellow oil (43 mg, 66 % yield), purified by column chromatography (SiO_2, PE). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2 H), 7.67 – 7.65 (m, 2 H), 7.54 – 7.48 (m, 3 H), 7.47 – 7.43 (m, 3 H), 7.03 (s, 2 H), 5.79 (s, 1 H), 2.66 (s, 6 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.54, 140.50, 134.88, 132.98, 132.15, 129.84, 129.06, 128.91, 128.41, 128.22, 125.71, 122.95, 108.87, 88.50, 24.24, 21.36. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}Si$: 327.1564, found: 327.1535.

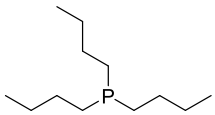
Scheme S1. The ligands evaluated in Pd-catalyzed of Si-C coupling of bromoalkynes (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .



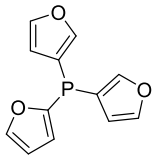
L1
N.D.



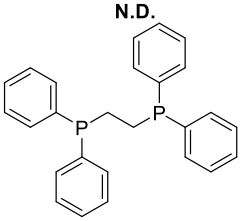
L2
N.D.



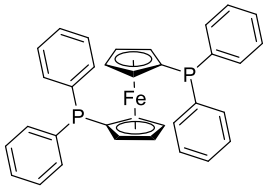
L3
N.D.



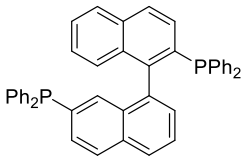
L4
N.D.



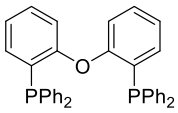
L5
N.D.



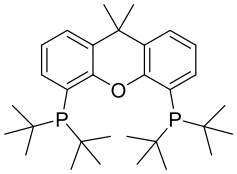
L6
N.D.



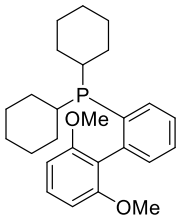
L7
N.D.



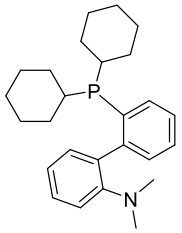
L8
N.D.



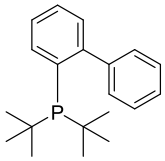
L9
N.D.



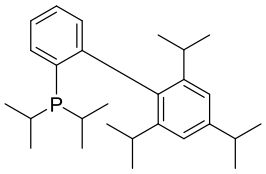
L10
N.D.



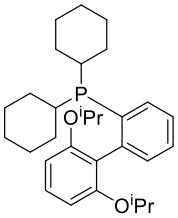
L11
N.D.



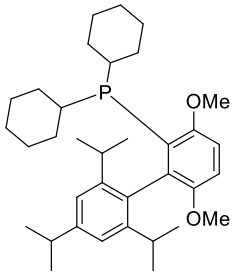
L12
N.D.



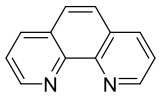
L13
N.D.



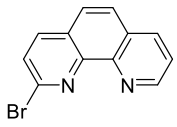
L14
N.D.



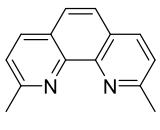
L15
N.D.



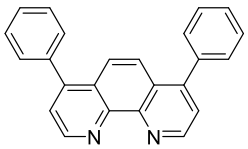
L16
N.D.



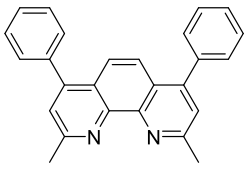
L17
N.D.



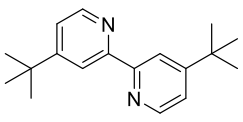
L18
N.D.



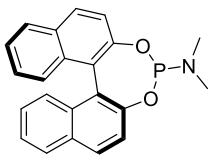
L19
N.D.



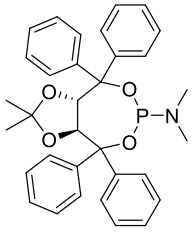
L20
N.D.



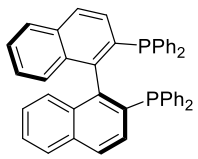
L21
N.D.



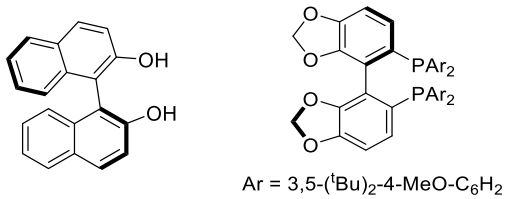
L24
N.D.



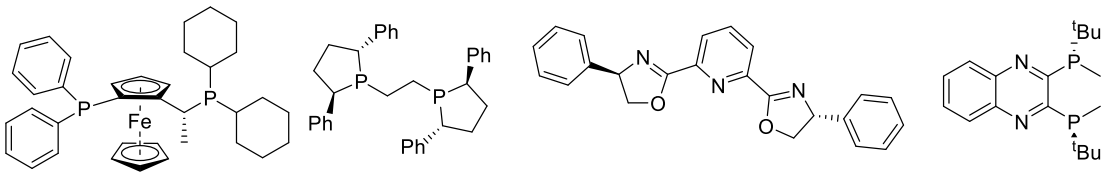
L25
N.D.



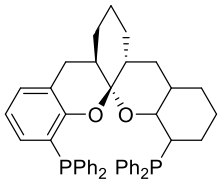
L26
N.D.



L27 **N.D.** **L28** **N.D.** **L29** **N.D.** **L30** **N.D.**

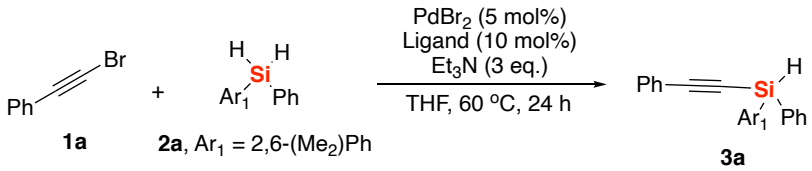


L31 **N.D.** **L32** **N.D.** **L33** **N.D.** **L34** **N.D.**



L35 **N.D.**

Note: Except Ligand **L9** and **L10**, all the other ligands were not effective to promote the Pd-catalyzed C(sp)-Si cross couping reaction of alkynyl bromide **1a** with hydrosilane **2a**.



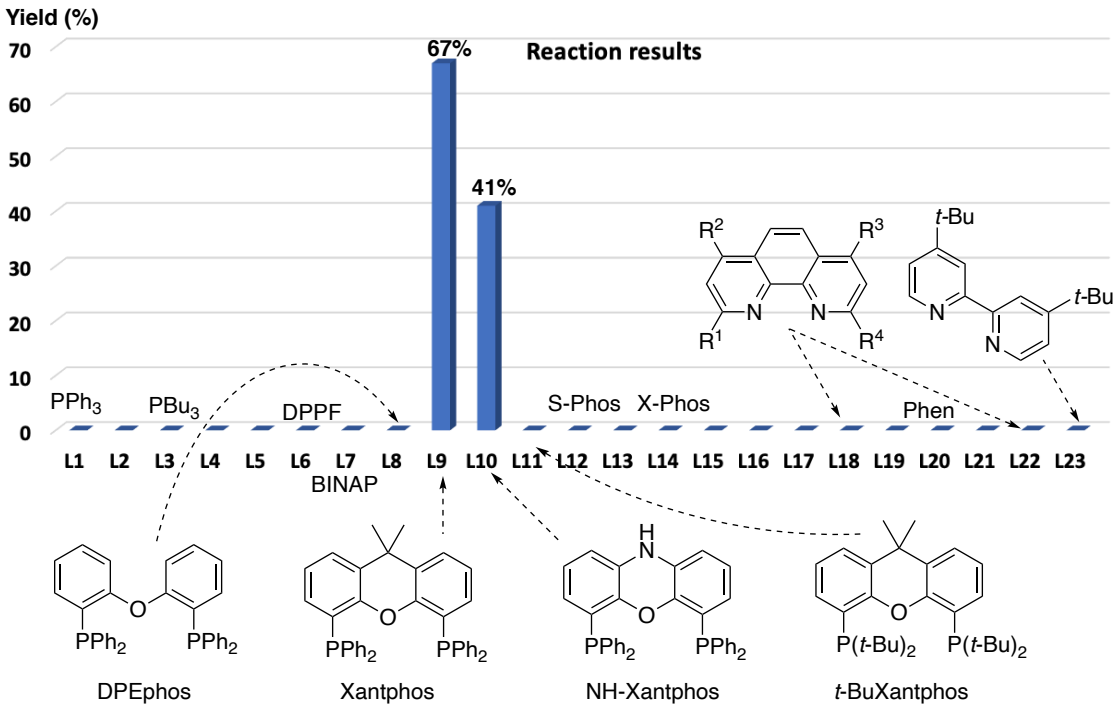
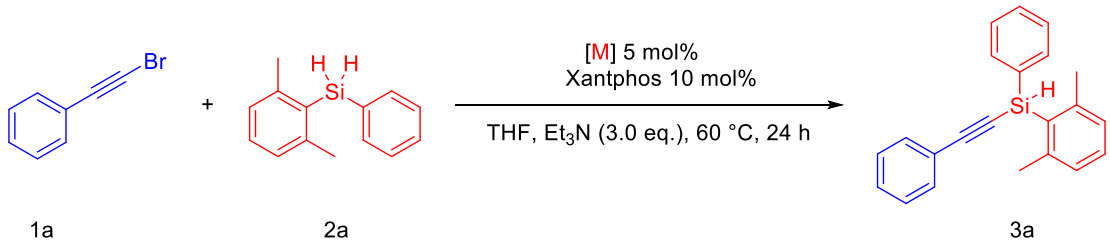


Table S1. Screening of transition metal catalyst for Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a).

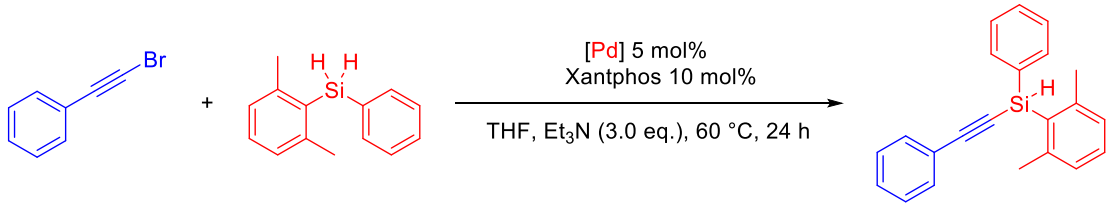


1a 2a 3a

Entry	Cat.	Yield of **3a** (%)[a]
1	$Cu(CH_3CN)_4PF_6$	N.D.
2	CuI	N.D.
3	$Ni(OAc)_2{\cdot}4H_2O$	N.D.
4	$Ni(acac)_2$	N.D.
5	$Co(acac)_2$	N.D.
6	$CoBr_2$	N.D.
7	$Fe(OTf)_2$	N.D.
8	$Fe(acac)_2$	N.D.
9	$Pd_2(dba)_3$	51
10	$PdCl_2[P(cy)_3]_2$	N.D.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Catalyst (5 mol%), Xantphos (10 mol%), Et_3N (0.6 mmol) and THF (2.0 mL) under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S2. Screening of palladium sources for Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a).

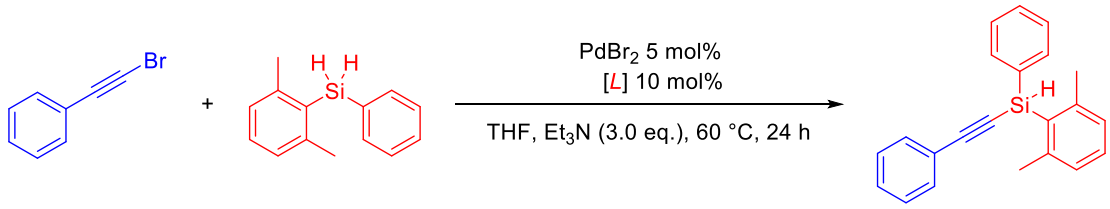


1a 2a 3a

Entry	Pd cat.	Yield of **3a** (%)[a]
1	$Pd(TFA)_2$	41
2	$Pd(cod)Cl_2$	41
3	$Pd(OAc)_2$	11
4	$Pd(CH_3CN)_2Cl_2$	28
5	$PdCl_2$	55
6	$PdBr_2$	67
7	PdI_2	19
8	$PdCl_2$(dppb)	43
9	$Pd(acac)_2$	60
10	$PdCl_2[P(cy)_3]_2$	N.D.
11	$PdCl_2$(dppf)	54
12	$Pd(CH_3CN)_4(BF_4)_2$	N.D.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), [Pd]Catalyst (5 mol%), Xantphos (10 mol%), Et_3N (0.6 mol%) and THF (2.0 mL) under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S3. Screening of ligands for Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

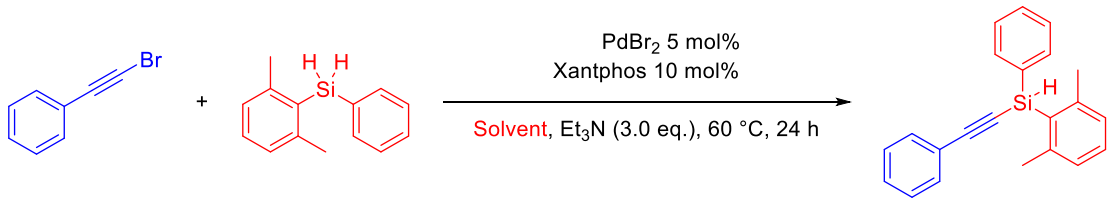


1a 2a 3a

Entry	Ligand	Yield of **3a** (%)[a]
1	Xantphos	67
2	NiXantphos	41
3	Other ligands	<5

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (5 mol%), L (10 mol%), Et_3N (0.6 mmol) and THF (2.0 mL) under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S4. Screening of Solvent for Pd-catalyzed of Si-C coupling of bromoalkynes (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

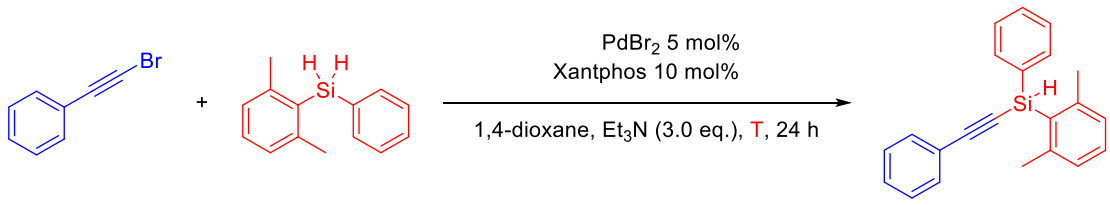


1a 2a 3a

Entry	Solvent	Yield of **3a** (%)[a]
1	THF	55
2	Toluene	27
3	DCM	17
4	DCE	12.5
5	CH_3CN	N.D.
6	1,4-Dioxane	59
7	Et_2O	37
8	DMSO	N.D.
9	DMF	N.D.
10	NMP	N.D.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (5 mol%), Xantphos (10 mol%), Et_3N (0.6 mmol), Solvent 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S5. The effect of temperature on the catalytic efficiency of Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

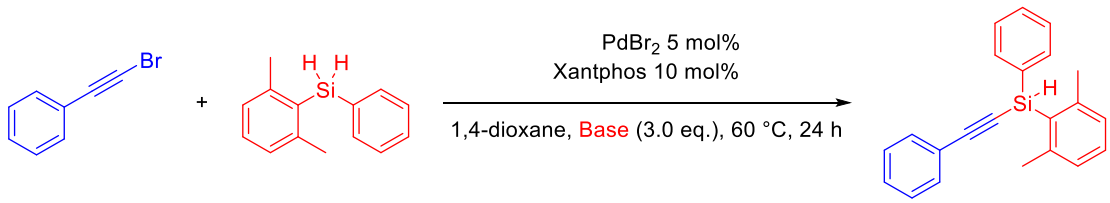


1a 2a 3a

Entry	Temp (°C)	Yield of **3a** (%)[a]
1	r.t.	43
2	60	56
3	80	43
4	100	42

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (5 mol%), Xantphos (10 mol%), Et_3N (0.6 mmol), 1,4-dioxane 2 mL under N_2 for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S6. Screening of inorganic or organic bases for Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .



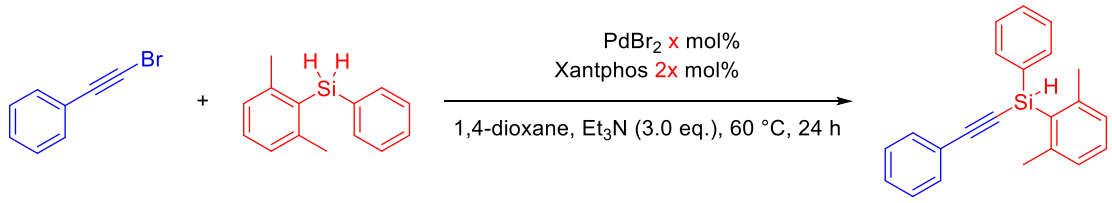
1a 2a 3a

Entry	Base	Yield of **3a** (%)[a]
1	Et_3N	51
2	NaOAc	N.D.
3	LiO^tBu	N.D.
4	NaO^tBu	N.D.
5	Cs_2CO_3	N.D.
6	K_3PO_4	N.D.
7	K_2CO_3	N.D.
8	DBU	N.D.
9	DIPA	N.D.

10	Pyridine	20
11	2,3-Lutidine	34
12	DABCO	N.D.
13	Cyclohexylamine	N.D.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (5 mol%), Xantphos (10 mol%), Base (0.6 mmol), 1,4-dioxane 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S7. Screening of the loading of catalyst and ligand for Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

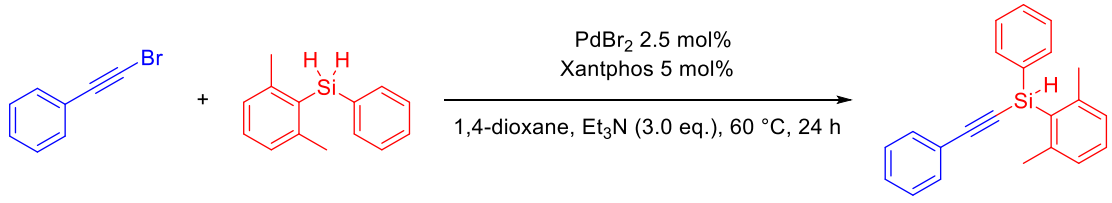


1a 2a 3a

Entry	$PdBr_2$ (x mol %)	XantPhos (2 x mol %)	Yield of **3a** (%)[a]
1	1.0	2.0	10
2	2.5	5.0	58
3	5.0	10.0	55
4	10.0	20.0	50

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (x mol%), Xantphos (2x mol%), Et_3N (0.6 mmol), 1,4-dioxane 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S8. The effect of additives on Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

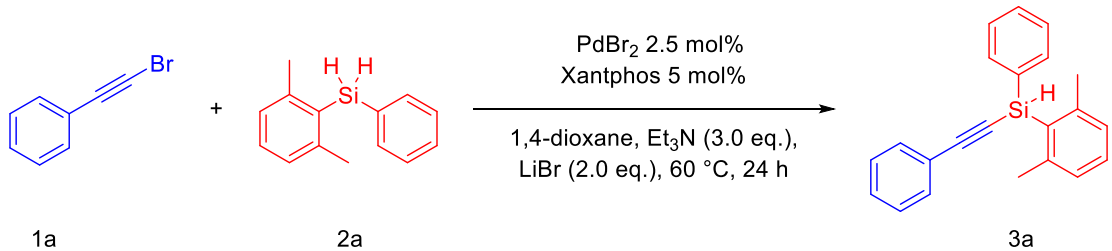


1a 2a 3a

Entry	Additives (2.0 eq.)	Yield of **3a** (%)[a]
1	CuF_2	N.D.
2	$CuBr_2$	N.D.
3	$Cu(OAc)_2$	N.D.
4	LiCl	48
5	LiBr	65
6	AgOAc	34
7	CsF_2	N.D.
8	KF	N.D.
9	NaI	16
10	$NaBHEt_3$	N.D.
11	AgF	N.D.
12	AgOTf	N.D.
13	TEMPO	Trace
14	TABA	N.D.
15	TBAI	54

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), 1,4-dioxane 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S9. The effect of the amount of alkynyl bromide on Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

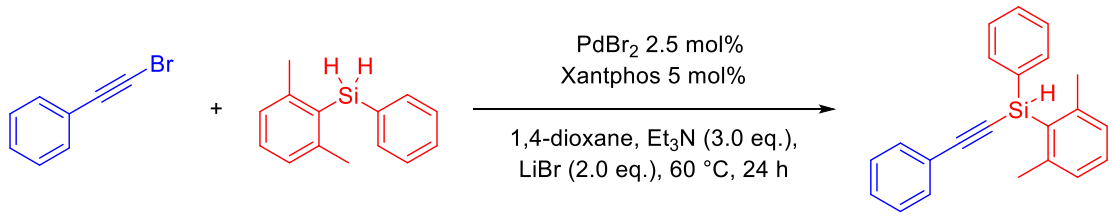


1a 2a 3a

Entry	**1a** (x eq.)	Yield of **3a** (%)[a]
1	1.0	35
2	2.0	35
3	3.0	25
4	4.0	13

Reaction conditions: **1a** (0.2x mmol), **2a** (0.2 mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S10. The effect of the amount of hydrosilane on Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

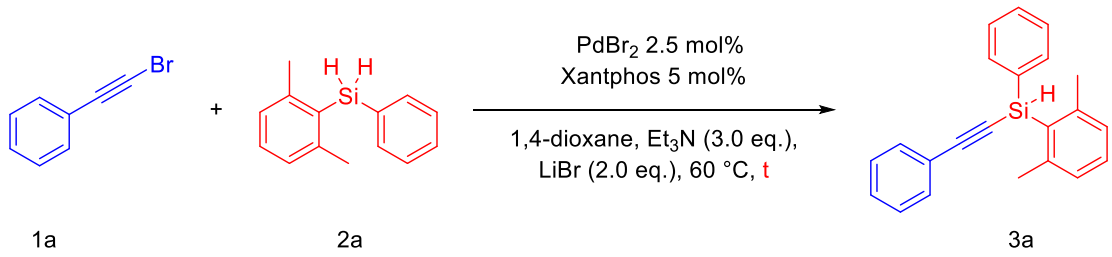


1a 2a 3a

Entry	**2a** (x eq.)	Yield of **3a** (%)[a]
1	1.5	44
2	2.0	66
3	3.0	70
4	4.0	61

Reaction conditions: **1a** (0.2 mmol), **2a** (0.2x mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C for 24 h. [a]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S11. The effect of reaction time on Pd-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .

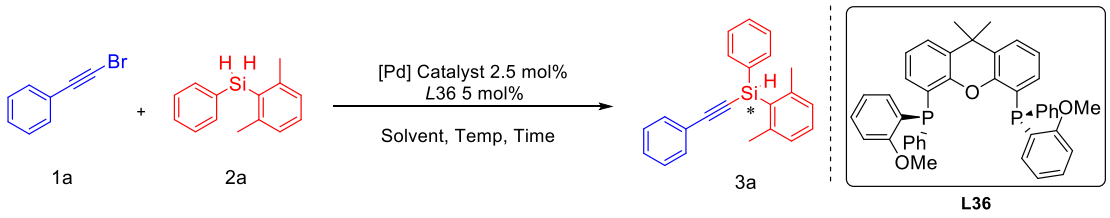


1a 2a 3a

Entry	Time	Yield of **3a** (%)[a]
1	12 h	67
2	24 h	68
3	48 h	78

Reaction conditions: **1a** (0.2 mmol), **2a** (0.2x mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C. [a]Yield by silica gel column chromatography.

Table S12. The optimization of reaction conditions for asymmetric Pd/L36-catalyzed of Si-C coupling of alkynyl bromide (1a) with (2,6-dimethylphenyl)(phenyl)silane (2a) .



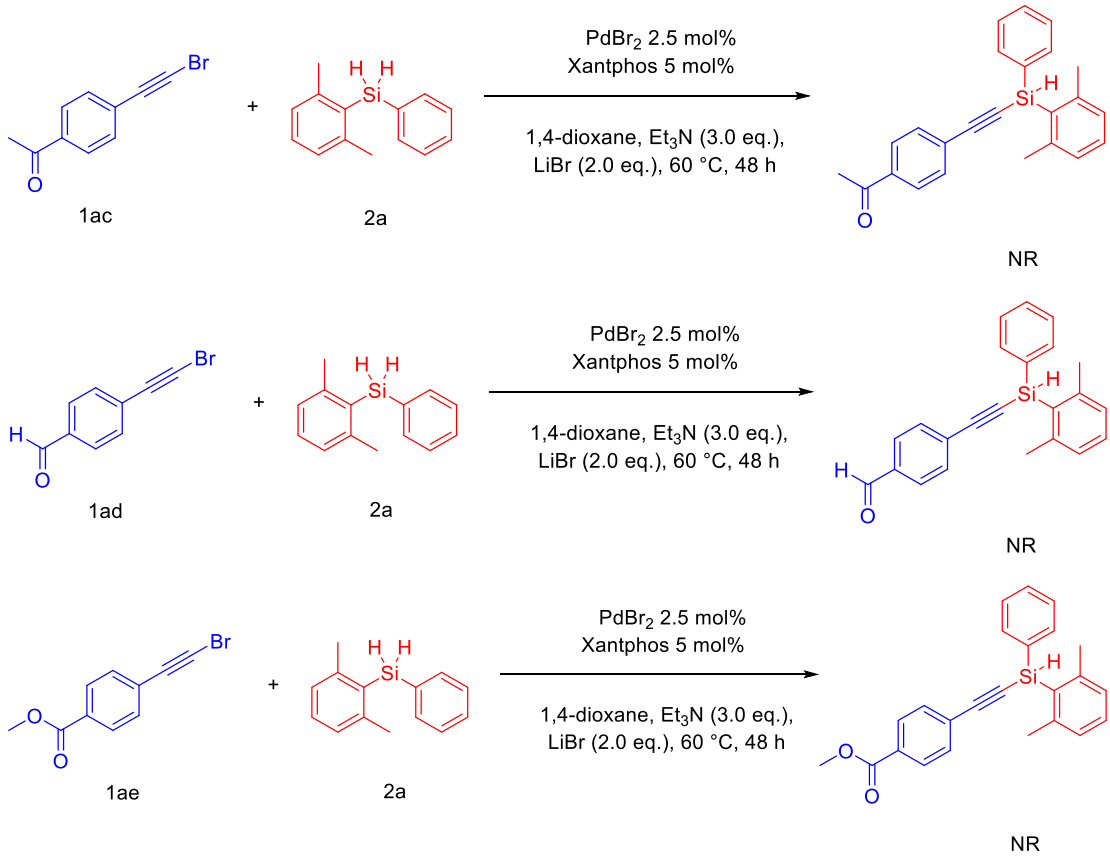
1a 2a 3a L36

Entry	Variation from "standard conditions"[a]	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]
1	none	37	58
2	With THF as solvent	14	27
3	at 25 °C	5	55
4	Reaction for 12 h	5	55
5	Without LiBr	23	55

6	With $Pd(acac)_2$ as Pd source	20	52
7	With $Pd_2(dba)_3$ as Pd source	30	51
8	With $PdCl_2$ as Pd source	25	51

[a]Standrad condition :**1a** (0.2 mmol), **2a** (0.6 mmol), $PdBr_2$ (2.5 mol%), **L36** (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol), 1,4-dioxane 2 mL under N_2 at 60 °C for 48 h. [b]Yield by silica gel column chromatography. [c]Determined by chiral HPLC.

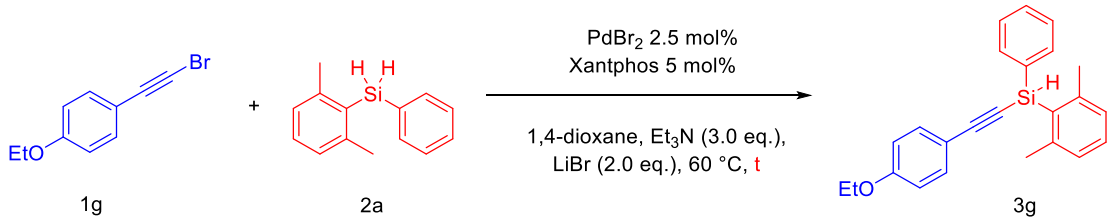
Scheme S2. Unreactive substrates on Pd-catalyzed of Si-C coupling of alkynyl bromides with (2,6-dimethylphenyl)(phenyl)silane.



Reaction conditions: Alkynyl bromides (0.2 mmol), **2a** (0.2x mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C for 48 h.

Table S13. GC-MS monitoring of the effect of substituents on aryl groups in brominated alkynes on reaction time.

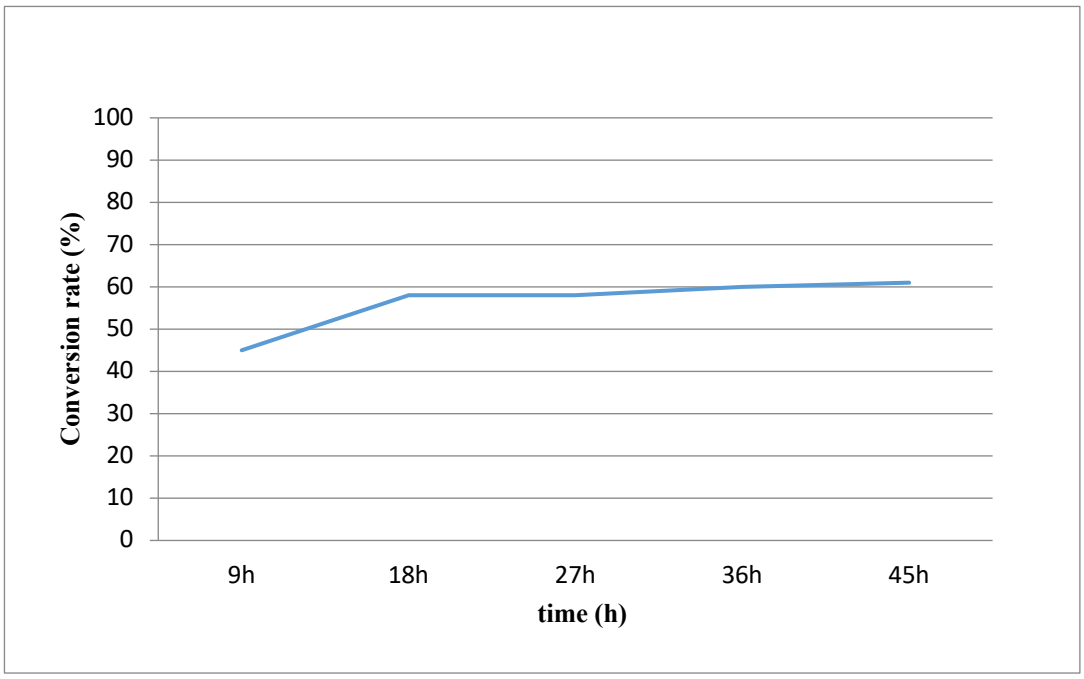
Example 1.



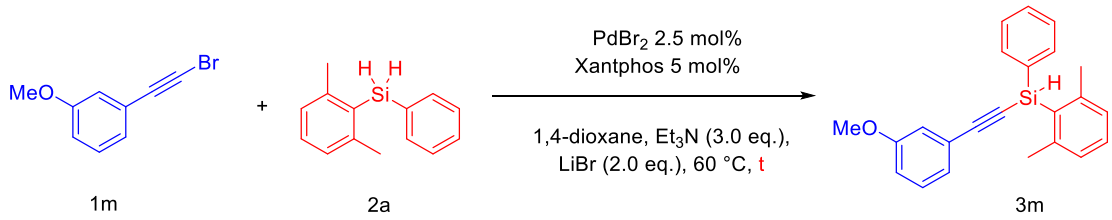
1g 2a 3g

Entry	Time (h)	Conversion (%)
1	9	45
2	18	58
3	27	58
4	36	60
5	45	61

Reaction conditions: **1g** (0.2 mmol), **2a** (0.6 mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C. The reaction was monitored by GC-MS every 9 h, and the yield of **3g** was determined by GC-MS.



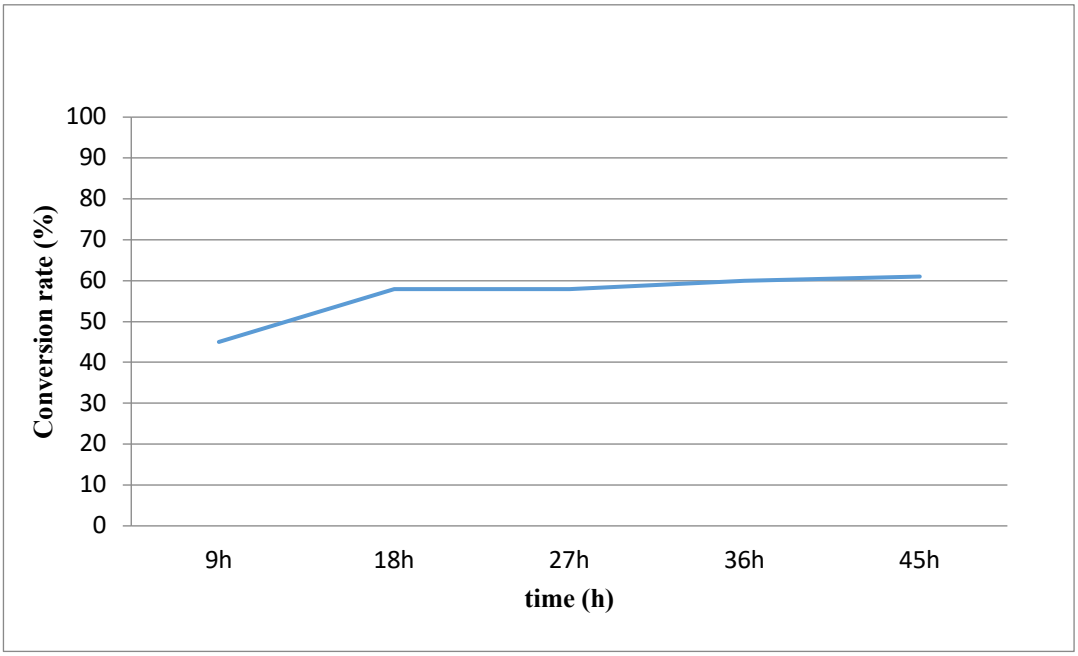
Example 2.



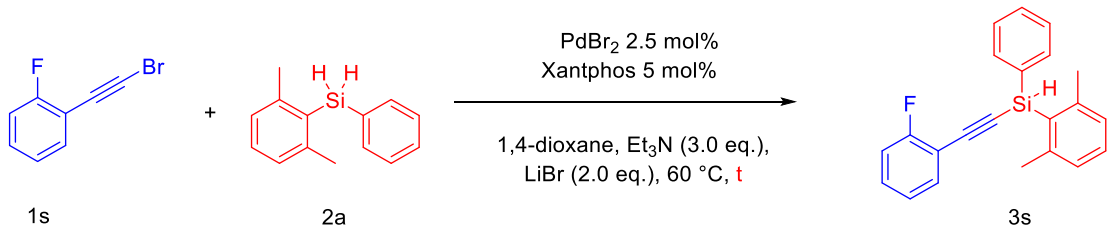
1m 2a 3m

Entry	Time(h)	Conversion (%)
1	9	38
2	18	55
3	27	58
4	36	59
5	45	60

Reaction conditions: **1m** (0.2 mmol), **2a** (0.6 mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C. The reaction was monitored by GC-MS every 9 h, and the yield of **3m** was determined by GC-MS.



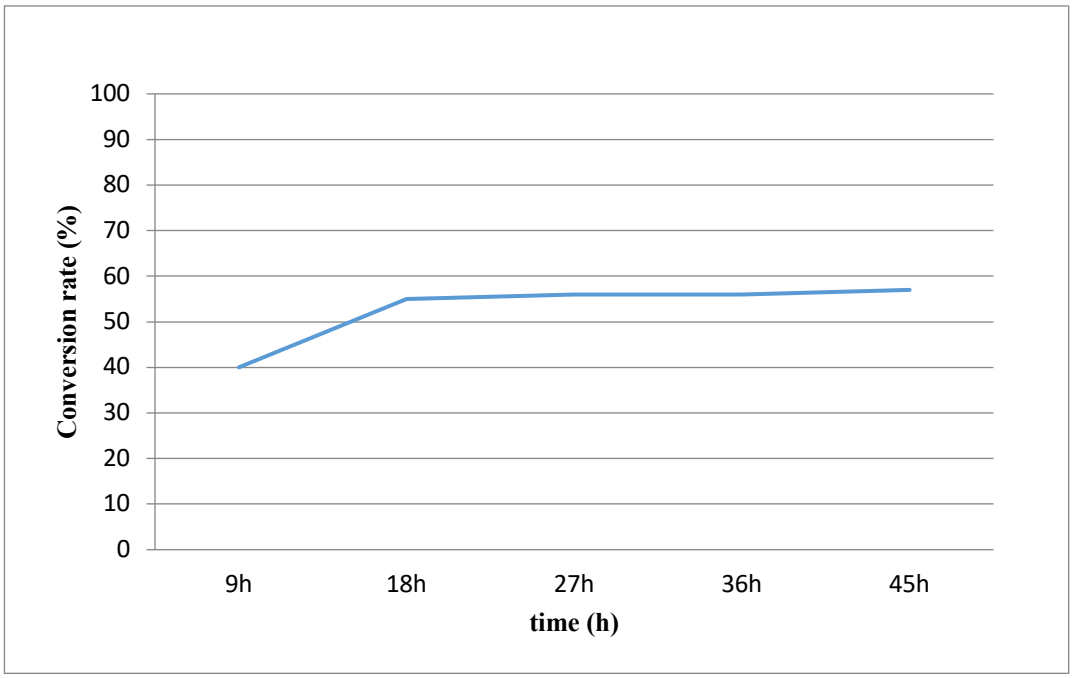
Example3.



1s 2a 3s

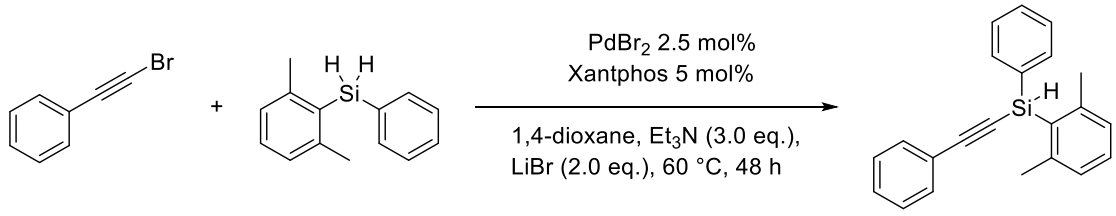
Entry	Time(h)	Conversion (%)
1	9	40
2	18	55
3	27	56
4	36	56
5	45	57

Reaction conditions: **1s** (0.2 mmol), **2a** (0.6 mmol), $PdBr_2$ (2.5 mol%), Xantphos (5 mol%), Et_3N (0.6 mmol), LiBr (0.4 mmol) 1,4-dioxane 2 mL under N_2 at 60 °C. The reaction was monitored by GC-MS every 9 h, and the yield of **3s** was determined by GC-MS.



6. Gram-scale synthesis and synthetic applications of alkynylsilane 3a

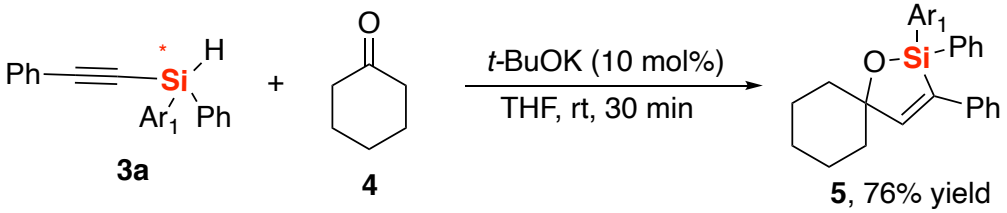
6.1 Gram-scale synthesis



3 mmol 9 mmol 0.7 g, 75% yield

A vial was charged with LiBr (0.52 g, 6.0 mmol, 2.0 equiv.), $PdBr_2$ (20 mg, 2.5 mol%), Xantphos (87 mg, 5 mol%) and evacuated under high vacuum and backfilled with N_2. Bromoalkynes (0.54g, 3 mmol), (2,6-dimethylphenyl)(phenyl)silane (9 mmol, 1.9 g, 3.0 equiv.), Et_3N (0.91 g, 9 mmol, 3.0 eq.), 1,4-dioxane (30 mL) was next added. The mixture was stirred at 60 ℃ for 48 hours. The crude product was purified by silica gel chromatography (petroleum et) to provide the desired product **3a** (0.7 g, 75% yield).

6.2 Synthetic applications



Prepared according to a previous reported method.[5] In a glove box, to a stirred solution of cyclohexanone (41 mg, 0.42 mmol, 1.0 equiv.) in 3 mL THF was added **3a** (142 mg, 0.50 mmol, 1.2 equiv.) followed by ^{t}BuOK (5 mg, 0.042 mmol, 0.1 equiv.). After stirring for 20 minutes, the reaction was quenched with an aqueous solution of saturated NH_4Cl and extracted twice with ether. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated to orange oil. The resulting residue was purified by column chromatography on silica gel (Hexane/CH_2Cl_2 = 5/1, v/v) to provide the desired product **5** as oil (130 mg, 76 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.58 – 7.53 (m, 2 H), 7.48 – 7.33 (m, 3 H), 7.23 – 7.08 (m, 7 H), 6.98 (s, 1 H), 6.96 (s, 1H), 2.25 (s, 6 H), 1.86 (m, 3 H), 1.73 – 1.50 (m, 6 H), 1.42 – 1.33 (m,

1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 156.25, 145.23, 140.84, 139.75, 138.54, 134.99, 134.27, 130.63, 130.37, 128.88, 128.74, 127.99, 127.75, 127.07, 85.03, 39.08, 26.12, 25.28, 23.50, 22.99. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{28}H_{31}OSi$: 411.2139, found: 411.2112.

7. Reference

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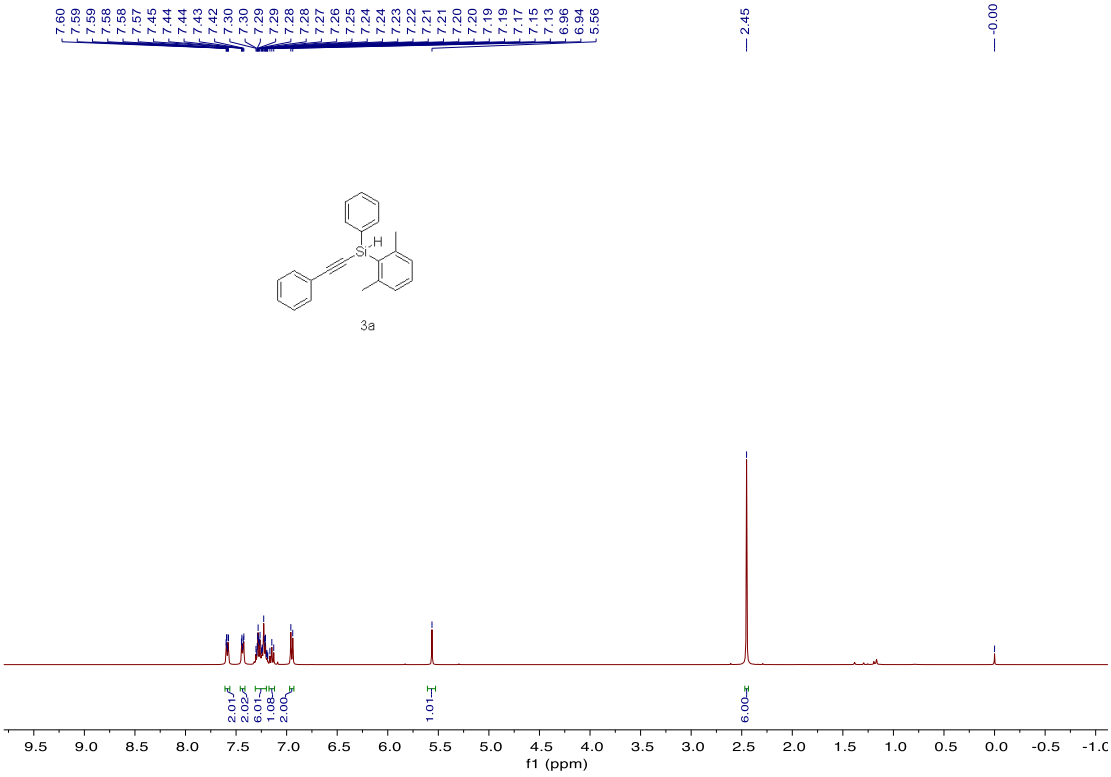
[3]. Zijlstra, H.; Leon, T.; de Cozar, A.; Fonseca Guerra, C.; Byrom, D.; Riera, A.; Verdaguer, X.; Bickelhaupt, F. M., Stereodivergent SN2@P Reactions of Borane Oxazaphospholidines: Experimental and Theoretical Studies, *J. Am. Chem. Soc* **2013**, *135*, 4483−4491.

[4]. Holz, J.; Rumpel, K.; Spannenberg, A.; Paciello, R.; Jiao, H.; Börner, A., P-Chirogenic Xantphos Ligands and Related Ether Diphosphines: Synthesis and Application in Rhodium-Catalyzed Asymmetric Hydrogenation. *ACS Catal.* **2017**, *7*, 6162-6169.

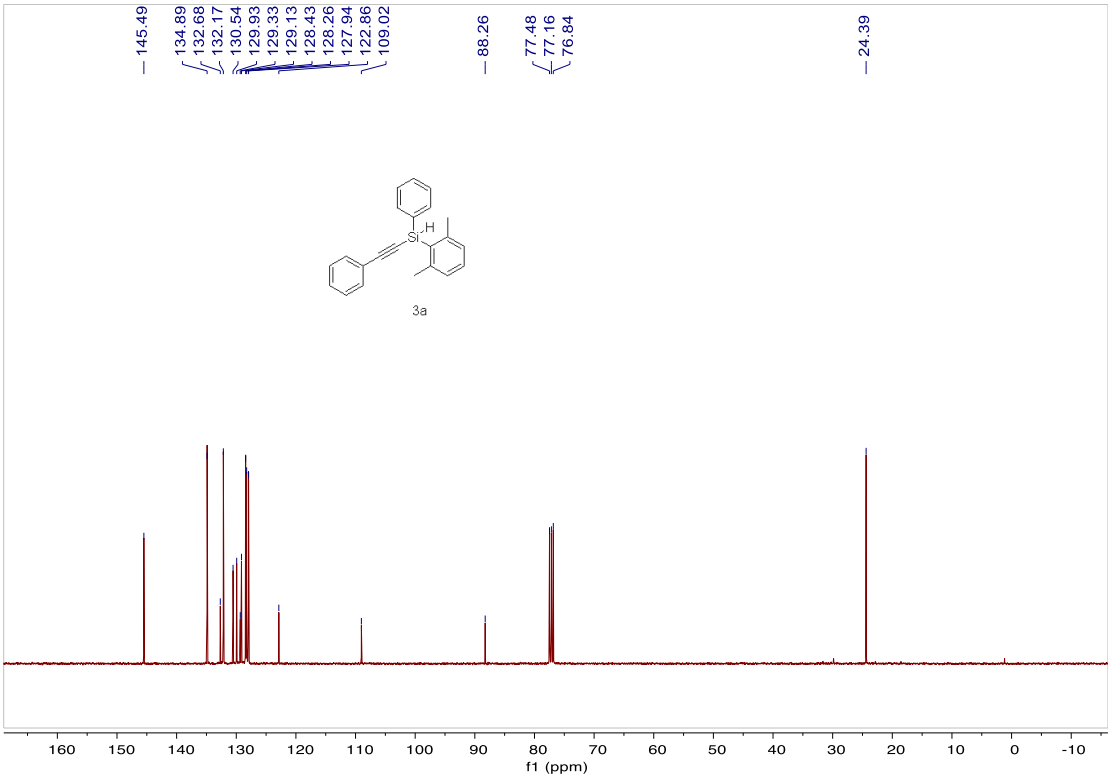
[5]. Maifeld, S. V.; Lee, D., Unusual Tandem Alkynylation and trans-Hydrosilylation to form Oxasilacyclopentenes. *Org. Lett.* **2005**, *7*, 4995-4998.

8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

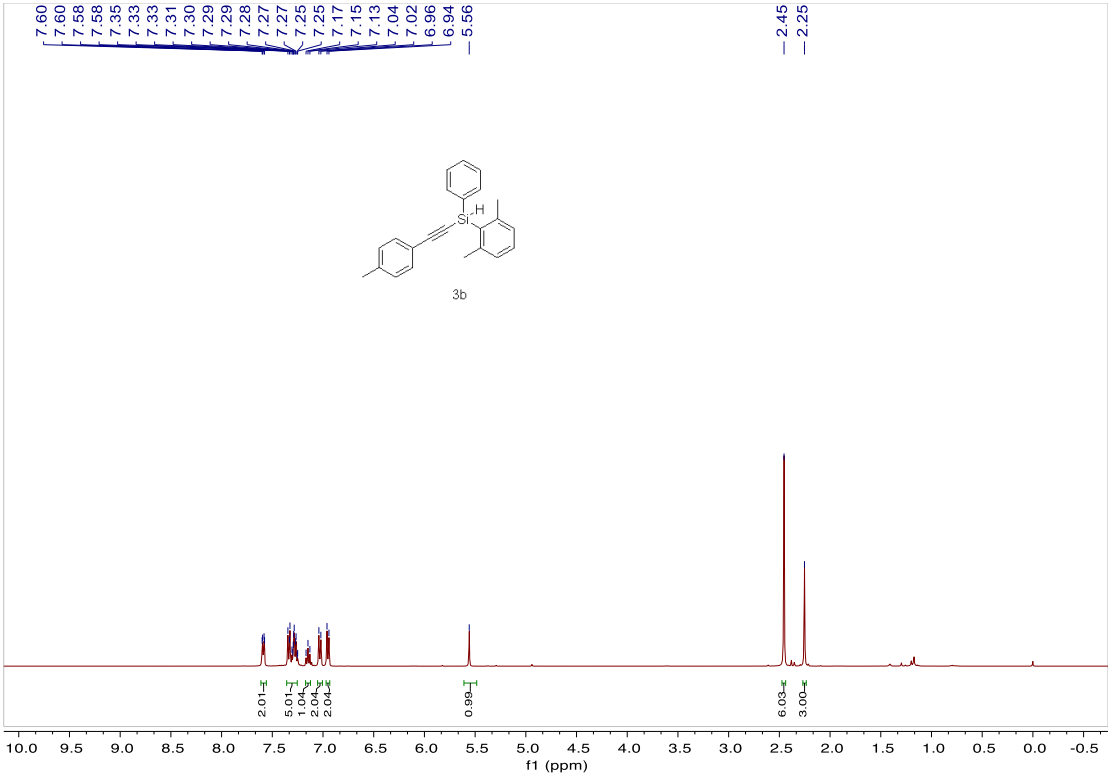
^{1}H NMR of 3a



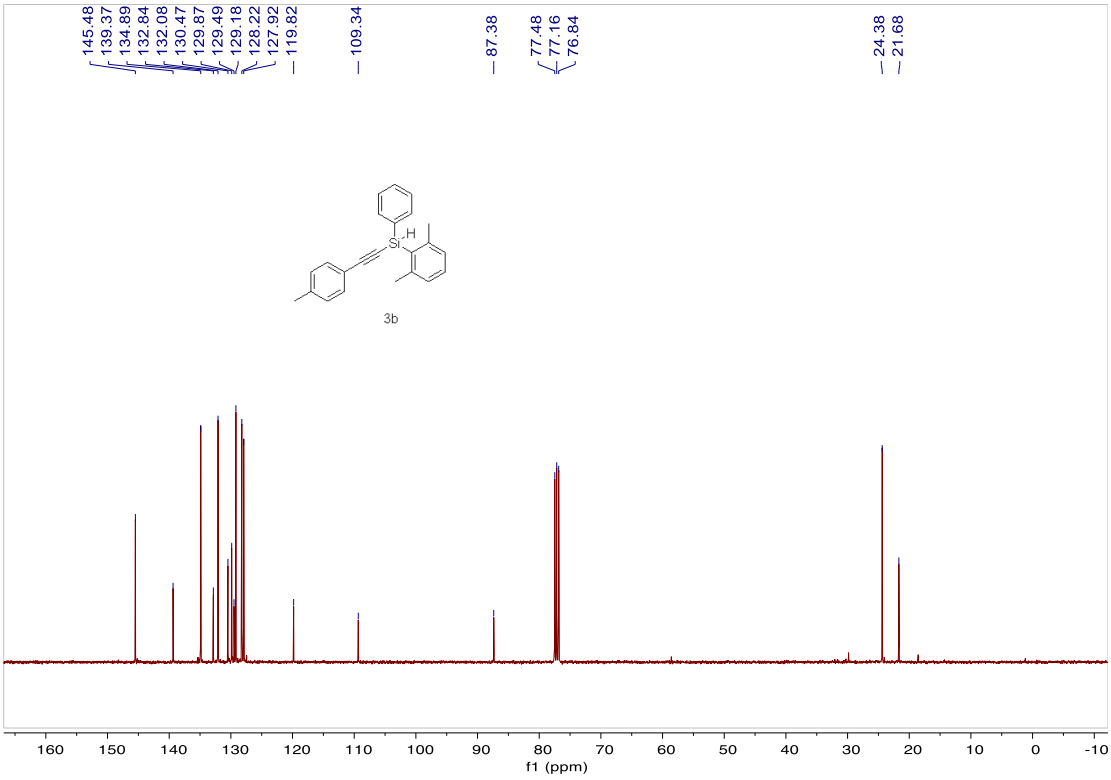
^{13}C NMR of 3a



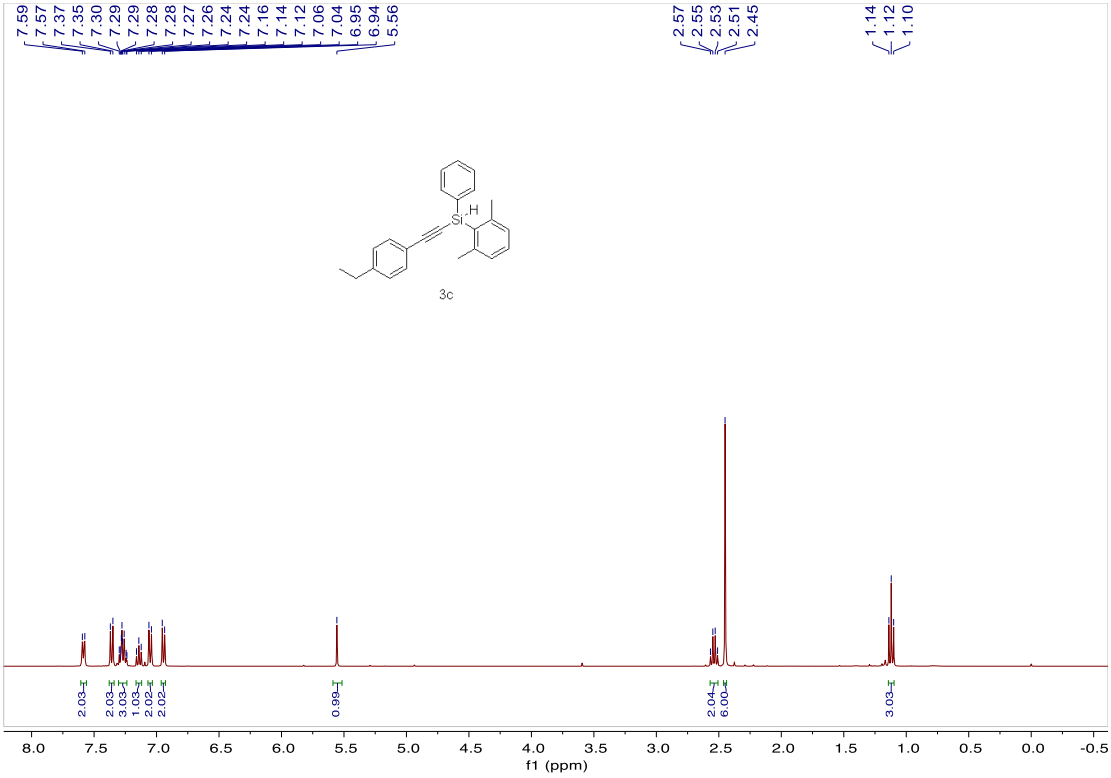
^{1}H NMR of 3b



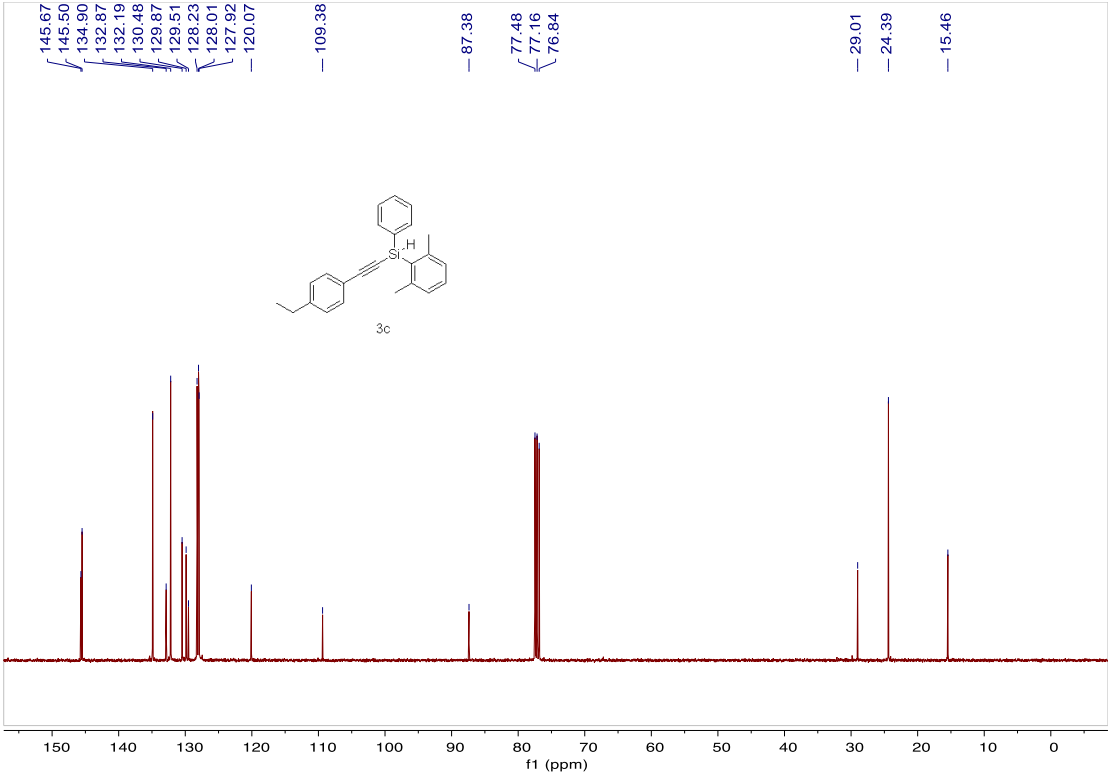
^{13}C NMR of 3b



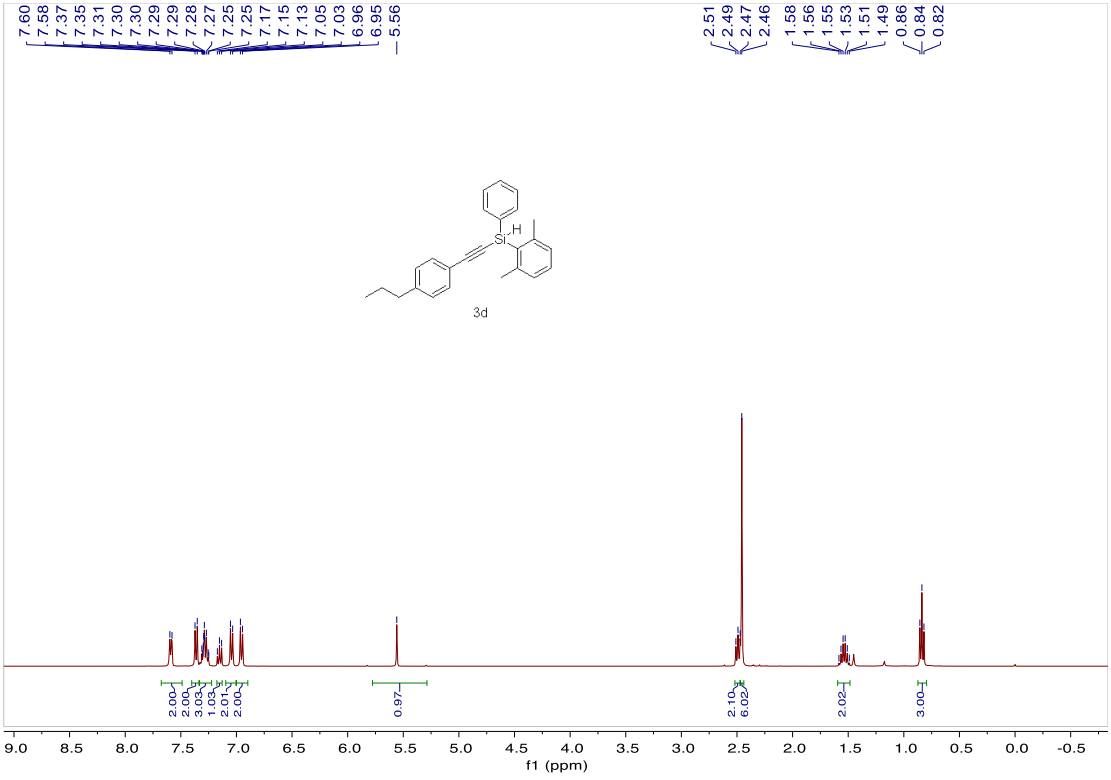
^{1}H NMR of 3c



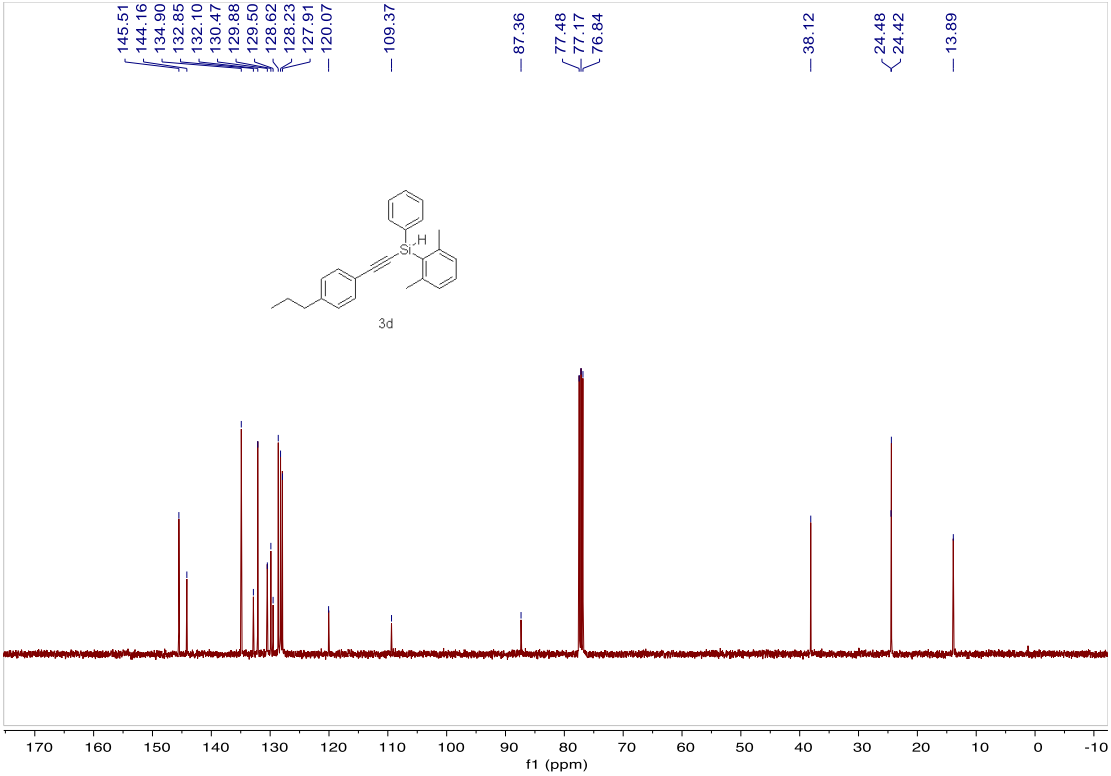
^{13}C NMR of 3c



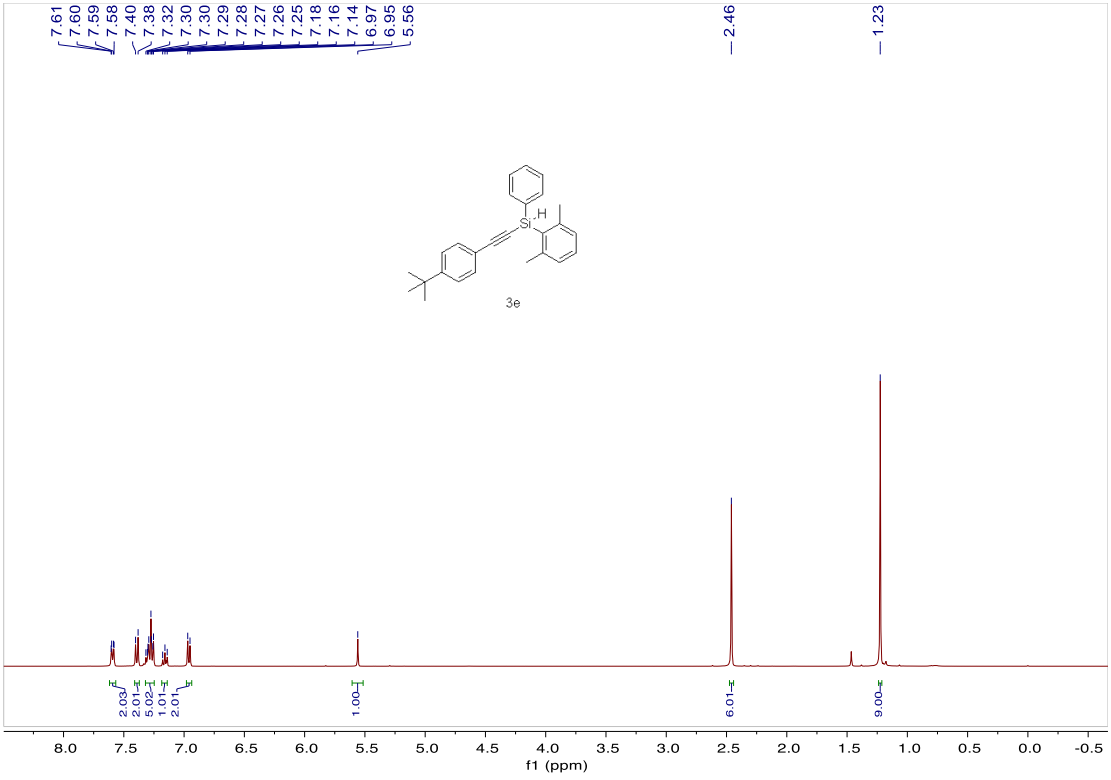
^{1}H NMR of 3d



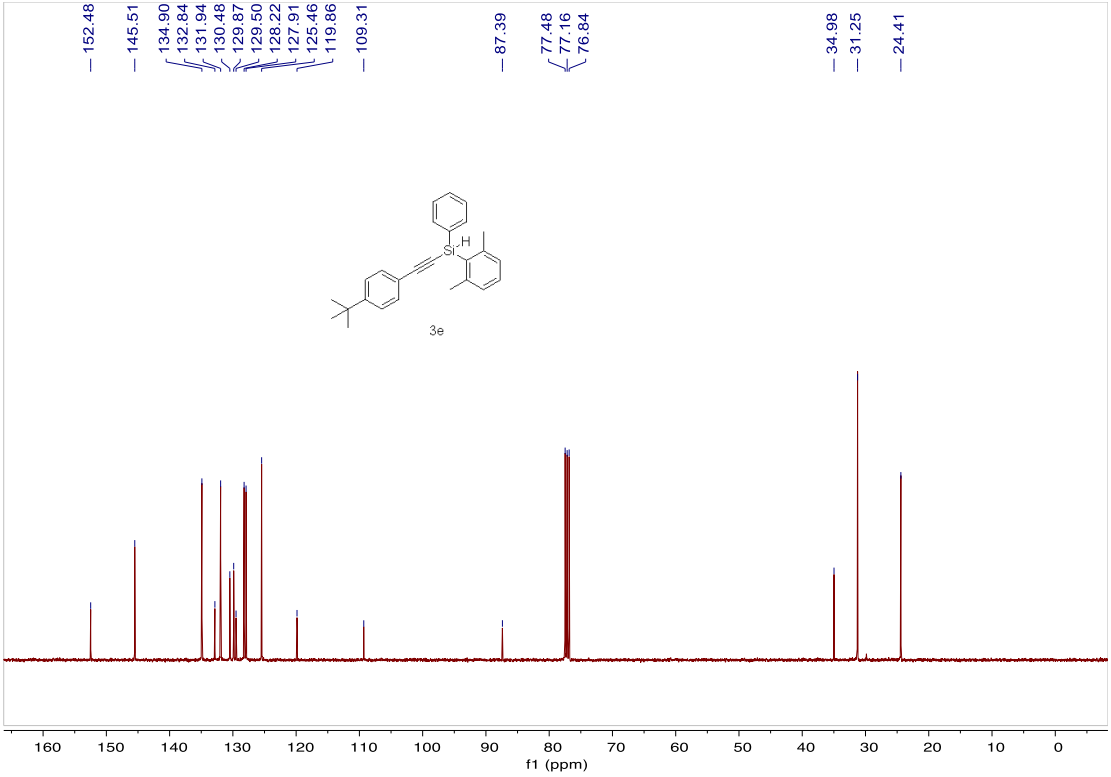
^{13}C NMR of 3d



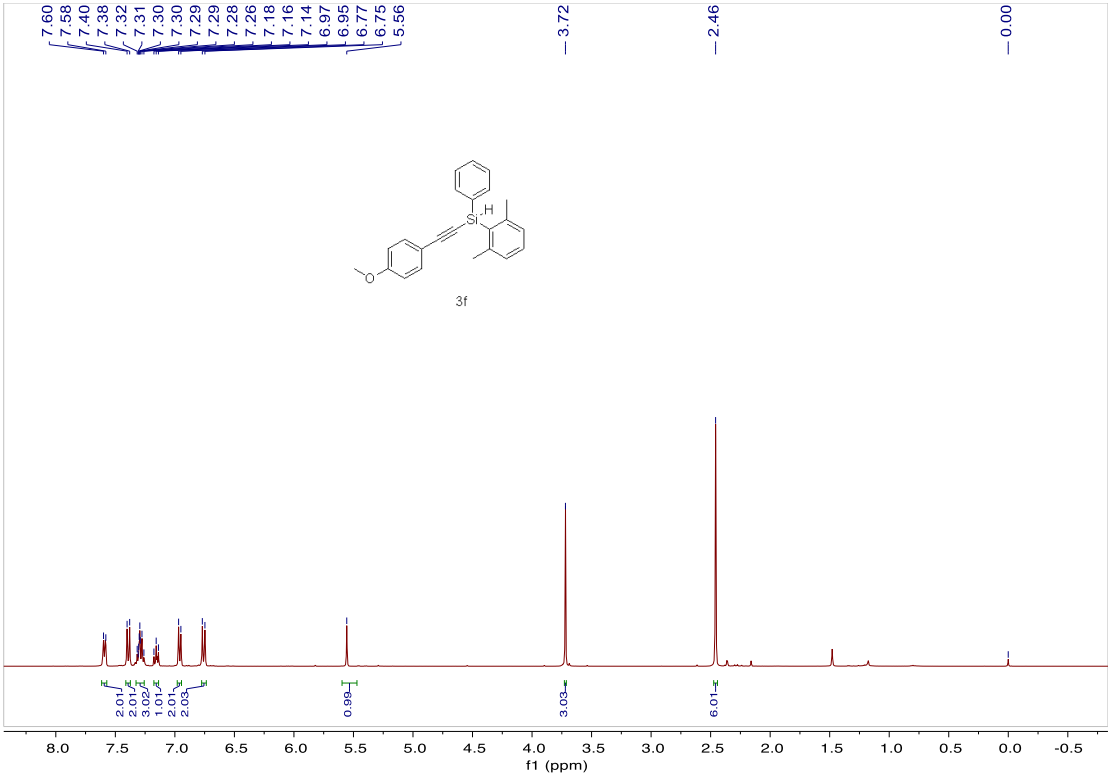
^{1}H NMR of 3e



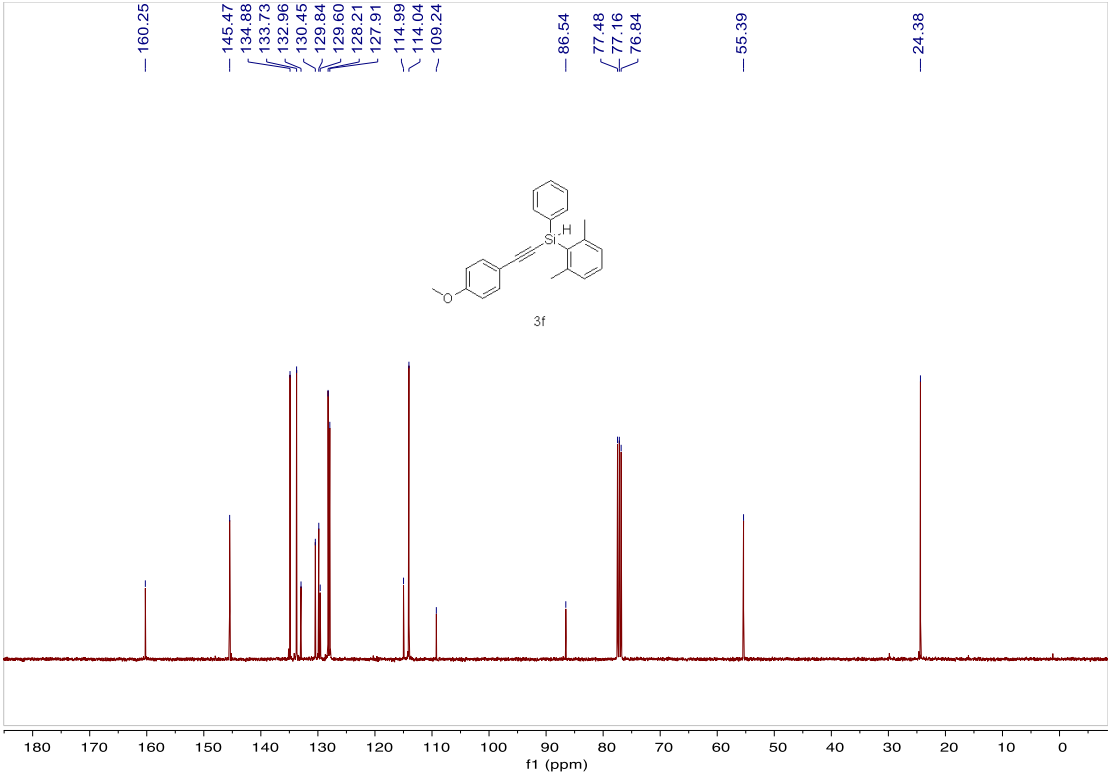
^{13}C NMR of 3e



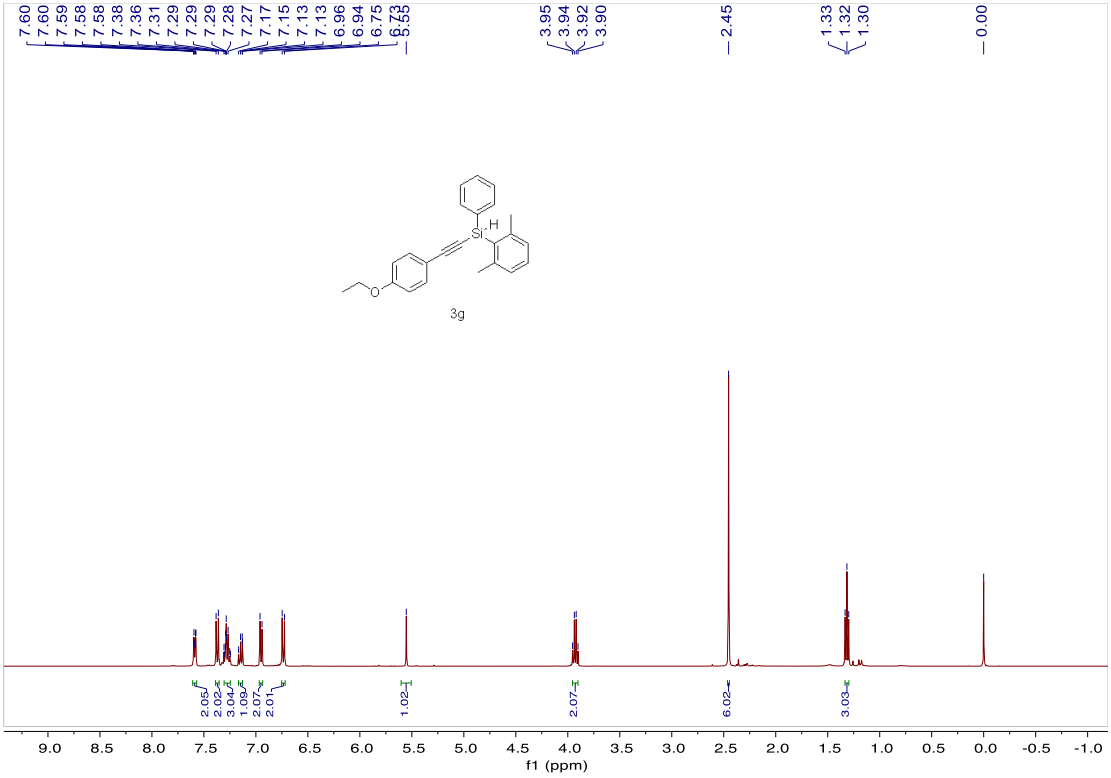
^{1}H NMR of 3f



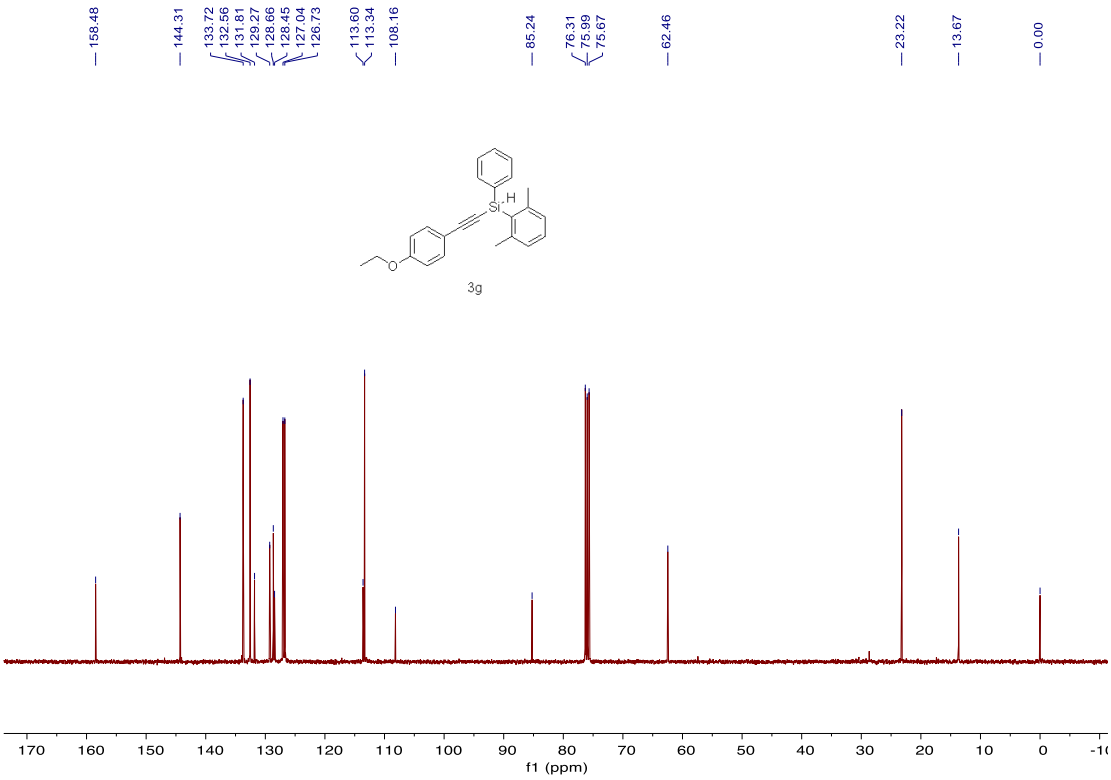
^{13}C NMR of 3f



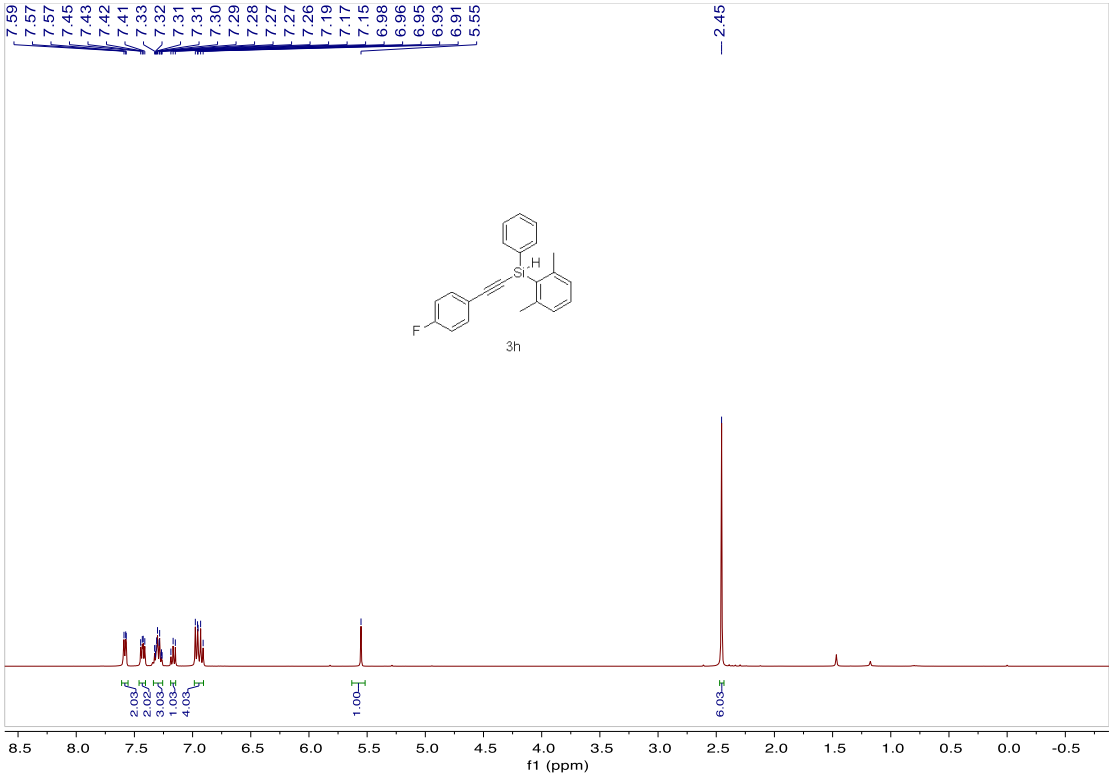
^{1}H NMR of 3g



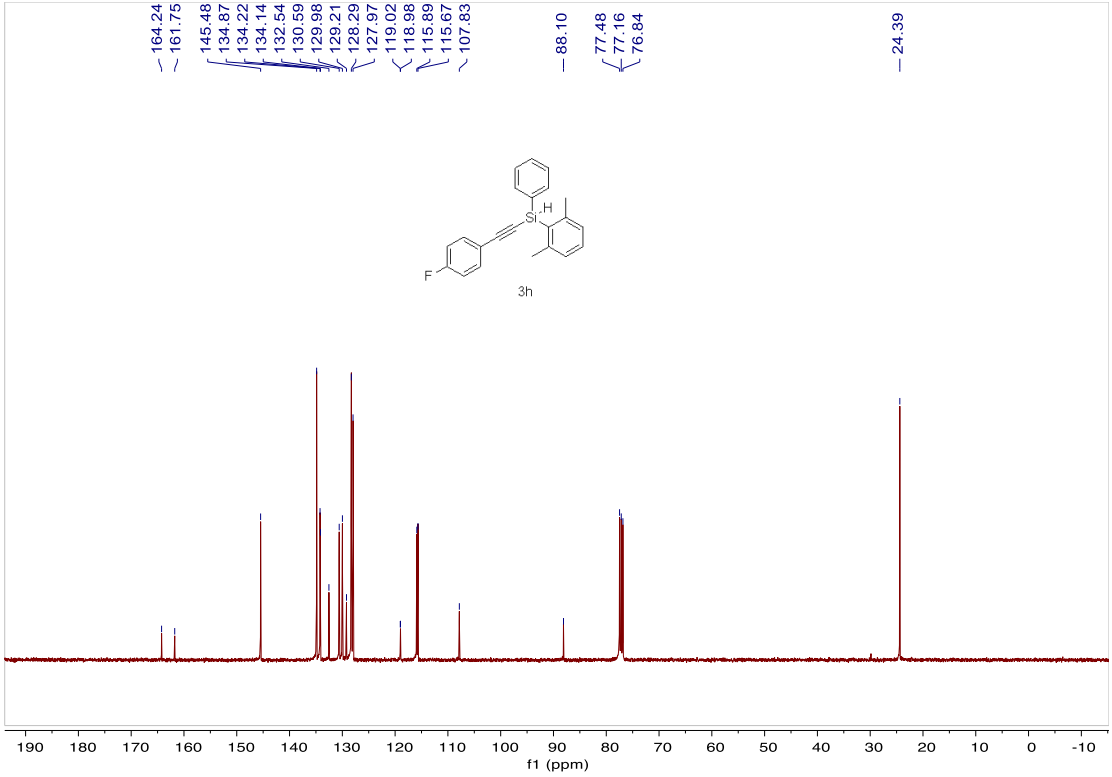
^{13}C NMR of 3g



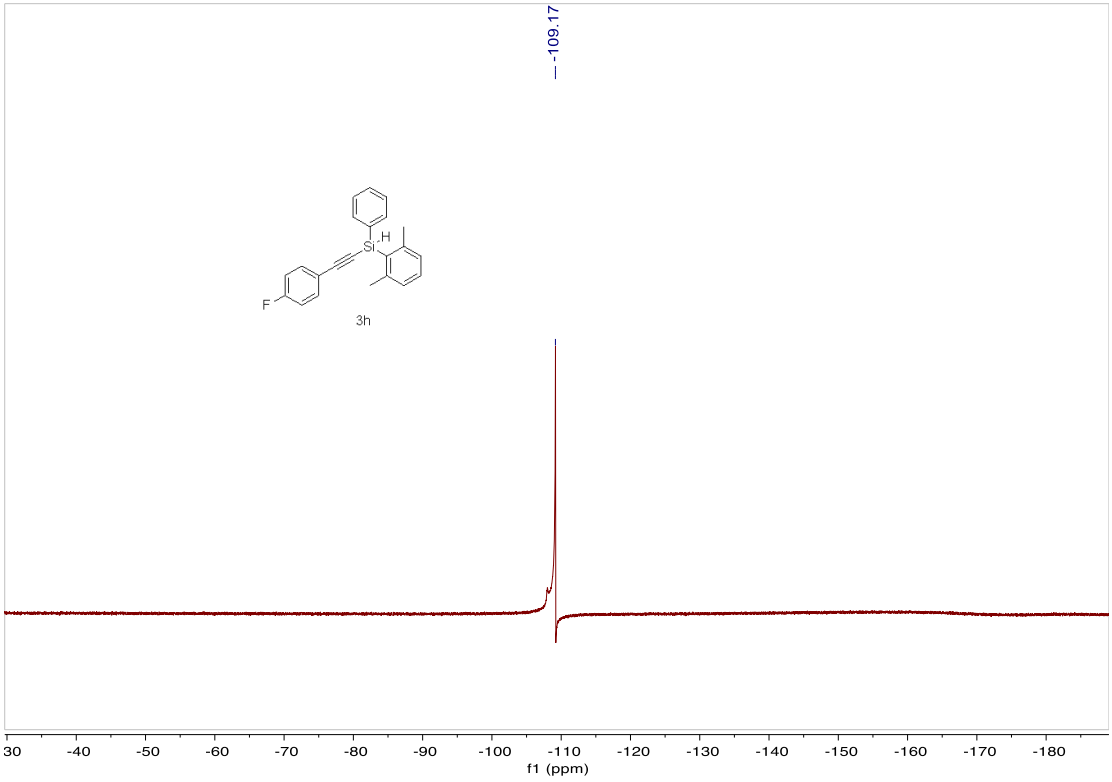
^{1}H NMR of 3h



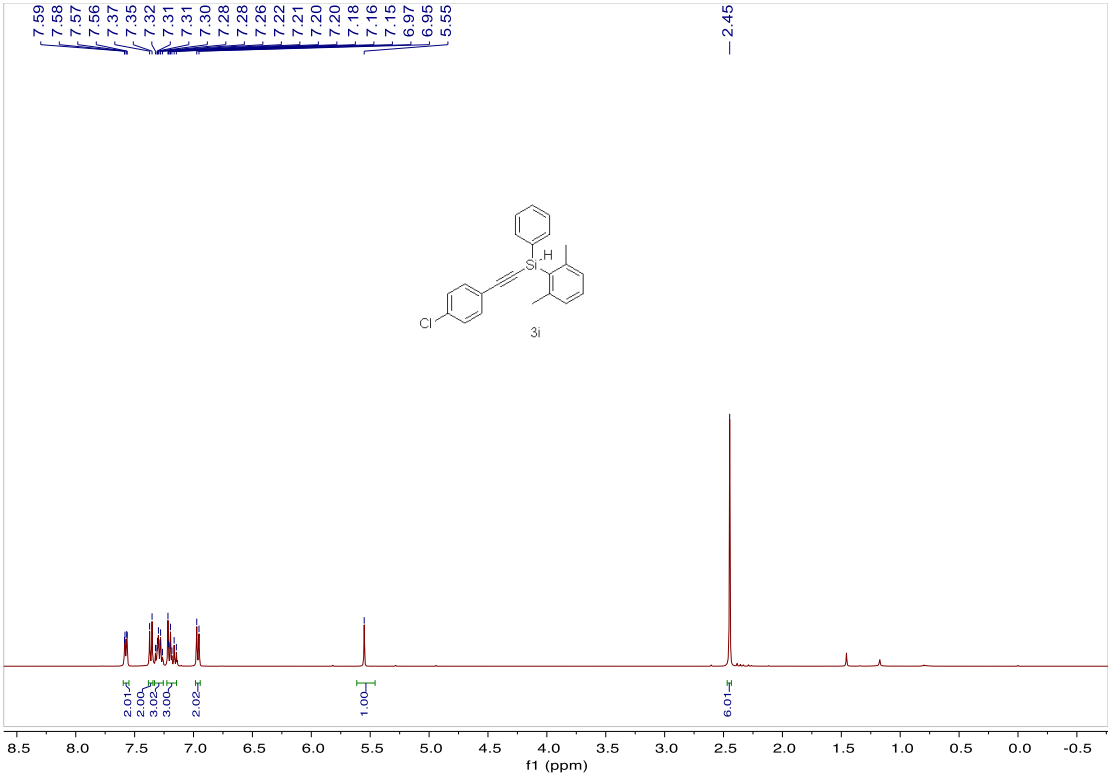
^{13}C NMR of 3h



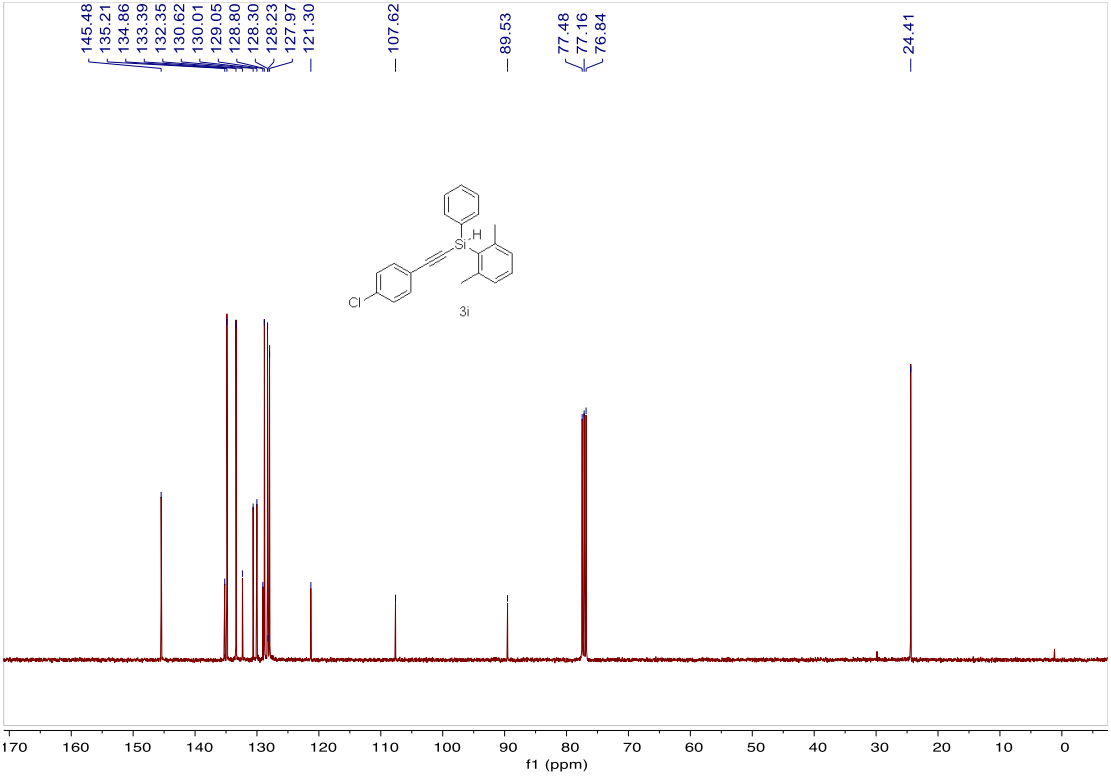
^{19}F NMR of 3h


-109.17
Si
H
F
3h
30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

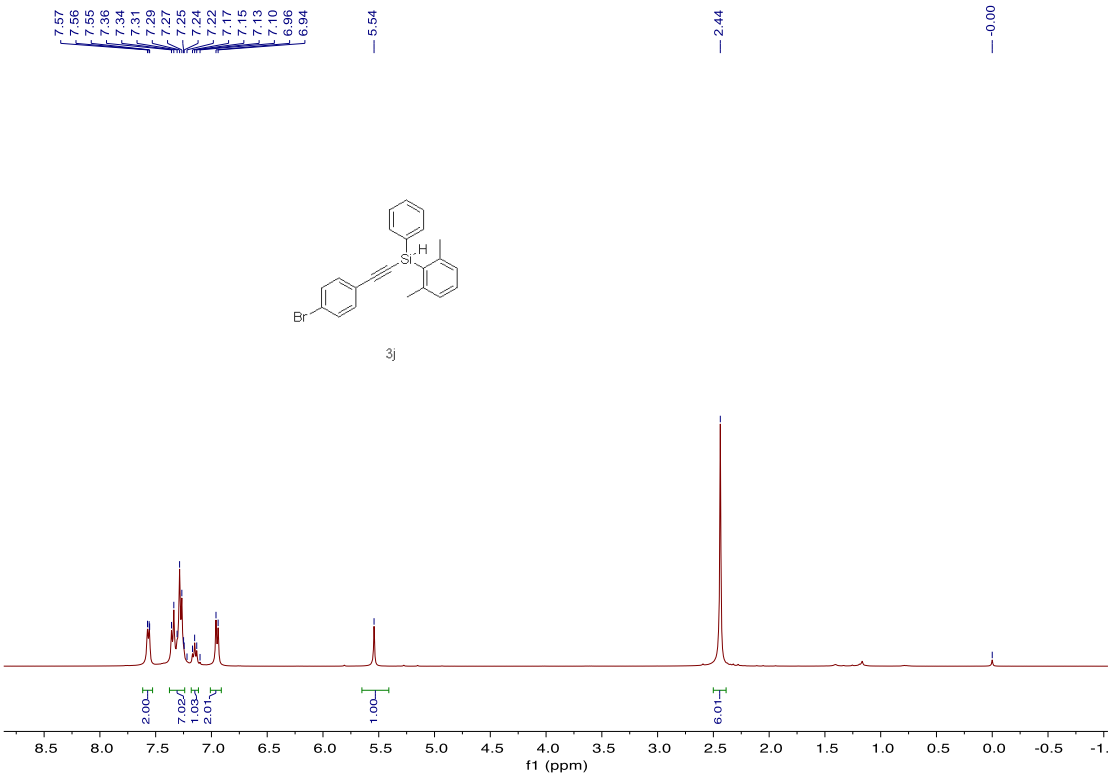
^{1}H NMR of 3i



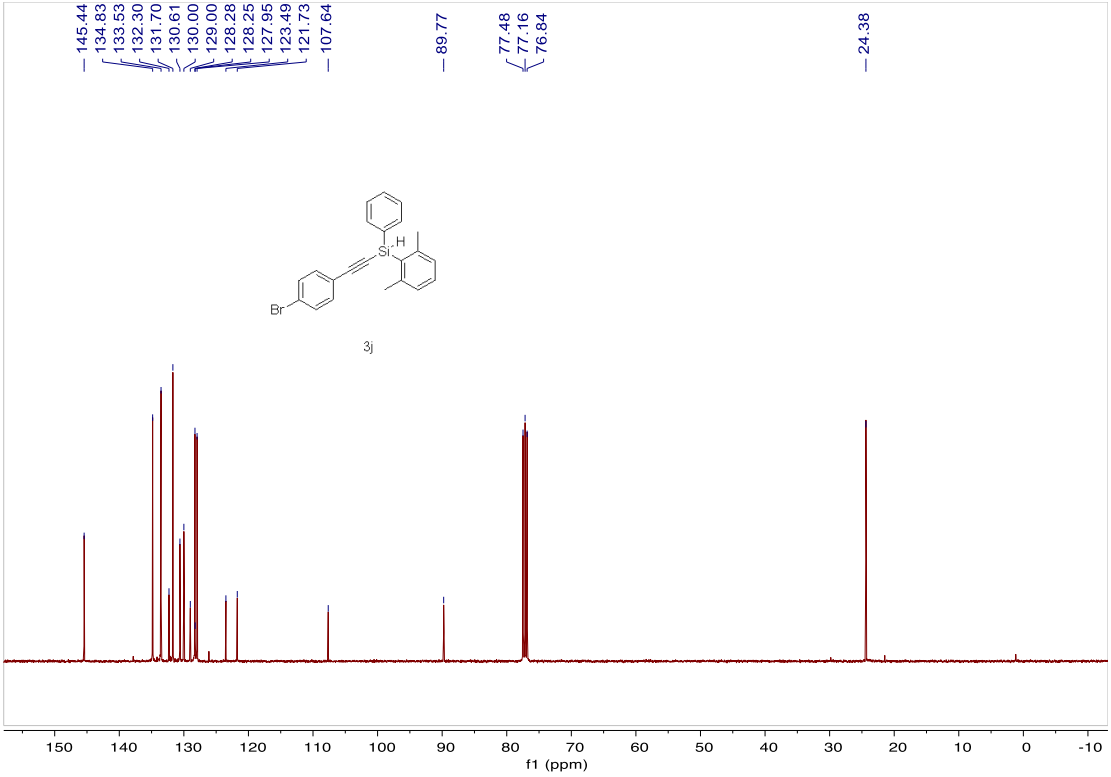
^{13}C NMR of 3i



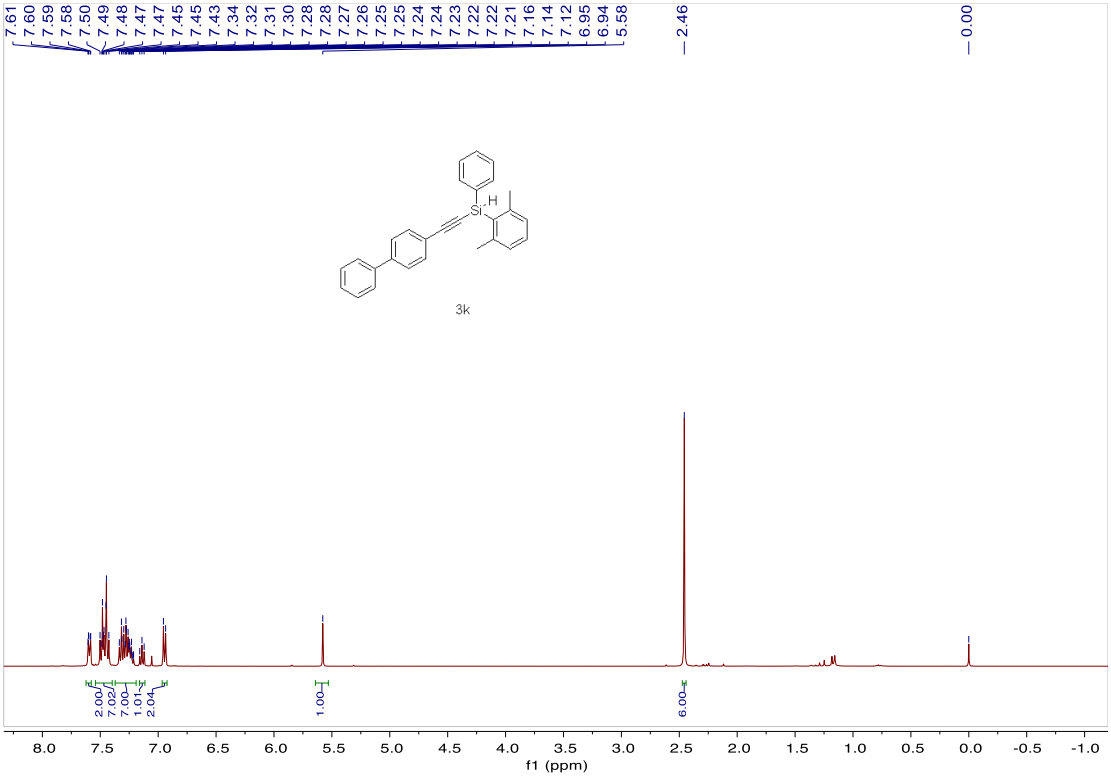
^{1}H NMR of 3j



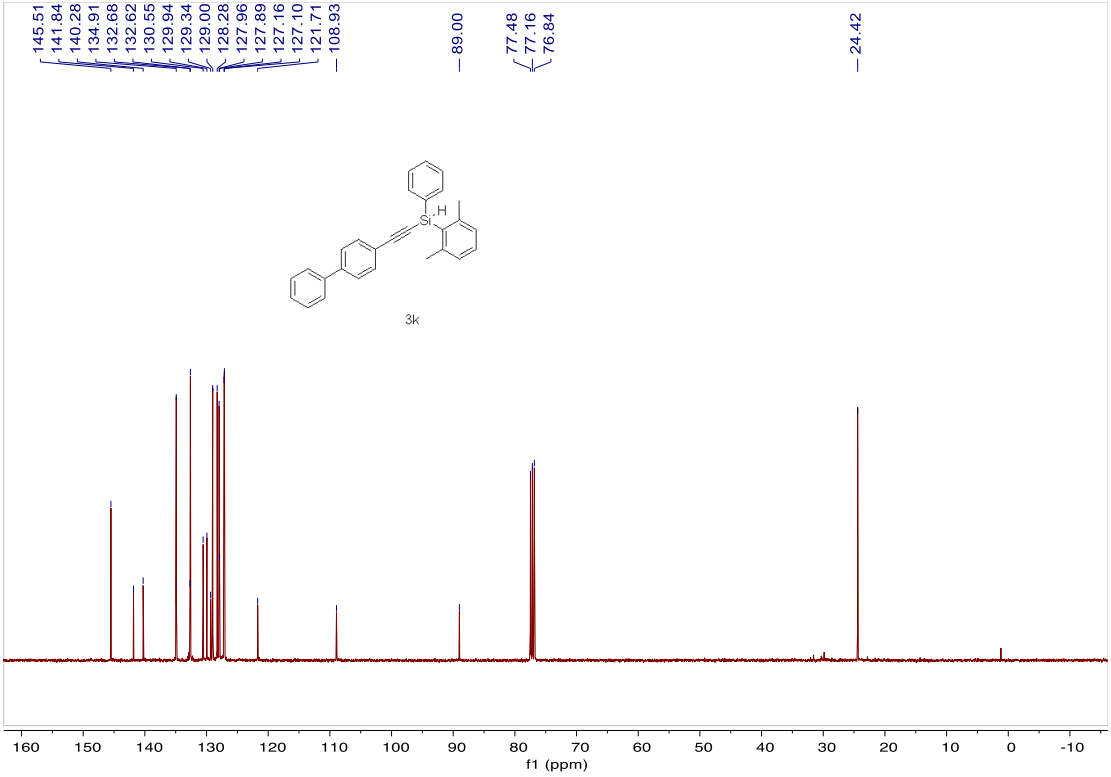
^{13}C NMR of 3j



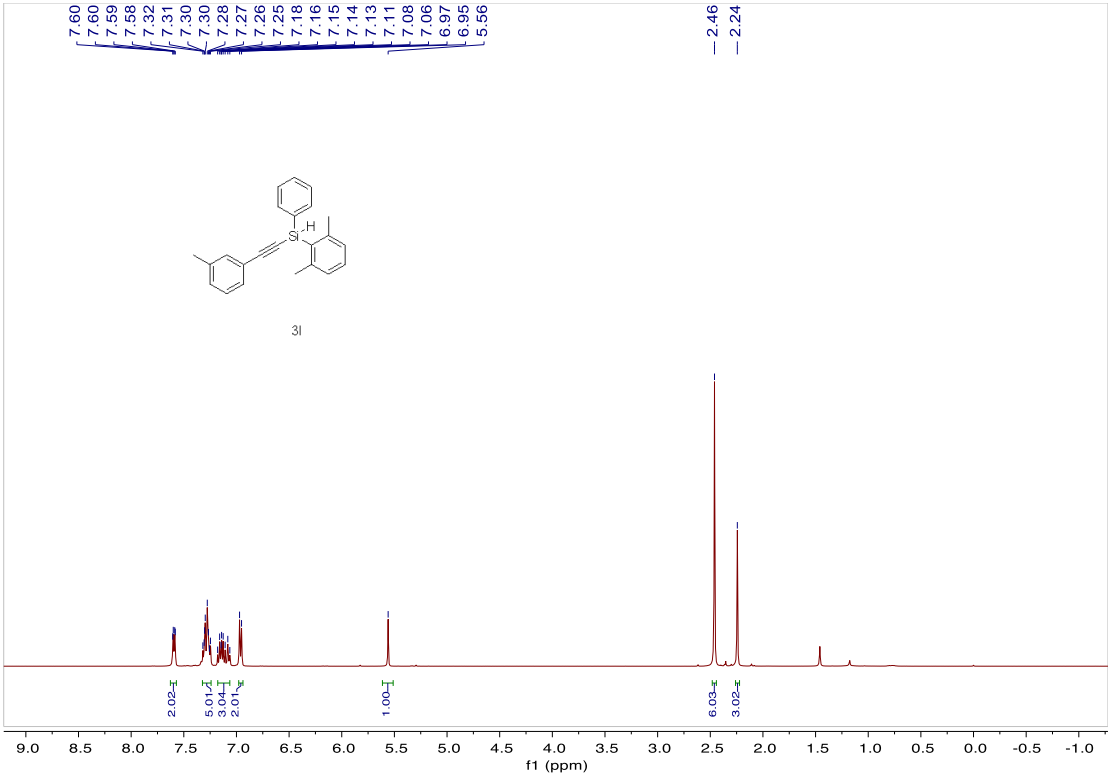
^{1}H NMR of 3k



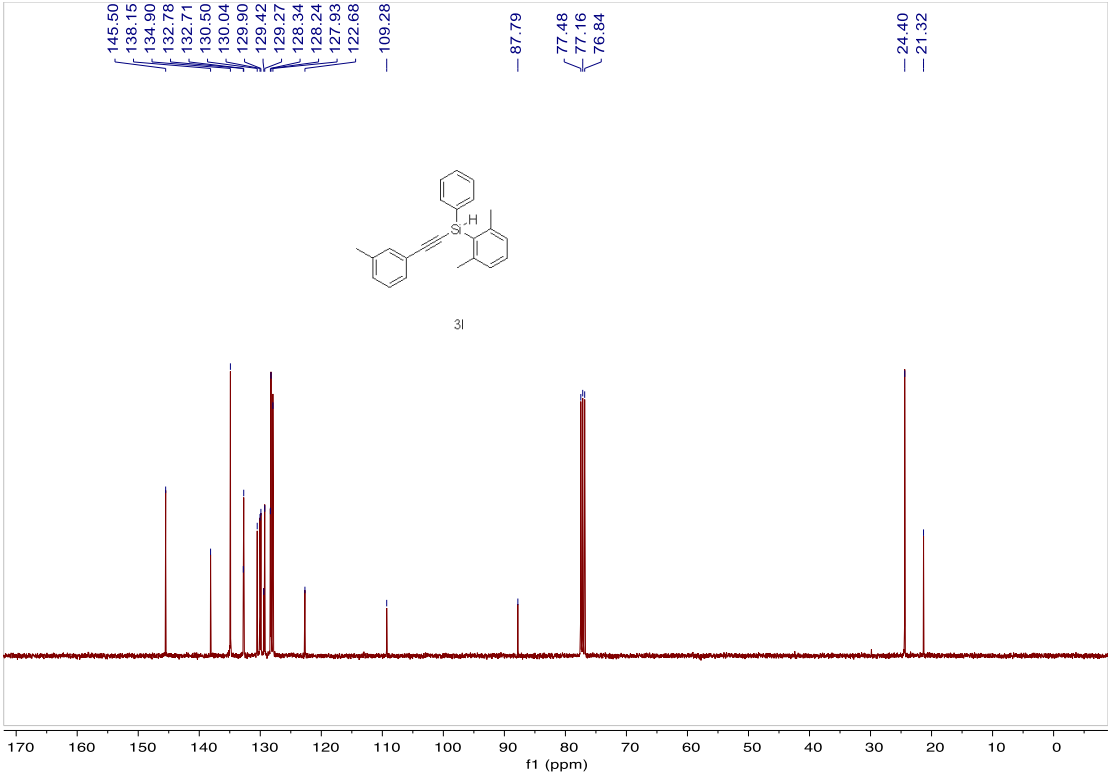
^{13}C NMR of 3k



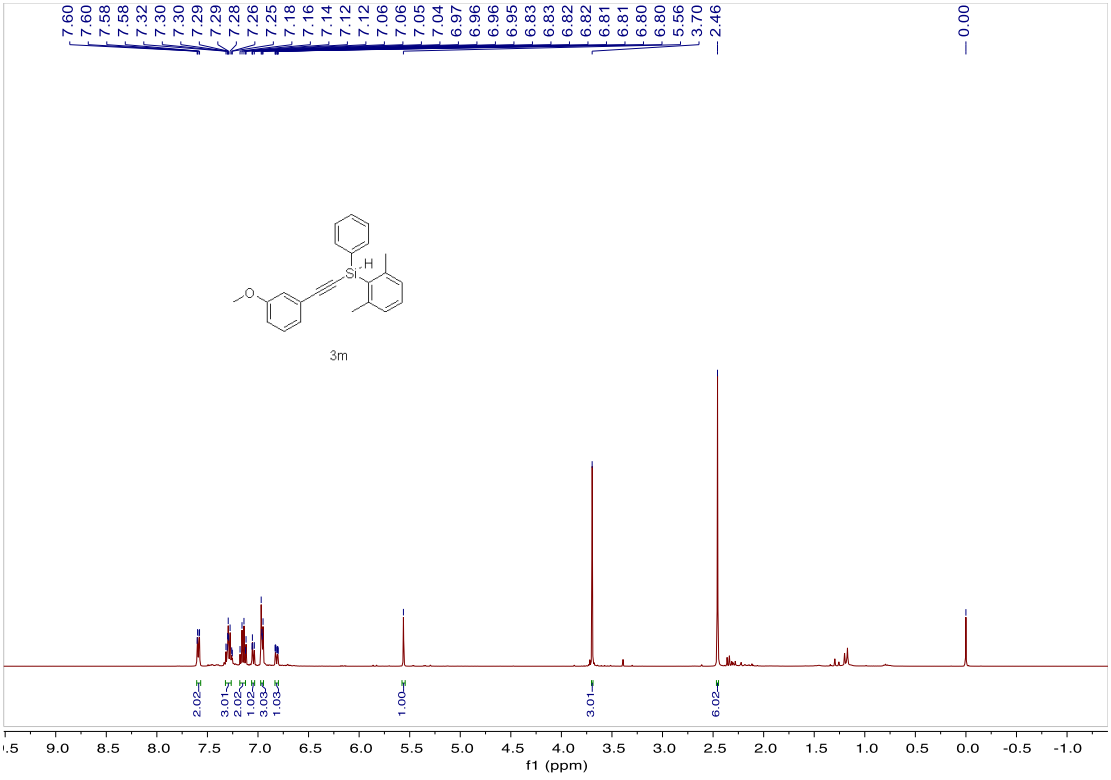
^{1}H NMR of 3l



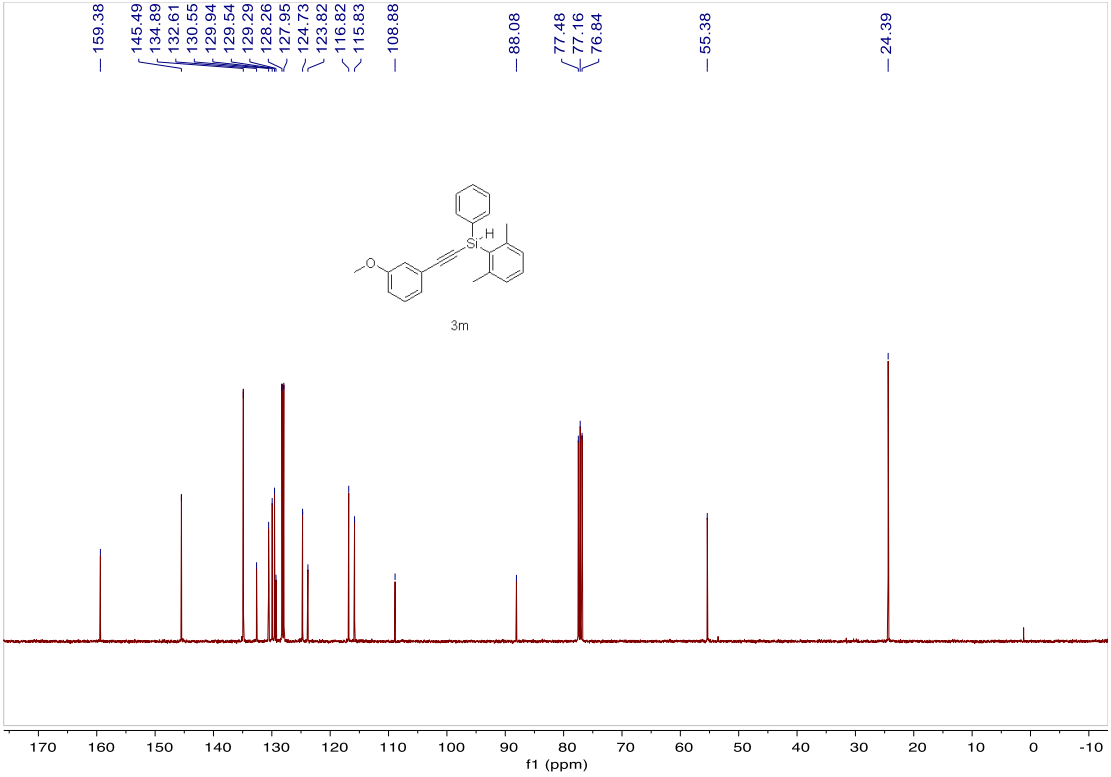
^{13}C NMR of 3l



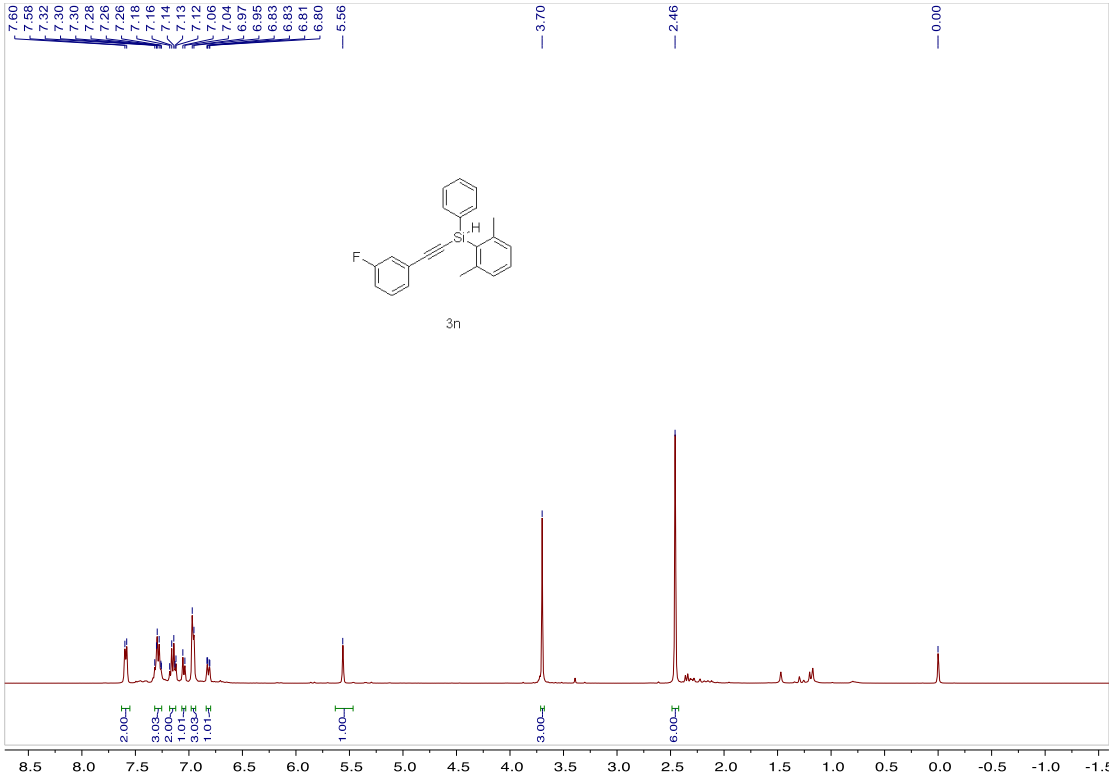
^{1}H NMR of 3m



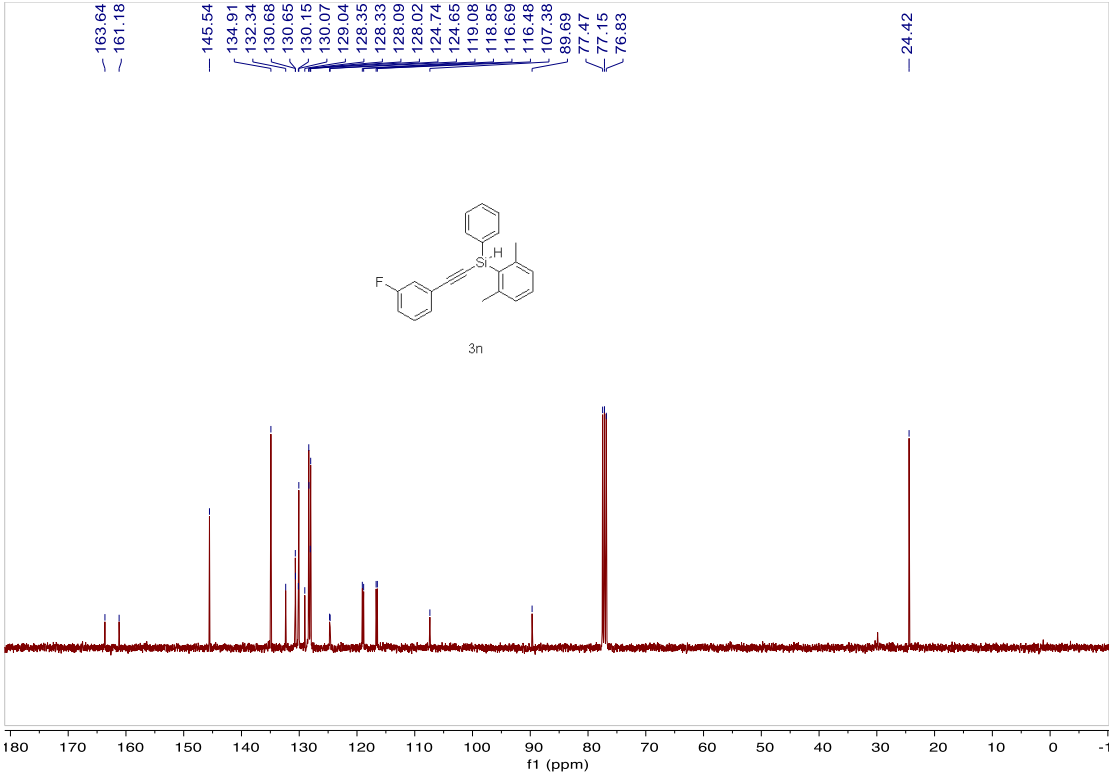
^{13}C NMR of 3m



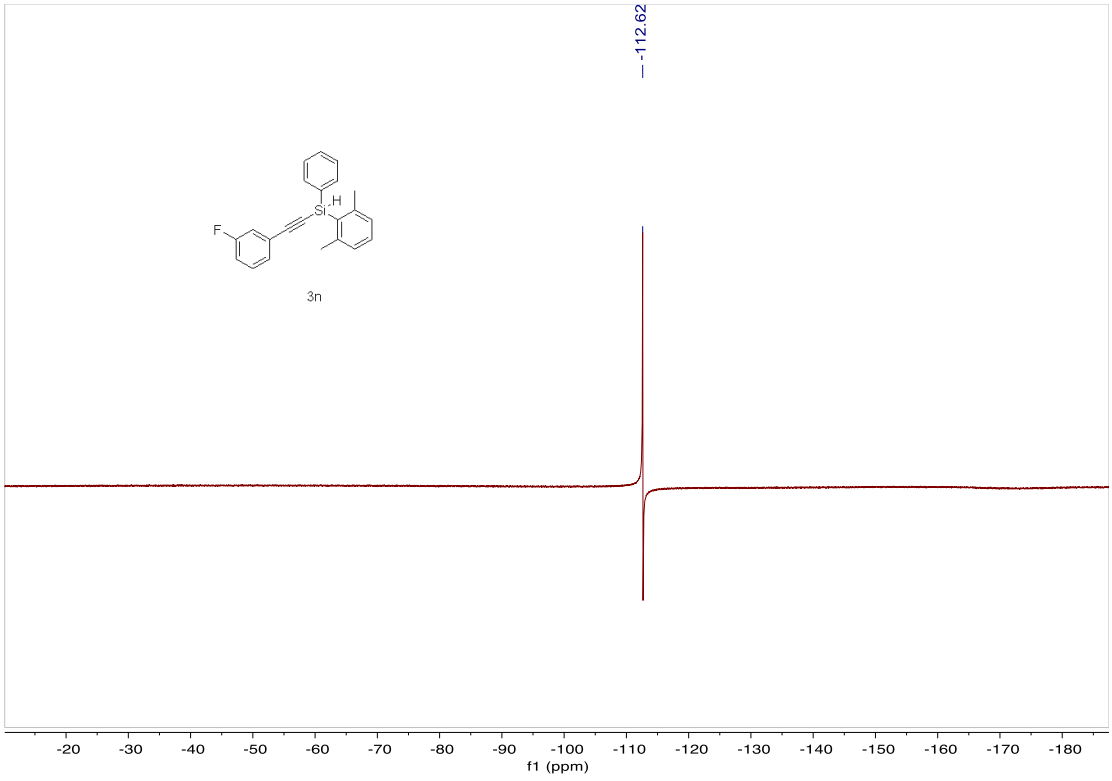
^{1}H NMR of 3n



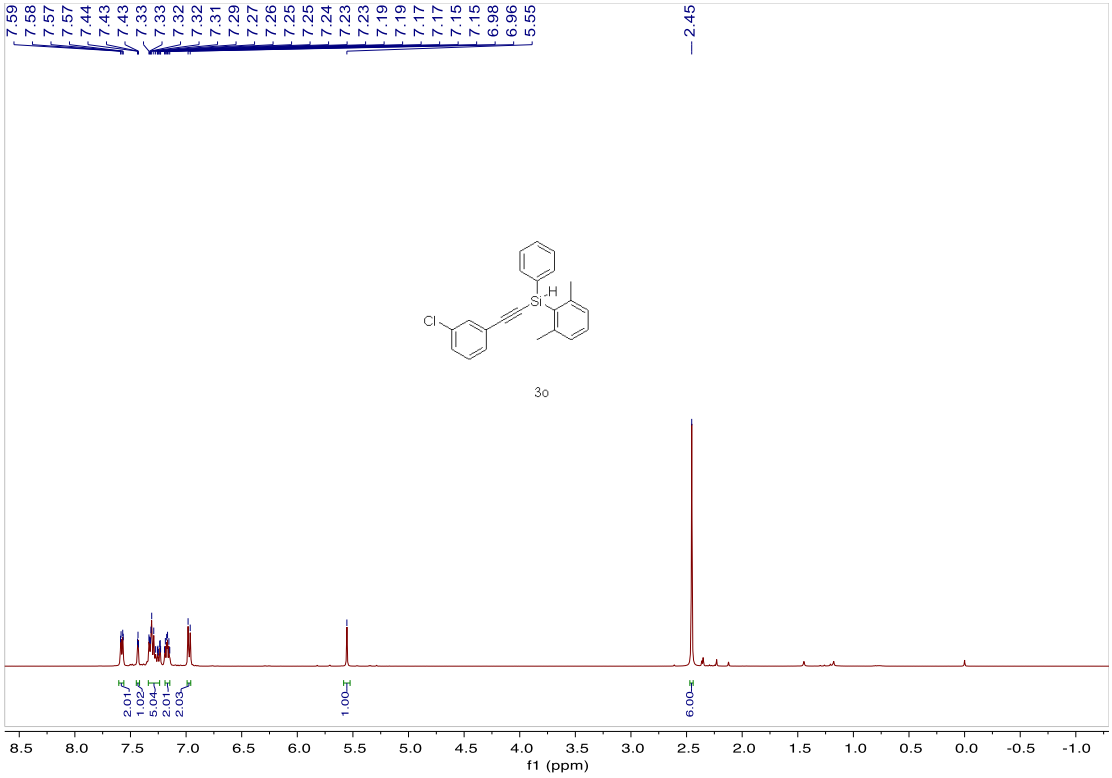
^{13}C NMR of 3n



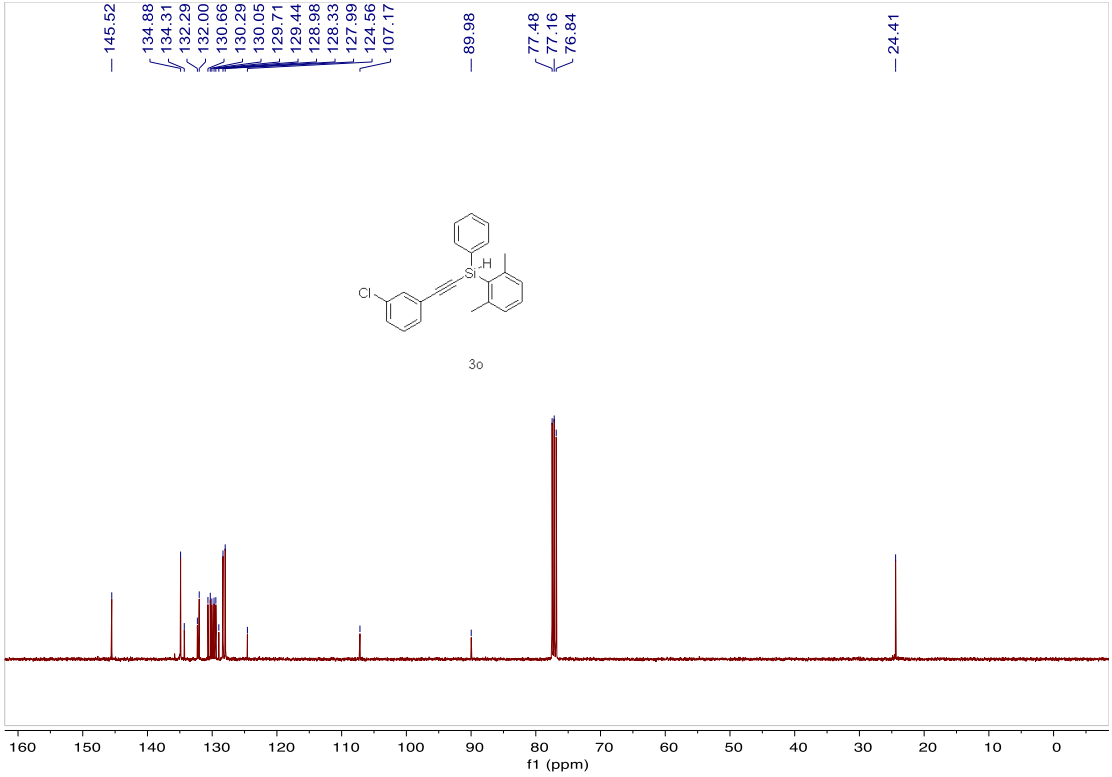
^{19}F NMR of 3n


-112.62
F
Si
H
3n
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

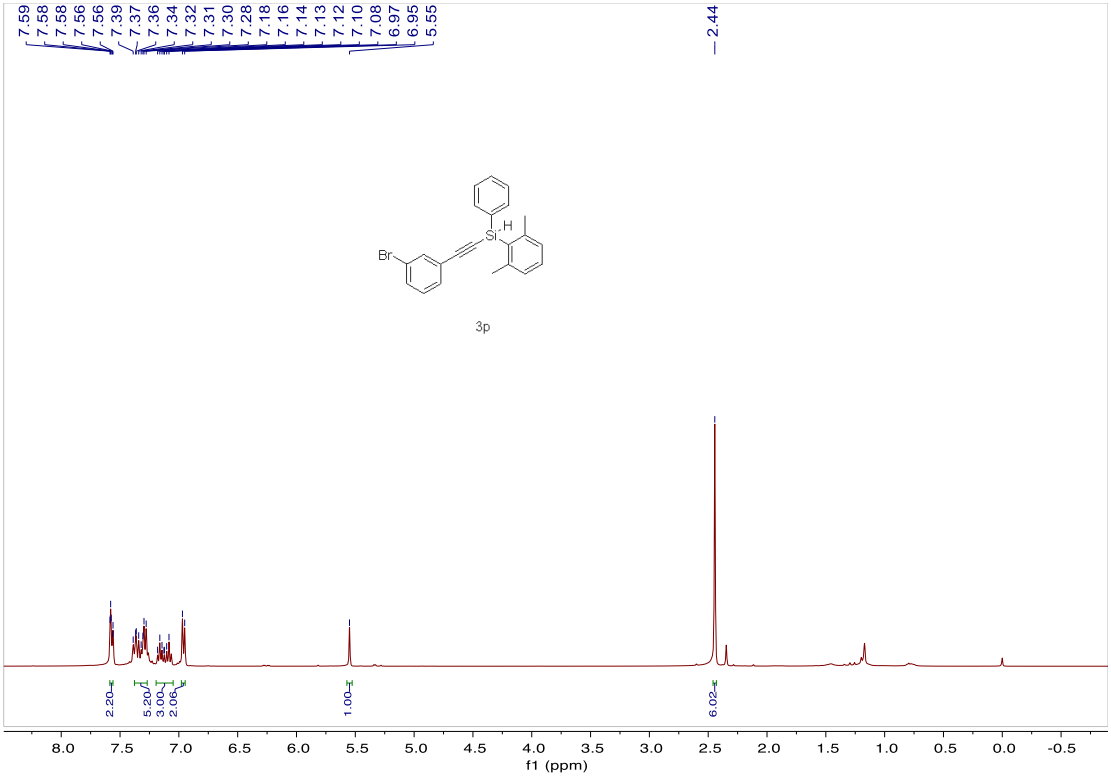
^{1}H NMR of 3o



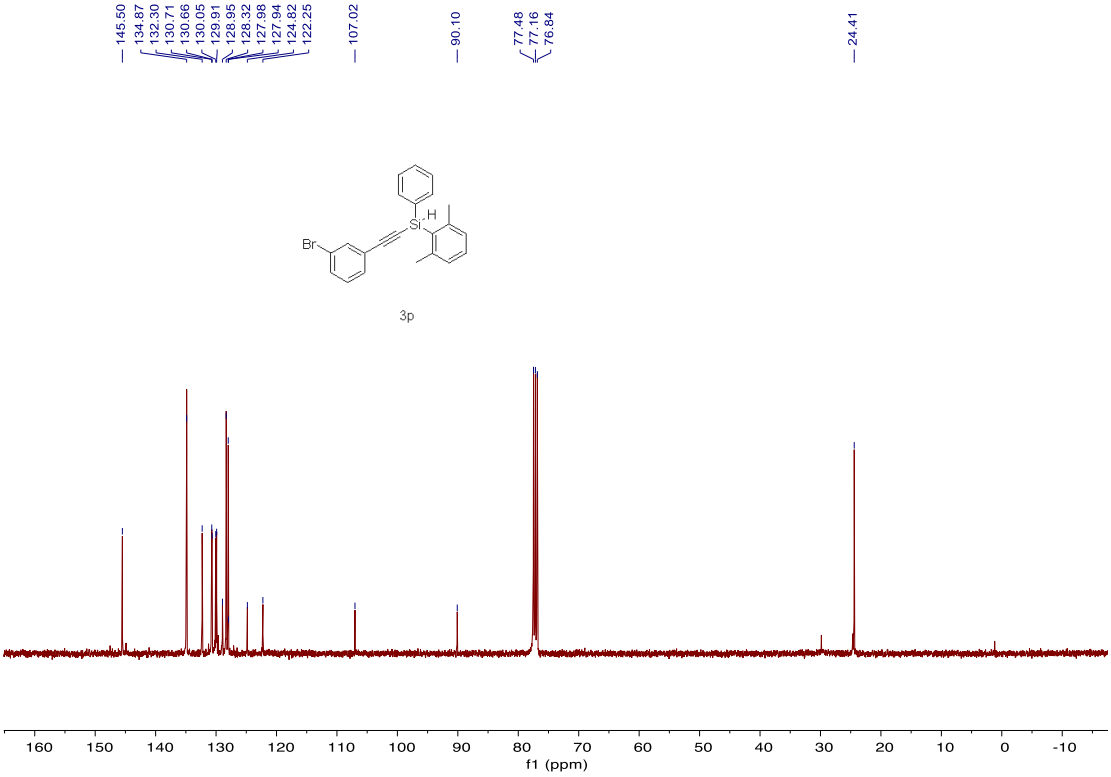
^{13}C NMR of 3o



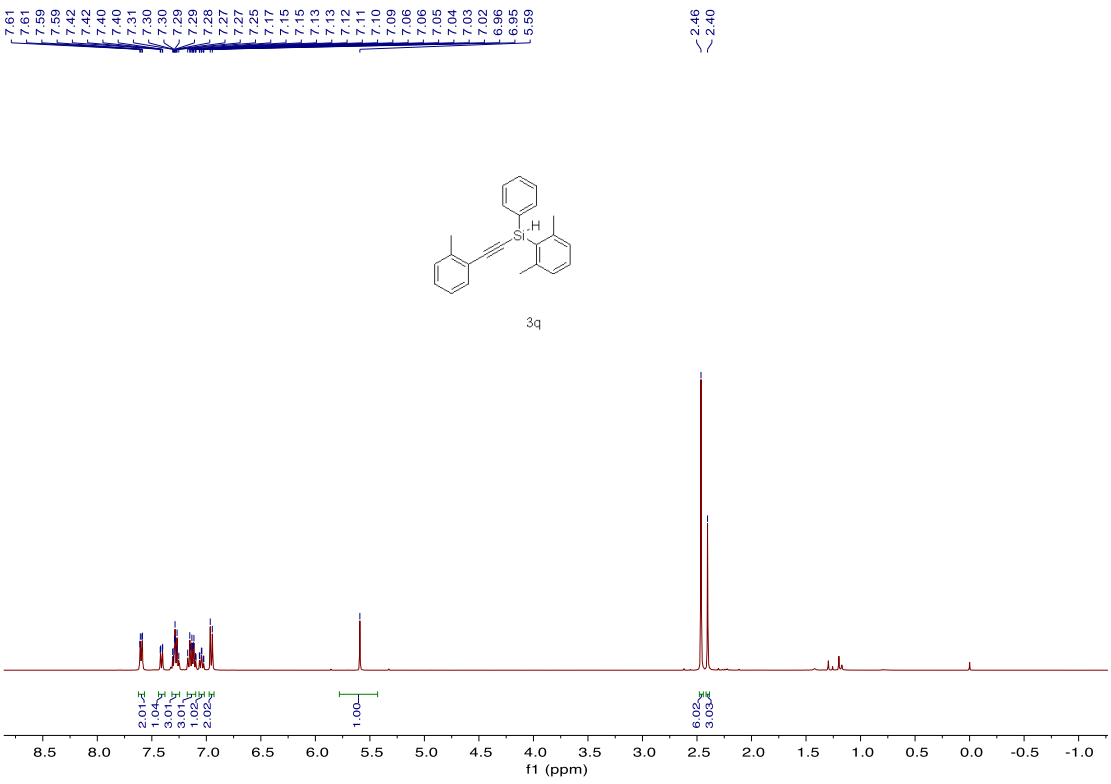
^{1}H NMR of 3p



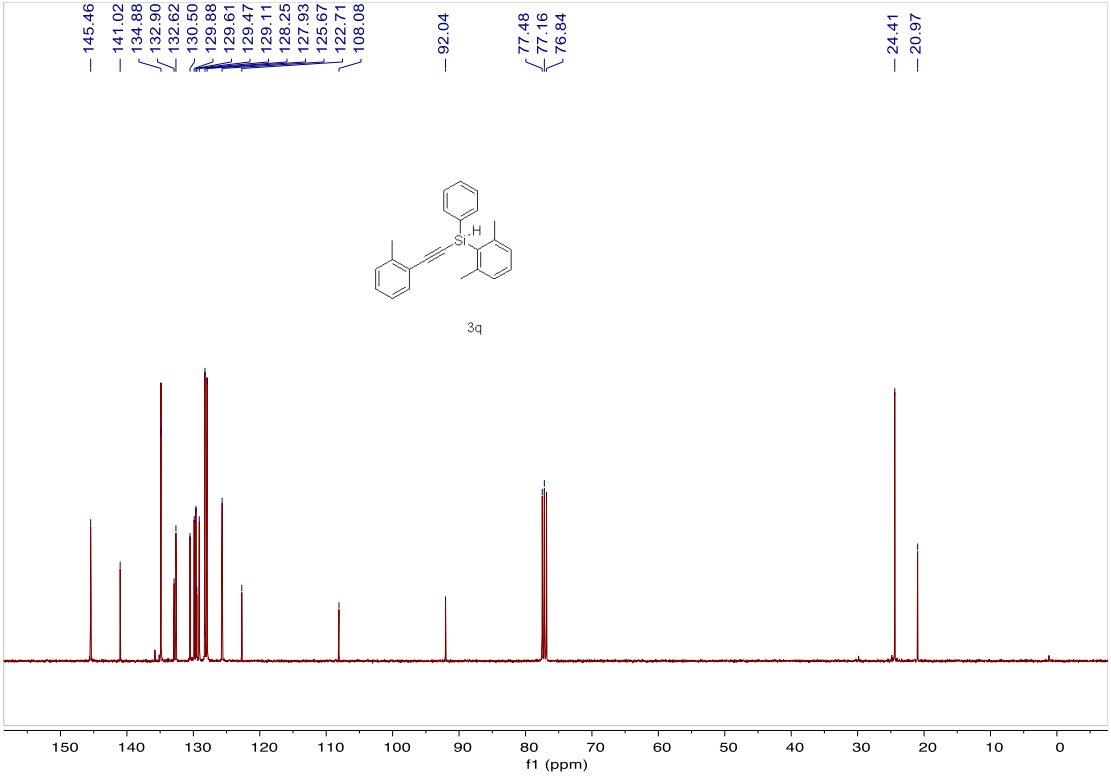
^{13}C NMR of 3p



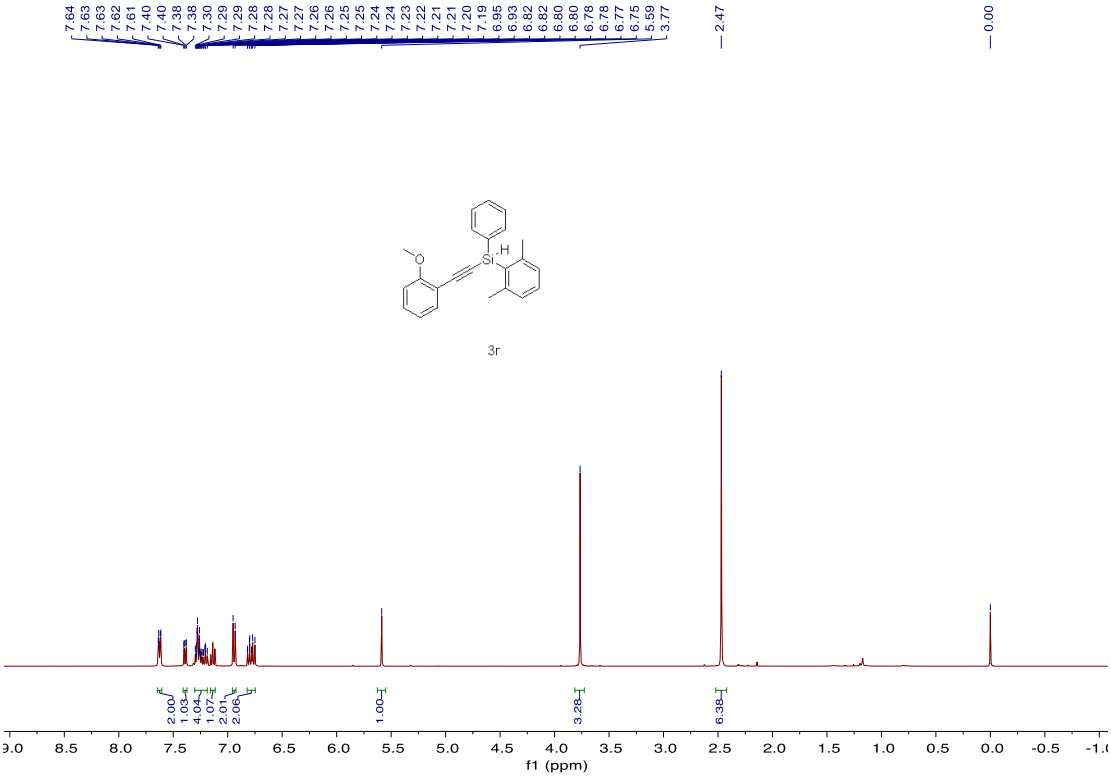
^{1}H NMR of 3q



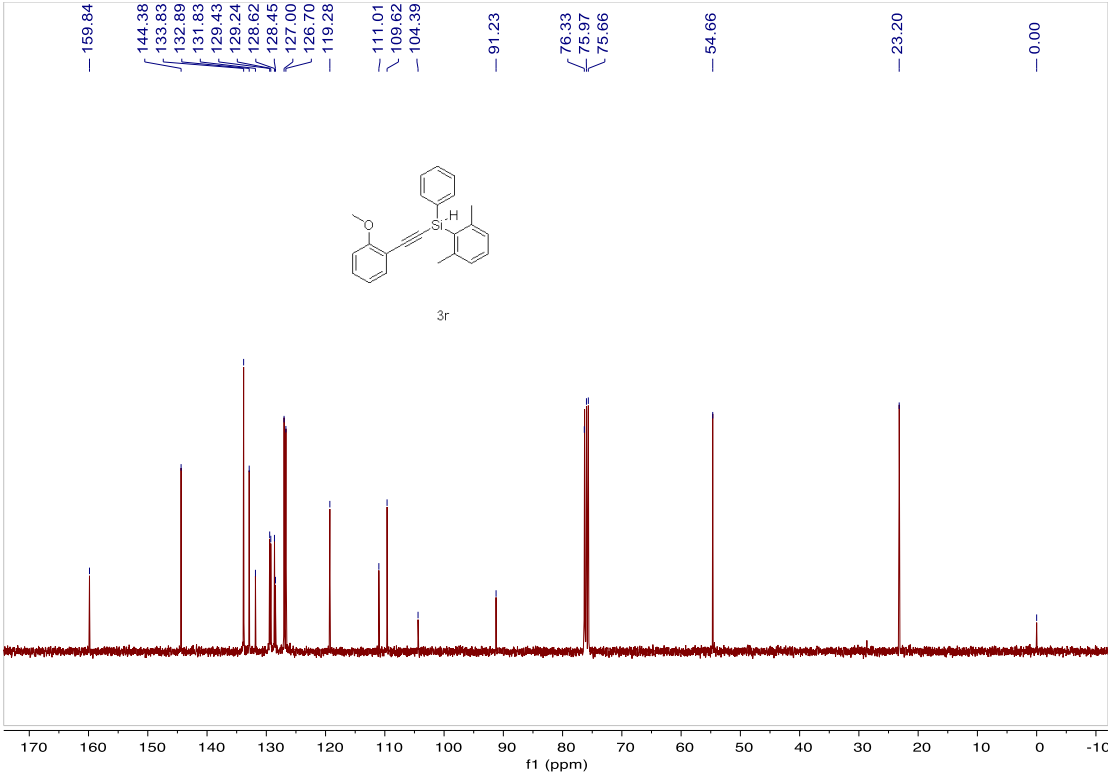
^{13}C NMR of 3q



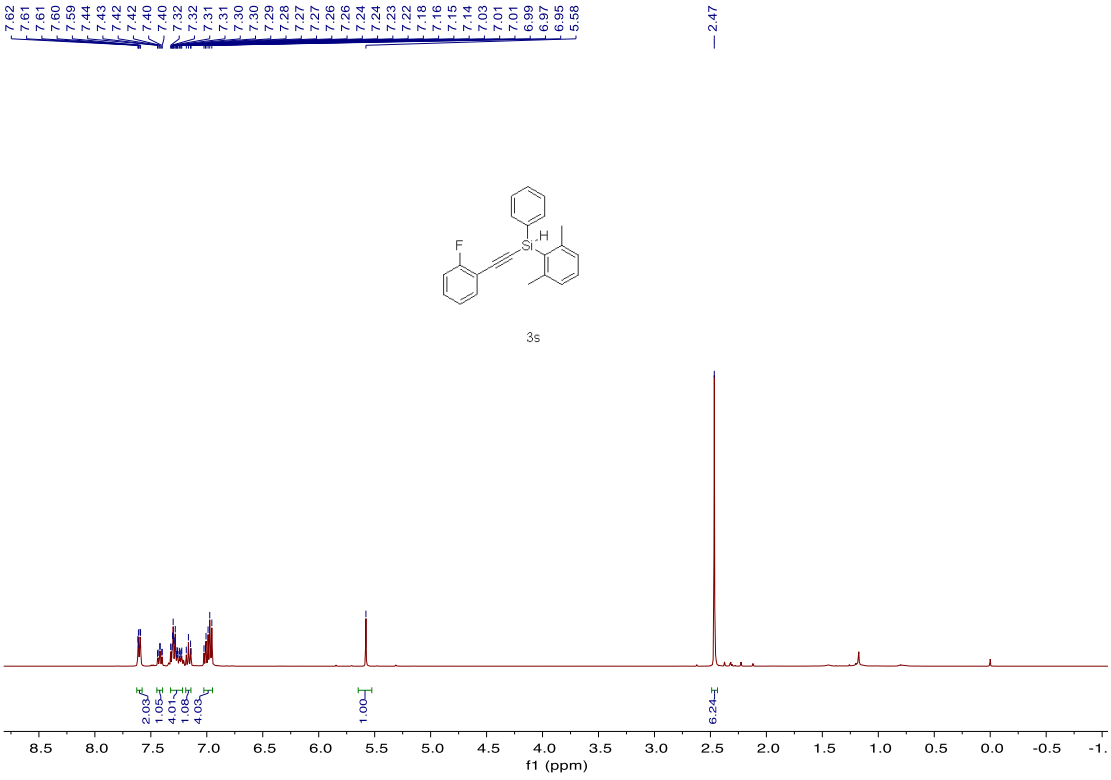
^{1}H NMR of 3r



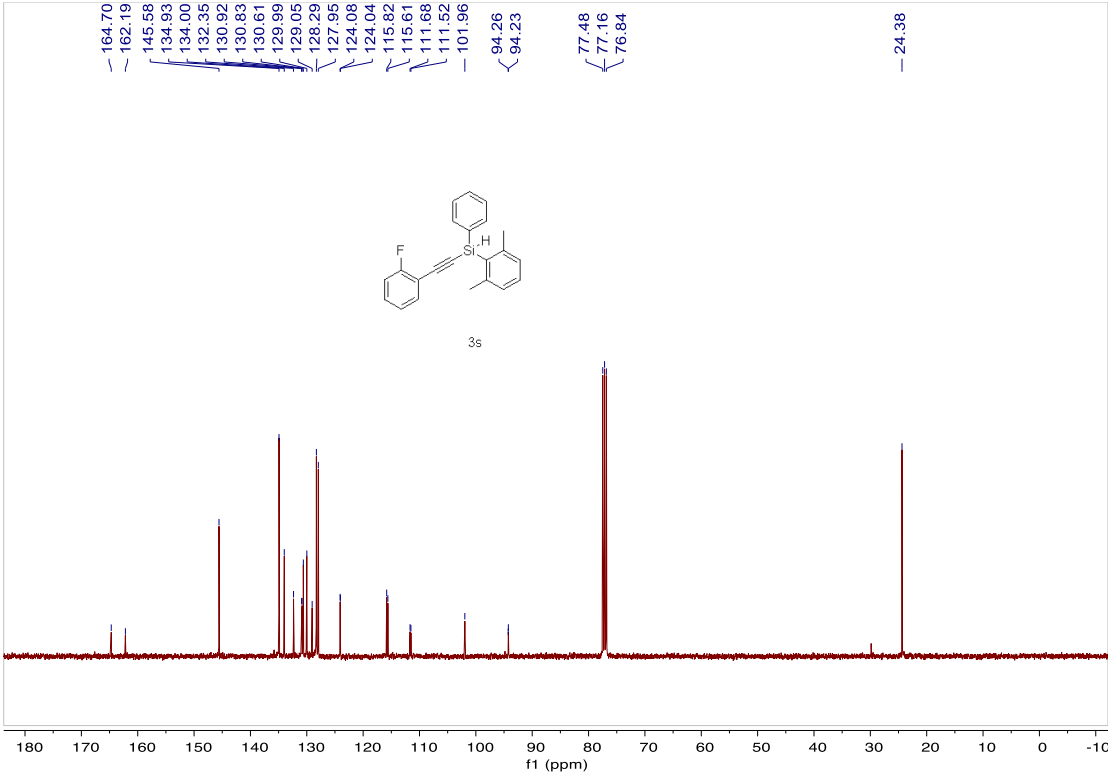
^{13}C NMR of 3r



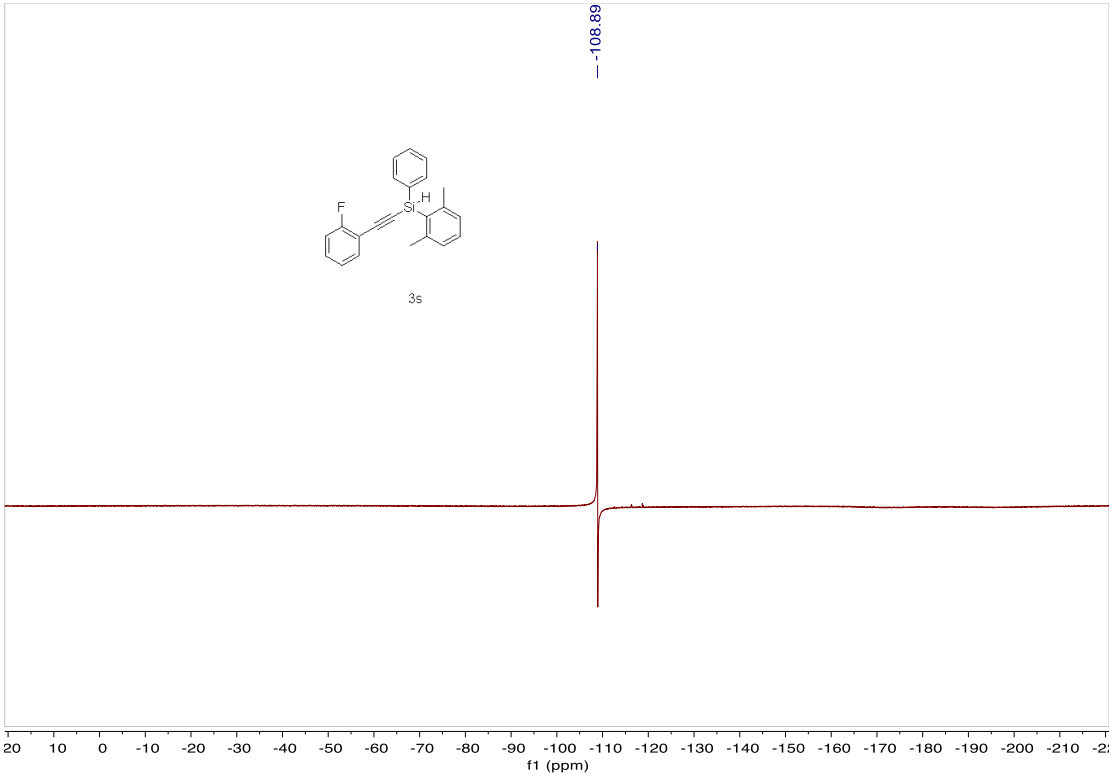
^{1}H NMR of 3s



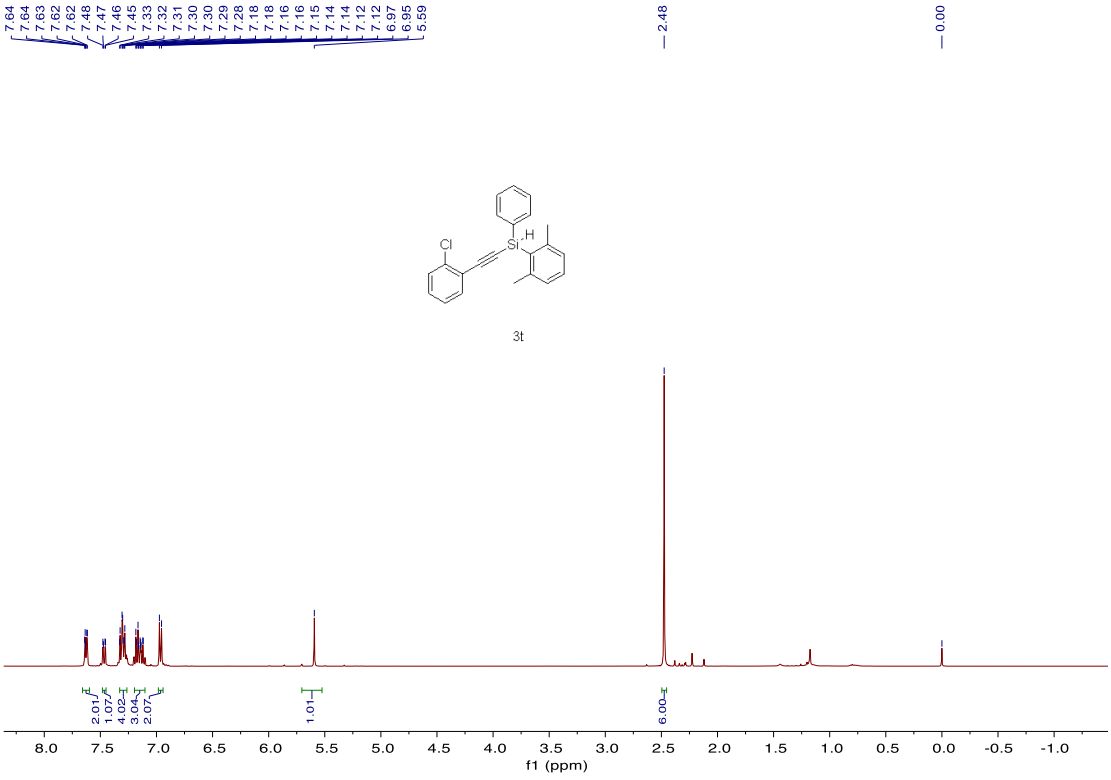
^{13}C NMR of 3s



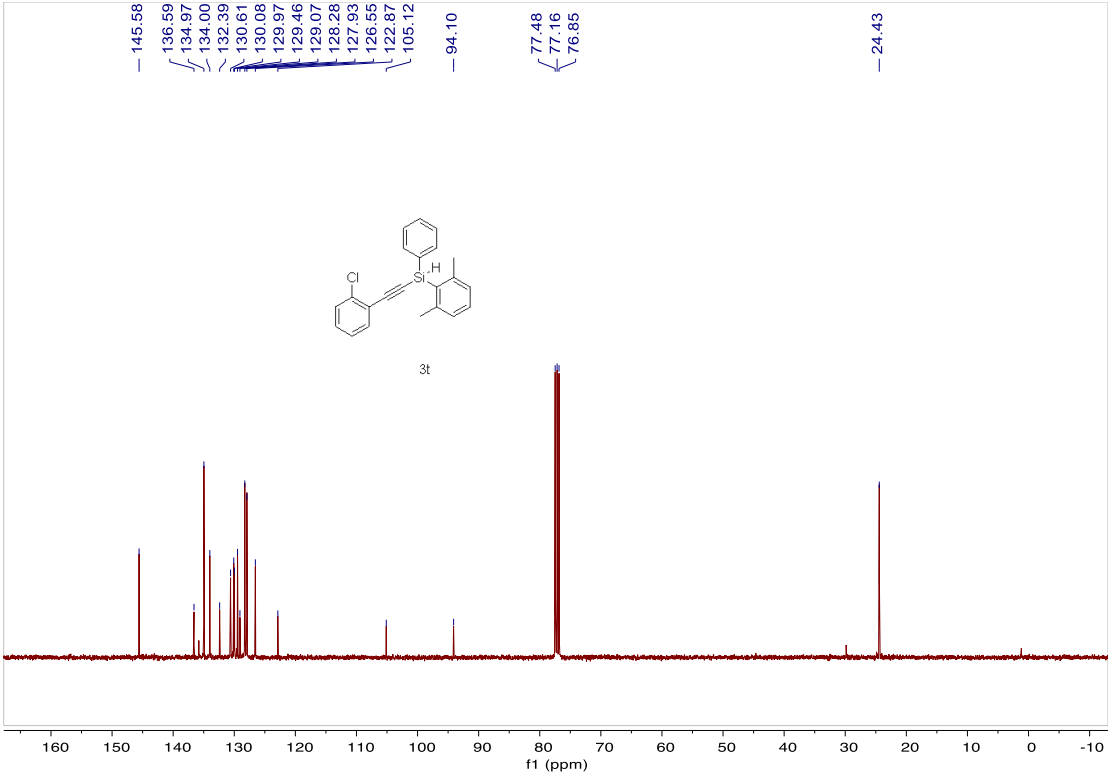
^{19}F NMR of 3s


-108.89
F
Si
H
3s
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

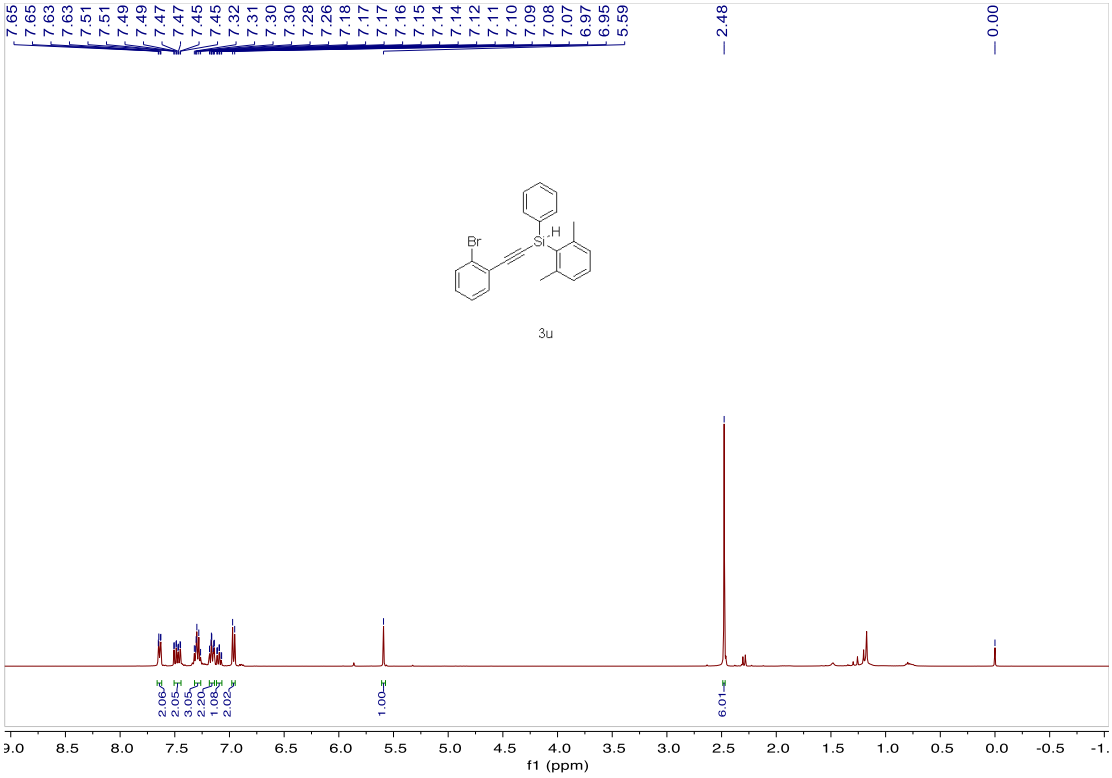
^{1}H NMR of 3t



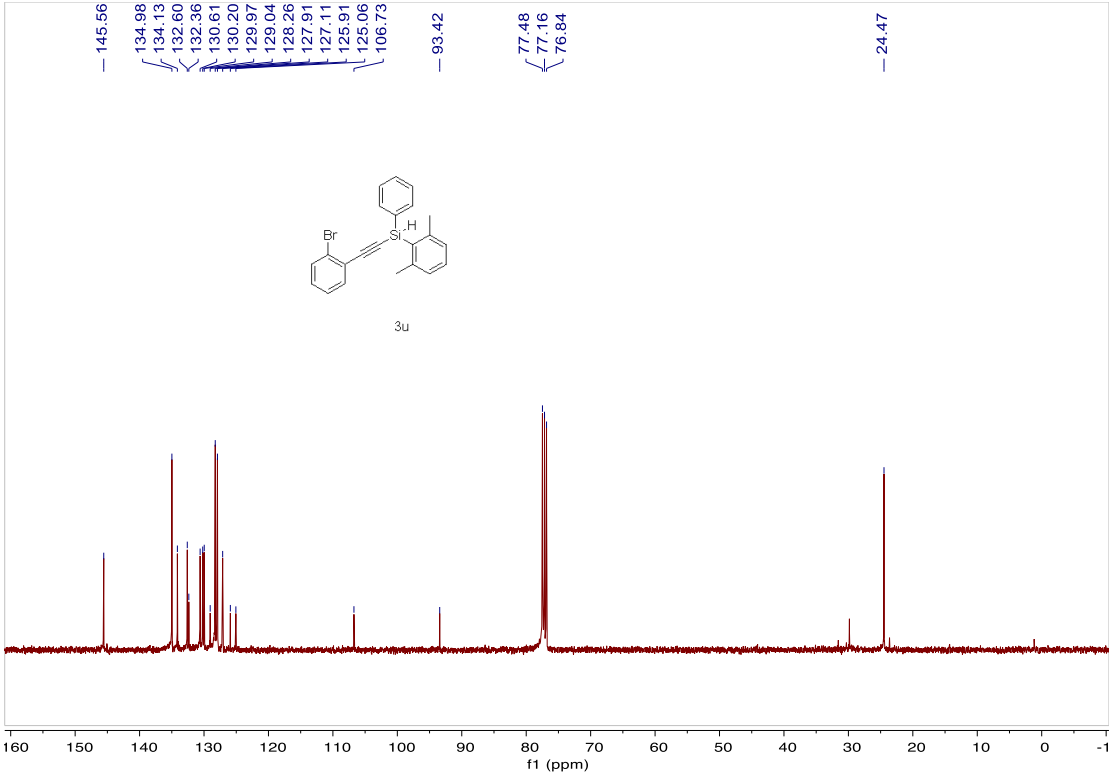
^{13}C NMR of 3t



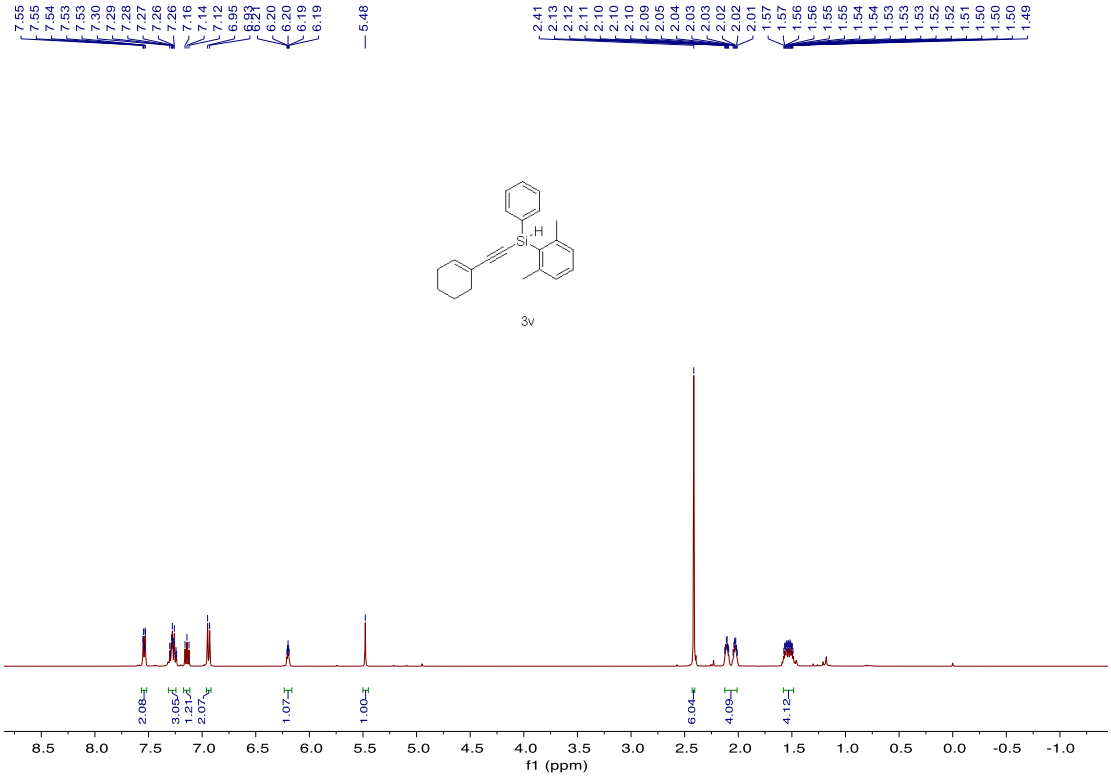
^{1}H NMR of 3u



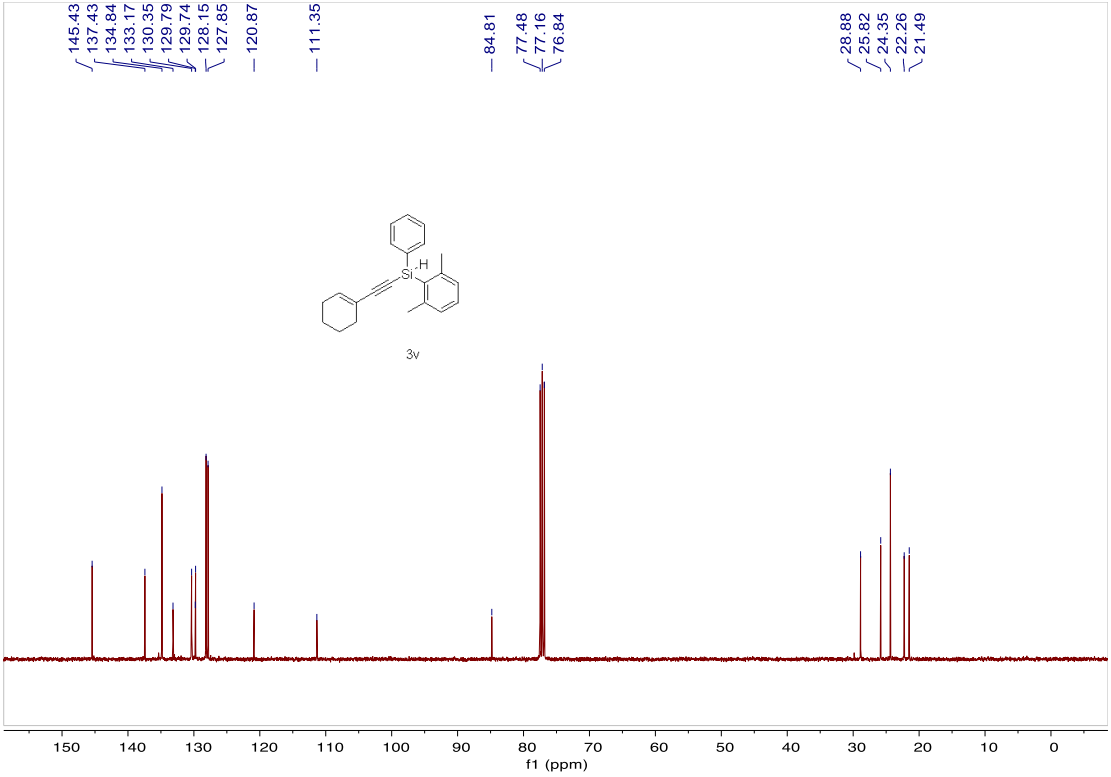
^{13}C NMR of 3u



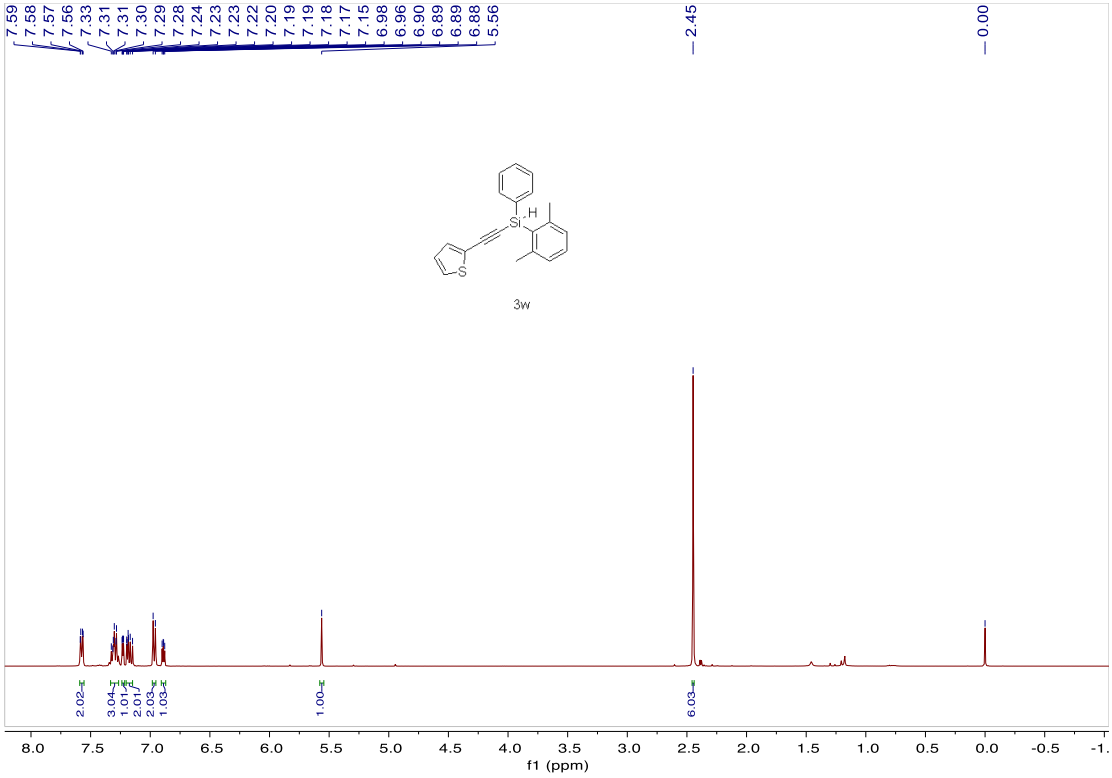
^{1}H NMR of 3v



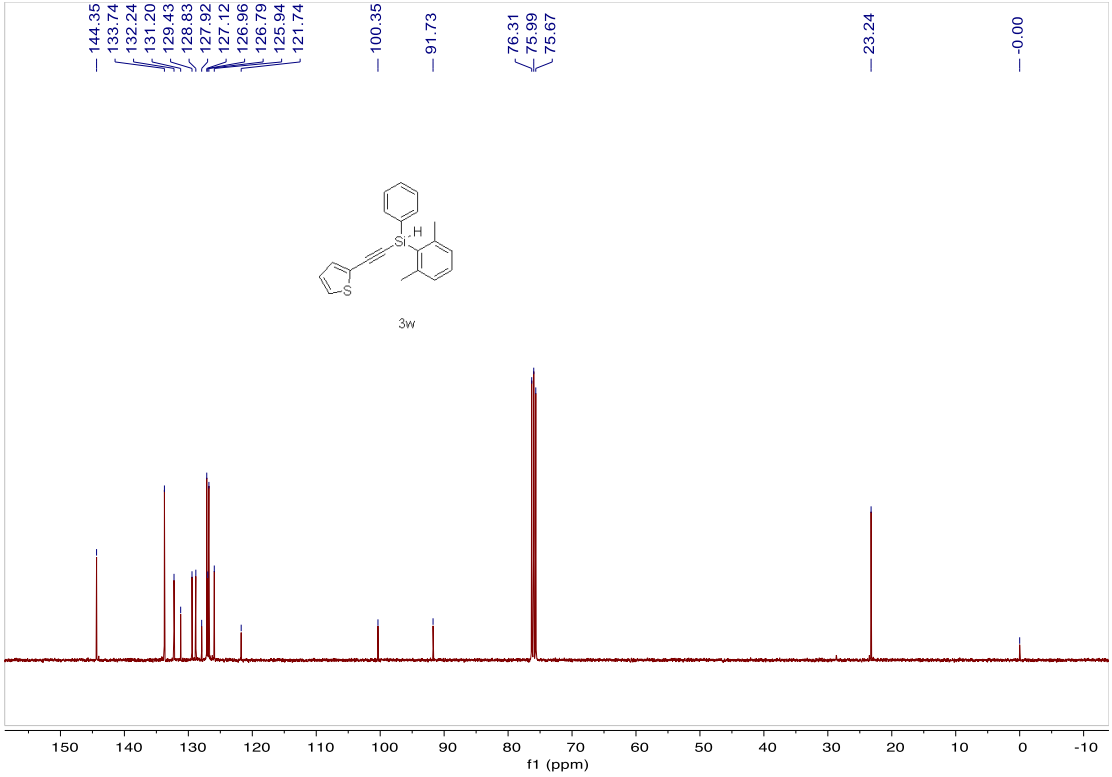
^{13}C NMR of 3v



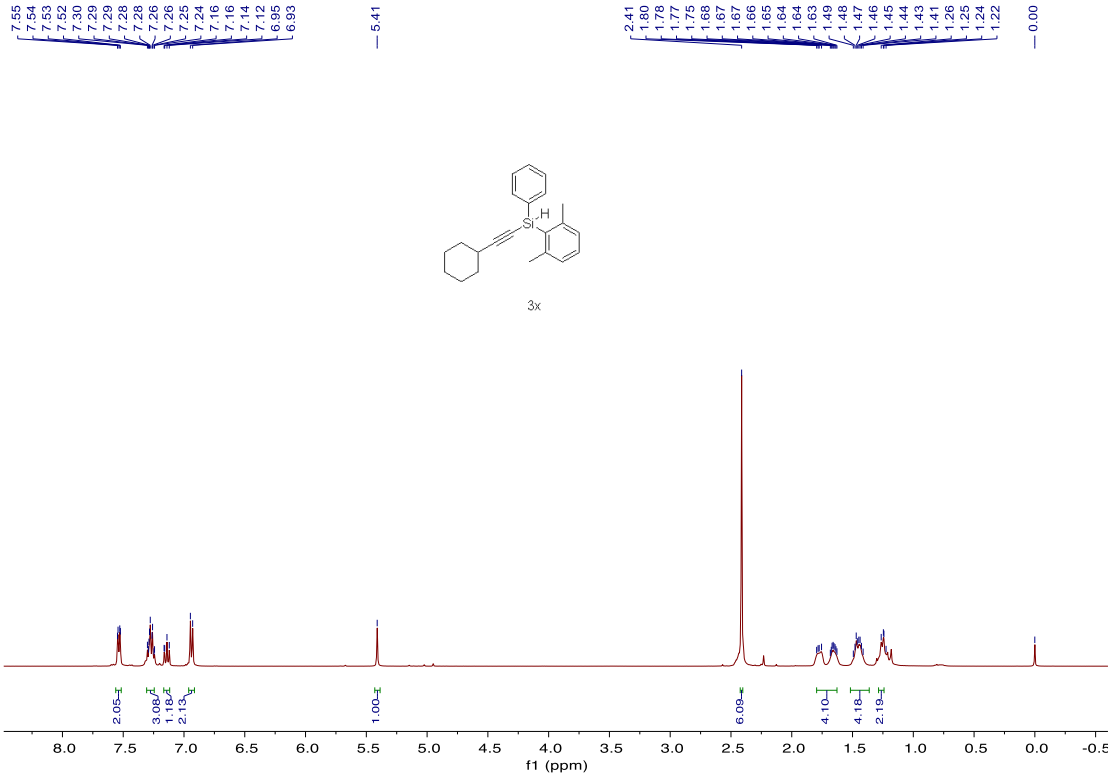
^{1}H NMR of 3w



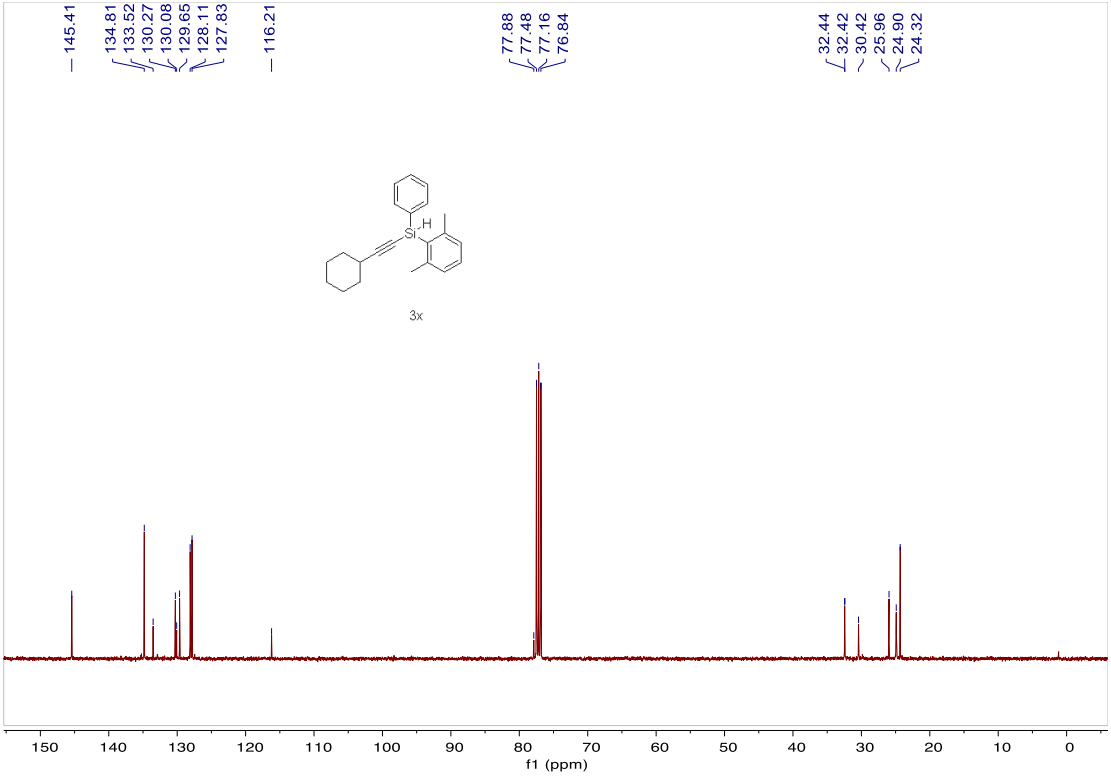
^{13}C NMR of 3w



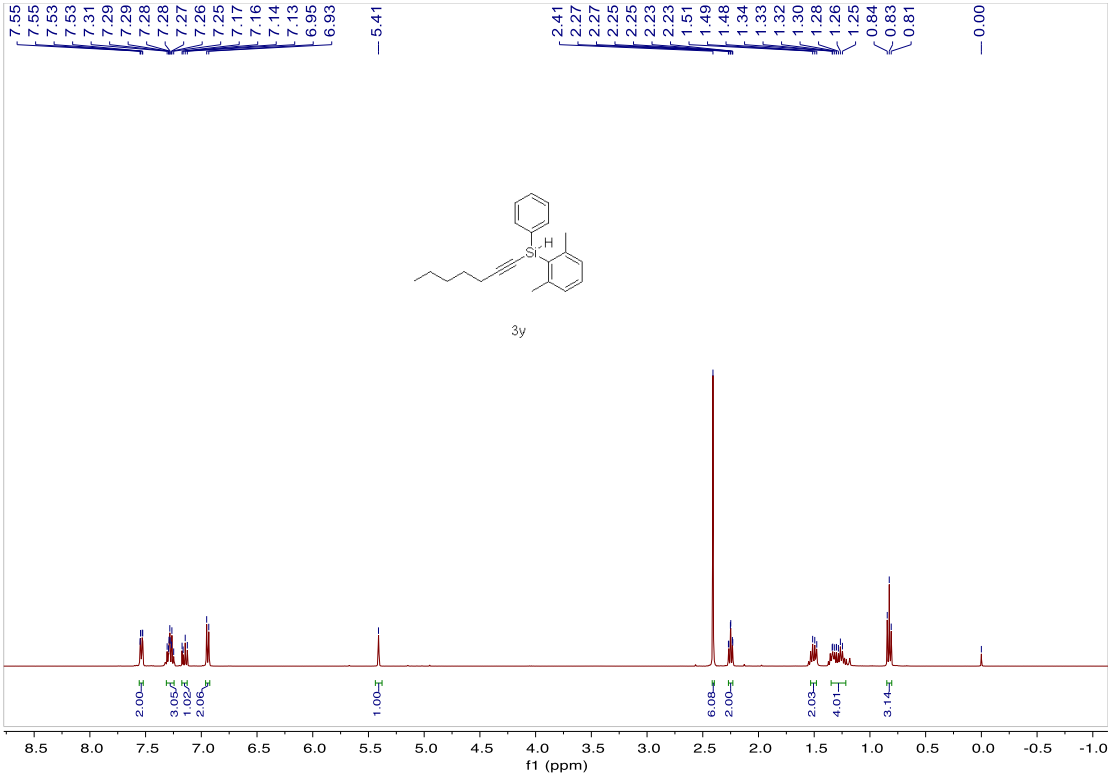
^{1}H NMR of 3x



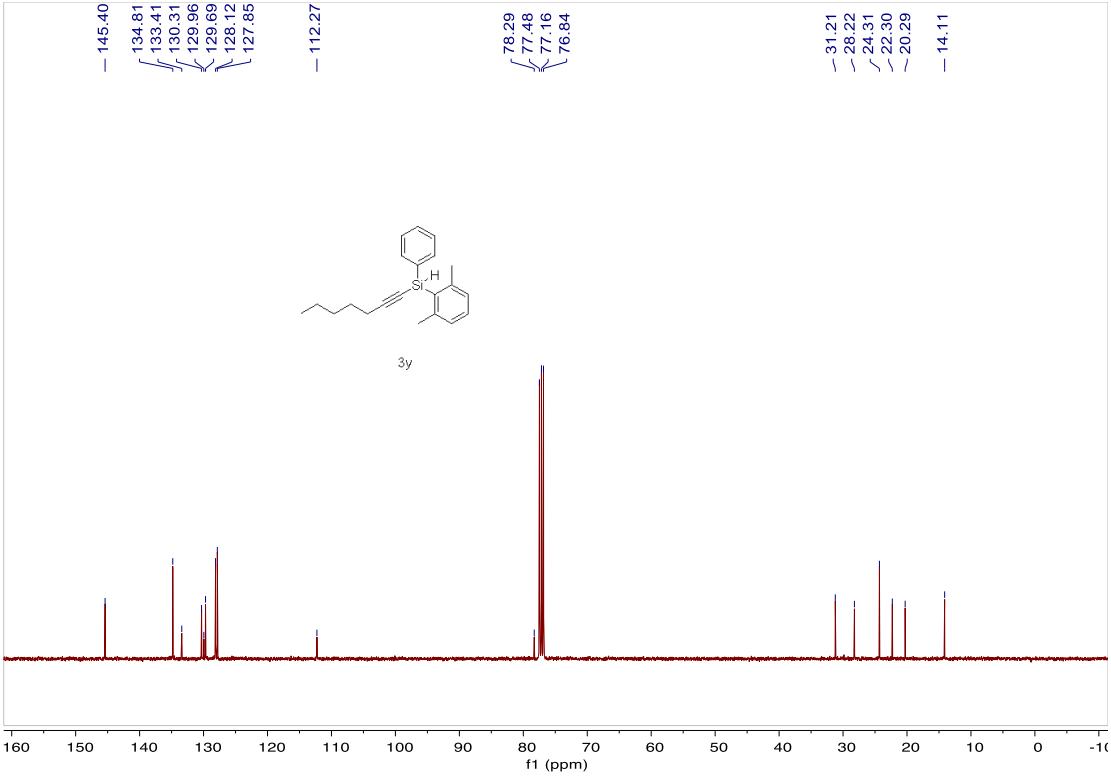
^{13}C NMR of 3x



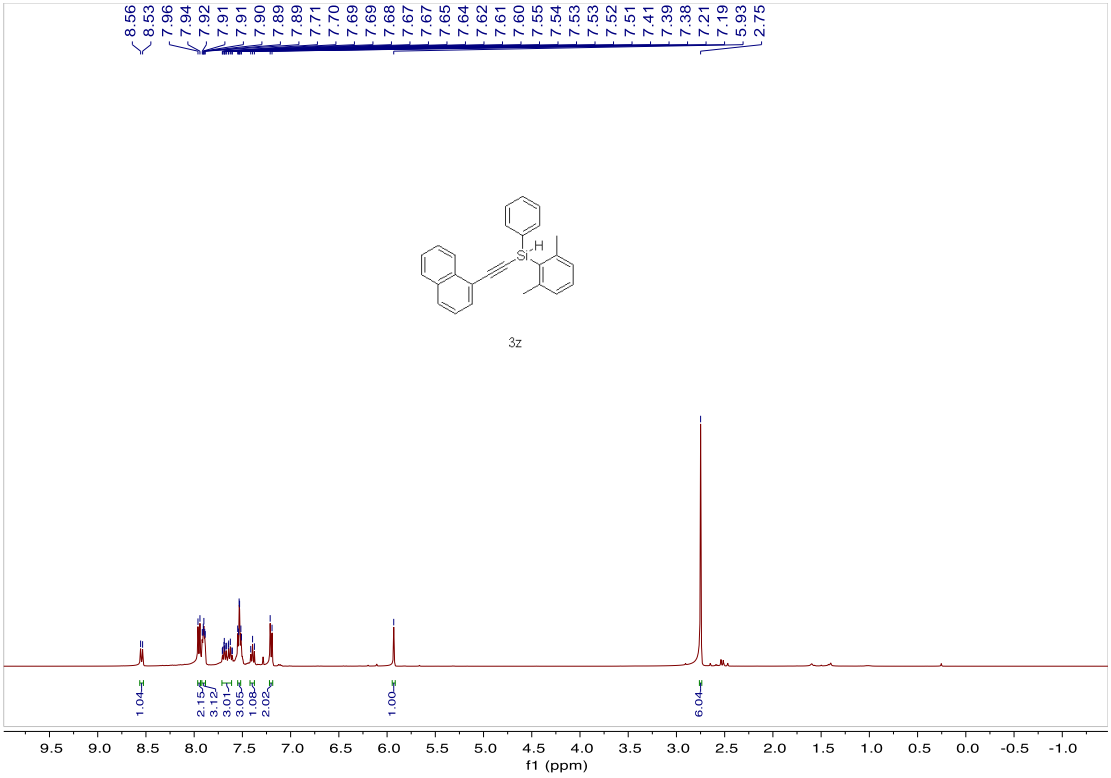
^{1}H NMR of 3y



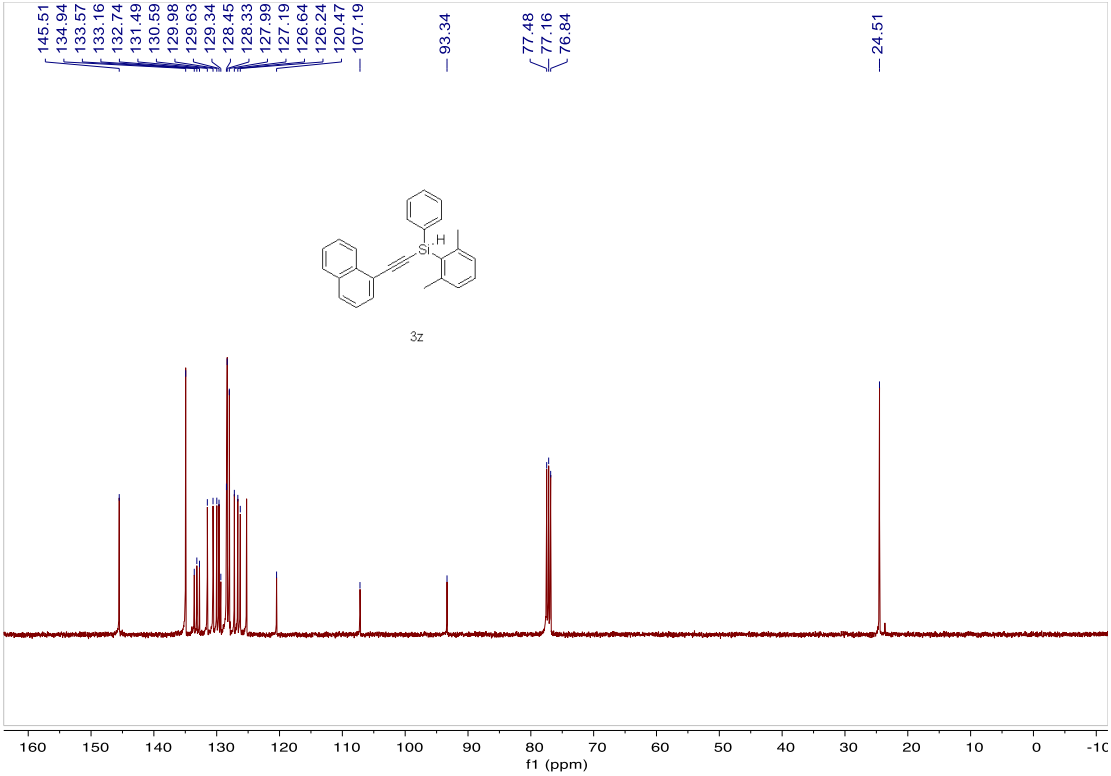
^{13}C NMR of 3y



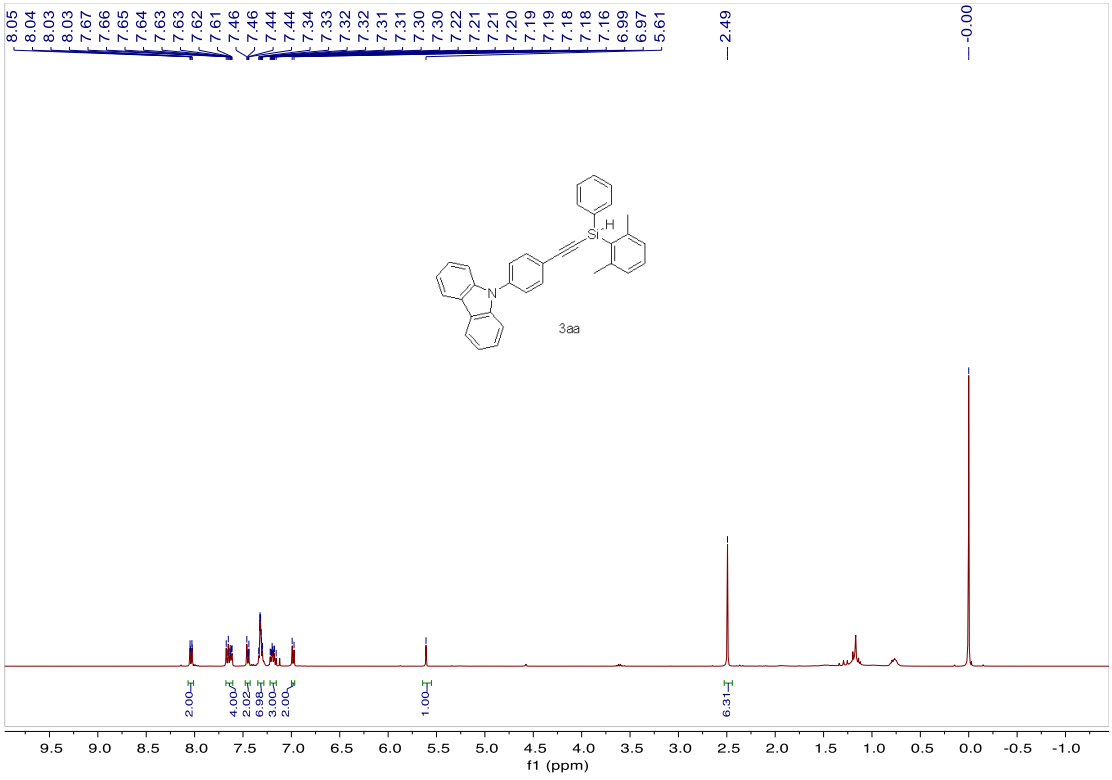
^{1}H NMR of 3z



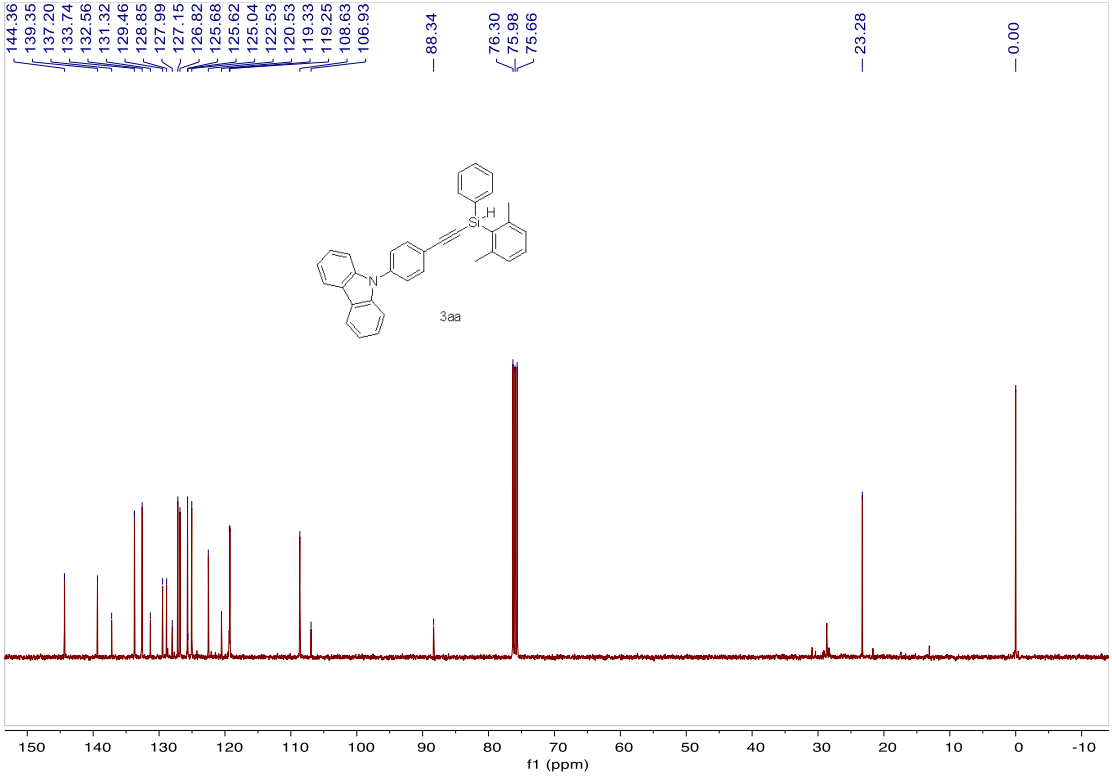
^{13}C NMR of 3z



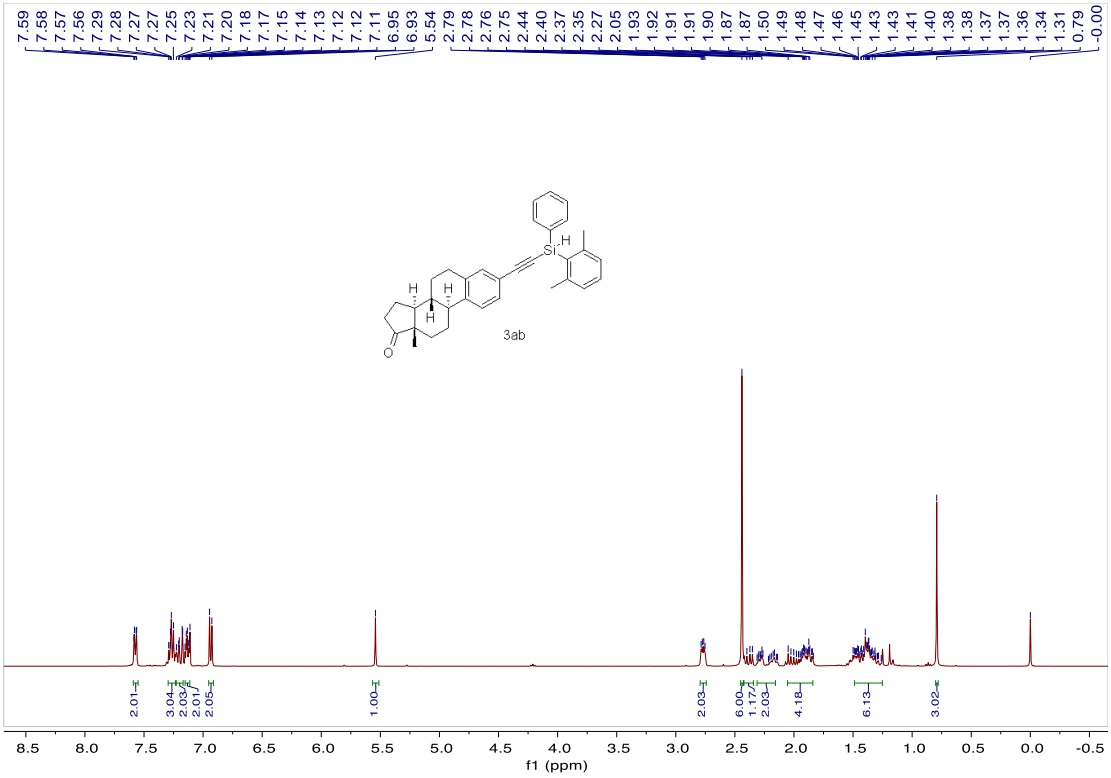
^{1}H NMR of 3aa



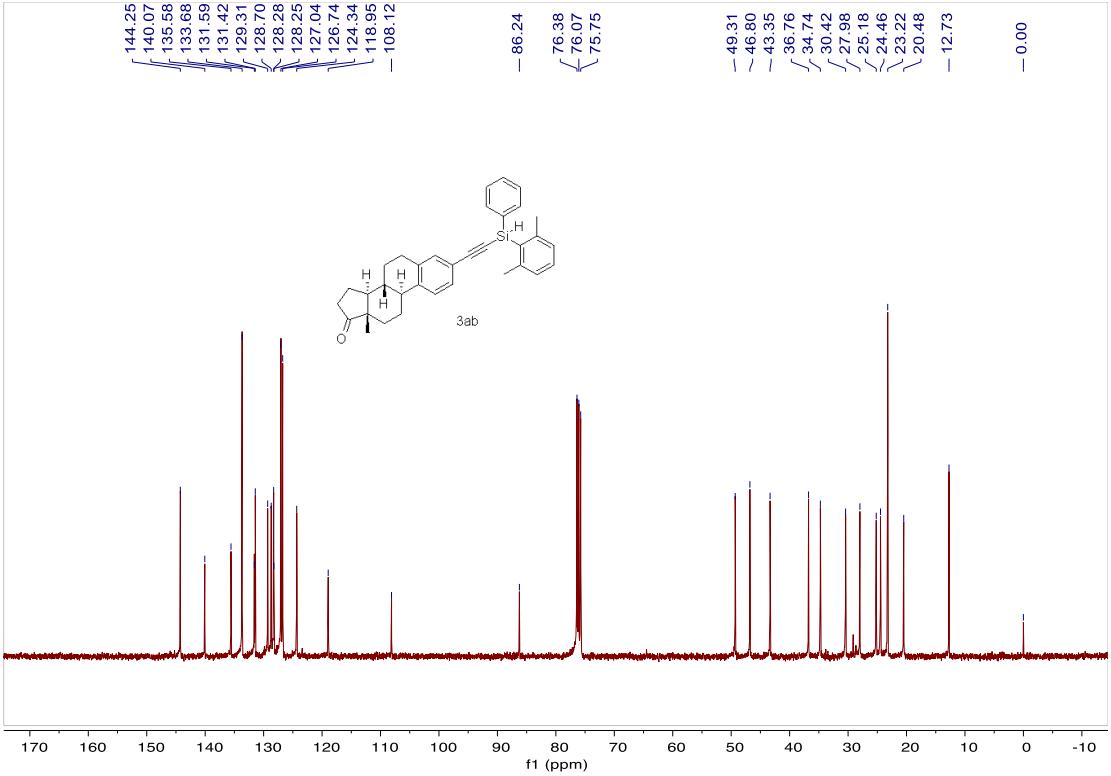
^{13}C NMR of 3aa



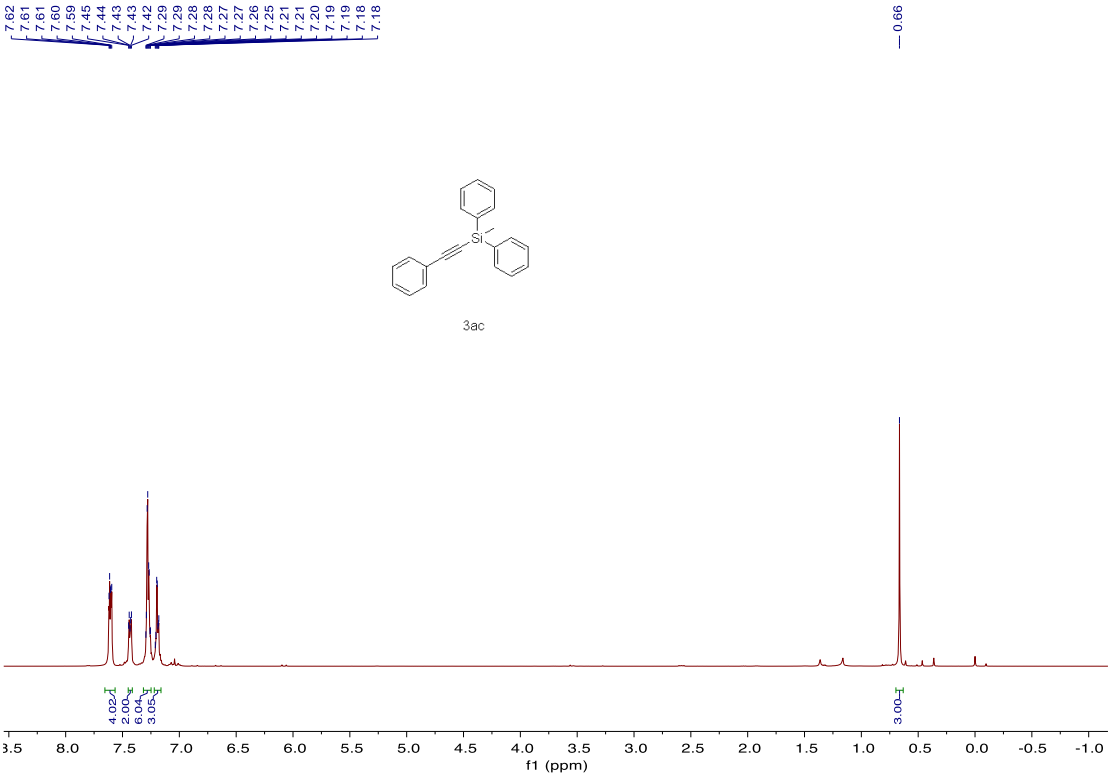
^{1}H NMR of 3ab



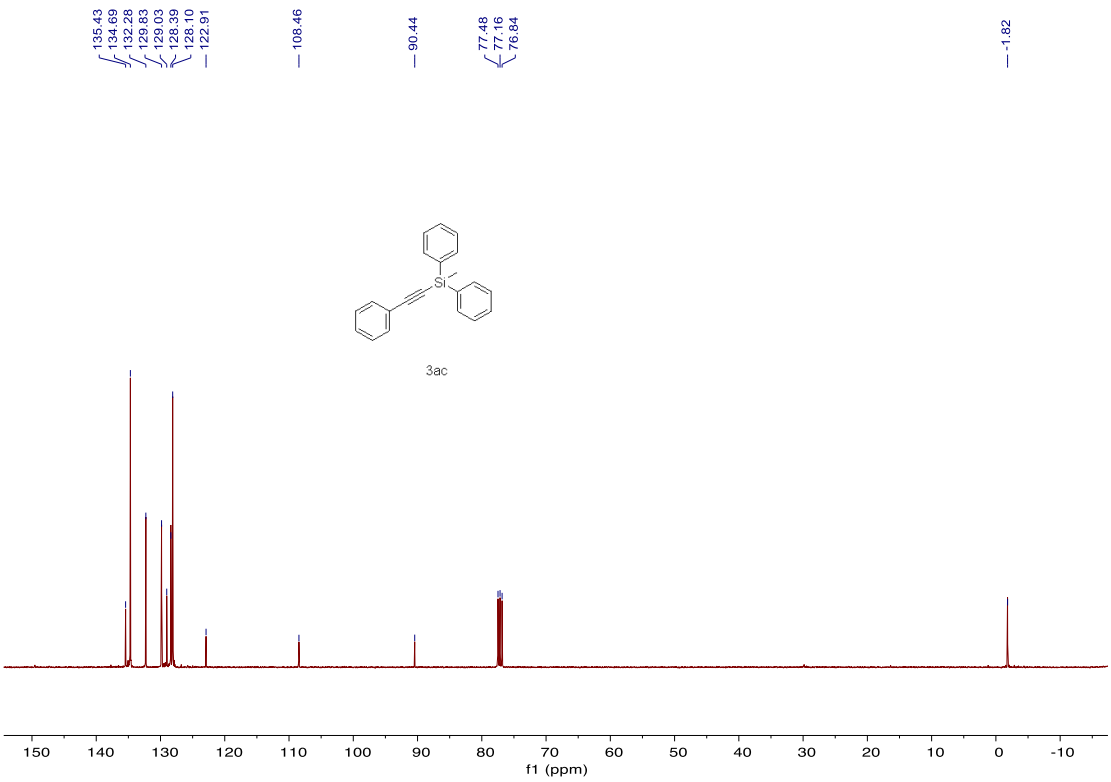
^{13}C NMR of 3ab



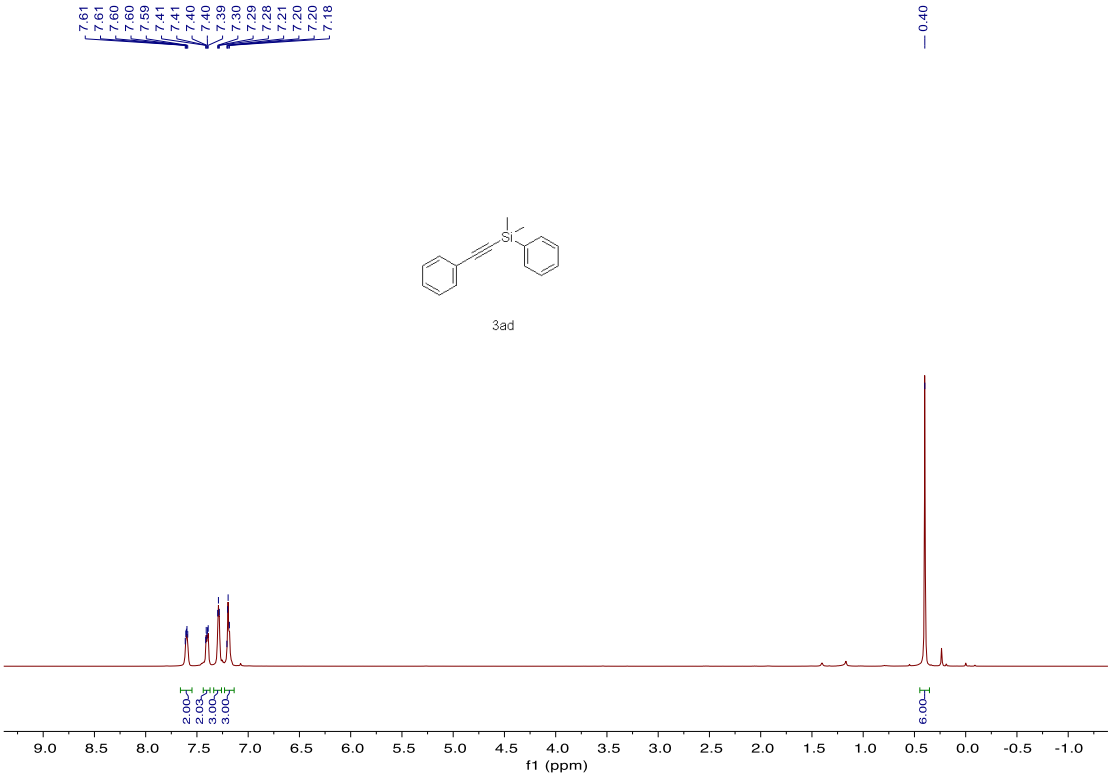
^{1}H NMR of 3ac



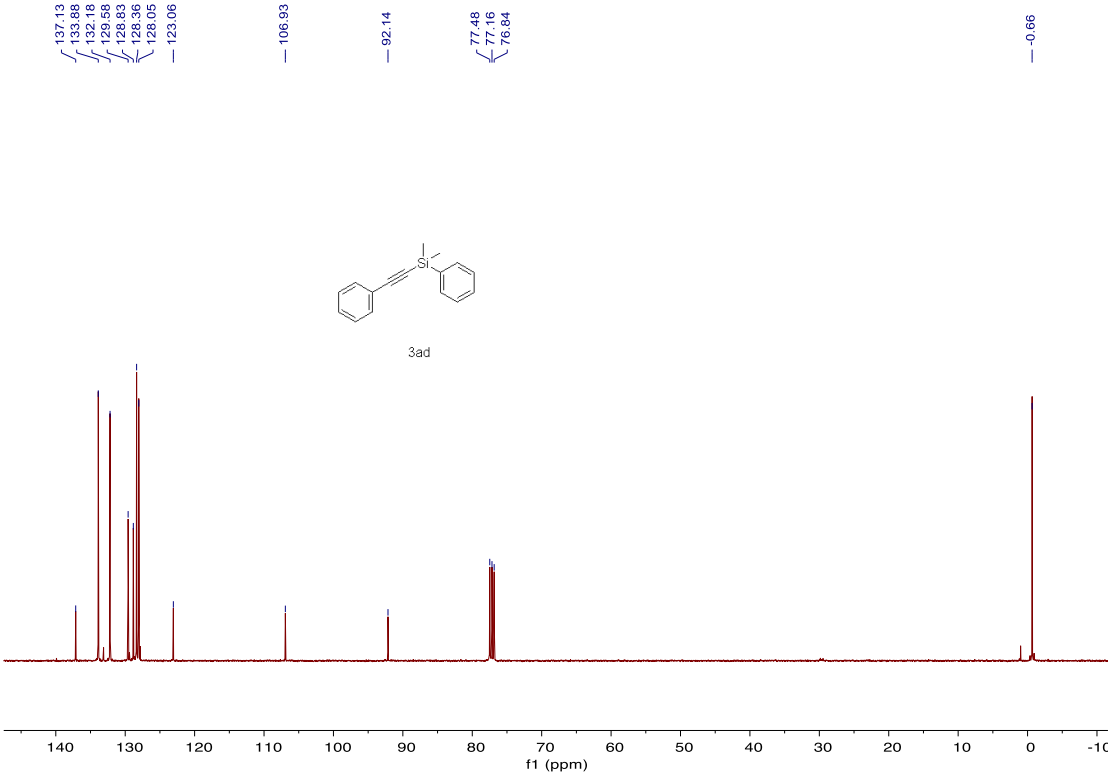
^{13}C NMR of 3ac



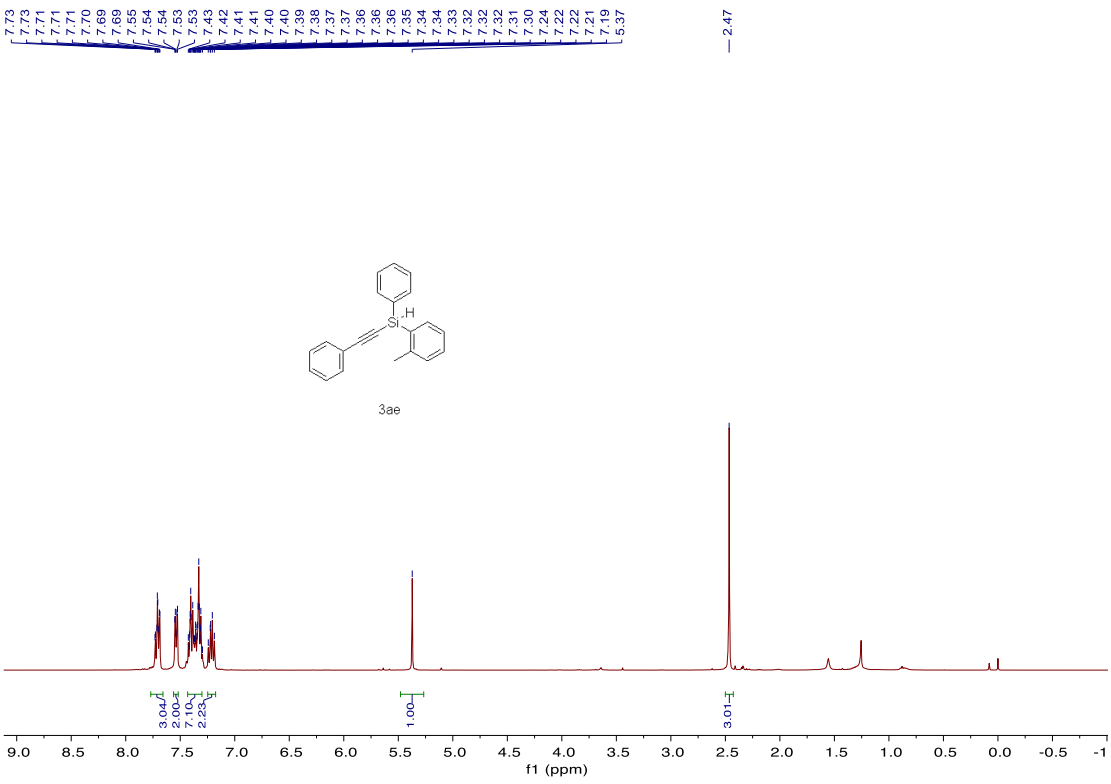
^{1}H NMR of 3ad



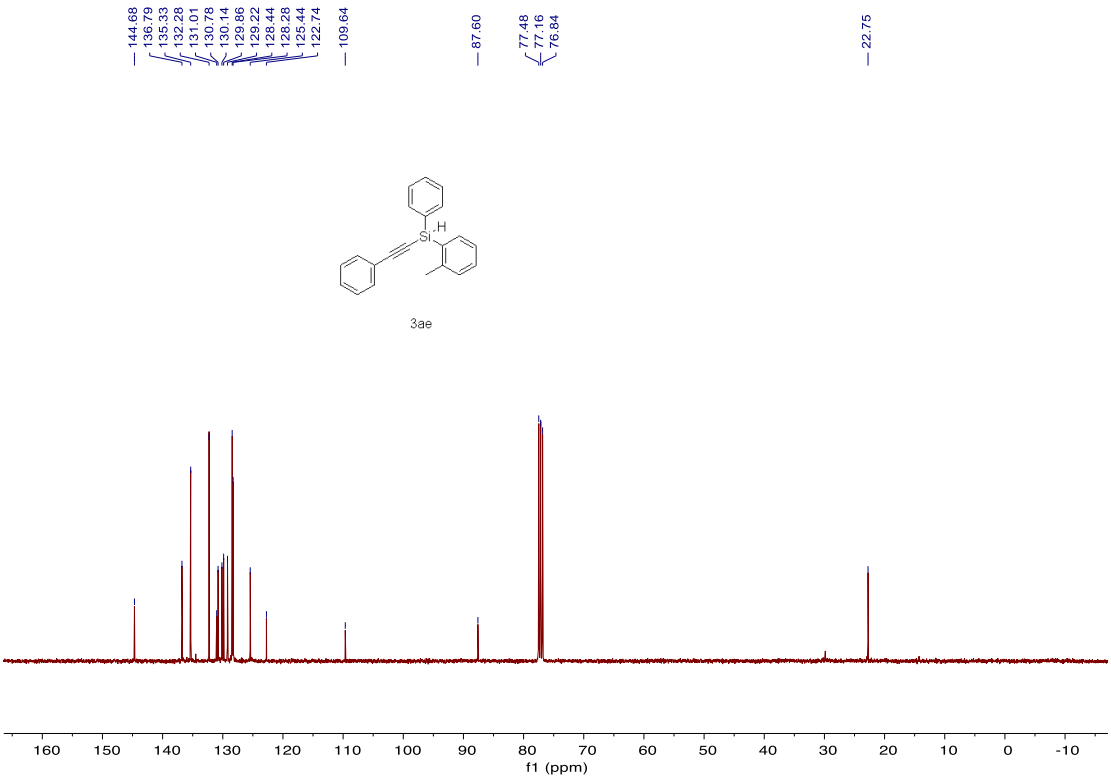
^{13}C NMR of 3ad



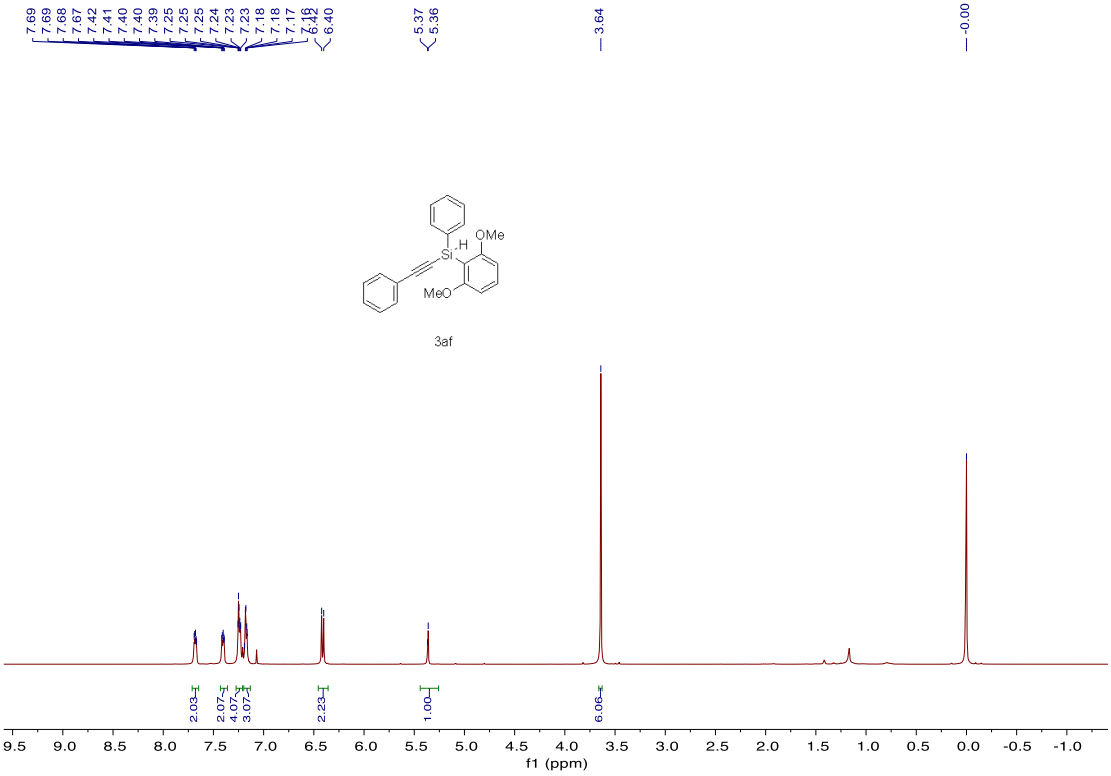
^{1}H NMR of 3ae



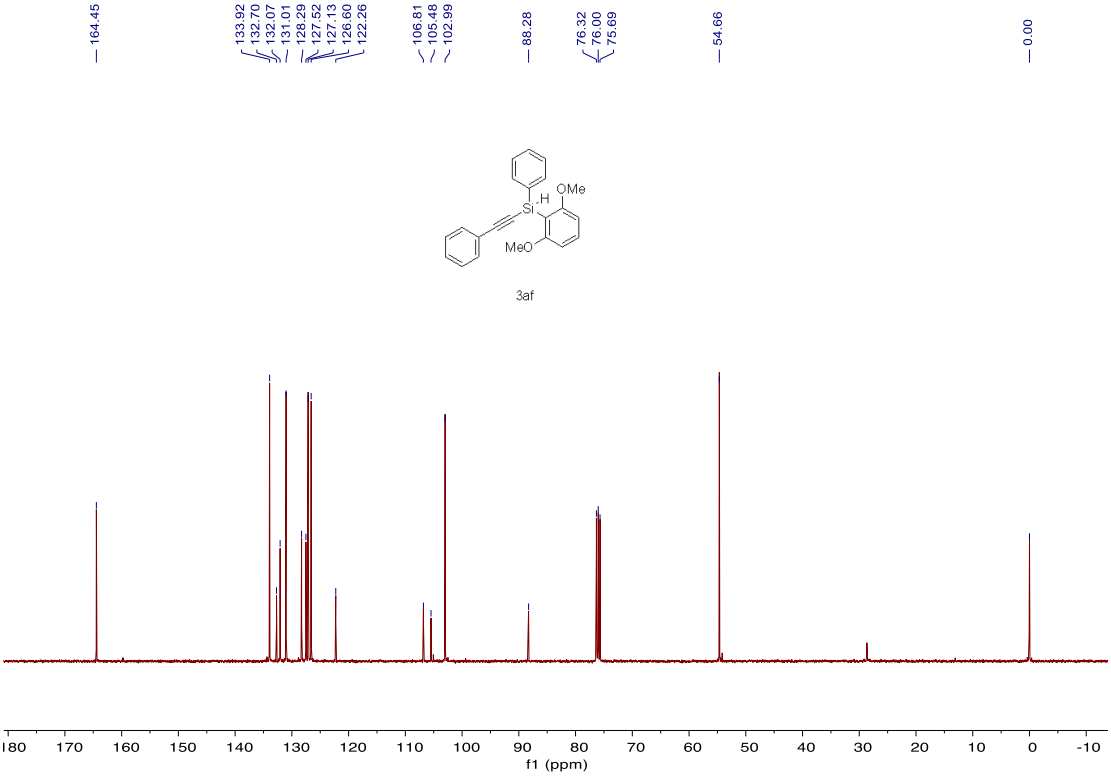
^{13}C NMR of 3ae



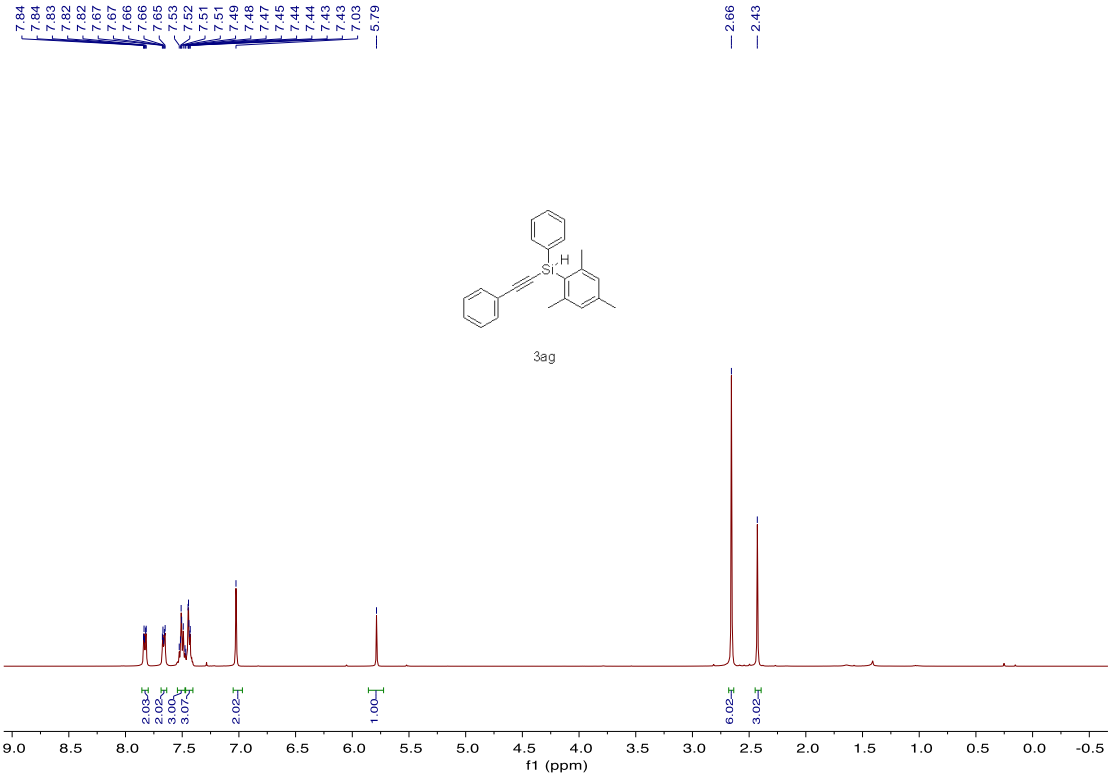
^{1}H NMR of 3af



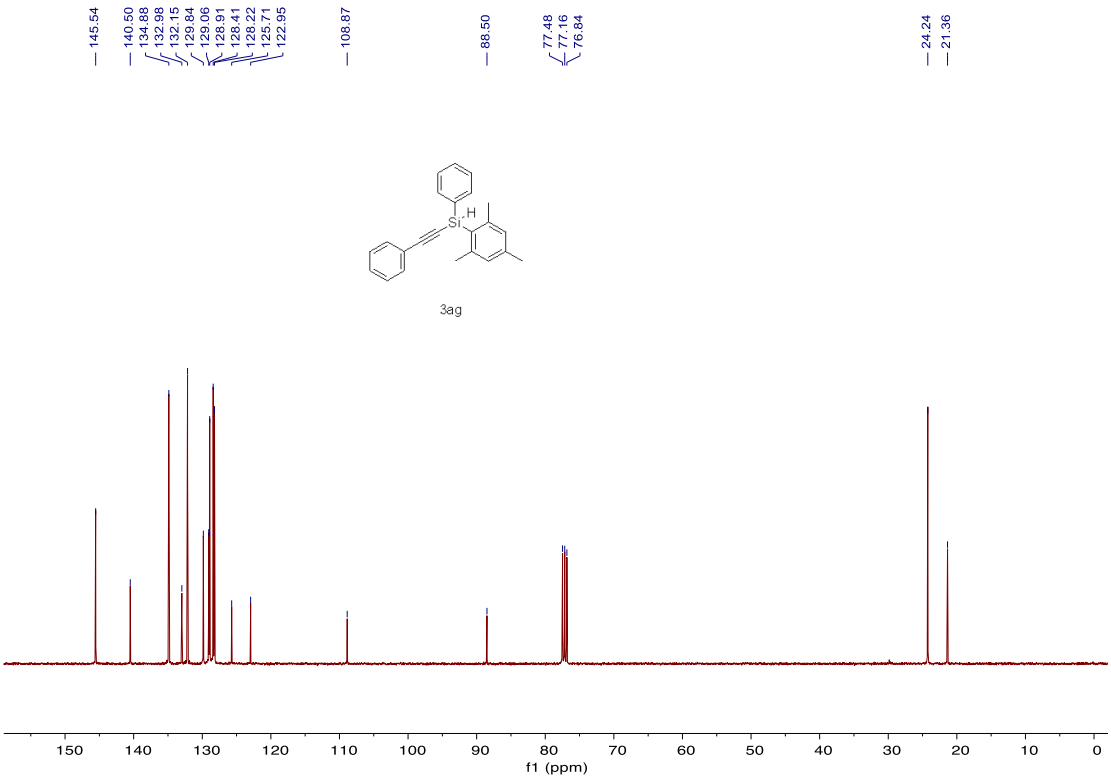
^{13}C NMR of 3af



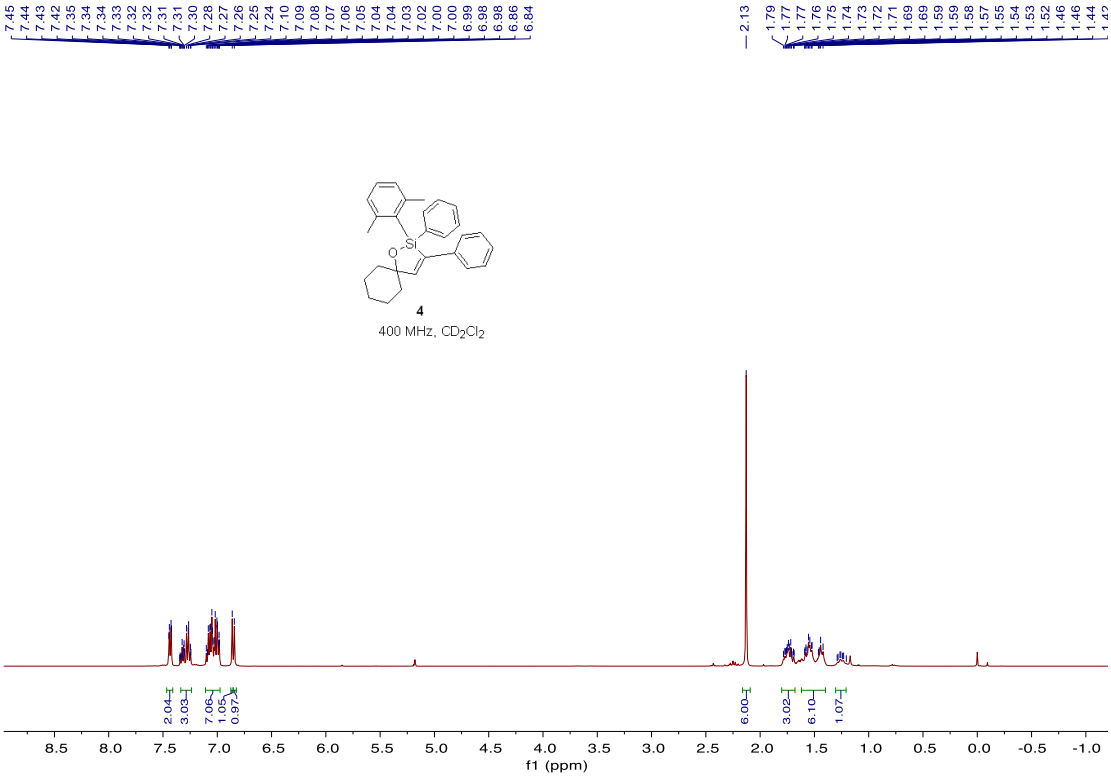
^{1}H NMR of 3ag



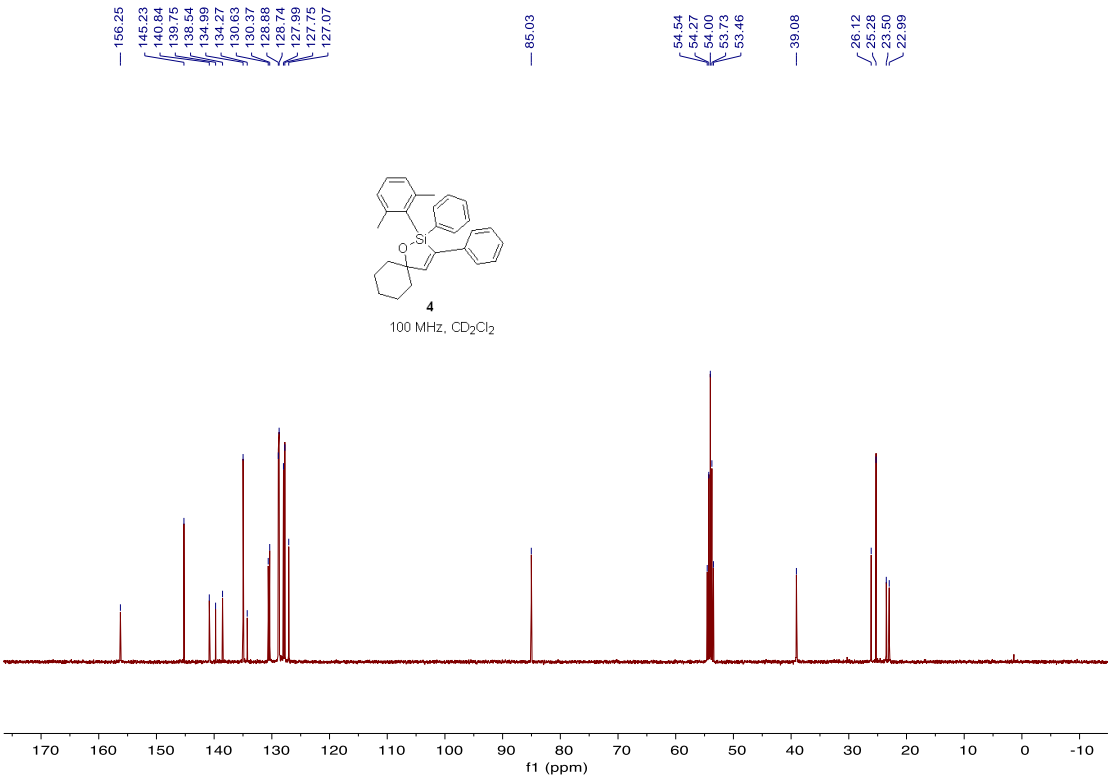
^{13}C NMR of 3ag



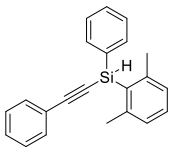
^{1}H NMR of 4



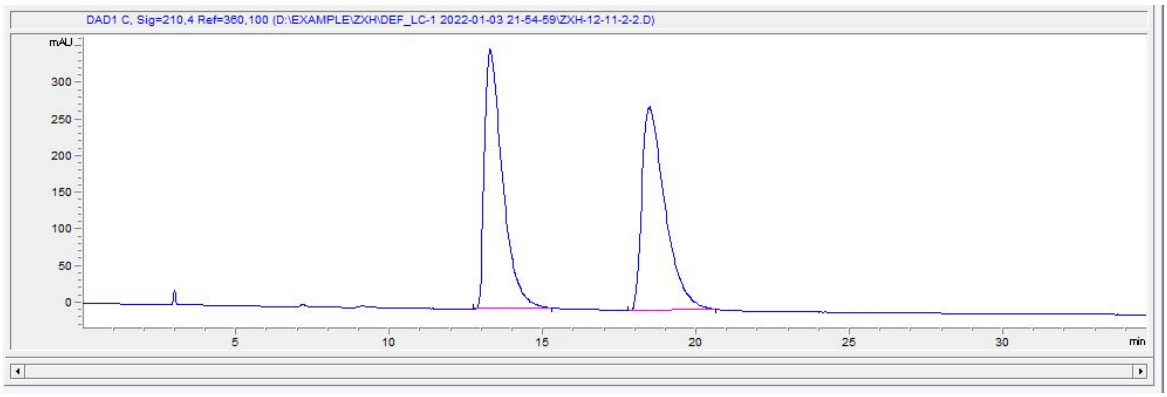
^{13}C NMR of 4



9. HPLC Spectra

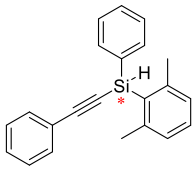


3a (race)

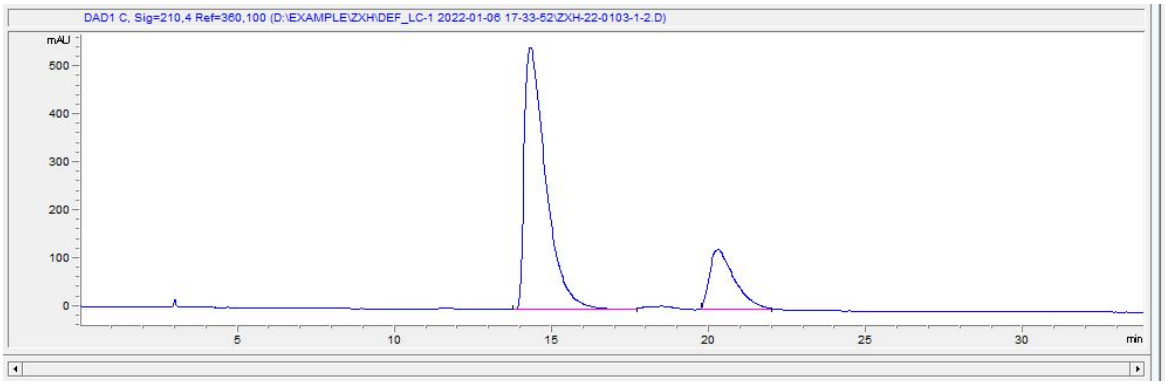


	Time/min	Area	Height	Area%
1	13.261	14548.6	354.2	50.023
2	18.459	14535.4	277.4	49.977

HPLC: optical purity = 0% ee; column: Chiralcel Pheromone, hexane/i-PrOH 100/0, 1.00 ml/min, t_1 = 13.261 min and t_2 = 18.459 min.



3a



	Time/min	Area	Height	Area%
1	14.304	26497.3	549.1	78.866
2	20.262	7100.2	126.7	21.134

HPLC: optical purity = 57% ee; column: Chiralcel Pheromone, hexane/i-PrOH 100/0, 1.00 ml/min, t_1 = 14.304 min and t_2 = 20.262 min.