Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regio- and Stereoselective Cobalt-Catalyzed Hydrosilylation of 1,3-Diynes with Primary and Secondary Silanes

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1. X-ray analysis of Co-5

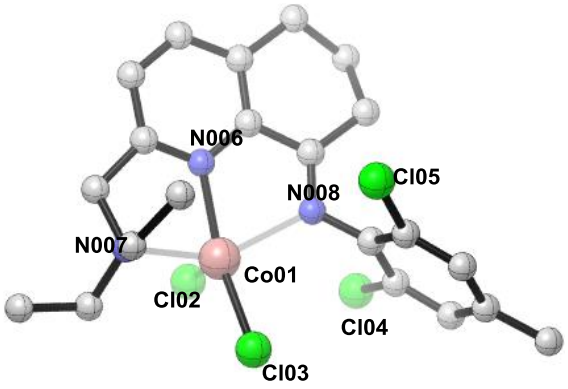


Figure S1. Solid structure of complex **Co-5**. Hydrogen atoms were emitted for clarity.

Table S1. Crystal data and structure refinement for Complex **Co-5.**

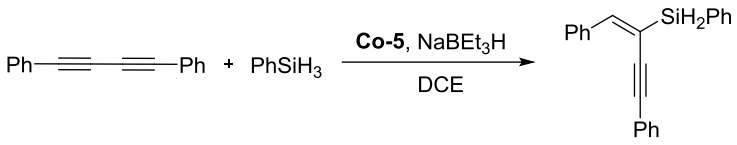
Identification code	LLL01
Empirical formula	$C_{21}H_{25}Cl_4CoN_3$
Formula weight	520.17
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.1201(4)
b/Å	12.8517(3)
c/Å	14.6087(4)
α/°	90
β/°	106.5640(10)
γ/°	90
Volume/Å^3	2540.99(12)
Z	4
ρ_{calc}g/cm^3	1.360
μ/mm^{-1}	9.254
F(000)	1068.0
Crystal size/mm3	0.2 ×0.2 ×0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	9.34 to 129.992
Index ranges	-16 ≤ h ≤ 16, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17

Reflections collected	46749
Independent reflections	4292 [R_{int} = 0.0607, R_{sigma} = 0.0289]
Data/restraints/parameters	4292/0/265
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0794
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.24

Table S2. Bond lengths [Å] and angles [°] for **Ni1**.

selected bond lengths [Å]		selected angles [°]	
Co(1)−Cl(2)	2.3233(6)	Cl(3)−Co(1)−Cl(2)	109.71(2)
Co(1)−Cl(3)	2.2730(6)	N(6)−Co(1)−N(7)	76.66(6)
Co(1)−N(6)	2.0597(17)	N(6)−Co(1)−N(8)	73.99(6)
Co(1)−N(7)	2.2138(17)	N(7)−Co(1)−Cl(2)	99.71(5)
Co(1)−N(8)	2.2146(17)	N(7)−Co(1)−Cl(3)	99.18(5)
		N(7)−Co(1)−N(8)	139.48(6)
		N(8)−Co(1)−Cl(2)	110.03(5)
		N(8)−Co(1)−Cl(3)	96.05(5)

2. Optimizations for the Hydrosilylation of 1,3-Diynes

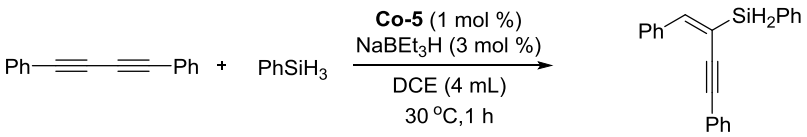


2a

Entry	Temp. (°C)	**Cat.** (mol%)	Time (min)	Solvent (mL)	Yield (%)[b]
1	0	**Co-5** (2)	25	DCE (1)	51
2	10	**Co-5** (2)	25	DCE (1)	58
3	20	**Co-5** (2)	25	DCE (1)	72
4	30	**Co-5** (2)	25	DCE (1)	84
5	40	**Co-5** (2)	25	DCE (1)	81
6	30	**Co-5** (0.1)	25	DCE (1)	-
7	30	**Co-5** (0.5)	25	DCE (1)	64
8	30	**Co-5** (1)	25	DCE (1)	82
9	30	**Co-5** (2)	25	DCE (1)	84
10	30	**Co-5** (1)	15	DCE (1)	62
11	30	**Co-5** (1)	25	DCE (1)	82
12	30	**Co-5** (1)	30	DCE (1)	87
13	30	**Co-5** (1)	40	DCE (1)	84
14	30	**Co-5** (1)	30	/	80
15	30	**Co-5** (1)	30	DCE (0.3)	89
16	**30**	**Co-5** (1)	**30**	**DCE (0.5)**	**91**
17	30	**Co-5** (1)	30	DCE (0.7)	88
18	30	**Co-5** (1)	30	DCE (1)	87

[a]Reaction conditions: 1,4-diphenylbuta-1,3-diyne (101 mg, 0.5 mmol), $PhSiH_3$ (162 mg, 3.0 eq.), Cat. (x mol%), $NaBEt_3H$ (3x mol%). [b]Yield of **2a** was determined by GC analysis with *N*-dodecane as internal standard.

3. Procedure for gram scale reaction

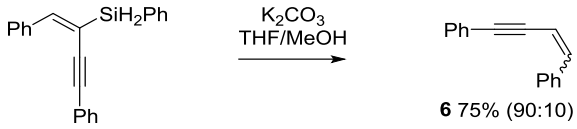


2a Yield: 85% (92:8)

To a Young tube, was charged with **Co-5** (20.8 mg, 0.04 mmol), **1a** (808 mg, 4 mmol), DCE (4.0 mL) and $PhSiH_3$ (1.30 g, 12 mmol). After stirring the resultant mixture for 30 s, $NaHBEt_3$ (120 μL, 0.12 mmol) was added to the tube. The mixture was stirred at 30 ^oC for 1 h. The residue was then purified by flash column chromatography using petroleum ether as eluent to afford **2a** (1.03 g, 85%) as a colorless oil.

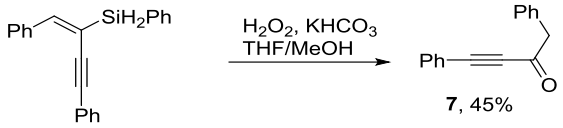
4. Derivations of the hydrosilylation product.

4.1 Desilylation of 2a.



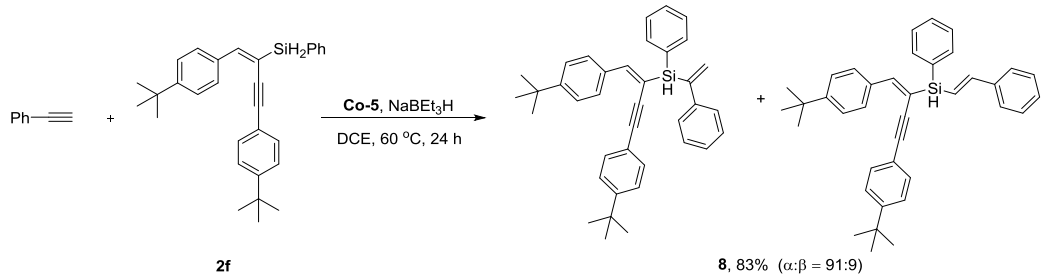
To a tube with 0.5 mL of THF and 0.5 mL of MeOH was added **2a** (62 mg, 0.2 mmol) and K_2CO_3 (55 mg, 0.4 mmol). The mixture was stirred at room temperature for 12 hours. The solution was concentrated under vacuum and the crude product was purified by flash column chromatography using petroleum ether as eluents yielding **6** (30 mg, Yield: 75%) as a colorless oil.

4.2 Oxidation of 2a.

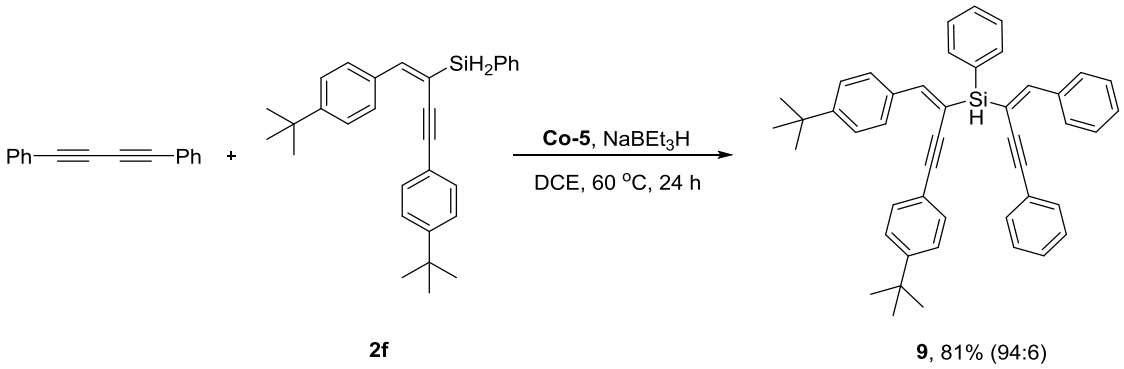


To a tube with 0.5 mL of THF and 0.5 mL of MeOH was added **2a** (155 mg, 0.5 mmol), 30% H_2O_2 aqua. (0.9 mL, 3 mmol,) and $KHCO_3$ (50 mg, 0.5 mmol). The mixture was stirred at room temperature for 15 hours. Then, anhydrous $Na_2S_2O_3$ (0.52 g) was added to quench the excess oxidant. Extracted the mixture with ethyl acetate, dried over sodium sulfate, filtered and concentrated under vacuum. The residue was purified by flash column chromatography using petroleum ether and ethyl acetate (30:1) as eluents to afford **7** (50 mg ,45%) as a yellow oil.

4.3 Second hydrosilylation of 2f.



To a Young tube, was added **Co-5** (6.3 mg, 0.012 mol, 4 mol%), **2f** (127 mg, 0.3 mmol), DCE (0.3 mL) and phenylacetylene (40 mg, 0.39 mmol). After stirring the mixture for 30 s, $NaHBEt_3$ (36 μL, 1.0 mol/L, 0.036 mmol) was added to the tube. The resulted mixture was stirred at 60 °C for 24 h. Then, the reaction temperature was allowed to cool to room temperature and the solvent was removed by vacuum and the crude mixture was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to give the corresponding product **8** as a yellow oil. (130 mg, 83% yield).

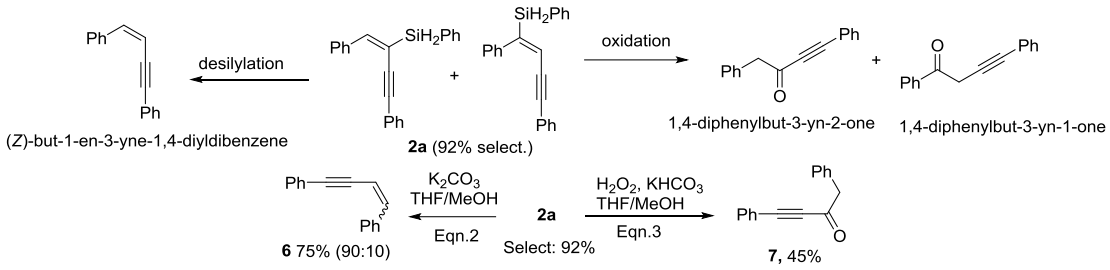


To a Young tube, was added **Co-5** (6.3 mg, 0.012 mol), **2f** (127 mg, 0.3 mmol), **2a** (79 mg, 0.39 mmol), DCE (0.3 mL). After stirring the mixture for 30 s, $NaHBEt_3$ (36 μL, 0.036 mmol, 1.0 mol/L) was added to the tube. The resulted mixture was stirred at 60 °C for 24 h. Then, the reaction temperature was allowed to cool to room temperature and the solvent was removed by vacuum and the crude mixture was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to give the corresponding product **9** as a white solid. (151 mg, 81% yield).

5. The analysis of the major side-product.

The major by-product was assigned as *trans* 1,2-addition product because of the following reasons:

(1) As the following scheme shown, if the by-product was *cis* 2,1-addition outcome, desilylation of the mixiture should only deliver (*Z*)-but-1-en-3-yne-1,4-diyldibenzene. And the oxidation of **2a** will produce both 1,4-diphenylbut-3-yn-2-one and 1,4-diphenylbut-3-yn-1-one. However, actually for the derivation of **2a** (select. 92%), we found that the desilylation of **2a** under K_2CO_3/MeOH gave 1,3-enyne **6** in 75% yield (*Z*:*E* = 90:10) (eqn. 2). Moreover, the oxidation of **2a** with hydrogen peroxide under basic condition only afforded 1,4-diphenylbut-3-yn-2-one **7** in 45% yield (eqn. 3). The results were listed in Scheme 2 in the manuscript.



(2) With **2i** (81% select.) as the model compound, ^{1}H-^{1}H correlations and 2D NOESY NMR detection was performed. The spectra was shown below. If the side reaction was *cis*-2,1-addition, **2i'-*Z*** was the major side product. And the contact between H^3 and H^4 should be clearly observed from 2D NOESY NMR analysis. However, the Figures S3 indicated a contact between H^1 and H^2, but the contact of H^3 and H^4 was not observed. Therefore, we proposed that **2i-*E*** was the major side product.

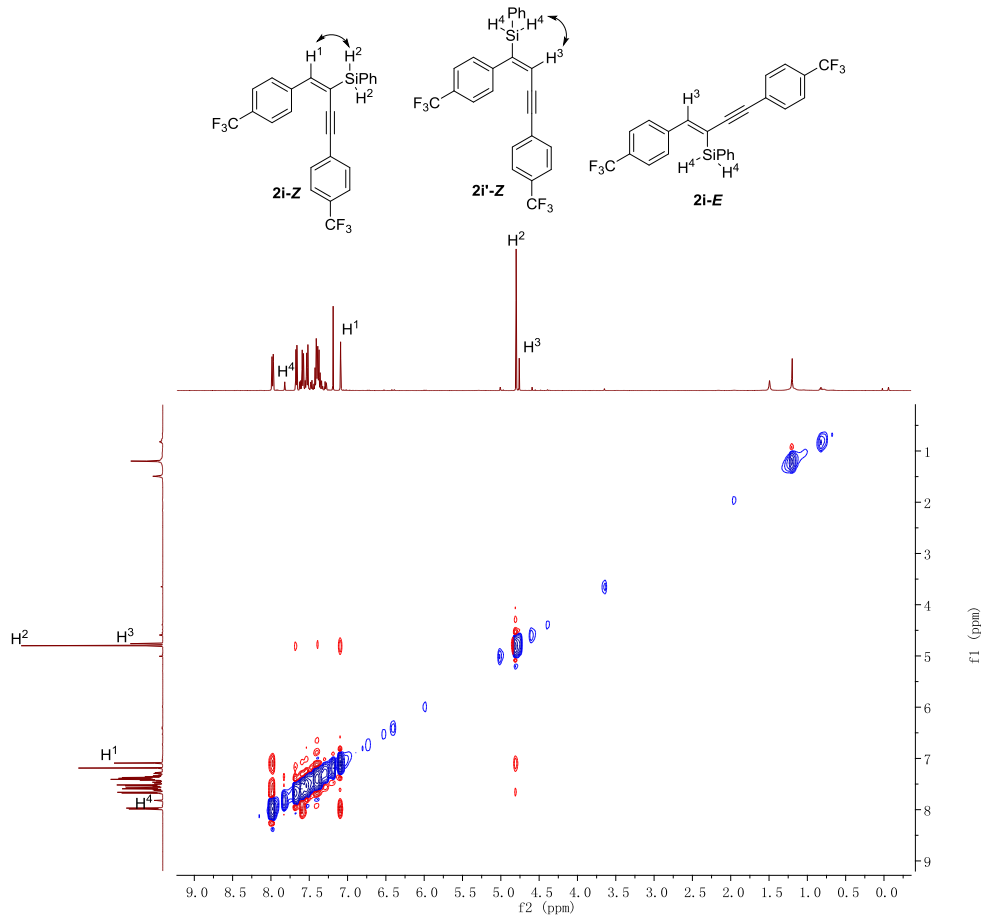


Figure S2. ^{1}H-^{1}H correlations and 2D NOESY NMR of **2i**.

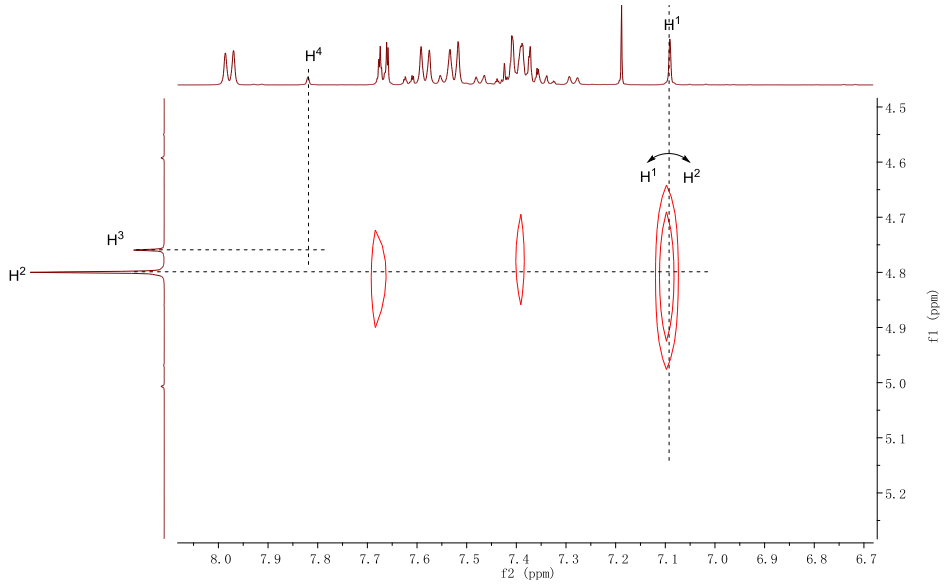
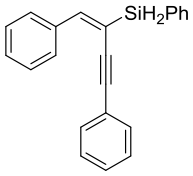
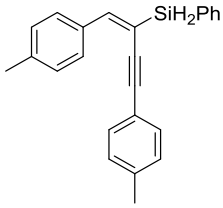


Figure S3. ^{1}H-^{1}H correlations and 2D NOESY NMR of **2i.**

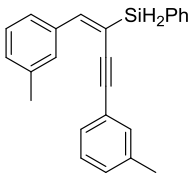
6. Spectra of products



***(E)*-(1,4-diphenylbut-1-en-3-yn-2-yl)phenylsilane (2a)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (132 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.47 – 7.40 (m, 7H), 7.38 – 7.33 (m, 4H), 7.11 (s, 1H), 4.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 137.3, 135.8, 131.4, 130.7, 130.2, 129.1, 129.0, 128.8, 128.4, 128.3, 128.2, 123.9, 115.1, 101.3, 89.7. HRMS-EI *(m/z)*: Calc. for $C_{22}H_{18}Si$ $[M]^+$ 310.1178, found 310.1183.

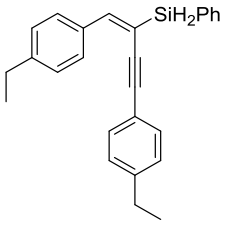


***(E)*-(1,4-di-p-tolylbut-1-en-3-yn-2-yl)phenylsilane (2b)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (128 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.47 – 7.41 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 1H), 4.85 (s, 2H), 2.39(s, 3H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 139.2, 138.3, 135.7, 134.8, 131.3, 130.9, 130.1, 129.1, 129.0, 129.0, 128.1, 120.9, 113.7, 101.3, 89.4, 21.5, 21.5. HRMS-EI *(m/z)*: Calc. for $C_{24}H_{22}Si$ $[M]^+$ 338.1491, found 338.1496.

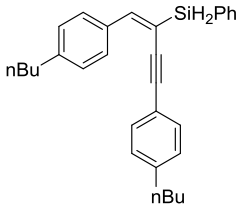


***(E)*-(1,4-di-m-tolylbut-1-en-3-yn-2-yl)phenylsilane (2c)**: The title compound was purified by column chromatography (PE) to afford the product as a pale

yellow oil (140 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 6.5 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.18 – 7.12 (m, 2H), 7.07 (s, 1H), 4.86 (s, 2H), 2.40 (s, 3H), 2.35 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 138.0, 137.8, 137.4, 135.8, 132.0, 130.8, 130.1, 129.9, 129.6, 129.1, 128.5, 128.3, 128.1, 126.2, 123.8, 114.8, 101.4, 89.6, 21.5, 21.2. HRMS-EI *(m/z)*: Calc. for $C_{24}H_{22}Si$ $[M]^+$ 338.1491, found 338.1496.

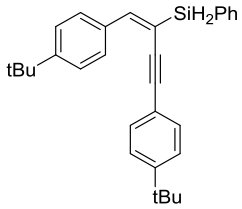


***(E)*-(1,4-bis(4-ethylphenyl)but-1-en-3-yn-2-yl)phenylsilane (2d)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (152 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.76 (m, 2H), 7.47 – 7.41 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.07 (s, 1H), 4.86 (s, 2H), 2.72 – 2.65 (m, 4H), 1.29 – 1.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 145.6, 144.7, 135.7, 135.1, 131.4, 131.0, 130.1, 129.1, 128.9, 128.1, 127.9, 127.8, 121.2, 113.8, 101.3, 89.4, 28.9, 28.8, 15.4. HRMS-EI *(m/z)*: Calc. for $C_{26}H_{26}Si$ $[M]^+$ 366.1804, found 366.1809.

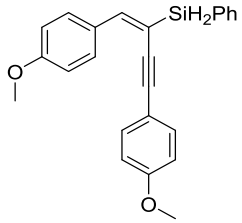


***(E)*-(1,4-bis(4-butylphenyl)but-1-en-3-yn-2-yl)phenylsilane (2e)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (160 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.74 (m, 2H), 7.46 – 7.40 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 1H), 4.85 (s, 2H), 2.66 – 2.60 (m, 4H), 1.65 – 1.58 (m, 4H), 1.40 – 1.34 (m, 4H), 0.97 – 0.92 (m, 6H).

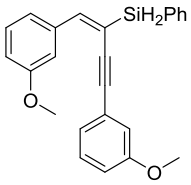
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 144.3, 143.4, 135.7, 135.1, 131.3, 131.0, 130.1, 129.0, 128.5, 128.4, 128.1, 121.2, 113.7, 101.4, 89.4, 35.6, 35.6, 33.4 , 33.4, 22.4, 22.3, 13.9, 13.9. HRMS-EI *(m/z)*: Calc. for $C_{30}H_{34}Si$ $[M]^+$ 422.2430, found 422.2435.



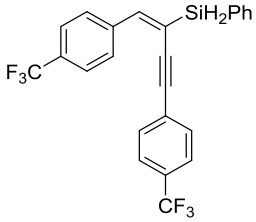
***(E)*-(1,4-bis(4-(tert-butyl)phenyl)but-1-en-3-yn-2-yl)phenylsilane (2f)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (156 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.75 (m, 2H), 7.49 – 7.41 (m, 5H), 7.39 (s, 4H), 7.08 (s, 1H), 4.86 (s, 2H), 1.36 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 151.5, 147.9, 135.7, 134.8, 131.1, 131.0, 130.1, 128.8, 128.1, 125.4, 125.3, 121.1, 114.0, 101.4, 89.4, 34.8, 34.8, 31.2, 31.2. HRMS-EI *(m/z)*: Calc. for $C_{30}H_{34}Si$ $[M]^+$ 422.2430, found 422.2435.



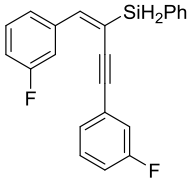
***(E)*-(1,4-bis(4-methoxyphenyl)but-1-en-3-yn-2-yl)phenylsilane (2g)**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a pale yellow oil (135 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.77 – 7.75 (m, 2H), 7.50 – 7.42 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.89 – 6.85 (m, 2H), 4.85 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 159.6, 147.1, 135.7, 134.0, 132.8, 131.1, 130.8, 130.5, 130.0, 128.1, 116.3, 114.2, 114.0, 113.7, 111.9, 100.7, 88.9, 55.3. HRMS-EI *(m/z)*: Calc. for $C_{24}H_{22}O_2Si$ $[M]^+$ 370.1389, found 370.1372.



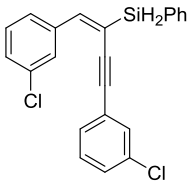
***(E)*-(1,4-bis(3-methoxyphenyl)but-1-en-3-yn-2-yl)phenylsilane (2h)**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a pale yellow oil (151 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.76 – 7.74 (m, 2H), 7.48 – 7.40 (m, 4H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.92 – 6.86 (m, 3H), 4.85 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 159.4, 148.4, 138.6, 135.8, 130.7, 130.2, 129.4, 129.3, 128.2, 124.8, 123.9, 122.1, 116.2, 115.7, 115.3, 115.0, 113.1, 101.7, 89.6, 55.3. HRMS-EI *(m/z)*: Calc. for $C_{24}H_{22}O_2Si$ $[M]^+$ 370.1389, found 370.1374.



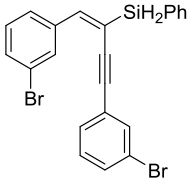
***(E)*-(1,4-bis(4-(trifluoromethyl)phenyl)but-1-en-3-yn-2-yl)phenylsilane (2i)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (158 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.72 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.44 (m, 5H), 7.16 (s, 1H), 4.87 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 140.1, 135.7, 131.6, 130.5 (q, $J_{C\text{-}F}$ = 32.4 Hz) , 130.1 (q, $J_{C\text{-}F}$ = 32.9 Hz), 129.0, 128.3, 127.1, 125.3 (q, $J_{C\text{-}F}$ = 3.2 Hz), 125.2 (d, $J_{C\text{-}F}$ = 3.8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 270.6 Hz), 123.8 (d, $J_{C\text{-}F}$ = 270.6 Hz), 118.2, 100.7, 91.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -62.8. HRMS-EI *(m/z)*: Calc. for $C_{24}H_{16}F_6Si$ $[M]^+$ 446.0925, found 446.0928.



***(E)*-(1,4-bis(3-fluorophenyl)but-1-en-3-yn-2-yl)phenylsilane (2j):** The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (143 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 10.5 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.38 – 7.27 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.02 (m, 4H), 4.85 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (d, J_{C-F} = 31.5 Hz), 161.6 (d, J_{C-F} = 32.9 Hz), 147.4 (d, J_{C-F} = 2.6 Hz), 139.2 (d, J_{C-F} = 7.8 Hz), 135.7, 130.4, 130.2, 130.1, 130.0 (d, J_{C-F} = 8.6 Hz), 129.8 (d, J_{C-F} = 8.2 Hz), 128.3, 127.3 (d, J_{C-F} = 2.9 Hz), 125.1 (d, J_{C-F} = 2.7 Hz), 118.1 (d, J_{C-F} = 22.5 Hz), 116.6, 116.1 (d, J_{C-F} = 21.4 Hz), 115.8 (d, J_{C-F} = 21.1 Hz), 115.1 (d, J_{C-F} = 22.4 Hz), 100.8 (d, J_{C-F} = 3.5 Hz), 90.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7, -112.8. HRMS-EI (m/z): Calc. for $C_{22}H_{16}F_2Si$ $[M]^+$ 346.0989, found 346.0974.

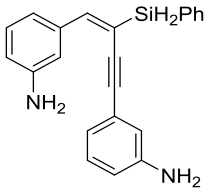


***(E)*-(1,4-bis(3-chlorophenyl)but-1-en-3-yn-2-yl)phenylsilane (2k)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (133 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.73 – 7.72 (m, 2H), 7.71 – 7.68 (m, 1H), 7.51 – 7.46 (m, 1H), 7.46 – 7.42 (m, 2H), 7.39 (s, 1H), 7.35 – 7.27 (m, 5H), 7.04 (s, 1H), 4.84 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 138.8, 135.7, 134.3, 134.3, 131.3, 130.4, 130.1, 129.6, 129.6, 129.1, 128.7, 128.6, 128.3, 127.3, 125.2, 116.8, 100.6, 90.4. HRMS-EI *(m/z)*: Calc. for $C_{22}H_{16}Cl_2Si$ $[M]^+$ 378.0398, found 346.0393.

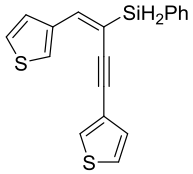


***(E)*-(1,4-bis(3-bromophenyl)but-1-en-3-yn-2-yl)phenylsilane (2l)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (182 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.75 – 7.69 (m, 3H), 7.57 (s, 1H), 7.51 – 7.39 (m, 6H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 4.84 (s, 2H). ^{13}C NMR (125 MHz,

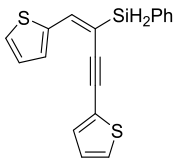
$CDCl_3$) δ 147.1, 139.0, 135.7, 134.3, 132.0, 131.6, 131.5, 130.4, 130.1, 129.9, 129.8, 128.3, 127.7, 125.4, 122.5, 122.3, 116.8, 100.5, 90.5. HRMS-EI *(m/z)*: Calc. for $C_{22}H_{16}Br_2Si$ $[M]^+$ 465.9388, found 465.9407.



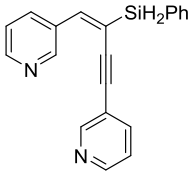
***(E)*-3,3'-(2-(phenylsilyl)but-1-en-3-yne-1,4-diyl)dianiline (2m)**: The title compound was purified by column chromatography (PE:EA=5:1) to afford the product as a pale yellow oil (134 mg, 79% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 – 7.69 (m, 2H), 7.51 – 7.42 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.05 – 7.01 (m, 1H), 6.99 (s, 1H), 6.66 – 6.55 (m, 4H), 5.23 (s, 2H), 5.12 (s, 2H), 4.75 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.4, 149.3, 149.2, 137.9, 135.9, 130.9, 130.6, 129.7, 129.4, 128.8, 123.6, 119.2, 117.0, 116.4, 115.9, 115.1, 114.8, 113.3, 102.3, 88.8. HRMS (APCI $^+$) *m/z* calcd for $C_{22}H_{21}N_2Si$, $[M+H]^+$ 341.1369. Found: 341.1469



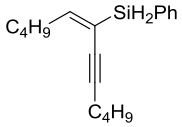
***(E)*-(1,4-di(thiophen-3-yl)but-1-en-3-yn-2-yl)phenylsilane (2n)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (129 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.8 Hz, 1H), 7.76 – 7.72 (m, 3H), 7.47 – 7.40 (m, 4H), 7.31 – 7.28 (m, 2H), 7.12 – 7.09 (m, 2H), 4.82 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 140.0, 135.7, 130.7, 130.2, 129.6, 128.3, 128.1, 127.9, 126.6, 125.4, 125.2, 122.9, 113.0, 95.9, 89.8. HRMS-EI *(m/z)*: Calc. for $C_{18}H_{14}S_2Si$ $[M]^+$ 322.0306, found 322.0307.



***(E)*-(1,4-di(thiophen-2-yl)but-1-en-3-yn-2-yl)phenylsilane (2o)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (137 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.50 – 7.39 (m, 4H), 7.33 (d, *J* = 5.2 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.27 (d, *J* = 3.6 Hz, 1H), 7.08 – 7.02 (m, 2H), 4.85 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 141.4, 135.7, 131.7, 130.5, 130.4, 130.2, 128.2, 128.1, 127.8, 127.2, 126.5, 124.0, 110.9, 96.4, 94.4. HRMS-EI *(m/z)*: Calc. for $C_{18}H_{14}S_2Si$ $[M]^+$ 322.0306, found 322.0310.

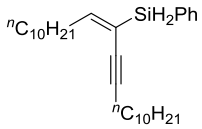


***(E)*-3,3'-(2-(phenylsilyl)but-1-en-3-yne-1,4-diyl)dipyridine (2p)**: The title compound was purified by column chromatography (PE:EA=5:1) to afford the product as a yellow oil (84 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.60 (s, 1H), 8.56 – 8.51 (m, 2H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.41 (m, 2H), 7.35 – 7.30 (m, 1H), 7.27 – 7.25(m, 1H), 7.10 (m, 1H), 4.86 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 150.5, 149.8, 148.9, 145.4, 138.2, 135.7, 135.1, 132.8, 130.5, 129.7, 128.3, 123.3, 123.1, 120.5, 118.0, 98.7, 92.0. HRMS-EI *(m/z)*: Calc. for $C_{20}H_{16}N_2Si$ $[M]^+$ 312.1083, found 312.1078.

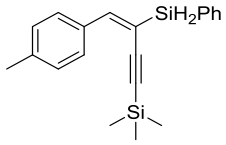


***(E)*-dodec-5-en-7-yn-6-yl-phenylsilane (2q)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (50% NMR yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.63 (m, 2H), 7.43 – 7.36 (m, 3H), 6.30 (t, *J* = 7.0 Hz, 1H), 4.60 (s, 2H), 2.41 (q, J = 7.1 Hz, 2H), 2.36 (t, J = 6.9 Hz, 2H), 1.52 – 1.44 (m, 4H), 1.43 – 1.35 (m, 4H), 0.93 – 0.90 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 135.5, 131.3, 129.8, 127.9, 116.6, 99.0, 79.0,

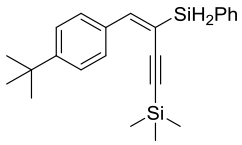
32.3, 31.0, 30.8, 22.4, 21.8, 19.5, 13.9, 13.6. HRMS-EI *(m/z)*: Calc. for $C_{18}H_{26}Si$ $[M]^+$ 270.1804, found 270.1820.



***(E)*-tetracos-11-en-13-yn-12-yl-phenylsilane (2r)**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (52% NMR yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 2H), 7.43 – 7.36 (m, 3H), 6.29 (t, *J* = 7.0 Hz, 1H), 4.60 (s, 2H), 2.42 (q, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.45−1.38 (m, 4H), 1.30−1.22 (m, 28H), 0.90−0.87 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 135.5, 131.3, 129.8, 127.9, 116.5, 99.0, 79.0, 32.6, 31.9, 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.6, 28.4, 22.7, 19.8, 19.2, 14.1. HRMS-EI *(m/z)*: Calc. for $C_{30}H_{50}Si$ $[M]^+$ 438.3682, found 438.3685.

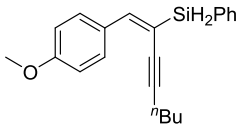


***(E)*-trimethyl(3-(phenylsilyl)-4-(p-tolyl)but-3-en-1-yn-1-yl)silane (2s)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (96 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.73 – 7.71 (m, 2H), 7.47 – 7.38 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.02 (s, 1H), 4.78 (s, 2H), 2.38 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 139.5, 135.8, 134.7, 130.8, 130.1, 129.1, 128.9, 128.0, 113.8, 107.3, 105.4, 21.5, -0.1. HRMS-EI *(m/z)*: Calc. for $C_{20}H_{24}Si_2$ $[M]^+$ 320.1417, found 320.1431.

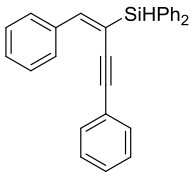


***(E)*-(4-(4-(tert-butyl)phenyl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2t)**: The title compound was purified by column

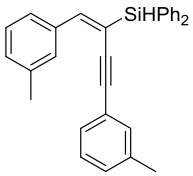
chromatography (PE) to afford the product as a colorless oil (144 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.75 – 7.74 (m, 2H), 7.47 – 7.41 (m, 5H), 7.07 (s, 1H), 4.82 (s, 2H), 1.38 (s, 9H), 0.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 149.3, 135.7, 134.6, 130.8, 130.1, 128.9, 128.0, 125.1, 114.0, 107.4, 105.4, 34.8, 31.2, -0.1. HRMS-EI *(m/z)*: Calc. for $C_{23}H_{30}Si_2$ $[M]^+$ 362.1886, found 362.1903.



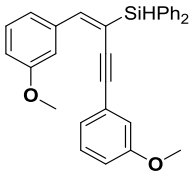
***(E)*-(1-(4-methoxyphenyl)oct-1-en-3-yn-2-yl)phenylsilane (2u)**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a pale yellow oil (133 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.38 (m, 3H), 6.91 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.74 (s, 2H), 3.83 (s, 3H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.57 – 1.52 (m, 2H), 1.46 – 1.41 (m, 2H), 0.94 – 0.90 (m, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 146.7, 135.7, 131.3, 130.8, 130.7, 130.3, 129.9, 128.0, 113.5, 112.9, 102.7, 80.9, 55.3, 30.8, 20.0, 13.6. HRMS-EI *(m/z)*: Calc. for $C_{21}H_{24}OSi$ $[M]^+$ 320.1596, found 320.1590.



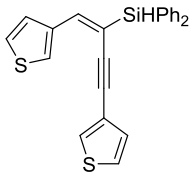
***(E)*-(1,4-diphenylbut-1-en-3-yn-2-yl)diphenylsilane (4a)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (172 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.77 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.49 – 7.39 (m, 8H), 7.37 – 7.29 (m, 6H), 7.14 (s, 1H), 5.38 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 137.5, 135.8, 132.6, 131.4, 130.1, 129.1, 129.1, 128.3, 128.3, 128.2, 128.1, 124.0, 117.1, 101.8, 90.2.



***(E)*-(1,4-di-m-tolylbut-1-en-3-yn-2-yl)diphenylsilane (4b)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (180 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 4H), 7.48 – 7.40 (m, 6H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.08 (m, 6H), 5.36 (s, 1H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 137.9, 137.8, 137.5, 135.8, 132.7, 132.0, 130.0, 129.8, 129.7, 129.0, 128.4, 128.2, 128.2, 128.0, 126.3, 123.9, 116.8, 102.0, 90.2, 21.5, 21.2.

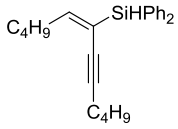


***(E)*-(1,4-bis(3-methoxyphenyl)but-1-en-3-yn-2-yl)diphenylsilane (4c)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (200 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.78 – 7.74 (m, 4H), 7.48 – 7.40 (m, 7H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.84 (m, 1H), 6.80 (s, 1H), 5.36 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 159.3, 148.6, 138.7, 135.8, 132.5, 130.0, 129.4, 129.3, 128.1, 124.9, 123.8, 122.2, 117.3, 116.0, 115.7, 114.9, 113.1, 102.2, 90.1, 55.3, 55.3.

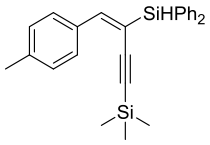


***(E)*-(1,4-di(thiophen-3-yl)but-1-en-3-yn-2-yl)diphenylsilane (4d)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (183 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.3

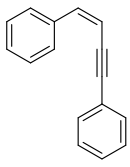
Hz, 1H), 7.79 – 7.71 (m, 5H), 7.49 – 7.40 (m, 6H), 7.33 – 7.29 (m, 2H), 7.27 – 7.25 (m, 1H), 7.11 (s, 1H), 7.02 (dd, *J* = 5.0, 1.1 Hz, 1H), 5.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 140.2, 135.8, 132.6, 130.1, 129.6, 128.1, 128.1, 126.6, 125.3, 125.2, 123.0, 115.1, 96.5, 90.3.



***(E)*-dodec-5-en-7-yn-6-yldiphenylsilane (4e)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (147 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.44 – 7.34 (m, 6H), 6.29 (t, *J* = 7.0 Hz, 1H), 5.10 (s, 1H), 2.44 (q, *J* = 7.2 Hz, 2H), 2.32 (t, *J* = 6.9 Hz, 2H), 1.45 – 1.38 (m, 4H), 1.37 – 1.29 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 135.7, 133.2, 129.7, 127.8, 118.5, 99.3, 79.3, 32.2, 31.0, 31.0, 22.4, 21.8, 19.5, 13.9, 13.6.

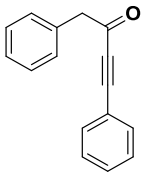


***(E)*-(3-(diphenylsilyl)-4-(p-tolyl)but-3-en-1-yn-1-yl)trimethylsilane (4f)**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (170 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.68 (m, 4H), 7.46 – 7.36 (m, 7H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.03 (s, 1H), 5.25 (s, 1H), 2.37 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 139.4, 135.8, 134.7, 132.7, 129.9, 129.1, 128.8, 127.9, 115.9, 107.9, 105.8, 21.5, -0.3. HRMS-EI *(m/z)*: Calc. for $C_{26}H_{28}Si_2$ $[M]^+$ 396.1730, found 396.1720.

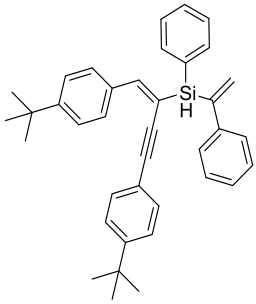


***(Z)*-but-1-en-3-yne-1,4-diyldibenzene (6)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (30 mg, 75%

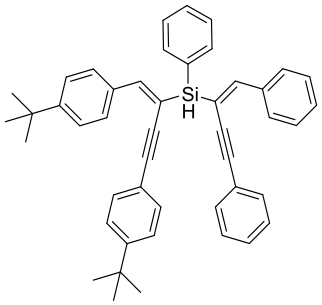
yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.42 – 7.32 (m, 6H), 6.72 (d, *J* = 11.9 Hz, 1H), 5.95 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.6, 131.5, 128.8, 128.5, 128.4, 128.4, 128.3, 123.5, 107.4, 95.9, 88.3.



1,4-diphenylbut-3-yn-2-one (7)[2]: The title compound was purified by column chromatography (PE:EA=30:1) to afford the product as a yellow oil (50 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.35 – 7.31 (m, 3H), 3.94 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2, 133.3, 133.1, 130.8, 129.9, 128.7, 128.6, 127.4, 119.9, 92.9, 87.7, 52.2.



***(E)*-(1,4-bis(4-(*tert*-butyl)phenyl)but-1-en-3-yn-2-yl)(phenyl)(1-phenylvinyl)silane (8)**: The title compound was purified by column chromatography (PE:EA=75:1) to afford the product as a yellow oil (130 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.44 (m, 6H), 7.40 – 7.31 (m, 7H), 7.30 – 7.26 (m, 2H), 7.10 (s, 1H), 6.36 (d, *J* = 2.3 Hz, 1H), 5.98 (d, *J* = 2.3 Hz, 1H), 5.31 (s, 1H), 1.39 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 151.4, 148.3, 145.4, 143.0, 135.8, 135.0, 132.3, 131.2, 129.0, 128.5, 128.0, 127.4, 127.1, 126.9, 125.3, 125.3, 121.2, 115.8, 101.8, 121.2, 89.8, 34.9, 34.8, 31.3, 31.2. HRMS-ESI *(m/z)*: Calc. for $C_{38}H_{40}Si$ $[M+Na]^+$ 547.2791, found 547.2786.



((*E*)-1,4-bis(4-(*tert*-butyl)phenyl)but-1-en-3-yn-2-yl)((*E*)-1,4-diphenylbut-1-en-3-yn-2-yl)phenylsilane (9): The title compound was purified by column chromatography (PE:EA=75:1) to afford the product as a white solid (151 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 4H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.38 (m, 8H), 7.38 – 7.34 (m, 3H), 7.32 (s, 3H), 7.29 – 7.26 (m, 4H), 7.24 (s, 1H), 5.23 (s, 1H), 1.36 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 151.3, 148.8, 148.6, 148.4, 137.5, 135.8, 135.0, 132.1, 131.5, 131.1, 130.2, 129.2, 129.0, 128.3, 128.2, 128.0, 128.0, 125.3, 125.1, 124.1, 121.2, 116.4, 115.1, 101.8, 101.6, 90.2, 89.7, 34.8, 34.8, 31.2, 31.2. HRMS-ESI *(m/z)*: Calc. for $C_{38}H_{40}Si$ $[M+K]^+$ 663.2844, found 663.2836.

(E)-(1,4-diphenylbut-1-en-3-yn-2-yl)phenylsilane (2a)

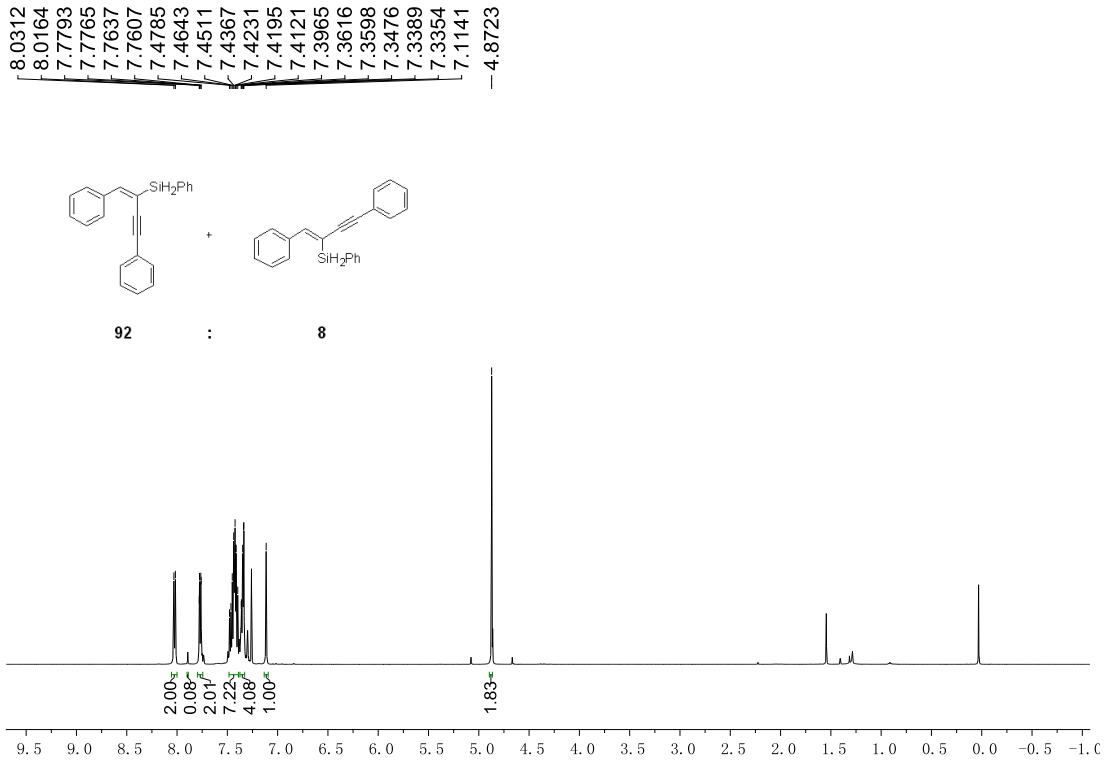


Figure S4. ^{1}H NMR (500 MHz) spectrum of **2a** in $CDCl_3$

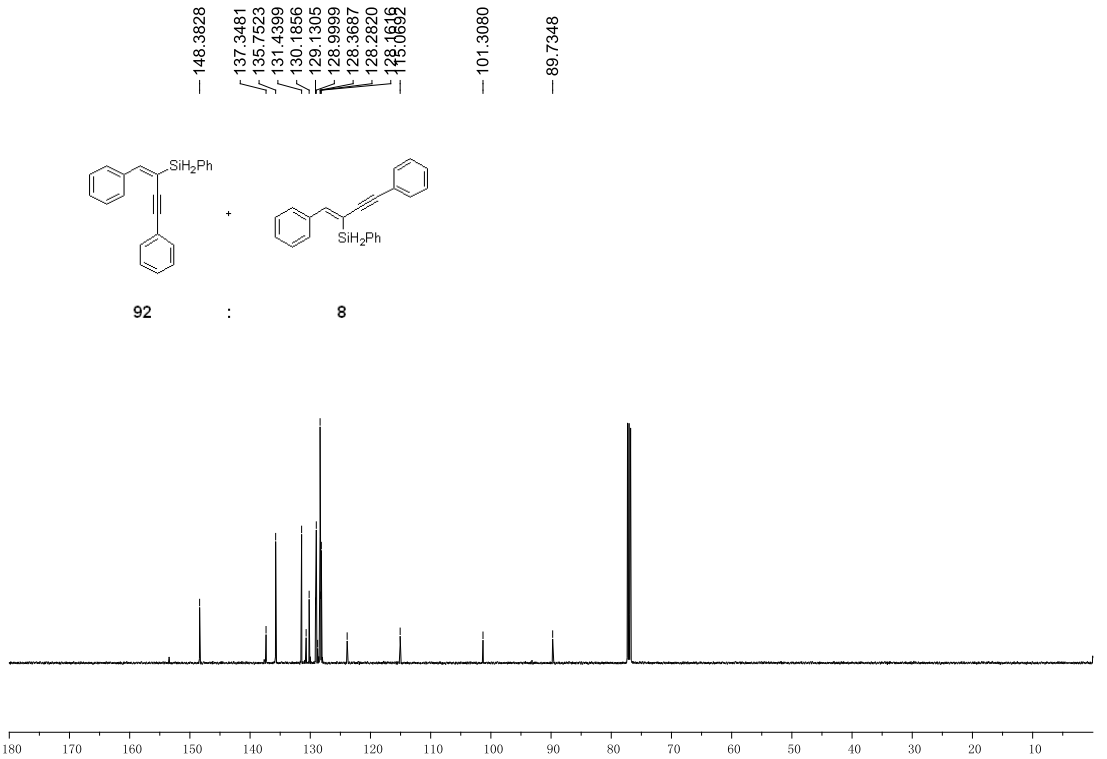


Figure S5. ^{13}C NMR (125 MHz) spectrum of **2a** in $CDCl_3$

(E)-(1,4-di-p-tolylbut-1-en-3-yn-2-yl)phenylsilane (2b)

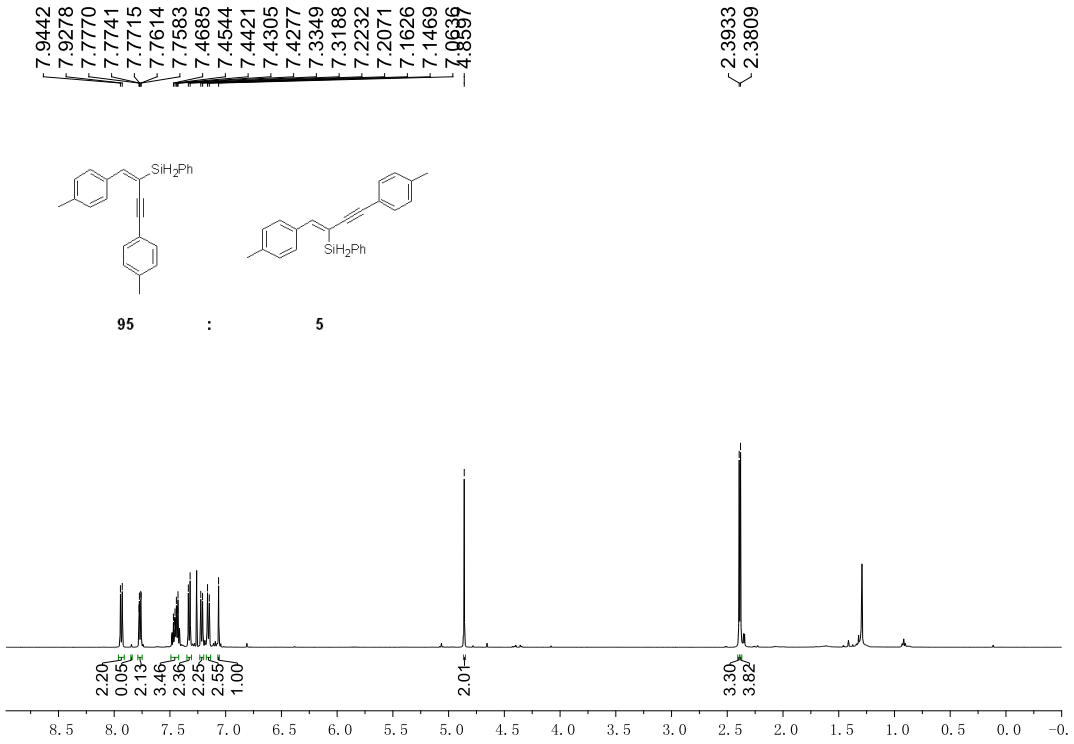


Figure S6. ^{1}H NMR (500 MHz) spectrum of **2b** in $CDCl_3$

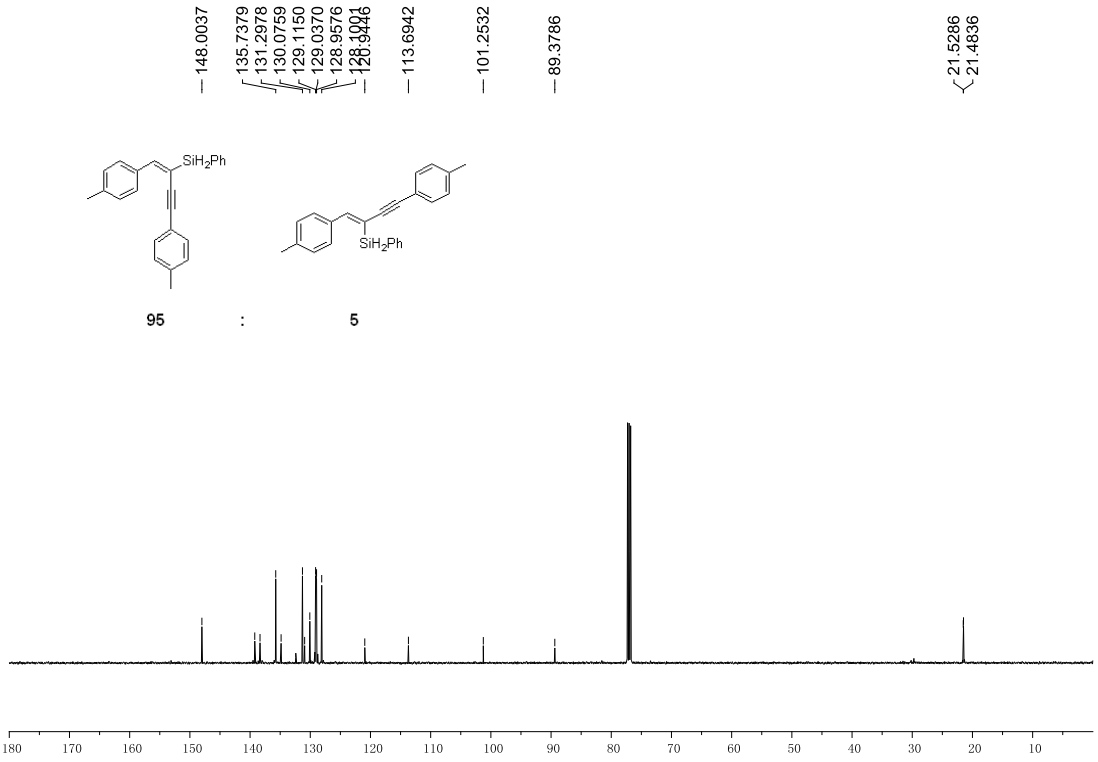


Figure S7. ^{13}C NMR (125 MHz) spectrum of **2b** in $CDCl_3$

(E)-(1,4-di-m-tolylbut-1-en-3-yn-2-yl)phenylsilane (2c)

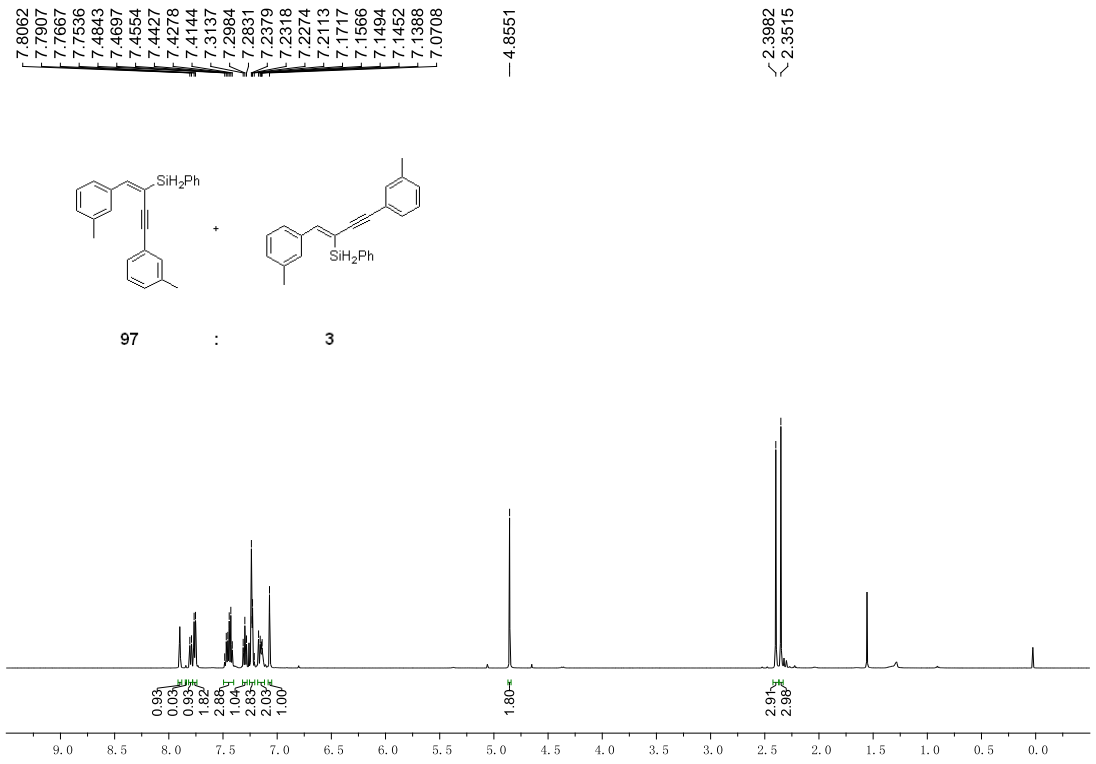


Figure S8. ^{1}H NMR (500 MHz) spectrum of **2c** in $CDCl_3$

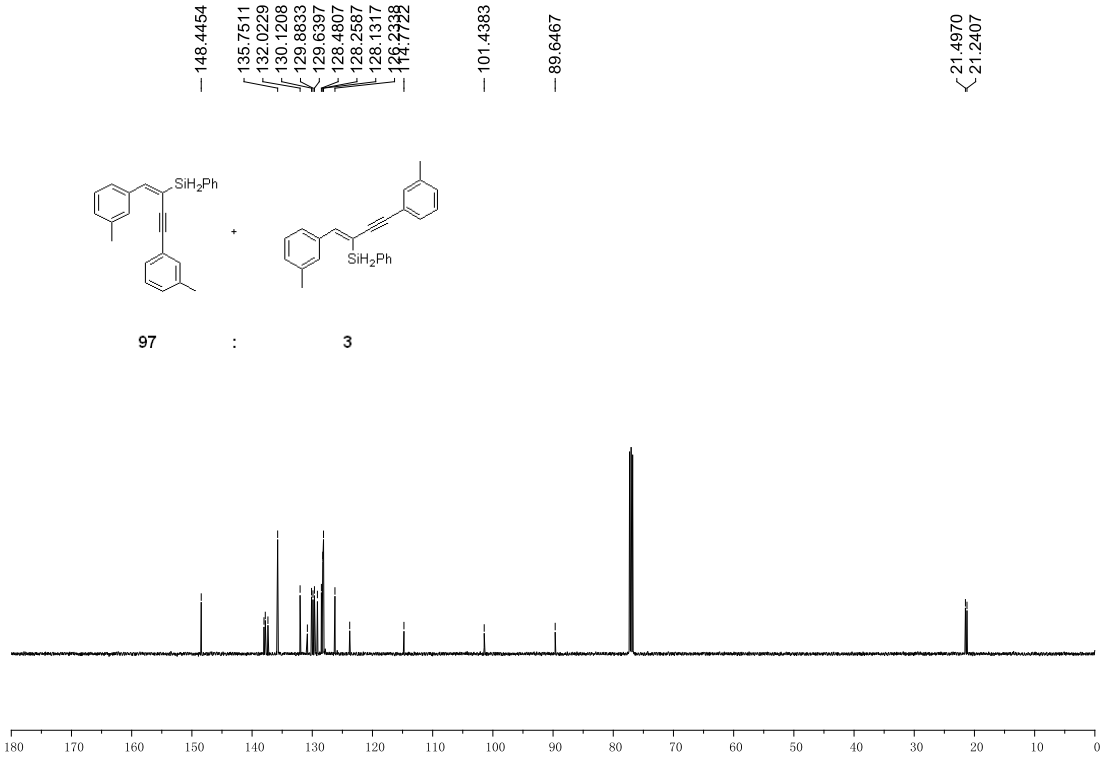


Figure S9. ^{13}C NMR (125 MHz) spectrum of **2c** in $CDCl_3$

(E)-(1,4-bis(4-ethylphenyl)but-1-en-3-yn-2-yl)phenylsilane (2d)

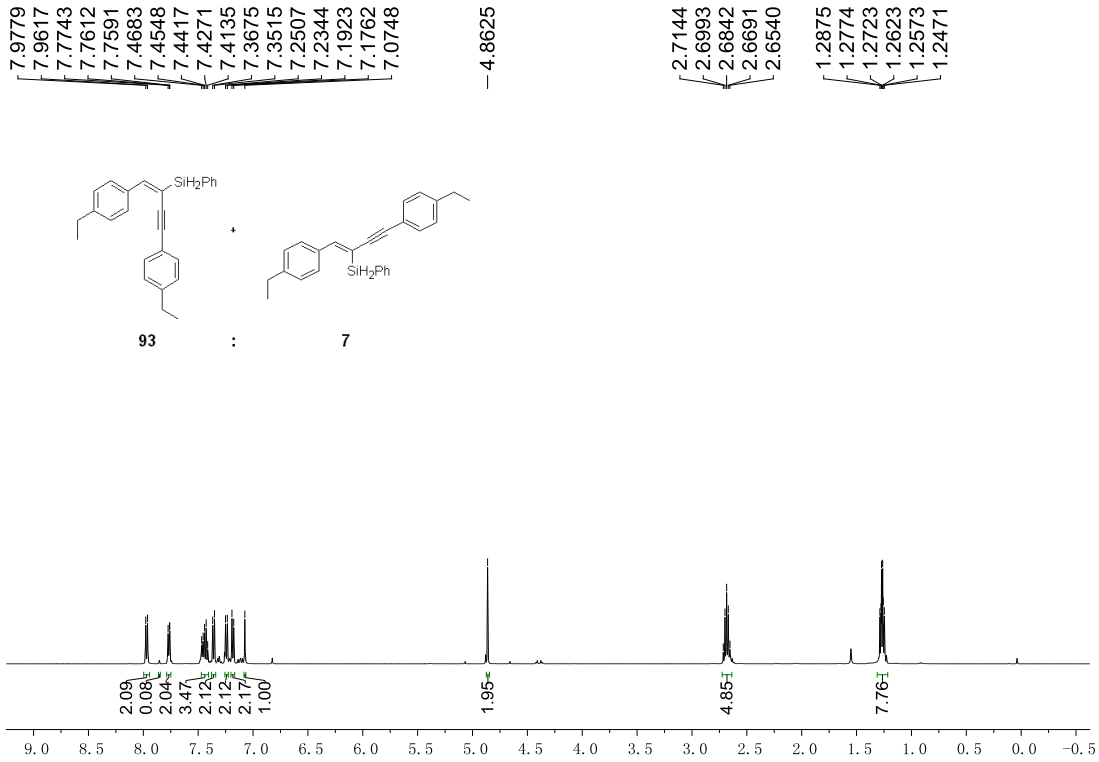


Figure S10. ^{1}H NMR (500 MHz) spectrum of **2d** in $CDCl_3$

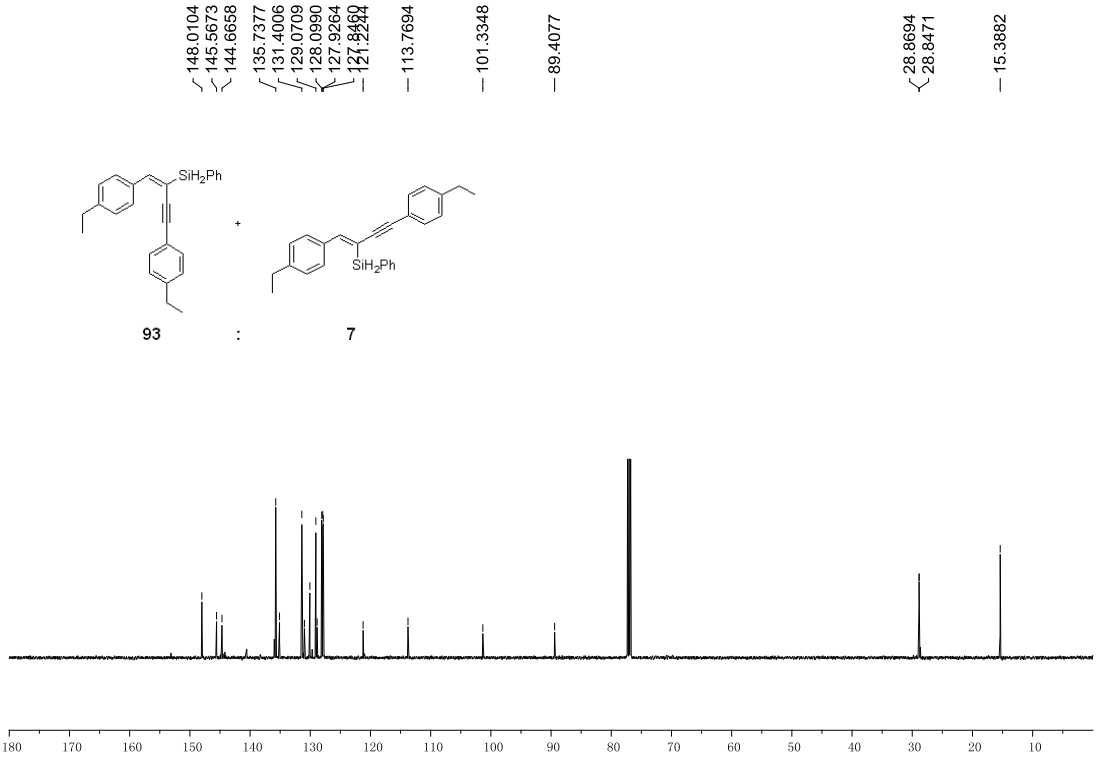


Figure S11. ^{13}C NMR (125 MHz) spectrum of **2d** in $CDCl_3$

(E)-(1,4-bis(4-butylphenyl)but-1-en-3-yn-2-yl)phenylsilane (2e)

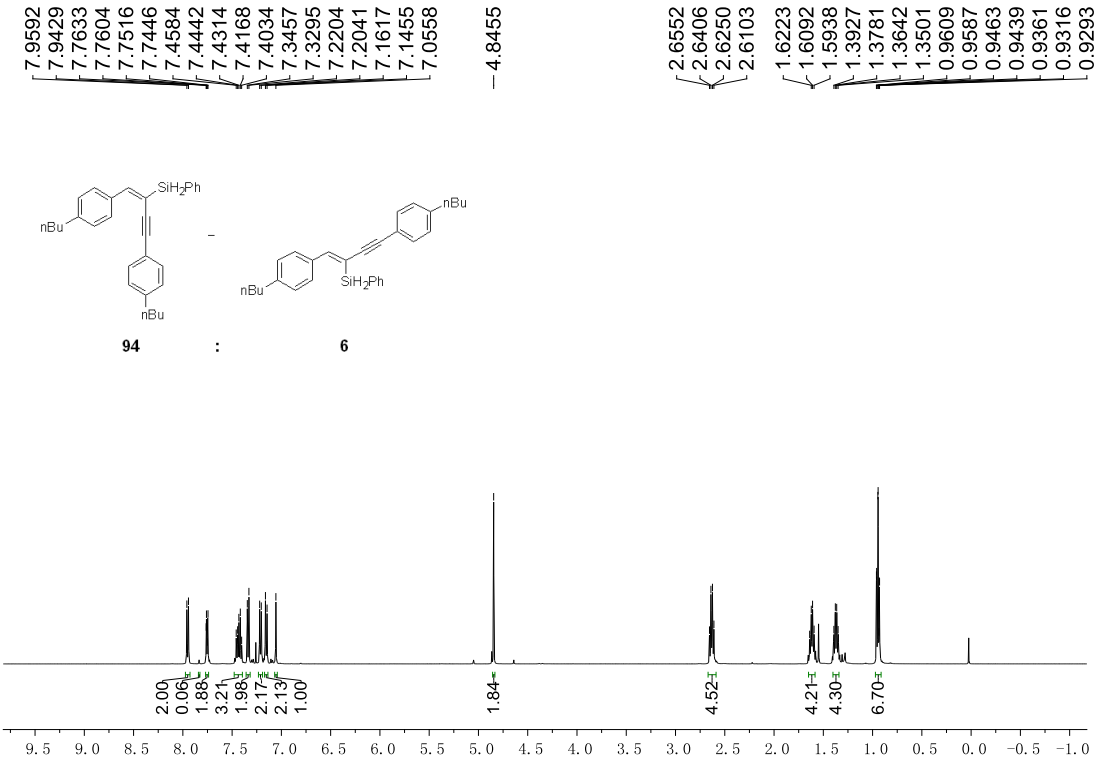


Figure S12. ^{1}H NMR (500 MHz) spectrum of **2e** in $CDCl_3$

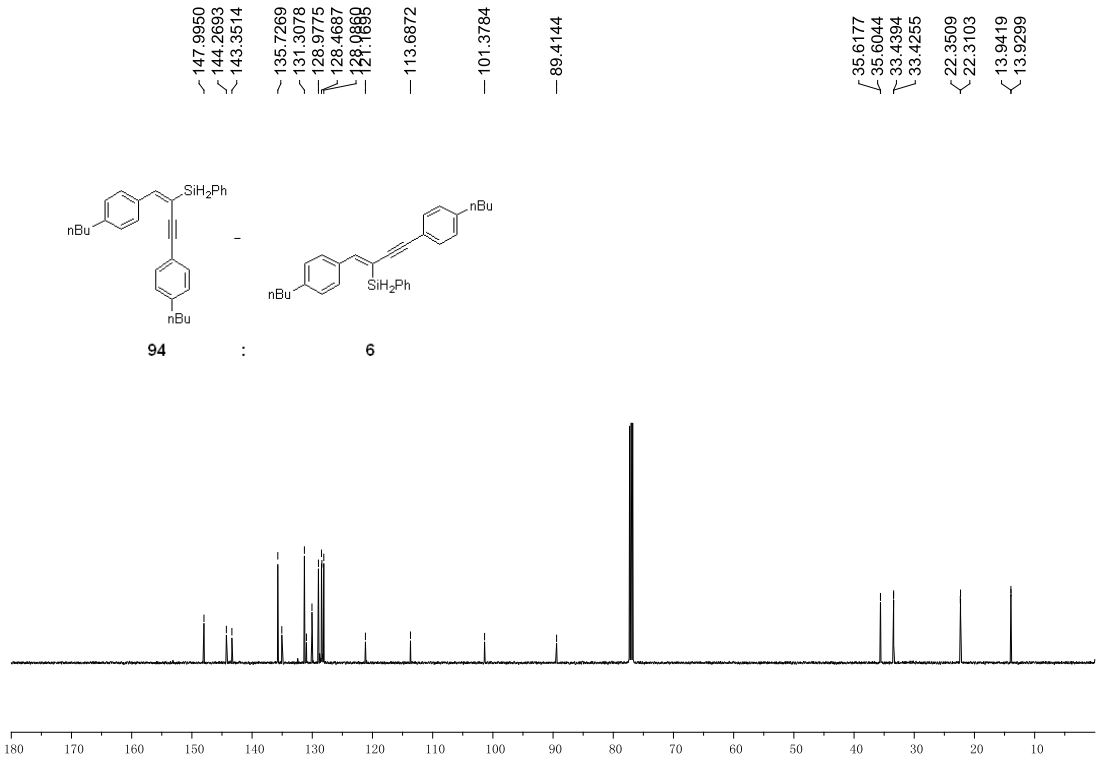


Figure S13. ^{13}C NMR (125 MHz) spectrum of **2e** in $CDCl_3$

(E)-(1,4-bis(4-(tert-butyl)phenyl)but-1-en-3-yn-2-yl)phenylsilane (2f)

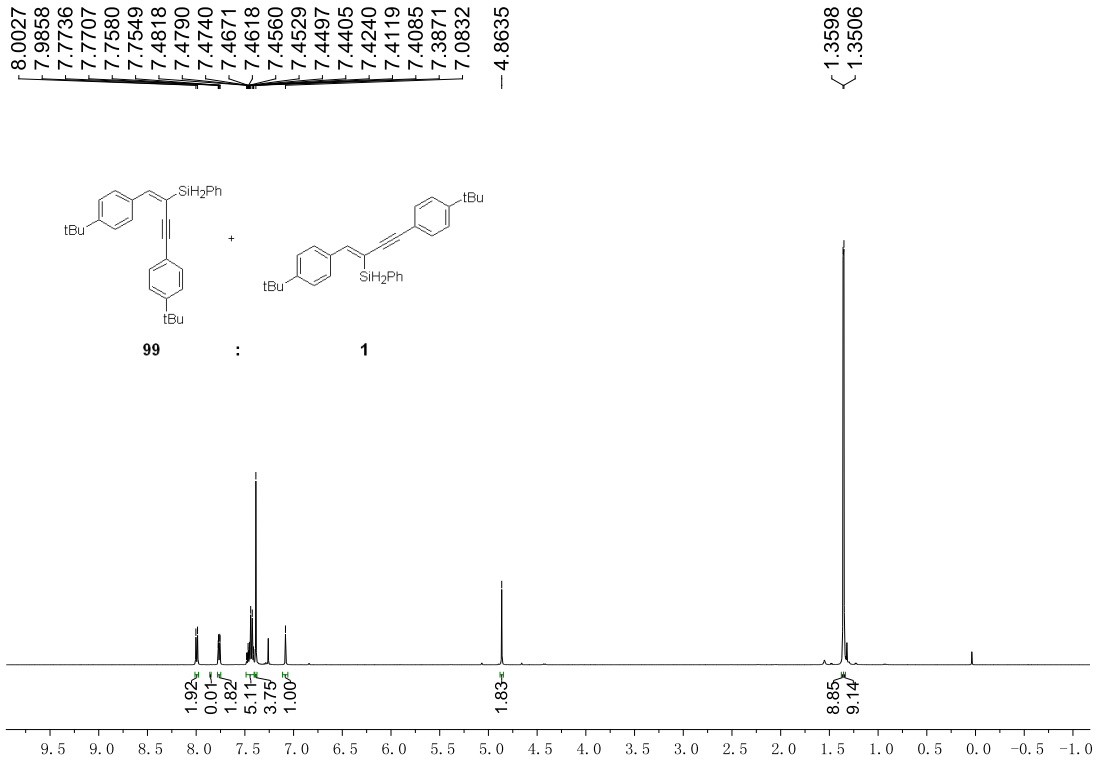


Figure S14. ^{1}H NMR (500 MHz) spectrum of **2f** in $CDCl_3$

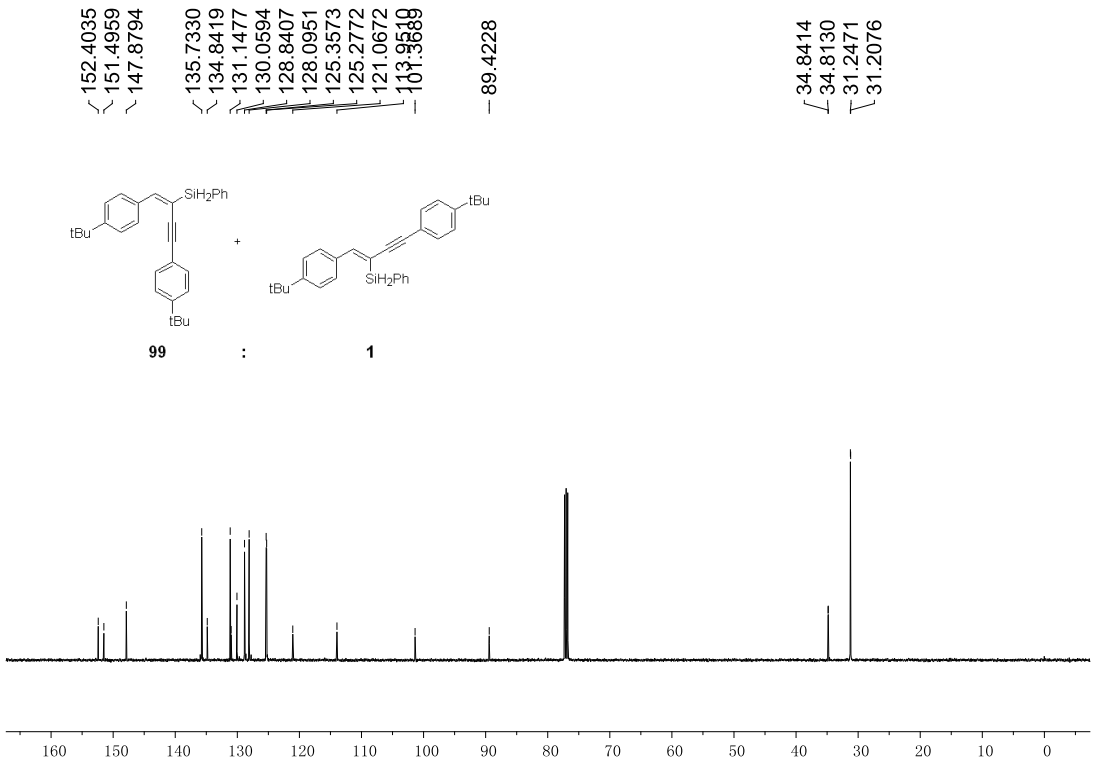


Figure S15. ^{13}C NMR (125 MHz) spectrum of **2f** in $CDCl_3$

(E)-(1,4-bis(4-methoxyphenyl)but-1-en-3-yn-2-yl)phenylsilane (2g)

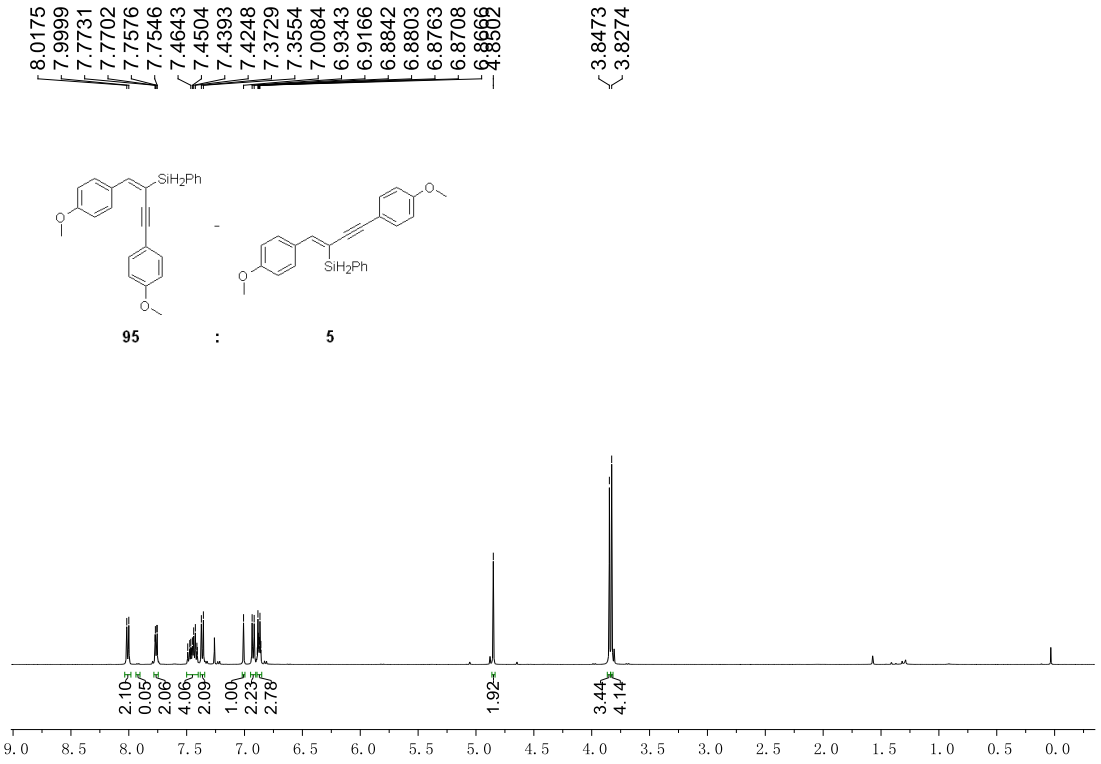


Figure S16. ^{1}H NMR (500 MHz) spectrum of **2g** in $CDCl_3$

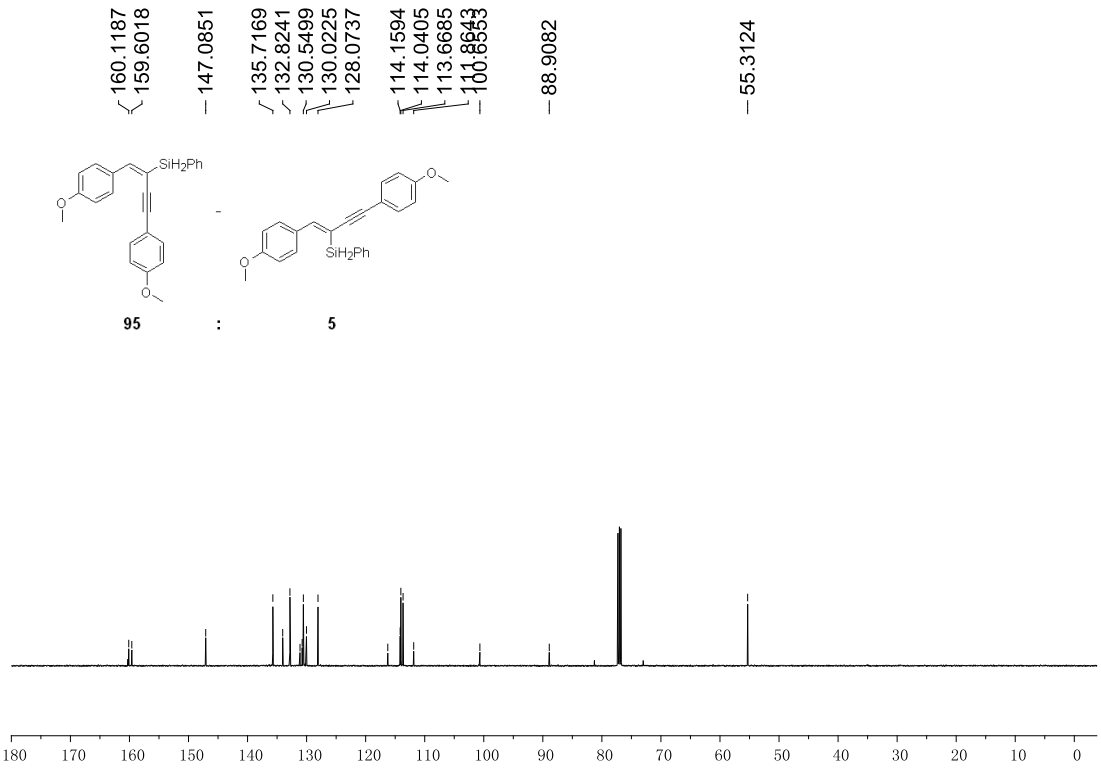


Figure S17. ^{13}C NMR (125 MHz) spectrum of **2g** in $CDCl_3$

(E)-(1,4-bis(3-methoxyphenyl)but-1-en-3-yn-2-yl)phenylsilane (2h)

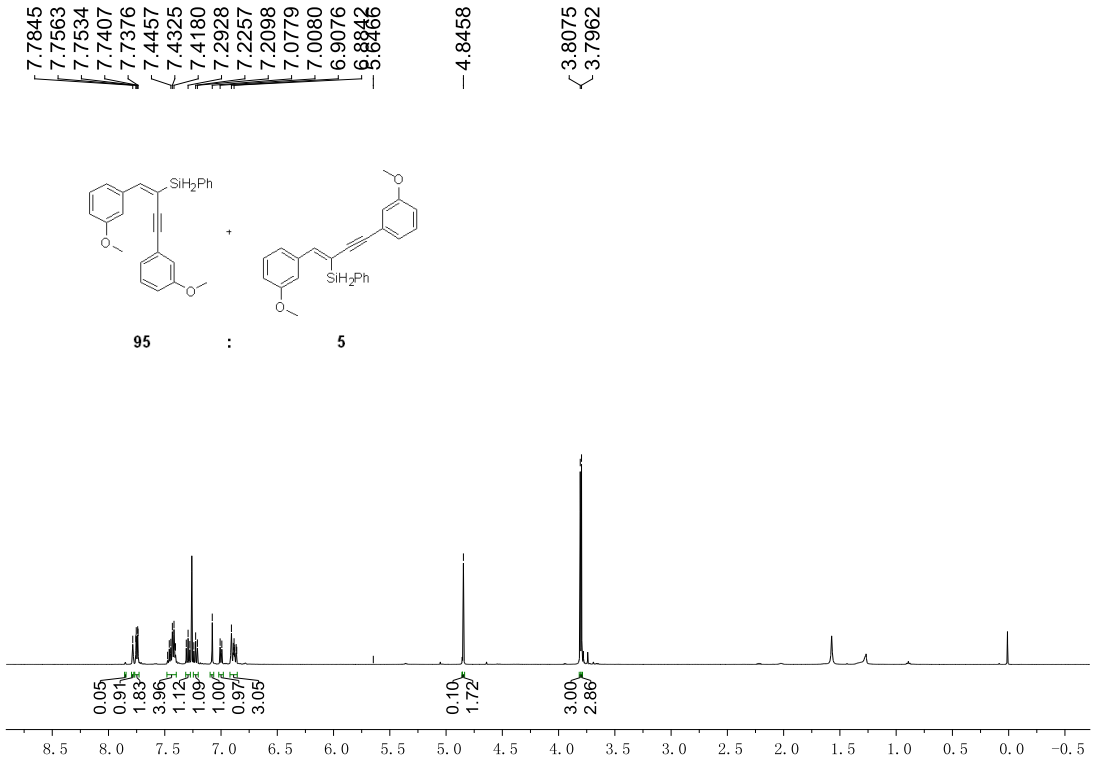


Figure S18. ^{1}H NMR (500 MHz) spectrum of **2h** in $CDCl_3$

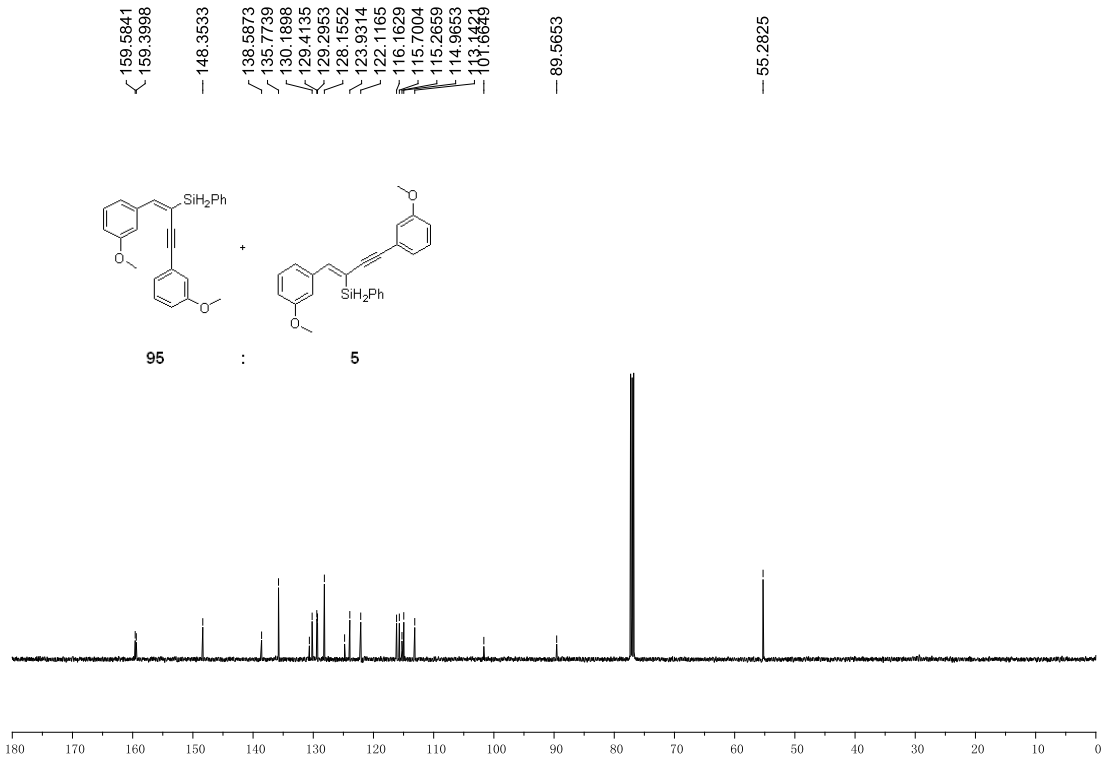


Figure S19. ^{13}C NMR (125 MHz) spectrum of **2h** in $CDCl_3$

(E)-(1,4-bis(4-(trifluoromethyl)phenyl)but-1-en-3-yn-2-yl)phenylsilane (2i)

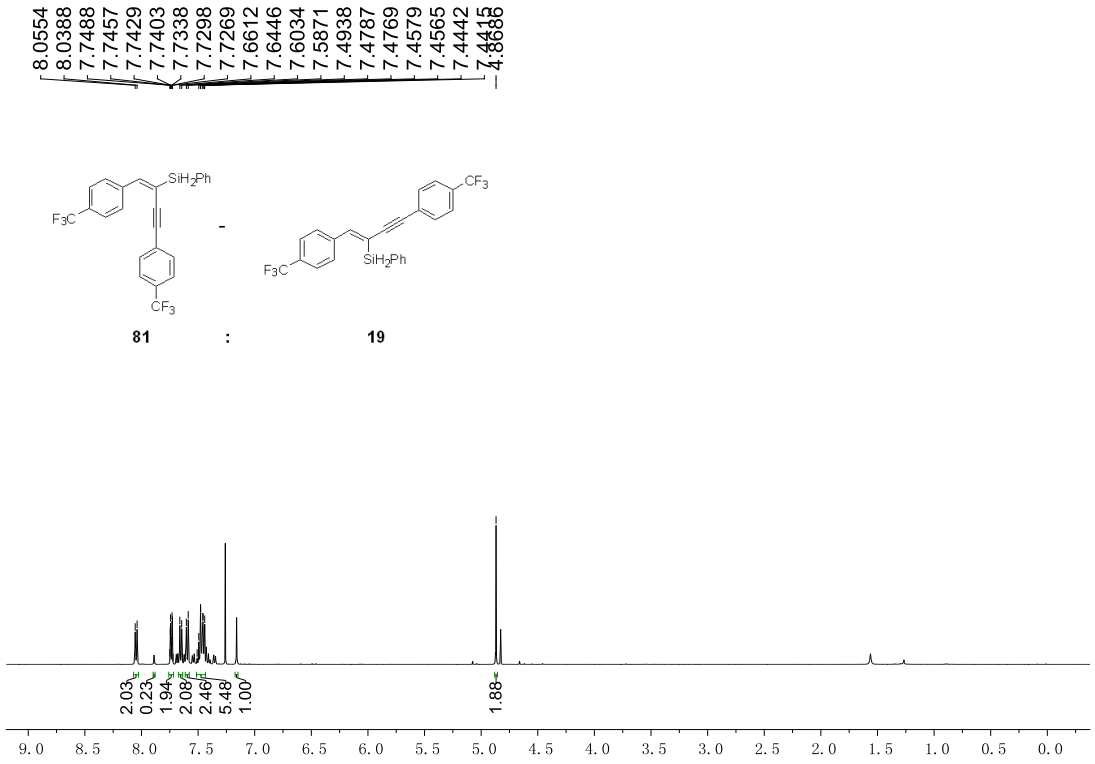


Figure S20. ^{1}H NMR (500 MHz) spectrum of **2i** in $CDCl_3$

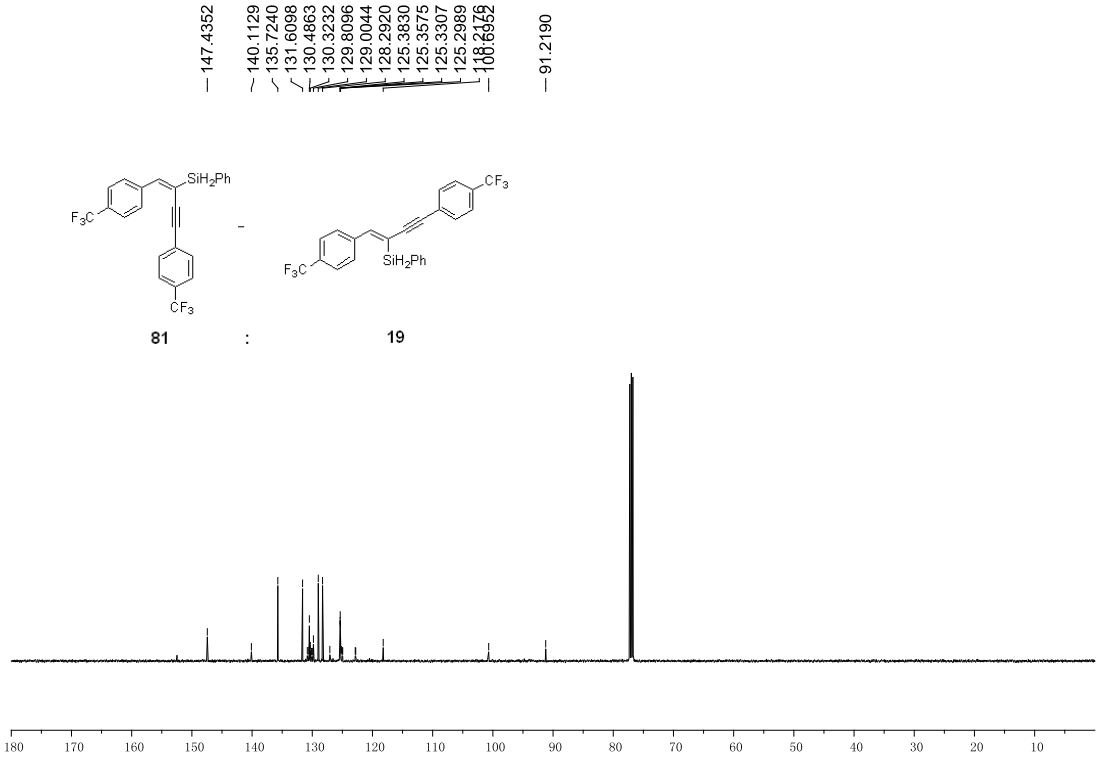


Figure S21. ^{13}C NMR (125 MHz) spectrum of **2i** in $CDCl_3$

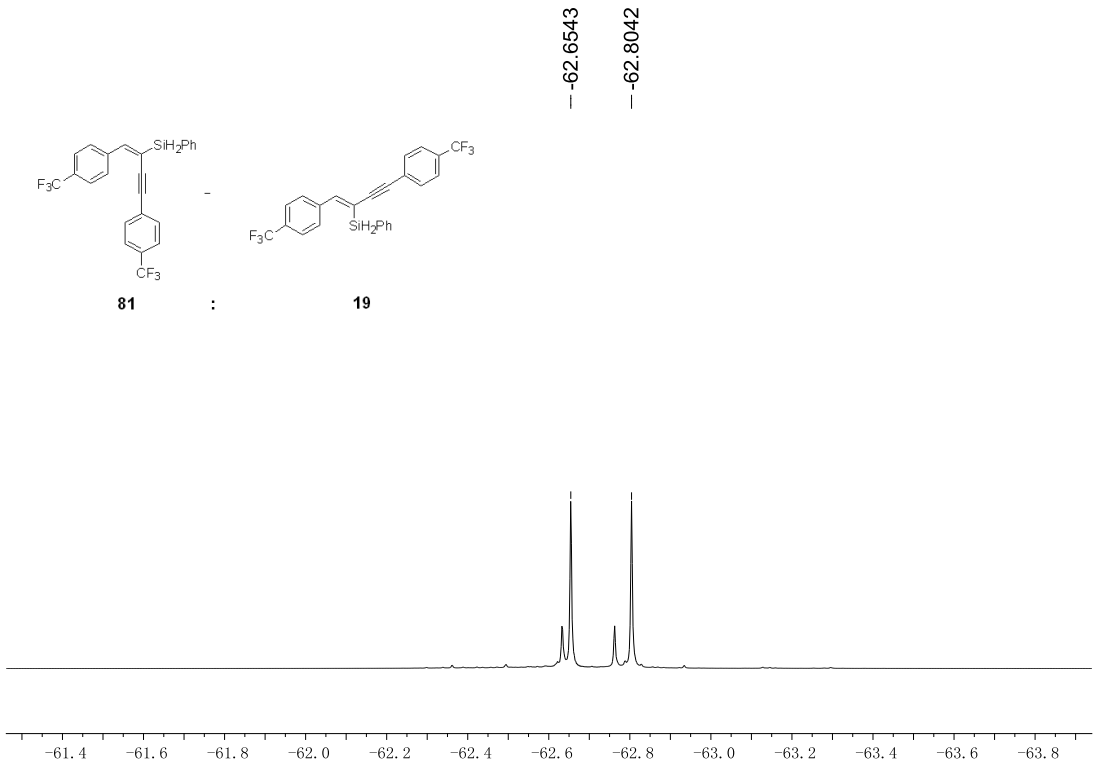


Figure S22. ^{19}F NMR (376 MHz) spectrum of **2i** in $CDCl_3$

(E)-(1,4-bis(3-fluorophenyl)but-1-en-3-yn-2-yl)phenylsilane (2j)

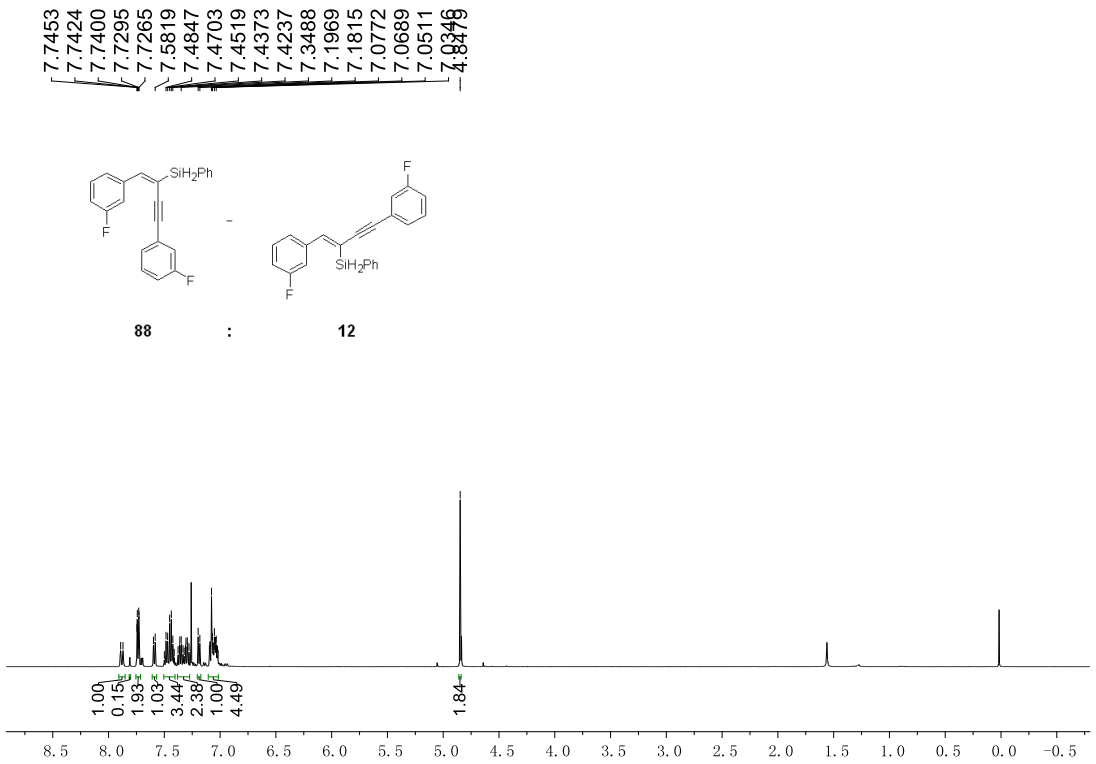


Figure S23. ^{1}H NMR (500 MHz) spectrum of **2j** in $CDCl_3$

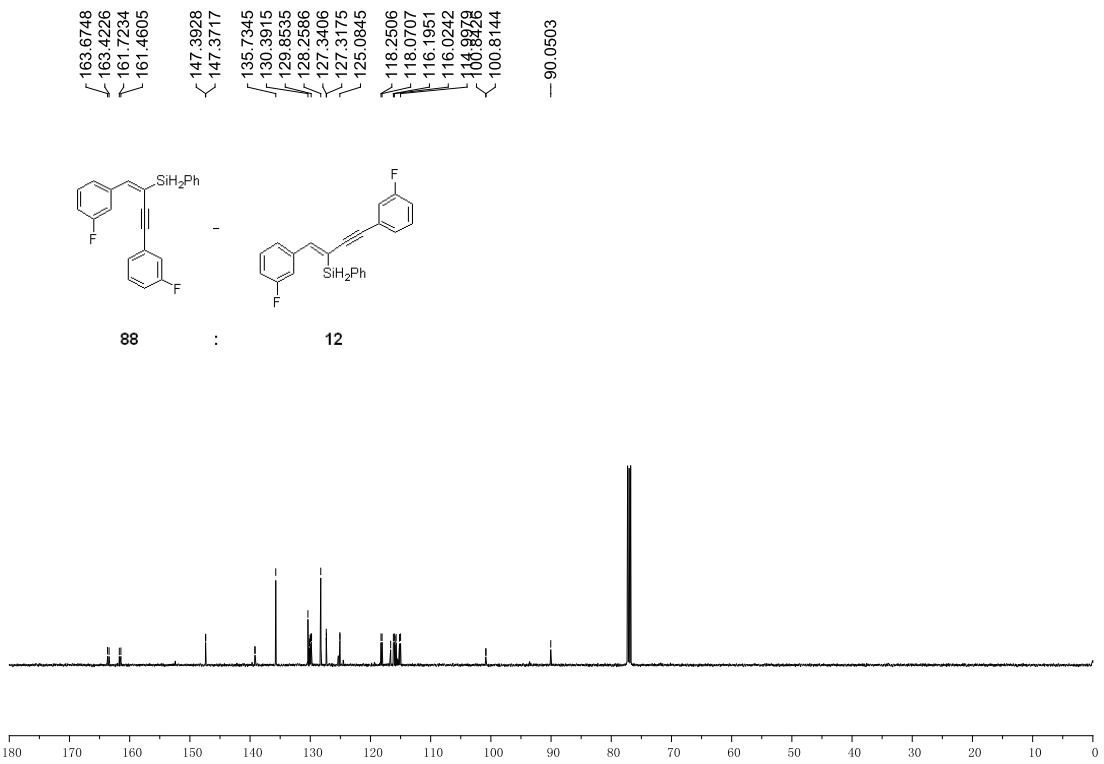


Figure S24 ^{13}C NMR (125 MHz) spectrum of **2j** in $CDCl_3$

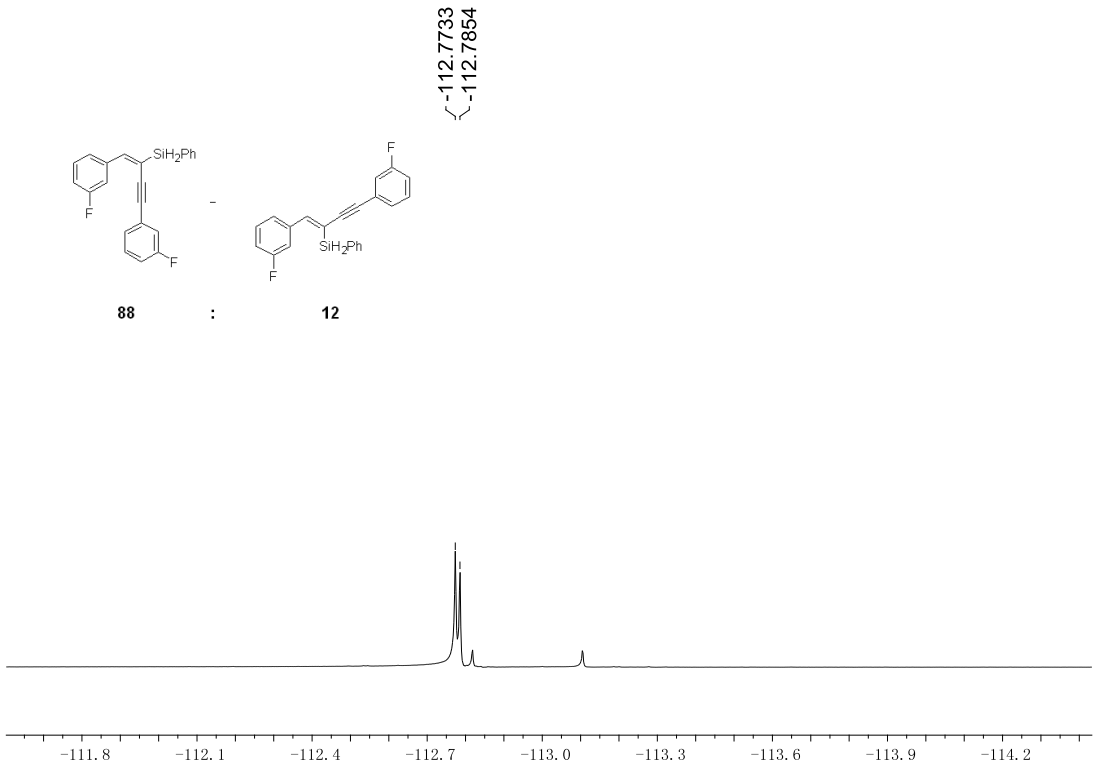


Figure S25. ^{19}F NMR (376 MHz) spectrum of **2i** in $CDCl_3$

(E)-(1,4-bis(3-chlorophenyl)but-1-en-3-yn-2-yl)phenylsilane (2k)

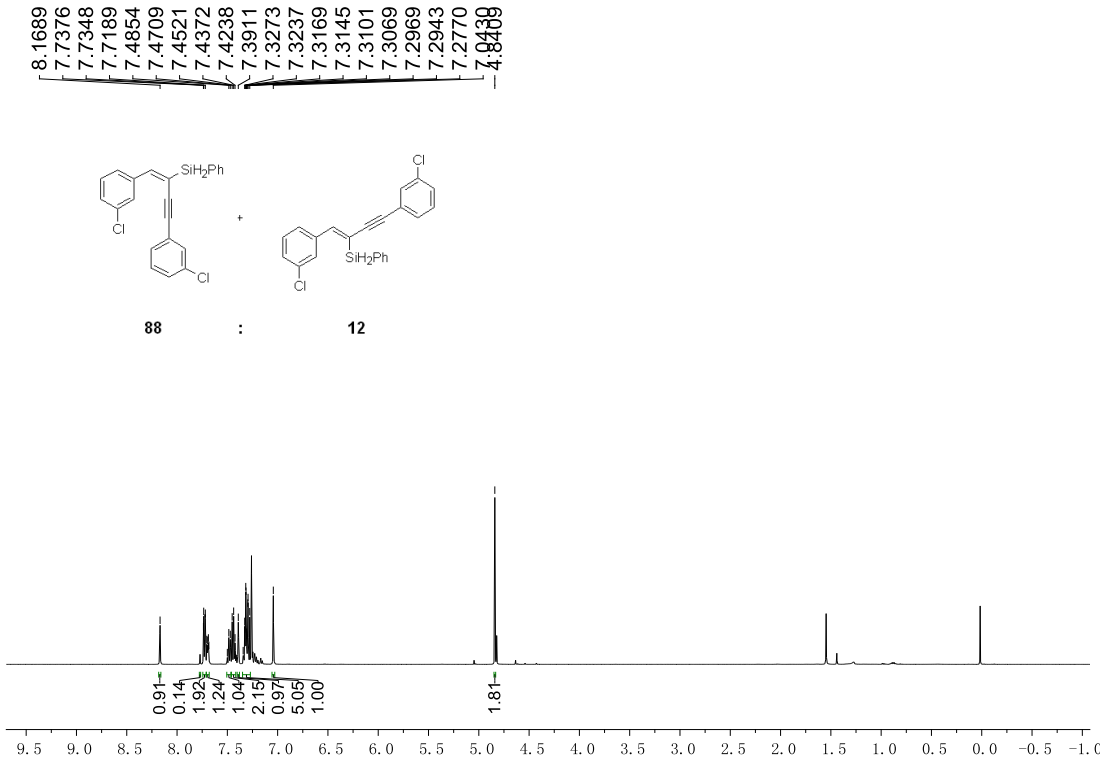


Figure S26. ^{1}H NMR (500 MHz) spectrum of **2k** in $CDCl_3$

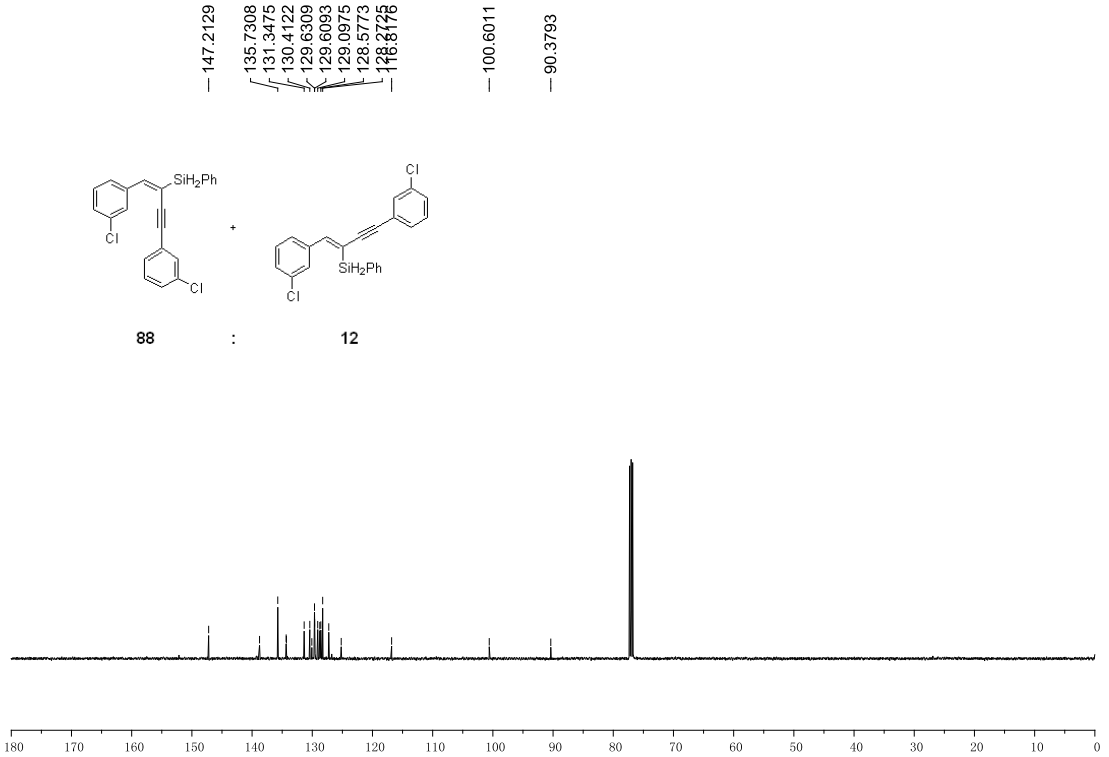


Figure S27 ^{13}C NMR (125 MHz) spectrum of **2k** in $CDCl_3$

(E)-(1,4-bis(3-bromophenyl)but-1-en-3-yn-2-yl)phenylsilane (2l)

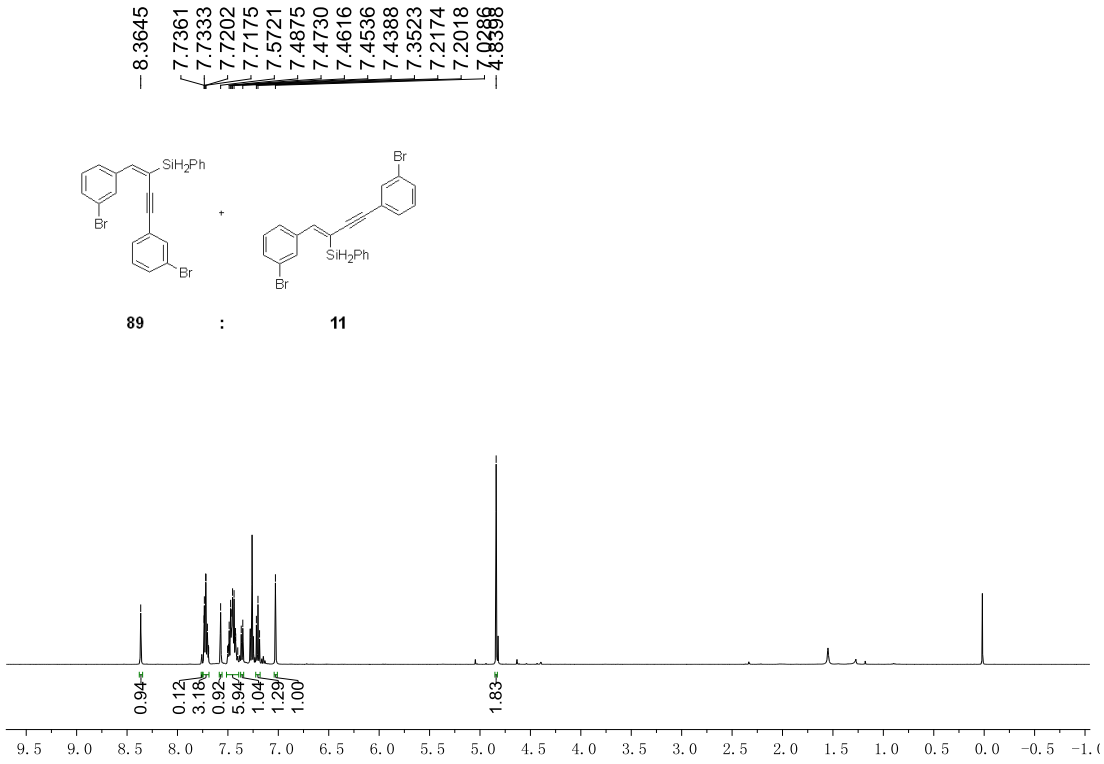


Figure S28. ^{1}H NMR (500 MHz) spectrum of **2l** in $CDCl_3$

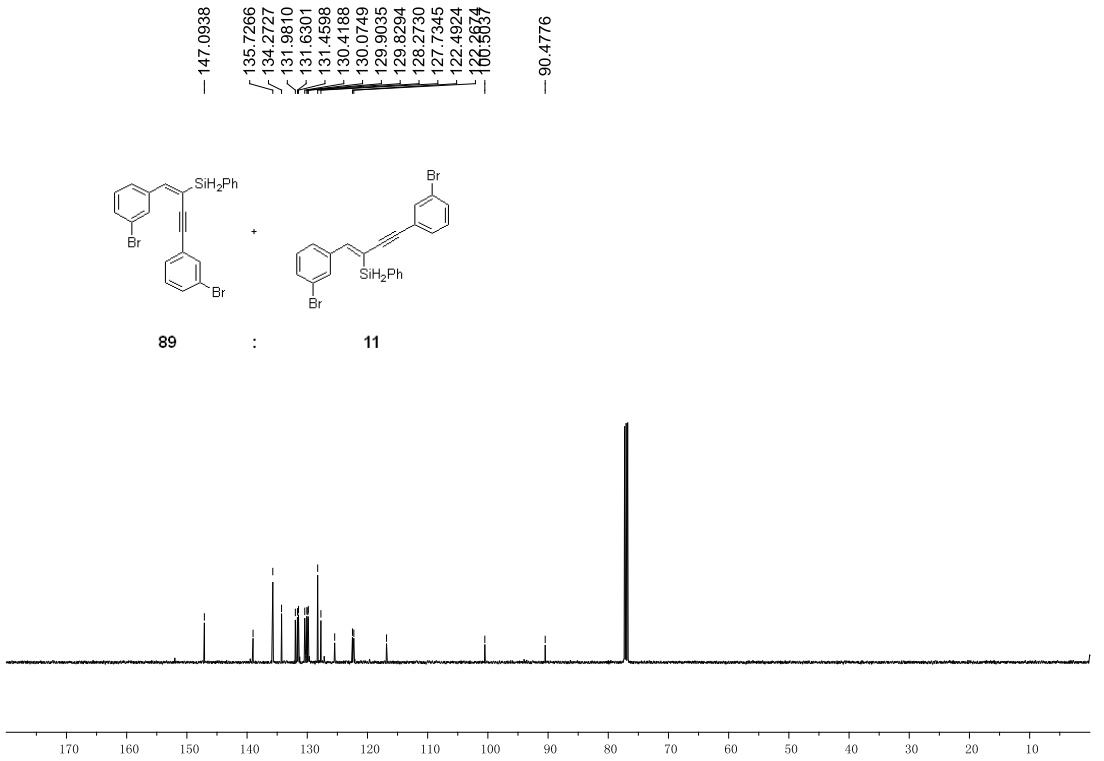


Figure S29 ^{13}C NMR (125 MHz) spectrum of **2l** in $CDCl_3$

(E)-3,3'-(2-(phenylsilyl)but-1-en-3-yne-1,4-diyl)dianiline (2m)

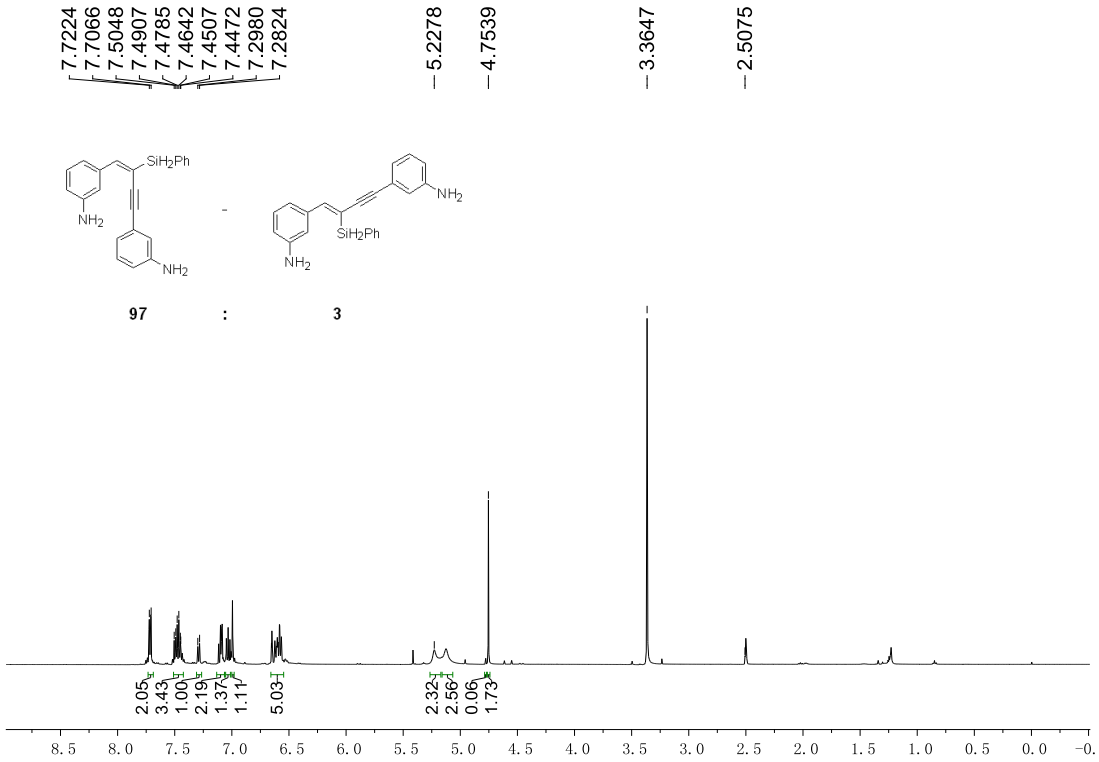


Figure S30. ^{1}H NMR (500 MHz) spectrum of **2m** in DMSO-*d*6

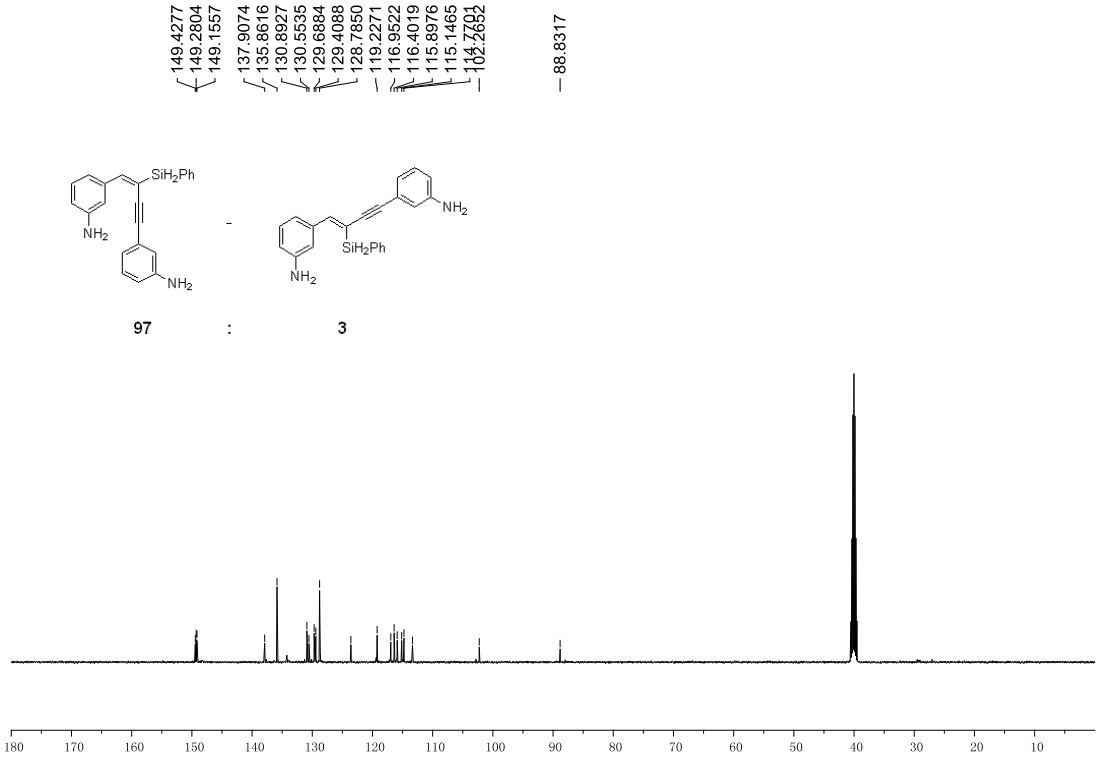


Figure S31 ^{3}C NMR (125 MHz) spectrum of **2m** in DMSO-*d*6

(E)-(1,4-di(thiophen-3-yl)but-1-en-3-yn-2-yl)phenylsilane (2n)

Figure S32. ^{1}H NMR (500 MHz) spectrum of **2n** in $CDCl_3$

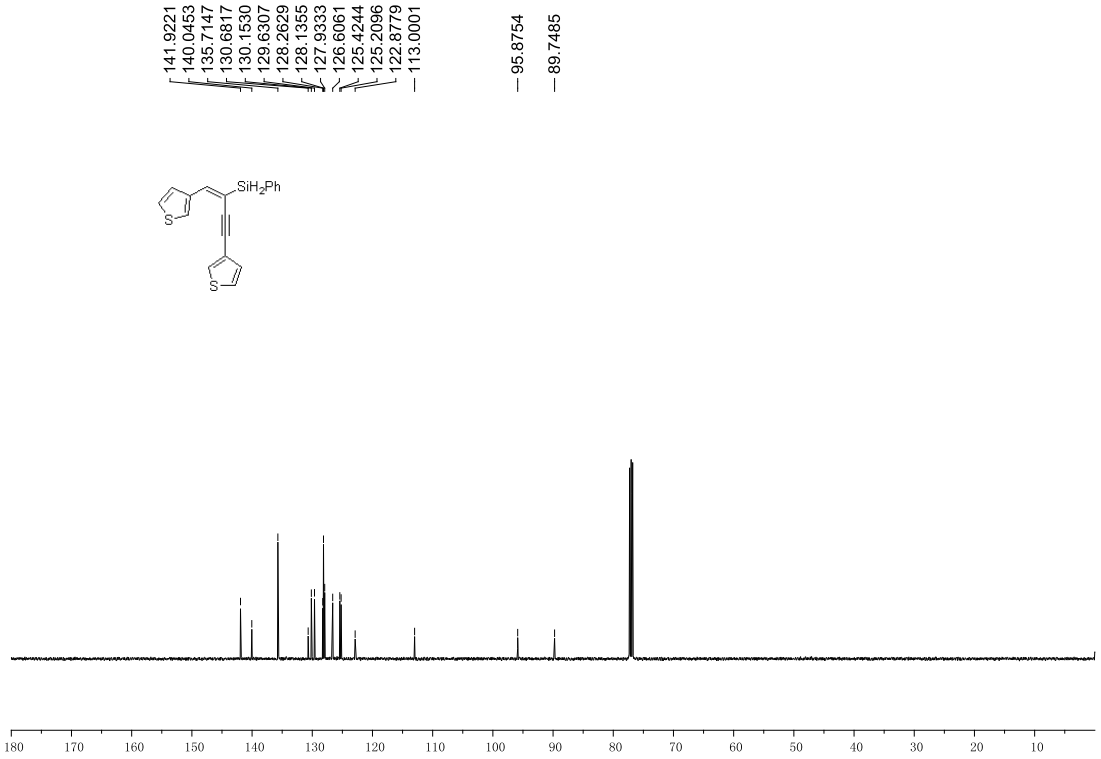


Figure S33 ^{13}C NMR (125 MHz) spectrum of **2n** in $CDCl_3$

(E)-(1,4-di(thiophen-2-yl)but-1-en-3-yn-2-yl)phenylsilane (2o)

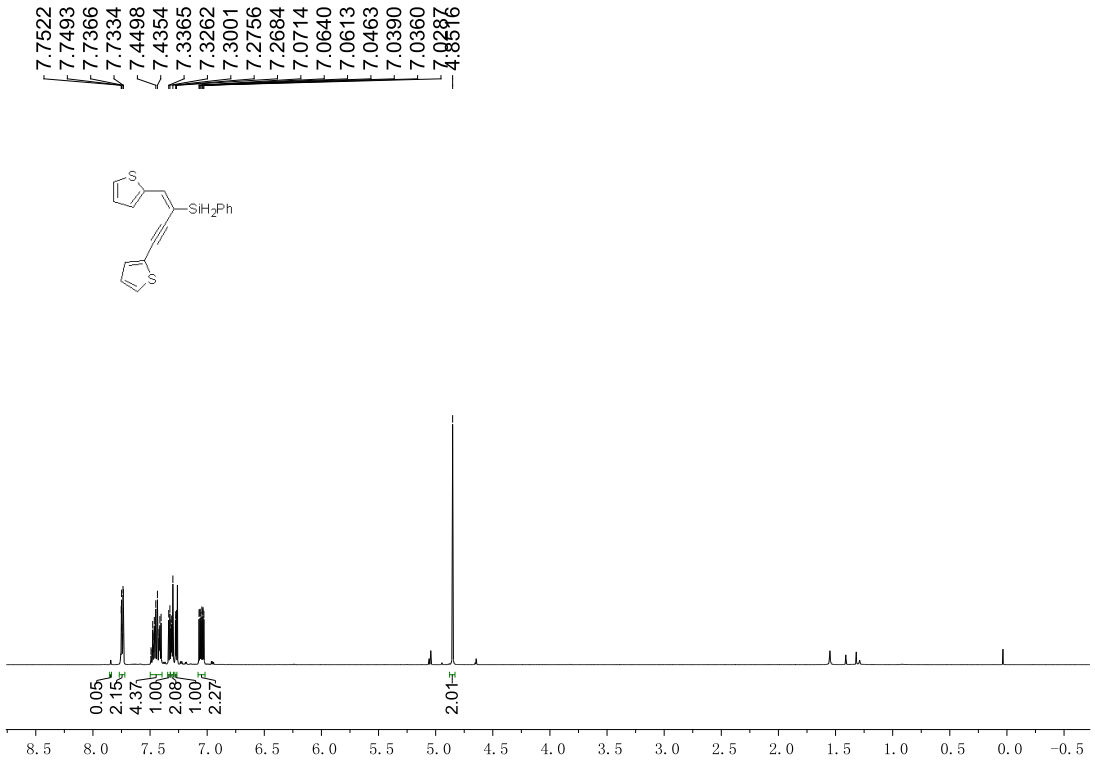


Figure S34. ^{1}H NMR (500 MHz) spectrum of **2o** in $CDCl_3$

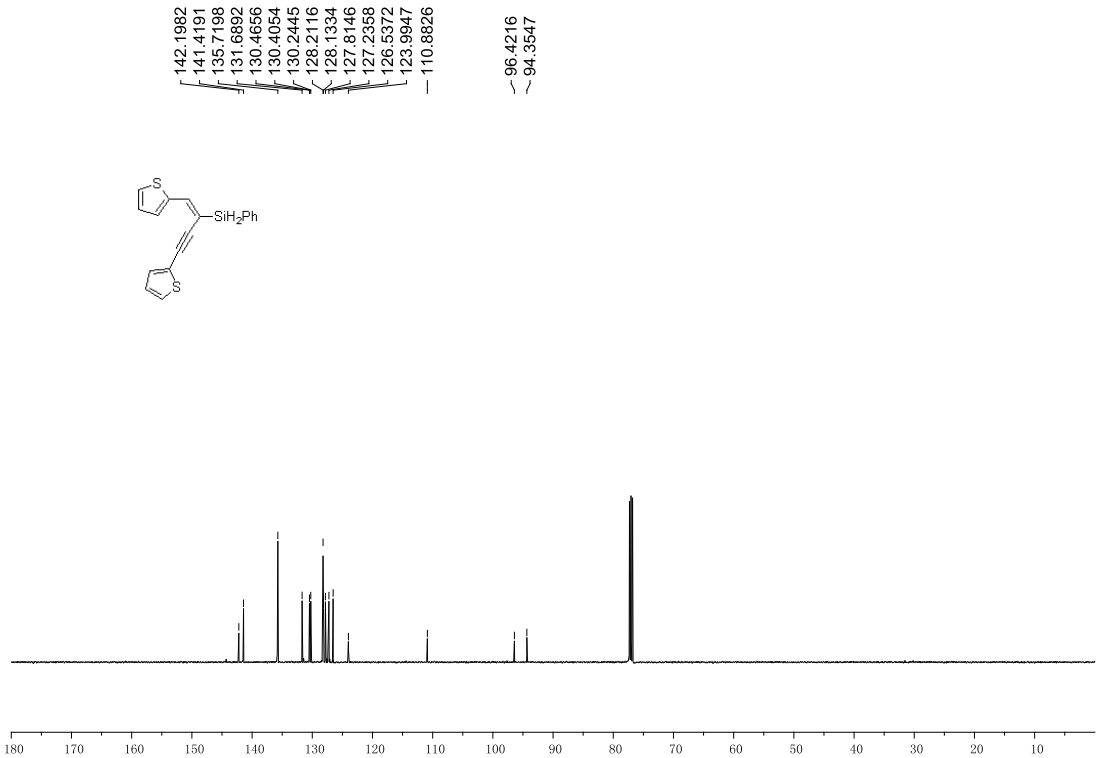


Figure S35 ^{13}C NMR (125 MHz) spectrum of **2o** in $CDCl_3$

(E)-3,3'-(2-(phenylsilyl)but-1-en-3-yne-1,4-diyl)dipyridine (2p)

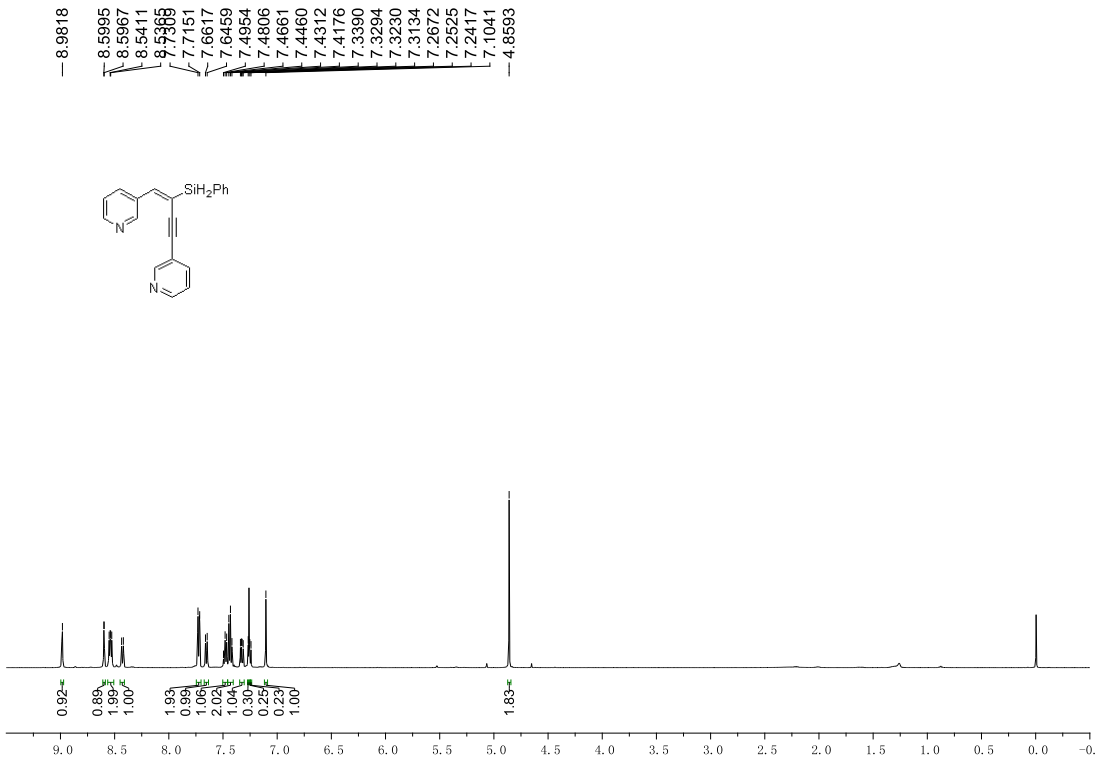


Figure S36. ^{1}H NMR (500 MHz) spectrum of **2p** in $CDCl_3$

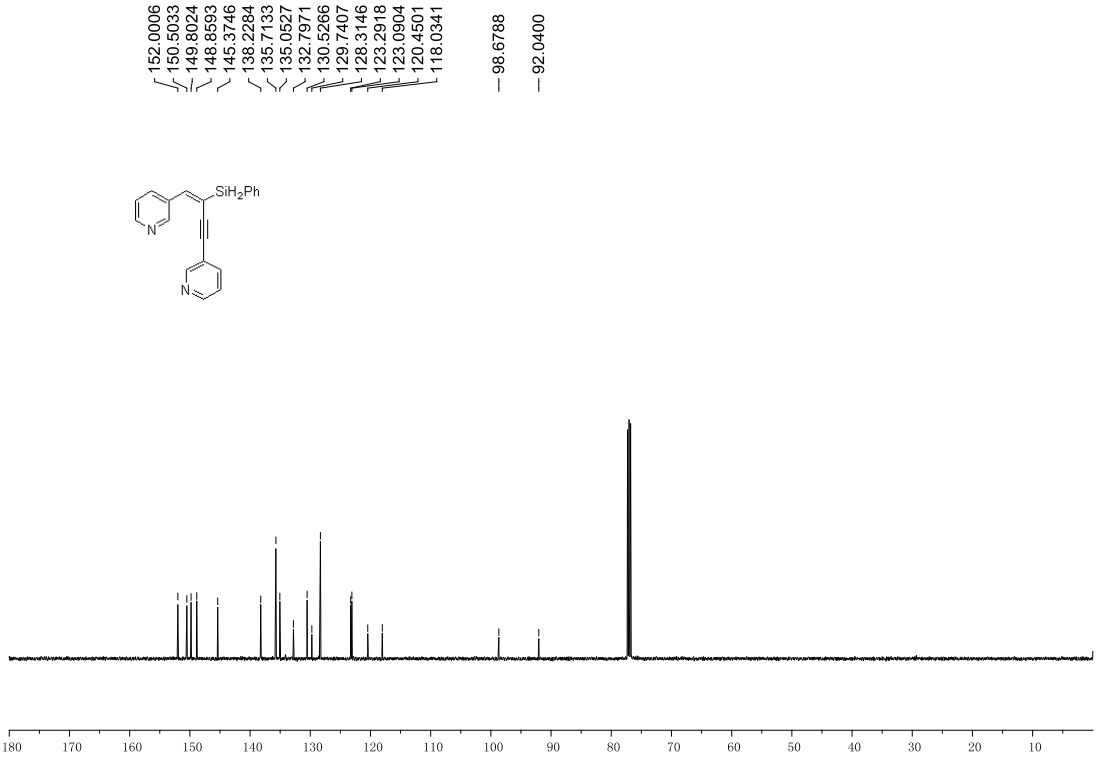


Figure S37 ^{13}C NMR (125 MHz) spectrum of **2p** in $CDCl_3$

(E)-dodec-5-en-7-yn-6-yl-phenylsilane (2q)

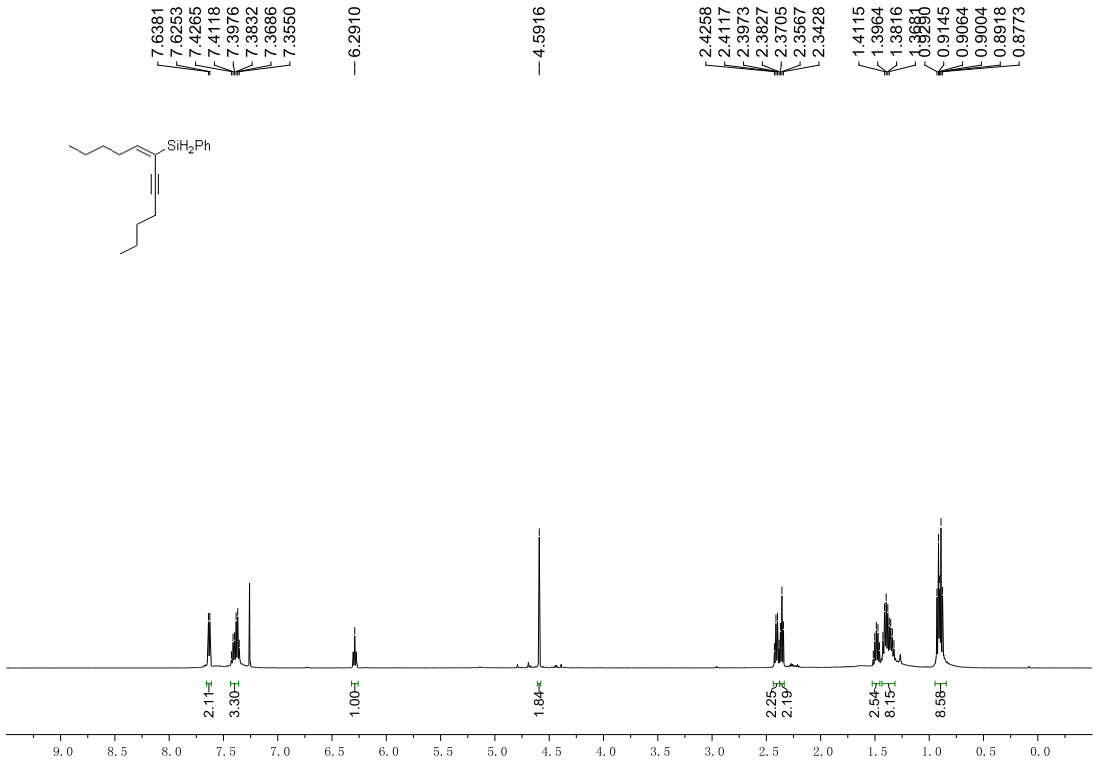


Figure S38. ^{1}H NMR (500 MHz) spectrum of **2q** in $CDCl_3$

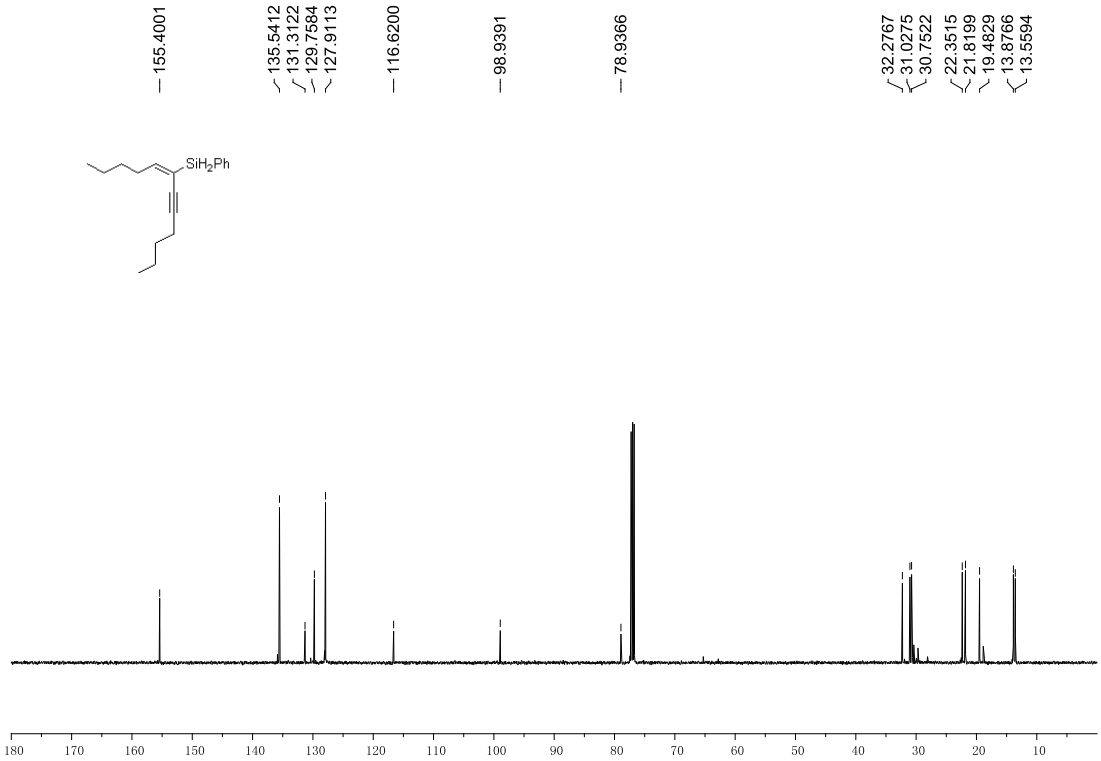


Figure S39 ^{13}C NMR (125 MHz) spectrum of **2q** in $CDCl_3$

(E)-tetracos-11-en-13-yn-12-yl-phenylsilane (2r)

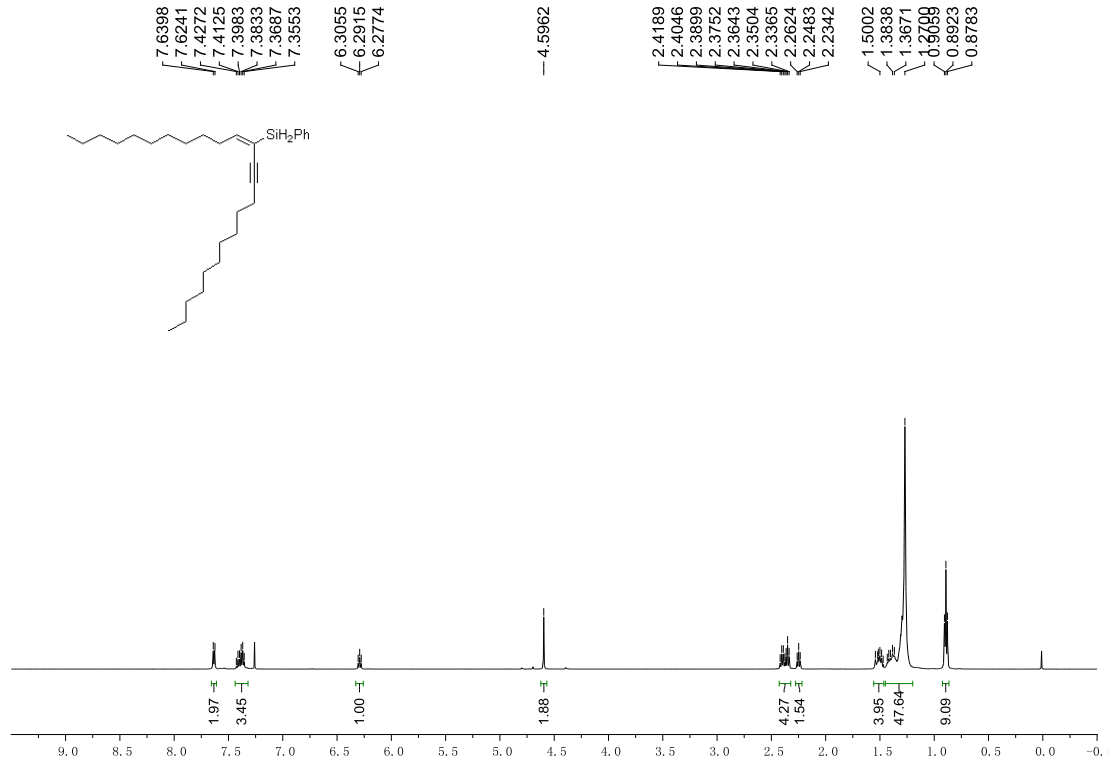


Figure S40. ^{1}H NMR (500 MHz) spectrum of **2r** in $CDCl_3$

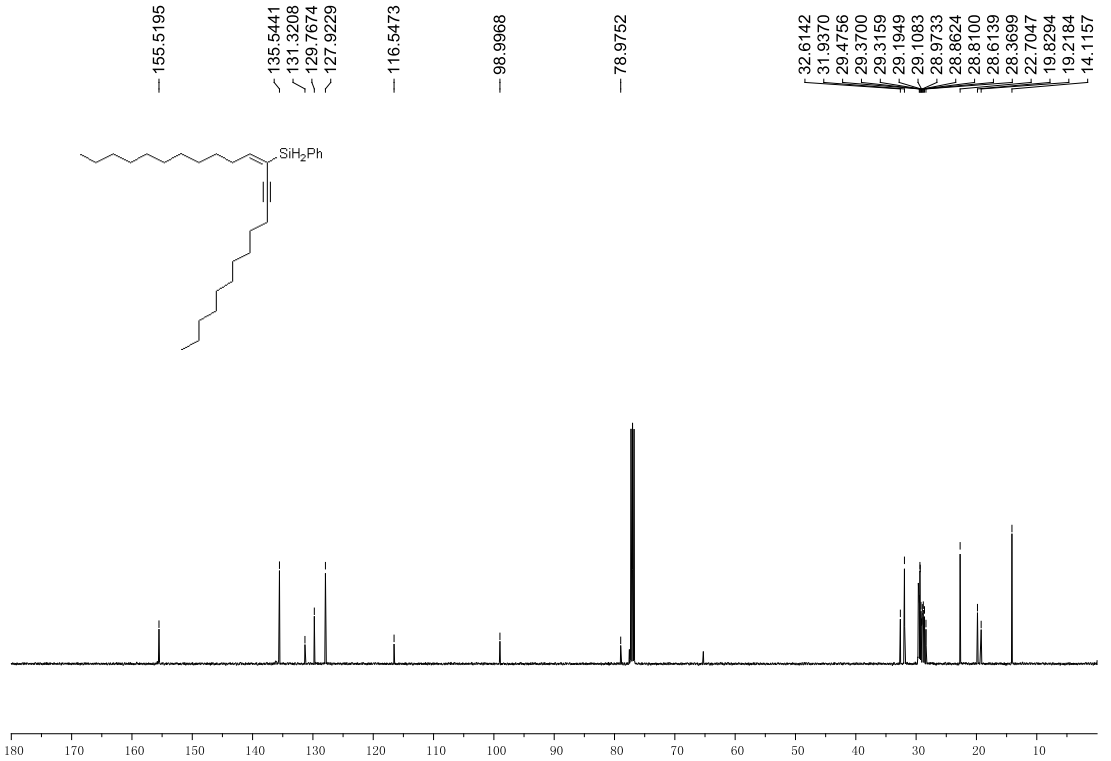


Figure S41 ^{13}C NMR (125 MHz) spectrum of **2r** in $CDCl_3$

(E)-trimethyl(3-(phenylsilyl)-4-(p-tolyl)but-3-en-1-yn-1-yl)silane (2s)

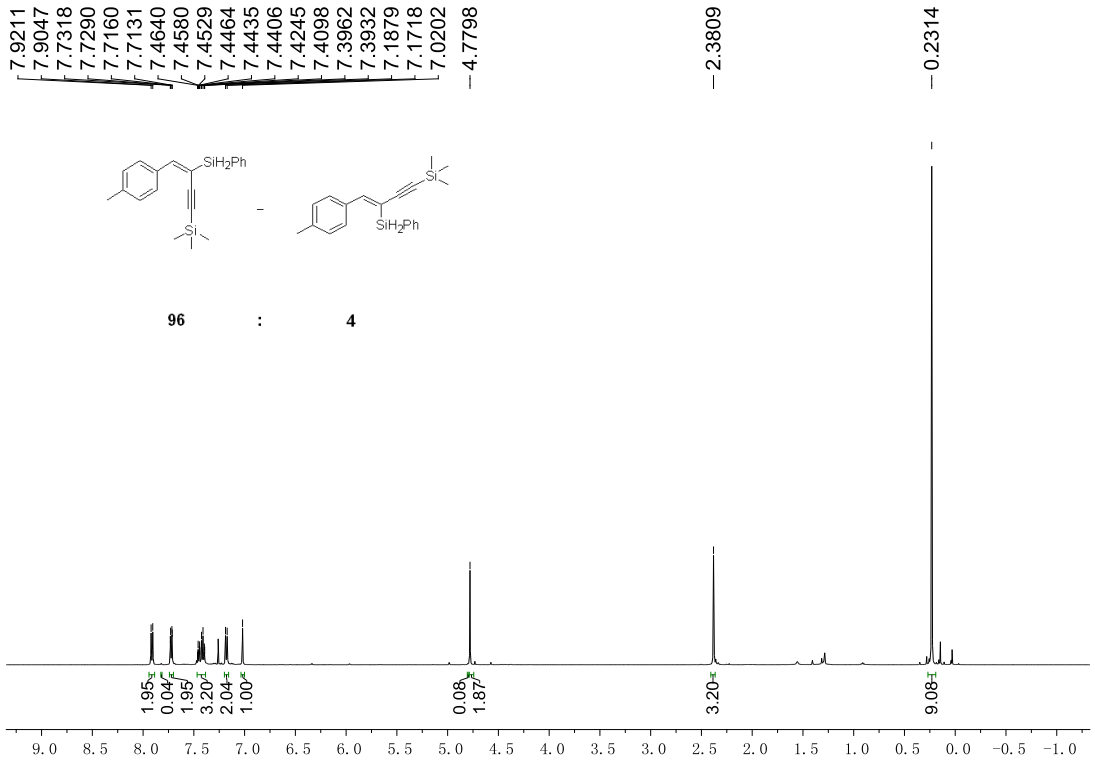


Figure S42. ^{1}H NMR (500 MHz) spectrum of **2s** in $CDCl_3$

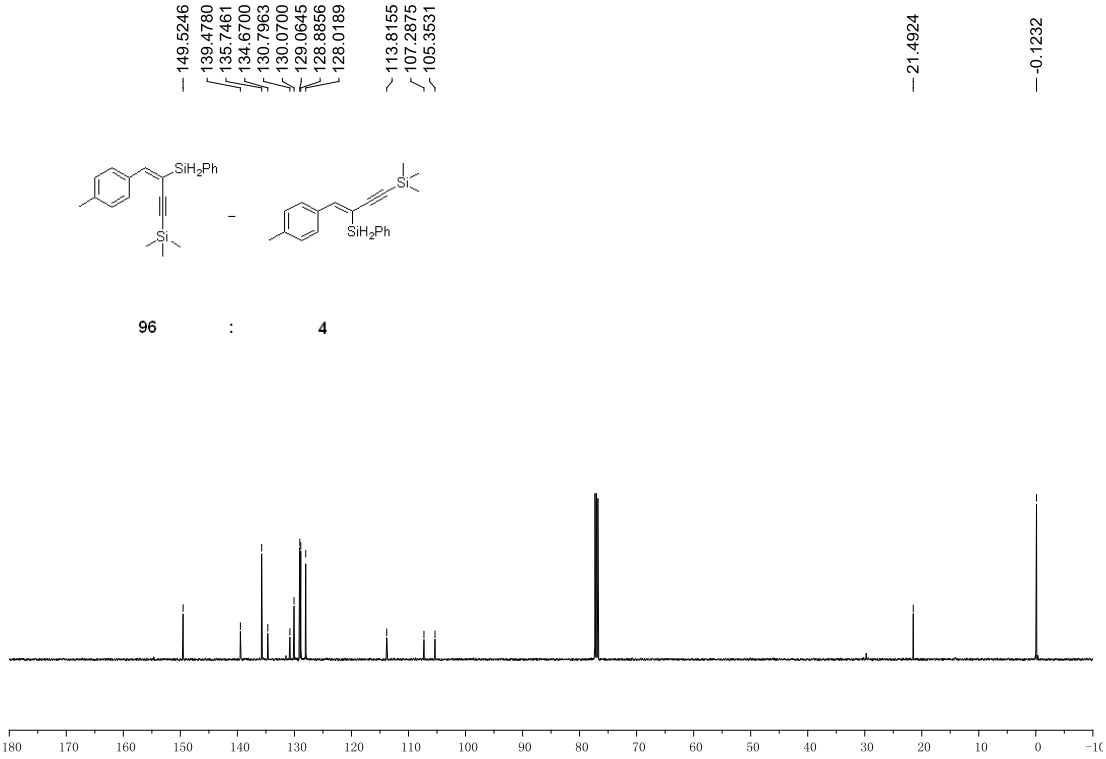


Figure S43 ^{13}C NMR (125 MHz) spectrum of **2s** in $CDCl_3$

(E)-(4-(4-(tert-butyl)phenyl)-3-(phenylsilyl)but-3-en-1-yn-1-yl)trimethylsilane (2t)

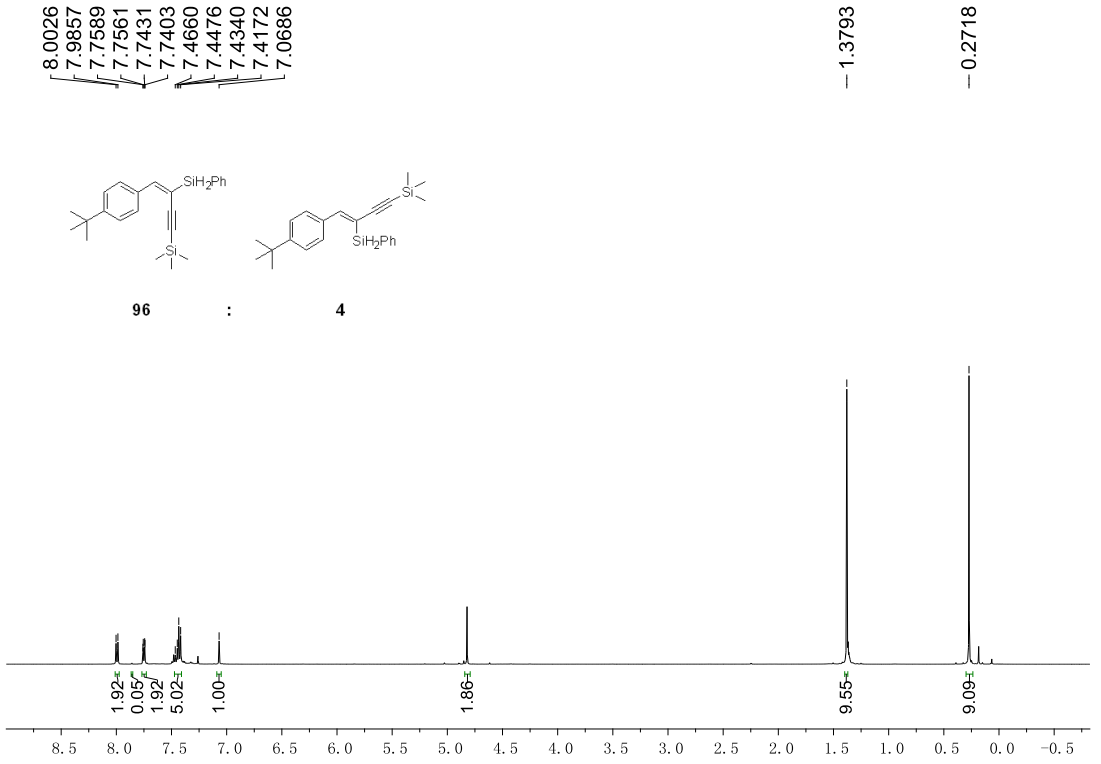


Figure S44. ^{1}H NMR (500 MHz) spectrum of **2t** in $CDCl_3$

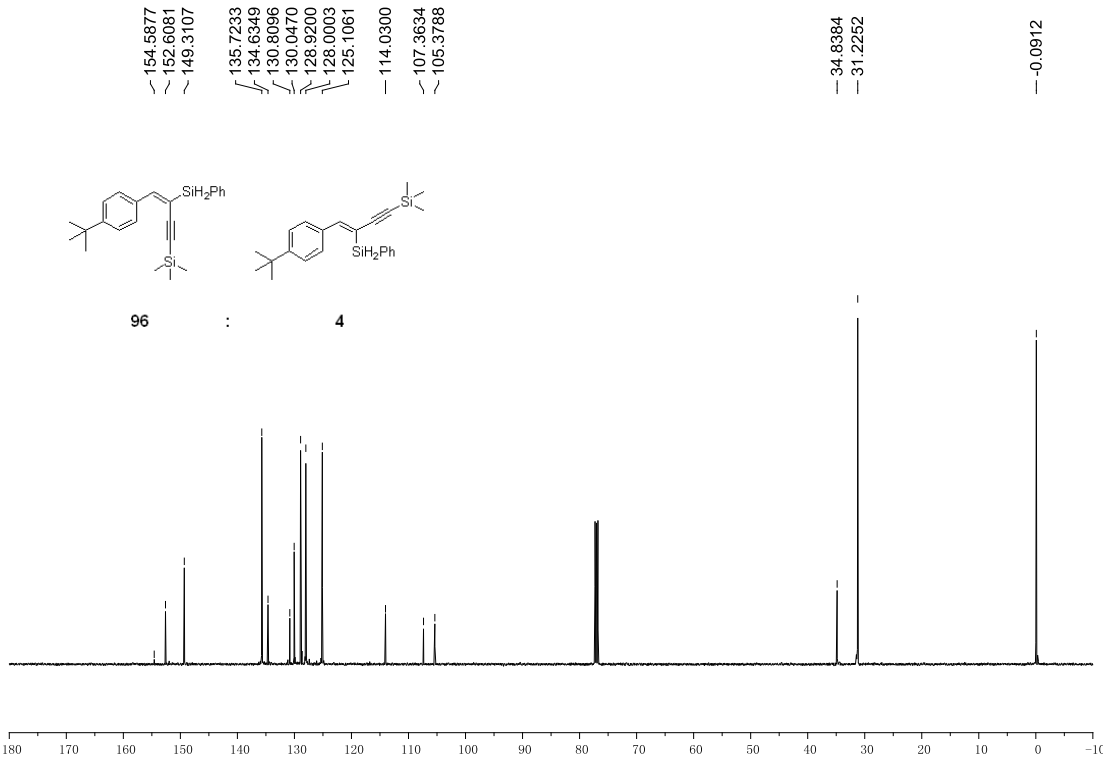


Figure S45 ^{13}C NMR (125 MHz) spectrum of **2t** in $CDCl_3$

(E)-(1-(4-methoxyphenyl)oct-1-en-3-yn-2-yl)phenylsilane (2u)

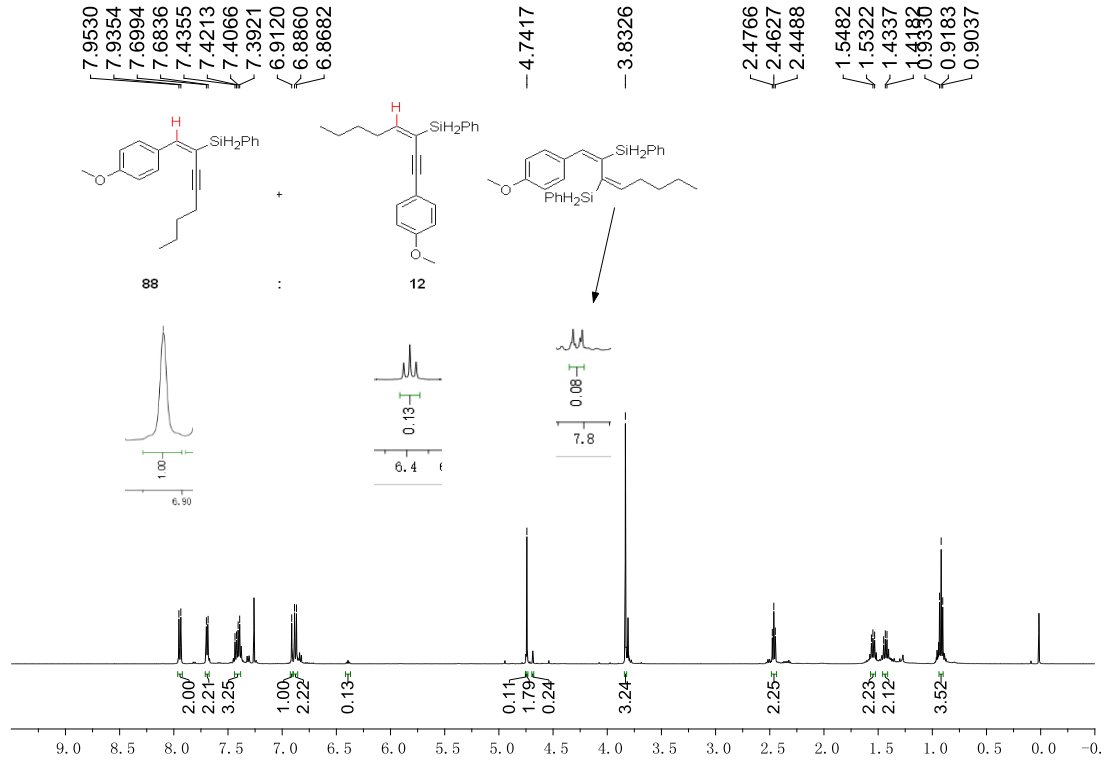


Figure S46. ^{1}H NMR (500 MHz) spectrum of **2u** in $CDCl_3$

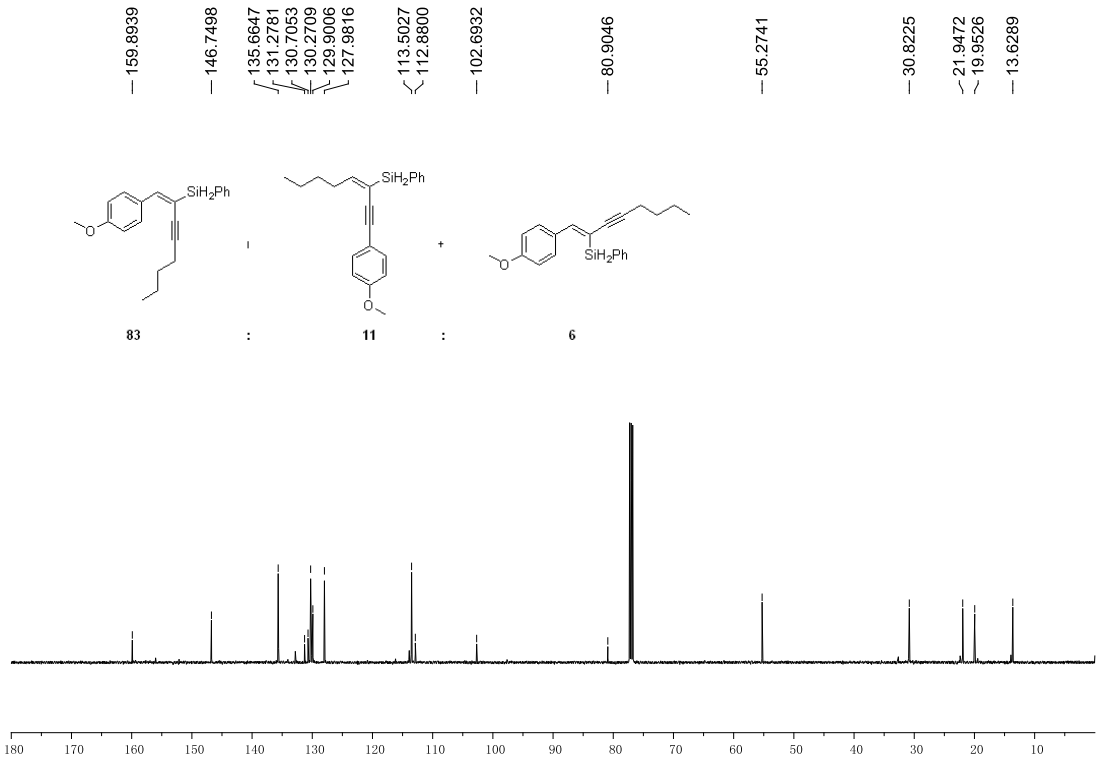


Figure S47 ^{13}C NMR (125 MHz) spectrum of **2u** in $CDCl_3$

(E)-(1,4-diphenylbut-1-en-3-yn-2-yl)diphenylsilane (4a)

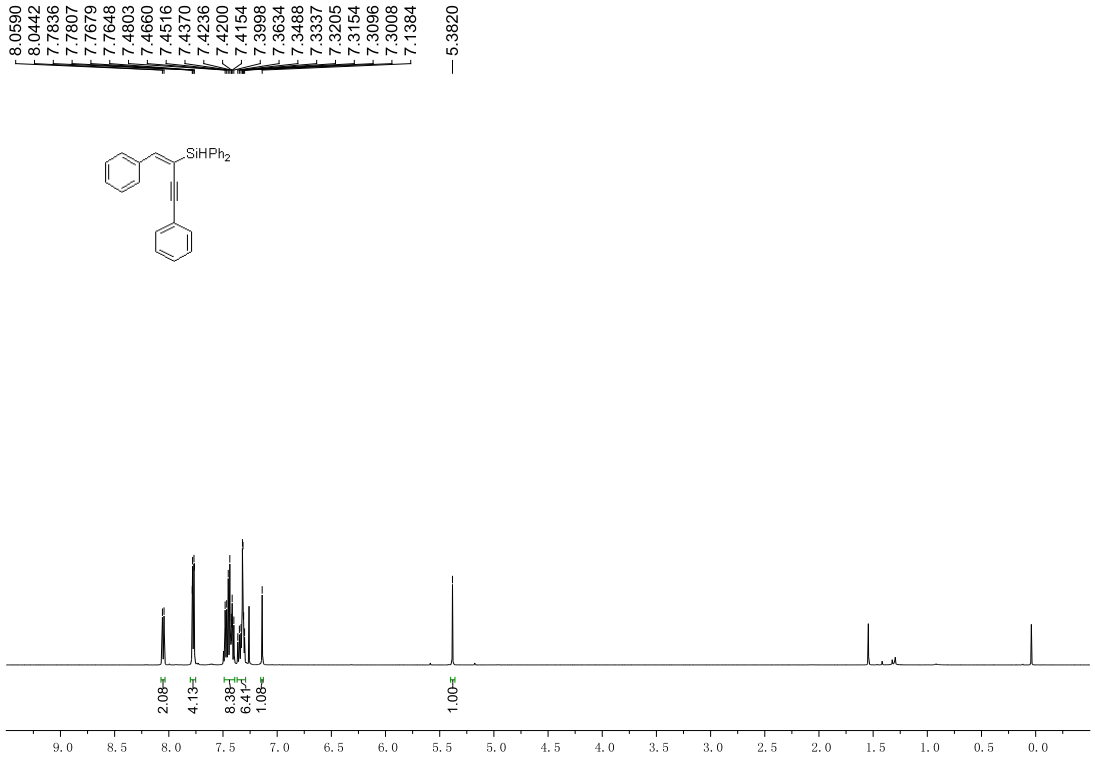


Figure S48. ^{1}H NMR (500 MHz) spectrum of **4a** in $CDCl_3$

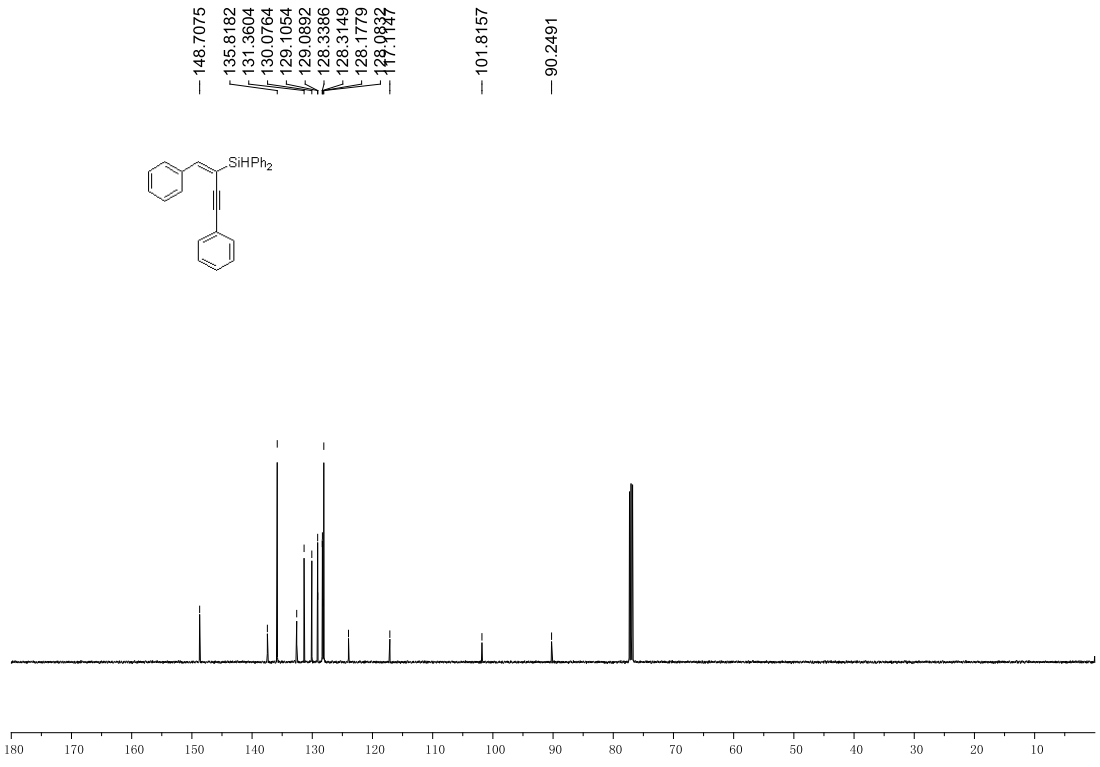


Figure S49 ^{13}C NMR (125 MHz) spectrum of **4a** in $CDCl_3$

(E)-(1,4-di-m-tolylbut-1-en-3-yn-2-yl)diphenylsilane (4b)

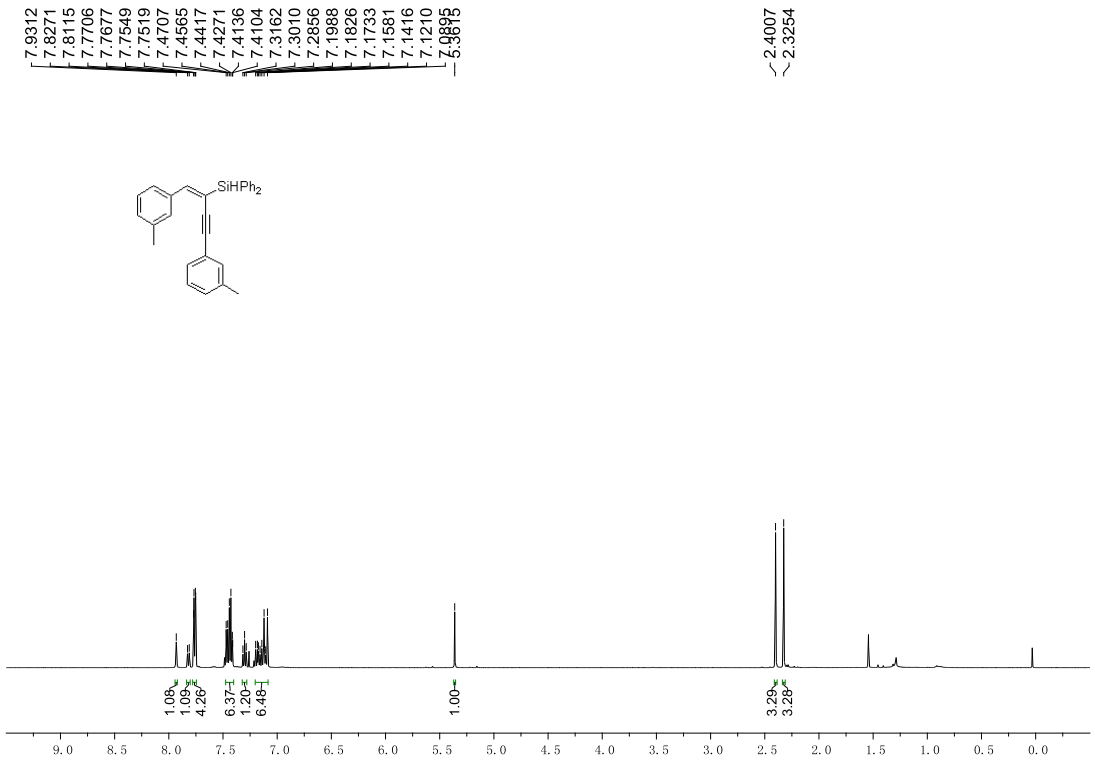


Figure S50. ^{1}H NMR (500 MHz) spectrum of **4b** in $CDCl_3$

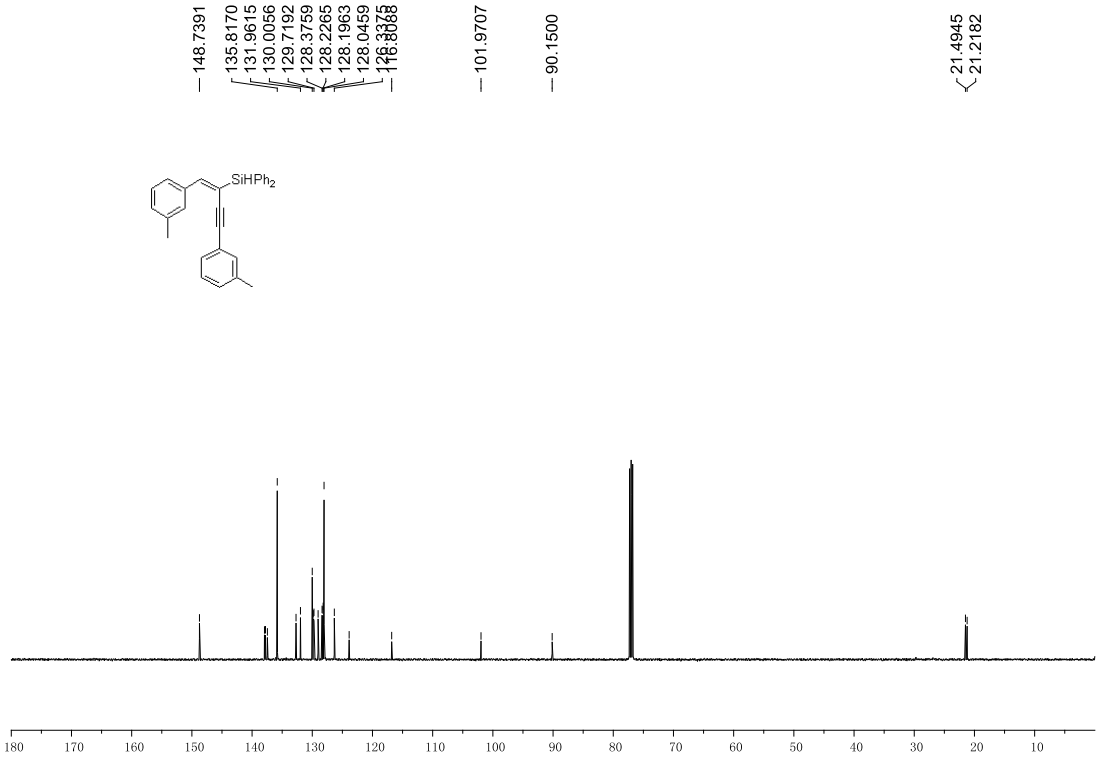


Figure S51 ^{13}C NMR (125 MHz) spectrum of **4b** in $CDCl_3$

(E)-(1,4-bis(3-methoxyphenyl)but-1-en-3-yn-2-yl)diphenylsilane (4c)

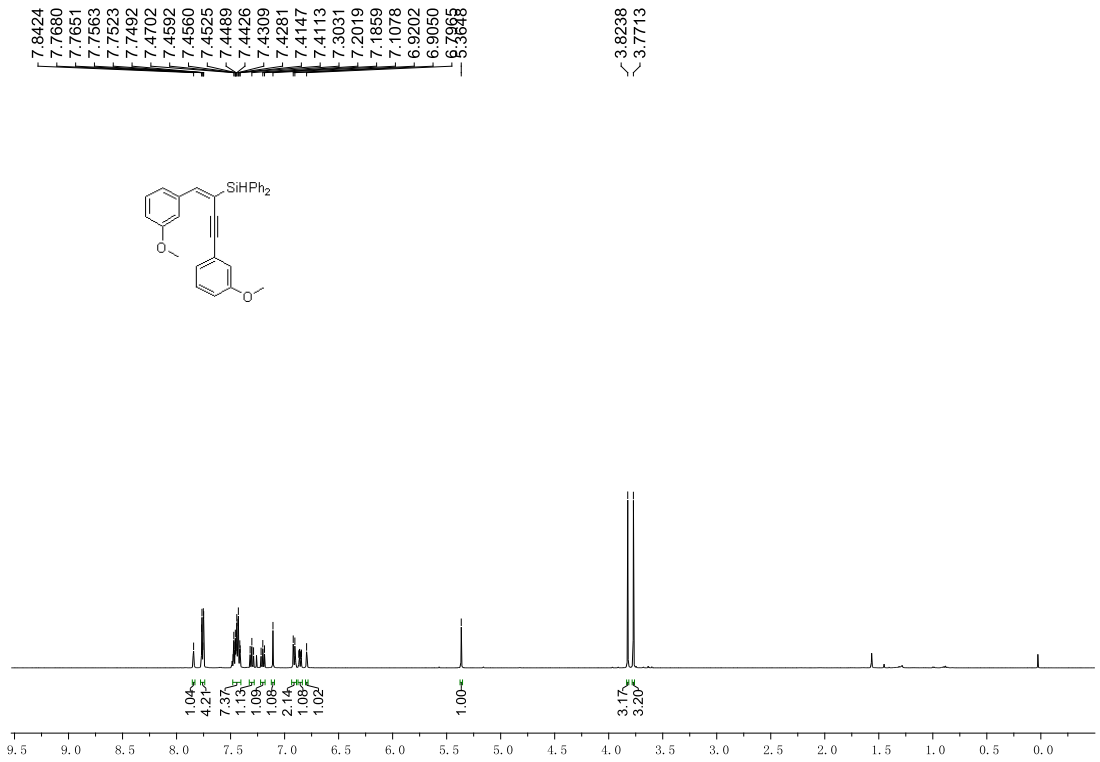


Figure S52. ^{1}H NMR (500 MHz) spectrum of **4c** in $CDCl_3$

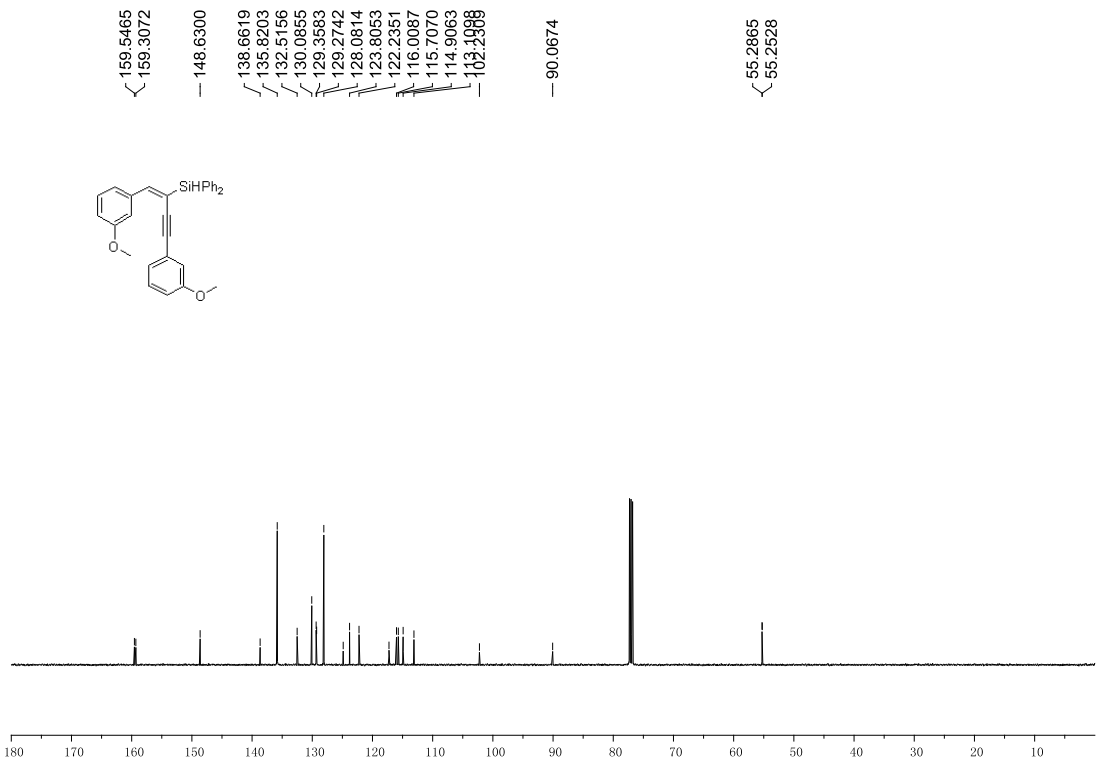


Figure S53 ^{13}C NMR (125 MHz) spectrum of **4c** in $CDCl_3$

(E)-(1,4-di(thiophen-3-yl)but-1-en-3-yn-2-yl)diphenylsilane (4d)

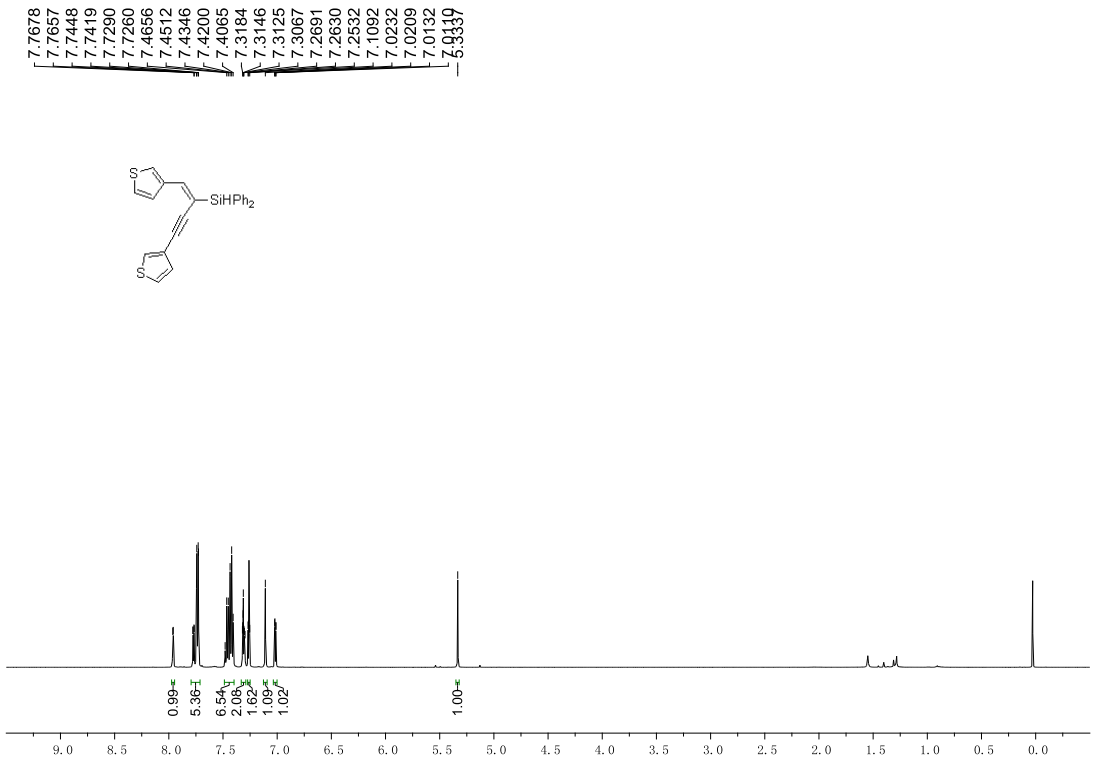


Figure S54. ^{1}H NMR (500 MHz) spectrum of **4d** in $CDCl_3$

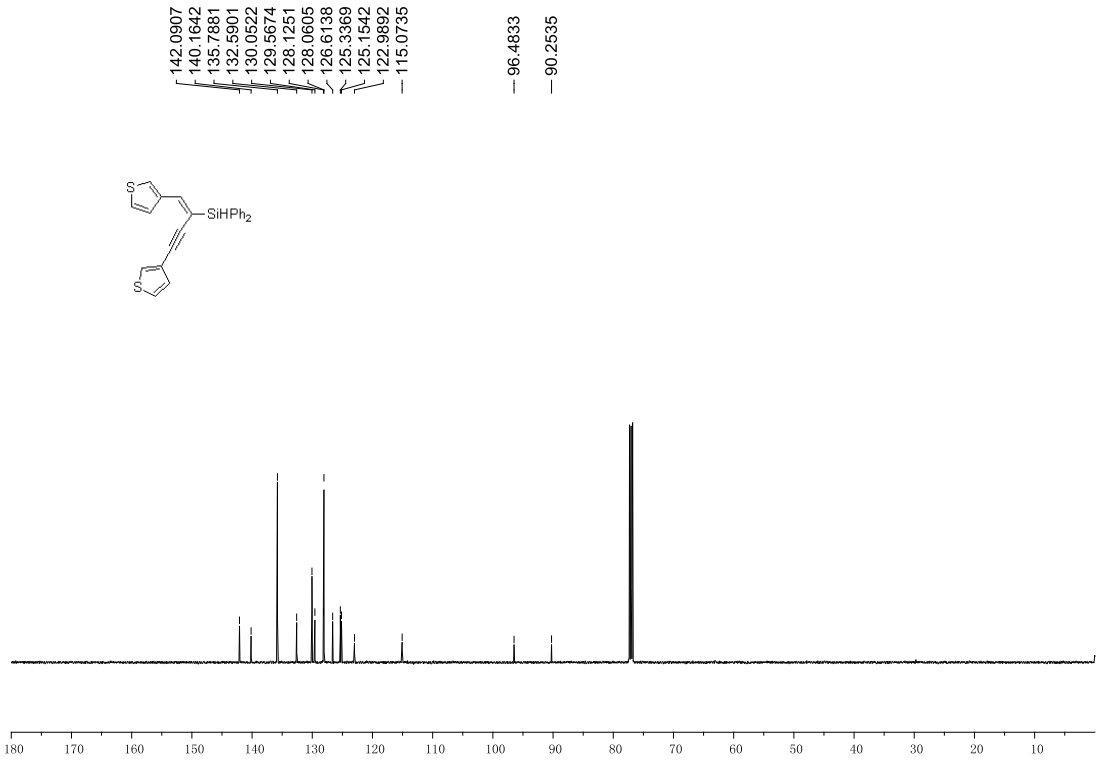


Figure S55 ^{13}C NMR (125 MHz) spectrum of **4d** in $CDCl_3$

(E)-dodec-5-en-7-yn-6-yldiphenylsilane (4e)

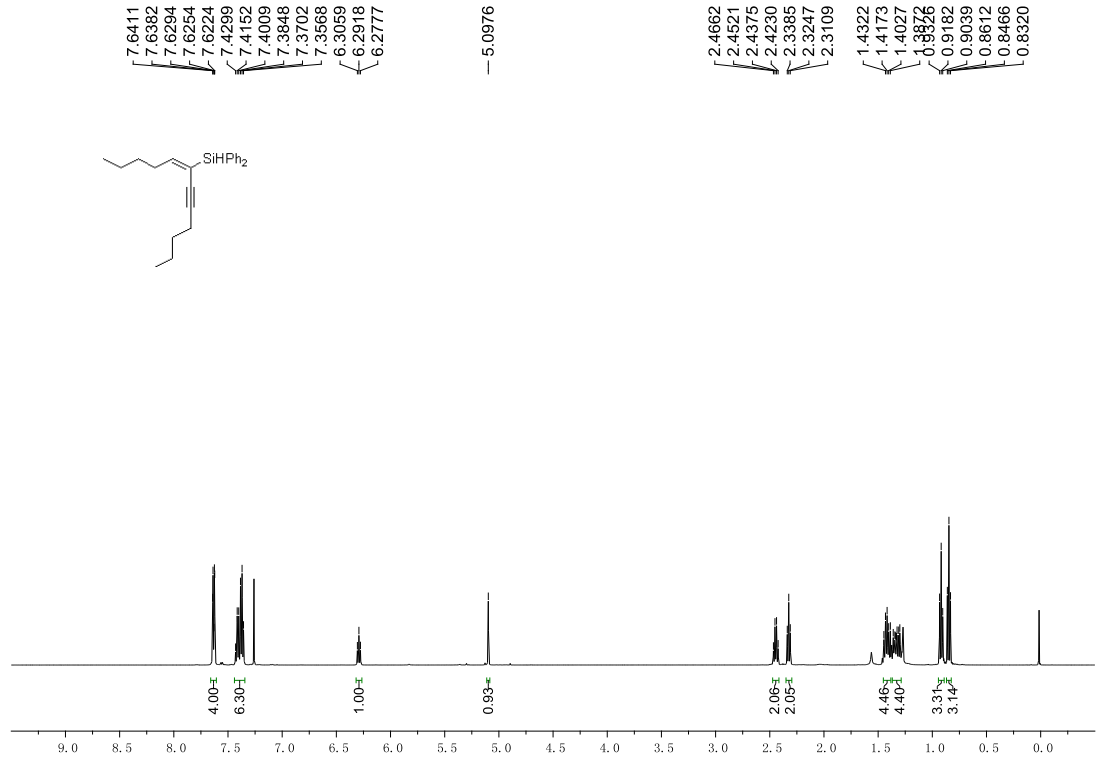


Figure S56. ^{1}H NMR (500 MHz) spectrum of **4e** in $CDCl_3$

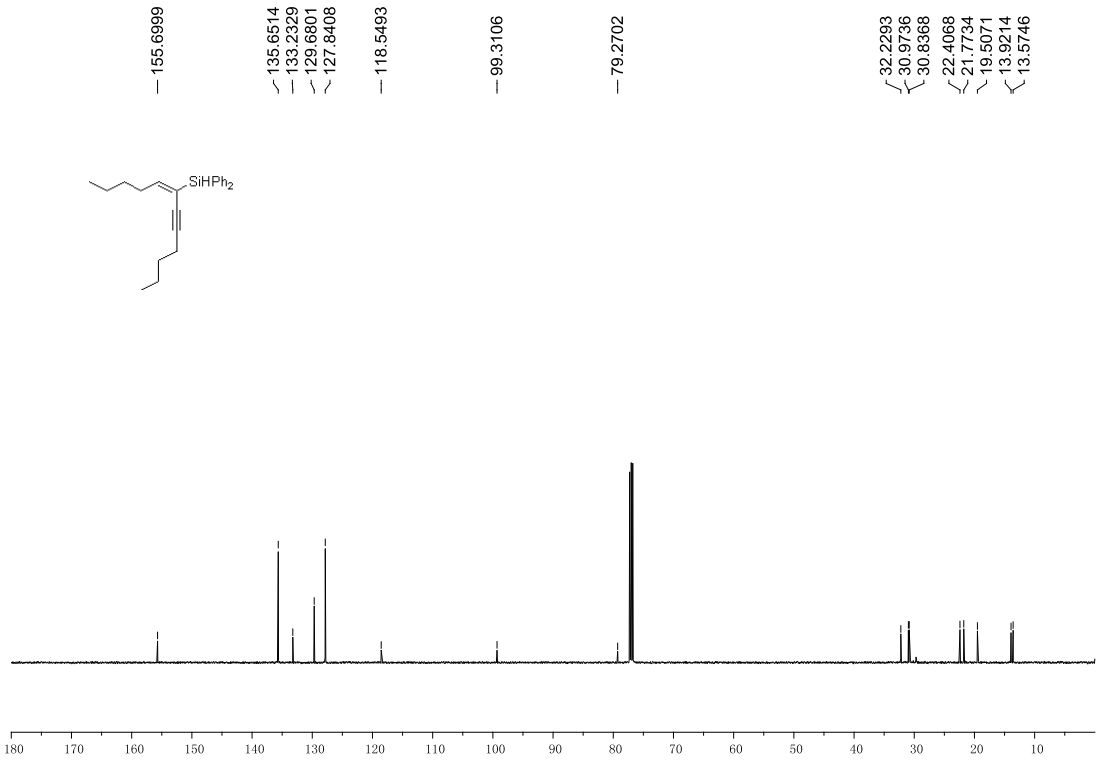


Figure S57 ^{13}C NMR (125 MHz) spectrum of **4e** in $CDCl_3$

(E)-(3-(diphenylsilyl)-4-(p-tolyl)but-3-en-1-yn-1-yl)trimethylsilane (4f)

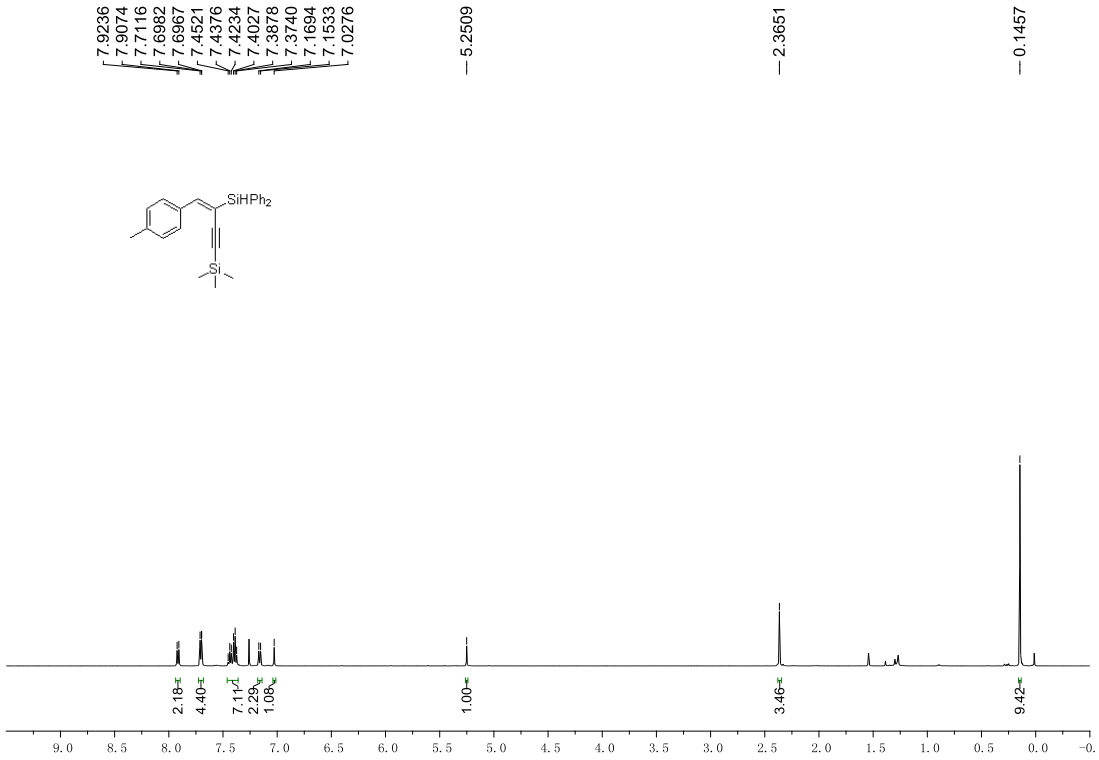


Figure S58. ^{1}H NMR (500 MHz) spectrum of **4f** in $CDCl_3$

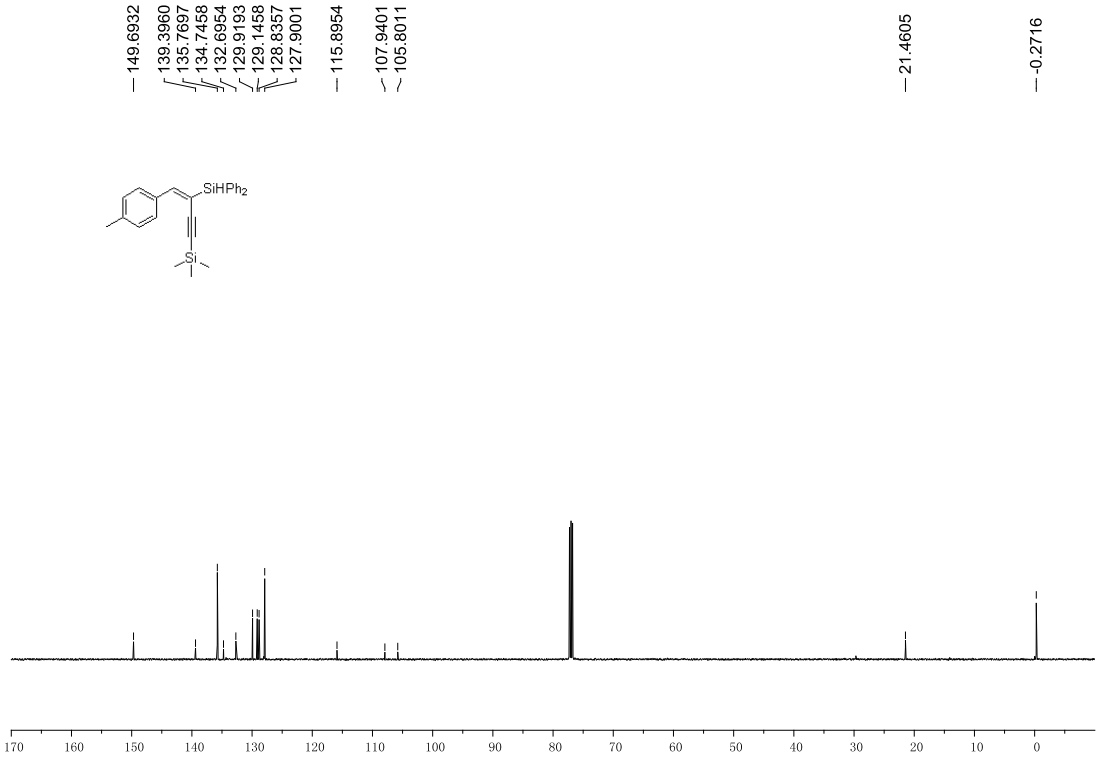


Figure S59 ^{13}C NMR (125 MHz) spectrum of **4f** in $CDCl_3$

(Z)-but-1-en-3-yne-1,4-diyldibenzene (6)

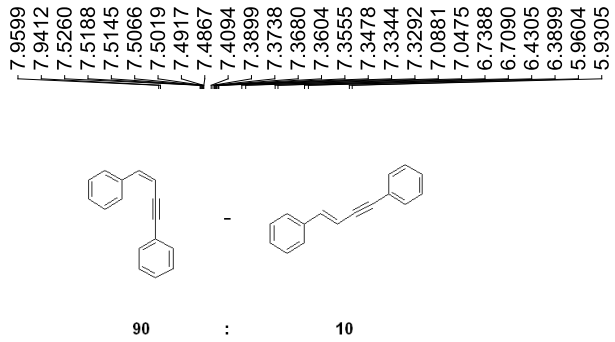


Figure S60. ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$

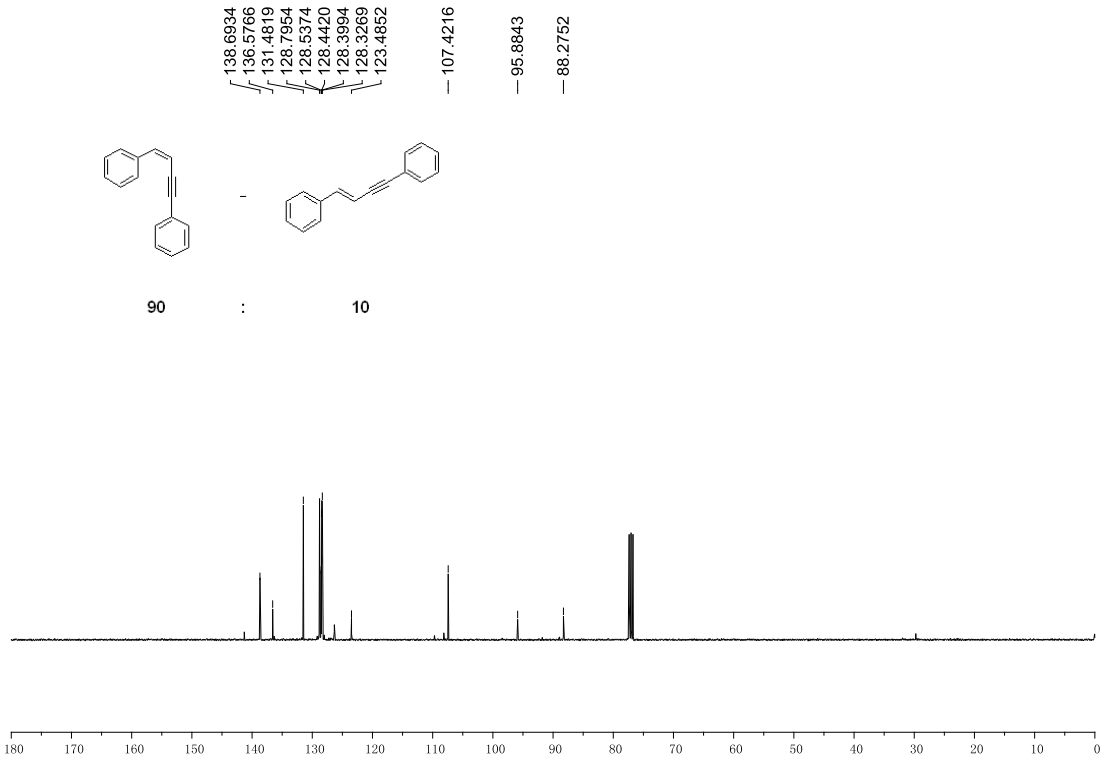


Figure S61 ^{13}C NMR (100 MHz) spectrum of 6 in $CDCl_3$

1,4-diphenylbut-3-yn-2-one (7)

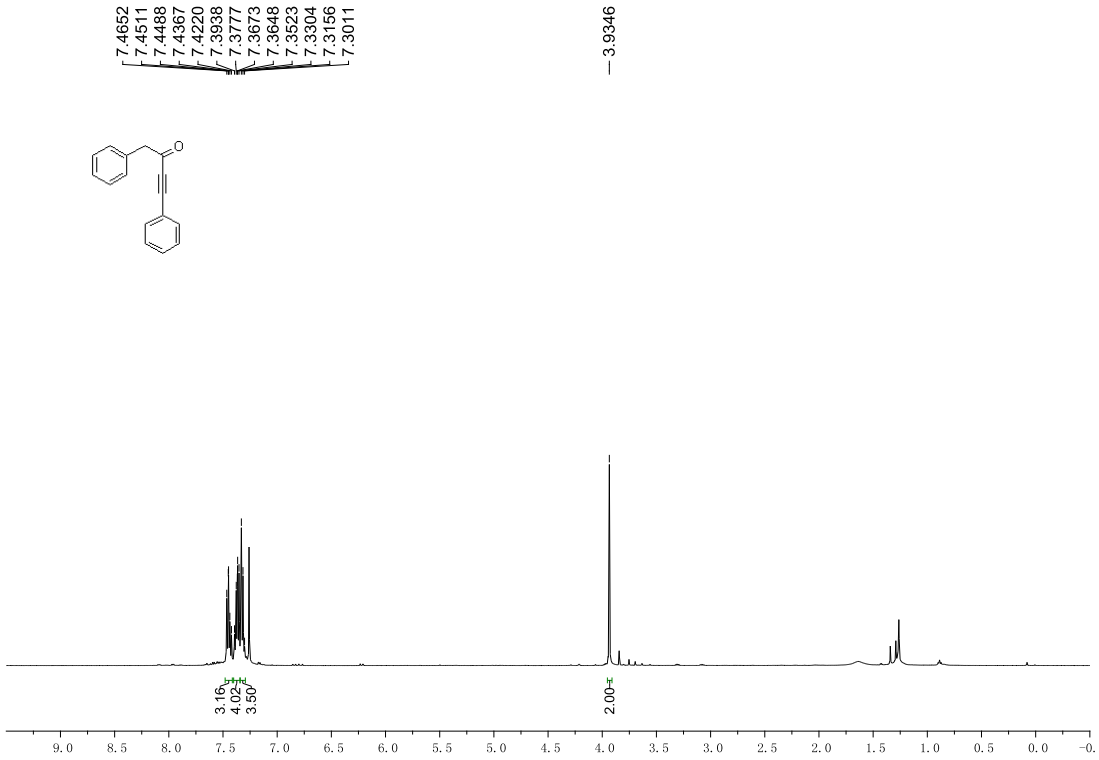


Figure S62. ^{1}H NMR (500 MHz) spectrum of **7** in $CDCl_3$

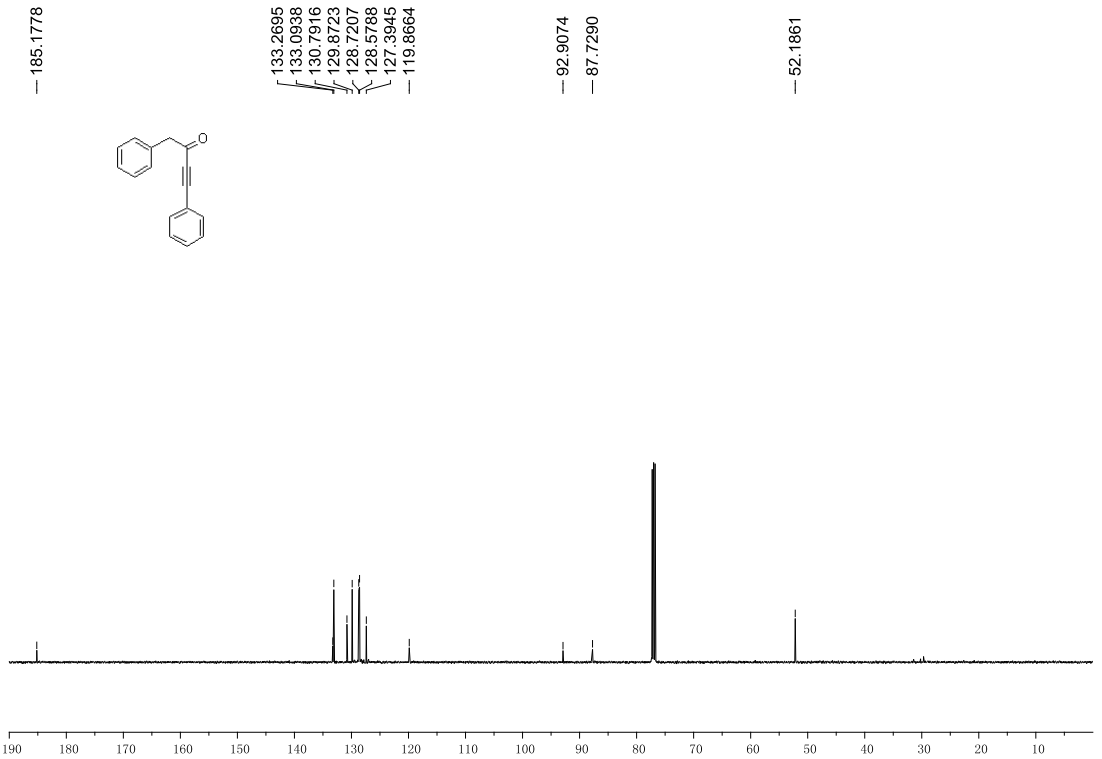


Figure S63 ^{13}C NMR (125 MHz) spectrum of **7** in $CDCl_3$

***(E)*-(1,4-bis(4-(*tert*-butyl)phenyl)but-1-en-3-yn-2-yl)(phenyl)(1-phenylvinyl)silane (8)**

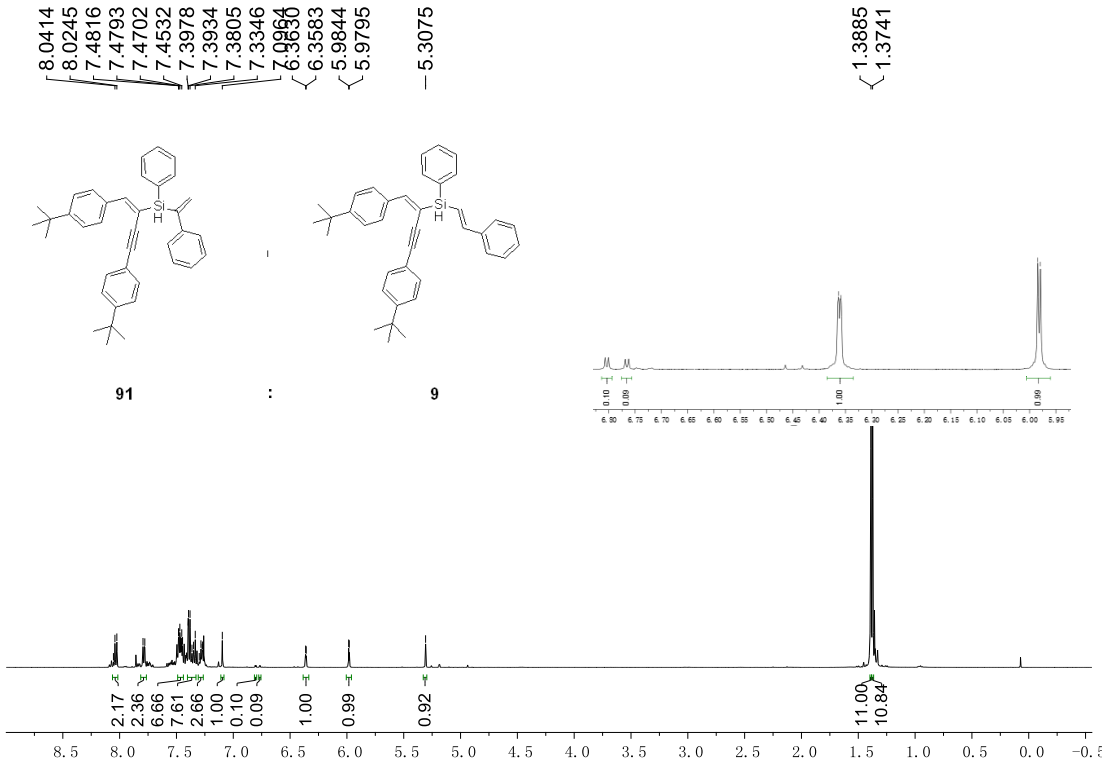


Figure S64. ^{1}H NMR (500 MHz) spectrum of **8** in $CDCl_3$

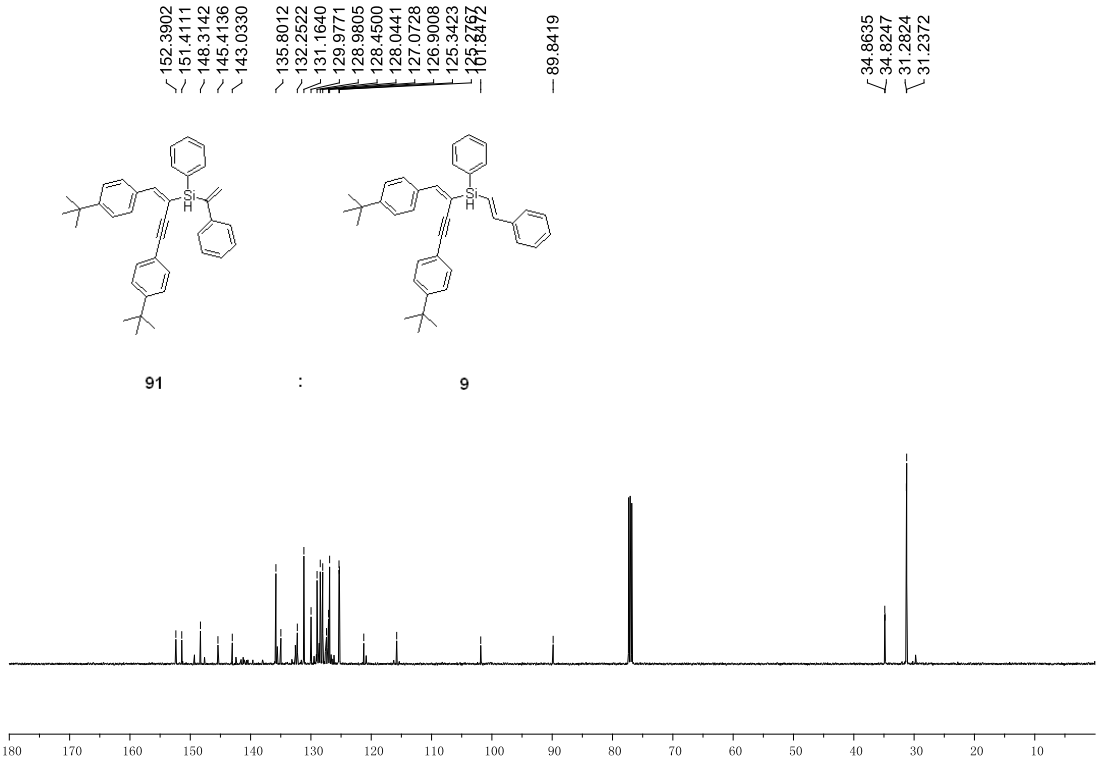


Figure S65 ^{13}C NMR (125 MHz) spectrum of **8** in $CDCl_3$

((*E*)-1,4-bis(4-(*tert*-butyl)phenyl)but-1-en-3-yn-2-yl)((*E*)-1,4-diphenylbut-1-en-3-yn-2-yl)phenylsilane (9)

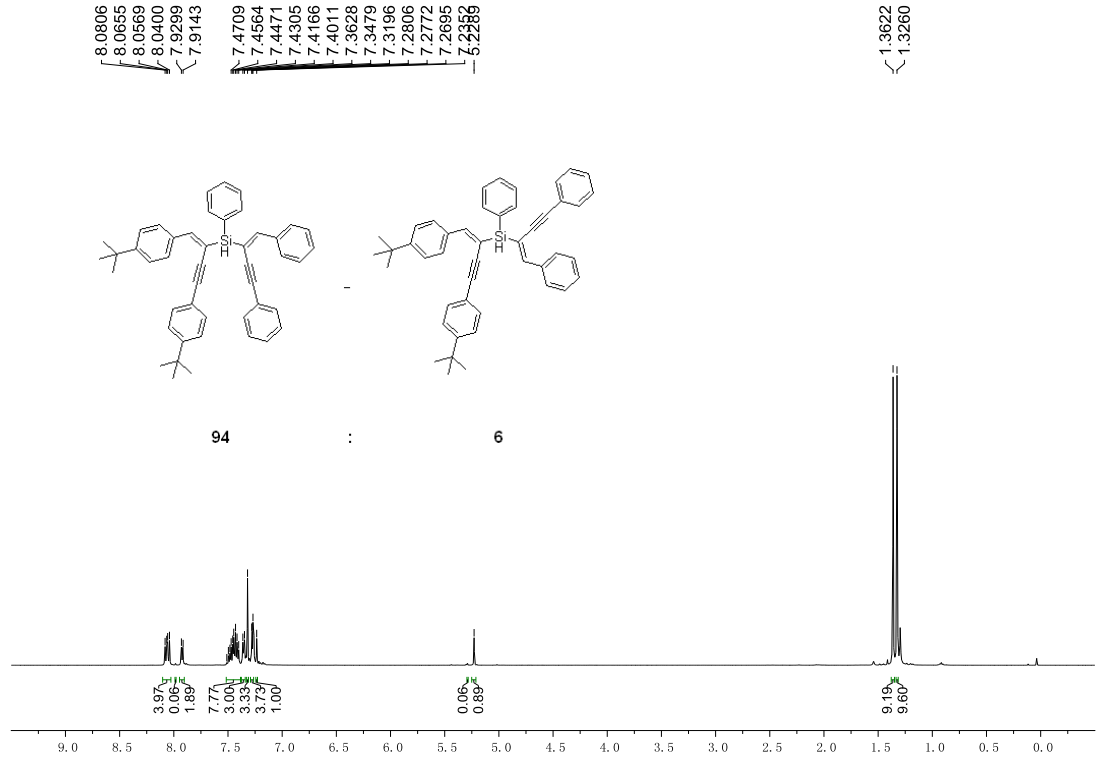


Figure S66. ^{1}H NMR (500 MHz) spectrum of **9** in $CDCl_3$

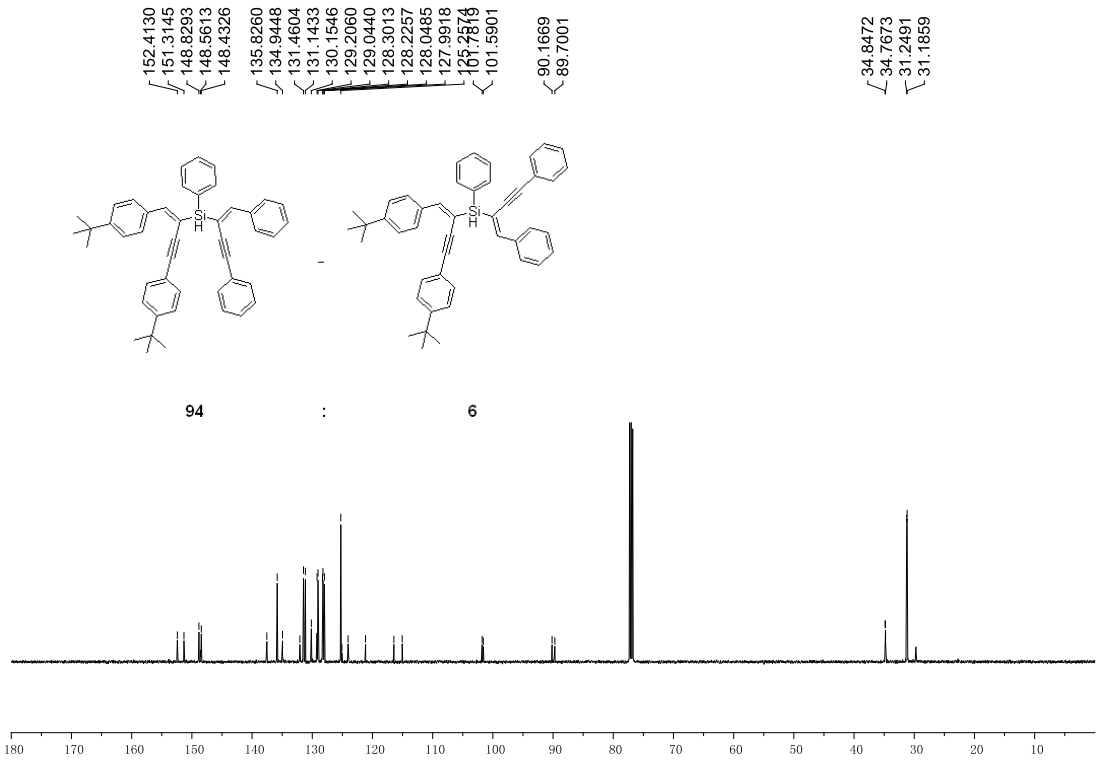


Figure S67 ^{13}C NMR (125 MHz) spectrum of **9** in $CDCl_3$

7. References

1. D. Kong, B. Hu, M. Yang, D. Chen and H. Xia, Highly Regio- and Stereoselective Tridentate NCNN Cobalt-Catalyzed 1,3-Diyne Hydrosilylation, *Organometallics*, 2019, **38**, 4341-4350.
2. H. L. Sang, Y. Hu and S. Ge, Cobalt-Catalyzed Regio- and Stereoselective Hydrosilylation of 1,3-Diynes To Access Silyl-Functionalized 1,3-Enynes, *Org Lett*, 2019, **21**, 5234-5237.