Cu-Catalyzed Regiodivergent and Stereospecific Silylation of 2,3-Disubstituted 1,3-Dienes

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried (100°C) or in anhydrous solvents under N_2, applying standard Schlenk techniques. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added through a weak N_2 counter-flow. Cooling baths were prepared in Dewar vessels, filled with ice/water (0°C), cooled acetone (> -78°C) or dry ice/acetone (-78°C). Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40 °C using a rotary eva*p*orator, and unless otherwise stated, the remaining compound was dried in high vacuum at ambient temperature. All given yields are isolated yields of chromatographically and NMR spectroscopically pure materials, unless otherwise stated.

Chemicals

Chemicals were purchased from commercial suppliers (including Energy Chemical, Bidepharm, Aladdin, Meryer, Sinopharm) and used without further purification unless otherwise stated.

Solvents

Solvents (CH_2Cl_2, $CHCl_3$, Et_2O, THF) were dried by distillation from an appropriate drying agent. In addition, more solvents (acetone, DMF, DMSO, EtOAc, EtOH, MeOH, MTBE, *n*-hexane) were purchased from commercial suppliers and dried over molecular sieves.

Gas

Dry N_2 were purchased from Hangzhou Jingong Materials with > 99.9% purity.

Column Chromatography

Column chromatography (CC) was carried out using silica gel (60 Å, 230−400 mesh, particle size 0.040−0.063 mm) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy

^1H, ^{13}C, nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500, AV-400 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequency are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted, processed with program MestReNova 14.0, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^1H NMR spectra ($CDCl_3$ δ 7.26, THF δ 1.72, 3.58, C_6D_6 δ 7.16), and are

reported as follows: chemical shift δ in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.2, THF δ 67.21, 25.31, C_6D_6 δ 128.1). All spectra are broadband decoupled unless otherwise noted.

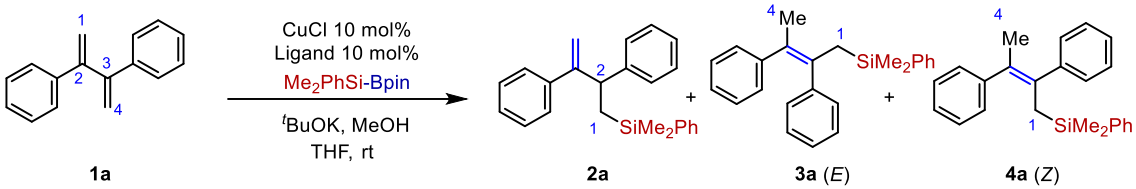
Mass Spectrometry

Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker micro QII-ESI-TOF. The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak.

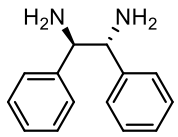
2. Reaction screening

Optimization of reaction conditions: In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with diene **1a** (20.6 mg, 0.1 mmol, 1 equiv.), *t*-BuOK (2.24 mg, 0.02mmol, 0.2 equiv), CuCl (1.0 mg, 0.01 mmol, 0.1 equiv), ligand (0.01 mmol, 0.1 equiv), then the mixture was dissolved in THF (0.5 mL). Next, Me_2PhSi-Bpin and MeOH (8 µL 0.2 mmol, 2 equiv) was added sequentially at room temperature. The reaction mixture was kept stirring for 4-12 h. The yields and conversions were determined by ^1H NMR analysis with dibromomethane as an internal standard. Ratios of isomers were determined by GC analysis.

Table S1. Optimization of the reaction



Entry	Ligands	[Si-B] (eq)	Conv. (%)	Yields (%)		rr	*E*:*Z*
				2a	**3a+4a**	**2a:(3a+4a)**	**3a:4a**
1	**L1**	1.5	96	15	77	1:5	4:1
2	**L2**	1.1	48	2	27	1:13	5:1
3	**L3**	1.1	85	11	71	1:6	2:1
4	**L4**	1.1	>99	30	69	2:1	2:1
5	**L5**	1.1	88	22	65	1:3	2:1
6	**L6**	1.1	>99	55	43	1:1	3:1
7	**L7**	1.1	57	15	30	1:2	2:1
8	**L8**	1.1	63	14	33	1:2	2:1
9	**L9**	1.1	21	20	-	>20:1	-
10	**L10**	1.1	32	3	27	1:9	1:5
11	**L11**	1.1	no rxn	-	-	-	-
12	**L12**	1.1	no rxn	-	-	-	-
13	**L13**	1.1	no rxn	-	-	-	-
14	**L14**	1.1	no rxn	-	-	-	-
15	**L15**	1.1	no rxn	-	-	-	-
16	**L16**	1.1	no rxn	-	-	-	-
17	**L17**	1.1	no rxn	-	-	-	-
18	**L18**	1.1	no rxn	-	-	-	-
19	PCy_3	1.1	69	54	4	14:1	-
20	PCy_3	1.3	>99	96	2	>20:1	-
21	PCy_3	1.5	87	78	9	9:1	3:1



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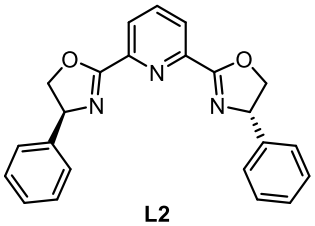

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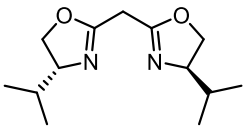

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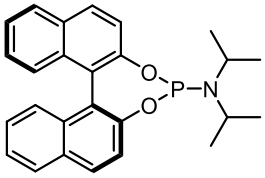

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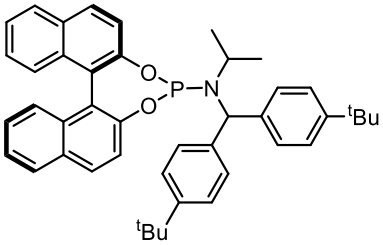

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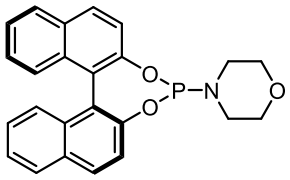

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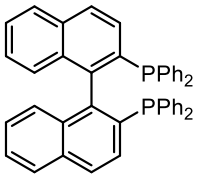

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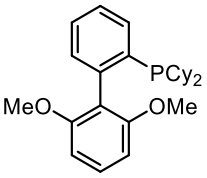

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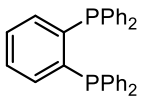

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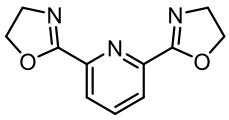

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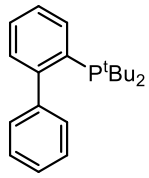

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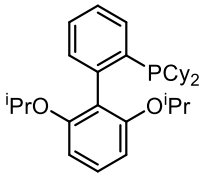

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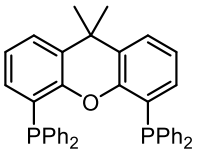

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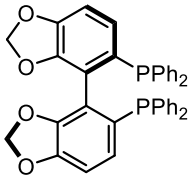

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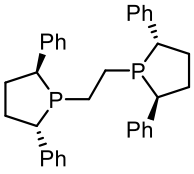

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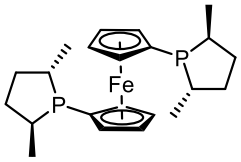

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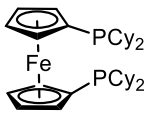

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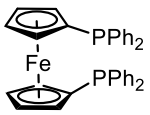
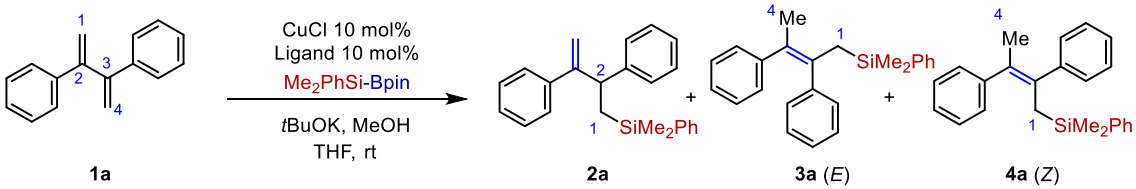


L18

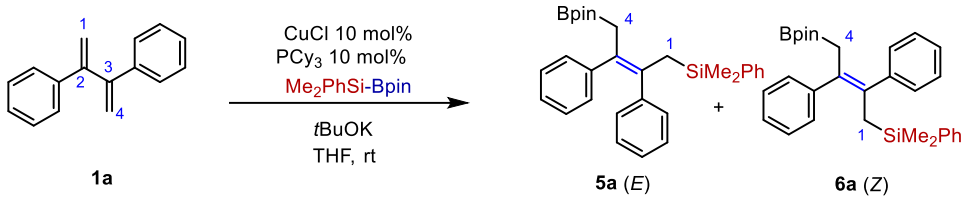
Table S2. Solvent optimization of the protosilylations.



1a **2a** **3a** (*E*) **4a** (*Z*)

Entry	Ligands	solvent	Conv. (%)	Yields (%)		rr	*E*:*Z*
				2a	**3a+4a**	**2a:(3a+4a)**	**3a:4a**
1	PCy_3	THF	>99	96	2	>20:1	-
2	PCy_3	DCM	No rxn	-	-	-	-
3	PCy_3	ToL	81	74	6	12:1	7:1
4	PCy_3	DMF	70	10	38	1:4	12:1
5	PCy_3	*n*-Hexane	77	70	6	10:1	8:1
6	**L1**	THF	96	15	77	1:5	4:1
7	**L1**	DCM	16	-	9	1:3	6:1
8	**L1**	ToL	15	-	14	1:4	7:1
9	**L1**	DMF	48	-	27	1:19	10:1
10	**L1**	*n*-Hexane	No rxn	-	-	-	-

Table S3. Solvent optimization of the borosilylation.

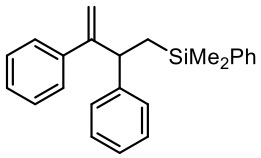


Entry	solvent	Conv. (%)	Yields (%)		*E*:*Z*
			5a	**6a**	**5a:6a**
1	THF	>99	95	-	>20:1
2	DCM	19	4	-	-
3	ToL	>99	30	60	1:2
4	DMF	83	-	20	1:10
5	*n*-Hexane	>99	74	24	3:1

3. General procedure of the 2,1-protosilylation

General procedure of the 2,1-protosilylation reaction: In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with substrate **1** (0.2 mmol, 1 equiv.), *t*-BuOK (0.04 mmol, 0.2 equiv), CuCl (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), then the mixture was dissolved in THF (1 mL). Next, Me_2PhSi-Bpin (0.26 mmol, 1.3 equiv.) and MeOH (0.4 mmol, 2 equiv.) was added sequentially at room temperature. The reaction mixture was kept stirring for 8h. The reaction mixture was purified by silica gel column chromatography (pure PEE) to afford product **2** as the main product in corresponding yields.

(2,3-diphenylbut-3-en-1-yl)dimethyl(phenyl)silane (**2a**)



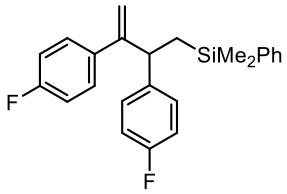
0.2 mmol scale, s.m. (starting material, the same as following) 41.2 mg, obtain product 62.2 mg, 91% yield, colorless oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.36–7.31 (m, 3H), 7.24–7.09 (m, 10H), 5.29 (s, 1H), 5.20 (s, 1H), 3.90 (t, *J* = 8.0 Hz, 1H), 1.48 (dd, *J* = 14.8, 6.1 Hz, 1H), 1.38 (dd, *J* = 14.8, 9.3 Hz, 1H), 0.11 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 144.8, 142.6, 139.4, 133.7, 129.0, 128.3, 128.2, 128.1, 127.8, 127.2, 127.0, 126.3, 113.0, 46.4, 23.0, -2.0, -2.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{26}SiNa$ 365.1696; Found 365.1744.

(2,3-bis(4-fluorophenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2b**)



0.2 mmol scale, s.m. 48.4 mg, obtain product 61.7 mg, 82% yield, colorless oily liquid.

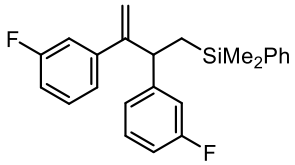
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.28 (m, 5H), 7.06–7.01 (m, 4H), 6.90–6.83 (m, 4H), 5.21 (s, 1H), 5.17 (s, 1H), 3.80 (t, *J* = 8.1Hz, 1H), 1.43 (dd, *J* = 14.8, 5.8 Hz, 1H), 1.32 (dd, *J* = 14.8, 9.7 Hz, 1H), 0.09 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 160.9, 153.1, 140.1, 139.0, 133.7, 129.5, 129.1, 128.6, 127.9, 115.2, 114.8, 112.9, 45.9, 22.9, -2.0, -2.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6, -117.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_2Si$ 379.1688; Found 379.1583.

(2,3-bis(3-fluorophenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2c**)



0.2 mmol scale, s.m. 48.4 mg, obtain product 87.4 mg, 96% yield, colorless oily liquid.

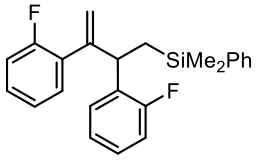
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.38–7.31 (m, 3H), 7.18–7.12 (m, 2H), 6.90–6.76 (m, 6H), 5.32 (s, 1H), 5.24 (s, 1H), 3.82 (t, *J* = 8.1 Hz, 1H), 1.45 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.34 (dd, *J* = 14.8, 9.2 Hz, 1H), 0.12 (s, 3H), 0.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.7, 154.3, 149.3, 146.6, 140.9, 135.7, 131.8, 131.2, 130.0, 126.0, 124.7, 117.0, 116.2, 116.1, 115.4, 48.2, 25.0, 0.0, -0.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5, -113.7.

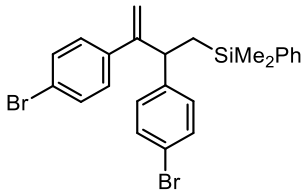
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_2Si$ 379.1688; Found 379.1629.

(2,3-bis(2-fluorophenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2d**)



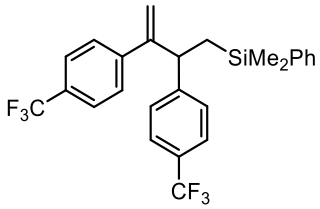
0.2 mmol scale, s.m. 48.4 mg, obtain product 70.3 mg, 93% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.35–7.37 (m, 3H), 7.21–7.01 (m, 3H), 7.01–6.90 (m, 4H), 6.87–6.80 (m, 1H), 5.34 (s, 1H), 5.19 (s, 1H), 4.30 (t, *J* = 7.8 Hz, 1H), 1.44 (d, *J* = 7.7 Hz, 2H), 0.16 (s, 3H), 0.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 158.5, 148.7, 139.3, 133.6, 130.8, 130.6, 130.3, 129.8, 128.9, 128.7, 128.0, 127.8, 123.9, 123.7, 115.6, 115.2, 39.2, 20.8, -2.6, -2.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7, -117.7.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_2Si$ 379.1688; Found 379.1677.

(2,3-bis(4-bromophenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2e**)



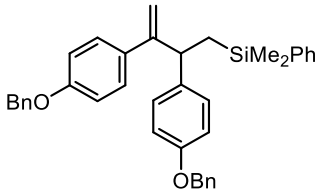
0.2 mmol scale, s.m. 73.2 mg, obtain product 44.0 mg, 44% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.14 (m, 9H), 6.84 (m, 4H), 5.16 (s, 1H), 5.10 (s, 1H), 3.66 (t, *J* = 8.1 Hz, 1H), 1.33 (dd, *J* = 14.8, 6.0 Hz, 1H), 1.21 (dd, *J* = 14.7, 9.5 Hz, 1H), 0.01 (s, 3H), 0.00 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 143.4, 141.1, 138.7, 133.7, 131.5, 131.3, 129.9, 129.1, 128.6, 127.9, 121.3, 120.2, 113.6, 45.9, 22.7, -2.0, -2.6.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{24}H_{24}Br_2SiK$ 536.9646; Found 536.9653.

(2,3-bis(4-(trifluoromethyl)phenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2f**)



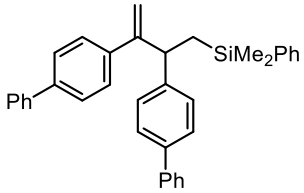
0.2 mmol scale, s.m. 68.4 mg, obtain product 79.4 mg, 83% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.28 (m, 9H), 7.19–7.16 (m, 4H), 5.36 (s, 1H), 5.30 (s, 1H), 3.95–3.86 (t, *J* = 8.1 Hz, 1H), 1.48 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.38 (dd, *J* = 14.8, 9.2 Hz, 1H), 0.15 (s, 3H), 0.11 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 148.3, 145.6, 138.5, 133.6, 129.2, 128.4, 128.0, 127.2, 125.4, 125.2, 115.1, 46.3, 22.8, -2.2, -2.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3, -62.5.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{26}H_{24}F_6SiK$ 517.1183; Found 517.1448

(2,3-bis(4-(benzyloxy)phenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2g**)



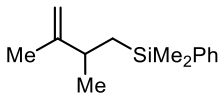
0.2 mmol scale, s.m. 83.6 mg, obtain product 82.1 mg, 74% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.29 (m, 15H), 7.11–7.02 (m, 4H), 6.84–6.78 (m, 4H), 5.22 (s, 1H), 5.10 (s, 1H), 5.01–5.00 (m, 4H), 3.82 (t, *J* = 7.9 Hz, 1H), 1.44 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.33 (dd, *J* = 14.7, 9.4 Hz, 1H), 0.10 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 157.3, 153.5, 139.5, 137.4, 137.3, 137.2, 135.3, 133.8, 129.1, 128.9, 128.7, 128.7, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 114.7, 114.4, 111.7, 70.1, 45.5, 23.1, -2.0, -2.6.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{38}O_2SiNa$ 577.2533; Found 577.2532.

(2,3-di([1,1'-biphenyl]-4-yl)but-3-en-1-yl)dimethyl(phenyl)silane (**2h**)



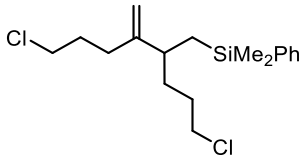
0.2 mmol scale, s.m. 71.6 mg, obtain product 87.8 mg, 89% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 4H), 7.49–7.40 (m, 10H), 7.38–7.32 (m, 4H), 7.30–7.29 (m, 2H), 7.27–7.23 (m, 3H), 5.42 (s, 1H), 5.28 (s, 1H), 4.01 (t, *J* = 7.7 Hz, 1H), 1.54 (dd, *J* = 14.7, 6.5 Hz, 1H), 1.46 (dd, *J* = 14.8, 9.0 Hz, 1H), 0.17 (s, 3H), 0.15 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 144.1, 141.4, 141.1, 140.0, 139.3, 139.1, 133.8, 129.0, 128.9, 128.8, 128.6, 127.9, 127.3, 127.3, 127.1, 127.1, 126.9, 113.2, 45.9, 23.2, -2.0, -2.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{34}SiNa$ 517.2322; Found 517.2339.

(2,3-dimethylbut-3-en-1-yl)dimethyl(phenyl)silane (**2i**)



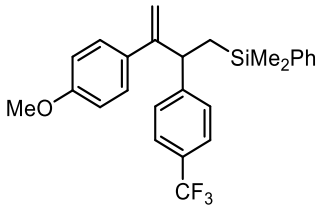
0.4 mmol scale, s.m. 32.9 mg, obtain product 40.9 mg, 47% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.45 (m, 2H), 7.44–7.29 (m, 3H), 4.67 (s, 1H), 4.59 (s, 1H), 2.36 (h, *J* = 6.9 Hz, 1H), 1.64 (s, 3H), 1.00 (m, 4H), 0.83 (dd, *J* = 14.8, 7.7 Hz, 1H), 0.30 (s, 3H), 0.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 140.0, 133.7, 128.9, 127.8, 108.5, 37.6, 23.2, 22.7, 18.7, -2.1, -2.3.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}SiNa$ 241.1383; Found 241.1280.

(6-chloro-2-(3-chloropropyl)-3-methylenehexyl)dimethyl(phenyl)silane (**2j**)



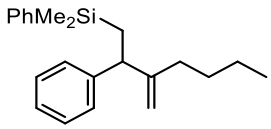
0.2 mmol scale, s.m. 41.2 mg, obtain product 53.9 mg, 82% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.36–7.32 (m, 3H), 4.77 (s, 1H), 4.68 (s, 1H), 3.50 (t, *J* = 6.5 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.22 (p, *J* = 7.0 Hz, 1H), 2.05–1.92 (m, 2H), 1.87–1.72 (m, 2H), 1.65–1.52 (m, 2H), 1.46 (t, *J* = 7.6 Hz, 2H), 0.97 (dd, *J* = 14.9, 8.1 Hz, 1H), 0.89 (dd, *J* = 14.9, 6.5 Hz, 1H), 0.29 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 139.5, 133.7, 129.0, 127.8, 109.8, 45.3, 45.1, 42.7, 33.7, 30.6, 30.5, 28.3, 21.6, -2.2, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{29}Cl_2Si$ 343.1410; Found 343.1678.

(3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)dimethyl(phenyl)silane (**2k**)



0.1 mmol scale, s.m. 30.4 mg, obtain product 40.1 mg, 91% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.28 (m, 7H), 7.22–7.20 (m, 2H), 7.10–7.03 (m, 2H), 6.77–6.70 (m, 2H), 5.28 (s, 1H), 5.14 (s, 1H), 3.90 (t, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 1.50 (dd, *J* = 14.9, 6.4 Hz, 1H), 1.36 (dd, *J* = 14.9, 9.1 Hz, 1H), 0.14 (s, 3H), 0.12 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 152.4, 149.3, 138.9, 134.4, 133.7, 129.1, 128.4, 128.0, 127.9, 125.2, 113.6, 112.4, 55.3, 46.3, 23.0, -2.2, -2.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{26}H_{27}F_3OSiK$ 479.1415; Found 479.1379.

dimethyl(3-methylene-2-phenylheptyl)(phenyl)silane (**2l**)

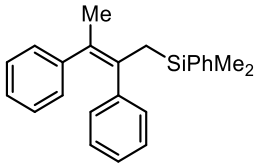


0.2 mmol scale, s.m. 37.2 mg, obtain product 57.8 mg, 90% yield, colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 2H), 7.31–7.25 (m, 3H), 7.22–7.13 (m, 3H), 7.11–7.05 (m, 2H), 4.97 (s, 1H), 4.75 (s, 1H), 3.29 (t, *J* = 7.8 Hz, 1H), 1.89–1.65 (m, 2H), 1.38–1.06 (m, 6H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.06 (s, 3H), 0.00 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 145.6, 139.7, 133.7, 128.9, 128.2, 128.0, 127.8, 126.2, 108.2, 47.6, 34.2, 30.1, 22.6, 21.6, 14.1, -2.1, -2.7.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{30}SiNa$ 345.2009; Found 345.2047.

4. General procedure of the 4,1-protosilylation

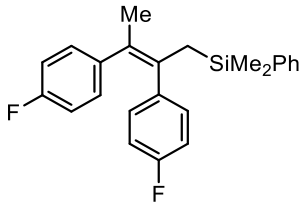
General procedure of the 4,1-protosilylation reaction: In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with substrate **1** (0.2 mmol, 1 equiv.), *t*-BuOK (0.04 mmol, 0.2 equiv), CuCl (0.02 mmol, 10 mol%), **L1** or **L2** (0.024 mmol, 12 mol%), then the mixture was dissolved in THF (1 mL). Next, Me_2PhSi-Bpin (0.3 mmol, 1.5 equiv.) and MeOH (0.4 mmol, 2 equiv.) was added sequentially at room temperature. The reaction mixture was kept stirring for 12h, then the mixture was purified by silica gel column chromatography (pure PEE) to afford compound **3** as the major product in corresponding yields.

(*E*)-(2,3-diphenylbut-2-en-1-yl)dimethyl(phenyl)silane (**3a**)



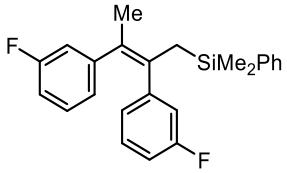
0.2 mmol, s.m. 41.2 mg, obtain 50.0 mg, 73% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.30 (m, 5H), 7.22–7.11 (m, 2H), 7.08–6.86 (m, 8H), 2.32 (s, 2H), 1.95 (s, 3H), 0.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.5, 135.1, 133.7, 130.5, 130.1, 129.5, 129.1, 127.8, 127.6, 127.5, 125.7, 125.4, 26.0, 21.9, -2.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{26}SiNa$ 365.1696; Found 365.1690.

(*E*)-(2,3-bis(4-fluorophenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3b**)



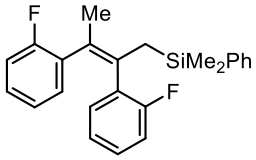
0.2 mmol, s.m. 48.4 mg, obtain 70.2 mg, 93% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.29 (m, 5H), 7.07–6.98 (m, 2H), 6.90–6.68 (m, 6H), 2.27 (s, 2H), 1.91 (s, 3H), 0.12 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 160.0, 140.7, 134.5, 133.6, 133.6, 131.4, 130.9, 129.8, 129.1, 127.8, 114.6, 114.5, 26.2, 21.9, -2.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8, -117.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_2Si$ 379.1688; Found 379.1965.

(*E*)-(2,3-bis(3-fluorophenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3c**)



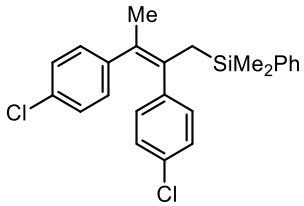
0.2 mmol, s.m. 48.4 mg, obtain 70.9 mg, 94% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.38–7.31 (m, 3H), 7.03–6.96 (m, 2H), 6.75–6.54 (m, 6H), 2.27 (s, 2H), 1.90 (s, 3H), 0.14 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 161.4, 147.0, 146.4, 138.8, 135.0, 133.6, 130.3, 129.2, 129.0, 127.8, 125.8, 125.1, 116.7, 116.2, 112.9, 112.7, 26.1, 21.7, -2.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3, -114.4.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_2Si$ 379.1688; Found 379.1509.

(*E*)-(2,3-bis(2-fluorophenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3d**)



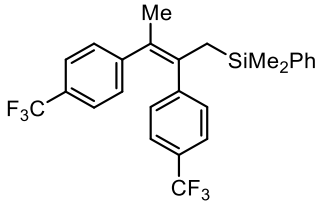
0.2 mmol, s.m. 48.4 mg, obtain 69.3 mg, 92% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.44 (m, 2H), 7.37–7.28 (m, 3H), 7.05–6.91 (m, 2H), 6.90–6.70 (m, 6H), 2.32 (s, 2H), 1.96 (s, 3H), 0.19 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.8, 139.1, 133.6, 132.2, 132.0, 131.8, 131.5, 131.3, 131.1, 129.0, 128.2, 127.9, 127.8, 123.3, 123.3, 115.2, 115.0, 24.6, 20.6, -2.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8, -115.0.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{24}F_2SiNa$ 401.1508; Found 401.1516.

(*E*)-(2,3-bis(4-chlorophenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3m**)



0.2 mmol, s.m. 54.8 mg, obtain 63 mg, 77% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.38–7.29 (m, 3H), 7.06–6.96 (m, 4H), 6.85–6.74 (m, 4H), 2.26 (s, 2H), 1.89 (s, 3H), 0.13 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 143.1, 142.5, 138.8, 134.8, 133.6, 131.3, 130.7, 129.2, 128.3, 127.9, 127.8, 113.6, 45.9, 26.2, 21.8, -2.3.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{24}Cl_2SiNa$ 433.0917; Found 433.0949.

(*E*)-(2,3-bis(4-(trifluoromethyl)phenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3f**)



0.1 mmol, s.m. 34.2 mg, obtain 43.5 mg, 91% yield, colorless oil

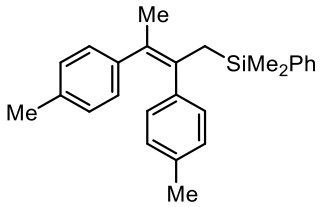
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 7.20–7.08 (m, 7H), 6.87–6.73 (m, 4H), 2.17 (s, 2H), 1.80 (s, 3H), 0.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.6, 138.4, 135.7, 133.6, 130.7, 130.2, 129.6, 129.3, 128.3, 128.0, 127.9, 127.7, 125.7, 124.7, 123.0, 26.3, 21.8, -2.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3, -62.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}F_6Si$ 479.1624; Found 479.1634.

(*E*)-(2,3-di-p-tolylbut-2-en-1-yl)dimethyl(phenyl)silane (**3n**)



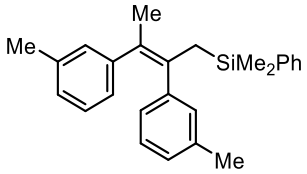
0.2 mmol, s.m. 46.8 mg, obtain 66.1 mg, 89% yield, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.43 (m, 2H), 7.39–7.30 (m, 3H), 7.15–6.73 (m, 8H), 2.28 (s, 2H), 2.22 (s, 6H), 1.91 (s, 3H), 0.10 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 141.5, 139.6, 135.0, 134.7, 134.5, 133.7, 129.9, 129.8, 129.3, 129.0, 128.3, 128.3, 127.7, 26.1, 22.1, 21.2, -2.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{30}SiNa$ 393.2009; Found 393.2074.

(*E*)-(2,3-di-m-tolylbut-2-en-1-yl)dimethyl(phenyl)silane (**3o**)



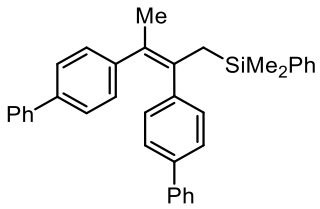
0.2 mmol, s.m. 46.8 mg, obtain 62.5 mg, 84% yield, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.46 (m, 2H), 7.40–7.31 (m, 3H), 6.95–6.88 (m, 2H), 6.84–6.62 (m, 6H), 2.31 (s, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 1.96 (s, 3H), 0.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.4, 139.6, 136.8, 136.7, 135.0, 133.7, 130.7, 130.1, 129.0, 127.7, 127.6, 127.3, 127.3, 127.2, 126.6, 126.3, 126.1, 25.9, 21.9, 21.5, 21.5, -2.3.

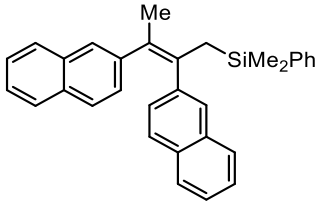
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{30}SiNa$ 393.2009; Found 393.2107.

(*E*)-(2,3-di([1,1'-biphenyl]-4-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**3h**)



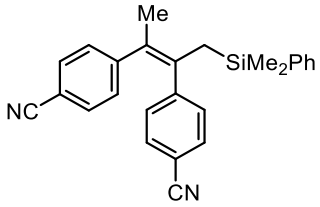
0.1 mmol, s.m. 35.8 mg, obtain 42 mg, 85% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.44 (m, 8H), 7.42–7.27 (m, 11H), 7.10–6.94 (m, 4H), 2.38 (s, 2H), 2.00 (s, 3H), 0.16 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.5, 141.0, 140.9, 139.3, 138.2, 138.0, 135.1, 133.7, 130.6, 130.1, 130.0, 129.0, 128.9, 128.8, 128.8, 127.8, 127.1, 127.0, 126.9, 126.3, 126.2, 26.2, 21.9, -2.3.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{36}H_{34}SiK$ 533.2061; Found 533.2276.

(*E*)-(2,3-di(naphthalen-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**3p**)



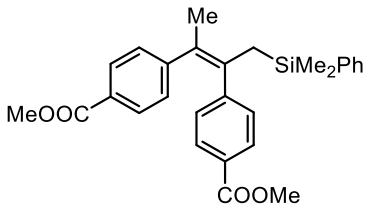
0.1 mmol, s.m. 30.6 mg, obtain 36.2 mg, 82% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.28 (m, 17H), 7.15–6.97 (m, 2H), 2.49 (s, 2H), 2.09 (s, 3H), 0.12 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.0, 139.3, 135.6, 133.8, 133.7, 133.4, 133.3, 131.9, 131.7, 130.8, 129.1, 129.1, 128.7, 128.5, 127.9, 127.8, 127.7, 127.5, 126.9, 126.9, 125.6, 125.6, 125.4, 125.2, 26.6, 22.3, -2.3.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{30}SiNa$ 465.2009; Found 465.2210.

(*E*)-4,4'-(1-(dimethyl(phenyl)silyl)but-2-ene-2,3-diyl)dibenzonitrile (**3q**)



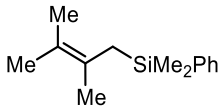
0.2 mmol, s.m. 51.2 mg, obtain 69.7 mg, 89% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.23 (m, 9H), 6.98–6.88 (m, 4H), 2.31 (s, 2H), 1.93 (s, 3H), 0.16 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 148.6, 137.9, 136.4, 133.6, 131.8, 131.7, 131.2, 130.6, 130.1, 129.4, 127.9, 118.9, 118.8, 110.0, 109.7, 26.3, 21.5, -2.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}N_2SiNa$ 415.1601; Found 415.1609.

(*E*)-4,4'-(1-(dimethyl(phenyl)silyl)but-2-ene-2,3-diyl)dibenzoate (**3r**)



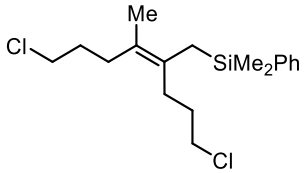
0.1 mmol, s.m. 32.2 mg, obtain 43.5 mg, 95% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 4H), 7.49–7.28 (m, 5H), 7.01–6.94 (m, 2H), 6.94–6.87 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.33 (s, 2H), 1.94 (s, 3H), 0.12 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 167.1, 149.6, 149.1, 138.6, 136.0, 133.6, 131.1, 130.0, 129.4, 129.3, 129.1, 129.1, 127.9, 127.7, 127.4, 52.1, 26.2, 21.6, -2.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{30}O_4SiNa$ 481.1806; Found 481.1818.

(2,3-dimethylbut-2-en-1-yl)dimethyl(phenyl)silane (**3i**)



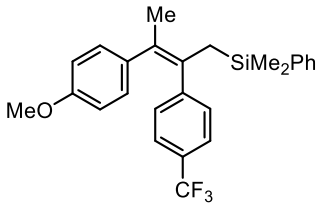
0.4 mmol, s.m. 32.86 mg, obtain 40.0 mg, 46% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.37–7.32 (m, 3H), 1.76 (s, 2H), 1.63 (s, 3H), 1.56 (s, 3H), 1.50 (s, 3H), 0.28 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 133.6, 128.9, 127.8, 124.5, 121.6, 25.0, 21.3, 21.1, 20.6, -2.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{23}Si$ 219.1564; Found 219.1325.

(*E*)-(6-chloro-2-(3-chloropropyl)-3-methylhex-2-en-1-yl)dimethyl(phenyl)silane (**3j**)



0.2 mmol, s.m. 41.2 mg, obtain 53.7 mg, 78% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.39–7.31 (m, 3H), 3.46 (dt, *J* = 16.9, 6.6 Hz, 4H), 2.14 (dd, *J* = 8.9, 6.4 Hz, 2H), 2.01 (dd, *J* = 9.4, 6.1 Hz, 2H), 1.83–1.75 (m, 4H), 1.73 (s, 2H), 1.46 (s, 3H), 0.30 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.6, 129.9, 129.1, 127.9, 125.7, 45.2, 45.1, 31.9, 31.8, 31.4, 31.0, 22.5, 19.0, -2.1.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{28}Cl_2SiNa$ 365.1230; Found 365.1749.

(E)-(3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)dimethyl(phenyl)silane (**3k**)



0.1 mmol, s.m. 30.4 mg, obtain 41.0 mg, 93% yield, colorless oil

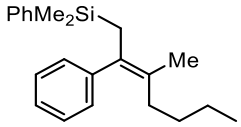
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.35–7.28 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.79–6.74 (m, 2H), 6.63-6.58 (m, 2H), 3.71 (s, 3H), 2.30 (s, 2H), 1.94 (s, 3H), 0.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 148.6, 138.8, 136.7, 133.6, 133.4, 131.6, 130.5, 130.4, 129.1, 127.8, 124.5, 113.2, 55.2, 25.9, 22.1, -2.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3.

HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{26}H_{27}F_3OSiK$ 479.1415; Found 479.1285.

dimethyl(phenyl)(2-(1-phenylethylidene)hexyl)silane (**3l**)



0.2 mmol, s.m. 37.2 mg, obtain 55.5 mg, 86% yield, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–6.94 (m, 10H), 2.02 (s, 2H), 1.84–1.78 (m, 2H), 1.56 (s, 3H), 1.30–1.16 (m, 2H), 1.11–1.02 (m, 2H), 0.71 (t, J = 7.3 Hz, 3H), 0.00 (s, 6H).

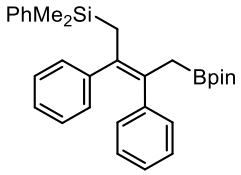
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 139.8, 133.6, 132.1, 129.2, 128.8, 127.8, 127.7, 125.9, 35.2, 31.3, 25.4, 22.7, 18.6, 14.2, -2.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{30}SiNa$ 345.2009; Found 345.1999.

5.General procedure of the 4,1-borosilylation

General procedures of the borosilylation: In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with substrate **1** (0.2 mmol, 1 equiv.), *t*BuOK (0.04 mmol, 0.2 equiv), CuCl (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), then the mixture was dissolved in THF (1 mL) at room temperature. Next, Me_2PhSi-Bpin (0.26 mmol, 1.3 equiv.) was added. The reaction mixture was kept stirring for 4h, then the mixture was purified by silica gel column chromatography to afford compound **5** as the major product in corresponding yields.

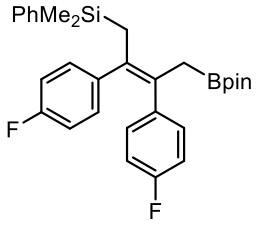
(*E*)-(2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5a**)



0.2 mmol, s.m. 41.2 mg, obtain 88.4 mg, 94% yield, colorless oil

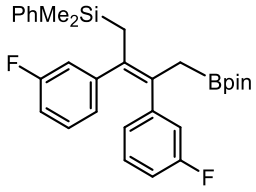
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.35 (m, 2H), 7.35–7.23 (m, 3H), 7.04–6.83 (m, 10H), 2.30 (s, 2H), 2.00 (s, 2H), 1.00 (s, 12H), 0.04 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.5, 139.6, 134.0, 133.7, 131.6, 130.3, 130.0, 128.9, 127.7, 127.3, 125.5, 125.3, 83.2, 25.9, 24.7, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{38}BO_2Si$ 468.2765; Found 468.3064.

(*E*)-(2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5b**)



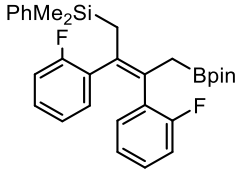
0.2 mmol, s.m. 48.4 mg, obtain 91.2 mg, 90% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.29 (m, 5H), 6.87–6.80 (m, 4H), 6.78–6.65 (m, 4H), 2.29 (s, 2H), 2.00 (s, 2H), 1.06 (s, 12H), 0.12 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 159.6, 140.6, 140.1, 139.2, 133.6, 133.5, 131.7, 131.5, 131.0, 129.0, 127.7, 114.4, 114.2, 83.3, 26.0, 24.7, -2.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2, -117.6.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{35}BF_2O_2SiNa$ 526.2396; Found 526.2819.

(*E*)-(2,3-bis(3-fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5c**)



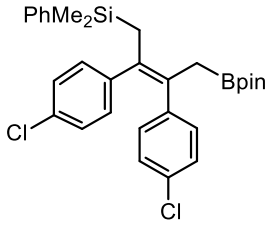
0.2 mmol, s.m. 48.4 mg, obtain 81.8 mg, 81% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.07 (m, 5H), 6.88–6.72 (m, 4H), 6.58–6.48 (m, 4H), 2.16 (s, 2H), 1.85 (s, 2H), 0.95 (s, 12H), 0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 161.1, 146.8, 146.5, 139.0, 133.8, 133.6, 131.5, 129.1, 128.8, 127.8, 125.9, 125.7, 116.8, 116.7, 112.6, 83.4, 25.8, 24.8, -2.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6, -114.8.
HRMS (ESI) m/z: $[M+H]^+$ $C_{30}H_{36}BF_2O_2Si$ 504.2577; Found 504.2370.

(*E*)-(2,3-bis(2-fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5d**)



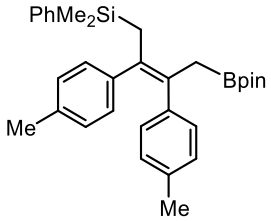
0.2 mmol, s.m. 48.4 mg, obtain 86.0 mg, 85% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.42 (m, 2H), 7.30–7.27(m, 3H), 7.02–6.65 (m, 8H), 2.34 (s, 2H), 2.07 (s, 2H), 1.11 (s, 12H), 0.17 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.9, 139.4, 133.6, 131.9, 131.7, 128.9, 128.8, 127.9, 127.8, 127.7, 123.1, 123.0, 114.9, 114.9, 83.2, 24.8, 24.5, -2.5.
^{19}F NMR (471 MHz, $CDCl_3$) δ -113.5, -114.3.
HRMS (ESI) m/z: $[M+H]^+$ $C_{30}H_{36}BF_2O_2Si$ 504.2577; Found 504.2326.

(*E*)-(2,3-bis(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5m**)



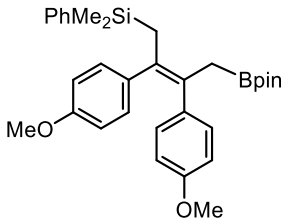
0.2 mmol, s.m. 54.8 mg, obtain 71.6 mg, 67% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.27 (m, 5H), 7.05–6.92 (m, 4H), 6.88–6.76 (m, 4H), 2.28 (s, 2H), 1.98 (s, 2H), 1.06 (s, 12H), 0.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.6, 139.0, 133.7, 133.6, 131.5, 131.3, 131.3, 131.2, 131.2, 129.1, 127.8, 127.7, 83.3, 25.9, 24.7, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{36}BCl_2O_2Si$ 536.1986; Found 536.2217.

(*E*)-dimethyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-di-p-tolylbut-2-en-1-yl)silane (**5n**)



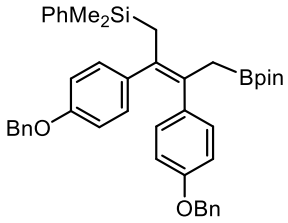
0.2 mmol, s.m. 46.8 mg, obtain 86.8 mg, 88% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 2H), 7.26–7.19 (m, 3H), 6.76–6.70 (m, 8H), 2.22 (s, 2H), 2.12 (s, 3H), 2.11 (s, 3H), 1.92 (s, 2H), 0.97 (s, 12H), 0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 141.6, 139.9, 134.7, 134.4, 133.7, 133.4, 131.0, 130.1, 129.8, 128.8, 128.1, 127.7, 83.1, 25.9, 24.9, 24.7, 21.2, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{42}BO_2Si$ 496.3078; Found 496.2871.

(*E*)-(2,3-bis(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5s**)



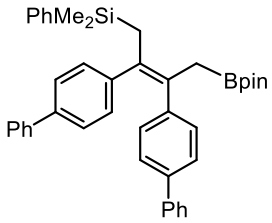
0.2 mmol, s.m. 53.2 mg, obtain 33.7 mg, 32% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.27–7.20 (m, 3H), 6.81–6.71 (m, 4H), 6.55–6.42 (m, 4H), 3.62 (s, 3H), 3.61 (s, 3H), 2.20 (s, 2H), 1.91 (s, 2H), 0.96 (s, 12H), 0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 139.7, 137.6, 137.0, 133.7, 133.0, 132.3, 132.2, 131.3, 131.0, 130.4, 128.9, 128.7, 128.6, 127.7, 112.8, 83.1, 55.2, 24.7, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{42}BO_4Si$ 528.2976; Found 528.2947.

(*E*)-(2,3-bis(4-(benzyloxy)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5g**)



0.1 mmol, s.m. 41.8 mg, obtain 49.7 mg, 73% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.28 (m, 15H), 6.92–6.81 (m, 4H), 6.71–6.60 (m, 4H), 4.97 (s, 2H), 4.96 (s, 2H), 2.30 (s, 2H), 2.01 (s, 2H), 1.04 (s, 12H), 0.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 156.3, 139.7, 137.9, 137.4, 137.3, 133.7, 133.0, 131.3, 131.0, 130.5, 128.9, 128.6, 128.6, 128.0, 127.9, 127.7, 127.5, 113.9, 113.8, 83.1, 69.9, 29.9, 25.9, 24.7, -2.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{44}H_{50}BO_4Si$ 680.3602; Found 680.2622.

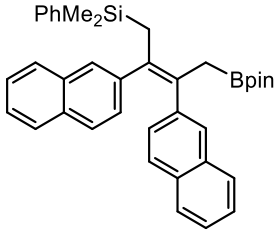
(*E*)-(2,3-di([1,1'-biphenyl]-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5h**)



0.2 mmol, s.m. 71.6 mg, obtain 115.0 mg, 93% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 6H), 7.41–7.27 (m, 13H), 7.06–7.01 (m, 4H), 2.40 (s, 2H), 2.10 (s, 2H), 1.06 (s, 12H), 0.15 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.5, 141.2, 141.0, 139.5, 137.9, 137.8, 134.0, 133.7, 131.3, 130.8, 130.5, 128.9, 128.7, 127.7, 127.0, 126.9, 126.9, 126.1, 126.0, 83.3, 29.9, 26.0, 24.7, -2.2.

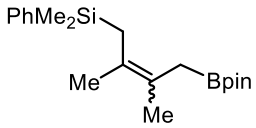
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{46}BO_2Si$ 620.3391; Found 620.3116.

(*E*)-(2,3-di(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5p**)



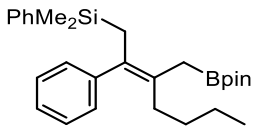
0.2 mmol, s.m. 61.2 mg, obtain 99.5 mg, 92% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.43 (m, 8H), 7.41–7.27 (m, 9H), 7.05–7.01 (m, 2H), 2.50 (s, 2H), 2.21 (s, 2H), 1.00 (s, 12H), 0.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.0, 139.5, 134.5, 133.7, 133.3, 133.2, 132.0, 131.7, 131.7, 129.4, 129.0, 128.7, 128.0, 127.9, 127.8, 127.7, 127.5, 126.7, 126.6, 125.4, 125.4, 125.2, 125.0, 83.2, 26.3, 24.7, -2.2.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{41}BO_2SiNa$ 590.2895; Found 590.2818.

(2,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)dimethyl(phenyl)silane (**5i**)



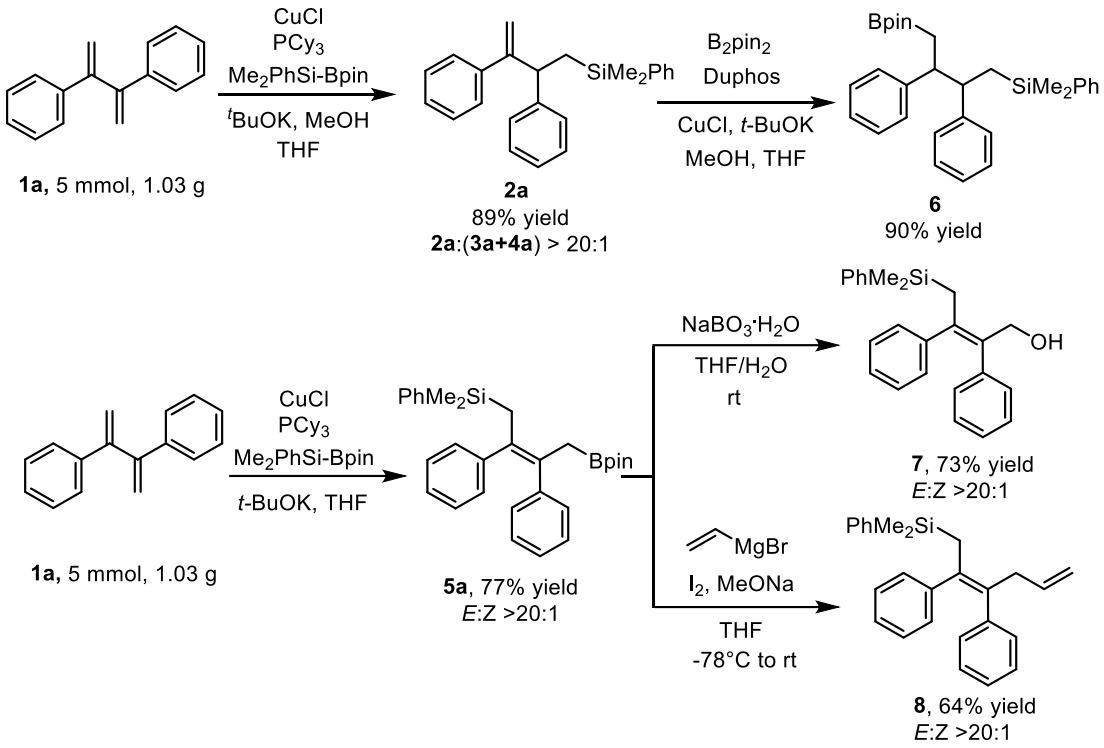
0.4 mmol, s.m. 32.9 mg, obtain 106.7 mg, 78% yield, colorless oil, E:Z = 1:1.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.35–7.32 (m, 3H), 1.77 (s, 2H), 1.66 (s, 2H), 1.57 (s, 3H), 1.54 (s, 3H), 1.23 (d, J = 3.6 Hz, 12H), 0.28 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 133.7, 128.8, 127.8, 123.5, 122.3, 83.1, 25.0, 25.0, 21.6, 21.4, 20.4, -2.0.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{38}BO_2Si$ 468.2765; Found 468.3064

(*E*)-dimethyl(phenyl)(2-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hept-2-en-1-yl)silane (**5l**)



0.2 mmol, s.m. 37.2 mg, obtain 61.6 mg, 69% yield, colorless oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H), 7.25–7.12 (m, 5H), 7.10–6.99 (m, 3H), 2.05 (s, 2H), 1.87 (t, *J* = 8.1 Hz, 2H), 1.66 (s, 2H), 1.30–1.22 (m, 2H), 1.18 (s, 12H), 1.11–1.05 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H), 0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 140.1, 133.6, 131.1, 130.4, 129.4, 128.7, 127.7, 127.6, 125.7, 83.1, 34.8, 31.4, 25.2, 24.9, 22.8, 14.2, -2.2.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{28}H_{43}BO_2SiK$ 488.2793; Found 488.2831.

6. Synthetic applications



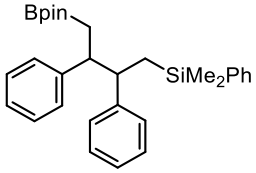
Scheme **S1**. Synthetic application

Gram scale reactions:

In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with substrate **1a** (1.03 g, 5 mmol, 1 equiv.), *t*-BuOK (112 mg, 1 mmol, 0.2 equiv), CuCl (50 mg, 0.5 mmol, 0.1 equiv), PCy_3 (140 mg, 0.5 mmol, 0.1 equiv), then the mixture was dissolved in THF (10 mL). Next, Me_2PhSi-Bpin (1.70 g, 6.5 mmol, 1.3 equiv.) and MeOH (0.4 mL, 2 equiv.) was added sequentially at room temperature. The reaction mixture was kept stirring for 8h. the reaction mixture was purified by silica gel column chromatography to afford compound **2a** as the main product (1.52 g, 89% yield).

In a glove box, a Schlenk tube equipped with a magnetic stir bar was charged with substrate **1a** (1.03 g, 5 mmol, 1 equiv.), *t*-BuOK (112 mg, mmol, 0.2 equiv), CuCl (50 mg, 0.5 mmol, 0.1 equiv), PCy_3 (140 mg, 0.5 mmol, 0.1 equiv), then the mixture was dissolved in THF (10 mL) at room temperature. Next, Me_2PhSi-Bpin (1.70 g, 6.5 mmol, 1.3 equiv.) was added. The reaction mixture was kept stirring for 4h. the reaction mixture was purified by silica gel column chromatography to afford compound **5a** as the main product (1.81 g, 77% yield).

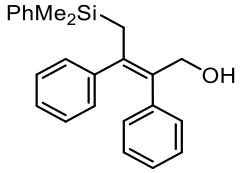
(2,3-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)dimethyl (phenyl)silane (**6**)



A Schlenk tube equipped with a magnetic stir bar was charged with CuCl (0.5 mg, 0.05 mmol, 0.05 equiv), Duphos (1.5 mg, 0.05 mmol, 0.05 equiv), and *t*-BuOK (11.2 mg, 0.1 mmol, 1.0 equiv), then the mixture was evacuated and refilled with N_2 for 3 times. The mixture was dissolved in THF (2 mL) at room temperature and stirred for 10 min, until a yellow homogeneous solution was obtained. Then $B_2(pin)_2$ (30.4 mg, 0.15 mmol,1.5 equiv) was added and stirring was continued for another 10 min at room temperature. Next, **2a** (34.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (8 µL, 0.2 mmol,2.0 equiv) was added. The reaction mixture was continued stirring at room temperature for 24 h. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 for three times. The obtained residue was purified by silica gel column chromatography to afford the desired product **6** (42.2 mg, 90% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.11 (m, 13H), 7.11–7.05 (m, 2H), 2.95–2.88 (m, 1H), 2.74–2.68 (m, 1H), 1.02–0.96 (m, 2H), 0.89 (d, *J* = 5.9 Hz, 12H), 0.85 (dd, *J* = 11.0, 2.7 Hz, 1H), 0.78 (dd, *J* = 15.2, 5.0 Hz, 1H), -0.17 (s, 3H), -0.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 145.2, 139.6, 133.6, 128.9, 128.7, 128.6, 128.1, 128.0, 127.6, 126.2, 126.0, 82.8, 50.7, 50.1, 24.7, 24.5, 20.9, -1.9, -3.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{39}BO_2SiNa$ 492.2741; Found 492.2792.

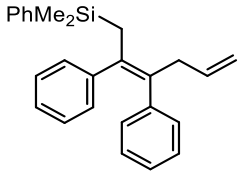
(*Z*)-4-(dimethyl(phenyl)silyl)-2,3-diphenylbut-2-en-1-ol (**7**)



To a mixture of boronic ester **5a** (93.6 mg, 0.2 mmol, 1 equiv) and $NaBO_3$•$4H_2O$ (153.85 mg, 2.0 mmol, 10 equiv) was added in THF:H_2O (1:1). The resulting reaction mixture was stirred for 1 hours at room temperature. Then the aqueous layer was extracted with CH_2Cl_2 and the combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressured. The crude product was purified by flash column chromatography on silica gel to afford the desired product **7** (52 mg, 73 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.47 (m, 2H), 7.341–7.32 (m, 3H), 7.12–6.88 (m, 10H), 4.24 (d, *J* = 6.1 Hz, 2H), 2.41 (s, 2H), 0.99 (t, *J* = 6.2 Hz, 1H), 0.09 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.0, 138.9, 138.3, 134.3, 133.8, 130.2, 129.8, 129.4, 128.0, 127.7, 126.4, 126.2, 63.6, 26.2, -2.7.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{26}OSiNa$ 381.1645; Found 381.1642.

(*E*)-(2,3-diphenylhexa-2,5-dien-1-yl)dimethyl(phenyl)silane (**8**)

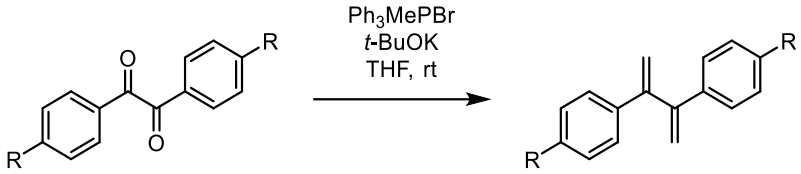


To a solution of boronic ester **5a** (70.2 mg, 0.15 mmol, 1.0 equiv) in THF (1 mL), vinyl magnesium bromide (1M, 0.6 mL, 4.0 equiv) was added dropwise at 0°C, and the resulting solution was stirred for 30 min at room temperature. After cooling the reaction mixture at -78 °C, a solution of iodine (76.2 mg, 4.0 equiv) in anhydrous THF (1 mL) was added dropwise followed by stirring for 20 min. Next, a solution of NaOMe (40.5 mg, 5 equiv) in methanol (1 mL) was added. The mixture of the reaction was continued stirring at room temperature for 6 hours. After full consumption of starting material, the reaction mixture was purified by silica gel column chromatography to afford the desired product **8** (35.2 mg, 64 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.40–7.30 (m, 3H), 7.09–6.93 (m, 8H), 6.90–6.85 (m, 2H), 5.64 (ddt, *J* = 16.5, 10.0, 6.2 Hz, 1H), 5.03–4.87 (m, 2H), 3.07 (dt, *J* = 6.3, 1.7 Hz, 2H), 2.32 (s, 2H), 0.09 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.4, 139.2, 136.5, 135.3, 133.7, 132.8, 130.2, 130.1, 129.1, 127.8, 127.5, 125.9, 125.5, 115.2, 39.5, 25.4, -2.4.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{28}SiNa$ 391.1852; Found 391.1940.

7. Substrates preparation

Procedure A

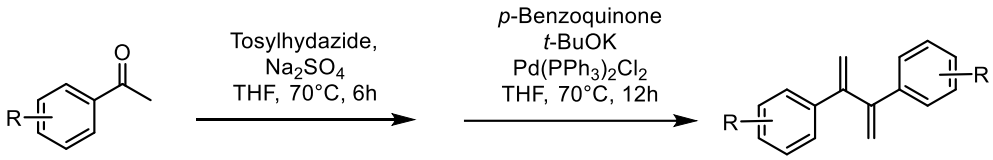


1a, 1b, 1e, 1m, 1n were prepared according to **procedure A**.

A mixture of Ph_3MePBr (2.5 equiv) and *t*-BuOK (3.0 equiv) was stirred at 0°C for 30 minutes in THF (0.1M). Then 1 equiv. of ketone was added and kept stirring for 2 h. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with NH_4Cl and dry it with anhydrous Na_2SO_4. The residue was separated and purified using silica gel column chromatography, resulting in solid product.

The structures **1a, 1b, 1e, 1m, 1n** were confirmed by comparison of the NMR spectra with the literature[1].

Procedure B



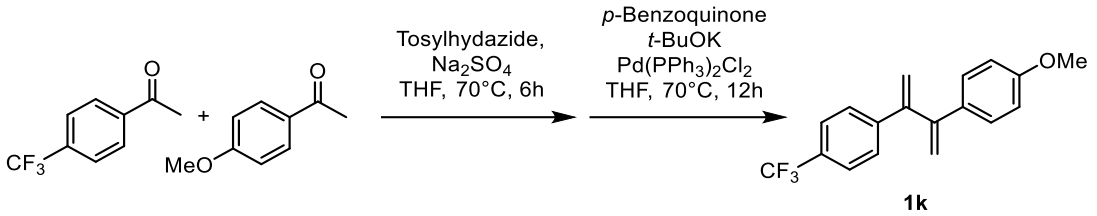
1c, **1d**, **1f**, **1g**, **1h**, **1i**, **1o**, **1p**, **1q**, **1r** were prepared according to **Procedure B**.

A mixture of ketone (1.0 equiv), tosylhydrazide (1.0 equiv), and Na_2SO_4 (1.0 equiv) was stirred at 70°C for 6h in THF (0.1M). Then, *p*-benzoquinone (2.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.05 equiv), and *t*-BuOLi (3.75 equiv) were charged, and the resulting mixture was stirred under an nitrogen atmosphere at 70°C for 12h. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with NH_4Cl and dry it with anhydrous Na_2SO_4. Vacuum concentration was used to remove the solvent and obtain a residue. The residue was separated and purified using silica gel column chromatography, resulting in a solid product.

The structures **1c**, **1d**, **1f**, **1g**, **1h**, **1i**, **1o**, **1p**, **1q**, **1r** were confirmed by comparison of the NMR spectra with the literature[1].

Procedure C

1k was prepared according to **Procedure C**.

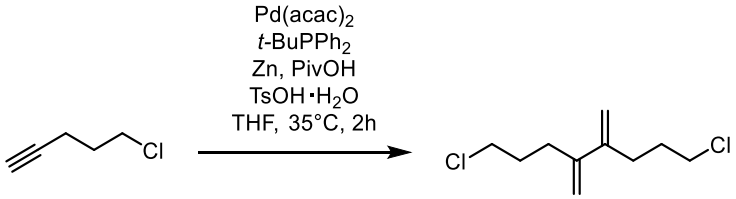


1k

A mixture of 4'-(Trifluoromethyl)acetophenone (0.88 g, 5.0 mmol, 1.0 equiv), 4'-Methoxyacetophenone (0.75 g, 5.0 mmol, 1.0 equiv), tosylhydrazide (1.86 g, 10.0 mmol, 2.0 equiv), and Na_2SO_4 (1.42 g, 10.0 mmol, 2.0 equiv) in THF (50 mL) was stirred at 70°C for 6 h. Then, *p*-benzoquinone (2.16 g, 20.0 mmol, 4.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.5 mmol, 0.1 equiv), and *t*-BuOLi (2.82 g, 35 mmol, 7 equiv) were added under N_2 flow, and the resulting mixture was stirred under nitrogen atmosphere at 70°C for 12h. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with NH_4Cl and dry it with anhydrous Na_2SO_4. The residue was separated and purified using silica gel column chromatography, resulting in a solid product of **1k** (0.64 g, 42% yield).

The structure **1k** was confirmed by comparison of the NMR spectra with the literature[2].

Procedure D

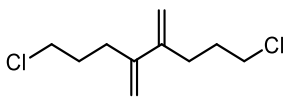


1j

1j was prepared according to **Procedure D**.

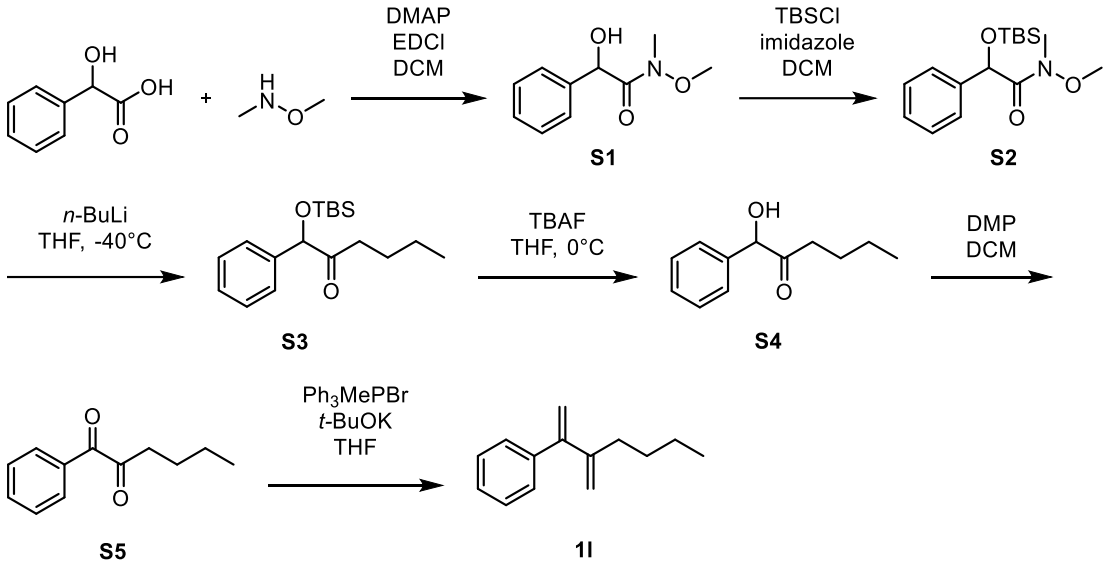
A mixture of $Pd(acac)_2$ (90 mg, 0.03 equiv), *t*-$BuPPh_2$ (145 mg, 0.06 equiv), $TsOH{\cdot}H_2O$ (950 mg, 0.5 equiv), PivOH (1.53 g, 1.5 equiv), Zn (650 mg, 1.0 equiv) and 5-chloropent-1-yne (1.1 mL, 10 mmoL, 1.0 equiv) was stirred at 35°C for 2h in THF (30 mL). Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with NH_4Cl and dry it with anhydrous Na_2SO_4. Vacuum concentration was used to remove the solvent and obtain a residue. The residue was separated and purified using silica gel column chromatography, resulting in a liquid product of **1j** (358 mg, 17% yield).

1,8-dichloro-4,5-dimethyleneoctane (**1j**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (s, 2H), 5.01 (s, 2H), 3.54 (t, J = 6.5 Hz, 4H), 2.41 (t, J = 7.2 Hz, 4H), 1.95–1.88 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 113.3, 44.8, 31.5, 31.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{17}Cl_2$ 207.0702; Found 207.0698.

Procedure E



1l was prepared according to **Procedure E**.

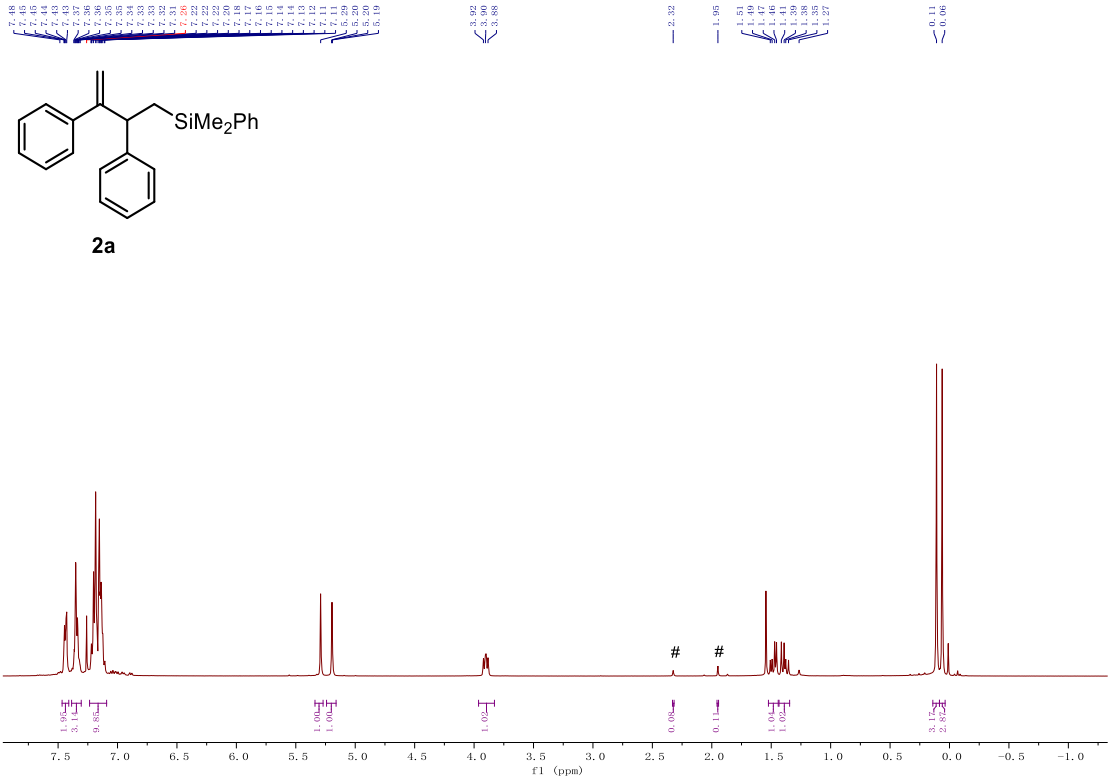
S1-S3 are synthesized according to the method reported by Malins et al[3].

Add substrate **S3** (1.0 equiv) and TBAF (1.0 equiv) to double ended flask with a magnet, and dissolve in THF (15 mL). The reaction mixture was cooled to 0°C for 1-2 hours. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with salt water and dry it with anhydrous Na_2SO_4. Vacuum concentration was used to remove the solvent and obtain a residue. The residue was separated and purified using silica gel column chromatography, resulting in a liquid product of **S4**.
The structure **S4** was confirmed by comparison of the NMR spectra with the literature[4].

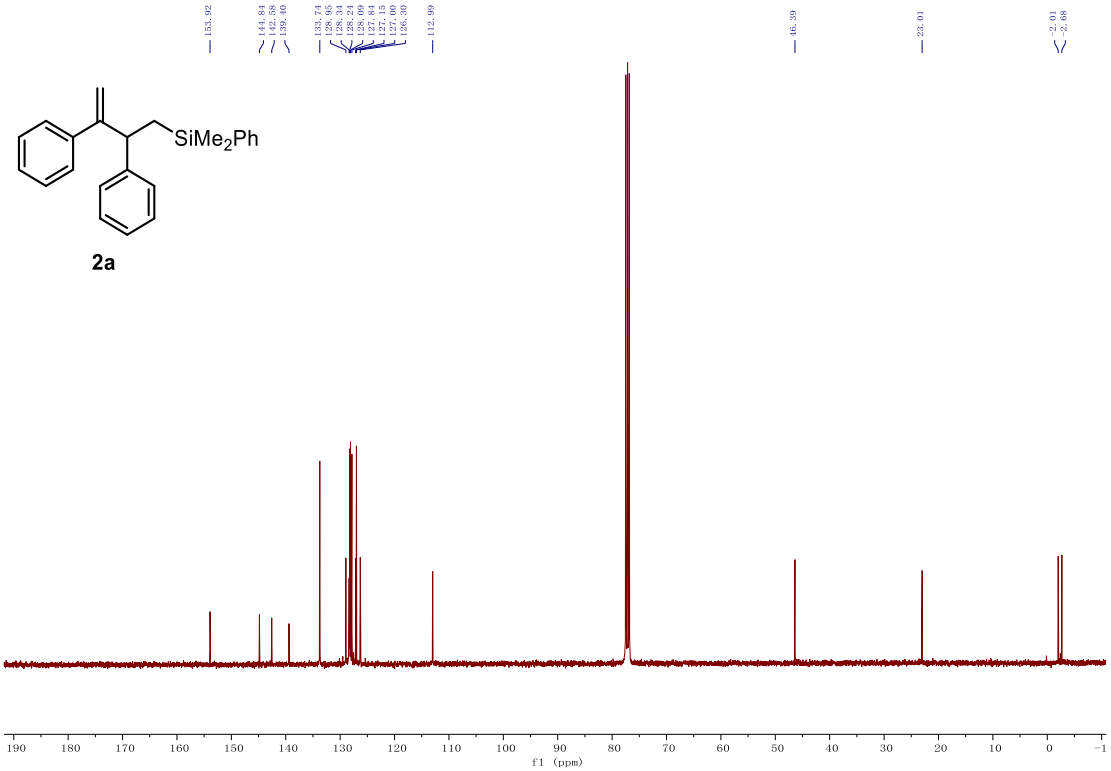
Add substrate **S4** (1.0 equiv), and DMP (1.5 equiv) to double ended flask with a magnet, and dissolve in CH_2Cl_2 (15 mL). The reaction mixture was at room temperature for 1-2 hours. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with salt water and dry it with anhydrous Na_2SO_4. Vacuum concentration was used to remove the solvent and obtain a residue. The residue was separated and purified using silica gel column chromatography, resulting in a liquid product of **S5**.
The structure **S5** was confirmed by comparison of the NMR spectra with the literature[5].

A mixture of Ph_3MePBr (2.5 equiv) and *t*-BuOK (3.0 equiv) was stirred at 0°C for 30 minutes in THF (0.1M). Then add 1-phenylhexane-1,2-dione (1.0 equiv) and stir for 2 h. Carefully track the reaction using TLC until all starting materials are consumed. Extract and separate the organic layer with CH_2Cl_2, wash the combined organic layer with salt water and dry it with anhydrous Na_2SO_4. Vacuum concentration was used to remove the solvent and obtain a residue. The residue was separated and purified using silica gel column chromatography, resulting in a liquid product of **1l**.
The structure **1l** was confirmed by comparison of the NMR spectra with the literature[6].

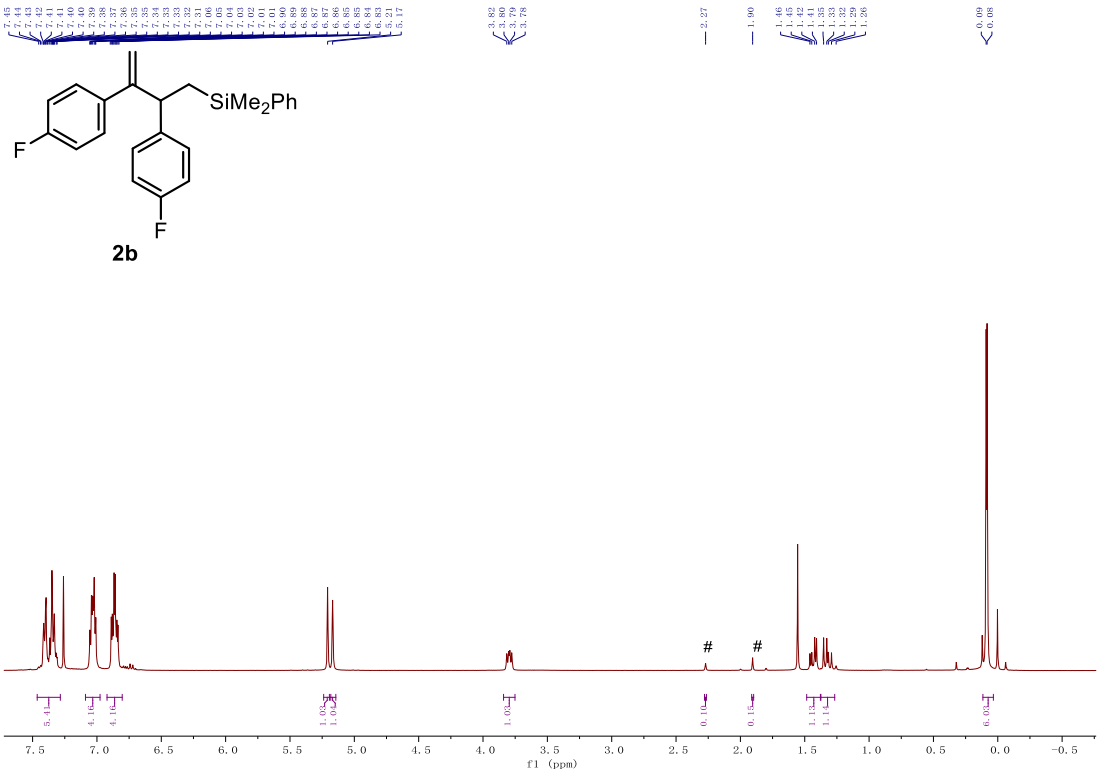
8. NMR spectra



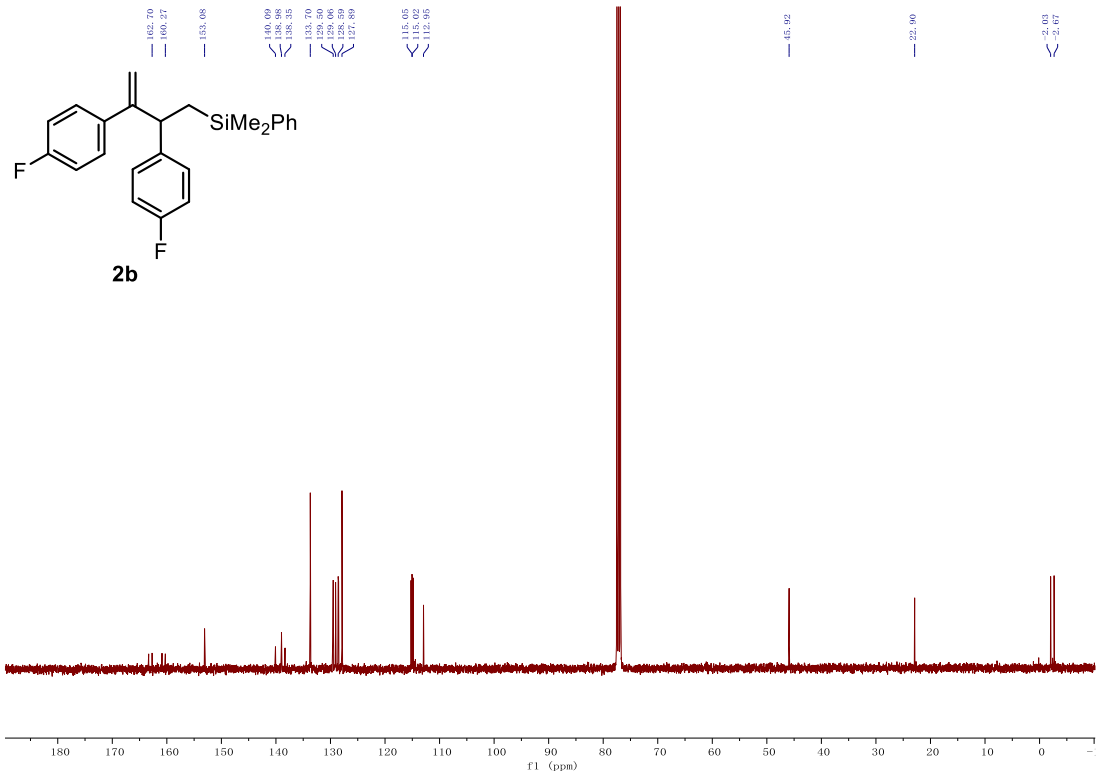
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



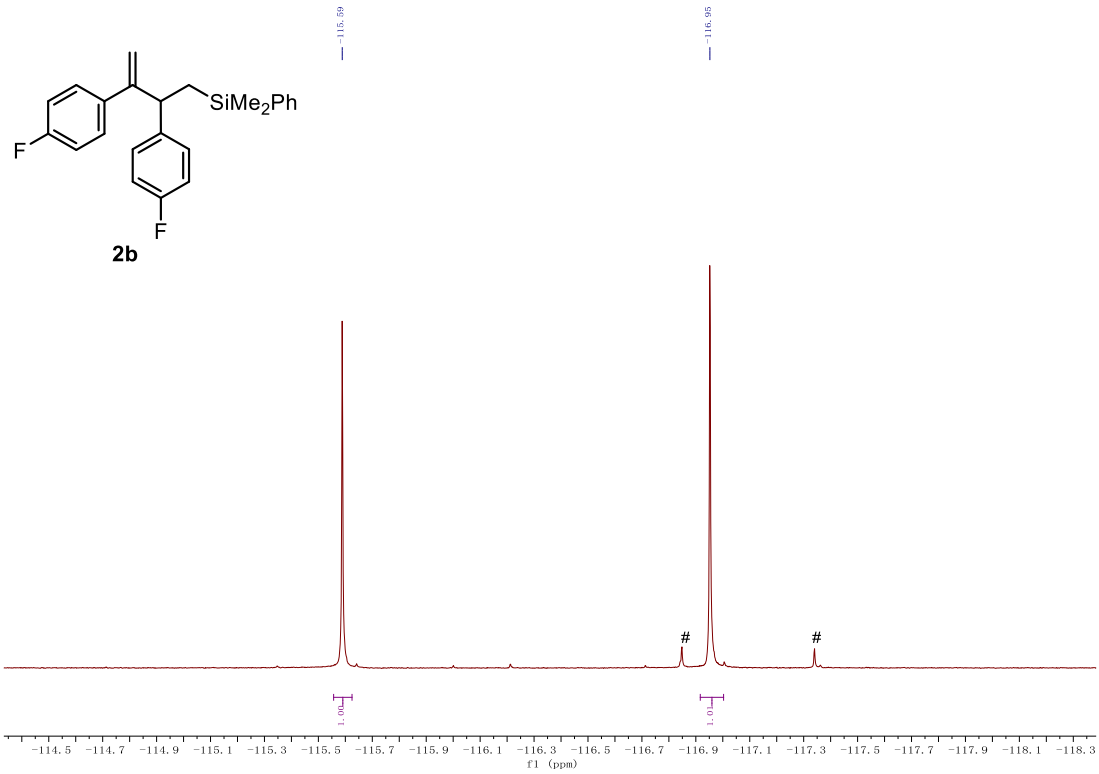
^{13}C NMR, $CDCl_3$, 101 MHz



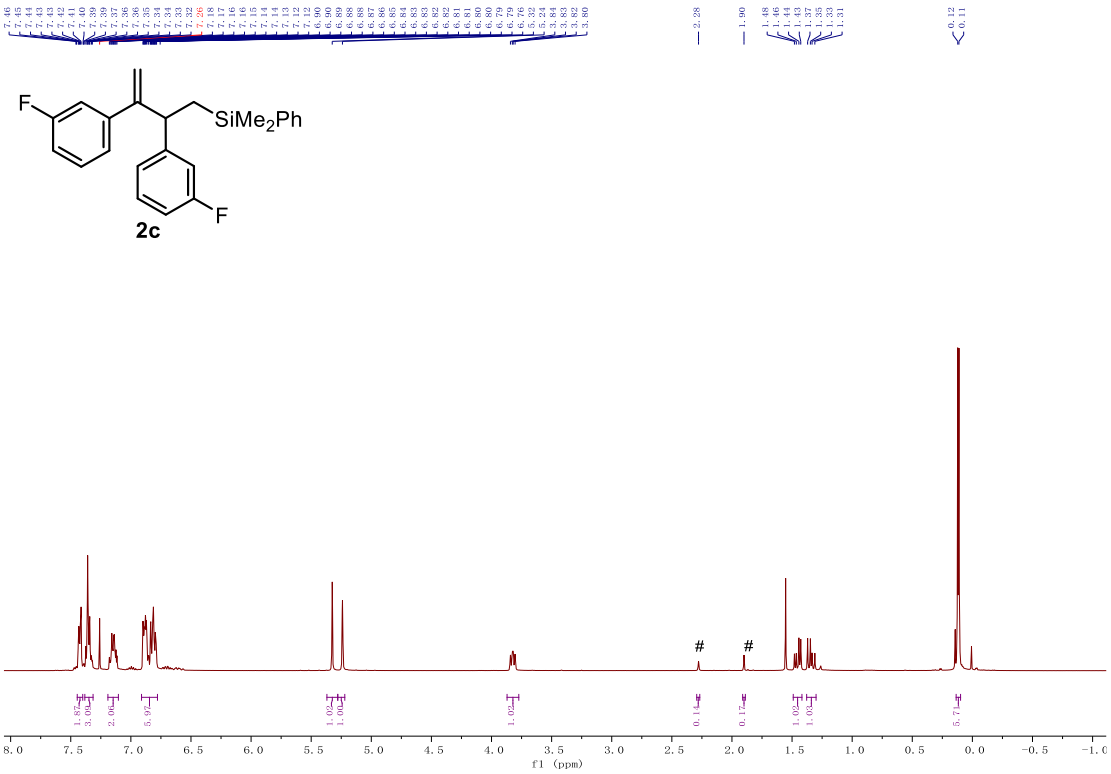
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



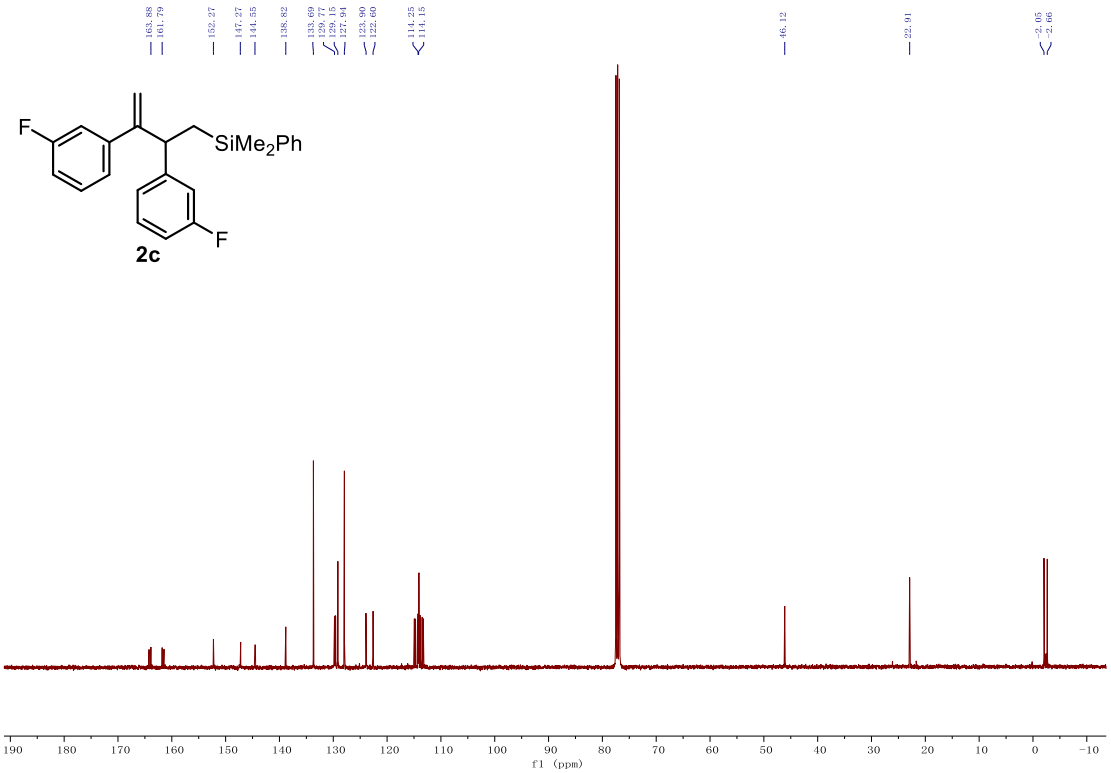
^{13}C NMR, $CDCl_3$, 101 MHz



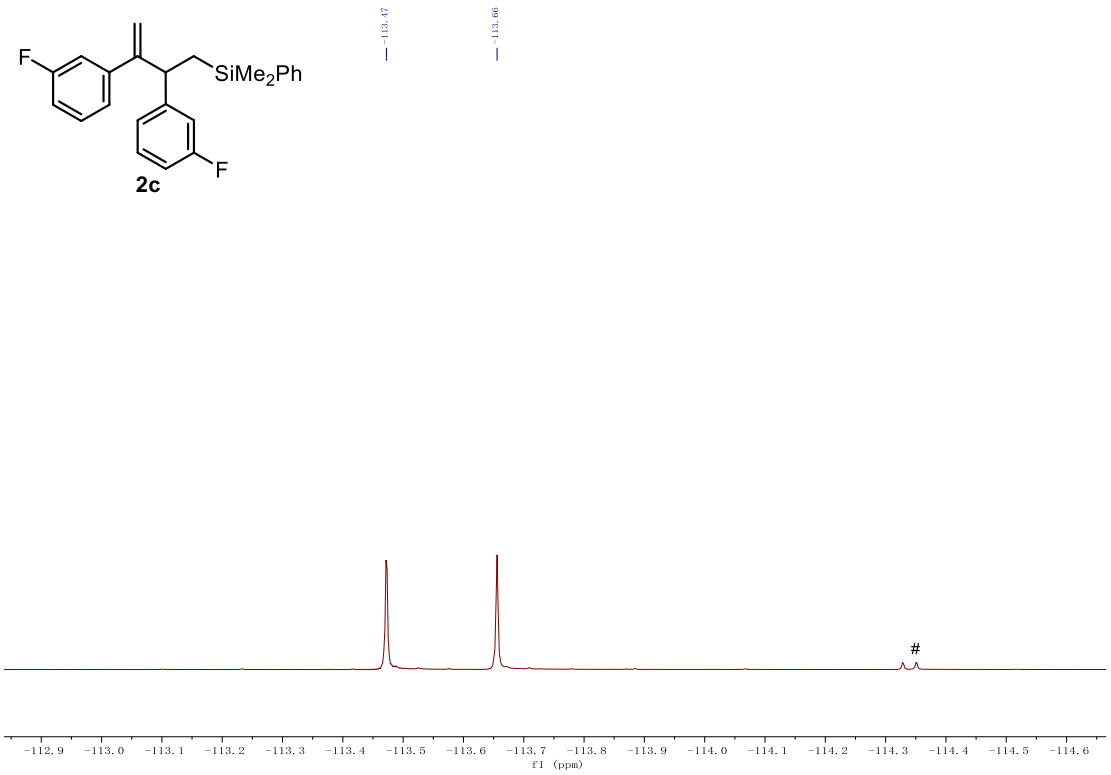
^{19}F NMR, $CDCl_3$, 376 MHz (# was attributed to 4,1-protosilylation isomer)



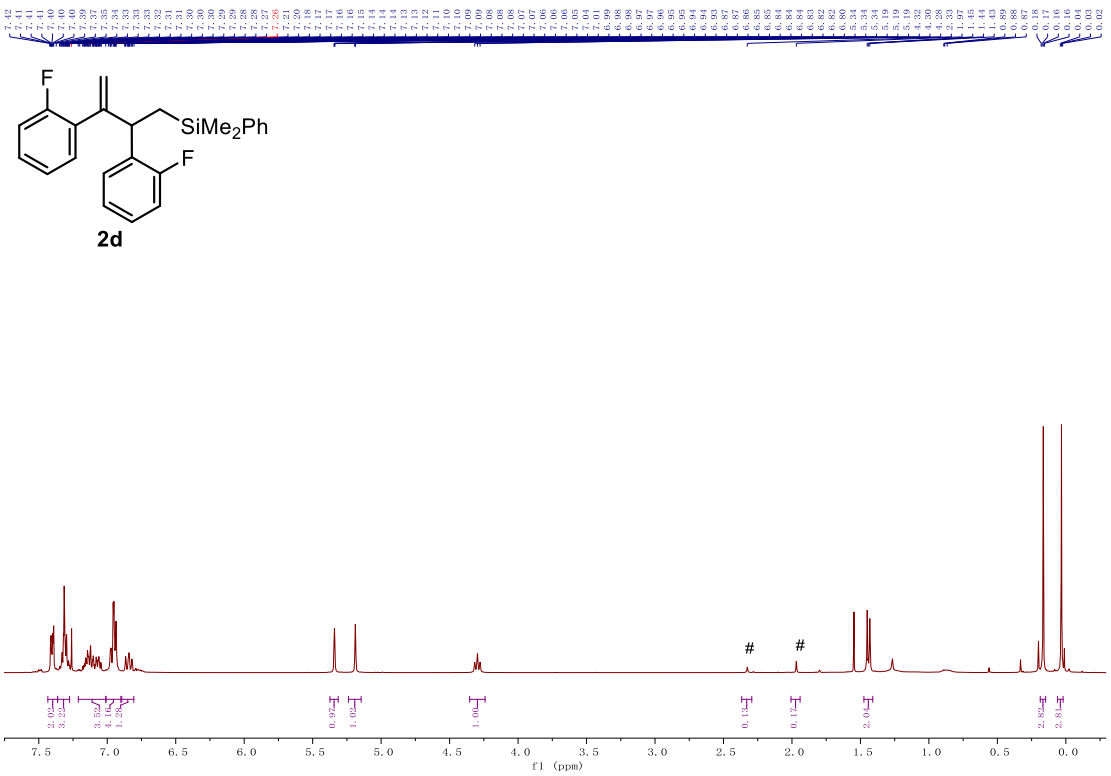
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



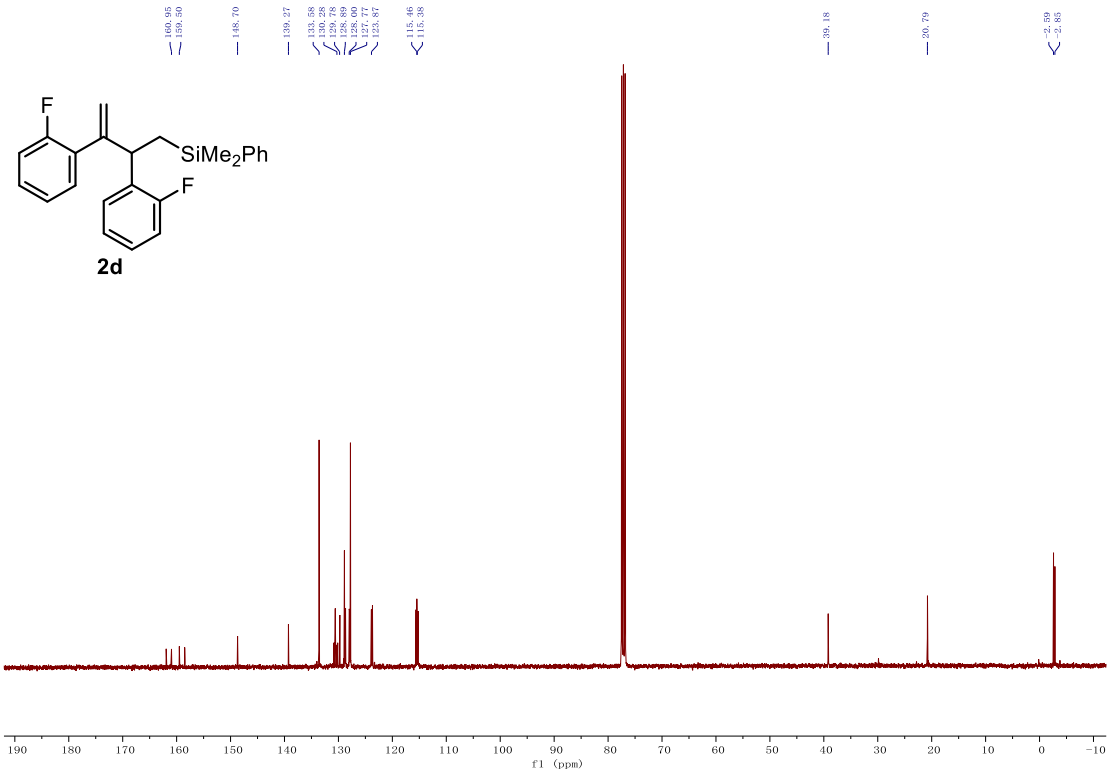
^{13}C NMR, $CDCl_3$, 101 MHz



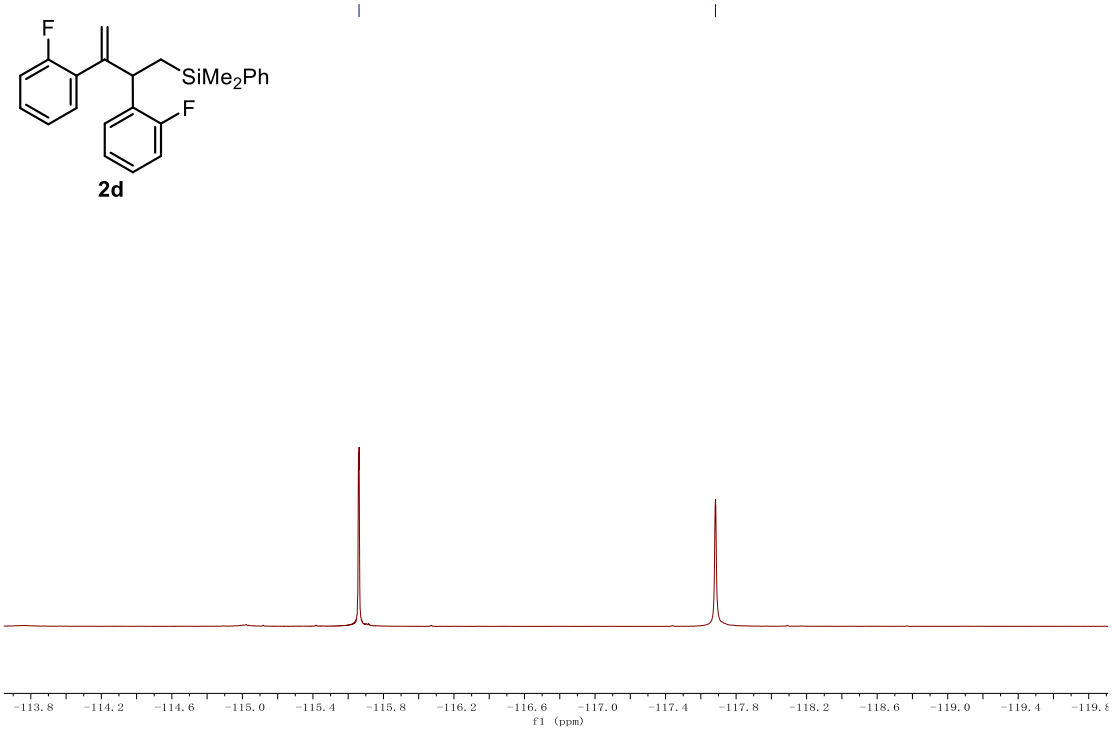
^{19}F NMR, $CDCl_3$, 376 MHz (# was attributed to 4,1-protosilylation isomer)



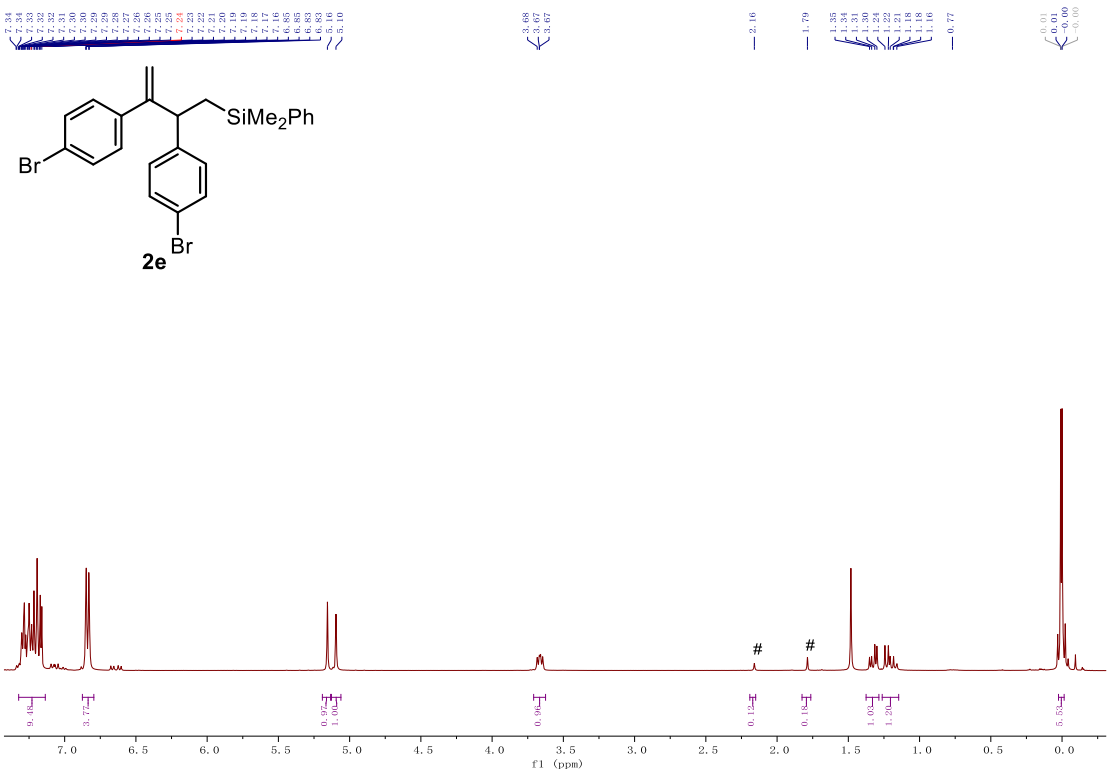
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



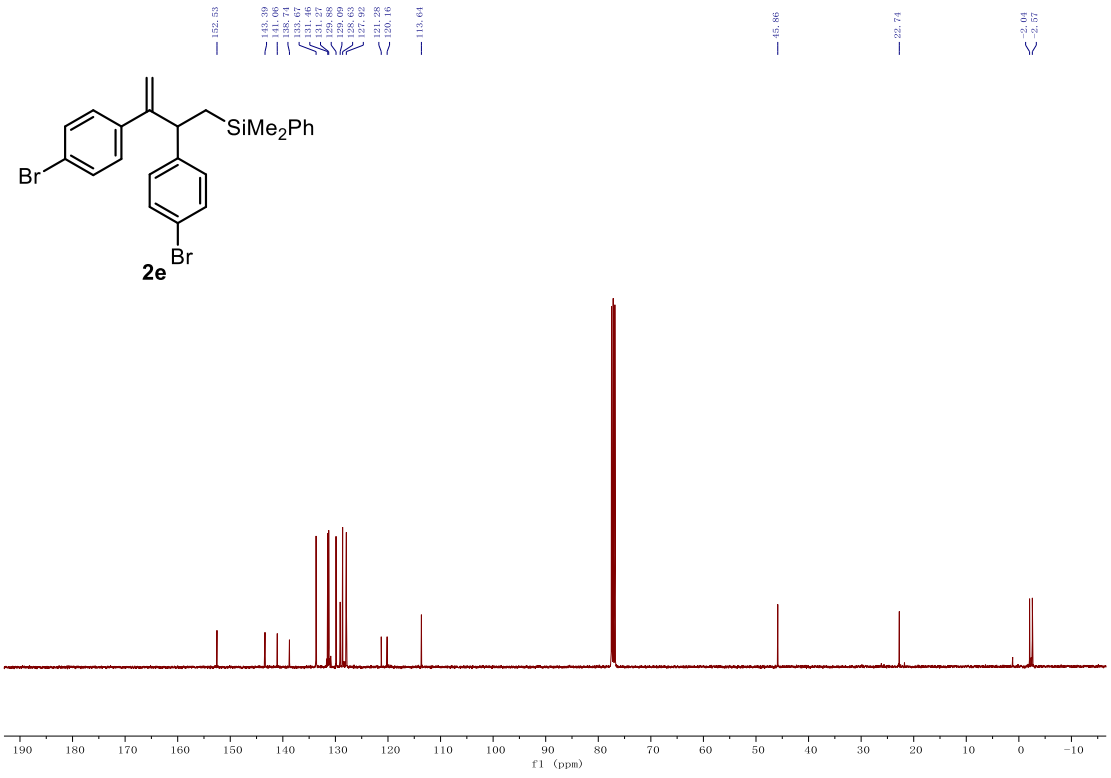
^{13}C NMR, $CDCl_3$, 101 MHz



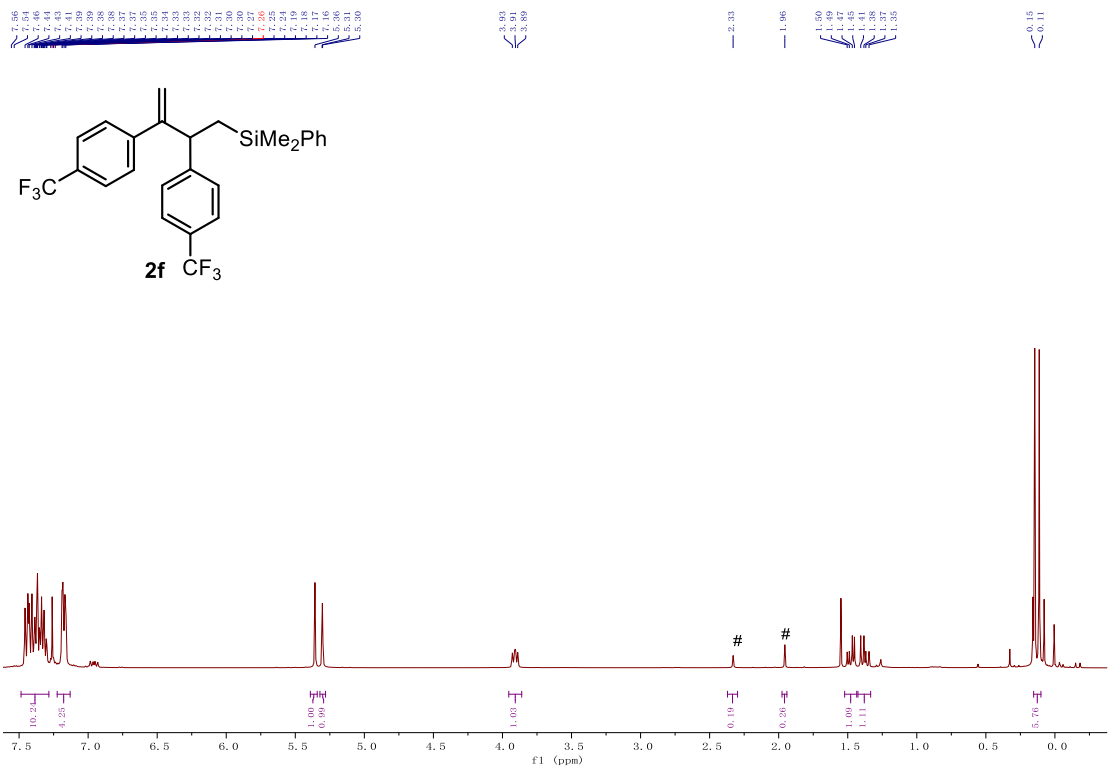
^{19}F NMR, $CDCl_3$, 376 MHz



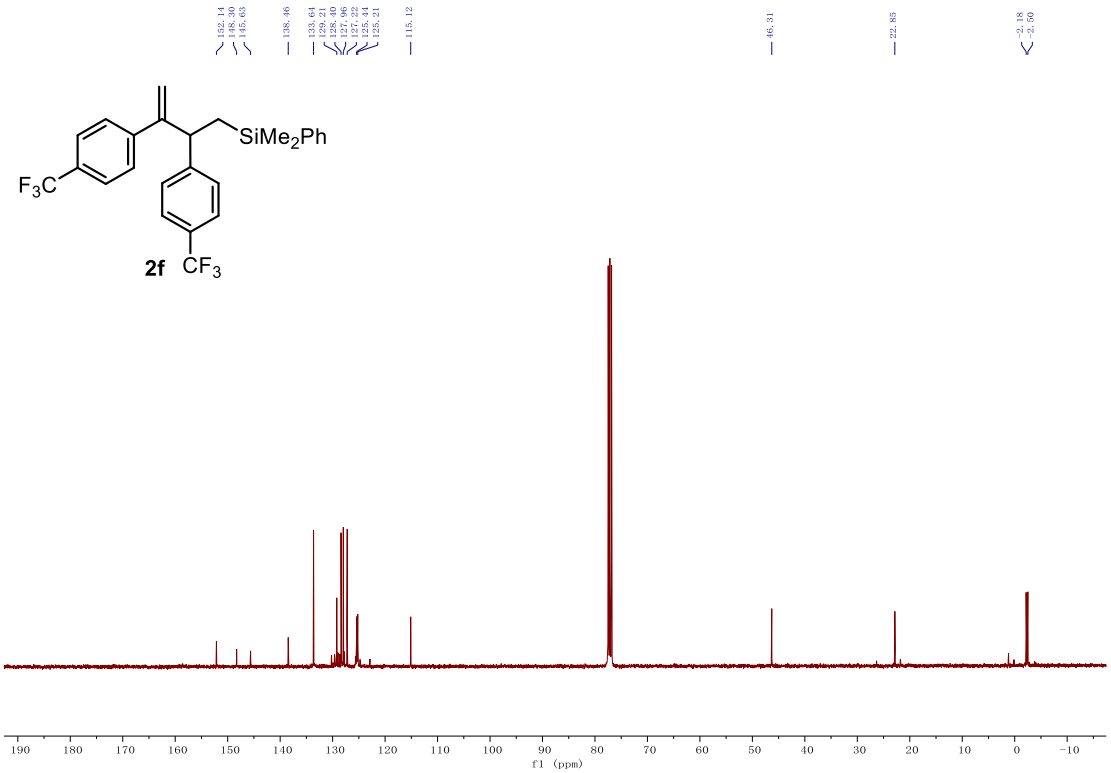
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



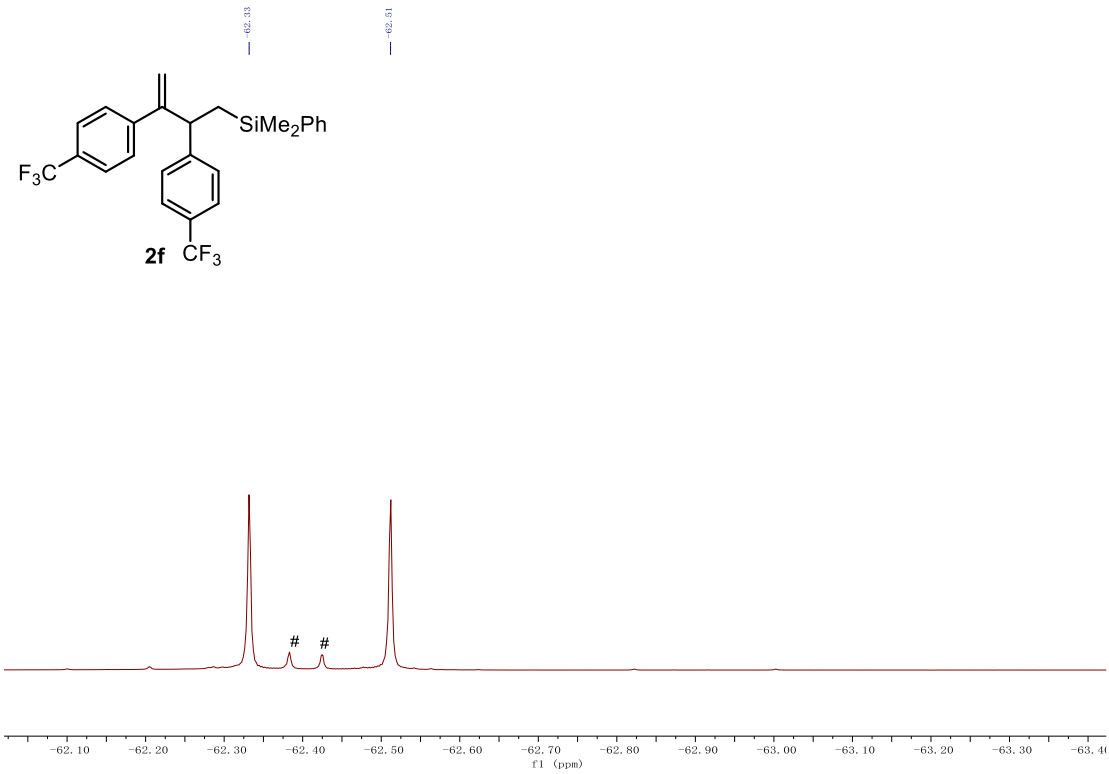
^{13}C NMR, $CDCl_3$, 101 MHz



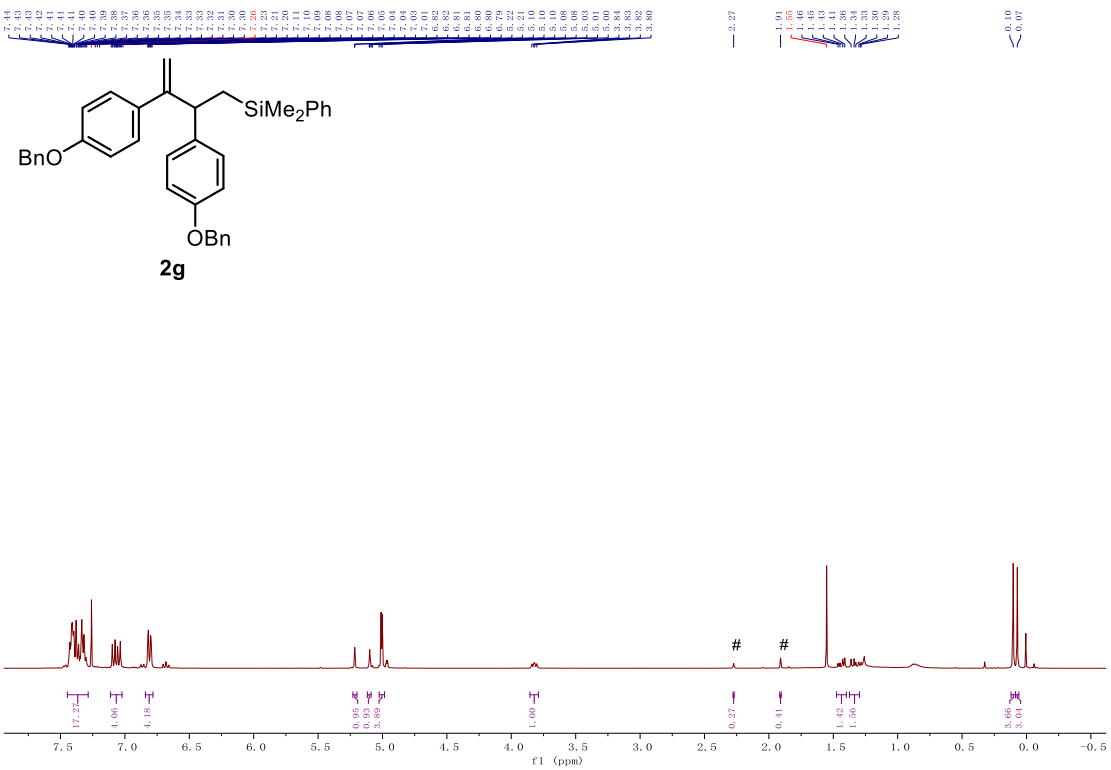
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



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

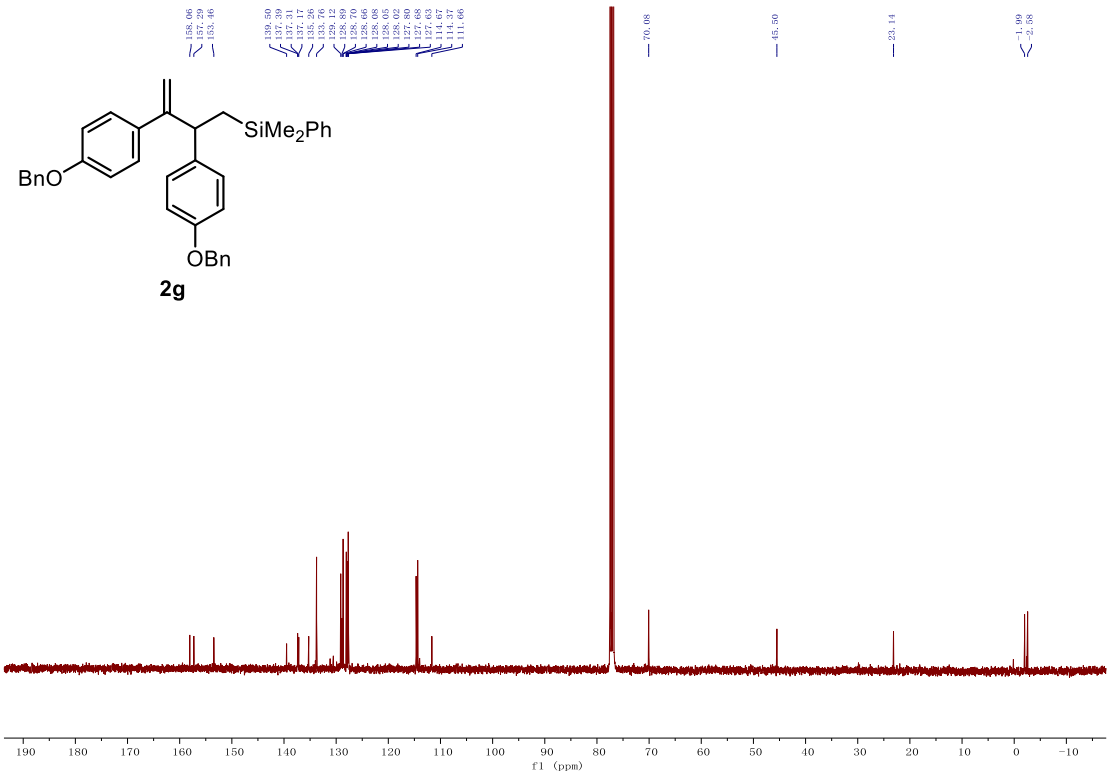


^{19}F NMR, $CDCl_3$, 376 MHz (# was attributed to 4,1-protosilylation isomer)



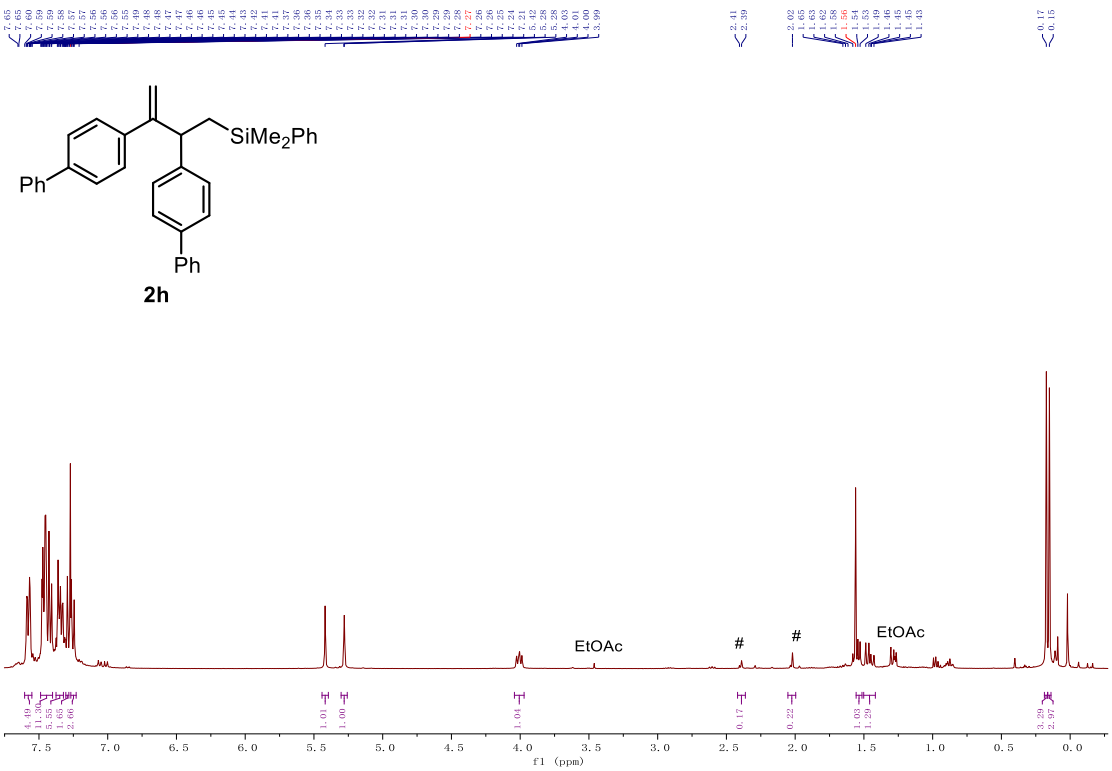
2g

^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)

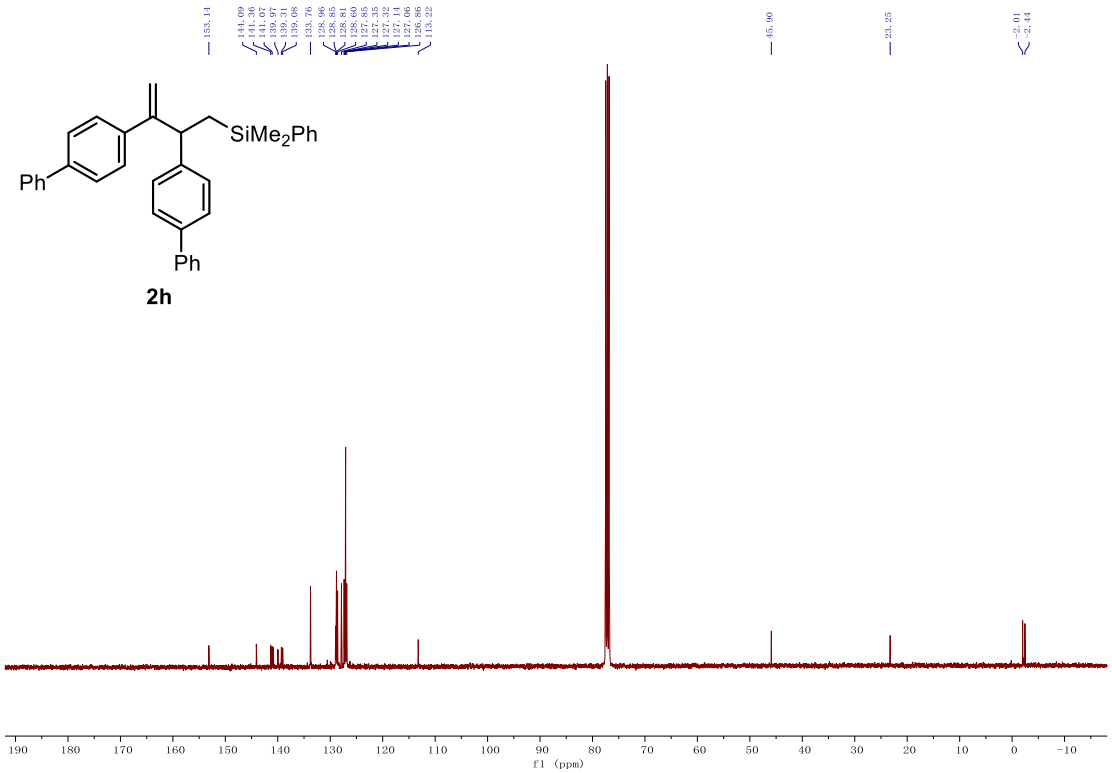


2g

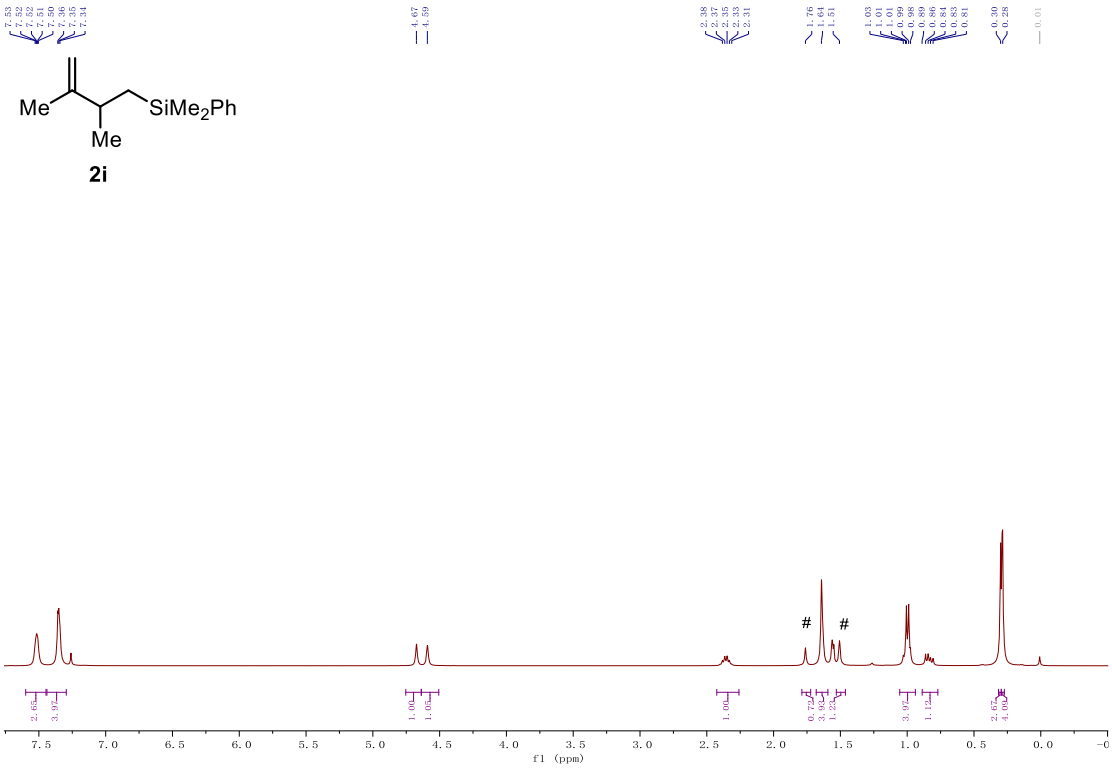
^{13}C NMR, $CDCl_3$, 101 MHz



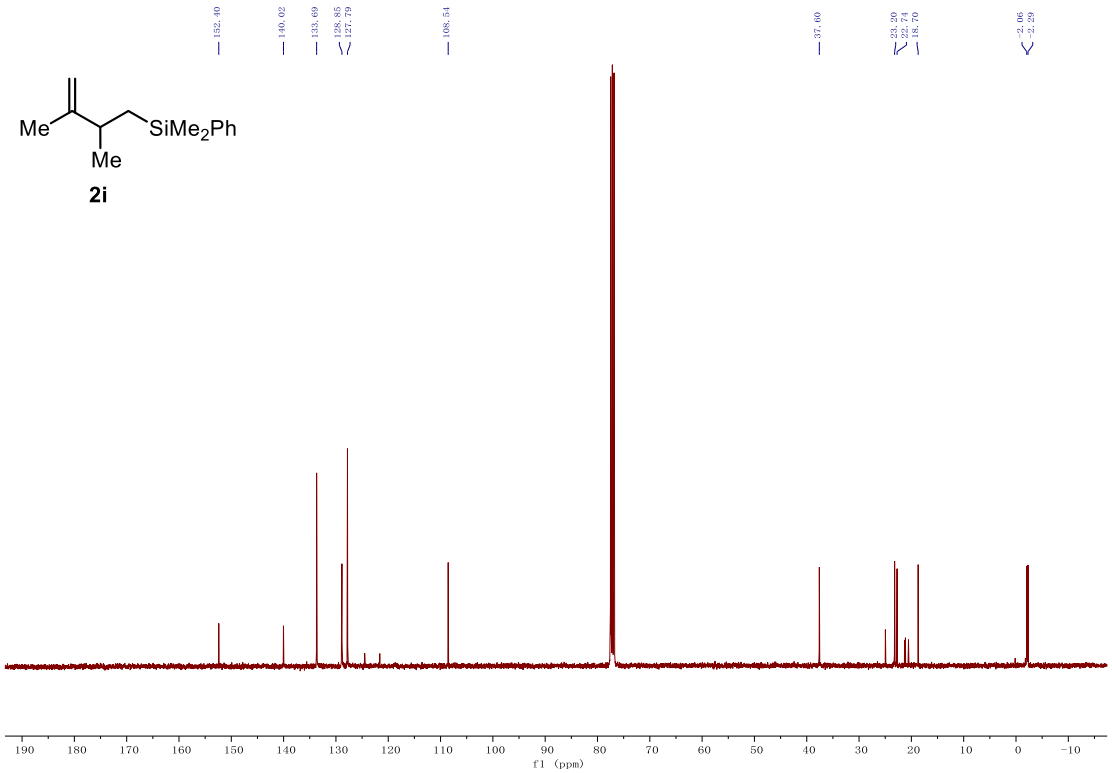
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



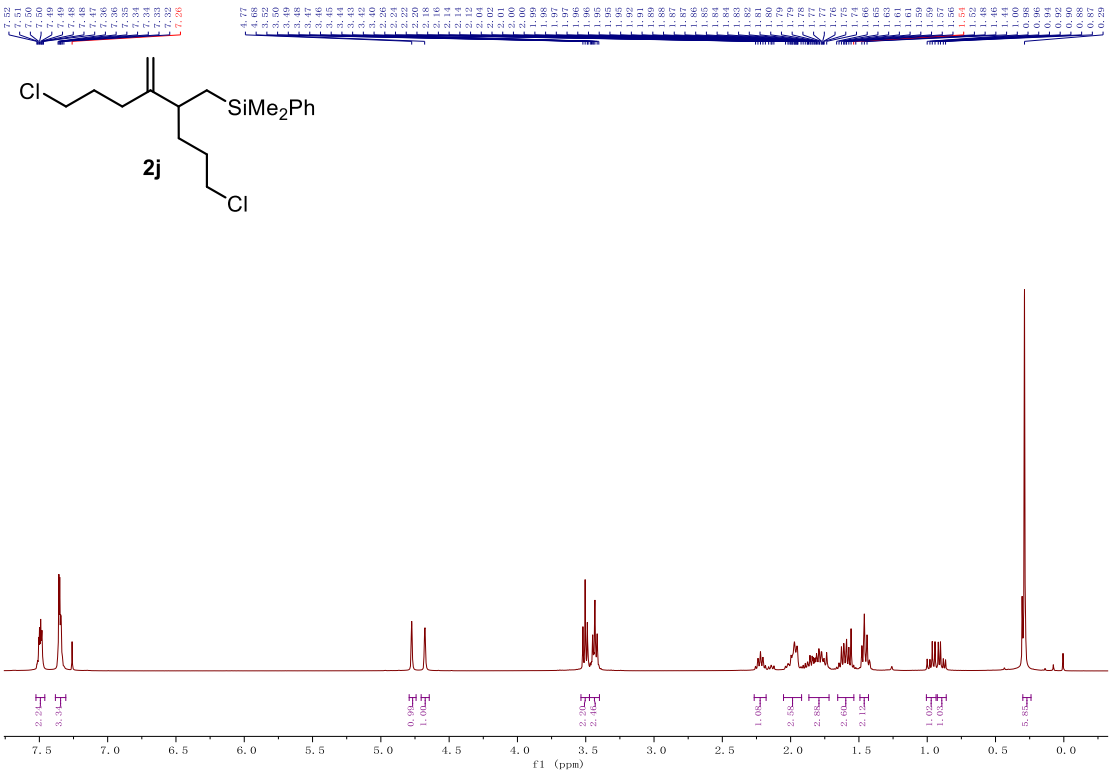
^{13}C NMR, $CDCl_3$, 101 MHz



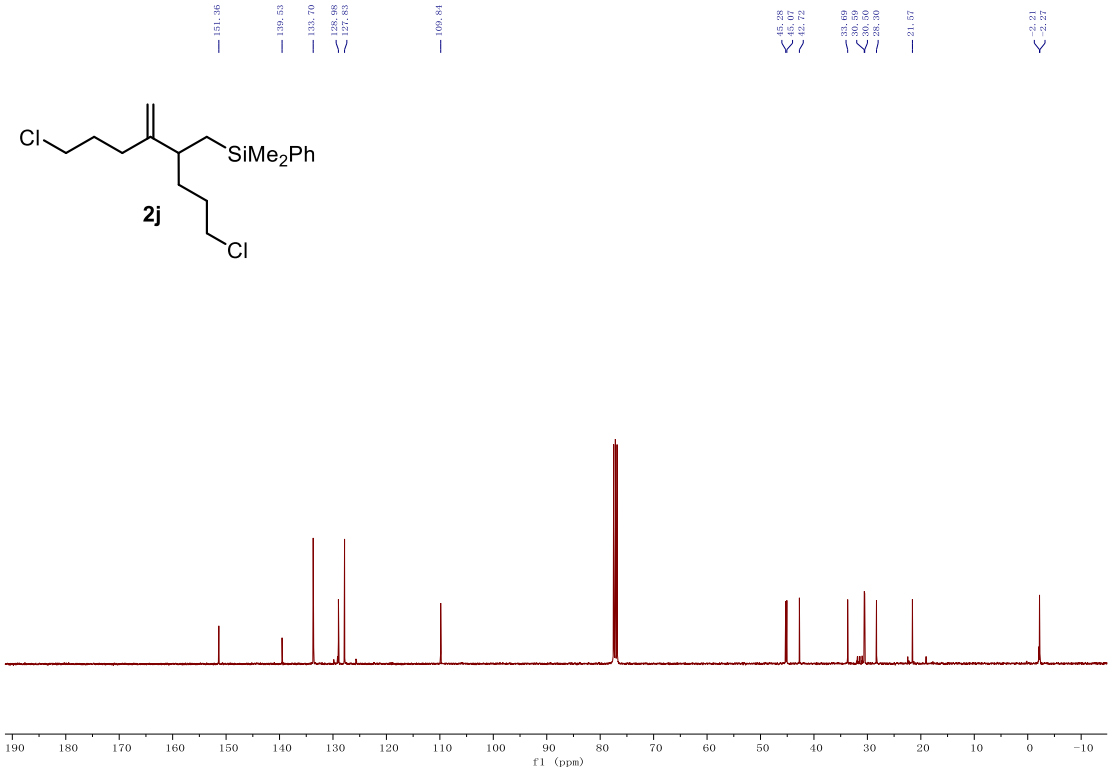
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



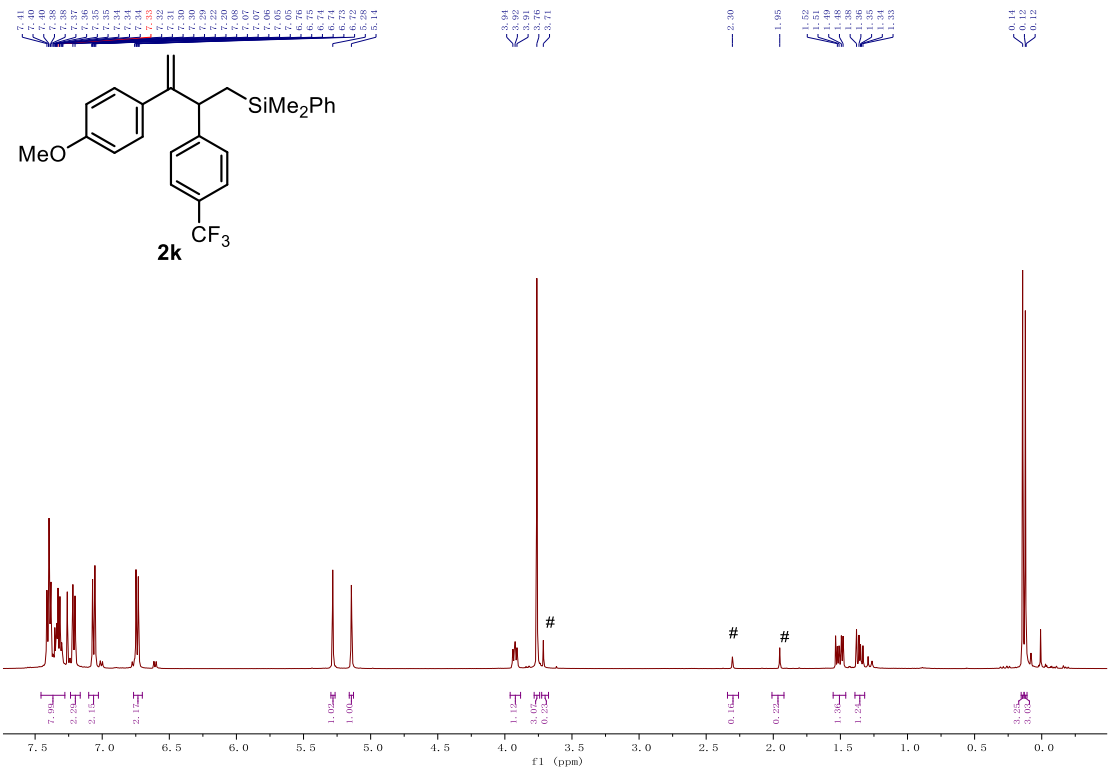
^{13}C NMR, $CDCl_3$, 101 MHz



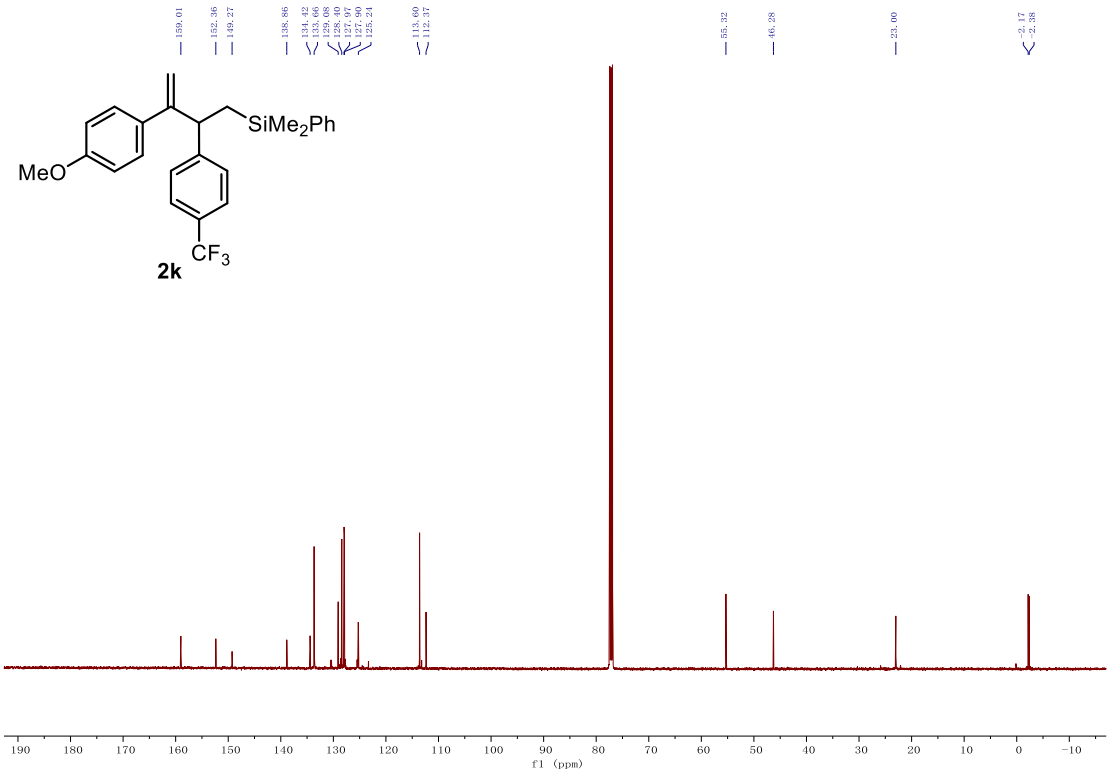
^{1}H NMR, $CDCl_3$, 400 MHz



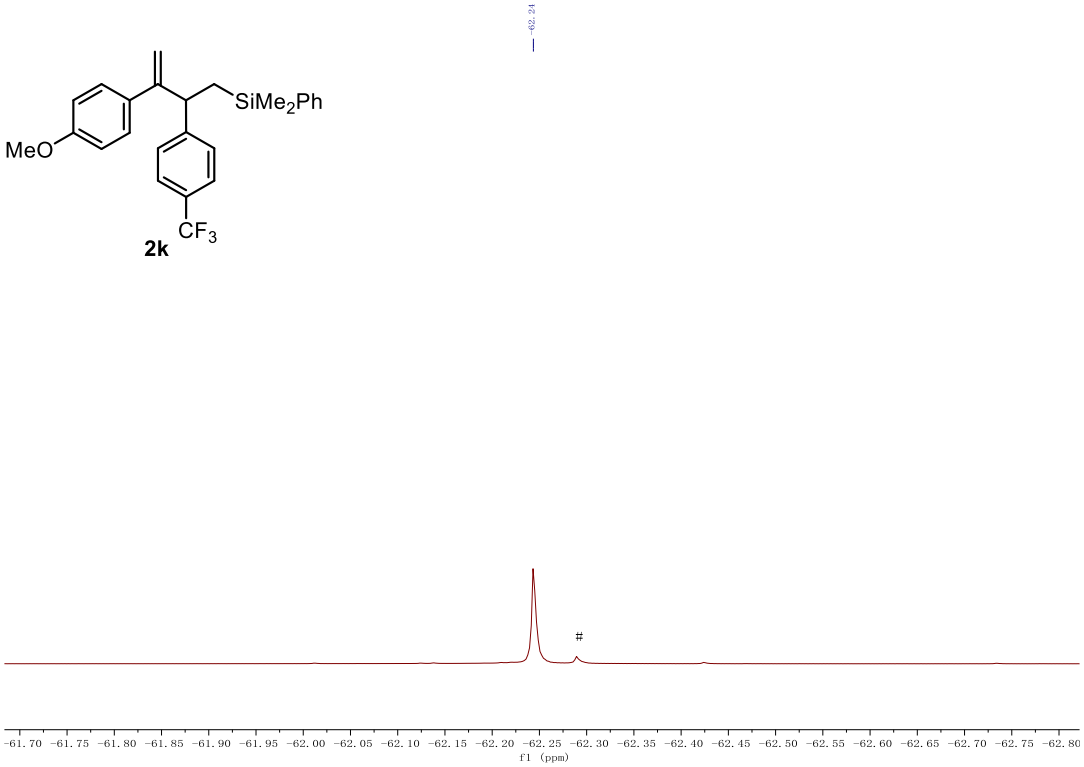
^{13}C NMR, $CDCl_3$, 101 MHz



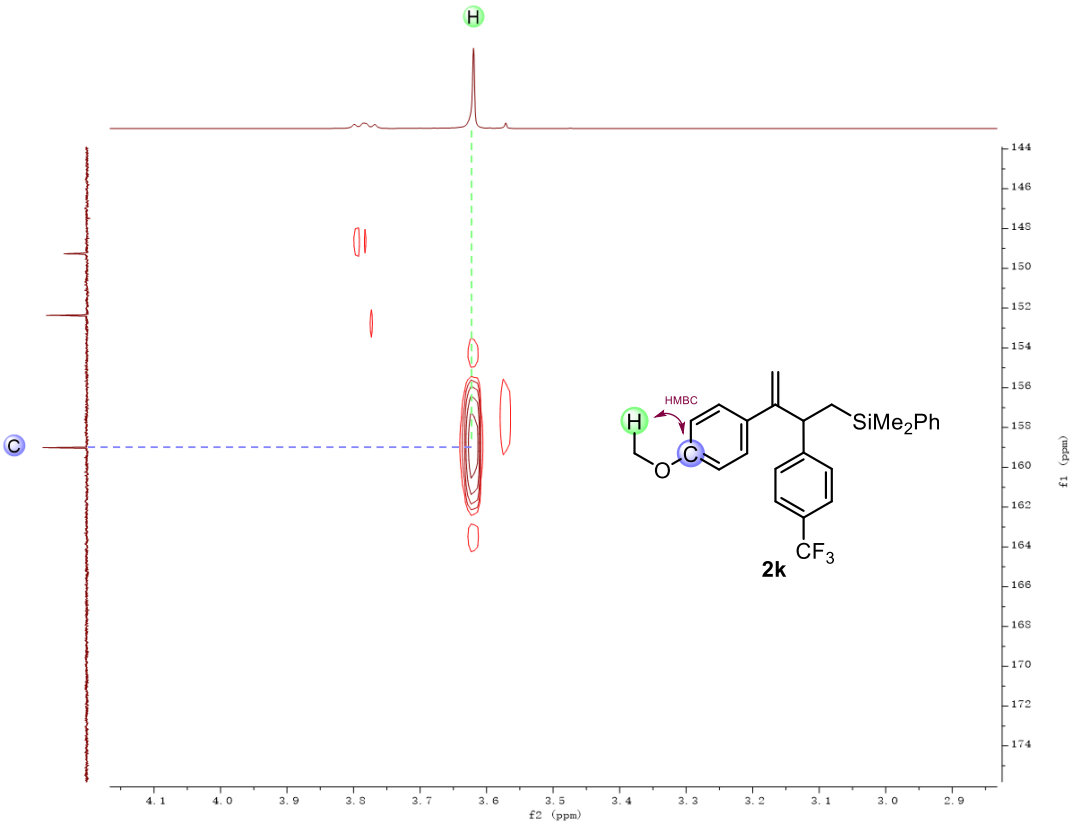
^{1}H NMR, $CDCl_3$, 400 MHz (# was attributed to 4,1-protosilylation isomer)



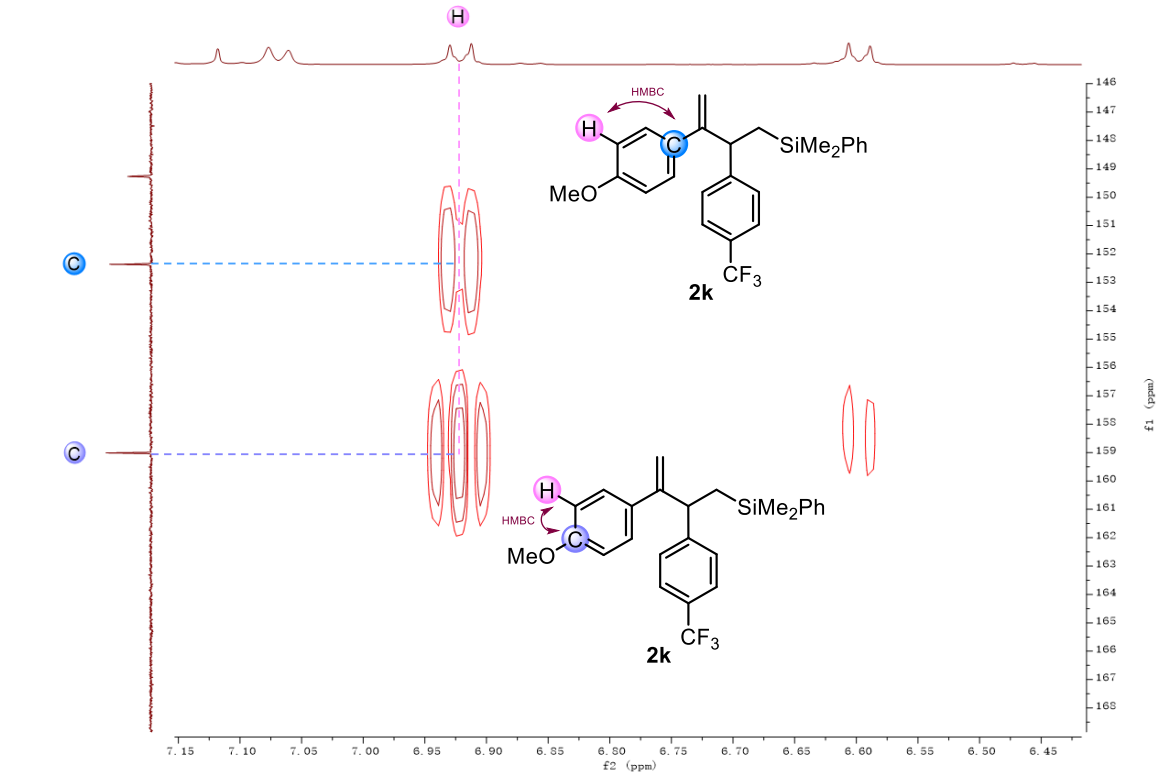
^{13}C NMR, $CDCl_3$, 101 MHz



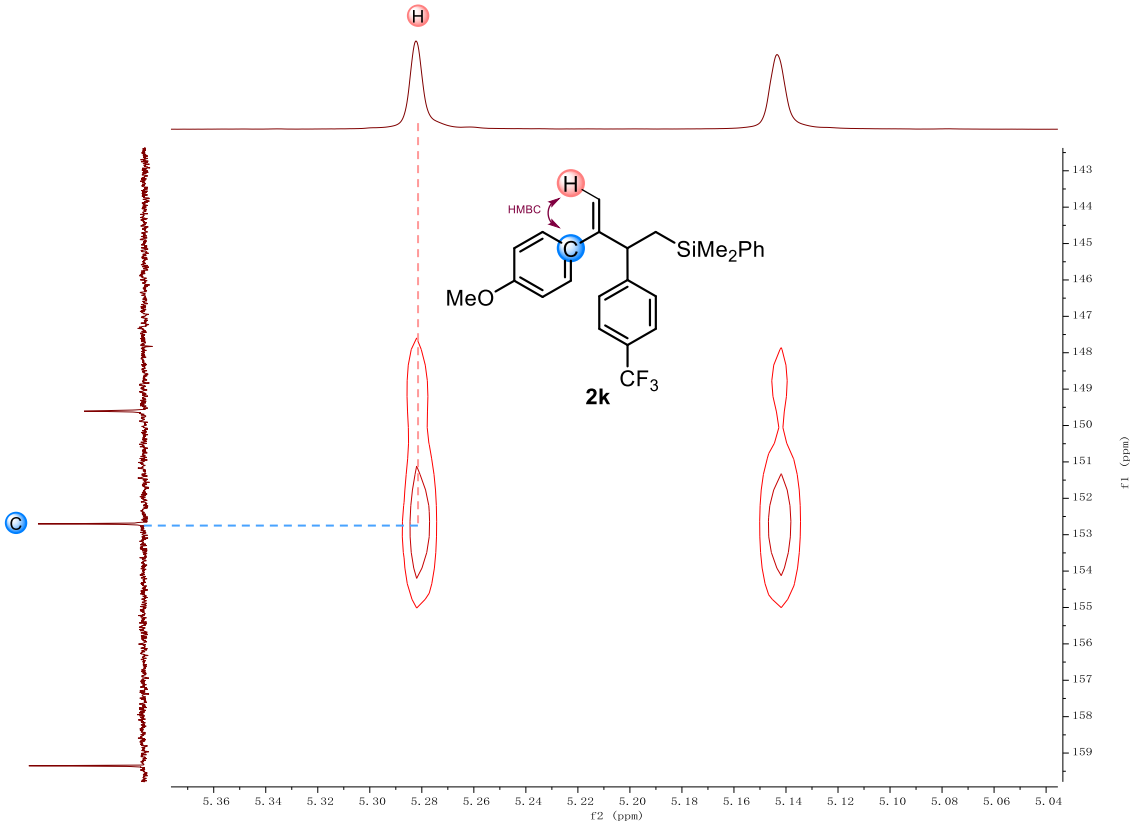
^{19}F NMR, $CDCl_3$, 376 MHz (# was attributed to 4,1-protosilylation isomer)



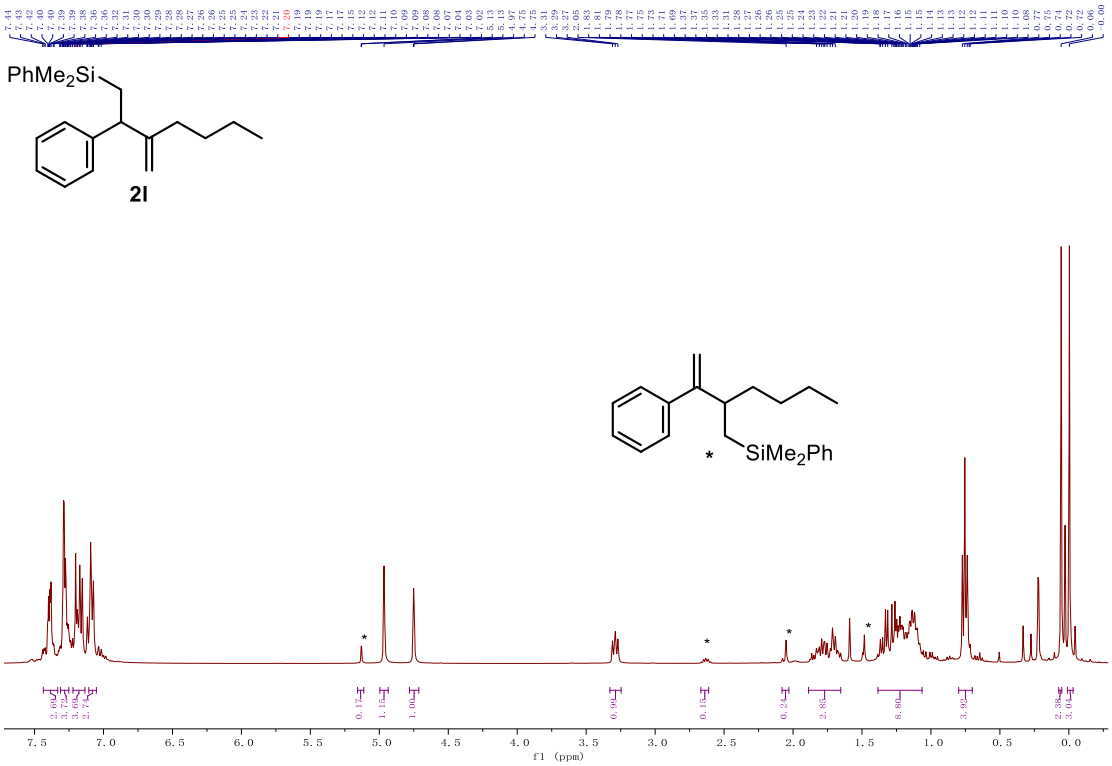
^{1}H, ^{13}C-HMBC



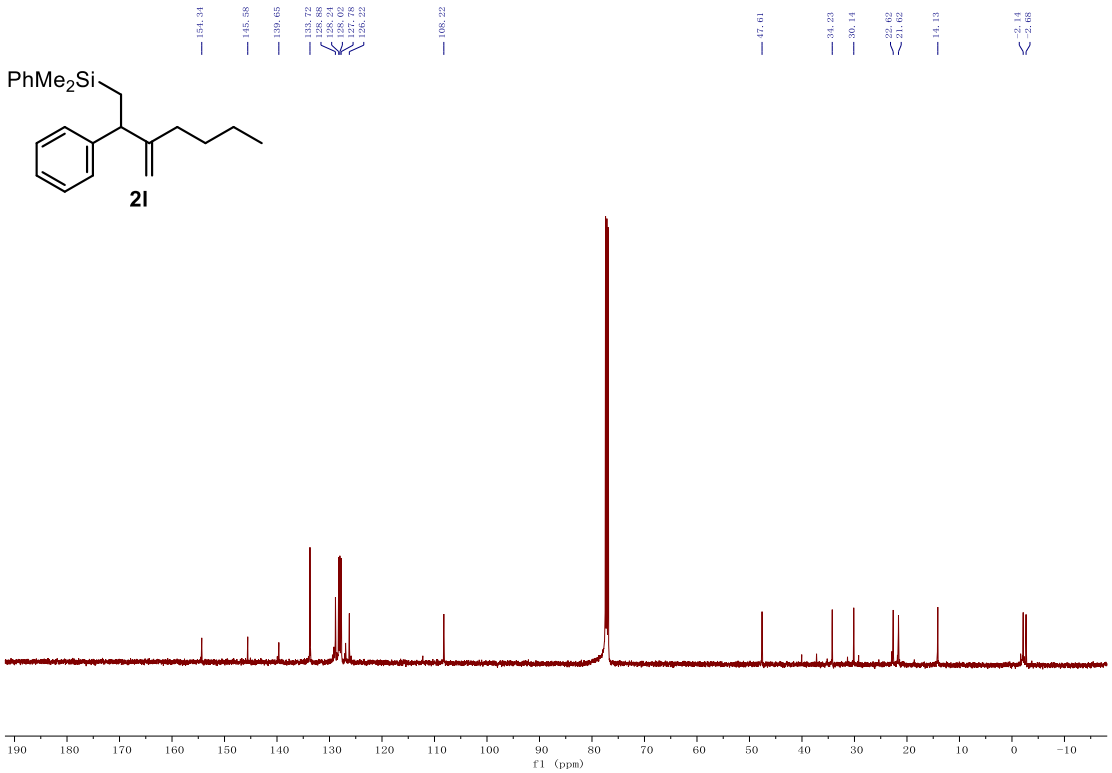
^{1}H, ^{13}C-HMBC



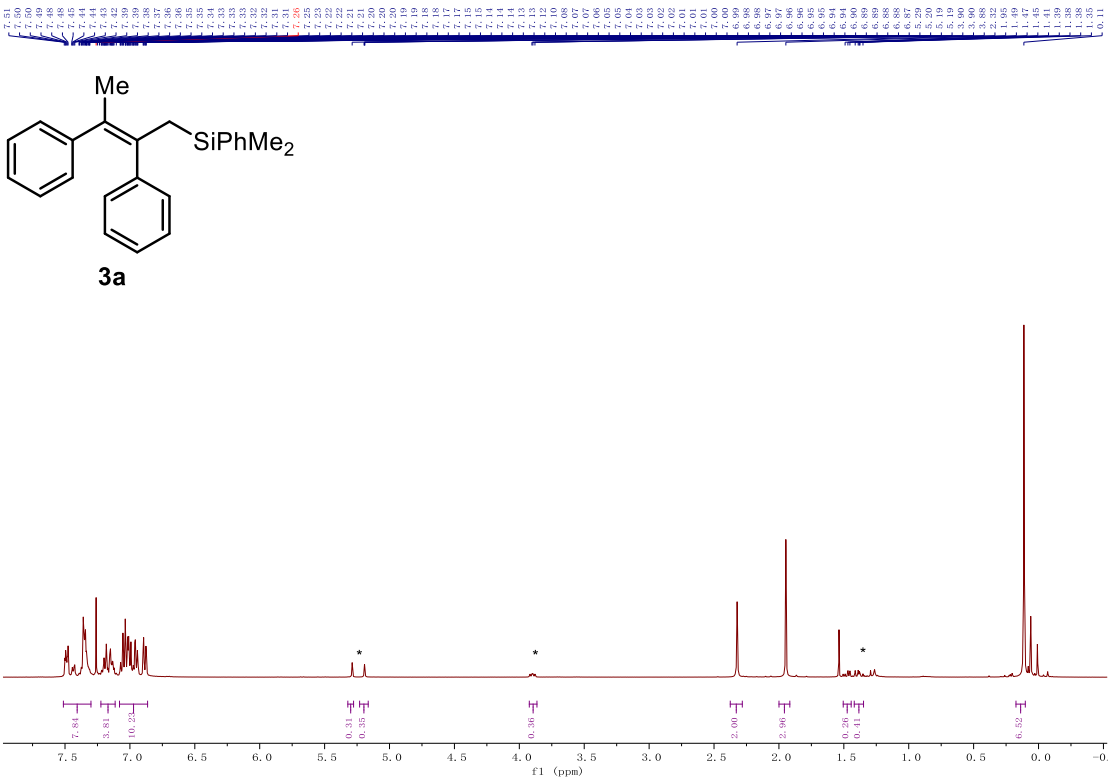
^{1}H, ^{13}C-HMBC



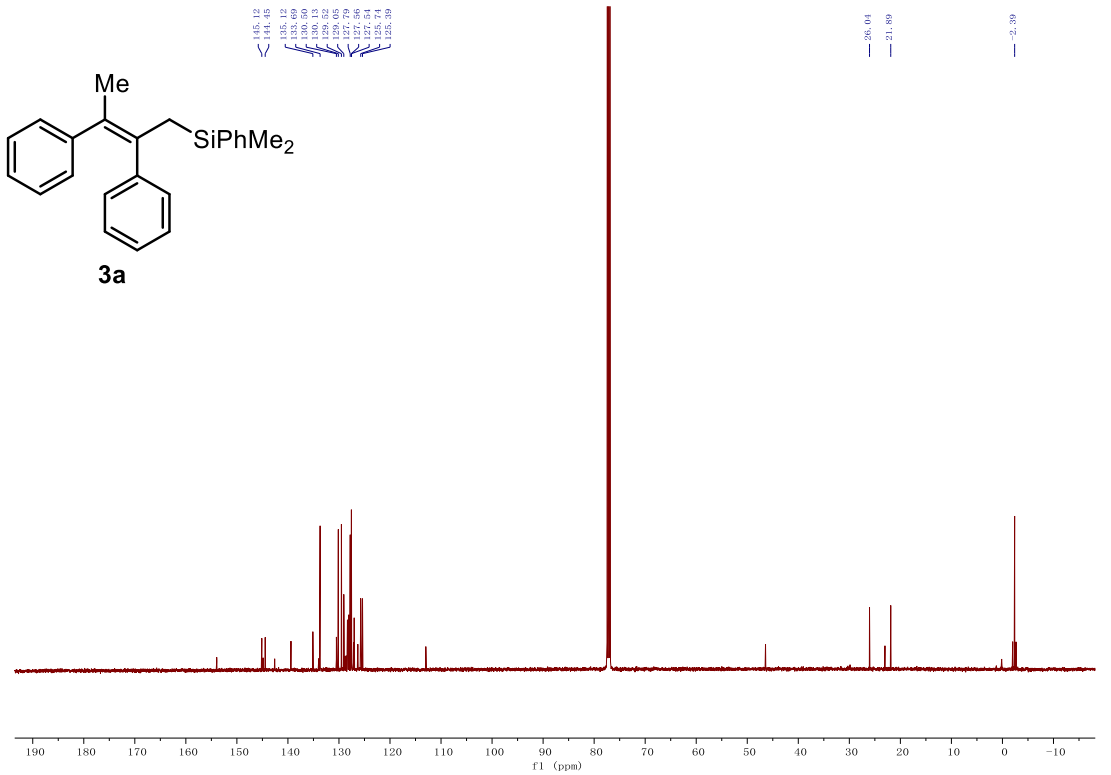
^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to regioisomer as indicated)



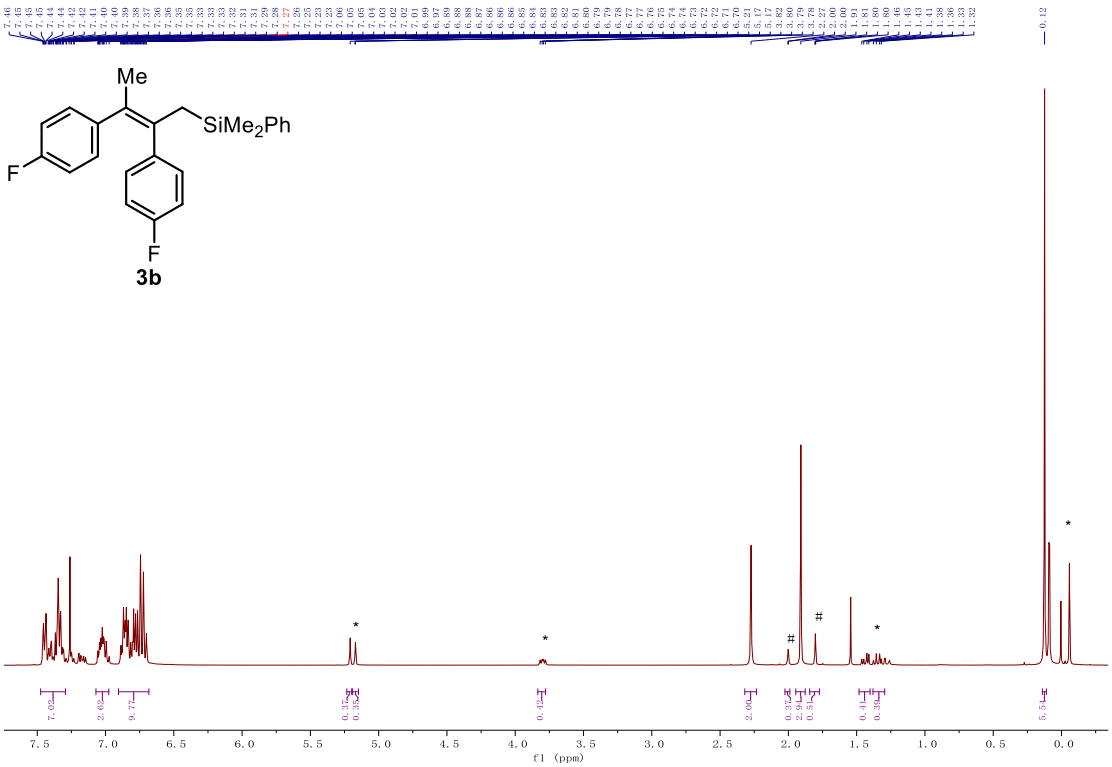
^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to 2,1-protosilylation isomer)

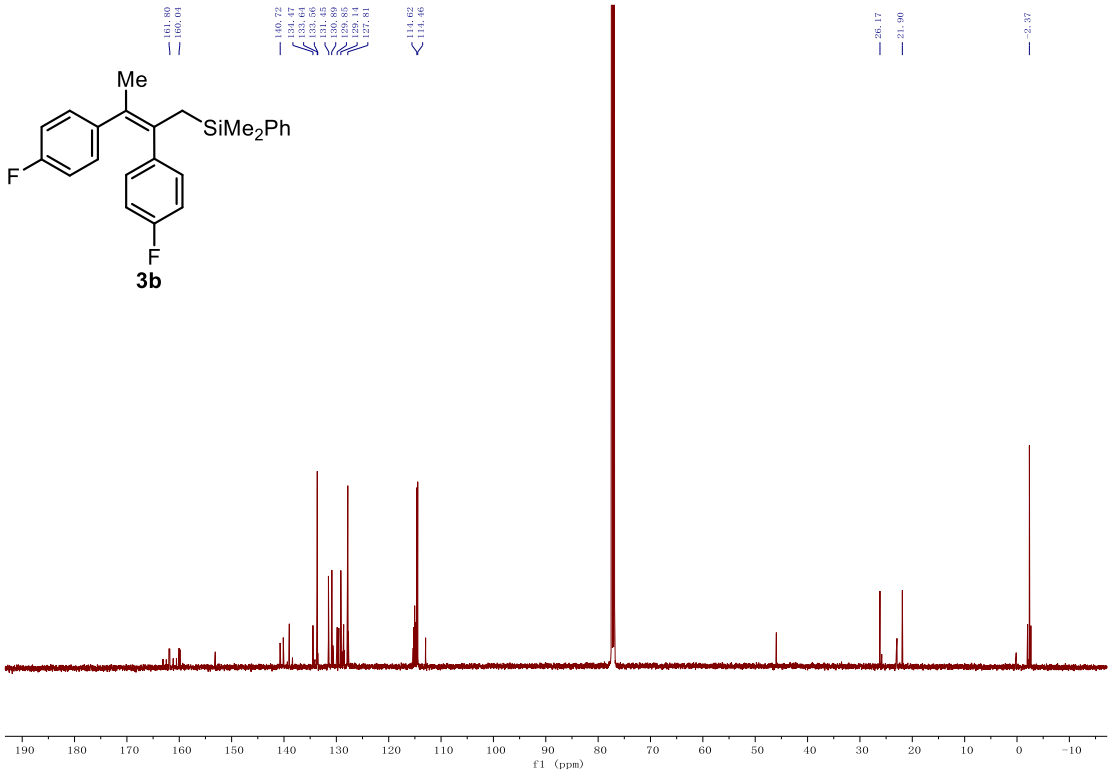


^{13}C NMR, $CDCl_3$, 101 MHz

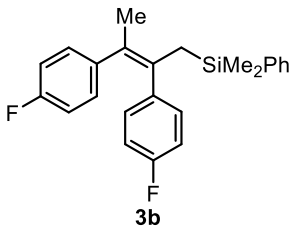


^{1}H NMR, $CDCl_3$, 400 MHz

(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



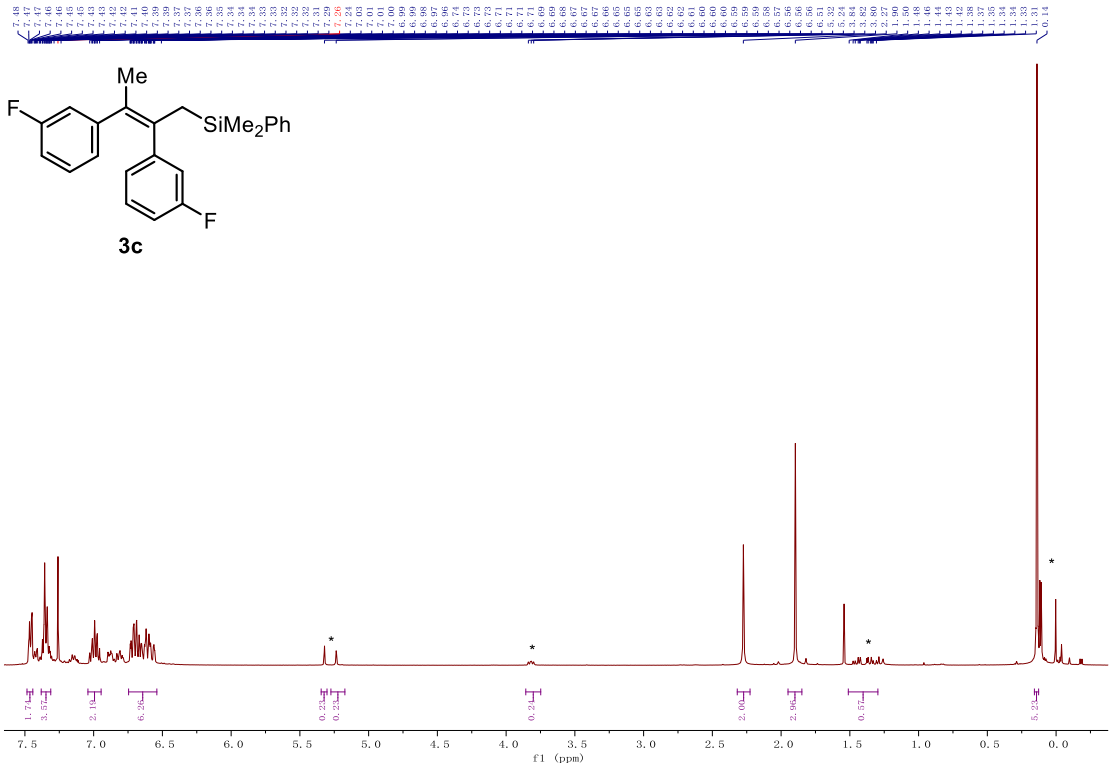
^{13}C NMR, $CDCl_3$, 101 MHz



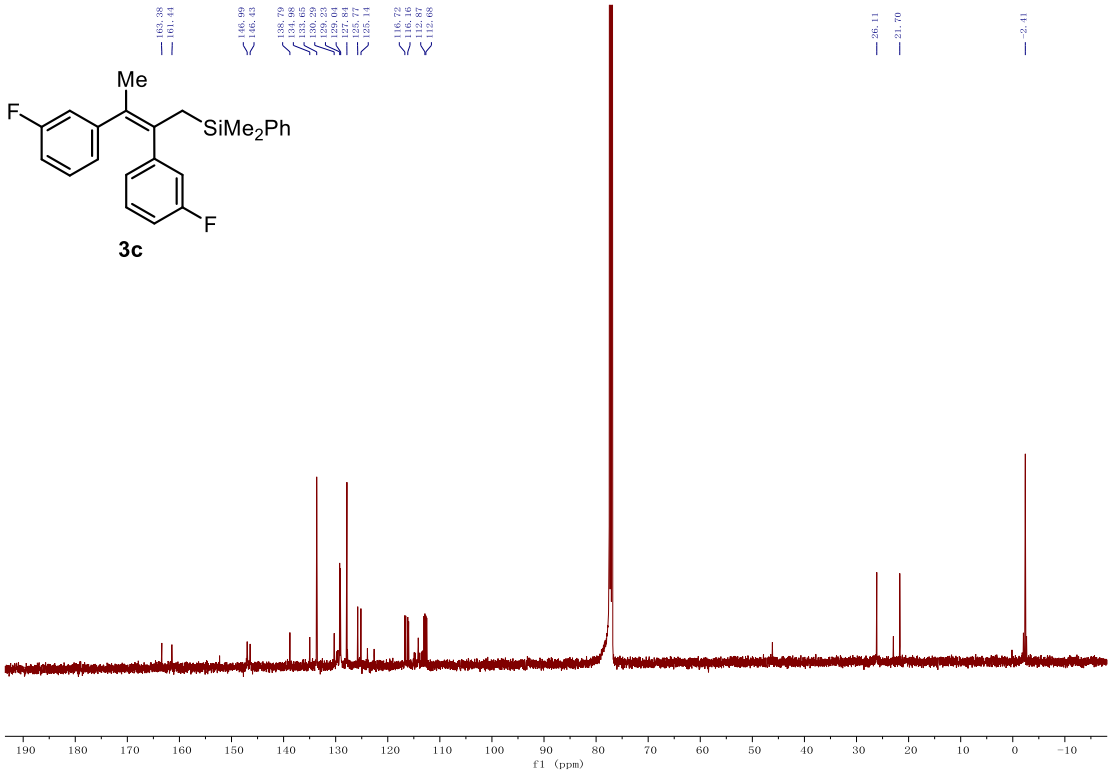
3b

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

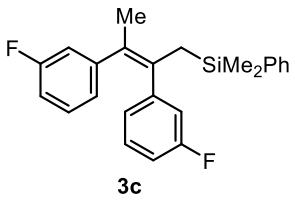
(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



^{1}H NMR, $CDCl_3$, 400 MHz(* was attributed to 2,1-protosilylation isomer)



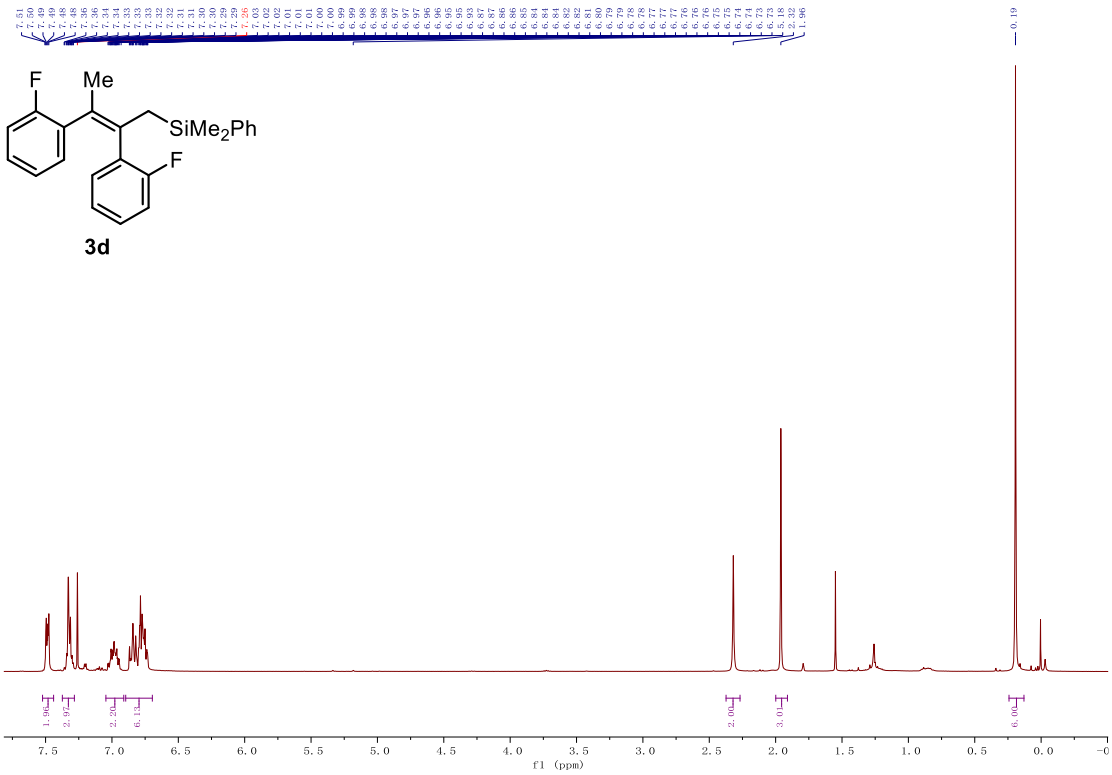
^{13}C NMR, $CDCl_3$, 101 MHz



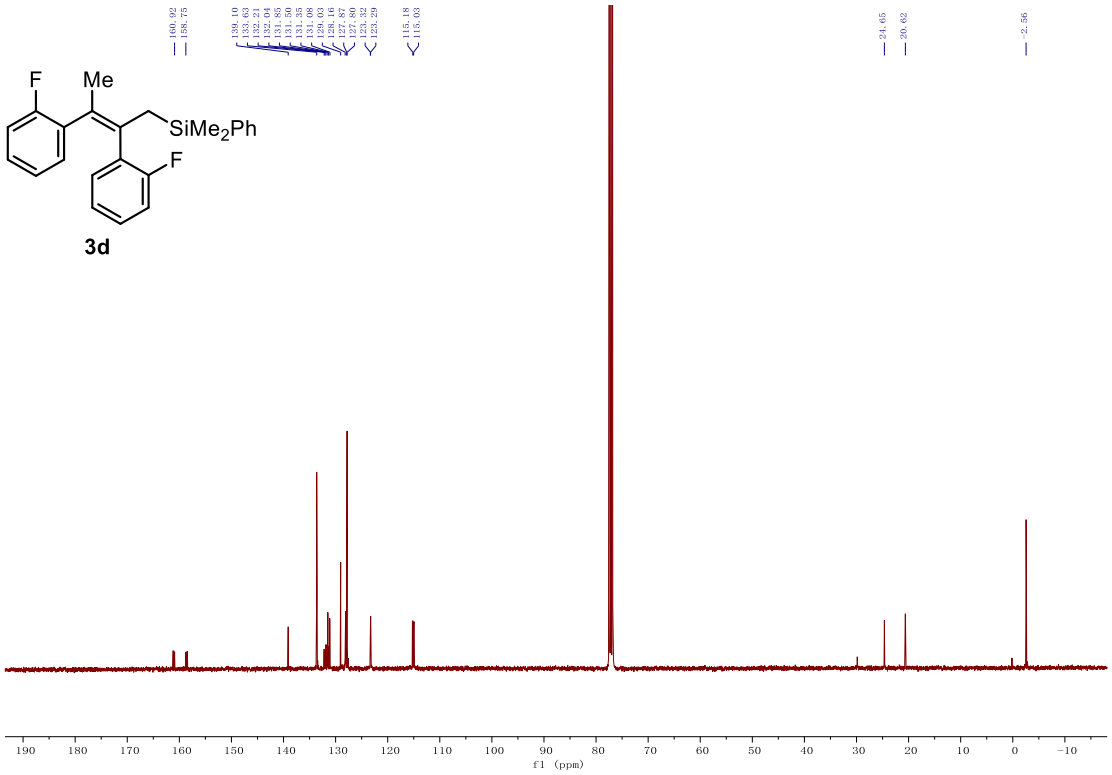
3c

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

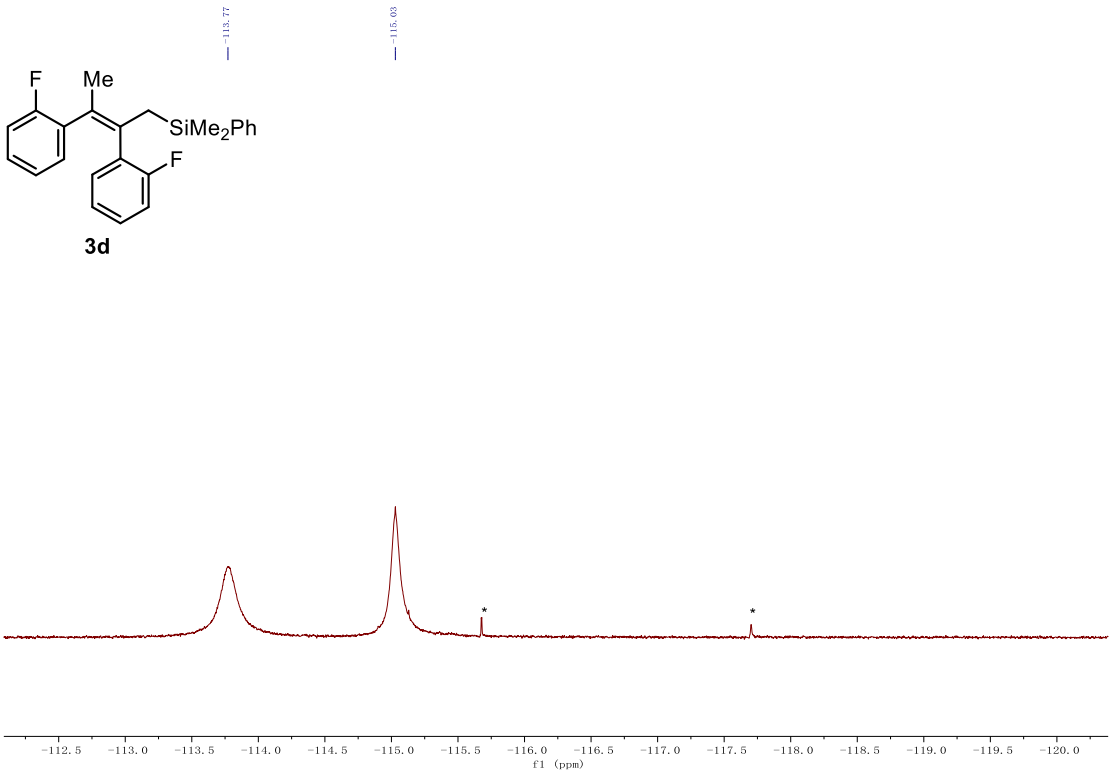
(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



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

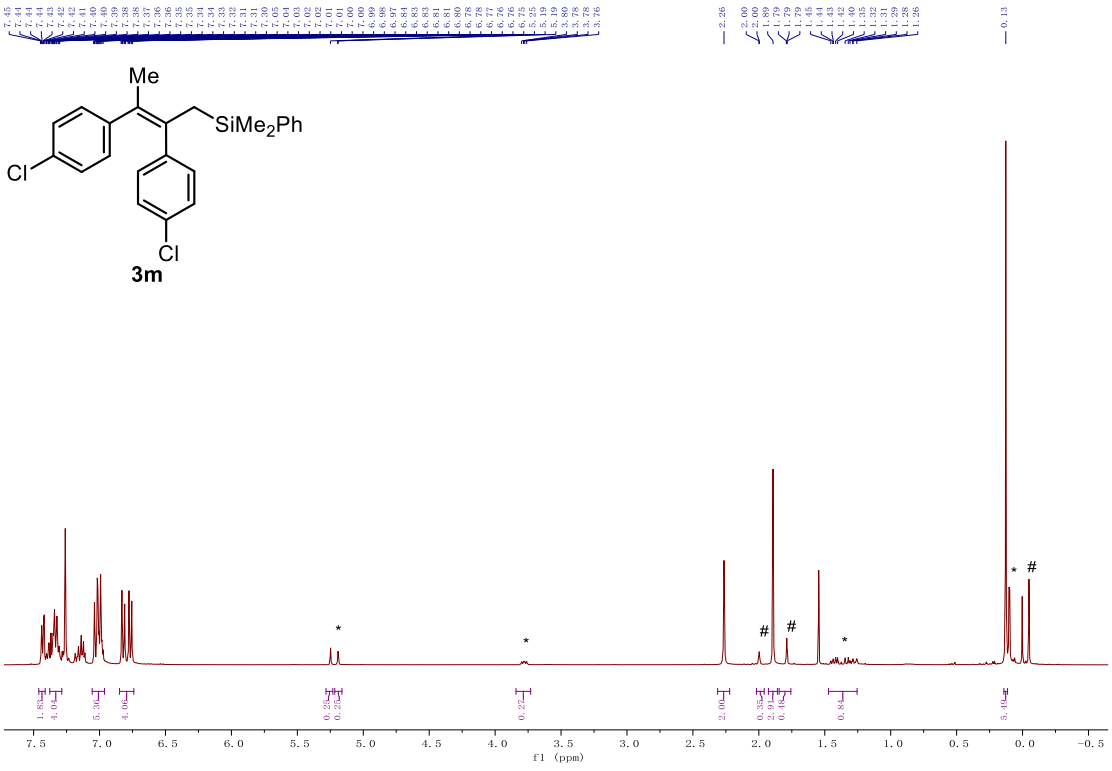


^{13}C NMR, $CDCl_3$, 101 MHz



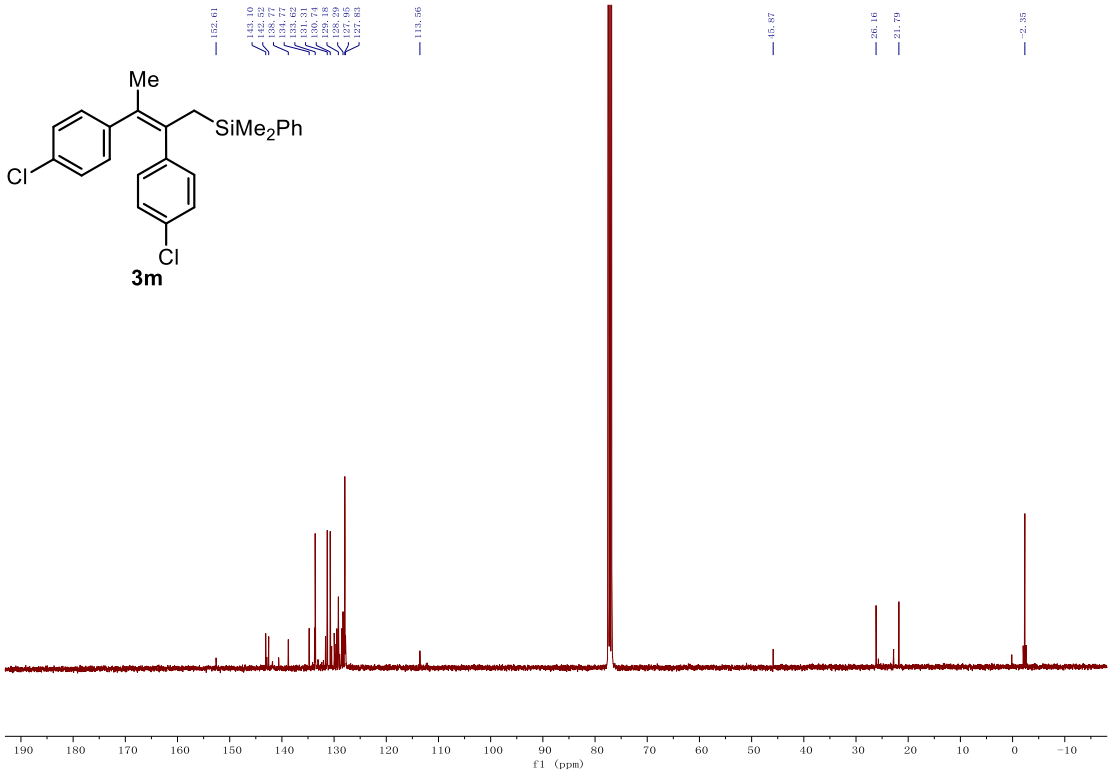
3d

^{19}F NMR, $CDCl_3$, 376 MHz (* was attributed to 2,1-protosilylation isomer)

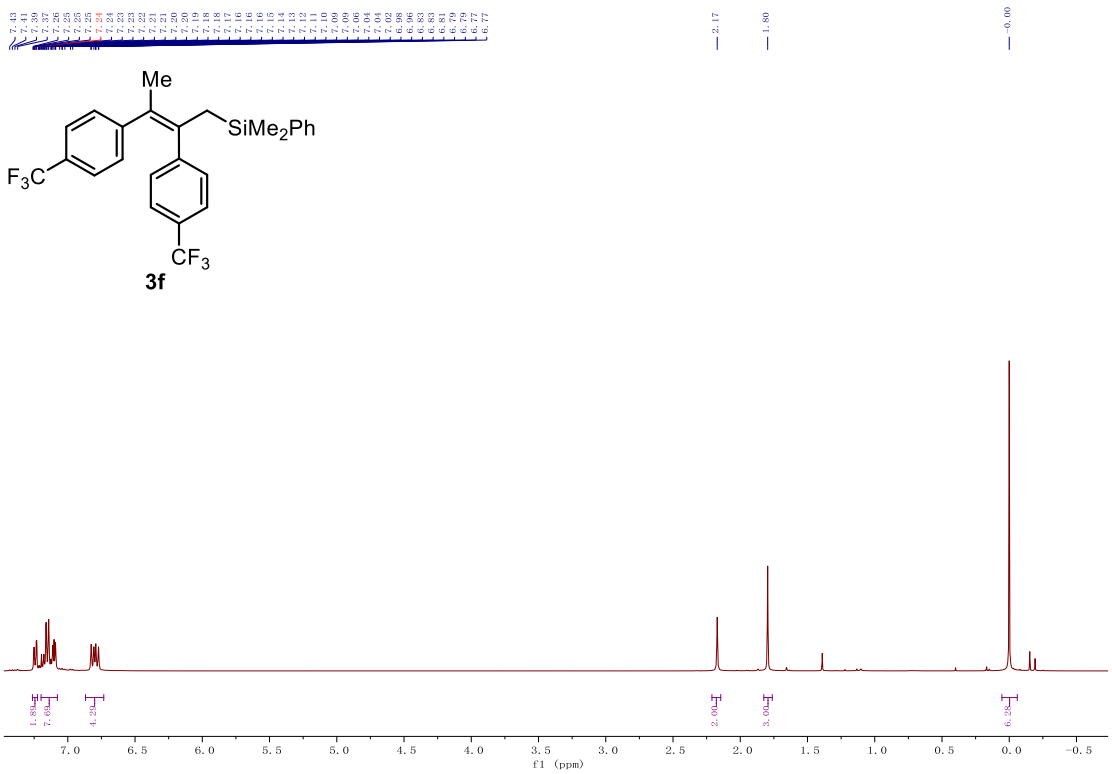


^{1}H NMR, $CDCl_3$, 400 MHz

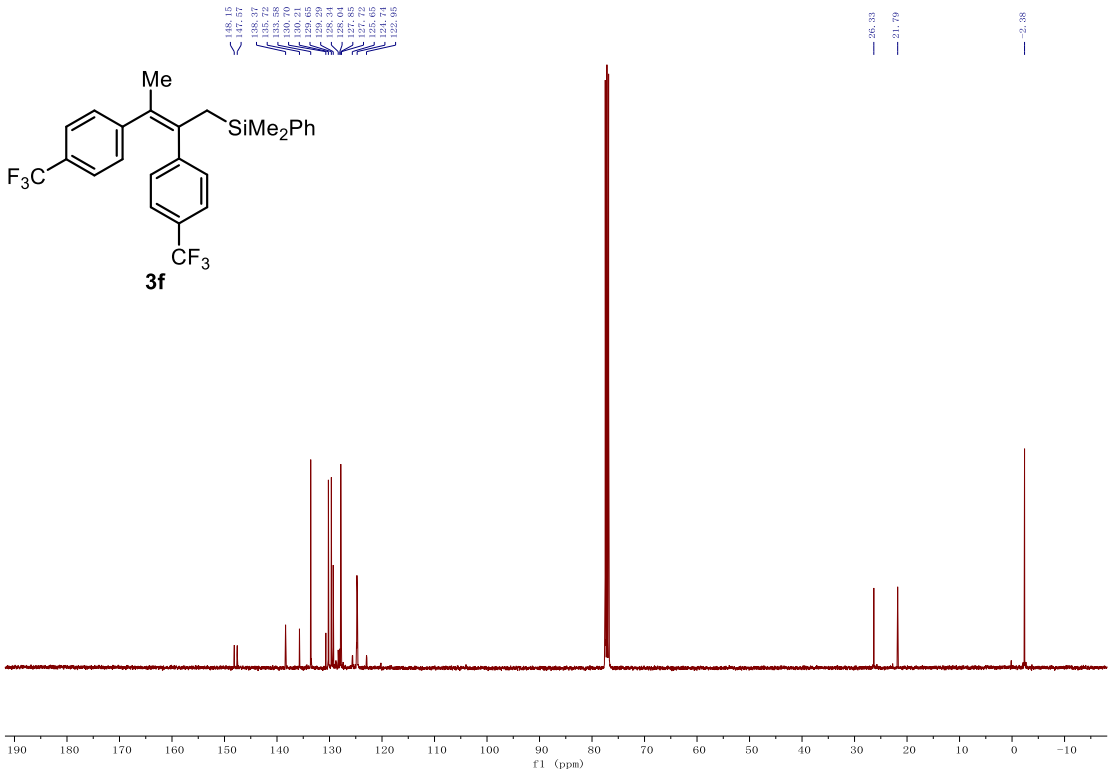
(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



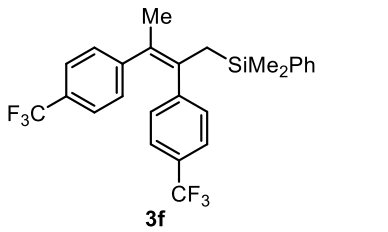
^{13}C NMR, $CDCl_3$, 101 MHz



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

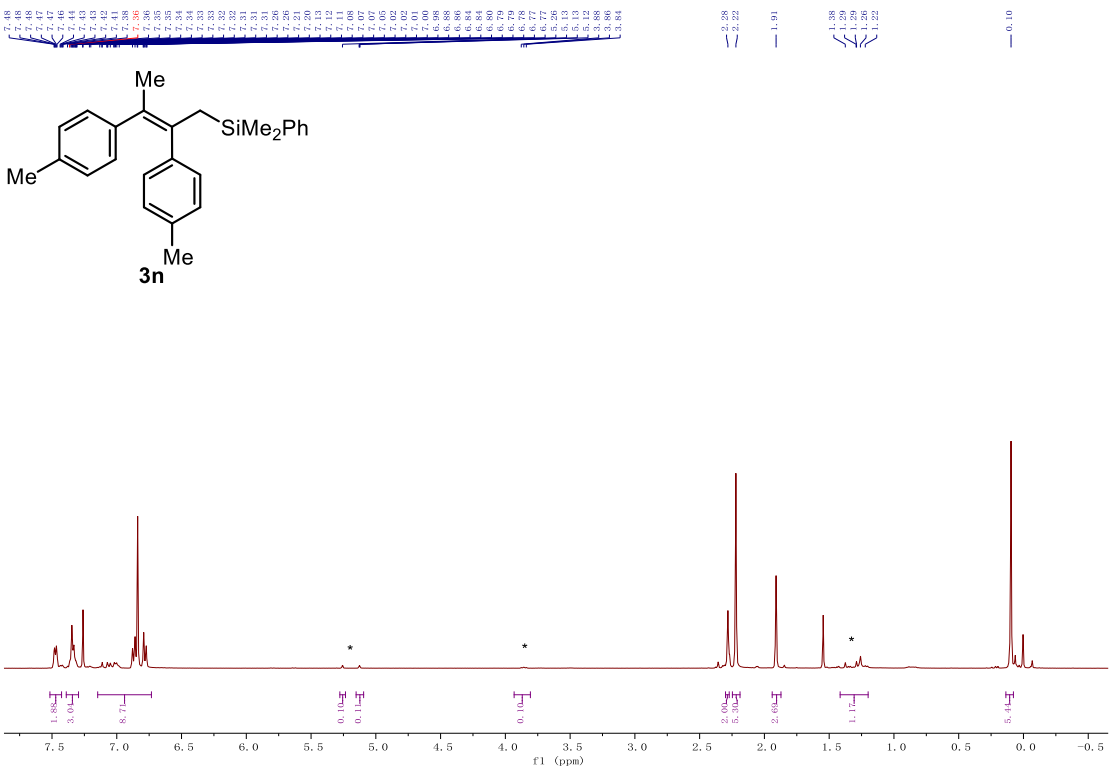


^{13}C NMR, $CDCl_3$, 101 MHz

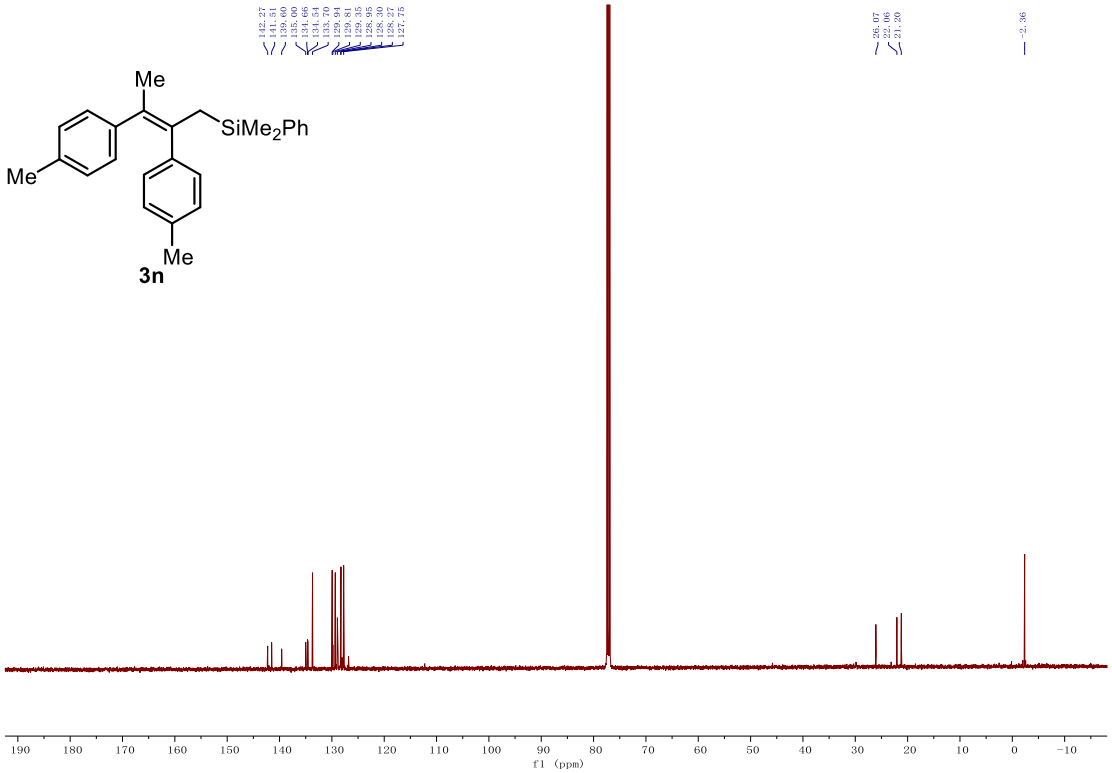


3f

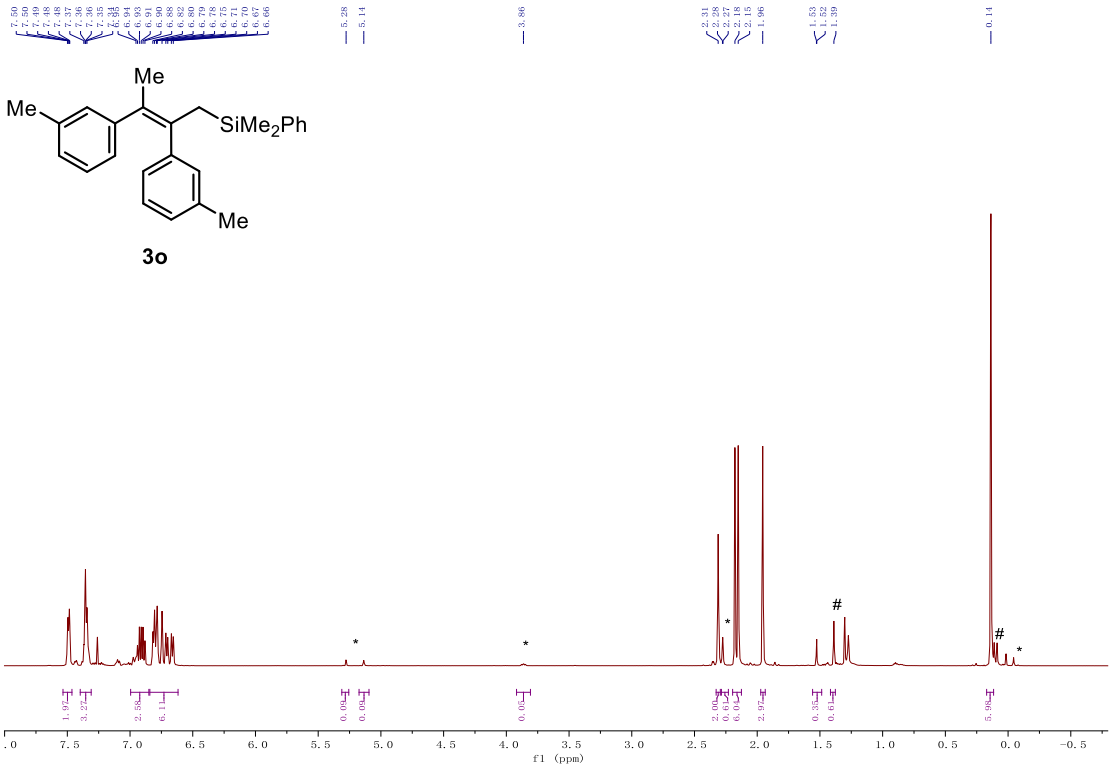
^{19}F NMR, $CDCl_3$, 376 MHz



^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to 2,1-protosilylation isomer)

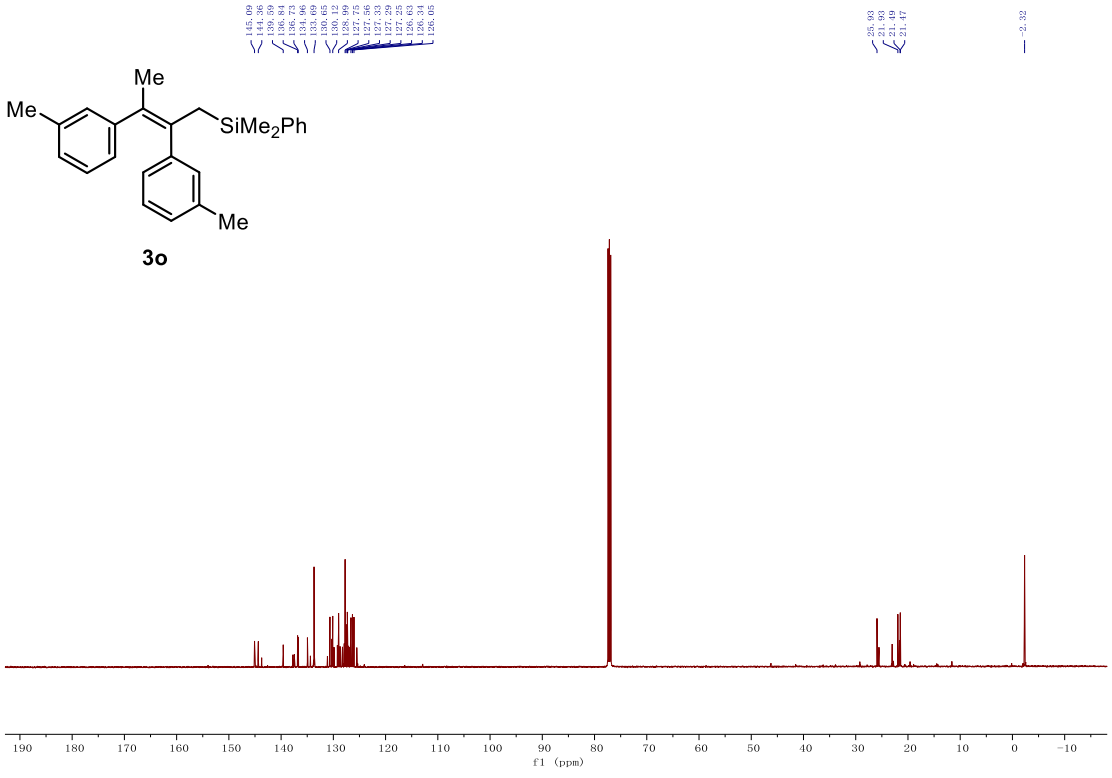


^{13}C NMR, $CDCl_3$, 101 MHz

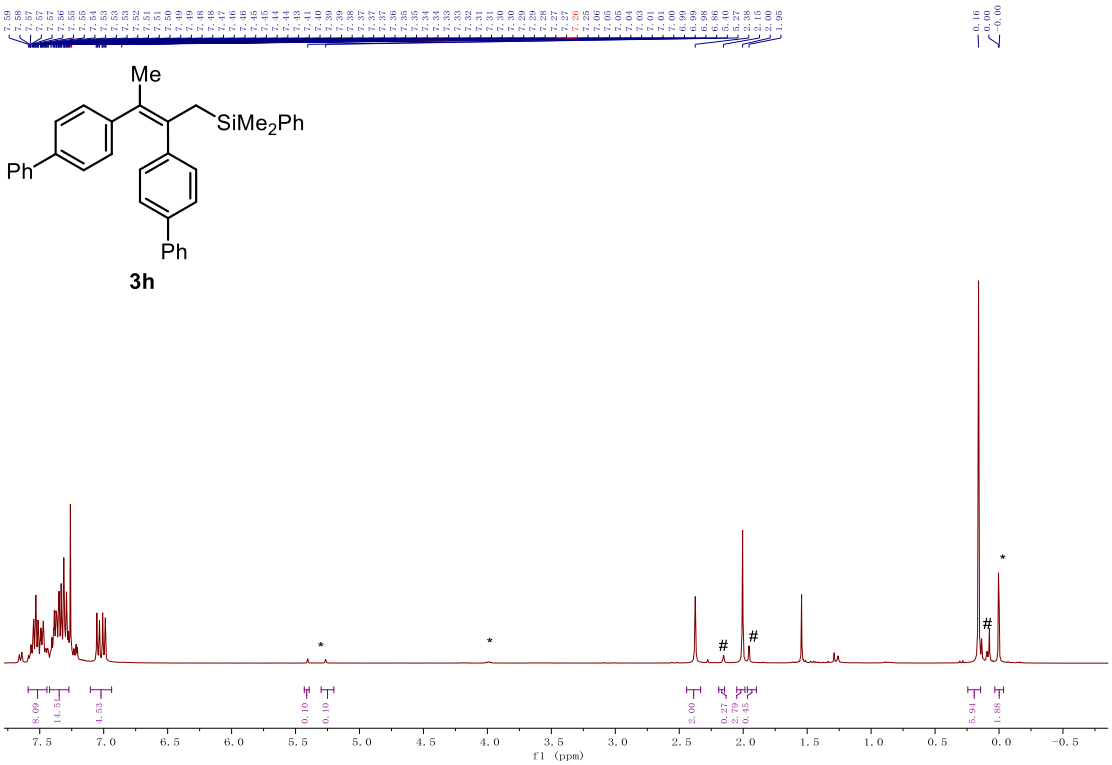


^{1}H NMR, $CDCl_3$, 400 MHz

(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)

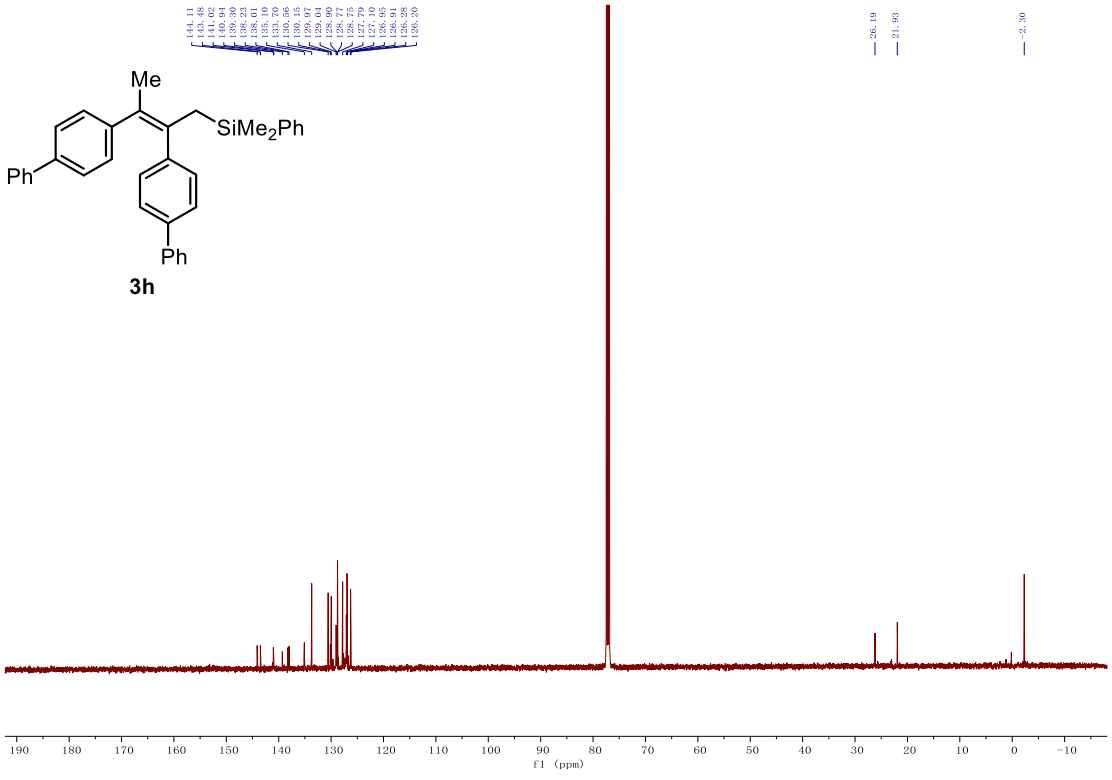


^{13}C NMR, $CDCl_3$, 101 MHz

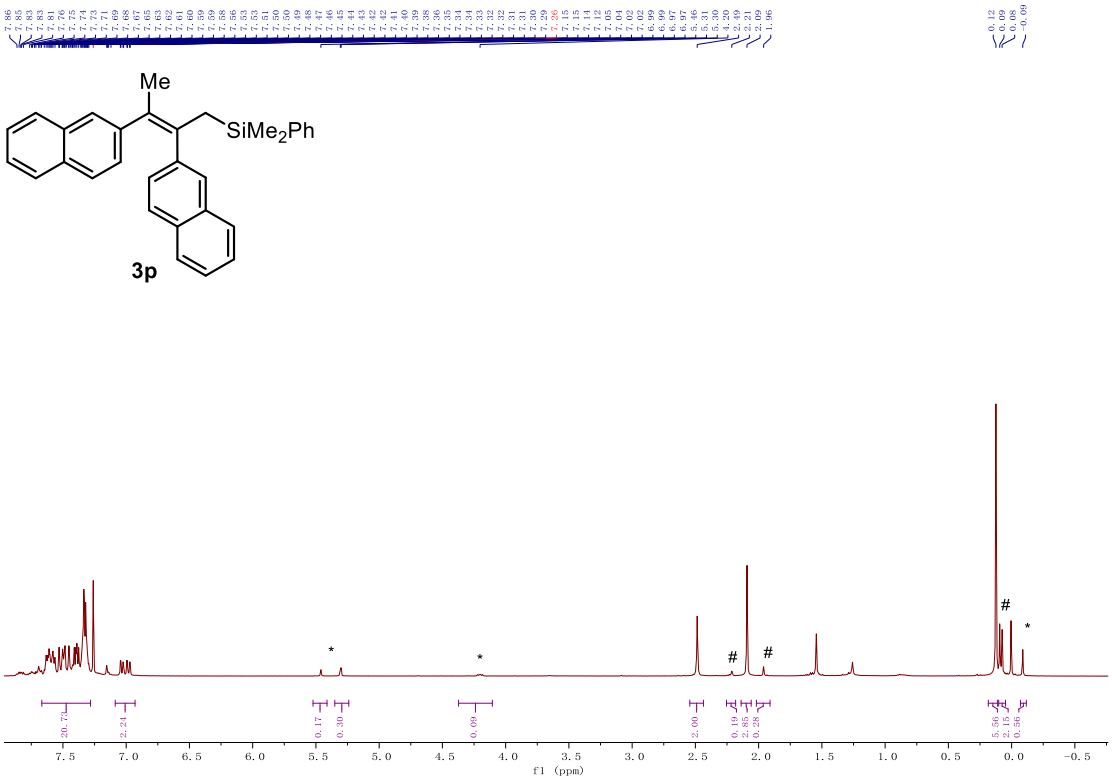


^{1}H NMR, $CDCl_3$, 400 MHz

(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)

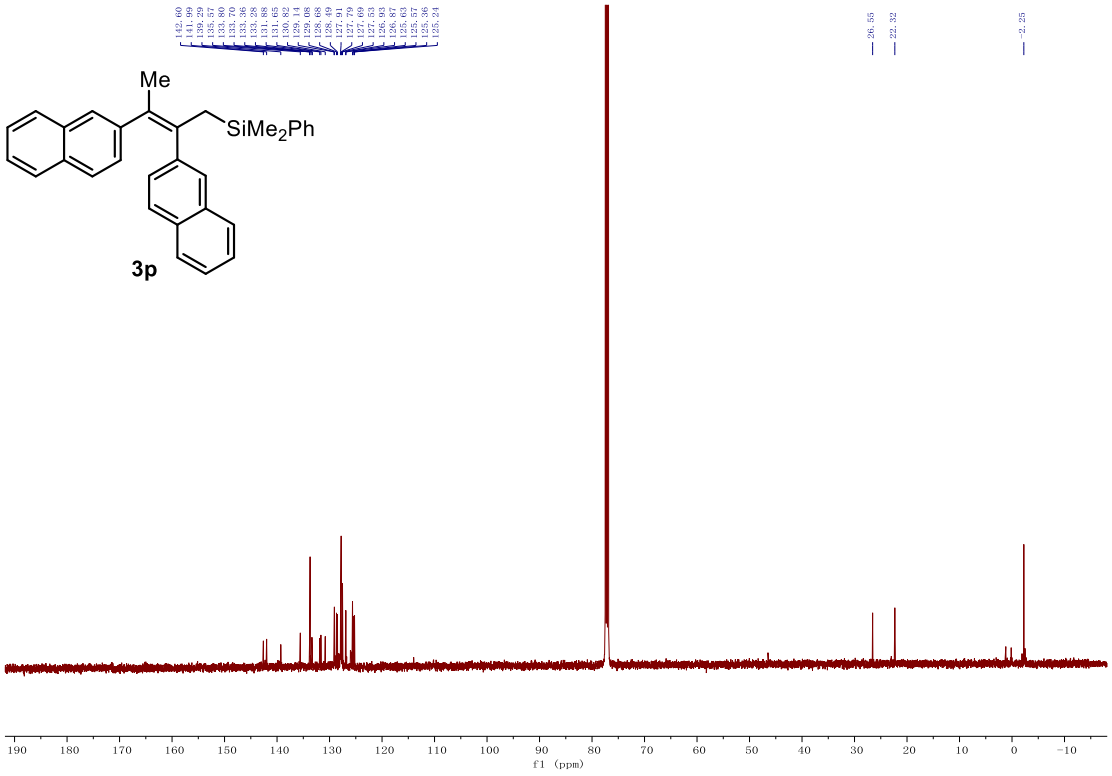


^{13}C NMR, $CDCl_3$, 101 MHz

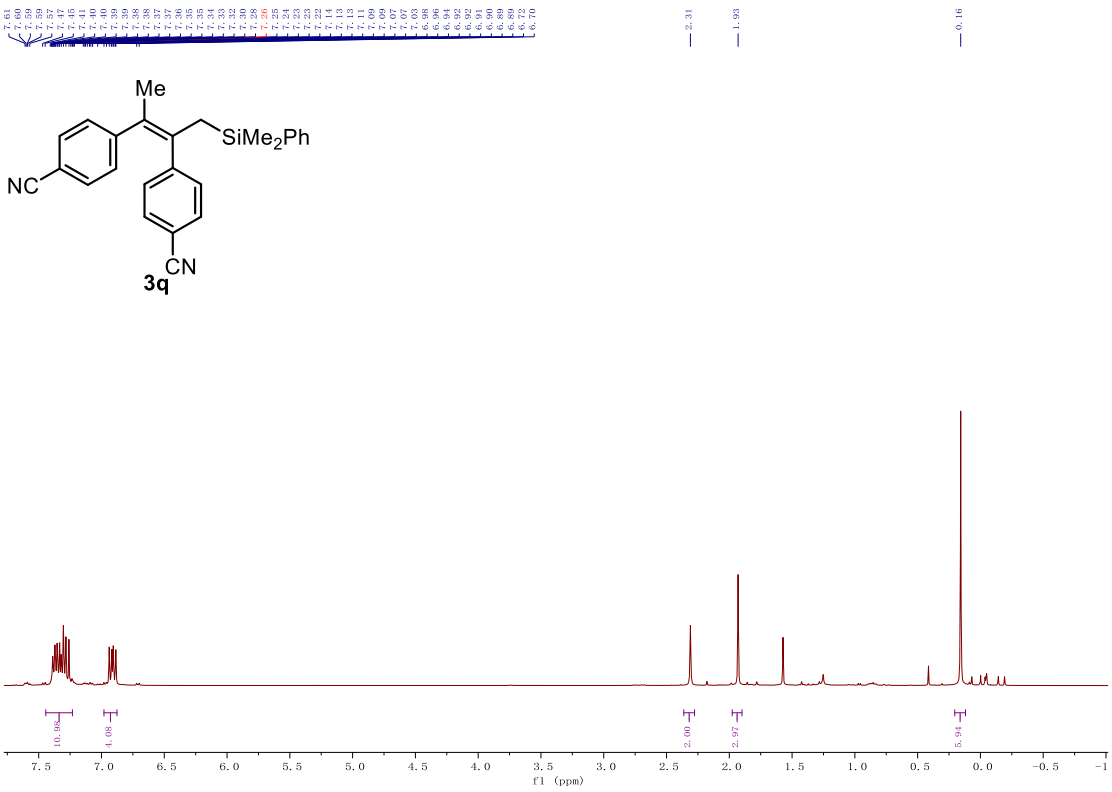


^{1}H NMR, $CDCl_3$, 400 MHz

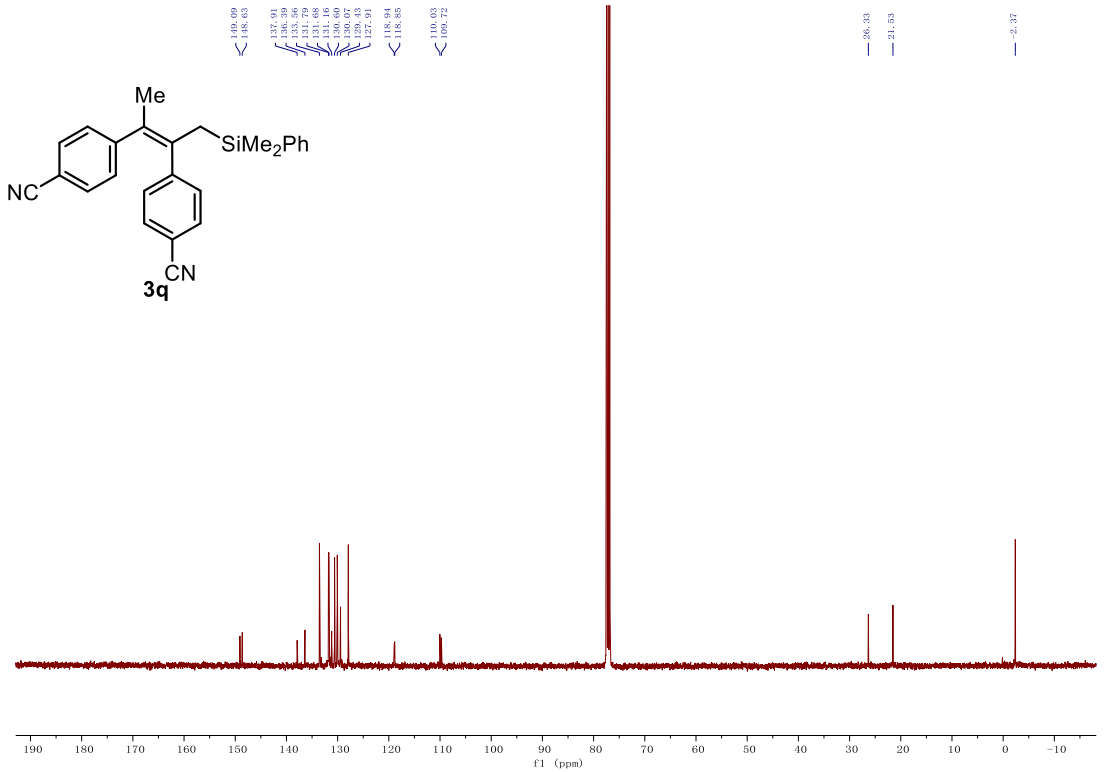
(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



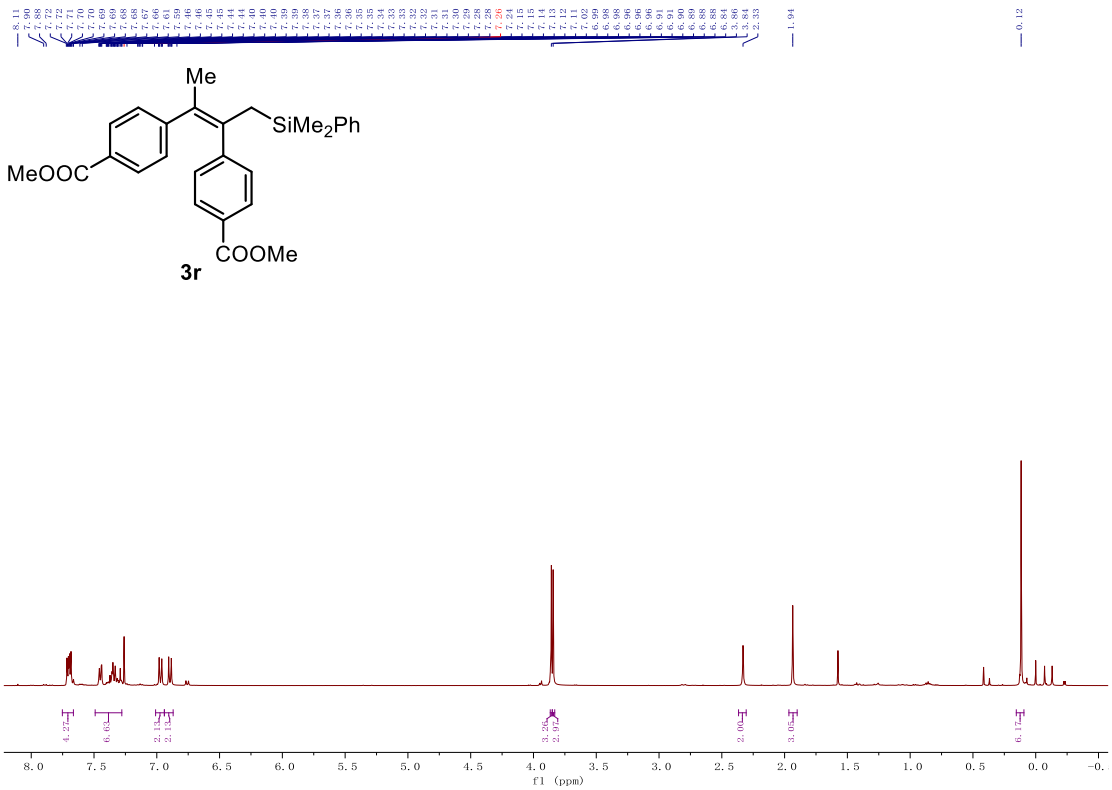
^{13}C NMR, $CDCl_3$, 101 MHz



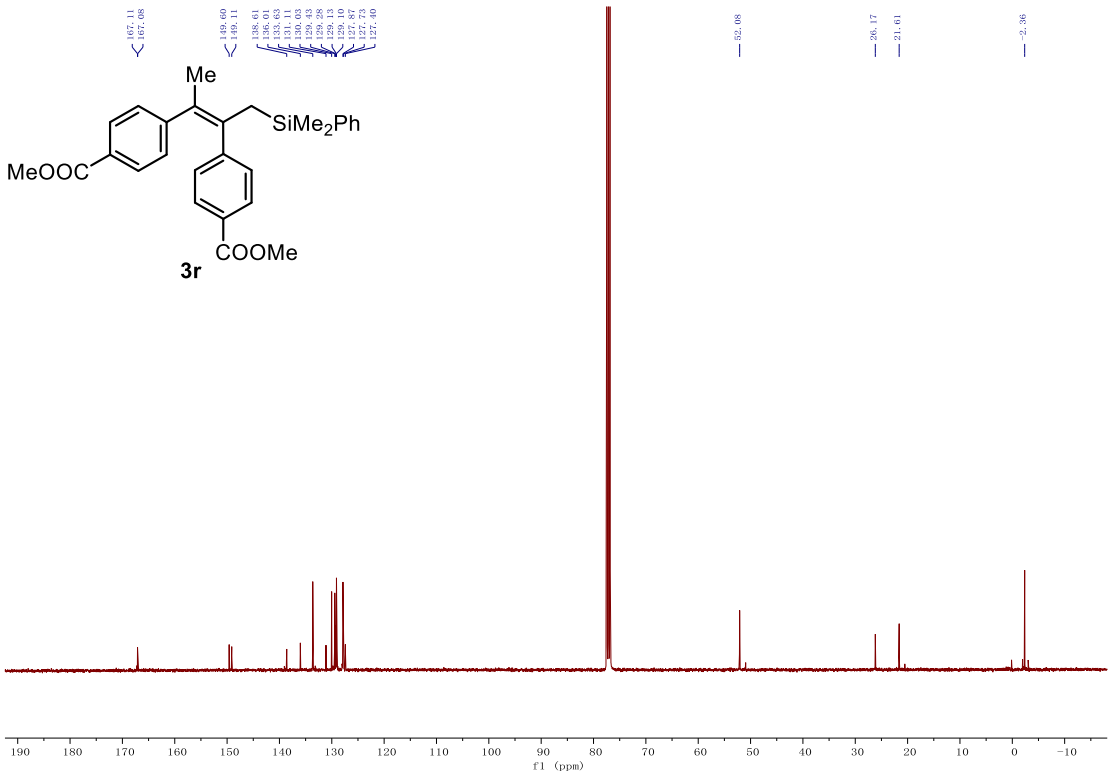
^{1}H NMR, $CDCl_3$, 400 MHz



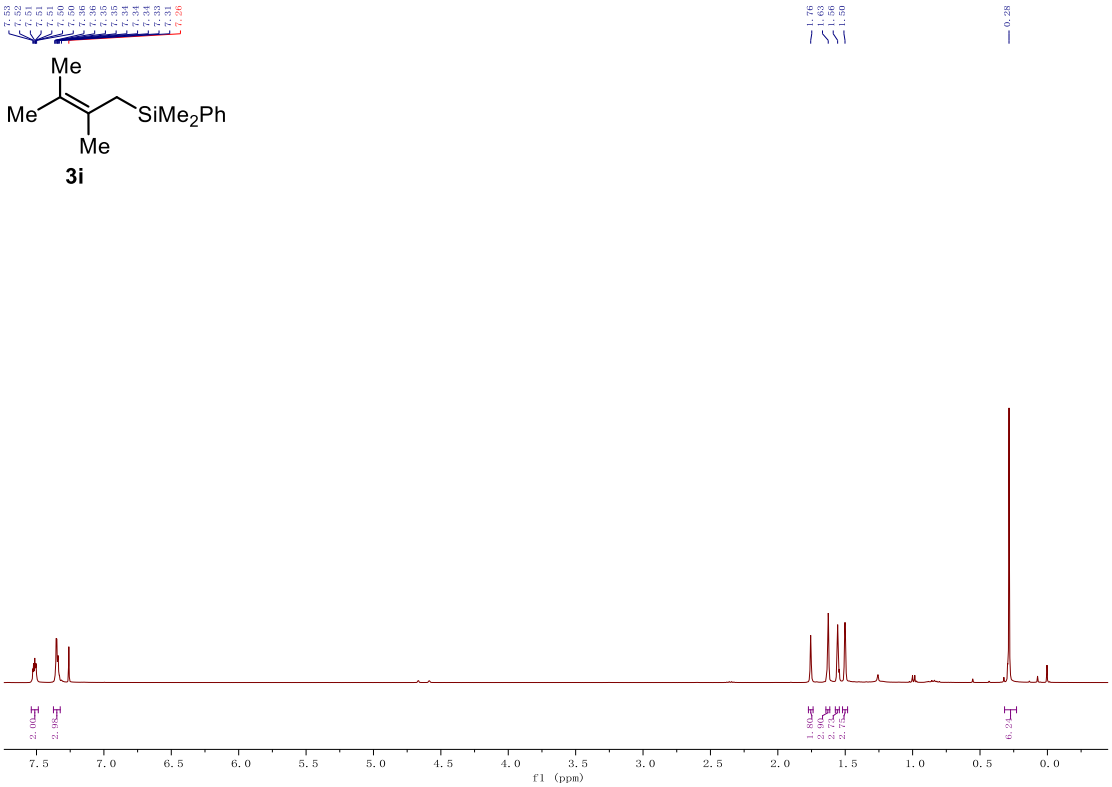
^{13}C NMR, $CDCl_3$, 101 MHz



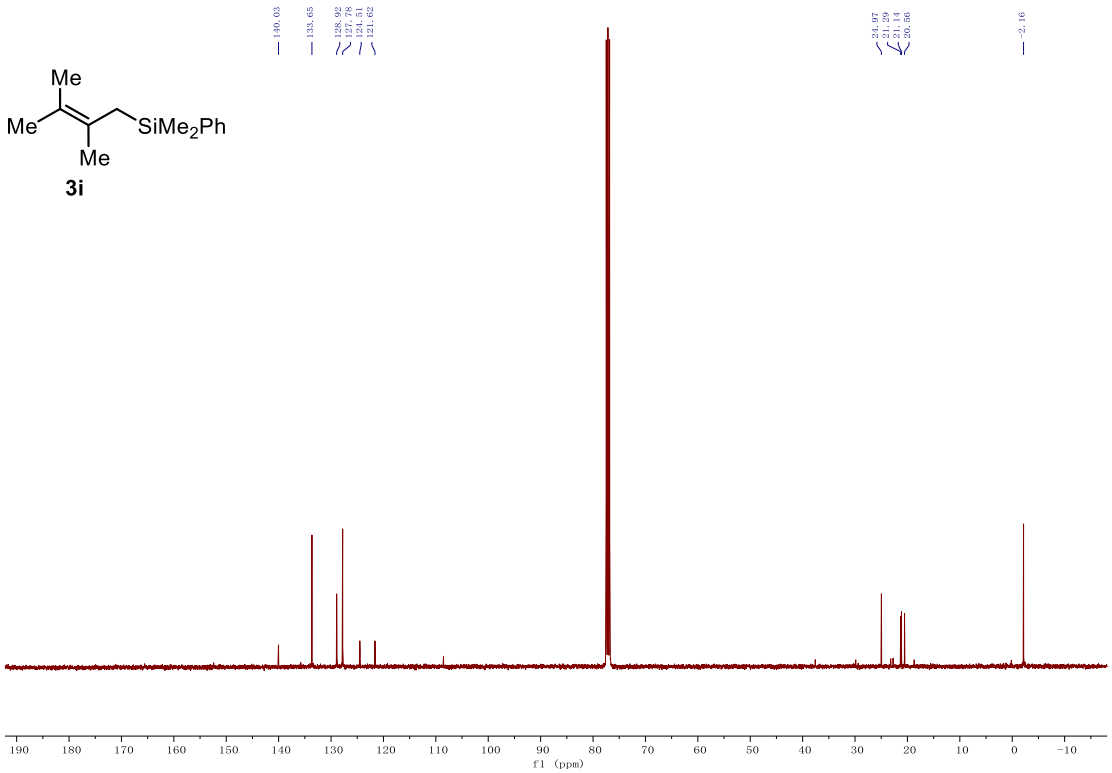
^{1}H NMR, $CDCl_3$, 400 MHz



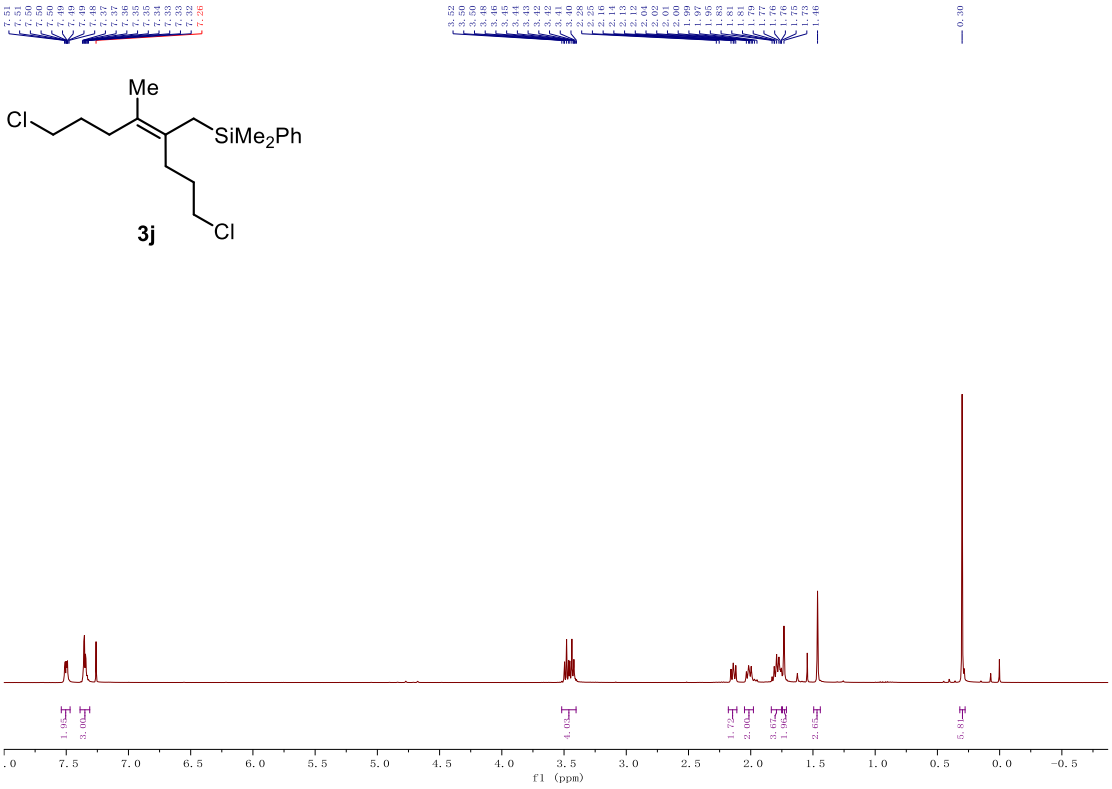
^{13}C NMR, $CDCl_3$, 101 MHz



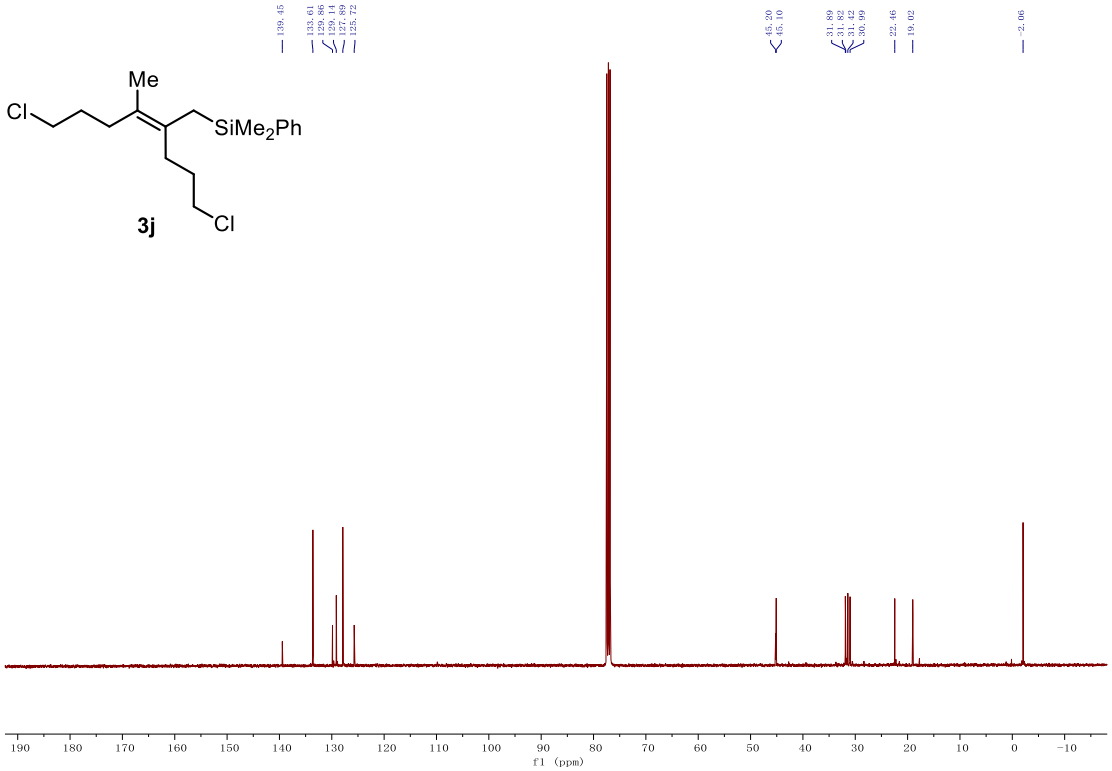
^{1}H NMR, $CDCl_3$, 400 MHz



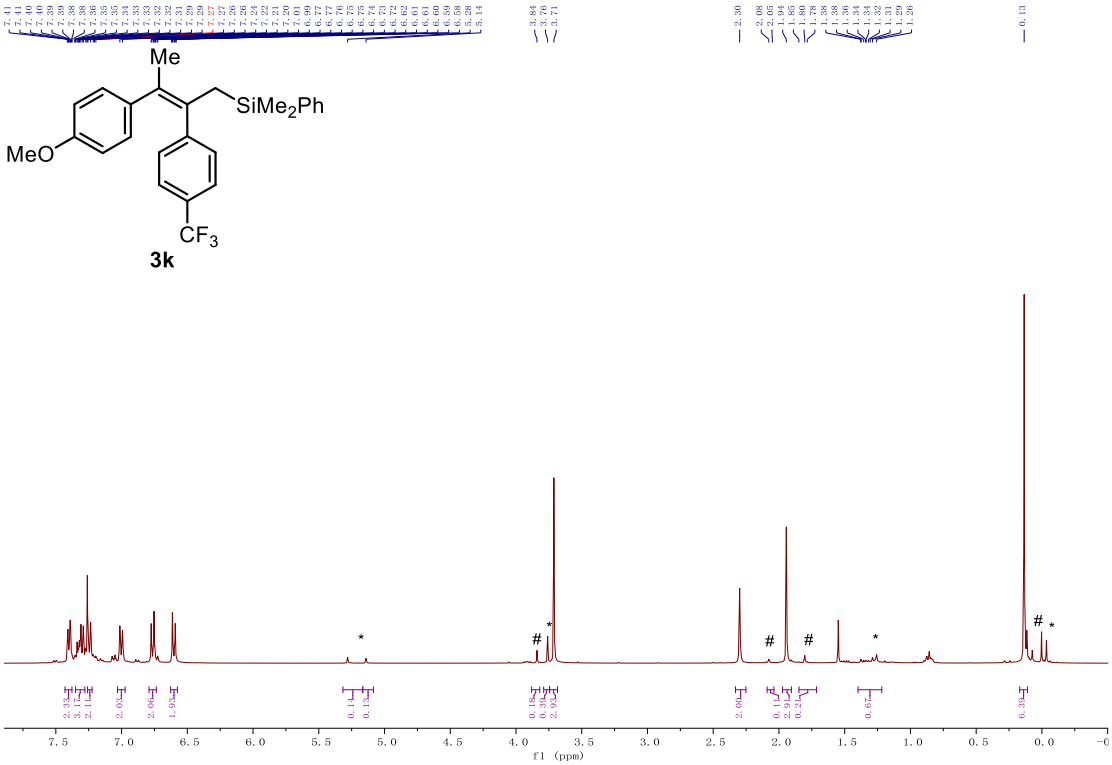
^{13}C NMR, $CDCl_3$, 101 MHz



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

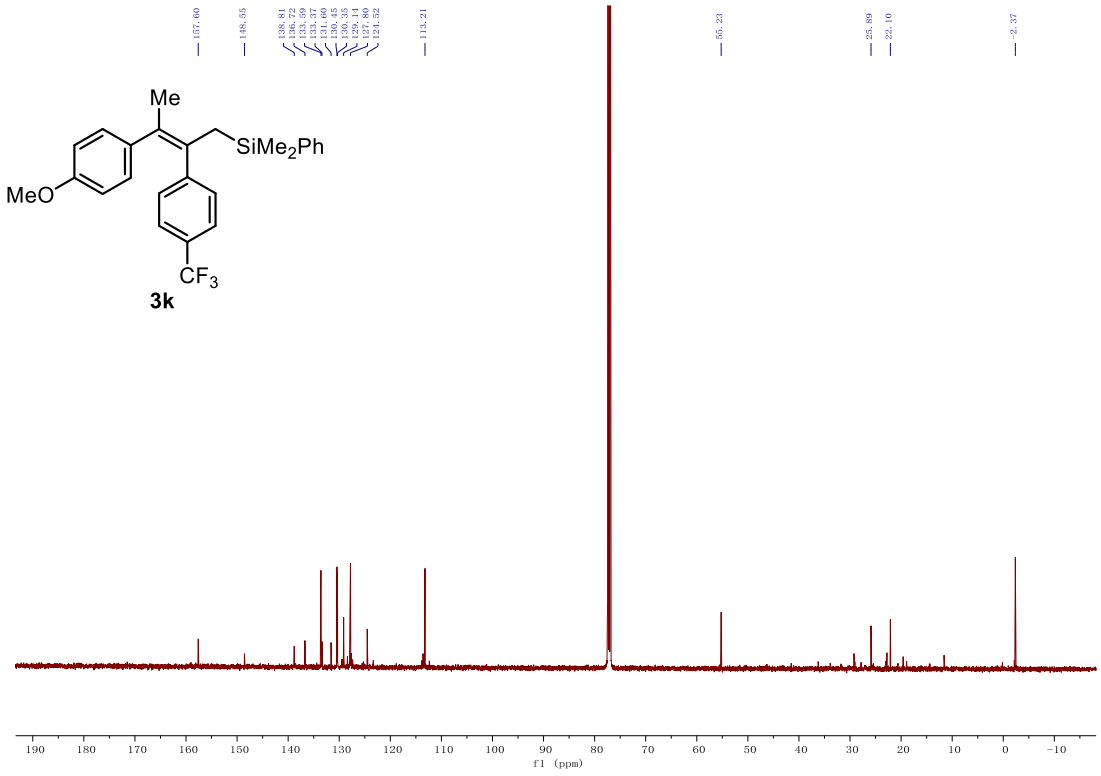


^{13}C NMR, $CDCl_3$, 101 MHz

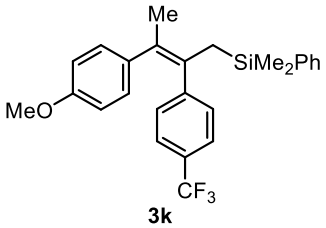


^{1}H NMR, $CDCl_3$, 400 MHz

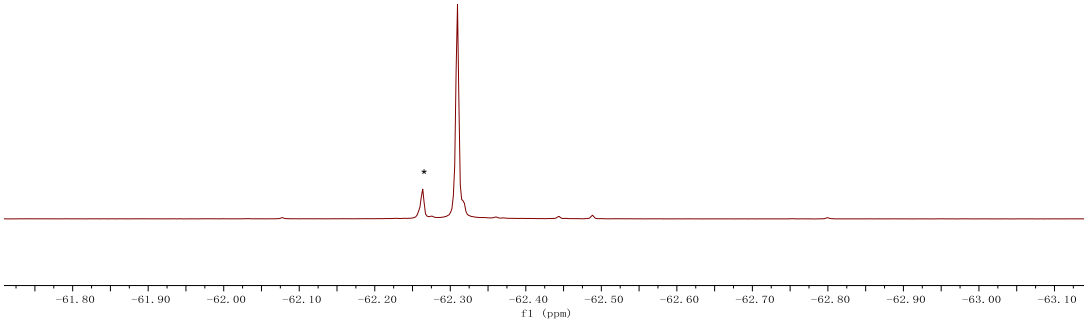
(* was attributed to 2,1-protosilylation isomer, # was attributed to (*Z*)-4,1-protosilylation isomer)



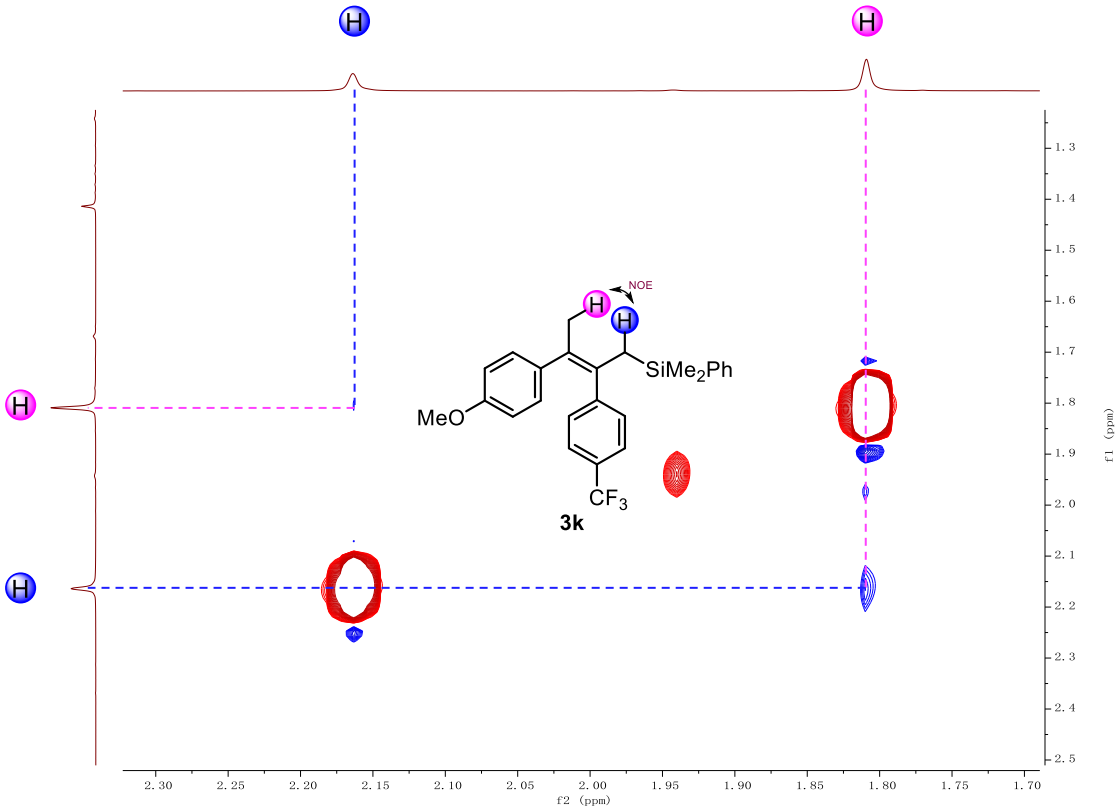
^{13}C NMR, $CDCl_3$, 101 MHz



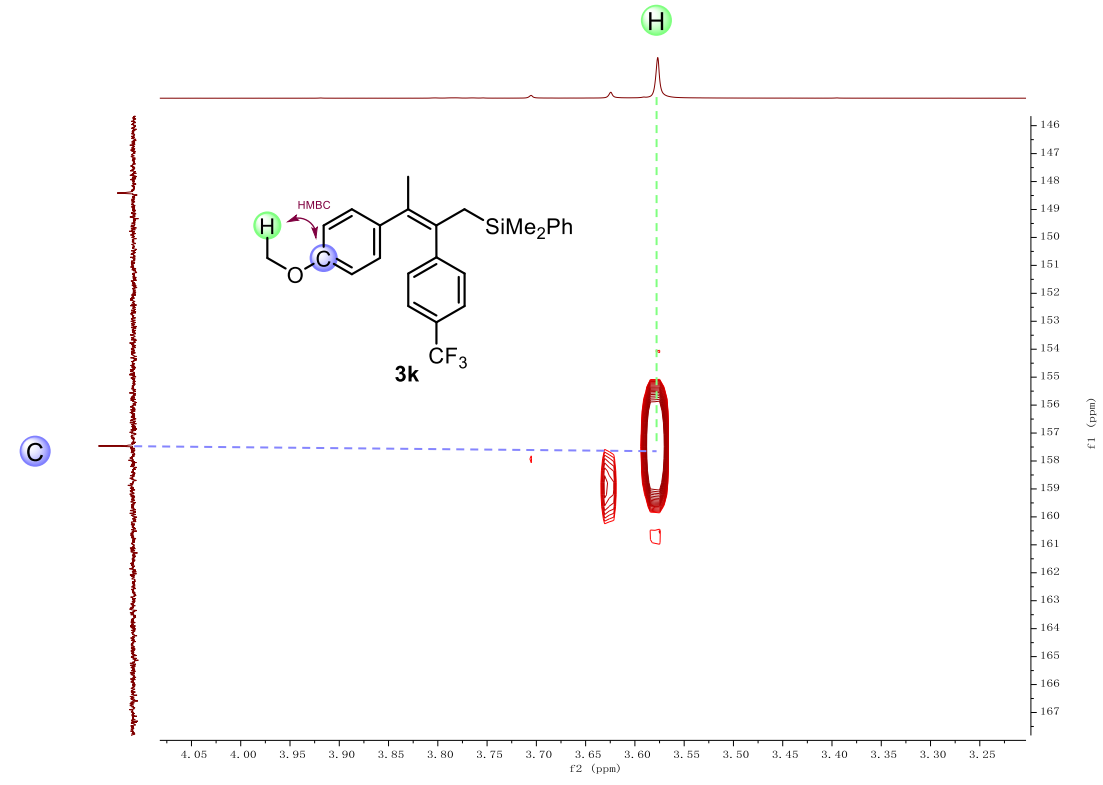
3k

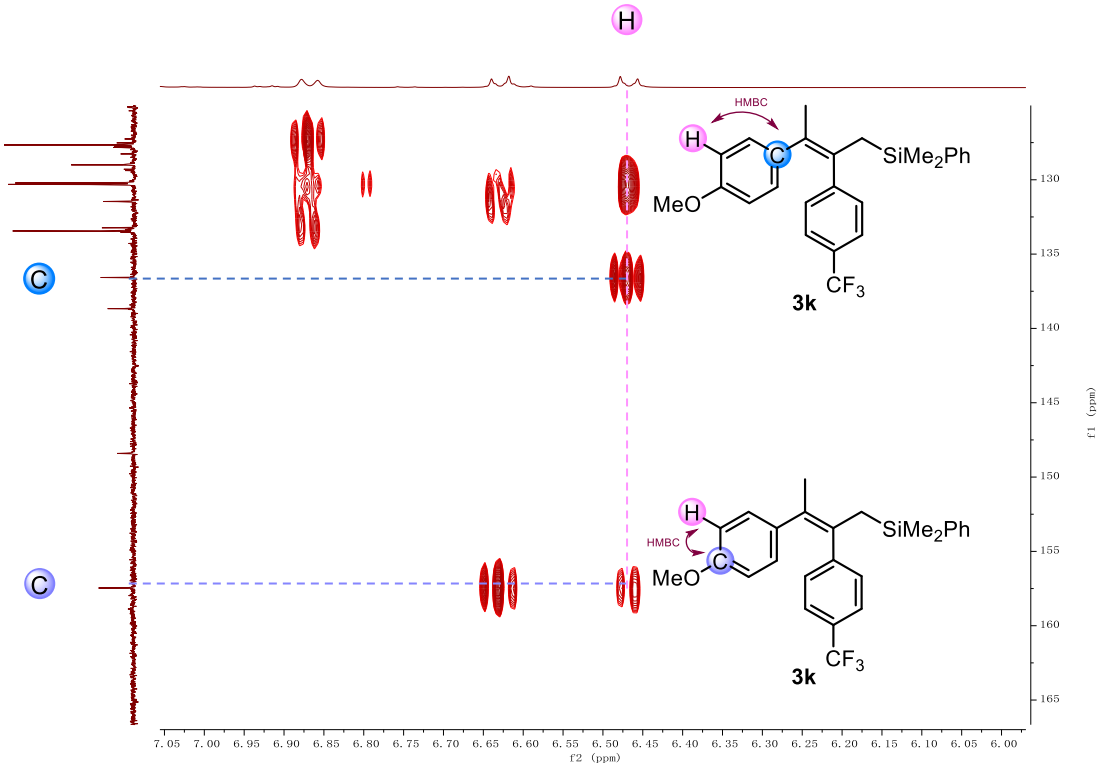


^{19}F NMR, $CDCl_3$, 376 MHz

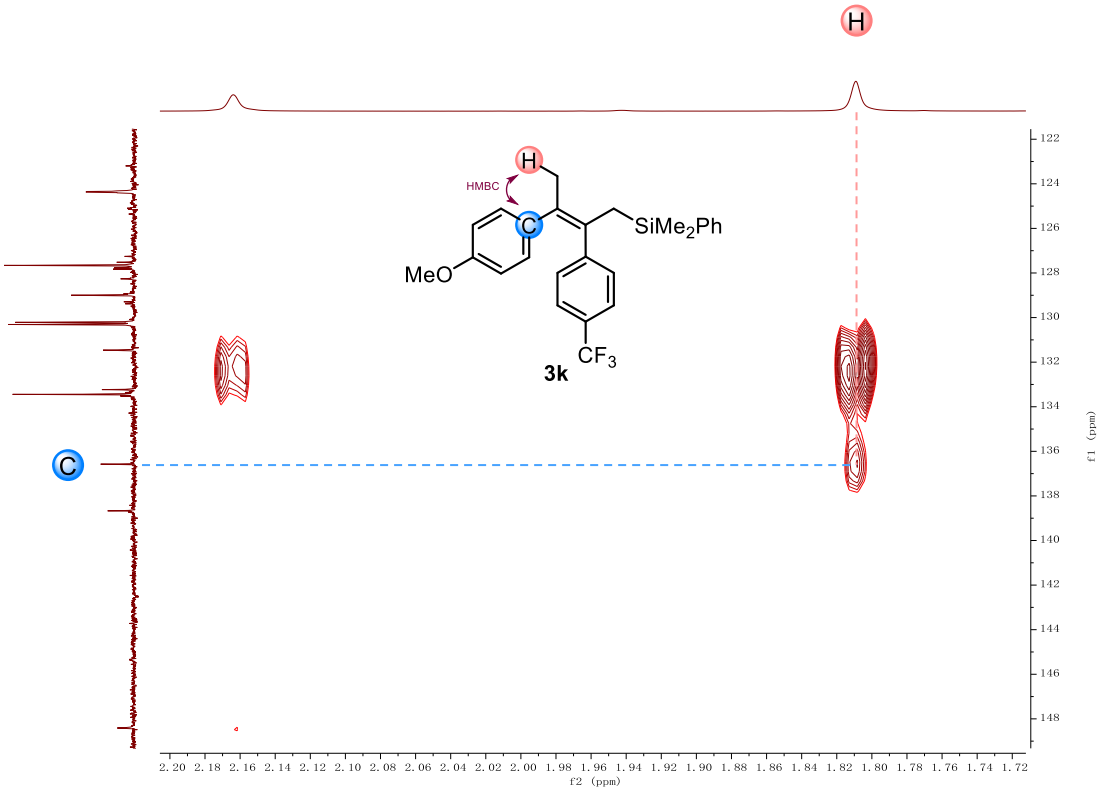


^{1}H, ^{1}H – NOESY

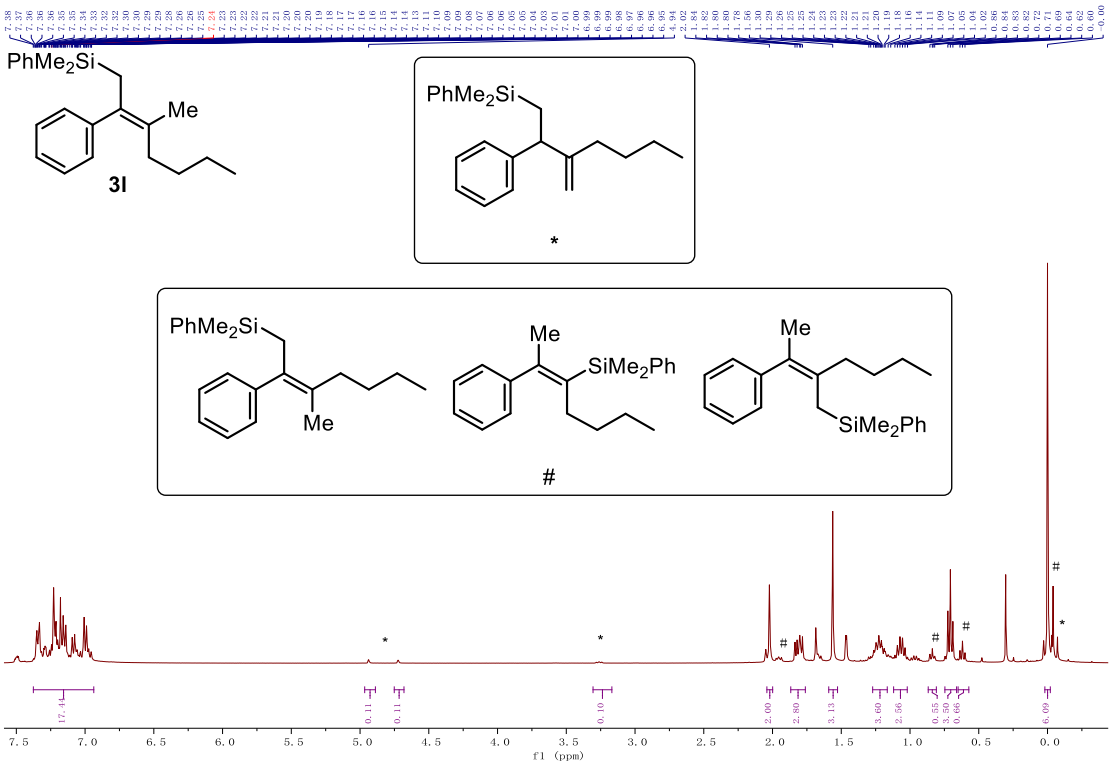

H
C
HMBC
H
C
O
SiMe2Ph
CF3
3k
f2 (ppm)
f1 (ppm)


H
C
C
HMBC
H
C
MeO
SiMe2Ph
CF3
3k
HMBC
H
C
MeO
SiMe2Ph
CF3
3k
f2 (ppm)
f1 (ppm)

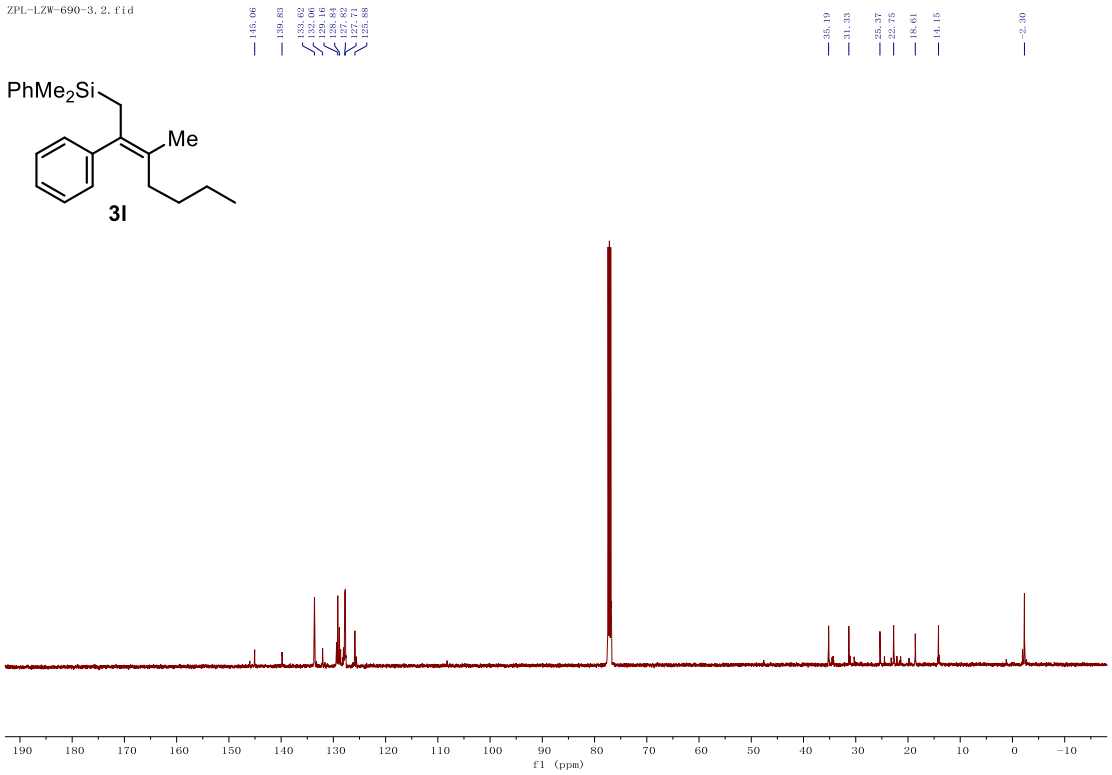
^{1}H, ^{13}C-HMBC


H
HMBC
C
SiMe2Ph
MeO
CF3
3k
C
122
124
126
128
130
132
134
136
138
140
142
144
146
148
f1 (ppm)
2.20 2.18 2.16 2.14 2.12 2.10 2.08 2.06 2.04 2.02 2.00 1.98 1.96 1.94 1.92 1.90 1.88 1.86 1.84 1.82 1.80 1.78 1.76 1.74 1.72
f2 (ppm)

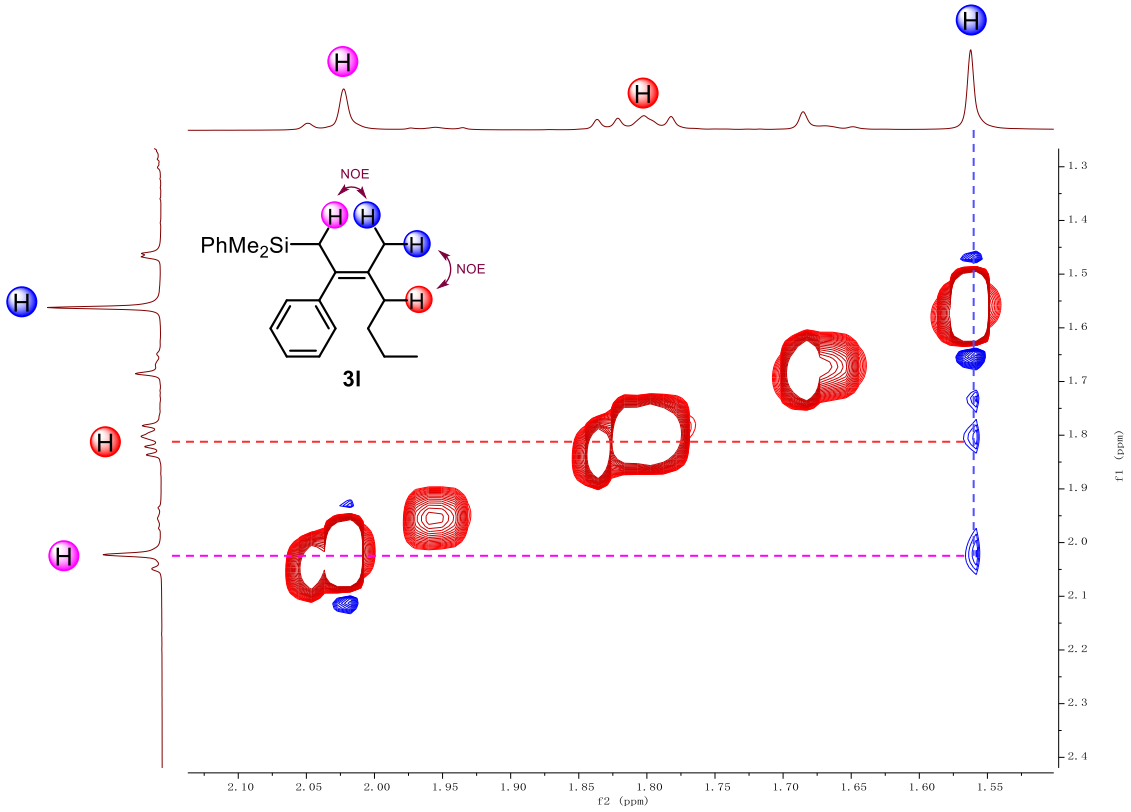
^{1}H, ^{13}C-HMBC



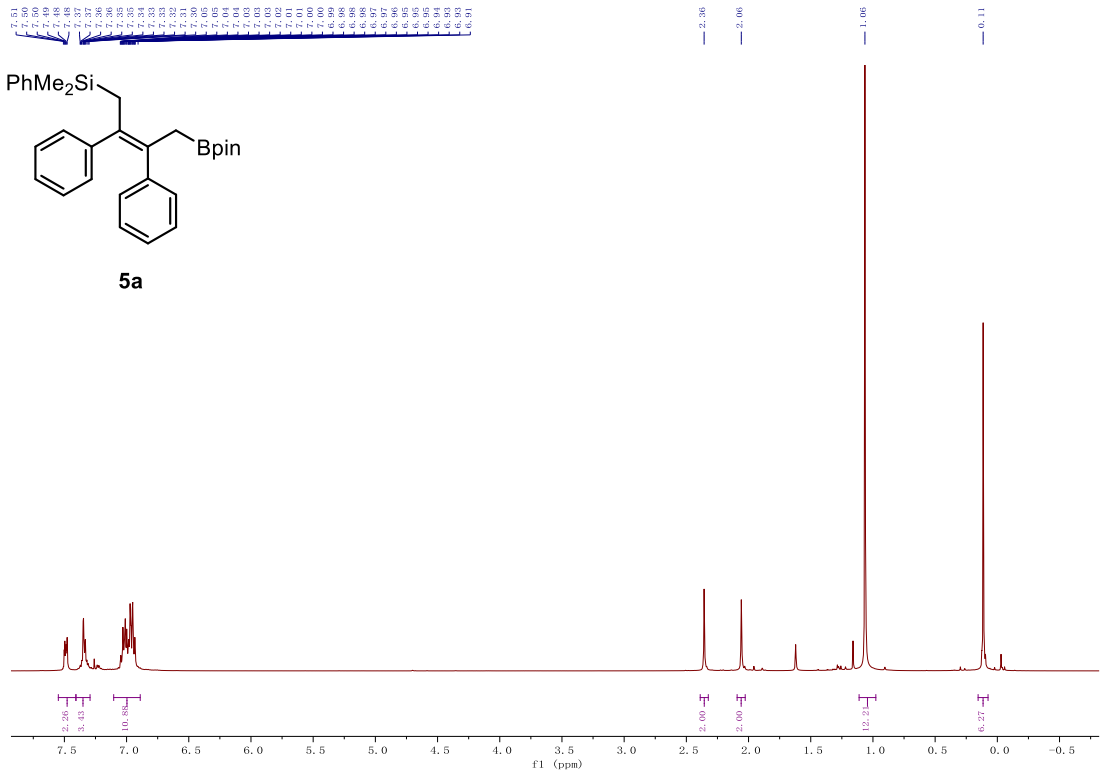
^{1}H NMR, $CDCl_3$, 400 MHz (* and # were attributed to plausible regioisomers as indicated)



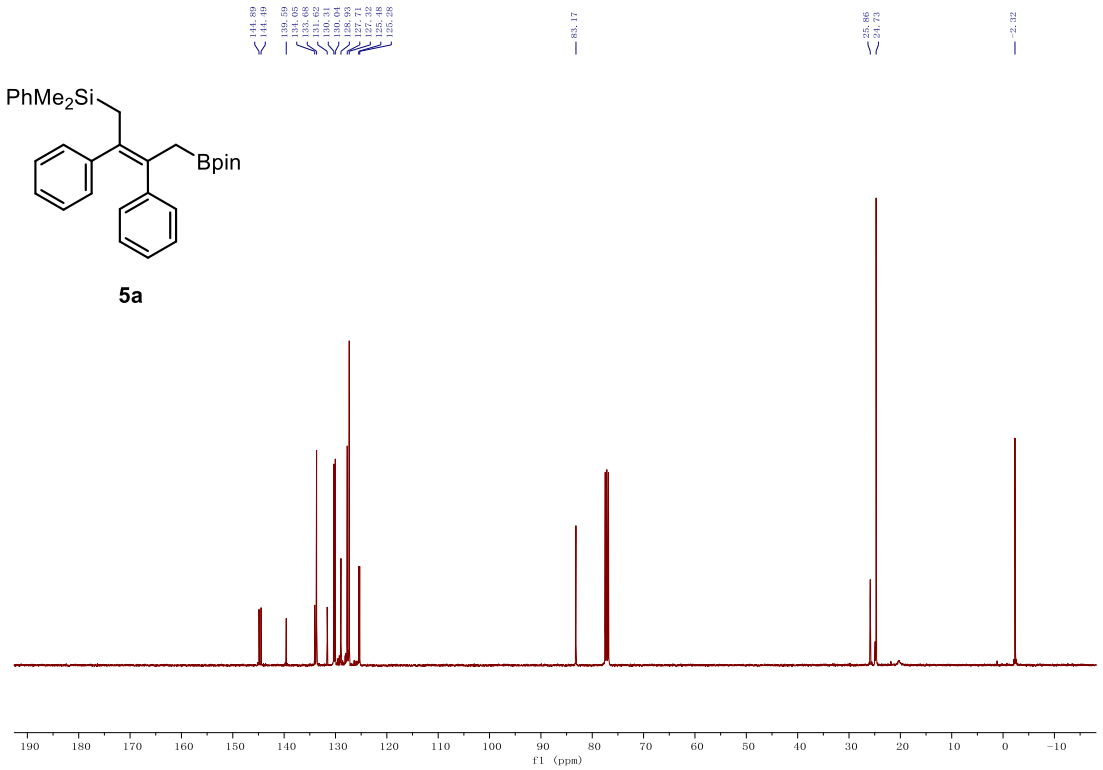
^{13}C NMR, $CDCl_3$, 101 MHz



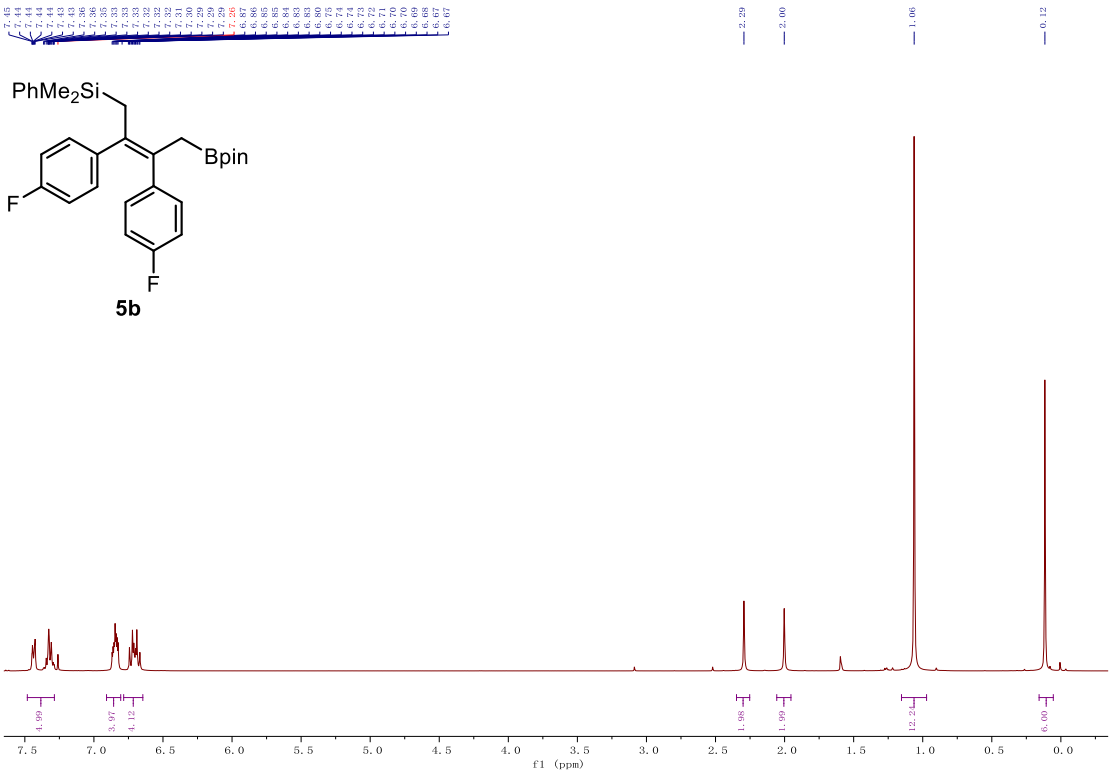
^{1}H, ^{1}H - NOESY



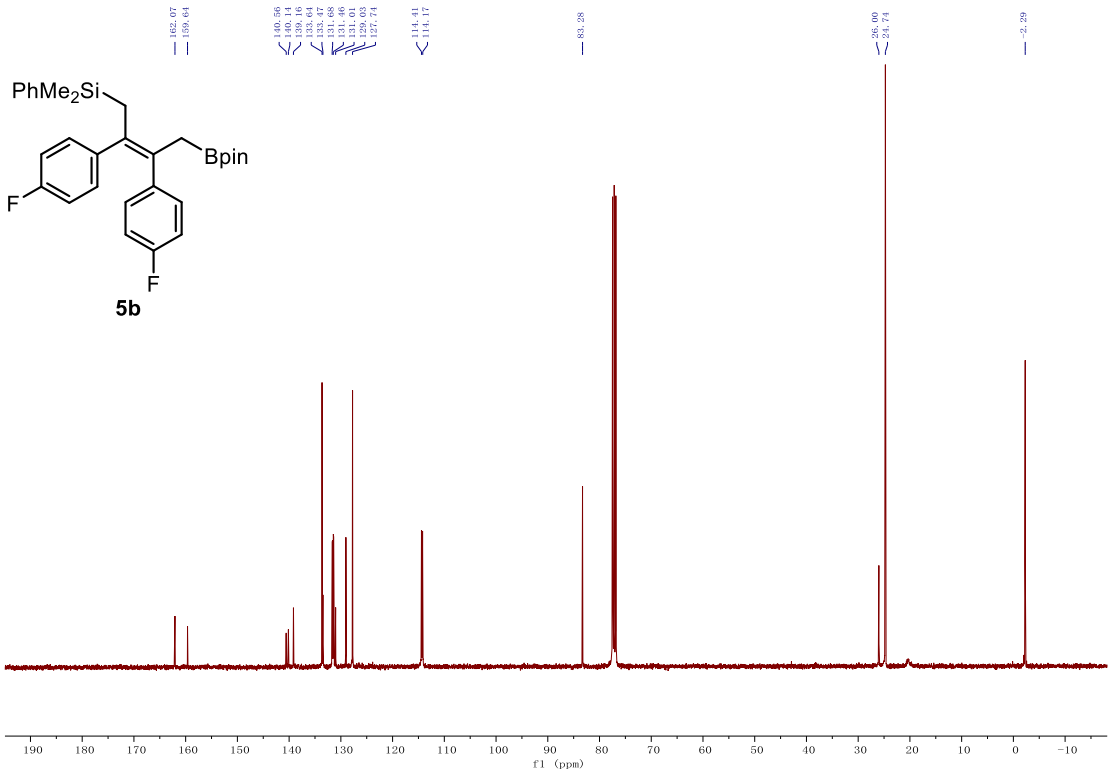
^{1}H NMR, $CDCl_3$, 400 MHz



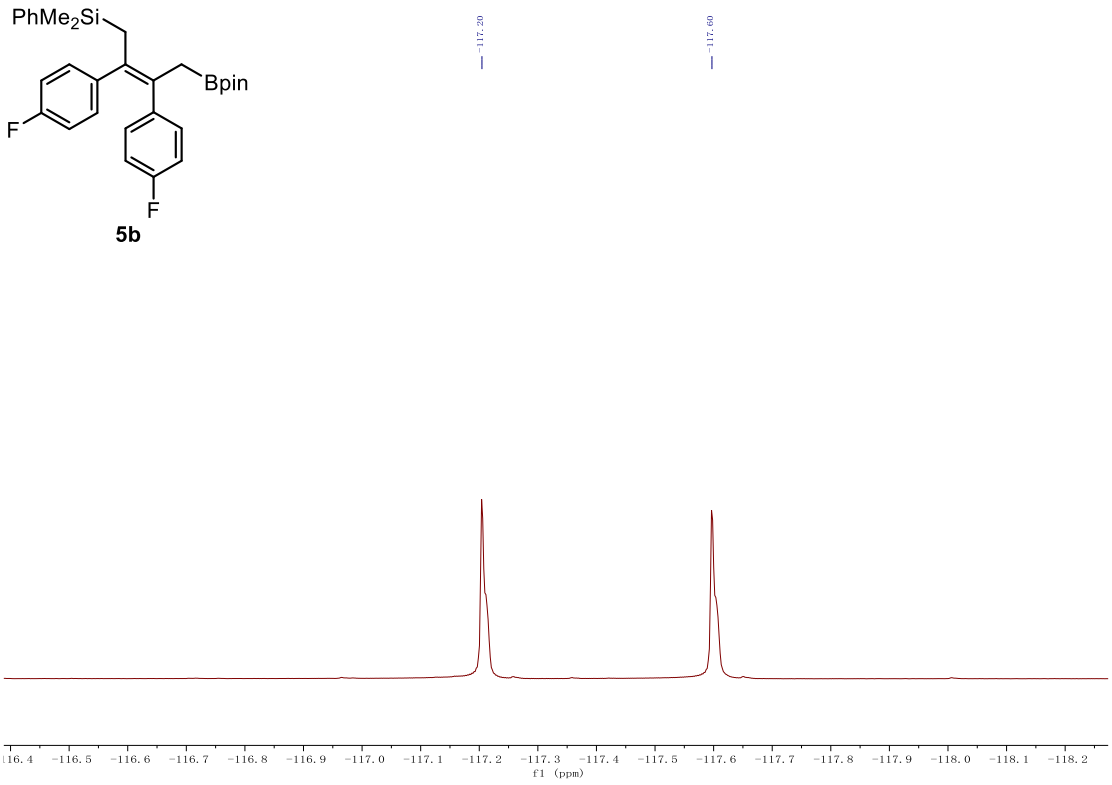
^{13}C NMR, $CDCl_3$, 101 MHz



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

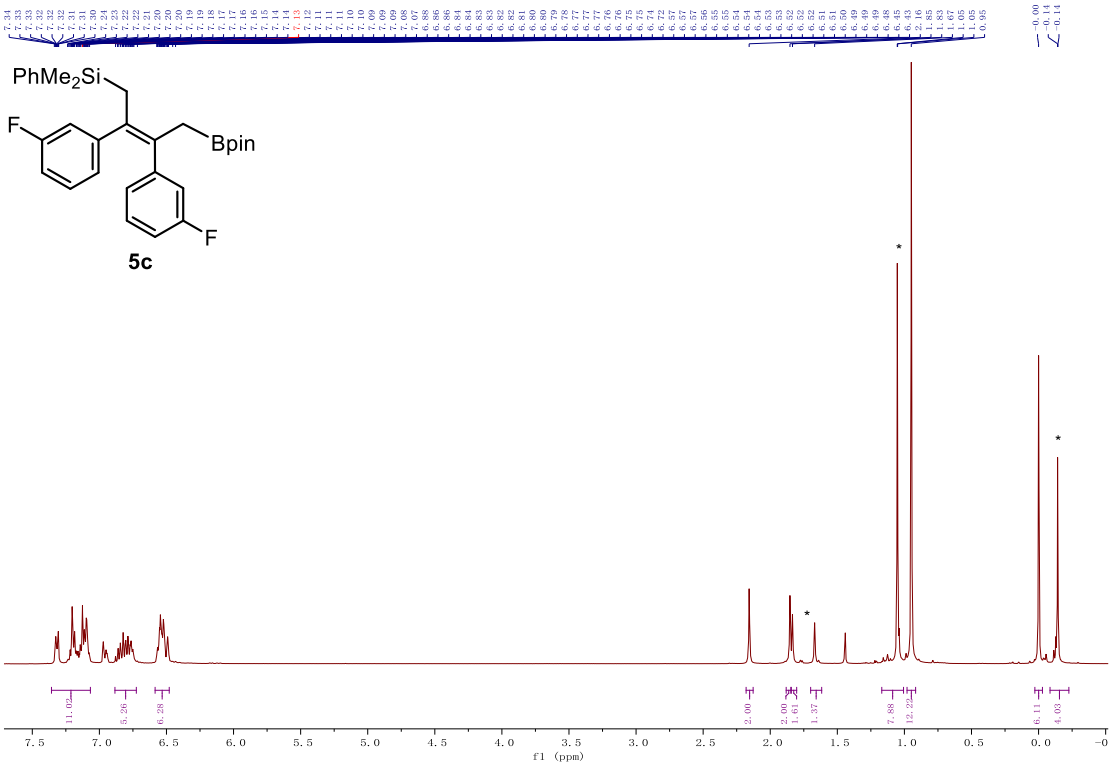


^{13}C NMR, $CDCl_3$, 101 MHz

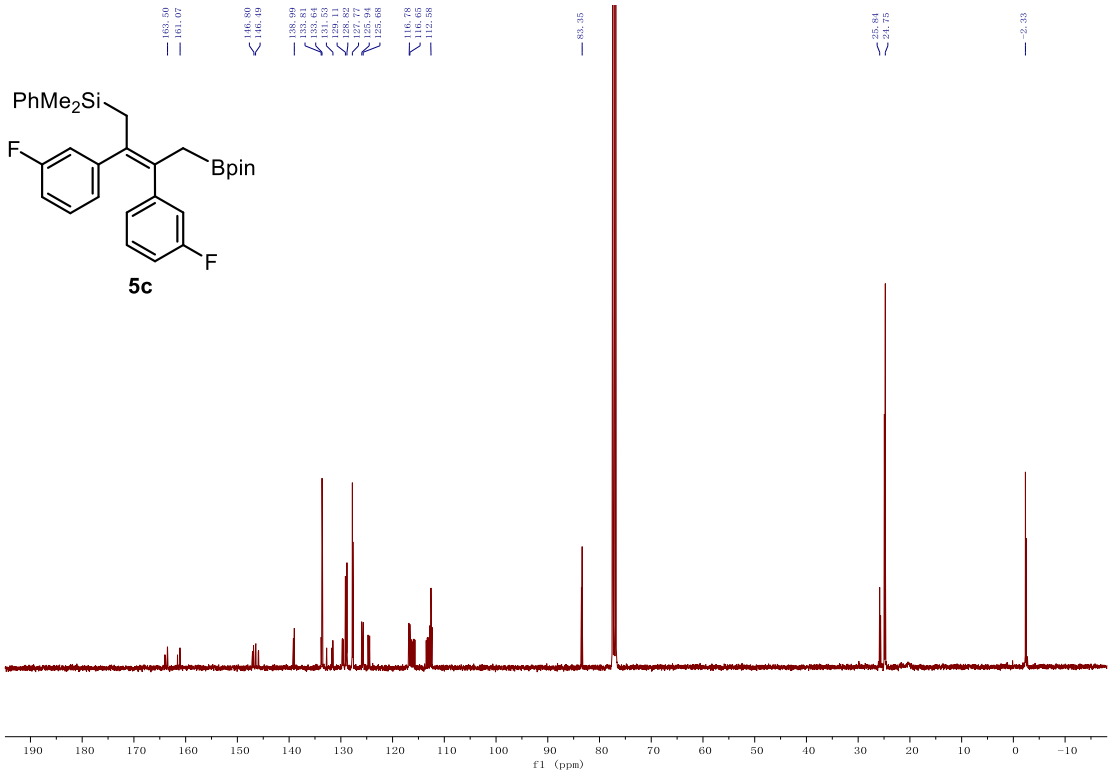


5b

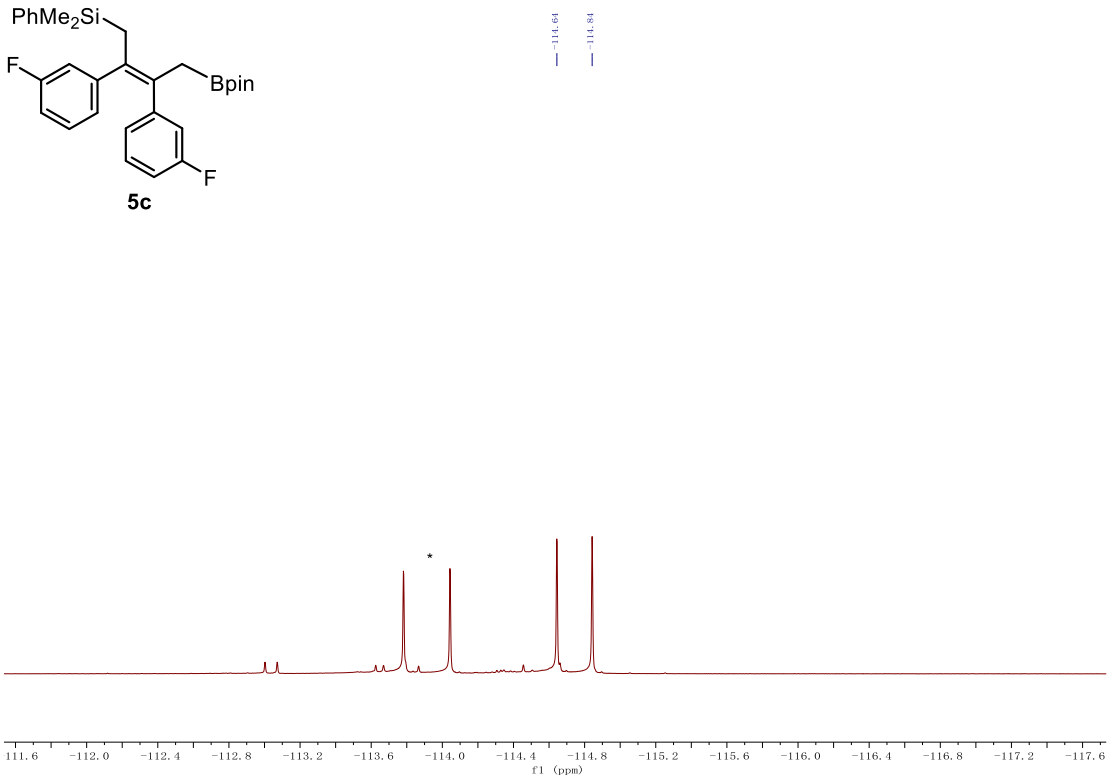
^{19}F NMR, $CDCl_3$, 376 MHz



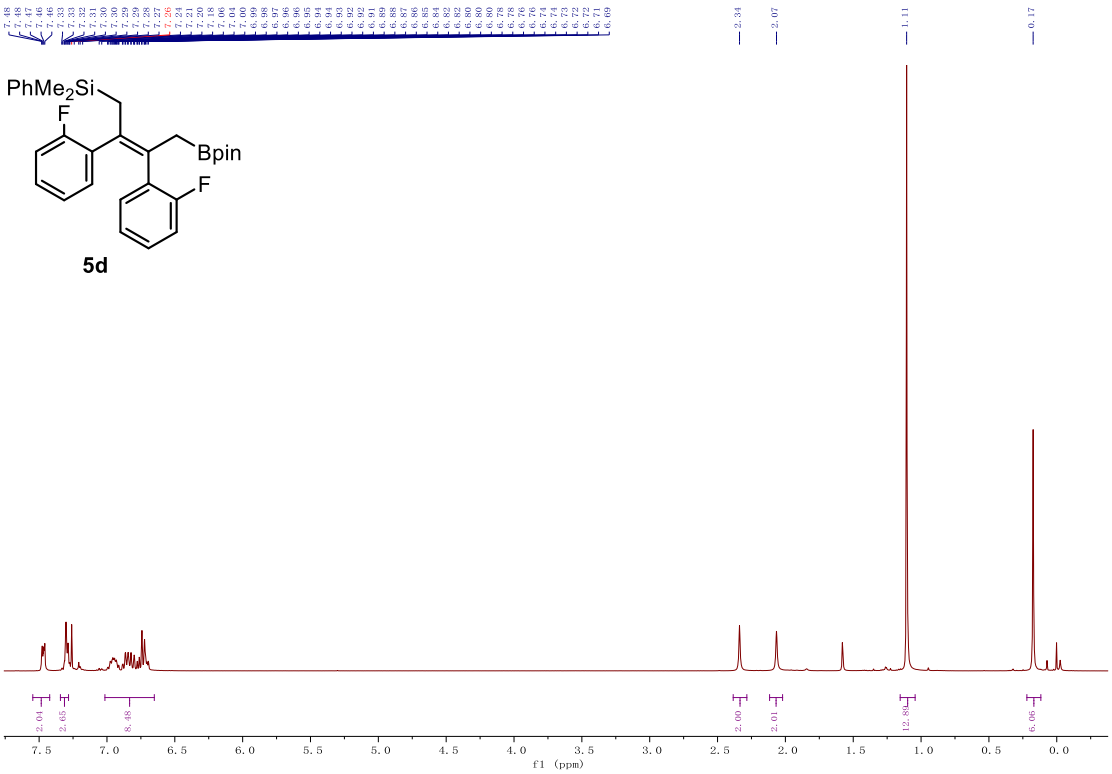
^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to (*Z*)-4,1-borosilylation isomer.)



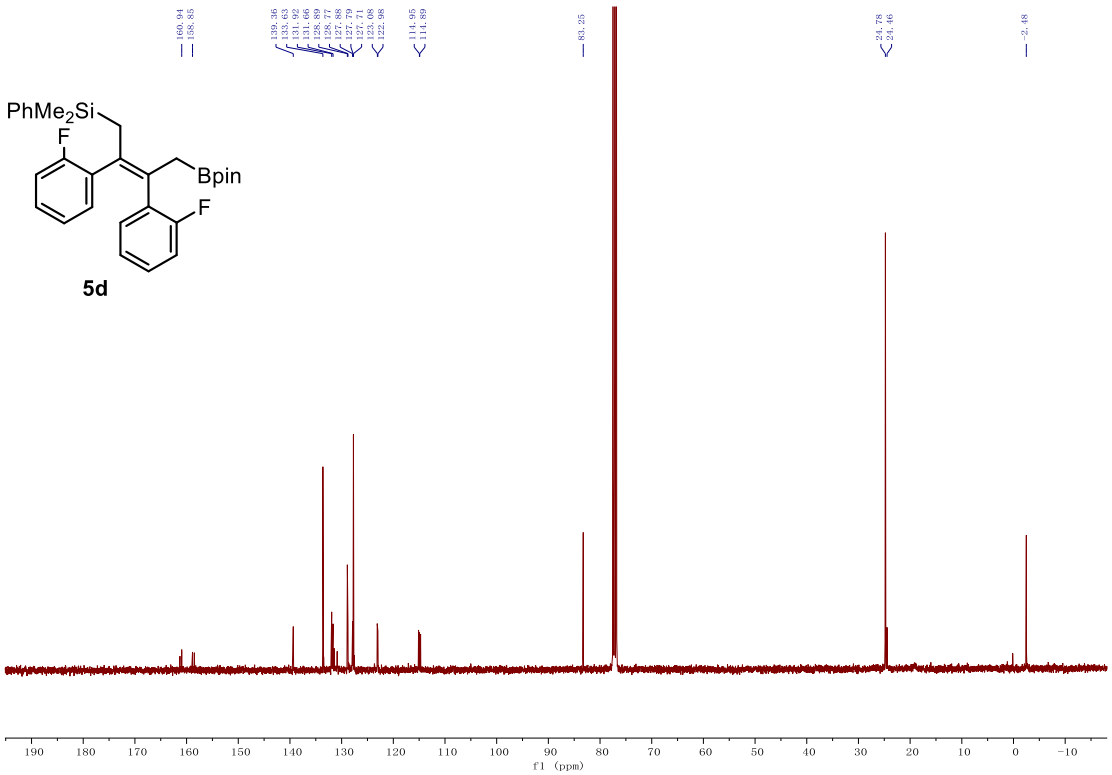
^{13}C NMR, $CDCl_3$, 101 MHz



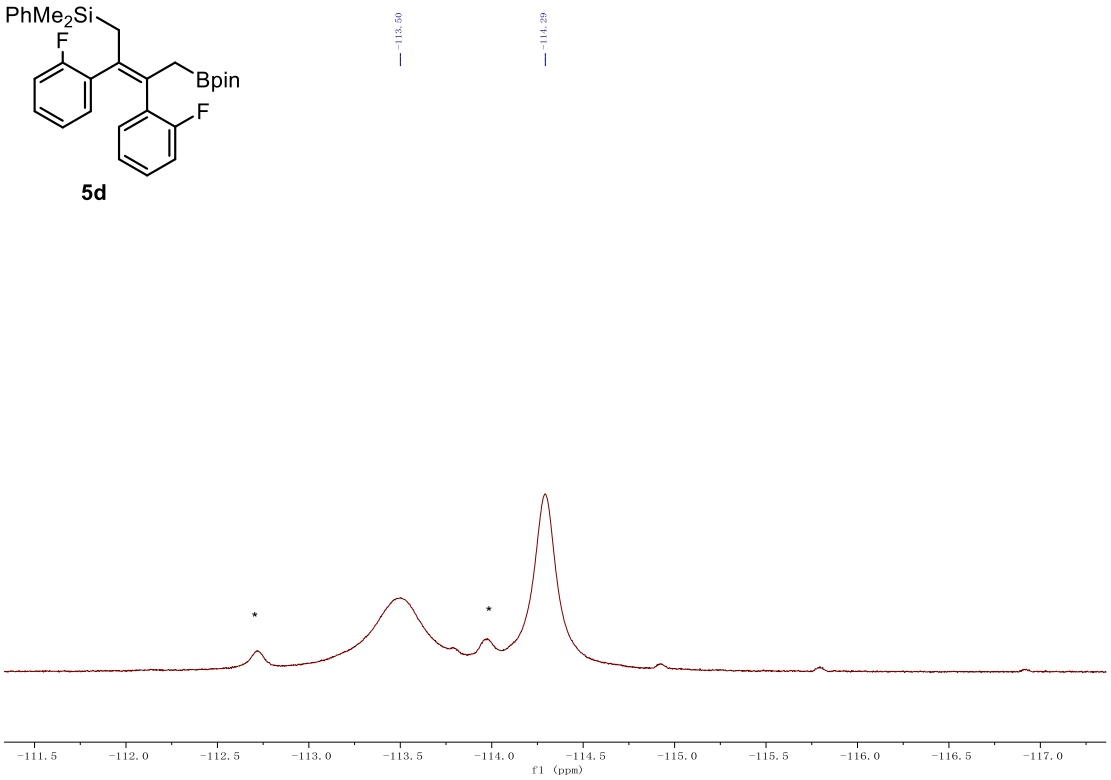
^{19}F NMR, $CDCl_3$, 376 MHz (* was attributed to (*Z*)-4,1-borosilylation isomer.)



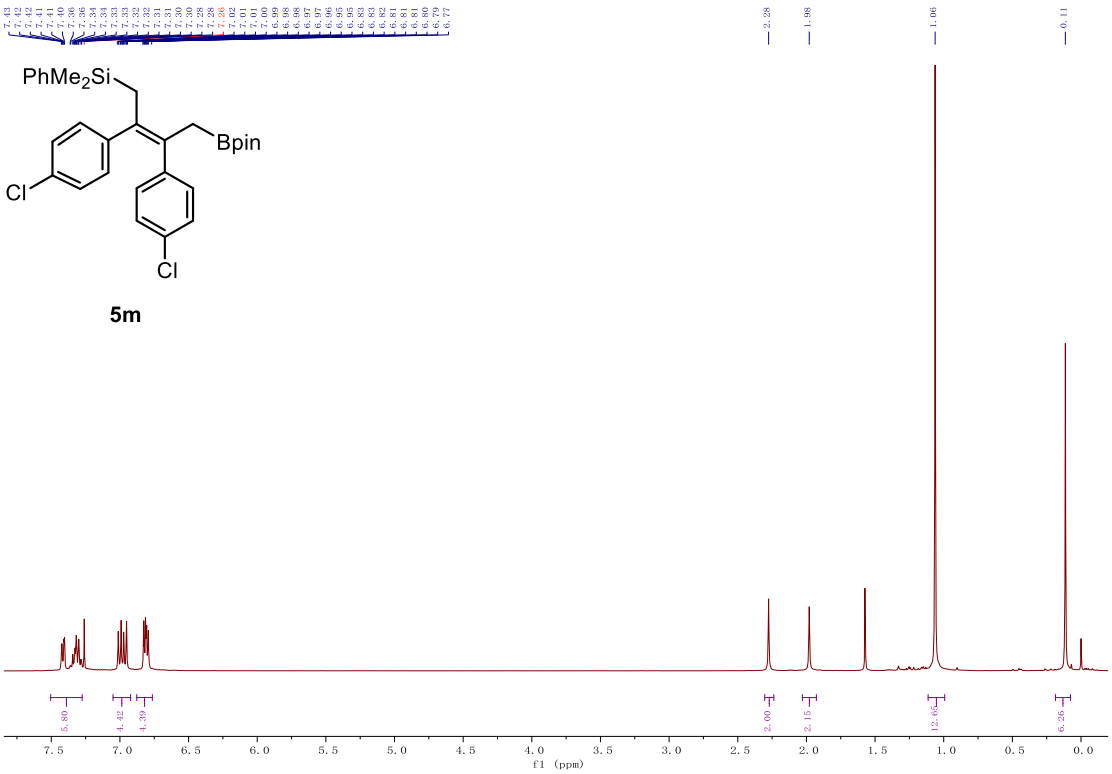
^{1}H NMR, $CDCl_3$, 400 MHz



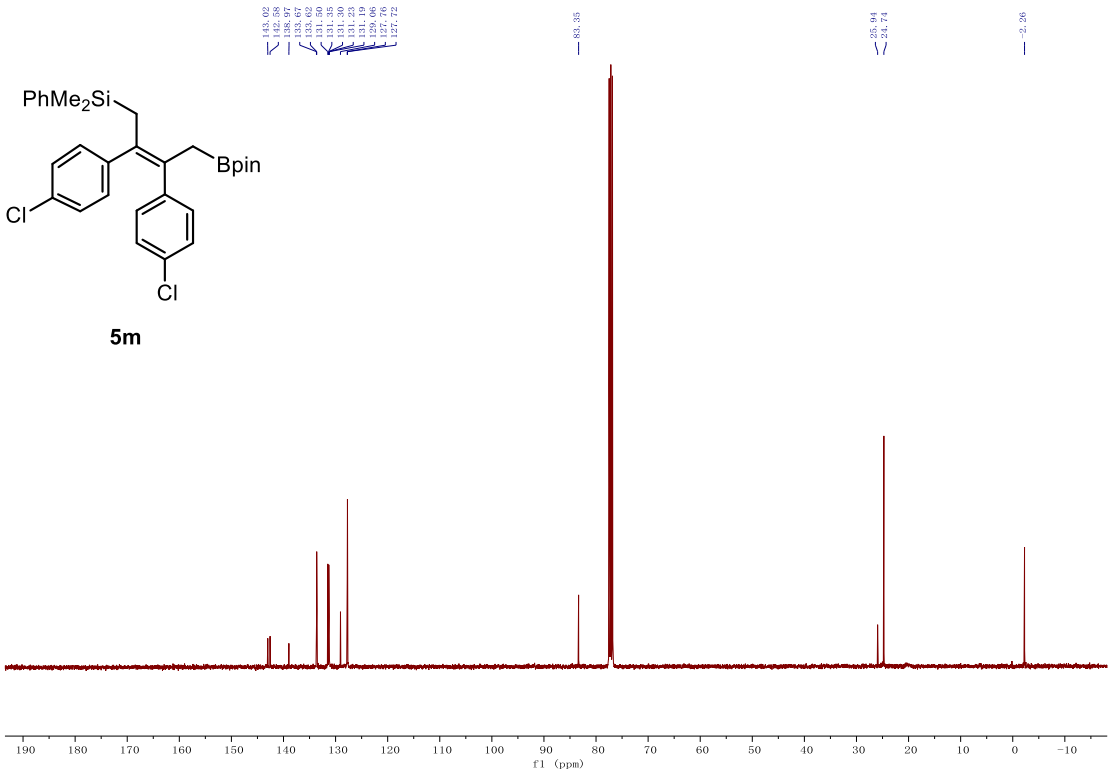
^{13}C NMR, $CDCl_3$, 101 MHz



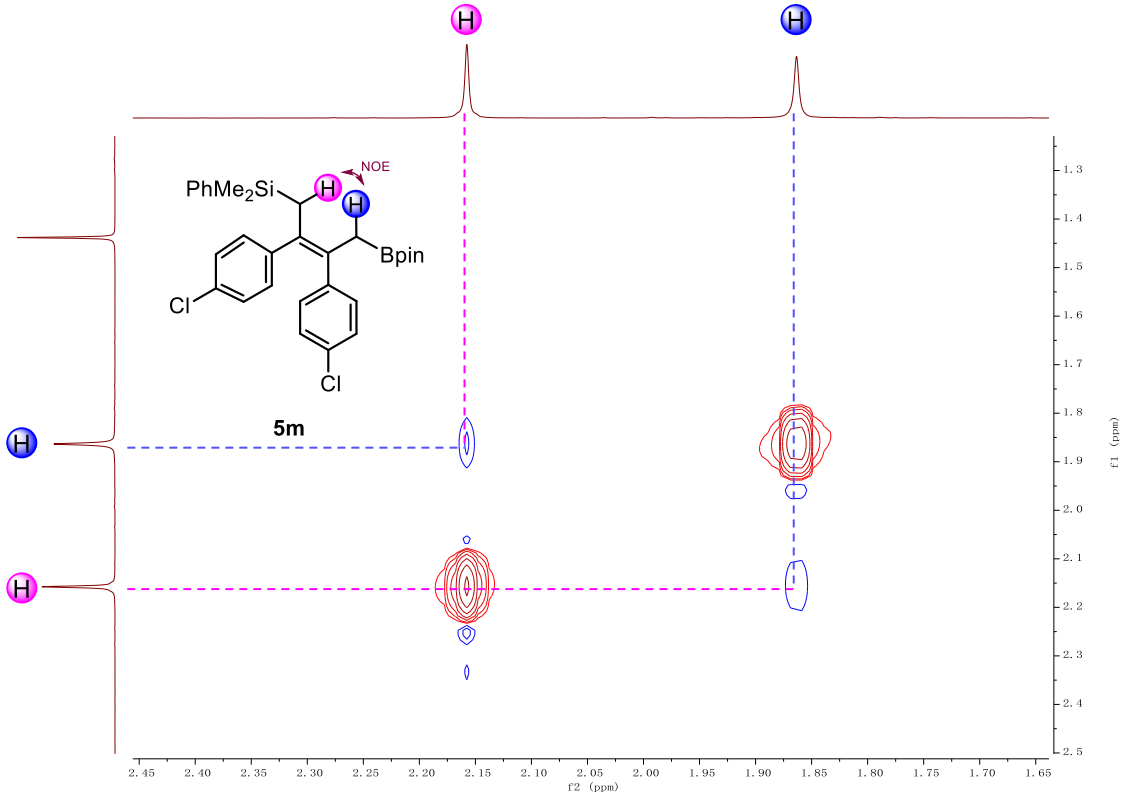
^{19}F NMR, $CDCl_3$, 376 MHz (* was attributed to (*Z*)-4,1-borosilylation isomer.)



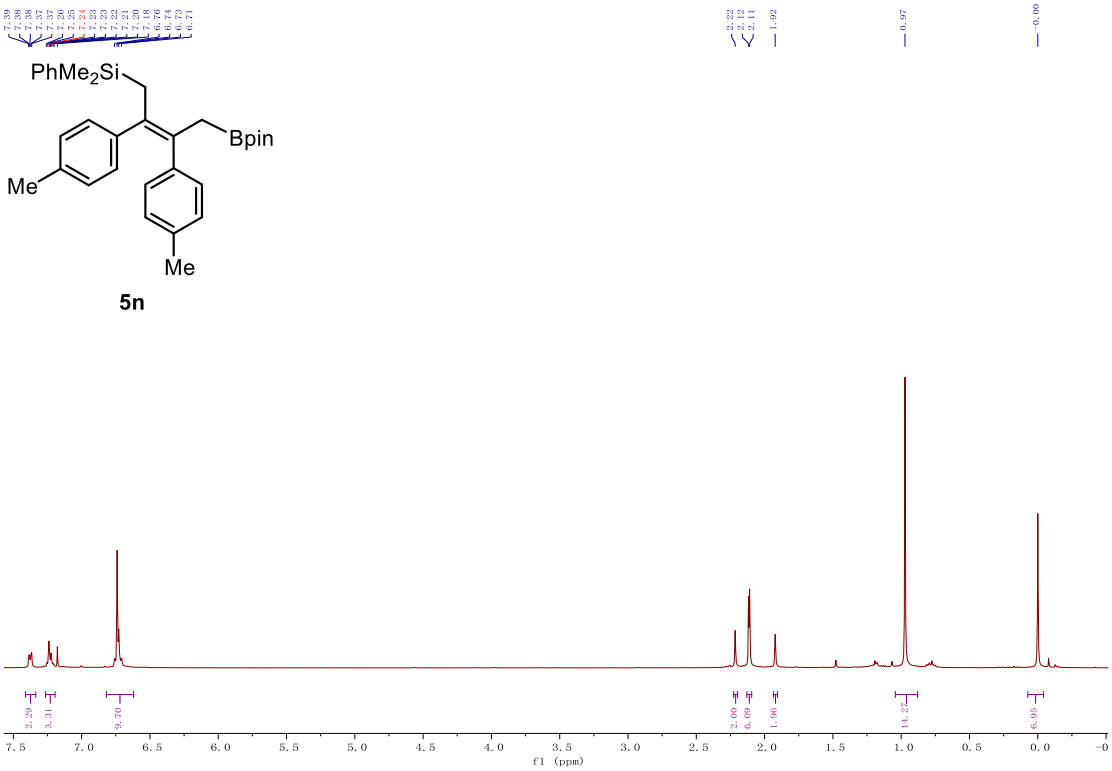
^{1}H NMR, $CDCl_3$, 400 MHz



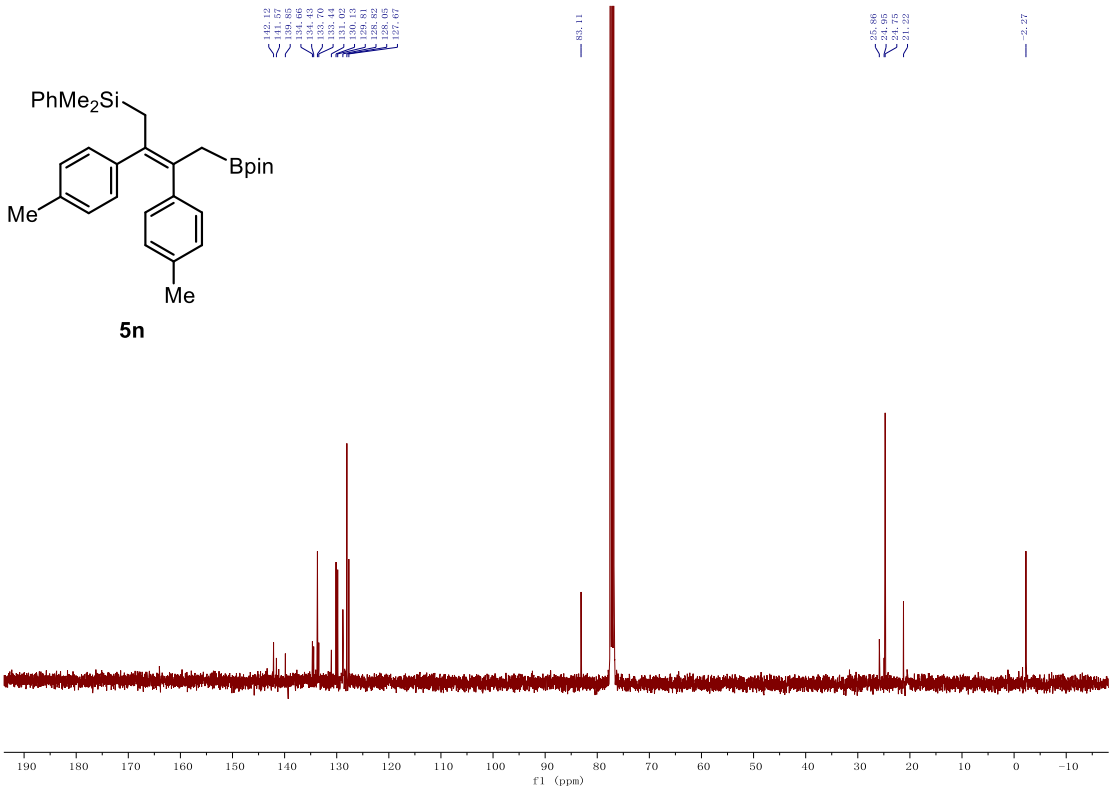
^{13}C NMR, $CDCl_3$, 101 MHz



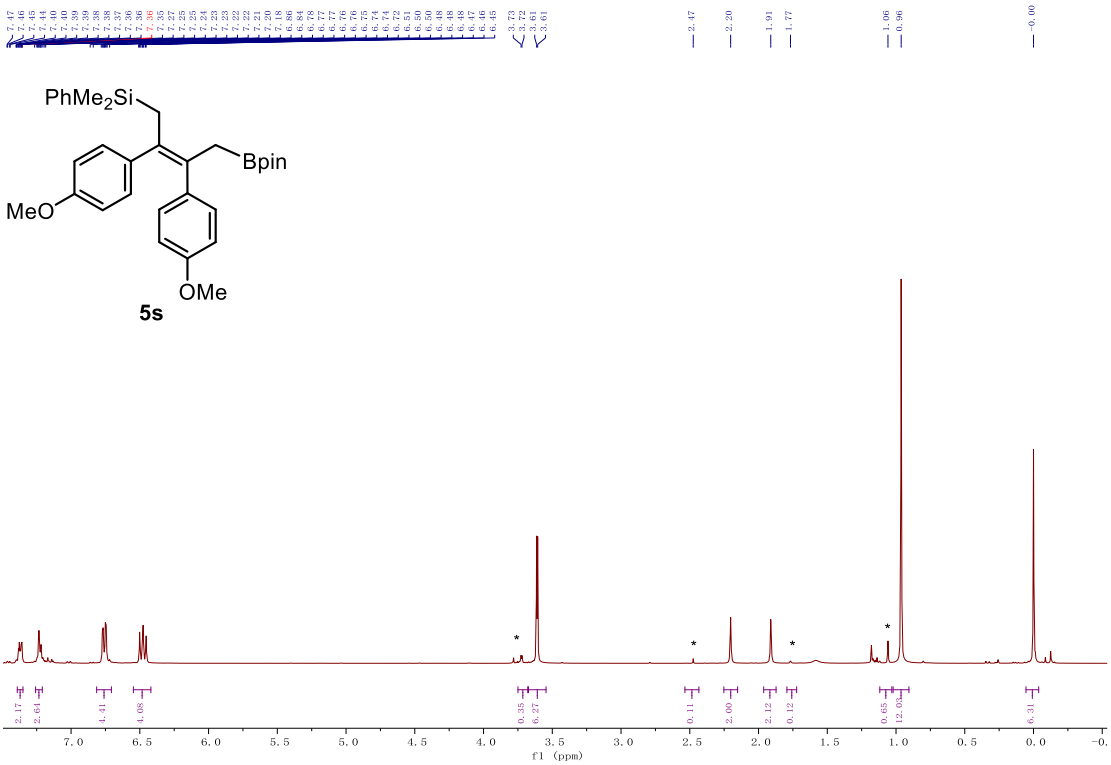
^{1}H, ^{1}H - NOESY



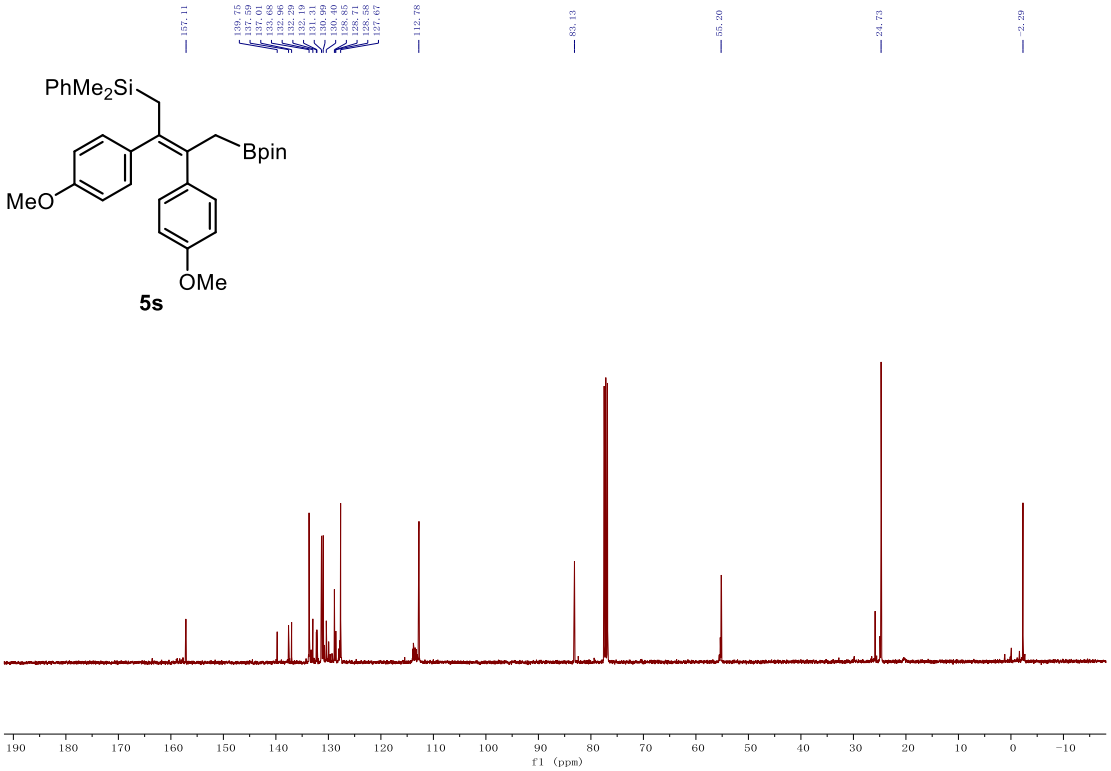
^{1}H NMR, $CDCl_3$, 400 MHz



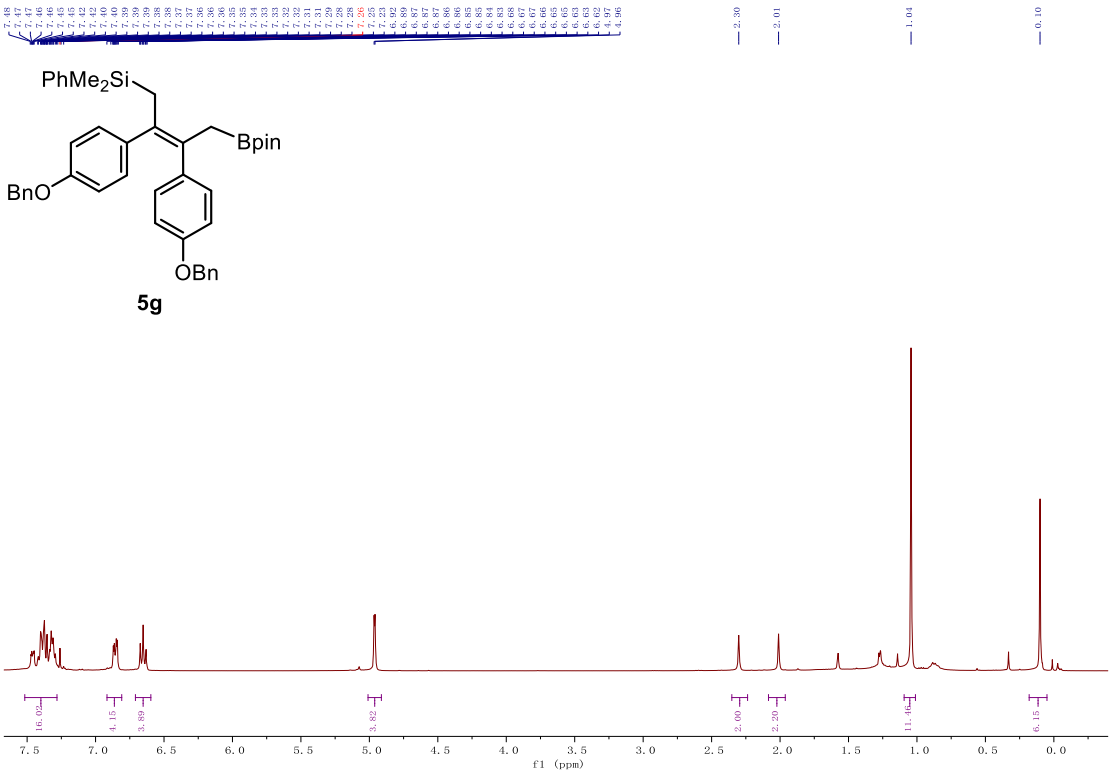
^{13}C NMR, $CDCl_3$, 101 MHz



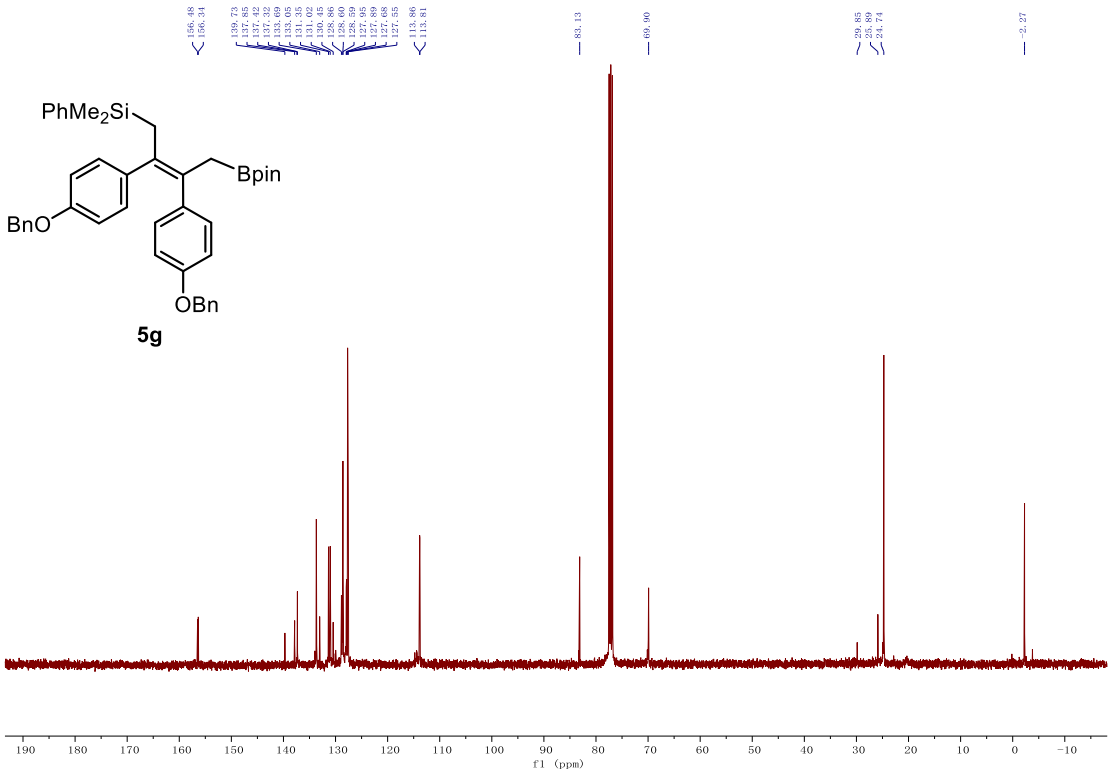
^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to (*Z*)-4,1-borosilylation isomer.)



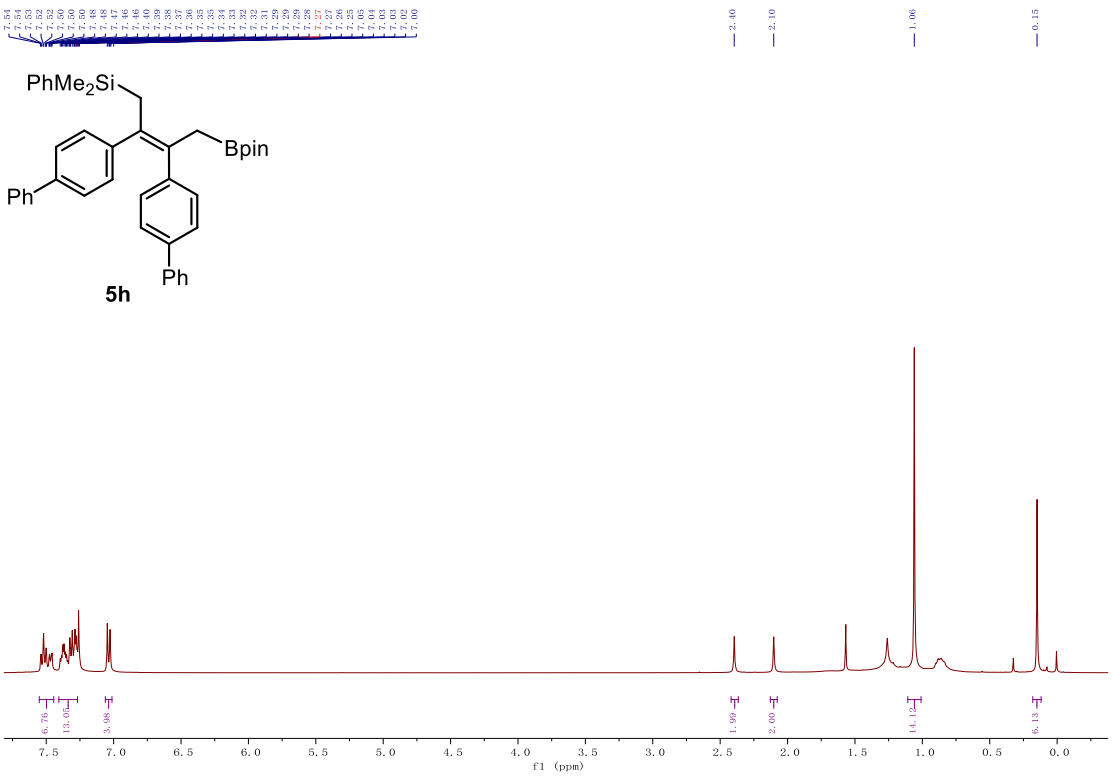
^{13}C NMR, $CDCl_3$, 101 MHz



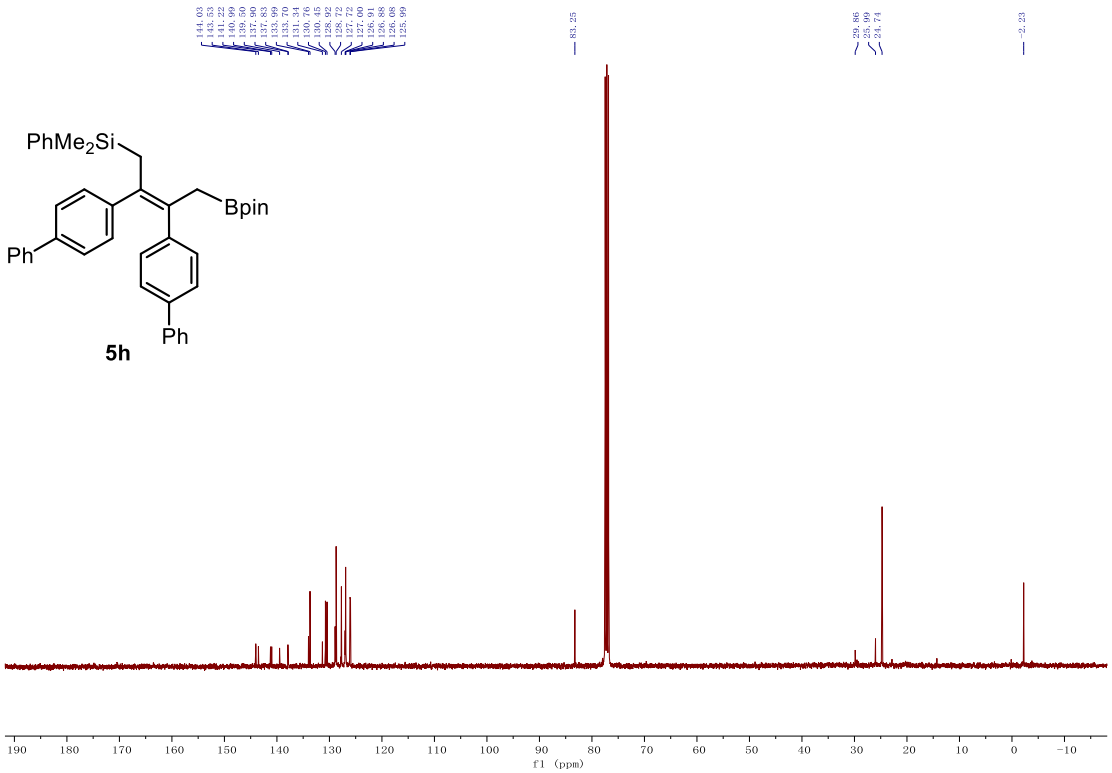
^{1}H NMR, $CDCl_3$, 400 MHz



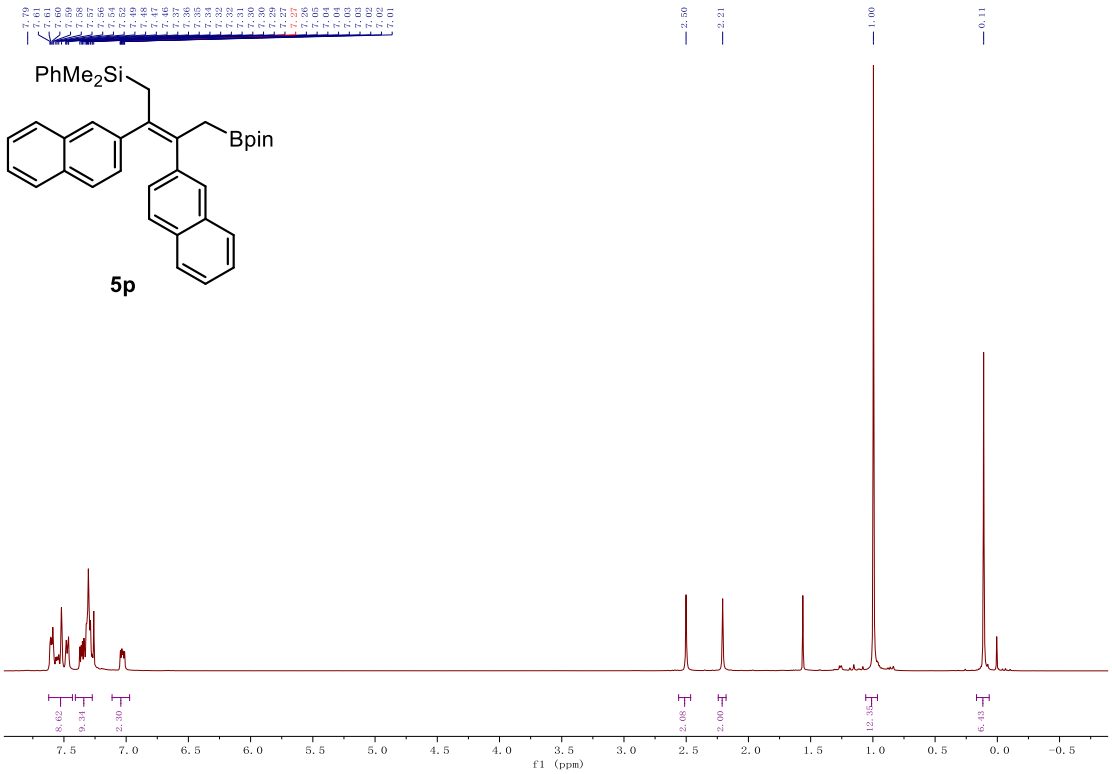
^{13}C NMR, $CDCl_3$, 101 MHz



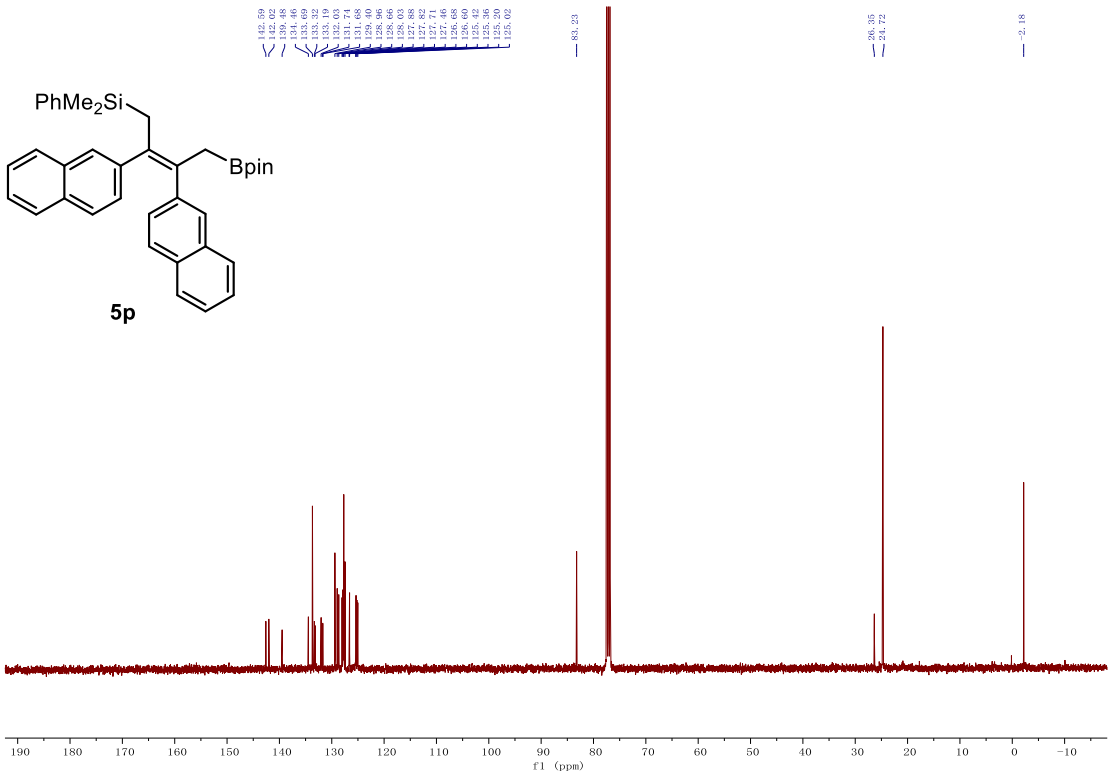
^{1}H NMR, $CDCl_3$, 400 MHz



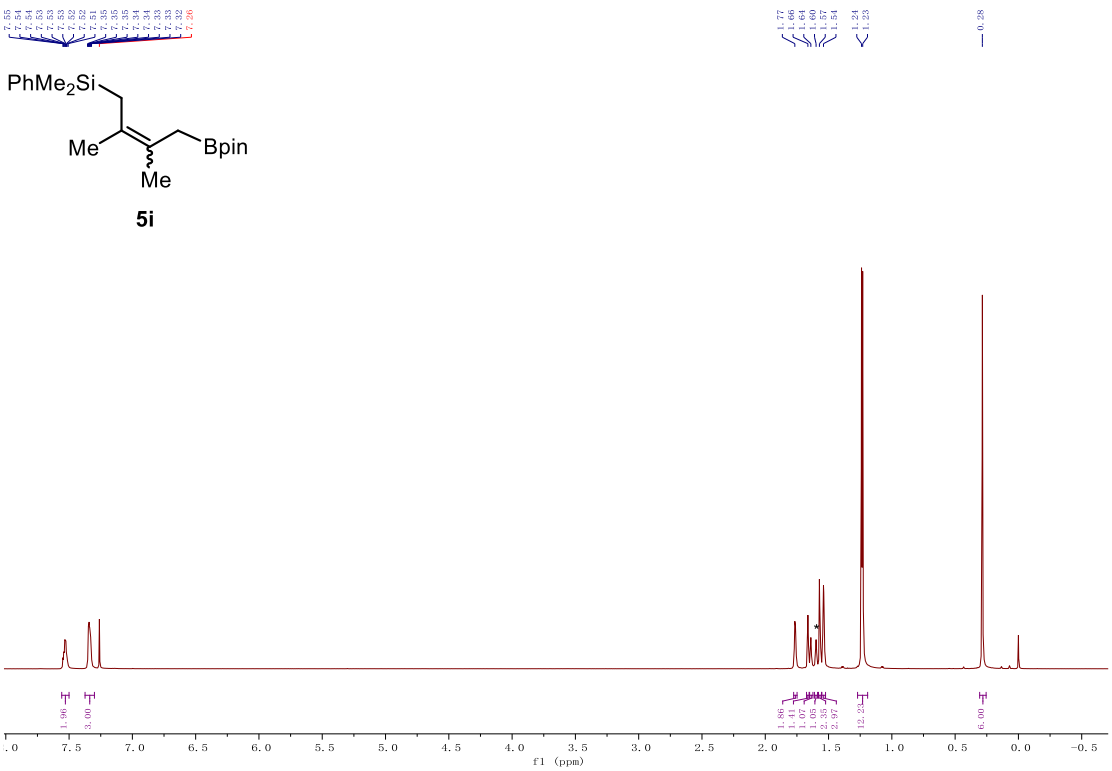
^{13}C NMR, $CDCl_3$, 101 MHz



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

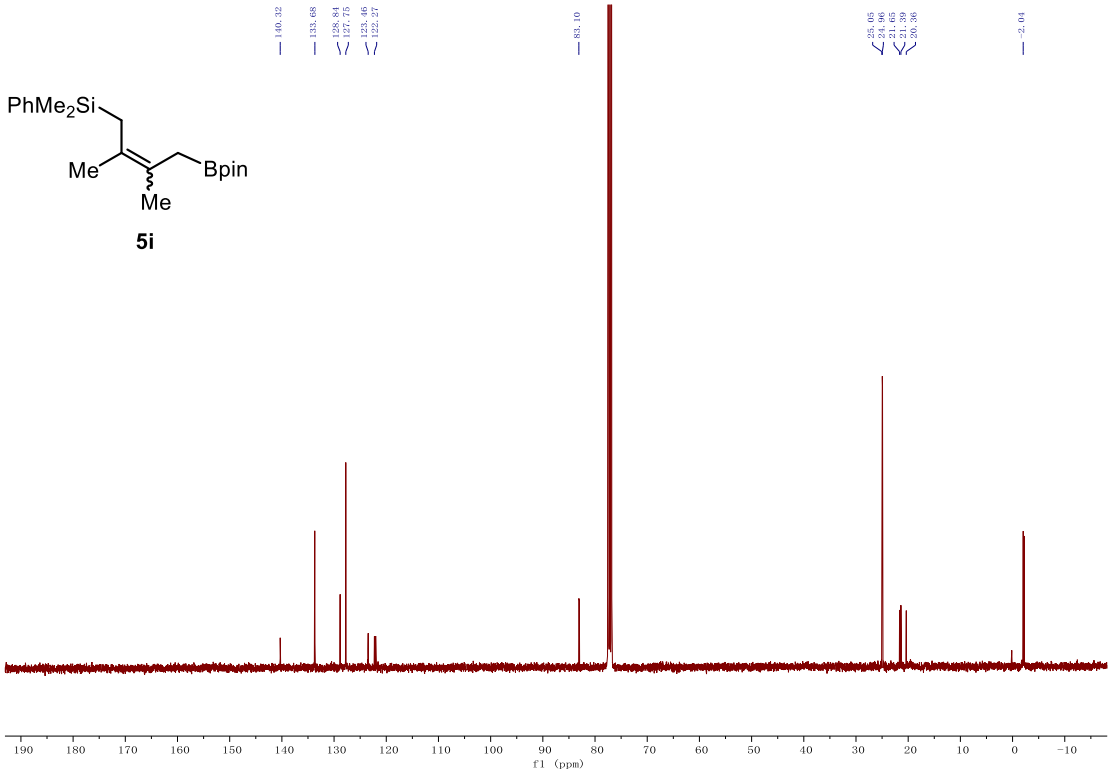


^{13}C NMR, $CDCl_3$, 101 MHz



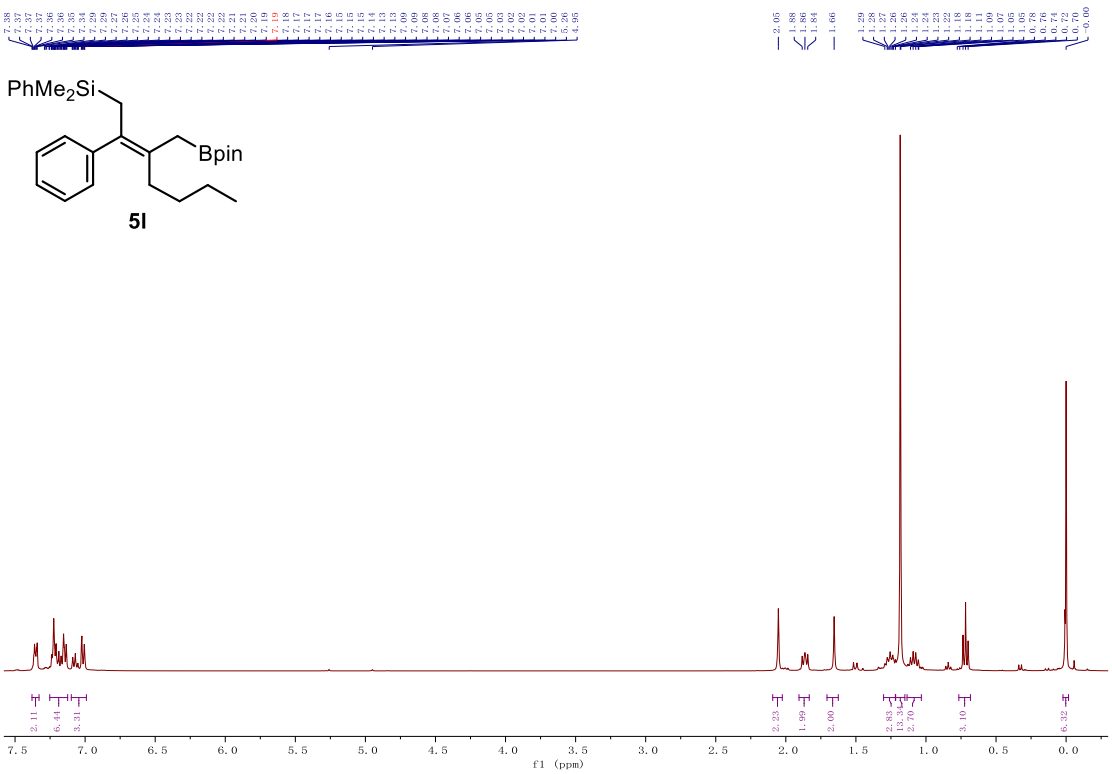
5i

^{1}H NMR, $CDCl_3$, 400 MHz (* was attributed to (*Z*)-4,1-borosilylation isomer.)

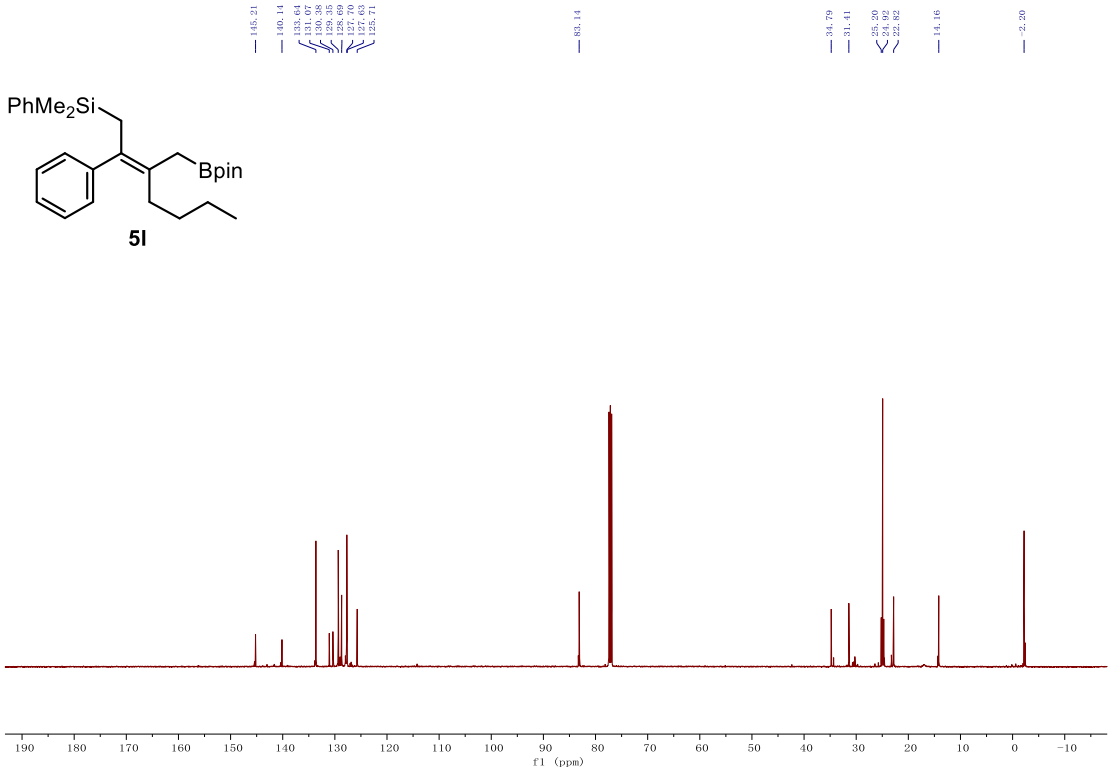


5i

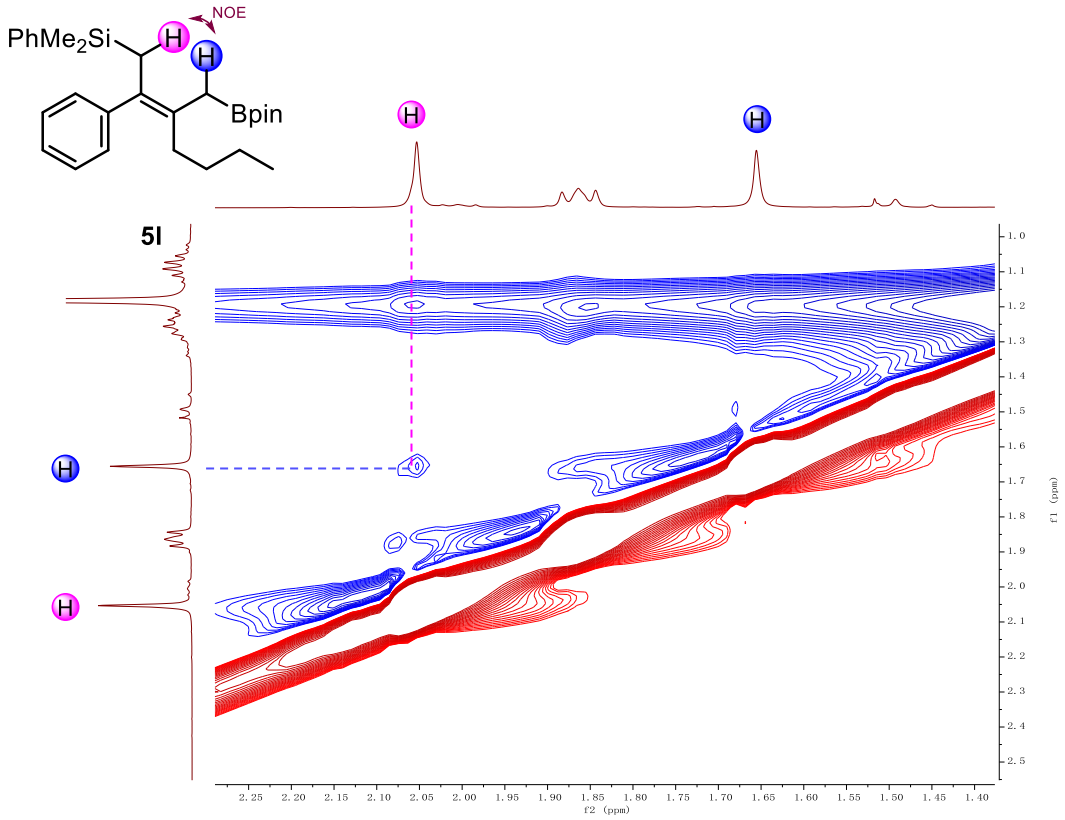
^{13}C NMR, $CDCl_3$, 101 MHz



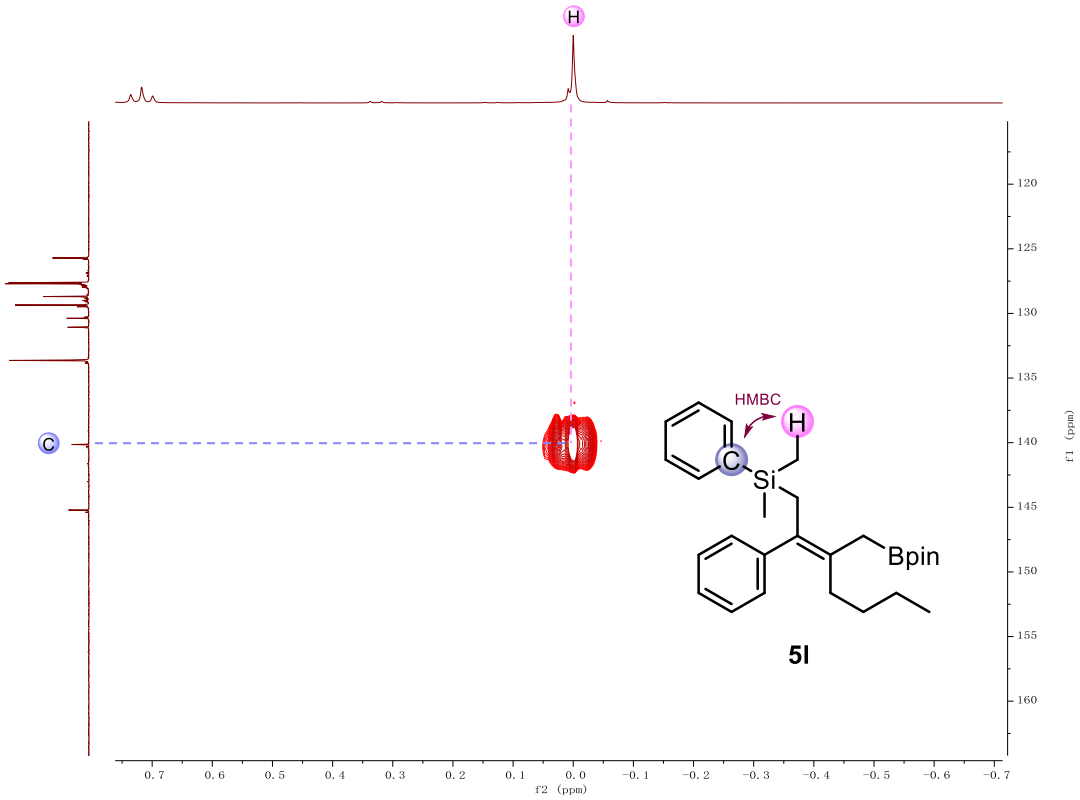
^{1}H NMR, $CDCl_3$, 400 MHz



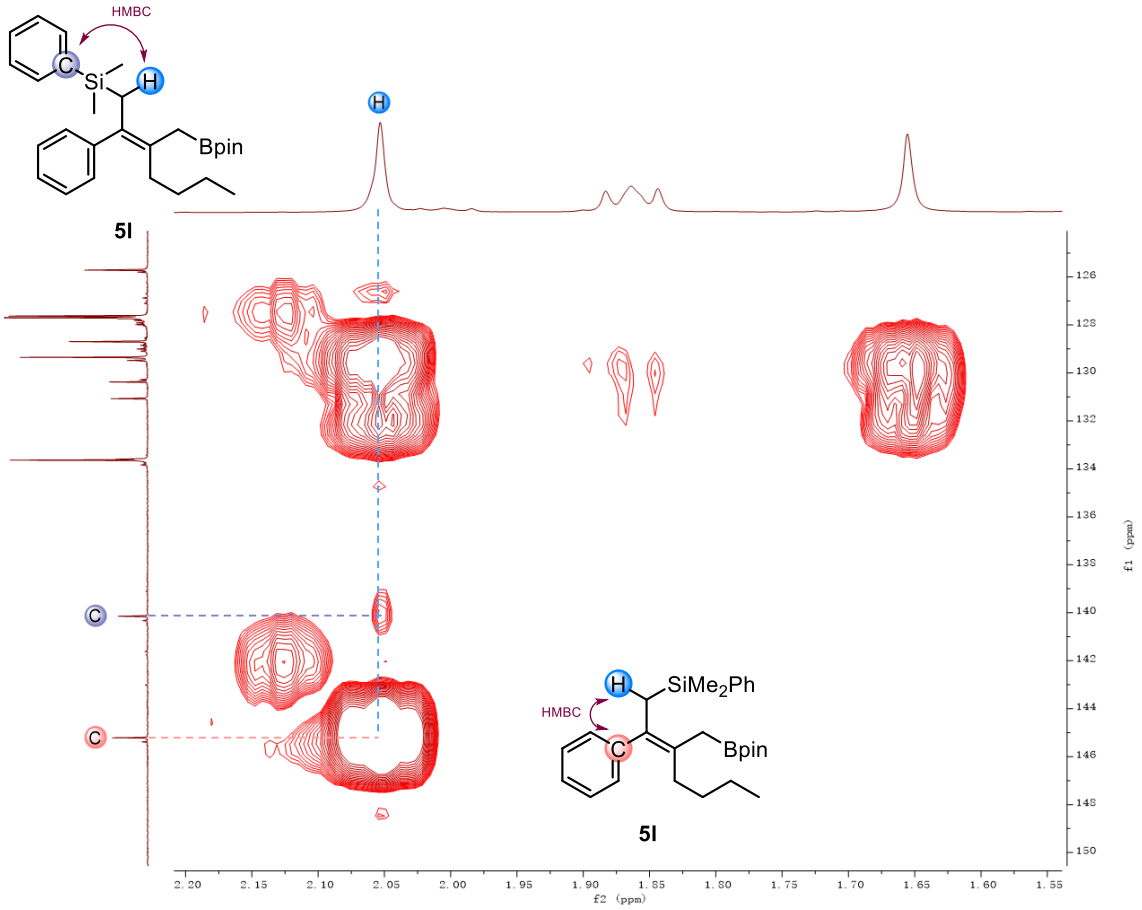
^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H, ^{1}H - NOESY



^{1}H, ^{13}C – HMBC


HMBC
C
Si
H
Bpin
5l
H
C
C
SiMe2Ph
HMBC
H
C
Bpin
5l
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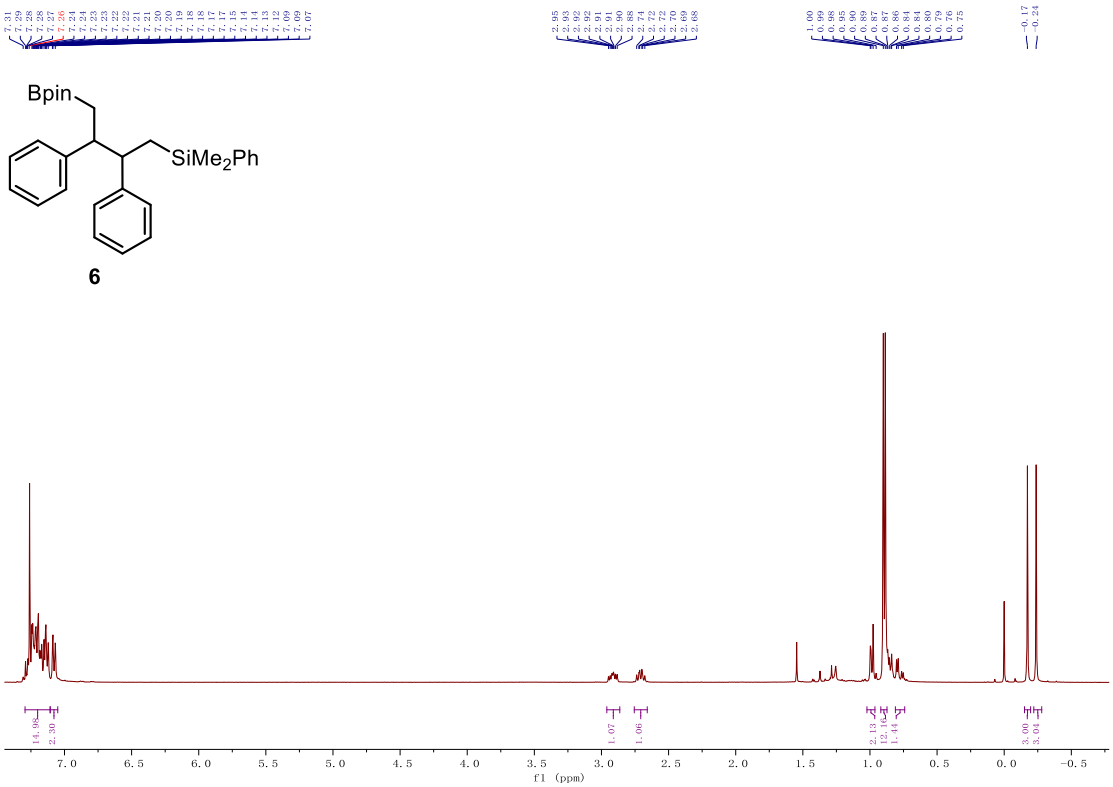
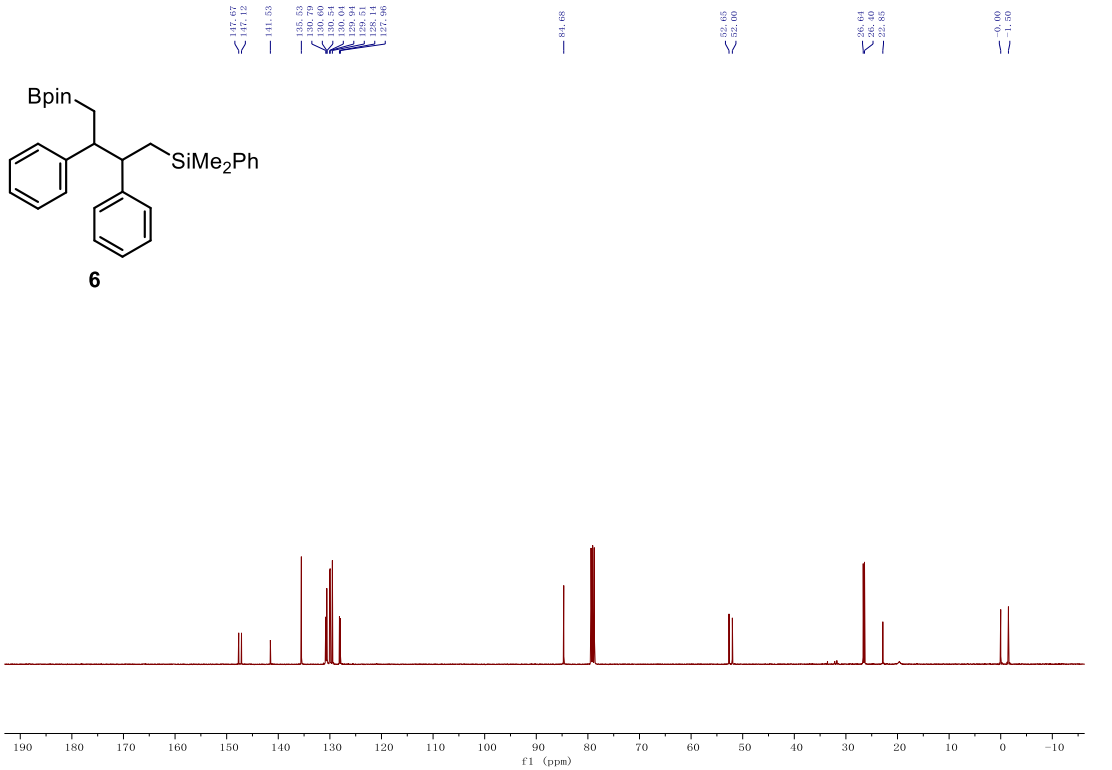
132
134
136
138
140
142
144
146
148
150
f1 (ppm)
2.20
2.15
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
f2 (ppm)

^{1}H, ^{13}C – HMBC



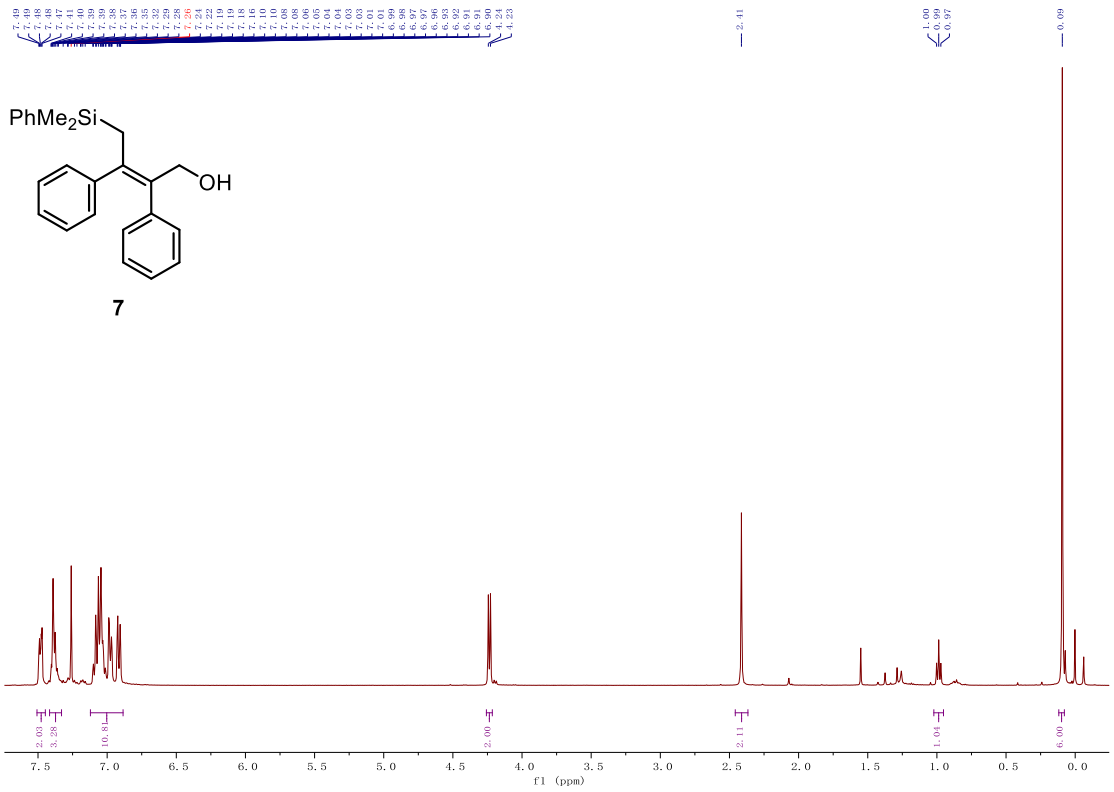
6

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

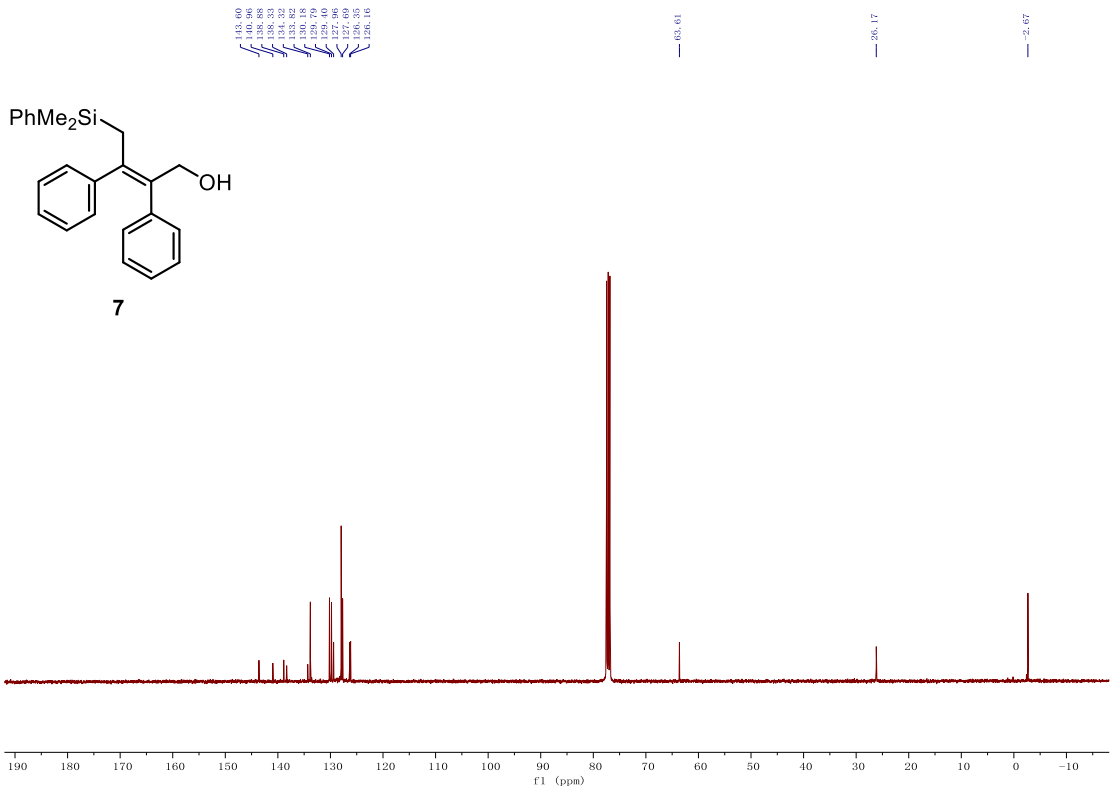


6

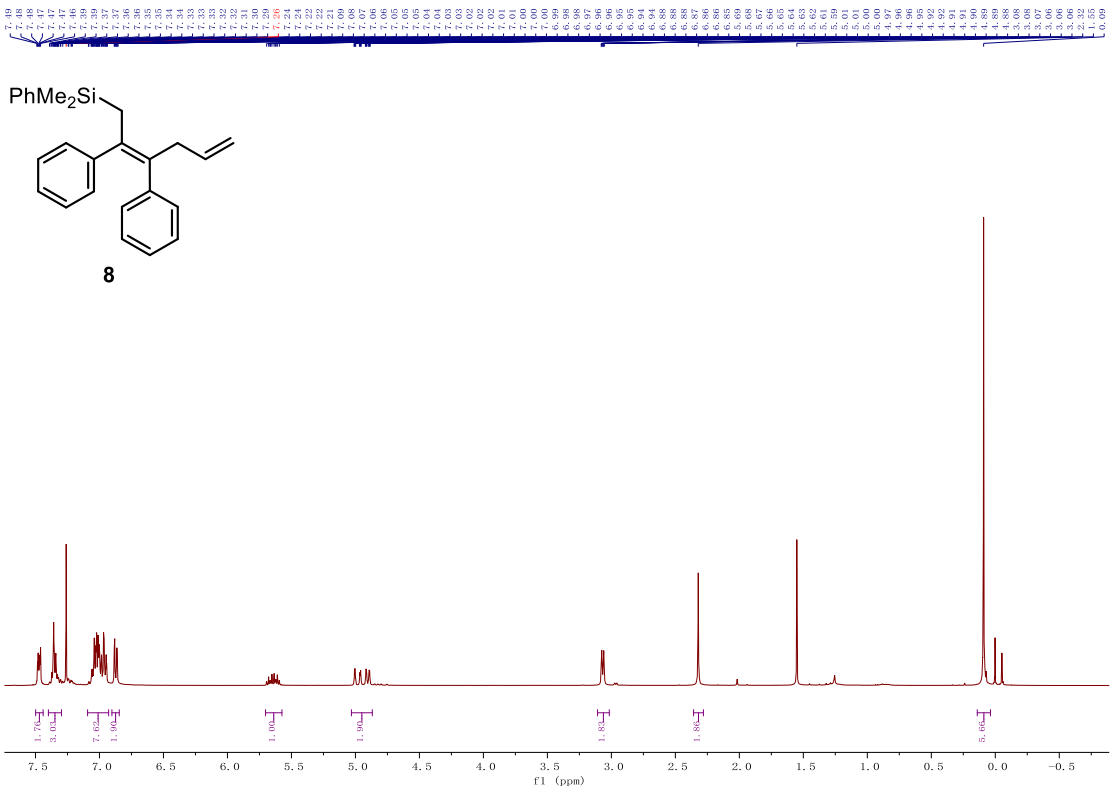
^{13}C NMR, $CDCl_3$, 101 MHz



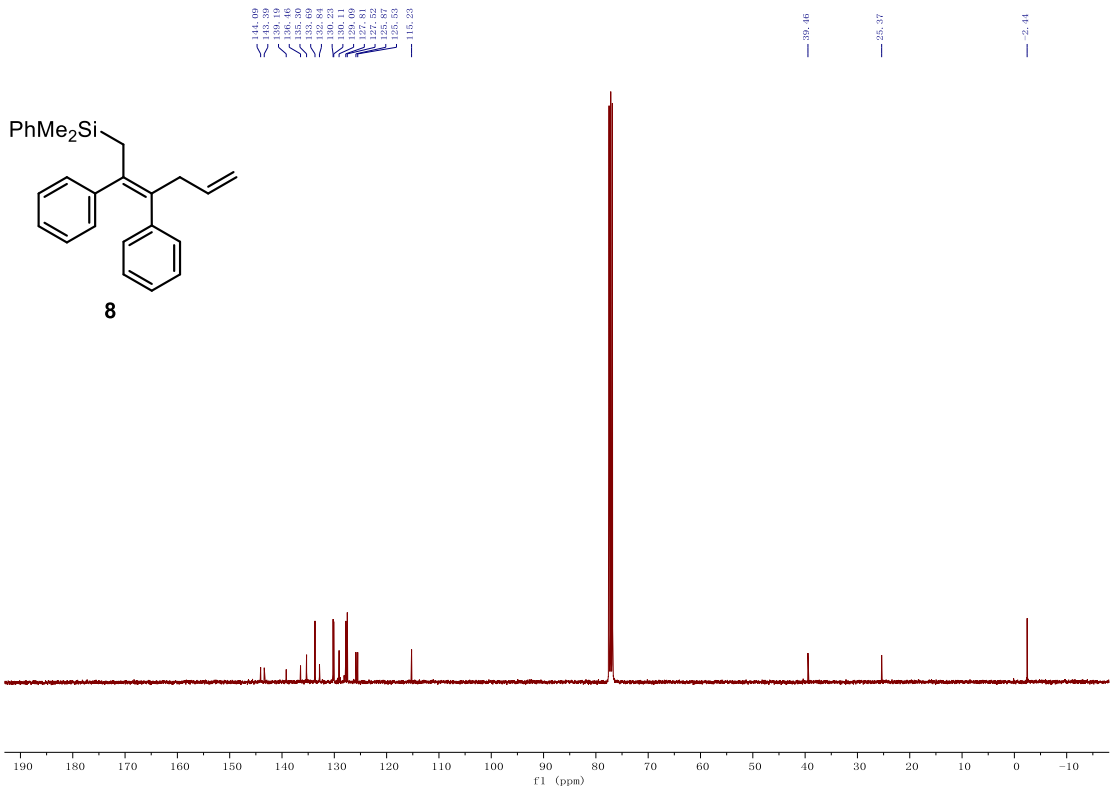
^{1}H NMR, $CDCl_3$, 400 MHz



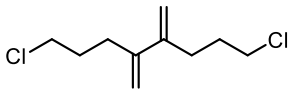
^{13}C NMR, $CDCl_3$, 101 MHz



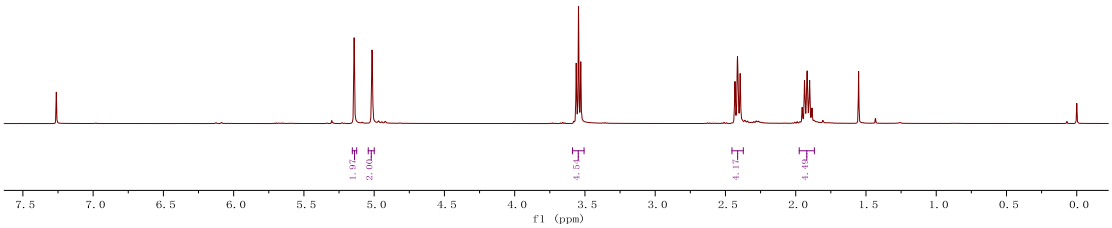
^{1}H NMR, $CDCl_3$, 400 MHz



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



1j



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

1j

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

9. References

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