Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iron-Catalyzed Cross-Electrophile Coupling of Bromostyrenes and Chlorosilanes

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I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents

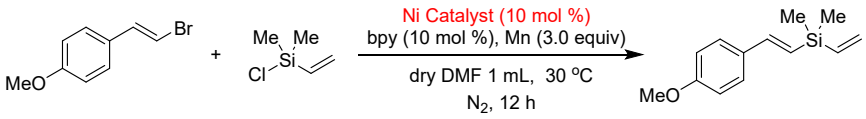
All operations were carried out under an atmosphere of nitrogen in a Schlenk line with magnetic stirring. DMF, THF, DMSO, DMA and so on were purchased (Sinopharm Group Co., China) and used directly. Deuterated solvents were used as received ($CDCl_3$ and DMSO-d_6 from Maclin Co., China). Nickel catalysts, iron catalysts, reductive, ligands were purchased from Bidepharm, Aldrich, Energy Chemicals, and TCI. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Procedures for the synthesis of the vinyl halides were synthesized according to the literature procedure.[1,2] All of the chlorosilanes were purchased from NY-Silicon (http://nanyuan-chem.com), which also could be synthesized according to the literature procedure.[3,4] Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

2. Physical Method

Column chromatography was performed using silica gel 300-400 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. Low resolution mass spectra were measured on Agilent 1260 Infinity II/6125 mass spectrometer. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Details of Optimization

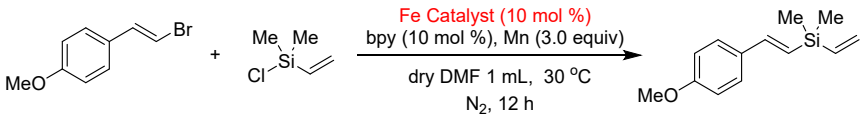
Table S1. Screening of Ni catalyst for the reaction of **1a** and **1b**



1a (0.2 mmol) **1b** (0.6 mmol) **1**

Entry	Ni Catalyst	yield% *Isolated yield*
1	$Ni(dppf)Cl_2$	75
2	$NiCl_2(PPh_3)_2$	27
3	$Ni(COD)_2$	29
4	$NiBr_2$	28
5	$Ni(OTf)_2$	60
6	NiF_2	58
7	$Ni(ClO_4)_2 \cdot 6H_2O$	30
8	$NiCl_2$	40
9	NiI_2	38
10	$NiBr_2 \cdot DME$	18
11	$Ni(acac)_2$	38
12	$Ni(TMHD)_2$	37
13	$NiCl_2 \cdot DME$	30

Table S2. Screening of Fe catalyst for the reaction of **1a** and **1b**

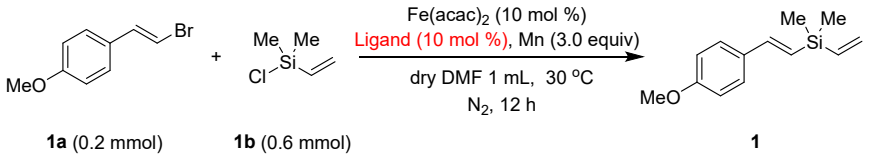


1a (0.2 mmol) **1b** (0.6 mmol) **1**

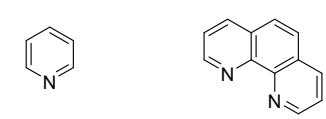
Entry	Fe Catalyst	yield% *Isolated yield*
1	$Cu(acac)_2$	no reaction
2	$Co(acac)_2$	8
3	$Fe(acac)_3$	76
4	$K_3[Fe(CN)_6]$	no reaction
5	$FeCl_3$	79
6	[Bmim]$FeCl_4$	83
7	Iron phthalocyanine	18
8	FeF_3	79

9	$Fe(OTf)_3$	70
10	$FeBr_3$	52
11	$Fe(acac)_2$	93
12	$FeCl_2$	43
13	FeAc	50
14	$Fe(NO_3)_3 \cdot 9H_2O$	no reaction
15	$Fe_2(SO_4)_3$	62
16	Ferric oxalate	no reaction
17	$FeSO_4$	64

Table S3. Screening of ligand for the reaction of **1a** and **1b**

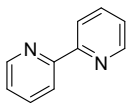


1a (0.2 mmol) **1b** (0.6 mmol) **1**

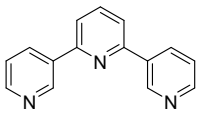


L1, 0%

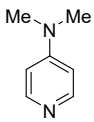
L2, 84%



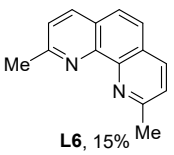
L3, 93%



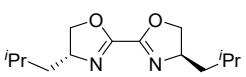
L4, 40%



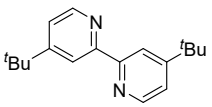
L5, 0%



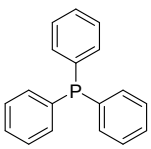
L6, 15%



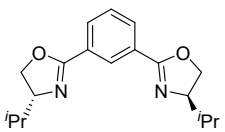
L7, 91%



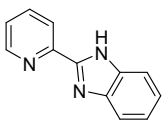
L8, 72%



L9, 17%

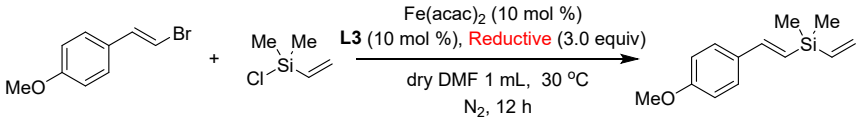


L10, 84%



L11, 23%

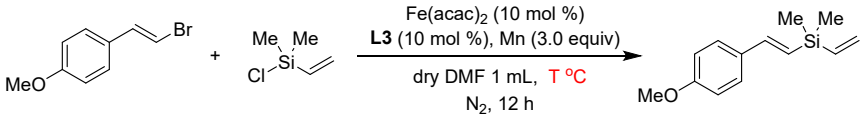
Table S4. Screening of reductive for the reaction of **1a** and **1b**



1a (0.2 mmol) **1b** (0.6 mmol) **1**

Entry	Reductive	yield% *Isolated yield*
1	Mn	93
2	Zn	no reaction
3	TDAE	no reaction
4	B_2pin_2 + LiOMe	no reaction

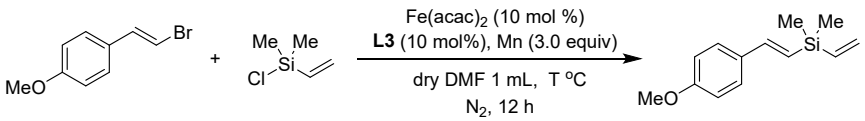
Table S5. Screening of temperature for the reaction of **1a** and **1b**



1a (0.2 mmol) **1b** (0.6 mmol) **1**

Entry	Temperature	yield% *Isolated yield*
1	0 °C	90
2	25 °C	80
3	30 °C	93
4	45 °C	71

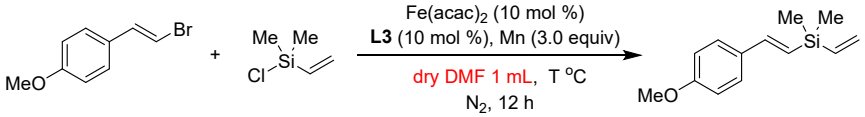
Table S6. Screening for the ratio of **1a** and **1b**



1a (0.2 mmol) **1b** (0.6 mmol) **1**

Entry	Variations	yield% *Isolated yield*
1	none	93
2	**1b** (1.0 equiv)	41
3	**1b** (1.5 equiv)	28
4	**1b** (2.0 equiv)	37
5	**1b** (2.5 equiv)	70
6	**1b** (2.7 equiv)	80
7	**1b** (2.8 equiv)	72

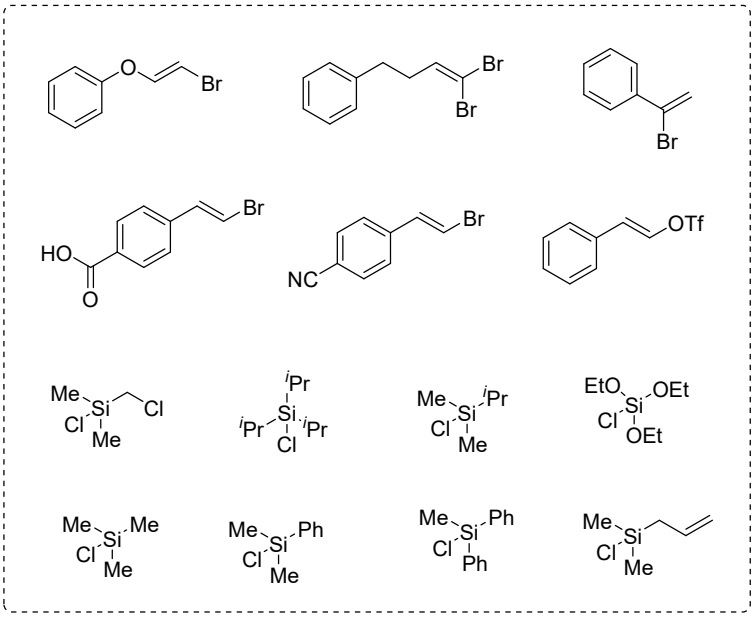
Table S7. Screening of solvent for the reaction of **1a** and **1b**



1a (0.2 mmol) **1b** (0.6 mmol) **1**

Entry	Solvent	yield% *Isolated yield*
1	none	93
2	DMA instead of DMF	74
3	DMSO instead of DMF	20
4	CH_3CN instead of DMF	no reaction
5	1,4-Dioxane instead of DMF	no reaction

Ineffective Substrates:



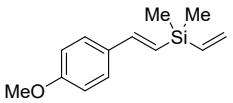
Part 3. Coupling of Vinyl Chlorosilanes with Vinyl Halides

1. General Procedure

General procedure for the reaction of vinyl chlorosilanes with vinyl halides (method A): To a dried Schlenk line was charged with vinyl halides (0.2 mmol, 100 mol%), 2,2'-bipyridine (3.12 mg, 0.02 mmol, 10 mol%), $Fe(acac)_2$ (5.08 mg, 0.02 mmol, 10 mol%) at 25 ℃. The Schlenk line was sealed with an atmosphere of nitrogen. Chlorodimethyl(vinyl)silane (72.39 mg, 0.6 mmol, 300 mol%) was added followed by addition of DMF (1 mL) via syringes. The reaction mixture was allowed to maintain 30 ℃ and stirred overnight. The reaction mixture was purified by column chromatograph to afford the product as a solid or oil.

2. Experimental Details

(*E*)-(4-Methoxystyryl)dimethyl(vinyl)silane (1)



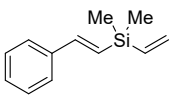
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (39.30 mg, 0.180 mmol) as a colorless oil. Moreover, when (*Z*)-alkenyl bromide was used, 57% yield of **1** was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.35 (m, 2H), 6.87–6.82 (m, 3H), 6.28 (d, J = 19.2 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.01 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 3.80 (s, 3H), 0.22 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.77, 144.39, 138.64, 132.32, 131.40, 127.81, 124.46, 114.02, 55.41, -2.71.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{13}H_{18}NaOSi$: 241.1019. Found: 241.1016.

(*E*)-Dimethyl(styryl)(vinyl)silane (2)



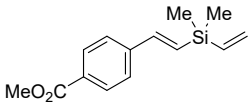
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 72% yield (27.2 mg, 0.144 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz,

1H), 6.90 (d, *J* = 19.1 Hz, 1H), 6.45 (d, *J* = 19.1 Hz, 1H), 6.22 (dd, *J* = 20.3, 14.6 Hz, 1H), 6.02 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.76 (dd, *J* = 20.3, 3.8 Hz, 1H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.86, 138.29, 132.42, 128.56, 128.12, 127.29, 126.47, -2.88.

Methyl (*E*)-4-(2-(dimethyl(vinyl)silyl)vinyl)benzoate (3)

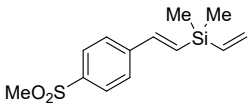


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (39.90 mg, 0.162 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H), 7.51–7.47 (m, 2H), 6.93 (d, *J* = 19.1 Hz, 1H), 6.60 (d, *J* = 19.1 Hz, 1H), 6.21 (dd, *J* = 20.3, 14.6 Hz, 1H), 6.04 (dd, *J* = 14.6, 3.7 Hz, 1H), 5.77 (dd, *J* = 20.3, 3.8 Hz, 1H), 3.91 (s, 3H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.02, 143.79, 142.57, 137.84, 132.86, 131.09, 130.02, 129.52, 126.44, 52.18, -2.93.

(*E*)-Dimethyl(4-(methylsulfonyl)styryl)(vinyl)silane (4)



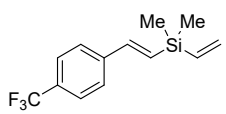
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (45.30 mg, 0.170 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91–7.88 (m, 2H), 7.61–7.58 (m, 2H), 6.93 (d, *J* = 19.2 Hz, 1H), 6.66 (d, *J* = 19.1 Hz, 1H), 6.21 (dd, *J* = 20.2, 14.6 Hz, 1H), 6.05 (dd, *J* = 14.6, 3.7 Hz, 1H), 5.77 (dd, *J* = 20.2, 3.7 Hz, 1H), 3.05 (s, 3H), 0.26 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.43, 142.64, 139.40, 137.40, 133.14, 133.04, 127.76, 127.15, 44.61, -3.10.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{19}O_2SSi$: 267.0870. Found: 267.0870.

(*E*)-Dimethyl(4-(trifluoromethyl)styryl)(vinyl)silane (5)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 54% yield (27.69 mg, 0.108 mmol) as a colorless oil.

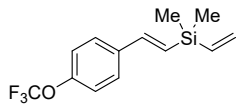
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 19.1 Hz, 1H), 6.58 (d, J = 19.2 Hz, 1H), 6.26–6.17 (m, 1H), 6.04 (dd, J = 14.6, 3.7 Hz, 1H), 5.77 (dd, J = 20.2, 3.8 Hz, 1H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.23, 137.70, 132.84, 130.95, 126.61, 125.58, 125.54, 125.50, 125.46, -3.03.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.46.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{13}H_{15}F_3NaSi$: 279.0787. Found: 279.0913.

(*E*)-Dimethyl(4-(trifluoromethoxy)styryl)(vinyl)silane (6)



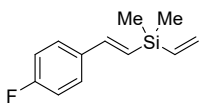
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 73% yield (39.76 mg, 0.146 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.43 (m, 2H), 7.18–7.15 (m, 2H), 6.87 (d, J = 19.1 Hz, 1H), 6.44 (d, J = 19.1 Hz, 1H), 6.21 (dd, J = 20.3, 14.6 Hz, 1H), 6.03 (dd, J = 14.6, 3.7 Hz, 1H), 5.76 (dd, J = 20.3, 3.8 Hz, 1H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.02, 143.29, 138.05, 137.14, 132.75, 130.48, 128.91, 127.81, 121.12, -2.88.

^{19}F NMR (471 MHz, $CDCl_3$): δ -57.86.

(*E*)-(4-Fluorostyryl)dimethyl(vinyl)silane (7)



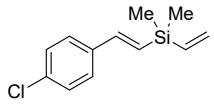
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 58% yield (23.80 mg, 0.116 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.36 (m, 2H), 7.04–6.97 (m, 2H), 6.85 (d, J = 19.2 Hz, 1H), 6.35 (d, J = 19.2 Hz, 1H), 6.21 (dd, J = 20.3, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.68 (d, J = 245.7 Hz), 143.55, 138.16, 134.56, 132.50, 128.05 (d, J = 7.6 Hz), 127.02, 115.52 (d, J = 21.4 Hz), -2.91.

^{19}F NMR (471 MHz, $CDCl_3$): δ -113.90.

(*E*)-(4-Chlorostyryl)dimethyl(vinyl)silane (8)

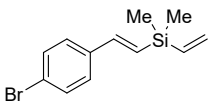


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 51% yield (22.72 mg, 0.152 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 19.1 Hz, 1H), 6.30 (d, J = 19.2 Hz, 1H), 6.08 (dd, J = 20.2, 14.6 Hz, 1H), 5.90 (dd, J = 14.6, 3.8 Hz, 1H), 5.63 (dd, J = 20.2, 4.4 Hz, 1H), 0.10 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.55, 138.10, 136.88, 133.83, 132.69, 128.80, 128.37, 127.77, -2.86.

(*E*)-(4-Bromostyryl)dimethyl(vinyl)silane (9)

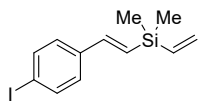


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 69% yield (36.88 mg, 0.138 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 6.84 (s, 1H), 6.44 (d, J = 19.1 Hz, 1H), 6.20 (dd, J = 20.2, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.50, 137.97, 137.22, 132.62, 131.66, 128.48, 127.99, 121.95, -2.97.

(*E*)-(4-Iodostyryl)dimethyl(vinyl)silane (10)



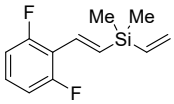
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 52% yield (32.68 mg, 0.104 mmol) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 19.2 Hz, 1H), 6.46 (d, J = 19.1 Hz, 1H), 6.20 (dd, J = 20.3, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.2, 3.8 Hz, 1H), 0.23 (d, J = 3.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.61, 137.94, 137.78, 137.62, 132.63, 128.62, 128.21, 93.59, -2.97.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{12}H_{16}ISi$: 315.0060. Found: 315.1574.

(*E*)-(2,6-Difluorostyryl)dimethyl(vinyl)silane (11)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 56% yield (25.13 mg, 0.112 mmol) as a colorless oil.

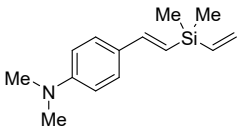
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18–7.10 (m, 1H), 6.92 (d, J = 19.8 Hz, 1H), 6.86 (t, J = 8.4 Hz, 2H), 6.76 (d, J = 19.8 Hz, 1H), 6.22 (dd, J = 20.2, 14.6 Hz, 1H), 6.03 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.15 (d, J = 7.6 Hz), 160.14 (d, J = 7.6 Hz), 137.80, 136.77 (t, J = 6.3 Hz), 132.73, 130.84 (t, J = 2.5 Hz), 128.44 (t, J = 10.1 Hz), 111.57 (dd, J = 20.6, 5.9 Hz), -3.11 (s).

^{19}F NMR (471 MHz, $CDCl_3$): δ -112.62.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{12}H_{15}F_2Si$: 225.0906. Found: 225.0350.

(*E*)-4-(2-(Dimethyl(vinyl)silyl)vinyl)-*N*,*N*-dimethylaniline (12)



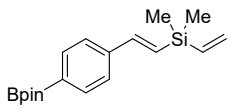
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 34% yield (49.68 mg, 0.068 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15–7.11 (m, 2H), 6.61 (d, J = 19.1 Hz, 1H), 6.48–6.45 (m, 2H), 6.05–5.94 (m, 2H), 5.78 (dd, J = 14.6, 3.9 Hz, 1H), 5.53 (dd, J = 20.3, 3.9 Hz, 1H), 2.75 (s, 6H), -0.00 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.50, 144.85, 138.97, 131.91, 127.52, 127.05, 121.29, 112.23, 40.48, -2.71.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{14}H_{22}NSi$: 232.1516. Found: 232.1531.

(*E*)-Dimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)(vinyl)silane (13)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 72% yield (45.3 mg, 0.144 mmol) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H), 7.46–7.42 (m, 2H), 6.92 (d, J = 19.1 Hz, 1H), 6.53 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.76 (dd, J = 20.3, 3.8 Hz, 1H), 1.35 (s, 12H), 0.24 (s, 6H).

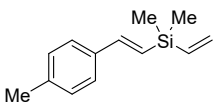
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.81, 140.85, 138.16, 135.06, 132.49, 128.69, 125.77, 83.82, 24.92, -2.93.

^{11}B NMR (161 MHz, $CDCl_3$): δ -62.12.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{28}BO_2Si$: 315.1946. Found: 315.1939.

M.p.: 86-87 ºC.

(*E*)-Dimethyl(4-methylstyryl)(vinyl)silane (14)



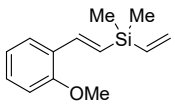
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 75% yield (30.36 mg, 0.150 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 19.1 Hz, 1H), 6.38 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.01 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 2.33 (s, 3H), 0.22 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.77, 138.46, 138.00, 135.64, 132.29, 129.26, 126.40, 125.87, 21.28, -2.85.

HRMS (ESI) m/z ($[M+K]^+$) calcd for $C_{13}H_{18}KSi$: 241.0809. Found: 241.0805.

(*E*)-(2-Methoxystyryl)dimethyl(vinyl)silane (15)



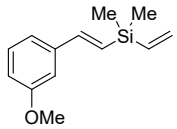
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 93% yield (40.62 mg, 0.186 mmol) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.7, 1.8 Hz, 1H), 7.32 (d, J = 19.4 Hz, 1H), 7.25–7.19 (m, 1H), 6.95–6.90 (m, 1H), 6.85 (dd, J = 8.2, 1.1 Hz, 1H), 6.43 (d, J = 19.3 Hz, 1H), 6.23 (dd, J = 20.3, 14.6 Hz, 1H), 6.00 (dd, J = 14.6, 3.8 Hz, 1H), 5.76 (dd, J = 20.3, 3.8 Hz, 1H), 3.83 (s, 3H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.70, 139.12, 138.60, 132.18, 129.15, 127.58, 127.43, 126.32, 120.62, 110.94, 55.50, -2.80.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{13}H_{19}OSi$: 219.1200. Found: 219.1193.

(*E*)-(3-Methoxystyryl)dimethyl(vinyl)silane (16)



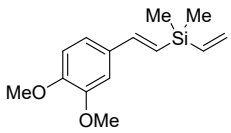
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (40.62 mg, 0.186 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 2.1 Hz, 1H), 6.87 (d, J = 19.1 Hz, 1H), 6.81 (dd, J = 8.2, 2.7 Hz, 1H), 6.44 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.76 (dd, J = 20.3, 3.8 Hz, 1H), 3.82 (s, 3H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.85, 144.66, 139.74, 138.19, 132.42, 129.48, 127.62, 119.21, 114.02, 111.36, 55.24, -2.94.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{13}H_{19}OSi$: 219.1200. Found: 219.1193.

(*E*)-(3,4-Dimethoxystyryl)dimethyl(vinyl)silane (17)



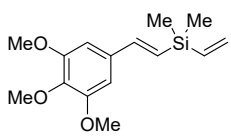
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (45.21 mg, 0.182 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (d, J = 1.9 Hz, 1H), 6.97 (dd, J = 8.3, 2.0 Hz, 1H), 6.86–6.81 (m, 2H), 6.28 (d, J = 19.1 Hz, 1H), 6.26–6.18 (m, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.76 (dd, J = 20.2, 3.8 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.29, 149.07, 144.49, 138.47, 132.30, 131.55, 124.67, 119.94, 110.97, 108.55, 55.96, 55.84, -2.82.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{14}H_{20}NaO_2Si$: 271.1125. Found: 271.1127.

(*E*)-Dimethyl(3,4,5-trimethoxystyryl)(vinyl)silane (18)



This compound was prepared from (*E*)-5-(2-iodovinyl)-1,2,3-trimethoxybenzene (64.03 mg, 0.2 mmol) according to the method A. After purification by column chromatography (SiO_2: 15% ethyl acetate in

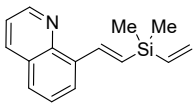
petroleum ether), the title compound was isolated in 87% yield (48.45 mg, 0.174 mmol) as a colorless oil. Moreover, when (*E*)-alkenyl bromide was used, 80% yield of **18** was obtained.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.82 (d, J = 19.0 Hz, 1H), 6.68 (s, 2H), 6.35 (d, J = 19.0 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.03 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 3.89 (s, 6H), 3.85 (s, 3H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.33, 144.61, 138.30, 138.20, 134.01, 132.47, 126.55, 103.46, 60.95, 56.08, -2.88.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{15}H_{22}NaO_3Si$: 301.1230. Found: 301.1270.

(*E*)-8-(2-(Dimethyl(vinyl)silyl)vinyl)quinoline (19)



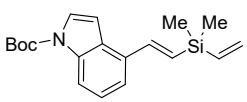
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 89% yield (42.61 mg, 0.178 mmol) as a yellows oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.33 (d, J = 19.5 Hz, 1H), 8.12 (dd, J = 8.3, 1.8 Hz, 1H), 7.99 (dd, J = 7.3, 1.4 Hz, 1H), 7.74 (dd, J = 8.2, 1.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.40 (dd, J = 8.2, 4.1 Hz, 1H), 6.73 (d, J = 19.4 Hz, 1H), 6.31 (dd, J = 20.3, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.81 (dd, J = 20.3, 3.8 Hz, 1H), 0.32 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.67, 145.64, 140.50, 138.55, 136.70, 136.16, 132.28, 129.87, 128.42, 127.80, 126.35, 125.54, 121.05, -2.78.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{15}H_{18}NSi$: 240.1203. Found: 240.1209.

***tert*-Butyl (*E*)-4-(2-(dimethyl(vinyl)silyl)vinyl)-1*H*-indole-1-carboxylate (20)**



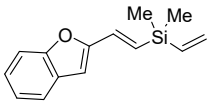
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (59.00 mg, 0.180 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 3.8 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 6.9 Hz, 1H), 7.27–7.25 (m, 1H), 6.80 (dd, J = 3.8, 0.8 Hz, 1H), 6.58 (d, J = 19.1 Hz, 1H), 6.26 (dd, J = 20.3, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.79 (dd, J = 20.3, 3.8 Hz, 1H), 1.67 (s, 9H), 0.27 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.80, 141.74, 138.31, 135.64, 132.50, 130.97, 129.03, 128.92, 126.08, 124.33, 119.36, 114.74, 105.29, 83.81, 28.25, -2.82.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{26}NO_2Si$: 328.1727. Found: 328.1754.

(*E*)-(2-(Benzofuran-2-yl)vinyl)dimethyl(vinyl)silane (21)



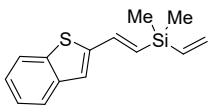
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 51% yield (23.20 mg, 0.102 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, J = 7.6, 1.3 Hz, 1H), 7.46–7.42 (m, 1H), 7.28–7.24 (m, 1H), 7.18 (td, J = 7.5, 1.0 Hz, 1H), 6.81 (d, J = 19.1 Hz, 1H), 6.67 (d, J = 19.0 Hz, 1H), 6.59 (d, J = 6.1 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.06 (d, J = 3.8 Hz, 1H), 5.78 (dd, J = 20.2, 3.8 Hz, 1H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.55, 155.01, 137.74, 132.94, 132.49, 130.11, 129.05, 124.92, 122.95, 121.34, 111.17, 104.96, -2.94.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{17}OSi$: 229.1043. Found: 229.1041.

(*E*)-(2-(Benzo[*b*]thiophen-2-yl)vinyl)dimethyl(vinyl)silane (22)

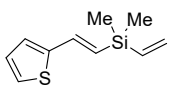


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 69% yield (33.73 mg, 0.138 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.75 (m, 1H), 7.72–7.67 (m, 1H), 7.34–7.27 (m, 2H), 7.17 (s, 1H), 7.08 (d, J = 18.7 Hz, 1H), 6.31 (d, J = 18.7 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.05 (dd, J = 14.6, 3.8 Hz, 1H), 5.79 (dd, J = 20.3, 3.7 Hz, 1H), 0.26 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.14, 140.22, 139.16, 137.95, 137.75, 132.81, 130.68, 124.86, 124.43, 123.82, 122.94, 122.37, -2.96.

(*E*)-Dimethyl(2-(thiophen-2-yl)vinyl)(vinyl)silane (23)



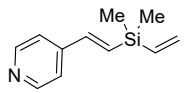
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 50% yield (19.50 mg, 0.100 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (dt, J = 5.0, 1.1 Hz, 1H), 7.01–6.91 (m, 3H), 6.25–6.13 (m, 2H), 6.01 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.2, 3.8 Hz, 1H), 0.21 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.18, 138.02, 137.35, 132.56, 127.49, 127.00, 125.82, 124.97, -2.91.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{10}H_{15}SSi$: 195.0658. Found: 195.0993.

(*E*)-4-(2-(Dimethyl(vinyl)silyl)vinyl)pyridine (24)



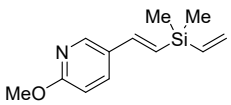
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 98% yield (37.1 mg, 0.196 mmol) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 19.1 Hz, 1H), 6.46 (d, J = 19.1 Hz, 1H), 6.21 (dd, J = 20.3, 14.7 Hz, 1H), 6.03 (dd, J = 14.6, 3.8 Hz, 1H), 5.76 (dd, J = 20.3, 3.8 Hz, 1H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.71, 138.05, 137.89 (d, J = 20.2 Hz), 132.73, 128.73, 128.31, 93.68, -2.87.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{11}H_{15}NNaSi$: 212.0866. Found: 212.1181.

(*E*)-5-(2-(Dimethyl(vinyl)silyl)vinyl)-2-methoxypyridine (25)



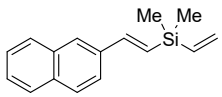
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (39.48 mg, 0.180 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 2.5 Hz, 1H), 7.73 (dd, J = 8.6, 2.5 Hz, 1H), 6.82 (d, J = 19.1 Hz, 1H), 6.71 (d, J = 8.6 Hz, 1H), 6.32 (d, J = 19.1 Hz, 1H), 6.21 (dd, J = 20.3, 14.6 Hz, 1H), 6.02 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 3.94 (s, 3H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.97, 146.10, 140.90, 138.12, 135.41, 132.53, 127.61, 126.53, 110.93, 53.60, -2.92.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{12}H_{18}NOSi$: 220.1152. Found: 220.1159.

(*E*)-Dimethyl(2-(naphthalen-2-yl)vinyl)(vinyl)silane (26)

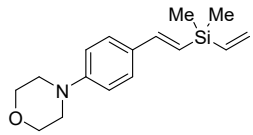


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 98% yield (46.73 mg, 0.196 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, J = 8.3, 2.0 Hz, 2H), 7.80 (d, J = 4.7 Hz, 2H), 7.69 (dd, J = 8.5, 1.8 Hz, 1H), 7.46 (tt, J = 6.9, 5.1 Hz, 2H), 7.09 (d, J = 19.1 Hz, 1H), 6.60 (d, J = 19.1 Hz, 1H), 6.27 (dd, J = 20.3, 14.6 Hz, 1H), 6.06 (dd, J = 14.6, 3.8 Hz, 1H), 5.81 (dd, J = 20.3, 3.8 Hz, 1H), 0.29 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.87, 138.28, 135.75, 133.63, 133.38, 132.49, 128.24, 128.18, 127.79, 127.71, 126.81, 126.26, 126.05, 123.37, -2.85.

(*E*)-4-(4-(2-(Dimethyl(vinyl)silyl)vinyl)phenyl)morpholine (27).



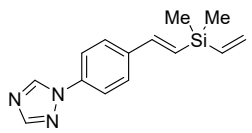
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 54% yield (29.53 mg, 0.108 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 2H), 6.88–6.85 (m, 2H), 6.81 (s, 1H), 6.27 (d, J = 15.8 Hz, 1H), 6.25–6.18 (m, 1H), 6.00 (dd, J = 14.6, 3.8 Hz, 1H), 5.75 (dd, J = 20.3, 3.8 Hz, 1H), 3.88–3.84 (m, 4H), 3.19–3.16 (m, 4H), 0.22 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.13, 144.39, 138.68, 132.15, 130.30, 127.48, 123.68, 115.31, 66.88, 49.06, -2.78.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{16}H_{24}NOSi$: 274.1622 Found: 274.1629.

(*E*)-1-(4-(2-(Dimethyl(vinyl)silyl)vinyl)phenyl)-1*H*-1,2,4-triazole (28)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 15% ethyl acetate in petroleum ether), the title compound was isolated in 61% yield (31.16 mg, 0.122 mmol) as a yellow oil.

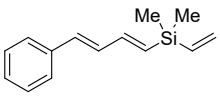
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.10 (s, 1H), 7.64 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7

Hz, 2H), 6.92 (d, J = 19.1 Hz, 1H), 6.52 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.2, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.7 Hz, 1H), 5.78 (dd, J = 20.3, 3.8 Hz, 1H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.60, 143.11, 140.74, 138.26, 137.83, 136.34, 132.71, 129.37, 127.71, 120.00, -2.99.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{18}N_3Si$: 256.1265. Found: 256.1265.

Dimethyl((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)(vinyl)silane (29)

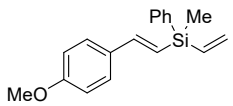


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 37% yield (15.95 mg, 0.064 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 6.6 Hz, 1H), 6.79 (dd, J = 15.1, 9.9 Hz, 1H), 6.71 (dd, J = 17.9, 10.1 Hz, 1H), 6.58 (d, J = 15.3 Hz, 1H), 6.18 (dd, J = 20.3, 14.6 Hz, 1H), 6.03–5.94 (m, 2H), 5.73 (dd, J = 20.3, 3.8 Hz, 1H), 0.19 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.31, 138.27, 137.18, 133.32, 132.56, 132.32, 131.59, 128.65, 127.77, 126.61, -2.91.

(*E*)-(4-Methoxystyryl)(methyl)(phenyl)(vinyl)silane (30)

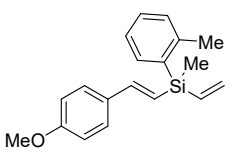


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 99% yield (55.53 mg, 0.198 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.55 (m, 2H), 7.42–7.34 (m, 5H), 6.91 (d, J = 19.1 Hz, 1H), 6.88–6.84 (m, 2H), 6.48–6.31 (m, 2H), 6.15 (dd, J = 14.6, 3.8 Hz, 1H), 5.82 (dd, J = 20.2, 3.8 Hz, 1H), 3.80 (s, 3H), 0.50 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.85, 146.15, 136.94, 136.34, 134.55, 134.29, 131.16, 129.23, 127.90, 127.87, 121.95, 113.94, 55.35, -4.14.

(*E*)-(4-Methoxystyryl)(methyl)(*o*-tolyl)(vinyl)silane (31)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 61% yield (35.93 mg, 0.122 mmol) as a

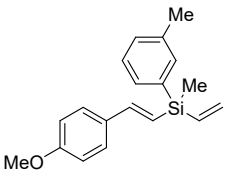
colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.4, 1.5 Hz, 1H), 7.41–7.37 (m, 2H), 7.29 (td, J = 7.5, 1.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 6.89 (d, J = 19.1 Hz, 1H), 6.87–6.83 (m, 2H), 6.51–6.38 (m, 2H), 6.13 (dd, J = 14.6, 3.6 Hz, 1H), 5.81 (dd, J = 20.3, 3.6 Hz, 1H), 3.80 (s, 3H), 2.45 (s, 3H), 0.54 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.78, 145.99, 137.17, 136.73, 136.42, 135.10, 134.14, 131.54, 131.16, 130.01, 127.85, 127.76, 122.07, 113.89, 55.29, 21.52, -4.17.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}OSi$: 295.1513. Found: 295.1449.

(*E*)-(4-Methoxystyryl)(methyl)(*m*-tolyl)(vinyl)silane (32)

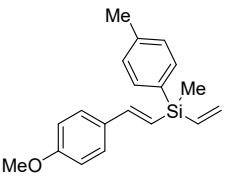


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (50.65 mg, 0.138 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (td, J = 7.8, 7.2, 3.4 Hz, 4H), 7.26 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 19.2 Hz, 1H), 6.88–6.83 (m, 2H), 6.47–6.32 (m, 2H), 6.14 (dd, J = 14.6, 3.7 Hz, 1H), 5.82 (dd, J = 20.3, 3.7 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H), 0.49 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.82, 146.04, 137.21, 136.77, 136.46, 135.14, 134.17, 131.58, 131.20, 130.06, 127.89, 127.80, 122.11, 113.93, 55.33, 21.56, -4.12.

(*E*)-(4-Methoxystyryl)(methyl)(*p*-tolyl)(vinyl)silane (33)



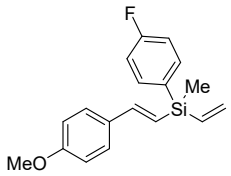
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (50.65 mg, 0.172 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.45 (m, 2H), 7.41–7.37 (m, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 19.1 Hz, 1H), 6.87–6.84 (m, 2H), 6.44–6.32 (m, 2H), 6.13 (dd, J = 14.6, 3.7 Hz, 1H), 5.81 (dd, J = 20.3, 3.8 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H), 0.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.80, 145.98, 139.12, 136.57, 134.60, 134.09, 133.20, 131.21, 128.73, 127.87, 122.23, 113.93, 55.32, 21.52, -4.04.

HRMS (ESI) m/z ([M+K]$^+$) calcd for $C_{19}H_{22}KOSi$: 333.1072. Found: 333.1075.

(*E*)-(4-Fluorophenyl)(4-methoxystyryl)(methyl)(vinyl)silane (34)



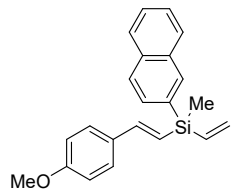
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 97% yield (57.89 mg, 0.194 mmol) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57–7.51 (m, 2H), 7.41–7.37 (m, 2H), 7.09–7.03 (m, 2H), 6.89 (d, J = 16.7 Hz, 1H), 6.87–6.84 (m, 2H), 6.42–6.30 (m, 2H), 6.15 (dd, J = 14.6, 3.7 Hz, 1H), 5.81 (dd, J = 20.3, 3.7 Hz, 1H), 3.81 (s, 3H), 0.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.87 (d, J = 248.2 Hz), 159.93, 146.38, 136.52 (d, J = 7.6 Hz), 136.14, 134.49, 132.38, 131.01, 127.92, 121.61, 115.10 (d, J = 20.2 Hz), 113.97, 55.32, -3.99.

M.p.: 48-49 ºC.

(*E*)-(4-Methoxystyryl)(methyl)(naphthalen-2-yl)(vinyl)silane (35)

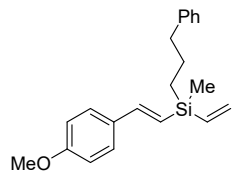


This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 63% yield (41.64 mg, 0.126 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 1.1 Hz, 1H), 7.82 (dt, J = 9.6, 6.9 Hz, 3H), 7.64 (dd, J = 8.1, 1.2 Hz, 1H), 7.48–7.45 (m, 2H), 7.42–7.38 (m, 2H), 6.95 (d, J = 19.1 Hz, 1H), 6.87–6.83 (m, 2H), 6.51–6.40 (m, 2H), 6.18 (dd, J = 14.6, 3.7 Hz, 1H), 5.87 (dd, J = 20.3, 3.7 Hz, 1H), 3.78 (s, 3H), 0.58 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.87, 146.36, 136.30, 135.36, 134.50, 134.37, 133.86, 133.00, 131.13, 130.68, 128.16, 127.94, 127.75, 127.05, 126.46, 125.93, 121.85, 113.96, 55.32, -4.02.

(*E*)-(4-Methoxystyryl)(methyl)(3-phenylpropyl)(vinyl)silane (36)



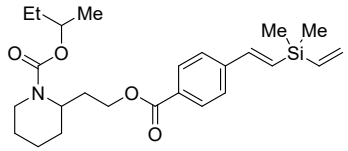
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 79% yield (50.96 mg, 0.158 mmol) as a

colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H), 7.29–7.24 (m, 2H), 7.17 (dt, J = 7.2, 3.8 Hz, 3H), 6.87–6.80 (m, 3H), 6.25 (d, J = 19.1 Hz, 1H), 6.19 (dd, J = 20.3, 14.7 Hz, 1H), 6.02 (dd, J = 14.6, 3.9 Hz, 1H), 5.74 (dd, J = 20.3, 3.9 Hz, 1H), 3.80 (s, 3H), 2.64 (t, J = 7.6 Hz, 2H), 1.74–1.64 (m, 2H), 0.79–0.72 (m, 2H), 0.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.69, 144.80, 142.59, 137.31, 132.86, 131.27, 128.55, 128.25, 127.71, 125.67, 123.07, 113.91, 55.30, 39.81, 25.96, 14.28, -4.84.

sec-Butyl (_E_)-2-(2-((4-(2-(dimethyl(vinyl)silyl)vinyl)benzoyl)oxy)ethyl)piperidine-1-carboxylate (37)



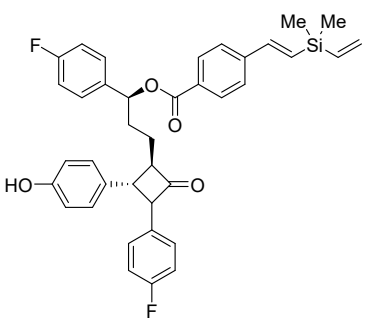
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 58% yield (51.46 mg, 0.116 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.3 Hz, 2H), 7.50–7.47 (m, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.60 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 4.74 (qd, J = 6.2, 2.0 Hz, 1H), 4.53 (s, 1H), 4.32 (q, J = 5.6, 4.8 Hz, 2H), 4.09 (s, 1H), 2.87 (t, J = 13.2 Hz, 1H), 2.22 (ddd, J = 12.8, 9.2, 6.8 Hz, 1H), 1.90 (dd, J = 14.2, 6.3 Hz, 1H), 1.74–1.53 (m, 8H), 1.18 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 7.5 Hz, 3H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.39, 155.60 (d, J = 3.8 Hz), 143.73, 142.46, 137.77, 132.76, 130.95, 129.95, 129.59, 126.32, 73.06, 62.69, 48.07, 29.73, 29.11, 25.55, 22.73, 19.82, 19.10, 9.78, -3.02, -3.62.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{25}H_{37}NNaO_4Si$: 466.2384. Found: 466.2398.

4-((1_R_,4_R_)-2-(4-Fluorophenyl)-4-((_S_)-3-(4-fluorophenyl)-3-hydroxypropyl)-3-oxocyclobutyl)phenyl 4-((_E_)-2-(dimethyl(vinyl)silyl)vinyl)benzoate (38)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 55% yield (68.51 mg, 0.110

mmol) as a white solid.

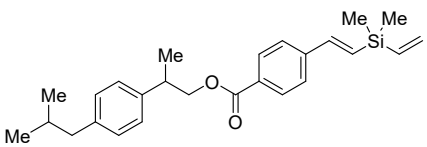
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17–8.08 (m, 2H), 7.56–7.51 (m, 2H), 7.40–7.33 (m, 2H), 7.23 (dd, J = 8.8, 5.1 Hz, 6H), 6.97 (dt, J = 23.9, 8.8 Hz, 4H), 6.79 (dd, J = 17.6, 10.9 Hz, 1H), 6.06–5.87 (m, 3H), 5.70 (dd, J = 19.4, 4.8 Hz, 1H), 5.44 (d, J = 10.9 Hz, 1H), 4.66 (t, J = 5.9 Hz, 1H), 4.63 (d, J = 2.4 Hz, 1H), 3.07 (td, J = 7.5, 2.4 Hz, 1H), 1.91 (ddd, J = 8.6, 6.4, 3.4 Hz, 2H), 1.87–1.81 (m, 2H), 0.11 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.25, 164.82, 151.07, 142.87, 140.34, 137.35, 135.91, 135.30, 133.89, 133.43, 130.57, 128.30, 127.47 (d, J = 8.8 Hz), 127.01, 126.39, 122.68, 118.41 (d, J = 8.8 Hz), 117.19, 116.02, 115.84, 115.19, 115.02, 74.00, 60.85, 60.65, 37.86, 25.02, -1.50, -1.73.

^{19}F NMR (471 MHz, $CDCl_3$): δ -115.57, -117.99.

M.p.: 87-88 ºC.

2-(4-Isobutylphenyl)propyl (*E*)-4-(2-(dimethyl(vinyl)silyl)vinyl)benzoate (39)



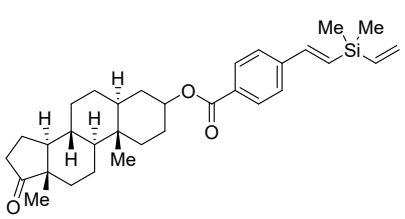
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 65% yield (52.86 mg, 0.130 mmol) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.47–7.44 (m, 2H), 7.20–7.18 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 19.1 Hz, 1H), 6.59 (d, J = 19.2 Hz, 1H), 6.21 (dd, J = 20.3, 14.6 Hz, 1H), 6.03 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 4.40 (dd, J = 10.7, 6.7 Hz, 1H), 4.35 (dd, J = 10.7, 7.5 Hz, 1H), 3.22 (q, J = 7.0 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 1.85 (dt, J = 13.5, 6.8 Hz, 1H), 1.38 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H), 0.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.33, 143.72, 142.43, 140.37, 140.10, 137.77, 132.75, 130.92, 129.89, 129.26, 127.07, 126.31, 70.06, 53.45, 45.07, 38.72, 30.24, 22.43, 18.07, -3.02.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{26}H_{34}NaO_2Si$: 429.2220. Found: 429.2207.

(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-2-(dimethyl(vinyl)silyl)vinyl)benzoate (40)



This compound was prepared according to the method A.

After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 51% yield (51.49 mg, 0.102 mmol) as a colorless oil.

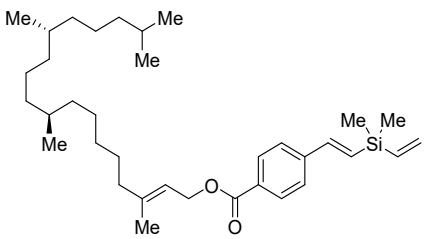
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.59 (d, J = 19.2 Hz, 1H), 6.21 (dd, J = 20.2, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 19.3, 3.8 Hz, 1H), 4.94 (tt, J = 10.9, 4.9 Hz, 1H), 2.47–2.41 (m, 1H), 2.10–2.04 (m, 1H), 1.98–1.92 (m, 2H), 1.80 (dt, J = 13.4, 3.2 Hz, 4H), 1.70–1.65 (m, 2H), 1.57–1.49 (m, 3H), 1.37–1.28 (m, 6H), 1.14–1.09 (m, 1H), 1.00 (dd, J = 11.7, 7.5 Hz, 1H), 0.90 (s, 3H), 0.87 (s, 3H), 0.78–0.73 (m, 1H), 0.25 (d, J = 1.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.93, 143.76, 141.71, 137.78, 133.39, 131.14, 130.13, 129.86, 126.24, 74.12, 54.36, 51.40, 47.82, 44.75, 36.79, 35.88, 35.74, 35.09, 34.09, 31.57, 30.85, 28.33, 27.56, 21.81, 20.52, 13.85, 12.32, -3.02.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{32}H_{45}O_3Si$: 505.3132. Found: 505.3142.

M.p.: 188-189 ºC.

(9*R*,13*R*,*E*)-3,9,13,17-Tetramethyloctadec-2-en-1-yl 4-((*E*)-2-(dimethyl(vinyl)silyl)vinyl) Benzoate (41)



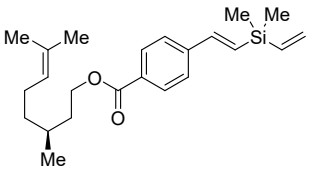
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 56% yield (60.36 mg, 0.112 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H), 7.49–7.46 (m, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.59 (d, J = 19.1 Hz, 1H), 6.21 (dd, J = 20.3, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.7 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 5.48–5.44 (m, 1H), 4.83 (d, J = 6.9 Hz, 2H), 2.04 (d, J = 6.4 Hz, 2H), 1.75 (s, 3H), 1.54–1.51 (m, 1H), 1.39 (d, J = 6.4 Hz, 2H), 1.37–1.33 (m, 2H), 1.32–1.26 (m, 8H), 1.18–1.01 (m, 10H), 0.87 (s, 3H), 0.86 (s, 3H), 0.84 (d, J = 6.6 Hz, 6H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.53, 143.79, 142.86, 142.36, 137.80, 132.75, 130.82, 129.96, 129.83, 126.30, 118.21, 61.97, 39.93, 39.42, 37.48, 37.42, 37.34, 36.68, 32.84, 32.71, 28.03, 25.09,

24.84, 24.51, 22.77, 22.68, 19.80, 16.52, 14.17, 0.04, -3.01.

(*S*)-3,7-dimethyloct-6-en-1-yl (*E*)-4-(2-(dimethyl(vinyl)silyl)vinyl)benzoate (42)



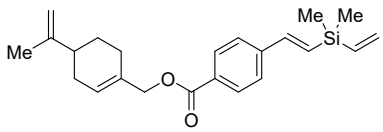
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 63% yield (46.70 mg, 0.126 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.97 (m, 2H), 7.50–7.46 (m, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.60 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.2, 14.7 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.2, 3.9 Hz, 1H), 5.12–5.08 (m, 1H), 4.37–4.33 (m, 2H), 2.00 (d, J = 8.9 Hz, 2H), 1.87–1.71 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.57 (t, J = 5.8 Hz, 1H), 1.46–1.37 (m, 2H), 0.97 (d, J = 6.6 Hz, 3H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.51, 143.75, 142.38, 137.78, 132.75, 131.42, 130.86, 129.89, 129.81, 126.31, 124.61, 63.54, 37.03, 35.55, 29.60, 25.75, 25.44, 19.56, 17.71, -3.01.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{23}H_{34}NaO_2Si$: 393.2220. Found: 393.2229.

(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl (*E*)-4-(2-(dimethyl(vinyl)silyl)vinyl)benzoate (43)



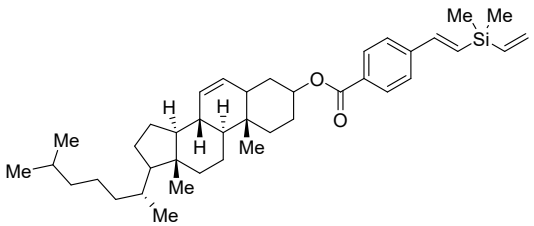
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (64.52 mg, 0.146 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.60 (d, J = 19.1 Hz, 1H), 6.22 (dd, J = 20.2, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.9 Hz, 1H), 5.84 (s, 1H), 5.77 (dd, J = 20.2, 3.9 Hz, 1H), 4.75–4.72 (m, 2H), 4.71 (s, 2H), 2.21–2.15 (m, 5H), 2.02 (d, J = 15.4 Hz, 1H), 1.88 (d, J = 12.1 Hz, 1H), 1.75 (s, 3H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.33, 149.66, 143.73, 142.48, 137.78, 132.77, 132.73, 130.96, 129.97, 129.65, 126.33, 125.71, 108.84, 68.88, 40.91, 30.52, 27.38, 26.11, 20.80, -2.37.

(8*S*,9*S*,10*S*,13*R*,14*S*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-

2,3,4,5,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-((*E*)-2-(dimethyl(vinyl)silyl)-vinyl)benzoate (44)



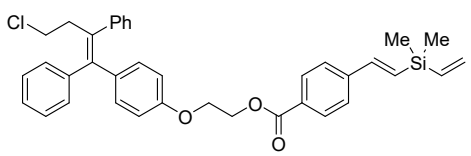
This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (97.38 mg, 0.162 mmol) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H), 7.49–7.46 (m, 2H), 6.93 (d, J = 19.1 Hz, 1H), 6.59 (d, J = 19.2 Hz, 1H), 6.22 (dd, J = 20.3, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.7 Hz, 1H), 5.77 (dd, J = 20.2, 3.8 Hz, 1H), 5.42 (d, J = 5.1 Hz, 1H), 4.85 (dtd, J = 12.1, 8.4, 4.5 Hz, 1H), 2.46 (d, J = 7.3 Hz, 2H), 2.01 (tt, J = 11.8, 4.0 Hz, 4H), 1.92 (dt, J = 13.2, 3.5 Hz, 1H), 1.84 (ddd, J = 13.1, 6.6, 3.7 Hz, 1H), 1.74 (dt, J = 11.7, 3.0 Hz, 1H), 1.58 (dd, J = 10.5, 3.6 Hz, 2H), 1.51 (q, J = 6.7 Hz, 4H), 1.46 (d, J = 4.6 Hz, 1H), 1.36–1.32 (m, 1H), 1.23 (d, J = 3.4 Hz, 1H), 1.21 (t, J = 3.4 Hz, 1H), 1.18 (d, J = 4.8 Hz, 1H), 1.16–1.14 (m, 1H), 1.13 (d, J = 2.0 Hz, 1H), 1.12 (d, J = 2.1 Hz, 1H), 1.09 (s, 1H), 1.07 (s, 3H), 1.00 (td, J = 11.2, 10.7, 5.0 Hz, 4H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 2.3 Hz, 3H), 0.86 (d, J = 2.3 Hz, 3H), 0.69 (s, 3H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.86, 143.80, 142.32, 139.74, 137.82, 132.75, 130.77, 130.13, 129.90, 126.27, 122.82, 74.63, 56.75, 56.19, 50.10, 42.38, 39.80, 39.57, 38.28, 37.10, 36.71, 36.24, 35.85, 31.58, 28.29, 28.07, 27.95, 24.35, 23.88, 22.87, 22.62, 21.11, 19.44, 18.77, 11.92, -3.00.

M.p.: 189-190 ºC.

2-(4-((*Z*)-4-Chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl 4-((*E*)-2-(dimethyl(vinyl)silyl) vinyl)benzoate (45)



This compound was prepared according to the method A. After purification by column chromatography (SiO_2: 40% ethyl acetate in petroleum ether), the title

compound was isolated in 59% yield (70.01 mg, 0.118 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2H), 7.47–7.44 (m, 2H), 7.38–7.35 (m, 2H), 7.30–7.27 (m, 3H), 7.19 (d, J = 6.2 Hz, 2H), 7.16–7.13 (m, 3H), 6.92 (d, J = 19.2 Hz, 1H), 6.82–6.79 (m, 2H), 6.61–6.57 (m, 3H), 6.21 (dd, J = 20.2, 14.6 Hz, 1H), 6.04 (dd, J = 14.6, 3.8 Hz, 1H), 5.77 (dd, J = 20.3, 3.8 Hz, 1H), 4.58–4.55 (m, 2H), 4.18–4.15 (m, 2H), 3.41 (t, J = 7.5 Hz, 2H), 2.92 (t, J = 7.5 Hz, 2H), 0.25 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.30, 156.77, 143.65, 142.85, 142.63, 141.66, 140.94, 137.72, 135.36, 135.33, 132.77, 131.78, 131.13, 130.06, 129.55, 129.40, 129.08, 128.38, 128.26, 126.99, 126.65, 126.31, 113.63, 65.77, 63.33, 42.85, 38.60, -3.04.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{37}H_{37}ClNaO_3Si$: 615.2093. Found: 615.2015.

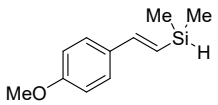
Part 4. Coupling of Chlorohydrosilanes with Vinyl Halides

1. General Procedure

General procedure for the reaction of chlorohydrosilanes with vinyl halides (method B): To a dried Schlenk line was charged with vinyl halides (0.2 mmol, 100 mol%), 2,2'-bipyridine (3.12 mg, 0.02 mmol, 10 mol%), $Fe(acac)_3$ (7.26 mg, 0.02 mmol, 10 mol%) at 25 ℃. The Schlenk line was sealed with an atmosphere of nitrogen. Chlorodimethylsilane (56.77 mg, 0.6 mmol, 300 mol%) was added followed by addition of DMF (1 mL) via syringes. The reaction mixture was allowed to maintain 35 ℃ and stirred overnight. The reaction mixture was purified by column chromatograph to afford the product as a solid or oil.

2. Experimental Details

(*E*)-(4-Methoxystyryl)dimethylsilane (46)

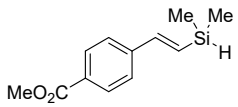


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 82% yield (31.16 mg, 0.162 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.35 (m, 2H), 6.91 (d, J = 19.0 Hz, 1H), 6.88–6.83 (m, 2H), 6.28 (dd, J = 19.1, 2.6 Hz, 1H), 4.20 (dq, J = 7.3, 3.7 Hz, 1H), 3.79 (s, 3H), 0.22 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.74, 144.81, 131.18, 127.73, 123.22, 114.75, 55.32, -3.85.

Methyl (*E*)-4-(2-(dimethylsilyl)vinyl)benzoate (47)

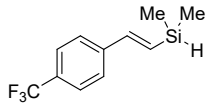


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 72% yield (31.73 mg, 0.144 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.98 (m, 2H), 7.51–7.47 (m, 2H), 6.99 (d, J = 19.1 Hz, 1H), 6.61 (dd, J = 19.1, 2.6 Hz, 1H), 4.22 (dq, J = 7.0, 3.4 Hz, 1H), 3.91 (s, 3H), 0.25 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.87, 144.22, 142.31, 129.91, 129.72, 128.21, 126.33, 52.08, -4.12.

(*E*)-Dimethyl(4-(trifluoromethyl)styryl)silane (48)



This compound was prepared according to the method B. After purification by column chromatography (SiO_2: petroleum ether), the title compound was isolated in 65% yield (29.94 mg, 0.130 mmol) as a colorless oil.

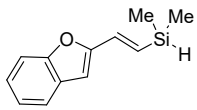
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 19.1 Hz, 1H), 6.58 (dd, J = 19.1, 2.6 Hz, 1H), 4.22 (dq, J = 6.6, 3.3 Hz, 1H), 0.26 (d, J = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.81, 141.45, 130.00, 129.77, 128.51, 126.63, 125.56 (dd, J = 7.7, 3.7 Hz), -4.11.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.51.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{11}H_{14}F_3Si$: 231.0811. Found: 231.0811.

(*E*)-(2-(Benzofuran-2-yl)vinyl)dimethylsilane (49)

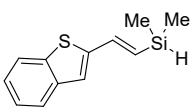


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (27.92 mg, 0.138 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 19.0 Hz, 1H), 6.66 (dd, J = 19.0, 2.8 Hz, 1H), 6.61 (s, 1H), 4.23 (h, J = 3.6 Hz, 1H), 0.25 (d, J = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.28, 154.94, 132.89, 128.92, 128.74, 124.89, 122.89, 121.28, 111.10, 105.35 -4.12.

(*E*)-(2-(Benzo[*b*]thiophen-2-yl)vinyl)dimethylsilane (50)

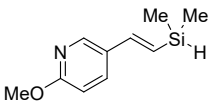


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (29.26 mg, 0.134 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77–7.72 (m, 1H), 7.70–7.66 (m, 1H), 7.33–7.26 (m, 2H), 7.13 (d, J = 18.8 Hz, 2H), 6.31 (dd, J = 18.8, 2.6 Hz, 1H), 4.27–4.16 (m, 1H), 0.25 (d, J = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.91, 140.19, 139.19, 138.46, 129.40, 124.92, 124.47, 123.86, 123.04, 122.38, -4.04.

(*E*)-5-(2-(Dimethylsilyl)vinyl)-2-methoxypyridine (51)

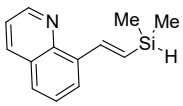


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 83% yield (31.71 mg, 0.164 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 2.5 Hz, 1H), 7.73 (dd, J = 8.6, 2.5 Hz, 1H), 6.89 (d, J = 19.1 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 6.33 (dd, J = 19.1, 2.6 Hz, 1H), 4.24–4.15 (m, 1H), 3.94 (s, 3H), 0.24 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.73, 144.81, 131.17, 129.71, 127.73, 123.22, 113.94, 55.32, -3.85.

(*E*)-8-(2-(Dimethylsilyl)vinyl)quinoline (52)

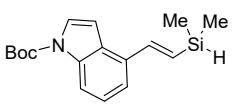


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (34.56 mg, 0.182 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (dd, J = 4.1, 1.8 Hz, 1H), 8.37 (d, J = 19.4 Hz, 1H), 8.14 (dd, J = 8.3, 1.8 Hz, 1H), 7.98 (dd, J = 7.3, 1.9 Hz, 1H), 7.75 (dd, J = 8.1, 1.4 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.41 (dd, J = 8.3, 4.1 Hz, 1H), 6.73 (dd, J = 19.3, 2.7 Hz, 1H), 4.32 (dt, J = 7.4, 3.7 Hz, 1H), 0.32 (d, J = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.68, 141.10, 136.63, 136.23, 128.88, 128.43, 127.88, 126.39, 125.67, 121.09, -3.82.

***tert*-Butyl (*E*)-4-(2-(dimethylsilyl)vinyl)-1*H*-indole-1-carboxylate (53)**



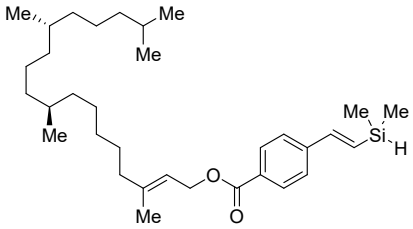
This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 20% ethyl acetate in petroleum ether), the title compound was isolated in 68% yield (41.00 mg, 0.136 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 3.7 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 19.1 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 6.81 (d, J = 3.8 Hz, 1H), 6.59 (dd, J = 19.1, 2.7 Hz, 1H), 4.26 (dq, J = 7.1, 3.6 Hz, 1H), 1.67 (s, 12H), 0.28 (d, J = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.79, 144.54, 142.30, 130.82, 128.92, 127.84, 126.54, 124.34,

119.38, 114.84, 105.24, 83.82, 28.24, -3.86.

(9*R*,13*R*,*E*)-3,9,13,17-Tetramethyloctadec-2-en-1-yl 4-((*E*)-2-(dimethylsilyl)vinyl)benzoate (54)

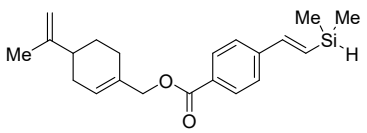


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (82.06 mg, 0.160 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H), 7.50–7.46 (m, 2H), 6.99 (d, J = 19.1 Hz, 1H), 6.59 (dd, J = 19.1, 2.7 Hz, 1H), 5.46 (t, J = 7.9 Hz, 1H), 4.84 (d, J = 6.9 Hz, 2H), 4.22 (dq, J = 7.1, 3.6 Hz, 1H), 2.05–2.02 (m, 2H), 1.76 (s, 3H), 1.54–1.50 (m, 1H), 1.41–1.38 (m, 2H), 1.34 (s, 2H), 1.32–1.26 (m, 8H), 1.18–1.01 (m, 10H), 0.87 (s, 3H), 0.86 (s, 3H), 0.84 (d, J = 6.7 Hz, 6H), 0.25 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.48, 144.32, 142.86, 142.21, 129.98, 129.92, 129.58, 126.29, 118.20, 61.60, 39.93, 39.42, 37.47, 37.41, 37.34, 36.67, 32.83, 32.71, 29.74, 28.02, 25.08, 24.84, 24.51, 22.77, 22.67, 19.77, 16.52, 0.04, -4.08.

(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl (*E*)-4-(2-(dimethylsilyl)vinyl)benzoate (55)



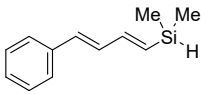
This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 64% yield (43.59 mg, 0.128 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–8.00 (m, 2H), 7.51–7.45 (m, 2H), 6.99 (d, J = 19.1 Hz, 1H), 6.60 (dd, J = 19.1, 2.6 Hz, 1H), 5.84 (s, 1H), 4.73 (dd, J = 4.1, 2.5 Hz, 2H), 4.71 (s, 2H), 4.22 (dq, J = 7.2, 3.6 Hz, 1H), 2.18 (dd, J = 8.0, 5.4 Hz, 4H), 2.04–1.96 (m, 1H), 1.90–1.84 (m, 1H), 1.74 (s, 3H), 1.53 (tt, J = 12.6, 8.9 Hz, 1H), 0.25 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.21, 148.55, 143.21, 141.26, 131.67, 128.93, 128.69, 128.65, 125.27, 124.65, 107.79, 67.82, 39.84, 29.46, 26.32, 25.44, 19.73, -5.15.

HRMS (ESI) m/z ([M+Na]$^+$) calcd for $C_{21}H_{28}NaO_2Si$: 363.1751. Found: 363.1755.

Dimethyl((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)silane (56)

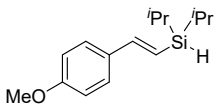


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 94% yield (35.41 mg, 0.188 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.39 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.24–7.21 (m, 1H), 6.84–6.71 (m, 2H), 6.63–6.55 (m, 1H), 6.03–5.93 (m, 1H), 4.15 (dq, J = 6.6, 3.6 Hz, 1H), 0.20 (d, J = 3.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.81, 137.11, 133.47, 131.39, 131.28, 128.66, 127.83, 126.64, -4.00.

(*E*)-Diisopropyl(4-methoxystyryl)silane (57)

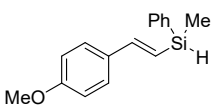


This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 64% yield (31.80 mg, 0.128 mmol) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 2H), 6.98 (d, J = 19.1 Hz, 1H), 6.90–6.85 (m, 2H), 6.21 (dd, J = 19.1, 4.7 Hz, 1H), 3.81 (s, 3H), 3.73 (dd, J = 4.7, 2.0 Hz, 1H), 1.06 (dd, J = 9.0, 2.9 Hz, 14H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.67, 147.03, 131.36, 127.68, 118.71, 113.90, 55.33, 18.86 (d, J = 34.0 Hz), 10.84.

(*E*)-(4-Methoxystyryl)(methyl)(phenyl)silane (58)



This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 74% yield (37.65 mg, 0.140 mmol) as a colorless oil.

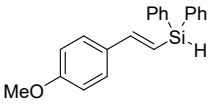
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.57 (m, 2H), 7.40–7.35 (m, 5H), 6.98 (d, J = 19.0 Hz, 1H), 6.87–6.84 (m, 2H), 6.37 (dd, J = 19.0, 3.0 Hz, 1H), 4.71 (p, J = 3.6 Hz, 1H), 3.79 (s, 3H), 0.49 (d, J = 3.8 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3): δ 159.91, 146.64, 135.92, 134.66, 131.00, 129.42, 127.97, 127.93,

120.77, 113.96, 55.32, -5.07.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{16}H_{19}OSi$: 255.1200. Found: 255.1192.

(*E*)-(4-Methoxystyryl)diphenylsilane (59)



This compound was prepared according to the method B. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 72% yield (45.57 mg, 0.138 mmol) as a colorless oil.

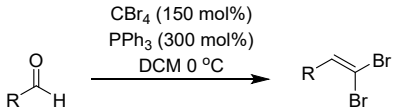
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.60 (m, 4H), 7.42–7.40 (m, 2H), 7.40–7.35 (m, 6H), 7.03 (d, J = 19.0 Hz, 1H), 6.88–6.84 (m, 2H), 6.58–6.50 (m, 1H), 5.23 (d, J = 3.3 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.08, 148.64, 135.56, 134.38, 130.45, 129.74, 128.06, 127.80, 118.49, 113.98, 54.26.

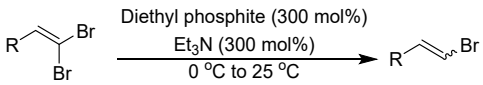
HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{21}H_{21}OSi$: 317.1356. Found: 317.1352.

Part 5. Preparation of Alkenyl Bromides

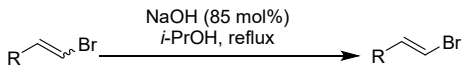
1. General Procedure



Step 1: To a flame-dried flask was added aldehyde (20 mmol, 100 mol%), CBr_4 (30 mmol, 150 mol%), and CH_2Cl_2 (80 mL). The flask was cooled to 0 °C in an ice bath, at which point a solution of PPh_3 (60 mmol, 300 mol%) in CH_2Cl_2 (70 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C under N_2 for 1 h. About half of the volume of CH_2Cl_2 was removed under reduced pressure. Pentane (100 mL) was added, and triphenylphosphine oxide (TPPO) precipitated out. After filtration and evaporation of the solvent, the residue was dissolved in pentane (50 mL) which led to further precipitation of TPPO. Filtration and evaporation of the solvent afforded the crud dibromide which was directly used for the next step.

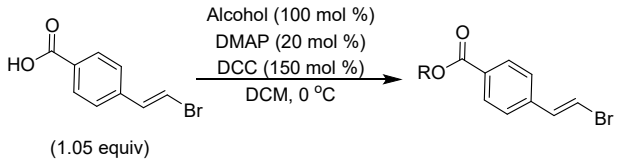


Step 2: To a solution of the crude dibromide (~ 20.0 mmol, 100 mol%) and NEt_3 (60 mmol, 300 mol%) in DMF (20 mL) was added dimethyl phosphonate (60.0 mmol, 300 mol%). The solution was stirred over night at room temperature. Water (60 mL) was added to the mixture, which was extracted with pentane (2 × 100 mL). The combined organic phases were washed with an aqueous solution of HCl (1 M, 55 mL) and dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography.



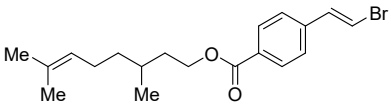
Step 3: The crude product (~20.0 mmol, 100 mol %) from the previous step was dissolved in *i*-PrOH (30 mL). Solid NaOH (17.0 mmol, 85 mol%) was added and the mixture was heated to reflux for 1.5 hours. The reaction mixture was cooled to room temperature, diluted with pentane (100 mL), and partitioned with distillated H_2O (2 × 100 mL). The organic phase was collected, and washed with an aqueous solution of HCl (1 M, 75 mL), dried over Na_2SO_4. The solvent was removed under

reduced pressure. The crude material was purified by flash chromatography.



Step 4: To a flame-dried flask was added acid (3.15 mmol, 105 mol %), DMAP (0.6 mmol, 20 mol %), DCC (4.5 mmol, 150 mol %), and CH_2Cl_2 (15 mL). The flask was cooled to 0 °C, at which point a solution of alcohol (3.0 mmol, 100 mol %) in CH_2Cl_2 (15 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C under N_2 over night. After the reaction was finished the CH_2Cl_2 was removed under reduced pressure. And The crude residue was purified by silicagel chromatography (hexanes) to give the target compound.

3,7-Dimethyloct-6-en-1-yl(*E*)-4-(2-bromovinyl)benzoate

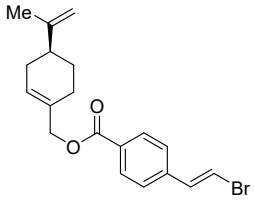


The title compound was prepared following the general procedure using (*E*)-4-(2-bromovinyl)benzoic acid (715 mg, 3.15 mmol, 1.05 equiv), citronellol (469 mg, 3.0 mmol, 1.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (990 mg) as a pale yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.97 (m, 2H), 7.38–7.32 (m, 2H), 7.14 (d, J = 14.0 Hz, 1H), 6.90 (s, 1H), 5.10 (tt, J = 7.1, 1.4 Hz, 1H), 4.39–4.31 (m, 2H), 2.01 (dh, J = 14.8, 7.4 Hz, 2H), 1.84–1.77 (m, 1H), 1.67 (s, 4H), 1.61–1.55 (m, 4H), 1.44–1.37 (m, 1H), 1.27–1.21 (m, 1H), 0.97 (d, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.18, 139.97, 136.39, 131.39, 130.08, 130.05, 125.93, 124.54, 109.30, 63.62, 36.97, 35.49, 29.56, 25.71, 25.39, 19.51, 17.67.

(*S*)-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl (*E*)-4-(2-bromovinyl)benzoate



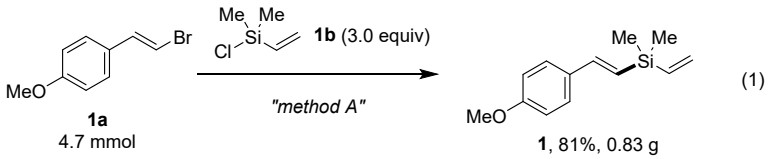
The title compound was prepared following the general procedure using (*E*)-4-(2-bromovinyl)benzoic acid (715 mg, 3.15 mmol, 1.05 equiv), perilla alcohol (476 mg, 3.0 mmol, 1.0 equiv). After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 87% yield (939 mg) as a pale yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H), 7.37–7.33 (m, 2H), 7.13 (d, J = 14.0 Hz, 1H), 6.91 (d, J = 14.0 Hz, 1H), 5.84 (s, 1H), 4.75–4.70 (m, 4H), 2.22–2.16 (m, 4H), 2.03–1.96 (m, 1H), 1.90–1.84 (m, 1H), 1.74 (s, 3H), 1.53 (ddt, J = 16.9, 12.7, 7.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.97, 149.53, 140.04, 136.37, 132.59, 130.16, 129.90, 125.94, 125.79, 109.37, 108.83, 68.95, 40.83, 30.47, 27.32, 26.46, 20.76.

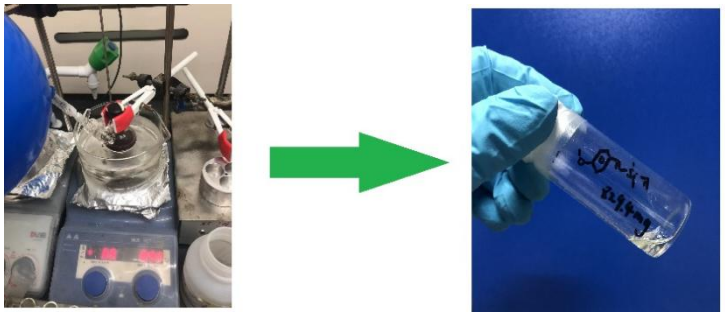
Part 6. Scale-up Experiments and Synthetic Applications

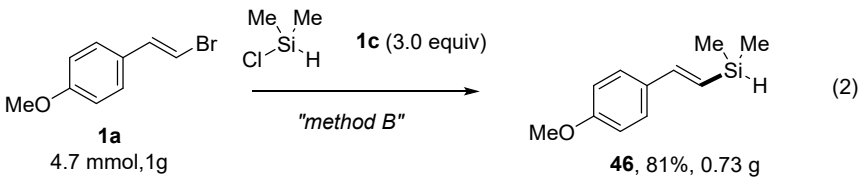
1. Scale-up Experiments



1a
4.7 mmol

1, 81%, 0.83 g (1)

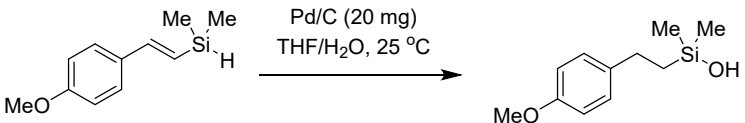




1a
4.7 mmol,1g

46, 81%, 0.73 g (2)

2. Hydration Reaction[4]

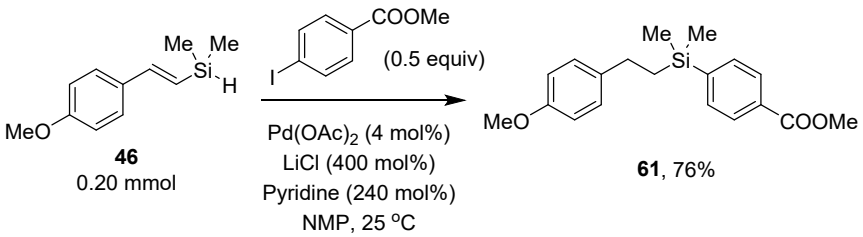


46
0.15 mmol

60, 66%

To a reaction tube equipped with a magnetic stir bar was added **46** (28.85 mg, 0.15 mmol), Pd/C (20 mg), and THF (1.6 mL), followed by addition of H_2O (0.3 mL). The reaction mixture was stirred overnight at room temperature. The reaction was quenched with water (10.0 mL) and extracted with ethyl acetate (3×15.0 mL). The combined organic layers was washed with water (15.0 mL), brine (20.0 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give compound **60** (20.82 mg, 66%, colorless oil).

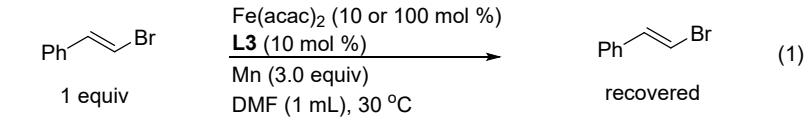
3. Cross-coupling Reaction[4]



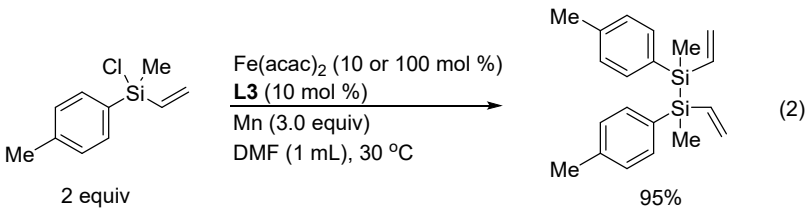
The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added methyl 4-iodobenzoate (26.21 mg, 0.10 mmol), LiCl (16.95 mg, 0.4 mmol), **46** (40.4 mg, 0.2 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), NMP (0.8 mL), and Pyridine (18.95 mg, 0.24 mmol). The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at room temperature for 24 h. After purification by column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound **61** was isolated in 76% yield (49.93 mg, 0.152 mmol) as a colorless oil.

Part 7. Mechanism Experiments

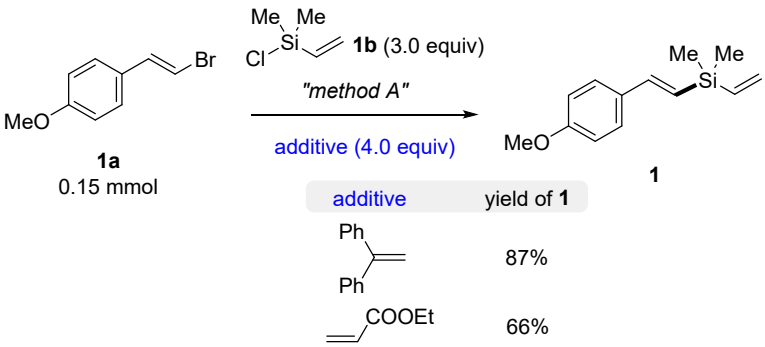
1. Control Experiments



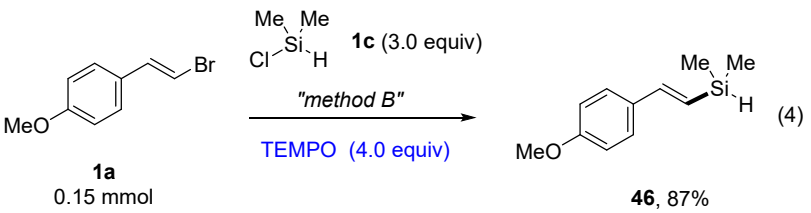
(1)



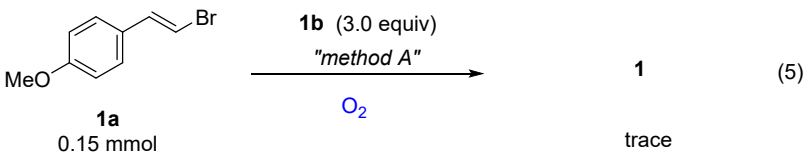
(2)



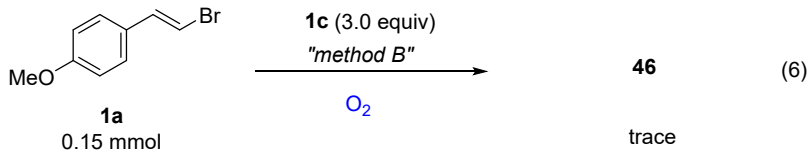
(3)



(4)

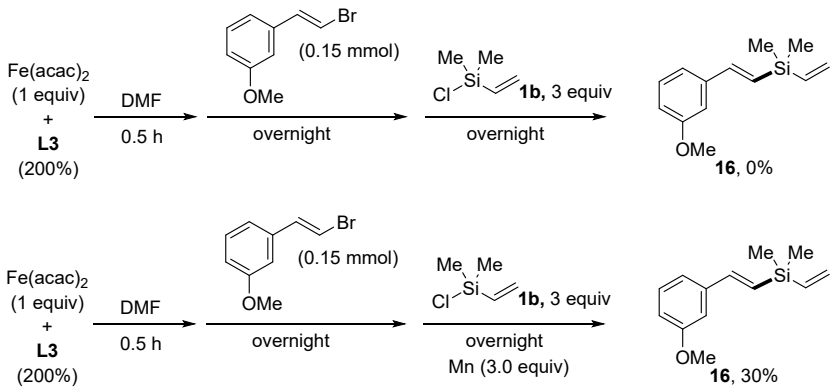


(5)



(6)

2. Stoichiometric Reaction of $Fe(acac)_2$ with Vinyl Bromide and Chlorosilanes



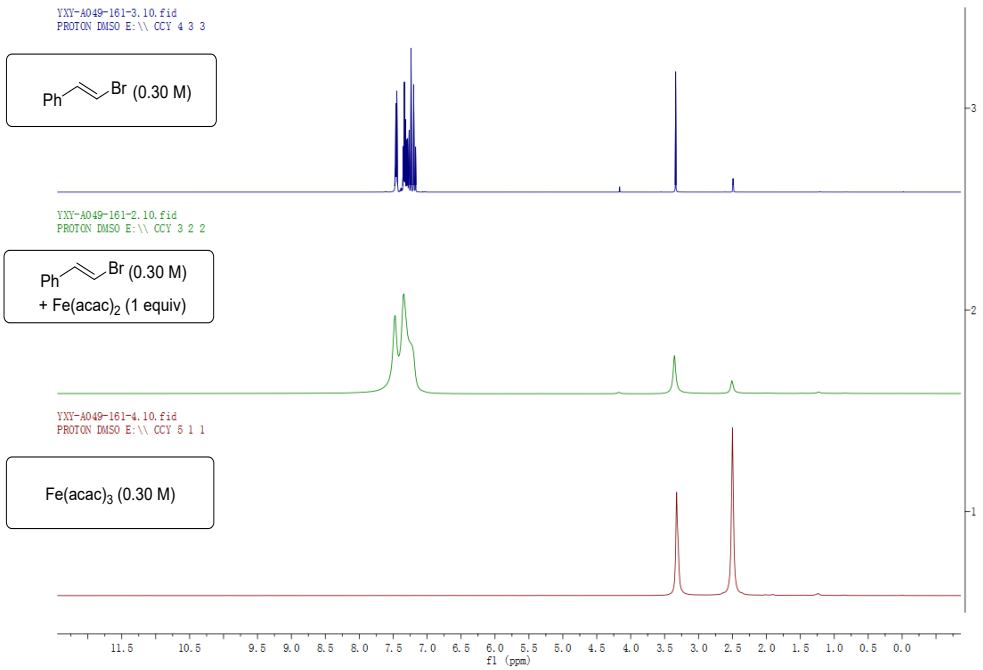


Figure S1. ^{1}H NMR (DMSO-d_6) spectra of the reaction of (*E*)-(2-bromovinyl)benzene with $Fe(acac)_2$.

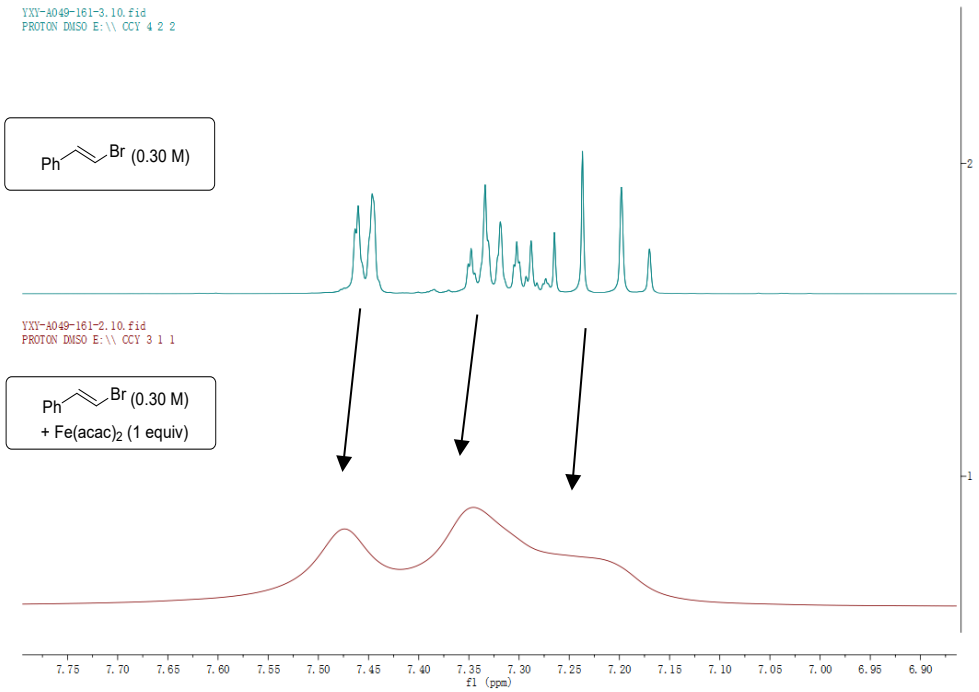
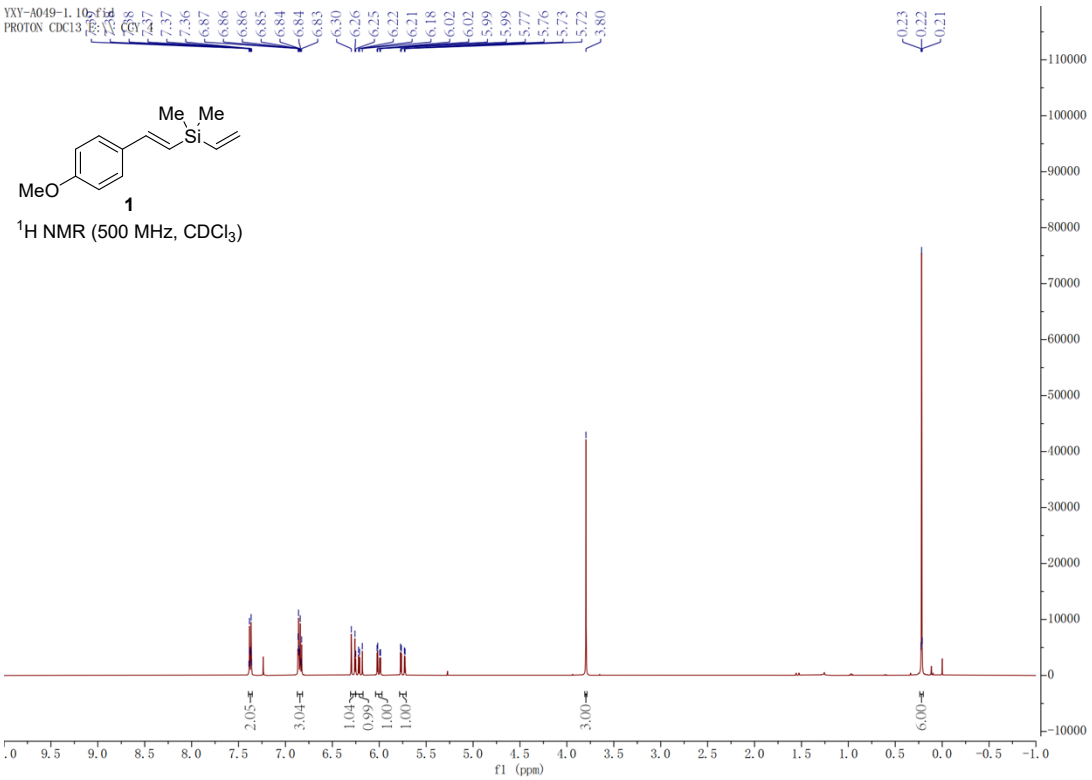
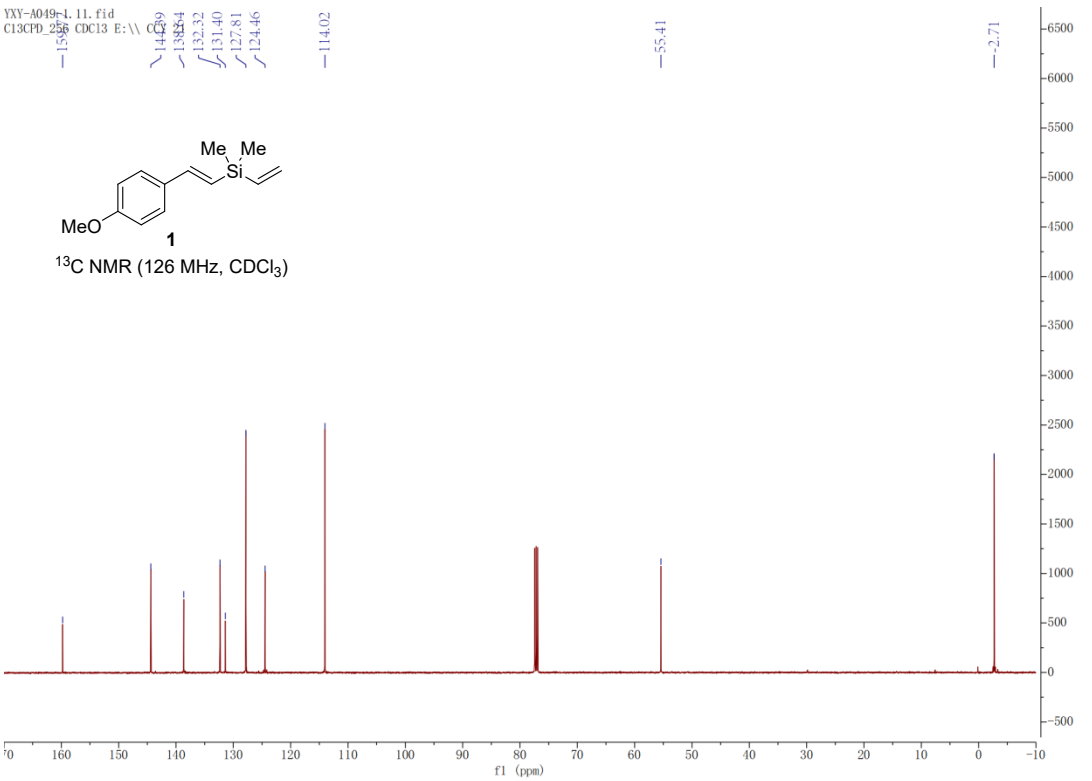
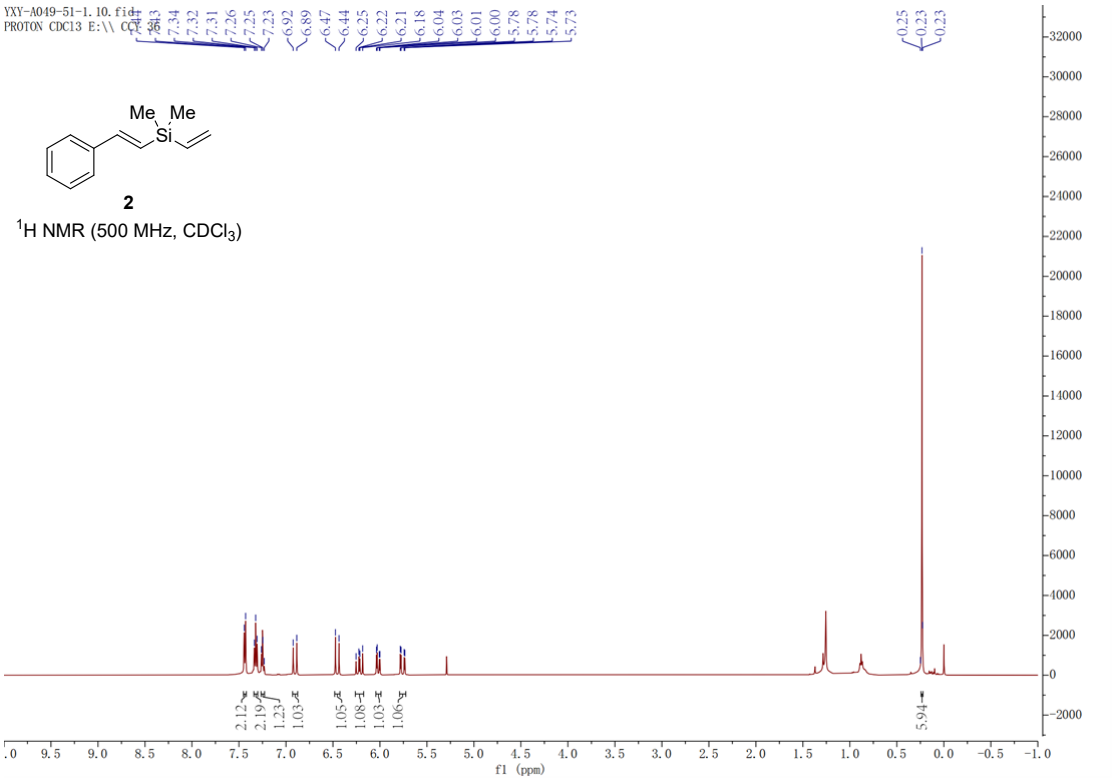


Figure S2. ^{1}H NMR (DMSO-d_6) partial spectra of the reaction of (*E*)-(2-bromovinyl)benzene with $Fe(acac)_2$.

II. Spectral Data for New Compounds

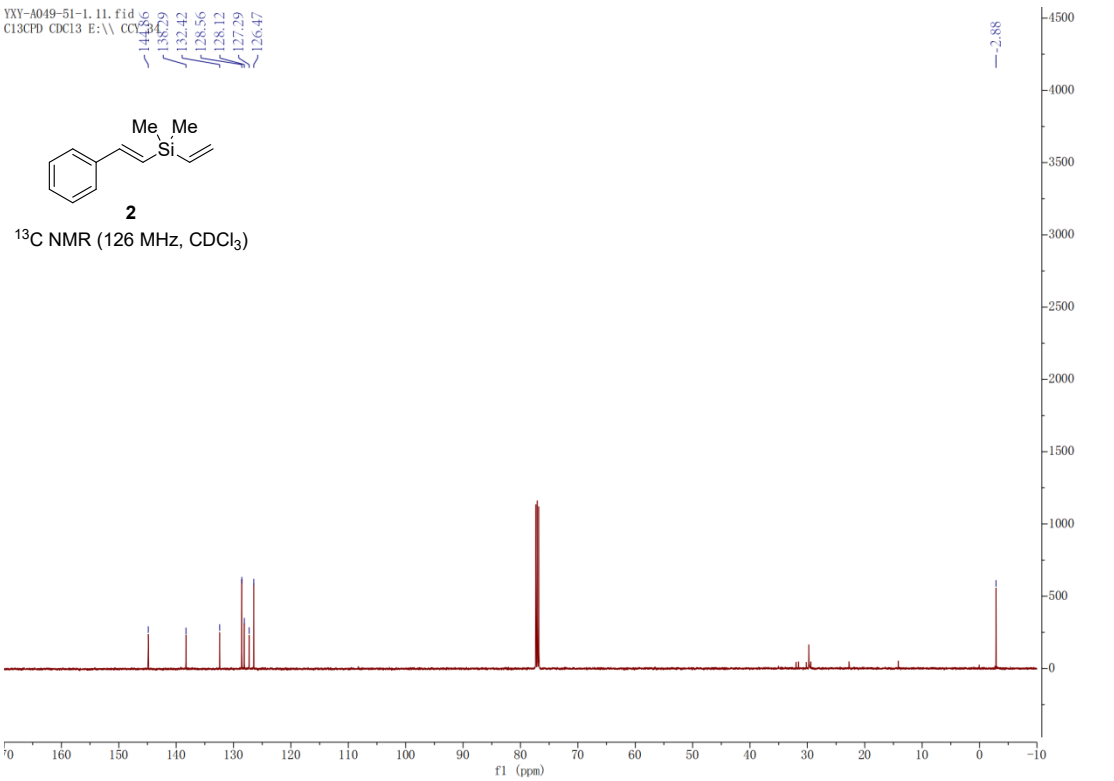






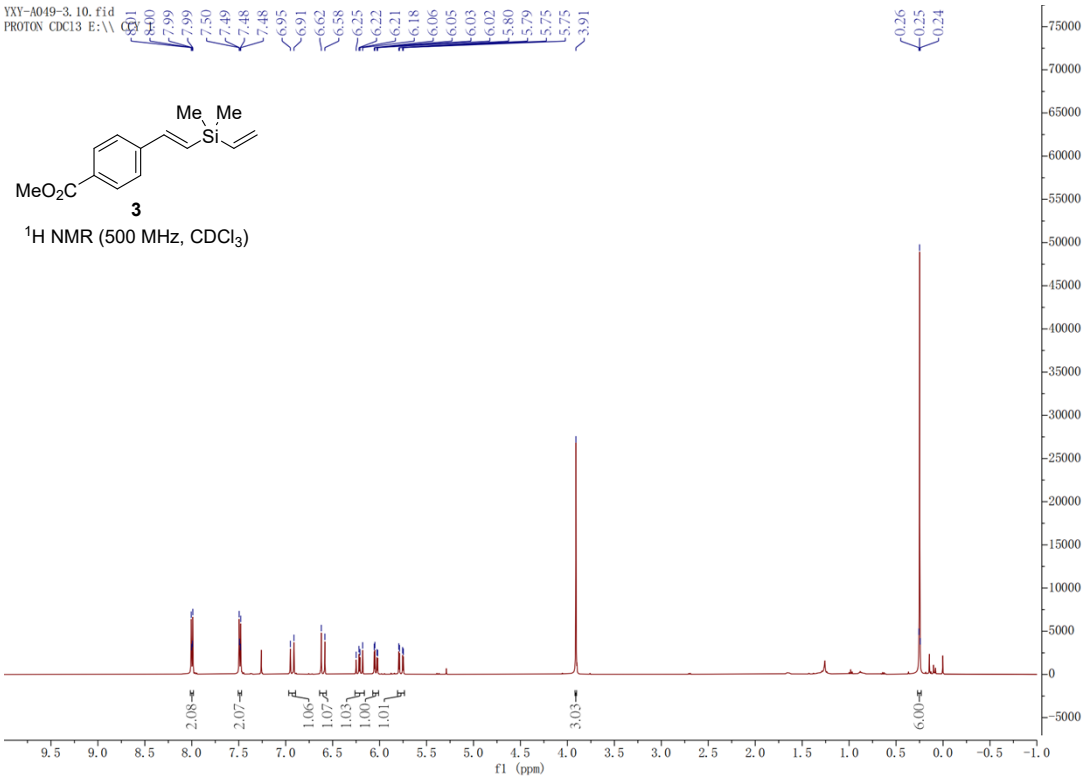
2

^{1}H NMR (500 MHz, $CDCl_3$)

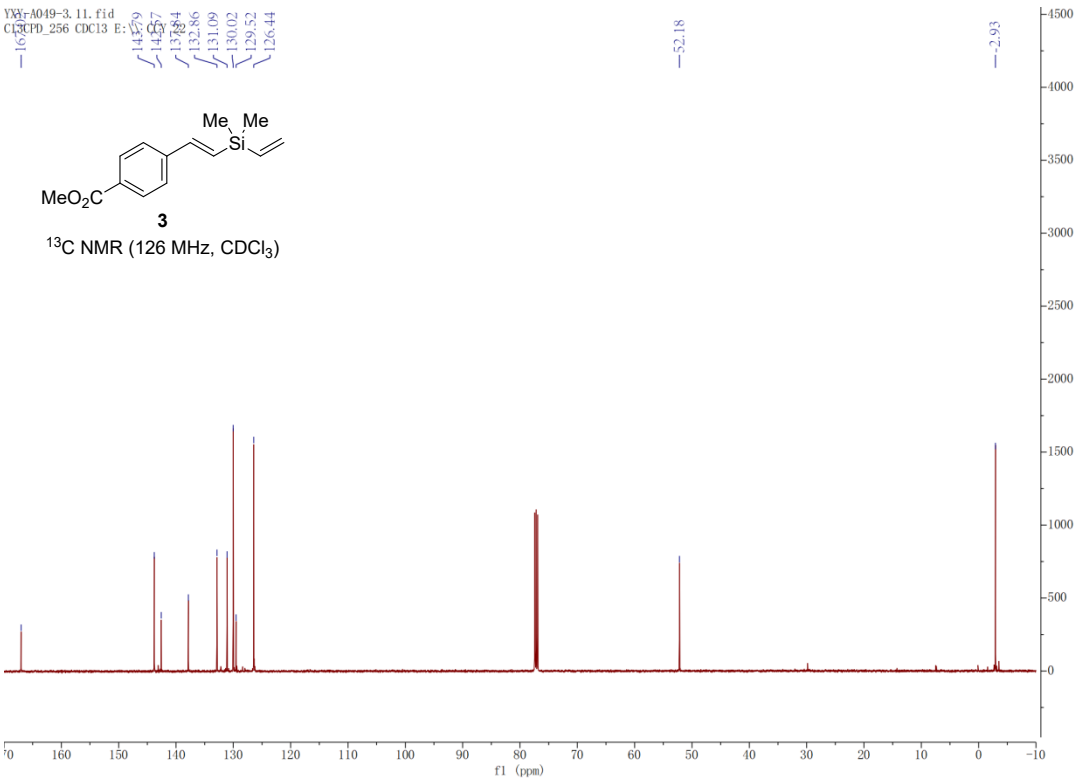


2

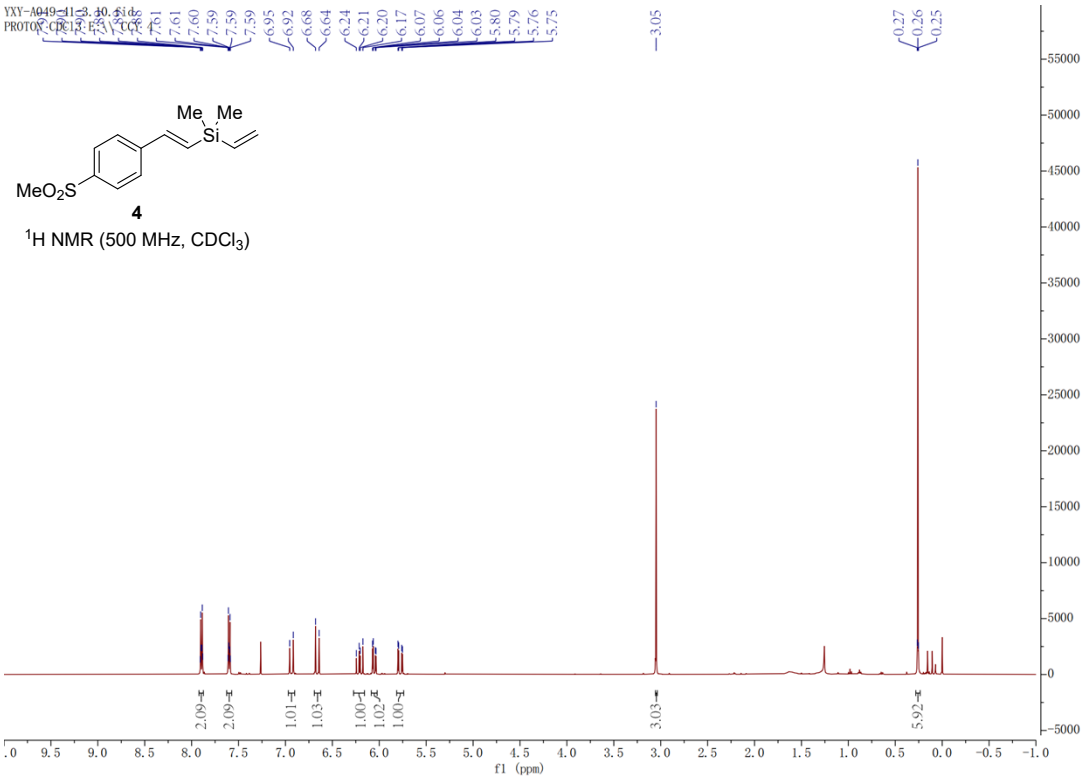
^{13}C NMR (126 MHz, $CDCl_3$)

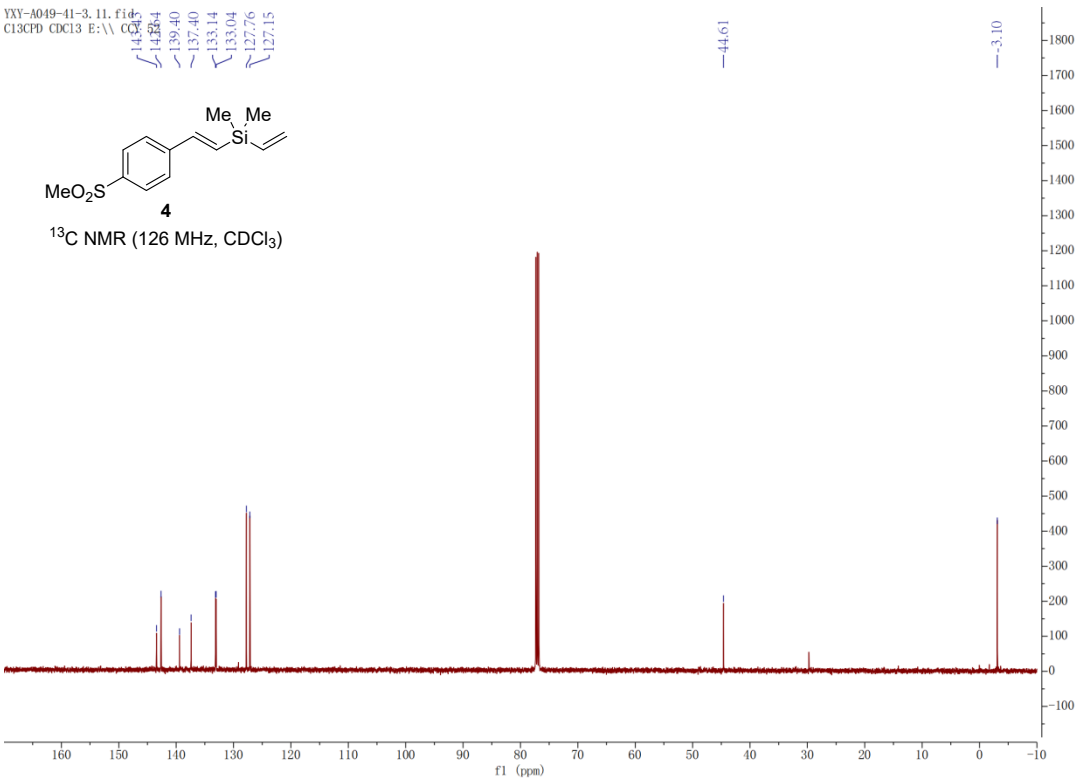


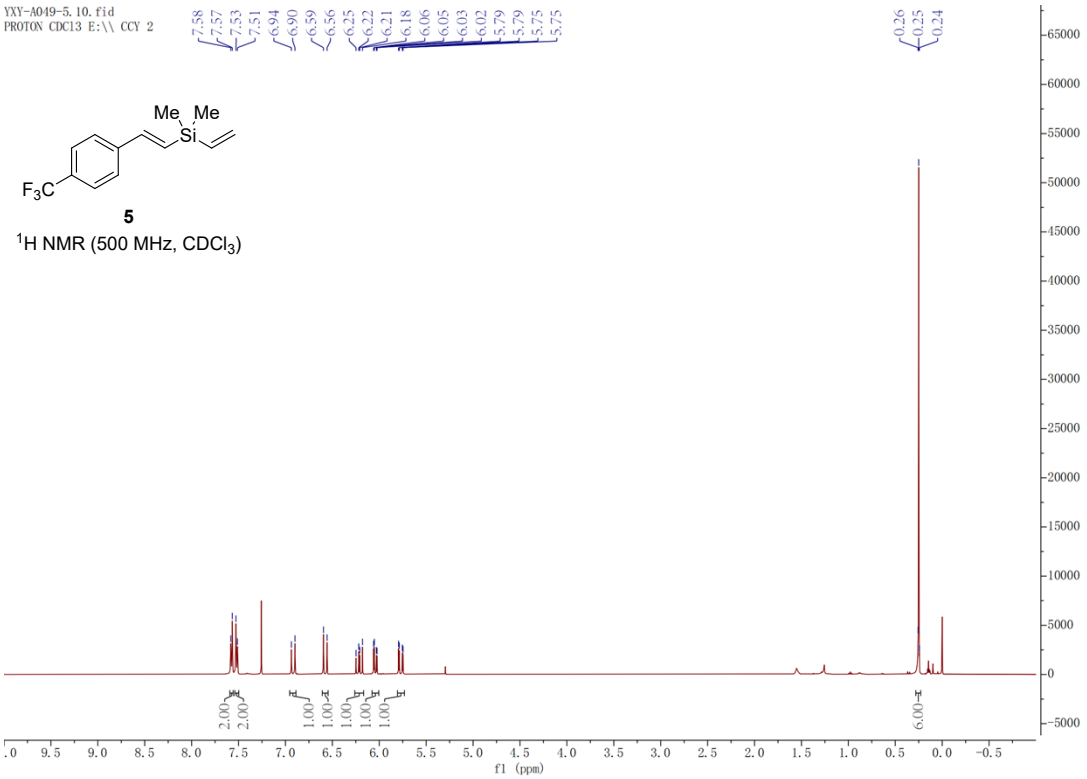
^{1}H NMR (500 MHz, $CDCl_3$)

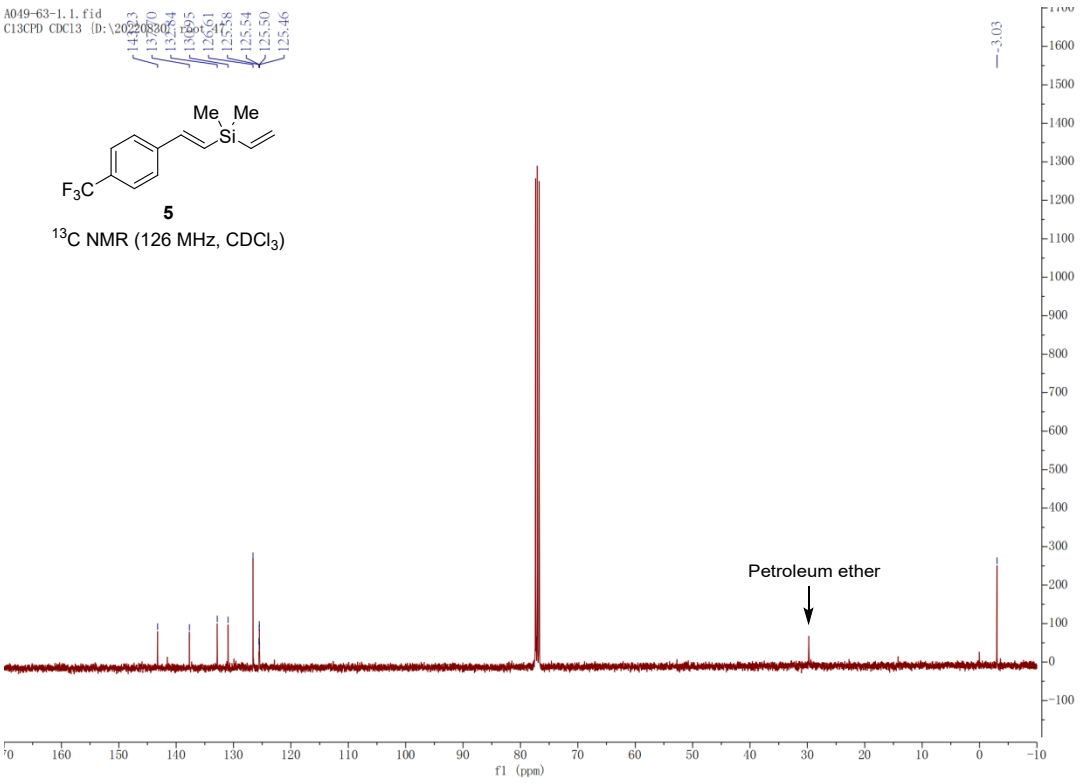


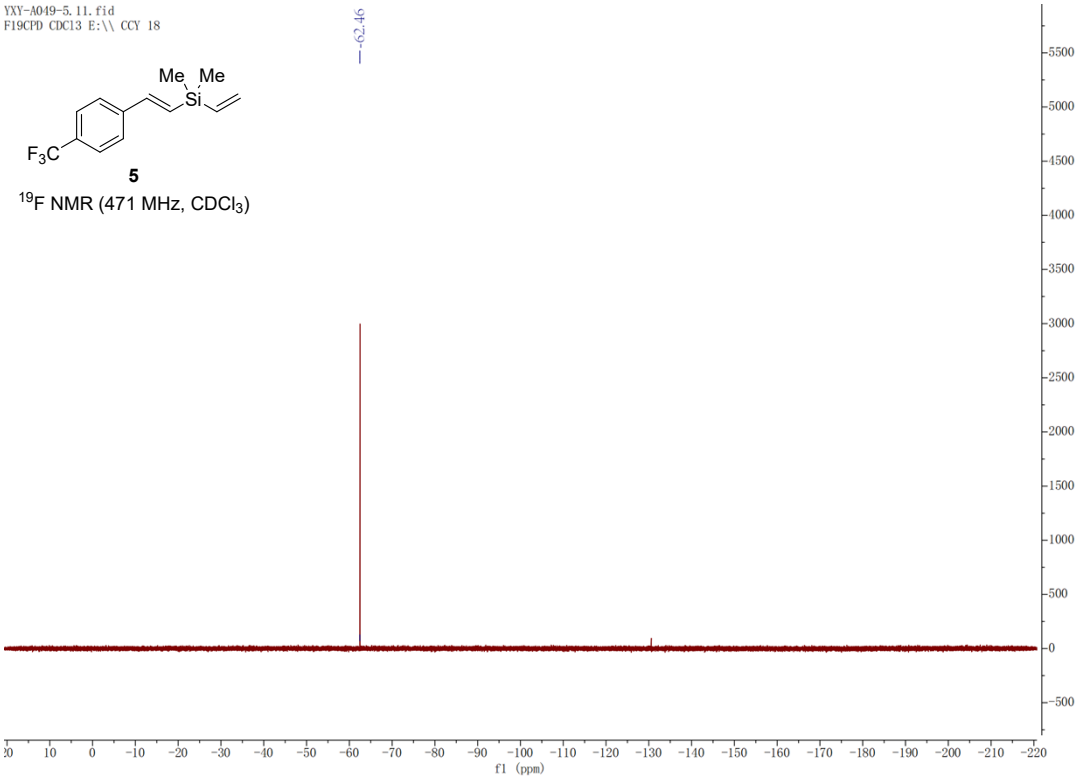
^{13}C NMR (126 MHz, $CDCl_3$)


Me Me
Si
MeO2S
4
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Me Me
Si
MeO2S
4
13C NMR (126 MHz, CDCl3)
f1 (ppm)

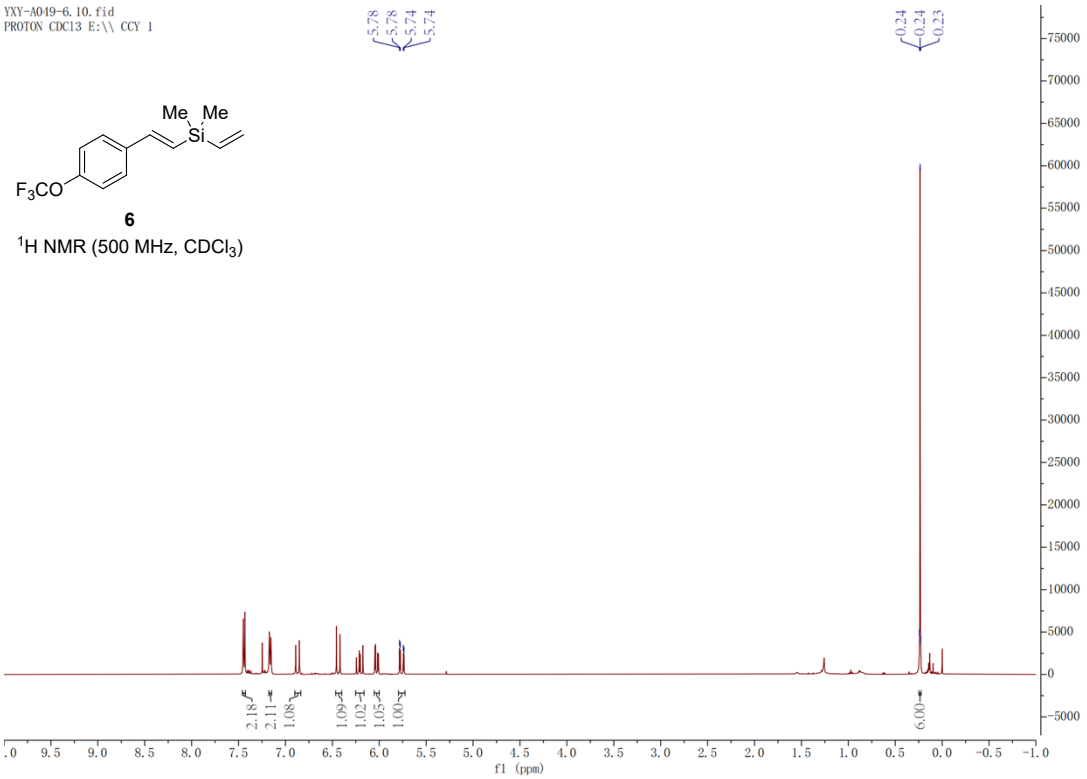

YXY-A049-5.10.fid
PROTON CDCl3 E:\\ CCY 2
Me Me
Si
F3C
5
1H NMR (500 MHz, CDCl3)
f1 (ppm)


A049-63-1.1.fid
C13CPD CDCl3
Me Me
Si
F3C
5
13C NMR (126 MHz, CDCl3)
Petroleum ether
f1 (ppm)



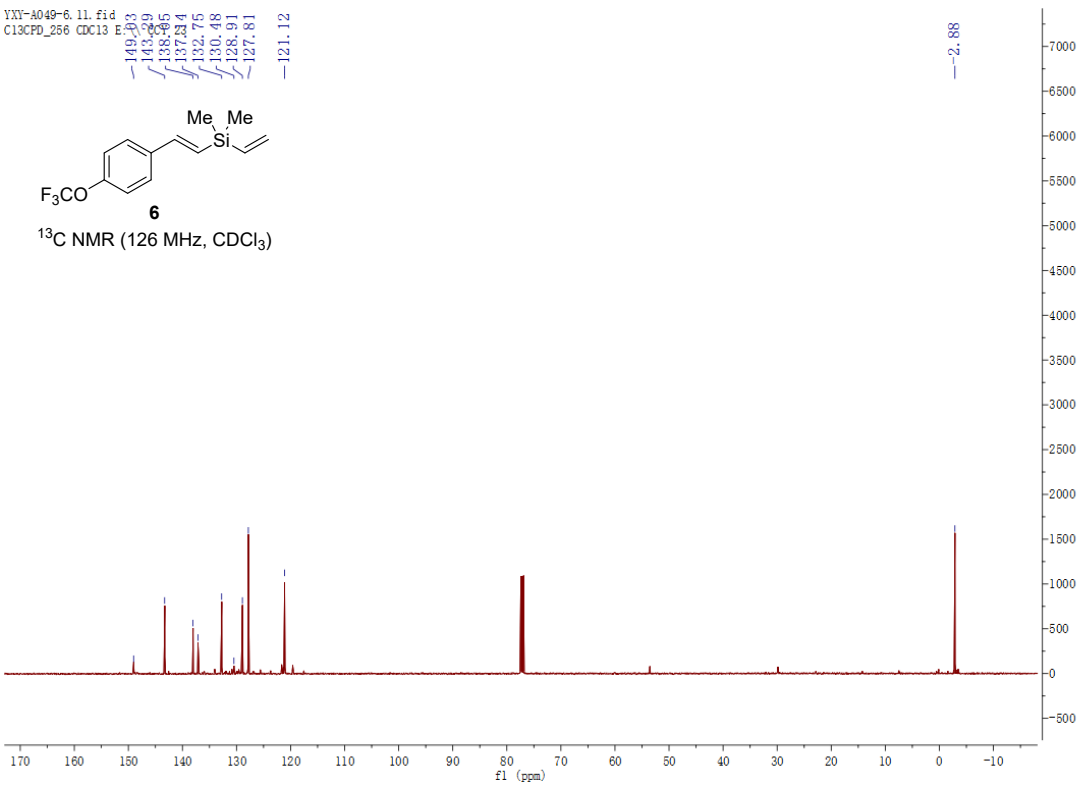
5

^{19}F NMR (471 MHz, $CDCl_3$)



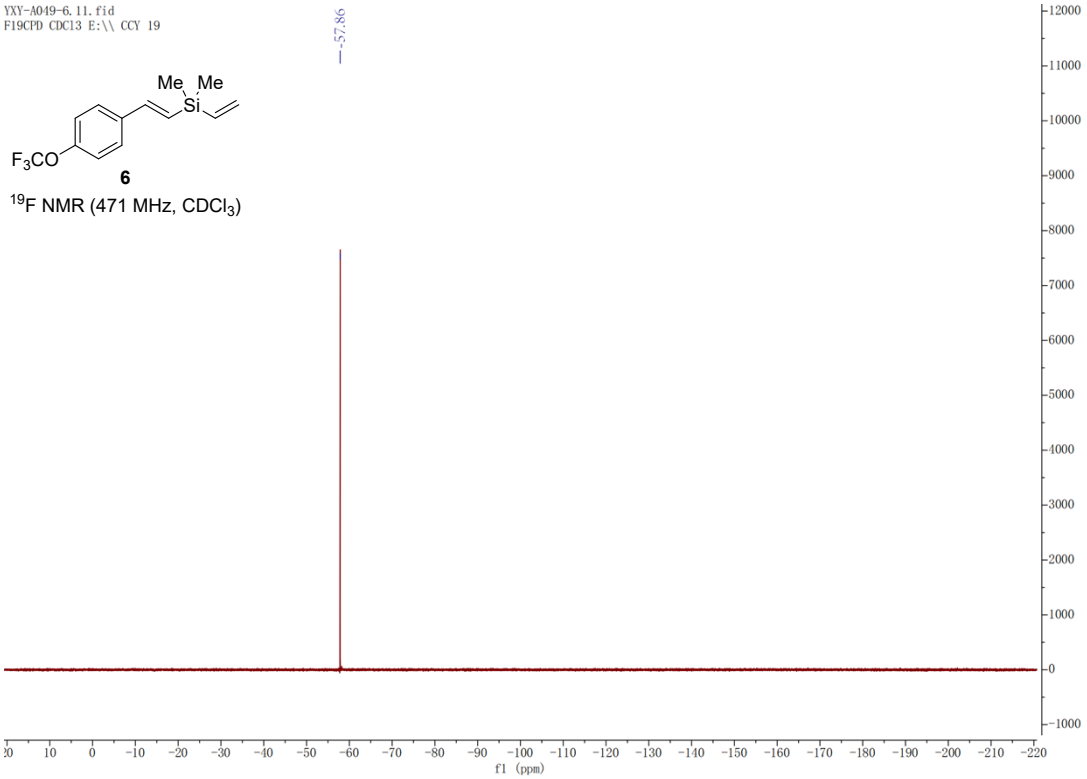
6

^{1}H NMR (500 MHz, $CDCl_3$)

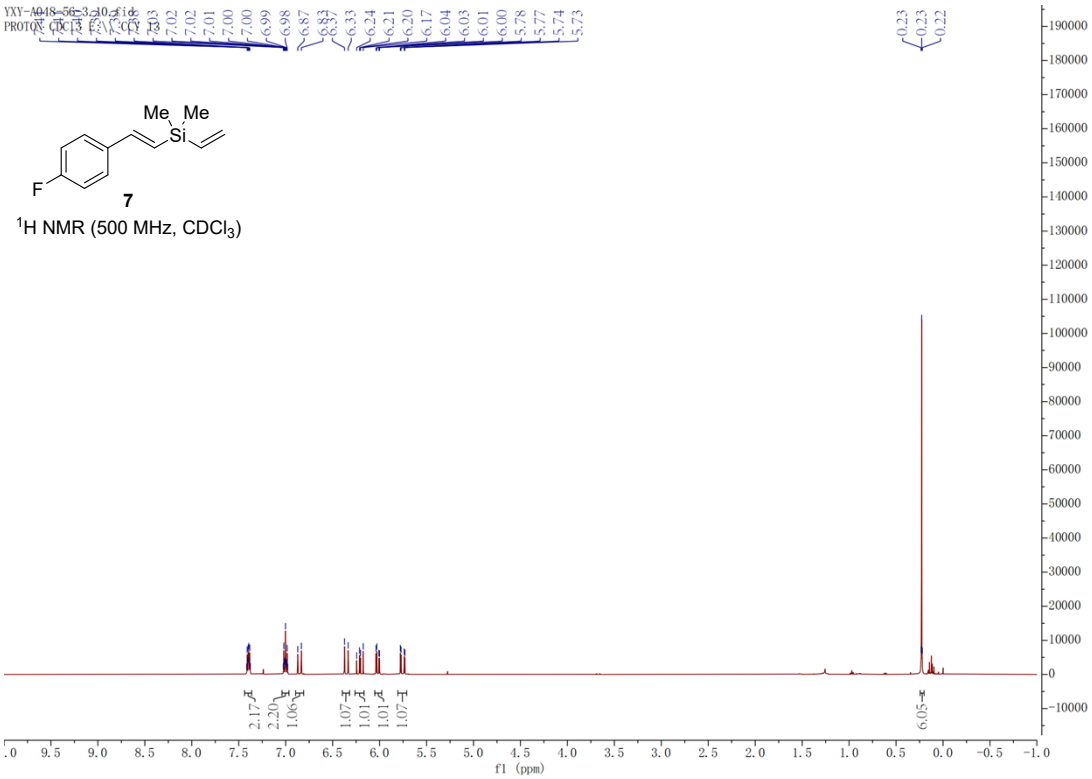


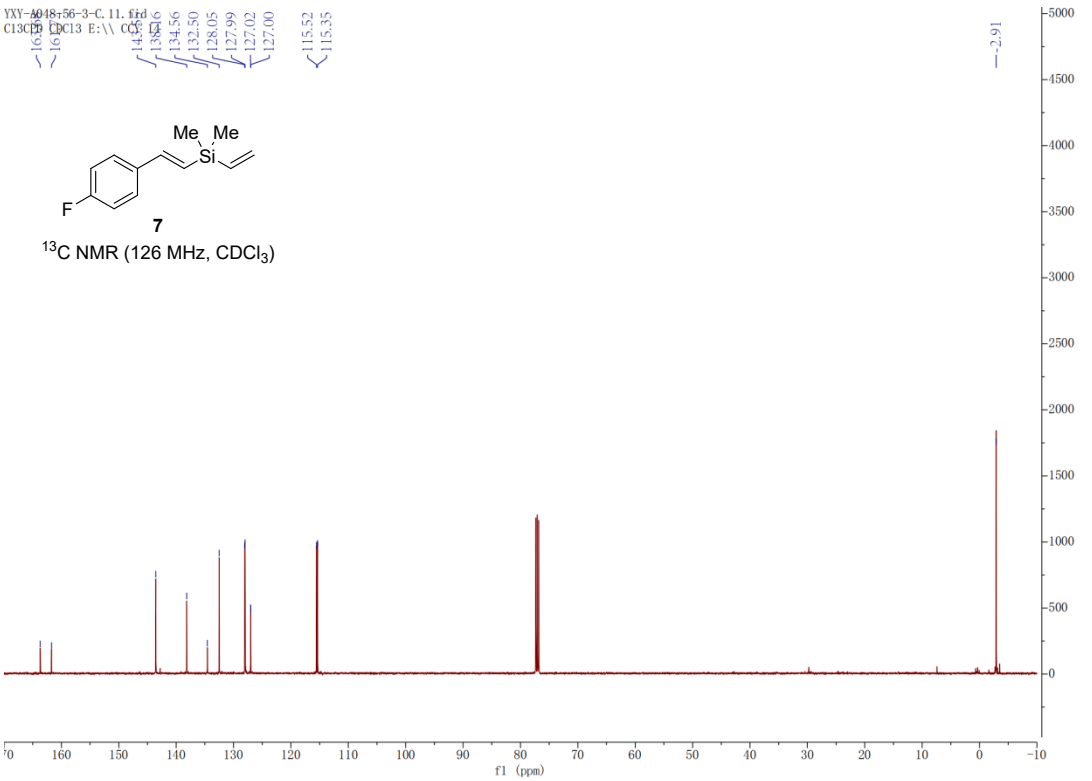
6

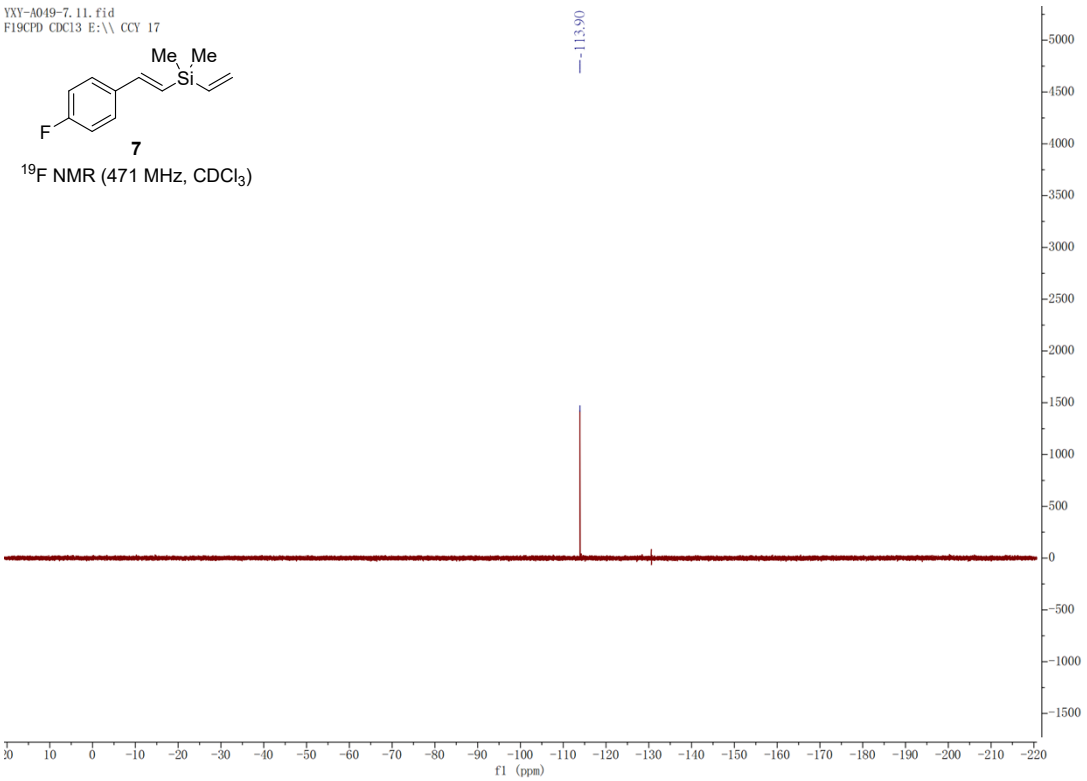
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

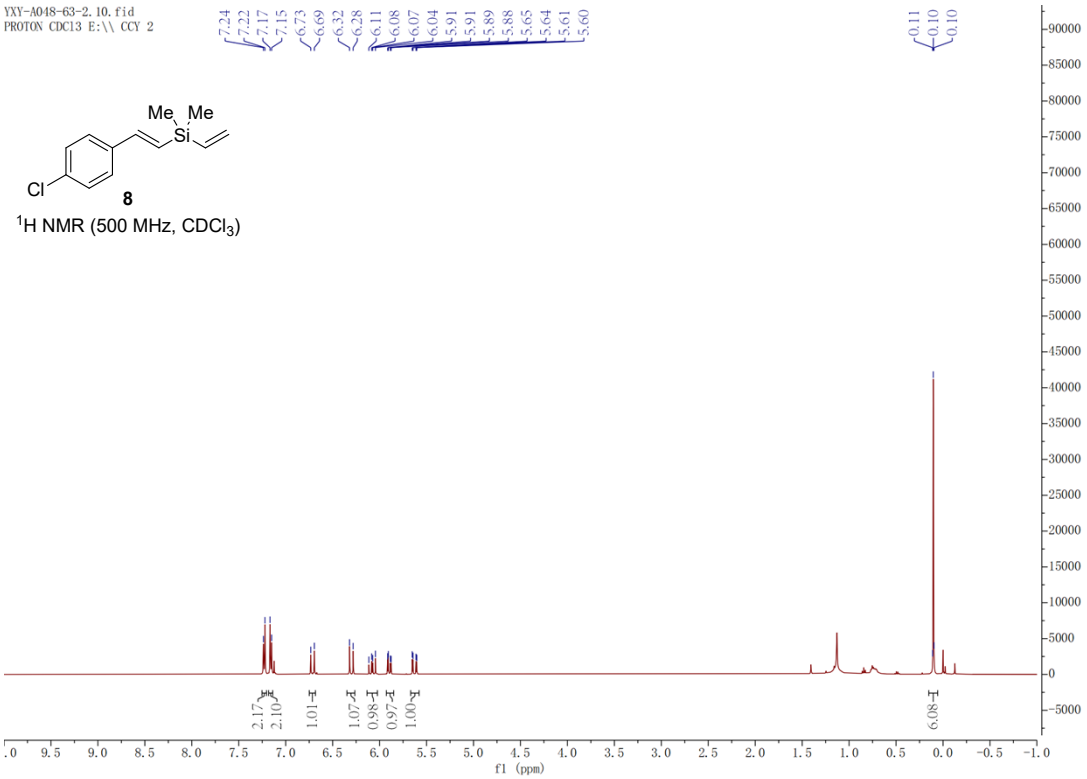

Me Me
Si
F
7
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Me Me
Si
F
7
13C NMR (126 MHz, CDCl3)
f1 (ppm)

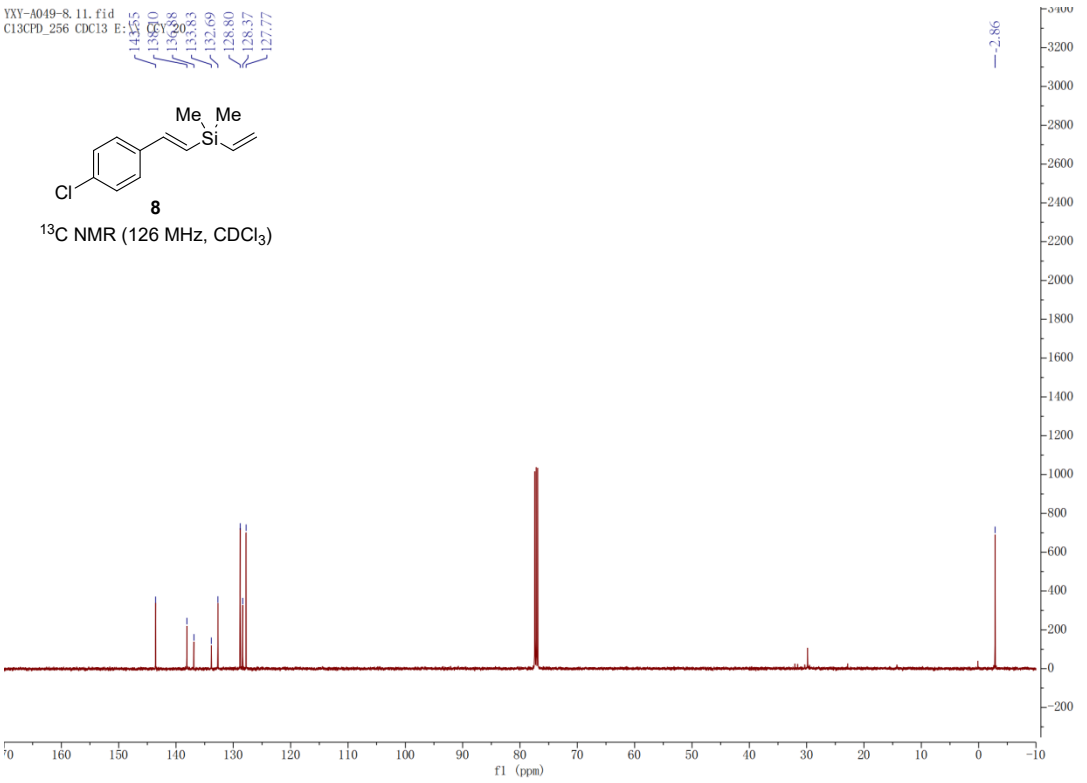


7

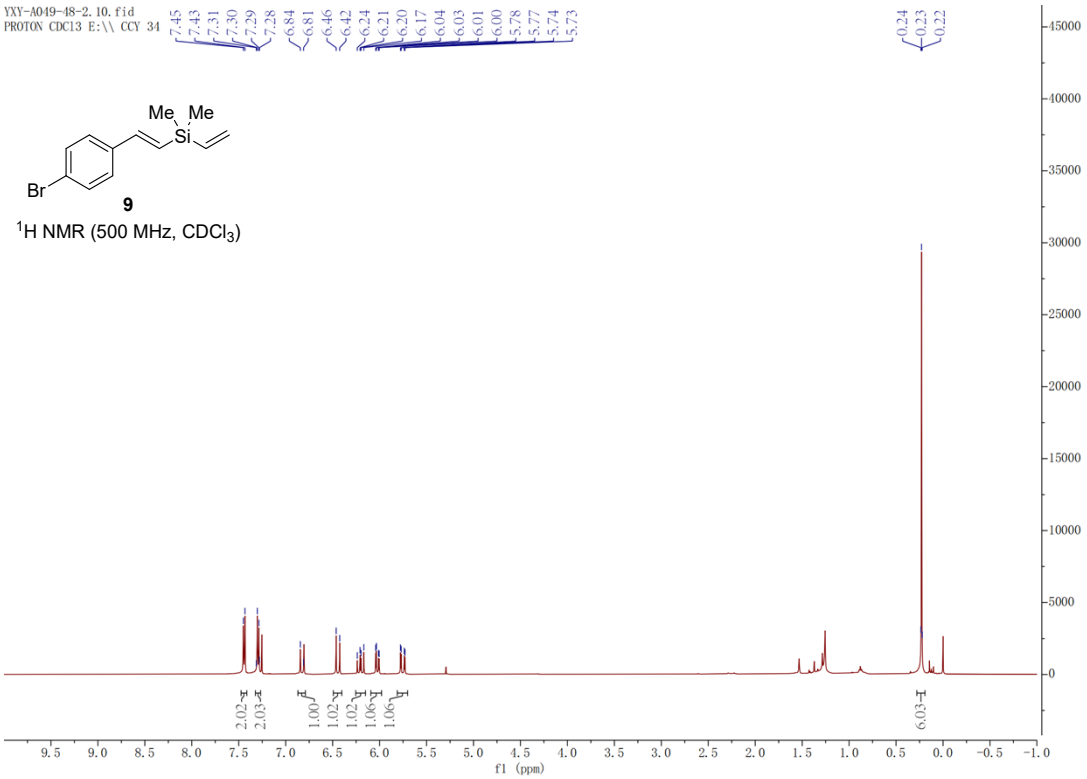
^{19}F NMR (471 MHz, $CDCl_3$)

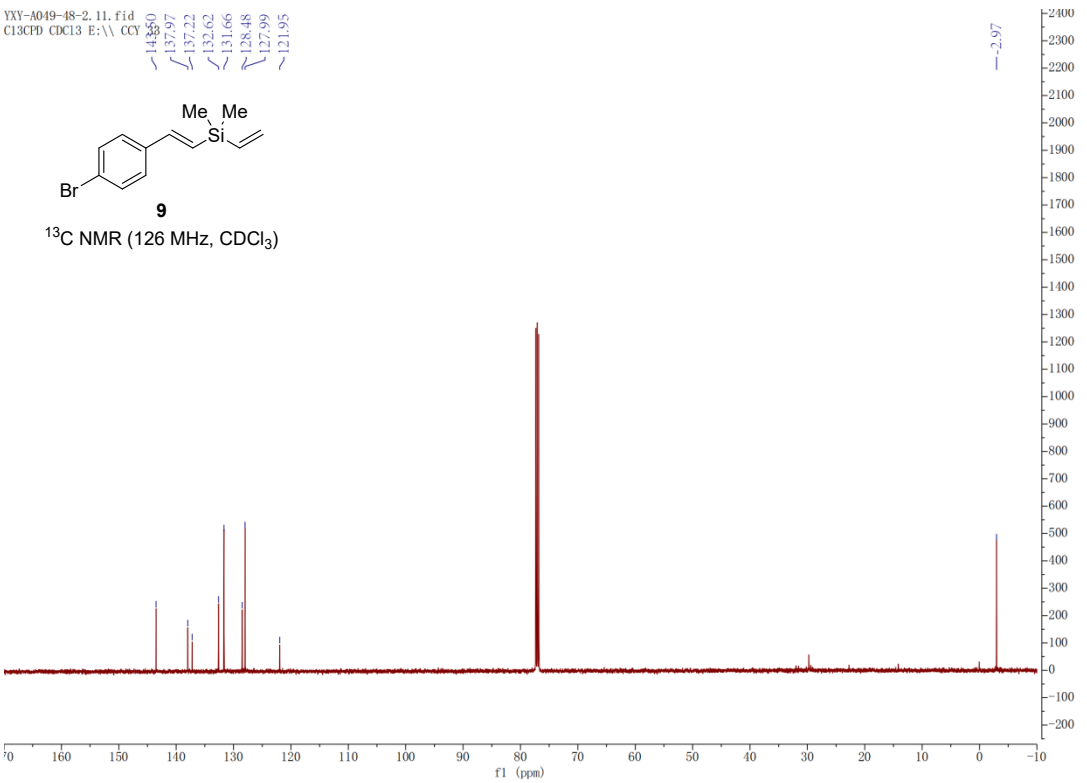


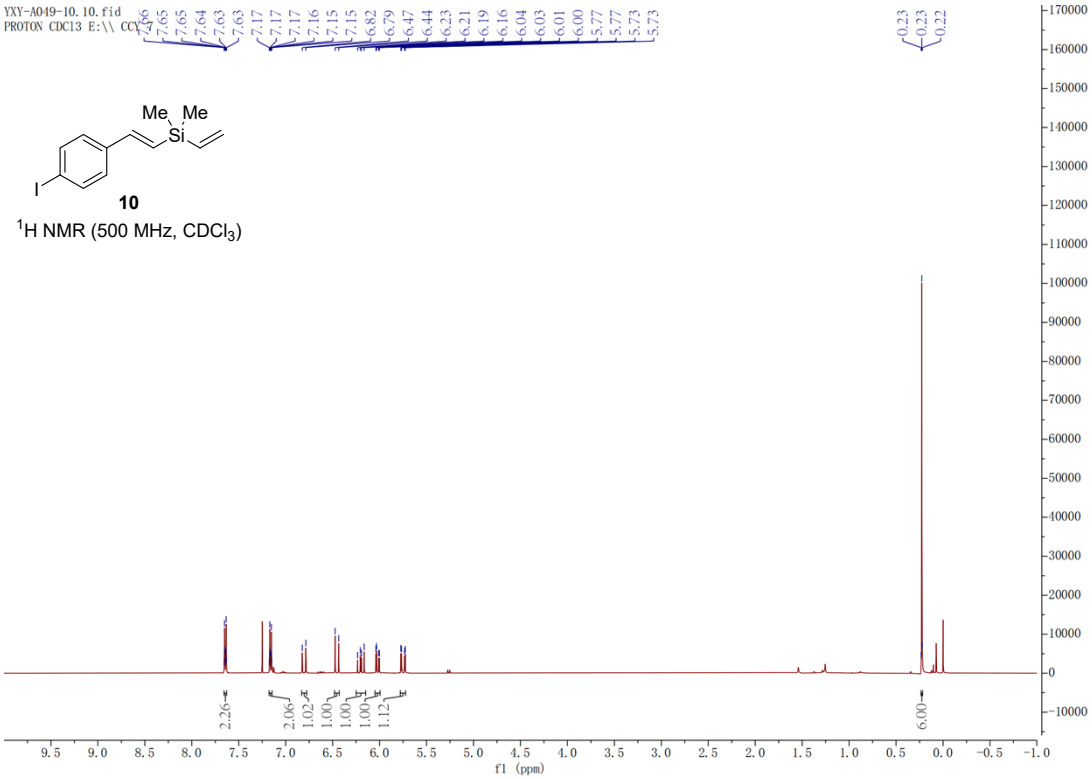
^{1}H NMR (500 MHz, $CDCl_3$)



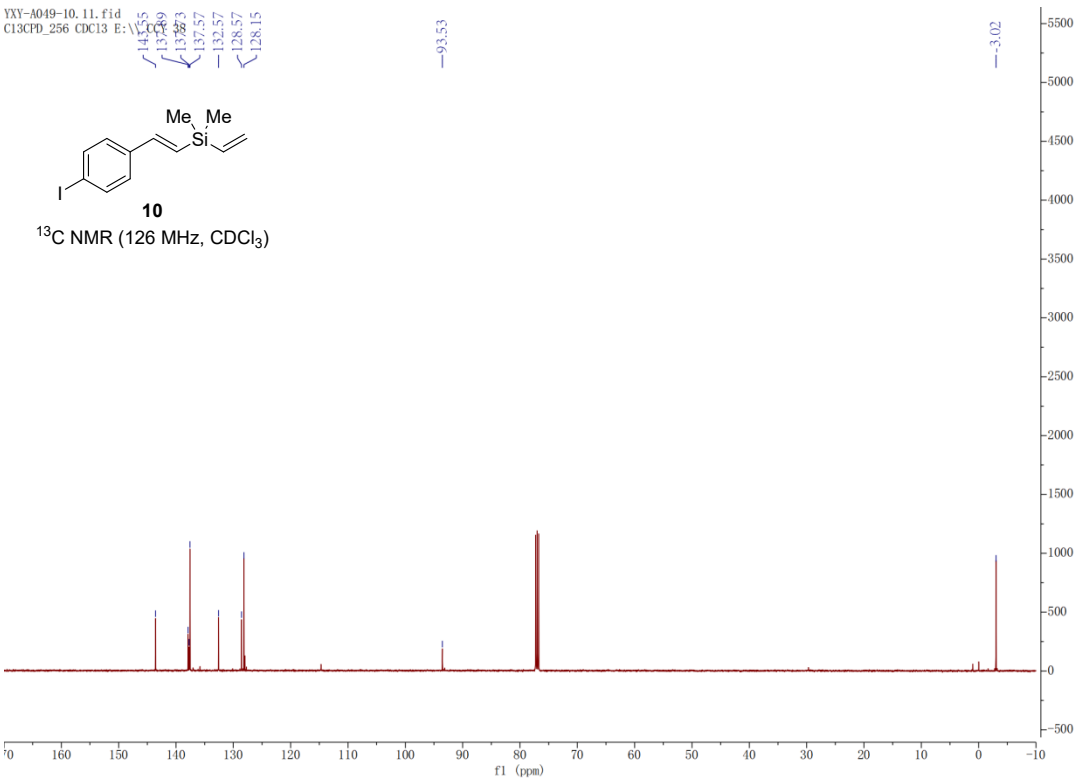
^{13}C NMR (126 MHz, $CDCl_3$)


YXY-A049-48-2.10.fid
PROTON CDCl3 E:\\ CCY 34
Me
Me
Si
Br
9
1H NMR (500 MHz, CDCl3)
f1 (ppm)

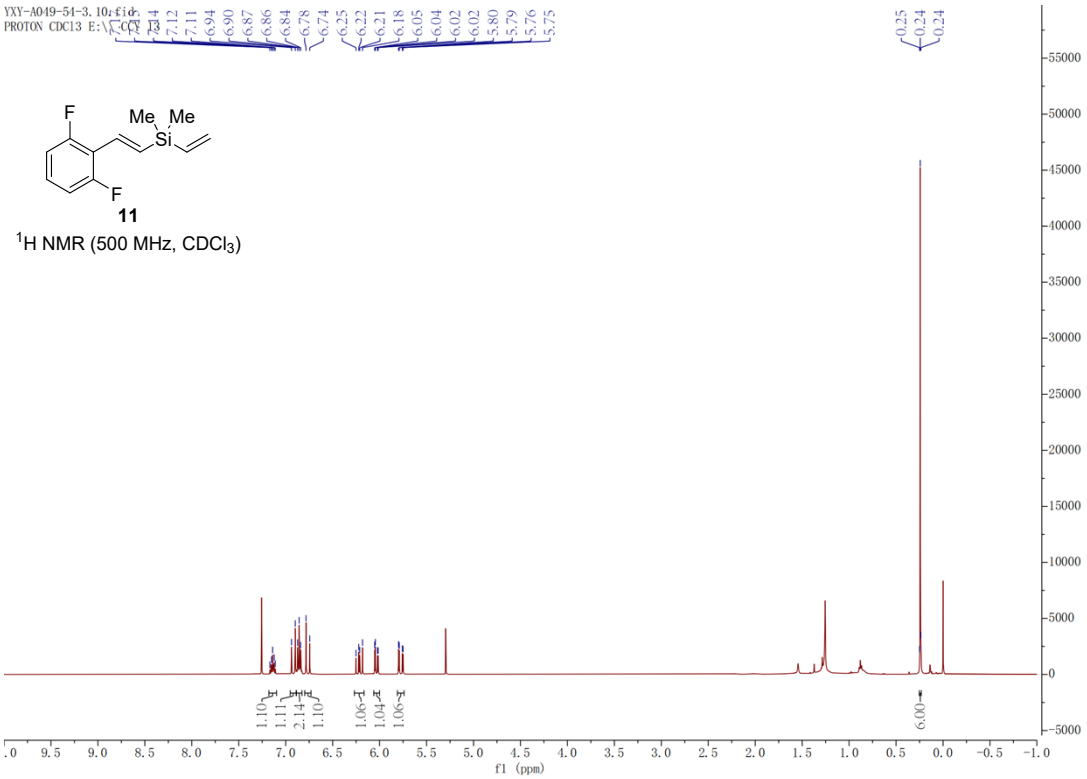

YXY-A049-48-2.11.fid
C13CPD CDCl3 E:\\ CCY 33
Me
Me
Si
Br
9
13C NMR (126 MHz, CDCl3)
f1 (ppm)

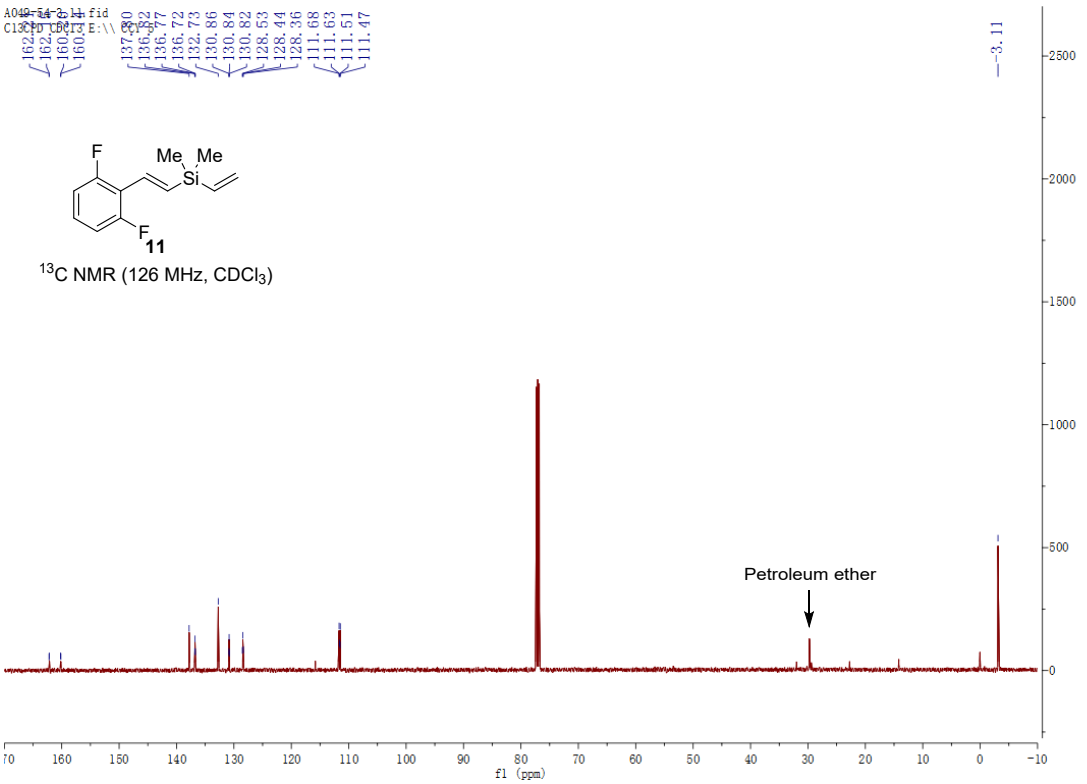


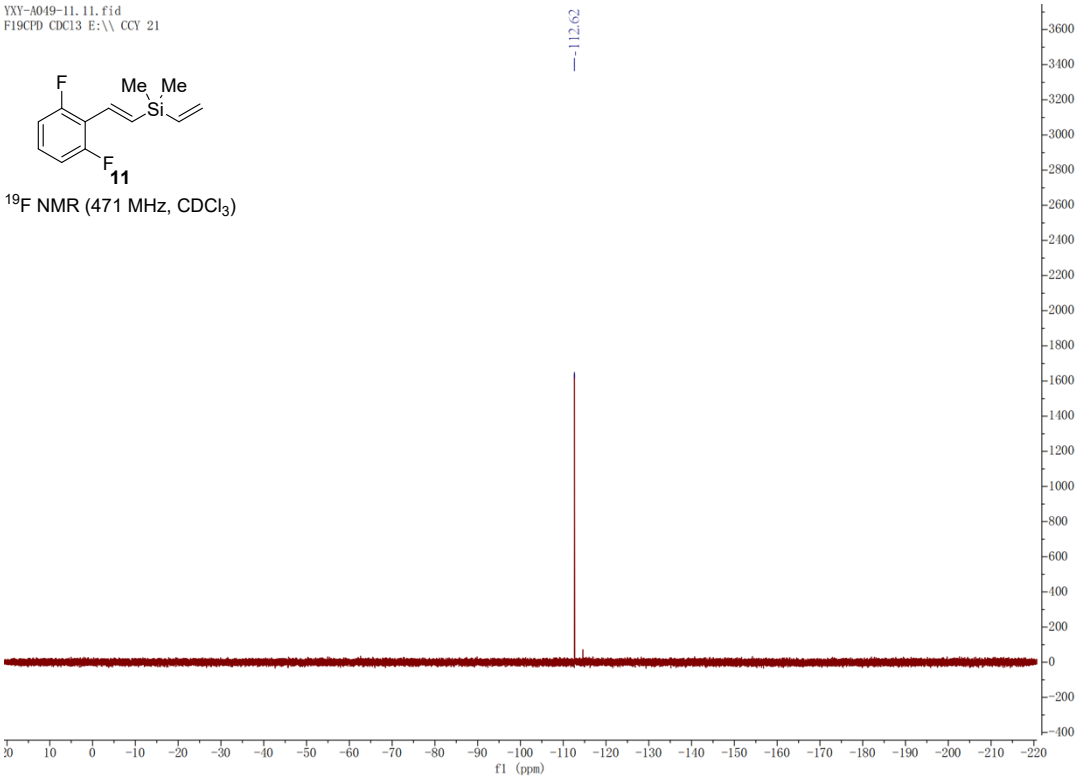
^{1}H NMR (500 MHz, $CDCl_3$)



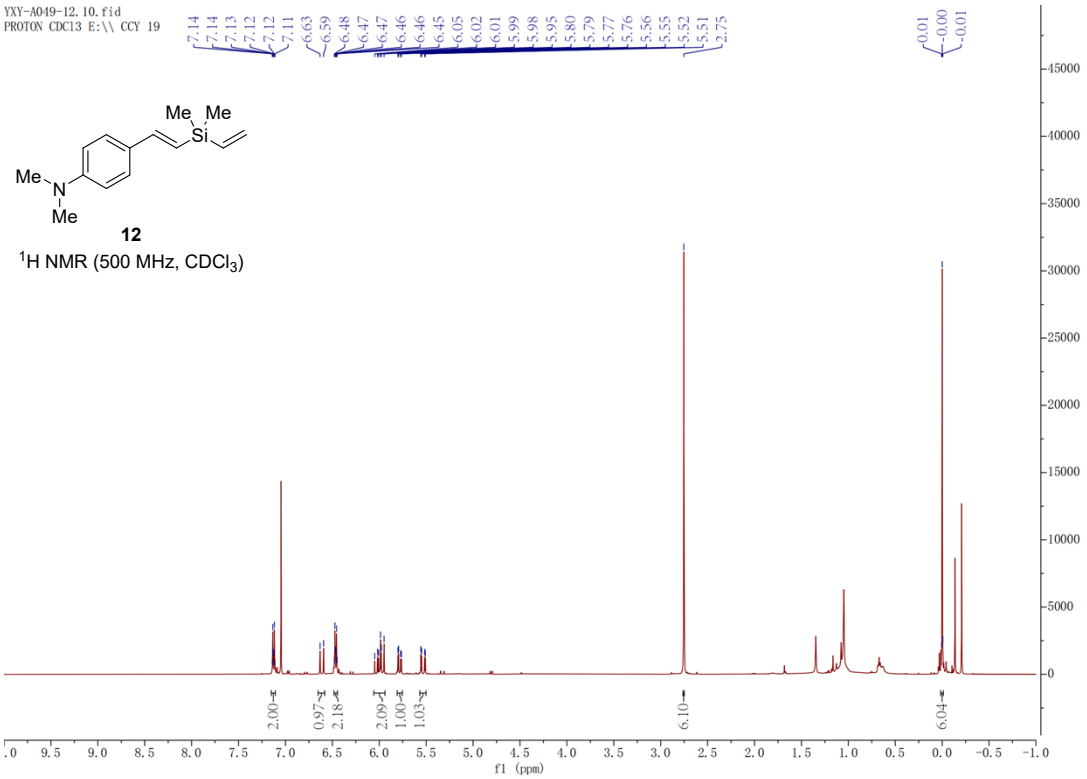
^{13}C NMR (126 MHz, $CDCl_3$)


F
Me
Me
Si
F
11
1H NMR (500 MHz, CDCl3)
f1 (ppm)


F
Me
Me
Si
F
11
13C NMR (126 MHz, CDCl3)
Petroleum ether
f1 (ppm)



^{19}F NMR (471 MHz, $CDCl_3$)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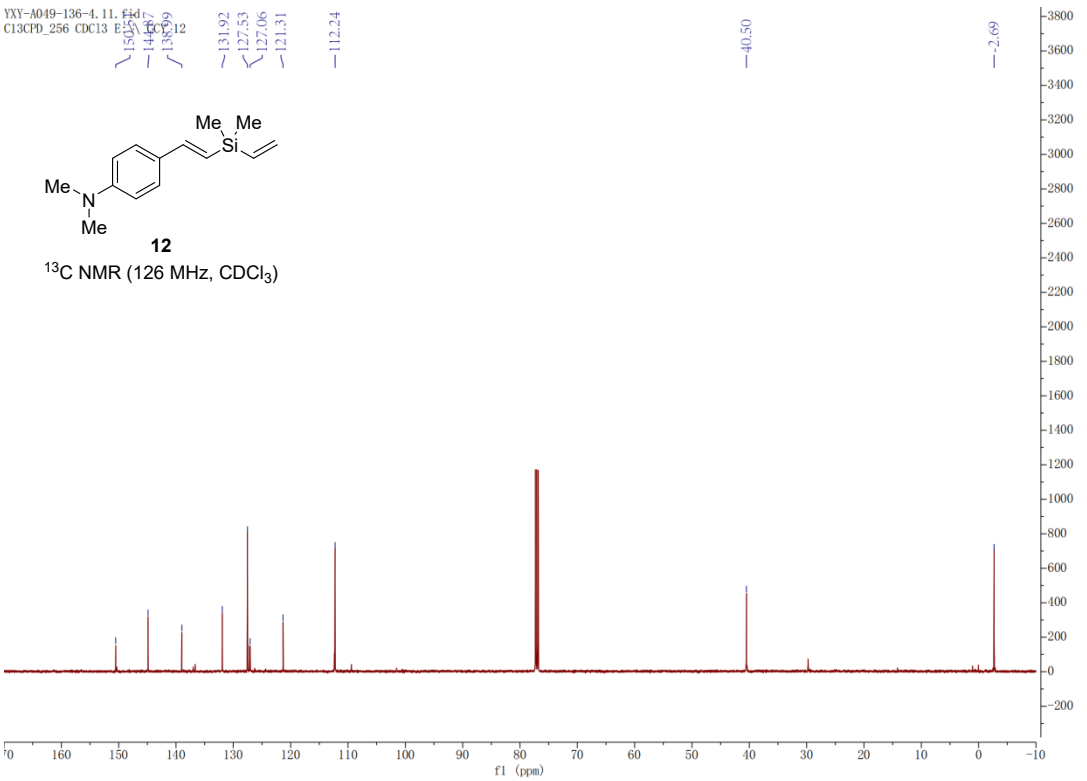
PROTON CDCl3 E:\\ CCY 19
Me
Me
Si
Me
N
Me
12
1H NMR (500 MHz, CDCl3)
f1 (ppm)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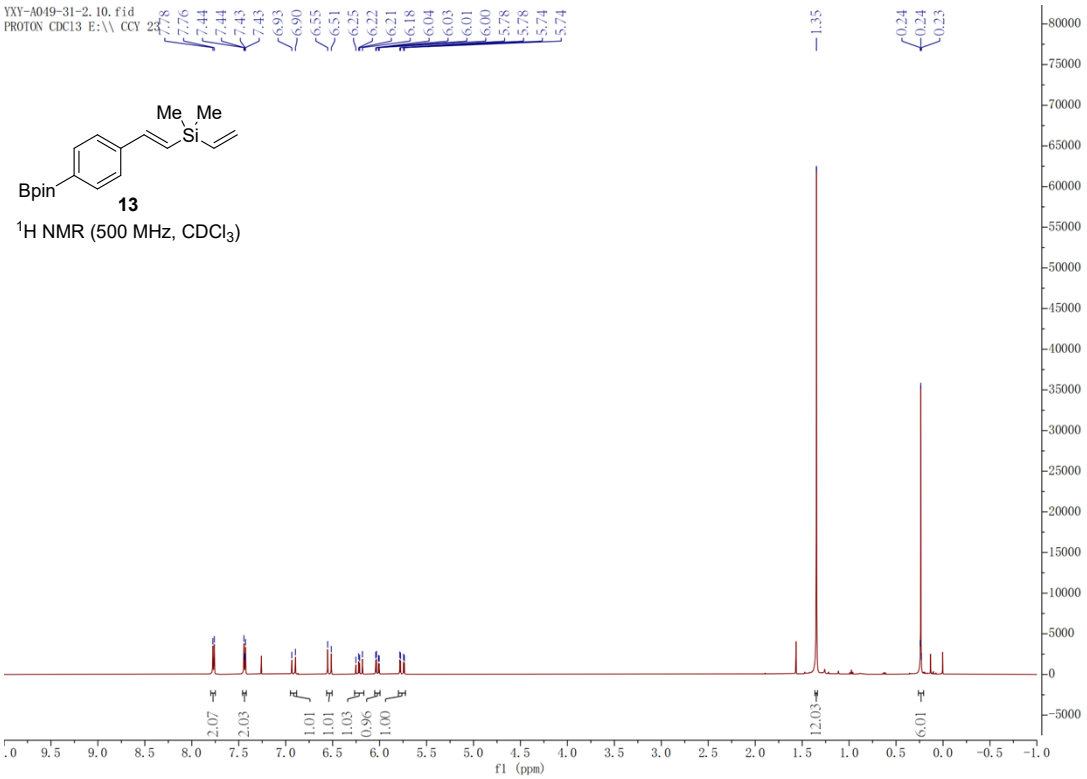
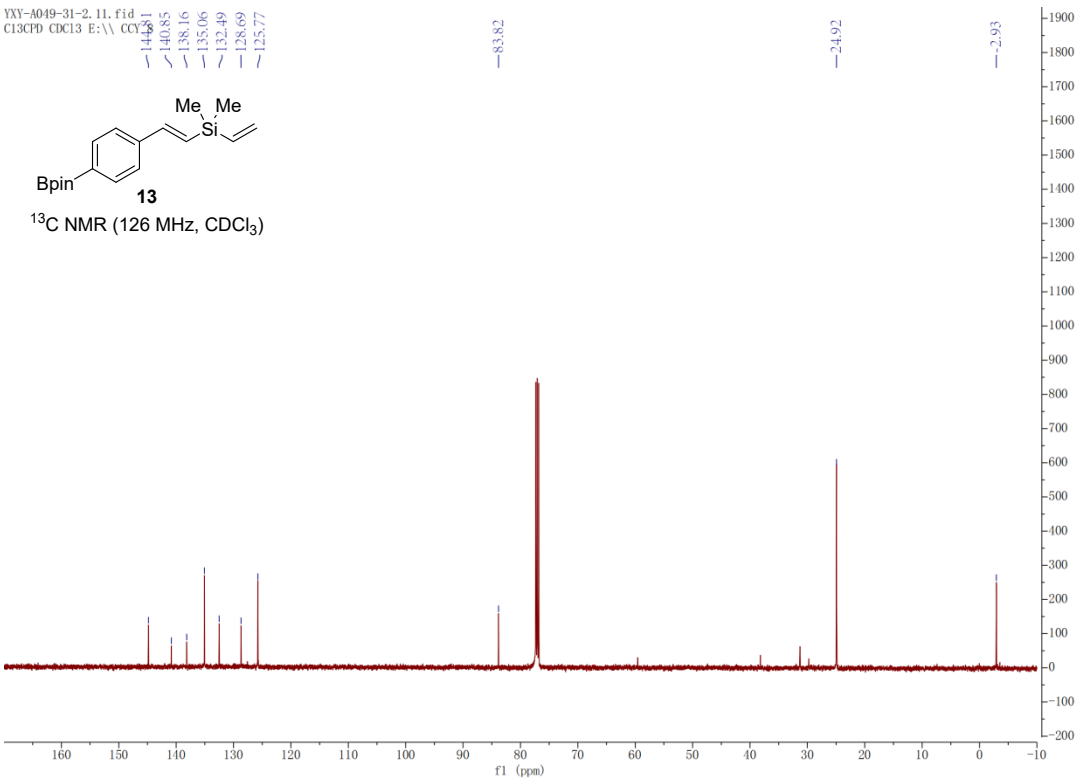
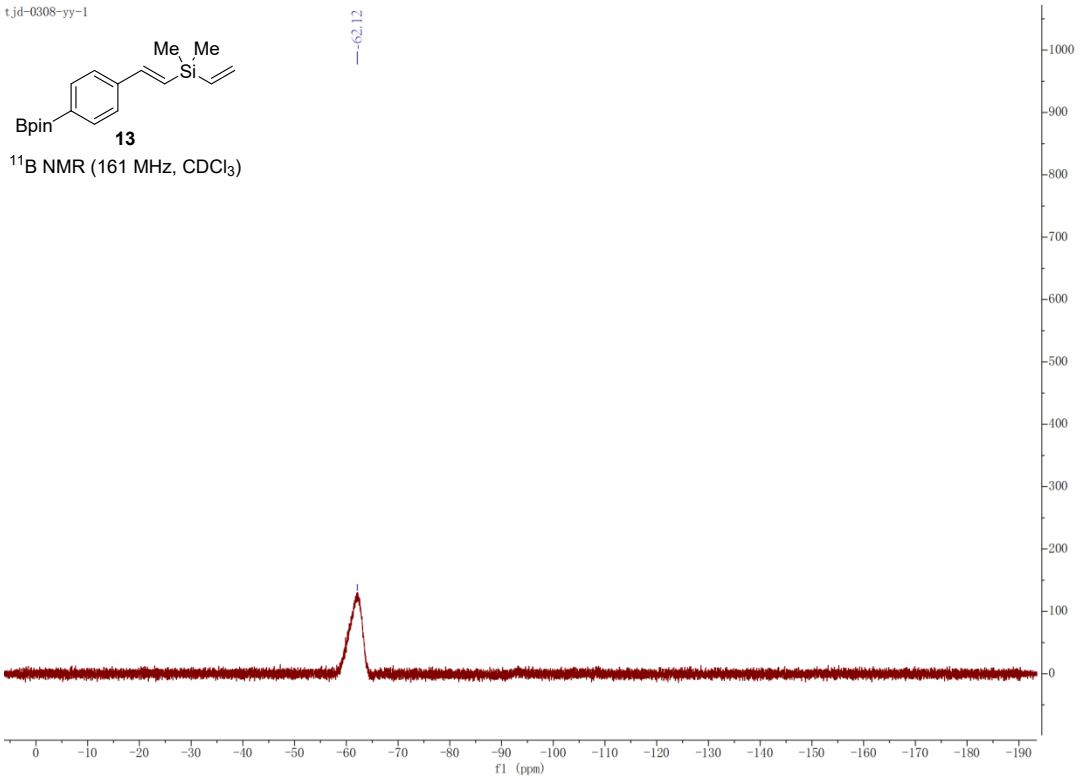
Me
Si
Me
N
Me
12
13C NMR (126 MHz, CDCl3)
f1 (ppm)



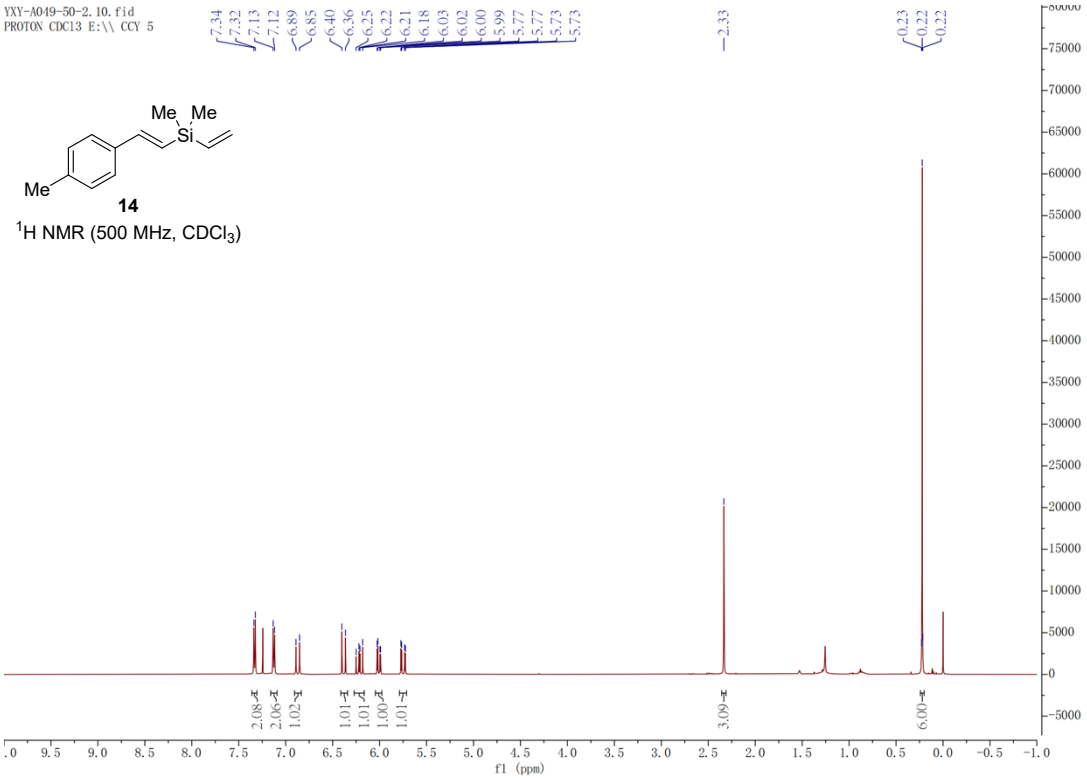
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

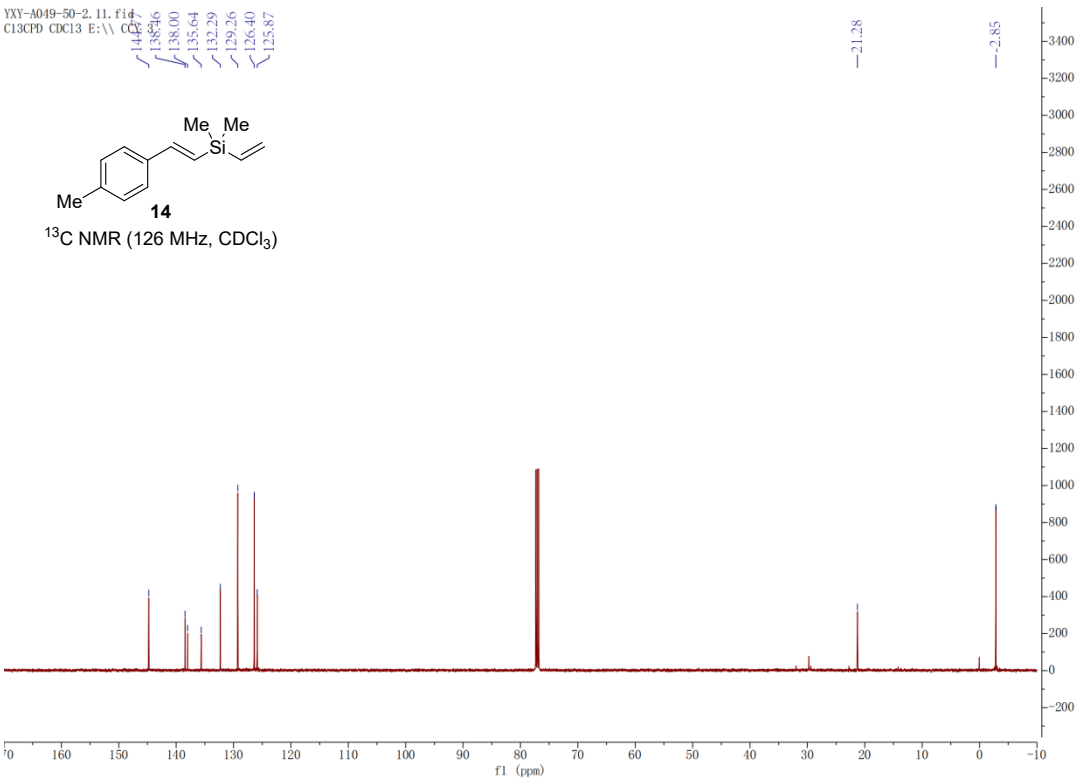


^{11}B NMR (161 MHz, $CDCl_3$)



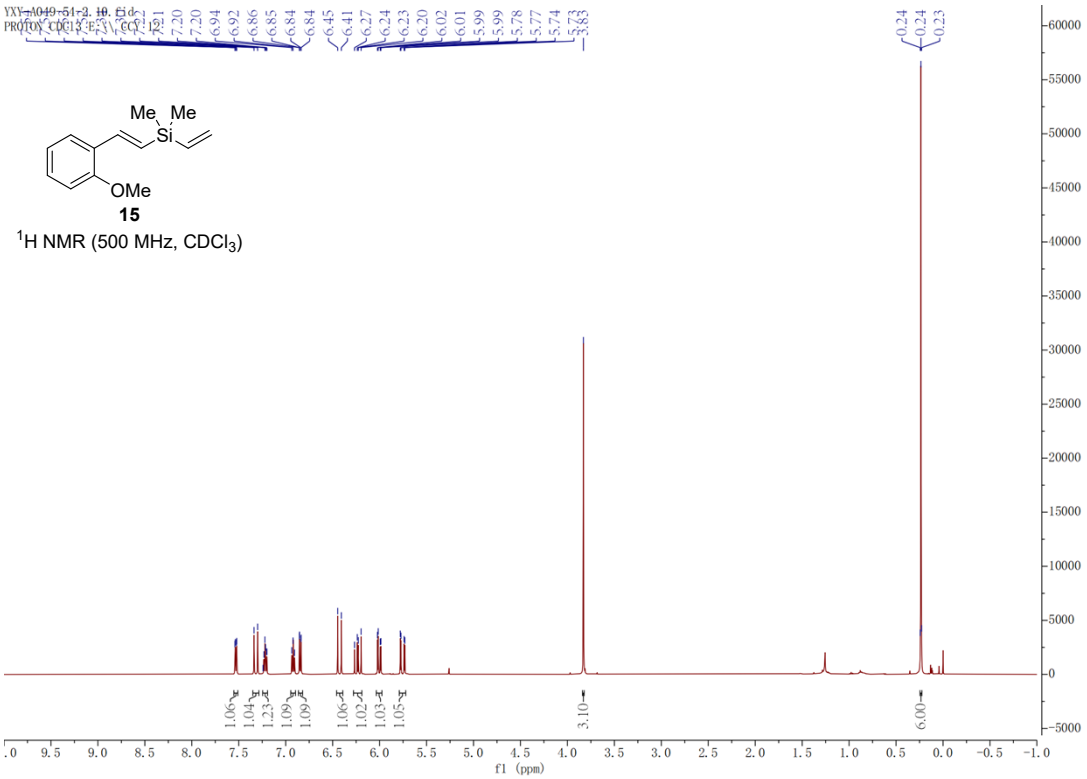
14

^{1}H NMR (500 MHz, $CDCl_3$)

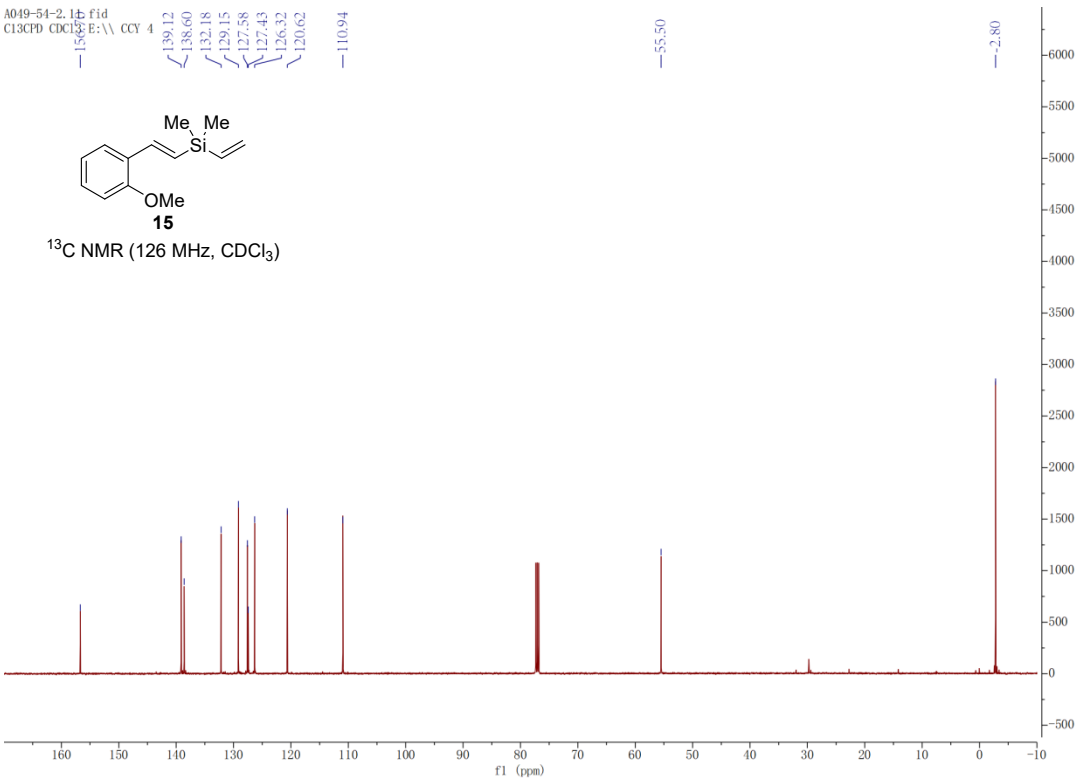


14

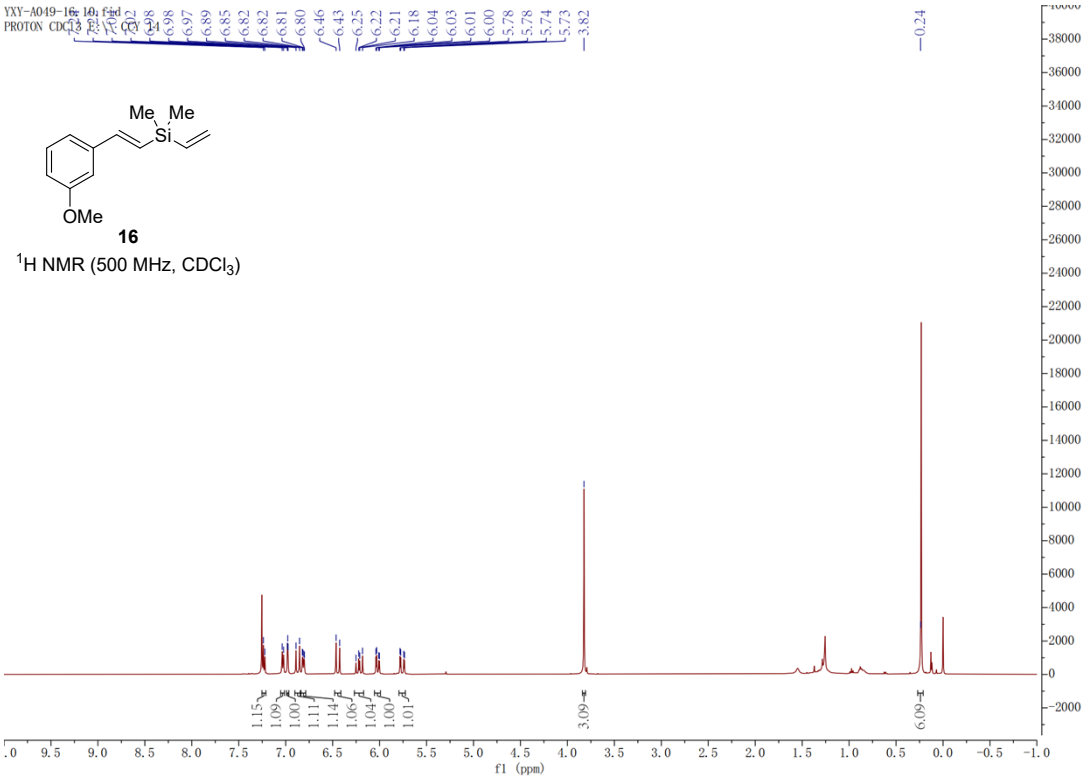
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

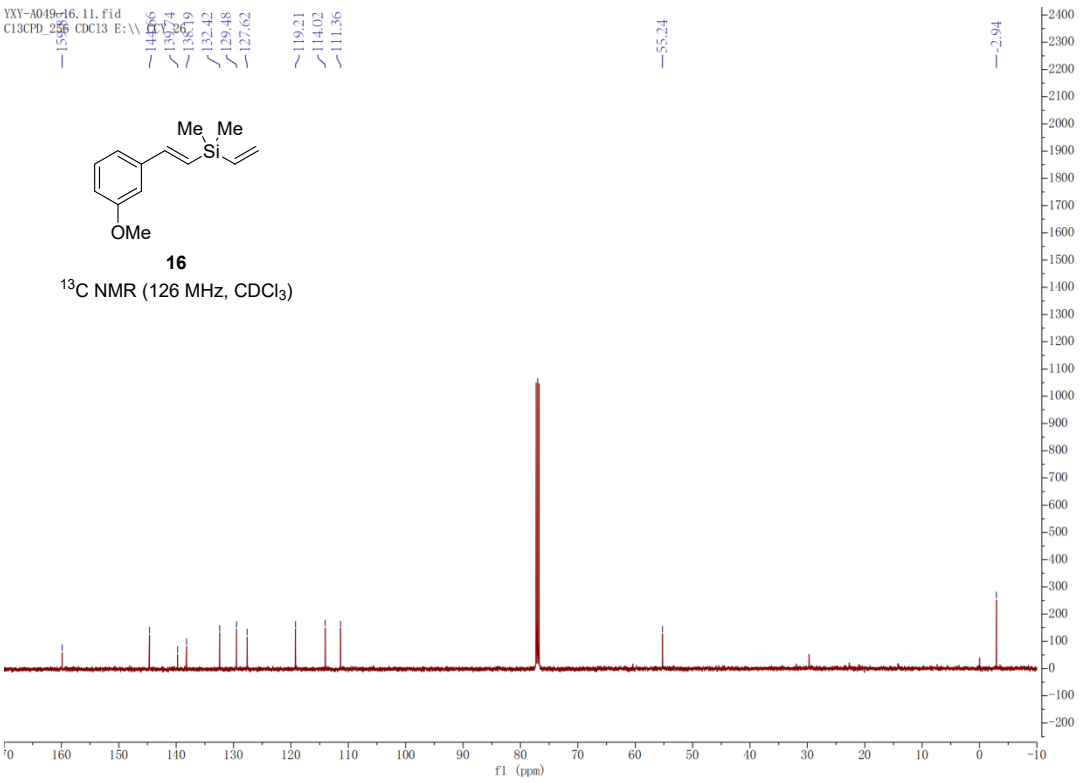


^{13}C NMR (126 MHz, $CDCl_3$)



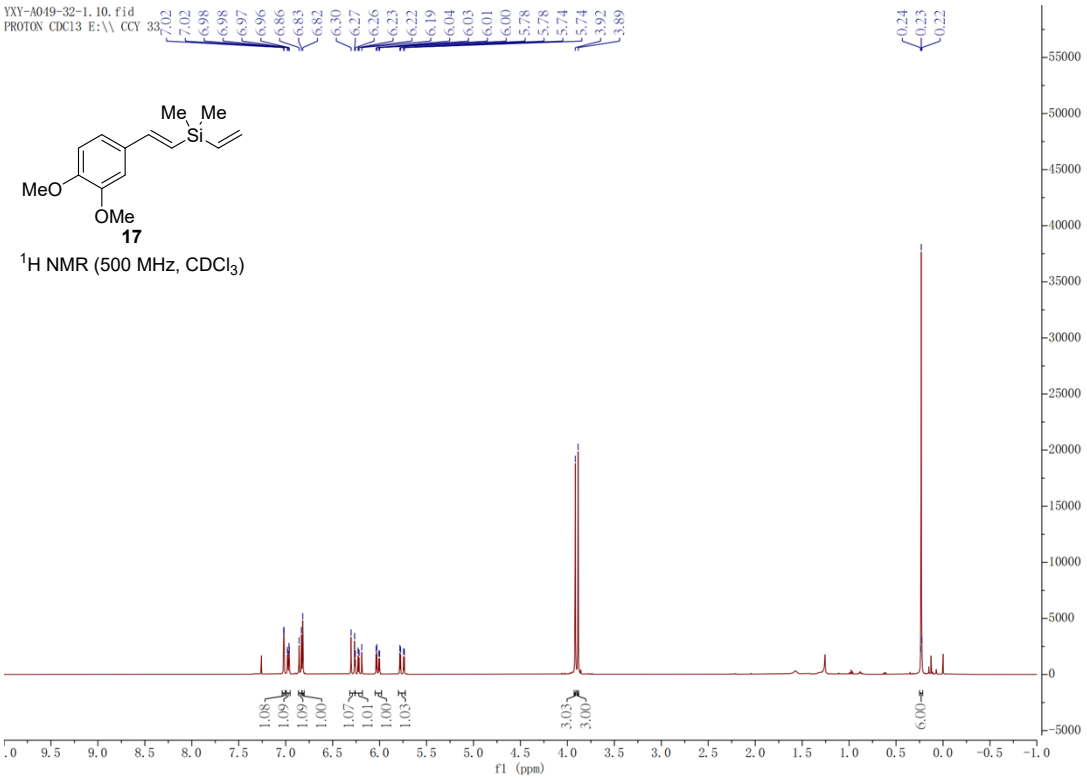
16

^{1}H NMR (500 MHz, $CDCl_3$)

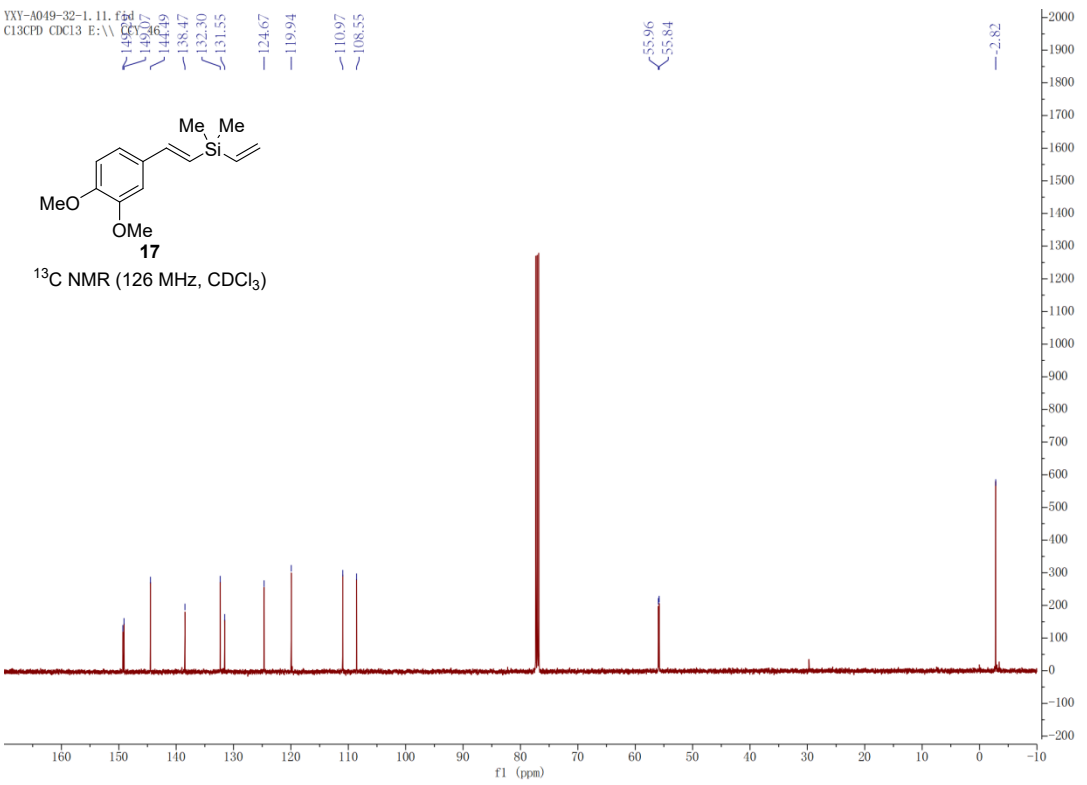


16

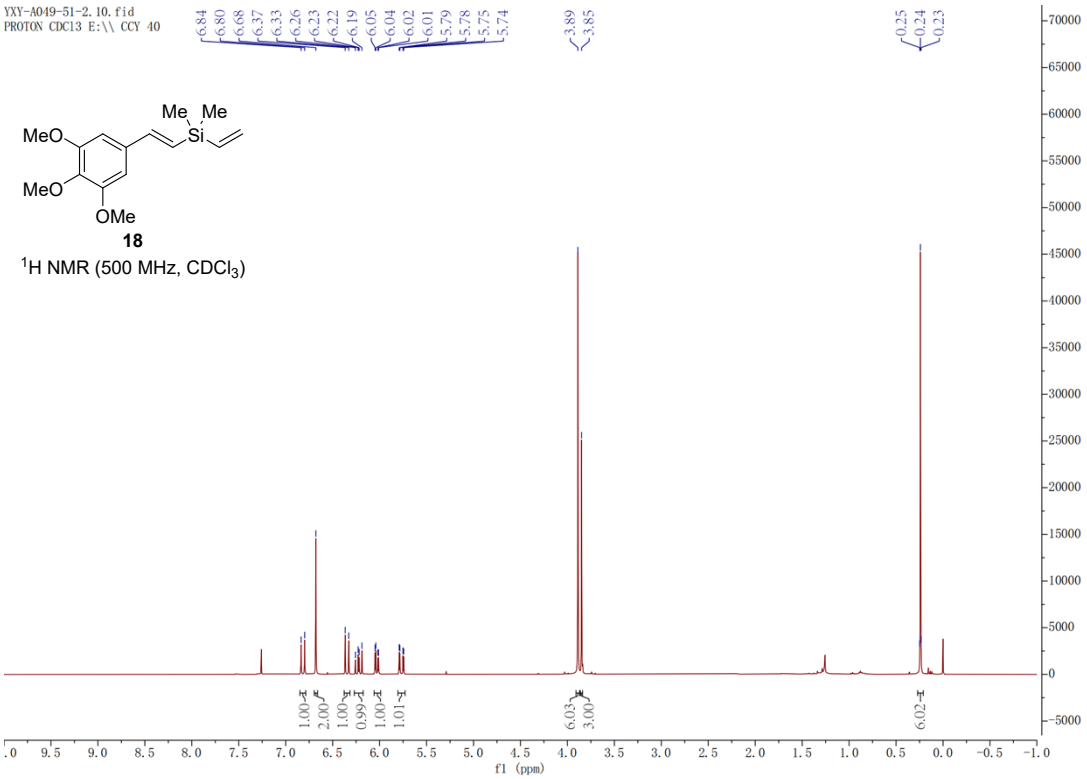
^{13}C NMR (126 MHz, $CDCl_3$)



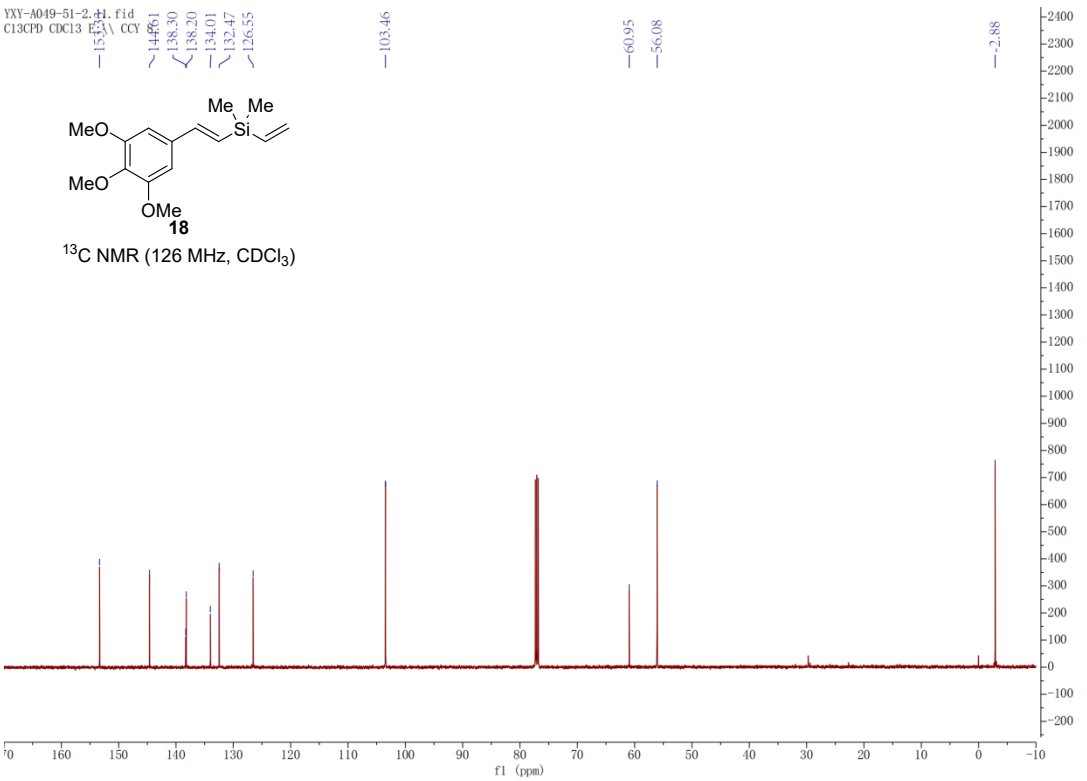
^{1}H NMR (500 MHz, $CDCl_3$)



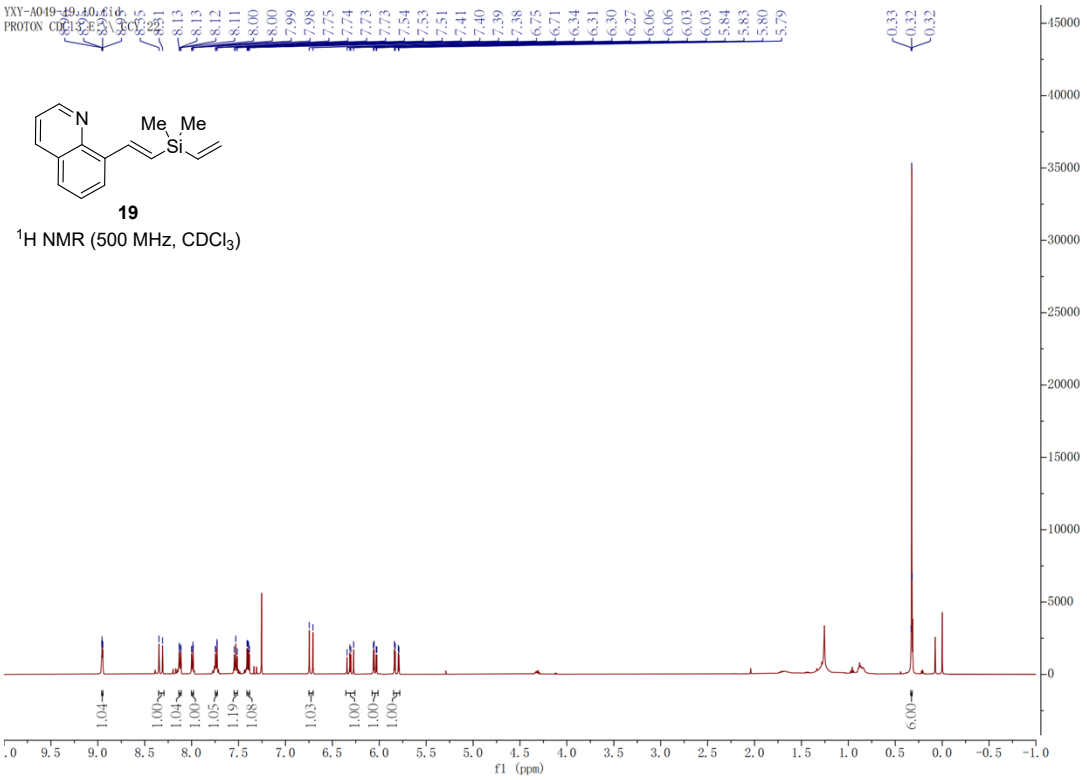
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

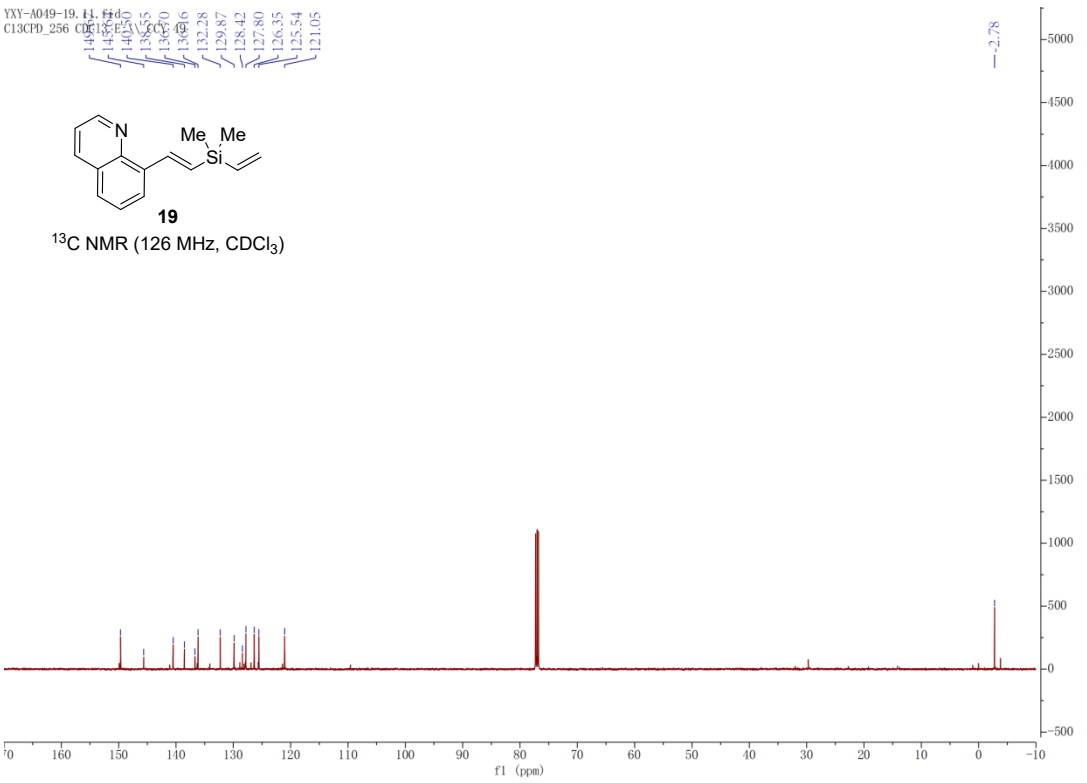


^{13}C NMR (126 MHz, $CDCl_3$)



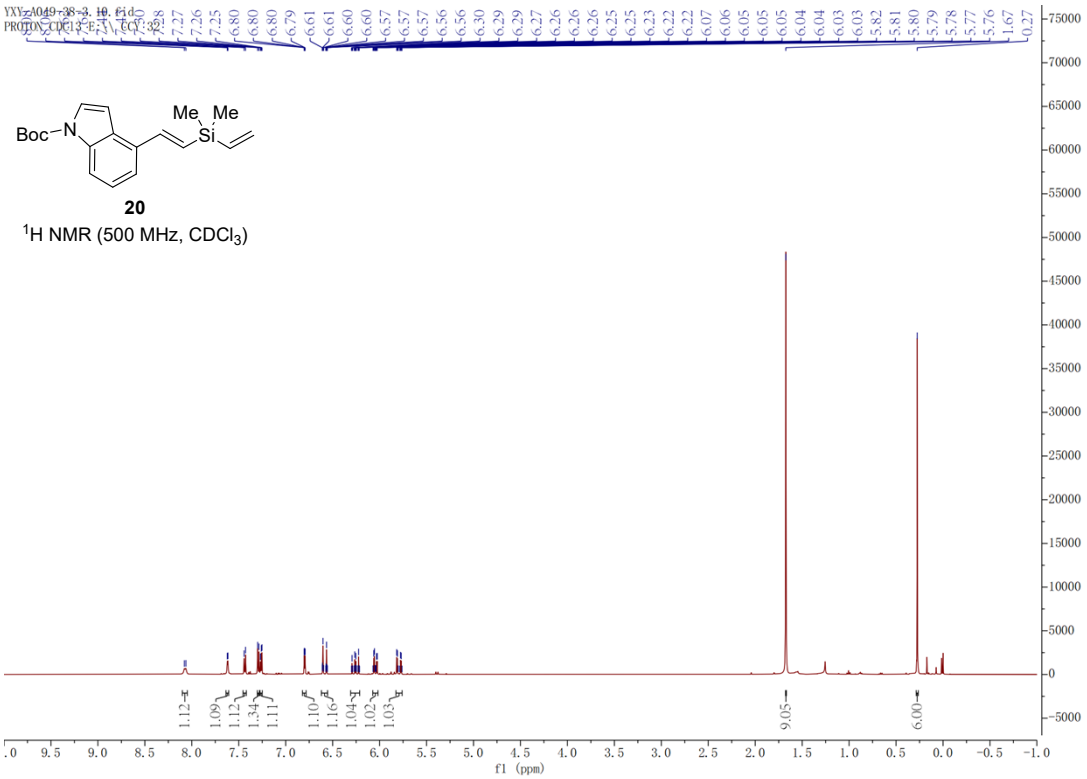
19

^{1}H NMR (500 MHz, $CDCl_3$)



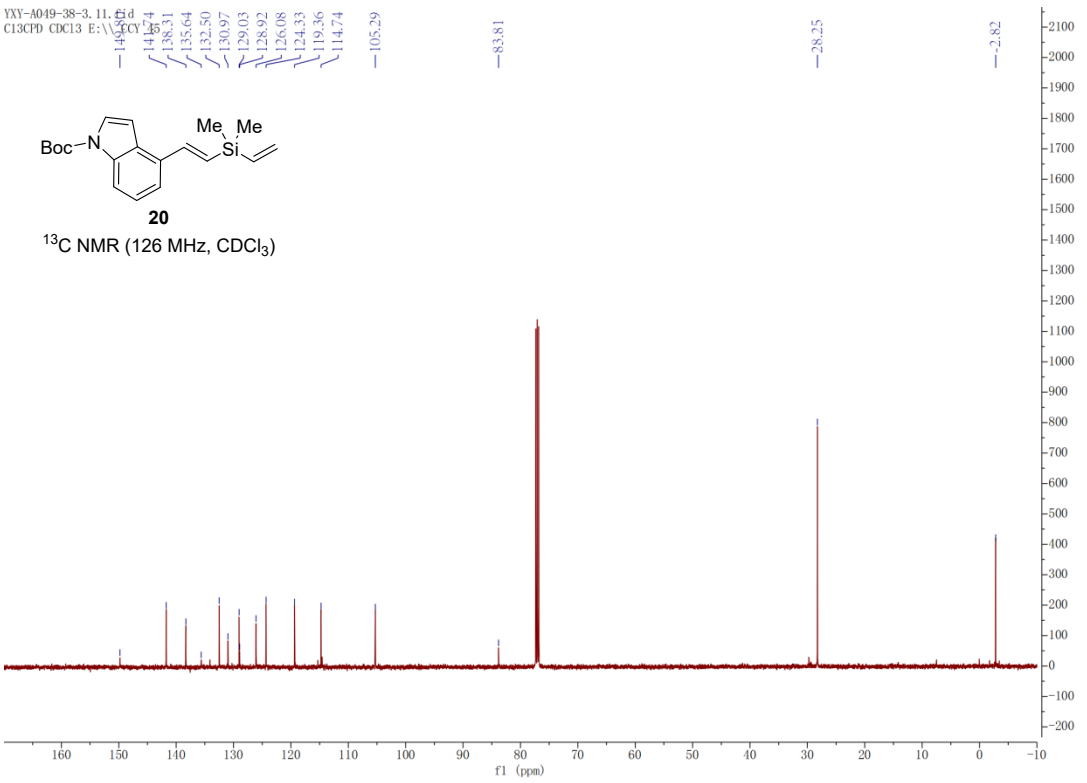
19

^{13}C NMR (126 MHz, $CDCl_3$)



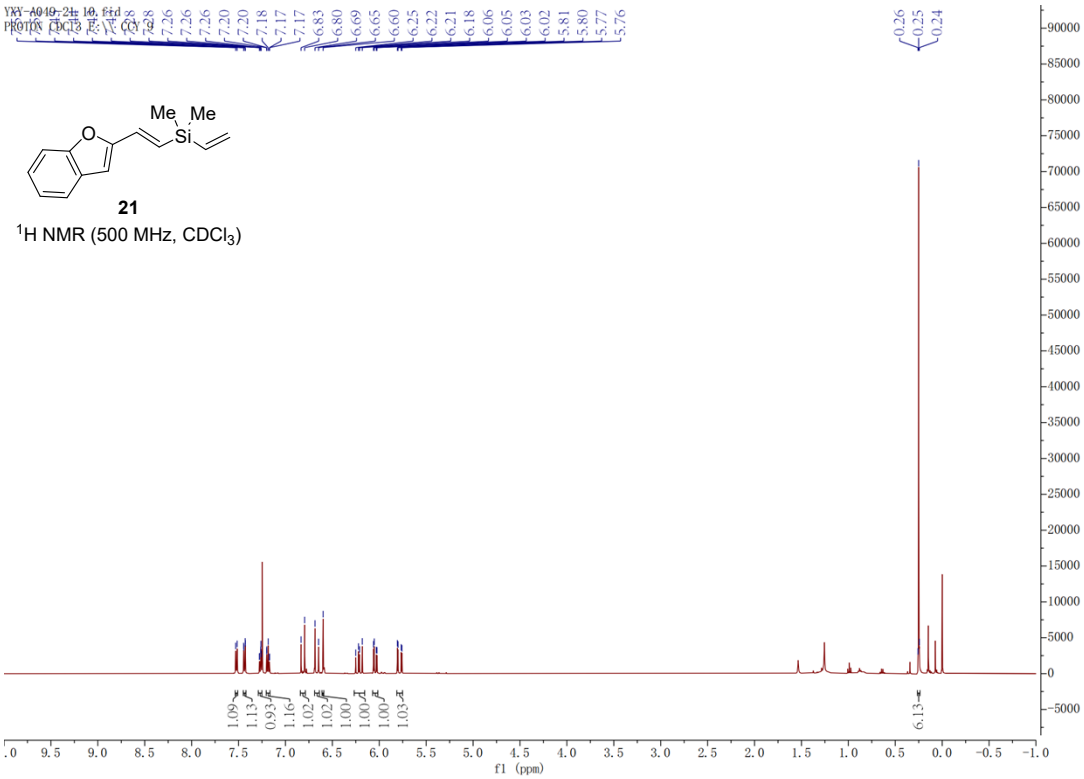
20

^{1}H NMR (500 MHz, $CDCl_3$)



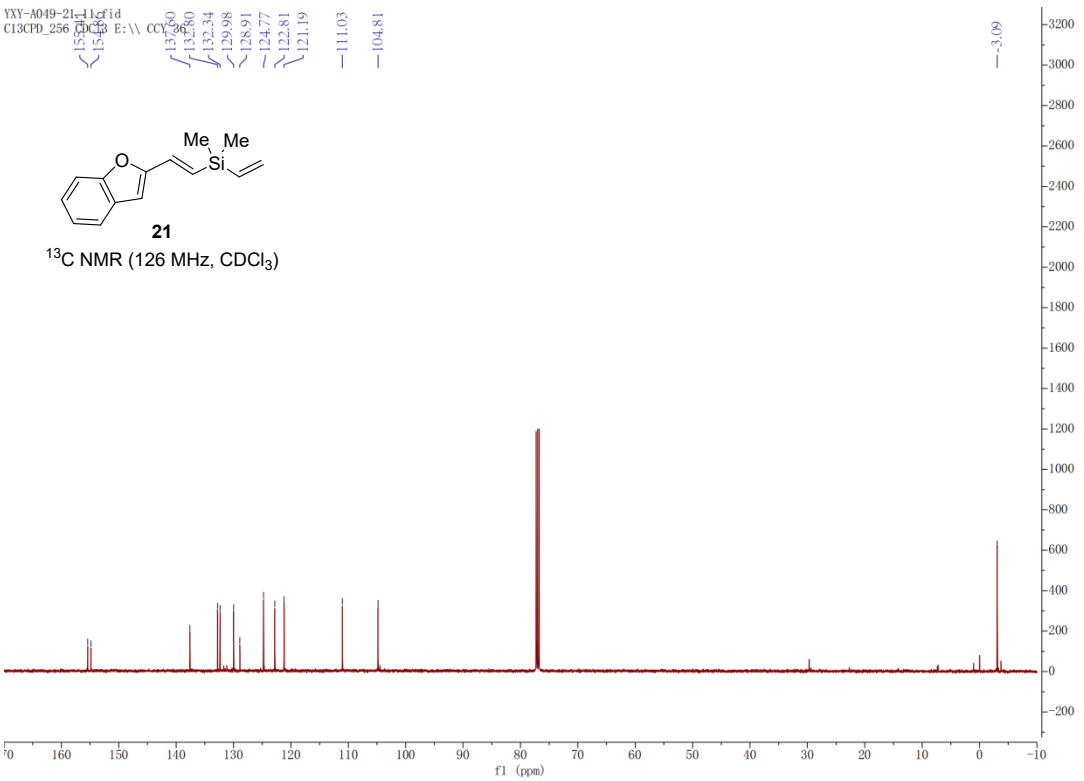
20

^{13}C NMR (126 MHz, $CDCl_3$)



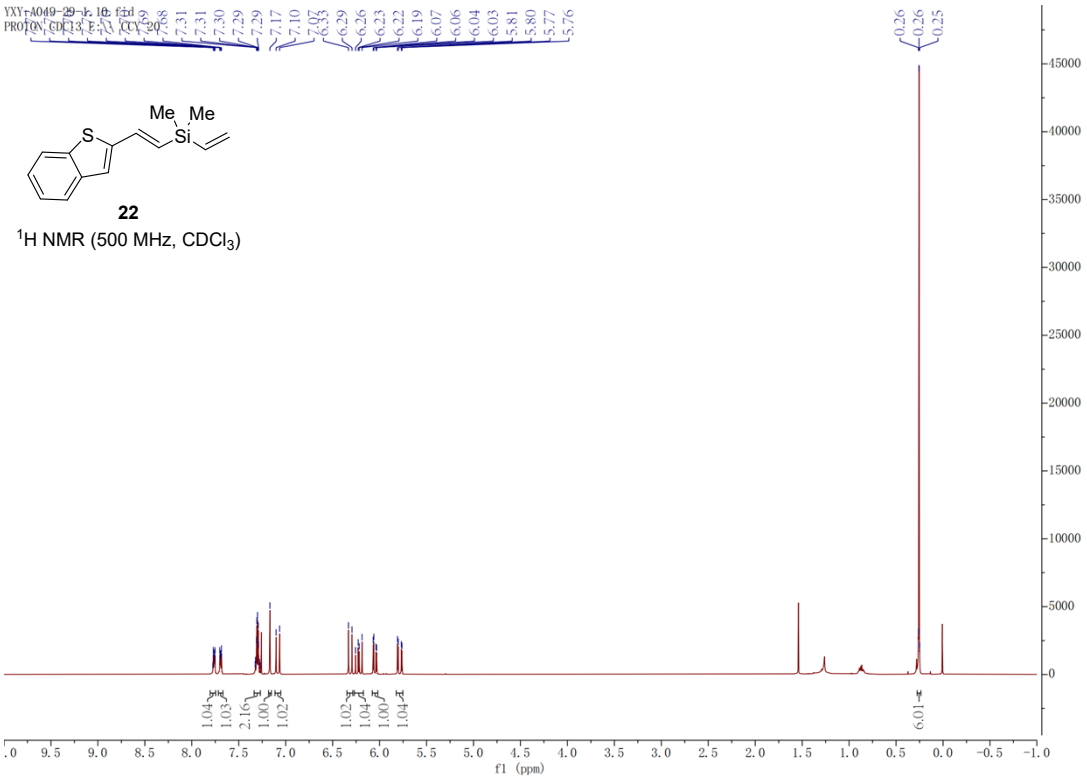
21

^{1}H NMR (500 MHz, $CDCl_3$)



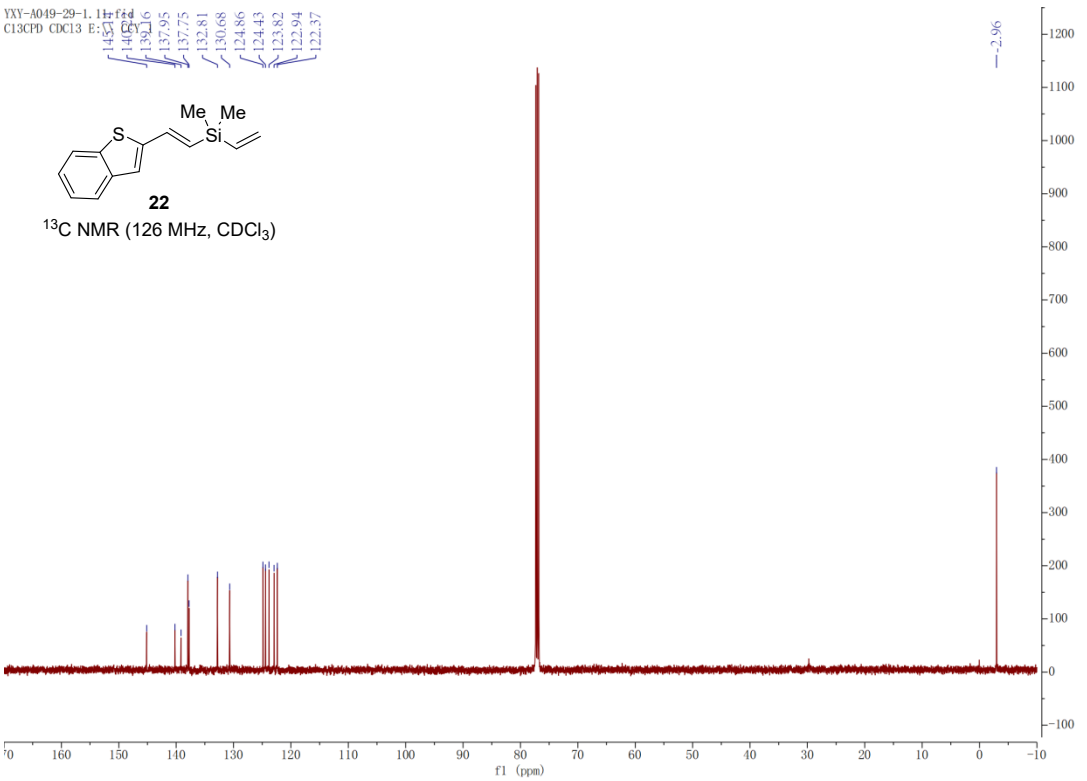
21

^{13}C NMR (126 MHz, $CDCl_3$)



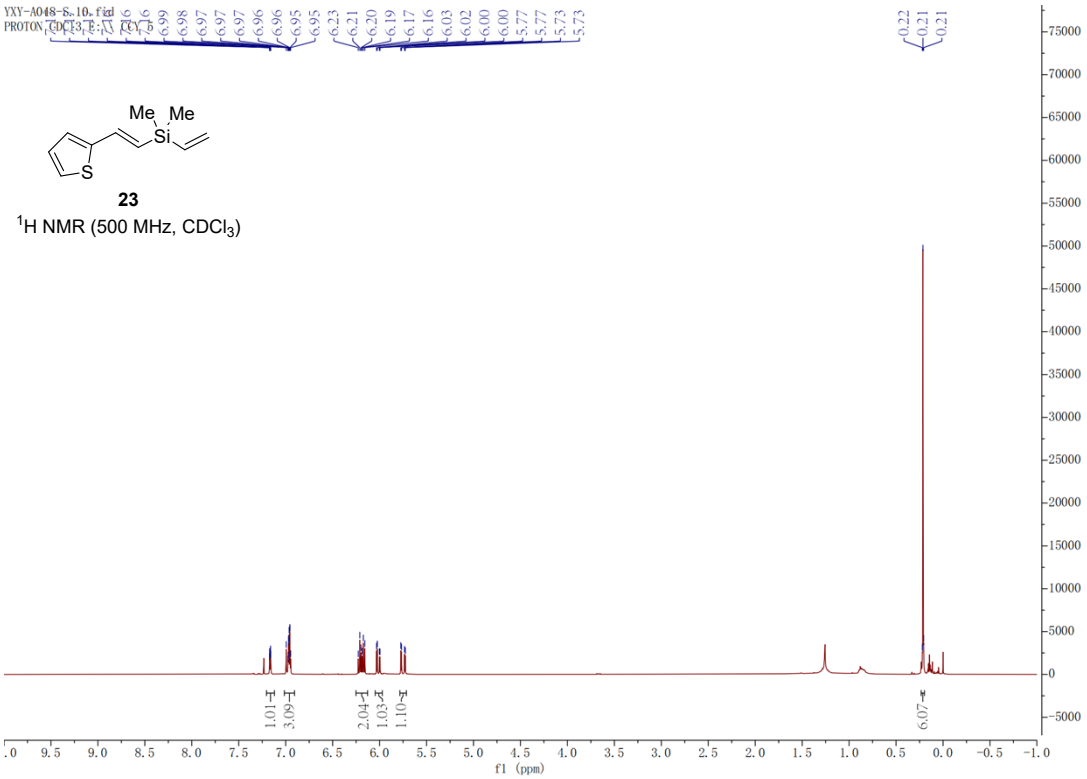
22

^{1}H NMR (500 MHz, $CDCl_3$)



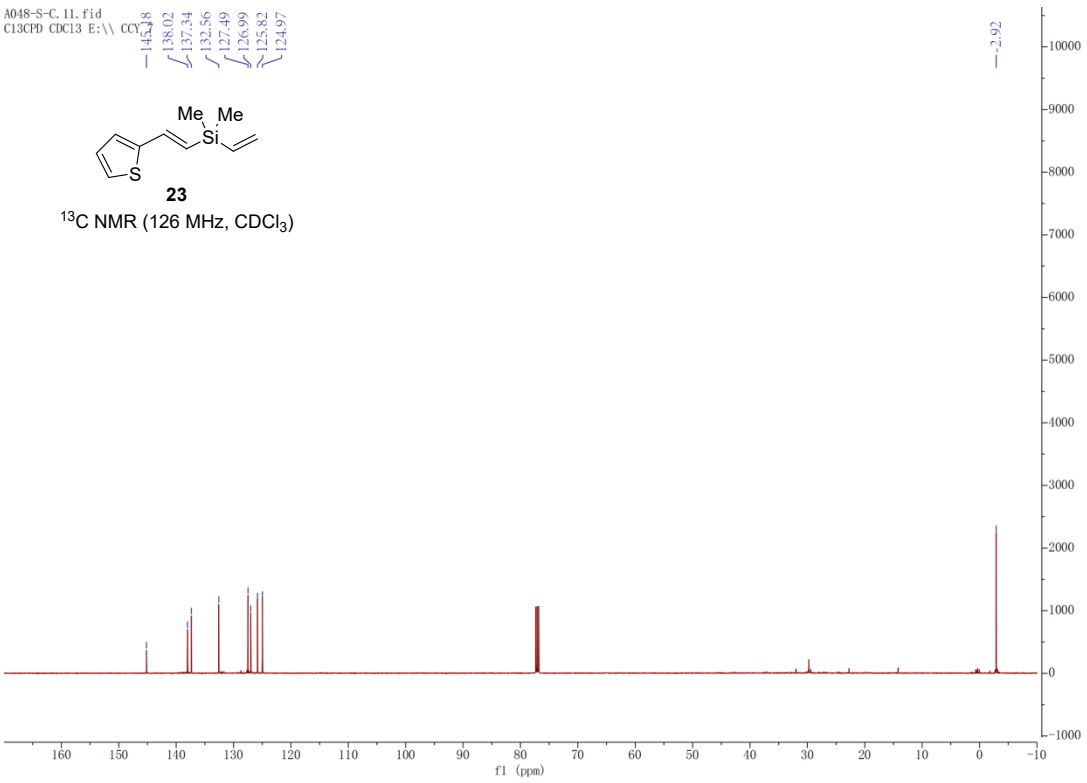
22

^{13}C NMR (126 MHz, $CDCl_3$)



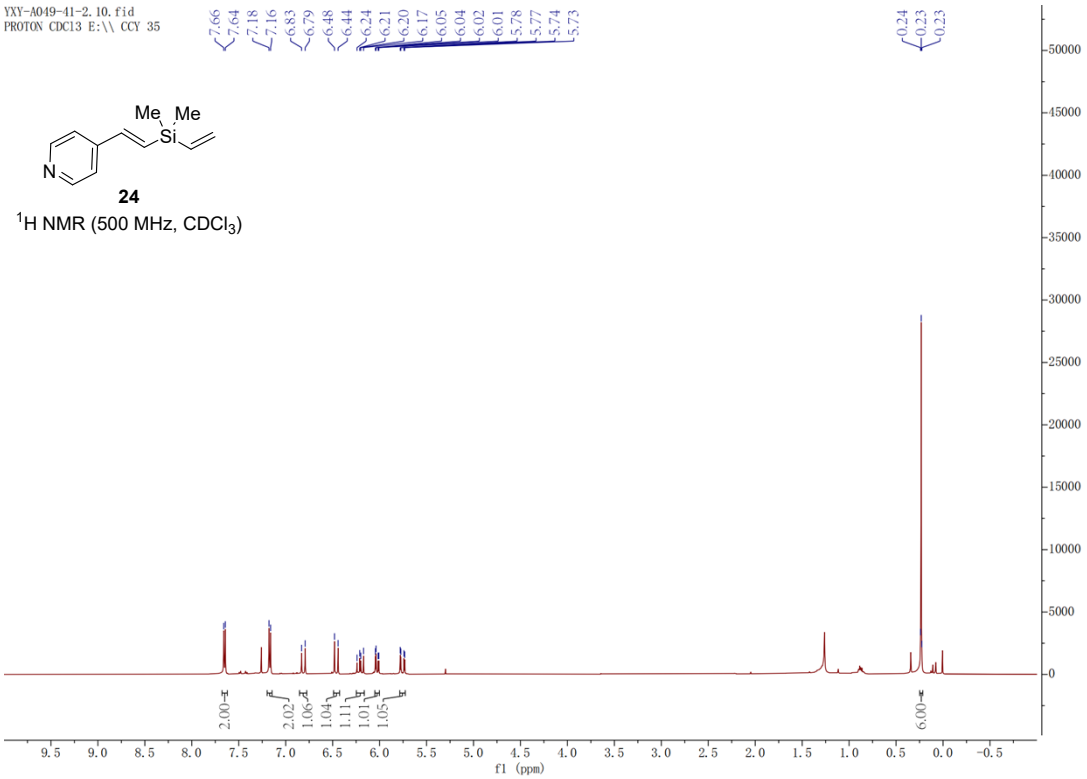
23

^{1}H NMR (500 MHz, $CDCl_3$)



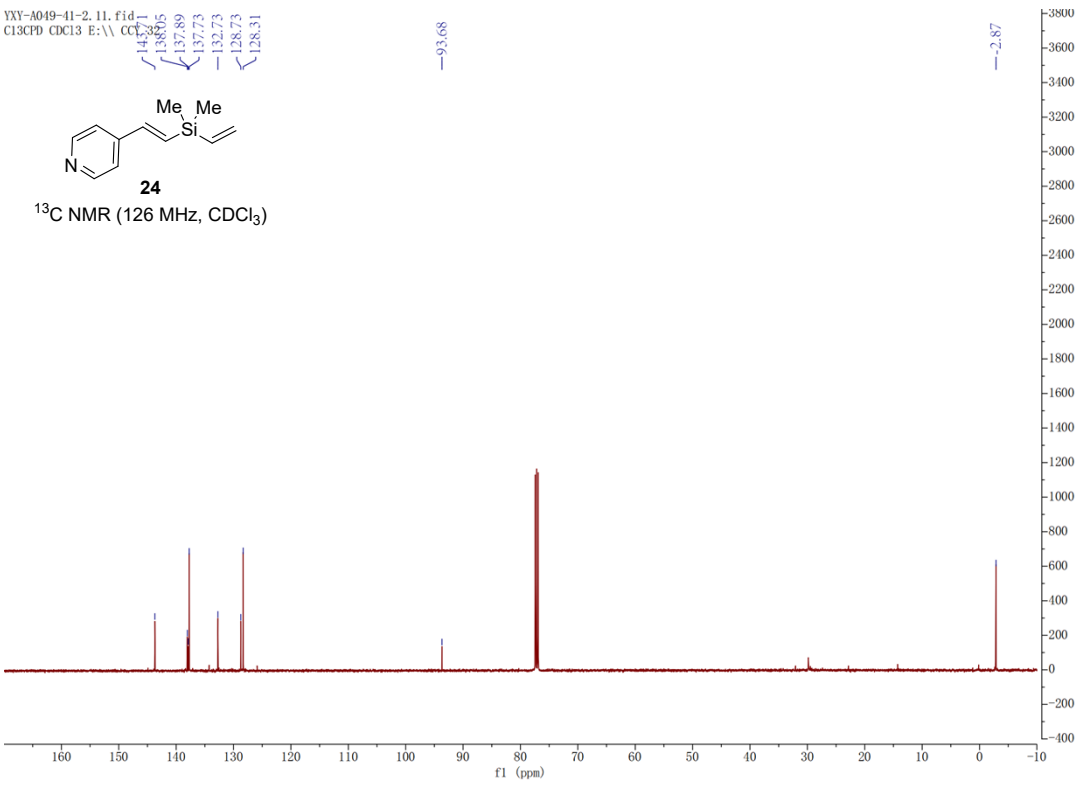
23

^{13}C NMR (126 MHz, $CDCl_3$)



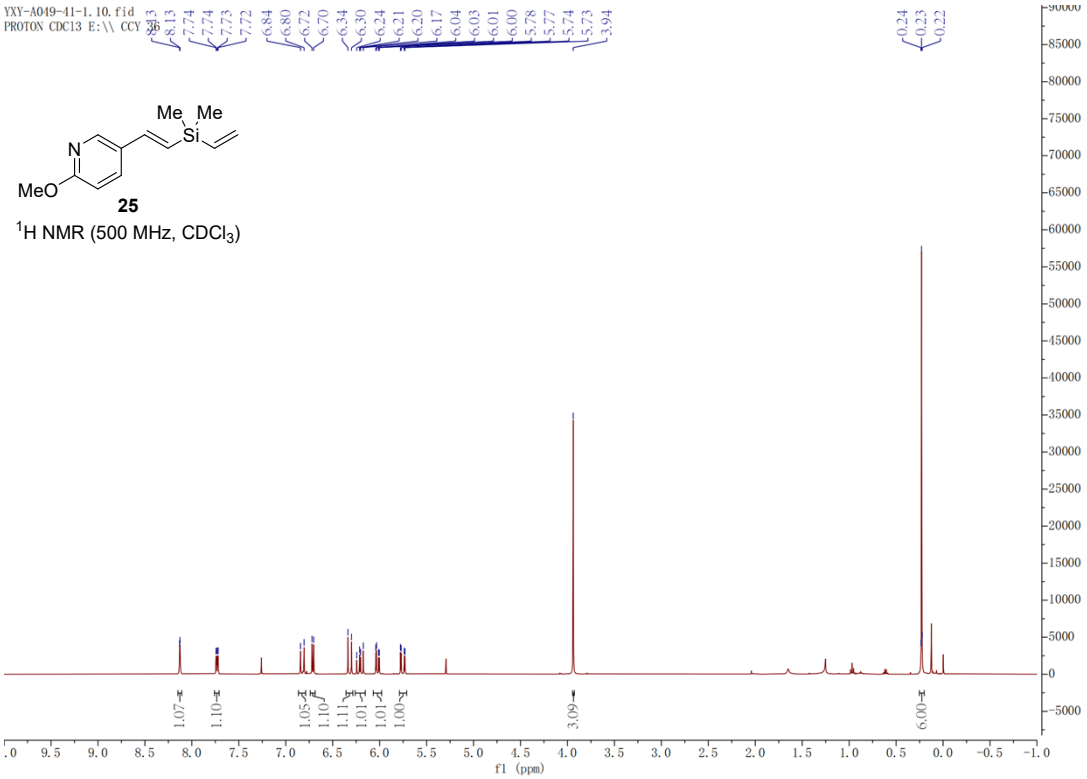
24

^{1}H NMR (500 MHz, $CDCl_3$)



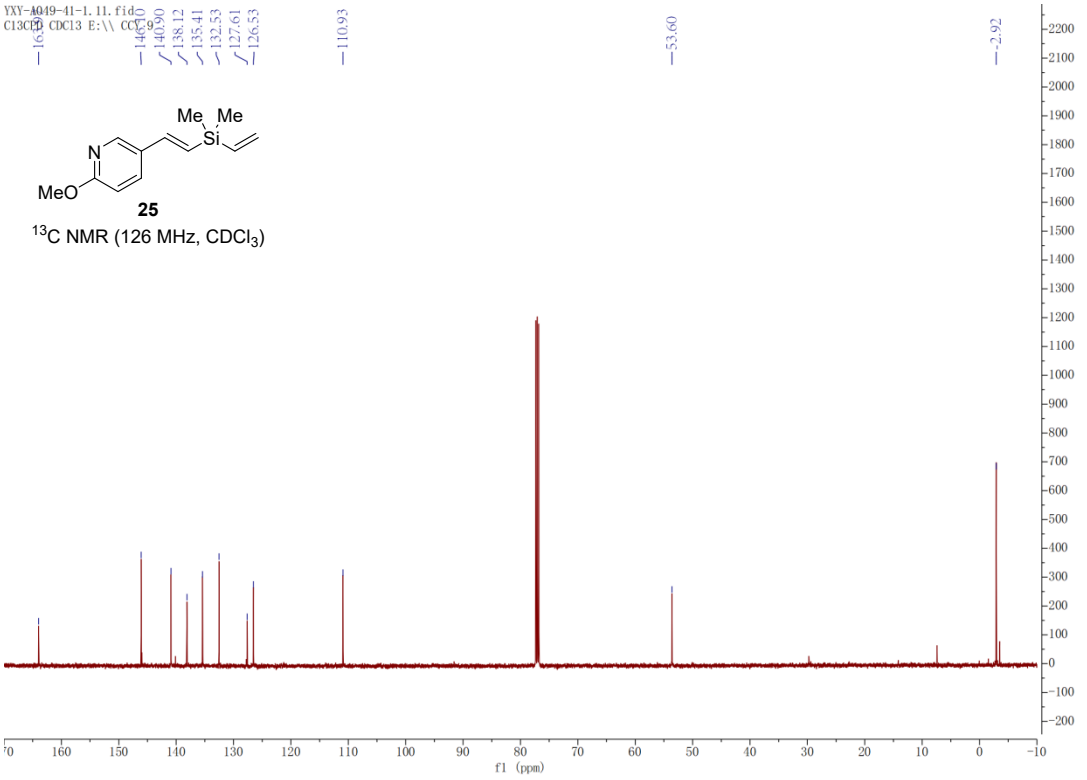
24

^{13}C NMR (126 MHz, $CDCl_3$)



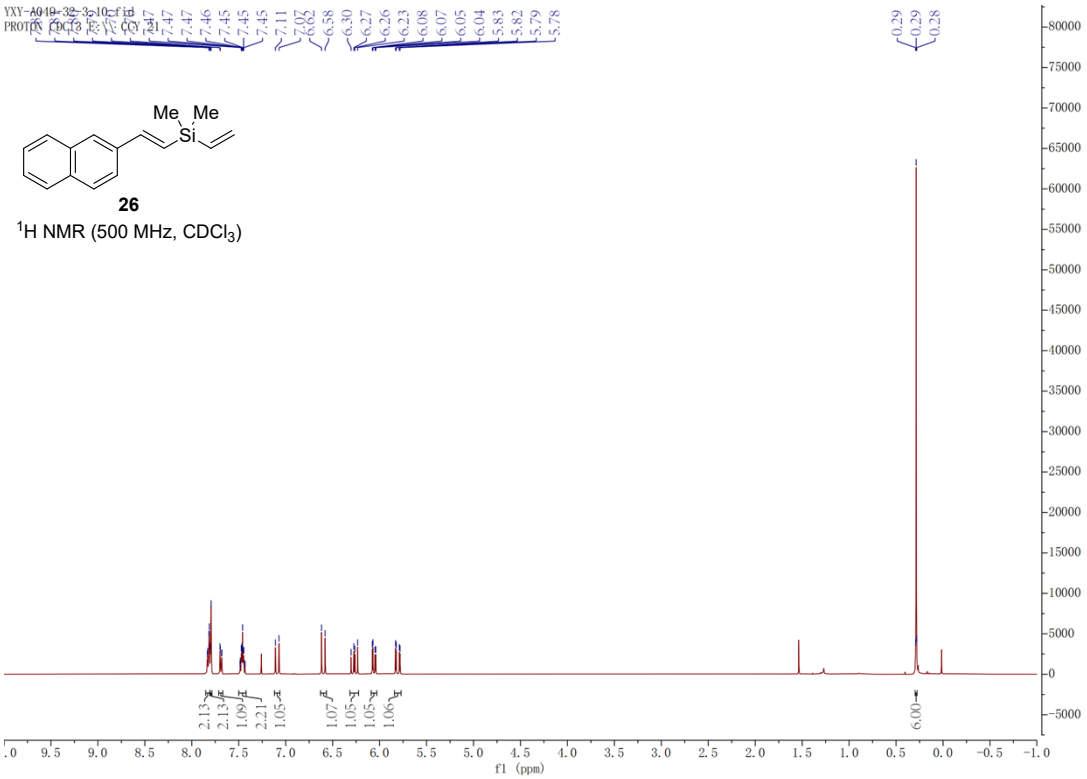
25

^{1}H NMR (500 MHz, $CDCl_3$)



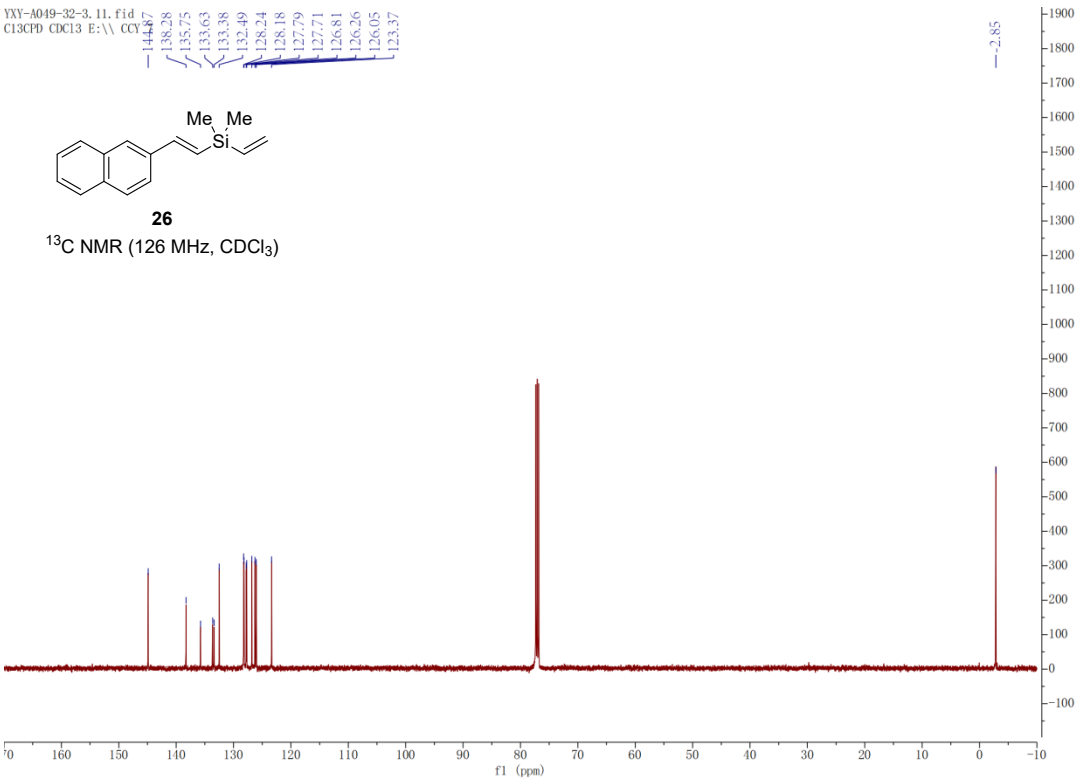
25

^{13}C NMR (126 MHz, $CDCl_3$)



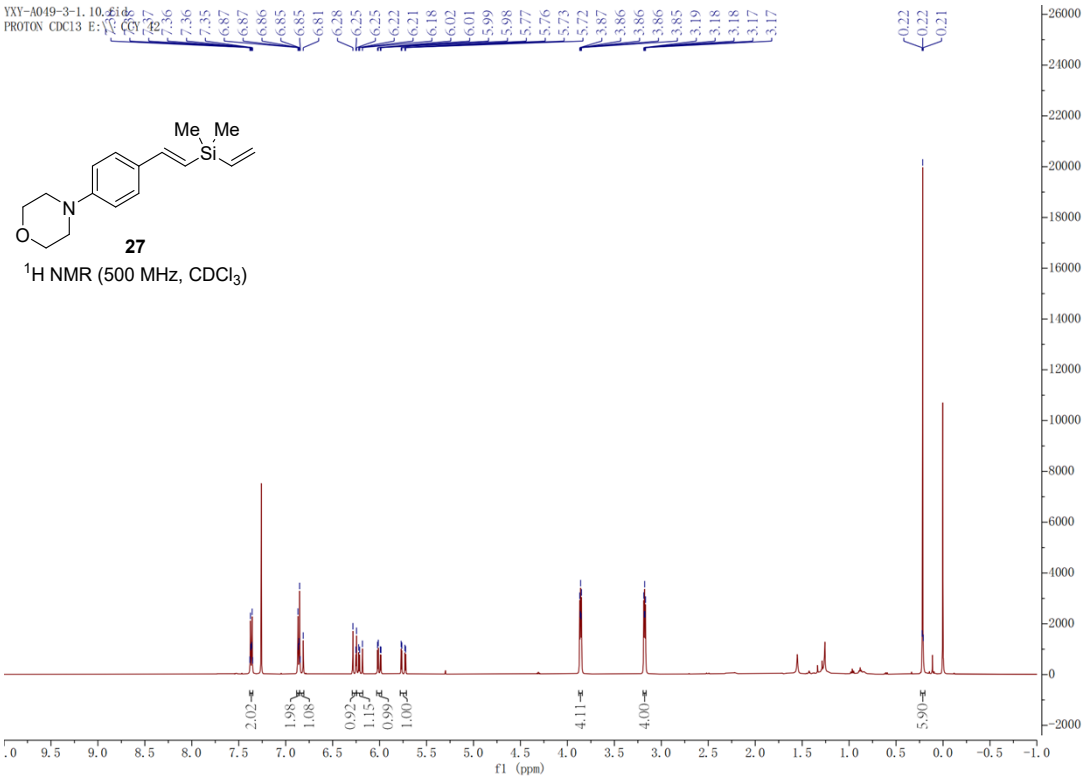
26

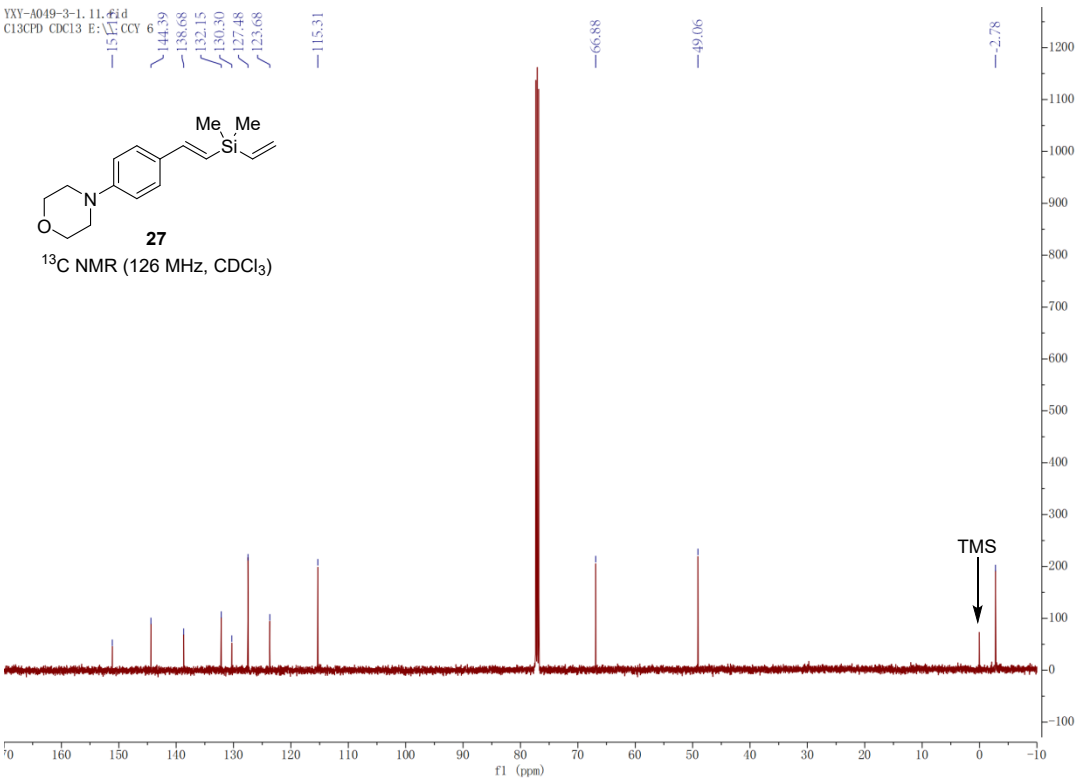
^{1}H NMR (500 MHz, $CDCl_3$)

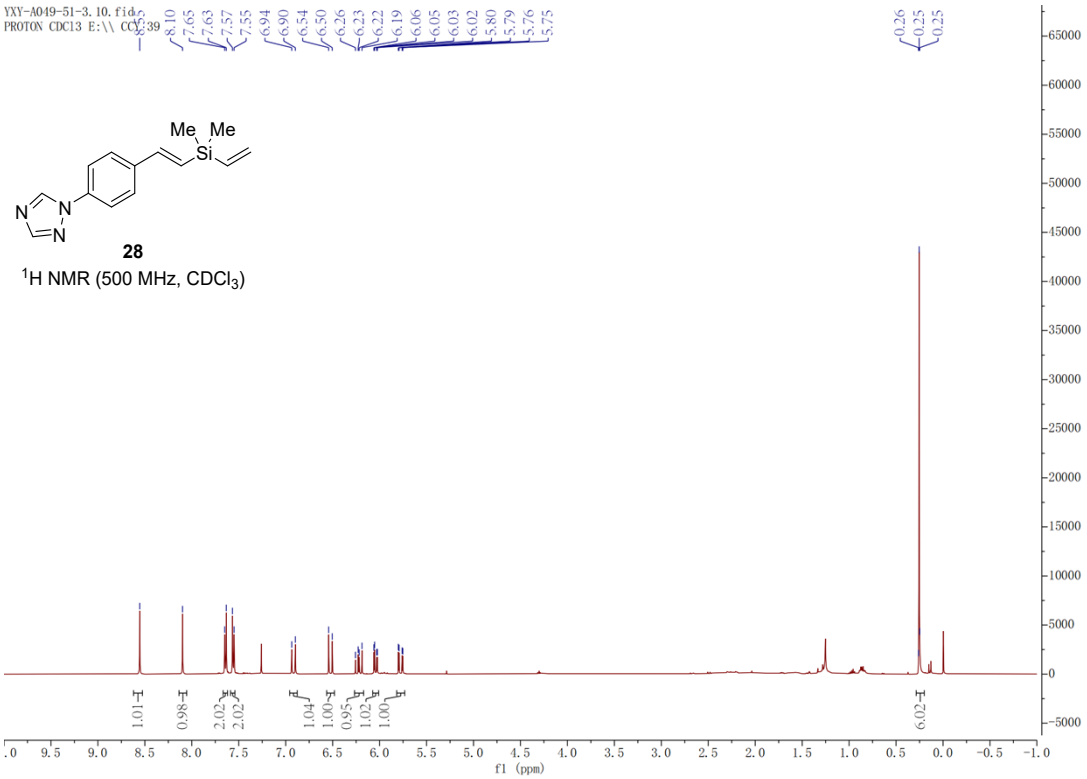


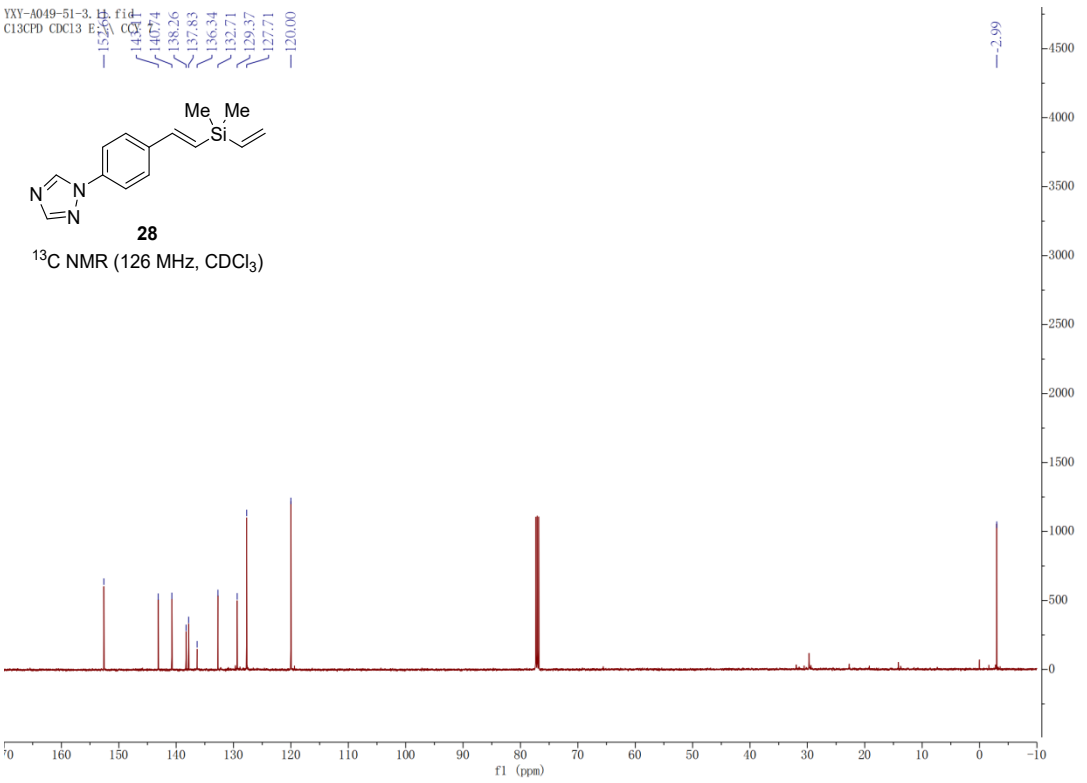
26

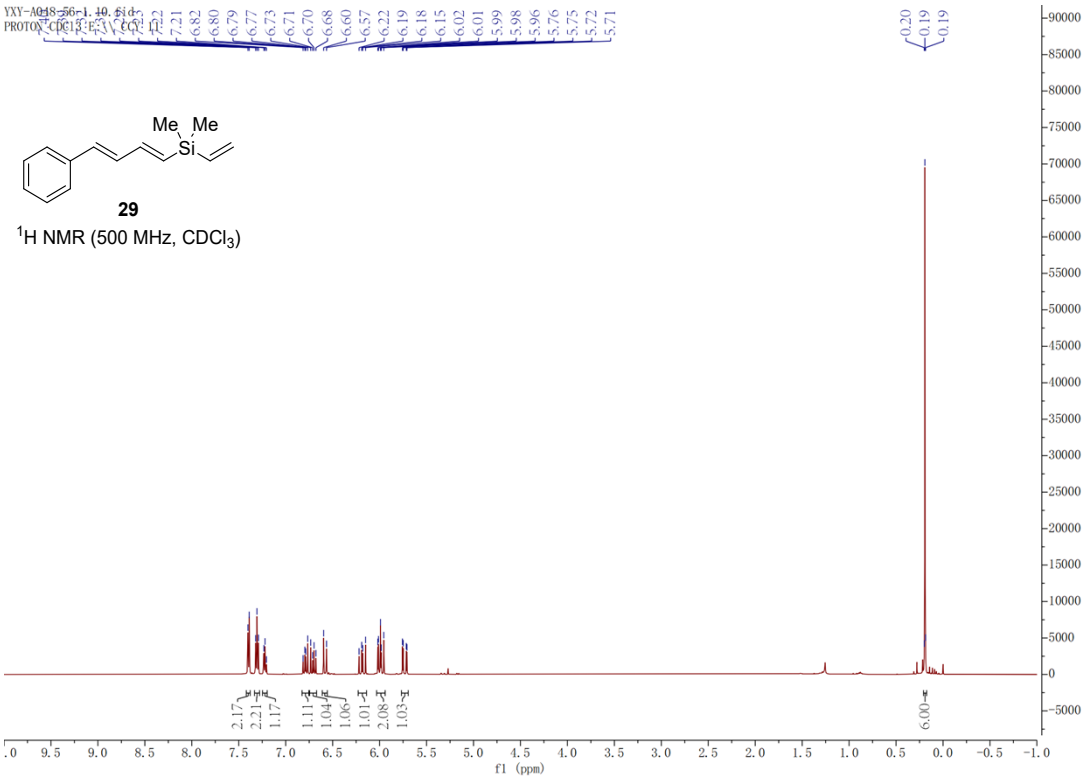
^{13}C NMR (126 MHz, $CDCl_3$)


Me Me
Si
N
O
27
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Me Me
Si
N
O
27
13C NMR (126 MHz, CDCl3)
TMS
f1 (ppm)

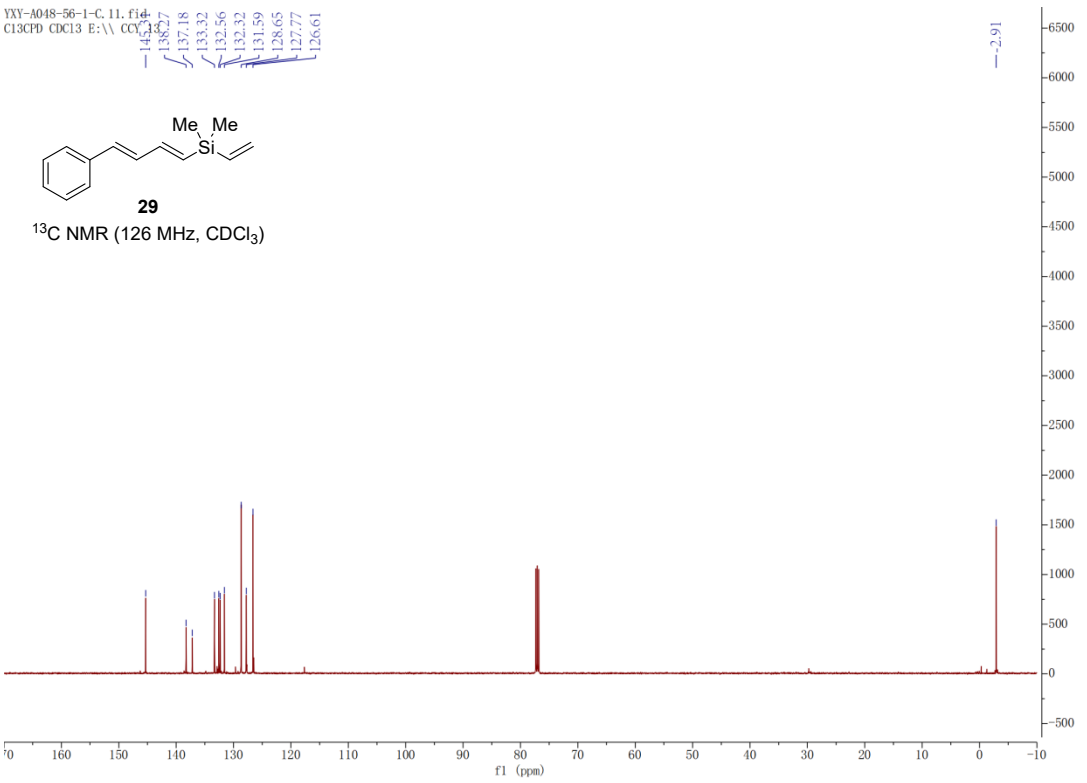

YXY-A049-51-3.10.fid
PROTON CDCl3 E:\\ CCU39
8.10
7.65
7.63
7.57
7.55
6.94
6.90
6.54
6.50
6.26
6.23
6.22
6.19
6.06
6.05
6.03
6.02
5.80
5.79
5.76
5.75
0.26
0.25
0.25
Me
Me
Si
N
N
N
28
1H NMR (500 MHz, CDCl3)
1.01
0.98
2.02
2.02
1.04
1.00
0.95
1.02
1.00
6.02
f1 (ppm)


YXY-A049-51-3.11.fid
C13CPD CDCl3 E:\\ CCU
152.64
143.41
140.74
138.26
137.83
136.34
132.71
129.37
127.71
120.00
77.24
77.00
76.75
-2.99
Me
Me
Si
N
N
N
28
13C NMR (126 MHz, CDCl3)
f1 (ppm)



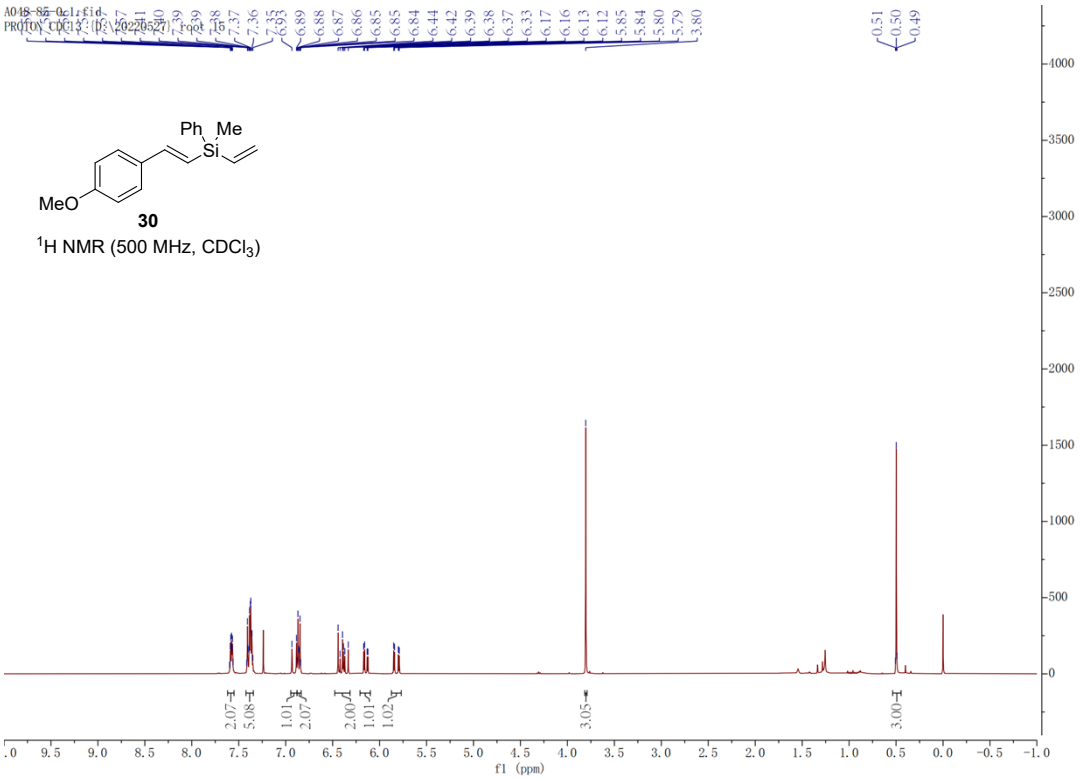
29

^{1}H NMR (500 MHz, $CDCl_3$)



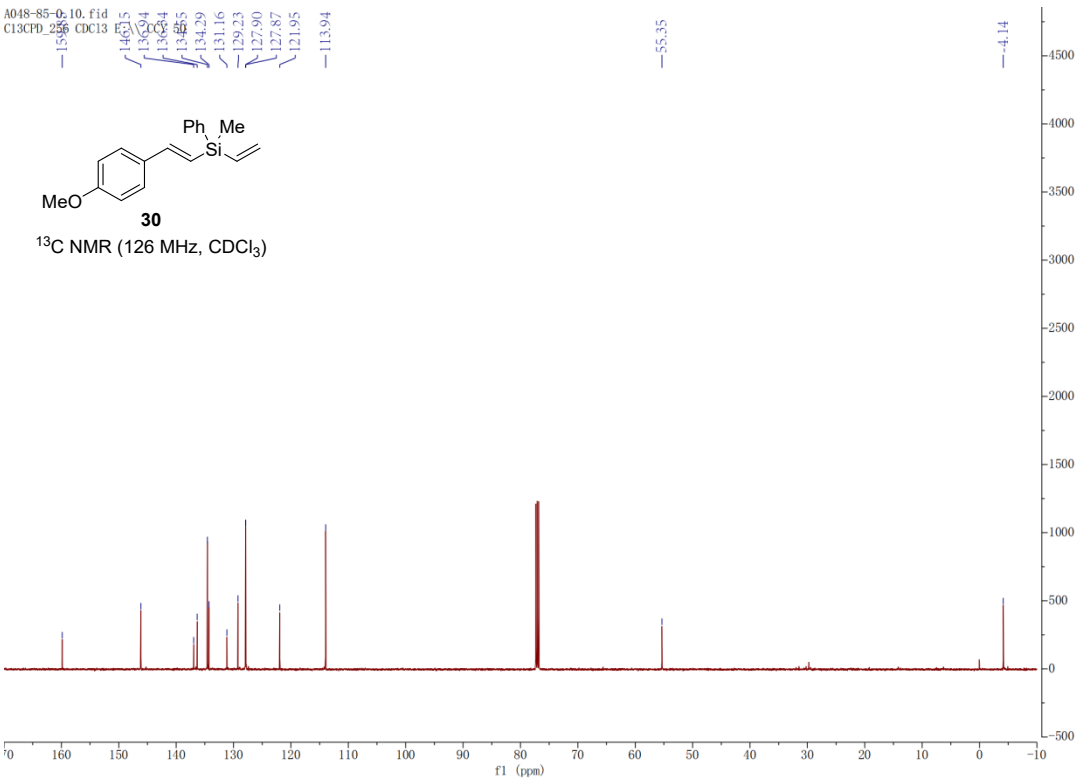
29

^{13}C NMR (126 MHz, $CDCl_3$)



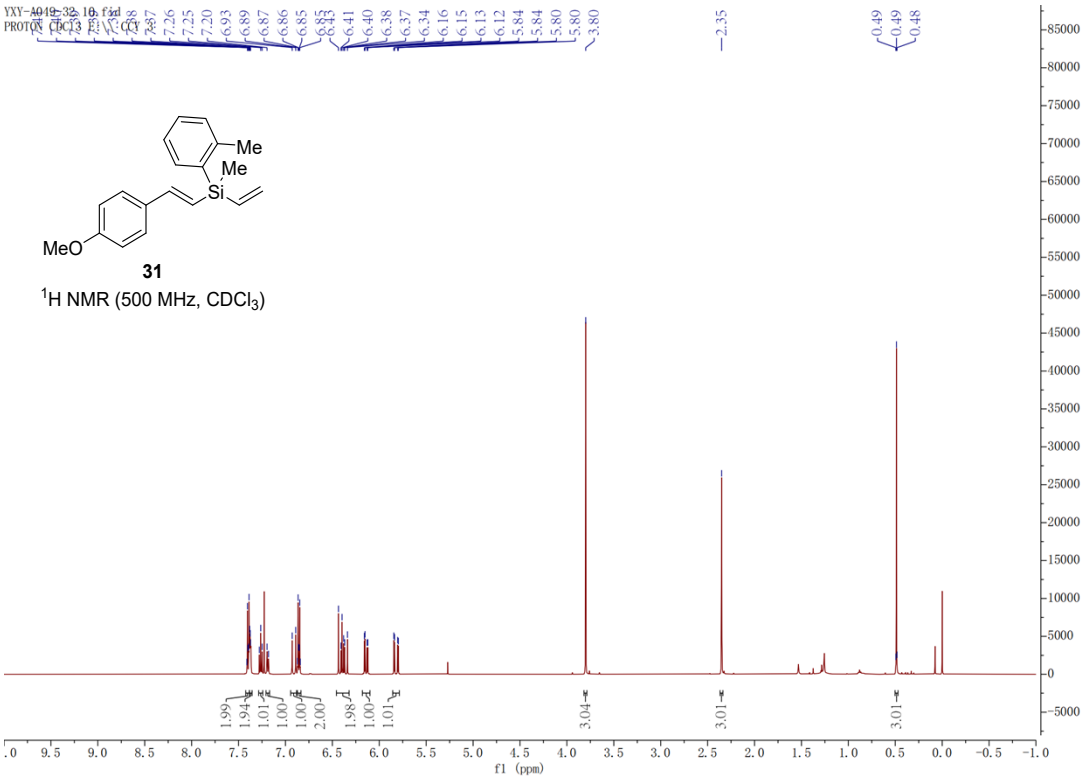
30

^{1}H NMR (500 MHz, $CDCl_3$)



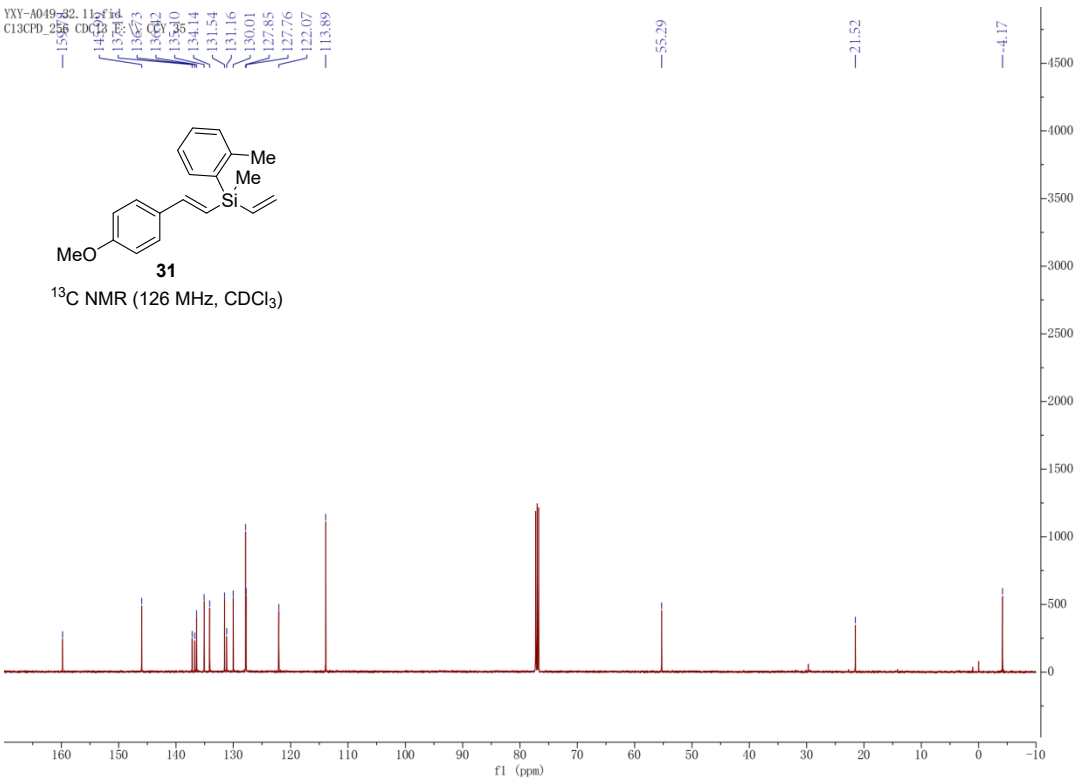
30

^{13}C NMR (126 MHz, $CDCl_3$)



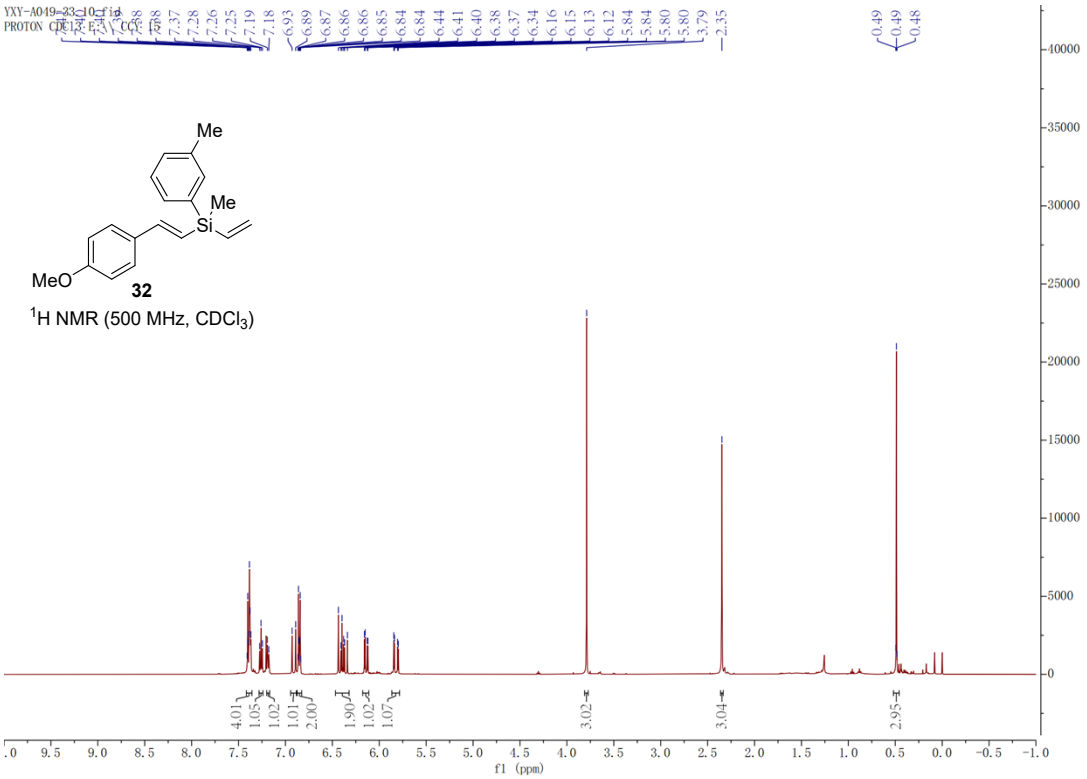
31

^{1}H NMR (500 MHz, $CDCl_3$)



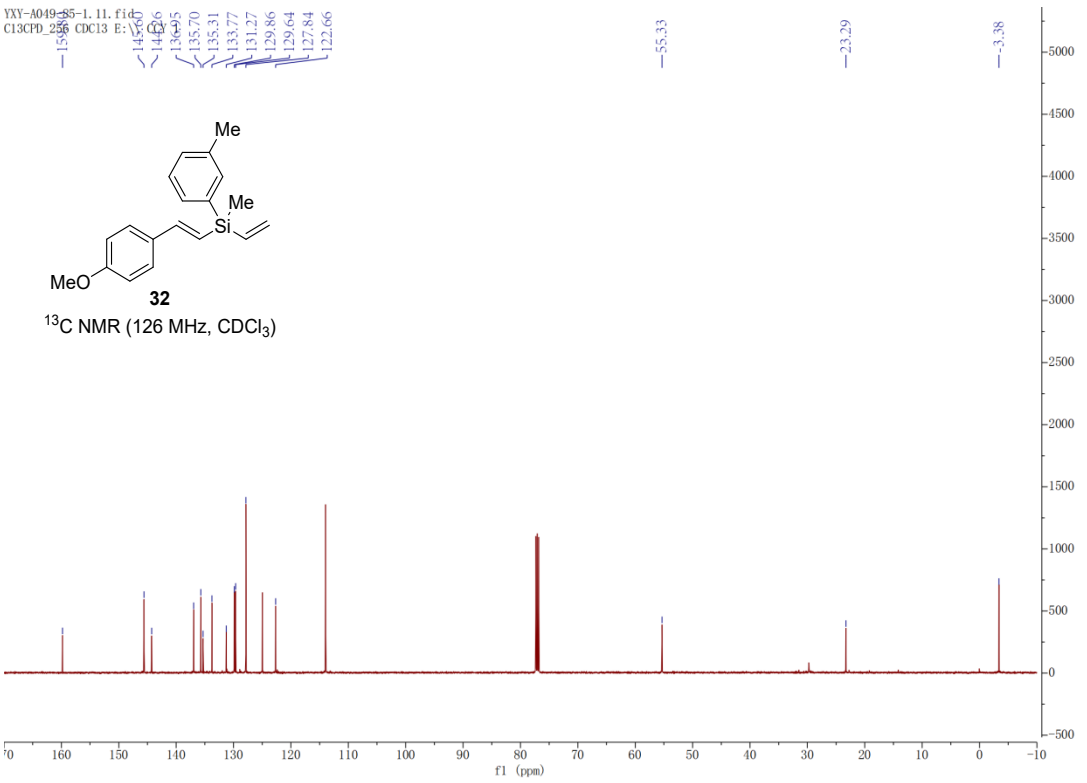
31

^{13}C NMR (126 MHz, $CDCl_3$)



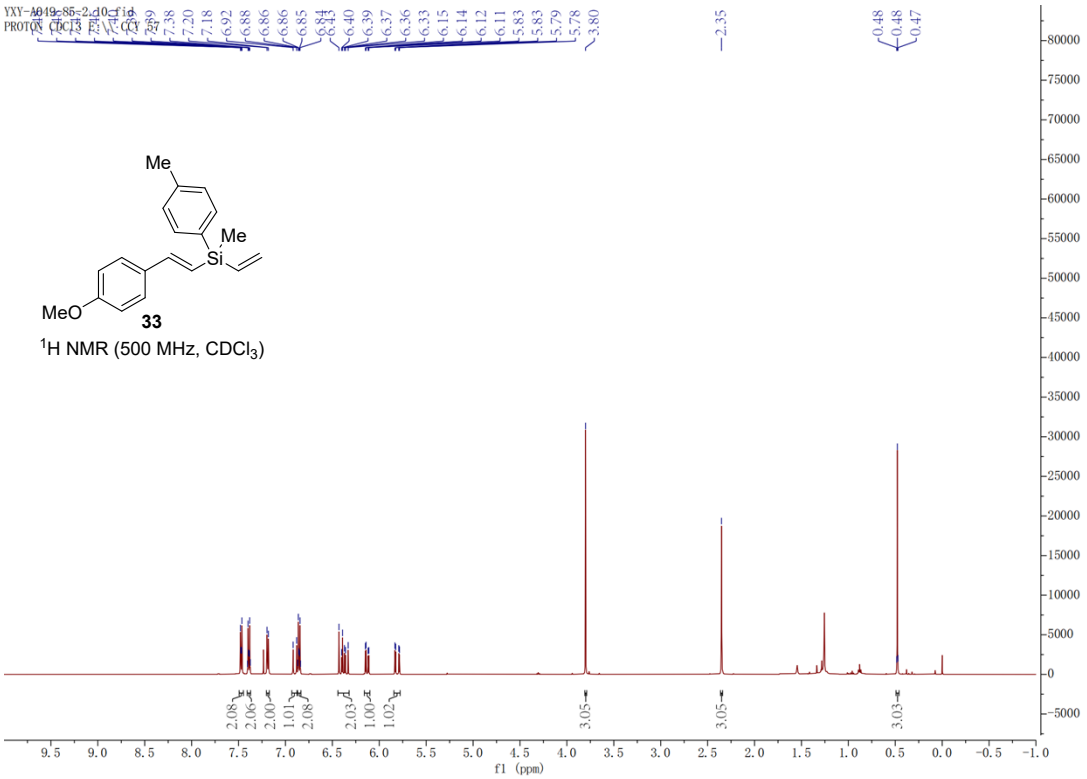
32

^{1}H NMR (500 MHz, $CDCl_3$)



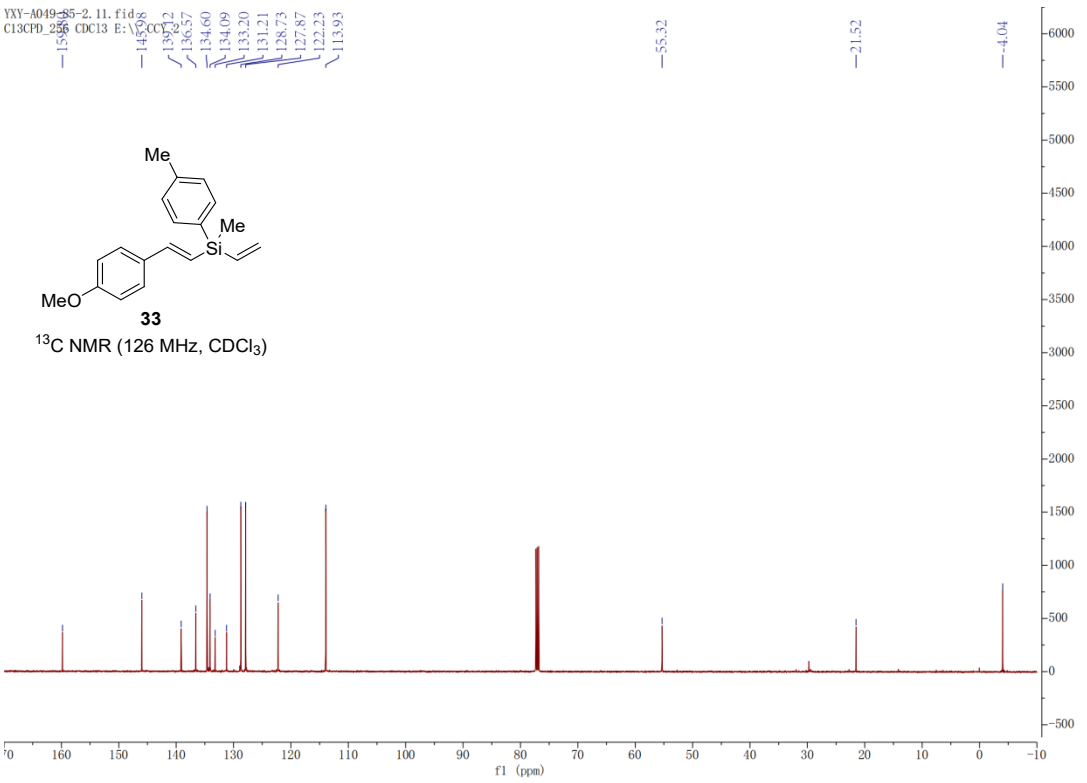
32

^{13}C NMR (126 MHz, $CDCl_3$)



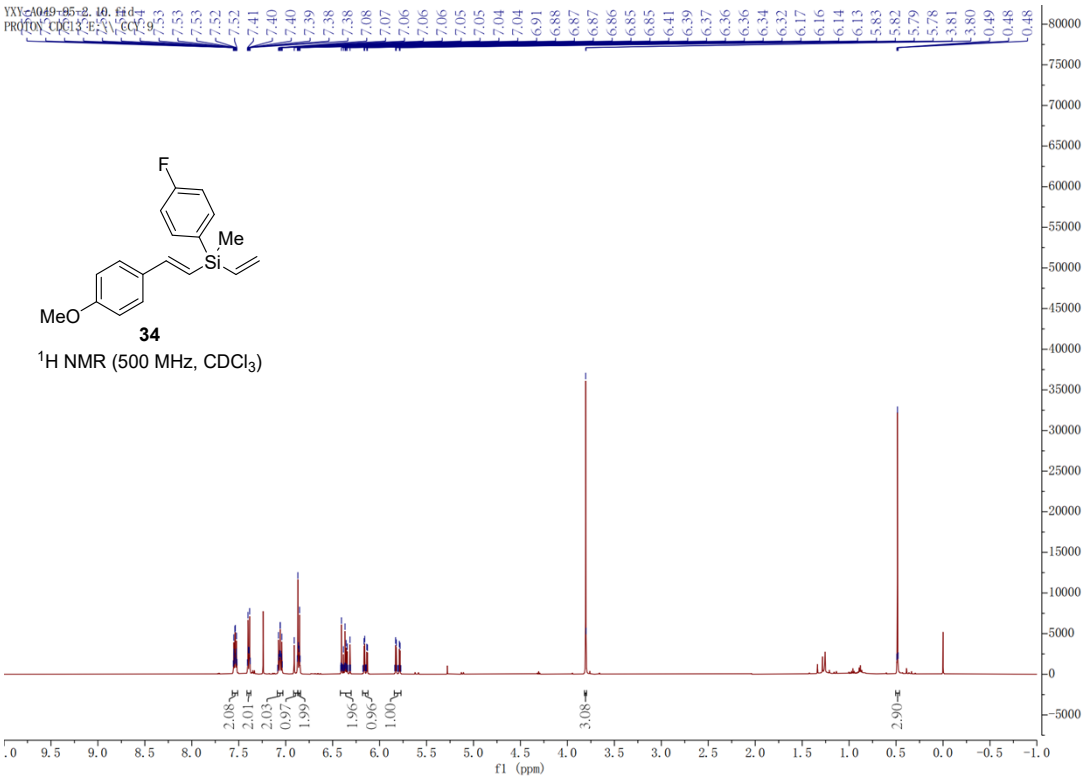
33

^{1}H NMR (500 MHz, $CDCl_3$)



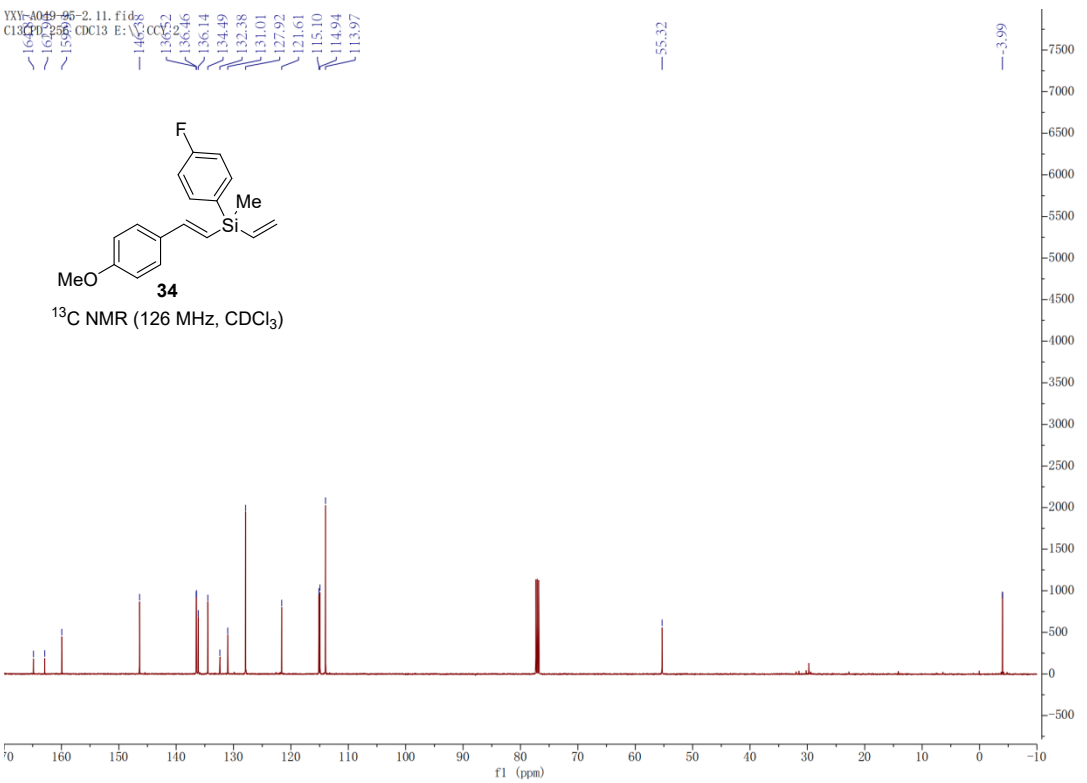
33

^{13}C NMR (126 MHz, $CDCl_3$)



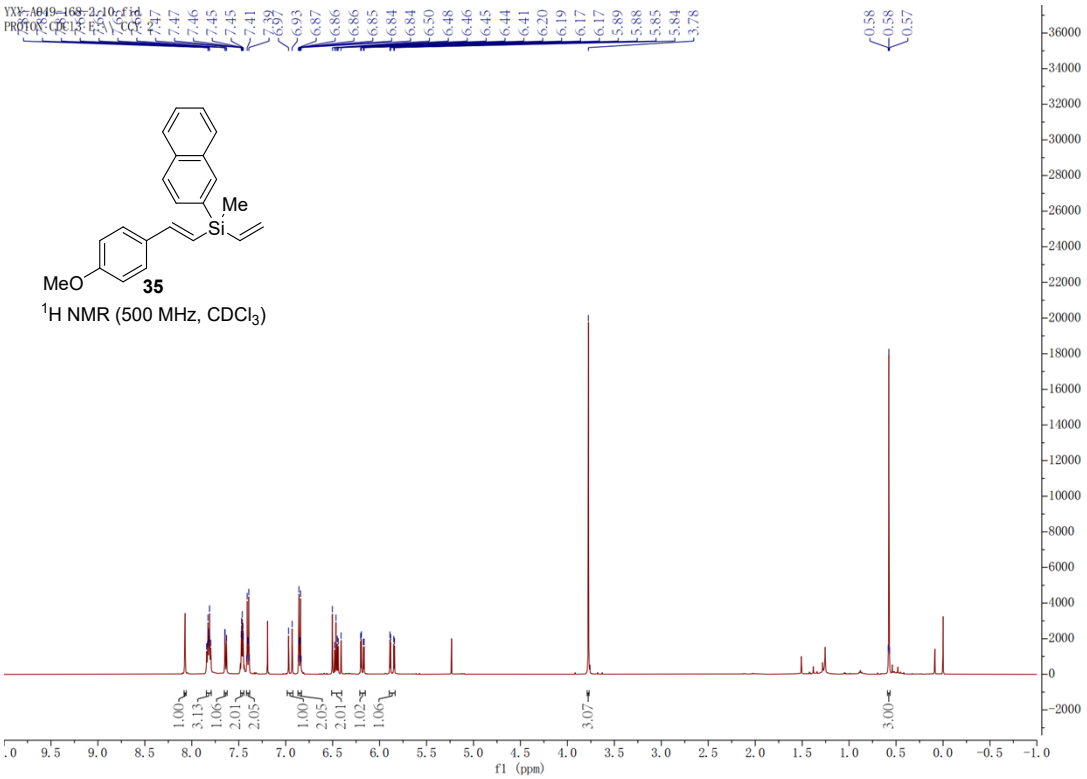
34

^{1}H NMR (500 MHz, $CDCl_3$)



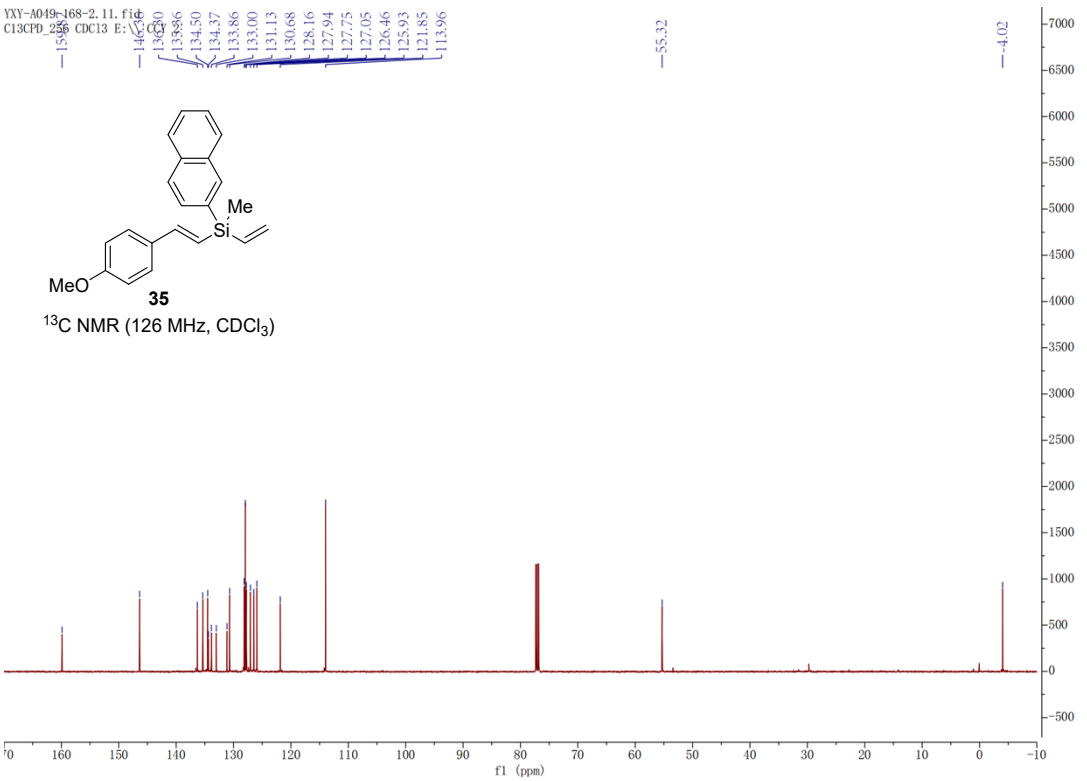
34

^{13}C NMR (126 MHz, $CDCl_3$)



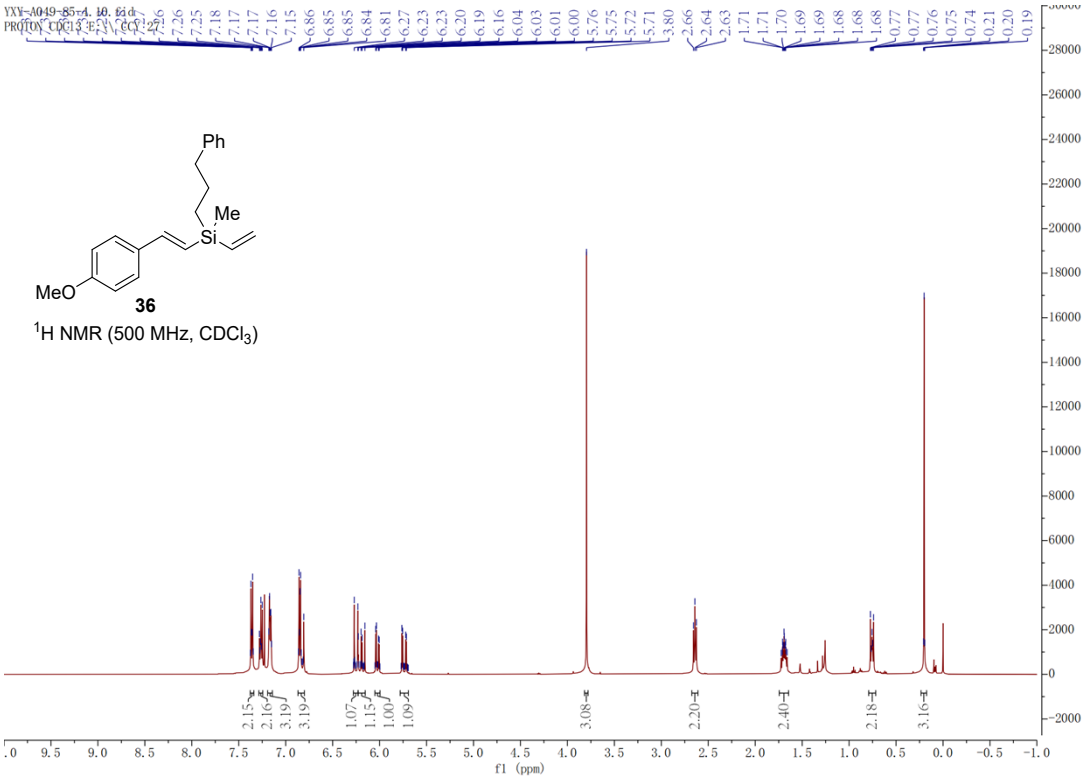
35

^{1}H NMR (500 MHz, $CDCl_3$)



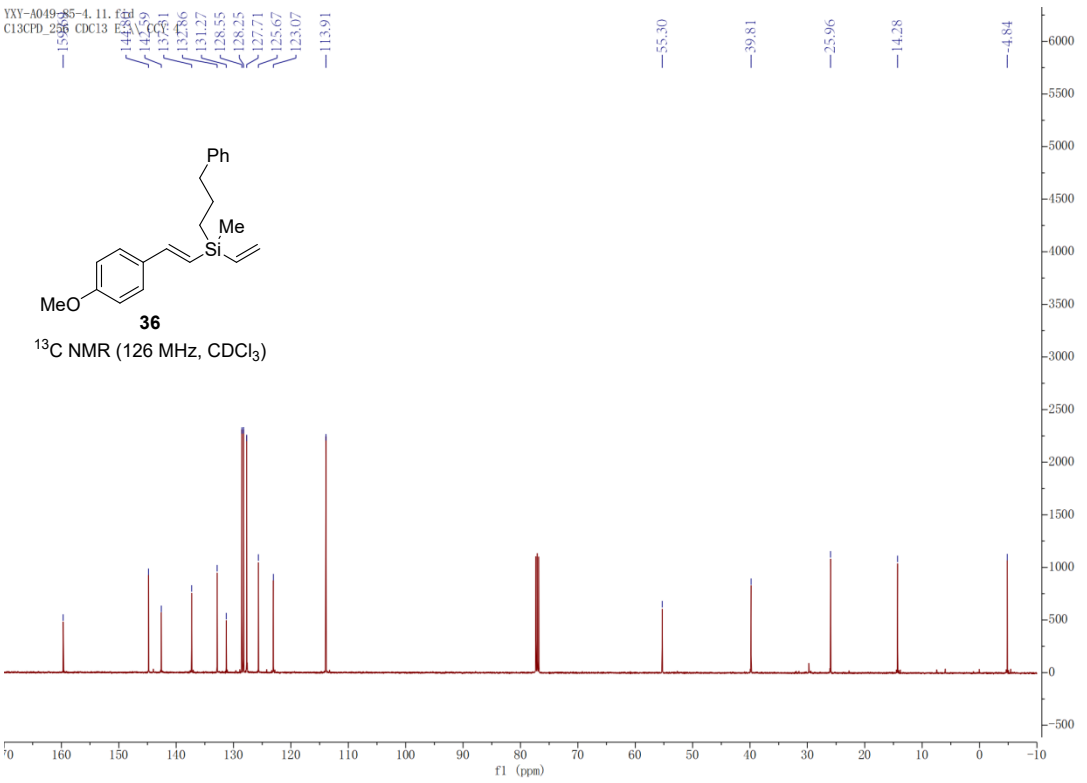
35

^{13}C NMR (126 MHz, $CDCl_3$)



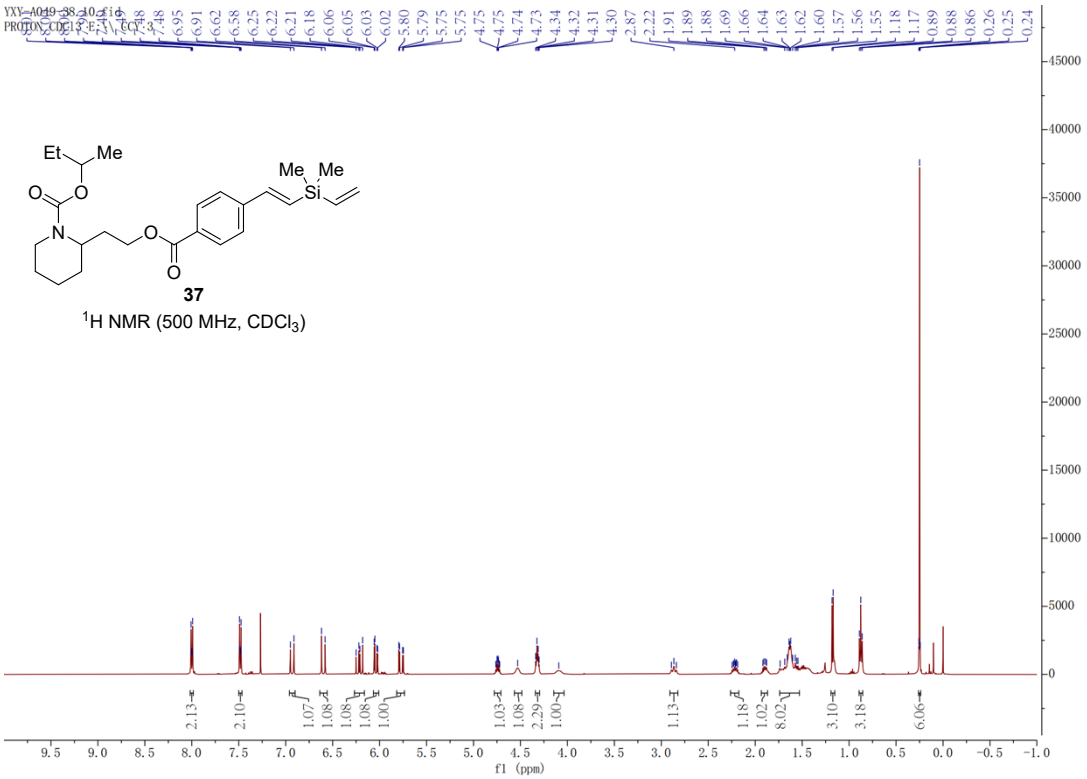
36

^{1}H NMR (500 MHz, $CDCl_3$)

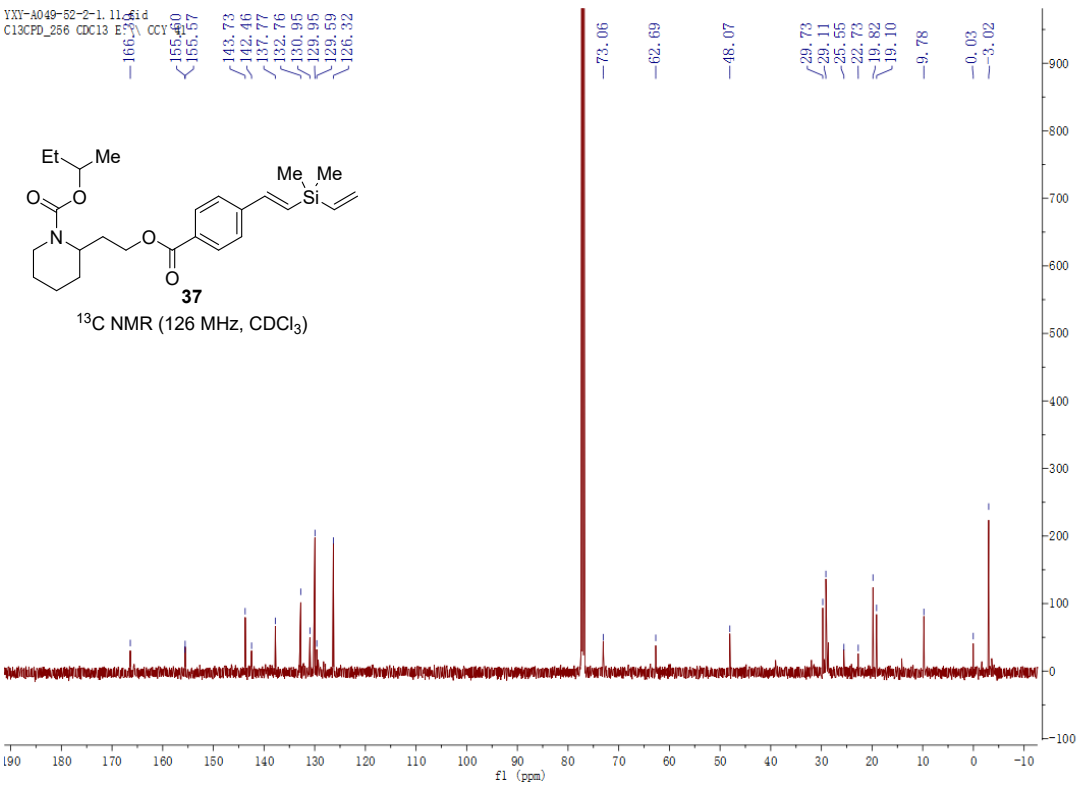


36

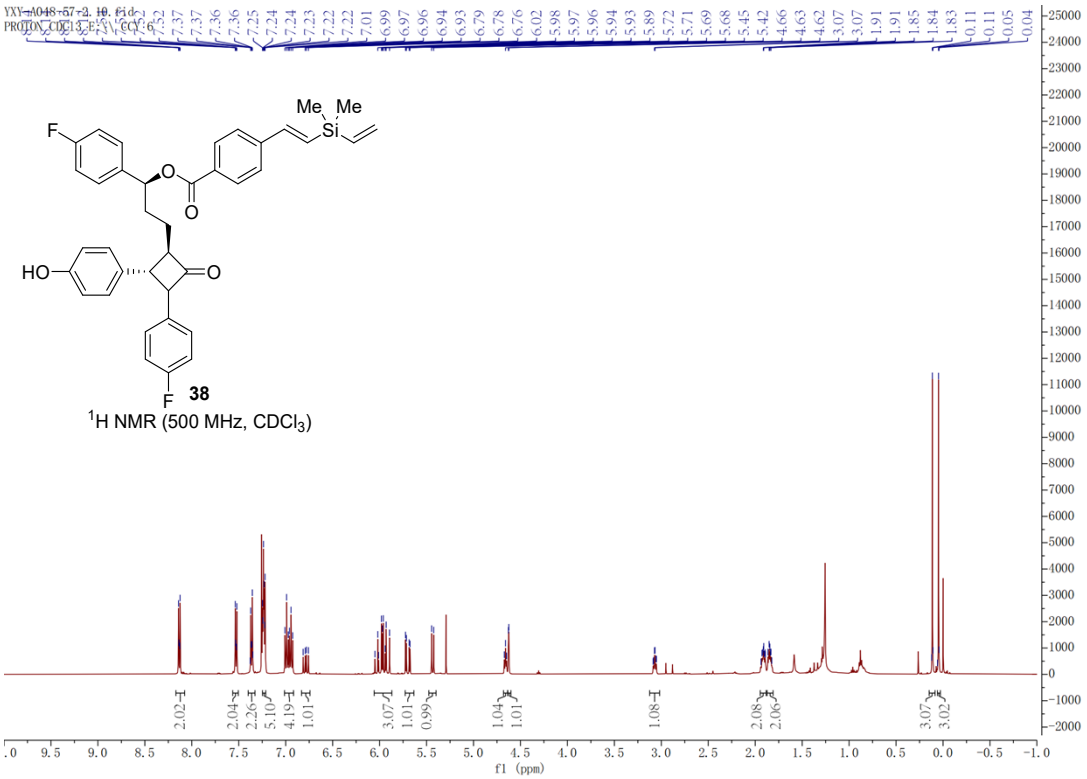
^{13}C NMR (126 MHz, $CDCl_3$)

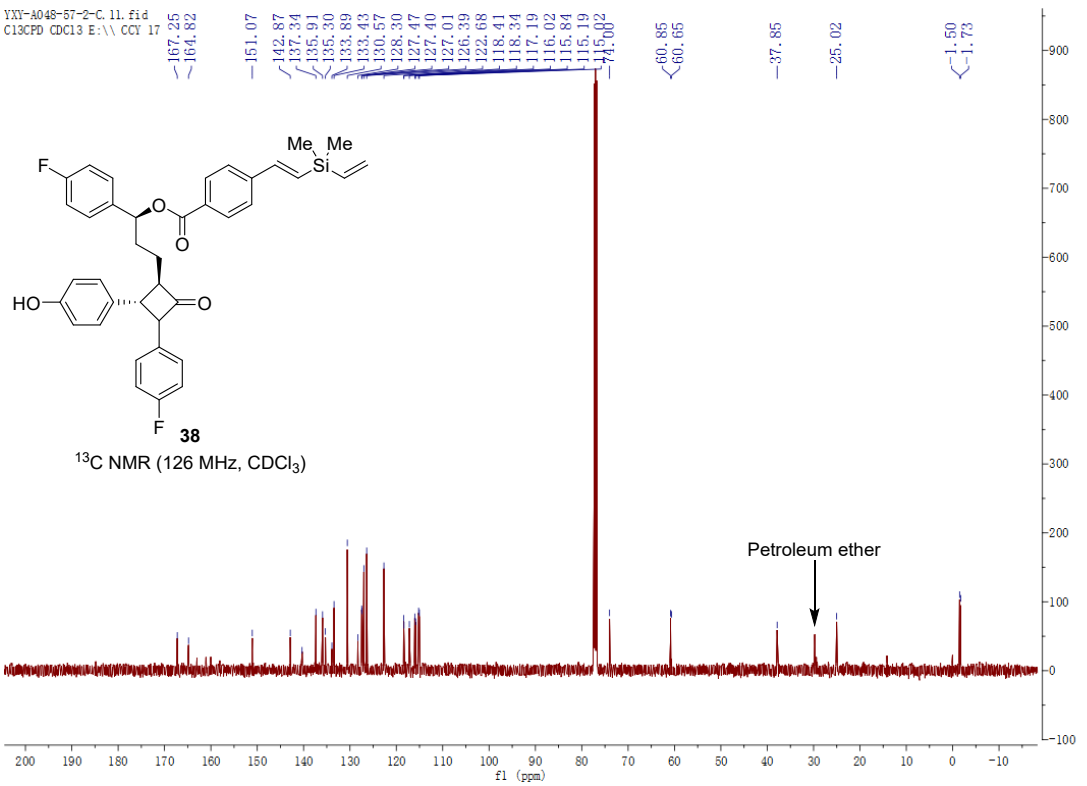


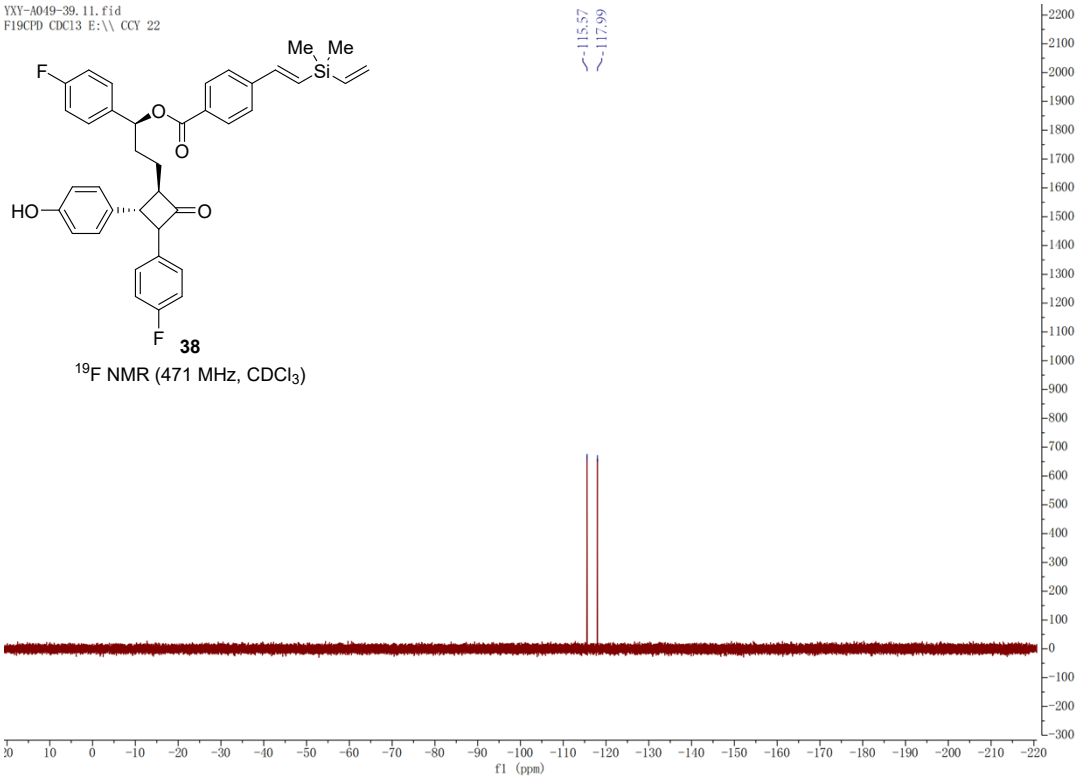
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

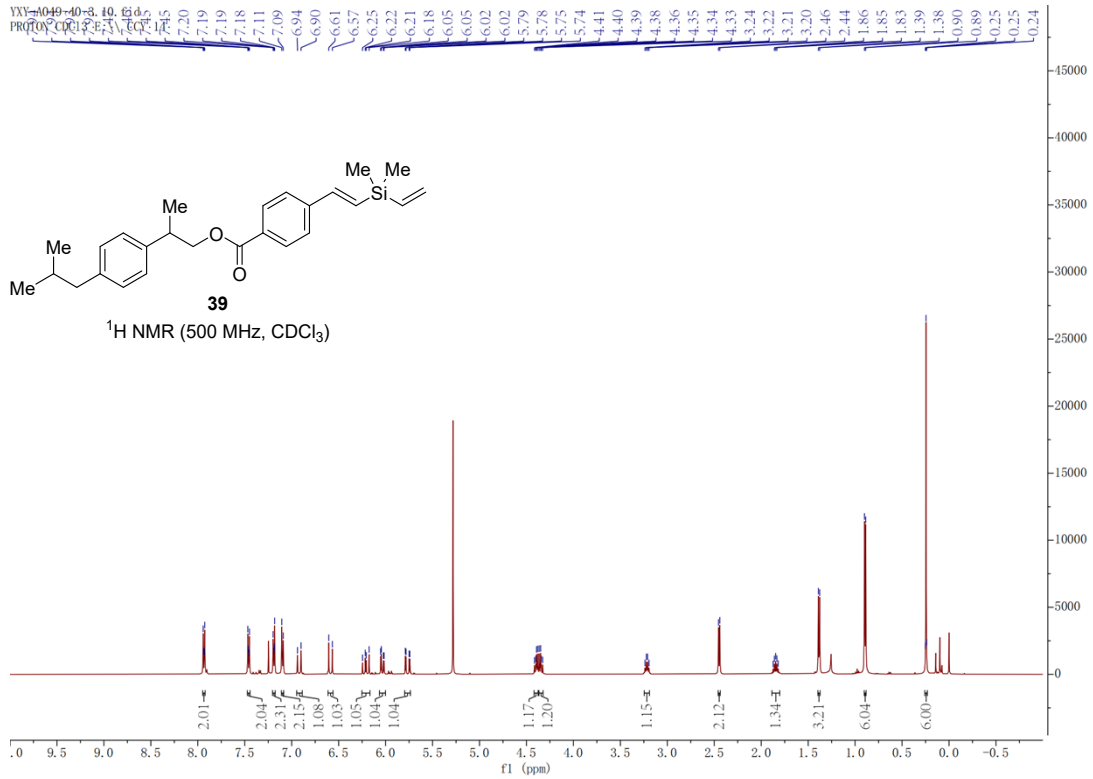

Me Me
Si
F
O
O
HO
O
F
38
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Me Me
Si
F
O
O
HO
O
F
38
13C NMR (126 MHz, CDCl3)
Petroleum ether
f1 (ppm)

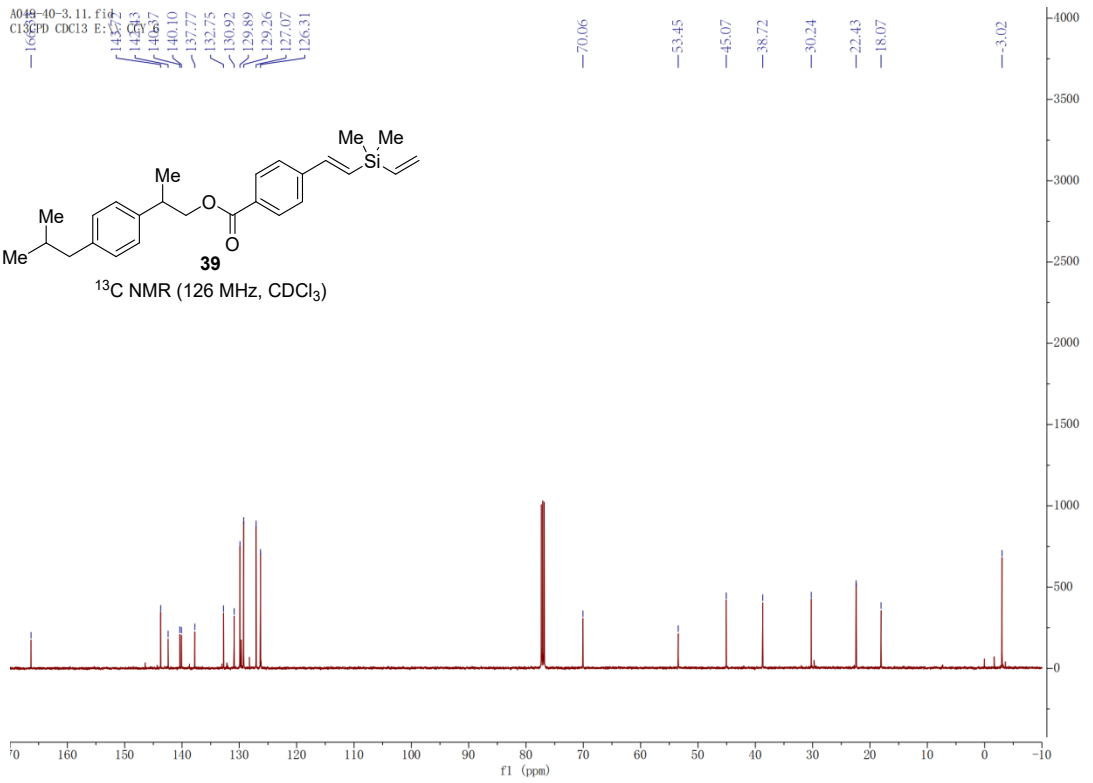


38

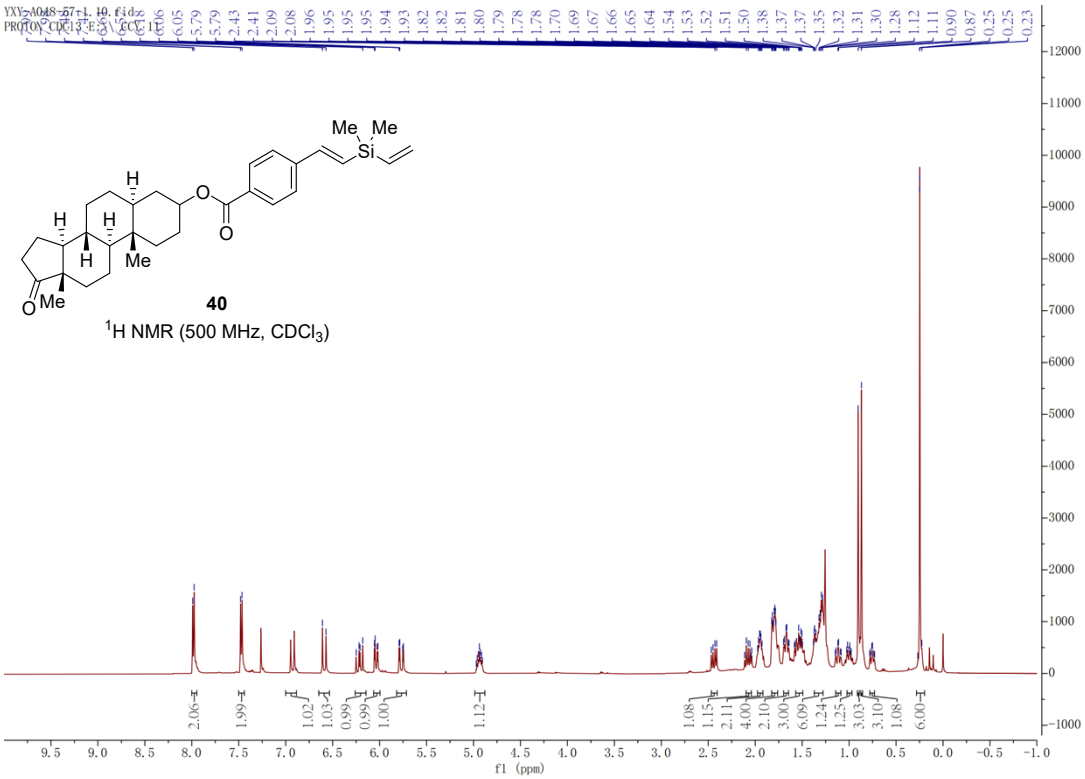
^{19}F NMR (471 MHz, $CDCl_3$)

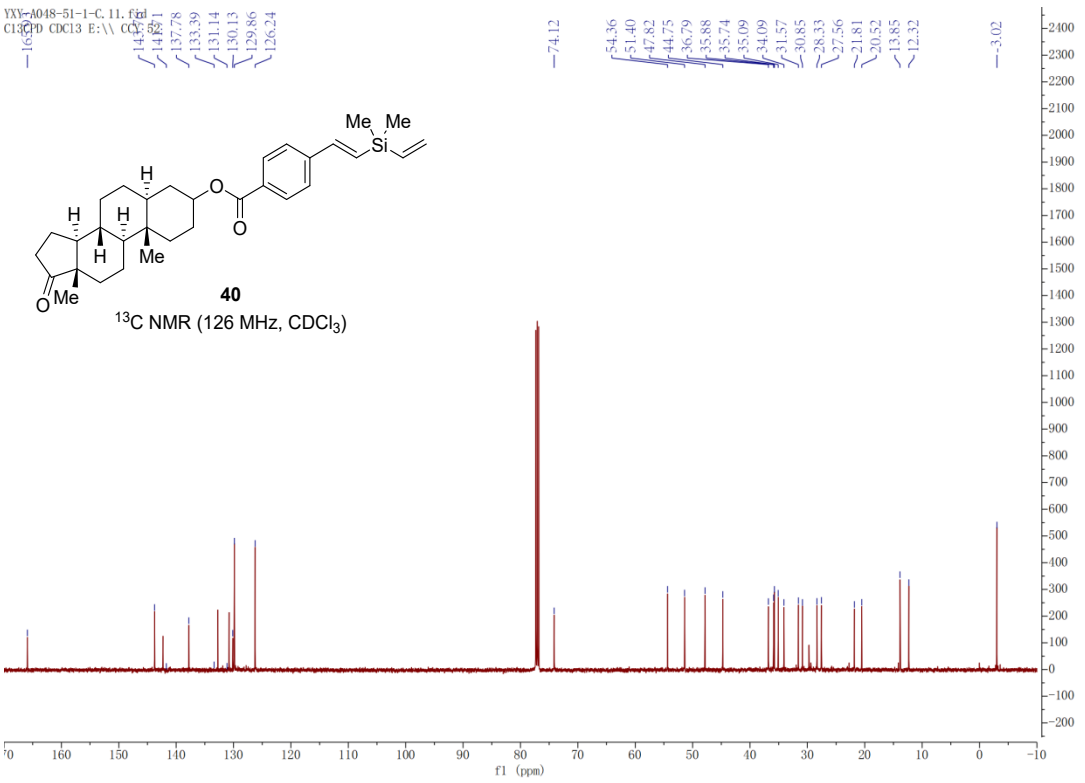


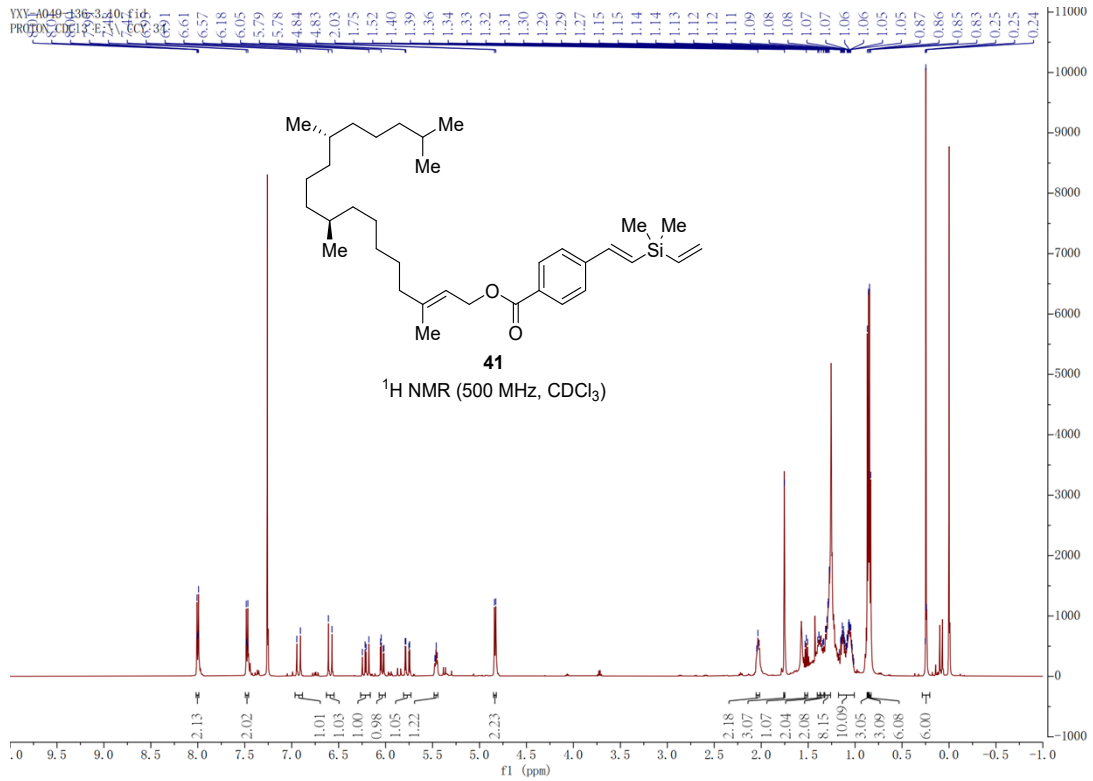
^{1}H NMR (500 MHz, $CDCl_3$)

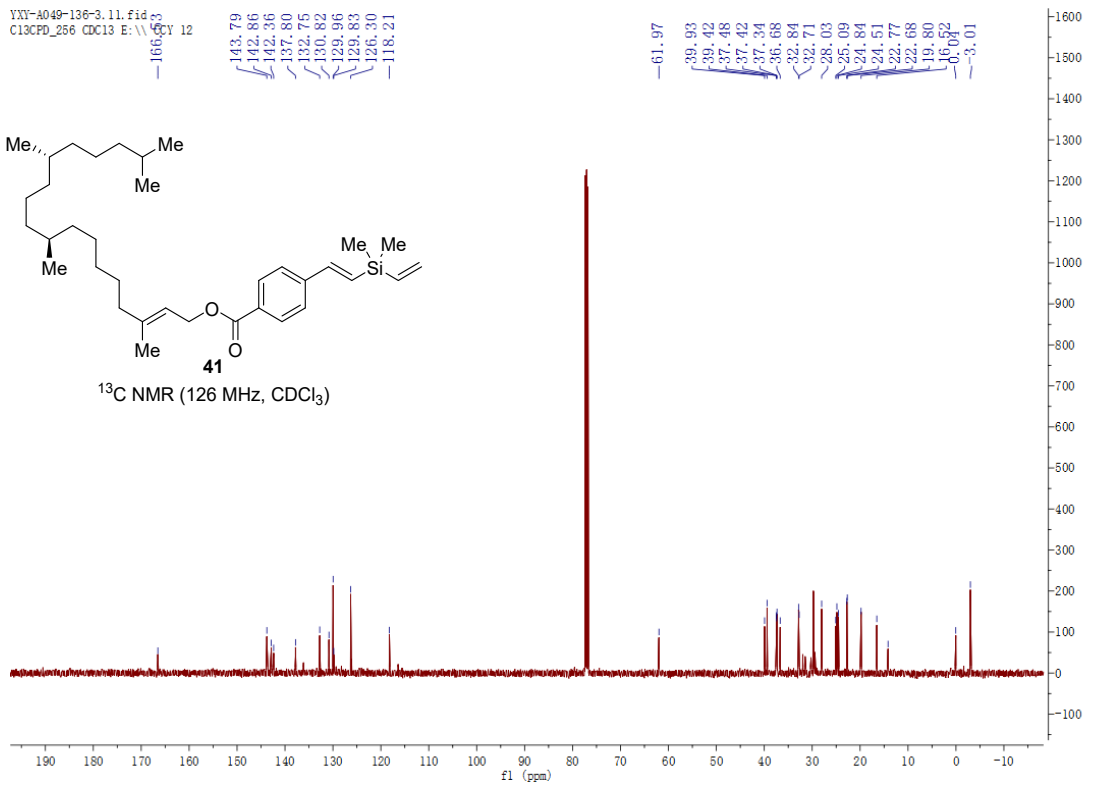


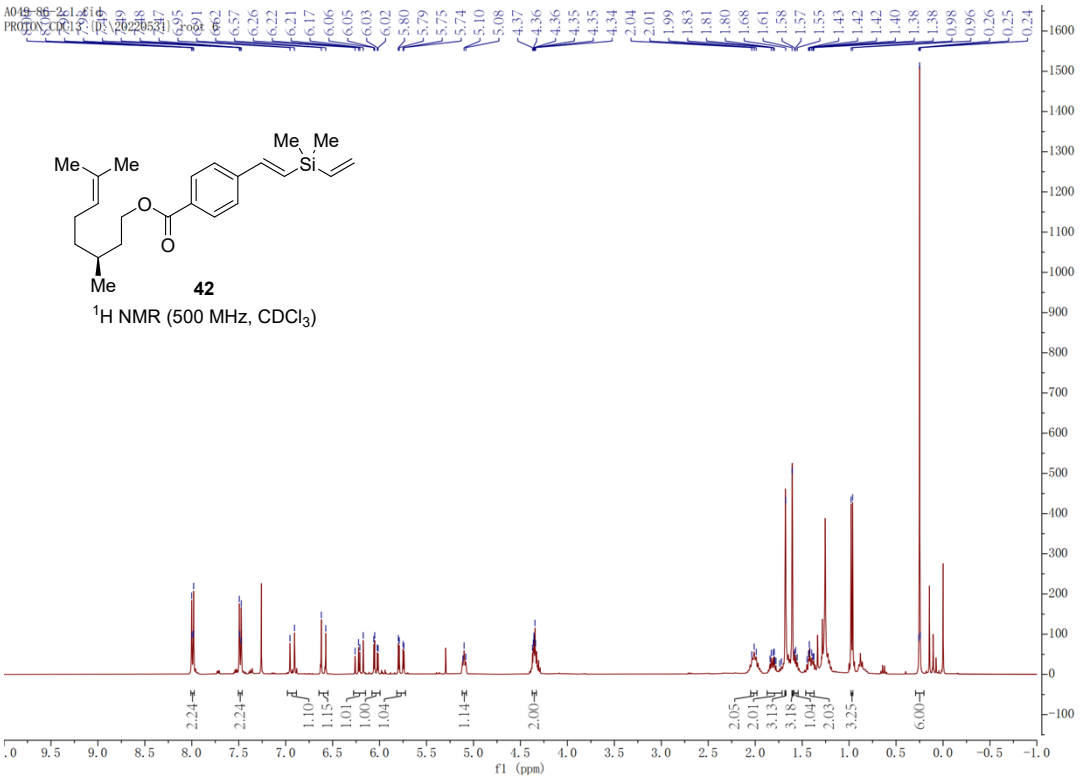
^{13}C NMR (126 MHz, $CDCl_3$)


Me Me
Si
H
O
O
H
H
H
Me
O
Me
40
1H NMR (500 MHz, CDCl3)
f1 (ppm)

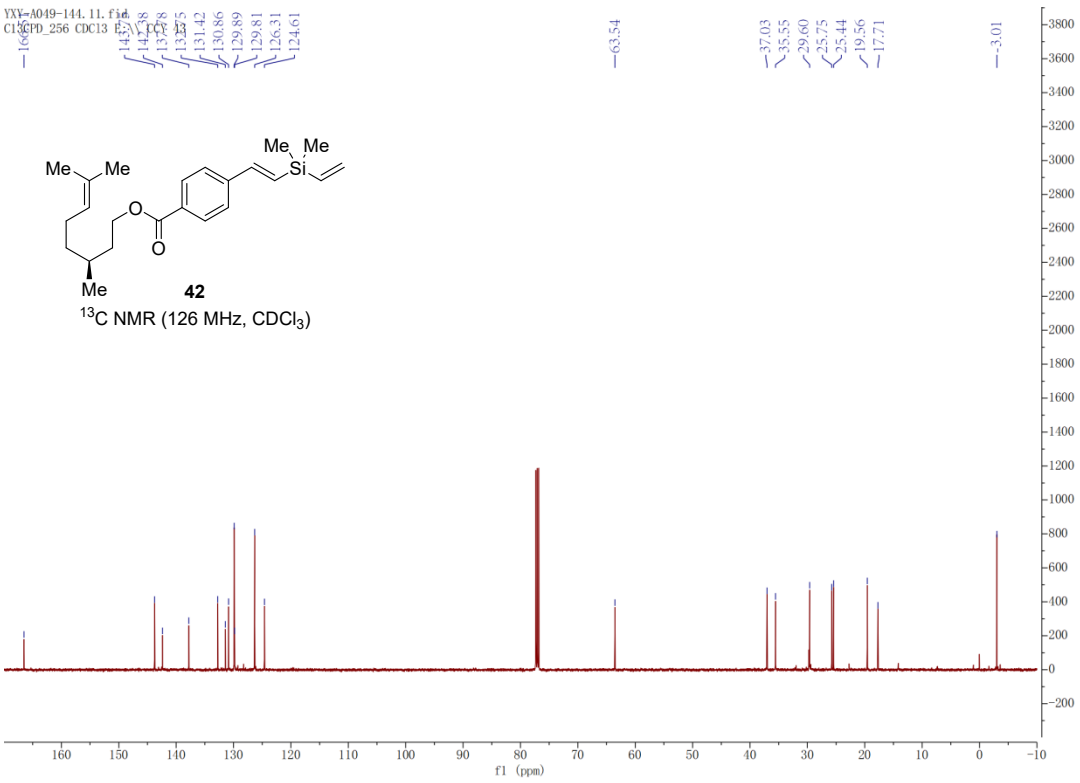

Me Me
Si
H
O
O
H
H
H
Me
O
Me
40
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Me
Me
Me
Me
Me
Si
O
Me
O
41
1H NMR (500 MHz, CDCl3)
f1 (ppm)

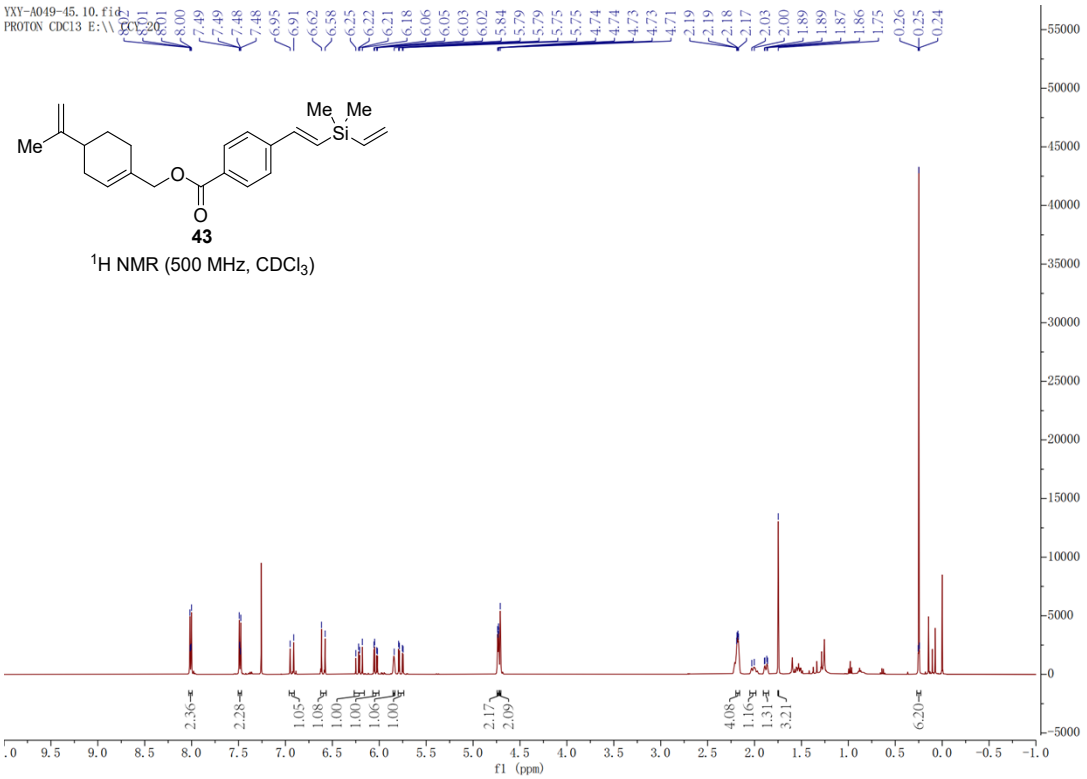

Me
Me
Me
Me
Me
Si
O
Me
O
41
13C NMR (126 MHz, CDCl3)
f1 (ppm)

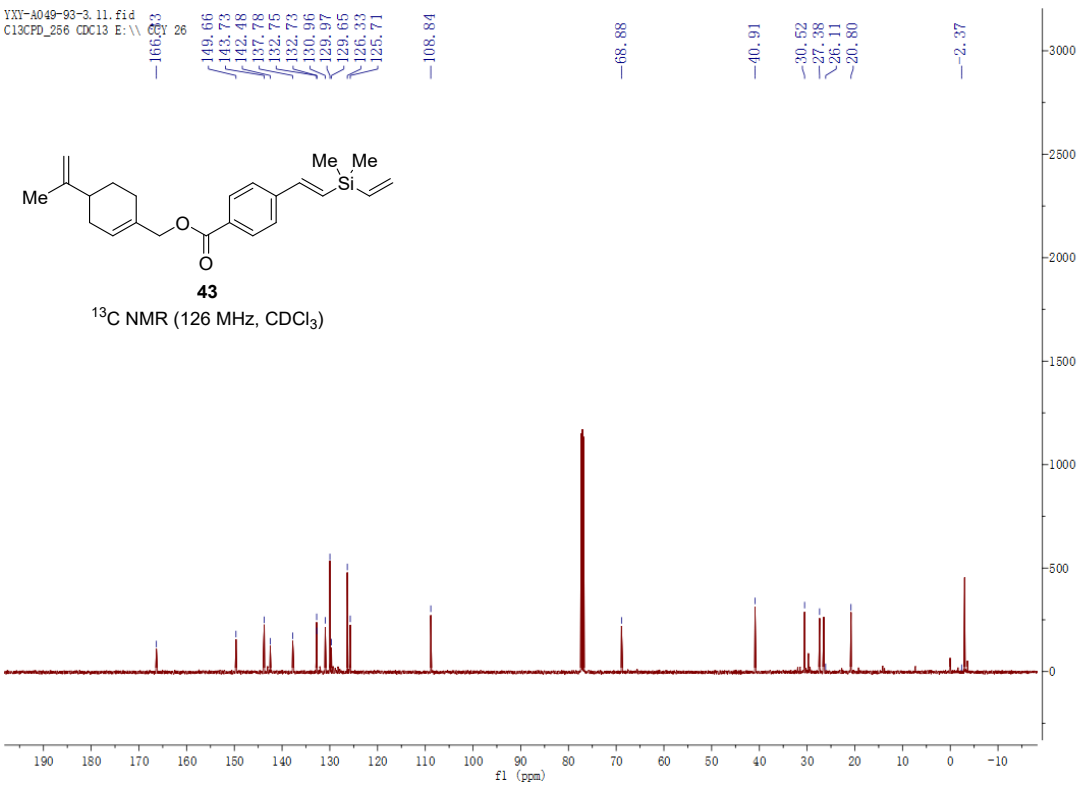


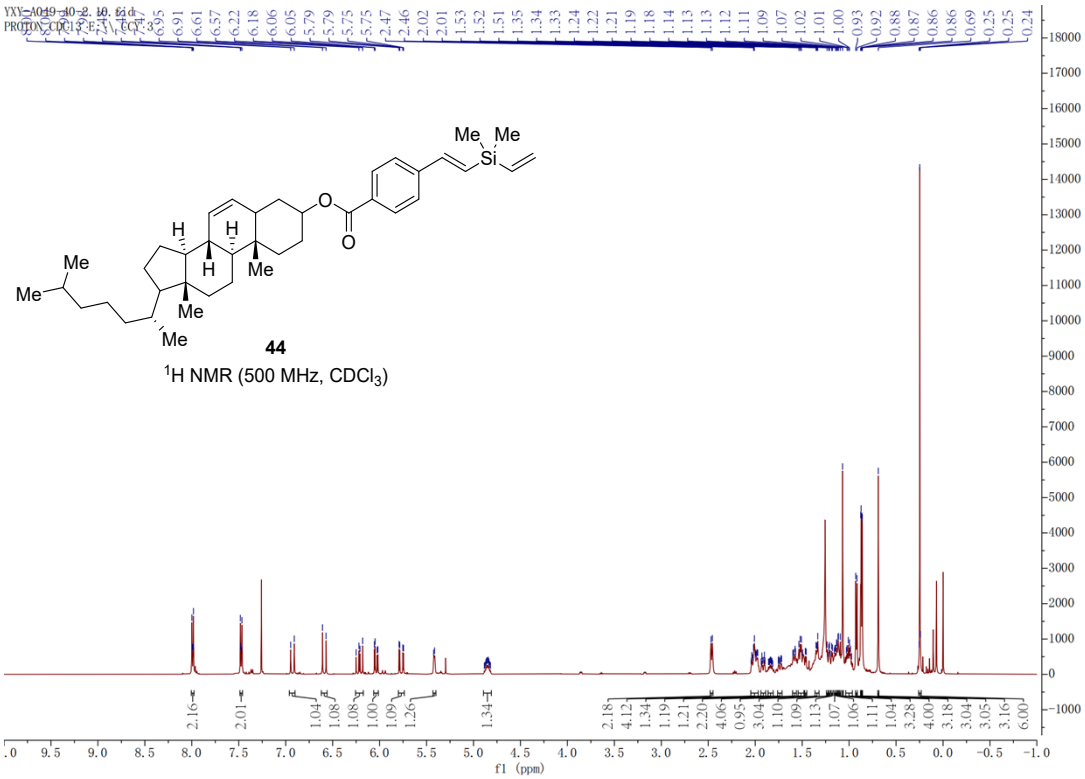
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

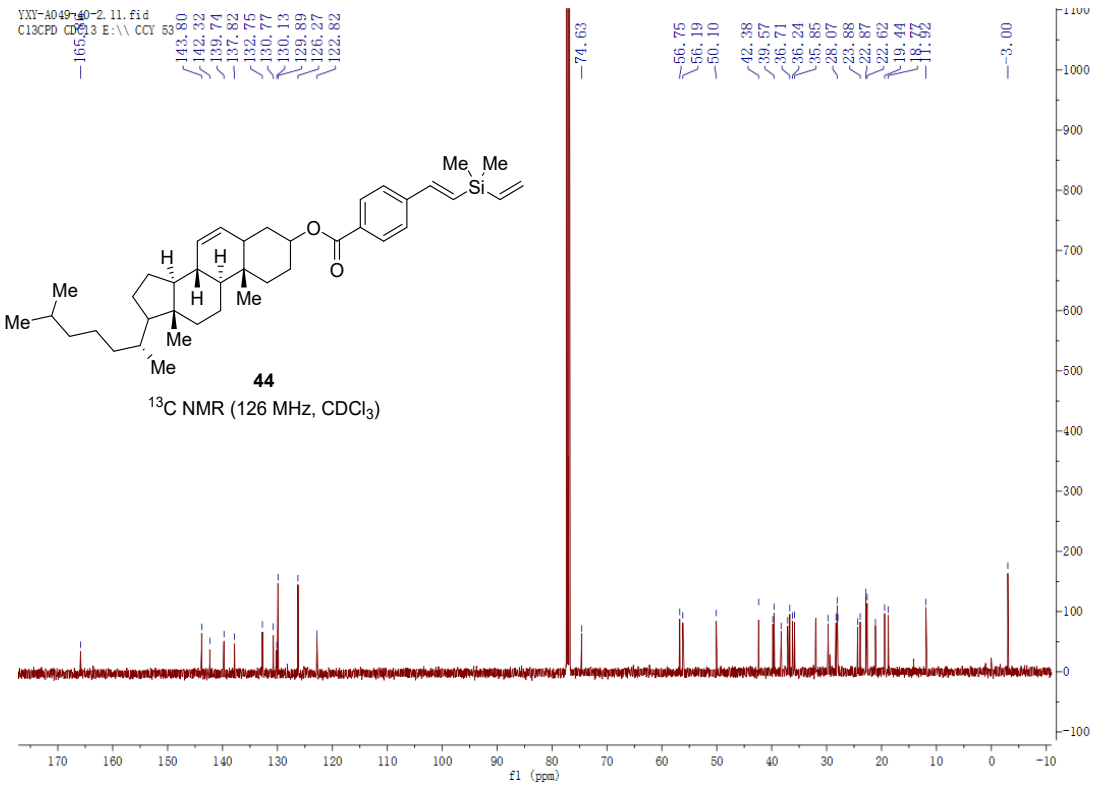

YXY-A049-45.10.fid
PROTON CDCl3 E:\\ CCY 26
Me
Me
Me
Si
O
O
43
1H NMR (500 MHz, CDCl3)
f1 (ppm)


YXY-A049-93-3.11.fid
C13CPD_256 CDCl3 E:\\ CCY 26
166.63
149.66
143.73
142.48
137.78
132.75
132.73
130.96
129.97
129.65
126.33
125.71
108.84
68.88
40.91
30.52
27.38
26.11
20.80
2.37
Me
Me
Me
Si
O
O
43
13C NMR (126 MHz, CDCl3)
f1 (ppm)



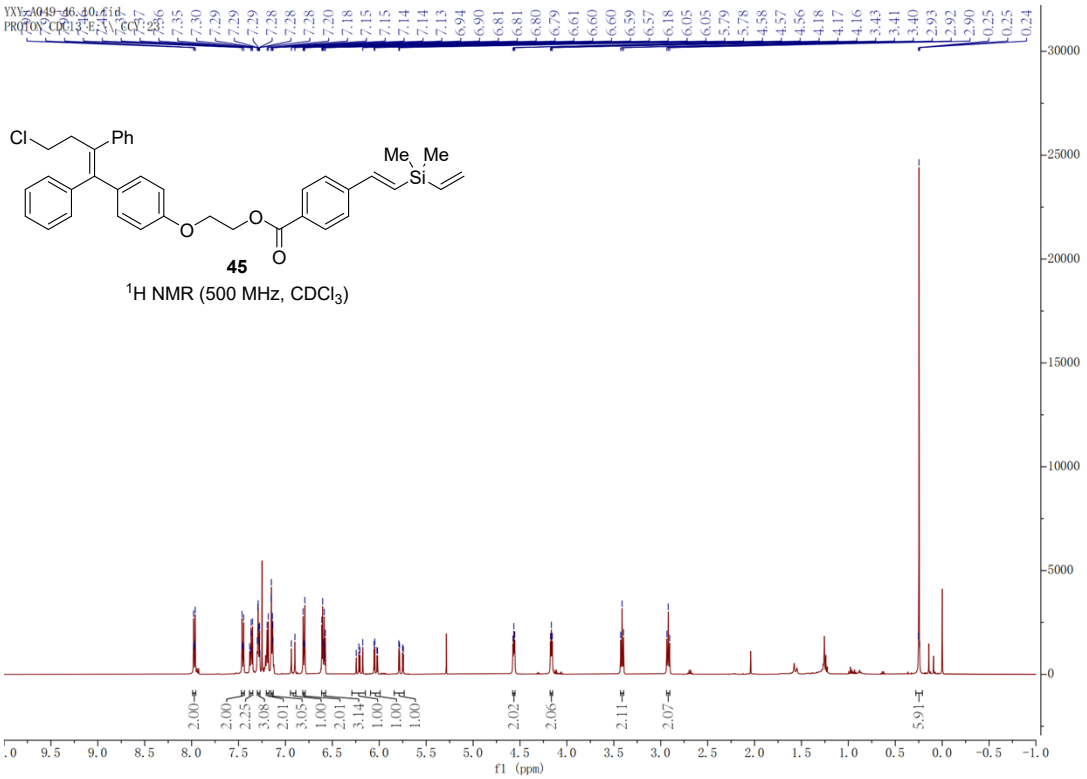
44

^{1}H NMR (500 MHz, $CDCl_3$)

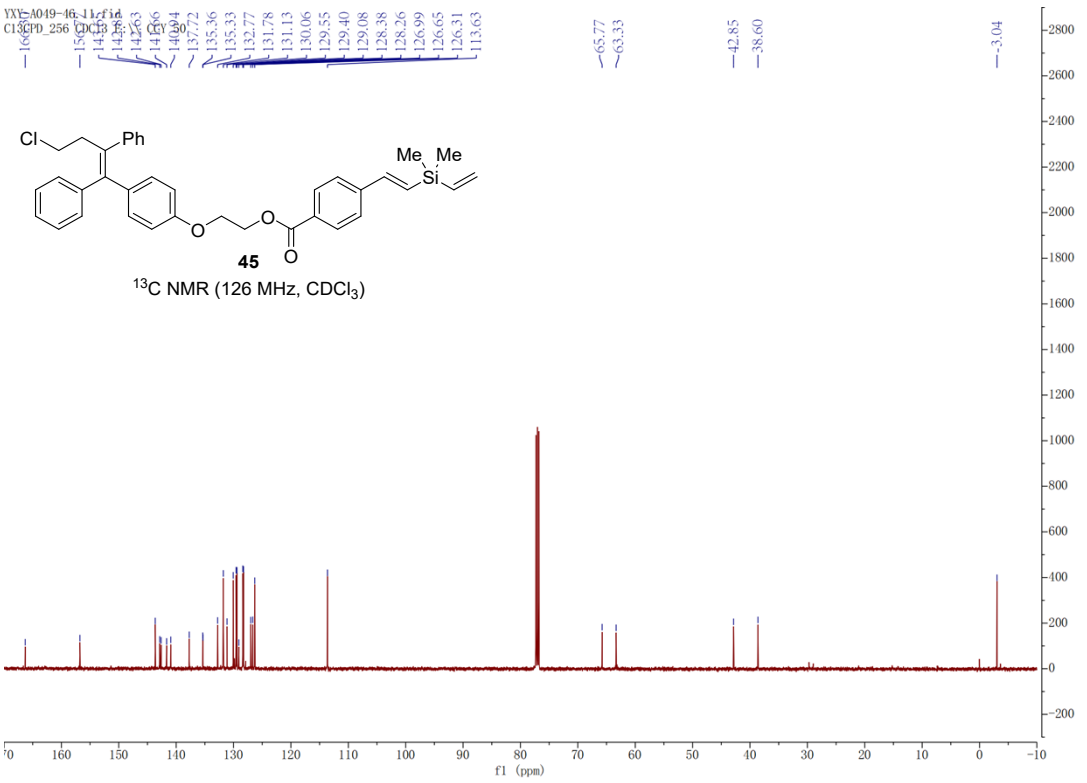


44

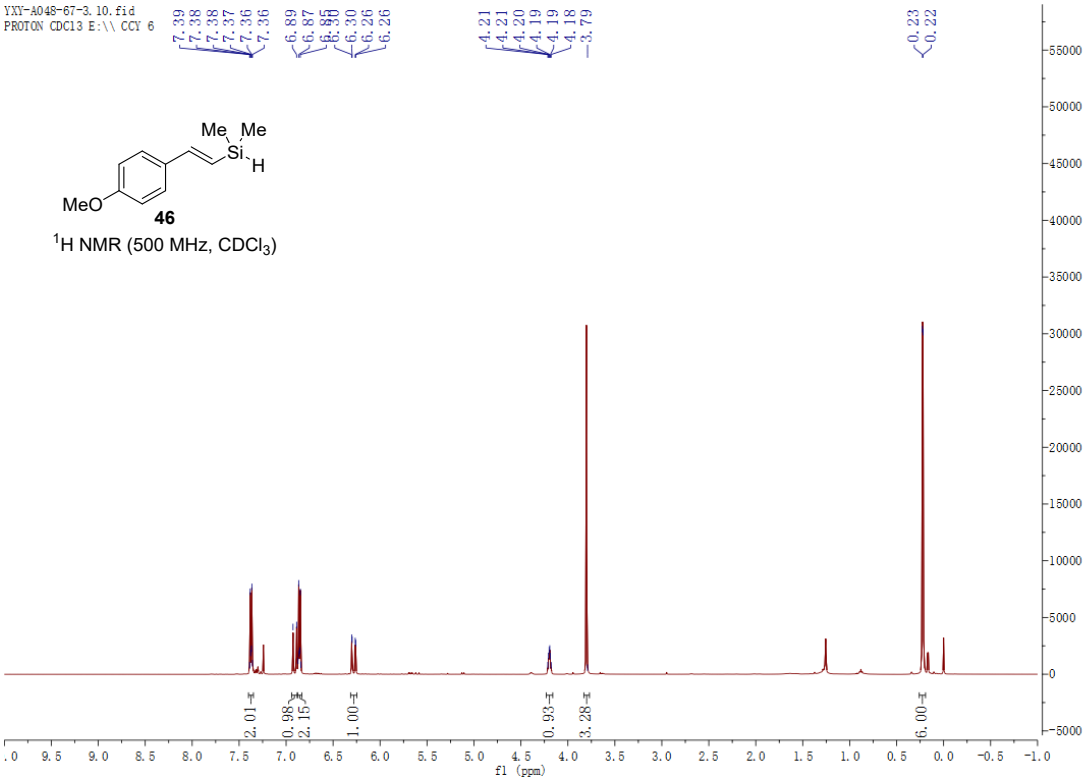
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

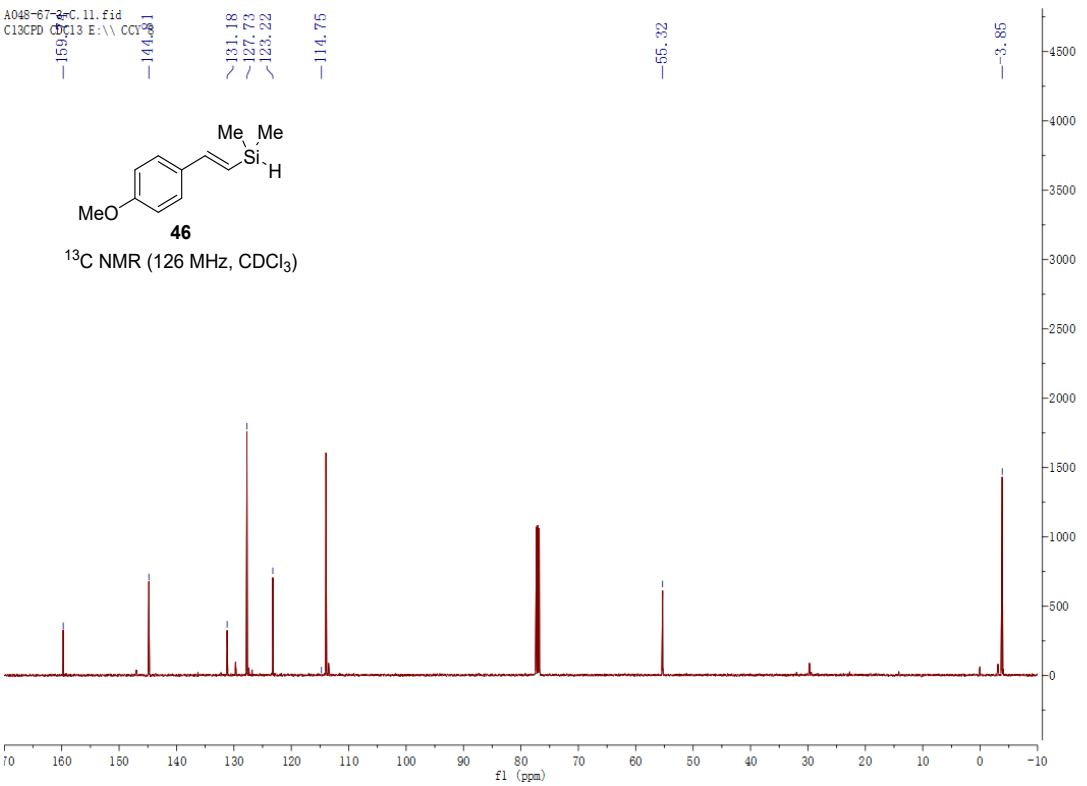


^{13}C NMR (126 MHz, $CDCl_3$)



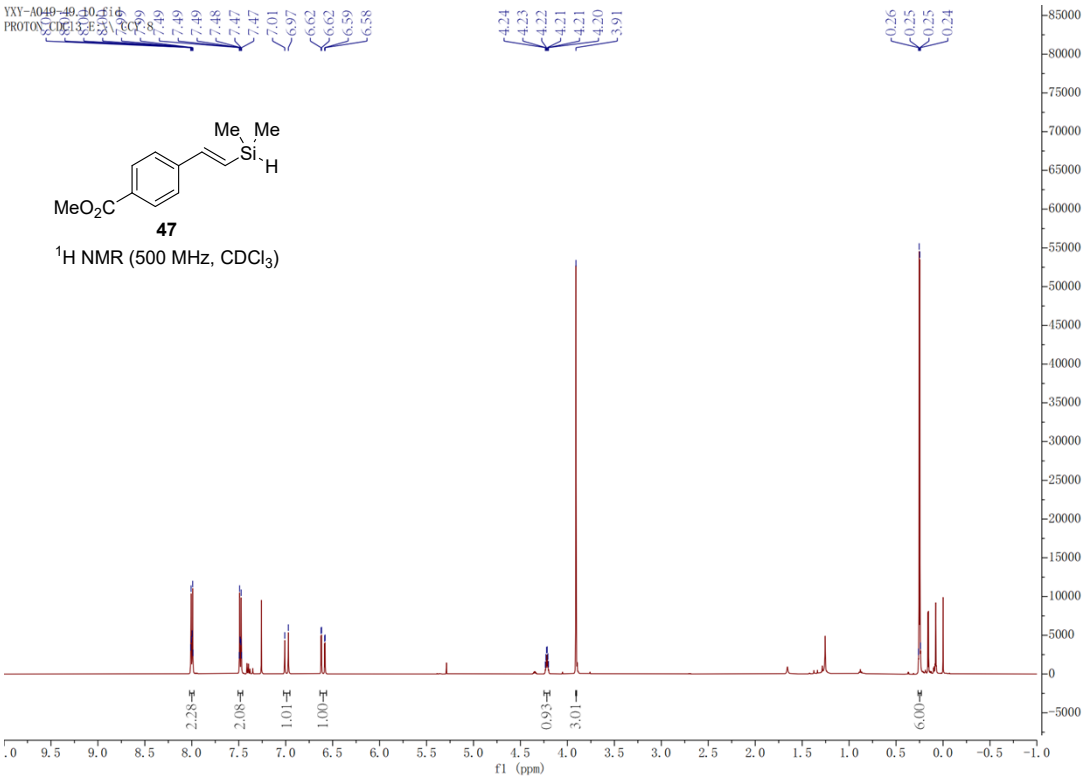
46

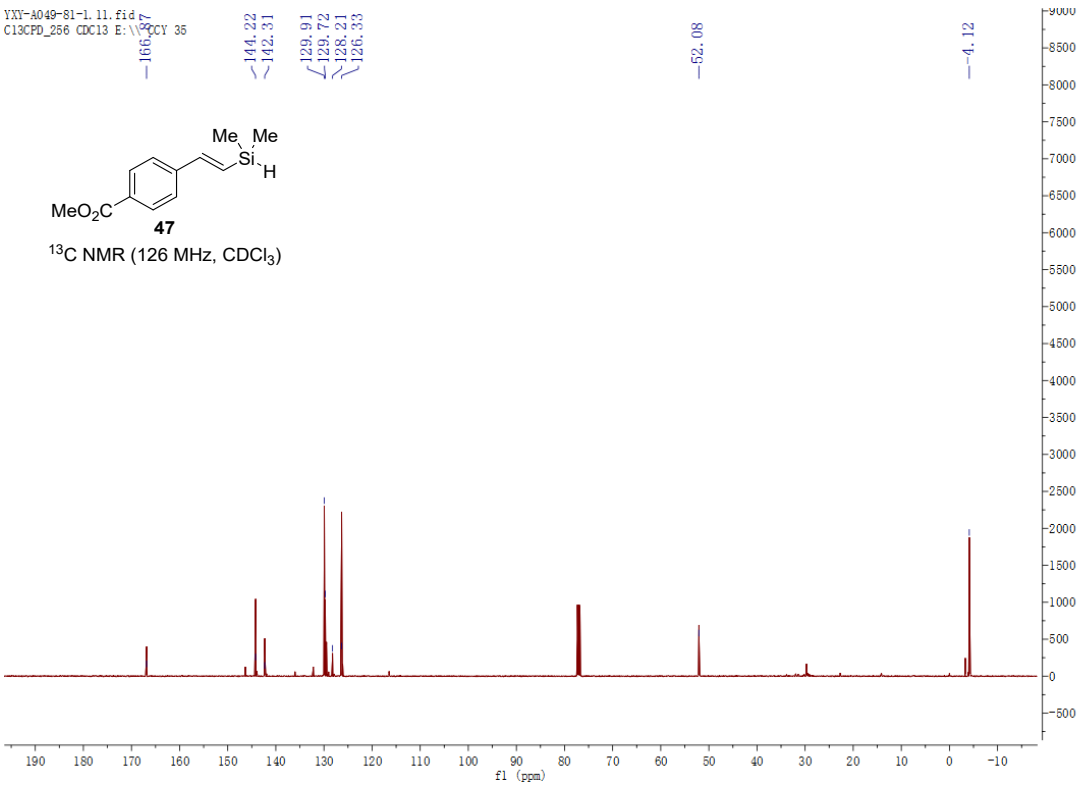
^{1}H NMR (500 MHz, $CDCl_3$)

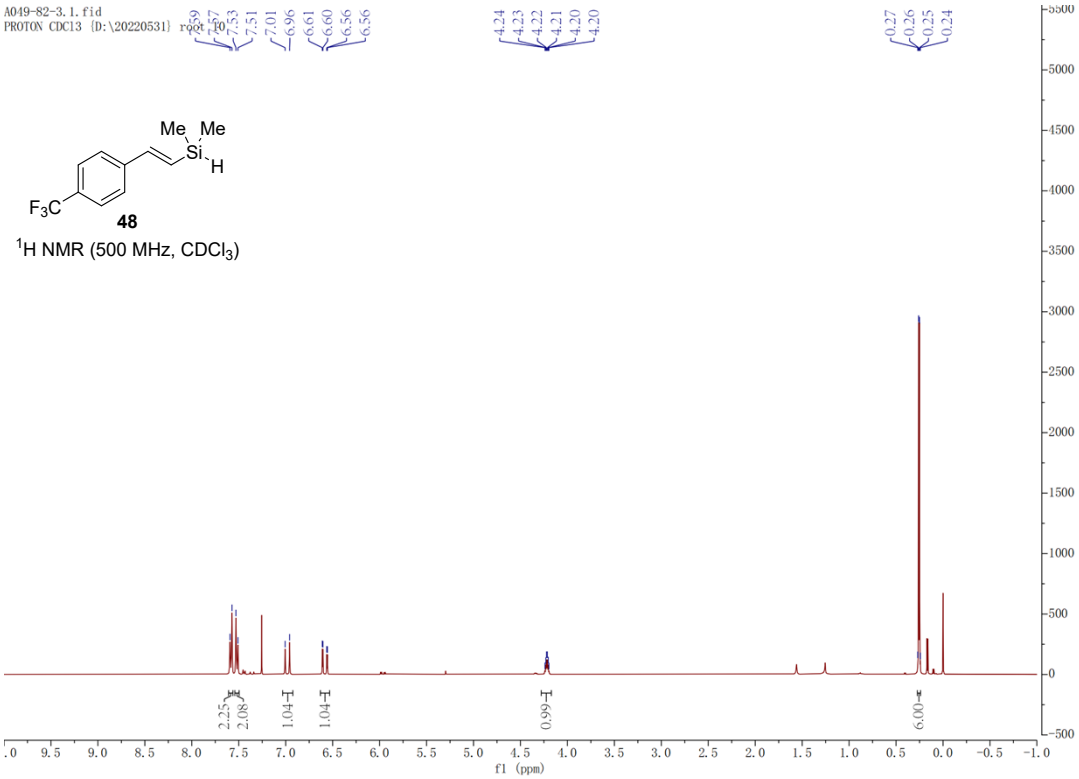


46

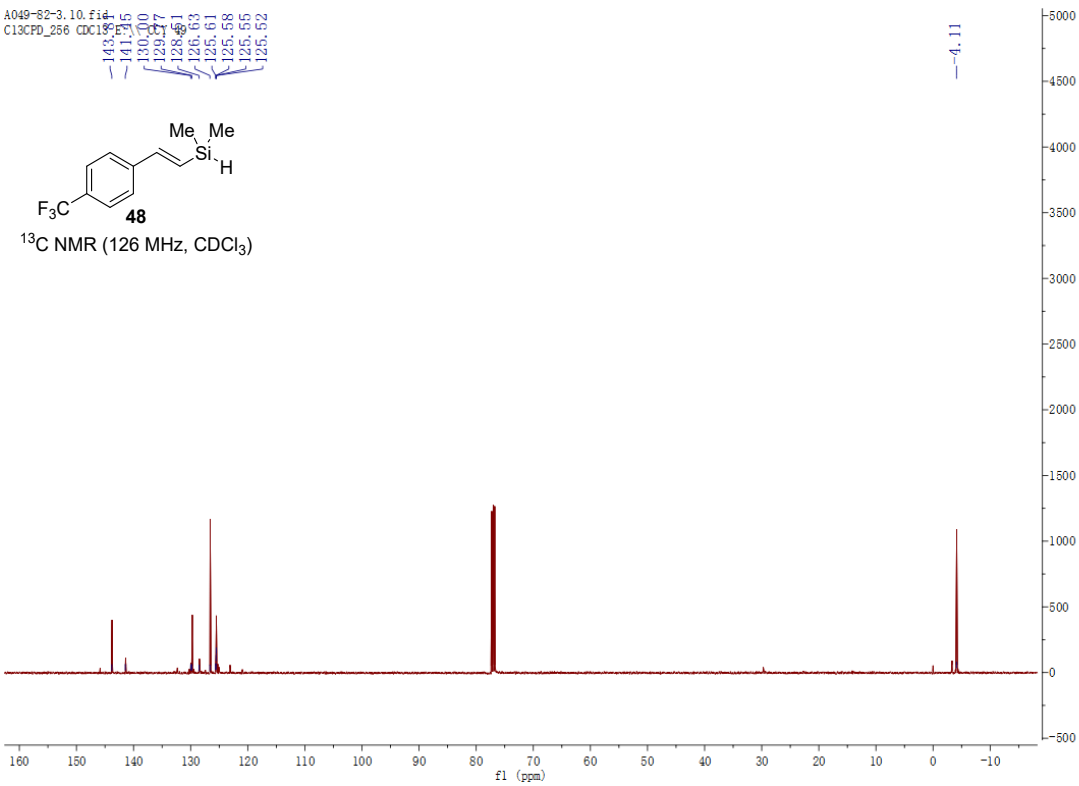
^{13}C NMR (126 MHz, $CDCl_3$)


Me Me
Si
H
MeO2C
47
1H NMR (500 MHz, CDCl3)
f1 (ppm)

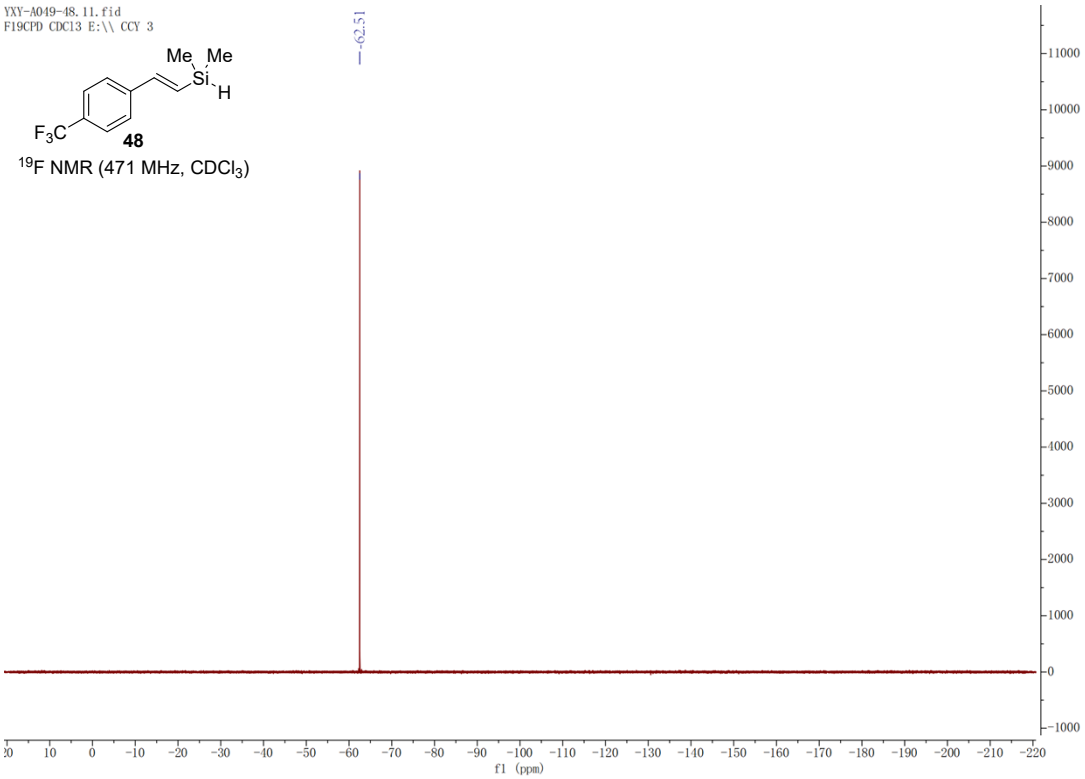

Me Me
Si
H
MeO2C
47
13C NMR (126 MHz, CDCl3)
f1 (ppm)



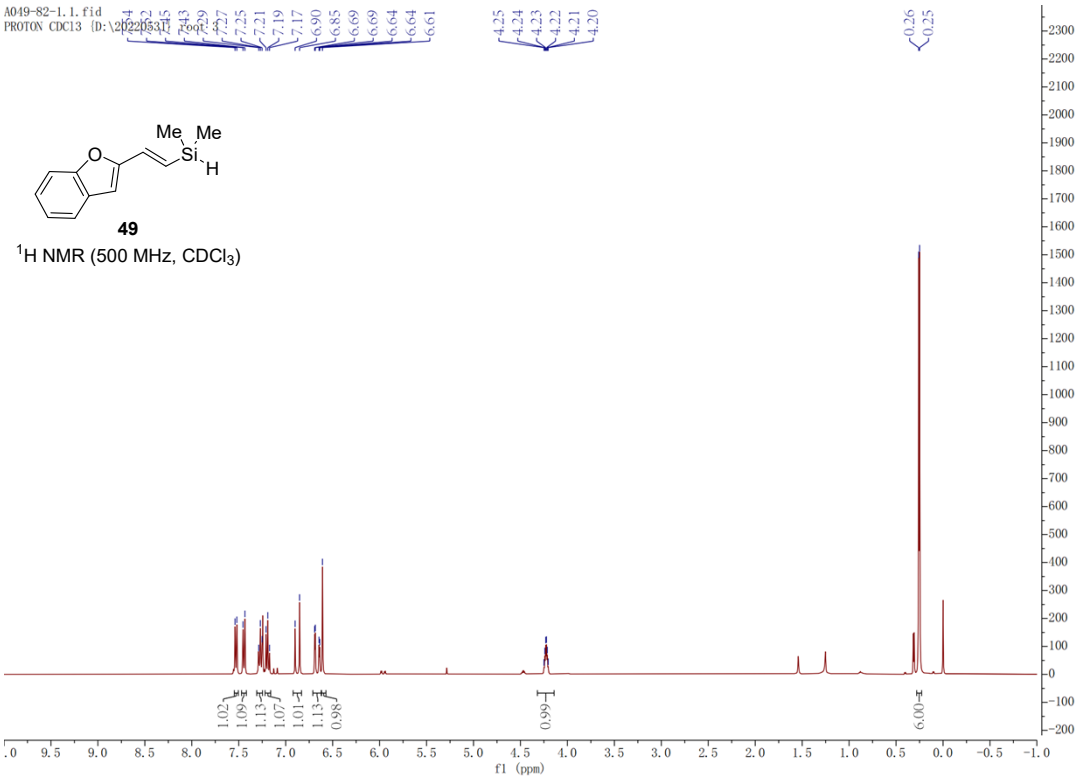
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

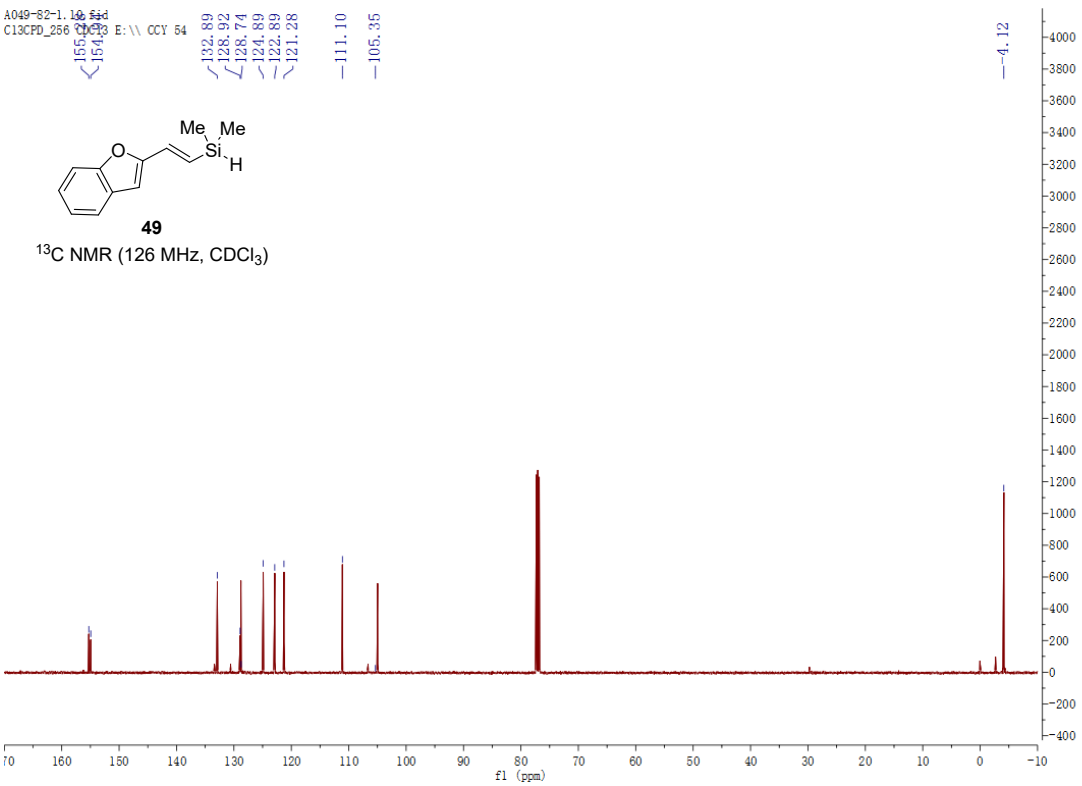


^{19}F NMR (471 MHz, $CDCl_3$)



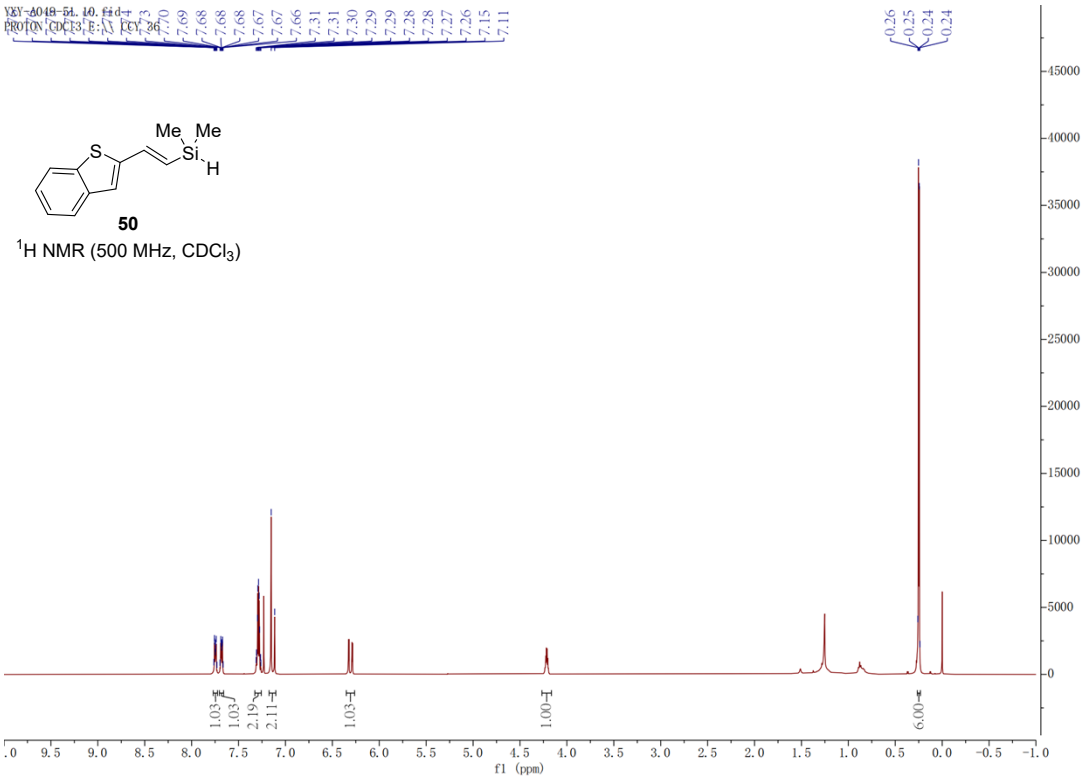
49

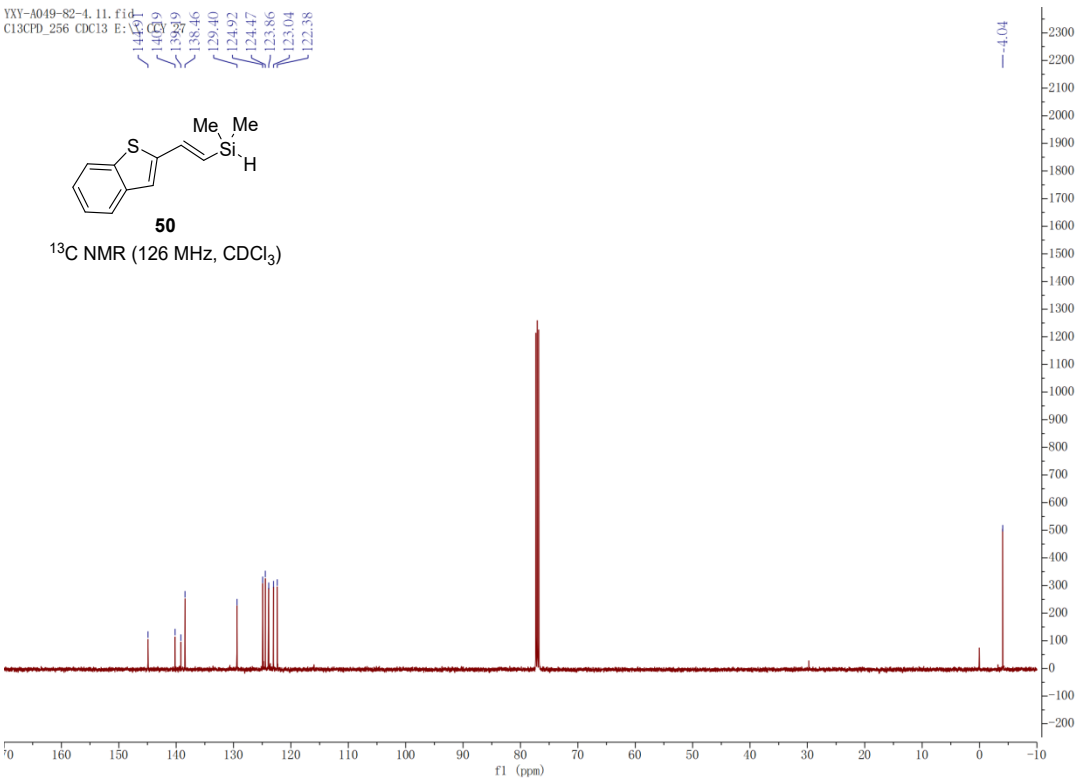
^{1}H NMR (500 MHz, $CDCl_3$)

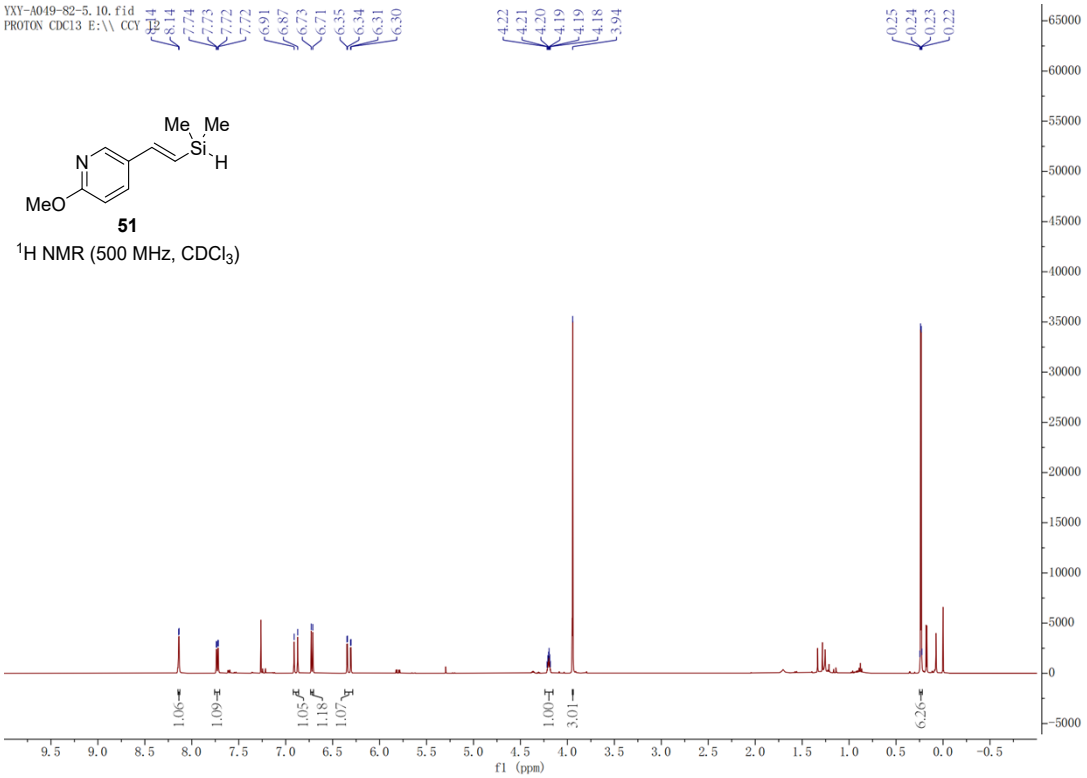


49

^{13}C NMR (126 MHz, $CDCl_3$)

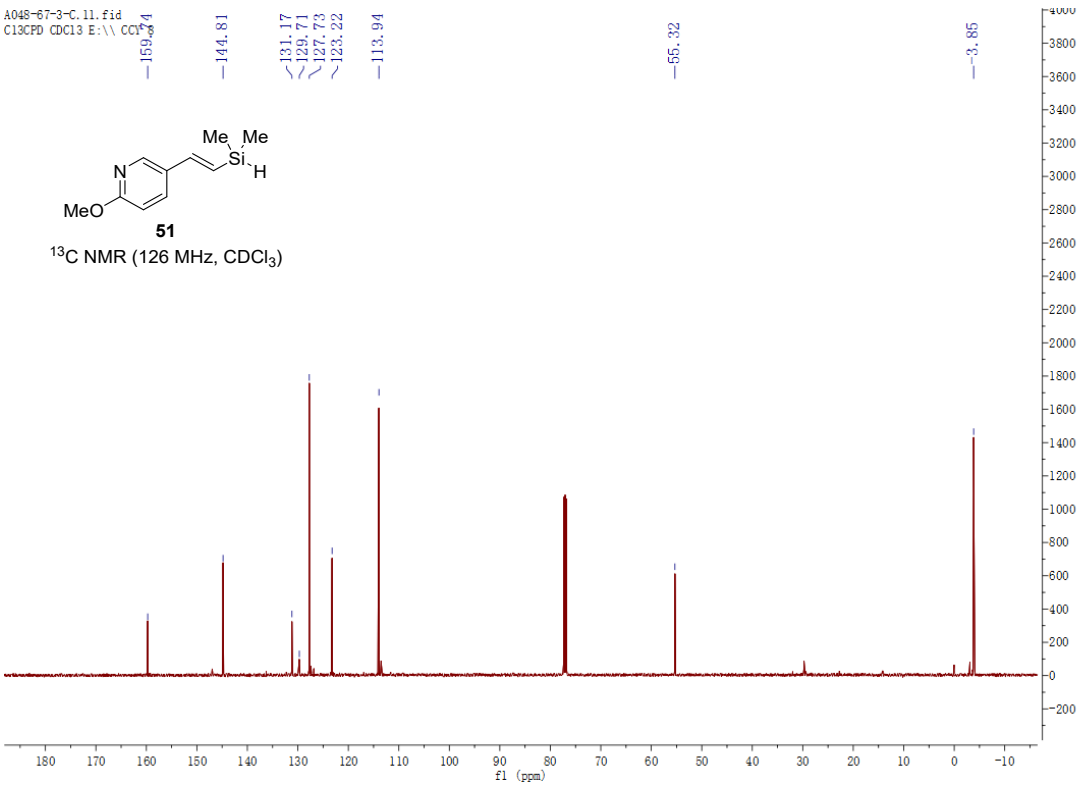

Me
Me
Si
H
S
50
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Me
Me
Si
H
S
50
13C NMR (126 MHz, CDCl3)
f1 (ppm)



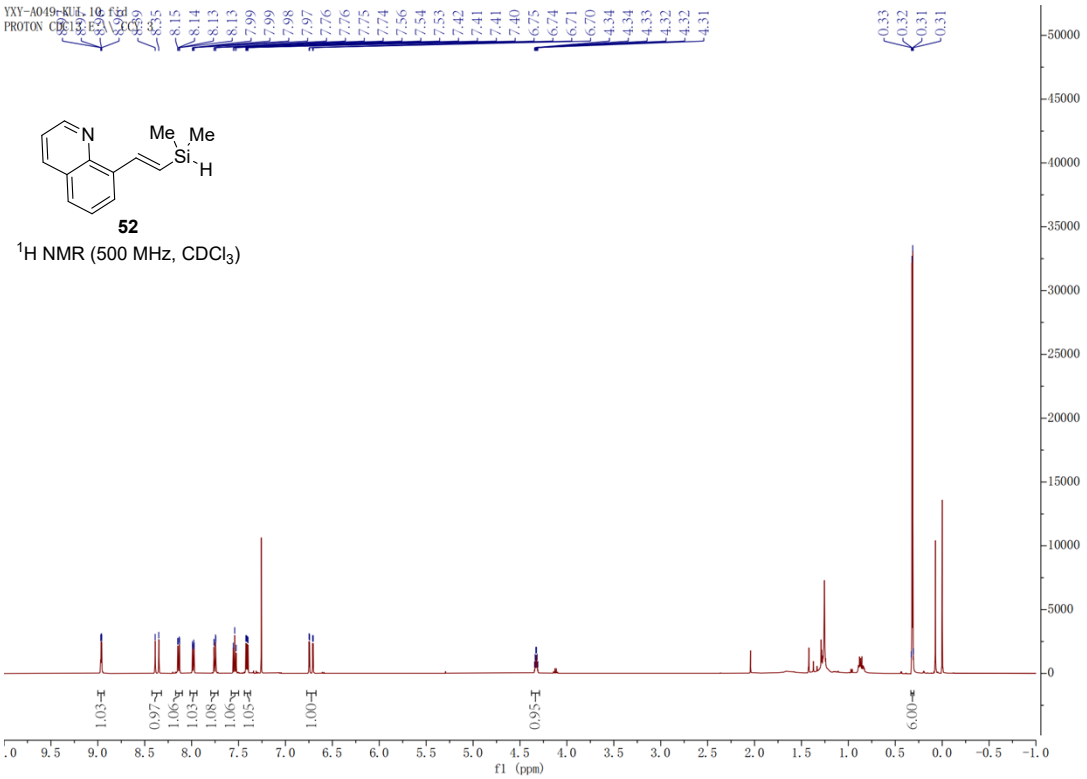
51

^{1}H NMR (500 MHz, $CDCl_3$)



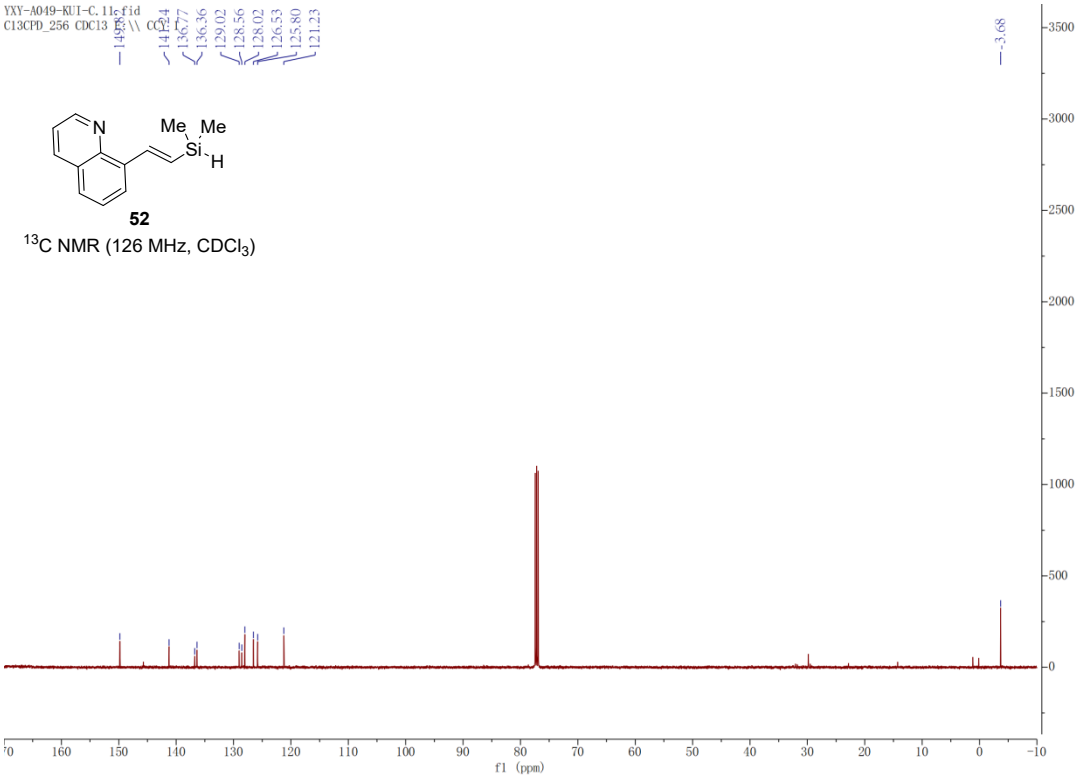
51

^{13}C NMR (126 MHz, $CDCl_3$)



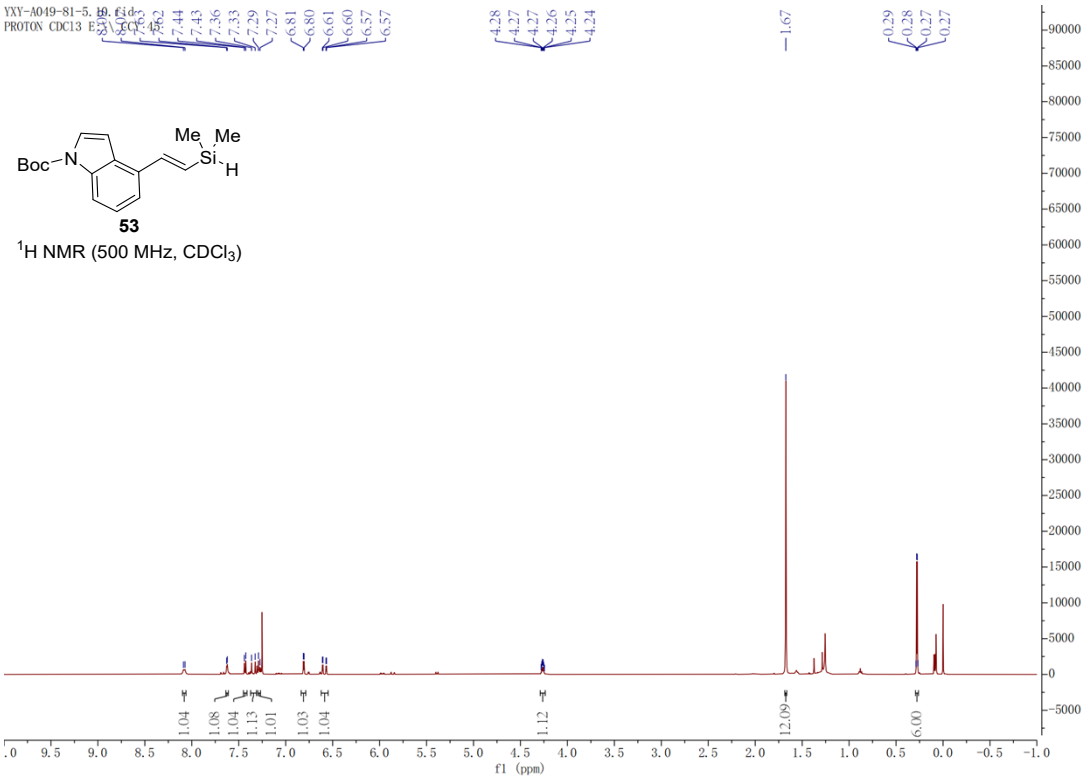
52

^{1}H NMR (500 MHz, $CDCl_3$)



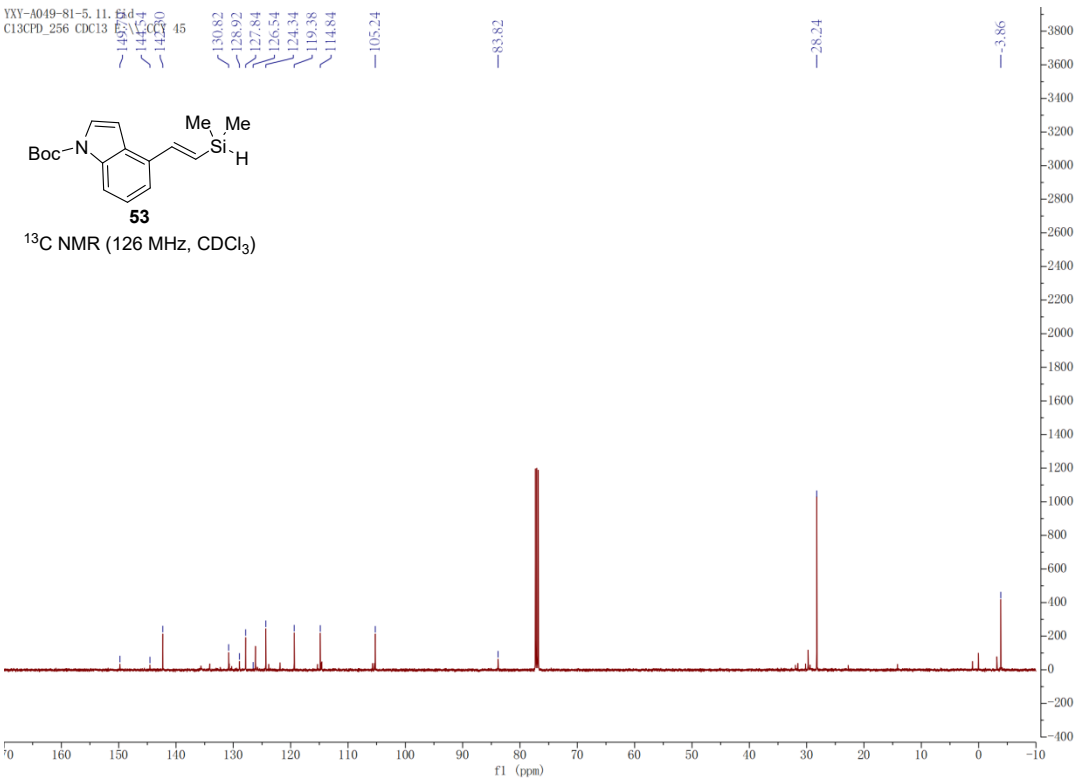
52

^{13}C NMR (126 MHz, $CDCl_3$)



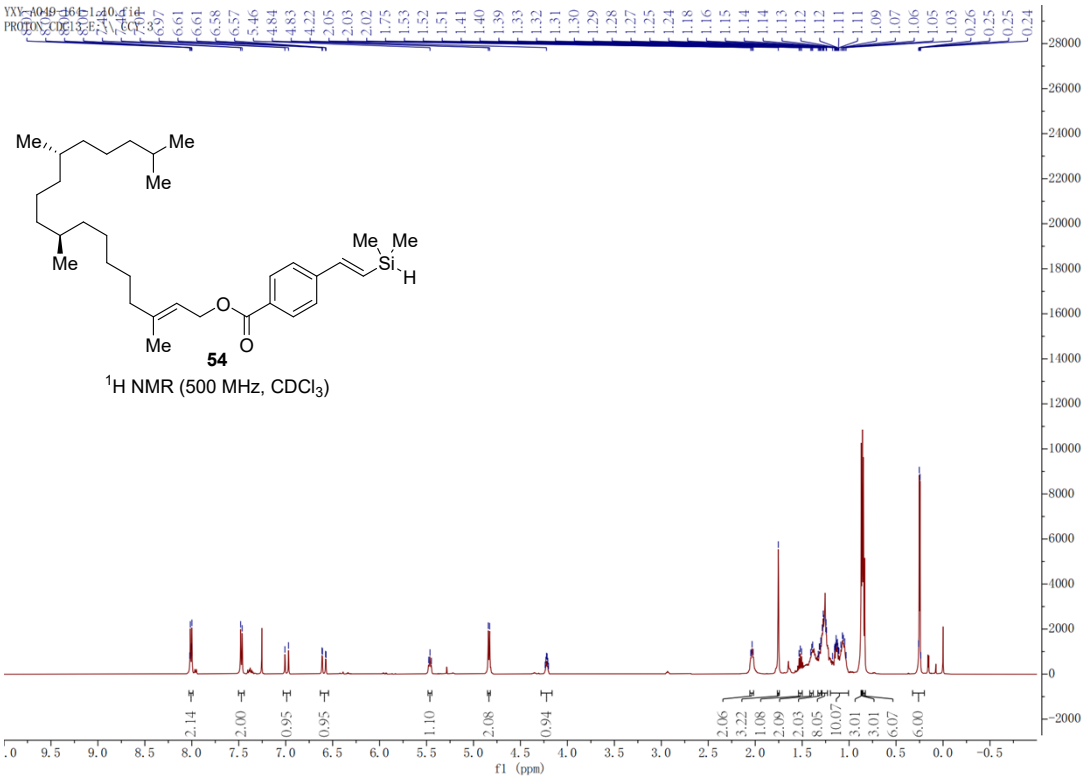
53

^{1}H NMR (500 MHz, $CDCl_3$)

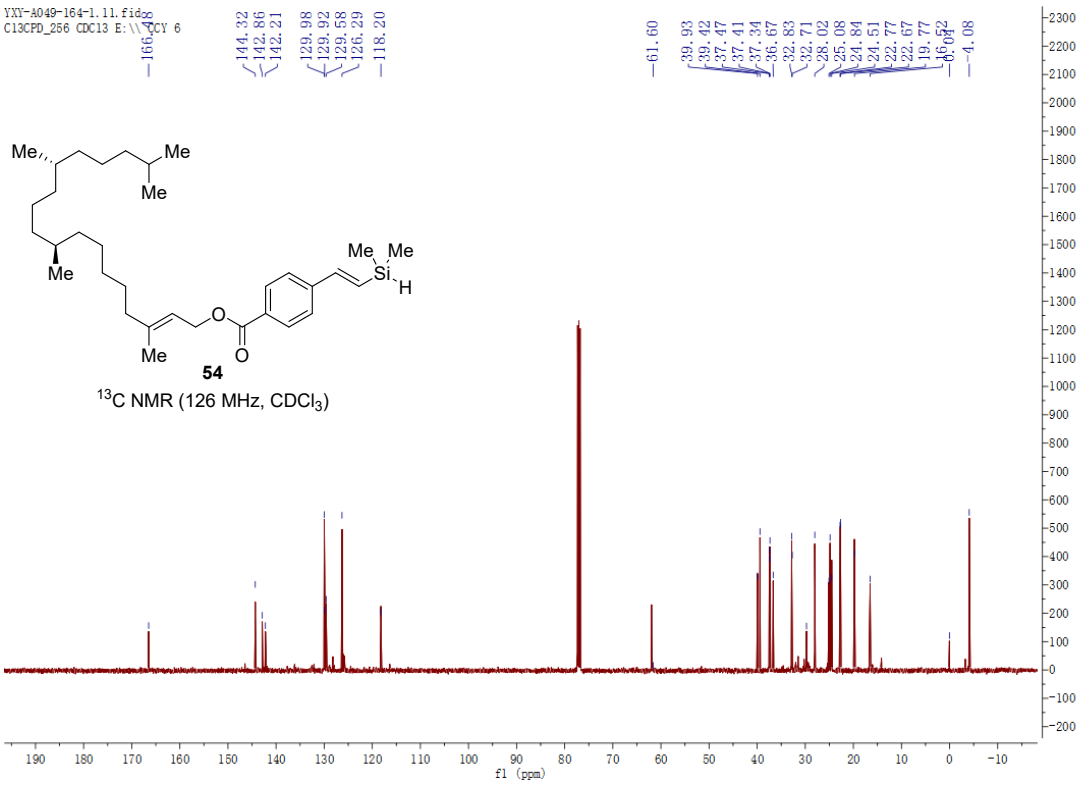


53

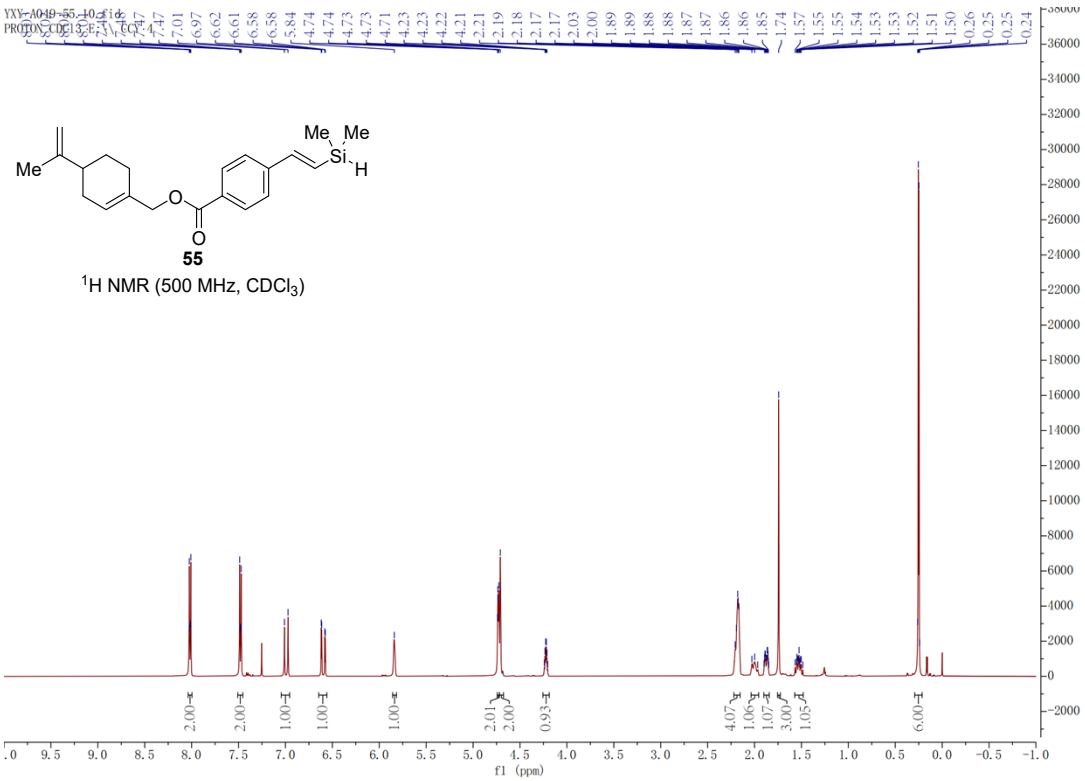
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

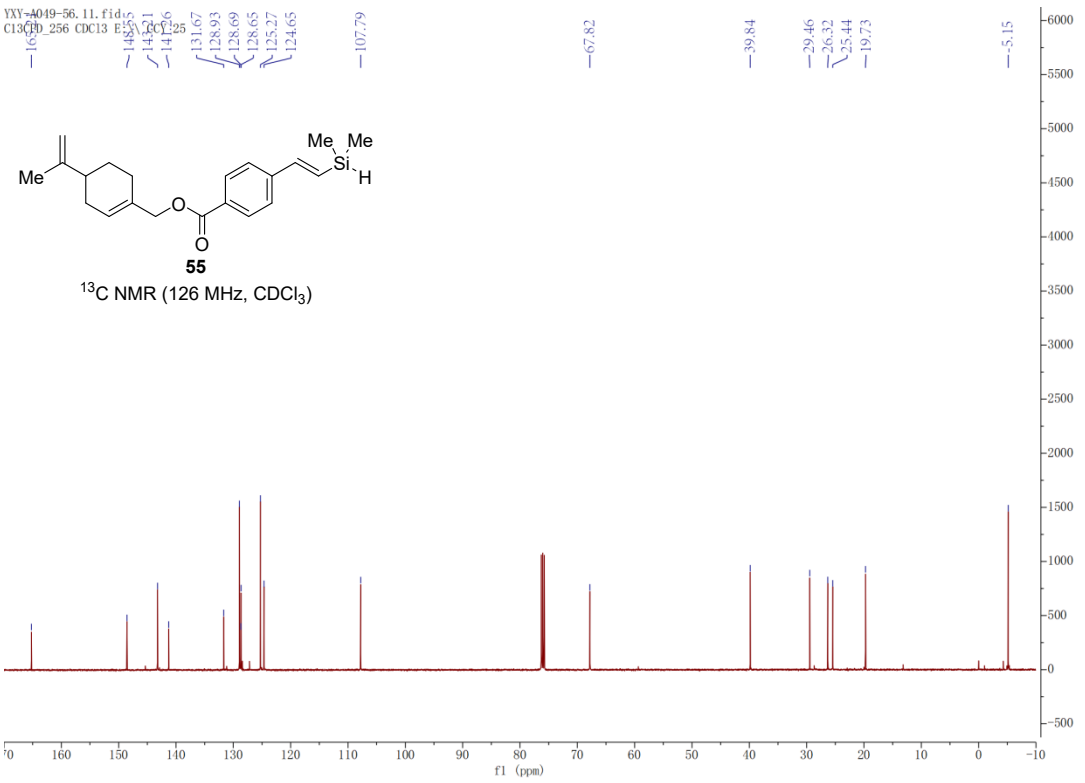


^{13}C NMR (126 MHz, $CDCl_3$)



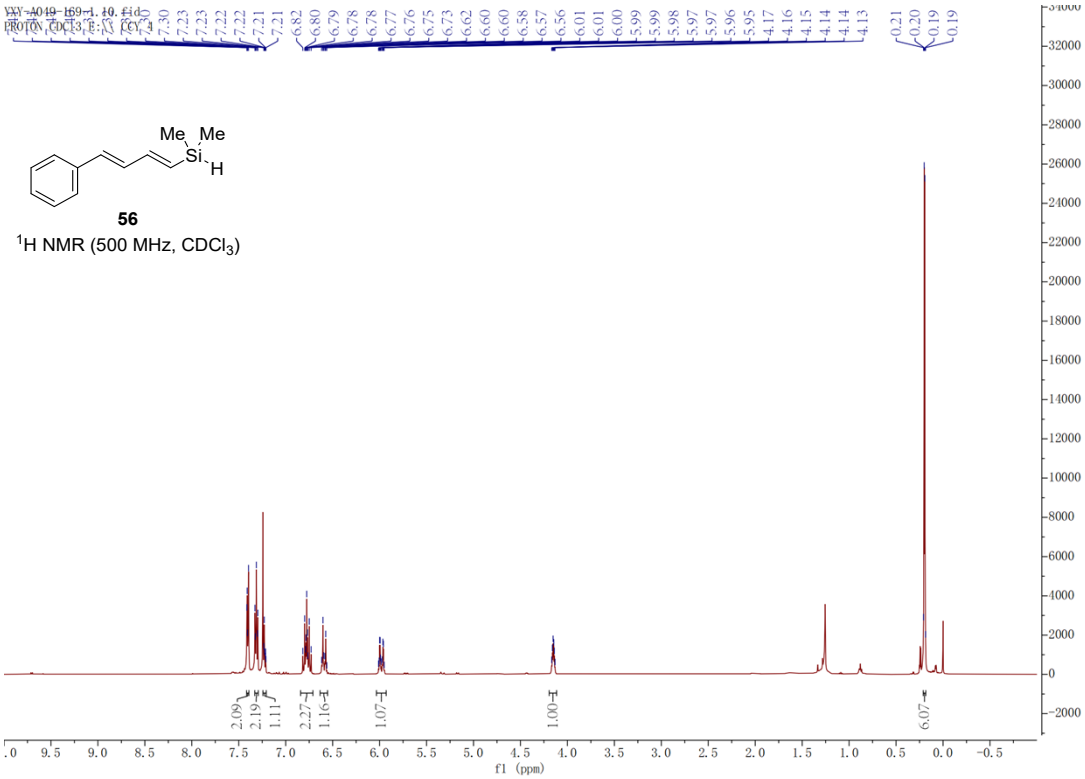
55

^{1}H NMR (500 MHz, $CDCl_3$)



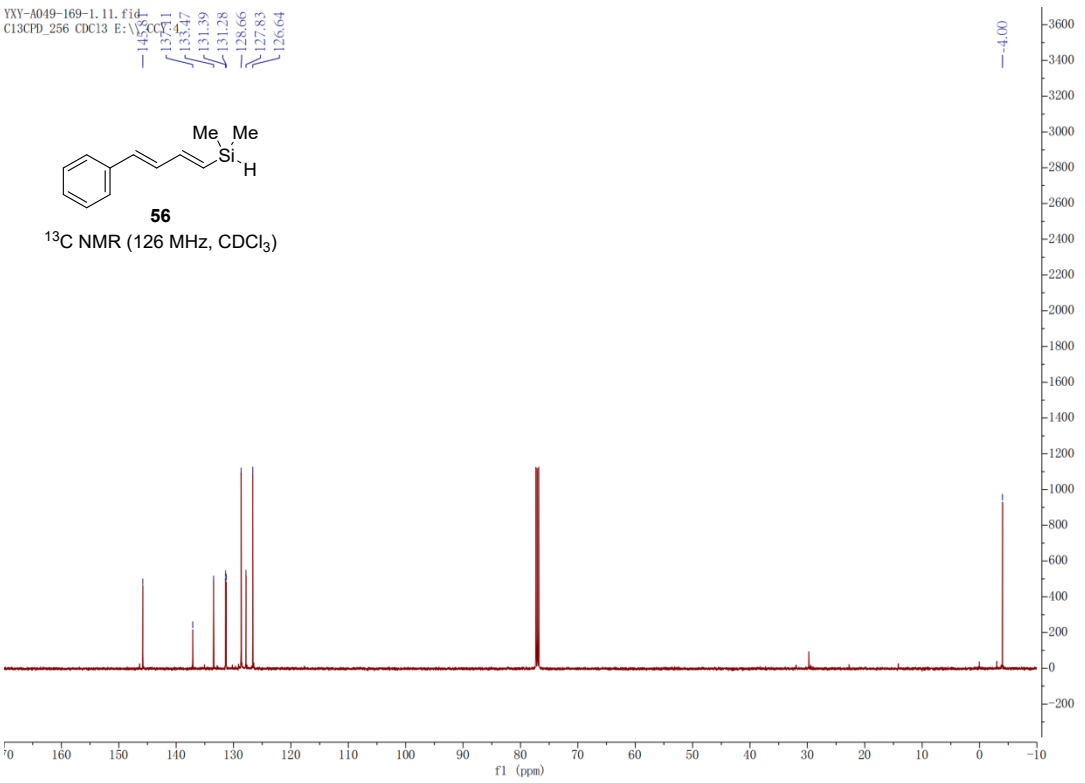
55

^{13}C NMR (126 MHz, $CDCl_3$)



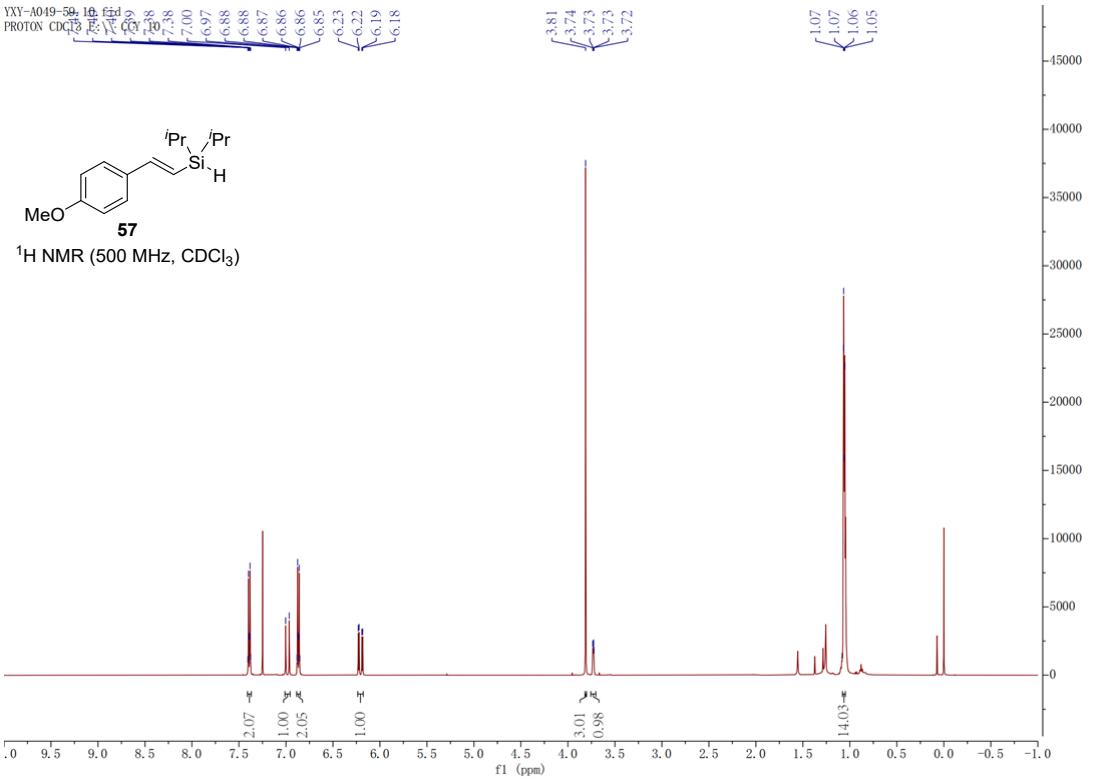
56

^{1}H NMR (500 MHz, $CDCl_3$)



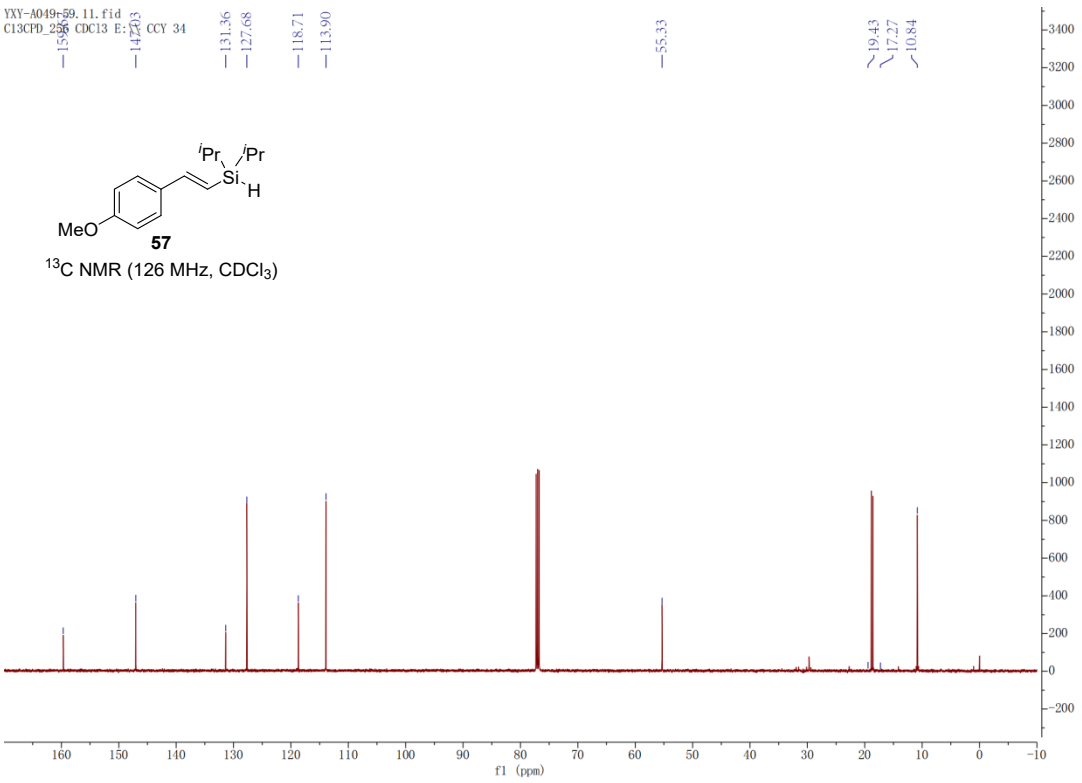
56

^{13}C NMR (126 MHz, $CDCl_3$)



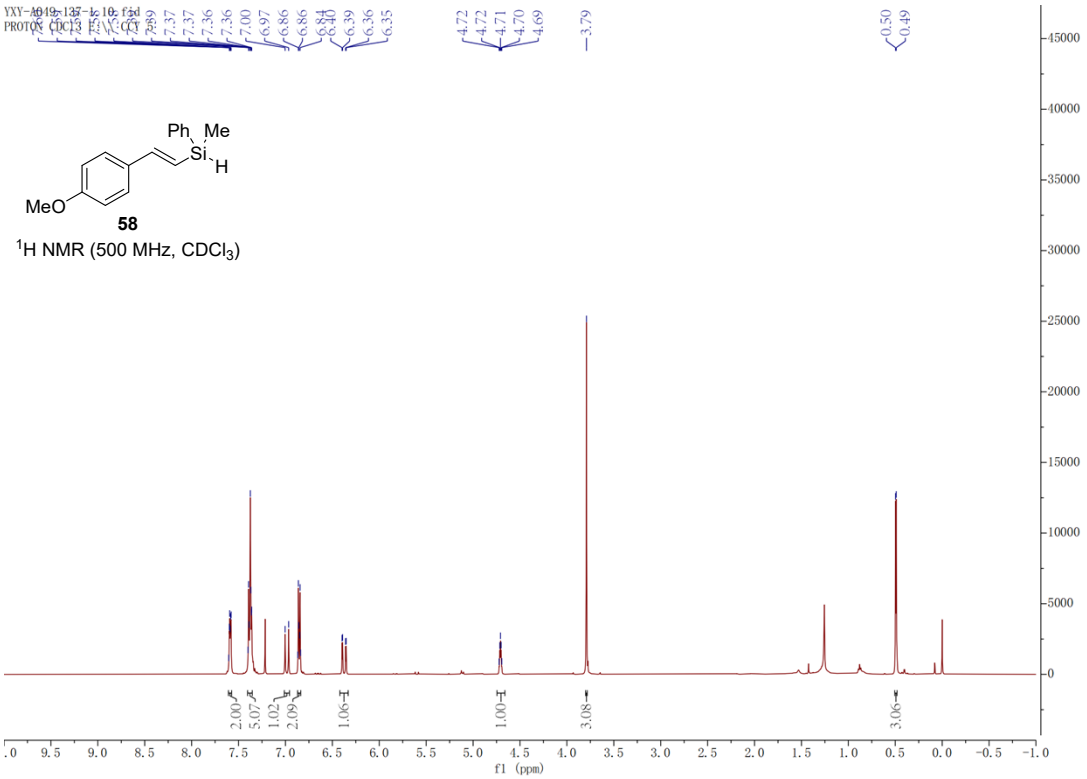
57

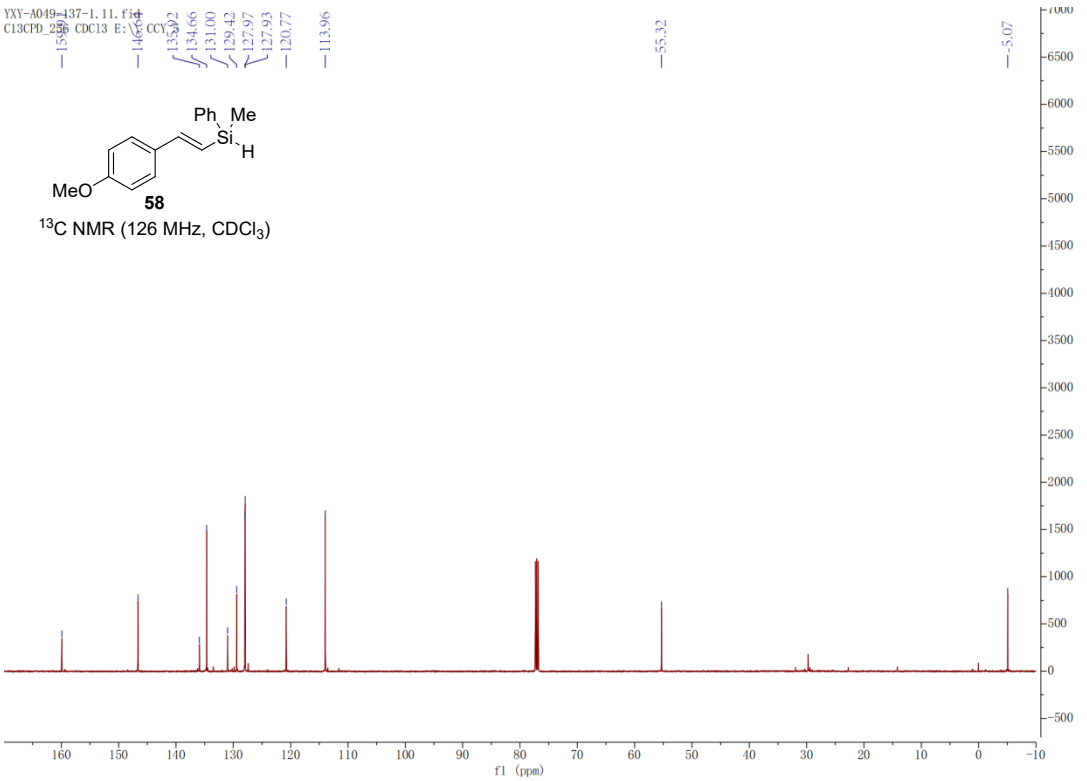
^{1}H NMR (500 MHz, $CDCl_3$)

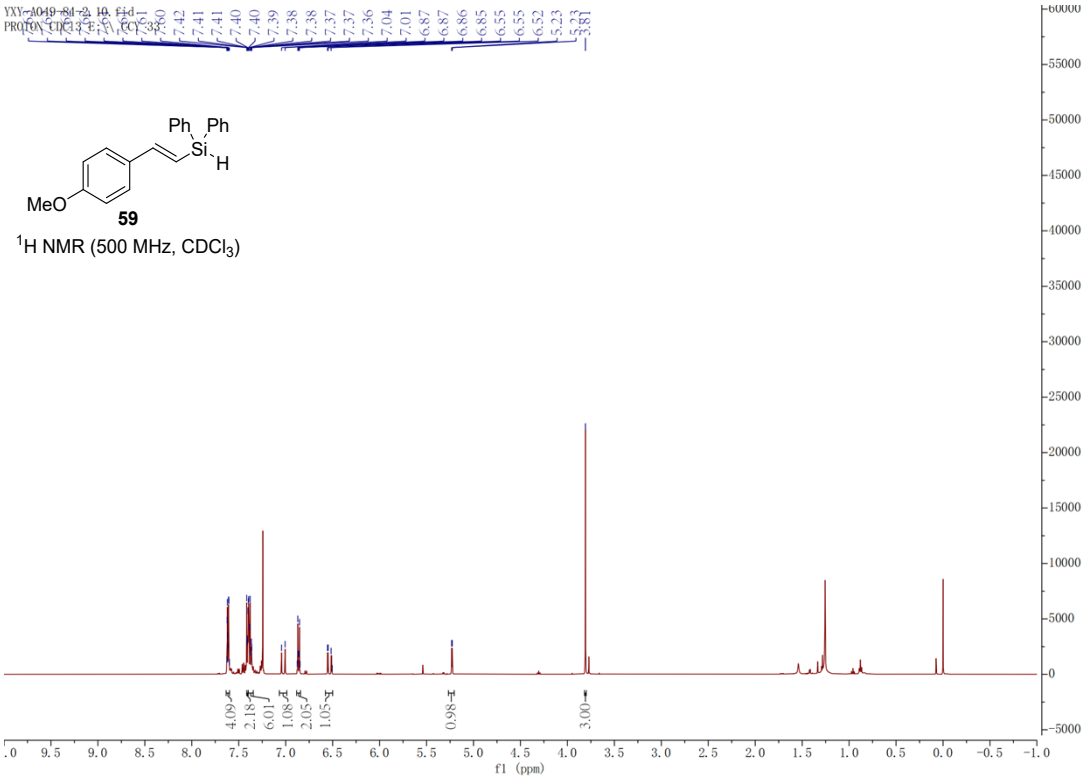


57

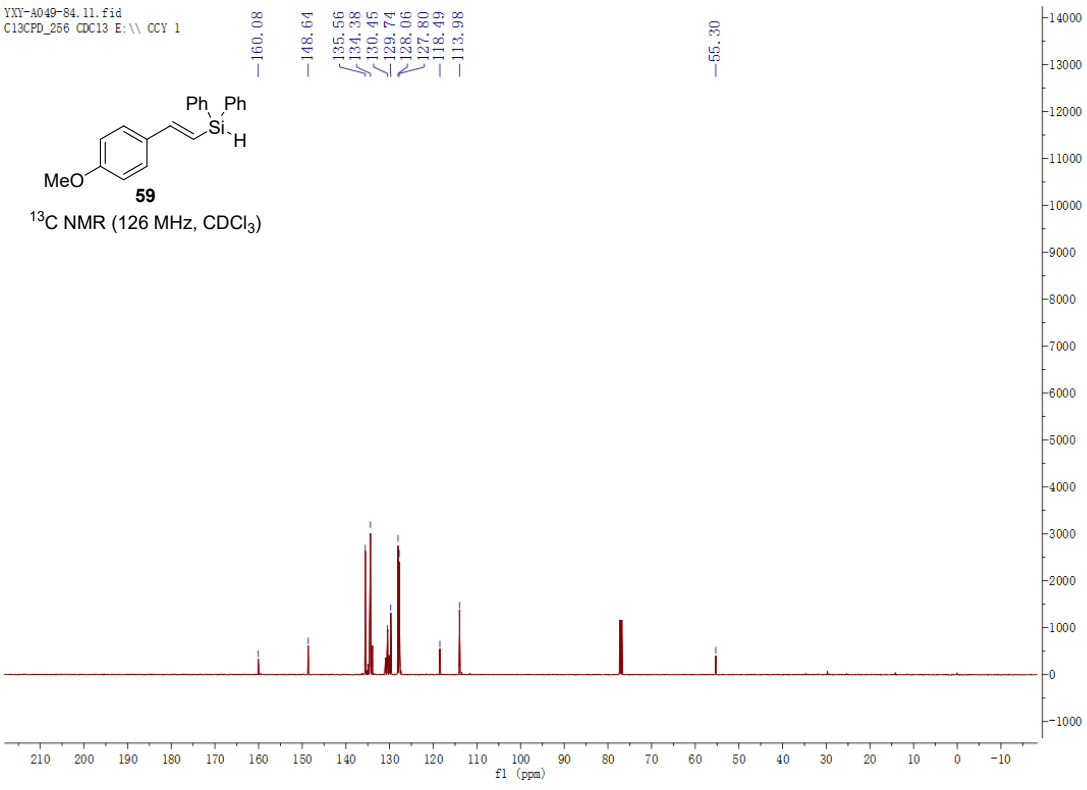
^{13}C NMR (126 MHz, $CDCl_3$)


Ph
Me
Si
H
MeO
58
1H NMR (500 MHz, CDCl3)
f1 (ppm)

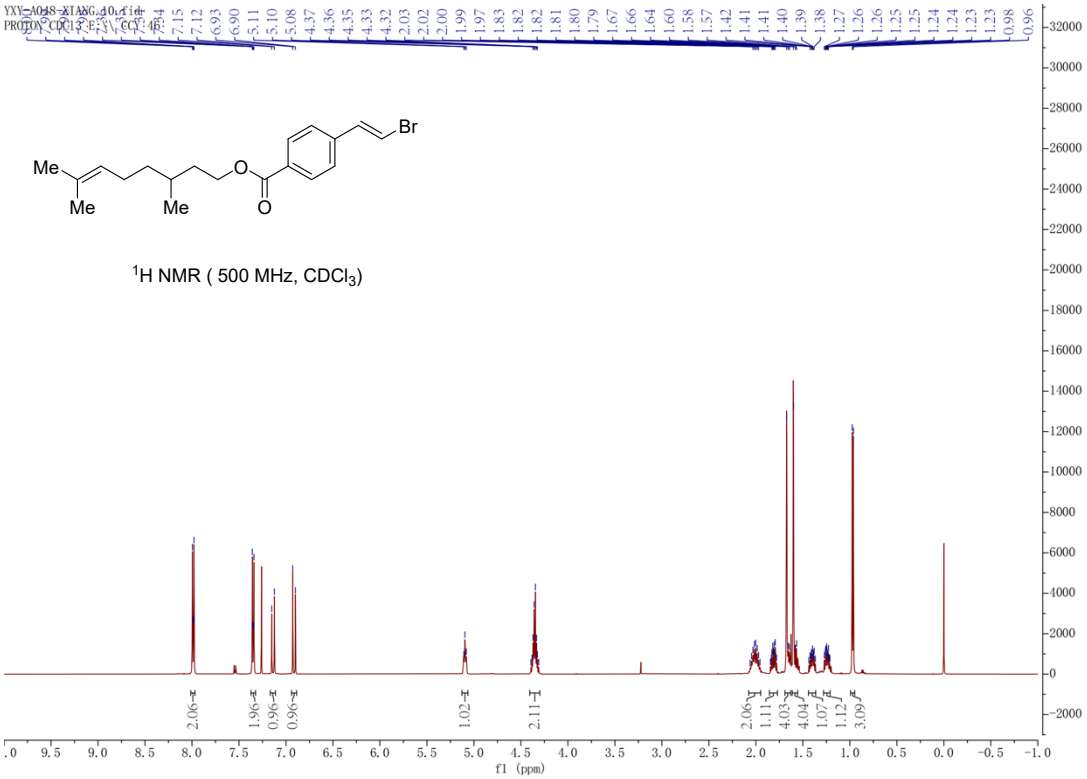

Ph
Me
Si
H
MeO
58
13C NMR (126 MHz, CDCl3)
f1 (ppm)



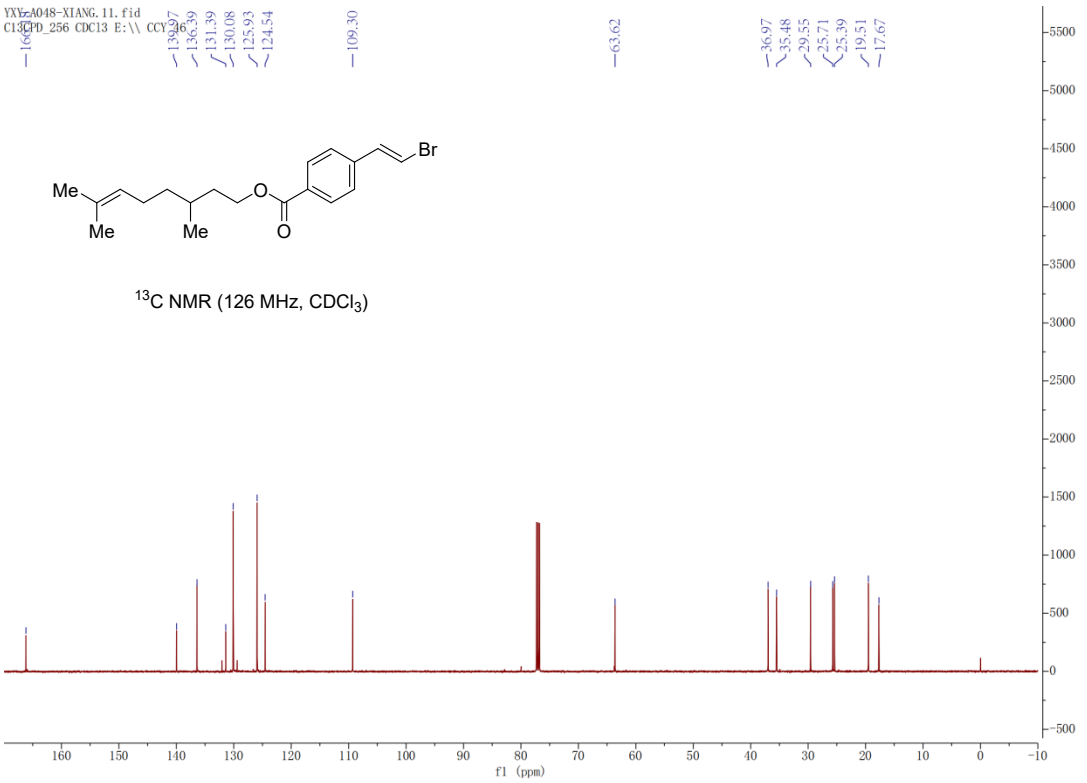
^{1}H NMR (500 MHz, $CDCl_3$)



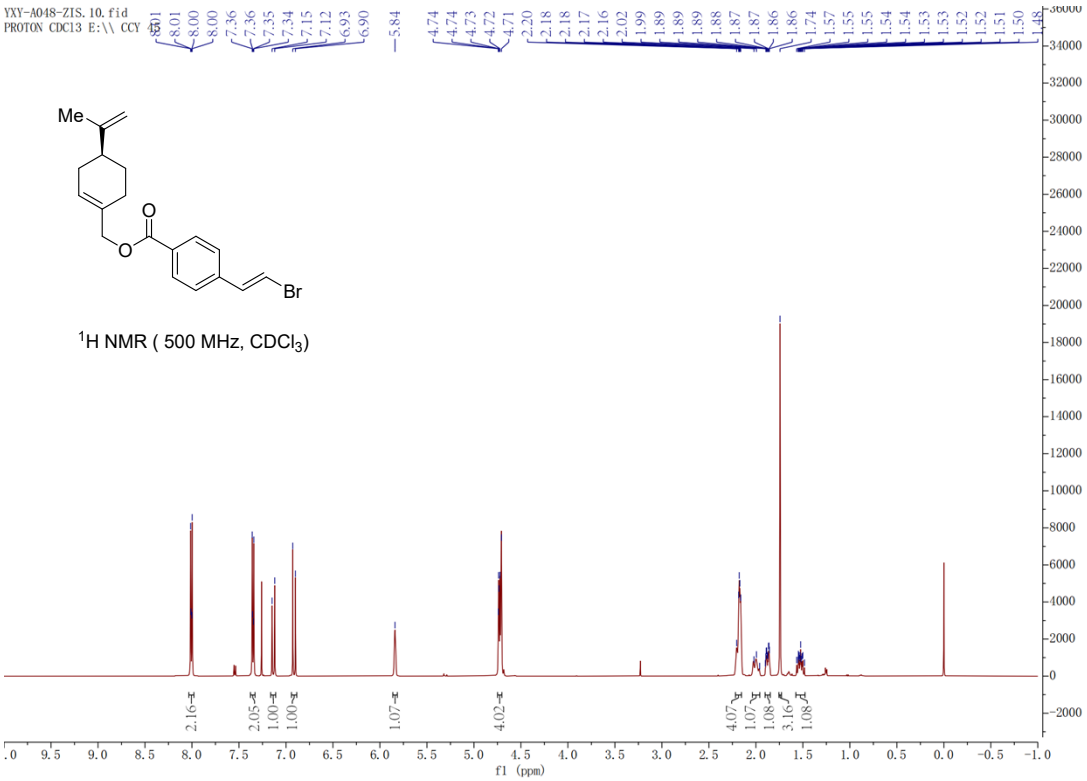
^{13}C NMR (126 MHz, $CDCl_3$)



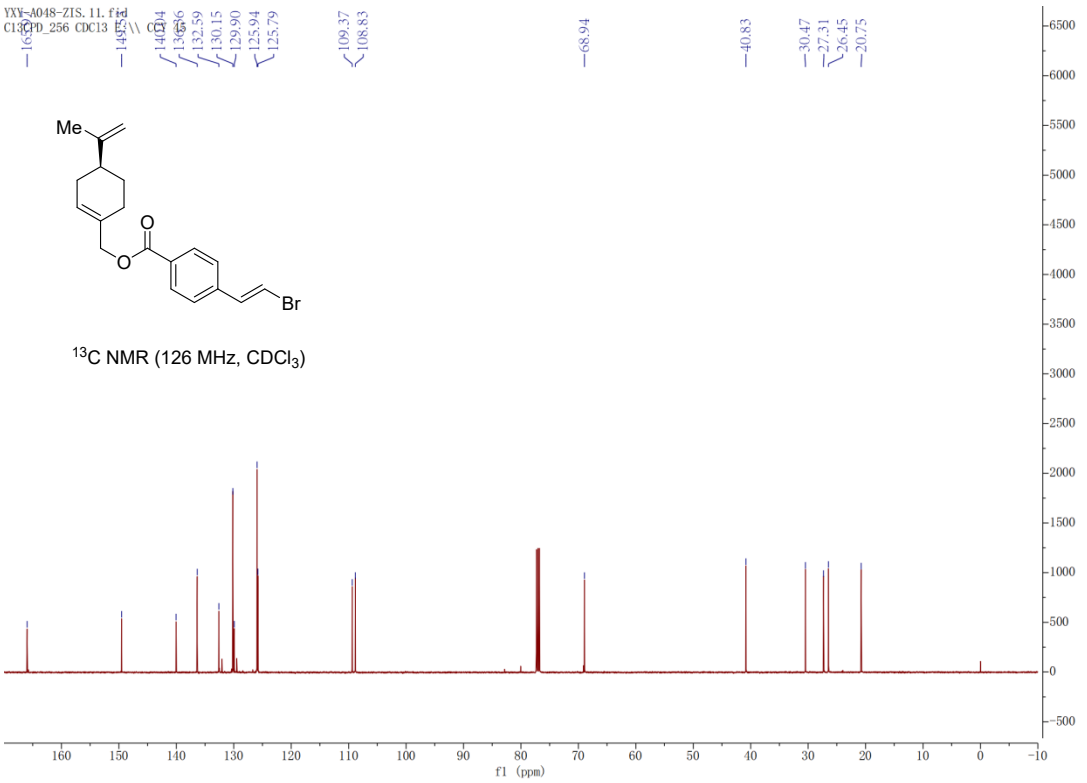
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

III. References

[1] Ye, Y.; Liu, J.; Xu, B.; Jiang, S.; Bai, R.; Li, S.; Xie, T.; Ye, X.-Y. *Chem. Sci.* **2021**, *12*, 13209.

[2] Ye, Y.; Qi, X.; Xu, B.; Lin, Y.; Xiang, H.; Zou, L; Ye, X.-Y.; Xie, T. *Chem. Sci.* **2022**, *13*, 6959.

[3] Duan, J.-C.; Wang, K.; Xu, G.-L.; Kang, S.-L.; Qi, L.-L.; Liu, X.-Y.; Shu, X.-Z. *Angew. Chem. Int. Ed.* **2020**, *59*, 23083.

[4] Zhao, Z.-Z.; Pang, X.-B.; Wei, X.-X.; Liu, X.-Y.; Shu, X.-Z. *Angew. Chem. Int. Ed.* **2022**, e202200215.