

Supporting Information

Palladium-catalyzed disilylation of *ortho*-halophenylethylenes enabled by 2-pyridone ligand

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1. General Information

Unless otherwise noted, reagents received from commercial suppliers (Adamas, Bidepharm, Macklin, TCI, Aladdin, Energy, Sigma-Aldrich, etc.) were used as received. Solvents dried with molecular sieves were obtained from J&K, Macklin, Energy or Acros and used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) supplied by Yantai Jiangyou Silicon Material Company (China). Visualization was accomplished with UV light or basic aqueous potassium permanganate (KMnO₄). Chromatography was conducted using forced flow (flash chromatography) of the indicated solvent system on 300-400 mesh silica gel (Silicycle flash F60). Preparative TLC was performed on silica gel 60 HSGF254 plates (Yantai Jiangyou) and observation of plates was carried out under UV light (254 nm).

Nuclear Magnetic Resonance (NMR) spectra were acquired on Varian mercury-400 and Bruker AM-400 spectrometers. Chemical shifts are reported in δ ppm referenced to internal SiMe₄ (TMS) standard or residual solvent peaks: TMS (δ 0.00 ppm) for ¹H NMR in Chloroform-*d* and DMSO-*d*₆; solvents' carbon resonances (Chloroform-*d* δ 77.00 and DMSO-*d*₆ δ 39.50) for ¹³C NMR. Multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (sextet), m (multiplet), and br (broad).

2. Reaction Development

Optimization of Reaction Conditions

To a 10 mL sealed tube charged with a stir bar were added a mixture of Pd precursor, ligand, base, and additives (if applicable). The sealed tube was capped with a Teflon thread plug, and then degassed and backfilled with argon (this procedure was repeated three times). Then hexamethyldisilane (**1**), 1-iodo-2-vinylbenzene (**2a**) and solvent were added under argon. The tube was sealed and the reaction mixture was stirred at a certain temperature for the specified amount of time. After the reaction mixture was cooled to room temperature, dodecane (internal standard, 12.5 μ L) and dichloromethane (2 mL) were added. An aliquot (0.1 mL) from the mixture was further diluted with dichloromethane and filtered and then analyzed by GC-FID. The yield and conversion were calculated against a calibration curve obtained for the authentic product and starting materials.

Note: when the loading of Pd precursor or ligand was too low to weigh accurately, a solution of the Pd precursor or ligand in the same solvent applied for the reaction was prepared in a certain concentration and used instead of the pure form.

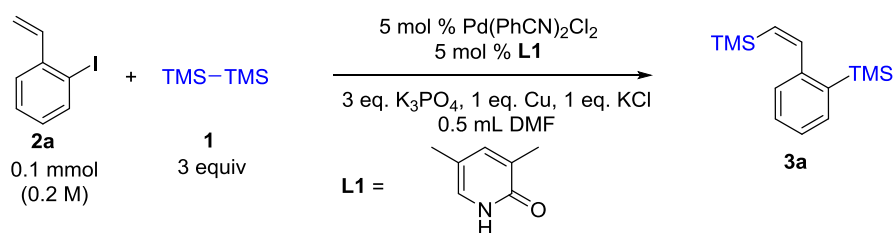
Table S1 Initial Screening of Reaction Conditions

entry	variation/additive	T/°C	conversion (%) ^a	3a (%) ^a
1	--	35 (62h)	8	2
2	--	60 (36h)	70	6
3	+ 0.5 eq. HCOOH	35 (86h)	10	1.6
4	2.5 mol % Pd ₂ (dba) ₃ ·HCCl ₃	35 (86h)	24	0.7
5	as substrate	80 (15h)	100	1
6	as substrate	80 (15h)	100	1.5

^aGC yield using dodecane as an internal standard.**Table S2** Screening of the reaction conditions

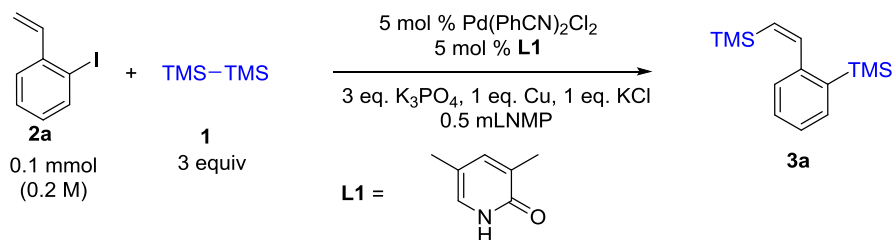
entry	variation/additive	T/°C	conversion (%) ^a	3a (%) ^a
1	--	60 (16h)	77	27
2	10 mol % L1	60 (21h)	100	25
3	--	35 (74h)	55	21
4	1 mol % Pd(PhCN) ₂ Cl ₂ , 4 mol % L1	60 (74h)	89	13
5	as substrate	60 (24h)	100	14
6	0.5 mL DMF	40 (71h)	100	37
7	0.5 mL DMF, 5 mol % L1	40 (33h)	100	37
8	0.5 mL DMF, Pd(OAc) ₂ instead	40 (71h)	100	37

^aGC yield using dodecane as an internal standard.

Table S3 Selected Conditions Screening

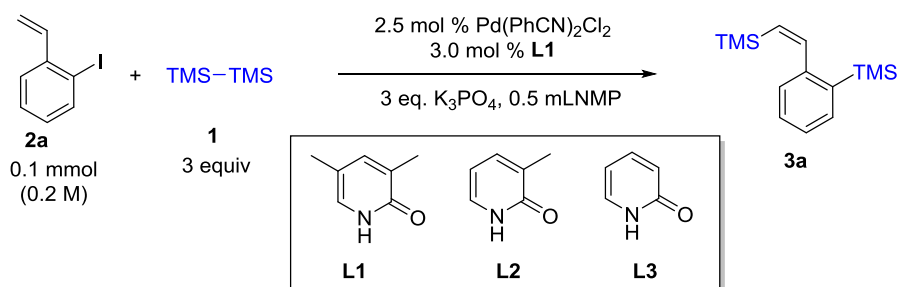
entry	variation/additive	T/°C	conversion (%) ^a	3a (%) ^a
1	10 mol % CuCl	50 (12h)	100	43
2	without Cu & KCl	50 (15h)	100	29
3	Cs ₂ CO ₃ as base	50 (17h)	45	19
4	KO ^t Bu as base	50 (12h)	100	0
5	DMA as solvent	50 (12h)	100	48
6	NMP as solvent	50 (12h)	100	49

^aGC yield using dodecane as an internal standard.

Table S4 Screening of additives

entry	variation/additive	T/°C	conversion (%) ^a	3a (%) ^a
1	10 mol % CuCl	50 (15h)	100	51
2	20 mol % CuCl	50 (15h)	100	60
3	10 % CuCl, 2.5 % Pd, 3.0% L1	50 (15h)	100	68
4	20 mol % CuCl, without Cu	50 (15h)	100	57
5	20 mol % CuCl, without Cu & KCl	50 (15h)	100	65
6	10 mol % CuCl, 5 eq. TMS ₂	50 (15h)	100	54
7	10 mol % CuCl, additional 1 eq. Cs ₂ CO ₃	50 (15h)	100	55

^aGC yield using dodecane as an internal standard.

Table S5 Screening of ligands and the equivalents of additives and catalysts

entry	variation/additive	T/°C	conversion (%) ^a	3a (%) ^a
1	20 mol % CuCl	50 (16h)	85	65
2	30 mol % CuCl	50 (16h)	73	53
3	50 mol % CuCl	50 (16h)	75	55
4	20 % CuCl, 1 % Pd, 1.2% L1	50 (40h)	100	81.5
5	20 % CuCl, 1 % Pd, 1.4% L1	50 (40h)	100	82.3
6	0.2 mmol scale, 20 % CuCl 1 % Pd, 1.2% L1 , 0.5 mL DMF	50 (40h)	100	78
7	20 % CuCl, 1 % Pd, 1.4% L2	50 (35h)	100	84
8	20 % CuBr, 1 % Pd, 1.4% L2	60 (16h)	100	84
9	20 % CuI, 1 % Pd, 1.4% L2	60 (16h)	100	86
10	20 % CuCl, 1 % Pd, 1.4% L3	60 (16h)	100	83
11	20 % CuI, 0.5 % Pd, 0.7% L2	60 (23h)	100	87

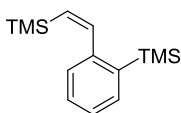
^aGC yield using dodecane as an internal standard.

3. Preparation of Substrates

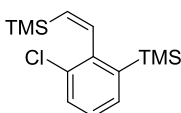
The substrates *ortho*-halophenylethylenes (**2**) are all known compounds and were synthesized according to the reported procedures¹.

4. General Procedure for the Disilylation Reaction of *ortho*-Halophenylethylenes

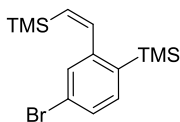
Standard reaction conditions: To a 10 mL sealed tube charged with a stir bar was added a mixture of CuI (11.4 mg, 0.06 mmol, 20 mol %), K₃PO₄ (192 mg, 0.9 mmol, 3 equiv.) and P(*o*-Tol)₃ (3.7 mg, 0.012 mmol, 4 mol %, if applied for *ortho*-bromophenylethylenes). The tube was capped with a Teflon thread plug, and then degassed and backfilled with argon (this procedure was repeated three times). Then Pd(PhCN)₂Cl₂ (0.0015 mmol, 0.5 mol %, an NMP solution was used instead of the pure form), 3-methylpyridin-2(1H)-one (0.0021 mmol, 0.7 mol %, an NMP solution was used instead of the pure form), *ortho*-halophenylethylene (0.3 mmol, 1 equiv), hexamethyldisilane (186 μ L, 0.9 mmol, 3 equiv) and NMP (1.5 mL) were added under argon. The tube was sealed immediately and the reaction mixture was stirred at 60°C for 24-48 h (*ortho*-iodophenylethylene) or 70°C for 14-18 h (*ortho*-bromophenylethylene). After cooling to room temperature, the mixture was poured into water (15 mL), extracted with petroleum ether, dried over Na₂SO₄ and concentrated. The pure product was then isolated by flash column chromatography unless otherwise noted.



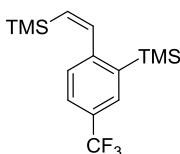
3a: 66.5 mg, 89% yield. Colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 14.9, 1H), 7.48 (dd, *J* = 7.2, 1.6, 1H), 7.30 (td, *J* = 7.4, 1.6, 1H), 7.27 – 7.21 (m, 1H), 7.19 (d, *J* = 7.1, 1H), 5.86 (d, *J* = 14.9, 1H), 0.29 (s, 9H), -0.09 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ = 148.6, 146.9, 137.7, 133.7, 133.2, 128.6, 128.5, 126.4, 0.0, -0.2. HRMS (FI): *m/z* for C₁₄H₂₄Si₂ [M]⁺ calcd.: 248.1411, found: 48.1410.



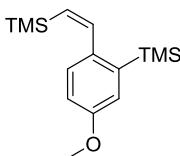
3b: 84.1 mg, 98% yield. Colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.27 (d, *J* = 15.1, 1H), 7.16 (ddd, *J* = 8.0, 7.2, 0.8, 1H), 6.08 (d, *J* = 15.3, 1H), 0.27 (s, 9H), -0.16 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ = 144.7, 142.8, 140.9, 136.7, 132.9, 132.1, 129.8, 127.5, 0.1, -1.3. HRMS (FI): *m/z* for C₁₄H₂₃ClSi₂ [M]⁺ calcd.: 282.1021, found: 282.1019.



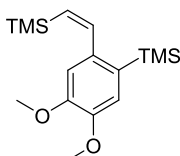
3c: 83.3 mg, 85% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.53 (d, $J = 14.8$, 1H), 7.40 – 7.32 (m, 2H), 7.32 (d, $J = 7.8$, 1H), 5.91 (d, $J = 14.8$, 1H), 0.27 (s, 9H), -0.05 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.6, 146.9, 136.5, 135.3, 134.8, 131.5, 129.2, 123.1, 0.0, -0.3. **HRMS** (FI): m/z for $\text{C}_{14}\text{H}_{23}\text{BrSi}_2$ $[\text{M}]^+$ calcd.: 326.0516, found: 326.0515.



3d: 93.5 mg, 98% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.62 – 7.54 (m, 2H), 7.30 (d, $J = 7.9$, 1H), 5.99 (d, $J = 15.0$, 1H), 0.34 (s, 9H), -0.06 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 150.4, 147.1, 139.1, 135.2, 130.3 (q, $J = 3.7$), 128.8, 128.5 (q, $J = 31.9$), 125.3 (q, $J = 3.8$), 124.5 (q, $J = 272.3$), 0.0, -0.4. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.35. **HRMS** (FI): m/z for $\text{C}_{15}\text{H}_{23}\text{F}_3\text{O}_2$ $[\text{M}]^+$ calcd.: 316.1282, found: 316.1283.

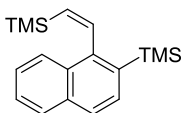


3e: 78.3 mg, 94% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.55 (d, $J = 14.7$, 1H), 7.14 (dd, $J = 8.4$, 0.7, 1H), 7.02 (d, $J = 2.8$, 1H), 6.81 (dd, $J = 8.3$, 2.8, 1H), 5.78 (d, $J = 14.7$, 1H), 3.80 (s, 3H), 0.28 (s, 9H), -0.07 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 158.1, 148.1, 139.5, 139.3, 132.2, 129.9, 120.1, 112.5, 55.1, 0.1, -0.3. **HRMS** (FI): m/z for $\text{C}_{15}\text{H}_{26}\text{OSi}_2$ $[\text{M}]^+$ calcd.: 278.1517, found: 278.1516.

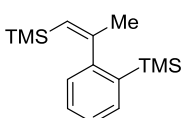


3f: 73.7 mg, 80% yield. White solid. **Melting point:** 41-43 °C. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.57 (d, $J = 14.8$, 1H), 6.97 (s, 1H), 6.79 (s, 1H), 5.81 (d, $J = 14.8$, 1H), 3.90 (s, 3H), 3.90 (s, 3H),

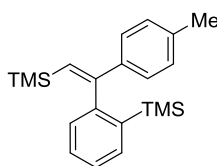
0.28 (s, 9H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.8, 148.3, 147.2, 140.2, 132.2, 129.3, 116.6, 112.6, 55.8, 55.7, 0.1, -0.10. HRMS (FI): m/z for $\text{C}_{16}\text{H}_{28}\text{O}_2\text{Si}_2$ $[\text{M}]^+$ calcd.: 308.1622, found: 308.1626.



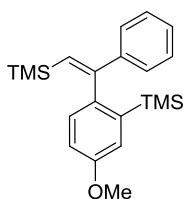
3g: 88.1 mg, 98% yield. Colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.08 (m, 1H), 7.83 – 7.76 (m, 1H), 7.75 – 7.67 (m, 2H), 7.58 (d, $J = 8.3$, 1H), 7.49 – 7.38 (m, 2H), 6.25 (d, $J = 15.4$, 1H), 0.35 (s, 9H), -0.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.5, 144.7, 136.9, 134.2, 133.6, 131.8, 130.0, 127.8, 126.7, 126.0, 125.8, 125.4, 0.3, -1.3. HRMS (FI): m/z for $\text{C}_{18}\text{H}_{26}\text{Si}_2$ $[\text{M}]^+$ calcd.: 298.1568, found: 298.1569.



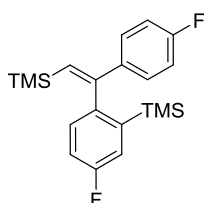
3h: 78.0 mg, 99% yield. Colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 1H), 7.30 – 7.18 (m, 2H), 7.03 – 6.96 (m, 1H), 5.57 (q, $J = 1.4$, 1H), 2.13 (d, $J = 1.4$, 3H), 0.29 (s, 9H), -0.26 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.8, 150.6, 136.7, 134.6, 128.4, 128.4, 128.3, 125.9, 31.8, 0.9, -0.4. HRMS (FI): m/z for $\text{C}_{15}\text{H}_{26}\text{Si}_2$ $[\text{M}]^+$ calcd.: 262.1568, found: 262.1565.



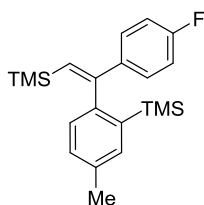
3i: 98% yield. Colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 1H), 7.43 – 7.29 (m, 2H), 7.16 (m, 3H), 7.07 (d, $J = 8.1$, 2H), 6.35 (s, 1H), 2.33 (s, 3H), -0.01 (s, 9H), -0.16 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 148.0, 140.1, 138.6, 137.4, 134.7, 130.9, 128.7, 128.3, 128.0, 126.9, 126.4, 21.1, 0.3, -0.4. HRMS (FI): m/z for $\text{C}_{21}\text{H}_{30}\text{Si}_2$ $[\text{M}]^+$ calcd.: 338.1881, found: 338.1886.



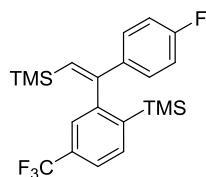
3j: 104.5 mg, 98% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 5H), 7.13 – 7.06 (m, 2H), 6.92 – 6.87 (m, 1H), 6.34 (s, 1H), 3.86 (s, 3H), -0.07 (s, 9H), -0.16 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 158.0, 157.4, 143.3, 140.3, 140.2, 132.2, 129.7, 128.0, 127.5, 127.1, 121.1, 112.3, 55.1, 0.1, -0.3. **HRMS** (FI): m/z for $\text{C}_{21}\text{H}_{30}\text{OSi}_2$ $[\text{M}]^+$ calcd.: 354.1830, found: 354.1834.



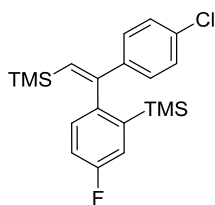
3k: 101.8 mg, 94% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 3H), 7.22 (dd, $J = 8.3, 5.6$, 1H), 7.15 (td, $J = 8.3, 2.7$, 1H), 7.04 (t, $J = 8.7$, 2H), 6.41 (s, 1H), 0.06 (s, 9H), -0.06 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 162.5 (d, $J = 247.9$), 161.8 (d, $J = 248.0$), 155.4, 143.4 (d, $J = 3.2$), 141.8 (d, $J = 3.7$), 139.1 (d, $J = 3.2$), 132.5 (d, $J = 6.8$), 129.9 (d, $J = 1.8$), 128.7 (d, $J = 8.1$), 121.4 (d, $J = 18.9$), 115.1 (d, $J = 20.9$), 114.9 (d, $J = 21.4$), 0.0, -0.4. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -114.62 (tt, $J = 8.7, 5.4$), -116.07 (td, $J = 8.9, 5.5$). **HRMS** (FI): m/z for $\text{C}_{20}\text{H}_{26}\text{F}_2\text{Si}_2$ $[\text{M}]^+$ calcd.: 360.1536, found: 360.1537.



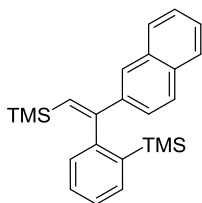
3l: 103.7 mg, 97% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.34 (d, $J = 1.9$, 1H), 7.23 – 7.15 (m, 3H), 7.03 (d, $J = 7.7$, 1H), 6.92 (t, $J = 8.7$, 2H), 6.26 (s, 1H), 2.39 (s, 3H), -0.05 (s, 9H), -0.18 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 162.4 (d, $J = 247.3$), 156.6, 144.7, 139.4 (d, $J = 3.2$), 138.2, 135.8, 135.7, 130.9, 129.1, 129.1 (d, $J = 1.8$), 128.7 (d, $J = 8.0$), 114.8 (d, $J = 21.3$), 21.4, 0.3, -0.4. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -115.12 (tt, $J = 8.6, 5.4$). **HRMS** (FI): m/z for $\text{C}_{21}\text{H}_{29}\text{FSi}_2$ $[\text{M}]^+$ calcd.: 356.1786, found: 356.1784.



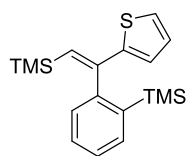
3m: 121.7 mg, 99% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.70 (d, $J = 7.8$, 1H), 7.65 – 7.54 (m, 1H), 7.42 (d, $J = 1.9$, 1H), 7.25 – 7.13 (m, 2H), 6.97 (t, $J = 8.7$, 2H), 6.38 (s, 1H), -0.00 (s, 9H), -0.17 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 162.6 (d, $J = 248.3$), 155.2, 148.3, 143.9 (q, $J = 1.2$), 138.5 (d, $J = 3.3$), 135.5, 130.6 (q, $J = 32.3, 32.3, 32.3$), 130.5 (d, $J = 1.8$), 128.7 (d, $J = 8.1$), 127.2 (q, $J = 3.7, 3.6, 3.6$), 124.1 (q, $J = 272.4, 272.3, 272.3$), 123.1 (q, $J = 3.8, 3.8, 3.8$), 115.1 (d, $J = 21.5$), 0.0, -0.55. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62, -114.16 (tt, $J = 8.7, 5.4$). **HRMS** (FI): m/z for $\text{C}_{21}\text{H}_{26}\text{F}_4\text{Si}_2$ $[\text{M}]^+$ calcd.: 410.1504, found: 410.1498.



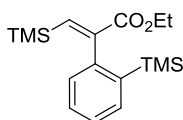
3n: 107.6 mg, 95% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 3H), 7.18 – 7.13 (m, 2H), 7.10 (dd, $J = 8.3, 5.6$, 1H), 7.05 (td, $J = 8.4, 2.7$, 1H), 6.37 (s, 1H), -0.03 (s, 9H), -0.17 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 161.8 (d, $J = 248.1$), 155.3, 143.1 (d, $J = 3.4$), 141.9 (d, $J = 3.6$), 141.2, 133.6, 132.6 (d, $J = 6.7$), 130.8, 128.2, 128.2, 121.4 (d, $J = 18.8$), 115.1 (d, $J = 20.7$), 0.1, -0.45. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -115.95 (td, $J = 8.8, 5.5$). **HRMS** (FI): m/z for $\text{C}_{20}\text{H}_{26}\text{ClF}\text{Si}_2$ $[\text{M}]^+$ calcd.: 376.1240, found: 376.1235.



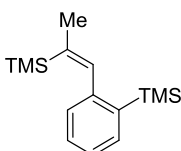
3o: 110.0 mg, 98% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 2H), 7.70 – 7.63 (m, 2H), 7.62 – 7.57 (m, 1H), 7.46 – 7.33 (m, 5H), 7.24 – 7.19 (m, 1H), 6.54 (s, 1H), -0.07 (s, 9H), -0.15 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 157.3, 147.7, 139.9, 138.9, 134.8, 133.1, 132.8, 131.0, 129.9, 128.5, 128.5, 127.7, 127.4, 127.0, 126.6, 126.0, 126.0, 124.3, 0.4, -0.4. **HRMS** (FI): m/z for $\text{C}_{24}\text{H}_{30}\text{Si}_2$ $[\text{M}]^+$ calcd.: 374.1881, found: 374.1887.



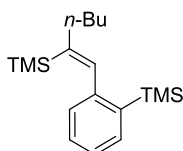
3p: 98.3 mg, 99% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 1H), 7.38 – 7.28 (m, 2H), 7.19 (dd, $J = 5.1, 1.2$, 1H), 7.18 – 7.11 (m, 1H), 6.85 (dd, $J = 5.1, 3.6$, 1H), 6.40 (dd, $J = 3.6, 1.2$, 1H), 6.20 (s, 1H), 0.08 (s, 9H), -0.19 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 151.3, 149.8, 146.8, 138.9, 134.7, 130.0, 128.3, 127.8, 127.4, 126.8, 125.6, 0.5, -0.4. **HRMS** (FI): m/z for $\text{C}_{18}\text{H}_{26}\text{SSi}_2$ $[\text{M}]^+$ calcd.: 330.1288, found: 330.1293.



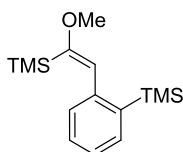
3q: 80.9 mg, 84% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 1H), 7.32 – 7.27 (m, 2H), 7.24 (s, 1H), 7.06 – 6.97 (m, 1H), 4.27 – 4.07 (m, 2H), 1.22 (t, $J = 7.1, 7.1$, 3H), 0.19 (s, 9H), -0.19 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.0, 149.2, 145.2, 144.0, 138.6, 134.3, 130.0, 128.2, 126.7, 61.1, 14.2, 0.5, -1.1. **HRMS** (FI): m/z for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{Si}_2$ $[\text{M}]^+$ calcd.: 320.1622, found: 320.1624.



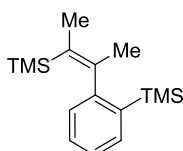
3r: 64.7 mg, 82% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.45 (dd, $J = 7.0, 1.7$, 1H), 7.29 (s, 1H), 7.28 – 7.22 (m, 1H), 7.21 (td, $J = 7.3, 1.6$, 1H), 7.08 (d, $J = 7.0$, 1H), 1.95 (d, $J = 1.7$, 3H), 0.26 (s, 9H), -0.16 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 146.9, 143.2, 139.6, 137.7, 133.7, 129.3, 128.4, 126.0, 24.5, -0.2, -0.6. **HRMS** (FI): m/z for $\text{C}_{15}\text{H}_{26}\text{Si}_2$ $[\text{M}]^+$ calcd.: 262.1568, found: 262.1563.



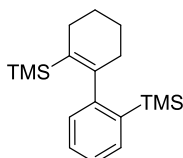
3s: 64.1 mg, 70% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.46 (dd, $J = 7.3, 1.6$, 1H), 7.30 (s, 1H), 7.26 (td, $J = 7.4, 1.7$, 1H), 7.21 (td, $J = 7.3, 1.5$, 1H), 7.12 (d, $J = 7.1$, 1H), 2.26 (m, 2H), 1.53 – 1.34 (m, 4H), 0.95 (t, $J = 7.2$, 3H), 0.26 (s, 9H), -0.15 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 147.2, 144.2, 143.1, 137.7, 133.7, 129.3, 128.4, 126.0, 38.2, 32.4, 22.7, 14.0, 0.2, -0.2. **HRMS** (FI): m/z for $\text{C}_{18}\text{H}_{32}\text{Si}_2$ $[\text{M}]^+$ calcd.: 304.2037, found: 304,2035.



3t: 80.4 mg, 96% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.47 (dd, $J = 7.1, 1.9$, 1H), 7.30 – 7.17 (m, 2H), 7.11 (d, $J = 7.3$, 1H), 6.54 (s, 1H), 3.64 (s, 3H), 0.29 (s, 9H), -0.12 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 164.3, 143.8, 139.1, 133.8, 130.7, 128.5, 125.8, 115.3, 54.6, -0.1, -1.1. **HRMS** (FI): m/z for $\text{C}_{15}\text{H}_{26}\text{OSi}_2$ $[\text{M}]^+$ calcd.: 278.1517, found: 278.1512.

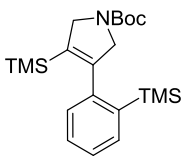


3u: 76.4 mg, 92% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 1H), 7.27 – 7.18 (m, 2H), 6.97 – 6.90 (m, 1H), 1.95 (q, $J = 1.1$, 3H), 1.77 (q, $J = 1.1$, 3H), 0.23 (s, 9H), -0.31 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 153.0, 148.2, 137.2, 134.6, 131.4, 128.8, 128.3, 125.6, 23.9, 17.5, 0.7, -0.7. **HRMS** (FI): m/z for $\text{C}_{16}\text{H}_{28}\text{Si}_2$ $[\text{M}]^+$ calcd.: 276.1724, found: 276.1721.



3v: 74.4 mg, 82% yield. Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.48 (dd, $J = 7.2, 1.8$, 1H), 7.27 – 7.18 (m, 2H), 6.95 (dd, $J = 7.0, 1.7$, 1H), 2.28 – 2.05 (m, 4H), 1.81 – 1.73 (m, 2H), 1.73 – 1.61 (m, 1H), 1.58 – 1.51 (m, 1H), 0.27 (s, 9H), -0.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ

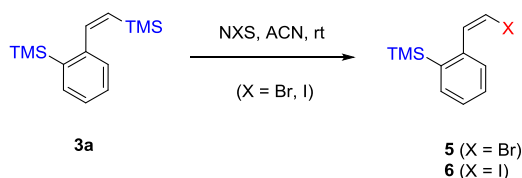
152.2, 149.6, 137.5, 134.7, 133.0, 129.2, 128.3, 125.6, 35.5, 28.3, 23.0, 22.6, 1.0, -0.9. **HRMS** (FI): m/z for $C_{18}H_{30}Si_2 [M]^+$ calcd.: 302.1881, found: 302.1877.



3w: 105.3 mg, 90% yield. Colorless oil. **1H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 1H), 7.33 – 7.27 (m, 2H), 7.09 – 7.01 (m, 1H), 4.46 – 4.16 (m, 4H), 1.54 – 1.44 (m, 9H), 0.25 (s, 9H), -0.15 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.2, 154.0, 149.8, 149.6, 142.5, 138.3, 138.2, 134.8, 134.7, 134.4, 134.3, 129.0, 128.5, 128.5, 126.8, 79.4, 79.3, 61.2, 61.0, 58.21, 58.19, 28.6, 28.5, 0.7, 0.6, -1.2, -1.3. **HRMS** (FI): m/z for $C_{21}H_{35}O_2NSi_2 [M]^+$ calcd.: 389.2201, found: 389.2204.

5. Synthetic Transformations of the Disilylated Product **3a**

5.1 Vinyl Halogenation Reaction

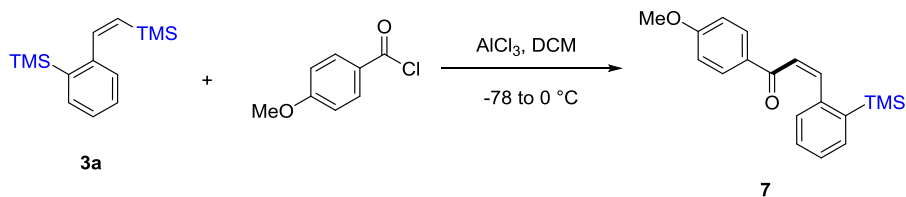


To the solution of NXS (0.3 mmol, 1 equiv.) in 2 mL CH_3CN at rt (20 °C) was added **3a** (0.3 mmol, 1 equiv., 74.6 mg, 84 μ L). After stirring at rt for 6 h, the reaction mixture was poured into water and extracted with petroleum ether. The combined extract was dried over Na_2SO_4 , concentrated in *vacuo* and purified by flash column chromatography (petroleum ether) to give the product **5/6**.

5: 72.5 mg, 95% yield, colorless oil. **1H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, $J = 7.3$, 2H), 7.38 (td, $J = 7.5$, 1.5, 1H), 7.34 – 7.27 (m, 2H), 6.52 (d, $J = 7.8$, 1H), 0.30 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.1, 138.8, 134.9, 134.3, 128.9, 128.7, 127.1, 108.6, -0.3. **HRMS** (FI): m/z for $C_{11}H_{15}BrSi [M]^+$ calcd.: 254.0121, found: 254.0125.

6: 78.1 mg, 86% yield, colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.55 (d, J = 6.9, 1H), 7.50 (d, J = 8.2, 1H), 7.45 – 7.34 (m, 2H), 7.31 (td, J = 7.2, 1.8, 1H), 6.66 (d, J = 8.3, 1H), 0.29 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 144.0, 141.6, 138.4, 134.3, 128.8, 128.5, 127.2, 83.8, -0.3. **HRMS** (FI): m/z for $\text{C}_{11}\text{H}_{15}\text{Si}$ $[\text{M}]^+$ calcd.: 301.9982, found: 301.9980.

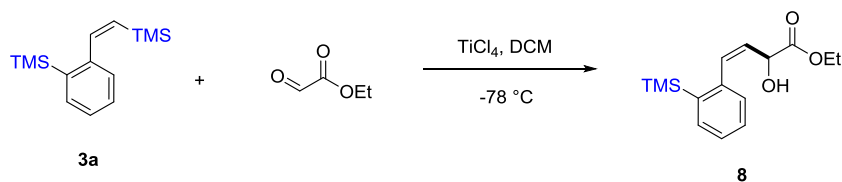
5.2 Acylation of **3a**



To the solution of 4-methoxybenzoyl chloride (0.33 mmol, 56.3 mg, 45 μL , 1.1 equiv.) in DCM (0.6 mL) at -78 °C under argon was added AlCl_3 (0.36 mmol, 48 mg, 1.2 equiv.), then a solution of **3a** (0.3 mmol, 1 equiv., 74.6 mg, 84 μL) in 0.4 mL DCM was added slowly into the mixture. The reaction mixture was stirred at -78 °C for 1 h and then the temperature was slowly elevated to 0 °C in 20 min. After cooling to -78 °C, a solution of Et_3N and MeOH in DCM was added slowly to quench the reaction. A solution of oxalic acid in water was added followed by extraction with EtOAc. The combined extract was dried over Na_2SO_4 , concentrated in *vacuo* and purified by flash column chromatography (petroleum ether/EtOAc 15 : 1) to give the product **7** (74.7 mg, 80% yield) as a yellowish oil. This product is rather unstable and will be transformed into the more stable *trans*-isomer under common experimental operation.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.87 (d, J = 8.9, 2H), 7.48 (dd, J = 7.3, 1.6, 1H), 7.32 (d, J = 12.5, 1H), 7.25 – 7.06 (m, 3H), 6.82 (d, J = 8.9, 2H), 6.64 (d, J = 12.5, 1H), 3.81 (s, 3H), 0.38 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 193.1, 163.4, 141.6, 140.5, 138.4, 134.1, 131.2, 130.2, 129.3, 128.7, 127.32, 127.31, 113.6, 55.4, -0.0. **HRMS** (FI): m/z for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{Si}$ $[\text{M}]^+$ calcd.: 310.1384, found: 310.1381.

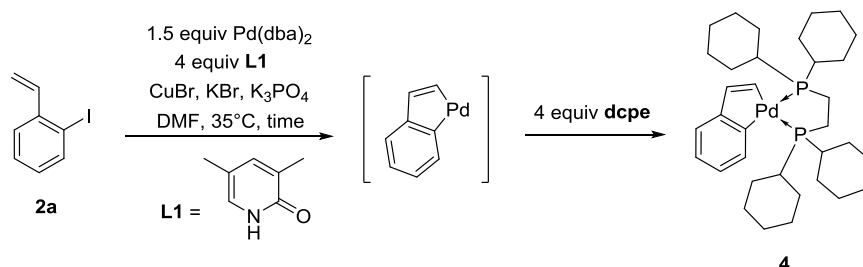
5.3 Substitution Reaction of 3a with Ethyl Glyoxylate



According to the reported procedure,² to the solution of ethyl glyoxylate (50% in toluene, 0.33 mmol, 67.4 mg, 1.1 equiv.) in DCM (0.4 mL) at -78 °C under argon was added a solution of TiCl₄ (0.36 mmol, 68.3 mg, 39.5 μL, 1.2 equiv.) in 0.4 mL DCM, then a solution of **3a** (0.3 mmol, 1 equiv., 74.6 mg, 84 μL) in 0.4 mL DCM was added slowly into the mixture. The reaction mixture was stirred at -78 °C for 1 h and then a solution of Et₃N and MeOH in DCM was added slowly to quench the reaction. A solution of oxalic acid in water was added followed by extraction with EtOAc. The combined extract was dried over Na₂SO₄, concentrated in *vacuo* and purified by flash column chromatography (petroleum ether/EtOAc 5 : 1) to give the product **8** (70.0 mg, 84% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.2, 1.5, 1H), 7.45 (d, *J* = 7.5, 1H), 7.36 (td, *J* = 7.5, 1.5, 1H), 7.28 (td, *J* = 7.4, 1.4, 1H), 7.04 (d, *J* = 11.2, 1H), 5.66 (dd, *J* = 11.2, 9.9, 1H), 4.84 (dd, *J* = 10.0, 5.1, 1H), 4.25 (q, *J* = 7.2, 2H), 3.01 (d, *J* = 5.2, 1H), 1.29 (t, *J* = 7.2, 3H), 0.32 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.2, 141.4, 139.0, 136.6, 134.3, 129.4, 128.8, 127.2, 126.9, 67.3, 62.2, 14.1, -0.3. HRMS (FI): *m/z* for C₁₅H₂₂O₃Si [M]⁺ calcd.: 278.1333, found: 278.1332.

6. The Influence of the Equivalent of 2-Pyridone Ligand on the Formation of Aryl-Vinyl-Palladacycle Species



Synthesis and characterization of the Aryl-Vinyl-Palladacycle complex **4** have been reported.^{1c}

Table S6

entry	time	variation	4 (%) ^a
1	5 s	--	0
2	25 s	--	4
3	50 s	--	7
4	80 s	--	7
5	2 min	--	9
6	4 min	--	9
7	2 min	without L1	0
8	25s	CuBr, KBr	12
9	50s	CuBr, KBr	13
10	2 min	CuBr, KBr	15
11	4 min	CuBr, KBr	17

^aDetermined by ³¹P NMR using Ph₃PO as an internal standard.

For in situ Capturing of Aryl-Vinyl-Palladacycle species:

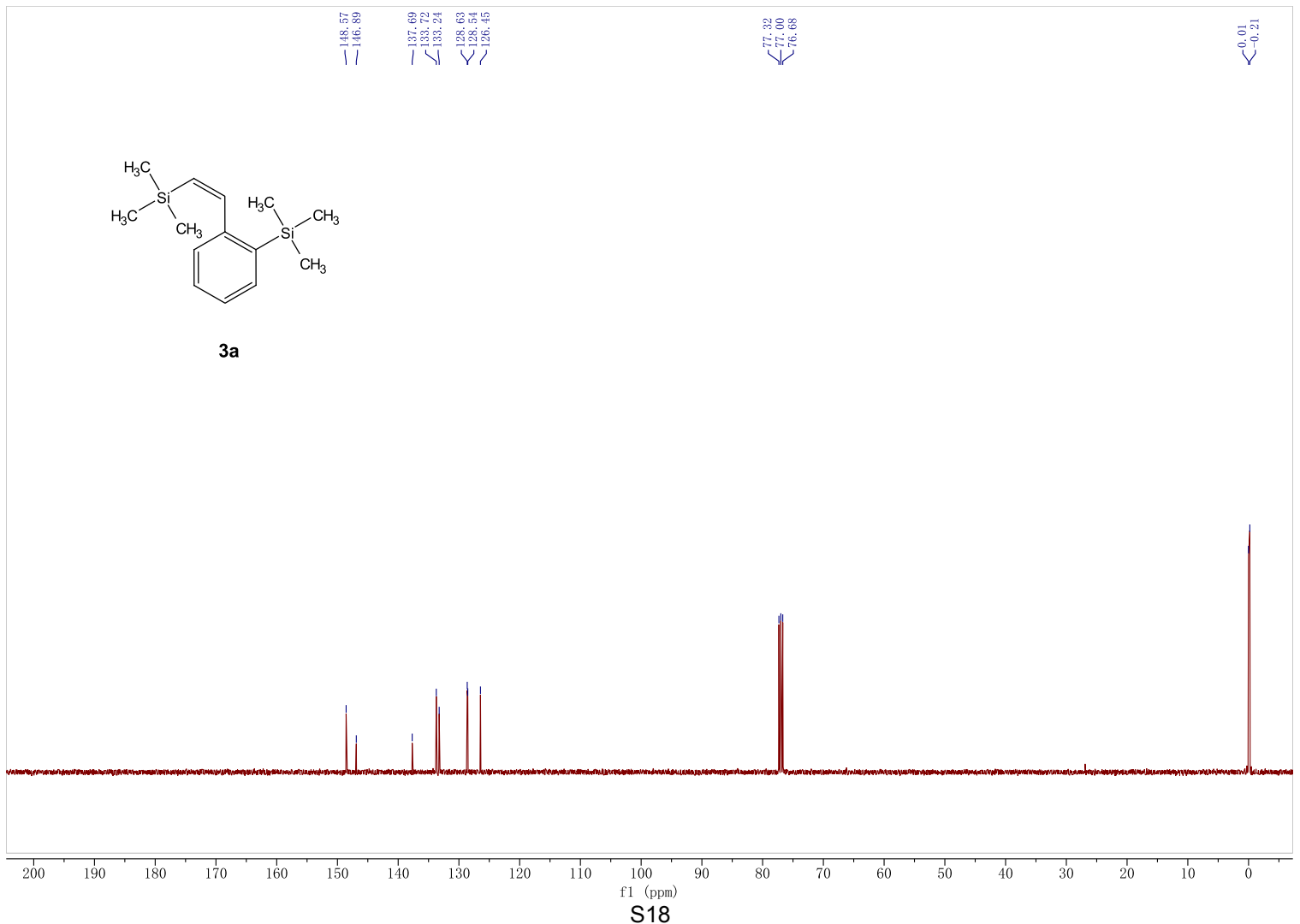
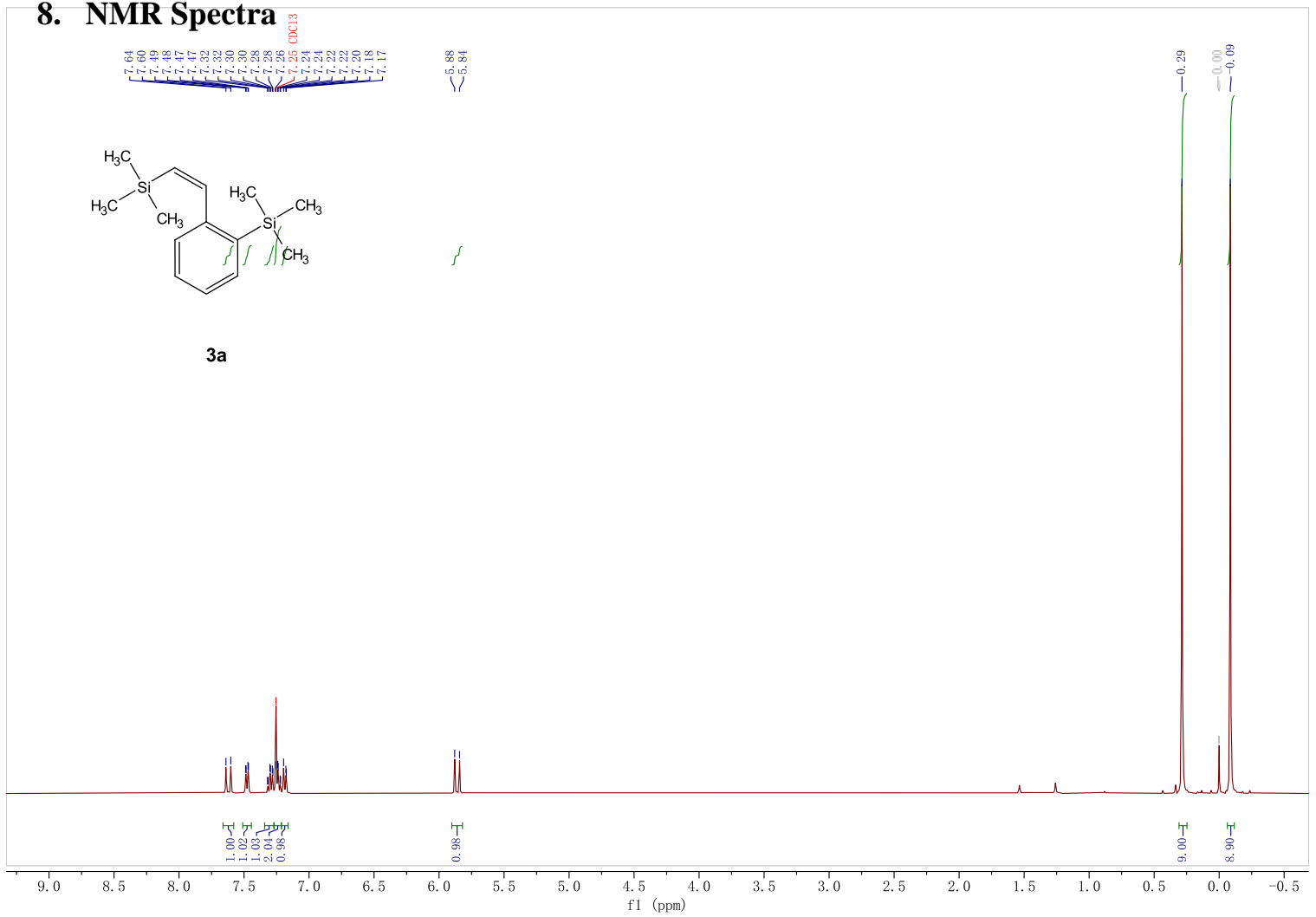
To a 5 mL sealed tube charged with a stir bar was added a mixture of Pd(dba)₂ (2.2 mg, 3.75 μmol), 3,5-dimethylpyridin-2(1H)-one (**L1**) (1.2 mg, 10 μmol), K₃PO₄ (21.2 mg, 0.1 mmol), and a ground mixture of CuBr and KBr (12.2 mg, containing 2.0 μmol CuBr and 0.1 mmol KBr). The tube was capped with a Teflon thread plug, and then degassed and backfilled with argon (this procedure was repeated three times). DMF (0.6 mL) was added and the mixture was stirred at 35°C for 30 s. Then a DMF solution of *ortho*-iodophenylethylene (10.2 μL, containing 2.5 μmol solute) was added and,

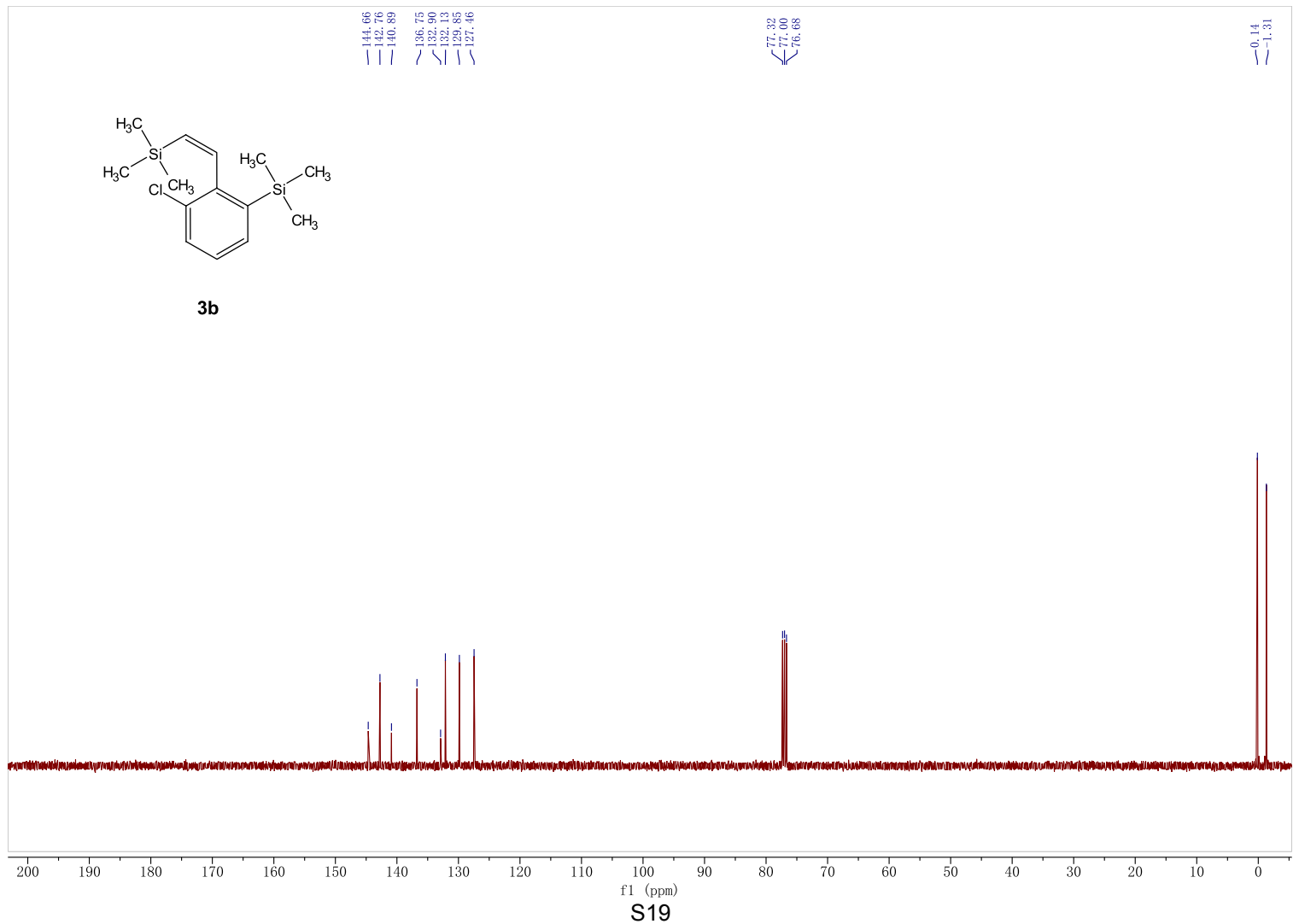
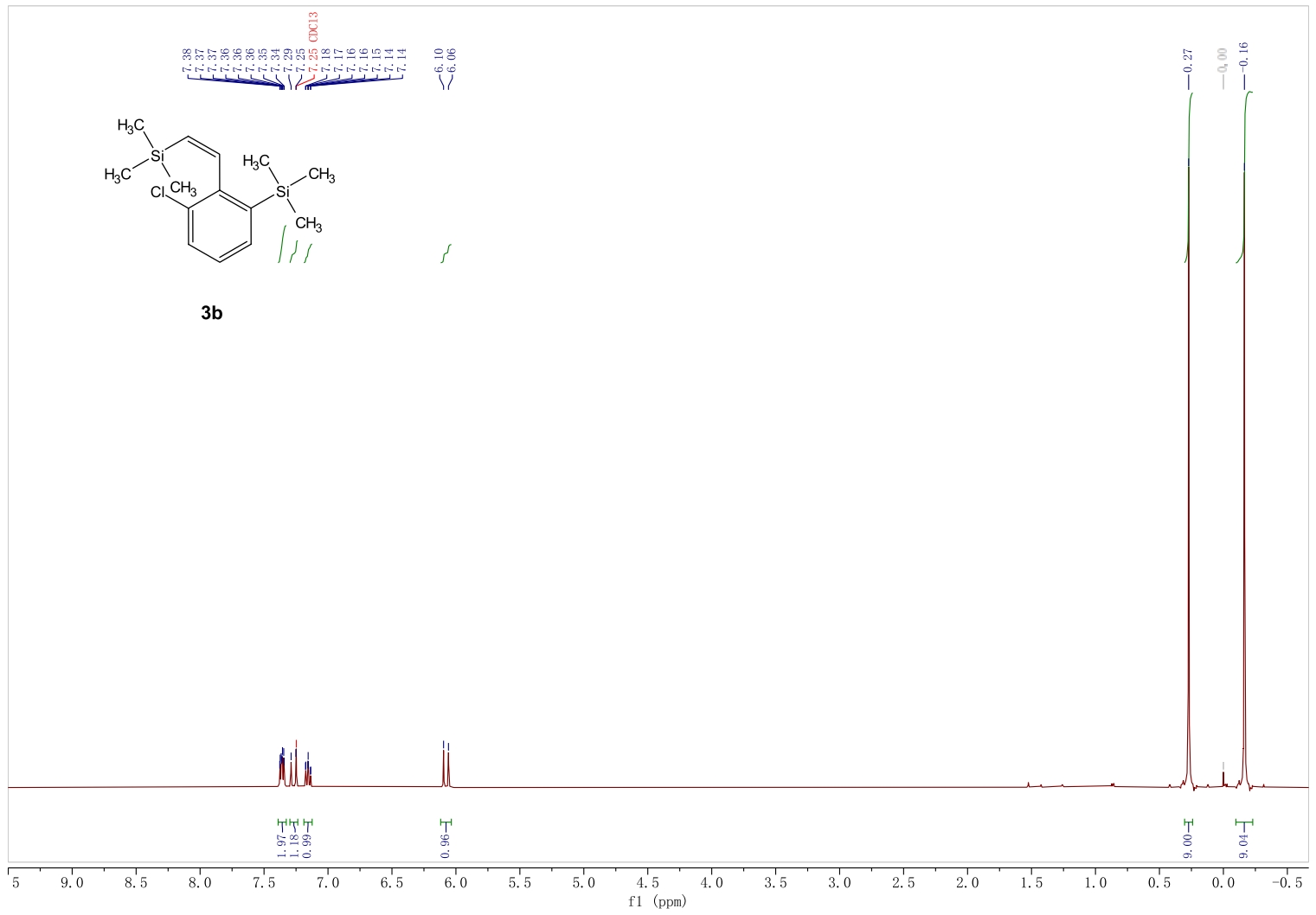
after stirring for 50s, a freshly prepared CH₂Cl₂ solution of 1,2-bis(dicyclohexylphosphino)ethane (**dcpe**) (80 μL, containing 4.2 mg, 10 μmol **dcpe**) was added, followed with a DMF solution of Ph₃PO (12.5 μL, containing 2.95 μmol solute) as internal standard. The resulting mixture was transferred to an NMR tube under argon and submitted to NMR analysis.

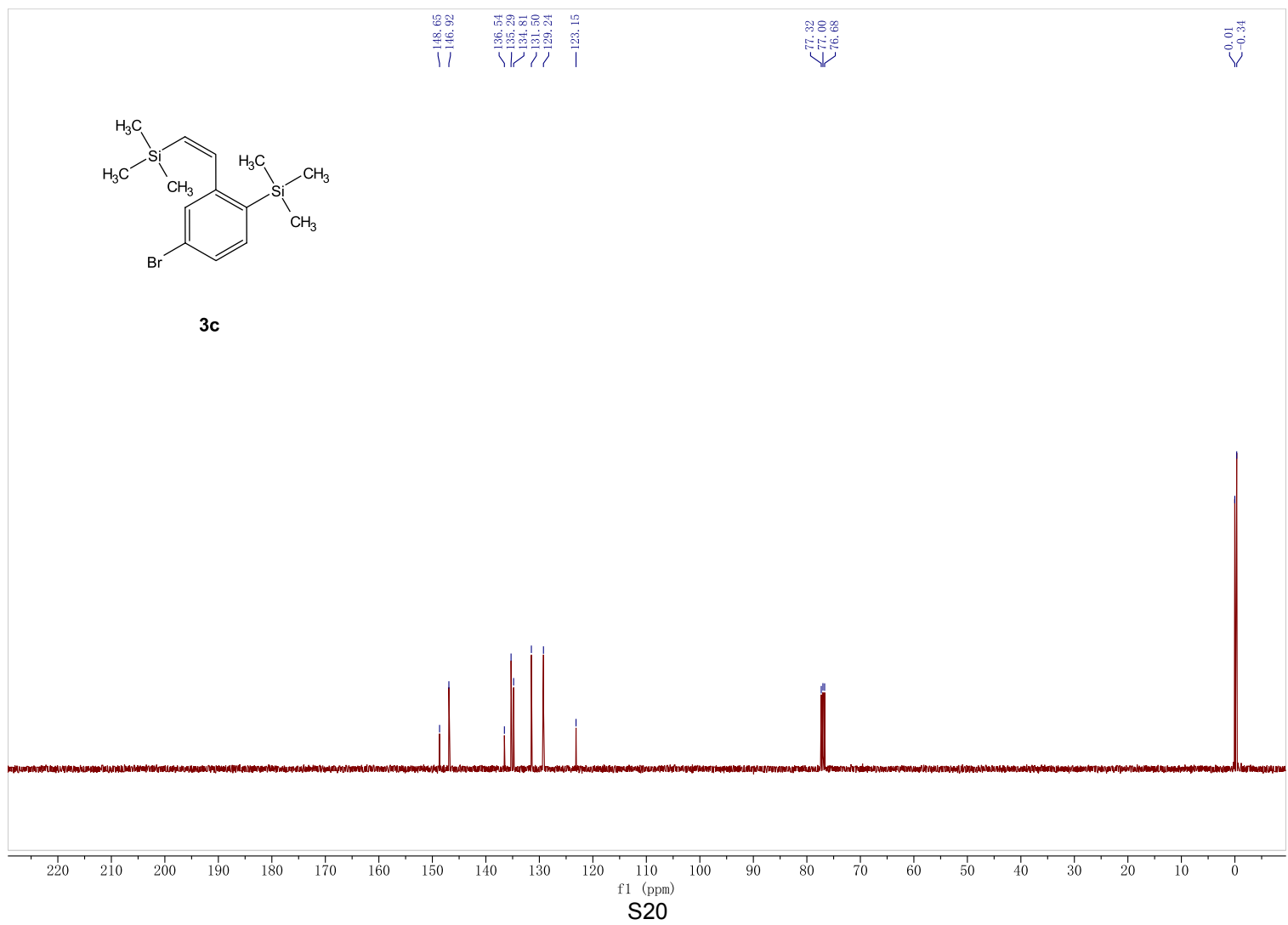
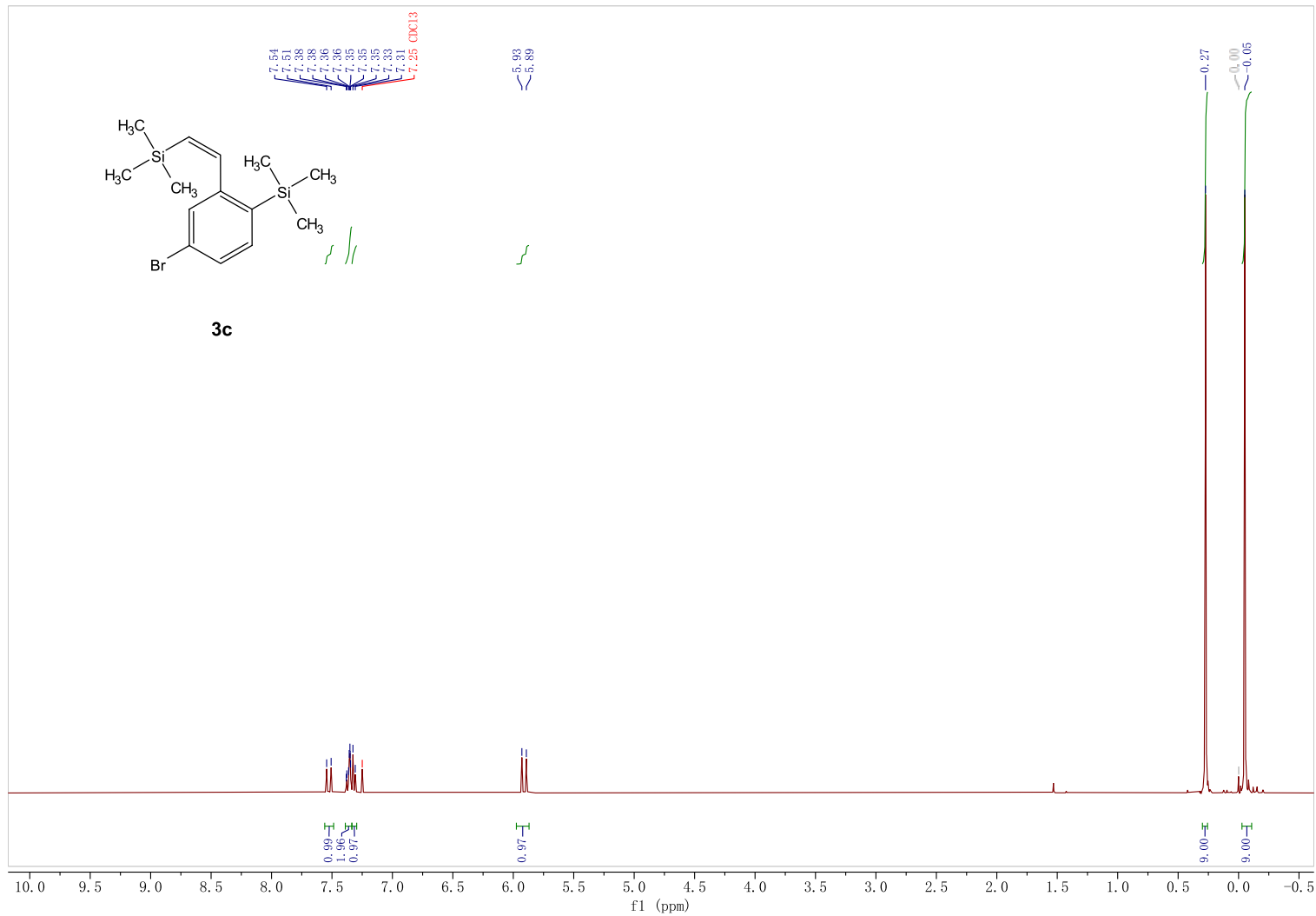
7. References

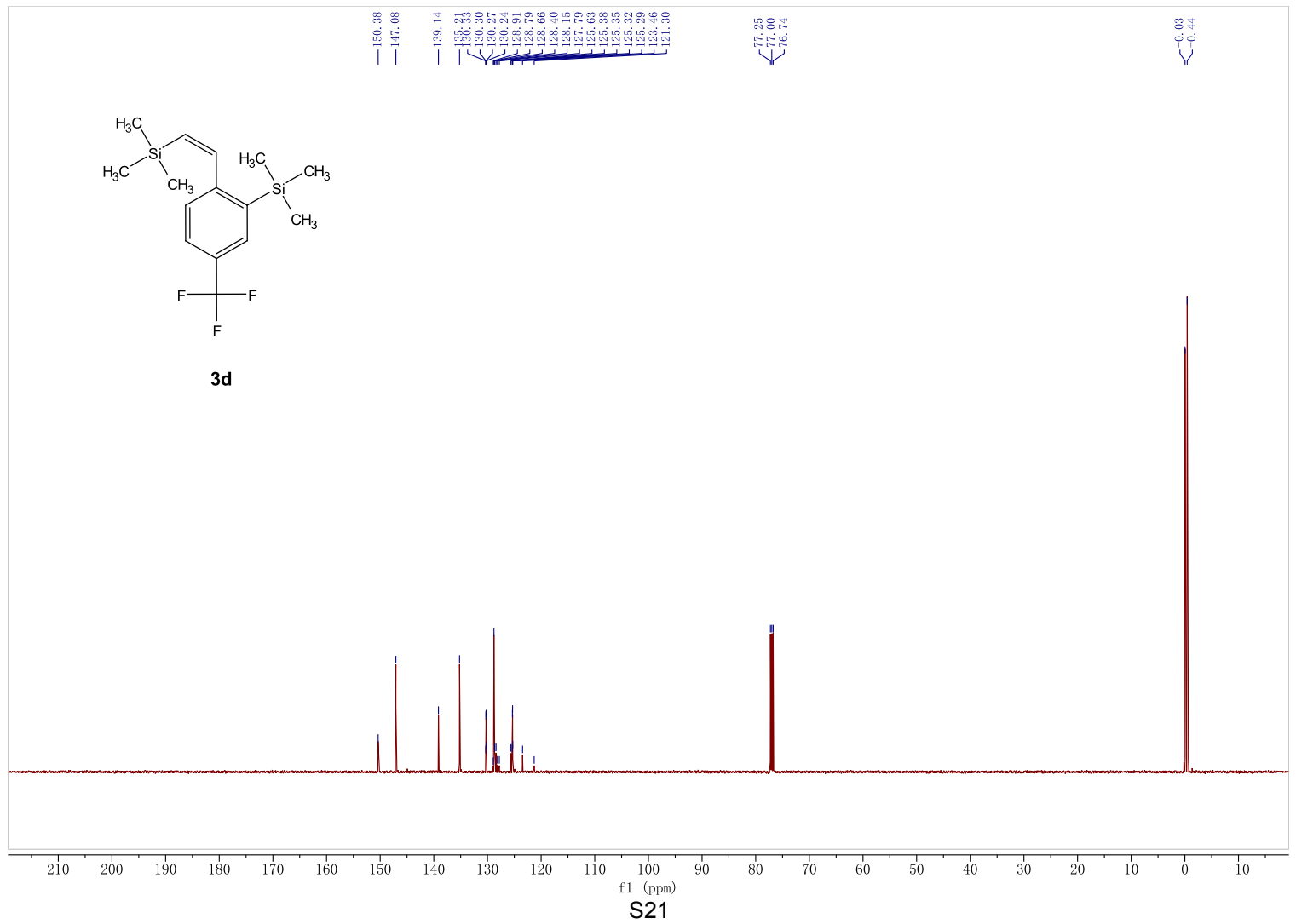
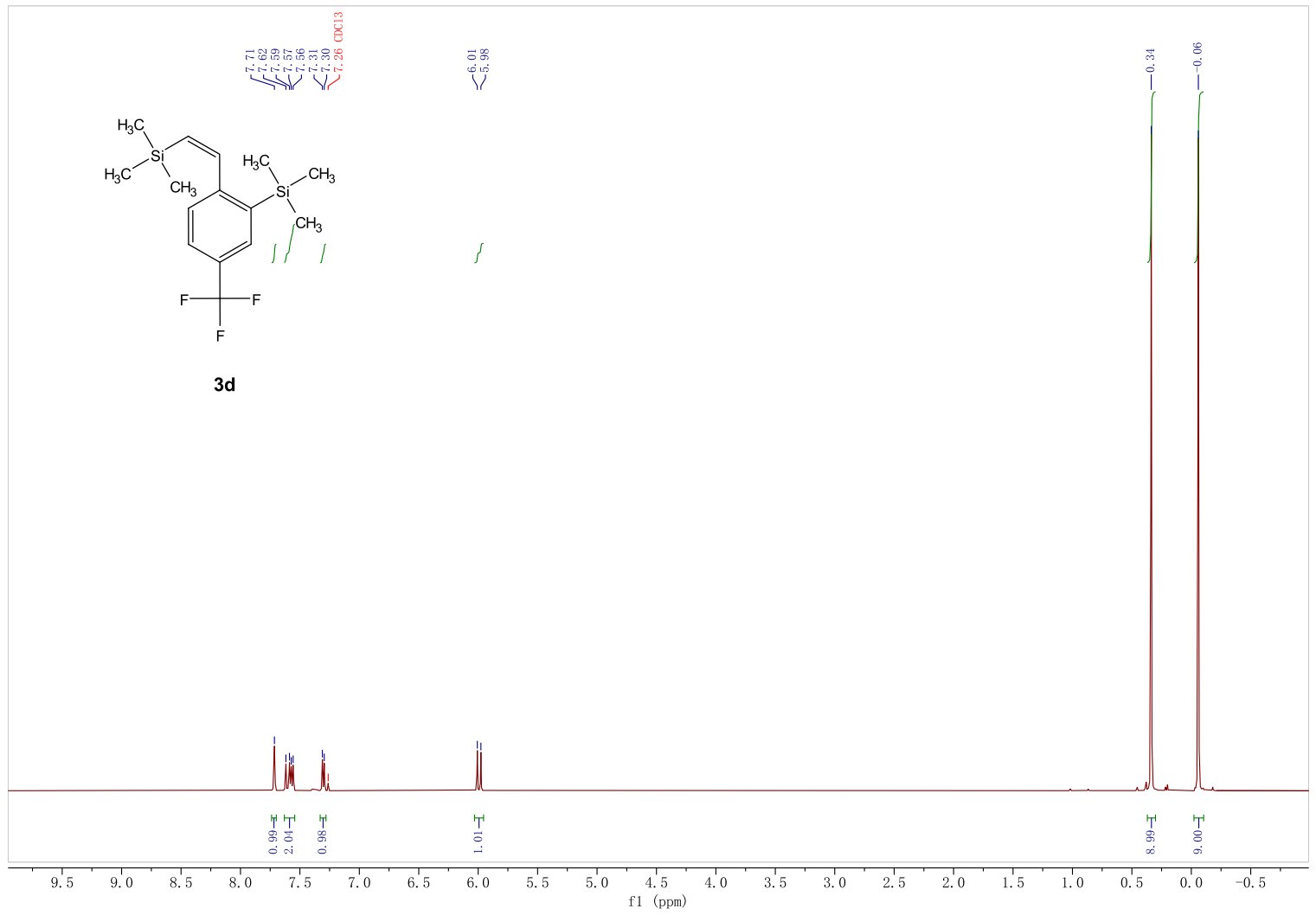
- 1 (a) T.-J. Hu, G. Zhang, Y.-H. Chen, C.-G. Feng and G.-Q. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 2897; (b) M.-Y. Li, P. Han, T.-J. Hu, D. Wei, G. Zhang, A. Qin, C.-G. Feng, B. Z. Tang and G.-Q. Lin, *iScience*, 2020, **23**, 100966; (c) B.-B. Zhu, W.-B. Ye, Z.-T. He, S.-S. Zhang, C.-G. Feng and G.-Q. Lin, *ACS Catal.*, 2021, **11**, 12123.
- 2 K. Mikami, H. Wakabayashi and T. Nakai, *J. Org. Chem.*, 1991, **56**, 4337.

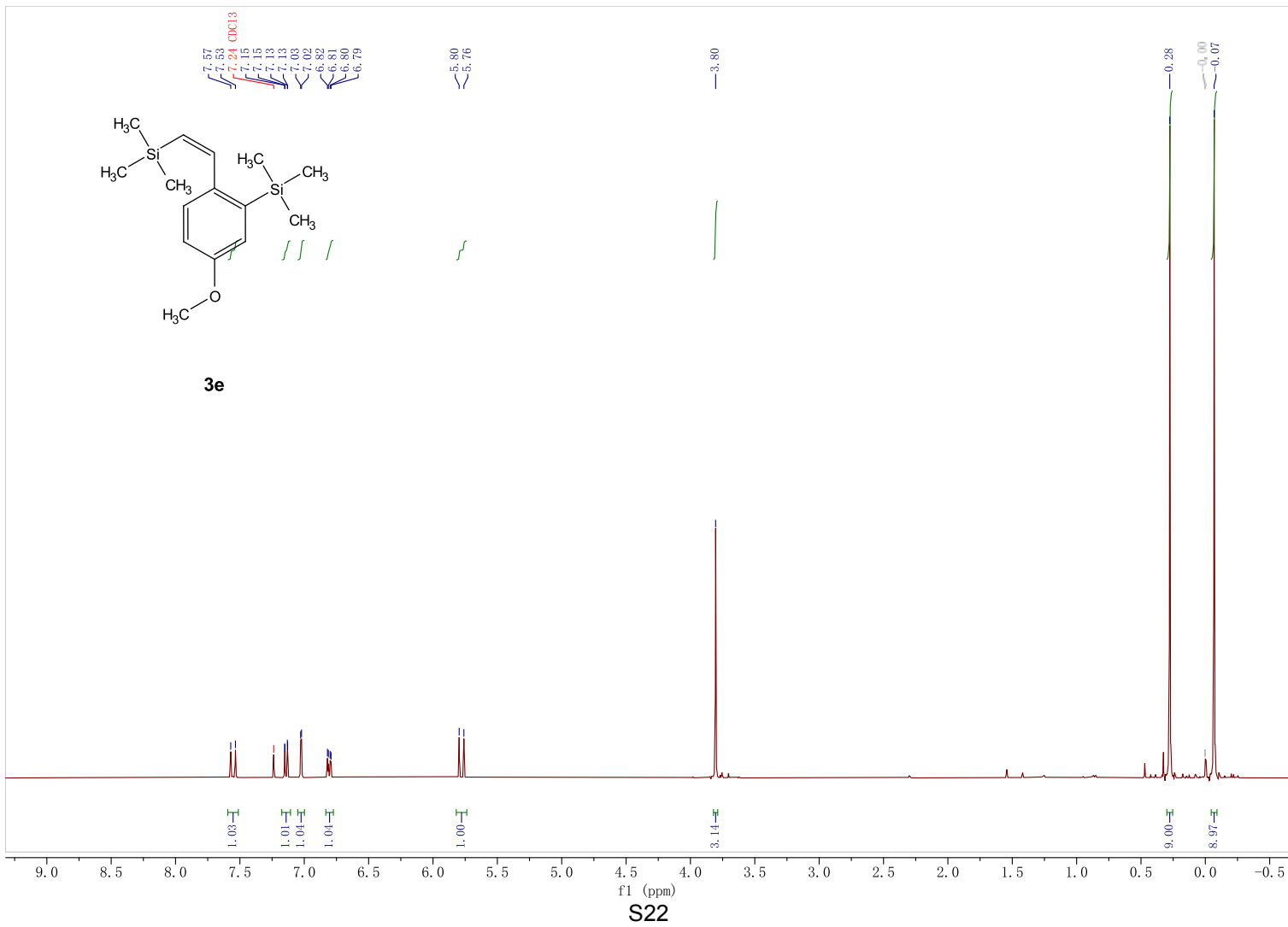
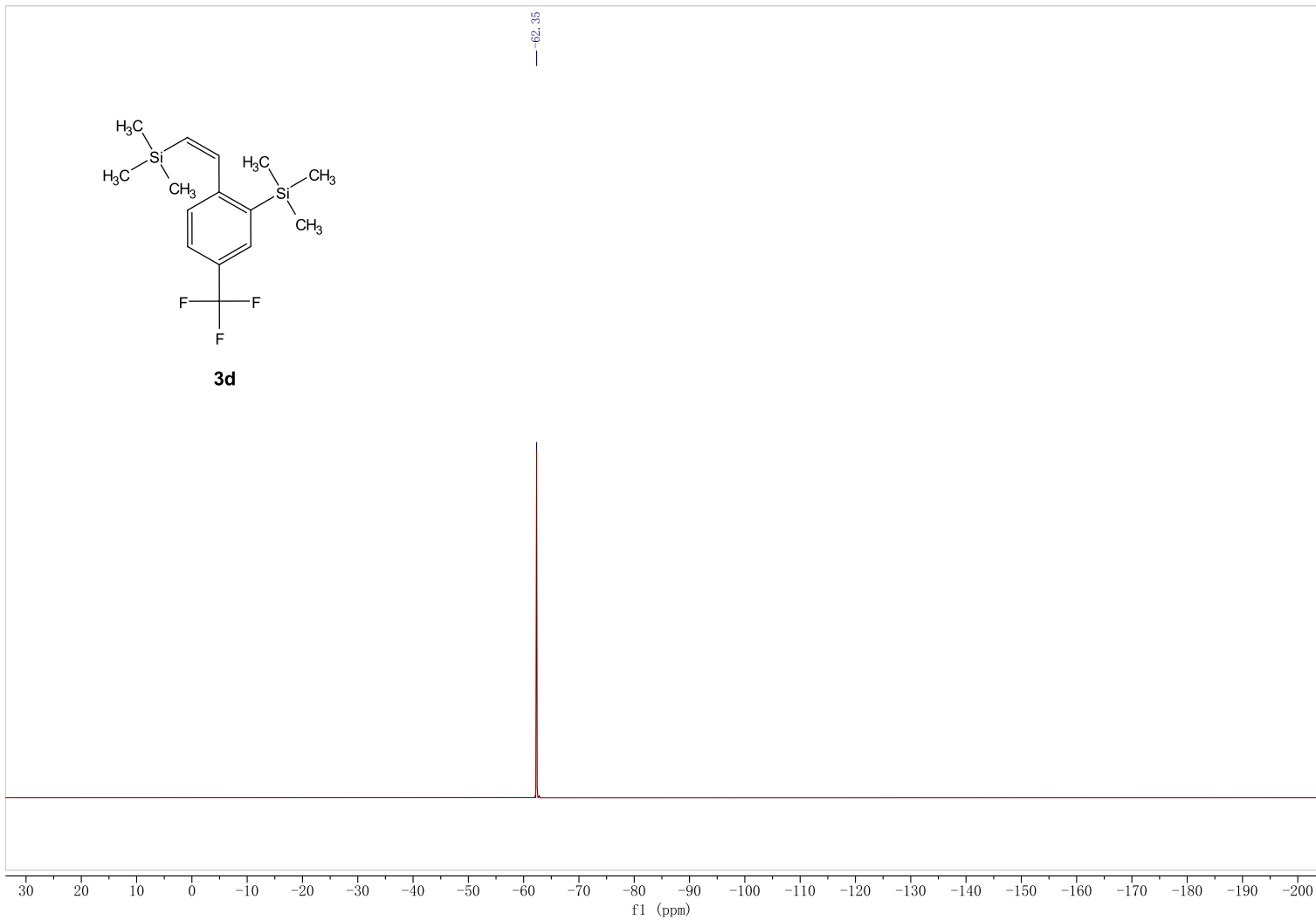
8. NMR Spectra

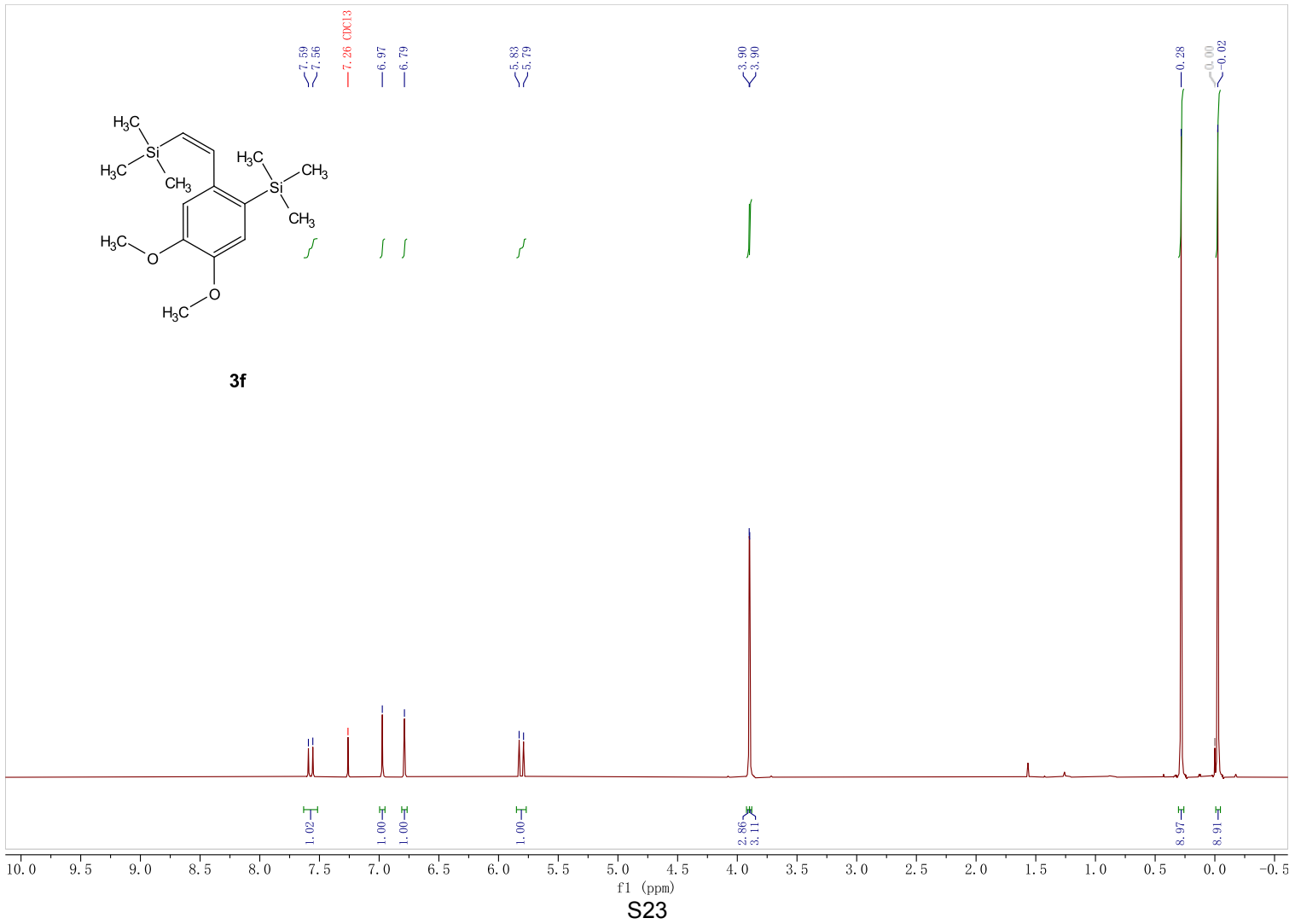
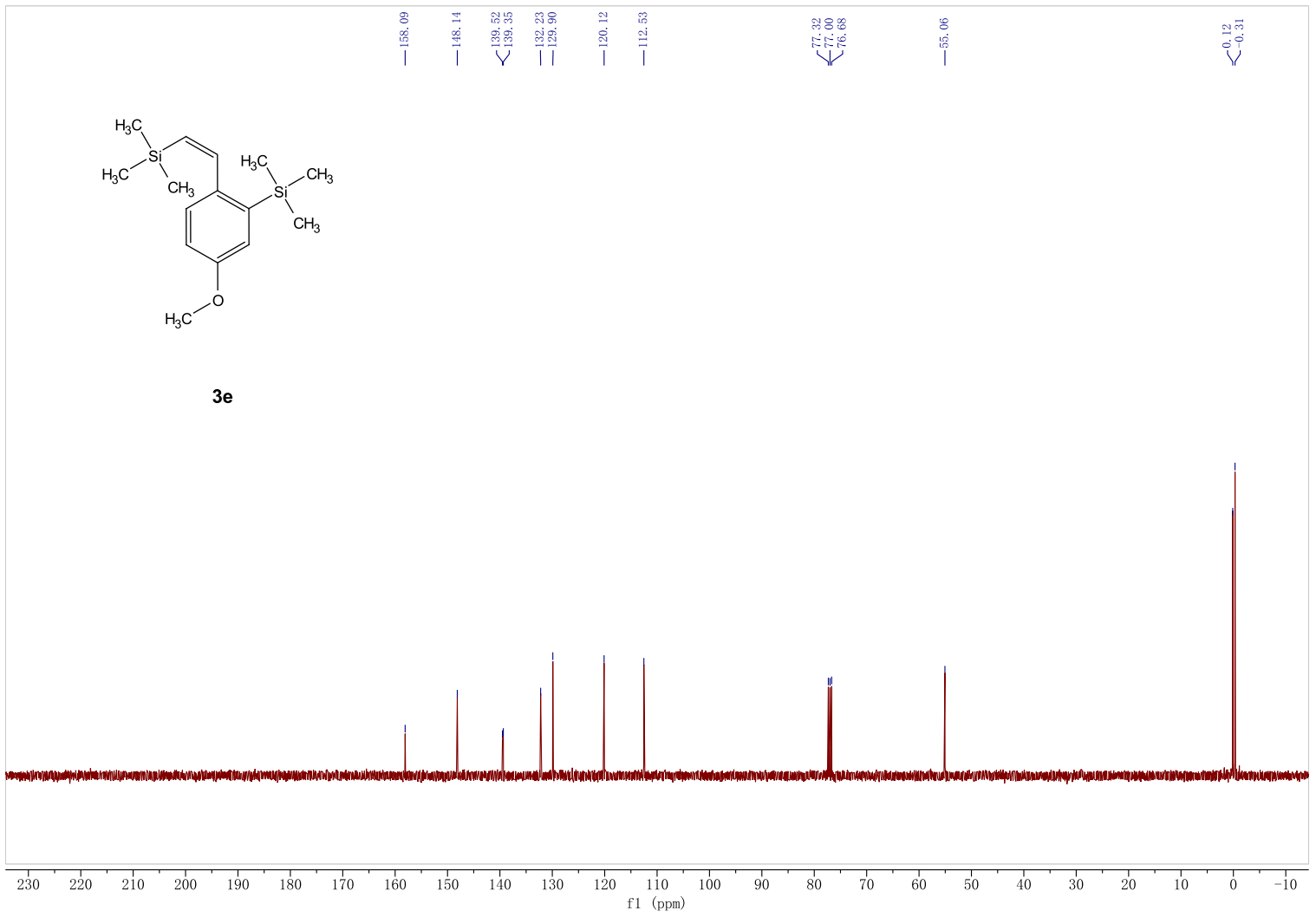


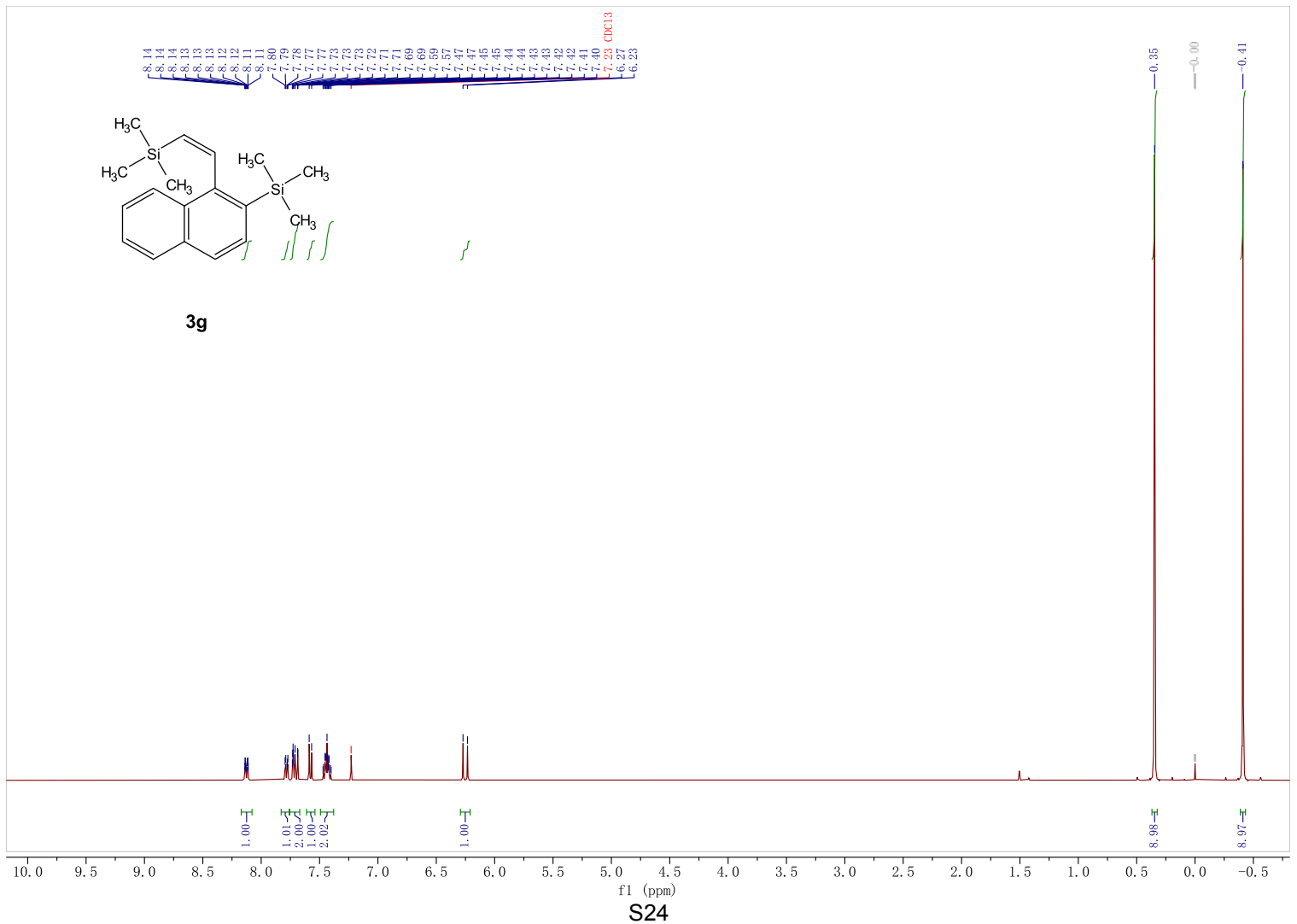
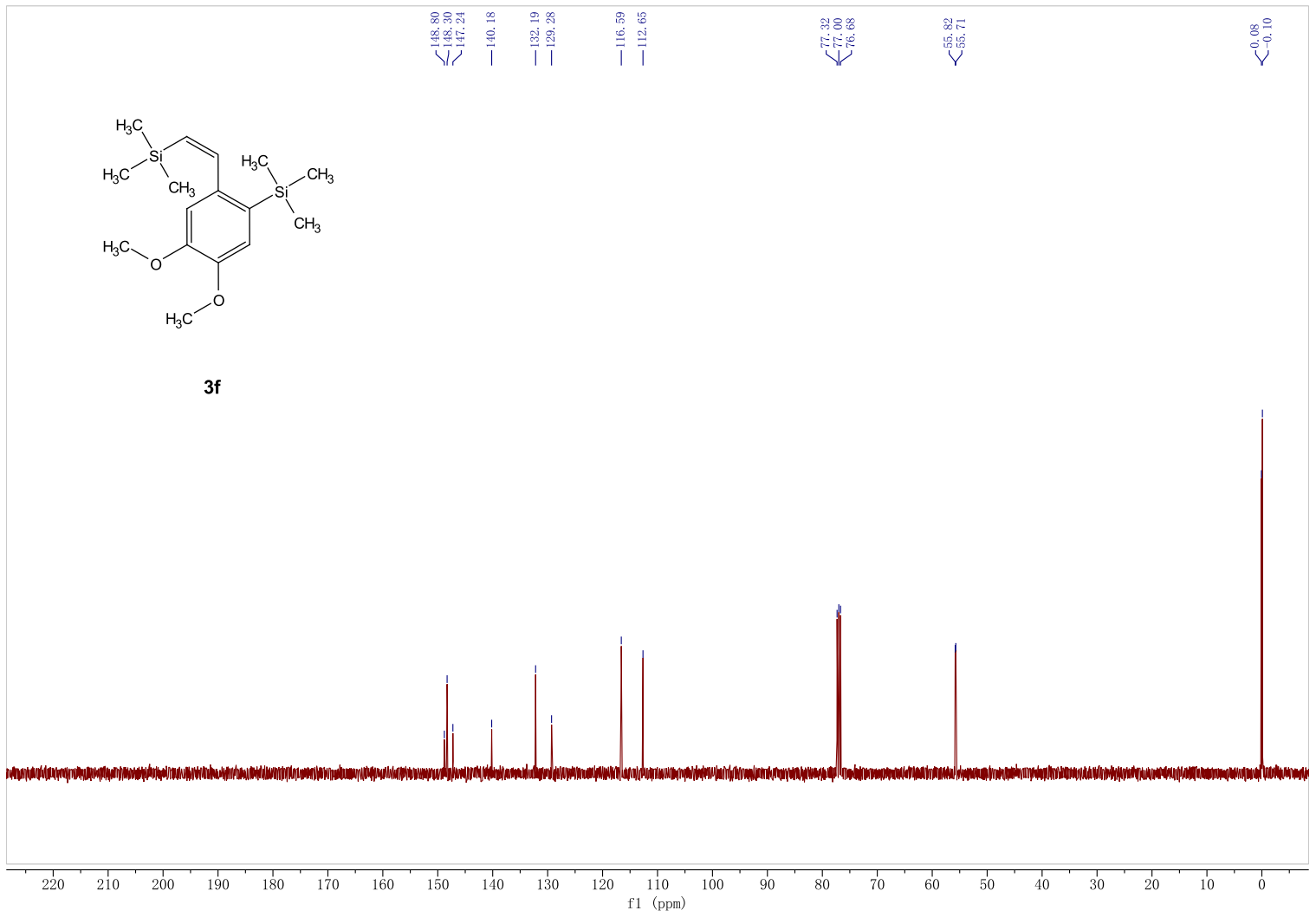


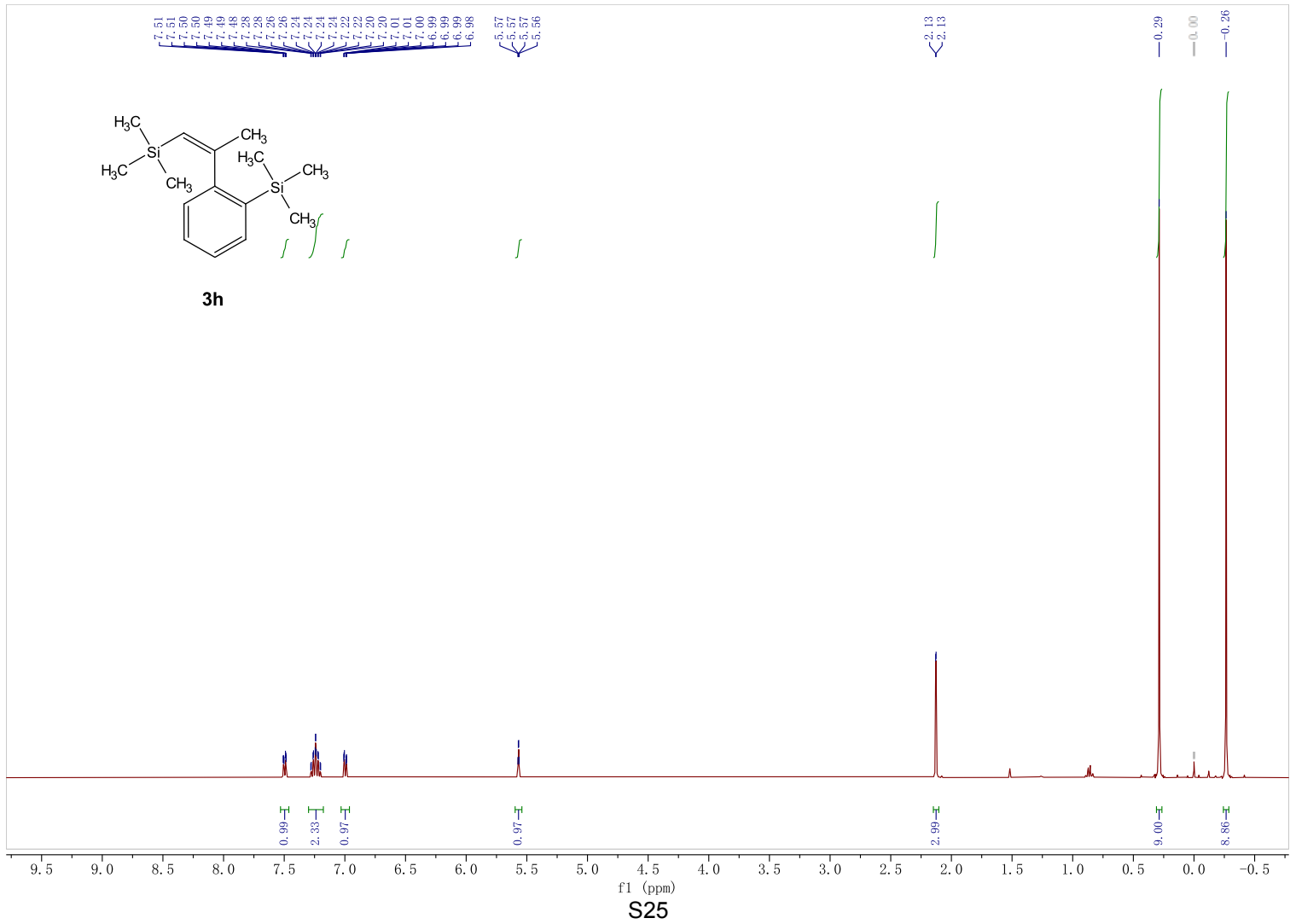
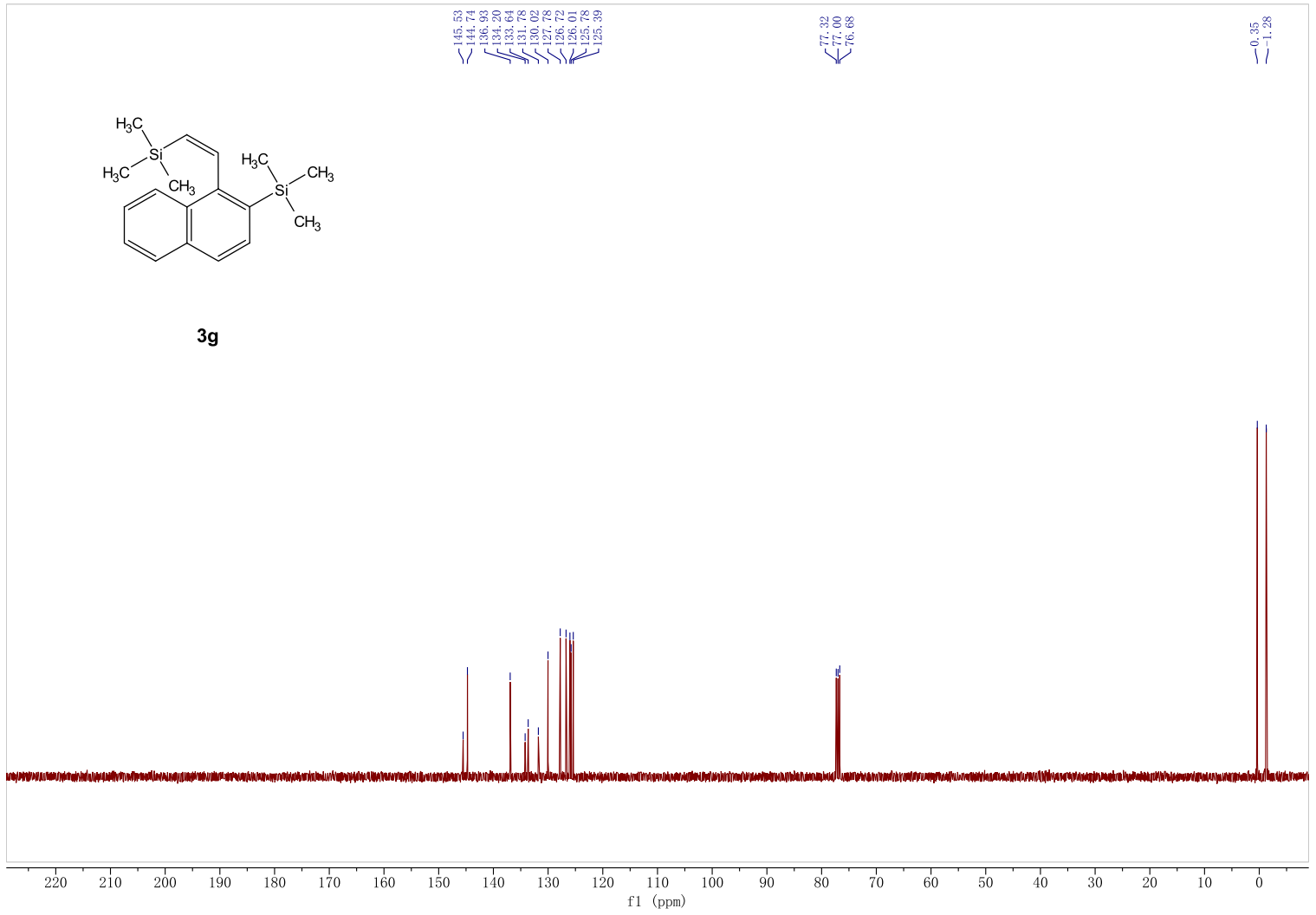


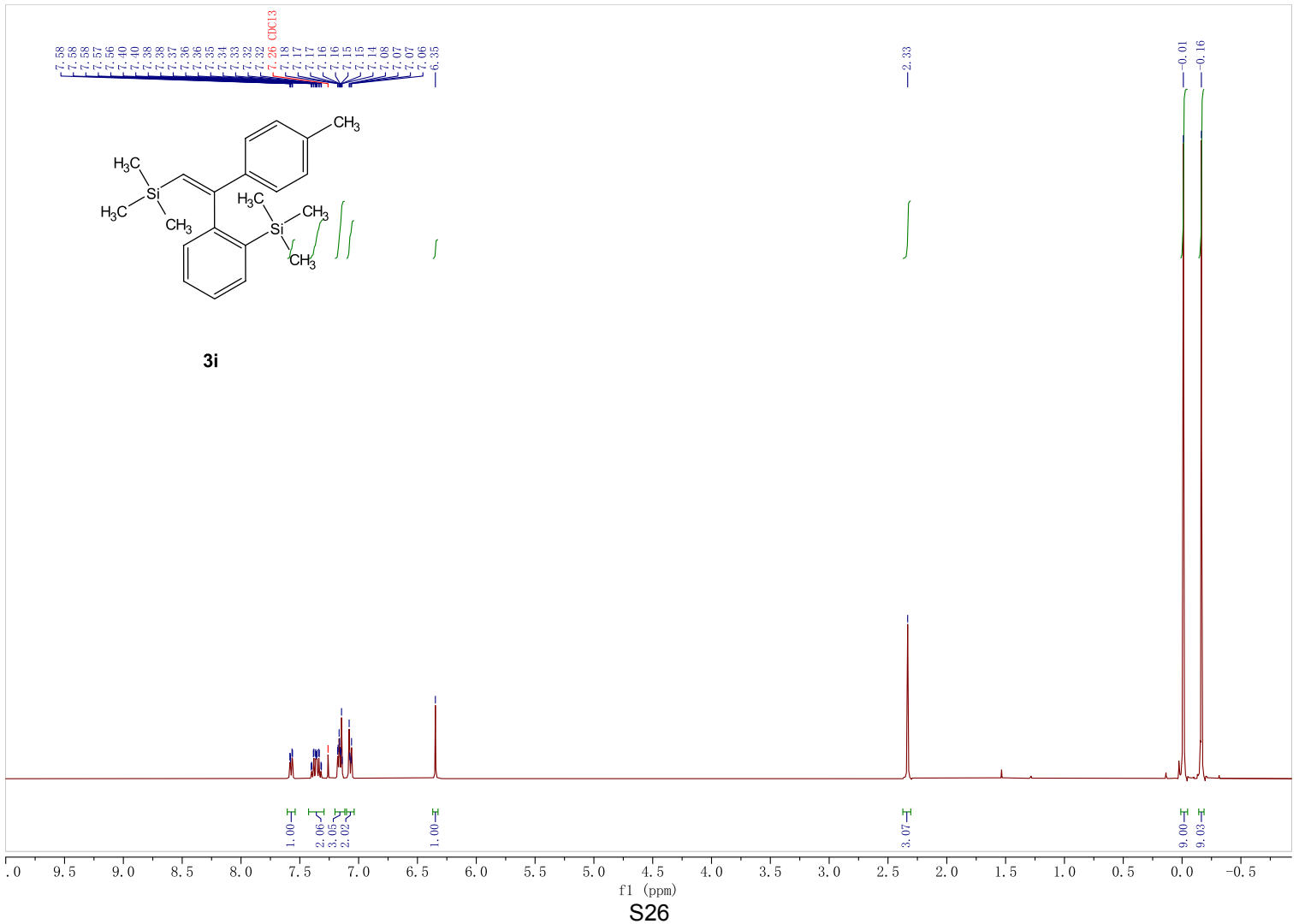
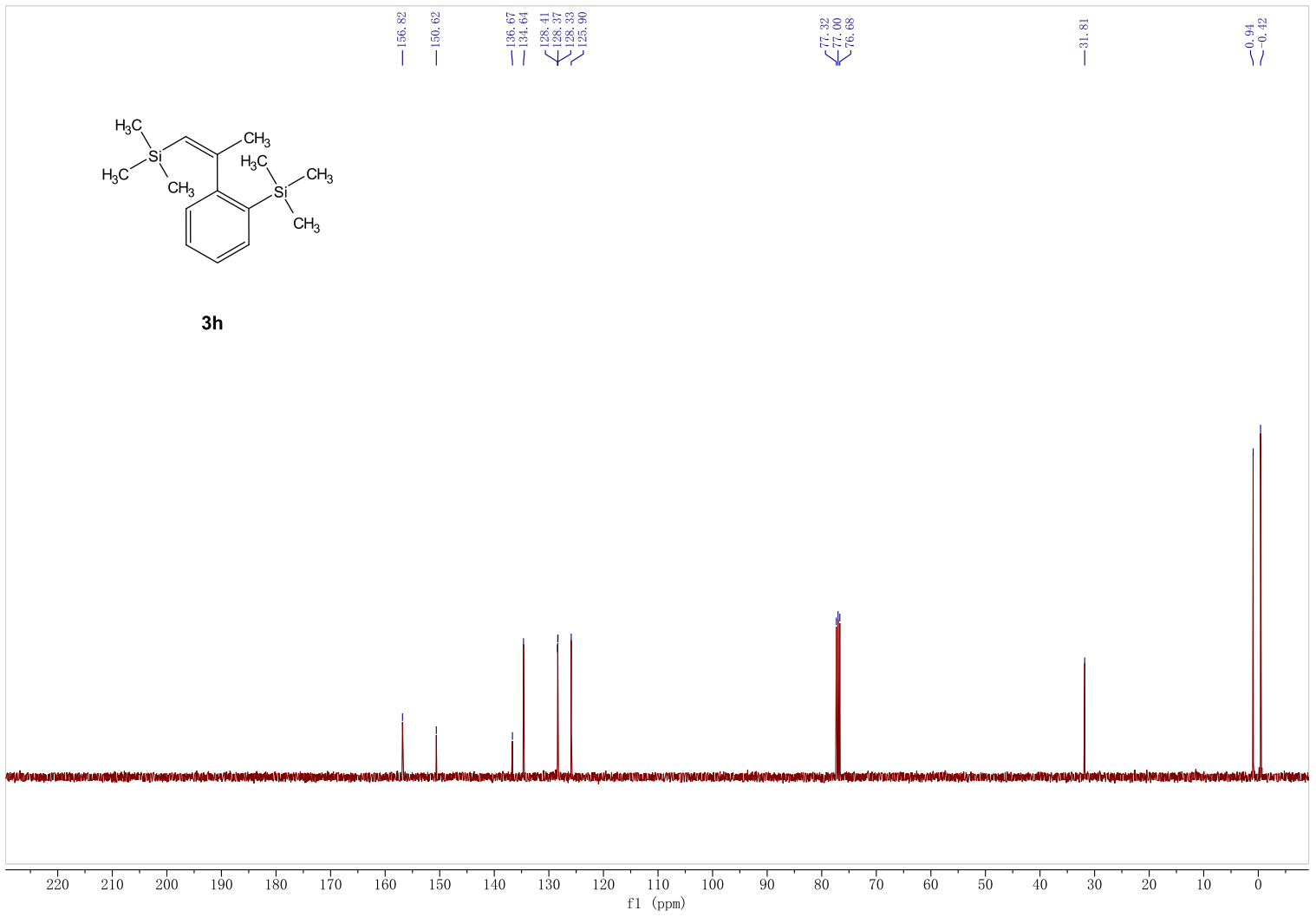


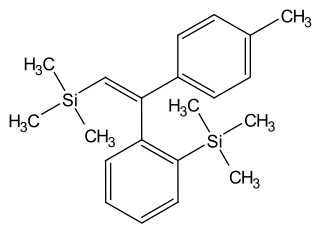




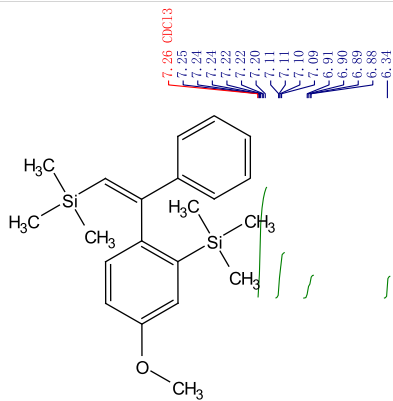
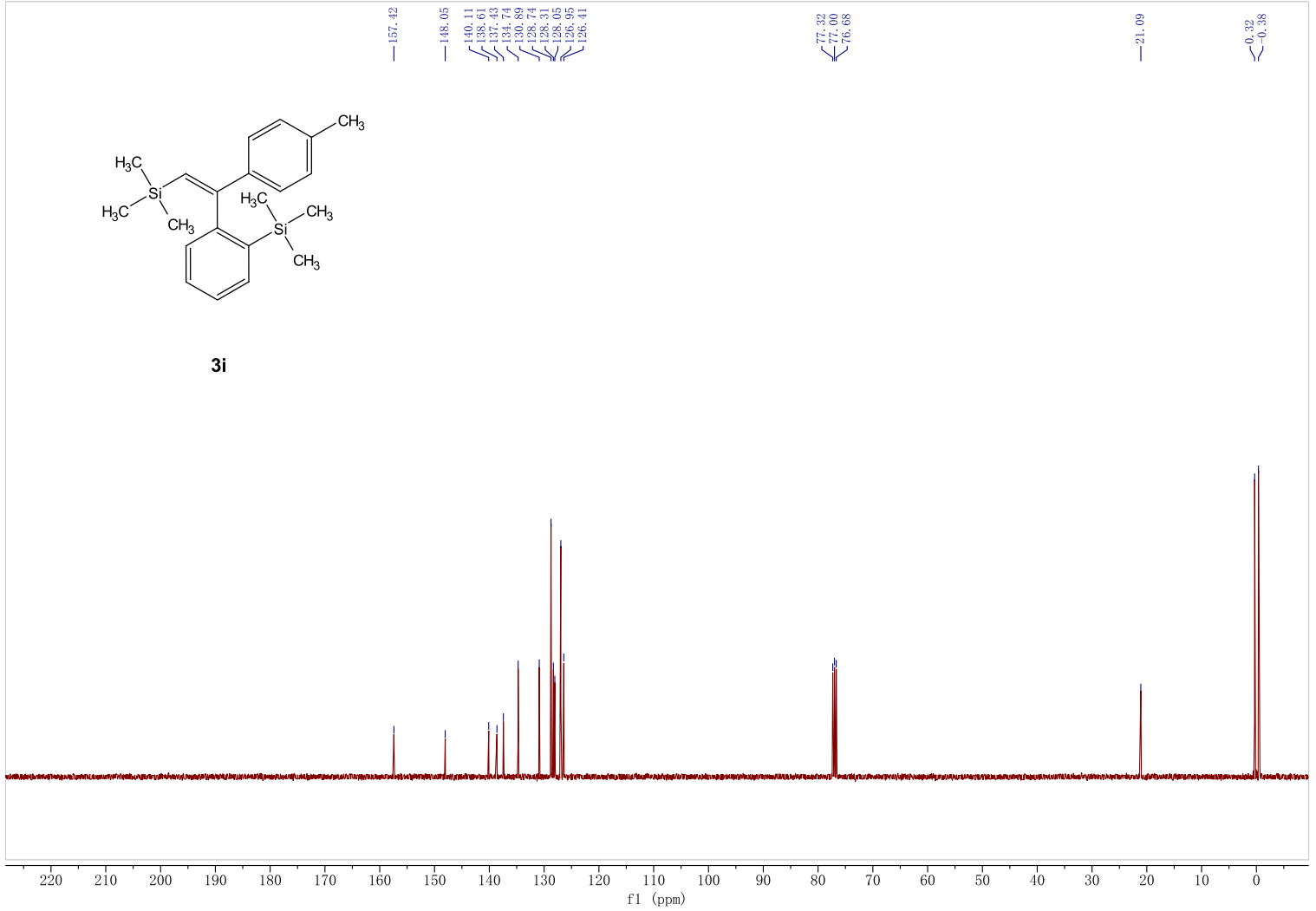




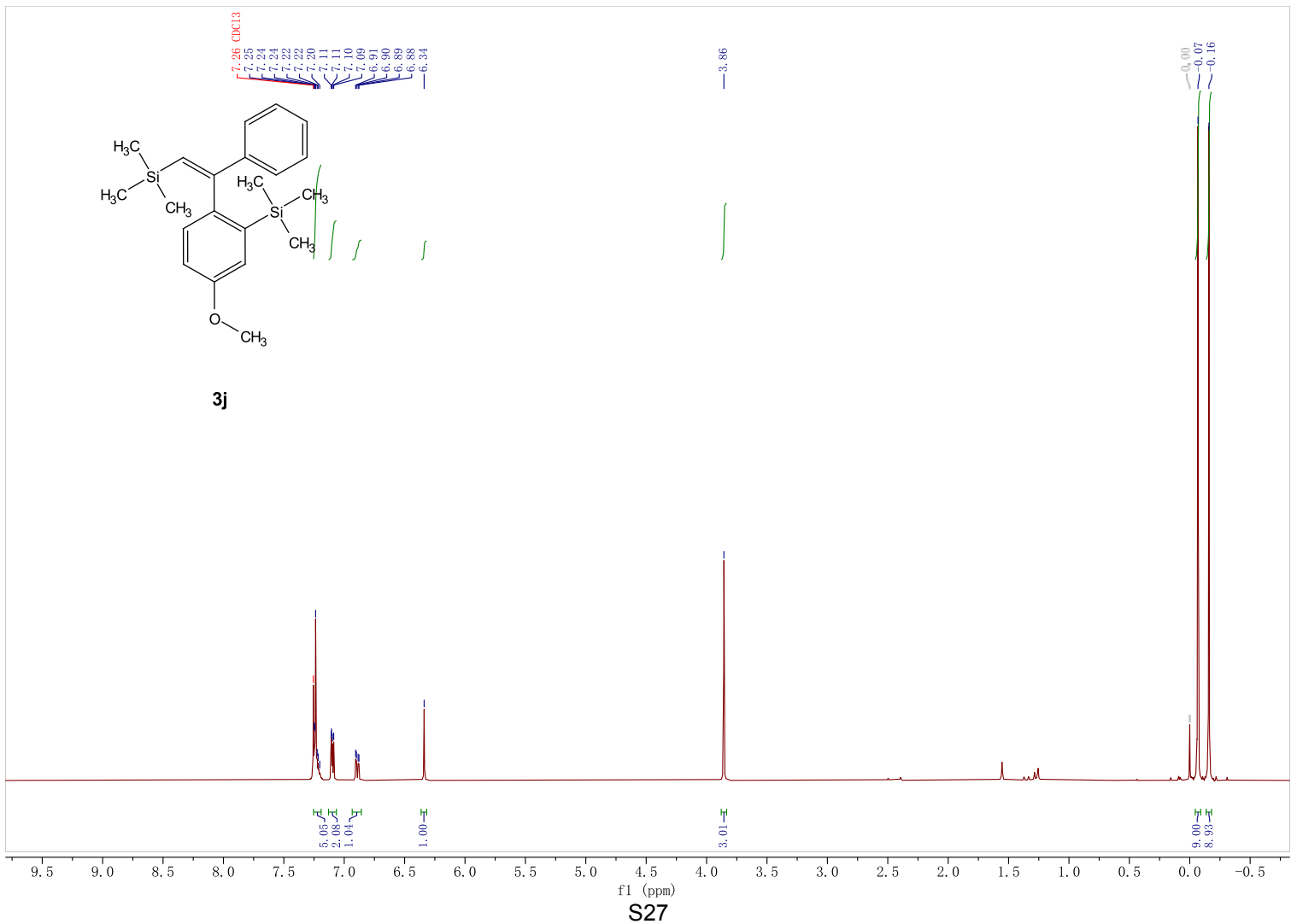


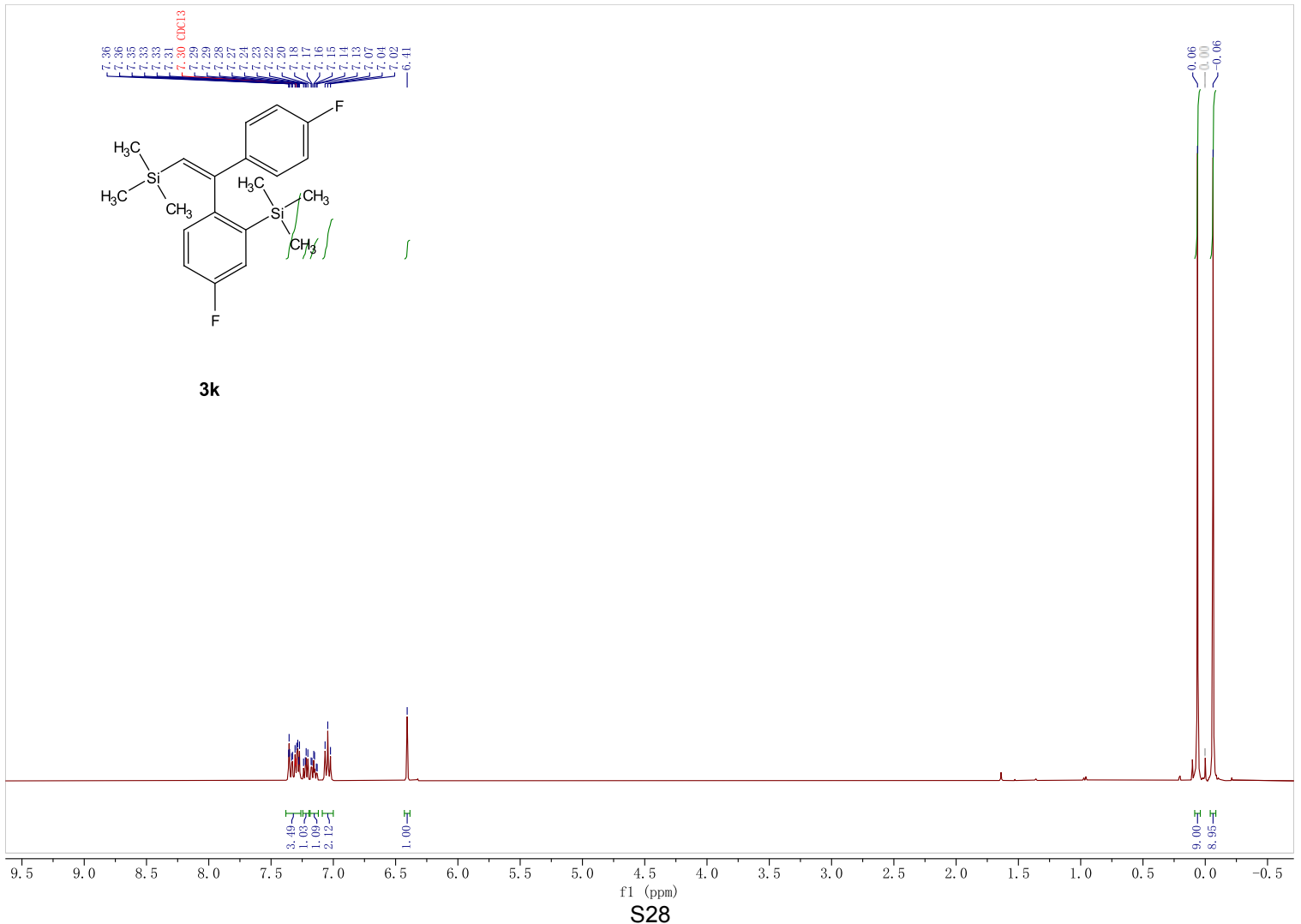
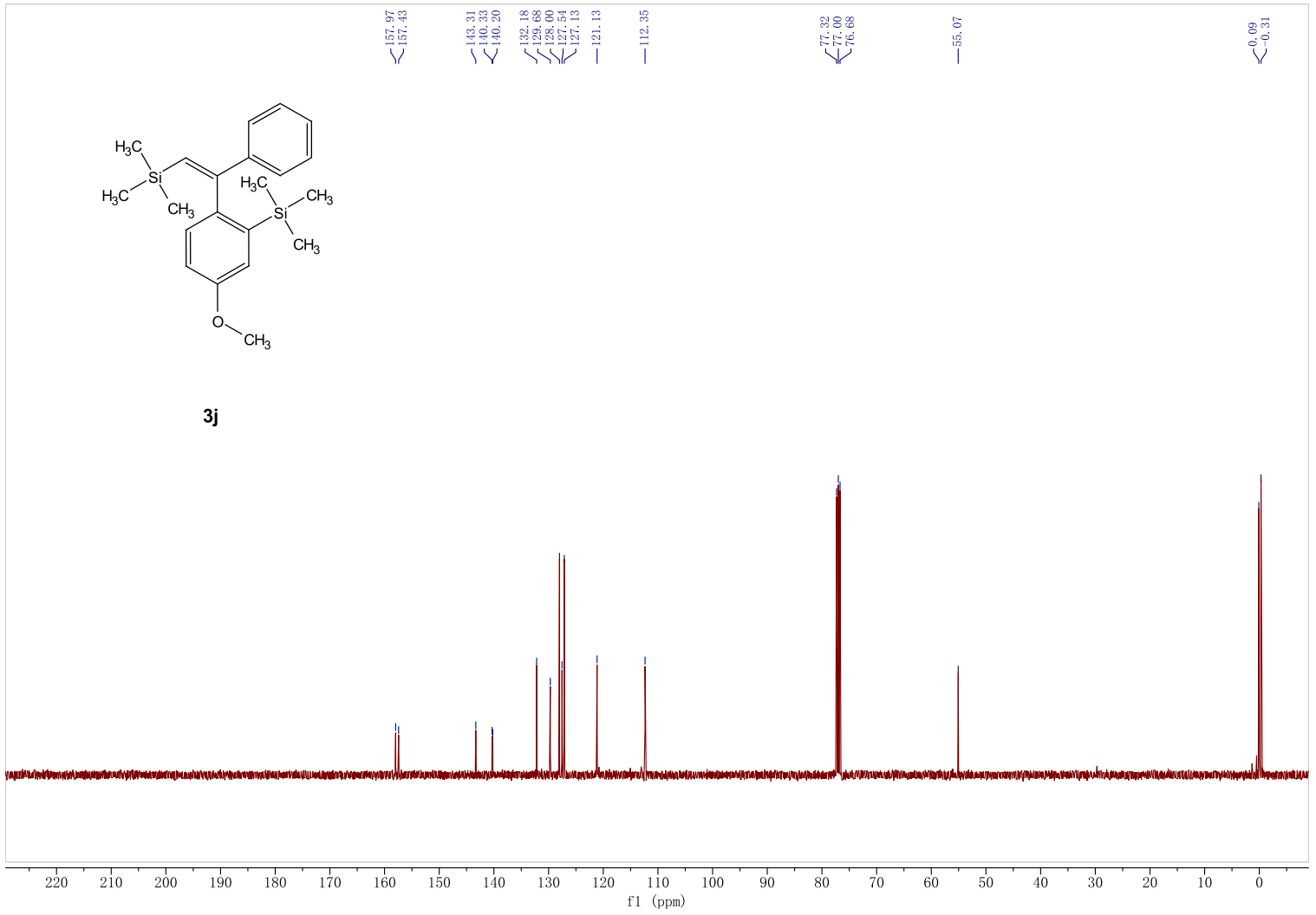


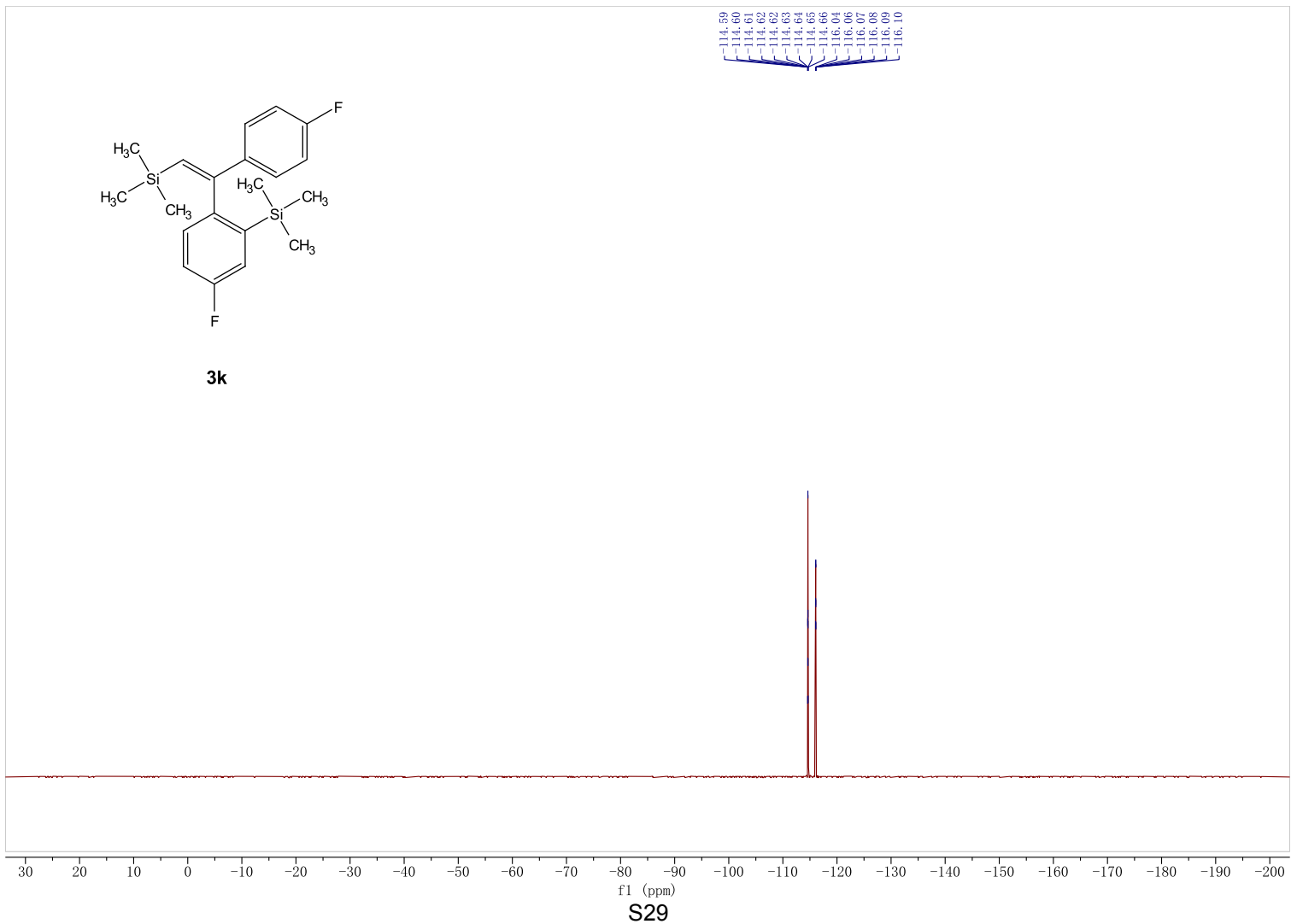
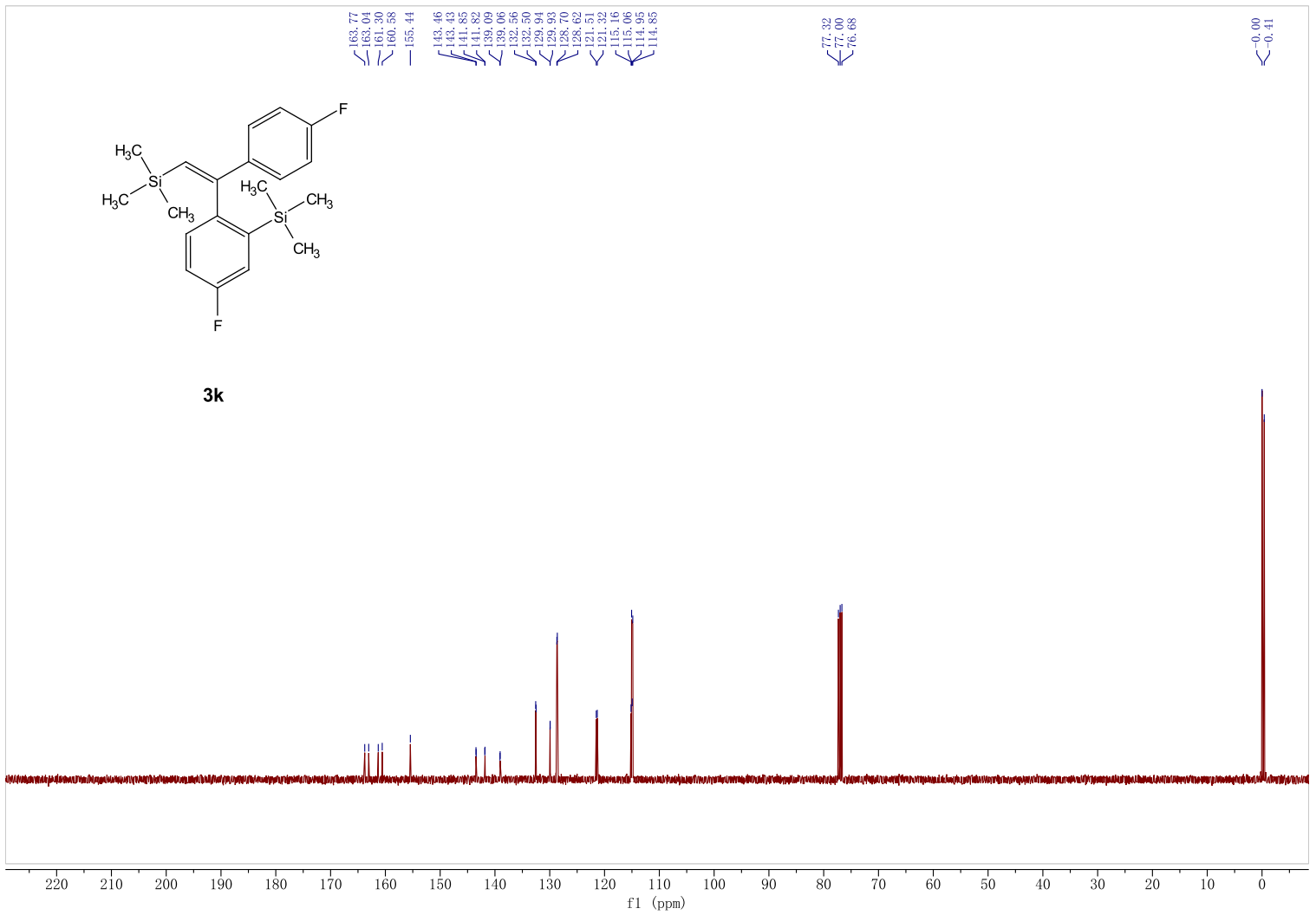
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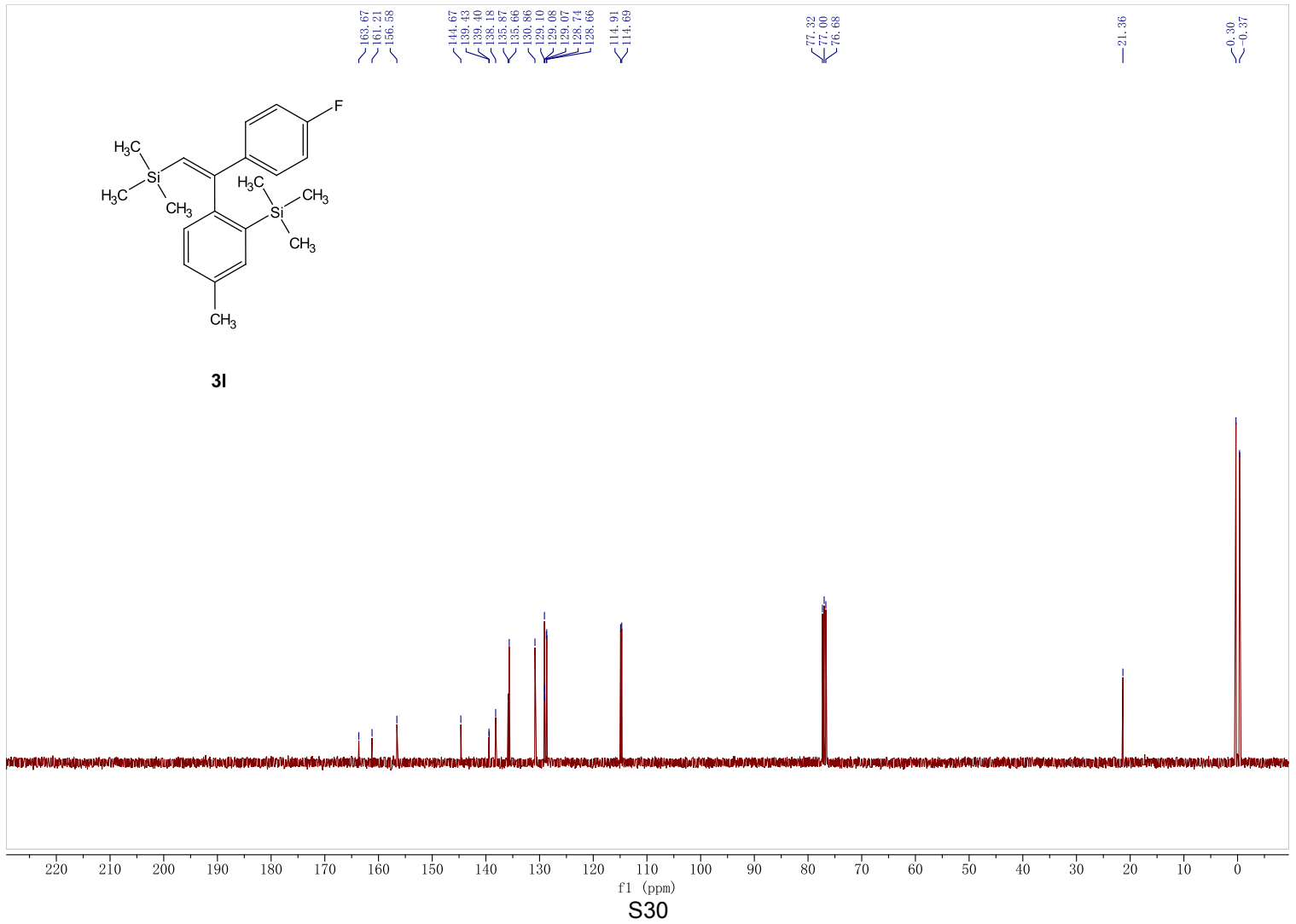
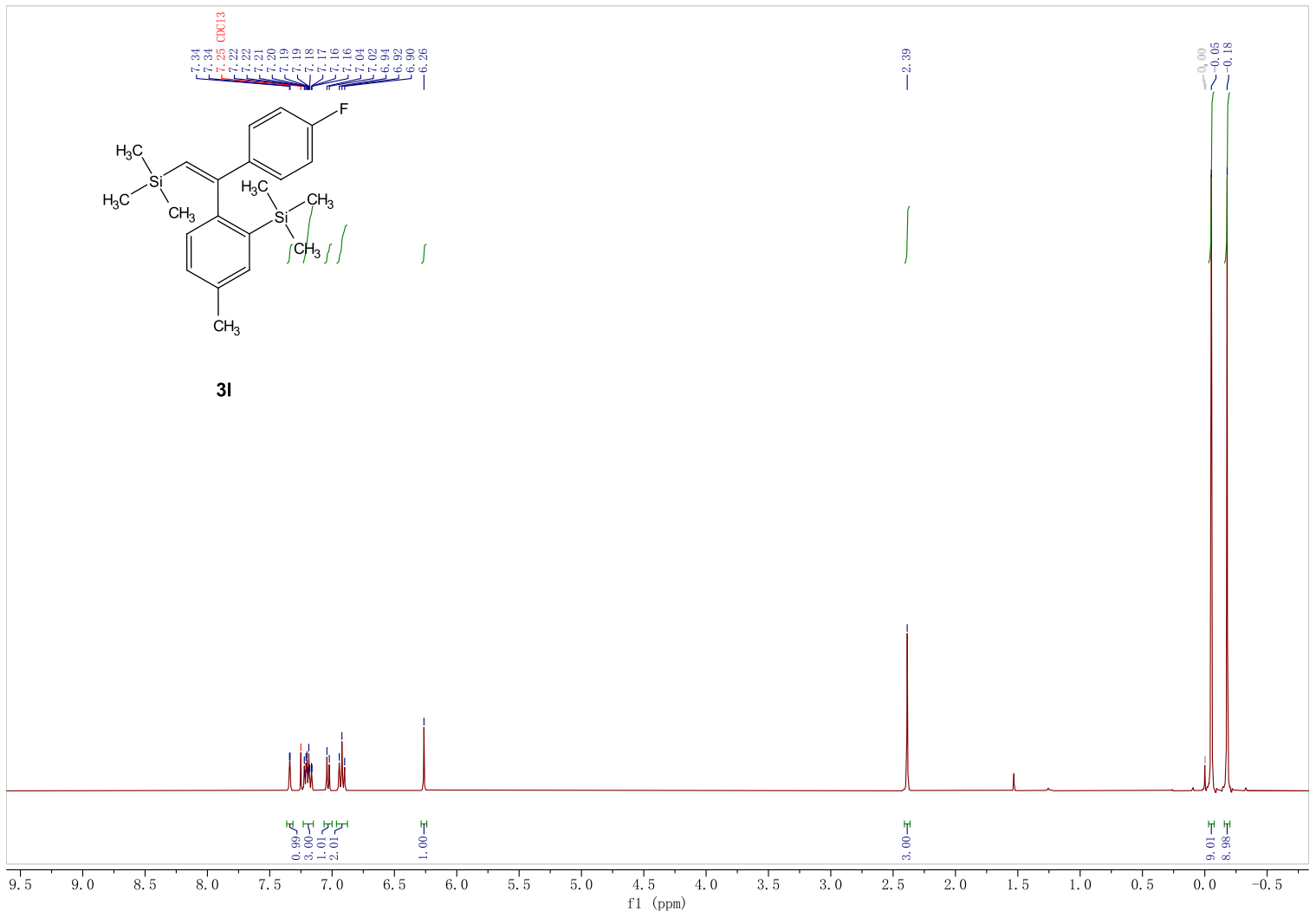


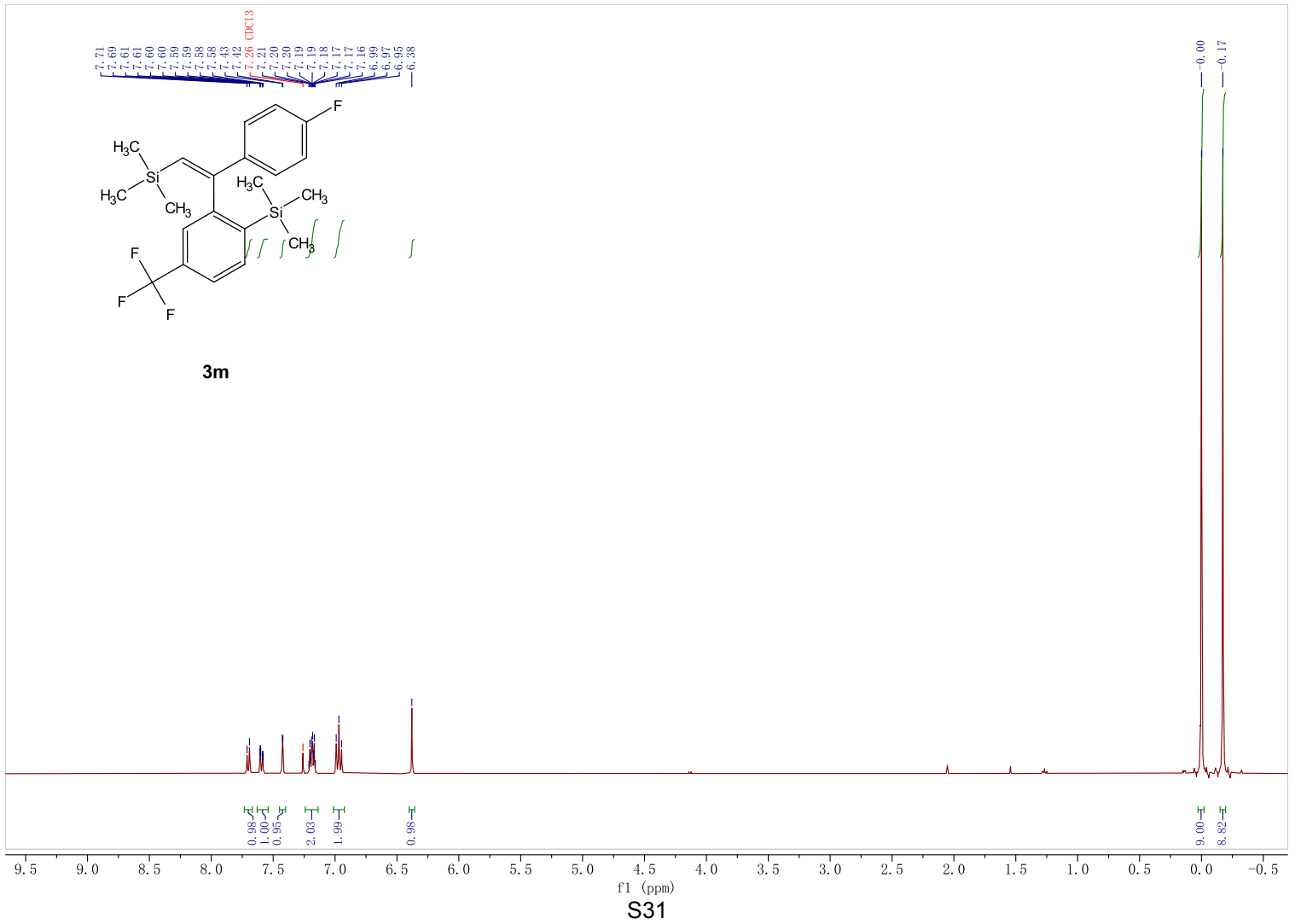
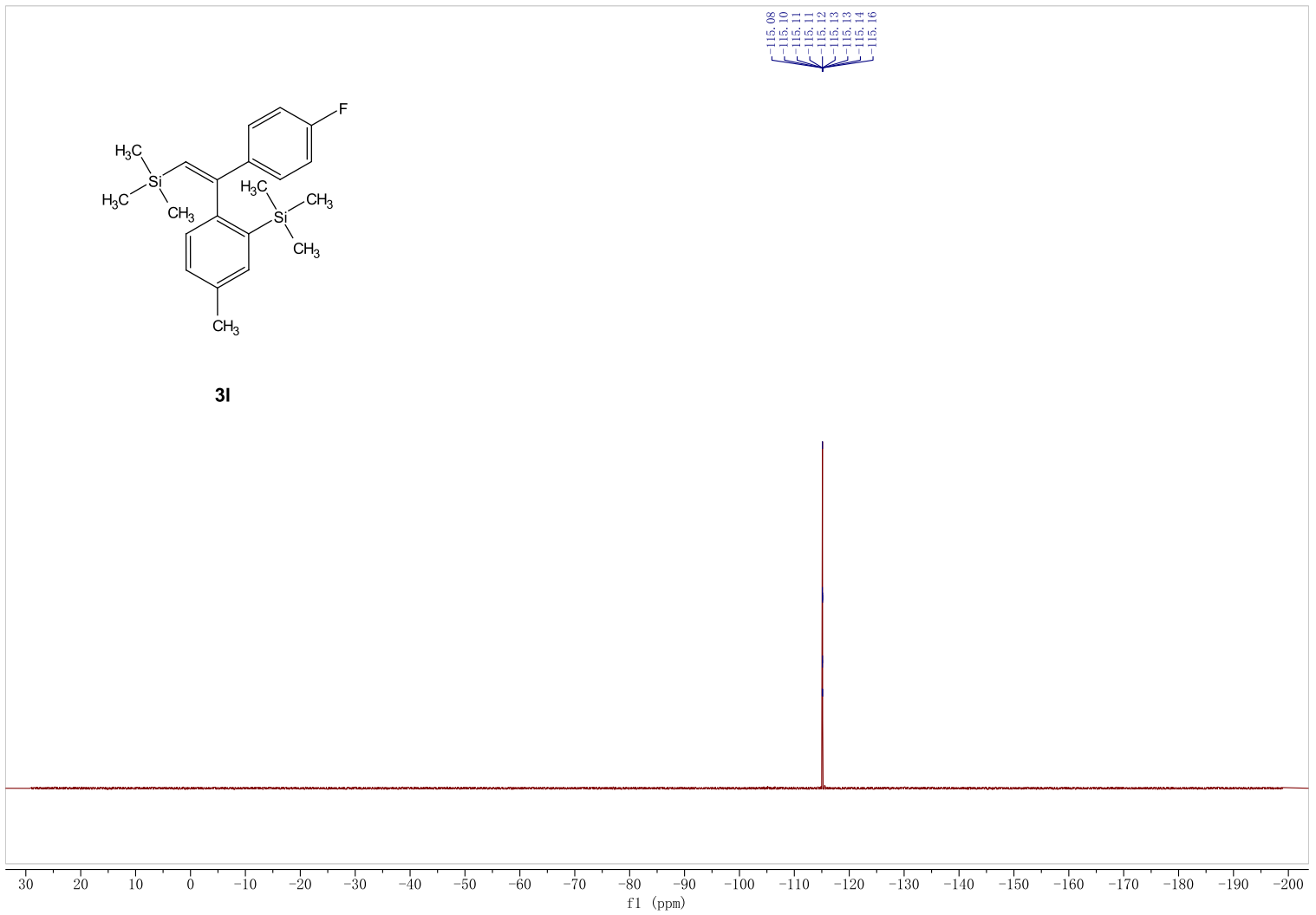
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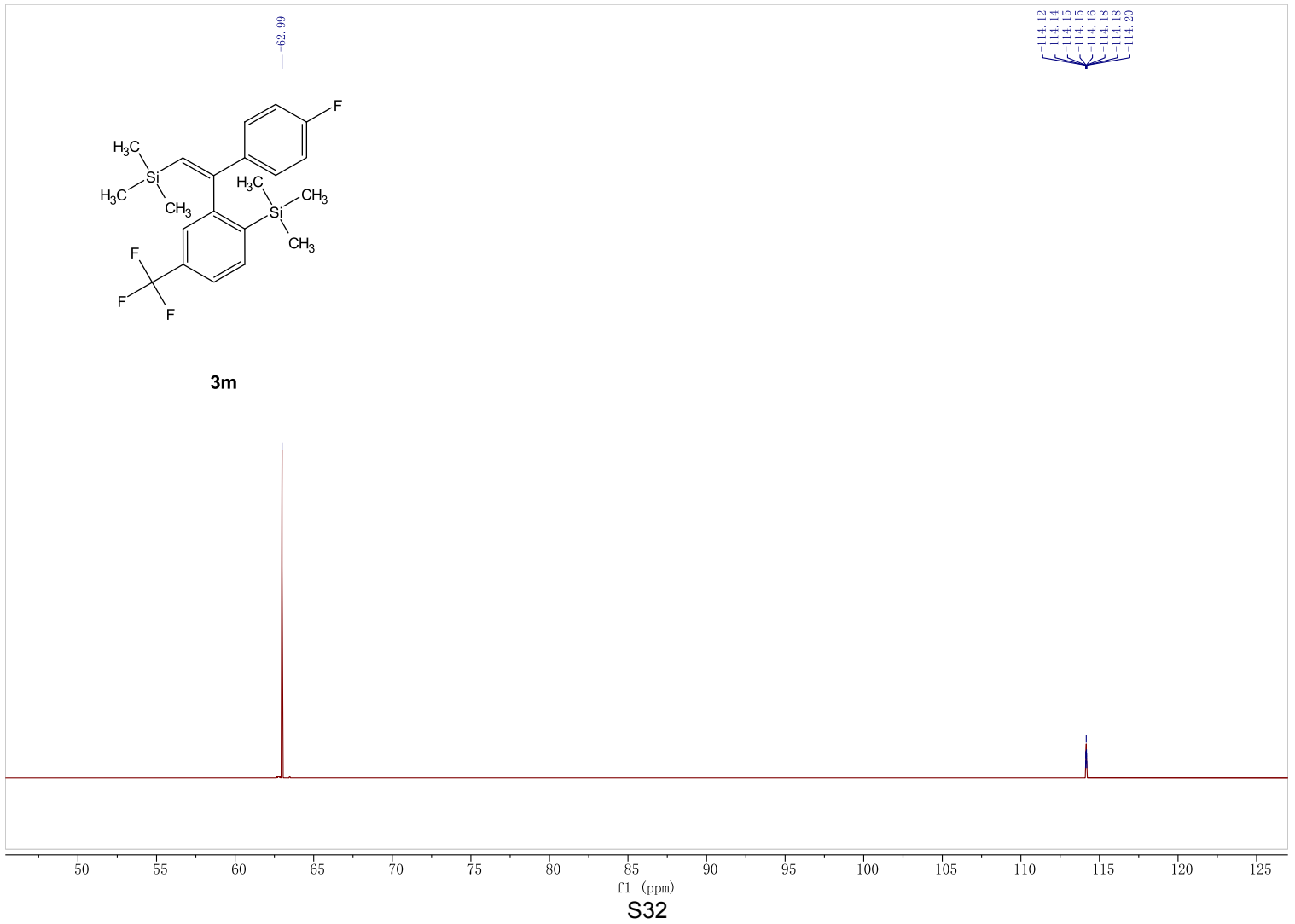
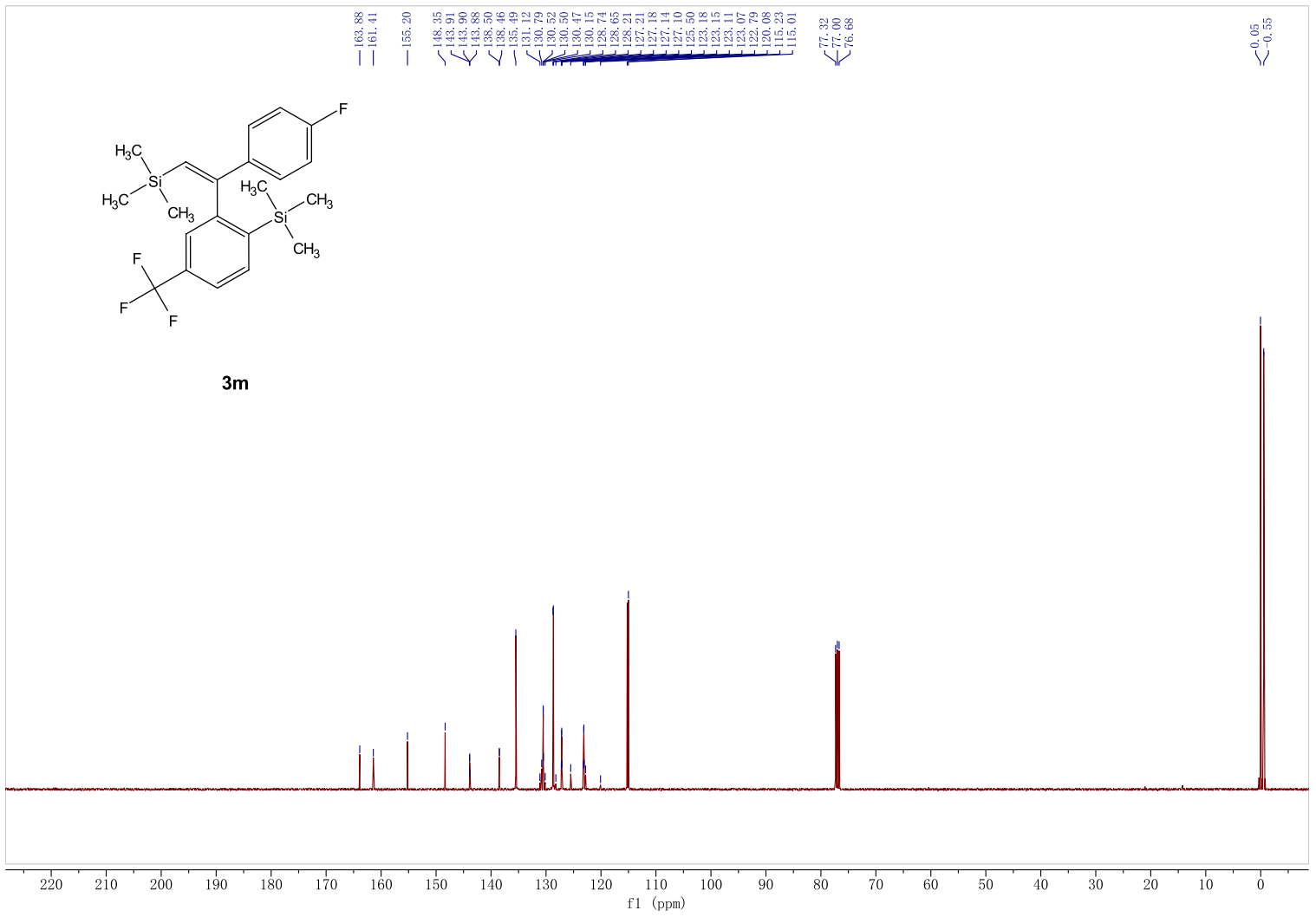


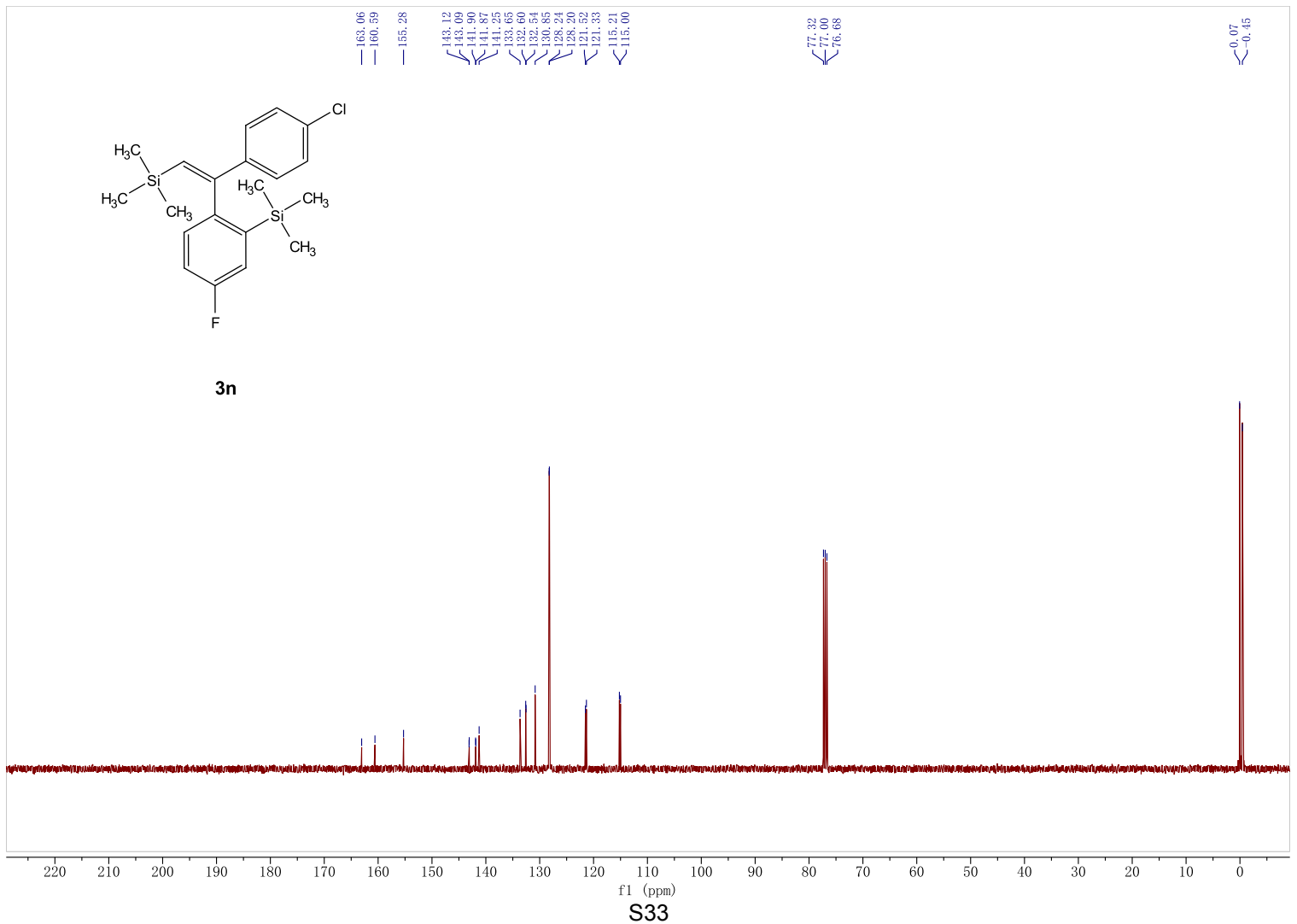
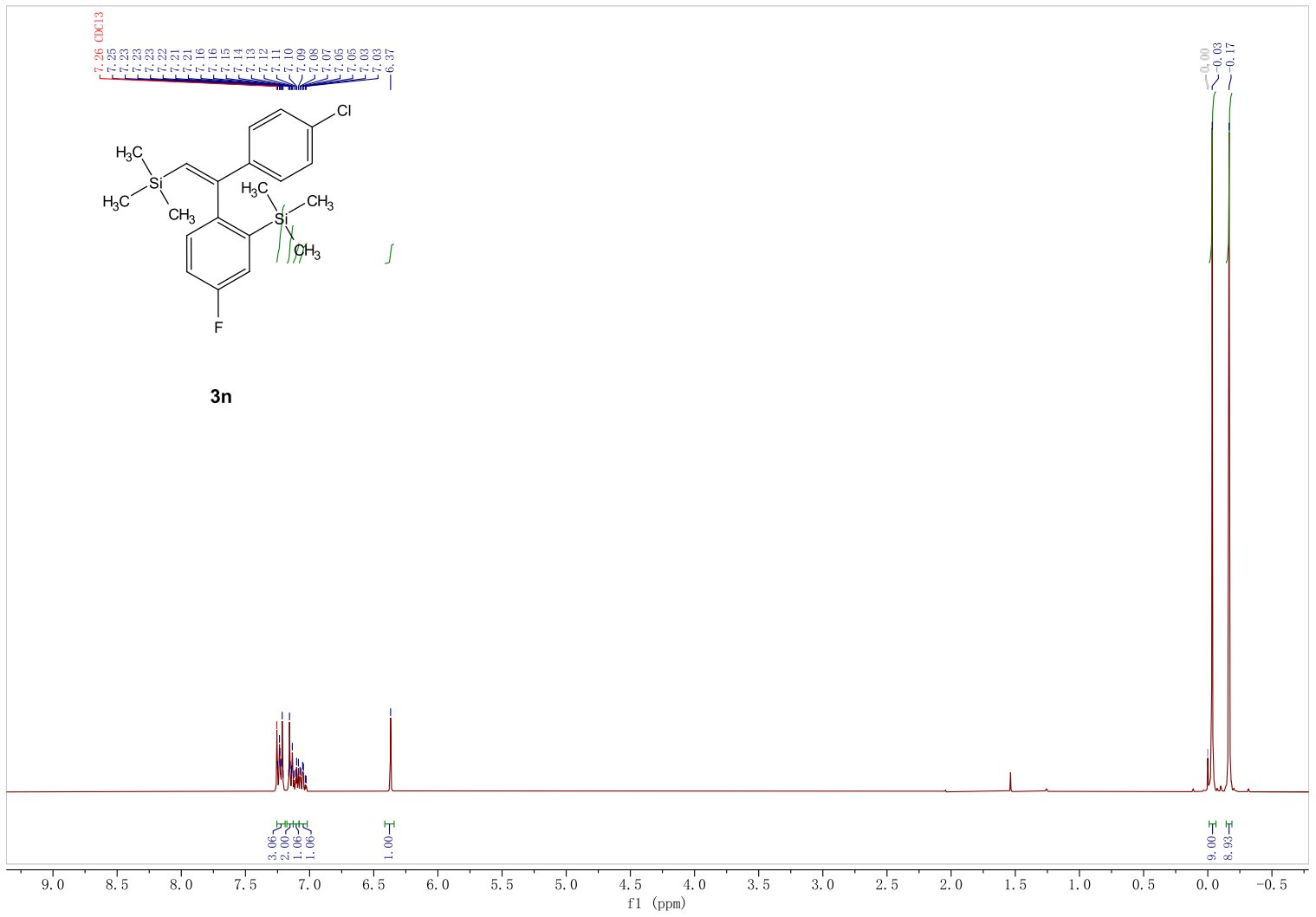


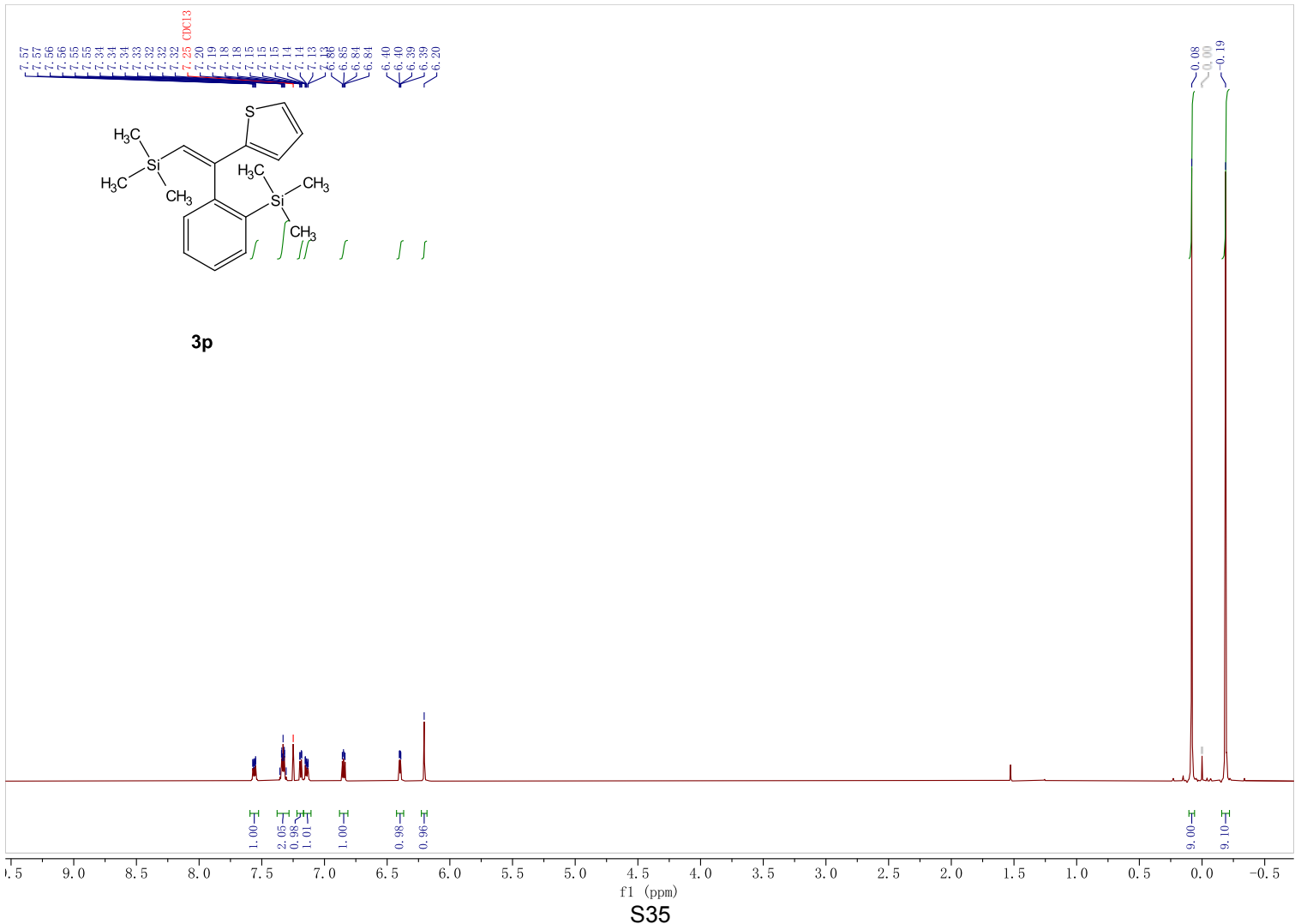
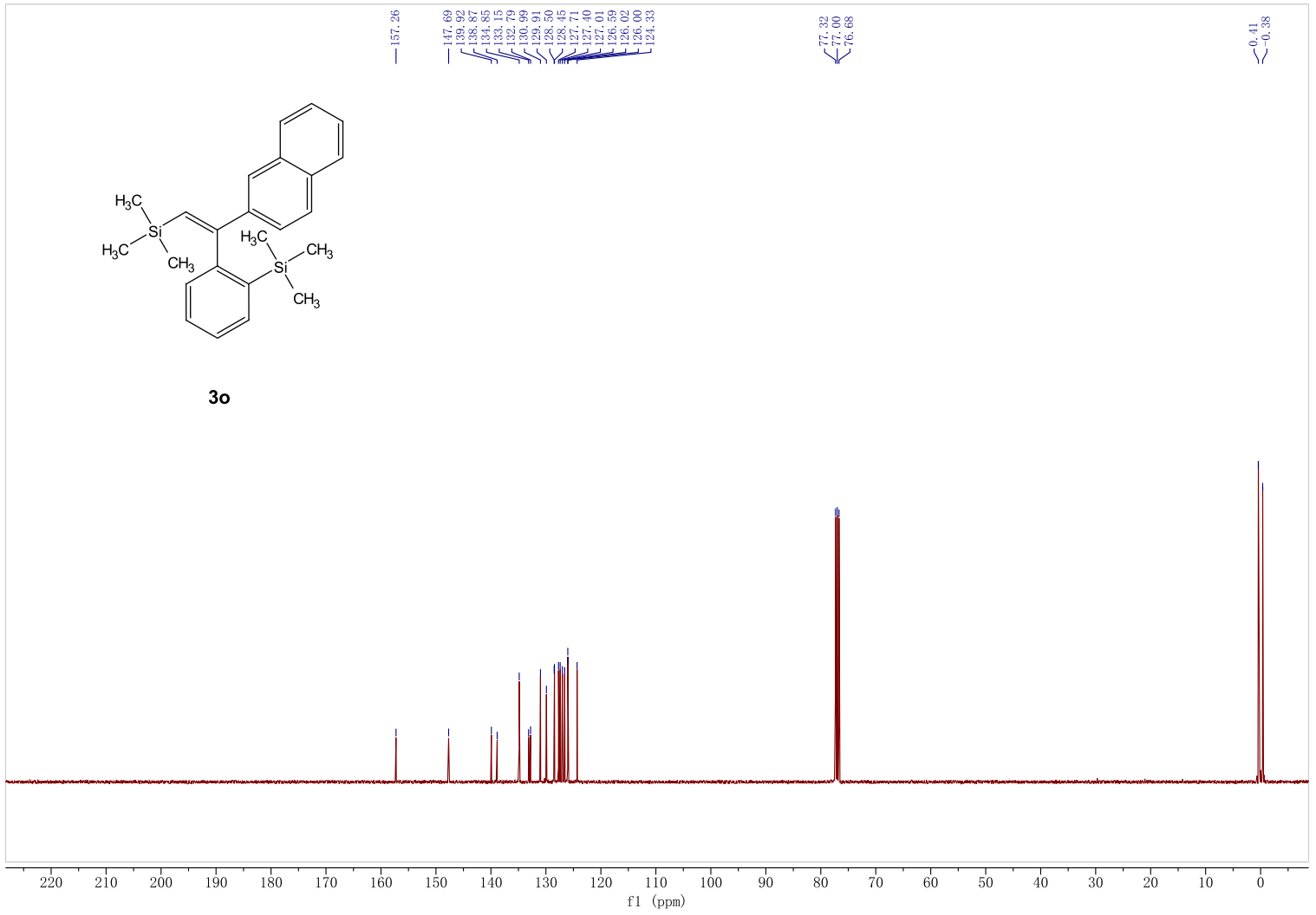


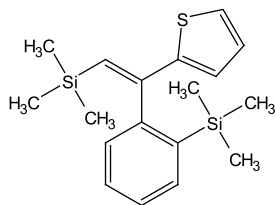










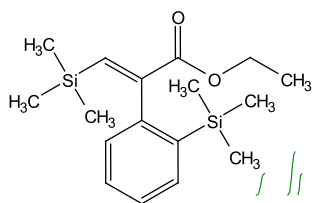
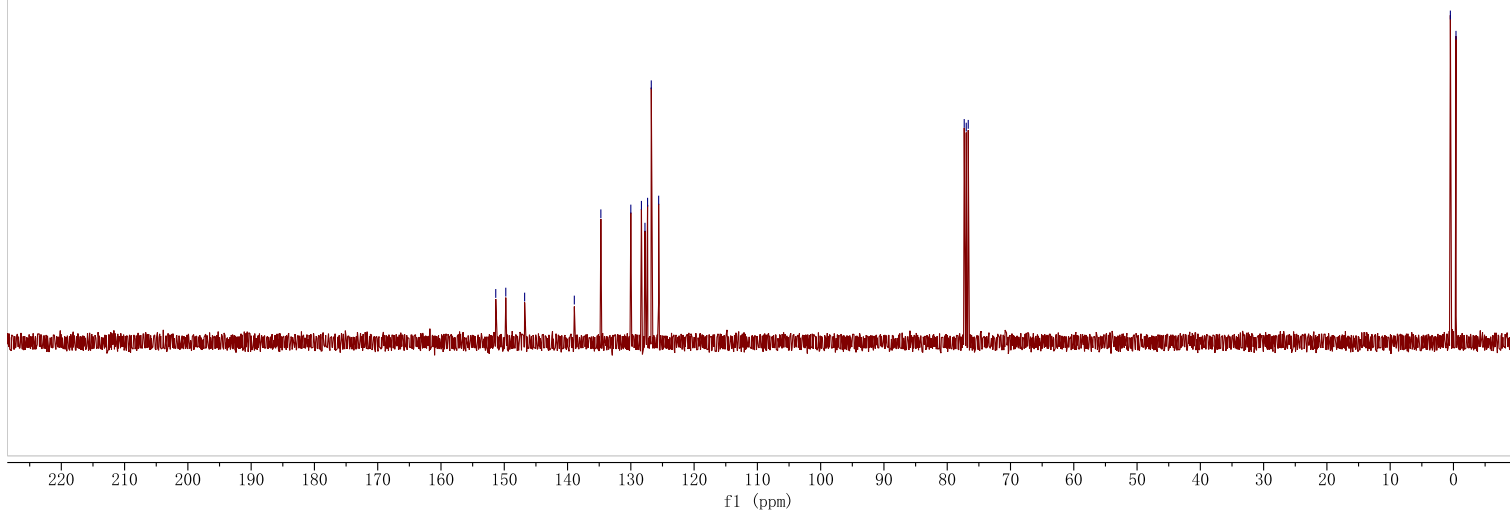


3p

151.35
149.77
146.79
138.93
136.74
136.61
128.33
127.77
127.36
126.77
125.61

77.32
77.00
76.68

0.49
-0.40



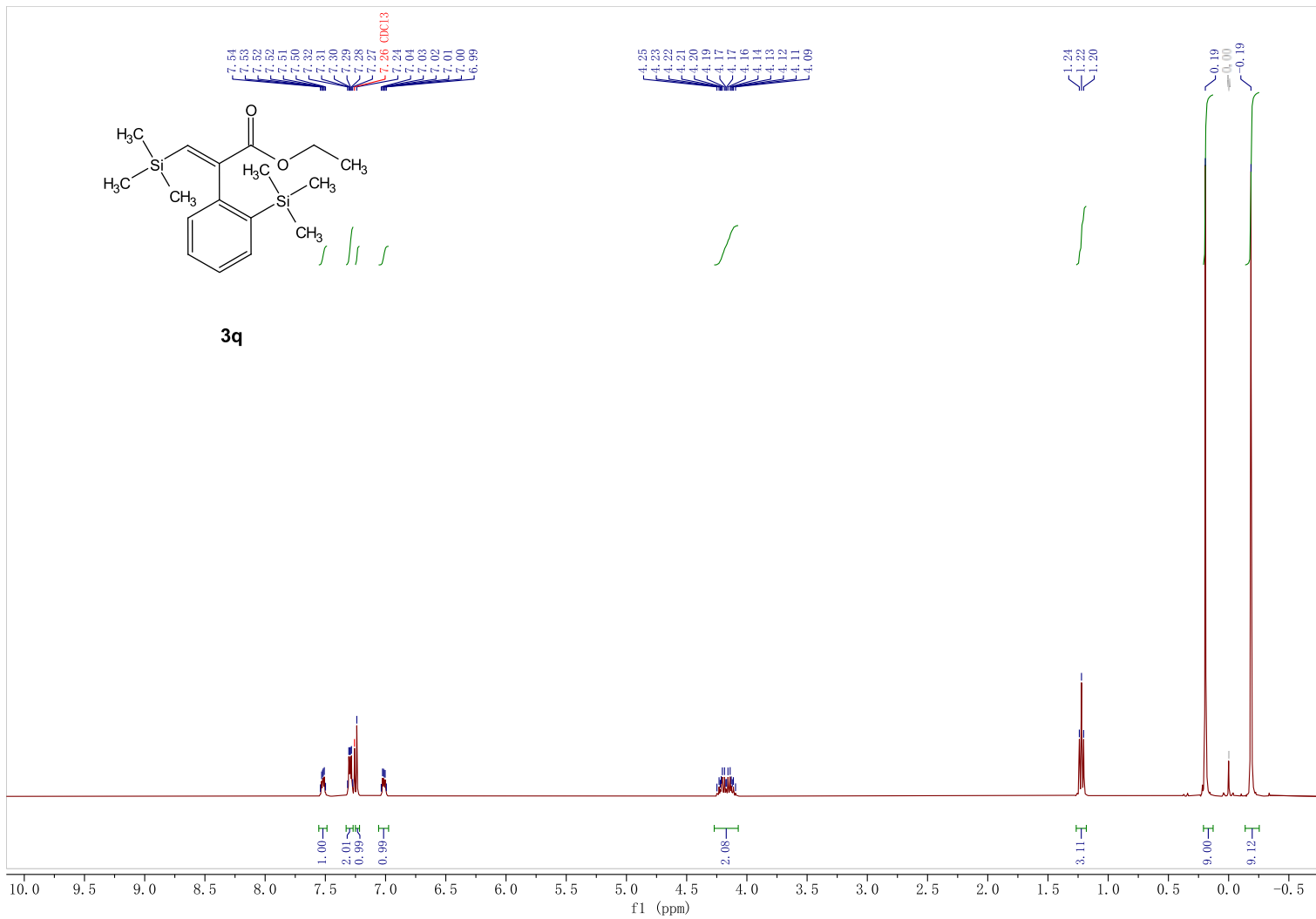
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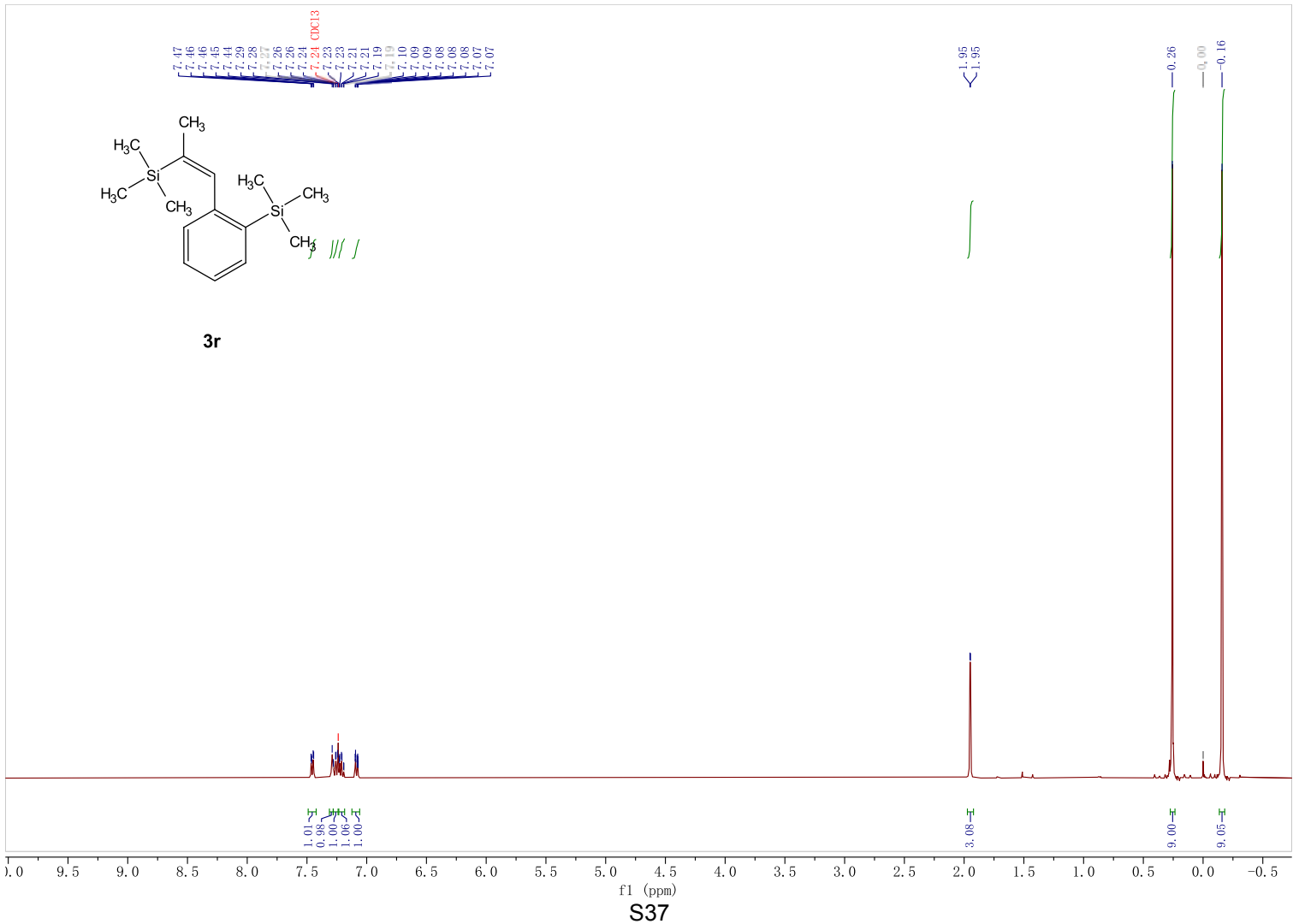
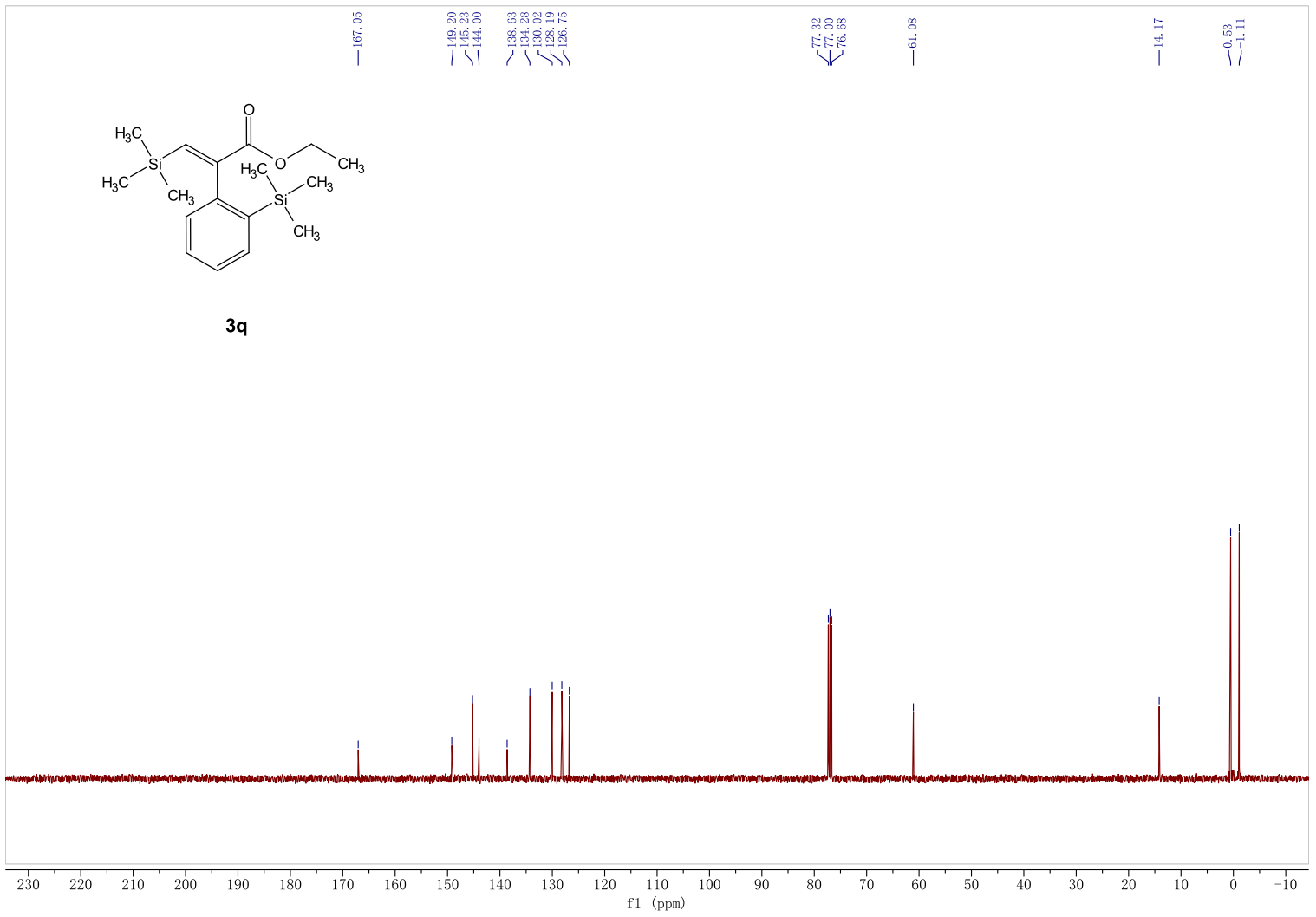
7.54
7.53
7.52
7.51
7.50
7.32
7.31
7.30
7.29
7.27
7.26 CDCl3
7.24
7.04
7.03
7.02
7.01
7.00
6.99

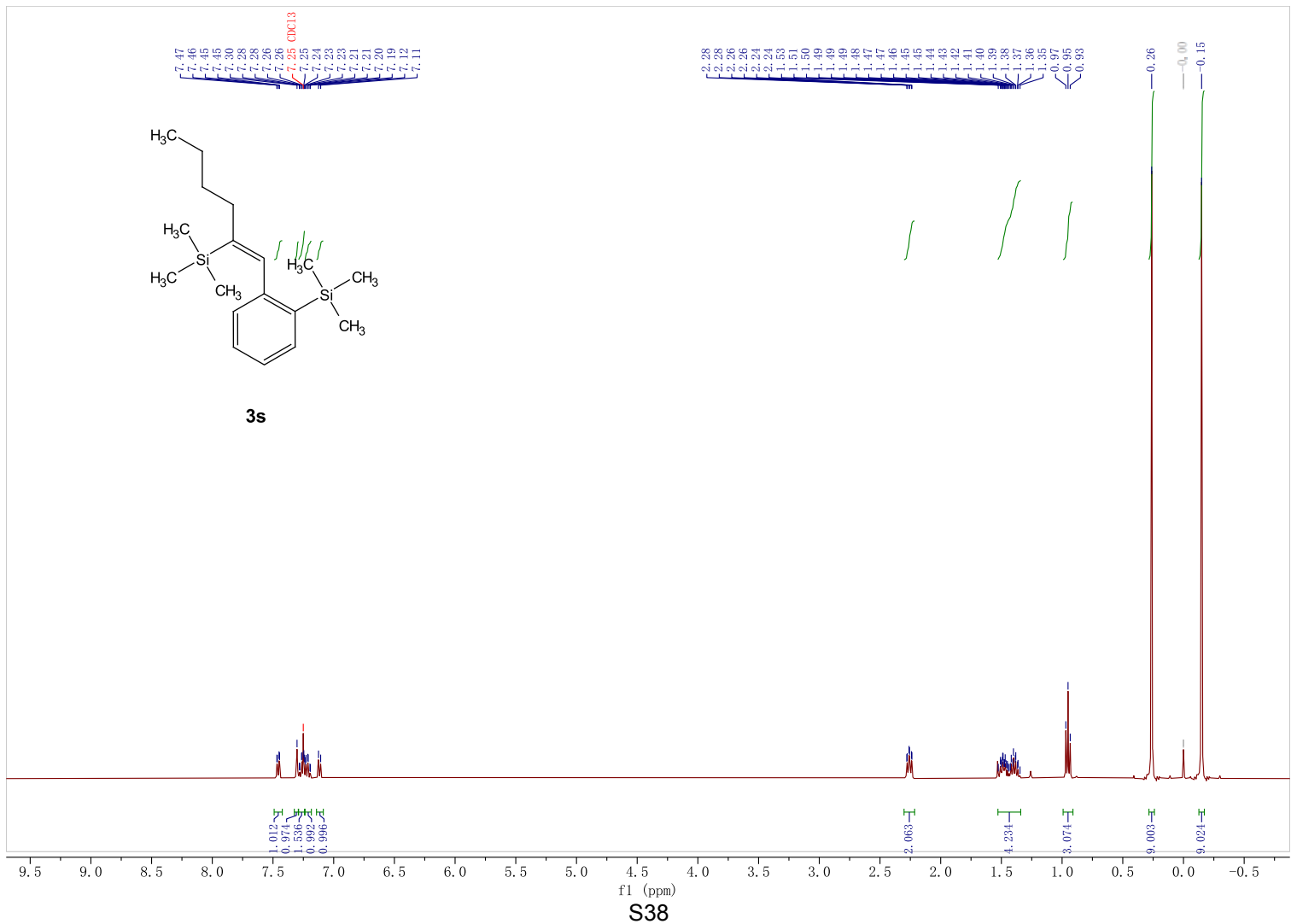
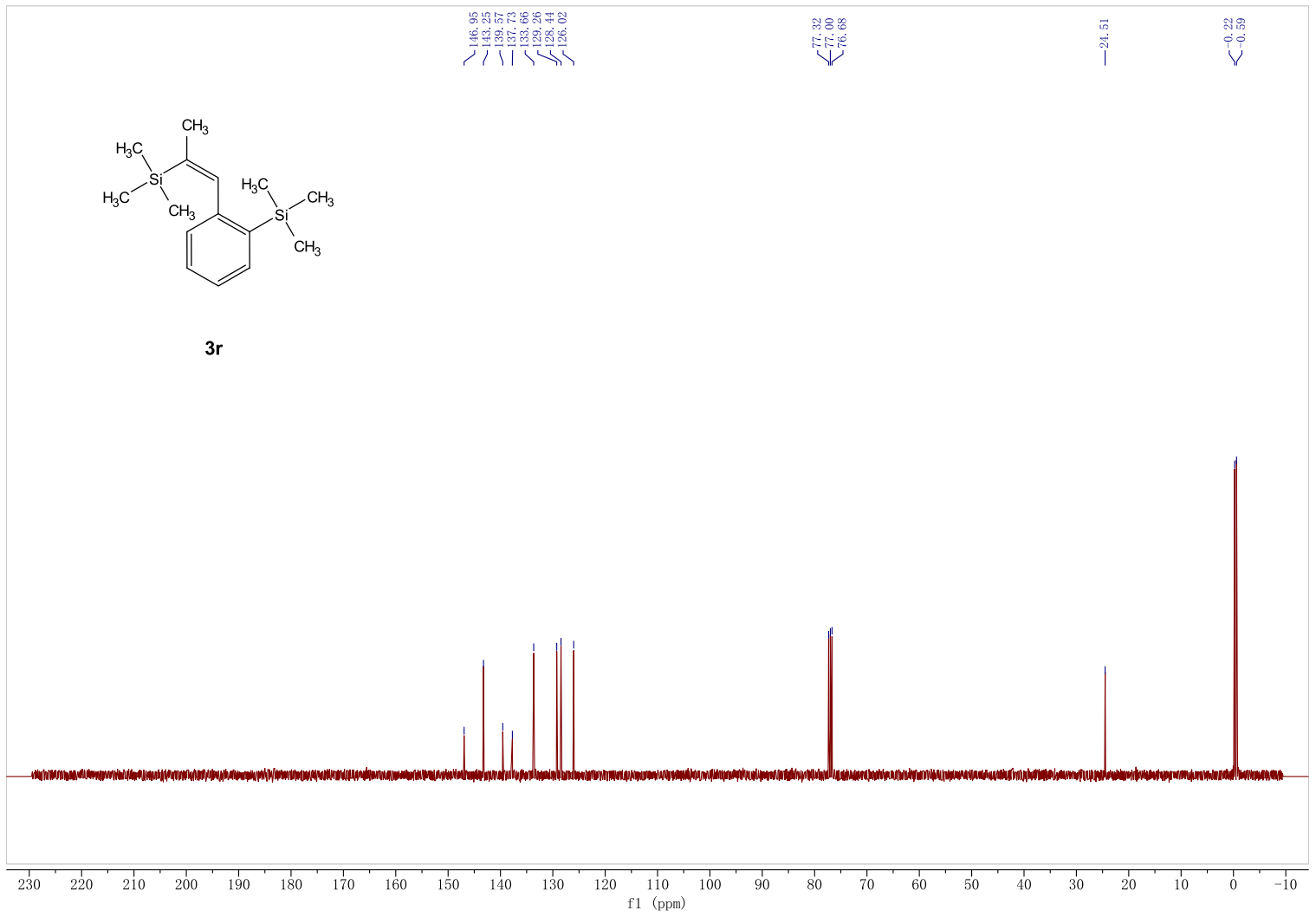
4.25
4.23
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4.17
4.16
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4.13
4.12
4.11
4.09

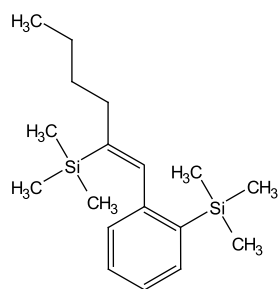
1.24
1.22
1.20

0.19
-0.00
-0.19

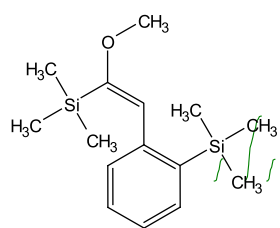
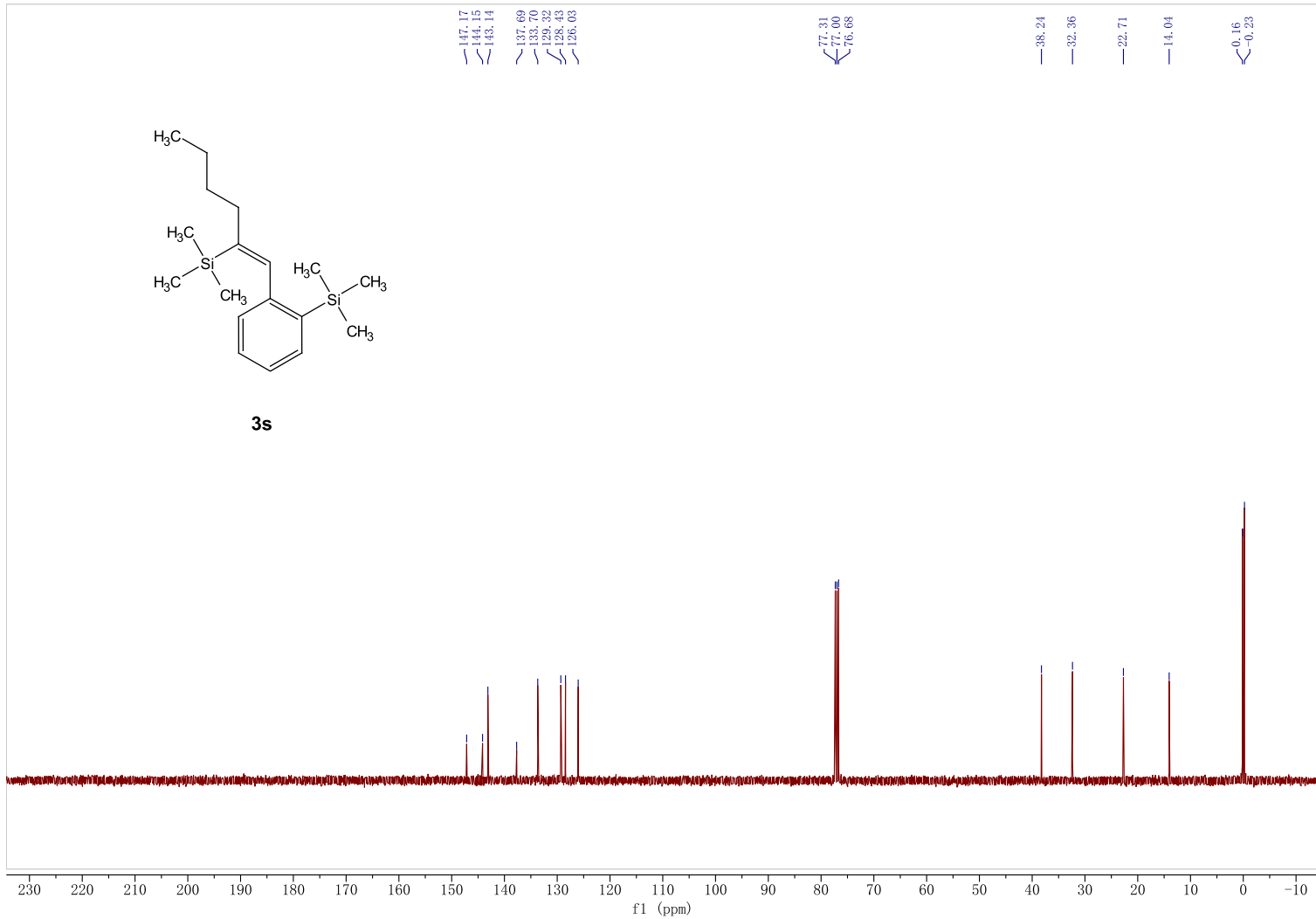








3s



3t

