Asymmetric Retro-[1, 4]-Brook Rearrangement of 3-Silyl Allyloxysilanes via Chirality Transfer from Silicon to Carbon

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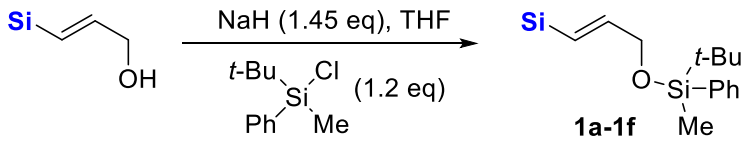
1. General Methods

Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4(conc.)/anisaldehyde/EtOH stains. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian and Bruker) and 600 MHz (Agilent), ^{13}C NMR spectra were recorded at 100 MHz (Bruker) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. CCl_4, *n*-hexane，*n*-heptane, HMPA and DMF were distilled from CaH_2. DCM, THF and Et_2O were distilled from sodium. All spectral data obtained for new compounds are reported here.

2. Experimental Procedures and Spectral Data of Products

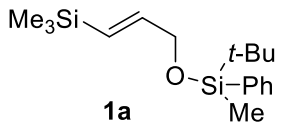
2.1. General Procedure to Synthesize 3-Silyl Allyloxysilanes1a-1f



To a suspension of NaH (186 mg, 4.64 mmol) in THF (2.0 mL) under argon atmosphere was added 3-silyl allylic alcohol[1] (3.2 mmol in 6.5 mL THF) slowly at 0 °C. The mixture was stirred for 10 min before adding *t*-BuMePhSiCl (814 mg, 3.84 mmol). After 30 min, the reaction was quenched at 0 °C by careful addition of H_2O followed by neutralization (pH = 7) with aq. 10% HCl. The mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 1-2% of EtOAc/petroleum ether) afforded **1a-1f**.

Preparation of 1a

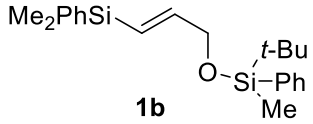
1. Z. -L. Song, Z. Lei, L. Gao, X. Wu, L.- J. Li, *Org. Lett.* **2010**, *12*, 5298-5301.



1a

1a: 85% yield, a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.39 (s, 3H), 0.97 (s, 9H), 4.21-4.28 (m, 2H), 6.00 (d, 1H, *J* =18.6 Hz), 6.13 (dt, 1H, J_1 = 18.6 Hz, J_2 = 4.2 Hz), 7.37-7.41 (m, 3H), 7.58 (d, 2H, *J* =6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, -1.3, 18.4, 25.9, 65.8, 127.5, 128.2, 129.3, 134.5, 135.8, 144.8; IR (neat) cm^{-1} 2955, 2934, 2857, 1467, 1251, 1113, 871, 853, 781; HRMS (MALDI, m/z) calcd for $C_{17}H_{31}OSi_2Na$ $(M+Na)^+$: 329.1727, found 329.1736.

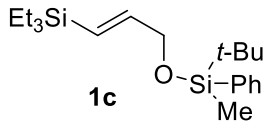
Preparation of 1b



1b

1b: 75% yield, a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.35 (s, 6H), 0.38 (s, 3H), 0.95 (s, 9H), 4.22-4.30 (m, 2H), 6.11-6.23 (m, 2H), 7.36-7.40 (m, 6H), 7.53-7.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.1, -2.5, 18.4, 25.9, 65.6, 125.8, 127.5, 127.7, 128.9, 129.4, 133.8, 134.5, 135.7, 138.9, 146.8; IR (neat) cm^{-1} 2956, 2891, 2856, 1466, 1253, 1113, 858, 823, 732; HRMS (MALDI, m/z) calcd for $C_{22}H_{32}OSi_2Na$ $(M+Na)^+$: 391.1884, found 391.1894.

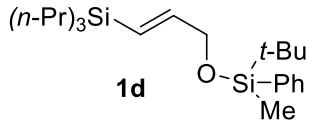
Preparation of 1c



1c

1c: 80% yield, a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.36 (s, 3H), 0.56 (q, 6H, *J* = 8.0 Hz), 0.91-0.95 (m, 18H), 4.18-4.27 (m, 2H), 5.91 (d, 1H, *J* = 18.8 Hz), 6.11 (dt, 1H, J_1 = 18.8 Hz, J_2 = 3.6 Hz), 7.33-7.39 (m, 3H),7.55 (d, 2H, *J* = 6.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.1, 4.3, 18.4, 25.9, 65.9, 124.3, 127.4,129.3, 134.5, 135.9, 146.1; IR (neat) cm^{-1} 2954, 2878, 2878, 1464, 1113, 827, 783, 732; HRMS (MALDI, m/z) calcd for $C_{20}H_{36}OSi_2Na$ $(M+Na)^+$: 371.2197, found 371.2202.

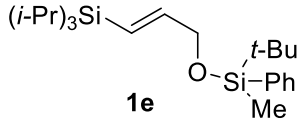
Preparation of 1d



1d

1d: 90% yield, a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 3H), 0.56-0.61 (m, 18H), 0.96 (s, 9H), 0.98 (t, 9H, *J* = 8.0 Hz), 1.31-1.39 (m, 6H), 4.20-4.28 (m, 2H), 5.94 (d, 1H, *J* = 18.8 Hz), 6.12 (dt, 1H, J_1 = 18.8 Hz, J_2 = 3.6 Hz), 7.35-7.40 (m, 3H),7.57 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1,15.4, 17.4, 18.4, 18.5, 25.9, 65.9, 125.5, 127.5, 129.3, 134.5, 135.9, 145.6; IR (neat) cm^{-1} 2955, 2928, 2862, 1462, 1254, 1113, 1063, 824, 785; HRMS (MALDI, m/z) calcd for $C_{23}H_{42}OSi_2K$ $(M+K)^+$: 429.2406, found 429.2402.

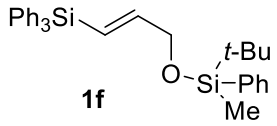
Preparation of 1e



1e

1e: 82% yield, a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 3H), 0.95 (s, 9H), 1.05-1.07 (m, 21H), 4.23-4.31 (m, 2H), 5.93 (d, 1H, *J* = 18.8 Hz), 6.18 (dt, 1H, J_1 = 18.8 Hz, J_2 = 3.6 Hz), 7.35-7.40 (m, 3H), 7.57 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1,10.9, 18.4, 18.6, 25.9, 65.9, 121.9, 127.5, 129.3, 134.5, 135.9, 144.8; IR (neat) cm^{-1} 2933, 2893, 2862, 1463, 1254, 1113, 882, 827 ; HRMS (MALDI, m/z) calcd for $C_{23}H_{42}OSi_2K$ $(M+K)^+$: 429.2406, found 429.2403.

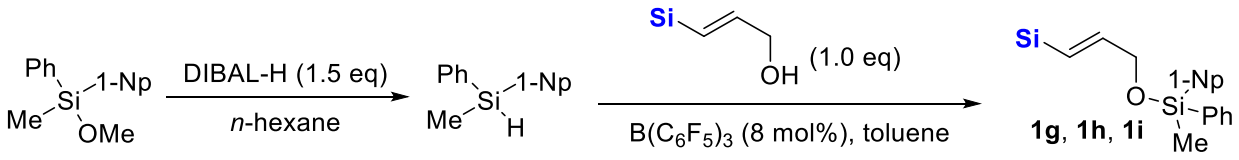
Preparation of 1f



1f

1f: 94% yield, white solid, m.p. 84°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 3H), 0.97 (s, 9H), 4.29-4.37 (m, 2H), 6.25 (dt, 1H, J_1 = 18.4 Hz, J_2 = 3.2Hz), 6.64 (d, 1H, *J* = 18.4 Hz), 7.34-7.45 (m, 12H), 7.54 (d, 6H, *J* = 6.8 Hz), 7.57 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, 18.4, 25.9, 65.4, 121.4, 127.6, 127.8, 129.4, 129.5, 134.4, 134.7, 135.6, 135.9, 150.8; IR (neat) cm^{-1} 3065, 3045, 2934, 2834, 2856, 1617, 1465, 1425, 1256, 1183, 1108, 1020, 838, 789; HRMS (MALDI, m/z) calcd for $C_{32}H_{36}OSi_2Na$ $(M+Na)^+$: 515.2197, found 515.2207.

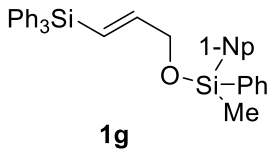
2.2. General Procedure to Synthesize 3-Silyl Allyloxysilanes 1g-1i



To a solution of 1-NpPhMeSiOMe [2](834 mg, 3.0 mmol) in anhyd *n*-hexane (15 mL) was added DIBAL-H (4.5 mL, 4.5 mmol, 1M solution in hexane) slowly at 0 °C under argon. The mixture was heated to reflux overnight. The reaction was quenched at 0°C by careful addition of H_2O followed by neutralization (pH = 7) with aq. 10% HCl. The mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: petroleum ether) afforded 1-NpPhMeSiH (700 mg, 94% yield).

3-silyl allylic alcohol (0.86 mmol), 1-NpPhMeSiH (213 mg, 0.86 mmol) and $B(C_6F_5)_3$ (36 mg, 0.069 mmol) in toluene (1.5 mL) was reacted at 90 ºC for 3 h. The reaction mixture was purified by silica gel flash column chromatography (gradient eluent: 1-5% of EtOAc/petroleum ether) to afford **1g**, **1h**, **1i**.

Preparation of 1g

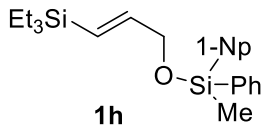


1g

1g: 85% yield, white solid, m.p. 131°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 3H), 4.42-4.43 (m, 2H), 6.26 (dt, 1H, J_1 = 18.4 Hz, J_2 = 3.6 Hz), 6.63 (d, 1H, J = 18.4 Hz), 7.34-7.53 (m, 21 H),7.65 (d, 2H, J = 6.8 Hz), 7.82 (d, 1H, J = 6.8 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 8.22 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.7, 65.9, 122.2, 124.9, 125.5,126.0, 127.8, 127.9, 128.5, 128.8, 129.4, 129.8, 130.8, 133.3, 133.6, 134.3, 134.5, 135.2, 135.9, 136.3, 136.9, 150.2; IR (neat) cm^{-1} 3058, 2962, 2864, 1425, 1257, 1108, 859, 822, 783; HRMS (MALDI, m/z) calcd for $C_{38}H_{34}OSi_2Na$ $(M+Na)^+$: 585.2040, found 585.2040.

Preparation of 1h

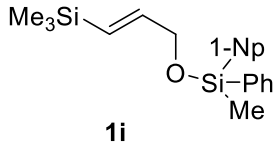
2. L. H. Sommer, C. L. Frye, G. A. Parker, K. W. Michael, *J. Am. Chem. Soc.* **1964**, *86*, 3271-3276.



1h

1h: 75% yield, a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (q, 6H, *J* = 8.0 Hz), 0.85 (s, 3H), 0.96 (t, 9H, *J* = 8.0 Hz), 4.36-4.38 (m, 2H), 5.95 (d, 1H, *J* = 18.8 Hz), 6.19 (dt, 1H, J_1 = 18.8 Hz, J_2 = 4.0 Hz), 7.39-7.46 (m, 4H),7.45-7.53 (m, 2H), 7.68 (d, 2H, *J* = 6.8 Hz), 7.84 (d, 1H, *J* = 6.8 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 8.25 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.6, 3.4, 7.3, 66.5, 124.9, 125.4, 125.5, 125.9, 127.9, 128.6, 128.7, 129.8, 130.7, 133.3, 133.8, 134.3, 135.2, 136.5, 136.9, 145.5; IR (neat) cm^{-1} 3051, 2953, 2909, 2875, 1425, 1216, 1113, 1014, 828, 783; HRMS (MALDI, m/z) calcd for $C_{26}H_{34}OSi_2K$ $(M+K)^+$: 457.1780, found 457.1779.

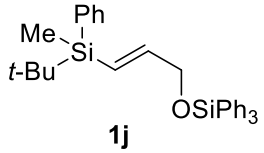
Preparation of 1i



1i

1i: 78% yield, a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.85 (s, 3H), 4.33-4.34 (m, 2H), 5.99 (d, 1H, *J* = 18.4 Hz), 6.15 (dt, 1H, J_1 = 18.8 Hz, J_2 = 4.0 Hz), 7.37-7.45 (m, 4H), 7.47-7.53 (m, 2H), 7.67 (d, 2H, *J* = 6.8 Hz), 7.84 (d, 1H, *J* = 6.8 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.95 (d, 1H, *J* = 8.0 Hz), 8.23 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.7, -1.4, 66.3, 124.9, 125.5, 125.9, 127.9, 128.6, 128.8, 129.3, 129.8, 130.7, 133.3, 133.8, 134.3, 135.2, 136.5, 136.9, 144.2; IR (neat) cm^{-1} 3050, 2957, 2929, 1590, 1427, 1255, 1118, 1082, 834, 700; HRMS (MALDI, m/z) calcd for $C_{23}H_{28}OSi_2Na$ $(M+Na)^+$: 399.1571, found 399.1575.

Preparation of 1j

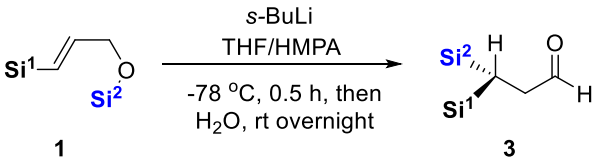


1j

1j: Using the same procedure as that used for **1f**: NaH (186mg, 4.64 mmol), THF (2.0 mL), 3-silyl allylic alcohol (3.2mmol in 6.5 mL THF), 0 °C, 10 min; then Ph_3SiCl (1.13g, 3.84 mmol) 0 °C afford **1j**, 82% yield, white solid, m.p. 52°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 3H), 0.95 (s,

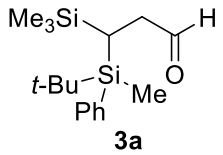
9H), 4.50-4.51 (m, 2H), 6.30 (dt, 1H, J_1 = 18.8 Hz, J_2 = 3.2 Hz), 6.40 (d, 1H, J = 18.8 Hz), 7.32 (t, 1H, J = 6.8 Hz), 7.38-7.52 (m, 11H), 7.55 (d, 2H, J = 6.8 Hz), 7.72 (d, 6H, J = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.8, 17.1, 26.6, 66.5, 123.3, 127.4, 127.7, 127.9, 128.8, 130.0,129.8, 130.0, 134.1, 134.9, 135.2, 135.3,135.4,135.6, 147.3; IR (neat) cm^{-1} 3065, 2951, 2926, 2852, 1464, 1426, 1364, 1257, 1115, 784, 705; HRMS (MALDI, m/z) calcd for $C_{32}H_{36}OSi_2K$ $(M+K)^+$: 531.1936, found 531.1938.

2.3. Screening of Silyl Groups



To a solution **1** (0.15 mmol) in anhyd THF (0.5 mL) and anhyd HMPA (0.60 mmol) under argon atmosphere was added *s*-BuLi (0.60 mL of 1.0 M solution in pentane, 0.60 mmol) at -78 °C. After stirring for 30 min, the reaction was quenched with H_2O and was warmed to room temperature with stirring overnight. The combined organic layers were diluted with Et_2O (5.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 1-5% of EtOAc /petroleum ether) afforded aldehyde **3**.

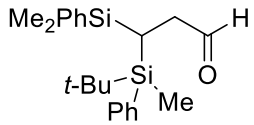
<u>Preparation of 3a</u>



3a: 62% yield, a yellow oil; (*dr* = 56:44). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.28 (s, 9H), 0.37 (s, 3H), 0.89 (s, 9H), 1.29 (dd, 1H, J_1 = 7.6 Hz, J_2 = 3.2 Hz), 2.69 (dd, 1H, J_1 = 19.6 Hz, J_2 = 7.6 Hz), 2.94 (dd, 1H, J_1 = 19.6 Hz, J_2 = 3.2 Hz), 7.32-7.33 (m, 3H), 7.48-7.52 (m, 2H), 9.84 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.4, 0.4. 1.0. 18.8, 28.1, 41.3, 127.6, 128.9, 134.6, 137.0, 201.9; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 9H), 0.36 (s, 3H), 0.95 (s, 9H), 1.19 (dd, 1H, J_1 = 7.6 Hz, J_2 = 3.2 Hz), 2.60 (dd, 1H, J_1 = 19.6 Hz, J_2 = 7.6 Hz), 2.71 (dd, 1H, J_1 = 19.6

Hz, J_2 = 3.2 Hz), 7.32-7.33 (m, 3H), 7.48-7.52 (m, 2H), 9.64 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -5.7, -0.1, 1.7, 18.5, 27.7, 42.6, 127.4, 128.8, 134.7, 137.6, 201.6; IR (neat) cm^{-1} 3069, 3049, 2958, 2858, 1466, 1423, 1363, 1255, 1107, 1013, 837, 788; HRMS (MALDI, m/z) calcd for $C_{17}H_{30}OSi_2K$ $(M+K)^+$: 345.1467, found 345.1466.

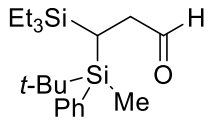
Preparation of 3b



3b

3b: 65% yield, a yellow oil; (*dr* = 53:47). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.23 (s, 3H), 0.31 (s, 3H), 0.87 (s, 9H), 1.56 (dd, 1H, J_1 = 7.2 Hz, J_2 = 3.2 Hz), 2.59-2.74 (m, 1H), 2.83 (dd, 1H, J_1 = 19.6 Hz, J_2 = 3.2 Hz), 7.24-7.32 (m, 7H), 7.43-7.49 (m, 3H), 9.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, -1.5, -1.0, 1.0, 18.9, 27.9, 41.4, 127.5, 127.7, 128.8, 129.0, 133.9, 134.7, 136.9, 139.1, 201.0; ***minor- isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.12 (s, 3H), 0.18 (s, 3H), 0.31 (s, 3H), 0.86 (s, 9H), 1.49 (dd, 1H, J_1 = 7.2 Hz, J_2 = 3.2 Hz), 2.59-2.74 (m, 2H), 7.24-7.32 (m, 7H), 7.43-7.49 (m, 3H), 9.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.7, -2.2, -1.2, 0.5, 18.6, 27.7, 42.5, 127.4, 127.6, 128.8, 128.9,133.8,134.8, 137.0, 139.0, 201.4; IR (neat) cm^{-1} 2958, 2932, 1719, 1424, 1363, 1108, 1013, 820, 791; HRMS (MALDI, m/z) calcd for $C_{22}H_{32}OSi_2K$ $(M+K)^+$: 407.1623, found 407.1815.

Preparation of 3c

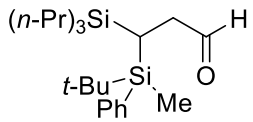


3c

3c: 53% yield, a yellow oil; (*dr* = 67:33). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17-0.29 (m, 6H), 0.39 (s, 3H), 0.78 (t, 9H, *J* = 8.0 Hz), 0.88 (s, 9H), 1.43 (dd, 1H, J_1 = 7.2 Hz, J_2 = 3.6 Hz), 2.71 (dd, 1H, J_1 = 20.0 Hz, J_2 = 7.2 Hz), 2.92 (dd, 1H, J_1 = 20.0 Hz, J_2 = 3.6 Hz), 7.29-7.35 (m, 3H), 7.53 (d, 2H, *J* = 7.2 Hz), 9.83 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, -2.1, 3.9, 7.6, 19.0, 28.1, 41.3, 127.4, 128.9, 134.5, 137.6, 201.8; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 3H),

0.52 (ddd, 6H, J_1 = 15.2 Hz, J_2 = 7.6 Hz, J_3 = 3.6 Hz), 0.85-0.89 (m, 9H), 0.96 (s, 9H), 1.31 (dd, 1H, J_1 = 7.6 Hz, J_2 = 3.6 Hz), 2.63 (dd, 1H, J_1 = 20.0 Hz, J_2 = 7.6 Hz), 2.77 (dd, 1H, J_1 = 20.0 Hz, J_2 = 3.6 Hz), 7.29-7.35 (m, 3H), 7.53 (d, 2H, J = 7.2 Hz), 9.64 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -5.2, -2.8, 4.3, 7.6, 18.9, 27.9, 42.4, 127.5, 128.9, 134.8, 137.1, 201.6; IR (neat) cm^{-1} 2955, 2933, 2879, 1703, 1465, 1422, 1007, 786, 733; HRMS (MALDI, m/z) calcd for $C_{20}H_{36}OSi_2Na$ $(M+Na)^+$: 371.2197, found 371.2195.

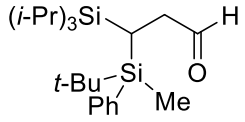
Preparation of 3d



3d

3d: 50% yield, a yellow oil; (*dr* = 65:35). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11-0.26 (m, 6H), 0.38 (s, 3H), 0.79 (t, 9H, J = 7.2 Hz), 0.88 (s, 9H), 1.11-1.16 (m, 6H), 1.38 (dd, 1H, J_1 = 6.4 Hz, J_2 = 3.6 Hz), 2.69 (dd, 1H, J_1 = 20.0 Hz, J_2 = 6.4 Hz), 2.90 (dd, 1H, J_1 = 20.0 Hz, J_2 = 3.6 Hz), 7.30-7.32 (m, 3H), 7.52 (d, 2H, J = 7.2 Hz), 9.82 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, -1.6, 15.9, 17.5, 18.5, 19.1, 28.1, 41.3, 127.4, 128.9, 134.6, 137.6, 201.8; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 3H), 0.44-0.48 (m, 6H), 0.87 (t, 9H, J = 7.2 Hz), 0.95 (s, 9H), 1.18-1.28 (m, 7H), 2.62 (dd, 1H, J_1 = 20.0 Hz, J_2 = 7.6 Hz), 2.79 (dd, 1H, J_1 = 20.0 Hz, J_2 = 3.2 Hz), 7.30-7.32 (m, 3H), 7.52 (d, 2H, J = 7.2 Hz), 9.65 (s, 1H);; ^{13}C NMR (150 MHz, $CDCl_3$) δ -5.2, -2.2, 16.3, 17.6, 18.6, 18.9, 27.9, 42.5, 127.5, 128.8, 134.8, 137.1, 201.6; IR (neat) cm^{-1} 2956, 2895, 2865, 1708, 1422, 1217, 1106, 1064, 760, 736; HRMS (MALDI, m/z) calcd for $C_{23}H_{42}OSi_2Na$ $(M+Na)^+$: 413.2666, found 413.2675.

Preparation of 3e

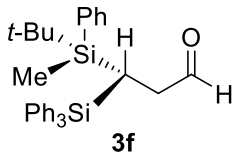


3e

3f: 45% yield, a yellow oil; (*dr* = 83:17). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (s, 3H), 0.71-0.79 (m, 3H), 0.89 (s, 9H), 0.90 (d, 9H, J = 7.6 Hz), 0.96 (d, 9H, J = 7.6 Hz), 1.74 (dd, 1H, J_1

= 4.4 Hz, J_2 = 4.4 Hz), 2.88 (dd, 1H, J_1 = 20.8 Hz, J_2 = 4.4 Hz), 3.01 (dd, 1H, J_1 = 20.8 Hz, J_2 = 4.4 Hz), 7.26-7.35 (m, 3H), 7.60 (d, 2H, J = 6.8 Hz), 9.86 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -6.6, -4.1, 12.5, 19.2, 19.5, 19.6, 28.2, 42.1, 127.1, 128.9, 135.1, 137.4, 201.9; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47 (s, 3H), 0.71-0.79 (m, 3H), 0.89 (s, 9H), 0.90 (d, 9H, J = 7.6 Hz), 0.96 (d, 9H, J = 7.6 Hz), 1.74 (dd, 1H, J_1 = 4.4 Hz, J_2 = 4.4 Hz), 3.01 (dd, 1H, J_1 = 20.8 Hz, J_2 = 4.4 Hz), 3.12 (dd, 1H, J_1 = 20.8 Hz, J_2 = 4.4 Hz), 7.26-7.35 (m, 3H), 7.60 (d, 2H, J = 6.8 Hz), 9.76 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -6.6, -3.9, 13.2, 19.2, 19.5, 19.6, 28.1, 42.1, 127.1, 128.9, 135.1, 137.4, 201.9; IR (neat) cm^{-1} 2934, 2863, 1706, 1464, 1420, 1235, 1008, 822, 781; HRMS (MALDI, m/z) calcd for $C_{23}H_{42}OSi_2Na$ $(M+Na)^+$: 413.2666, found 413.2672.

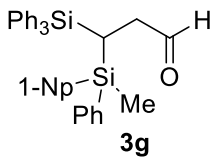
Preparation of 3f



3f

3f: 60% yield, white solid, m.p. 94°C; (*dr* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.85 (s, 9H), 2.53 (t, 1H, J = 4.4 Hz) (major), **2.27 (t, 1H, *J* = 4.4 Hz) (minor)**, 3.05 (dd, 1H, J_1 = 20.0 Hz, J_2 = 4.4 Hz), 3.16 (dd, 1H, J_1 = 20.0 Hz, J_2 = 4.4 Hz), 6.96 (t, 2H, J = 7.2 Hz), 7.13 (t, 3H, J = 7.2 Hz), 7.20-7.26 (m, 6H), 7.31 (t, 3H, J = 7.2 Hz), 7.40 (d, 6H, J = 7.2 hz), 9.58 (s, 1H) (major), **9.32 (s, 1H) (minor)**; ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.1, -2.1, 19.2, 27.7, 42.6, 126.8, 127.5, 128.4, 129.1, 134.6, 134.9, 135.9, 200.8; IR (neat) cm^{-1} 3068, 3049, 2959, 2931, 2857, 1717, 1685, 1467, 1426, 1285, 1162, 1106, 1019, 789; HRMS (MALDI, m/z) calcd for $C_{32}H_{36}OSi_2Na^+$: 515.2197, found 515.2199.

Preparation of 3g

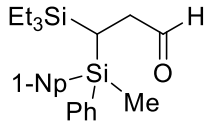


3g

3g: 65% yield, white solid, m.p 80°C; (*dr* = 65:35). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.54 (s, 3H), 2.80-2.88 (m, 2H), 2.96-2.98 (m, 1H), 7.19-7.36 (m, 11H), 7.41 (t, 4H, J = 7.2 Hz), 7.50 (d, 4H, J = 7.2 Hz), 7.55-7.59 (m, 3H), 7.73 (d, 1H, J = 7.2 Hz), 7.79-7.82 (m, 3H), 7.95 (d,

1H, *J* = 7.2 Hz), 9.24 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -0.6, 1.0, 42.4, 124.9, 125.1, 125.5, 127.7, 127.8, 128.7, 128.9, 129.1, 129.4, 130.3, 133.5, 133.8, 134.5, 135.0, 135.4, 136.0, 136.6, 137.1, 200.5; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52 (s, 3H), 2.80-2.88 (m, 2H), 2.96-2.98 (m, 1H), 7.19-7.36 (m, 11H), 7.41 (t, 4H, *J* = 7.2 Hz), 7.50 (d, 4H, *J* = 7.2 Hz), 7.55-7.59 (m, 3H), 7.73 (d, 1H, *J* = 7.2 Hz), 7.79-7.82 (m, 3H), 7.95 (d, 1H, *J* = 7.2 Hz), 9.09 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -0.6, 1.0, 42.8, 125.1, 125.2, 125.7, 127.7, 127.9, 128.5, 129.0, 129.2, 129.5, 130.2, 133.5, 133.8, 134.7, 135.2, 135.5, 135.9, 136.6, 137.1, 200.9; IR (neat) cm^{-1} 3064, 2963, 2917, 1713, 1423, 1401, 1102, 1023, 801, 700; HRMS (MALDI, m/z) calcd for $C_{38}H_{34}OSi_2Na$ $(M+Na)^+$: 585.2040, found 585.2042.

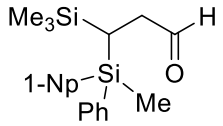
Preparation of 3h



3h

3h: 73% yield, a colorless oil; (*dr* = 83:17). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24-0.42 (m, 6H), 0.77 (t, 9H, *J* = 8.0 Hz), 0.82 (s, 9H), 1.91 (dd, 1H, J_1 = 5.2 Hz, J_2 = 5.2 Hz), 2.75-2.88 (m, 2H), 7.31-7.48 (m, 6H), 7.54-7.56 (m, 2H), 7.73-7.84 (m, 2H), 7.88 (d, 1H, *J* = 8.0 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 9.66 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -1.8, 0.00, 3.9, 7.5, 41.6, 124.9, 125.4, 125.7, 127.9, 128.5, 128.9, 129.1, 130.5, 133.5, 134.6, 134.9, 135.1, 137.0, 137.6, 201.40; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24-0.42 (m, 6H), 0.67 (t, 9H, *J* = 8.0 Hz), 0.85 (s, 9H), 1.76 (dd, 1H, J_1 = 5.2 Hz, J_2 = 5.2 Hz), 2.75-2.88 (m, 2H), 7.31-7.48 (m, 6H), 7.54-7.56 (m, 2H), 7.73-7.84 (m, 2H), 7.88 (d, 1H, *J* = 8.0 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 9.57 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ-1.7, 0.09, 4.1, 7.7, 41.9, 125.0, 125.4, 125.6, 127.8, 128.6, 129.0, 129.2, 130.5\4, 133.5, 134.6, 134.9, 135.1, 137.0, 137.6, 201.45; IR (neat) cm^{-1} 3050, 2955, 2910, 1718, 1461, 1422, 1382, 1105, 1011, 795, 708; HRMS (MALDI, m/z) calcd for $C_{26}H_{34}OSi_2Na$ $(M+Na)^+$: 441.2040, found 441.2035.

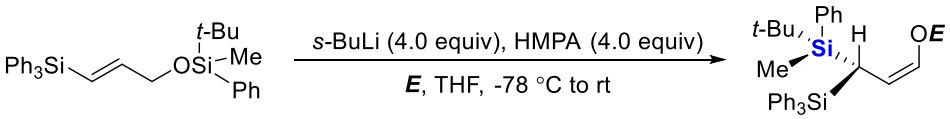
Preparation of 3i



3i

3i: 63% yield, a colorless oil; (*dr* = 86:14). ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.24 (s, 9H), 0.79 (s, 3H), 1.78 (dd, 1H, J_1 = 7.6 Hz, J_2 = 3.6 Hz), 2.73-2.87 (m, 2H), 7.32-7.48 (m, 6H), 7.55 (d, 2H, *J* = 6.8 Hz), 7.77(d, 1H, *J* = 6.8 Hz),7.82-7.89 (m, 2H), 8.01(d, 1H, *J* = 8.0 Hz), 9.72 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -2.1, -0.4, 3.4, 41.6, 124.9, 125.4, 125.8, 127.9, 128.4, 128.9, 129.1, 130.5, 133.4, 134.5, 134.8, 134.9, 137.1, 137.4, 201.5; ***minor- isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) -0.14 (s, 9H), 0.79 (s, 3H), 1.61-1.64 (m, 1H), 2.73-2.87 (m, 2H), 7.32-7.48 (m, 6H), 7.55 (d, 2H, *J* = 6.8 Hz), 7.77 (d, 1H, *J* = 6.8 Hz), 7.82-7.89 (m, 2H), 8.01(d, 1H, *J* = 8.0 Hz), 9.67 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -1.1, -0.2, 3.6, 41.9, 124.9, 125.4, 125.6, 127.9, 128.5, 129.0, 129.2, 130.4, 133.5, 134.6, 134.8, 134.9, 137.1, 137.4, 201.6; IR (neat) cm^{-1} 3042, 2954, 2849, 1718, 1421, 1383, 1251, 1103, 1063, 1023, 838, 785; HRMS (MALDI, m/z) calcd for $C_{23}H_{28}OSi_2Na$ $(M+Na)^+$: 399.1571, found 399.1571.

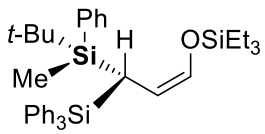
2.4. Reactions with Electrophiles



1f **4** [*dr* = 90:10]

To a solution of **1f** (75mg, 0.15 mmol) in anhyd THF (0.5 mL) and anhyd HMPA (104 μL, 0.60 mmol) under argon atmosphere was added *s*-BuLi (0.60 mL of 1.0 M solution in pentane, 0.60 mmol) at -78 °C. After stirring for 30 min, electrophiles (0.75 mmol) was added and the resulting solution was warmed to room temperature with stirring for 2 h. The mixture was diluted with Et_2O (5.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 1-5% of EtOAc /petroleum ether) afforded **4**.

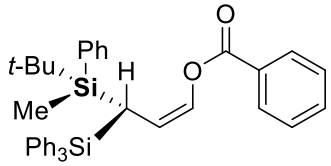
Preparation of 4a



4a

4a: 60% yield, a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 3H), 0.73 (q, 6H, *J* = 8.0 Hz), 0.87 (s, 9H), 1.04 (t, 9H, *J* = 8.0 Hz), 3.39 (d, 1H, *J* = 12.4 Hz) (major), 3.14 (d, 1H, *J* = 12.4 Hz) (minor), 4.65 (dd, 1H, J_1 = 12.4 Hz, J_2 = 5.6 Hz) (major), 4.58 (dd, 1H, J_1 = 12.4 Hz, J_2 = 5.6 Hz) (minor), 6.16 (d, 1H, *J* = 5.6 Hz), 7.02 (t, 2H, *J* = 7.6 Hz), 7.16-7.22 (m, 9H), 7.28 (t, 3H, *J* = 7.6 Hz), 7.41 (d, 6H, *J* = 7.6 Hz),; ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.4, 4.7, 6.7, 7.8, 19.3, 27.4, 107.1, 126.8, 127.2, 127.3, 128.1, 128.7, 134.9, 135.7, 136.0, 136.1, 137.3; IR (neat) cm^{-1} 3068, 3047, 2957, 2880, 2855, 1637, 1463, 1425, 1264, 1103, 1009, 847, 736; HRMS (MALDI, m/z) calcd for $C_{38}H_{50}OSi_3Na$ $(M+Na)^+$: 629.3062, found 629.3058.

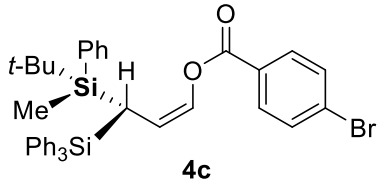
Preparation of 4b



4b

4b: 65% yield, white solid, m.p. 114°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.86 (s, 9H), 3.45 (d, 1H, *J* = 13.2 Hz) (major), 3.14 (d, 1H, *J* = 13.2 Hz) (minor), 5.31 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.17 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 7.06 (t, 2H, *J* = 7.6 Hz), 7.13 (t, 6H, *J* = 7.6 Hz), 7.19-7.26 (m, 7H), 7.40 (d, 6H, *J* = 7.6 Hz) 7.57 (t, 2H, *J* = 7.6 Hz), 7.67 (t, 1H, *J* = 7.6 Hz), 8.18 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.2, 11.6, 19.4, 27.3, 113.6, 127.1, 127.4, 128.5, 128.7, 129.1, 129.6, 129.8, 132.4, 133.4, 134.5, 134.7, 136.0, 136.7, 163.2; IR (neat) cm^{-1} 3041, 2962, 2928, 2855, 1715, 1424, 1267, 1104, 1043, 947, 799, 702; HRMS (MALDI, m/z) calcd for $C_{39}H_{40}O_2Si_2Na$ $(M+Na)^+$: 619.2459, found 619.2455.

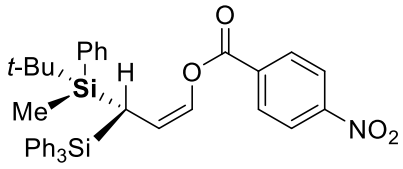
Preparation of 4c



4c

4c: 65% yield, white solid, m.p. 49°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 3H), 0.85 (s, 9H), 3.38 (d, 1H, *J* = 13.2 Hz) (major), 3.07 (d, 1H, *J* = 13.2 Hz) (minor), 5.34 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.19 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 7.07 (t, 2H, *J* = 7.6 Hz), 7.12-7.18 (m, 7H), 7.20-7.28 (m, 6H),7.38 (d, 6H, *J* = 7.6 Hz), 7.70 (d, 2H, *J* = 7.6 Hz), 7.99 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, 11.9, 19.4, 27.3, 113.9, 127.2, 127.4, 128.4, 128.5, 128.7, 129.1, 131.2, 132.1, 132.3, 134.3, 134.6, 135.9, 136.6, 162.5.; IR (neat) cm^{-1} 3068, 2925, 2854, 1732, 1590, 1480, 1395, 1260, 1175, 818, 782; HRMS (MALDI, m/z) calcd for $C_{39}H_{39}O_2Si_2BrNa$ $(M+Na)^+$: 697.1564, found 697.1562.

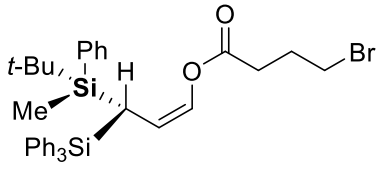
Preparation of 4d



4d

4d: 60% yield, white solid, m.p. 151°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.174 (s, 3H), 0.87 (s, 9H), 3.36 (d, 1H, *J* = 13.2 Hz) (major), 3.03 (d, 1H, *J* = 13.2 Hz) (minor), 5.45 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.28 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 7.07-7.16 (m, 8H), 7.19 (d, 1H, *J* = 6.0 Hz) 7.23-7.28 (m, 6H), 7.38 (d, 6H, *J* = 7.6 Hz), 8.24 (d, 2H, *J* = 8.8 Hz), 8.40 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.0, 12.4, 19.4, 27.3, 115.0, 123.8, 127.2, 127.4, 128.7, 129.2, 130.8, 132.2, 134.2, 134.6, 134.9, 135.9, 136.6, 150.7, 161.3; IR (neat) cm^{-1} 3051, 2956, 2925, 2852, 1733, 1526, 1425, 1351, 1264, 1046, 819; HRMS (MALDI, m/z) calcd for $C_{39}H_{39}NO_4Si_2Na$ $(M+Na)^+$: 664.2310, found 664.2316.

Preparation of 4e

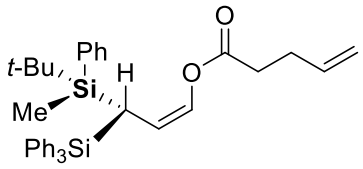


4e

4e: 67% yield, white viscous liquid;; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 3H), 0.84 (s, 9H), 2.23 (tt, 2H, J_1 = 6.8 Hz, J_2 = 6.8 Hz), 2.65 (t, 2H, *J* = 6.8 Hz), 3.25 (d, 1H, *J* = 12.8 Hz), 3.50 (t, 2H, *J* = 6.8 Hz), 5.20 (dd, 1H, J_1 = 12.8 Hz, J_2 = 6.0 Hz) (major), 5.13 (dd, 1H, J_1 = 12.8 Hz, J_2 = 6.0 Hz)

(minor), 7.00 (d, 1H, *J* = 6.0 Hz), 7.06 (t, 2H, *J* = 7.6 Hz), 7.18 (t, 9H, *J* = 7.6 Hz), 7.25-7.31 (m, 3H), 7.37 (d, 6H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.2, 11.3, 19.4, 27.3, 27.6, 32.3, 32.5, 112.9, 127.1, 127.4, 128.5, 129.1, 132.1, 134.5, 134.7, 136.0, 136.5, 169.1; IR (neat) cm^{-1} 3069, 3048, 2958, 2929, 2856, 1750, 1466, 1427, 1255, 1216, 1107, 818, 781; HRMS (MALDI, m/z) calcd for $C_{36}H_{41}O_2Si_2Na$ $(M+Na)^+$: 663.1721, found 663.1727.

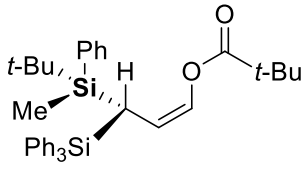
Preparation of 4f



4f

4f: 50% yield, white viscous liquid;; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.83 (s, 9H), 2.44-2.49 (m, 2H), 2.55-2.59 (m, 2H), 3.26 (d, 1H, *J* = 13.2 Hz) (major), 2.96 (d, 1H, *J* = 13.2 Hz) (minor), 5.08 (d, 1H, *J* = 10.0 Hz), 5.12-5.19 (m, 2H), 5.89 (ddt, 1H, J_1 = 16.8 Hz, J_2 = 10.0 Hz, J_3 = 6.0 Hz), 7.01 (d, 1H, *J* = 6.0 Hz), 7.05 (t, 2H, *J* = 7.2 Hz), 7.16-7.20 (m, 9H), 7.25-7.31 (m, 3H), 7.37 (d, 6H, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.3, 11.1, 19.4, 27.3, 28.7, 33.5, 112.6, 115.8, 127.0, 127.3, 128.4, 129.0, 132.2, 134.6, 134.7, 136.0, 136.4, 136.5, 169.5; IR (neat) cm^{-1} 3070, 3048, 2958, 2928, 2856, 1752, 1427, 1234, 1151, 1106, 818, 782; HRMS (MALDI, m/z) calcd for $C_{37}H_{42}O_2Si_2Na$ $(M+Na)^+$: 597.2616, found 597.2612.

Preparation of 4g

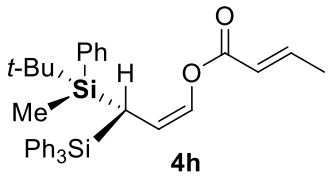


4g

4g: 66% yield, white viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.84 (s, 9H), 1.33 (s, 9H), 3.28 (d, 1H, *J* = 13.2 Hz) (major), 2.97 (d, 1H, *J* = 13.2 Hz) (minor), 5.17 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.05 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 7.00-7.06 (m, 3H), 7.15-7.19 (m, 8H), 7.21-7.24 (m, 1H), 7.29 (t, 3H, *J* = 7.2 Hz) 7.36 (d, 6H, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, 11.0, 19.4, 27.2, 38.9, 112.6, 127.0, 127.3, 127.4,128.4, 129.0, 132.4,

134.6, 134.7, 135.9, 136.5, 174.9; IR (neat) cm^{-1} 3069, 3049, 2929, 1743, 1477, 1427, 1393, 1367, 1276, 1133, 1053, 817; HRMS (MALDI, m/z) calcd for $C_{37}H_{44}O_2Si_2Na$ $(M+Na)^+$: 599.2772, found 599.2772.

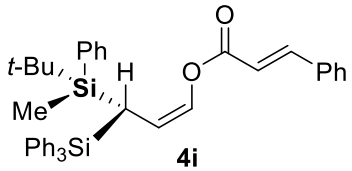
Preparation of 4h



4h

4h: 50% yield, white viscous liquid;; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.83 (s, 9H), 2.02 (d, 3H, *J* = 6.8 Hz), 3.32 (d, 1H, *J* = 13.2 Hz) (major), 3.03(d, 1H, *J* = 13.2 Hz) (minor), 5.16 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.04 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 6.04 (d, 1H, *J* = 15.6 Hz) (major), 5.89 (d, 1H, *J* = 15.6 Hz) (minor), 7.04-7.07 (m, 3H), 7.15-7.21 (m, 10H), 7.28 (t, 3H, *J* = 7.2 Hz), 7.38 (d, 6H, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.3, 11.0, 18.4, 19.3, 27.3, 112.8, 121.9, 127.0, 127.3, 128.4, 129.0, 132.2, 134.6, 134.7, 136.0, 136.6, 146.3, 162.9; IR (neat) cm^{-1} 3048, 3018, 2929, 2856, 1733, 1648, 1466, 1429, 1104, 819, 782; HRMS (MALDI, m/z) calcd for $C_{36}H_{40}O_2Si_2Na$ $(M+Na)^+$: 583.2459, found 583.2461.

Preparation of 4i

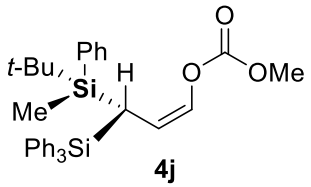


4i

4i: 55% yield, white solid, m.p. 165°C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H), 0.86 (s, 9H), 3.38 (d, 1H, *J* = 13.2 Hz) (major), 3.08 (d, 1H, *J* = 13.2 Hz) (minor), 5.23 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.4 Hz) (major), 5.10 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.4 Hz) (minor), 6.58 (d, 1H, *J* = 16.0 Hz) (major), 6.43 (d, 1H, *J* = 16.0 Hz) (minor), 7.06 (t, 2H, *J* = 7.6 Hz), 7.12 (d, 1H, *J* = 6.4 Hz), 7.18 (t, 6H, *J* = 7.6 Hz), 7.23-7.29 (m, 6H), 7.40 (d, 6H, *J* = 7.6 Hz), 7.47-7.48 (m, 3H), 7.63-7.65 (m, 2H), 7.84 (d, 1H, *J* = 16.0 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.3, 11.3, 19.4, 27.3, 113.1, 117.1, 127.1, 127.4, 128.3, 128.5, 129.0, 129.1, 130.7, 132.3, 134.3, 134.6, 134.7, 136.0, 136.6, 146.1, 163.5; IR (neat) cm^{-1} 3048, 2927, 2853, 1734, 1634, 1425, 1149, 1105, 815; HRMS (MALDI, m/z) calcd for

$C_{41}H_{42}O_2Si_2Na$ $(M+Na)^+$: 645.2616, found 645.2617.

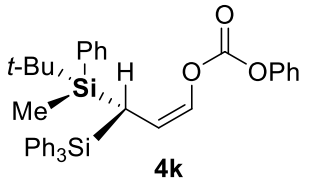
Preparation of 4j



4j

4j: 70% yield, white viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.83 (s, 9H), 3.26 (d, 1H, *J* = 13.2 Hz) (major), 2.98 (d, 1H, *J* = 13.2 Hz) (minor), 3.88 (s, 3H) (major), 3.78 (s, 3H) (minor), 5.14 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.01 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor) , 6.74 (d, 1H, *J* = 6.0 Hz) (major), 6.67 (d, 1H, *J* = 6.0 Hz) (minor), 7.02 (t, 2H, *J* = 7.6 Hz), 7.17 (t, 9H, *J* = 7.6 Hz), 7.25-7.30 (m, 3H), 7.39 (d, 6H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.4, 10.6, 19.3, 27.3, 55.1, 112.9, 127.0, 127.3, 128.4, 128.9, 133.6, 134.4, 134.8, 136.1, 136.2, 153.3; IR (neat) cm^{-1} 3069, 3048, 2960, 2928, 2855, 1762, 1464, 1432, 1260, 1105, 1029, 948, 792; HRMS (MALDI, m/z) calcd for $C_{34}H_{38}O_3Si_2Na$ $(M+Na)^+$: 573.2252, found 573.2249.

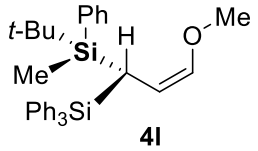
Preparation of 4k



4k

4k:70% yield, white solid, m.p. 68°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.85 (s, 9H), 3.25 (d, 1H, *J* = 13.2 Hz) (major), 2.92 (d, 1H, *J* = 13.2 Hz) (minor), 5.24 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.10 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 6.83 (d, 1H, *J* = 6.0 Hz), 7.03 (t, 2H, *J* = 7.6 Hz), 7.16-7.21 (m, 8H), 7.25-7.29 (m, 5H), 7.39-7.46 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.4, 10.9, 19.4, 27.3, 113.9, 120.9, 121.0, 126.3, 127.0, 127.4, 128.5, 129.1, 129.5, 129.6, 133.5, 134.3, 134.8, 136.1, 150.9; IR (neat) cm^{-1} 3065, 2916, 2926, 1773, 1489, 1426, 1258, 1104, 1074 872, 797; HRMS (MALDI, m/z) calcd for $C_{39}H_{40}O_3Si_2Na$ $(M+Na)^+$: 635.2408, found 635.2414.

Preparation of 4l

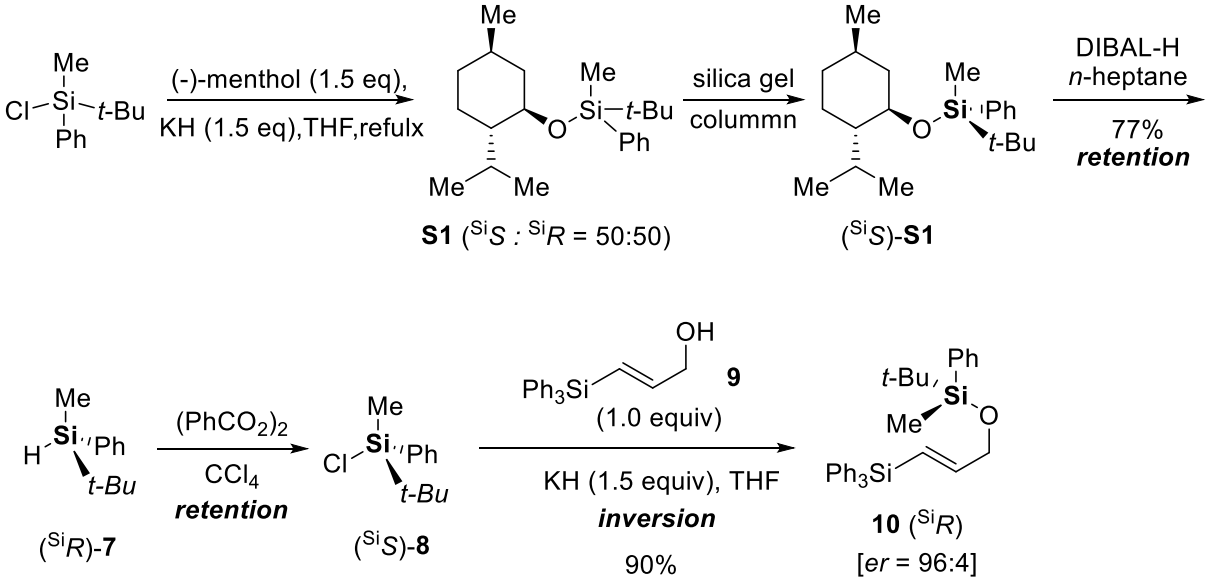


4l

4l: 40% yield, white viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.83 (s, 9H), 3.26 (d, 1H, *J* = 13.2 Hz) (major), 2.97 (d, 1H, *J* = 13.2 Hz) (minor)，3.88 (s, 3H) (major), 3.79 (s, 3H) (minor), 5.14 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (major), 5.01 (dd, 1H, J_1 = 13.2 Hz, J_2 = 6.0 Hz) (minor), 6.74 (d, 1H, *J* = 6.0 Hz) (major), 6.67 (d, 1H, *J* = 6.0 Hz) (minor), 7.02 (t, 2H, *J* = 7.2 Hz), 7.17 (t, 8H, *J* = 7.2 Hz), 7.22-7.29 (m, 4H), 7.39 (d, 6H, *J* = 7.6 Hz),; ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.4, 8.7, 19.3, 27.4, 59.0, 104.8, 126.8, 127.2, 128.1, 128.7, 134.8, 135.4, 136.0, 136.9, 144.1; IR (neat) cm^{-1} 3068, 2925, 2852, 1426, 1262, 1104, 819, 781; HRMS (MALDI, m/z) calcd for $C_{33}H_{38}OSi_2Na$ $(M+Na)^+$: 529.2353, found 529.2349.

2.5. Preparation of Enantiomerically Defined 10 and Its Retro-[1,4]-Brook Rearrangement to Form 11.

Preparation of 10



To a suspension of KH (1.13 g, 8.5 mmol, 30 % w/w) in THF (4.0 mL) was added (-)-menthol (1.32 g, 8.5 mmol) in THF (6.0 mL) at 0 °C under argon atmosphere. After refluxed for 3 h, a solution of *t*-BuPhMeSiCl (1.2 g, 5.66 mmol) in THF (3.0 mL) was added at room temperature. Heating at reflux for 20 h, the mixture was quenched with careful addition of H_2O followed by neutralization (pH = 7) with aq. 10% HCl. The organic layer was separated and the aqueous phase was extracted

with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with cyclohexane as eluent, affording a mixture of (^{Si}R)-**S1** and (^{Si}S)-**S1** (1.01g, 60%, *dr* = 50:50) as a colorless oil. After repeated flash chromatography, (^{Si}S)-**S1** and (^{Si}R)-**S1** were separated as colorless oil.

To a solution of (^{Si}S)-**S1** (620 mg, 1.86 mmol) in dry *n*-heptane (9.0 mL) was added DIBAL-H (5.0 mL, 7.47 mmol, 1M solution in hexane) slowly at 0 °C under argon atmosphere. The mixture was heated at reflux for 5 h before quenching at 0 °C with careful addition of H_2O followed by neutralization (pH = 7) with aq. 10% HCl. The mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: petroleum ether) afforded colorless oil (^{Si}R)-**7**[3] (308 mg, 93% yield). HPLC (Phenomenex Lux® 5μm Cellulose-3 column, solvent *n*-heptane, flow rate 0.7ml/min): t_R=5.083 min for (^{Si}R)-**7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.34 (d, 3H, *J* = 3.6 Hz), 0.95 (s, 9H,), 4.14 (q, 1H, *J* = 3.6 Hz), 7.34-7.39 (m, 3H), 7.52-7.55 (m, 2H). $[\alpha]_D^{25}$ -2.4 (c = 1.0, $CHCl_3$).

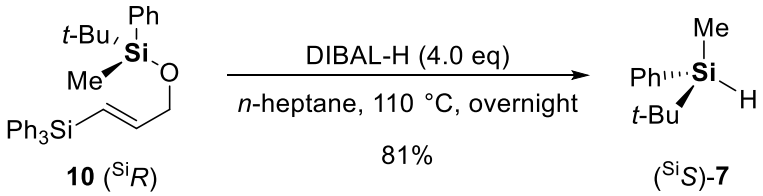
To a solution of (^{Si}R)-**7** (360 mg, 2.02 mmol) in CCl_4 (14.0 mL) was added benzoyl peroxide (50 mg, 0.2 mmol). The mixture was refluxed for 21 h followed by stirring for 3.5 h at room temperature.[4] The solvent of the mixture was removed under reduced pressure. The crude product (^{Si}S)-**8** was used without purification in next step.

To a suspension of KH (270 mg, 2.02 mmol, 30 % w/w)) in THF (1.0 mL) under argon atmosphere was added **9** (420 mg, 1.35 mmol in 1.0 mL THF) slowly at 0 °C. The mixture was stirred for 10 min before adding a solution of (^{Si}S)-**8** in 1.2 mL THF at -78 °C. The reaction was maintained at -78 °C for 12 h, and then quenched at 0 °C by careful addition of H_2O followed by neutralization (pH = 7) with aq. 10% HCl. The mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 1-2% of EtOAc/petroleum ether) afforded white solid (^{Si}R)-**10** (600 mg, 90% yield, *er* = 96:4, m.p 44 °C), HPLC (Chiralpak OD column, *n*-hexane, 1.5 mL/min, UV 220 nm, t_{major} = 8.621 min, t_{minor} =

3. V. T. Trepohl, R. Fröhlich, M. Oestreich, *Tetrahedron* **2009**, *65*, 6510-6518.
4. K. Igawa, N. Kokan, K. Tomooka, *Angew. Chem*. **2010**, *122*, 740; *Angew. Chem. Int. Ed.* **2010**, *49*, 728-731.

13.227 min), $[\alpha]_D^{20}$ = +6.78 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 3H), 0.97 (s, 9H), 4.29-4.38 (m, 2H), 6.25 (dt, 1H, J_1 = 18.4 Hz, J_2 = 3.2 Hz), 6.65 (d, 1H, *J* = 18.4 Hz), 7.37-7.43 (m, 12H), 7.55 (d, 6H, *J* = 6.8 Hz), 7.58 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ -7.1, 18.4, 25.9, 65.4, 121.4, 127.6, 127.8, 129.4, 129.5, 134.4, 134.7, 135.6, 135.9, 150.8.

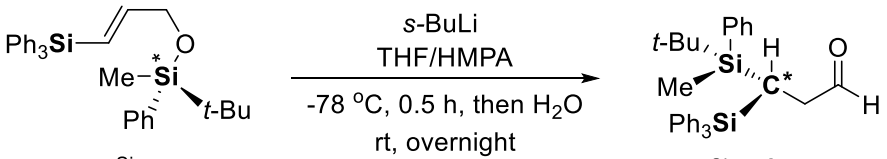
Reduction of (^{Si}R)-10 to (^{Si}S)-7



10 (^{Si}*R*) (^{Si}*S*)-**7**

To a solution of (^{Si}*R*)-**10** (0.16 mmol, 80 mg) in dry *n*-heptane (0.9 mL) under argon atmosphere was added DIBAL-H (1.80 mmol, 1.8 ml, 1.0 M solution in hexane) dropwise at 0 °C. Then the reaction mixture was subsequently heated to 110 °C and refluxed overnight. Finally, the reaction was cooled down to room temperature and quenched with H_2O followed by neutralization with aq. 10% HCl. The organic layer was separated and the aqueous layer was extracted with Et_2O for three times, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product via silica gel flash column chromatography (gradient eluent: cyclohexanes) afforded (^{Si}*S*)-**7** (22 mg, 81%, *er* = 93:7) as a colorless oil. HPLC (Phenomenex Lux® 5μm Cellulose-3 column, solvent *n*-heptane, flow rate 0.7ml/min): t_R=5.019 min for (^{Si}*R*)-**7** (minor enantiomer), t_R=5.164 min for (^{Si}*S*)-**7** (major enantiomer). $[\alpha]_D^{25}$ 1.4 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.34 (d, 3H, *J* = 3.6 Hz), 0.95 (s, 9H,), 4.14 (q, 1H, *J* = 3.6 Hz), 7.34-7.39 (m, 3H), 7.52-7.55 (m, 2H).

Preparation of 11



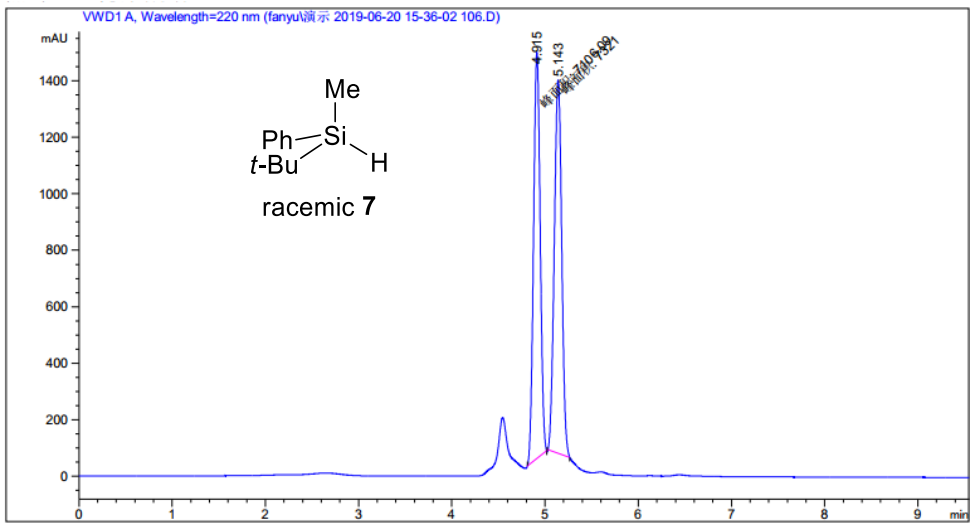
(^{Si}*R*)-**10**
90%, *er* = 96:4

(^{Si}*R*, ^{C}*S*)-**11**
60%, *dr* = 90:10; *er* = 96:4

To a solution (^{Si}*R*)-**10** (150 mg, 0.3 mmol) in anhyd THF (1.0 mL) and anhyd HMPA (0.2 mL, 1.20 mmol) under argon atmosphere was added *s*-BuLi (1.2 mL of 1.0 M solution in pentane,1.2

mmol) at -78 °C. After stirring for 30 min, the reaction was quenched with H_2O and was warmed to room temperature with stirring overnight. The combined organic layers were diluted with Et_2O (5.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 1-5% of EtOAc/petroleum ether) afforded pure white solid (^{Si}R, ^{C}S)-**11** (90 mg, 60% yield, *er* = 96:4, m.p. 116 °C), HPLC (Chiralpak OD column, 0.5% 2-propamol/*n*-hexane, 1.0 mL/min, UV 220 nm, t_{minor} = 8.671 min, t_{major} = 11.425 min), $[\alpha]_D^{20}$ = -12.75 (*c* = 1.0 in $CHCl_3$), the crystal of the product (^{Si}R, ^{C}S)-**11** was obtained from *n*-hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 3H), 0.86 (s, 9H), 2.54 (t, 1H, *J* = 4.8 Hz), 3.06 (dd, 1H, J_1 = 20.0 Hz, J_2 = 4.8 Hz), 3.17 (dd, 1H, J_1 = 20.0 Hz, J_2 = 4.8 Hz), 6.97 (t, 2H, *J* = 7.2 Hz), 7.14 (t, 3H, *J* = 7.2 Hz), 7.21-7.26 (m, 6H), 7.32 (t, 3H, *J* = 7.2 Hz), 7.40 (d, 6H, *J* = 7.2 hz), 9.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -7.1, -2.1, 19.2, 27.7, 42.6, 126.8, 127.5, 128.4, 129.1, 134.6, 134.9, 135.9, 200.8.

3. HPLC copies



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面积百分比报告

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排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=220 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
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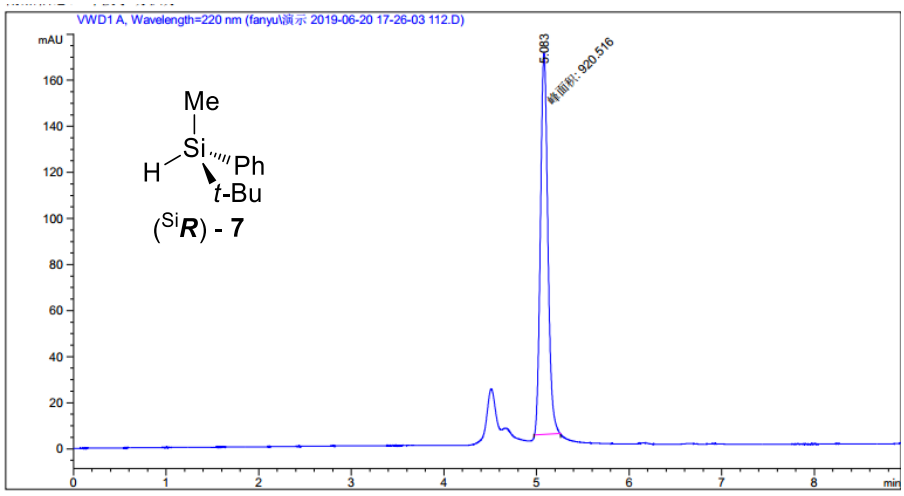
2	5.143	MM	0.0923	7321.00391	1322.43921	50.7448



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面积百分比报告

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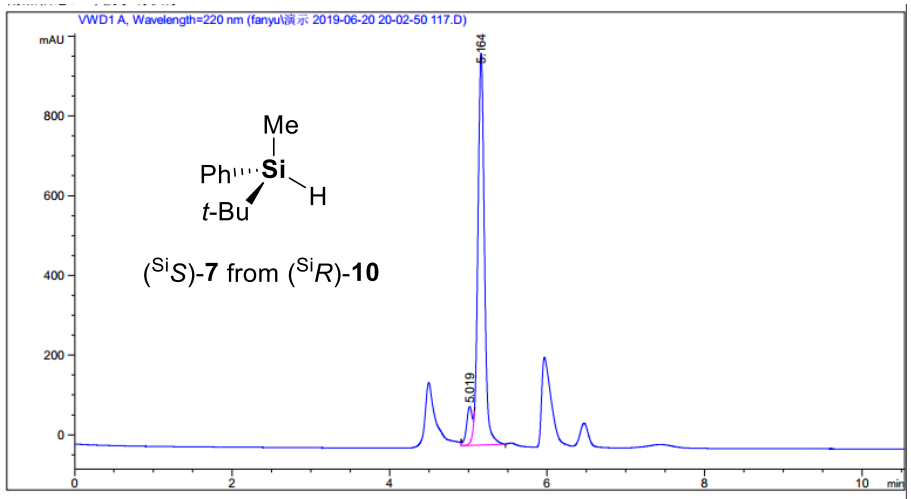
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=220 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.083	MM	0.0926	920.51563	165.59372	100.0000



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面积百分比报告

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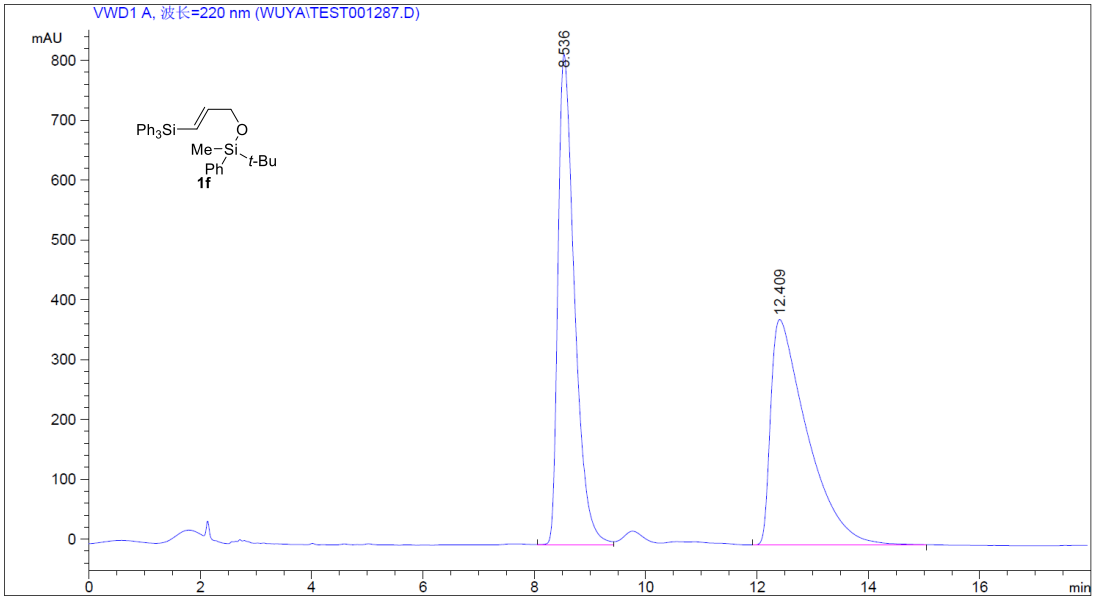
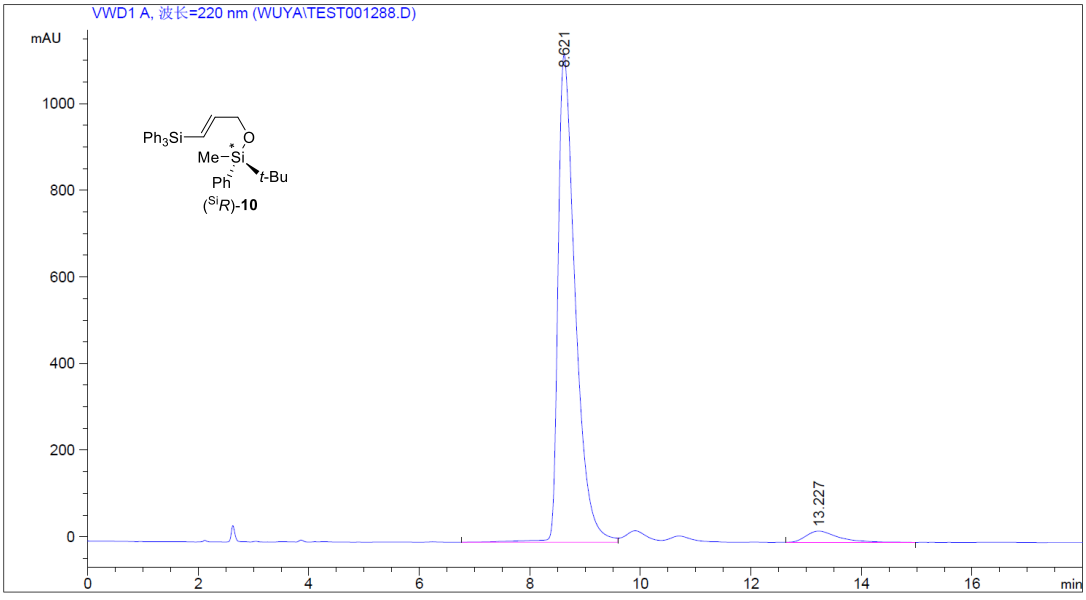
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, Wavelength=220 nm

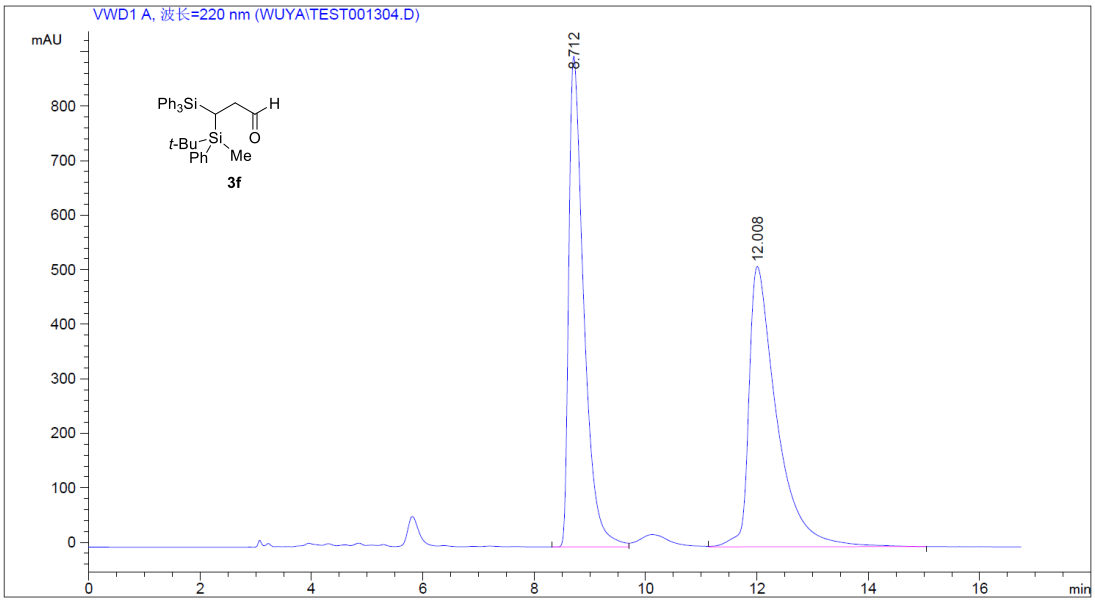
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.019	VV E	0.0731	435.45178	91.31609	7.0784
2	5.164	VB R	0.0893	5716.34570	983.28766	92.9216



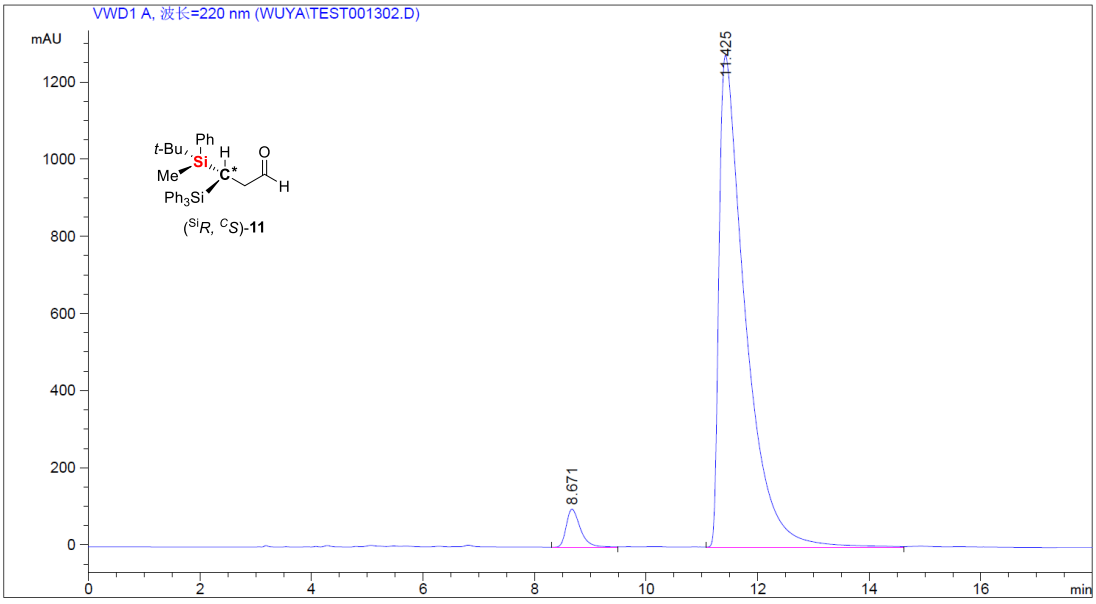
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.536	VV	0.3144	1.69726e4	819.49805	49.8143
2	12.409	VB	0.6590	1.70991e4	376.79620	50.1857



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.621	VV	0.3259	2.44341e4	1126.23804	95.7299
2	13.227	VV	0.6118	1089.89514	26.20897	4.2701



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.712	VV	0.2803	1.69041e4	900.02802	48.6755
2	12.008	VB	0.5051	1.78241e4	513.94238	51.3245



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.671	VV	0.2675	1734.27197	98.74428	4.0155
2	11.425	VV	0.4667	4.14548e4	1274.91125	95.9845

4. Computational Details

All calculations were performed using Gaussian 09 program package[1]. Geometries were fully optimized at the B3LYP-D3(BJ)/6-311G(d,p)[2,3] level in THF solvent and characterized by frequency analysis. The self-consistent reaction field (SCRF) method with SMD[4, 5] solvation model was used to evaluate solvent effect on reaction. The transition states were checked by intrinsic reaction coordinate (IRC) calculations.[6] The Gibbs free energies (G_{195K}) corrected by both solvent and zero-point vibrational effect were used in the discussions.

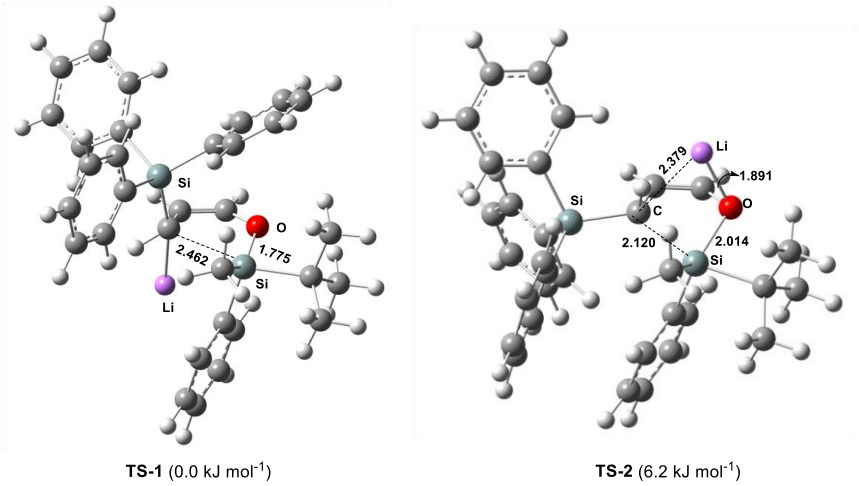


Figure 1. Optimized geometries of transition states TS-1 and TS-2 and their energy difference calculated at the B3LYP-D3(BJ)(SMD, THF)/6-311G(d,p) level.

References:

[1] Gaussian 09 (Revision E.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J.E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[2] A. D. Becke J. Chem. Phys. 1993, 98, 5648-5652.

[3] S. Grimme, J. Antony, S. Ehrlich, H. Krieg J. Chem. Phys. 2010, 132, 154104-154119.

[4] A. V. Marenich, C. J. Cramer, D. G. Truhlar J. Phys. Chem. B 2009, 113, 6378-6396.

[5] V. S. Bernales, A. V. Marenich, R. Contreras, C. J. Cramer, D. G. Truhlar J. Phys. Chem. B 2012, 116, 9122-9129.

[6] C. Gonzalez, H. B. Schlegel J. Chem. Phys. 1989, 90, 2154-2161.

Cartesian coordinates of all stationary points

TS-1

Zero-point correction= 0.57791 a.u.
Thermal correction to Gibbs Free Energy= 0.54226 a.u.
Sum of electronic and zero-point Energies= -1902.29890 a.u.
Sum of electronic and thermal Free Energies= -1902.33455 a.u.
The number of imaginary frequencies 1

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	1.513006	0.209771	-0.038878
2	6	0	1.426705	-1.606801	0.484105
3	6	0	2.082815	1.277170	1.417543
4	6	0	2.940352	0.334862	-1.292088
5	6	0	1.307637	-2.607795	-0.494503
6	6	0	1.204601	-3.952569	-0.148289
7	6	0	1.227831	-4.332391	1.192922
8	6	0	1.354796	-3.358413	2.180243
9	6	0	1.451936	-2.013583	1.825882
10	6	0	3.220710	0.906147	2.152529
11	6	0	3.715923	1.708219	3.178067
12	6	0	3.086591	2.913829	3.486022
13	6	0	1.472507	2.497437	1.739328
14	6	0	1.965085	3.309308	2.760469
15	6	0	3.053559	1.486688	-2.087561
16	6	0	4.104219	1.651034	-2.986634
17	6	0	3.931168	-0.647545	-1.430677
18	6	0	4.986634	-0.492010	-2.330074
19	6	0	5.075348	0.657338	-3.111813
20	1	0	1.294444	-2.334005	-1.543011

21	1	0	1.105930	-4.704122	-0.924182
22	1	0	1.147779	-5.378983	1.465335
23	1	0	1.374982	-3.643901	3.226443
24	1	0	1.547553	-1.272757	2.611504
25	1	0	3.732021	-0.022292	1.919894
26	1	0	4.593659	1.396001	3.733590
27	1	0	3.470670	3.541538	4.282501
28	1	0	0.597745	2.825849	1.189343
29	1	0	1.472952	4.248302	2.990254
30	1	0	2.306033	2.270364	-2.003558
31	1	0	4.167079	2.550540	-3.589970
32	1	0	3.879955	-1.551100	-0.833437
33	1	0	5.738558	-1.268893	-2.420258
34	1	0	5.893846	0.779498	-3.812700
35	14	0	-2.046735	-0.283617	0.173939
36	6	0	-3.220415	1.068398	-0.486995
37	6	0	-1.342590	0.280080	1.845625
38	6	0	-3.835482	0.946882	-1.750433
39	6	0	-4.675999	1.944719	-2.253523
40	6	0	-4.932161	3.085951	-1.498293
41	6	0	-4.343339	3.226492	-0.240191
42	6	0	-3.496121	2.236569	0.253063
43	1	0	-2.102296	0.260640	2.630739
44	1	0	-0.941192	1.289042	1.775220
45	1	0	-3.663106	0.055892	-2.343429
46	1	0	-5.133703	1.822769	-3.228947
47	1	0	-5.587463	3.859208	-1.882542
48	1	0	-4.547135	4.108958	0.356441
49	1	0	-3.044353	2.370014	1.229511
50	1	0	-0.531091	-0.371122	2.170114
51	6	0	-0.072998	0.819275	-0.799912
52	6	0	-0.171265	0.251738	-2.187339
53	6	0	-0.954666	-0.842149	-2.281120
54	8	0	-1.637681	-1.299582	-1.222624
55	1	0	0.418389	0.561562	-3.047356

56	1	0	-1.077628	-1.434214	-3.184307
57	3	0	-1.602629	1.820760	-1.786398
58	1	0	0.015504	1.923350	-0.773899
59	6	0	-3.275075	-1.695462	0.798935
60	6	0	-4.221439	-1.180552	1.899401
61	6	0	-2.425941	-2.846770	1.370101
62	6	0	-4.163632	-2.253733	-0.326406
63	1	0	-4.958846	-1.954175	2.154273
64	1	0	-4.780242	-0.295345	1.576540
65	1	0	-3.697703	-0.926045	2.823124
66	1	0	-1.749690	-3.258221	0.616207
67	1	0	-1.815368	-2.521992	2.217592
68	1	0	-3.066438	-3.666937	1.726074
69	1	0	-3.570970	-2.667269	-1.142700
70	1	0	-4.818188	-1.481142	-0.742474
71	1	0	-4.813538	-3.050608	0.063442

TS-2

Zero-point correction= 0.57809 a.u.

Thermal correction to Gibbs Free Energy= 0.54252 a.u.

Sum of electronic and zero-point Energies= -1902.29660 a.u.

Sum of electronic and thermal Free Energies= -1902.33217 a.u.

The number of imaginary frequencies 1

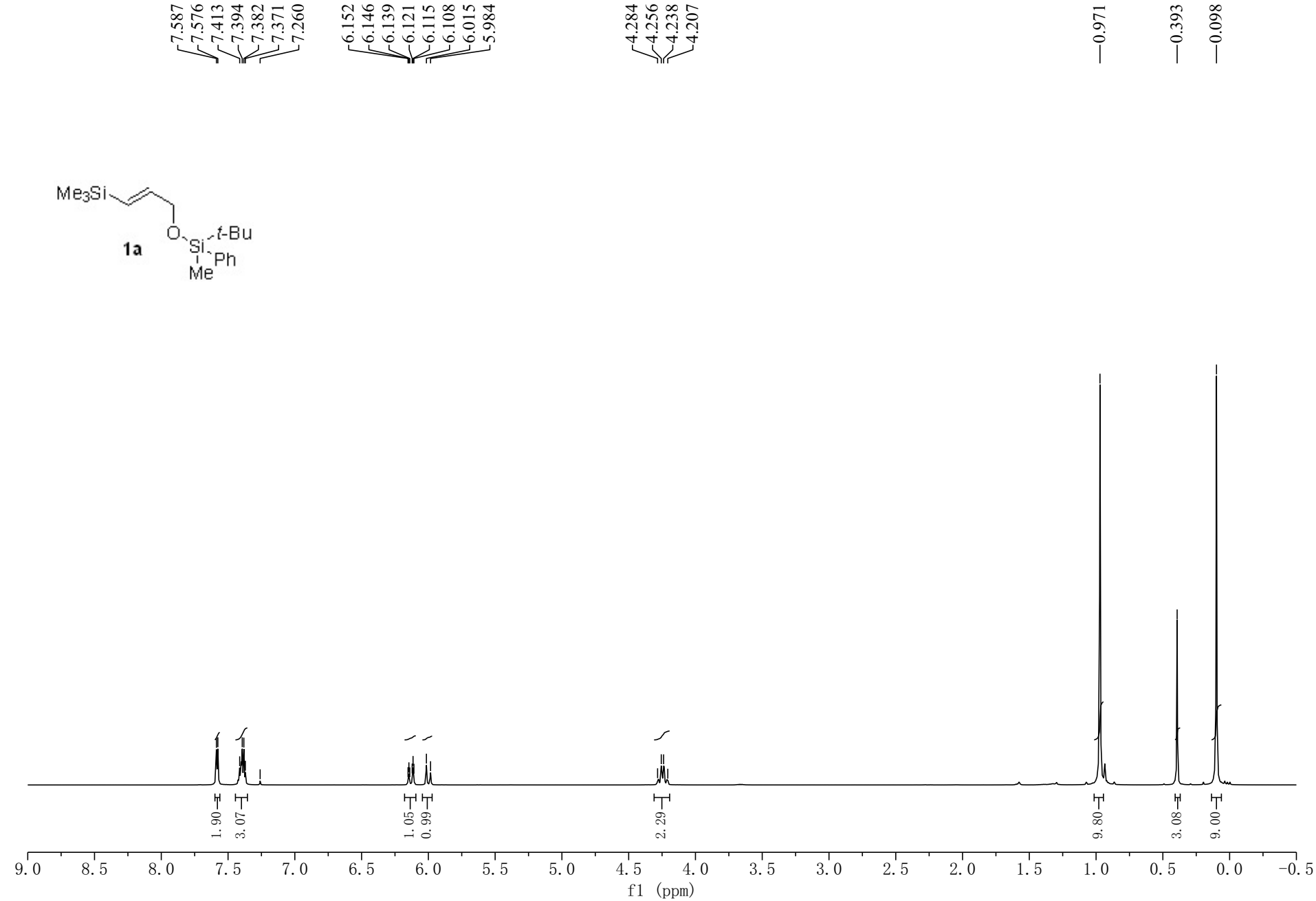
Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.795872	2.099449	-4.261161
2	6	0	-2.272167	2.356924	-4.395897
3	6	0	-2.656946	2.621289	-5.660703
4	8	0	-1.662069	2.771407	-6.568169
5	1	0	-2.999017	2.197220	-3.608608
6	1	0	-3.678220	2.724672	-6.016202
7	3	0	-1.260478	4.162171	-5.351718

8	1	0	-0.207834	3.037157	-4.154135
9	14	0	-0.139346	1.508729	-6.188474
10	6	0	0.130256	1.656378	-8.163517
11	14	0	-0.424185	1.297316	-2.591304
12	6	0	1.218639	0.375212	-2.460779
13	6	0	-1.823054	0.133411	-2.078688
14	6	0	-0.351180	2.673944	-1.285729
15	6	0	2.420046	1.090677	-2.323401
16	6	0	3.647241	0.438314	-2.243449
17	6	0	3.700045	-0.954290	-2.297421
18	6	0	2.519943	-1.684116	-2.418774
19	6	0	1.294043	-1.024043	-2.494192
20	6	0	-2.537972	0.341574	-0.888995
21	6	0	-3.574505	-0.510734	-0.509347
22	6	0	-3.918906	-1.593708	-1.315232
23	6	0	-2.188106	-0.962926	-2.876331
24	6	0	-3.221749	-1.817746	-2.501684
25	6	0	-0.993098	3.907254	-1.476204
26	6	0	-0.981481	4.893771	-0.490723
27	6	0	0.302339	2.466329	-0.059801
28	6	0	0.319515	3.447144	0.929587
29	6	0	-0.322677	4.665965	0.715637
30	1	0	2.399561	2.174527	-2.279810
31	1	0	4.560907	1.013570	-2.140813
32	1	0	4.654235	-1.466052	-2.237663
33	1	0	2.551587	-2.767724	-2.452837
34	1	0	0.389162	-1.611862	-2.584351
35	1	0	-2.286796	1.179818	-0.249185
36	1	0	-4.112491	-0.328024	0.414712
37	1	0	-4.725157	-2.257253	-1.022229
38	1	0	-1.667088	-1.150618	-3.803866
39	1	0	-3.482540	-2.655797	-3.138618
40	1	0	-1.522698	4.103174	-2.402751
41	1	0	-1.487255	5.837841	-0.663179
42	1	0	0.809467	1.525526	0.124940

43	1	0	0.833887	3.261373	1.866270
44	1	0	-0.310135	5.431386	1.483659
45	6	0	1.676653	1.822639	-5.658636
46	1	0	1.780907	2.849062	-5.287389
47	1	0	1.938886	1.168201	-4.826880
48	1	0	2.420177	1.686116	-6.443719
49	6	0	-0.661109	-0.312577	-6.073709
50	6	0	0.255909	-1.303788	-5.691826
51	6	0	-1.969589	-0.726006	-6.375402
52	6	0	-0.115181	-2.644983	-5.601865
53	1	0	1.276604	-1.029363	-5.452032
54	6	0	-2.348033	-2.065208	-6.290430
55	1	0	-2.711417	0.005225	-6.674459
56	6	0	-1.421147	-3.030812	-5.900112
57	1	0	0.614653	-3.387161	-5.295787
58	1	0	-3.367627	-2.354353	-6.522320
59	1	0	-1.713652	-4.072666	-5.829347
60	6	0	-1.133616	1.375191	-8.994376
61	1	0	-0.904216	1.444774	-10.068122
62	1	0	-1.515639	0.366169	-8.814716
63	1	0	-1.930590	2.083336	-8.769364
64	6	0	0.630993	3.070109	-8.509873
65	1	0	0.841309	3.158821	-9.585858
66	1	0	-0.119113	3.827356	-8.262951
67	1	0	1.555797	3.323467	-7.981470
68	6	0	1.185235	0.631696	-8.624573
69	1	0	0.862289	-0.394520	-8.426467
70	1	0	1.342552	0.718652	-9.709062
71	1	0	2.159115	0.768126	-8.150480

WY-5-45-2A H1 CDCl3 600M Hz



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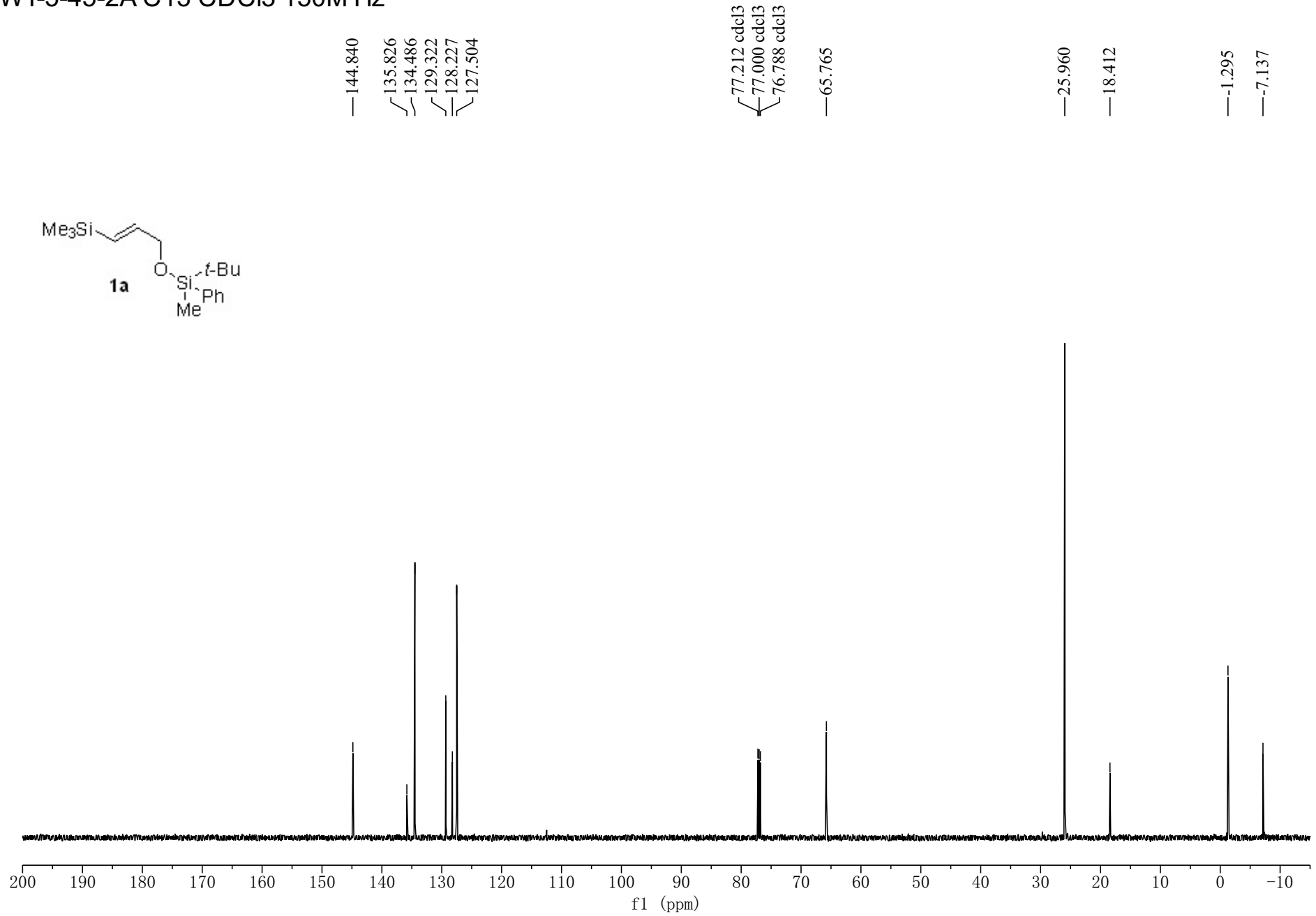

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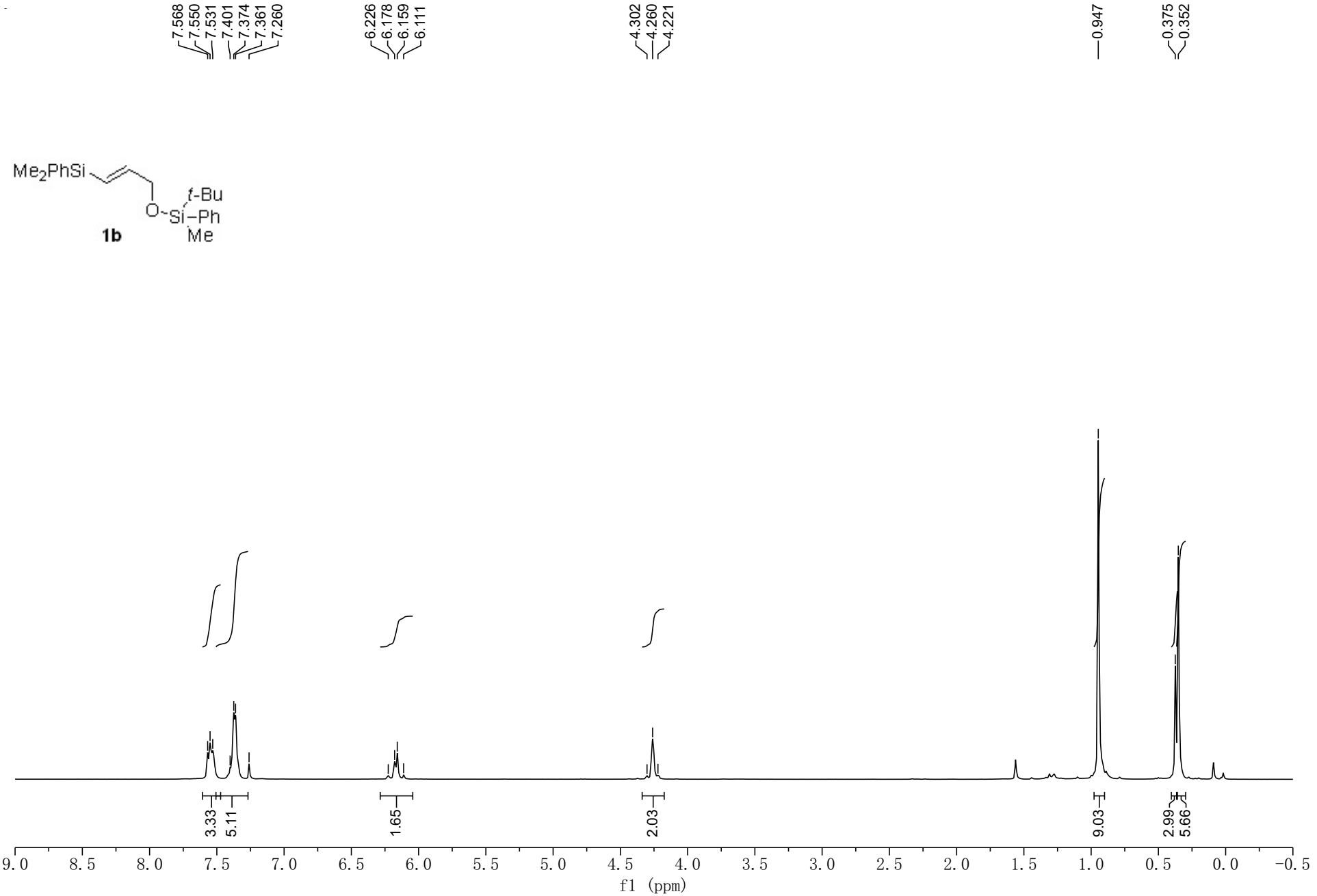

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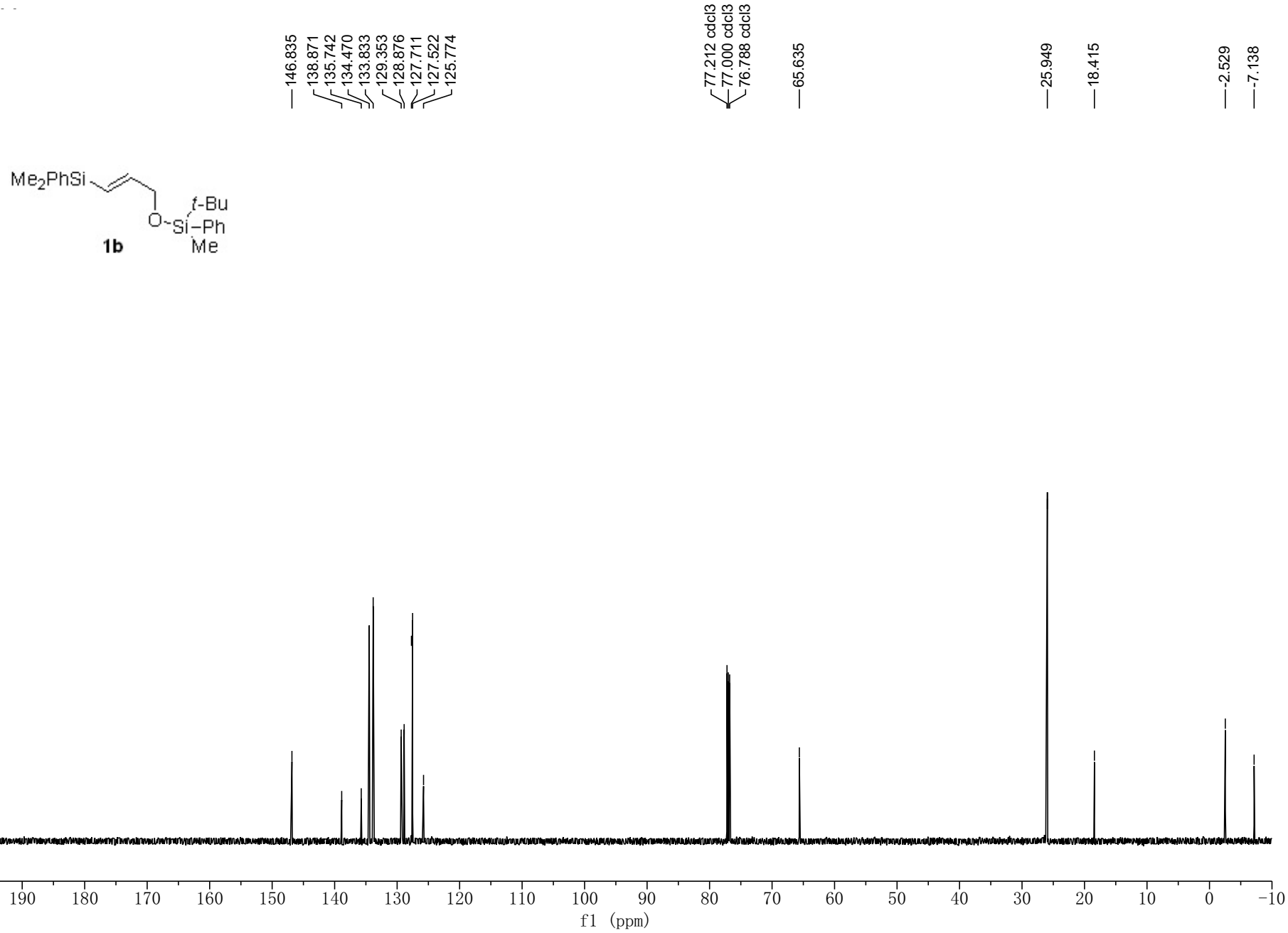

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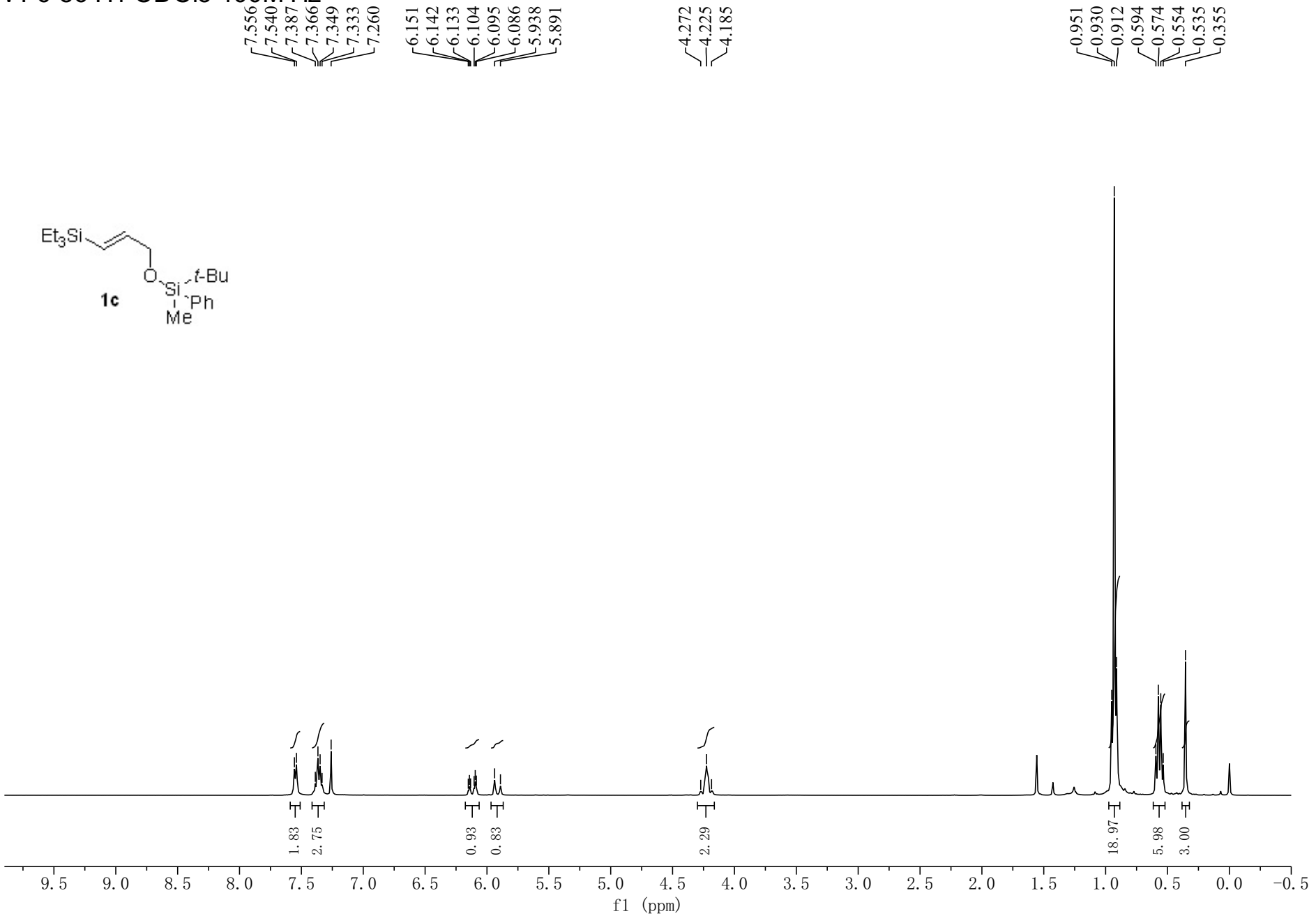
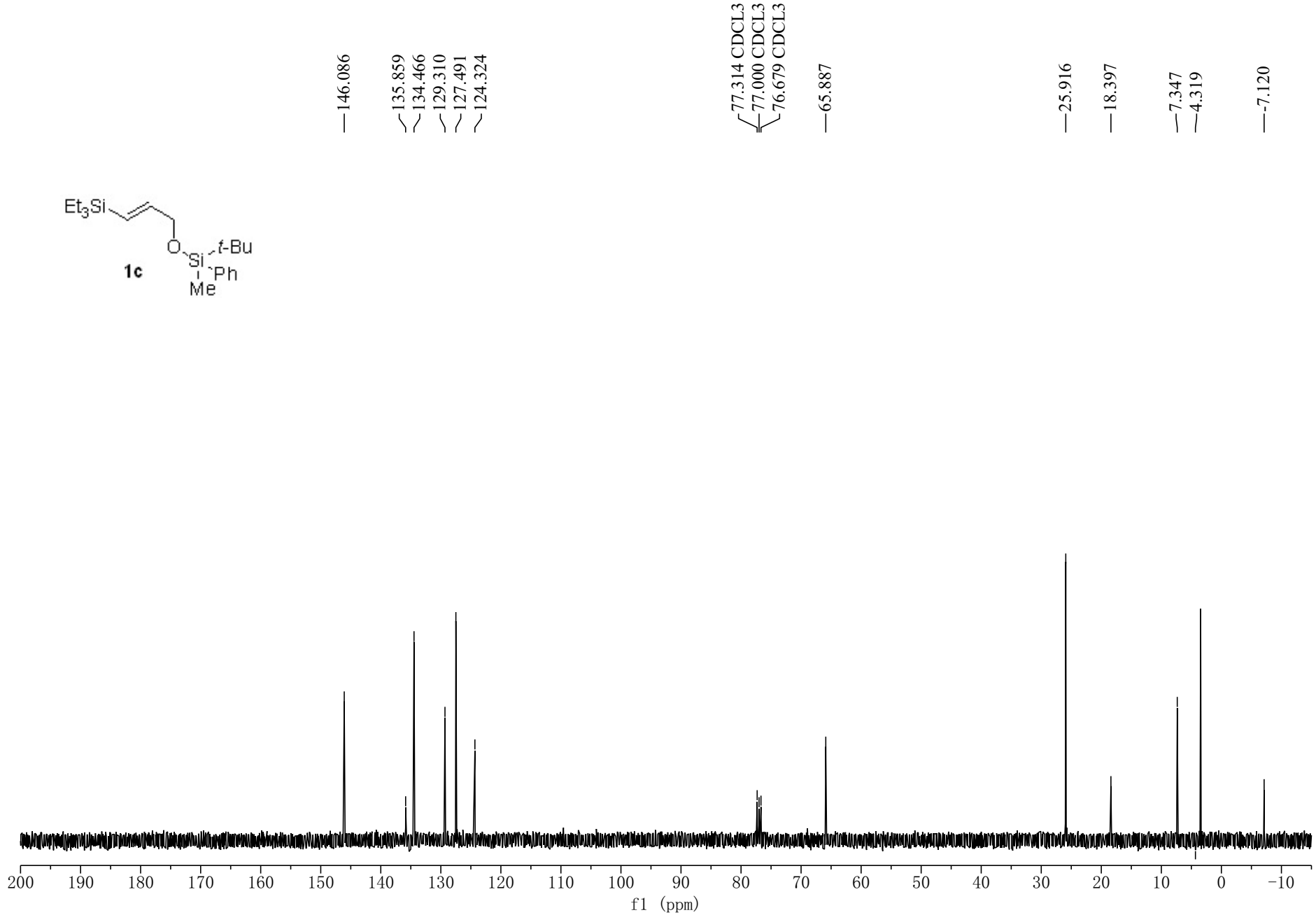
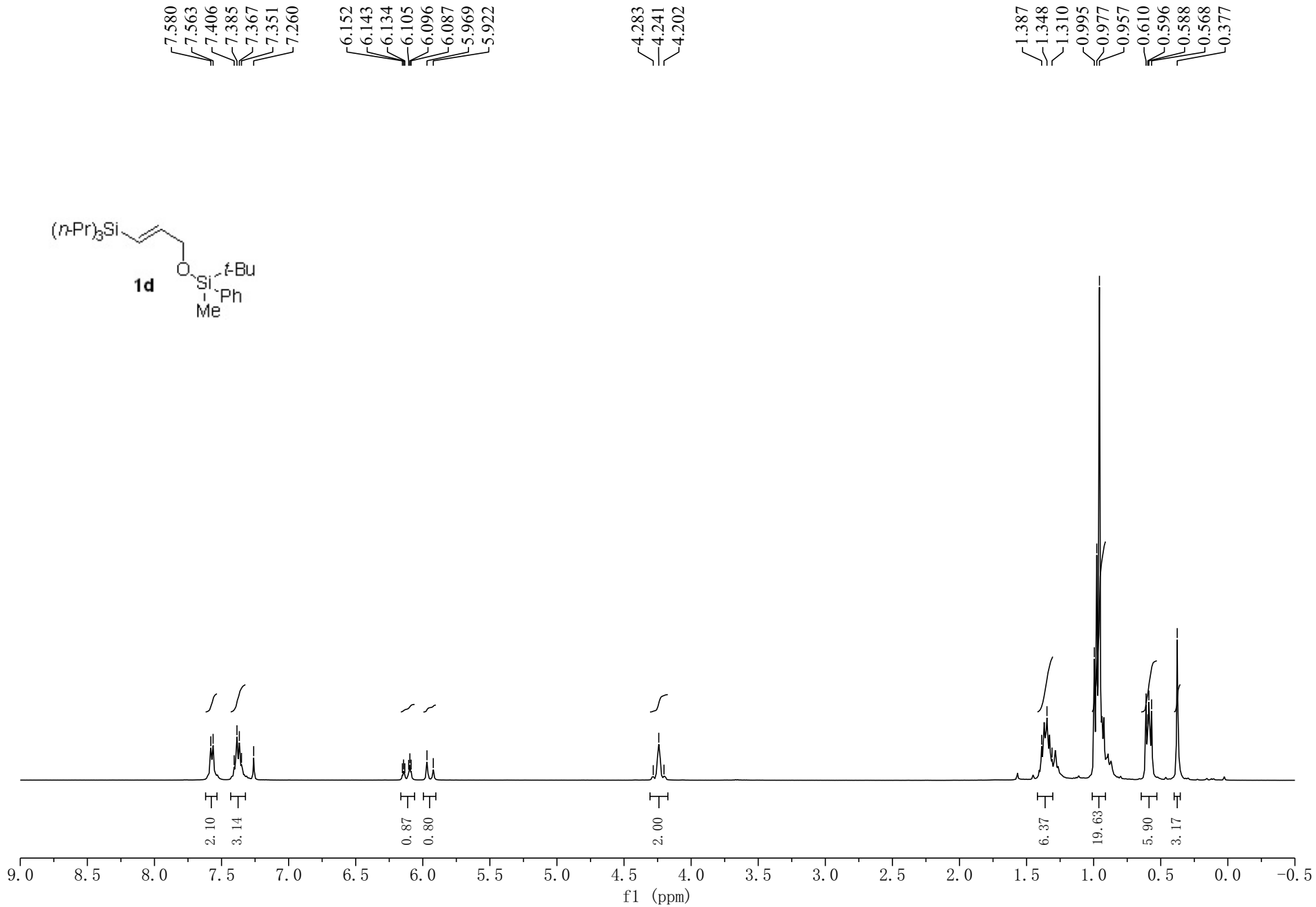


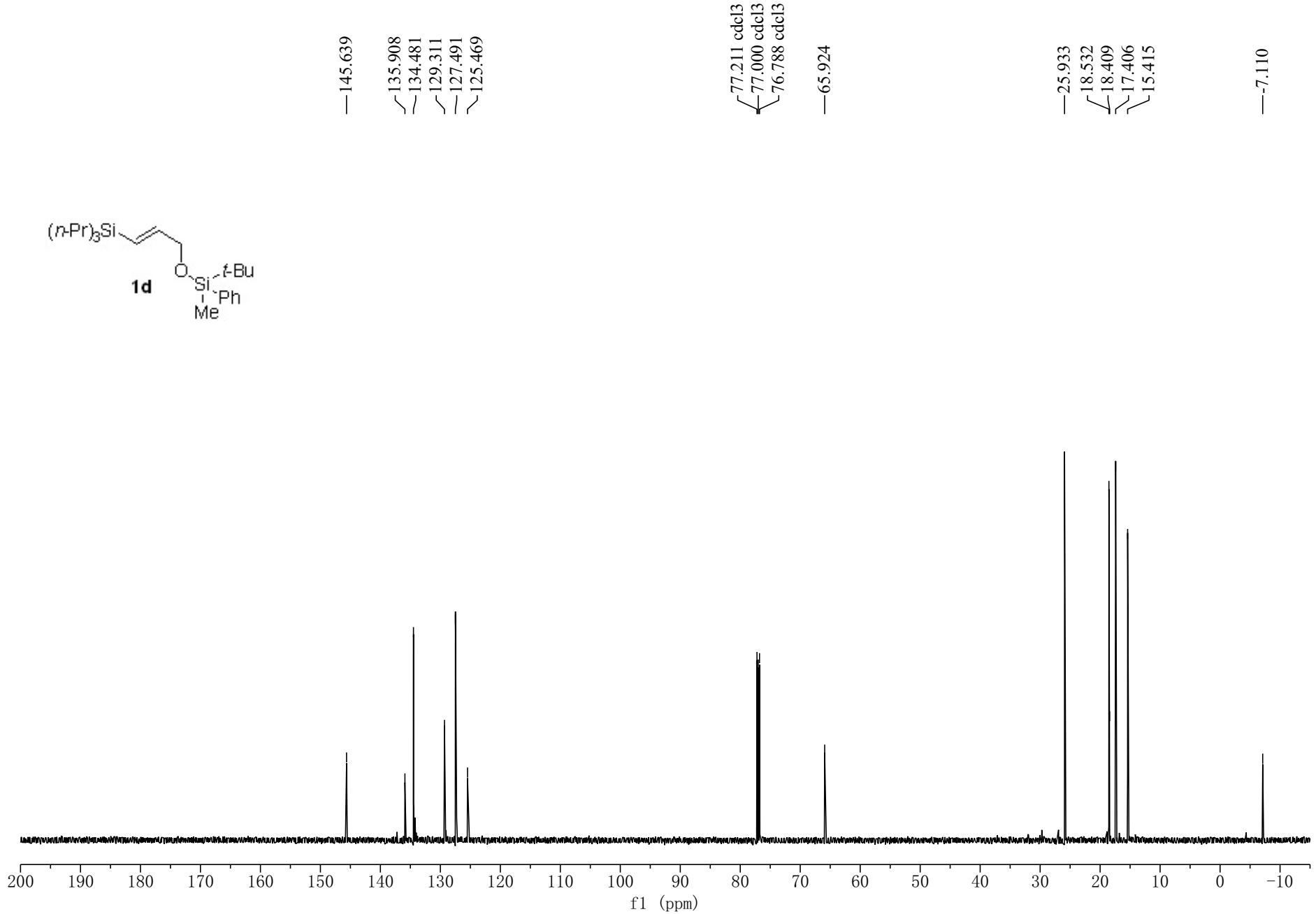
WY-6-86 C13 CDCl3 100M Hz



WY-6-27 H1 CDCl3 400M Hz



WY-6-27 C13 CDCL3 150M Hz



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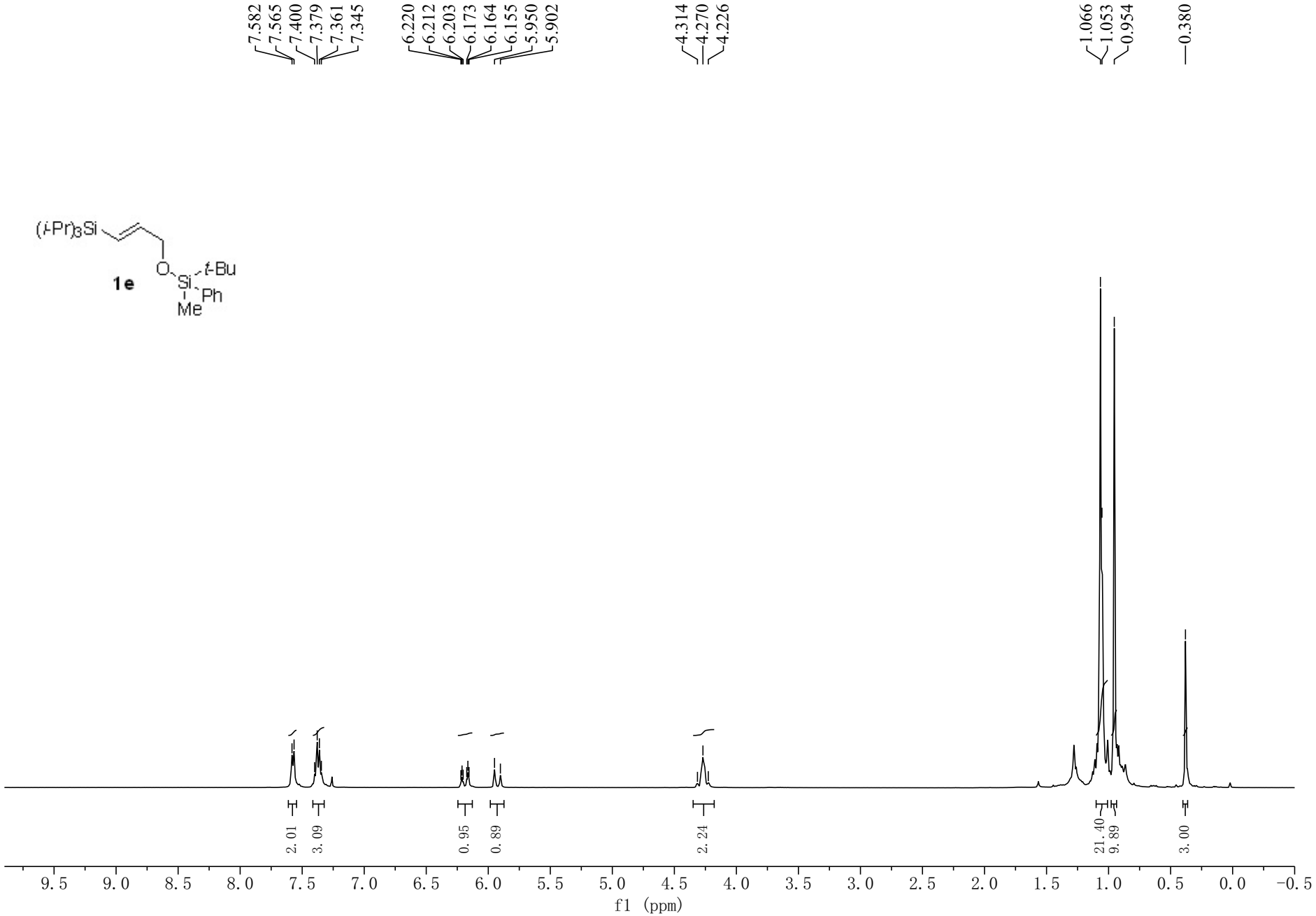
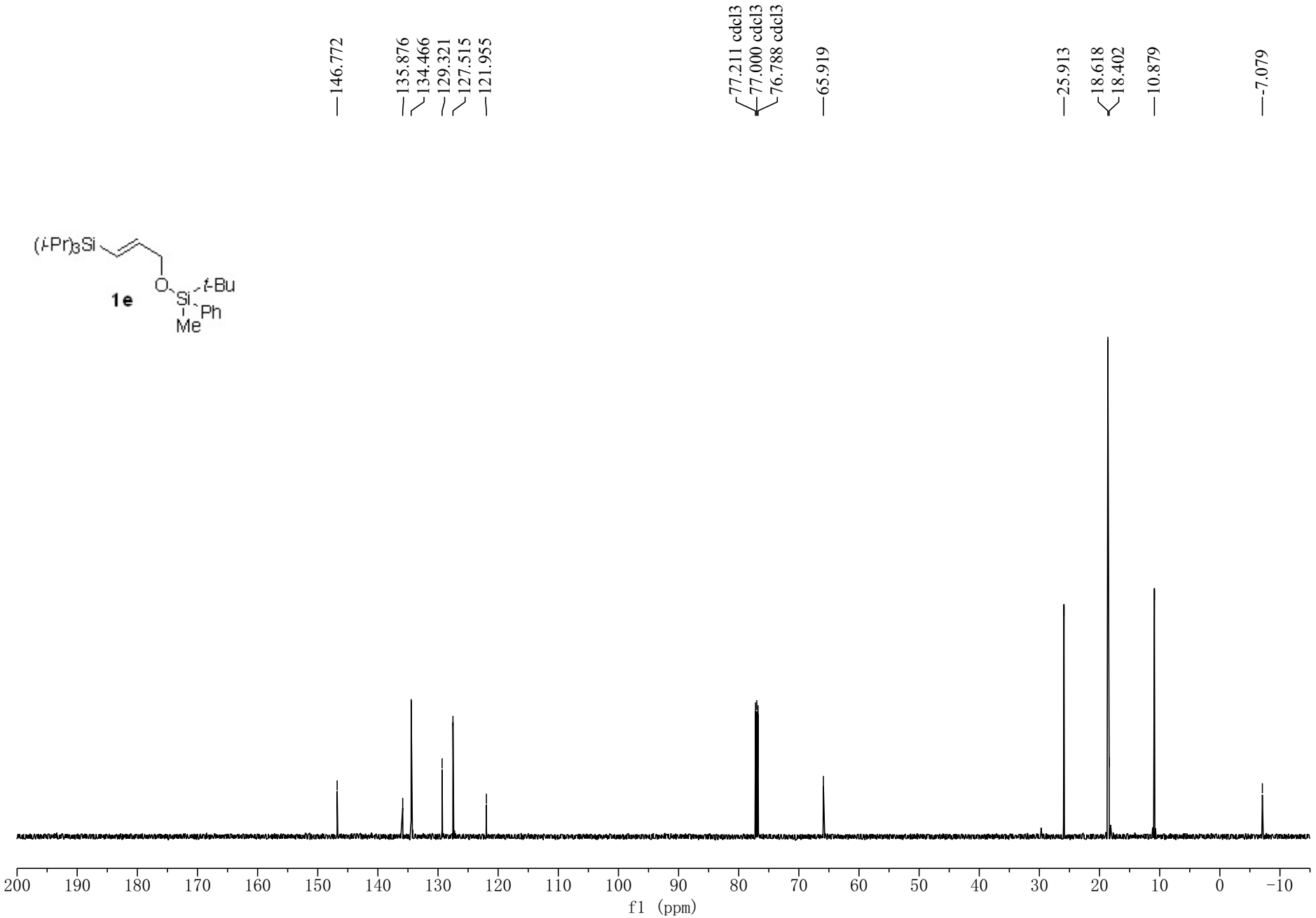


WY-6-28 C13 CDCl3



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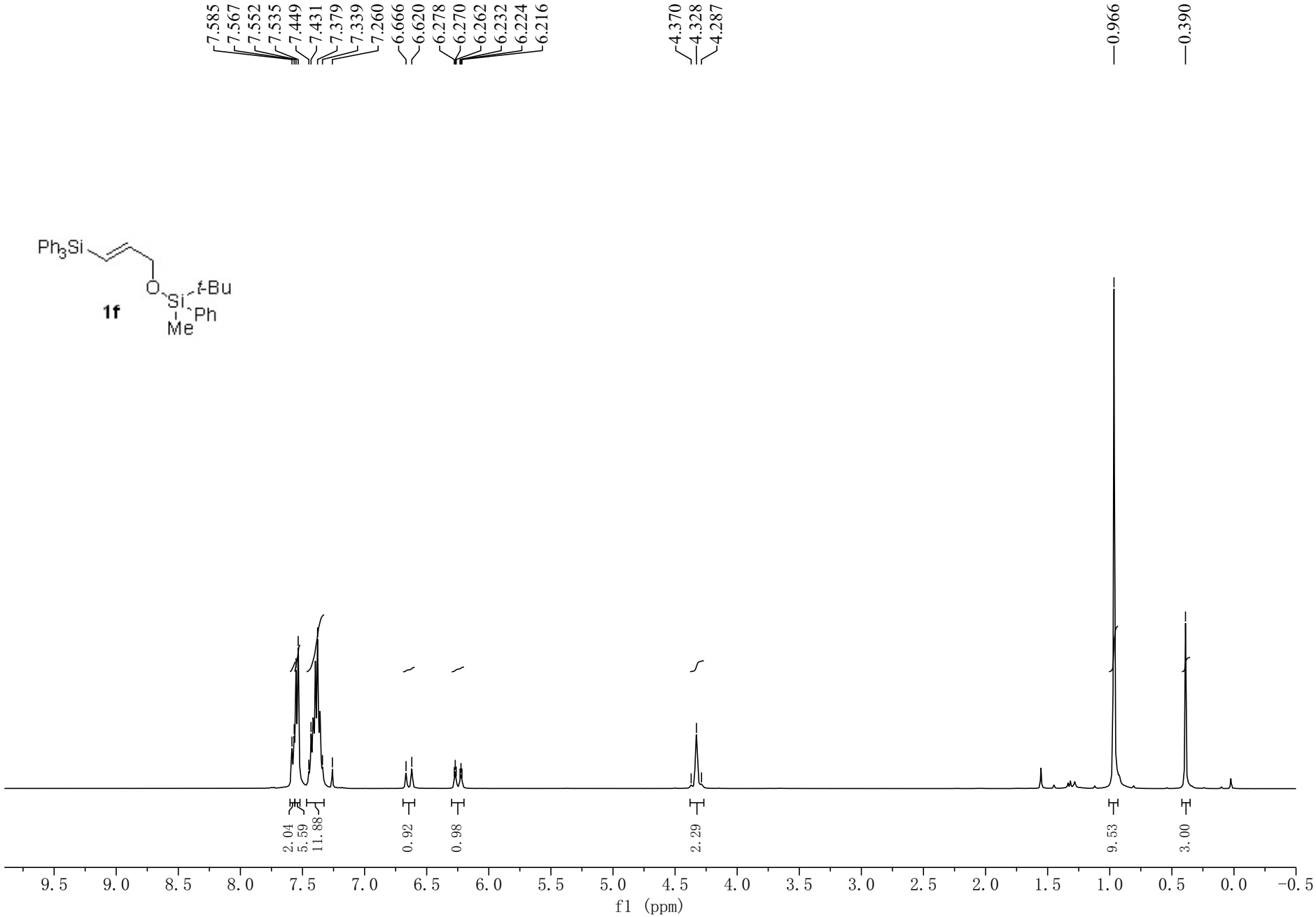
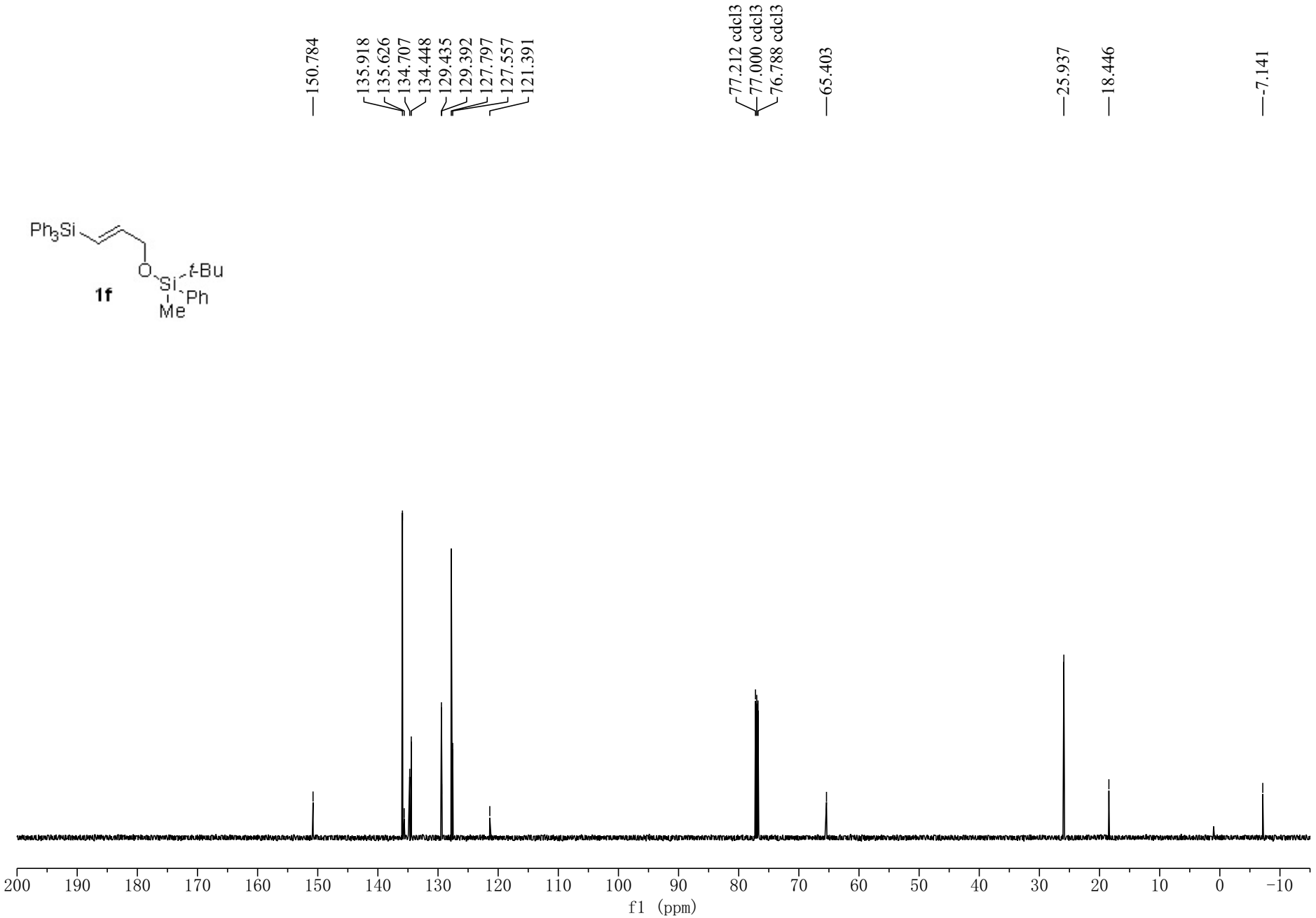
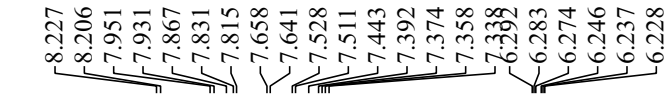
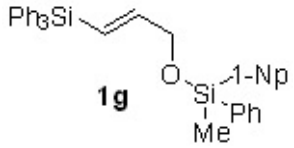


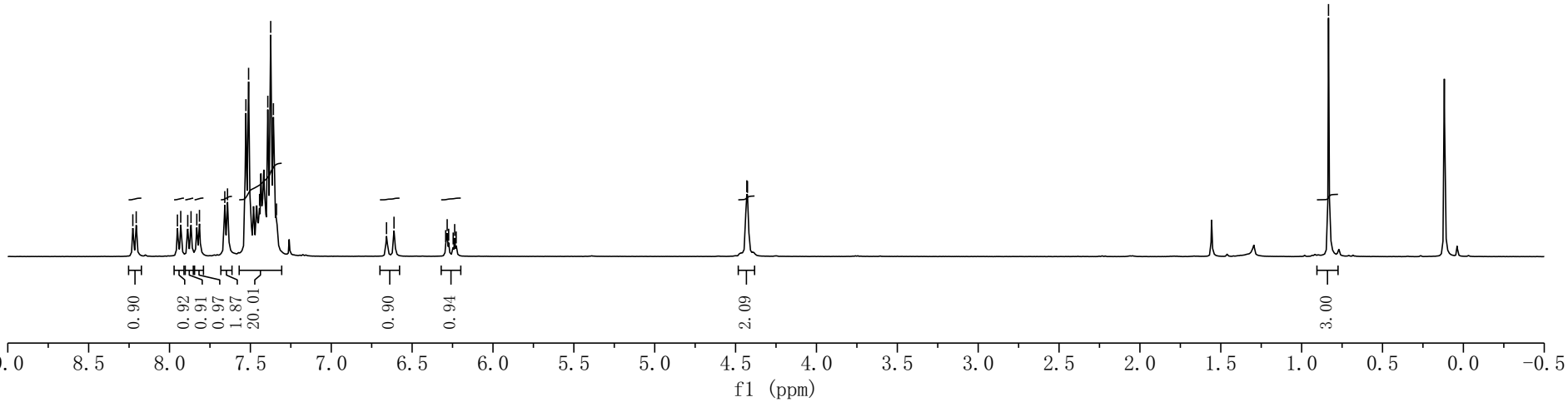
WY-5-66 C13 CDCl3 150M Hz



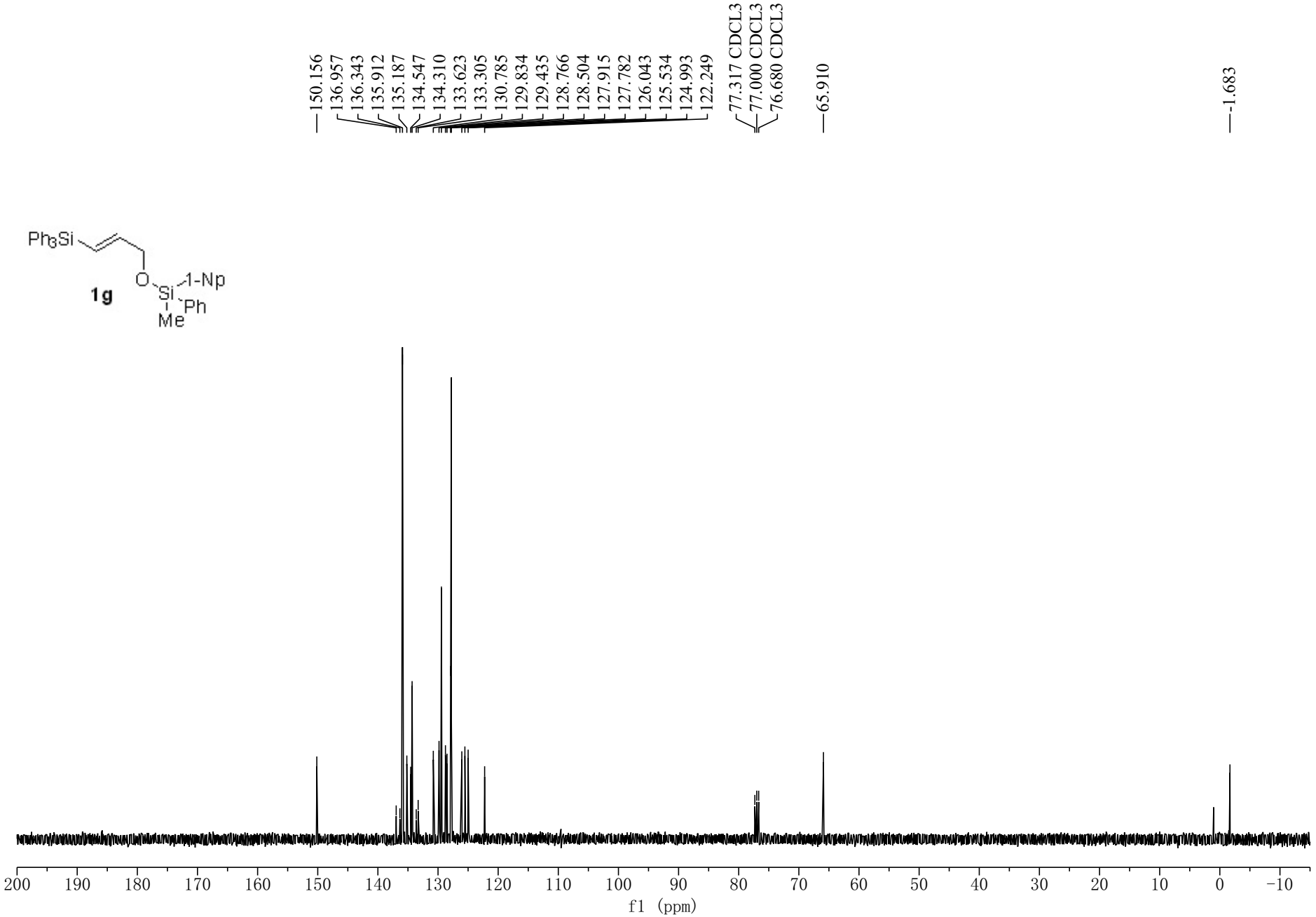
WY-6-63 H1 CDl3 400M Hz



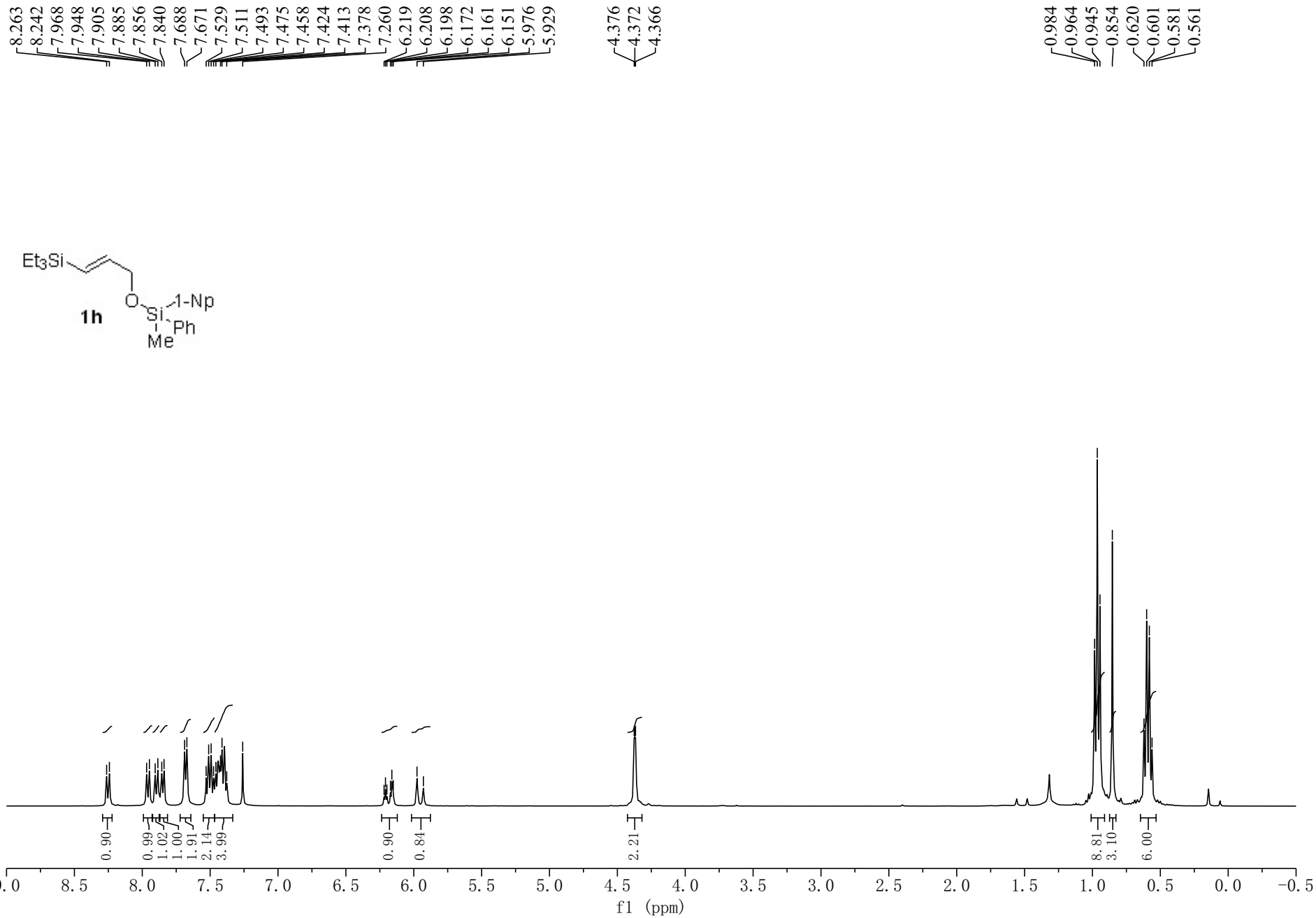




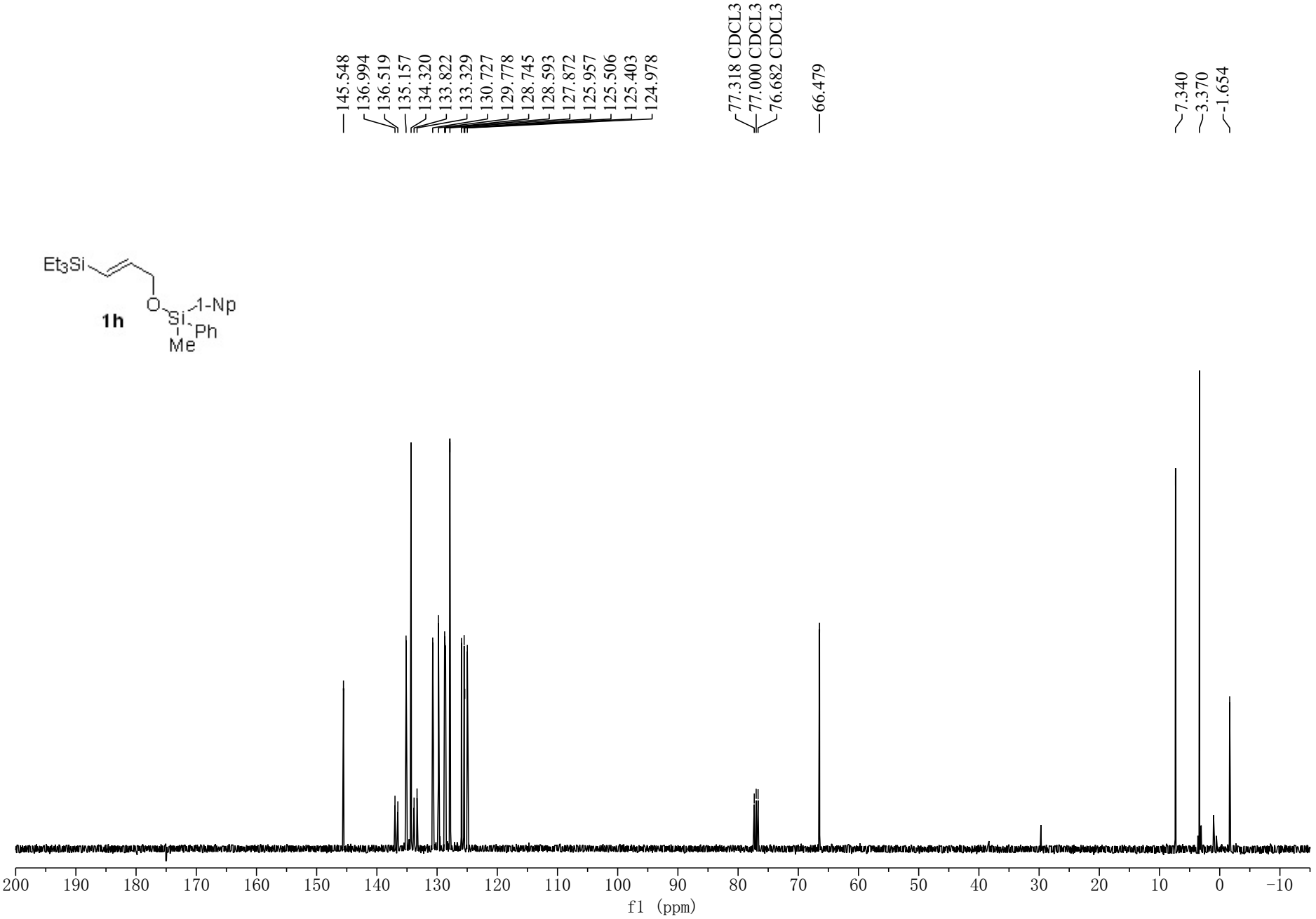
WY-6-63 C13 CDl3 100M Hz



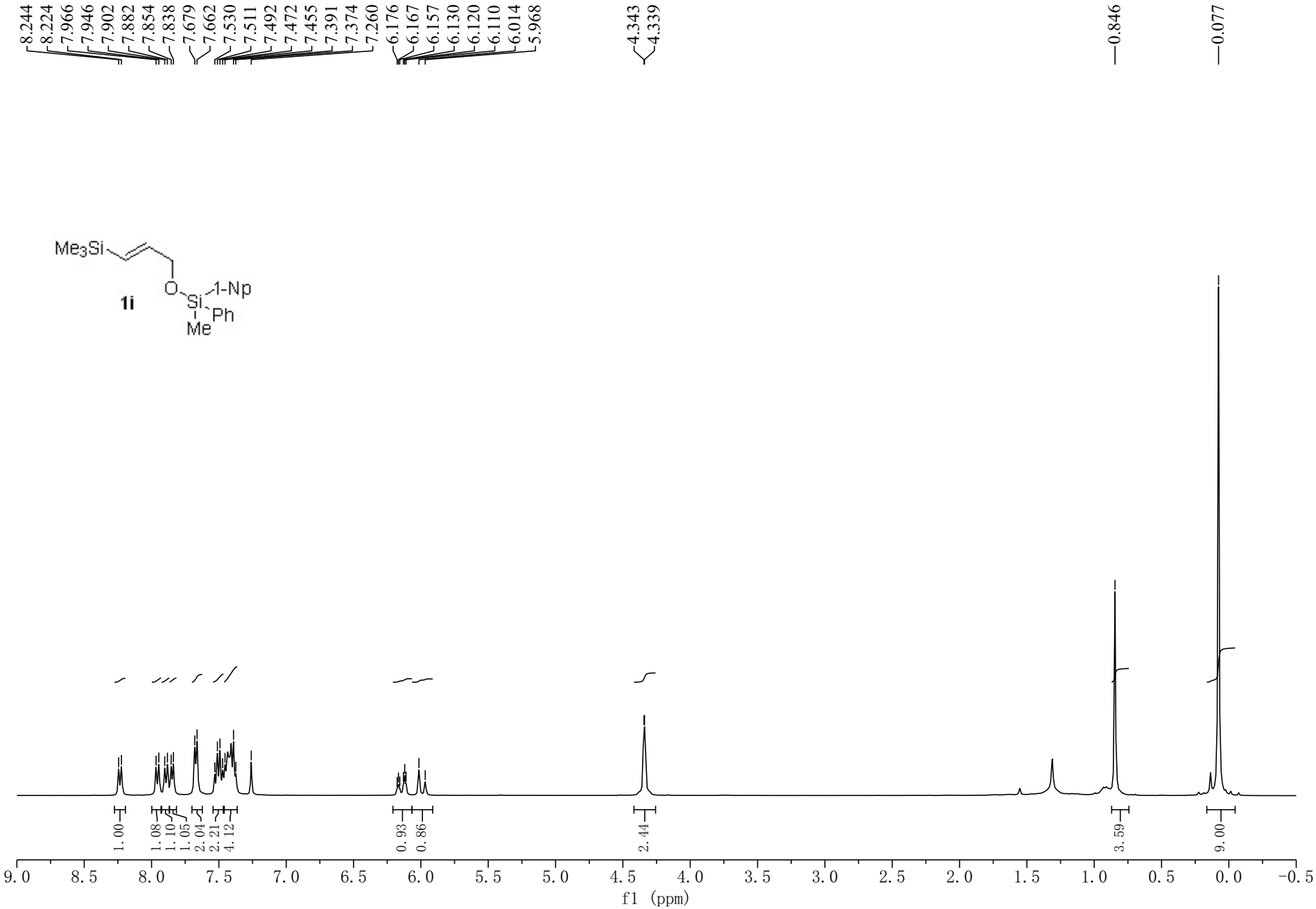
WY-6-75-2 H1 CDCl3 400M Hz



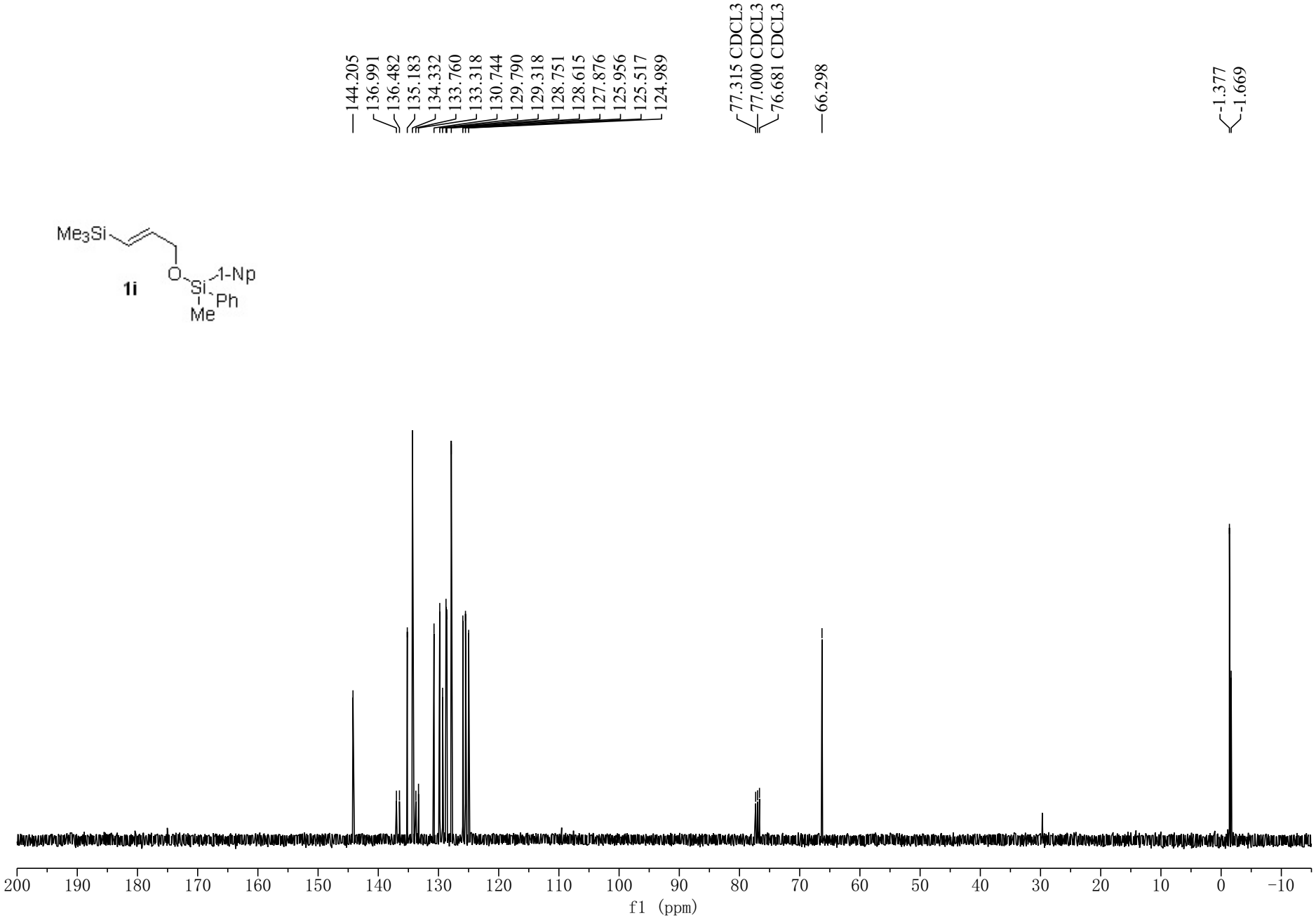
WY-6-73 C13 CDCl3 100M Hz



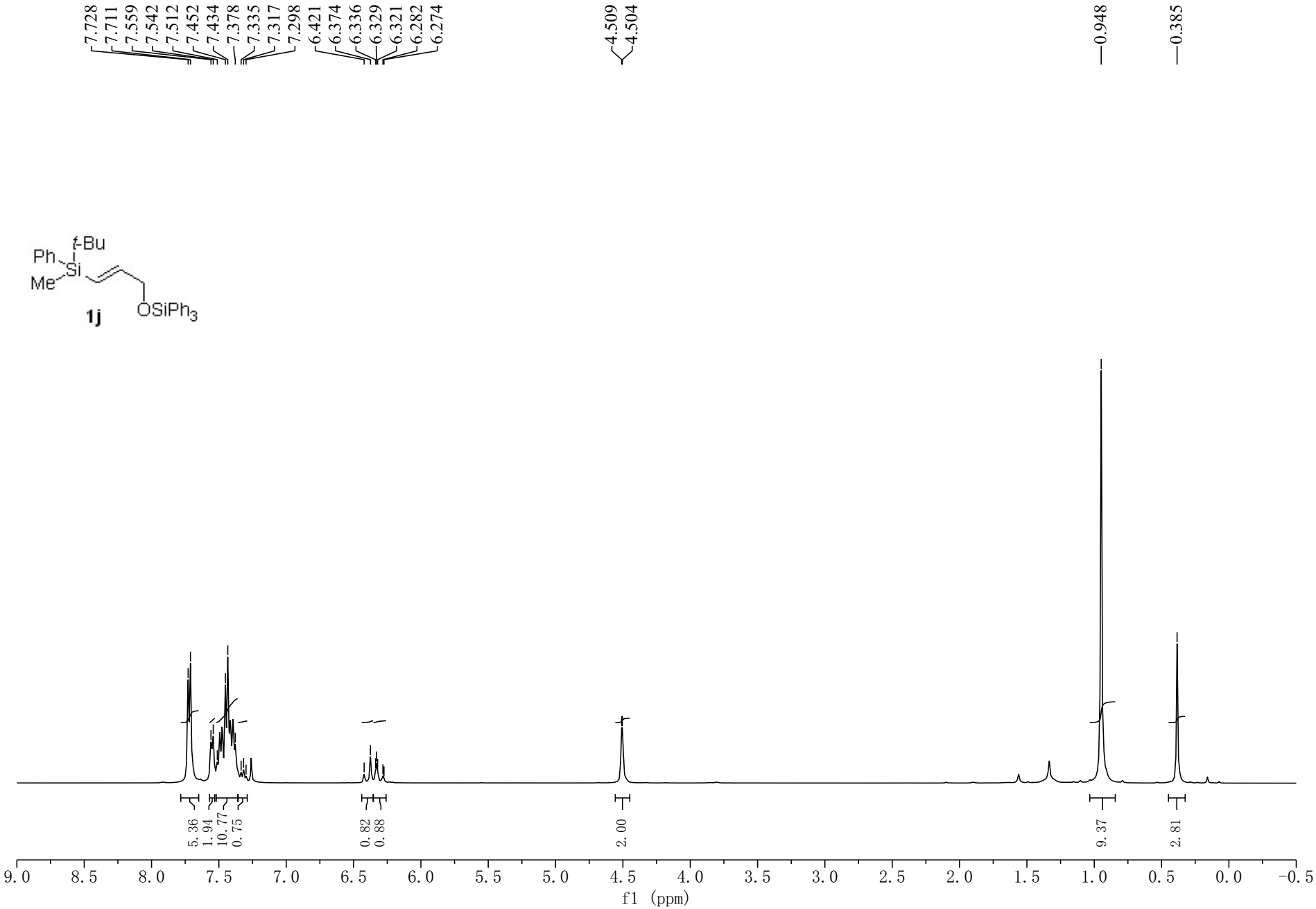
WY-6-75-1 H1 CDCl3 400M Hz



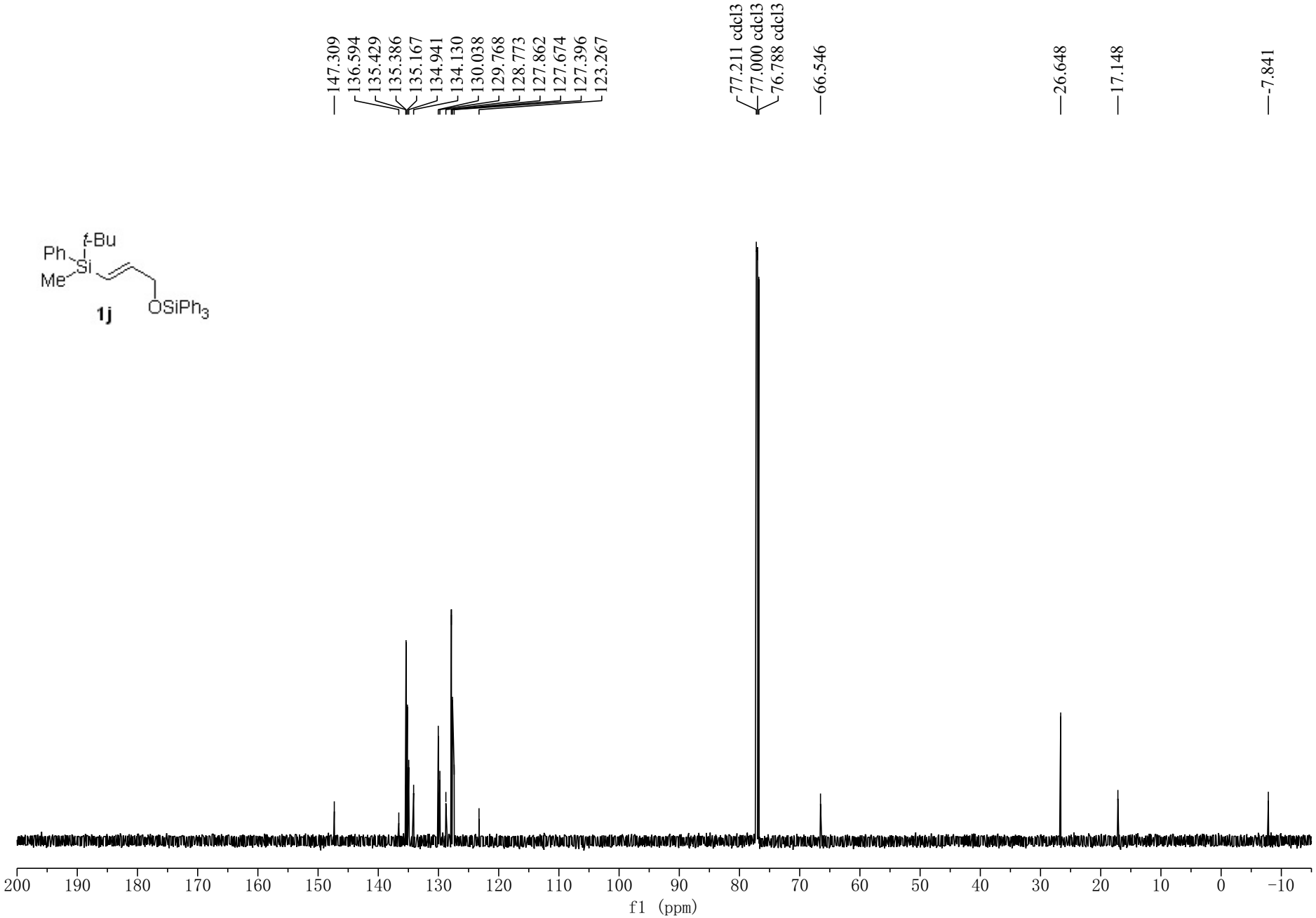
WY-6-75-1 C13 CDCl3 100M Hz



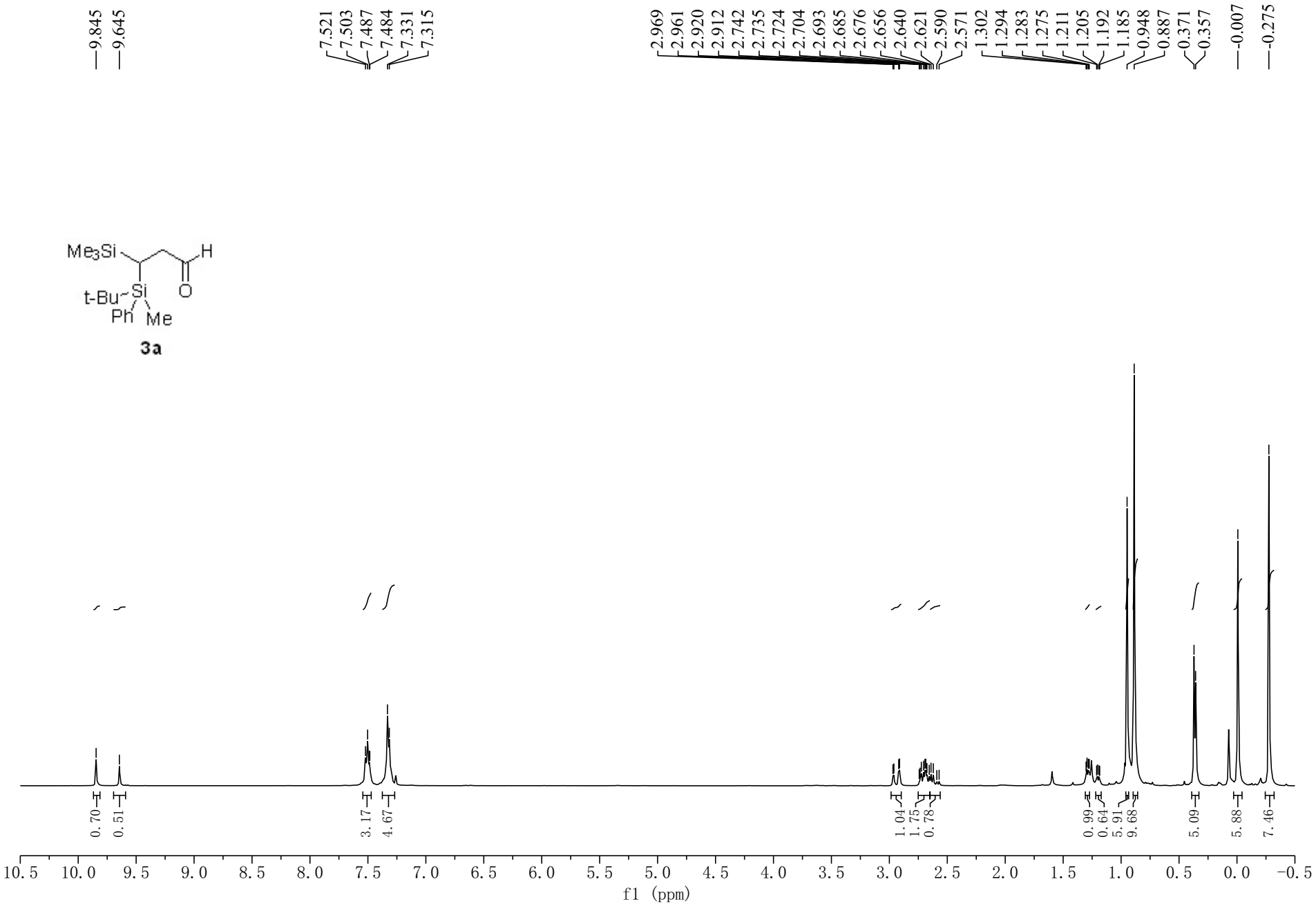
WY-6-11 H1 CDCl3 400M Hz



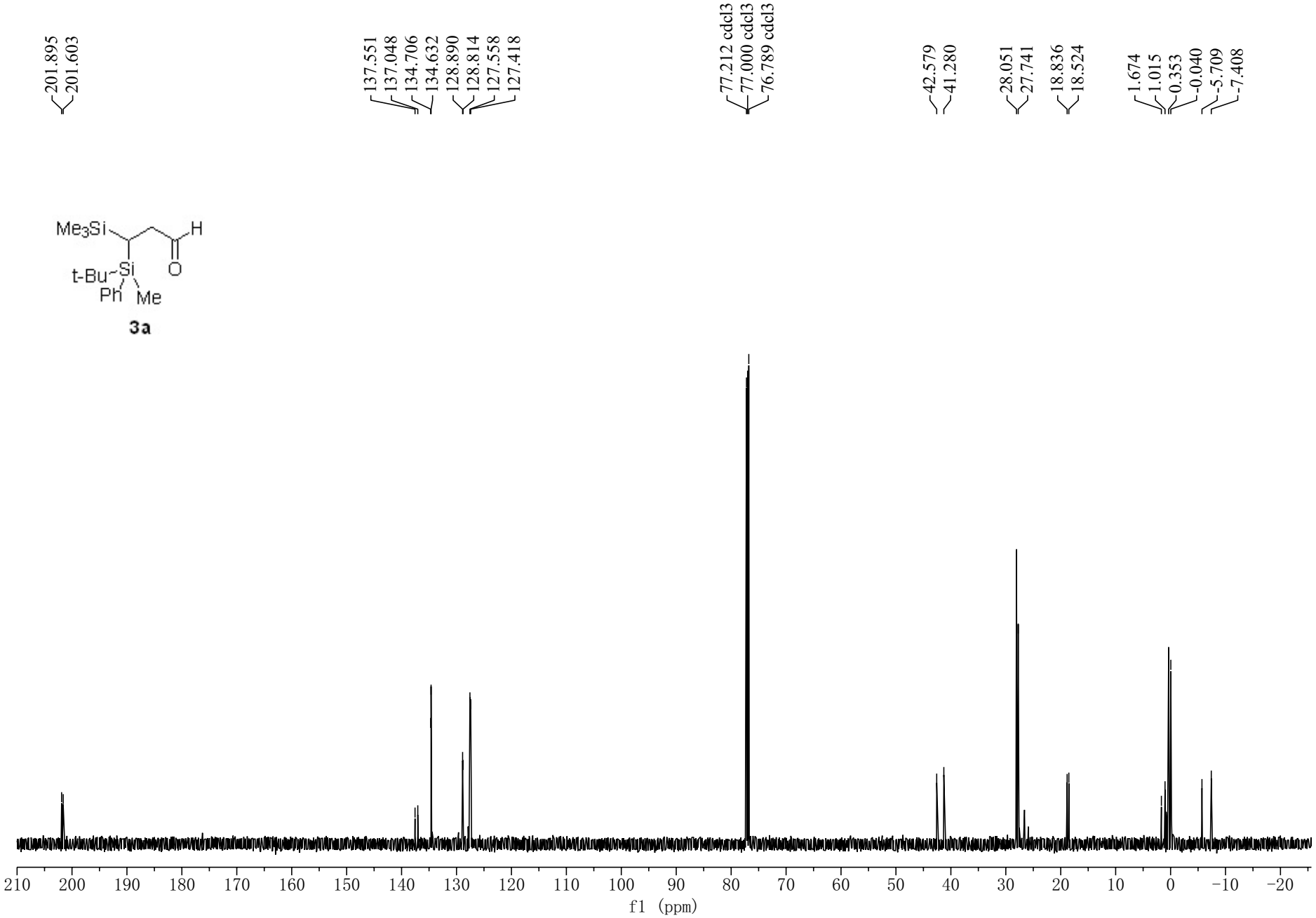
WY-6-45 C13 CDCl3 150M Hz



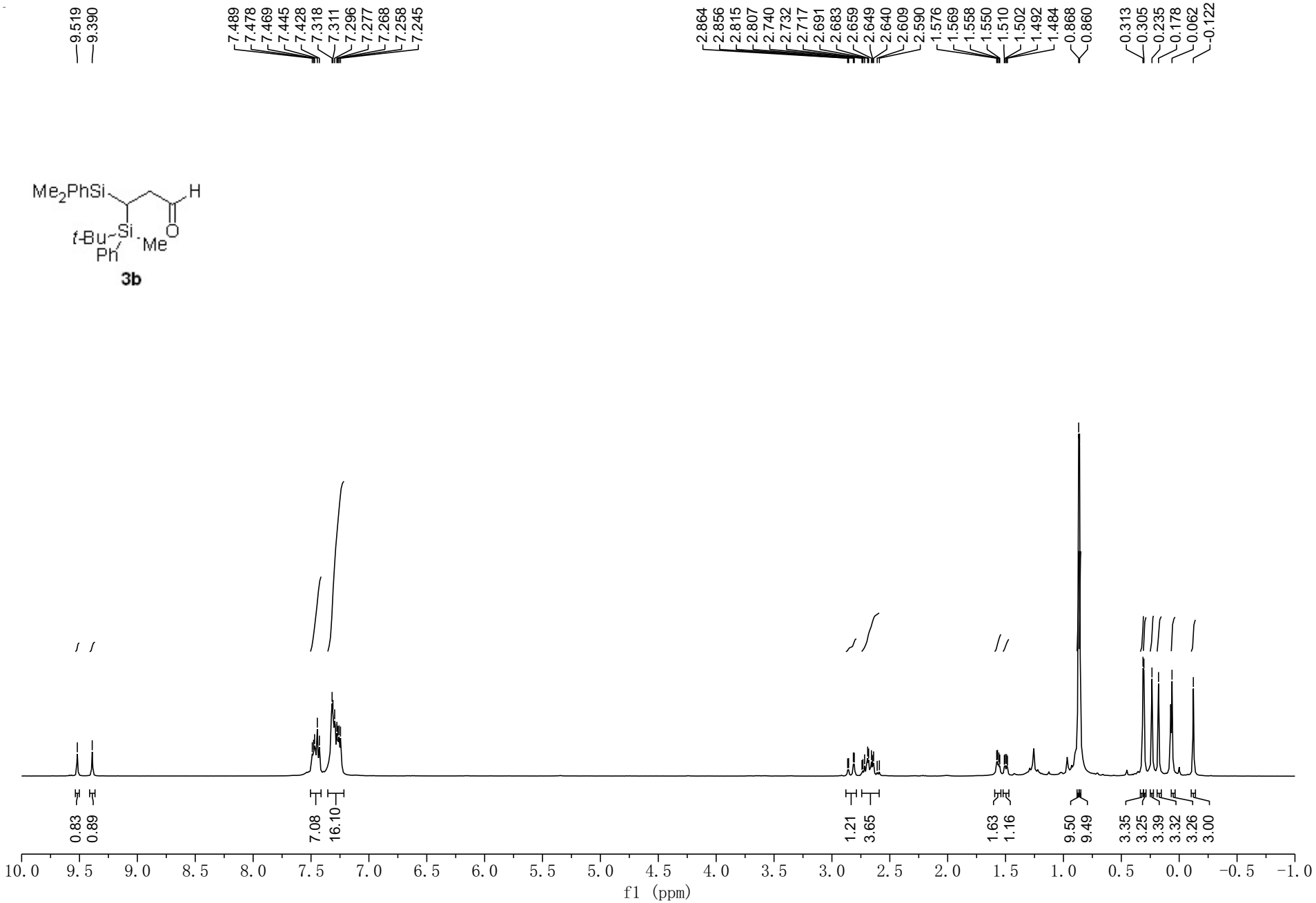
WY-7-104-2 H1 CDCl3 400M Hz



WY-5-68 C13 CDCl3 150M Hz

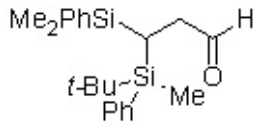


WY-6-7 H1 CDCl3 400M

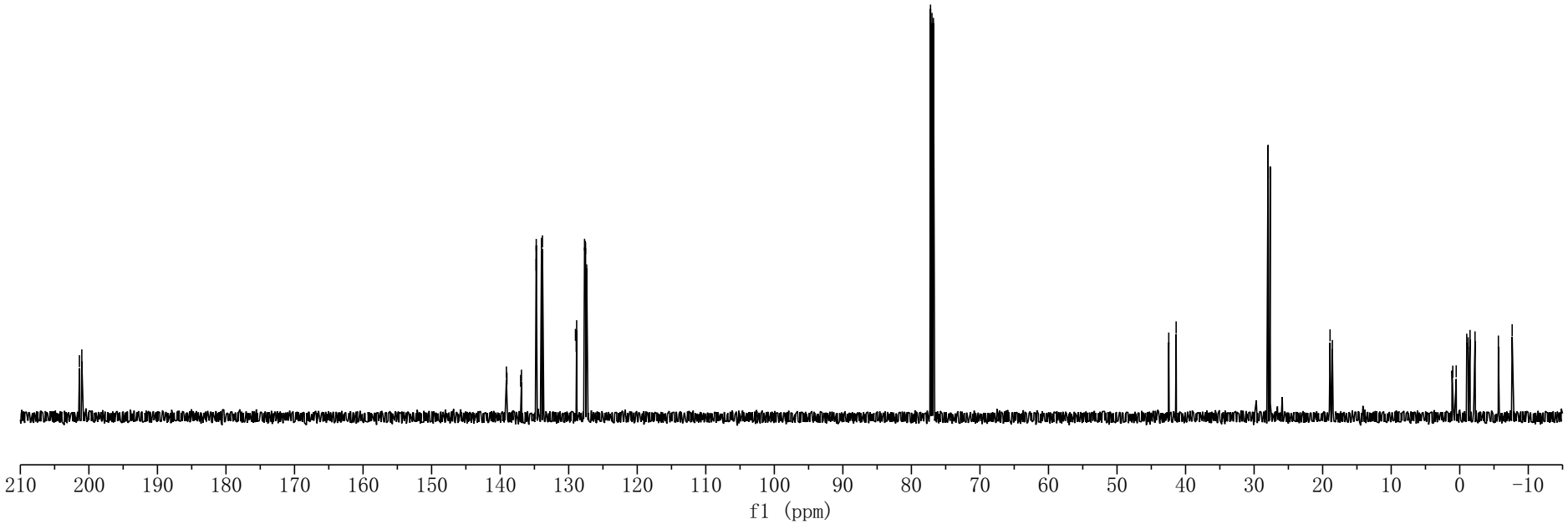


WY-6-7 C13 CDCl3

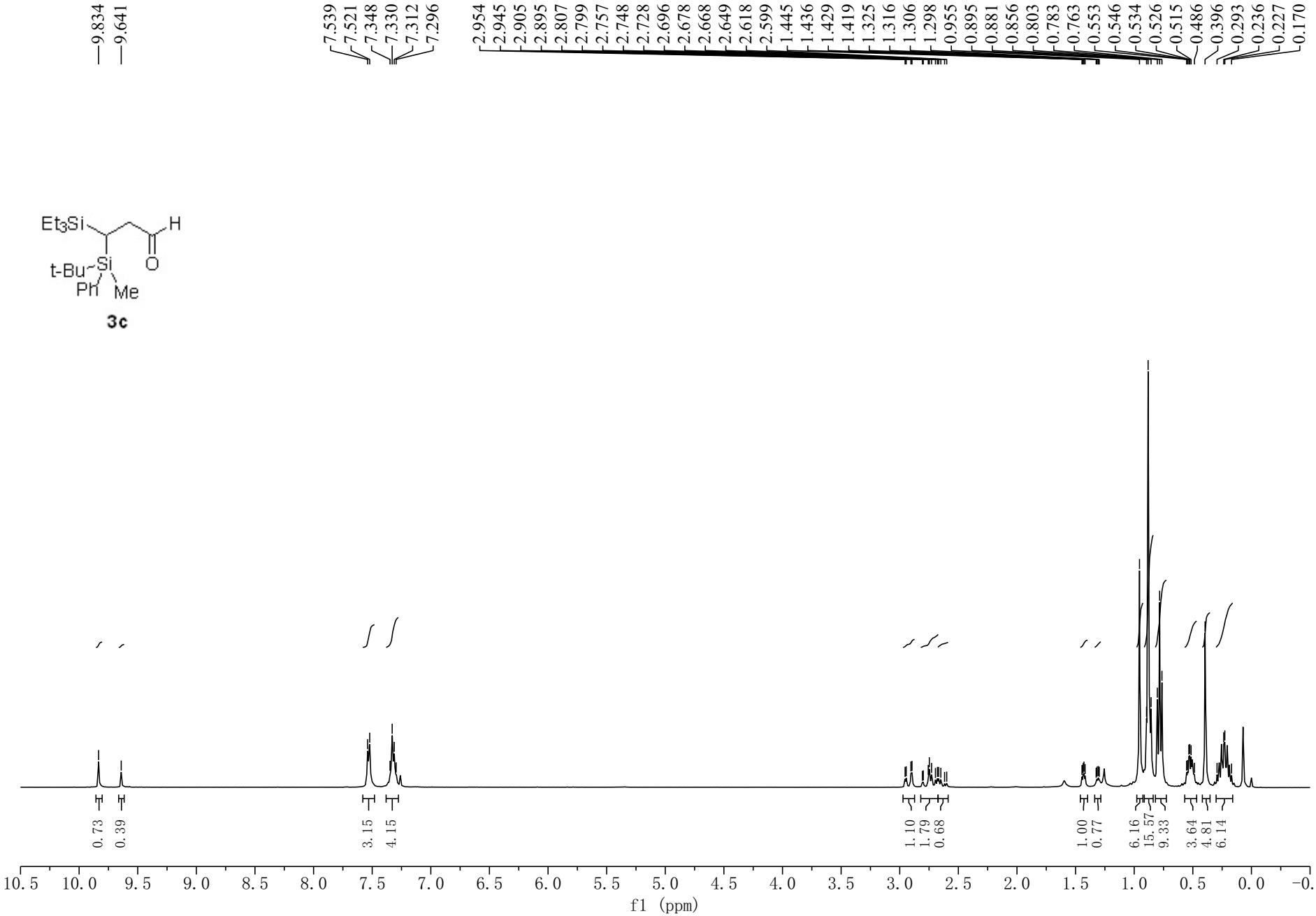
201.379
201.033
139.085
139.015
137.006
136.890
134.745
134.731
133.968
133.825
129.010
128.900
128.838
128.820
127.687
127.598
127.539
127.376
77.212 cdcl3
77.000 cdcl3
76.788 cdcl3
42.452
41.374
27.965
27.655
18.919
18.581
1.014
0.514
-1.023
-1.221
-1.501
-2.229
-5.640
-7.650



3b

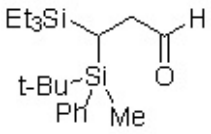


WY-7-19-2B H1 CDCl3 400M Hz

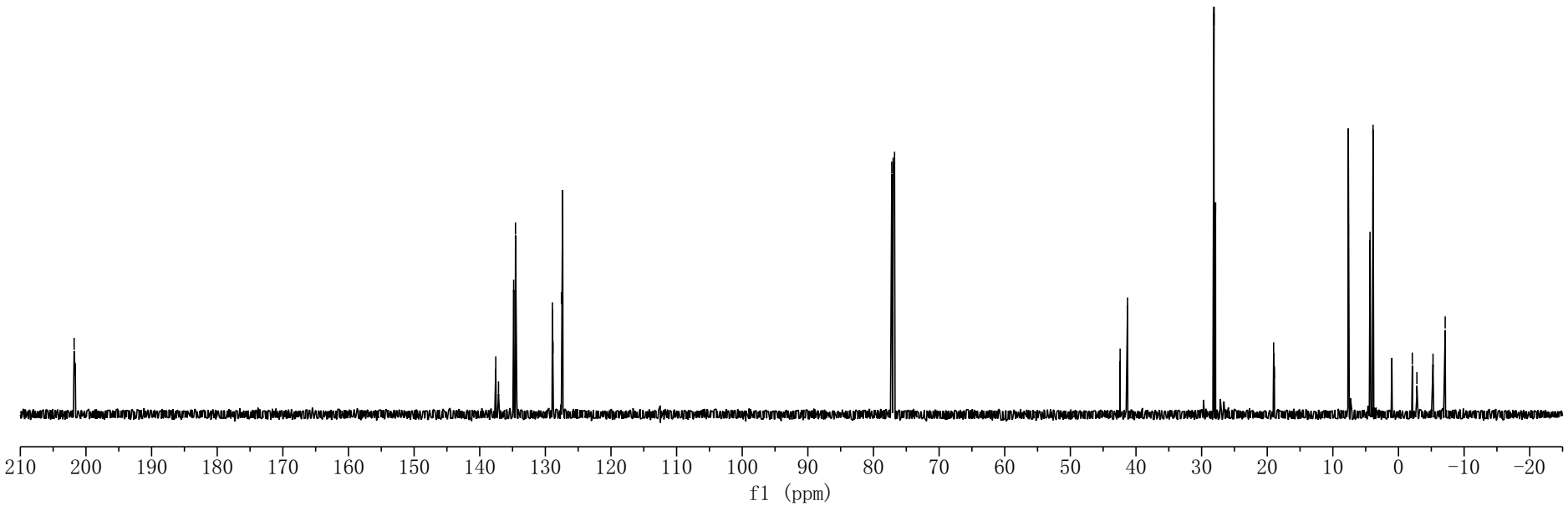


WY-6-62 C13 CDCl3 150M Hz

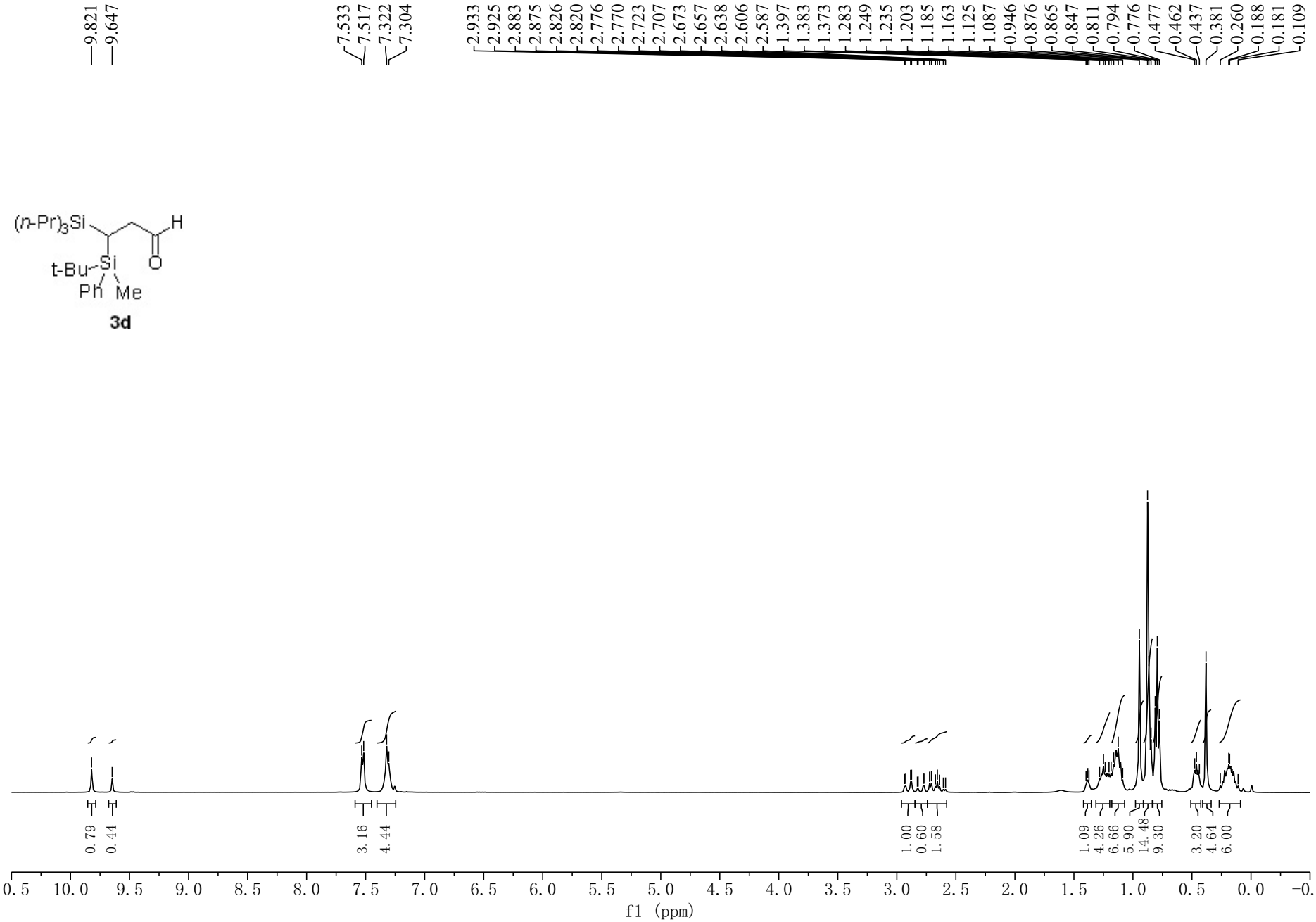
201.804
201.612
137.556
137.135
134.824
134.549
128.924
128.840
127.544
127.360
77.212 cdcl3
77.000 cdcl3
76.788 cdcl3
42.418
41.281
28.117
27.882
19.026
18.911
7.649
7.627
4.339
3.879
-2.109
-2.805
-5.260
-7.116



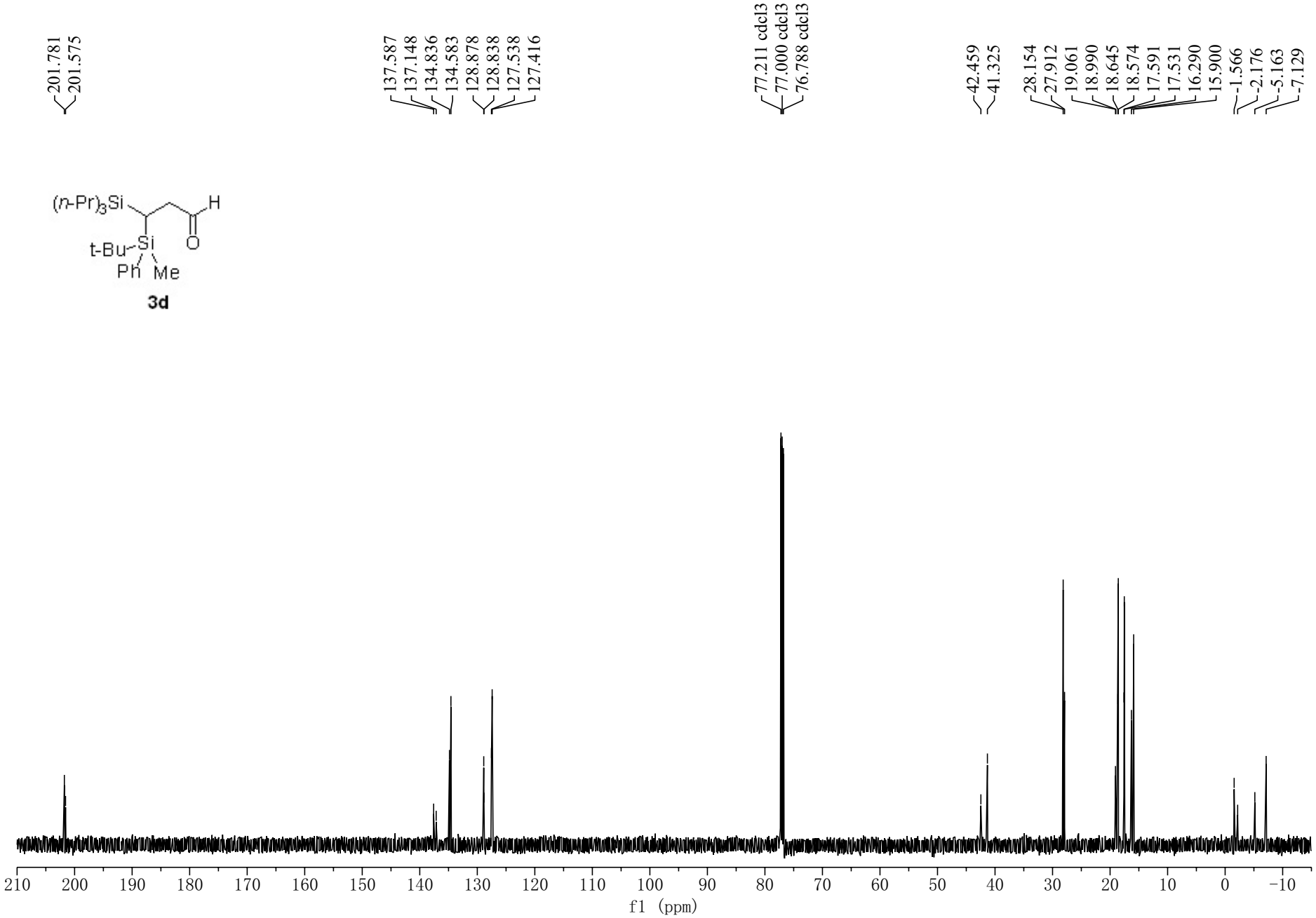
3c



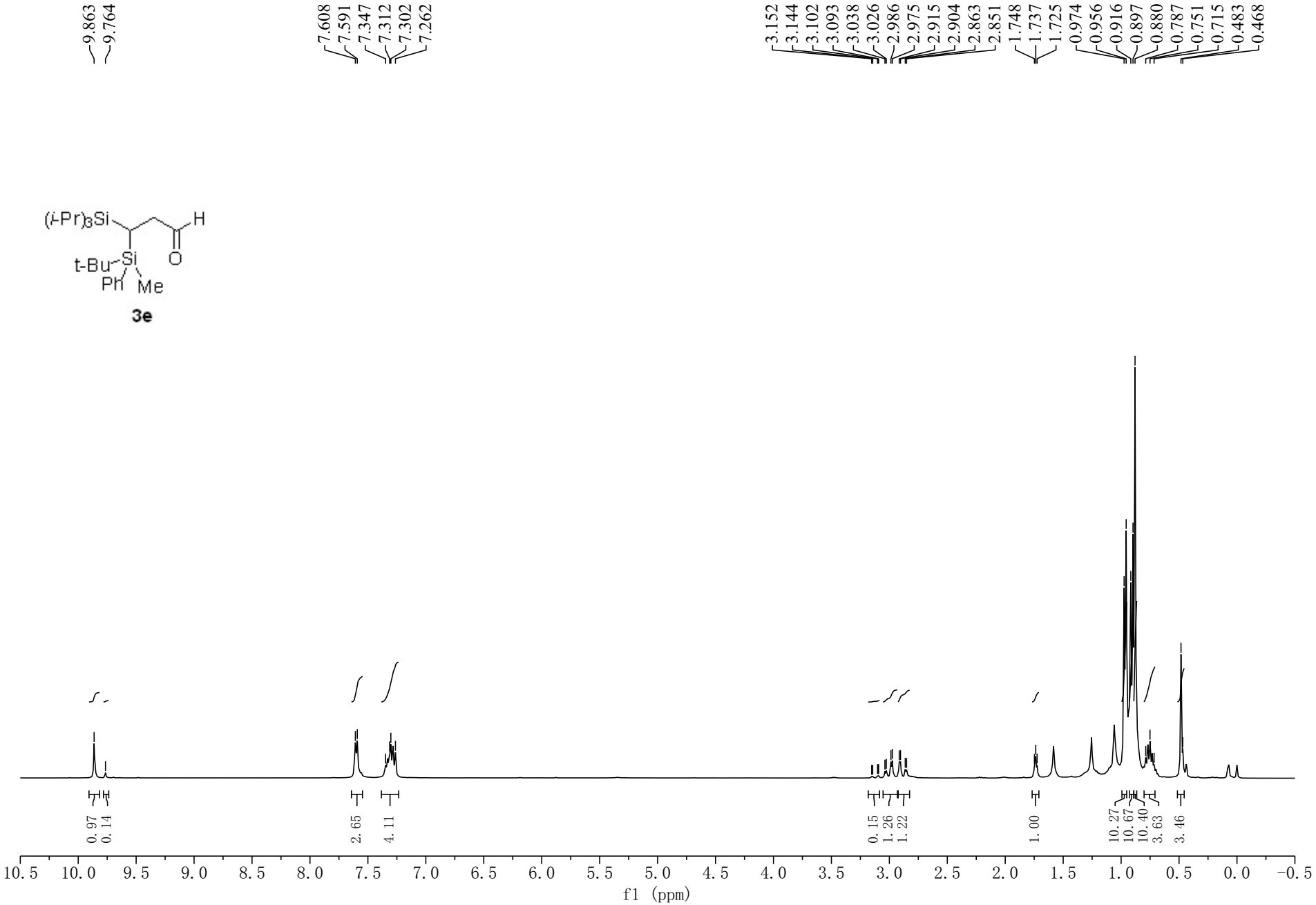
WY-6-29-2 H1 CDl3 400M Hz



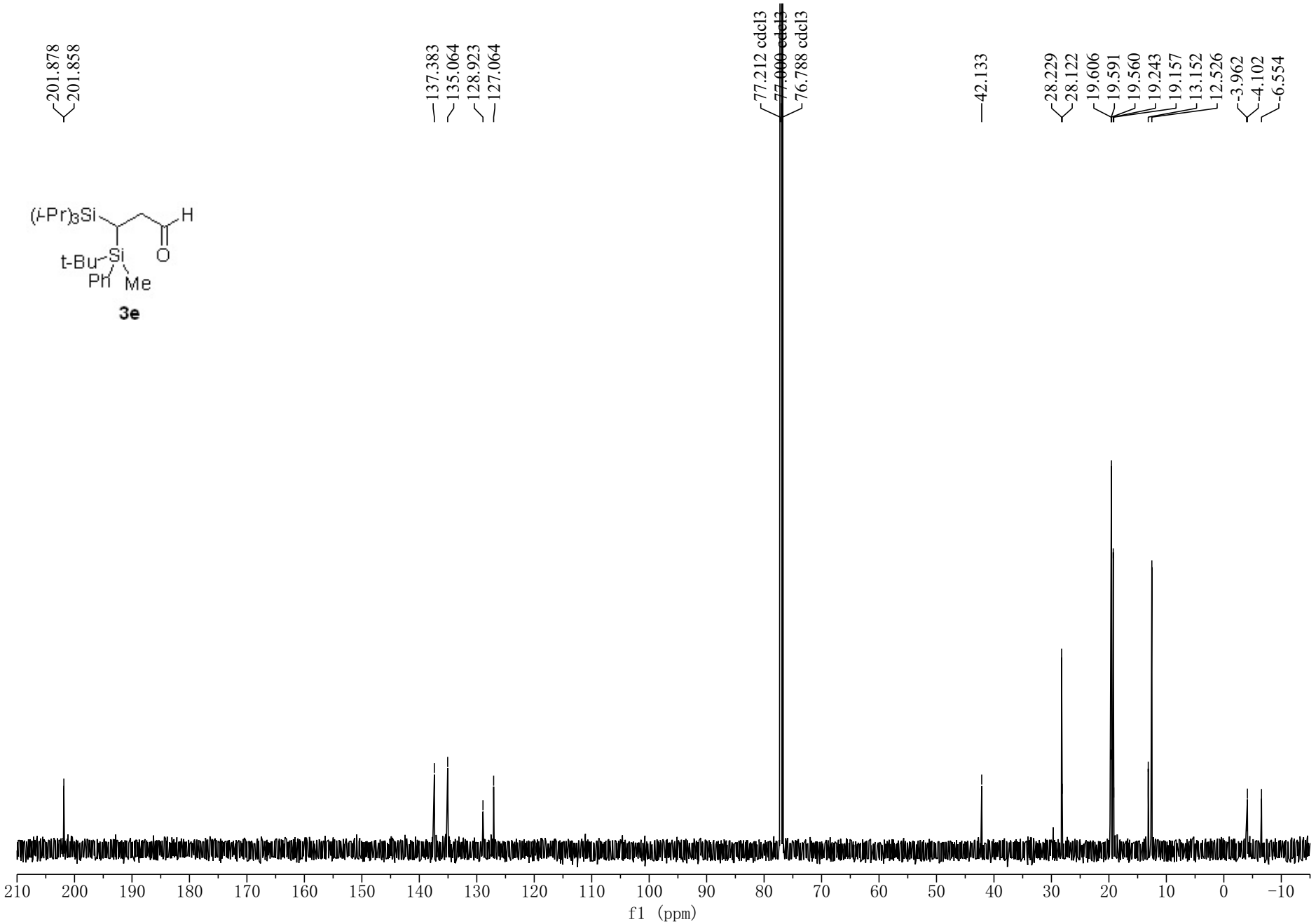
WY-6-29-2 C13 CDCl3 150M Hz



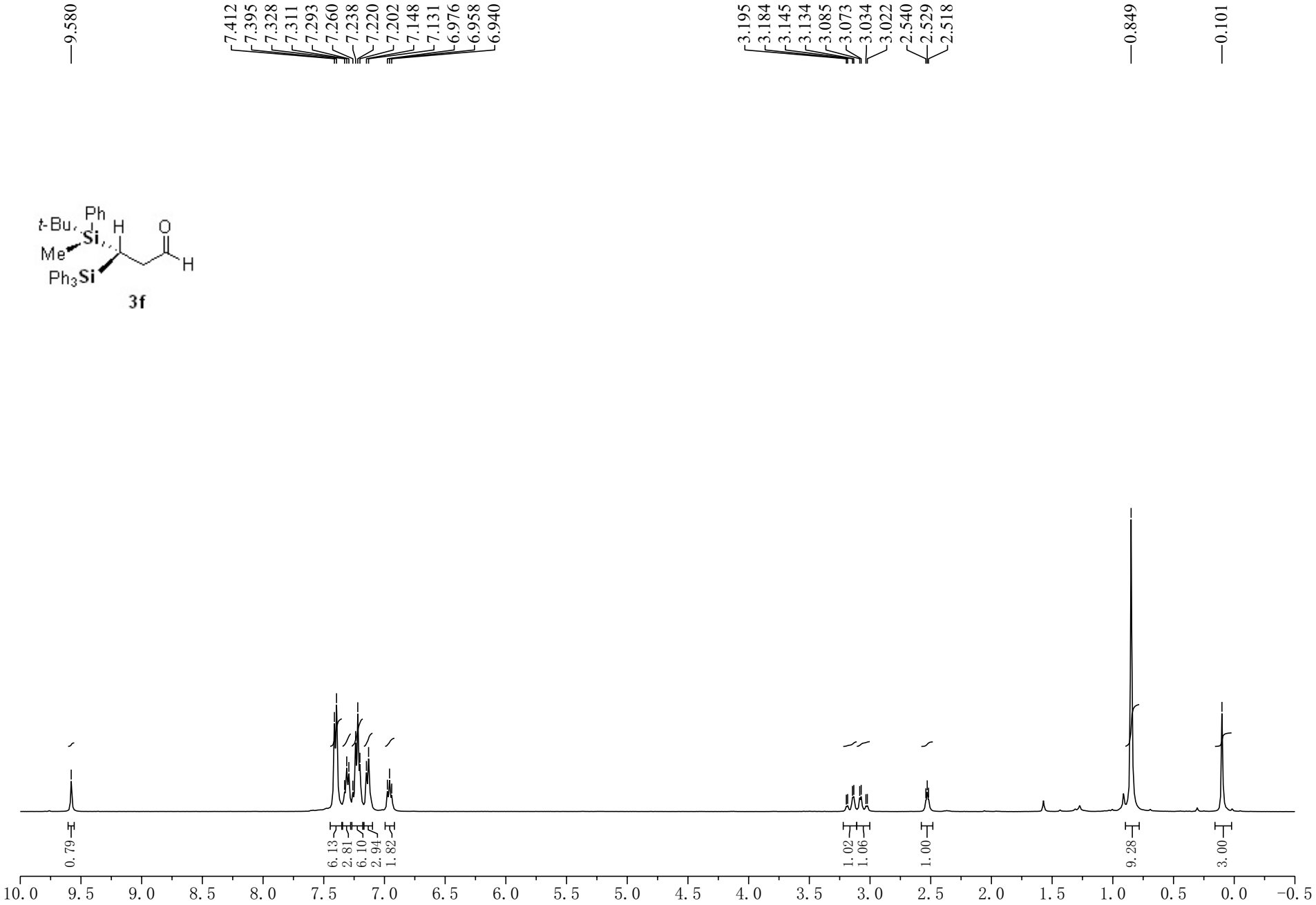
WY-6-30-2B H1 CDCl3 400M Hz



WY-6-30-2B C13 CDCl3 150M Hz



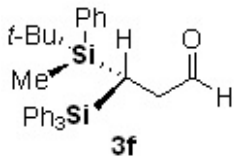
WY-8-6-2 H1 CDCl3 400M HZ



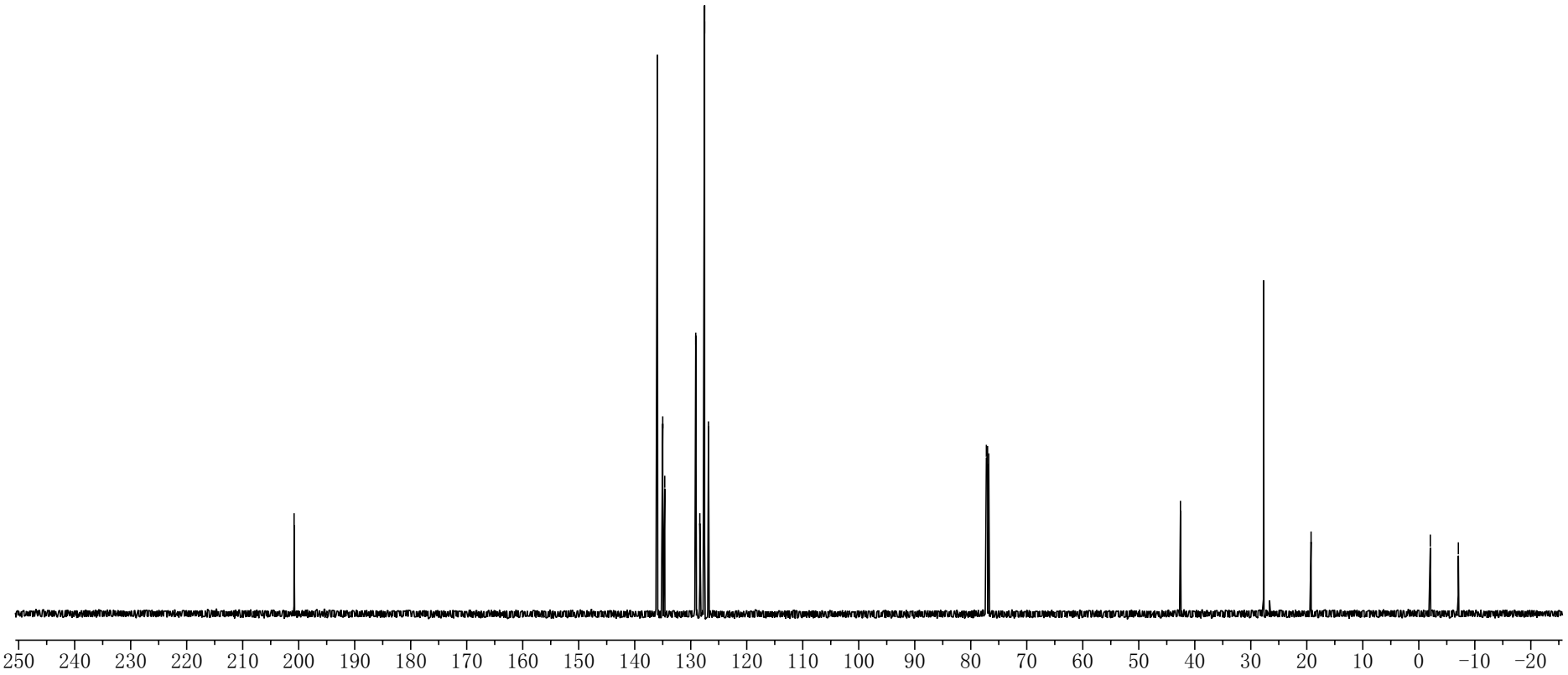
3f

WY-8-6-2 C13 CDCl3 100M Hz

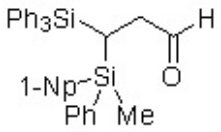
200.823
135.951
134.999
134.641
129.105
128.378
127.526
126.831
77.211 cdcl3
77.000 cdcl3
76.788 cdcl3
42.557
27.707
19.233
-2.057
-7.064



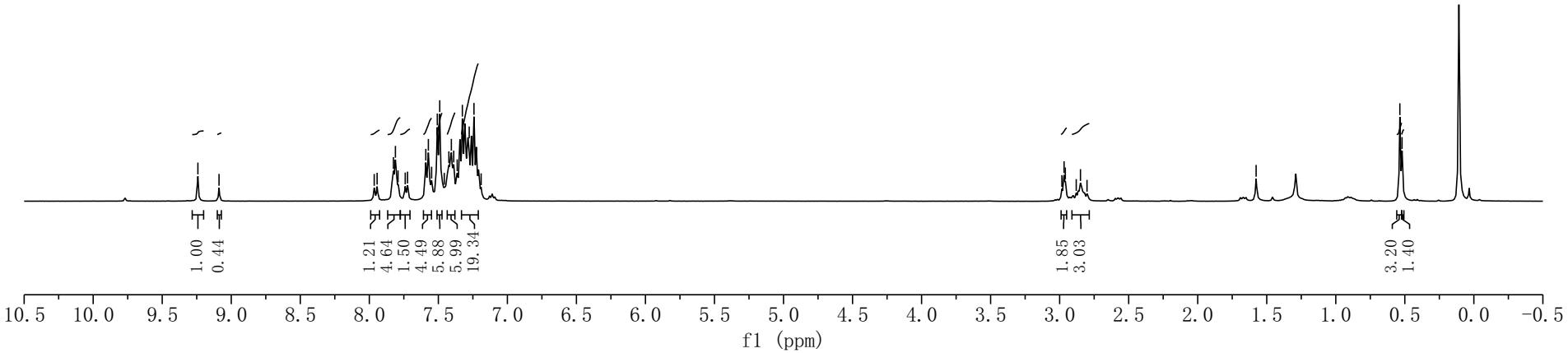
3f



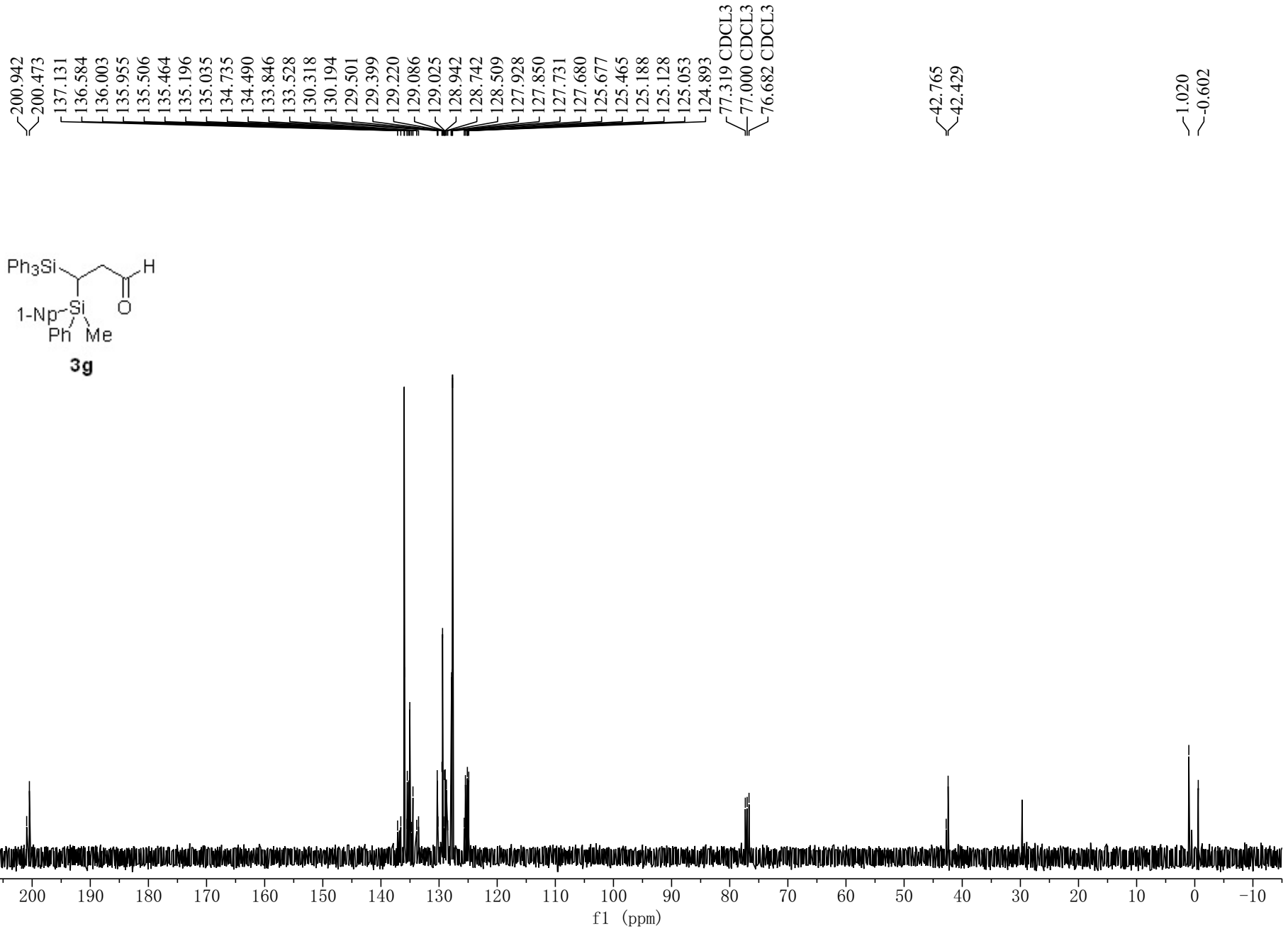
WY-6-67 H1 CDCl3 400M Hz



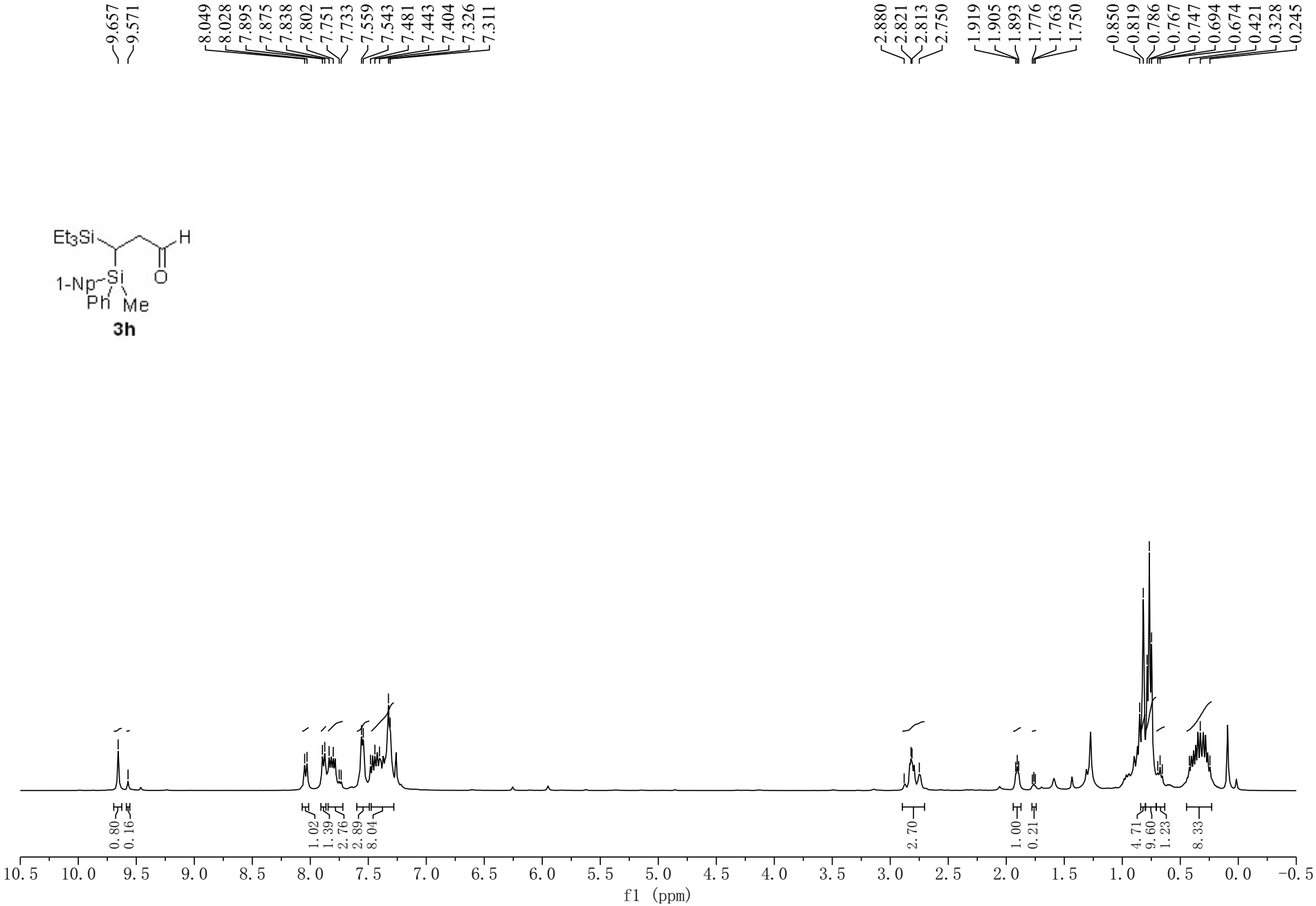
3g



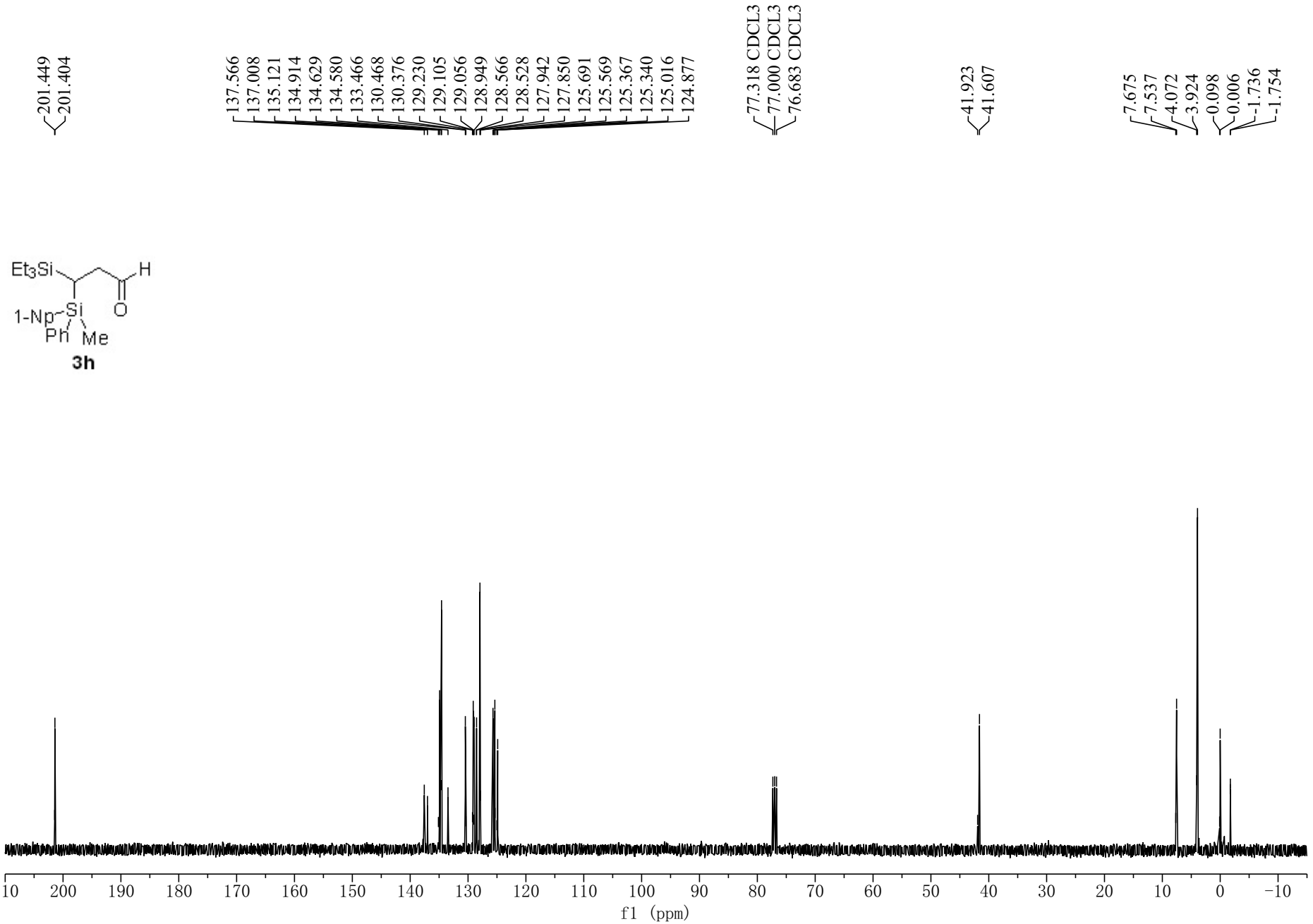
WY-6-66 C13 CDCl3 100M Hz



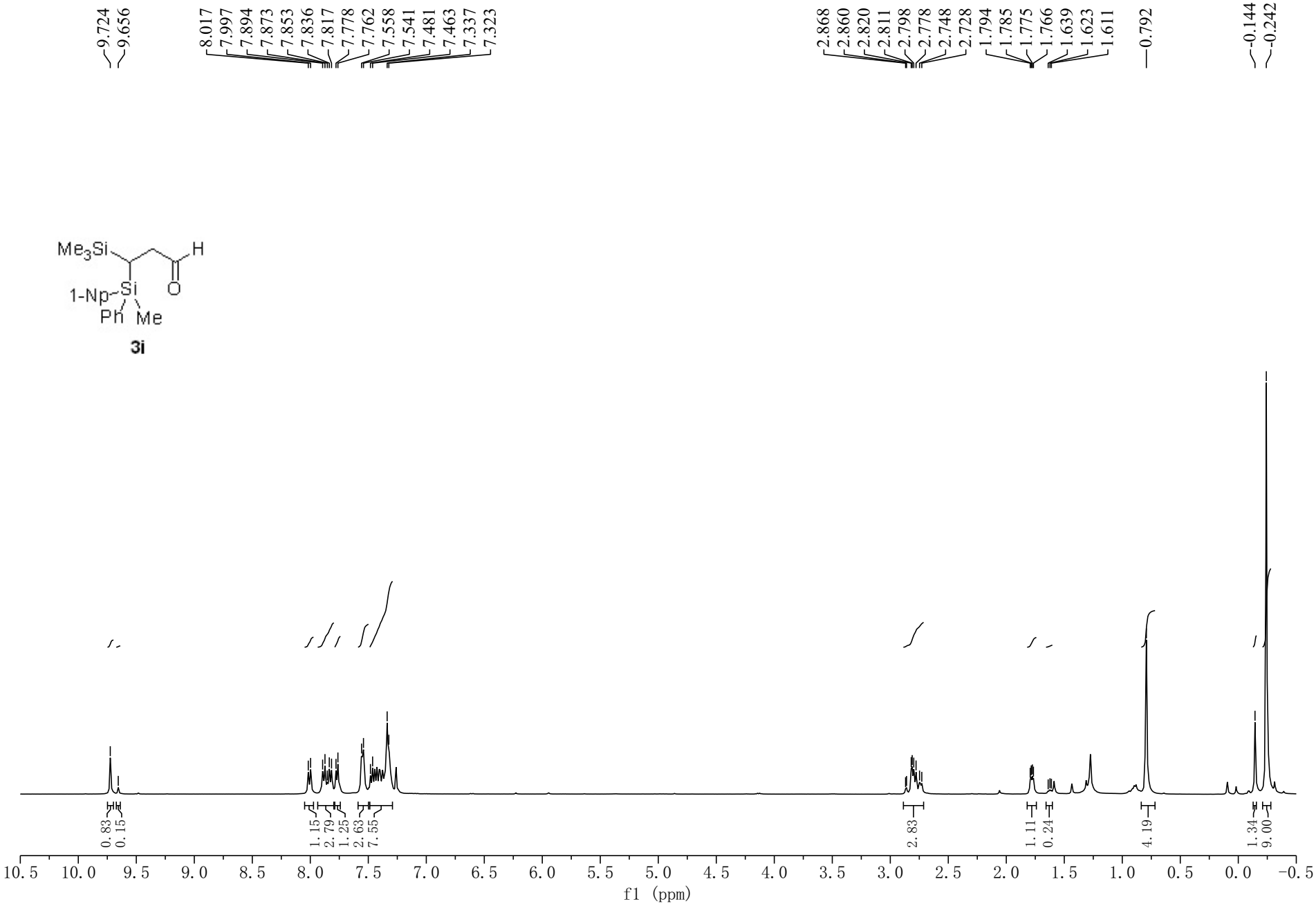
CH-1-20 H1 CDCl3 400M Hz



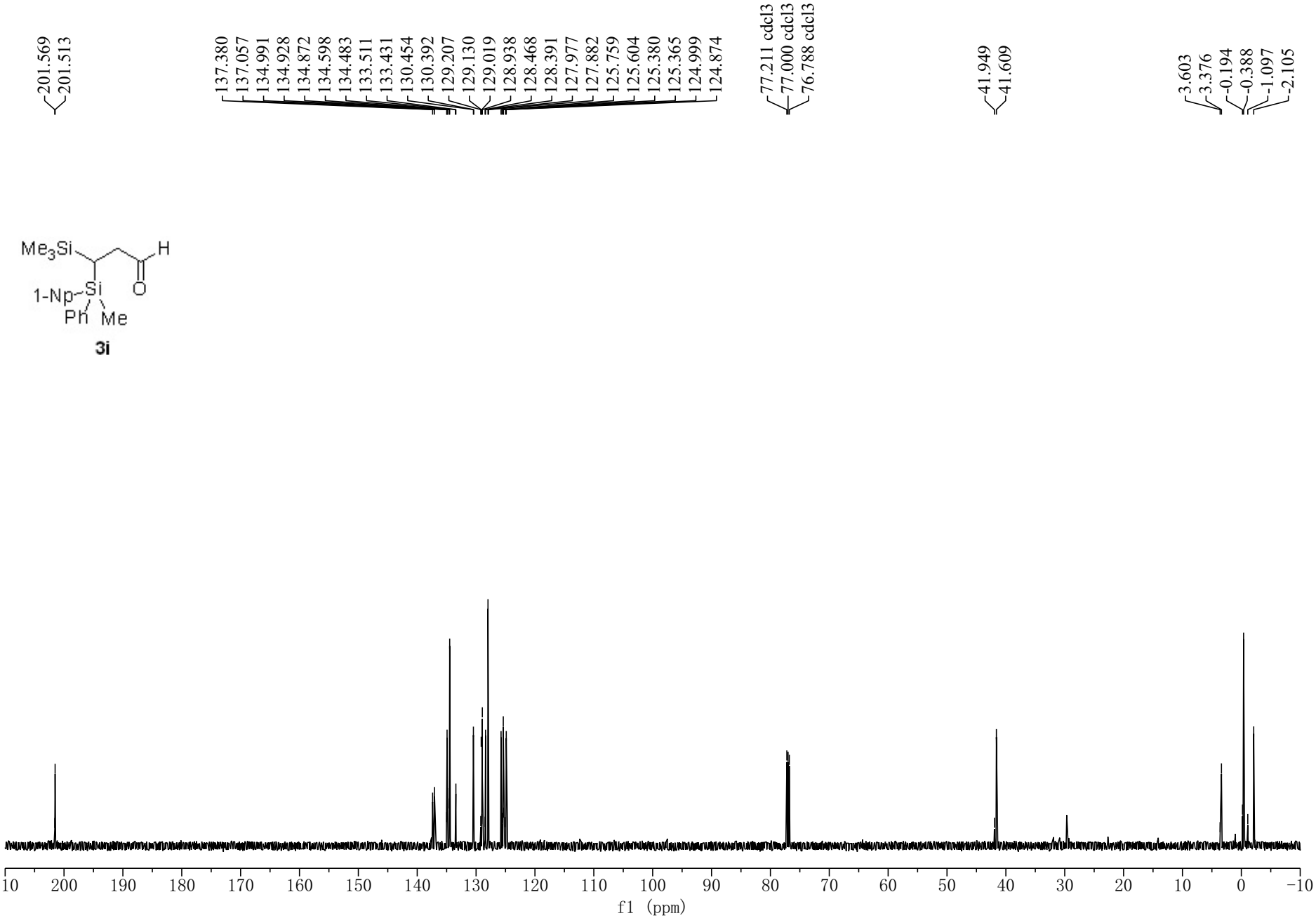
WY-6-82B C13 CDCl3 100M Hz



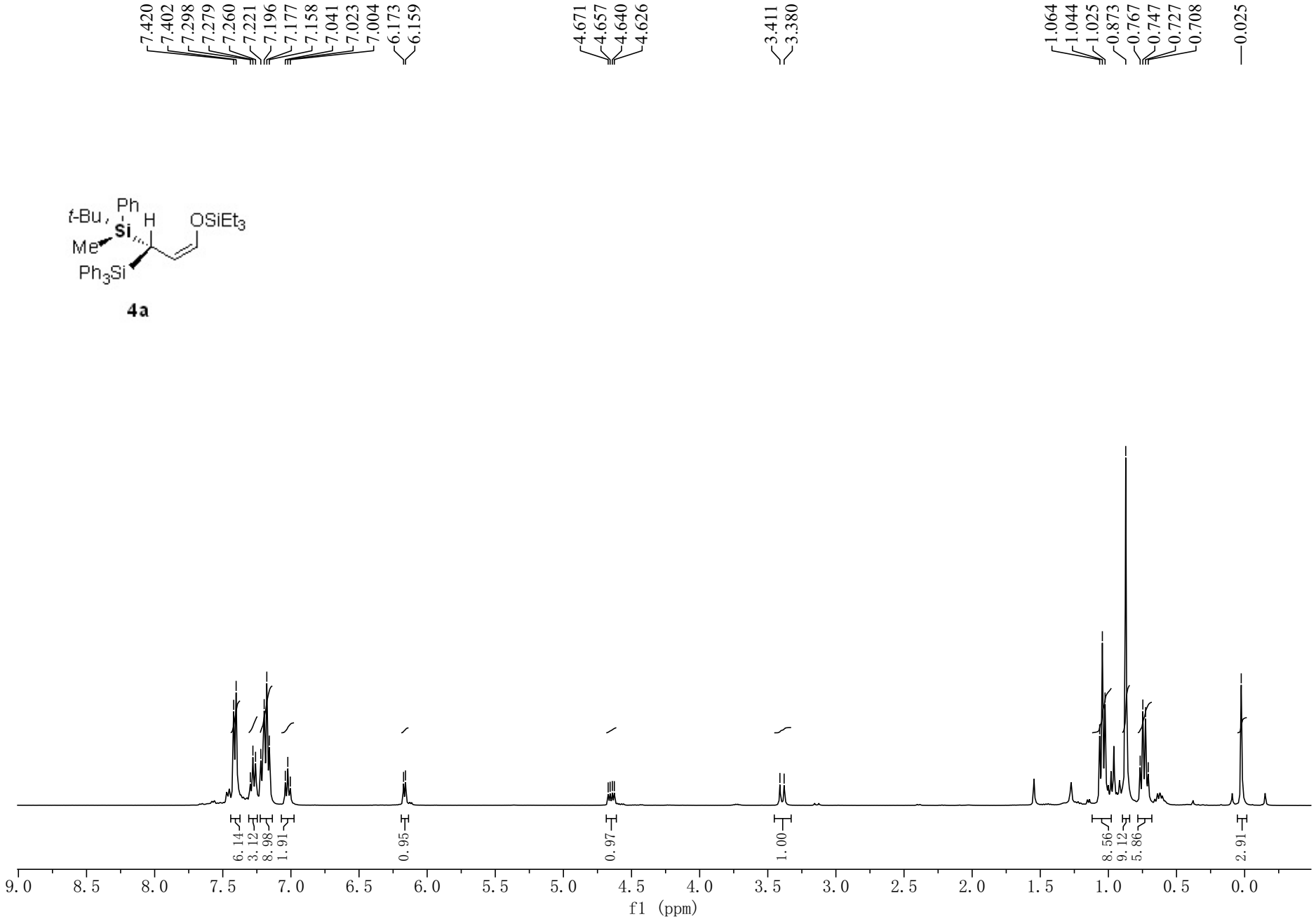
CH-1-21 H1 CDCl3 400M Hz



CH-1-21 C13 CDCl3 150M Hz

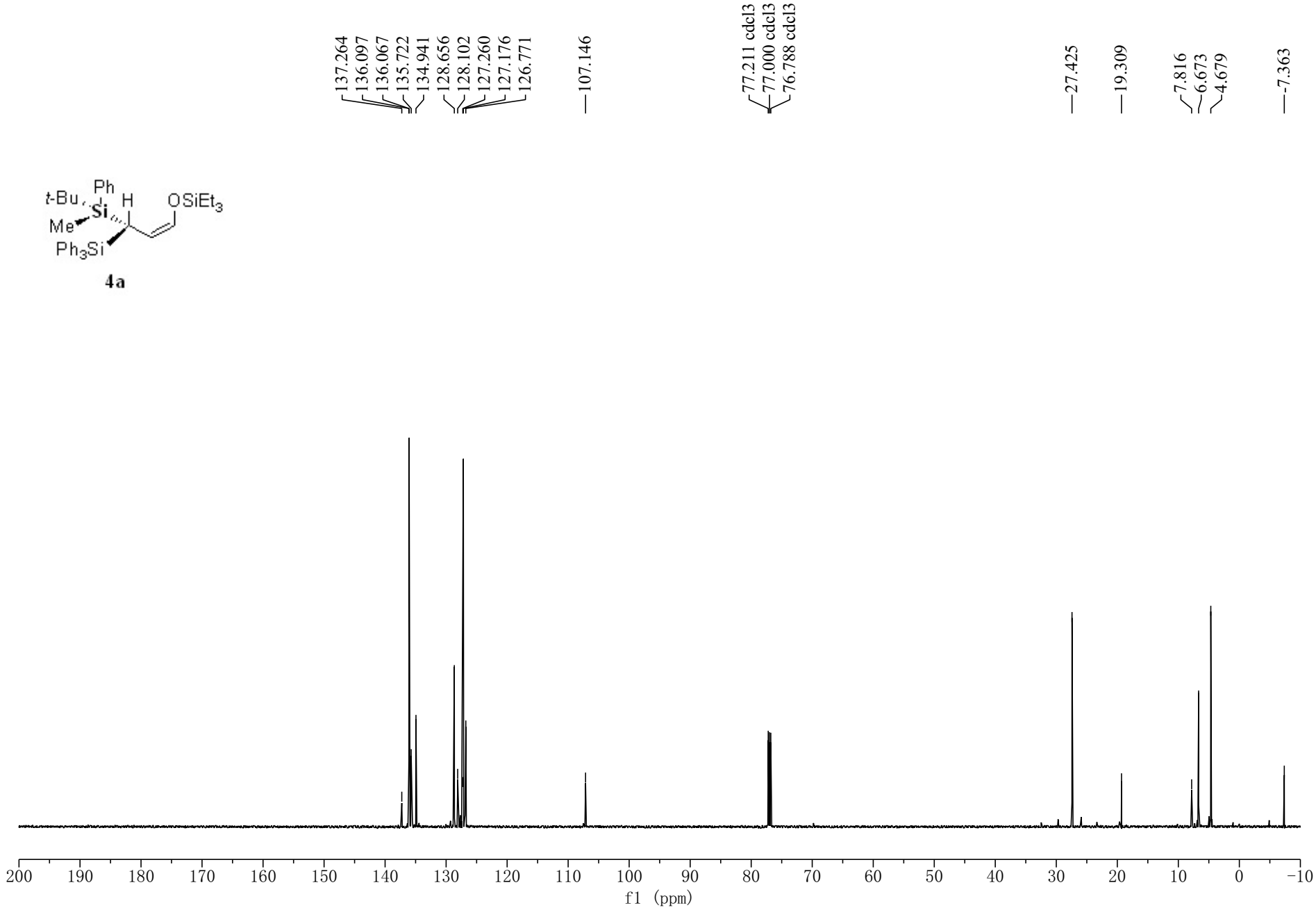


WY-7-43A H1 CDCl3 400M Hz



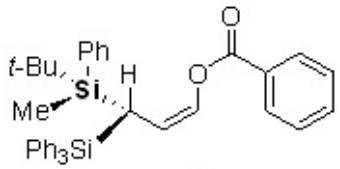
4a

WY-7-43A C13 CDCl3 150M Hz

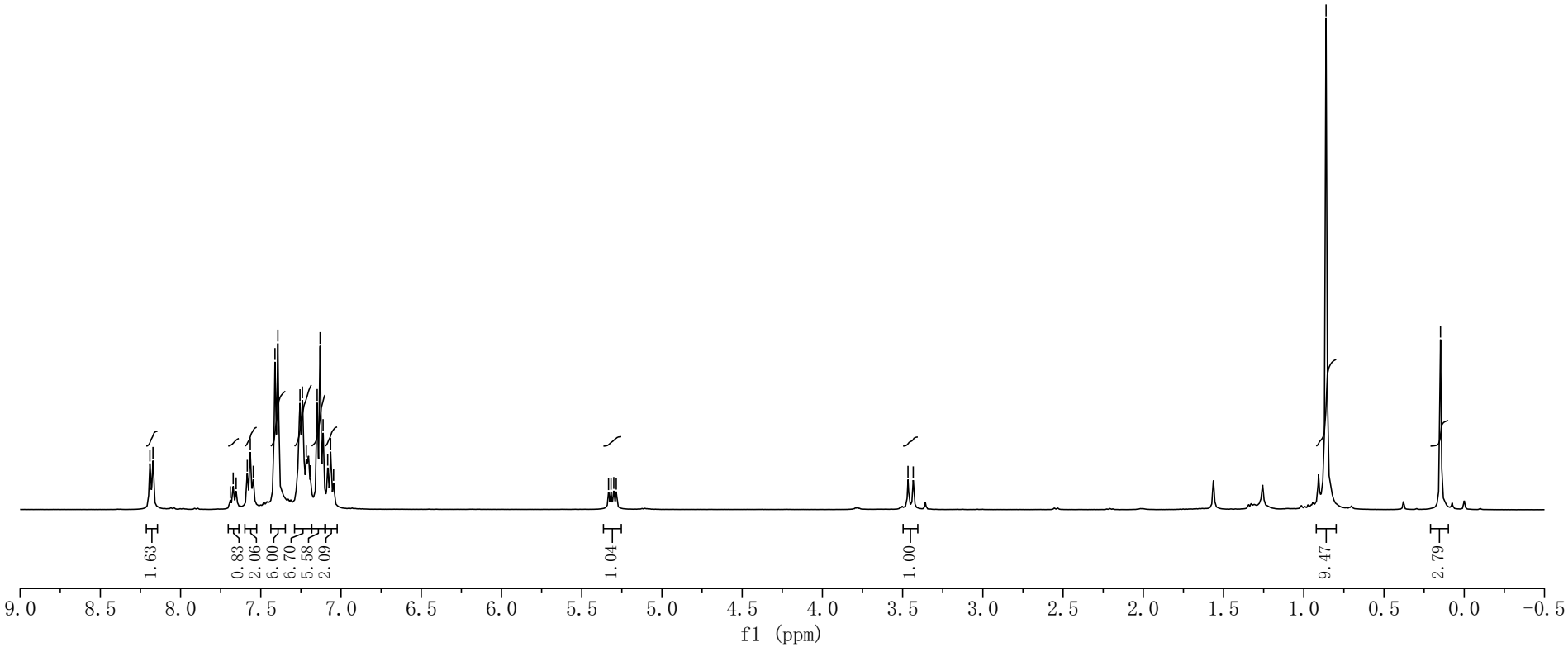


WY-7-51-3 H1 CDCl3 400M Hz

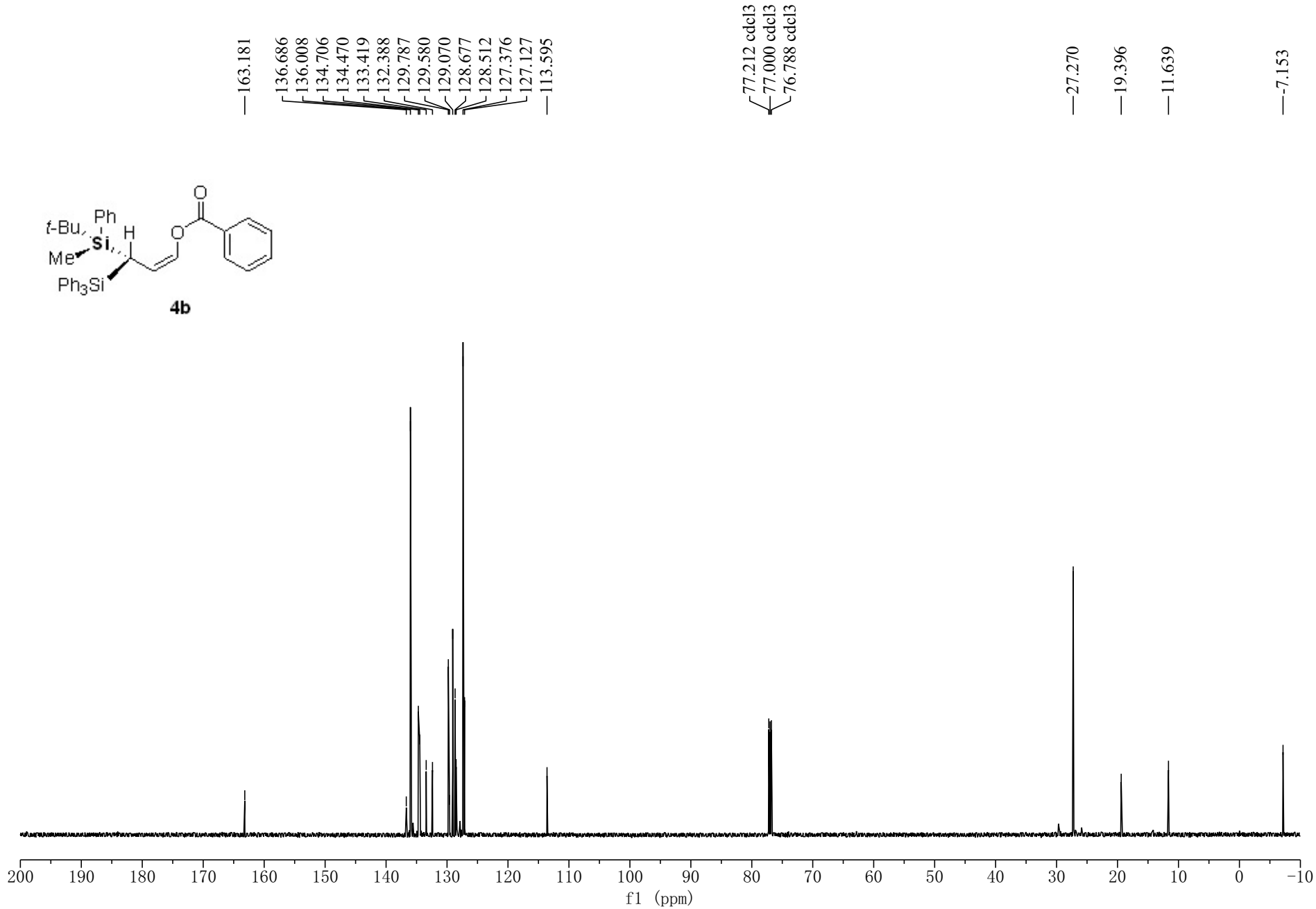
8.191
8.172
7.690
7.672
7.654
7.584
7.565
7.547
7.412
7.393
7.256
7.241
7.216
7.191
7.149
7.130
7.112
7.083
7.065
7.046
5.333
5.317
5.300
5.285
3.467
3.434
0.861
0.148



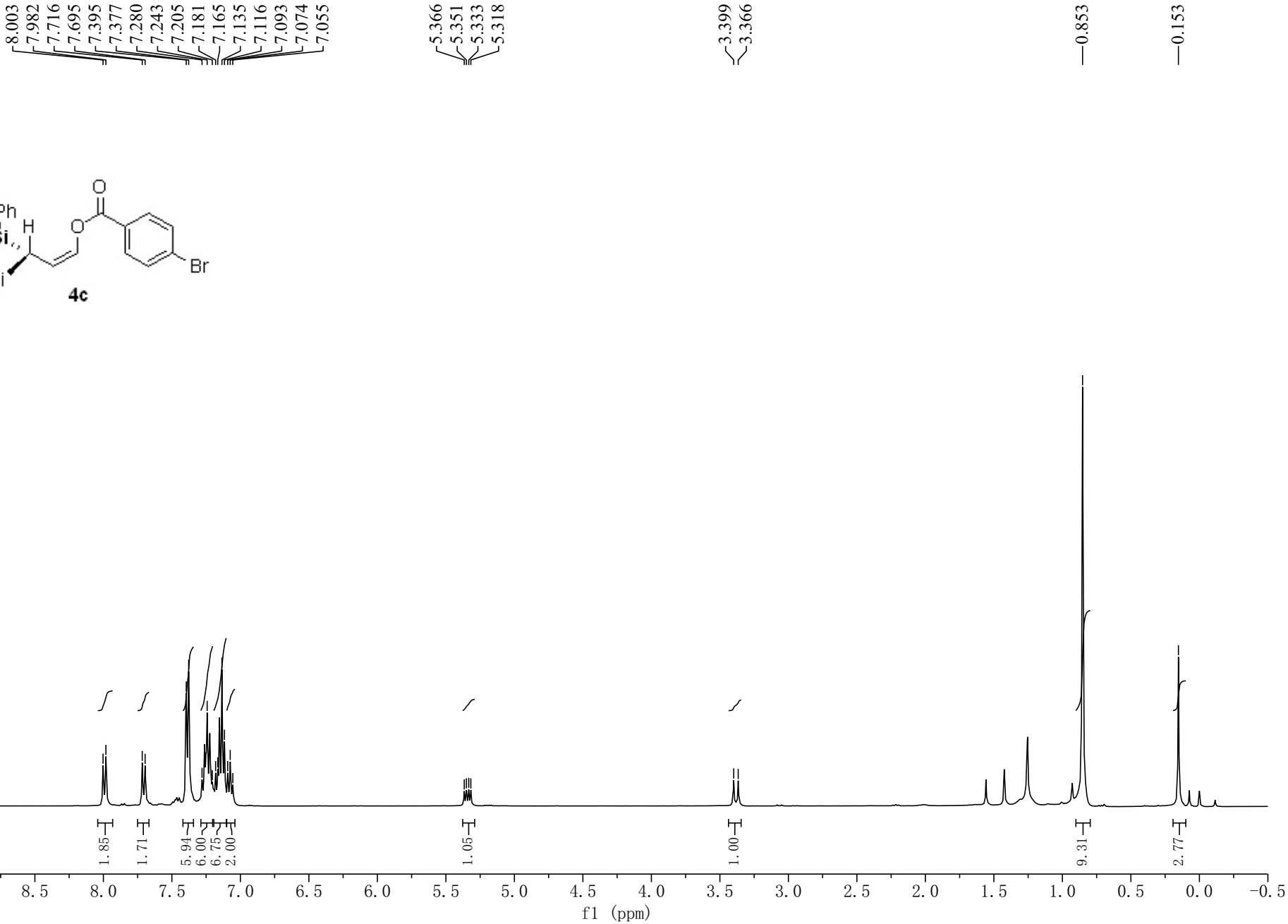
4b



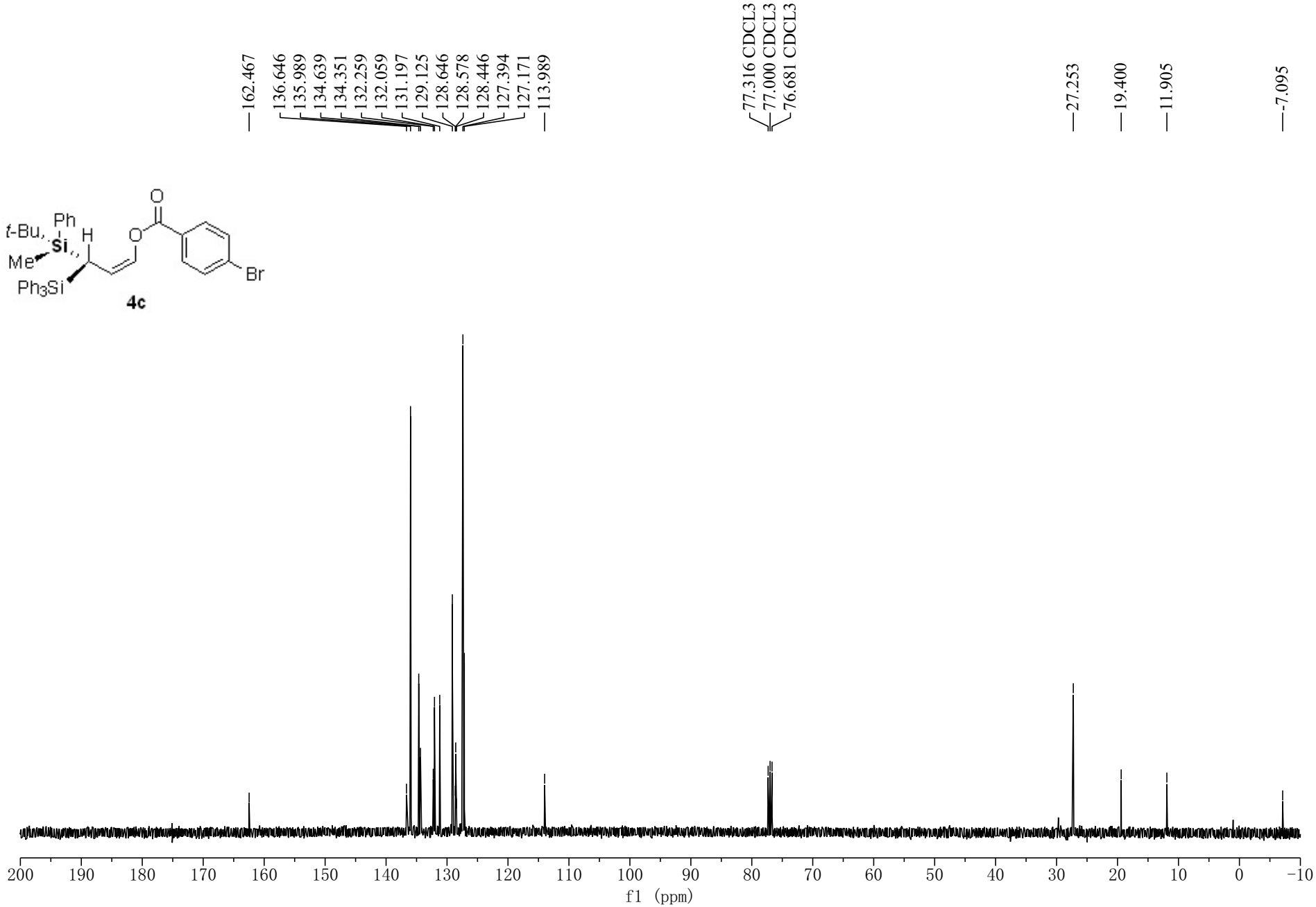
WY-7-51-3 C13 CDCl3 150M Hz



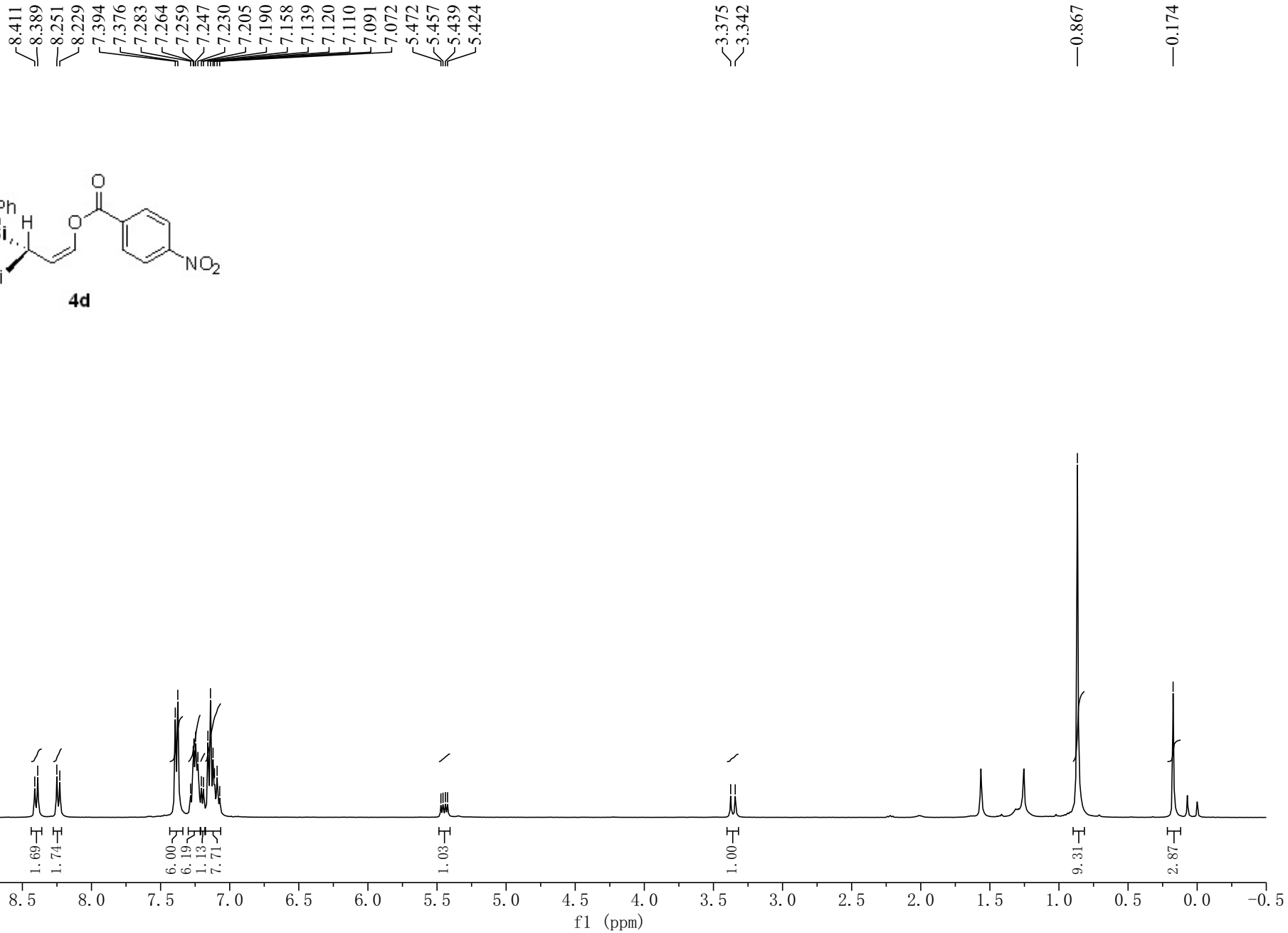
WY-7-44 H1 CDCl3 400M Hz



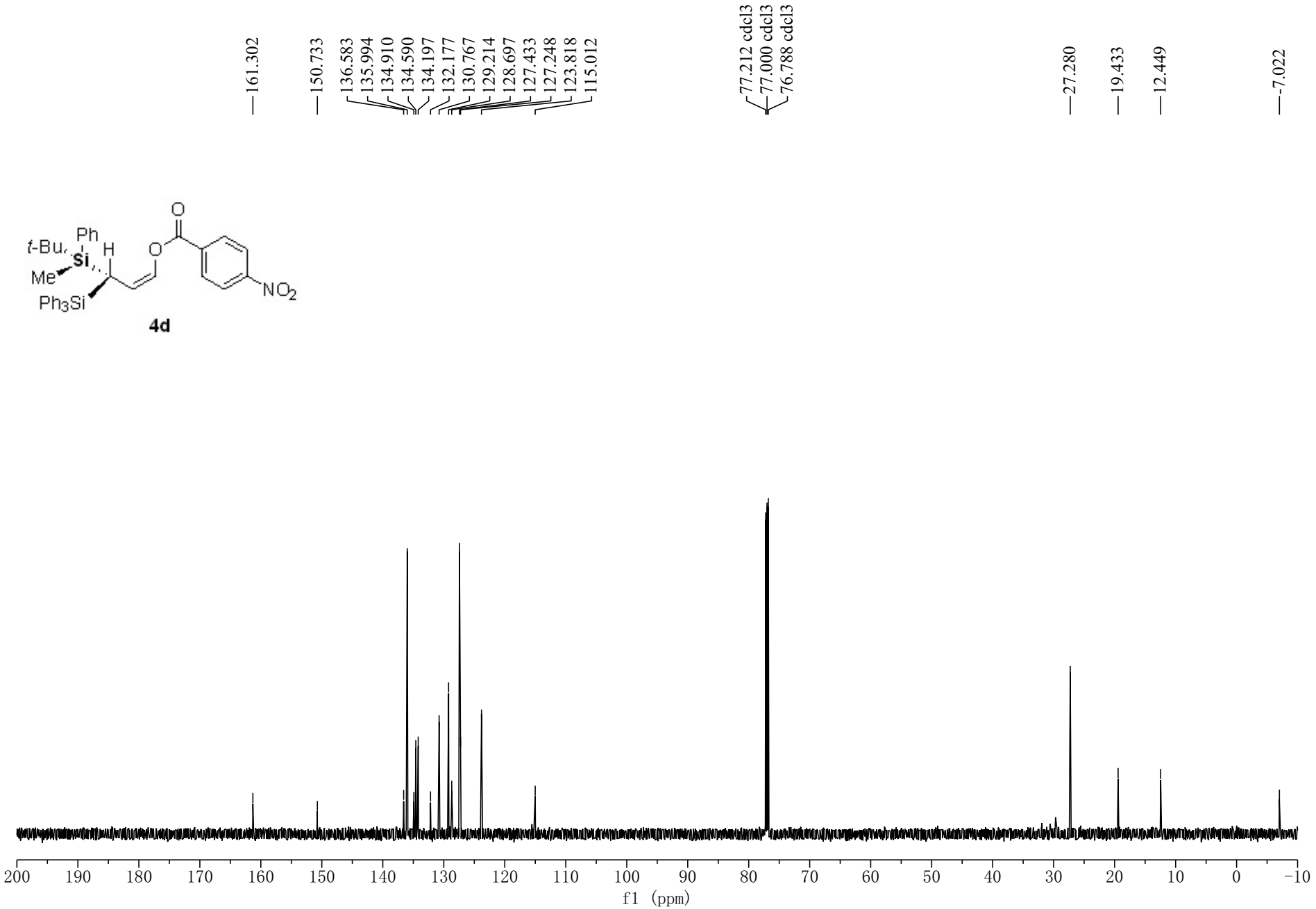
WY-7-44 C13 CDCl3 150M Hz



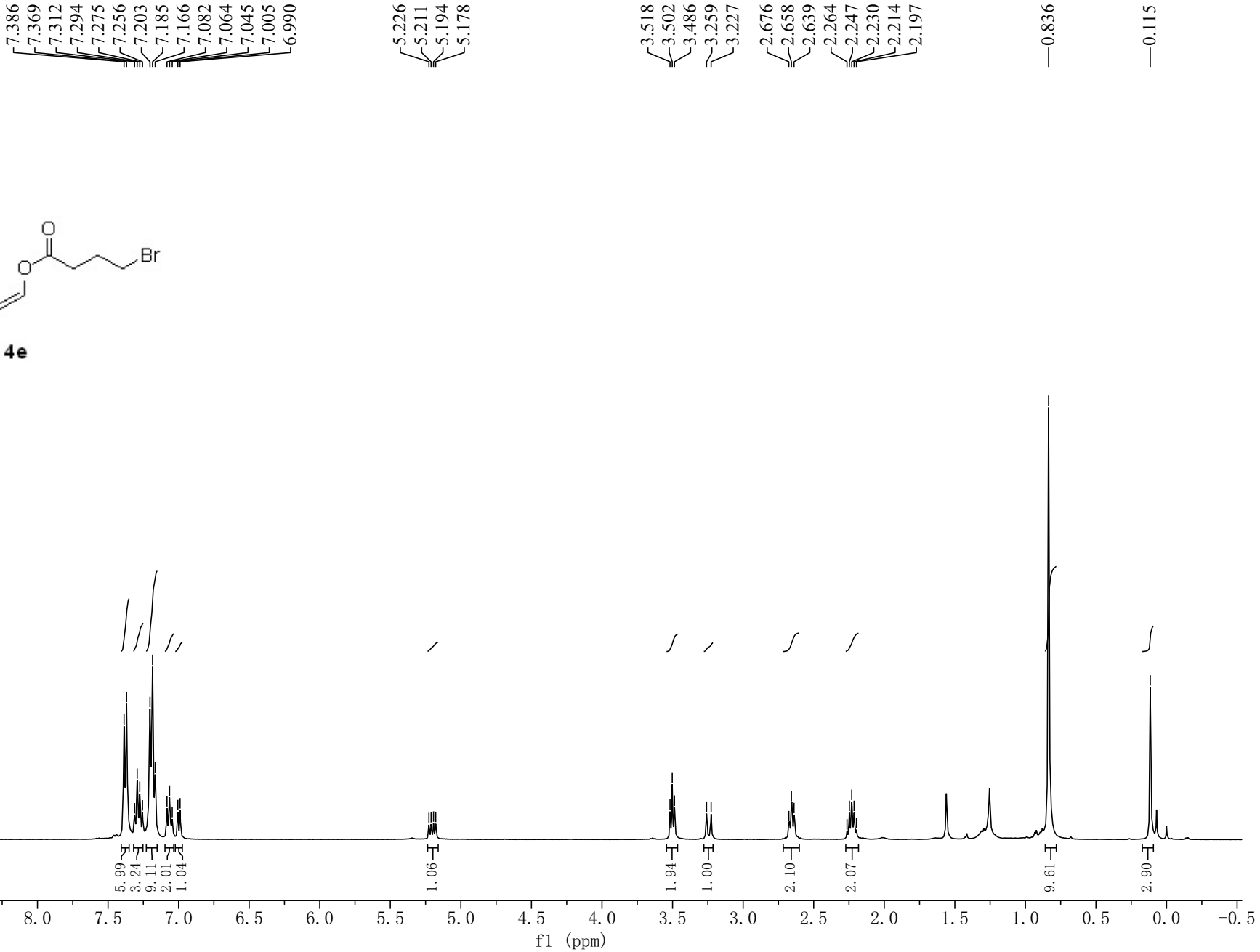
WY-7-109-1 H1 CDCl3 400M Hz



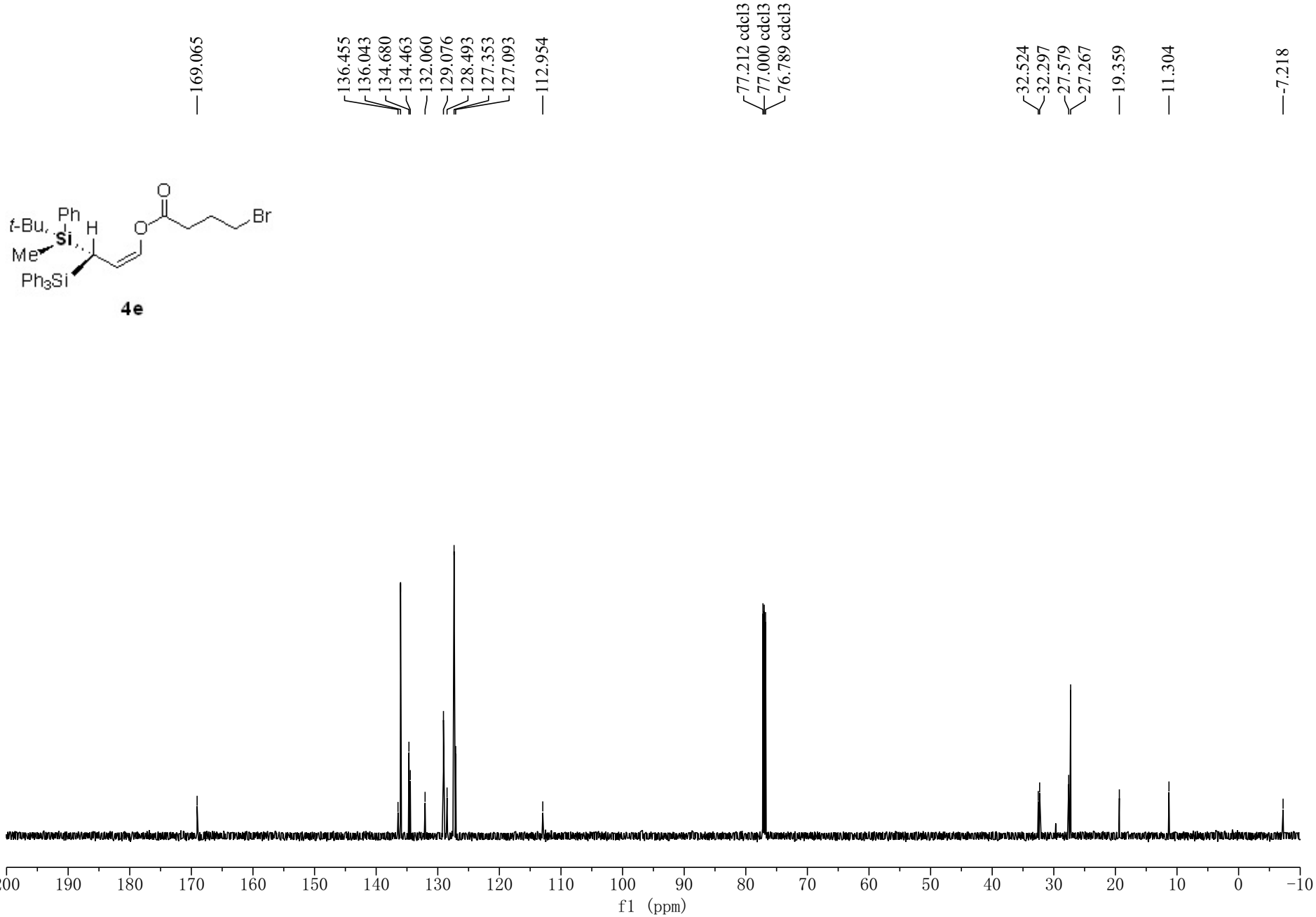
WY-7-109-1 C13 CDCl3 150M Hz



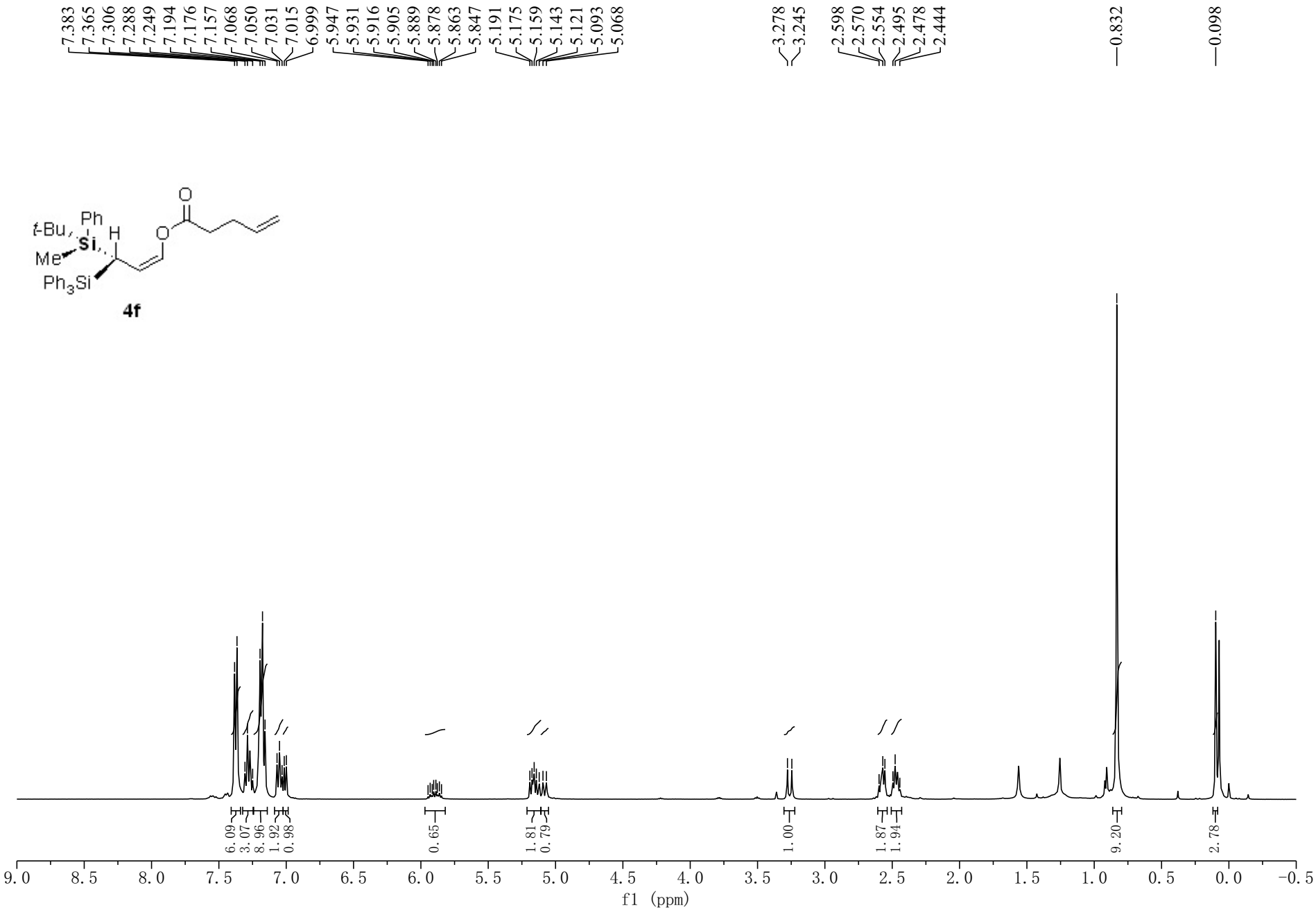
WY-7-108-1 H1 CDCl3 400M Hz



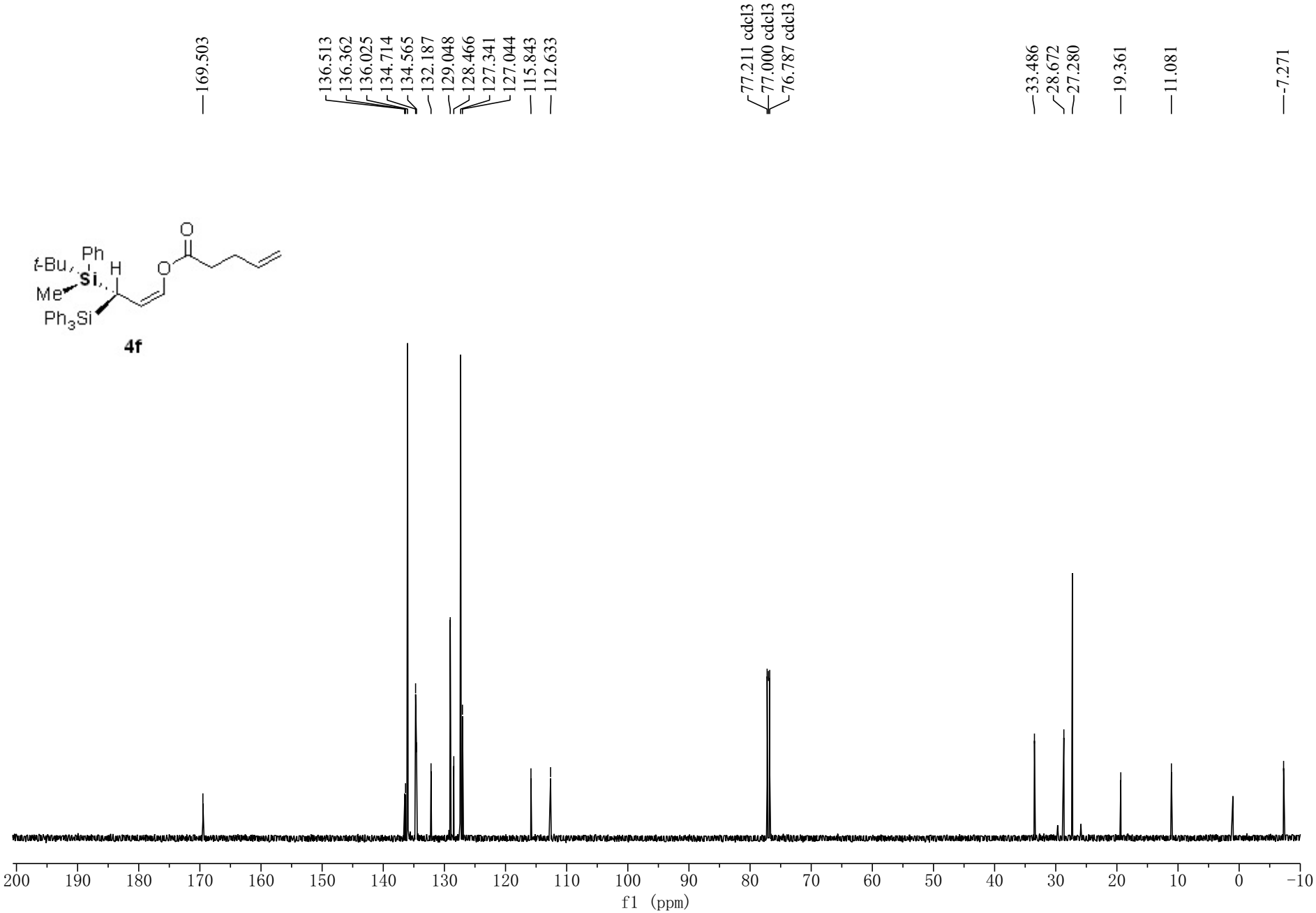
WY-7-108-1 C13 CDCl3 150M Hz



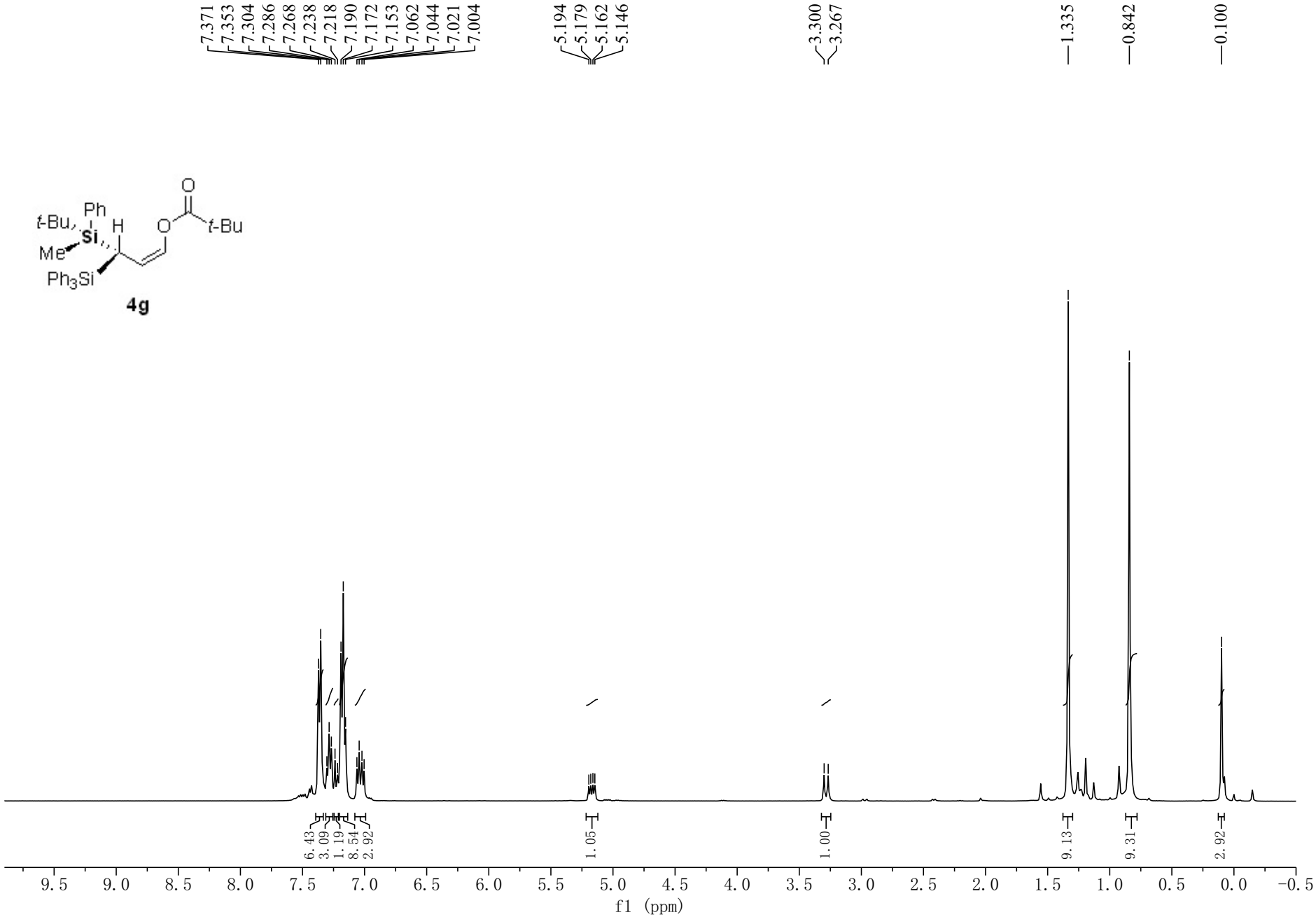
WY-7-74-2B-2 H1 CDCl3 400M Hz



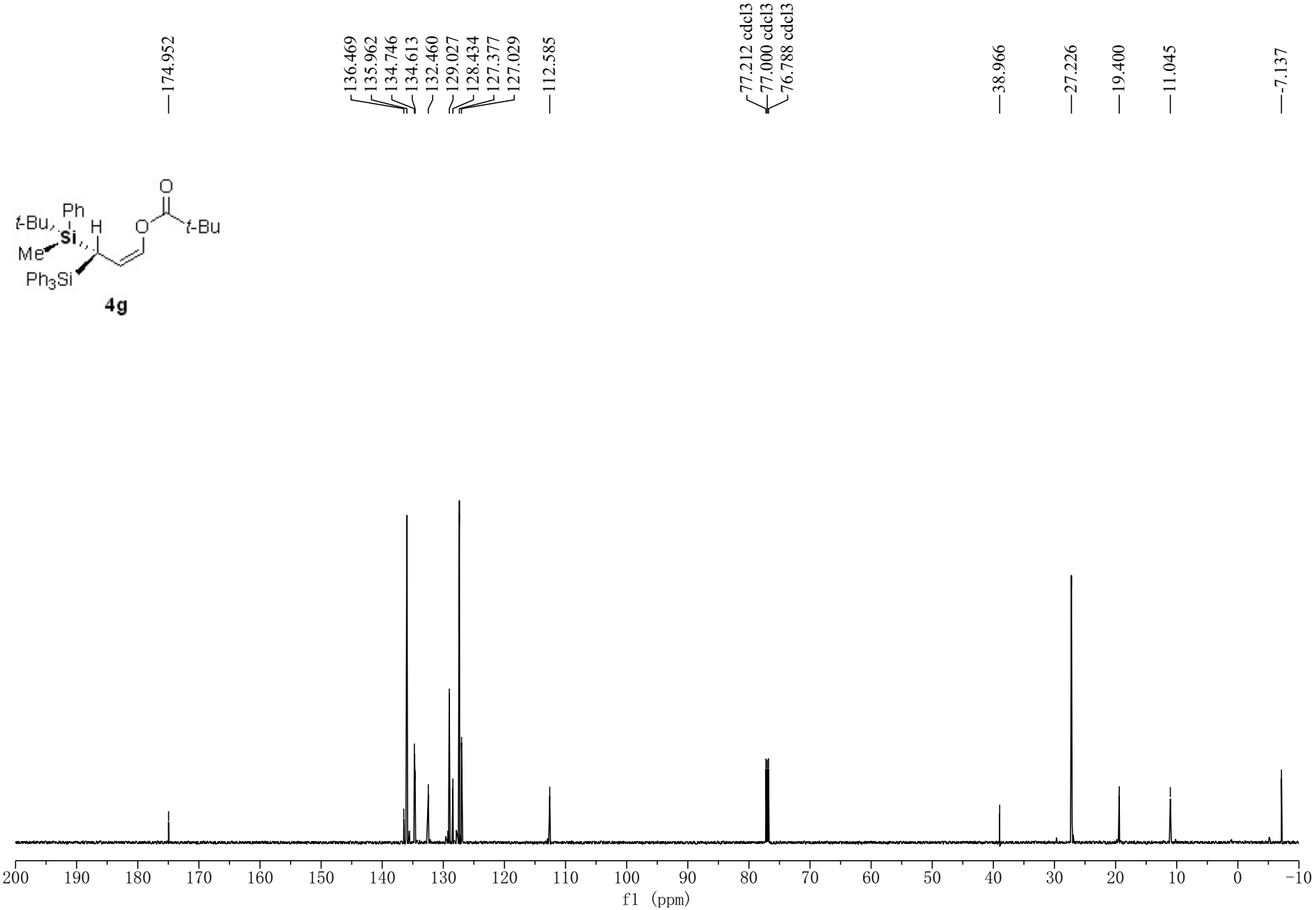
WY-7-74-2B-2 C13 CDCl3 150M Hz



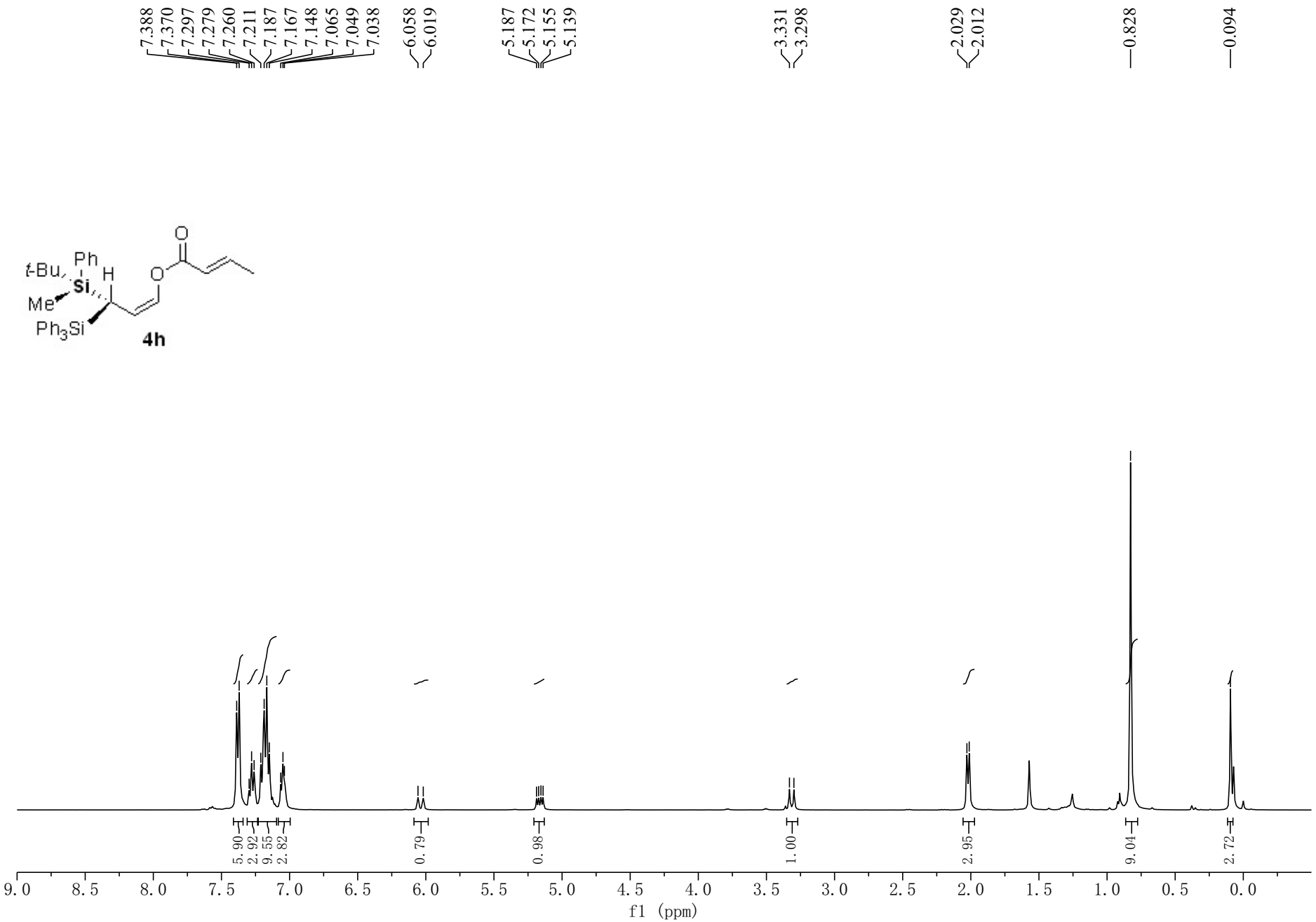
WY-7-45B-1 H1 CDCl3 400M Hz



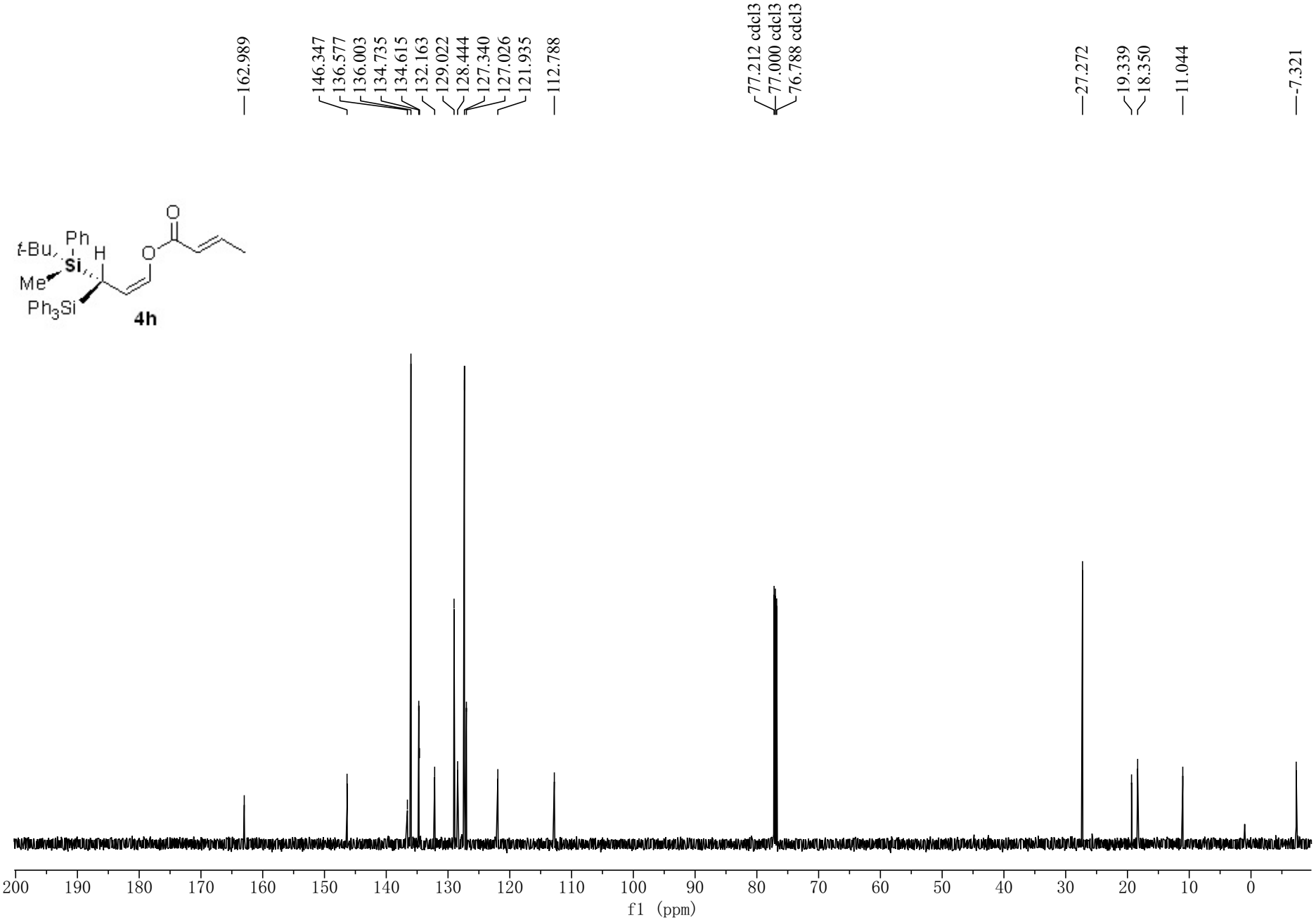
WY-7-45B-1 C13 CDCl3 150M Hz



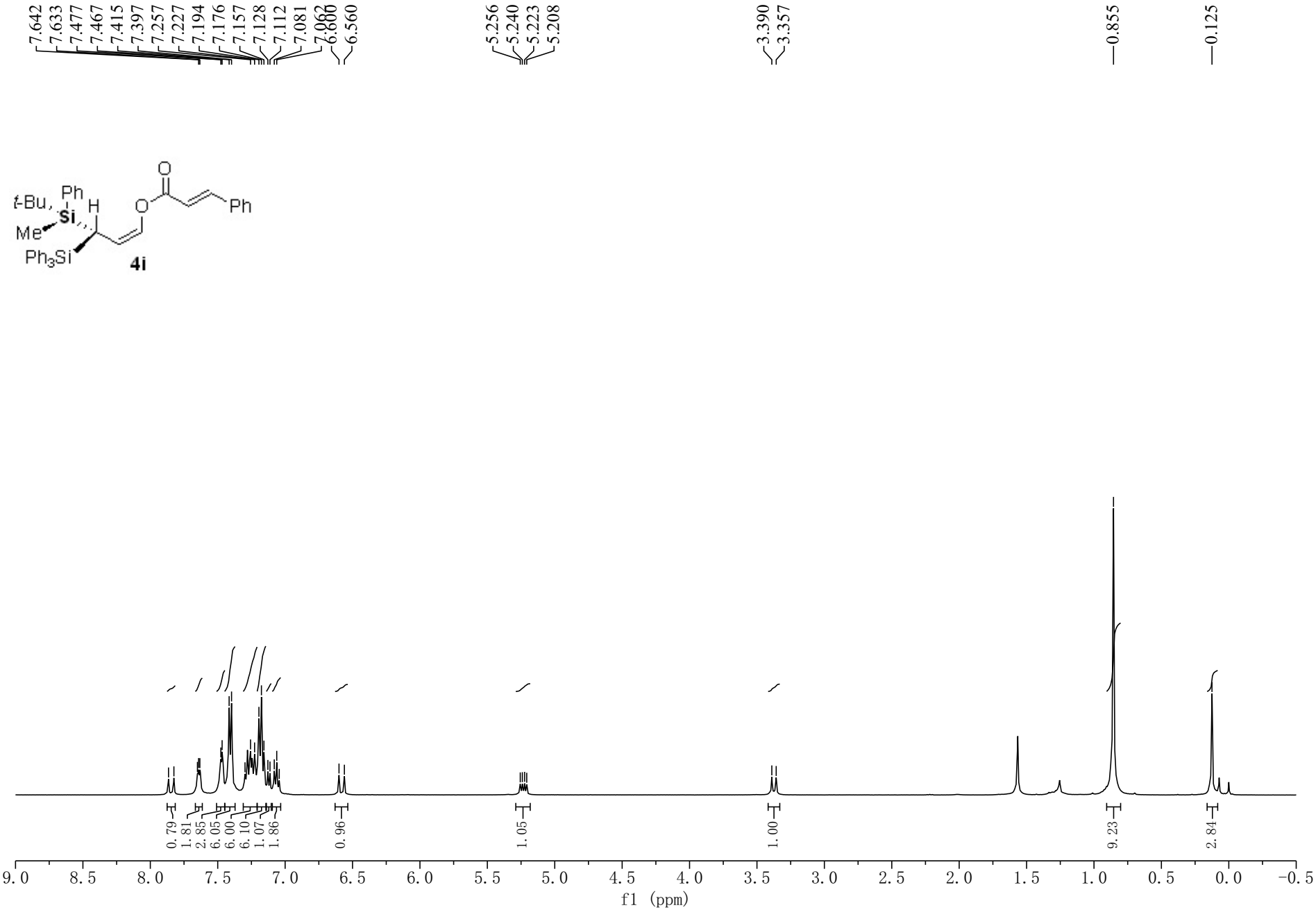
Gui-2-57B-2 H1 CDCl3 400M Hz



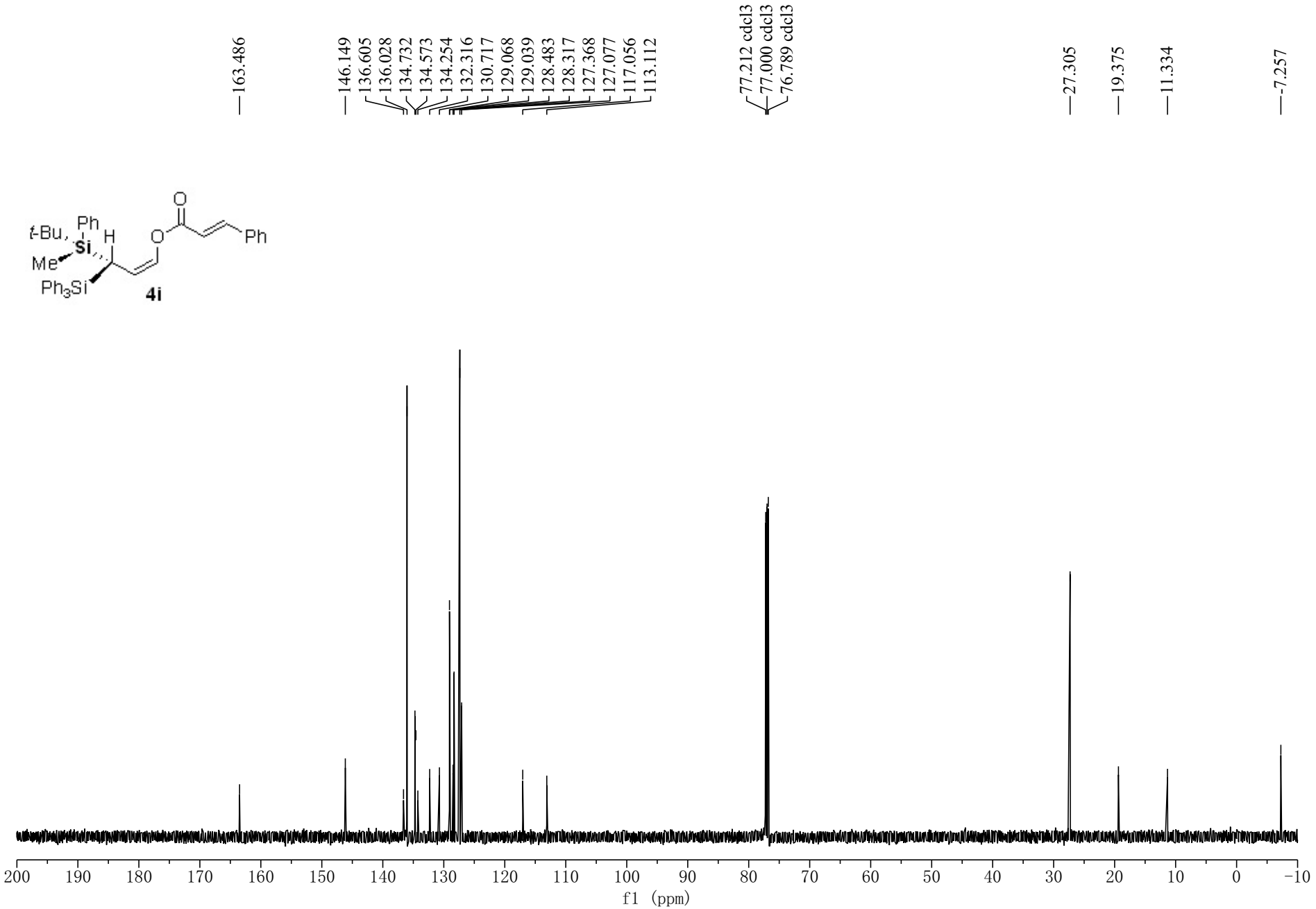
Gui-2-57B-2 C13 CDCl3 150M Hz



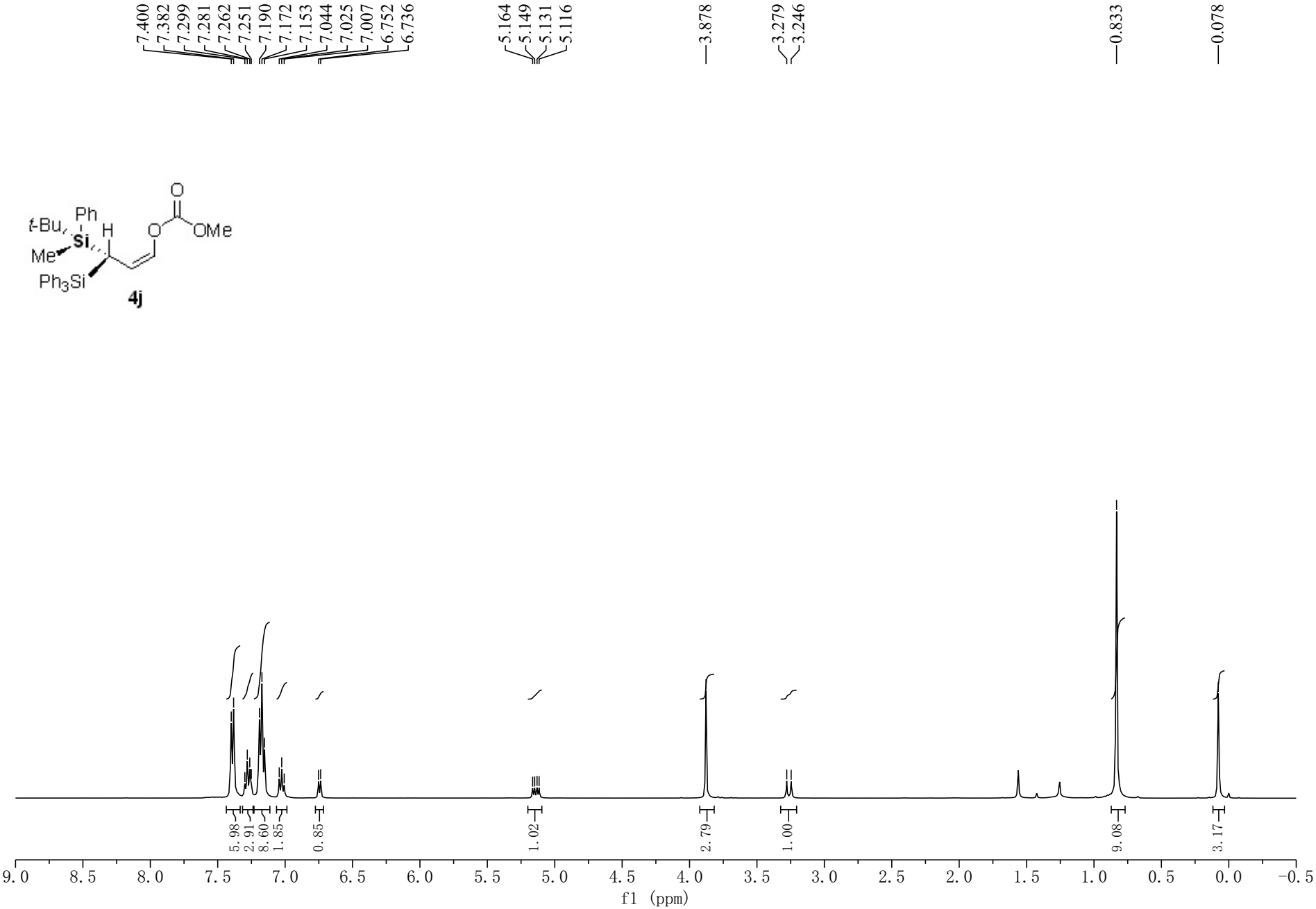
Gui-2-58B-3 H1 CDCl3 400M Hz



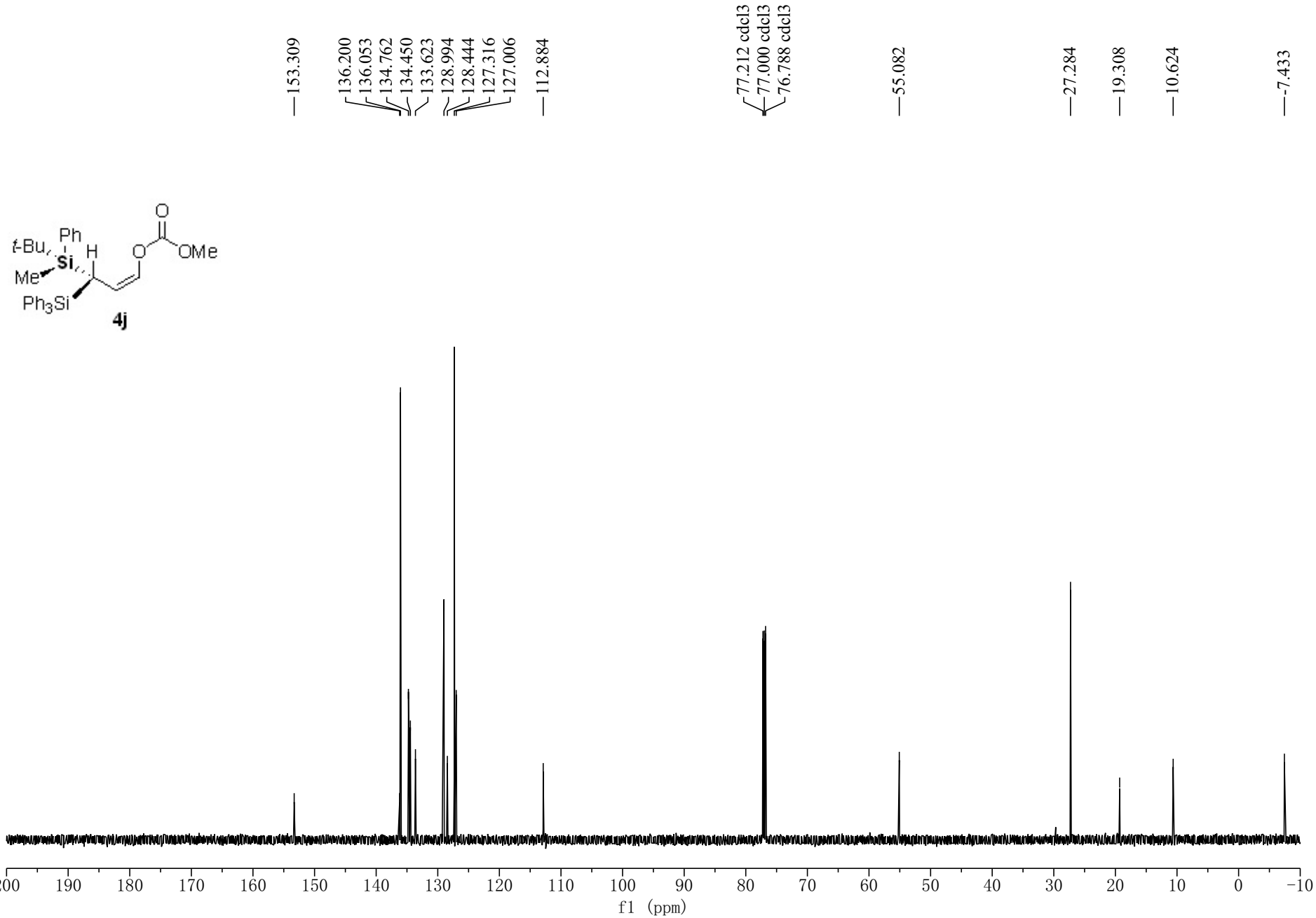
Gui-2-58B-3 C13 CDCl3 100M Hz



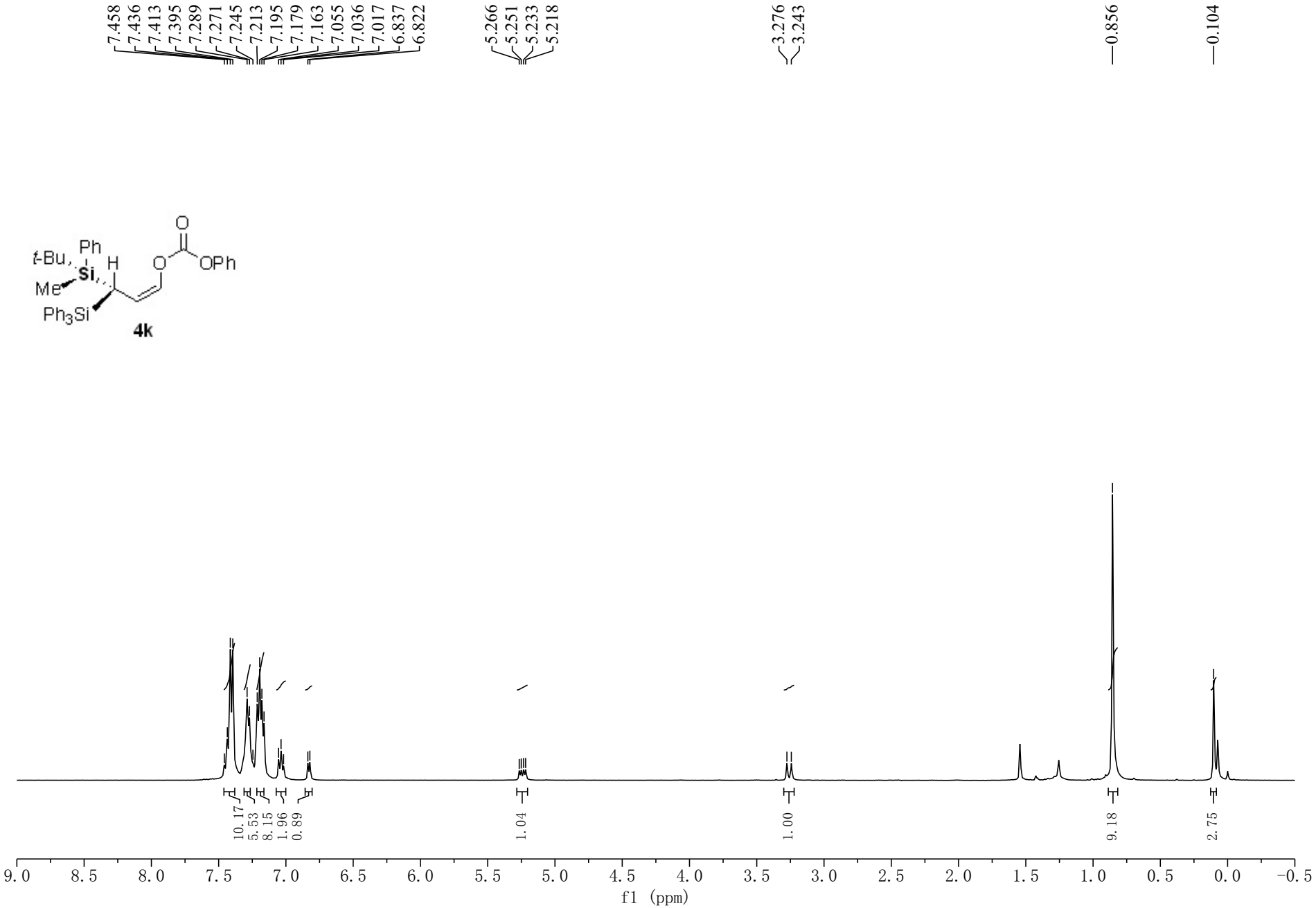
WY-7-58B H1 CDCl3 400M Hz



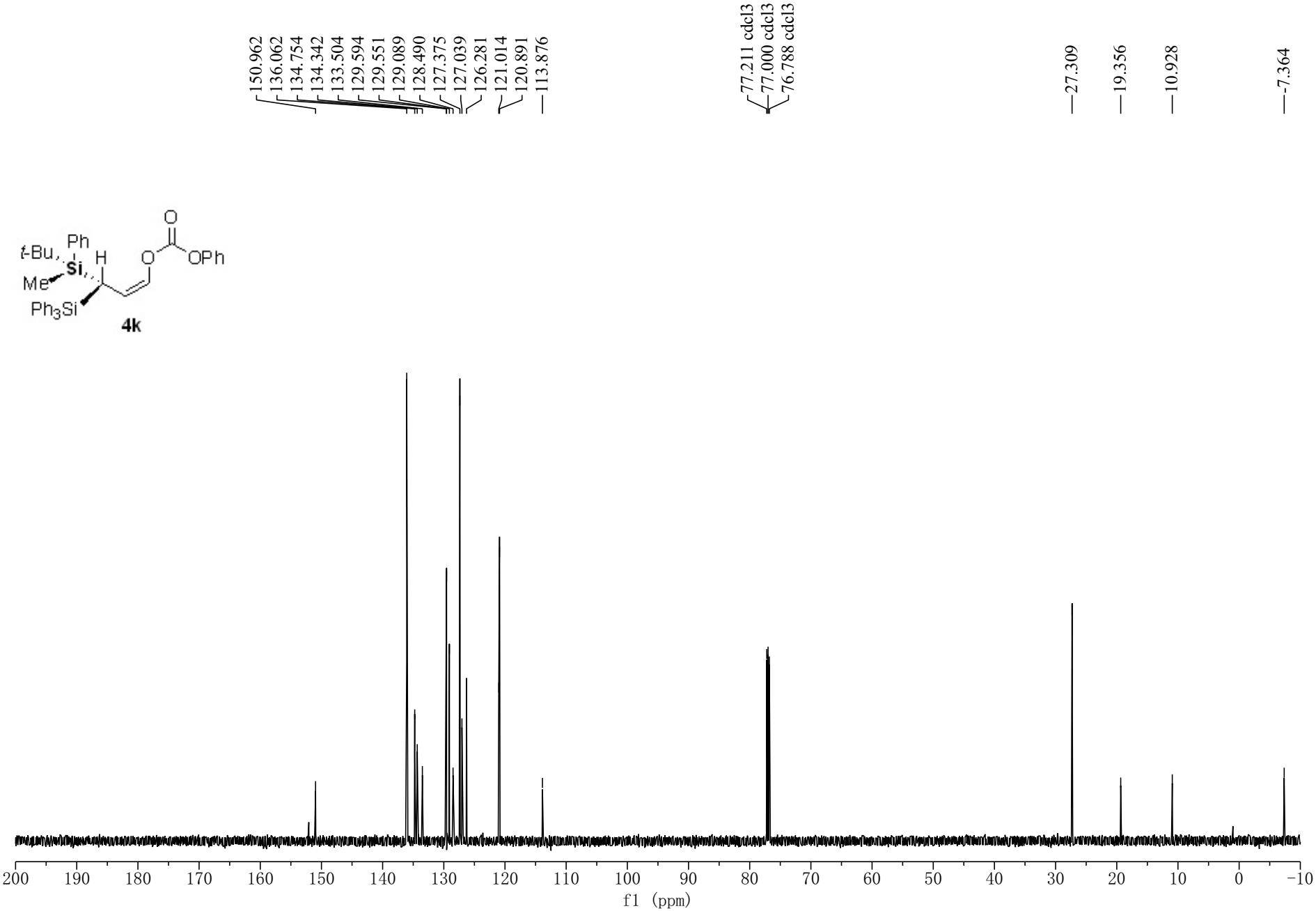
WY-7-58B C13 CDCl3 150M Hz



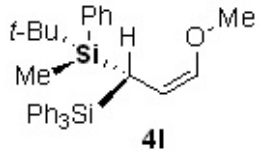
Gui-2-59-P-3 C13 CDCl3 150M Hz



Gui-2-59-P-3 C13 CDCl3 150M Hz



CH-0308 H1 CDCl3 400M Hz



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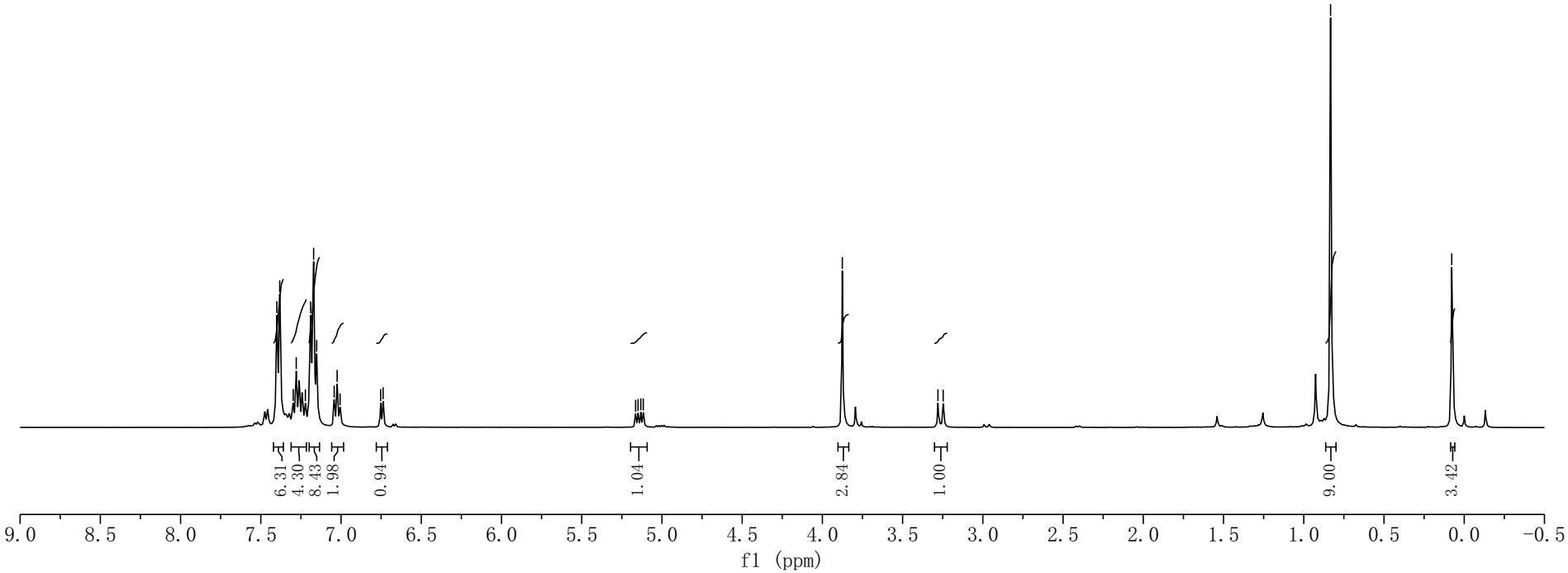
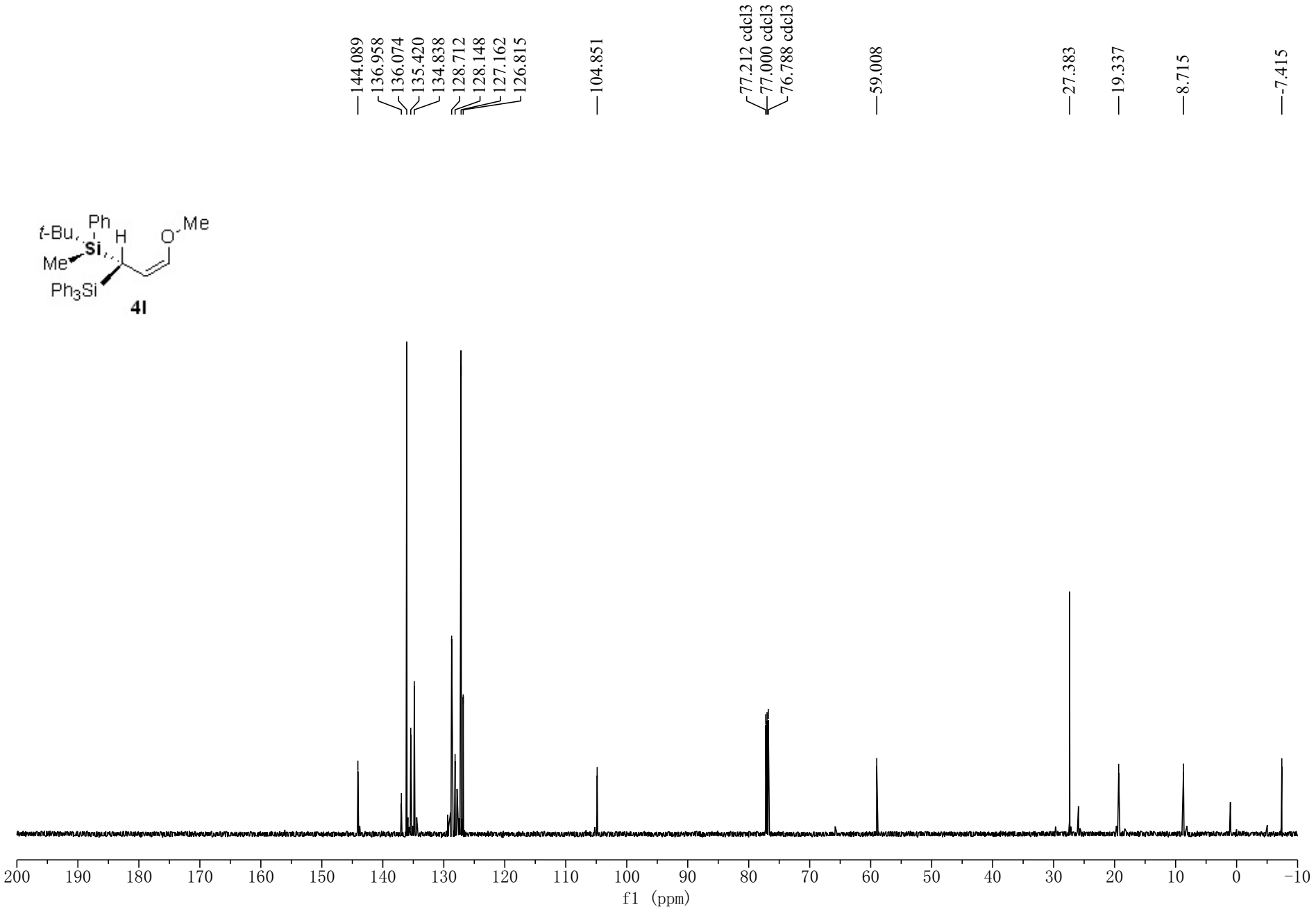
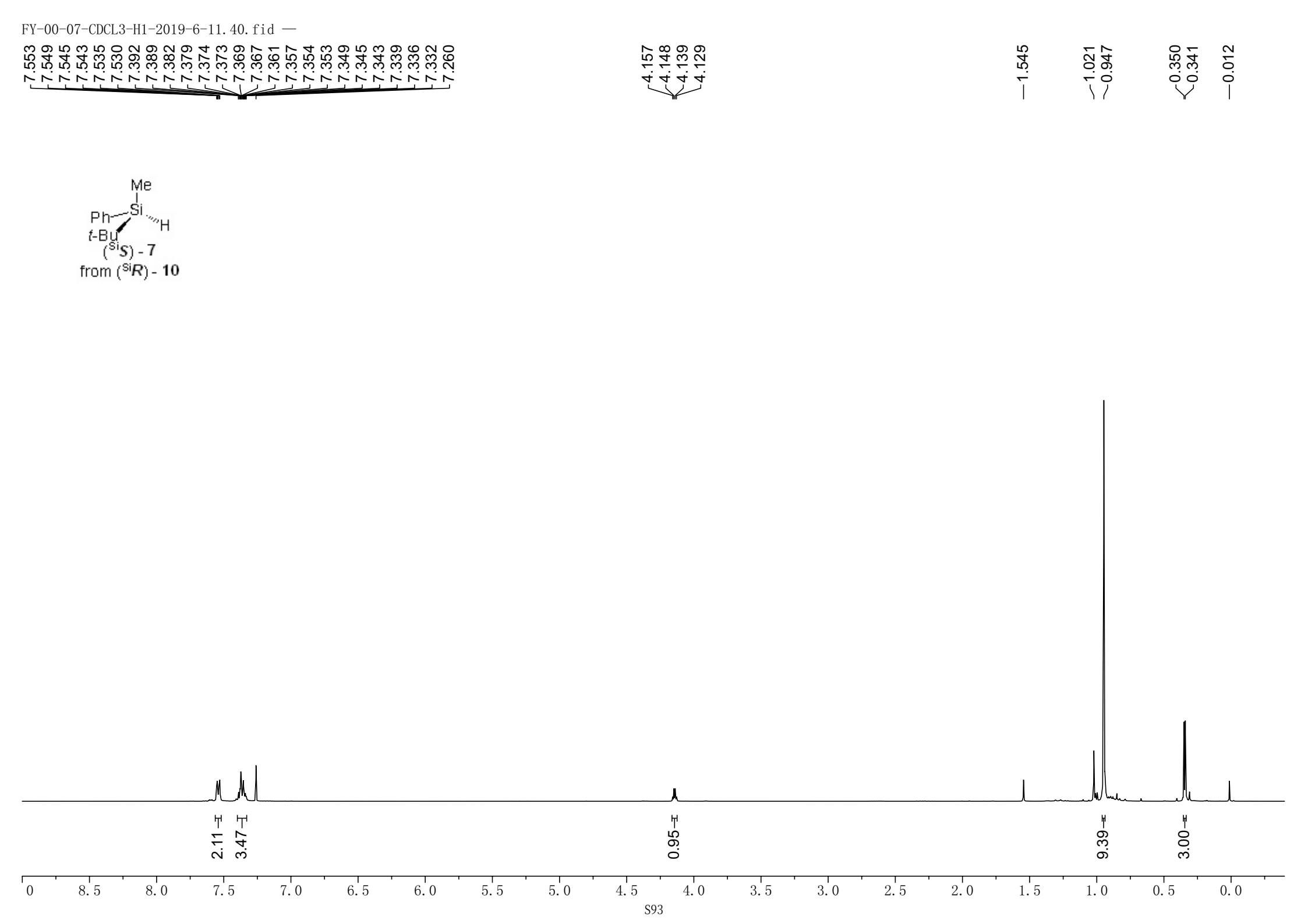


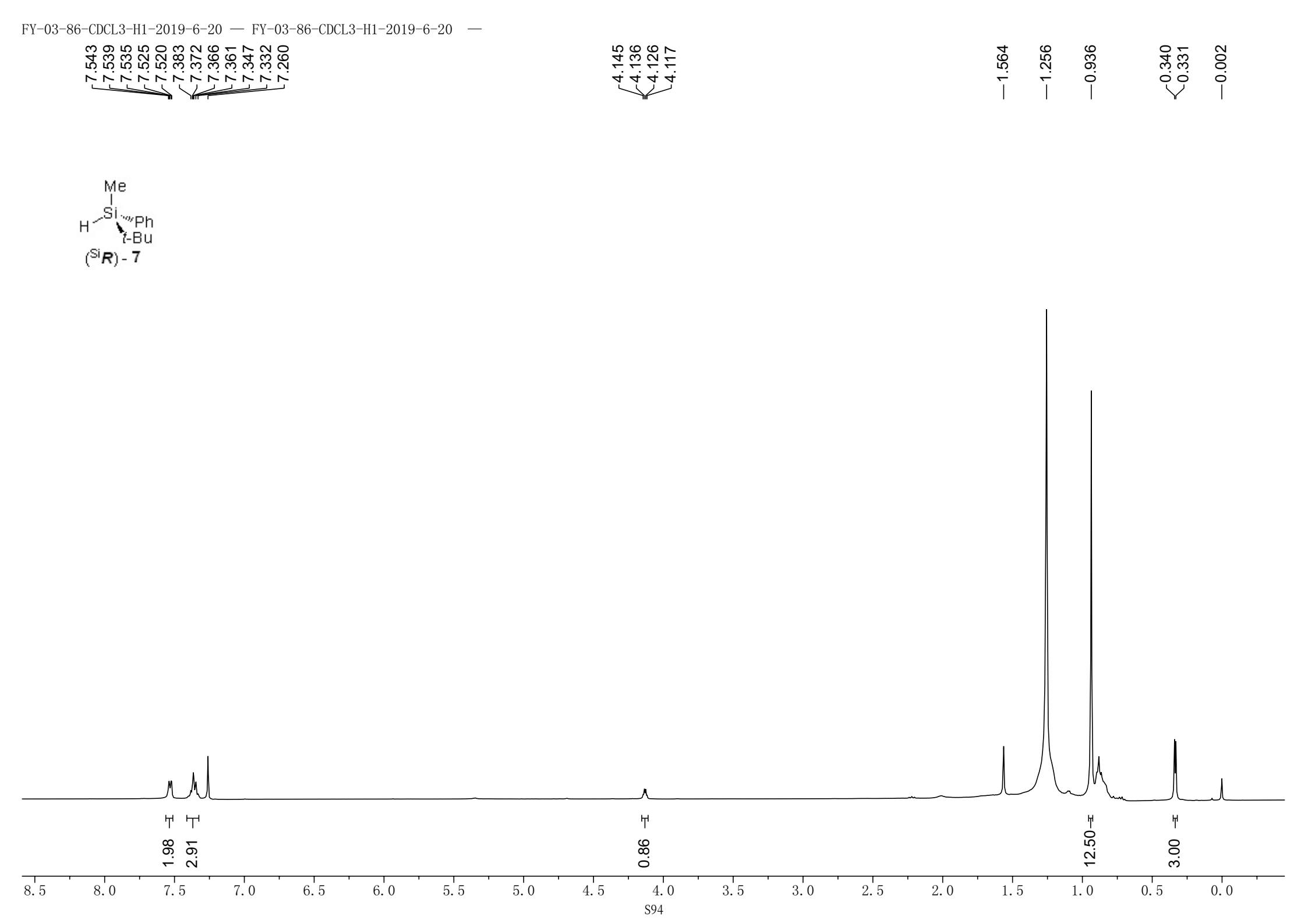
WY-7-93-3 C13 CDCl3 150M Hz



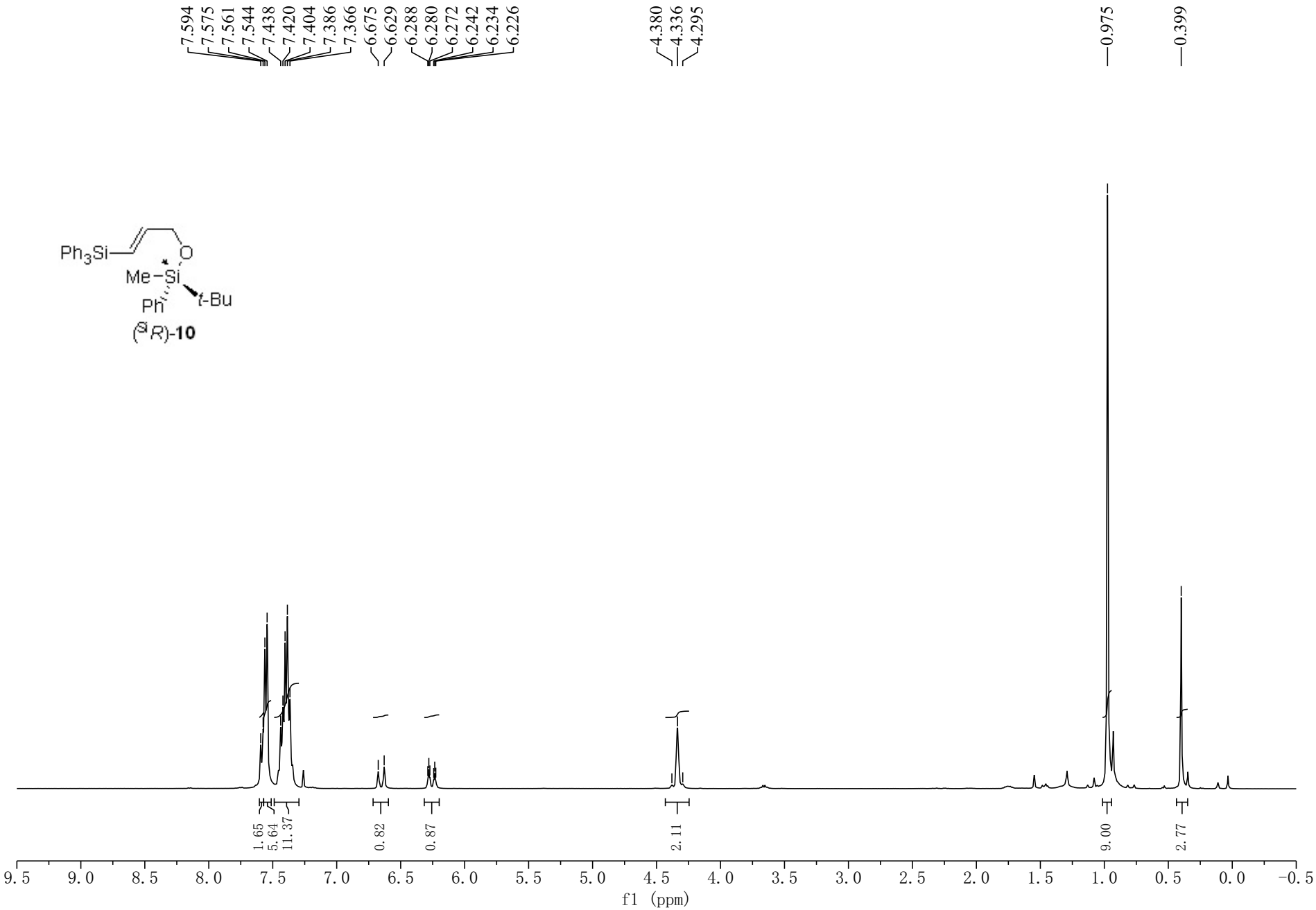
FY-00-07-CDCL3-H1-2019-6-11.40.fid



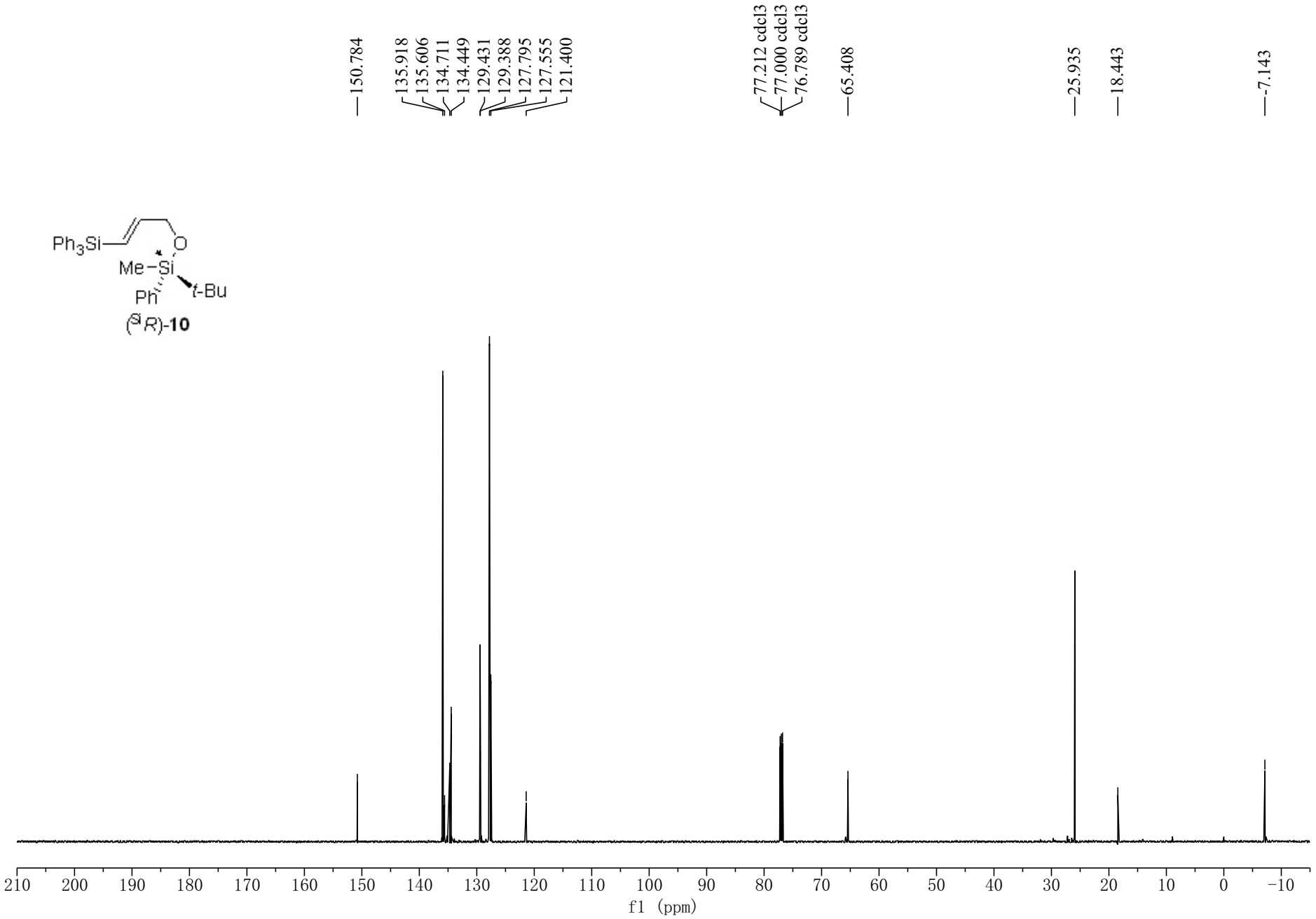
FY-03-86-CDCL3-H1-2019-6-20 — FY-03-86-CDCL3-H1-2019-6-20 —



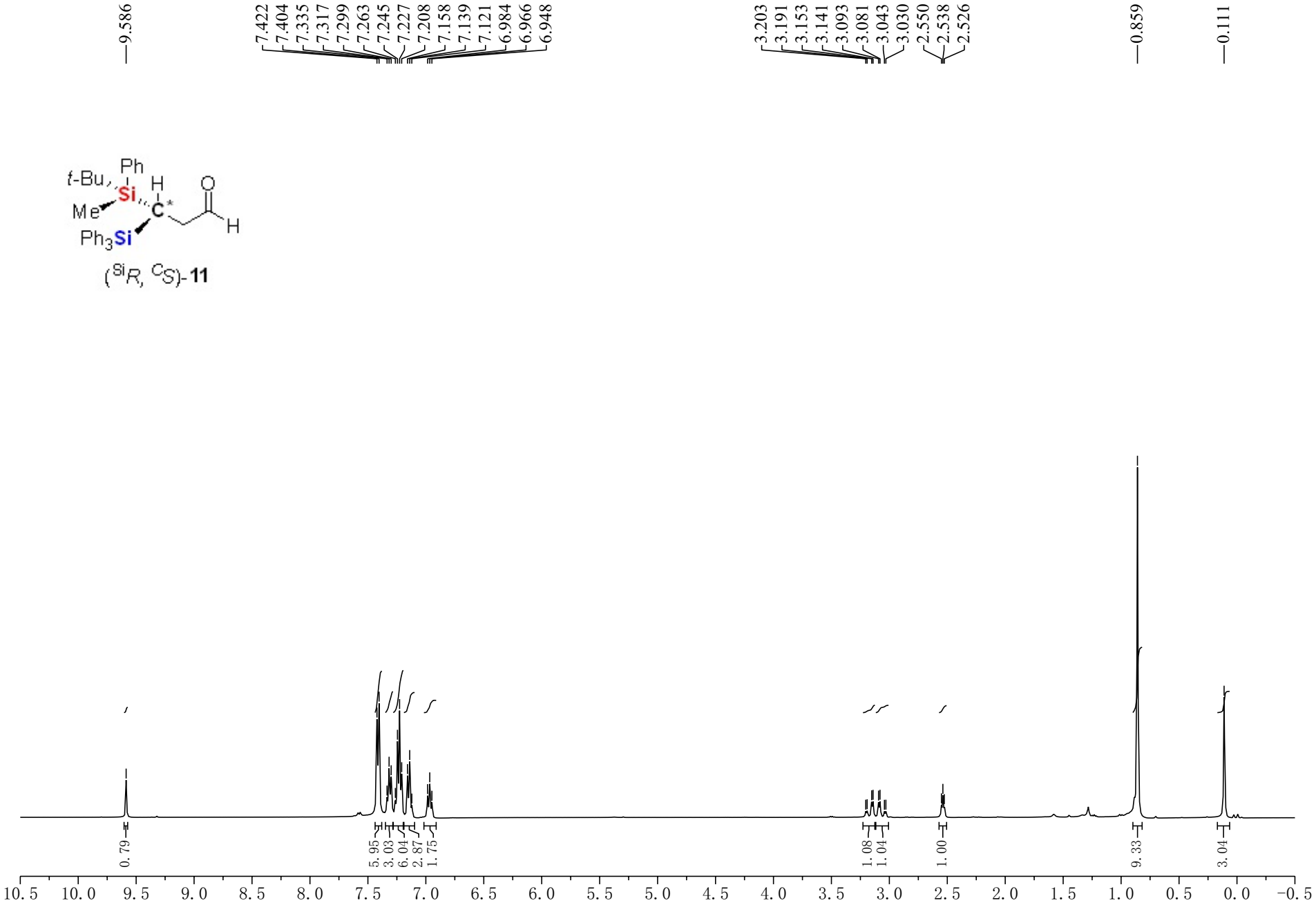
WY-7-80 H1 CDCl3 400M Hz



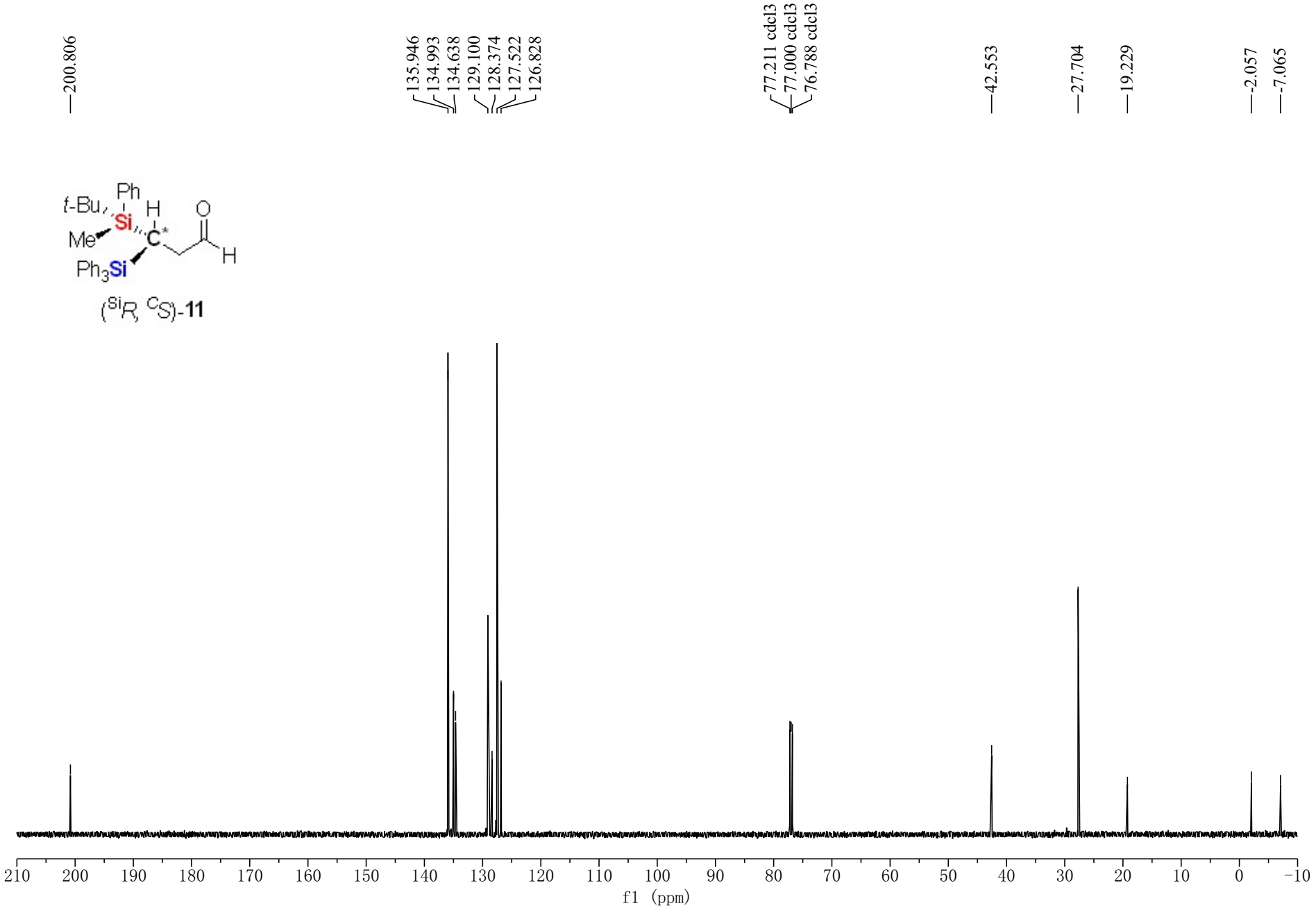
WY-7-80 C13 CDCl3 150M Hz



WY-8-12-1 H1 CDCl3 400M Hz



WY-8-12-1 C13 CDCl3 100M Hz



(SiR, CS)-**11**