

Supporting Information

Iron Porphyrin-Catalyzed Insertion Reaction of

***N*-Tosylhydrazone-Derived Carbenes into X-H (X = Si, Sn,**

Ge) Bonds

En-Hui Wang,^a Yuan-Ji Ping,^b Zong-Rui Li,^b Hongling Qin,^b Zhen-Jiang Xu,^{*b} and

Chi-Ming Che^{*b,c}

^a School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai, P. R. China

^b Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, 354 Feng Lin Road, Shanghai 200032, P. R. China.

^c Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

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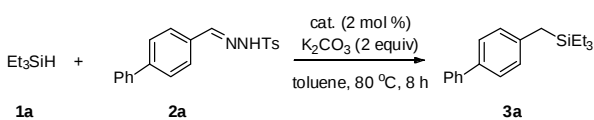
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1. General Information

All reagents purchased from commercial sources were used as received. The solvents toluene, THF and 1,4-dioxane were distilled from sodium. The silica gel for column chromatography was supplied as 300-400 mesh from Haiyang Chemicals (Qingdao, China). The ^1H and ^{13}C NMR spectra were recorded on a Varian Inova spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^1H and 77.16 ppm for ^{13}C in CDCl_3). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). The MS spectra were recorded on Agilent Technologies 5973N. High resolution mass spectra (HRMS) were recorded on Agilent Technologies 6224 by using ESI method or Waters Micromass GCT Premier by using EI method. GC analysis was performed with Shimadzu GC-2010 plus. Microwave reactions were performed with CEM Discover SP microwave synthesizer. *N*-Tosylhydrazones¹ and metal porphyrin catalysts² were prepared according to the known procedures.

2. Screen of metal complexes

Table S1. Screen of the catalysts^a

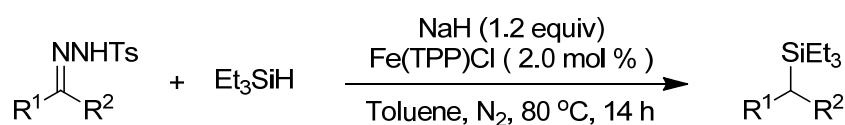
		
entry	catalyst	yield ^b (%)
1	Cu(OTf) ₂	25
2	CuCl ₂	32
3	CuI	16
4	CuBr	16
5	Rh(TPFPP)Cl	ND
6	Rh(TPP)Cl	50
7	Rh(TPP)Me	ND
8	Co(TPP)	32
9	Co(TTP)	20
10	Co(TPFPP)	ND
11	Fe(TPFPP)Cl	ND
12	Fe(TPP)Cl	62
13	Fe(TTP)Cl	30

14	Fe(<i>p</i> -ClTPP)Cl	ND
15	Fe(TPP)Cl	76 ^{c,d}

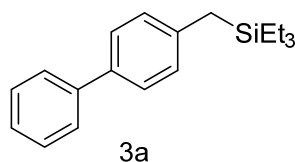
^aUnless otherwise specified, reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), cat. (2 mol%) and K₂CO₃ (0.4 mmol, 2 equiv) were reacted in toluene (2 mL) at 80 °C for 8 hours. ^bGC yield. ^cReactions were done at 80 °C for 14 h. ^dIsolated yield.

3. Synthesis and Analytical Data of compounds

The Fe(TPP)Cl catalyzed carbene insertion reaction into Et₃SiH was performed according to the general procedure given below:



General procedure: To a flame-dried sealed tube were added *N*-tosylhydrazone (0.2 mmol, 1.0 equiv), NaH (9.6 mg, 60 wt%, 0.24 mmol, 1.2 equiv), Fe(TPP)Cl (2.86 mg, 4.0 μmol, 0.02 equiv), triethylsilane (64 μl, 0.4 mmol, 2.0 equiv) and dry toluene (2.0 mL, 0.1 M) under Ar atmosphere. Then the tube was sealed and heated at 80 °C for additional 14 h. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was purified by flash column chromatography on silica gel (eluting with petroleum ether) to afford product as a colorless oil.

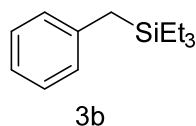


3a ([1,1'-biphenyl]-4-ylmethyl)triethylsilane:

Colorless oil. 51 mg, Yield: 90 %

¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.36 (m, 4H), δ 7.36 – 7.29 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.18 (s, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H).

EI-MS *m/z* (relative intensity): 282 (M⁺, 32), 115 (100), 87 (82), 168 (47), 167 (38), 59 (25), 165 (24), 57 (23). The spectroscopic data were identical in all respects to those previously reported³.

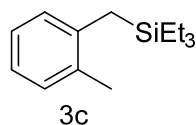


3b benzyltriethylsilane:

Colorless oil. 30 mg, Yield: 72 %

¹H NMR (400 MHz, CDCl₃): δ 7.21 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 2.11 (s, 2H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.53 (q, *J* = 8.0 Hz, 6H) .

EI-MS m/z (relative intensity): 206 (M^+ , 19.5), 115 (100), 87 (93), 121 (8021), 59 (26), 179 (25), 180 (23), 178 (13). The spectroscopic data were identical in all respects to those previously reported.³



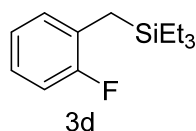
3c triethyl(2-methylbenzyl)silane:

Colorless oil. 38 mg, Yield: 86 %

^1H NMR (400 MHz, CDCl_3): δ 7.15 – 7.03 (m, 2H), 7.03 – 6.96 (m, 2H), 2.27 (s, 3H), 2.12 (s, 2H), 0.93 (t, J = 8.0 Hz, 9H), 0.56 (q, J = 8.0 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.3, 134.7, 130.2, 128.9, 125.8, 124.1, 20.5, 18.7, 7.5, 3.7.

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{Si}$ [M] $^+$ 220.1647, found 220.1651.



3d triethyl(2-fluorobenzyl)silane:

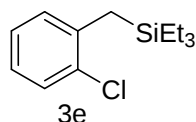
Colorless oil. 21 mg, Yield: 46 %

^1H NMR (400 MHz, CDCl_3): δ 7.10 – 6.92 (m, 4H), 2.11 (d, J = 2.1 Hz, 2H), 0.94 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H).

^{19}F NMR (376 MHz, CDCl_3): δ -117.07 – -117.35 (m).

^{13}C NMR (100 MHz, CDCl_3): δ 160.5 (d, J = 242.3 Hz), 130.5 (d, J = 5.1 Hz), 127.9 (d, J = 17.1 Hz), 125.5 (d, J = 7.7 Hz), 123.8 (d, J = 3.4 Hz), 115.1 (d, J = 22.5 Hz), 14.4 (d, J = 2.5 Hz), 7.3, 3.3.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{FSi}$ [M] $^+$ 224.1397, found 224.1404.



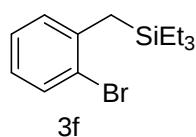
3e (2-chlorobenzyl)triethylsilane:

Colorless oil. 34 mg, Yield: 71 %

^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, J = 6.6 Hz, 1H), 7.14 – 7.05 (m, 2H), 7.03 – 6.96 (m, 1H), 2.30 (s, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.3, 132.8, 130.0, 129.5, 126.5, 125.3, 19.5, 7.5, 3.6.

EI-MS m/z (relative intensity): 240 (M^+ , 1.62), 87 (100), 115 (79), 211 (67), 59 (30), 213 (25), 91 (18), 93 (14). The spectroscopic data were identical in all respects to those previously reported³.



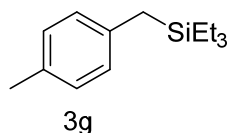
3f (2-bromobenzyl)triethylsilane:

Colorless oil. 31 mg, Yield: 54 %

^1H NMR (400 MHz, CDCl_3): δ 7.49 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.15 (td, $J = 7.4, 1.3$ Hz, 1H), 7.08 (dd, $J = 7.7, 1.9$ Hz, 1H), 6.96 – 6.88 (m, 1H), 2.34 (s, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.59 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.1, 132.8, 129.8, 127.2, 125.6, 123.7, 22.2, 7.4, 3.6.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{SiBr}$ $[\text{M}]^+$ 284.0596, found 284.0602.



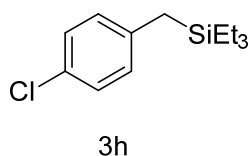
3g triethyl(4-methylbenzyl)silane:

Colorless oil. 23 mg, Yield: 52 %

^1H NMR (400 MHz, CDCl_3): δ 7.03 (d, $J = 7.6$ Hz, 2H), 6.93 (d, $J = 7.6$ Hz, 2H), 2.30 (s, 3H), 2.07 (s, 2H), 0.94 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 137.4, 133.2, 129.0, 128.1, 21.1, 21.0, 7.5, 3.1.

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{Si}$ $[\text{M}]^+$ 220.1647, found 220.1650.

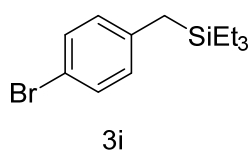


3h (4-chlorobenzyl)triethylsilane:

Colorless oil. 47 mg, Yield: 97 %

^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 2.07 (s, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.51 (q, $J = 8.0$ Hz, 6H).

EI-MS m/z (relative intensity): 240 (M^+ , 12.2), 115 (100), 87 (90), 59 (24), 155 (14), 213 (25), 91 (18), 93 (14). The spectroscopic data were identical in all respects to those previously reported³.



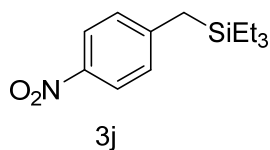
3i (4-bromobenzyl)triethylsilane:

Colorless oil. 47 mg, Yield: 83 %

^1H NMR (400 MHz, CDCl_3): δ 7.31 (d, $J = 8.5$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 2.05 (s, 1H), 0.91 (t, $J = 8.0$ Hz, 5H), 0.50 (q, $J = 8.0$ Hz, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.9, 131.3, 129.9, 117.4, 21.4, 7.4, 3.0.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{SiBr}$ $[\text{M}]^+$ 284.0596, found 284.0599.



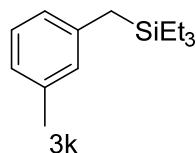
3j triethyl(4-nitrobenzyl)silane:

Colorless oil. 42 mg, Yield: 83 %

^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 2H), 2.25 (s, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 150.2, 144.9, 128.5, 123.8, 23.3, 7.3, 3.0.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Si}$ $[\text{M}]^+$ 251.1342, found 251.1343.



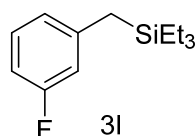
3k triethyl(3-methylbenzyl)silane:

Colorless oil. 36 mg, Yield: 81 %

^1H NMR (400 MHz, CDCl_3): δ 7.11 (t, $J = 7.4$ Hz, 1H), 6.92 – 6.79 (m, 3H), 2.32 (s, 3H), 2.08 (s, 2H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.53 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 140.7, 137.7, 129.1, 128.1, 125.3, 124.7, 21.6, 21.6, 7.4, 3.2.

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{Si}$ $[\text{M}]^+$ 220.1647, found 220.1642.



3l triethyl(3-fluorobenzyl)silane:

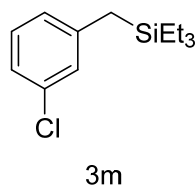
Colorless oil. 26 mg, Yield: 58 %

^1H NMR (400 MHz, CDCl_3): δ 6.98 – 6.84 (m, 4H), 2.06 (s, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.51 (q, $J = 8.0$ Hz, 6H).

^{19}F NMR (376 MHz, CDCl_3): δ -120.56 – -120.69 (m).

^{13}C NMR (100 MHz, CDCl_3): δ 160.3 (d, $J = 241.2$ Hz), 136.2 (d, $J = 3.1$ Hz), 129.2 (d, $J = 7.7$ Hz), 115.0 (d, $J = 21.0$ Hz), 20.8, 7.4, 3.1.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{FSi}$ $[\text{M}]^+$ 224.1367, found 224.1400.



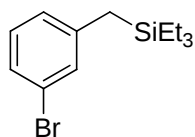
3m (3-chlorobenzyl)triethylsilane:

Colorless oil. 39 mg, Yield: 81 %

^1H NMR (400 MHz, CDCl_3): δ 7.13 (t, $J = 7.7$ Hz, 1H), 7.07 – 6.97 (m, 2H), 6.89 (d, $J = 7.7$, 1H), 2.08 (s, 2H), 0.93 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 134.0, 129.5, 128.1, 126.4, 124.1, 21.8, 7.4, 3.1.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{SiCl}$ $[\text{M}]^+$ 240.1101, found 240.1104.



3n

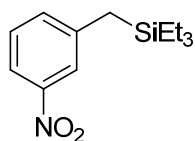
3n (3-bromobenzyl)triethylsilane:

Colorless oil. 40 mg, Yield: 71 %

^1H NMR (400 MHz, CDCl_3): δ 7.22 – 7.14 (m, 2H), 7.07 (t, $J = 7.7$ Hz, 1H), δ 6.94 (d, $J = 7.7$ Hz, 1H), 2.07 (s, 2H), 0.93 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.5 , 131.0 , 129.8 , 127.0 , 126.8 , 122.4 , 21.8 , 7.4 , 3.1 .

HRM (EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{SiBr}$ $[\text{M}]^+$ 284.0596, found 284.0604.



3o

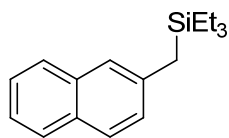
3o triethyl(3-nitrobenzyl)silane:

Colorless oil. 44 mg, Yield: 88 %

^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 7.7$ Hz, 1H), 7.87 (s, 1H), 7.39 – 7.29 (m, 2H), 2.22 (s, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.4 , 143.3 , 134.3 , 129.0 , 122.6 , 119.2 , 22.2 , 7.3 , 3.0 .

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Si}$ $[\text{M}]^+$ 251.1342, found 251.1346.



3p

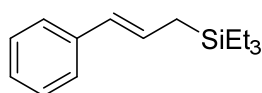
3p triethyl(naphthalen-2-ylmethyl)silane:

Colorless oil. 39 mg, Yield: 76 %

^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, $J = 7.7$ Hz, 1H), 7.73 (t, $J = 8.1$ Hz, 2H), 7.48 – 7.34 (m, 3H), 7.21 (dd, $J = 8.1$, 1.7 Hz, 1H), 2.29 (s, 2H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.56 (q, $J = 8.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 138.6 , 134.0 , 131.0 , 128.1 , 127.7 , 127.6 , 127.1 , 125.9 , 125.3 , 124.4 , 22.1 , 7.5 , 3.2 .

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{Si}$ $[\text{M}]^+$ 256.1647, found 256.1656.

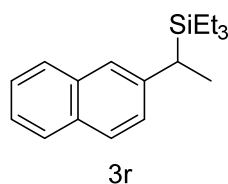


3q

3q cinnamyltriethylsilane:

Colorless oil. 13 mg, Yield: 28 %

^1H NMR (400 MHz, CDCl_3): δ 7.31-7.23 (m, 4H), 7.18-7.10 (m, 1H), 6.28-6.20 (m, 2H), 1.70 (dd, J = 5.0, 2.0 Hz, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H);
 EI-MS m/z (relative intensity): 232 (M^+ , 18.67), 115 (100), 87 (97), 59 (33), 116 (15), 117(11), 88 (10), 57 (10). The spectroscopic data were identical in all respects to those previously reported³.

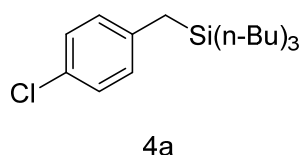


3r triethyl(1-(naphthalen-2-yl)ethyl)silane:

Colorless oil. 14 mg, Yield: 26 %

^1H NMR (400 MHz, CDCl_3): δ 7.81 – 7.69 (m, 3H), 7.49 (s, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.25 (dd, J = 8.0, 1.0 Hz, 1H), 2.49 (q, J = 7.5 Hz, 1H), 1.48 (d, J = 7.5 Hz, 3H), 0.91 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H).

EI-MS m/z (relative intensity): 270 (M^+ , 21), 115 (100), 87 (87.5), 59 (30), 57(24), 155(21.35), 55 (16), 154 (15). The spectroscopic data were identical in all respects to those previously reported³.



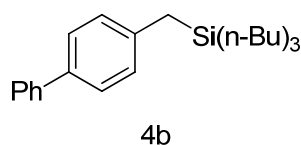
4a tributyl(4-chlorobenzyl)silane:

Colorless oil. 51 mg, Yield: 78 %

^1H NMR (400 MHz, CDCl_3): δ 7.15 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 2.04 (s, 2H), 1.37 – 1.14 (m, 12H), 0.86 (t, J = 7.1 Hz, 9H), 0.52 – 0.42 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.4, 129.5, 129.4, 128.3, 26.9, 26.1, 22.3, 13.9, 11.7.

EI-MS m/z (relative intensity): 324 (M^+ , 2), 143 (100), 199 (54), 59 (46), 87(34), 101(31), 155 (19), 91 (15). The spectroscopic data were identical in all respects to those previously reported³.



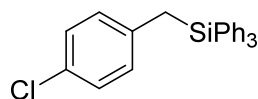
4b ([1,1'-biphenyl]-4-ylmethyl)tributylsilane:

Colorless oil. 50 mg, Yield: 68 %

^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 8.2 Hz, 2H), 7.54 – 7.38 (m, 4H), 7.37 – 7.29 (m, 1H), 7.11 (d, J = 8.2 Hz, 1H), 2.17 (s, 2H), 1.37-0.94 (m, 12H), 0.92 (t, J = 7.0 Hz, 9H), 0.62 – 0.50 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.4, 140.2, 136.8, 128.8, 128.6, 126.9, 126.9, 126.8, 26.9, 26.1, 22.5, 13.9, 11.9.

HRMS(EI) m/z calcd. for $\text{C}_{25}\text{H}_{38}\text{Si}$ [M]⁺ 366.2743, found 366.2738.



4c

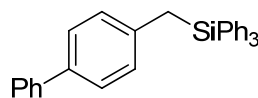
4c (4-chlorobenzyl)triphenylsilane:

White solid. m.p. 166-167 °C. 23 mg, Yield: 30 %

¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.37 (m, 9H), 7.38 – 7.32 (m, 6H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 2.90 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 137.0, 136.1, 133.9, 130.5, 130.3, 129.8, 128.2, 128.0, 23.1.

EI-MS *m/z* (relative intensity): 384 (M⁺, 2), 259 (100), 181 (89), 260 (30), 53(30), 182(70), 84 (25), 183 (15). The spectroscopic data were identical in all respects to those previously reported³.



4d

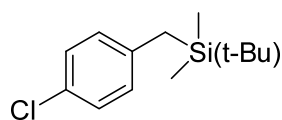
4d ([1,1'-biphenyl]-4-ylmethyl)triphenylsilane:

White solid. m.p. 146-148 °C . 70 mg, Yield: 82 %

¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.30 (m, 20H), 6.94 (d, *J* = 8.0 Hz, 2H), 2.99 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 141.0, 137.5, 137.2, 136.0, 134.1, 129.6, 129.6, 128.6, 127.8, 126.8, 126.7, 126.6, 23.2.

HRMS(EI) *m/z* calcd. for C₃₁H₂₆Si [M]⁺ 426.1804, found 426.1802.



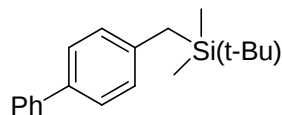
4e

4e tert-butyl(4-chlorobenzyl)dimethylsilane:

Colorless oil. 11 mg, Yield: 23 %

¹H NMR (400 MHz, CDCl₃): δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 2.06 (s, 2H), 0.90 (s, 9H), -0.12 (s, 6H).

EI-MS *m/z* (relative intensity): 240(M⁺,15), 73(100), 115 (87), 87 (26), 59(22), 183(21), 105 (19), 155 (18). The spectroscopic data were identical in all respects to those previously reported³.



4f

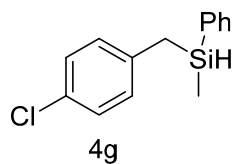
4f ([1,1'-biphenyl]-4-ylmethyl)(tert-butyl)dimethylsilane:

Colorless oil. 23 mg, Yield: 40 %

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.37 (m, 4H), 7.36 – 7.27 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.15 (s, 2H), 0.95 (s, 9H), -0.05 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 141.3, 140.1, 136.8, 128.8, 128.6, 127.0, 126.9, 126.9, 26.7, 22.4, 16.9, -6.4.

HRMS(EI) m/z calcd. for $C_{19}H_{26}Si$ $[M]^+$ 282.1804, found 282.1809.



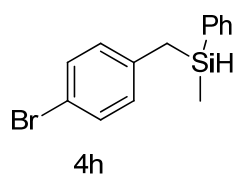
4g (4-chlorobenzyl)(methyl)(phenyl)silane:

Colorless oil. 31 mg, Yield: 63 %

1H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.42 (m, 2H), 7.40-7.33 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 4.43 (q, J = 3.7 Hz, 1H), 2.45 – 2.22 (m, 2H), 0.31 (d, J = 3.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 135.1, 134.5, 130.2, 129.7, 129.7, 128.5, 128.1, 23.2, -6.1.

HRMS(EI) m/z calcd. for $C_{14}H_{15}ClSi$ $[M]^+$ 246.0632, found 246.0629.



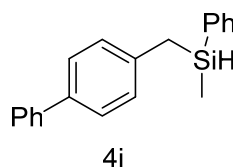
4h (4-bromobenzyl)(methyl)(phenyl)silane:

Colorless oil. 30 mg, Yield: 51 %

1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.5 Hz, 2H), 7.43 – 7.28 (m, 5H), 6.87 (d, J = 8.5 Hz, 2H), 4.44 (q, J = 3.5 Hz, 1H), 2.46 – 2.21 (m, 2H), 0.32 (d, J = 3.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.1, 134.5, 131.4, 130.2, 129.8, 128.1, 118.1, 23.3, -6.1.

HRMS(EI) m/z calcd. for $C_{14}H_{15}BrSi$ $[M]^+$ 290.0126, found 290.0136.



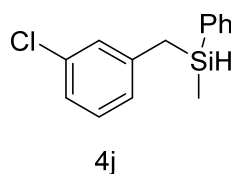
4i ([1,1'-biphenyl]-4-ylmethyl)(methyl)(phenyl)silane:

White solid. m.p. 42-44 °C . 43 mg, Yield: 75 %

1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.54-7.32 (m, 8H), 7.11 (d, J = 7.8 Hz, 2H), 4.51 (q, J = 3.7 Hz, 1H), 2.57 – 2.35 (m, 2H), 0.38 (d, J = 3.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.6, 137.4, 135.6, 134.6, 129.6, 128.9, 128.8, 128.0, 127.1, 127.0, 126.9, 23.4, -6.0.

HRMS(EI) m/z calcd. for $C_{20}H_{20}Si$ $[M]^+$ 288.1334, found 288.1337.

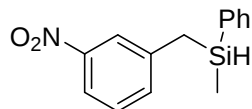


4j (3-chlorobenzyl)(methyl)(phenyl)silane:

Colorless oil. 31 mg, Yield: 63 %

^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, J = 7.8 Hz, 2H), 7.43 – 7.30 (m, 3H), 7.16 – 7.03 (m, 2H), 7.00 (s, 1H), 6.89 – 6.82 (m, 1H), 4.44 (q, J = 6.4, 5.0 Hz, 1H), 2.44 – 2.22 (m, 2H), 0.35 – 0.29 (m, 3H).
 ^{13}C NMR (100 MHz, CDCl_3): δ 141.6, 135.0, 134.5, 134.1, 129.8, 129.6, 128.4, 128.1, 126.6, 124.7, 23.7, -6.1.

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{ClSi}$ $[\text{M}]^+$ 246.0632, found 246.0639.



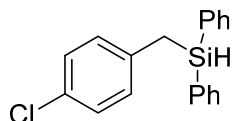
4k

4k methyl(3-nitrobenzyl)(phenyl)silane:

Colorless oil. 30 mg, Yield: 58 %

^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.2 Hz, 1H), 7.84 (s, 1H), 7.47 – 7.30 (m, 5H), 7.29 – 7.23 (m, 2H), 4.47 (q, J = 3.7 Hz, 1H), 2.56 – 2.39 (m, 2H), 0.35 (d, J = 3.7 Hz, 3H).
 ^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 141.6, 134.4, 134.3, 134.1, 129.9, 129.0, 128.0, 122.8, 119.6, 23.9, -6.3.

HRMS(EI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{Si}$ $[\text{M}]^+$ 257.0872, found 257.0876.



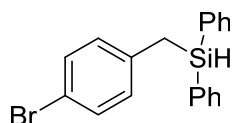
4l

4l (4-chlorobenzyl)diphenylsilane:

White solid. m.p. 80-82 °C . 27 mg, Yield: 44 %

^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.48 (m, 4H), 7.46 – 7.33 (m, 6H), 7.14 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.94 (t, J = 3.7 Hz, 1H), 2.67 (d, J = 3.7 Hz, 2H).
 ^{13}C NMR (100 MHz, CDCl_3): δ 142.9, 137.3, 135.3, 133.2, 130.4, 130.0, 128.5, 128.2, 22.0.

HRMS(EI) m/z calcd. for $\text{C}_{19}\text{H}_{17}\text{ClSi}$ $[\text{M}]^+$ 308.0788, found 308.0787.



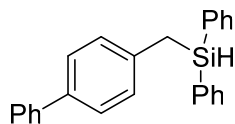
4m

4m (4-bromobenzyl)diphenylsilane:

White solid. m.p. 85-87 °C . 36 mg, Yield: 51 %

^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.44 (m, 4H), 7.44 – 7.29 (m, 6H), 7.25 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 4.91 (t, J = 3.5 Hz, 1H), 2.62 (d, J = 3.5 Hz, 2H).
 ^{13}C NMR (100 MHz, CDCl_3): δ 137.8, 135.3, 133.2, 131.4, 130.5, 130.0, 128.2, 118.3, 22.1.

HRMS(EI) m/z calcd. for $\text{C}_{19}\text{H}_{17}\text{BrSi}$ $[\text{M}]^+$ 352.0283, found 352.0293.



4n

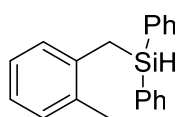
4n ([1,1'-biphenyl]-4-ylmethyl)diphenylsilane:

White solid. m.p. 110-111 °C . 27 mg, Yield: 39 %

^1H NMR (400 MHz, CDCl_3): δ 7.63 – 7.52 (m, 6H), 7.50 – 7.30 (m, 11H), δ 7.11 (d, J = 8.2 Hz, 1H), 5.03 (t, J = 3.8 Hz, 1H), 2.77 (d, J = 3.8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 138.2, 137.7, 135.3, 131.7, 129.8, 128.7, 128.7, 128.0, 127.2, 126.9, 126.8, 19.8.

HRMS(EI) m/z calcd. for $\text{C}_{25}\text{H}_{22}\text{Si}$ $[\text{M}]^+$ 350.1491, found 350.1490.



4o

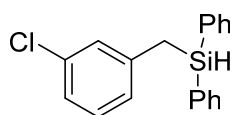
4o (2-methylbenzyl)diphenylsilane:

Colorless oil. 35 mg, Yield: 62 %

^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.44 (m, 4H), 7.45 – 7.30 (m, 6H), 7.11 – 6.85 (m, 4H), 4.91 (t, J = 3.7 Hz, 1H), 2.66 (d, J = 3.7 Hz, 2H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 140.1, 137.1, 135.4, 133.8, 130.2, 129.9, 129.3, 128.1, 125.9, 124.9, 20.3, 19.9.

HRMS(EI) m/z calcd. for $\text{C}_{20}\text{H}_{20}\text{Si}$ $[\text{M}]^+$ 288.1334, found 288.1342.



4p

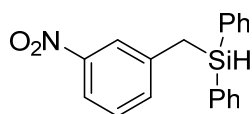
4p (3-chlorobenzyl)diphenylsilane:

Colorless oil. 33 mg, Yield: 54 %

^1H NMR (400 MHz, CDCl_3): δ 7.55 – 7.47 (m, 4H), 7.46 – 7.33 (m, 6H), 7.11 – 7.03 (m, 2H), 7.00 (s, 1H), 6.90 – 6.82 (m, 1H), 4.96 (t, J = 3.5 Hz, 1H), 2.67 (d, J = 3.5 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 140.9, 135.3, 134.1, 133.1, 130.1, 129.5, 128.8, 128.2, 126.9, 124.9, 22.4.

HRMS(EI) m/z calcd. for $\text{C}_{19}\text{H}_{17}\text{ClSi}$ $[\text{M}]^+$ 308.0788, found 308.0790.



4q

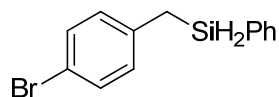
4q (3-nitrobenzyl)diphenylsilane:

Colorless oil. 20 mg, Yield: 31 %

^1H NMR (400 MHz, CDCl_3): δ 7.96 – 7.87 (m, 1H), 7.83 (s, 1H), 7.54 – 7.27 (m, 12H), 4.95 (s, 1H), 2.78 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.3, 141.2, 135.3, 134.8, 132.4, 130.3, 129.1, 128.3, 123.4, 119.9, 22.8.

HRMS(EI) m/z calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{Si}$ $[\text{M}]^+$ 319.1029, found 319.1037.



4r

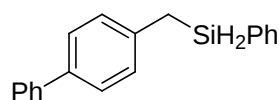
4r (4-bromobenzyl)(phenyl)silane:

Colorless oil. 13 mg, Yield: 24 %

^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, J = 8.4 Hz, 2H), 7.43 – 7.28 (m, 5H), 6.94 (d, J = 8.4 Hz, 2H), 4.39 (t, J = 3.3 Hz, 2H), 2.42 (t, J = 3.3 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 140.1, 138.2, 135.4, 131.6, 130.2, 130.1, 128.2, 118.5, 19.9.

HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{BrSi}$ $[\text{M}]^+$ 275.9970, found 275.9976.



4s

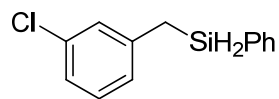
4s ([1,1'-biphenyl]-4-ylmethyl)(phenyl)silane:

Colorless oil. 13 mg, Yield: 24 %

^1H NMR (400 MHz, CDCl_3): δ 7.63 – 7.56 (m, 2H), δ 7.56 – 7.51 (m, 2H), δ 7.48 (d, J = 8.2 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.29 (m, 3H), 7.17 (d, J = 8.2 Hz, 2H), 4.46 (t, J = 3.9 Hz, 2H), 2.53 (t, J = 3.9 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.2, 138.4, 137.8, 135.4, 131.8, 130.0, 128.9, 128.8, 128.2, 127.3, 127.1, 127.0, 19.9.

HRMS(EI) m/z calcd. for $\text{C}_{19}\text{H}_{18}\text{Si}$ $[\text{M}]^+$ 274.1178, found 274.1182.



4t

4t (3-chlorobenzyl)(phenyl)silane:

Colorless oil. 12 mg, Yield: 26 %

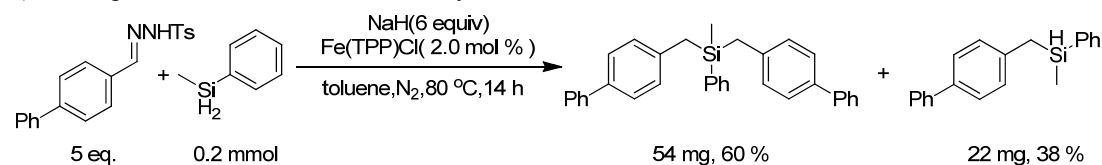
^1H NMR (400 MHz, CDCl_3): δ 7.53 – 7.45 (m, 2H), 7.44 – 7.32 (m, 3H), 7.22 – 7.08 (m, 2H), 7.07 (s, 1H), 6.94 (d, J = 7.0 Hz, 1H), 4.41 (t, J = 4.0 Hz, 2H), 2.44 (t, J = 4.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.3, 135.7, 135.4, 134.3, 130.1, 129.8, 128.4, 128.2, 126.6, 125.1, 20.2.

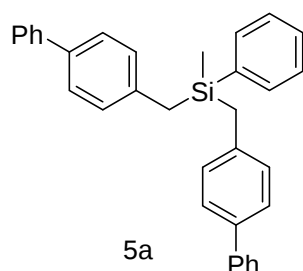
HRMS(EI) m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{ClSi}$ $[\text{M}]^+$ 232.0475, found 232.0472.

Fe(TPP)Cl catalyzed double Si-H insertion reaction:

a) One-pot double insertion of secondary Si-H bonds



To a flame-dried sealed tube were added *N*-tosylhydrazide (1 mmol, 5 equiv), NaH (48 mg, 60 wt%, 1.2 mmol, 6 equiv), Fe(TPP)Cl (2.86 mg, 4 μ mol, 0.02 equiv) and dry Toluene (2.0 mL, 0.1 M) inside a glove box. Then, methylphenylsilane (24.5 mg, 0.2 mmol, 1.0 equiv) was added and the tube was sealed and heated at 80 °C for additional 14 h. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was allowed to reach room temperature, and filtered through a short pad of silica gel with EtOAc as an eluent. The filtrate was evaporated under reduced pressure to leave a crude mixture, which was purified by column chromatography on silica gel (eluting with petroleum ether) to afford product.



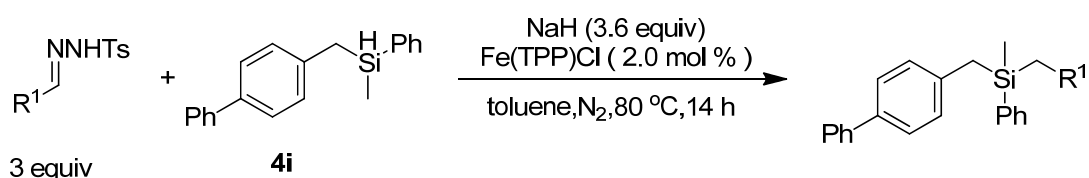
5a bis([1,1'-biphenyl]-4-ylmethyl)(methyl)(phenyl)silane. : Colorless oil. 54 mg, Yield: 60 %

^1H NMR (400 MHz, CDCl_3) : δ 7.64 (d, J = 7.3 Hz, 4H), 7.48 (q, J = 7.3 Hz, 10H), 7.39 (dt, J = 15.0, 7.3 Hz, 5H), δ 2.57 – 2.43 (m, 4H), 0.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) : δ 141.2, 138.4, 137.2, 136.5, 134.4, 129.5, 129.1, 128.8, 127.9, 126.9, 126.9, 23.9, -5.6.

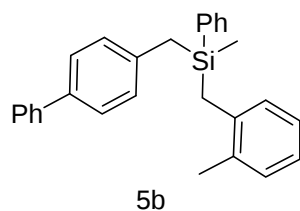
HRMS (ESI) m/z calcd. for $\text{C}_{33}\text{H}_{34}\text{NSi}$ [$\text{M}+\text{NH}_4$] $^+$ 472.2461, found 472.2455.

b) Second step insertion of **4i**:



To a flame-dried sealed tube were added *N*-tosylhydrazide (0.6 mmol, 3 equiv), NaH (28.8 mg, 60 wt%, 0.69 mmol, 3.6 equiv), Fe(TPP)Cl (2.86 mg, 4. μ mol, 0.02 equiv), **4i** ([1,1'-biphenyl]-4-ylmethyl)(methyl)(phenyl)silane (57.7 mg, 0.2 mmol, 1.0 equiv) and dry toluene (2.0 mL, 0.1 M) under Ar atmosphere. Then the tube was sealed and heated at 80 °C for additional

14 h. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was purified by column chromatography on silica gel (eluting with petroleum ether) to afford product.



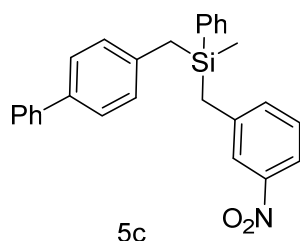
5b ([1,1'-biphenyl]-4-ylmethyl)(methyl)(2-methylbenzyl)(phenyl)silane:

Colorless oil. 39 mg, Yield: 50 %

^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.5$ Hz, 2H), 7.48 – 7.40 (m, 7H), 7.40 – 7.30 (m, 3H), 7.13 – 6.97 (m, 5H), 6.93 (dd, $J = 6.9, 2.0$ Hz, 1H), 2.55 – 2.38 (m, 4H), 2.04 (s, 3H), 0.24 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.1, 138.3, 137.6, 137.1, 136.8, 135.1, 134.1, 130.2, 129.3, 128.9, 128.9, 128.7, 127.7, 126.8, 126.8, 125.7, 124.5, 24.0, 21.1, 20.2, -5.7.

HRMS(EI) m/z calcd. for $\text{C}_{28}\text{H}_{28}\text{Si}$ $[\text{M}]^+$ 392.1960, found 392.1957.



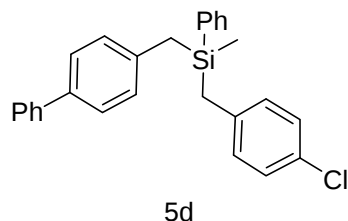
5c ([1,1'-biphenyl]-4-ylmethyl)(methyl)(3-nitrobenzyl)(phenyl)silane:

Colorless oil. 76 mg, Yield: 90 %

^1H NMR (400 MHz, CDCl_3): δ 7.93 – 7.85 (m, 1H), 7.70 (s, 1H), 7.60 – 7.53 (m, 2H), 7.47 – 7.19 (m, 11H), 7.10 (d, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 8.2$ Hz, 2H), 2.53 – 2.35 (m, 4H), 0.26 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 141.6, 141.0, 137.7, 137.6, 135.2, 134.6, 134.2, 129.9, 129.0, 129.0, 128.8, 128.1, 127.1, 127.1, 126.9, 123.1, 119.6, 24.6, 23.7, -5.8.

HRMS(ESI) m/z calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{NH}_4]^+$ 441.1998, found 441.1991.



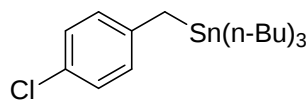
5d ([1,1'-biphenyl]-4-ylmethyl)(4-chlorobenzyl)(methyl)(phenyl)silane:

White solid. m.p. 54-56 °C. 53 mg, Yield: 64 %

^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.49 – 7.29 (m, 10H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 2.49 – 2.29 (m, 4H), 0.25 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.1, 138.2, 137.7, 137.3, 136.0, 134.3, 130.0, 129.8, 129.6, 129.0, 128.8, 128.3, 127.9, 127.0, 126.9, 23.8, 23.7, -5.8.

HRMS(EI) m/z calcd. for $C_{27}H_{25}ClSi$ $[M]^+$ 412.1414, found 412.1408.



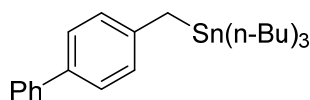
7a

7a tributyl(4-chlorobenzyl)stannane :

Colorless oil. 65 mg, Yield: 85 %

1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 2.26 (t, $J_{Sn-H} = 56$ Hz, 2H), 1.47 – 1.34 (m, 6H), 1.31 – 1.20 (m, 6H), 0.87 (t, $J = 7.3$ Hz, 9H), 0.80 (t, $J = 8.0$ Hz, 6H).

EI-MS m/z (relative intensity): 414(M^+ , 1), 177(100), 179 (97), 235 (70), 175(67), 291(55), 233 (55), 289 (44). The spectroscopic data were identical in all respects to those previously reported³.



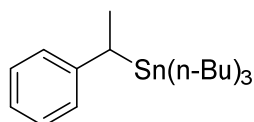
7b

7b ([1,1'-biphenyl]-4-ylmethyl)tributylstannane:

Colorless oil. 62 mg, Yield: 80 %

1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.39 (m, 4H), 7.33 – 7.26 (m, 1H), 7.06 (d, $J = 8.3$ Hz, 2H), 2.35 (t, $J_{Sn-H} = 28$ Hz, 2H), 1.52 – 1.37 (m, 6H), 1.36 – 1.19 (m, 6H), 0.92 – 0.80 (m, 15H).

EI-MS m/z (relative intensity): 457(M^+ , 1), 167(100), 179 (66), 177 (60), 291(60), 235(59), 289 (55), 287 (46). The spectroscopic data were identical in all respects to those previously reported³.



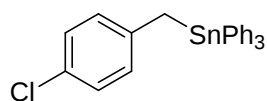
7c

7c tributyl(1-phenylethyl)stannane:

Colorless oil. 24 mg, Yield: 30 %

1H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, $J = 7.2$ Hz, 2H), 7.04 (d, $J = 7.2$ Hz, 2H), 7.00 (t, $J = 7.2$ Hz, 1H), 2.71 (q, $J = 7.8$ Hz, 1H), 1.58 (d, $J = 7.8$ Hz, 3H), 1.45 – 1.32 (m, 6H), 1.32 – 1.17 (m, 6H), 0.86 (t, $J = 7.8$ Hz, 9H), 0.82 – 0.74 (m, 6H).

EI-MS m/z (relative intensity): 474(M^+ , 2), 351(100), 197 (46), 125 (26), 89(22), 350(42), 195 (35), 89 (11). The spectroscopic data were identical in all respects to those previously reported³.



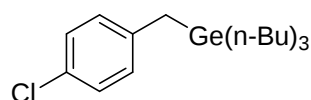
7d

7d (4-chlorobenzyl)triphenylstannane:

Colorless oil. 68 mg, Yield: 72 %

^1H NMR (400 MHz, CDCl_3): δ 7.47 – 7.32 (m, 15H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 2.95 (t, $J_{\text{Sn-H}} = 66$ Hz, 2H).

EI-MS m/z (relative intensity): 396(M^+ , 1), 179(100), 177 (92), 105 (64), 175(61), 235(57), 291 (44), 233 (43). The spectroscopic data were identical in all respects to those previously reported³.



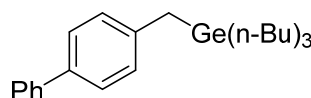
7e

7e tributyl(4-chlorobenzyl)germane:

Colorless oil. 73 mg, Yield: 99 %

^1H NMR (400 MHz, CDCl_3): δ 7.15 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 2.17 (s, 2H), 1.32 – 1.24 (m, 12H), 0.87 (t, $J = 6.9$ Hz, 9H), 0.74 – 0.62 (m, 6H).

EI-MS m/z (relative intensity): 370(M^+ , 1), 189(100), 133 (74), 89 (28), 55(26), 245(36), 187 (75), 89 (38). The spectroscopic data were identical in all respects to those previously reported³.



7f

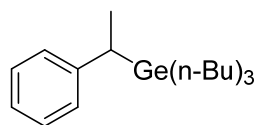
7f ([1,1'-biphenyl]-4-ylmethyl)tributylgermane:

Colorless oil. 73 mg, Yield: 89 %

^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 8.1$ Hz, 2H), 7.54 – 7.42 (m, 4H), 7.39 – 7.31 (m, 1H), 7.13 (d, $J = 8.1$ Hz, 2H), 2.32 (s, 2H), 1.43 – 1.29 (m, 12H), 0.94 (t, $J = 6.9$ Hz, 9H), 0.83 – 0.75 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.4, 141.2, 136.6, 128.8, 128.3, 126.9, 126.9, 126.8, 27.4, 26.7, 22.02, 13.9, 12.4.

HRMS(EI) m/z calcd. for $\text{C}_{25}\text{H}_{38}^{70}\text{Ge}$ [M]⁺ 408.2216, found 408.2211.



7g

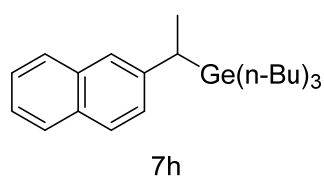
7g tributyl(1-phenylethyl)germane:

Colorless oil. 31 mg, Yield: 44 %

^1H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 2H), 7.09 – 7.01 (m, 3H), 2.49 (q, $J = 7.5$ Hz, 1H), 1.42 (d, $J = 7.5$ Hz, 3H), 1.33 – 1.16 (m, 10H), 0.85 (t, $J = 6.8$ Hz, 9H), 0.72 – 0.62 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.2, 128.1, 126.6, 124.1, 28.6, 27.5, 26.9, 16.2, 13.9, 11.3.

HRMS(EI) m/z calcd. for $\text{C}_{20}\text{H}_{36}^{70}\text{Ge}$ [M]⁺ 346.2060, found 346.2057.



7h tributyl(1-(naphthalen-2-yl)ethyl)germane:

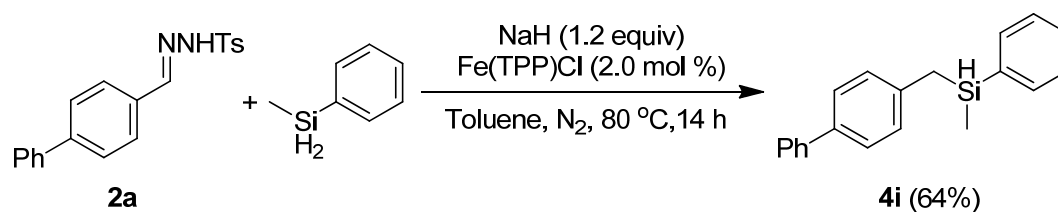
Colorless oil. 35 mg, Yield: 44 %

^1H NMR (400 MHz, CDCl_3) : δ 7.79 – 7.66 (m, 3H), 7.46 (s, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.26 – 7.18 (m, 1H), 2.67 (q, J = 7.5 Hz, 1H), 1.52 (d, J = 7.5 Hz, 3H), 1.31 – 1.19 (m, 12H), 0.88 – 0.78 (m, 9H), 0.76 – 0.62 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) : δ 145.0 , 133.9 , 131.3 , 127.6 , 127.4 , 127.3 , 126.8 , 125.8 , 124.4 , 123.6 , 28.9 , 27.5 , 26.8 , 16.3 , 13.9 , 11.4 .

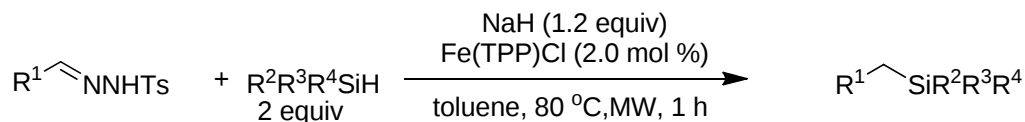
HRMS(EI) m/z calcd. for $\text{C}_{24}\text{H}_{38}^{70}\text{Ge}$ $[\text{M}]^+$ 396.2216, found 396.2206,.

Fe(TPP)Cl catalyzed gram scale reaction:



To a flame-dried sealed tube were added **2a** (1.0 g, 2.85 mmol, 1.0 equiv), NaH (137 mg, 60 wt%, 3.42 mmol, 1.2 equiv), Fe(TPP)Cl (40 mg, 0.02 equiv), methylphenylsilane (697mg, 5.71 mmol, 2.0 equiv) and dry Toluene (30 mL) under Ar atmosphere. Then the tube was sealed and heated at 80 °C for additional 14 h. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was purified by column chromatography on silica gel (eluting with petroleum ether) to afford product **4i** (444 mg, 64%)

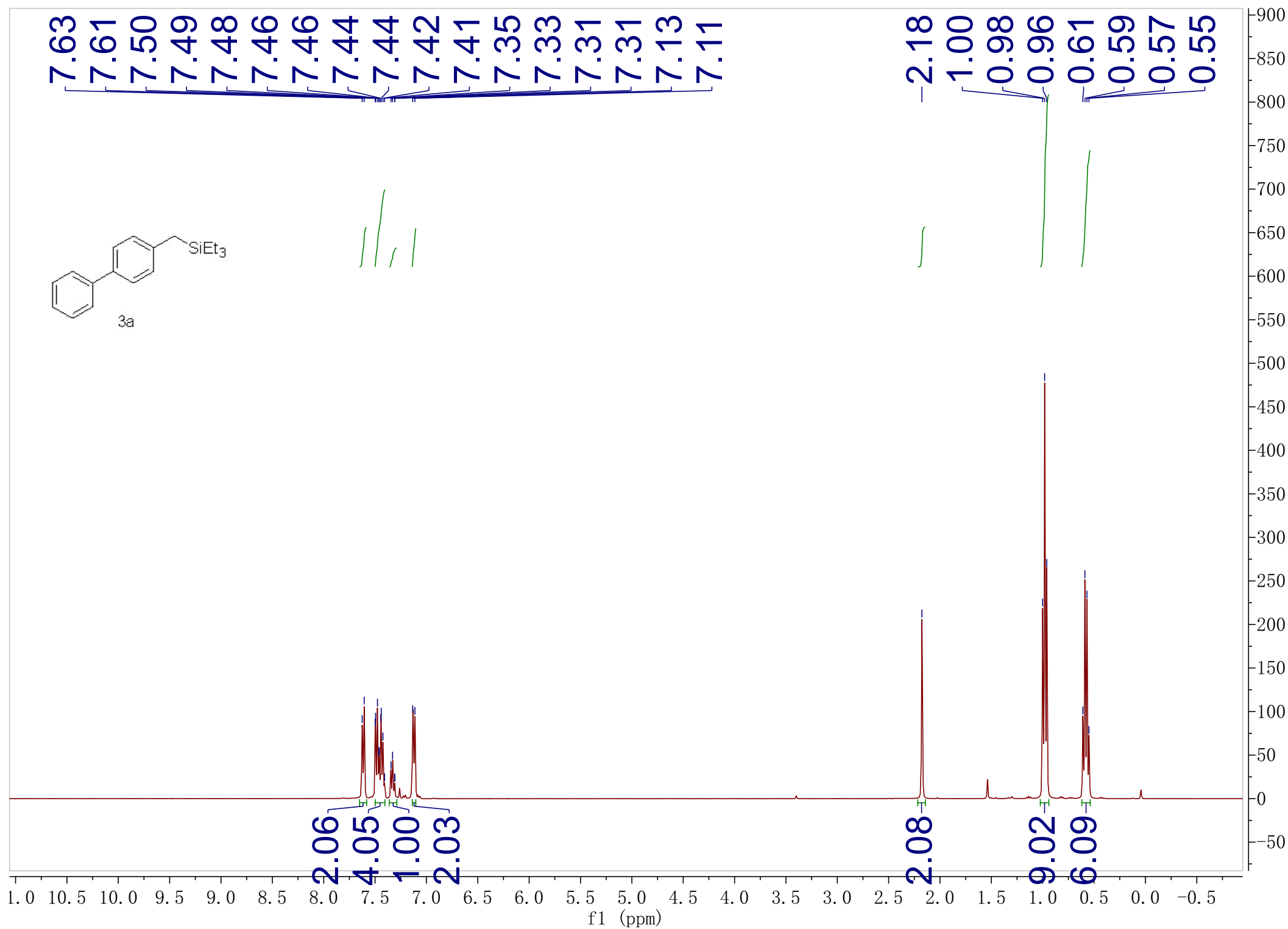
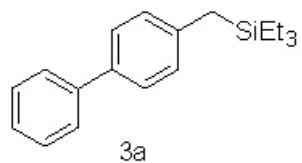
Fe(TPP)Cl catalyzed Si-H insertion under microwave irradiation:

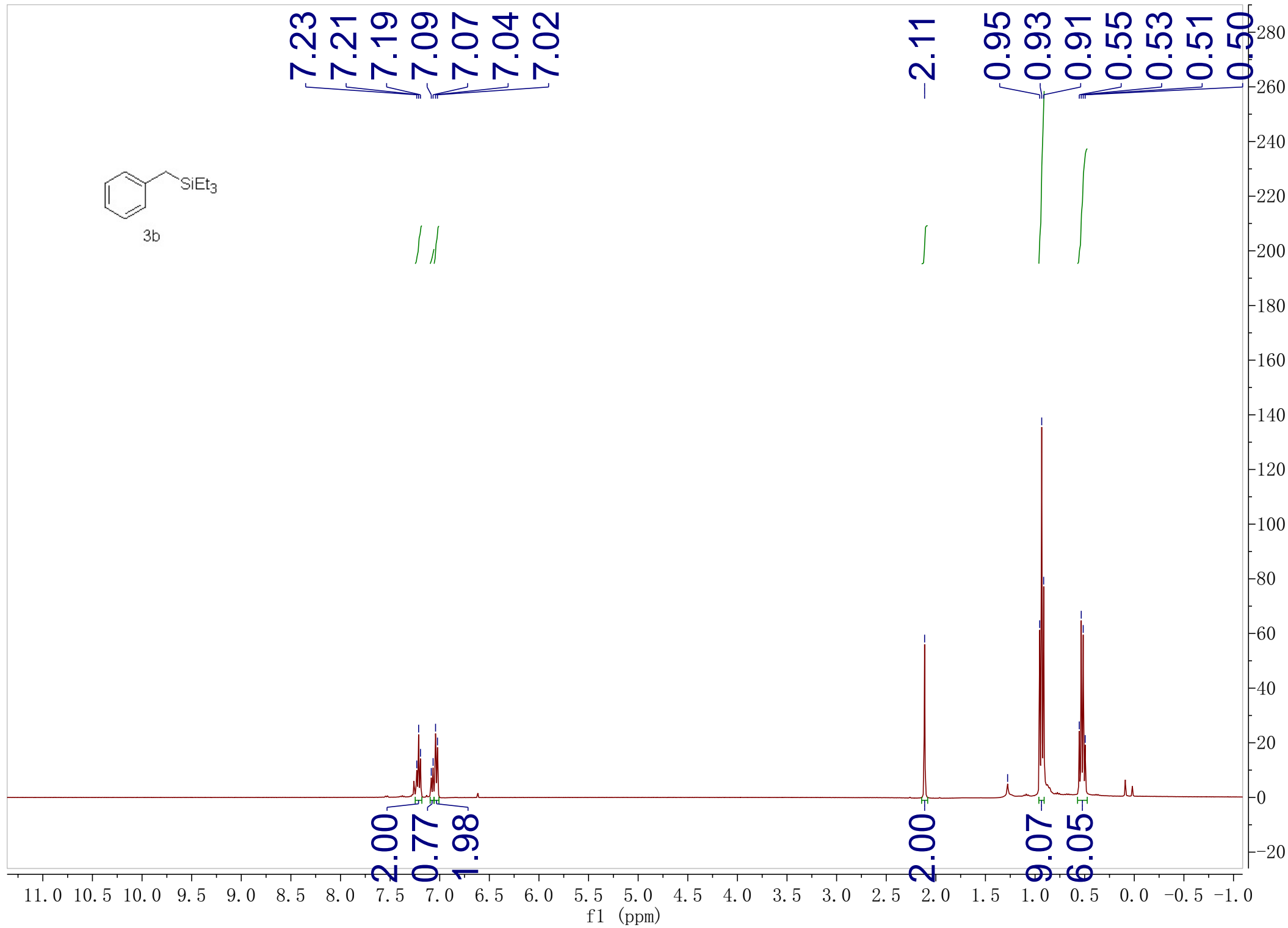
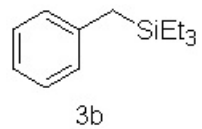


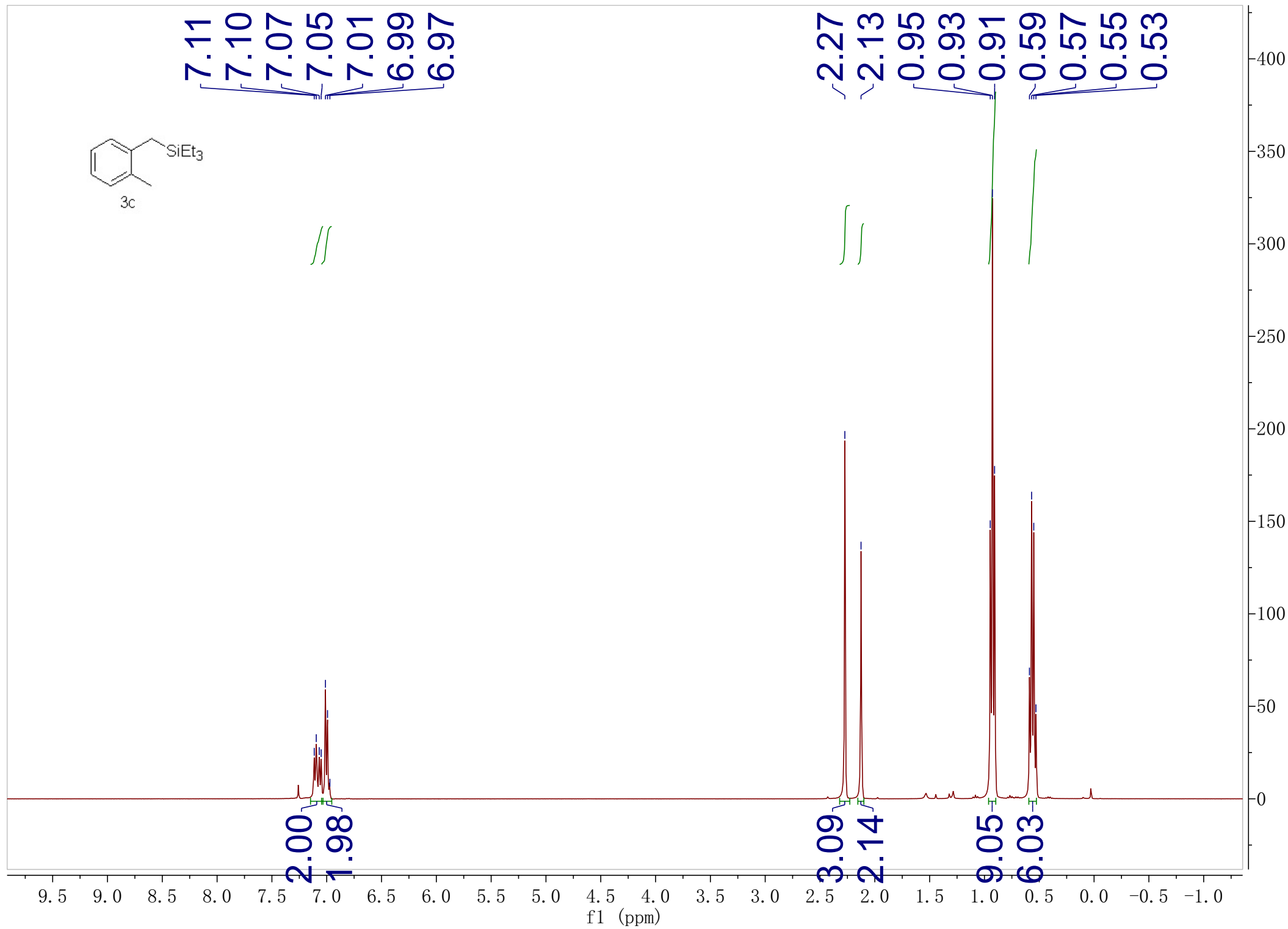
To a tube equipped with rubber stopper were added *N*-tosylhydrazone (0.2 mmol, 1.0 equiv), NaH (9.6 mg, 60 wt%, 0.24 mmol, 1.2 equiv), Fe(TPP)Cl (2.86 mg, 4.0 μmol , 0.02 equiv), silane (0.4 mmol, 2.0 equiv) and toluene (2.0 mL, 0.1 M) under air atmosphere. Then the tube was sealed and placed in Discover SP microwave synthesizer and reacted at 80 °C for 1 h. After completion the reaction was allowed to cool to room temperature and the crude reaction mixture was purified by column chromatography on silica gel (eluting with petroleum ether) to afford the insertion product.

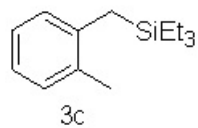
4. References and Notes

- [1] Creary, X.; Tam, W. W.; Albizati, K. F.; Stevens, R. V. *Org. Synth.* **1986**, *64*, 207.
- [2] (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chatterjee, A. *J. Am. Chem. Soc.* **1971**, *93*, 3162
- [3] Liu, Z.; Li, Q.; Yang, Y.; Bi, X. *Chem. Commun.* **2017**, *53*, 2503.



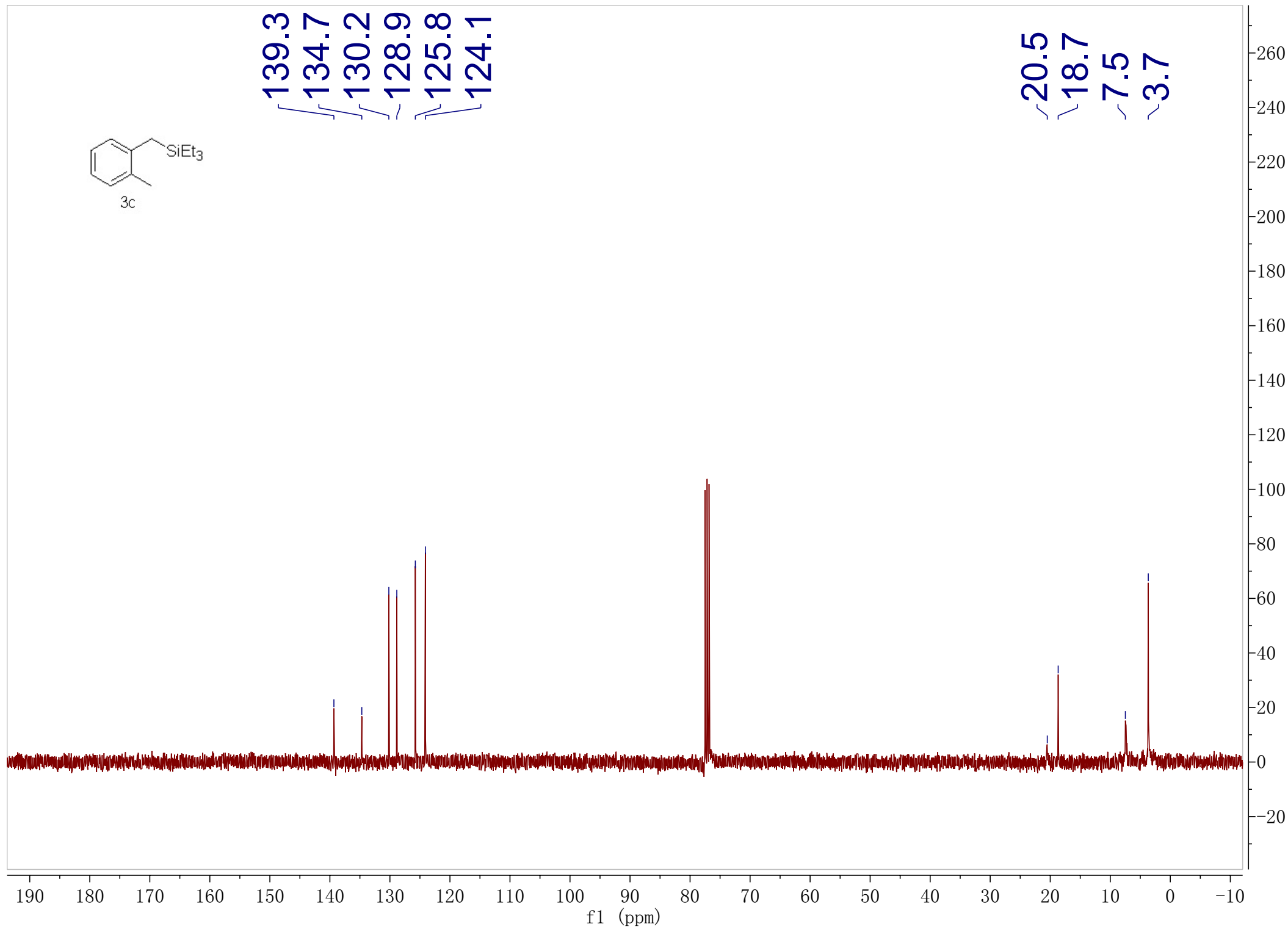


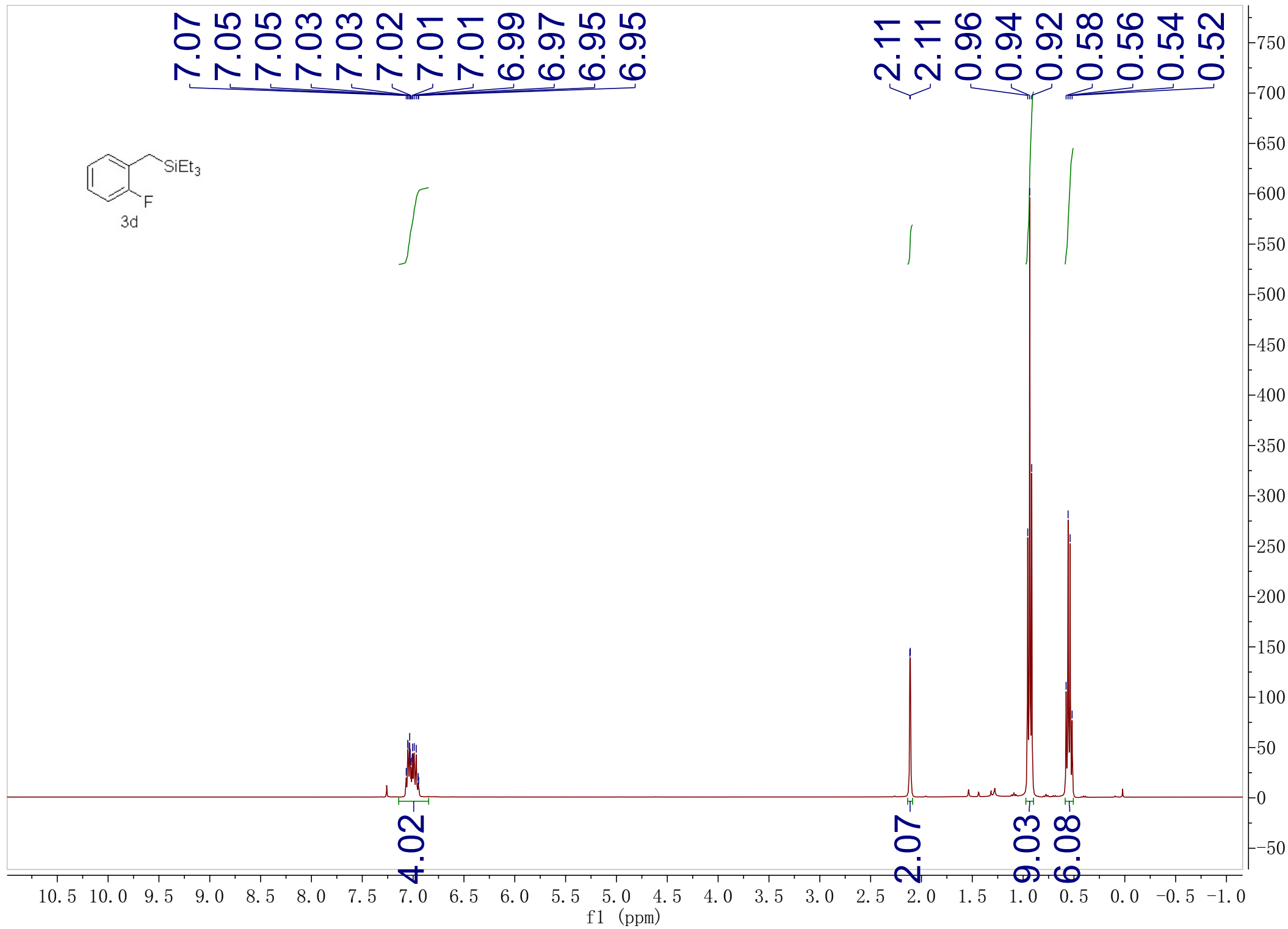


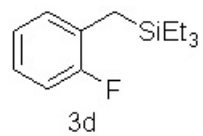


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130.2
128.9
125.8
124.1

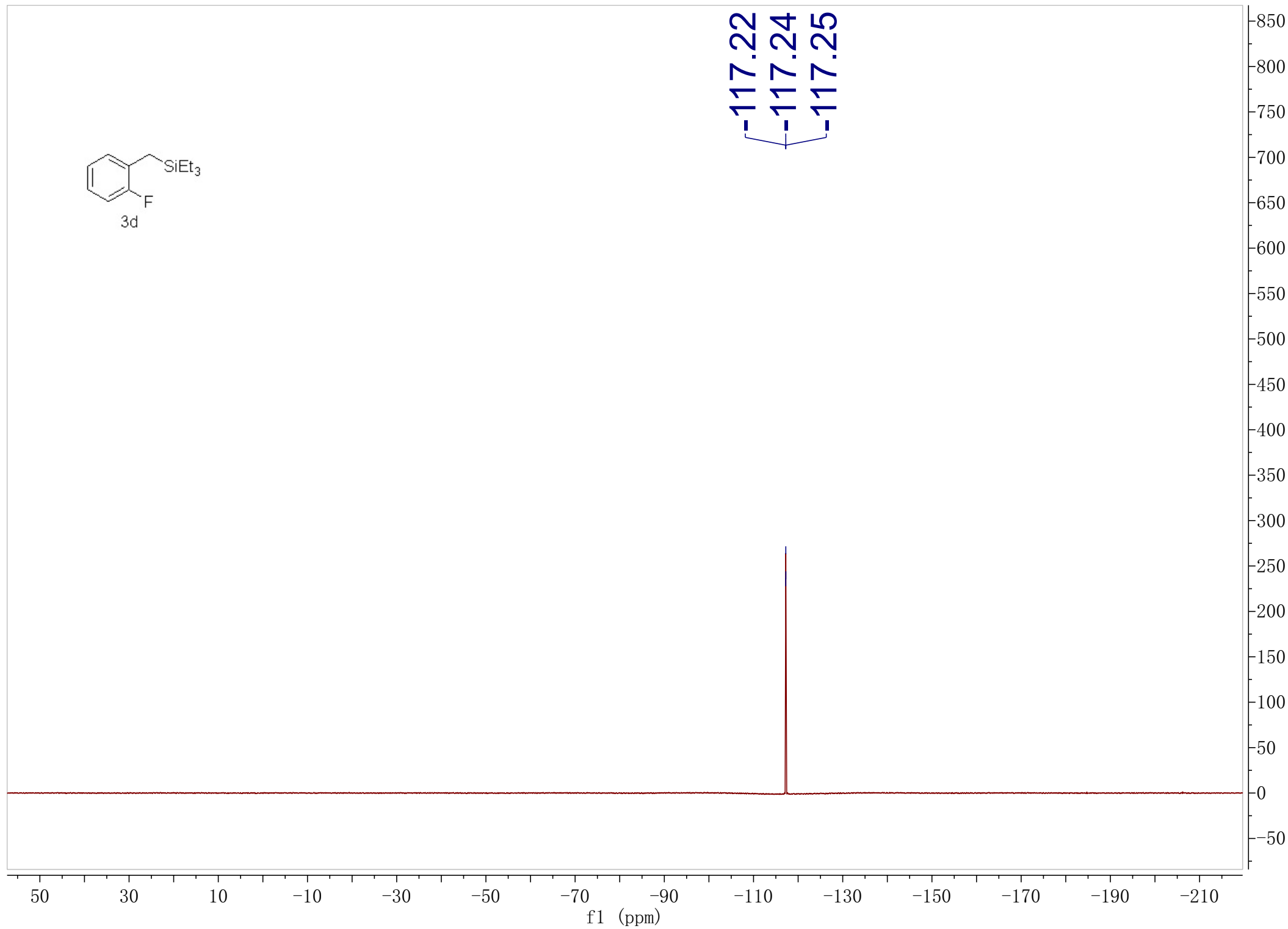
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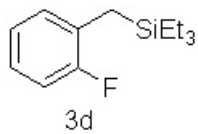






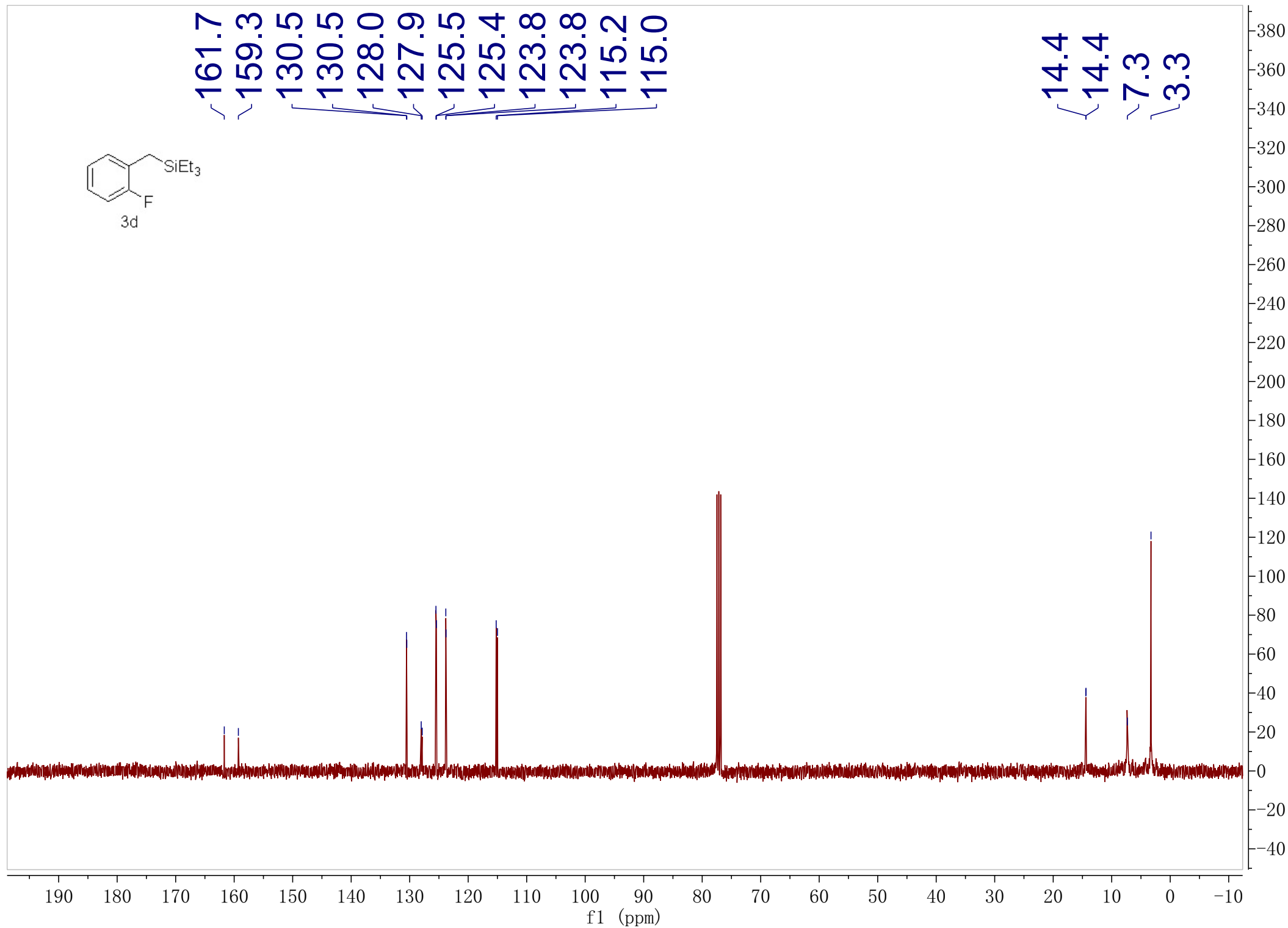
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117.25

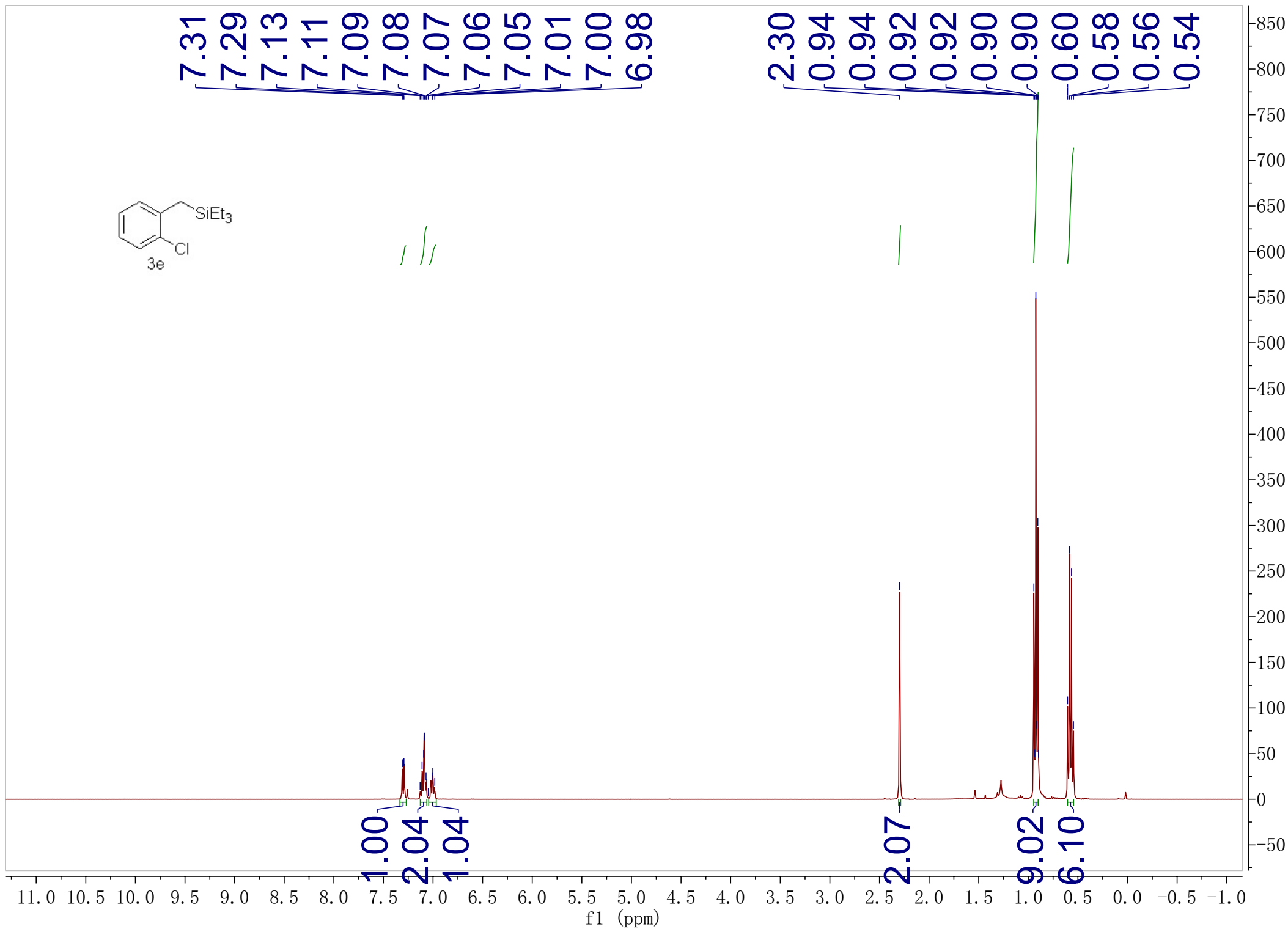
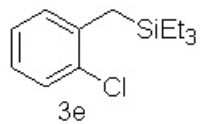


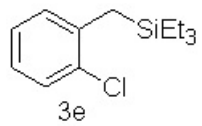


161.7
159.3
130.5
130.5
128.0
127.9
125.5
125.4
123.8
123.8
115.2
115.0

14.4
14.4
7.3
3.3

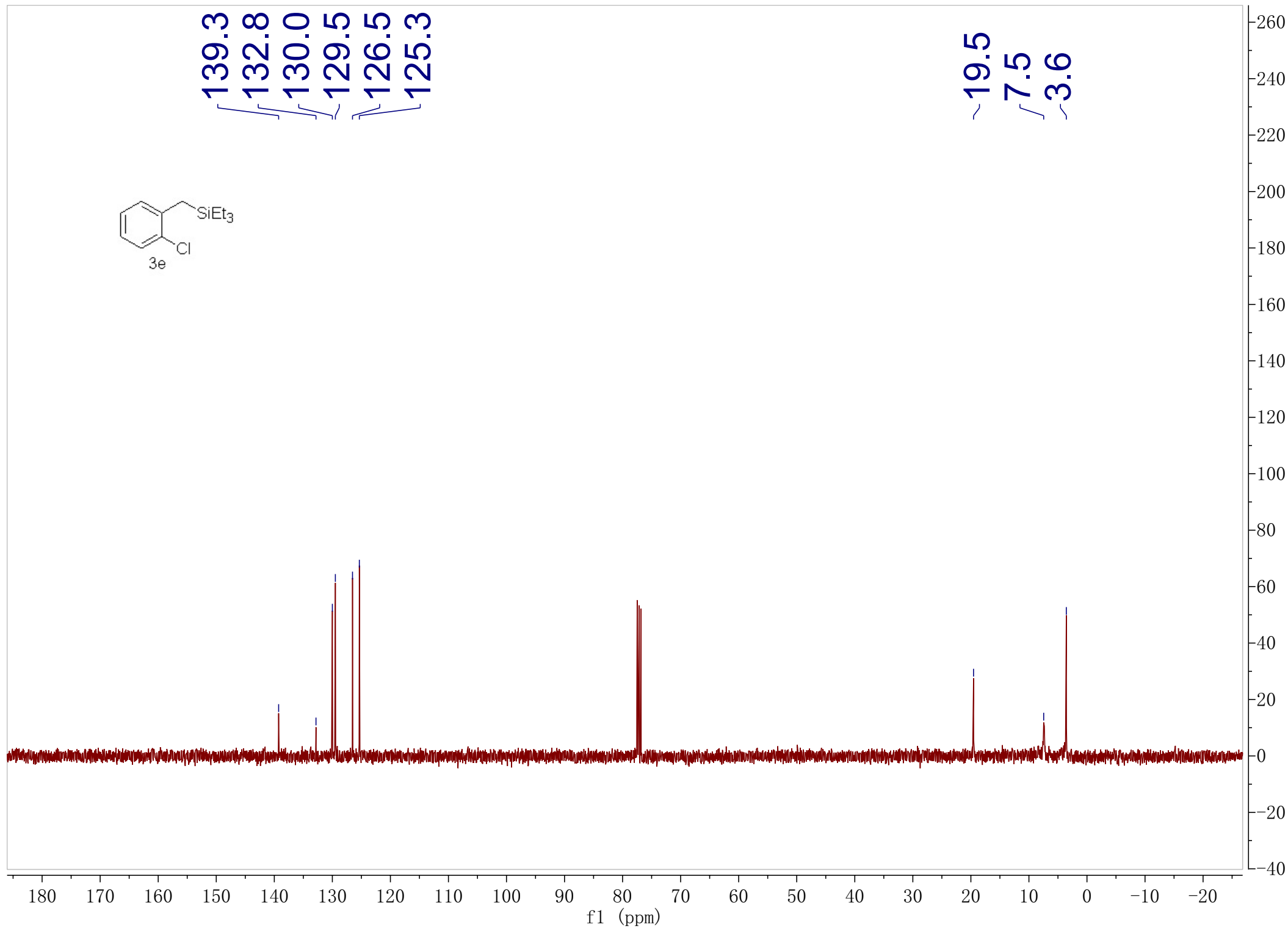


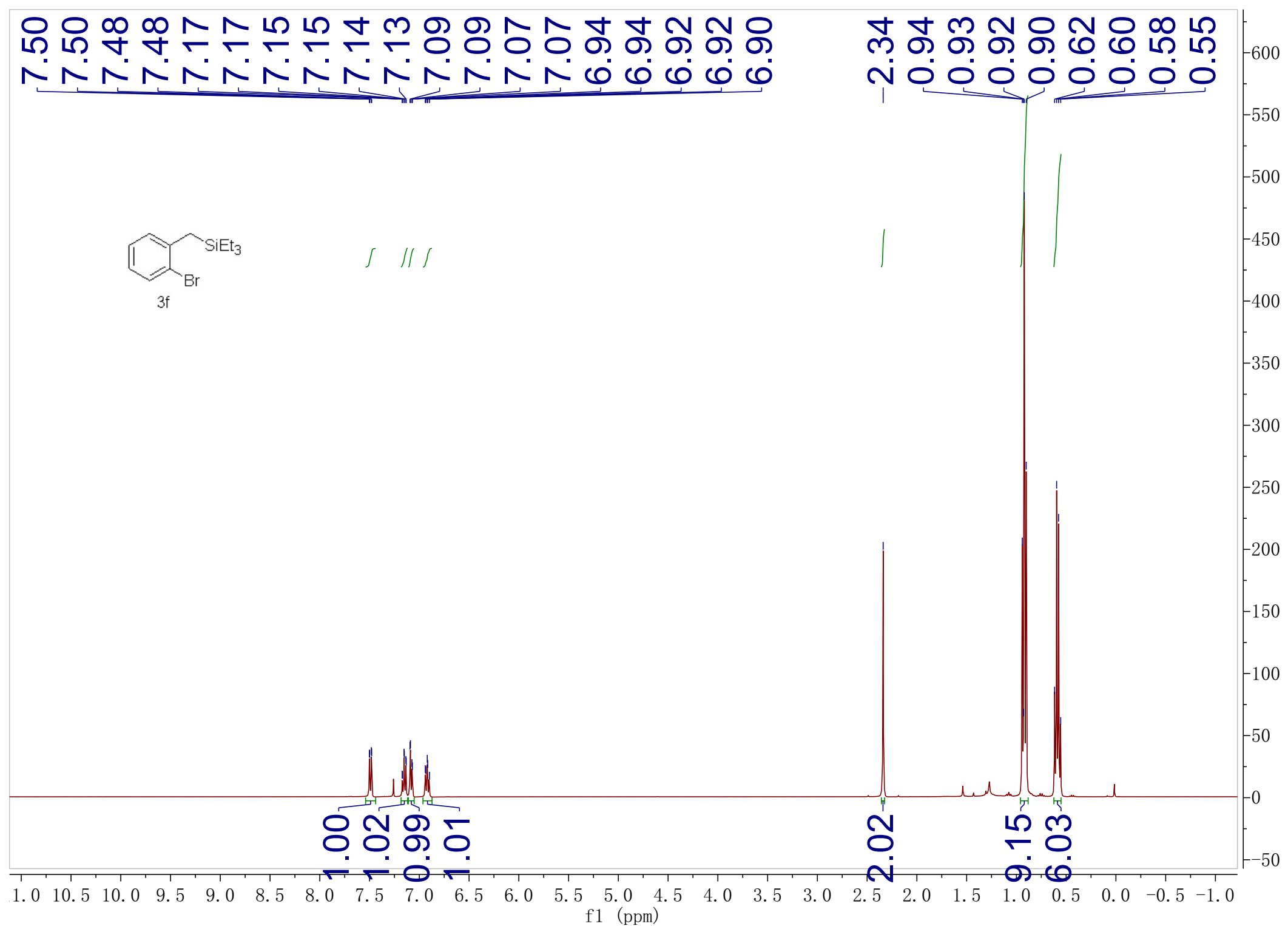
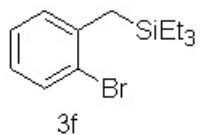


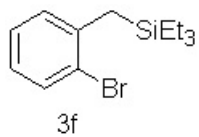


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132.8
130.0
129.5
126.5
125.3

~19.5
7.5
~3.6





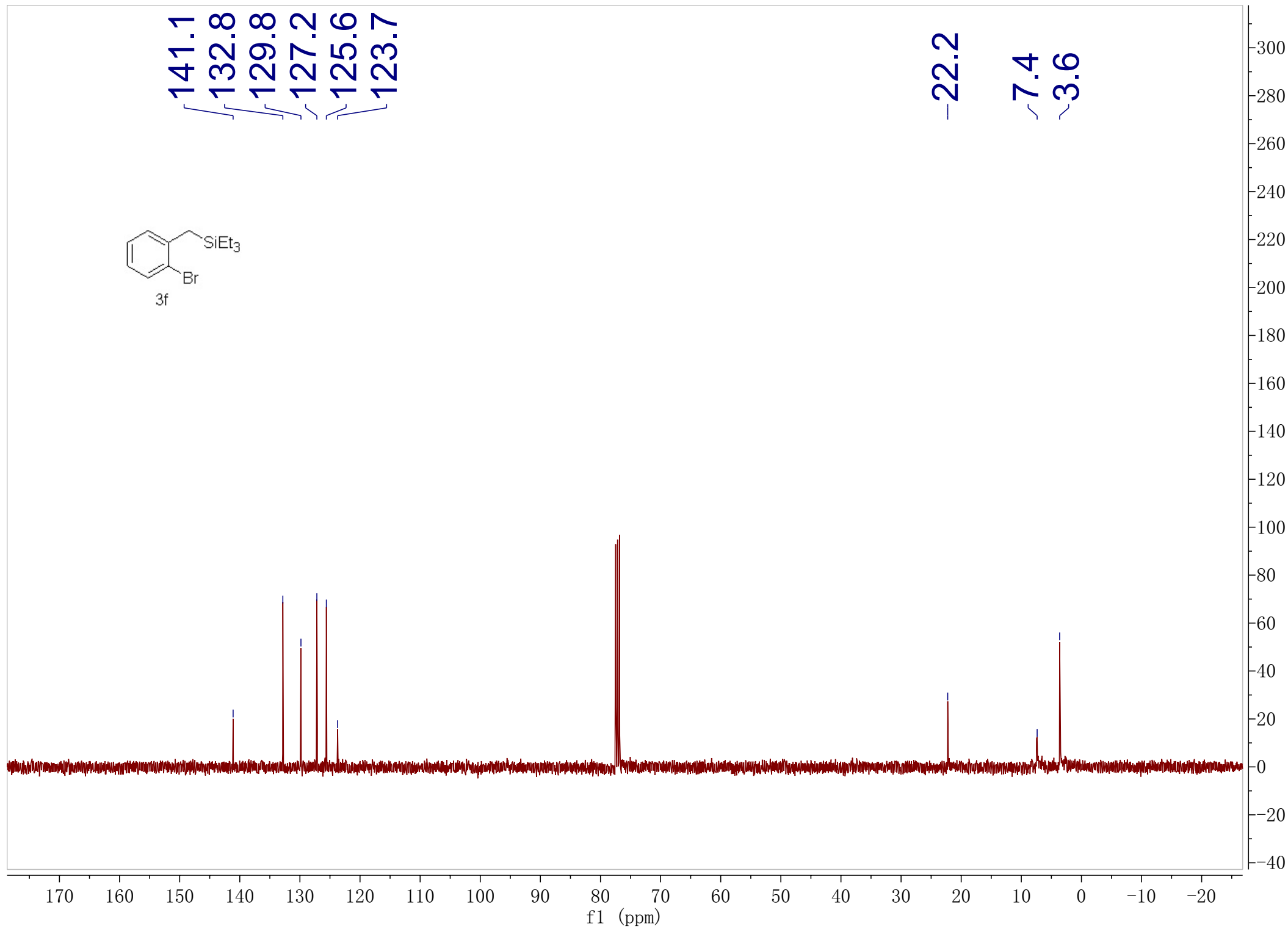


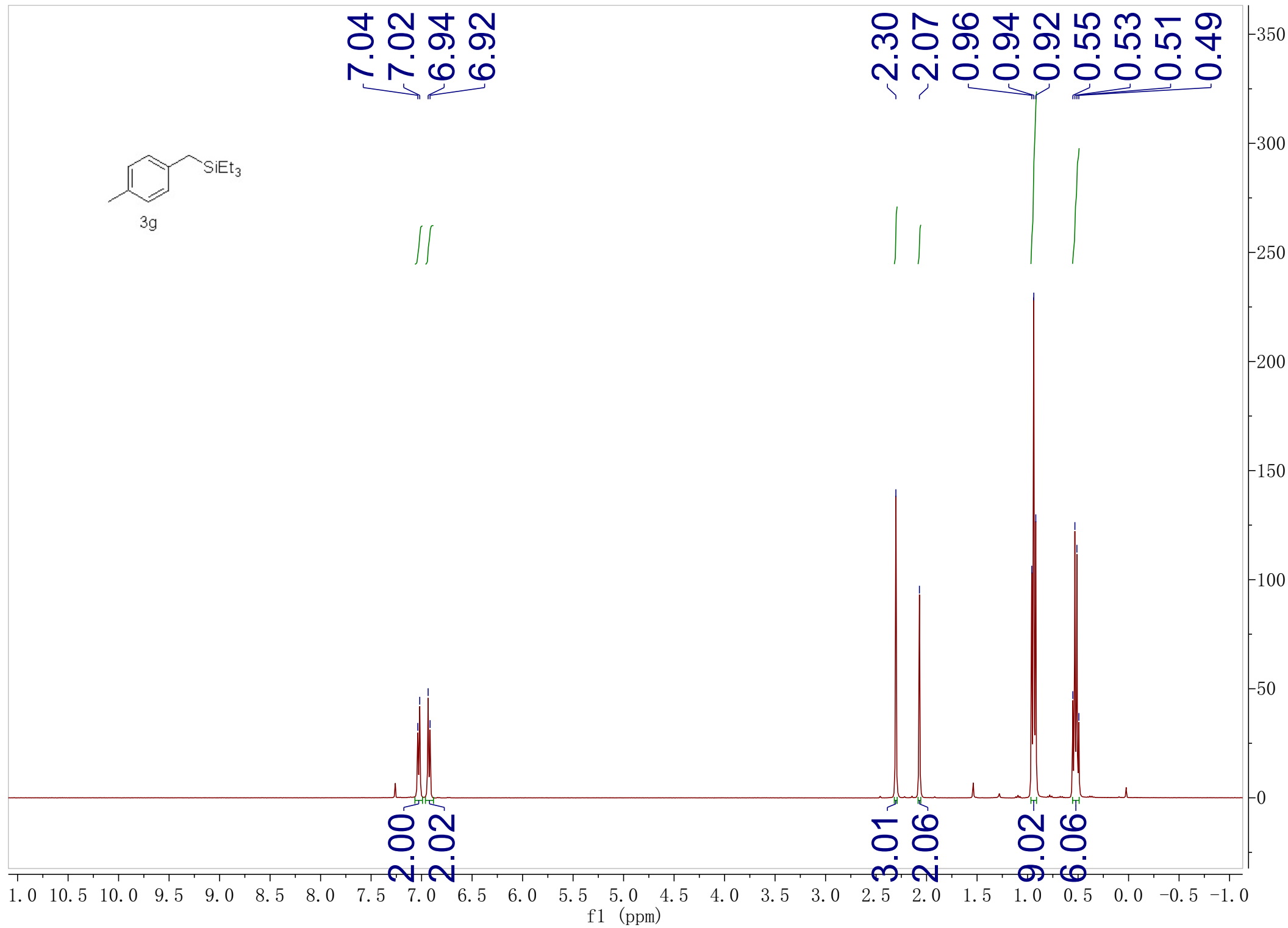
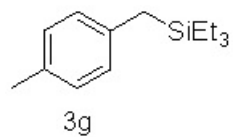
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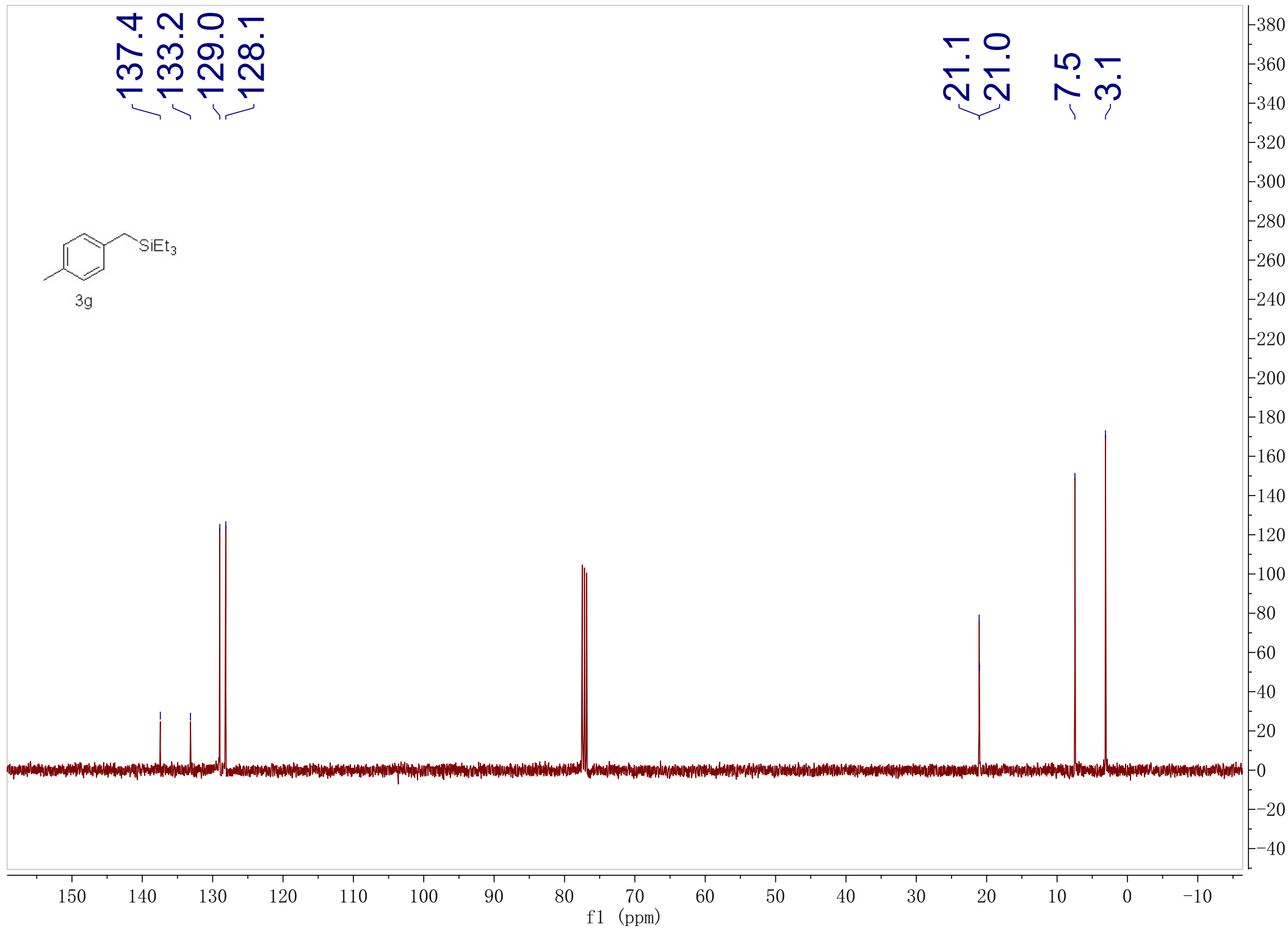
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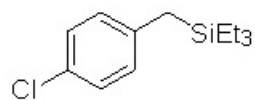
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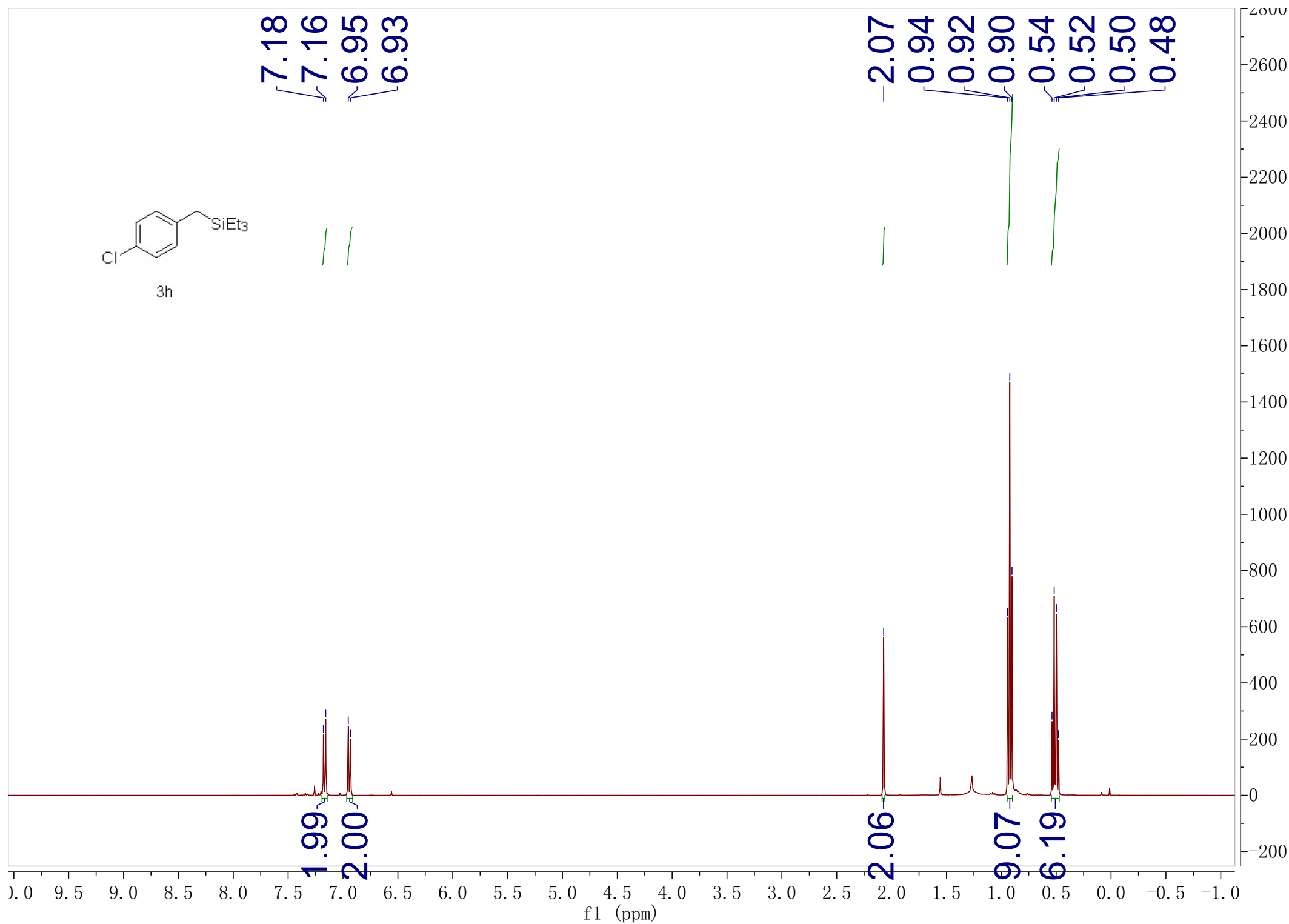
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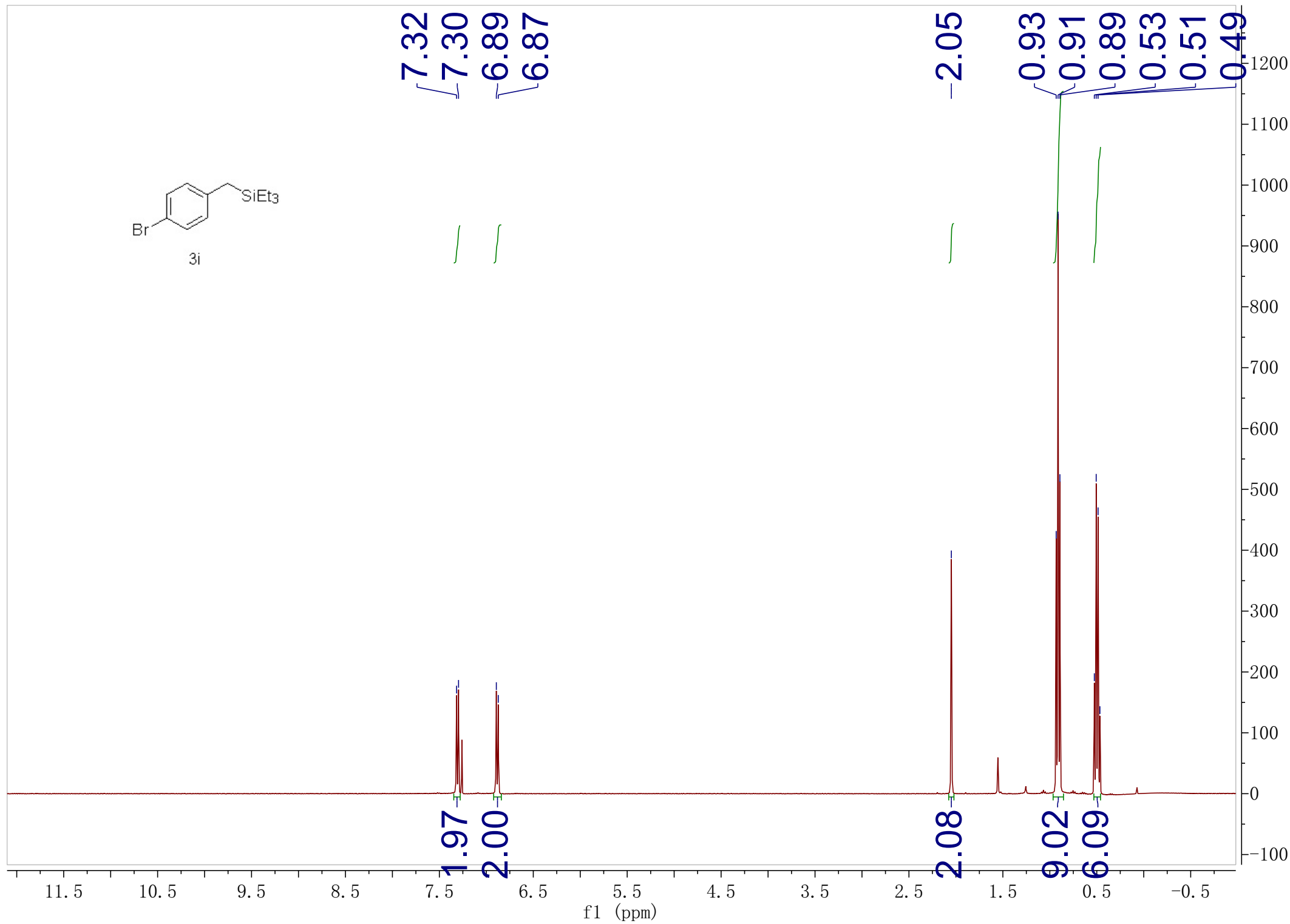
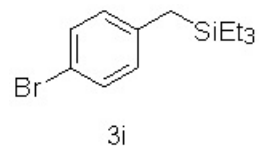
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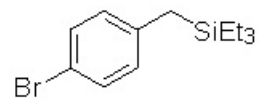
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0.52
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0.48

1.99
2.00

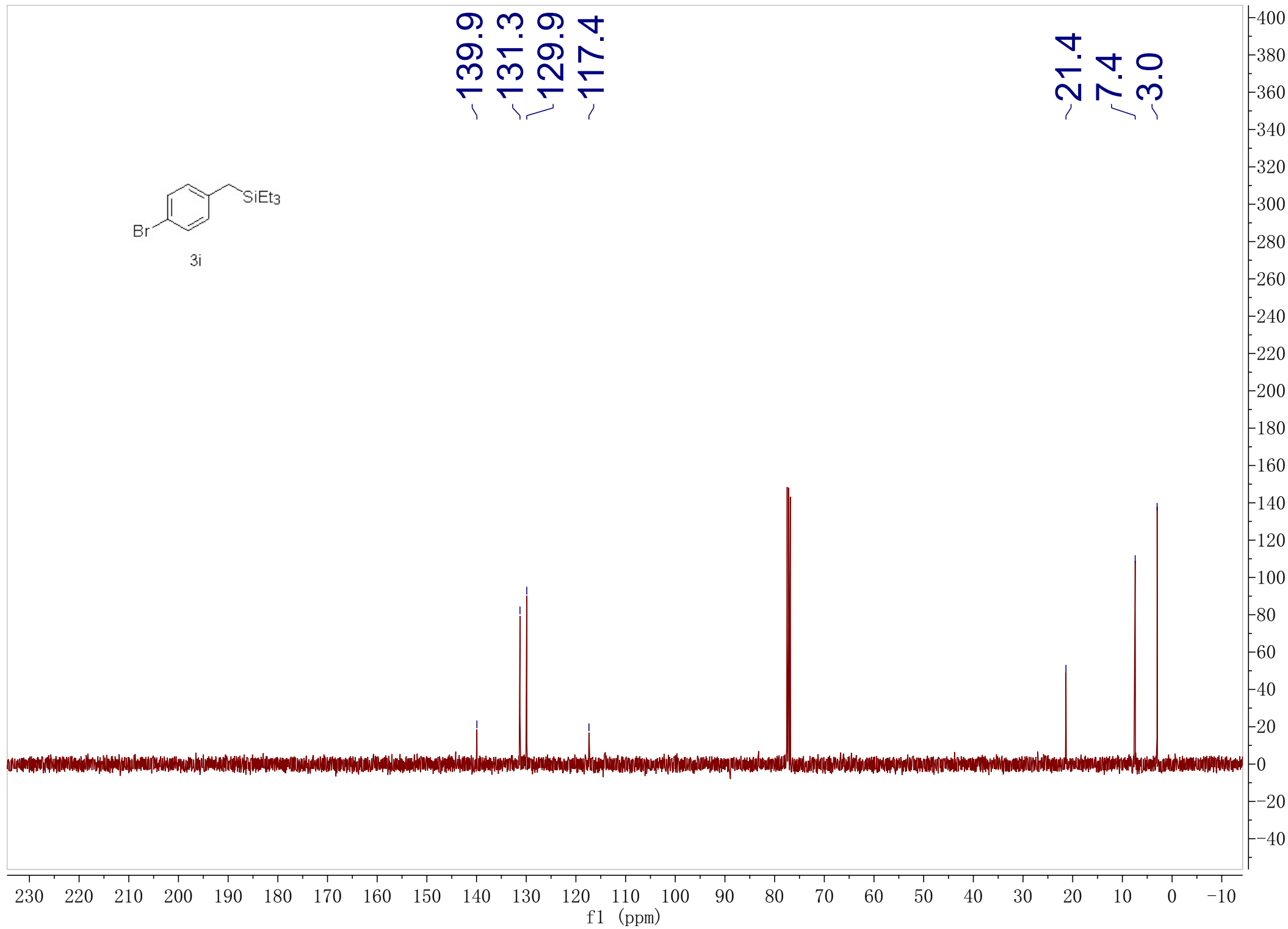
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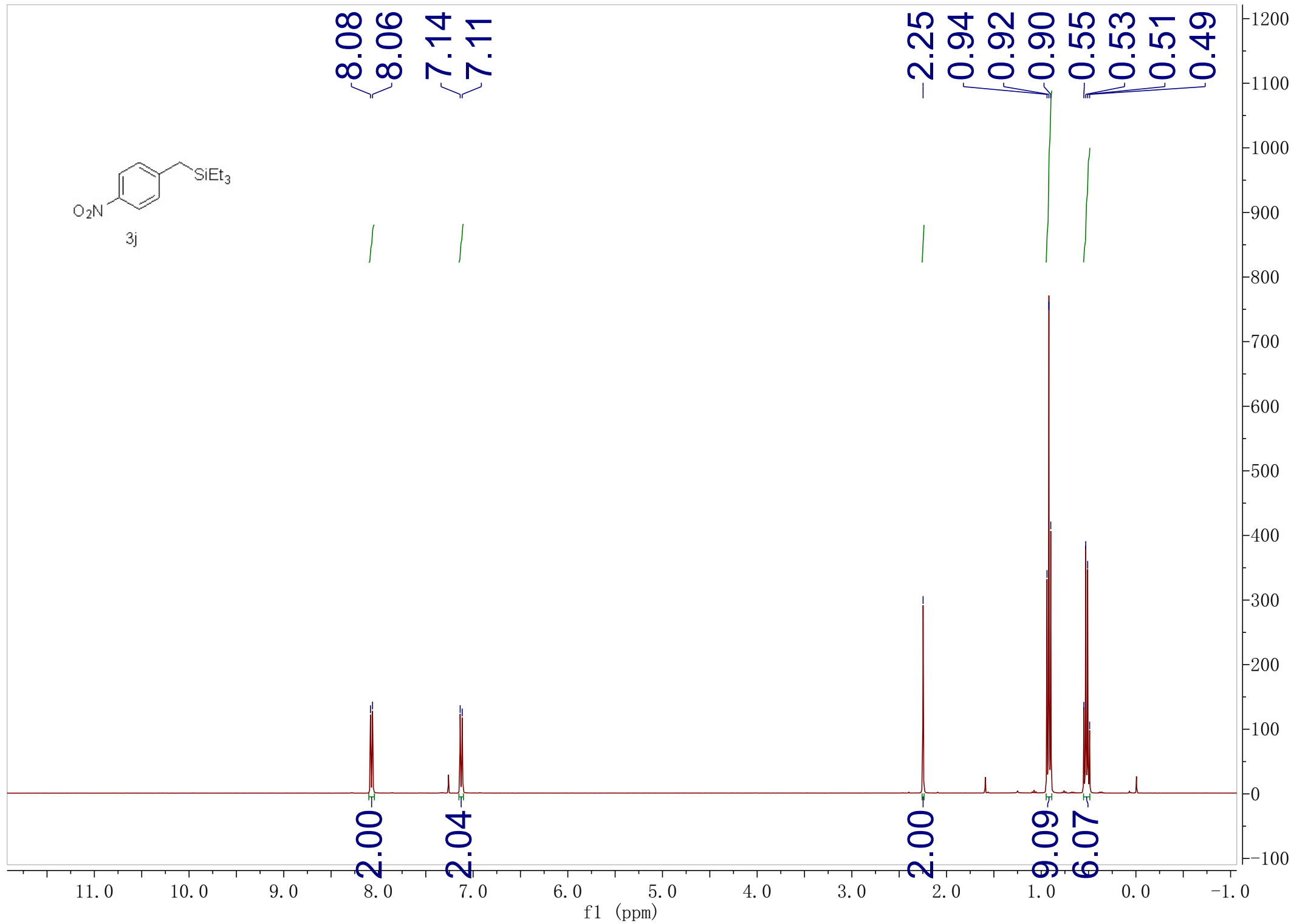
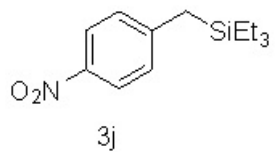


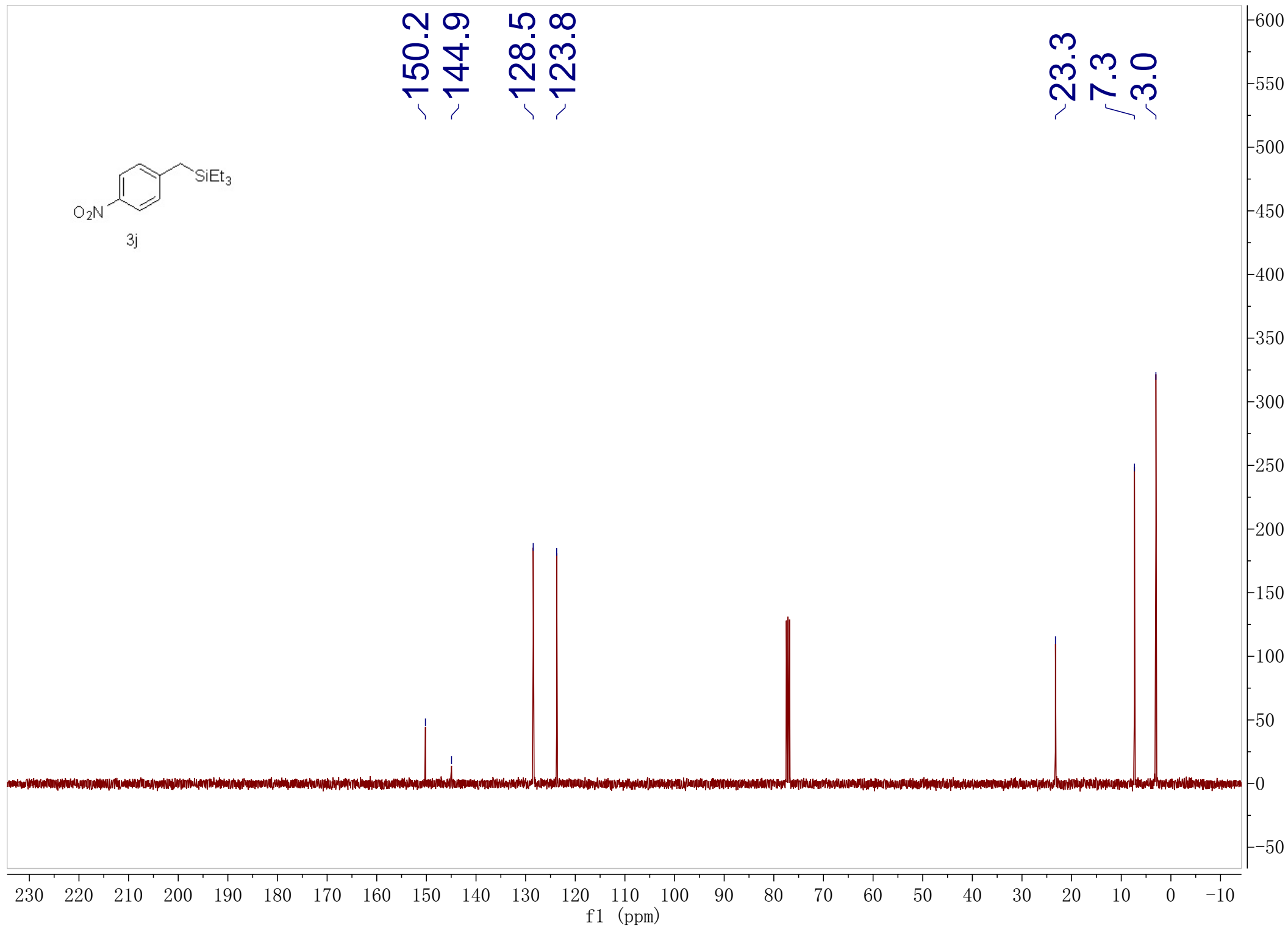
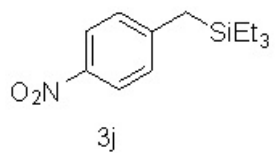


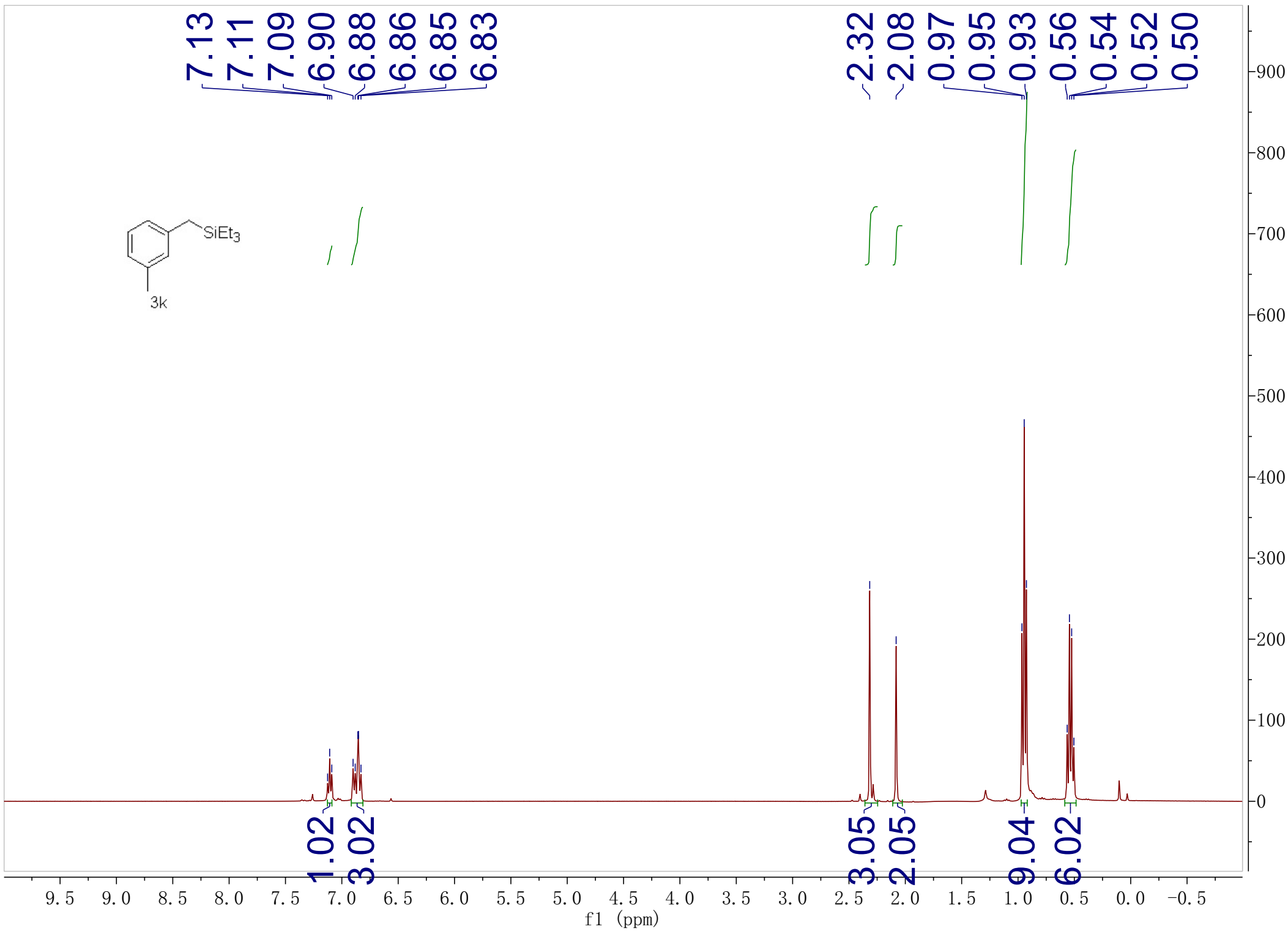
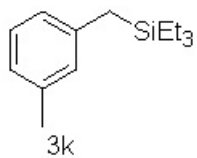


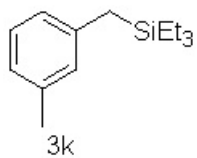
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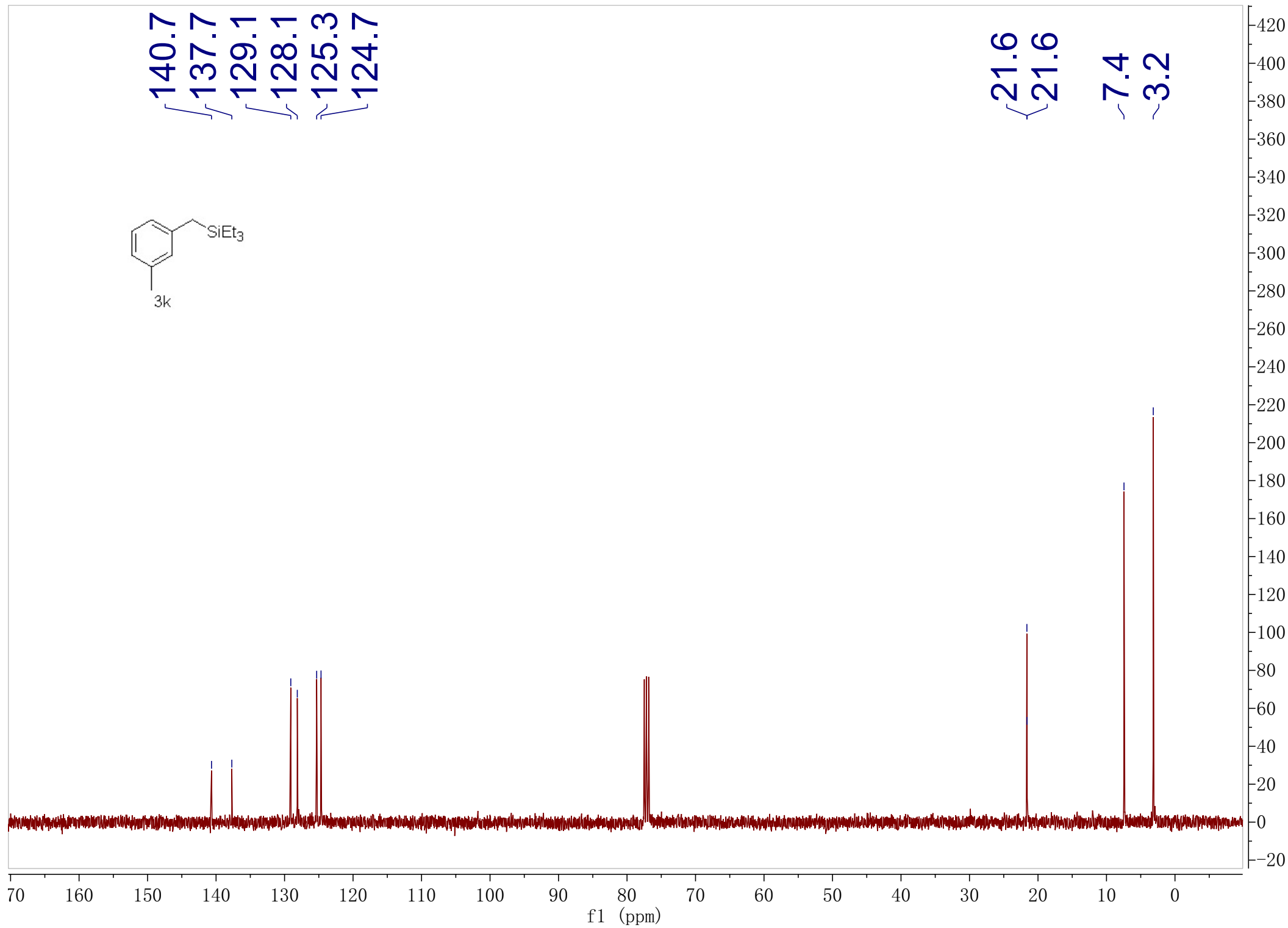


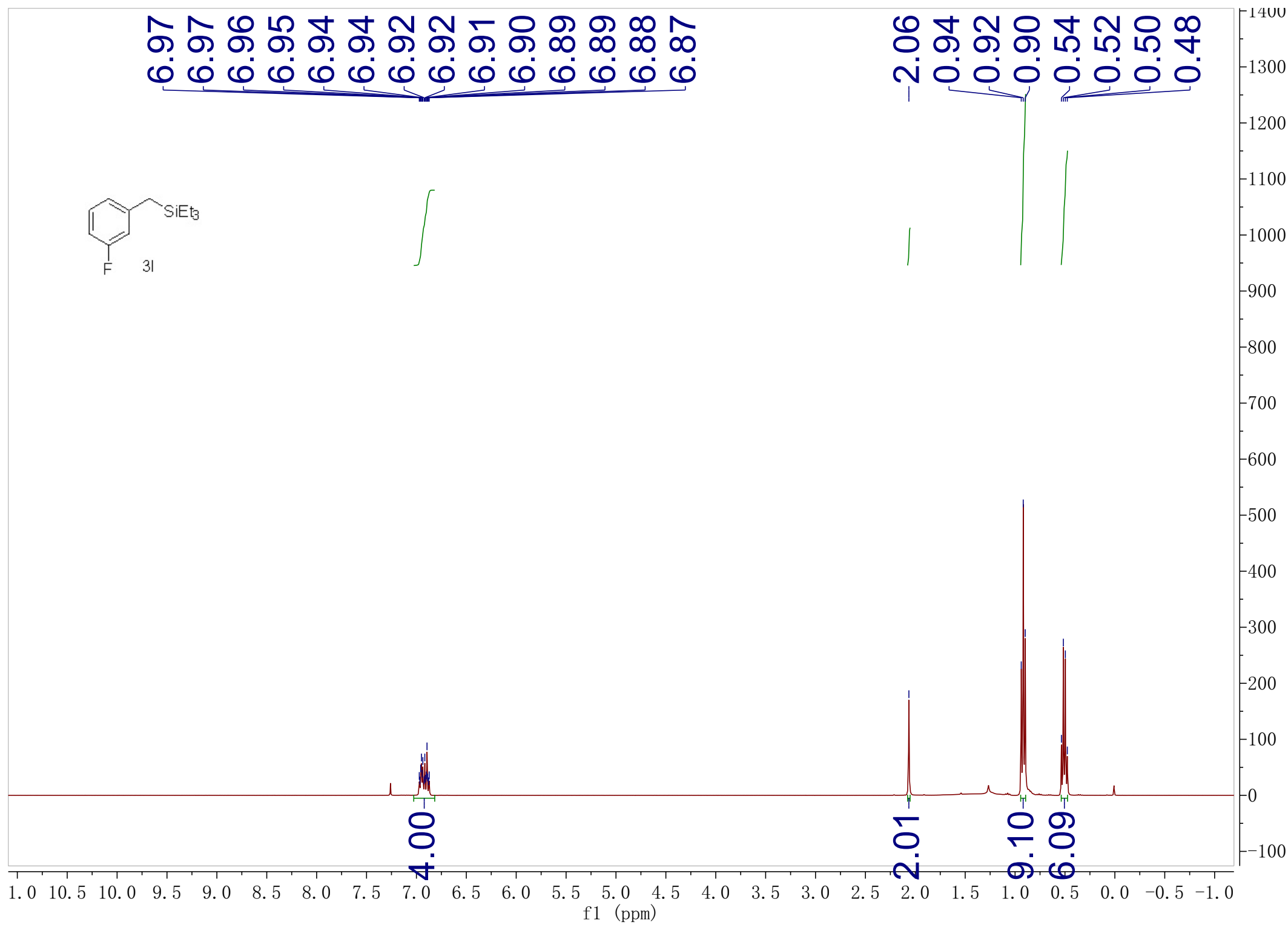


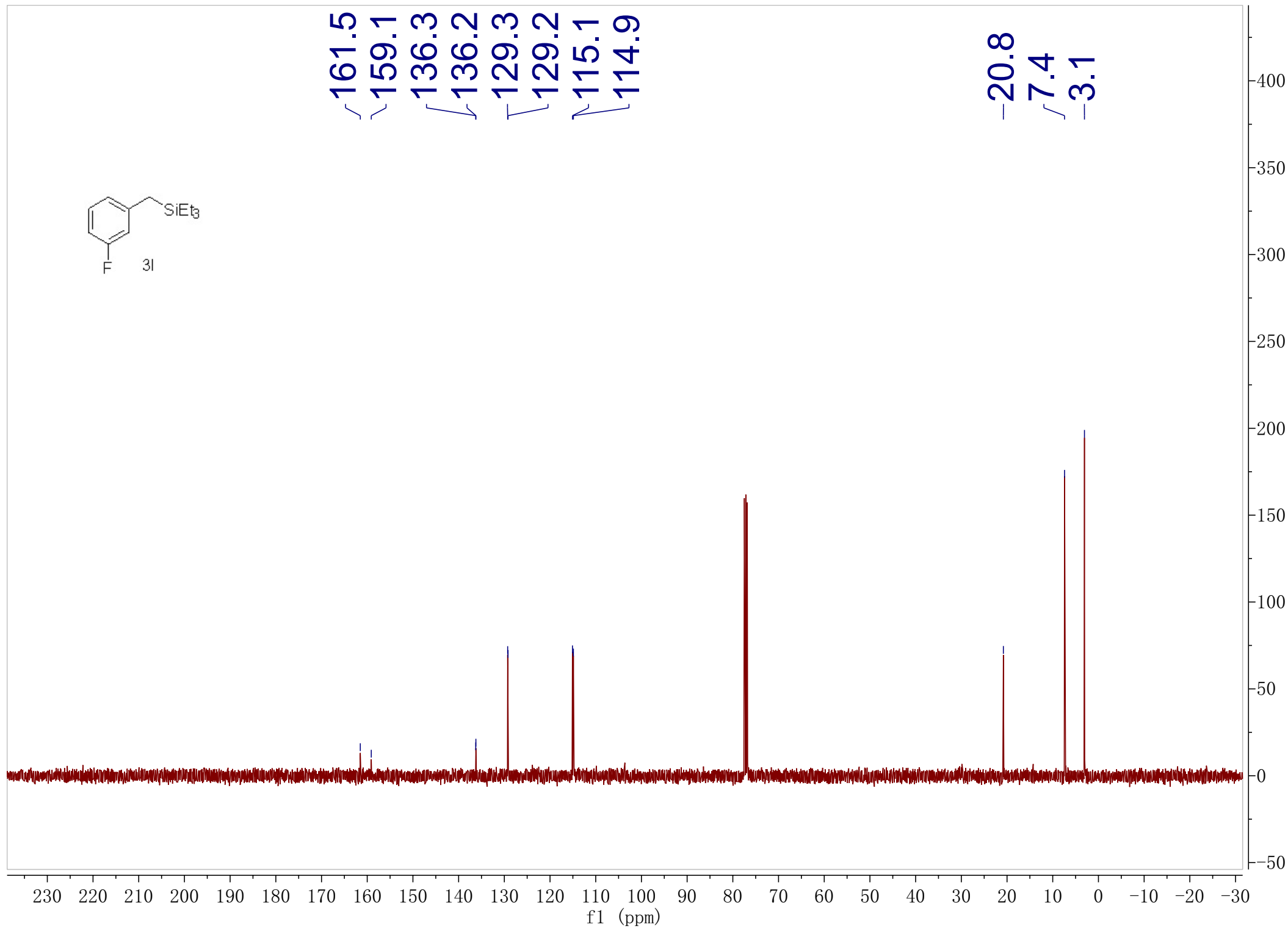
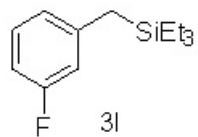
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124.7

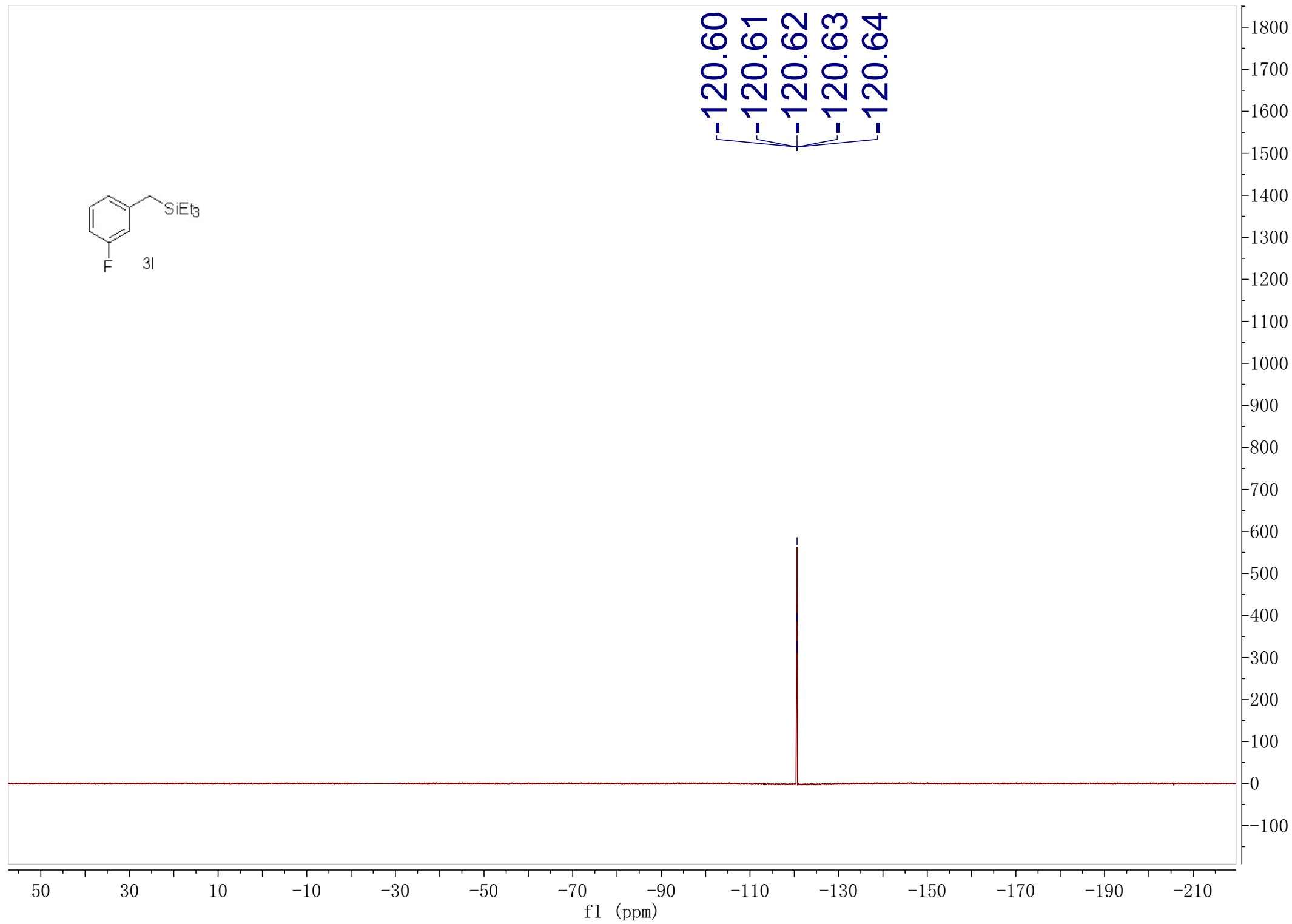
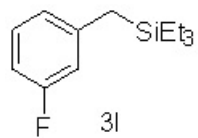
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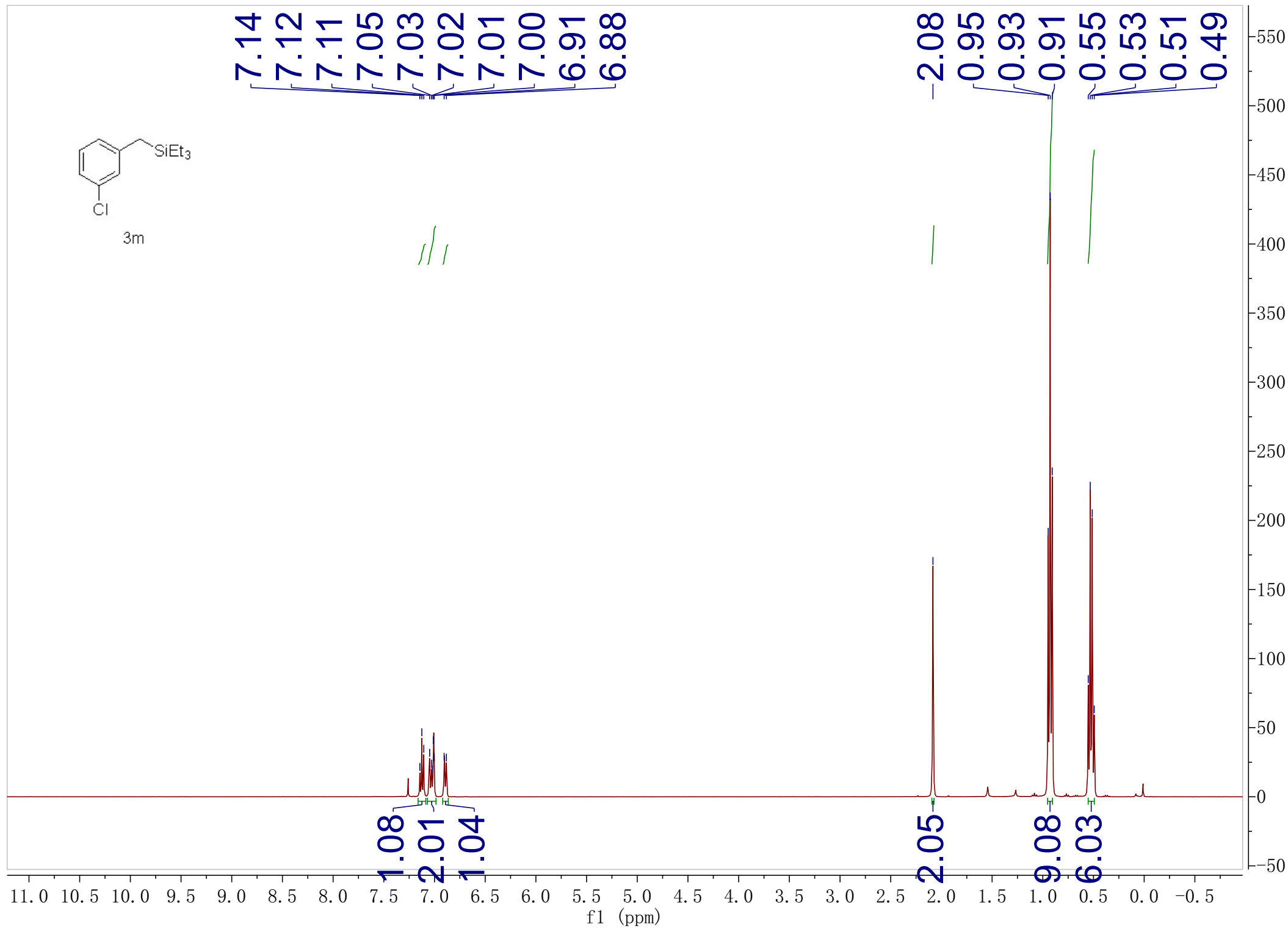
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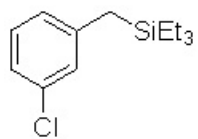








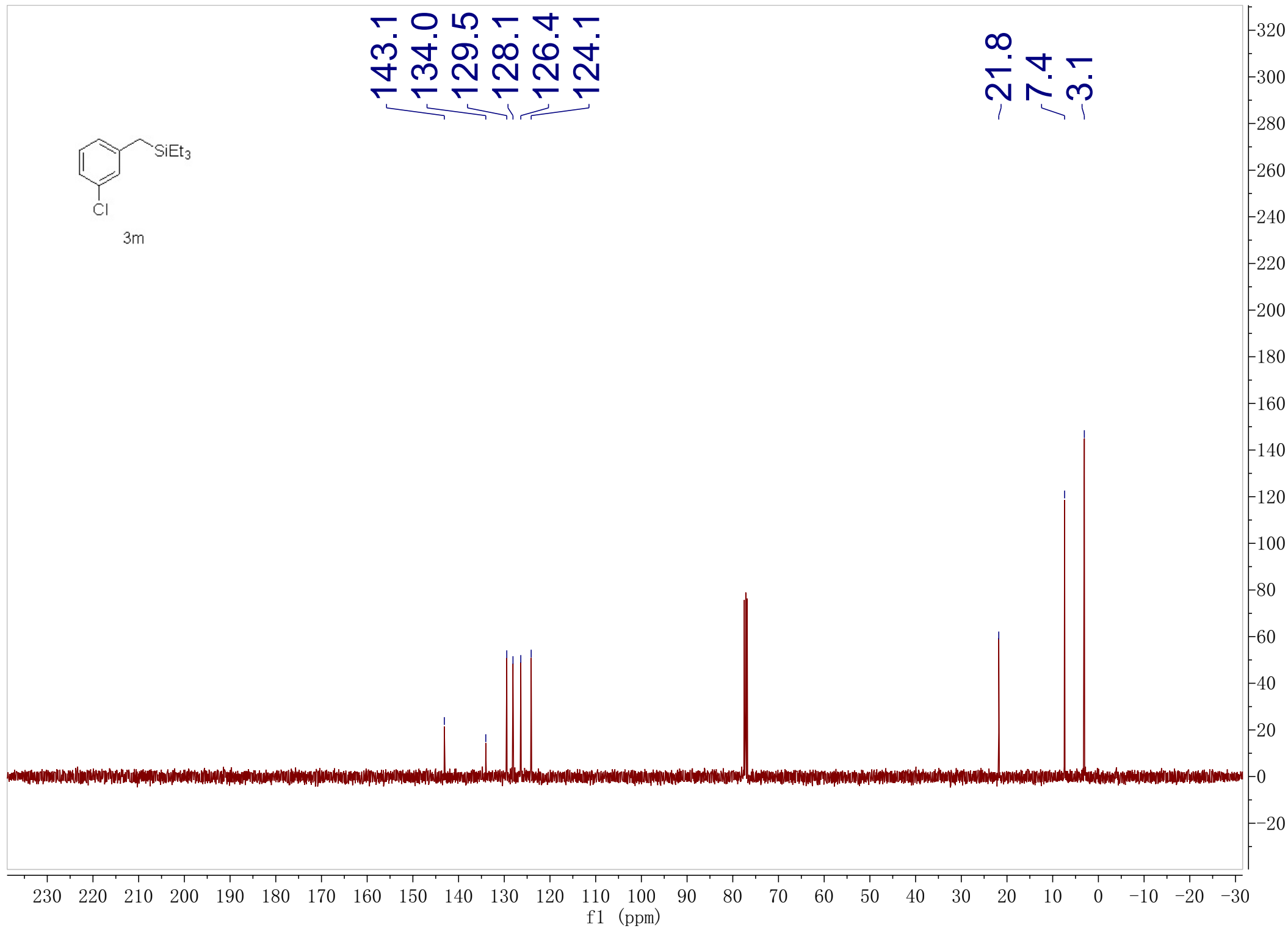


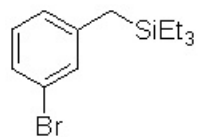


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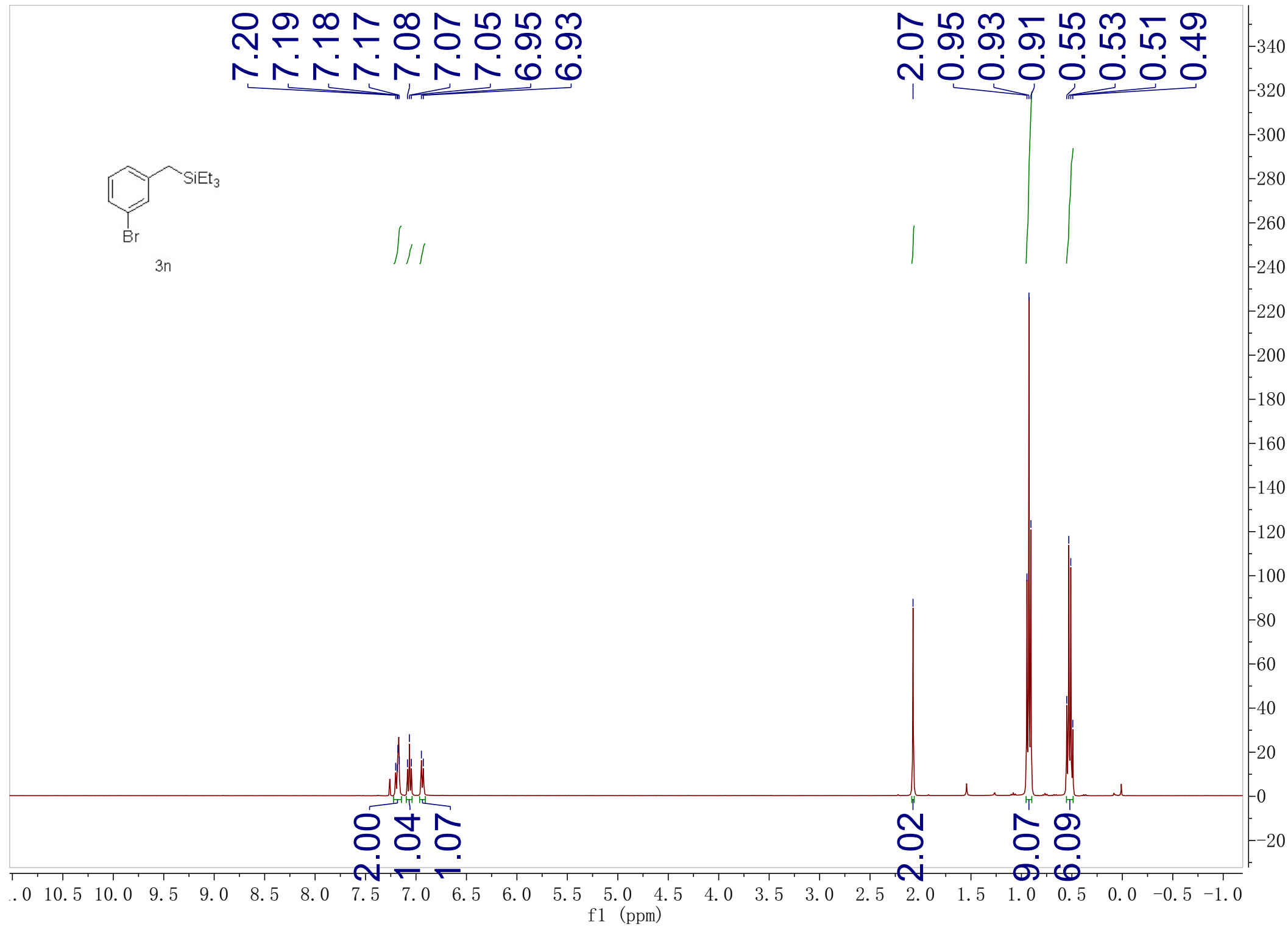
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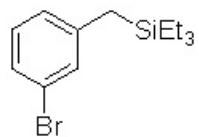
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3n

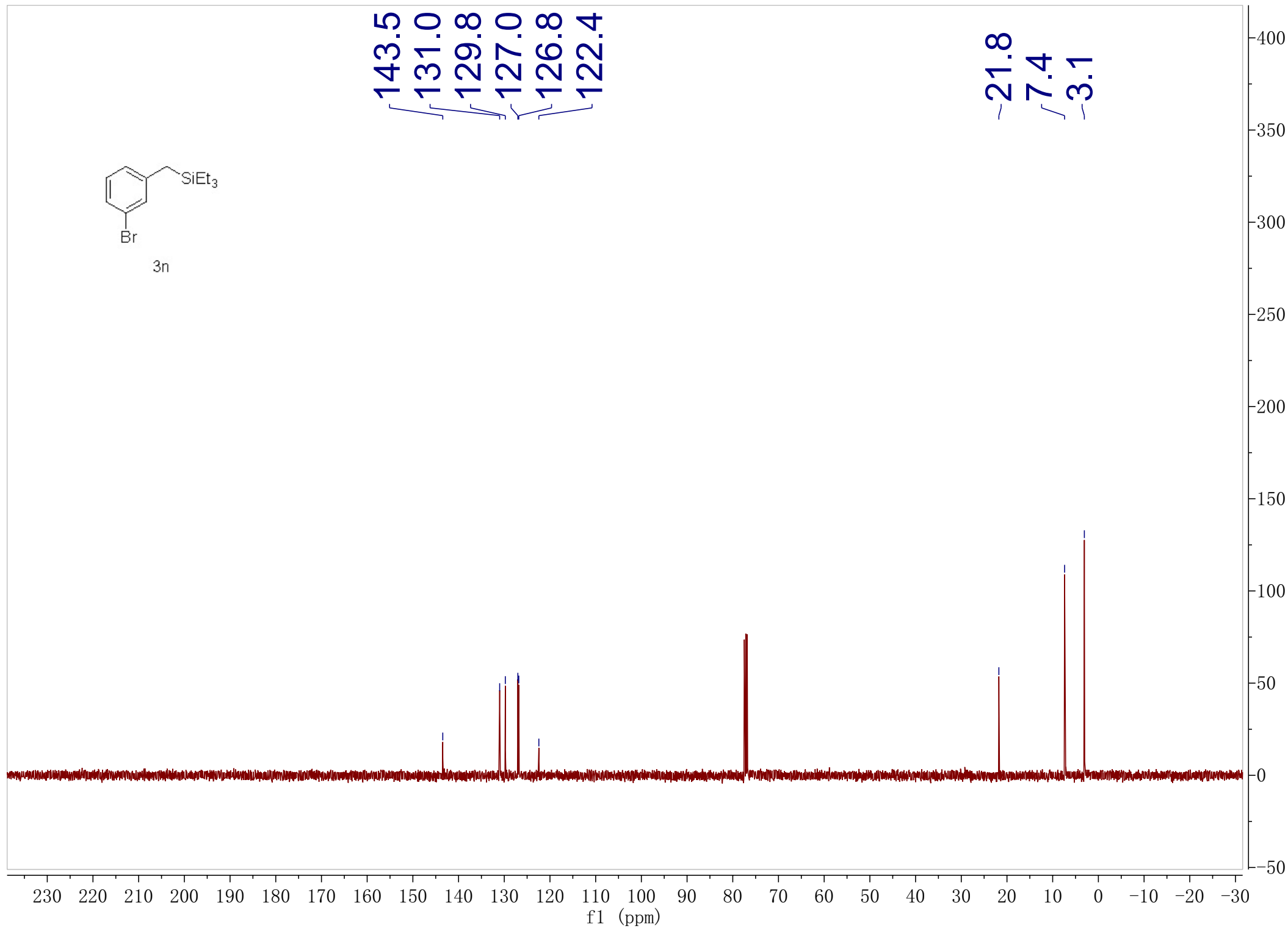


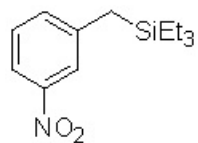


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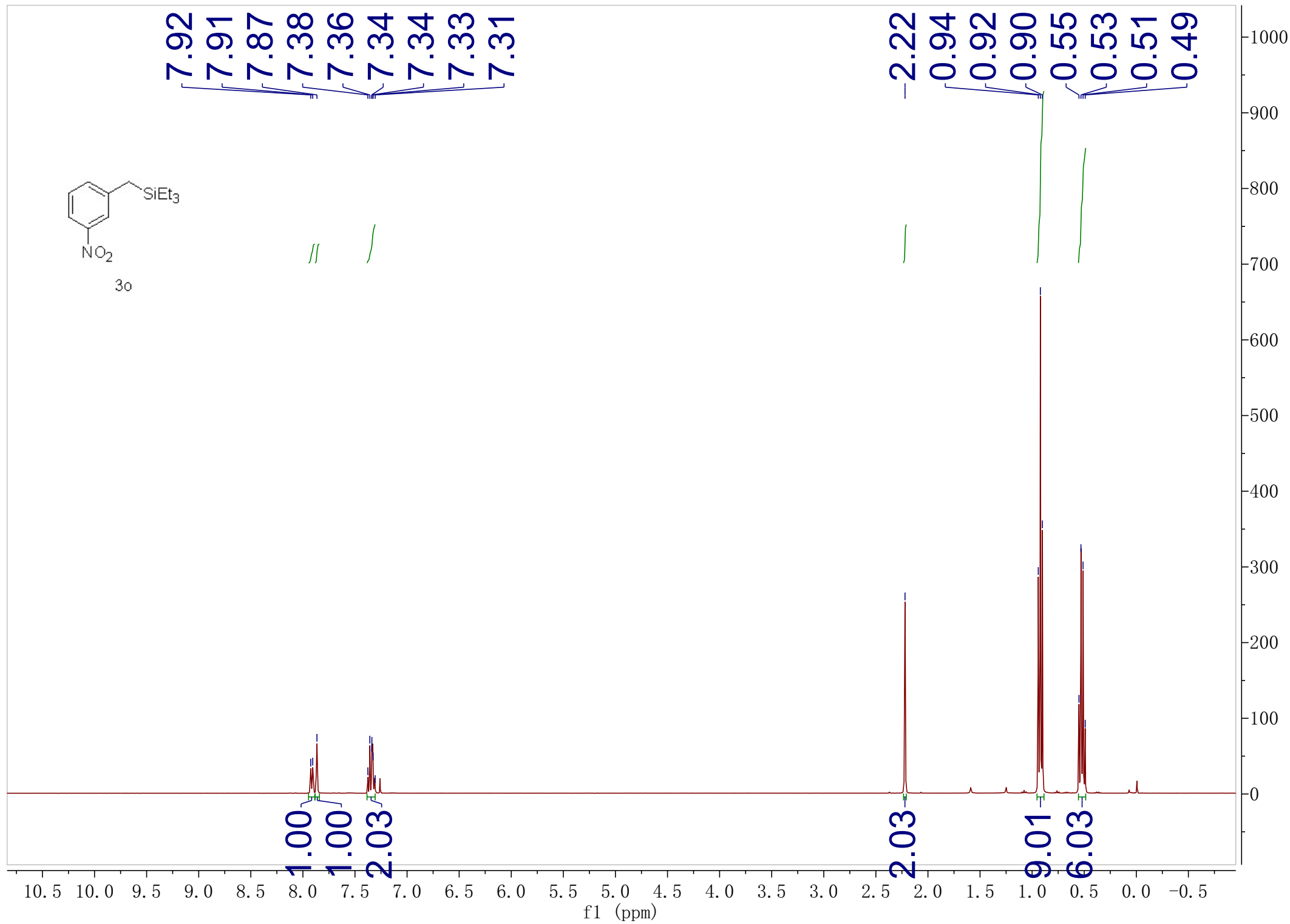
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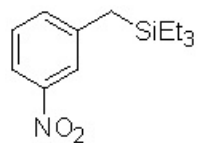
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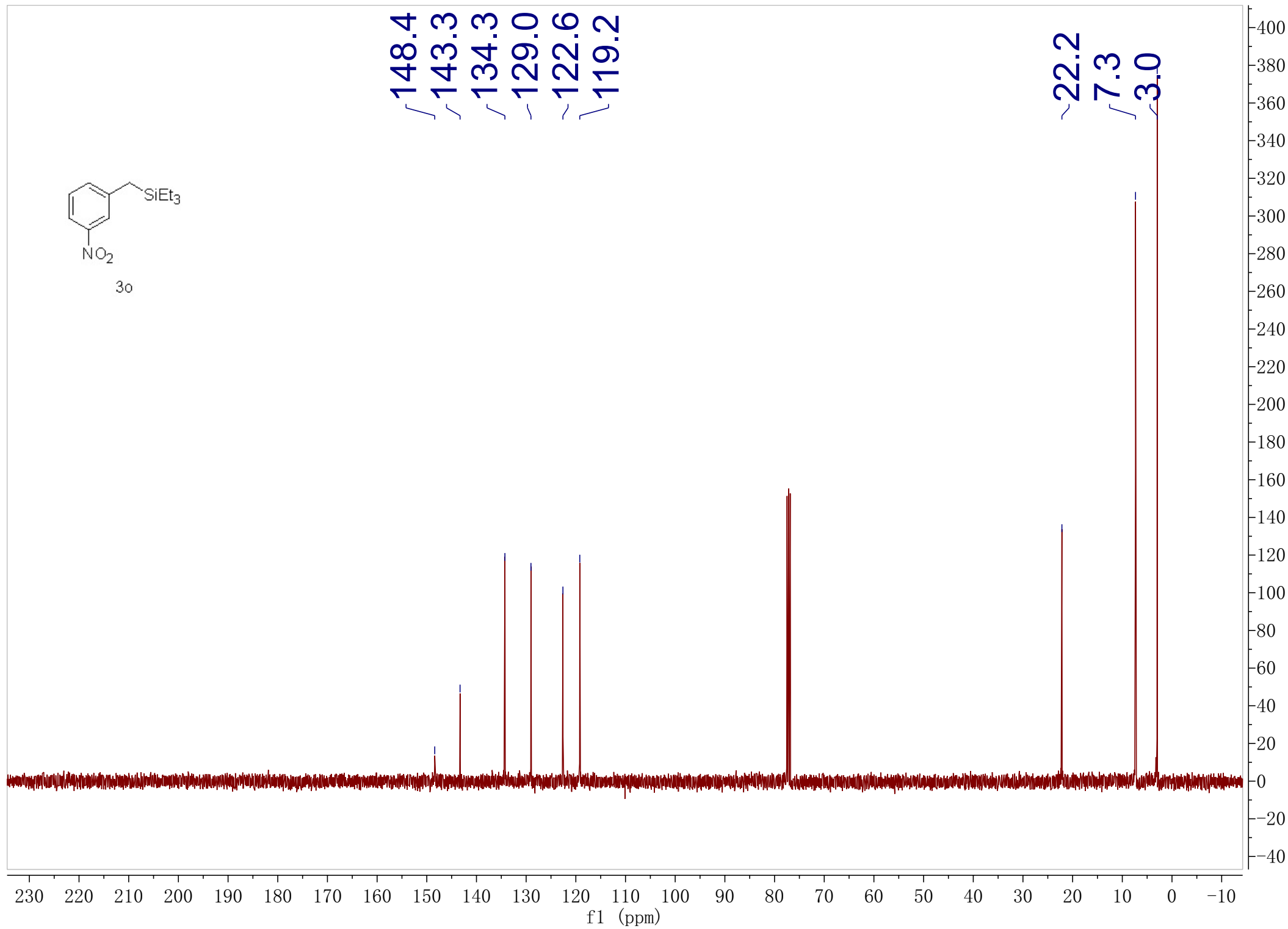


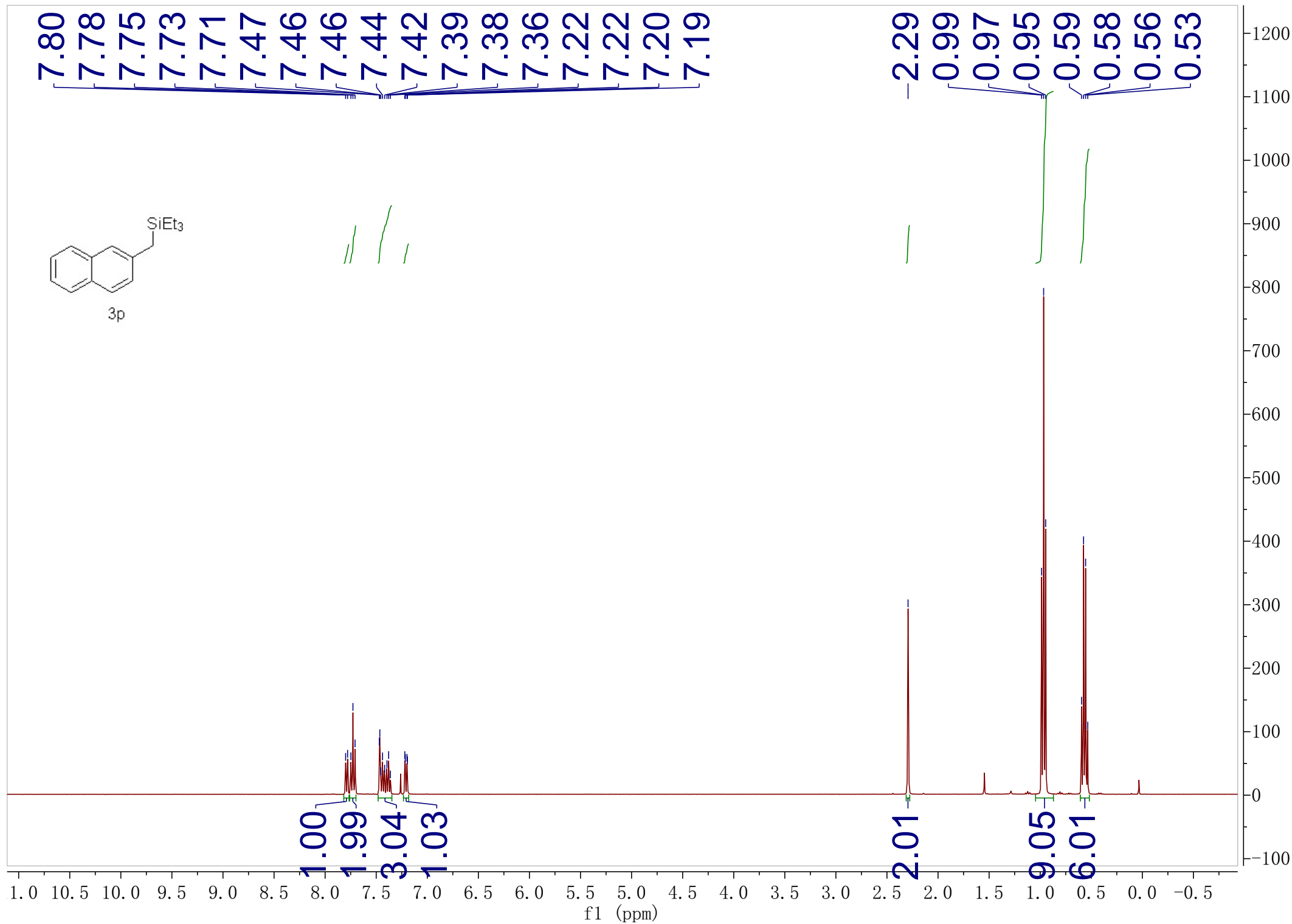
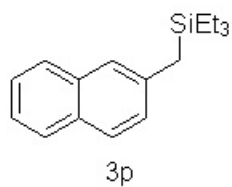
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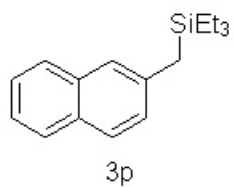




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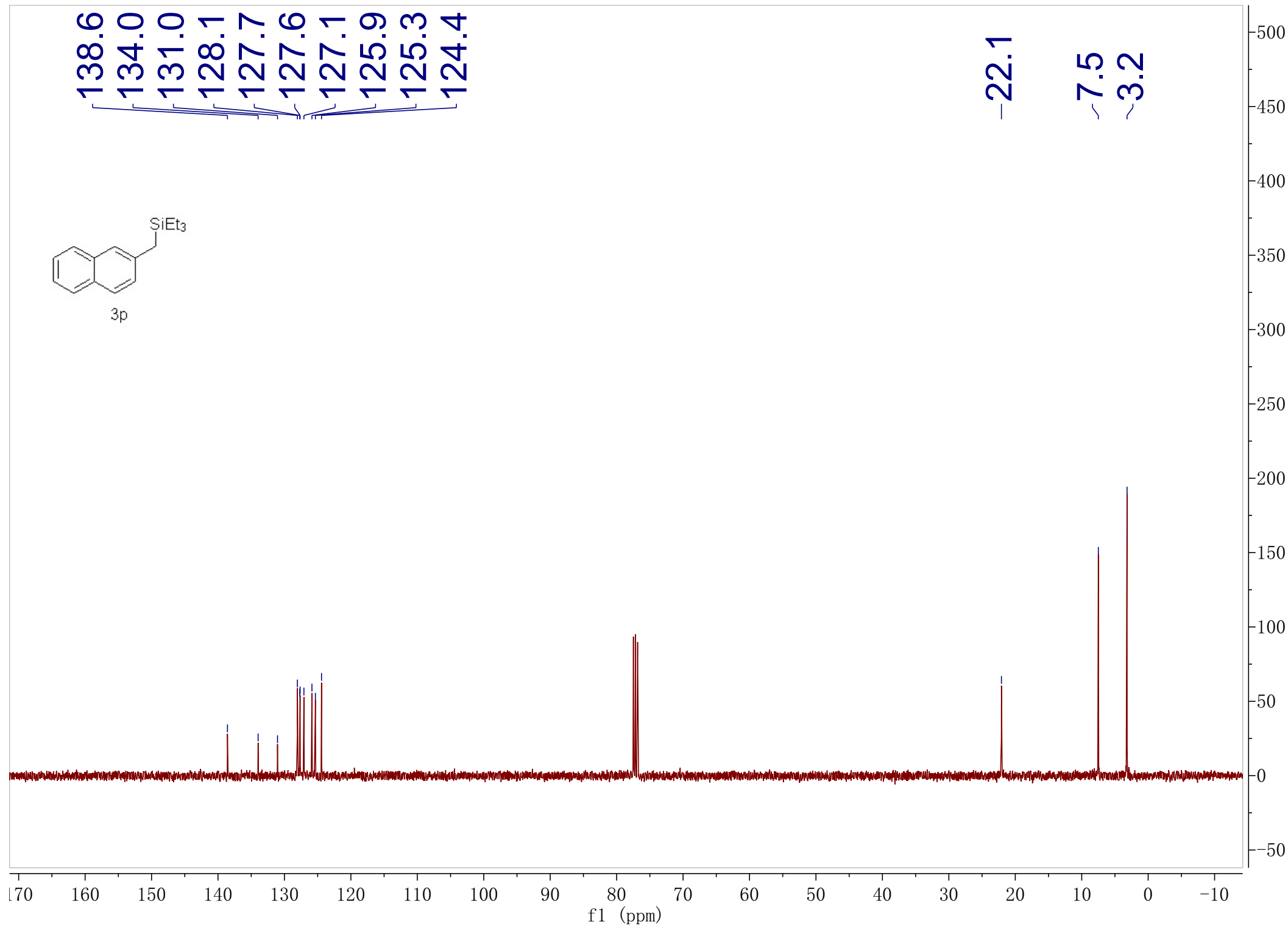


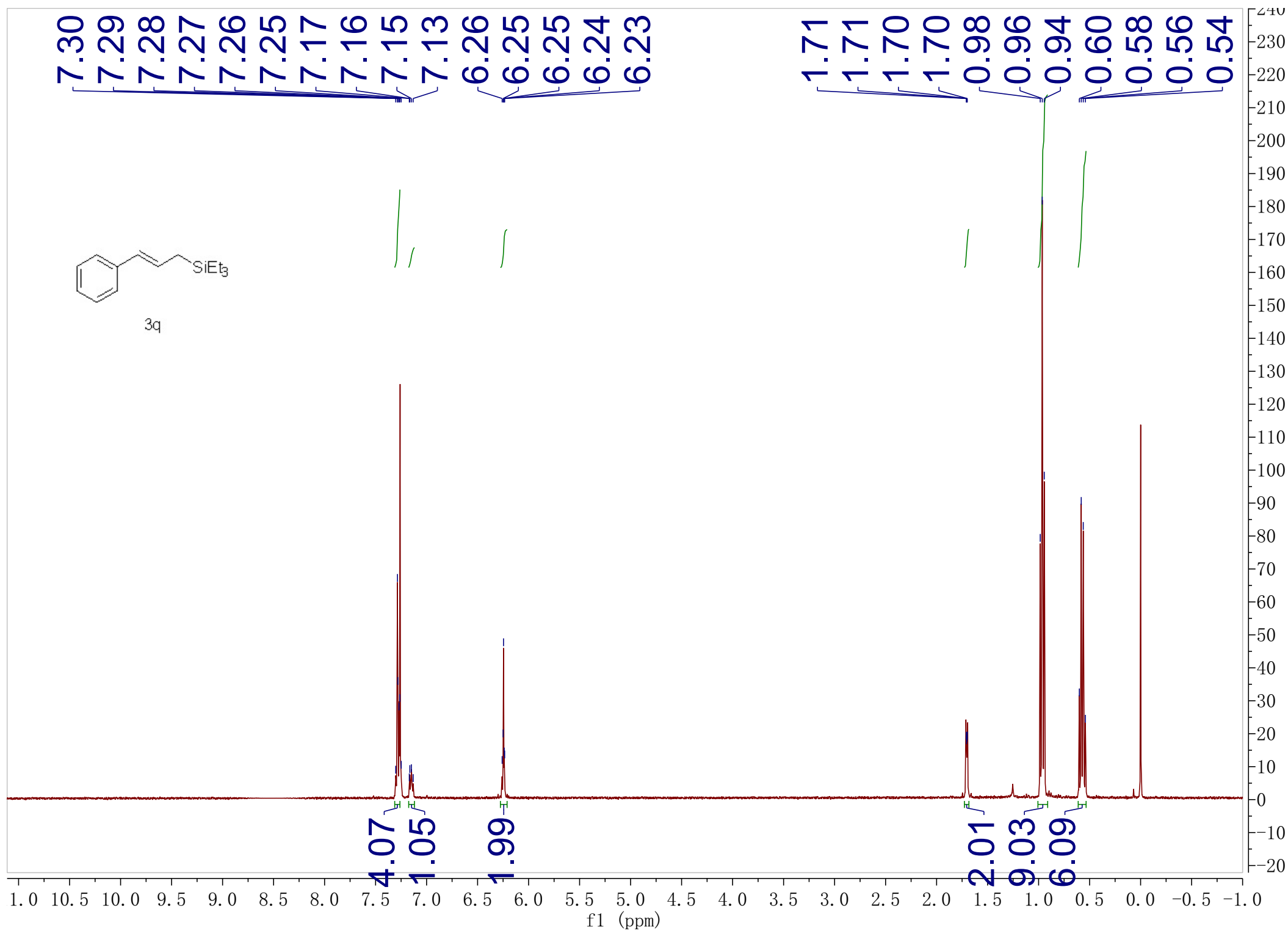
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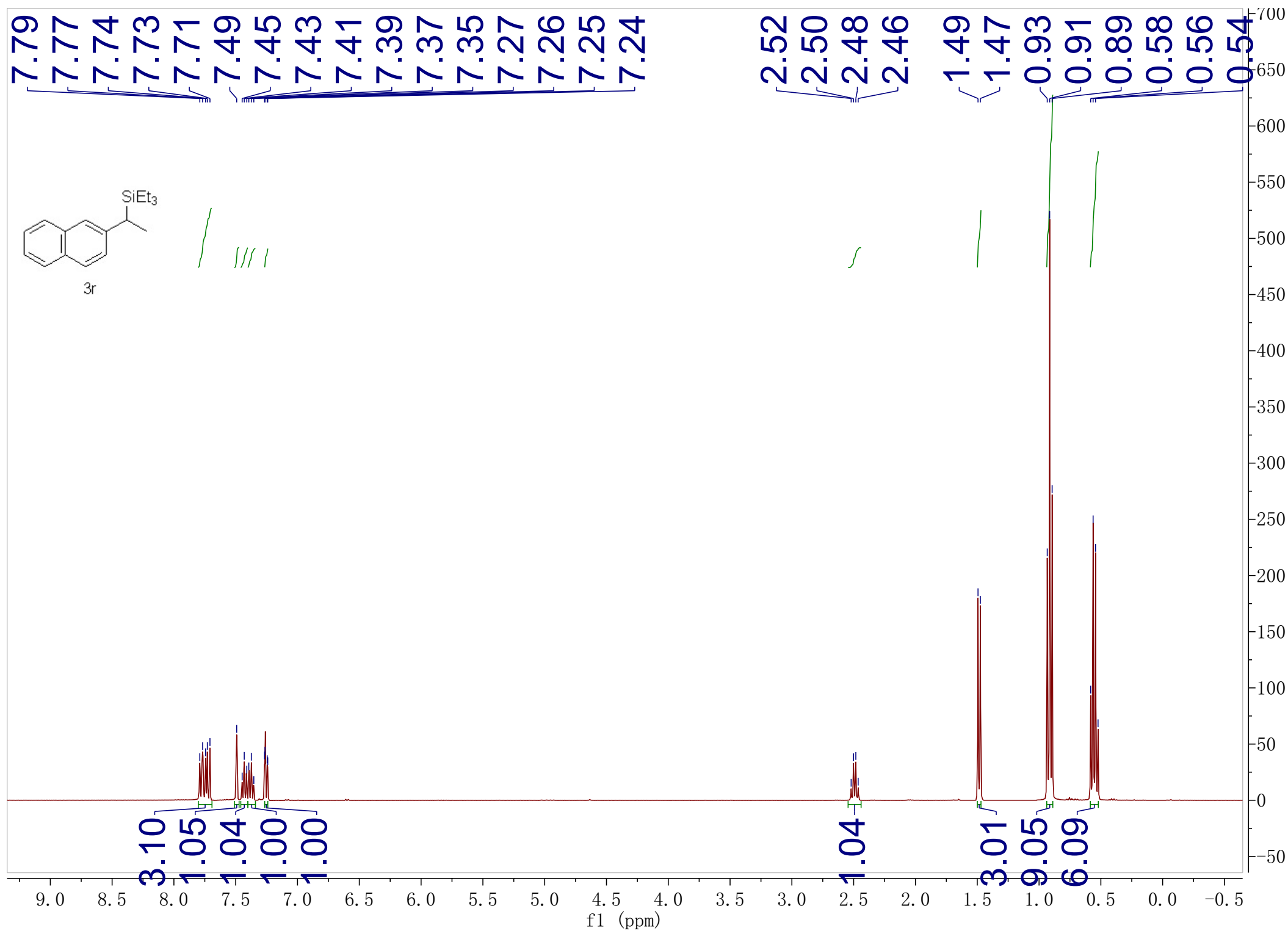
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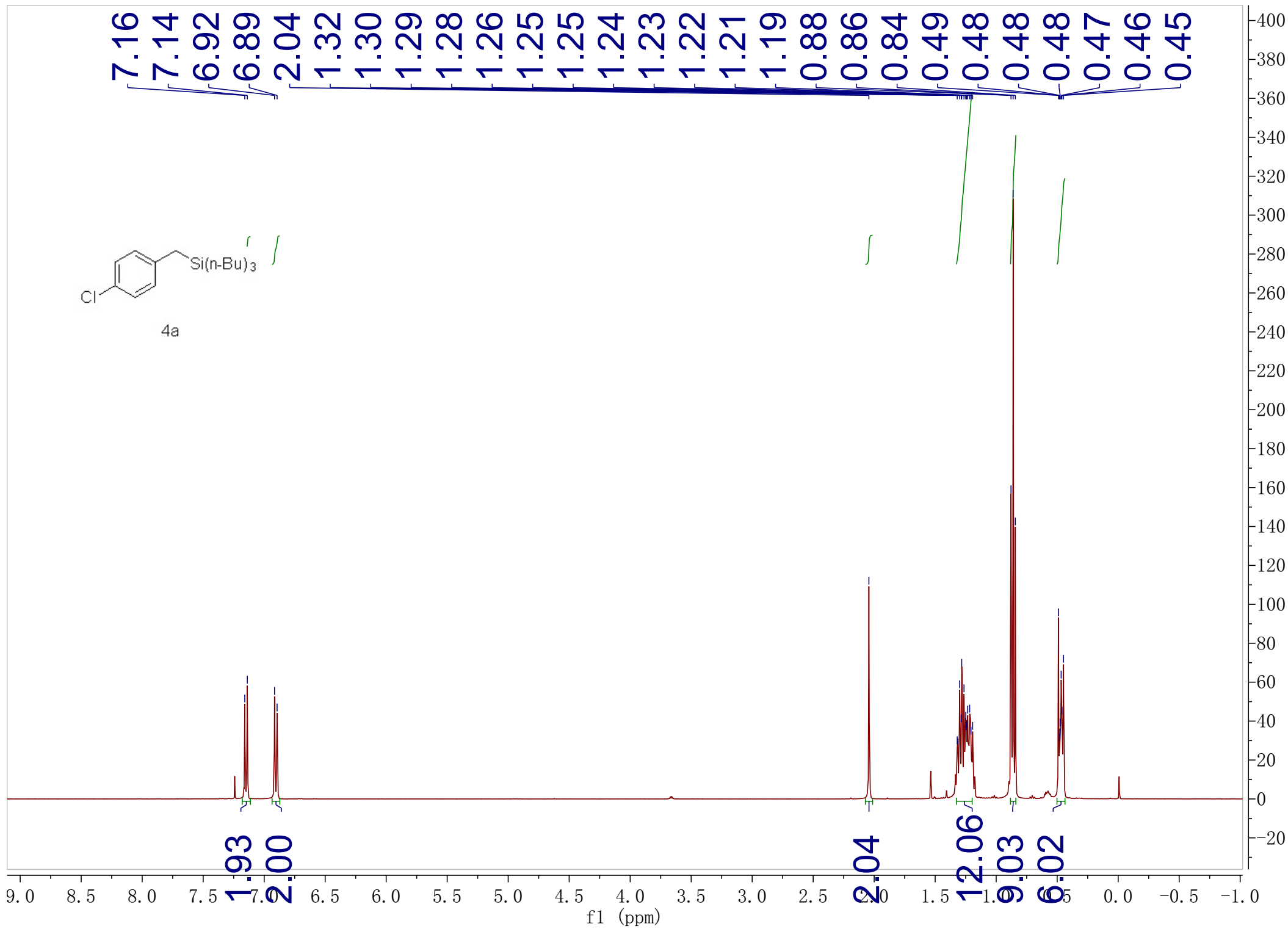
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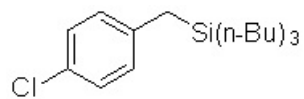
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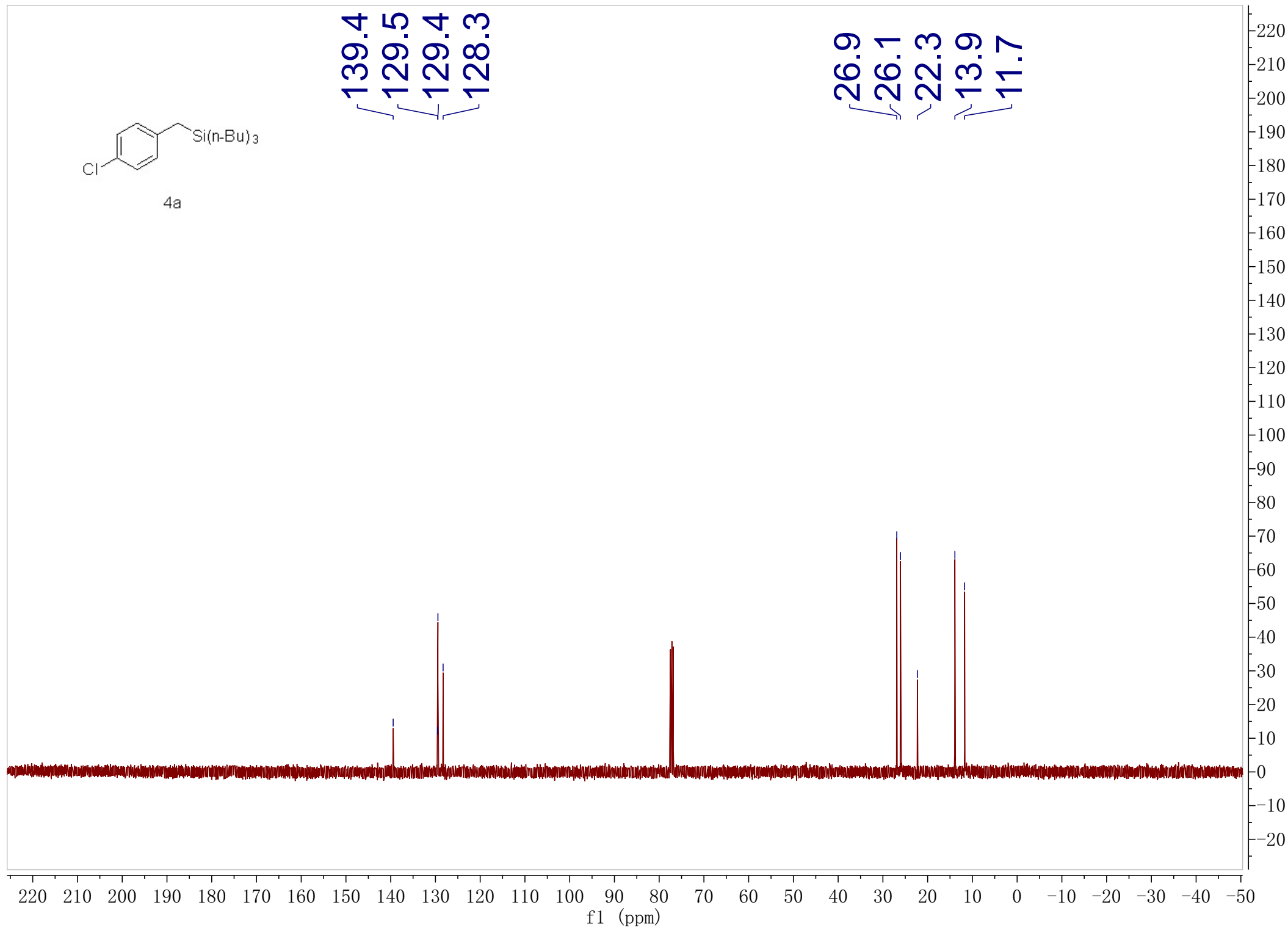


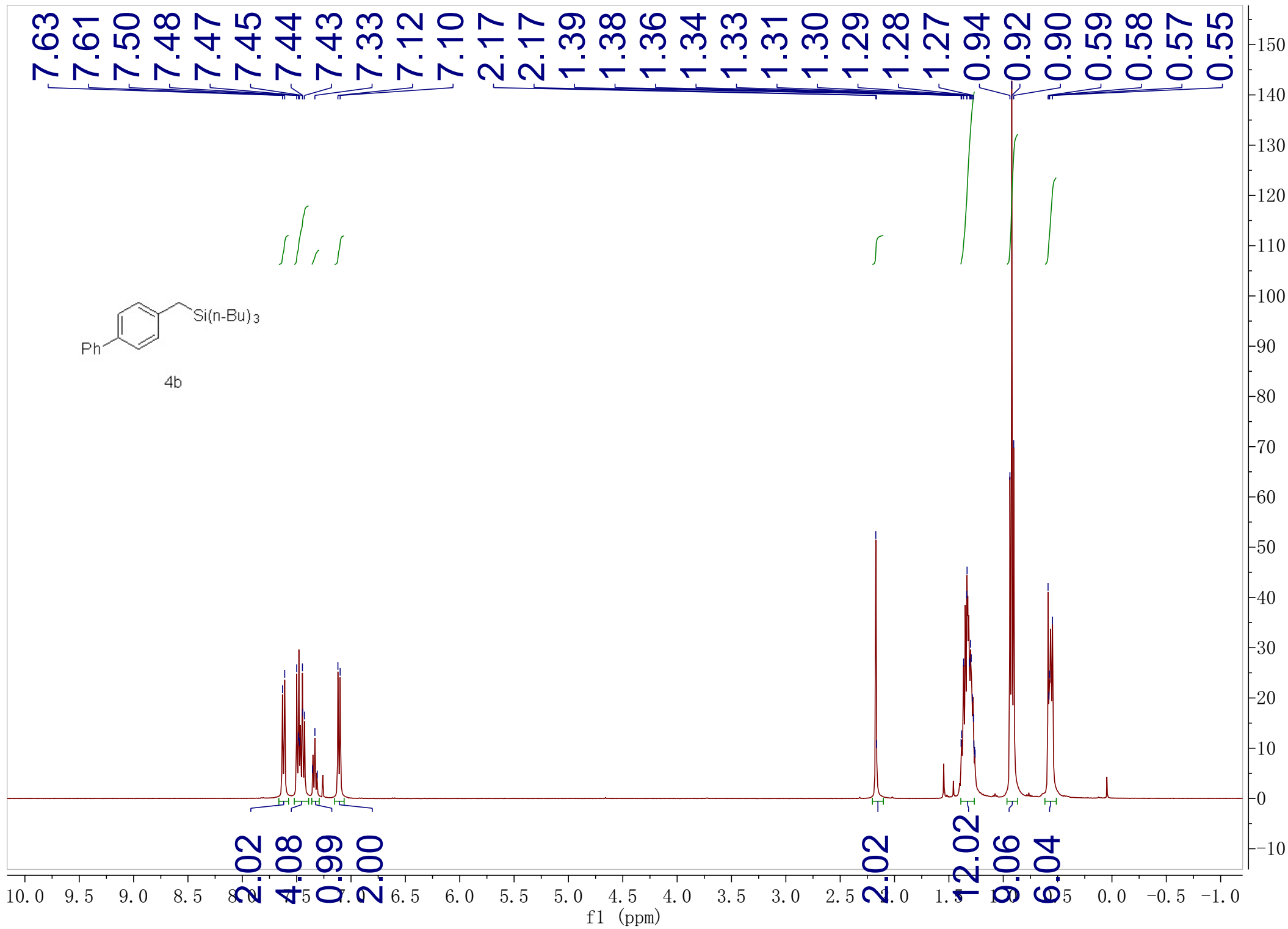


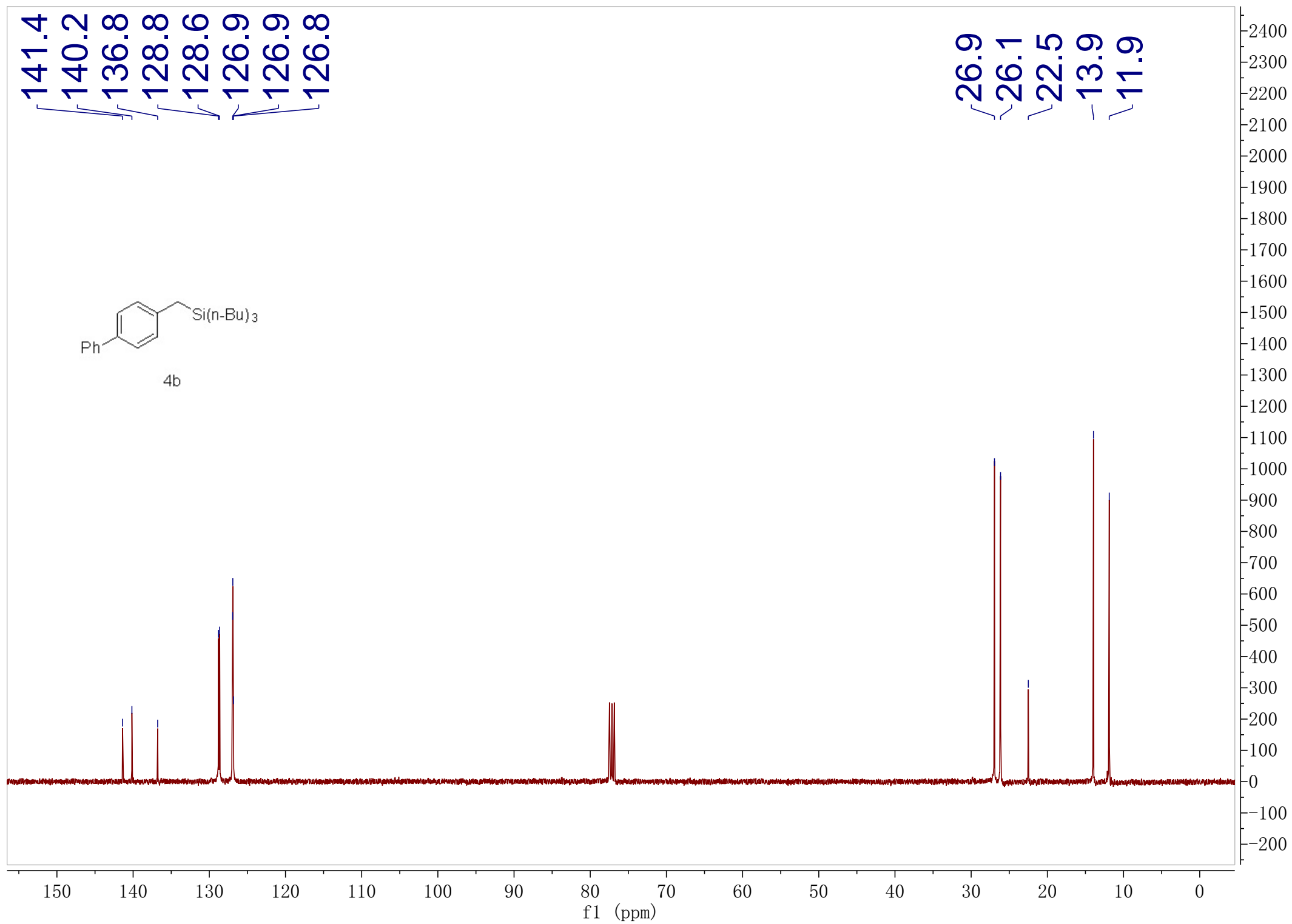
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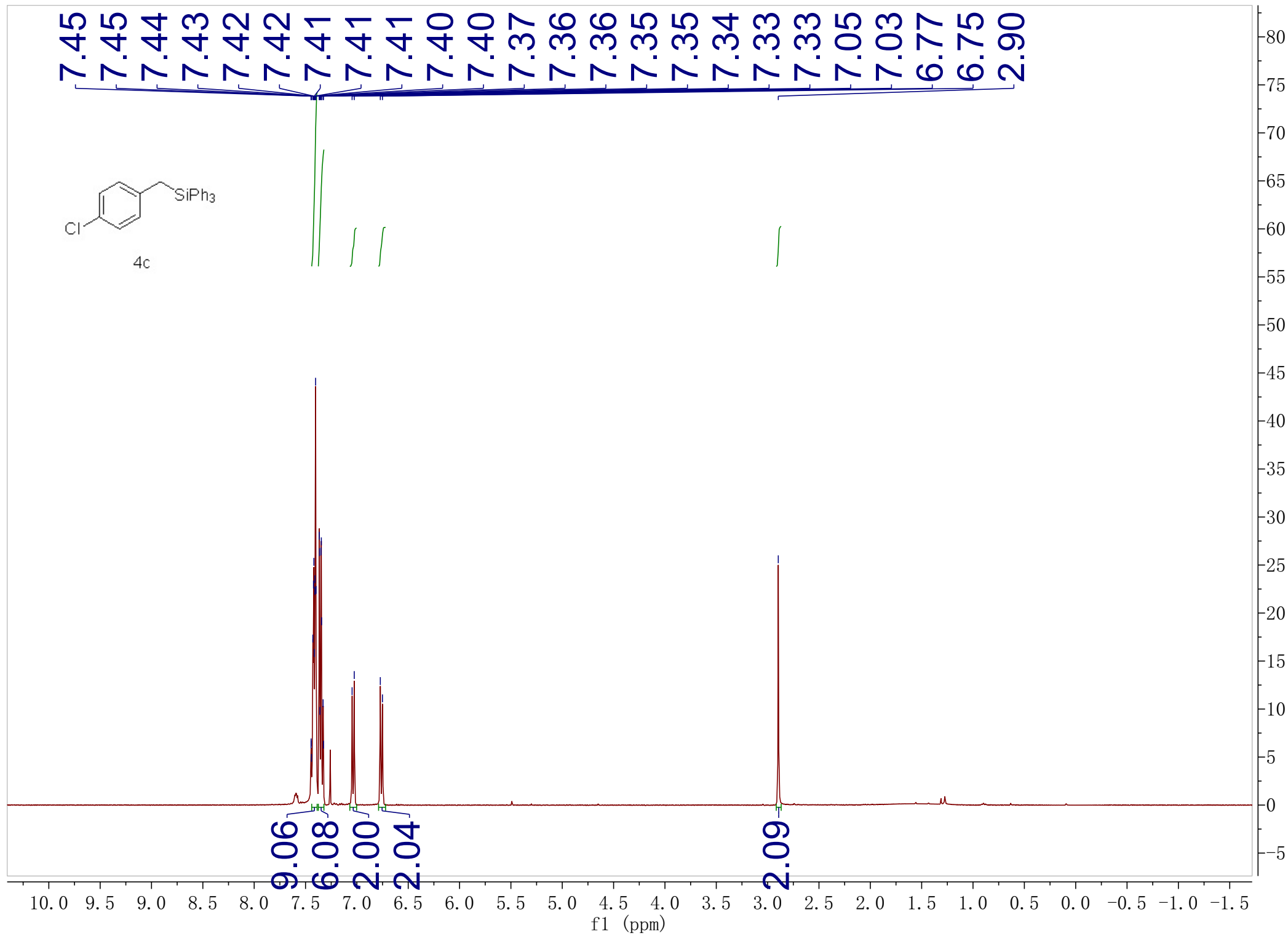
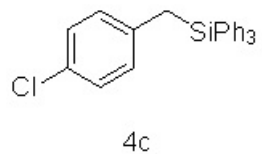
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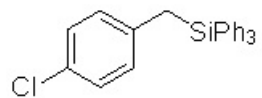
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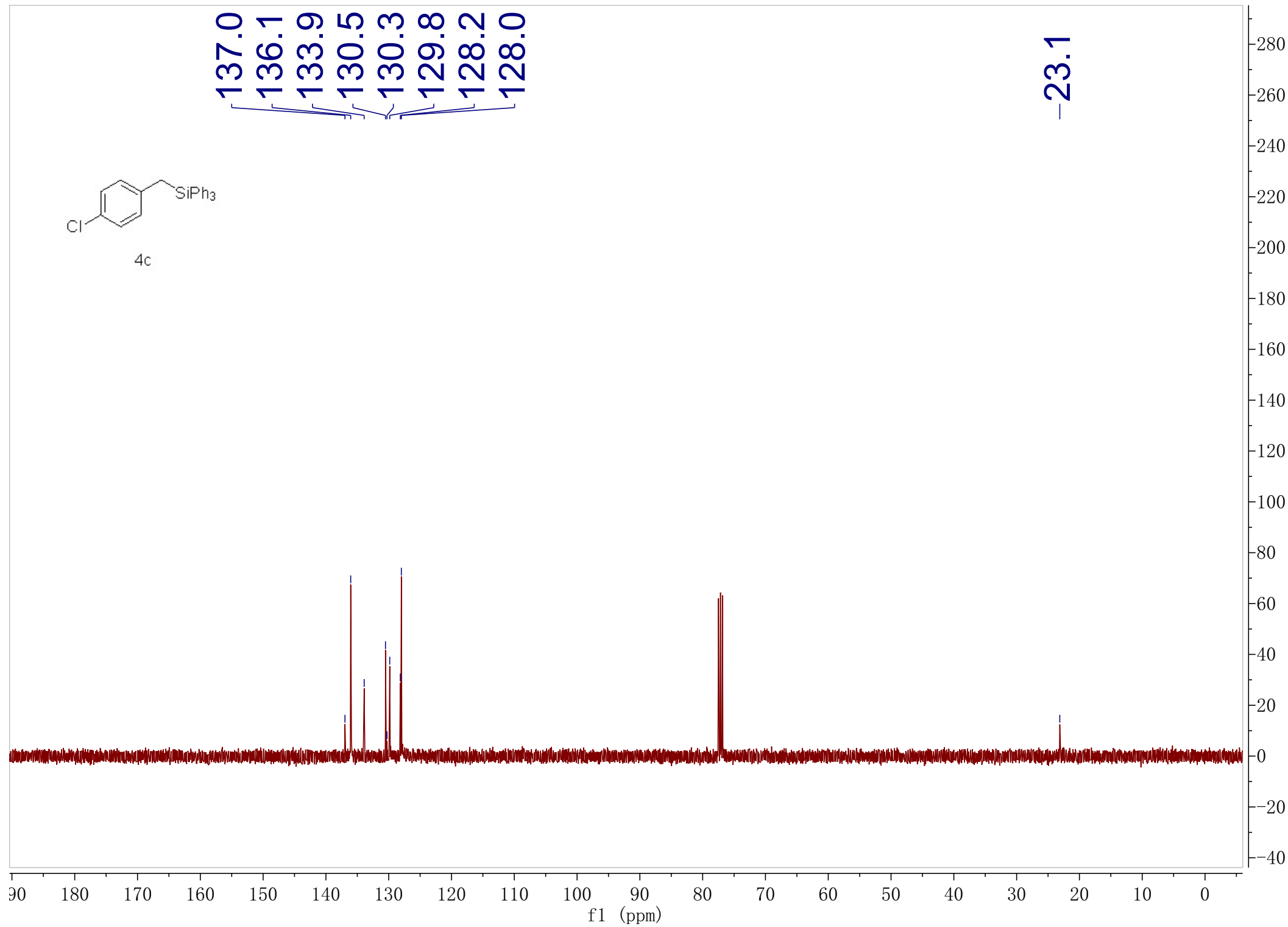


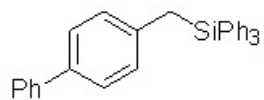


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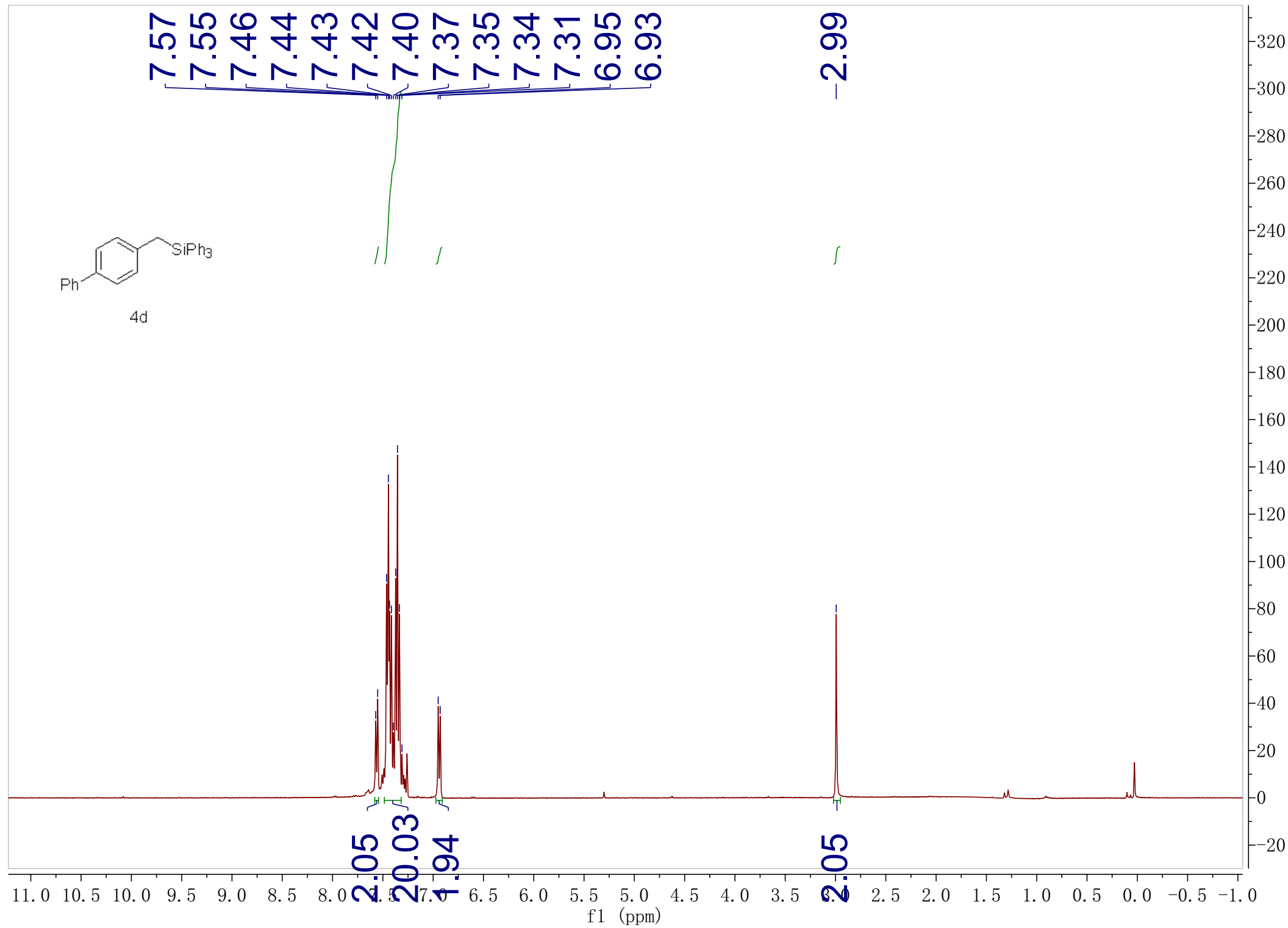
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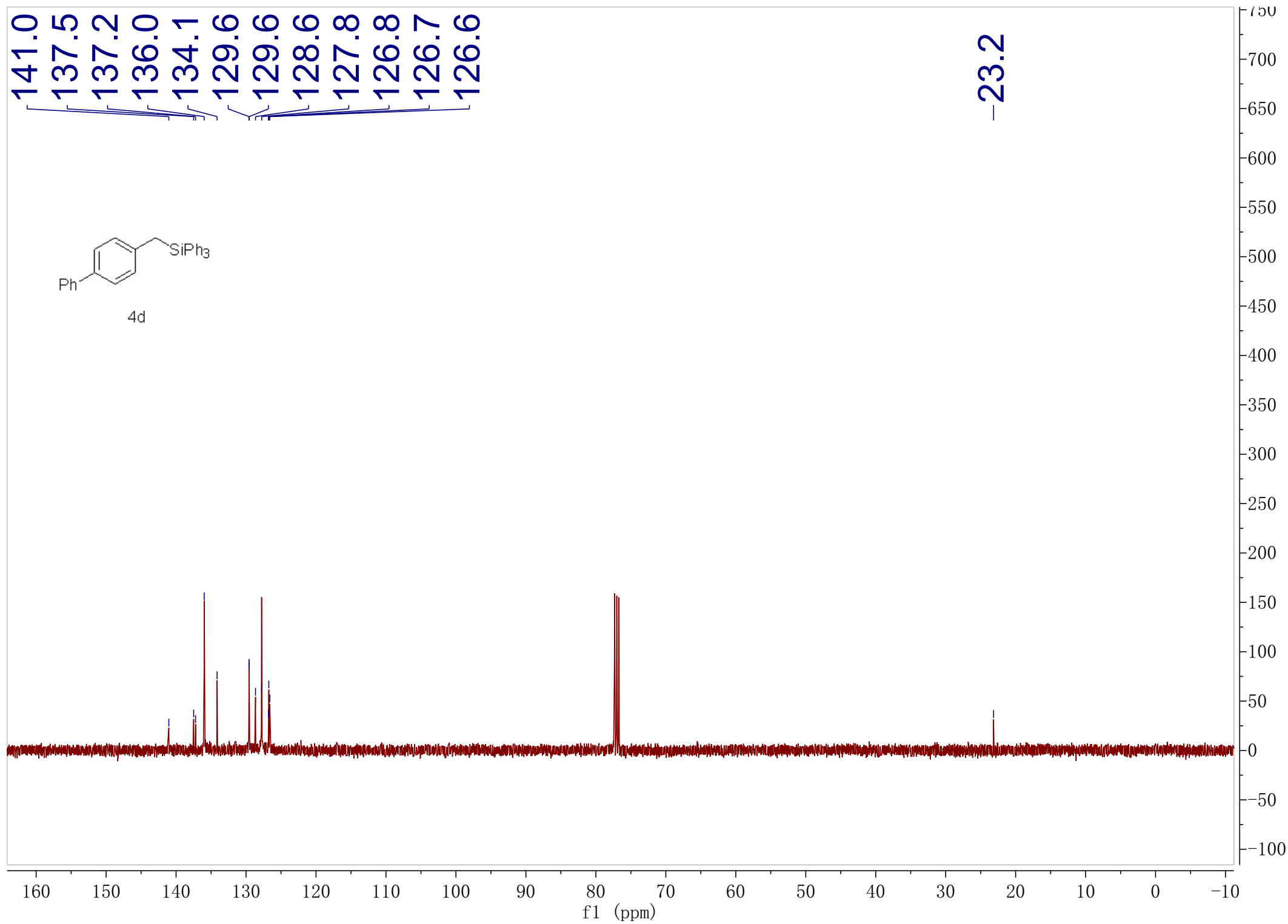
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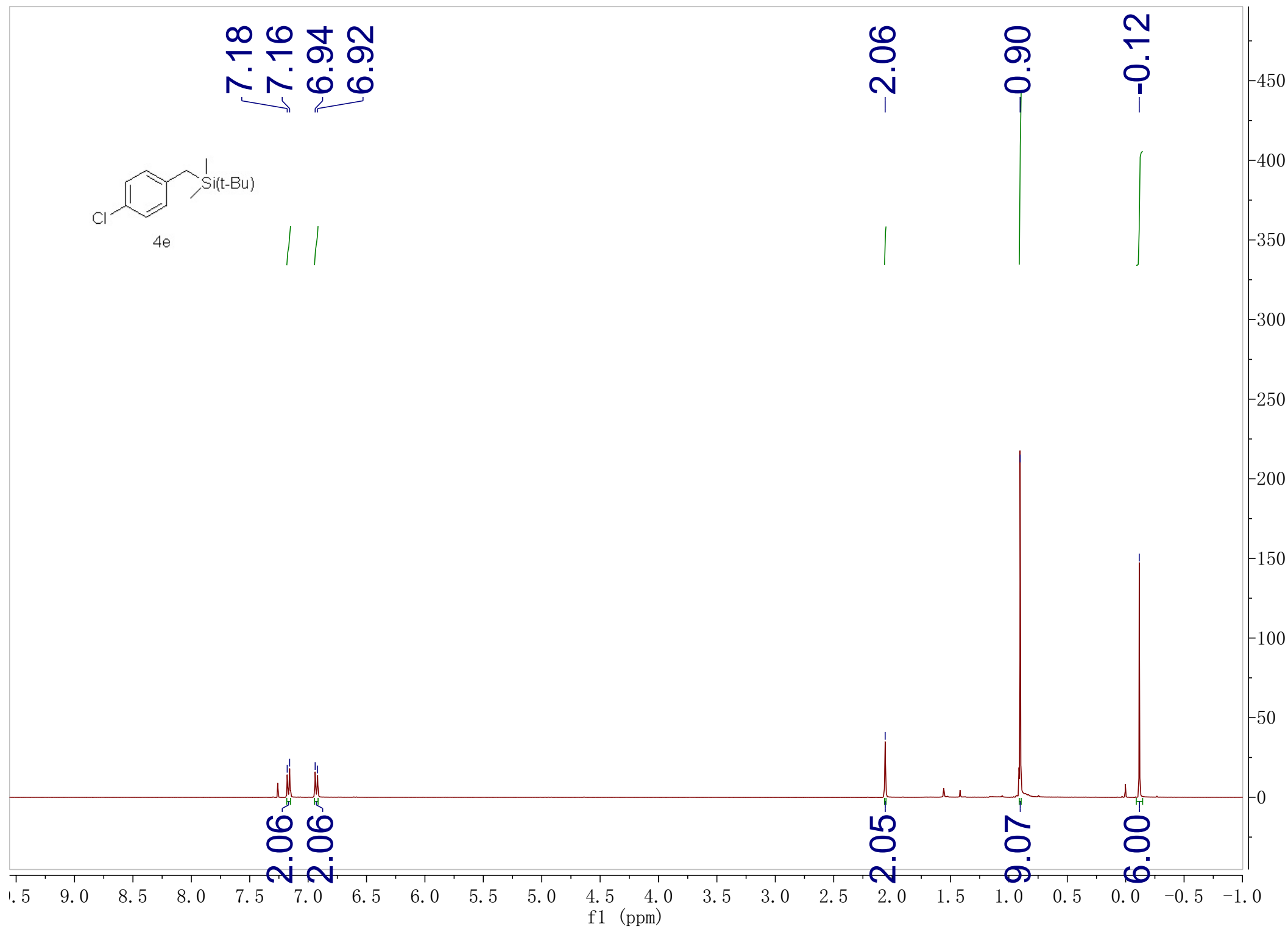


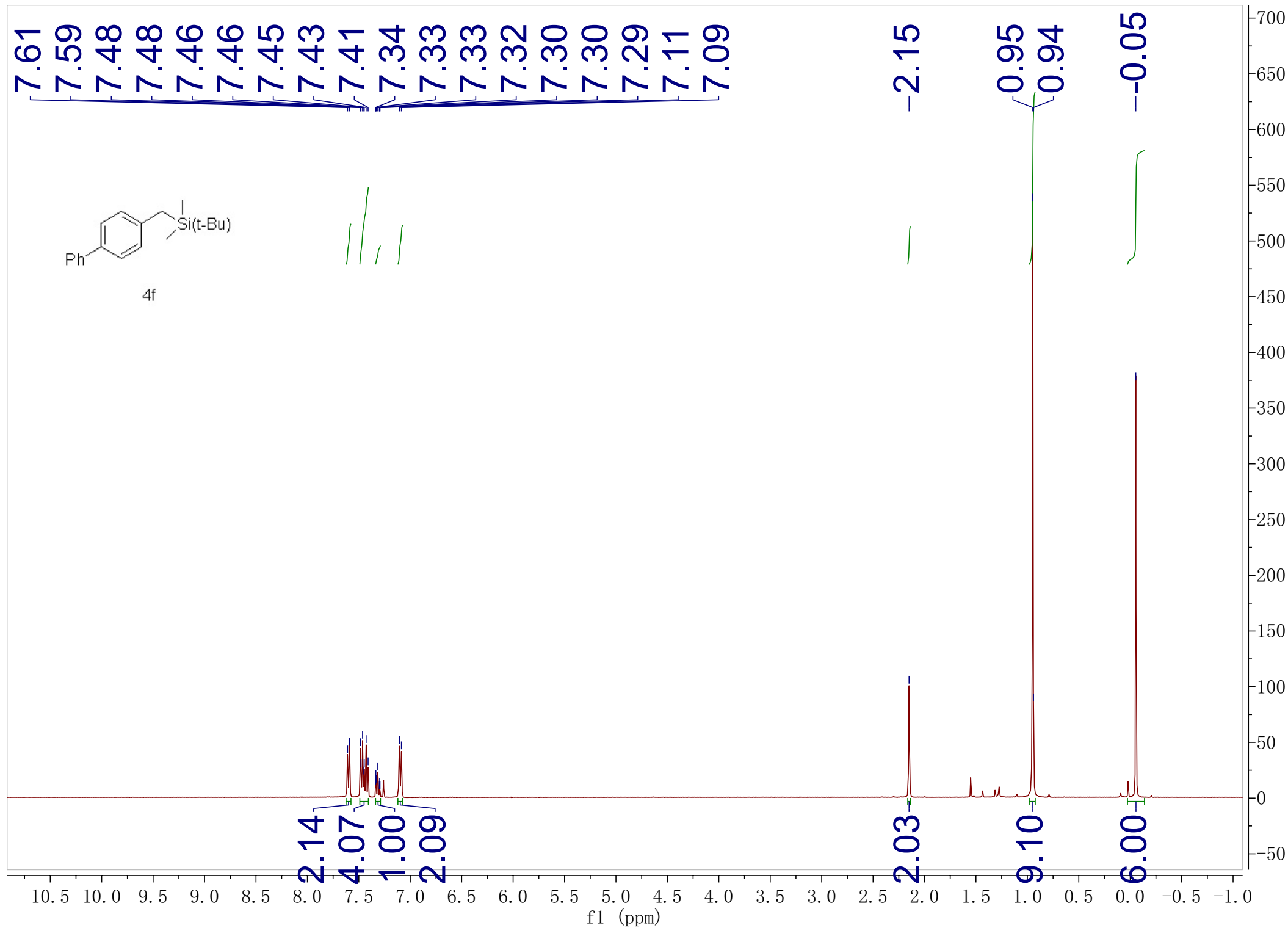


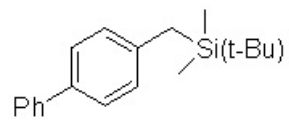
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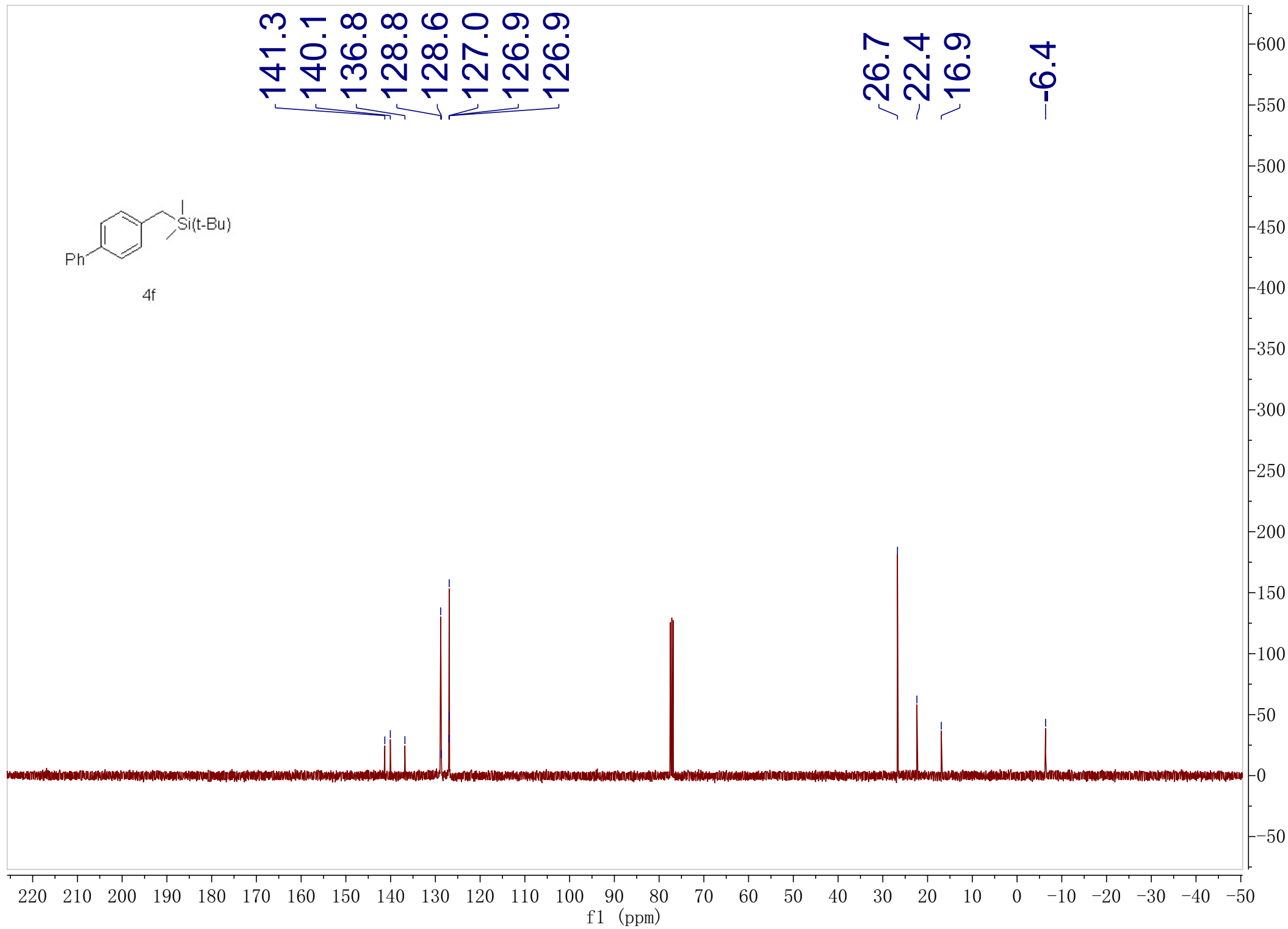


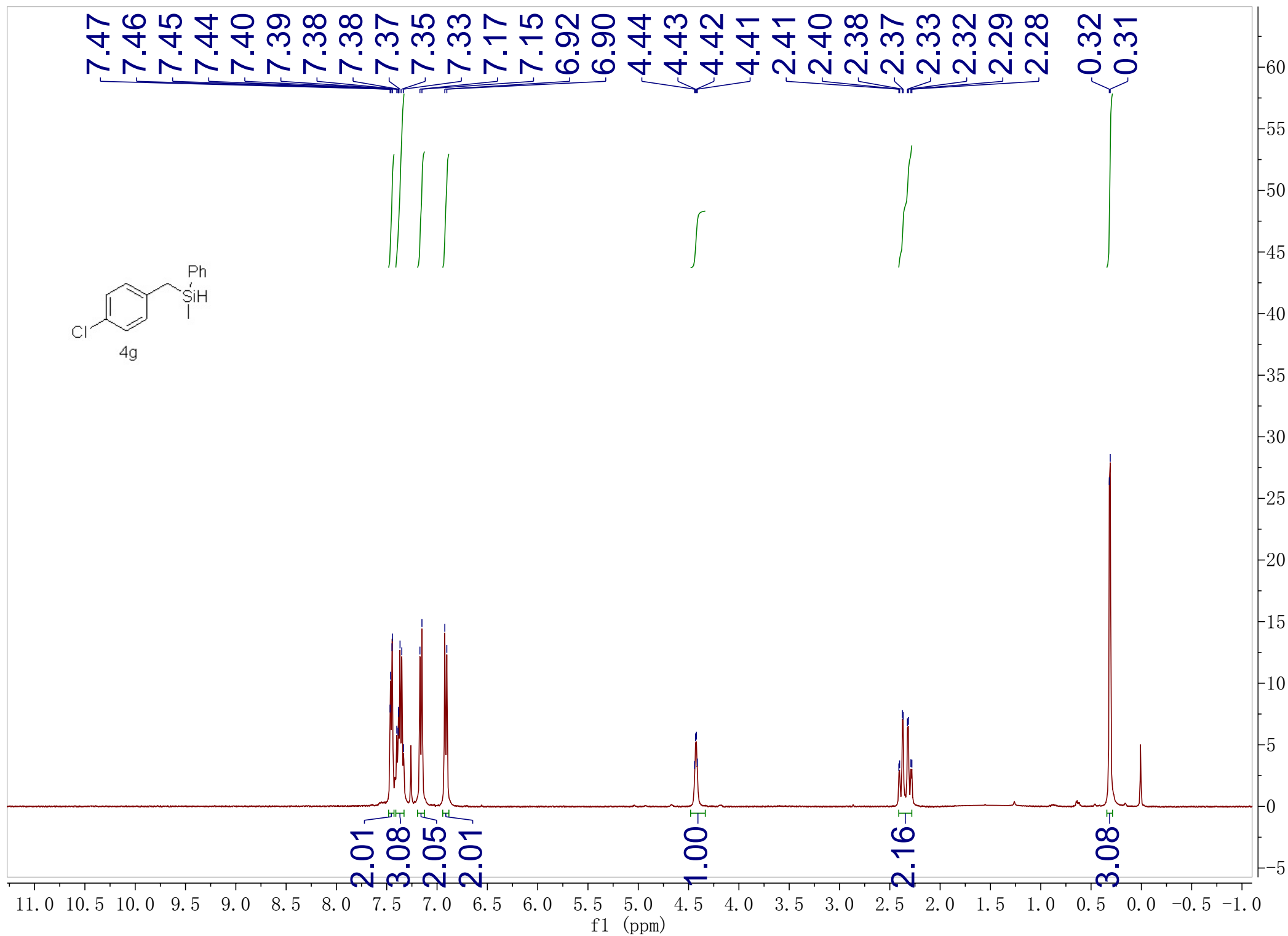
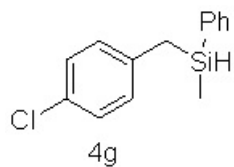


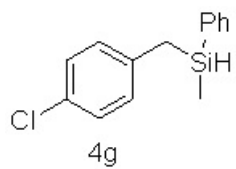
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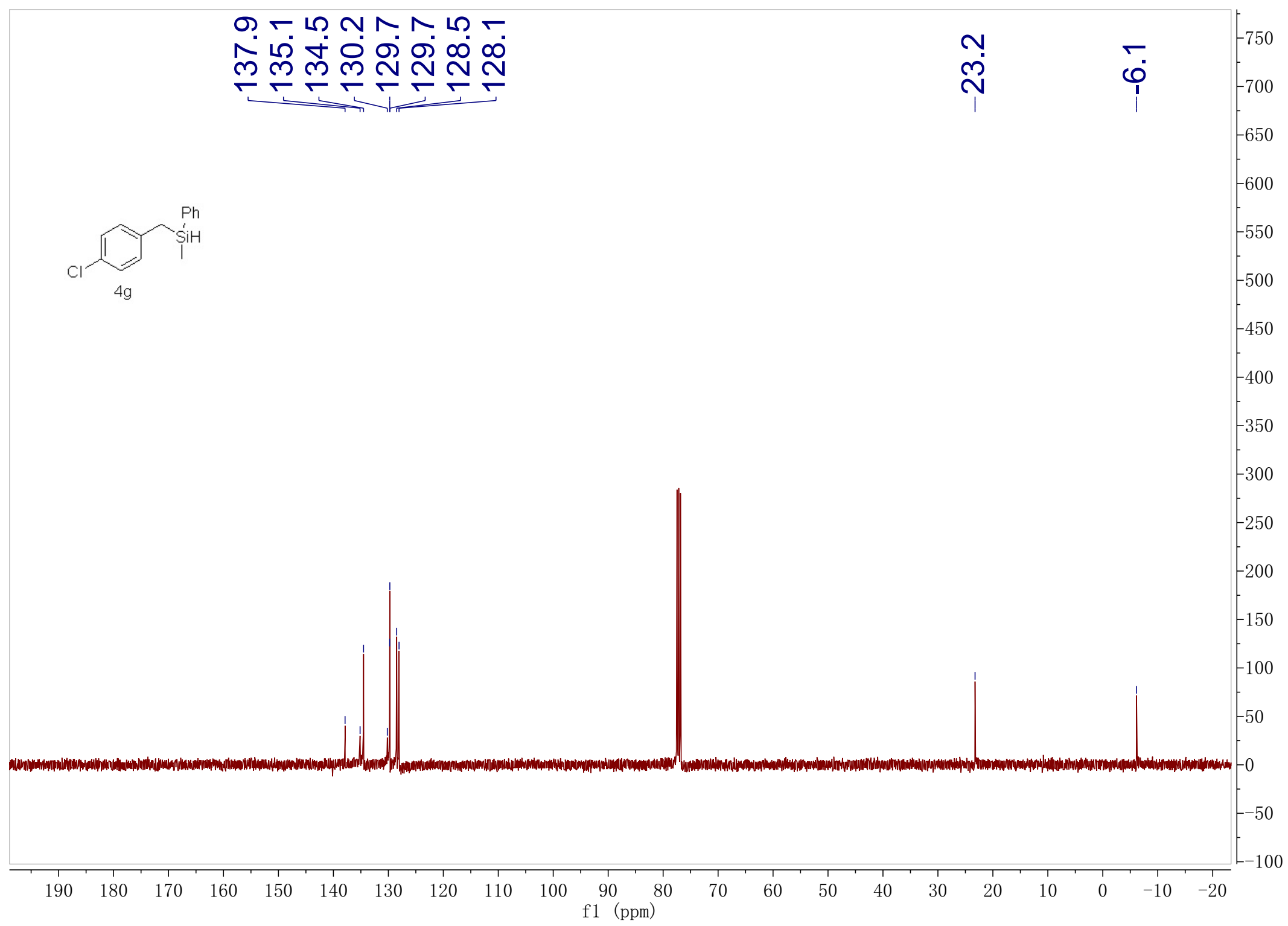


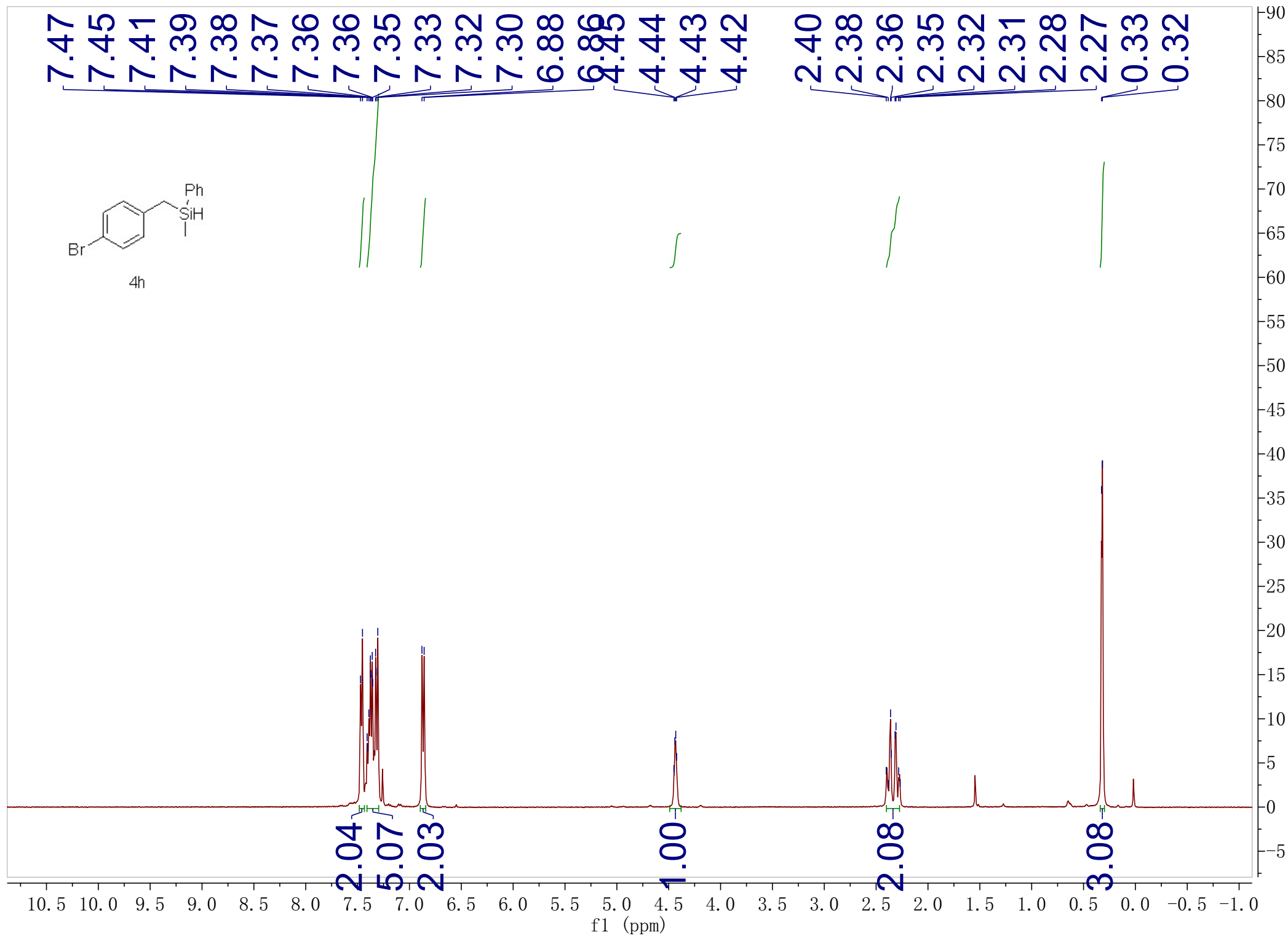


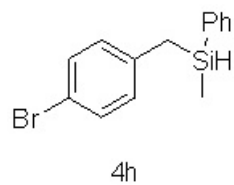
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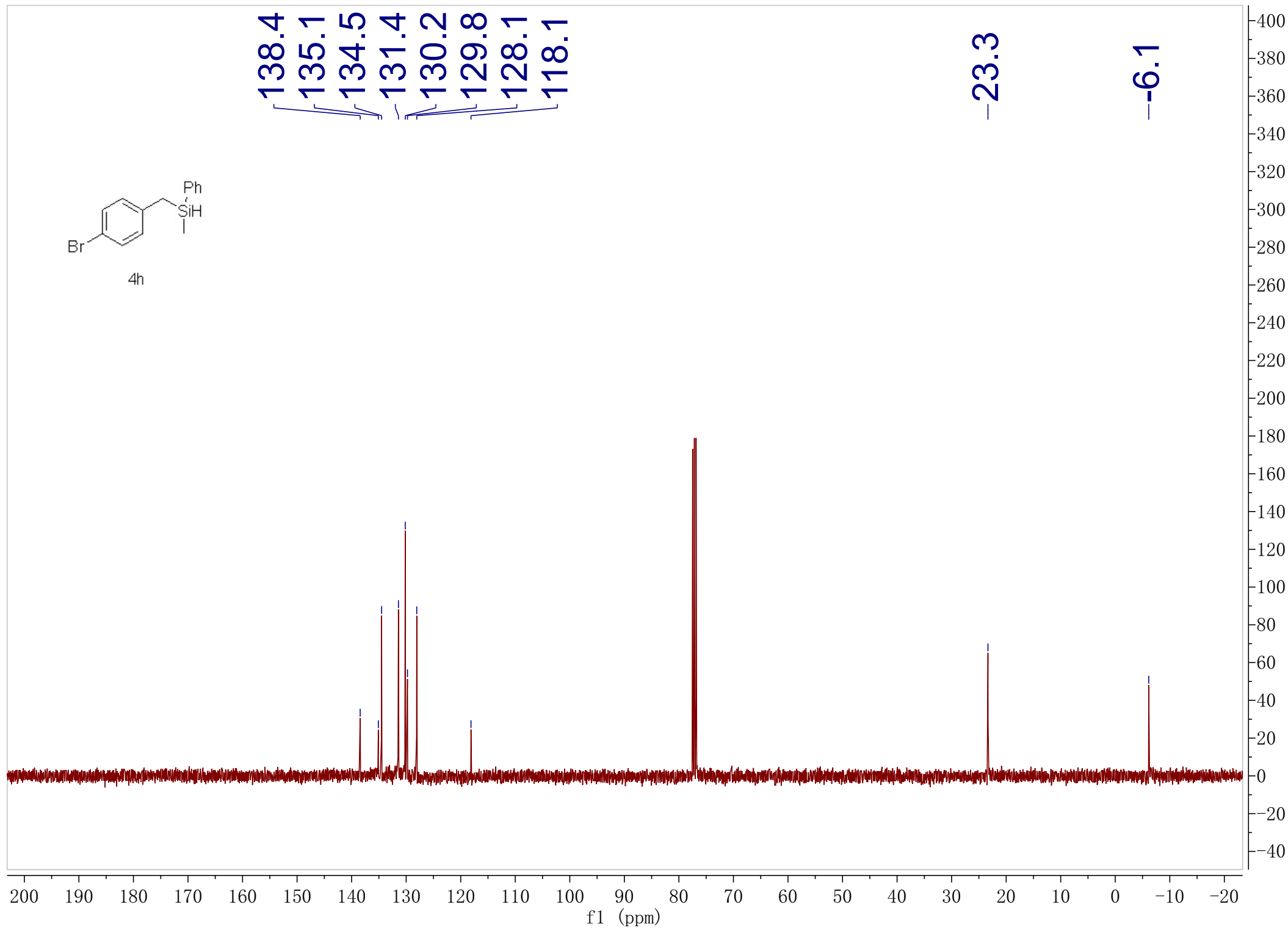


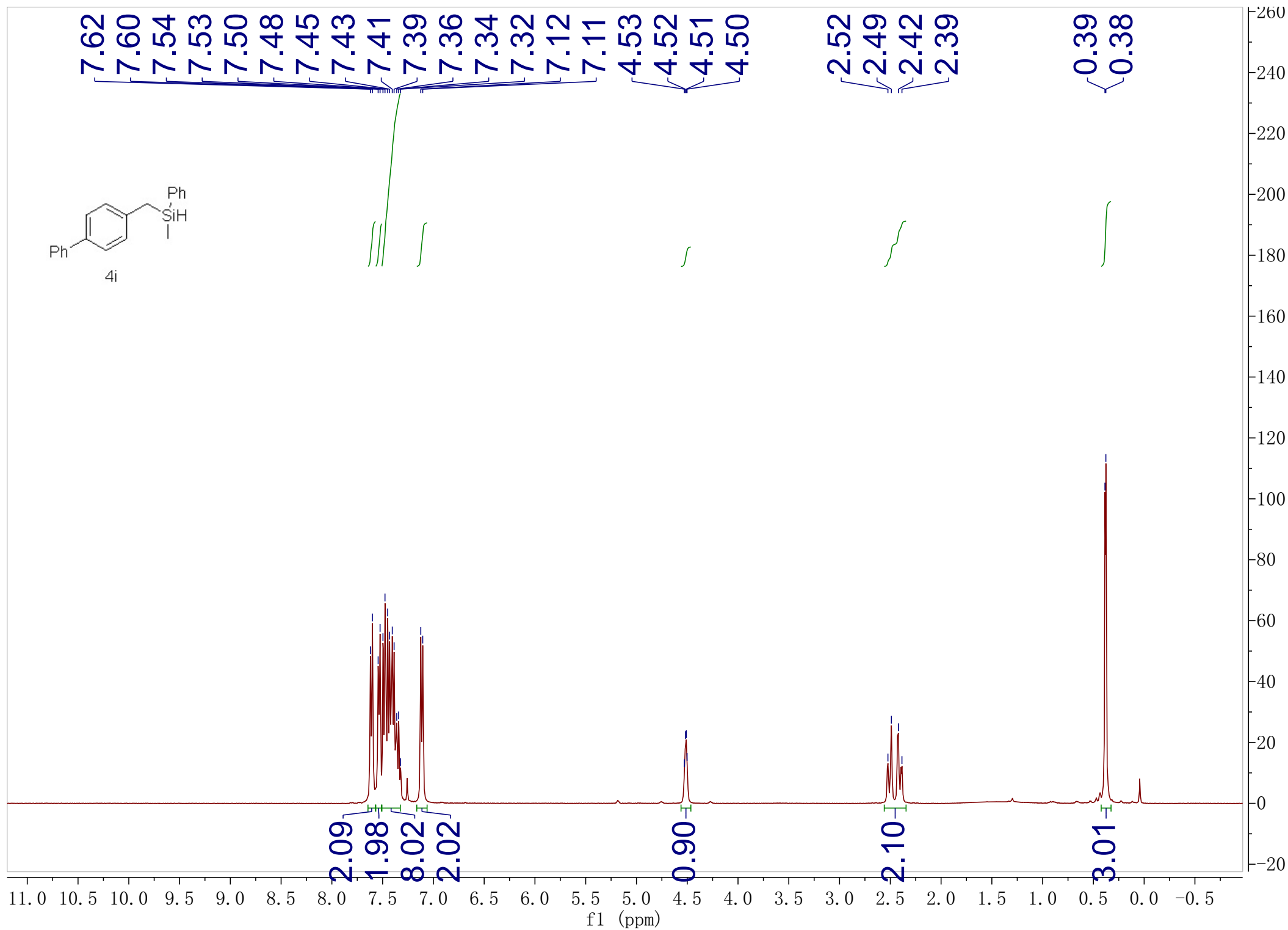


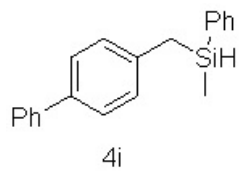
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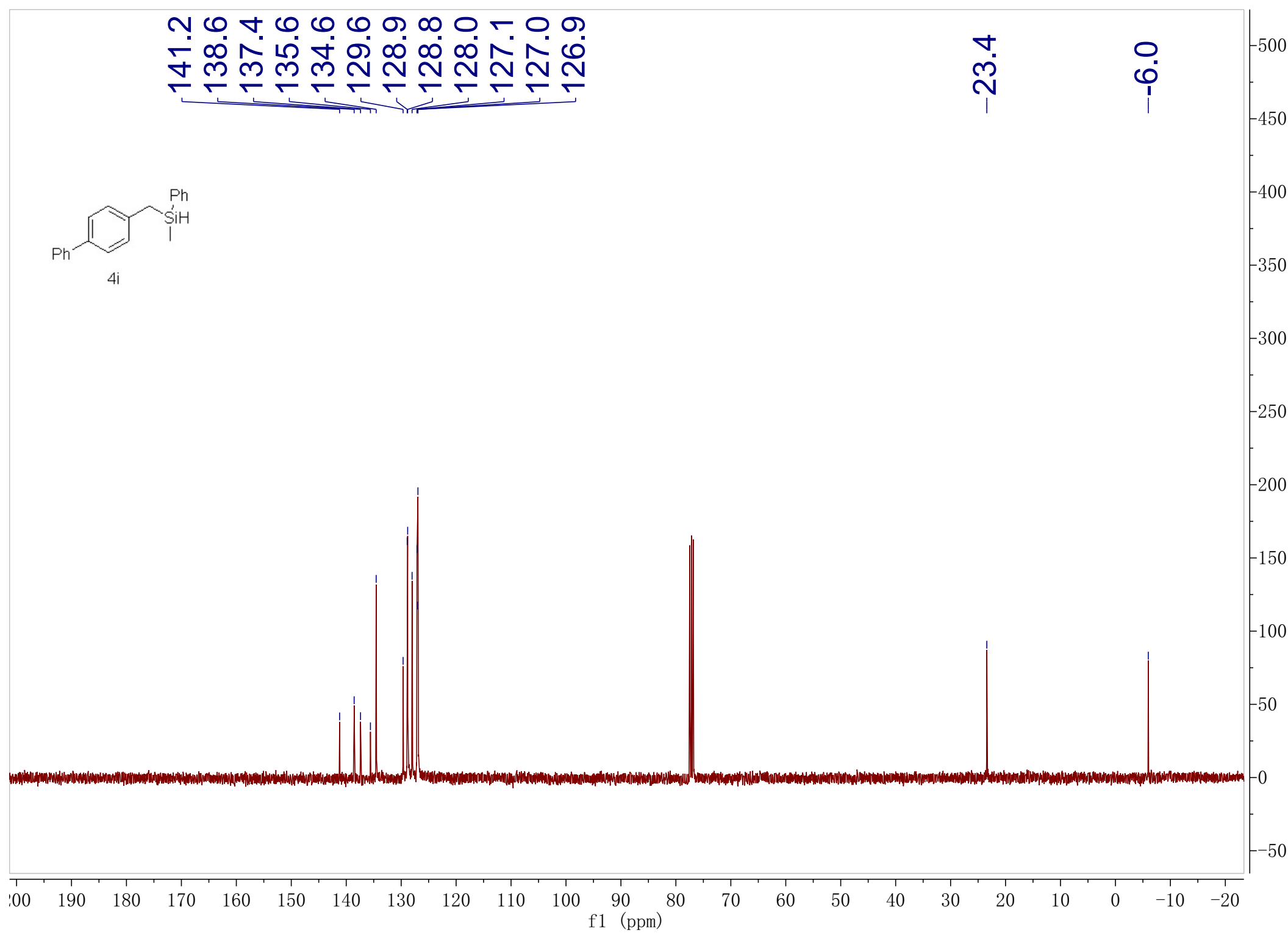


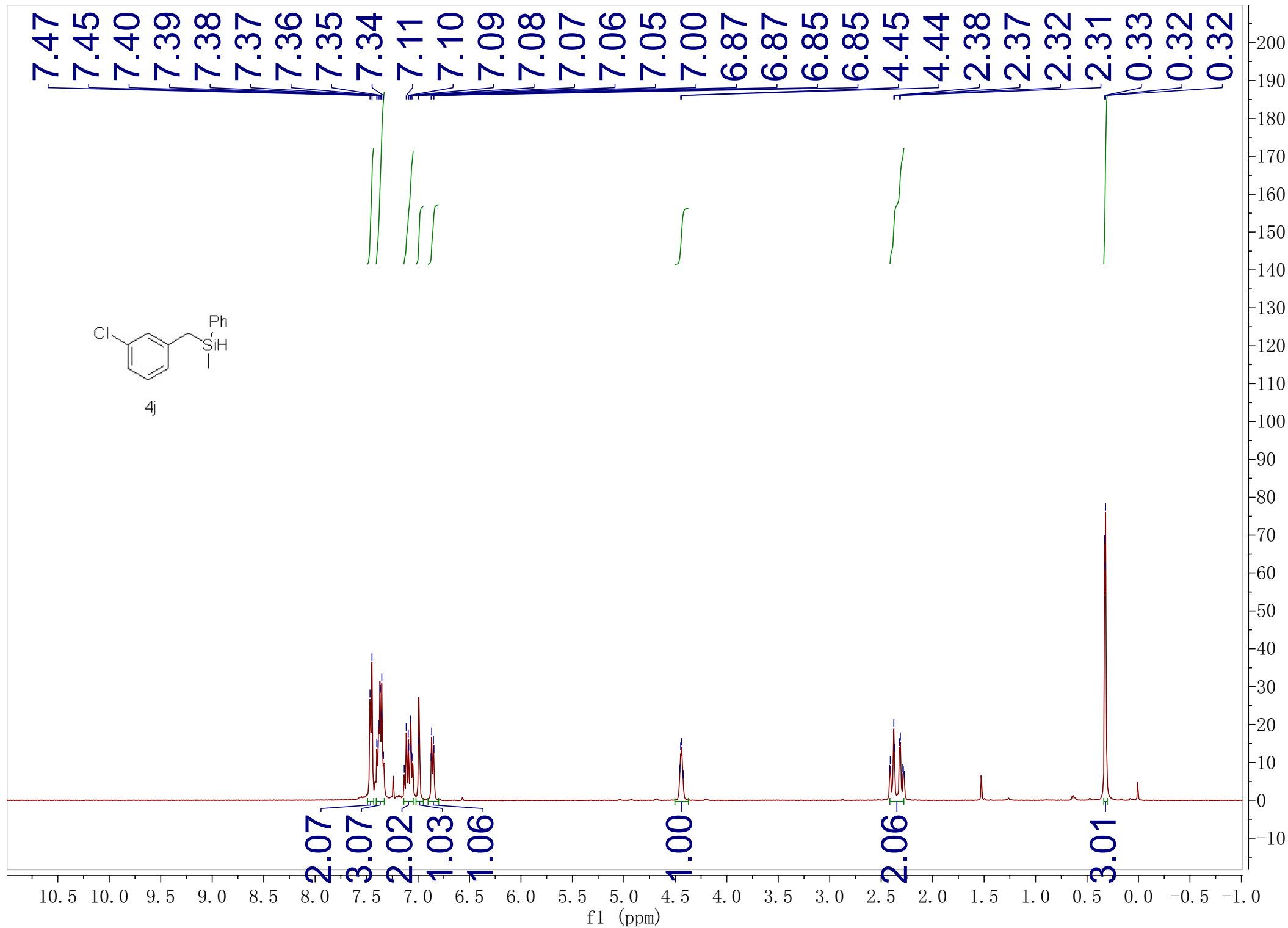


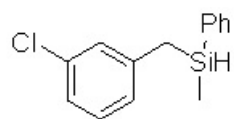
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-6.0





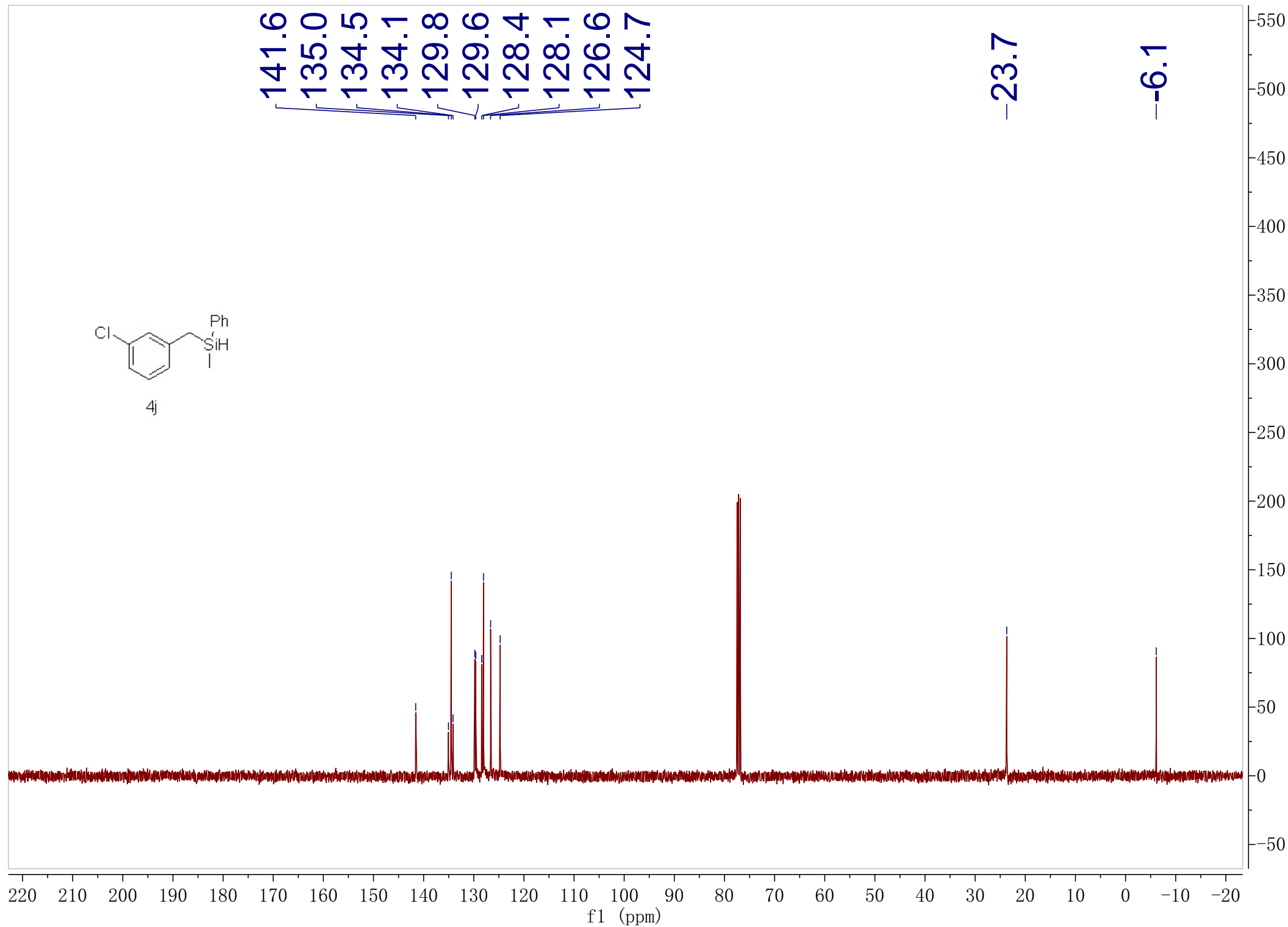


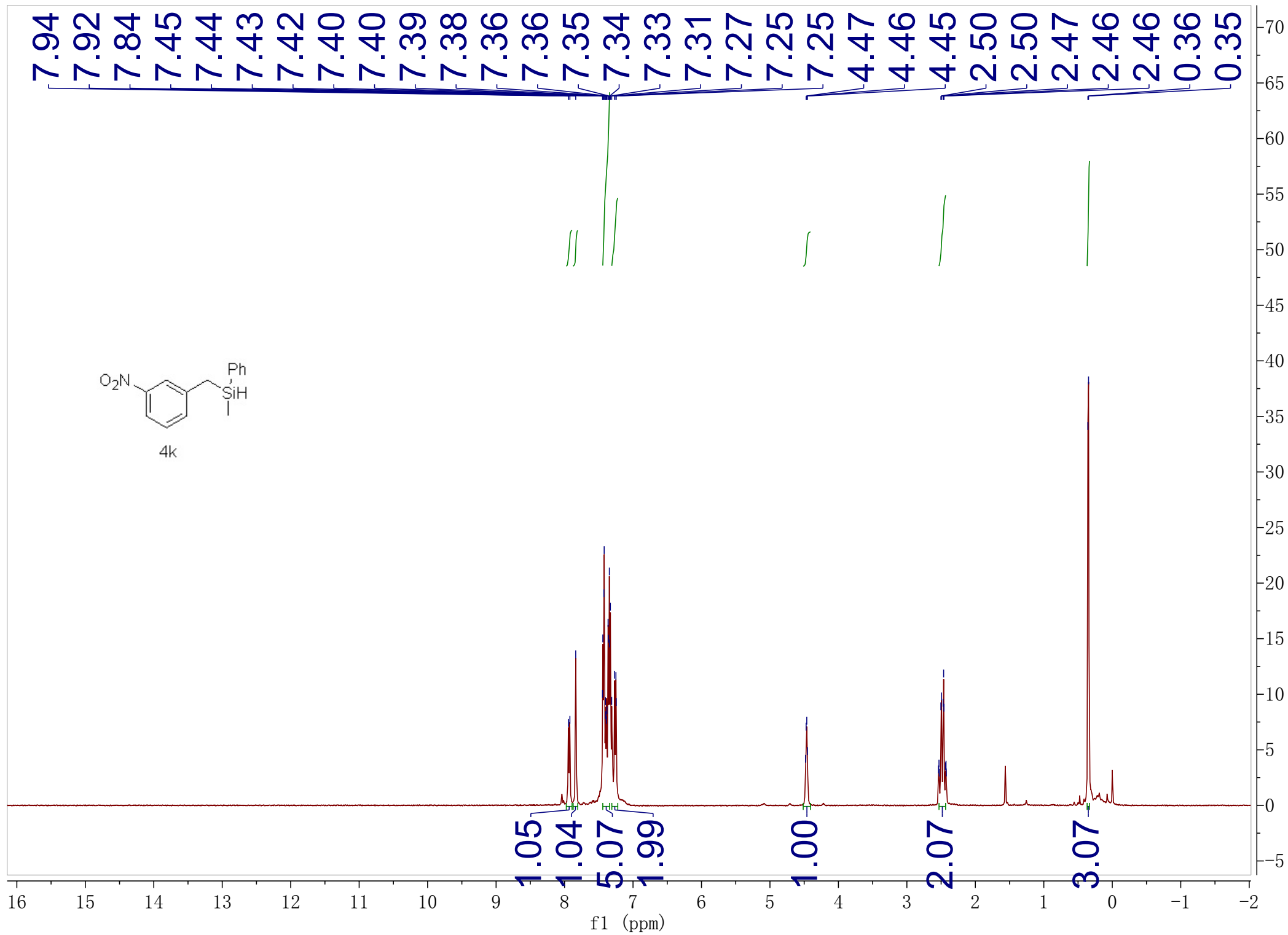
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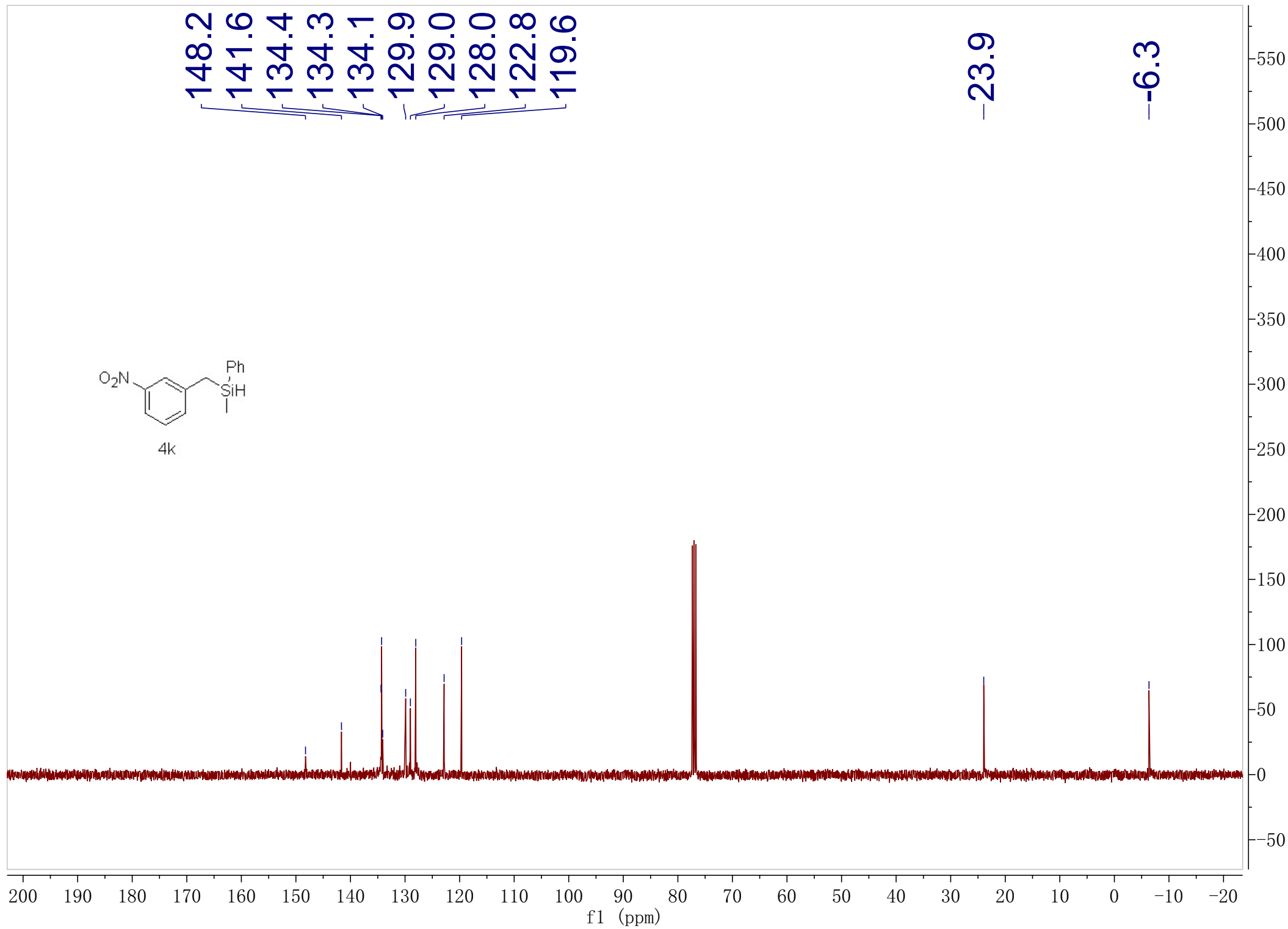
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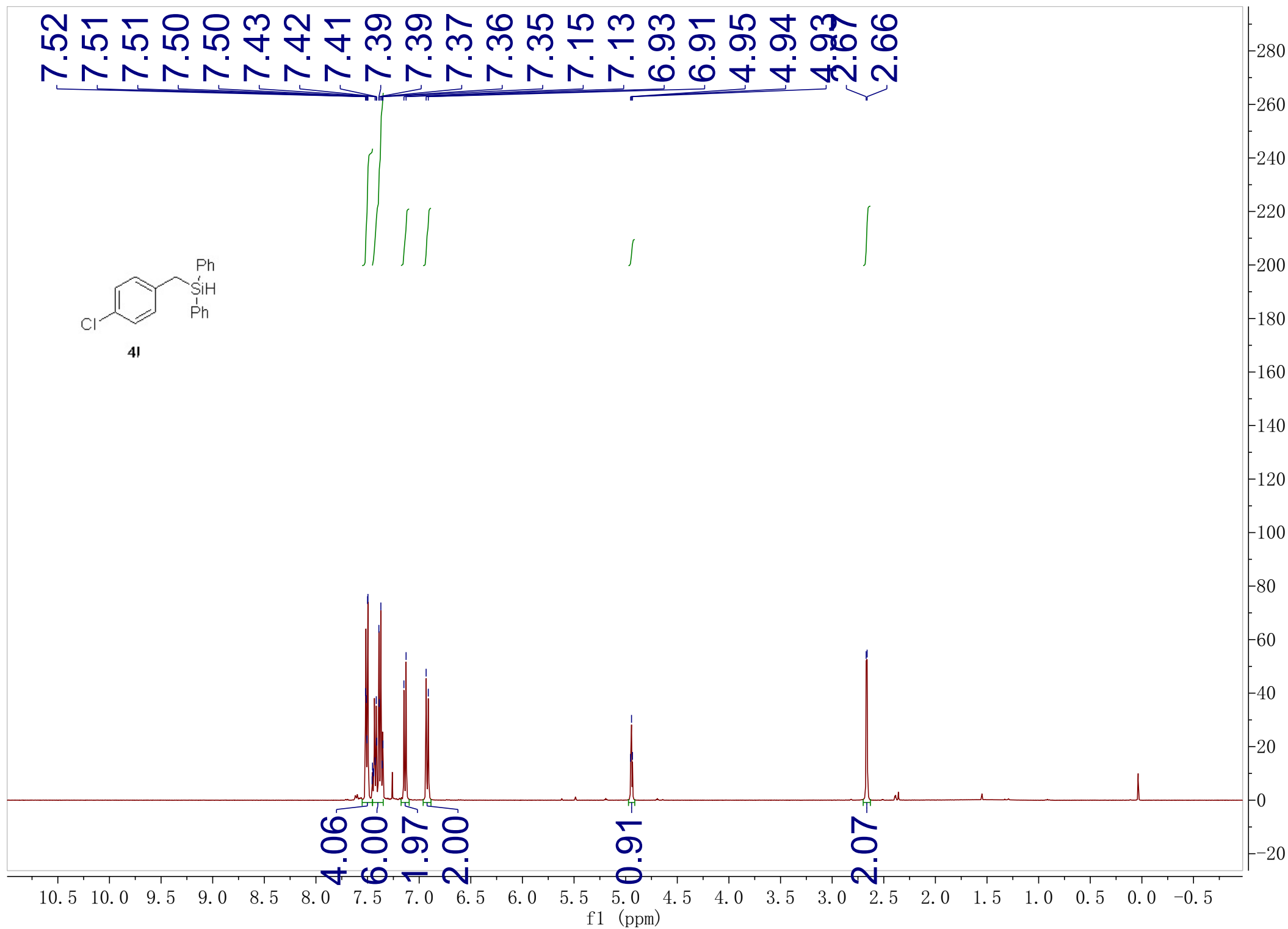
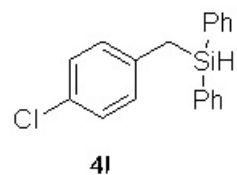
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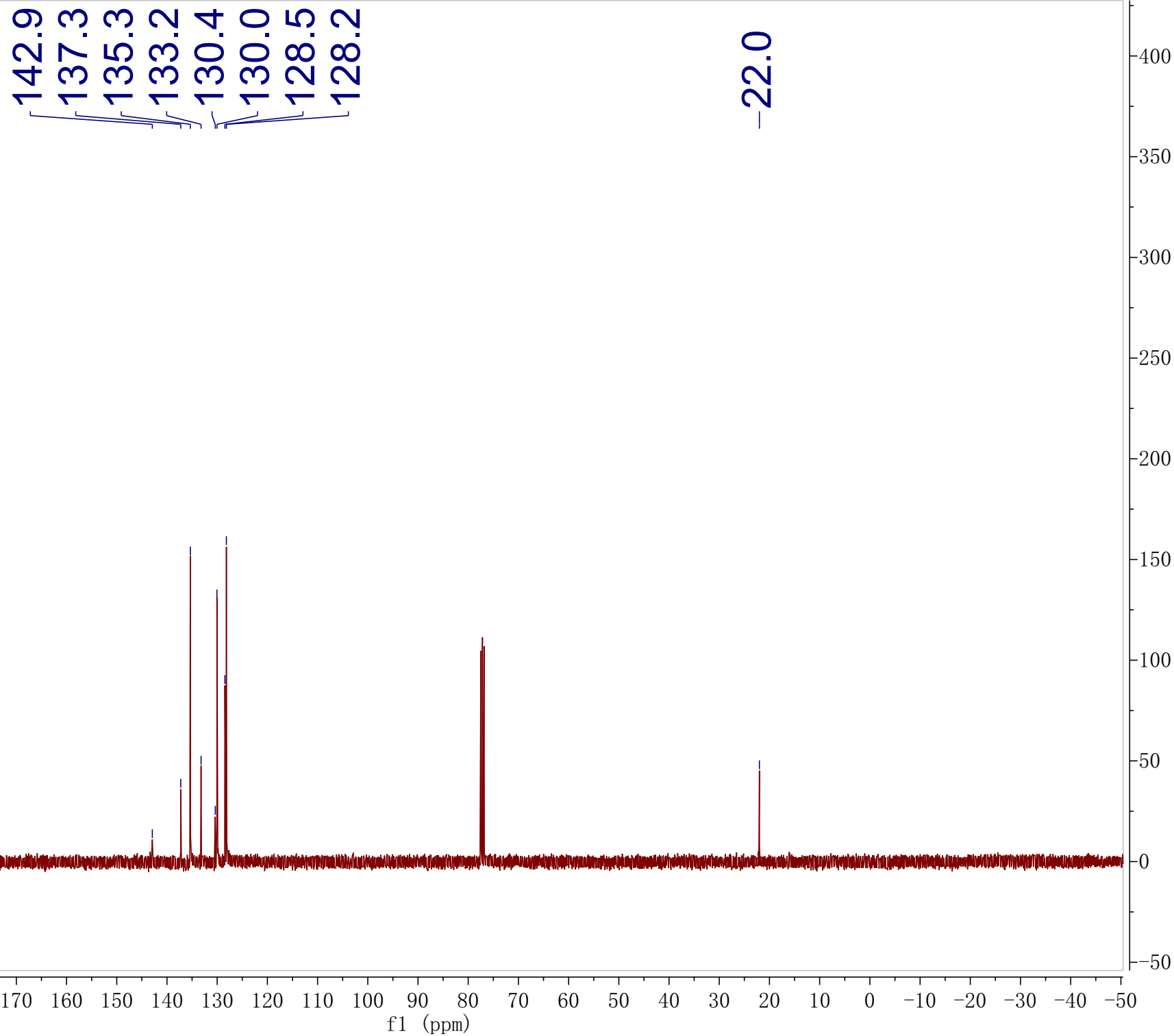
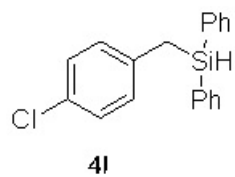
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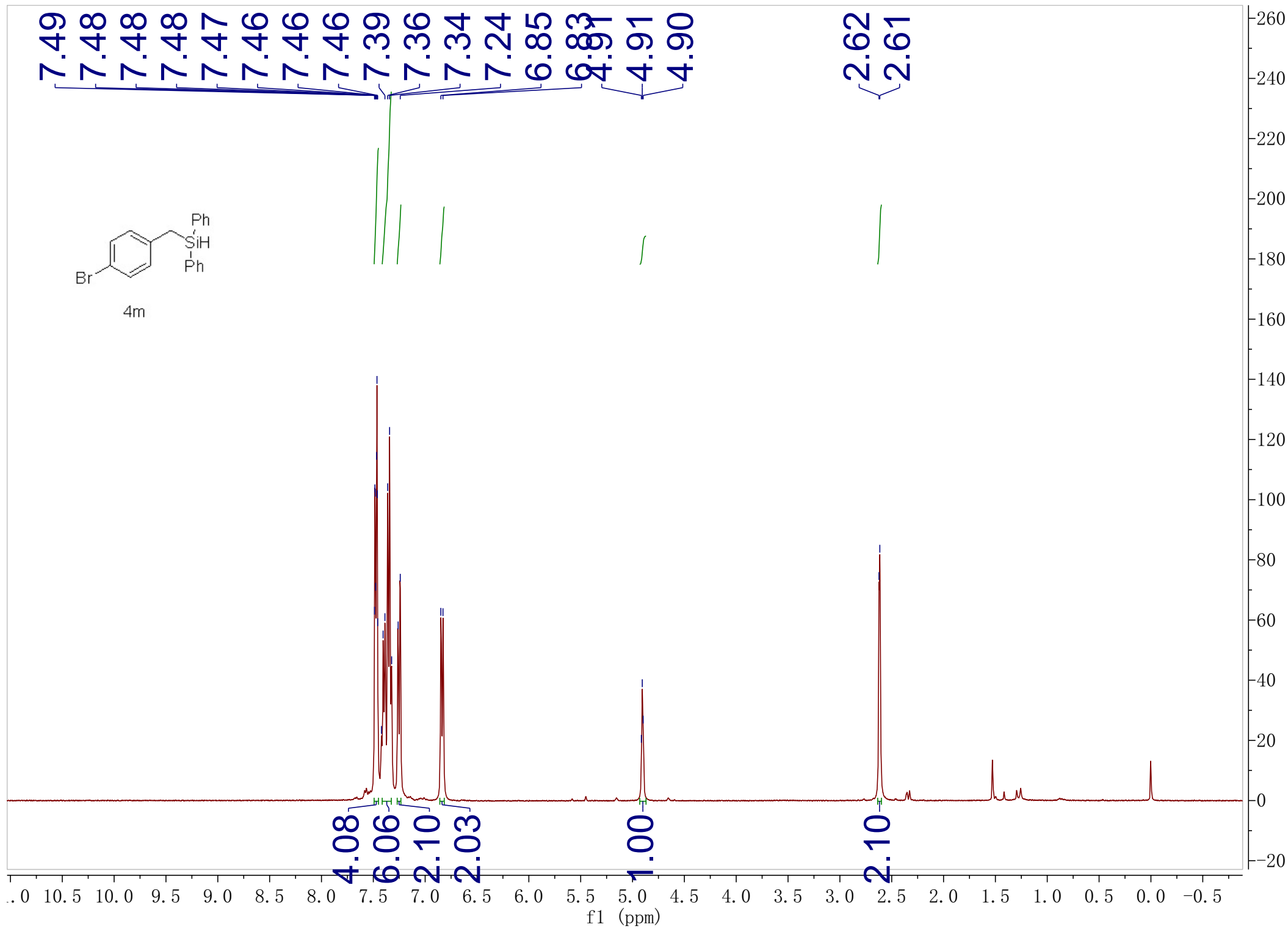


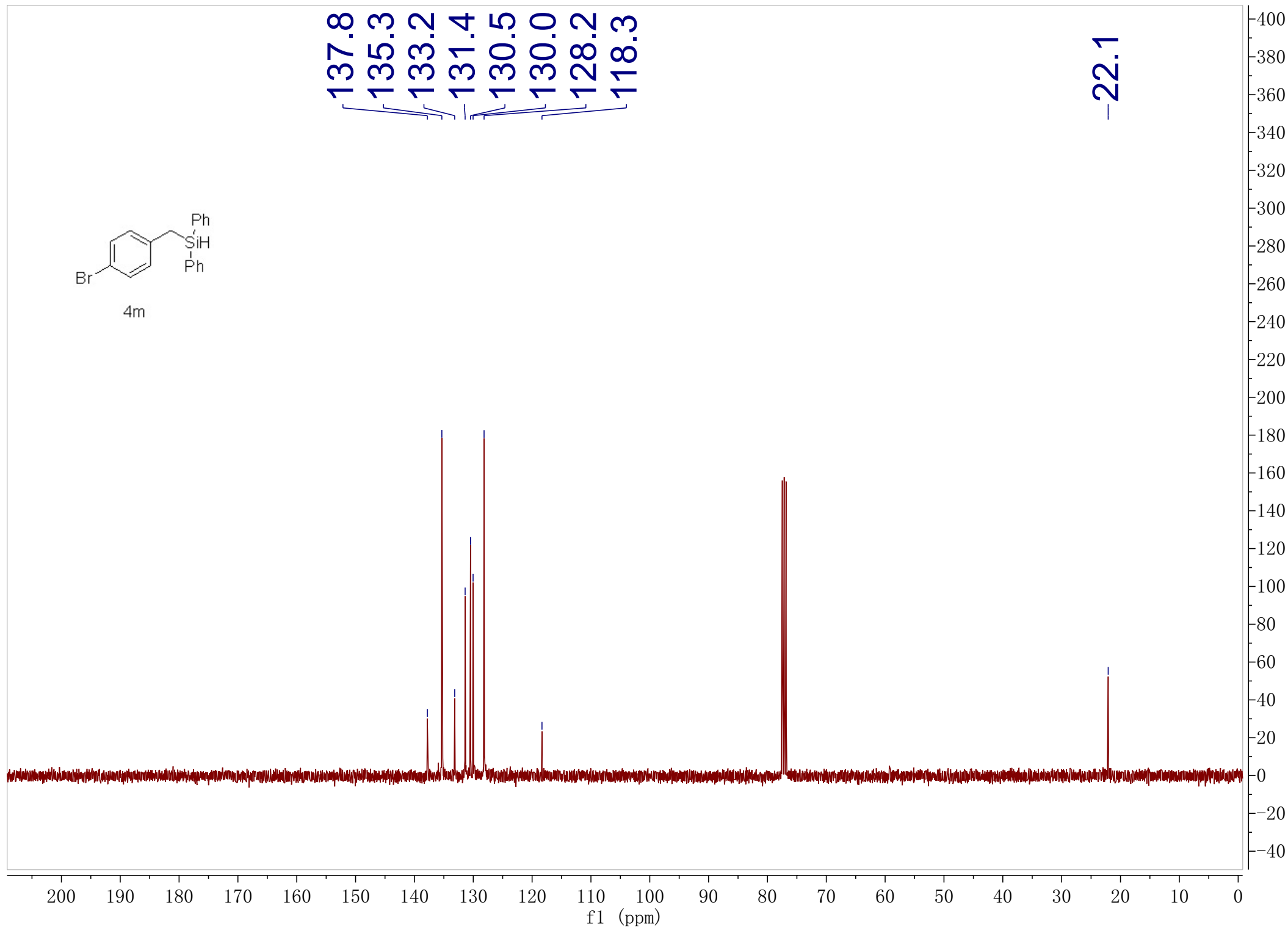
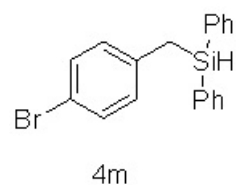


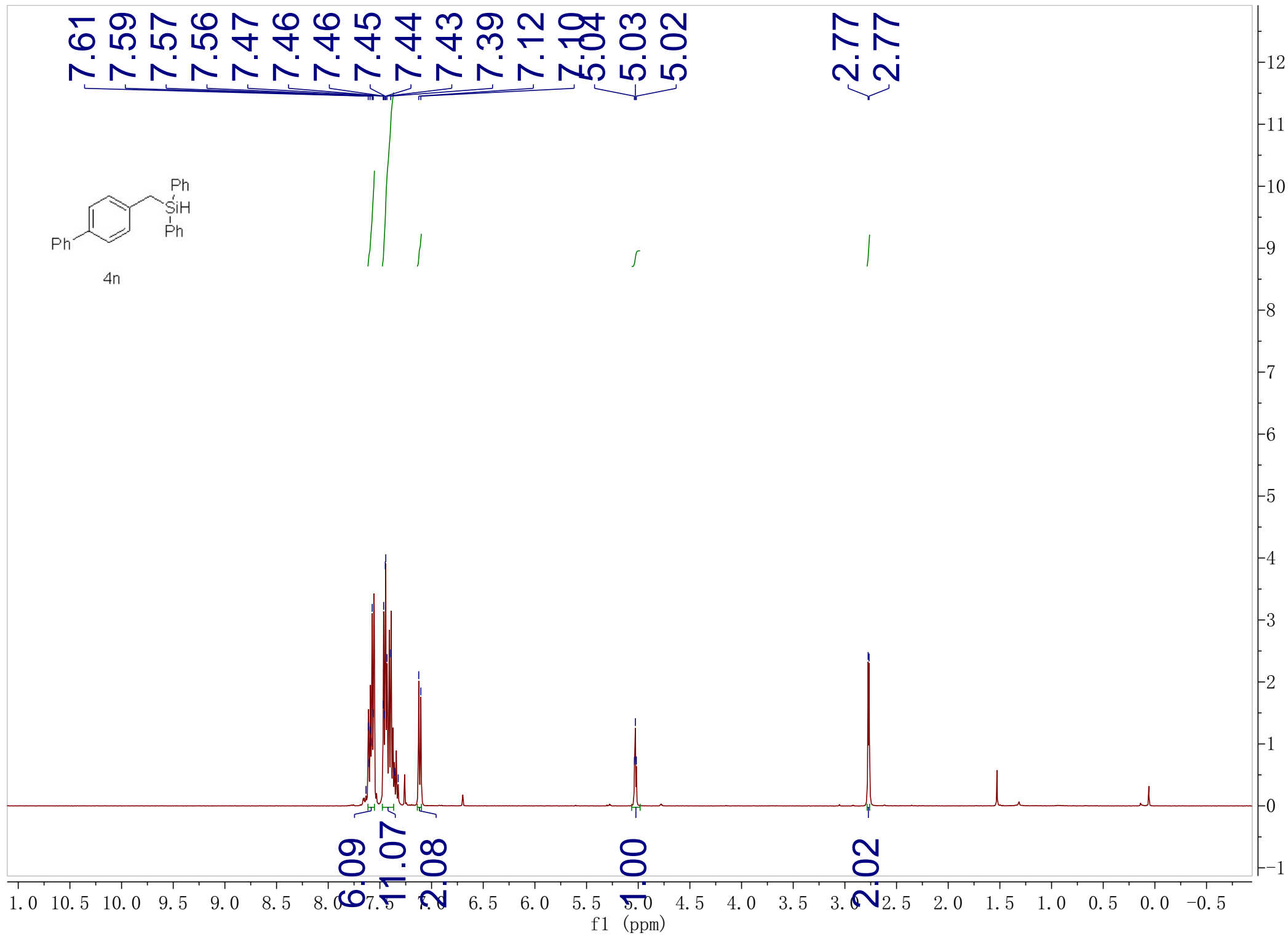


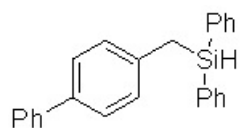




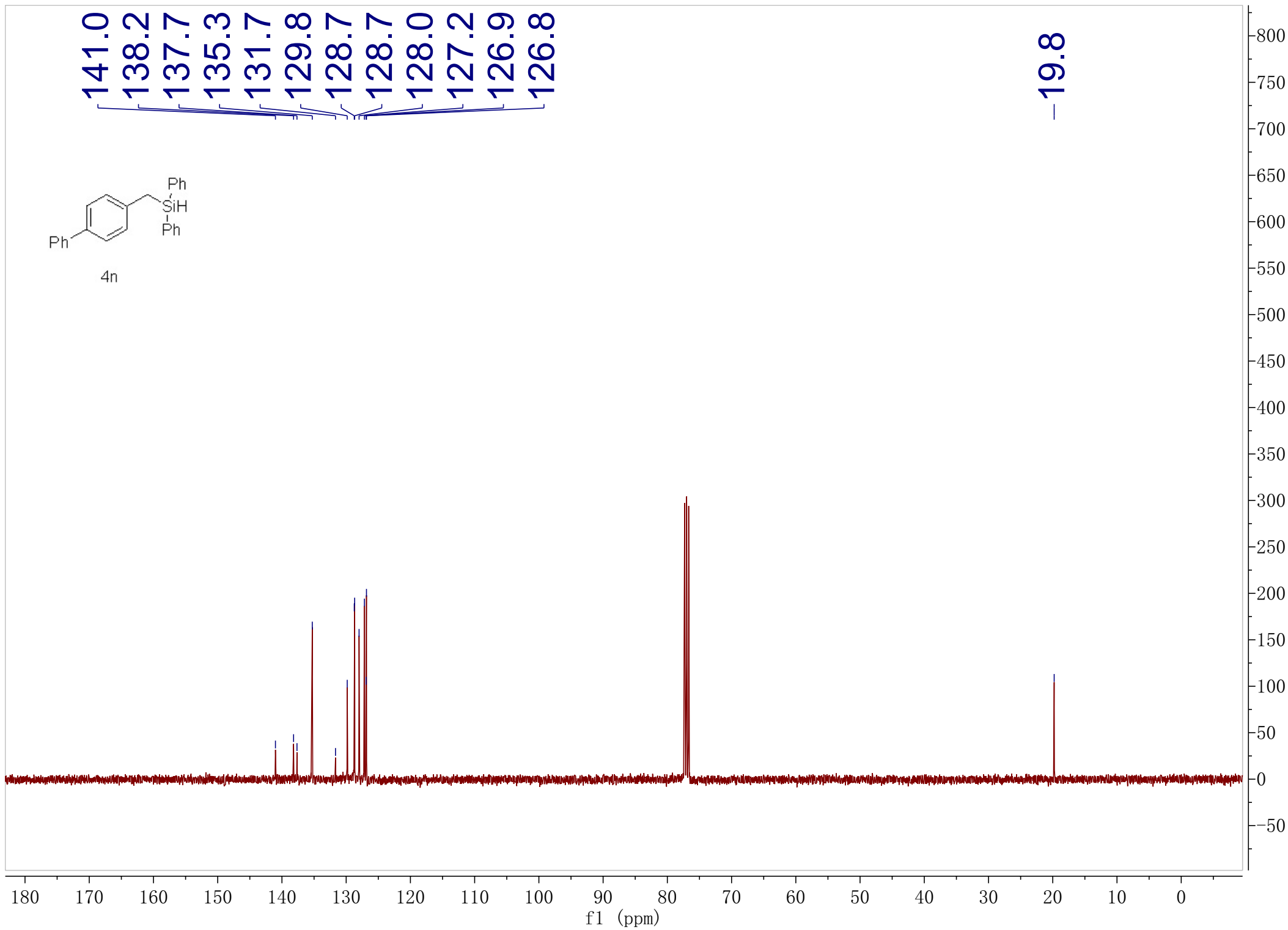


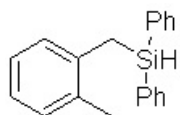




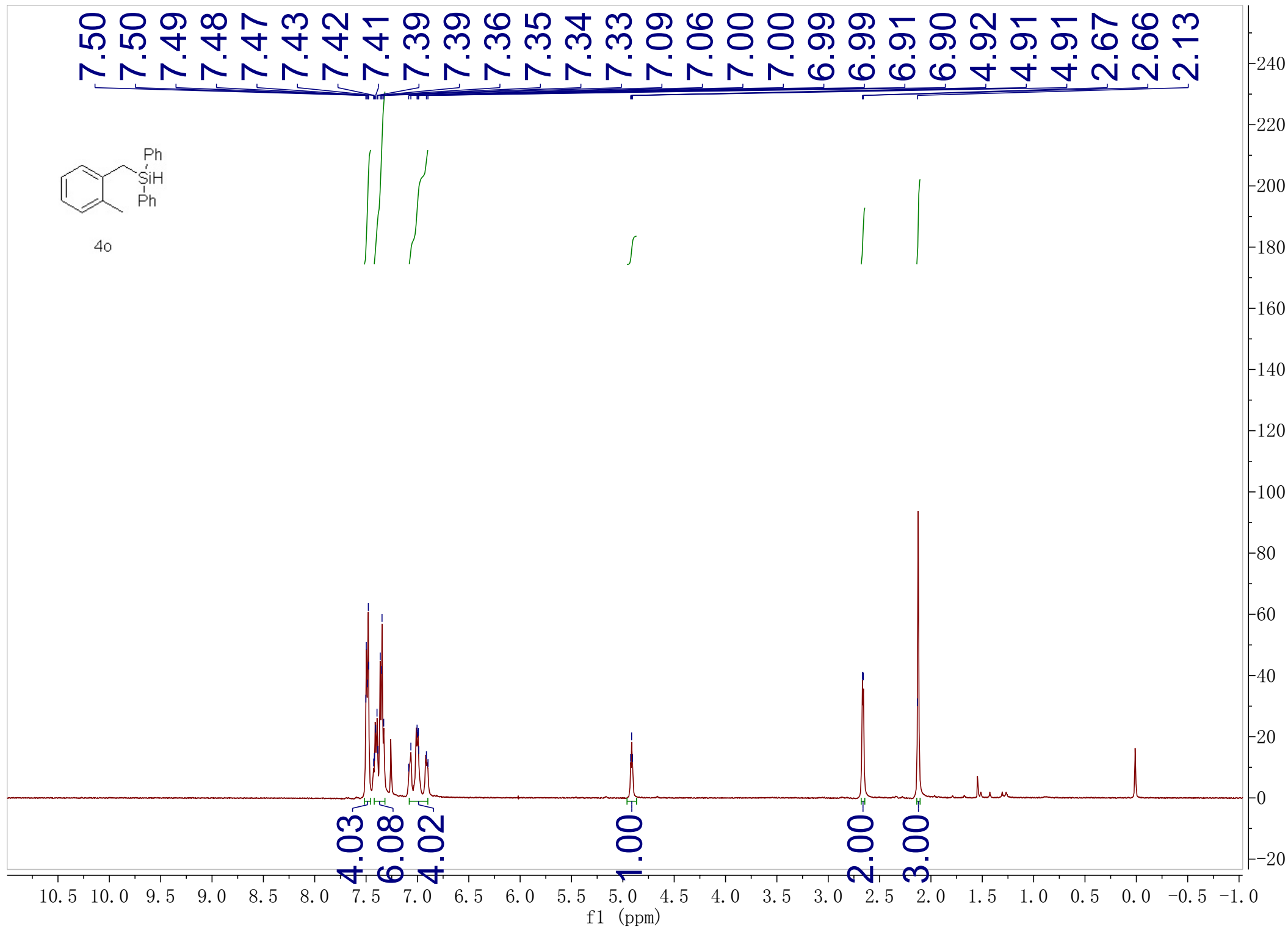


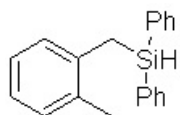
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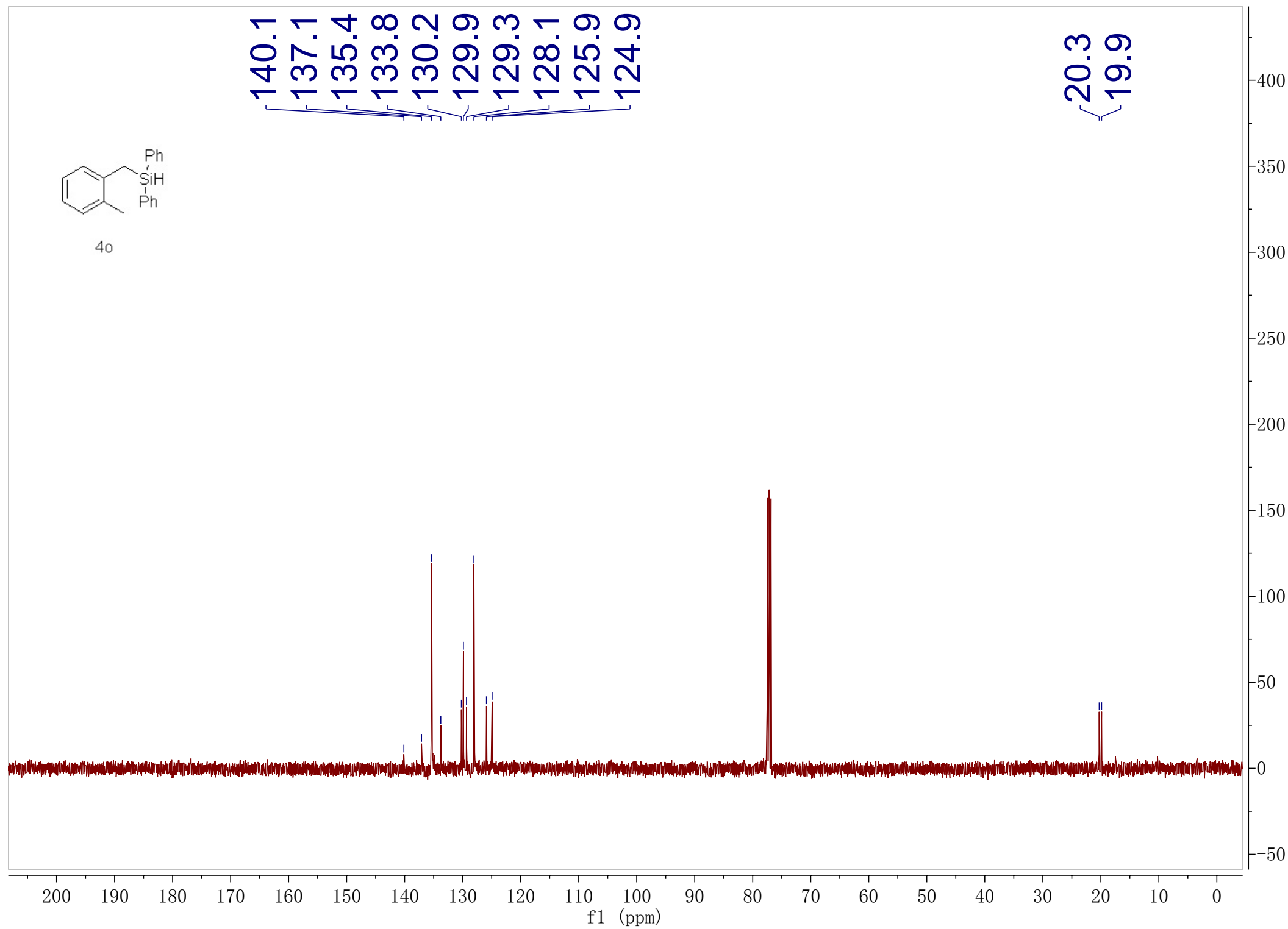


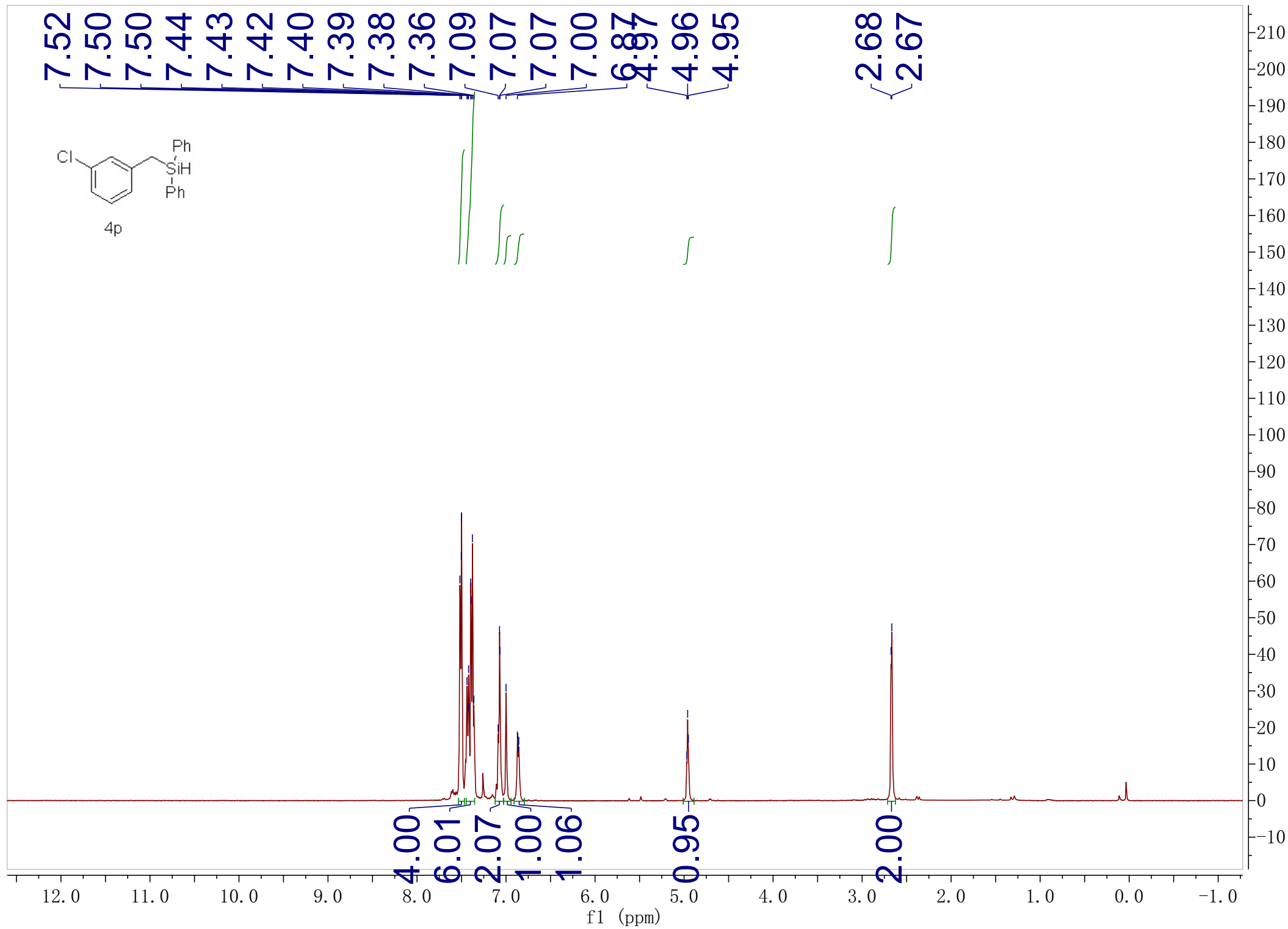


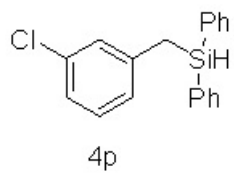
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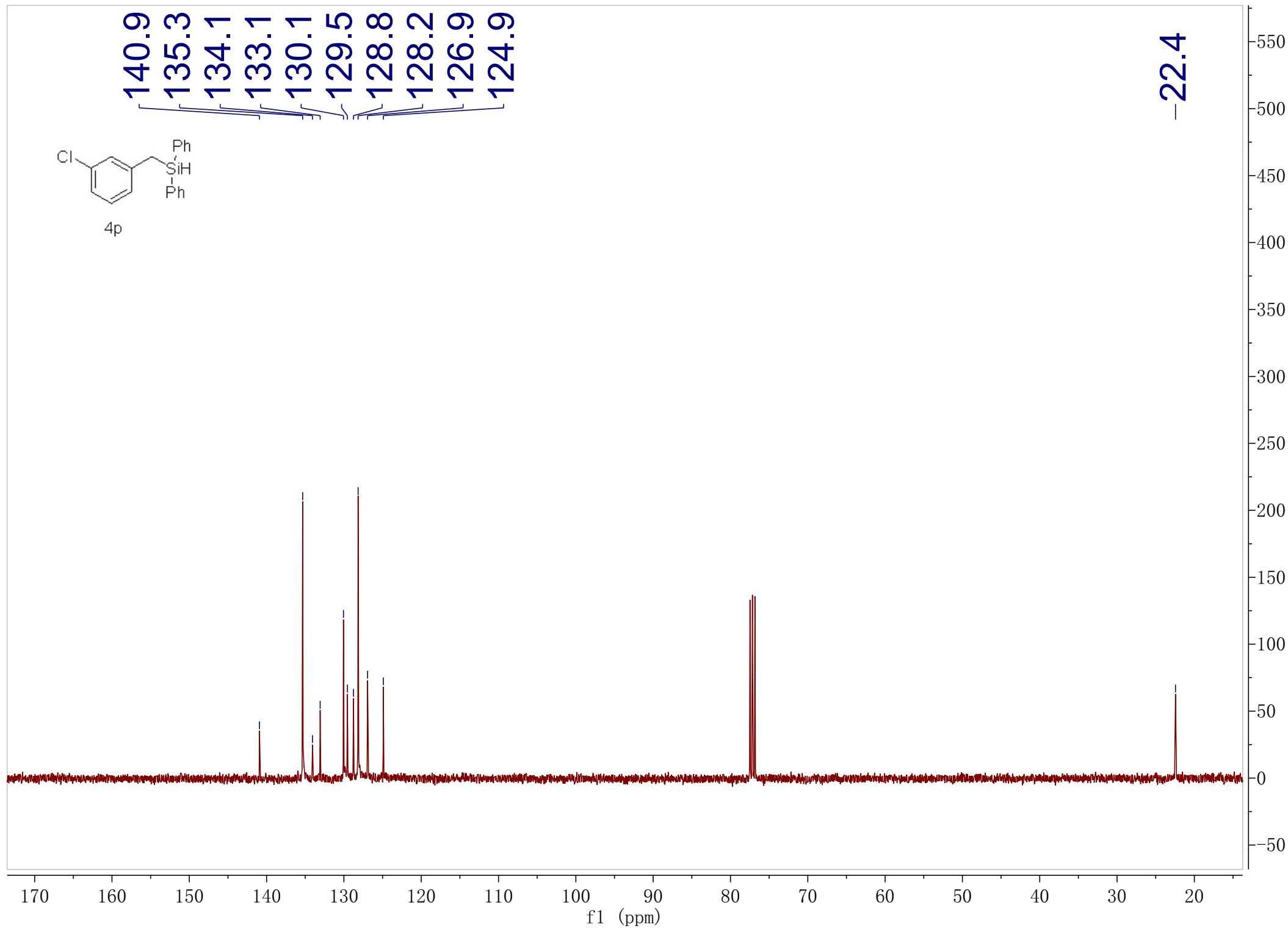


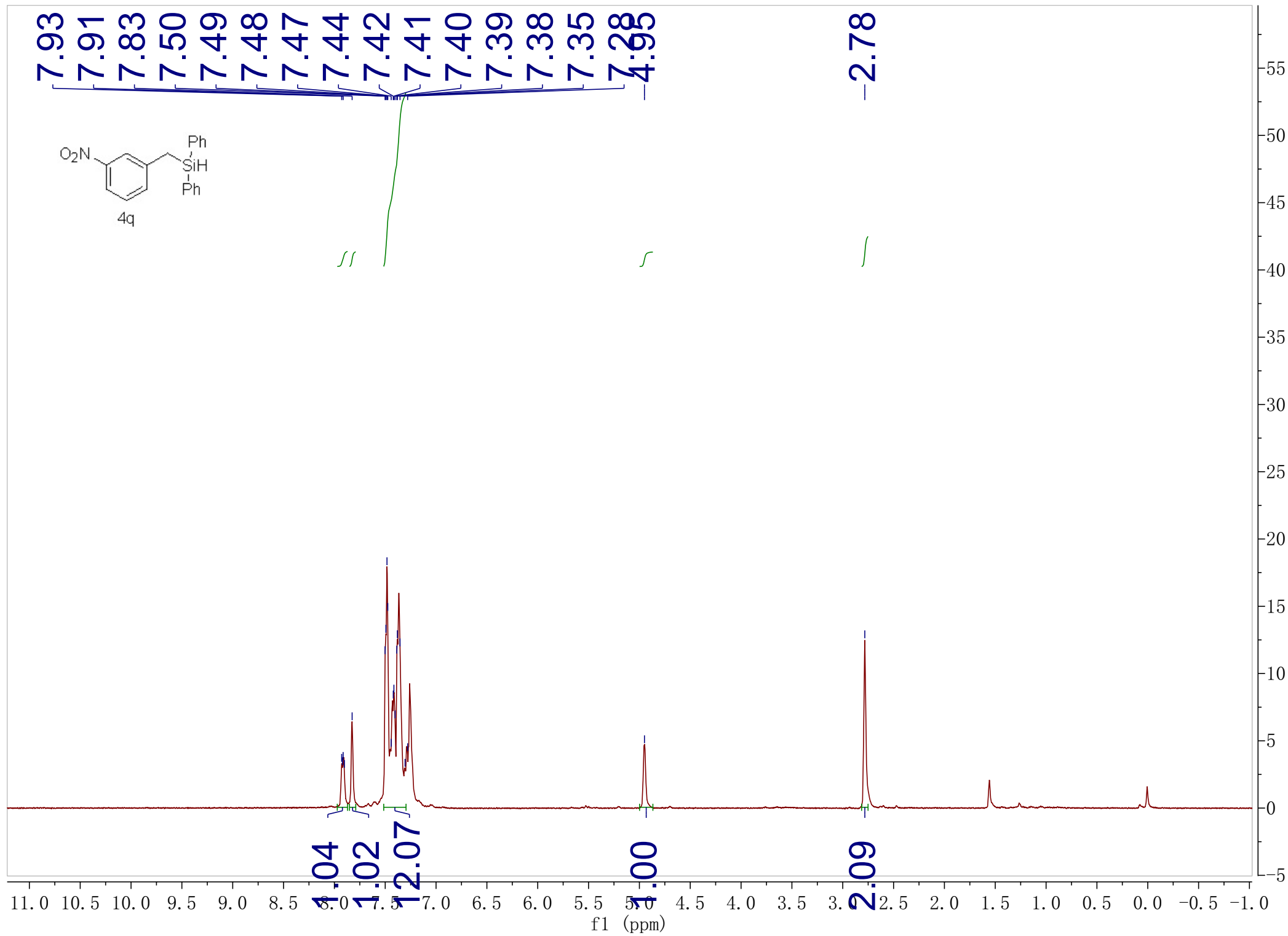


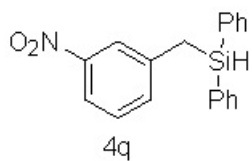


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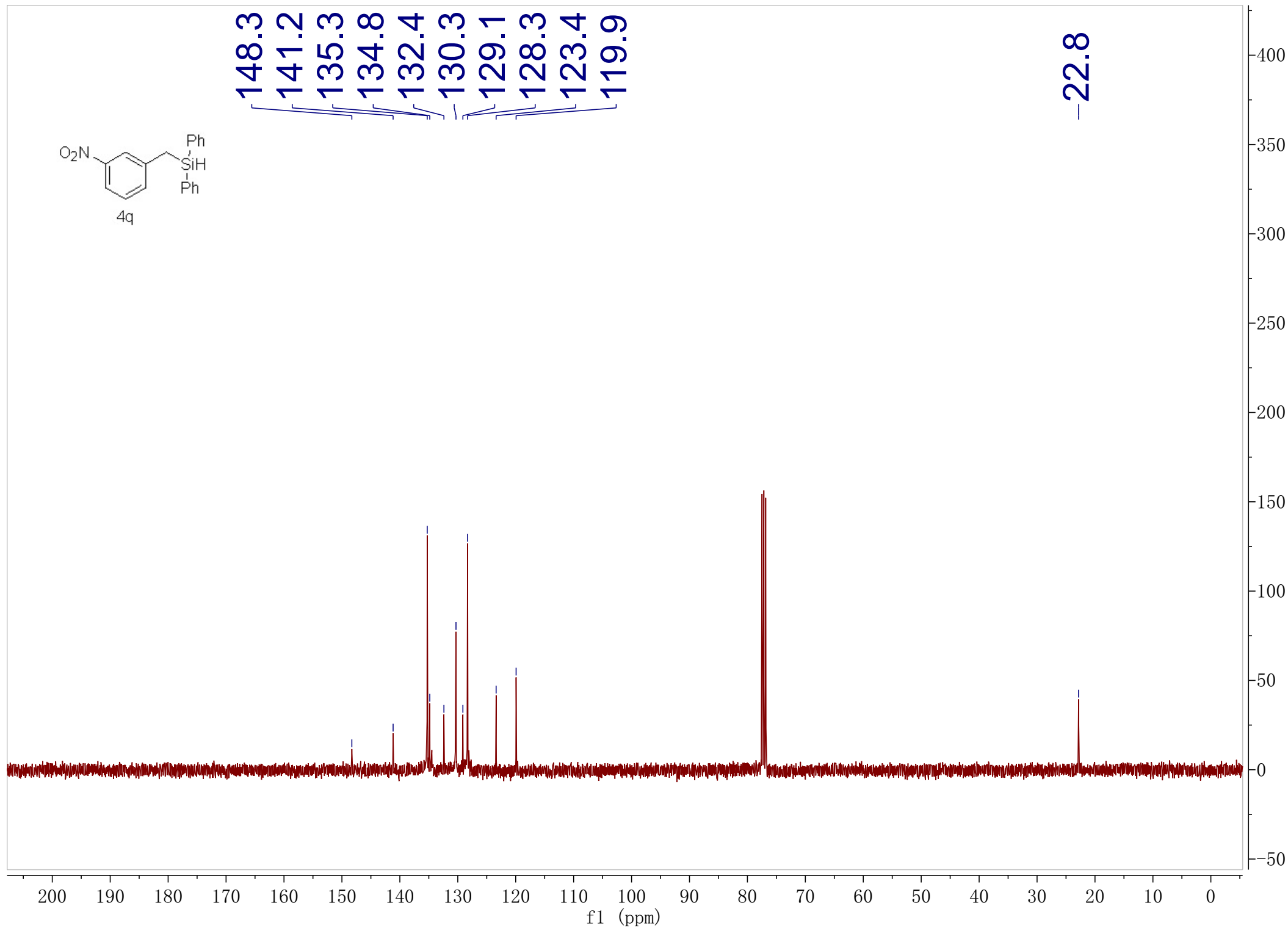


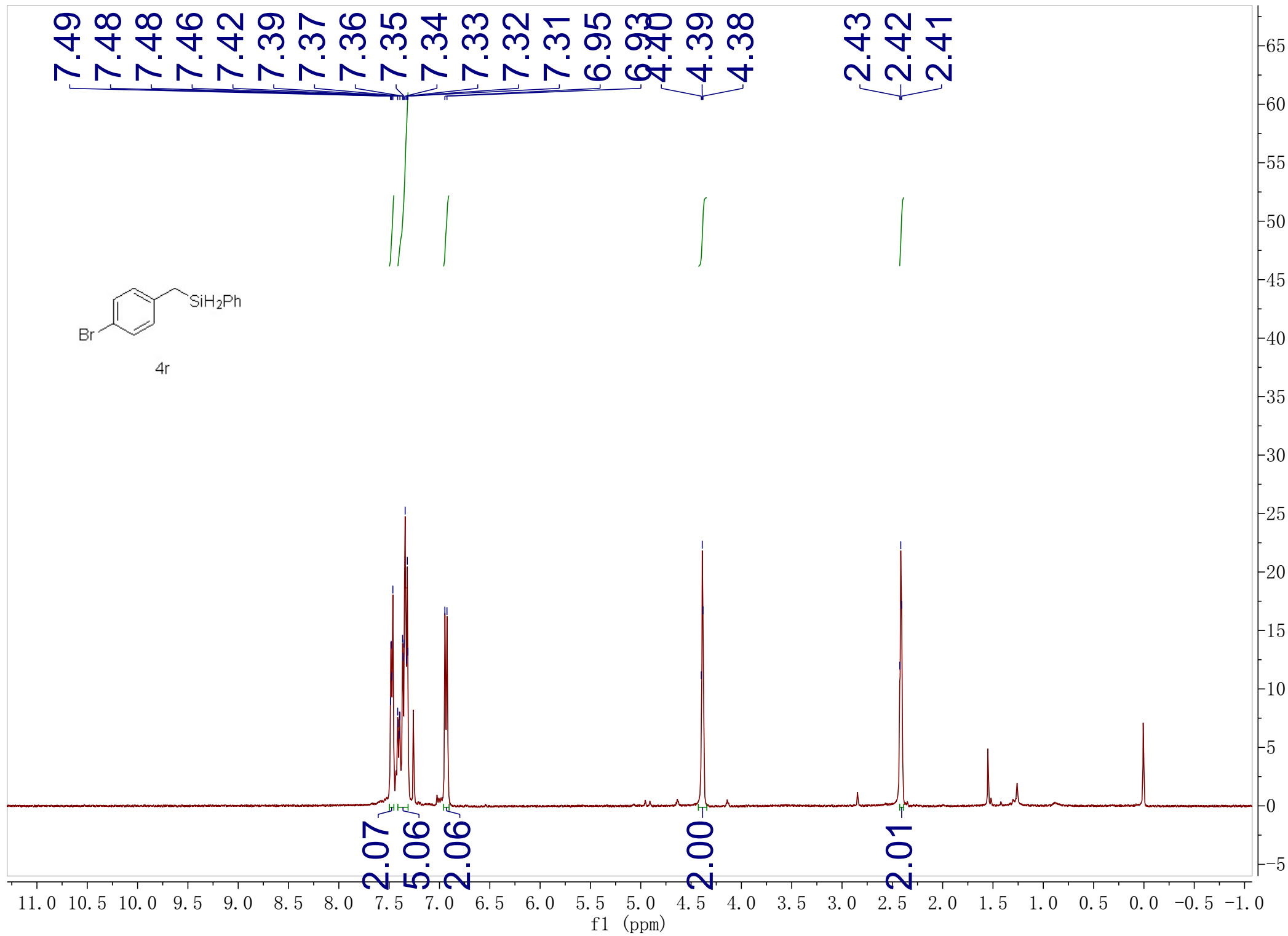


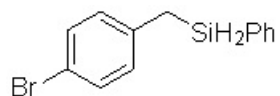


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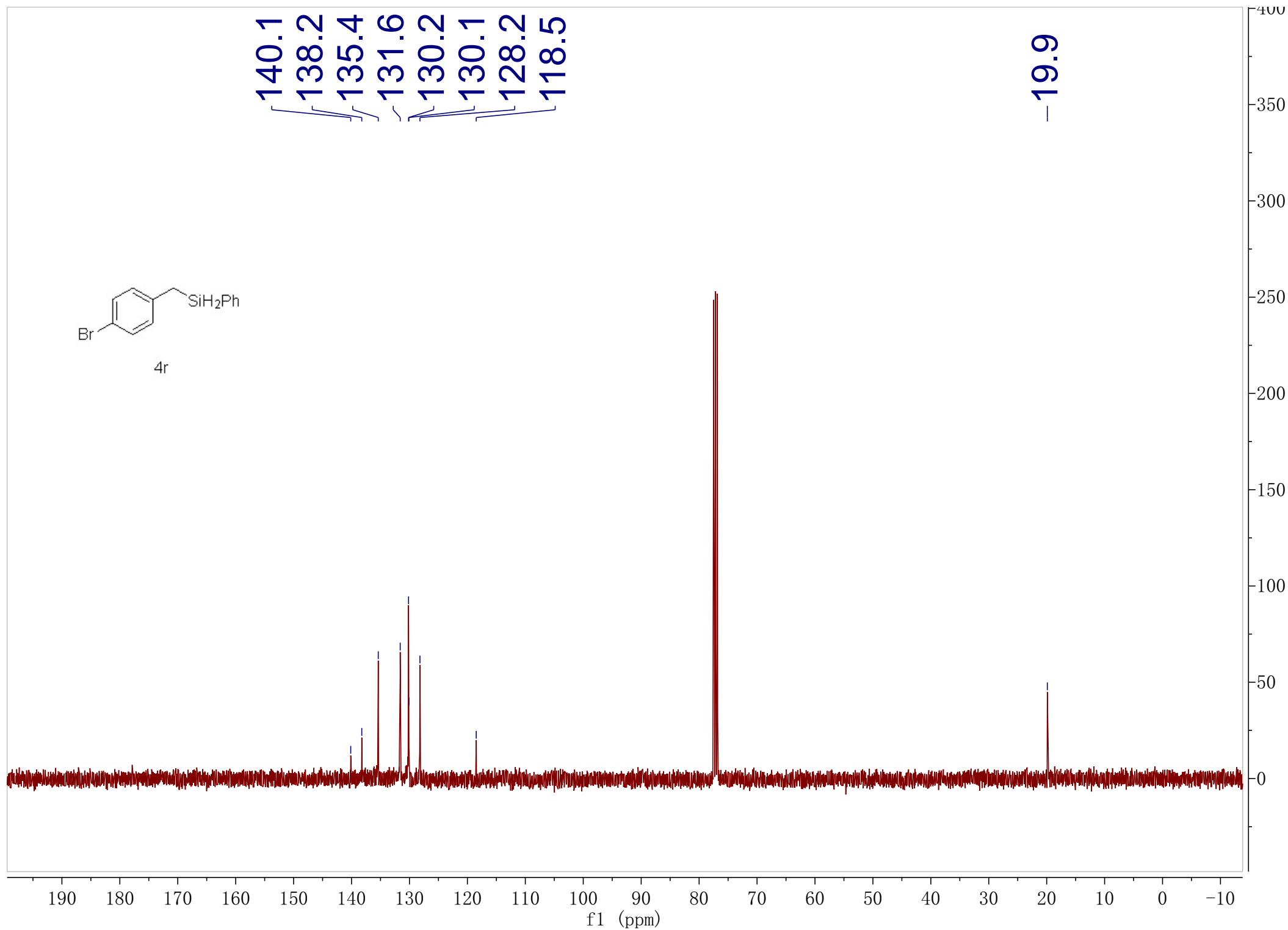


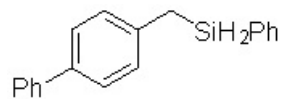


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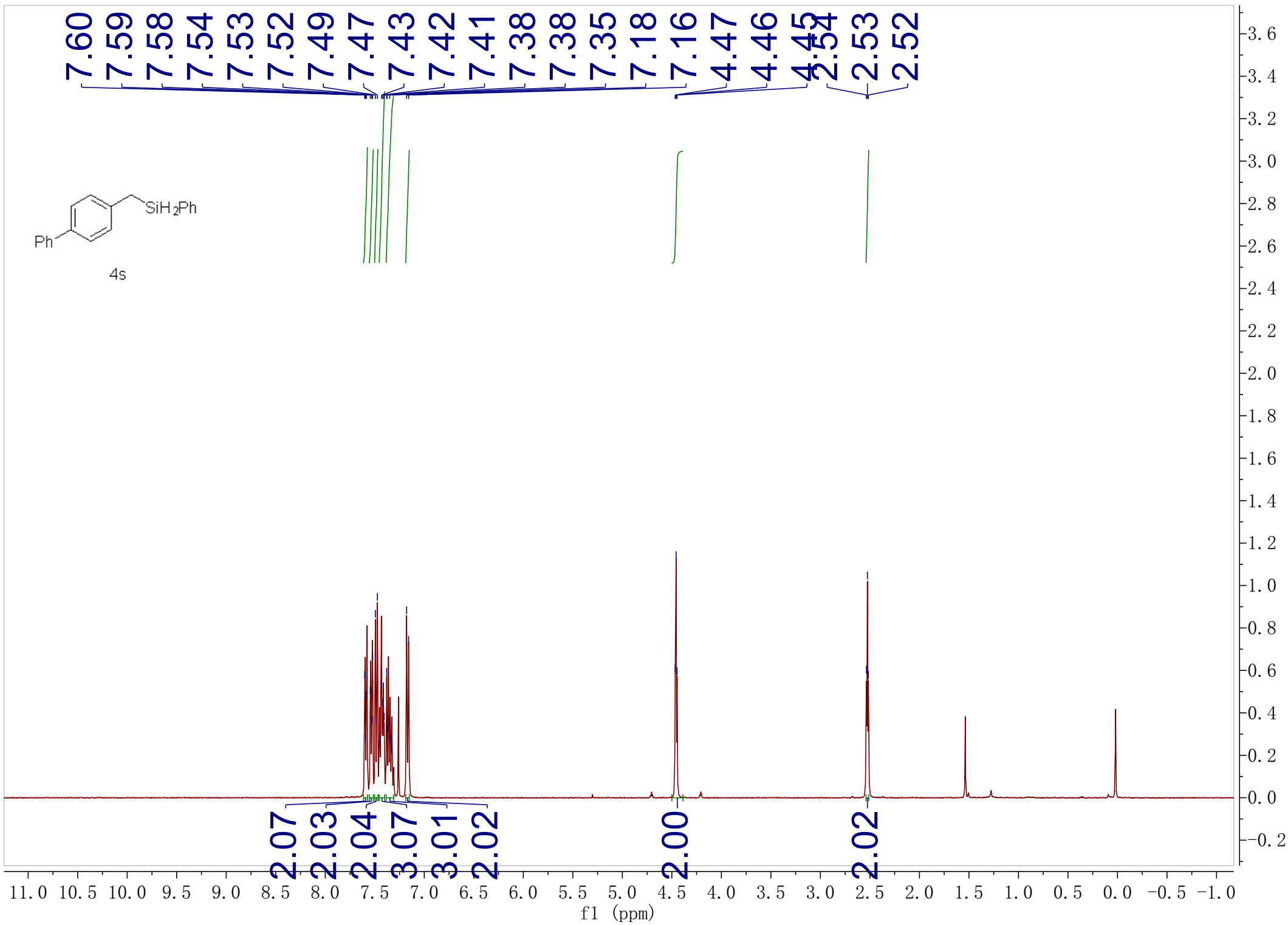
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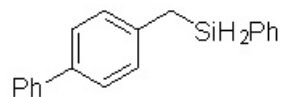
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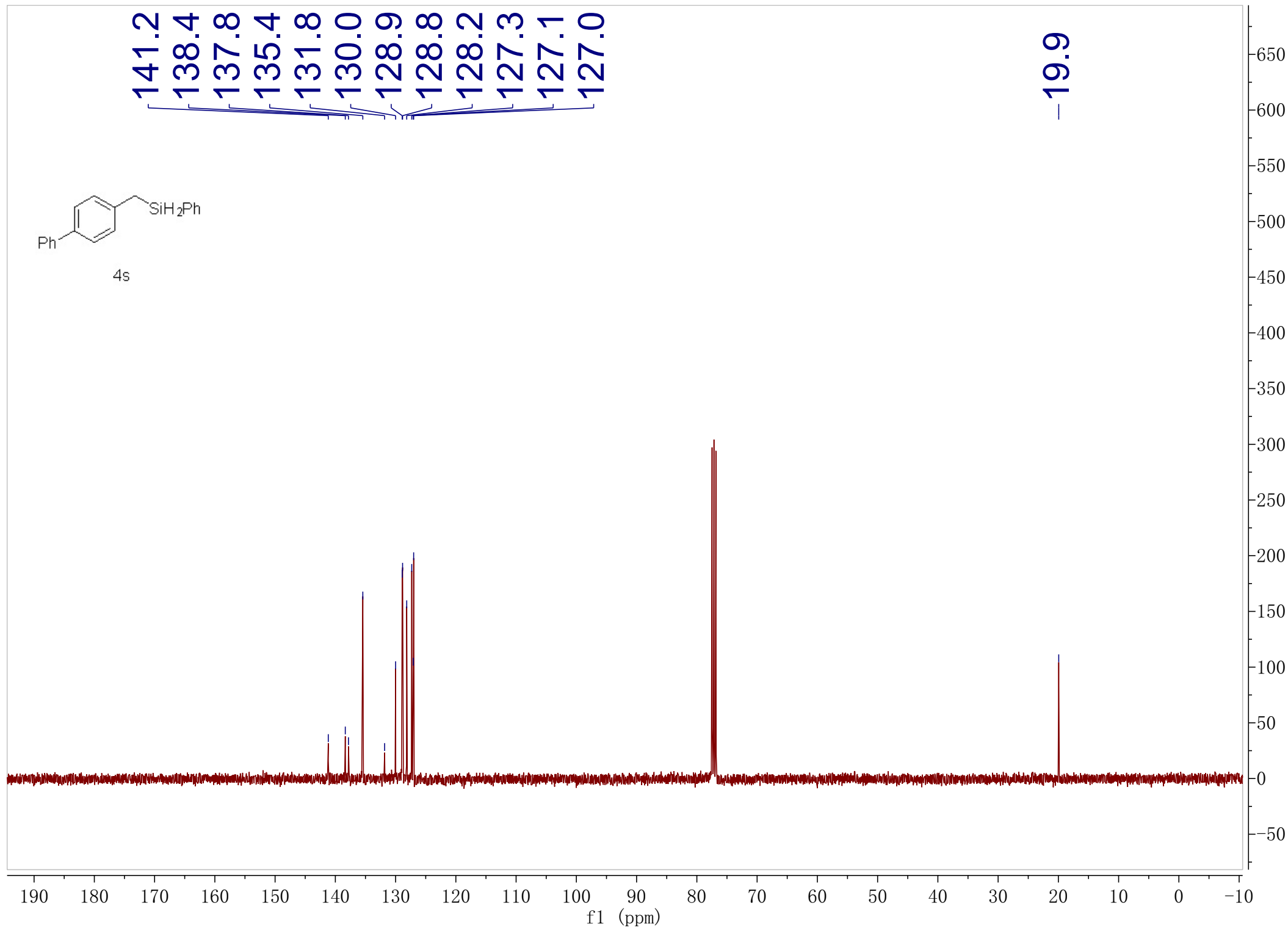


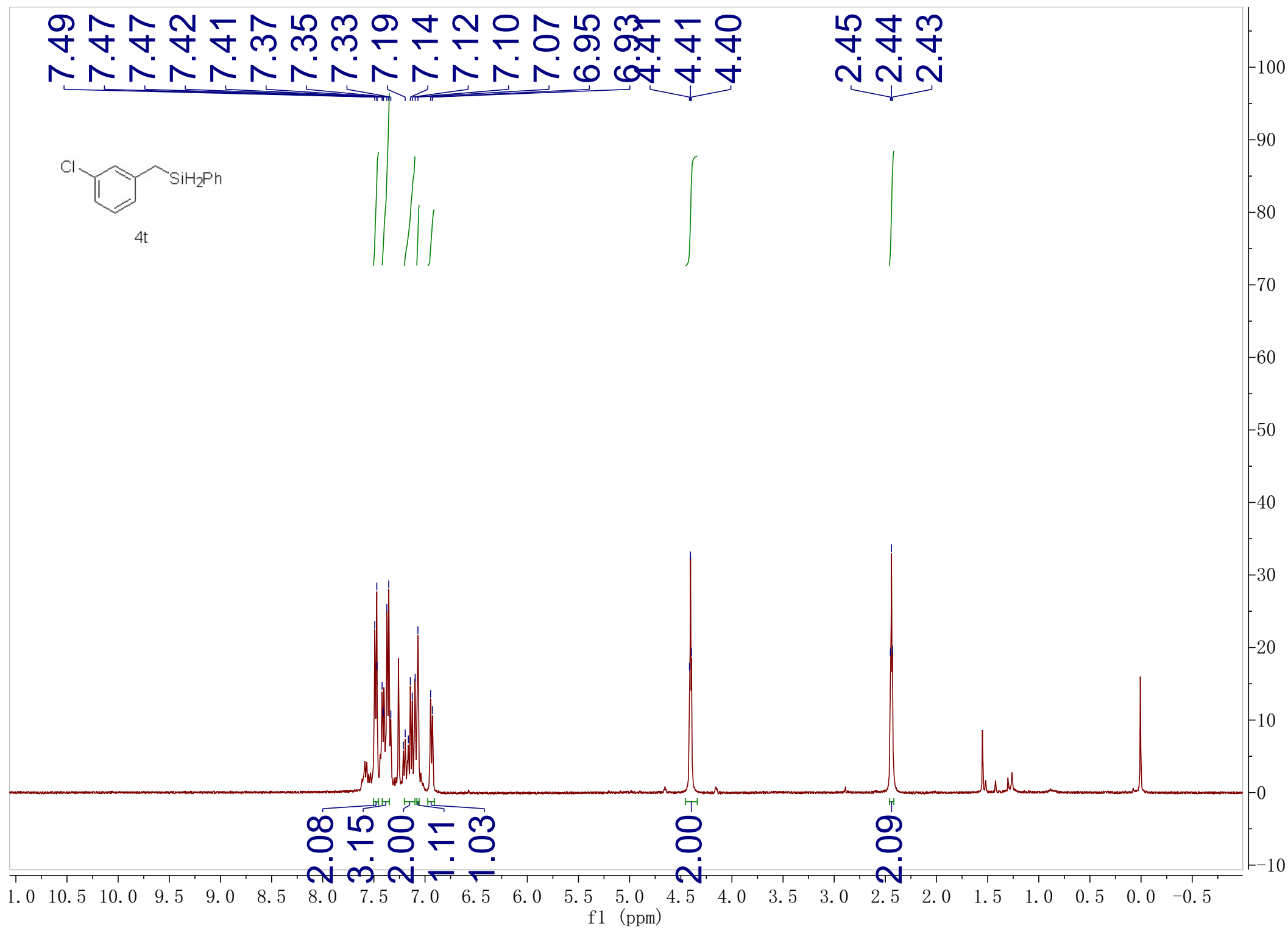


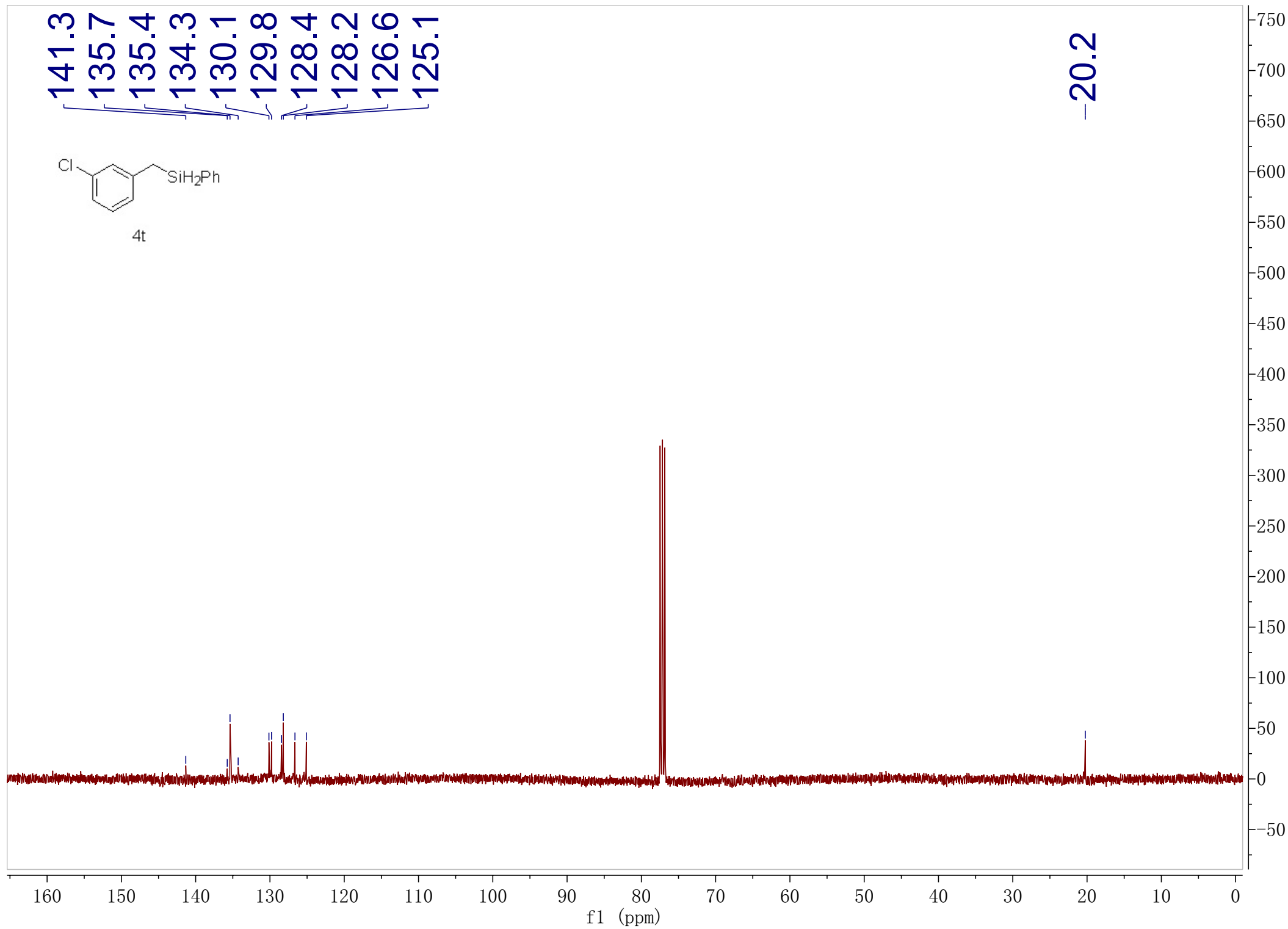
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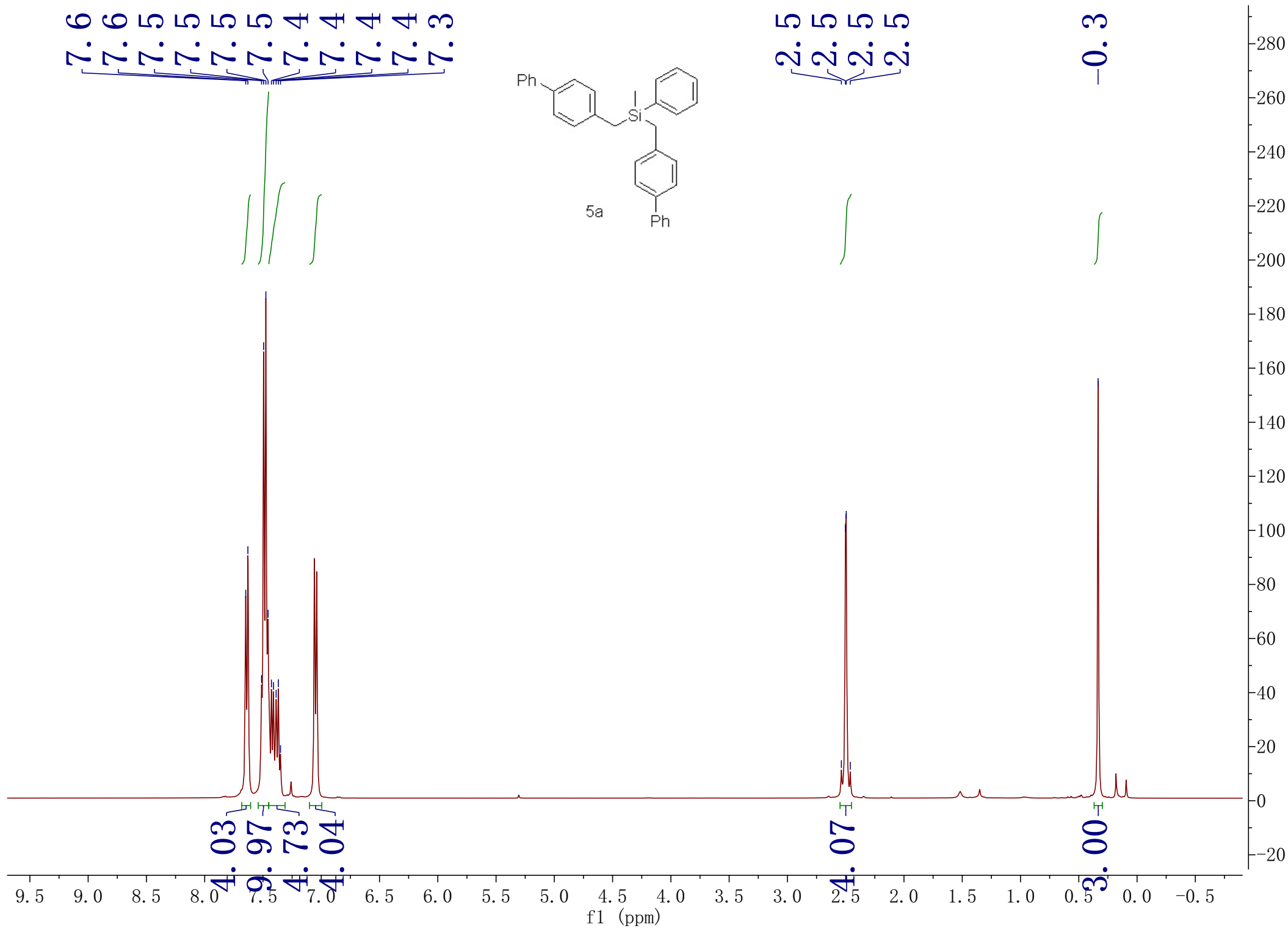
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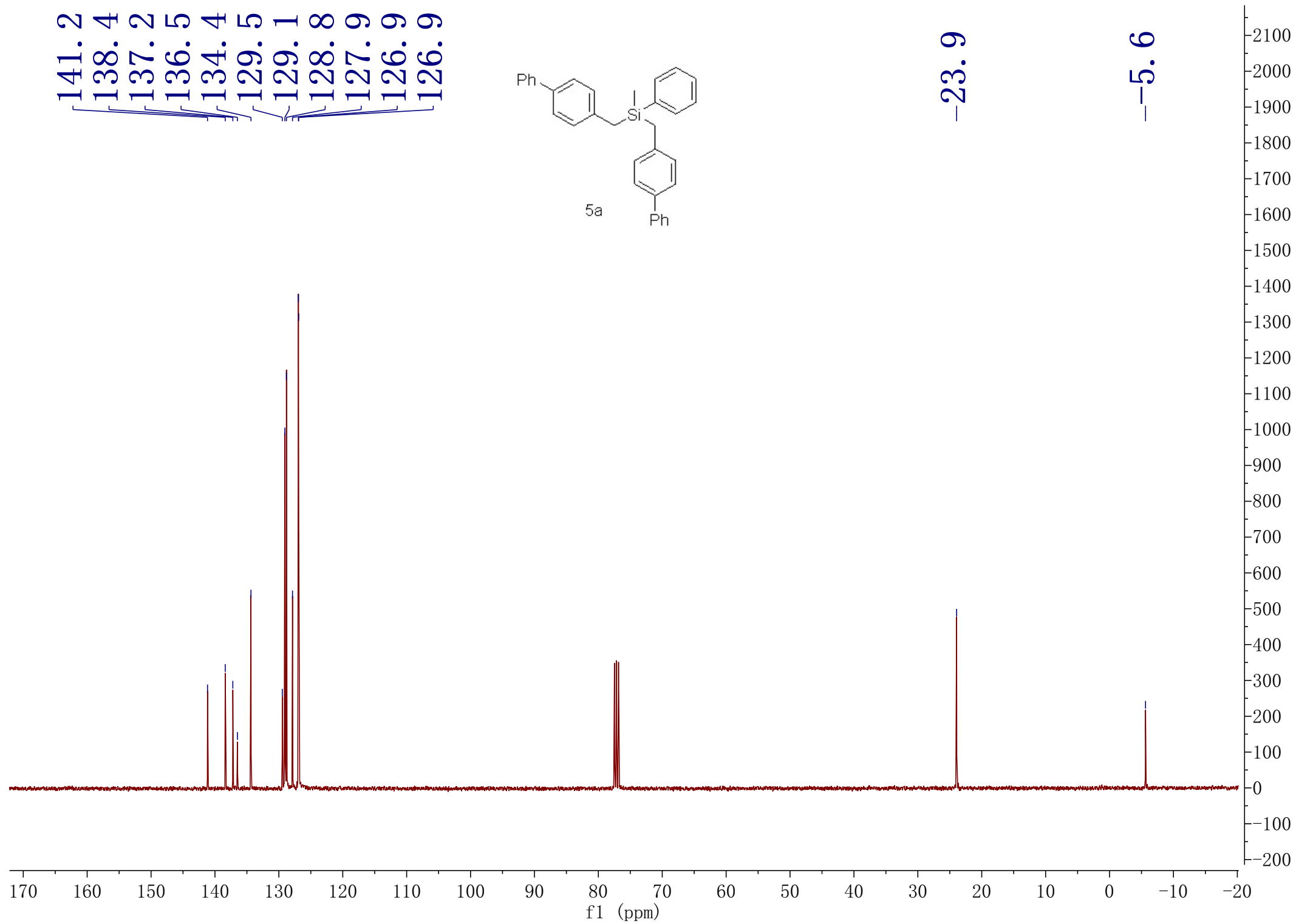
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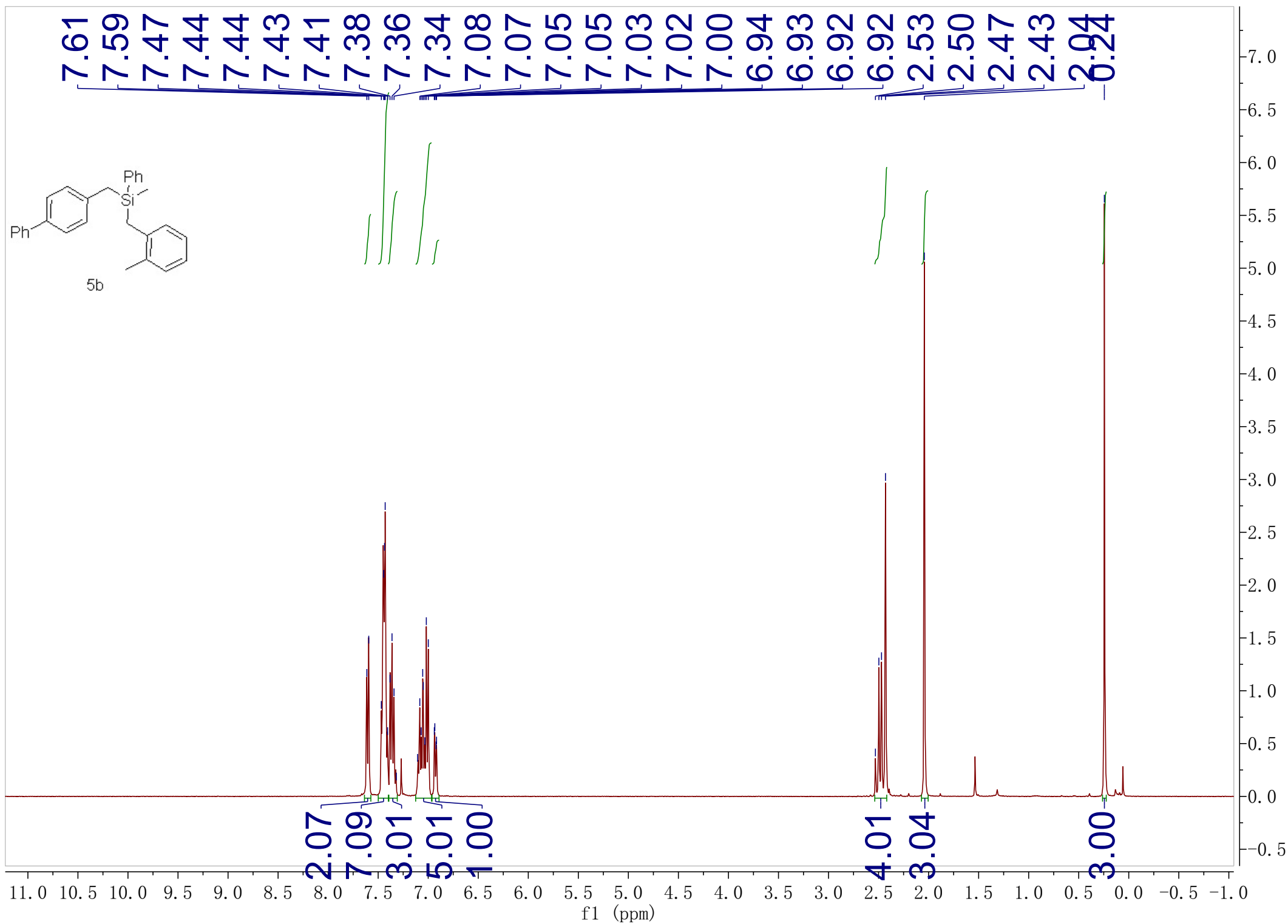
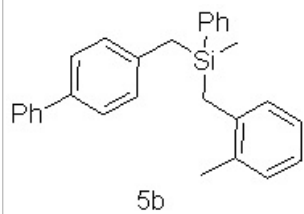


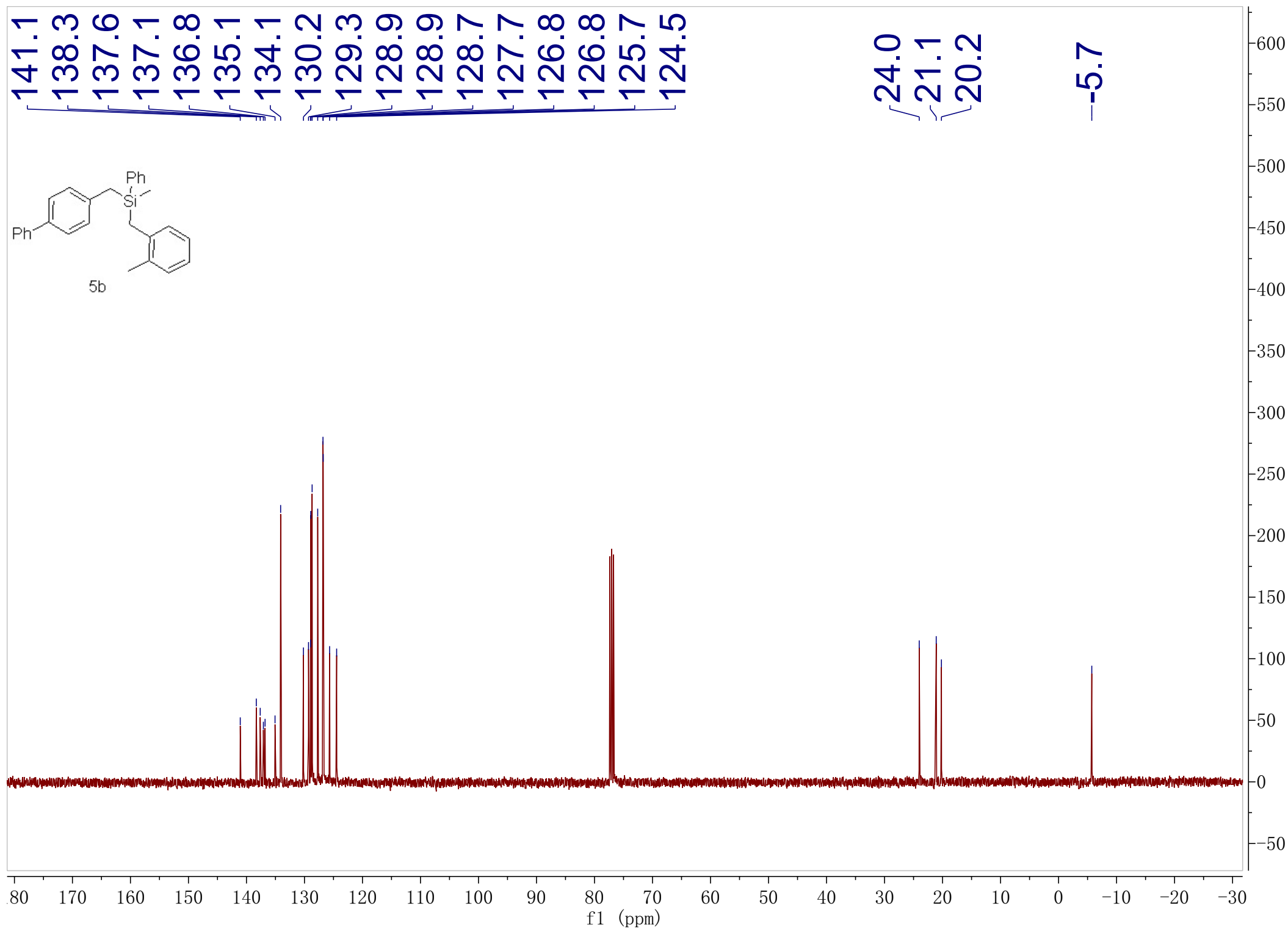
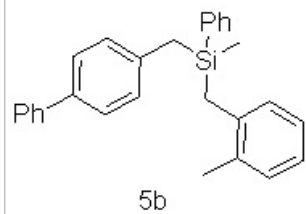


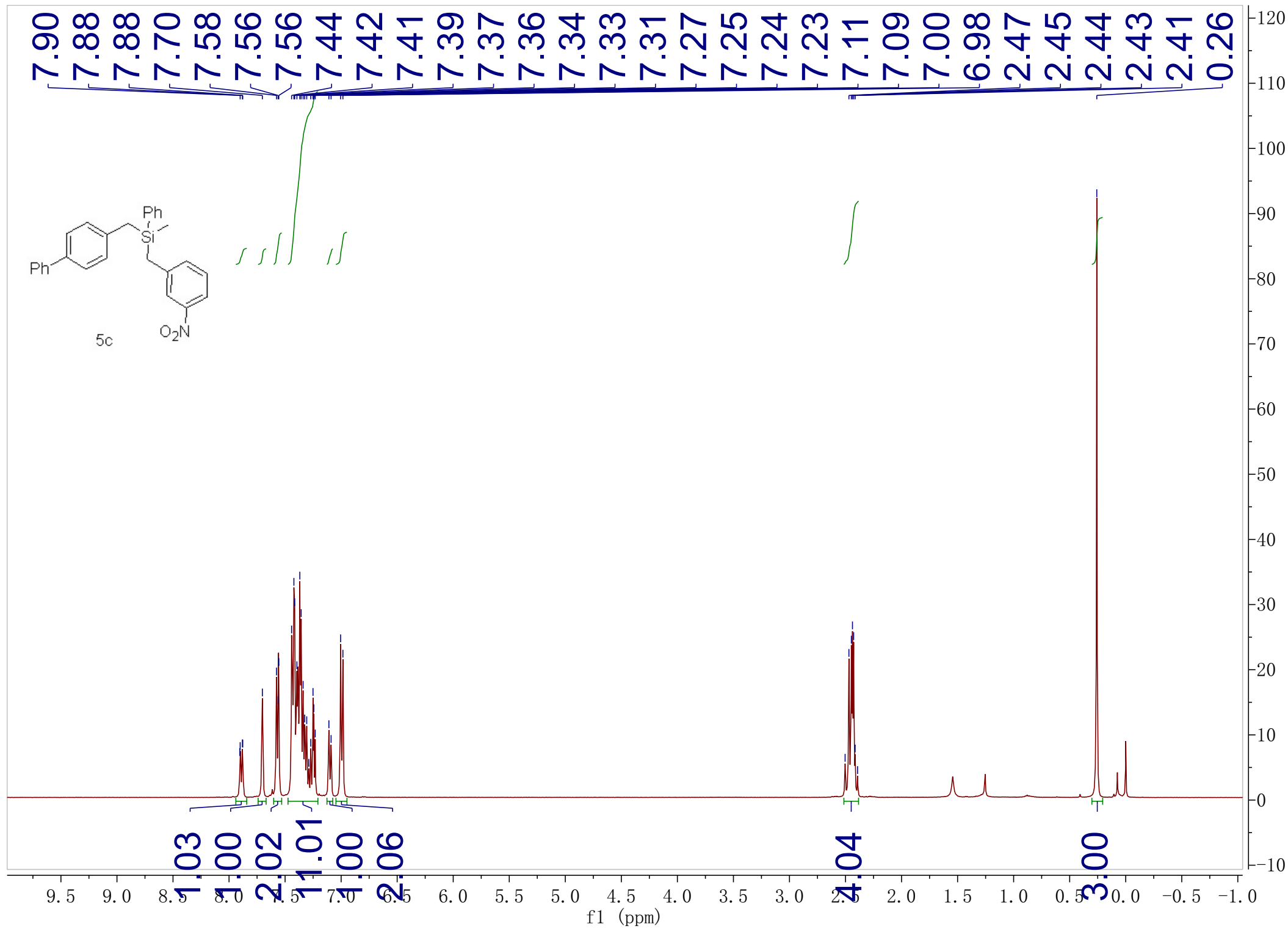


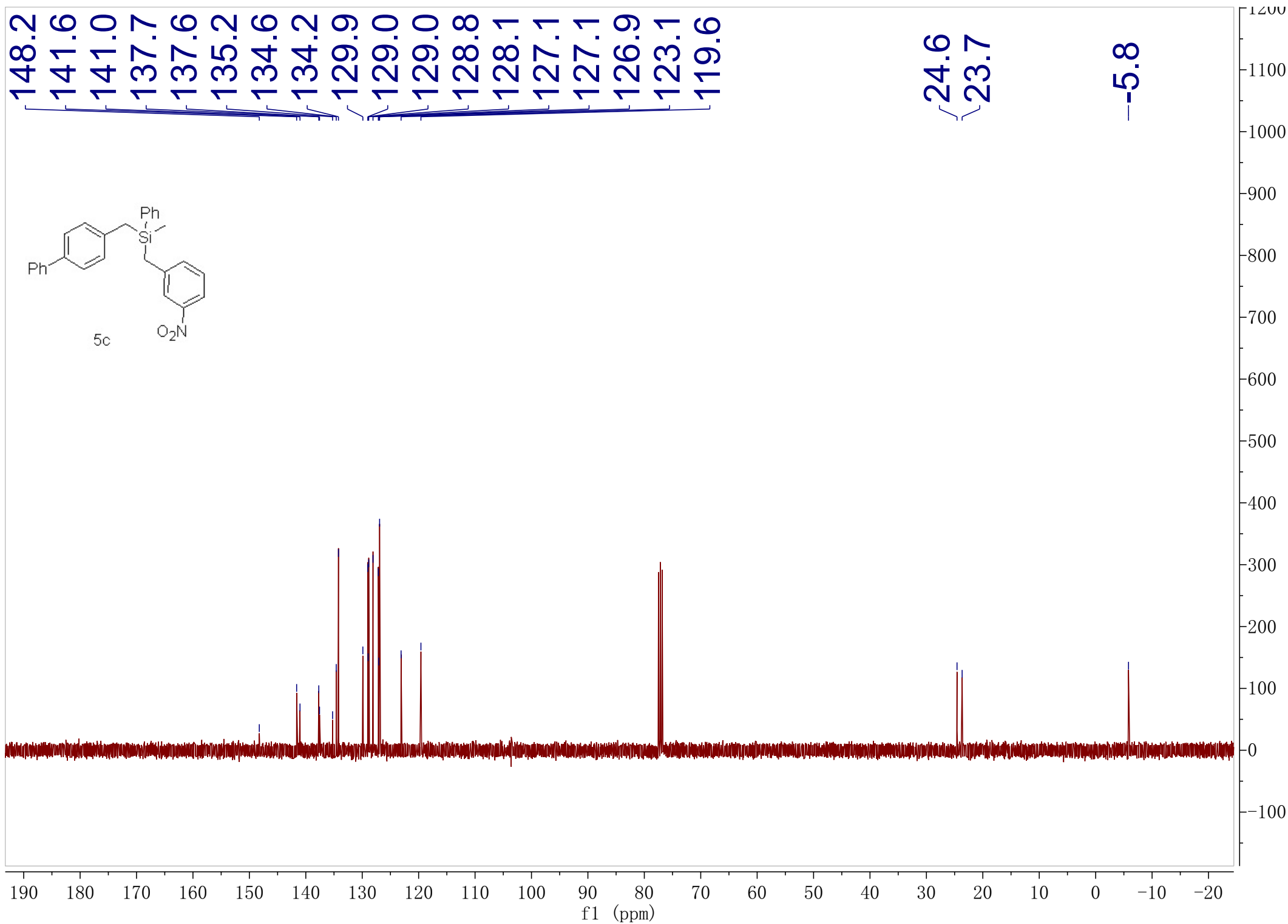


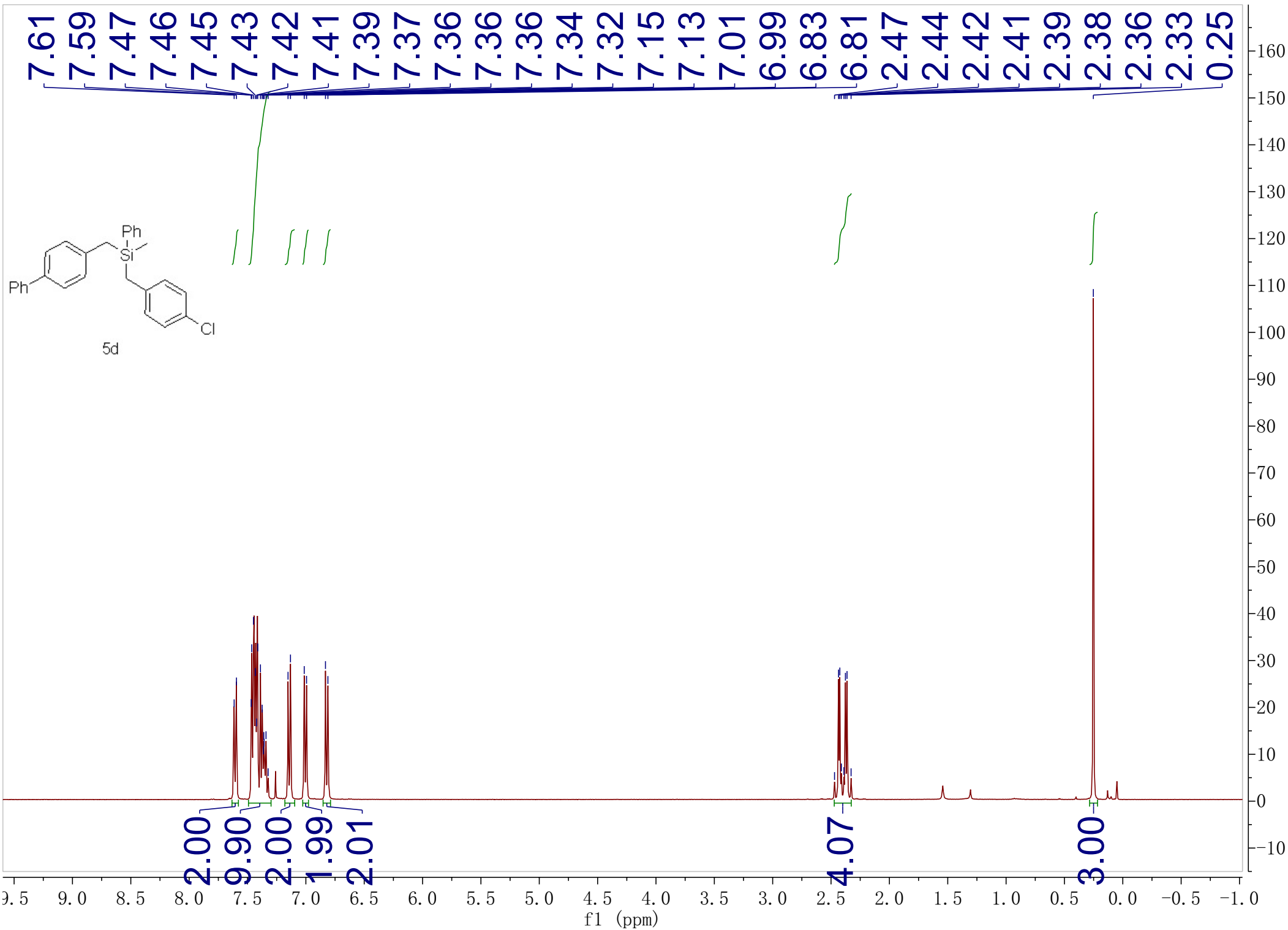


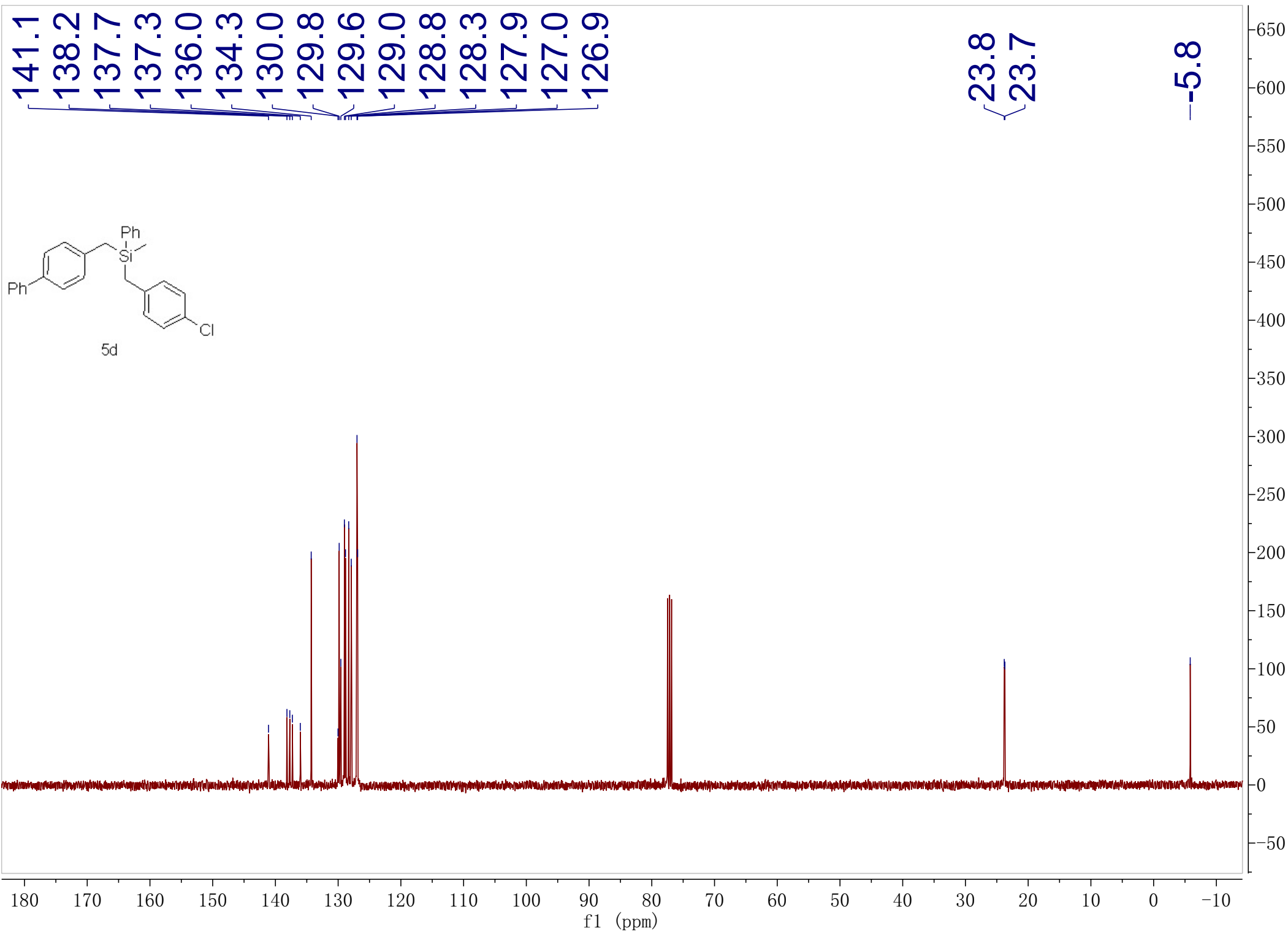
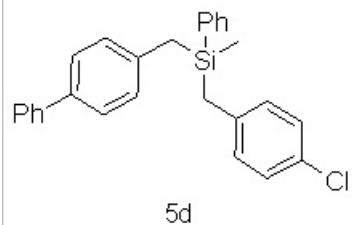


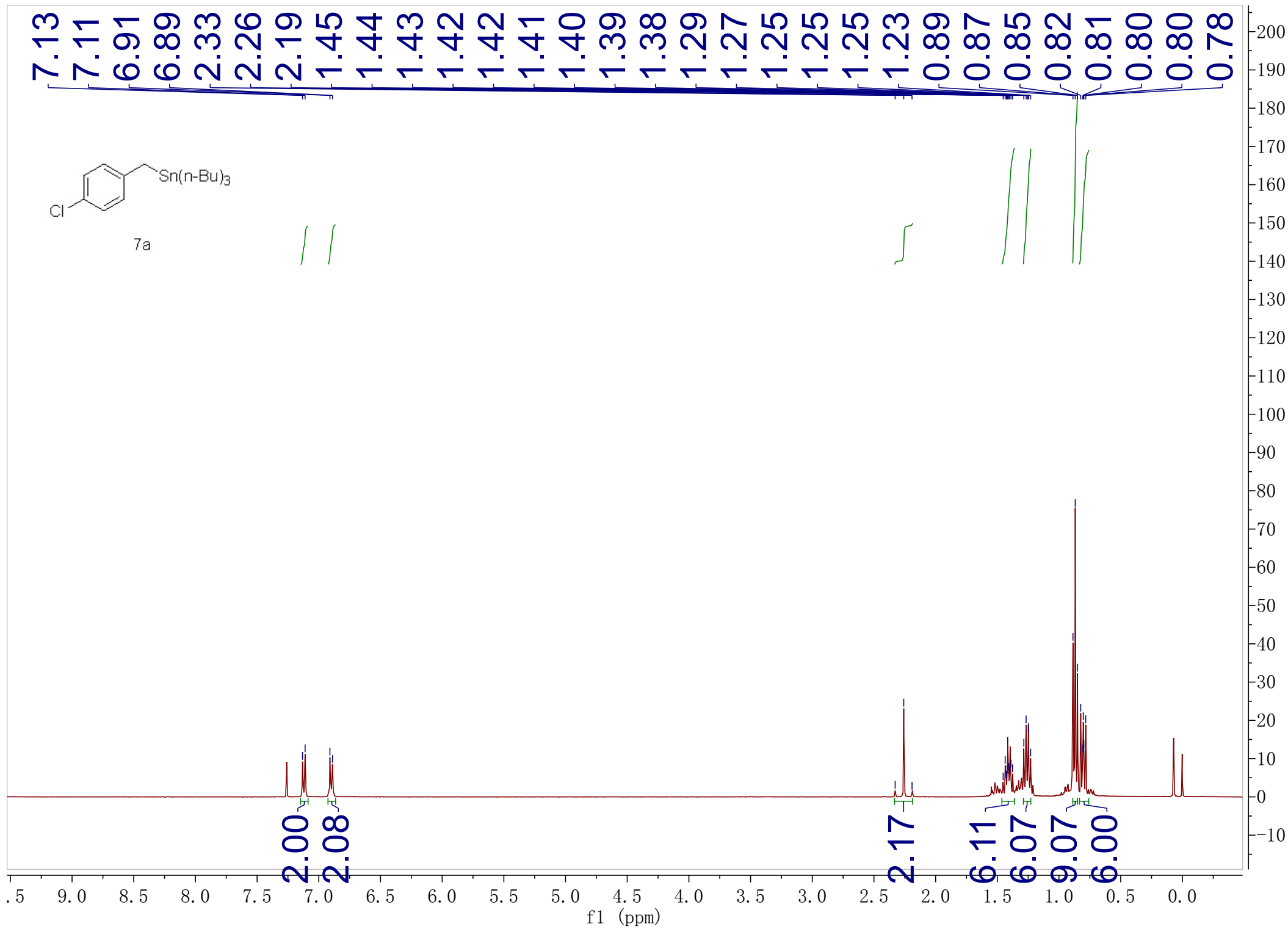


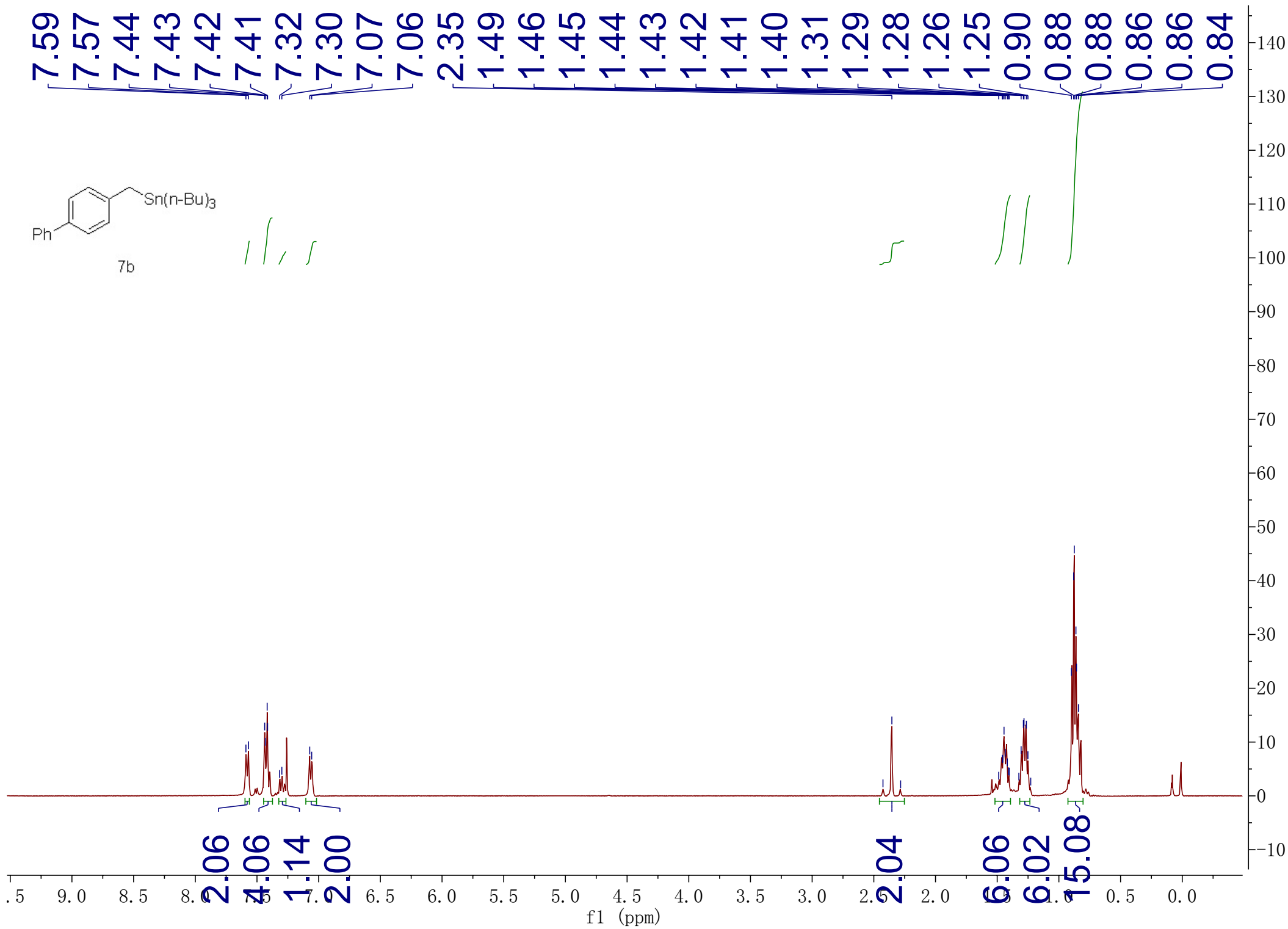


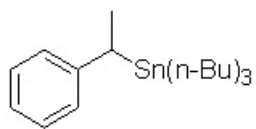




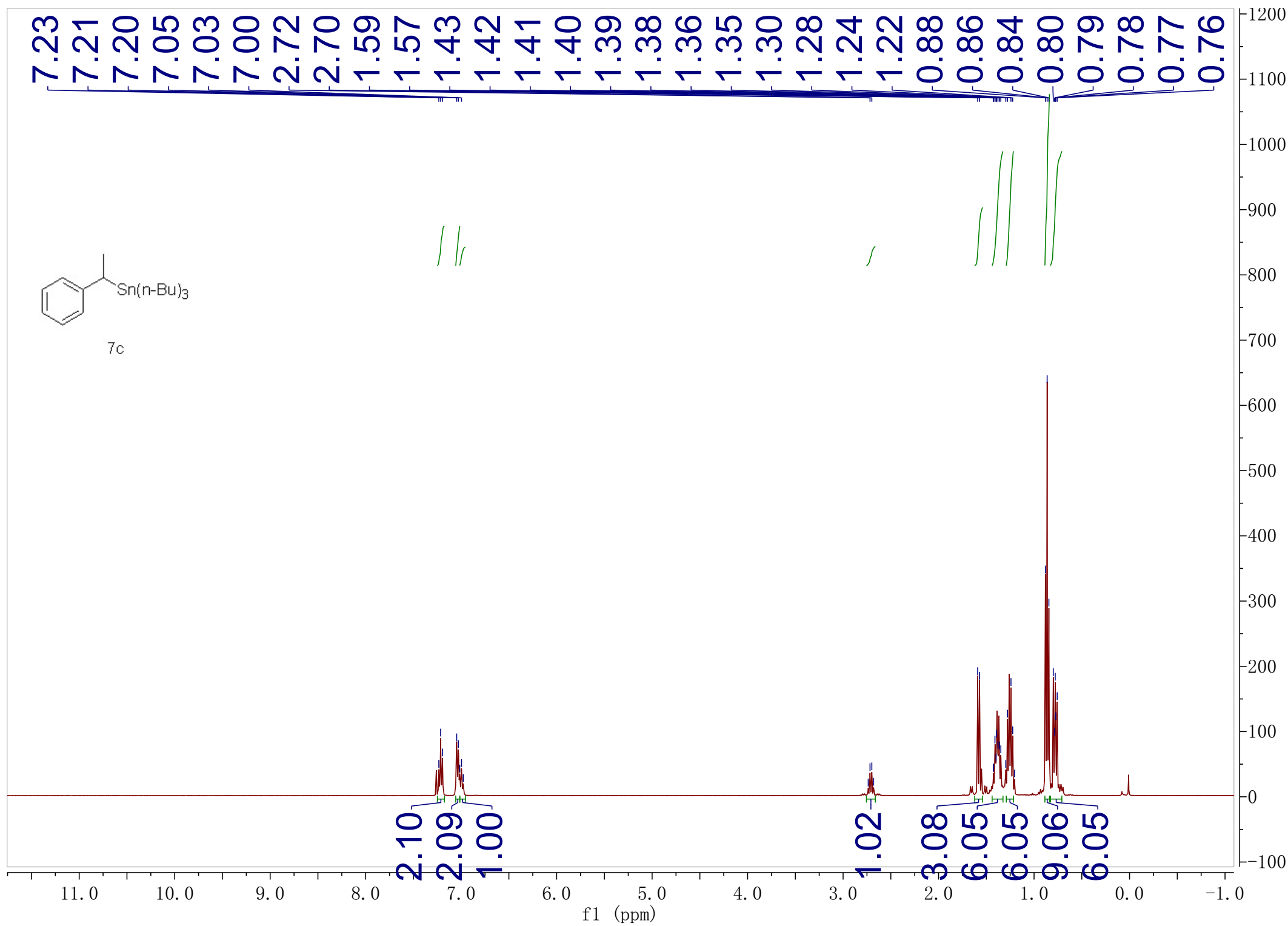


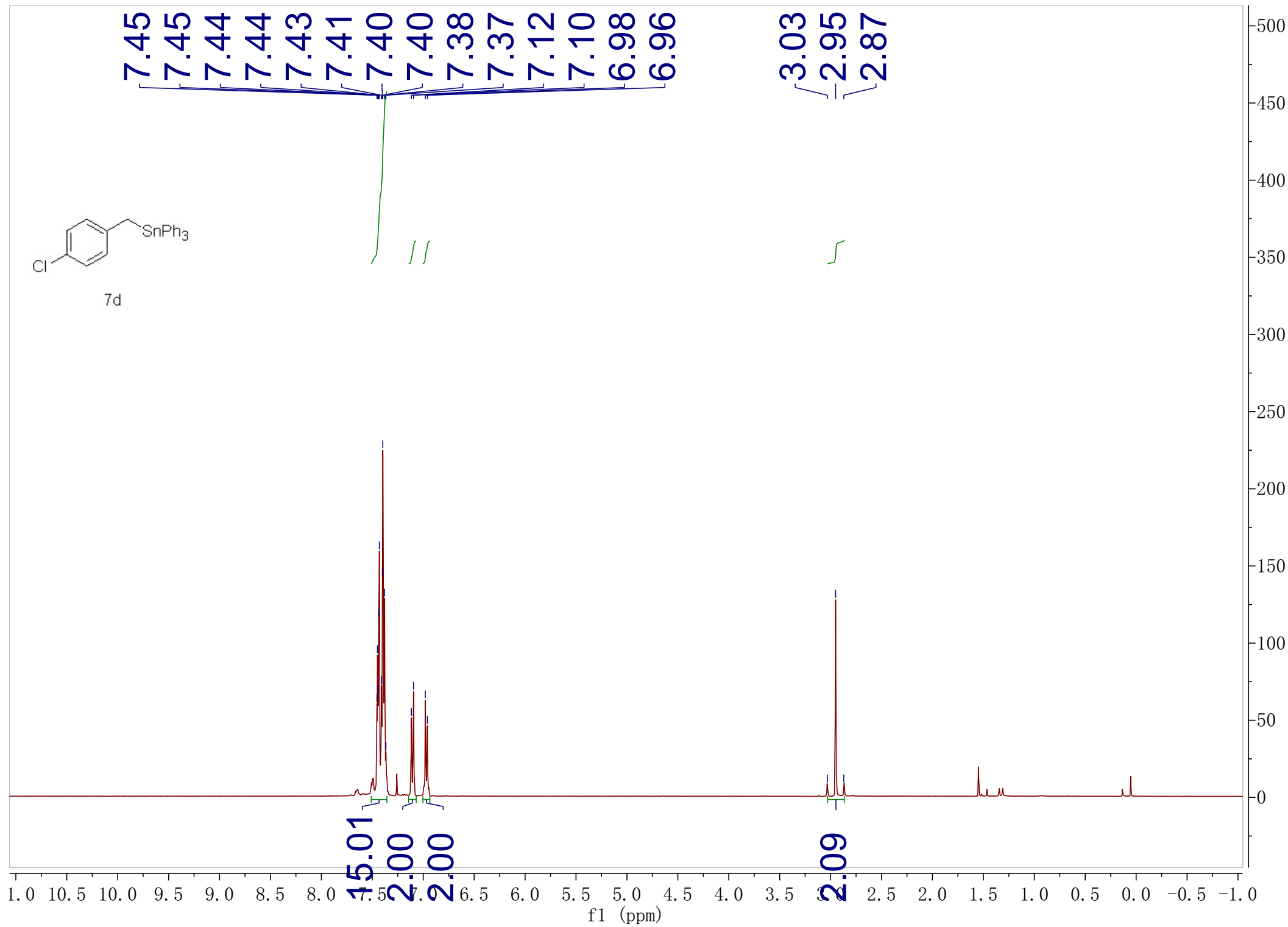


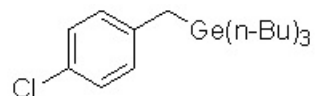




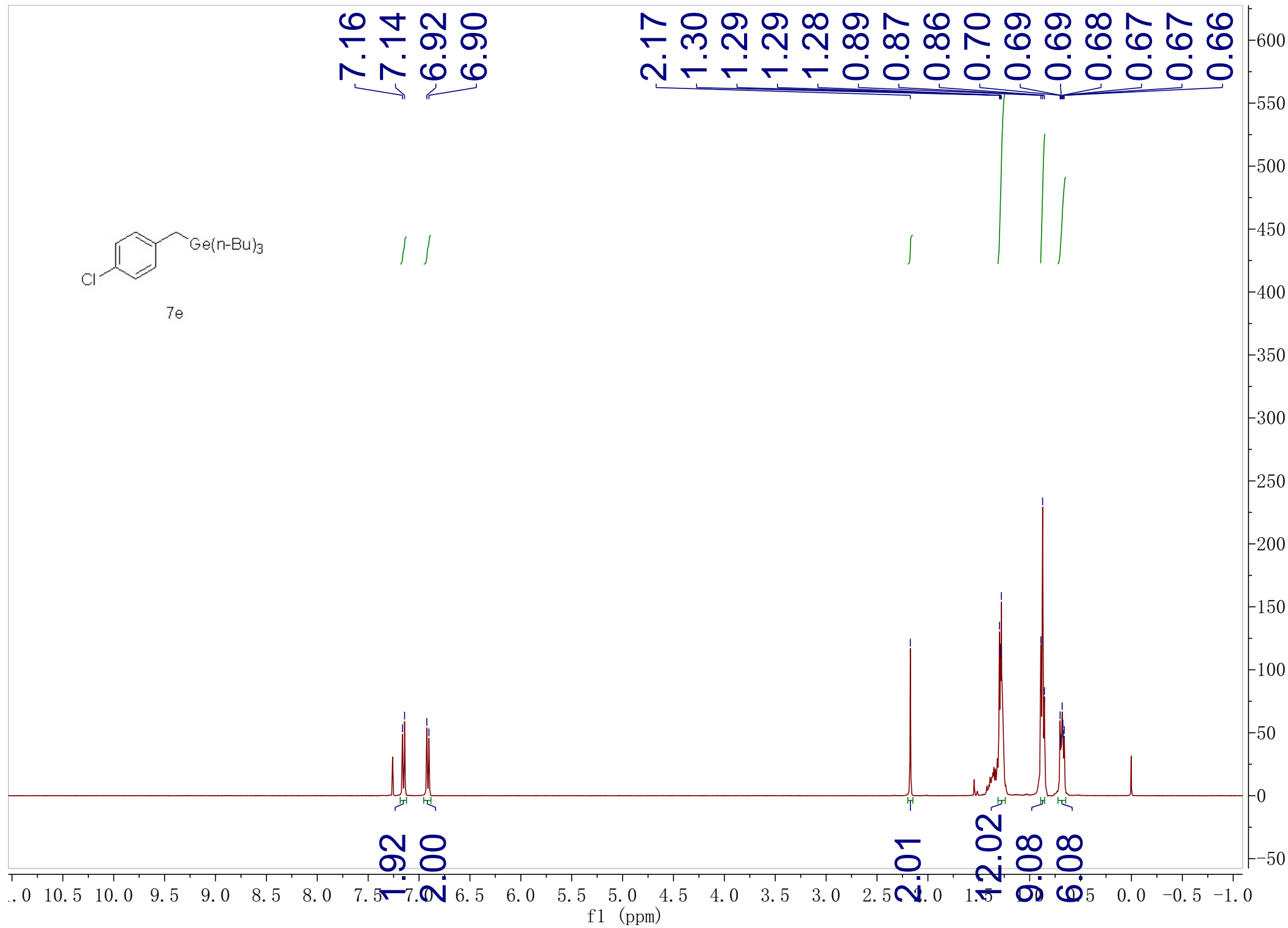
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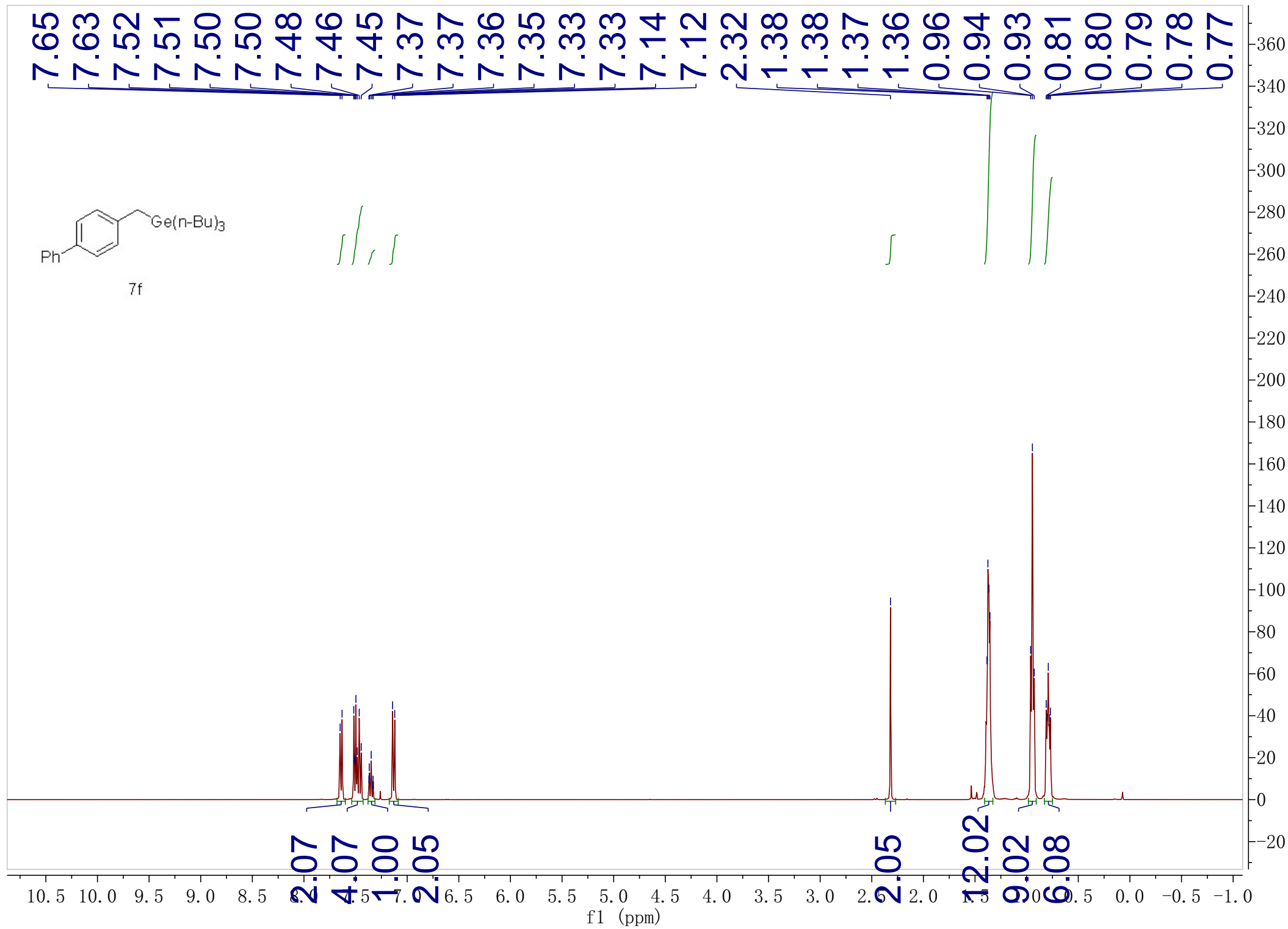


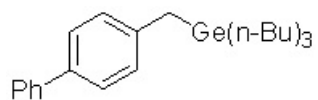




7e



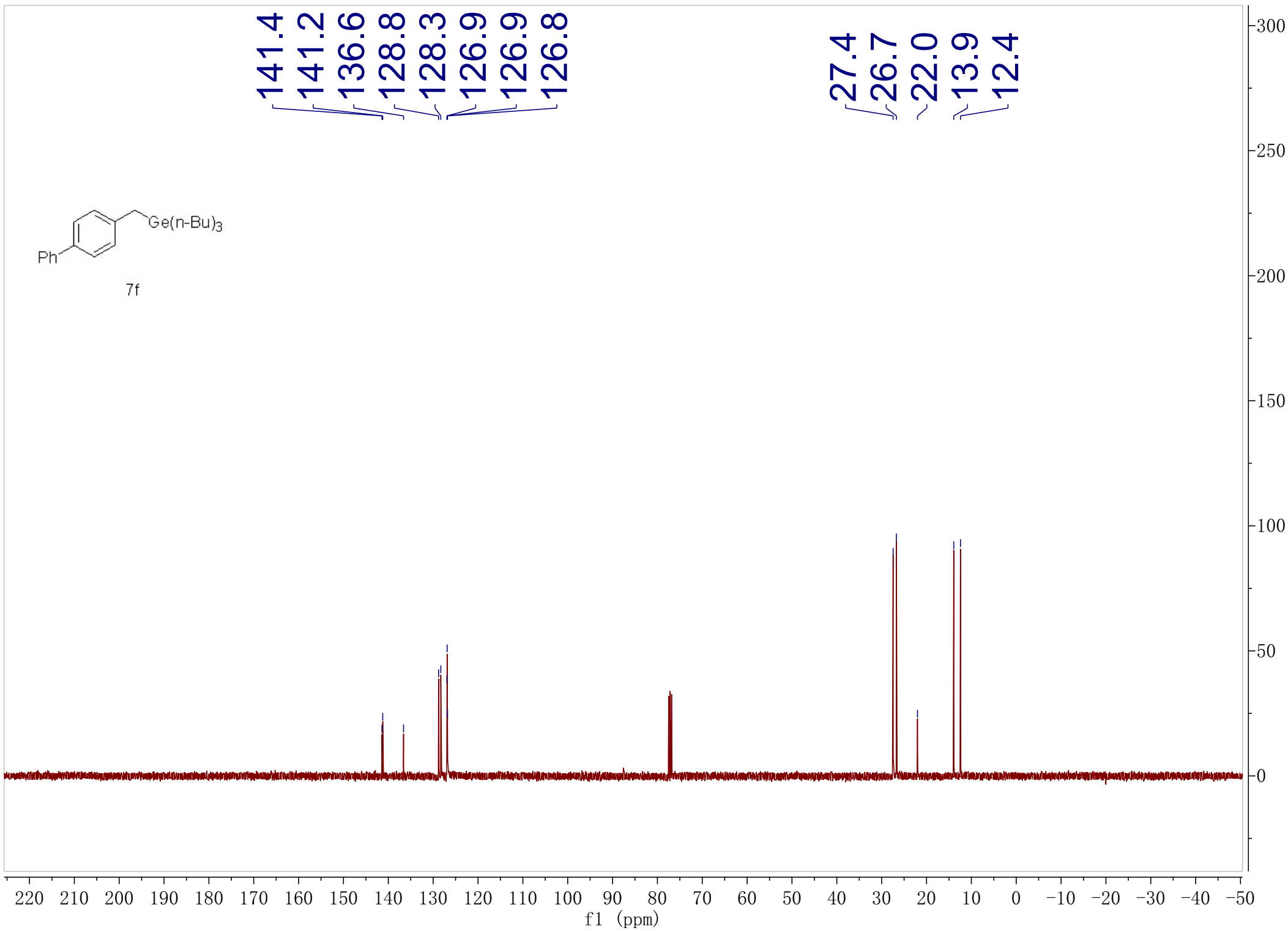


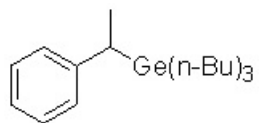


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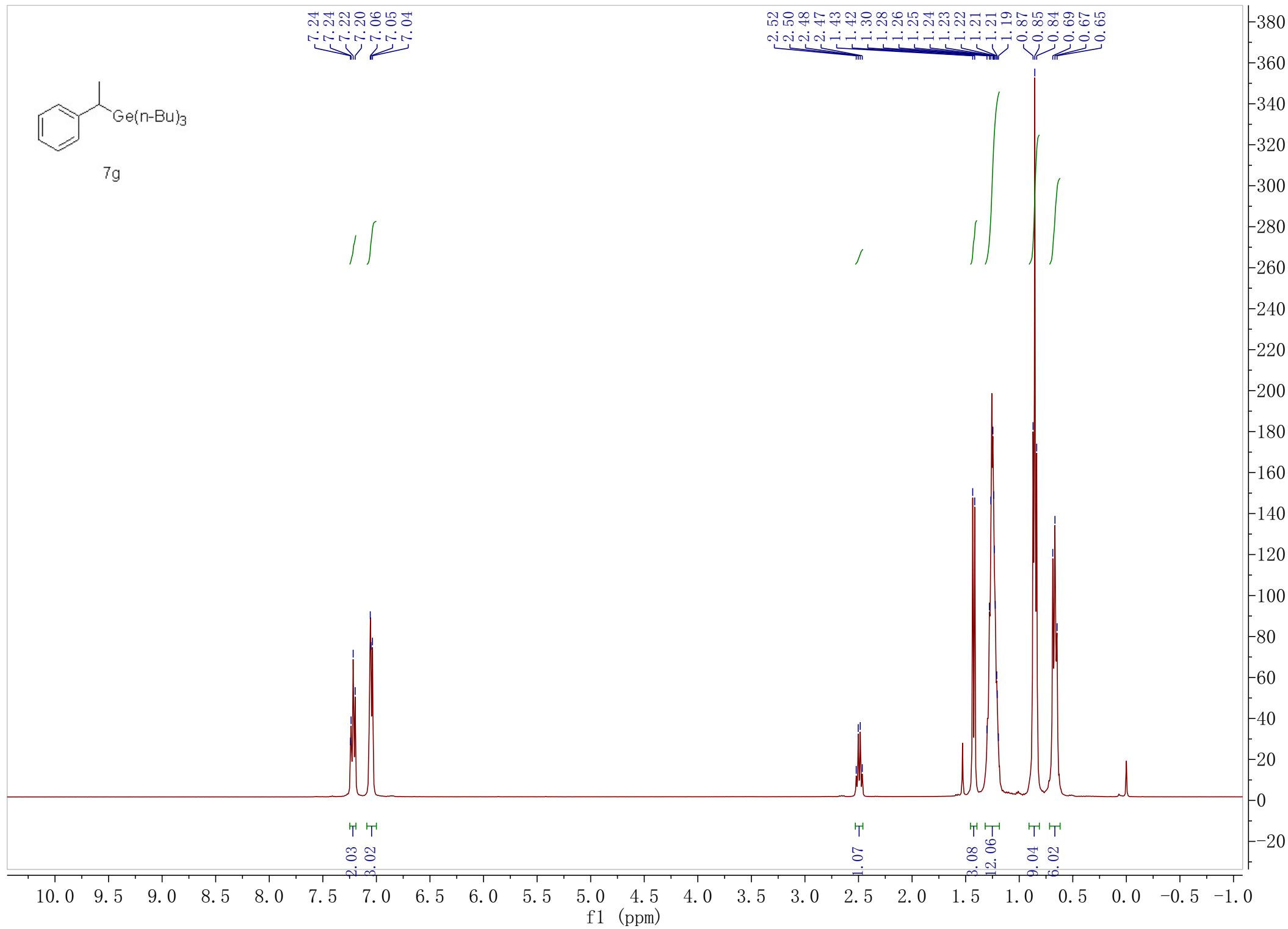
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141.2
136.6
128.8
128.3
126.9
126.9
126.8

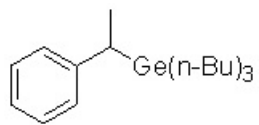
27.4
26.7
22.0
13.9
12.4





7g





7g

— 147.2

— 128.1

— 126.6

— 124.1

— 28.6

— 27.5

— 26.9

— 16.2

— 13.9

— 11.3

