

Electronic Supporting Information

Synthesis of Aryl Trimethylstannanes from Aryl Halides: An Efficient Photochemical method

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1. General reagent information

Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI and used as received or purified according to Purification of Common Laboratory Chemicals. Acetonitrile and methanol were purchased from Acros Organics and used directly without further purification. Distilled water was degassed with sonication under vacuum and then backfilled with argon for a total of at least three times. 1-iodo-4-(prop-2-yn-1-yloxy)benzene,^[1] 1-(allyloxy)-4-iodobenzene,^[2] 2-iodobenzofuran^[3] and 2-iodobenzo[b]thiophene^[4] were prepared according to the literature procedure.

2. General analytical information

NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^1H NMR spectra were recorded at 400 MHz in NMR solvents (CDCl_3) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance, ^{19}F NMR spectra were collected on at 376.5 MHz. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). The measurement of molecular mass was acquired with Thermo Trace 1300 GC-MS equipment using EI-MS mode.

3. General procedure for the synthesis of aryl trimethylstannanes



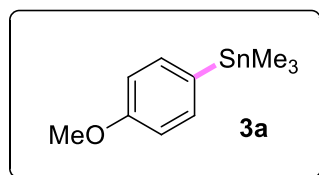
Figure S1. Photochemical reactor (The photochemistry instrument XPA-7 was purchased from Xujiang electromechanical plant, Nanjing, China)

A solution of the aryl halides (0.3 mmol), $(\text{SnMe}_3)_2$ (0.45 mmol), DIPEA (1.0 eq) and the additive reagents in MeCN (3.0 ml, $c = 0.1 \text{ M}$) was added into a quartz test tube containing a magnetic stirring bar and the mixture was purged with argon for 10 min. The tube was then capped with a

septum. The reaction mixture was irradiated using a 300 W high-pressure mercury lamp through a water-cooled quartz immersion well for 1 or 2 hours depending on the substrate. The reaction mixture was then concentrated and the stannylation product was purified by column chromatography on basic or neutral alumina (Note: some aryl stannanes are not stable on a silica gel column).

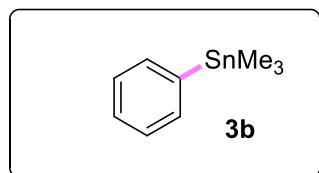
4. Spectra data of the photochemical stannylation products

Trimethyl(4-methoxyphenyl)stannane (**3a**)^[5]



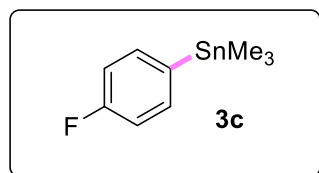
Flash chromatography (basic alumina, petroleum ether/EtOAc = 100/1) afforded **3a** (67.7 mg, 83%) as pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 0.29 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 136.8, 132.4, 113.9, 54.9, -9.5; IR (cm⁻¹): 2918, 2835, 1589, 1496, 1277, 1244, 1180, 1076, 1034, 769. EI-MS (*m/z*, relative intensity): 272 (*M*⁺, < 1), 257 (100), 255 (79), 253 (45), 227 (38), 225 (29), 223 (17), 135 (13), 121 (19). ¹¹⁹Sn NMR (149 MHz, CDCl₃) δ -26.13.

Trimethyl(phenyl)stannane (**3b**)^[5]



Flash chromatography (basic alumina, petroleum ether) afforded **3b** (45.7 mg, 63%); Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 5.6 Hz, 2H), 7.35 (m, 3H), 0.29 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 135.8, 128.2, 128.0, -9.6; IR (cm⁻¹): 2923, 2852, 1742, 1659, 1468, 1373, 1242, 1046, 938, 726. EI-MS (*m/z*, relative intensity): 242 (*M*⁺, < 1), 227 (100), 225 (71), 223 (46), 197 (49), 195 (40), 193 (27), 135 (24.5), 120 (52). ¹¹⁹Sn NMR (149 MHz, CDCl₃) δ -26.95.

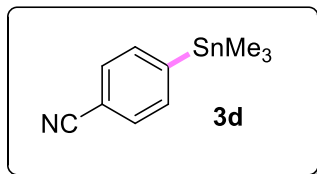
Trimethyl(4-fluorophenyl)stannane (**3c**)^[5]



Flash chromatography (basic alumina, petroleum ether) afforded **3c** (45.2 mg, 58%); Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.35 (dd, *J* = 9.6, 8.4 Hz, 2H), 0.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5 (d, *J* = 245 Hz), 137.3 (d, *J* = 6.0 Hz), 137.1 (d, *J* = 4.0 Hz), 115.2 (d, *J* = 19 Hz), -9.4; ¹⁹F NMR (376.5 MHz, CDCl₃) δ -113.2; IR (cm⁻¹): 2925,

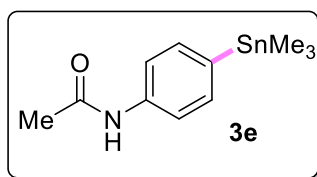
1743, 1580, 1490, 1373, 1242, 1163, 1049, 817, 767. EI-MS (m/z , relative intensity): 245 ($[M-15]^+$, 100), 243 (77), 241 (47), 215 (38), 213 (32), 211 (19), 139 (52), 135 (45). ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.11.

4-(Trimethylstannyl)benzonitrile (**3d**)^[5]



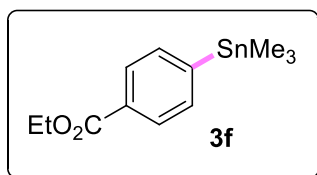
Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3d** (60.8 mg, 76% from 4-iodobenzonitrile; 57.6mg, 72% from 4-bromobenzonitrile; 44.8 mg, 56% from 4-chlorobenzonitrile); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.0, 2H), 7.58 (d, J = 8.4, 2H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 136.2, 130.7, 119.1, 111.7, -9.5; IR (cm^{-1}): 2921, 2227, 1740, 1380, 1244, 1066, 1046, 1018, 816, 773, 733. EI-MS (m/z , relative intensity): 267 (M^+ , 2), 252 (100), 250 (76), 248 (42), 222 (27), 220 (22), 135 (21), 120 (27). ^{119}Sn NMR (149 MHz, CDCl_3) δ -21.58.

N-(4-(trimethylstannyl)phenyl)acetamide (**3e**)



Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1 to 5/1) afforded **3e** (70.0 mg, 78%); Pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 8.8, 2H), 7.44 (d, J = 8.4, 2H), 7.15 (s, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 137.9, 136.4, 129.0, 119.5, 24.5, -9.5; IR (cm^{-1}): 3288, 2923, 1726, 1538, 1386, 1281, 1075, 1045, 943, 756. EI-MS (m/z , relative intensity): 299 (M^+ , 6), 284 (100), 282 (79), 280 (48), 254 (34), 252 (26), 250 (15), 135 (22), 120 (21). ^{119}Sn NMR (149 MHz, CDCl_3) δ -26.94. HRMS (ESI^+): Calculated for $\text{C}_{11}\text{H}_{11}\text{NOSnNa}$ ($M+\text{Na}$) $^+$: 322.0230, Found: 322.0225.

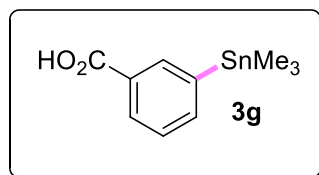
Ethyl 4-(trimethylstannyl)benzoate (**3f**)^[5]



Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3f** (75.3 mg, 80% from ethyl 4-iodobenzoate; 60.3 mg, 64% from ethyl 4-bromobenzoate); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.0, 2H), 7.58 (d, J = 8.0, 2H), 4.40 (m, 2H), 1.41 (t, J = 7.0, 3H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 149.4, 135.7, 130.1, 128.4, 60.8, 14.3, -9.6; IR (cm^{-1}): 2981, 2910, 1718, 1591, 1386, 1276, 1103, 1066, 771, 753. EI-MS (m/z , relative intensity): 299 ($[M-15]^+$, 100), 297 (76), 295 (47), 271 (32), 269 (42), 241 (15), 239 (12),

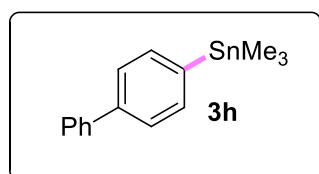
135 (26). ^{119}Sn NMR (149 MHz, CDCl_3) δ -25.07.

3-(Trimethylstannyl)benzoic acid (**3g**)^[6]



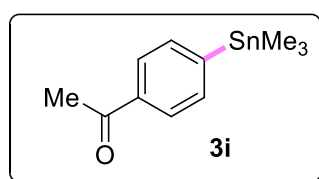
Flash chromatography (neutral alumina, $\text{MeOH}/\text{DCM} = 30/1$ to $10/1$) afforded **3g** (58.3 mg, 68%); white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (s, 1H), 8.06 (d, $J = 7.6$, 1H), 7.73 (d, $J = 6.8$, 1H), 7.45 (t, $J = 7.2$, 1H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 142.9, 141.1, 137.3, 130.0, 128.6, 127.9, -9.5; IR (cm^{-1}): 2922, 2853, 1682, 1585, 1430, 1261, 1134, 1106, 943, 768, 744. ^{119}Sn NMR (149 MHz, CDCl_3) δ -23.92.

[1,1'-Biphenyl]-4-yltrimethylstannane (**3h**)^[7]



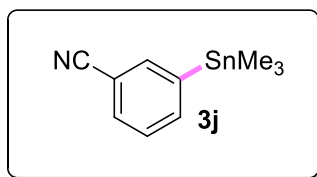
Flash chromatography (basic alumina, petroleum ether/ $\text{EtOAc} = 100/1$) afforded **3h** (81.1 mg, 85%); white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (m, 6H), 7.49 (t, $J = 7.6$, 2H), 7.40 (m, 1H), 0.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 141.1, 141.0, 136.2, 128.7, 127.2, 127.1, 126.7, -9.8; IR (cm^{-1}): 2982, 2915, 1741, 1653, 1457, 1380, 1280, 1243, 1007, 912, 757, 737. EI-MS (m/z , relative intensity): 318 (M^+ , 4), 303 (100), 201 (77), 299 (44), 273 (39), 271 (32), 269 (18), 152 (54). ^{119}Sn NMR (149 MHz, CDCl_3) δ -26.08.

1-(4-(Trimethylstannyl)phenyl)ethanone (**3i**)^[5]



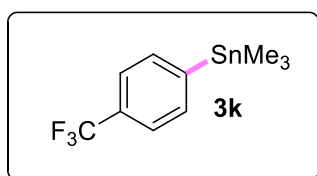
Flash chromatography (basic alumina, petroleum ether/ $\text{EtOAc} = 100/1 - 50/1$) afforded **3i** (56.2 mg, 66%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$, 2H), 7.62 (d, $J = 8.0$, 2H), 2.59 (s, 3H), 0.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 150.1, 136.7, 135.9, 128.7, 127.1, 26.5, -9.6; IR (cm^{-1}): 2982, 2913, 1740, 1685, 1587, 1386, 1207, 1188, 1057, 955, 773. EI-MS (m/z , relative intensity): 284 (M^+ , 3), 269 (100), 267 (79), 265 (46), 239 (38), 237 (29), 235 (17), 135 (22). ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.91.

3-(Trimethylstannyl)benzonitrile (**3j**)



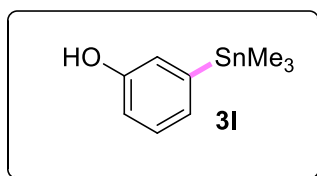
Flash chromatography (basic alumina, petroleum ether) afforded **3i** (62.4 mg, 78% from 3-iodobenzonitrile; 40.8mg, 51% from 3-bromobenzonitrile); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.71 (d, J = 7.6, 1H), 7.59 (m, 1H), 7.43 (t, J = 7.6, 1H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 150.1, 139.8, 139.1, 131.6, 128.2, 119.3, 112.1, -9.5; IR (cm^{-1}): 2983, 2920, 1733, 1683, 1540, 1389, 1257, 1244, 1102, 1075, 788, 737. EI-MS (m/z , relative intensity): 267 (M^+ , 1), 252 (100), 250 (77), 248 (48), 222 (28), 220 (23), 218 (13), 135 (20). ^{119}Sn NMR (149 MHz, CDCl_3) δ -20.66. Elemental analysis: Calculated for $\text{C}_{10}\text{H}_{13}\text{NSn}$: C: 45.17%; H: 4.93%; N:5.27, Found: C: 45.37%; H: 4.62%; N:4.96.

Trimethyl(4-(trifluoromethyl)phenyl)stannane (**3k**)^[5]



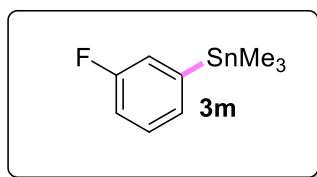
Flash chromatography (basic alumina, petroleum ether) afforded **3k** (57.7.1 mg, 62%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 7.6, 2H), 7.57 (d, J = 6.0, 2H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 136.0, 130.8 (q, J = 32 Hz), 125.6 (q, J = 270 Hz), 124.3 (q, J = 4.0 Hz), -9.6; ^{19}F NMR (376.5 MHz, CDCl_3) δ -62.8; IR (cm^{-1}): 2980, 1742, 1521, 1403, 1373, 1273, 1143, 1119, 1018, 962, 857, 764. EI-MS (m/z , relative intensity): 295 ($[\text{M}-15]^+$, 100), 293 (73), 291 (45), 265 (32), 263 (22), 260 (14), 126 (37), 107 (96). ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.91.

3-(Trimethylstannyl)phenol (**3l**)



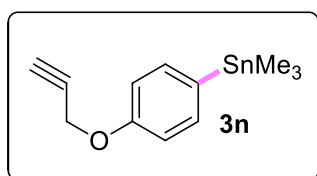
Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1) afforded **3l** (56.5 mg, 73%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.24 (t, J = 7.2, 1H), 7.05 (d, J = 6.8, 1H), 7.69 (d, J = 2.8, 1H), 6.79 (m, 1H), 4.88 (s, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 141.1, 129.2, 128.1, 122.3, 115.2, -9.6; IR (cm^{-1}): 3378, 2983, 2912, 1741, 1653, 1575, 1474, 1243, 1046, 995, 778. EI-MS (m/z , relative intensity): 258 (M^+ , 5), 243 (100), 241 (77), 239 (46), 213 (30), 211 (24), 209 (9), 135 (33), 133 (23). ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.85. Elemental analysis: Calculated for $\text{C}_9\text{H}_{14}\text{OSn}$: C: 42.07%; H: 5.49%, Found: C: 41.95%; H: 5.23%.

Trimethyl(3-fluorophenyl)stannane (**3m**)



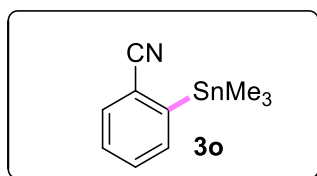
Flash chromatography (basic alumina, petroleum ether) afforded **3m** (48.3 mg, 62%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (m, 1H), 7.22 (m, 1H), 7.17 (m, 1H), 6.98 (m, 1H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.8 (d, $J = 249$ Hz), 145.1 (d, $J = 3.0$ Hz), 131.2 (d, $J = 3.0$ Hz), 129.4 (d, $J = 6$ Hz), 122.1 (d, $J = 17$ Hz), 115.1 (d, $J = 21$ Hz), -9.5; ^{19}F NMR (376.5 MHz, CDCl_3) δ -113.6; IR (cm^{-1}): 2985, 2921, 1742, 1653, 1591, 1471, 1373, 1256, 1208, 999, 781. EI-MS (m/z , relative intensity): 245 ($[\text{M}-15]^+$, 100), 243 (78), 241 (47), 215 (34), 213 (25), 211 (15), 139 (28), 133 (12). ^{119}Sn NMR (149 MHz, CDCl_3) δ -22.77. Elemental analysis: Calculated for $\text{C}_9\text{H}_9\text{FSn}$: C: 41.75%; H: 5.06%, Found: C: 41.63%; H: 5.18%.

Trimethyl(4-(prop-2-yn-1-yloxy)phenyl)stannane (**3n**)



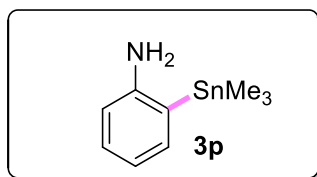
Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3n** (62.2 mg, 70%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.4$, 1H), 7.02 (d, $J = 8.4$, 1H), 4.70 (s, 2H), 2.53 (s, 1H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 136.8, 133.6, 131.6, 114.8, 78.6, 75.4, -9.5; IR (cm^{-1}): 3297, 2979, 2913, 1584, 1494, 1339, 1281, 1221, 1076, 1028 924, 770. EI-MS (m/z , relative intensity): 296 (M^+ , 2), 281 (37), 279 (28), 277 (15), 131 (30), 103 (100), 91 (14), 77 (6). ^{119}Sn NMR (149 MHz, CDCl_3) δ -26.09. Elemental analysis: Calculated for $\text{C}_{12}\text{H}_{16}\text{OSn}$: C: 48.86%; H: 5.47%, Found: C: 48.42%; H: 5.58%.

2-(Trimethylstannyl)benzonitrile (**3o**)^[5]



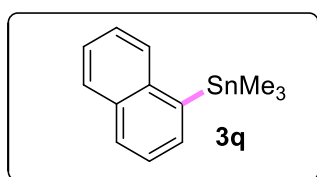
Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3o** (36.8 mg, 46%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$, 1H), 7.58 (d, $J = 7.2$, 1H), 7.52 (t, $J = 7.2$, 1H), 7.40 (t, $J = 7.6$, 1H), 0.44 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 136.3, 132.7, 131.5, 128.5, 120.3, 119.9, -9.0; IR (cm^{-1}): 2985, 2919, 1740, 1578, 1458, 1275, 1254, 1111, 1050, 764. EI-MS (m/z , relative intensity): 252 ($[\text{M}-15]^+$, 100), 250 (79), 248 (47), 222 (45), 220 (32), 218 (20), 135 (12), 120 (20). ^{119}Sn NMR (149 MHz, CDCl_3) δ -17.45.

2-(Trimethylstannyl)aniline (**3p**)^[8]



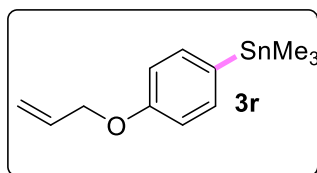
Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1- 5/1) afforded **3p** (36.2 mg, 47%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, J = 7.6, 1H), 7.16 (t, J = 7.6, 1H), 6.81 (t, J = 7.2, 1H), 6.68 (d, J = 8.0, 1H), 3.63 (s, 2H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 136.7, 129.8, 125.8, 118.9, 114.9, -9.2; IR (cm^{-1}): 3369, 2981, 2922, 1718, 1617, 1473, 1280, 1245, 1066, 1046, 753. EI-MS (m/z , relative intensity): 257 (M^+ , 10), 242 (100), 240 (77), 238 (43), 212 (74), 210 (62), 120 (19), 102 (24). ^{119}Sn NMR (149 MHz, CDCl_3) δ -33.58.

Trimethyl(naphthalen-1-yl)stannane (**3q**)^[9]



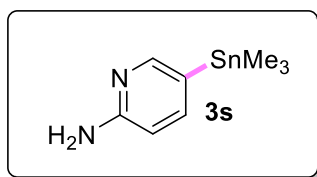
Flash chromatography (basic alumina, petroleum ether/EtOAc = 100/1) afforded **3q** (52.5 mg, 60%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (m, 3H), 7.58 (d, J = 6.4, 1H), 7.50 (m, 3H), 0.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 138.5, 134.5, 133.6, 129.8, 129.0, 128.7, 125.8, 125.4, 125.3, -8.4; IR (cm^{-1}): 3048, 2982, 2917, 1741, 1558, 1373, 1244, 1046, 791, 774. EI-MS (m/z , relative intensity): 292 (M^+ , 10), 277 (100), 275 (74), 273 (44), 247 (56), 245 (42), 243 (25), 141 (34). ^{119}Sn NMR (149 MHz, CDCl_3) δ -29.27.

(4-(Allyloxy)phenyl)trimethylstannane (**3r**)



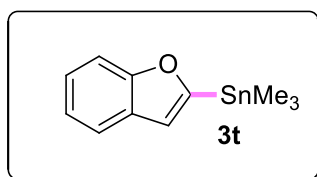
Flash chromatography (basic alumina, petroleum ether/EtOAc = 100/1) afforded **3r** (57.2 mg, 64%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 8.4, 2H), 6.95 (d, J = 8.4, 2H), 6.11 (m, 1H), 5.45 (dd, J = 1.6, 1.6, 1H), 5.31 (dd, J = 1.2, 1.6, 1H), 4.56 (d, J = 5.2, 2H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 136.8, 133.3, 132.6, 117.6, 114.7, 68.5, -9.5; IR (cm^{-1}): 3013, 2982, 2914, 1741, 1586, 1495, 1274, 1181, 1075, 768. EI-MS (m/z , relative intensity): 298 (M^+ , 3), 283 (42), 281 (34), 279 (19), 253 (8), 105 (100), 91 (17), 79 (8). ^{119}Sn NMR (149 MHz, CDCl_3) δ -26.97. Elemental analysis: Calculated for $\text{C}_{12}\text{H}_{18}\text{OSn}$: C: 48.53%; H: 6.11%, Found: C: 48.36%; H: 6.19%.

5-(Trimethylstannyl)pyridin-2-amine (**3s**)



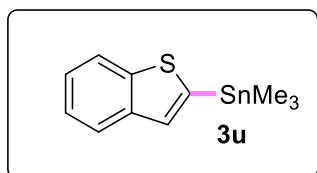
Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1 to 5/1) afforded **3s** (44.9 mg, 58%); white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.51 (m, 1H), 6.54 (d, J = 8.0, 1H), 4.78 (s, 2H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 153.1, 145.1, 123.8, 109.3, -9.6; IR (cm^{-1}): 3324, 2980, 2920, 1581, 1487, 1366, 1147, 1090, 822, 767. ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.95. HRMS (ESI^+): Calculated for $\text{C}_8\text{H}_{15}\text{N}_2\text{Sn}$ ($\text{M}+\text{H}$) $^+$: 259.0257, Found: 259.0248.

Benzofuran-2-yltrimethylstannane (**3t**)^[10]



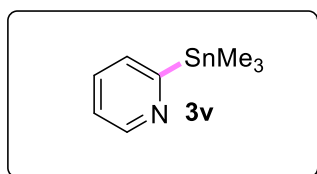
Flash chromatography (basic alumina, petroleum ether/EtOAc = 100/1) afforded **3r** (69.4 mg, 82%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 7.2, 1H), 7.50 (d, J = 8.0, 1H), 7.24 (m, 2H), 6.92 (s, 1H), 0.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 158.5, 127.9, 123.6, 122.1, 120.3, 117.5, 110.9, -9.3; IR (cm^{-1}): 3061, 2985, 2919, 1741, 1576, 1489, 1373, 1248, 1154, 1031, 928, 752. EI-MS (m/z , relative intensity): 282 (M^+ , 19), 267 (100), 265 (73), 263 (45), 237 (54), 235 (40), 131 (35), 89 (31). ^{119}Sn NMR (149 MHz, CDCl_3) δ -46.49.

Benzo[b]thiophen-2-yltrimethylstannane (**3u**)^[10]



Flash chromatography (basic alumina, petroleum ether/EtOAc = 100/1) afforded **3u** (61.7 mg, 69%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.6, 1H), 7.83 (d, J = 7.6, 1H), 7.43 (s, 1H), 7.35 (m, 2H), 0.44 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 140.9, 140.3, 131.9, 123.8, 123.5, 122.8, 121.9, -8.4; IR (cm^{-1}): 3055, 2985, 2920, 1792, 1558, 1436, 1288, 1244, 1047, 921, 744. EI-MS (m/z , relative intensity): 298 (M^+ , 21), 283 (100), 281 (76), 279 (46), 253 (60), 251 (22), 249 (28), 101 (75). ^{119}Sn NMR (149 MHz, CDCl_3) δ -24.17.

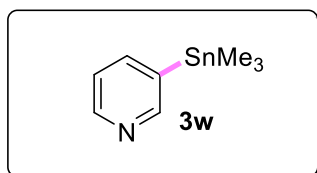
2-(Trimethylstannyl)pyridine (**3v**)^[10]



Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1 to 5/1) afforded **3v** (52.5

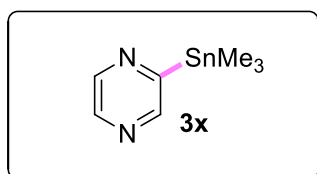
mg, 72%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.74 (d, $J = 4.8$, 1H), 7.53 (m, 1H), 7.45 (d, $J = 7.2$, 1H), 7.15 (m, 1H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 150.5, 133.5, 131.6, 122.3, -9.5; IR (cm^{-1}): 3356, 2923, 2852, 1743, 1507, 1458, 1373, 1273, 1242, 1049, 759. ^{119}Sn NMR (149 MHz, CDCl_3) δ -48.89.

3-(Trimethylstannyl)pyridine (**3w**)^[10]



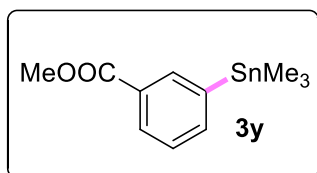
Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1 to 5/1) afforded **3w** (62.7 mg, 86% from 3-iodopyridine; 42% ^1H NMR yield from 3-bromopyridine); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.64 (s, 1H), 8.55 (d, $J = 3.6$, 1H), 7.79 (d, $J = 7.6$, 1H), 7.27 (m, 1H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 149.2, 143.8, 137.4, 123.9, -9.6; IR (cm^{-1}): 2982, 2923, 2853, 1740, 1588, 1466, 1243, 1050, 1029, 774. EI-MS (m/z , relative intensity): 243 (M^+ , 8), 228 (100), 226 (74), 224 (45), 198 (36), 196 (11), 194 (18), 135 (23). ^{119}Sn NMR (149 MHz, CDCl_3) δ -23.01.

2-(Trimethylstannyl)pyrazine (**3x**)^[11]



Flash chromatography (neutral alumina, petroleum ether/EtOAc = 10/1) afforded **3x** (59.3 mg, 81%); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.71 (t, $J = 2.0$, 1H), 8.59 (d, $J = 1.6$, 1H), 8.39 (d, $J = 2.4$, 1H), 0.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 150.6, 146.6, 143.3, 123.9, -9.5; IR (cm^{-1}): 3048, 2982, 2854, 1742, 1558, 1448, 1381, 1243, 1125, 1039, 776. EI-MS (m/z , relative intensity): 229 ($[\text{M}-15]^+$, 84), 227 (66), 225 (40), 199 (41), 197 (28), 165 (31), 135 (100), 120 (26). ^{119}Sn NMR (149 MHz, CDCl_3) δ -42.32.

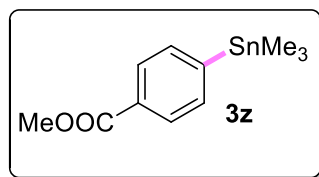
Methyl 3-(trimethylstannyl)benzoate (**3y**)^[12]



Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3y** (68.4 mg, 76% from methyl 3-bromobenzoate); Pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.98 (d, $J = 8.0$, 1H), 7.68 (d, $J = 6.8$, 1H), 7.42 (m, 1H), 3.92 (s, 1H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 142.7, 140.3, 136.6, 129.4, 129.3, 127.8, 52.0, -9.5; IR (cm^{-1}): 2985, 2951, 1724, 1584, 1436, 1277, 1216, 1047, 974, 772. EI-MS (m/z , relative intensity): 285 ($[\text{M}-15]^+$, 100), 283 (74), 281 (45), 255 (26), 253 (19), 251 (12), 195 (14), 135 (18). ^{119}Sn NMR (149 MHz, CDCl_3)

δ -24.02.

Methyl 4-(trimethylstannyl)benzoate (3z**)**^[12]

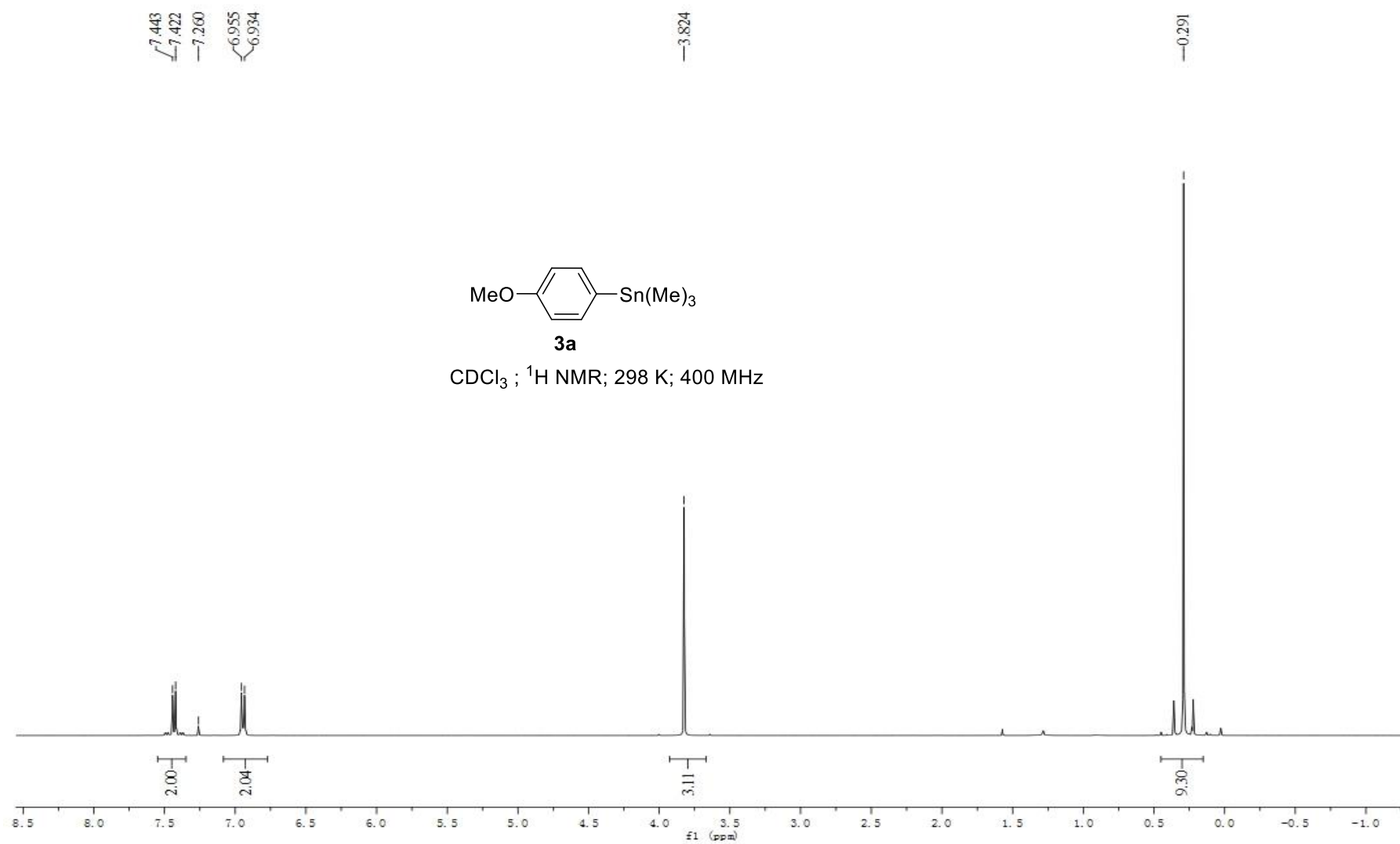


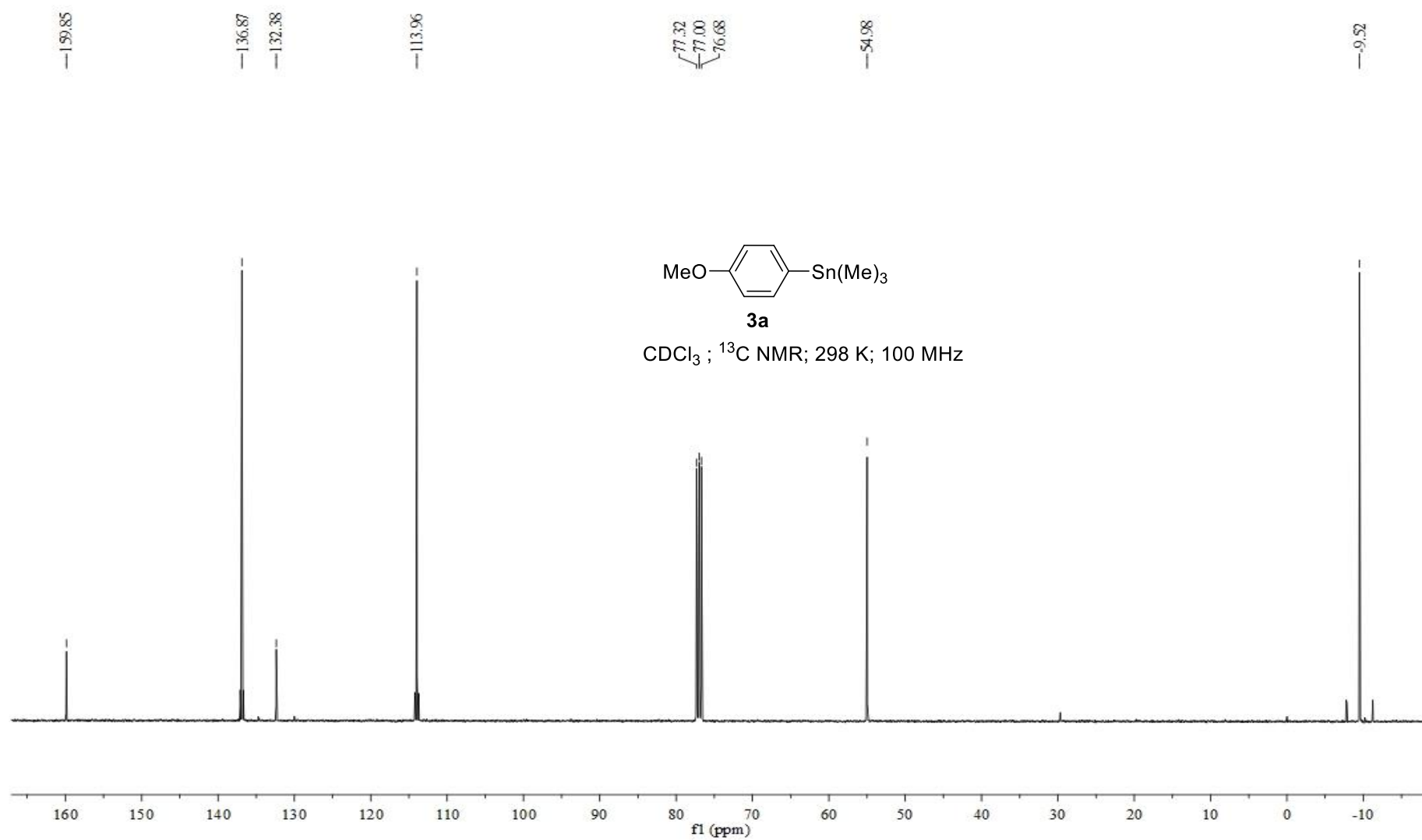
Flash chromatography (basic alumina, petroleum ether/EtOAc = 50/1) afforded **3z** (58.5 mg, 65% from methyl 4-bromobenzoate); Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.2, 1H), 7.58 (d, J = 6.8, 1H), 3.91 (s, 1H), 0.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 149.6, 135.7, 129.7, 128.5, 52.0, -9.5; IR (cm⁻¹): 2985, 2851, 1725, 1591, 1435, 1386, 1279, 1185, 1066, 1047, 772. EI-MS (m/z , relative intensity): 285 ([M-15]⁺, 100), 283 (78), 281 (46), 255 (33), 253 (26), 251 (15), 195 (11), 119 (23). ¹¹⁹Sn NMR (149 MHz, CDCl₃) δ -24.91.

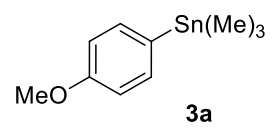
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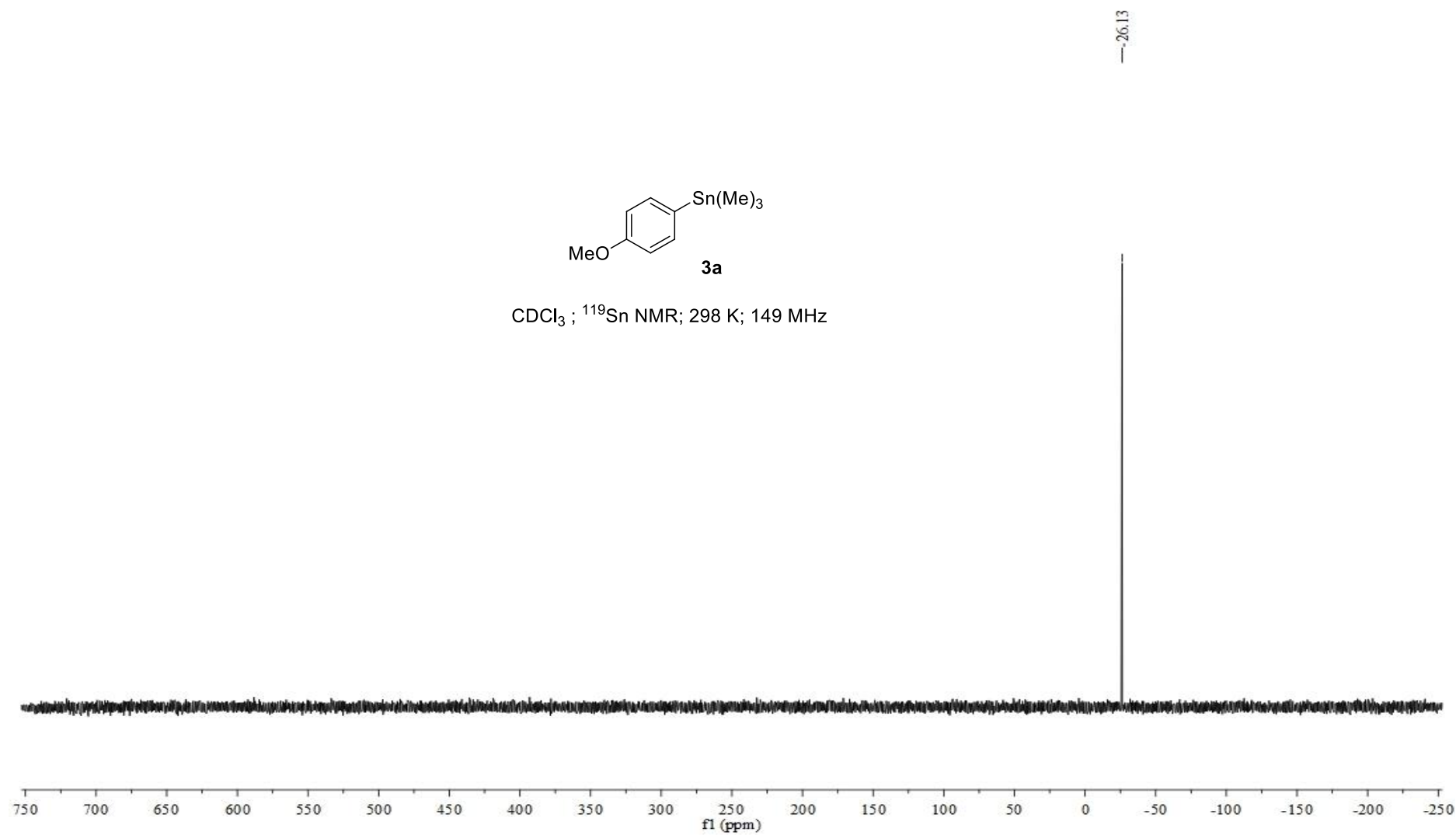
6. Copies of NMR Spectra

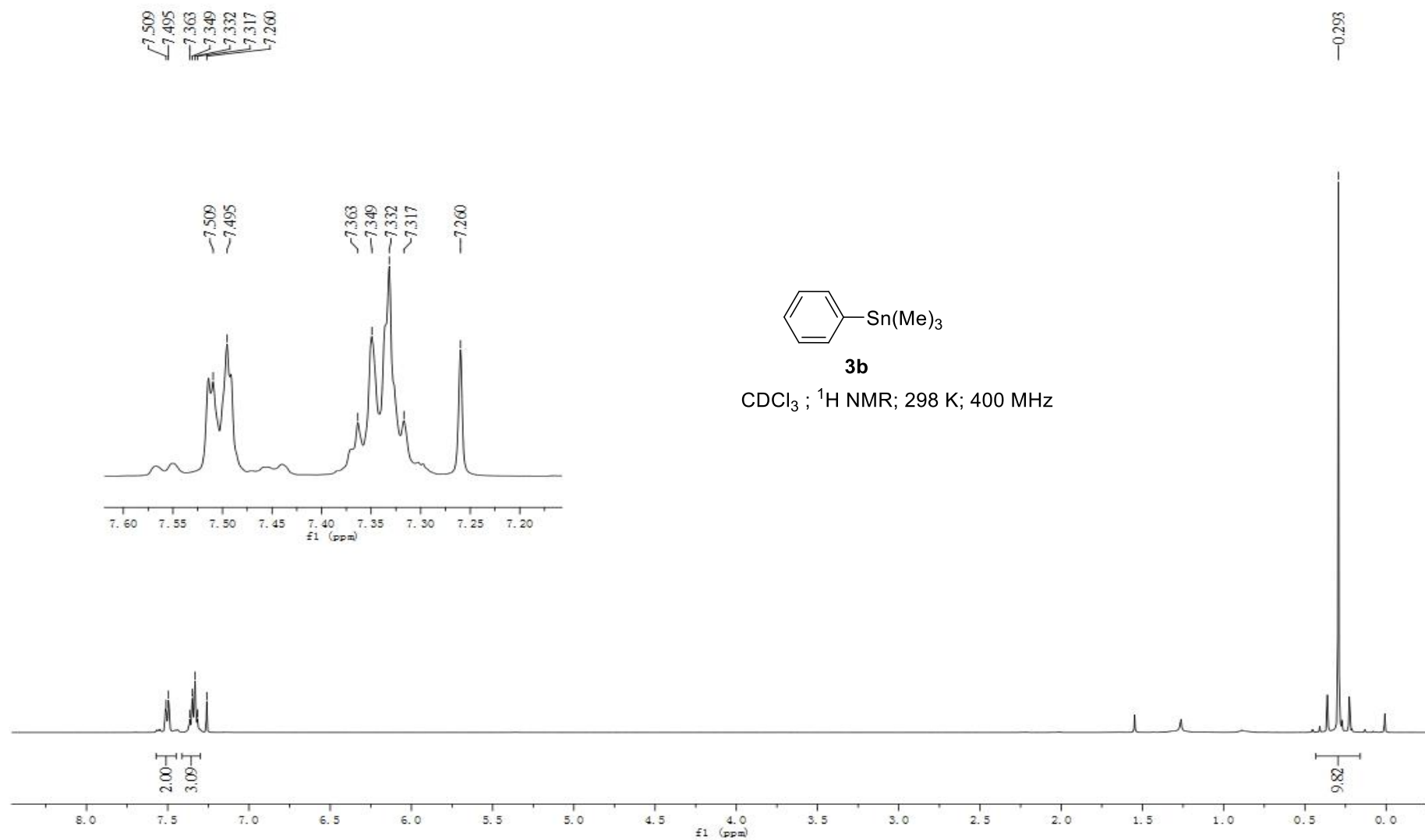


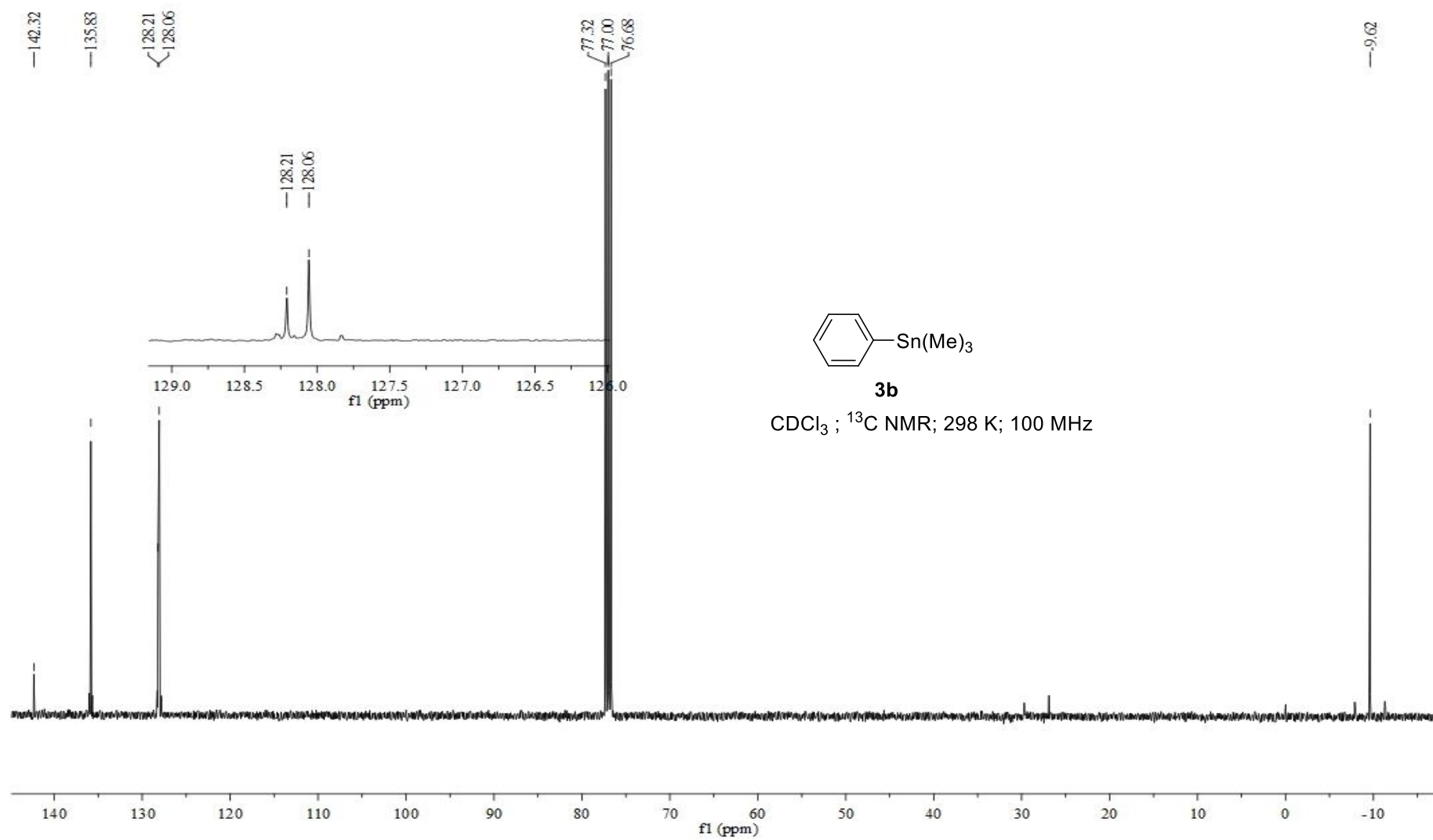


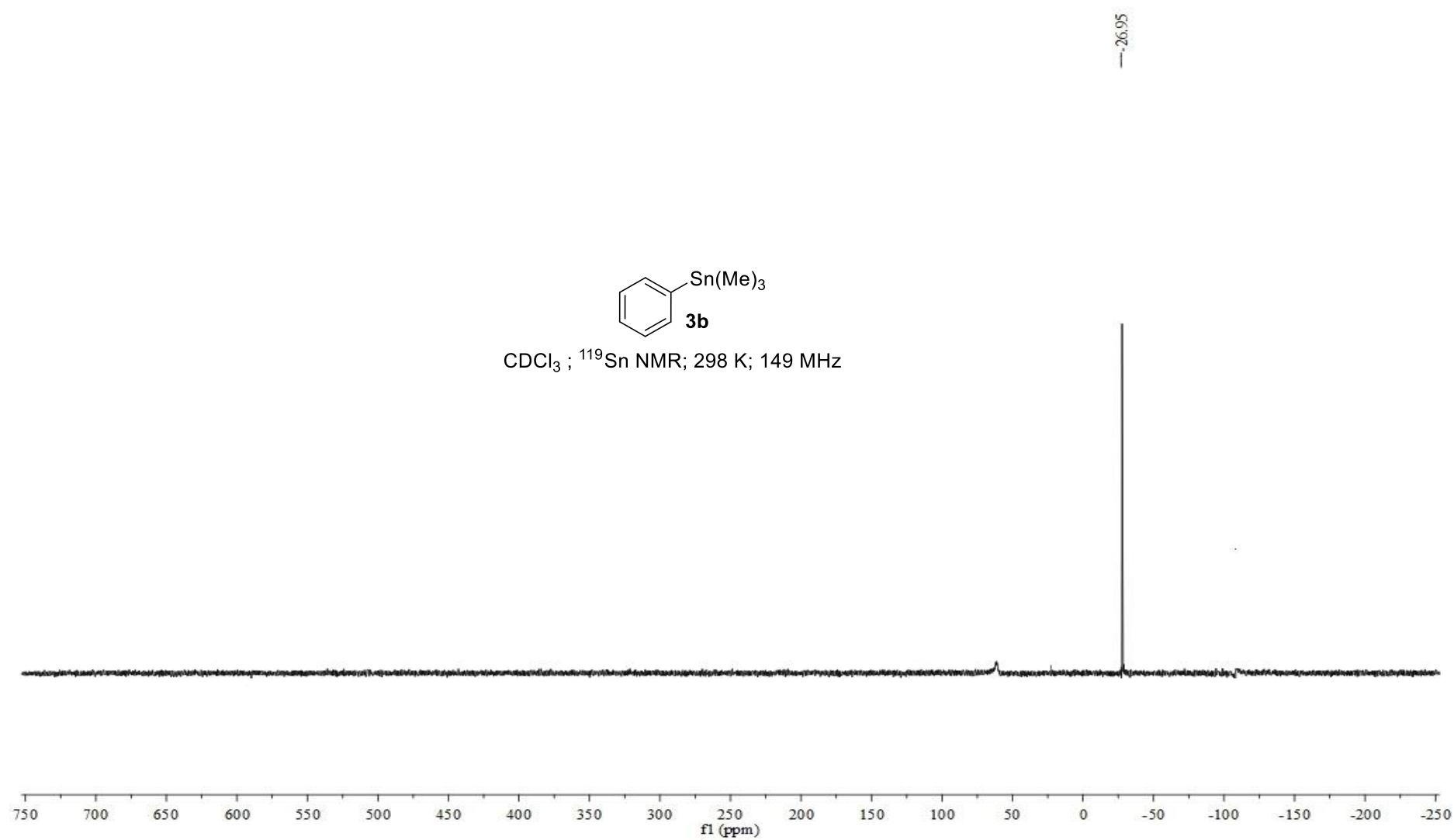


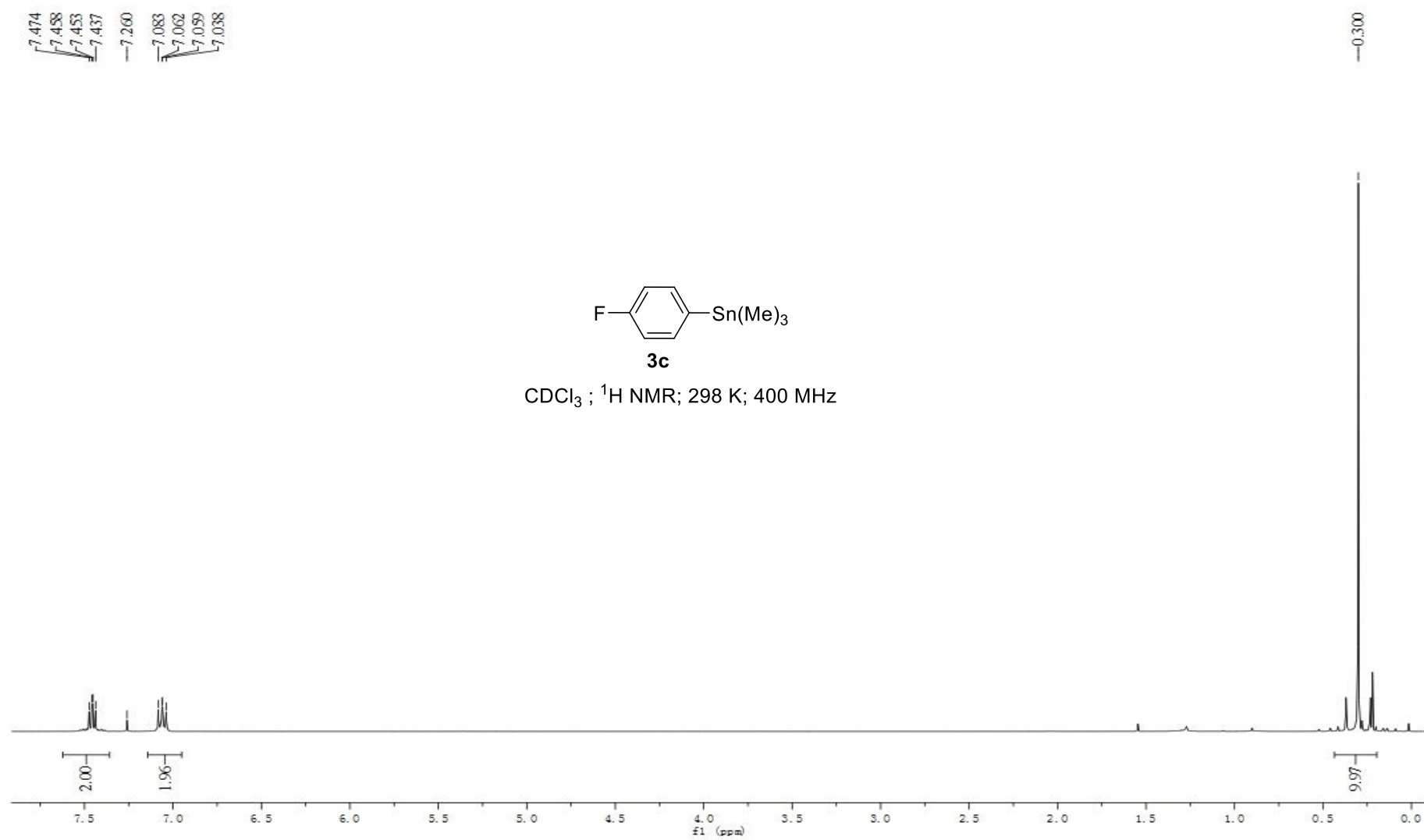
CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

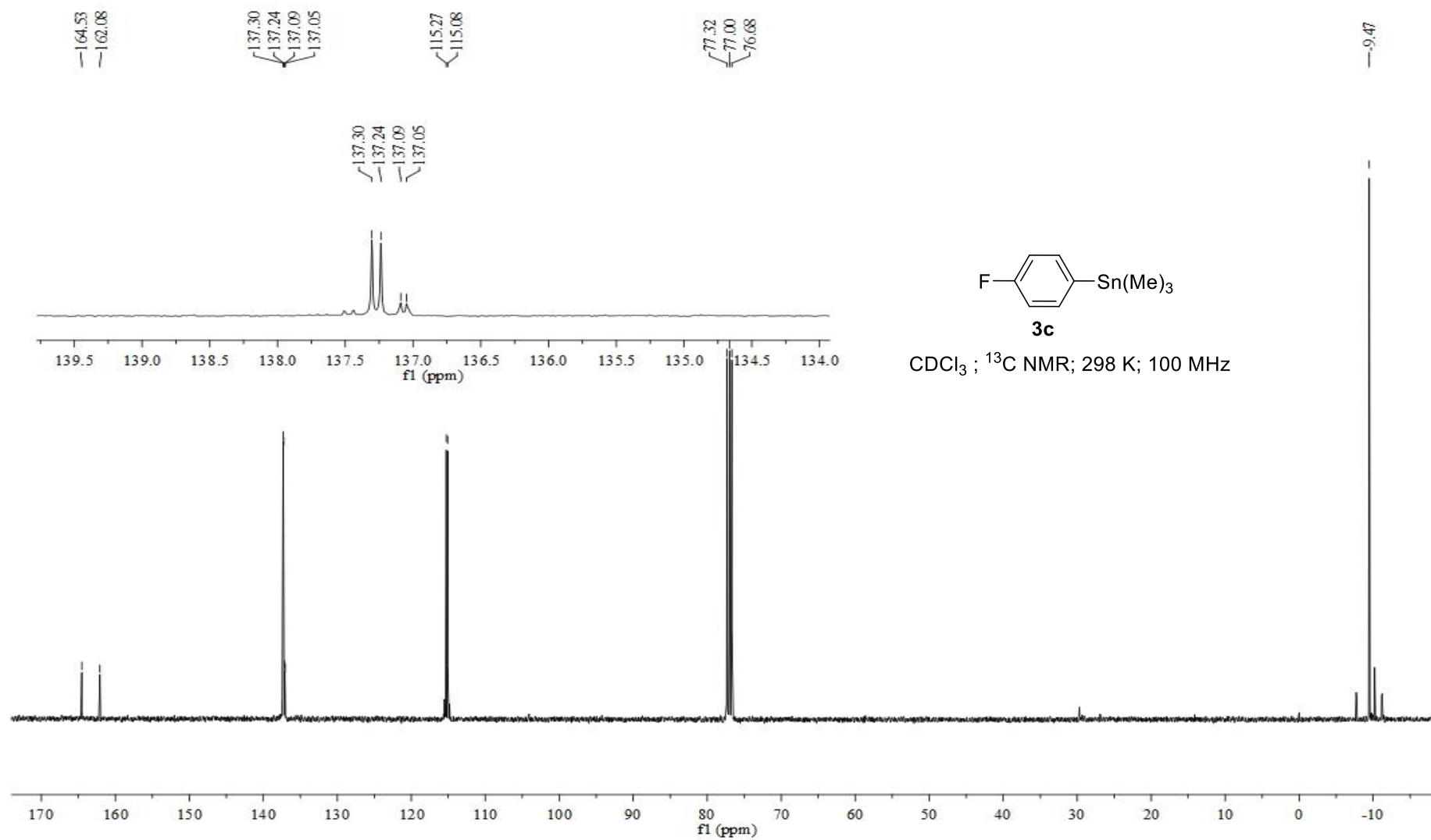


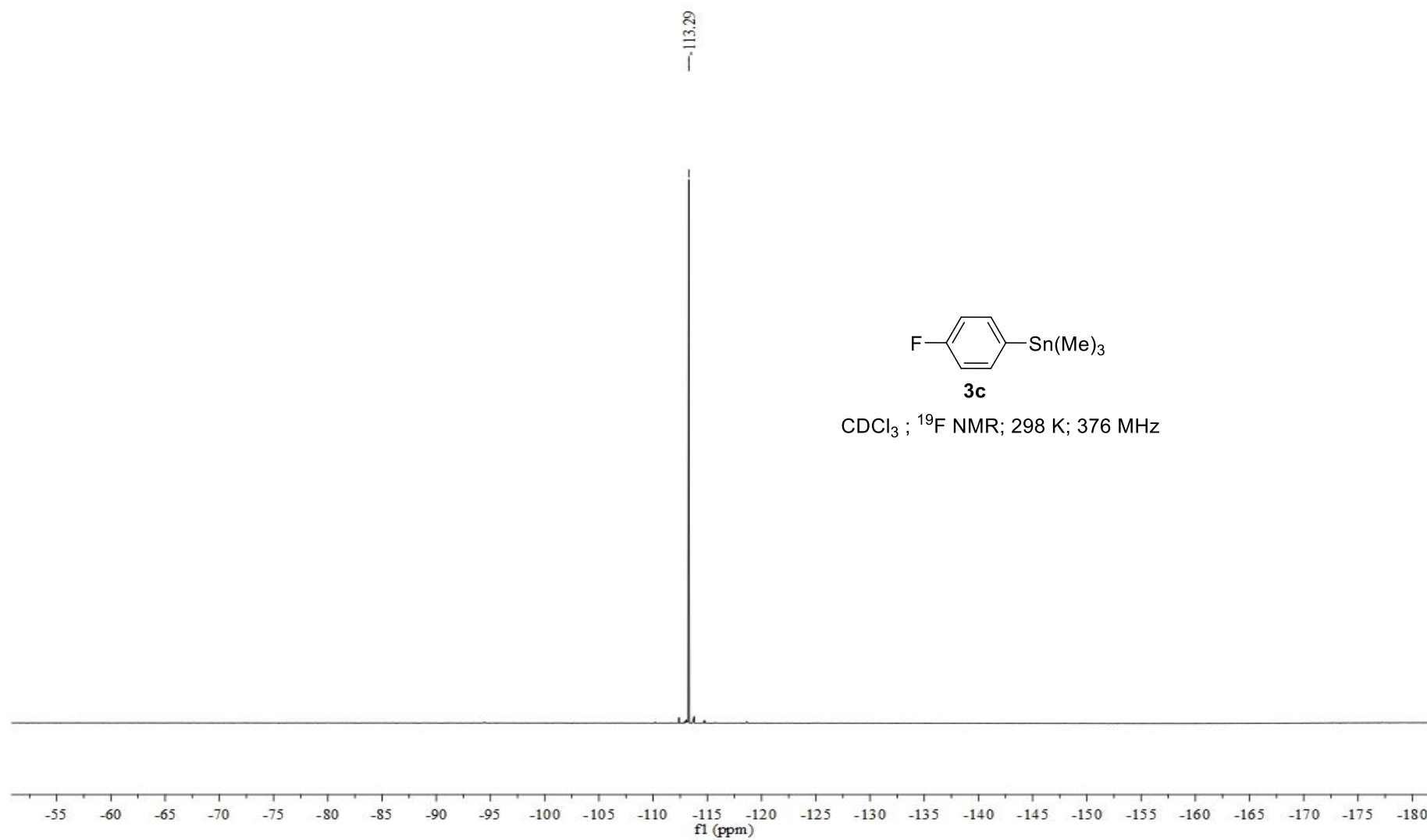


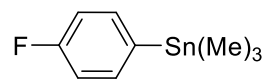






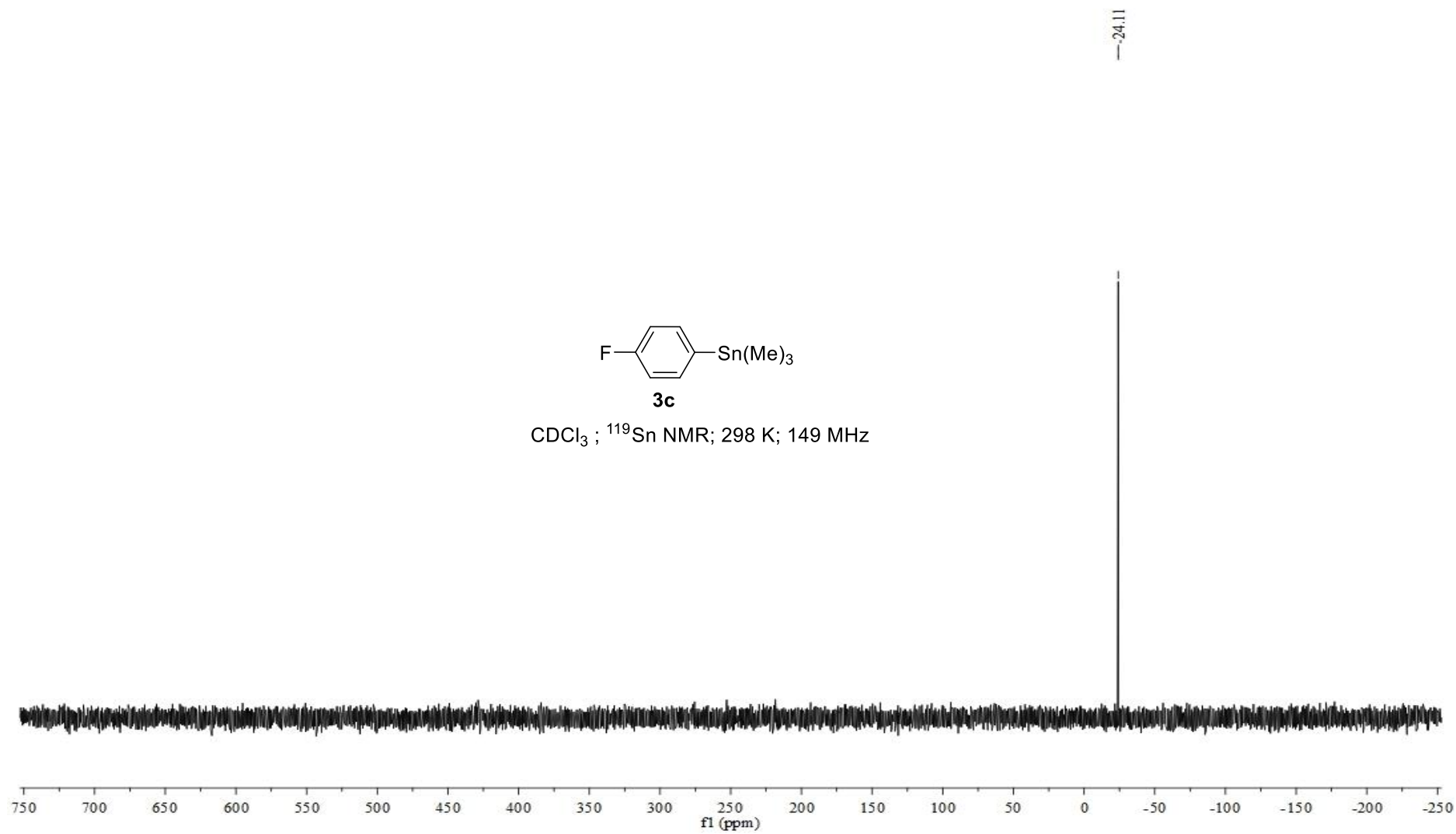


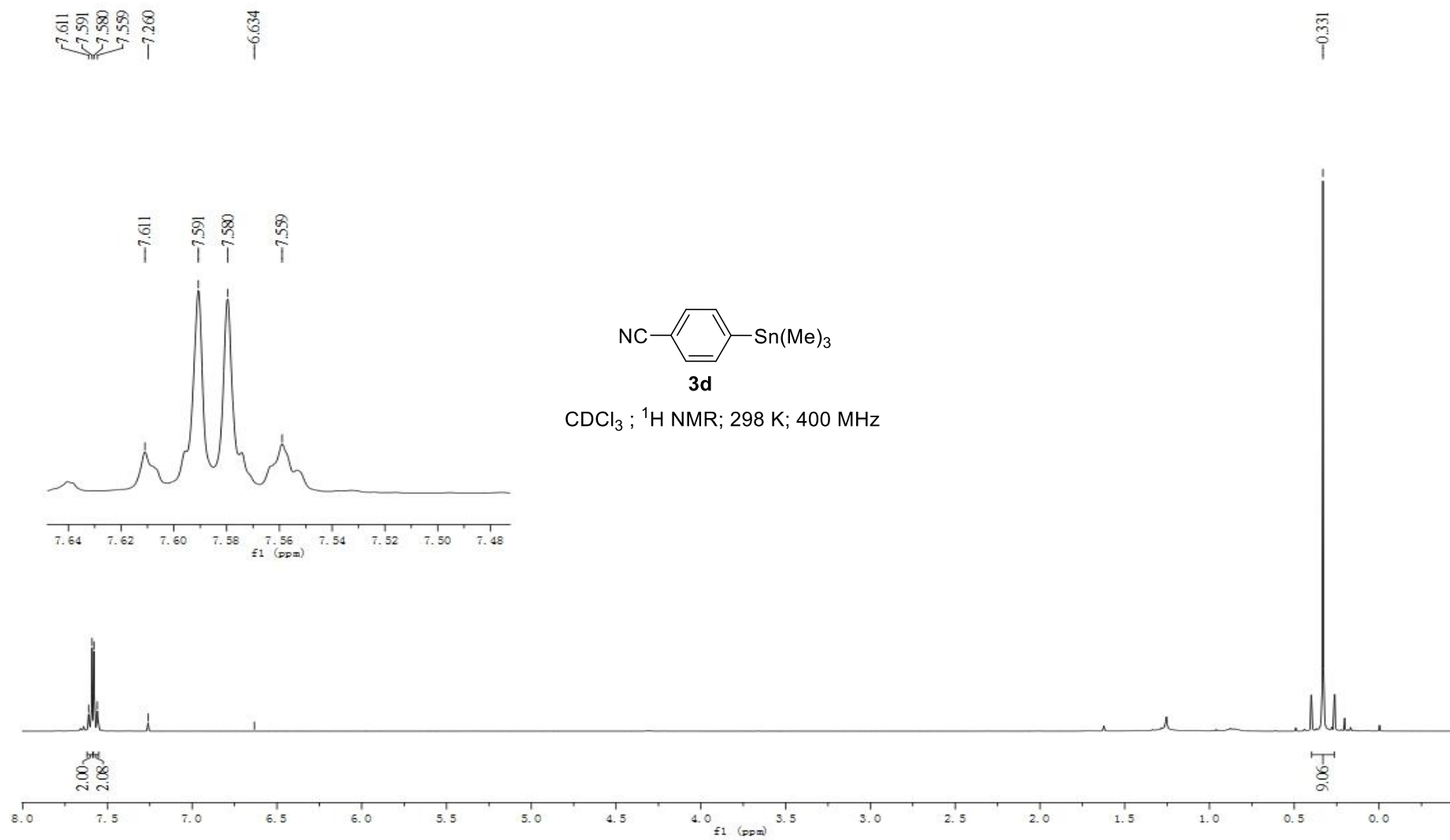


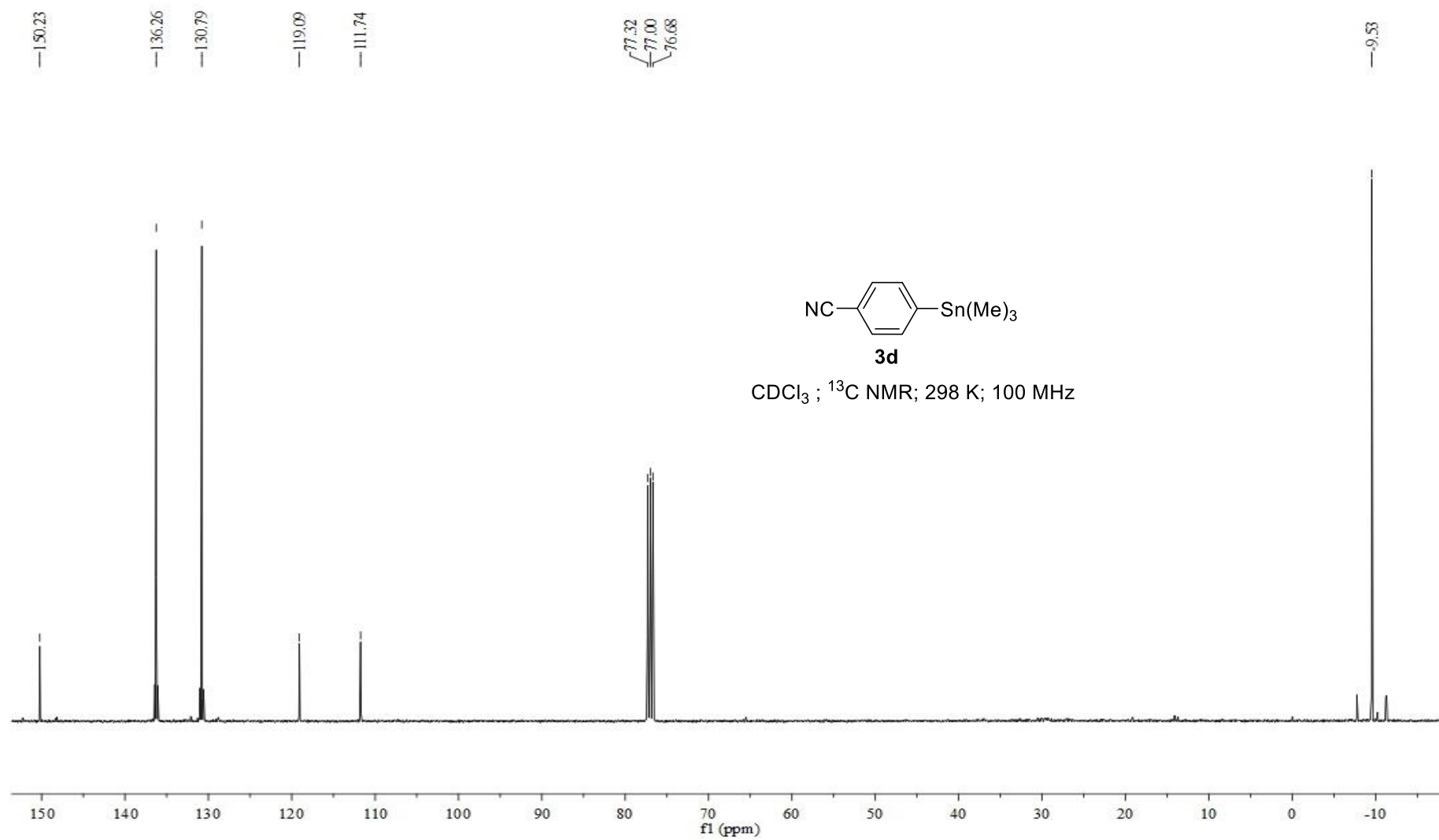


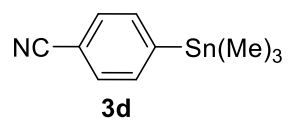
3c

CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

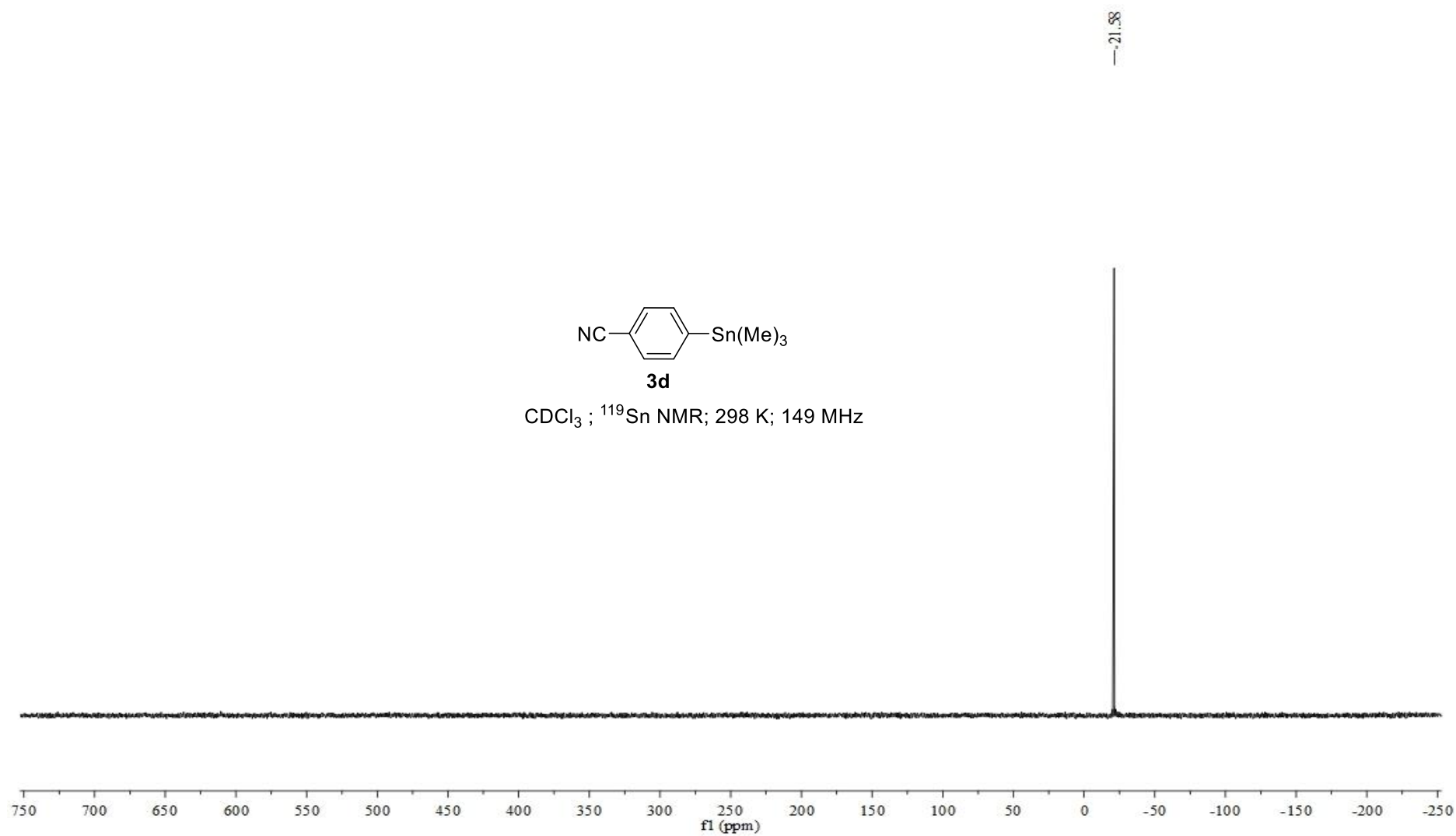


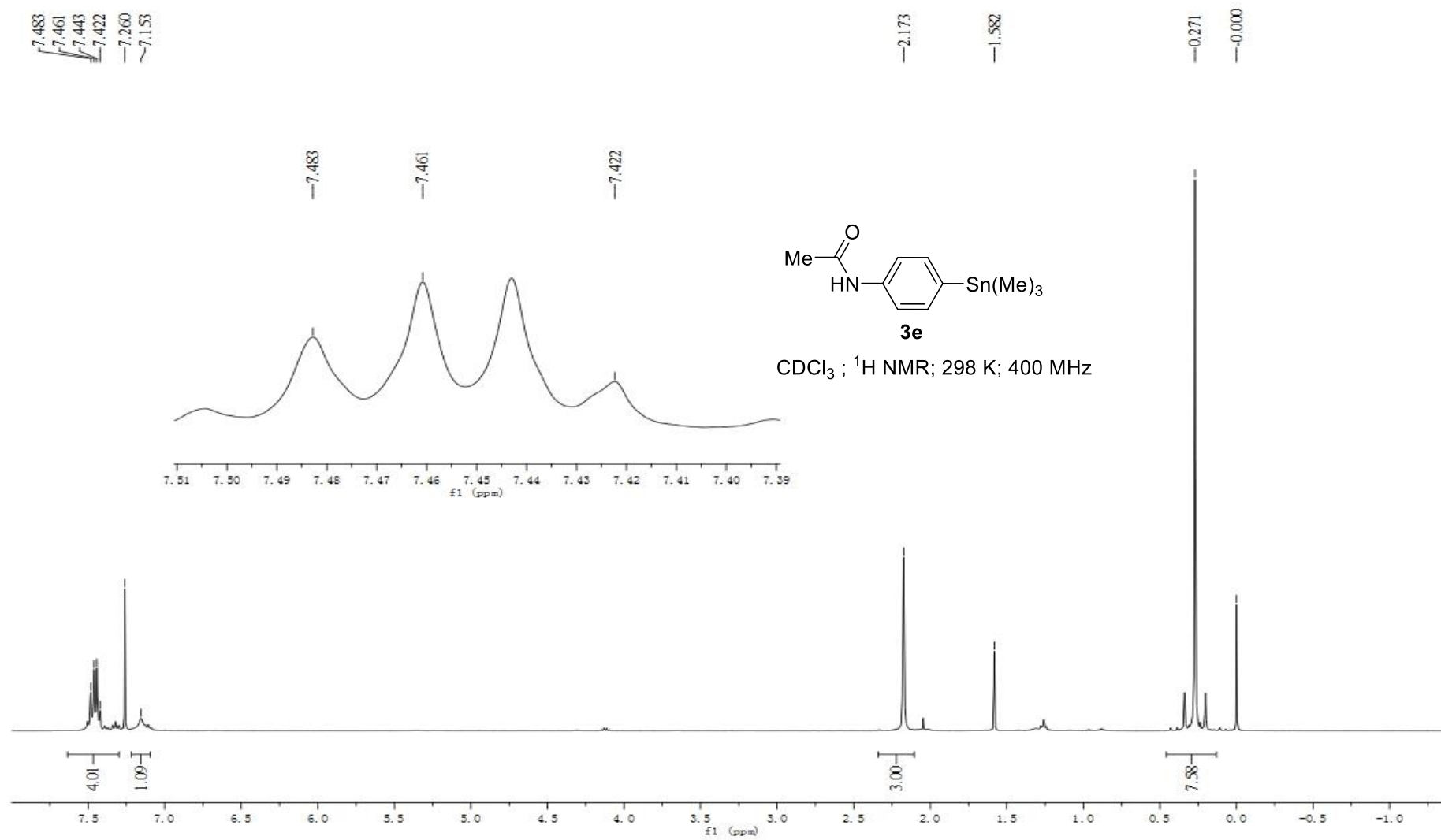


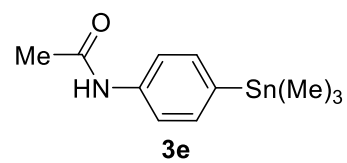




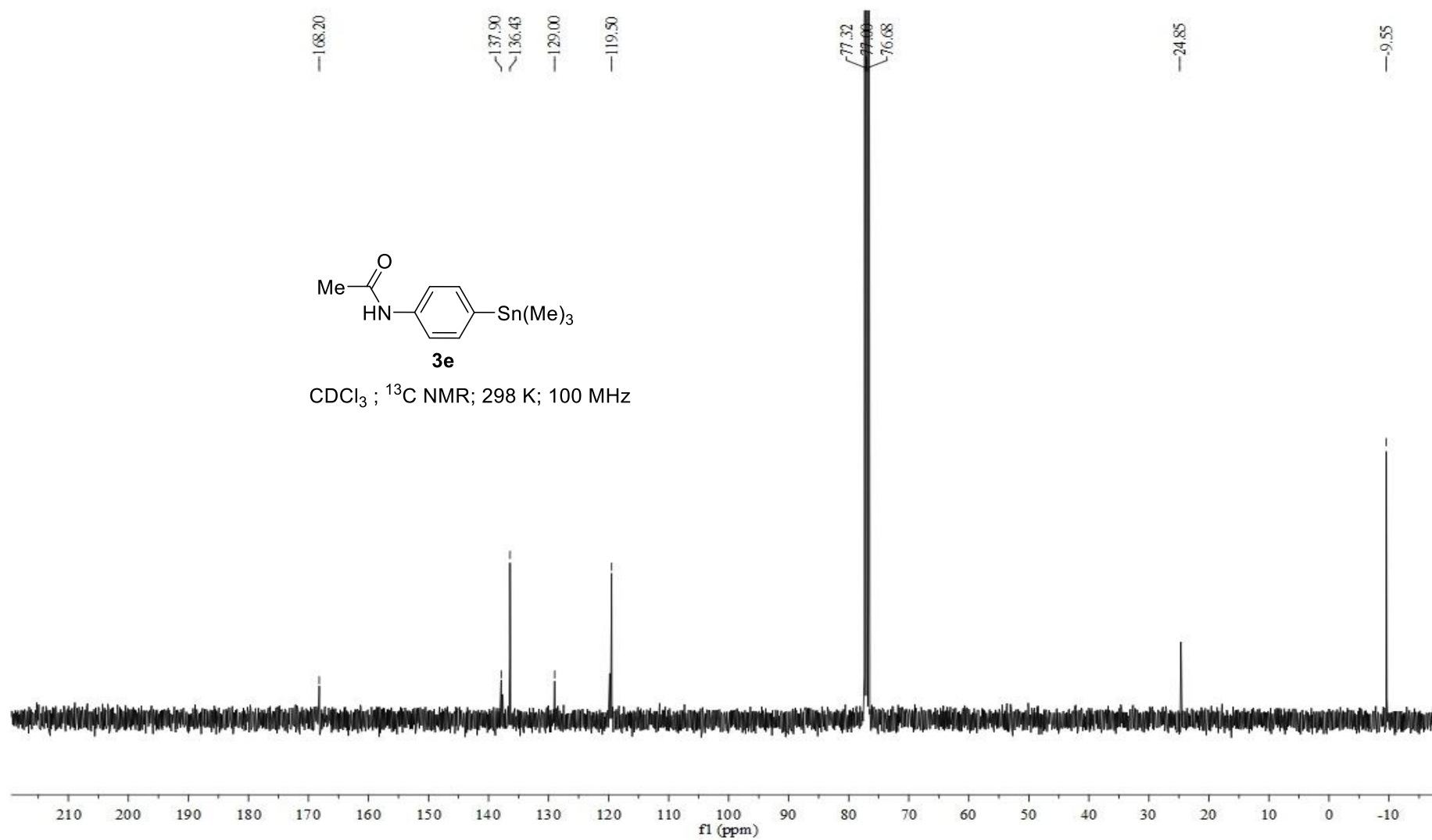
CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

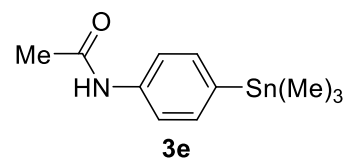




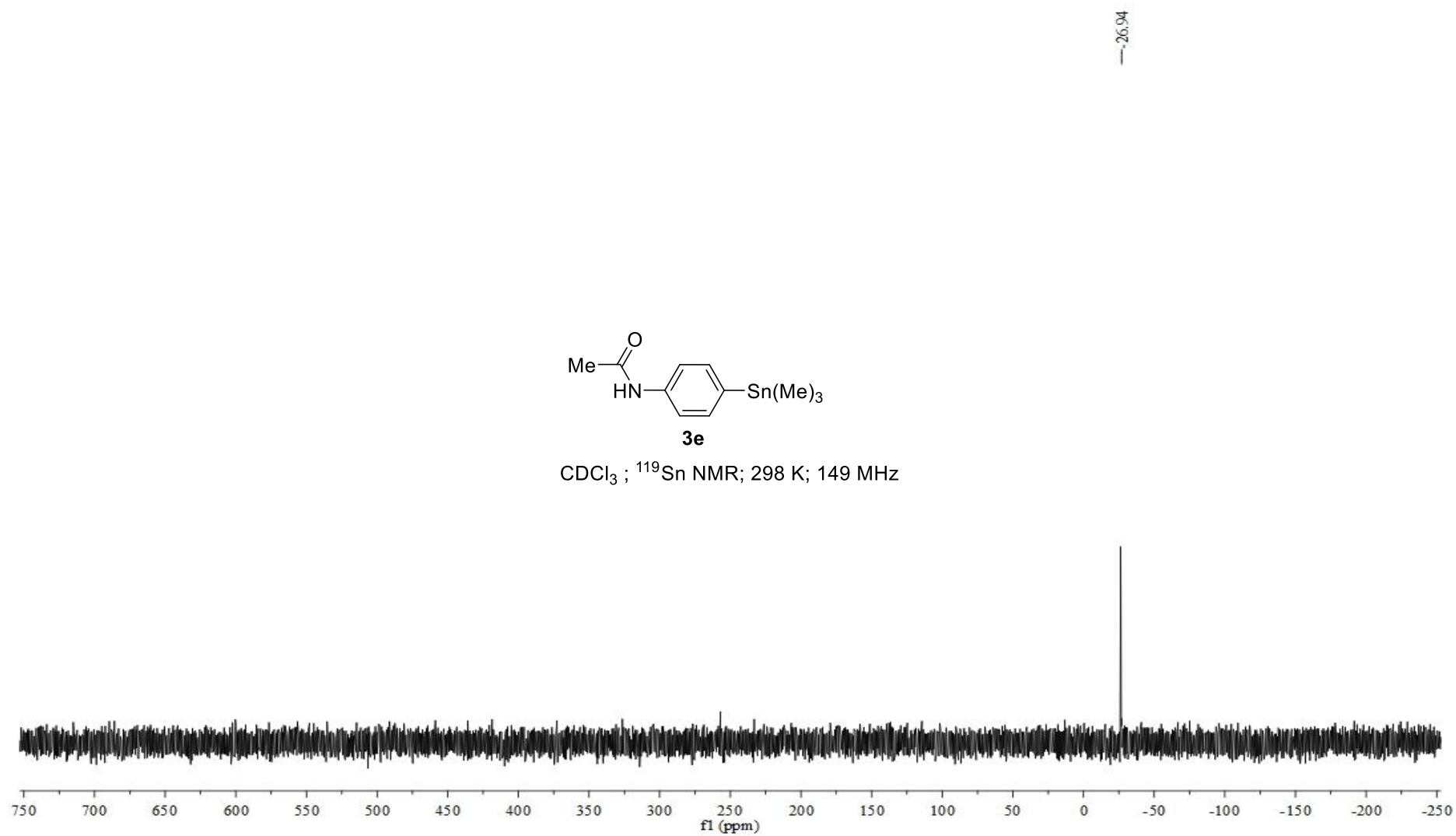


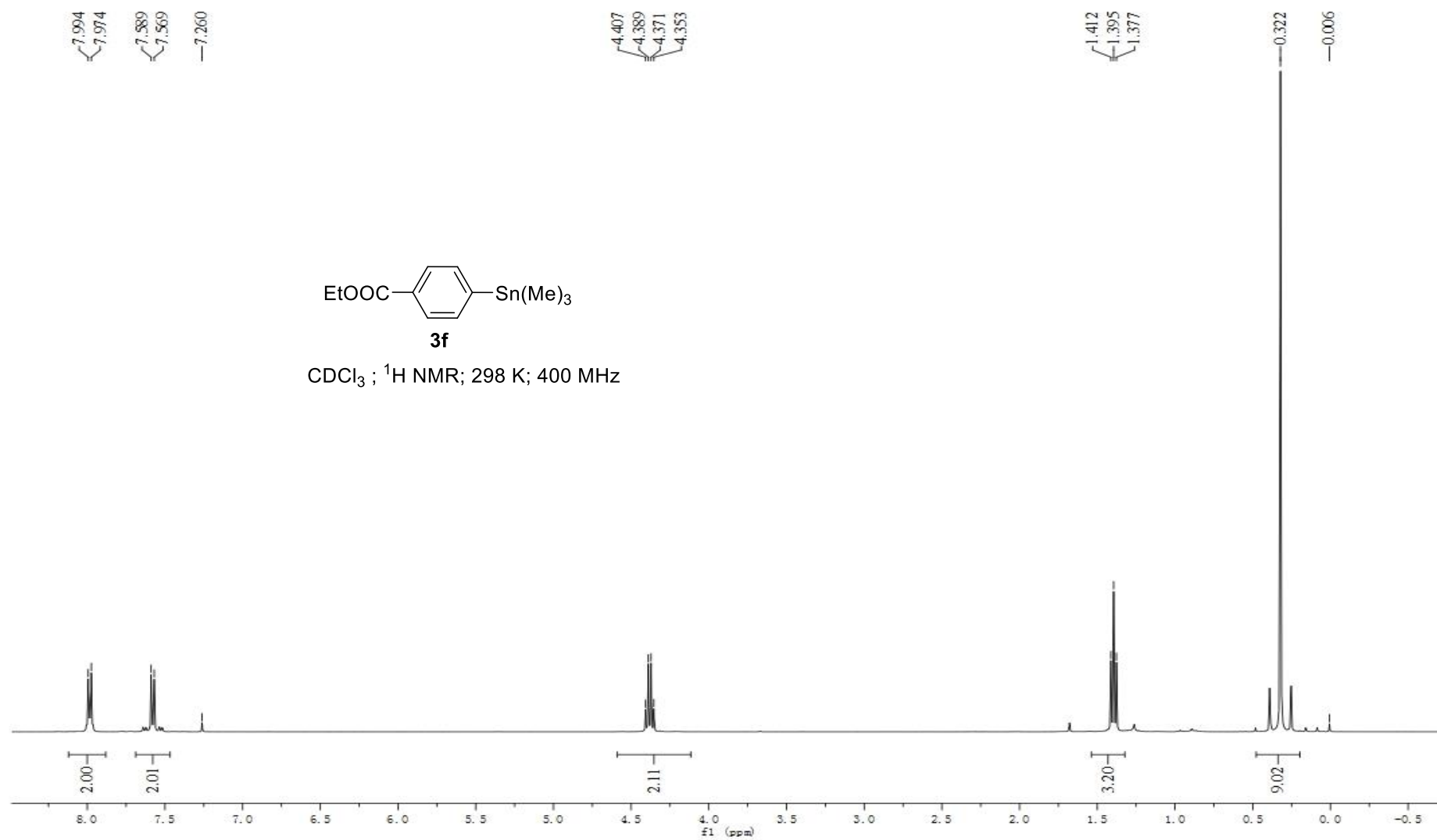
CDCl₃; ¹³C NMR; 298 K; 100 MHz

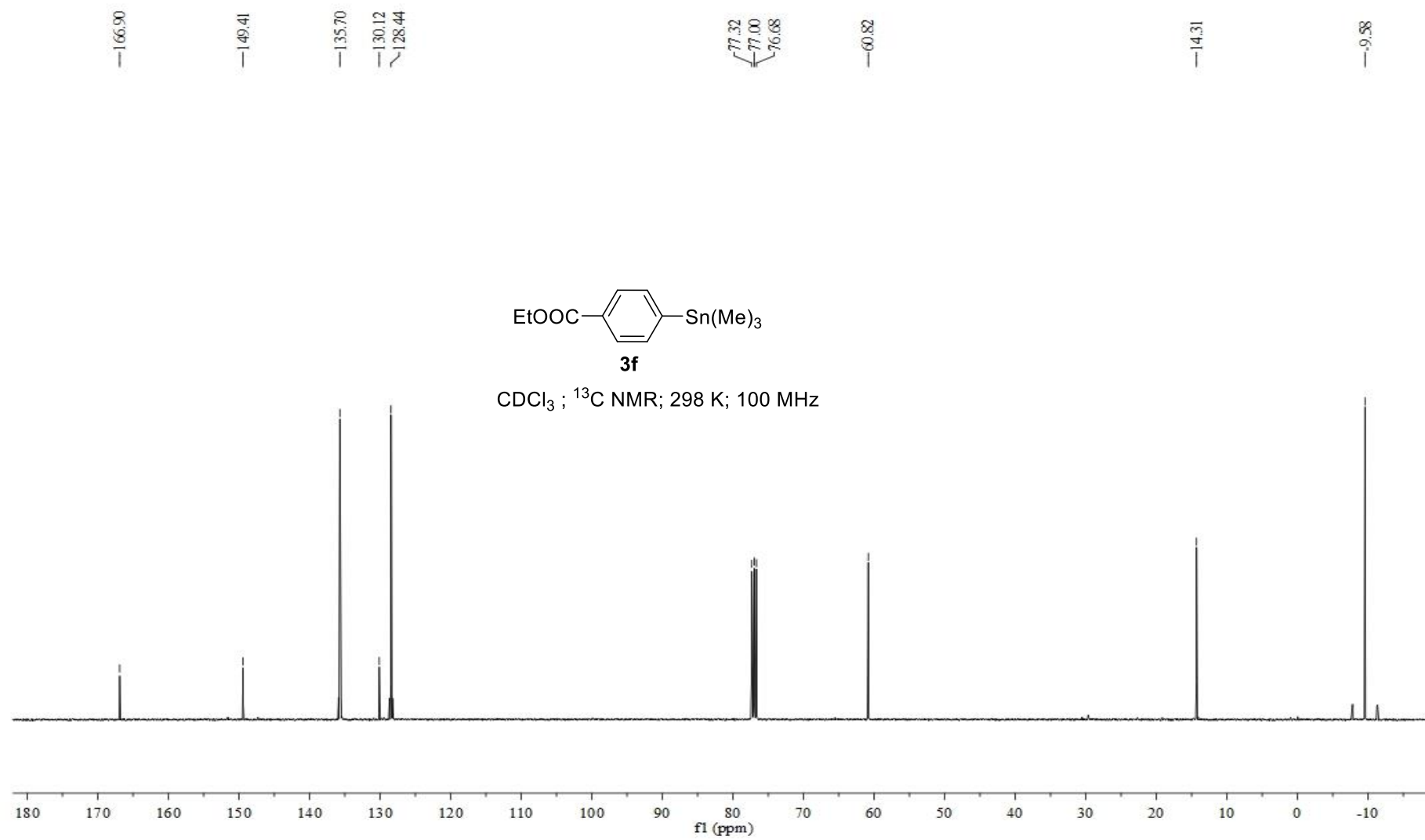


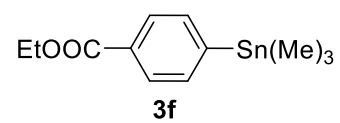


CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

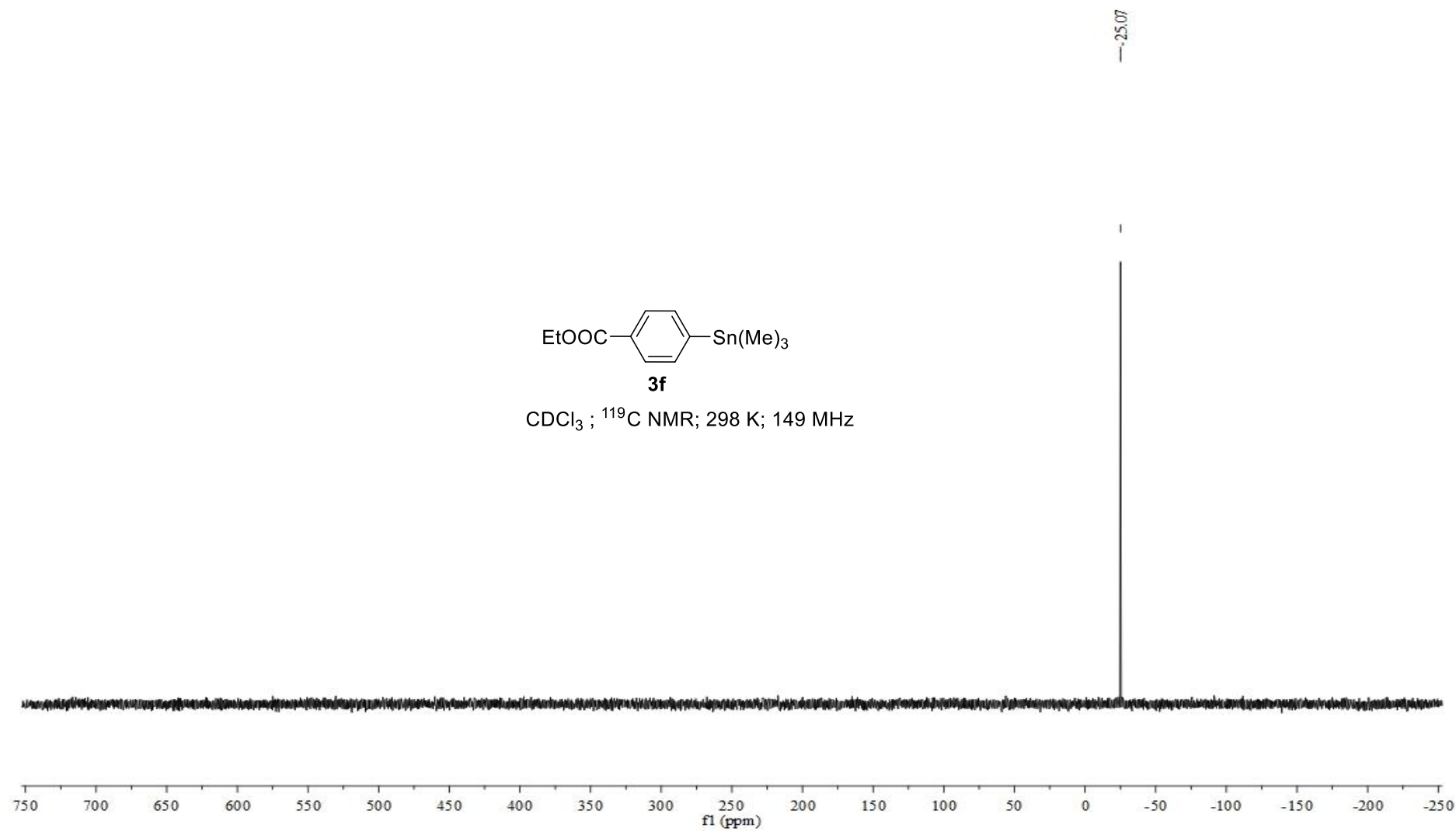


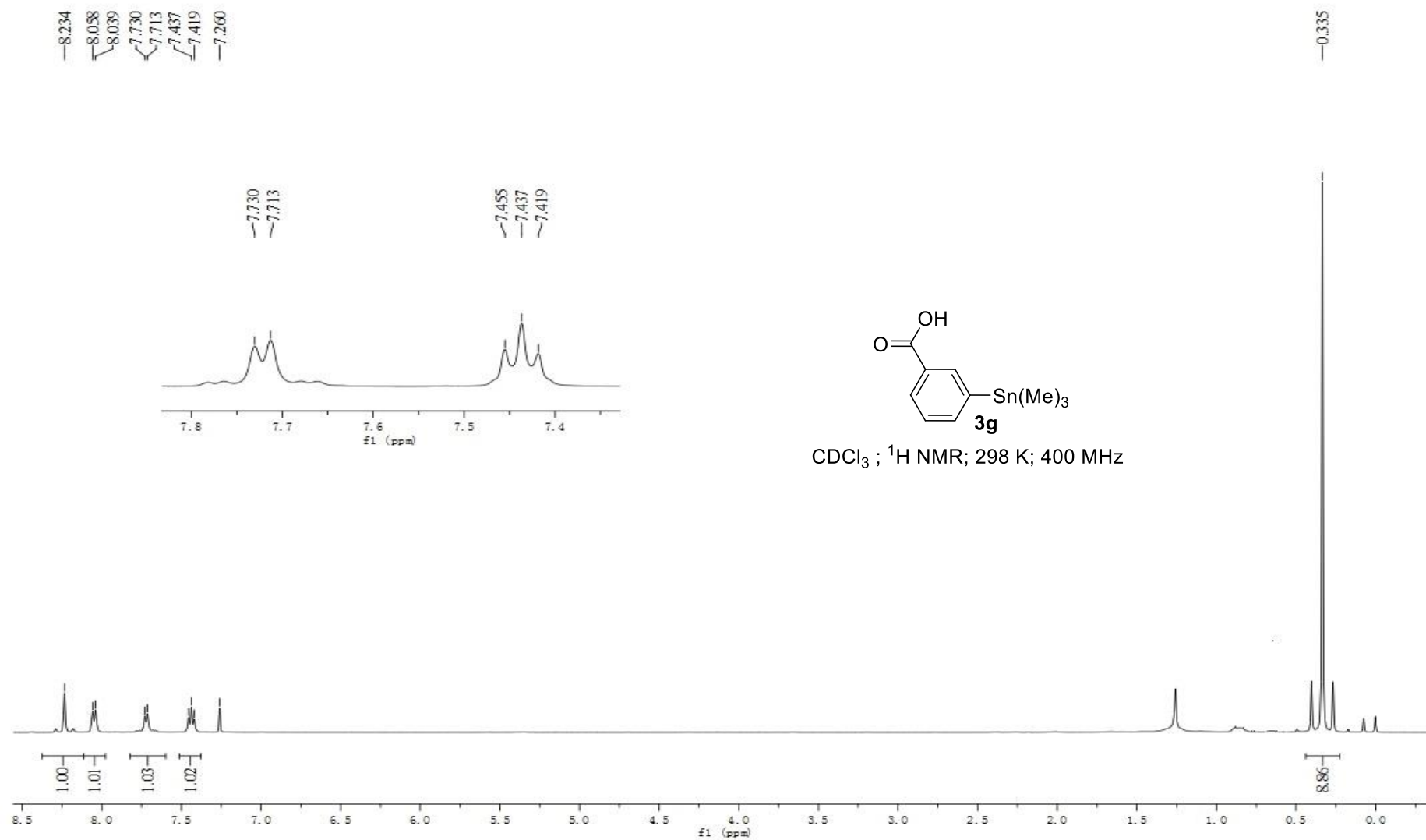


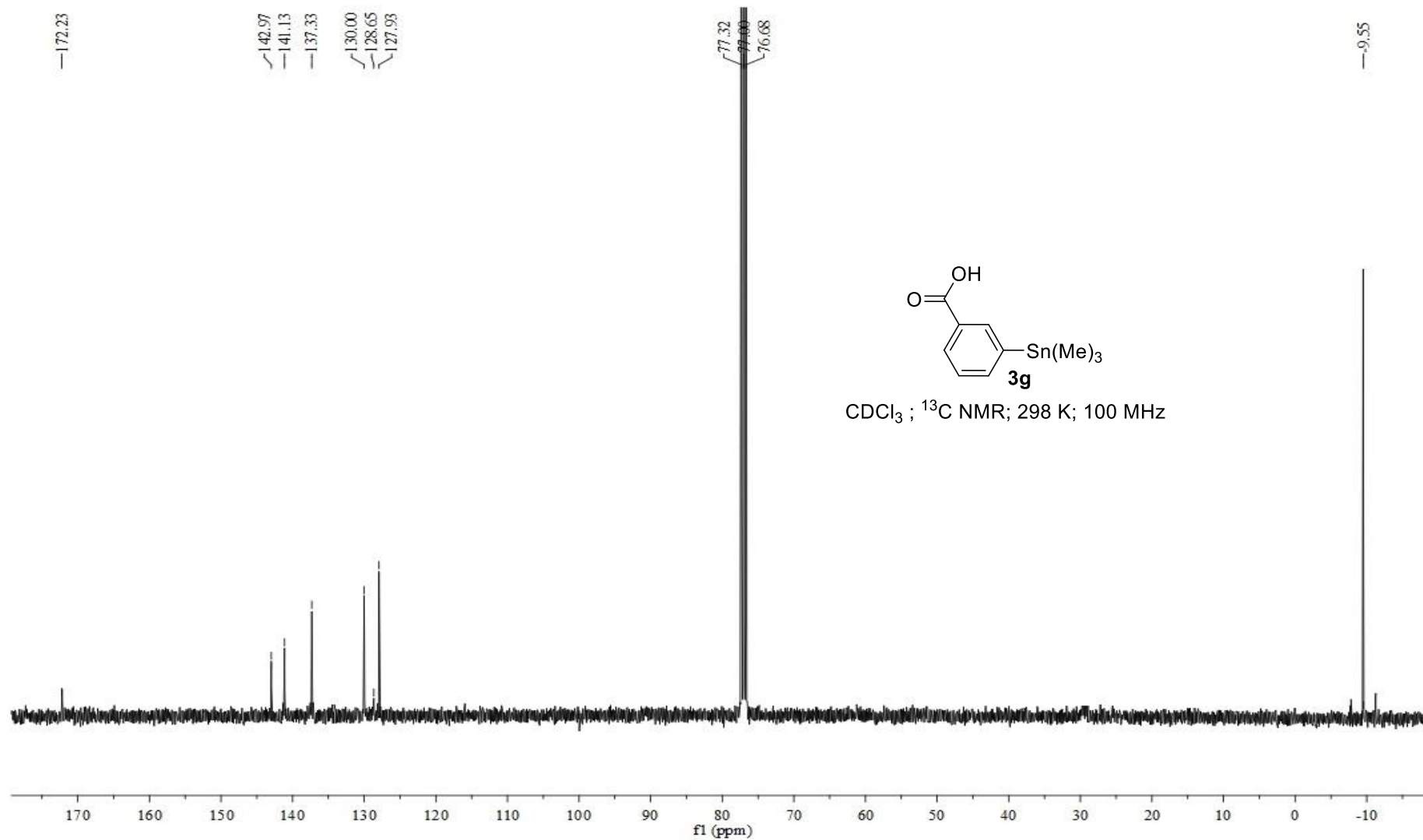


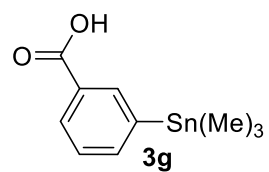


CDCl_3 ; ^{119}C NMR; 298 K; 149 MHz

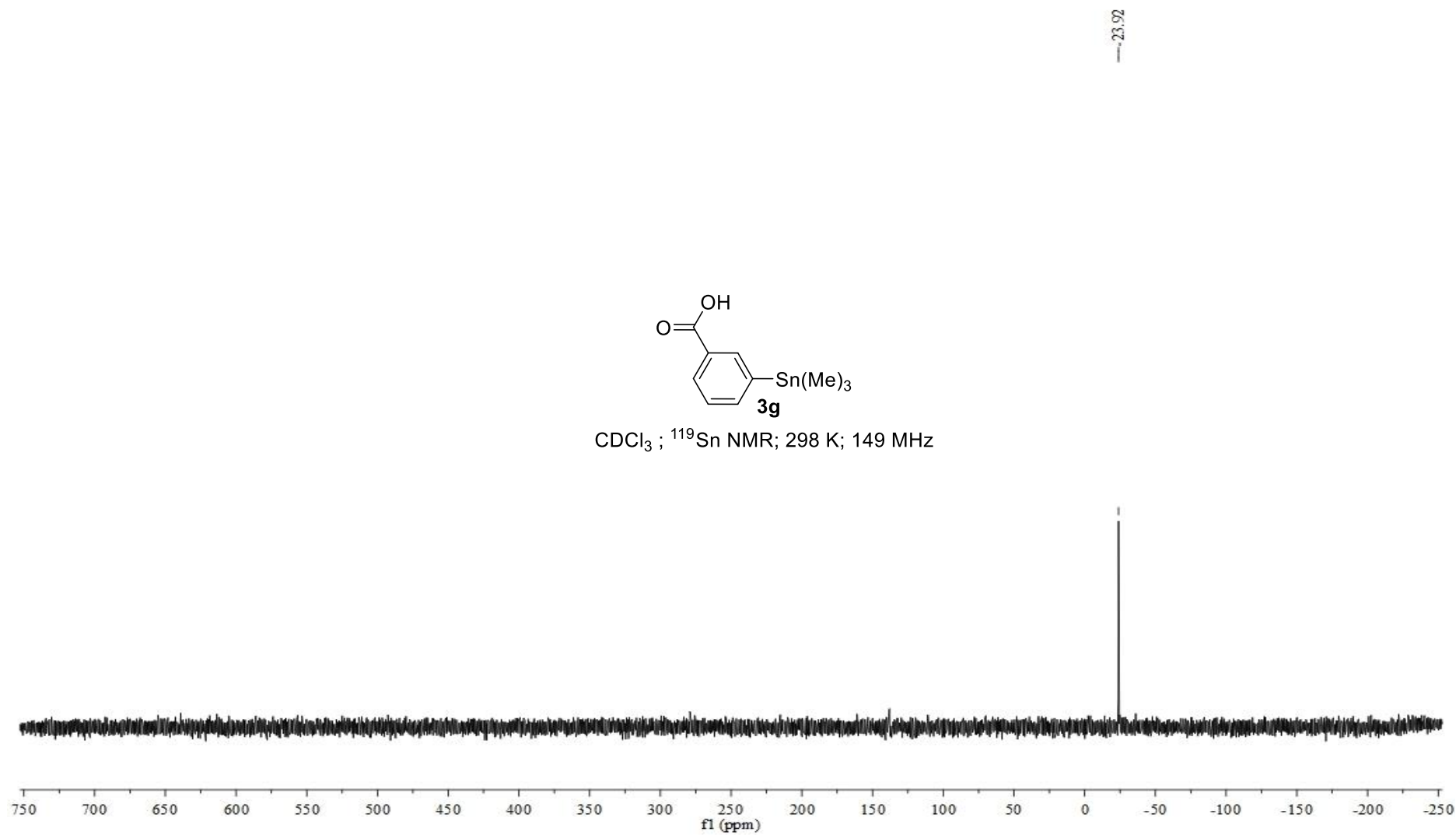


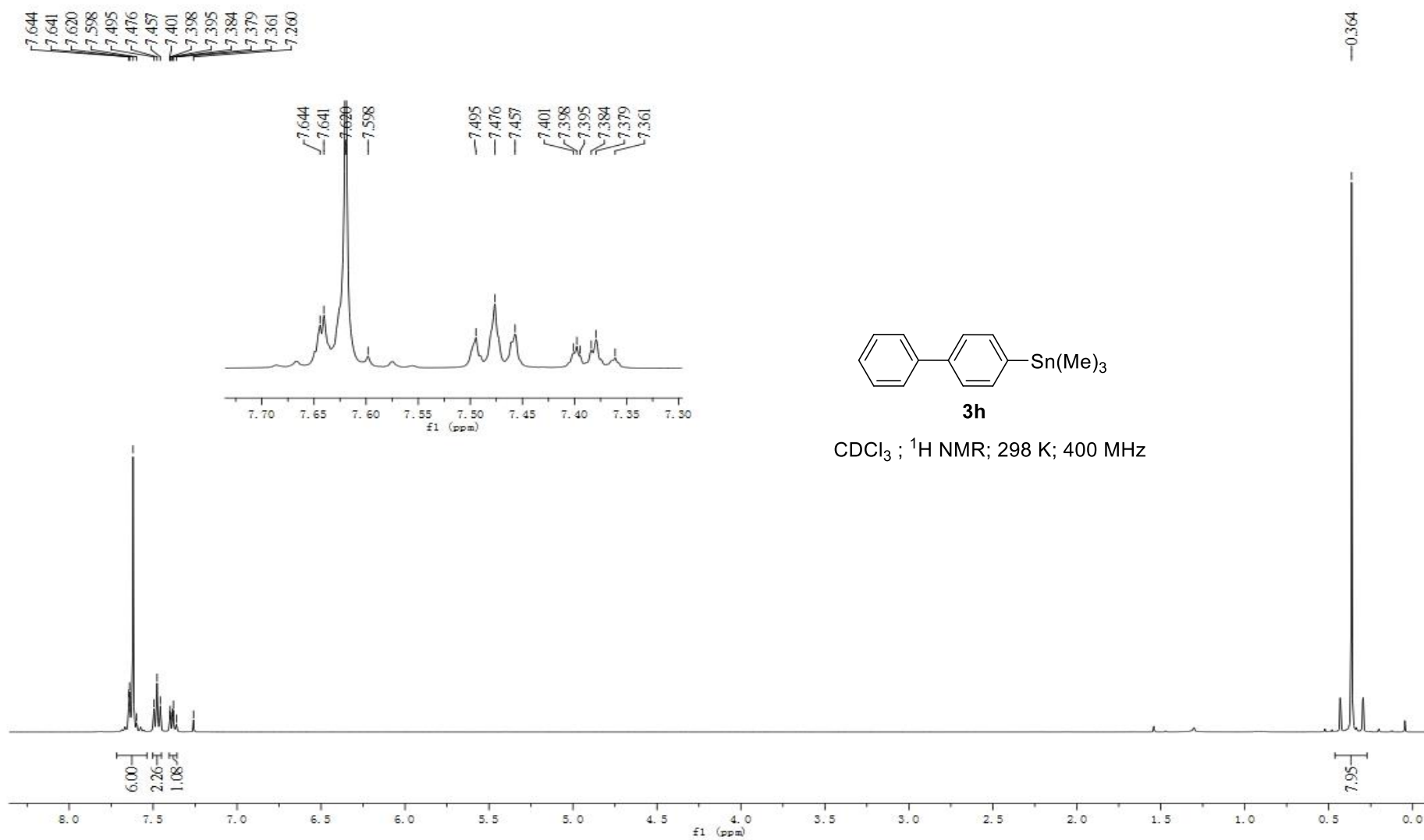


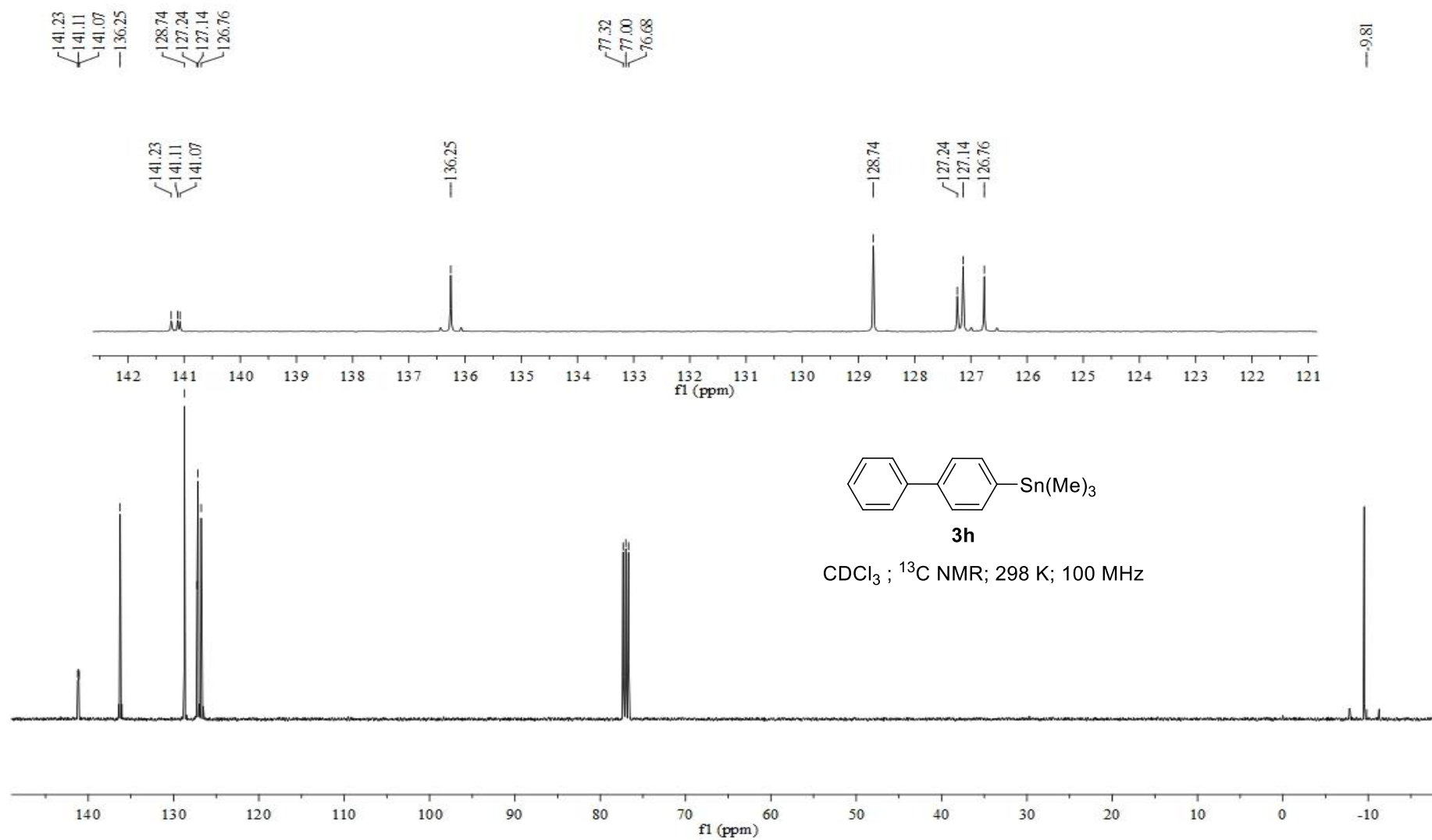


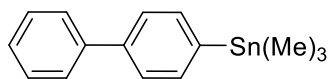


CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz



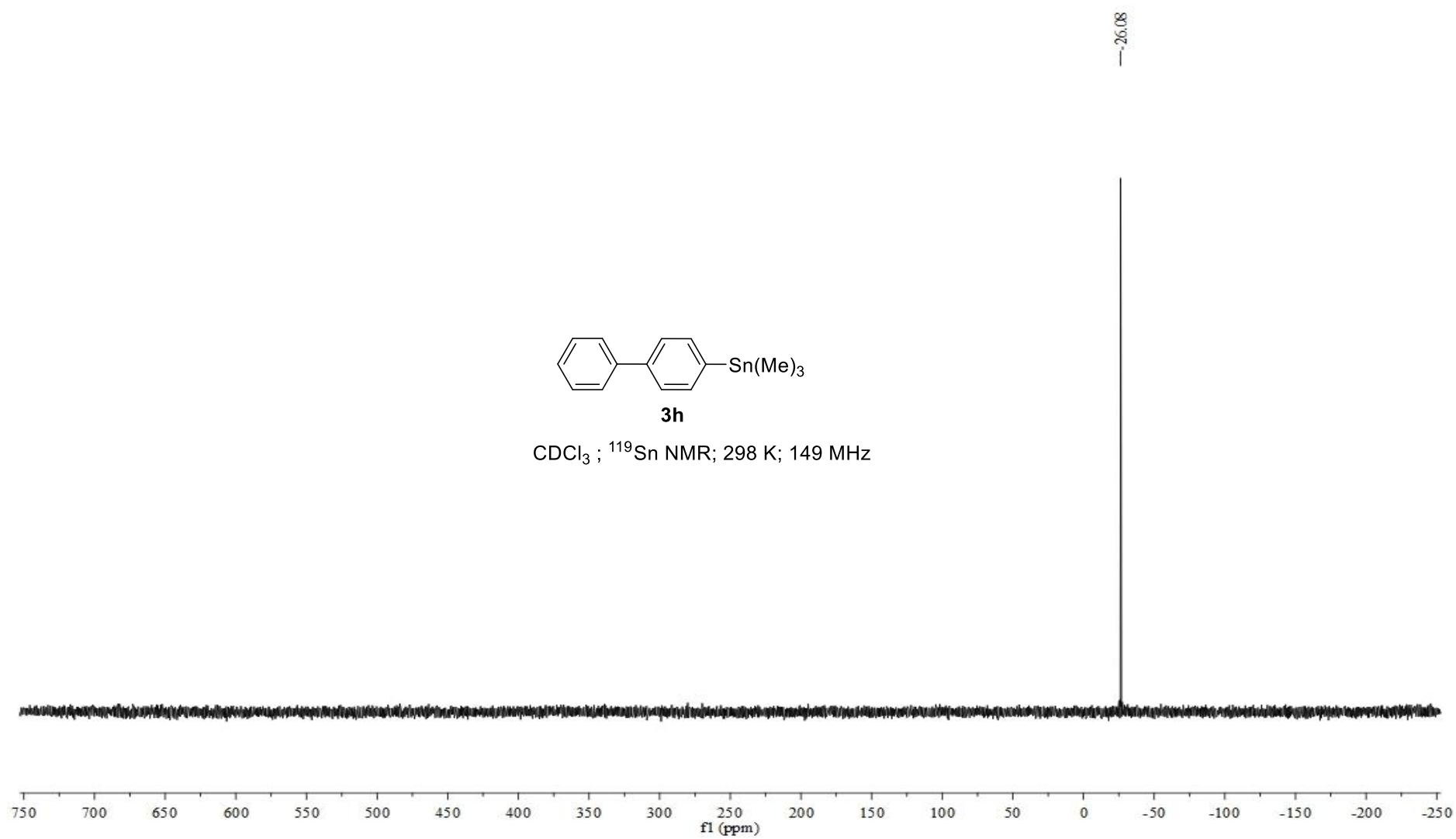


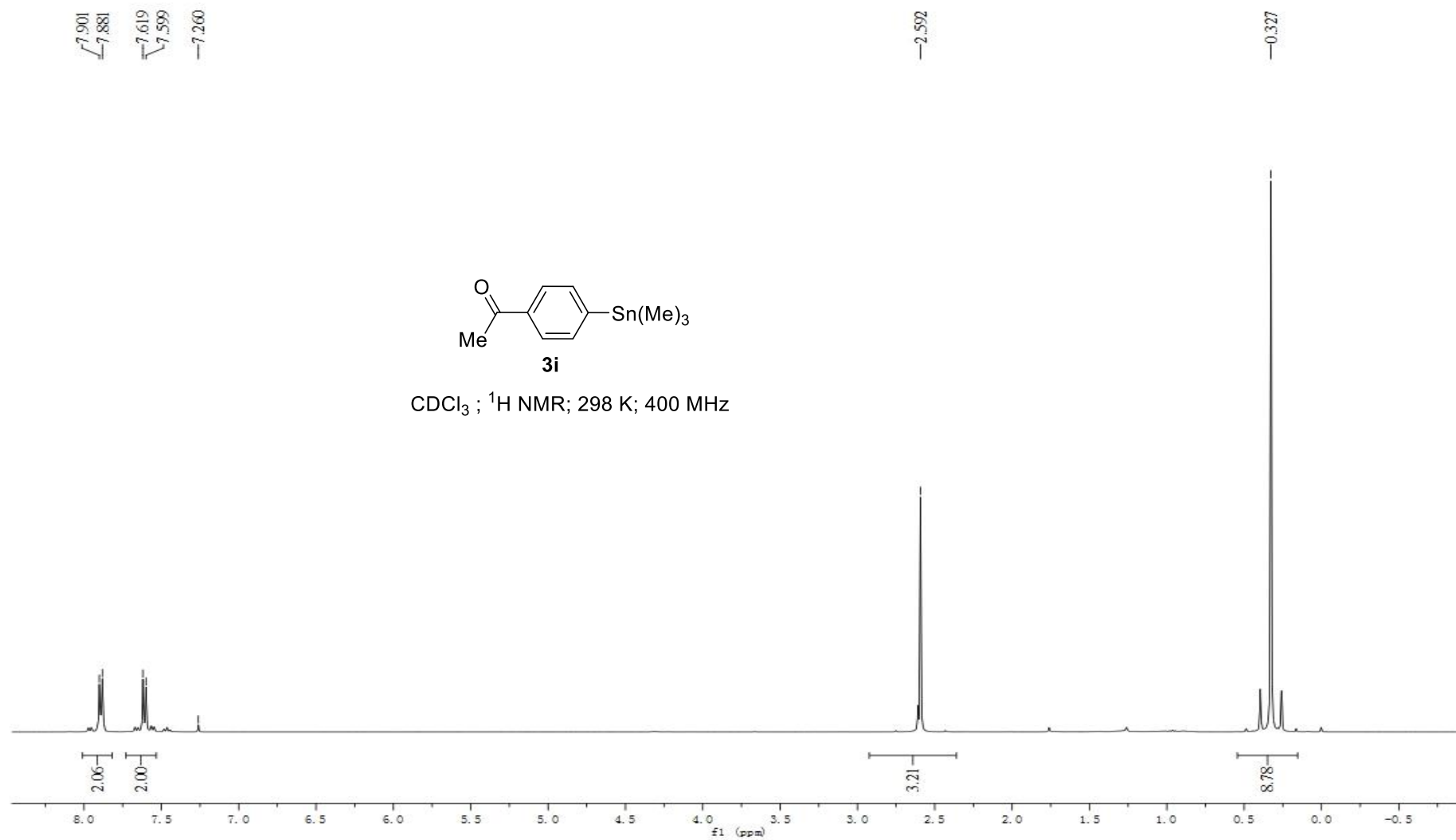


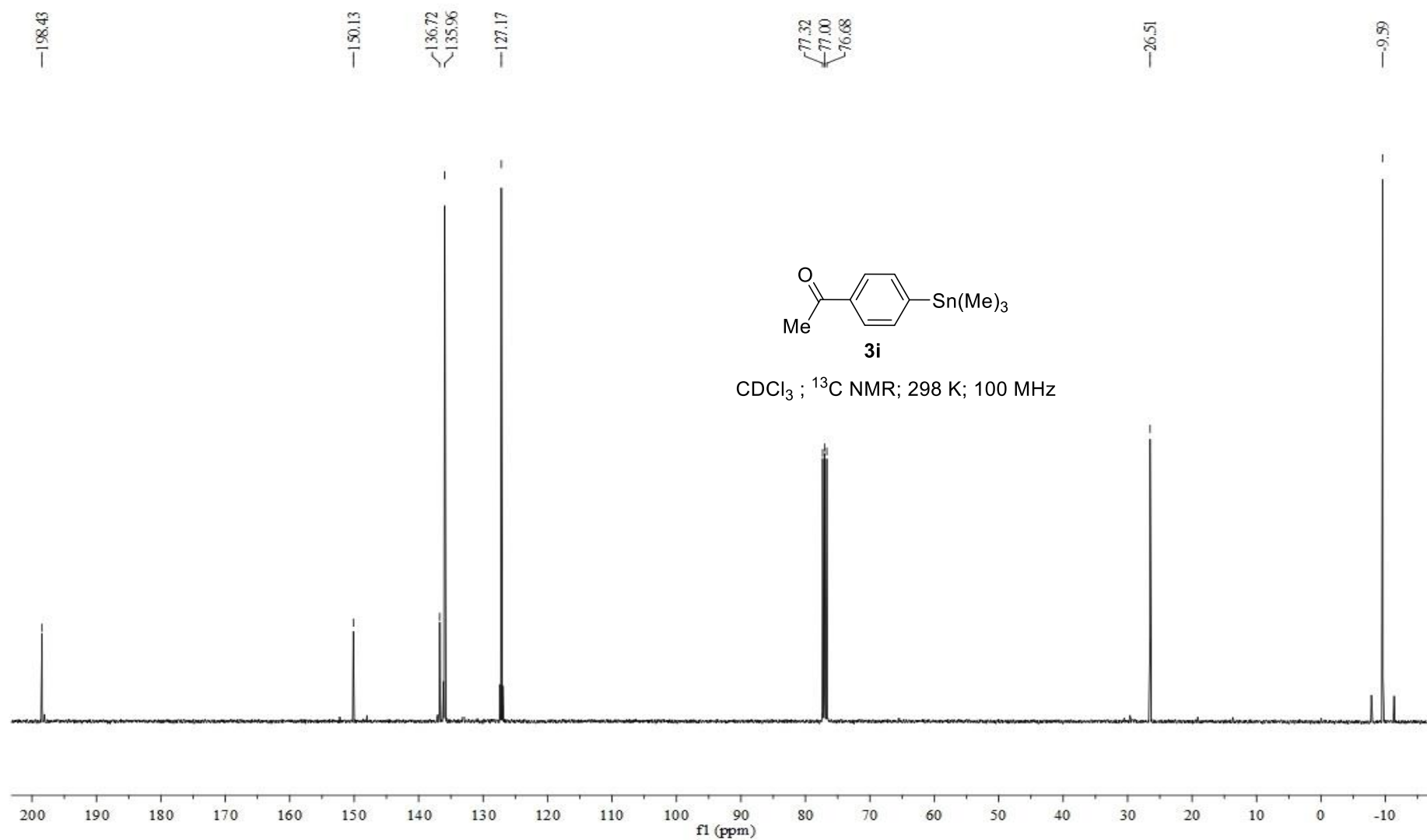


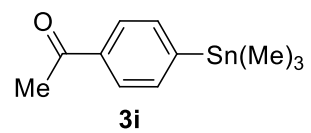
3h

CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

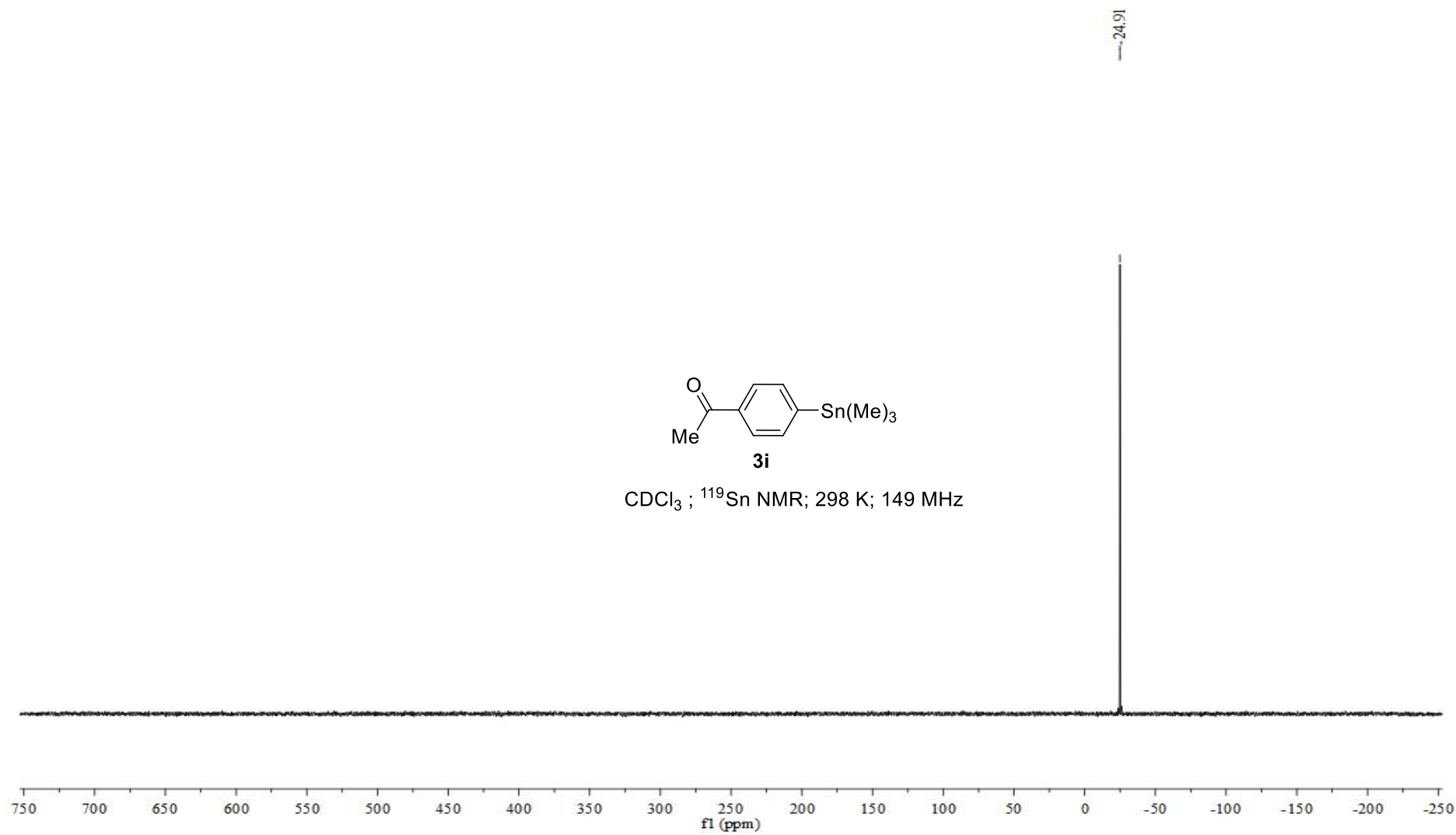


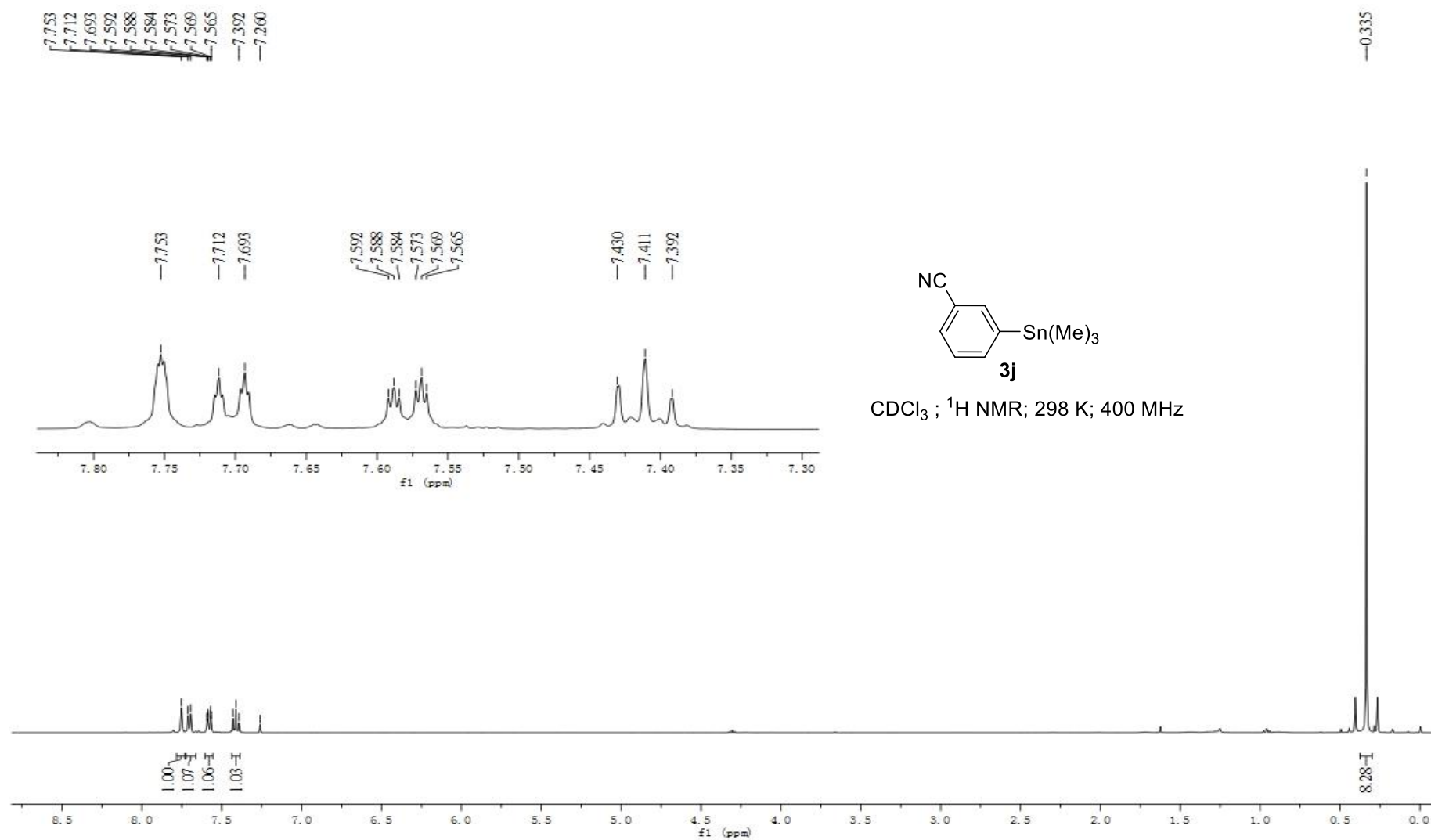


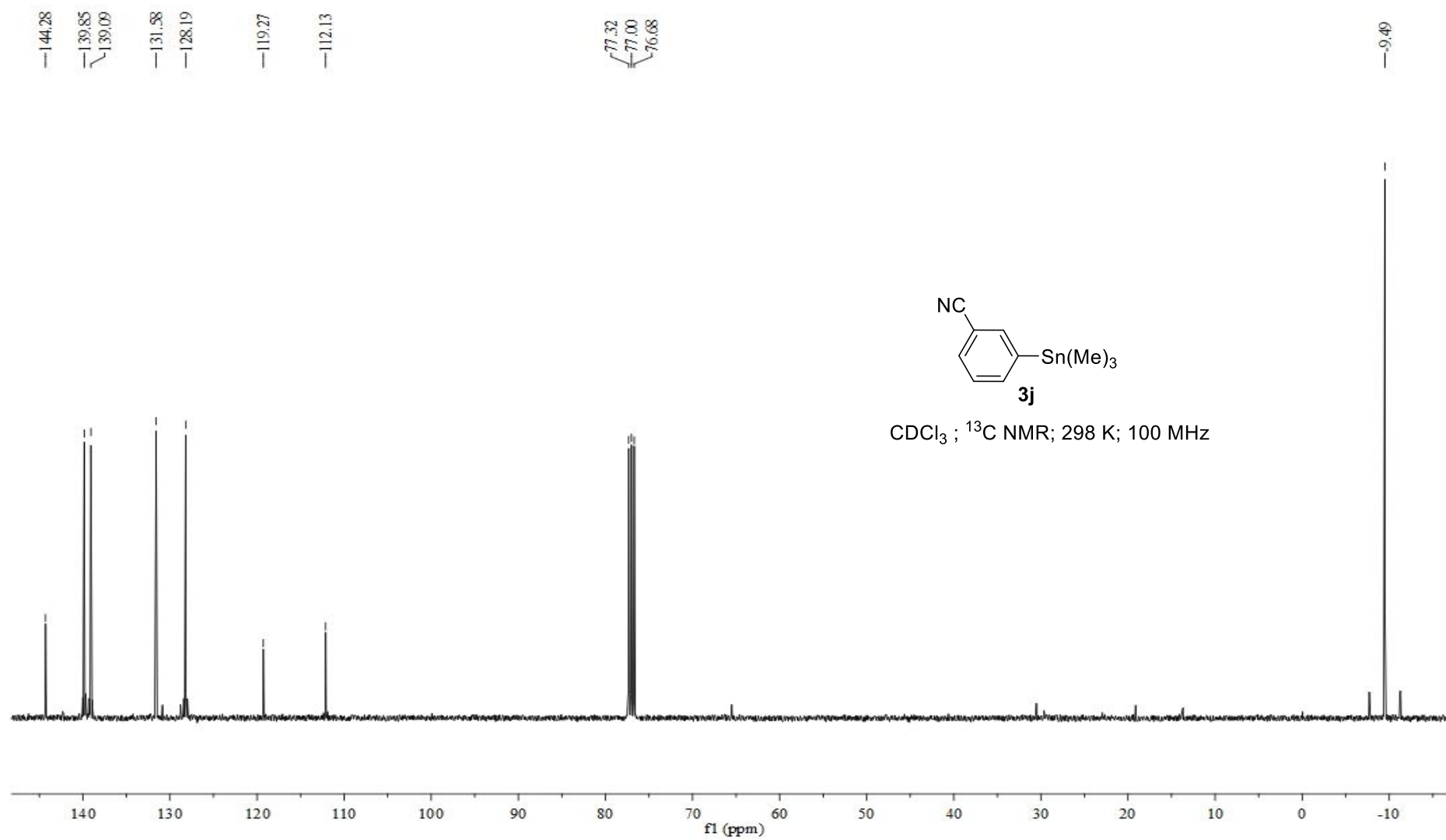


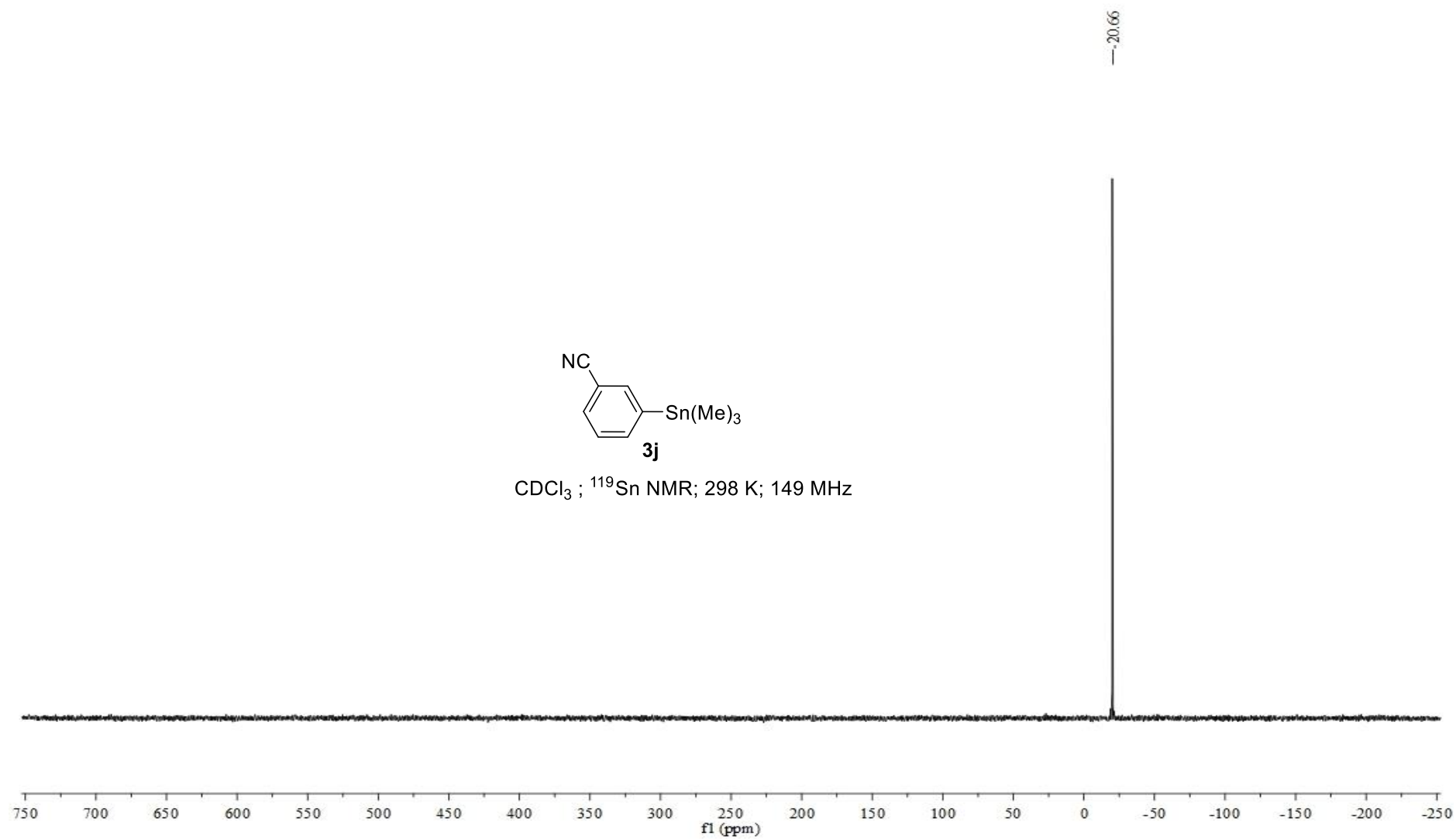


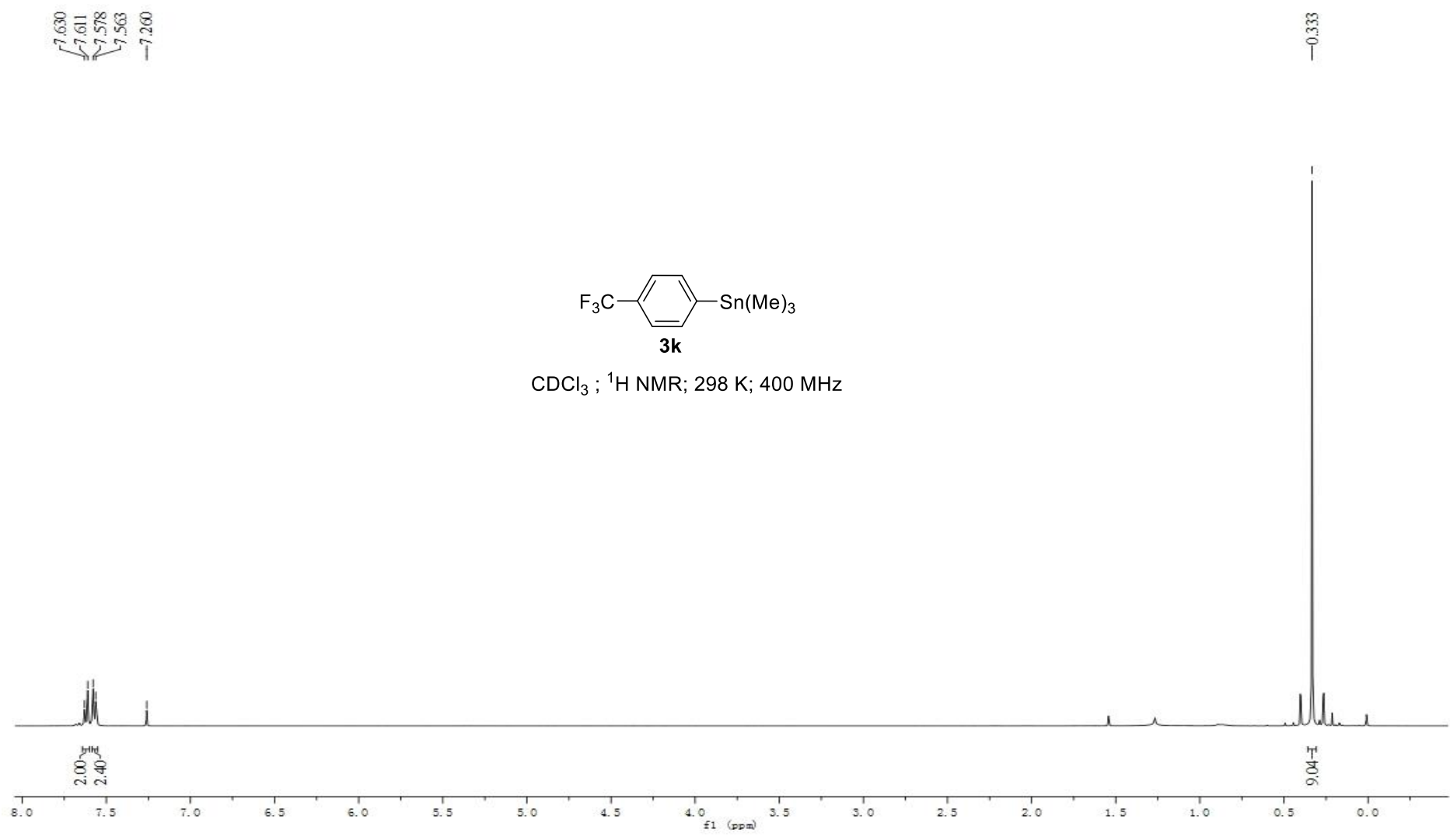
CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

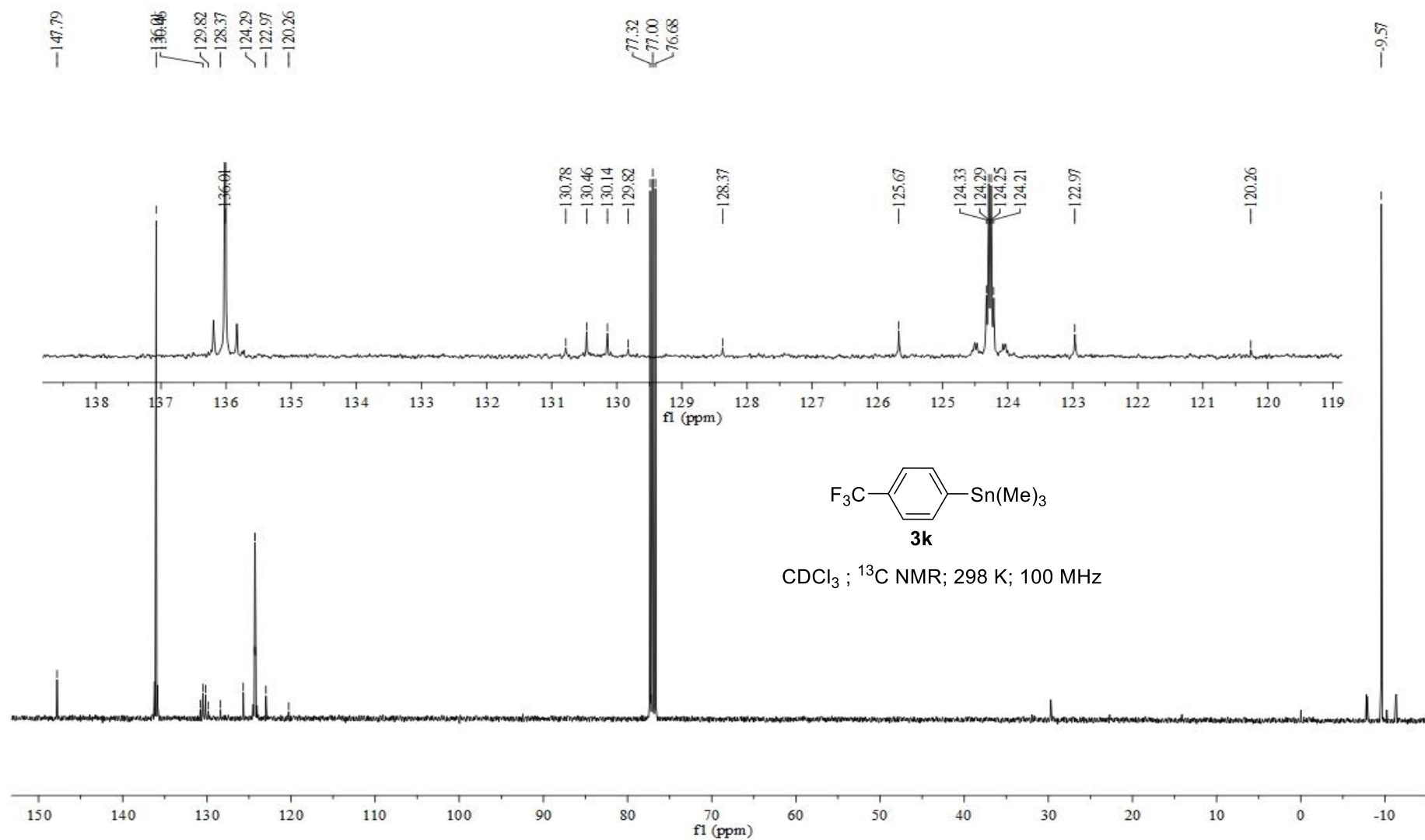


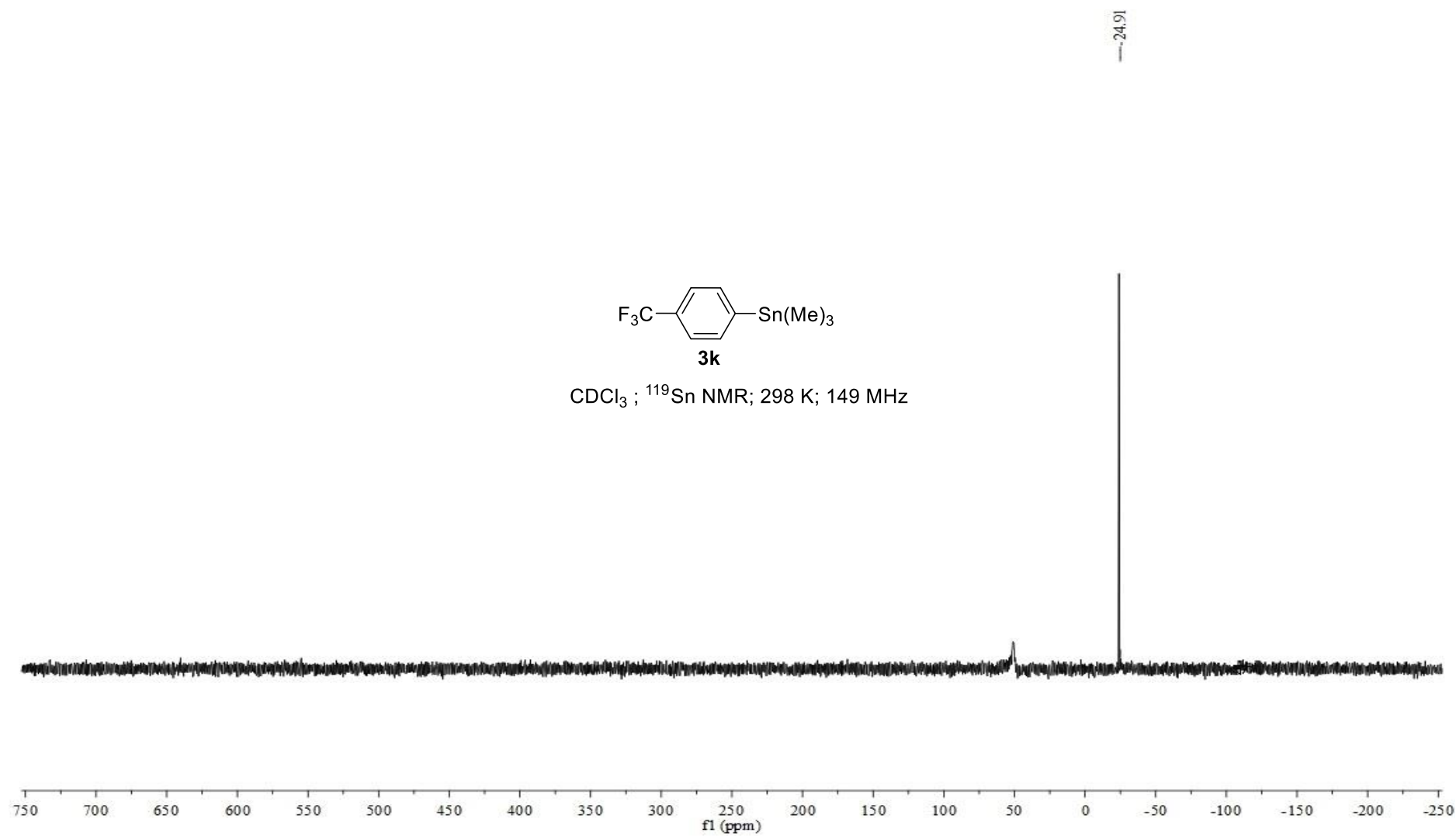


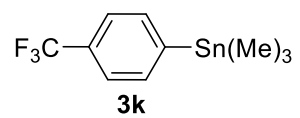




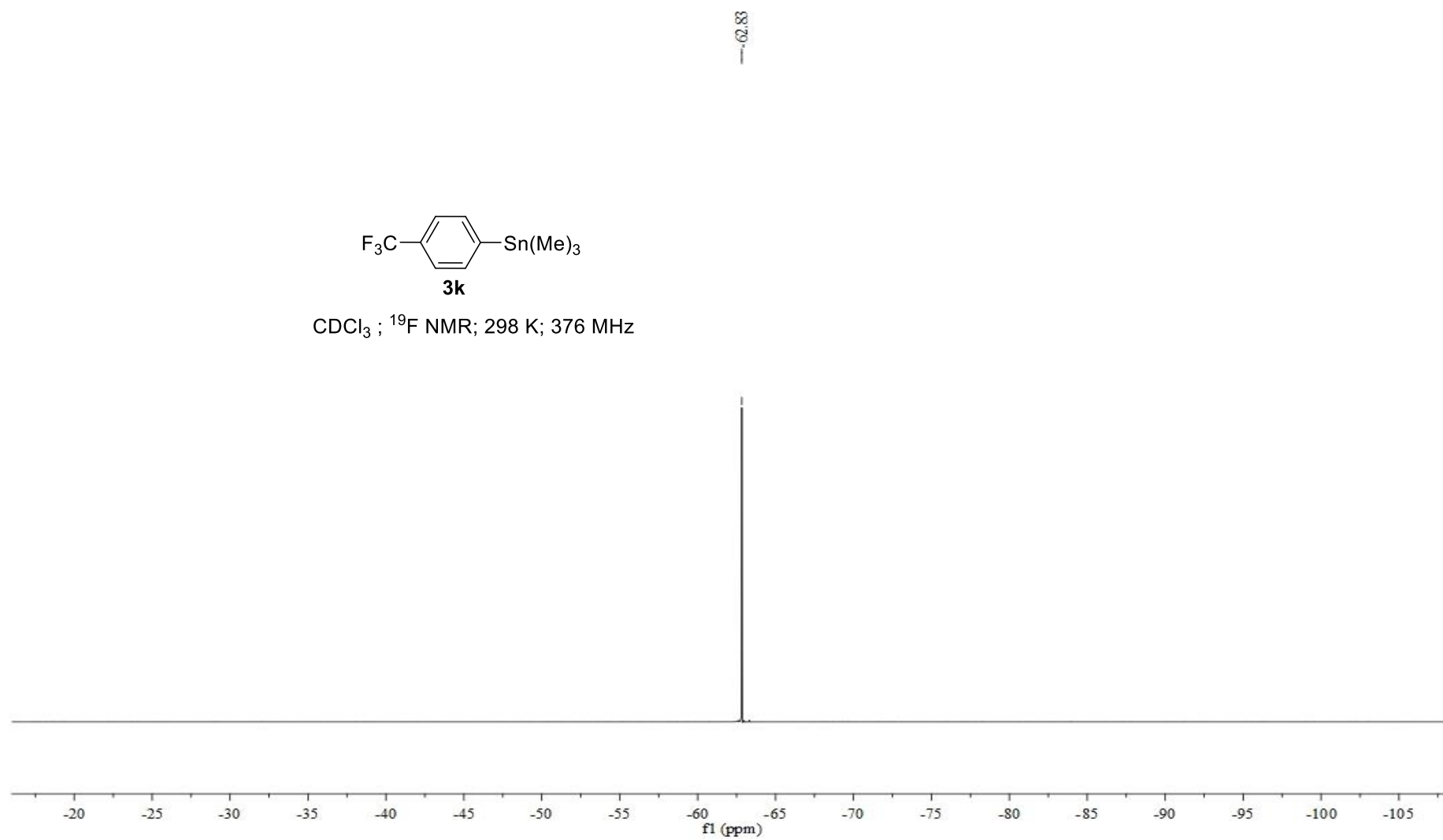


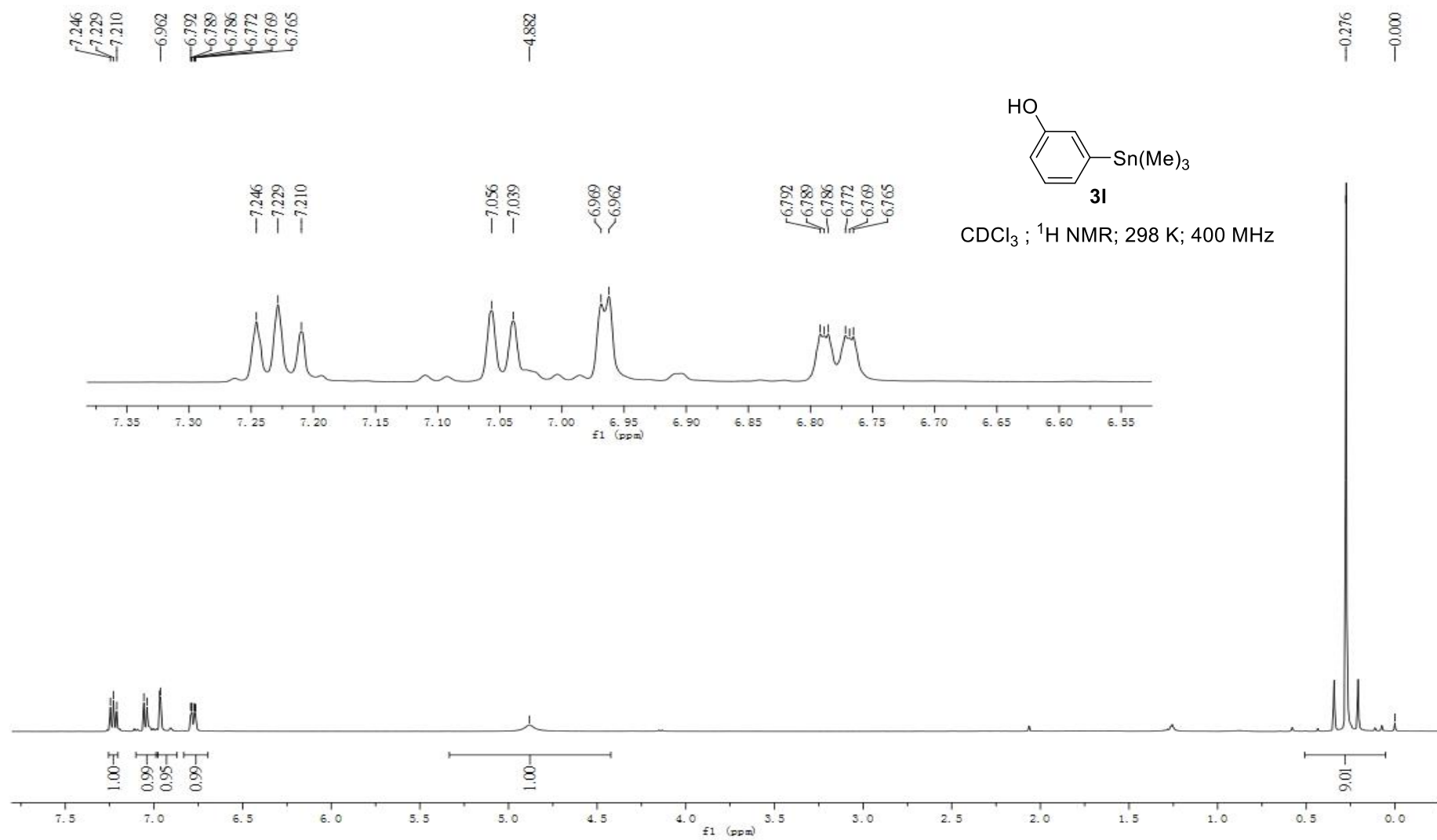


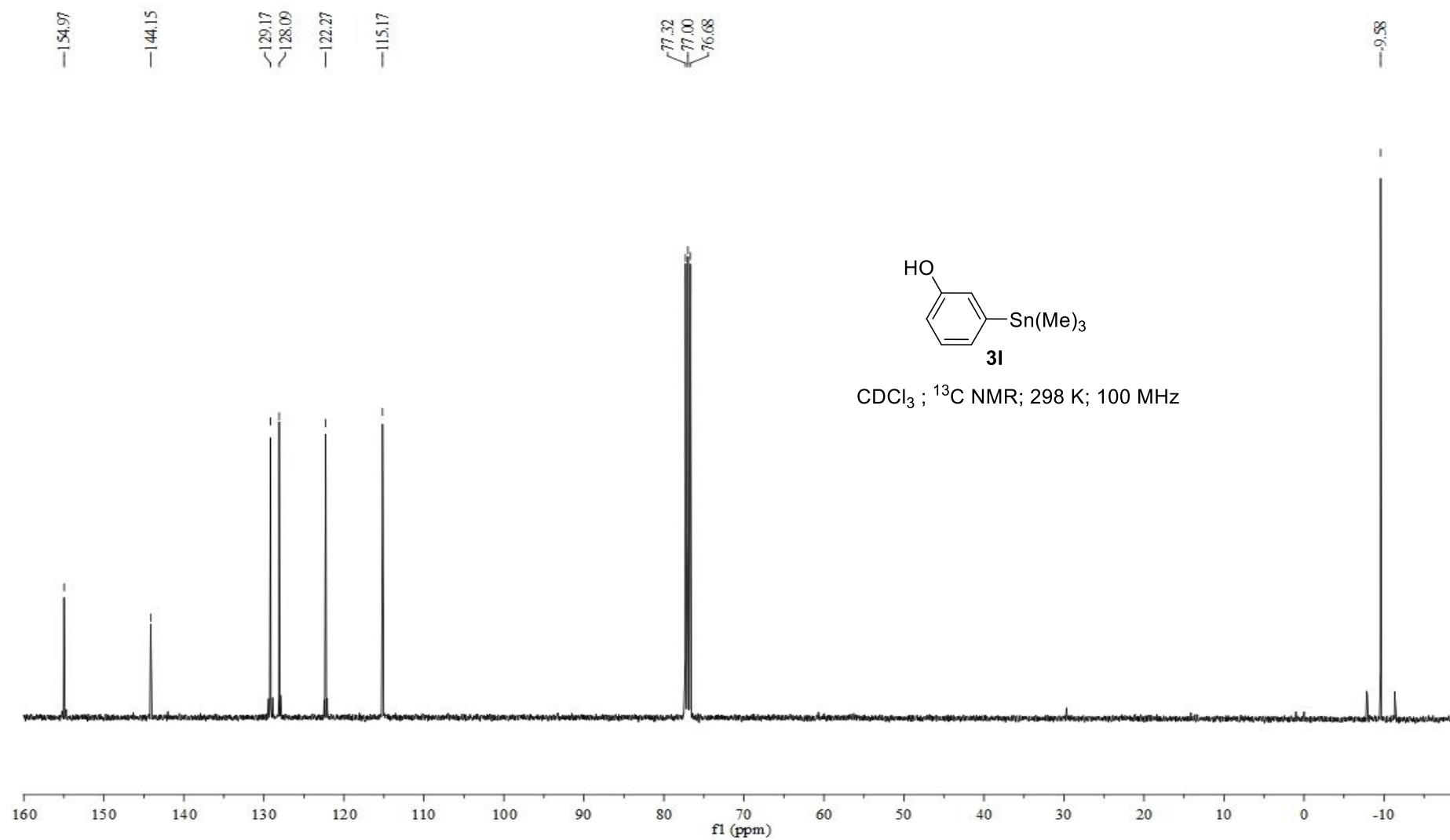


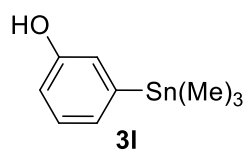


CDCl₃ ; ¹⁹F NMR; 298 K; 376 MHz



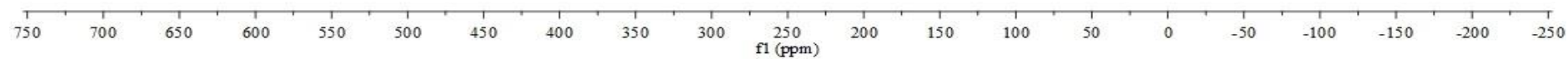


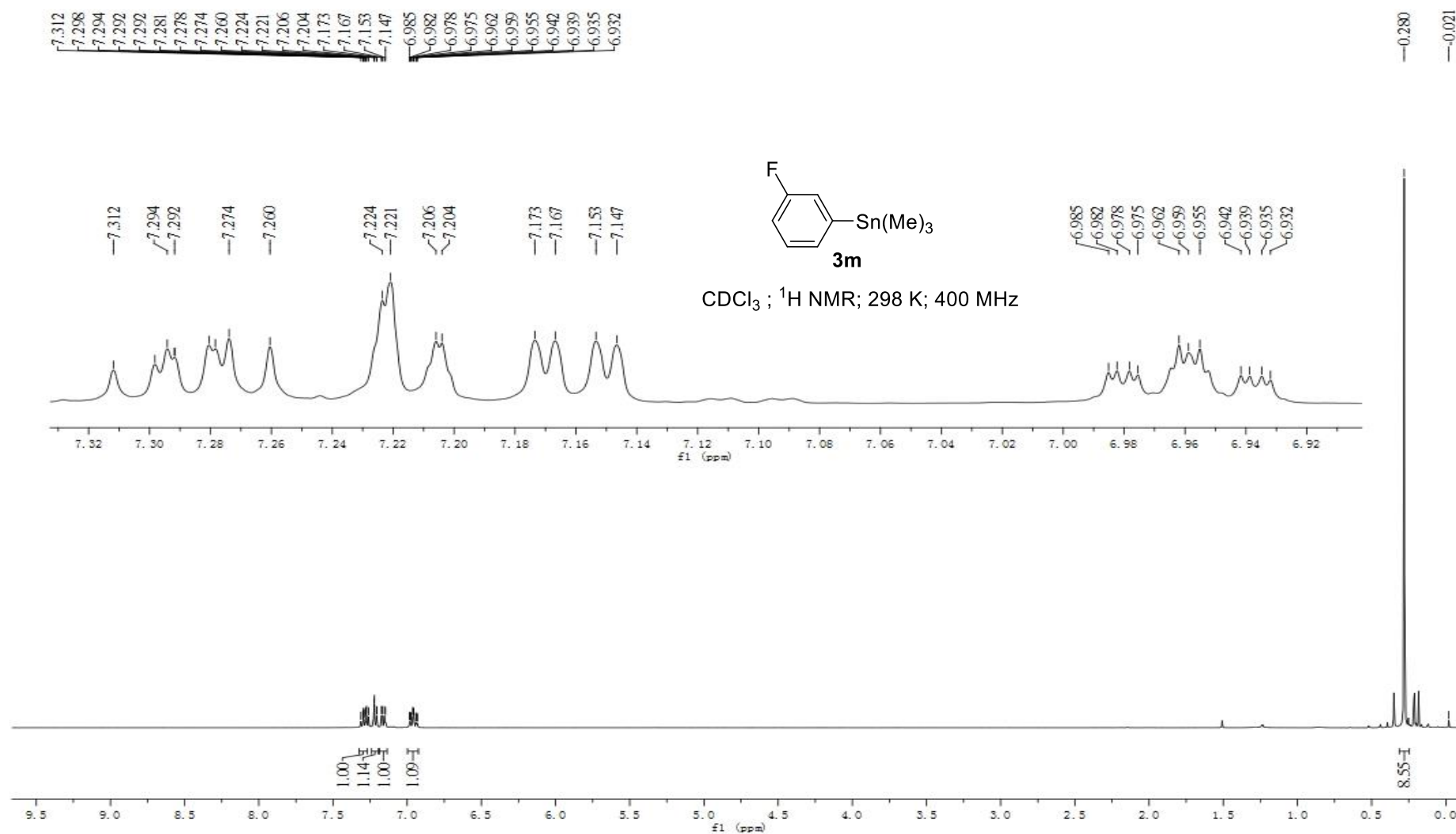


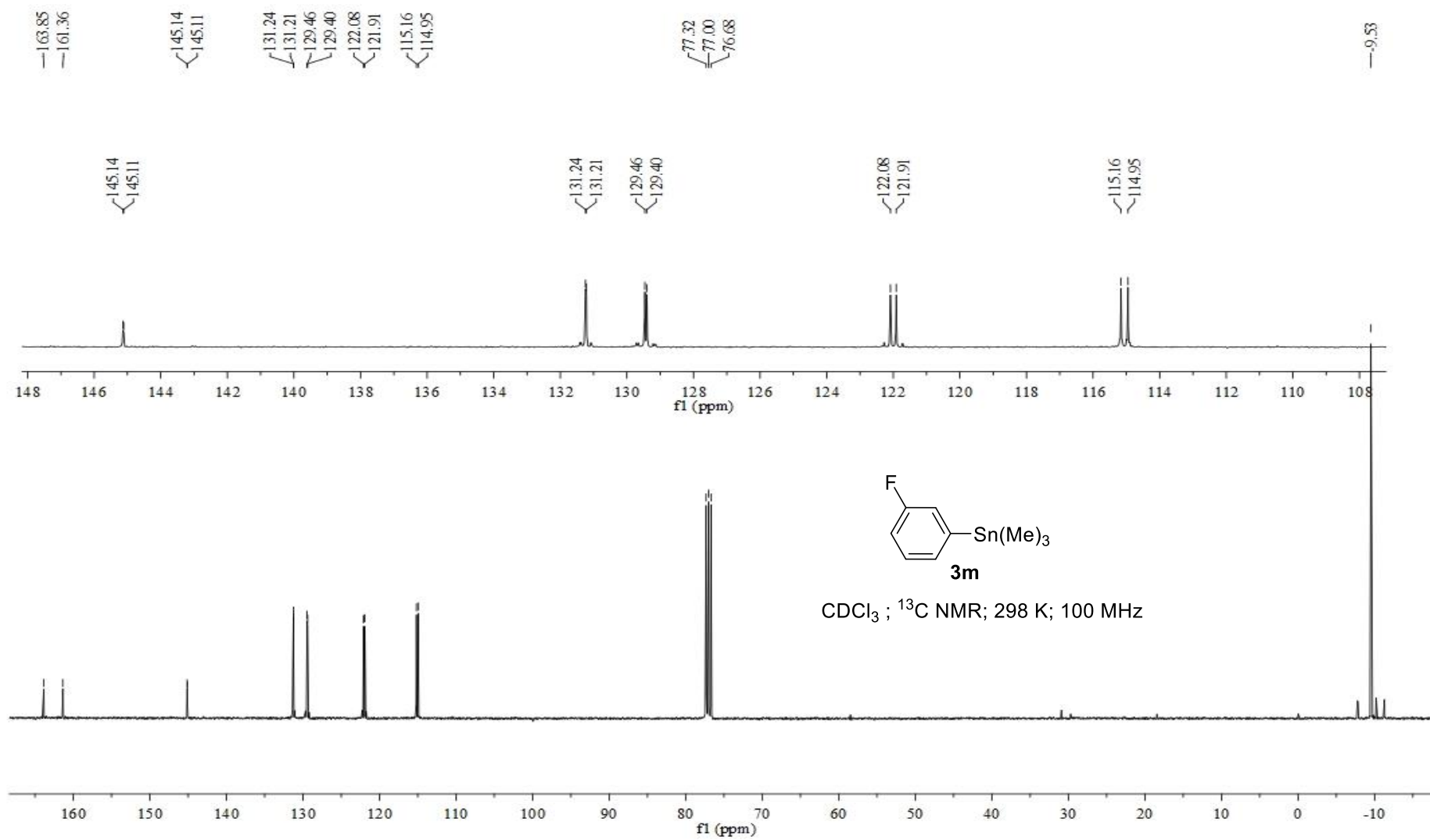


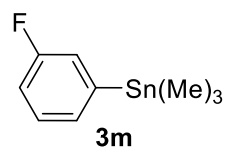
CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

—24.85

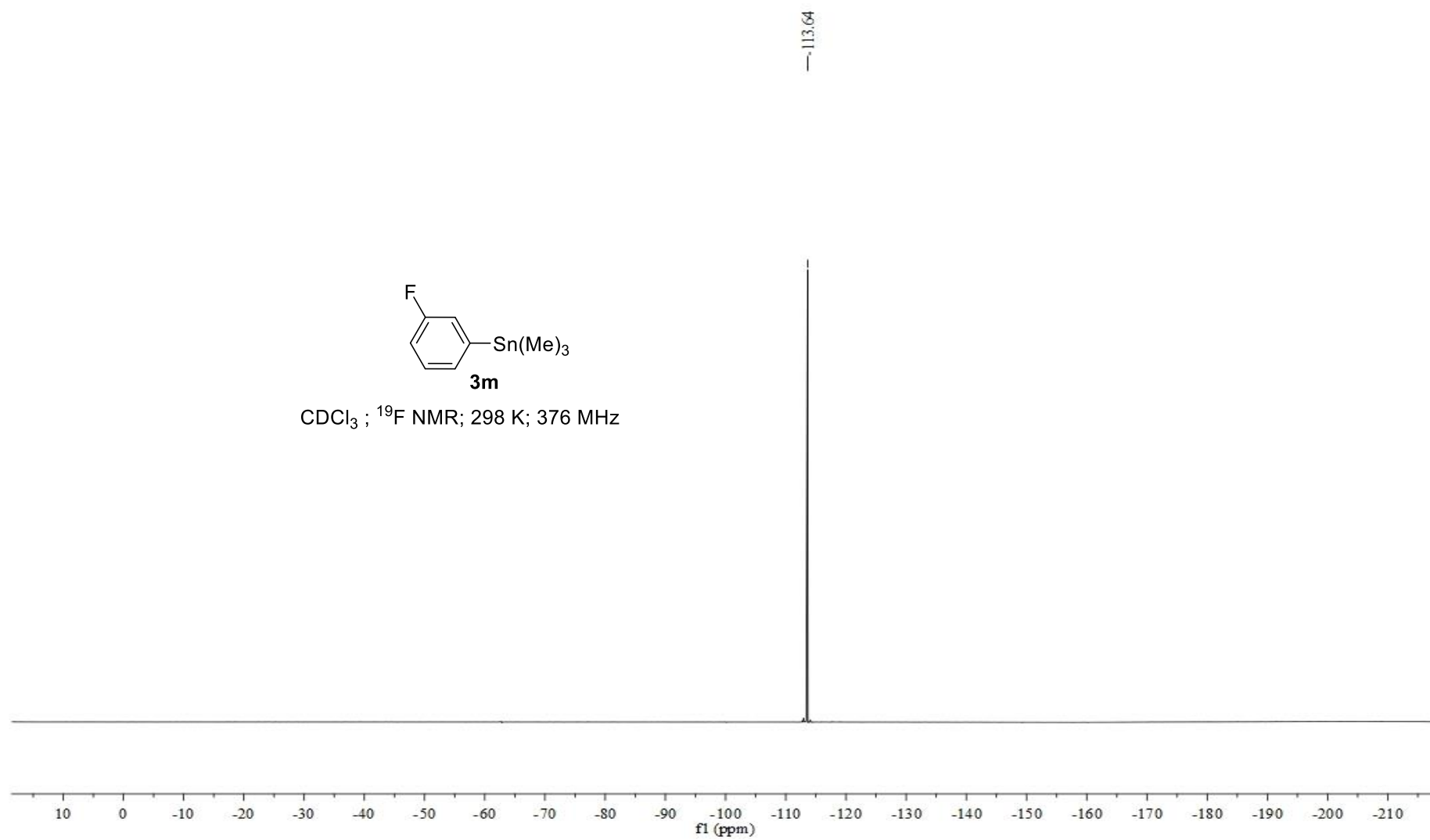


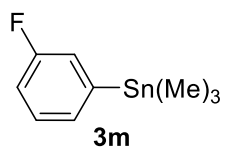




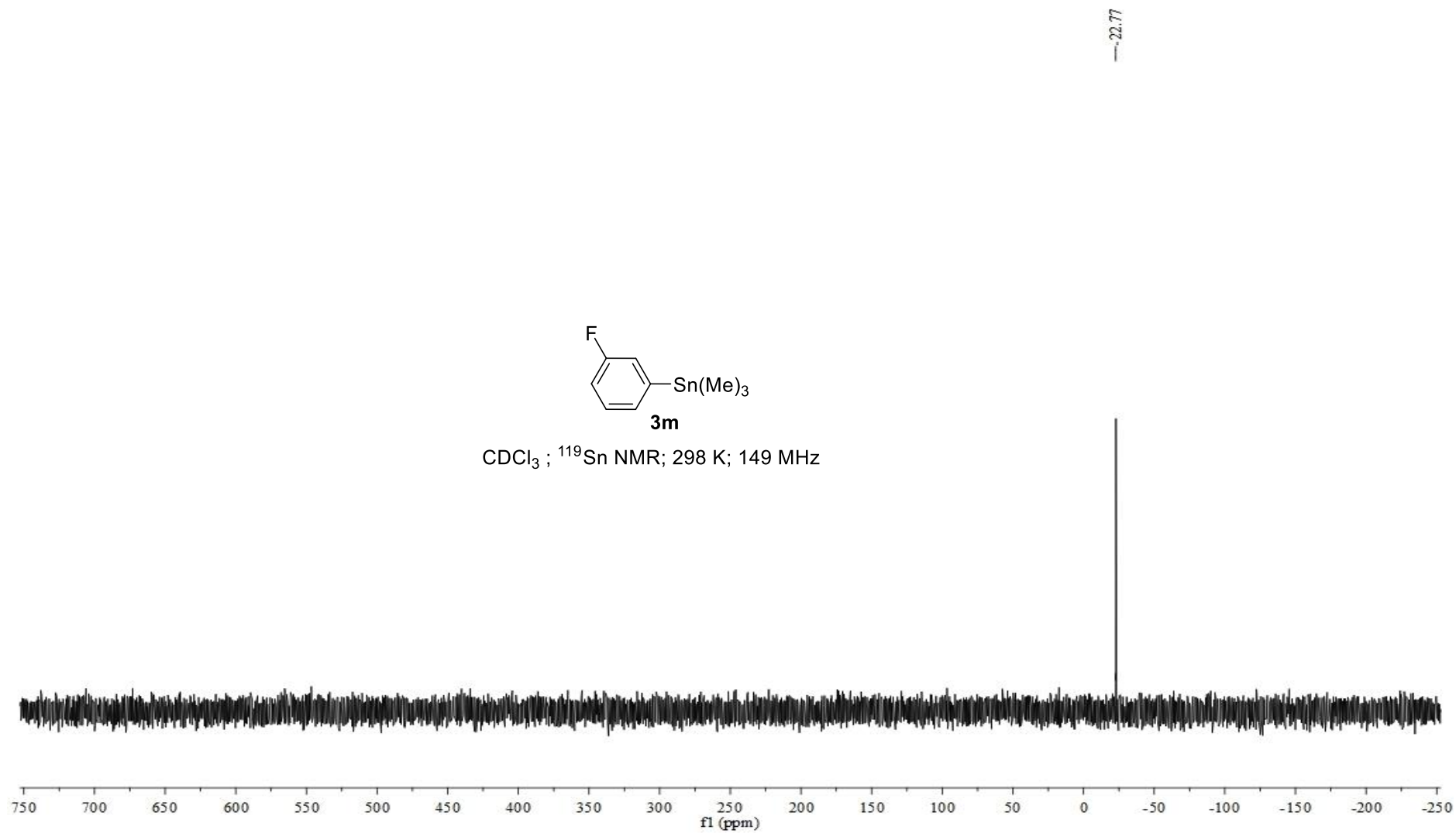


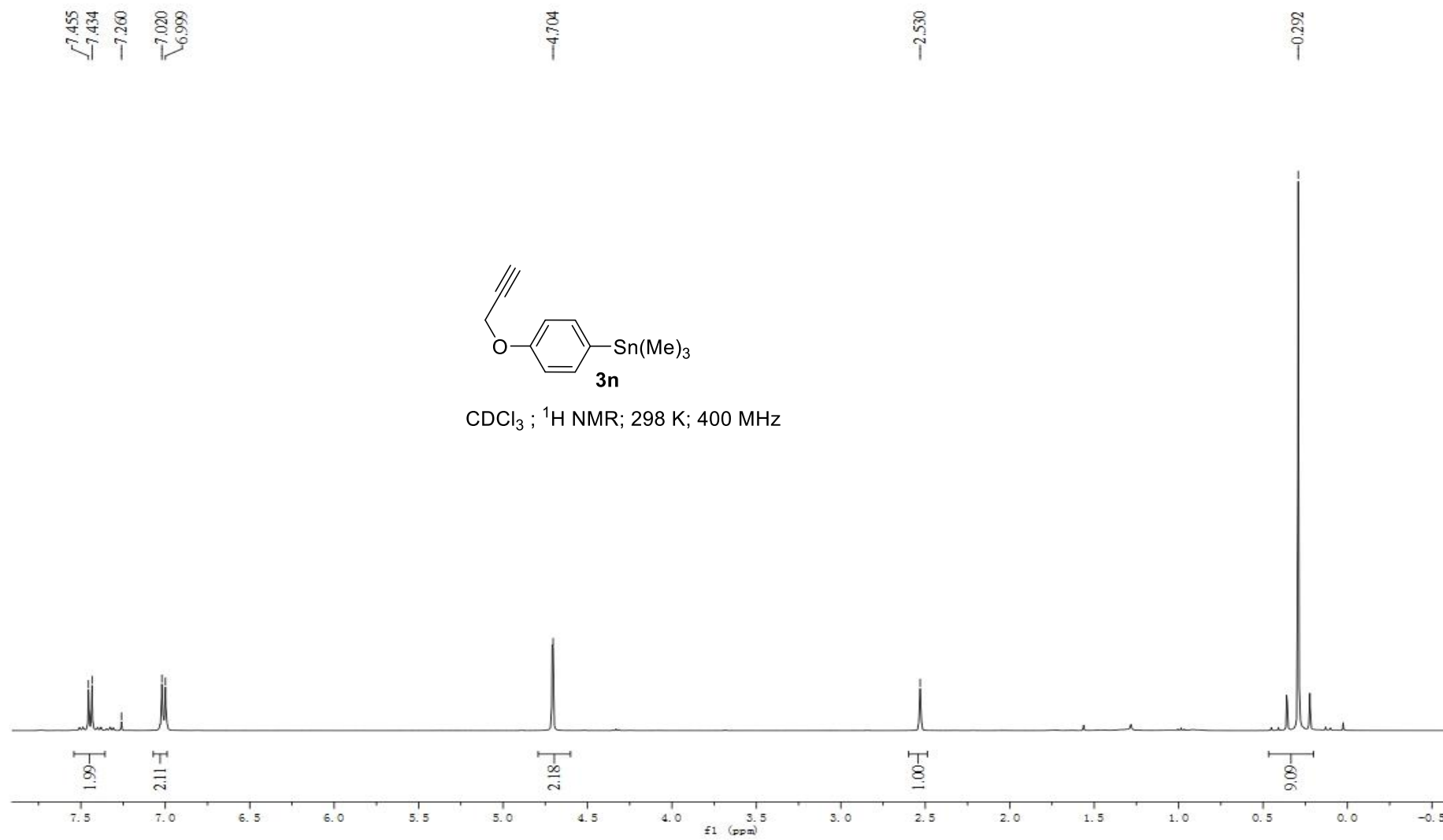
CDCl_3 ; ^{19}F NMR; 298 K; 376 MHz

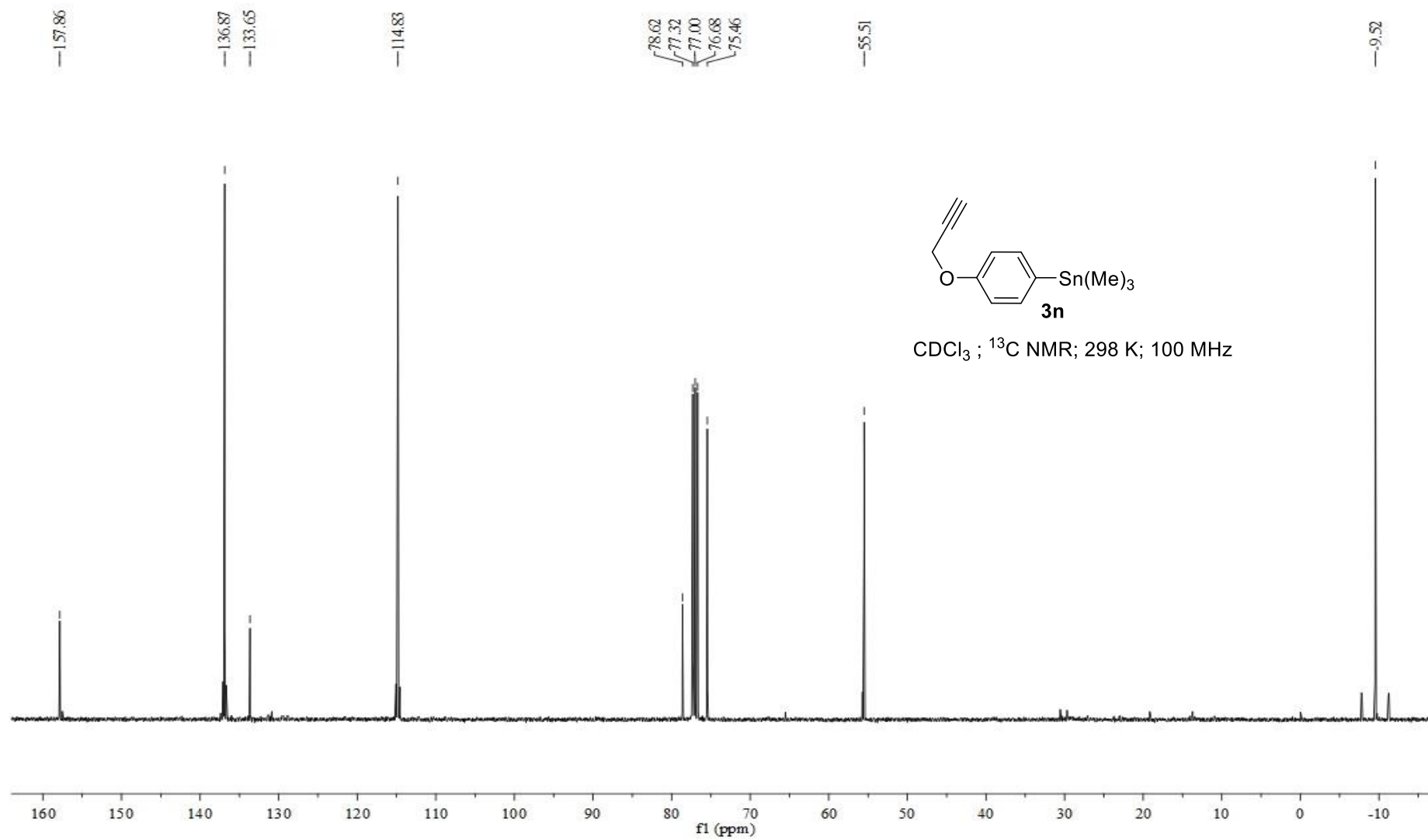


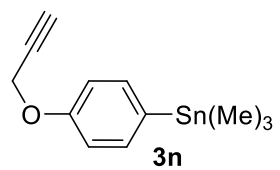


CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

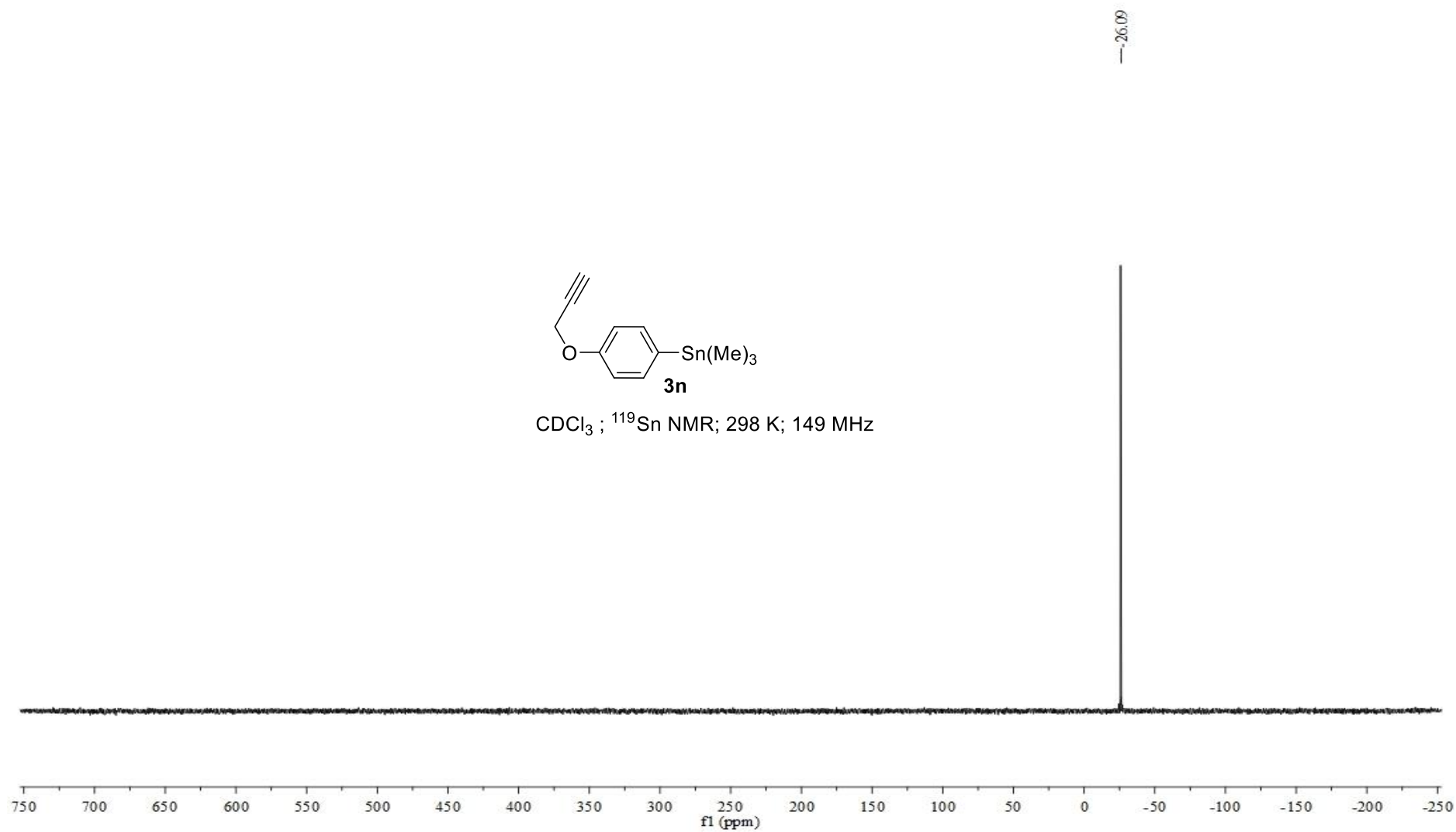


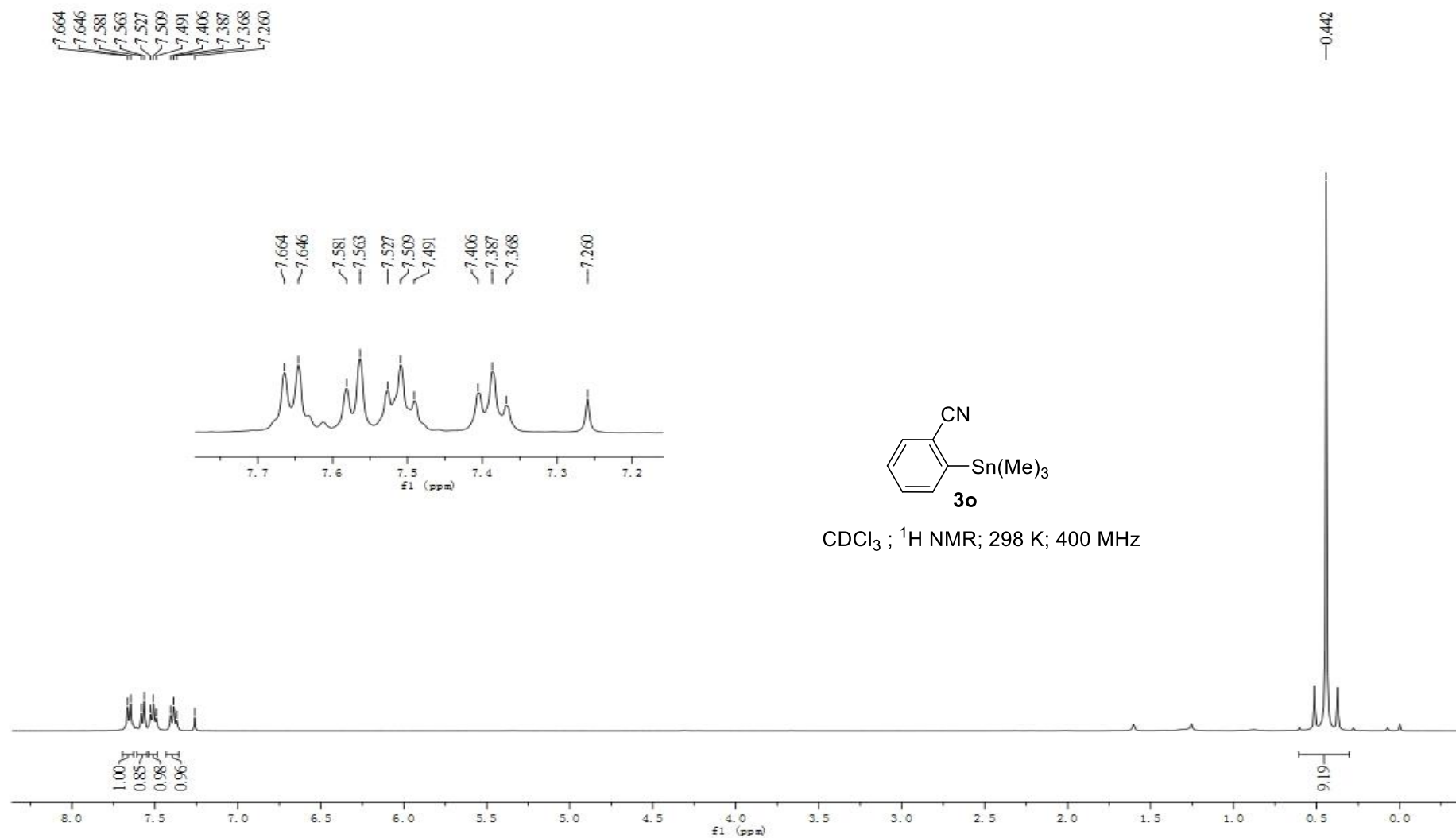


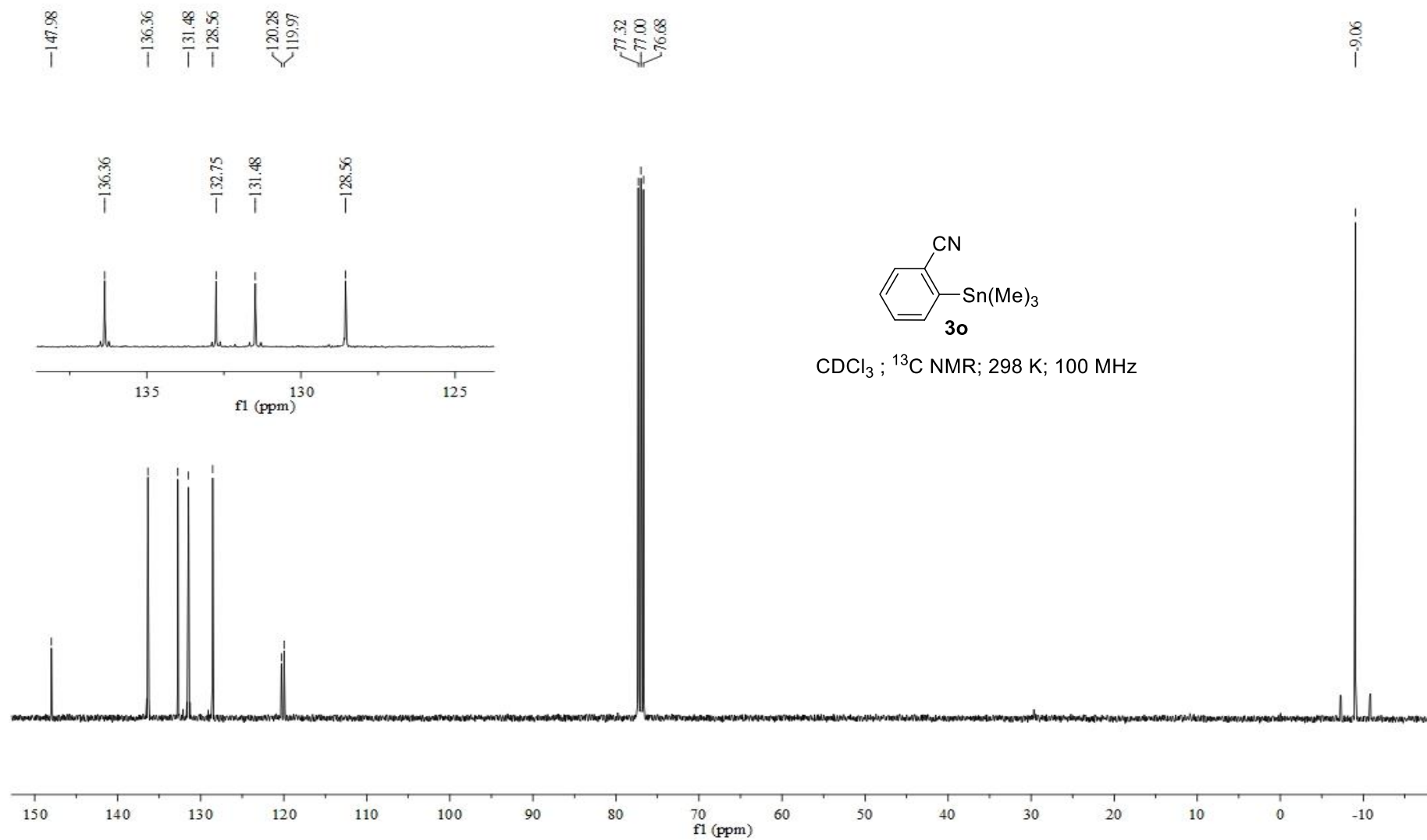


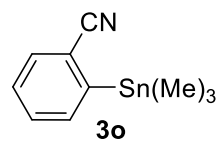


CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

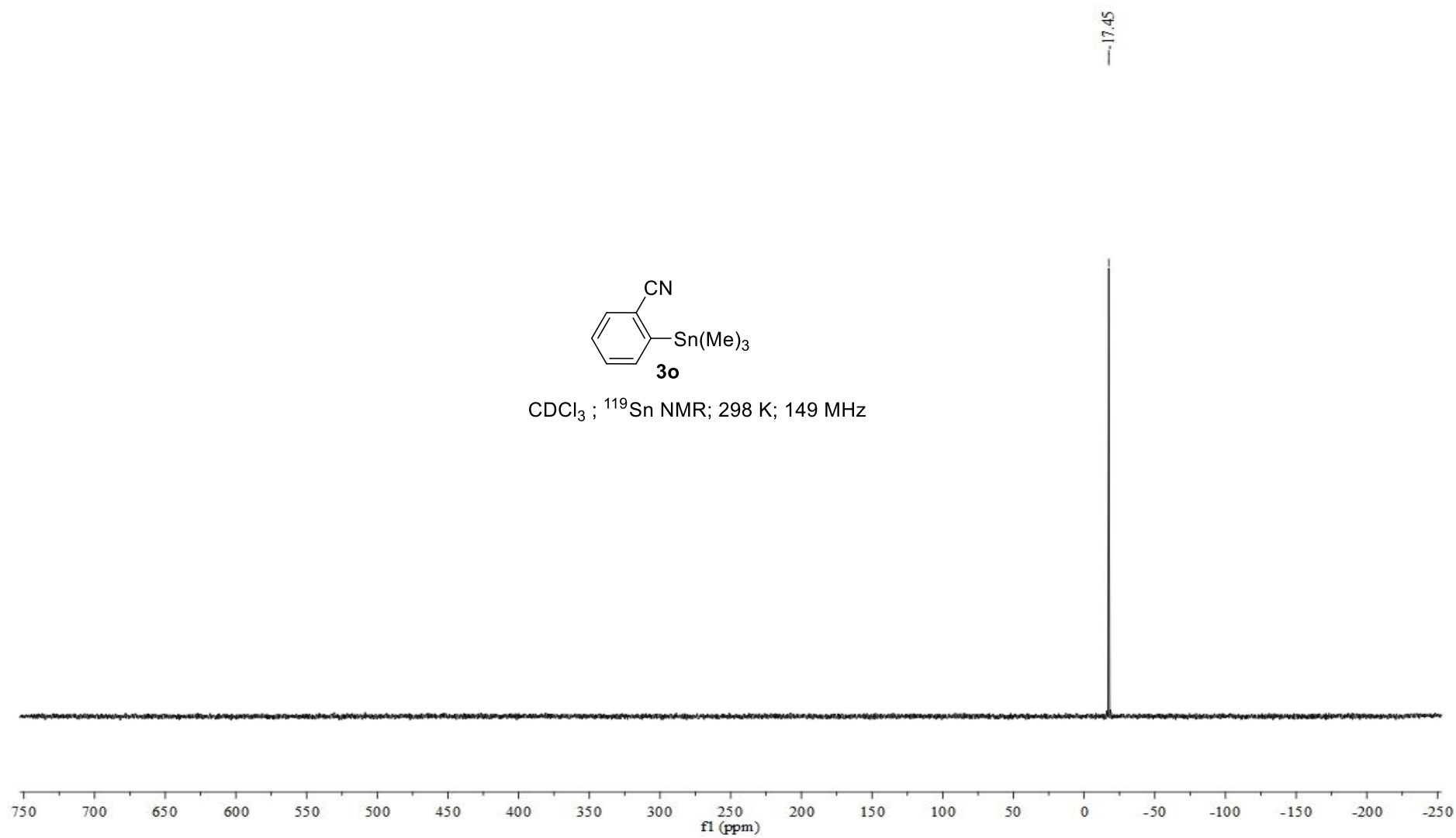


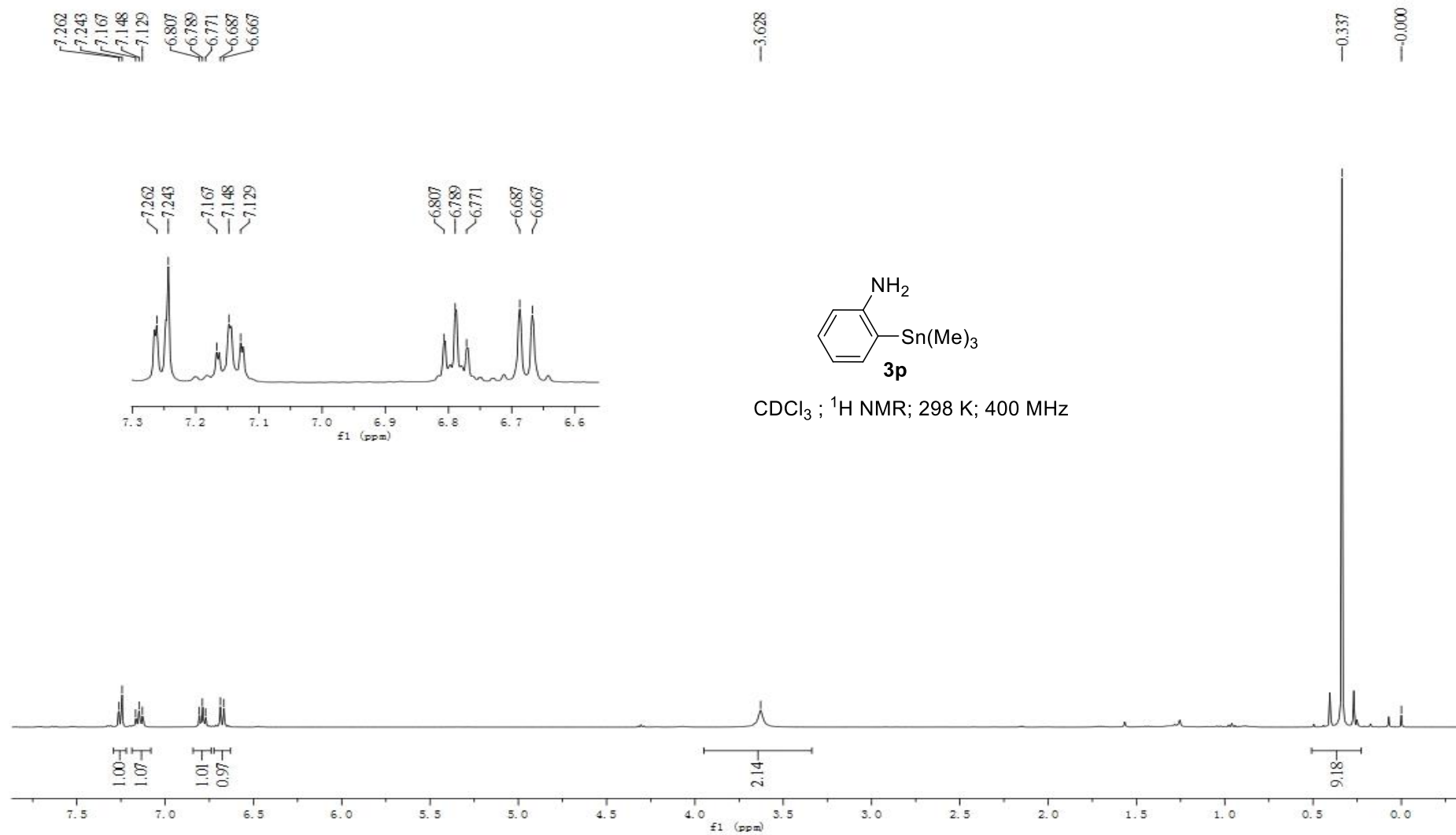


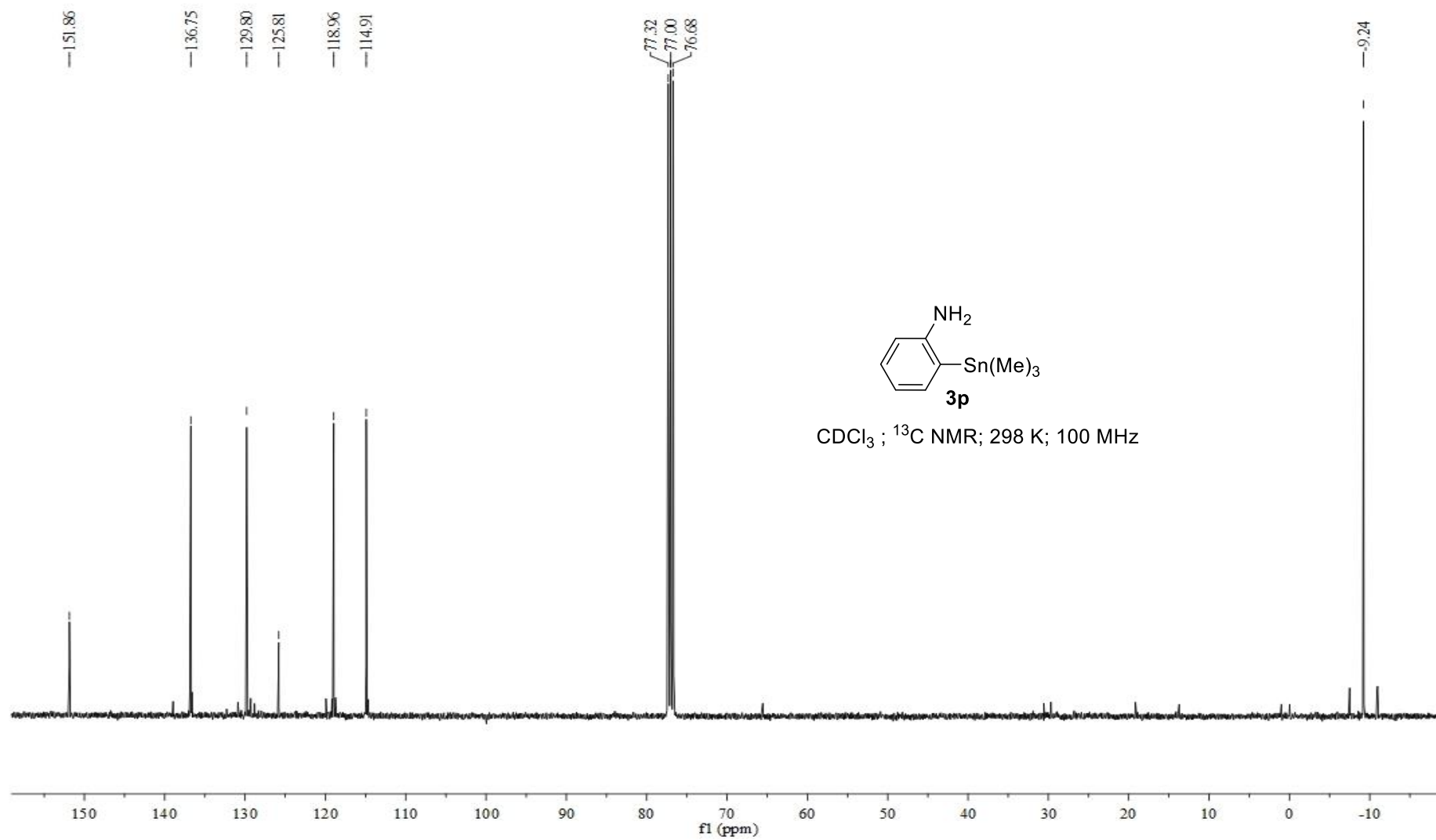


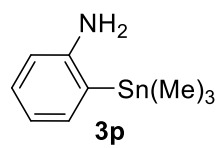


CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

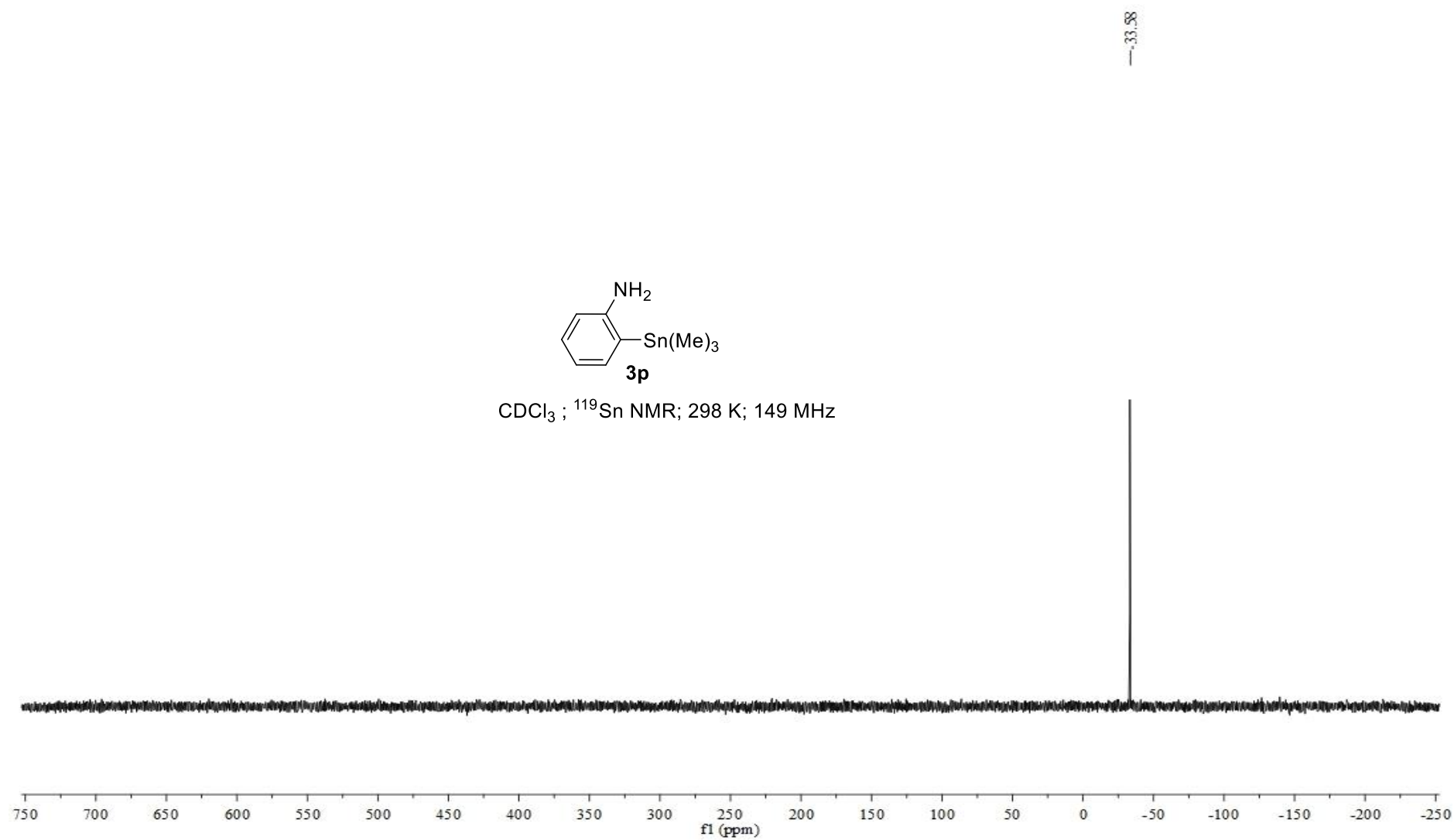


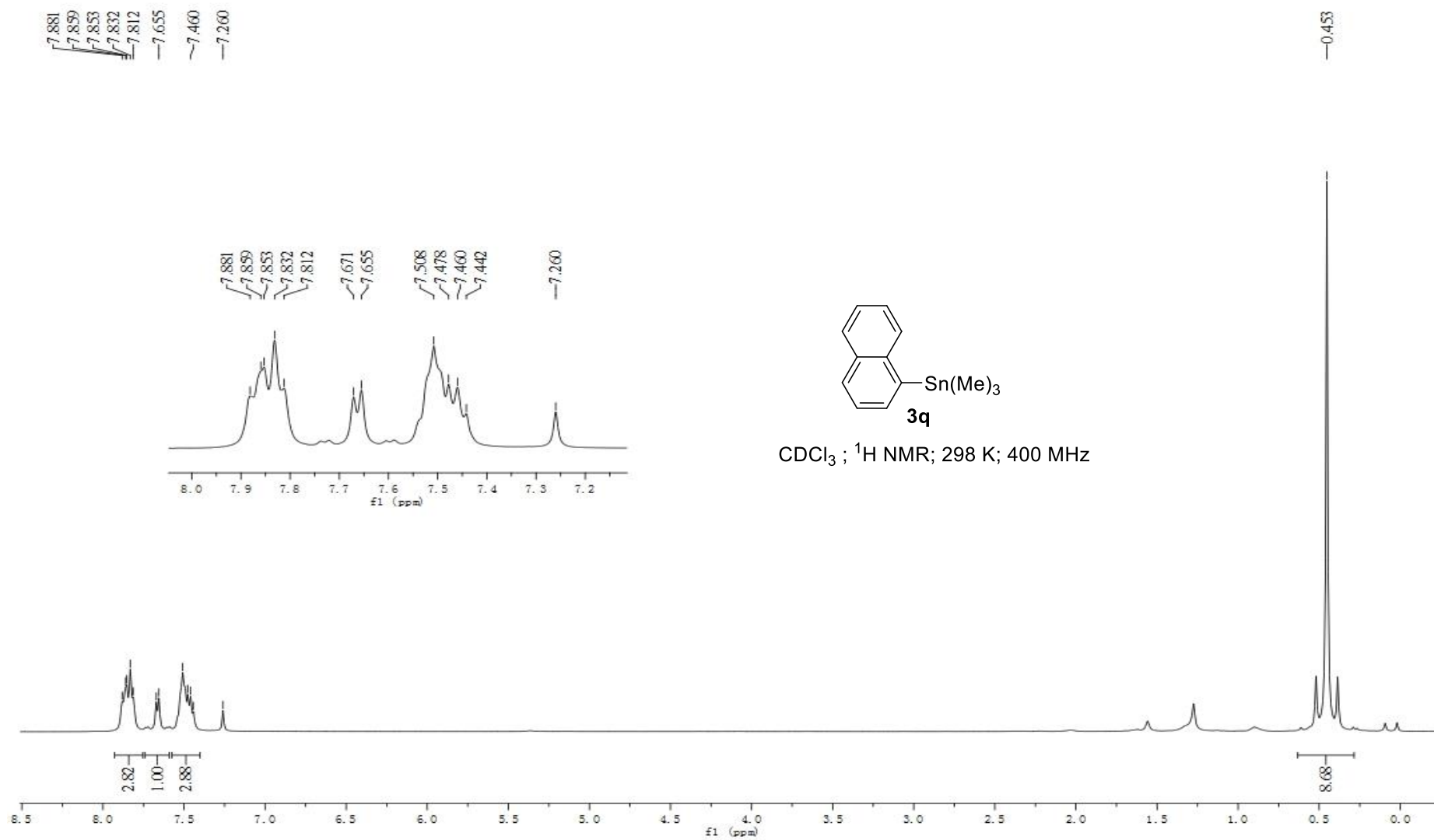


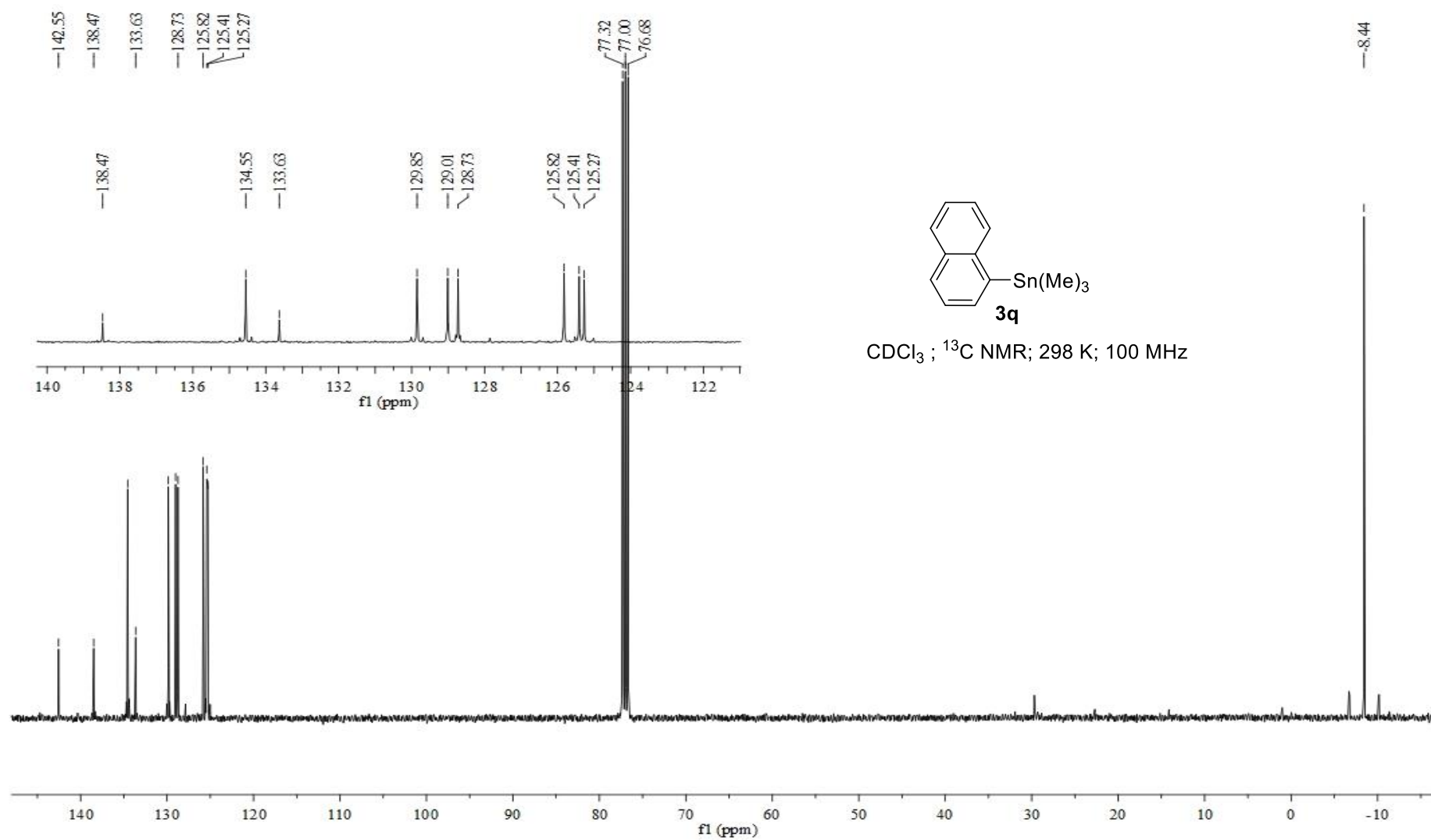


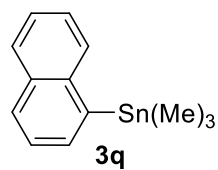


CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

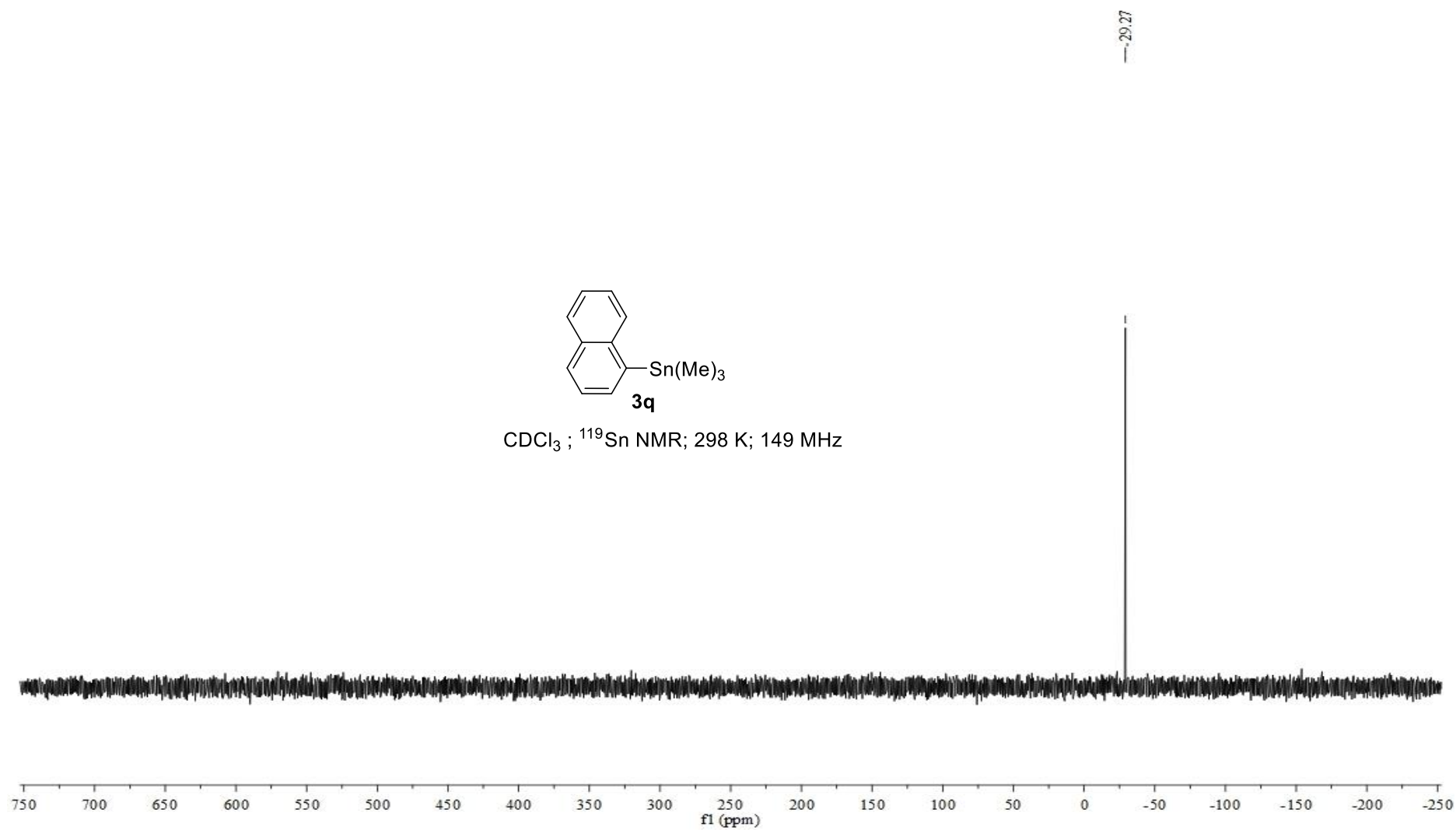


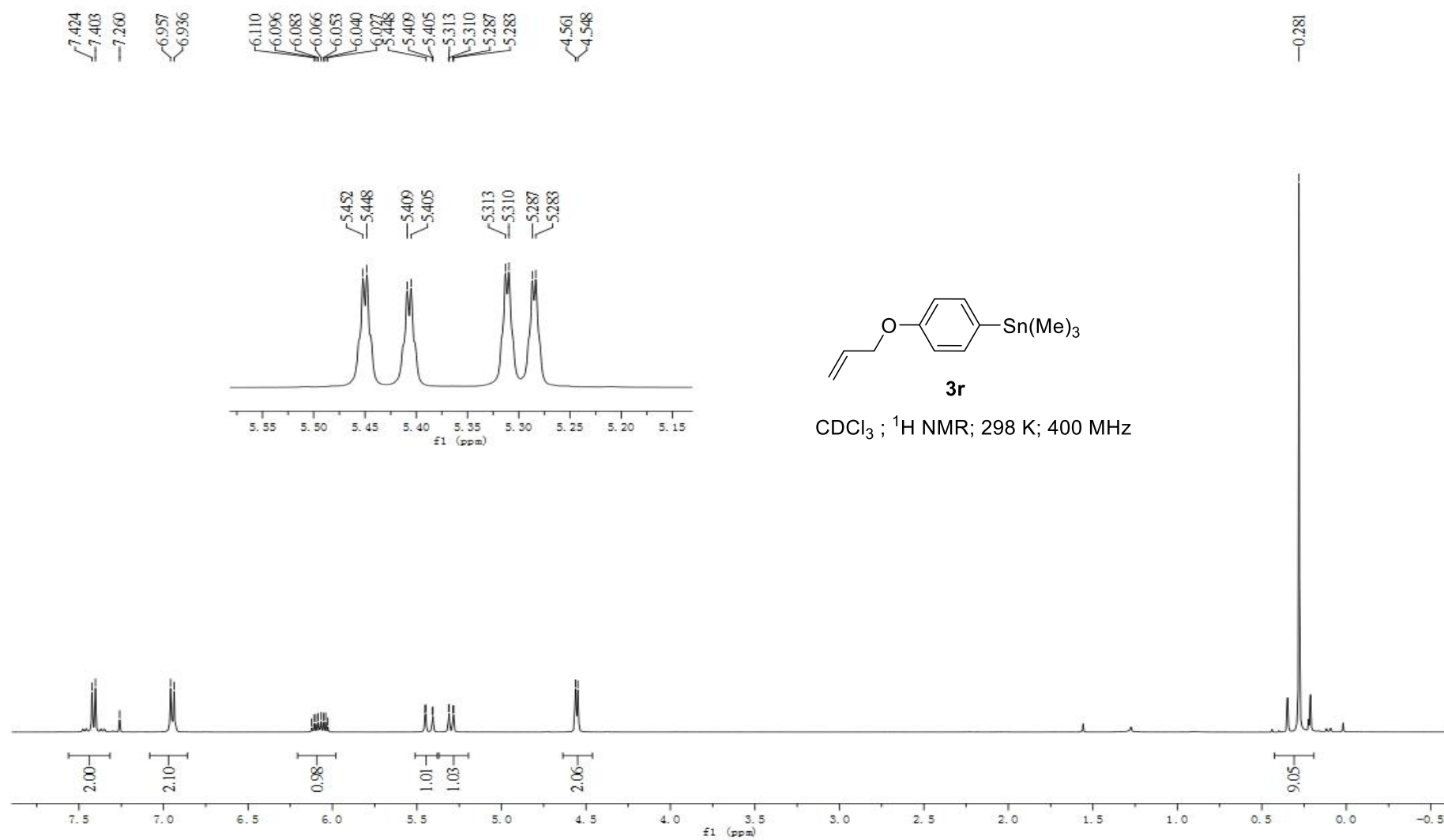


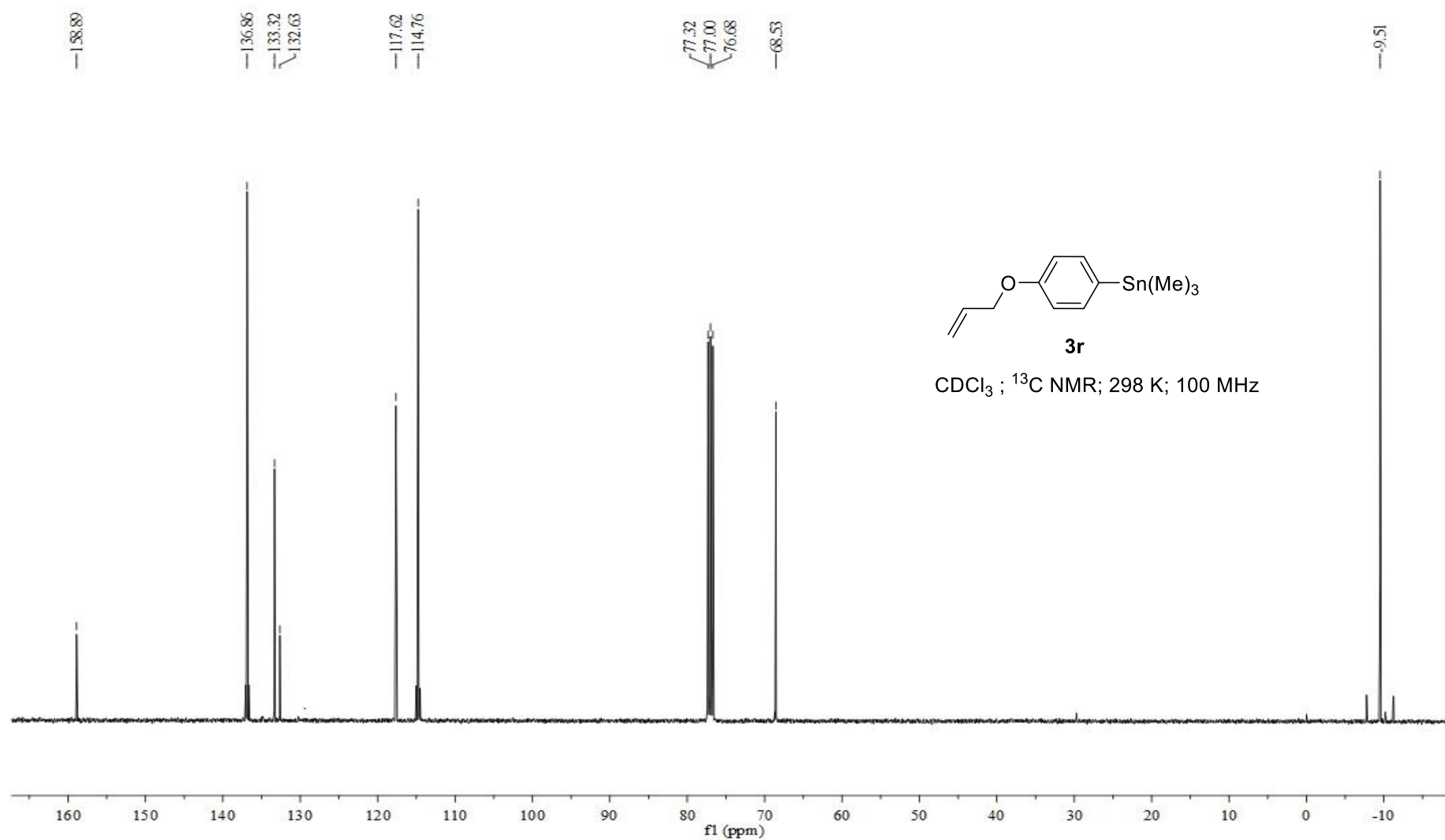


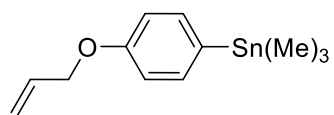


CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

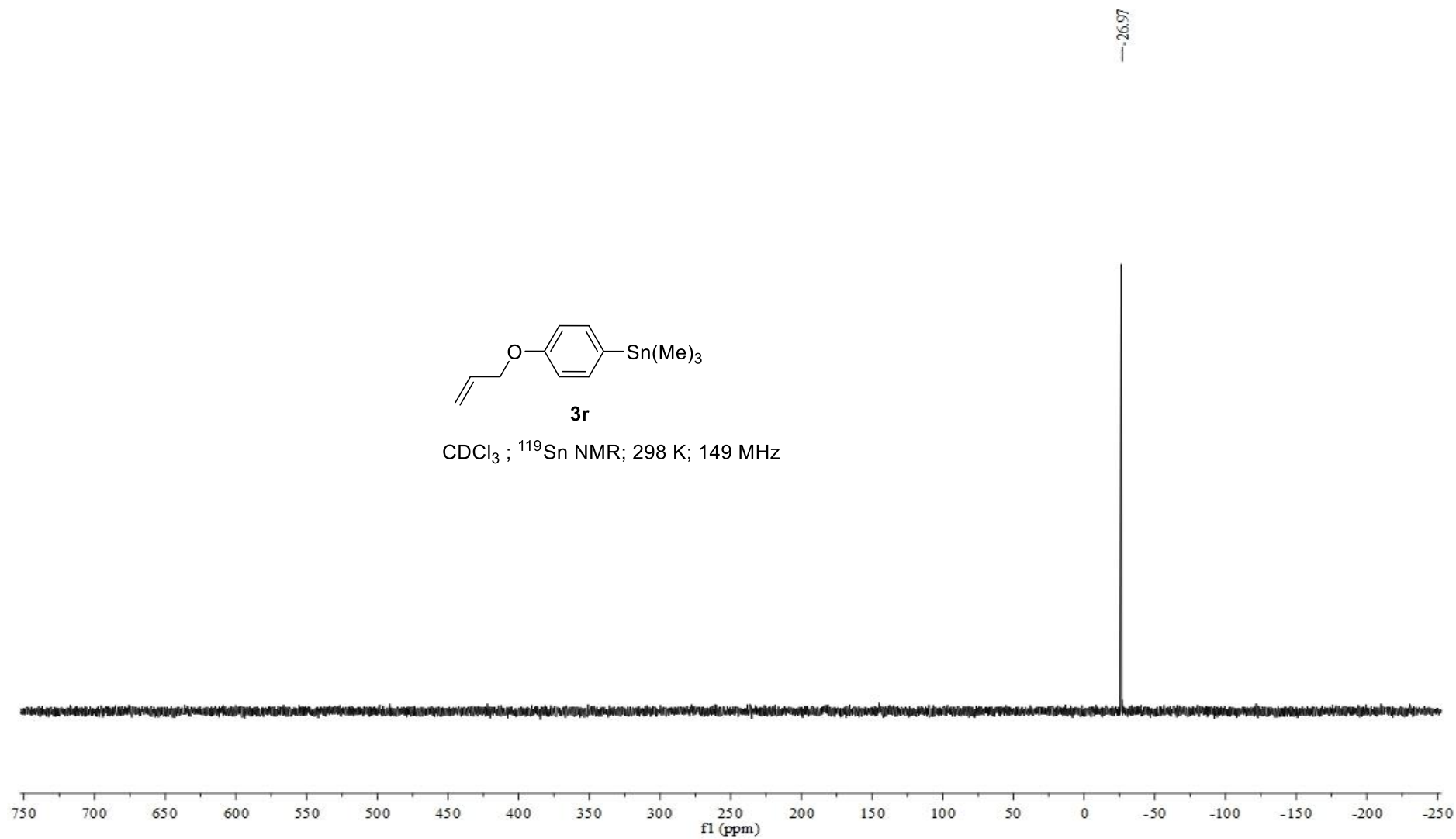


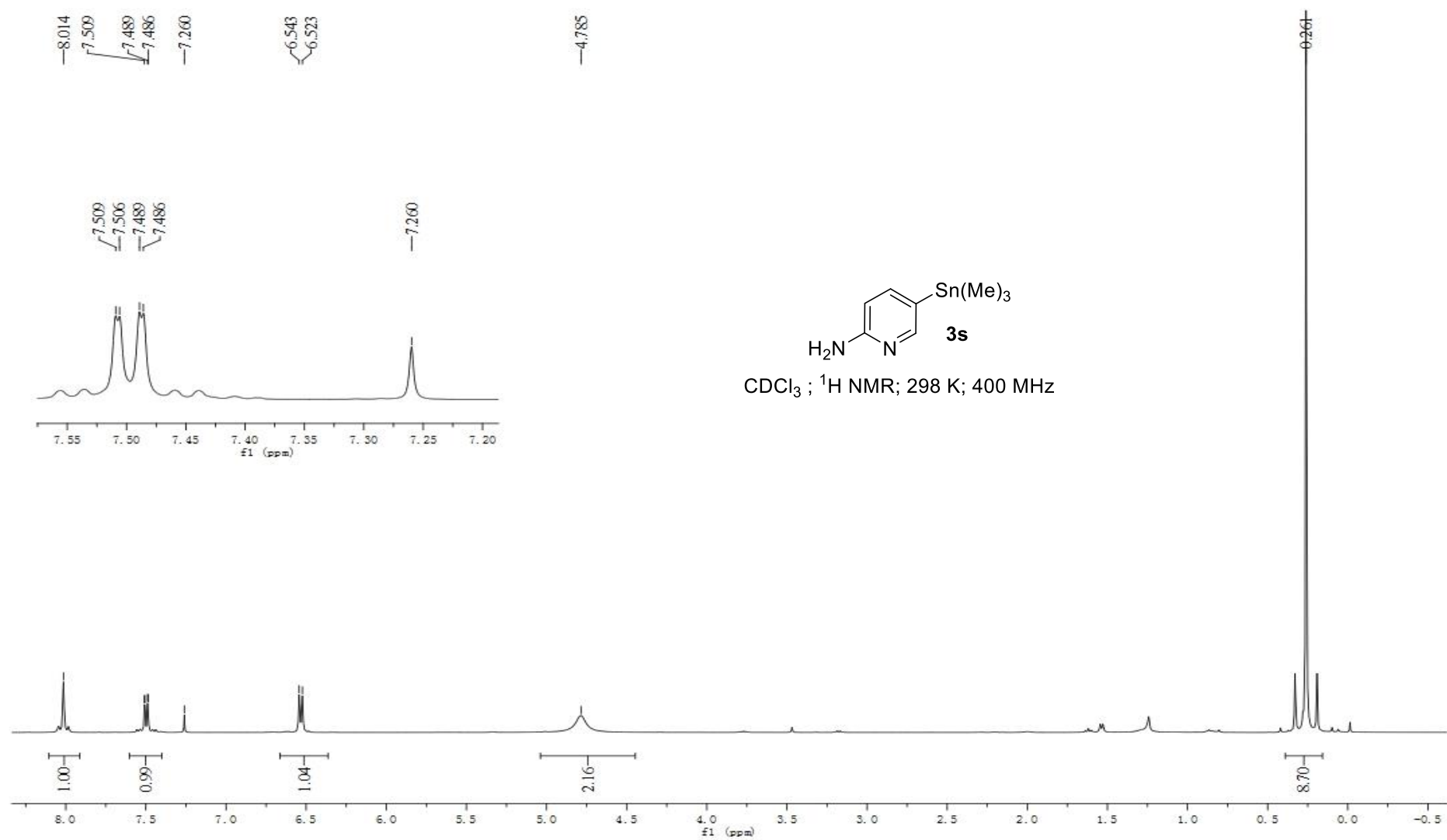


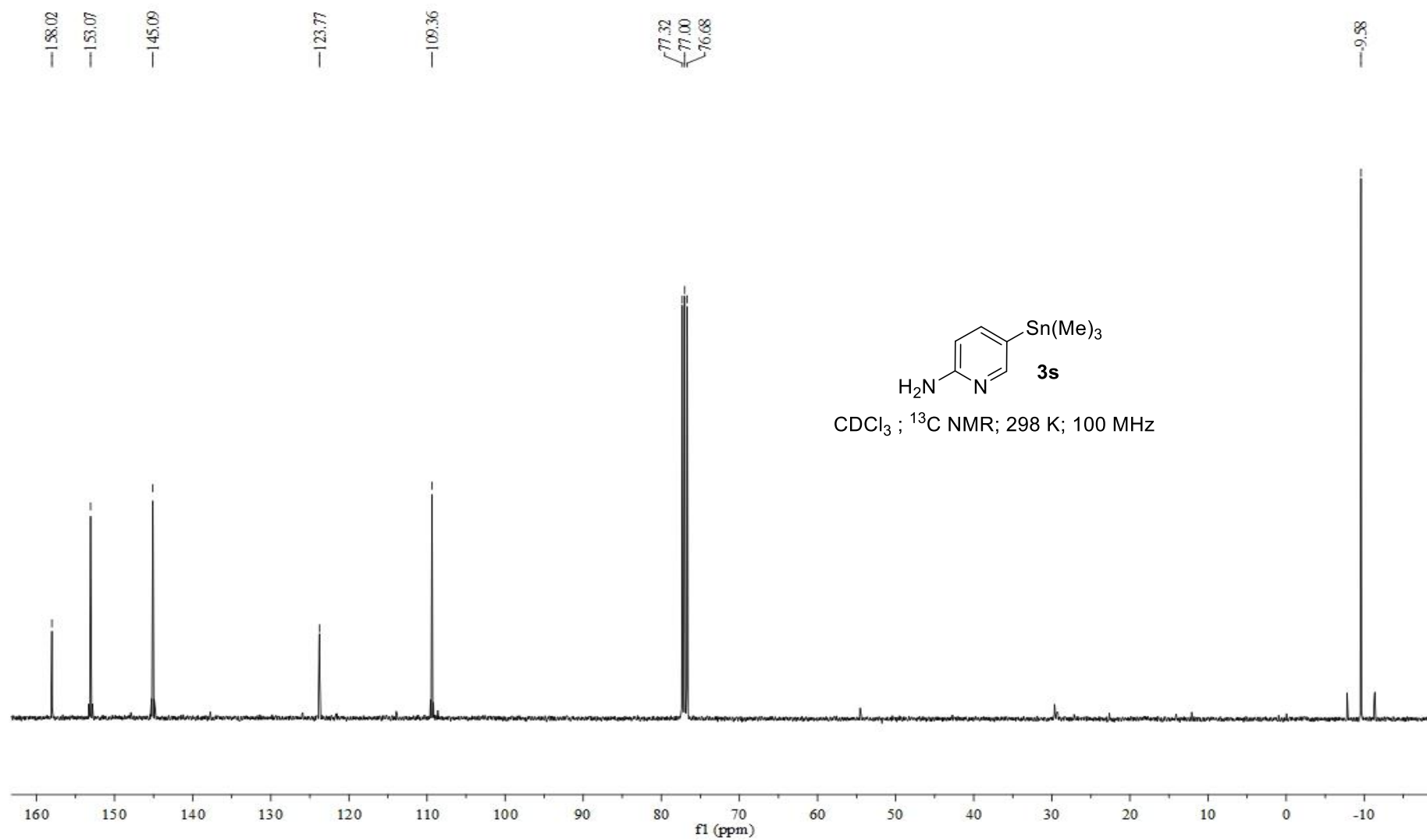


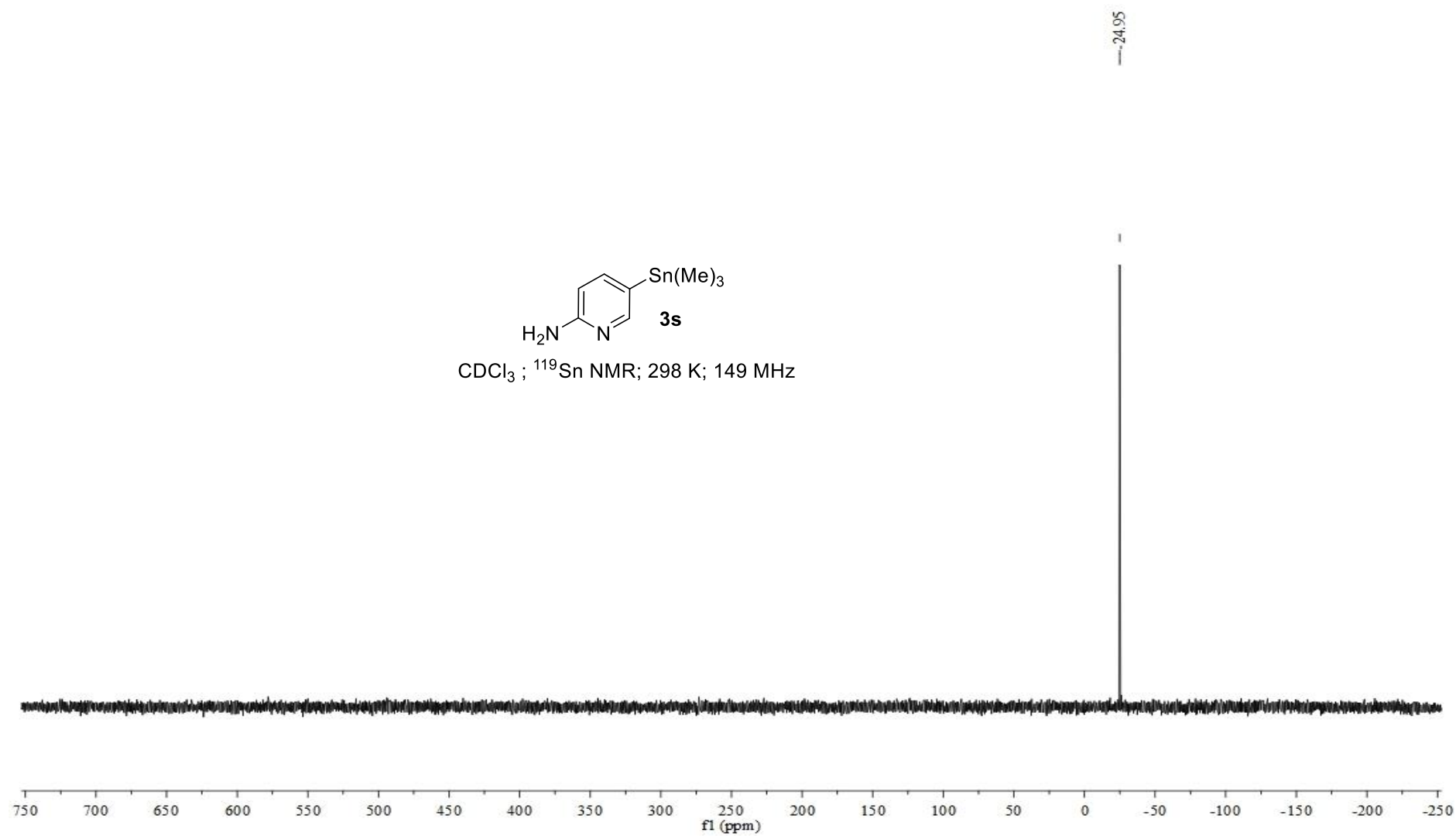
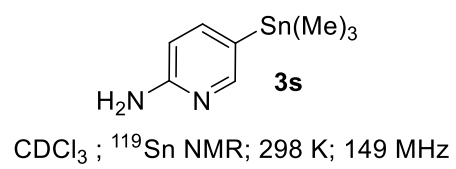


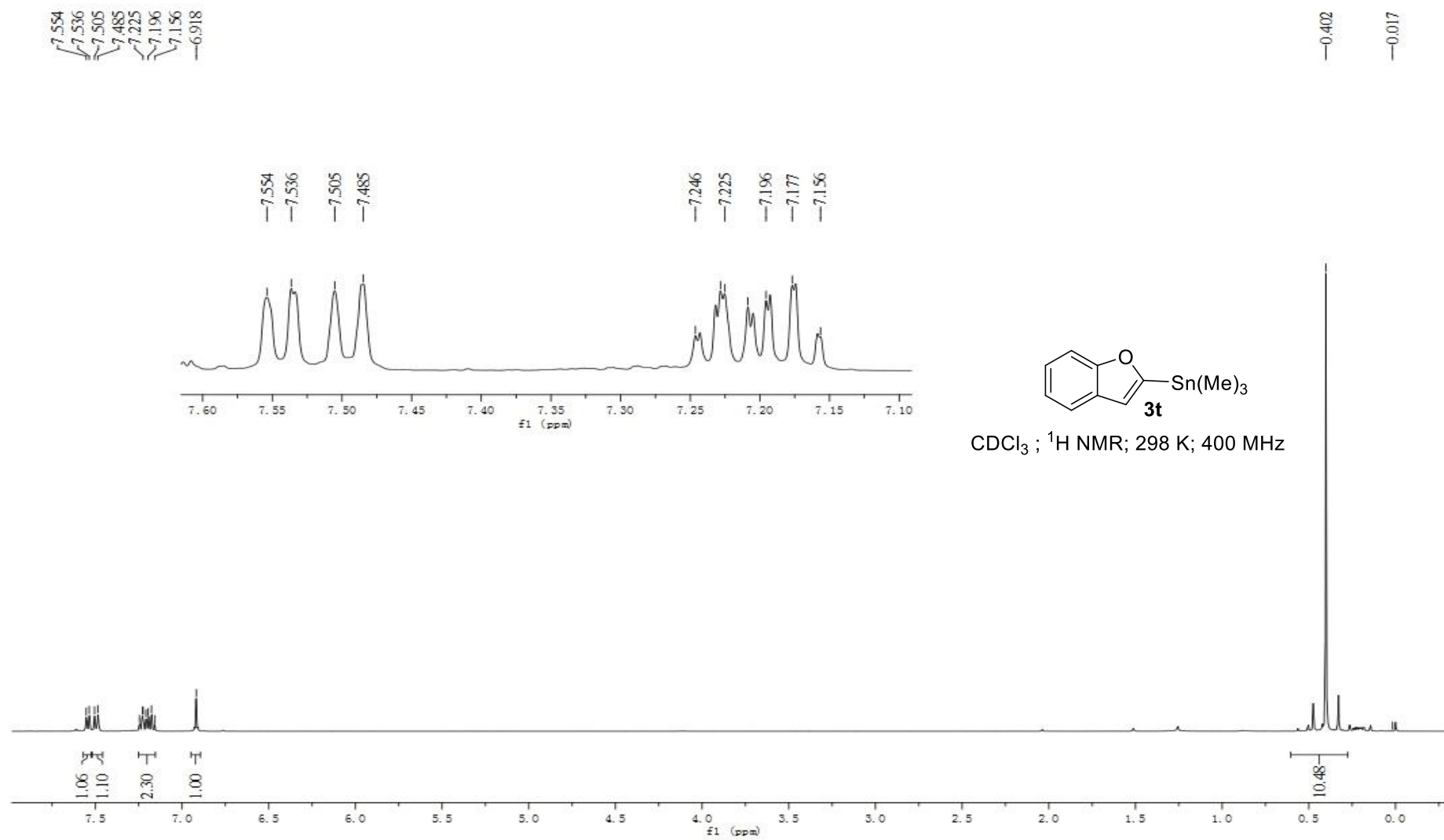
CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

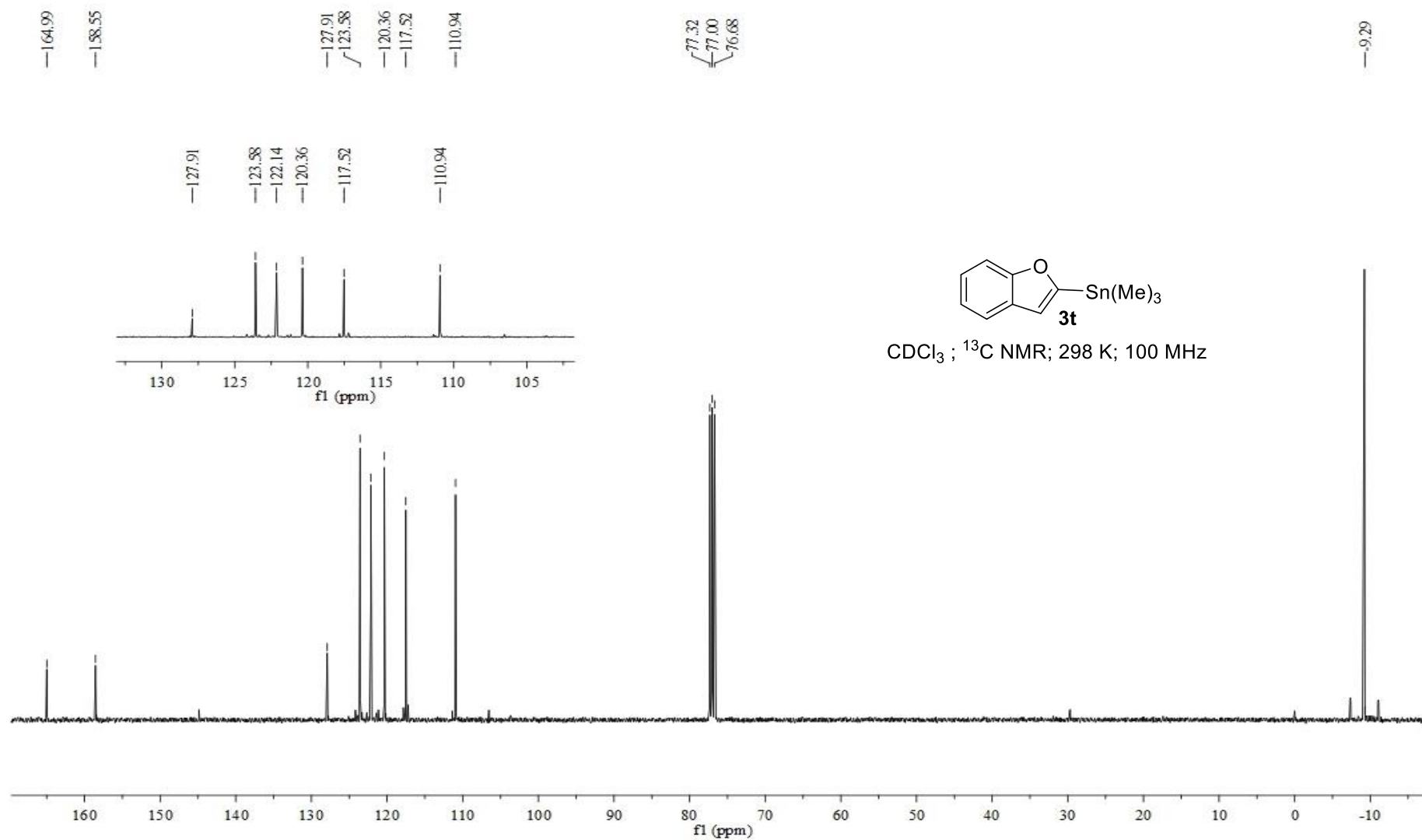


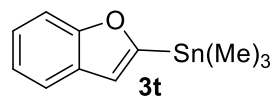




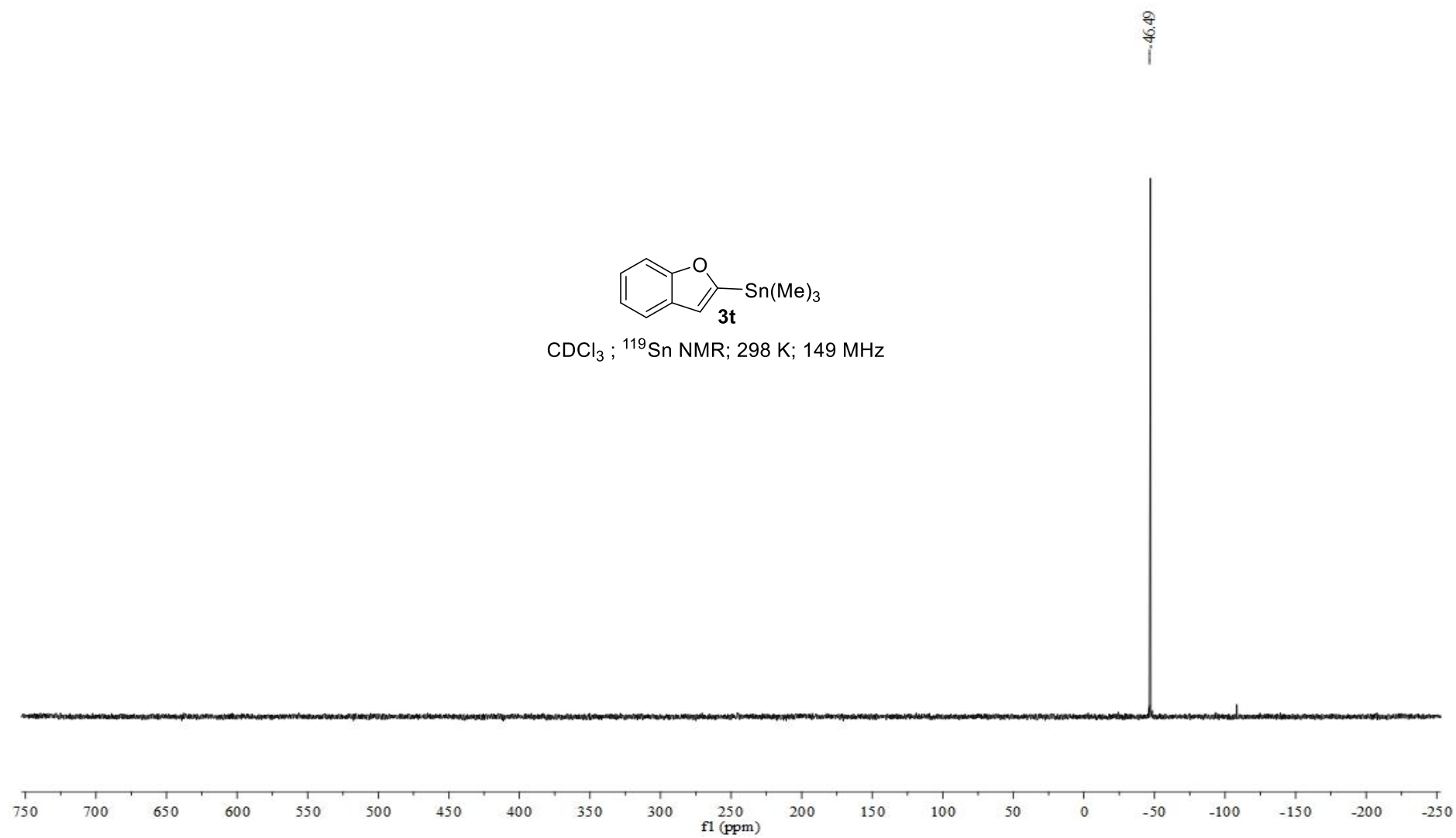


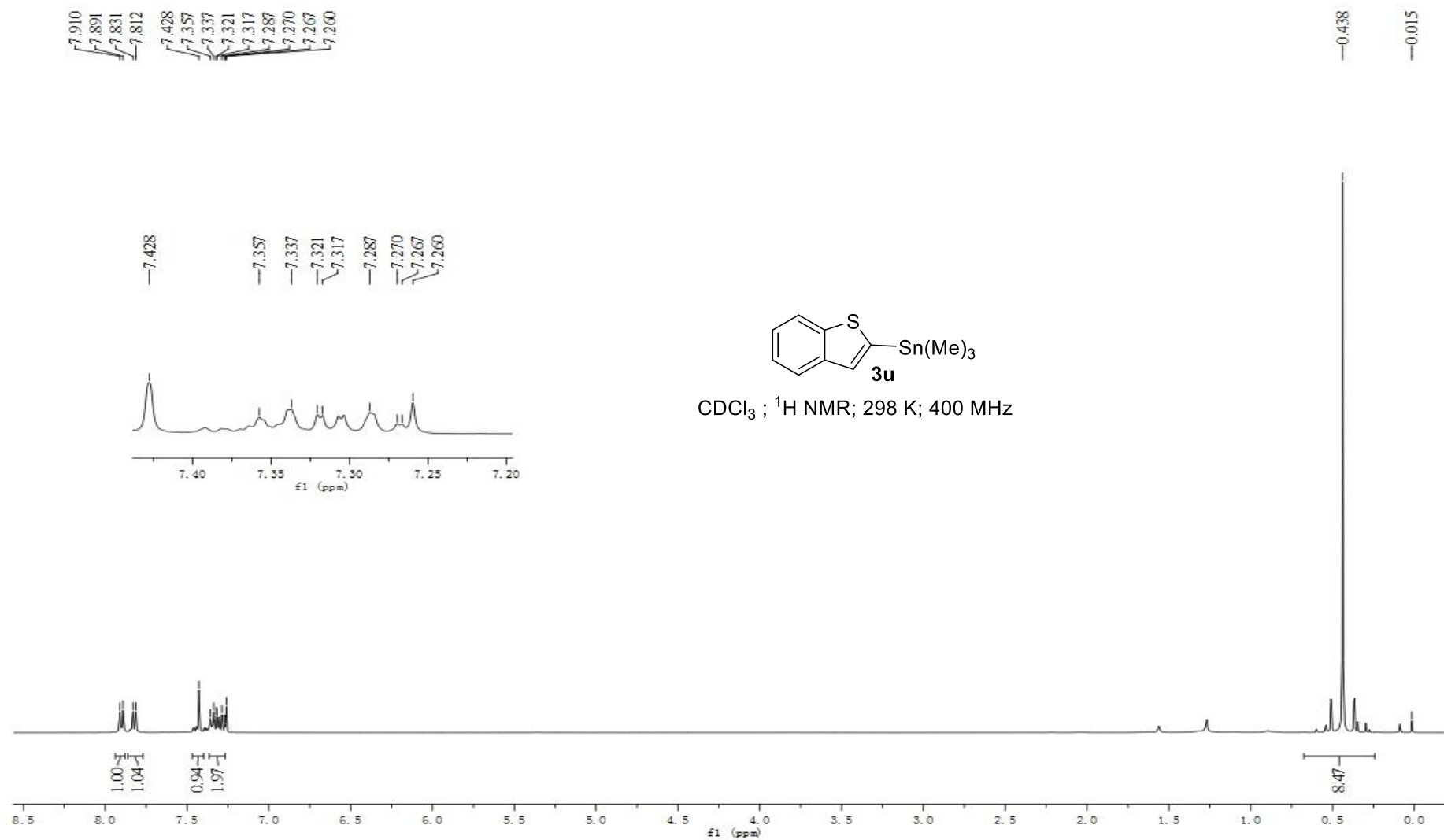


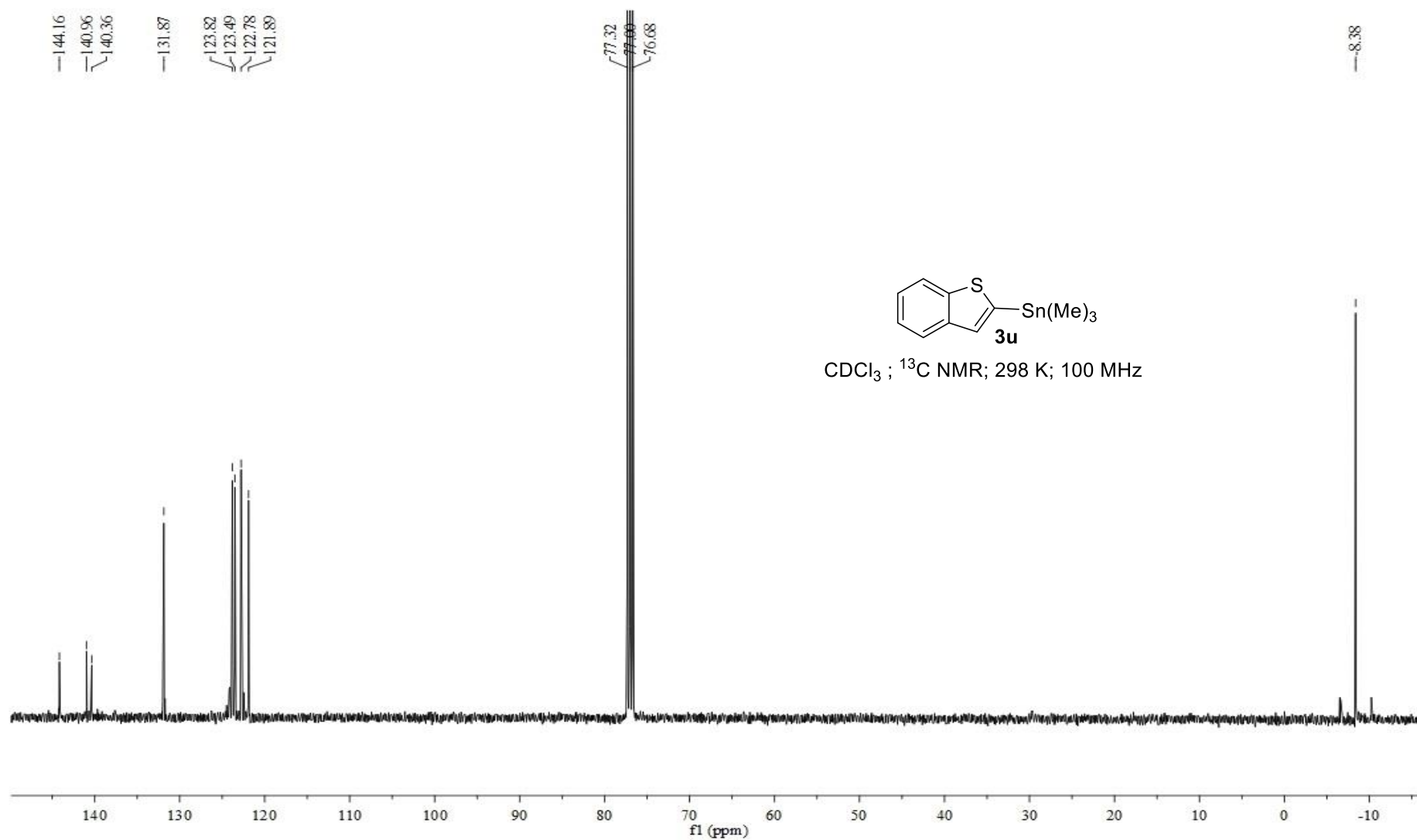


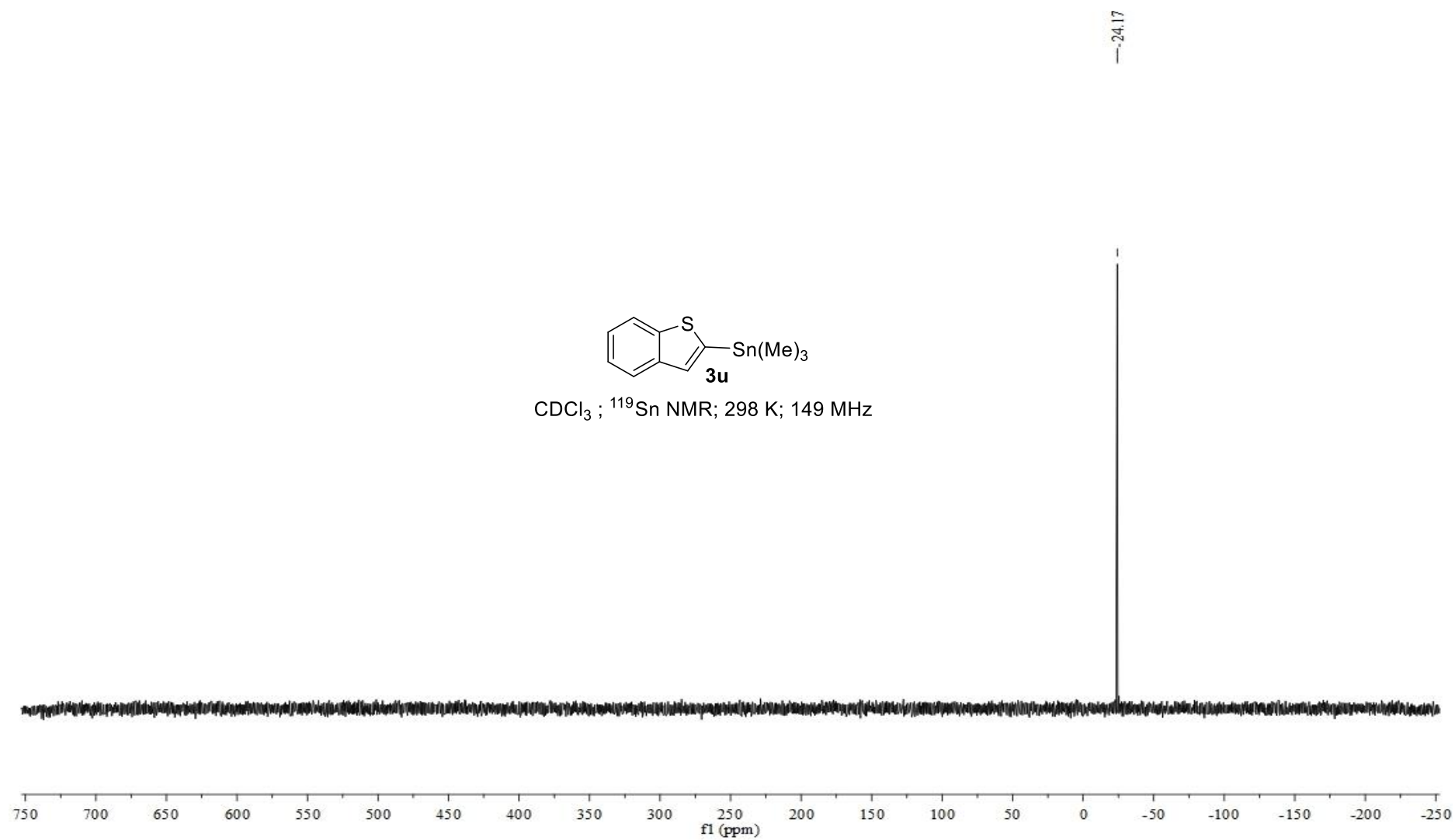


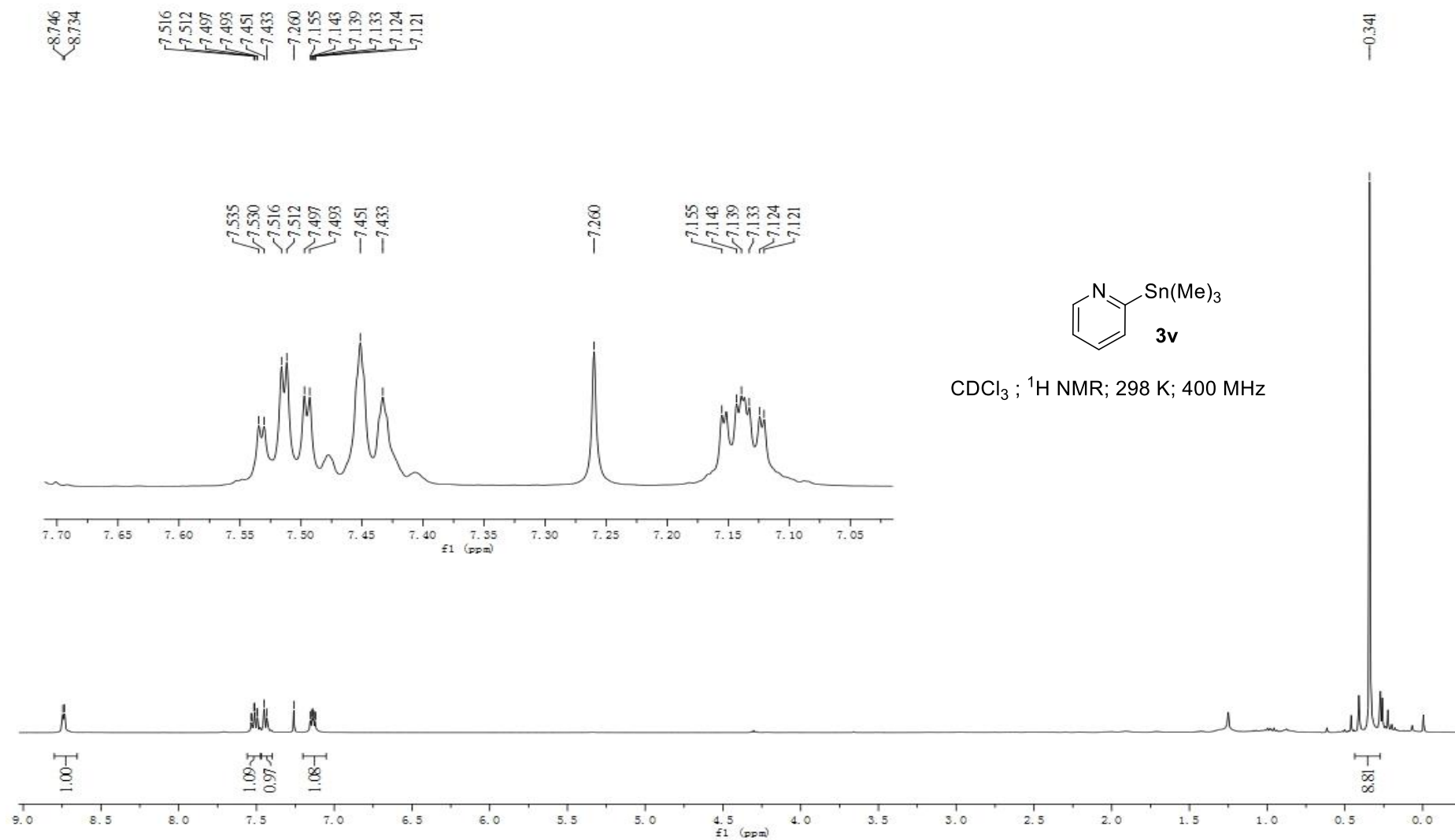
CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

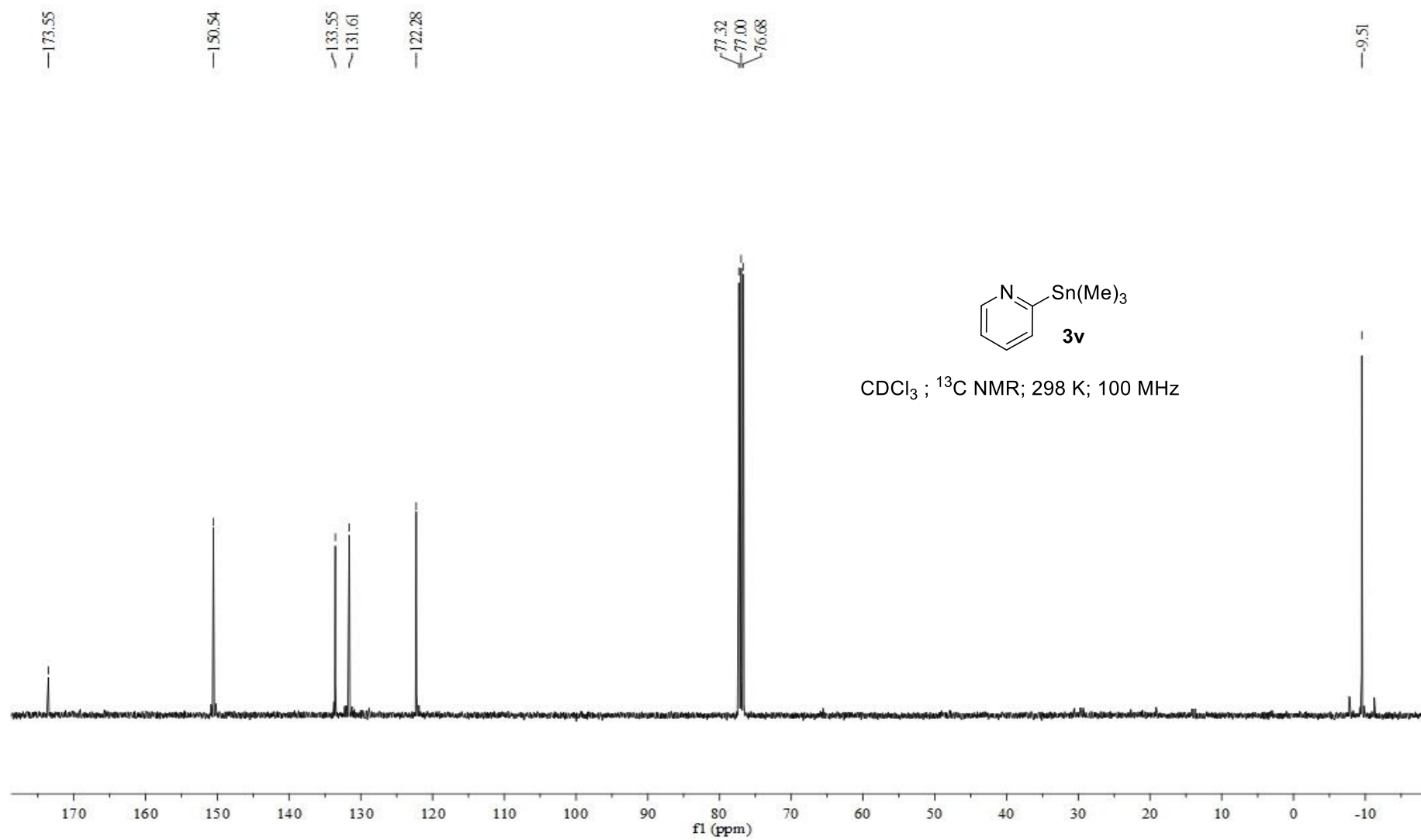


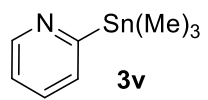




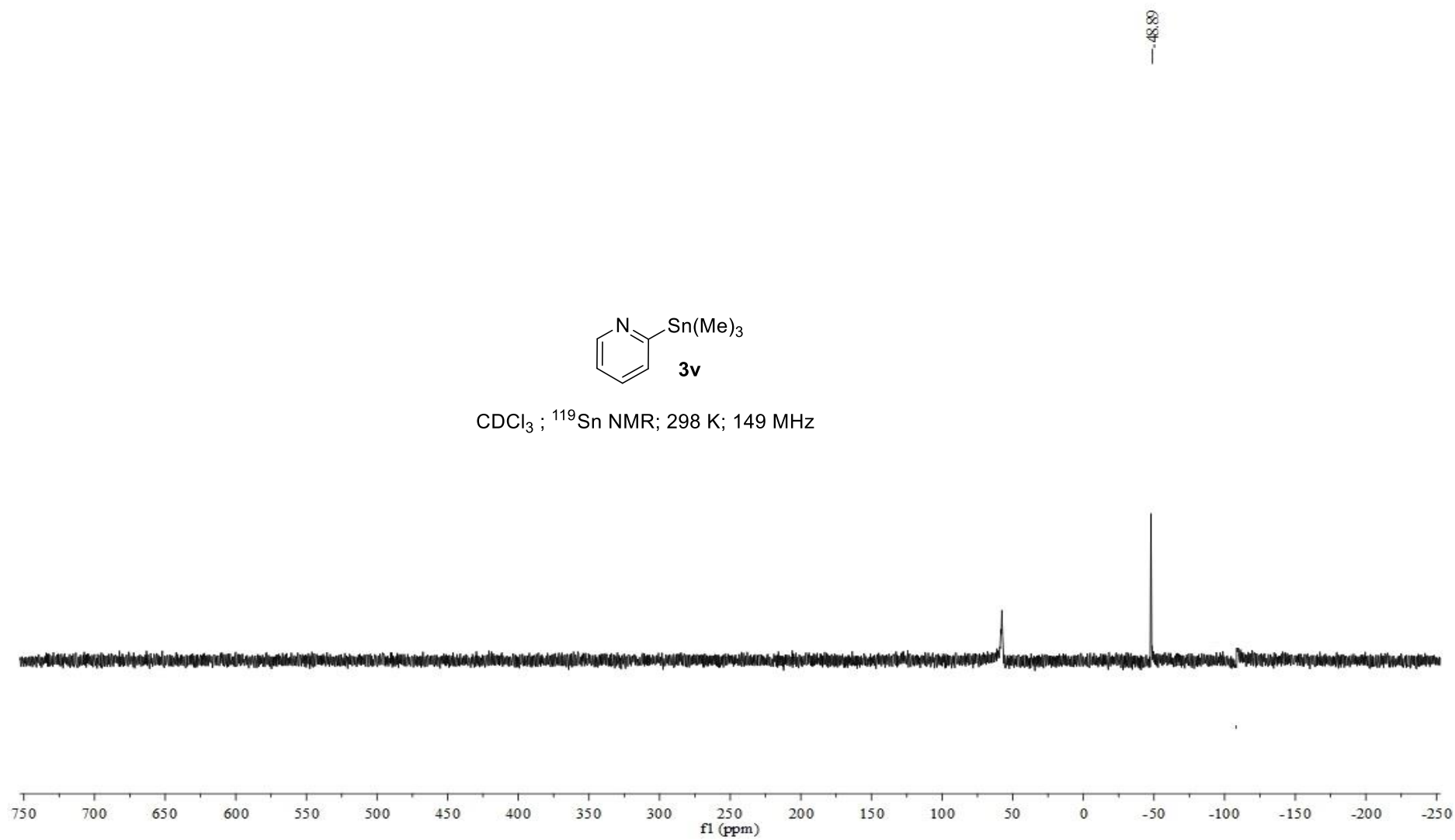


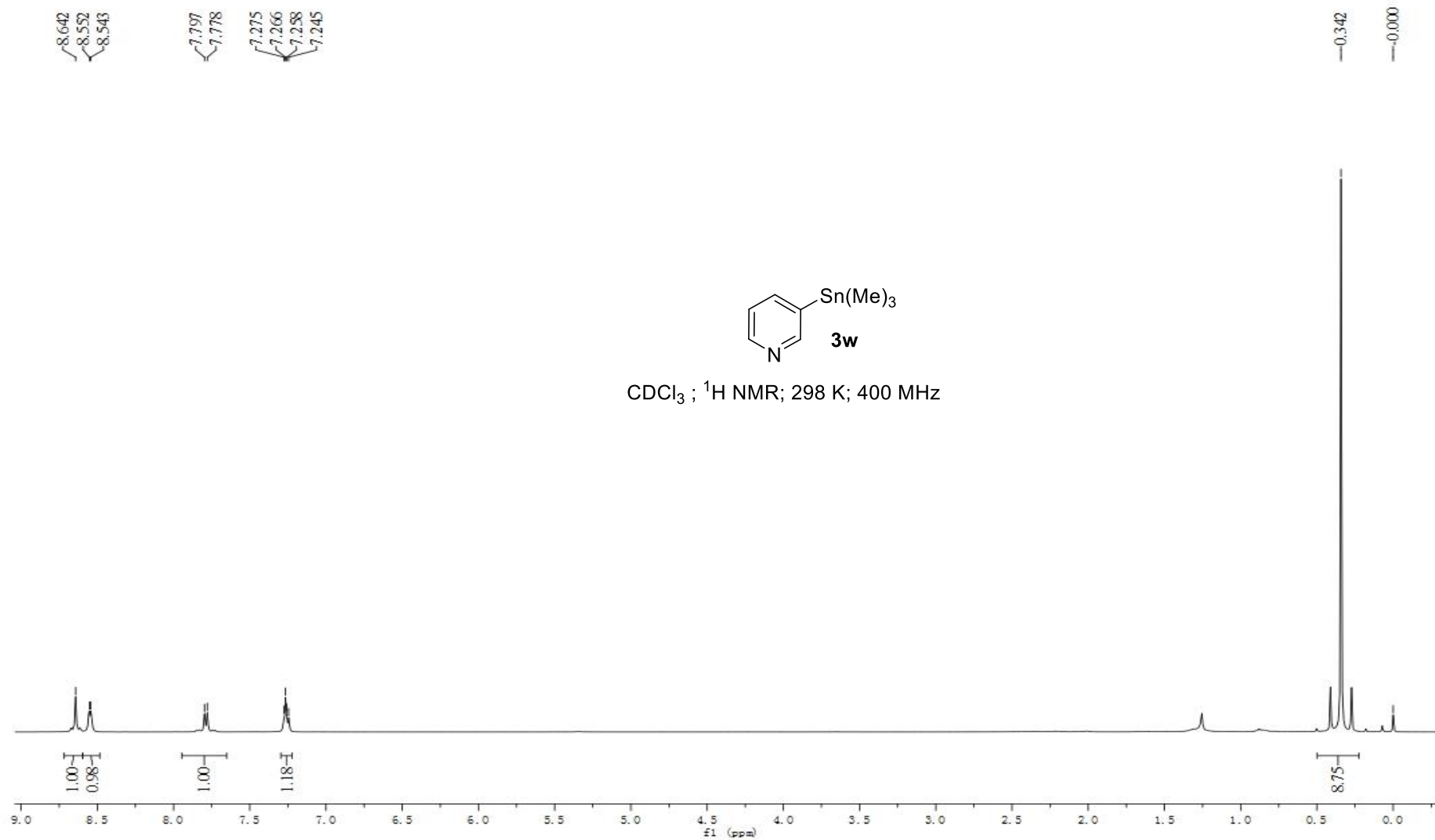


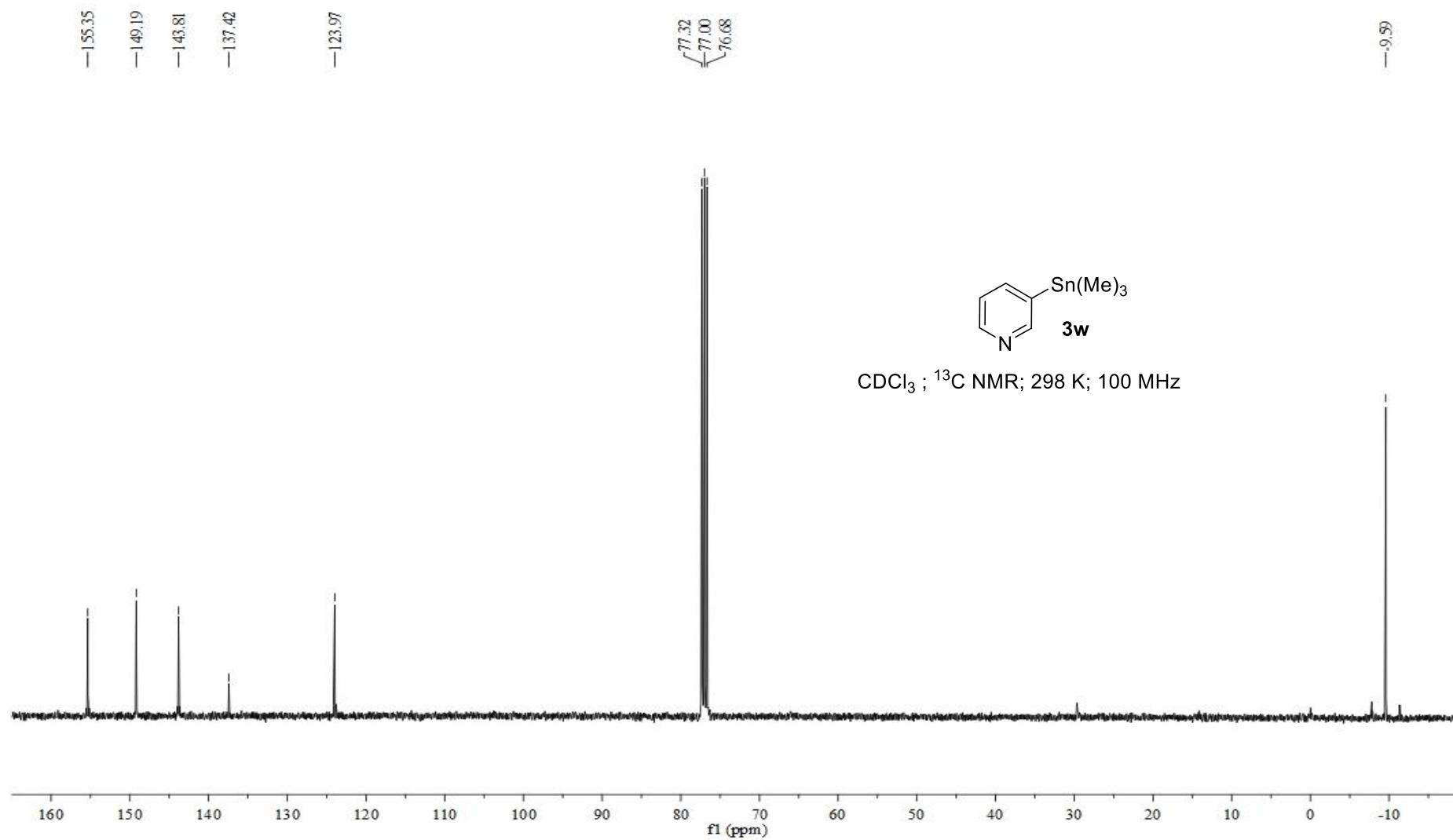


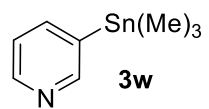


CDCl_3 ; ^{119}Sn NMR; 298 K; 149 MHz

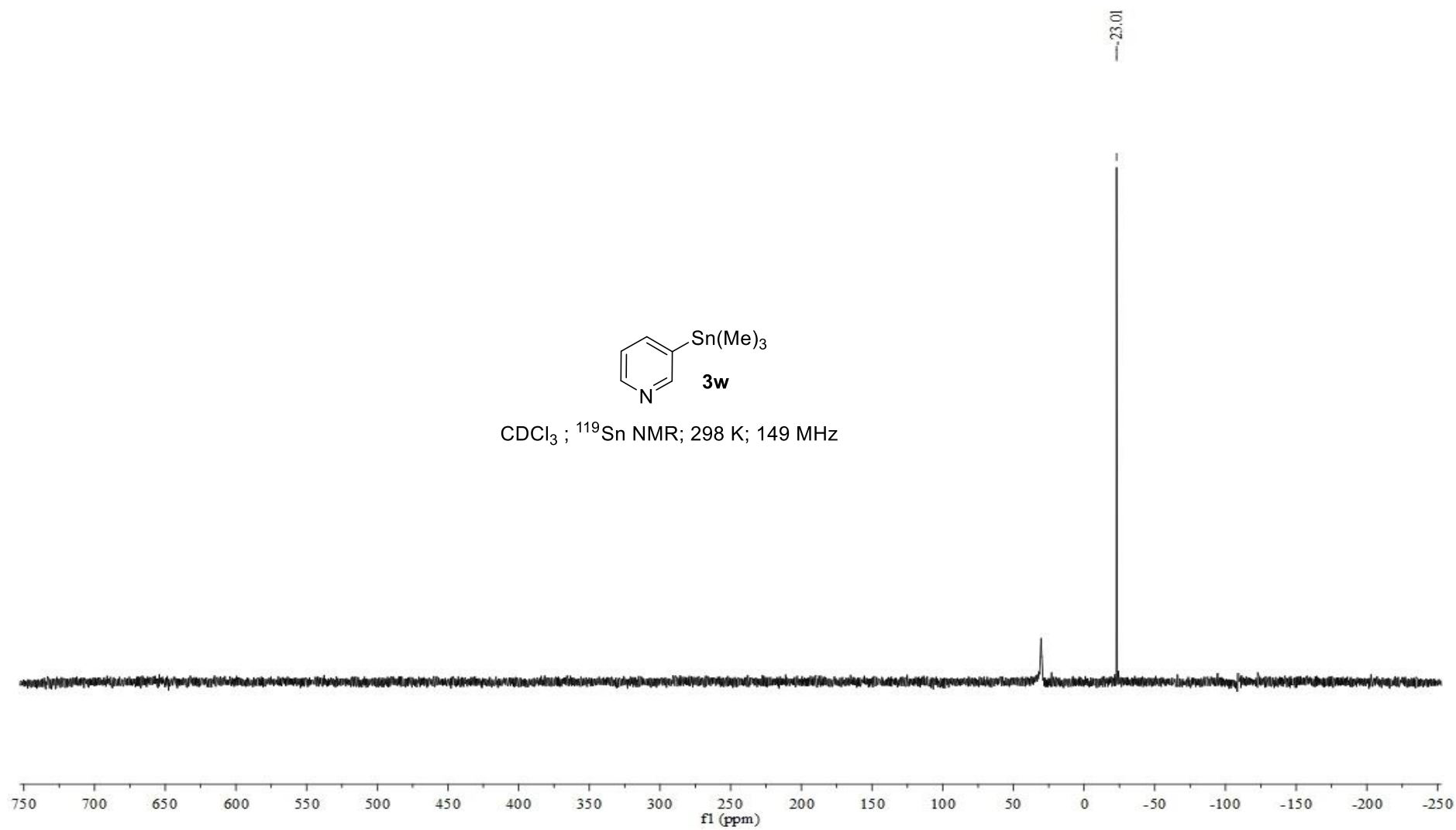


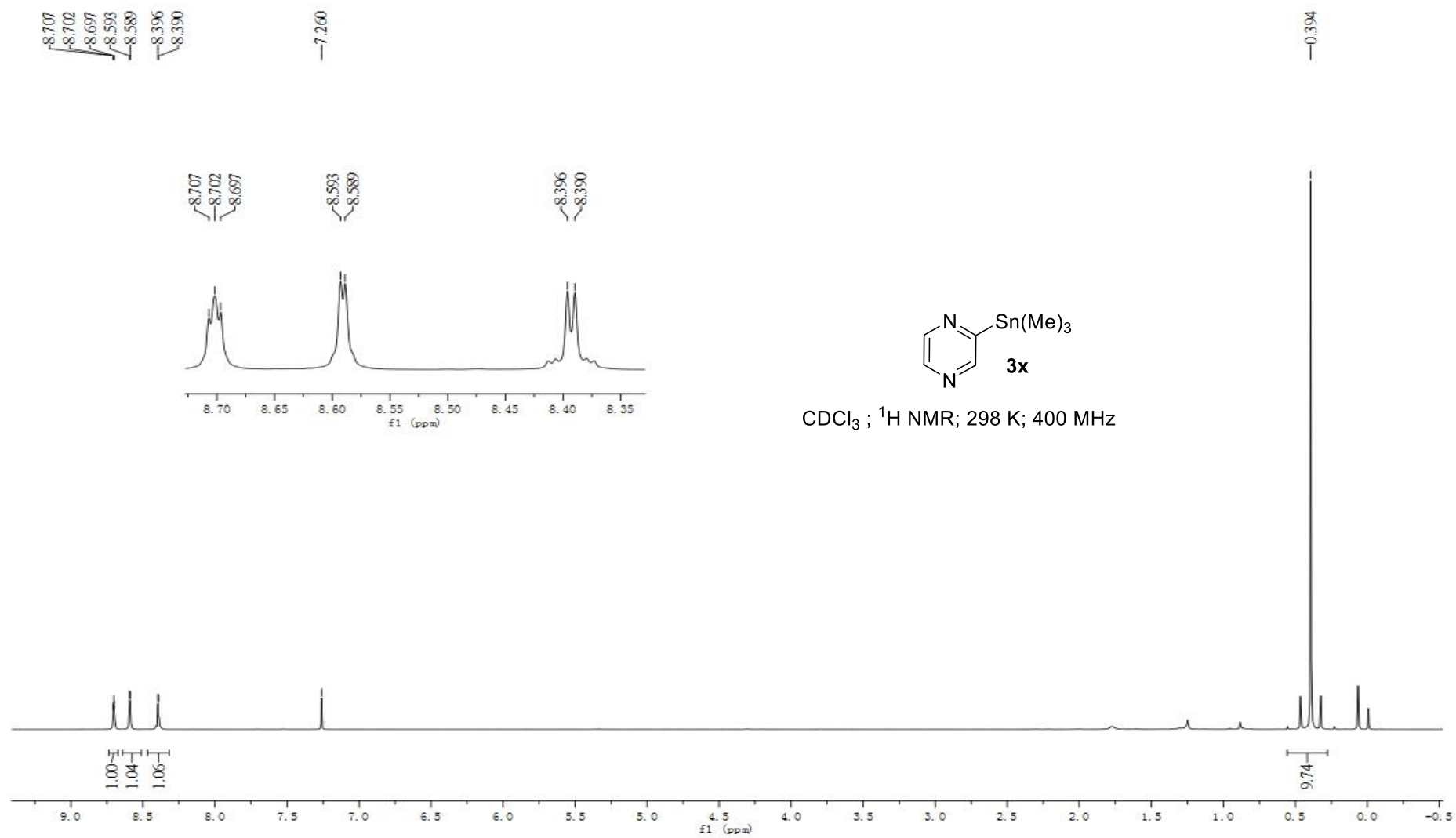


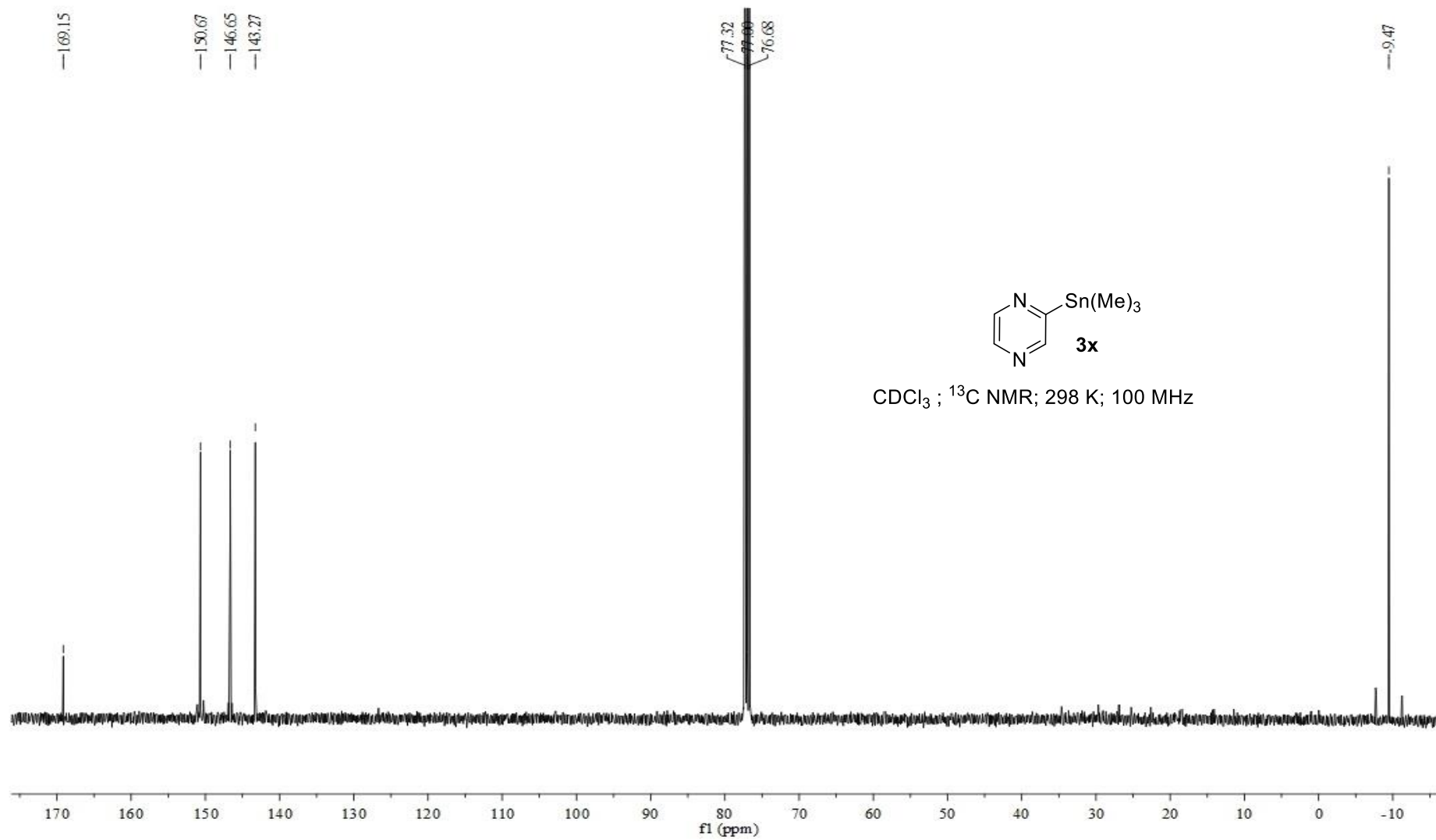


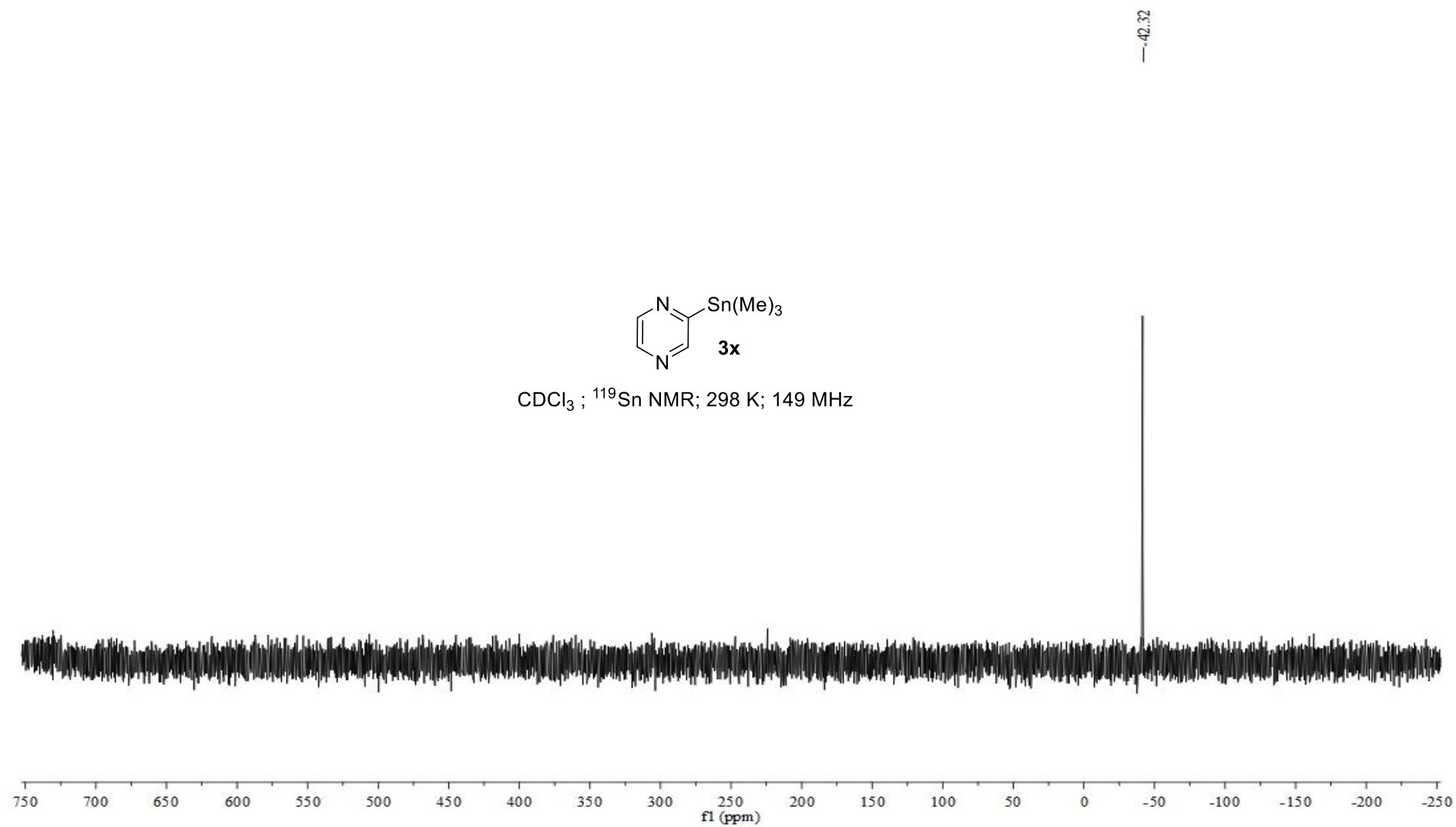


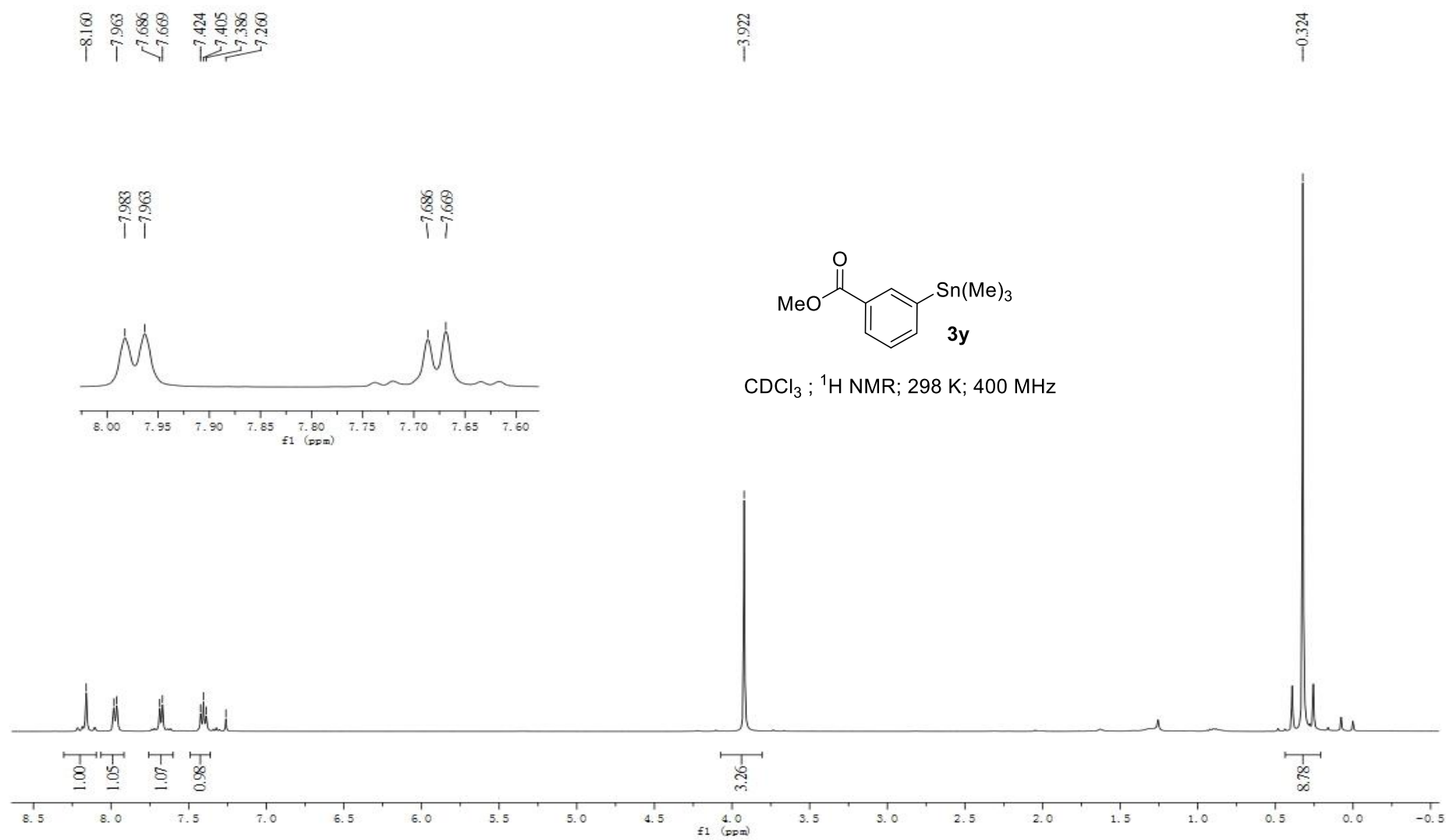
CDCl₃ ; ¹¹⁹Sn NMR; 298 K; 149 MHz

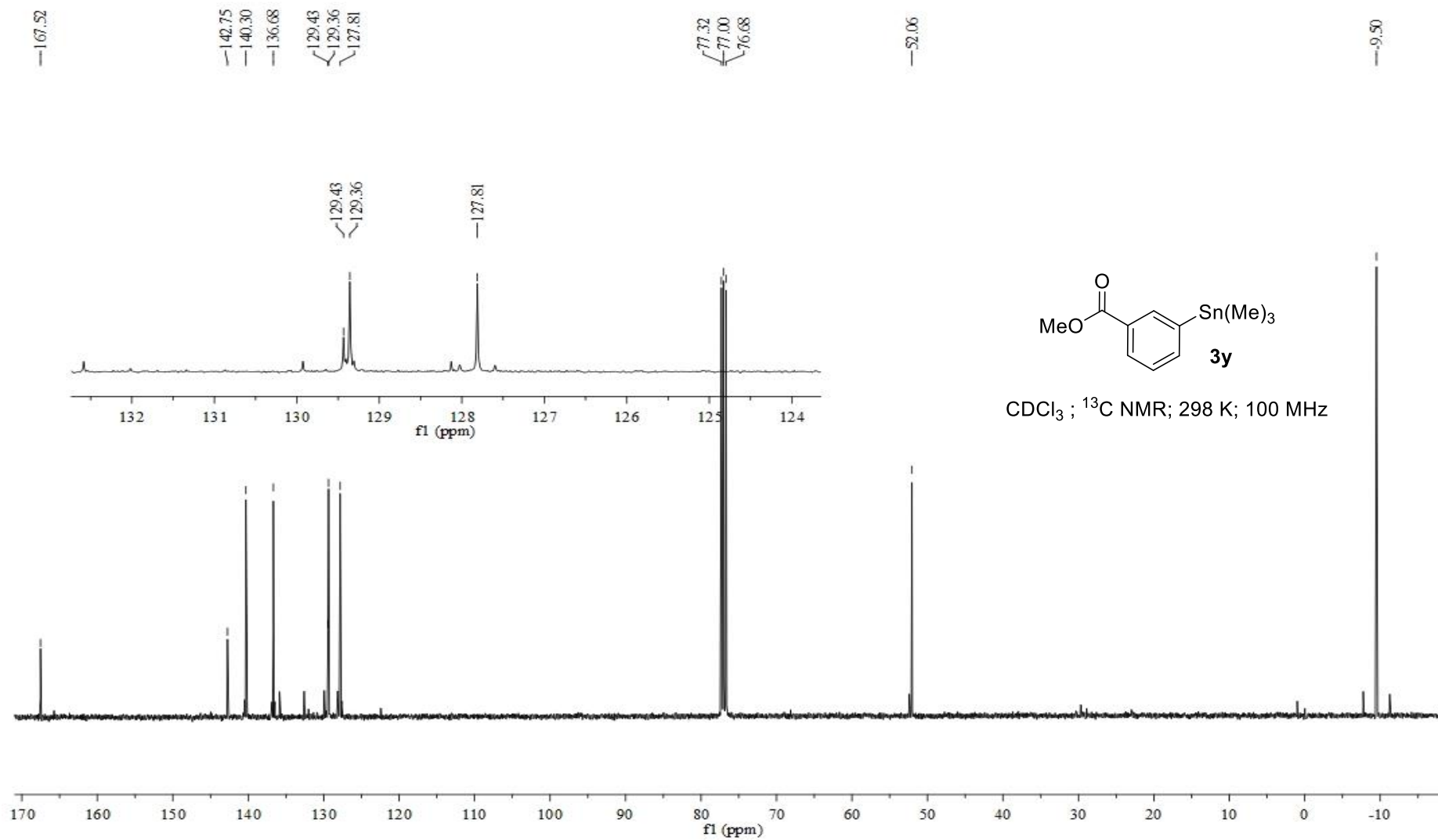


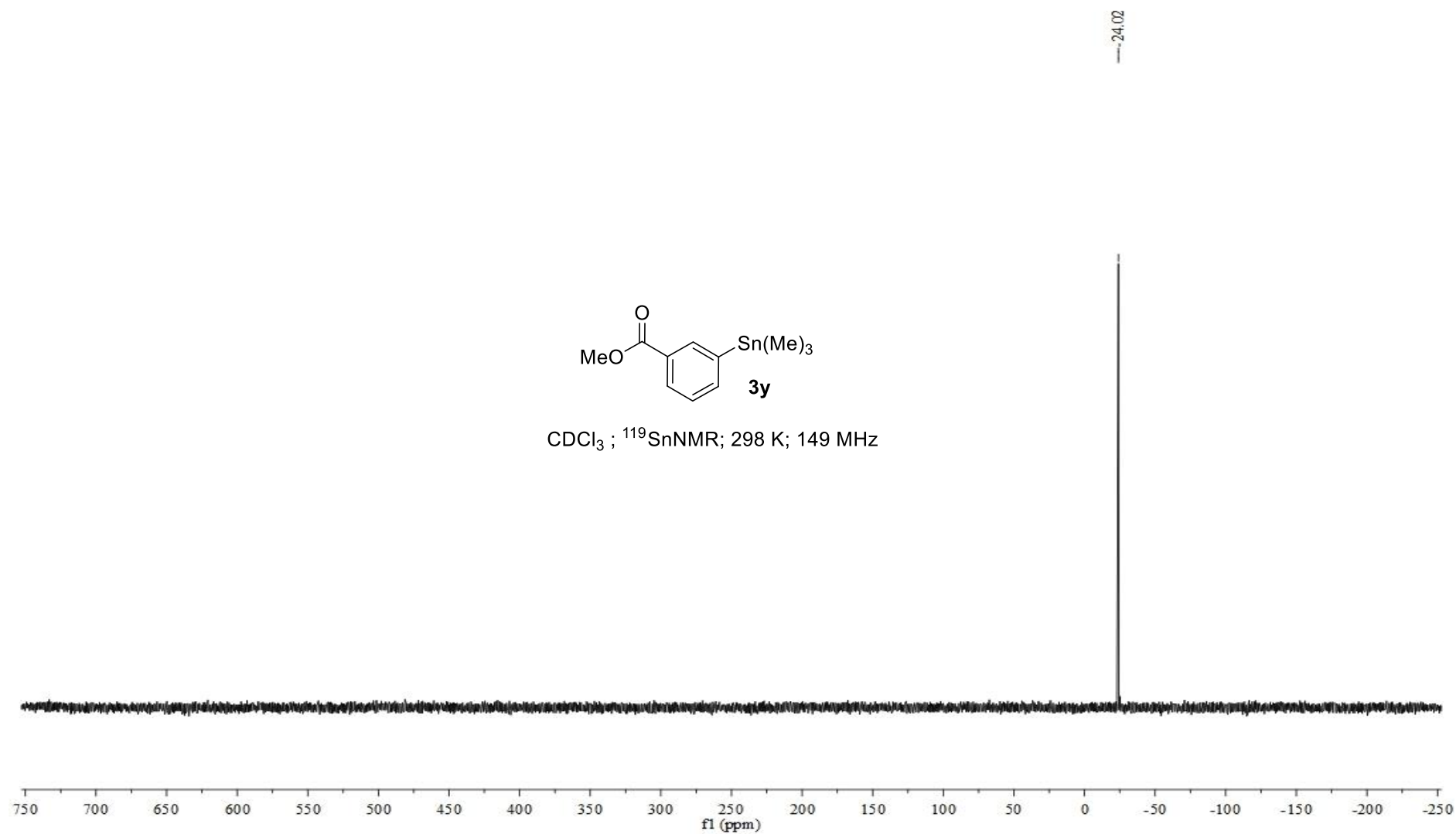


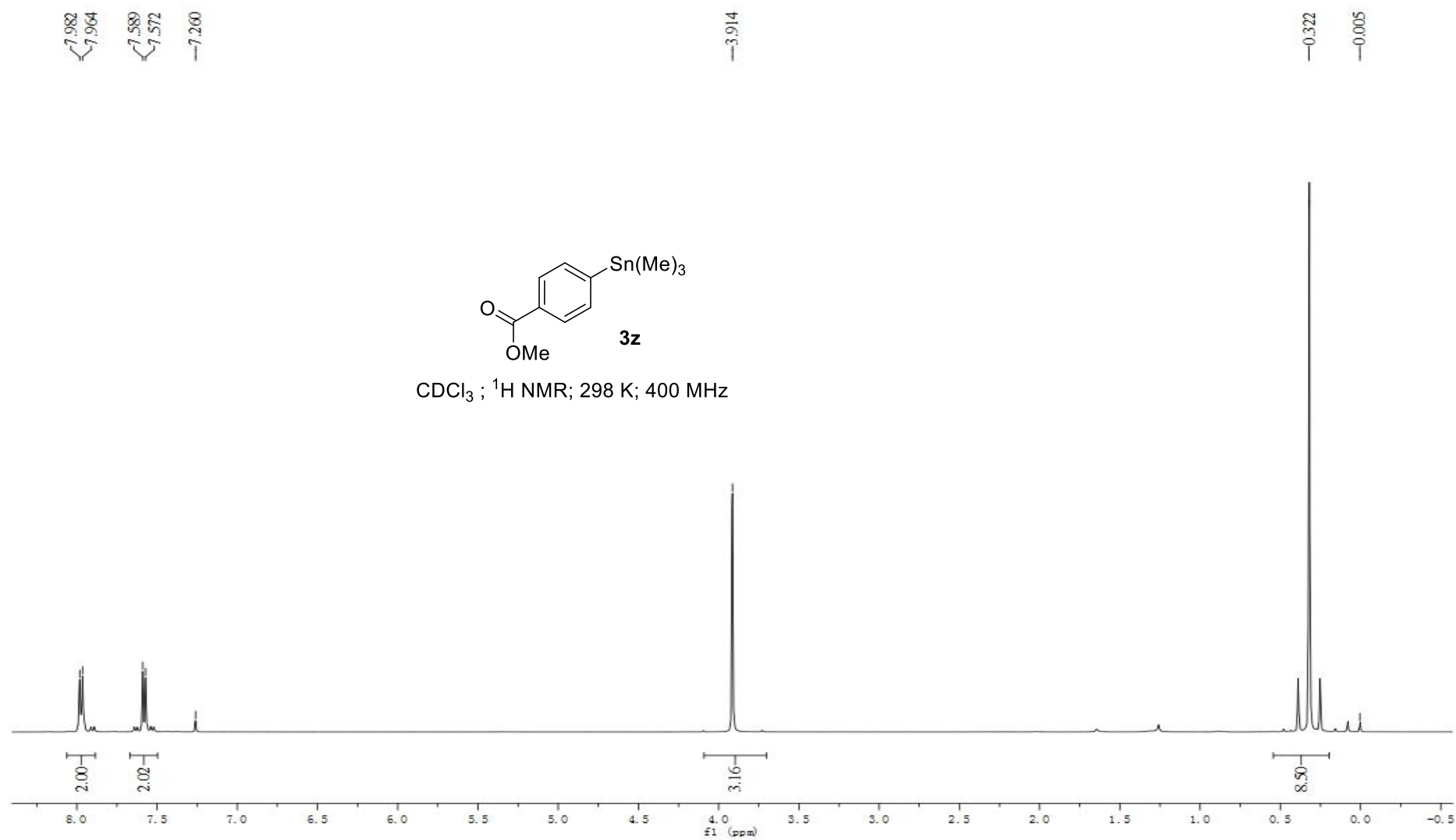


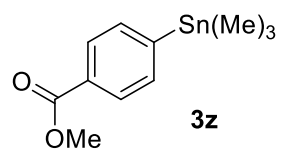












CDCl₃ ; ¹³C NMR; 298 K; 100 MHz

