

Iodine-mediated 1,2-aryl migration of primary benzhydryl amines

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1. General Information. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz (100 MHz for ^{13}C NMR) spectrometer. Chemical shift values are given in ppm (parts per million) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet; dd, doublet of doublets; and dt, doublet of triplets; tt, triplet of triplets. The coupling constants (J) are reported in hertz (Hz). Melting points were determined on a micromelting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a Q-TOF mass spectrometer equipped with an electrospray ion source (ESI), operated in the positive mode. Flash column chromatography was performed over 200–300 mesh silica gel. 1,2-Dichloromethane (DCE) and carbon tetrachloride (CCl_4) used in the synthesis of products **2** was analytical reagent grade and used without any pretreatment.

2. Preparation of Substrates 1. Substrate **1j** is commercially available and the other ones were prepared according to the following methods:

Method A.¹ A solution of 1,1-diarylethan-1-ol² (10 mmol) in anhydrous CH_2Cl_2 (30 mL) was treated with NaN_3 (1.43 g, 22 mmol) at room temperature, and then cooled to $-5\text{ }^\circ\text{C}$. A mixture of TFA (6.2 mL, 84 mmol) and CH_2Cl_2 (12.4 mL) was added dropwise slowly to the above reaction mixture under a nitrogen atmosphere. It was stirred at $-5\text{ }^\circ\text{C}$ for 15 min, then at $0\text{ }^\circ\text{C}$ for another 2–12 h. Upon the completion of the reaction (indicated by TLC), it was quenched with water (20 mL) dropwise slowly, followed by dropwise addition of 14% ammonia solution (20 mL). After vigorously stirred for 30 min, the resulting mixture was allowed to warm up slowly to room temperature, and extracted with CH_2Cl_2 ($3 \times 30\text{ mL}$). The combined organic layer was

dried over anhydrous Na₂SO₄ and concentrated to provide the crude azide intermediate.

A solution of the above crude azide in Et₂O (5 mL) was added dropwise to a suspension of lithium aluminum hydride (569 mg, 15 mmol) in Et₂O (15 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3 h, and then quenched with 1 N NaOH solution (pH > 10). The insoluble solid was filtered off and the filtrate was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated and purified through silica gel chromatography to yield substrates **1a–1b**, **1d**, **1f**, **1i**, **1k–1r**, **1t** and **1w–1aa**.

Method B.³ A Grignard reagent (30 mmol, 1 M or 3 M in Et₂O) was added dropwise (within 15 min) to a vigorously stirred solution of the corresponding nitrile (10 mmol) in Et₂O (40 mL) at room temperature under a nitrogen atmosphere. After further stirred for 40 min, the resulting mixture was treated with Ti(*i*-PrO)₄ (3 mL, 10 mmol) and stirred for another 24 h. Upon the completion of the reaction (indicated by TLC), it was quenched with 10% NaOH solution (40 mL) and filtered. The solid was washed with EtOAc (30 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and then purified through silica gel column chromatography to yield substrates **1c**, **1e**, **1g–1h**, **1s** and **1u–1v**.

1,1-Diphenylethan-1-amine (1a).⁴ Method A; eluent: EtOAc/petroleum ether (PE)/Et₃N 16:83:1; yield: 1.03 g, 52%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.35 (m, 4H), 7.30–7.26 (m, 4H, overlapped with the peak of chloroform), 7.21–7.18 (m, 2H), 1.86 (s, 2H), 1.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 128.2, 126.4, 126.2, 58.5, 31.9; HRMS (ESI-TOF) *m/z*: [M – NH₂]⁺ calcd for C₁₄H₁₃

181.1012, found 181.1008.

1,1-Diphenylpropan-1-amine (1b).³ Method A; eluent: EtOAc/PE/Et₃N 3:96:1; yield: 359 mg, 17%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.34 (m, 4H), 7.30–7.26 (m, 4H), 7.18 (tt, J = 7.2, 1.2 Hz, 2H), 2.25 (q, J = 7.2 Hz, 2H), 1.83 (s, 2H), 0.81 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 128.1, 126.7, 126.3, 61.3, 35.0, 8.6; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₅H₁₇NNa 234.1253, found 234.1254.

1,1-Diphenylbutan-1-amine (1c).⁵ Method B; eluent: EtOAc/PE/Et₃N 2:97:1; yield: 1.40 g, 62%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.33 (m, 4H), 7.30–7.25 (m, 4H), 7.19 (tt, J = 7.2, 1.6 Hz, 2H), 2.20–2.16 (m, 2H), 1.78 (s, 2H), 1.26–1.16 (m, 2H), 0.91 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 128.0, 126.5, 126.2, 61.0, 44.9, 17.5, 14.6; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₆H₁₇ 209.1325, found 209.1326.

2-Methyl-1,1-diphenylpropan-1-amine (1d). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 879 mg, 39%; light yellow solid; mp 61–62 °C (lit.³ mp 63–65 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.48 (m, 4H), 7.28–7.24 (m, 4H, overlapped with the peak of chloroform), 7.14 (t, J = 7.6 Hz, 2H), 2.96–2.86 (m, 1H), 1.62 (s, 2H), 0.85 (d, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9, 128.0, 126.5, 125.9, 63.7, 34.6, 17.6; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₆H₁₇ 209.1325, found 209.1323.

Cyclopropyldiphenylmethanamine (1e).⁶ Method B; eluent: EtOAc/PE/Et₃N 2:97:1; yield: 1.65 g, 74%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.38 (m, 4H), 7.30–7.26 (m, 4H), 7.21 (tt, J = 7.2, 1.6 Hz, 2H), 1.64 (s, 2H), 1.59–1.54 (m, 1H), 0.58–0.53 (m, 2H), 0.35–0.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 127.9, 127.2, 126.4, 60.5, 22.4, 1.7; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₆H₁₅

207.1168, found 207.1168.

Cyclobutyldiphenylmethanamine (1f). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 427 mg, 18%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.22 (m, 8H, overlapped with the peak of chloroform), 7.19–7.14 (m, 2H), 3.40–3.32 (m, 1H), 1.98–1.80 (m, 7H), 1.70–1.65 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 128.0, 126.9, 126.2, 62.0, 44.7, 23.6, 17.3; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₇H₁₉NNa 260.1410, found 260.1406.

Cyclopentyldiphenylmethanamine (1g). Method B; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.76 g, 70%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.43 (m, 4H), 7.27–7.23 (m, 4H, overlapped with the peak of chloroform), 7.14 (t, J = 7.6 Hz, 2H), 3.17–3.09 (m, 1H), 1.70 (s, 2H), 1.62–1.53 (m, 6H), 1.38–1.32 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 127.9, 126.7, 125.9, 62.9, 47.7, 28.1, 26.3; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₈H₁₉ 235.1481, found 235.1482.

Cyclohexyldiphenylmethanamine (1h). Method B; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.78 g, 67%; white solid; mp 84–86 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.45 (m, 4H), 7.26 (t, J = 7.6 Hz, 4H, overlapped with the peak of chloroform), 7.14 (t, J = 7.2 Hz, 2H), 2.45–2.39 (m, 1H), 1.76–1.58 (m, 7H), 1.39–1.26 (m, 2H), 1.16–0.93 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 128.0, 126.6, 125.9, 63.6, 45.9, 27.8, 26.9, 26.7; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₉H₂₁ 249.1638, found 249.1639.

2,2-Dimethyl-1,1-diphenylpropan-1-amine (1i). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 814 mg, 34%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.38 (m, 4H), 7.25–7.20 (m, 4H, overlapped with the peak of chloroform), 7.19–7.15 (m, 2H), 1.82 (s, 2H), 1.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 129.4, 127.0, 125.8, 67.4, 38.0, 28.1; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₇H₁₉

223.1481, found 223.1484.

Triphenylmethanamine (1j). White solid; mp 103–104 °C (lit.³ mp 101–102 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.21 (m, 15H, overlapped with the peak of chloroform), 2.27 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 128.1, 127.9, 126.6, 66.2; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₉H₁₇NNa 282.1253, found 282.1251.

1,1-Di-*p*-tolylethan-1-amine (1k). Method A; eluent: PE/Et₃N 99:1; yield: 1.35 g, 60%; light yellow solid; mp 39–41 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 8.0 Hz, 4H), 7.09 (d, J = 8.0 Hz, 4H), 2.31 (s, 6H), 1.82 (s, 2H), 1.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 135.8, 128.8, 126.1, 58.0, 32.1, 21.0; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₆H₁₉NNa 248.1410, found 248.1411.

1,1-Bis(4-methoxyphenyl)ethan-1-amine (1l).⁵ Method A; eluent: EtOAc/PE/Et₃N 3:96:1; yield: 1.78 g, 69%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.26 (m, 4H), 6.84–6.80 (m, 4H), 3.79 (s, 6H), 1.90 (s, 2H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 142.3, 127.2, 113.3, 57.5, 55.3, 32.3; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₆H₁₉NNaO₂ 280.1308, found 280.1306.

1,1-Di([1,1'-biphenyl]-4-yl)ethan-1-amine (1m). Method A; eluent: EtOAc/PE/Et₃N 20:79:1; yield: 2.52 g, 72%; white solid; mp 158–160 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.59–7.54 (m, 8H), 7.49 (d, J = 8.0 Hz, 4H), 7.42 (t, J = 7.6 Hz, 4H), 7.34–7.30 (m, 2H), 1.92 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 140.7, 139.2, 128.7, 127.2, 127.0, 126.9, 126.6, 58.1, 31.9; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₂₆H₂₁ 333.1638, found 333.1639.

1,1-Bis(4-fluorophenyl)ethan-1-amine (1n).⁶ Method A; eluent: EtOAc/PE/Et₃N 3:96:1; yield: 1.10 g, 47%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.30 (m, 4H), 7.00–6.94 (m, 4H), 1.86 (s, 2H), 1.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

161.4 (d, $J_{\text{C-F}} = 243.7$ Hz), 145.4 (d, $J_{\text{C-F}} = 3.3$ Hz), 127.8 (d, $J_{\text{C-F}} = 7.9$ Hz), 114.9 (d, $J_{\text{C-F}} = 20.9$ Hz), 57.7, 32.3; HRMS (ESI-TOF) m/z : $[\text{M} - \text{NH}_2]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{F}_2$ 217.0823, found 217.0824.

1,1-Bis(4-chlorophenyl)ethan-1-amine (1o). Method A; eluent: EtOAc/PE/Et₃N 3:96:1; yield: 958 mg, 36%; light yellow solid; mp 77–80 °C (lit.⁵ mp 73 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.24 (m, 8H, overlapped with the peak of chloroform), 1.87 (s, 2H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9, 132.4, 128.3, 127.6, 57.9, 31.9; HRMS (ESI-TOF) m/z : $[\text{M} - \text{NH}_2]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}_2$ 249.0232, found 249.0232.

1,1-Bis(4-(trifluoromethyl)phenyl)ethan-1-amine (1p). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.57 g, 47%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, $J = 8.0$ Hz, 4H), 7.50 (d, $J = 8.4$ Hz, 4H), 1.90 (s, 2H), 1.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 129.0 (q, $J_{\text{C-F}} = 32.3$ Hz), 126.5, 125.3 (q, $J_{\text{C-F}} = 3.9$ Hz), 124.1 (q, $J_{\text{C-F}} = 270.2$ Hz), 58.4, 31.6; HRMS (ESI-TOF) m/z : $[\text{M} - \text{NH}_2]^+$ calcd for $\text{C}_{16}\text{H}_{11}\text{F}_6$ 317.0759, found 317.0755.

1,1-Di-*m*-tolylethan-1-amine (1q). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.62 g, 72%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.21–7.13 (m, 6H), 7.02 (d, $J = 7.2$ Hz, 2H), 2.32 (s, 6H), 1.90 (s, 2H), 1.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.8, 137.6, 128.0, 127.1, 126.8, 123.3, 58.3, 31.9, 21.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{NNa}$ 248.1410, found 248.1406.

1,1-Bis(3-chlorophenyl)ethan-1-amine (1r). Method A; eluent: EtOAc/PE/Et₃N 2:97:1; yield: 1.78 g, 67%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.40 (m, 2H), 7.25–7.18 (m, 6H, overlapped with the peak of chloroform), 1.81 (s, 3H), 1.79 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 134.2, 129.6, 126.8, 126.3, 124.5, 58.2, 31.7; HRMS (ESI-TOF) m/z : $[\text{M} - \text{NH}_2]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}_2$ 249.0232, found

249.0229.

1,1-Di-*o*-tolylethan-1-amine (1s). Method B; eluent: EtOAc/PE/Et₃N 2:97:1; yield: 1.26 g, 56%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, J = 7.6, 0.8 Hz, 2H), 7.26–7.22 (m, 2H, overlapped with the peak of chloroform), 7.15 (td, J = 7.6, 1.6 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 1.85 (s, 3H), 1.82 (s, 2H), 1.75 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 146.9, 135.3, 132.3, 126.6, 126.1, 125.3, 58.8, 31.3, 21.4; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₆H₁₇ 209.1325, found 209.1328.

1,1-Bis(3,4-dimethylphenyl)ethan-1-amine (1t). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.32 g, 52%; dark yellow solid; mp 52–54 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.17–7.16 (m, 2H), 7.09–7.03 (m, 4H), 2.23 (m, 12H), 1.81 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 136.2, 134.4, 129.3, 127.4, 123.6, 57.8, 32.2, 20.1, 19.4; HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₈H₂₃NNa 276.1723, found 276.1721.

1,1-Bis(3,4-dichlorophenyl)ethan-1-amine (1u). Method B; eluent: EtOAc/PE/Et₃N 10:89:1; yield: 1.78 g, 53%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 2.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.15 (dd, J = 8.8, 2.4 Hz, 2H), 1.80 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 132.4, 130.9, 130.3, 128.1, 125.7, 57.7, 31.6; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₄H₉Cl₄ 316.9453, found 316.9457.

1,1-Bis(3,5-dimethylphenyl)ethan-1-amine (1v). Method B; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 811 mg, 32%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 4H), 6.85 (s, 2H), 2.28 (s, 12H), 1.79 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 137.4, 127.9, 123.9, 58.1, 32.1, 21.5; HRMS (ESI-TOF) m/z : [M – NH₂]⁺ calcd for C₁₈H₂₁ 237.1638, found 237.1639.

1,1-Di(naphthalen-2-yl)ethan-1-amine (1w). Method A; eluent: EtOAc/PE/Et₃N

10:89:1; yield: 1.43 g, 48%; white solid; mp 89–90 °C (lit.⁵ mp 89 °C); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.50–7.43 (m, 4H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 2H), 2.03 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 133.2, 132.2, 128.2, 128.0, 127.5, 126.2, 125.84, 125.78, 123.7, 58.8, 31.5; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₂H₁₉NNa 320.1410, found 320.1409.

1-Phenyl-1-(*p*-tolyl)ethan-1-amine (1x).⁷ Method A; eluent: EtOAc/PE/Et₃N 15:84:1; yield: 1.56 g, 74%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30–7.24 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 1.88 (s, 2H), 1.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 147.0, 135.9, 128.8, 128.1, 126.3, 126.2, 126.1, 58.2, 32.0, 21.0; HRMS (ESI-TOF) *m/z*: [M – NH₂]⁺ calcd for C₁₅H₁₅ 195.1168, found 195.1165.

1-(4-Chlorophenyl)-1-phenylethan-1-amine (1y).⁸ Method A; eluent: EtOAc/PE/Et₃N 15:84:1; yield: 950 mg, 41%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.19 (m, 9H, overlapped with the peak of chloroform), 1.83 (s, 2H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.4, 148.4, 132.1, 128.3, 128.2, 127.8, 126.6, 126.1, 58.2, 31.9; HRMS (ESI-TOF) *m/z*: [M – NH₂]⁺ calcd for C₁₄H₁₂Cl 215.0622, found 215.0619.

1-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-amine (1z). Method A; eluent: EtOAc/PE/Et₃N 5:94:1; yield: 1.06 g, 40%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.50 (m, 4H), 7.37–7.29 (m, 4H), 7.25–7.21 (m, 1H, overlapped with the peak of chloroform), 1.86 (s, 5H, overlapped with the peak of NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 153.8 (q, *J*_{C–F} = 1.4 Hz), 149.0, 128.8, 128.4, 126.7, 126.6, 126.1, 125.1 (q, *J*_{C–F} = 3.9 Hz), 124.2 (q, *J*_{C–F} = 270.2 Hz), 58.4, 31.8; HRMS (ESI-TOF) *m/z*: [M – NH₂]⁺ calcd for C₁₅H₁₂F₃ 249.0886, found 249.0889.

1-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethan-1-amine (1aa).⁹ Method A; eluent: EtOAc/PE/Et₃N 10:89:1; yield: 1.44 g, 55%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.30 (m, 2H), 7.28–7.22 (m, 4H, overlapped with the peak of chloroform), 6.84–6.81 (m, 2H), 3.79 (s, 3H), 1.82 (s, 2H), 1.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 148.6, 141.6, 132.0, 128.1, 127.6, 127.2, 113.4, 57.7, 55.2, 32.1; HRMS (ESI-TOF) *m/z*: [M – NH₂]⁺ calcd for C₁₅H₁₄ClO 245.0728, found 245.0723.

3. General Procedure for the Synthesis of Products 2. A stirred solution of the substrate **1** (0.5 mmol) in DCE (6 mL) and CCl₄ (2 mL) was treated with iodine (317 mg, 1.25 mmol) and Cs₂CO₃ (814 mg, 2.5 mmol) in sequence, and then heated to reflux (the reaction temperature was –5 °C then rt for **1l**; 70 °C for **1aa**) until TLC indicating that the conversion was complete. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure. The resulting residue was dissolved in MeOH (8 mL), and then treated with NaBH₄ (95 mg, 2.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. Upon completion of the reaction (indicated by TLC), it was quenched with 1 N NaOH (5 mL), and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated and purified through silica gel chromatography to yield the product **2**.

N-(1-Phenylethyl)aniline (2a).¹⁰ 3 h; eluent: EtOAc/PE 1:99; yield: 89 mg, 91%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.28 (m, 4H), 7.24–7.19 (m, 1H, overlapped with the peak of chloroform), 7.11–7.06 (m, 2H), 6.63 (tt, *J* = 7.6, 0.8 Hz, 1H), 6.51–6.48 (m, 2H), 4.47 (q, *J* = 6.8 Hz, 1H), 4.01 (s, 1H), 1.50 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 145.3, 129.1, 128.7, 126.9, 125.9, 117.3, 113.3, 53.5, 25.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₄H₁₆N 198.1277,

found 198.1276.

***N*-(1-Phenylpropyl)aniline (2b).**¹⁰ 2 h; eluent: EtOAc/PE 1:99; yield: 99 mg, 93%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.28 (m, 4H), 7.23–7.19 (m, 1H, overlapped with the peak of chloroform), 7.09–7.05 (m, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 7.6 Hz, 2H), 4.22 (t, J = 6.8 Hz, 1H), 4.06 (s, 1H), 1.89–1.74 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 144.0, 129.1, 128.5, 126.9, 126.5, 117.1, 113.2, 59.7, 31.7, 10.9; HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₅H₁₈N 212.1434, found 212.1433.

***N*-(1-Phenylbutyl)aniline (2c).**¹¹ 3 h; eluent: EtOAc/PE 1:99; yield: 34 mg, 30%; light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.28 (m, 4H), 7.21 (t, J = 6.8 Hz, 1H), 7.09–7.05 (m, 2H), 6.64–6.60 (m, 1H), 6.51–6.49 (m, 2H), 4.30 (t, J = 6.8 Hz, 1H), 4.06 (s, 1H), 1.84–1.69 (m, 2H), 1.48–1.30 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 144.3, 129.1, 128.5, 126.8, 126.4, 117.1, 113.2, 58.0, 41.2, 19.6, 14.0; HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₆H₂₀N 226.1590, found 226.1594.

***N*-(2-Methyl-1-phenylpropyl)aniline (2d).**¹¹ 3 h; eluent: EtOAc/PE 1:99; yield: 67 mg, 59%; yellow solid; mp 49–50 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.26 (m, 4H), 7.23–7.18 (m, 1H), 7.08–7.03 (m, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 7.6 Hz, 2H), 4.12 (d, J = 6.0 Hz, 2H, overlapped with the peak of NH₂), 2.09–1.97 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 142.5, 129.0, 128.2, 127.1, 126.7, 116.9, 113.2, 63.7, 34.9, 19.7, 18.6; HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₆H₂₀N 226.1590, found 226.1588.

***N*-(Cyclopropyl(phenyl)methyl)aniline (2e).**¹² 1.5 h; eluent: EtOAc/PE 1:99; yield: 109 mg, 98%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.39 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.21 (m, 1H, overlapped with the peak of chloroform),

7.08–7.03 (m, 2H), 6.62 (t, $J = 7.2$ Hz, 1H), 6.46 (d, $J = 7.6$ Hz, 2H), 4.38 (s, 1H), 3.64 (d, $J = 8.0$ Hz, 1H), 1.22–1.13 (m, 1H), 0.65–0.34 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 143.3, 129.1, 128.5, 127.0, 126.5, 117.2, 113.4, 63.0, 19.8, 4.2, 3.6; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{N}$ 224.1434, found 224.1435.

***N*-(Cyclobutyl(phenyl)methyl)aniline (2f).**¹³ 2 h; eluent: EtOAc/PE 1:99; yield: 81 mg, 68%; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.26 (m, 4H), 7.21–7.18 (m, 1H), 7.07–7.03 (m, 2H), 6.61 (t, $J = 7.6$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.15 (d, $J = 9.2$ Hz, 1H), 4.00 (s, 1H), 2.57–2.48 (m, 1H), 2.15–2.10 (m, 1H), 1.93–1.76 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 142.6, 129.1, 128.4, 127.0, 126.6, 117.2, 113.4, 63.8, 42.6, 26.2, 25.6, 17.6; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{N}$ 238.1590, found 238.1592.

***N*-(Cyclopentyl(phenyl)methyl)aniline (2g).**¹⁴ 2 h; eluent: EtOAc/PE 1:99; yield: 96 mg, 76%; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.26 (m, 4H), 7.19 (tt, $J = 7.2, 1.6$ Hz, 1H), 7.07–7.02 (m, 2H), 6.59 (t, $J = 7.2$ Hz, 1H), 6.50–6.48 (m, 2H), 4.18 (s, 1H), 4.07 (d, $J = 8.4$ Hz, 1H), 2.20–2.10 (m, 1H), 1.92–1.84 (m, 1H), 1.69–1.23 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 143.9, 129.0, 128.3, 126.9, 126.8, 116.9, 113.2, 63.0, 47.7, 30.1, 29.9, 25.20, 25.15; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{N}$ 252.1747, found 252.1749.

***N*-(Cyclohexyl(phenyl)methyl)aniline (2h).**¹³ 1 h; eluent: EtOAc/PE 1:99; yield: 109 mg, 82%; colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.26 (m, 4H), 7.22–7.17 (m, 1H), 7.08–7.02 (m, 2H), 6.59 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.50–6.47 (m, 2H), 4.14 (s, 1H), 4.11 (d, $J = 6.4$ Hz, 1H), 1.88 (d, $J = 12.4$ Hz, 1H), 1.77–1.60 (m, 4H), 1.53 (d, $J = 12.8$ Hz, 1H), 1.24–0.99 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 142.6, 129.0, 128.1, 127.2, 126.7, 116.9, 113.1, 63.3, 44.9, 30.2, 29.4, 26.39, 26.36, 26.32; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{N}$ 266.1903, found 266.1907.

***N*-(2,2-Dimethyl-1-phenylpropyl)aniline (2i).**¹³ 4.5 h; eluent: EtOAc/PE 1:99; yield: 22 mg, 18%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.25 (m, 4H), 7.22–7.18 (m, 1H), 7.06–7.02 (m, 2H), 6.60–6.56 (m, 1H), 6.49–6.46 (m, 2H), 4.26 (s, 1H), 4.04 (s, 1H), 0.99 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 141.1, 129.0, 128.5, 127.7, 126.8, 116.8, 113.1, 67.1, 34.9, 27.0; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₇H₂₂N 240.1747, found 240.1749.

***N*-Benzhydrylaniline (2j).**¹⁰ eluent: EtOAc/PE 1:99; yield: 128 mg, 98% (0.5 mmol, 2 h); 1.49 g, 96% (6 mmol, 8 h); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.30 (m, 8H), 7.27–7.23 (m, 2H overlapped with the peak of chloroform), 7.14–7.09 (m, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.55–6.53 (m, 2H), 5.49 (s, 1H), 4.23 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 143.0, 129.2, 128.8, 127.5, 127.4, 117.7, 113.5, 63.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₉H₁₈N 260.1434, found 260.1438.

4-Methyl-*N*-(1-(*p*-tolyl)ethyl)aniline (2k).¹⁵ 3 h; eluent: EtOAc/PE 1:99; yield: 88 mg, 78%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.4 Hz, 2H, overlapped with the peak of chloroform), 7.11 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 4.42 (q, *J* = 6.8 Hz, 1H), 3.77 (s, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 142.4, 136.3, 129.6, 129.3, 126.3, 125.8, 113.4, 53.4, 25.1, 21.1, 20.4; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₆H₂₀N 226.1590, found 226.1585.

4-Methoxy-*N*-(1-(4-methoxyphenyl)ethyl)aniline (2l).¹⁶ According to the *General Procedure*, the first-step rearrangement reaction was performed at –5 °C for 12 h and then rt for 16 h; eluent: EtOAc/PE 3:97; yield: 116 mg, 90%; brown oil; ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.25 (m, 2H), 6.87–6.83 (m, 2H), 6.71–6.67 (m, 2H), 6.49–6.45 (m, 2H), 4.37 (q, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 1.47 (d, *J* =

6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 151.8, 141.6, 137.5, 126.9, 114.7, 114.6, 114.0, 55.8, 55.3, 53.6, 25.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_2$ 258.1489, found 258.1485.

***N*-(1-([1,1'-Biphenyl]-4-yl)ethyl)-[1,1'-biphenyl]-4-amine (2m).** 2 h; eluent: EtOAc/PE 2:98; yield: 147 mg, 84%; white solid, mp 123–125 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.55 (m, 4H), 7.50–7.30 (m, 11H), 7.24–7.20 (m, 1H, overlapped with the peak of chloroform), 6.63–6.59 (m, 2H), 4.57 (q, J = 6.4 Hz, 1H), 4.18 (s, 1H), 1.57 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 144.1, 141.2, 140.9, 139.8, 130.2, 128.7, 128.6, 127.8, 127.4, 127.1, 127.0, 126.3, 126.2, 126.0, 113.5, 53.2, 25.0; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}$ 350.1903, found 350.1906.

4-Fluoro-*N*-(1-(4-fluorophenyl)ethyl)aniline (2n).¹⁷ 2 h; eluent: EtOAc/PE 1:99; yield: 52 mg, 45%; brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.28 (m, 2H), 7.02–6.96 (m, 2H), 6.82–6.76 (m, 2H), 6.42–6.37 (m, 2H), 4.38 (q, J = 6.8 Hz, 1H), 3.88 (s, 1H), 1.47 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.9, 159.5, 155.8, 153.5, 142.3, 139.6, 126.2 (d, $J_{\text{C-F}}$ = 7.9 Hz), 114.6 (d, $J_{\text{C-F}}$ = 5.6 Hz), 114.3 (d, $J_{\text{C-F}}$ = 4.6 Hz), 113.0 (d, $J_{\text{C-F}}$ = 7.3 Hz), 52.4, 24.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{N}$ 234.1089, found 234.1091.

4-Chloro-*N*-(1-(4-chlorophenyl)ethyl)aniline (2o).¹⁶ 2 h; eluent: EtOAc/PE 1:99; yield: 124 mg, 93%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.25 (m, 4H, overlapped with the peak of chloroform), 7.04–7.00 (m, 2H), 6.40–6.36 (m, 2H), 4.39 (q, J = 6.8 Hz, 1H), 4.03 (s, 1H), 1.48 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 143.3, 132.6, 129.0, 128.9, 127.2, 122.1, 114.4, 53.1, 25.1; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{N}$ 266.0498, found 266.0497.

4-(Trifluoromethyl)-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (2p). 6 h; eluent:

EtOAc/PE 1:99; yield: 135 mg, 81%; colorless solid; mp 80–81 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 8.4 Hz, 2H), 4.56 (q, J = 6.4 Hz, 1H), 4.38 (s, 1H), 1.55 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 148.4, 129.5 (q, $J_{\text{C-F}}$ = 32.2 Hz), 126.6 (q, $J_{\text{C-F}}$ = 3.8 Hz), 126.1, 125.9 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.8 (q, $J_{\text{C-F}}$ = 268.7 Hz), 124.1 ($J_{\text{C-F}}$ = 270.3 Hz), 119.3 ($J_{\text{C-F}}$ = 32.4 Hz), 112.5, 53.0, 24.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{F}_6\text{N}$ 334.1025, found 334.1022.

3-Methyl-*N*-(1-(*m*-tolyl)ethyl)aniline (2q). 5 h; eluent: EtOAc/PE 1:99; yield: 80 mg, 71%; light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.22–7.15 (m, 3H), 7.04–7.02 (m, 1H), 6.97 (t, J = 8.0 Hz, 1H), 6.48–6.46 (m, 1H), 6.37 (s, 1H), 6.31 (dd, J = 8.0, 2.4 Hz, 1H), 4.43 (q, J = 6.8 Hz, 1H), 3.90 (s, 1H), 2.33 (s, 3H), 2.21 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 145.3, 138.8, 138.1, 129.0, 128.5, 127.6, 126.5, 122.9, 118.1, 114.1, 110.2, 53.4, 24.9, 21.6, 21.5; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{N}$ 226.1590, found 226.1587.

3-Chloro-*N*-(1-(3-chlorophenyl)ethyl)aniline (2r). 1.5 h; eluent: EtOAc/PE 1:99; yield: 98 mg, 74%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.32 (m, 1H), 7.26–7.20 (m, 3H, overlapped with the peak of chloroform), 6.99 (t, J = 8.0 Hz, 1H), 6.64–6.61 (m, 1H), 6.46 (t, J = 2.0 Hz, 1H), 6.35–6.32 (m, 1H), 4.41 (q, J = 6.8 Hz, 1H), 4.09 (s, 1H), 1.49 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 146.8, 134.8, 134.6, 130.12, 130.06, 127.3, 125.9, 123.9, 117.5, 113.0, 111.4, 53.1, 24.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{N}$ 266.0498, found 266.0497.

2-Methyl-*N*-(1-(*o*-tolyl)ethyl)aniline (2s). 5 h; eluent: EtOAc/PE 1:99; yield: 45 mg, 40%; light yellow solid; mp 73–76 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.37 (m, 1H), 7.18–7.12 (m, 3H), 7.04 (d, J = 7.2 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.58 (t, J =

7.2 Hz, 1H), 6.22 (d, $J = 8.0$ Hz, 1H), 4.70 (q, $J = 6.8$ Hz, 1H), 3.84 (s, 1H), 2.44 (s, 3H), 2.22 (s, 3H), 1.50 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 142.8, 134.6, 130.6, 130.0, 127.1, 126.7, 126.6, 124.5, 121.5, 116.7, 110.6, 49.7, 23.3, 19.0, 17.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{N}$ 226.1590, found 226.1592.

***N*-(1-(3,4-Dimethylphenyl)ethyl)-3,4-dimethylaniline (2t).** 2.5 h; eluent: EtOAc/PE 1:99; yield: 70 mg, 55%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.12 (s, 1H), 7.10–7.04 (m, 2H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.39–6.38 (m, 1H), 6.26 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.38 (q, $J = 6.8$ Hz, 1H), 3.65 (s, 1H), 2.22 (d, $J = 6.8$ Hz, 6H), 2.11 (d, $J = 13.6$ Hz, 6H), 1.46 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.7, 143.1, 137.1, 136.7, 135.0, 130.2, 129.9, 127.2, 125.1, 123.3, 115.3, 110.6, 53.4, 25.1, 20.1, 20.0, 19.5, 18.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{N}$ 254.1903, found 254.1904.

3,4-Dichloro-*N*-(1-(3,4-dichlorophenyl)ethyl)aniline (2u). 3 h; eluent: EtOAc/PE 1:99; yield: 128 mg, 76%; light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.39 (m, 2H), 7.17–7.10 (m, 2H), 6.53 (d, $J = 2.8$ Hz, 1H), 6.28 (dd, $J = 8.8, 2.8$ Hz, 1H), 4.36 (q, $J = 6.8$ Hz, 1H), 4.08 (s, 1H), 1.49 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 144.6, 132.9, 132.7, 131.1, 130.8, 130.6, 127.7, 125.1, 120.4, 114.5, 112.8, 52.8, 24.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{Cl}_4\text{N}$ 333.9718, found 333.9722.

***N*-(1-(3,5-Dimethylphenyl)ethyl)-3,5-dimethylaniline (2v).** 3.5 h; eluent: EtOAc/PE 1:99; yield: 95 mg, 75%; light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.98 (s, 2H), 6.86 (s, 1H), 6.32 (s, 1H), 6.19 (s, 2H), 4.39 (q, $J = 6.8$ Hz, 1H), 3.92 (s, 1H), 2.29 (s, 6H), 2.18 (s, 6H), 1.47 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 145.3, 138.7, 138.0, 128.5, 123.7, 119.3, 111.3, 53.5, 24.7, 21.5, 21.4; HRMS

(ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{18}H_{24}N$ 254.1903, found 254.1907.

***N*-(1-(Naphthalen-2-yl)ethyl)naphthalen-2-amine (2w).**¹⁸ 4 h; eluent: EtOAc/PE 1:99; yield: 121 mg, 81%; yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.77 (m, 4H), 7.59 (t, J = 8.8 Hz, 2H), 7.53 (dd, J = 8.4, 1.6 Hz, 1H), 7.46–7.39 (m, 3H), 7.27–7.22 (m, 1H, overlapped with the peak of chloroform), 7.14–7.10 (m, 1H), 6.92 (dd, J = 8.8, 2.4 Hz, 1H), 6.67–6.66 (m, 1H), 4.76 (q, J = 6.8 Hz, 1H), 4.37 (s, 1H), 1.63 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.3, 134.9, 133.5, 132.7, 128.8, 128.5, 127.8, 127.6, 127.5, 127.4, 126.1, 125.99, 125.97, 125.5, 124.4, 124.3, 122.0, 118.0, 105.9, 53.8, 24.9; HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{22}H_{20}N$ 298.1590, found 298.1586.

4-Methyl-*N*-(1-phenylethyl)aniline (2x)¹⁹ and ***N*-(1-(*p*-Tolyl)ethyl)aniline (2x')**²⁰ 4 h; eluent: EtOAc/PE 1:99; yield: 81 mg, 76% (**2x:2x'** = 1:1.71, determined by the 1H NMR peaks of the $ArCH_3$ group); dark yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 3.5H), 7.32–7.28 (m, 3.5H), 7.26–7.19 (m, 3.8H, overlapped with the peak of chloroform), 7.13–7.06 (m, 3.9H), 6.91–6.88 (m, 3.4H), 6.65–6.61 (m, 1H), 6.52–6.49 (m, 1.9H), 6.44–6.41 (m, 3.4H), 4.47–4.42 (m, 2.7H), 3.91 (s, 2.5H), 2.31 (s, 3H), 2.18 (s, 5.1H), 1.50–1.48 (m, 8.1H); ^{13}C NMR (100 MHz, $CDCl_3$): **2x**: δ 147.4, 142.3, 136.4, 129.4, 129.2, 125.9, 117.2, 113.3, 53.2, 25.2, 21.2; **2x'**: δ 145.5, 145.1, 129.7, 128.7, 126.9, 126.4, 125.8, 113.5, 53.7, 25.1, 20.4; HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{15}H_{18}N$ 212.1434, found 212.1430.

***N*-(1-(4-Chlorophenyl)ethyl)aniline (2y)**²¹ and **4-Chloro-*N*-(1-phenylethyl)aniline (2y')**²¹ 4.5 h; eluent: EtOAc/PE 1:99; yield: 104 mg, 90% (**2y:2y'** = 1:1.45, determined by the 1H NMR peaks of the only CH_3 group); dark yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 11.8H, overlapped with the peak of chloroform), 7.11–7.07 (m, 2H), 7.03–6.99 (m, 2.9H), 6.65 (t, J = 7.6 Hz, 1H), 6.47 (d, J = 7.6 Hz,

2H), 6.43–6.39 (m, 2.9H), 4.46–4.40 (m, 2.5H), 4.03 (s, 2.4H), 1.50 (d, $J = 6.8$ Hz, 4.4H), 1.48 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): **2y**: δ 147.0, 143.8, 132.4, 129.2, 128.9, 127.3, 117.5, 113.3, 53.0, 25.2; **2y'**: δ 145.8, 144.7, 128.82, 128.76, 127.1, 125.8, 121.8, 114.4, 53.6, 25.1; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}$ 232.0888, found 232.0884.

***N*-(1-(4-(Trifluoromethyl)phenyl)ethyl)aniline (2z)¹⁹ and *N*-(1-Phenylethyl)-4-(trifluoromethyl)aniline (2z')**.²² 3 h; eluent: EtOAc/PE 1:99; yield: 102 mg, 77% (**2z:2z'** = 1:1.25, determined by the ^1H NMR peaks of the only CH_3 group); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.34–7.30 (m, 7.5H), 7.26–7.22 (m, 1.25H, overlapped with the peak of chloroform), 7.11–7.07 (m, 2H), 6.67 (t, $J = 7.2$ Hz, 1H), 6.51–6.45 (m, 4.5H), 4.55–4.49 (m, 2.3H), 4.33 (s, 2.3H), 1.54–1.51 (m, 6.8H); ^{13}C NMR (100 MHz, CDCl_3): **2z**: δ 149.4, 146.8, 129.2 (q, $J_{\text{C-F}} = 32.0$ Hz), 129.2, 126.2, 125.7 (q, $J_{\text{C-F}} = 3.8\text{Hz}$), 124.2 (q, $J_{\text{C-F}} = 272.2\text{Hz}$), 117.7, 113.3, 53.3, 25.1; **2z'**: δ 149.5, 144.2, 128.8, 127.2, 126.4 (q, $J_{\text{C-F}} = 3.8$ Hz), 125.8 (q, $J_{\text{C-F}} = 268.6$ Hz), 125.7, 118.7 (q, $J_{\text{C-F}} = 32.4$ Hz), 112.4, 53.2, 24.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}$ 266.1151, found 266.1154.

4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (2aa).²³ According to the *General Procedure*, the first-step rearrangement reaction was performed at 70 °C for 3 h; eluent: EtOAc/PE 1:99; yield: 27 mg, 21%; dark yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.26–7.22 (m, 2H, overlapped with the peak of chloroform), 7.04–7.00 (m, 2H), 6.87–6.83 (m, 2H), 6.44–6.40 (m, 2H), 4.39 (q, $J = 6.8$ Hz, 1H), 4.02 (s, 1H), 3.78 (s, 3H), 1.48 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 145.8, 136.6, 128.9, 126.8, 121.7, 114.4, 114.0, 55.2, 52.9, 25.0; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{ClNO}$ 262.0993, found 262.0988.

***N*-(1-(4-Chlorophenyl)ethyl)-4-methoxyaniline (2aa').**²⁴ According to the *General Procedure*, the first-step rearrangement reaction was performed at 70 °C for 3 h; eluent: EtOAc/PE 1:99; yield: 85 mg, 65%; dark yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.25 (m, 4H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 8.8 Hz, 2H), 4.37 (q, *J* = 6.8 Hz, 1H), 3.68 (m, 4H), 1.46 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 144.1, 141.2, 132.3, 128.8, 127.3, 114.8, 114.6, 55.7, 53.8, 25.2; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₅H₁₇ClNO 262.0993, found 262.0988.

4. Synthesis of Compound 3. According to the *General Procedure for the Synthesis of Products 2*, upon the completion of the first-step rearrangement of substrate **1j** (130 mg, 0.5 mmol), the reaction mixture was allowed to cool to room temperature. It was quenched with 5% Na₂S₂O₃ (5 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated to give the crude imine intermediate, which was re-dissolved in anhydrous THF (8 mL). The solution of the crude imine was cooled to –78 °C and treated with methyllithium (1.25 mL, 2 mmol, 1.6 M in Et₂O) under a nitrogen atmosphere. After stirred at the same temperature for 2 h, it was allowed to warm up to room temperature slowly and stirred for another 12 h. Upon completion of the reaction (indicated by TLC), it was quenched with water (5 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated and purified through silica gel chromatography (EtOAc/PE 1:99) to yield *N*-(1,1-diphenylethyl)aniline (**3**)²⁵ as colorless oil (136 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.44 (m, 4H), 7.33–7.29 (m, 4H), 7.25–7.21 (m, 2H, overlapped with the peak of chloroform), 7.04–6.99 (m, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.44–6.41 (m, 2H), 4.38 (s, 1H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 145.9, 128.7, 128.5, 126.9,

126.8, 117.5, 116.1, 62.4, 26.6; HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590, found 274.1591.

5. Synthesis of Compound 4. According to the procedure for the synthesis of **3**, the crude imine intermediate was obtained from substrate **1j** (130 mg, 0.5 mmol). It was re-dissolved in anhydrous THF (8 mL), cooled to 0 °C, and then treated with allyl magnesium bromide (1 mL, 1 mmol, 1 M in Et₂O) under a nitrogen atmosphere. After addition, the reaction mixture was allowed to warm up to room temperature and stirred for 12 h. Upon completion of the reaction (indicated by TLC), it was quenched with sat. NH₄Cl solution (5 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated and purified through silica gel chromatography (EtOAc/PE 1:99) to yield *N*-(1,1-diphenylbut-3-en-1-yl)aniline (**4**)²⁶ as yellow oil (124 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.0 Hz, 4H), 7.30 (t, J = 7.2 Hz, 4H), 7.21 (t, J = 7.2 Hz, 2H), 6.96 (t, J = 7.6 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 6.34 (d, J = 8.0 Hz, 2H), 5.53–5.43 (m, 1H), 5.08–5.03 (m, 2H), 4.65 (s, 1H), 3.25 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 144.8, 133.6, 128.6, 128.4, 127.3, 126.7, 119.6, 117.5, 116.0, 64.5, 44.9; HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{22}H_{21}NNa$ 322.1566, found 322.1565.

6. Synthesis of Compound 5. According to the procedure for the synthesis of **3**, the crude imine intermediate was obtained from substrate **1j** (130 mg, 0.5 mmol). It was re-dissolved in DMSO (5 mL), and then treated with phenylacetylene (77 mg, 0.75 mmol) and ^tBuOK (28 mg, 0.25 mmol). After stirred at 40 °C for 10 min, the reaction was quenched with 0.6 M K₂CO₃ solution (5 mL) and extracted with CH₂Cl₂ (3 × 15

mL). The combined organic layer was dried over anhydrous Na₂SO₄, concentrated and purified through silica gel chromatography (EtOAc/PE 1:99) to yield *N*-(1,1,3-triphenylprop-2-yn-1-yl)aniline (**5**) as a yellow solid (146 mg, 81% yield). mp 80–81 °C (lit.²⁷ mp 81 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.76–7.74 (m, 4H), 7.40–7.36 (m, 3H), 7.34–7.32 (m, 3H), 7.28–7.25 (m, 5H), 7.13–7.08 (m, 2H), 6.77–6.73 (m, 1H), 6.70–6.68 (m, 2H), 4.47 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 144.3, 131.7, 128.6, 128.4, 128.28, 128.26, 127.6, 126.9, 123.0, 118.6, 116.6, 90.9, 87.0, 63.7; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₇H₂₂N 360.1747, found 360.1749.

7. References

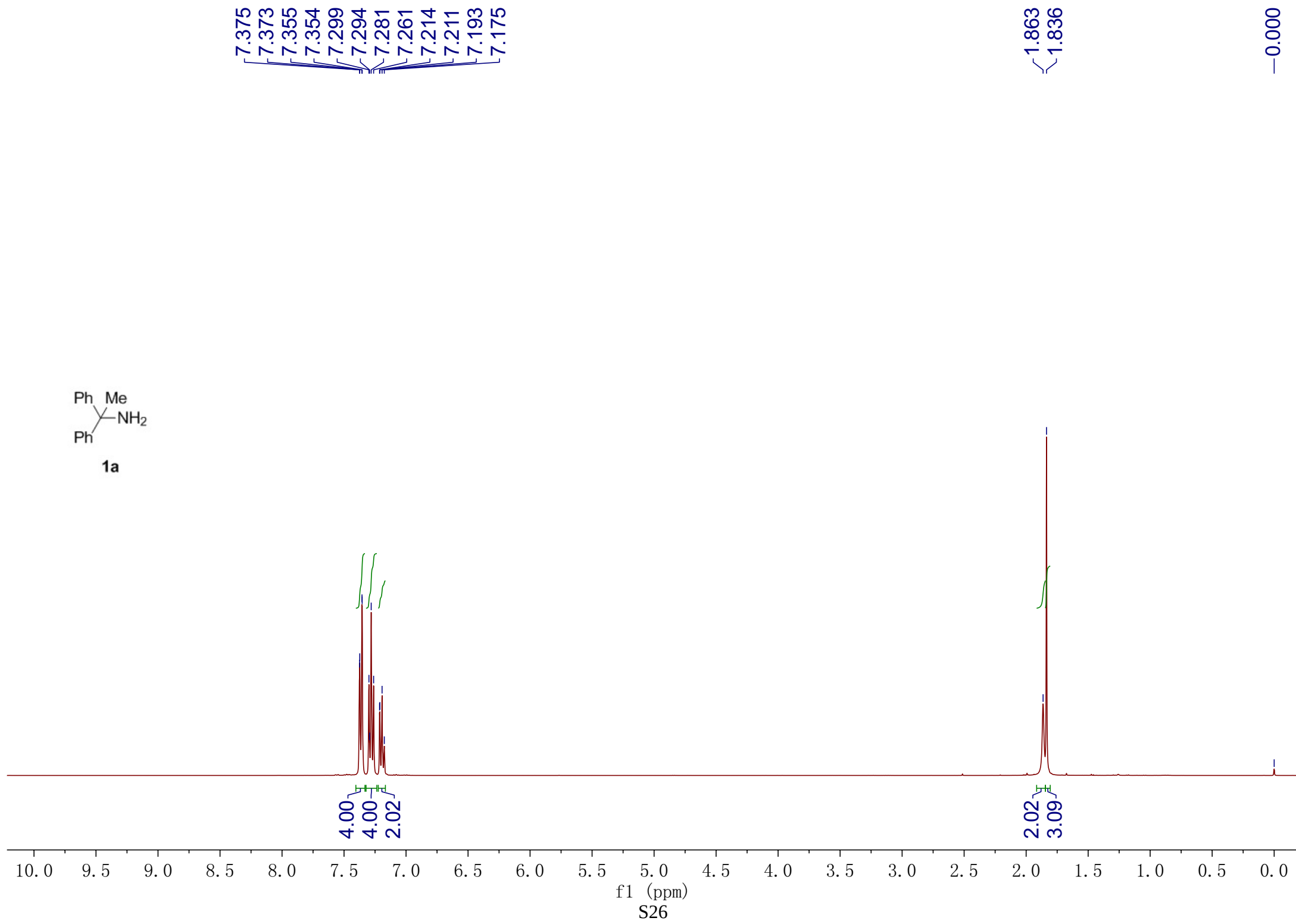
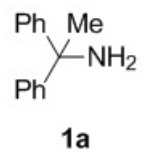
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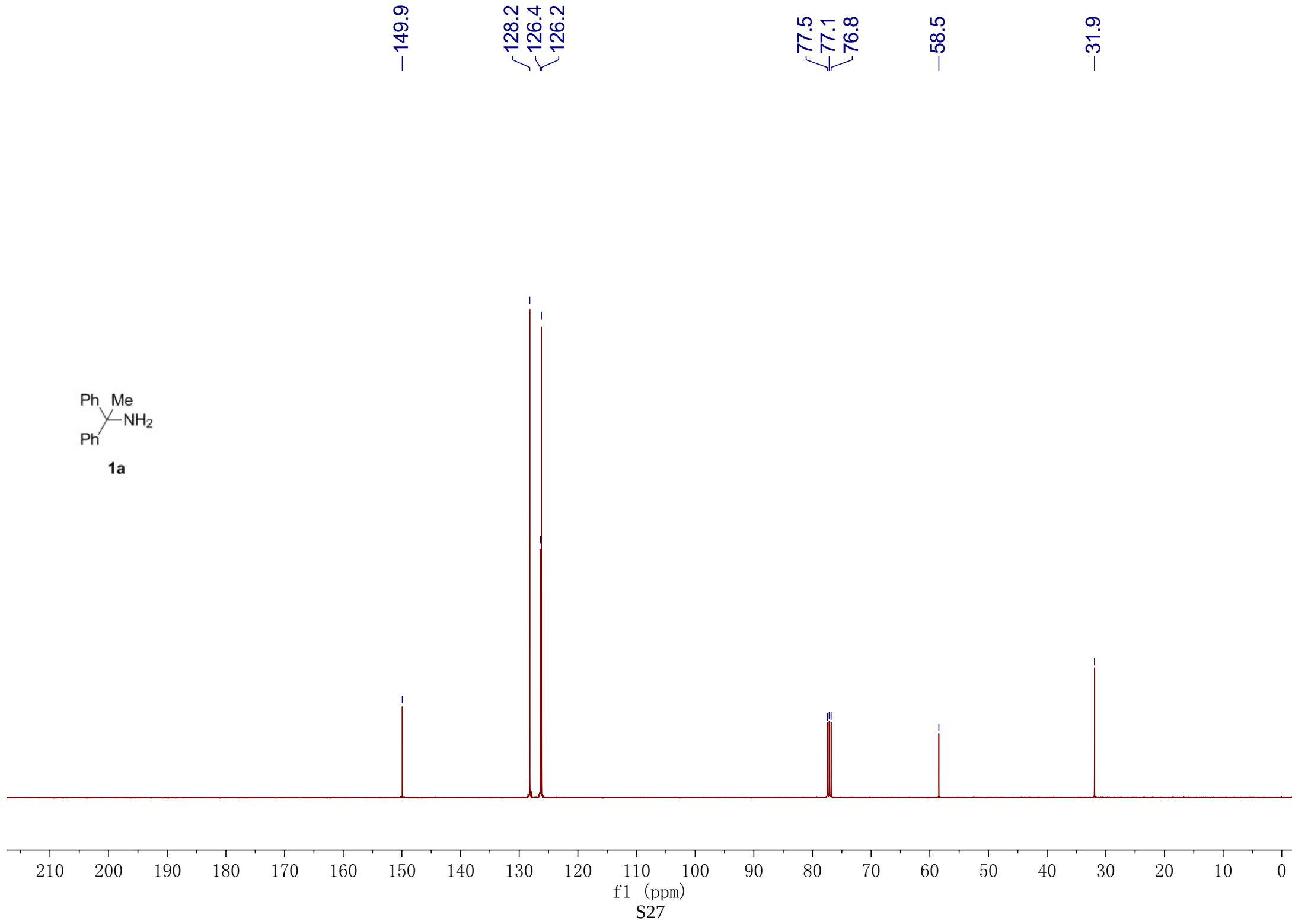
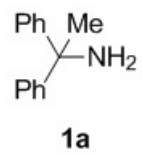
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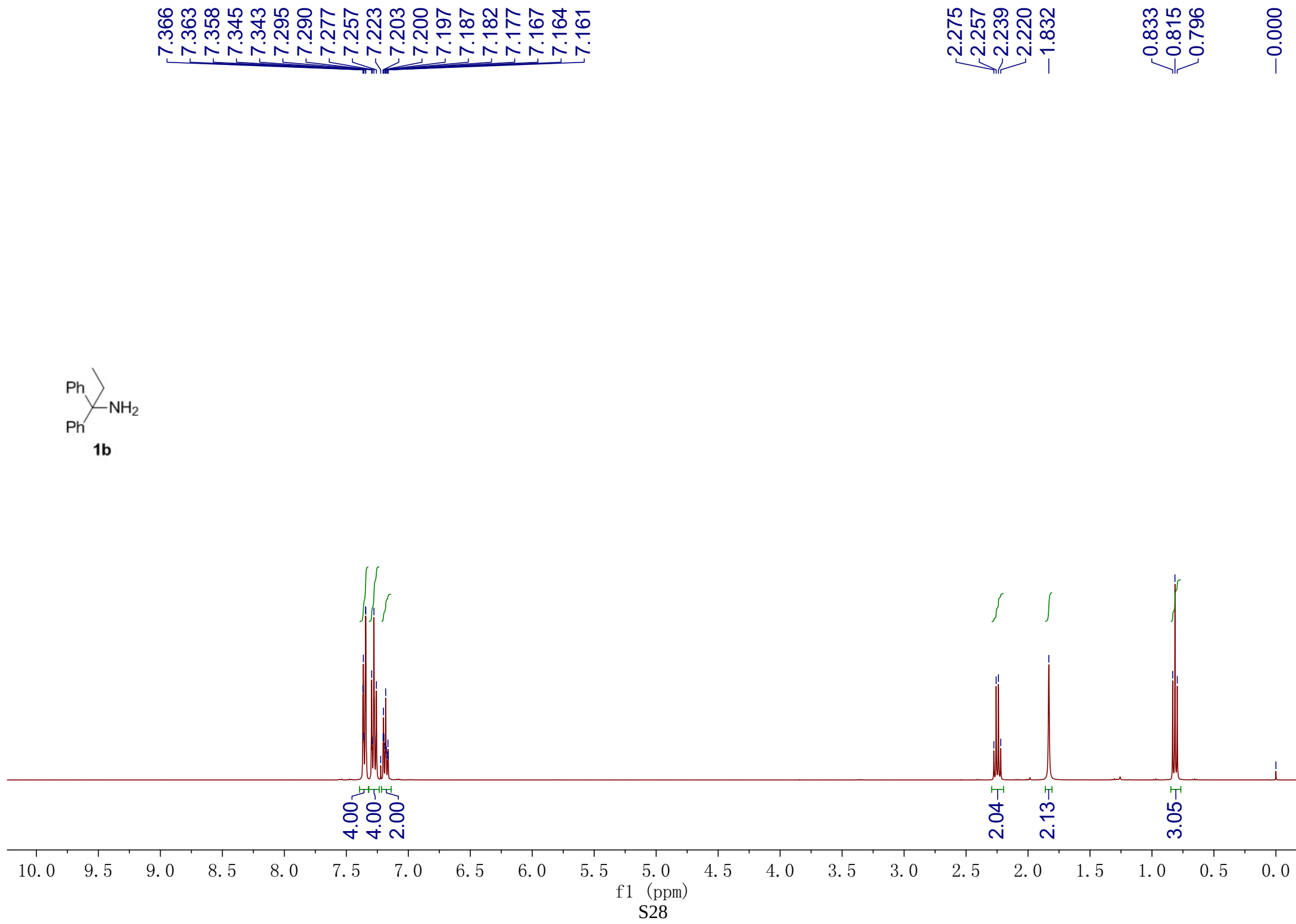
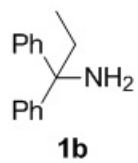
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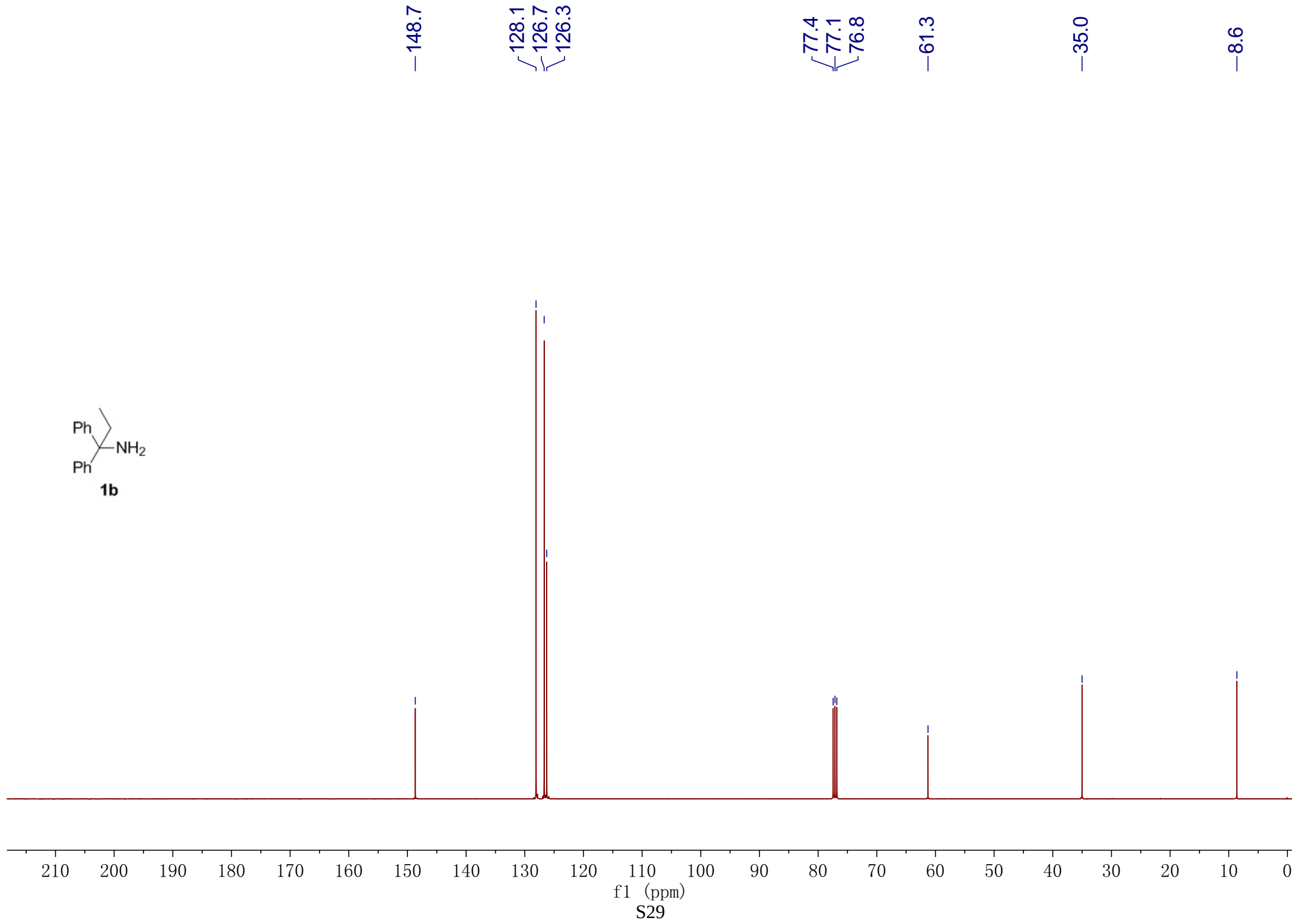
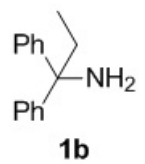
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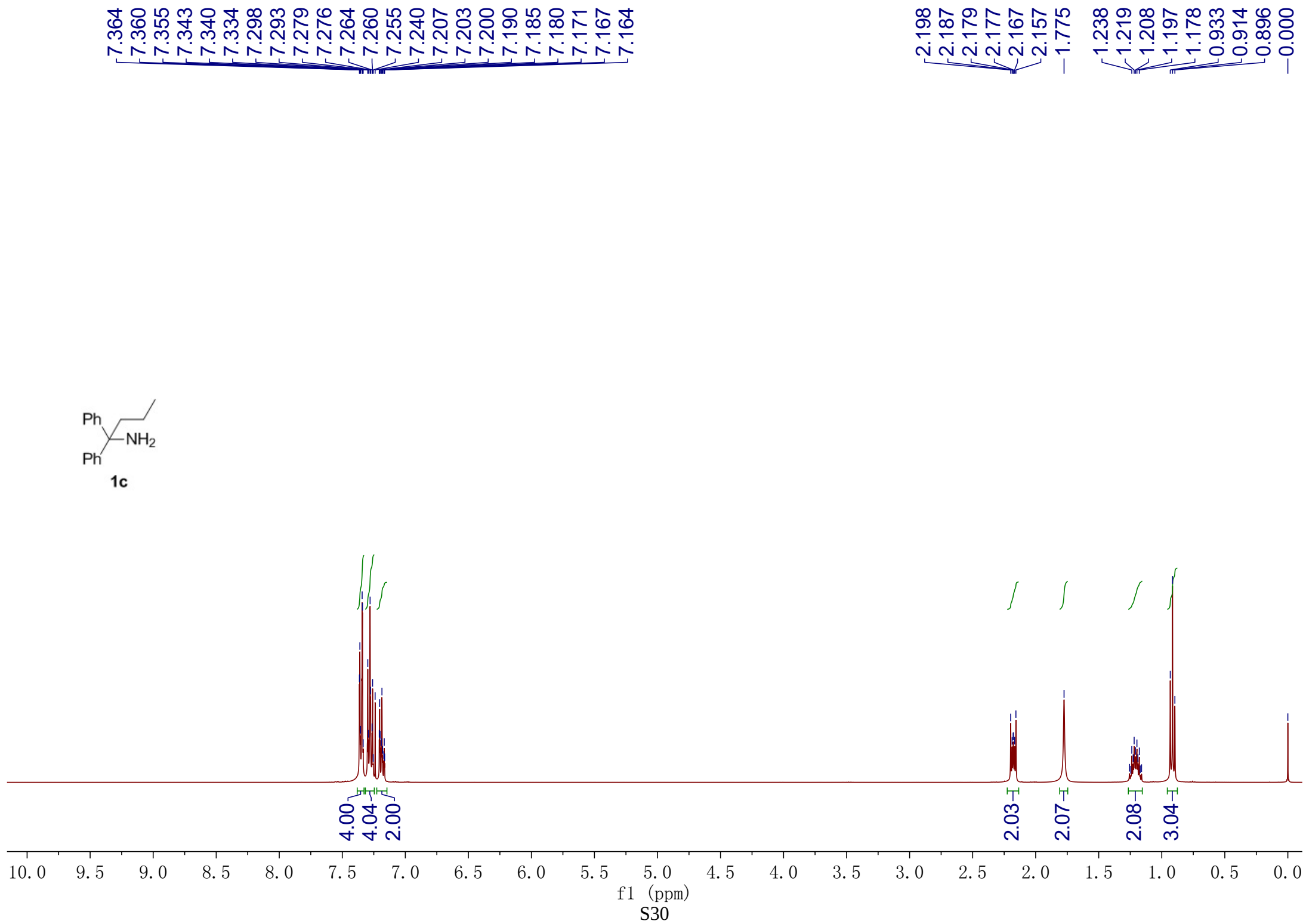
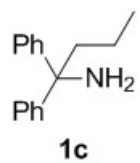
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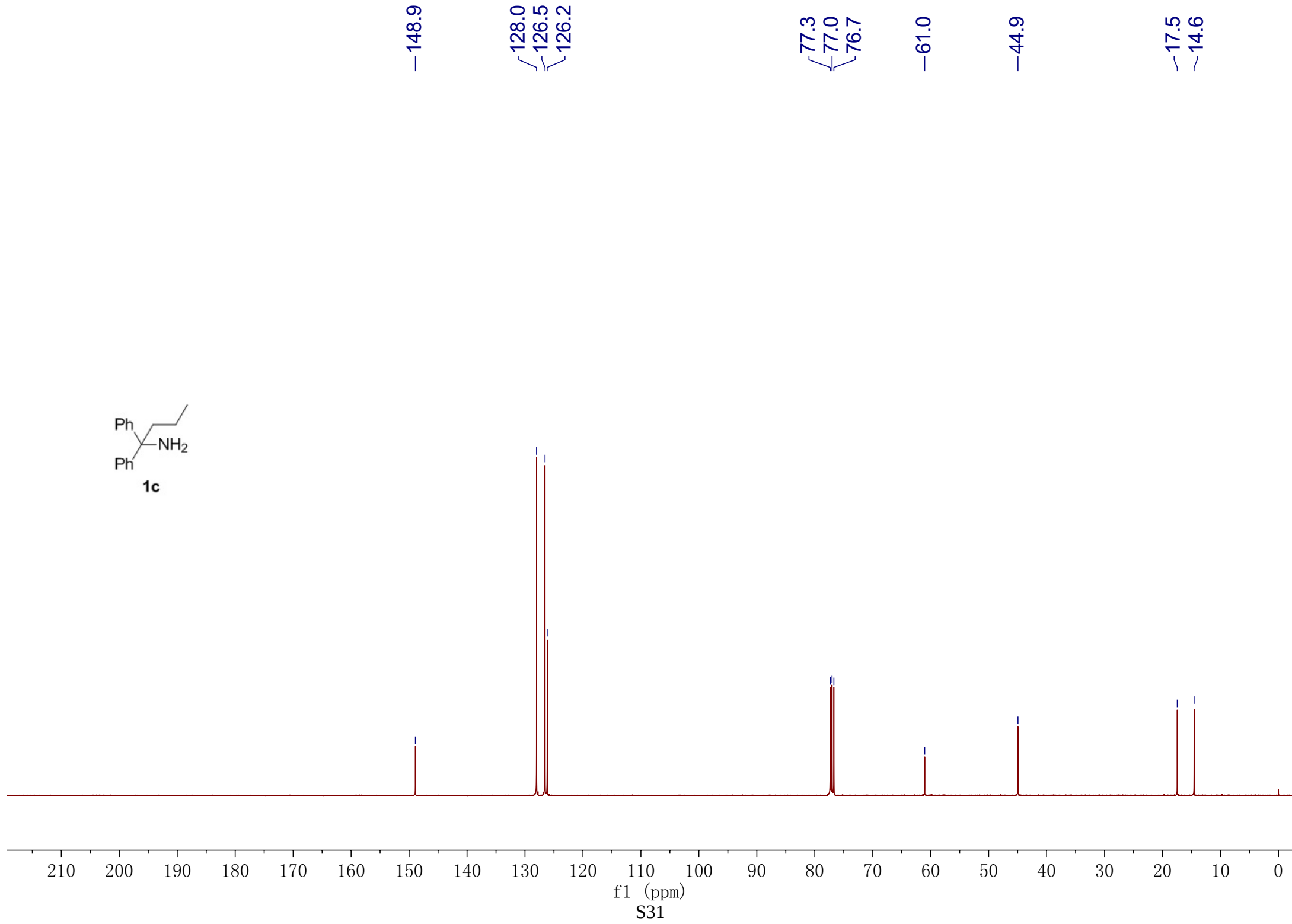
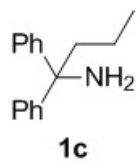


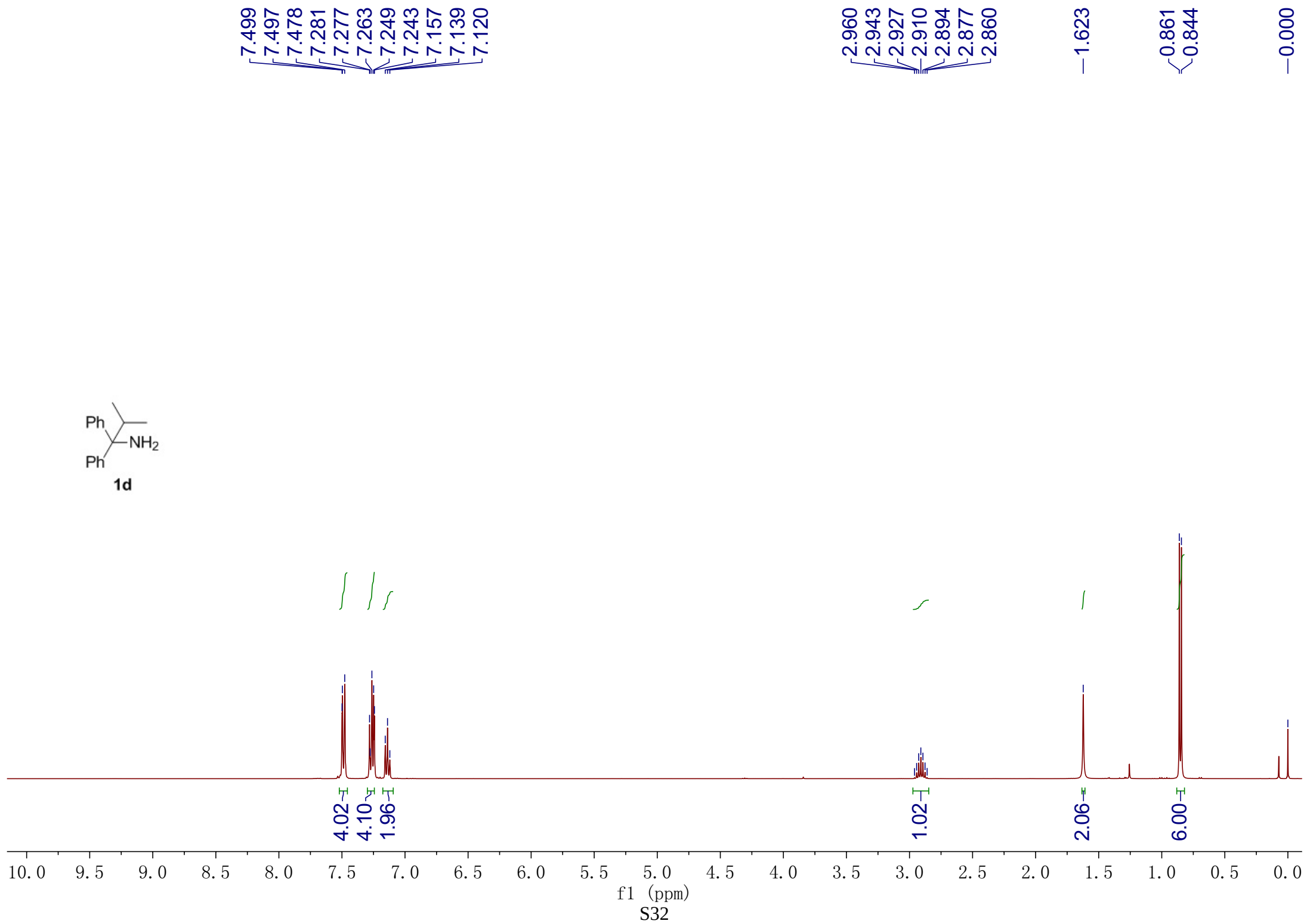
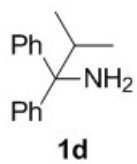


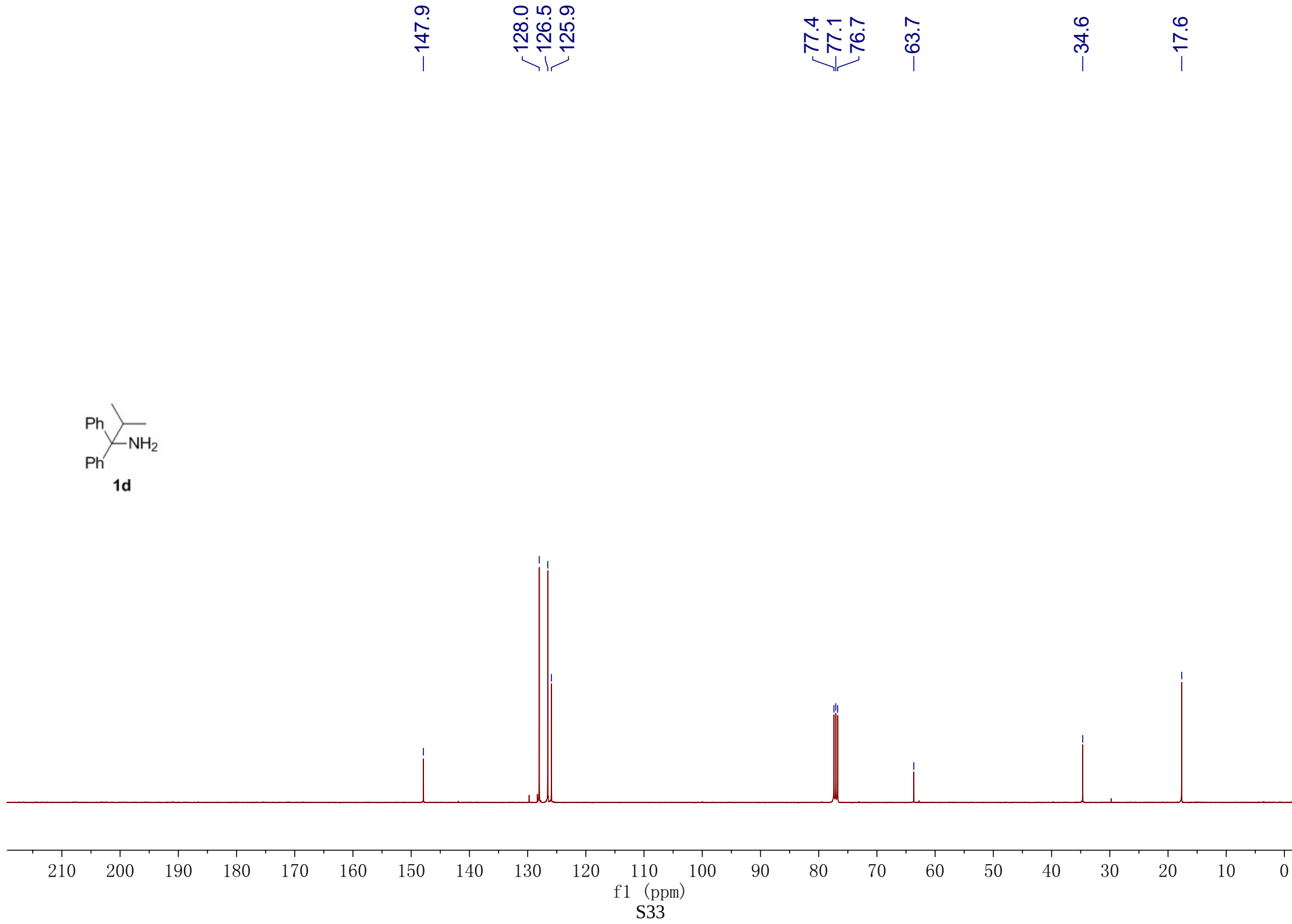
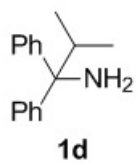


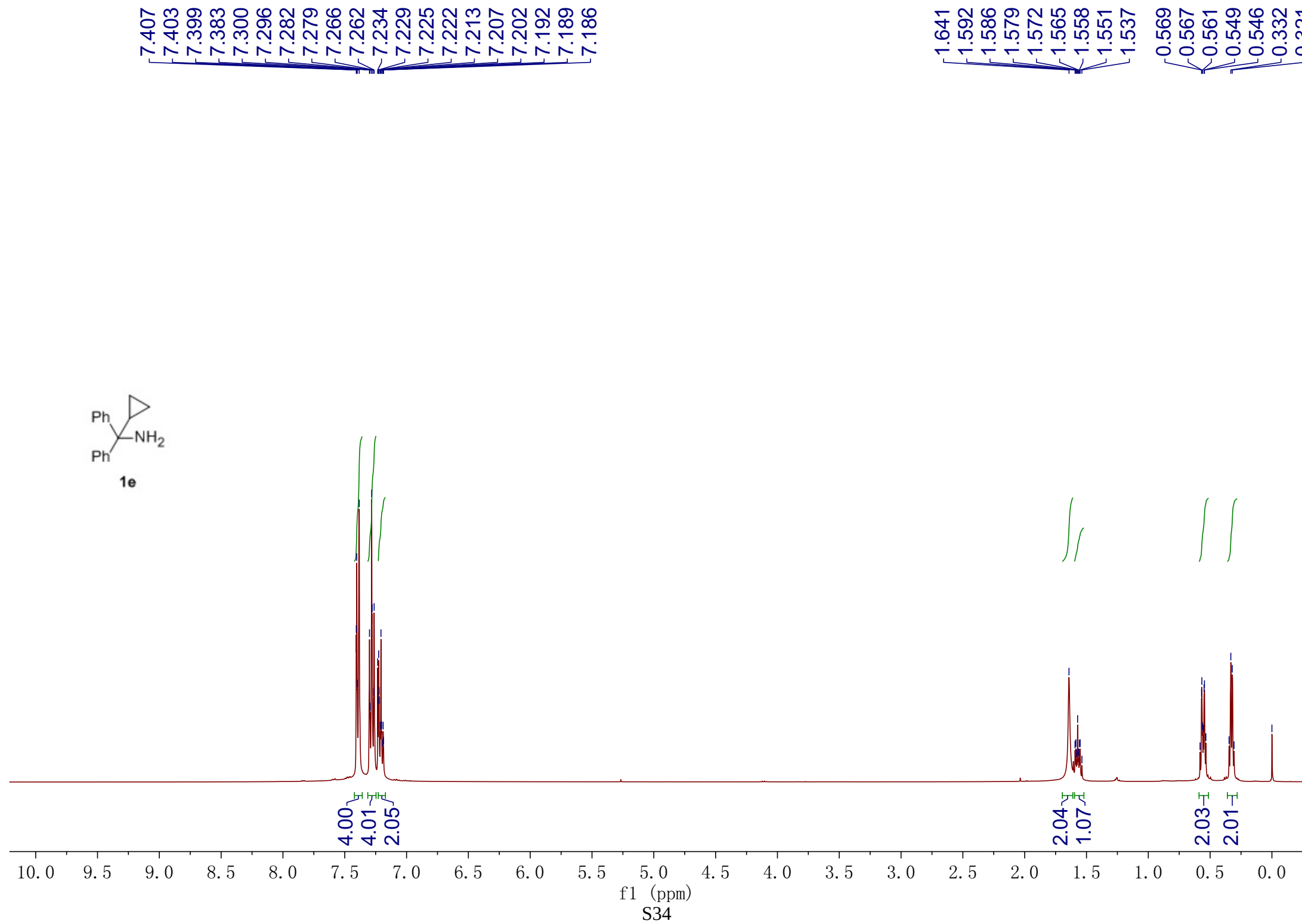
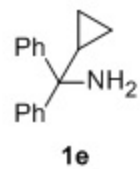


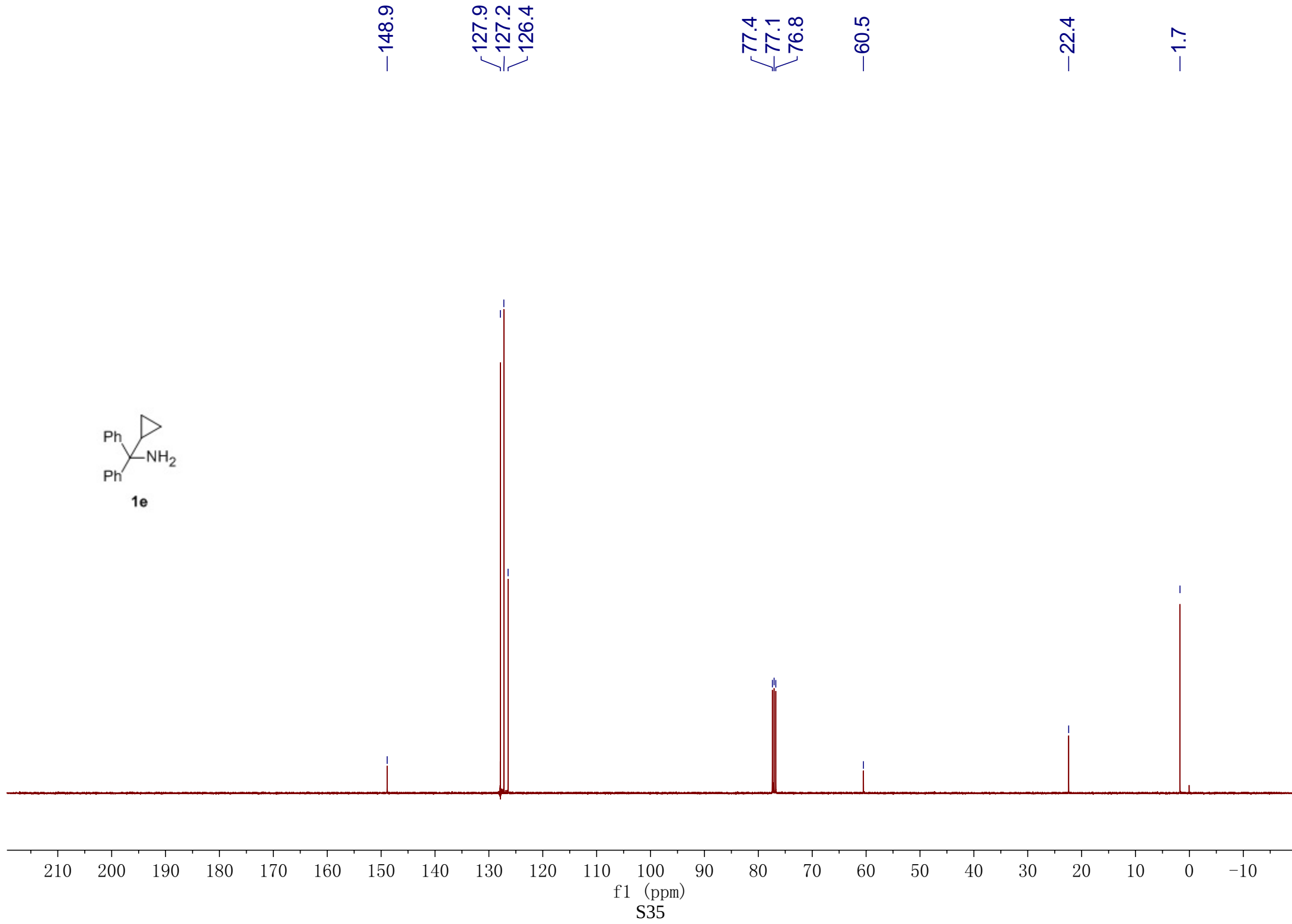
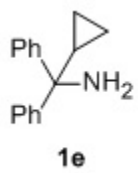


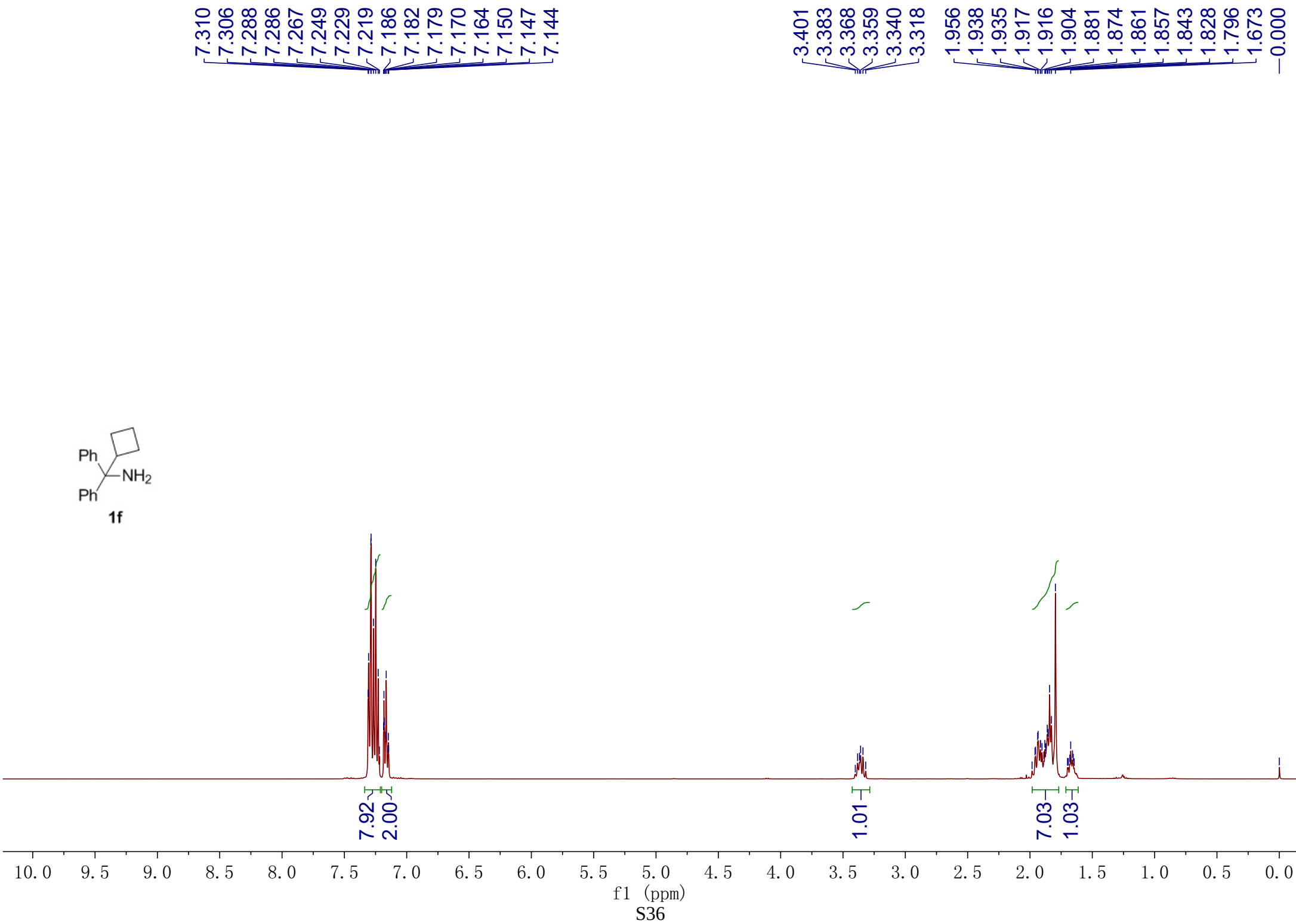
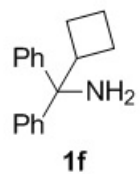


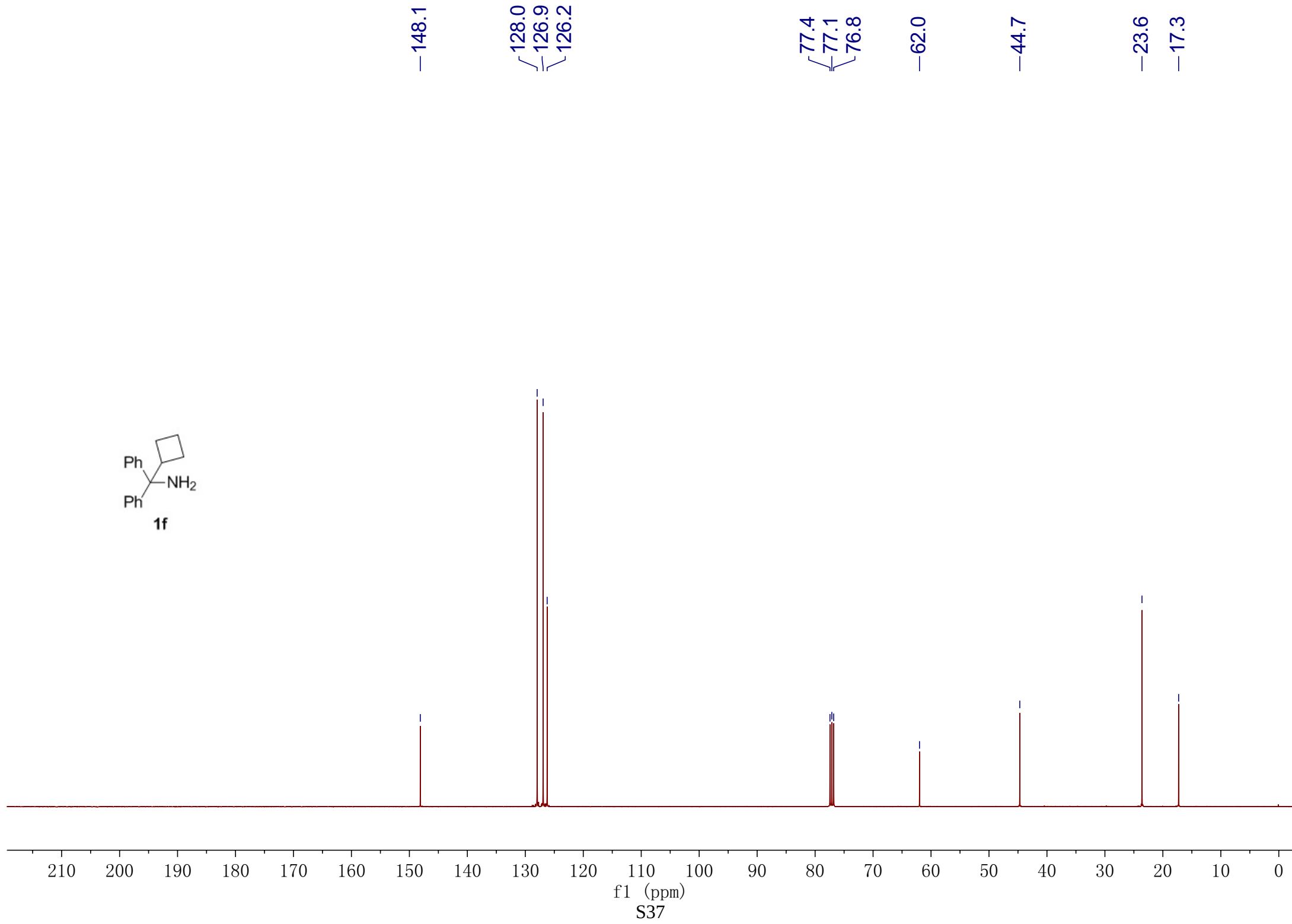
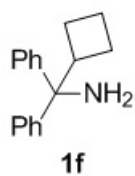


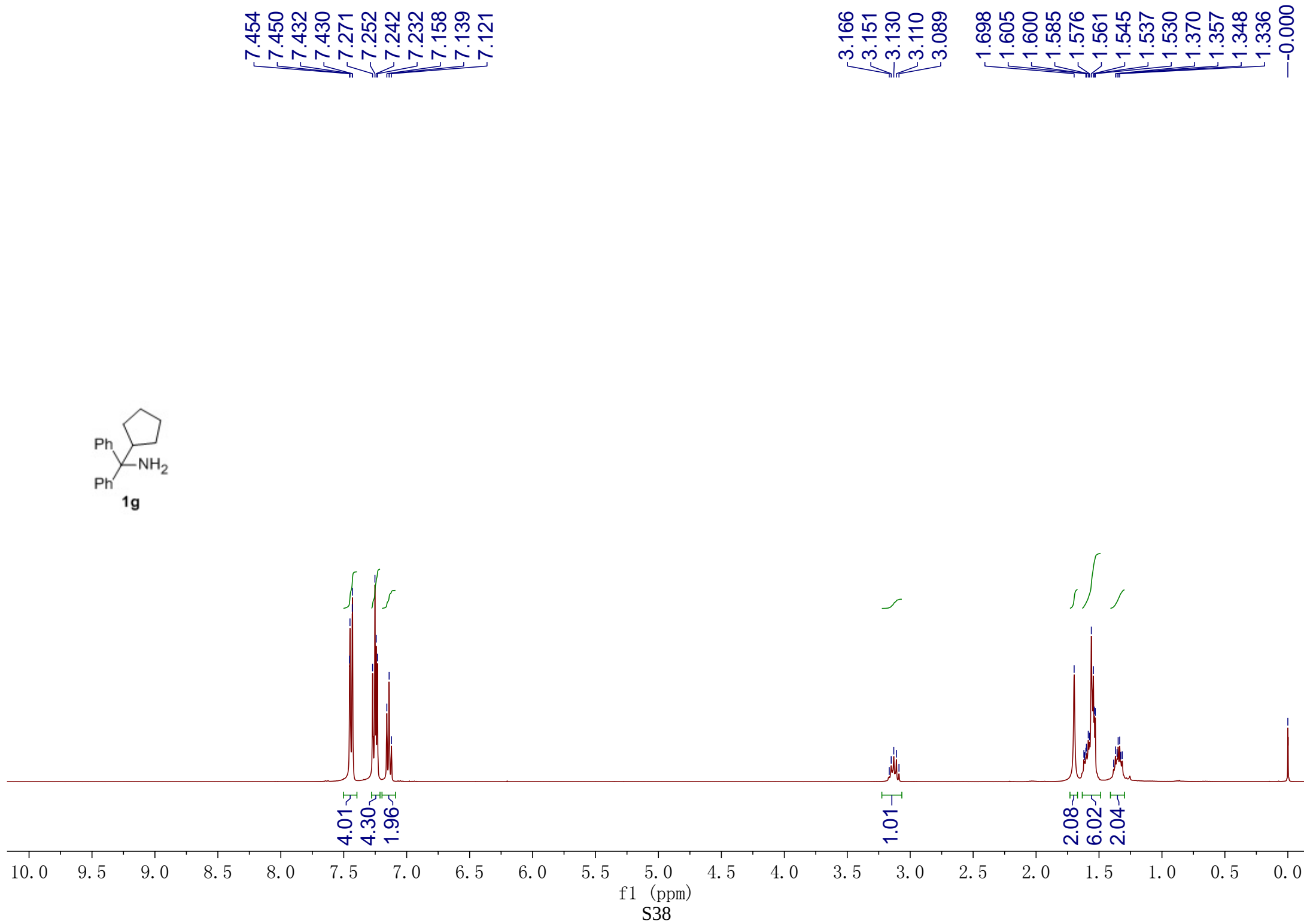
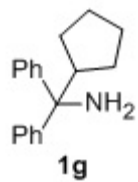


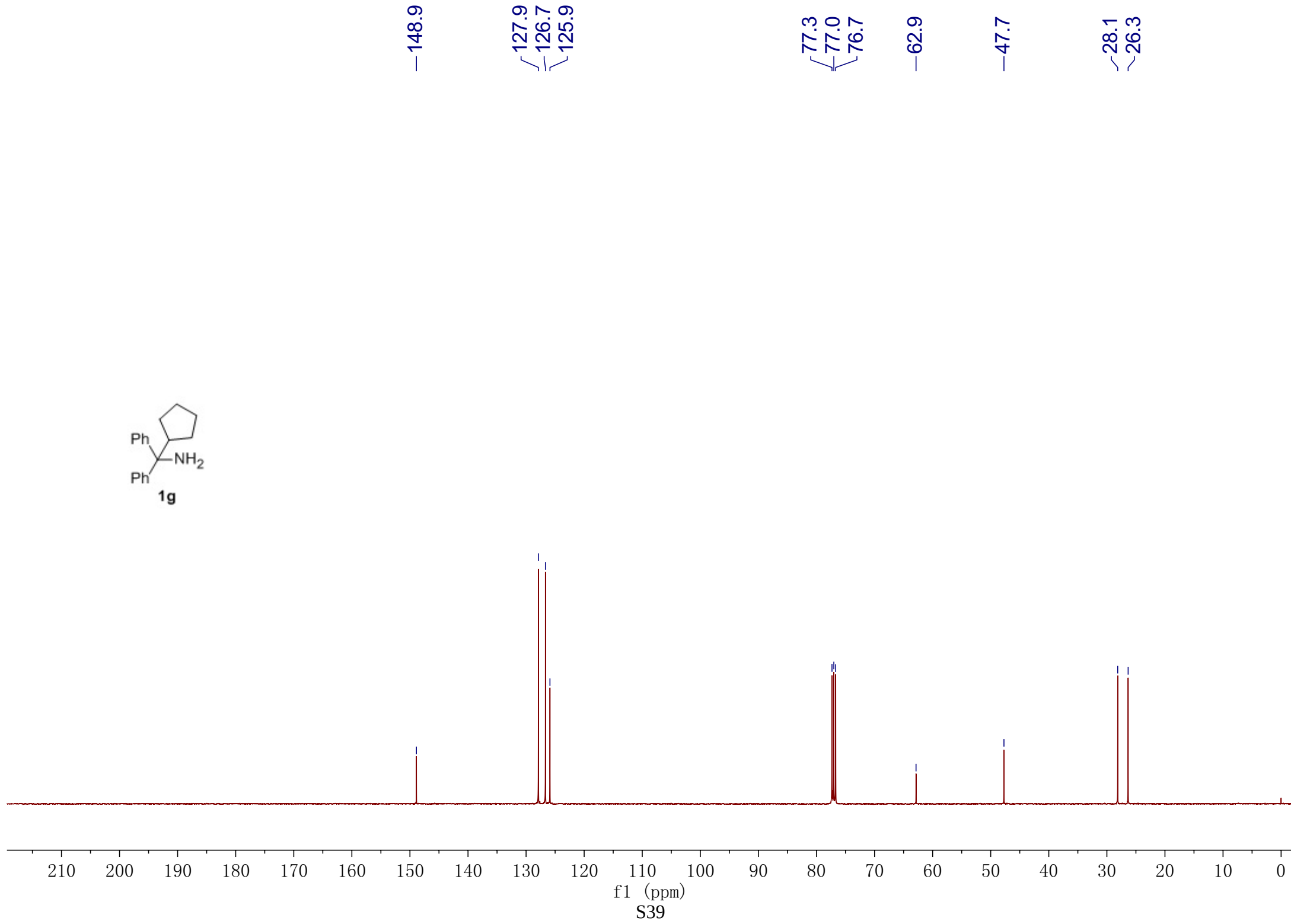
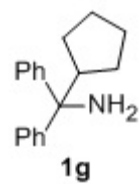


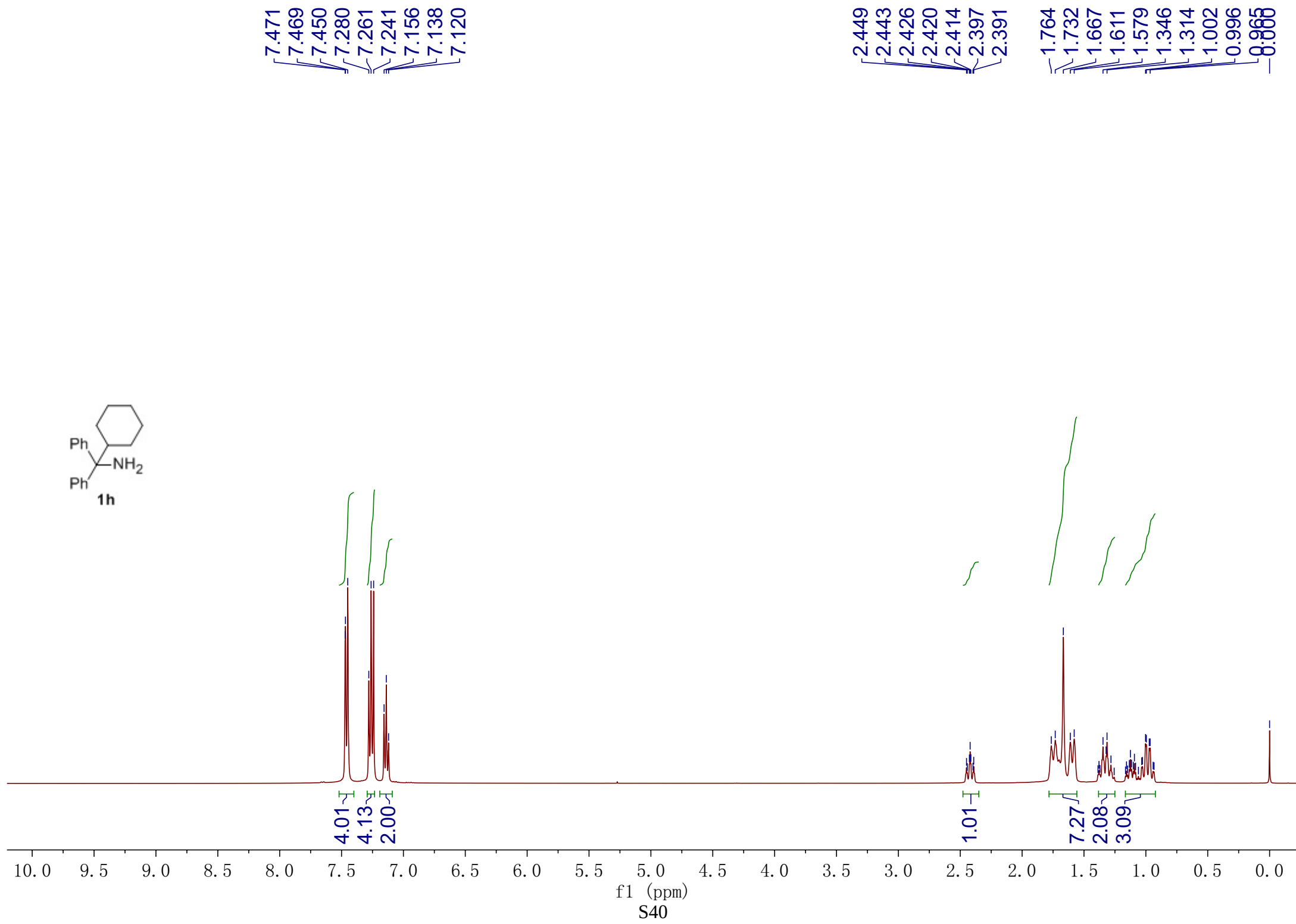
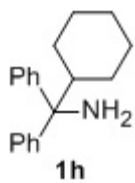


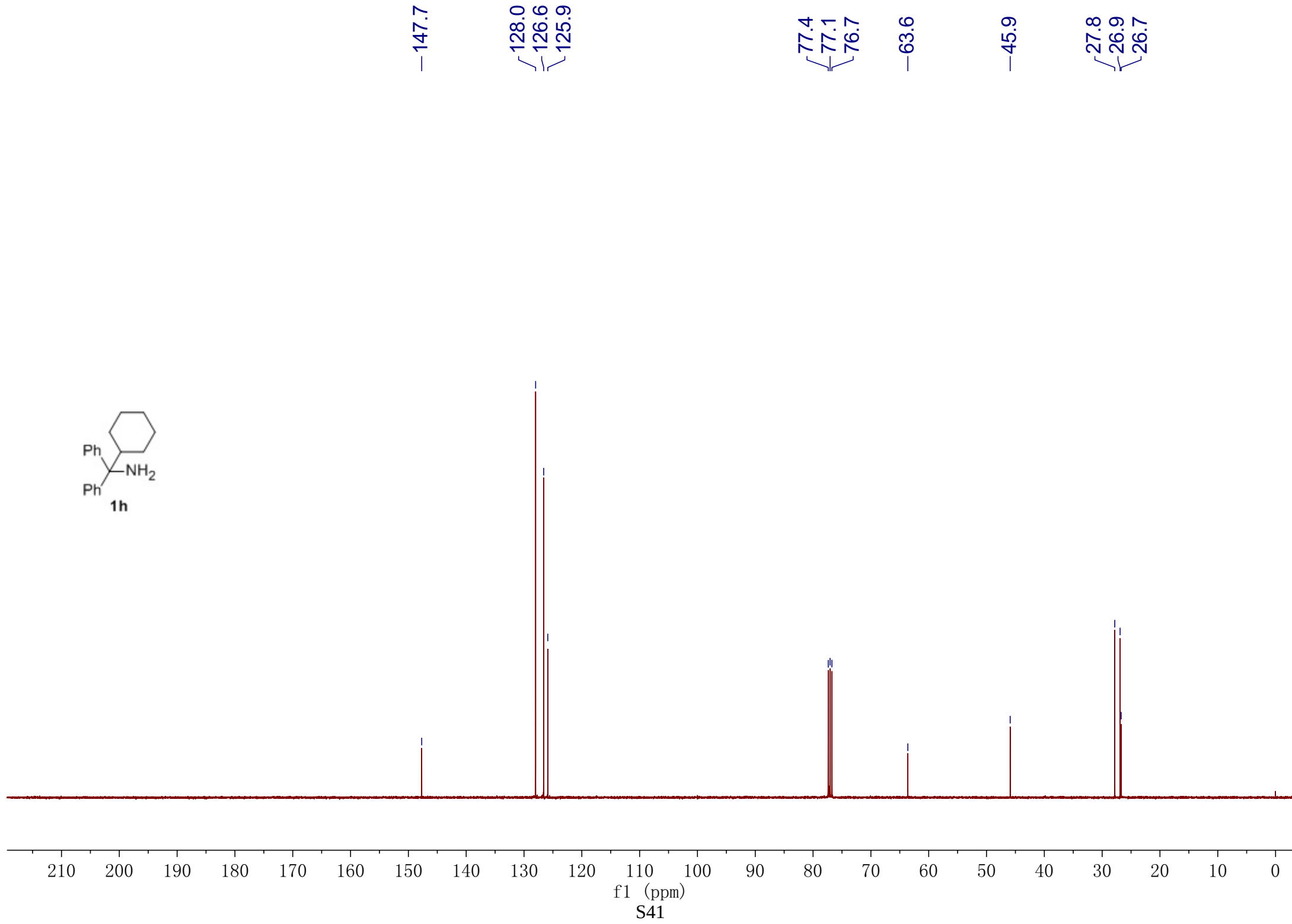
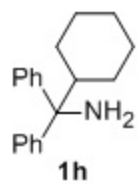


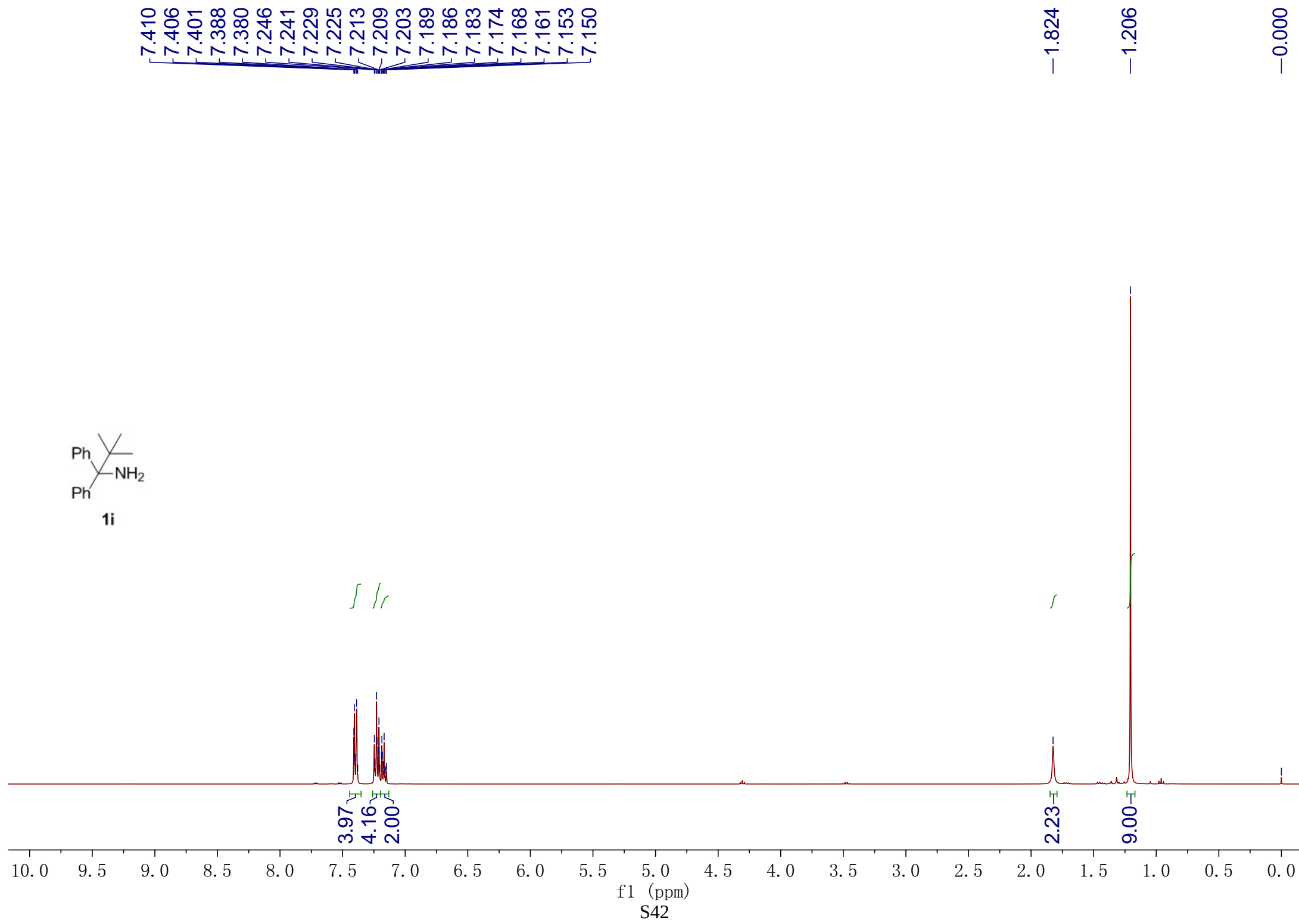


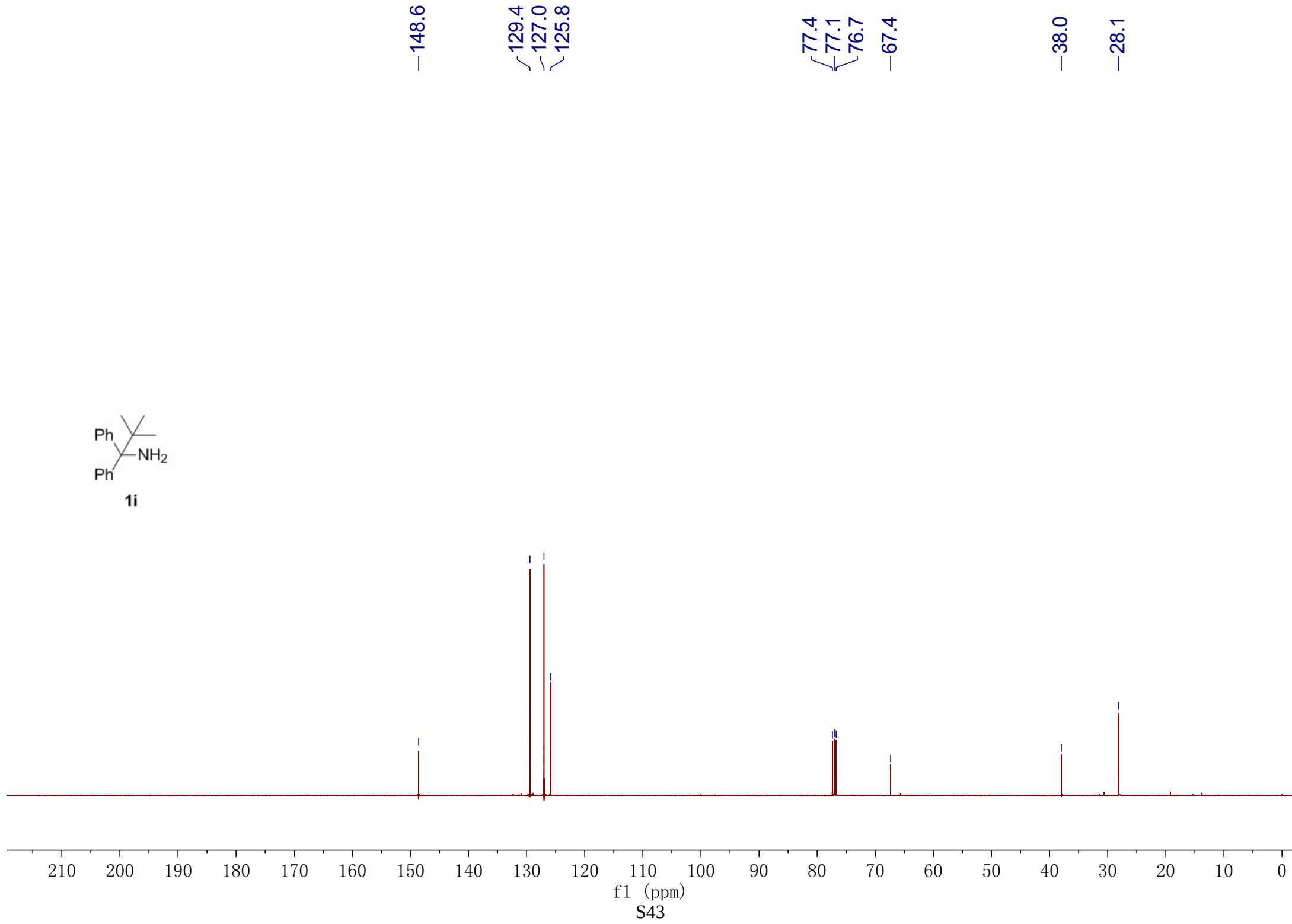
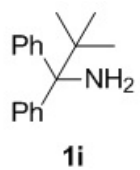


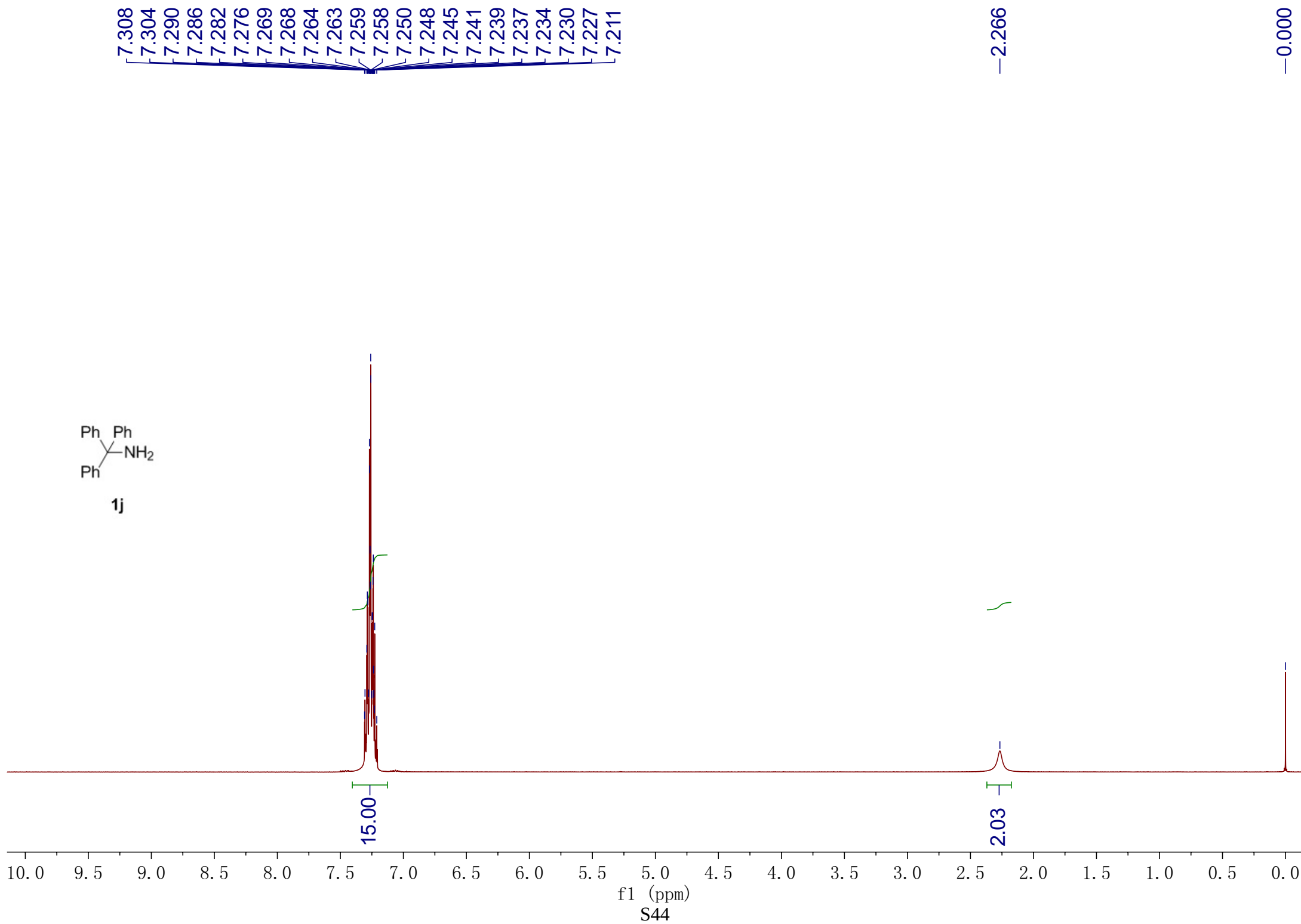
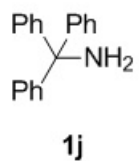


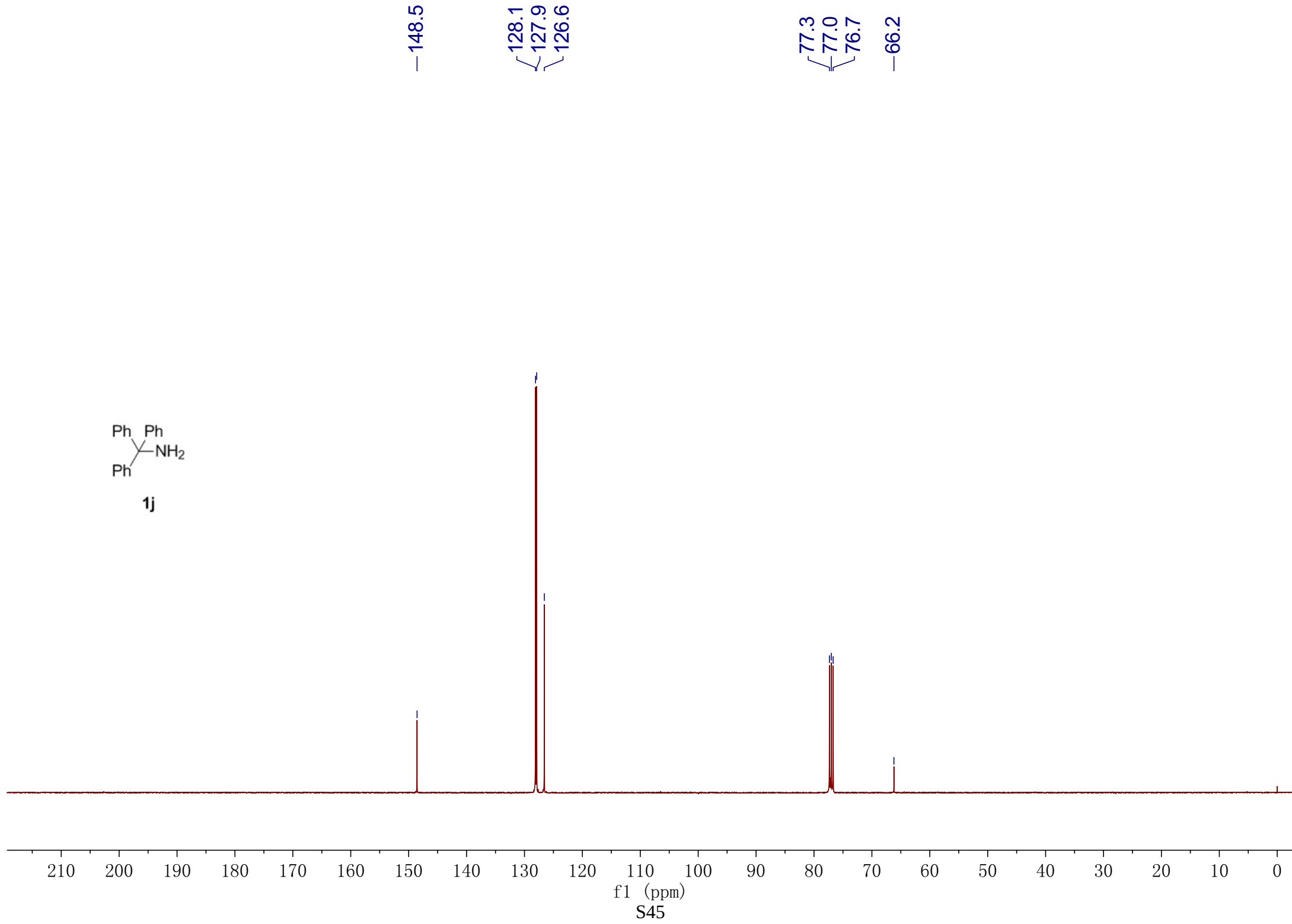
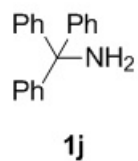


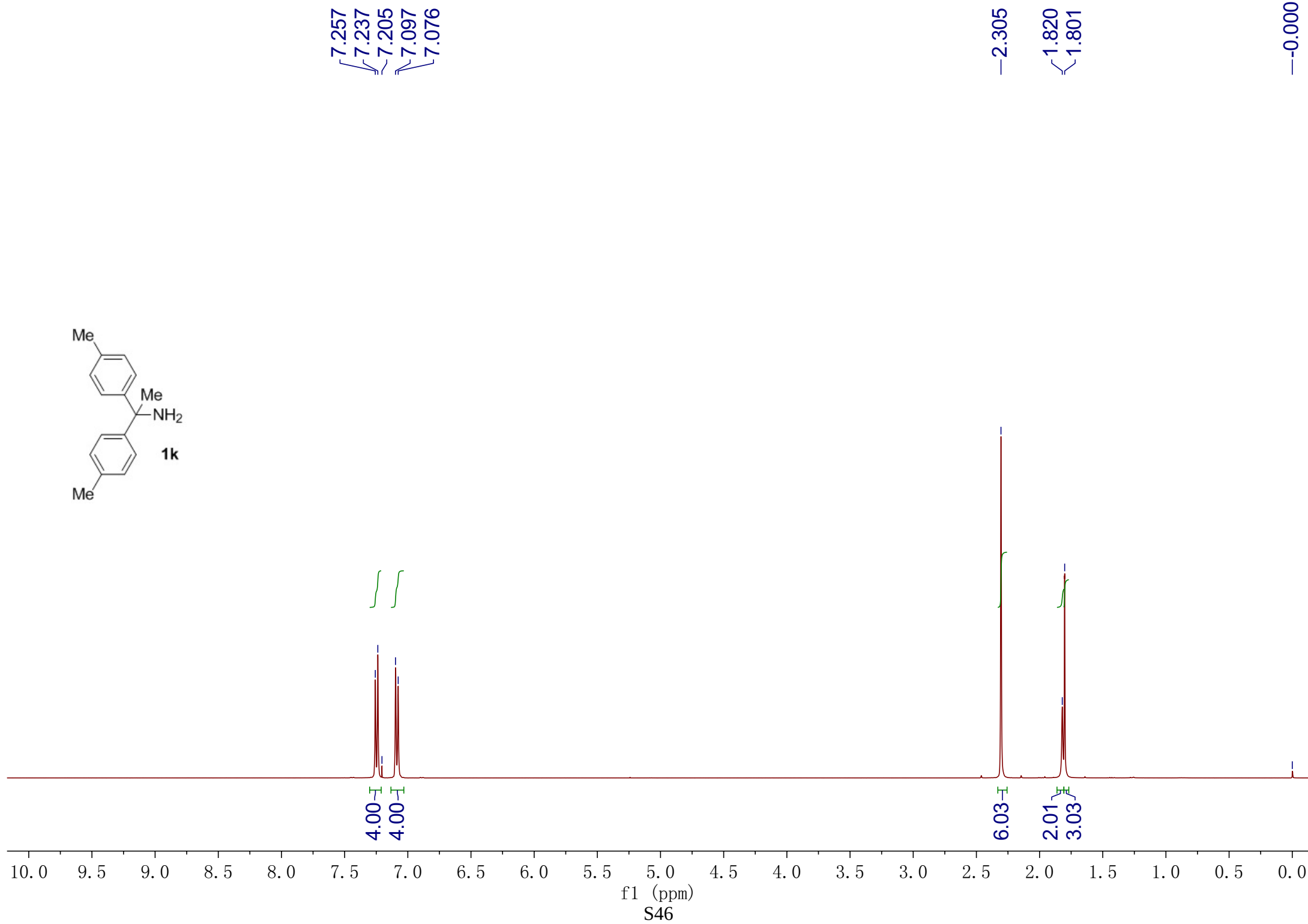
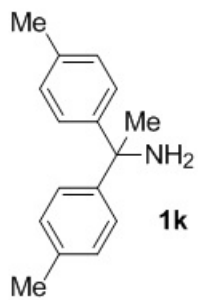


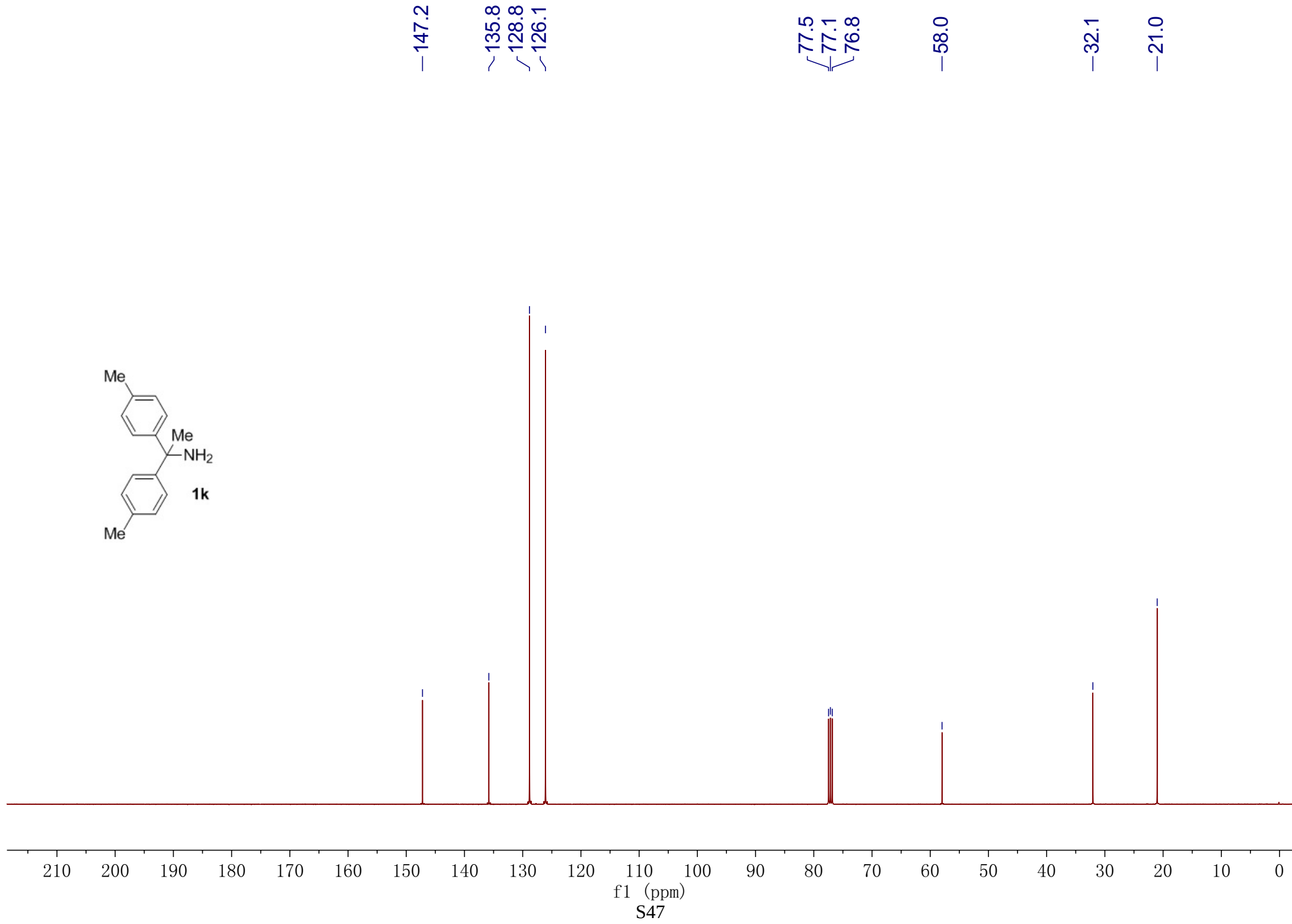
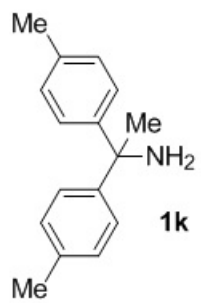


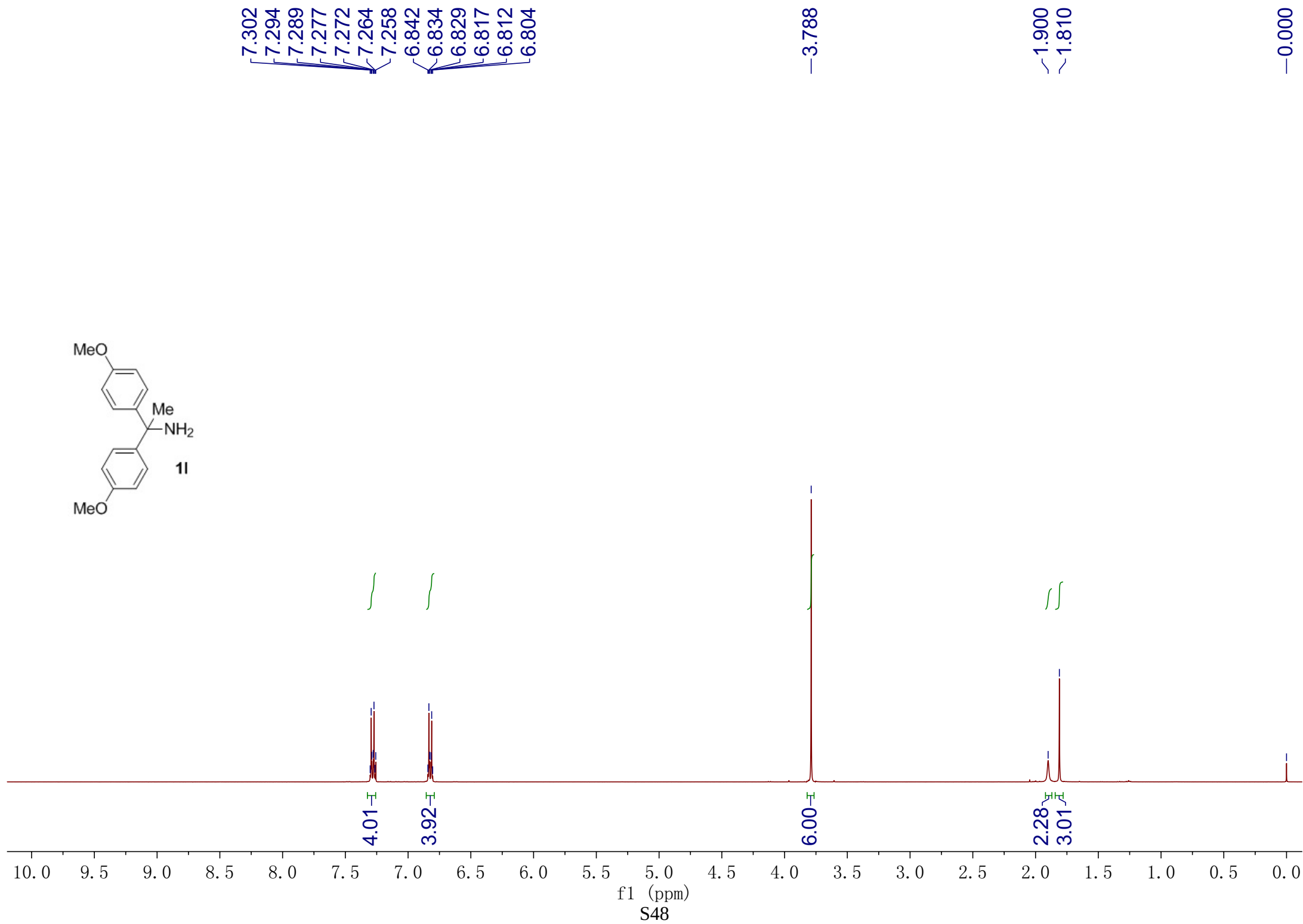
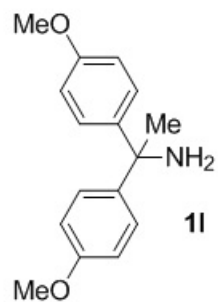


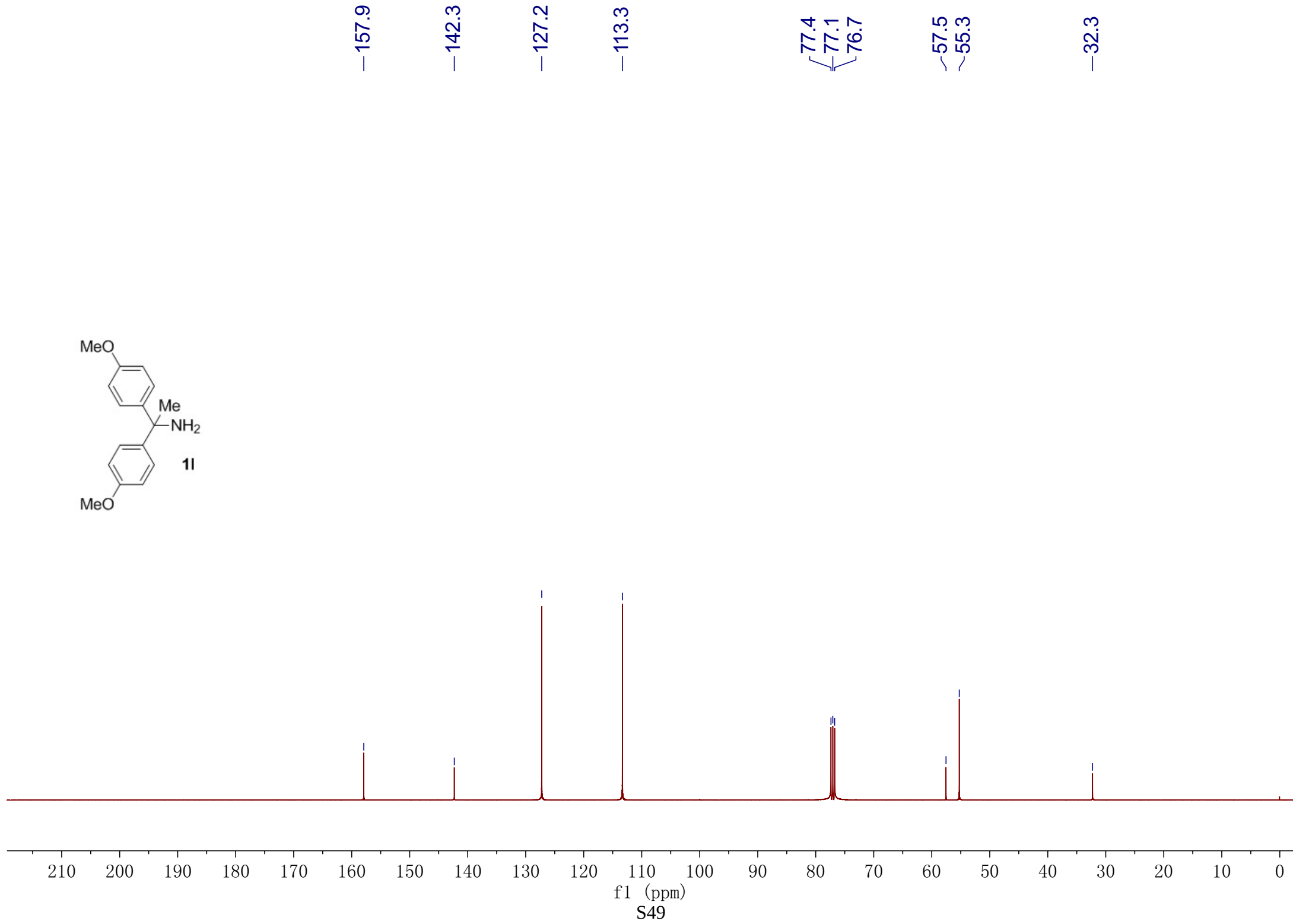
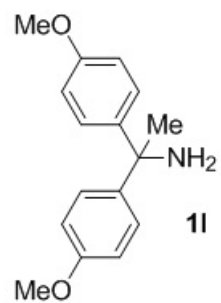


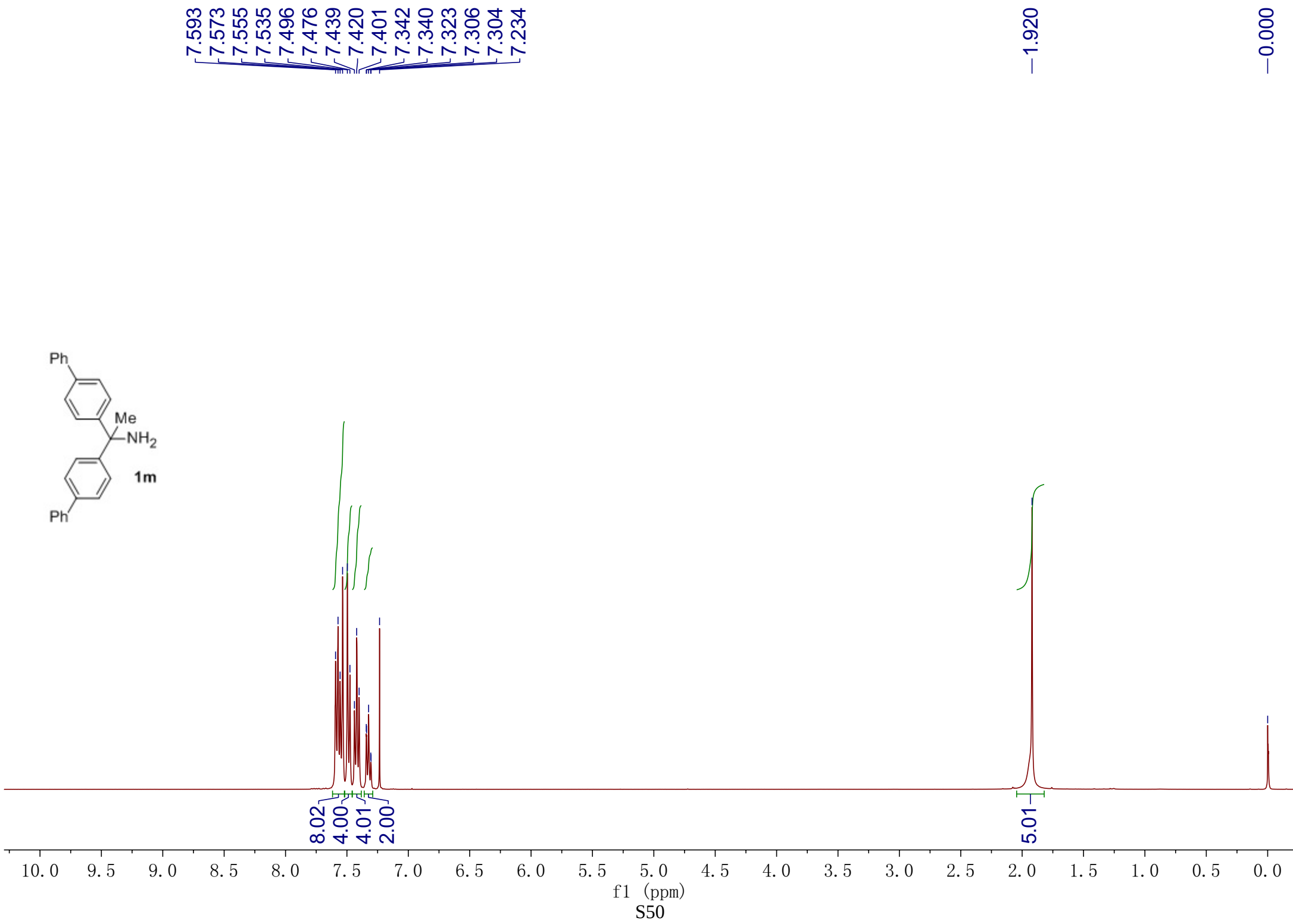
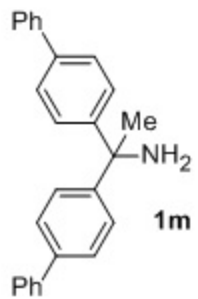


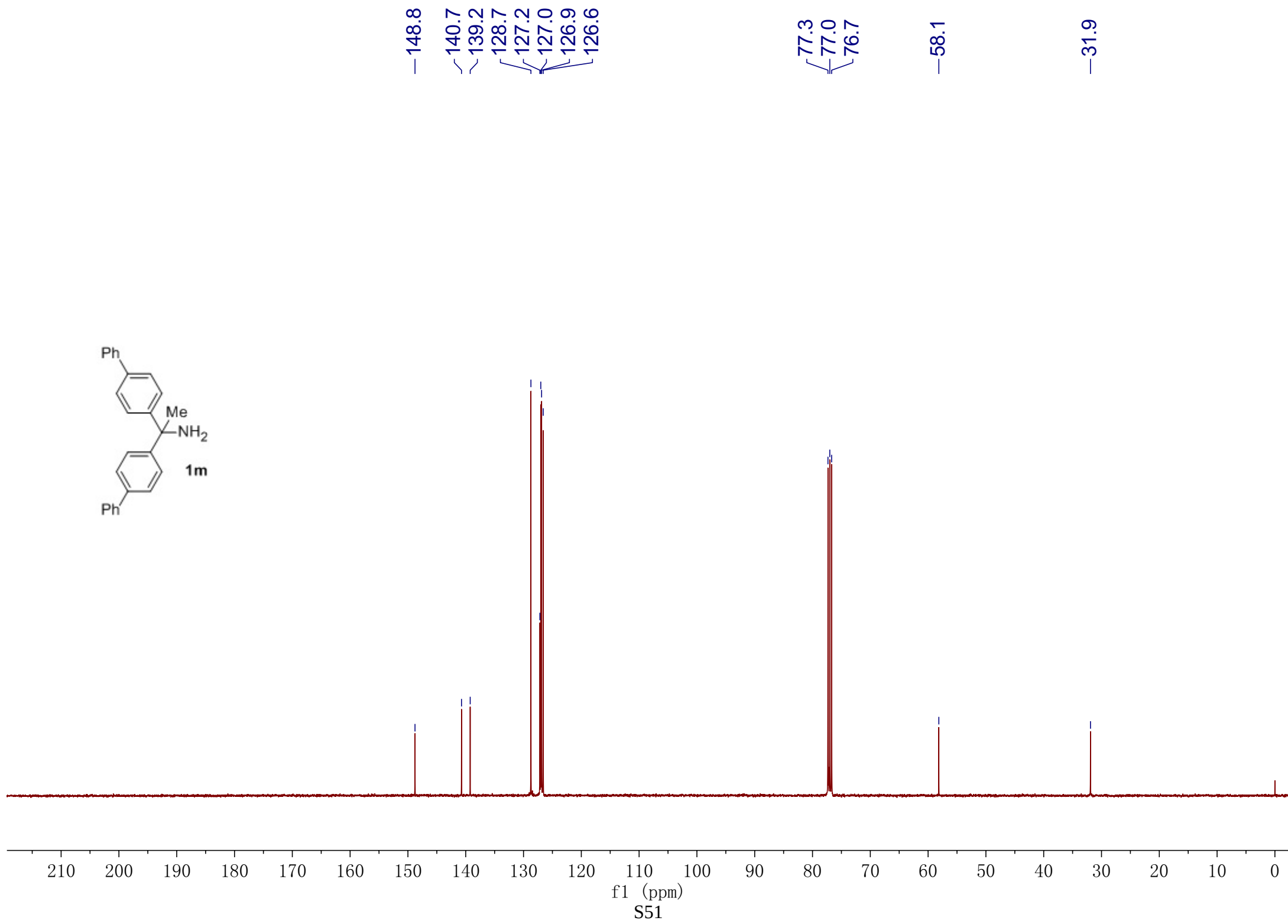
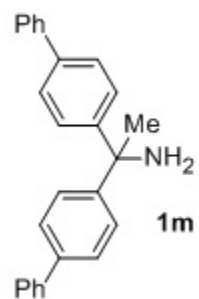


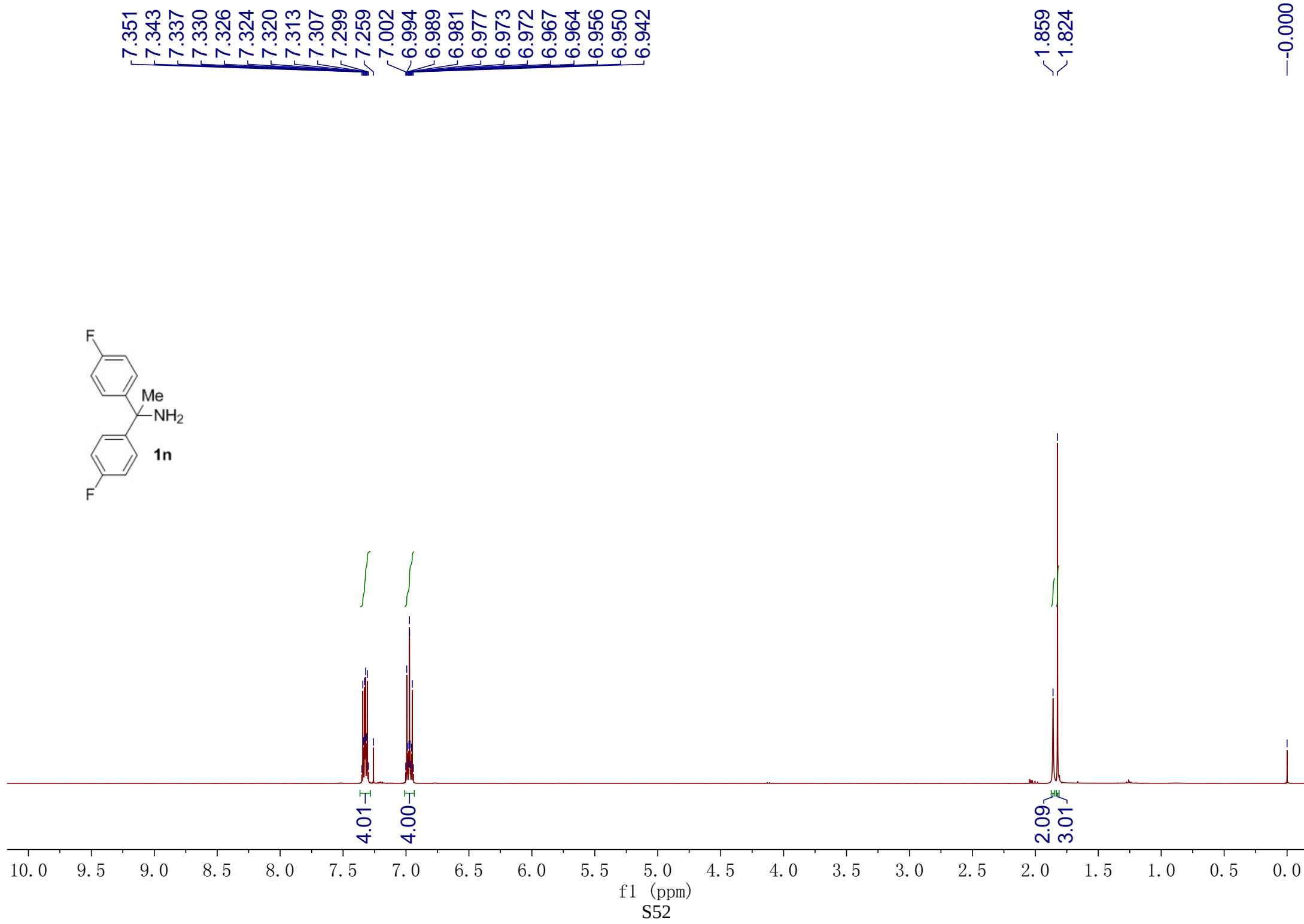
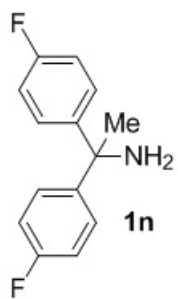


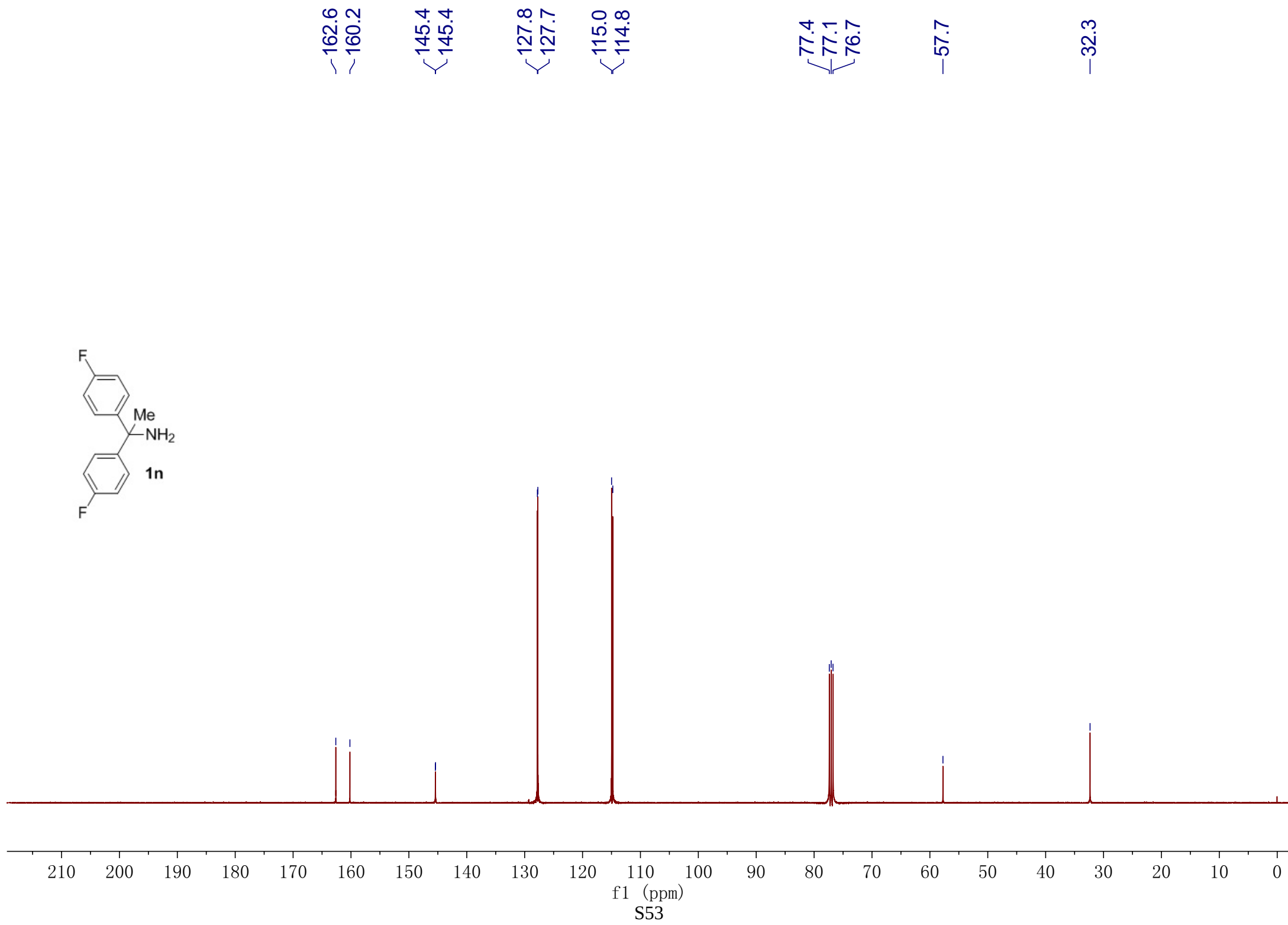
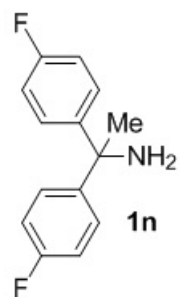


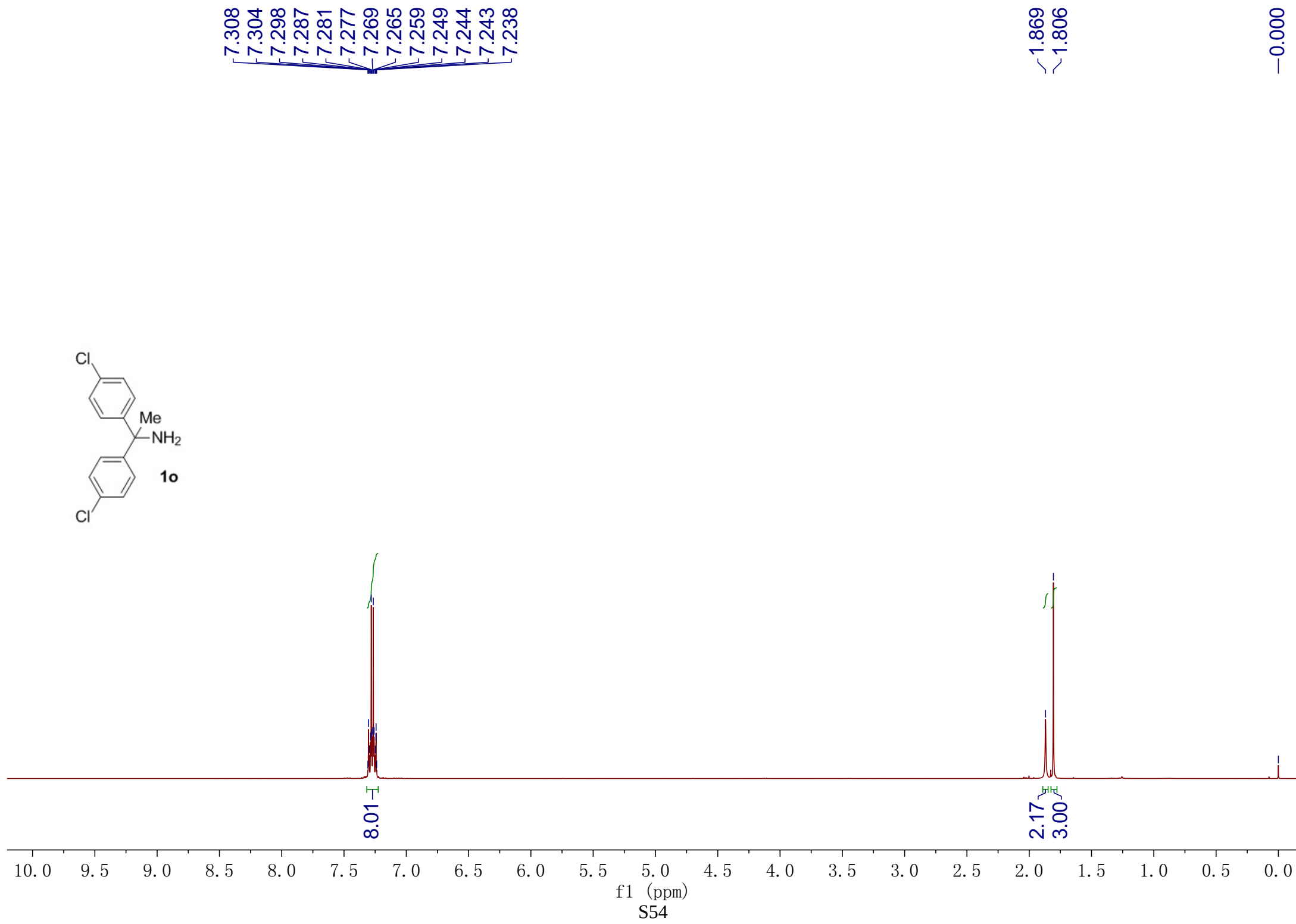
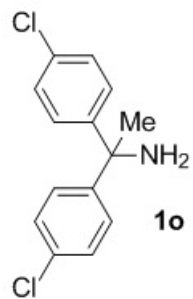


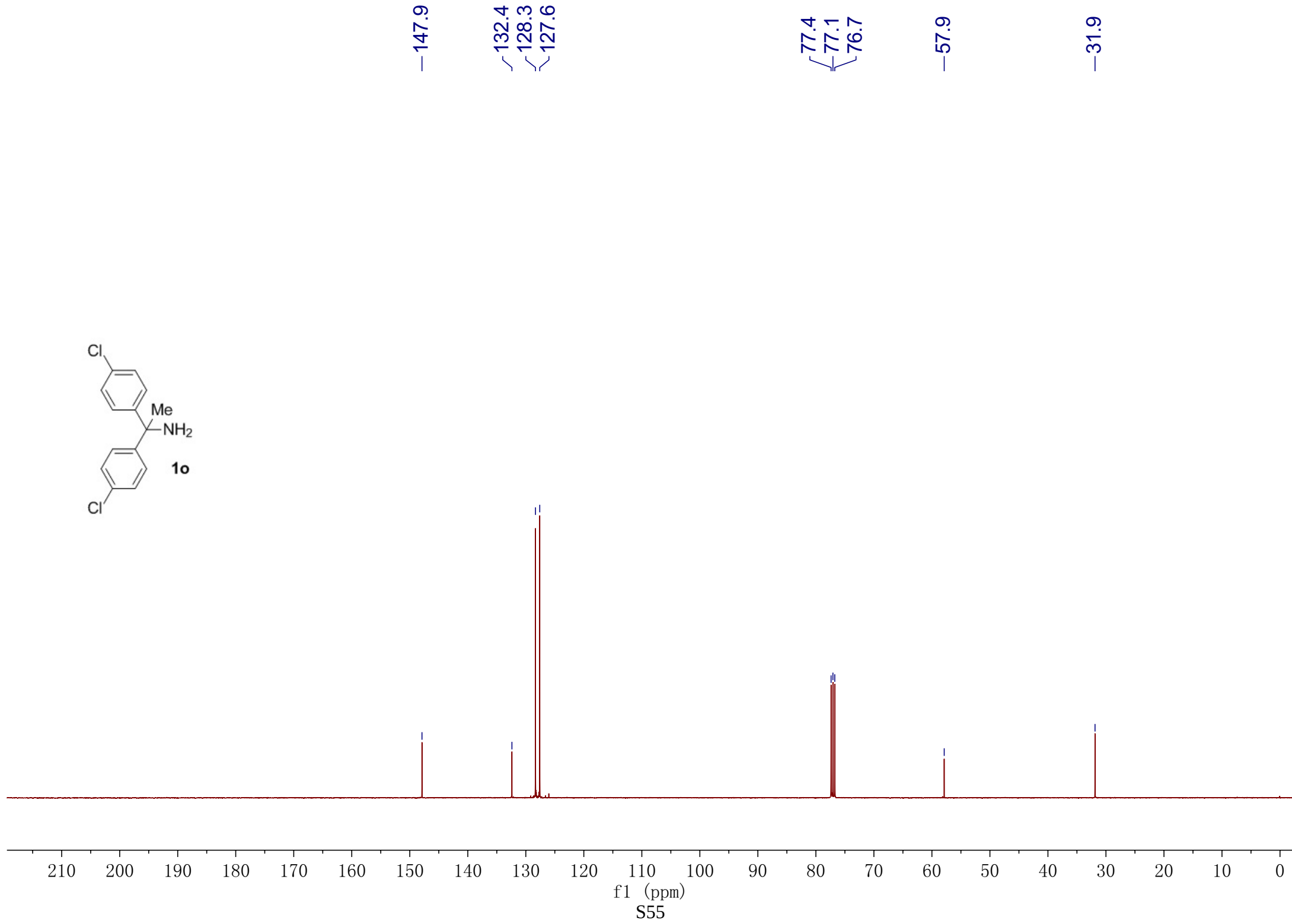
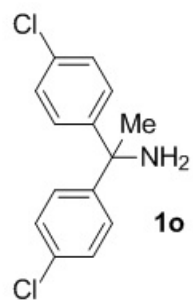


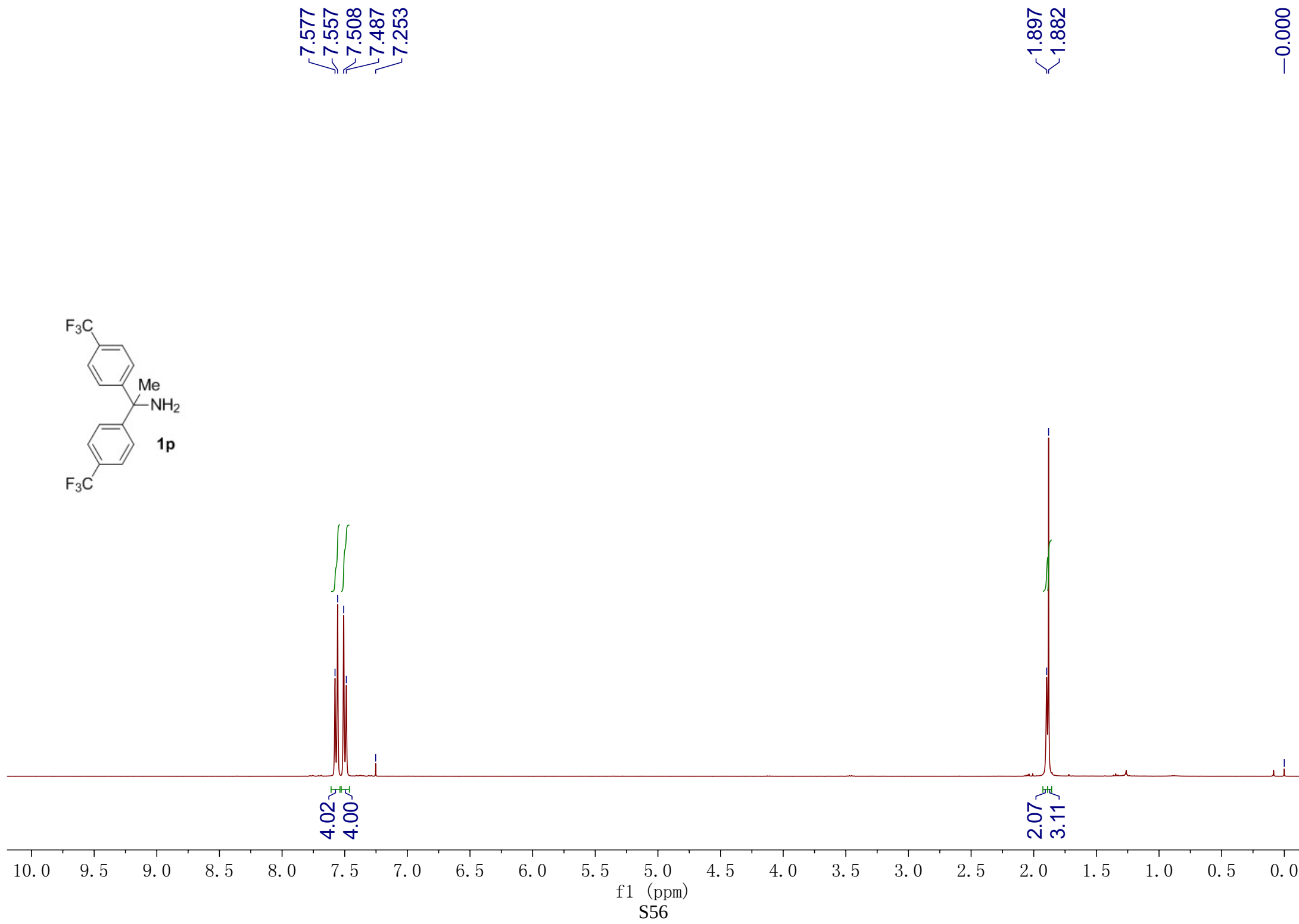
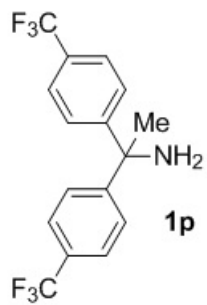


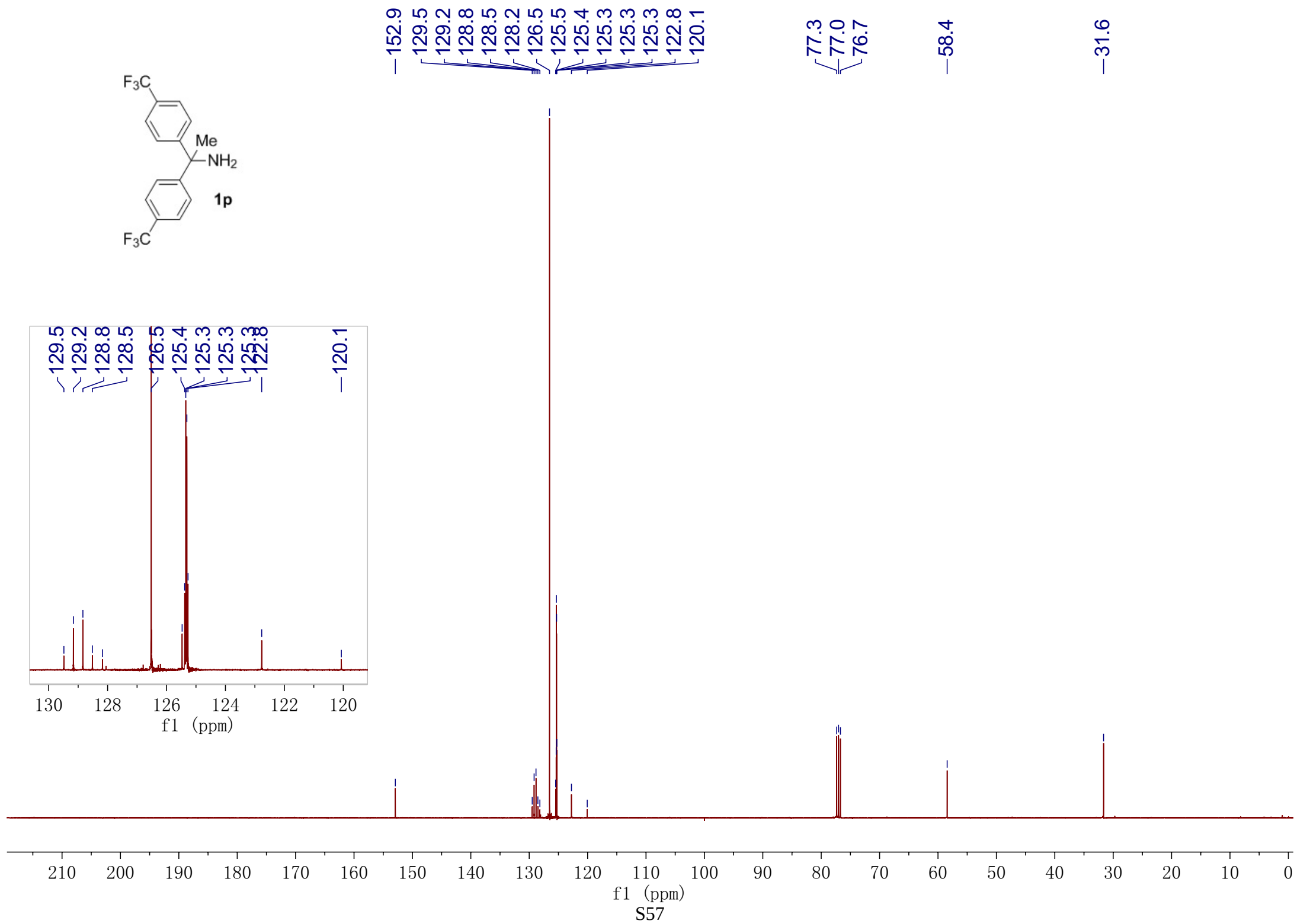
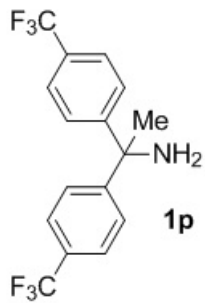


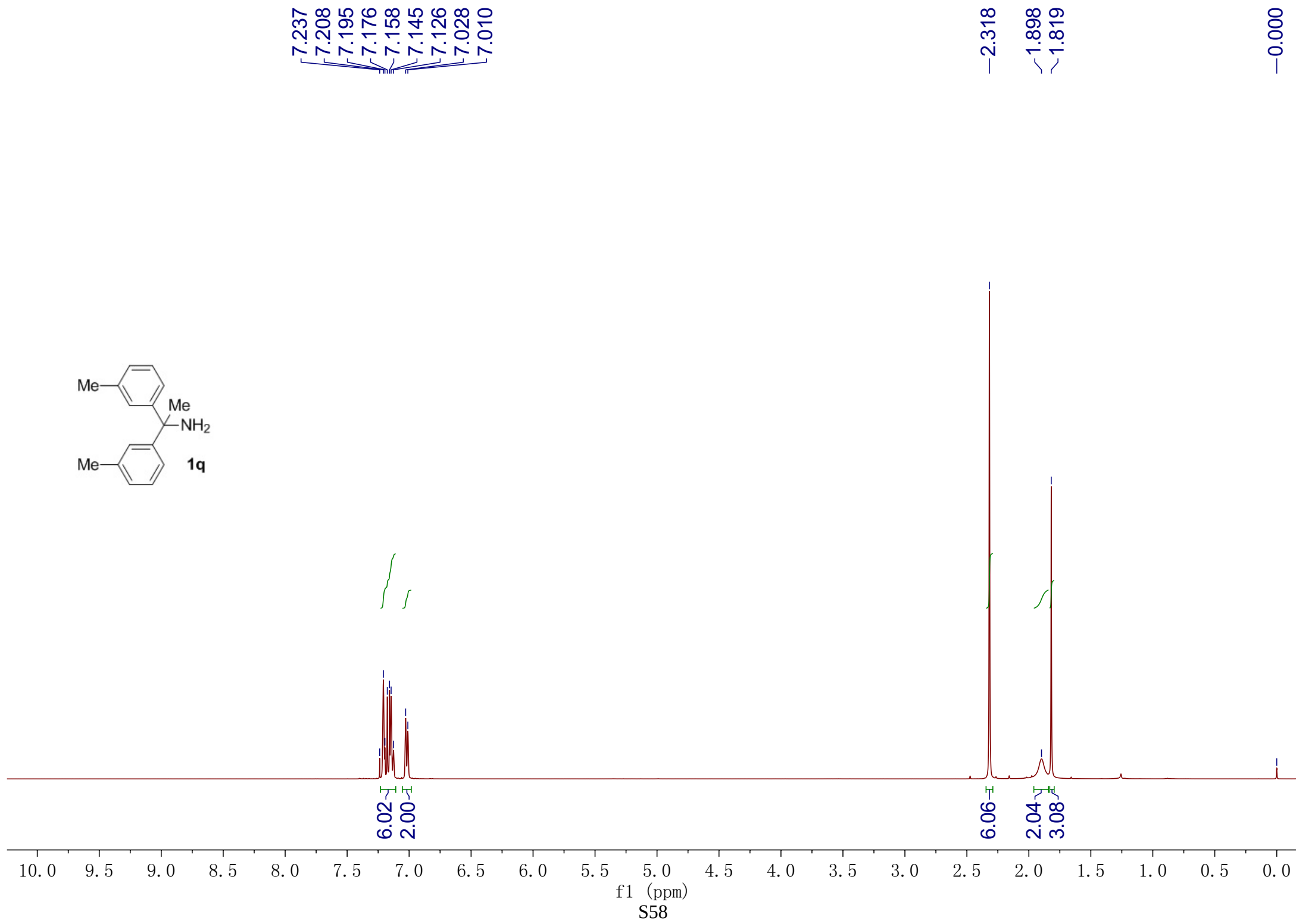
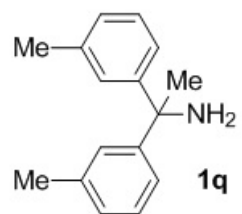


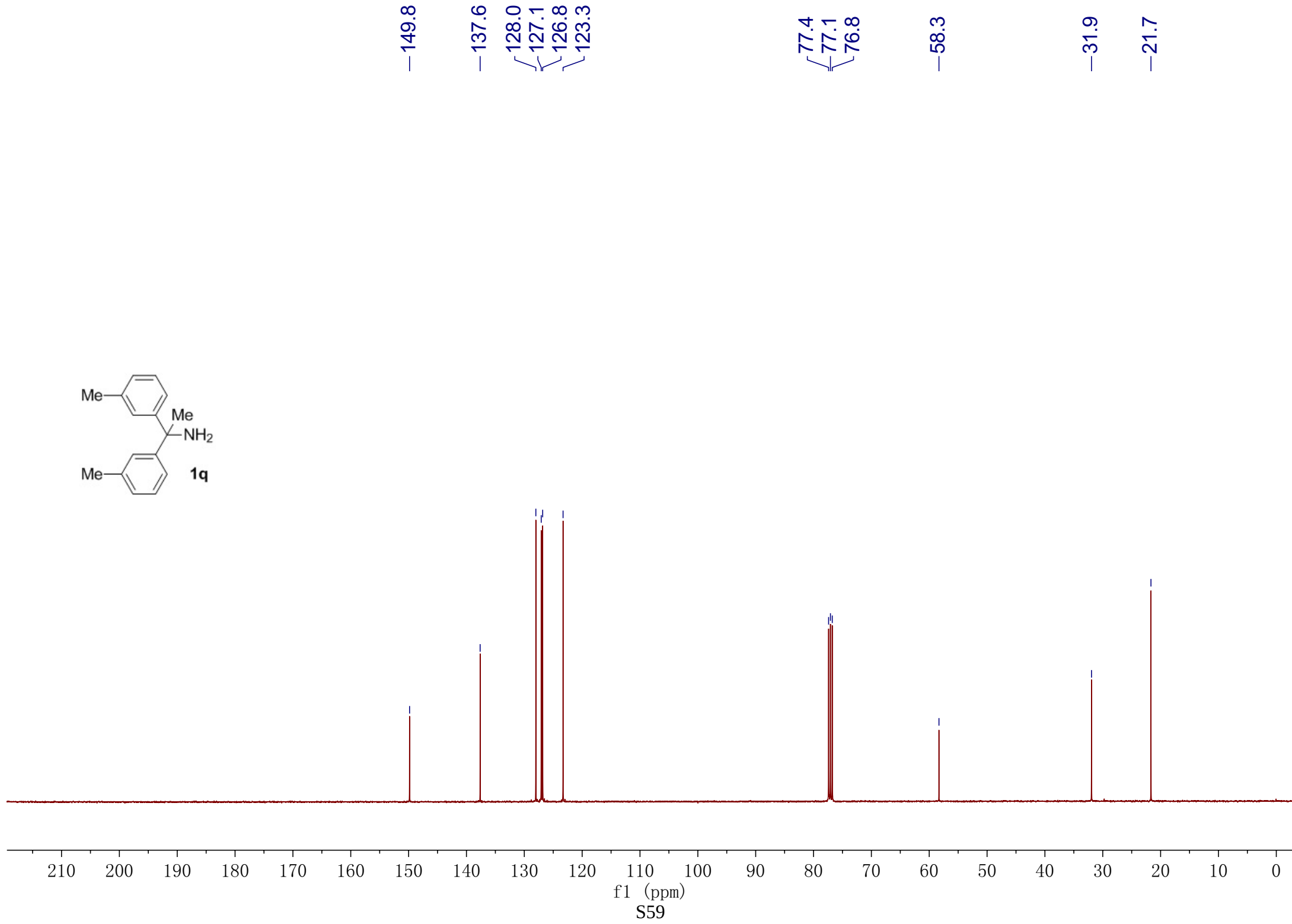
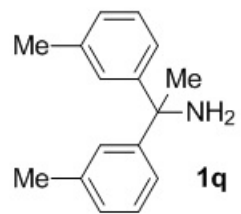


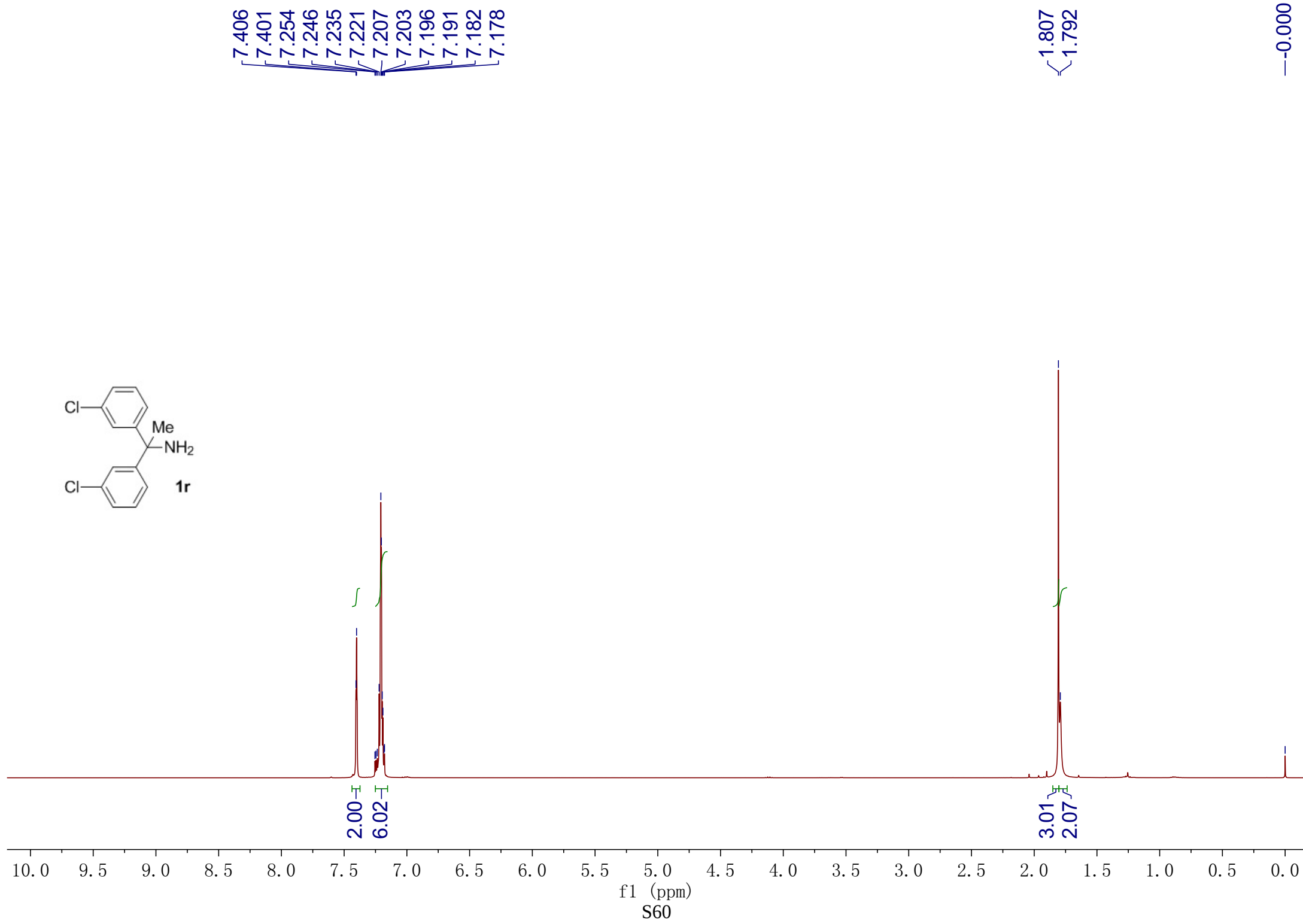
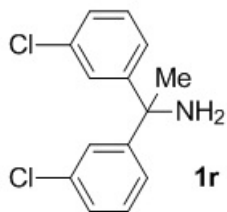


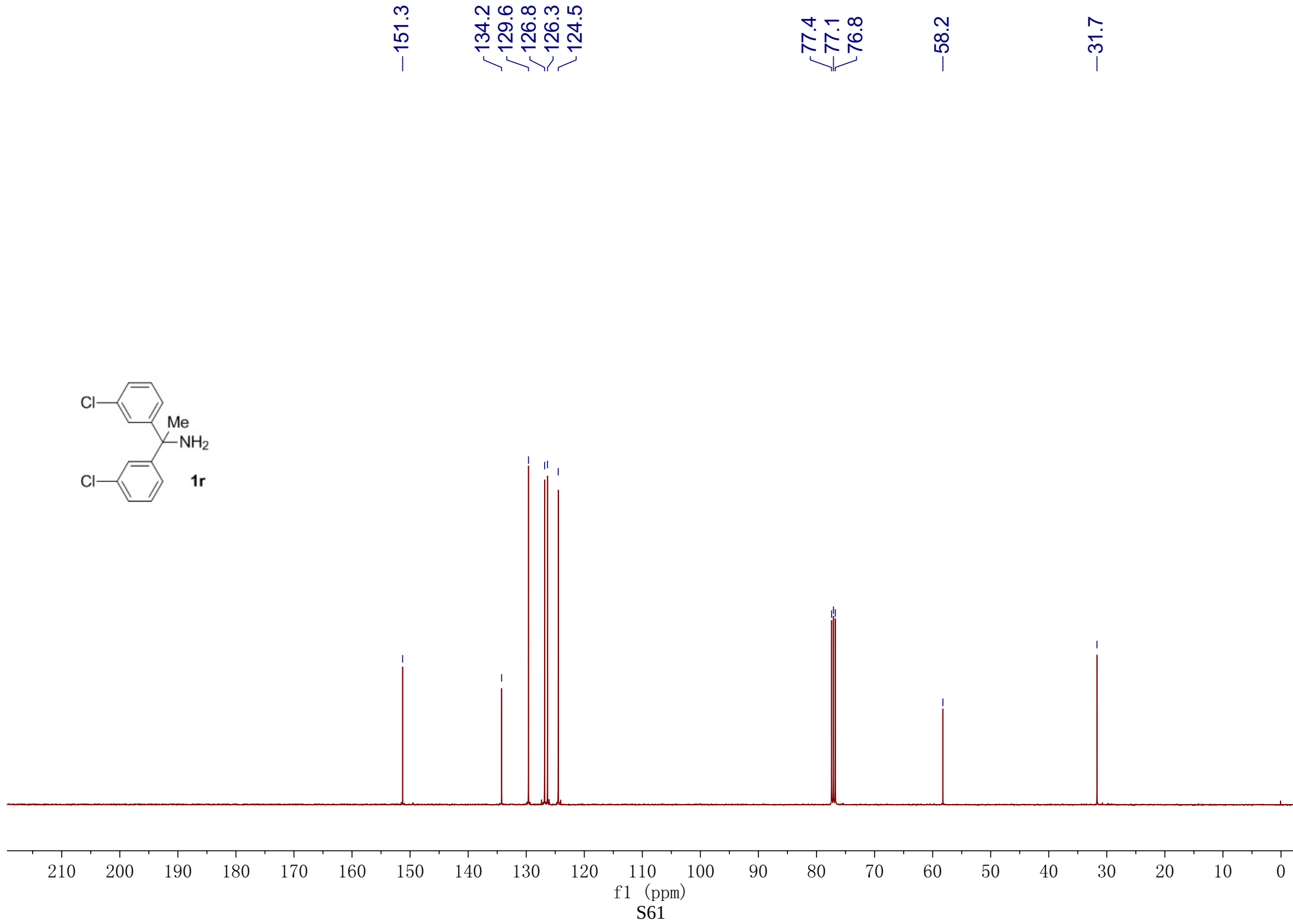
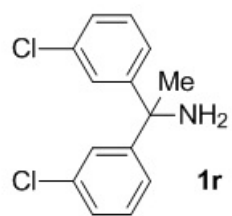


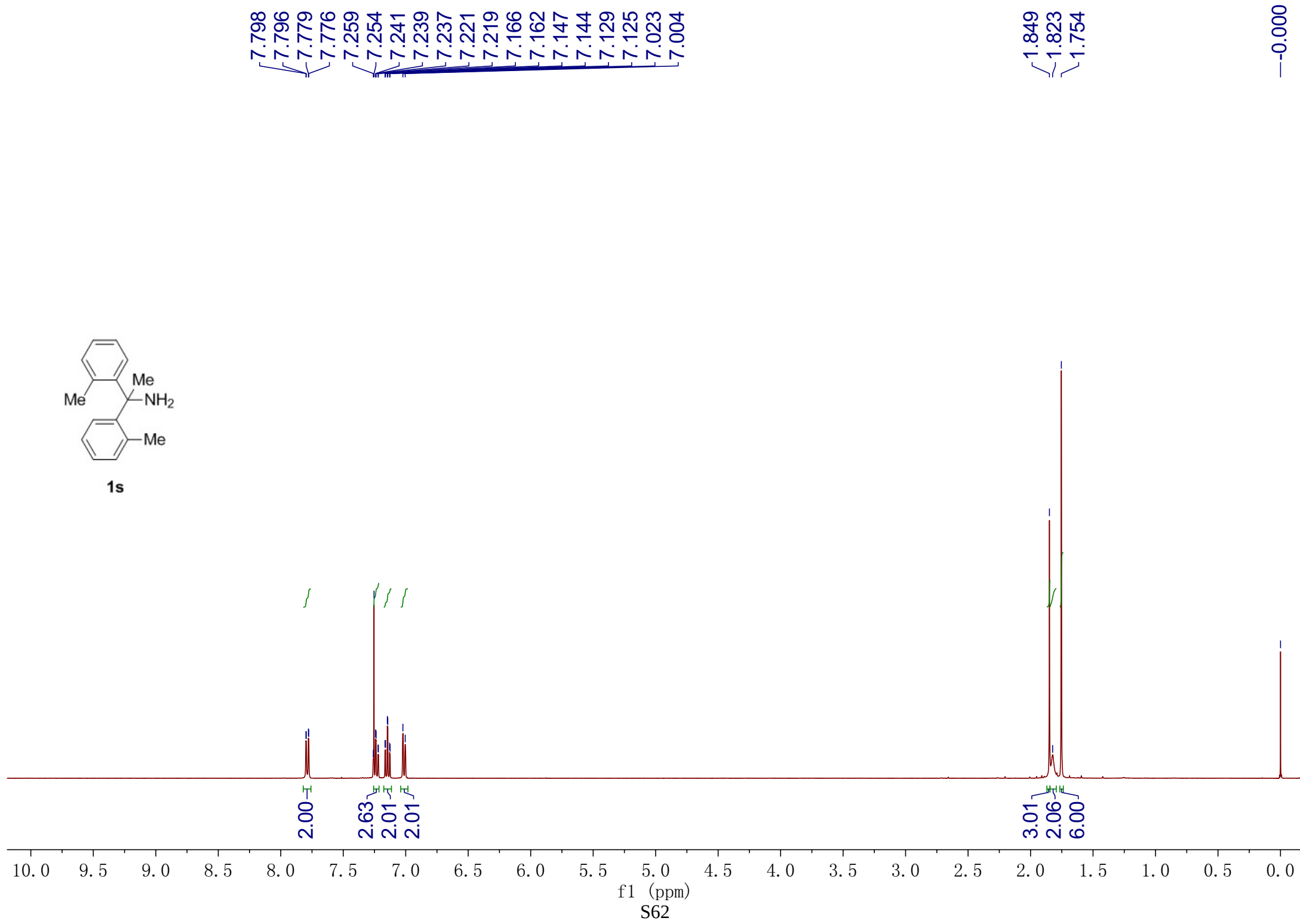
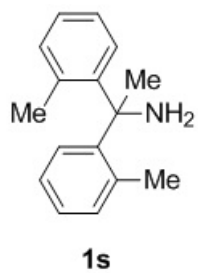


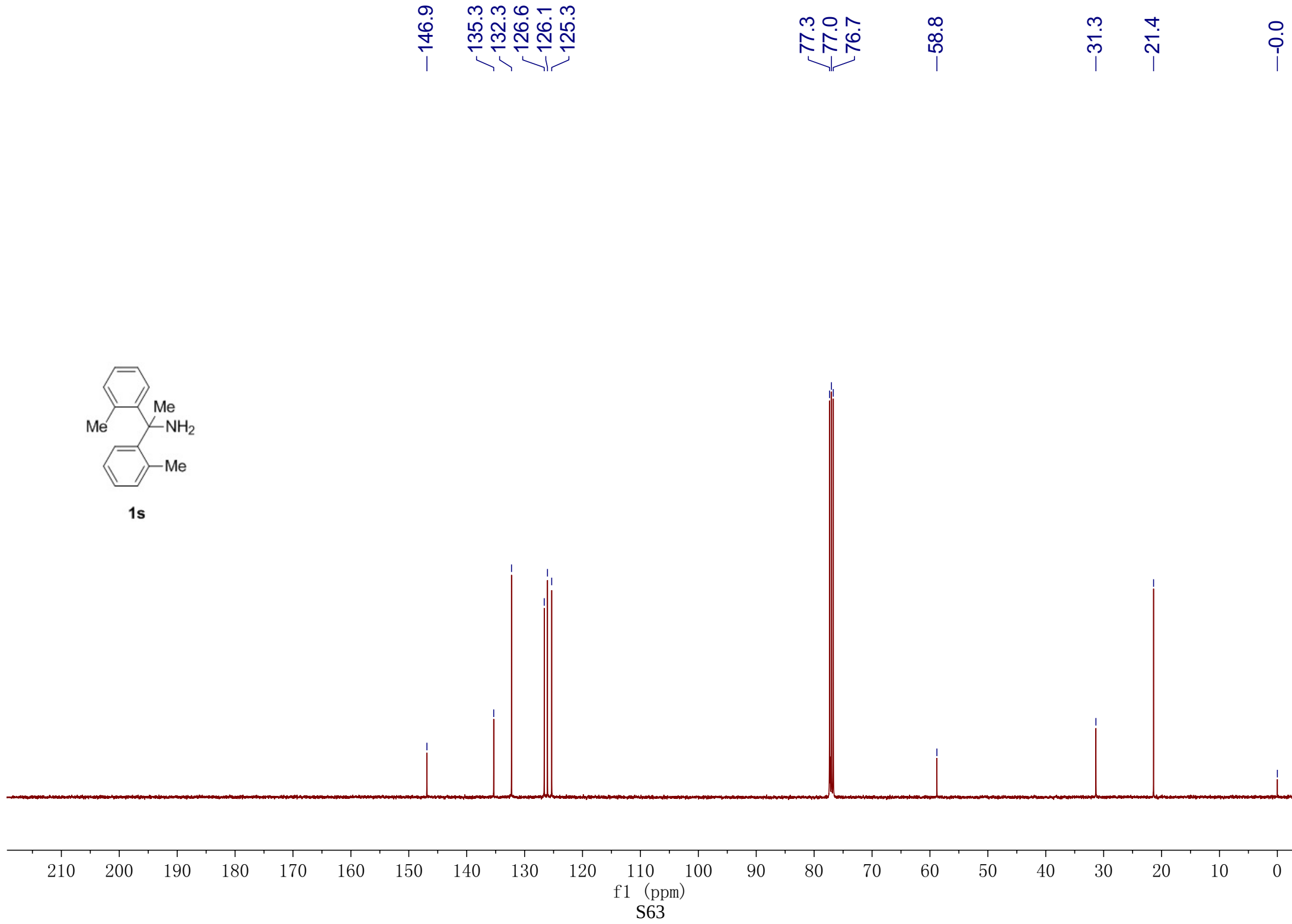
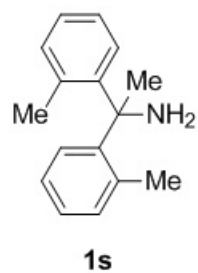


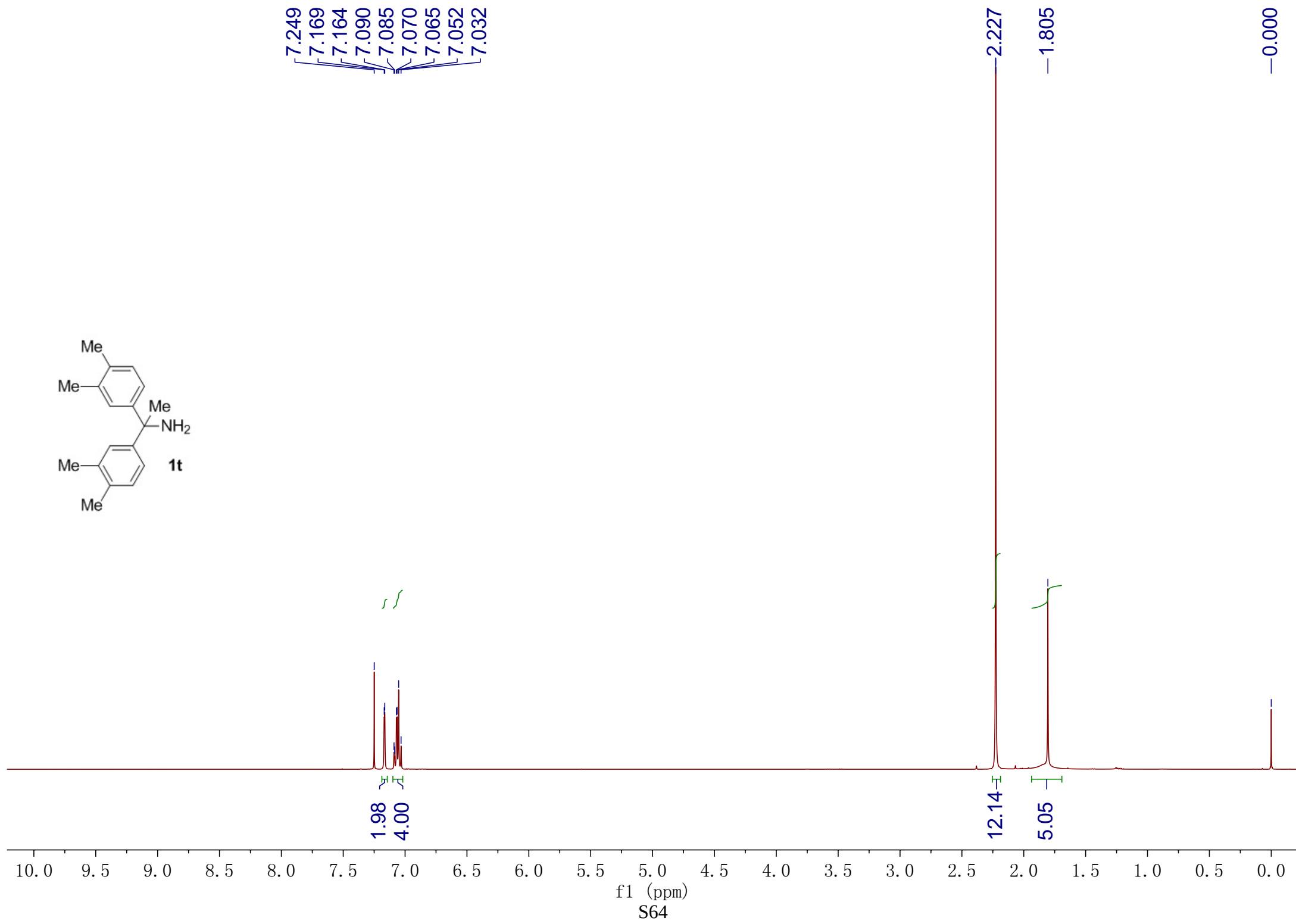
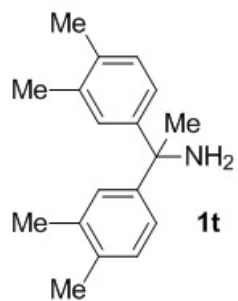


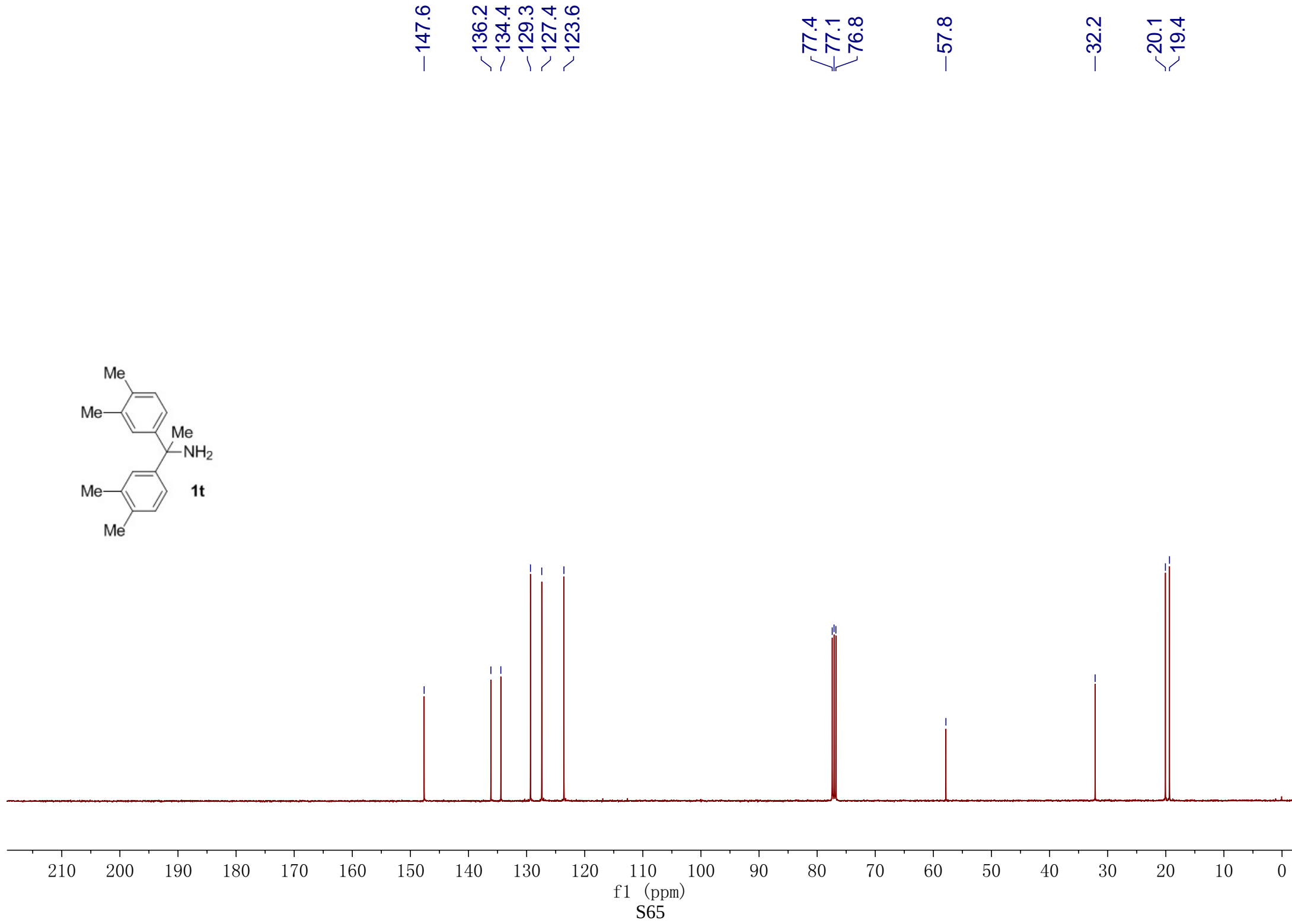
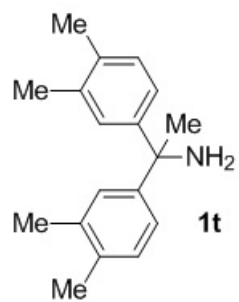


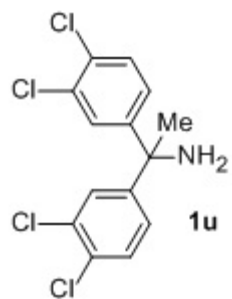








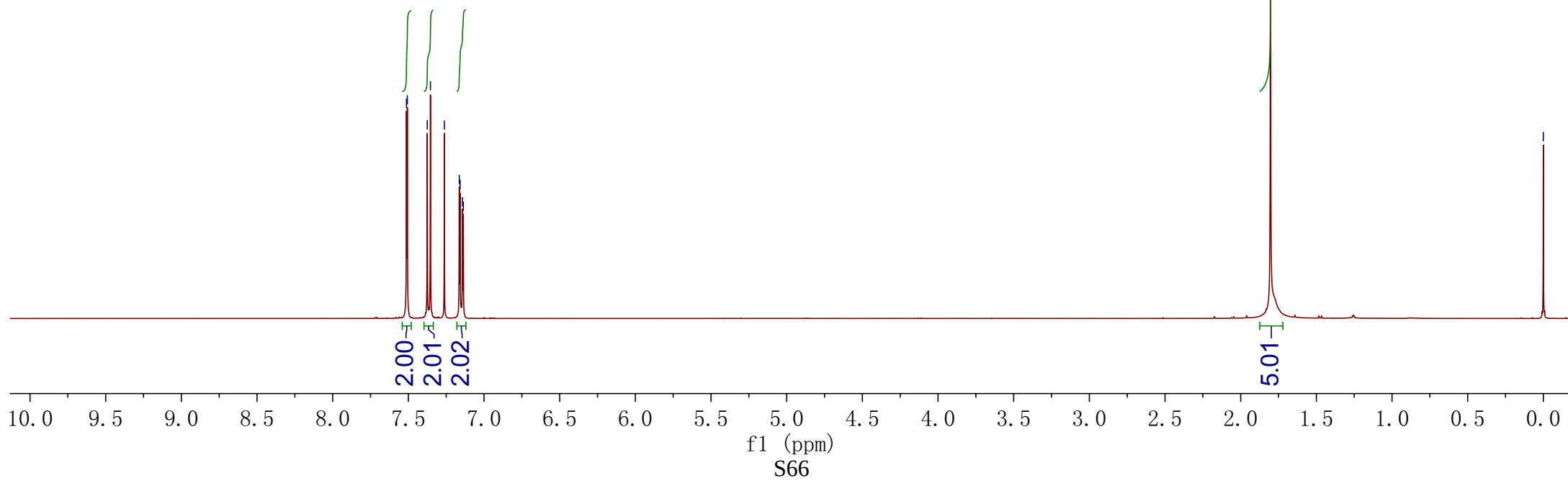


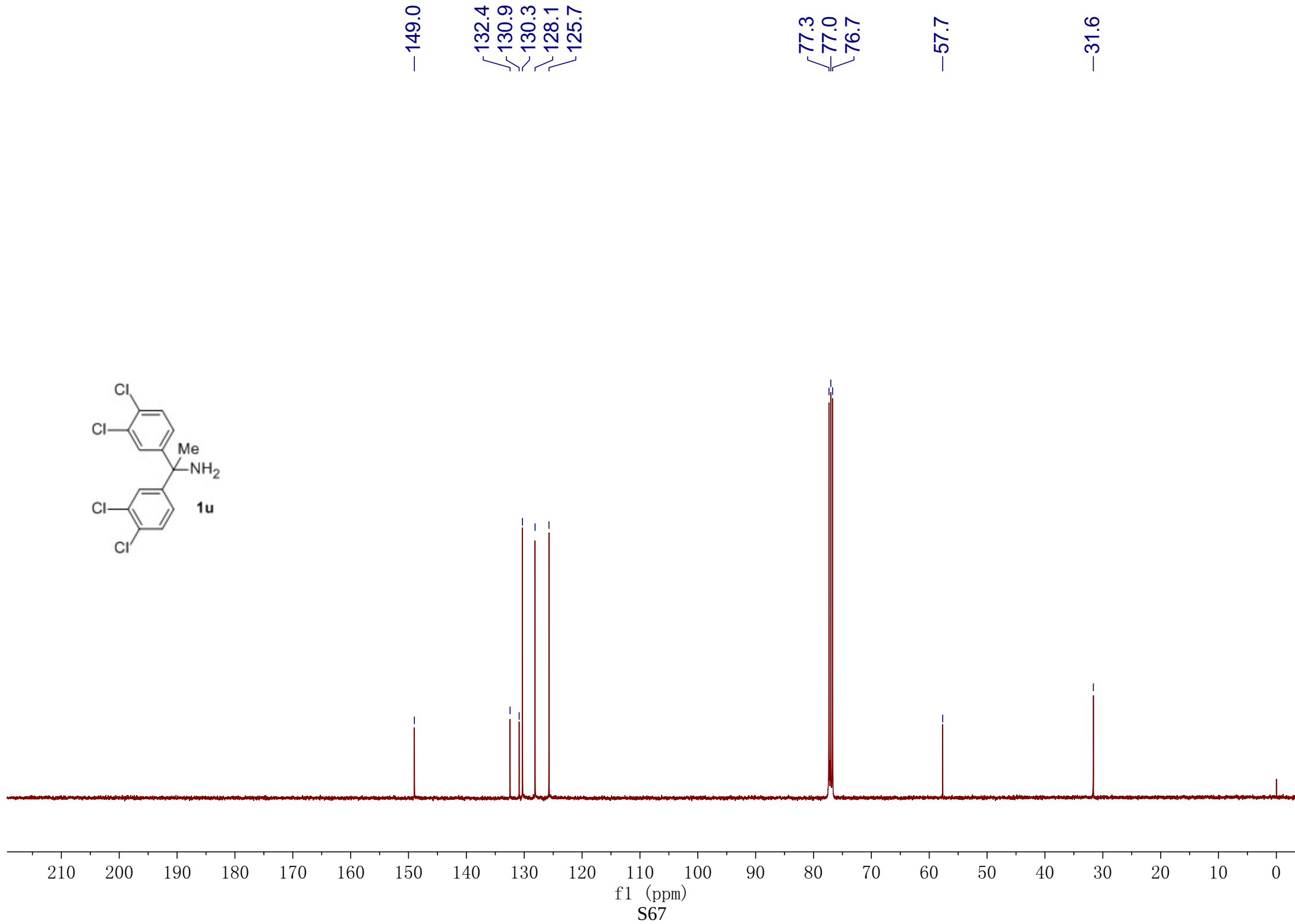
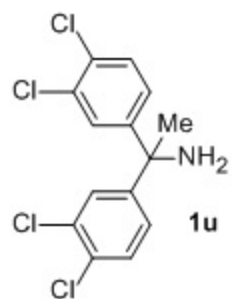


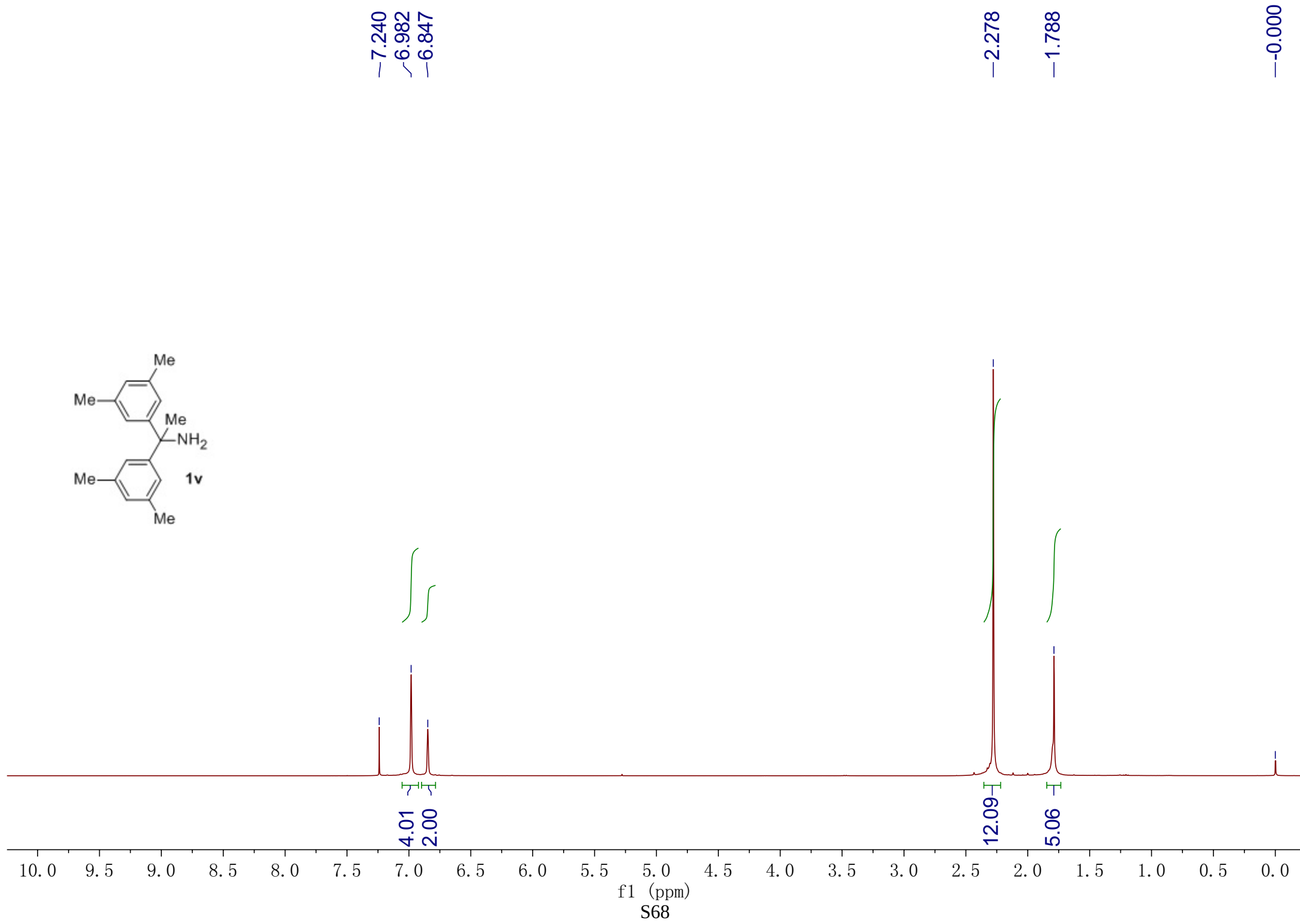
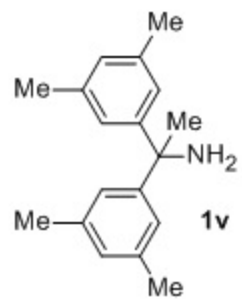
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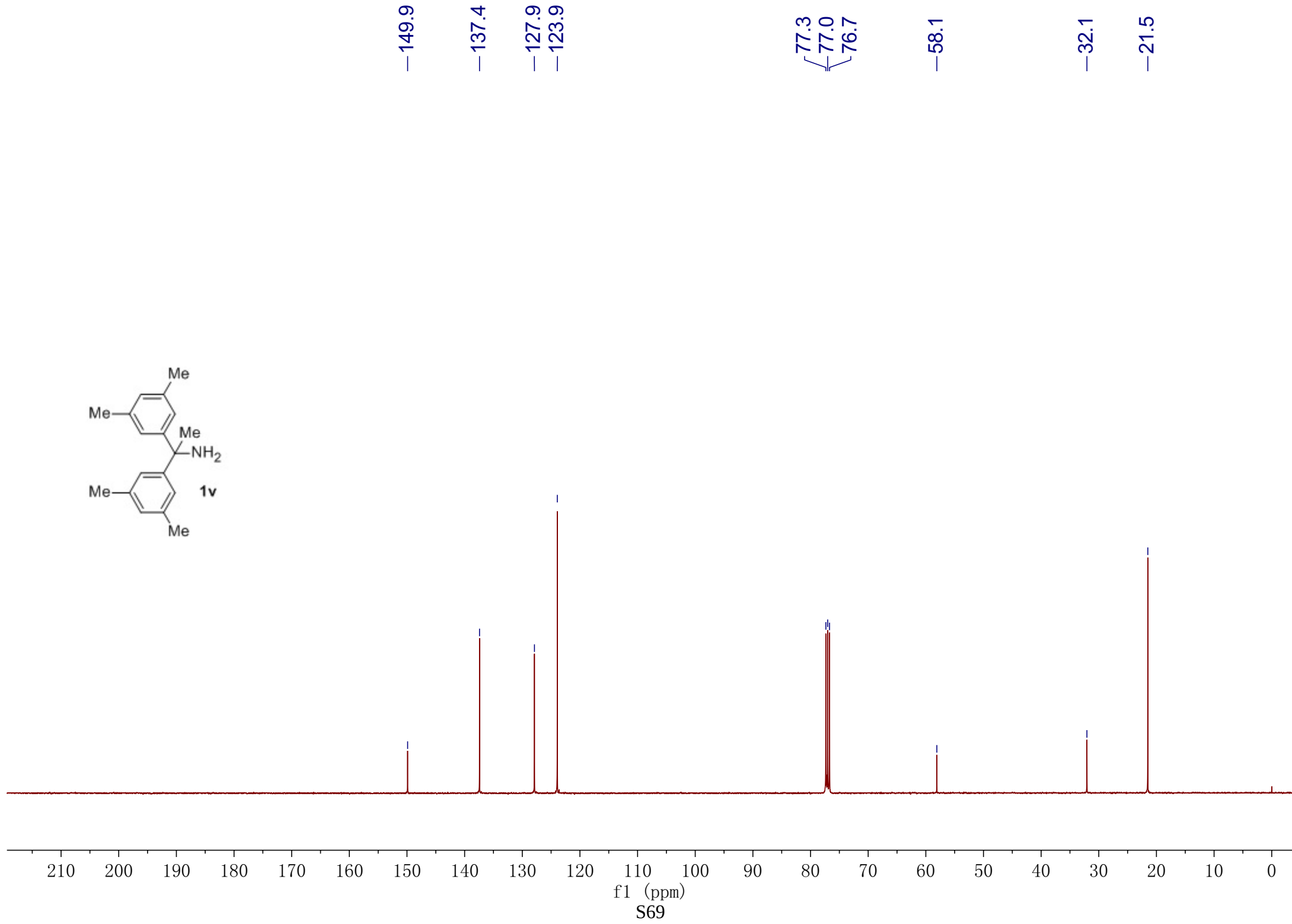
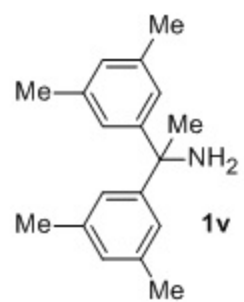
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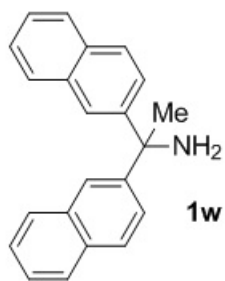
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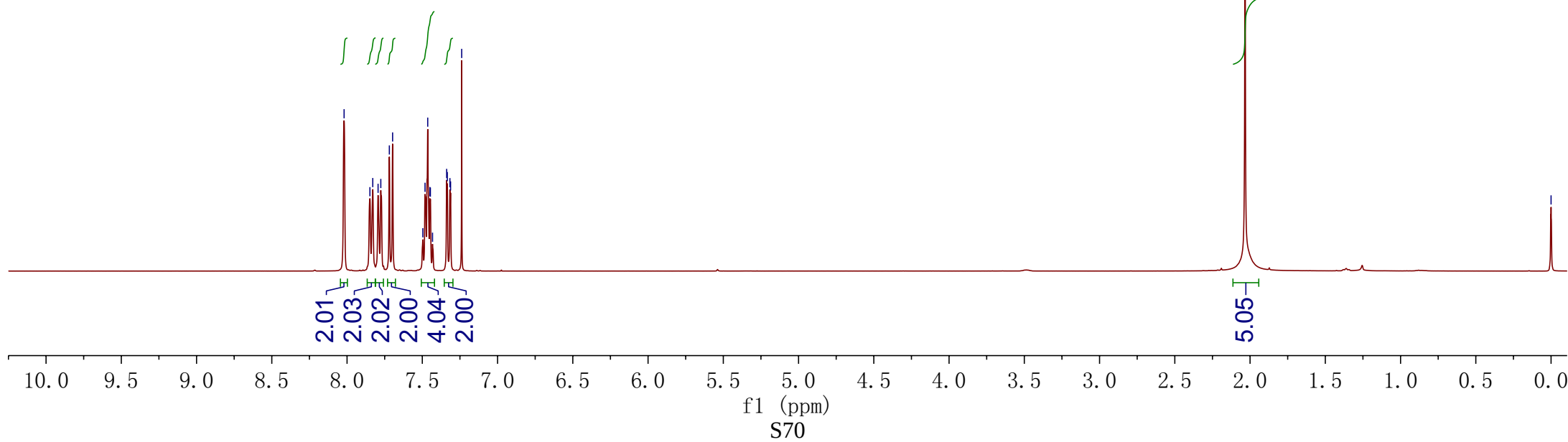


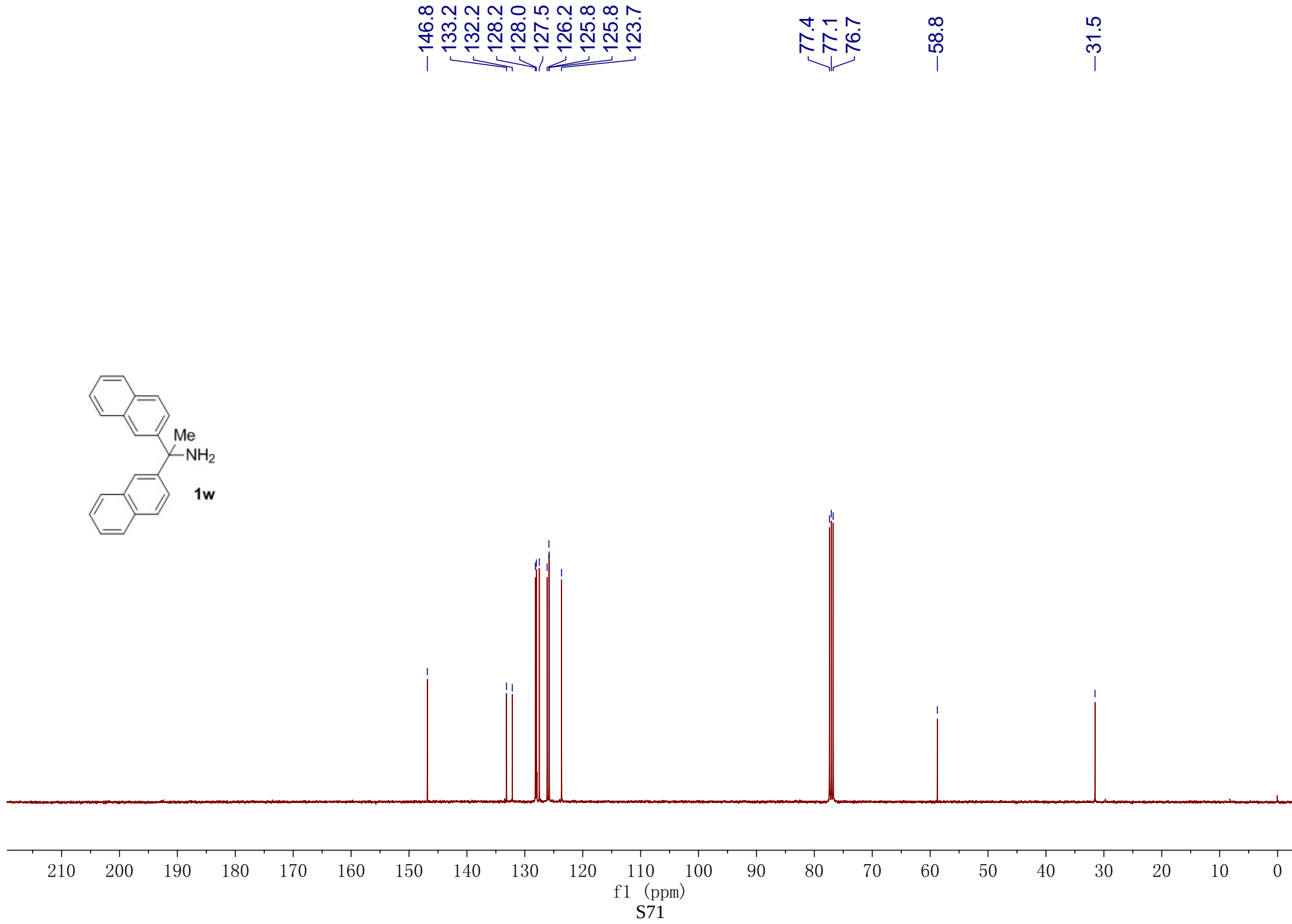
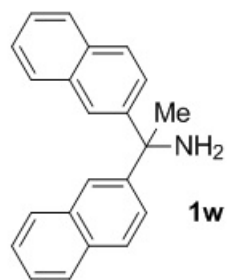


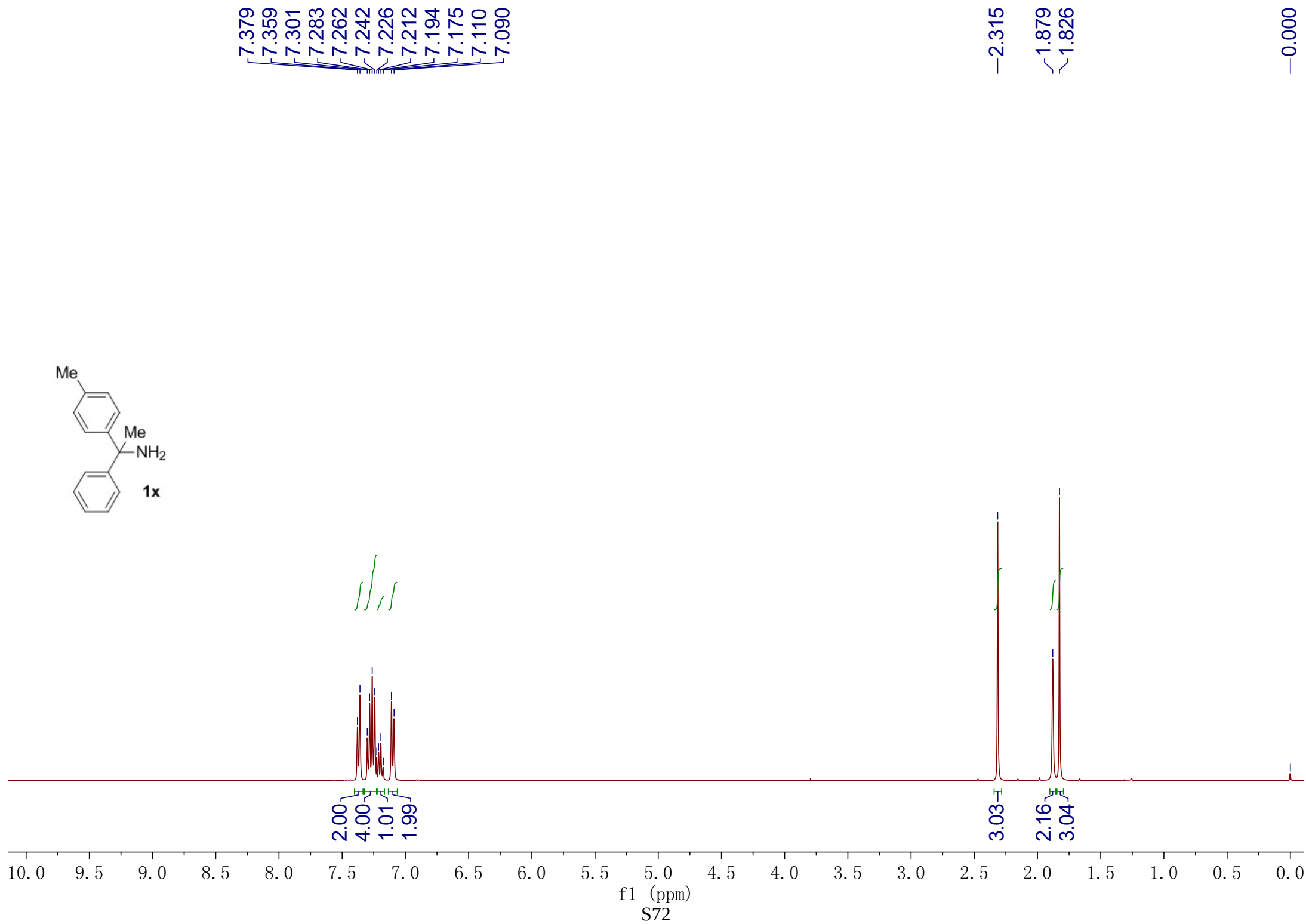
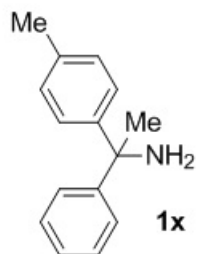
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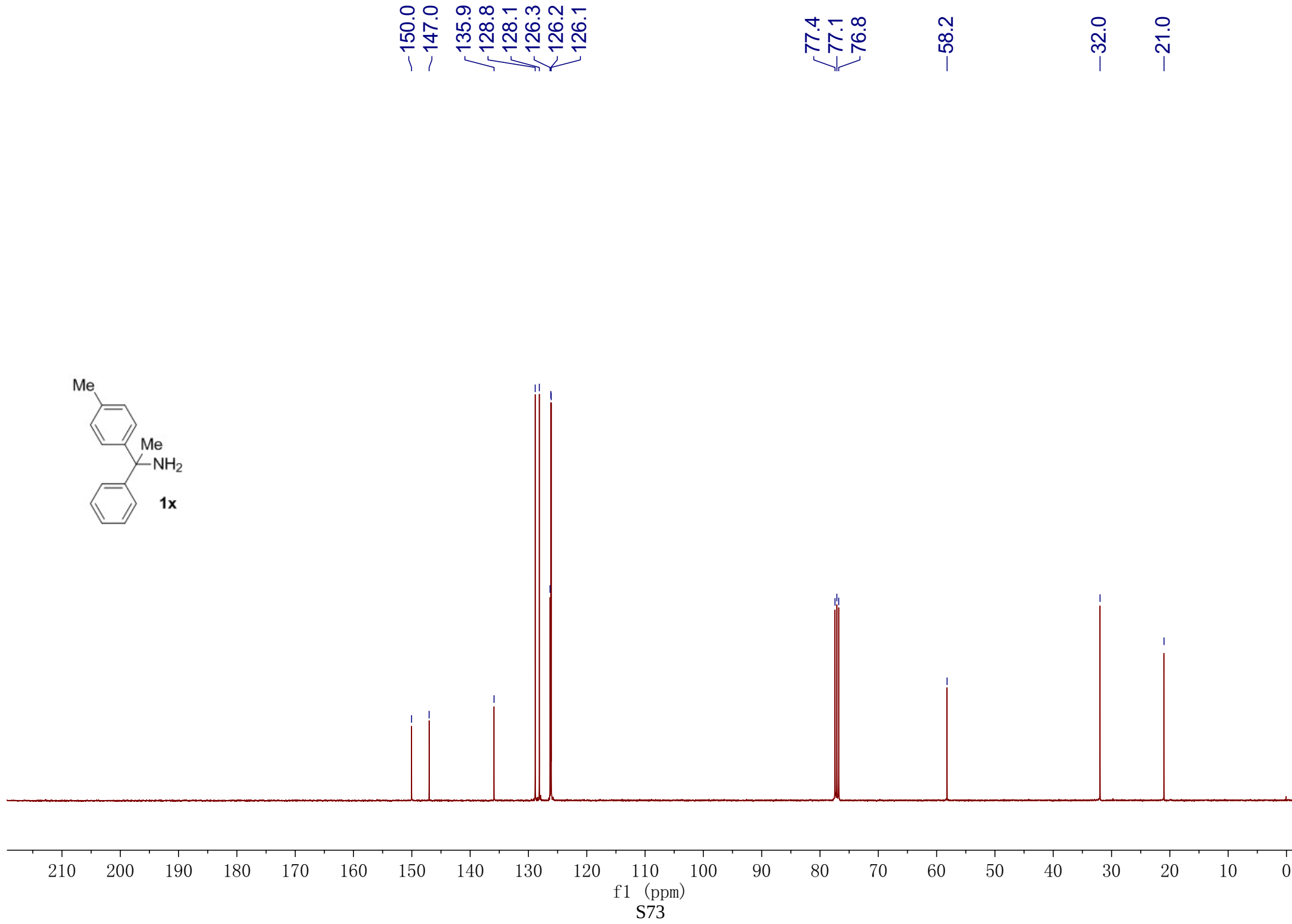
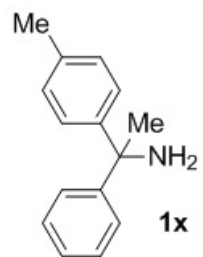
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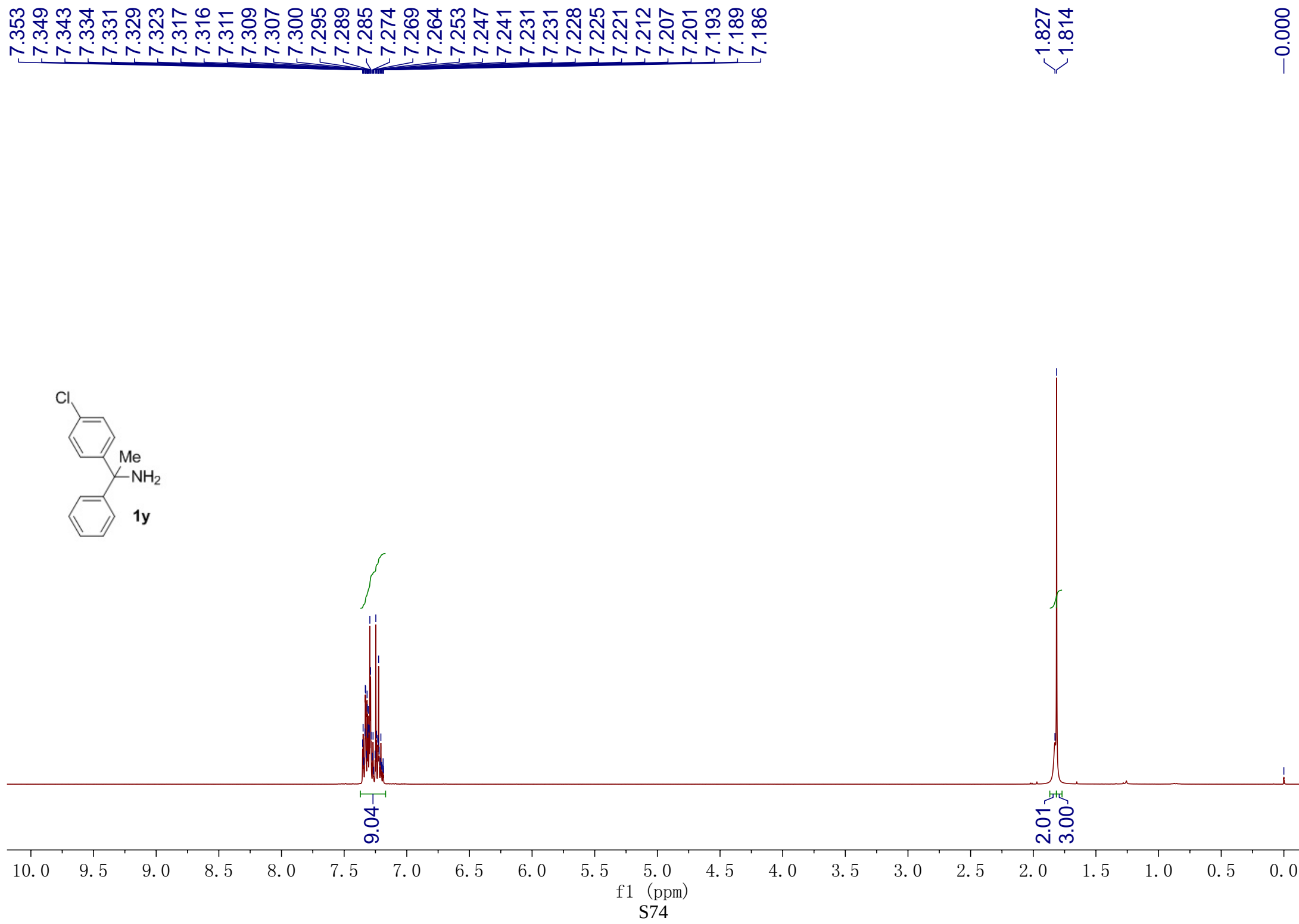
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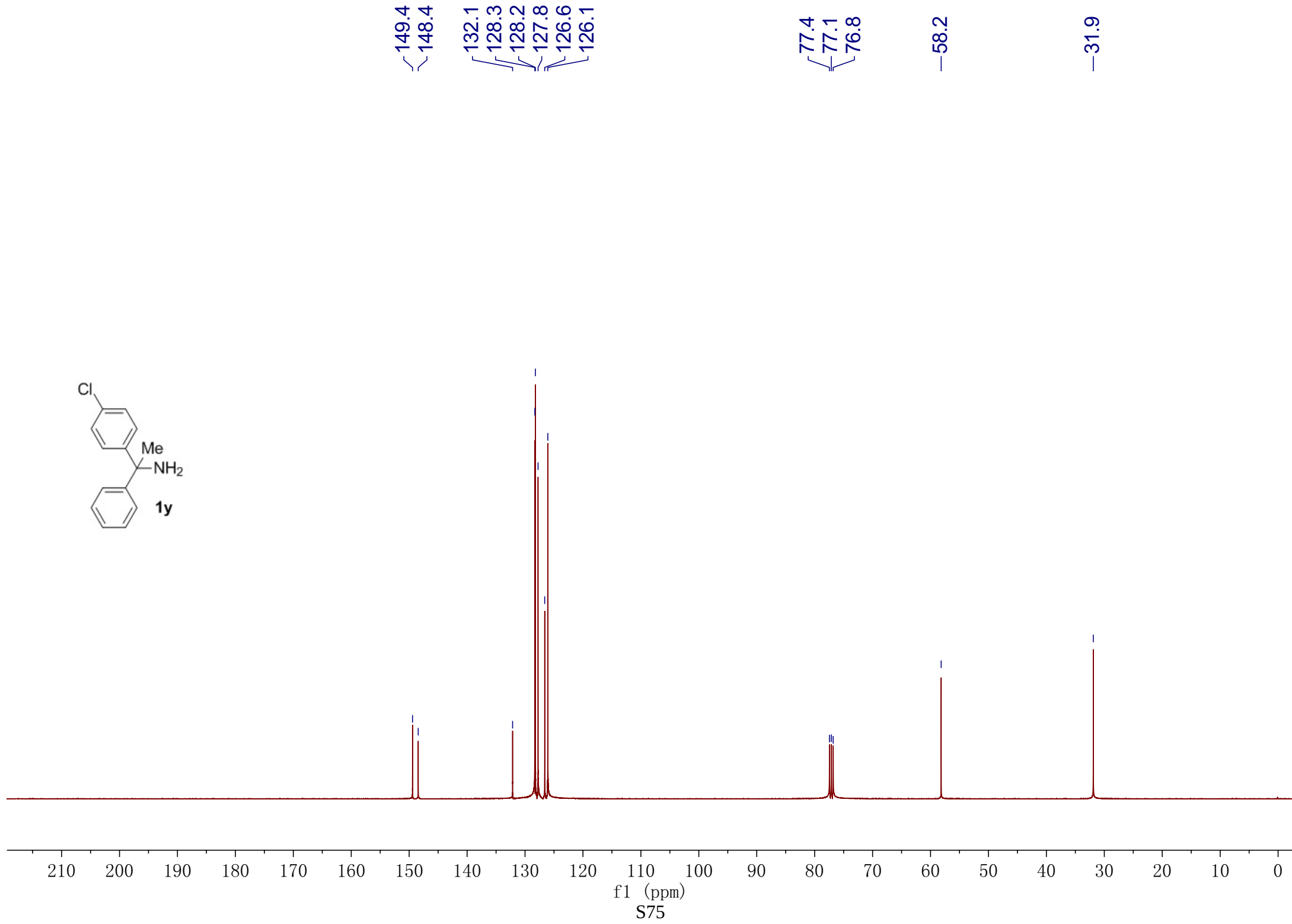
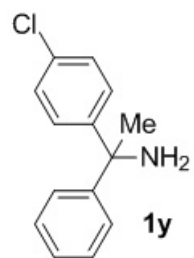








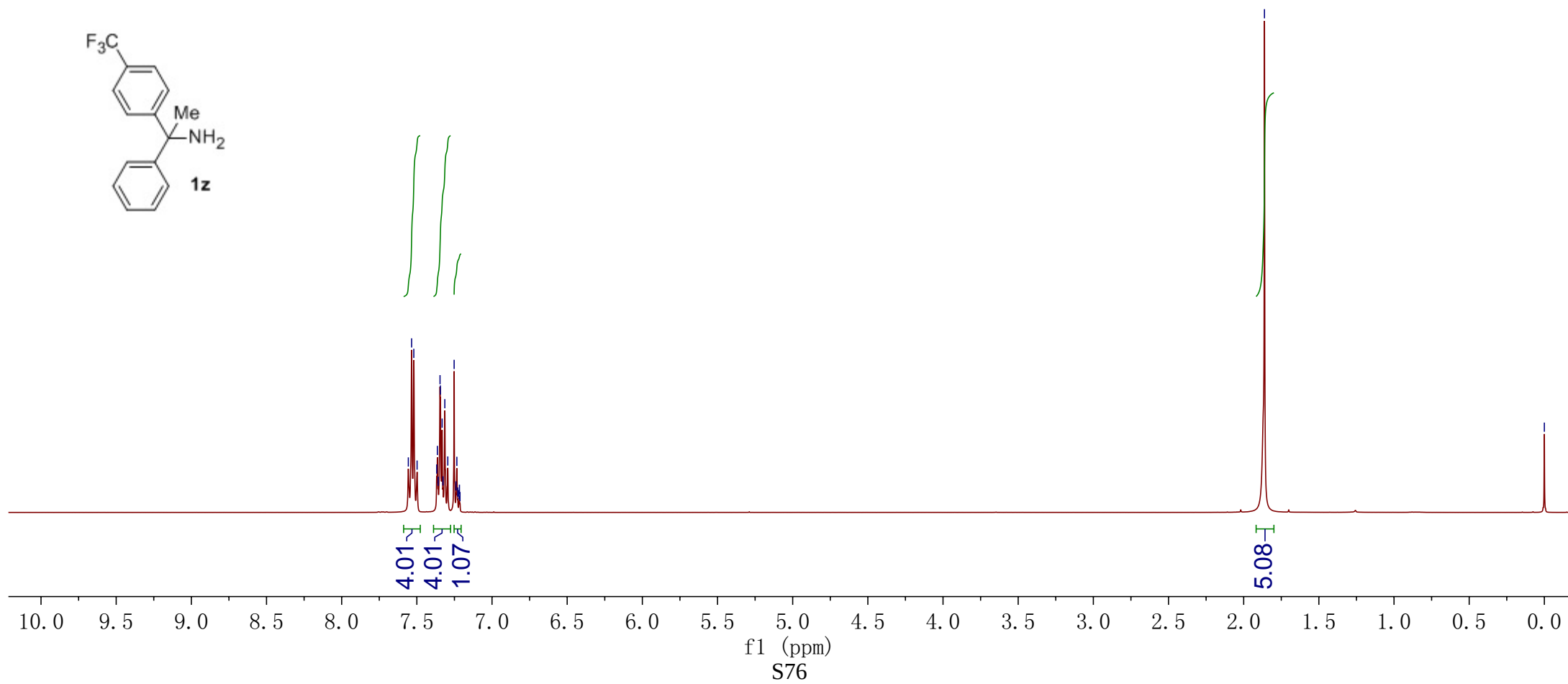
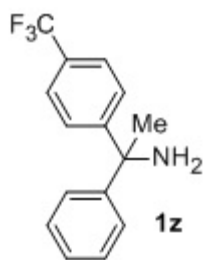


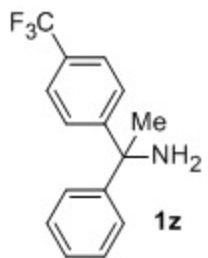


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—0.000



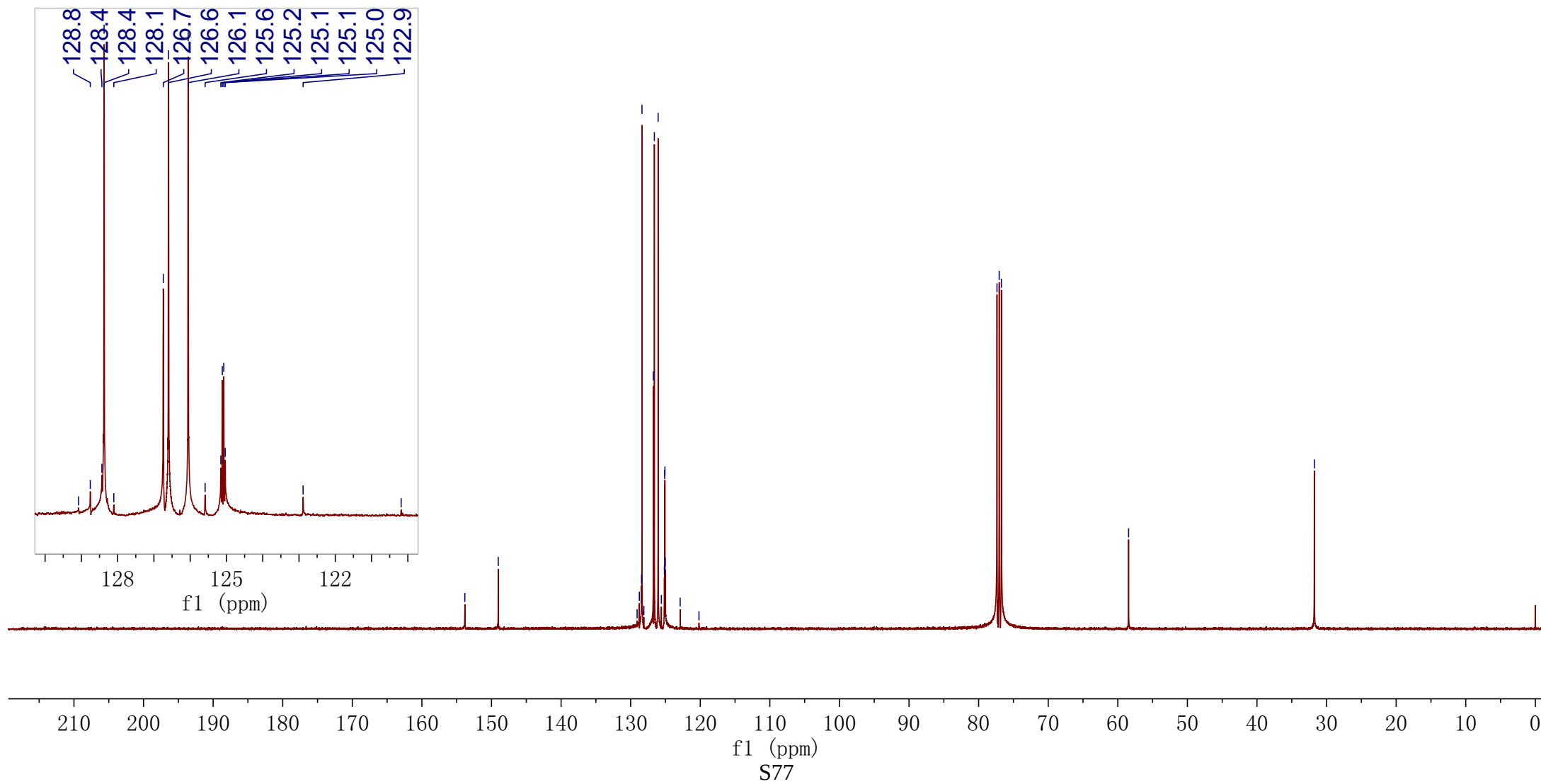


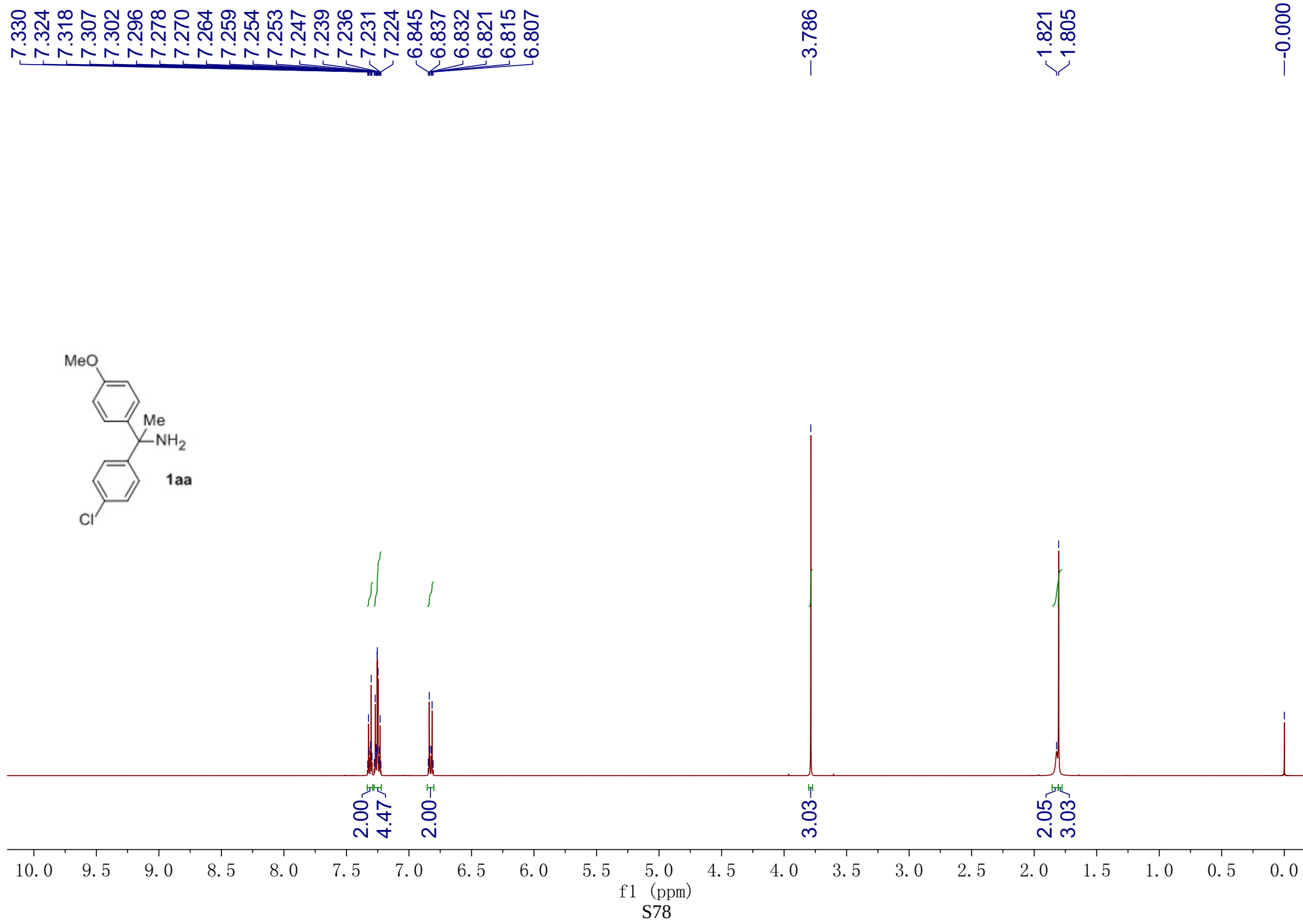
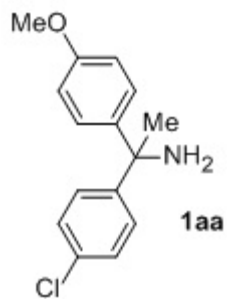
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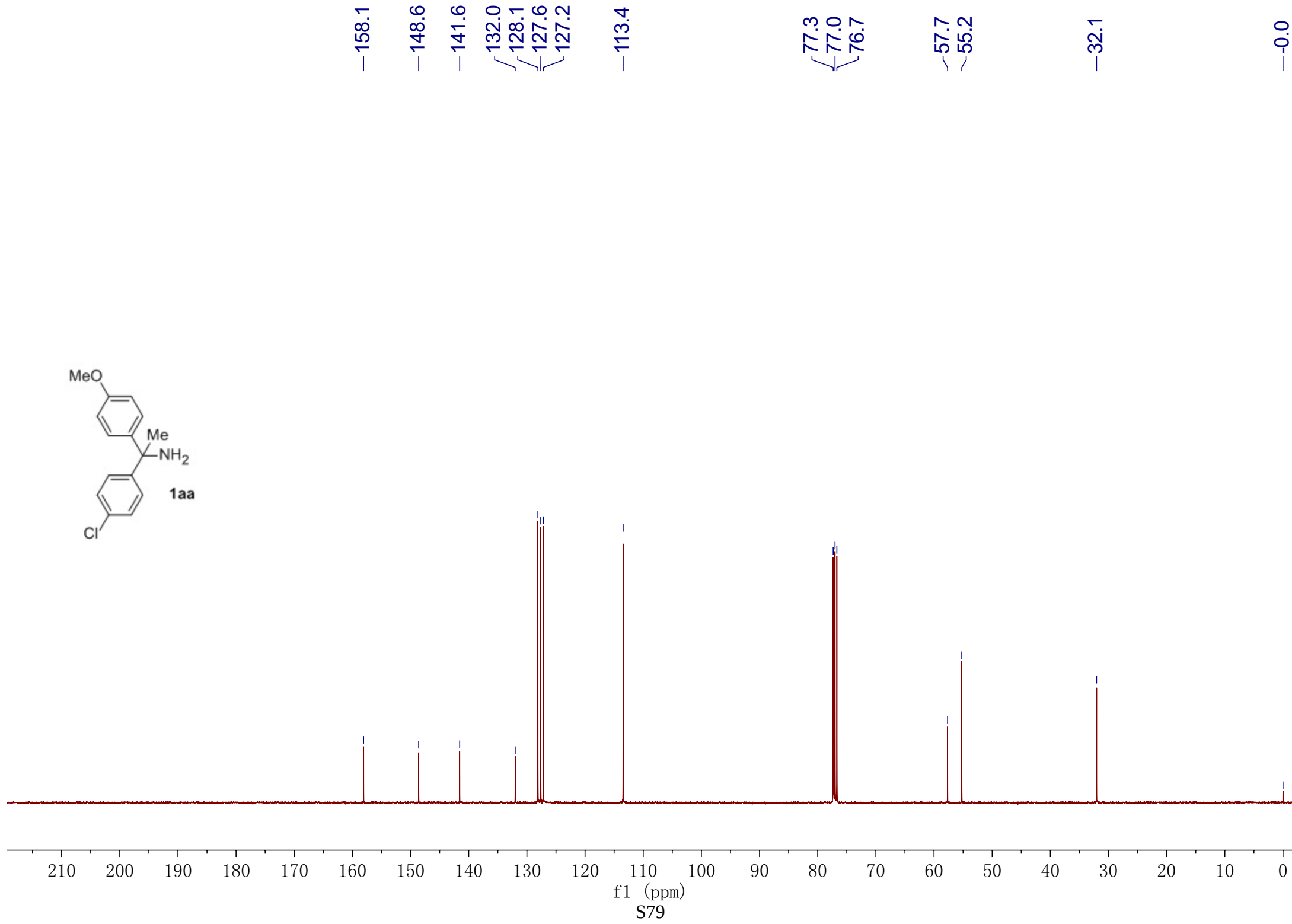
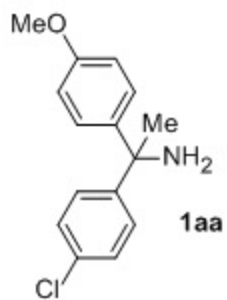
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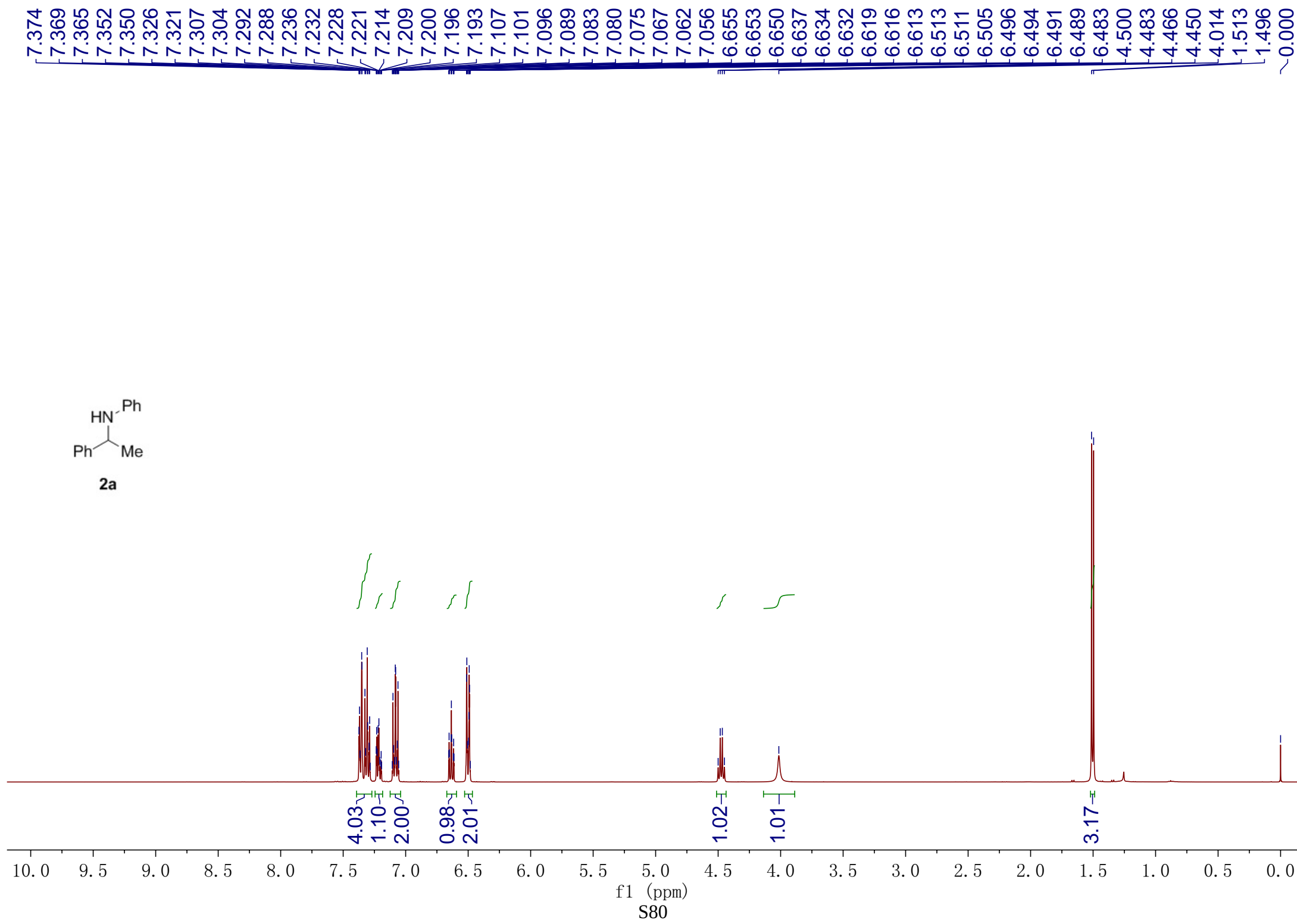
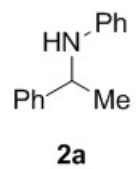
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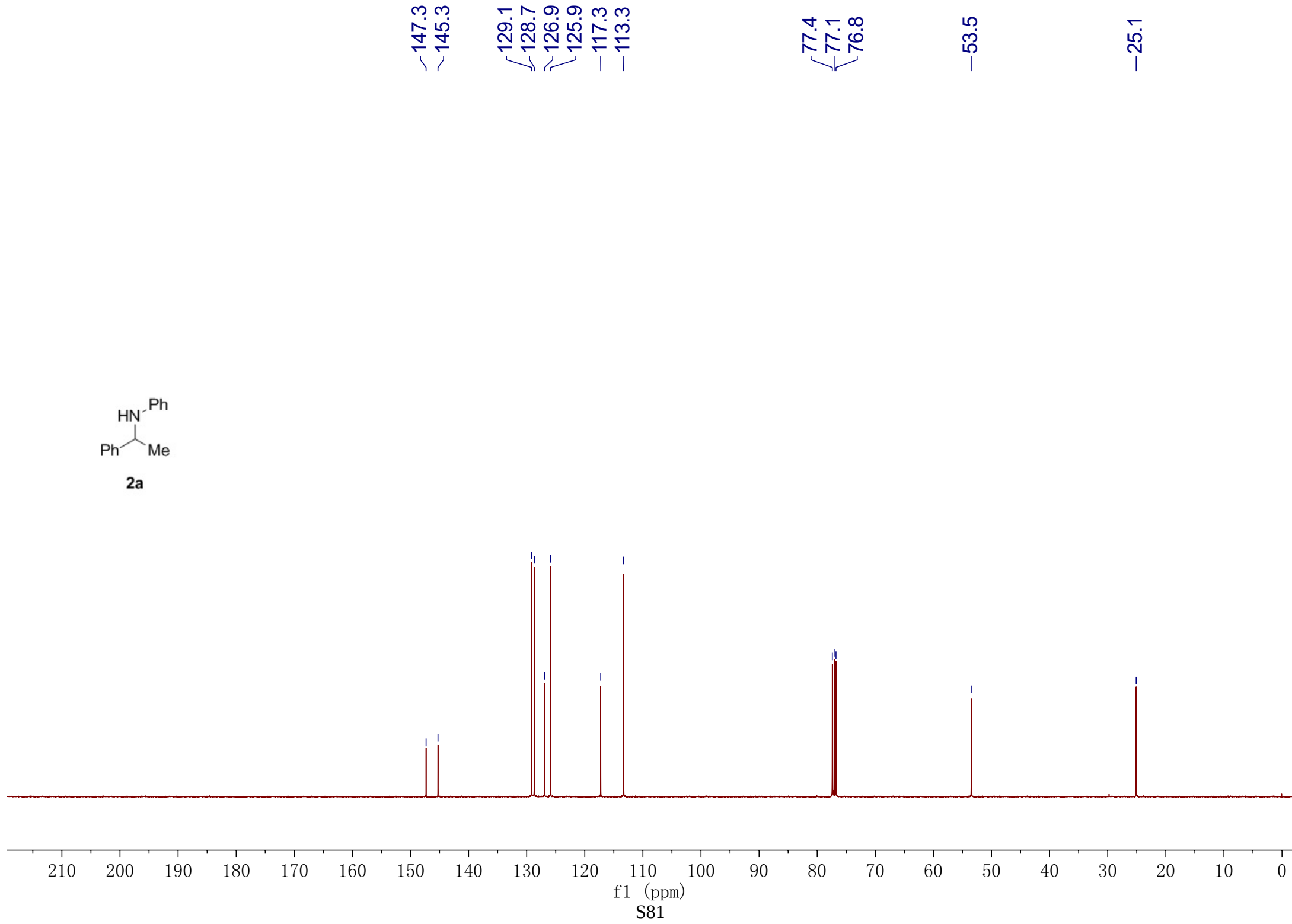
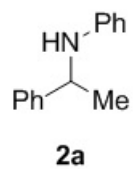
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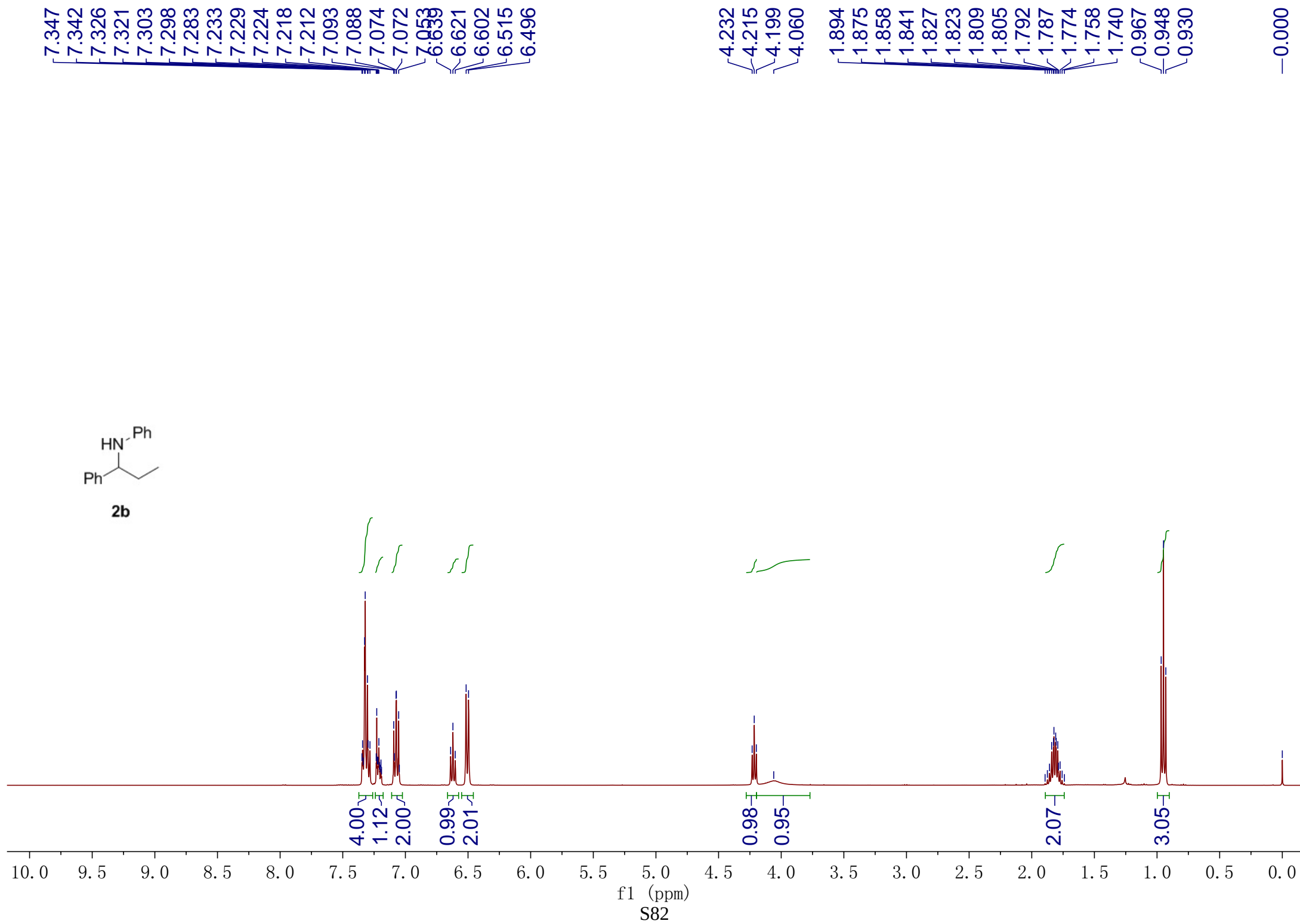
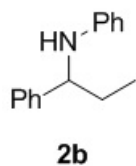


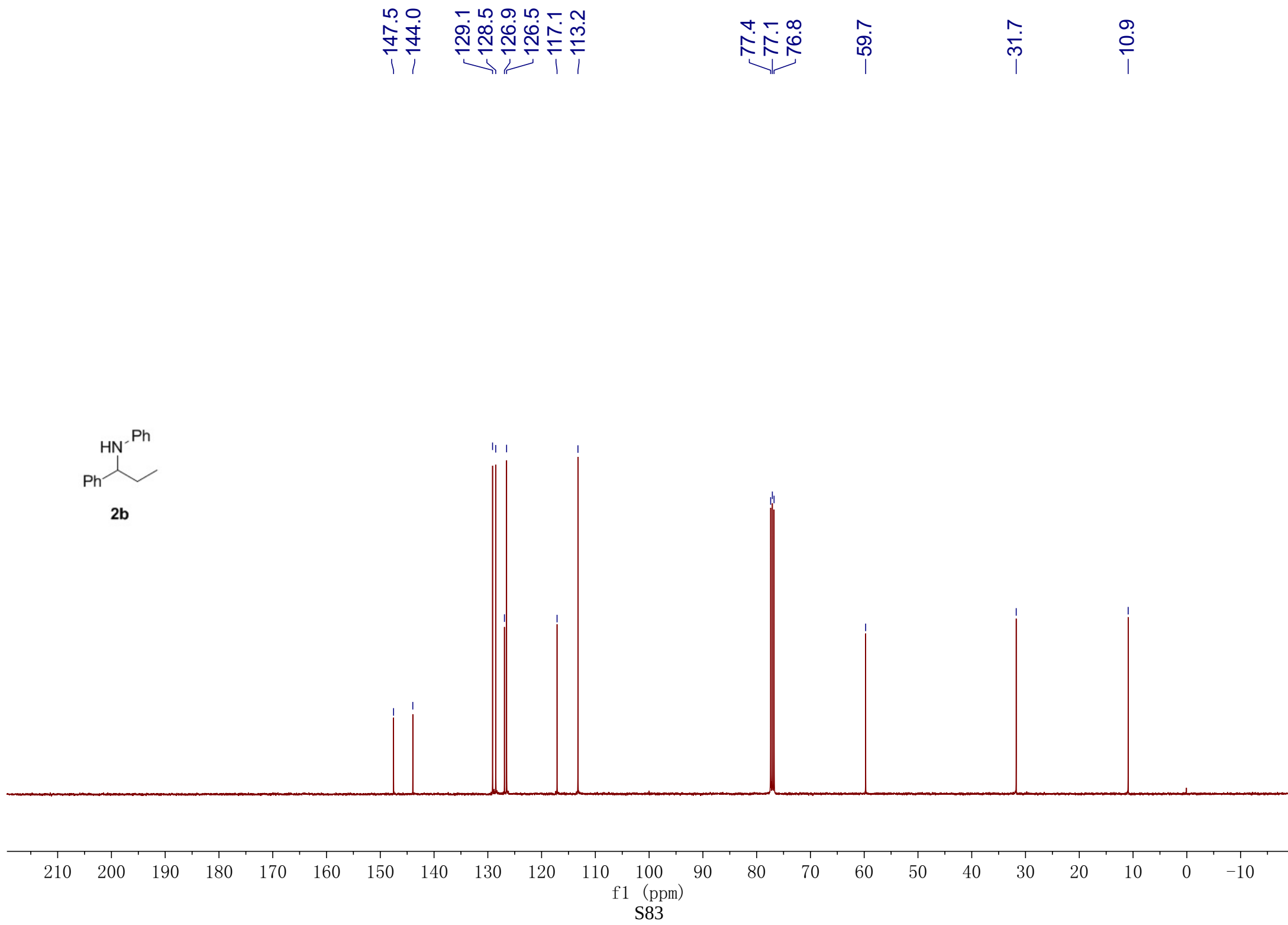
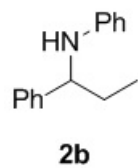


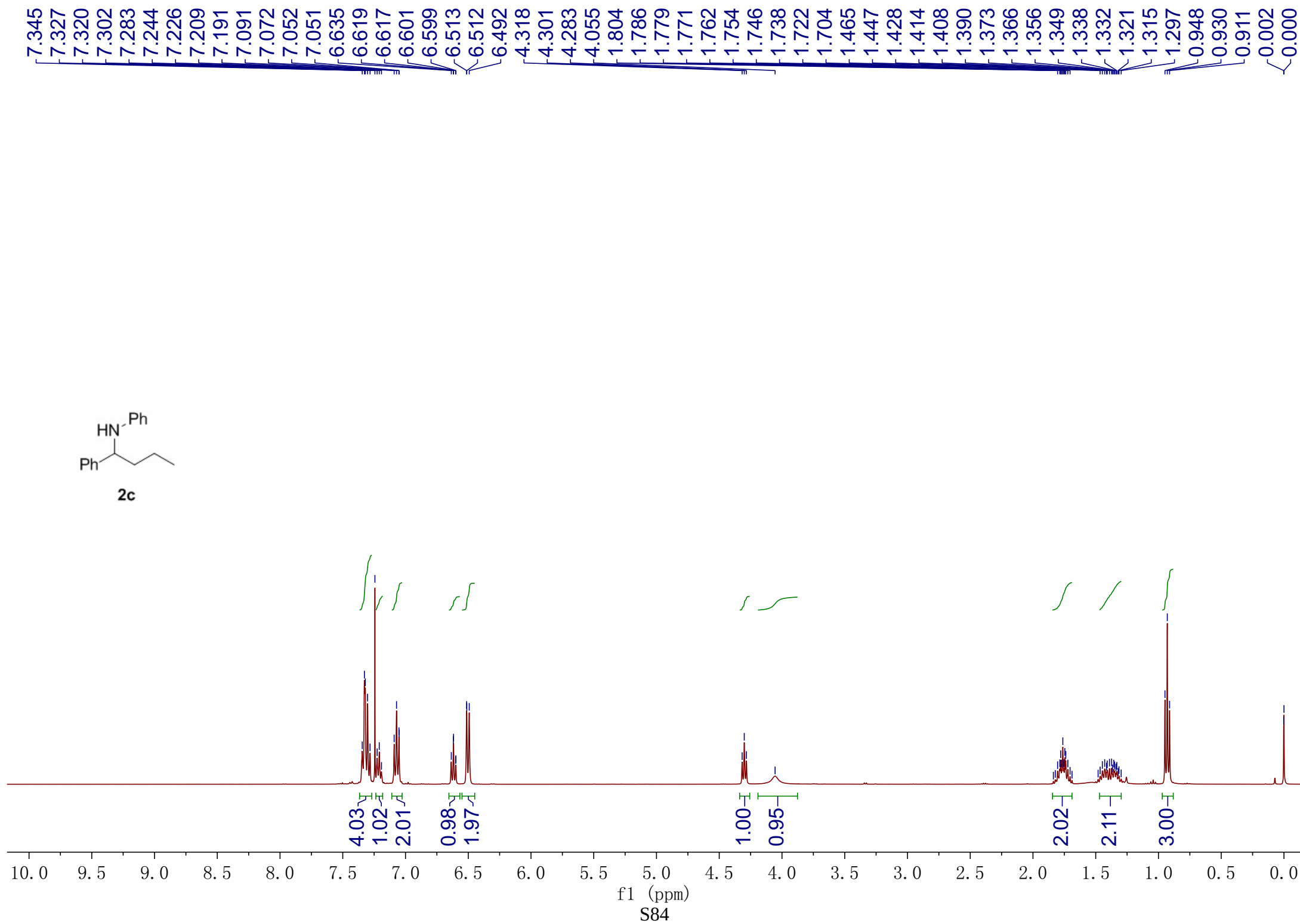
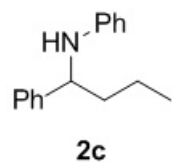


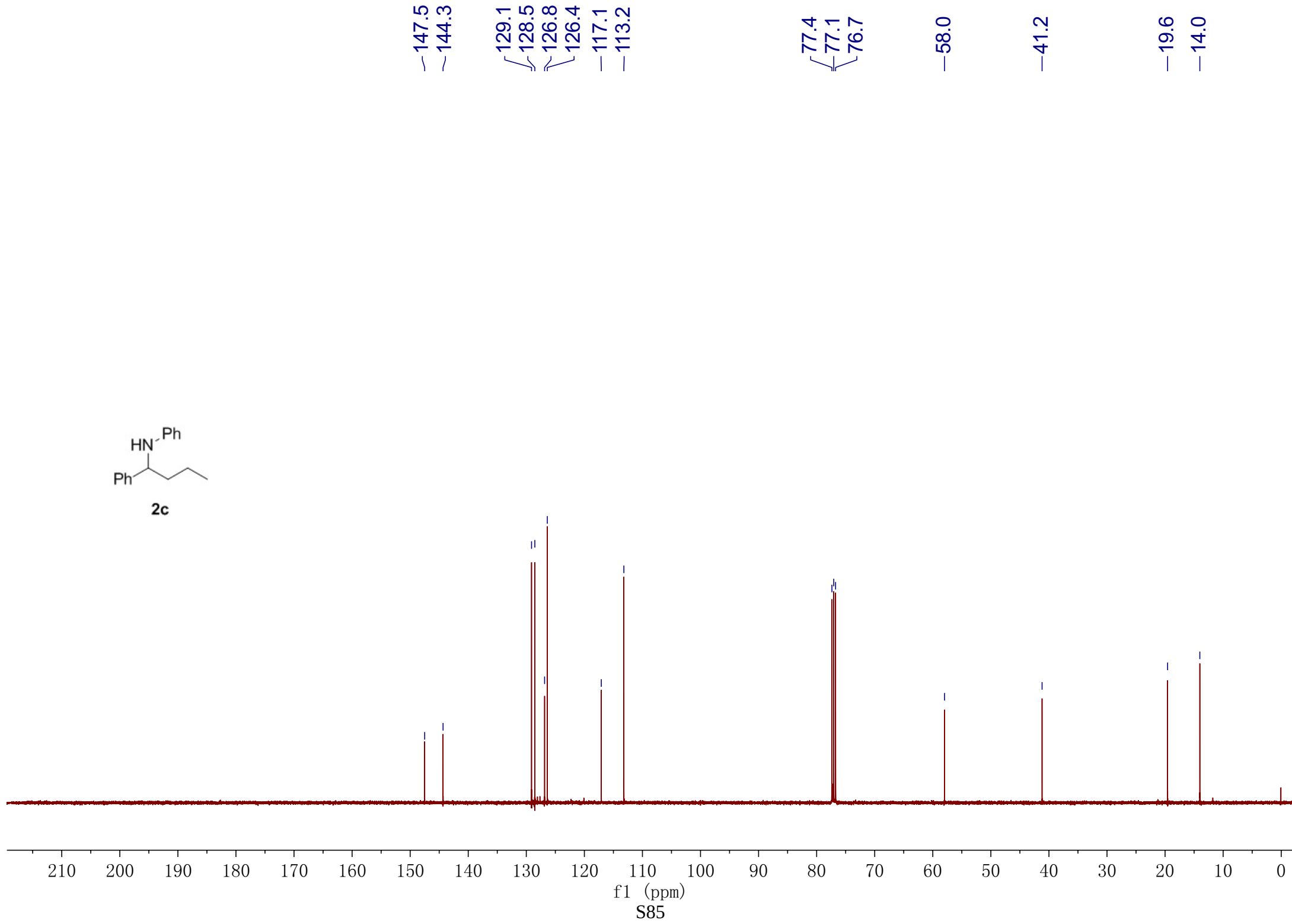
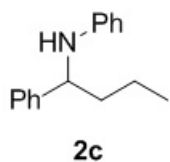


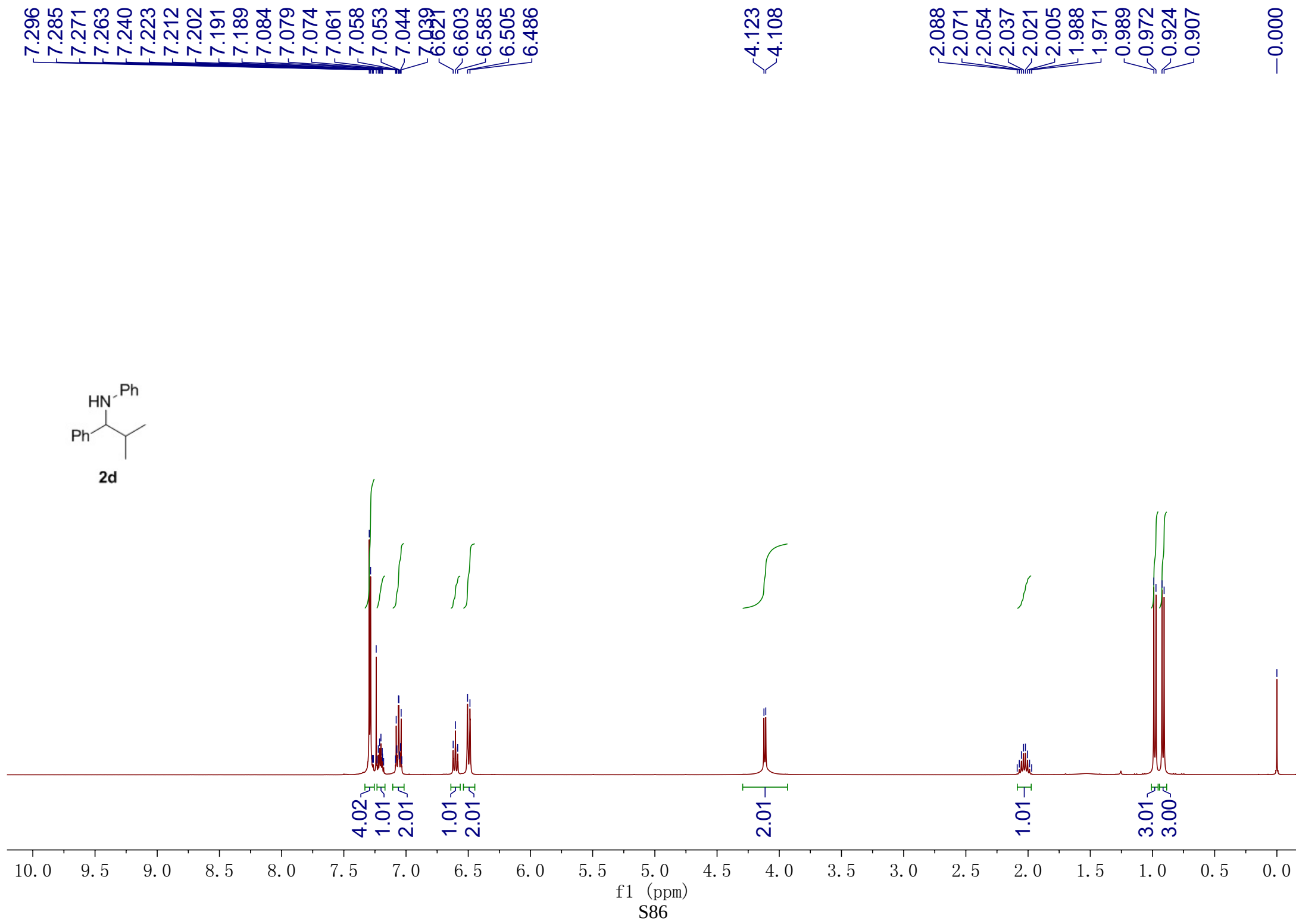
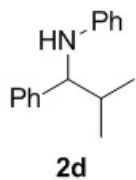


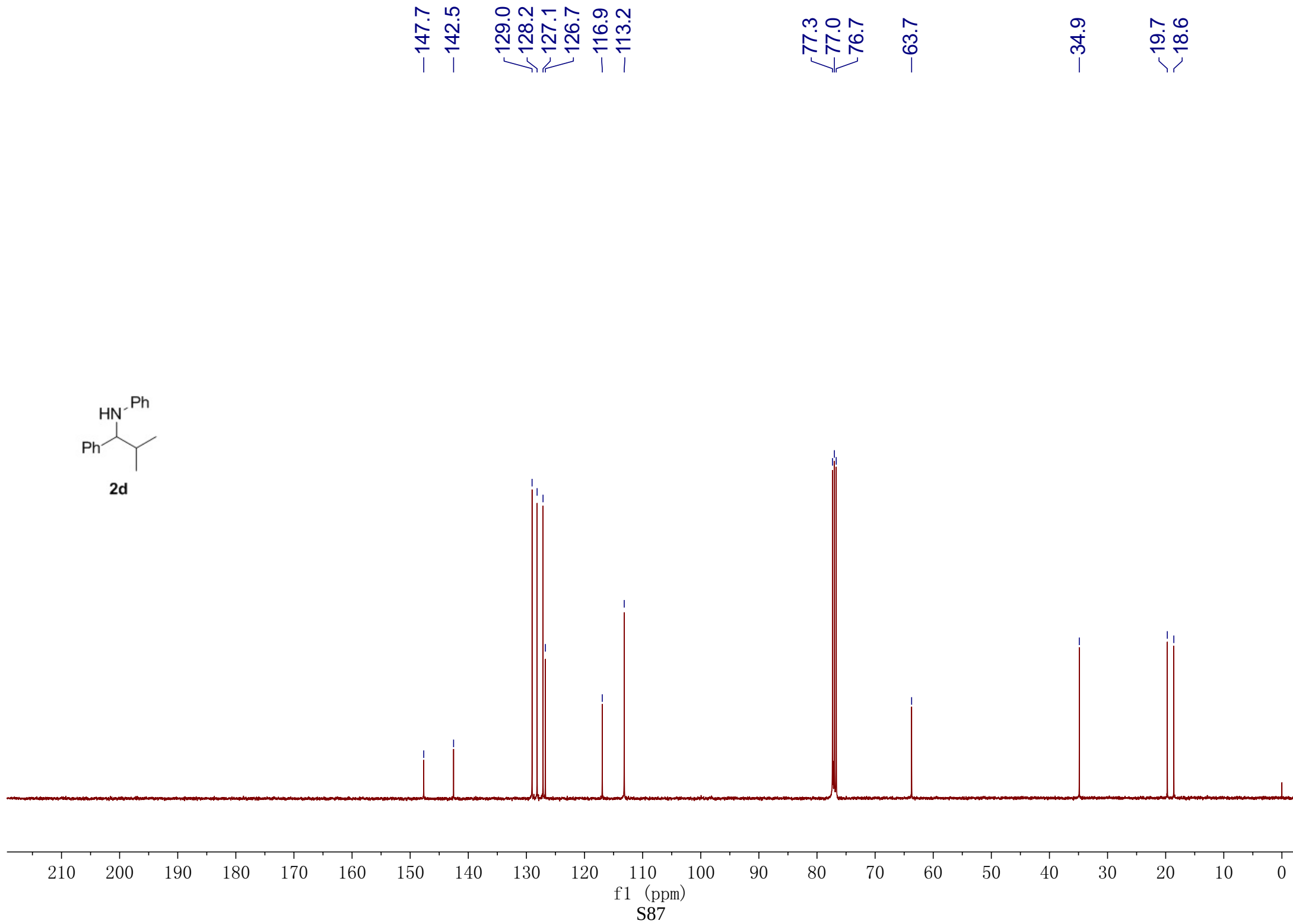
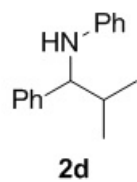


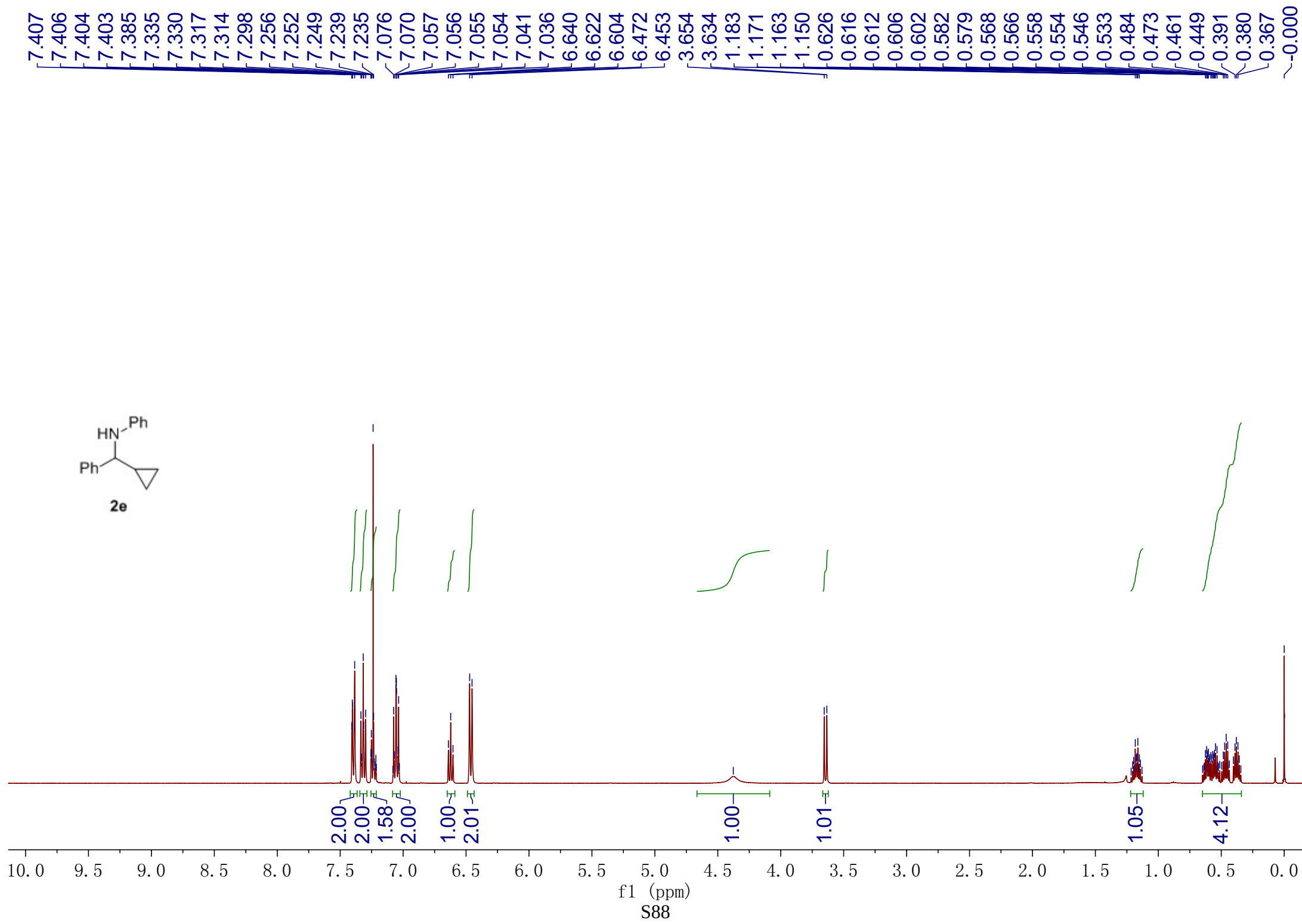
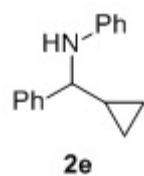


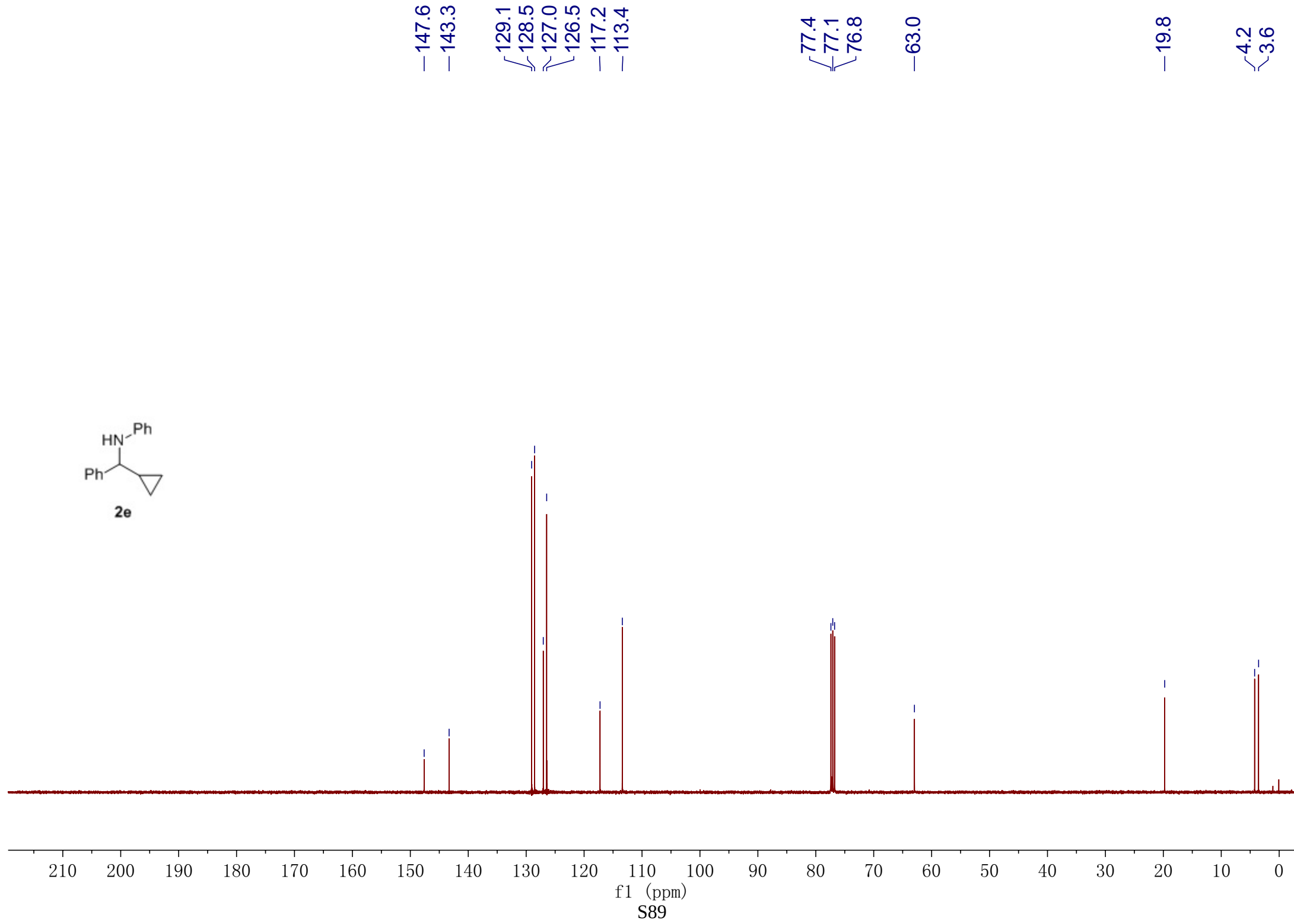
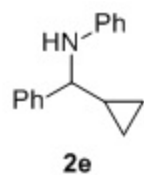


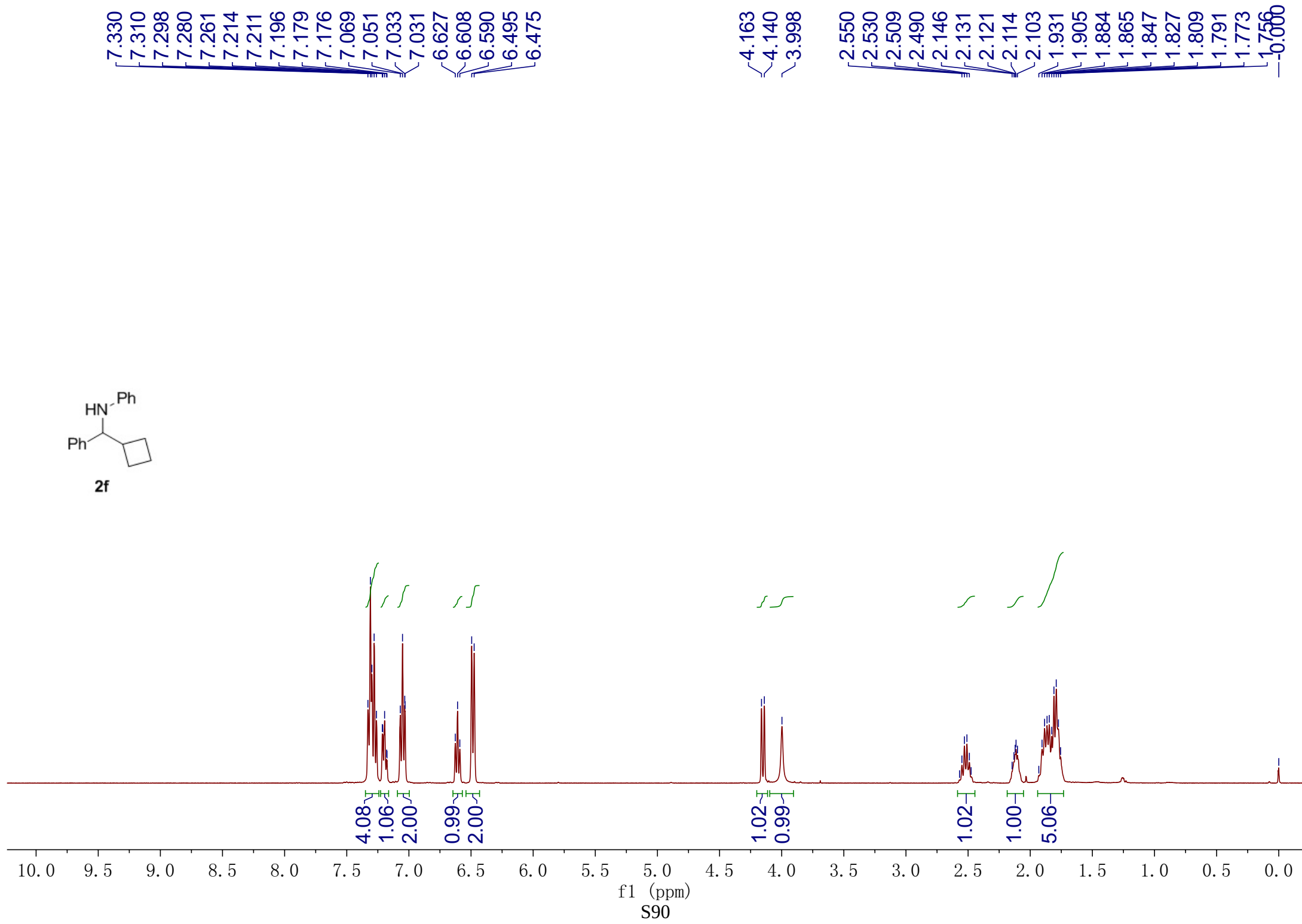
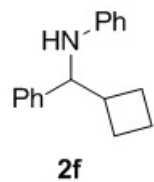


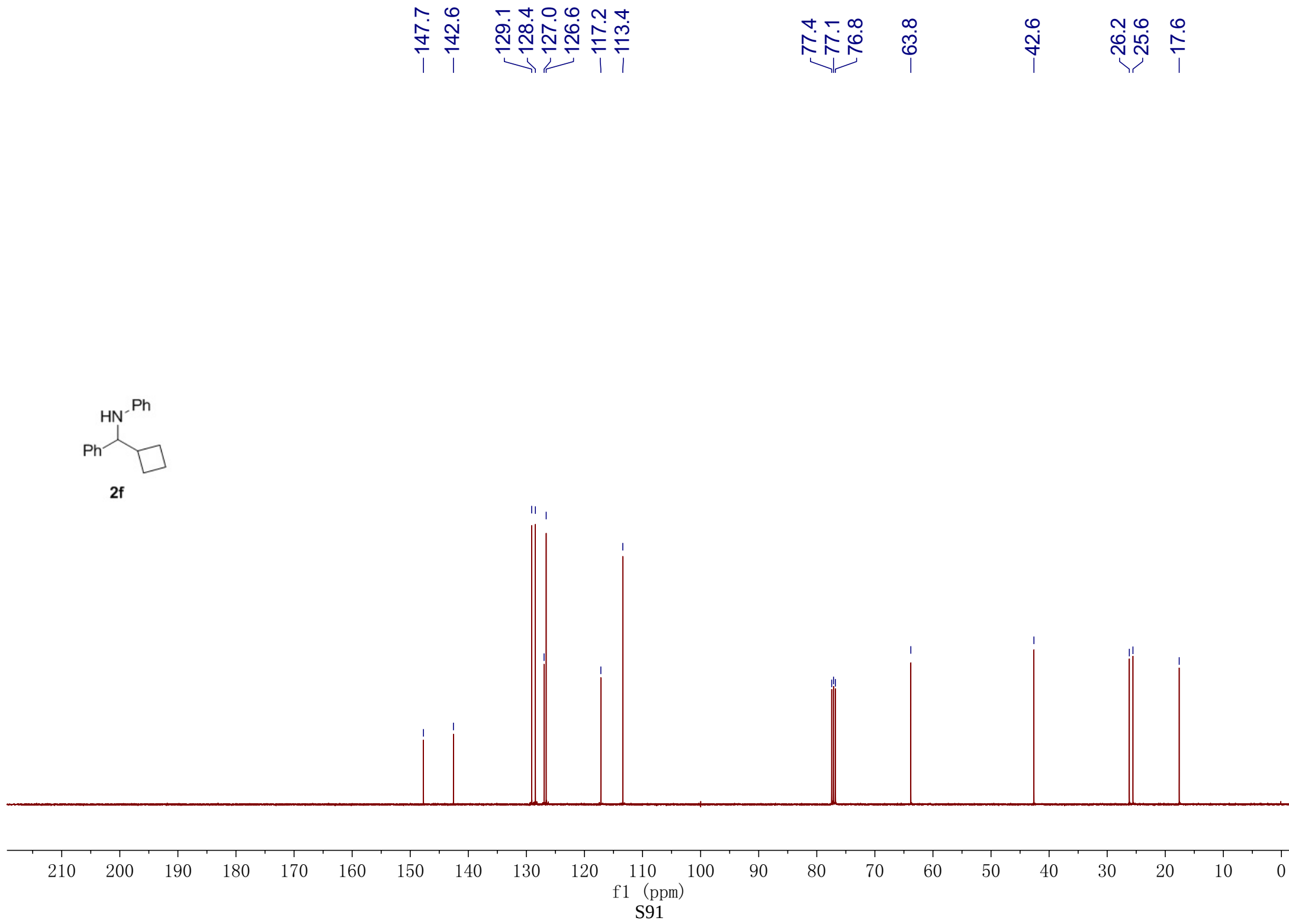
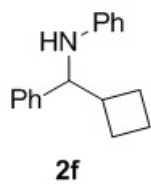


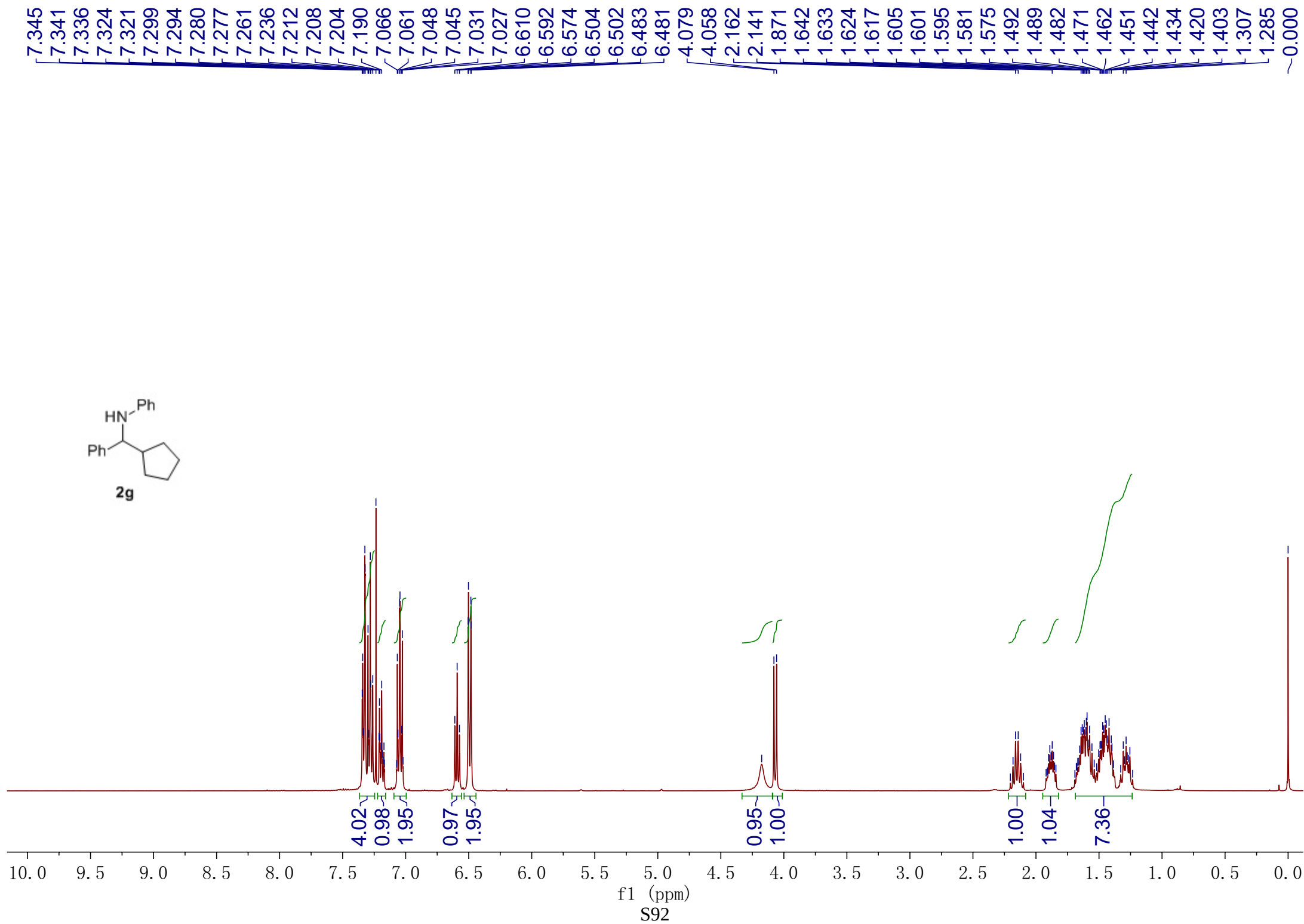
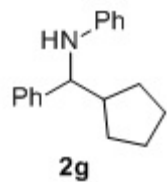


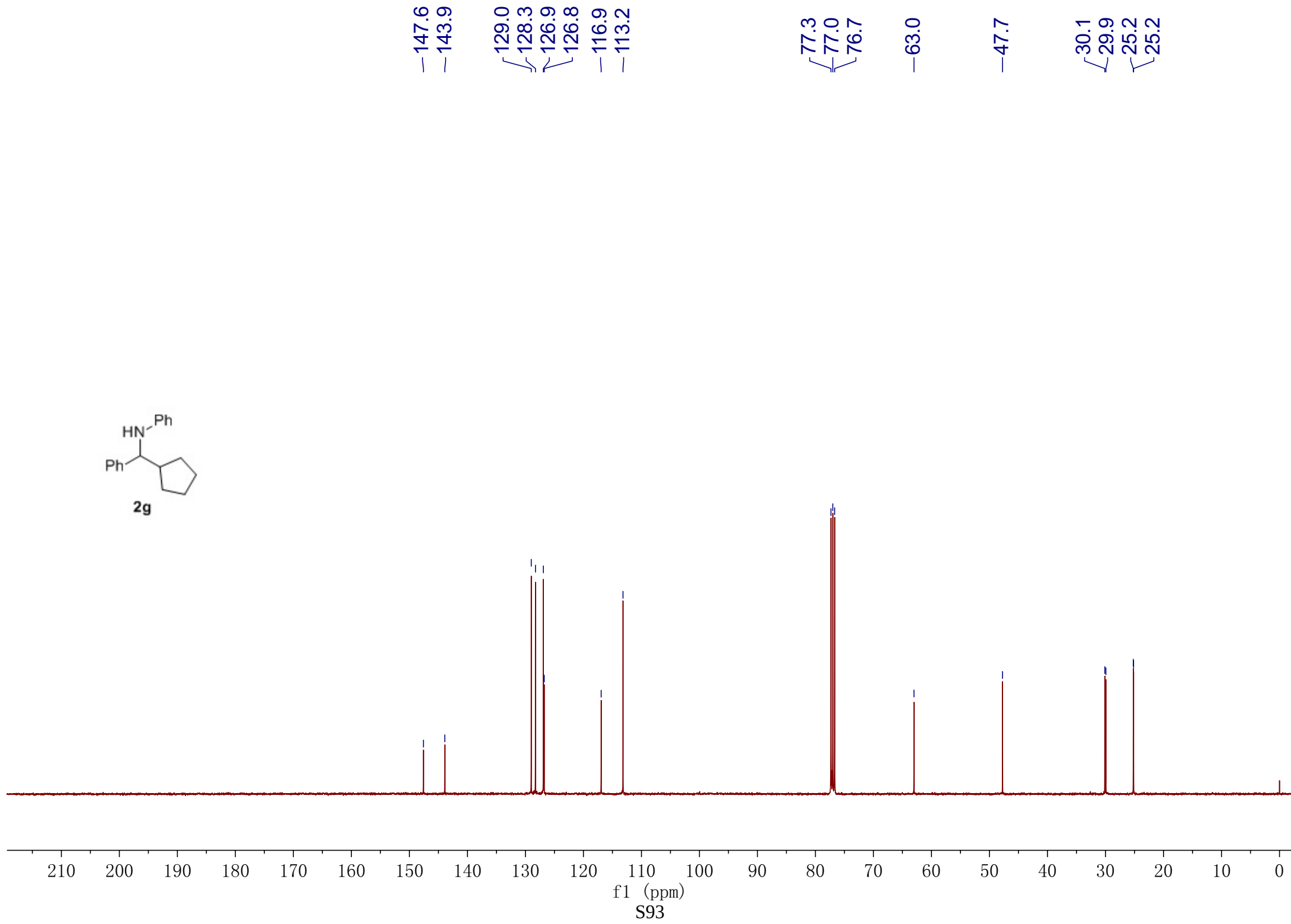
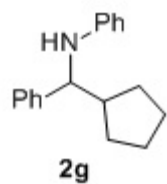


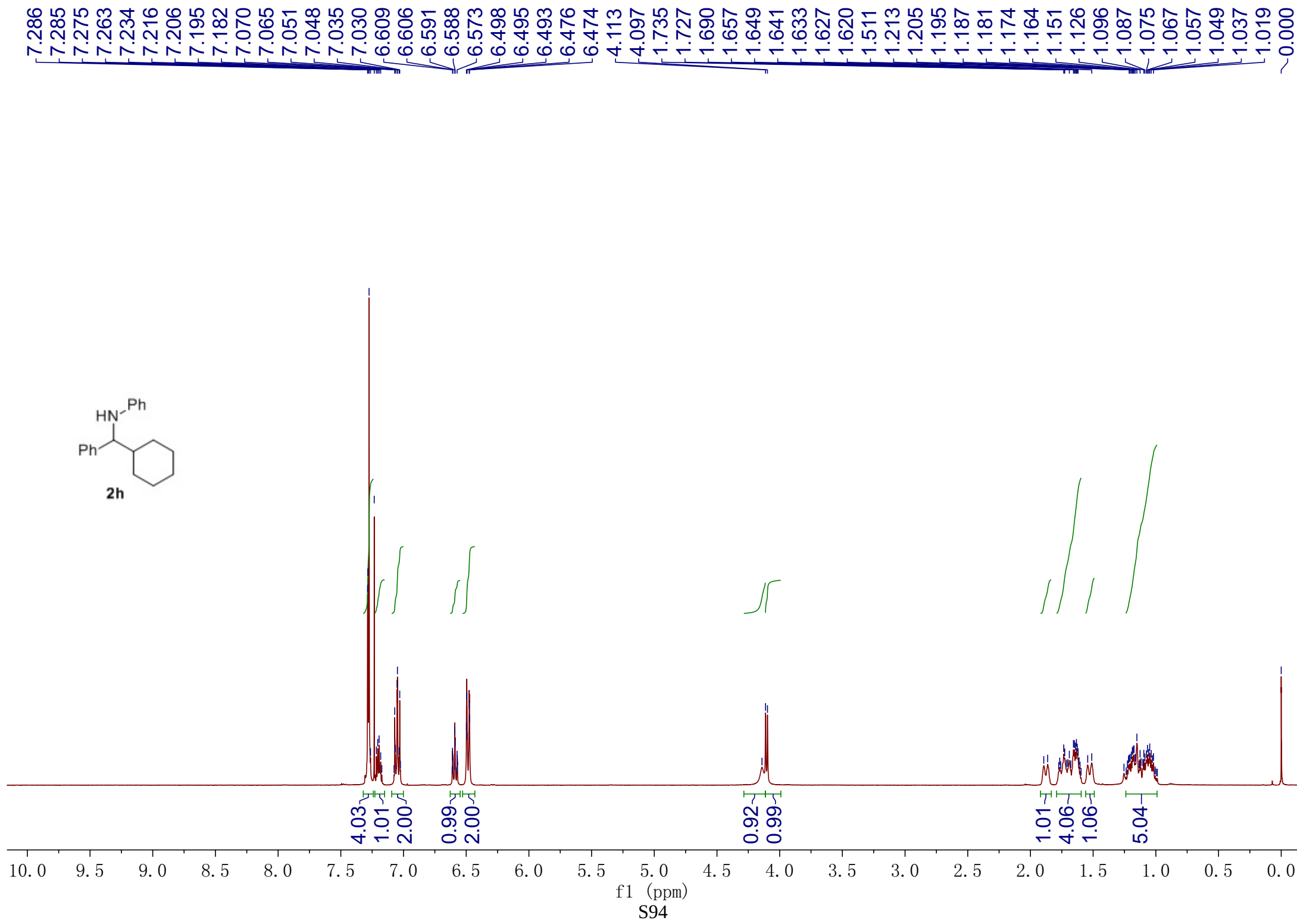
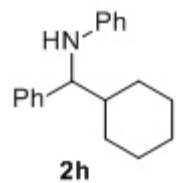


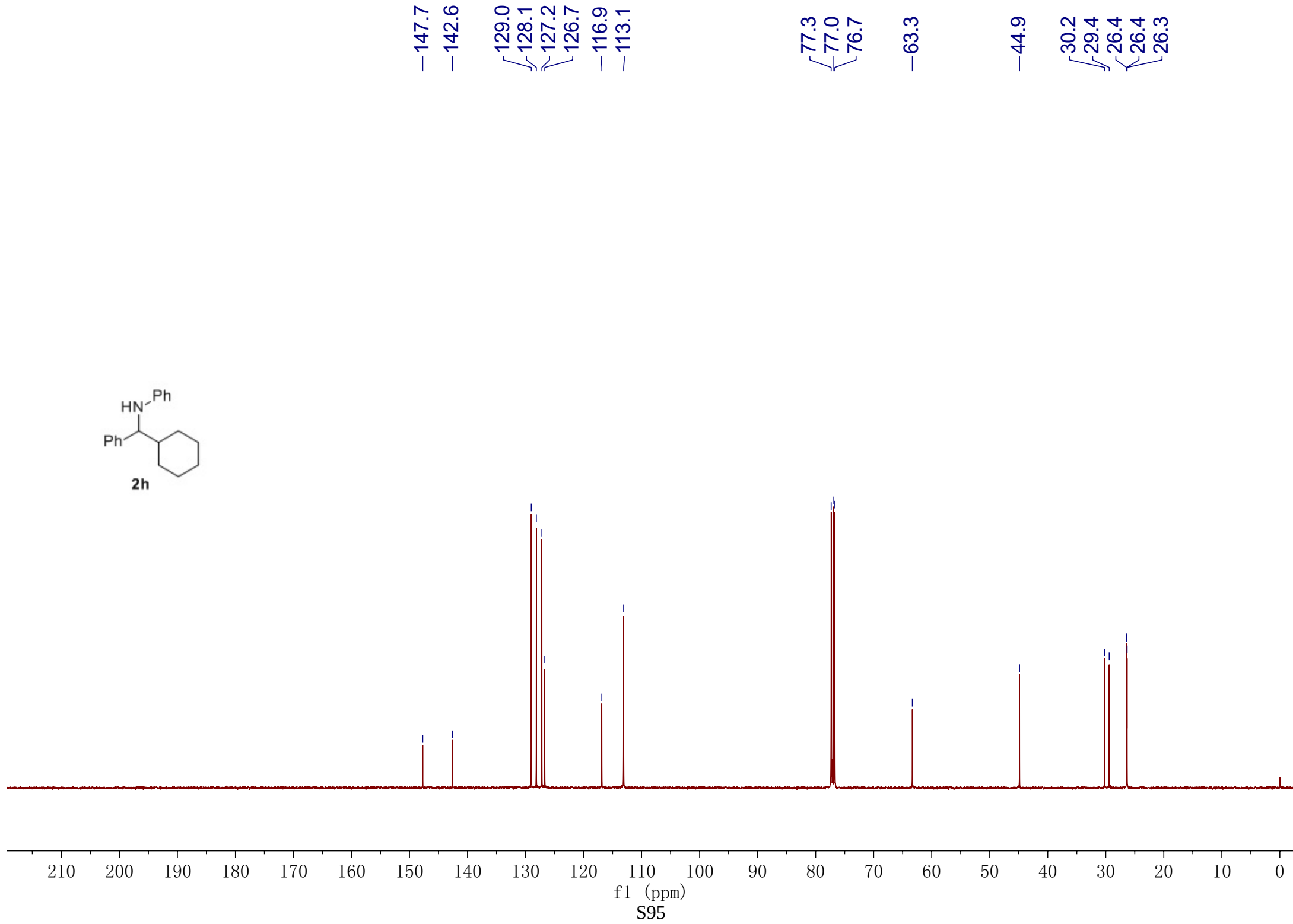
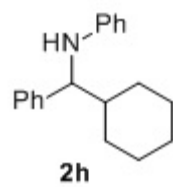


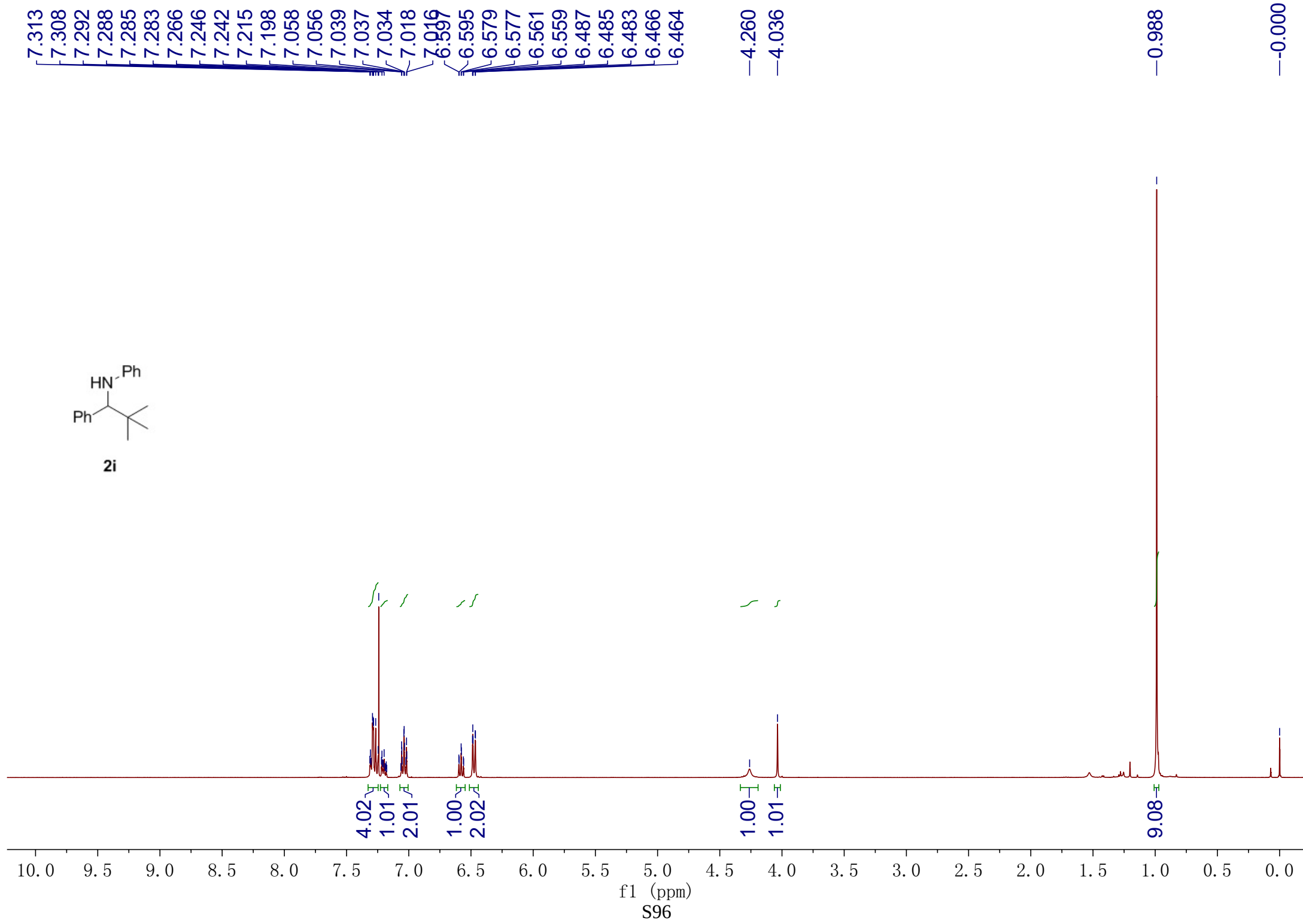
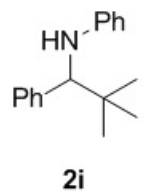


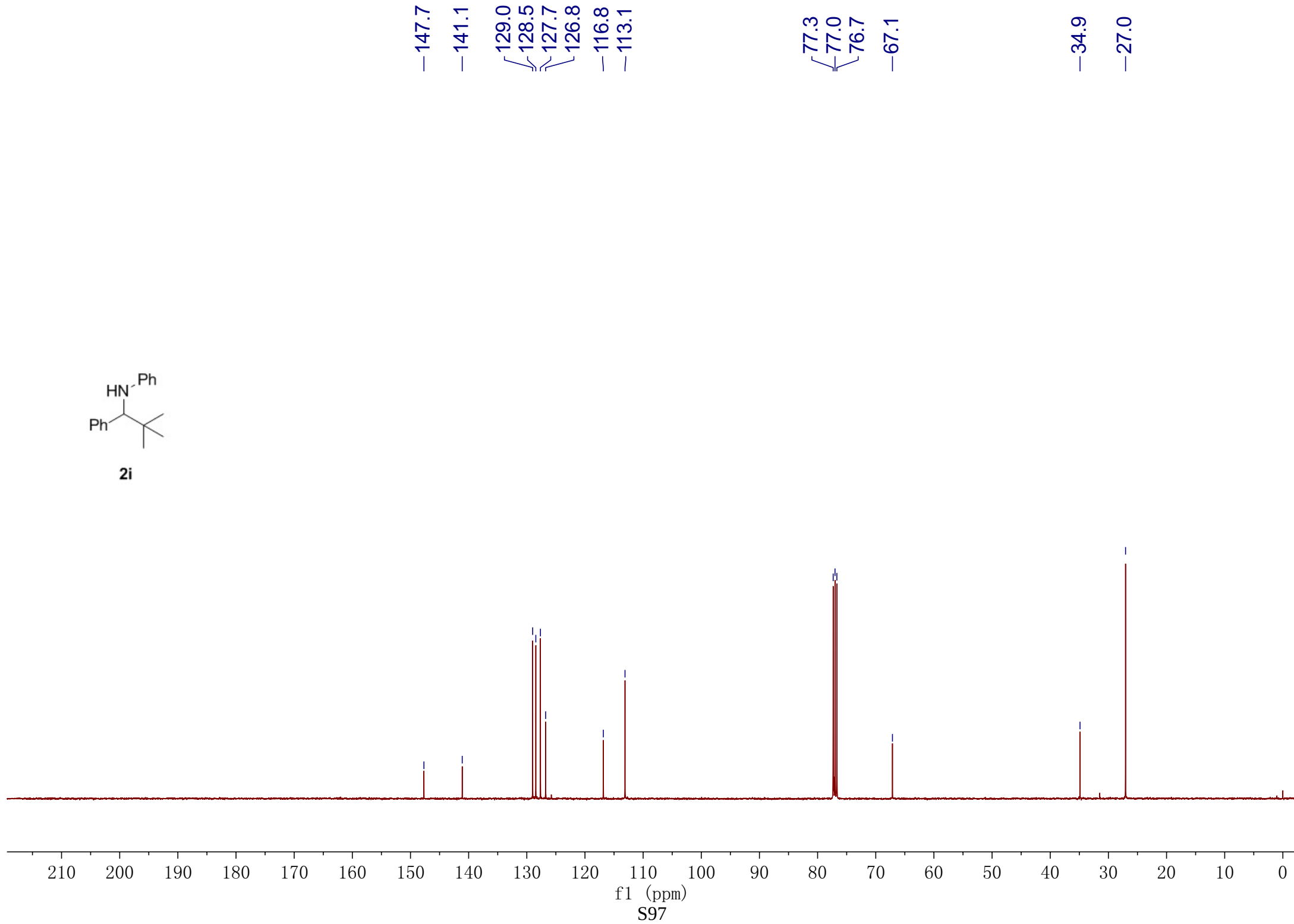
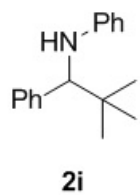


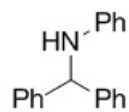




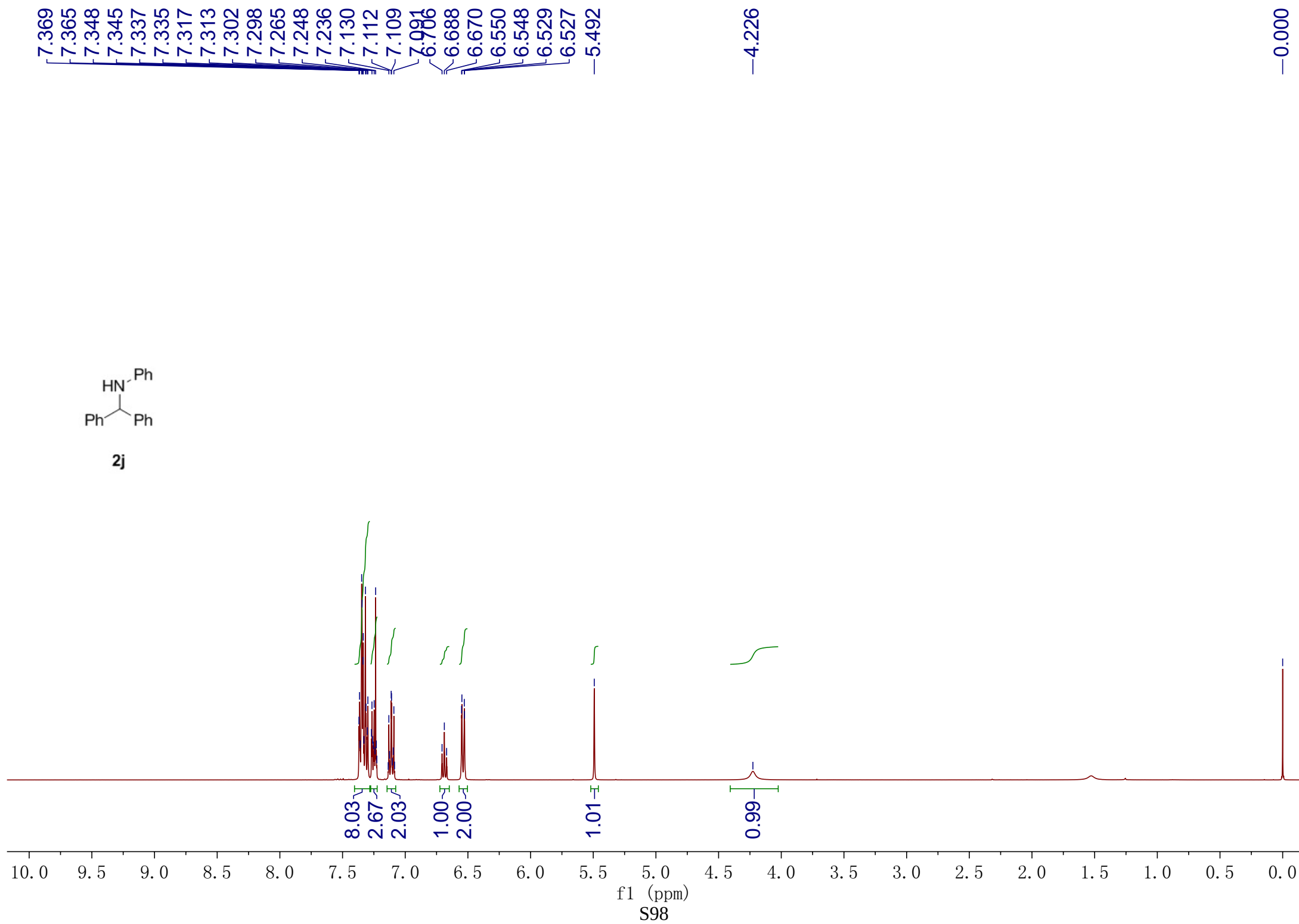


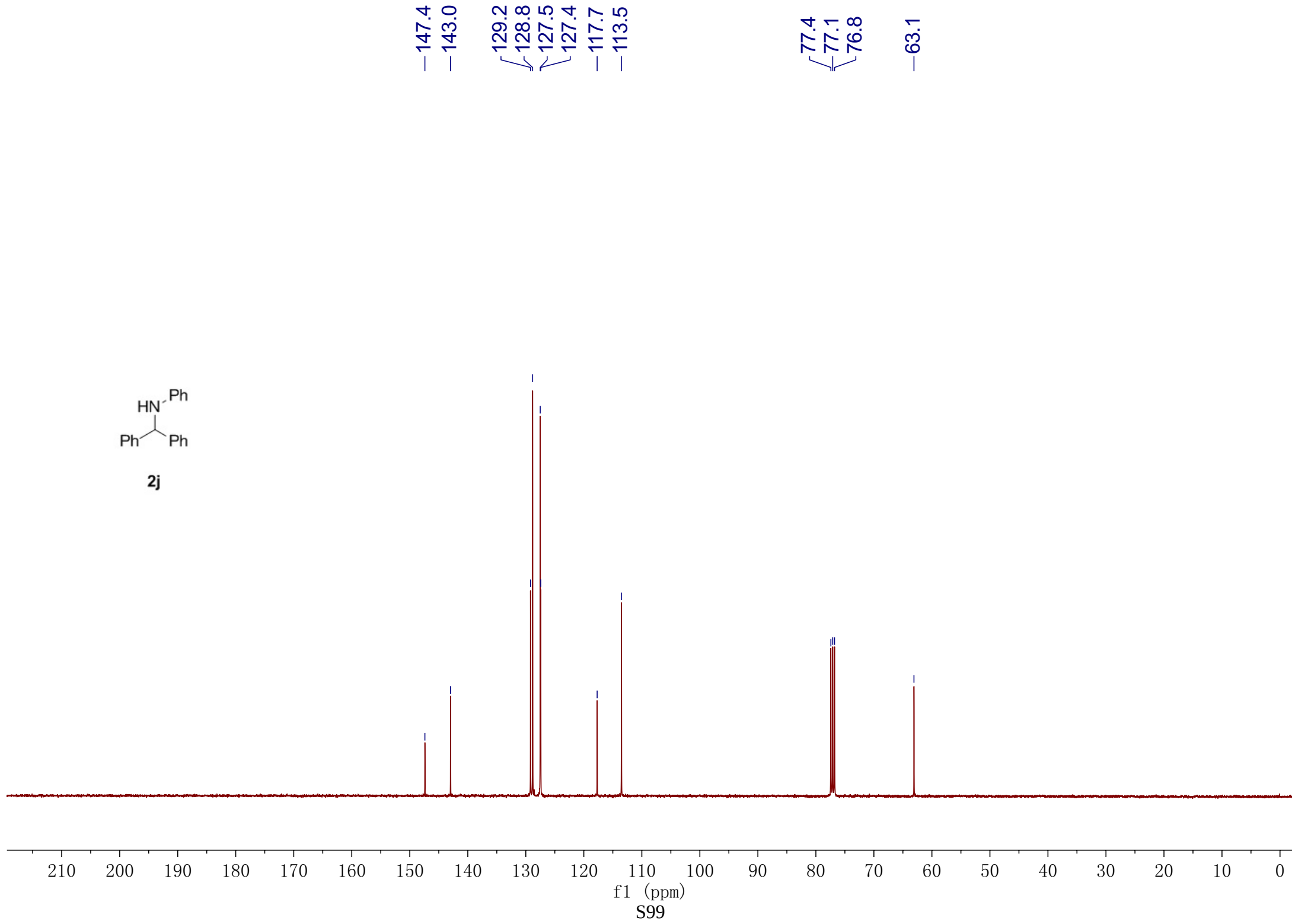
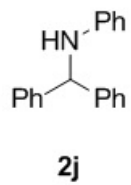


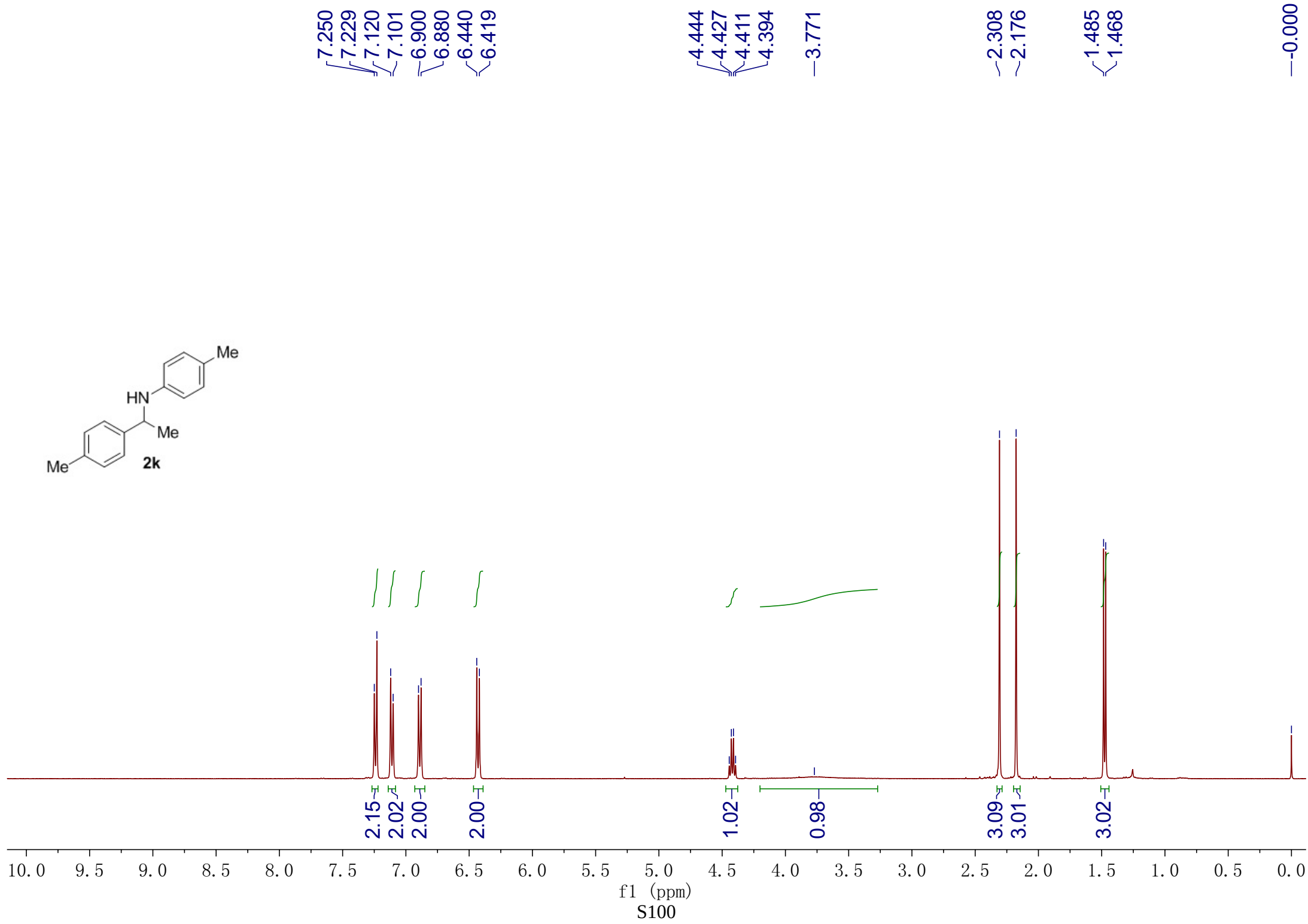
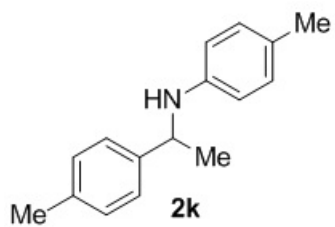


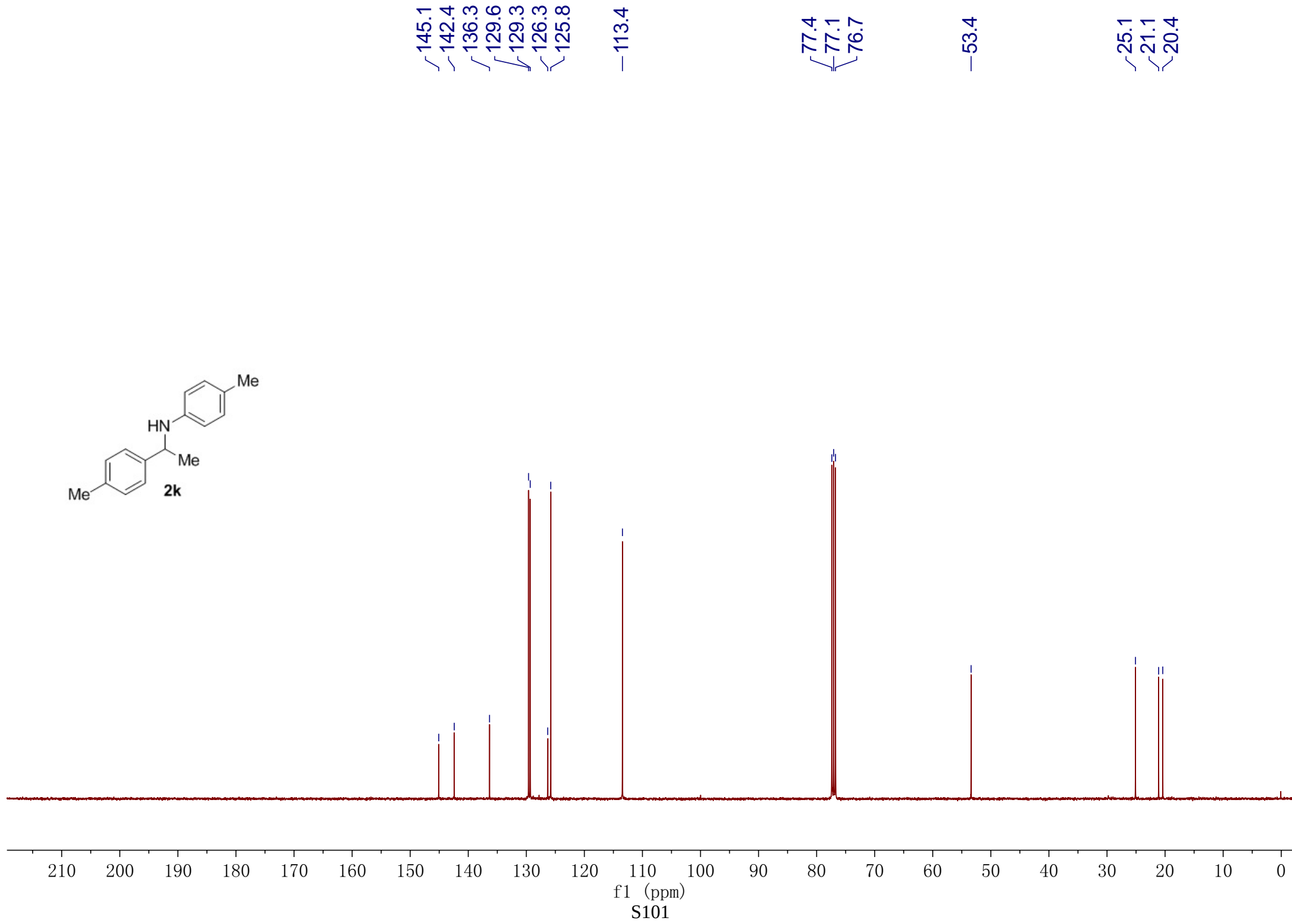
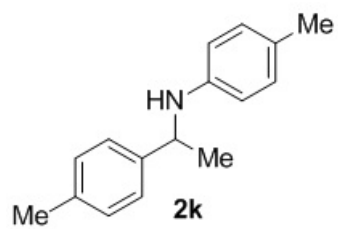


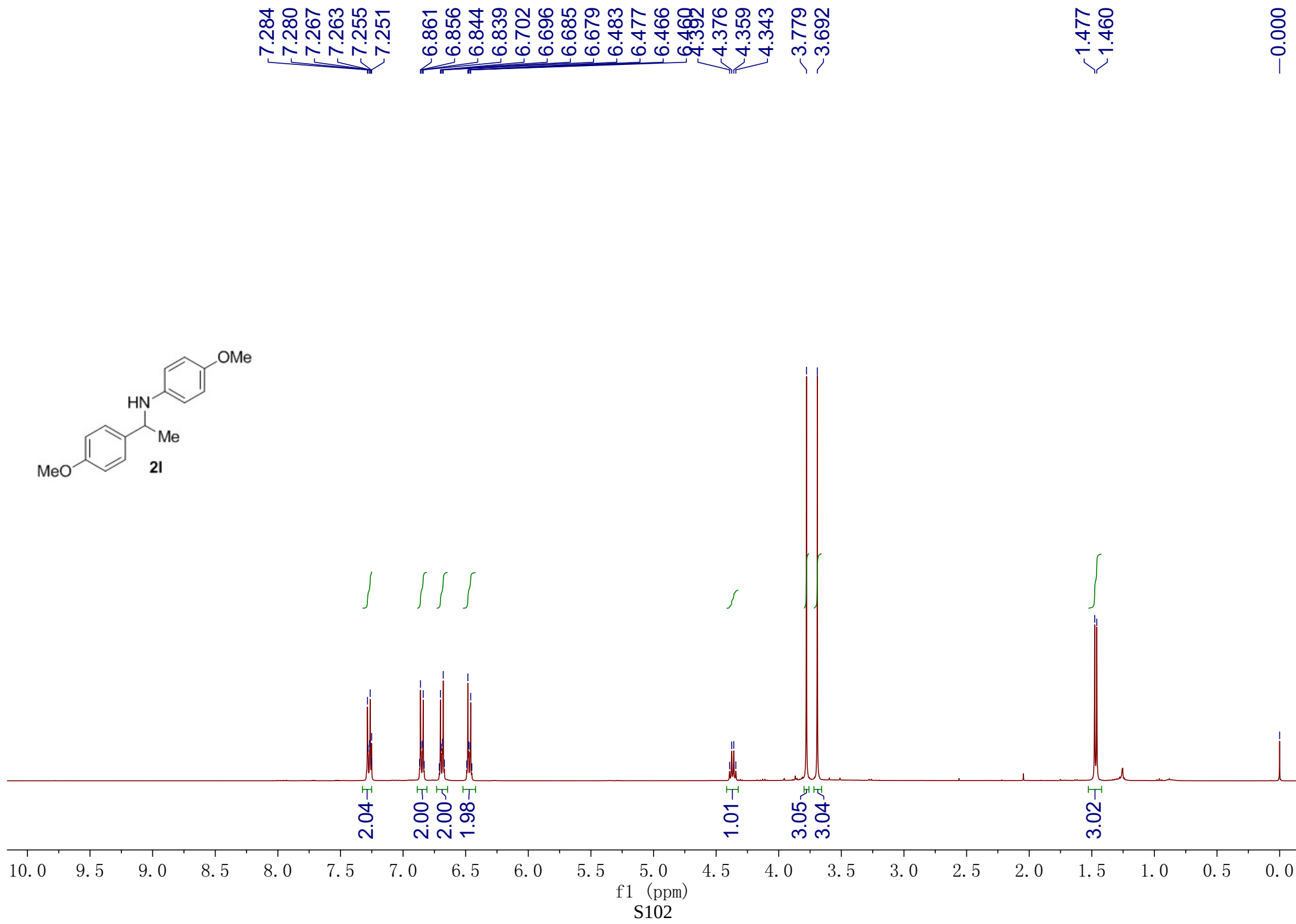
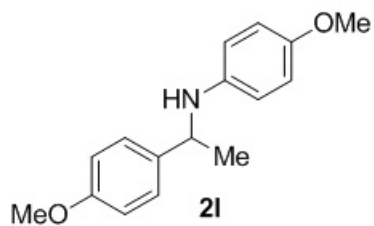
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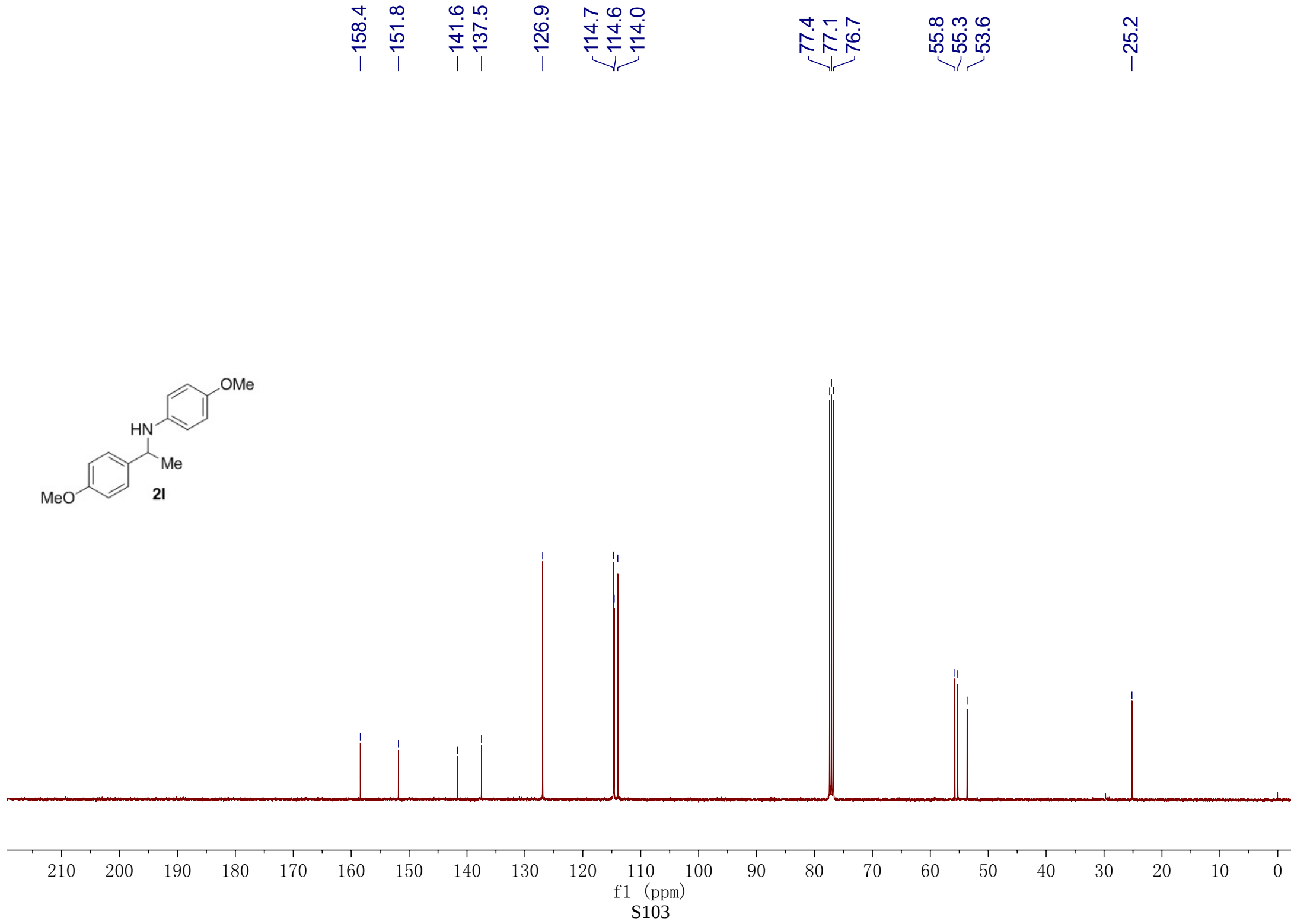
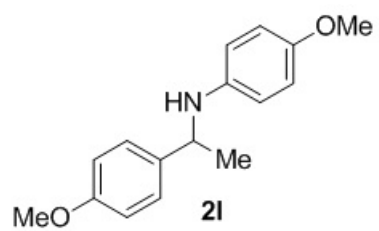


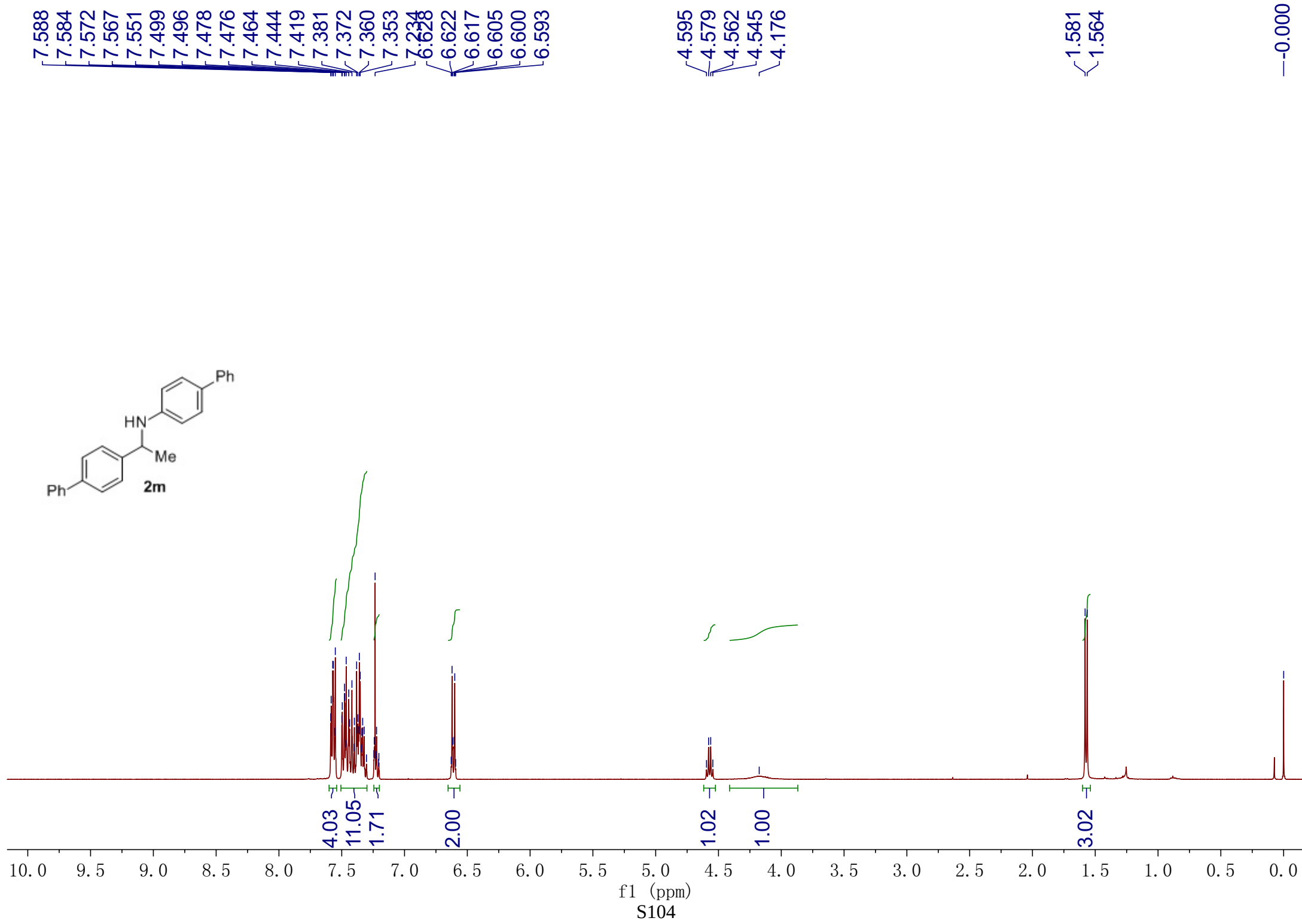


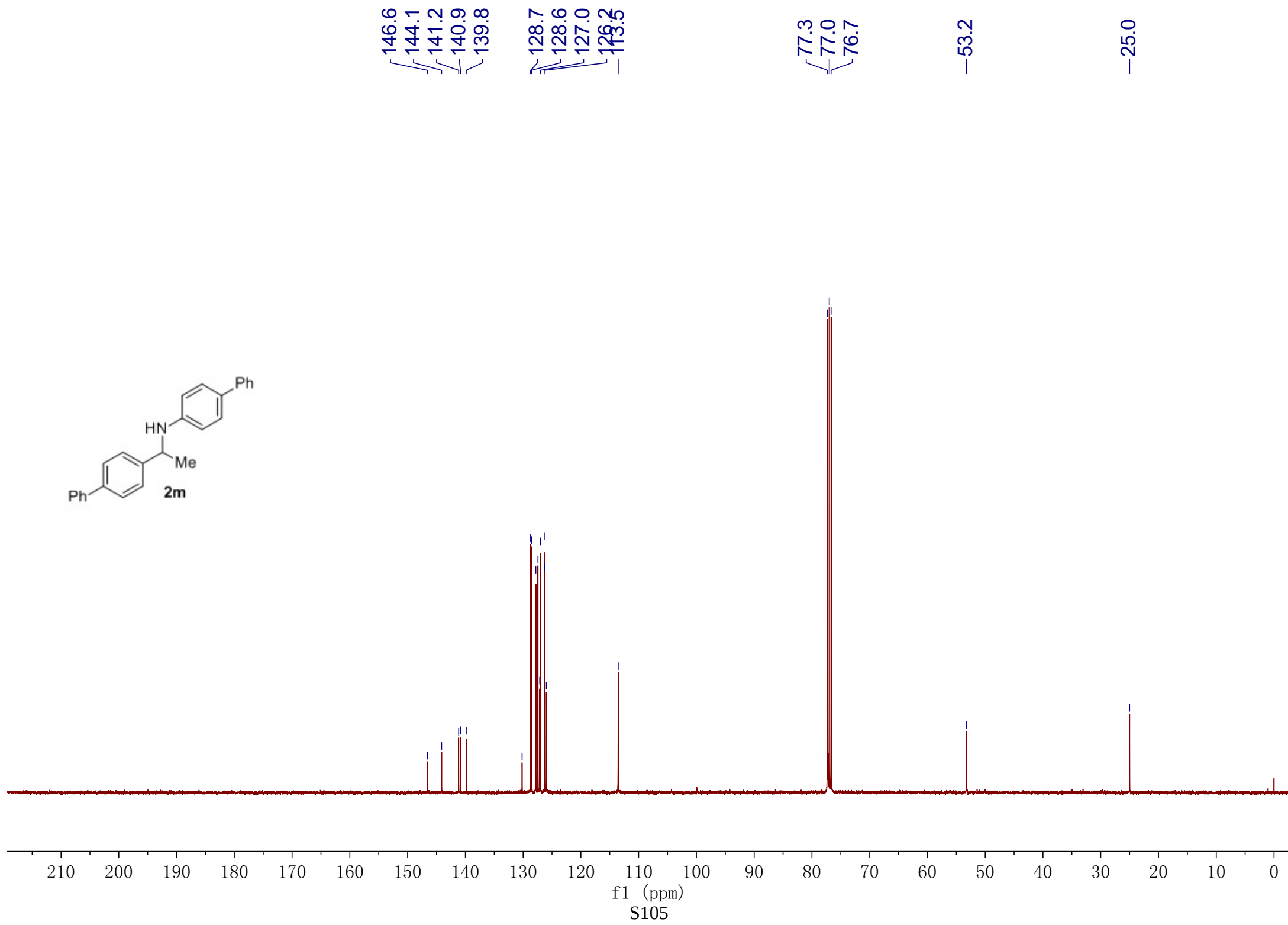
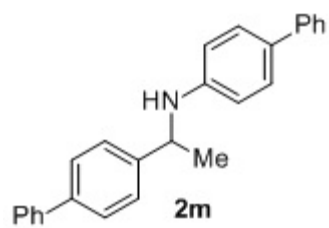


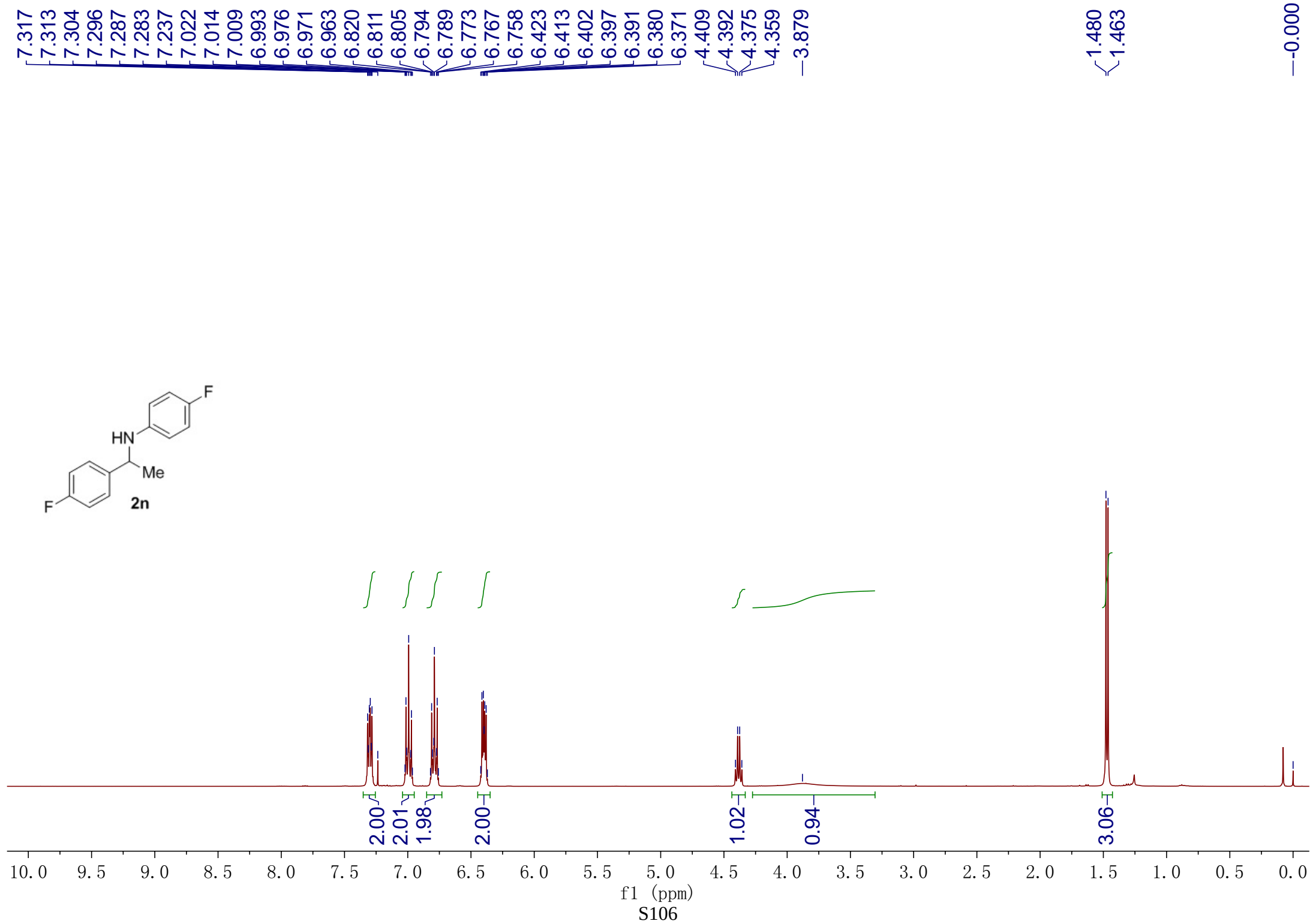
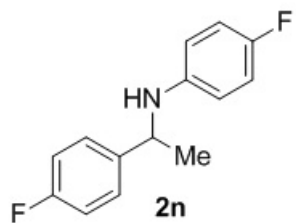


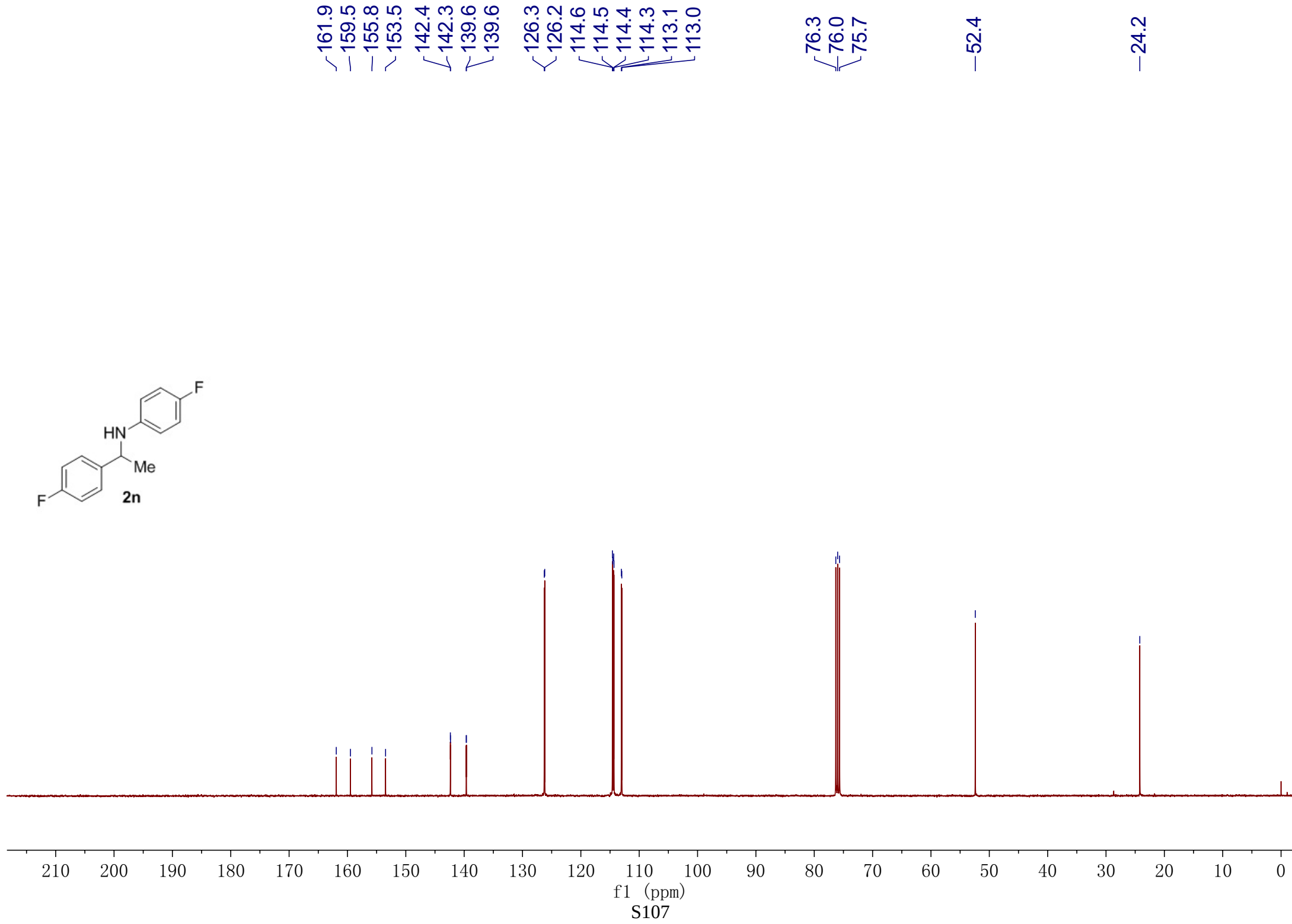
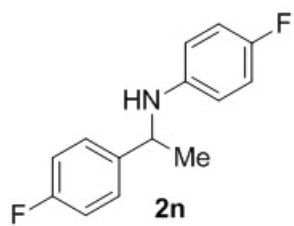


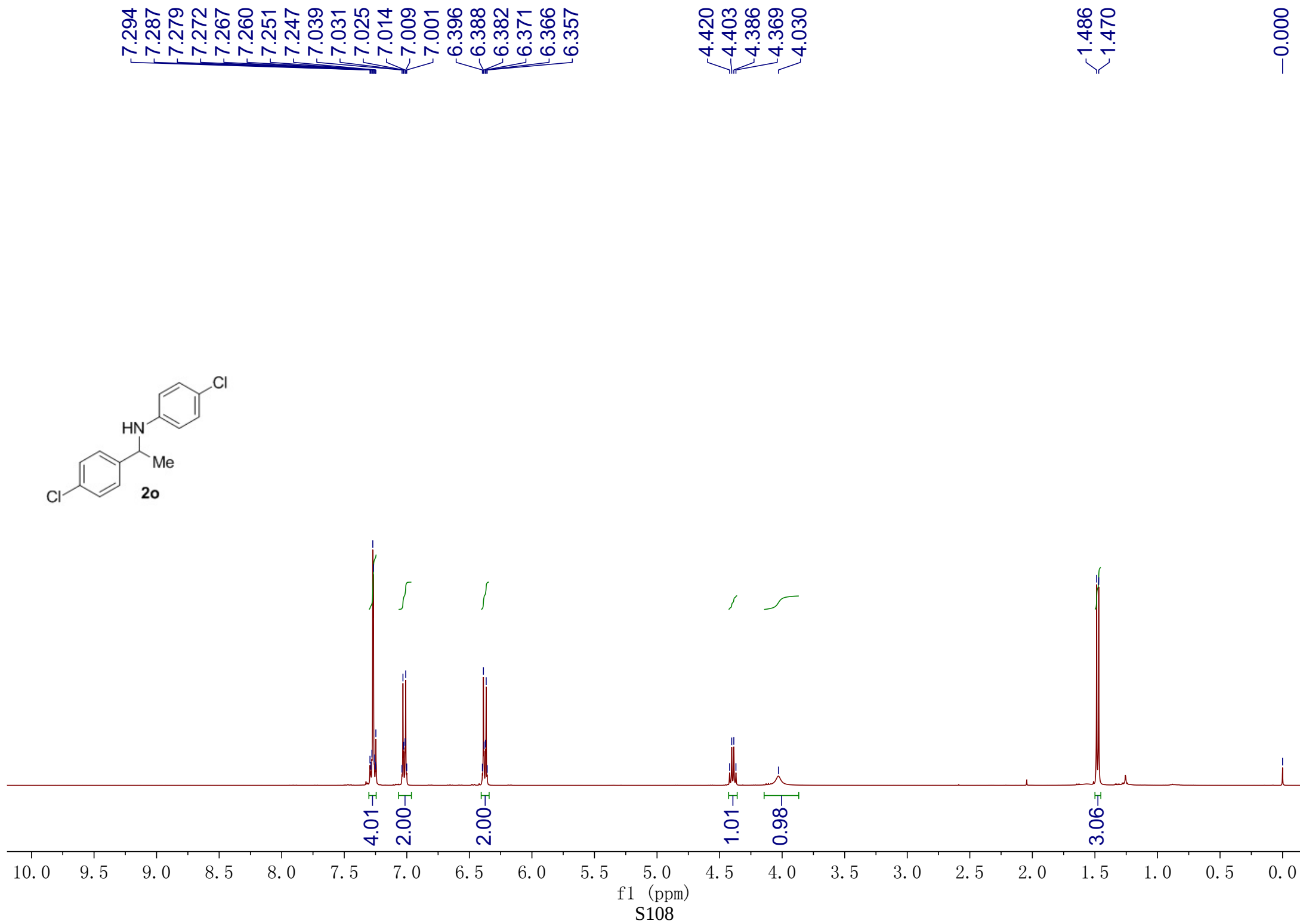
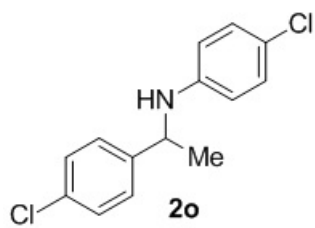


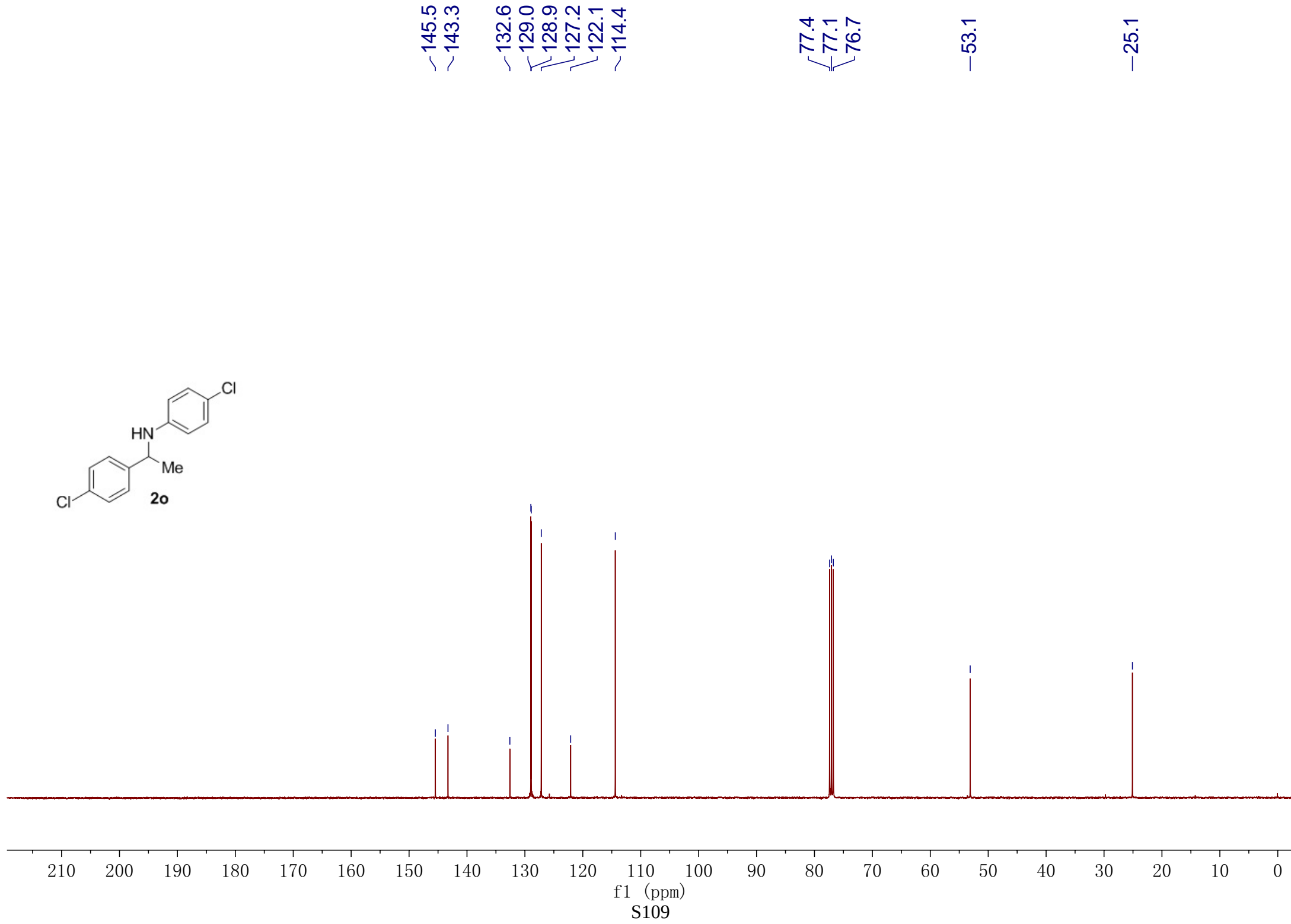
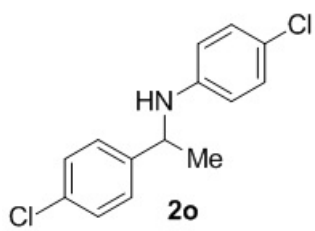


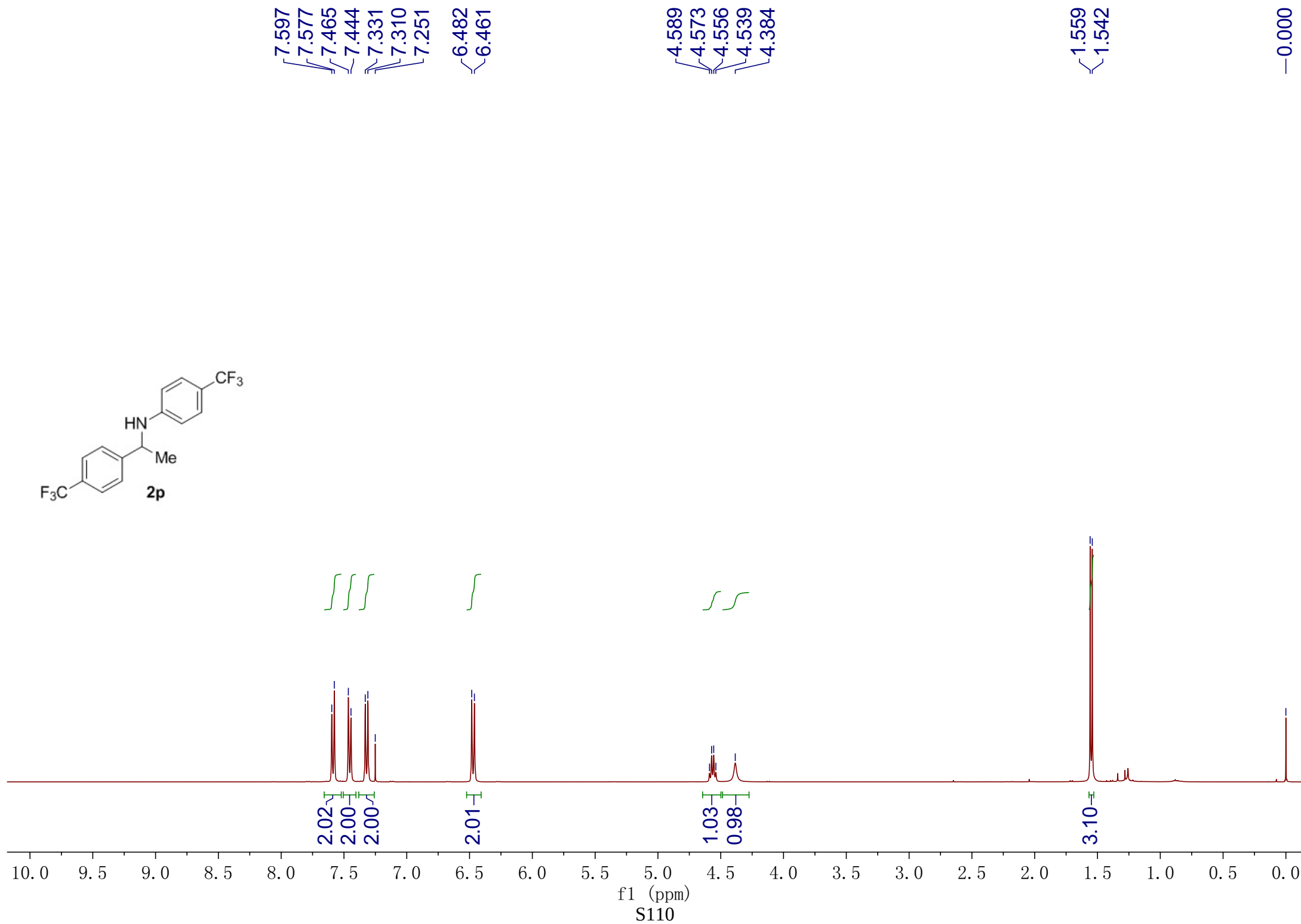
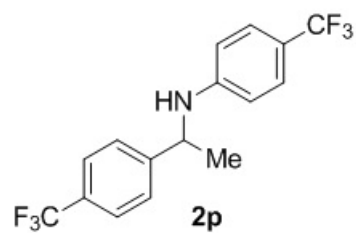


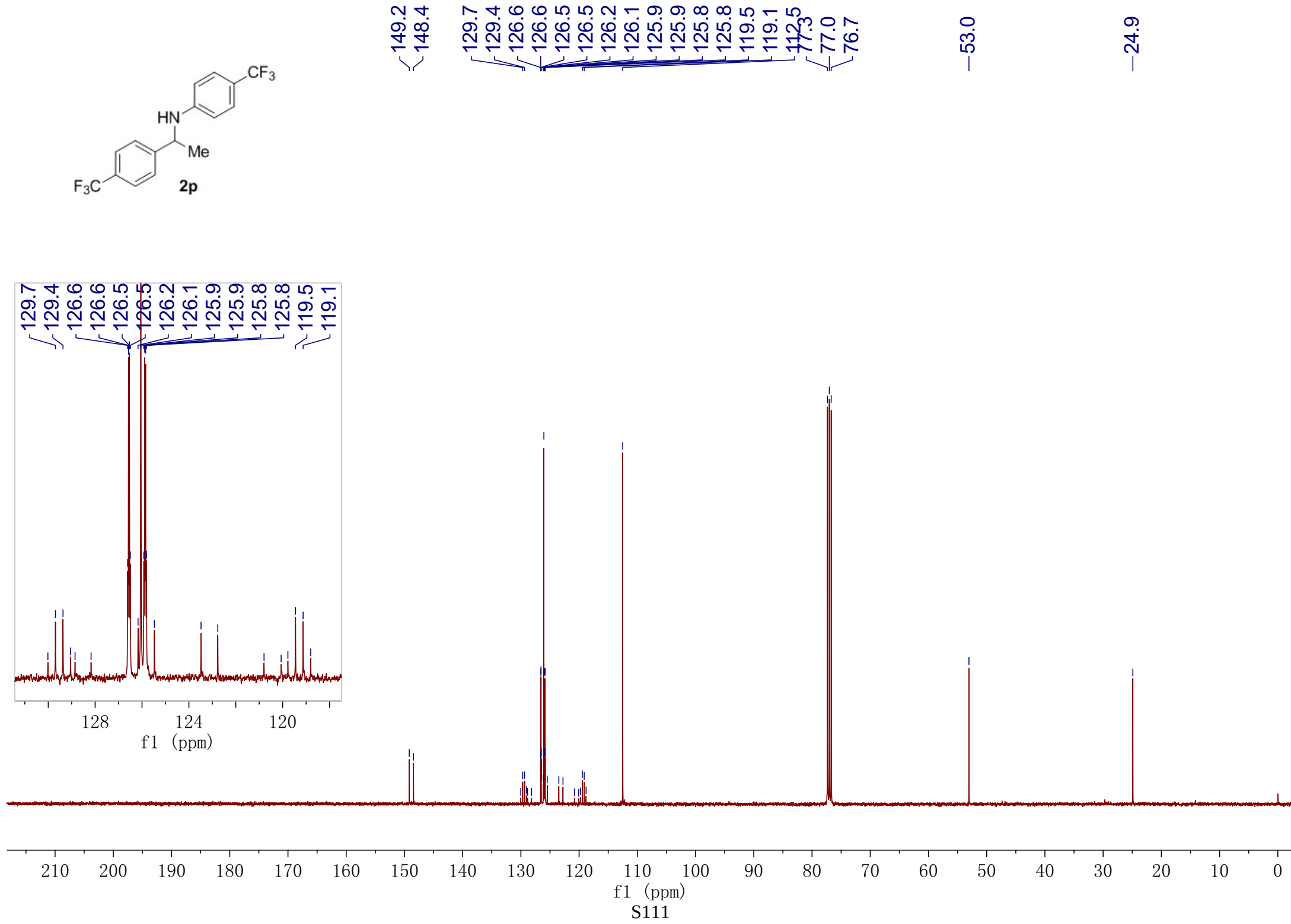
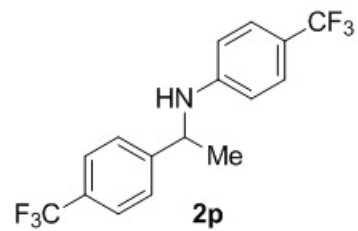


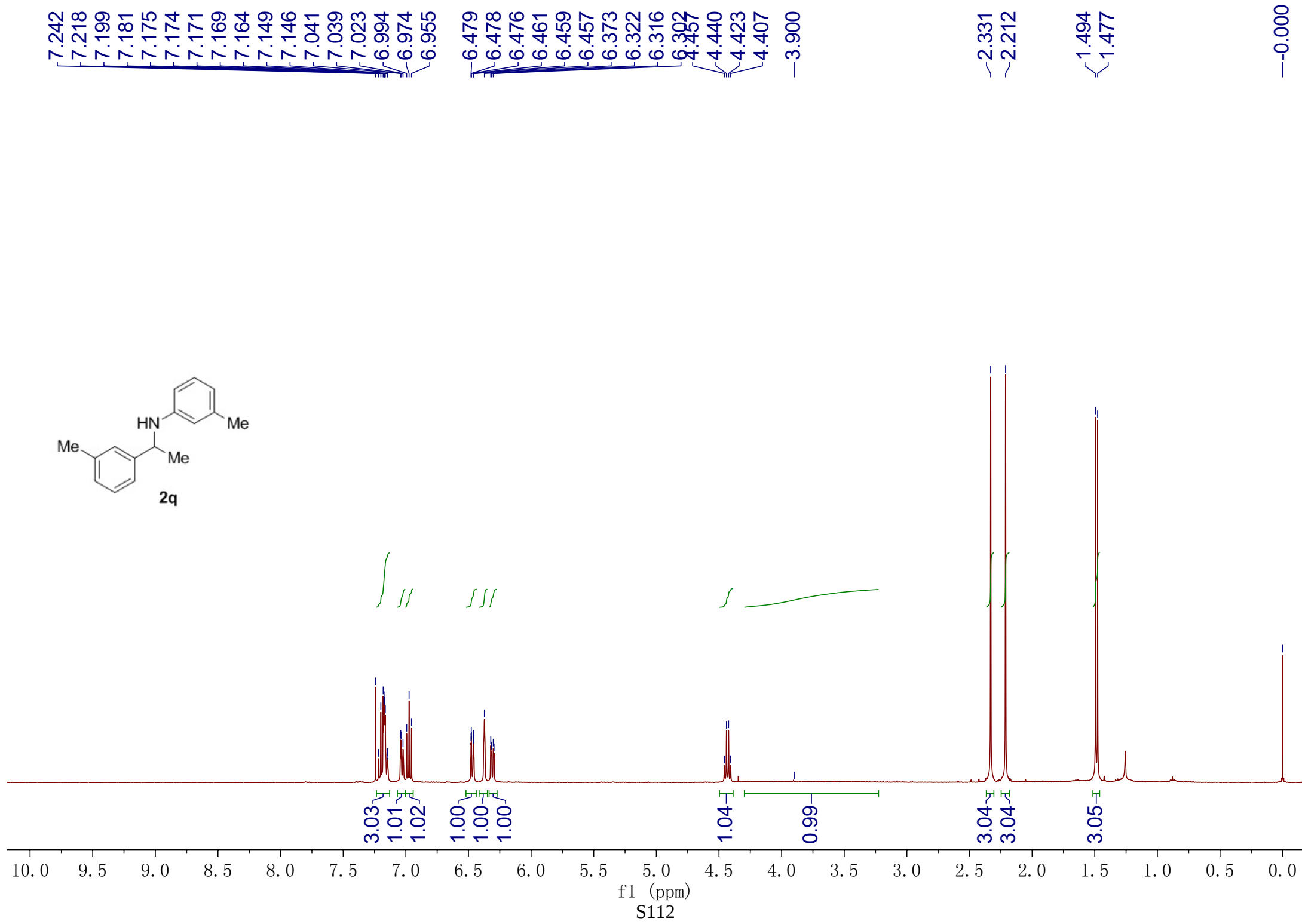
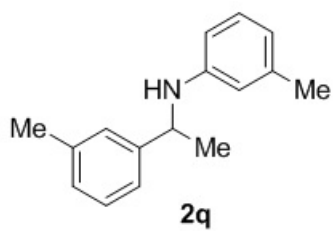


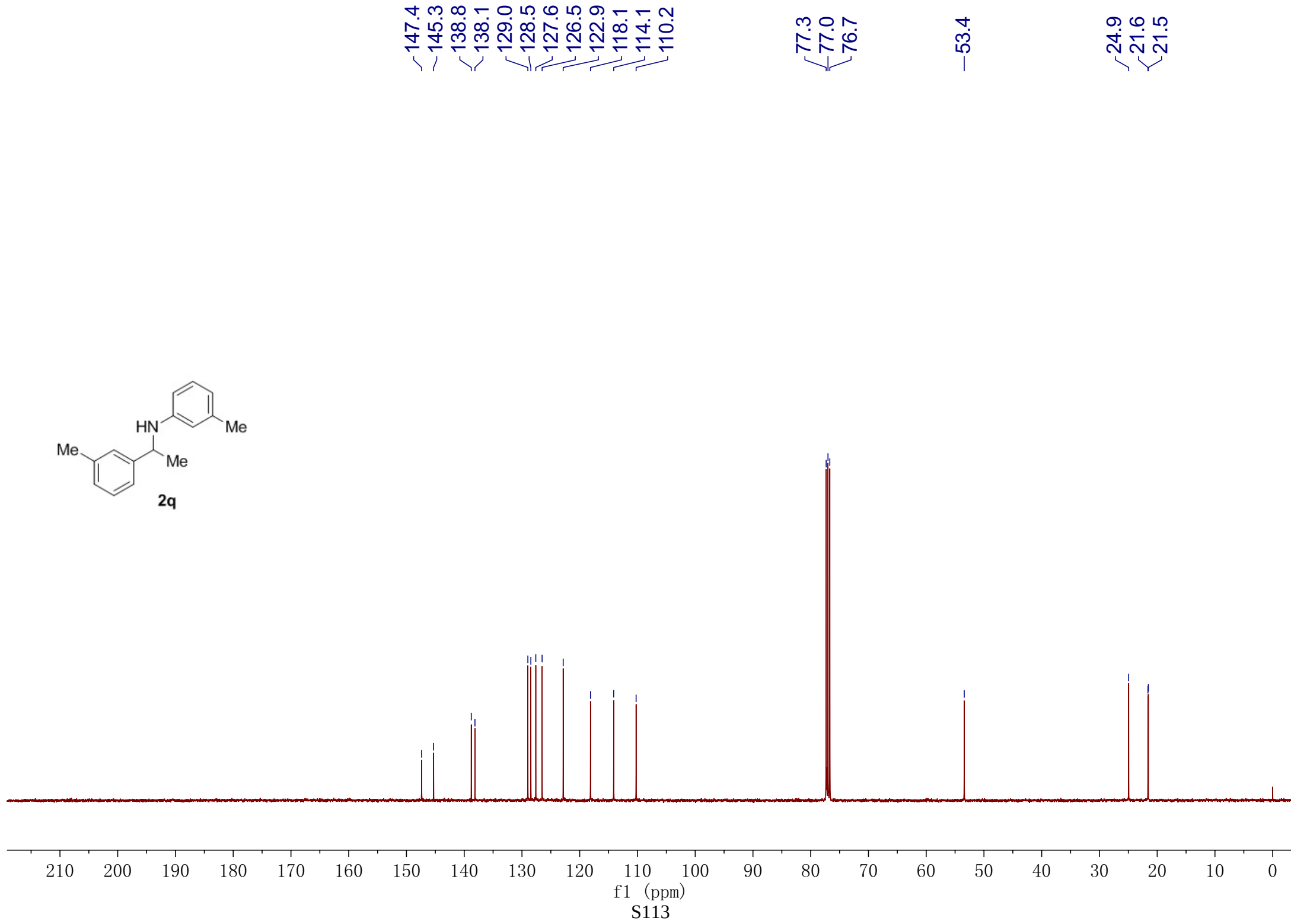
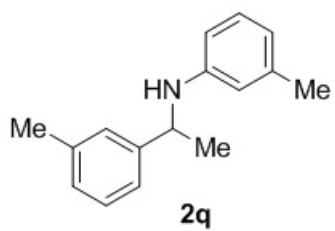


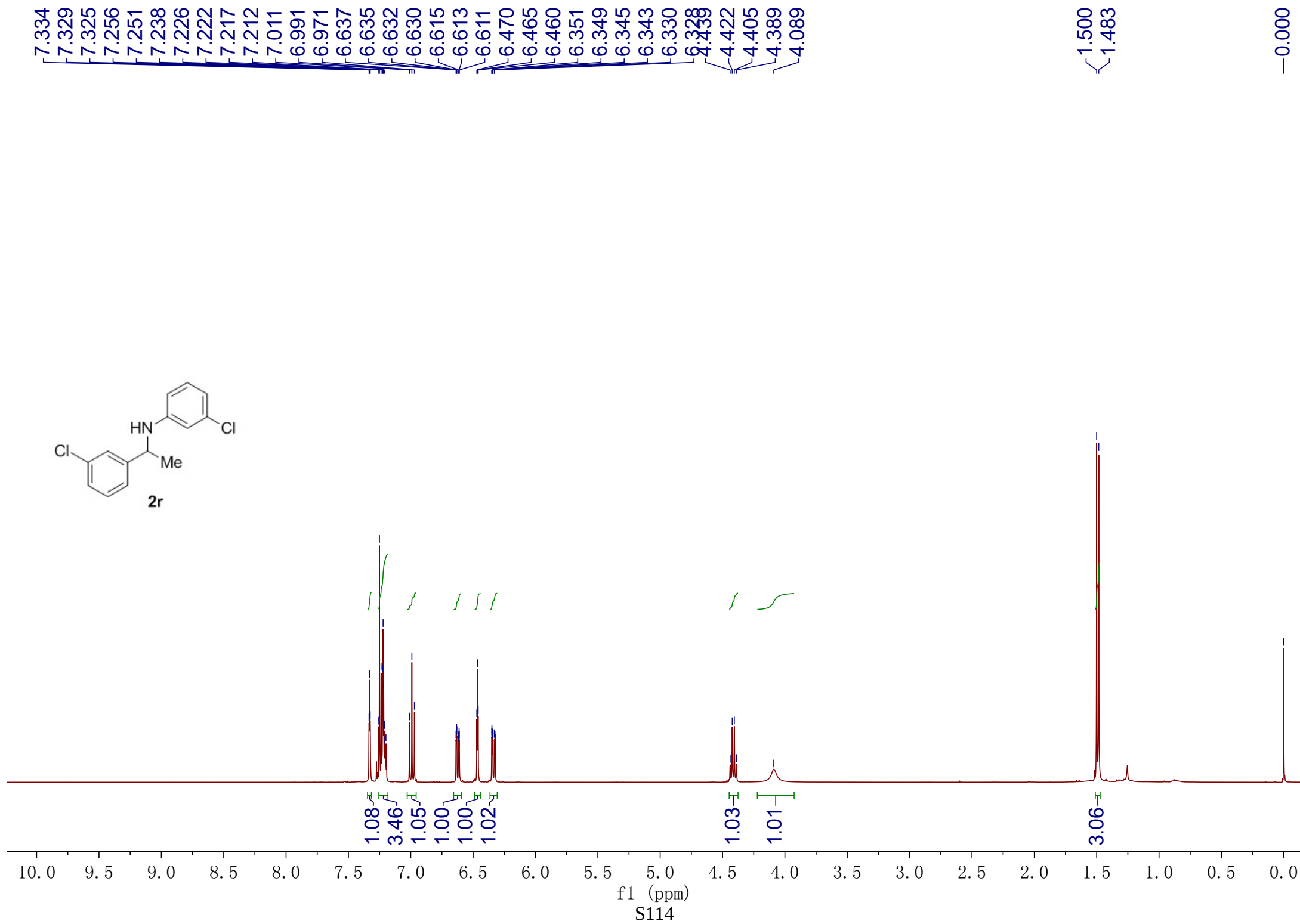
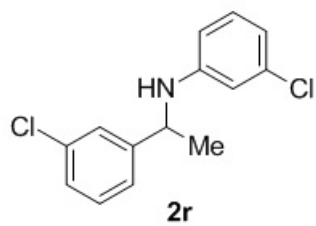


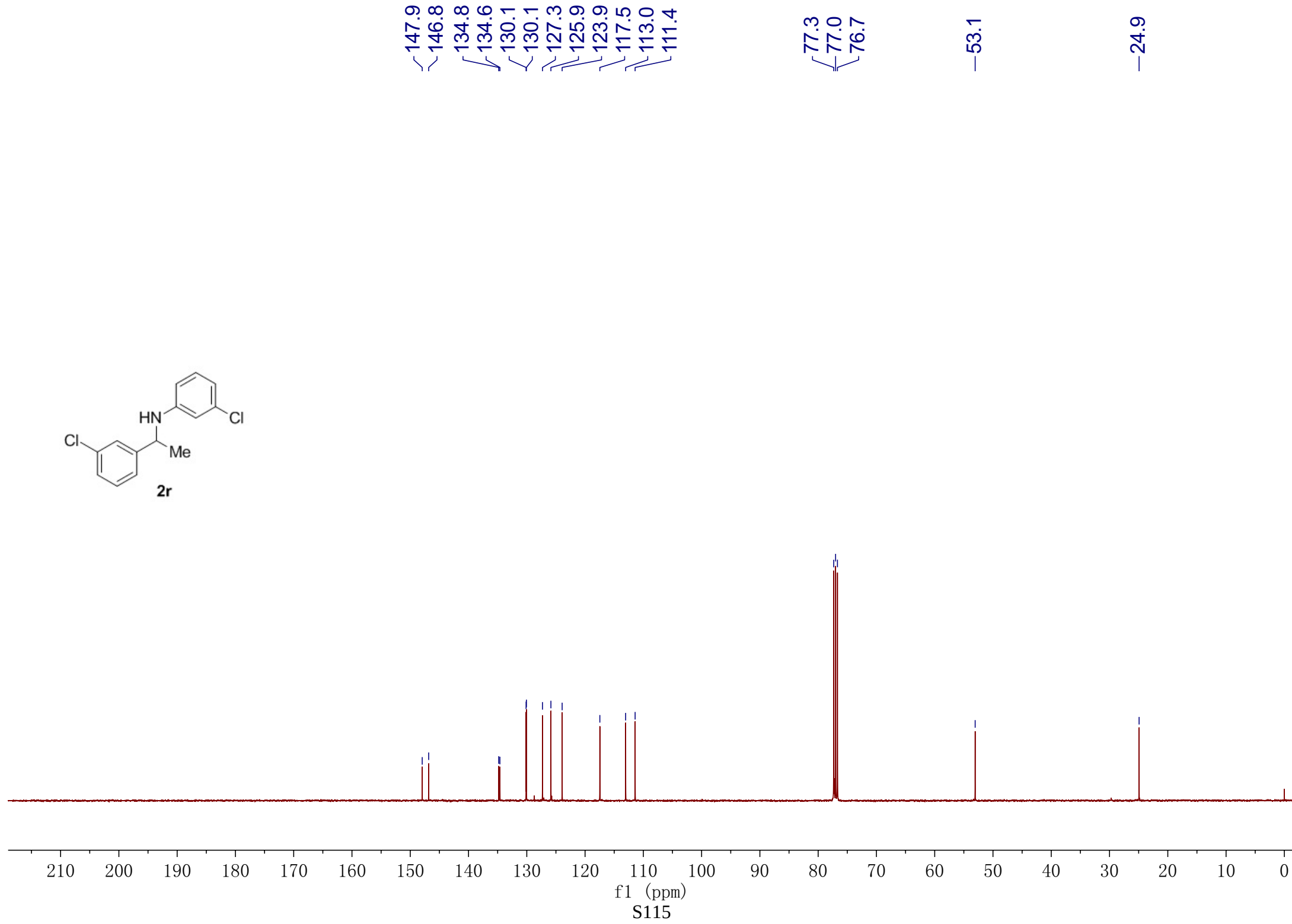
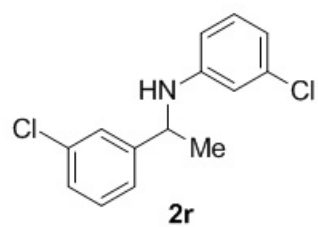


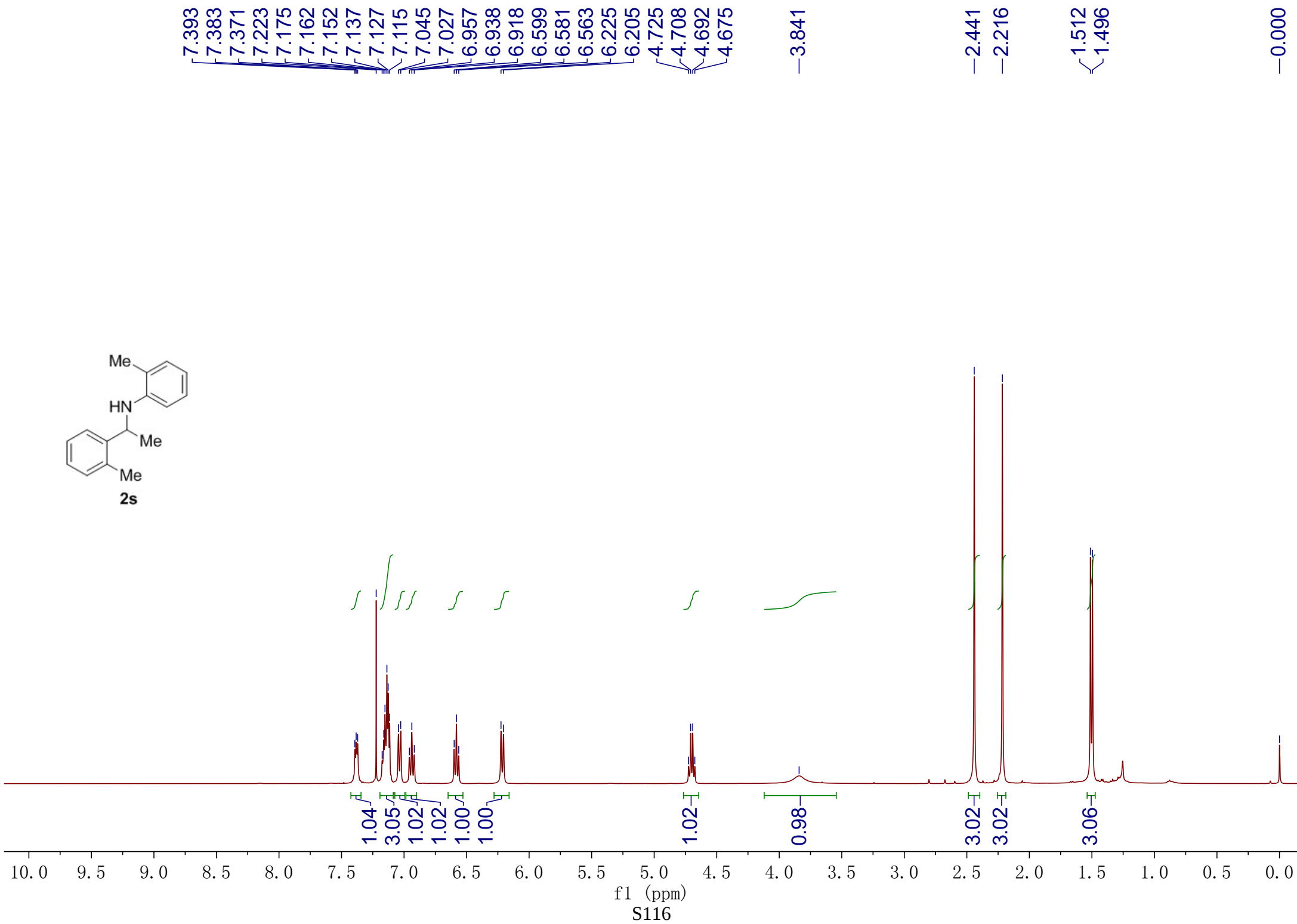


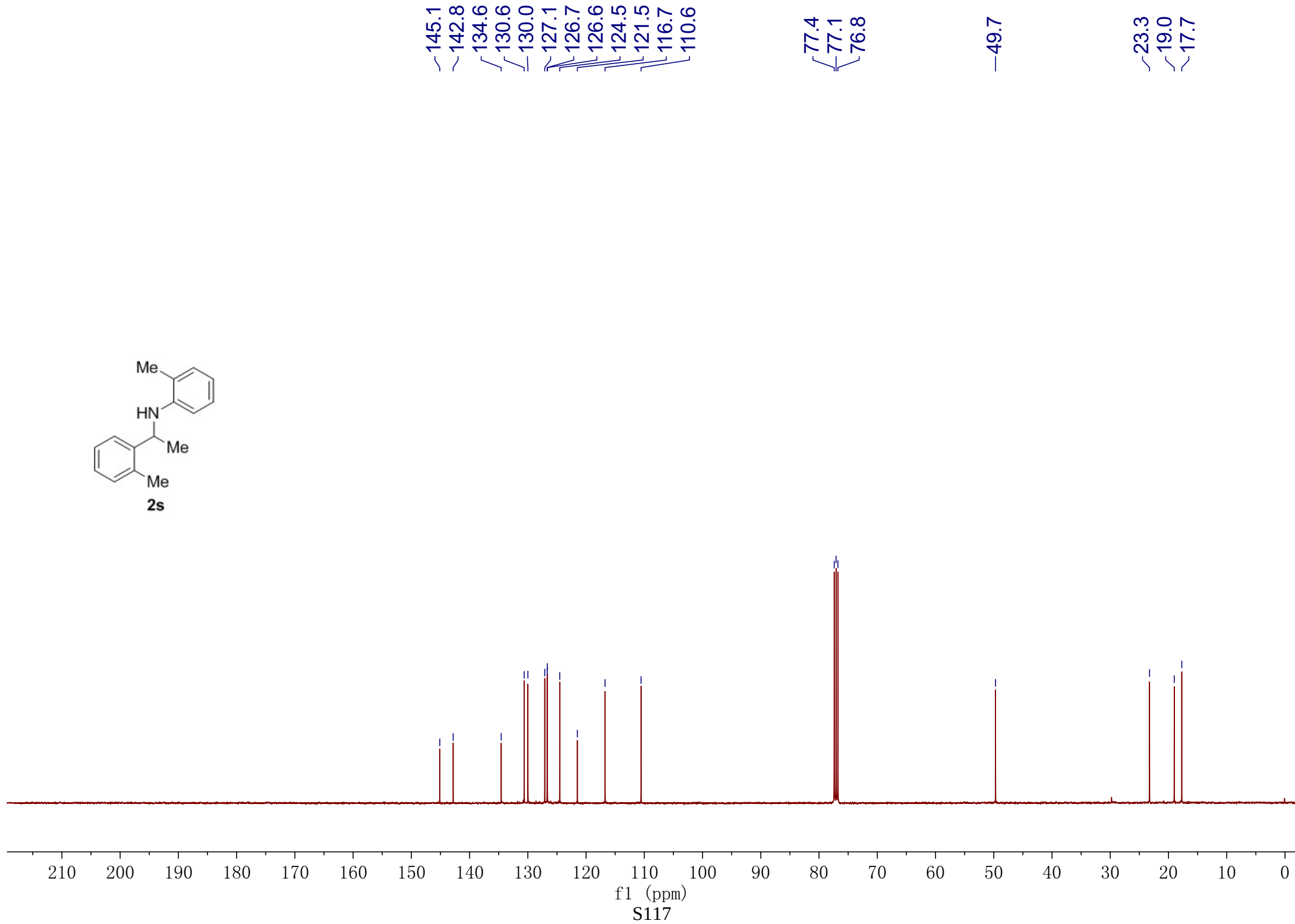
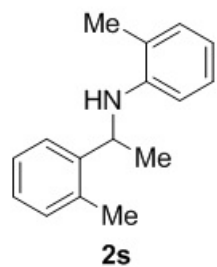


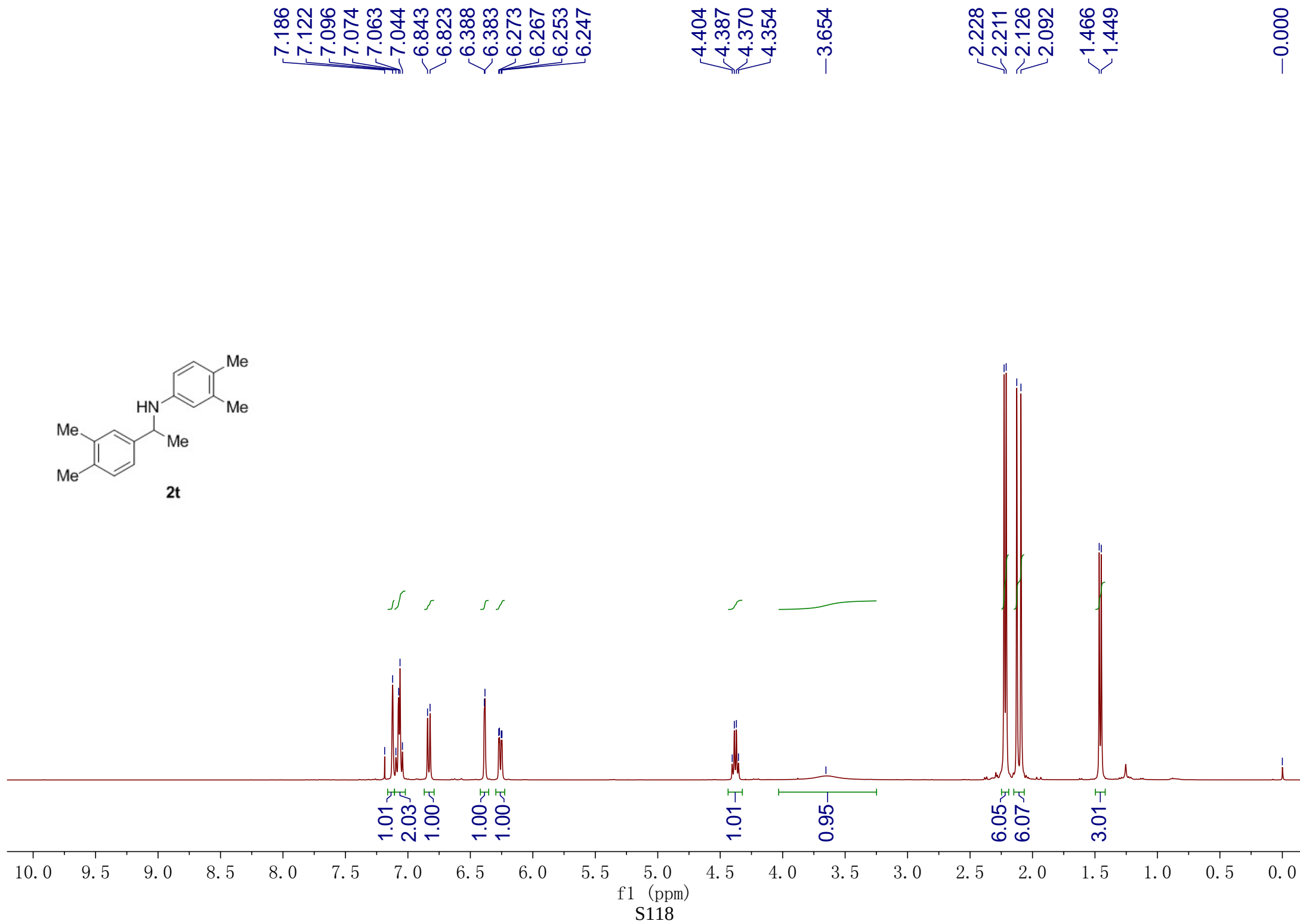
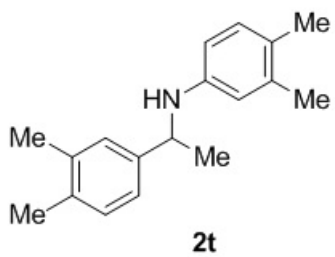


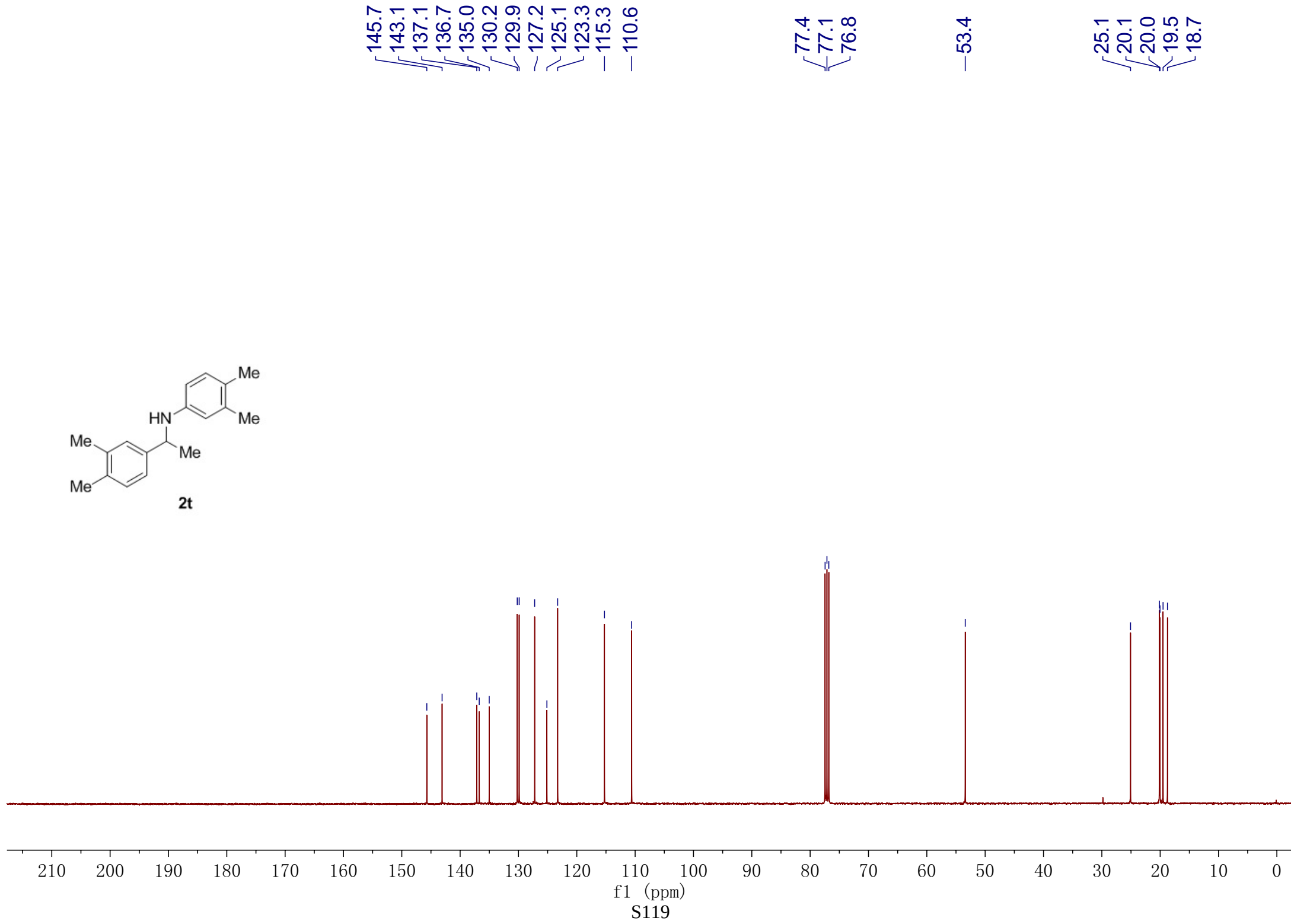
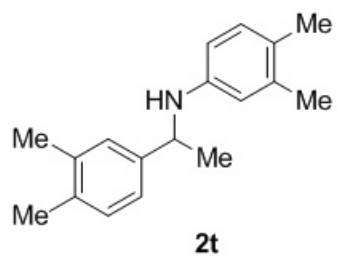


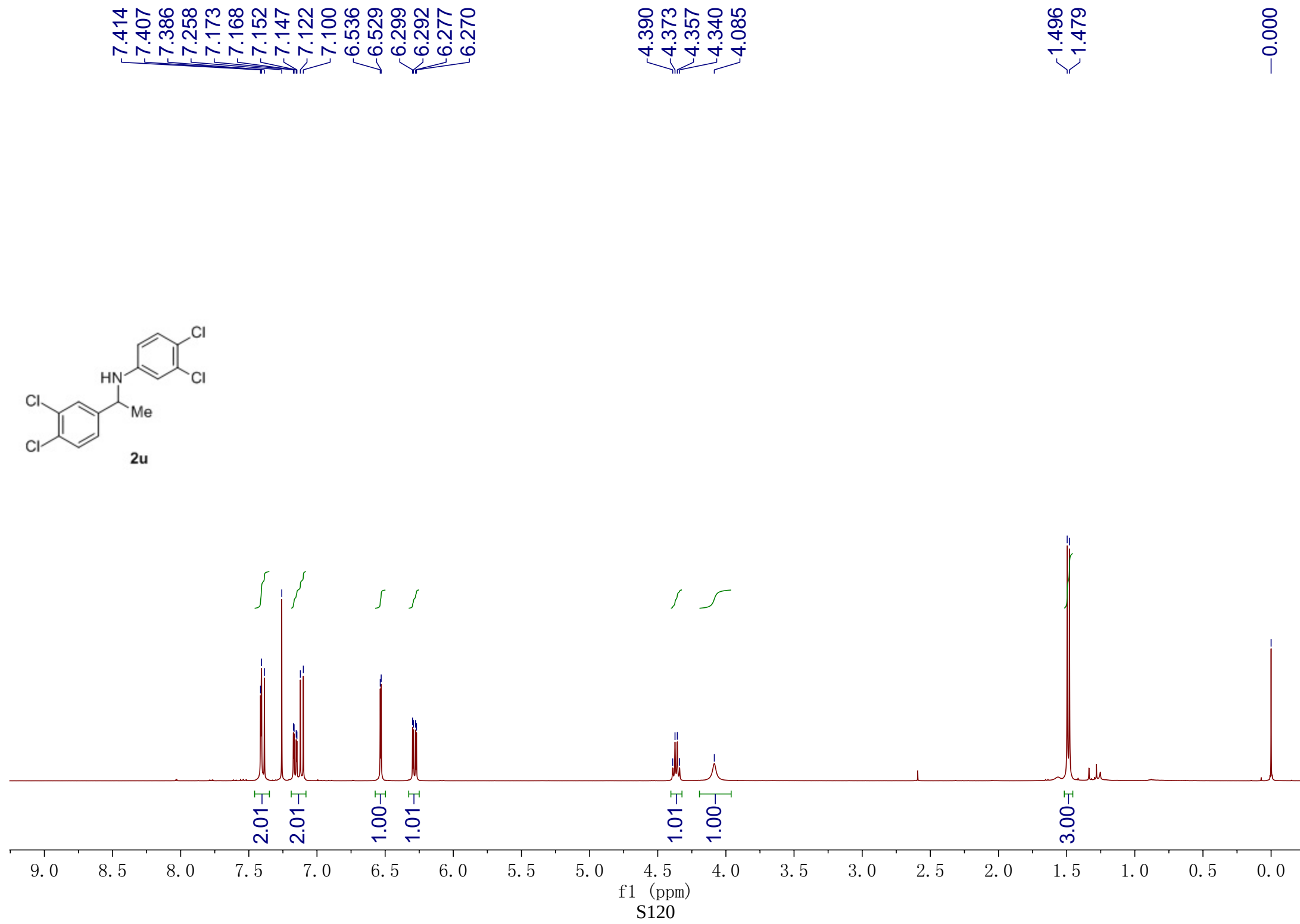
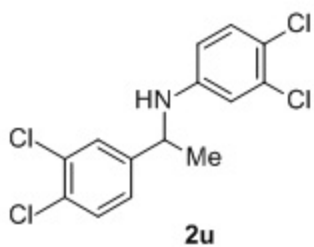


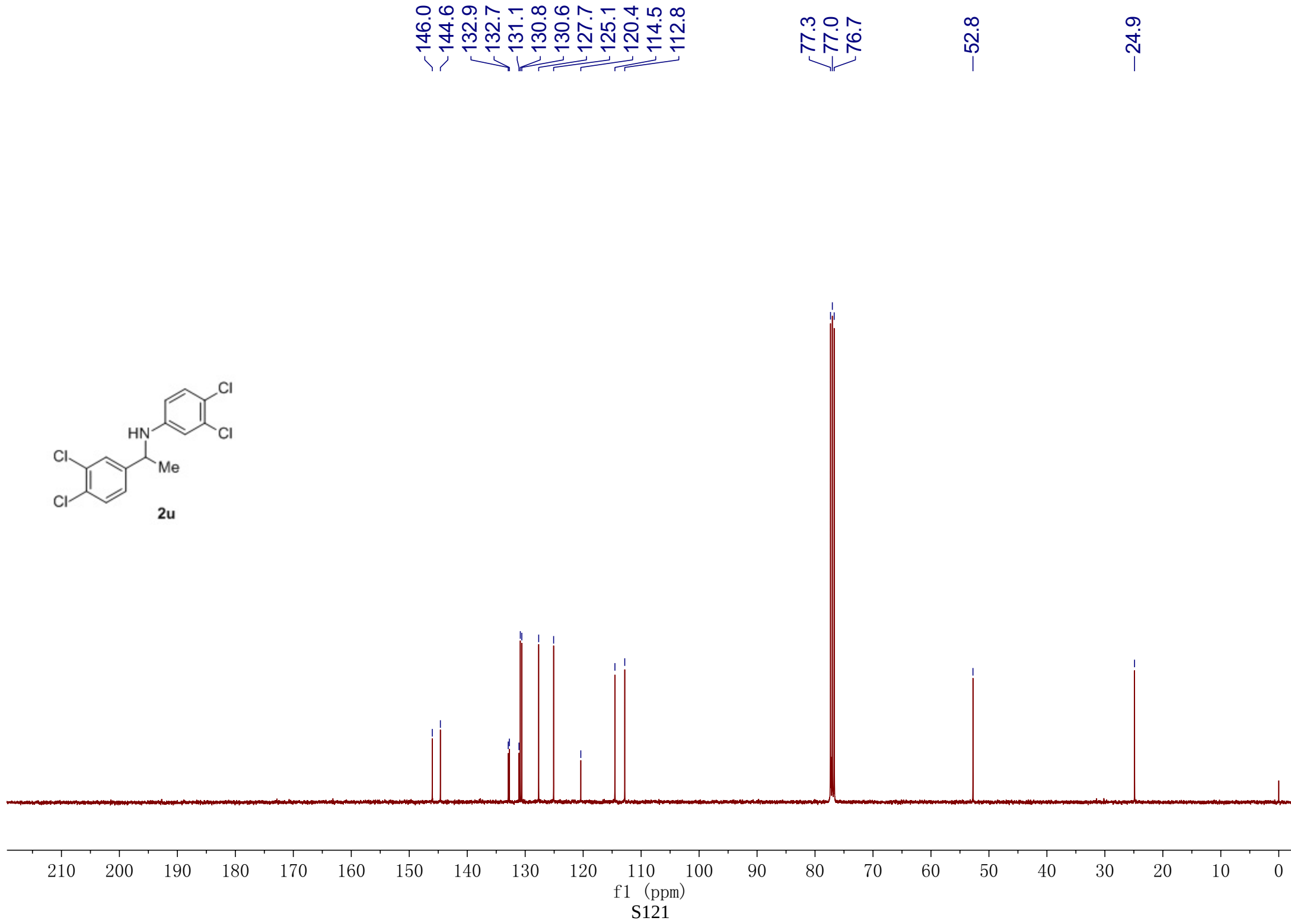
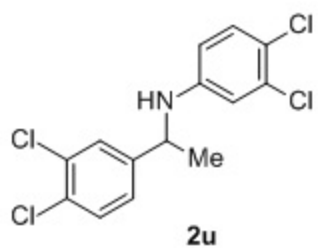


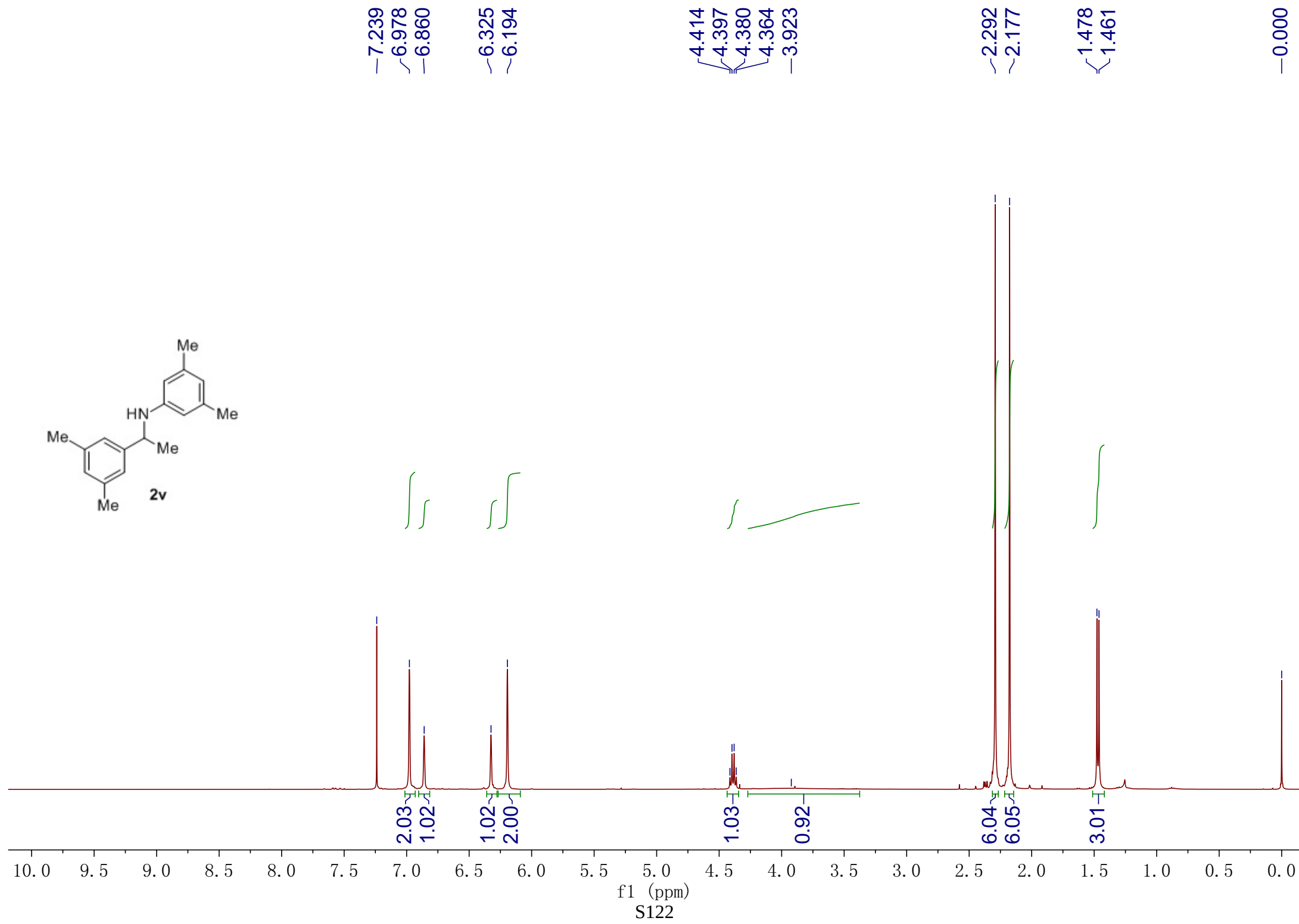
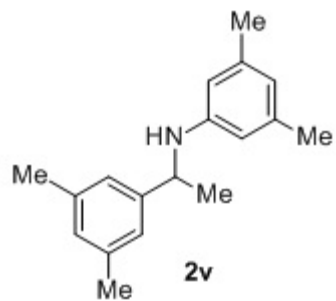


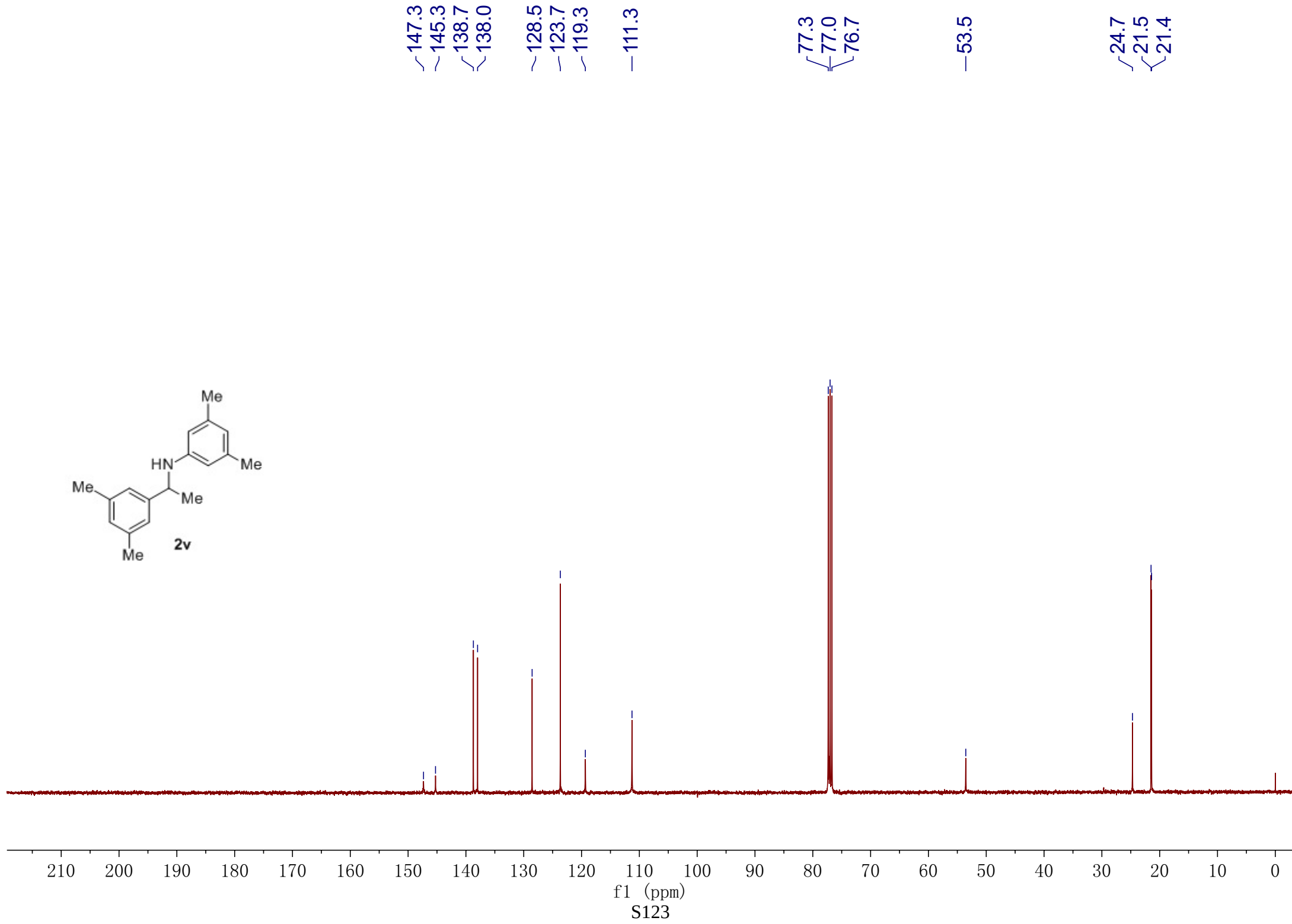
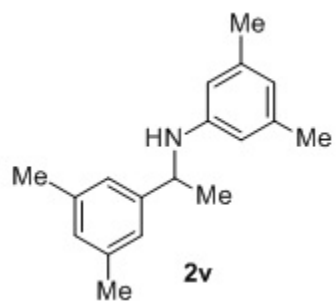


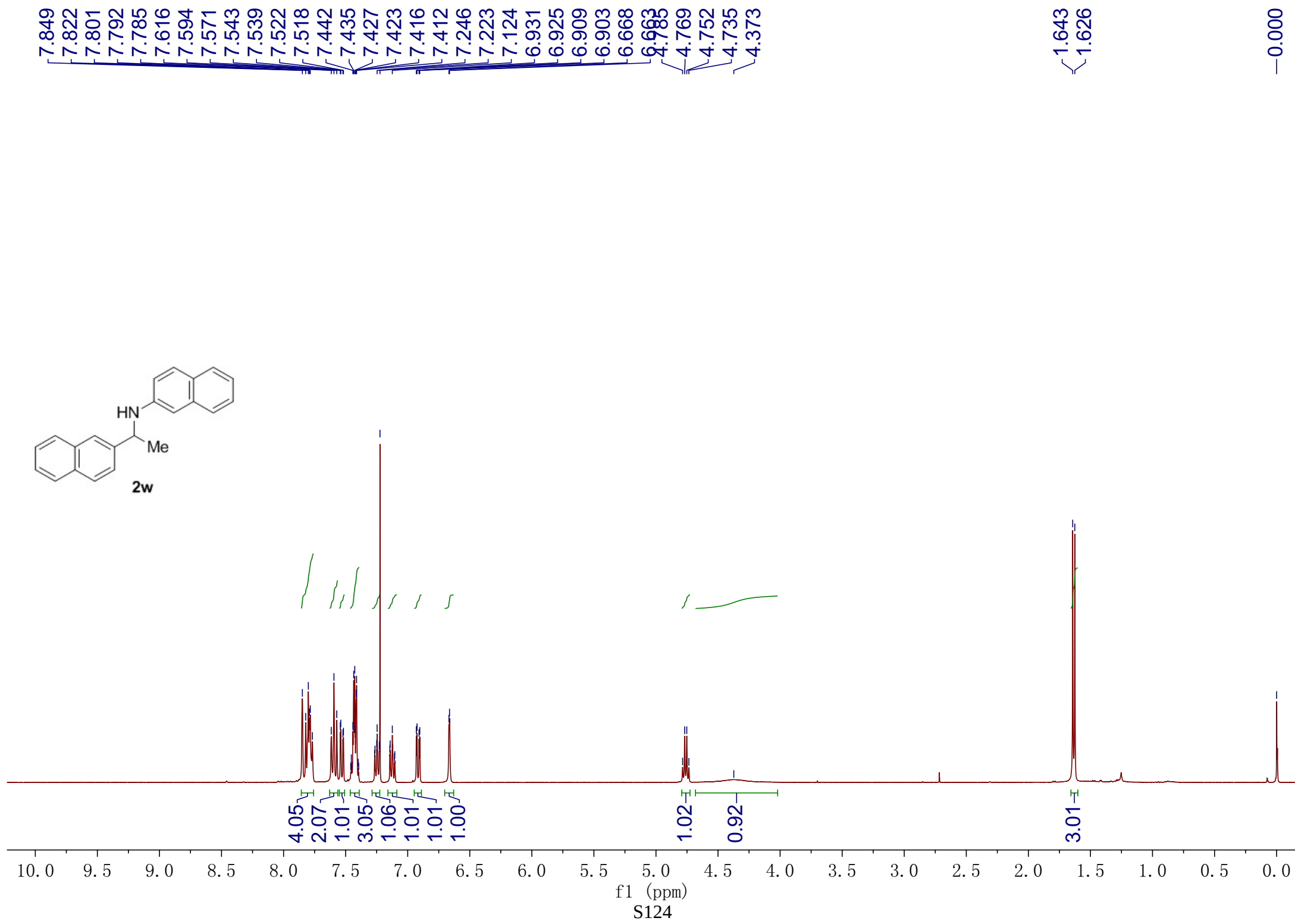
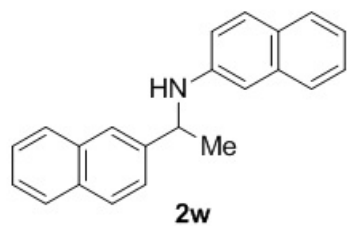


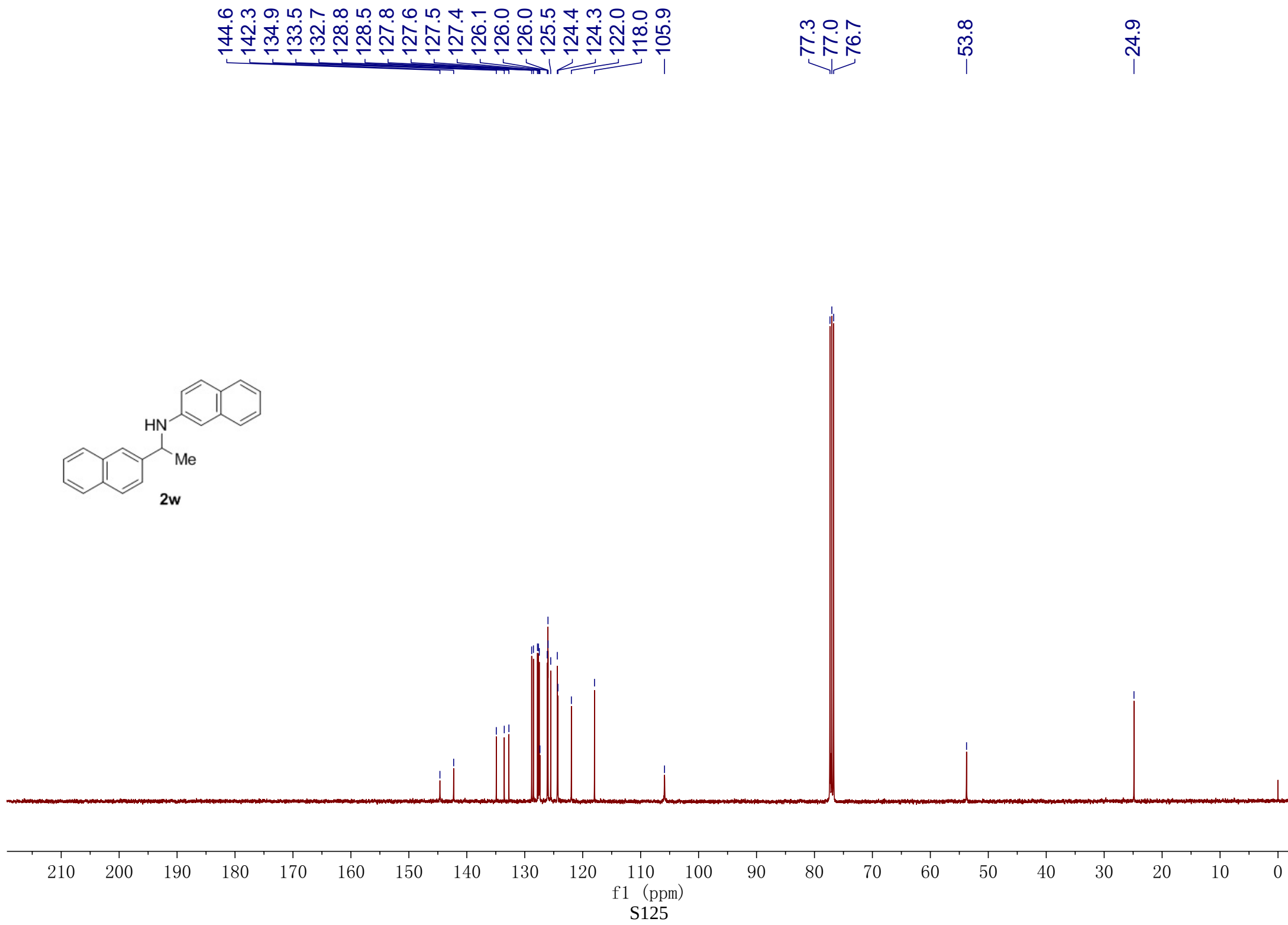
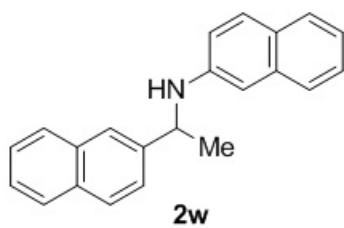


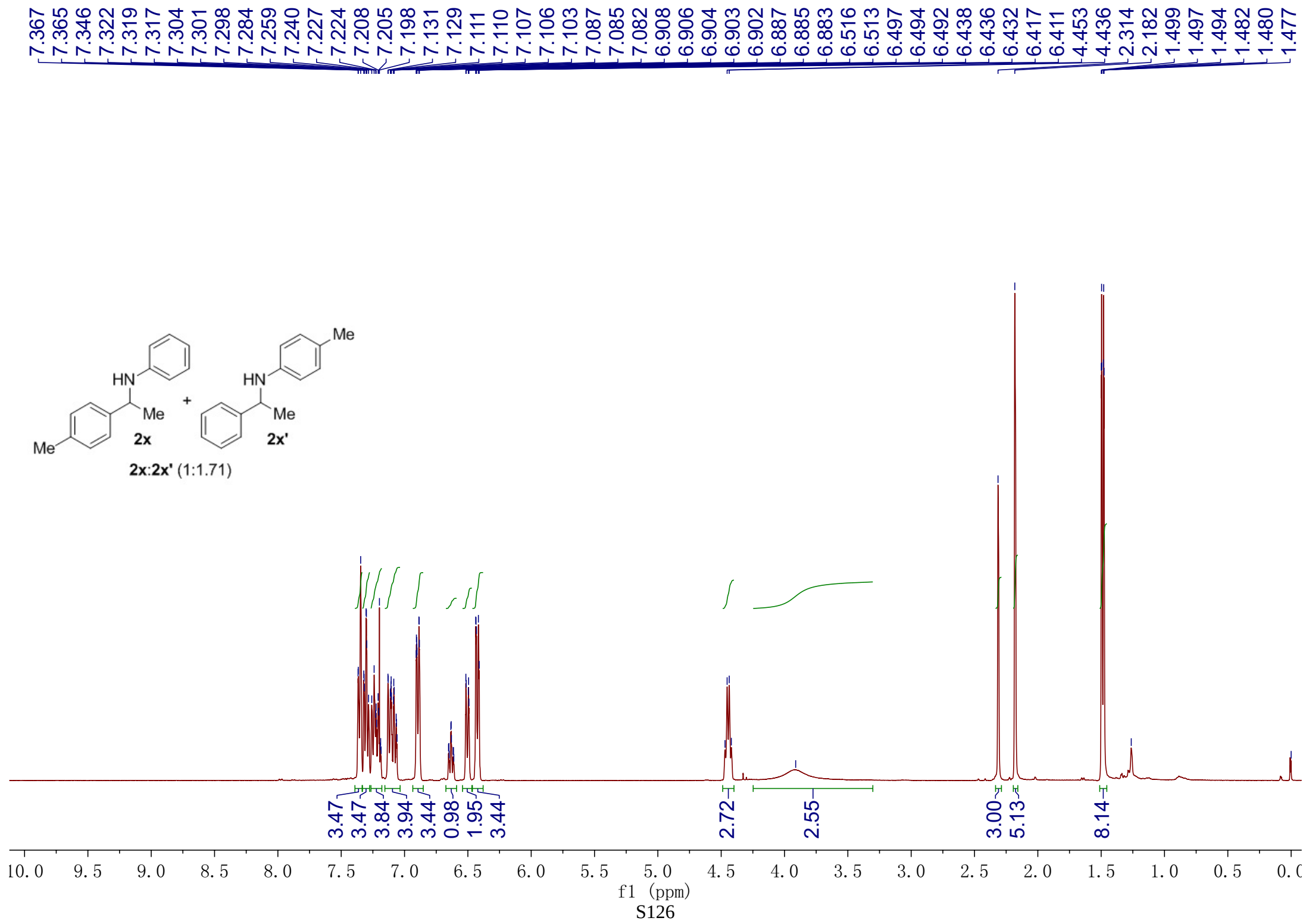


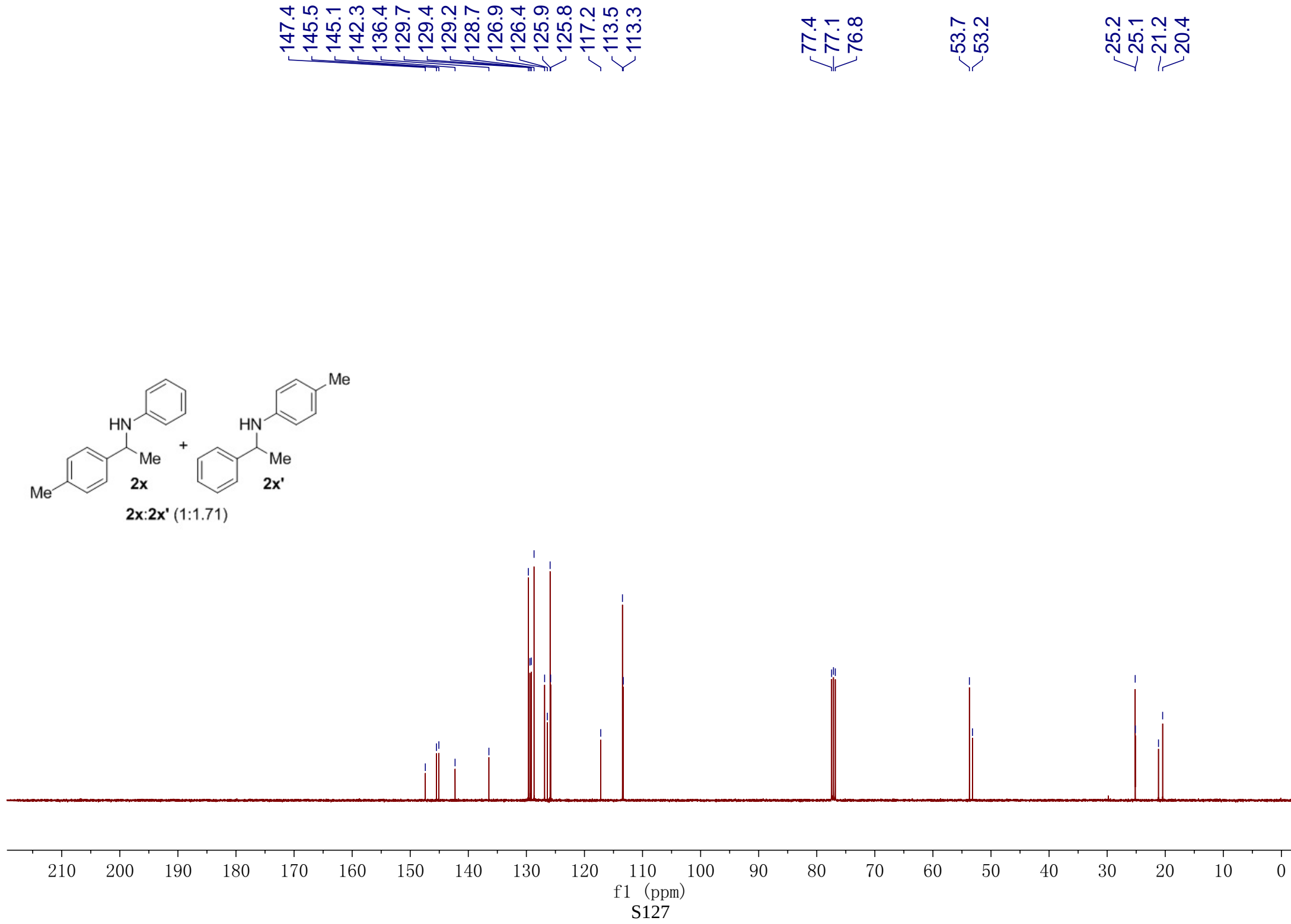
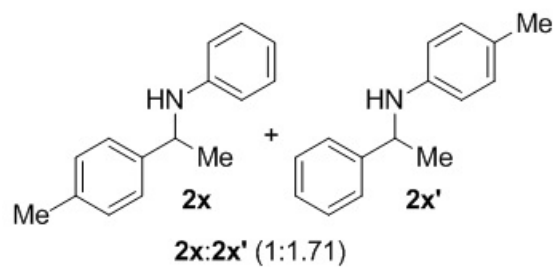


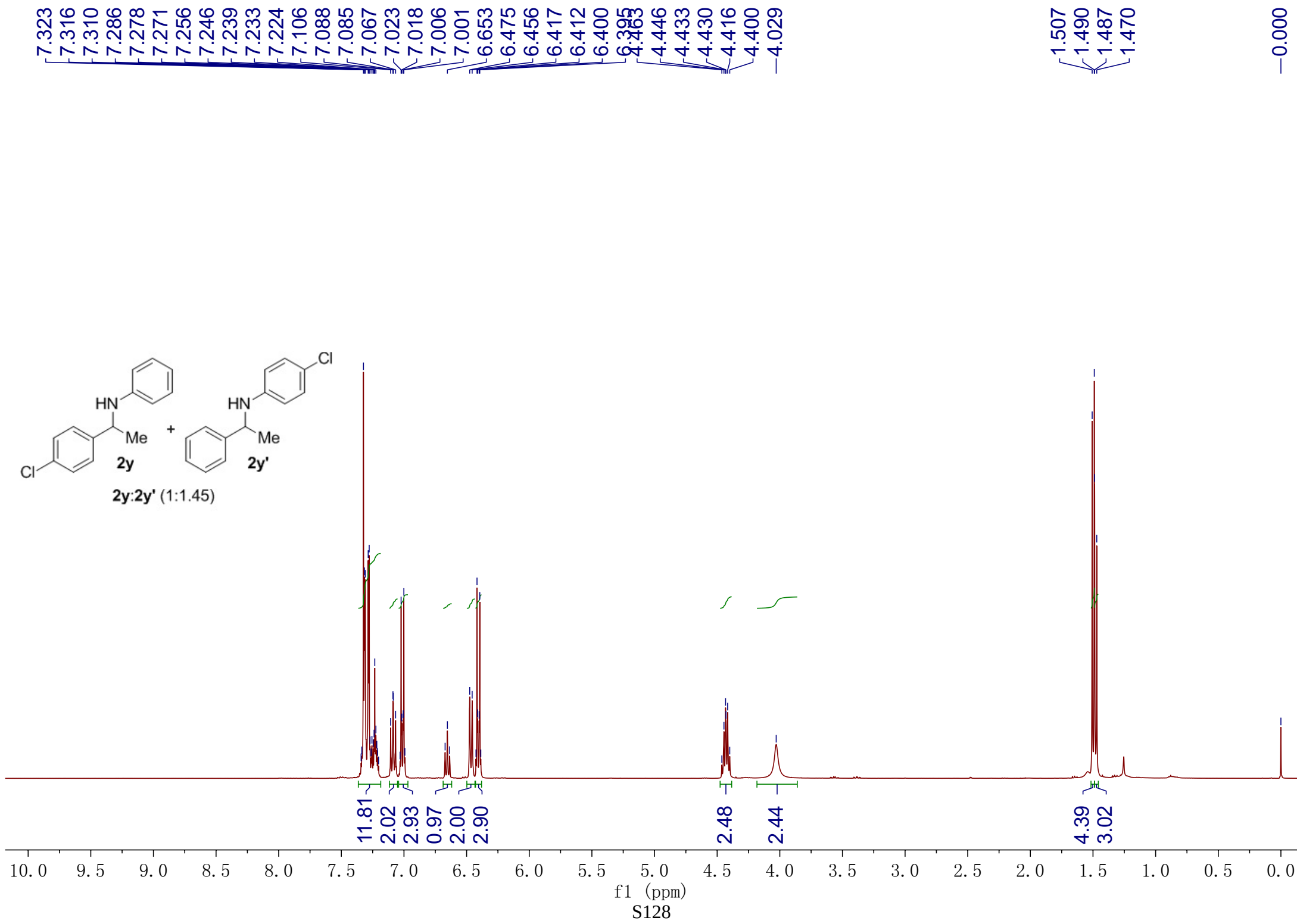


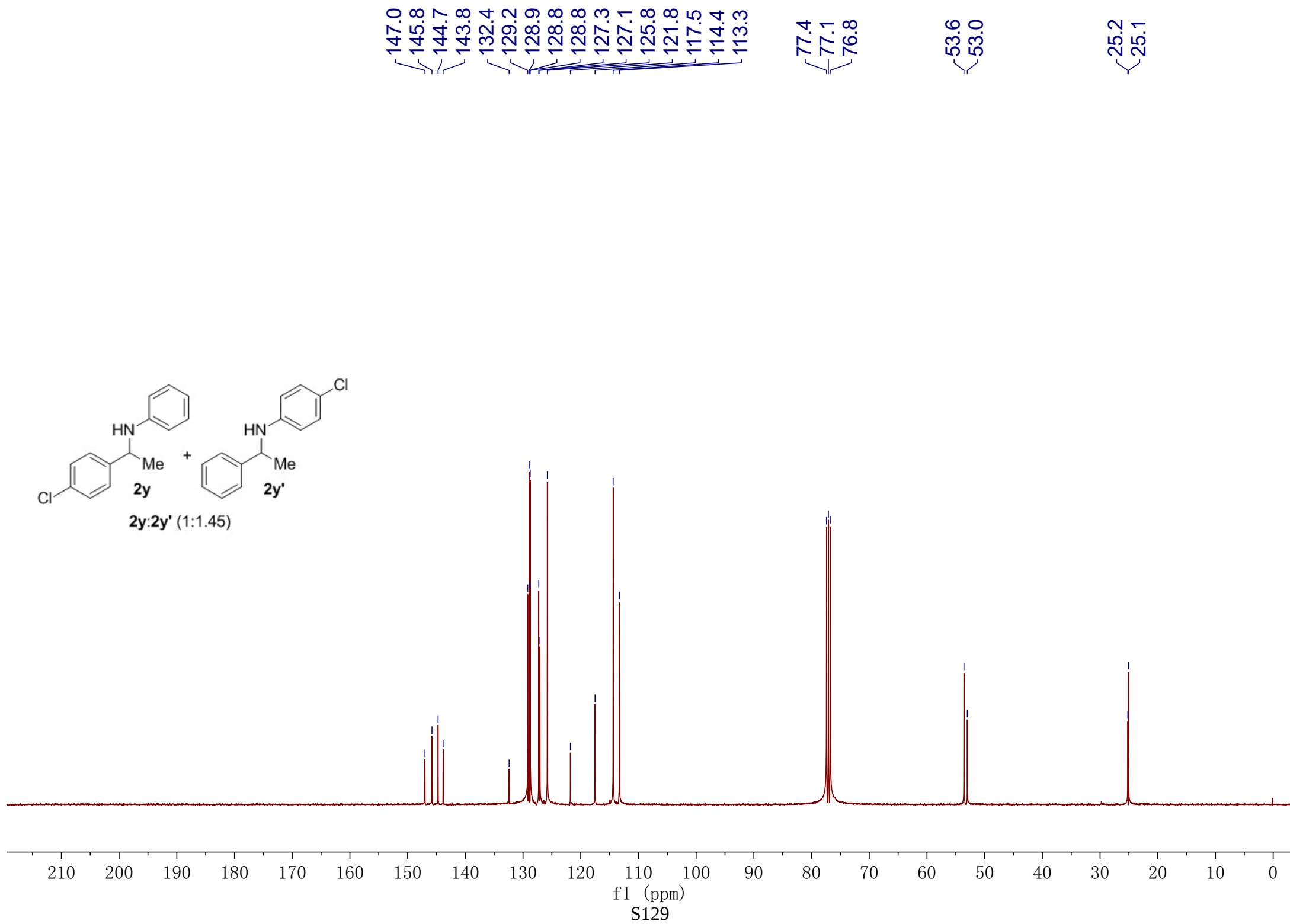
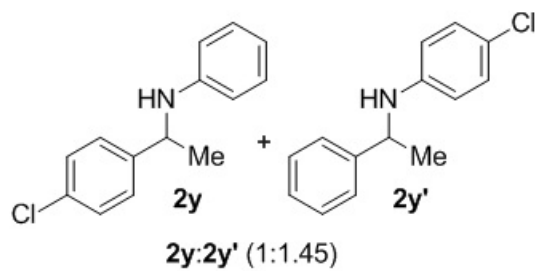


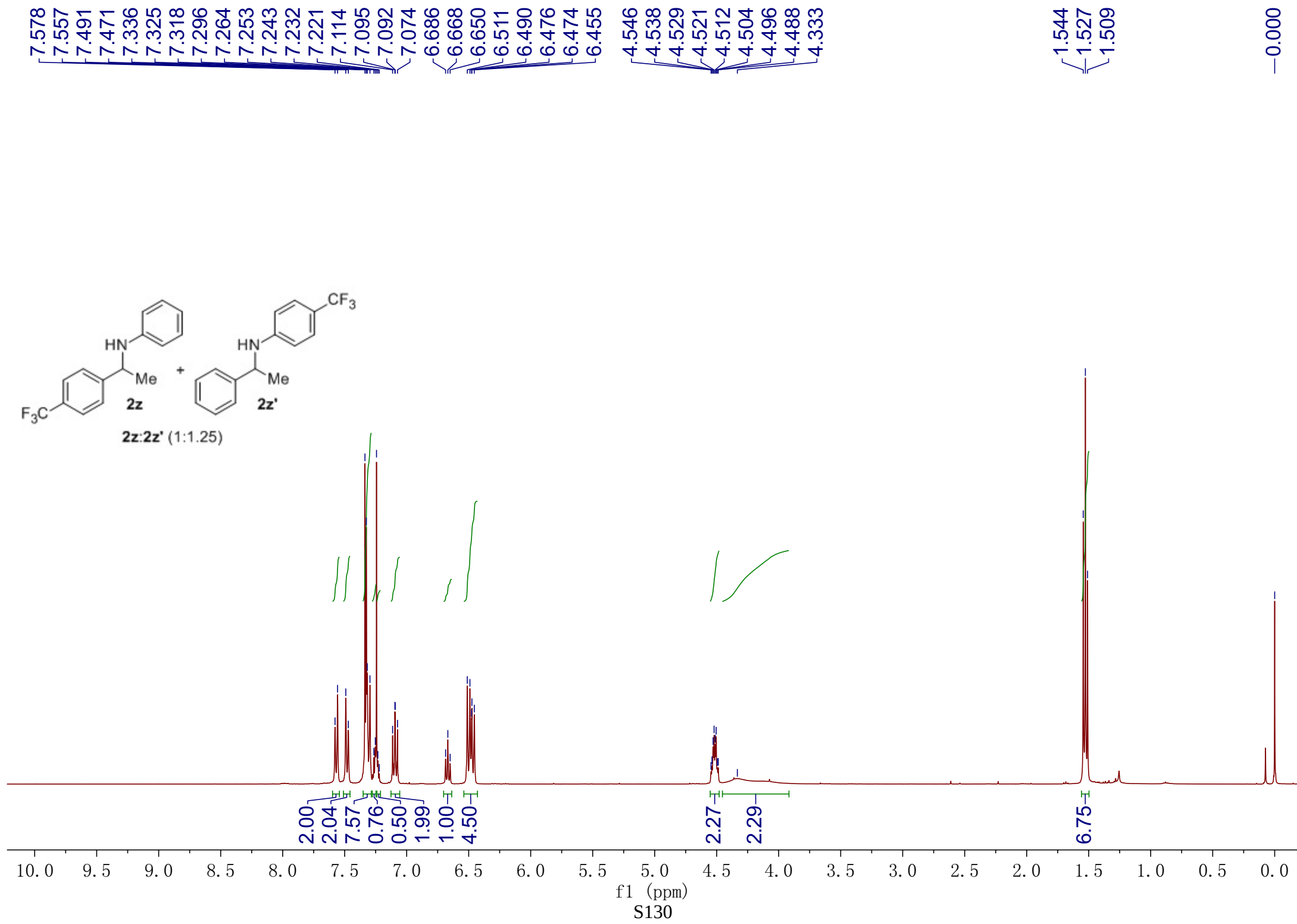


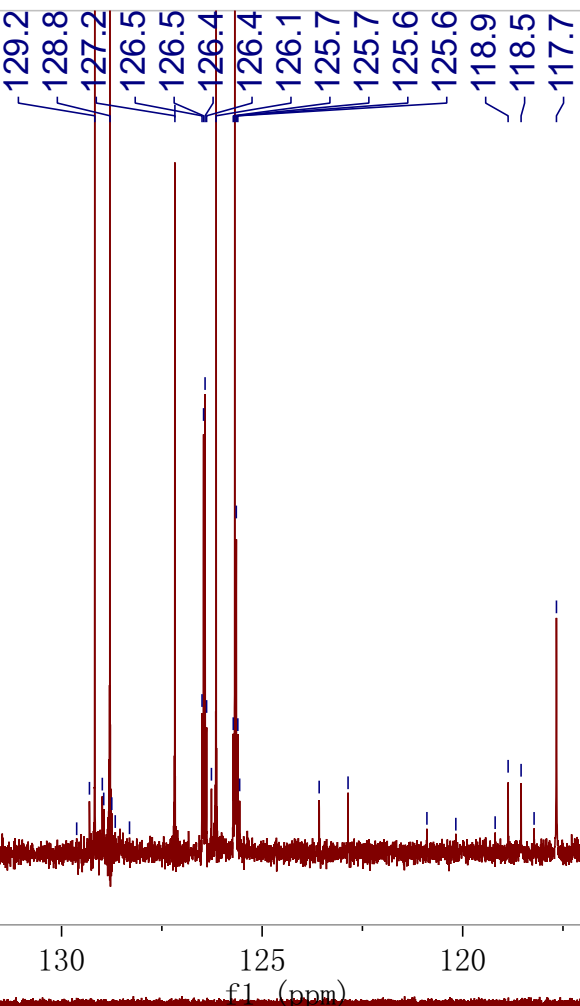
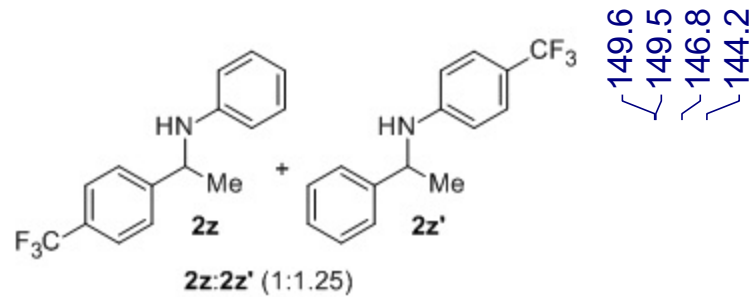










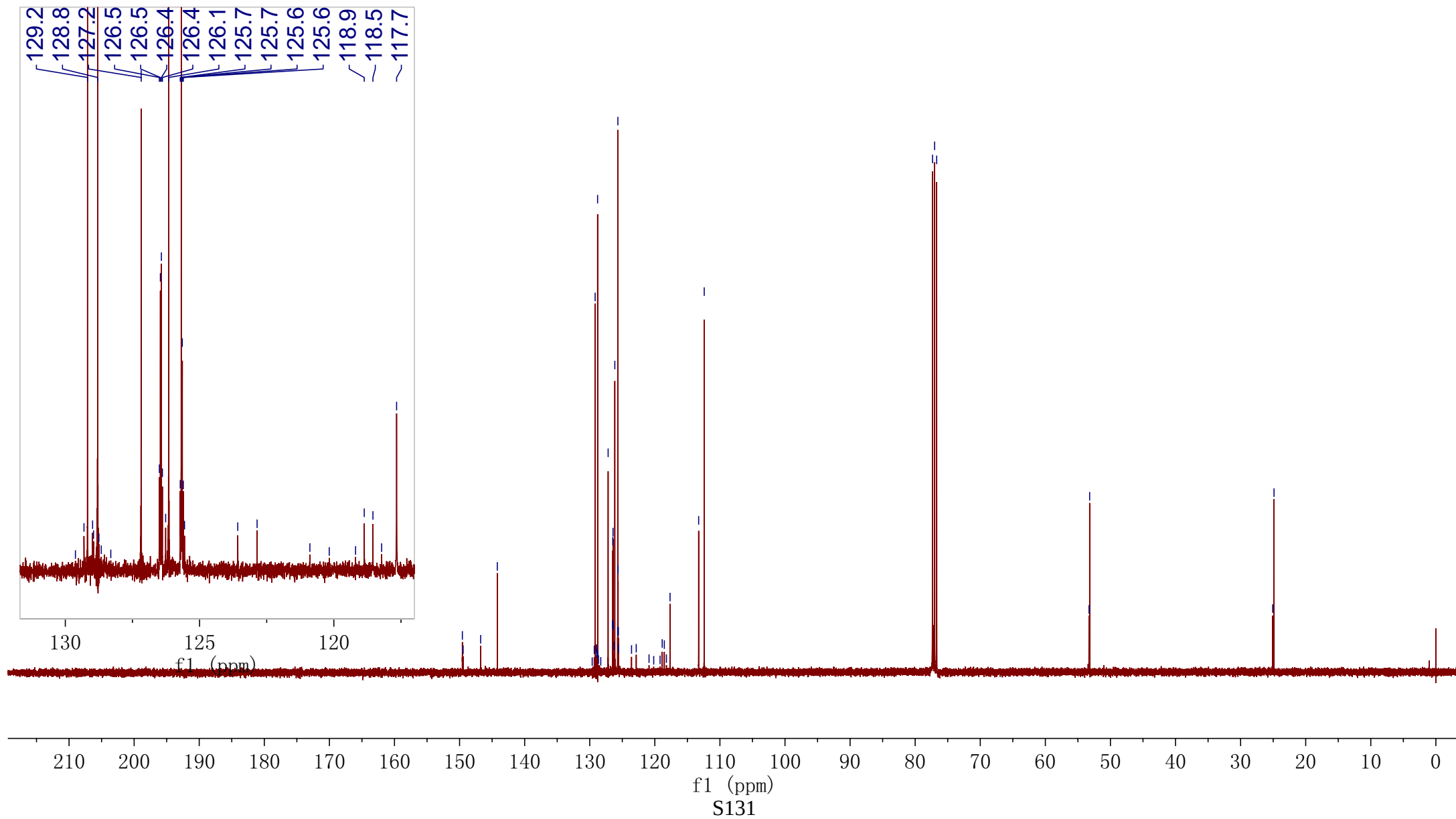


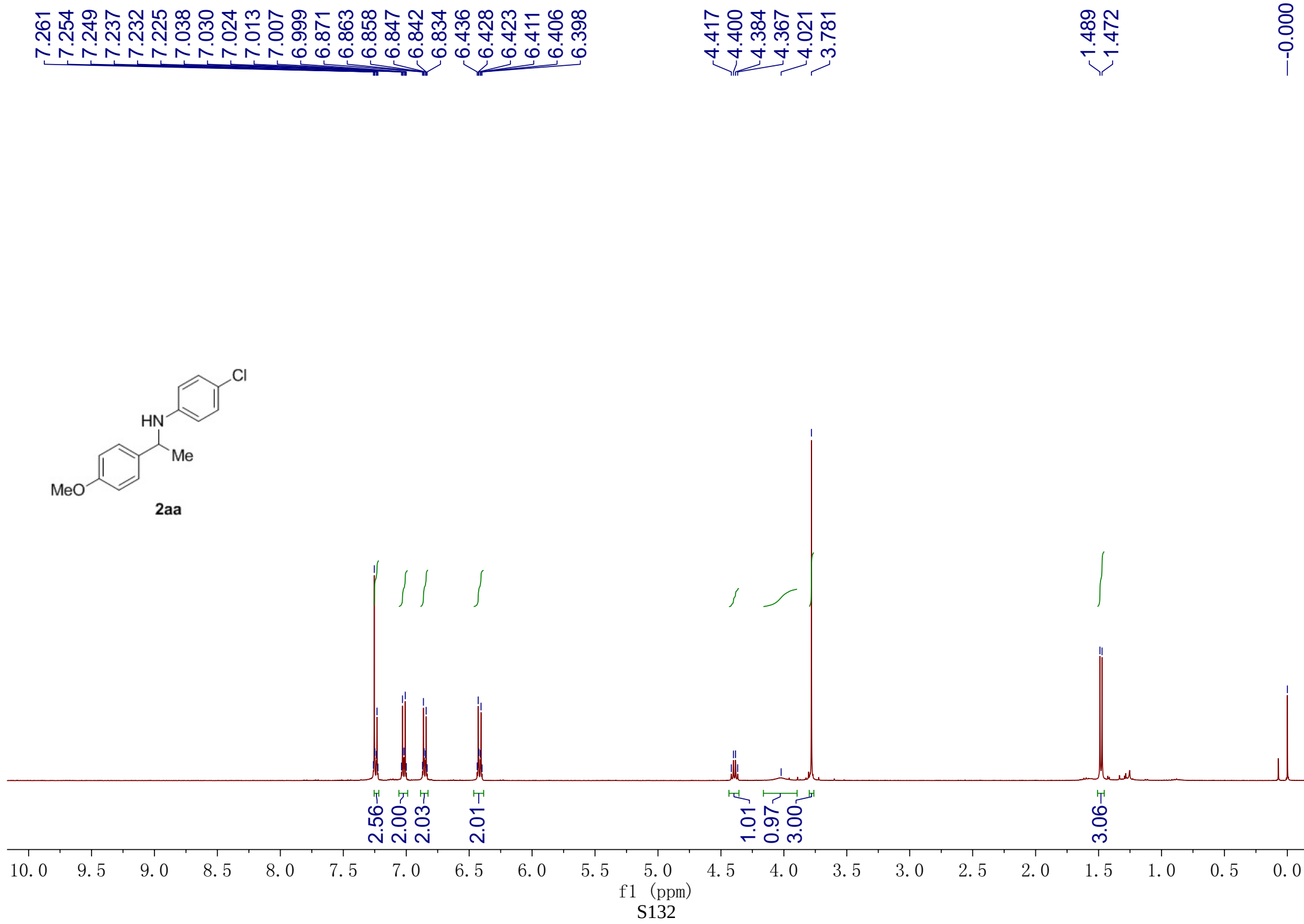
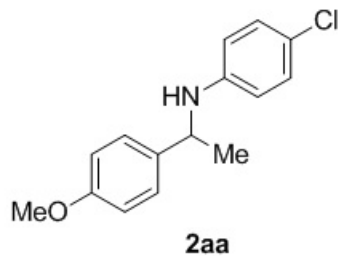
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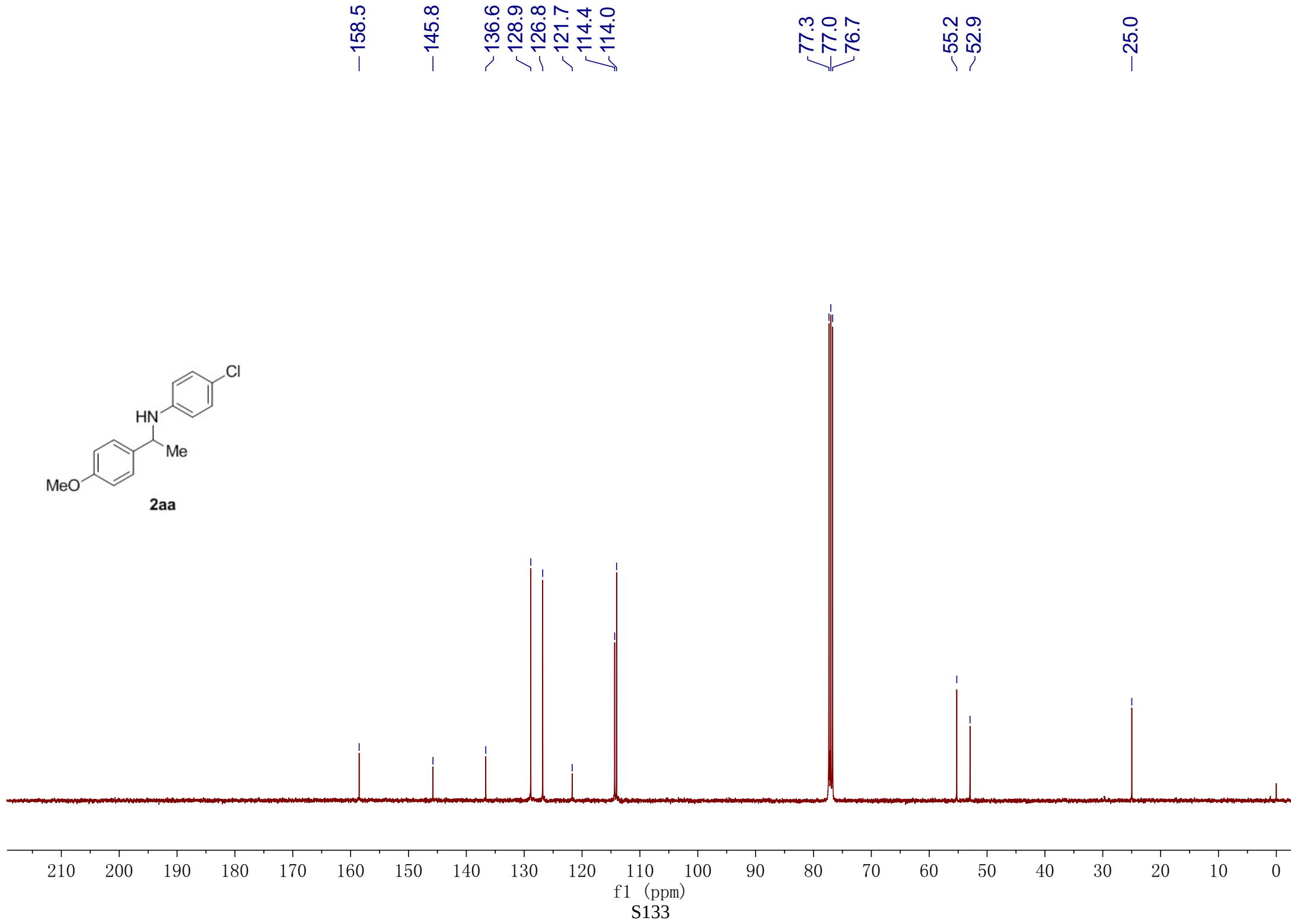
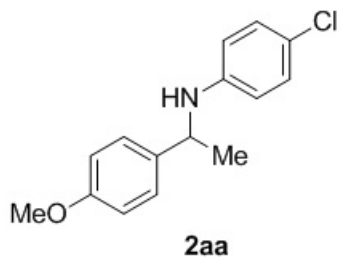
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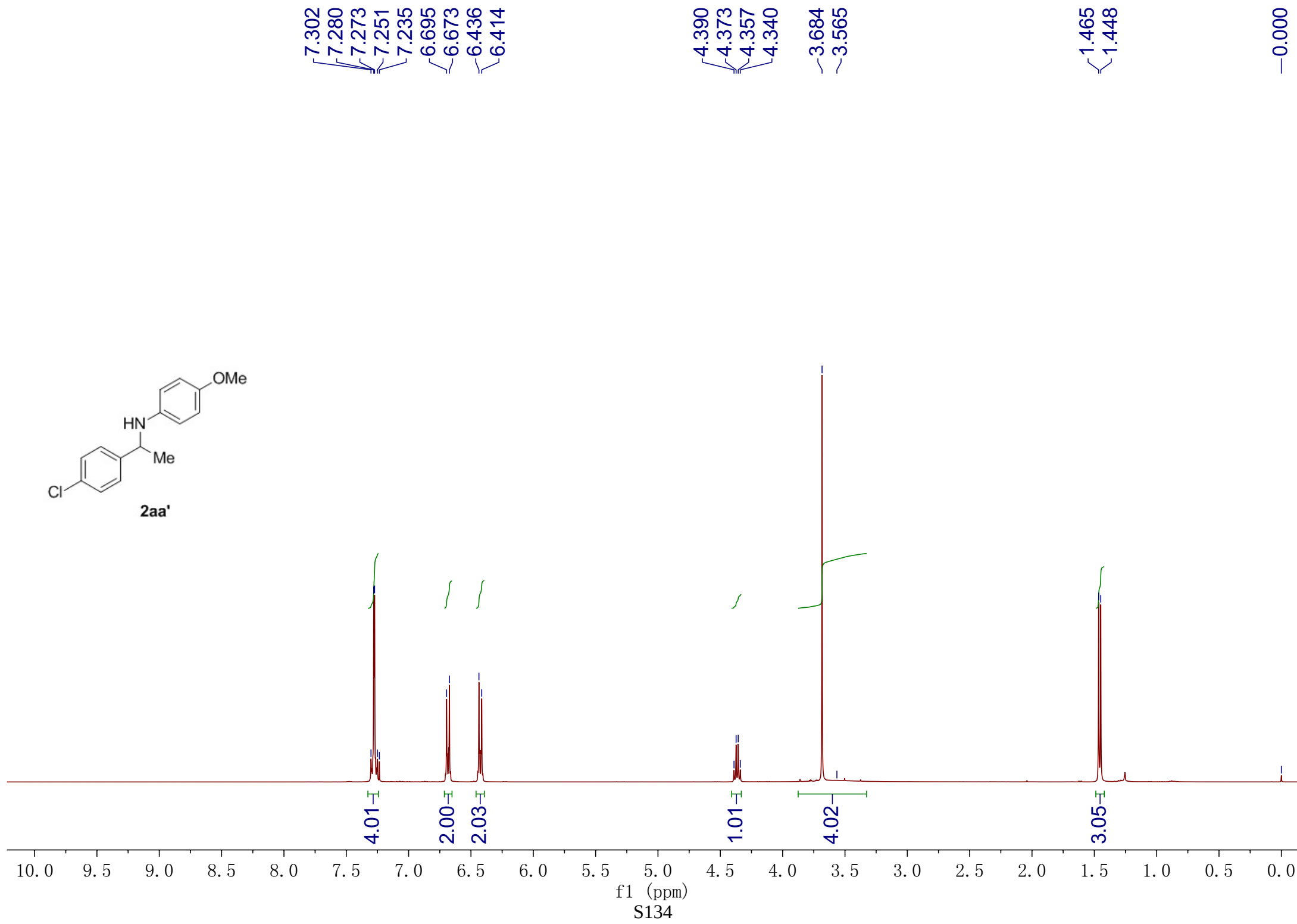
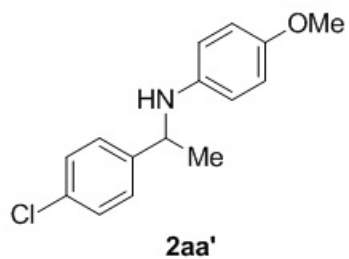
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 53.2

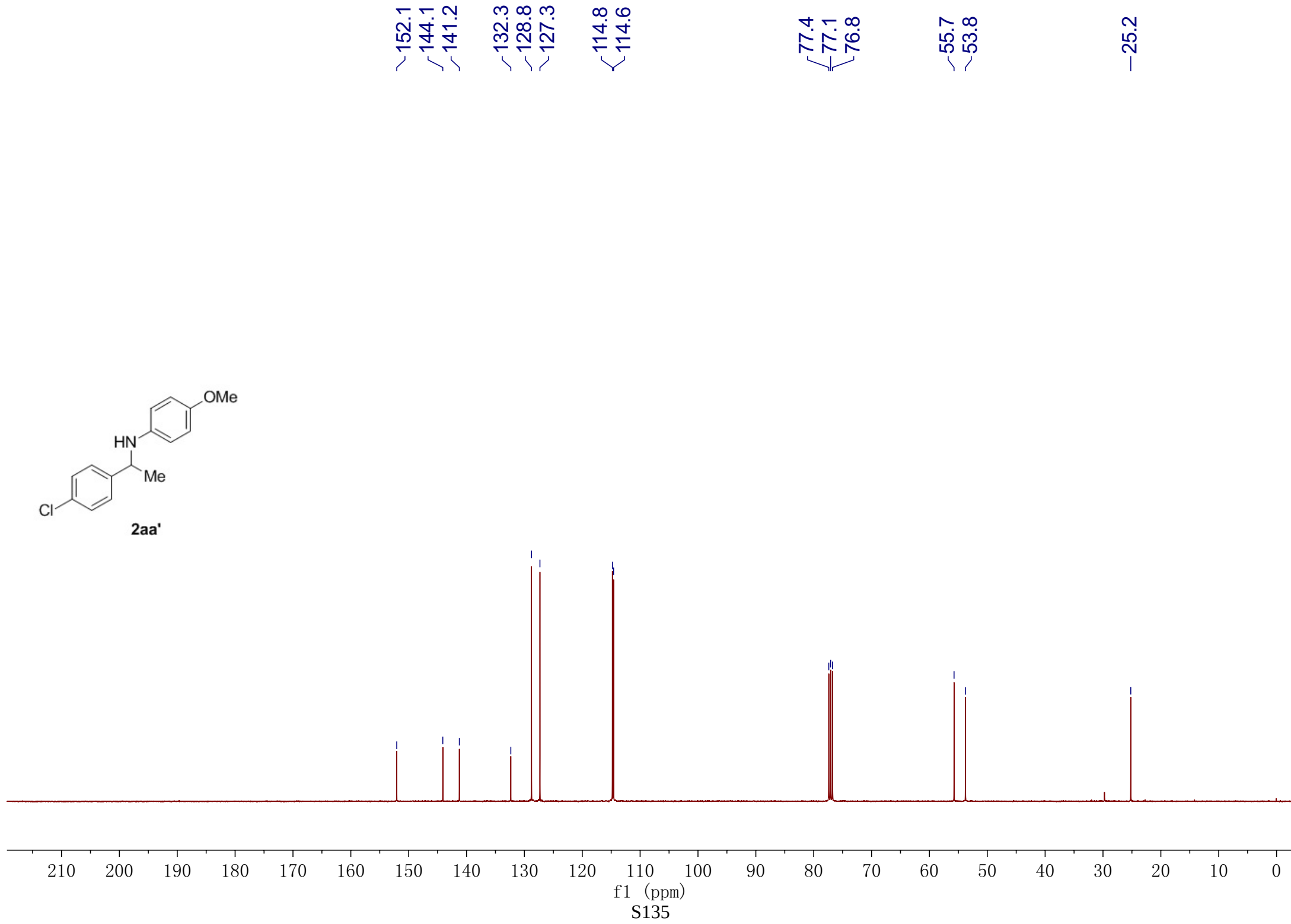
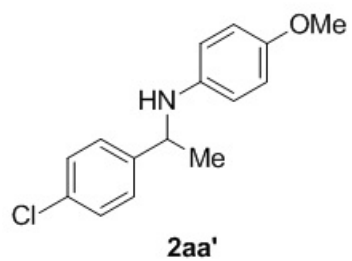
25.1
 24.9

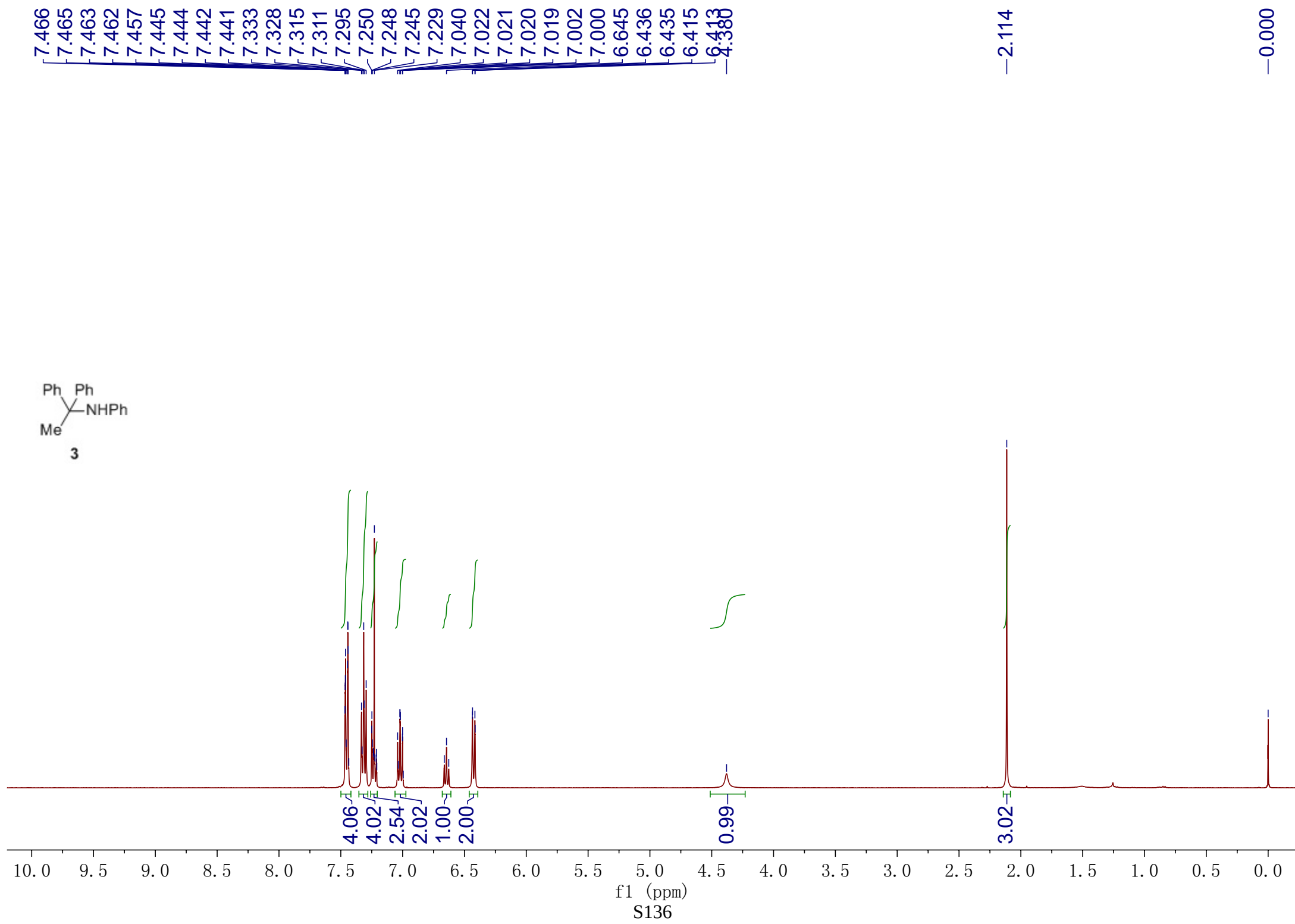
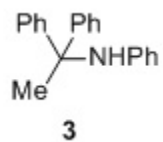


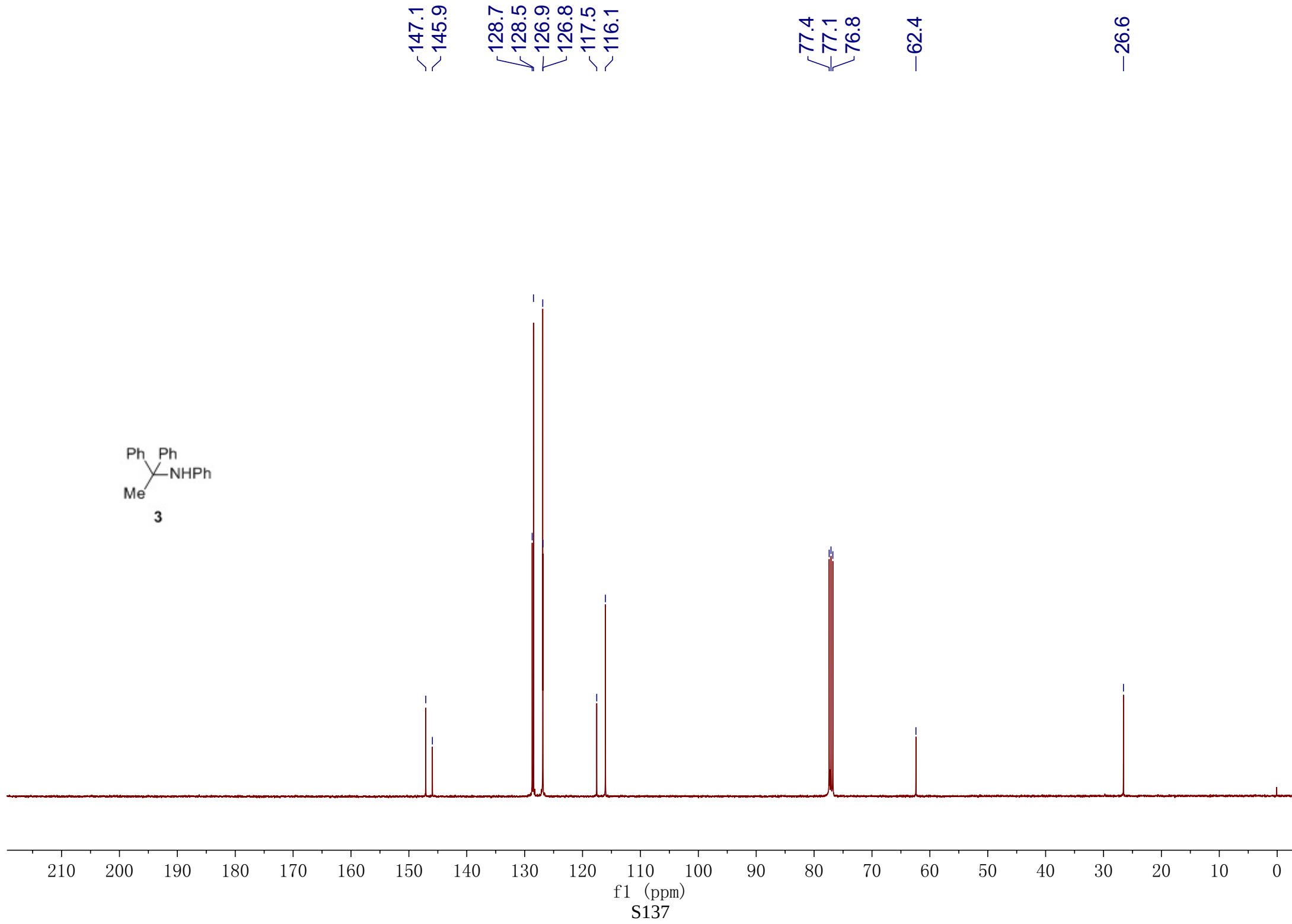
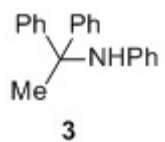


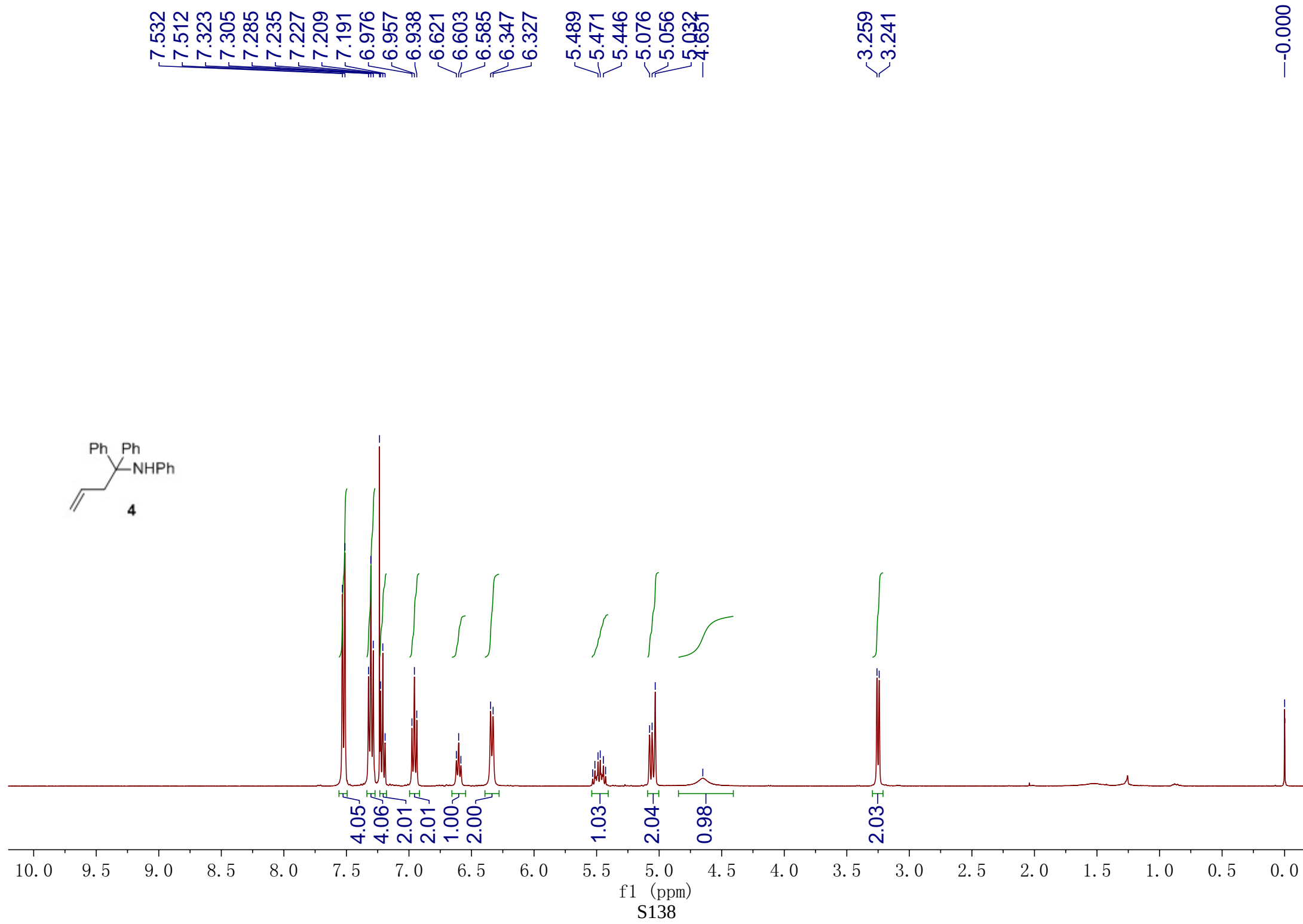


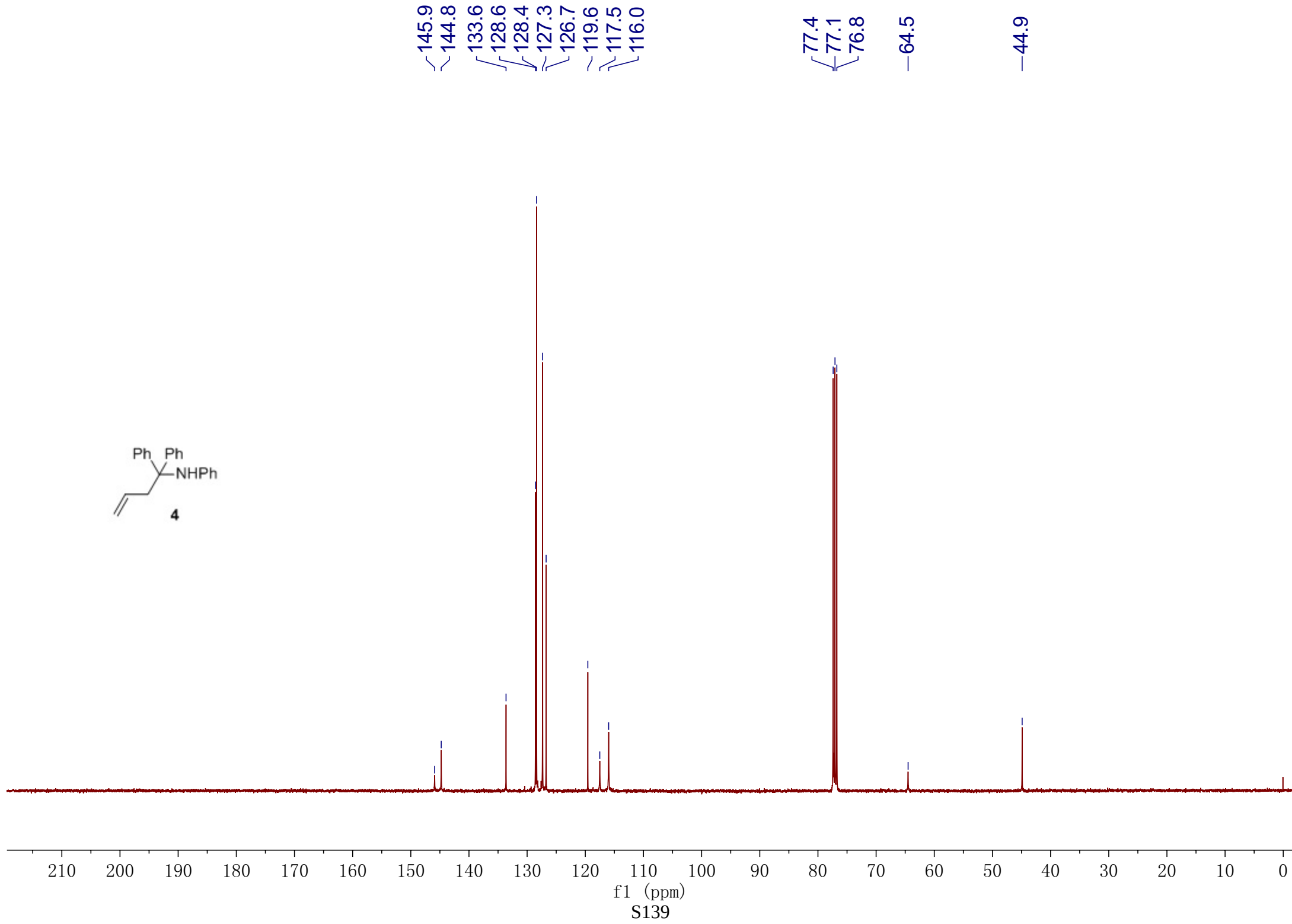
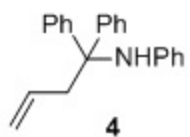


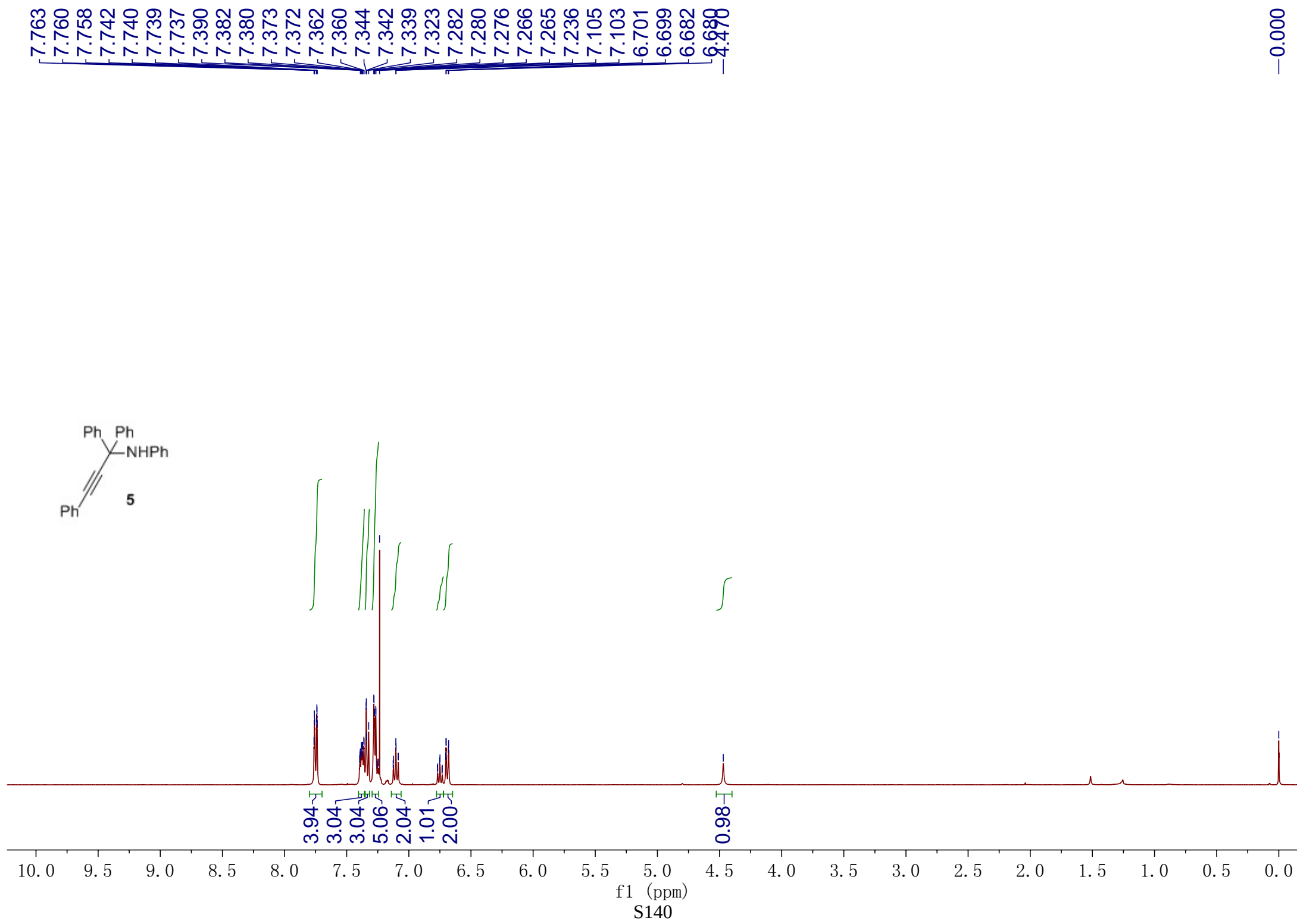
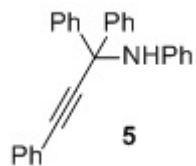


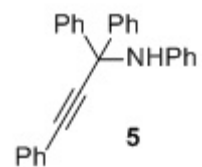












145.3
 144.3
 131.7
 128.6
 128.4
 128.3
 128.3
 127.6
 126.9
 123.0
 118.6
 116.6
 —90.9
 —87.0
 77.4
 77.1
 76.7
 —63.7

