

Catalyst-free Photochemical Reactions of Alkyl Dihydropyridines via Modulation of Chromophores and Light Wavelength

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Contents

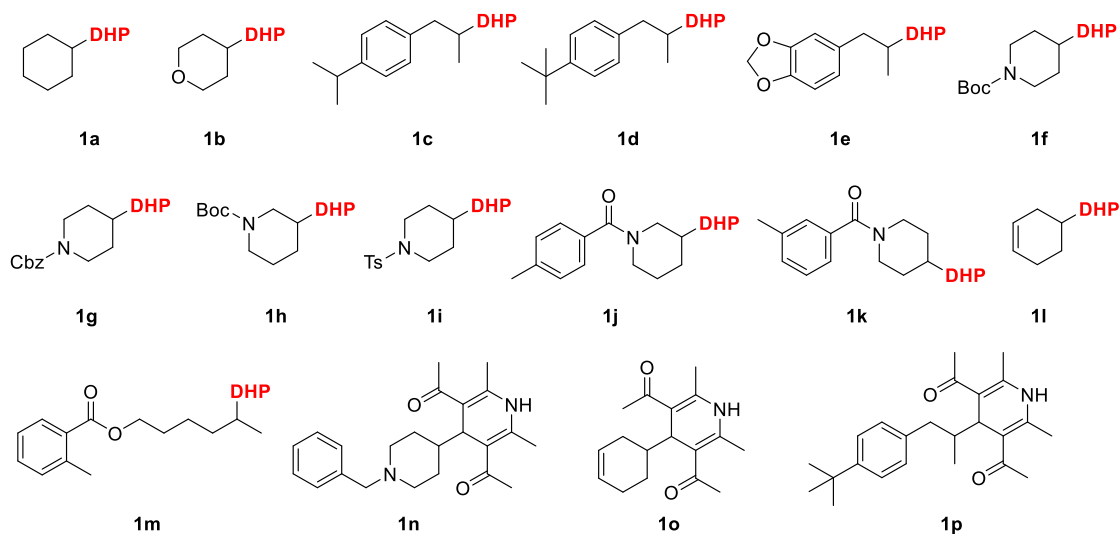
1. General.....	2
2. Synthesis of DHP starting material DHP 1	2
2.1 General procedure for the synthesis of DHP (1a-1l).....	2
2.2 General procedure for the synthesis of DHPs (1i-1k).....	3
3. The general procedure of trifluoromethylthiolation	4
4. General procedure for the synthesis of thioethers 5.....	5
5. Characteristic data.....	6
6. Copies of NMR Spectra	14
7. References.....	111

1. General

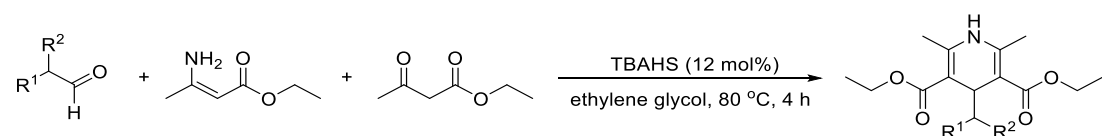
All commercial reagents were used without further purification. Flash column chromatography was performed with silica gel (100-200 mesh). All products were characterized by NMR. ^1H NMR (400 MHz, 600 MHz), ^{13}C NMR (100 MHz, 150 MHz) and ^{19}F NMR (376 MHz, 564 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in ppm from Chloroform- d ($\delta = 7.27$ ppm) or DMSO- d_6 ($\delta = 2.50$ ppm) for ^1H NMR and relative to Chloroform- d ($\delta = 77.2$ ppm) or DMSO- d_6 ($\delta = 39.5$ ppm) for ^{13}C NMR. ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (J), are reported in Hertz (Hz). High-Resolution Mass Spectra were obtained using the high-resolution mass spectrometers in the EI, ESI or APCI modes from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences Mass Spectral Facility. Thiosulfonates **4a-4e** are known compounds and were prepared using the literature procedure.¹

2. Synthesis of DHP starting material DHP 1

Synthesized DHP starting materials **1**: **1a-1b**², **1c-1f**³, **1g**⁴ are known compounds.



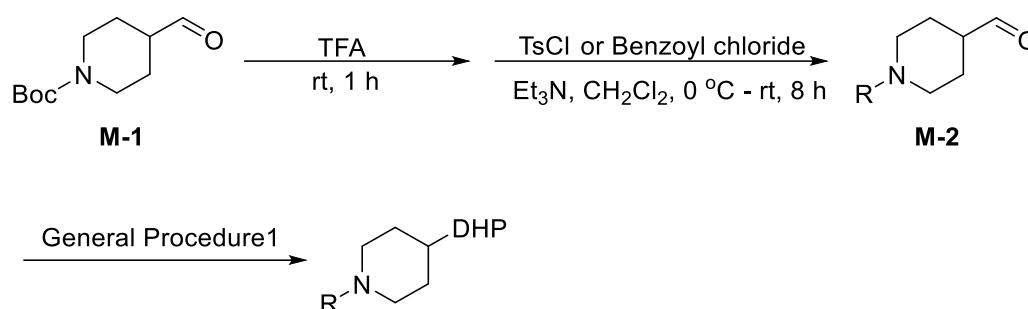
2.1 General procedure for the synthesis of DHP (**1a-1l**)



Procedure A. To a solution of aldehyde (1 equiv), ethyl 3-aminocrotonate (1 equiv), and ethyl acetoacetate (1 equiv) in ethylene glycol (2.5 M), Bu_4NHSO_4 (12 mol %) was added in one portion. The reactor was sealed and heated at 80°C for 4 h. After the

consumption of the aldehyde, the reaction mixture was cooled to rt and was diluted with EtOAc. Then the mixture was poured into a separatory funnel containing brine, and the aqueous layer was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and the excess solvent was removed in a vacuum. The crude mixture was purified by flash column chromatography on silica gel to give DHP product **1a-1l**.

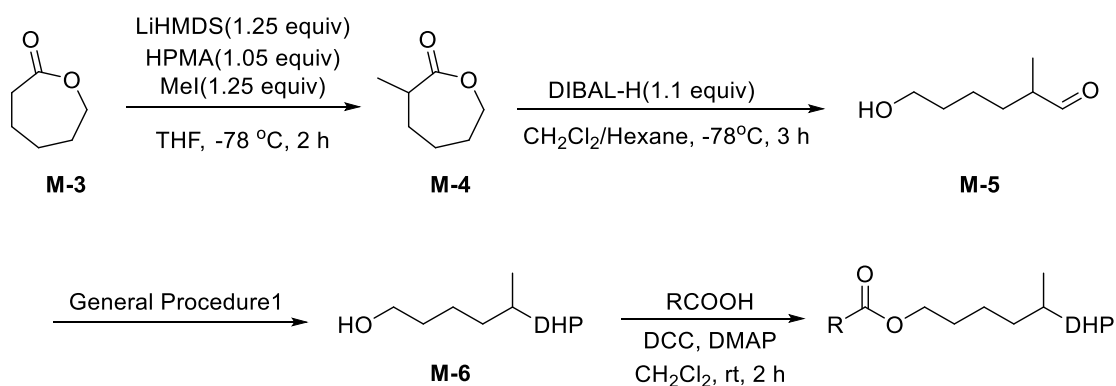
2.2 General procedure for the synthesis of DHPs (**1i-1k**)



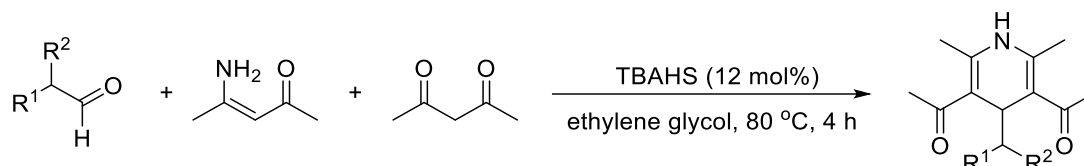
A solution of **M-1** (0.852 g, 4 mmol) in trifluoroacetic acid (TFA) (10 mL) was stirred for 1 h at room temperature. Trifluoroacetic acid was removed by a rotary evaporator to obtain the crude product without further purification.

A solution of TsCl or Benzoyl chloride (1.5 equiv, 6 mmol) in a mixture of Et₃N (2.5 equiv, 10 mmol, 1.012 g) and CH₂Cl₂ (16 mL) was cooled to 0 °C under nitrogen. Then the crude product obtained in the previous step was slowly added, and the reaction mixture was stirred for 8 h at room temperature. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was evaporated to dryness, and the residue was purified by flash column chromatography on silica gel to give **M-2**.

Synthesis of **1l**³

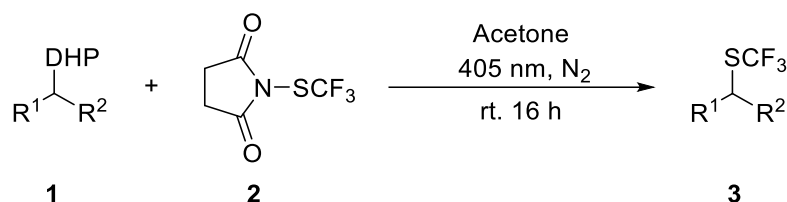


2.2 General procedure for the synthesis of DHP starting materials **1m-1n**.

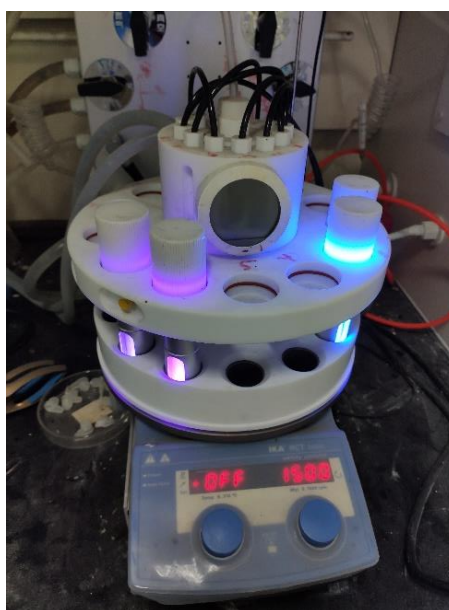
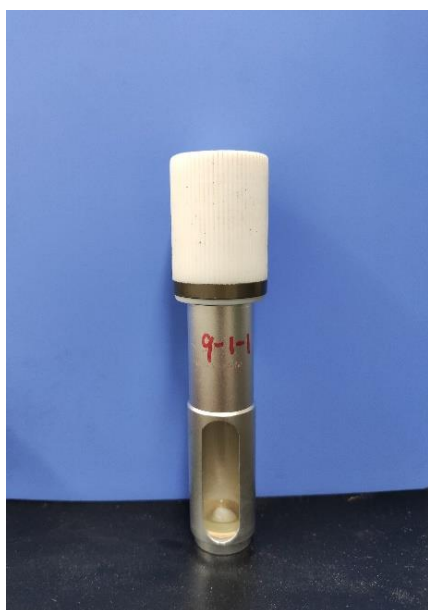


General procedure 2: Over a solution of aldehyde (1 equiv), ethyl (Z)-4-aminopent-3-en-2-one (1 equiv), and pentane-2,4-dione (1 equiv) in ethylene glycol (2.5 M) was added Bu₄NHSO₄ (12 mol %) in one portion. The vial was sealed and heated at 80 °C for 4 h. After the consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel containing brine and extracted with EtOAc three times. After drying over anhydrous Na₂SO₄, it was filtered and taken to dryness. The crude reaction mixture was purified by flash column chromatography on silica gel to give DHP product **1m-1n**.

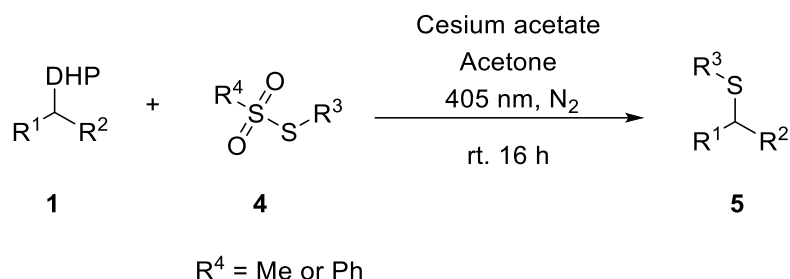
3. The general procedure of trifluoromethylthiolation



In the glove box, DHP **1** (1.2 equiv, 0.24 mmol), **2** (1 equiv, 0.2 mmol) was added to an oven-dried vial, then the dried acetone was added, the vial was sealed with a screw cap. The reaction mixture was vigorously stirred for 16 h at room temperature under irradiation of 405 nm wavelength blue LEDs. Then the vial was removed from the light source, and the mixture was concentrated under reduced pressure. The residue was purified by either flash column chromatography on silica gel or preparative TLC to give **3**.

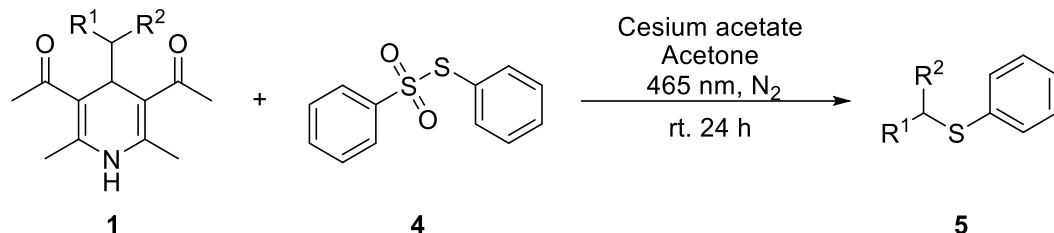


4. General procedure for the synthesis of thioethers **5**



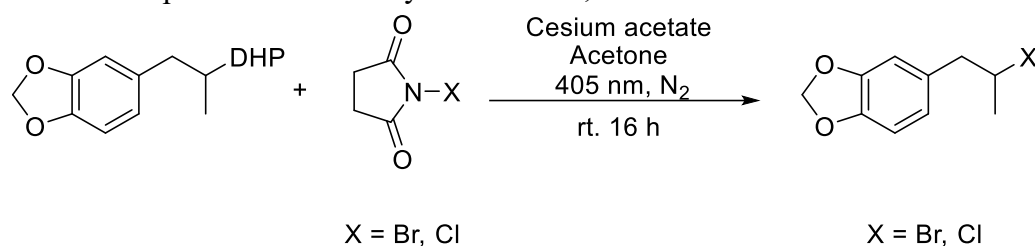
In a glove box, DHP **1** (1.2 equiv, 0.24 mmol), **4** (1 equiv, 0.2 mmol), cesium acetate (2.4 equiv, 0.48 mmol, 0.092 g) was added to an oven-dried vial; then the dried acetone was added, and the vial was sealed with a screw cap. The reaction mixture was vigorously stirred for 16 h at rt under irradiation of 405 nm wavelength blue LEDs. Then the vial was removed from the light source, and the solid was filtered off. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give **5**.

2.6 General procedure for the synthesis of **5o**, **5p**



General procedure 5: in the glove box, DHP **1** (1.2 equiv, 0.24 mmol), **4** (1 equiv, 0.2 mmol), Cesium acetate (2.4 equiv, 0.48 mmol, 0.092 g) was added to an oven-dried vial, then the dried acetone was added, the vial was sealed with a screw cap. The reaction mixture was vigorously stirred for 16 h at rt under irradiation of 465 nm wavelength blue LEDs. Then the vial was removed from the light source, and the solid was filtered off. The filtrate was concentrated under reduced pressure, and the crude product residue was purified by flash column chromatography on silica gel to give **5o** or **5p**.

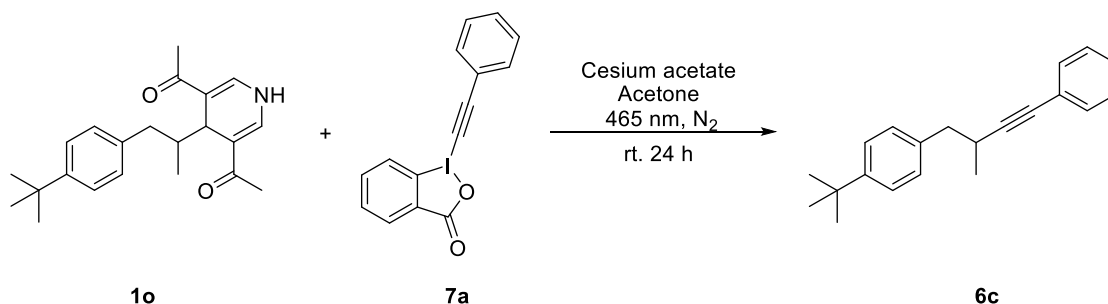
2.7 General procedure for the synthesis of **6a**, **6b**



General procedure 6: DHP **1** (1.2 equiv, 0.24 mmol), NBS or NCS (1 equiv, 0.2 mmol), Cesium acetate (2.4 equiv, 0.48 mmol, 0.092 g) was added to an oven-dried vial, then the dried acetone was added in the glove box, the vial was sealed with a screw cap. The

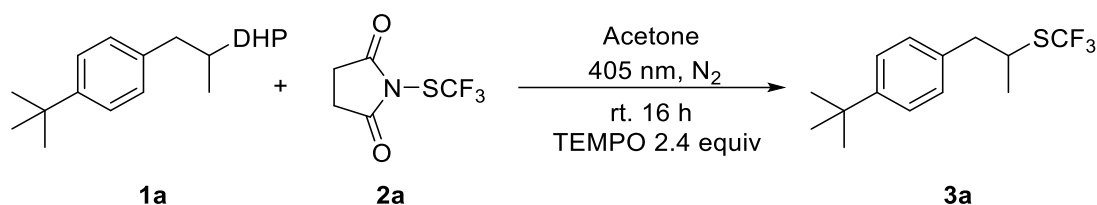
reaction mixture was vigorously stirred for 16 h at rt under irradiation of 405 nm wavelength blue LEDs. Then the vial was removed from the light source, and the solid was filtered off. The filtrate was concentrated under reduced pressure, and the crude product residue was purified by flash column chromatography on silica gel to give **6a** or **6b**.

2.8 Procedure for the synthesis of **6c**



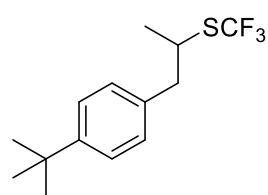
In the glove box, DHP **1o** (1.2 equiv, 0.24 mmol), **7a** (1 equiv, 0.2 mmol), Cesium acetate (2.4 equiv, 0.48 mmol, 0.092 g) was added to an oven-dried vial, then the dried acetone was added, the vial was sealed with a screw cap. The reaction mixture was vigorously stirred for 16 h at rt under irradiation of 465 nm wavelength blue LEDs. Then the vial was removed from the light source, and the solid was filtered off. The filtrate was concentrated under reduced pressure, and the crude product residue was purified by flash column chromatography on silica gel to give **6c**.

2.9 Procedure for radical quenching experiment



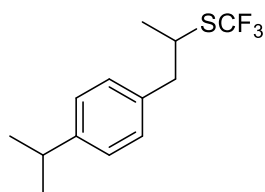
In a glove box, DHP **1a** (1.2 equiv, 0.12 mmol), **2a** (1 equiv, 0.1 mmol, 0.02 g), TEMPO (2.4 equiv, 0.24 mmol) was added to an oven-dried vial, then the dried acetone was added, the vial was sealed with a screw cap. The reaction mixture was vigorously stirred for 16 h at rt under irradiation of 405 nm wavelength blue LEDs. The yield of **3a** was analyzed by ^{19}F NMR spectroscopy by using trifluoromethoxybenzene as an internal standard.

5. Characteristic data

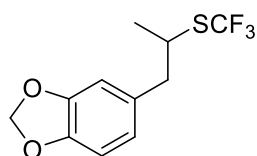


(1-(4-(Tert-butyl)phenyl)propan-2-yl)(trifluoromethyl)sulfane (**3a**). Colorless oil, 48 mg, 87% yield. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.36 (m, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 3.63 – 3.55 (m, 1H), 3.11 (dd, $J = 13.8, 5.4$ Hz, 1H), 2.80 (dd, $J = 13.8, 8.8$ Hz, 1H), 1.40 (d, $J = 6.9$ Hz, 3H), 1.36 (s, 9H). ^{13}C

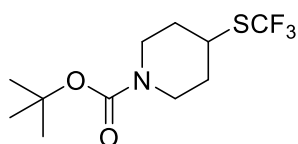
NMR (151 MHz, Chloroform-*d*) δ 149.8, 134.7, 131.2 (q, $J = 306.4$ Hz), 129.0, 125.4, 42.9, 42.0, 34.5, 31.4, 21.1. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -38.97. HRMS (EI): Calcd. for $\text{C}_{14}\text{H}_{19}\text{F}_3\text{S}$ [M^+]: m/z 276.1154; found: 276.1157.



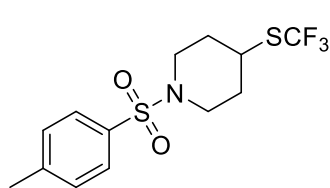
(1-(4-Isopropylphenyl)propan-2-yl)(trifluoromethyl)sulfane (**3b**). Colorless oil, 44 mg, 83% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, $J = 7.9$ Hz, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 3.59 – 3.48 (m, 1H), 3.06 (dd, $J = 13.8, 5.5$ Hz, 1H), 2.94–2.84 (m, 1H), 2.75 (dd, $J = 13.8, 8.8$ Hz, 1H), 1.35 (d, $J = 6.8$ Hz, 3H), 1.24 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.5, 135.0, 131.2 (d, $J = 306.4$ Hz), 129.2, 126.5, 43.0, 42.0, 33.7, 24.0, 21.1. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -38.99. HRMS (EI): Calcd. for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{S}$ [M^+]: m/z 262.0998; found: 262.0999.



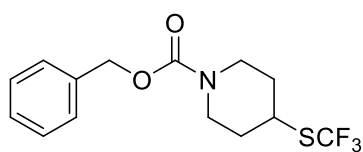
5-(2-((Trifluoromethyl)thio)propyl)benzo[d][1,3]dioxole (**3c**). Colorless oil, 43 mg, 81% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.75 (d, $J = 7.9$ Hz, 1H), 6.66 (s, 1H), 6.63 (d, $J = 7.9$ Hz, 1H), 5.94 (s, 2H), 3.53–3.44 (m, 1H), 2.99 (dd, $J = 13.9, 5.7$ Hz, 1H), 2.71 (dd, $J = 13.9, 8.6$ Hz, 1H), 1.35 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.7, 146.5, 131.5, 131.1 (q, $J = 306.4$ Hz), 122.4, 109.5, 108.2, 101.0, 43.1, 42.1, 21.0. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -38.98. HRMS (EI): Calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{F}_3\text{S}$ [M^+]: m/z 264.0426; found: 264.0421.



Tert-butyl 4-((trifluoromethyl)thio)piperidine-1-carboxylate (**3f**). Colorless oil, 43 mg, 76% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 3.94 (d, $J = 11.7$ Hz, 2H), 3.41–3.34 (m, 1H), 3.00 (t, $J = 11.1$ Hz, 2H), 2.08 – 1.97 (m, 2H), 1.70 – 1.63 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.5, 130.8 (q, $J = 306.7$ Hz), 79.9, 42.9, 41.5, 32.6, 28.4. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -38.99. HRMS (EI): Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{NF}_3\text{S}$ [M^+]: m/z 285.1005; found: 285.1003.

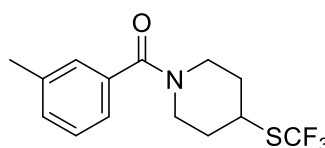


Tert-butyl 4-((trifluoromethyl)thio)piperidine-1-carboxylate⁵ (**3g**). White solid, 40 mg, 71% yield. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 3.57 (dt, $J = 9.7, 3.8$ Hz, 2H), 3.22–3.17 (m, 1H), 2.68 – 2.61 (m, 2H), 2.46 (s, 3H), 2.17 – 2.11 (m, 2H), 1.88–1.81 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.9, 132.8, 130.6 (q, $J = 306.7$ Hz), 129.8, 127.7, 45.3, 40.3, 32.1, 21.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -39.22.

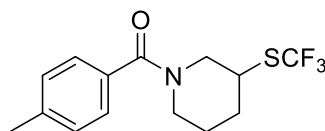


Benzyl 4-((trifluoromethyl)thio)piperidine-1-carboxylate (**3h**). Colorless oil, 53 mg, 82% yield. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 5.15 (s, 2H), 4.05 (s, 2H), 3.44–3.39 (m, 1H), 3.12 (s, 2H),

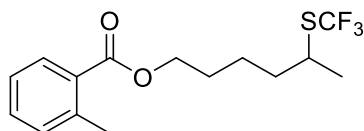
2.07 (s, 2H), 1.73 – 1.61 (m, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 155.0, 136.5, 130.8 (q, *J* = 306.7 Hz), 128.5, 128.1, 128.0. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -38.99. HRMS (EI): Calcd. for C₁₄H₁₆O₂NF₃S [M⁺]: *m/z* 319.0848; found: 319.0851.



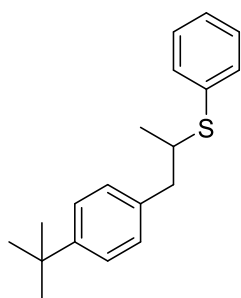
m-Tolyl(4-((trifluoromethyl)thio)piperidin-1-yl)methanone (**3i**). Colorless oil, 37 mg, 61% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.20 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 4.43 (s, 1H), 3.74 (s, 1H), 3.52-3.45 (m, 1H), 3.23-3.16 (m, *J* = 13.6, 10.6, 3.0 Hz, 2H), 2.37 (s, 3H), 2.10 (s, 2H), 1.73 (s, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 170.6, 138.5, 135.5, 130.7 (q, *J* = 306.8 Hz), 130.6, 128.4, 127.5, 123.7, 46.8, 41.3, 41.3, 33.5, 32.4, 21.4. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -38.99. HRMS (EI): Calcd. for C₁₄H₁₆ONF₃S [M⁺]: *m/z* 303.0905; found: 303.0901.



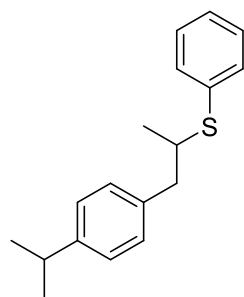
p-Tolyl(3-((trifluoromethyl)thio)piperidin-1-yl)methanone (**3j**). Colorless oil. 44 mg, 73% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.08 (s, 2H), 3.36 (s, 1H), 3.29 – 3.16 (m, 2H), 2.38 (s, 3H), 2.23 – 2.15 (m, 1H), 1.83 (s, 1H), 1.78 – 1.66 (m, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 171.0, 140.1, 132.4, 130.6 (q, *J* = 306.9 Hz), 129.1, 127.1, 41.2, 31.3, 29.7, 24.8, 21.4. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -39.23. HRMS (EI⁺): Calcd. for C₁₄H₁₆F₃NOS [M⁺]: *m/z* 303.0905; found: 303.0894.



5-((Trifluoromethyl)thio)hexyl 2-methylbenzoate (**3k**). Colorless oil. 44 mg, 89% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.24 (dt, *J* = 7.1, 3.0 Hz, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 3.33 (h, *J* = 6.8 Hz, 1H), 2.60 (s, 3H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.70 (dt, *J* = 13.1, 6.4 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.43 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 167.7, 140.1, 131.9, 131.7, 131.2 (q, *J* = 306.2 Hz), 130.5, 129.7, 125.7, 64.3, 41.0, 36.5, 28.4, 23.30, 22.3, 21.8. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -39.12. HRMS (EI): Calcd. for C₁₅H₁₉O₂F₃S [M⁺]: *m/z* 320.1052; found: 320.1048.



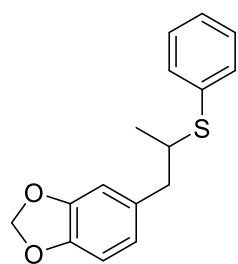
(1-(4-(Tert-butyl)phenyl)propan-2-yl)(phenyl)sulfane (**5a**). Yellowish oil. 48 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 4H), 7.24 – 7.19 (m, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.49-3.40 (m, *J* = 11.9, 9.0, 6.7, 5.4 Hz, 1H), 3.00 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.62 (dd, *J* = 13.7, 9.0 Hz, 1H), 1.30 (s, 9H), 1.23 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.2, 136.2, 135.3, 131.91, 128.9, 128.8, 126.8, 125.2, 44.5, 42.7, 34.4, 31.4, 20.3. HRMS (EI): Calcd. for C₁₉H₂₄S [M⁺]: *m/z* 284.1593; found: 284.1588.



(1-(4-Isopropylphenyl)propan-2-yl)(phenyl)sulfane (**5b**).

Yellowish oil. 49 mg, 91% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.24 – 7.19 (m, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 3.49 – 3.39 (m, 1H), 3.00 (dd, $J = 13.7, 5.2$ Hz, 1H), 2.92–2.82 (m, 1H), 2.62 (dd, $J = 13.7, 9.0$ Hz, 1H), 1.23 (d, $J = 6.9$ Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.9, 136.6, 135.3, 131.9, 129.1, 128.8, 126.8, 126.4, 44.5, 42.8, 33.7, 24.0, 20.2. HRMS

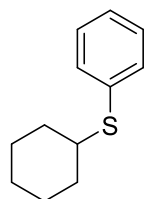
(EI): Calcd. for $\text{C}_{18}\text{H}_{22}\text{S}$ [M^+]: m/z 270.1437; found: 270.1435.



5-(2-(Phenylthio)propyl)benzo[d][1,3]dioxole (**5c**). Colorless oil.

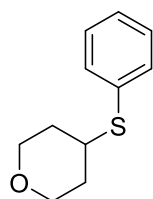
44 mg, 82% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.33 – 7.26 (m, 2H), 7.25 – 7.19 (m, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 6.65 (d, $J = 1.7$ Hz, 1H), 6.60 (dd, $J = 7.9, 1.7$ Hz, 1H), 5.92 (s, 2H), 3.43 – 3.34 (m, 1H), 2.93 (dd, $J = 13.7, 5.4$ Hz, 1H), 2.57 (dd, $J = 13.7, 8.9$ Hz, 1H), 1.22 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.5, 146.1, 135.1, 133.0,

132.0, 128.9, 126.9, 122.2, 109.5, 108.1, 100.9, 44.7, 42.9, 20.1. HRMS (EI): Calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$ [M^+]: m/z 272.0866; found: 272.0868.



Cyclohexyl(phenyl)sulfane⁶ (**5d**). Yellowish oil. 29 mg, 76% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.20 (dd, $J = 8.3, 6.2$ Hz, 1H), 3.14–3.07 (m, 1H), 1.98 (d, $J = 10.7$ Hz, 2H), 1.81 – 1.72 (m, 2H), 1.65 – 1.58 (m, 1H), 1.40 – 1.24 (m, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.2, 131.9, 128.7, 126.6, 46.6,

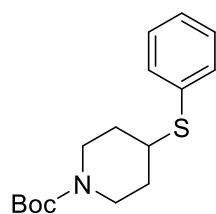
33.4, 26.1, 25.8.



4-(Phenylthio)tetrahydro-2H-pyran⁷ (**5e**). Yellow oil, 34 mg, 88% yield.

^1H NMR (600 MHz, Chloroform-*d*) δ 7.42 (dt, $J = 8.4, 1.9$ Hz, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 3.97 (dt, $J = 11.8, 3.8$ Hz, 2H), 3.43 (td, $J = 11.5, 2.4$ Hz, 2H), 3.29–3.24 (m, 1H), 1.93 – 1.87 (m, 2H), 1.67 (dt, $J = 11.0, 4.2$ Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 133.7,

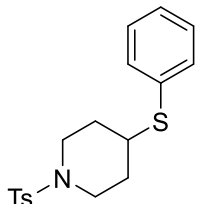
132.7, 128.9, 127.3, 67.3, 43.5, 33.2.

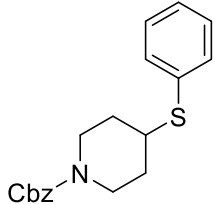


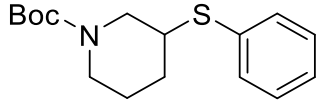
Tert-butyl 4-(phenylthio)piperidine-1-carboxylate⁷ (**5f**). Colorless oil.

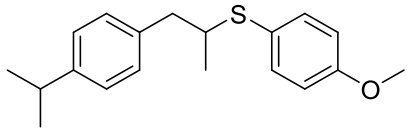
43 mg, 74% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dt, $J = 8.5, 2.0$ Hz, 2H), 7.33 – 7.24 (m, 3H), 3.96 (d, $J = 10.8$ Hz, 2H), 3.24–3.17 (m, 1H), 2.98 – 2.86 (m, 2H), 1.96 – 1.87 (m, 2H), 1.57–1.48 (m, 4.1 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.7, 133.8, 132.7, 128.9, 127.3, 79.6, 44.5, 43.5,

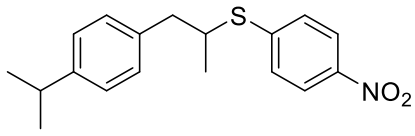
32.1, 28.4.


 4-(Phenylthio)-1-tosylpiperidine⁸ (**5g**). white solid, 43 mg, 62% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26 (q, *J* = 5.6 Hz, 3H), 3.58 (dt, *J* = 9.8, 4.0 Hz, 2H), 3.03-2.96 (m, 1H), 2.60 – 2.50 (m, 2H), 2.43 (s, 3H), 2.04 – 1.95 (m, 2H), 1.75-1.65 (m, 3.8 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 143.6, 133.3, 133.1, 132.8, 129.7, 129.0, 127.7, 127.5, 45.5, 43.5, 31.5, 21.6.

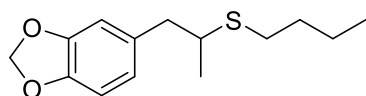

 Benzyl 4-(phenylthio)piperidine-1-carboxylate (**5h**). Yellow oil. 42 mg, 64% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.16 (m, 8H), 5.04 (s, 2H), 4.05 – 3.86 (m, 2H), 3.18-3.11 (m, 1H), 2.94 (t, *J* = 11.0 Hz, 2H), 1.85 (d, *J* = 11.2 Hz, 2H), 1.47 (d, *J* = 10.0 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 155.2, 136.8, 133.7, 132.8, 129.0, 128.5, 128.0, 127.9, 127.4, 67.2, 44.3, 43.4, 32.0. HRMS (EI): Calcd. for C₁₉H₂₁O₂NS [M⁺]: *m/z* 327.1288; found: 327.1283.


 Tert-butyl 3-(phenylthio)piperidine-1-carboxylate (**5i**). Colorless oil. 45 mg, 77% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 4.08 (s, 1H), 3.88 (d, *J* = 12.9 Hz, 1H), 3.18 – 3.04 (m, 1H), 2.84 (dd, *J* = 16.7, 6.4 Hz, 2H), 2.15 – 1.99 (m, 1H), 1.76 – 1.70 (m, 1H), 1.58 – 1.46 (m, 2H), 1.41 (s, 9H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 154.4, 134.2, 132.2, 131.3, 129.0, 127.0, 79.6, 50.1, 49.3, 43.8, 30.9, 29.7, 28.4, 25.2. HRMS (EI): Calcd. for C₁₆H₂₃O₂NS [M⁺]: *m/z* 293.1444; found: 293.1447.

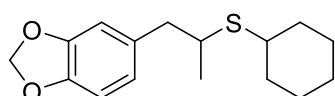

 (1-(4-Isopropylphenyl)propan-2-yl)(4-methoxyphenyl)sulfane (**5j**). Yellowish oil. 51 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.87 – 6.82 (m, 2H), 3.80 (s, 3H), 3.30 – 3.20 (m, 1H), 2.96 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.95-2.82 (m, 1H), 2.56 (dd, *J* = 13.6, 9.1 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 159.4, 146.8, 136.8, 135.6, 129.1, 126.3, 125.1, 114.4, 55.3, 45.8, 42.8, 33.7, 24.0, 20.2. HRMS (EI): Calcd. for C₁₉H₂₄OS [M⁺]: *m/z* 300.1542; found: 300.1541.


 (1-(4-Isopropylphenyl)propan-2-yl)(4-nitrophenyl)sulfane (**5k**). Yellow oil, 35 mg, 55% yield. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.69 (h, *J* = 6.6 Hz, 1H), 3.04 (dd, *J* = 13.8, 5.9 Hz, 1H), 2.91 (p, *J* = 6.9 Hz, 1H), 2.81 (dd, *J* = 13.8, 8.2 Hz, 1H), 1.39 (d, *J* = 6.7 Hz, 3H), 1.26 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 147.4, 146.9,

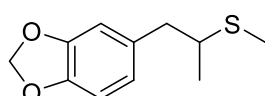
145.2, 135.6, 129.2, 127.9, 126.55 123.9, 43.2, 42.6, 33.7, 24.0, 20.3. HRMS (EI): Calcd. for C₁₈H₂₁O₂NS [M⁺]: m/z 315.1288; found: 315.1290.



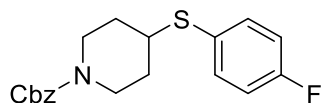
5-(2-(Butylthio)propyl)benzo[d][1,3]dioxole (**5l**). Yellowish oil, 43 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.3 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.93 (s, 2H), 2.97 – 2.86 (m, 2H), 2.60 – 2.50 (m, 3H), 1.58 – 1.51 (m, 2H), 1.44–1.35 (m, 2H), 1.22 – 1.19 (m, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 147.5, 146.0, 133.4, 122.2, 109.5, 108.1, 100.8, 43.5, 41.4, 31.9, 30.4, 22.2, 20.6, 13.7. HRMS (EI): Calcd. for C₁₄H₂₀O₂S [M⁺]: m/z 252.1179; found: 252.1176.



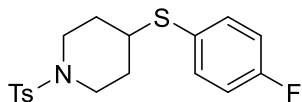
5-(2-(Cyclohexylthio)propyl)benzo[d][1,3]dioxole (**5m**). Yellowish oil, 27 mg, 48% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.69 – 6.66 (m, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 2H), 3.06 – 2.96 (m, 1H), 2.89 (dd, *J* = 13.6, 5.5 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.55 (dd, *J* = 13.6, 8.7 Hz, 1H), 1.94 (t, *J* = 10.1 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.65 – 1.59 (m, 1H), 1.34 – 1.23 (m, 5H), 1.19 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 147.4, 145.9, 133.5, 122.2, 109.6, 108.0, 100.8, 43.8, 42.4, 39.5, 34.1, 34.0, 26.2, 26.2, 25.9, 21.0. HRMS (EI): Calcd. for C₁₆H₂₂O₂S [M⁺]: m/z 278.1335; found: 278.1340.



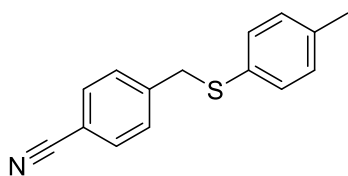
5-(2-(Methylthio)propyl)benzo[d][1,3]dioxole (**5n**). Yellowish oil, 32 mg, 76% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.74 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 6.66 – 6.62 (m, 1H), 5.93 (s, 2H), 2.91 – 2.81 (m, 2H), 2.63 – 2.54 (m, 1H), 2.09 (s, 3H), 1.22 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 147.5, 146.0, 133.4, 122.1, 109.5, 108.1, 100.8, 43.0, 42.9, 20.1, 13.7. HRMS (EI): Calcd. for C₁₁H₁₄O₂S [M⁺]: m/z 210.0715; found: 210.0706.



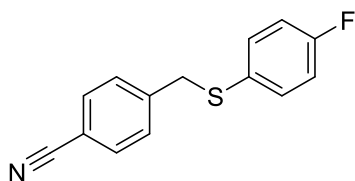
benzyl 4-((4-fluorophenyl)thio)piperidine-1-carboxylate (**5o**) white solid, 47 mg, 68% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.30 (m, 5H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.11 (s, 2H), 4.05 (s, 2H), 3.32 – 3.04 (m, 1H), 2.98 (t, *J* = 11.0 Hz, 2H), 1.90 (d, *J* = 10.1 Hz, 2H), 1.52 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 248.4 Hz), 155.3, 136.9, 135.9 (d, *J* = 8.5 Hz), 128.6, 128.5 (d, *J* = 3.6 Hz), 128.2, 128.0, 116.2 (d, *J* = 21.8 Hz), 67.3, 45.3, 43.5, 32.1. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ -113.45 – -113.64 (m). HRMS (EI): Calcd. for C₁₉H₂₀FN₂O₂S [M⁺]: m/z 345.1193; found: 345.1190.



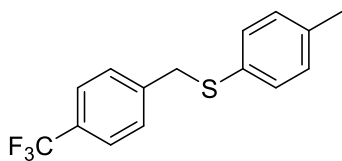
4-((4-fluorophenyl)thio)-1-tosylpiperidine (**5p**)⁹ white solid, 43 mg, 60% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 3.80 – 3.45 (m, 2H), 3.03 – 2.72 (m, 1H), 2.65 – 2.44 (m, 2H), 2.43 (s, 3H), 1.95 (dd, *J* = 13.5, 3.4 Hz, 2H), 1.72 – 1.62 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 248.5 Hz), 143.8, 136.0 (d, *J* = 8.4 Hz), 133.1, 129.8, 128.2 (d, *J* = 3.5 Hz), 127.8, 116.3 (d, *J* = 21.8 Hz), 45.6, 44.4, 31.5, 21.7. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.19 – -113.37 (m).



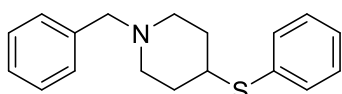
4-((p-tolylthio)methyl)benzotrile (**5q**)¹⁰ white solid, 29 mg, 62% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.04 (s, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.8, 137.5, 132.2, 131.7, 130.8, 129.9, 129.5, 118.9, 110.8, 39.8, 21.1.



4-(((4-fluorophenyl)thio)methyl)benzotrile (**5r**)¹¹ white solid, 27 mg, 56% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.26 (s, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 4.01 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.5 (d, *J* = 248.2 Hz), 143.4, 134.4 (d, *J* = 8.4 Hz), 132.3, 129.6, 129.3 (d, *J* = 3.4 Hz), 118.8, 116.3 (d, *J* = 21.8 Hz), 111.0, 40.4. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.30 – -113.53 (m).

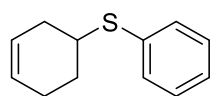


p-tolyl(4-(trifluoromethyl)benzyl)sulfane (**5s**)¹² white solid, 33 mg, 58% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.09 (s, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 142.3, 137.3, 131.6, 131.4, 129.9, 129.5, 129.2, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.1 Hz), 39.6, 21.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.37 (s).

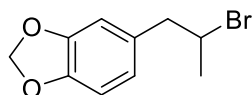


1-Benzyl-4-(phenylthio)piperidine¹³ (**5t**). Yellowish solid, 43 mg, 76% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.28 (m, 5H), 7.26 – 7.19 (m, 3H), 3.49 (s, 2H), 3.11-3.04 (m, 3.6 Hz, 1H), 2.84 (dt, *J* = 11.5, 3.3 Hz, 2H), 2.09 (t, *J* = 10.5 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.71 – 1.64 (m, 2H). ¹³C NMR (101 MHz,

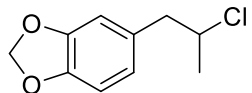
Chloroform-*d*) δ 138.2, 134.5, 132.3, 129.1, 128.8, 128.2, 127.0, 126.9, 63.1, 53.0, 44.5, 32.5.



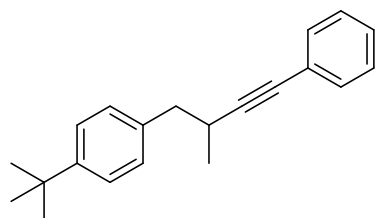
Cyclohex-3-en-1-yl(phenyl)sulfane¹⁴ (**5u**). Colorless oil, 28 mg, 74% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 8.4, 6.2 Hz, 1H), 5.74 – 5.58 (m, 2H), 3.41-3.34 (m, 1H), 2.46 – 2.35 (m, 1H), 2.23 – 2.00 (m, 4H), 1.70 – 1.59 (m, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 134.9, 131.9, 128.8, 126.8, 126.8, 125.3, 42.8, 31.9, 28.8, 24.8.



5-(2-Bromopropyl)benzo[d][1,3]dioxole³ (**6a**). Colorless oil, 44 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.76 (dd, *J* = 7.8, 2.5 Hz, 1H), 6.69 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 2.6 Hz, 2H), 4.28-4.19 (m, 1H), 3.16-3.10 (m, 2.2 Hz, 1H), 3.01-2.95 (m, 1H), 1.68 (dd, *J* = 6.6, 2.6 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.6, 146.4, 132.3, 122.3, 109.5, 108.2, 101.0, 50.8, 47.2, 25.6.

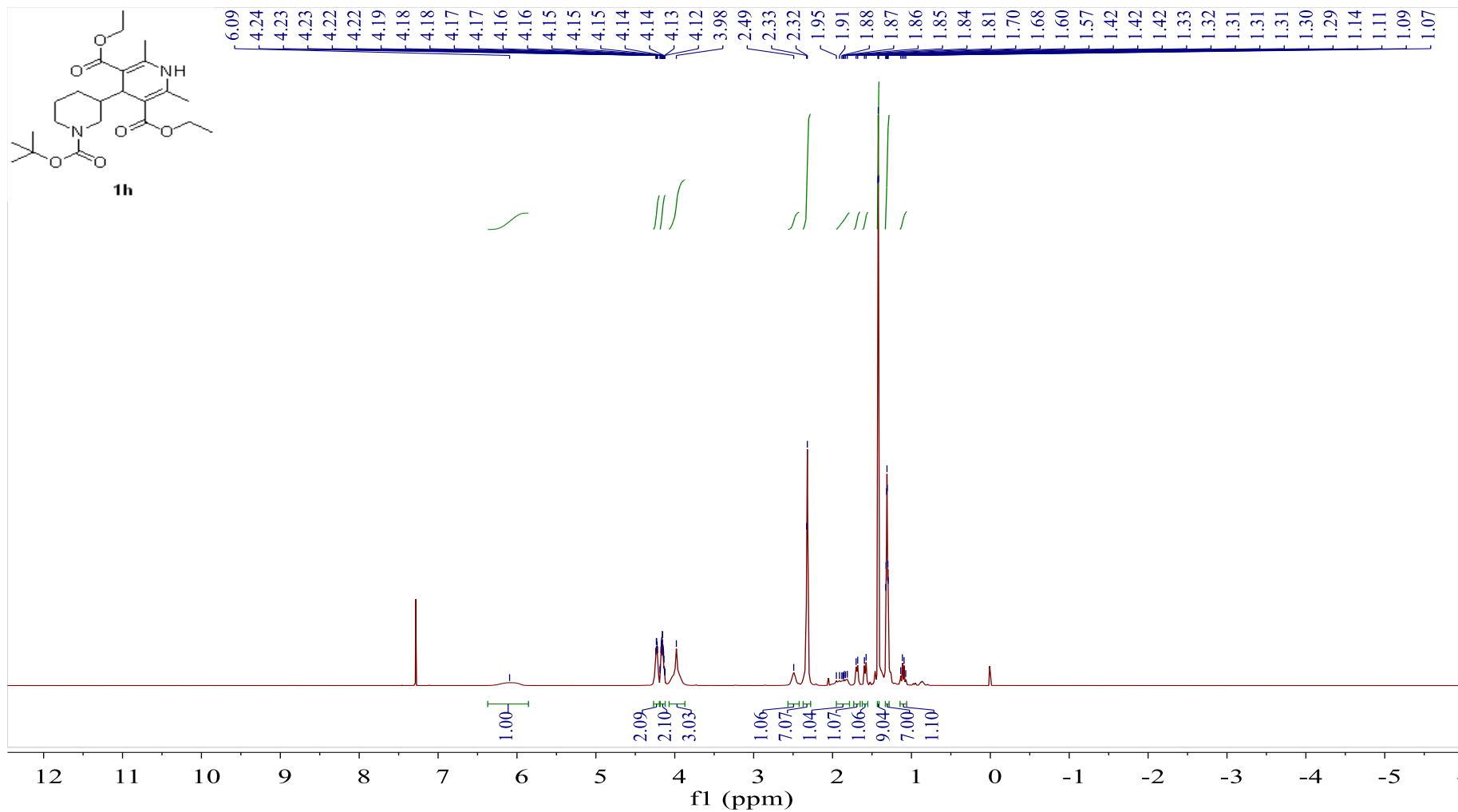


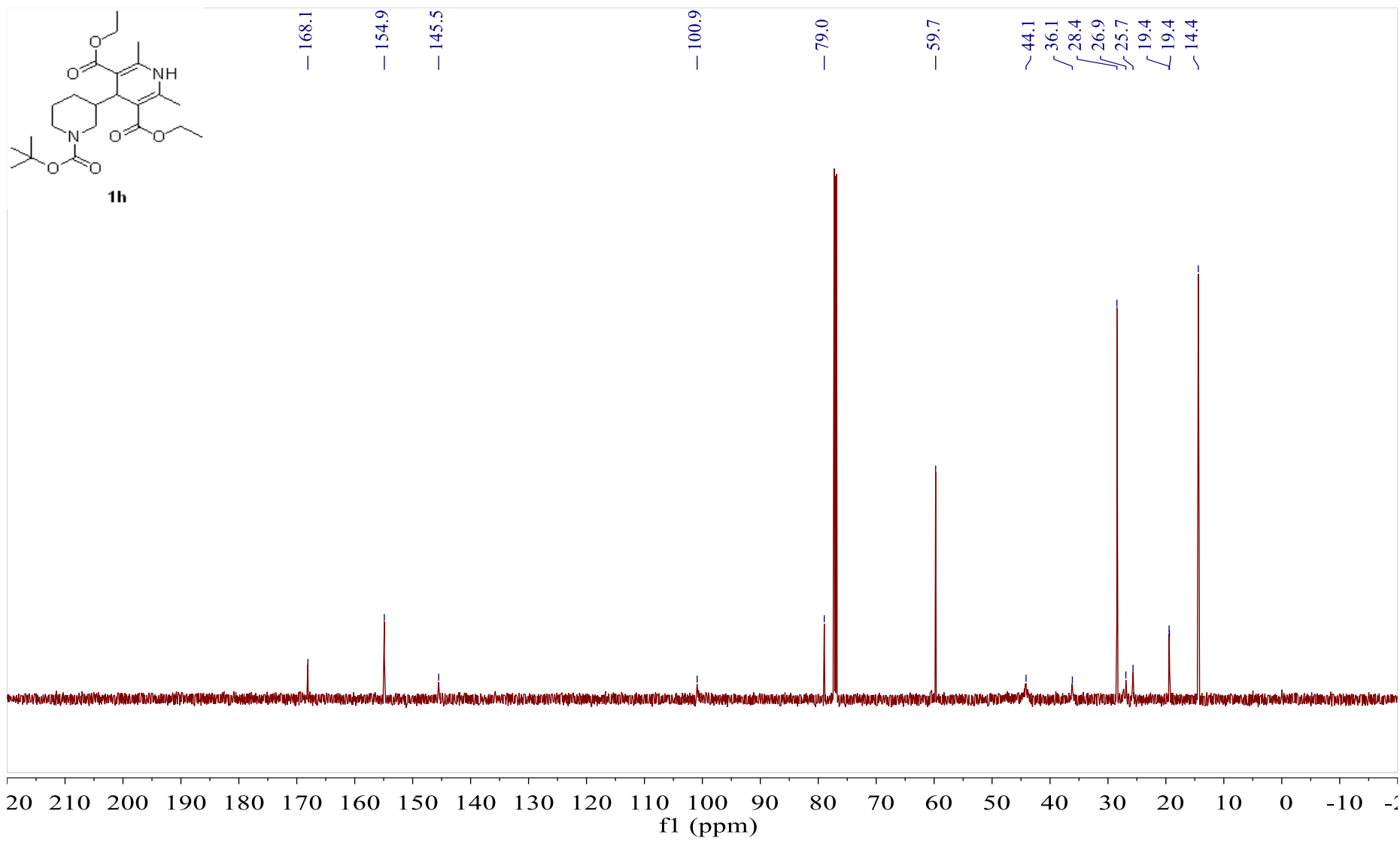
5-(2-Chloropropyl)benzo[d][1,3]dioxole³ (**6b**). Colorless oil, 34 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.75 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.70 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.94 (d, *J* = 2.1 Hz, 2H), 4.15 (h, *J* = 6.6 Hz, 1H), 2.99 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.87 (dd, *J* = 14.0, 6.7 Hz, 1H), 1.50 (dd, *J* = 6.5, 2.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.6, 146.4, 131.7, 122.4, 109.7, 108.2, 100.9, 58.7, 46.3, 24.6.

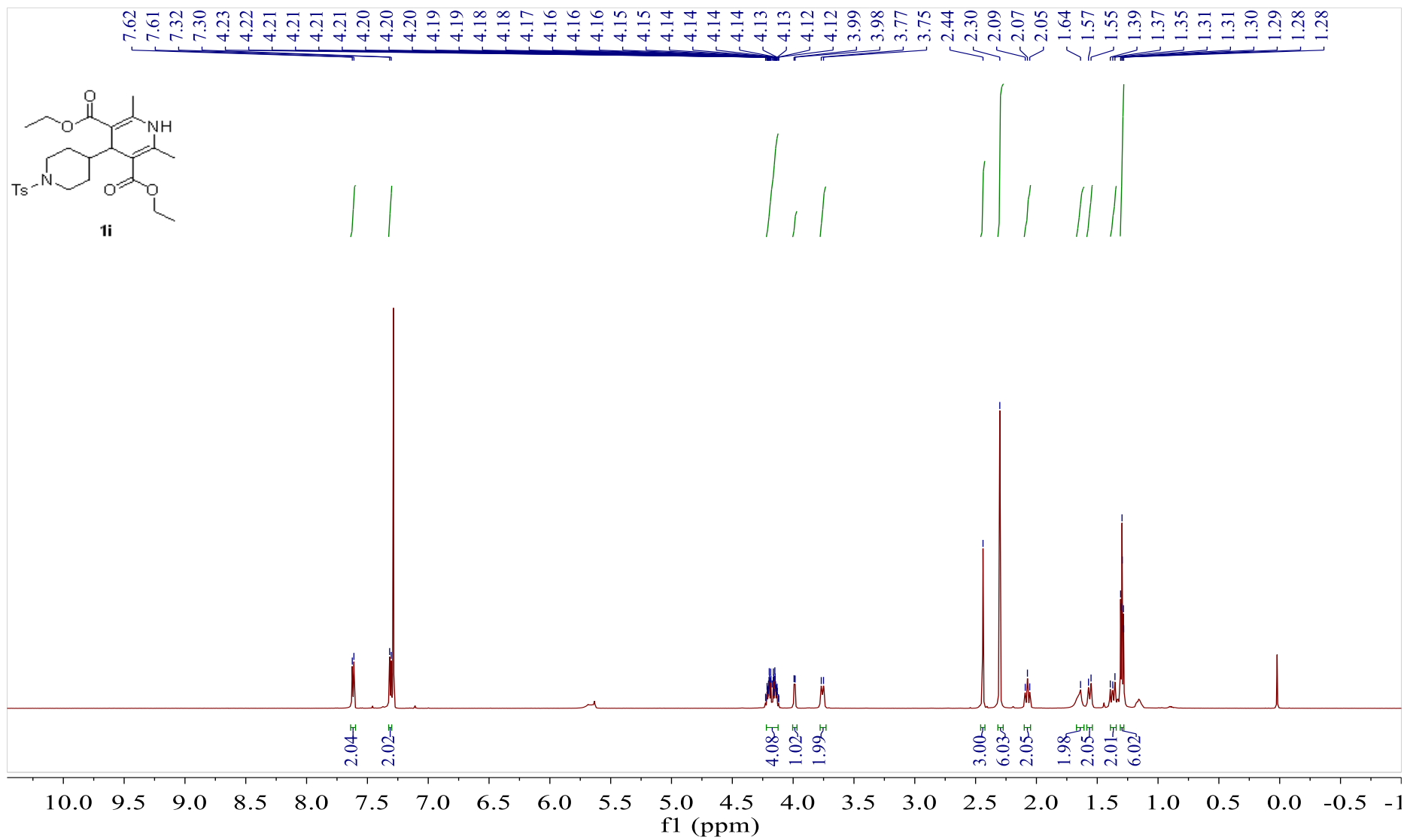


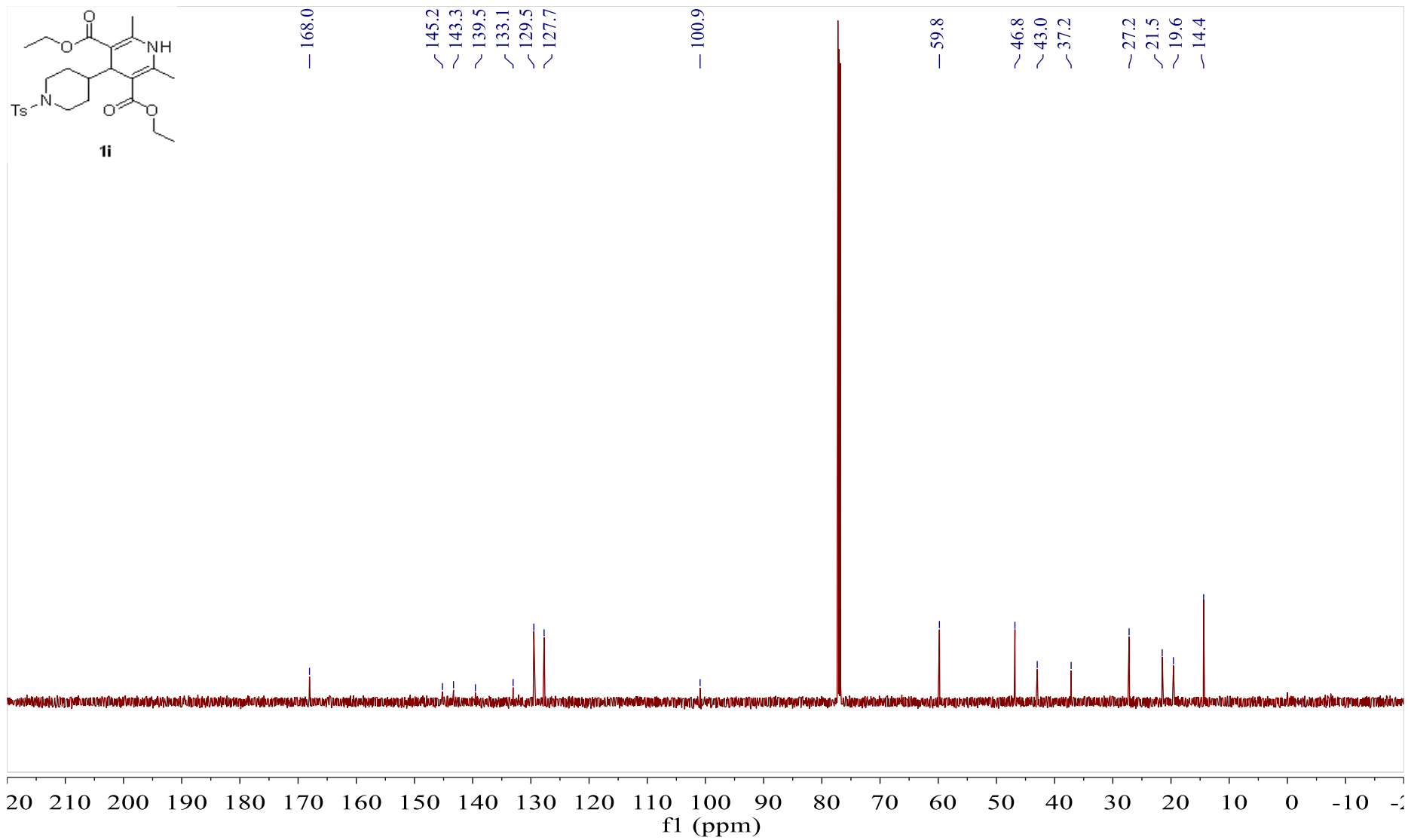
1-(Tert-butyl)-4-(2-methyl-4-phenylbut-3-yn-1-yl)benzene¹⁵ (**6c**). Yellowish oil, 41 mg, 75% yield. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 7.32-7.28 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.97 – 2.89 (m, 2H), 2.80 – 2.74 (m, 1H), 1.35 (s, 9H), 1.29 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 149.0, 136.6, 131.5, 129.0, 128.1, 127.5, 125.1, 124.0, 94.4, 81.4, 42.7, 34.4, 31.4, 28.6, 20.6.

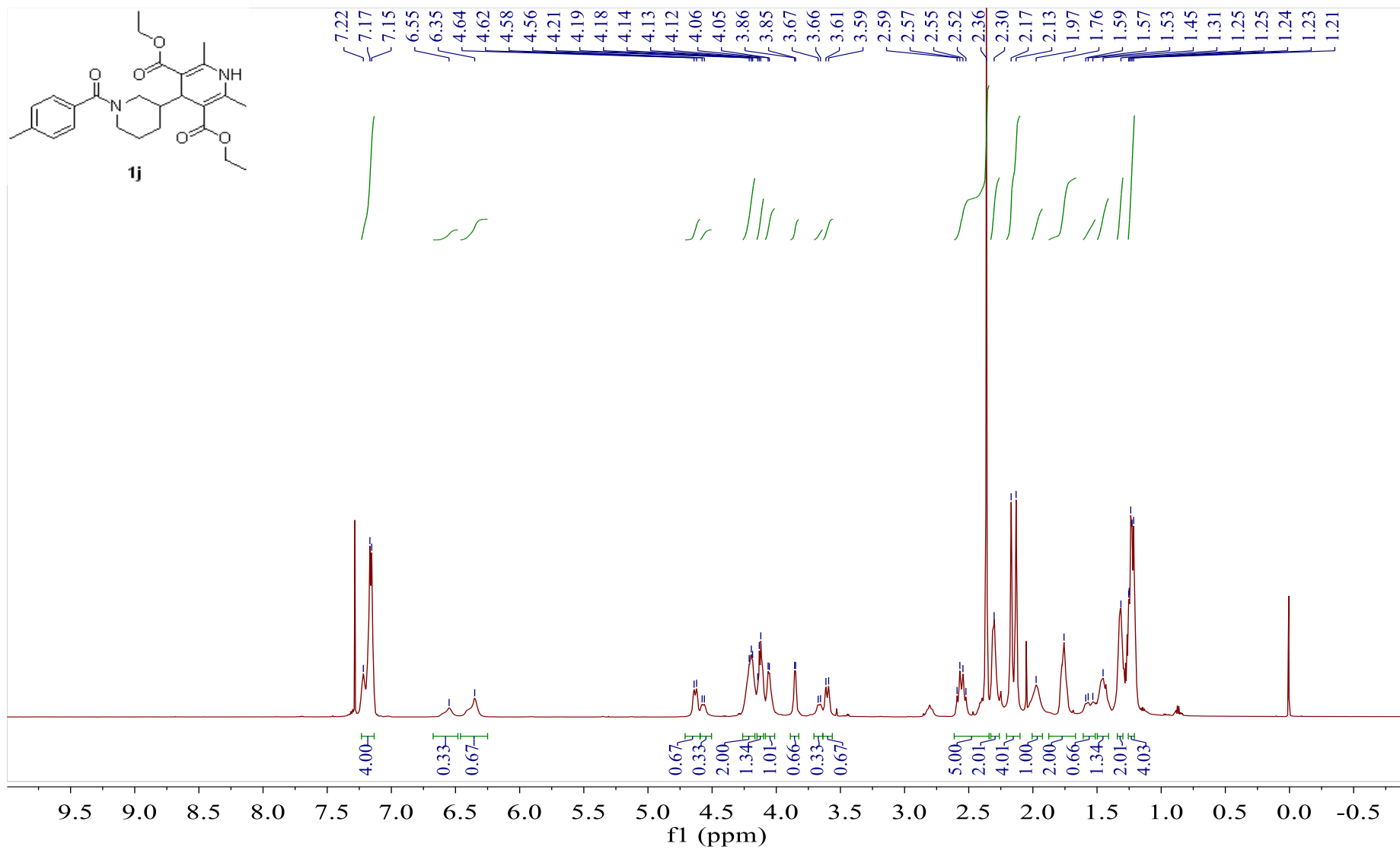
6. Copies of NMR Spectra

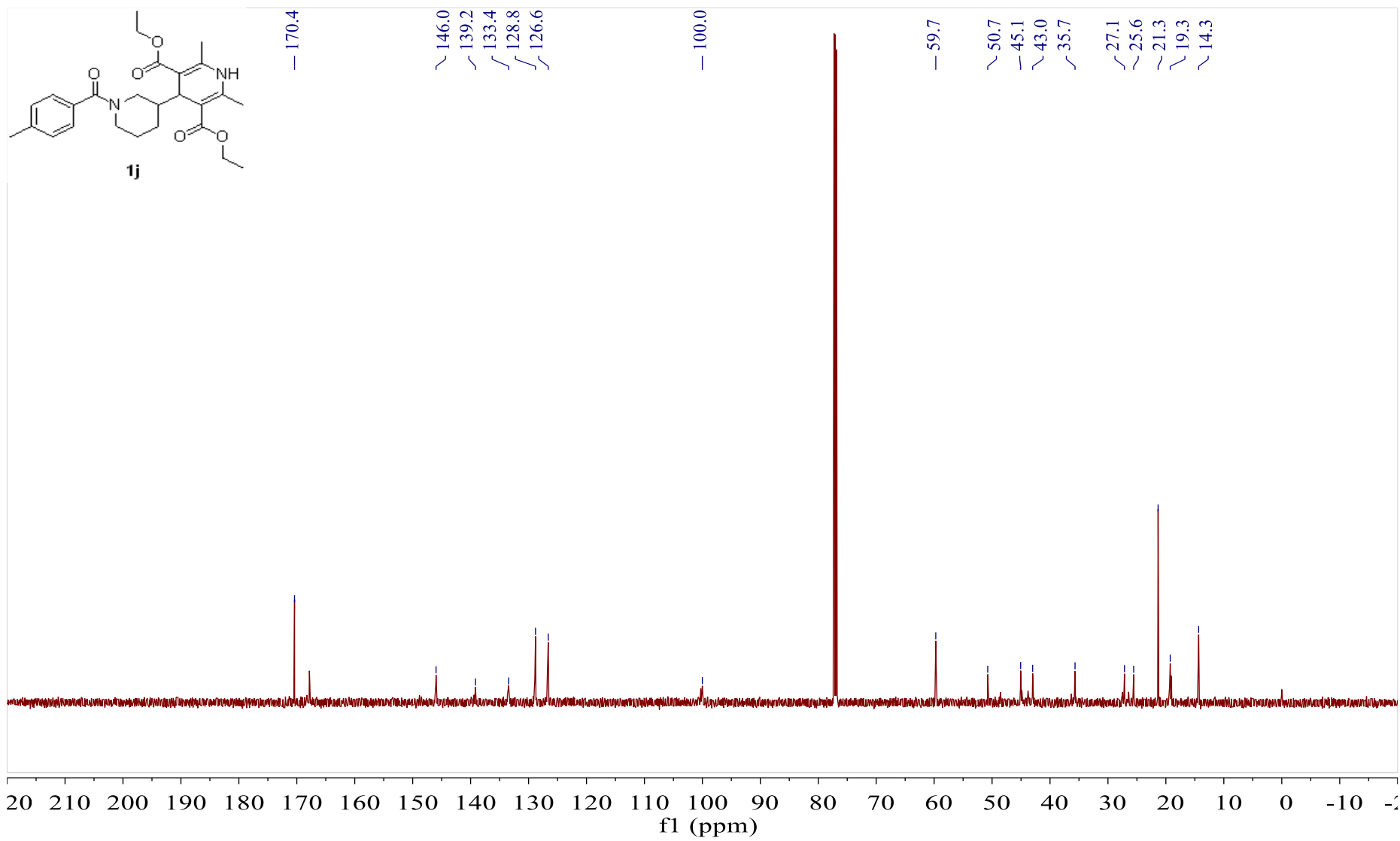


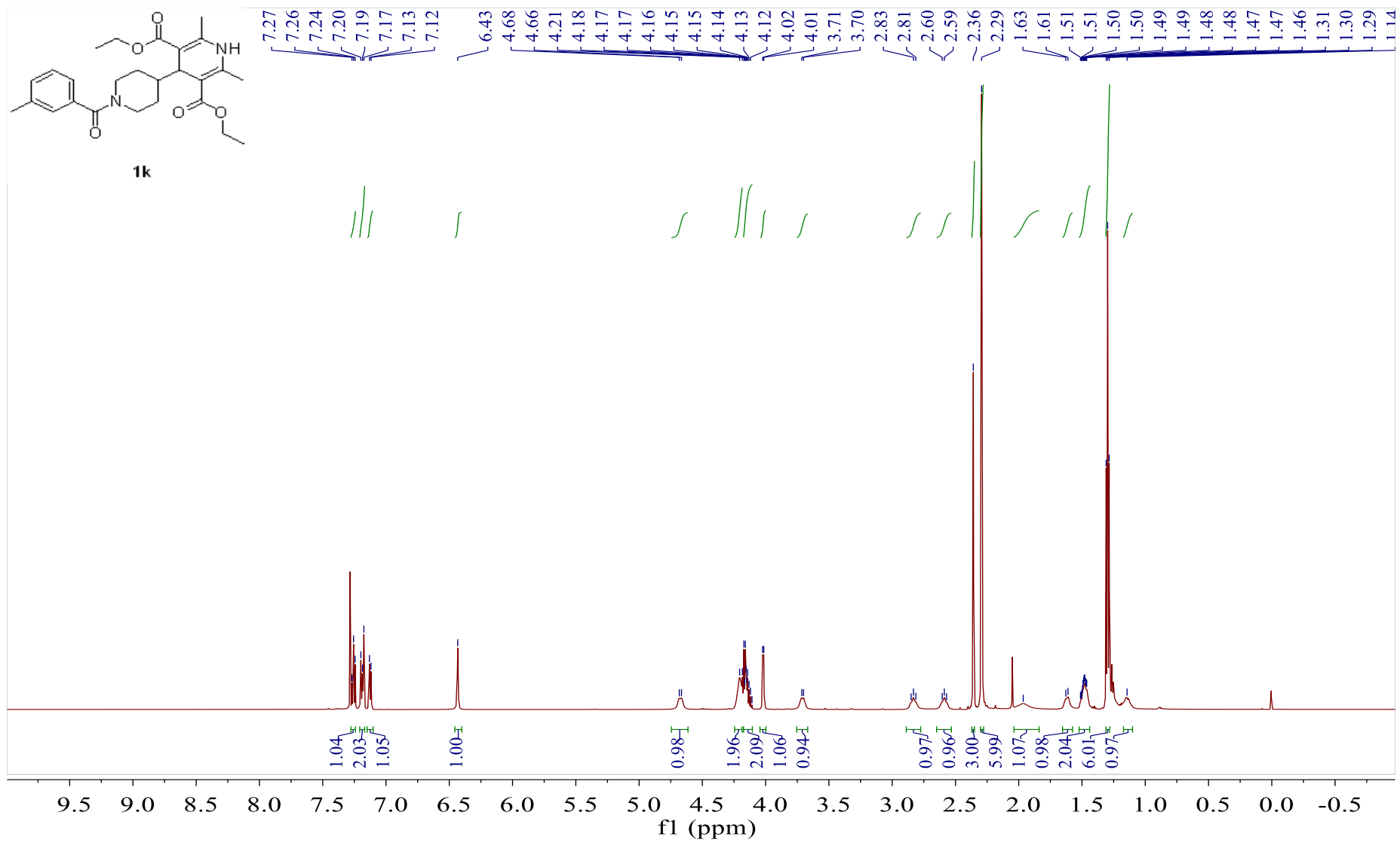


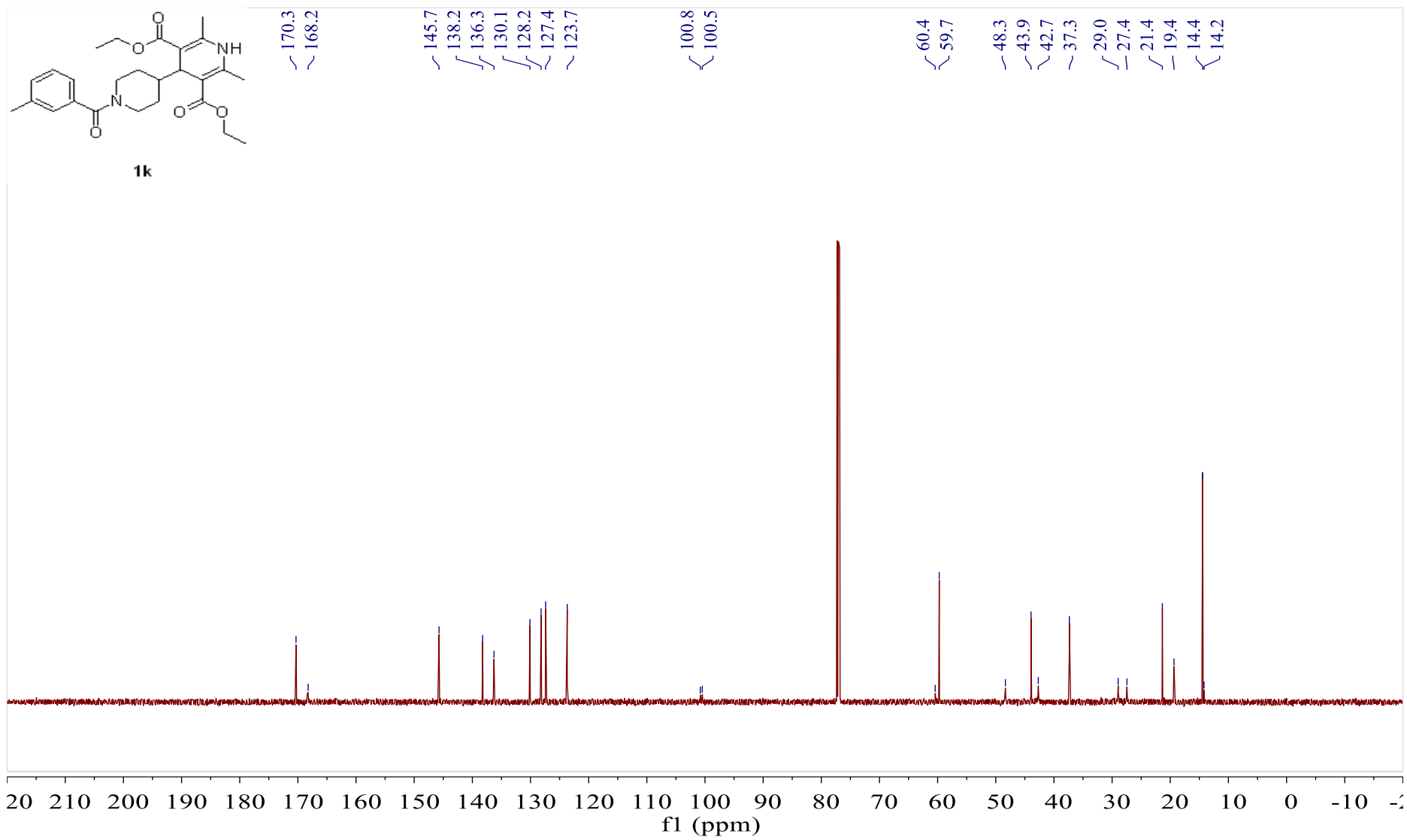


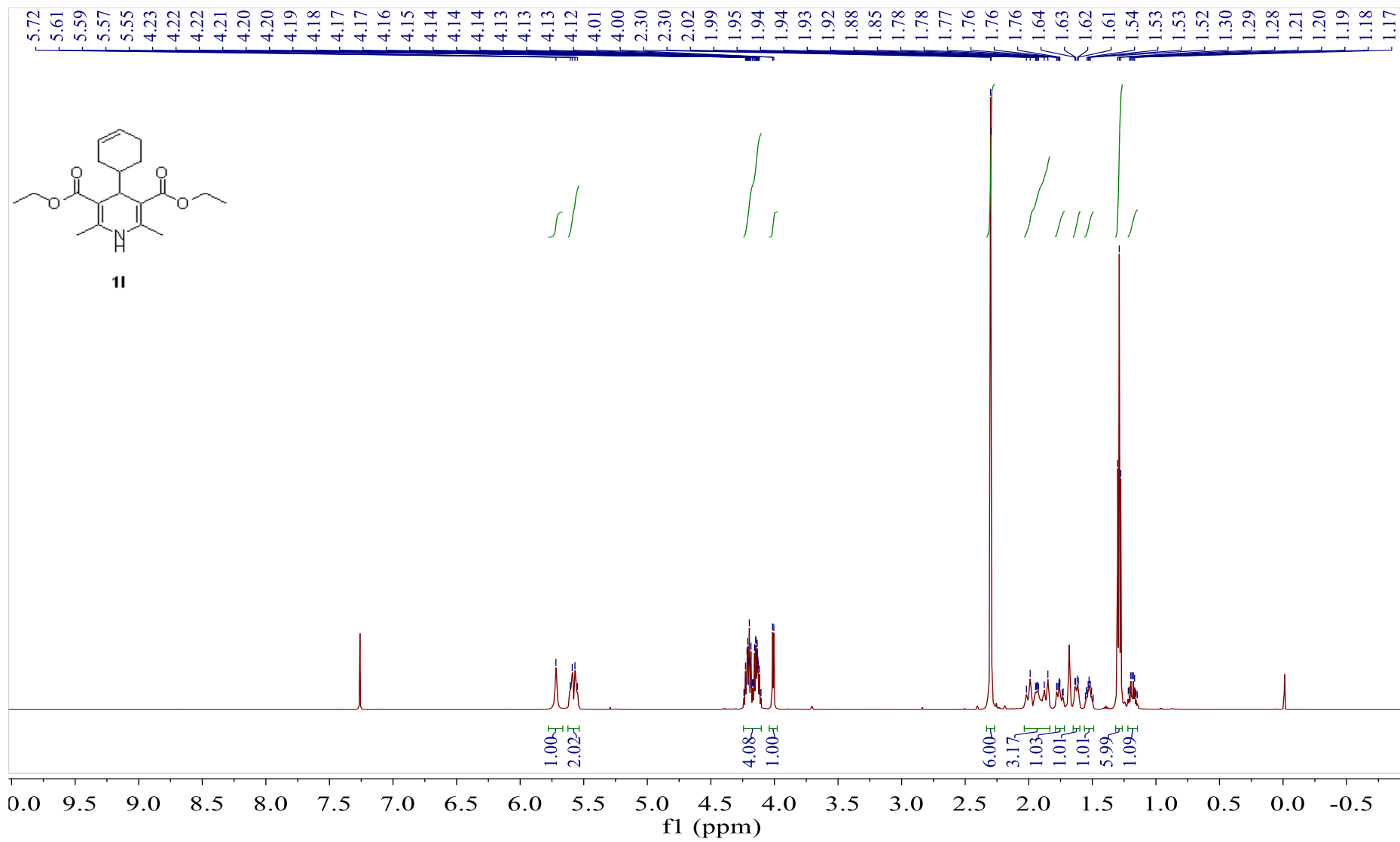


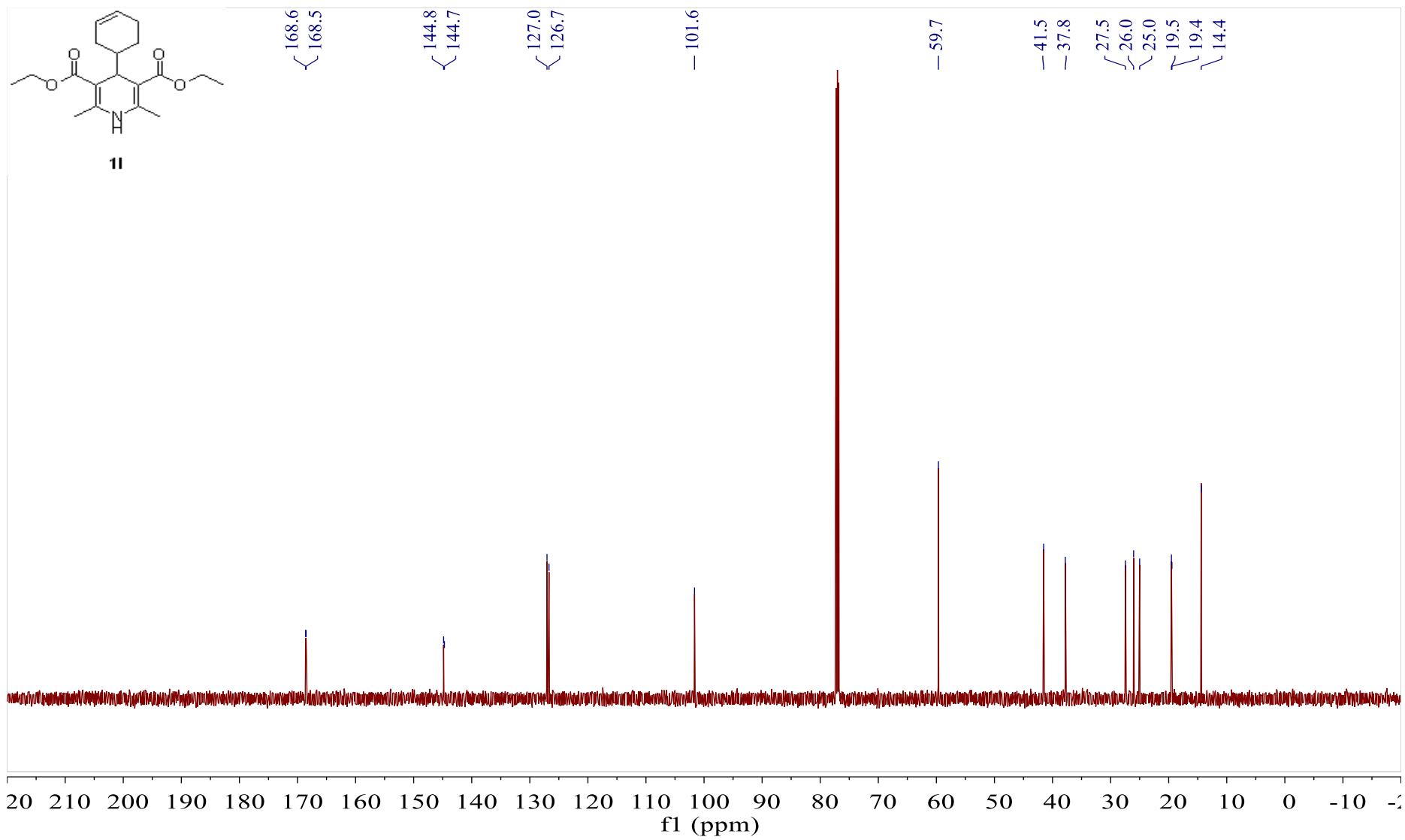


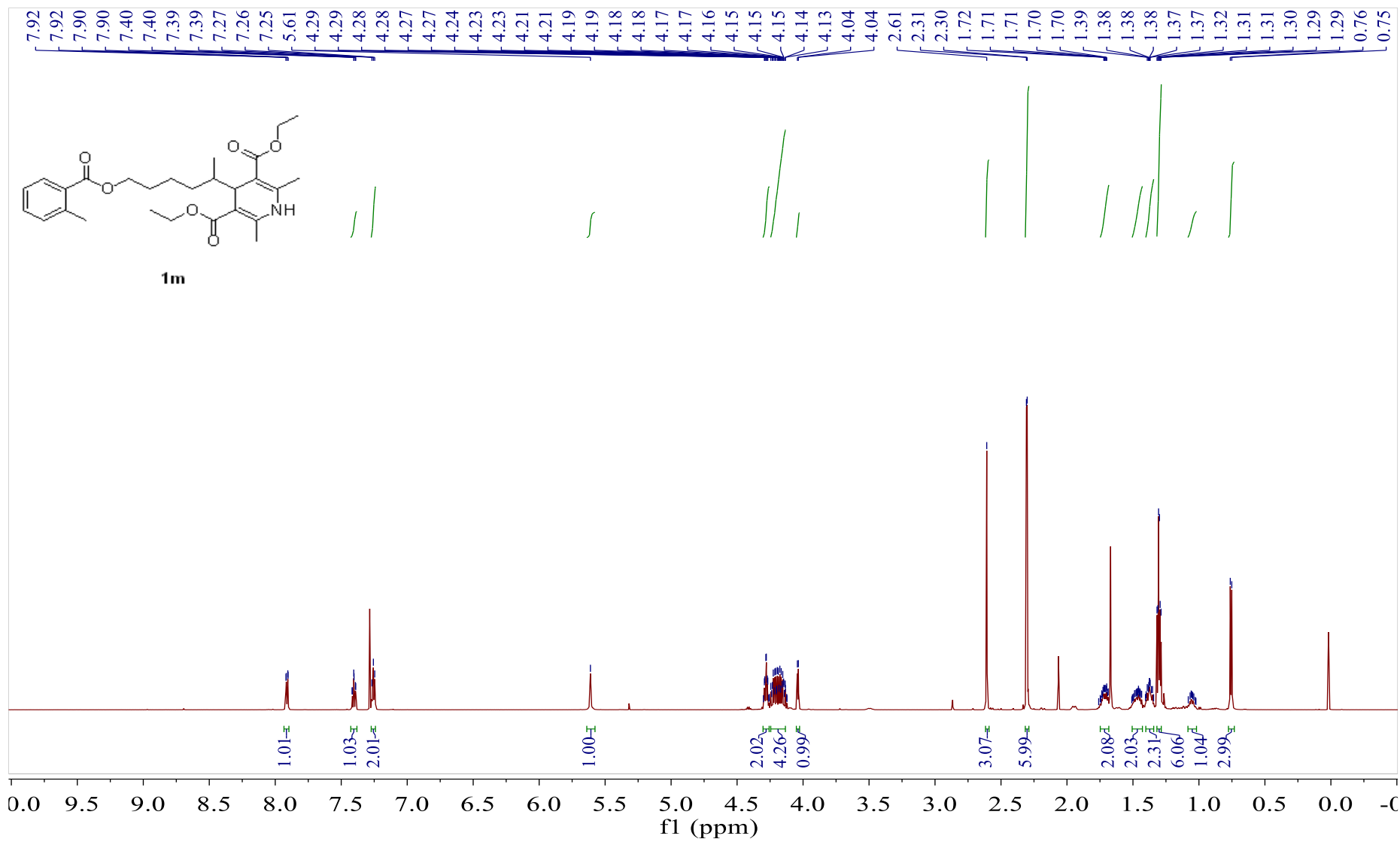


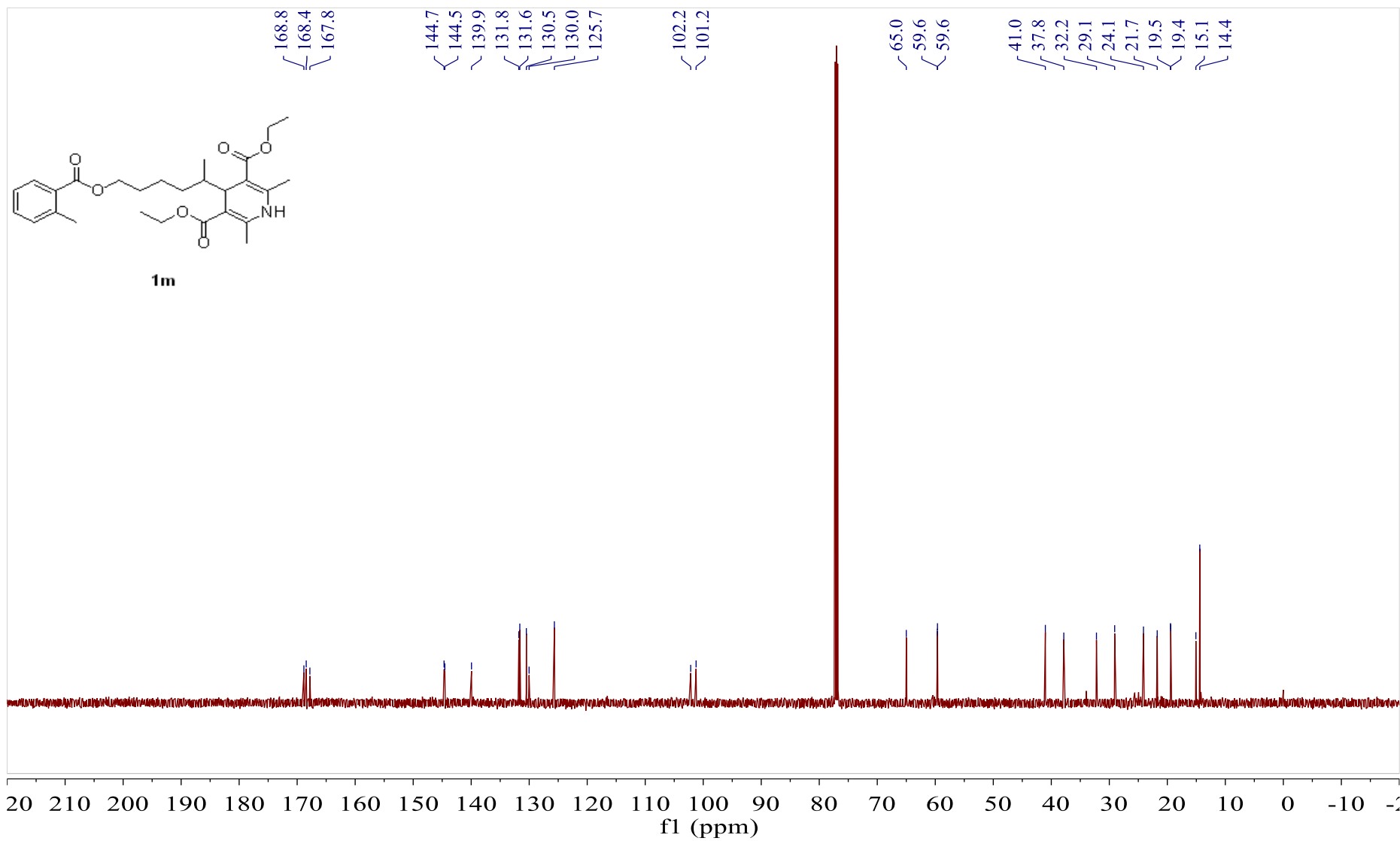


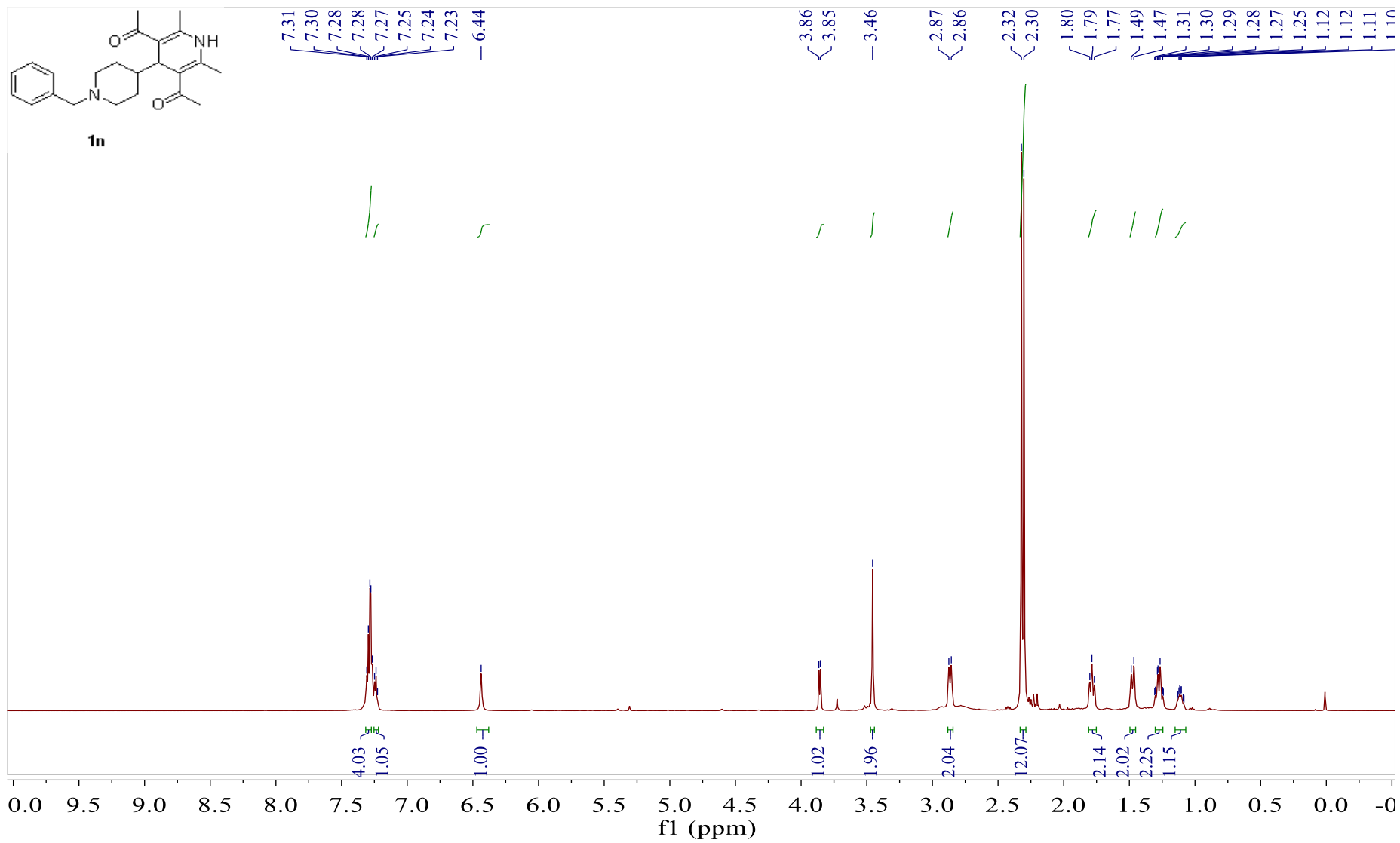


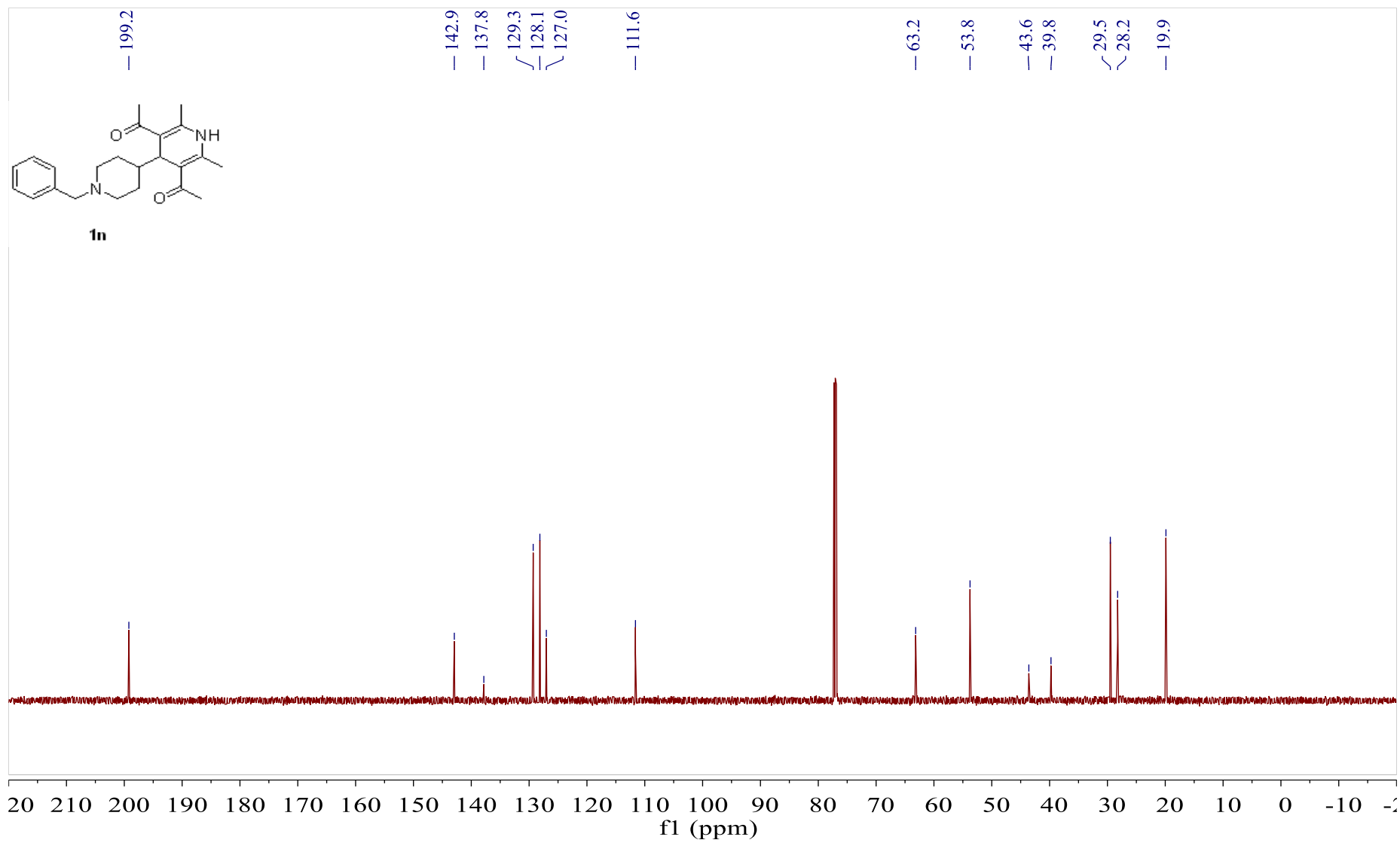


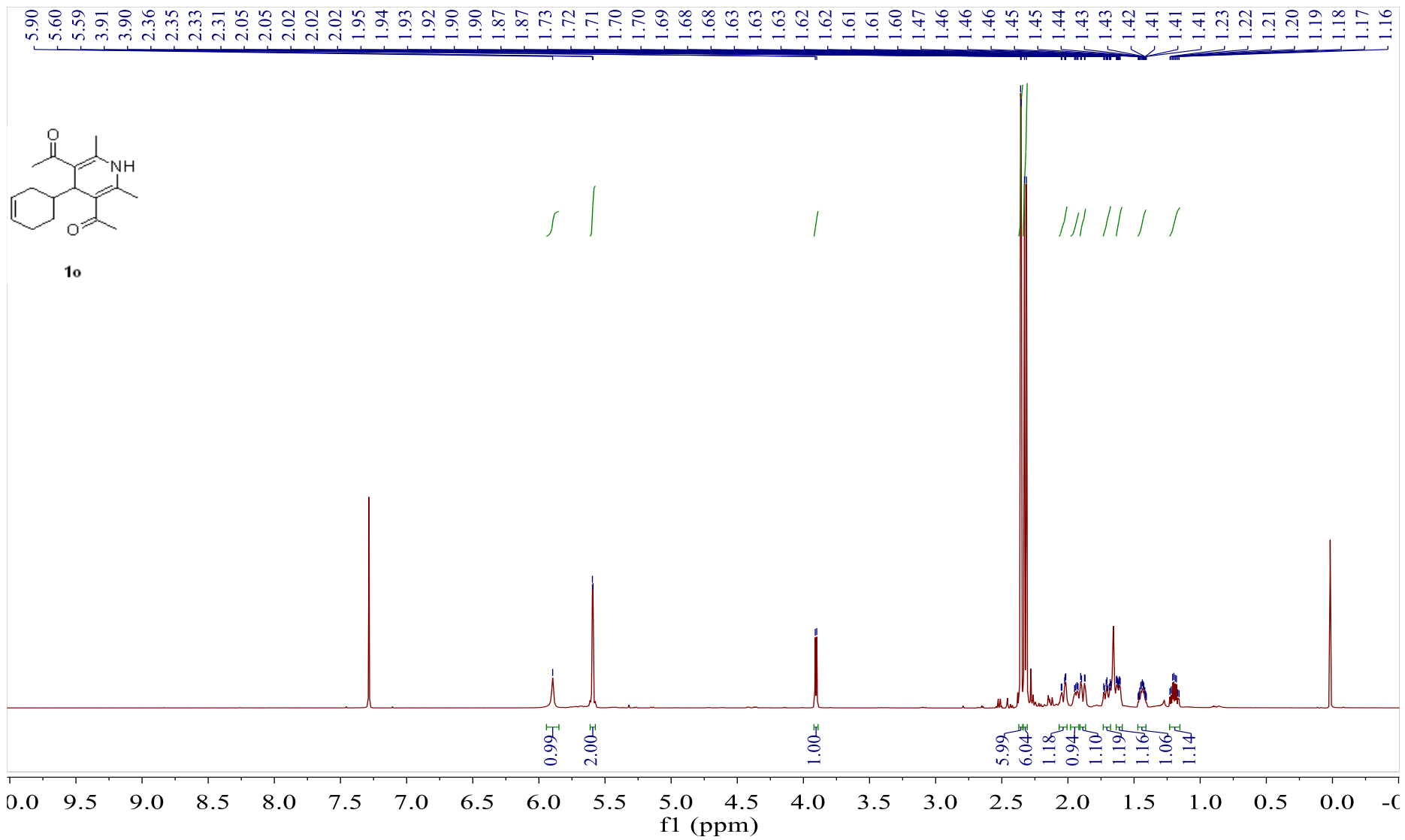


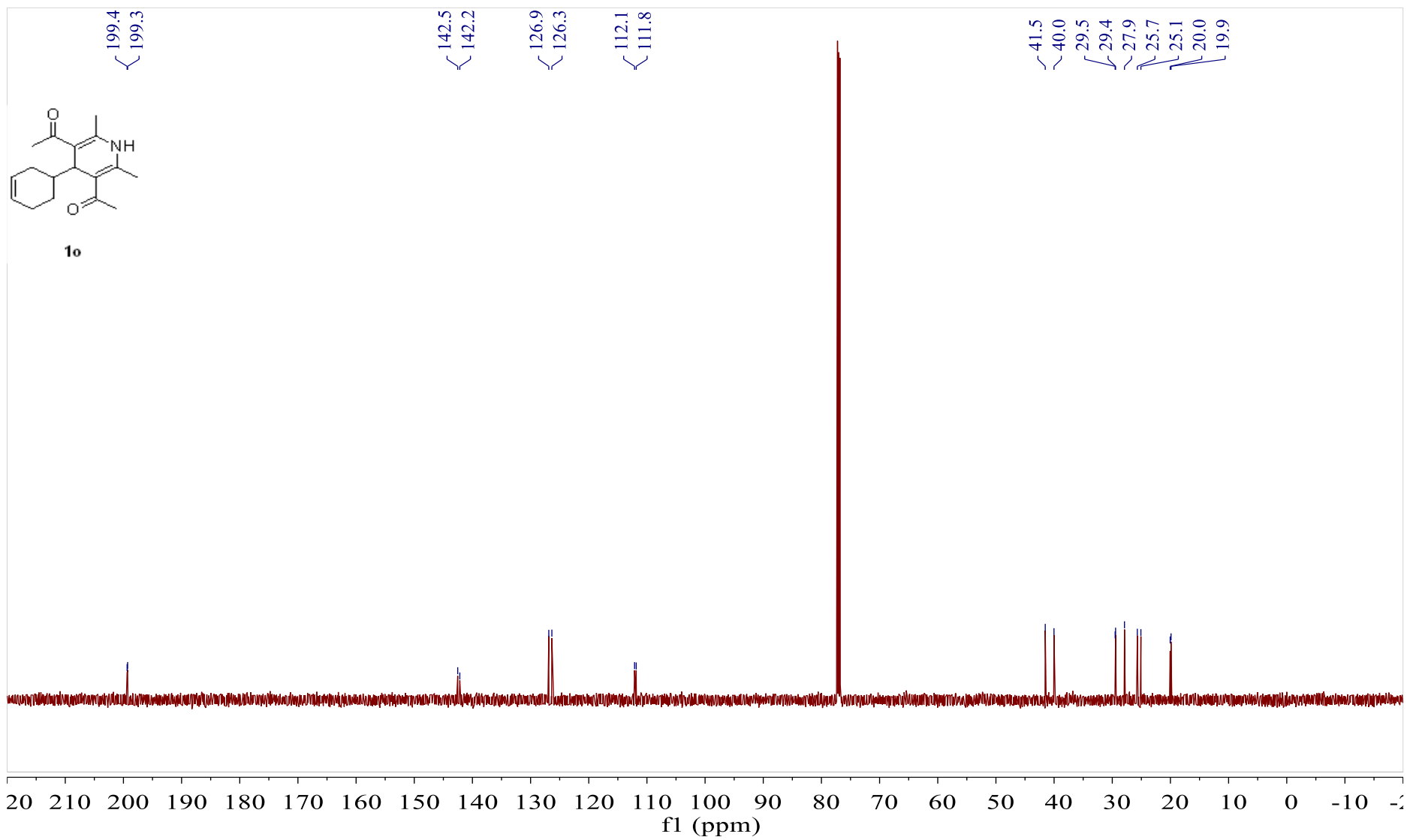


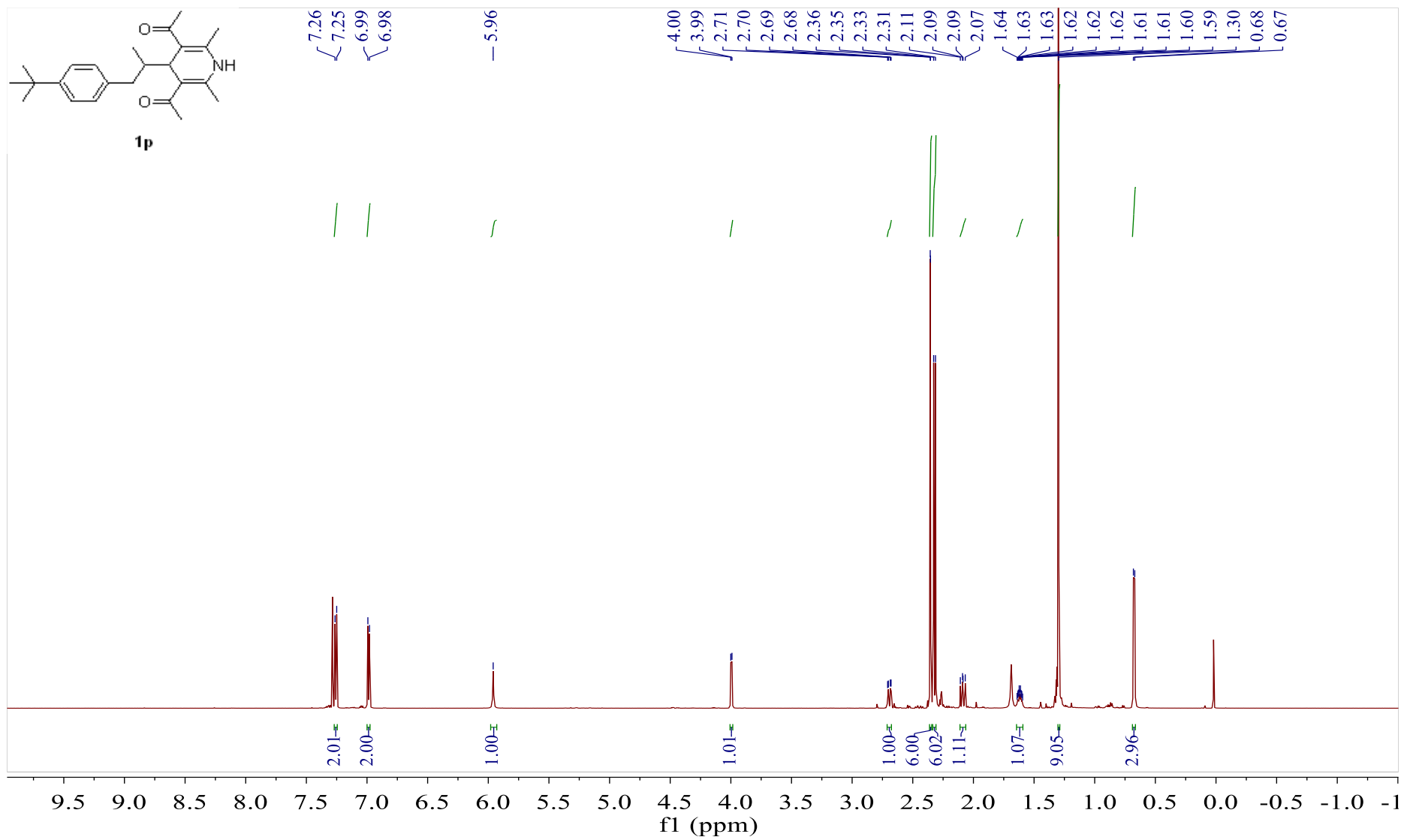


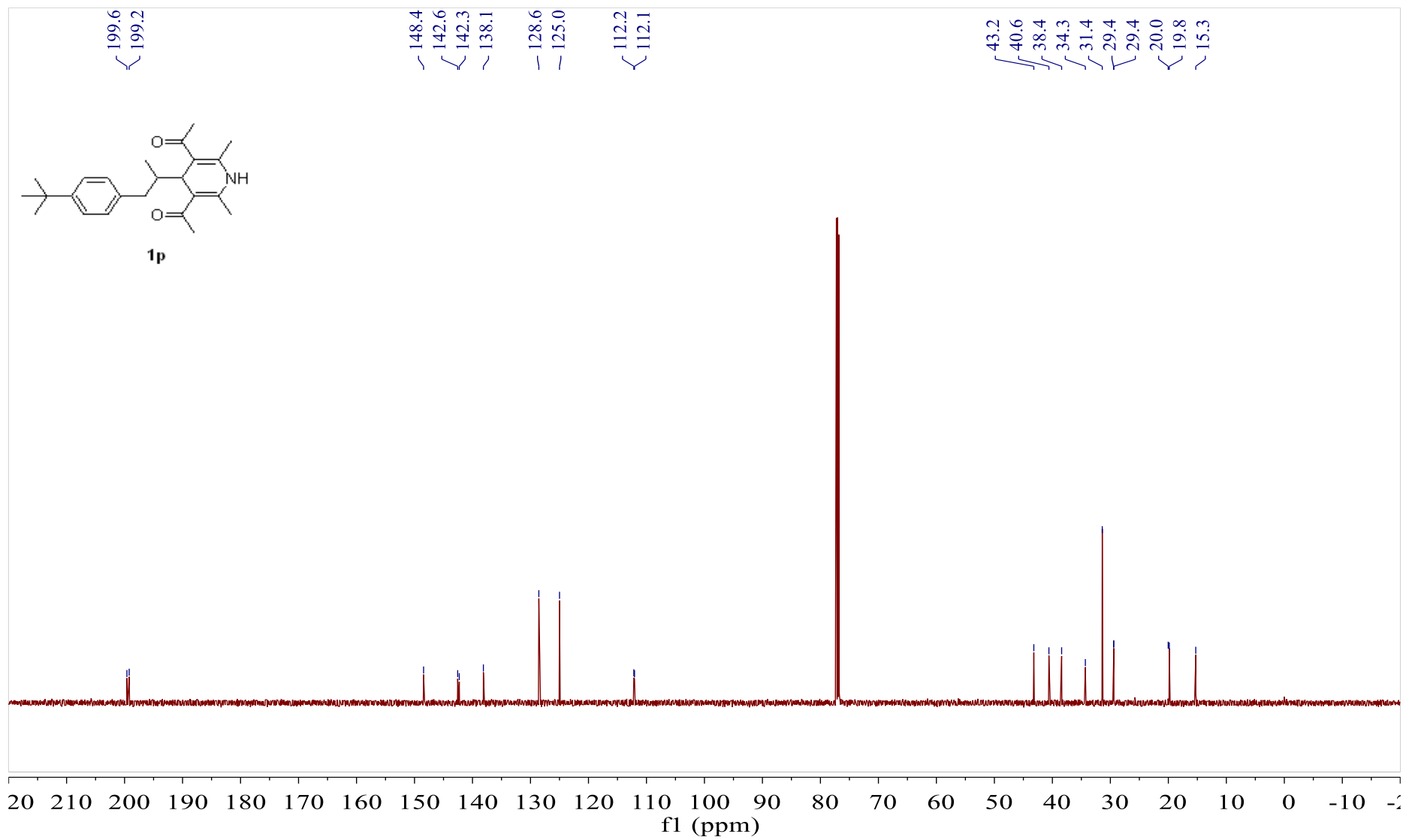


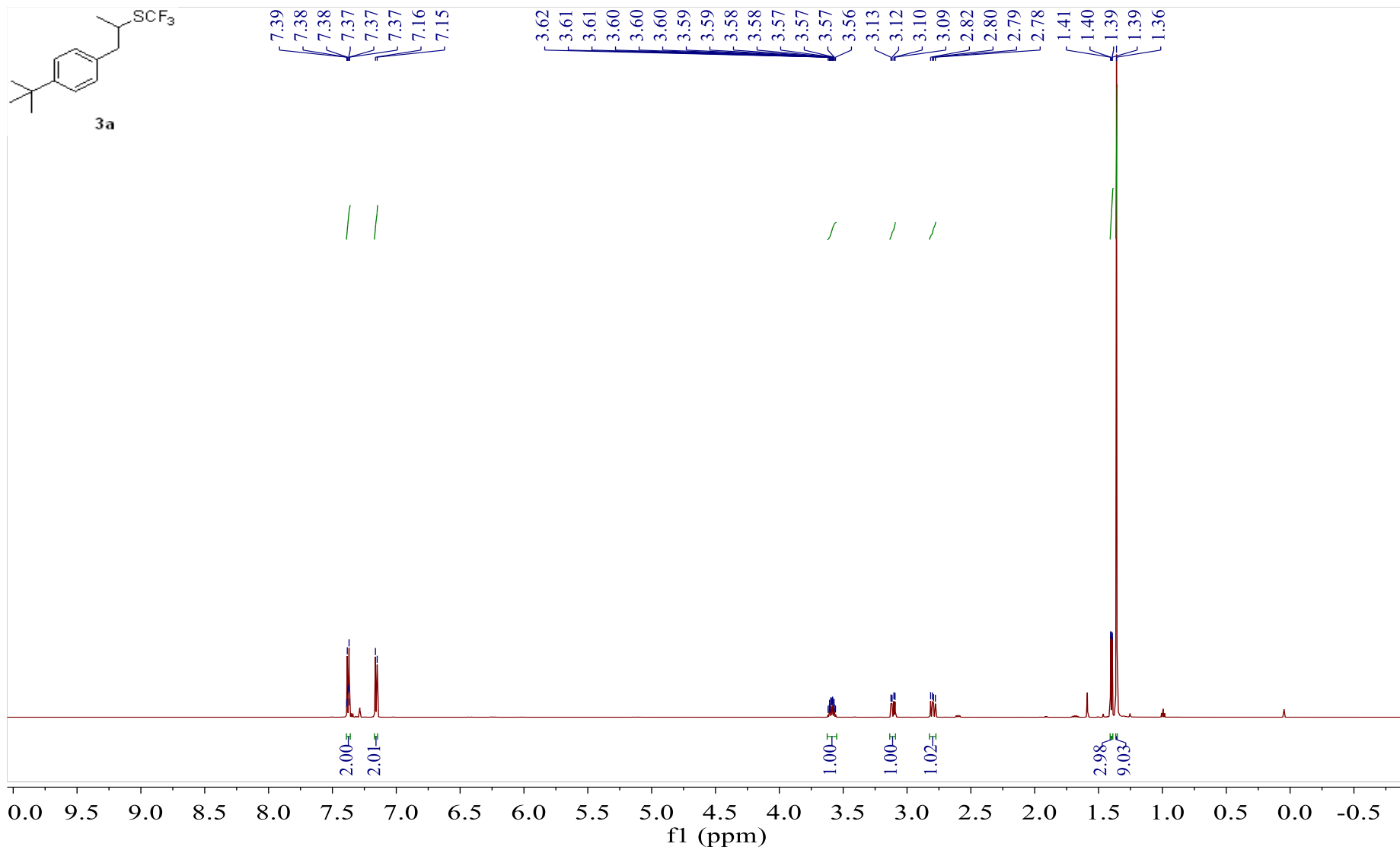


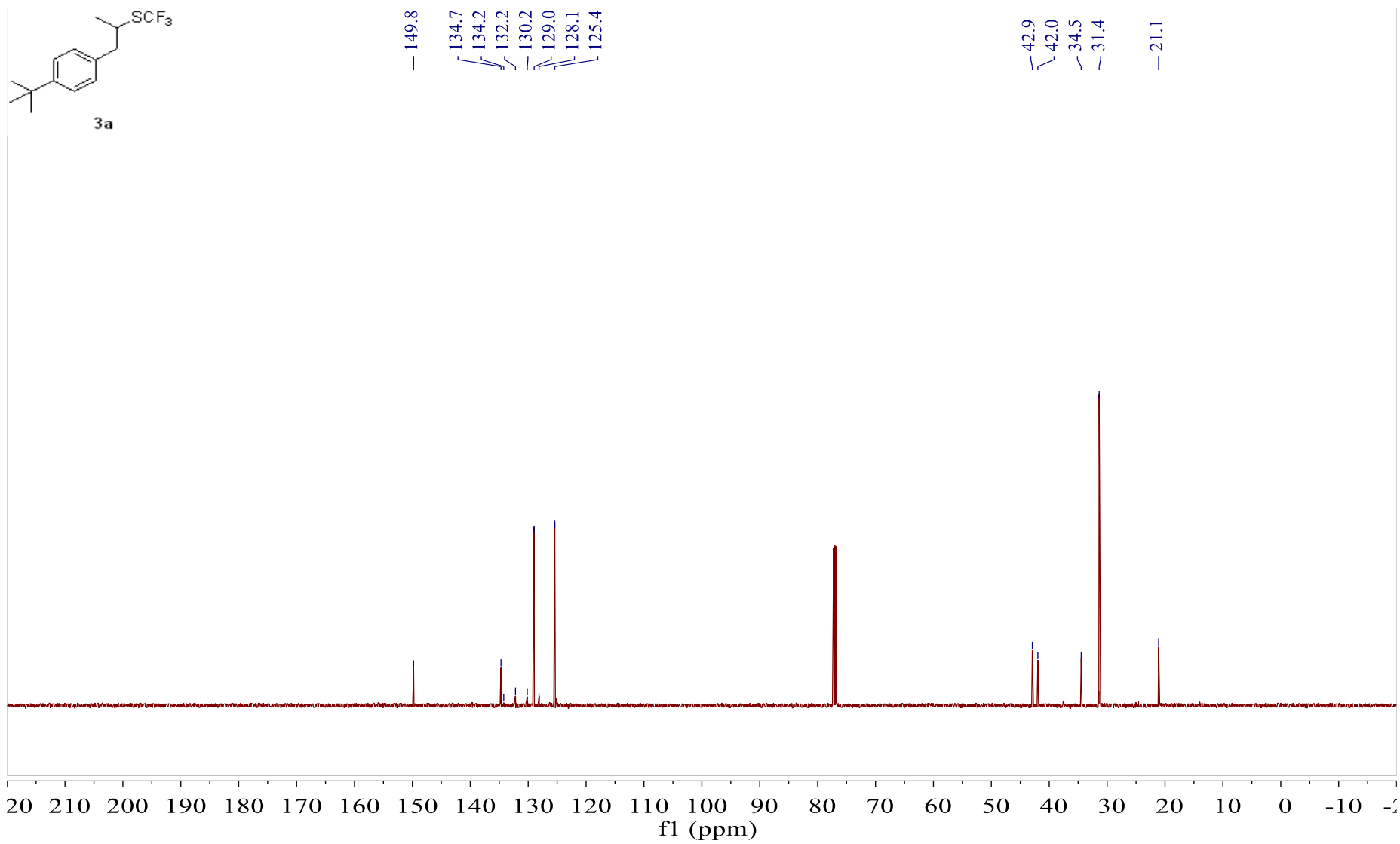


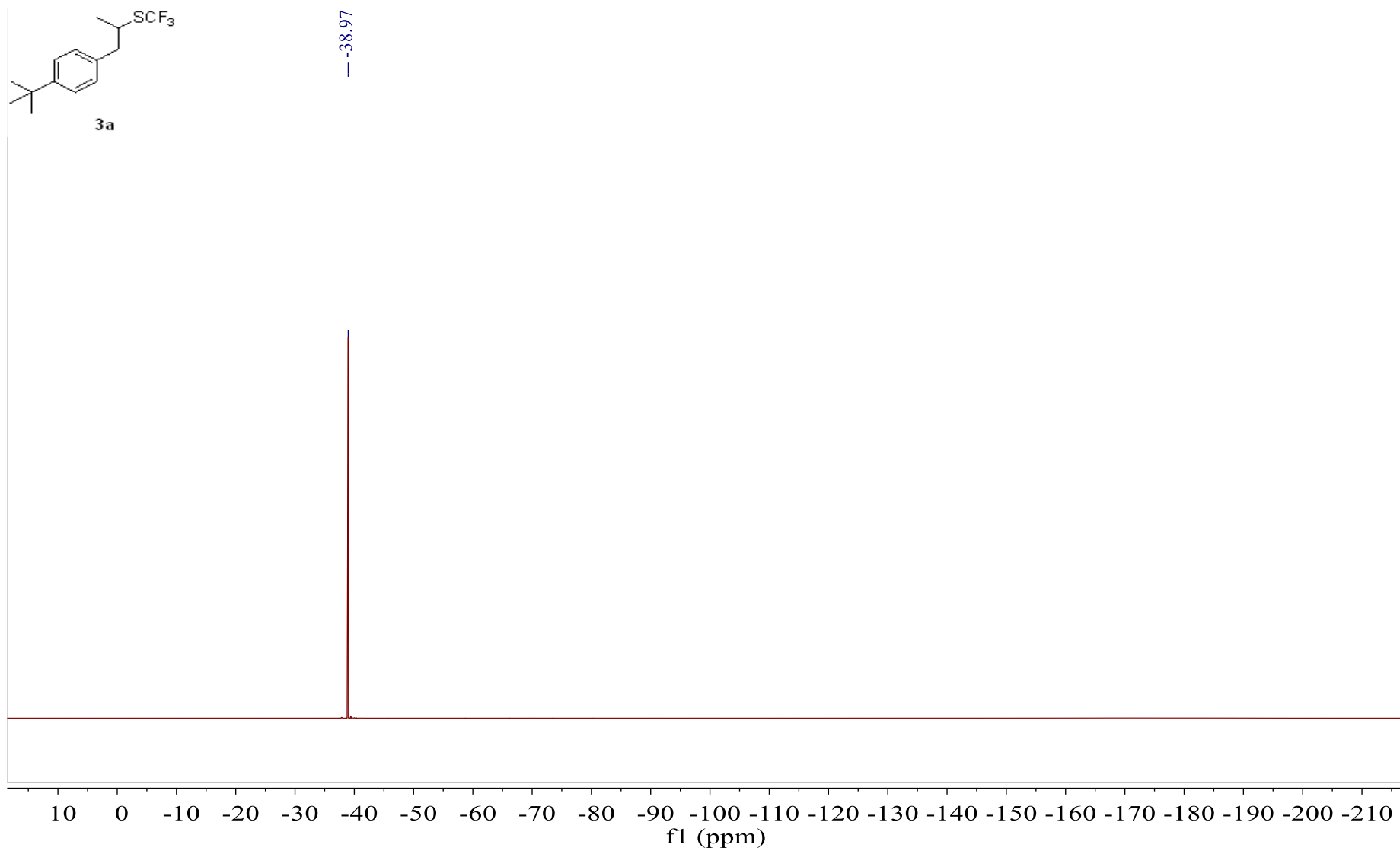


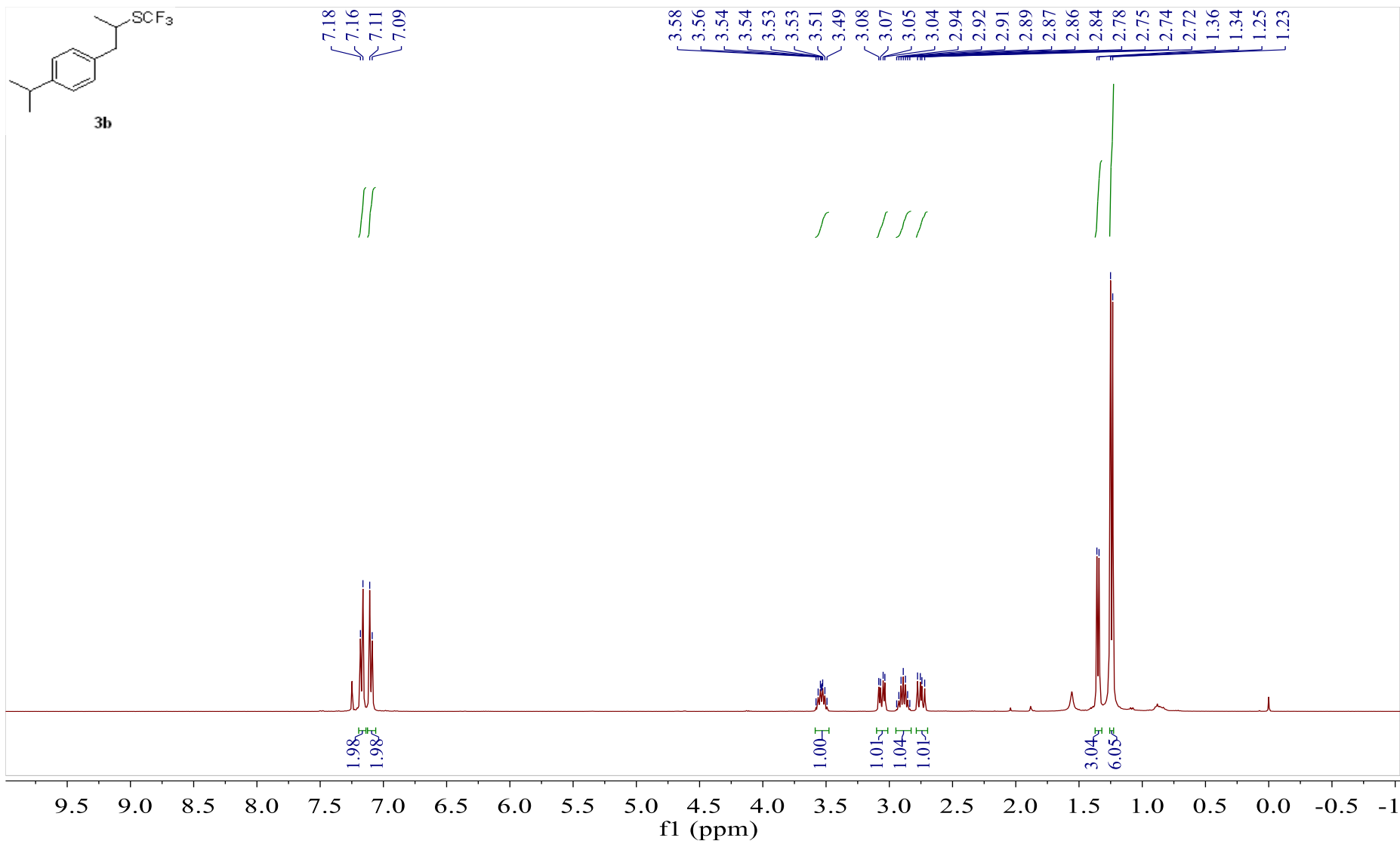


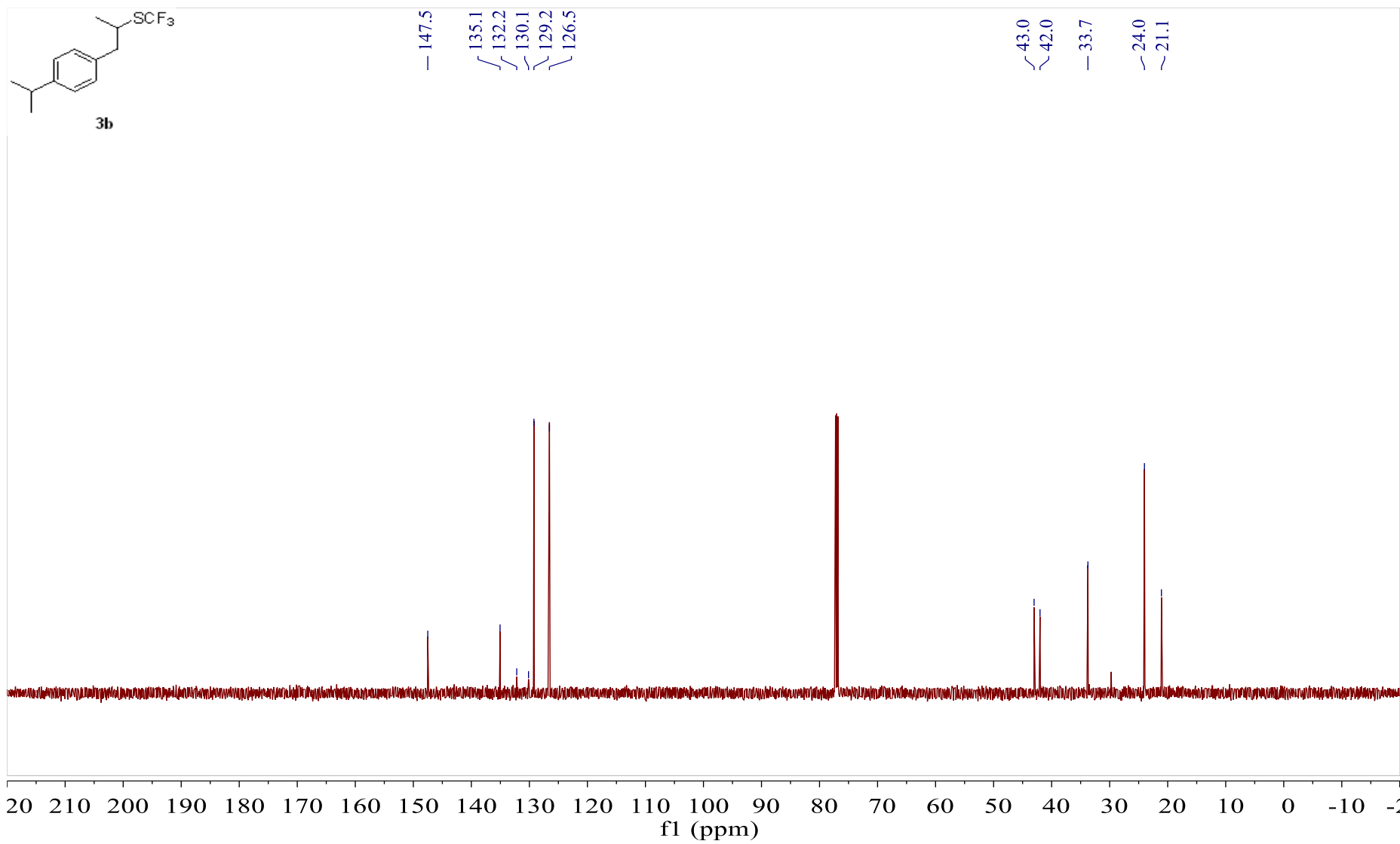


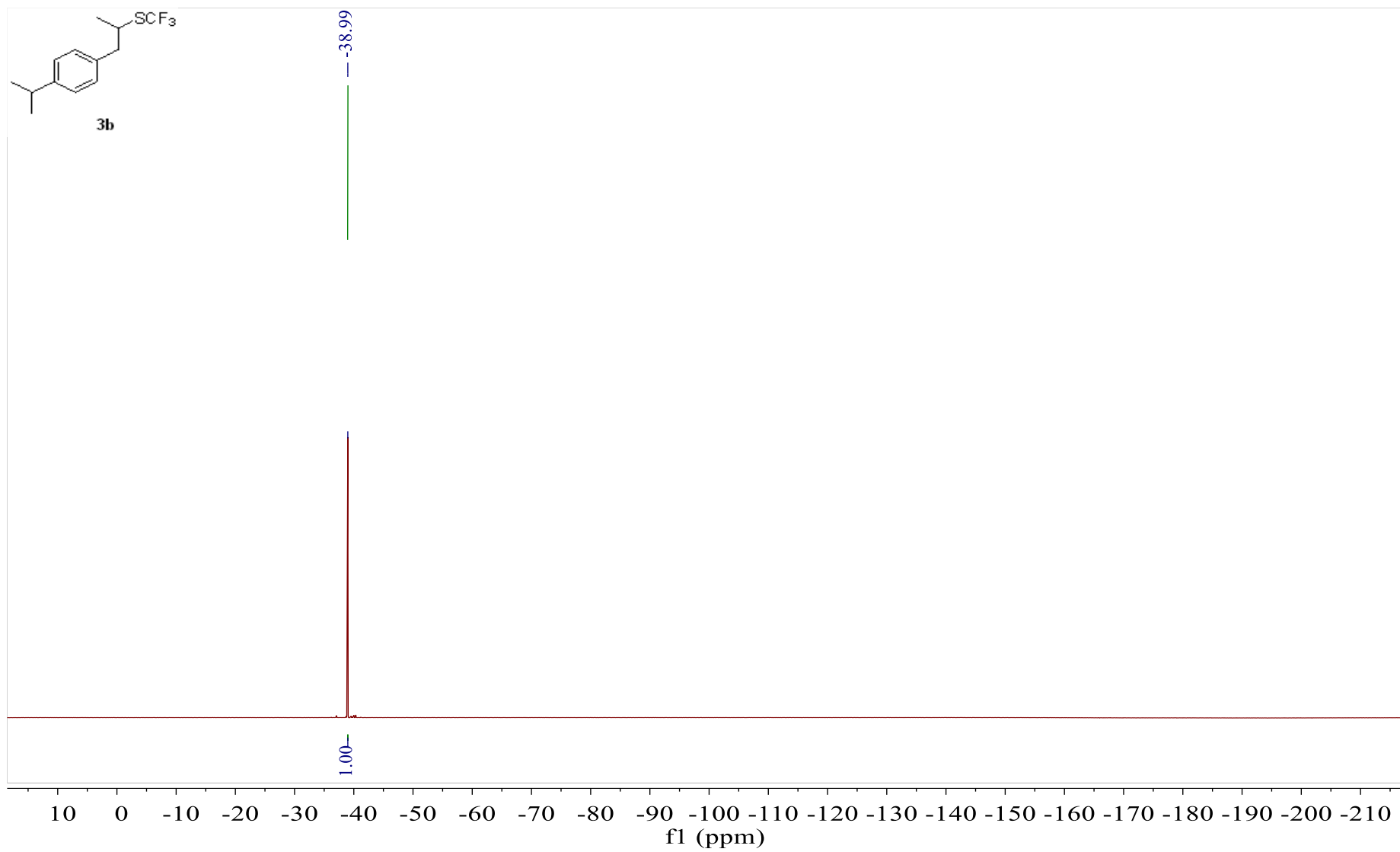


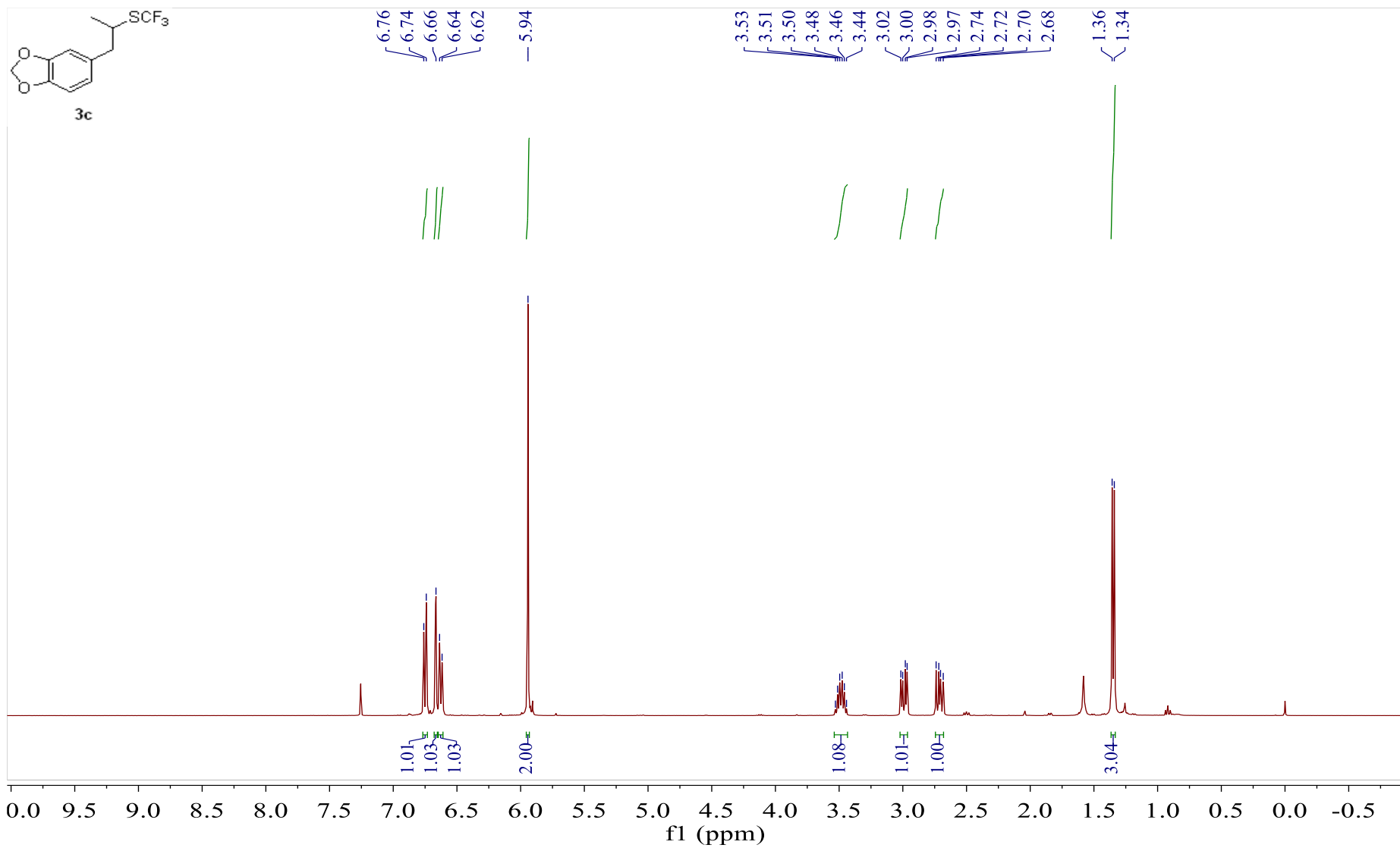


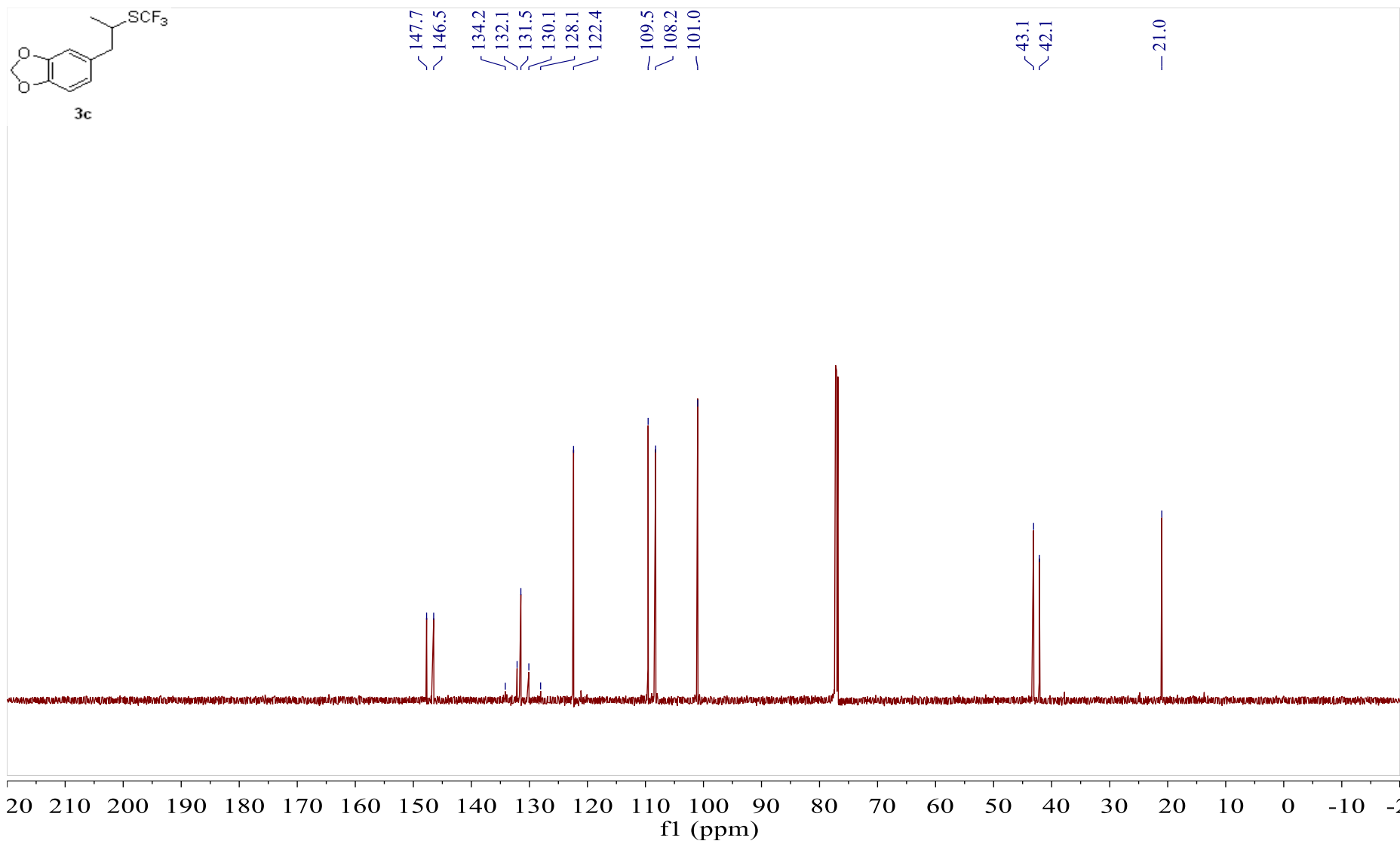


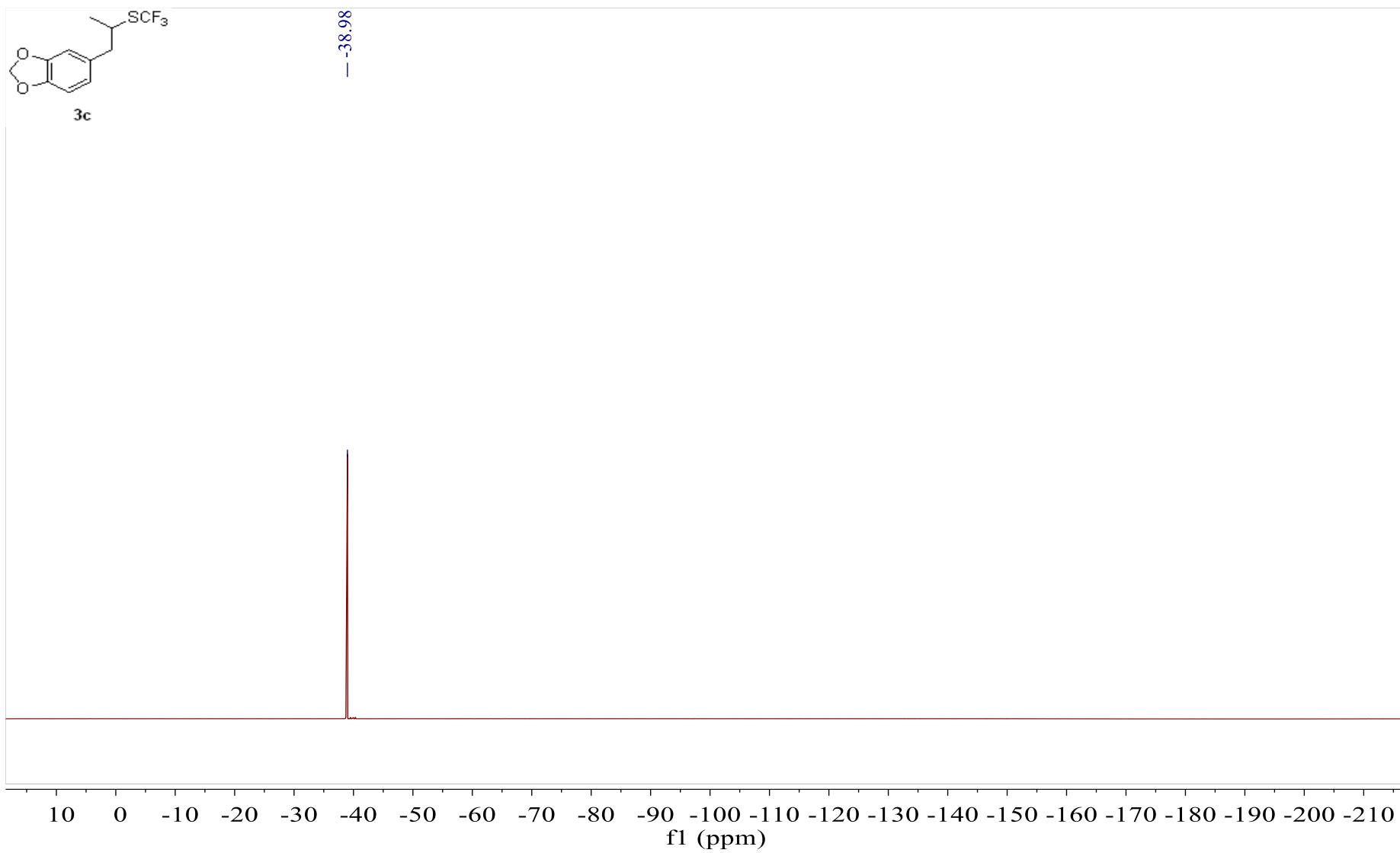


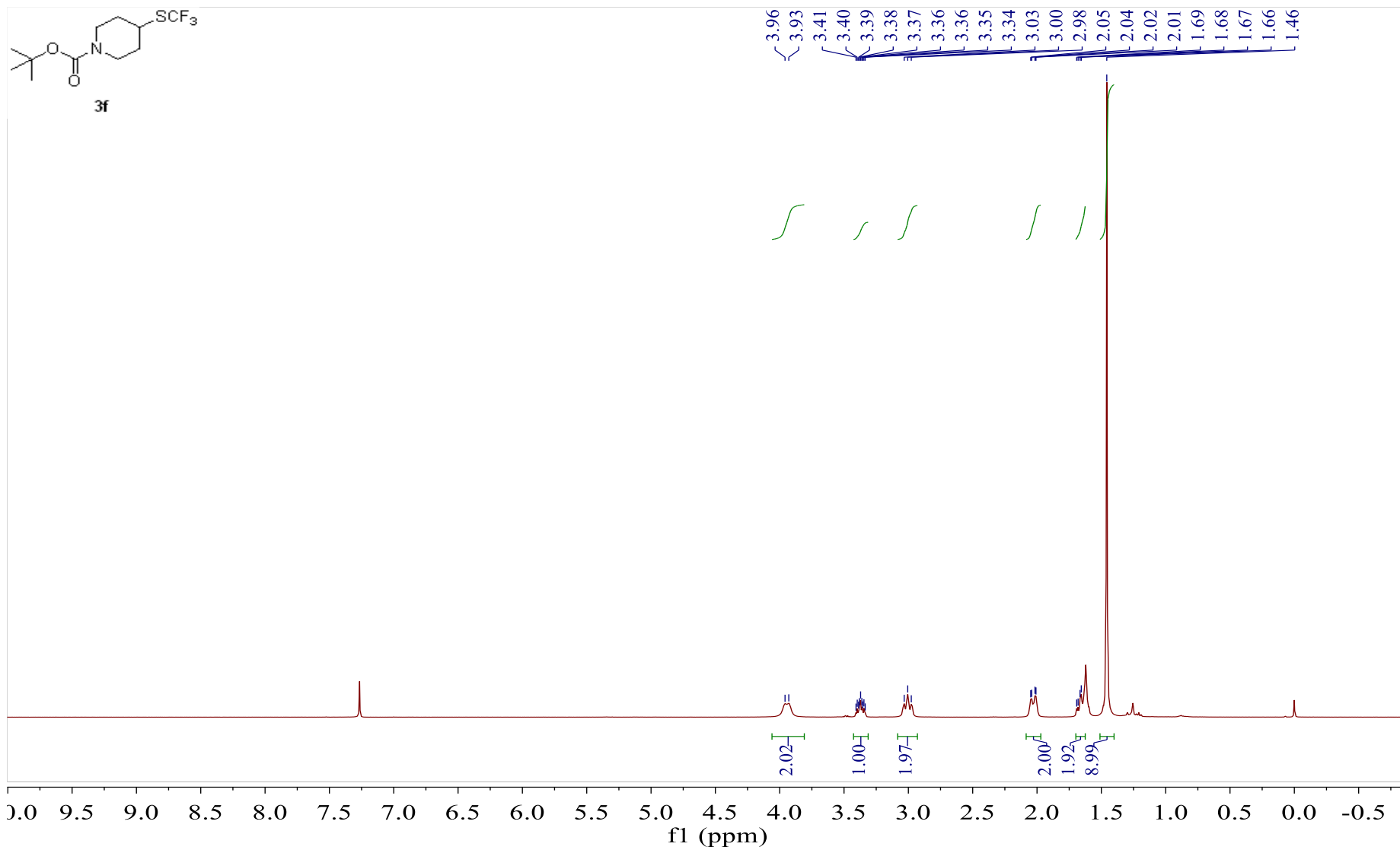


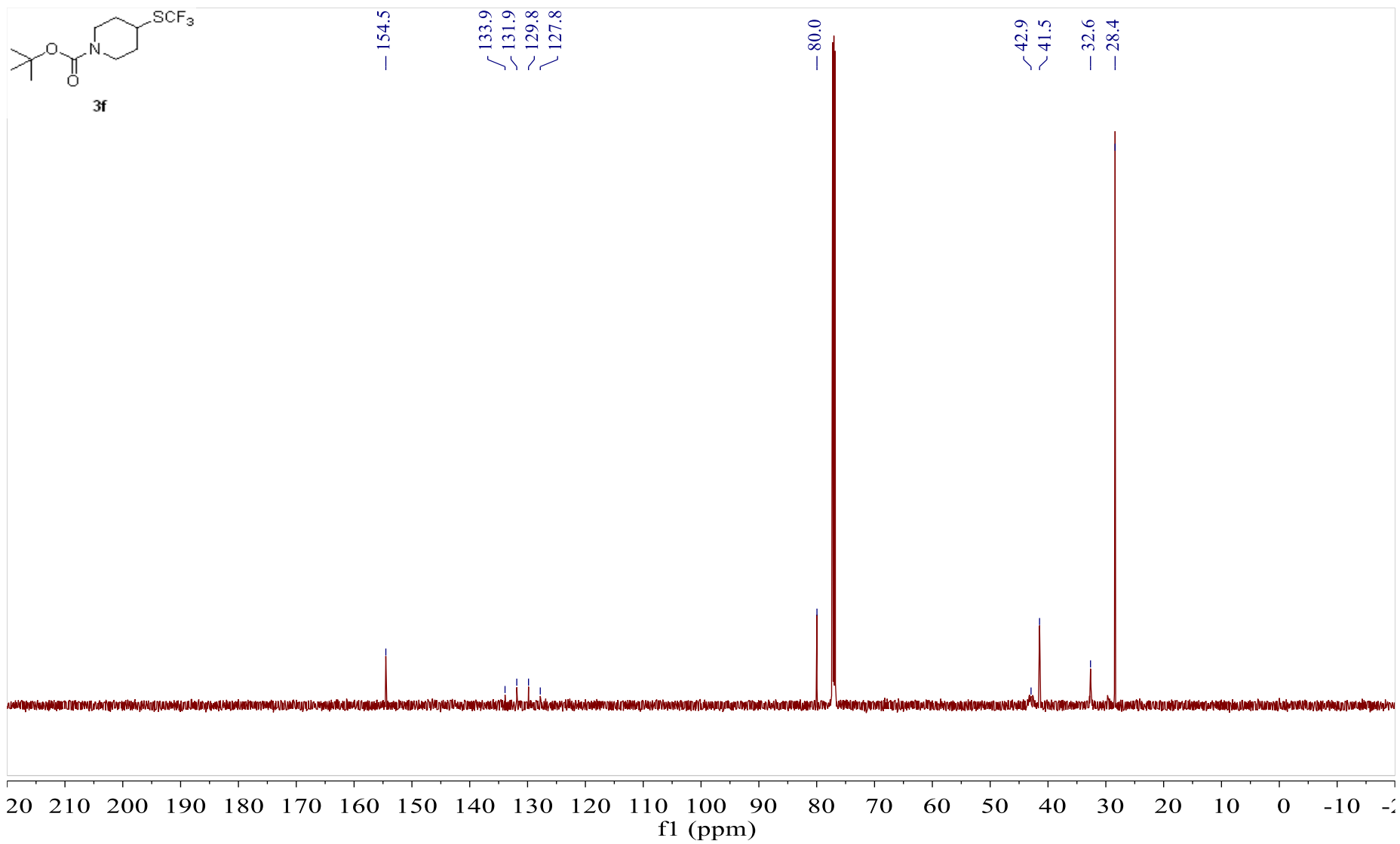


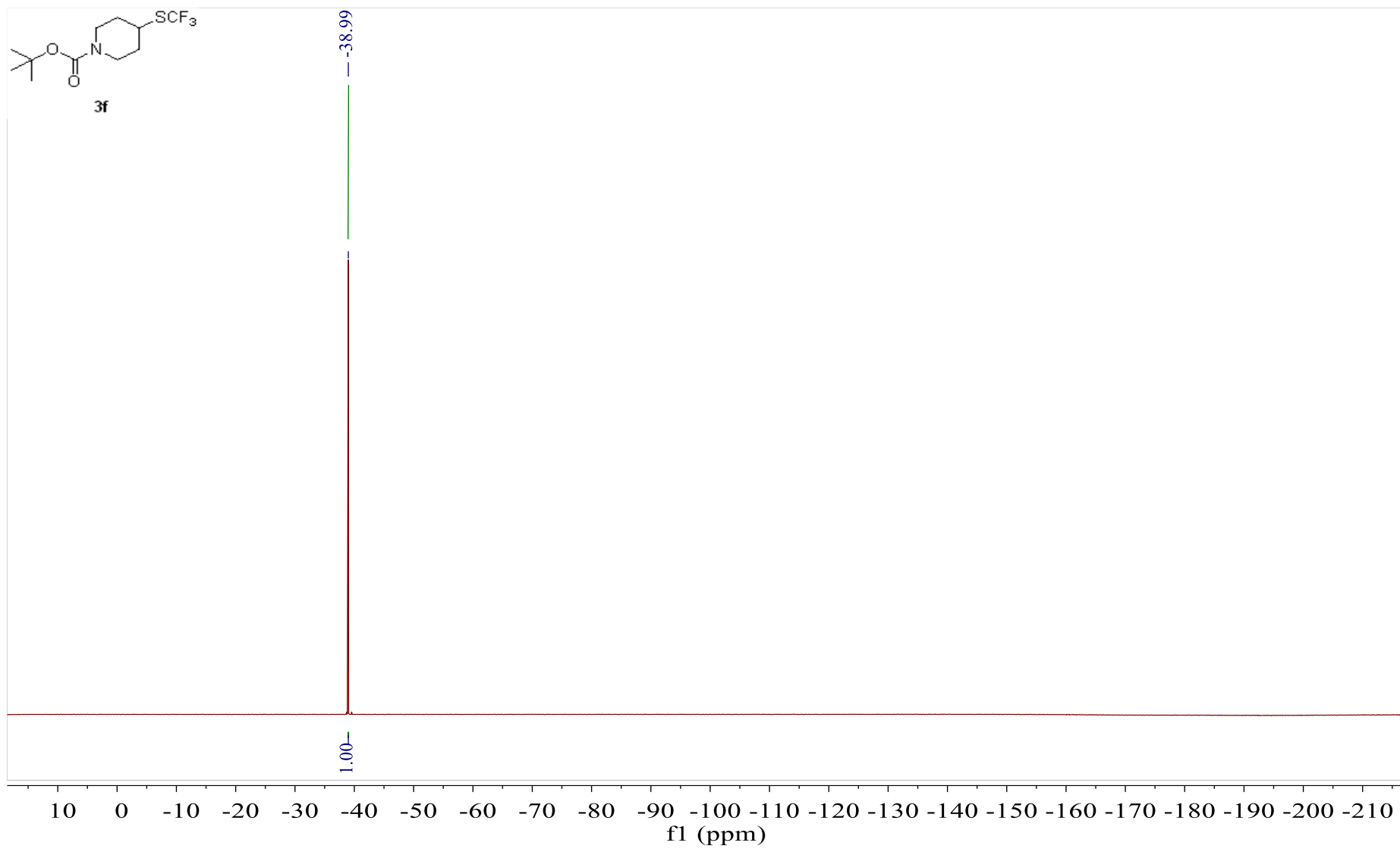


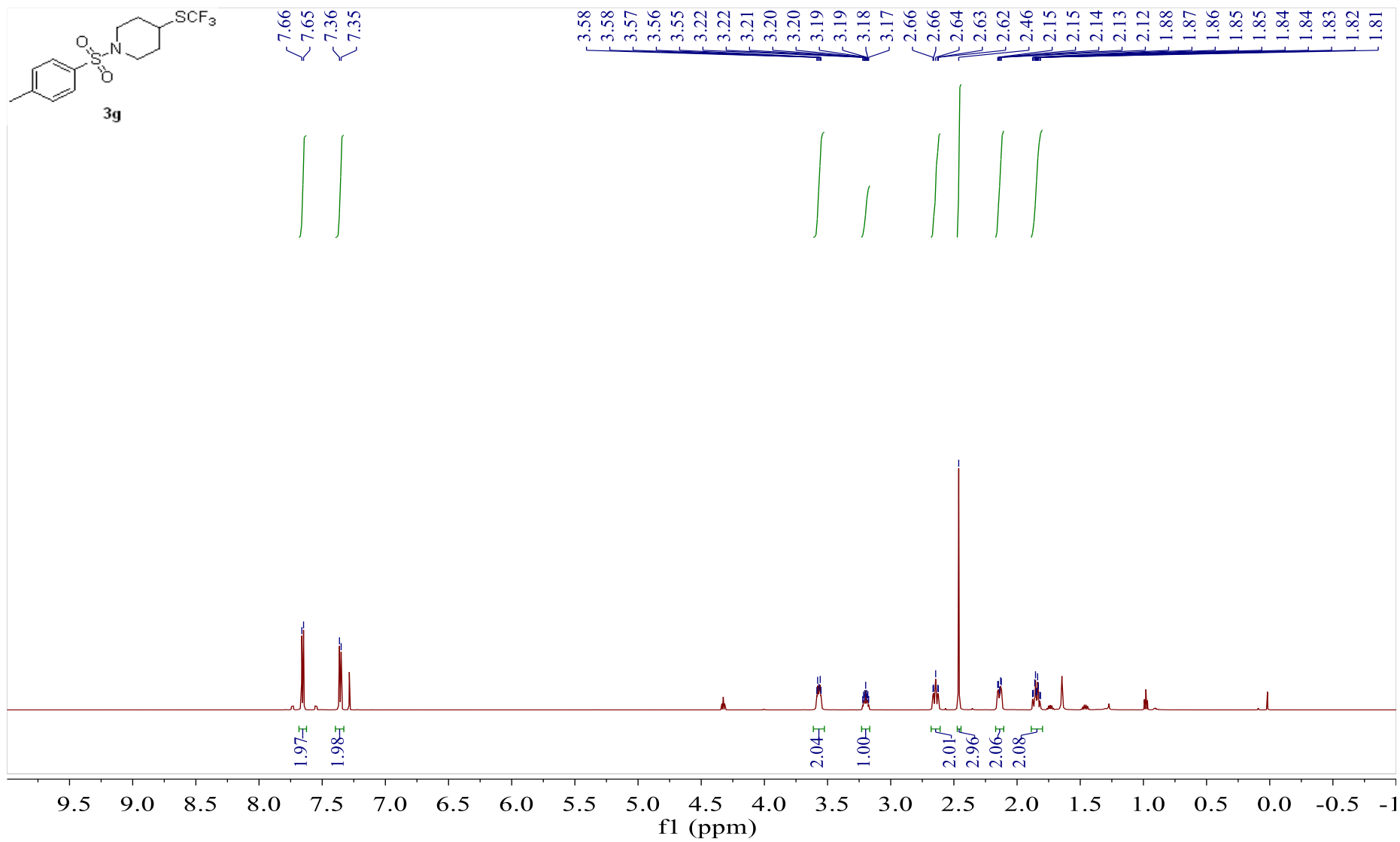


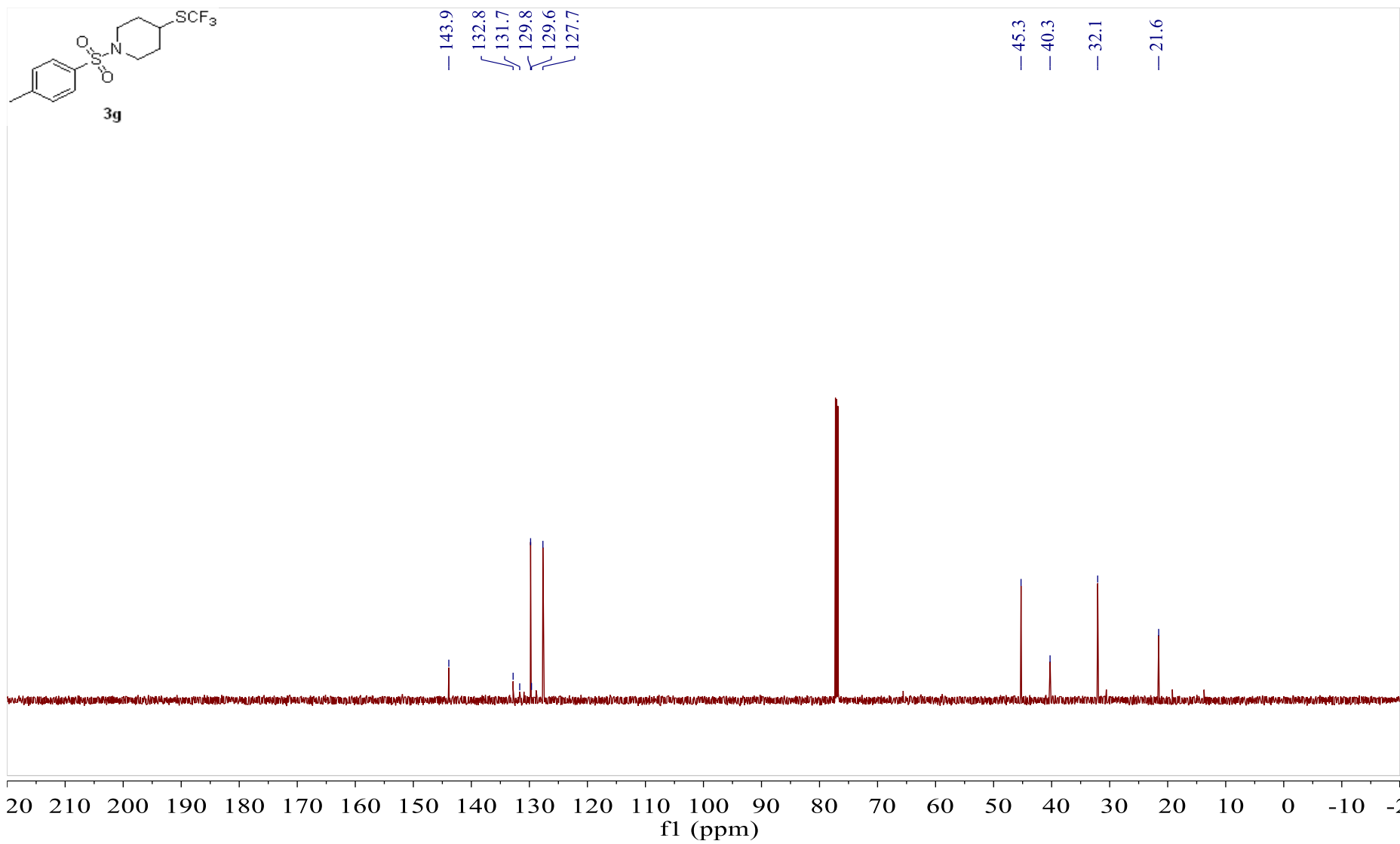


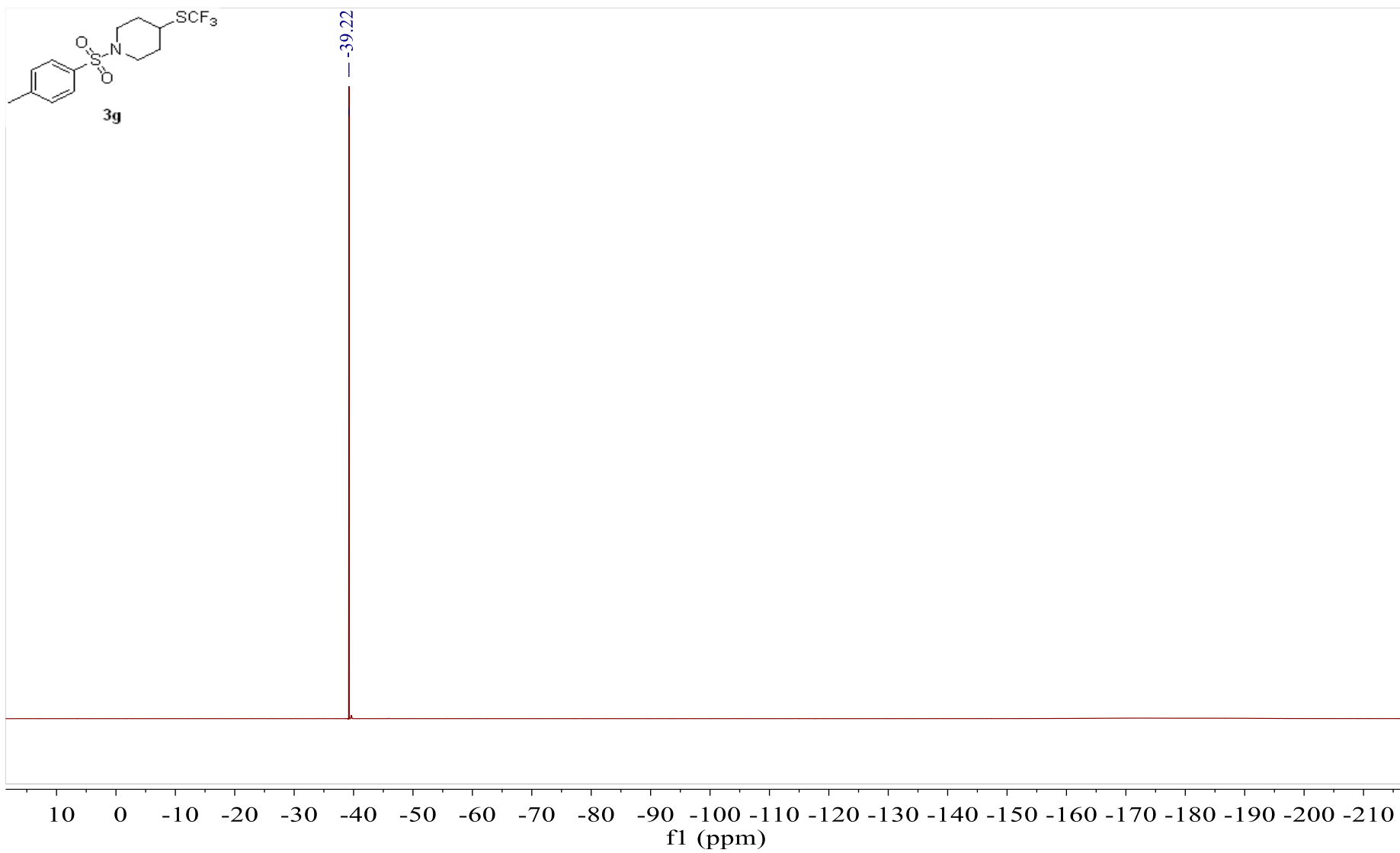


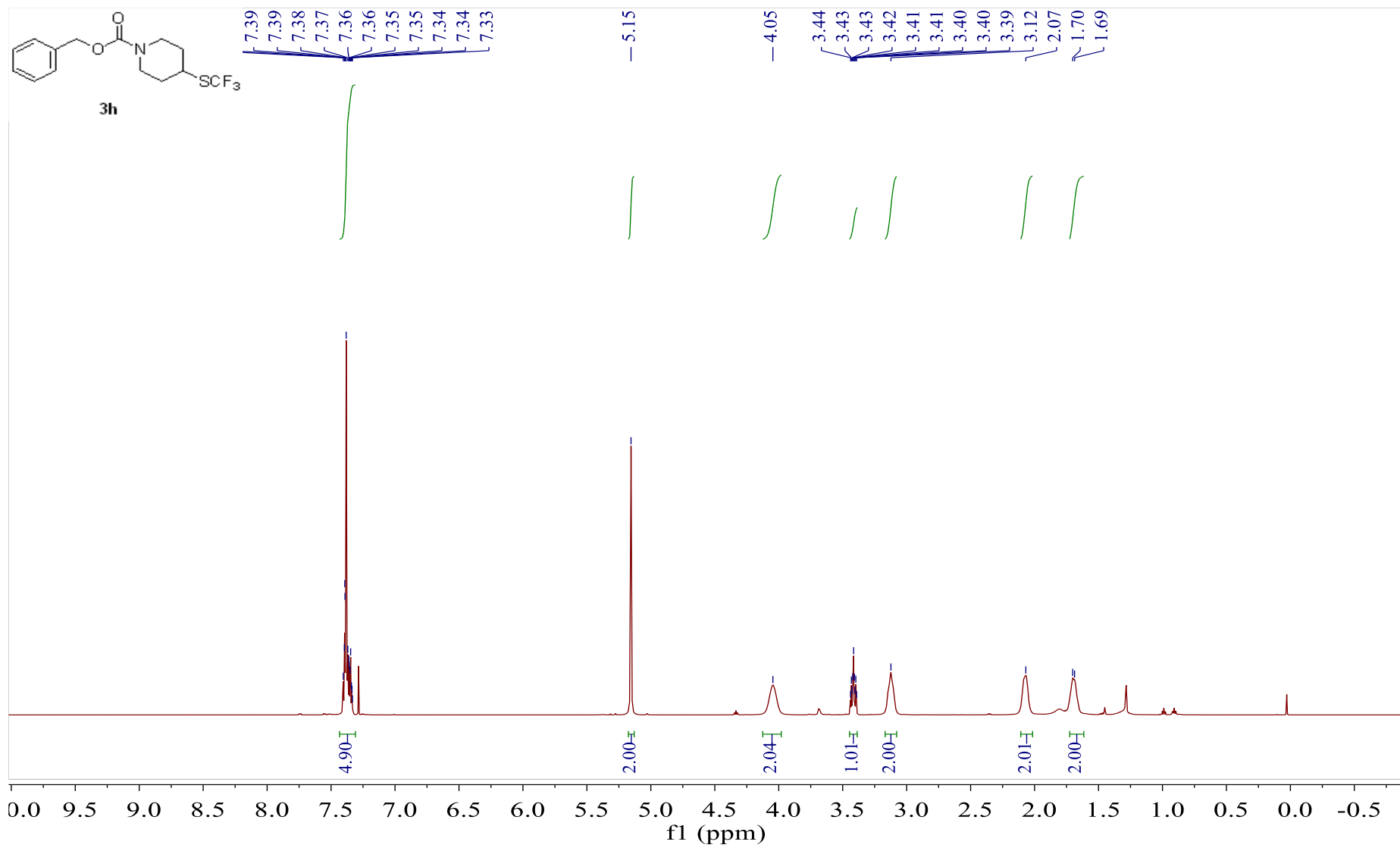


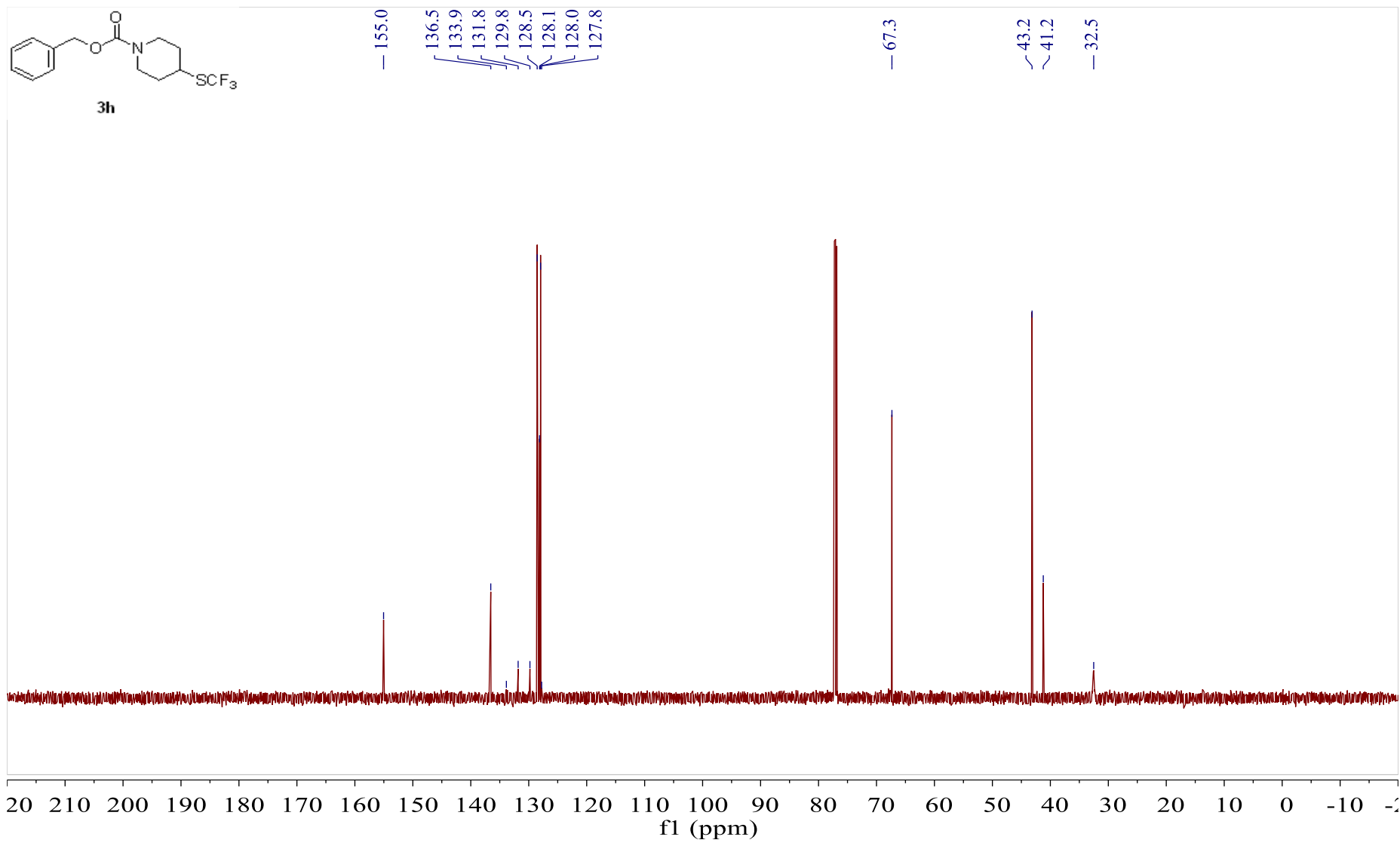


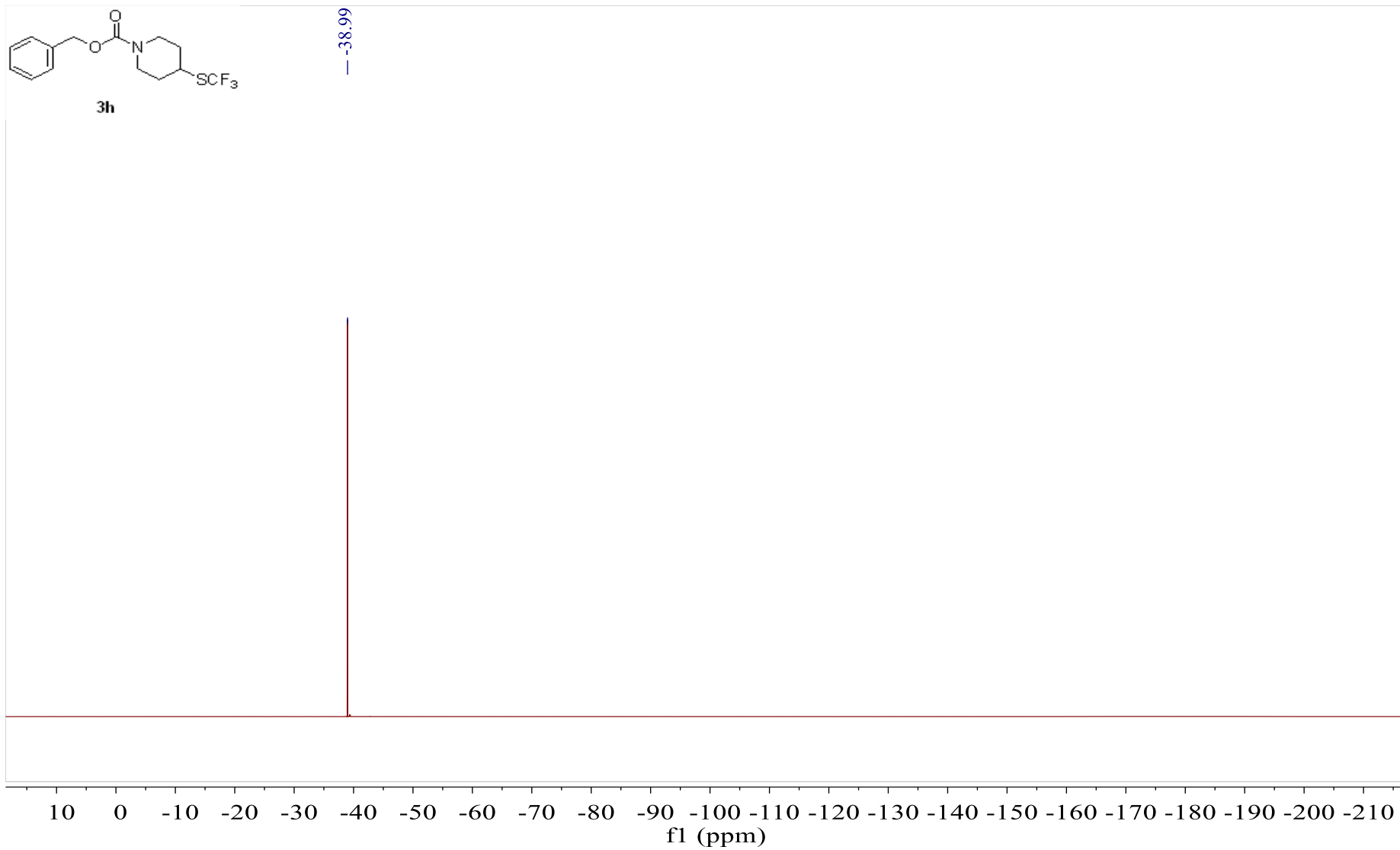


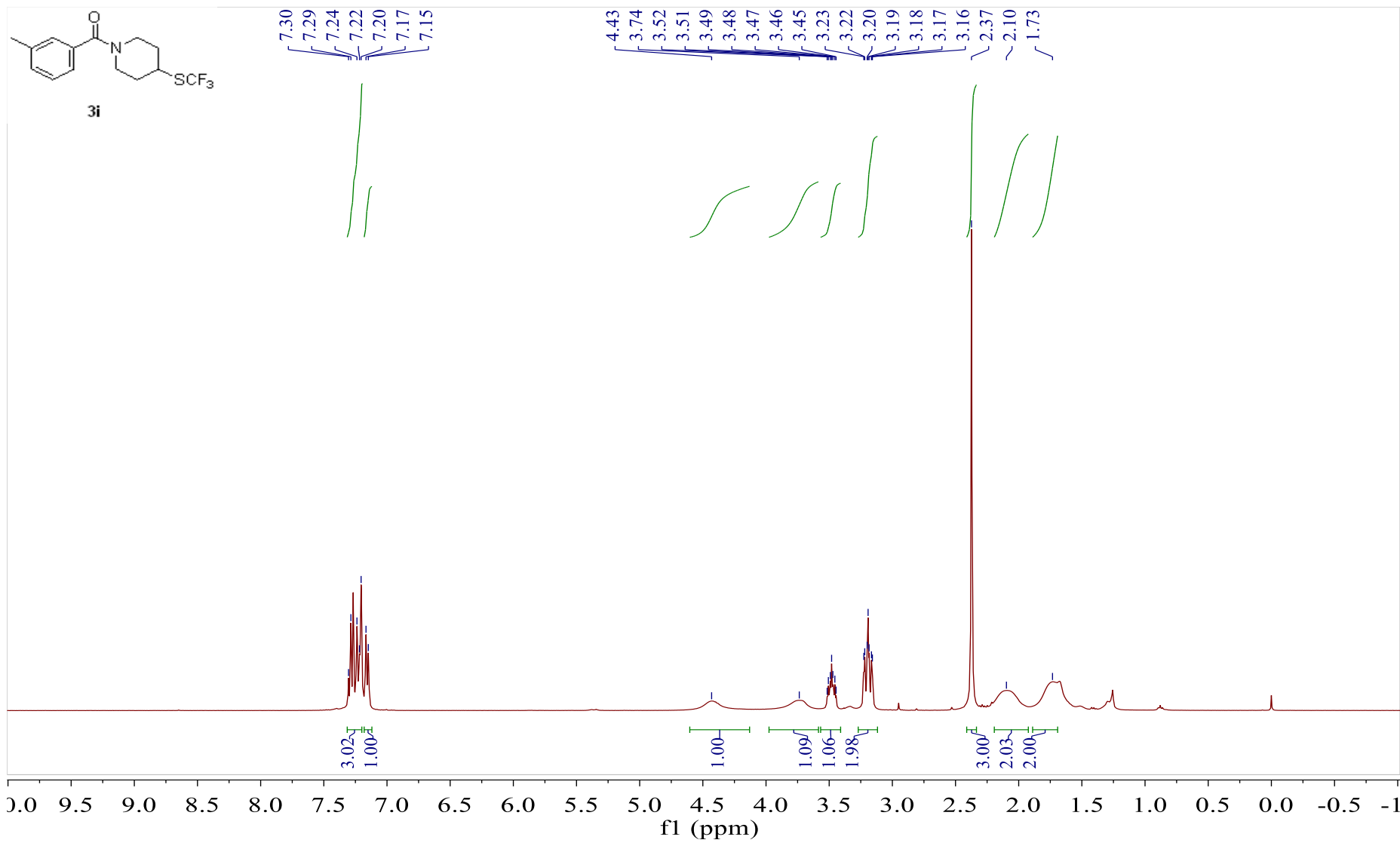


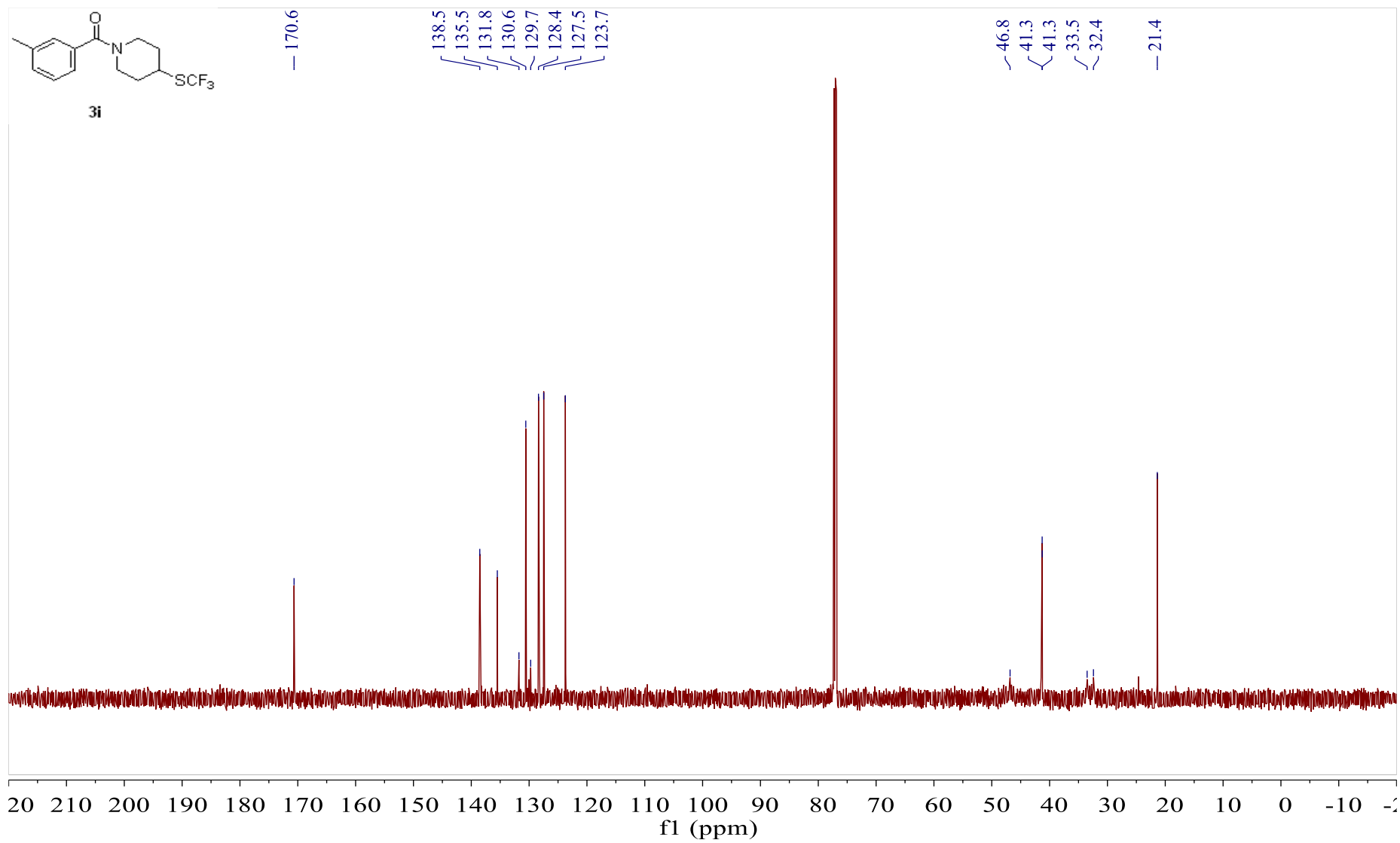


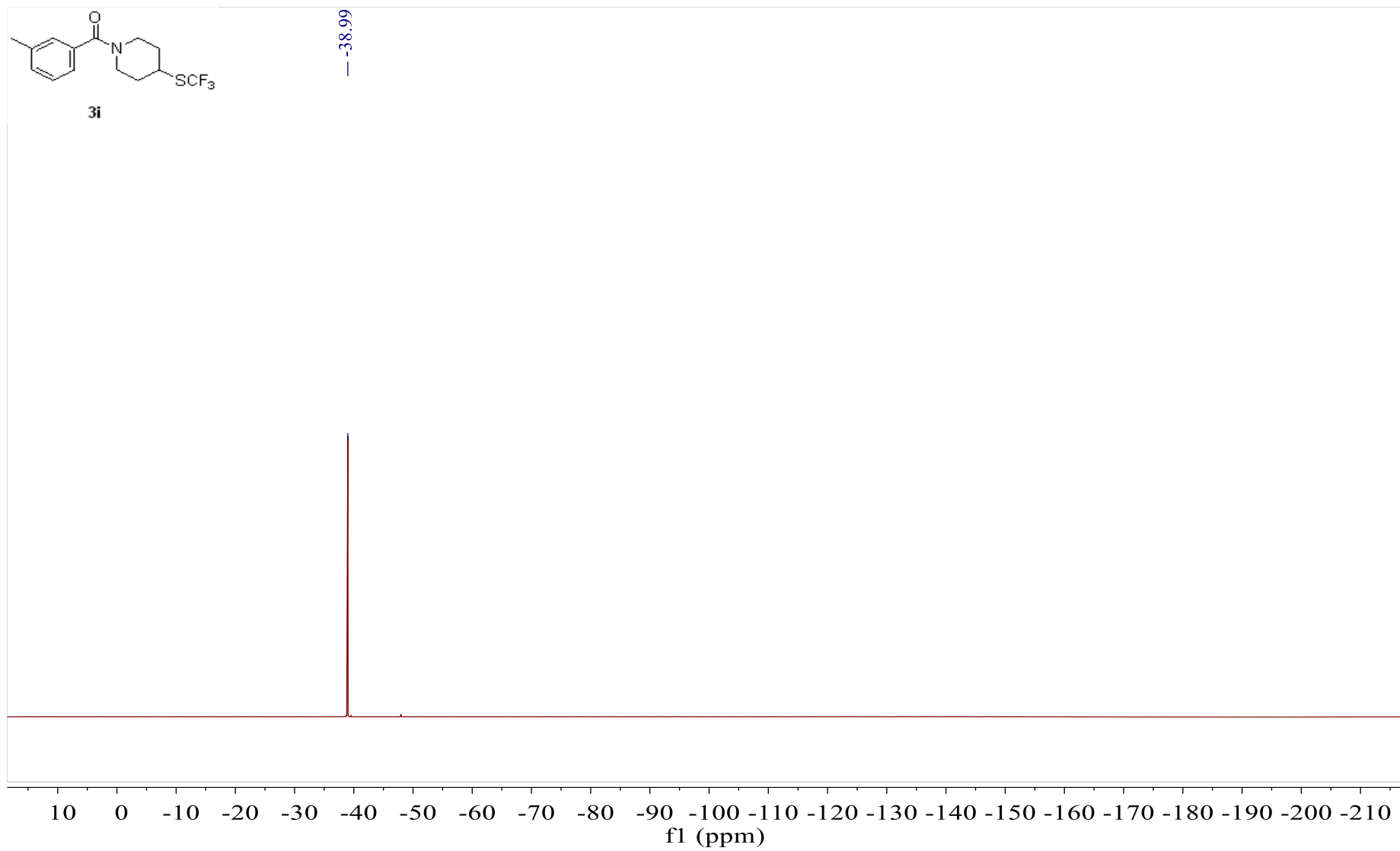


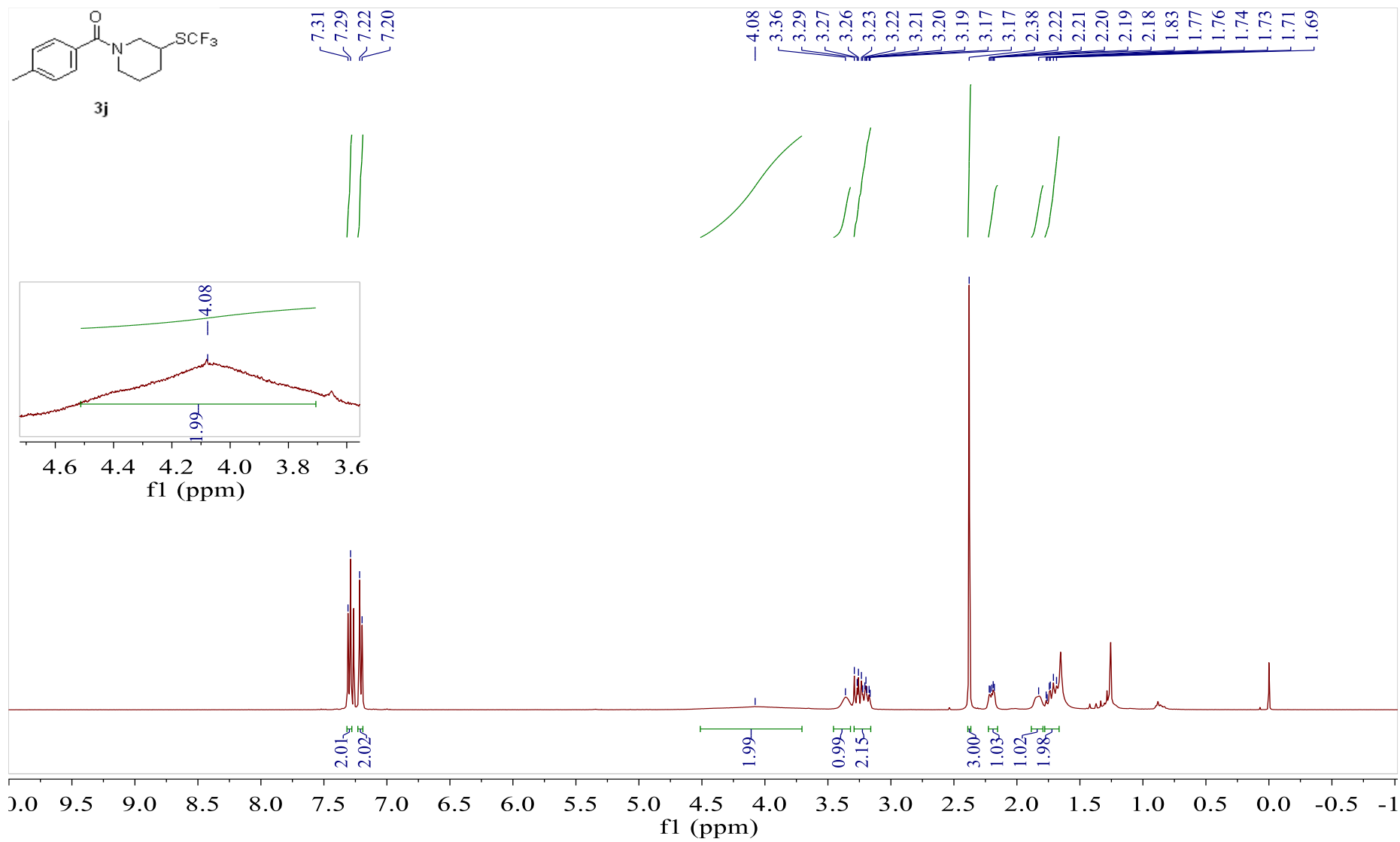


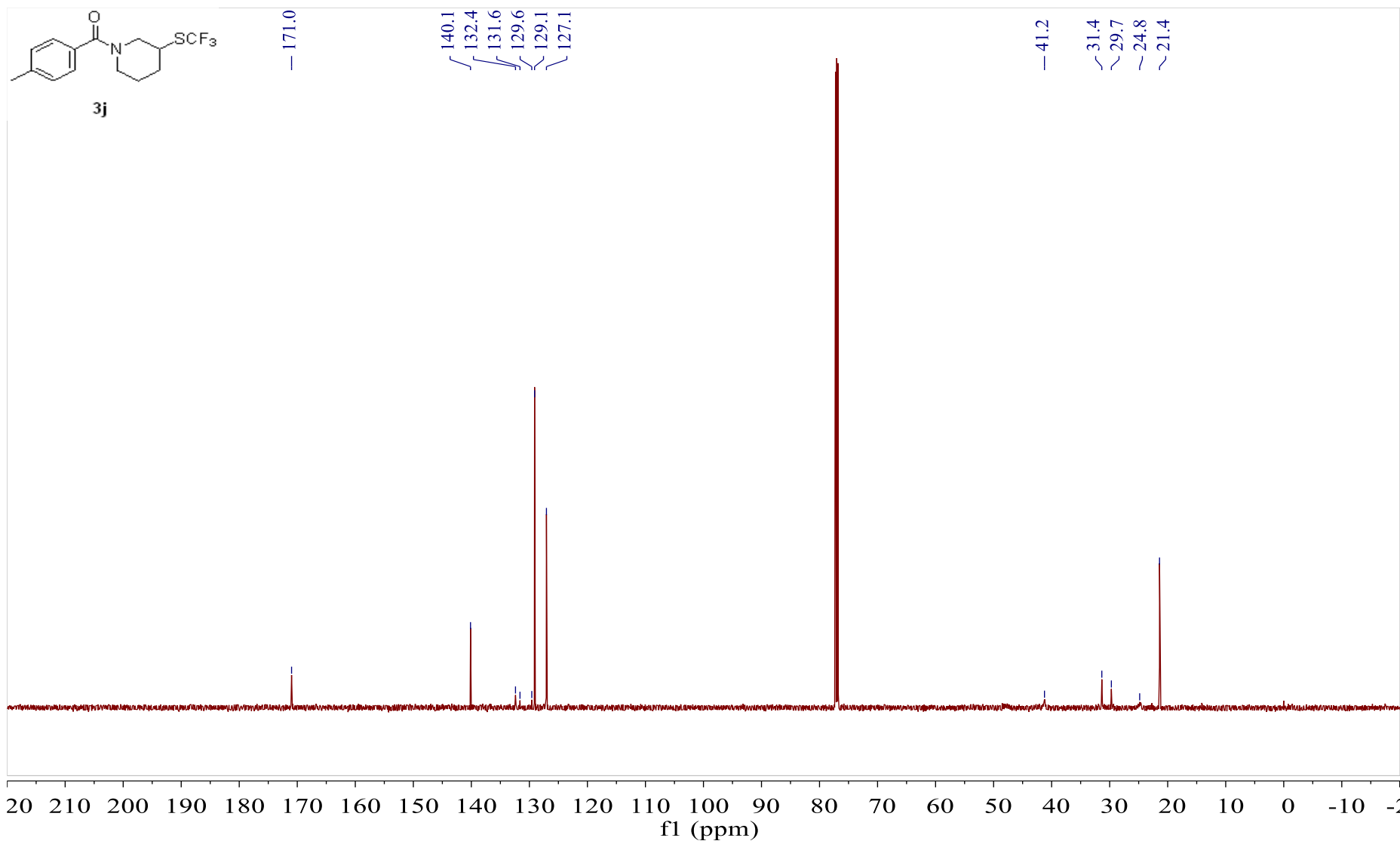


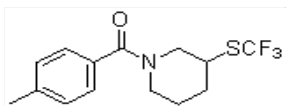






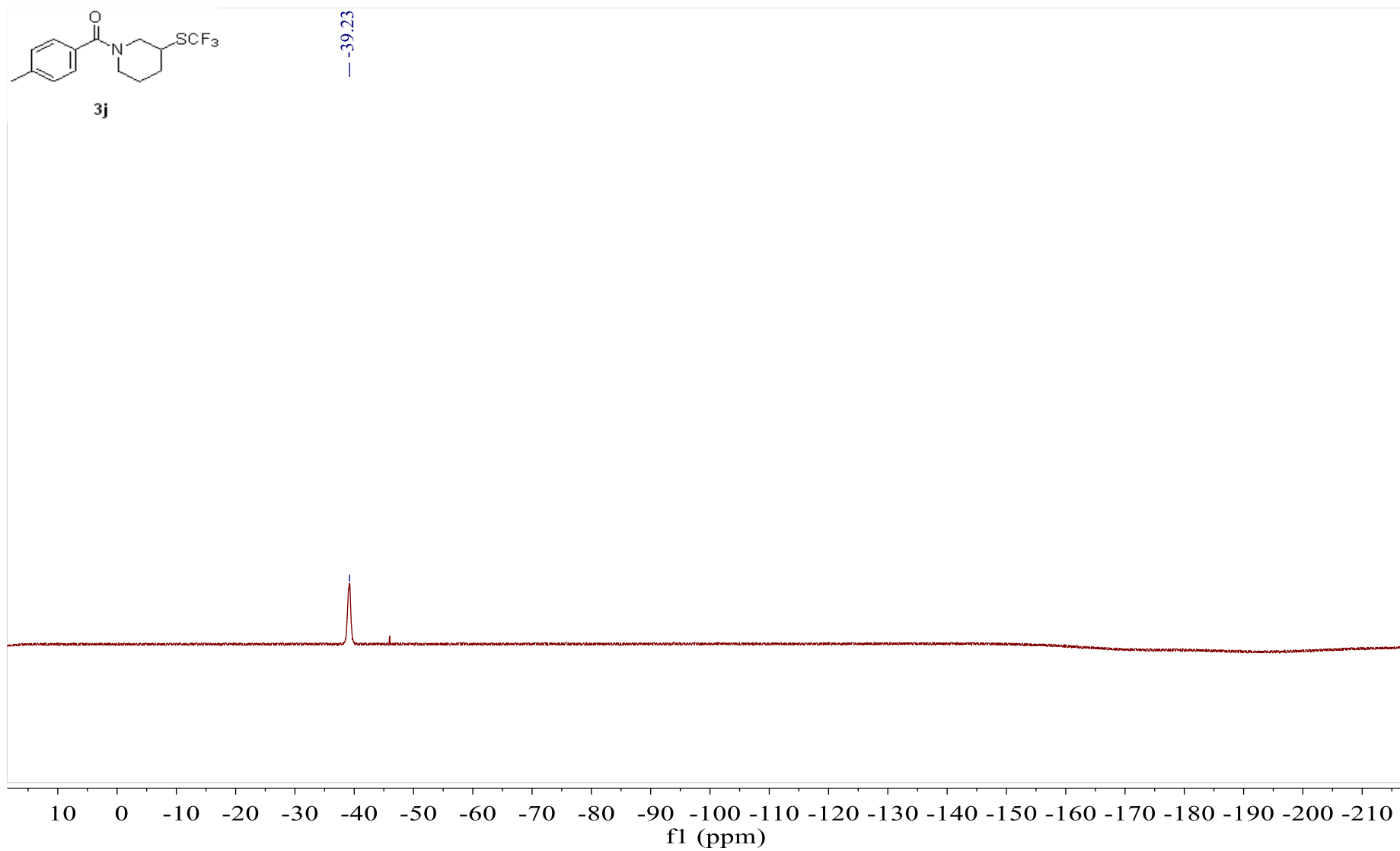


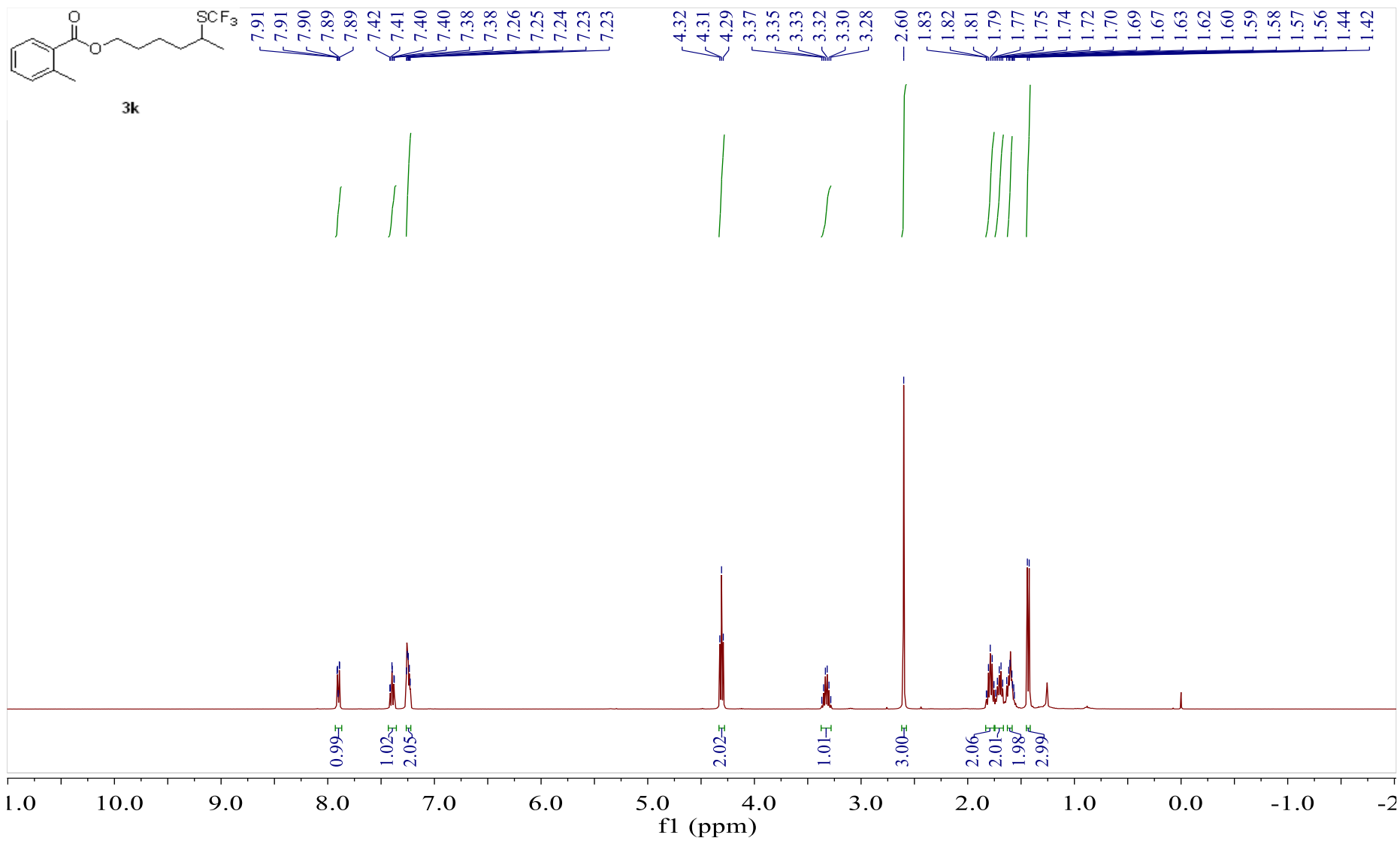


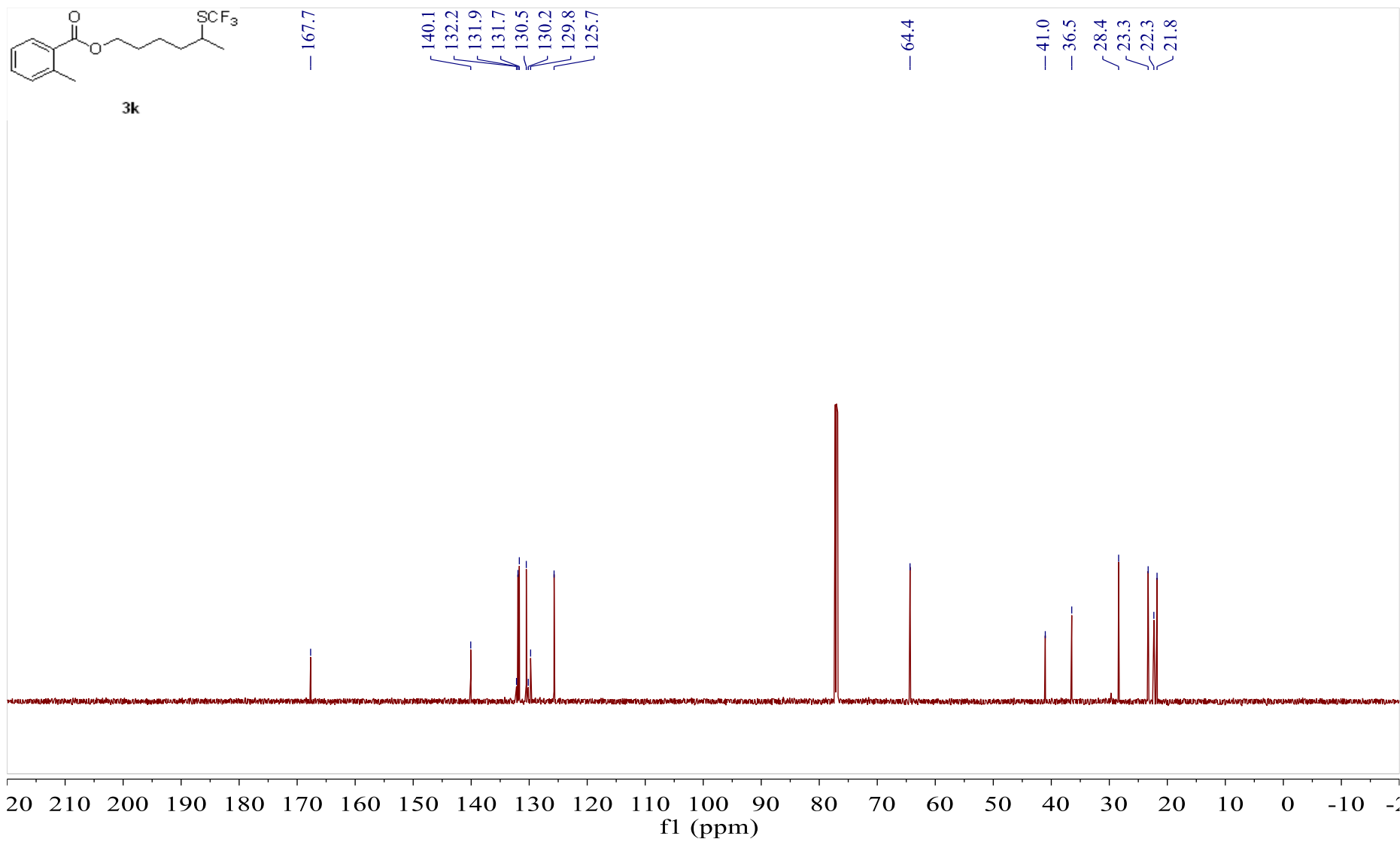


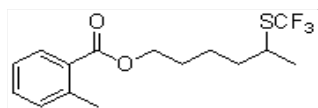
3j

— -39.23



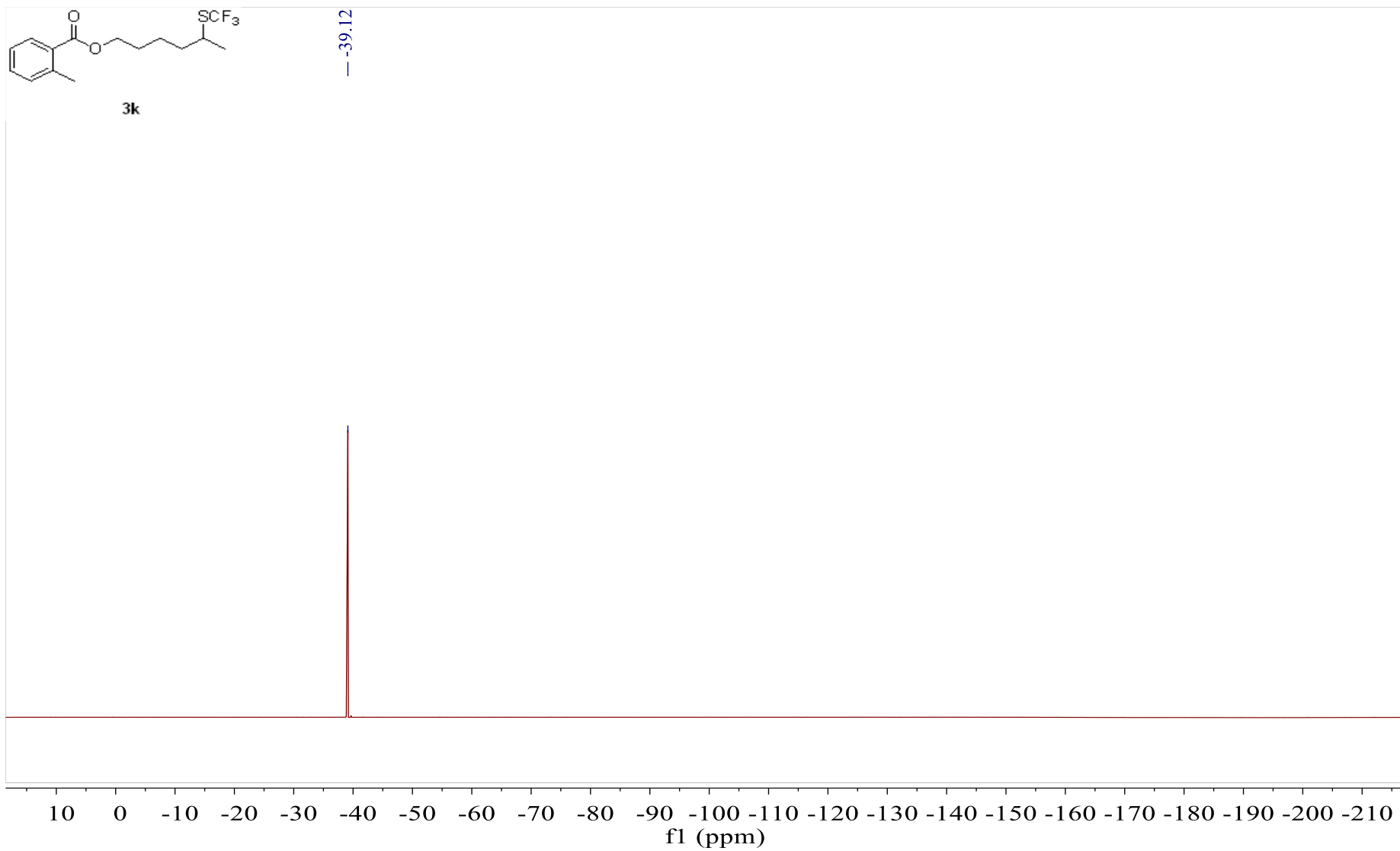


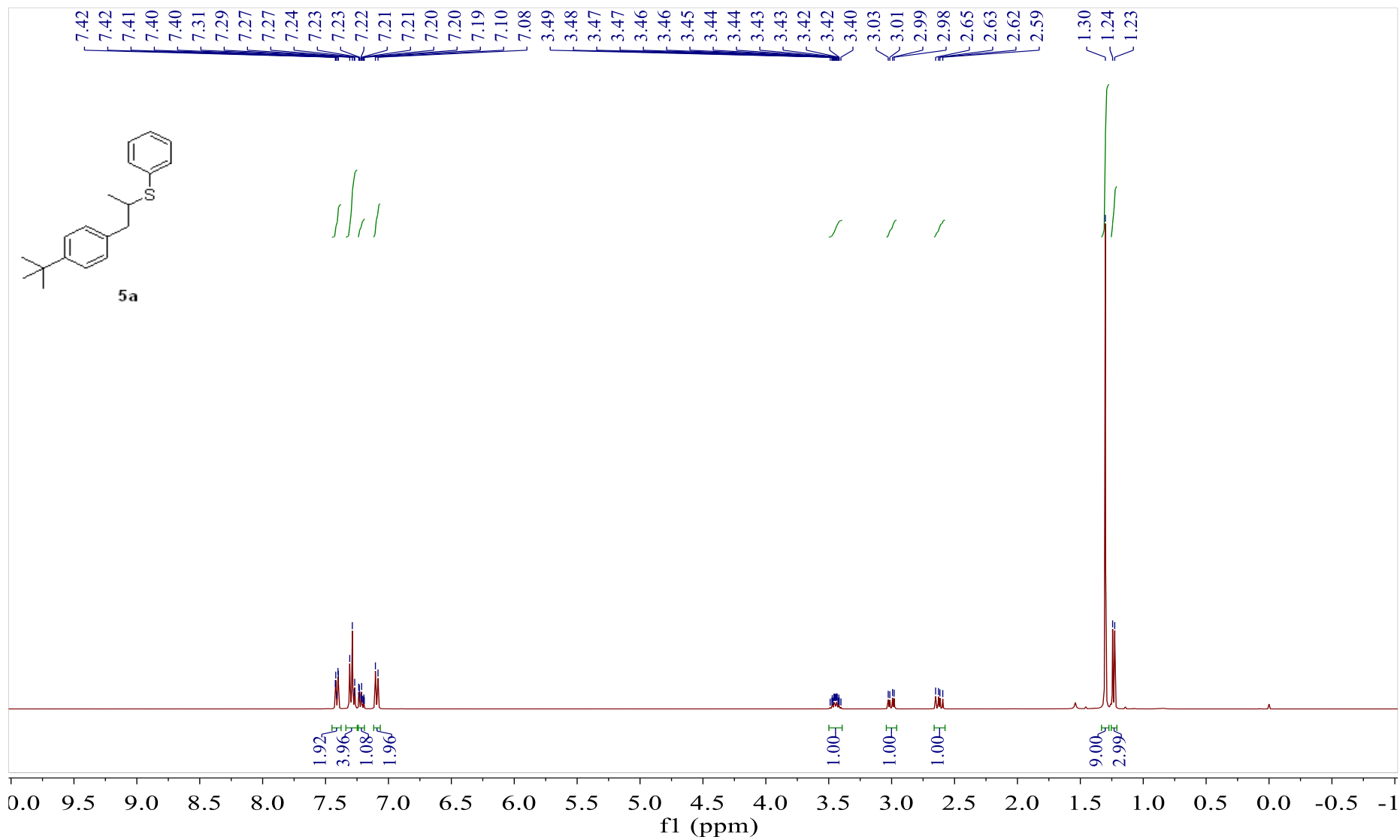


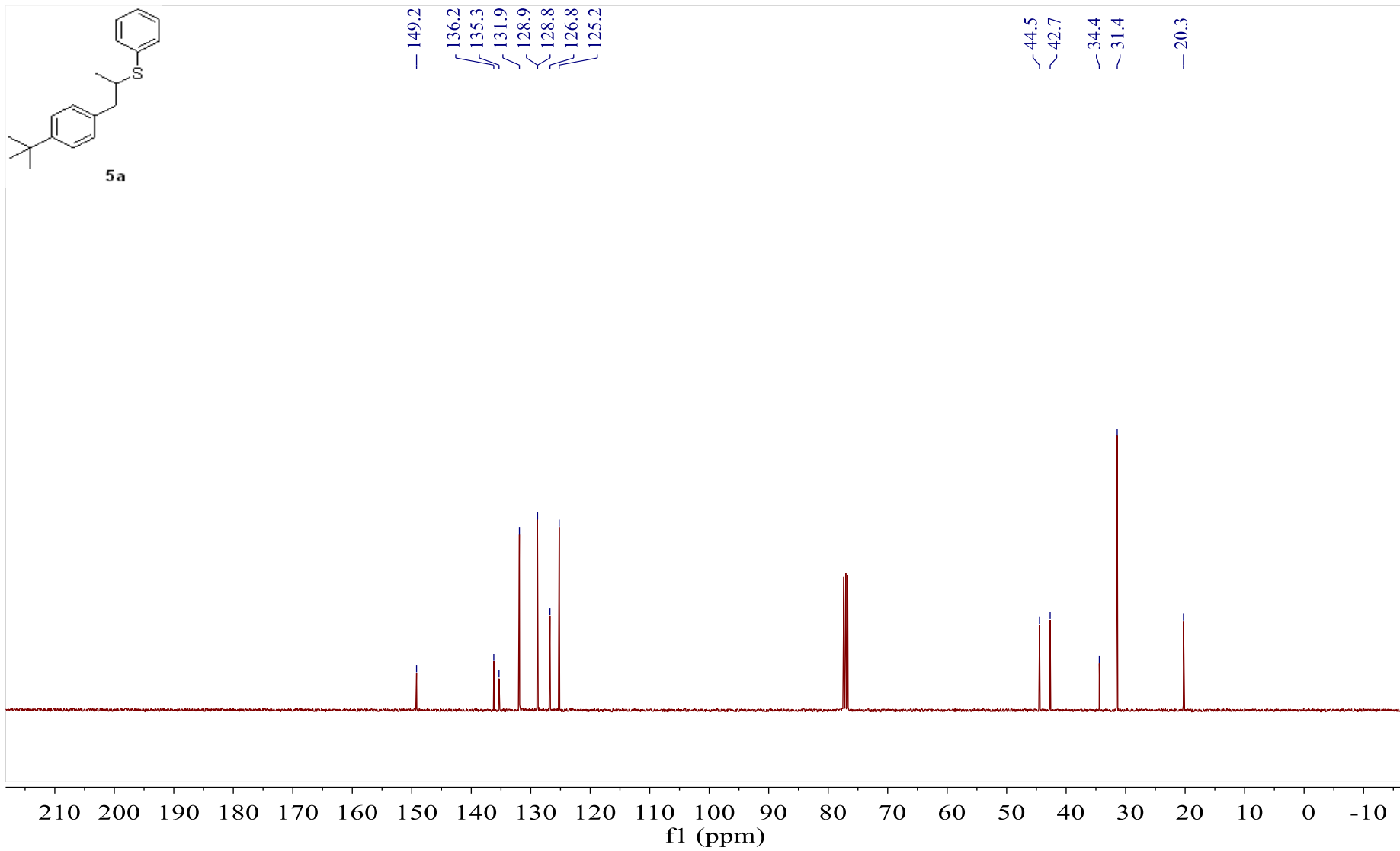


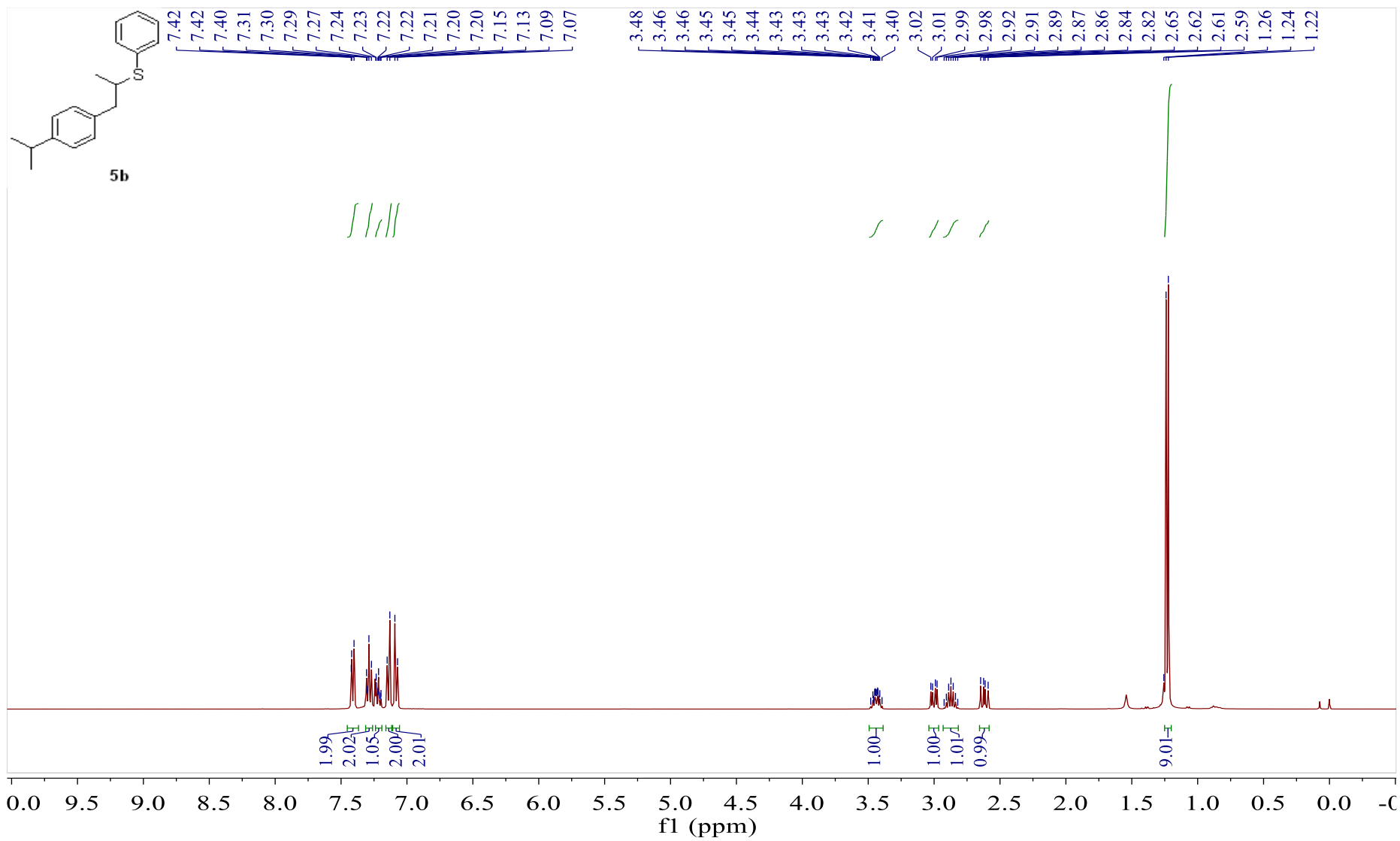
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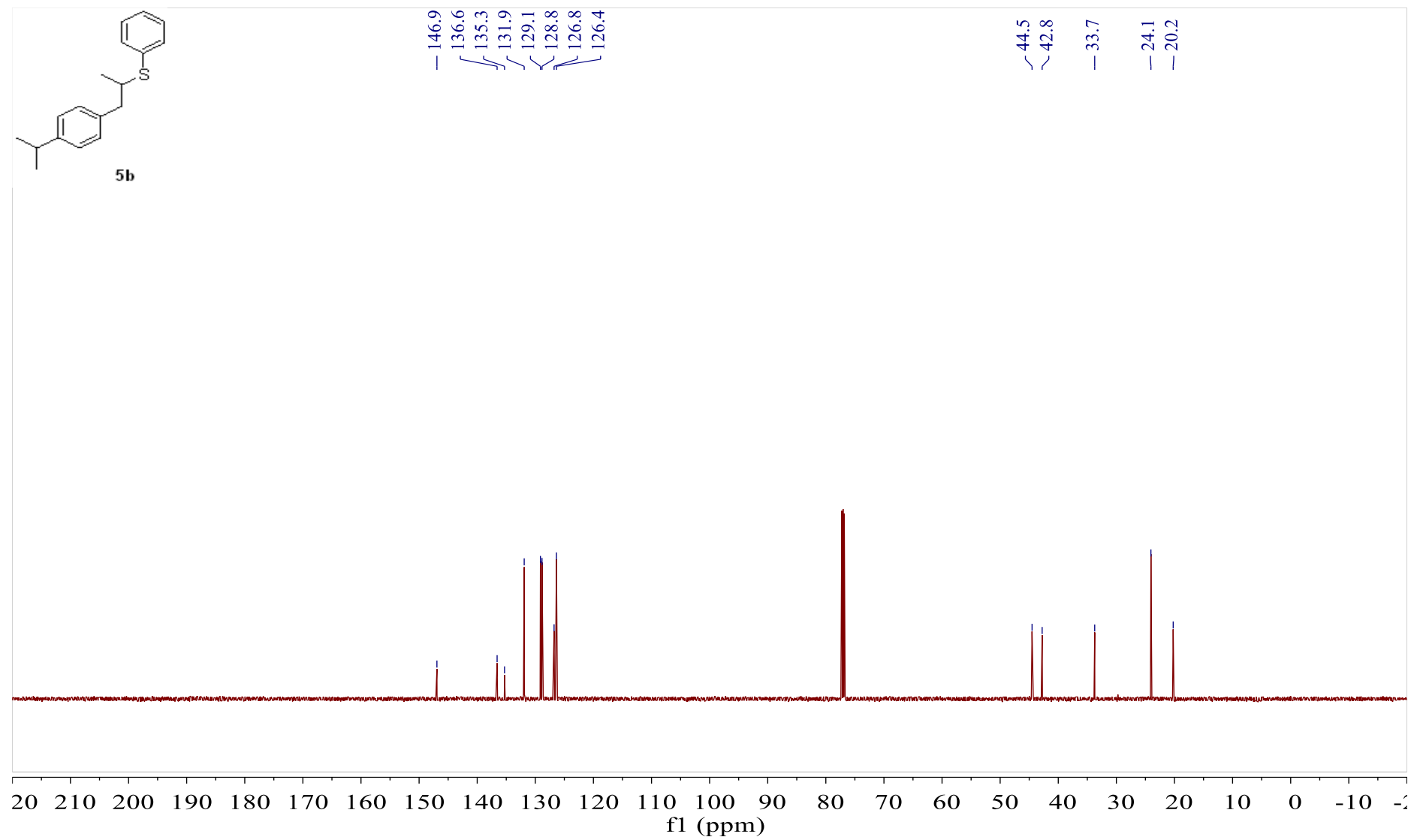
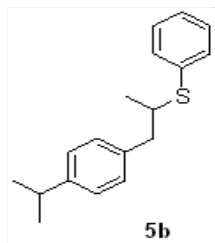
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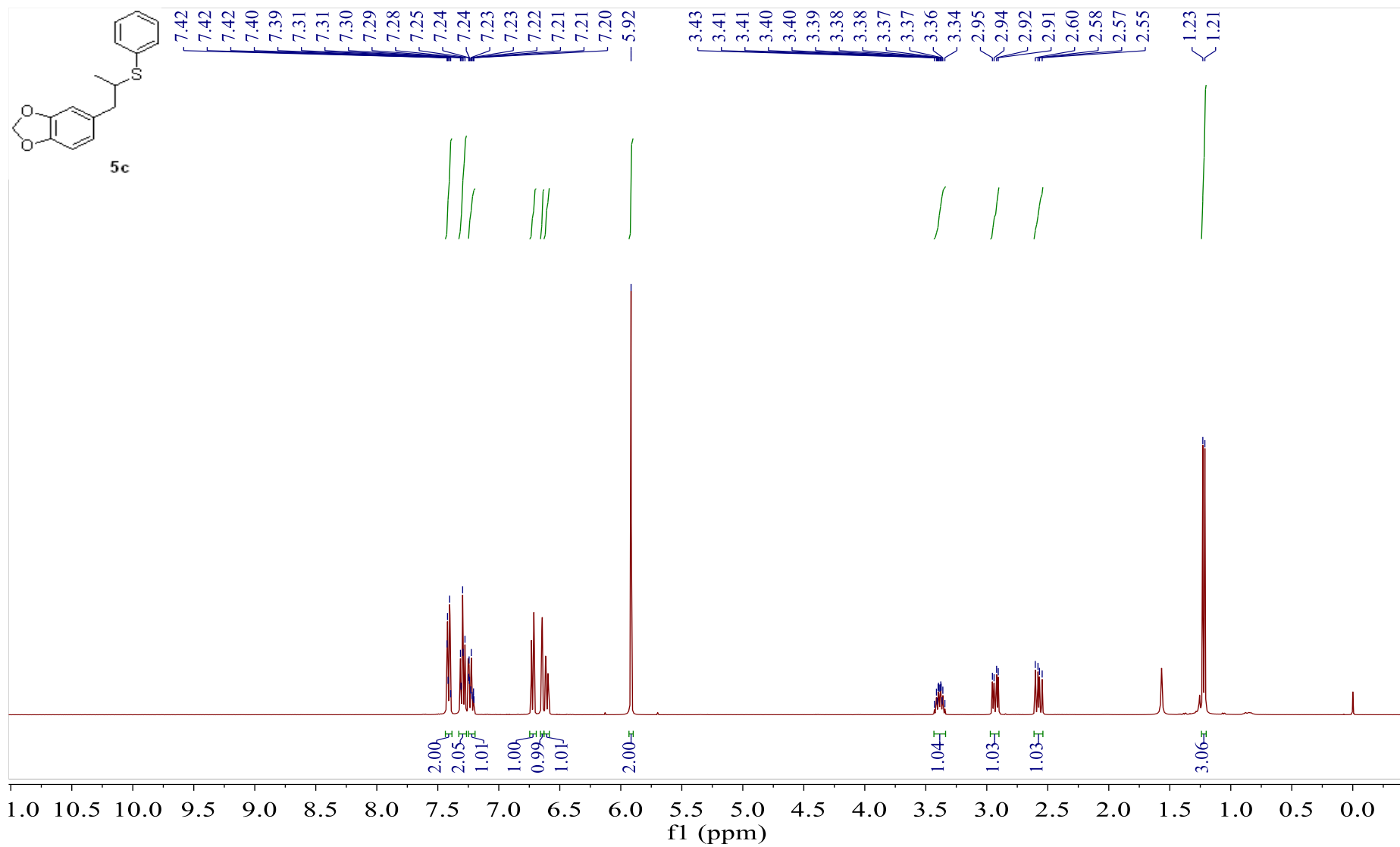


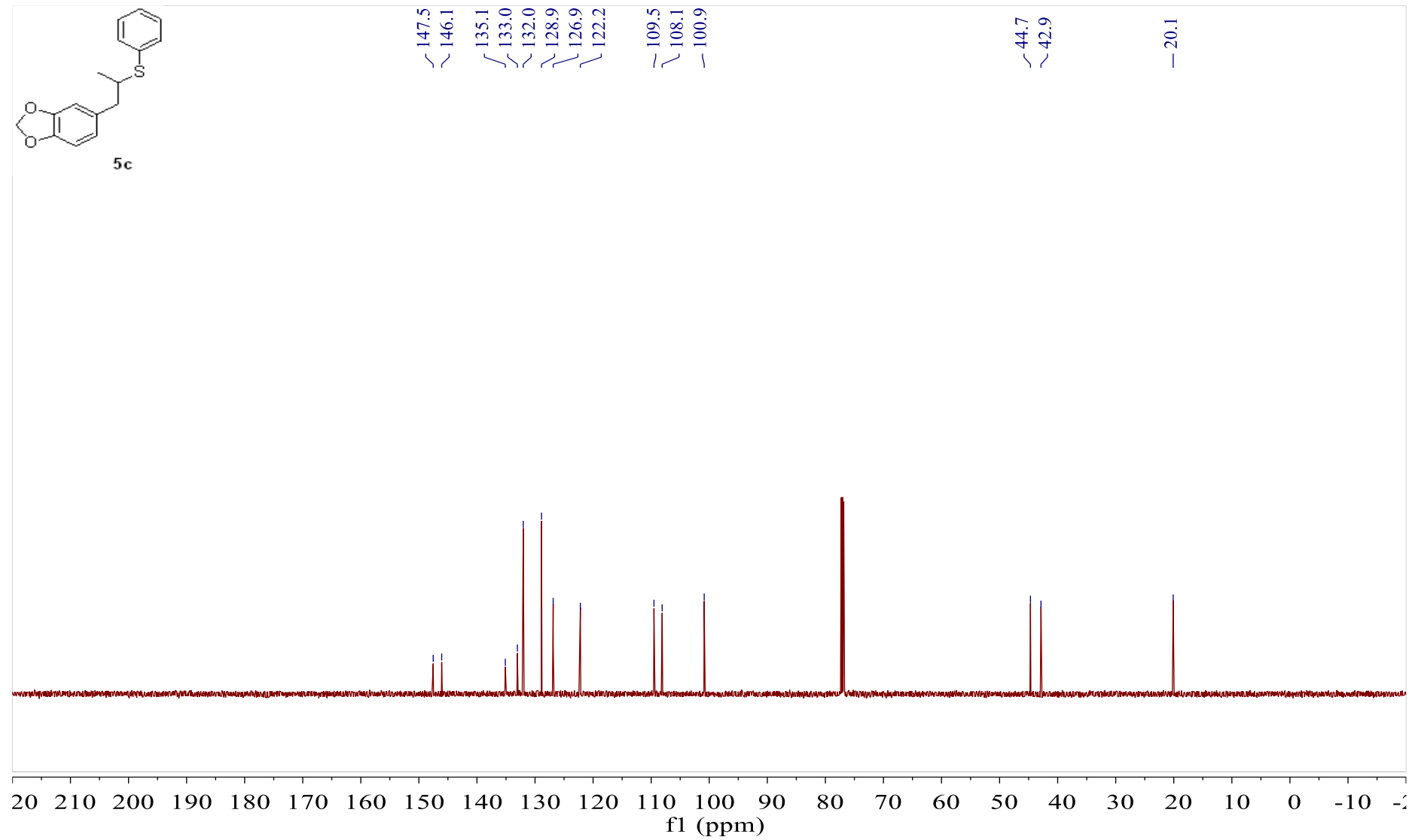
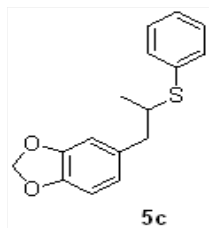


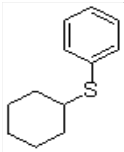




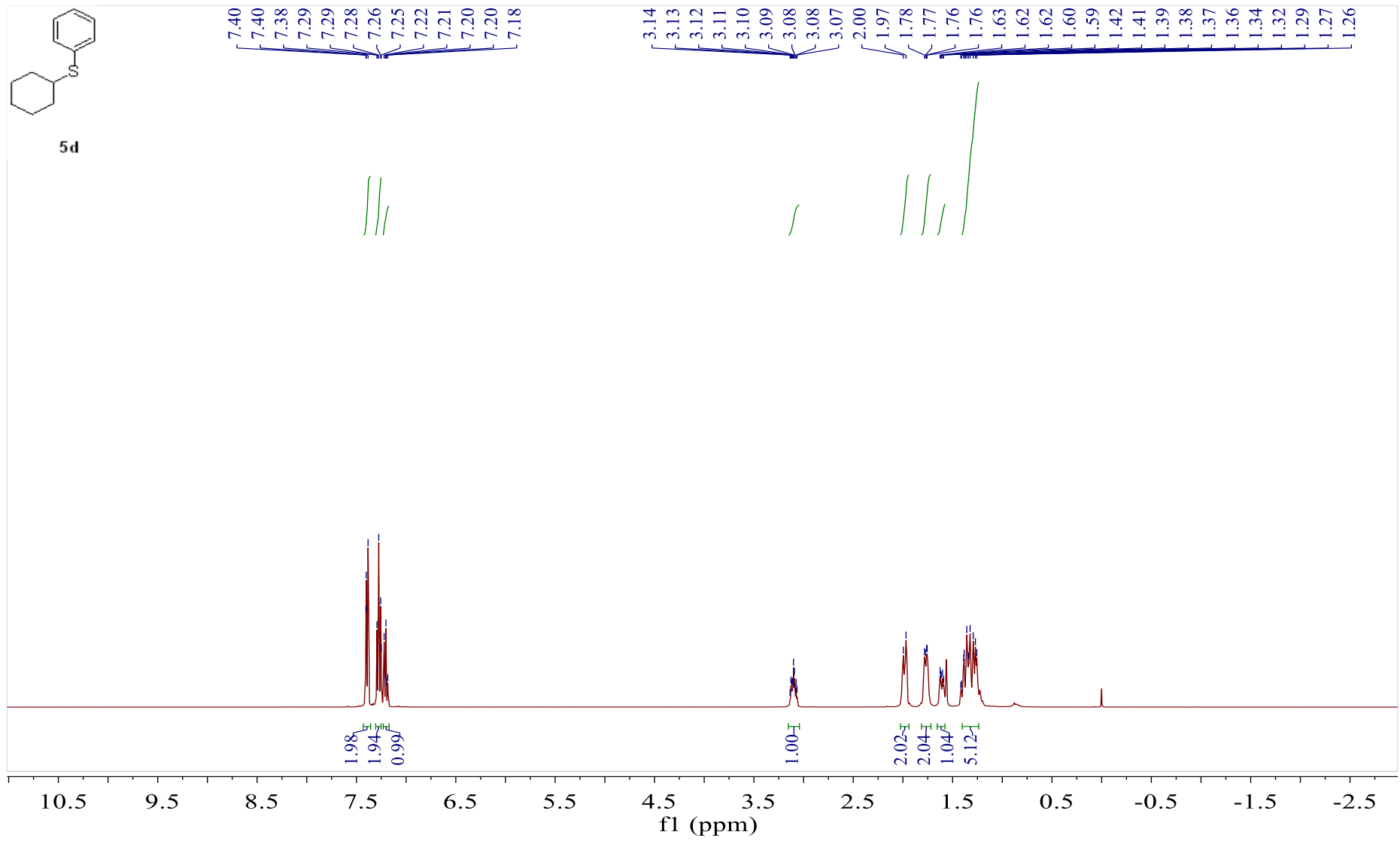


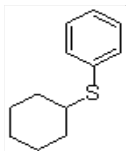




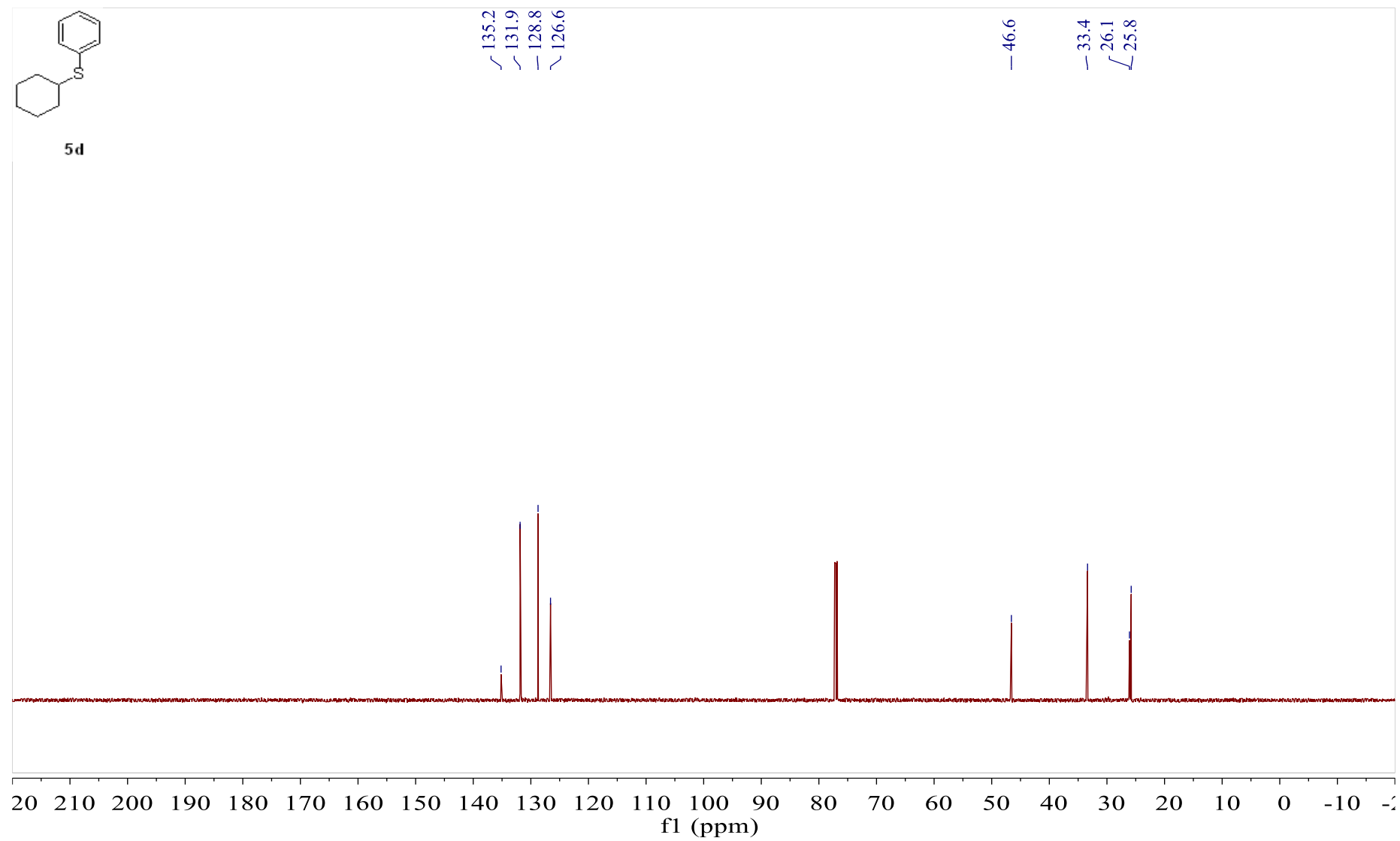


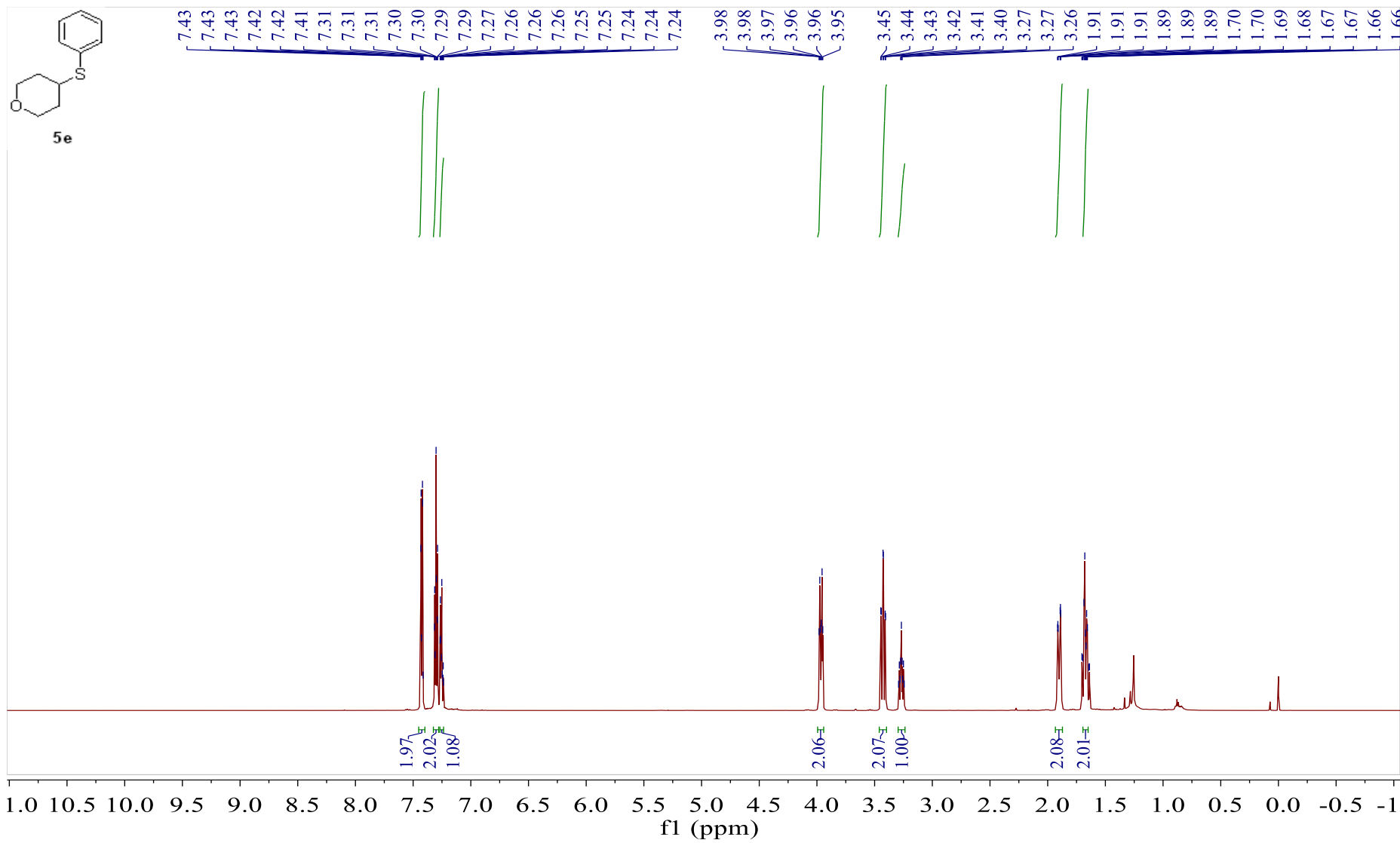
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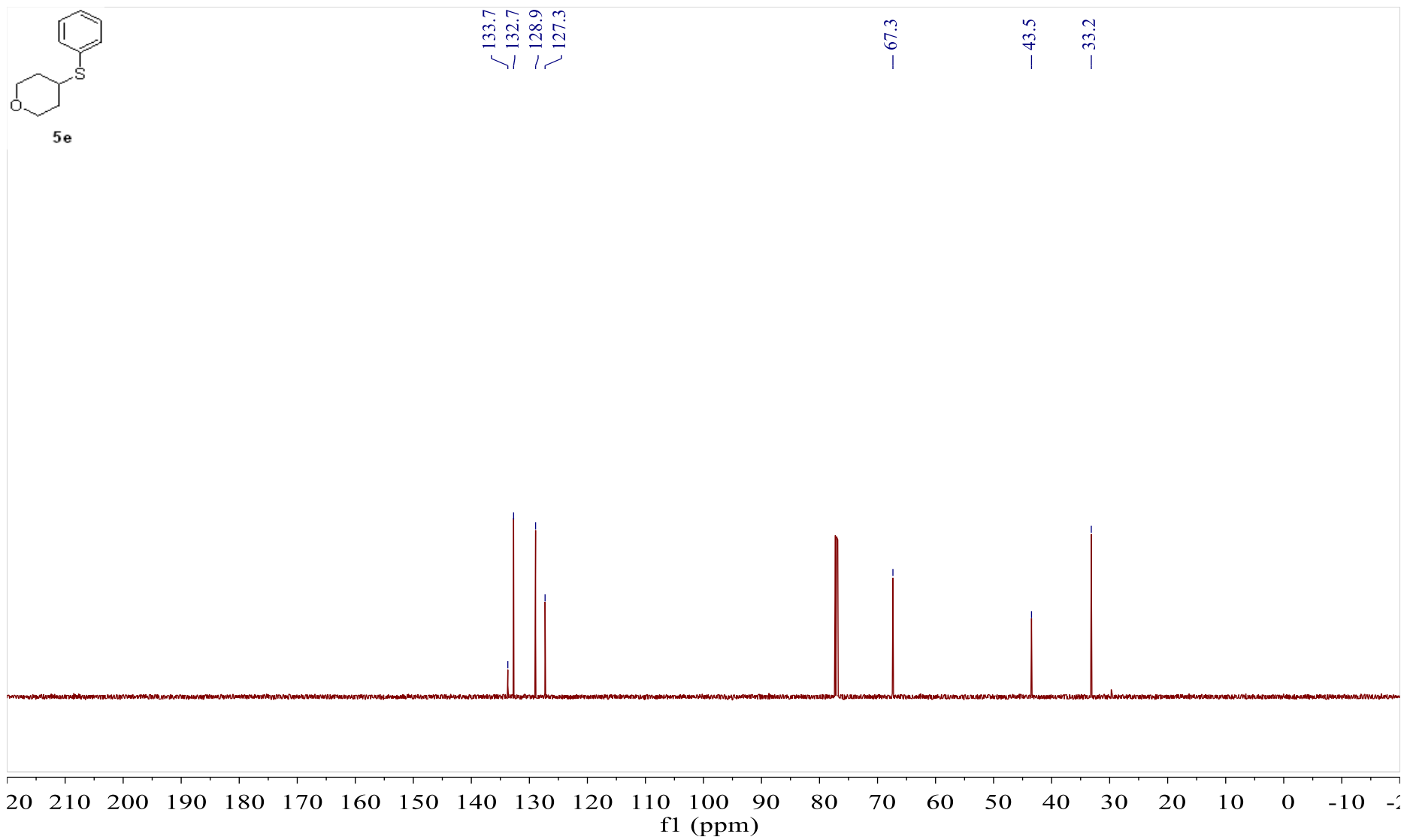


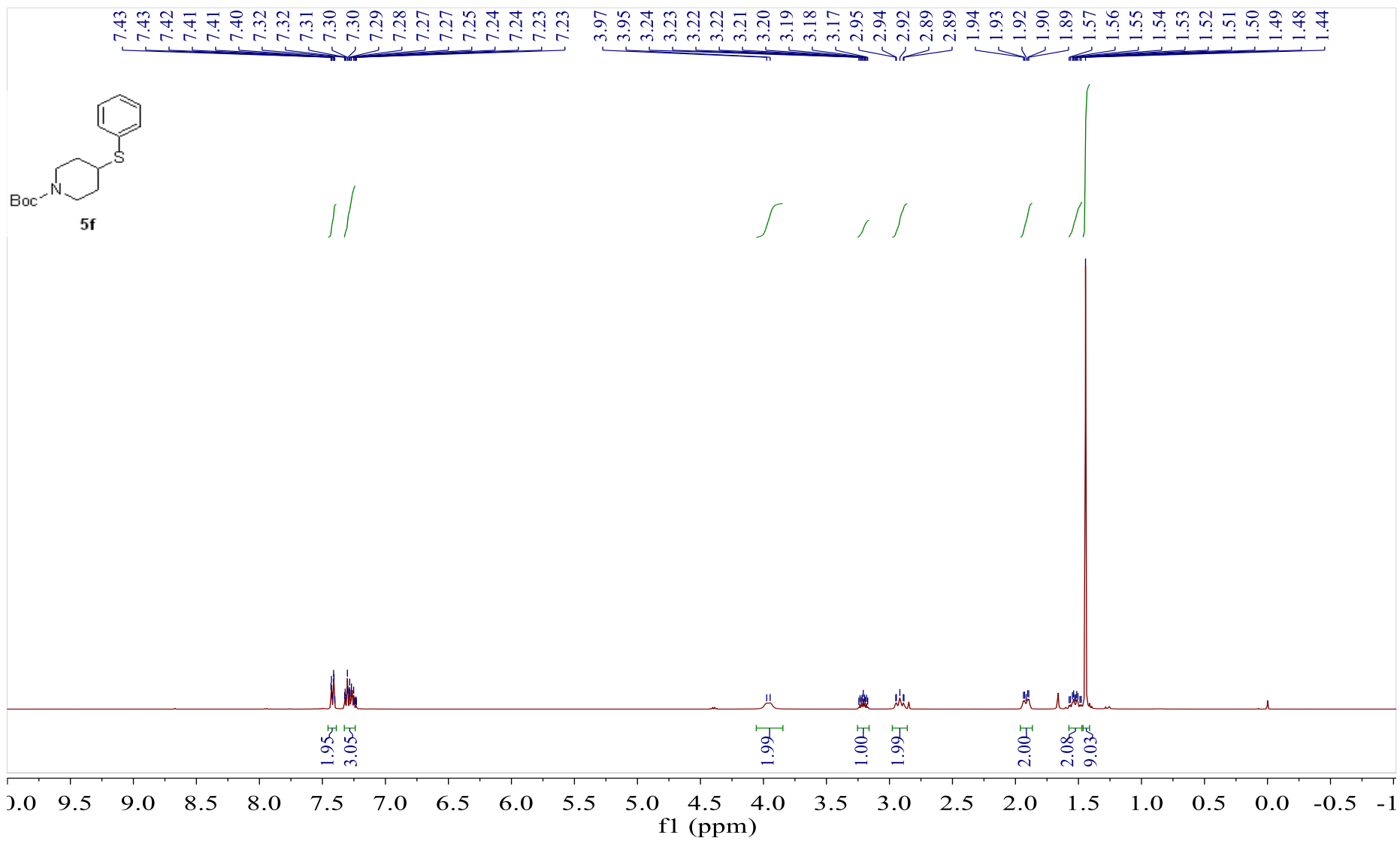


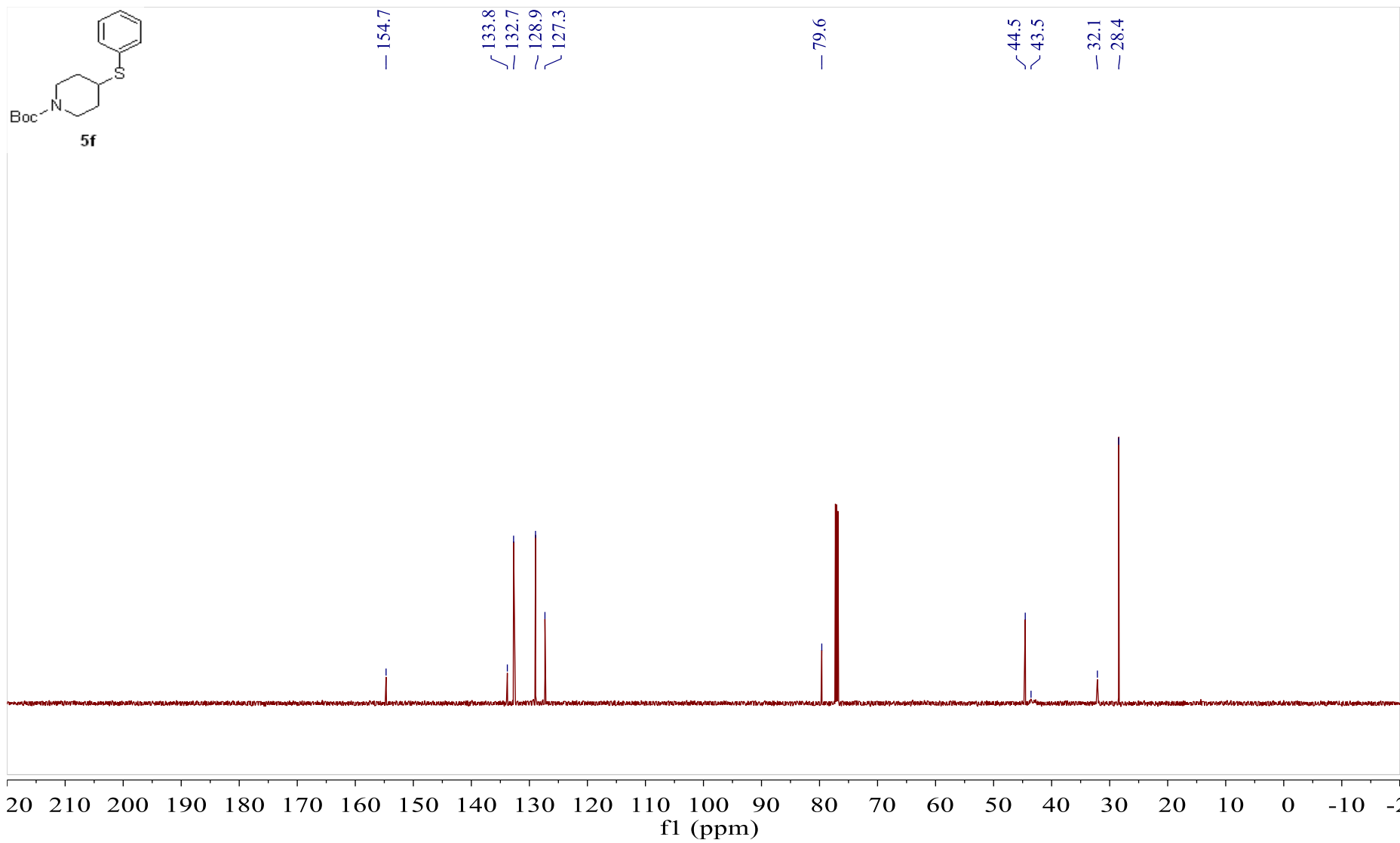
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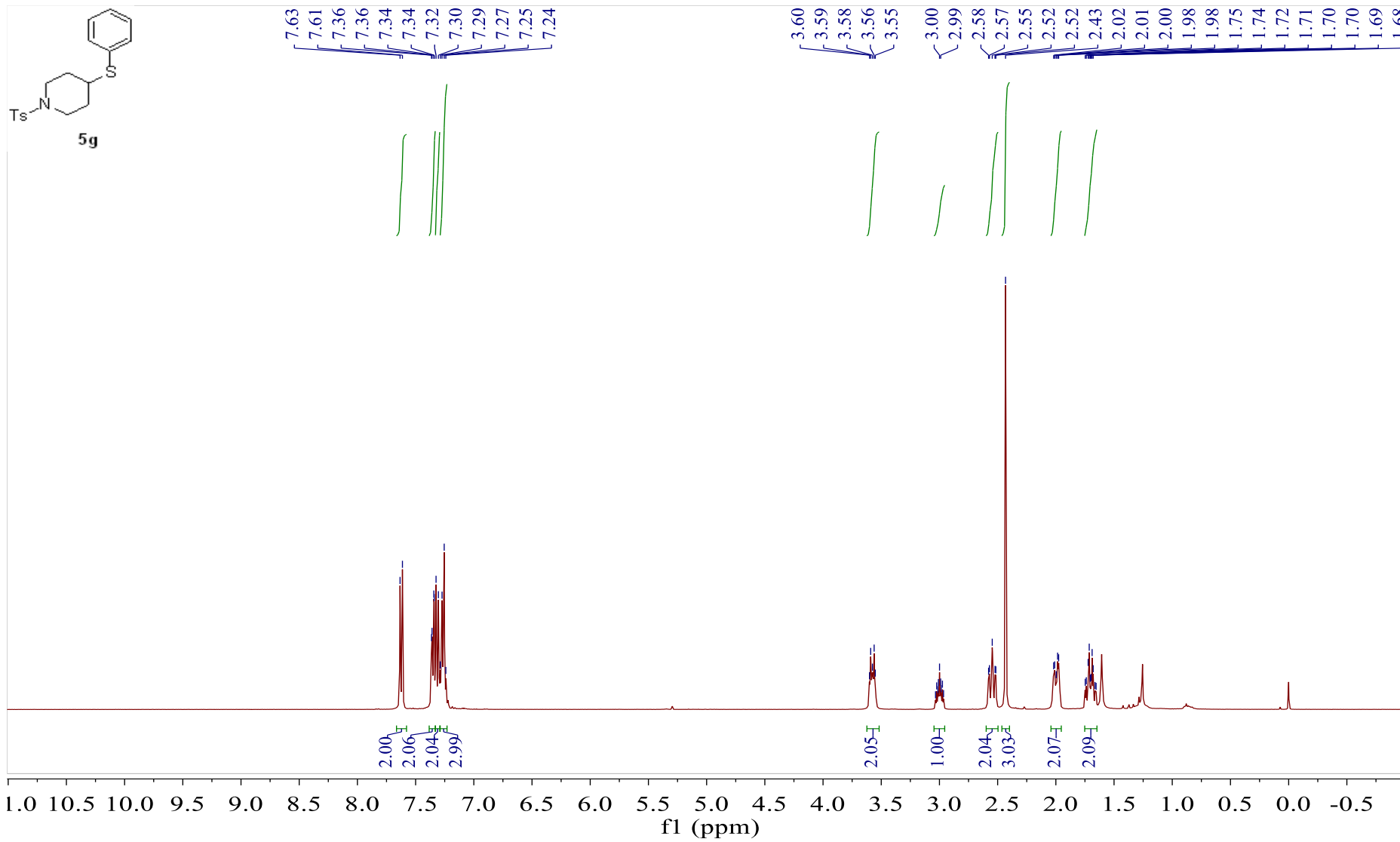


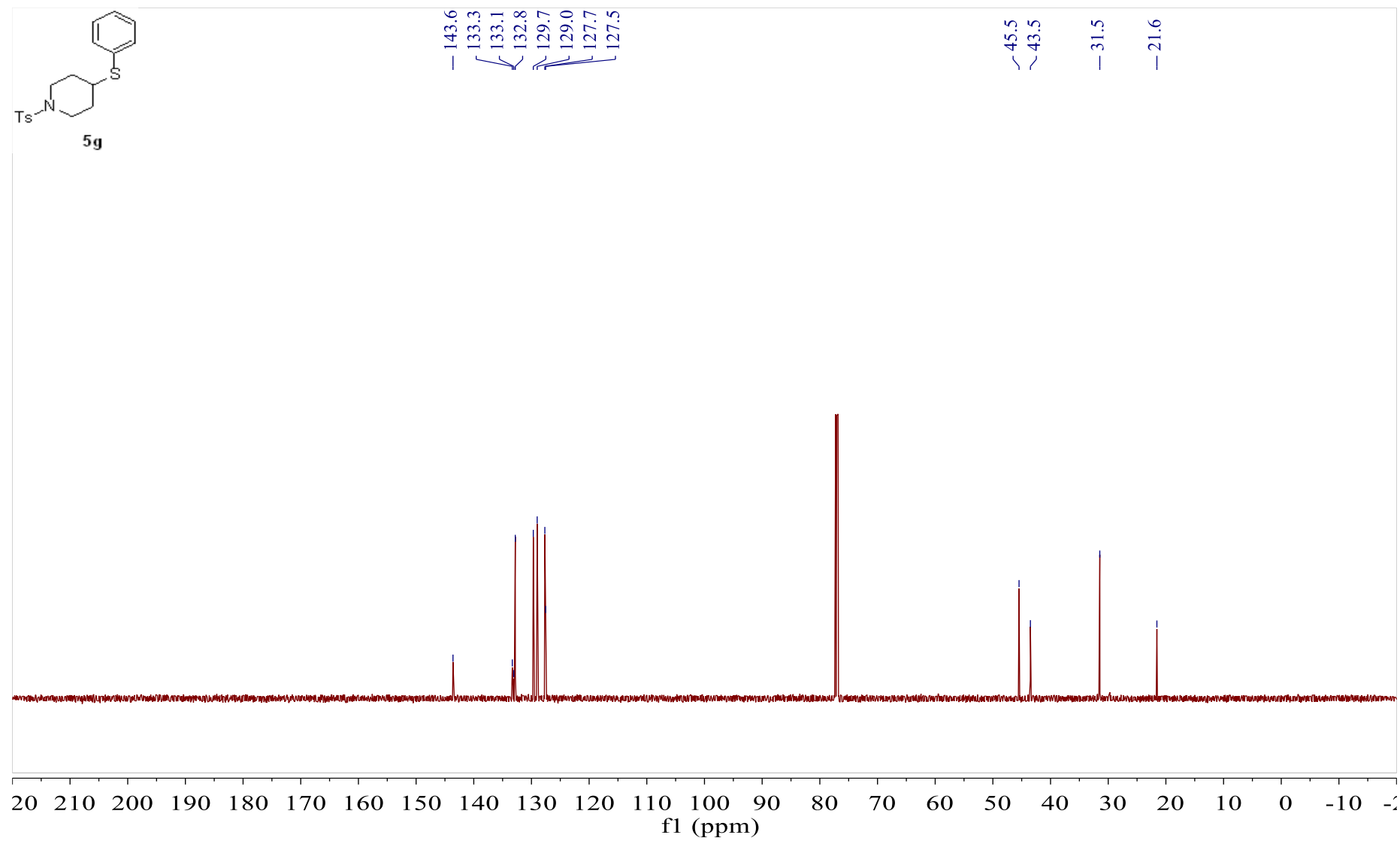
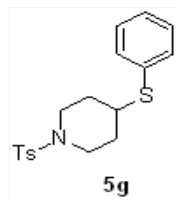


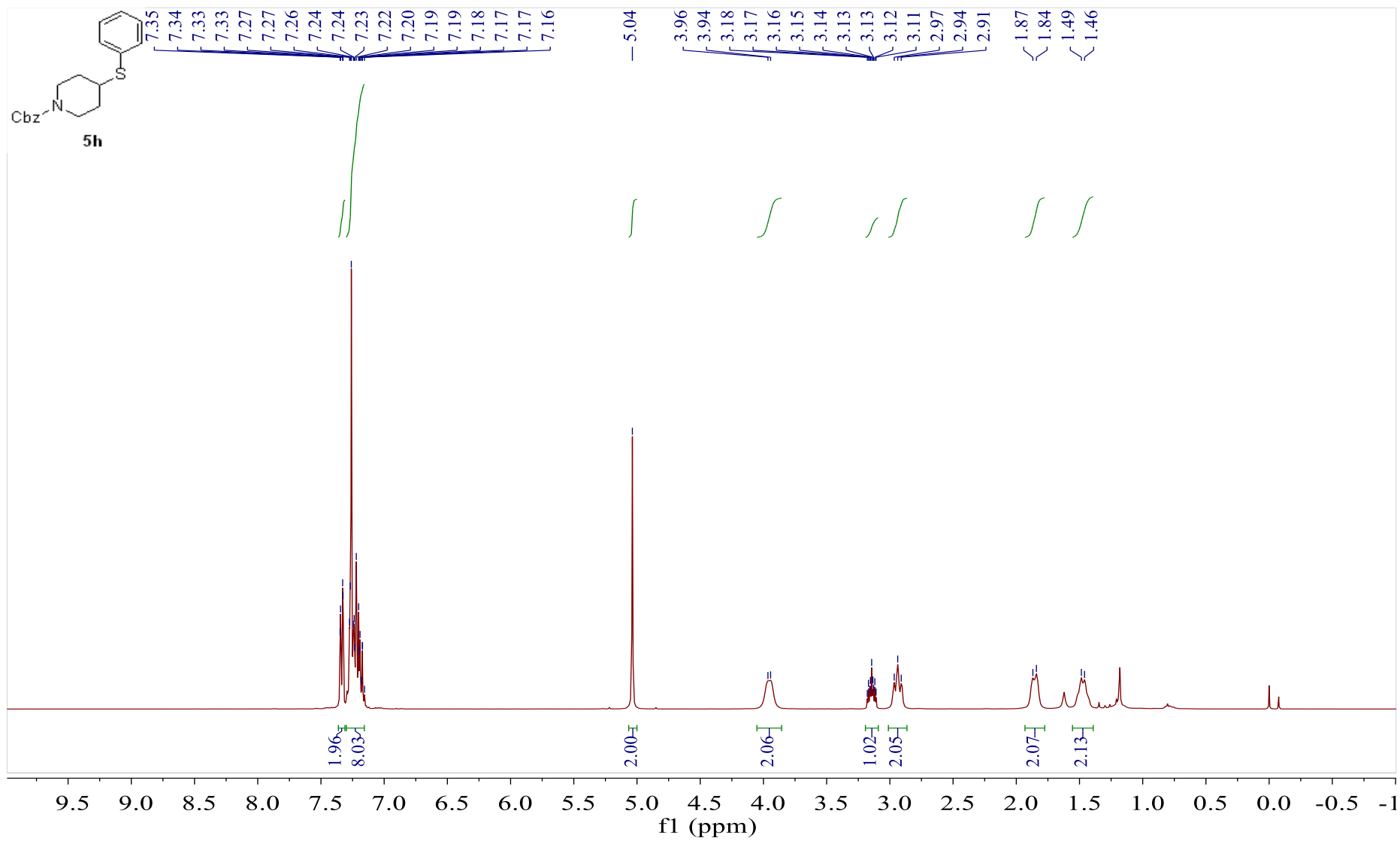


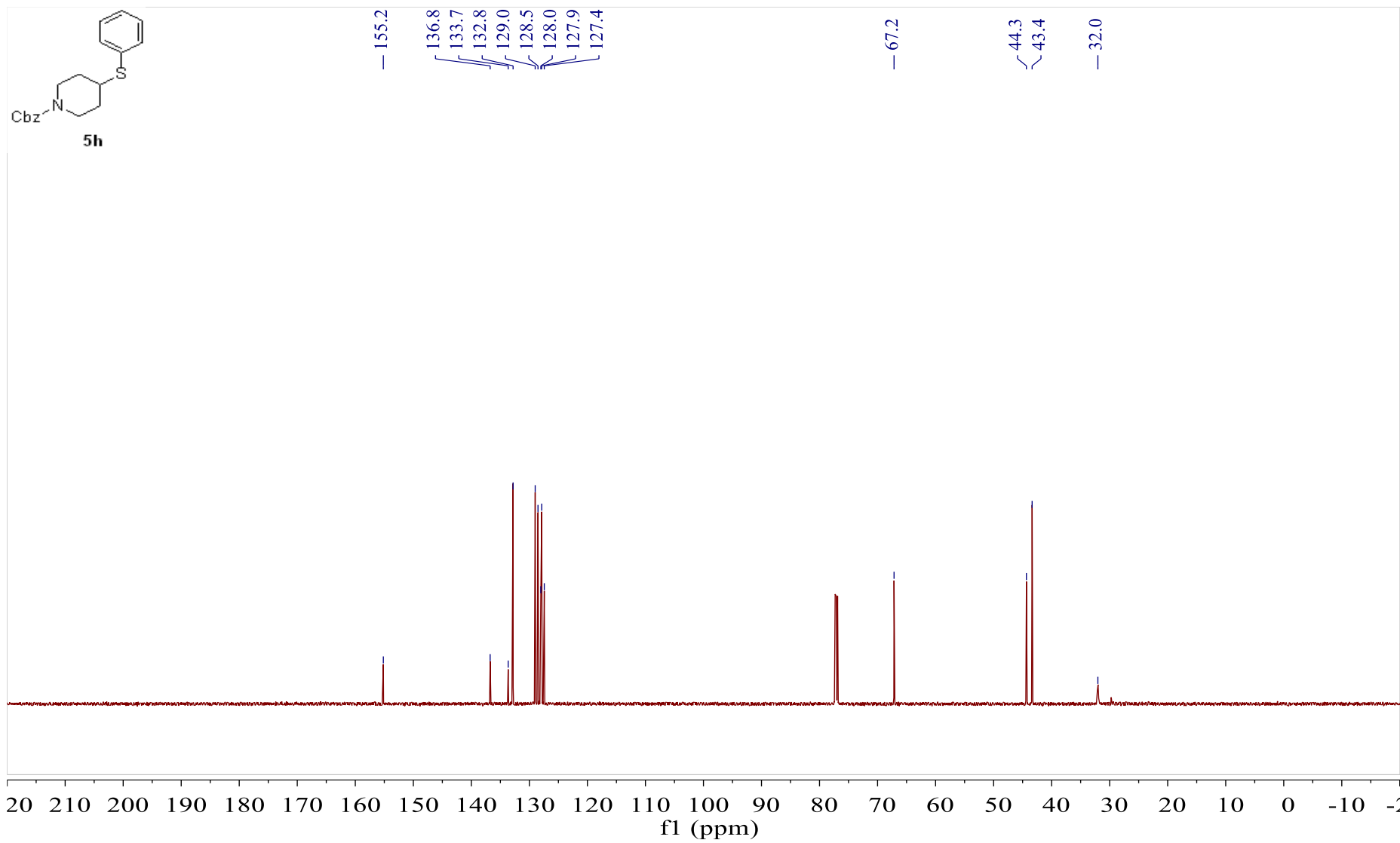


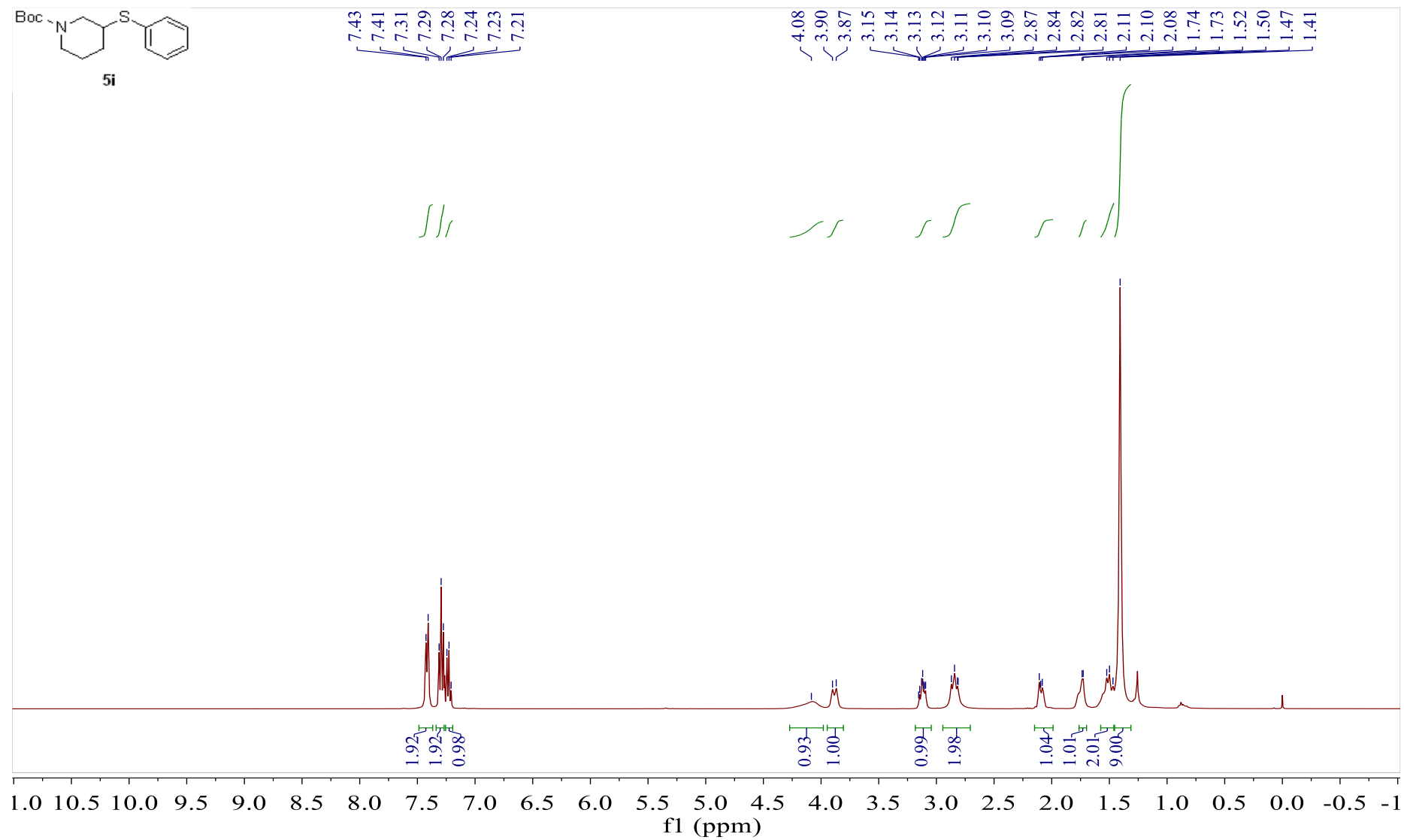
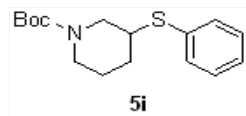


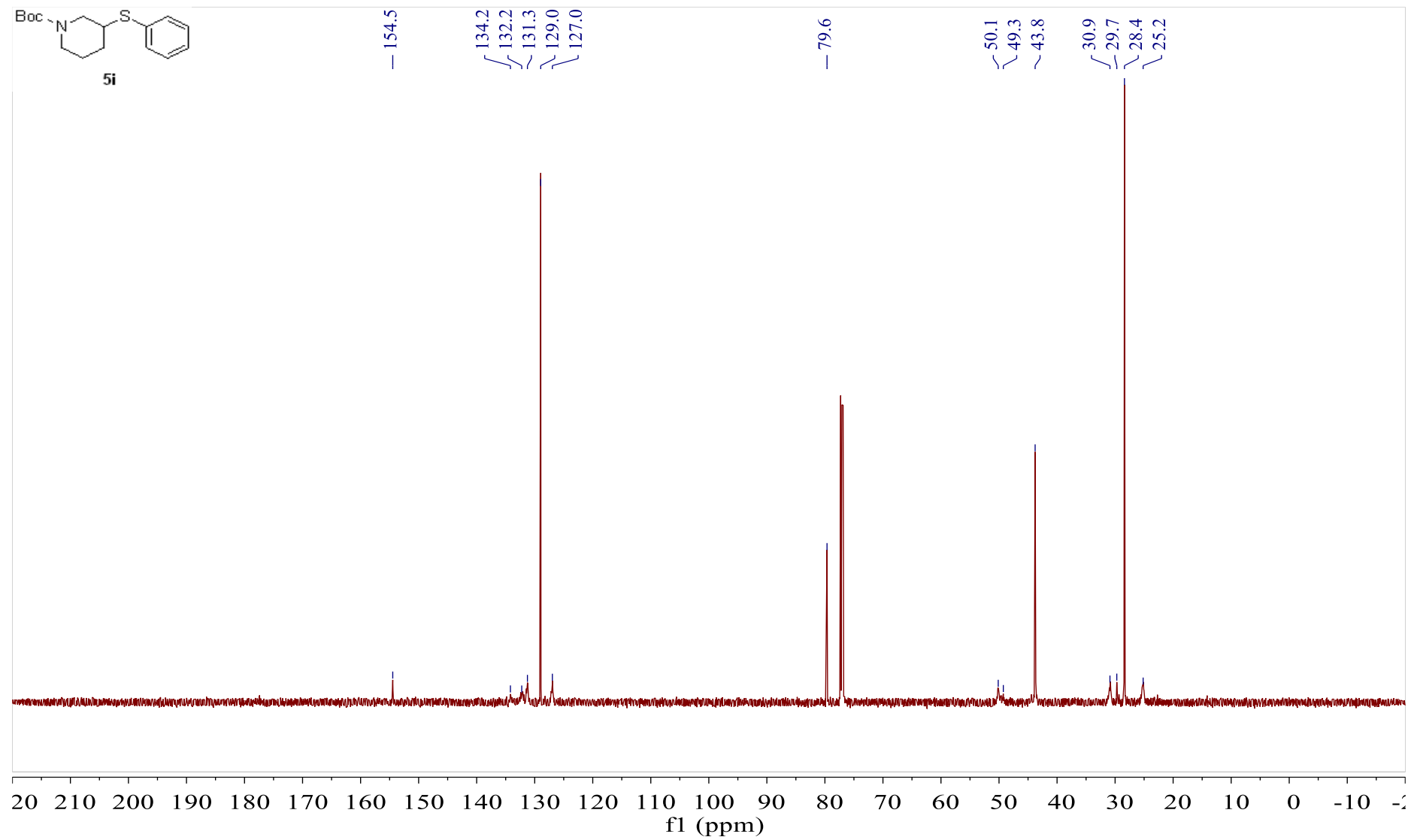
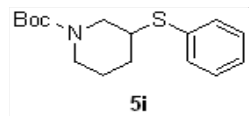


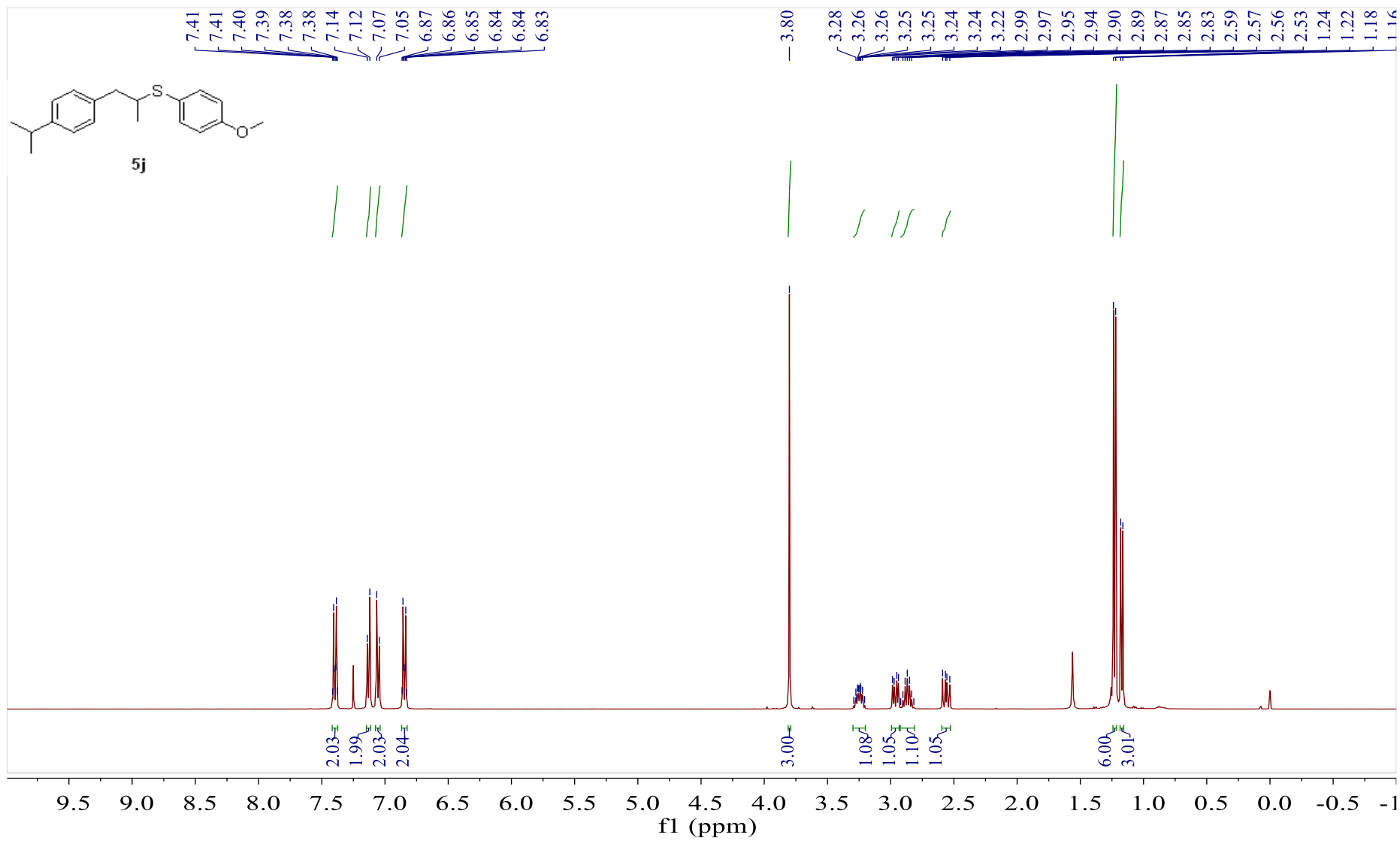


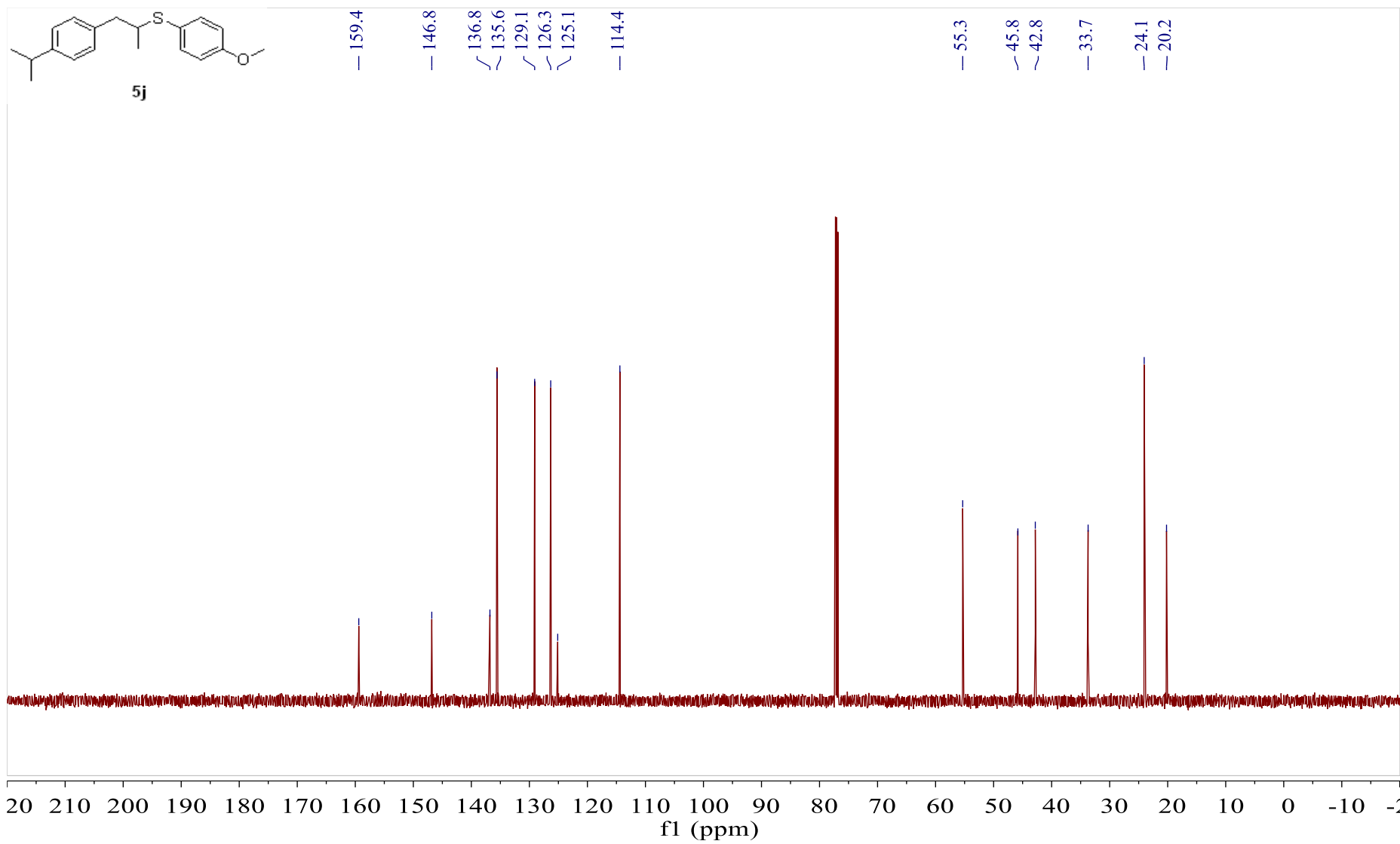


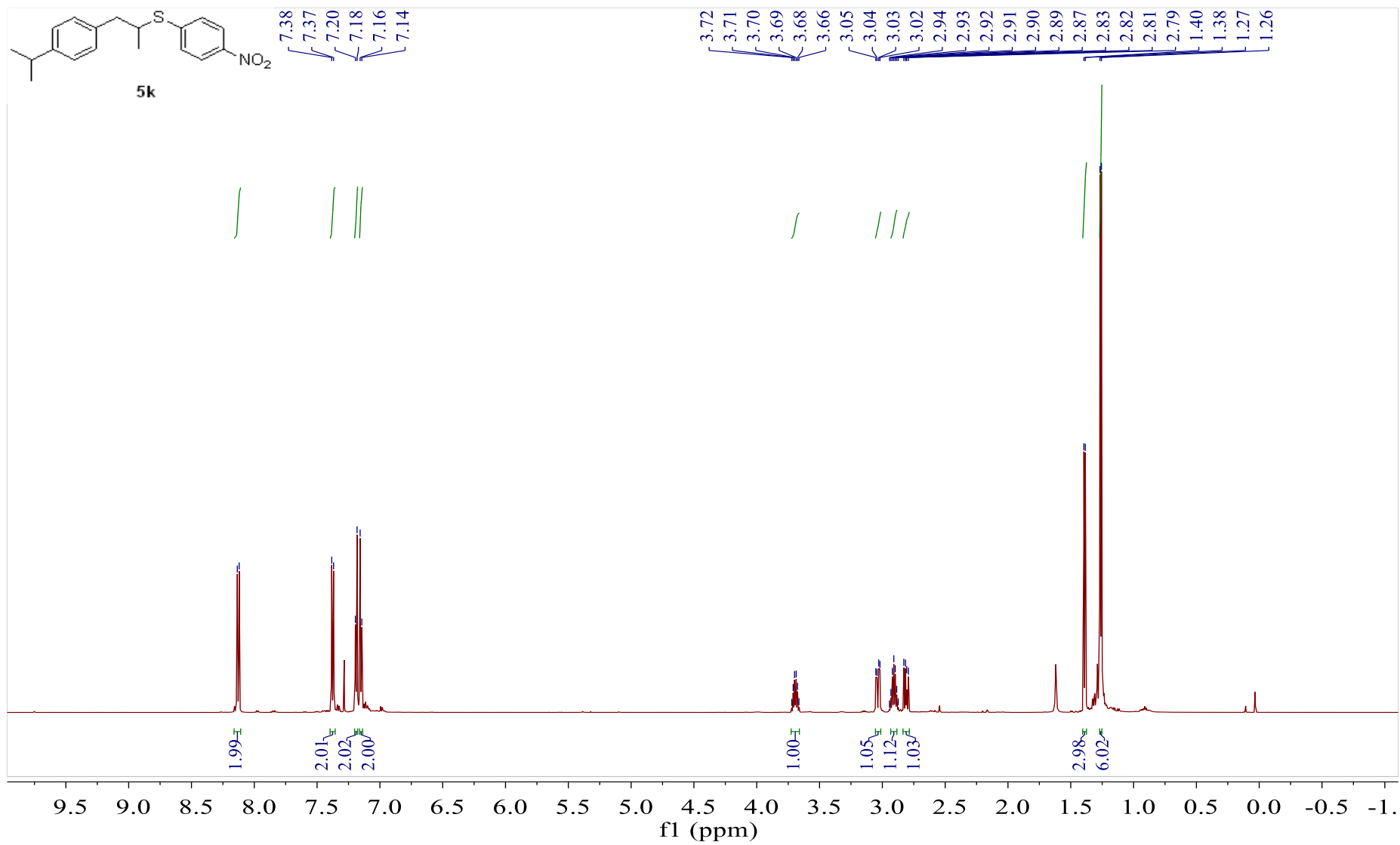


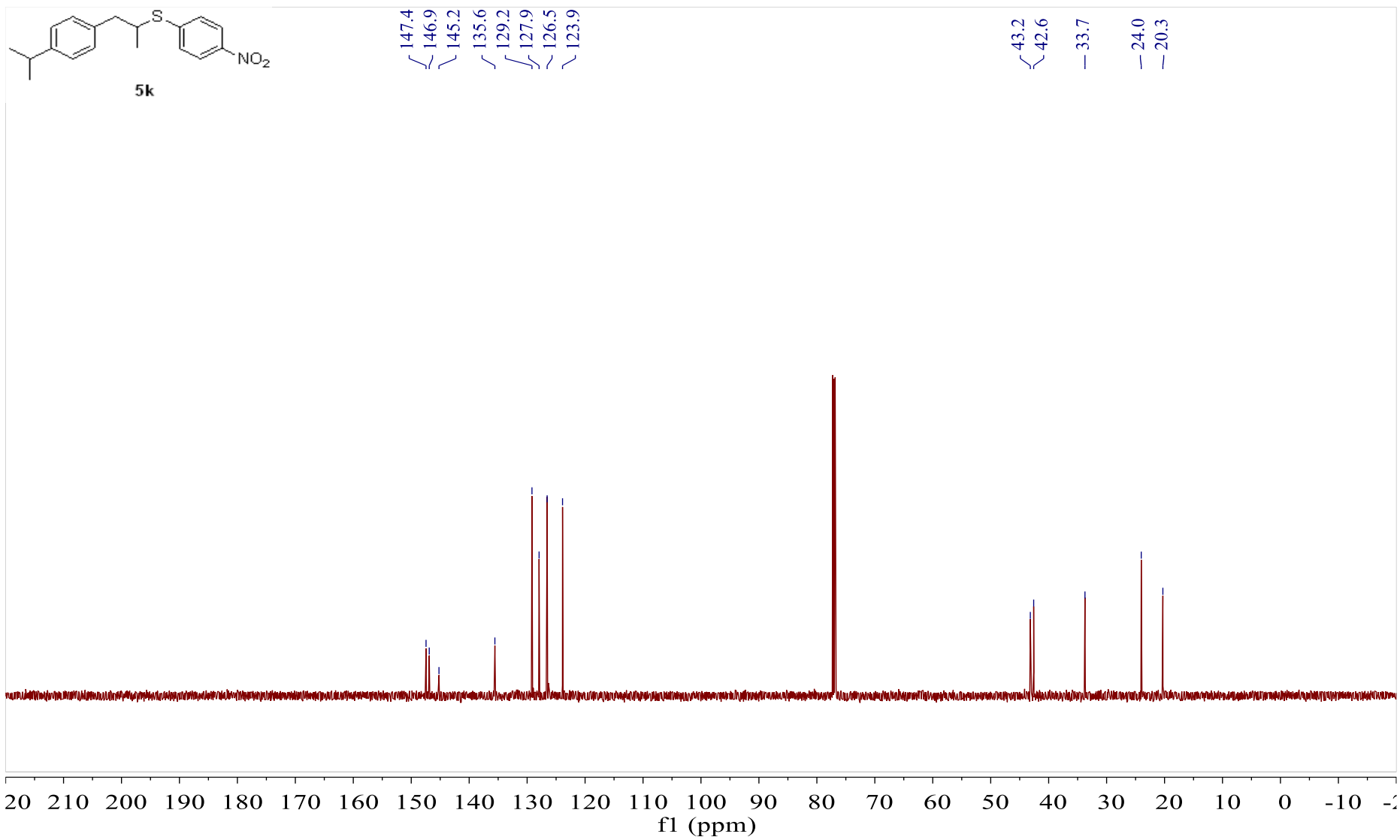


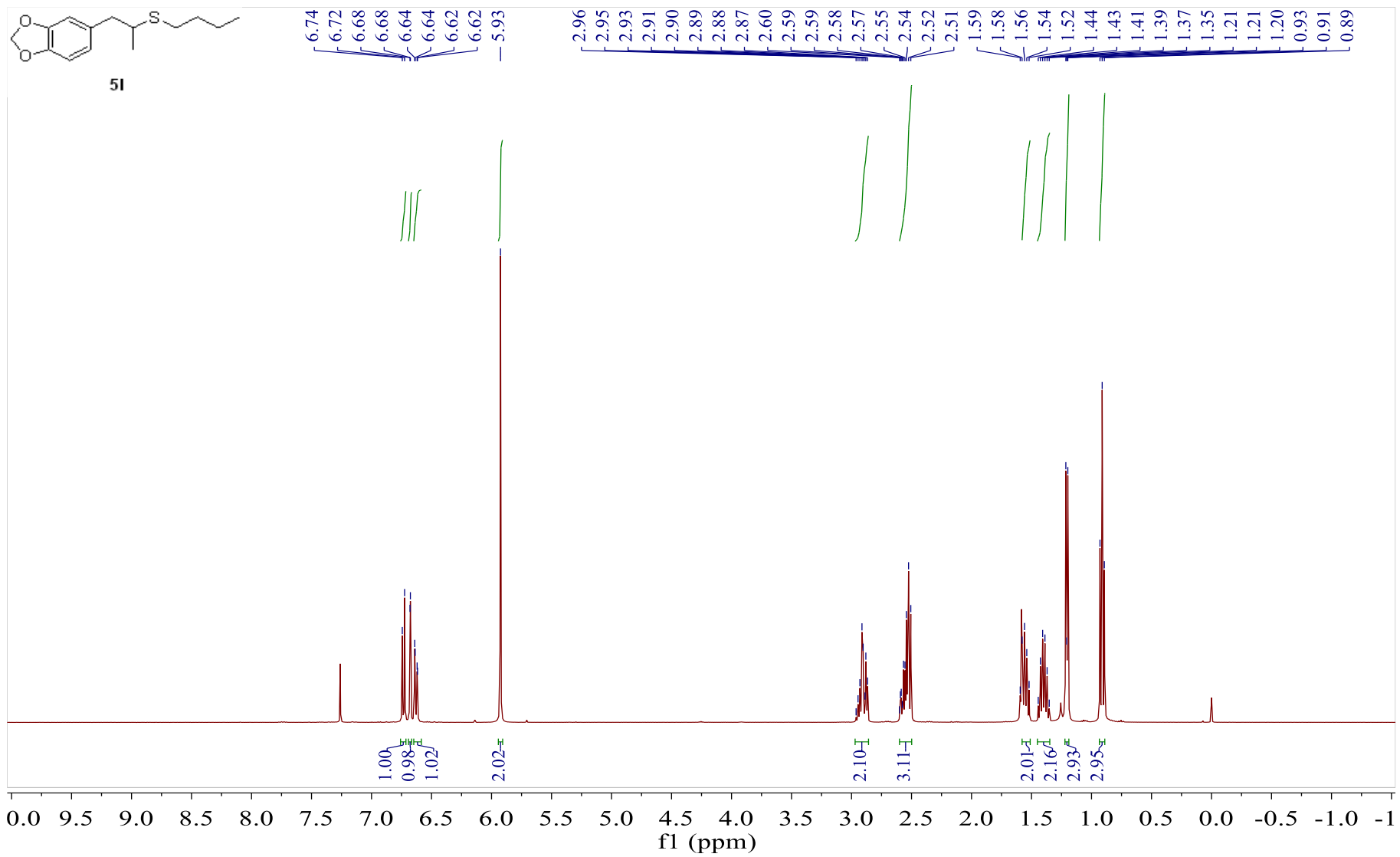


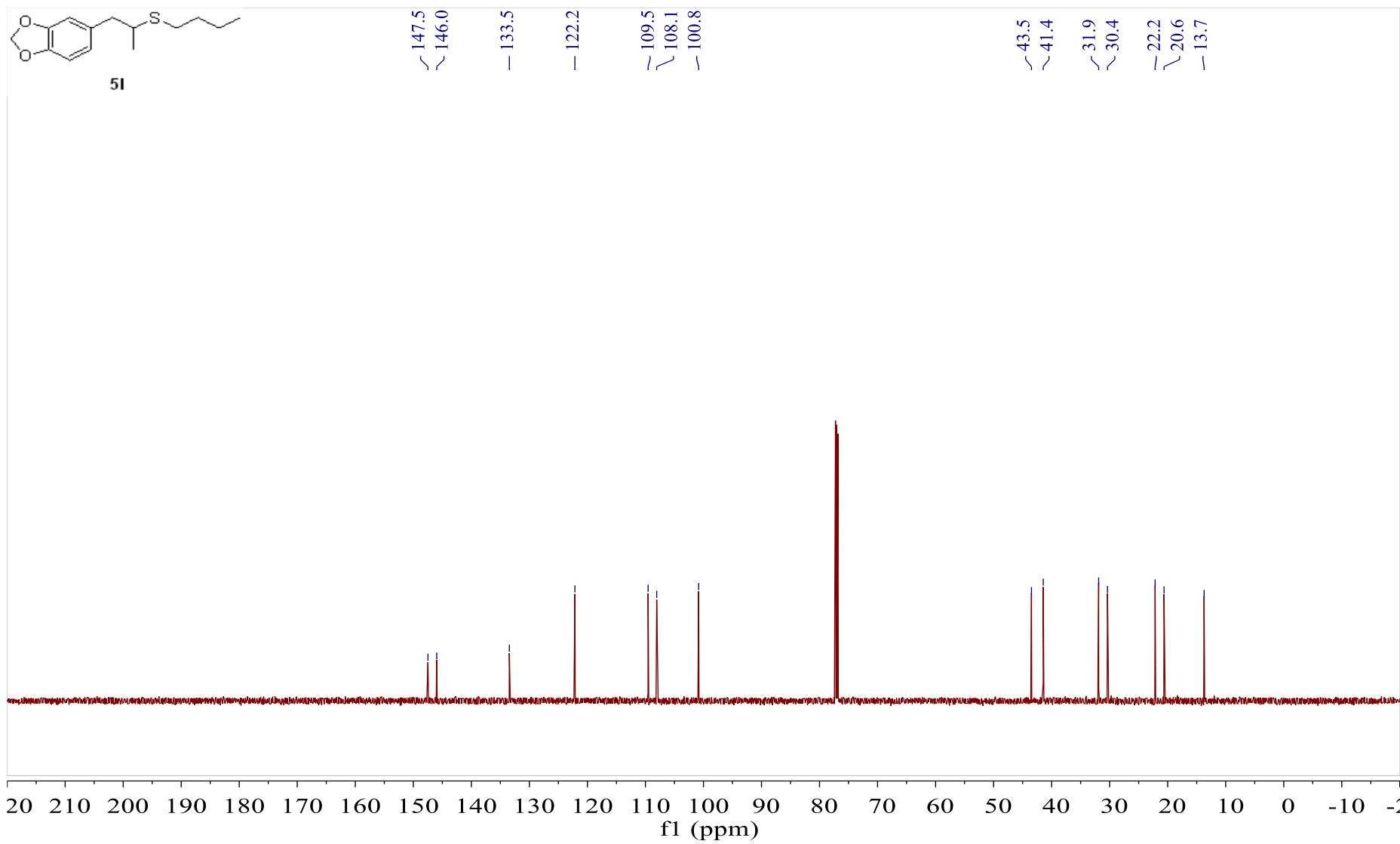


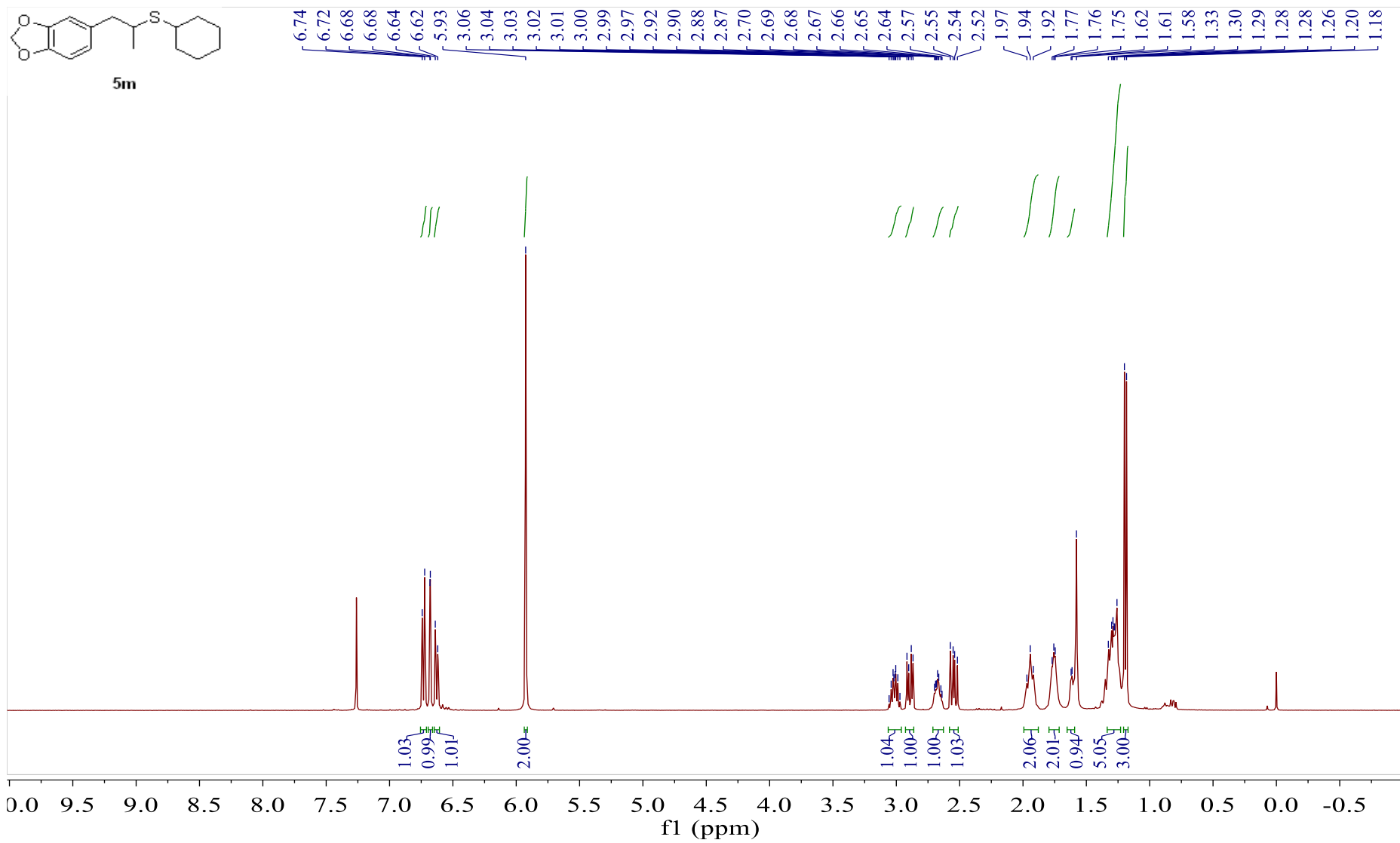


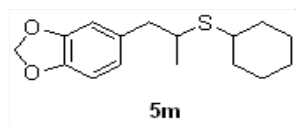












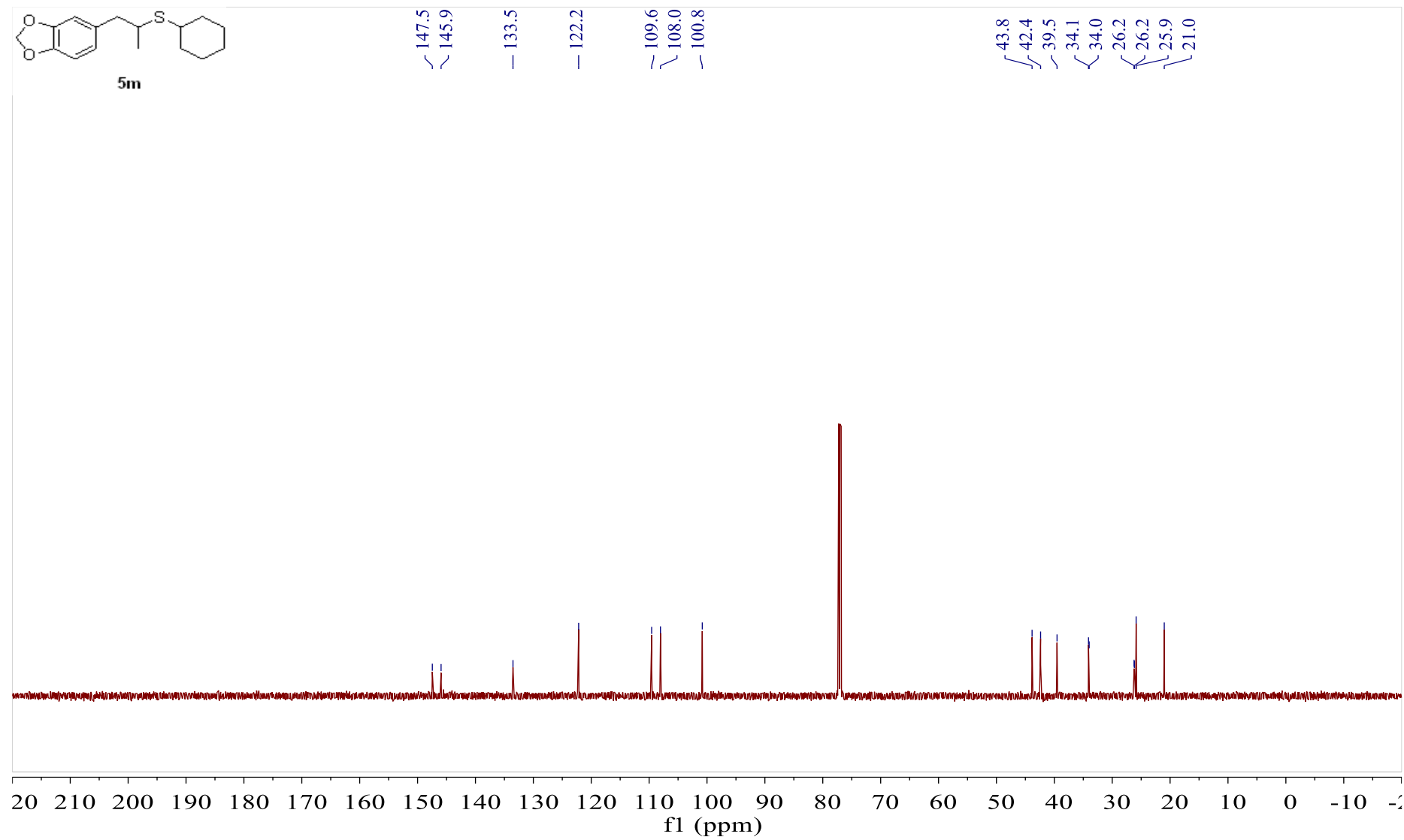
147.5
145.9

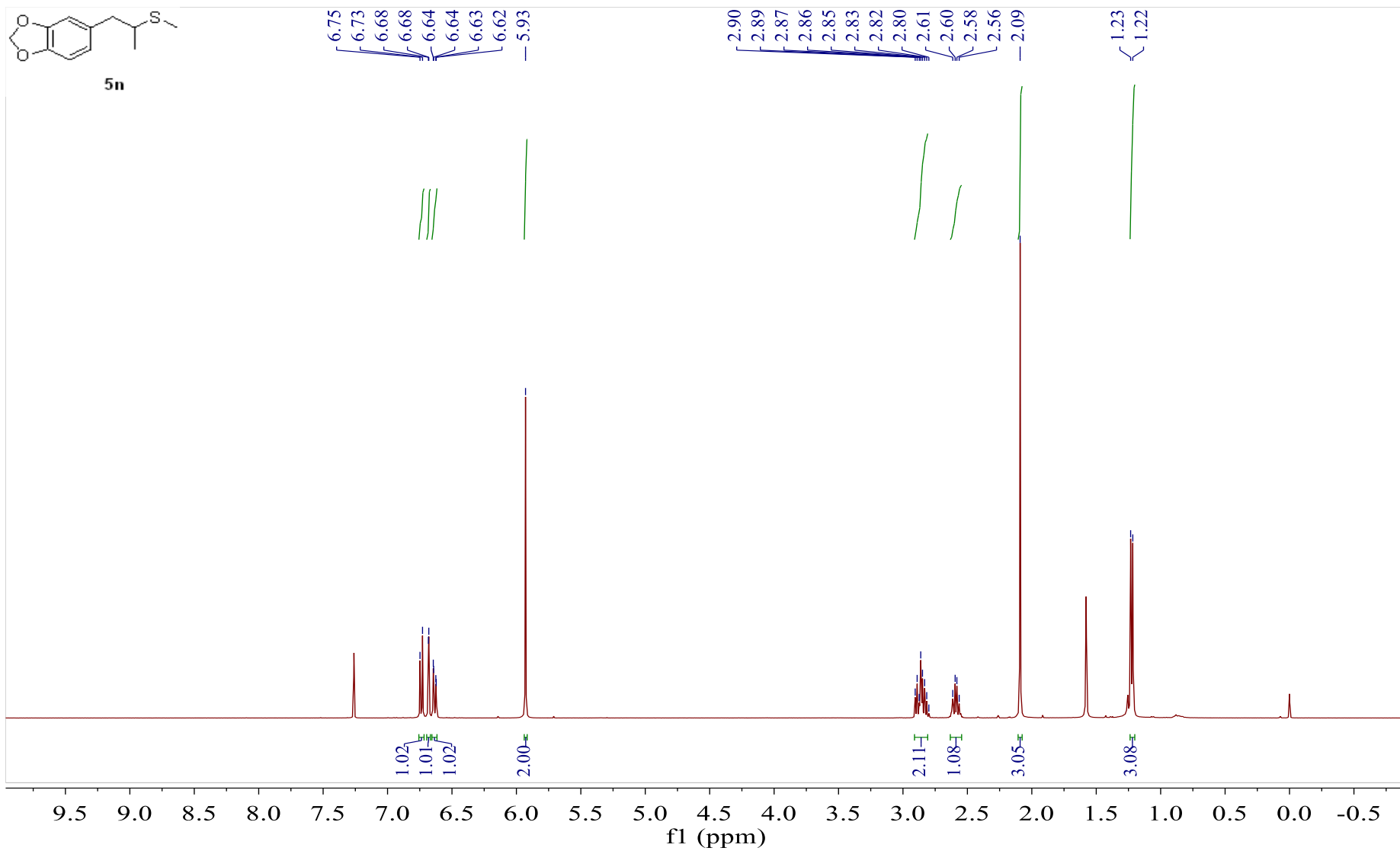
133.5

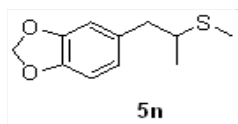
122.2

109.6
108.0
100.8

43.8
42.4
39.5
34.1
34.0
26.2
26.2
25.9
21.0







147.5
146.0

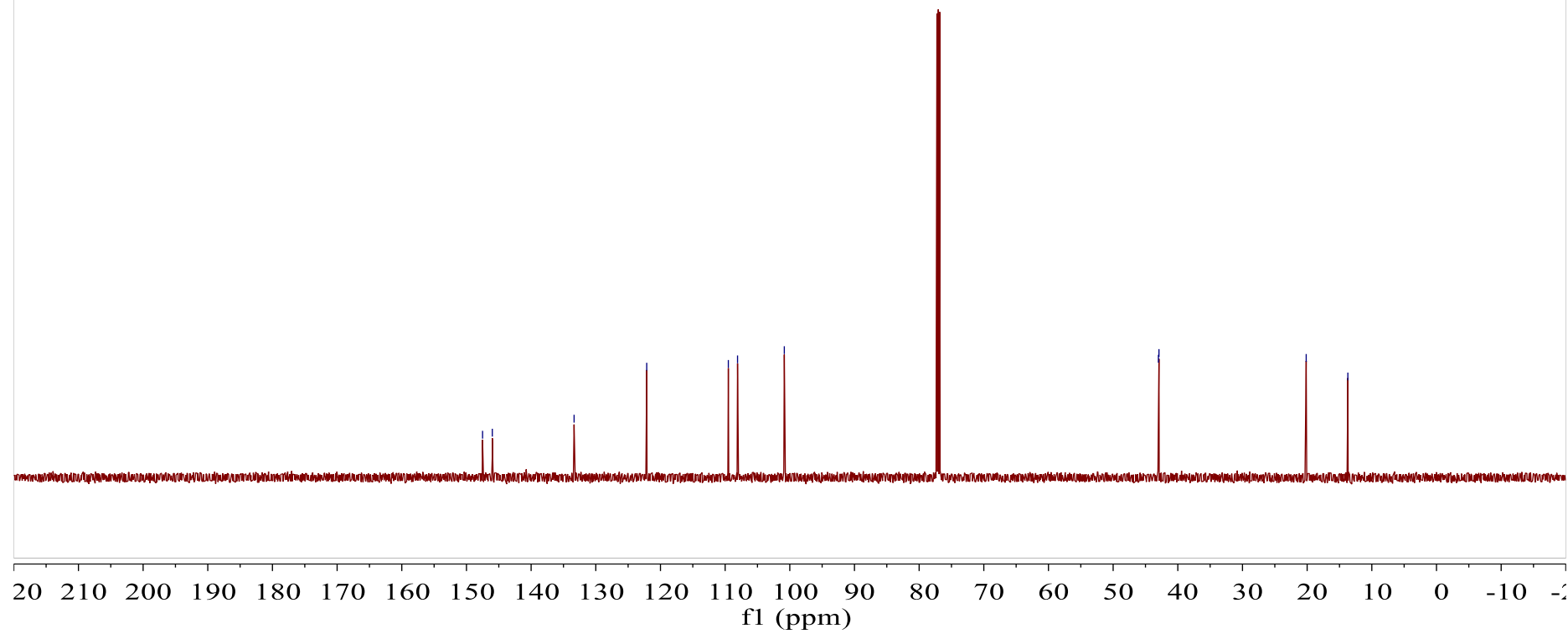
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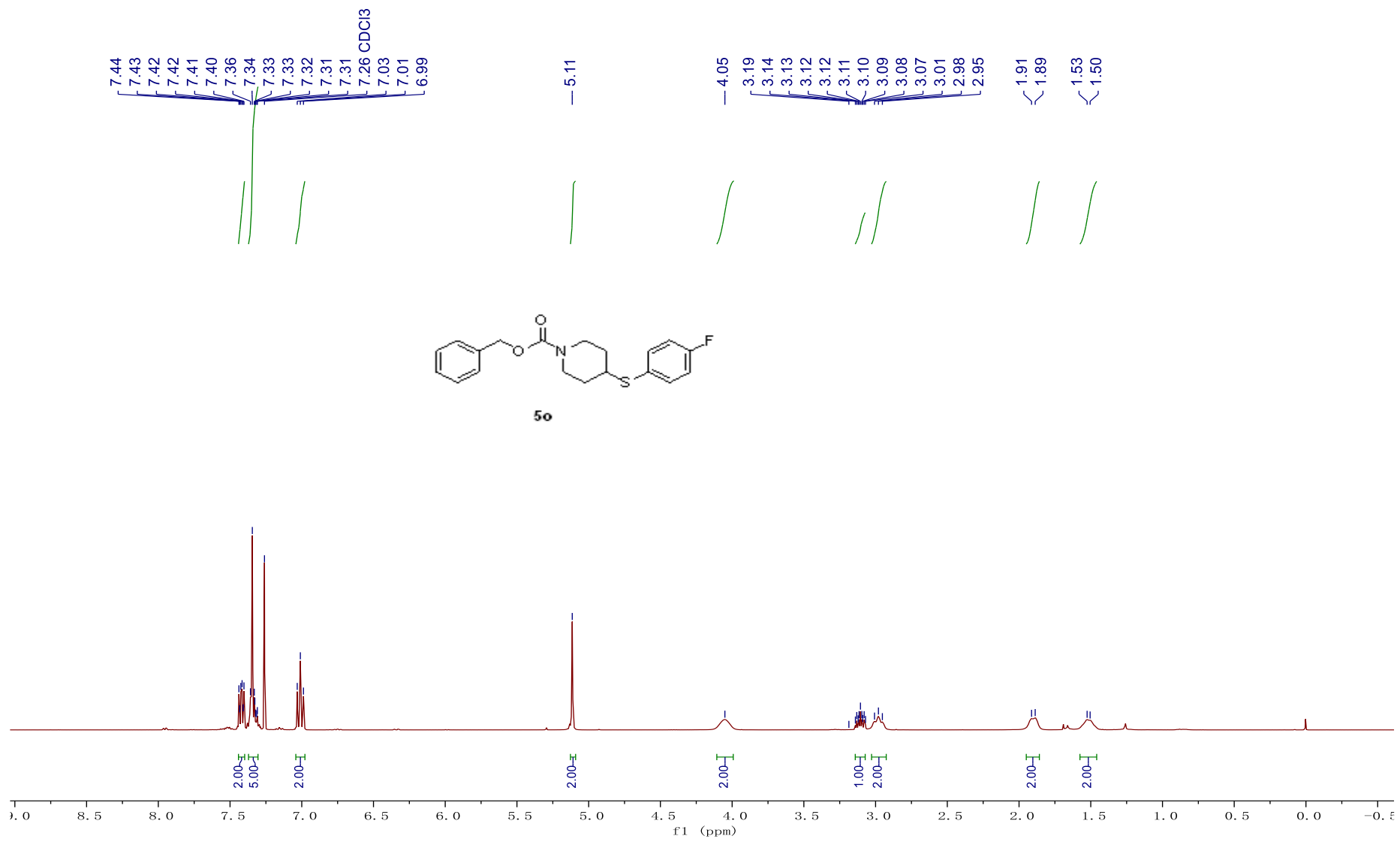
122.1

109.5
108.1
100.8

43.0
42.9

20.1
13.7





— 164.00
— 161.53
— 155.25

— 136.85
— 135.98
— 135.90
— 128.62
— 128.50
— 128.46
— 128.15
— 128.00

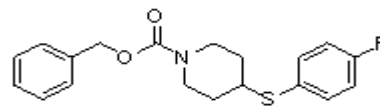
— 116.32
— 116.10

— 77.16 CDCl₃

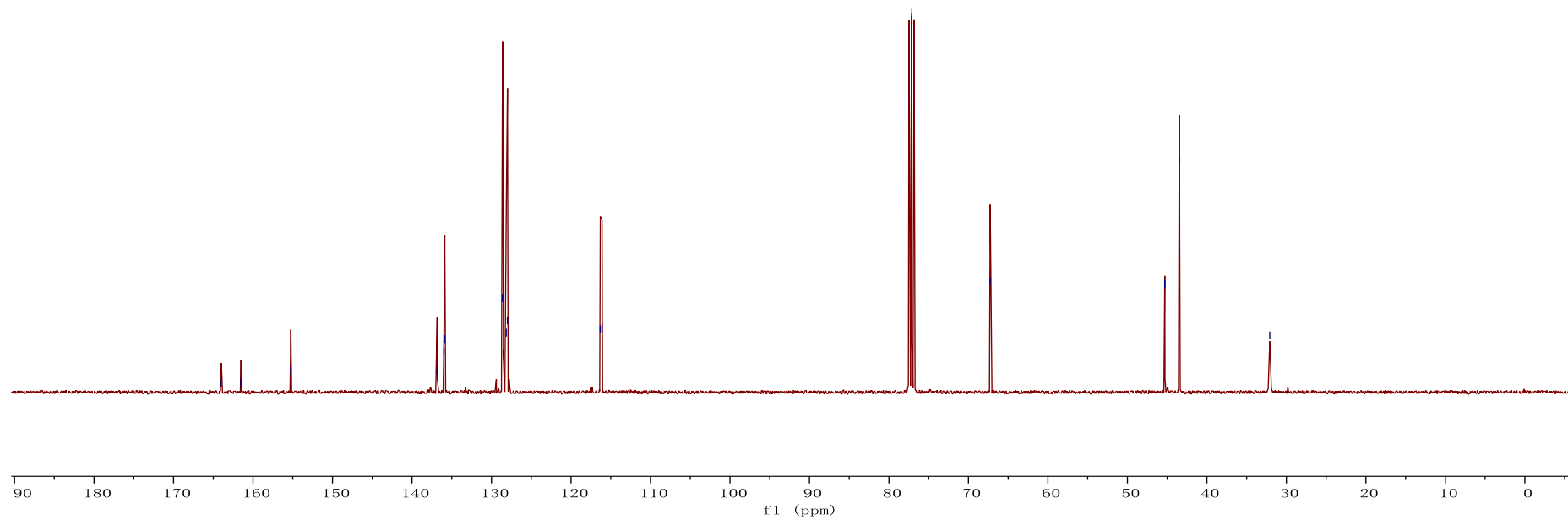
— 67.27

— 45.30
— 43.47

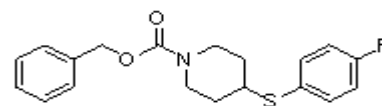
— 32.09



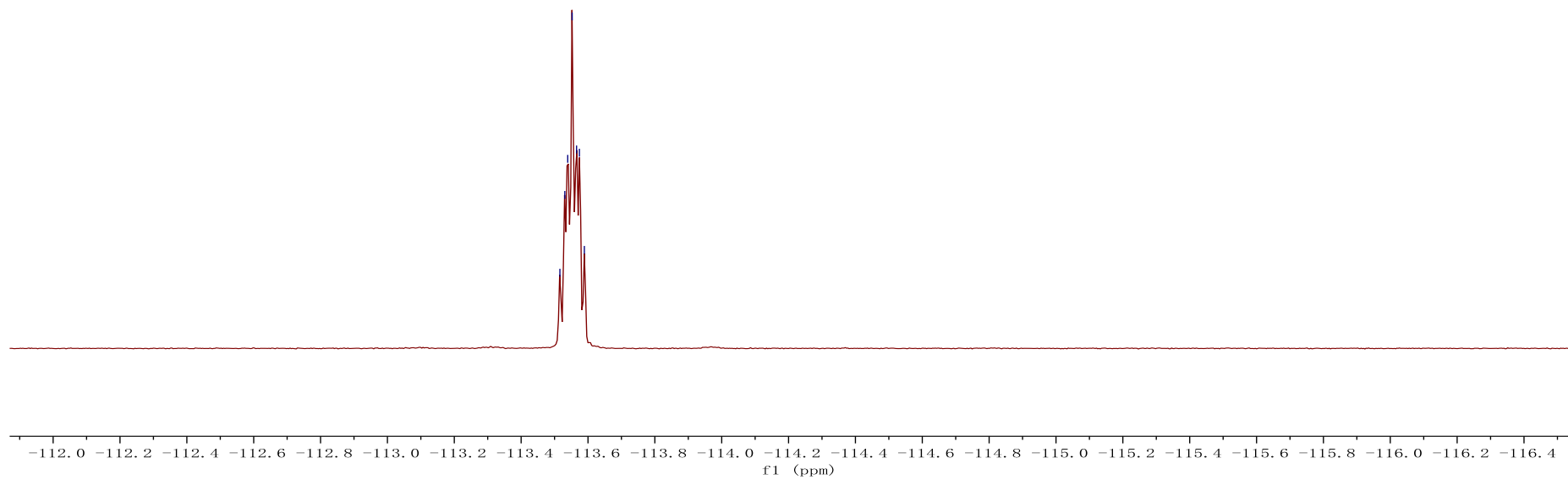
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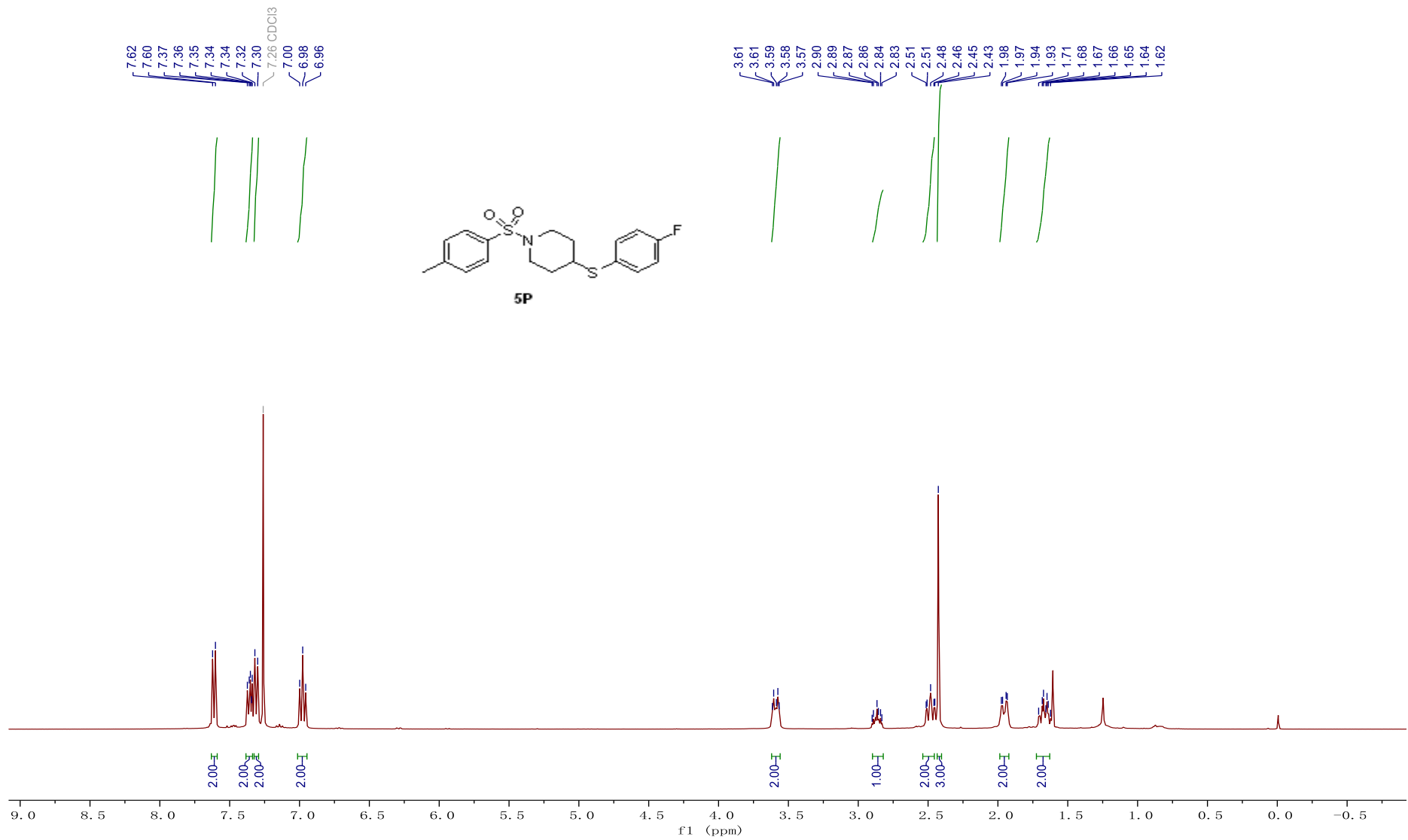


-113.52
-113.53
-113.54
-113.55
-113.57
-113.59



5o





— 164.03
— 161.56

— 143.77
— 136.02
— 135.93
— 133.09
— 129.81
— 128.19
— 128.15
— 127.80

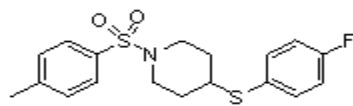
— 116.36
— 116.15

— 77.16 CDCl₃

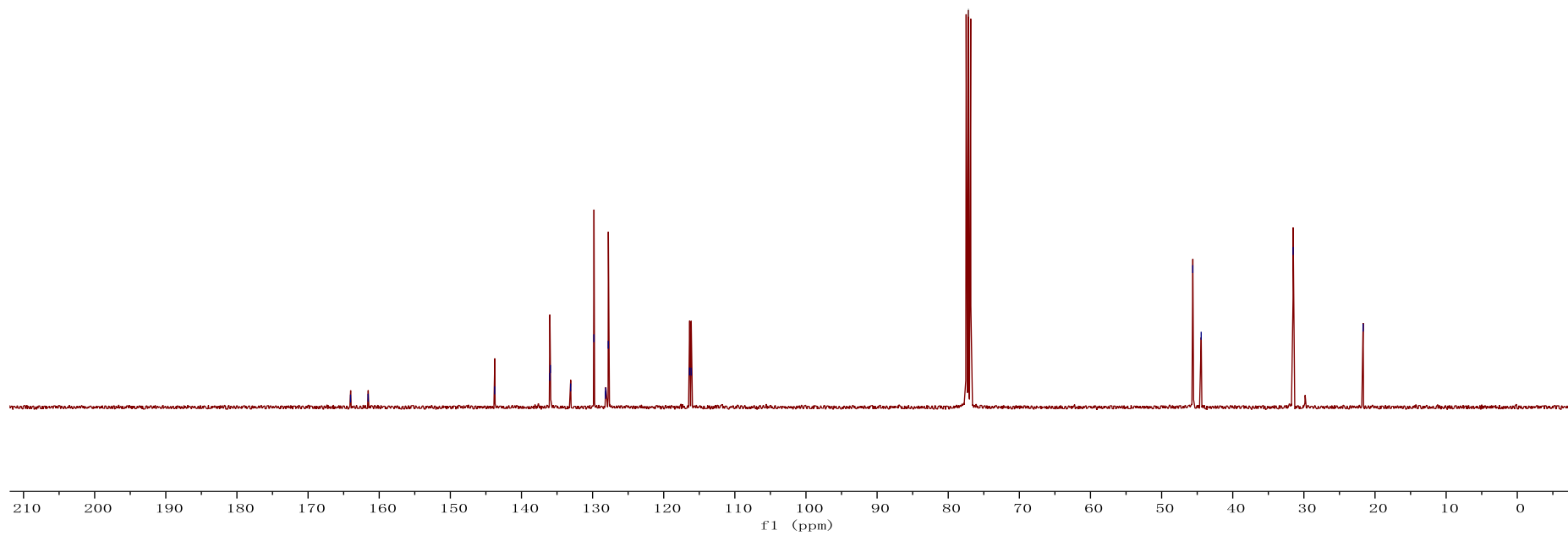
— 45.62
— 44.44

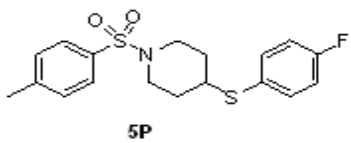
— 31.52

— 21.67

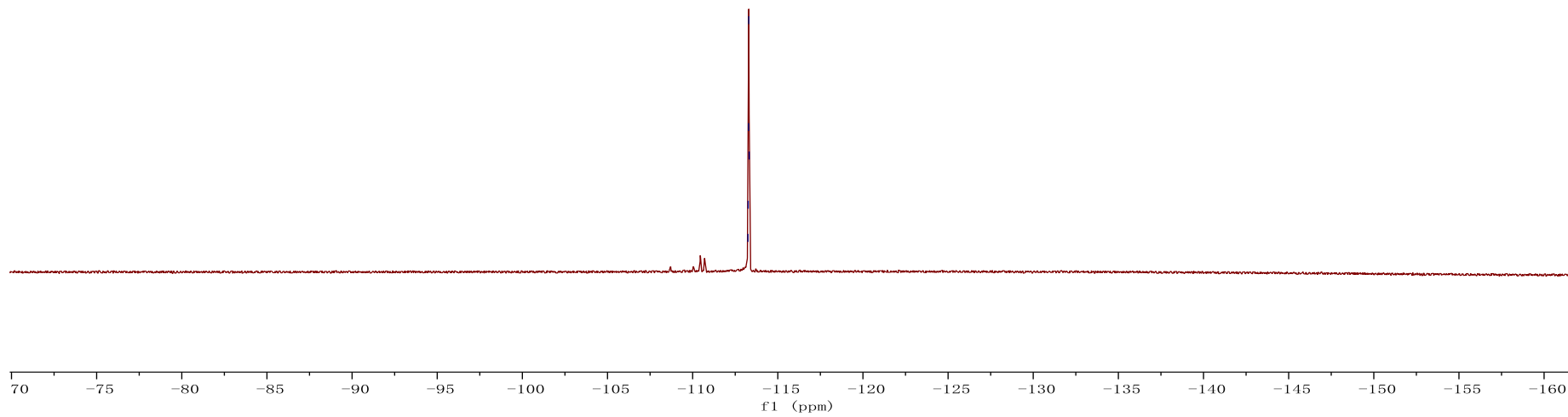


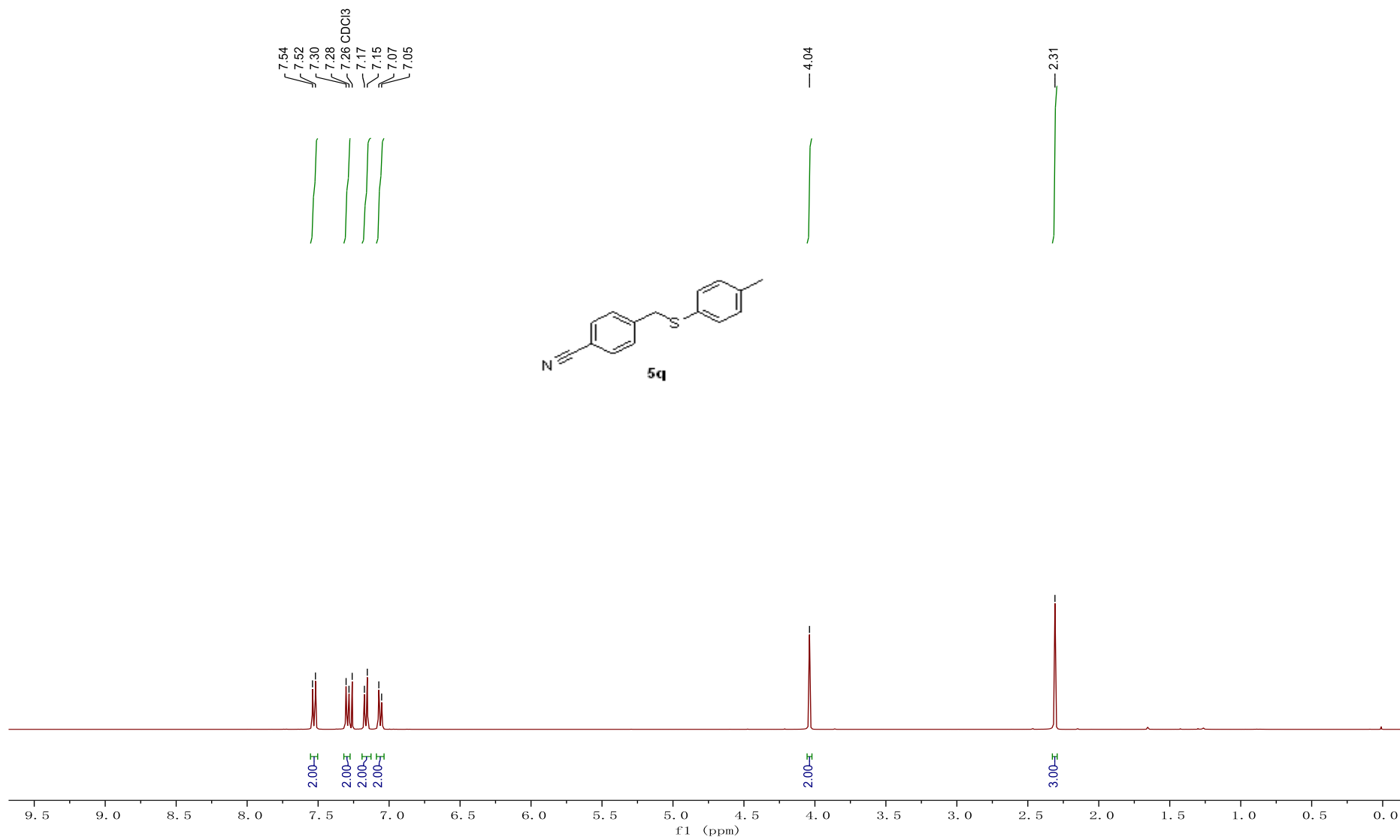
5P

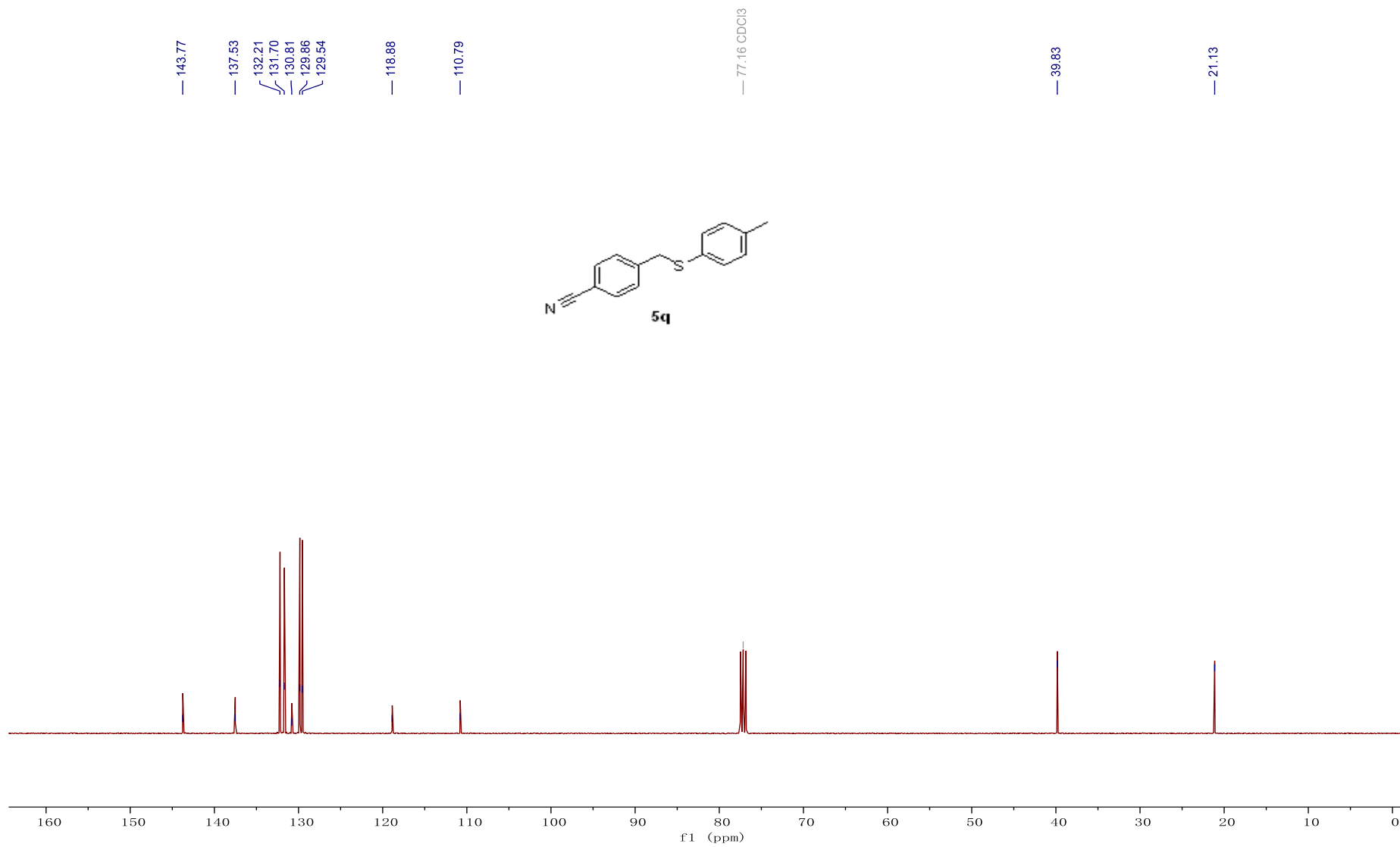


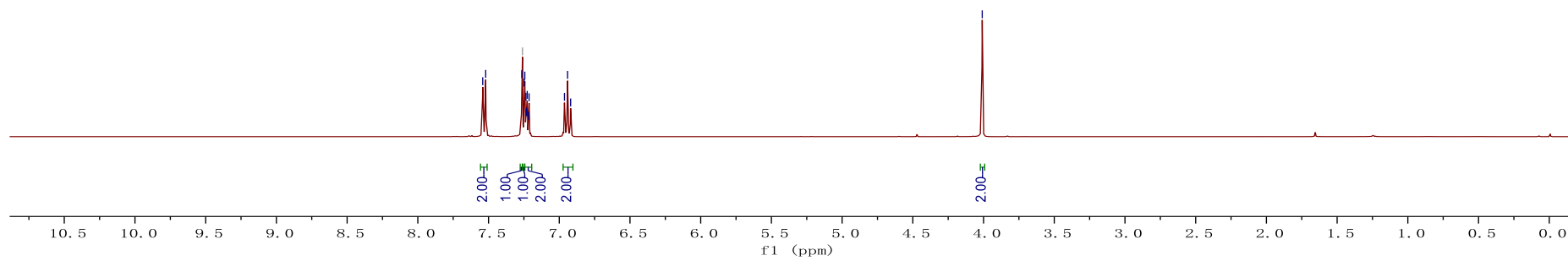
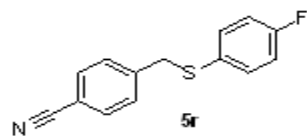
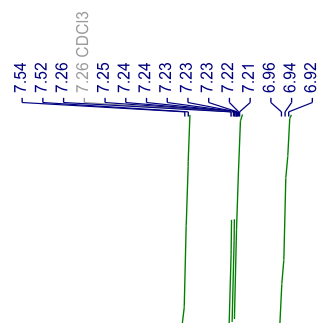


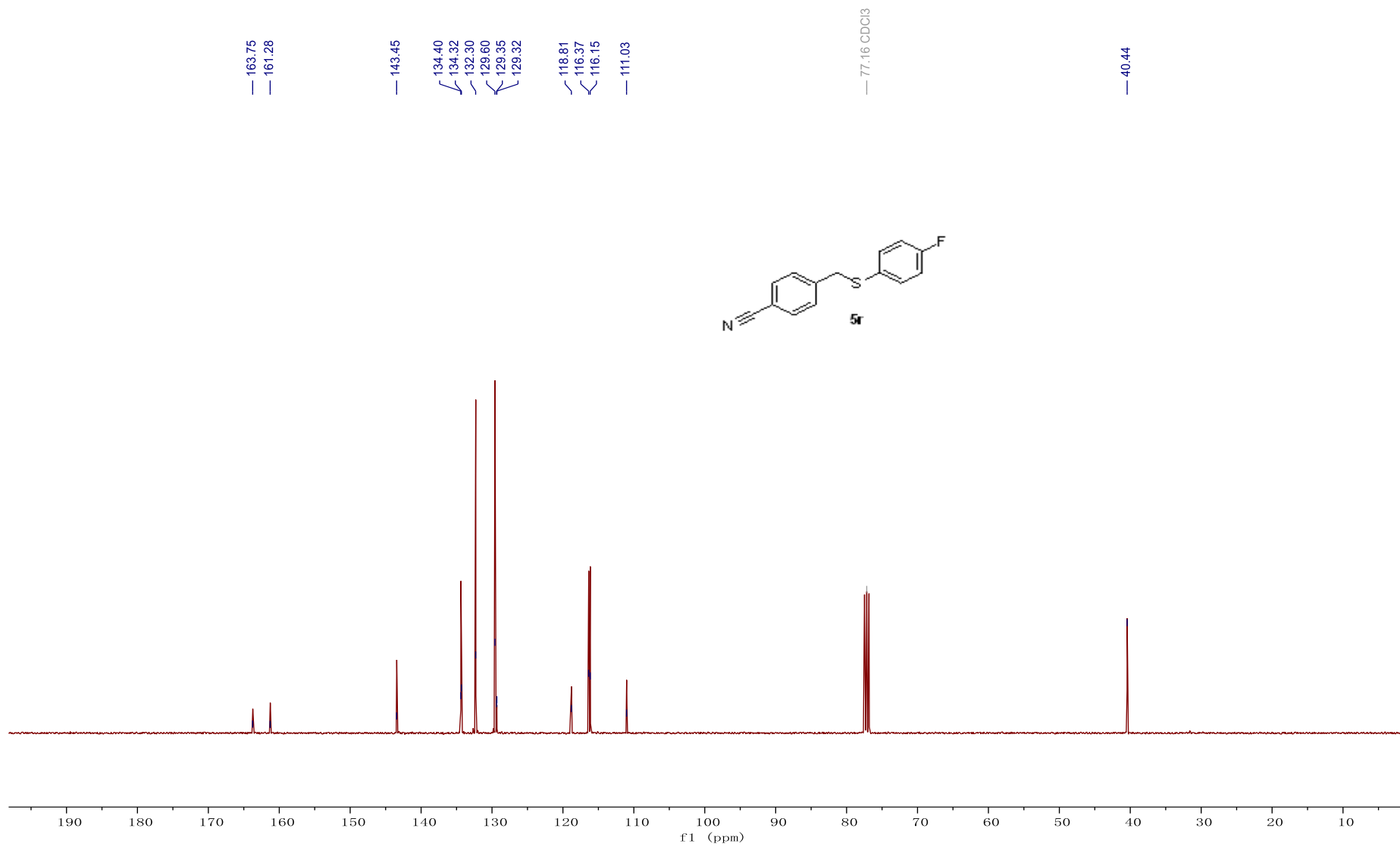
-113.25
-113.26
-113.28
-113.29
-113.32

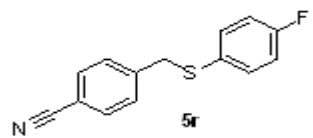




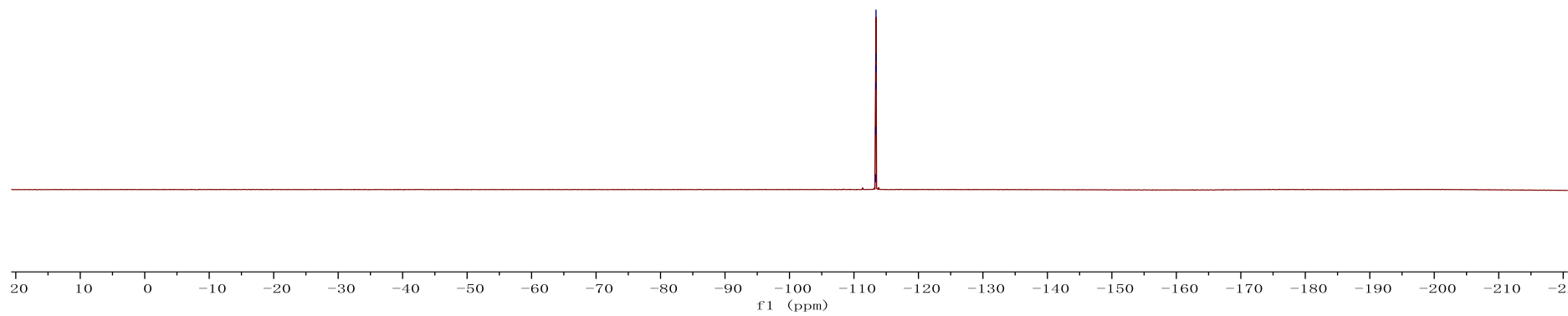


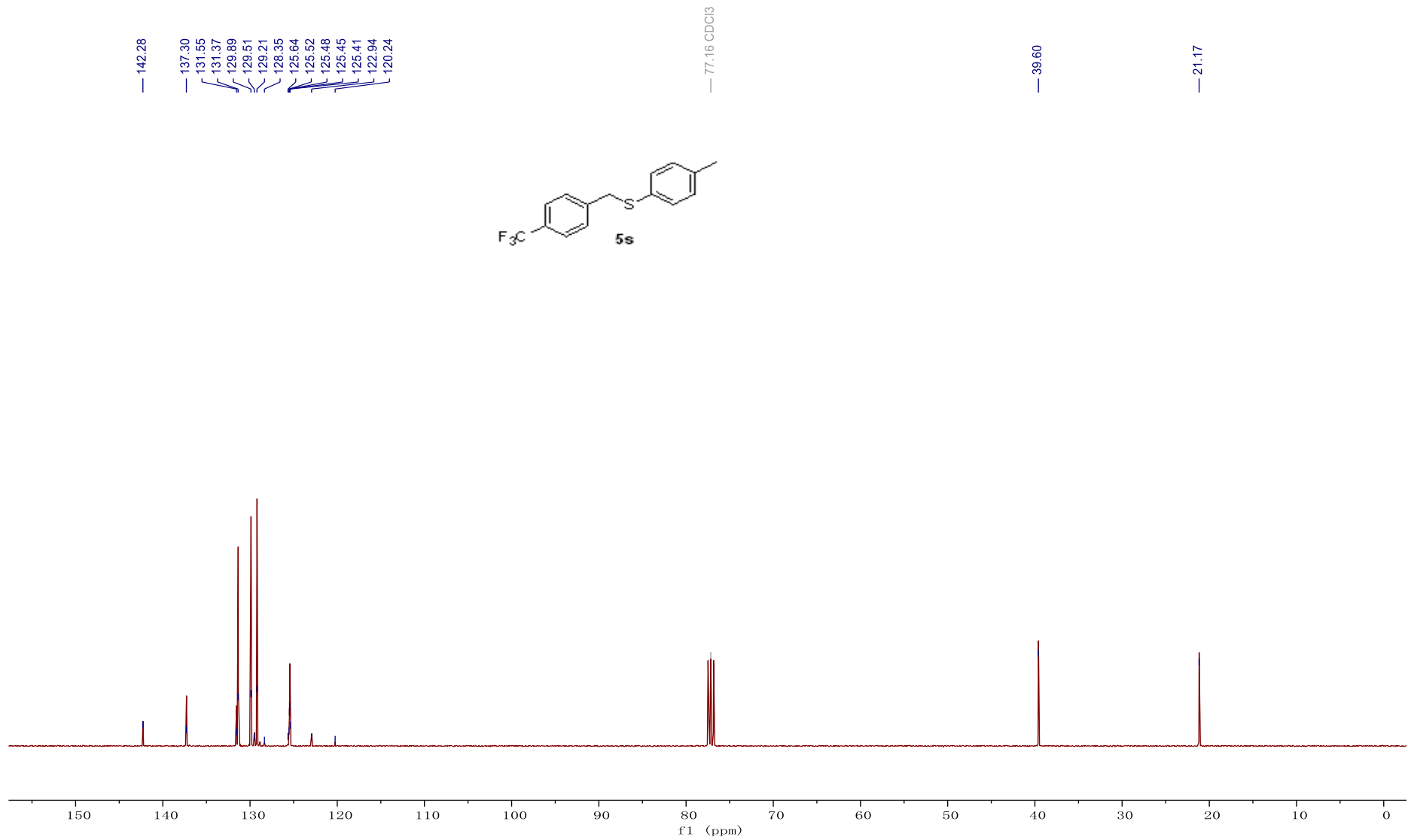


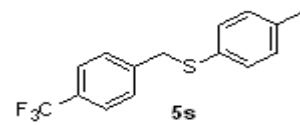




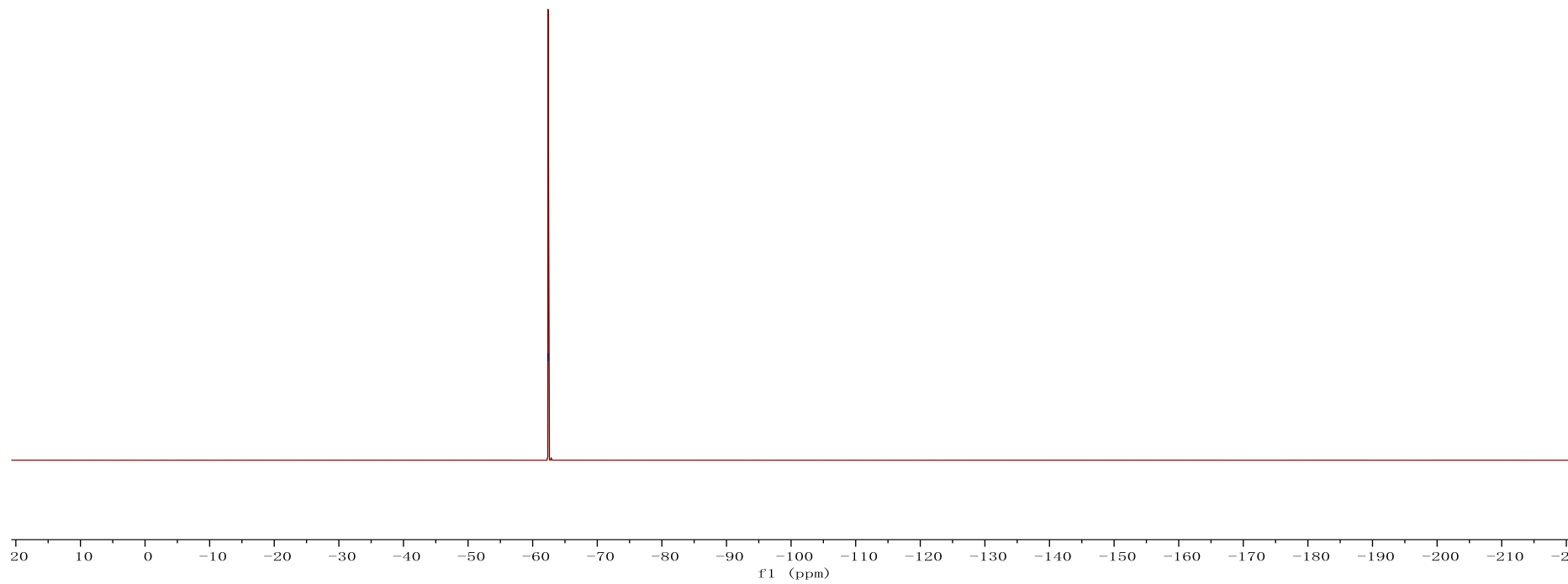
-113.36
-113.38
-113.39
-113.40
-113.41
-113.44

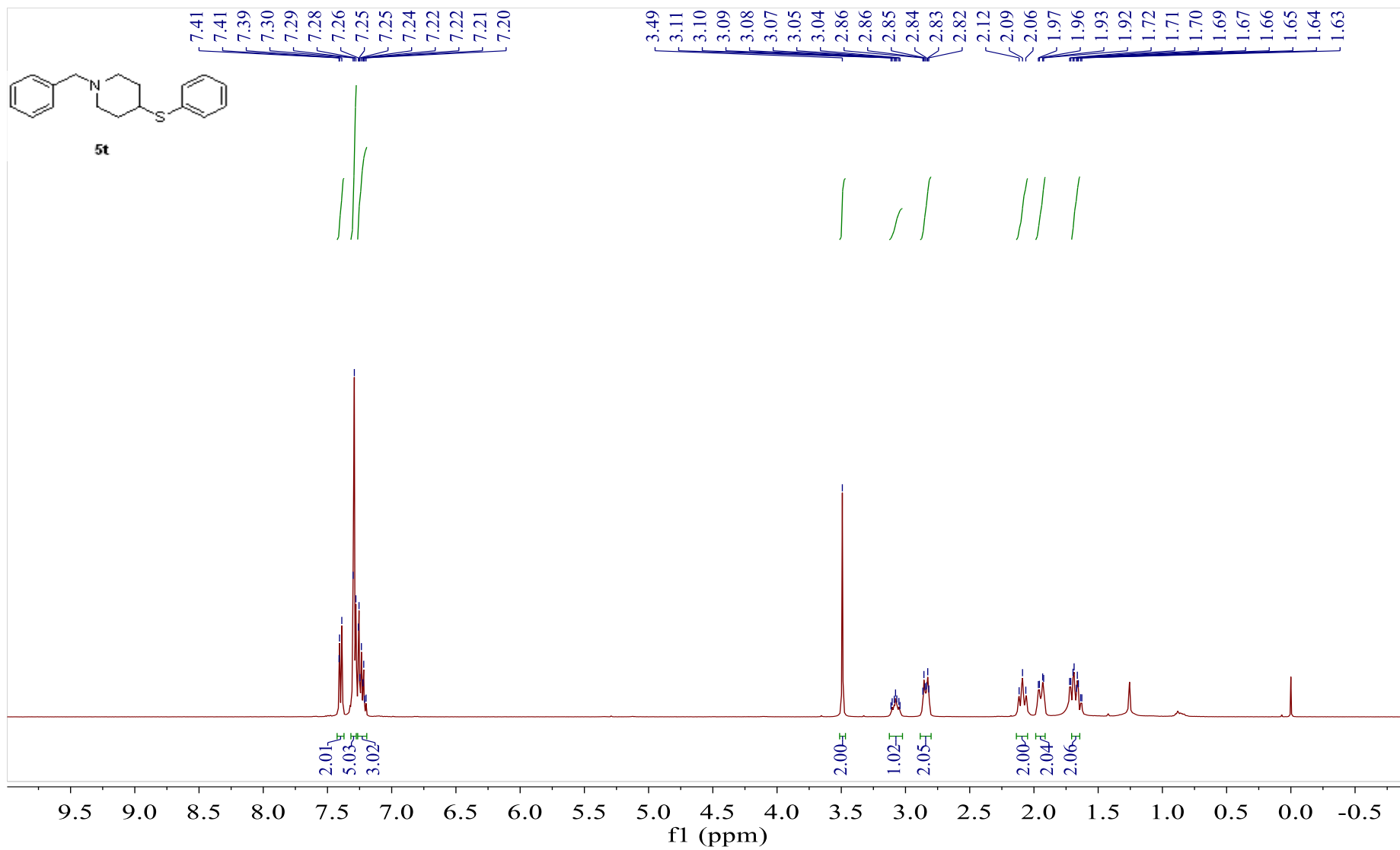


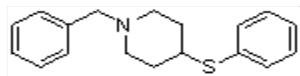




—62.37







5t

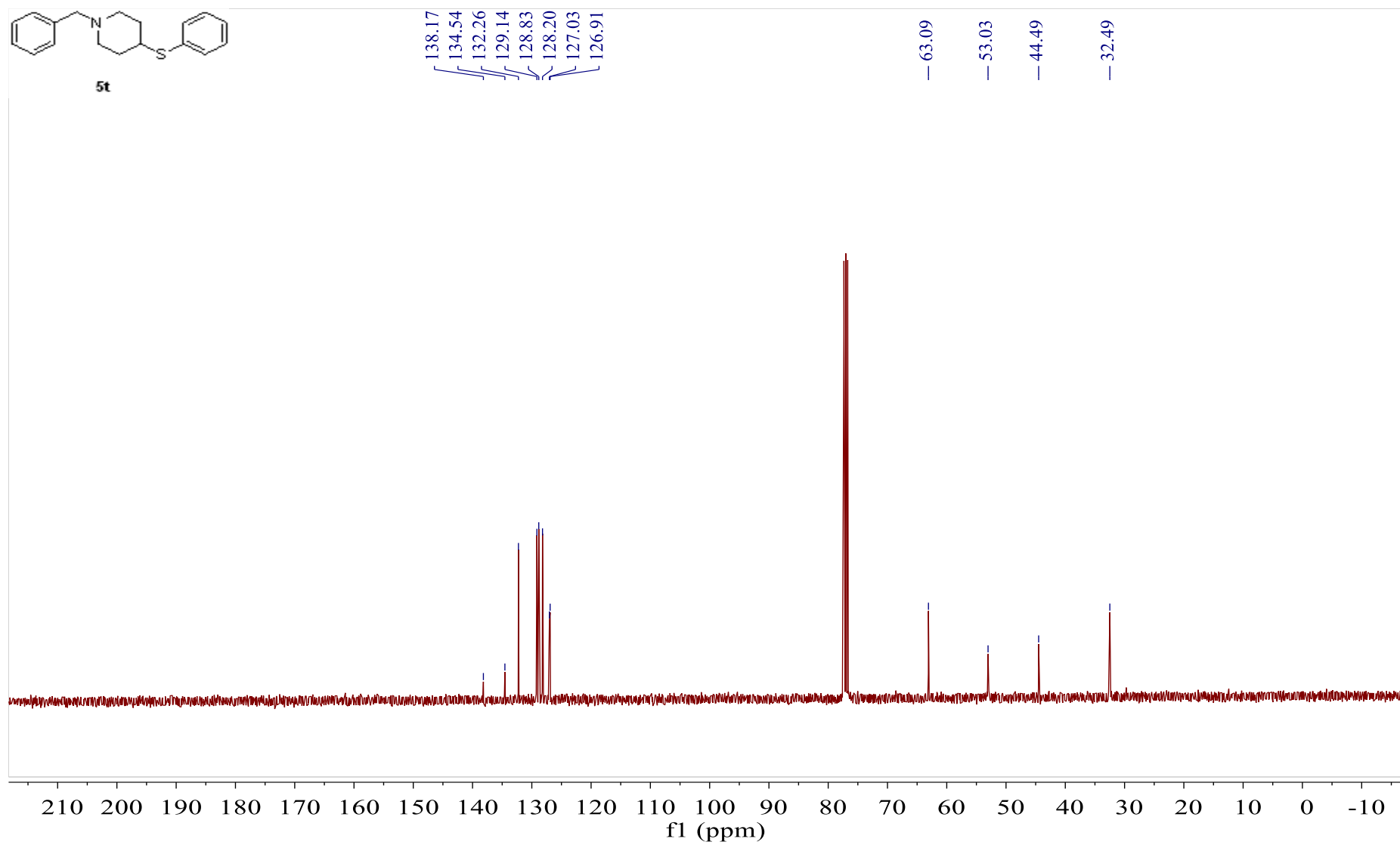
138.17
134.54
132.26
129.14
128.83
128.20
127.03
126.91

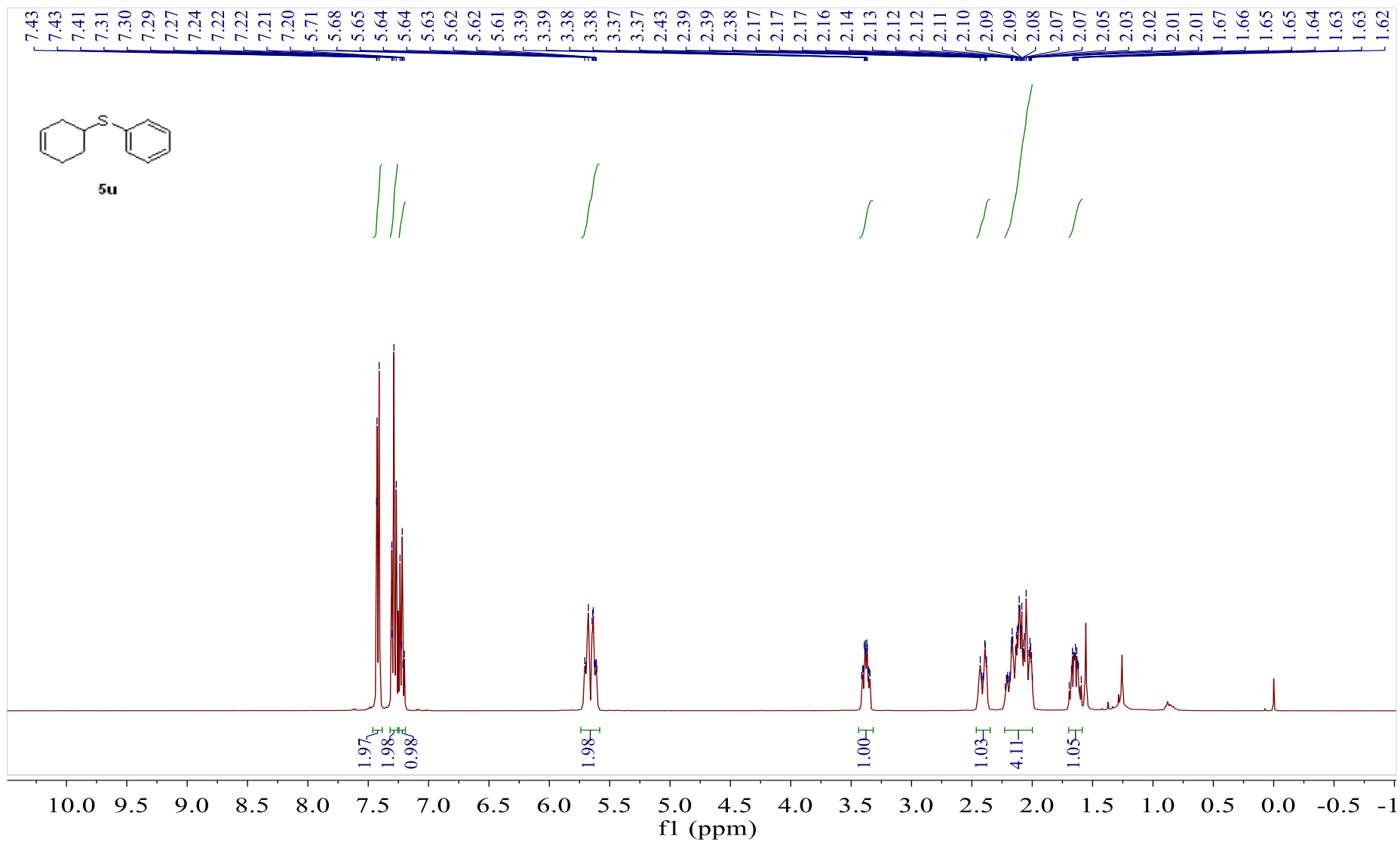
63.09

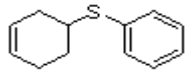
53.03

44.49

32.49





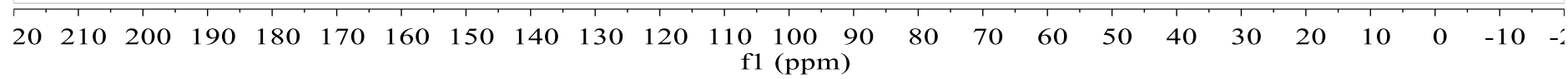


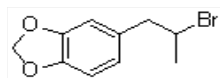
5u

134.92
131.88
128.83
126.77
126.76
125.32

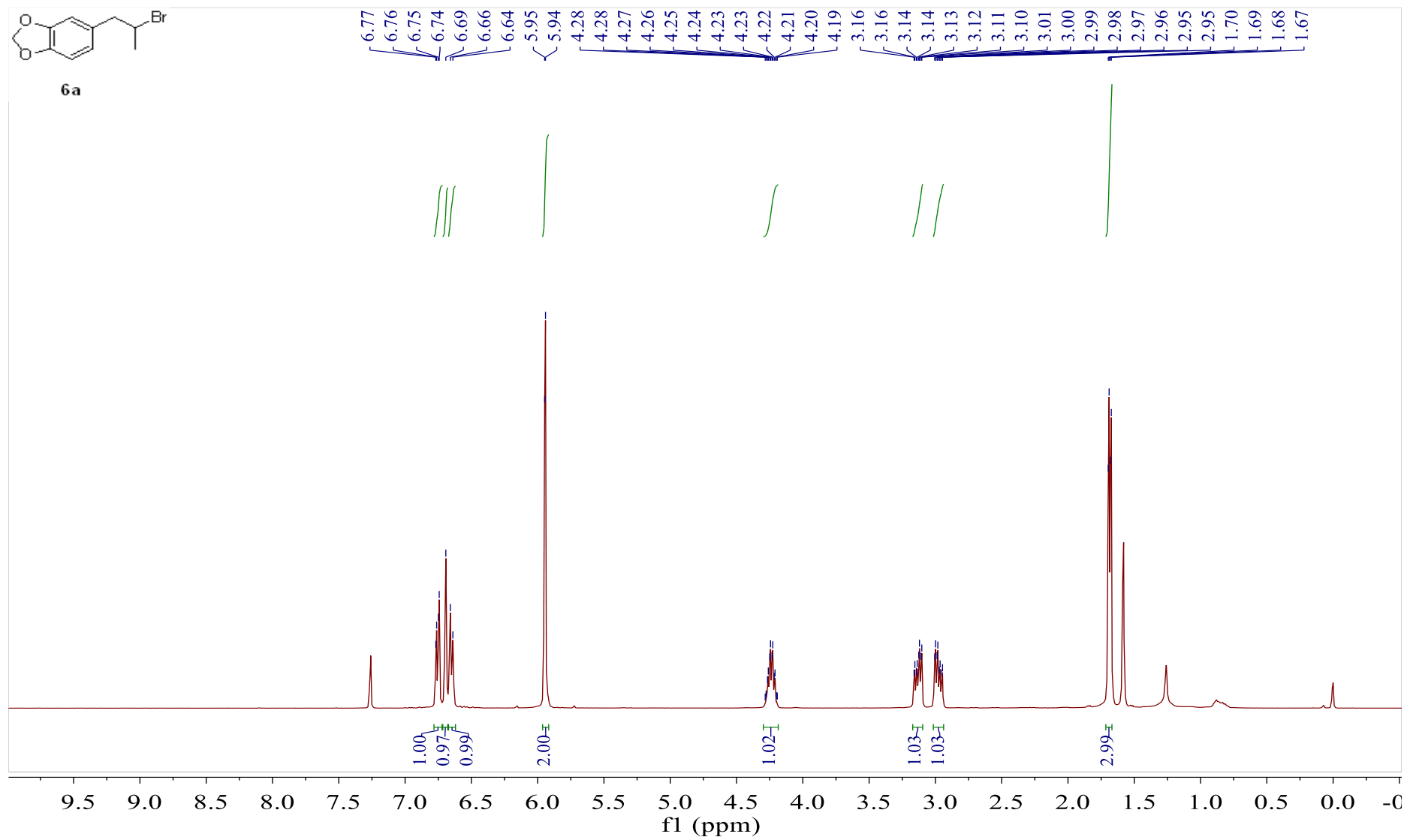
42.83

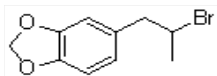
31.92
28.86
24.84



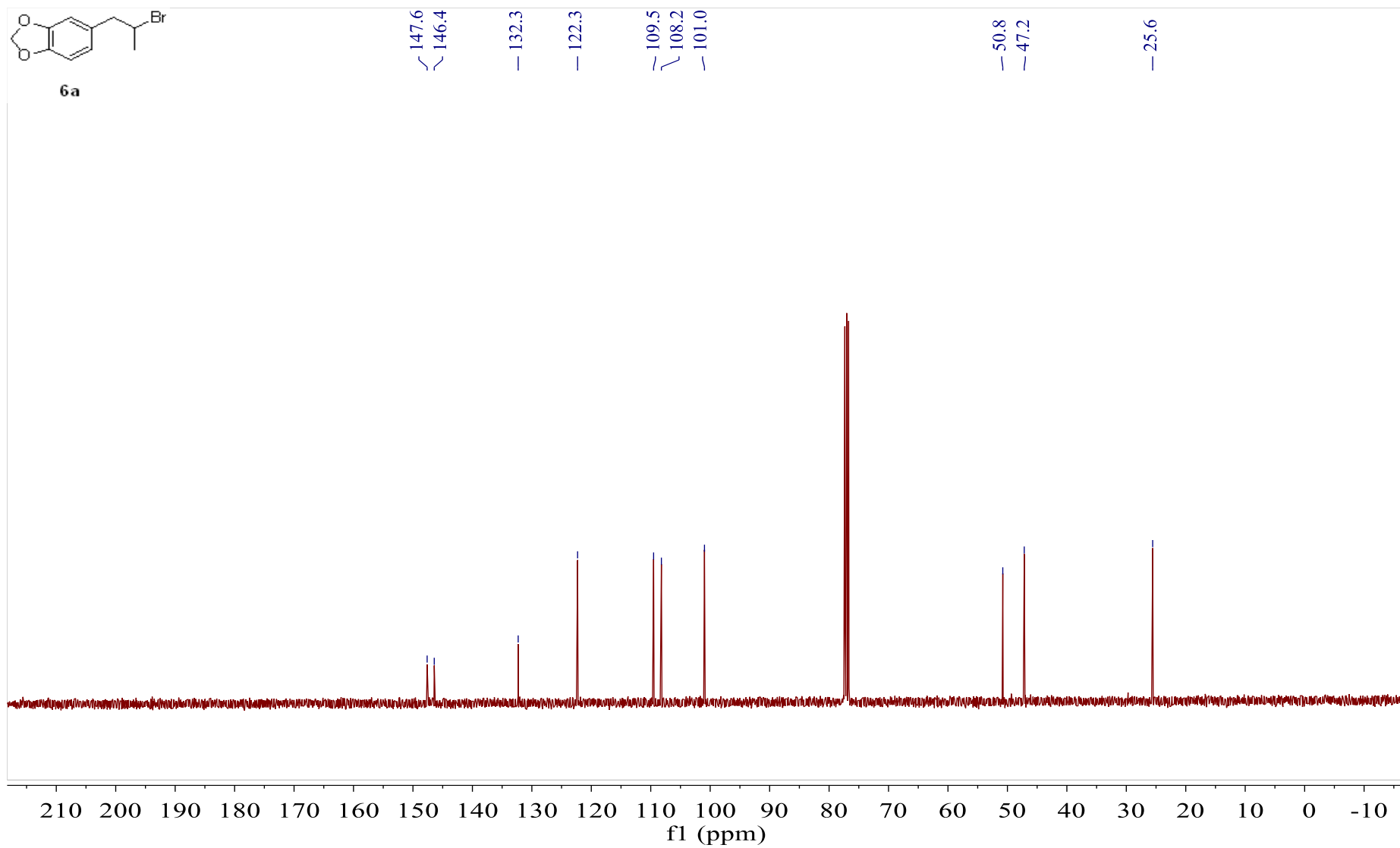


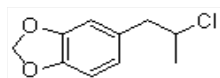
6a



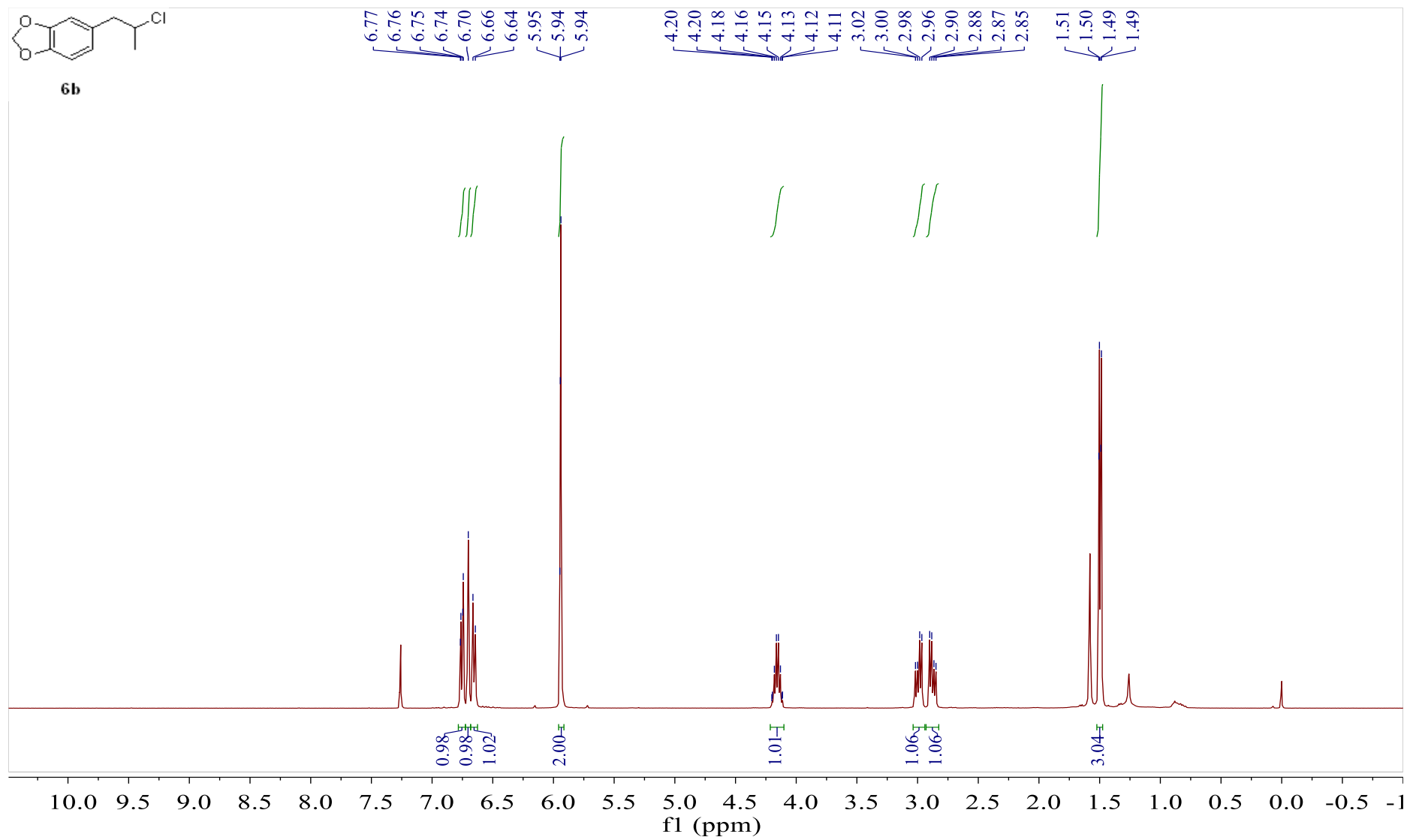


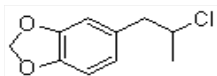
6a



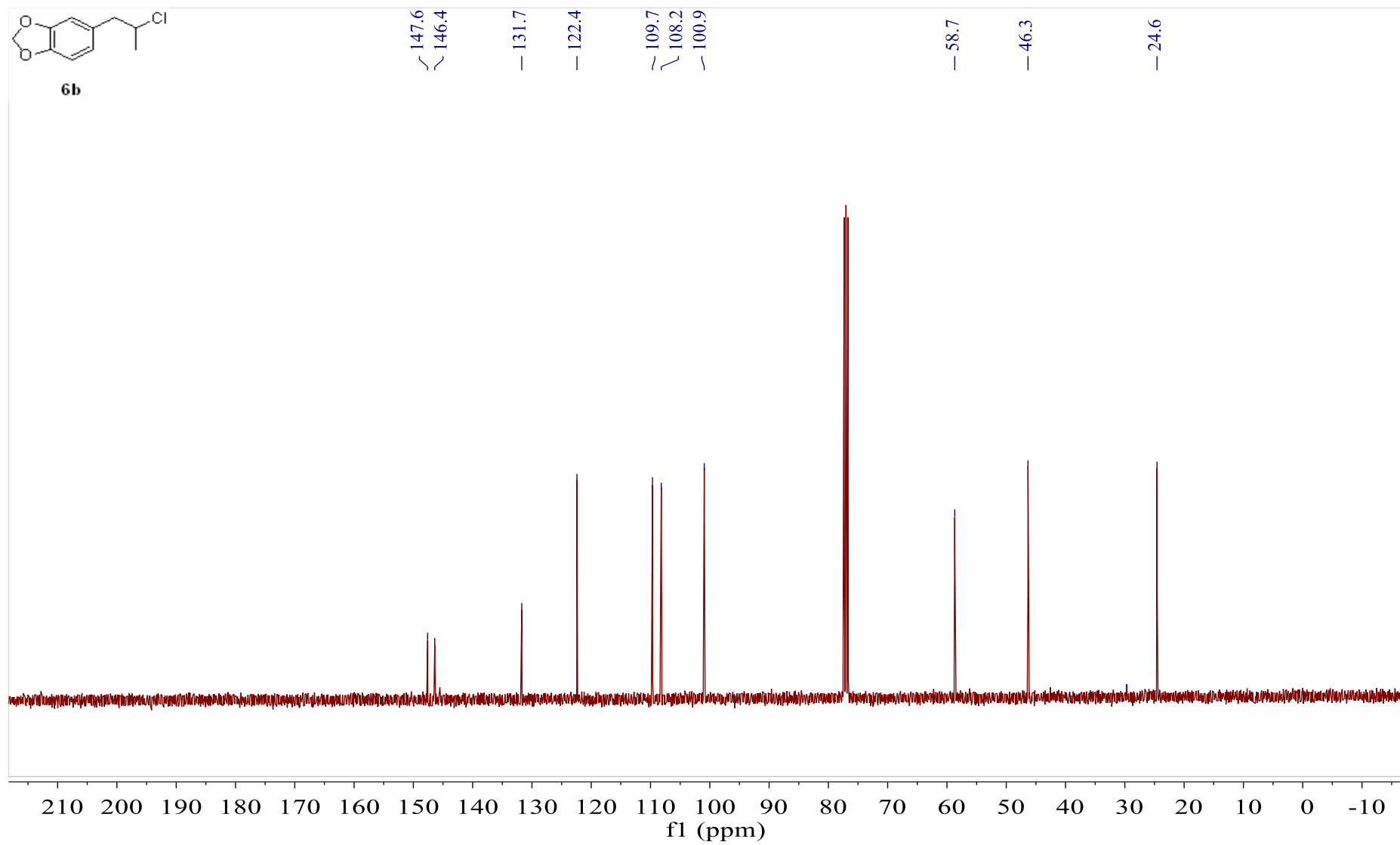


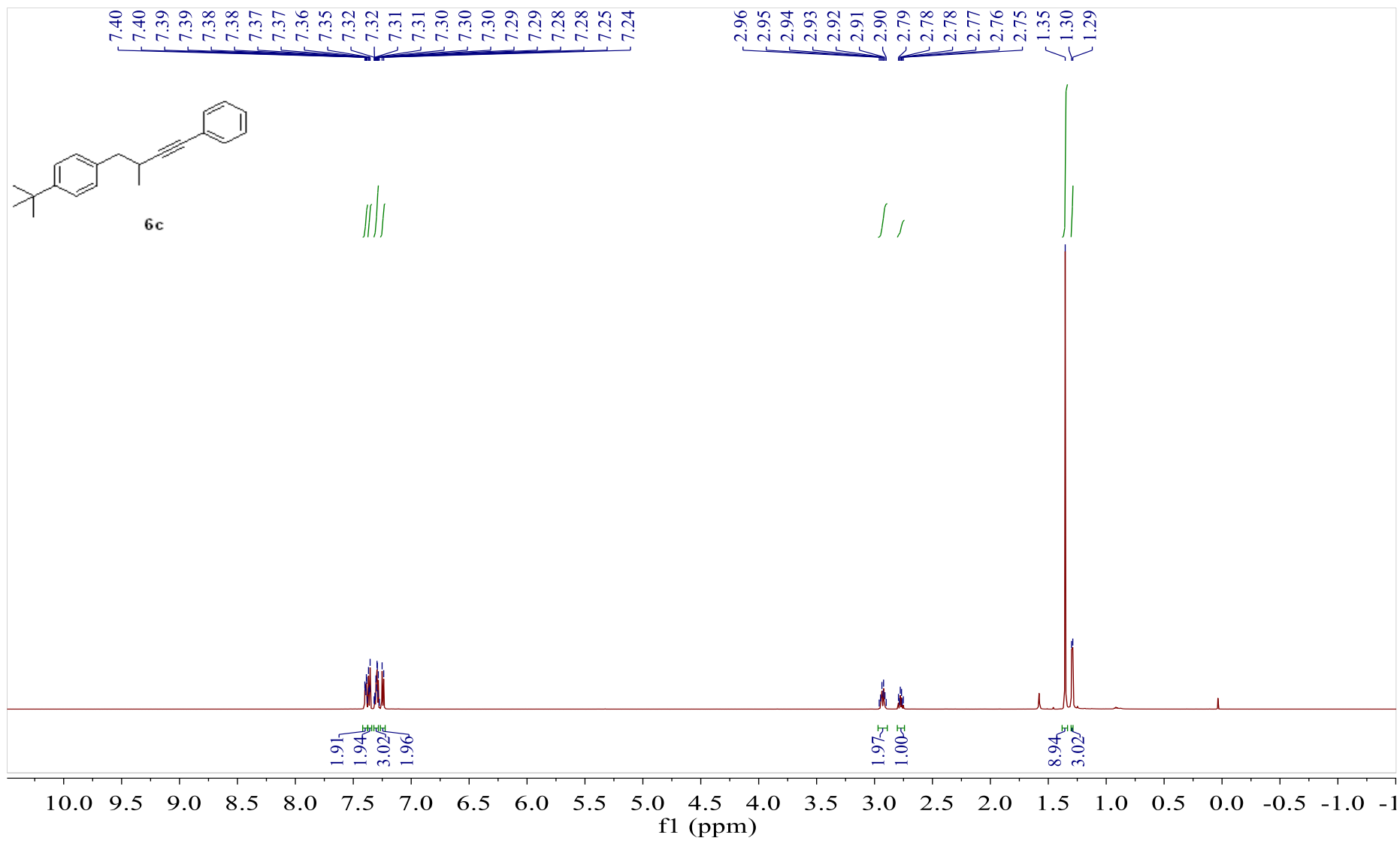
6b

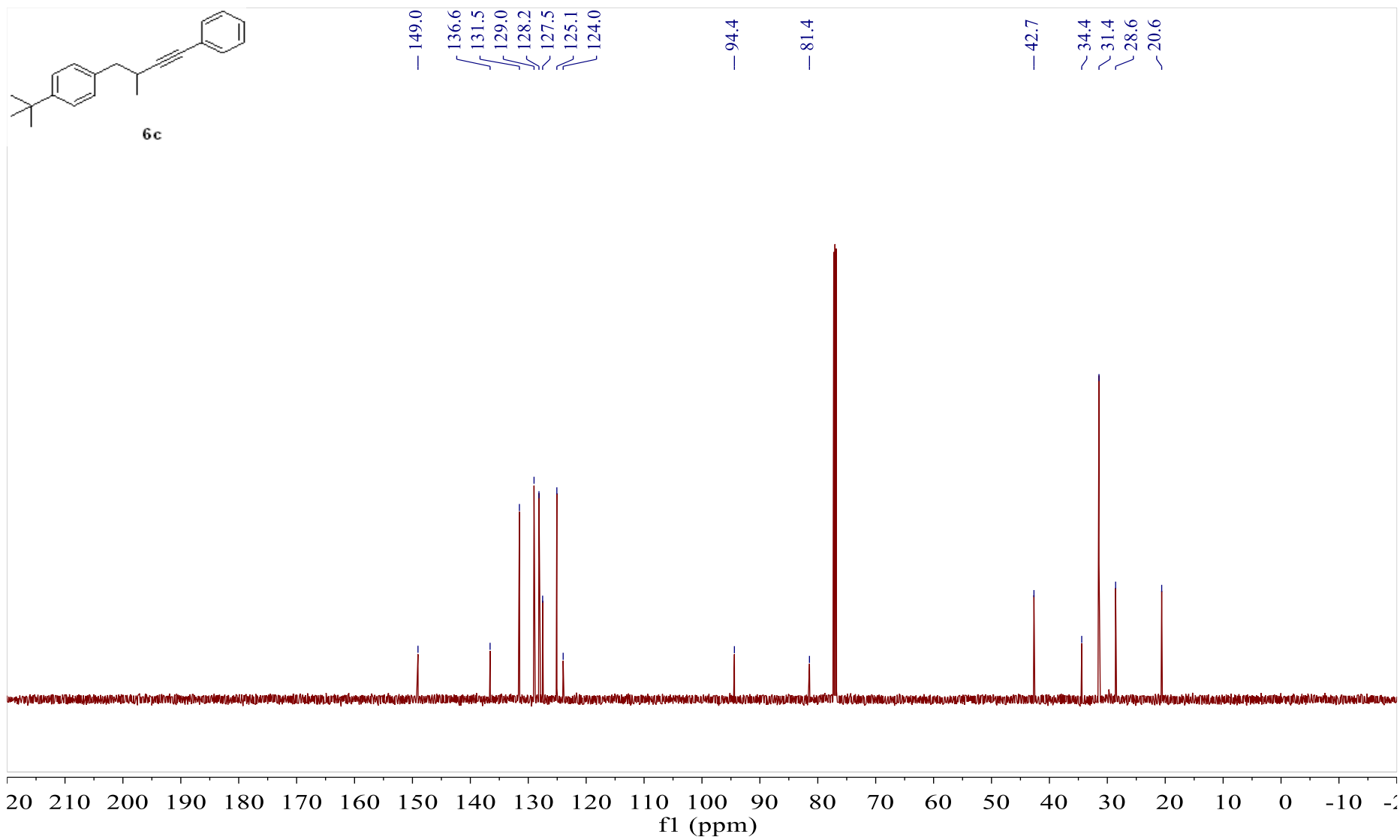




6b







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