

Supporting Information for:

**Copper-catalyzed carbonylation of anilines by diisopropyl
azodicarboxylate for the synthesis of carbamates**

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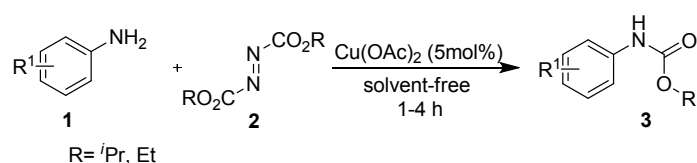
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1. General information

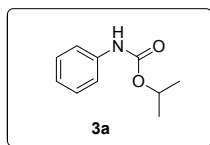
^1H , ^{13}C and ^{19}F NMR spectra were recorded at 400, 100 and 365 MHz respectively in CDCl_3 . Multiplicities were given as: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet and m = multiplet. Coupling constants, J were reported in Hertz unit (Hz). All products were further characterized by HRMS (ESI-TOF-Q). Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel 60 (200-300 mesh)). Analytical thin layer chromatography (TLC) plates (silica gel GF254) were analyzed under UV light. All reactions were carried out under argon atmosphere in dried glassware with magnetic stirring. Solvents were distilled by standard methods. Reagents were purchased from commercial suppliers and used without further purification unless otherwise noted.

2. Typical procedure for the synthesis of carbamates

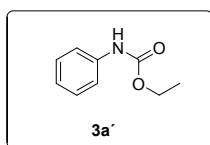


A 10 mL round bottom flask with a magnetic stir bar was charged with the mixture of aniline **1** (0.3 mmol), diisopropyl azodicarboxylate **2** (0.6 mmol) and $\text{Cu}(\text{OAc})_2$ (5 mol%, 2.7 mg) in Ar atmosphere. The resulting mixture was stirred at indicated temperature for required time. When the reaction was completed (detected by TLC), if necessary the reaction mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding carbamate **3** with hexane/ethyl acetate as the eluent.

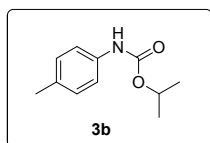
3. Characterization data of products



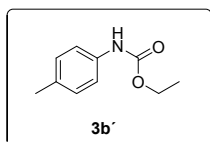
3a: Yield: 81% (43.6 mg), white solid, mp 89-91 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.38 (d, J = 8.0 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.04 (t, J = 7.2 Hz, 1 H), 6.64 (s, 1 H), 5.07-4.97 (m, 1 H), 1.29 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.3, 138.1, 129.0, 123.2, 118.6, 68.7, 22.1; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{13}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 202.0838, found 202.0827.



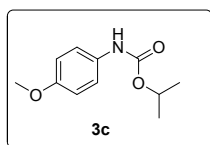
3a': Yield: 79% (39.3 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.38 (d, J = 7.6 Hz, 2 H), 7.28 (t, J = 7.6 Hz, 2 H), 7.04 (t, J = 7.2 Hz, 1 H), 6.78 (s, 1 H), 4.24-4.19 (m, 2 H), 1.29 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 138.0, 129.0, 123.3, 118.7, 61.2, 14.6.



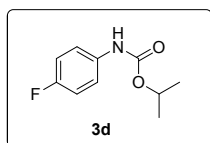
3b: Yield: 75% (43.5 mg), white solid, mp 52-54 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (d, J = 8.4 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 6.67 (s, 1 H), 5.04-4.98 (m, 1 H), 2.29 (s, 3 H), 1.28 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.5, 135.6, 132.7, 129.5, 118.8, 68.6, 22.1, 20.8; HRMS Calcd (ESI) m/z for $\text{C}_{11}\text{H}_{15}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 216.0995, found 216.0987.



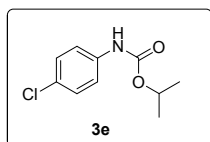
3b': Yield: 74% (39.8 mg), white solid, mp 50-52 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 8.0 Hz, 2 H), 6.69 (s, 1 H), 4.23-4.18 (m, 2 H), 2.29 (s, 3 H), 1.29 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.8, 135.4, 132.9, 129.5, 118.8, 61.1, 20.8, 14.6.



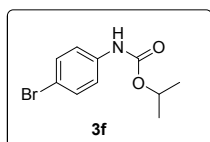
3c: Yield: 74% (46.6 mg), white solid, mp 63-65 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.28 (d, J = 7.6 Hz, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.60 (s, 1 H), 5.03-4.97 (m, 1 H), 3.77 (s, 3 H), 1.28 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.8, 153.7, 131.2, 120.6, 114.2, 68.5, 55.5, 22.1; HRMS Calcd (ESI) m/z for $\text{C}_{11}\text{H}_{15}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 232.0944, found 232.0935.



3d: Yield: 78% (46.2 mg), white solid, mp 89-91 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.35-7.32 (m, 2 H), 7.01-6.97 (m, 2 H), 6.56 (s, 1 H), 5.06-4.96 (m, 1 H), 1.29 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.1, 157.7, 153.5, 134.1, 120.4, 115.6 (d, J = 22.4 Hz), 68.9, 22.1; ^{19}F NMR (CDCl_3 , 376 MHz) δ -119.9 (s, 1 F); HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{12}\text{FNNaO}_2$ $[\text{M}+\text{Na}]^+$ 220.0744, found. 220.0734.

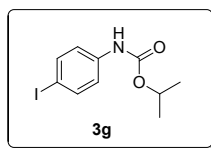


3e: Yield: 83% (53.2 mg), white solid, mp 106-108 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.33 (d, J = 8.8 Hz, 2 H), 7.25 (d, J = 8.8 Hz, 2 H), 6.64 (s, 1 H), 5.06-4.96 (m, 1 H), 1.29 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.1, 136.7, 129.0, 128.2, 119.8, 69.0, 22.1; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{12}\text{ClNNaO}_2$ $[\text{M}+\text{Na}]^+$ 236.0449, found 236.0447.

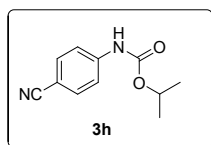


(3f): Yield: 82% (63.2 mg), white solid, mp 104-106 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.40 (d, J = 8.4 Hz, 2 H), 7.28 (d, J = 10.0 Hz, 2 H), 6.61 (s, 1 H), 5.06-4.96 (m, 1 H), 1.29 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.0, 137.2, 132.0, 120.1, 115.7, 69.1, 22.1; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{12}\text{BrNNaO}_2$ $[\text{M}+\text{Na}]^+$

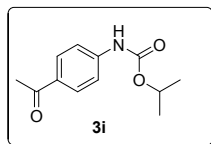
279.9944, found 279.9941.



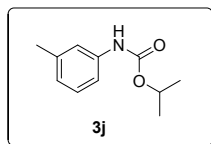
(3g): Yield: 66% (60.8 mg), almost white solid, mp 114-116 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (d, J = 8.8 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 6.54 (s, 1 H), 5.05-4.96 (m, 1 H), 1.29 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.0, 138.0, 137.9, 120.5, 86.1, 69.1, 22.1.



(3h): Yield: 48% (29.3 mg), white solid, mp 143-145 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 2 H), 7.02 (s, 1 H), 5.07-5.00 (m, 1 H), 1.31 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.6, 142.4, 133.3, 119.0, 118.2, 105.9, 69.6, 22.0; HRMS Calcd (ESI) m/z for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 227.0791, found 227.0783.

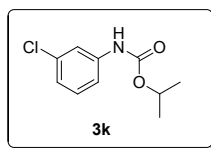


(3i): Yield: 52% (34.4 mg), white solid, mp 130-132 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 6.78 (s, 1 H), 5.07-5.01 (m, 1 H), 2.57 (s, 3 H), 1.32 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 197.1, 152.8, 142.8, 132.0, 129.9, 117.5, 69.3, 26.4, 22.0; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{15}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 244.0944, found 244.0940.

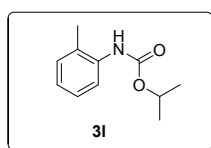


(3j): Yield: 71% (41.4 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.24 (d, J = 3.6 Hz, 1 H), 7.18-7.15 (m, 2 H), 6.85 (t, J = 2.0 Hz, 1 H), 6.64 (s, 1 H), 5.04-4.98 (s, 1 H), 2.31 (s, 3 H), 1.28 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.3, 138.9, 138.1, 128.8, 124.0, 119.3, 115.7, 68.7, 22.1, 21.5; HRMS Calcd (ESI) m/z for

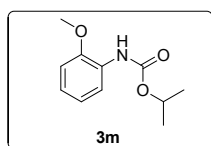
$C_{11}H_{15}NNaO_2$ $[M+Na]^+$ 216.0995, found 216.0991.



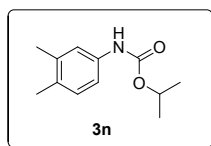
(3k): Yield: 81% (51.8 mg), transparent oil; 1H NMR ($CDCl_3$, 400 MHz) δ 7.51 (s, 1 H), 7.20 (d, $J = 4.8$ Hz, 2 H), 7.04-6.99 (m, 1 H), 6.64 (s, 1 H), 5.06-4.97 (m, 1 H), 1.30 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 139.3, 134.7, 130.0, 123.3, 118.6, 116.5, 69.1, 22.0; HRMS Calcd (ESI) m/z for $C_{10}H_{12}ClNNaO_2$ $[M+Na]^+$ 236.0449, found 236.0445.



(3l): Yield: 53% (30.7 mg), white solid, mp 63-65 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, $J = 4.4$ Hz, 1 H), 7.20 (t, $J = 7.6$ Hz, 1 H), 7.14 (d, $J = 7.2$ Hz, 1 H), 7.00 (t, $J = 7.6$ Hz, 1 H), 6.36 (s, 1 H), 5.06-4.97 (m, 1 H), 2.24 (s, 3 H), 1.30 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 136.1, 130.4, 126.9, 123.9, 121.0, 68.8, 22.1, 17.7; HRMS Calcd (ESI) m/z for $C_{11}H_{15}NNaO_2$ $[M+Na]^+$ 216.0995, found 216.0992.

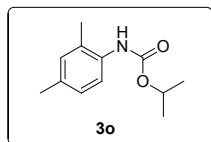


(3m): Yield: 45% (28.3 mg), transparent oil; 1H NMR ($CDCl_3$, 400 MHz) δ 8.10 (s, 1 H), 7.18 (s, 1 H), 7.00-6.93 (m, 2 H), 6.85 (dd, $J = 2.4, 7.6$ Hz, 1 H), 5.07-4.98 (m, 1 H), 3.85 (s, 3 H), 1.30 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 147.5, 127.9, 122.5, 121.1, 118.1, 109.9, 68.5, 55.6, 22.1; HRMS Calcd (ESI) m/z for $C_{11}H_{15}NNaO_3$ $[M+Na]^+$ 232.0944, found 232.0945.

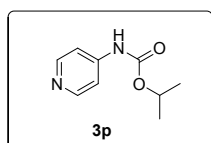


(3n): Yield: 79% (49.1 mg), white solid, mp 98-99 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 7.17 (s, 1 H), 7.09 (d, $J = 8.0$ Hz, 1 H), 7.03 (d, $J = 8.4$ Hz, 1 H), 6.54 (s, 1 H), 5.05-

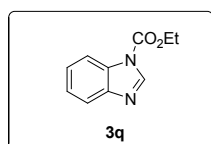
4.96 (m, 1 H), 2.20 (d, $J = 9.6$ Hz, 6 H), 1.28 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.4, 137.2, 135.8, 131.5, 130.0, 120.1, 116.2, 68.5, 22.1, 19.9, 19.1; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 230.1151, found .230.1153.



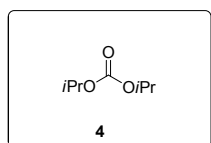
(3o): Yield: 73% (45.2 mg), white solid, mp 81-83 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.6 (s, 1 H), 6.99 (d, $J = 8.4$ Hz, 1 H), 6.96 (s, 1 H), 6.28 (s, 1 H), 5.05-4.96 (m, 1 H), 2.27 (s, 3 H), 2.20 (s, 3 H), 1.29 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.8, 133.7, 133.4, 131.0, 127.3, 121.6, 68.6, 22.1, 20.8, 17.6; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$ 230.1151, found 230.1156.



(3p): Yield: 30% (16.0 mg), white solid, mp 108-110 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.46 (d, $J = 6.0$ Hz, 2 H), 7.35 (d, $J = 6.0$ Hz, 2 H), 7.11 (s, 1 H), 5.07-5.01 (m, 1 H), 1.31 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.0, 150.2, 146.2, 112.6, 69.3, 22.0.

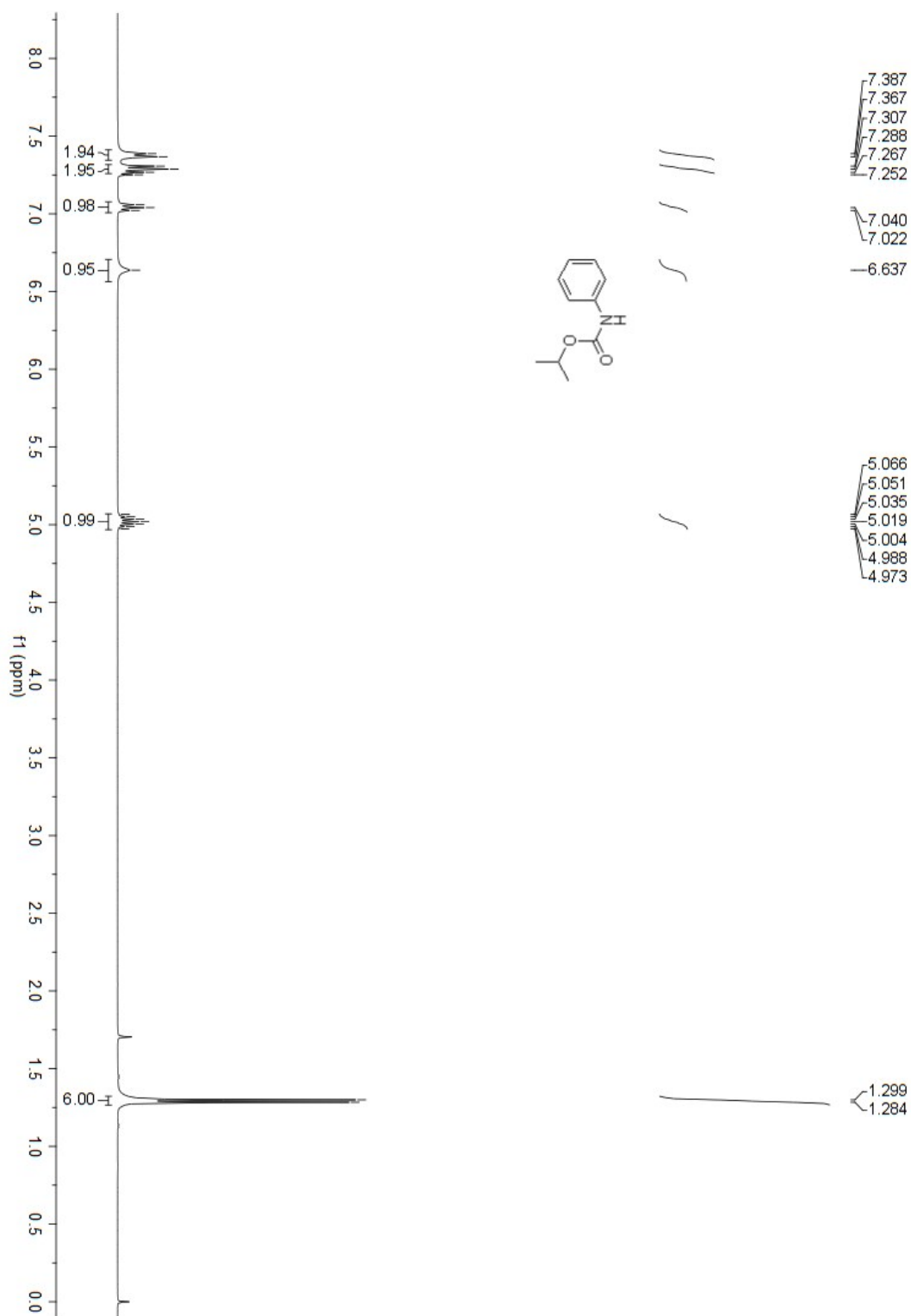
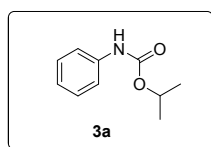


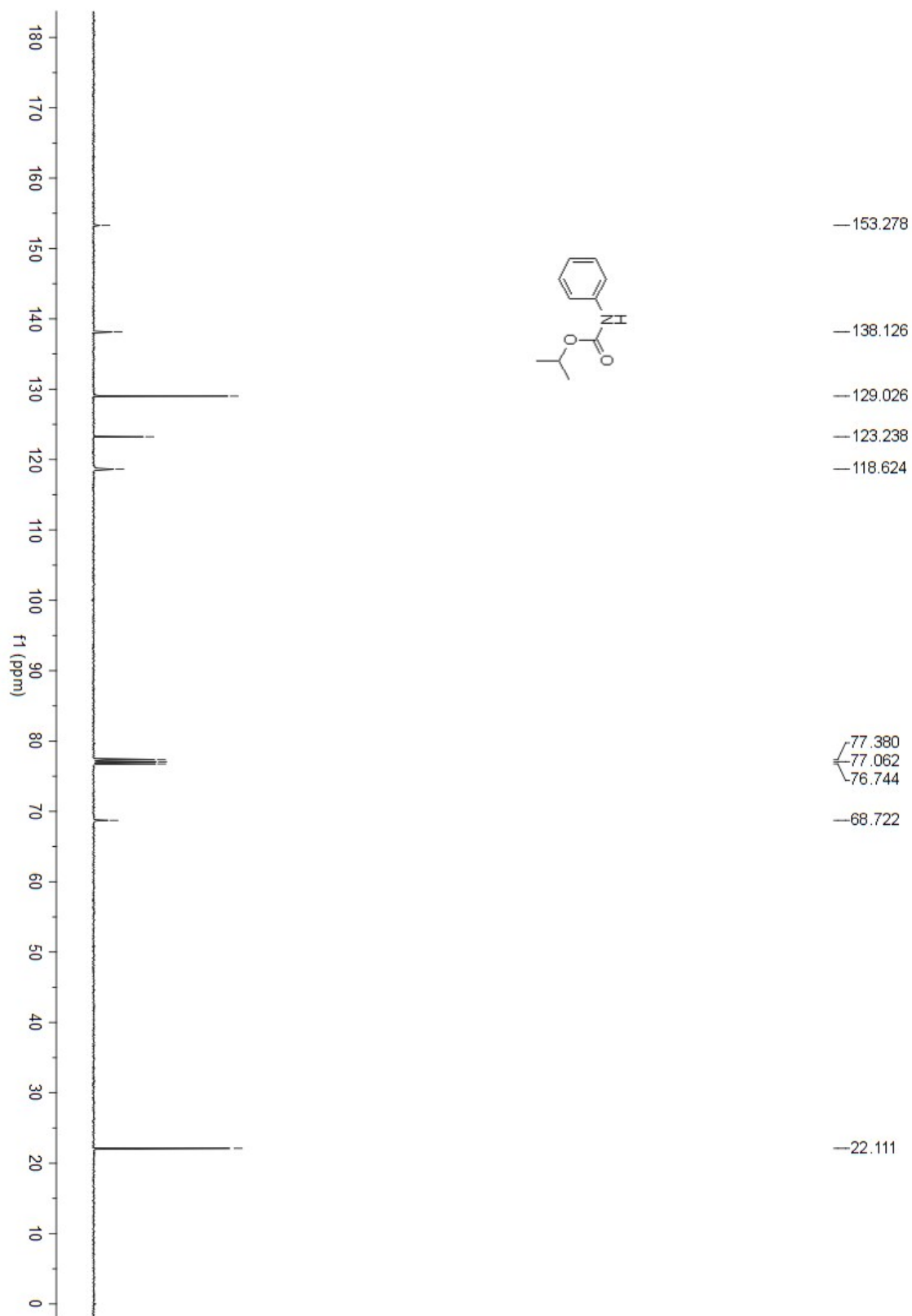
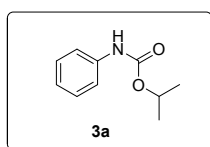
(3q): Yield: 78% (44.5 mg), white solid, mp 57-59 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.48 (s, 1 H), 8.03 (d, $J = 8.0$ Hz, 1 H), 7.80 (d, $J = 6.8$ Hz, 1 H), 7.43-7.35 (m, 2 H), 4.59-4.53 (m, 2 H), 1.51 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 149.5, 144.0, 141.7, 131.3, 125.4, 124.5, 120.7, 114.4, 64.2, 14.3; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 213.0634, found 213.0628.

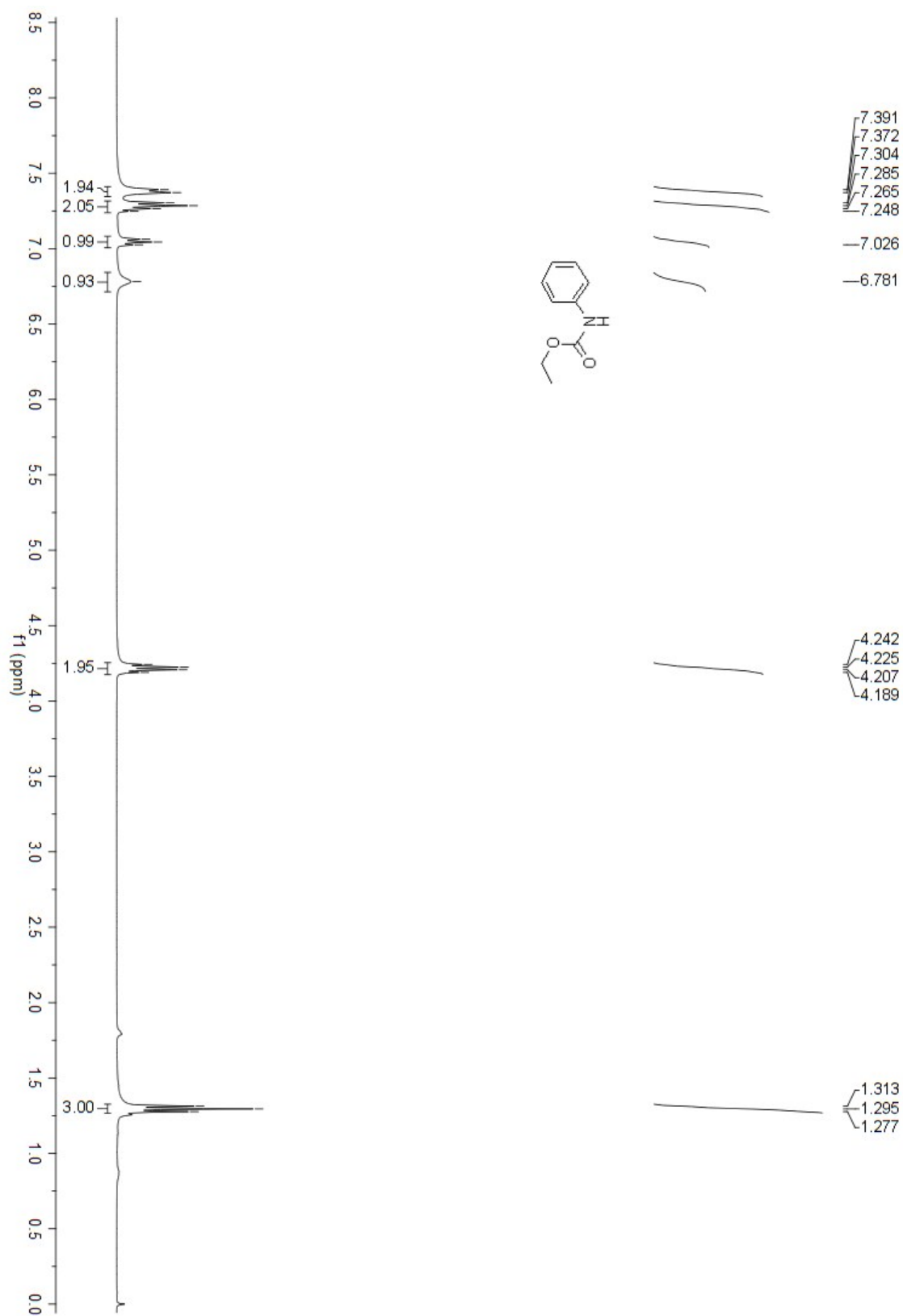
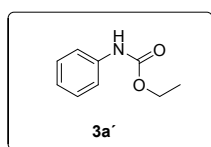


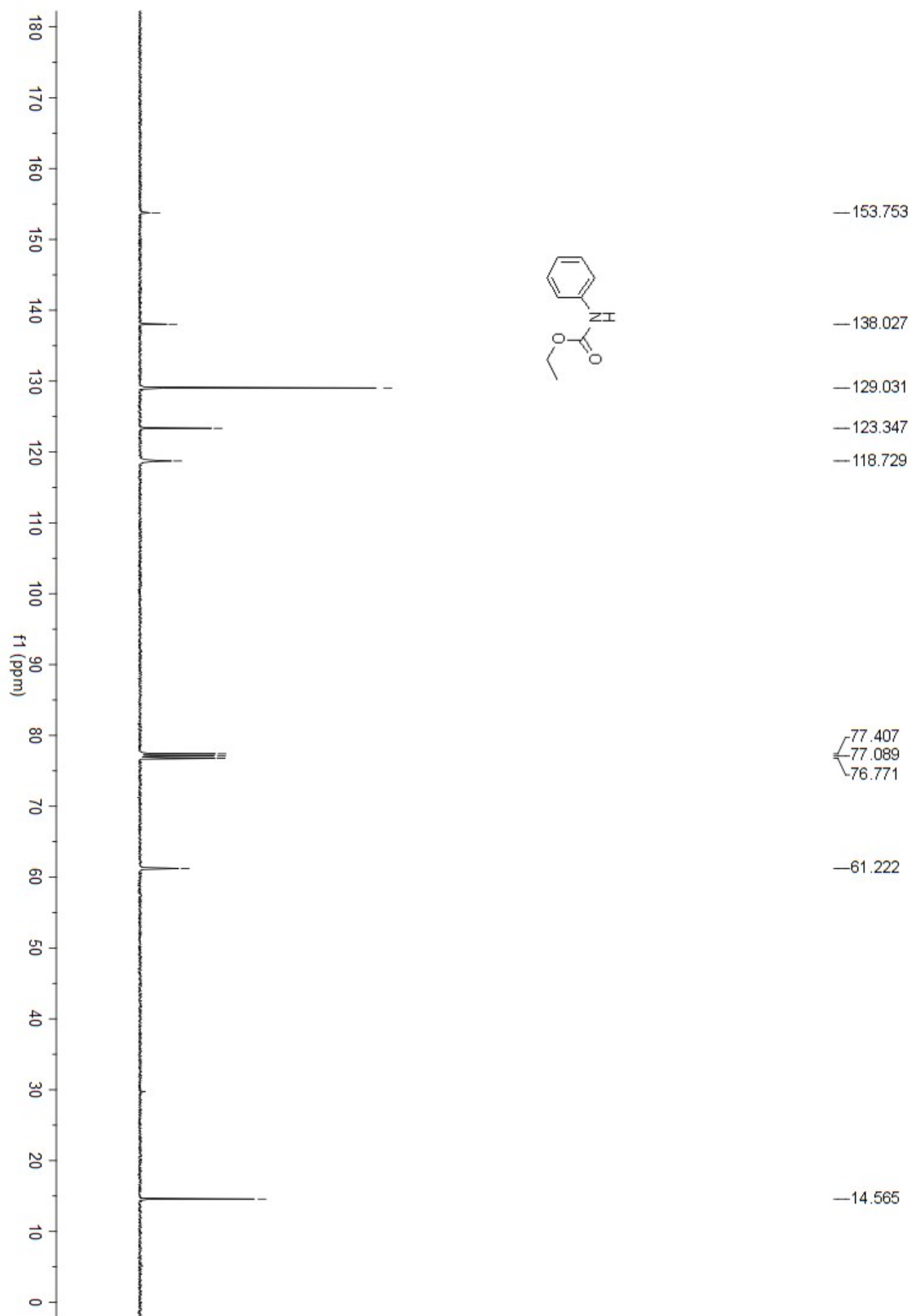
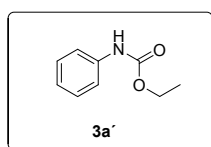
(4): ^1H NMR (CDCl_3 , 400 MHz) δ 5.00-4.94 (m, 2 H), 1.26 (d, $J = 6.4$ Hz, 12 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.4, 70.1, 22.0.

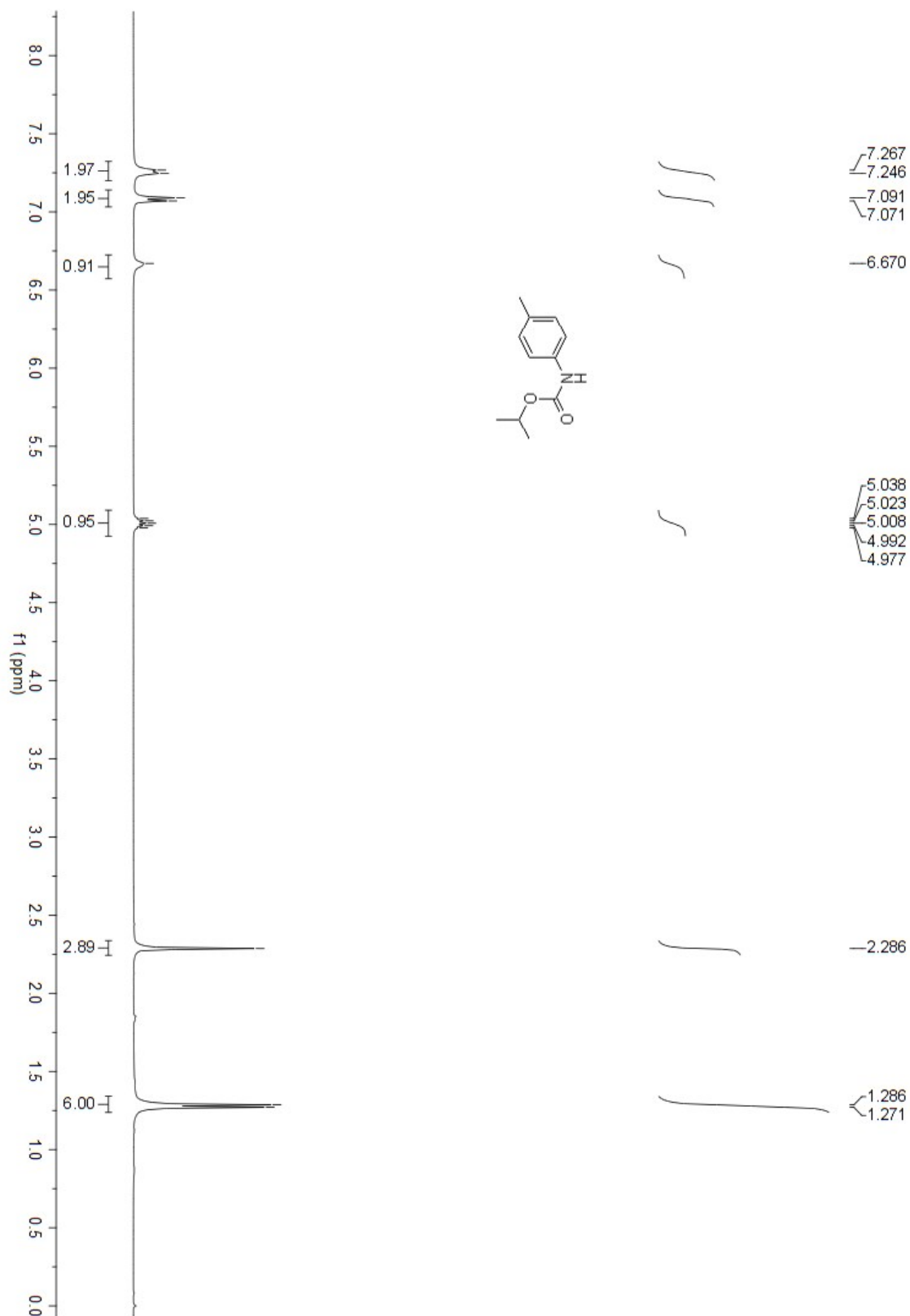
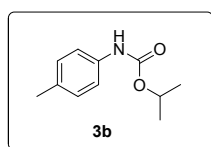
4. Copies of ^1H , ^{13}C and ^{19}F NMR spectra

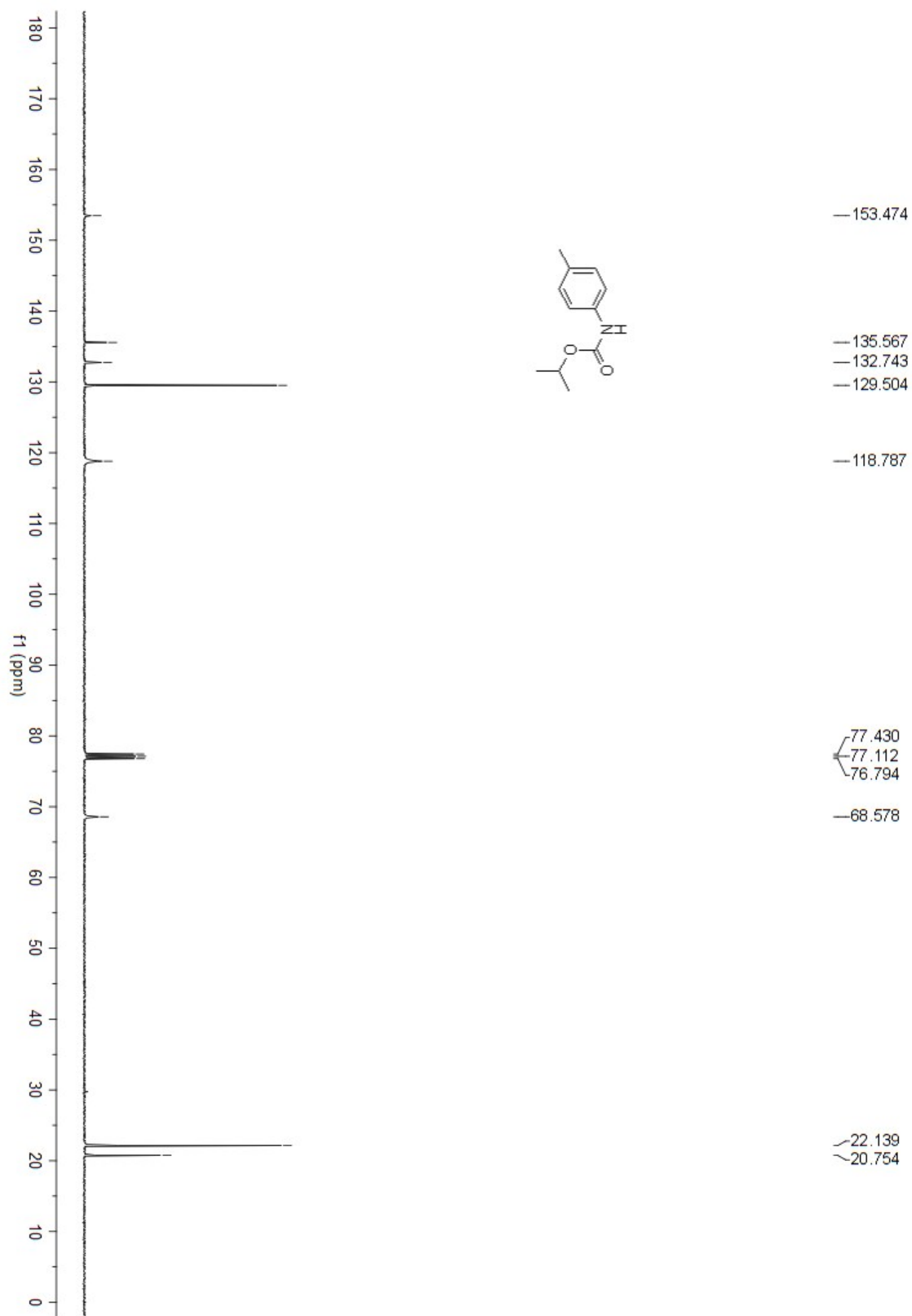
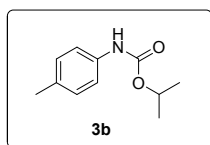


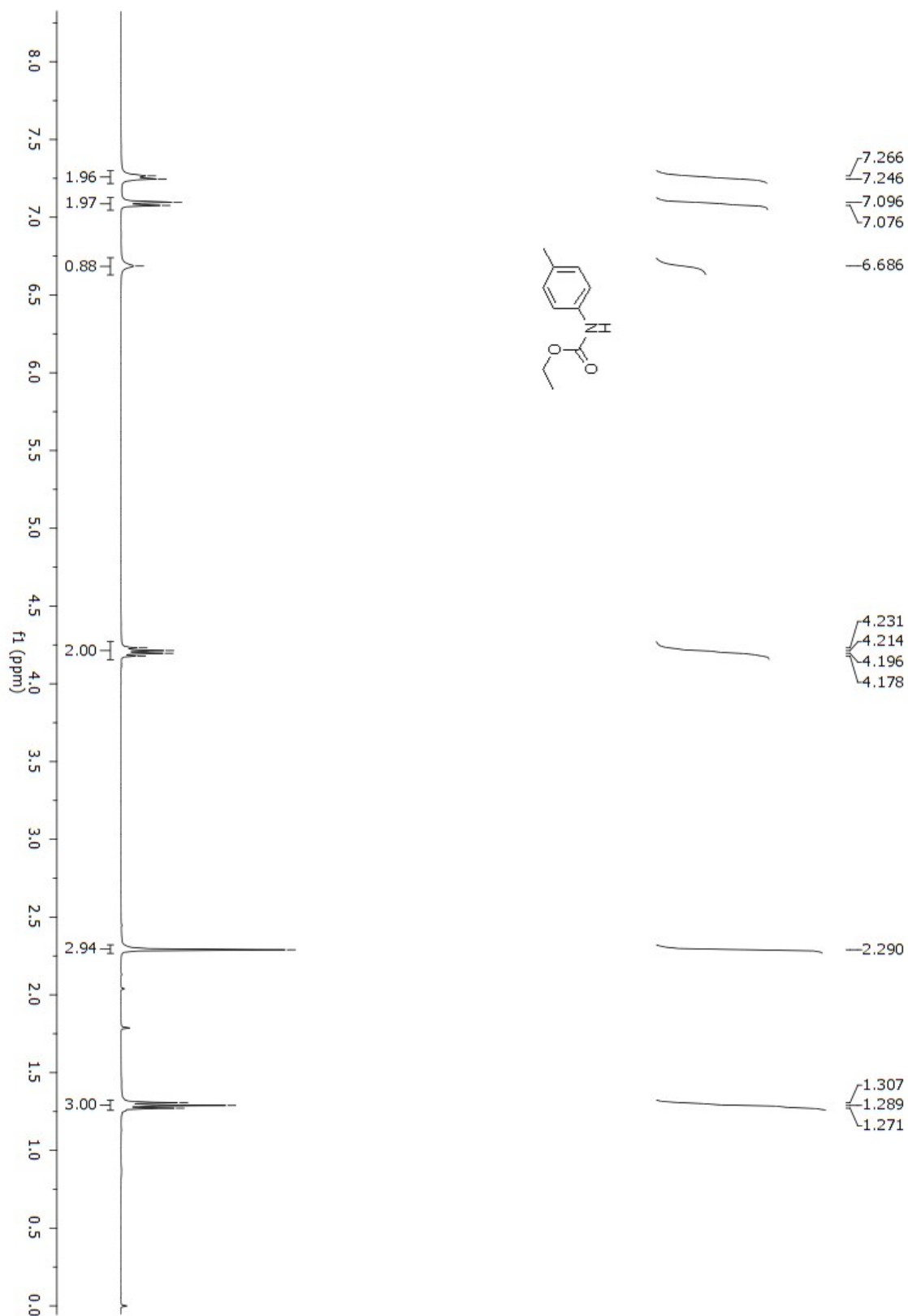
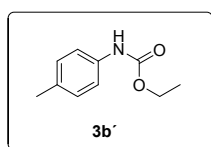


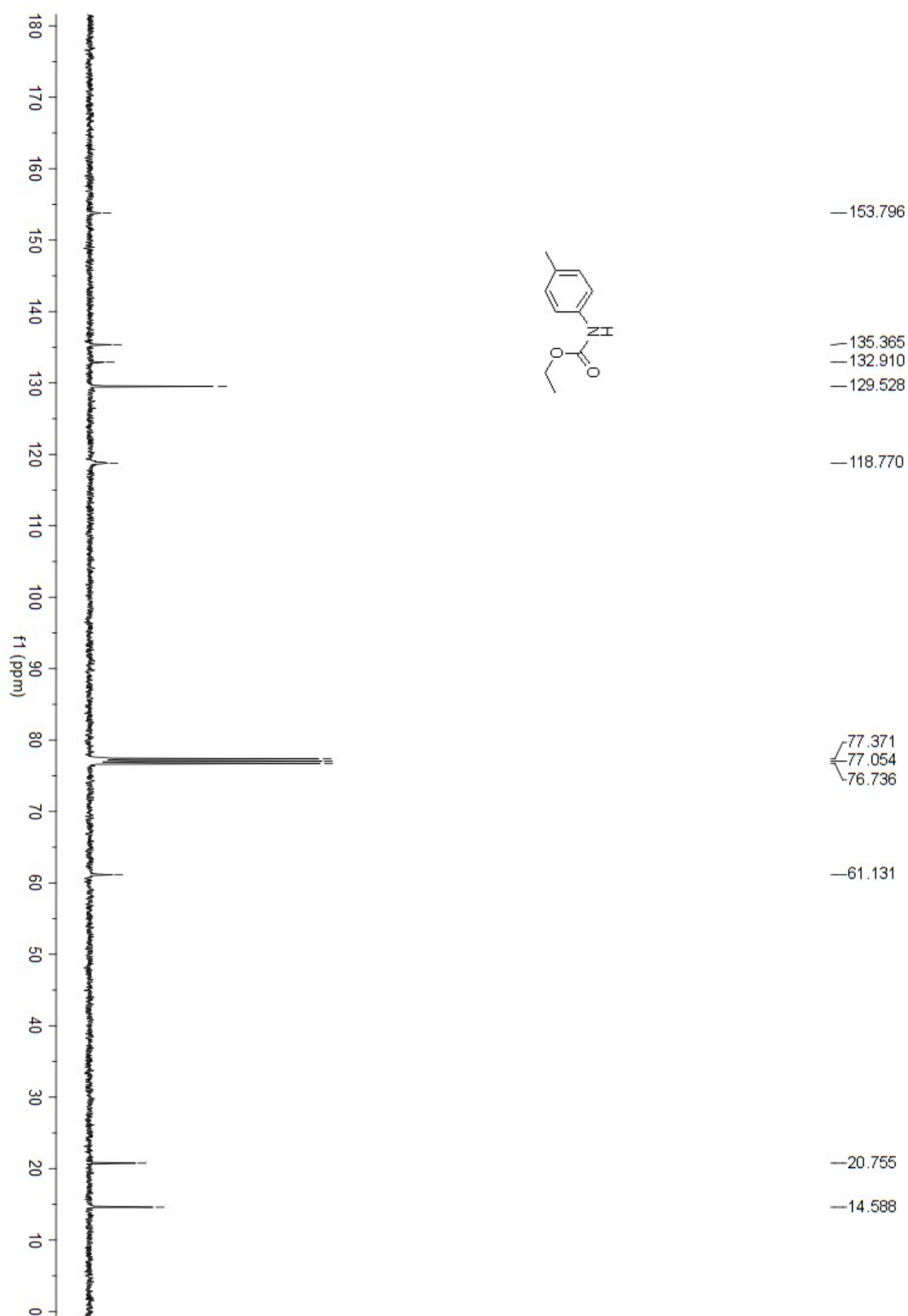
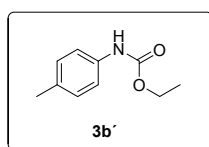


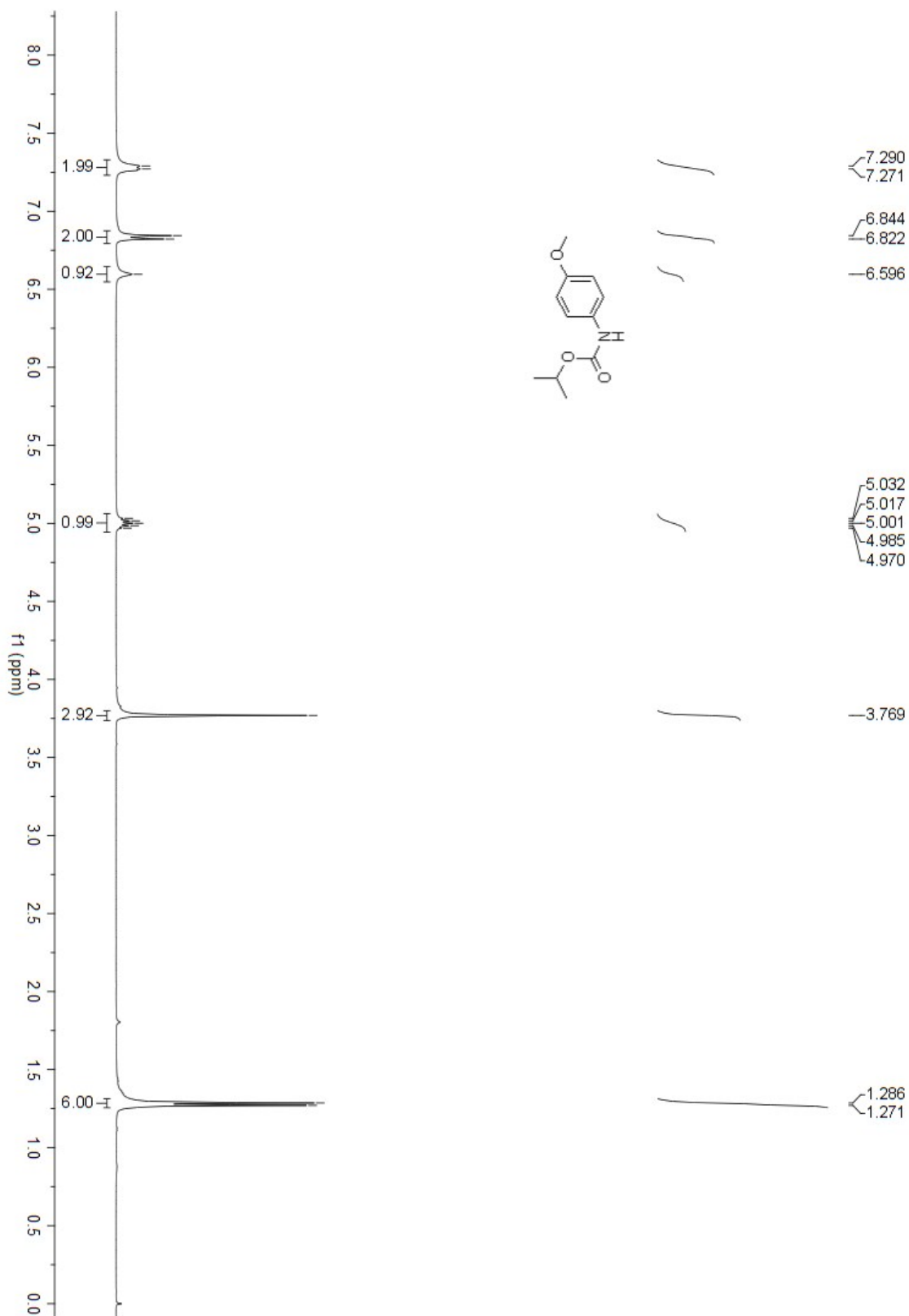
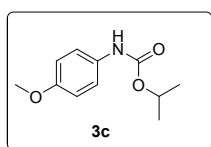


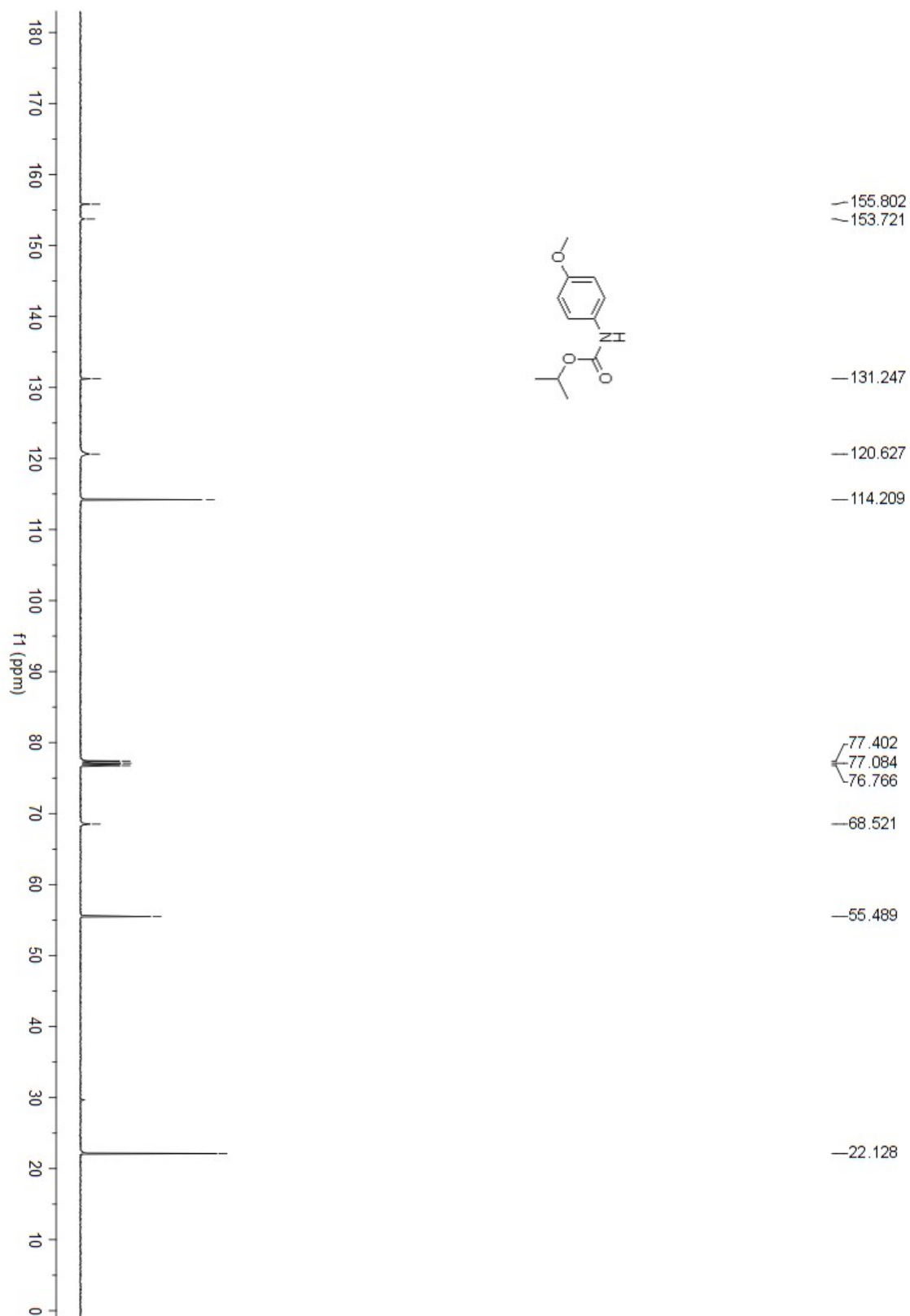
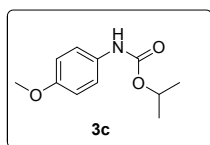


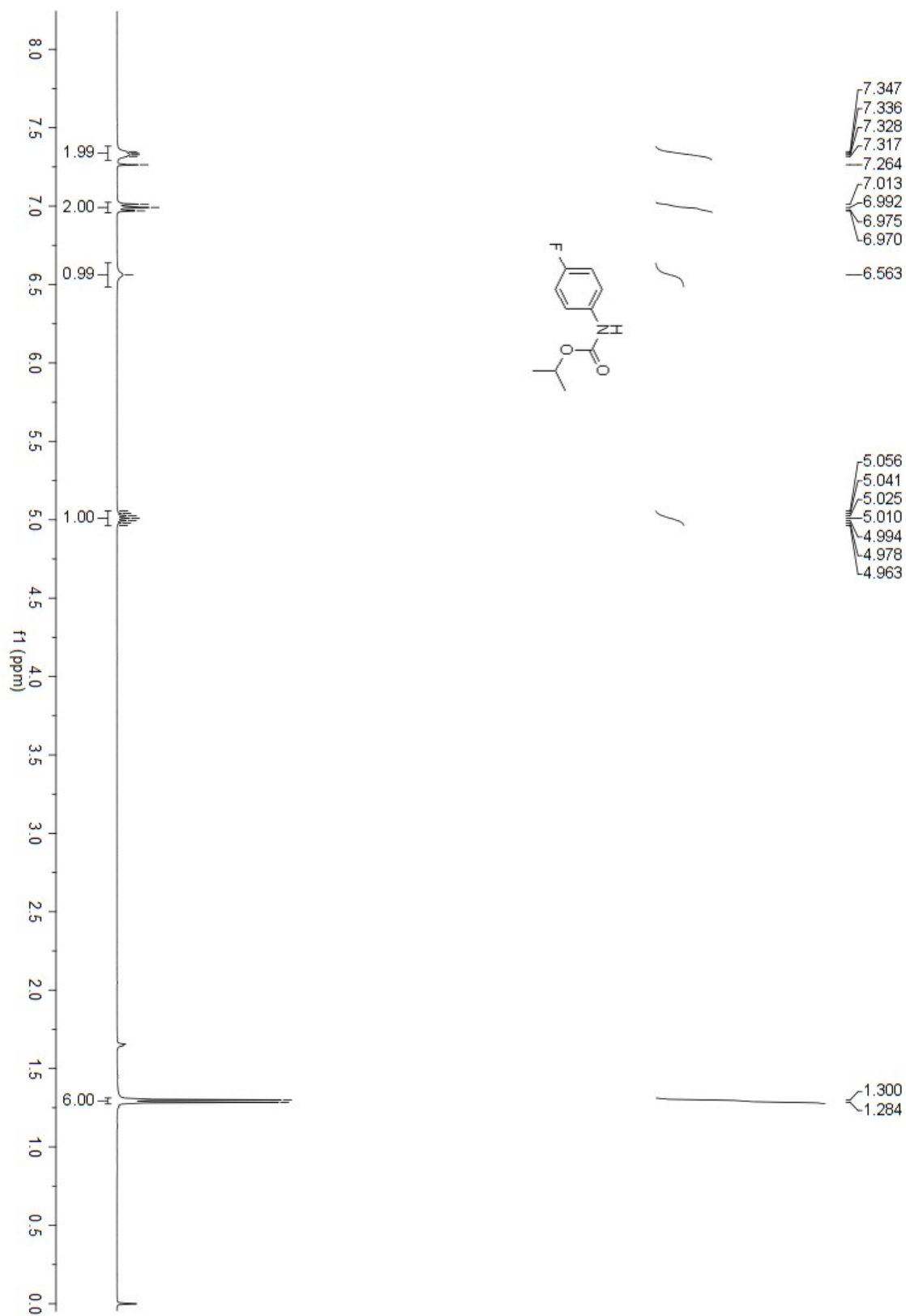
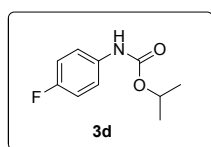


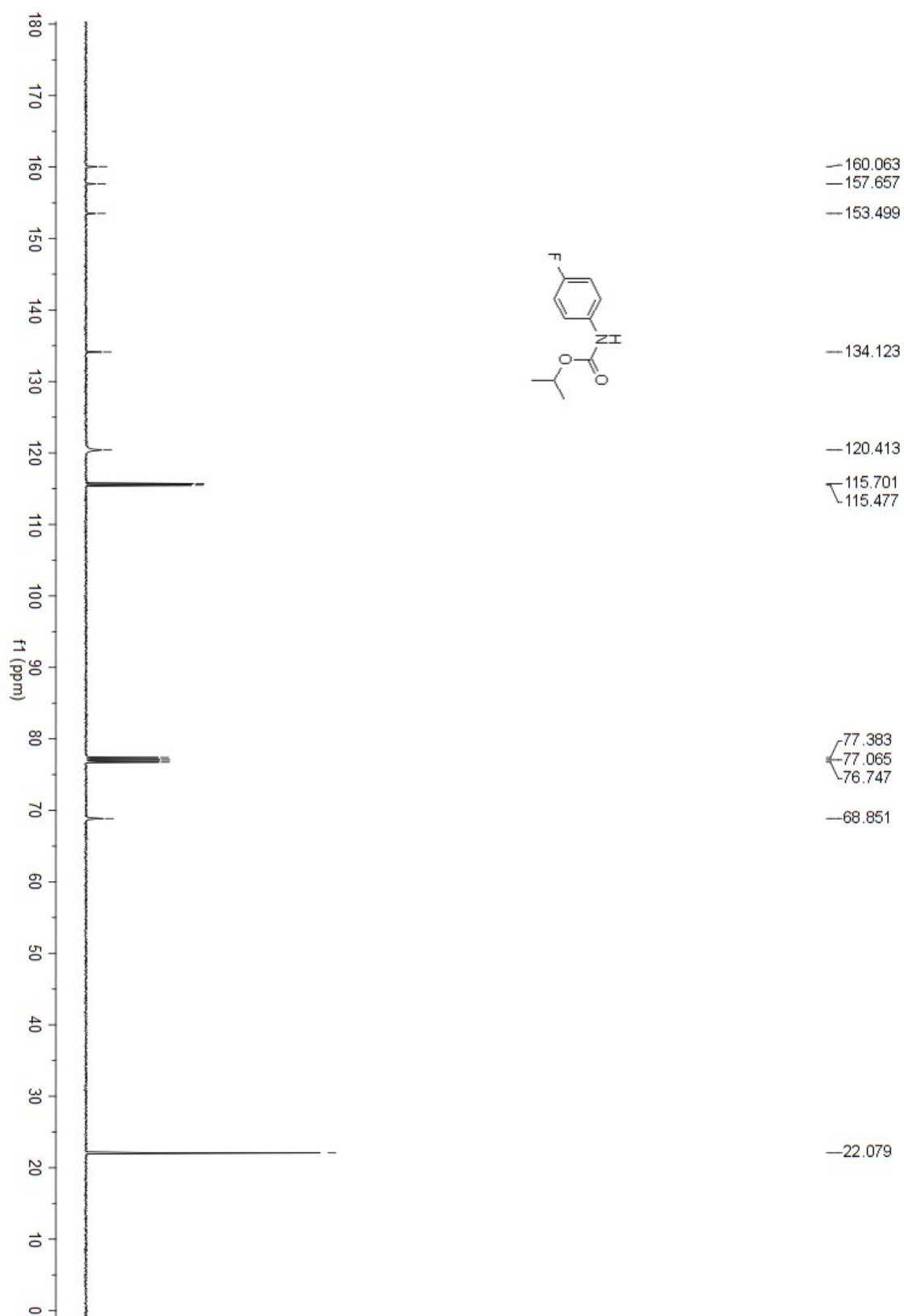
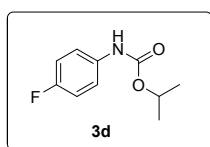


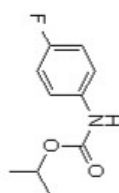
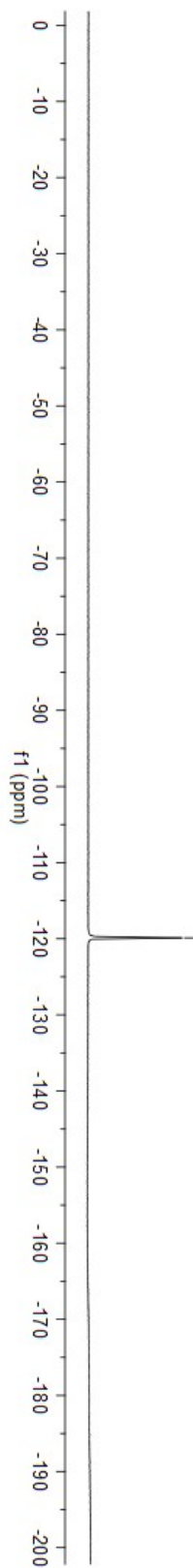
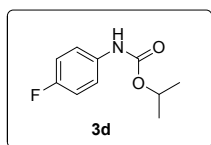




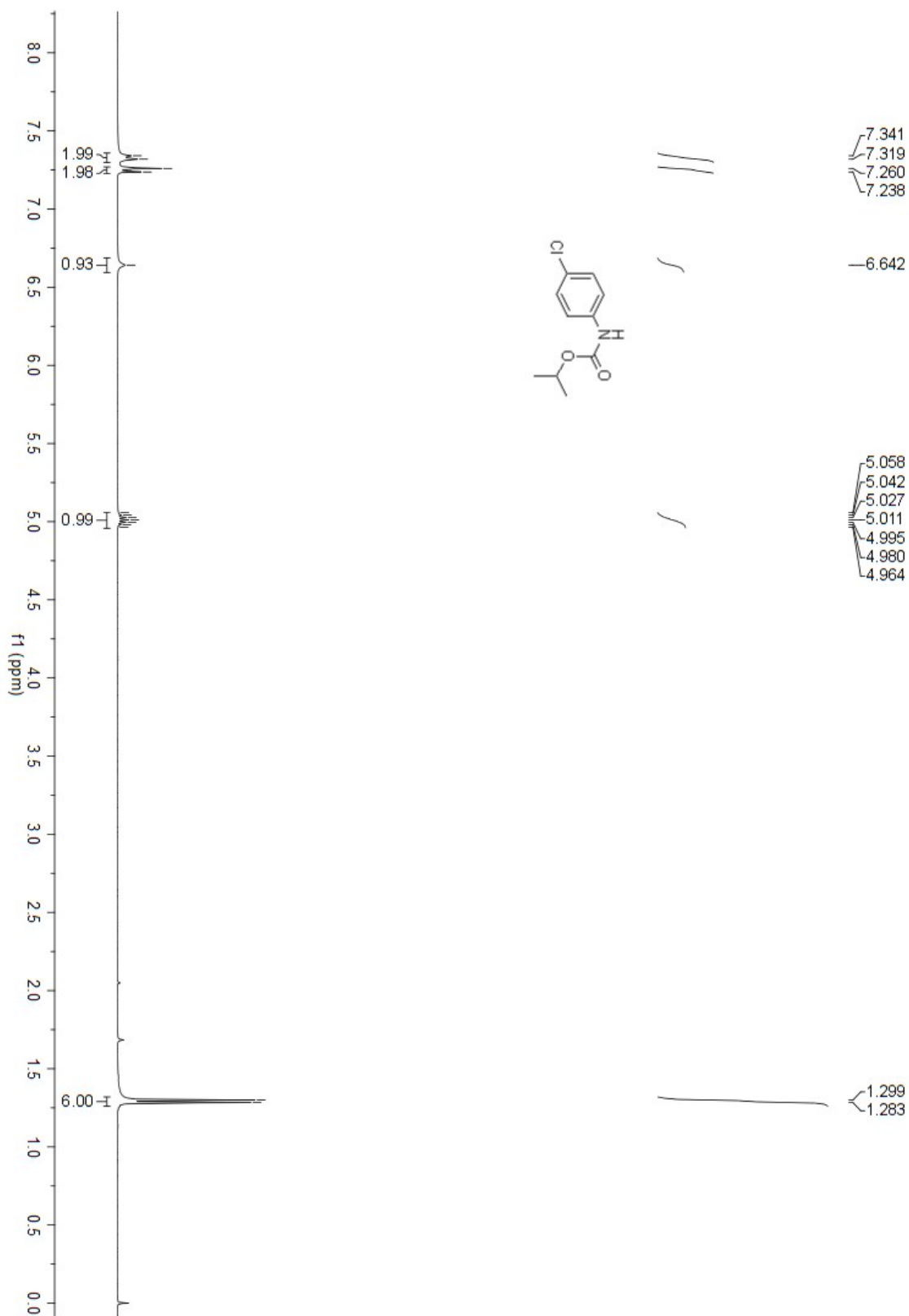
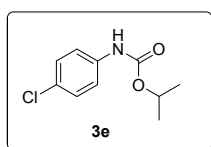


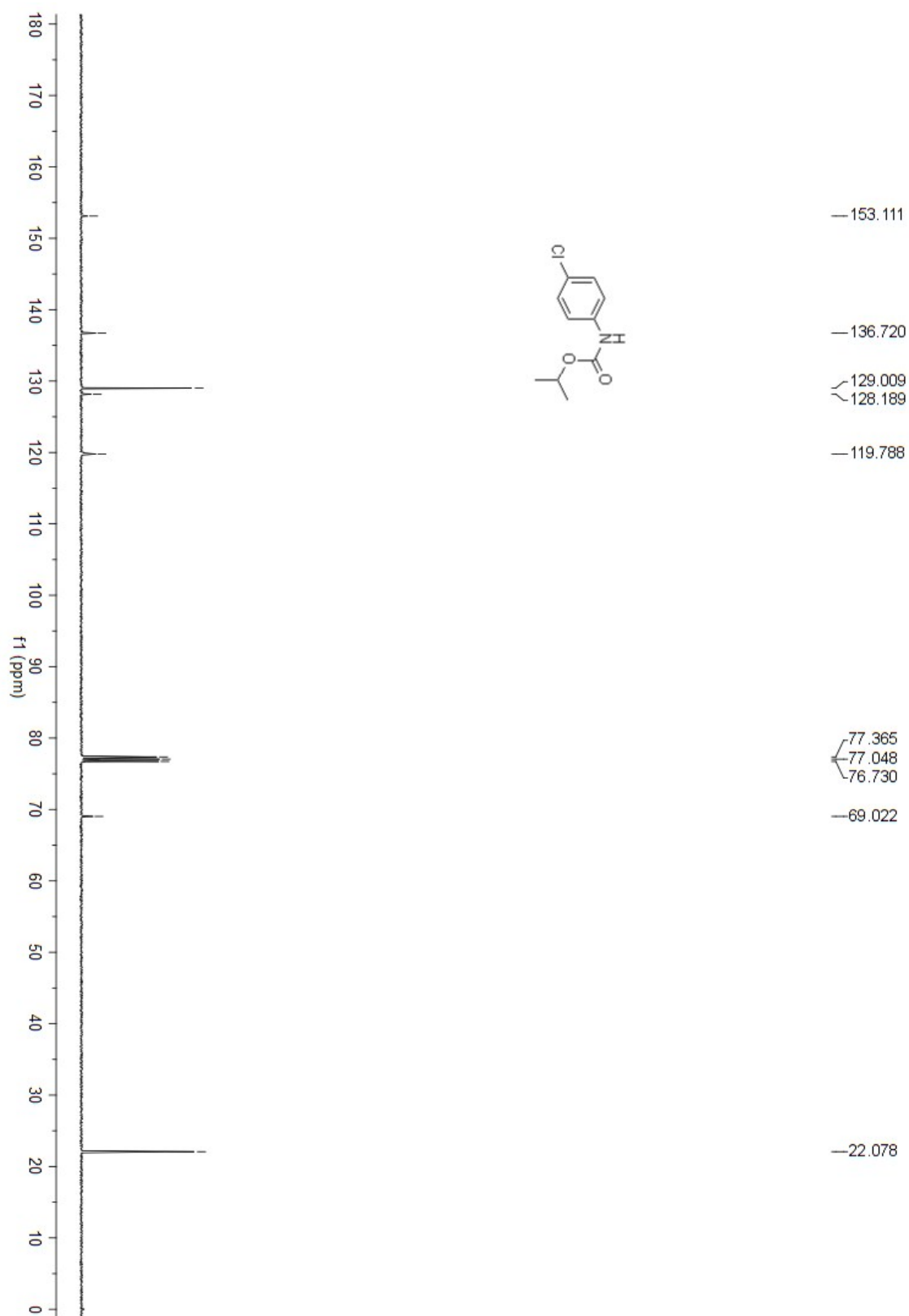
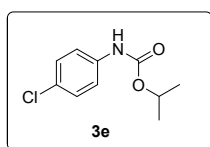


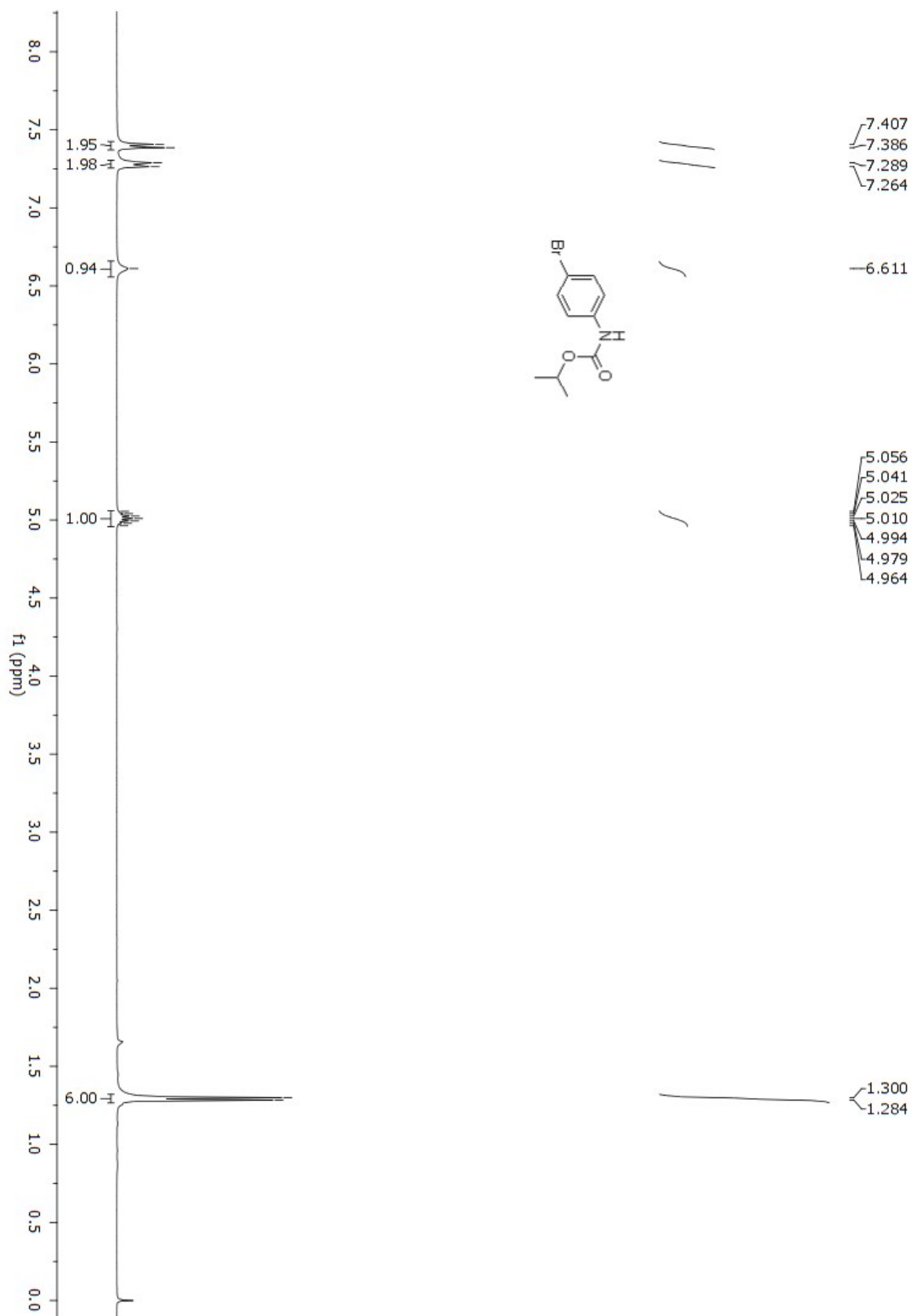
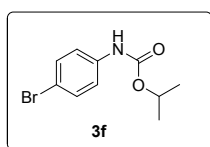


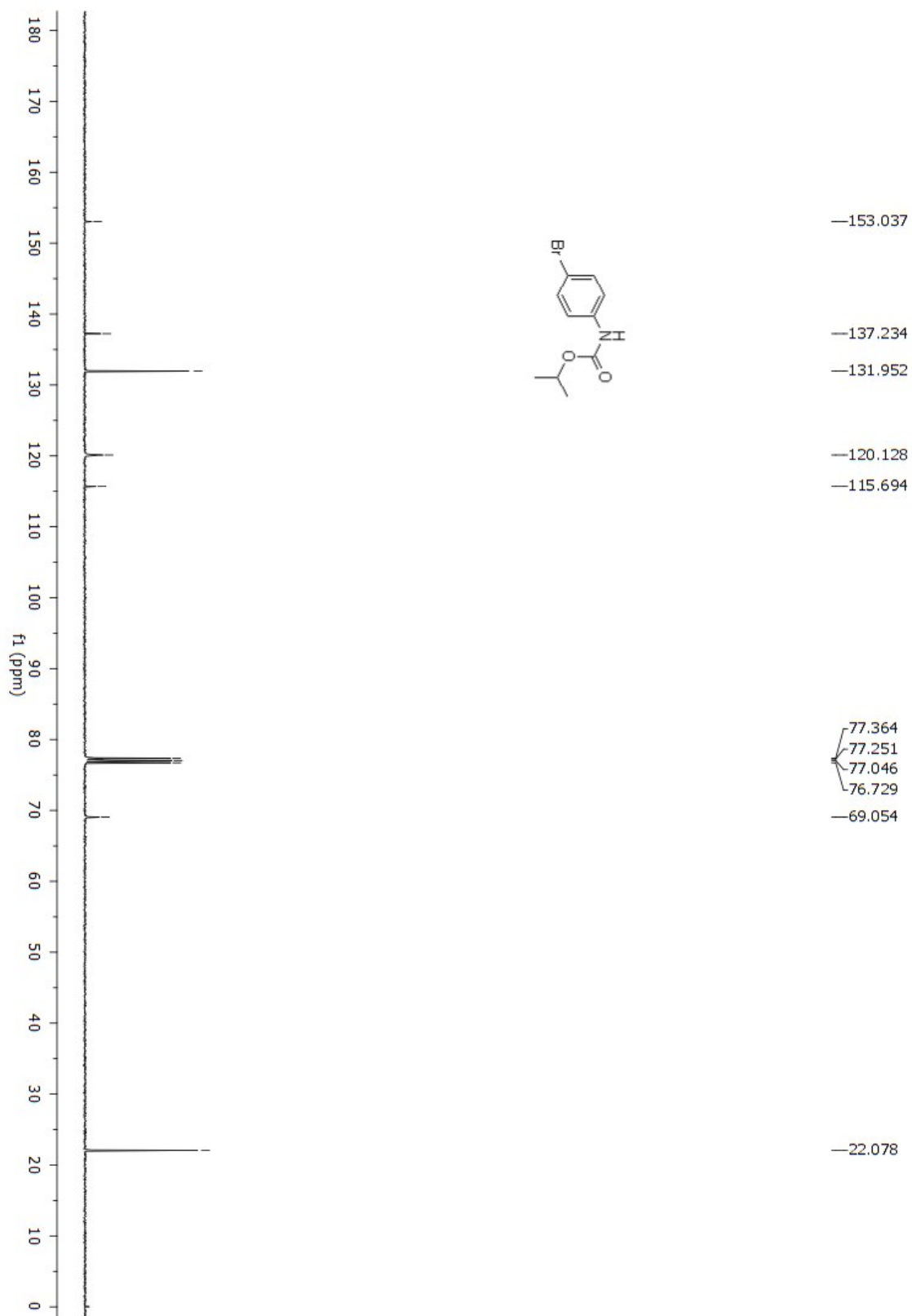
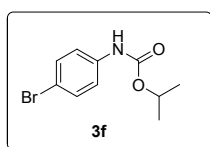


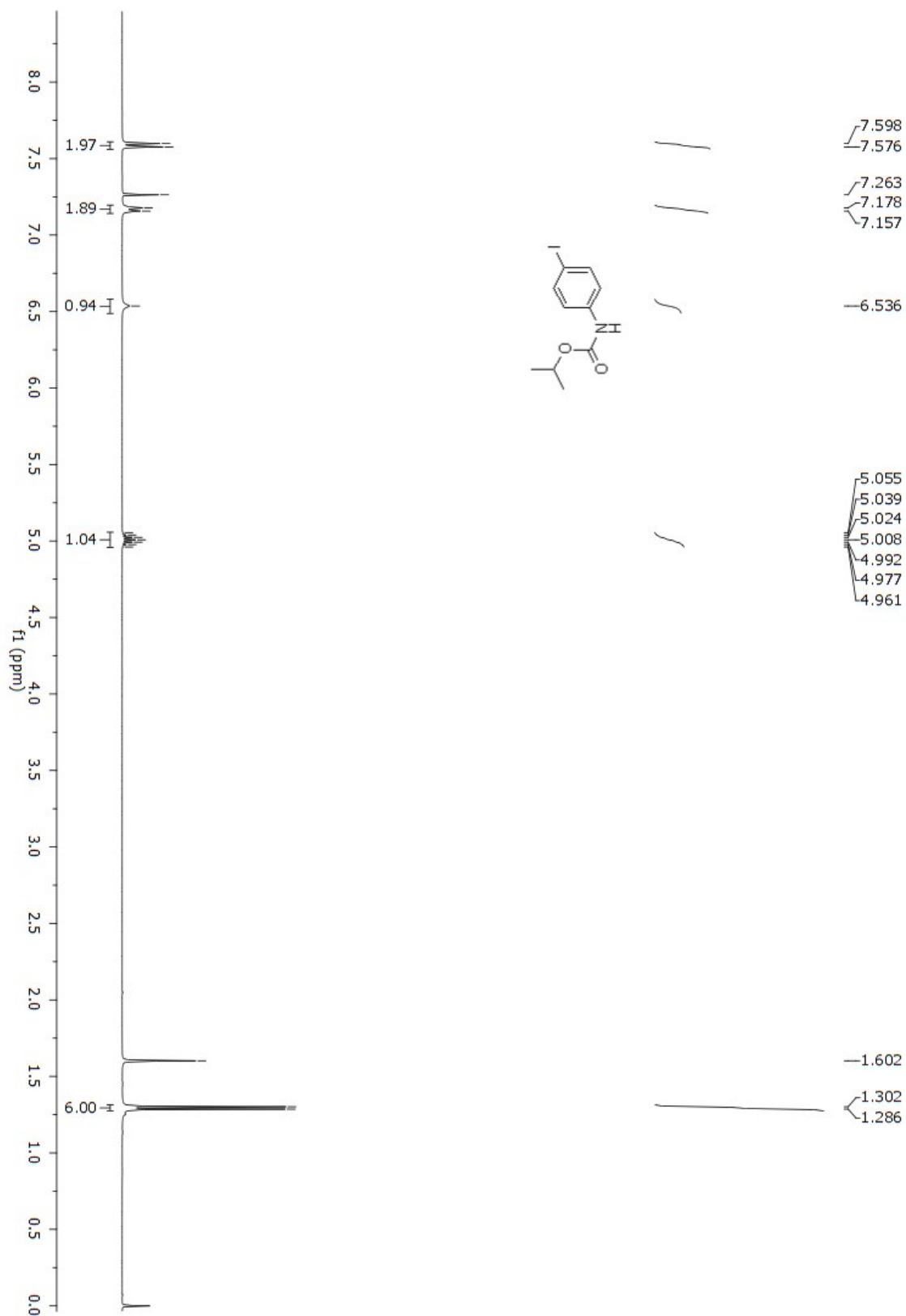
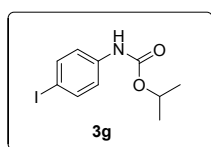
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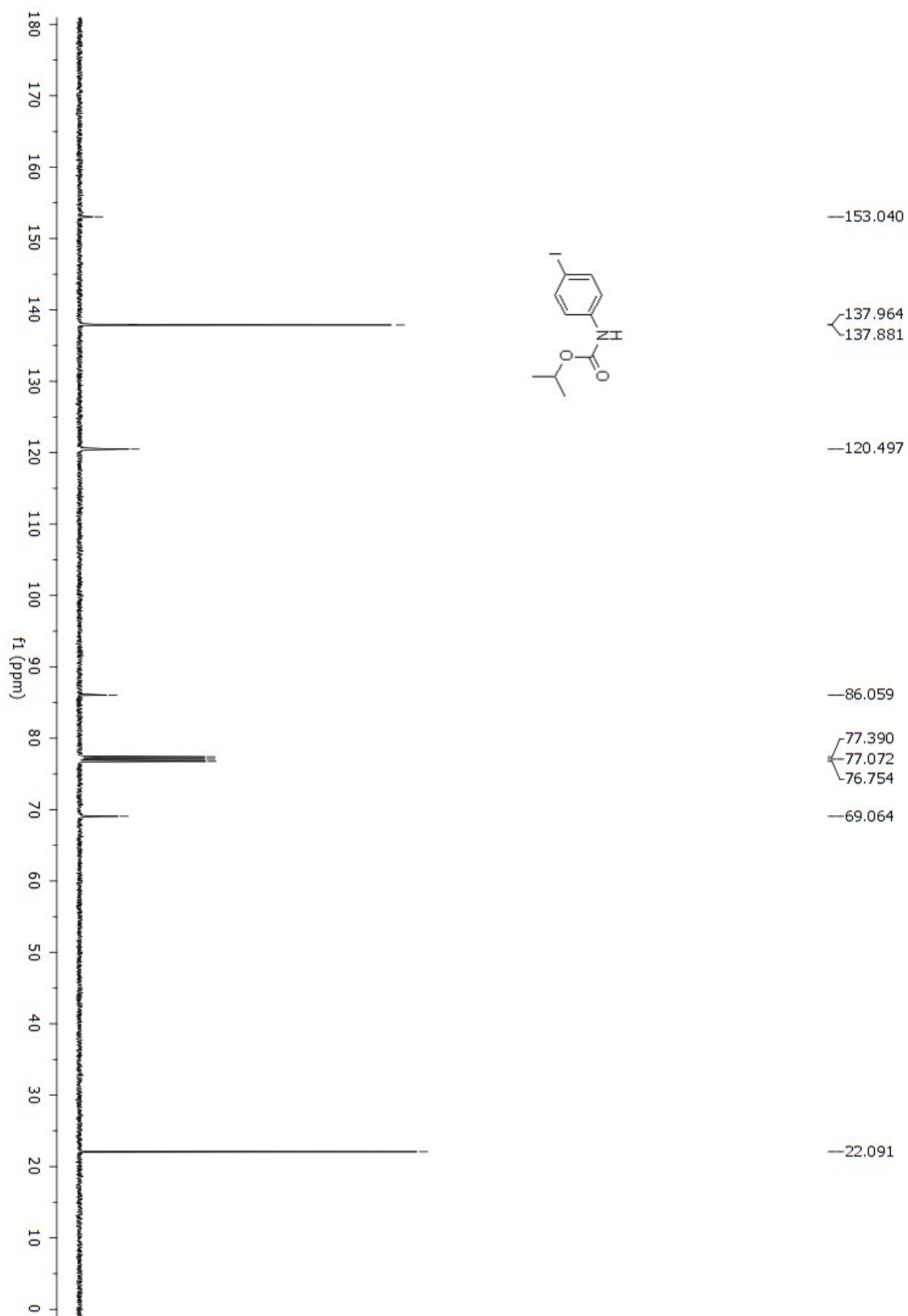
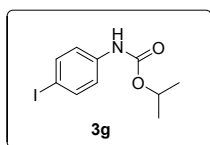


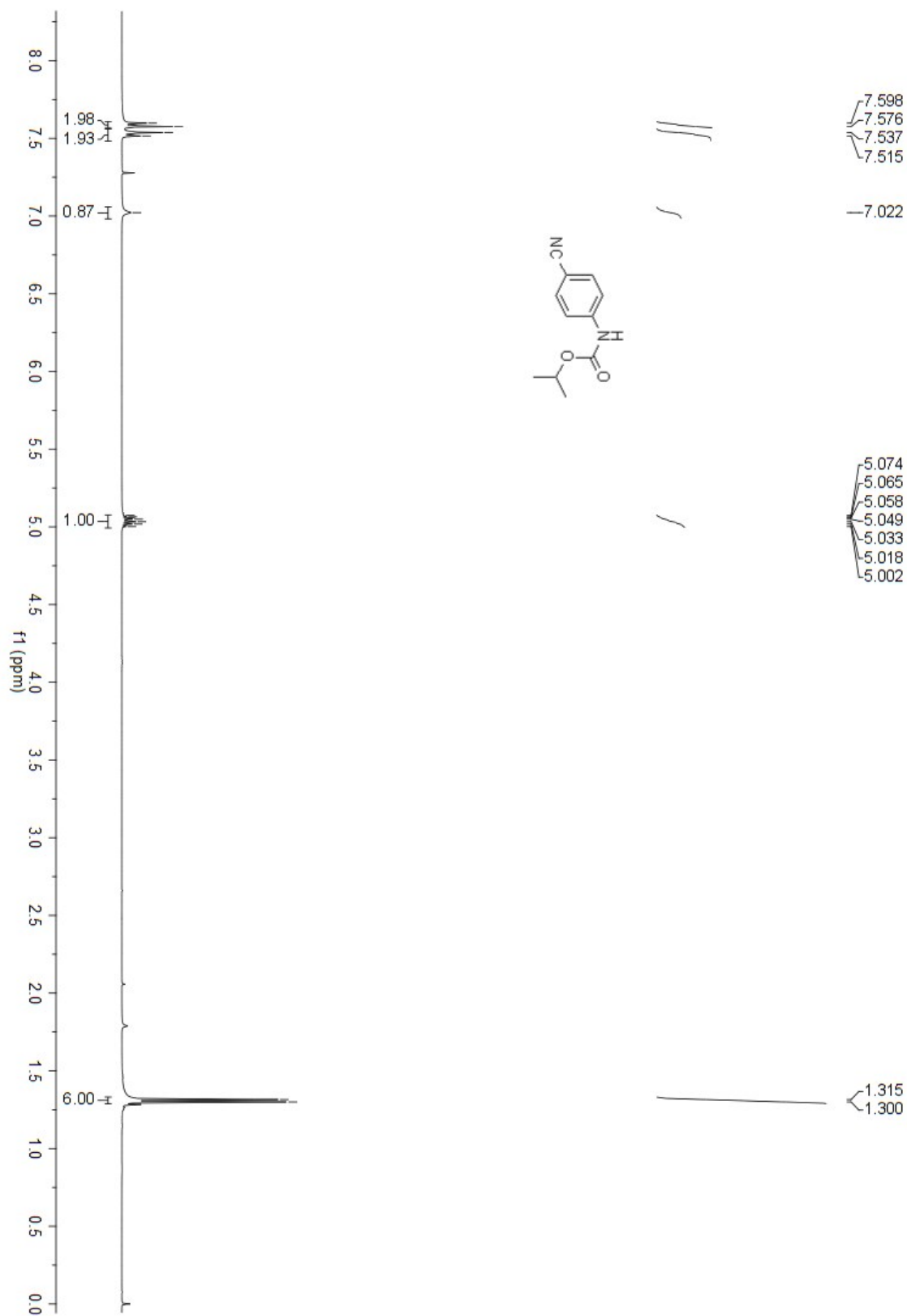
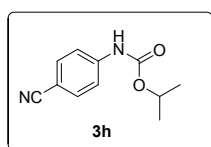


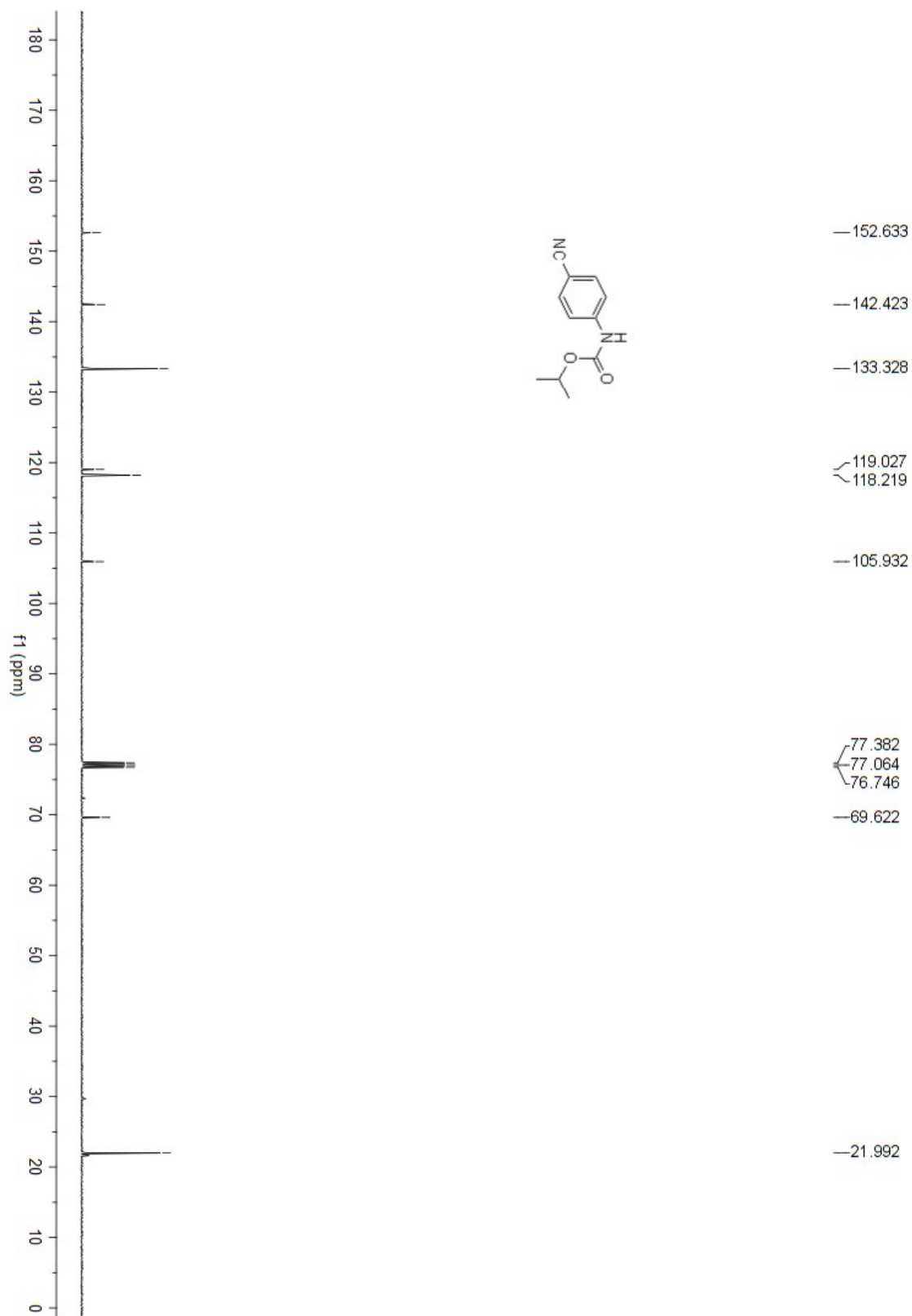
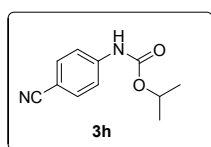


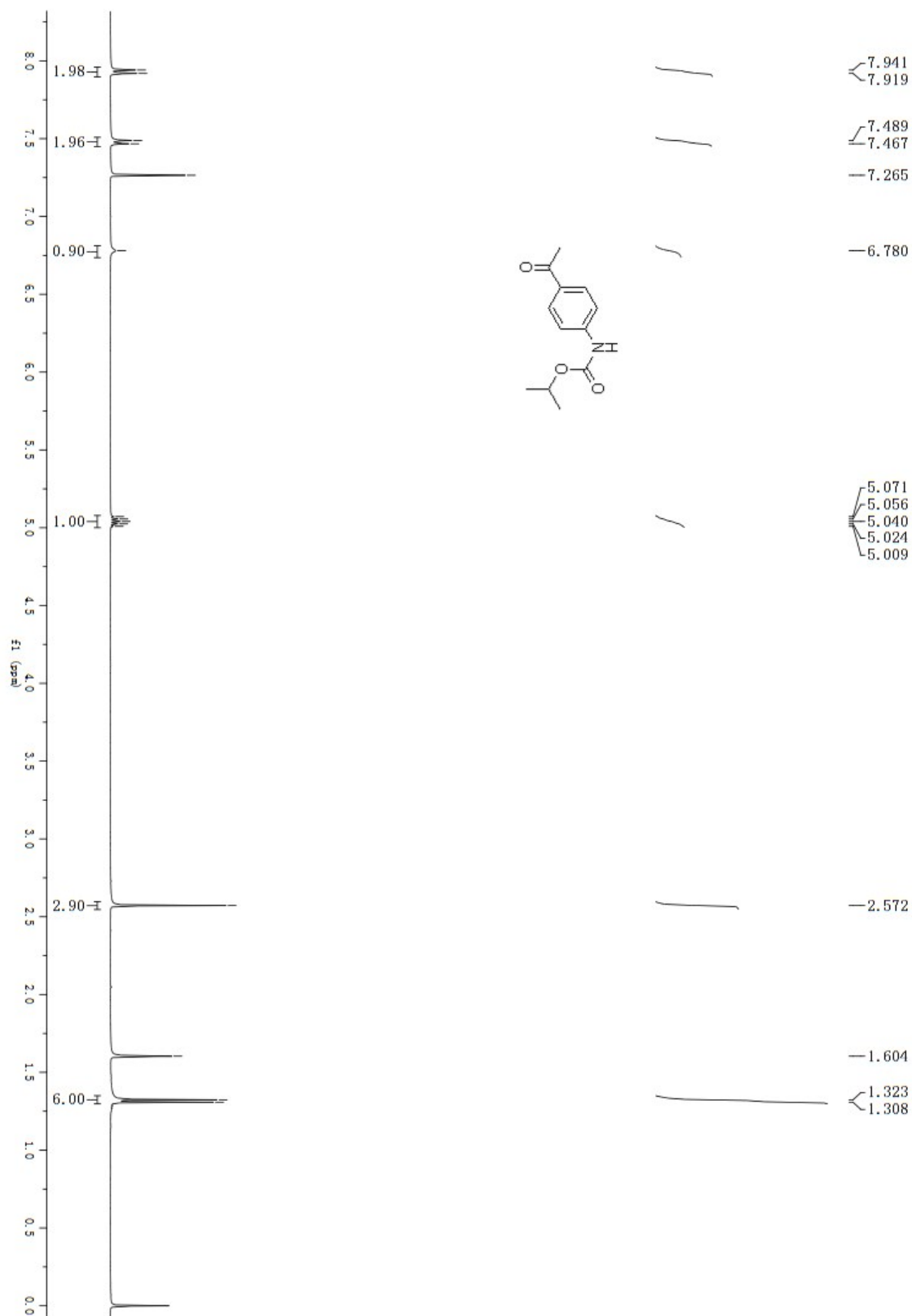
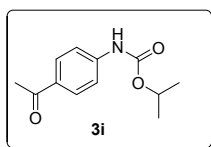


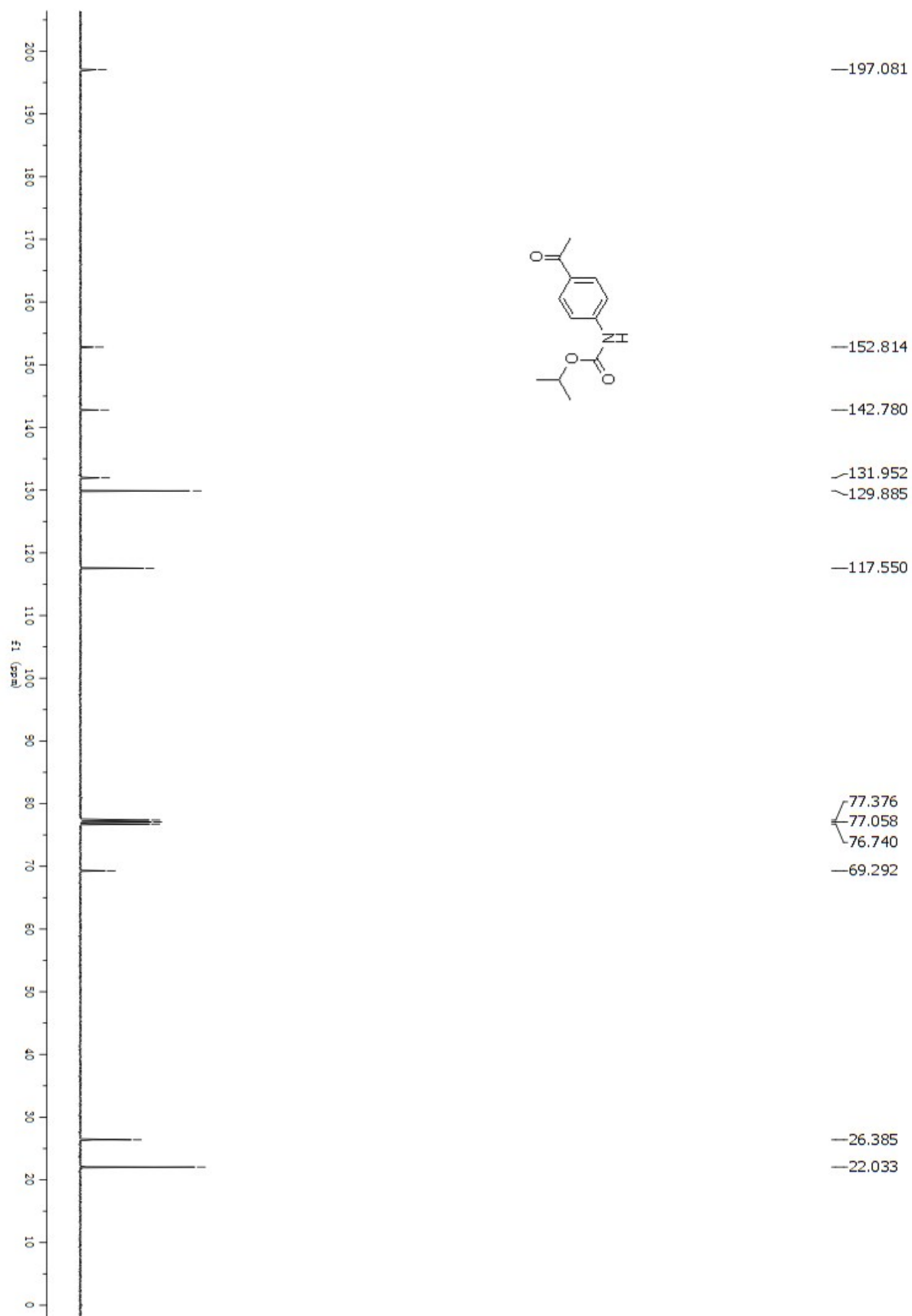
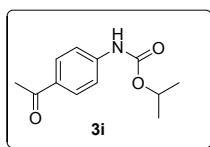


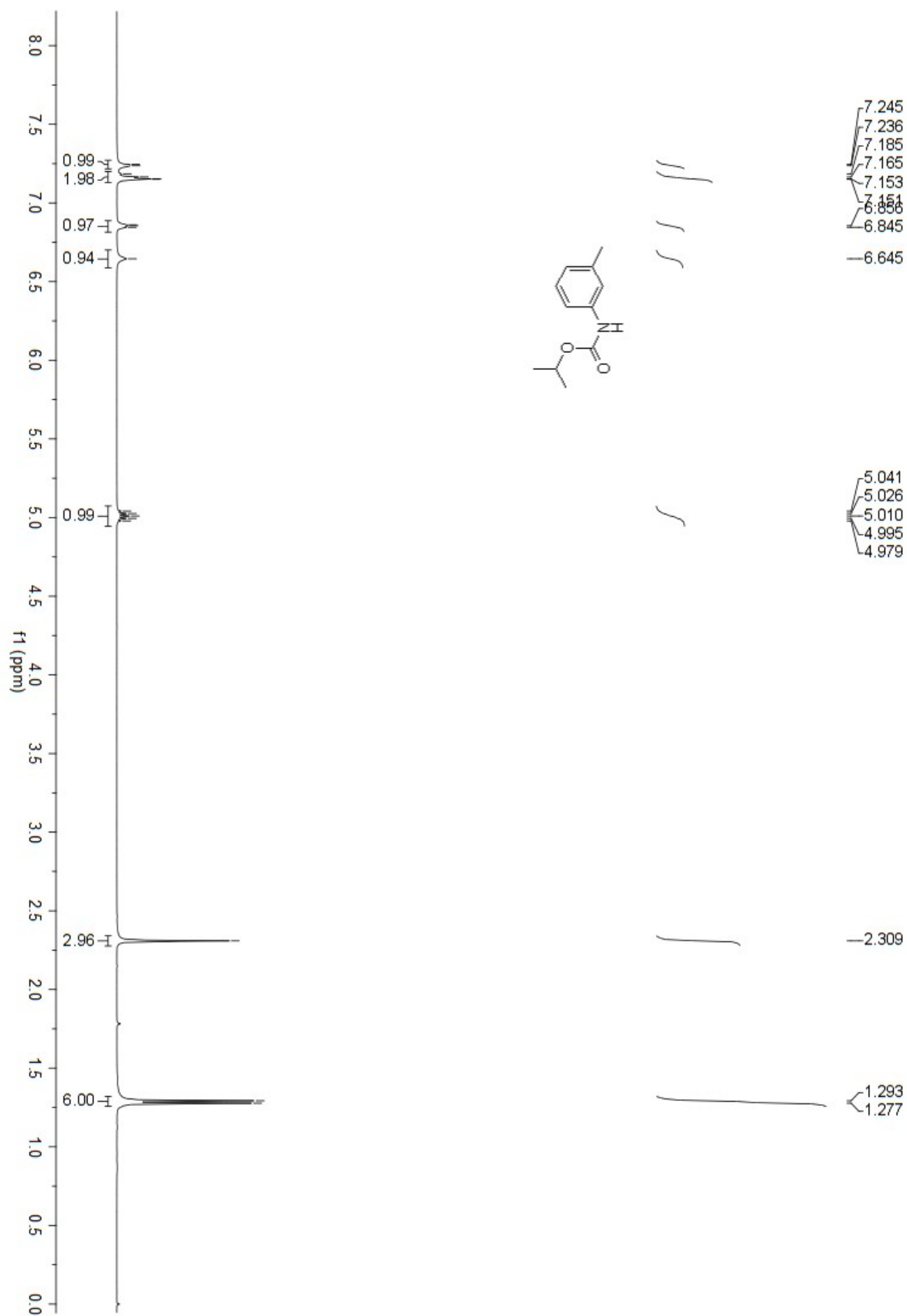
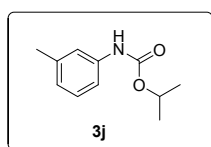


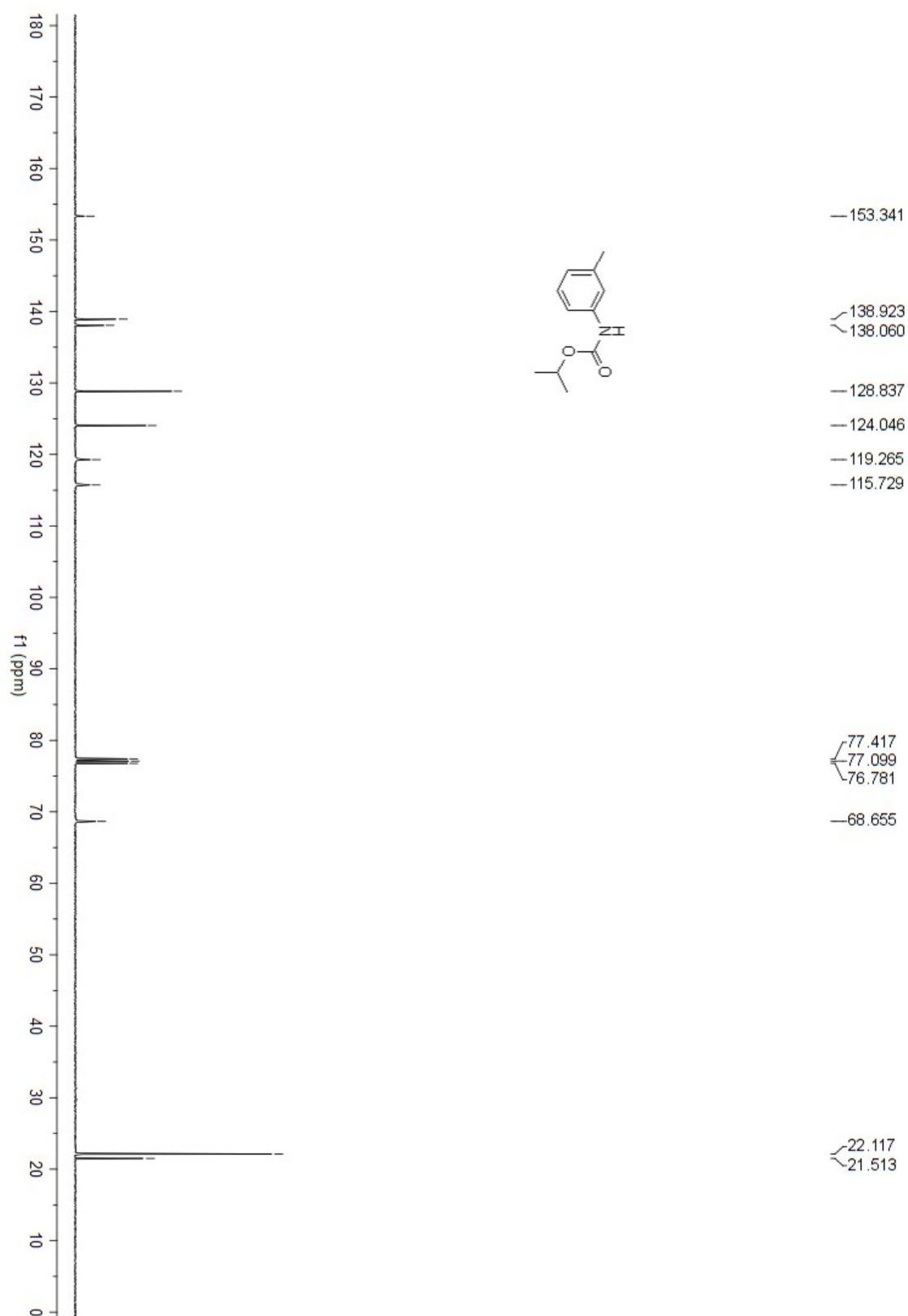
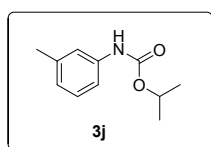


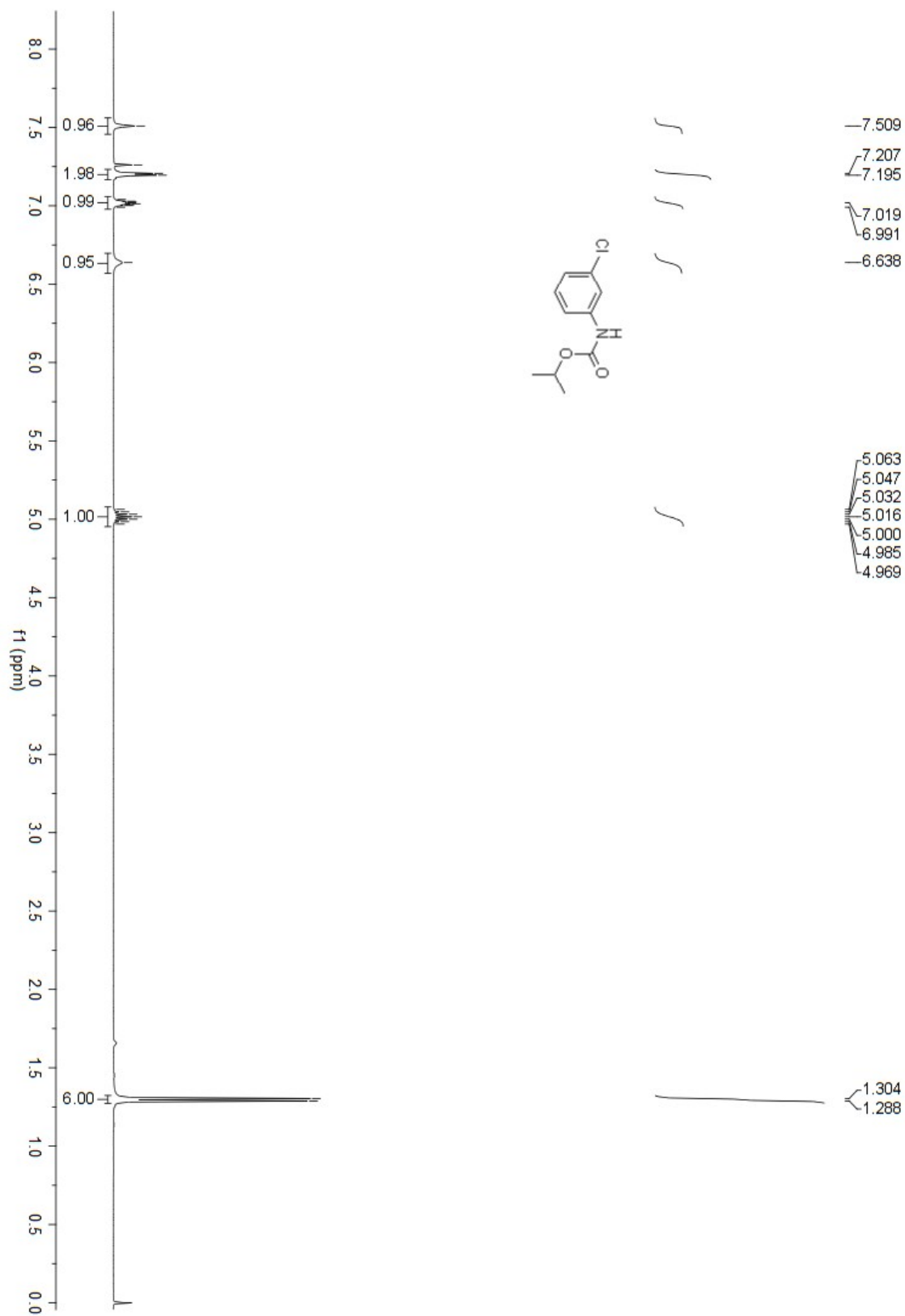
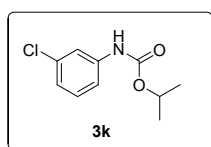


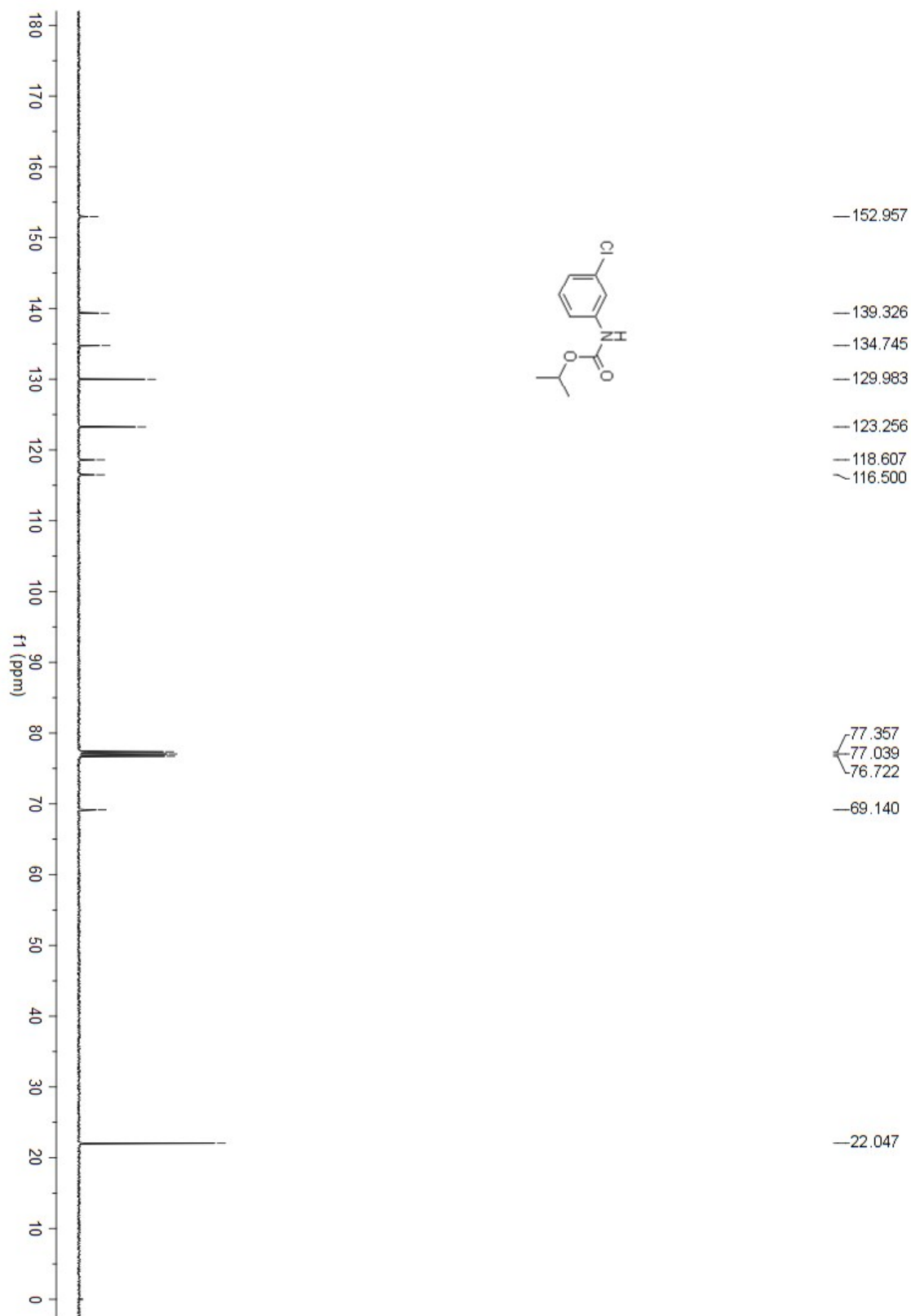
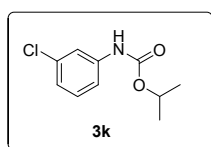


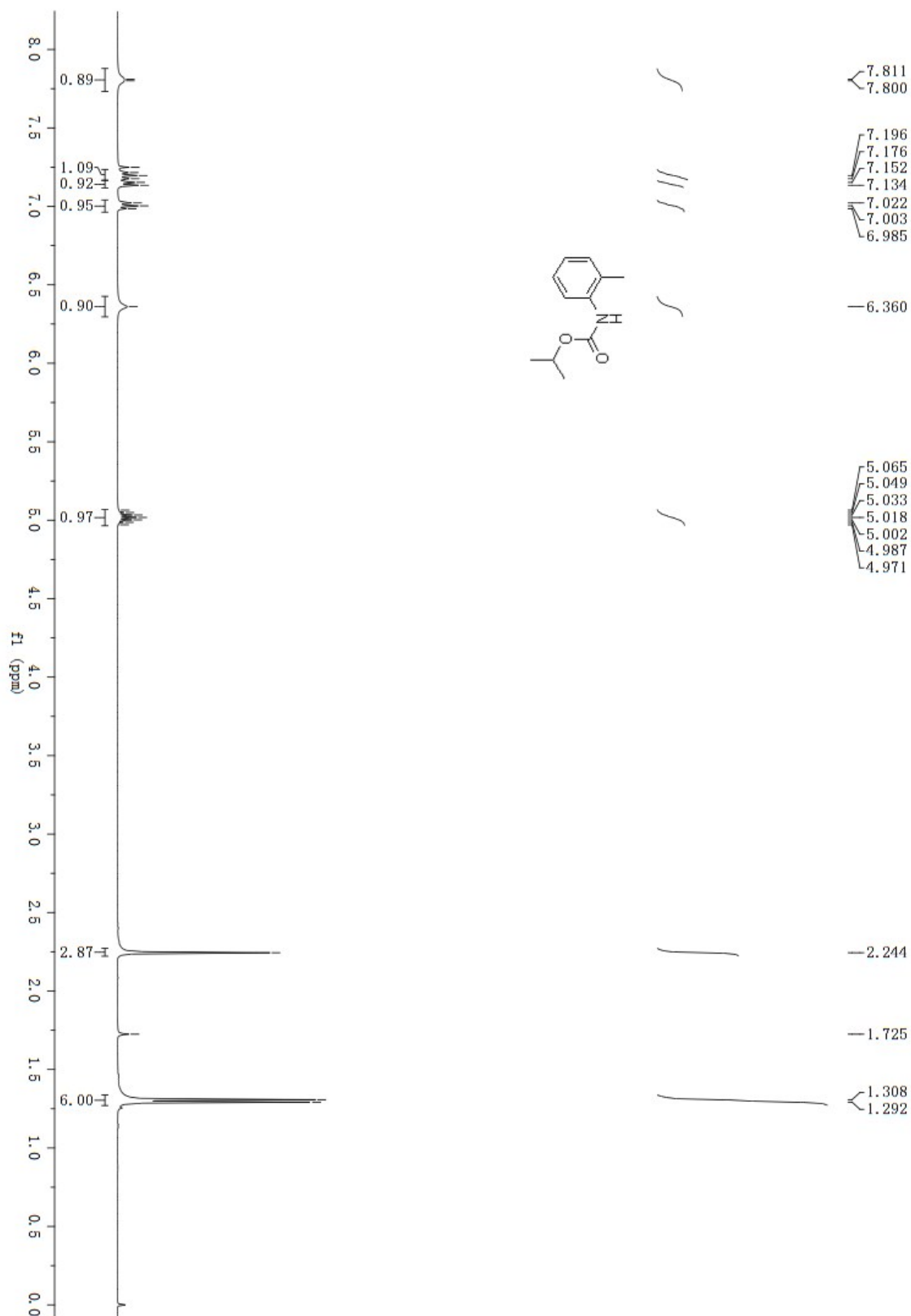
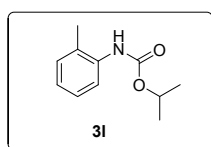


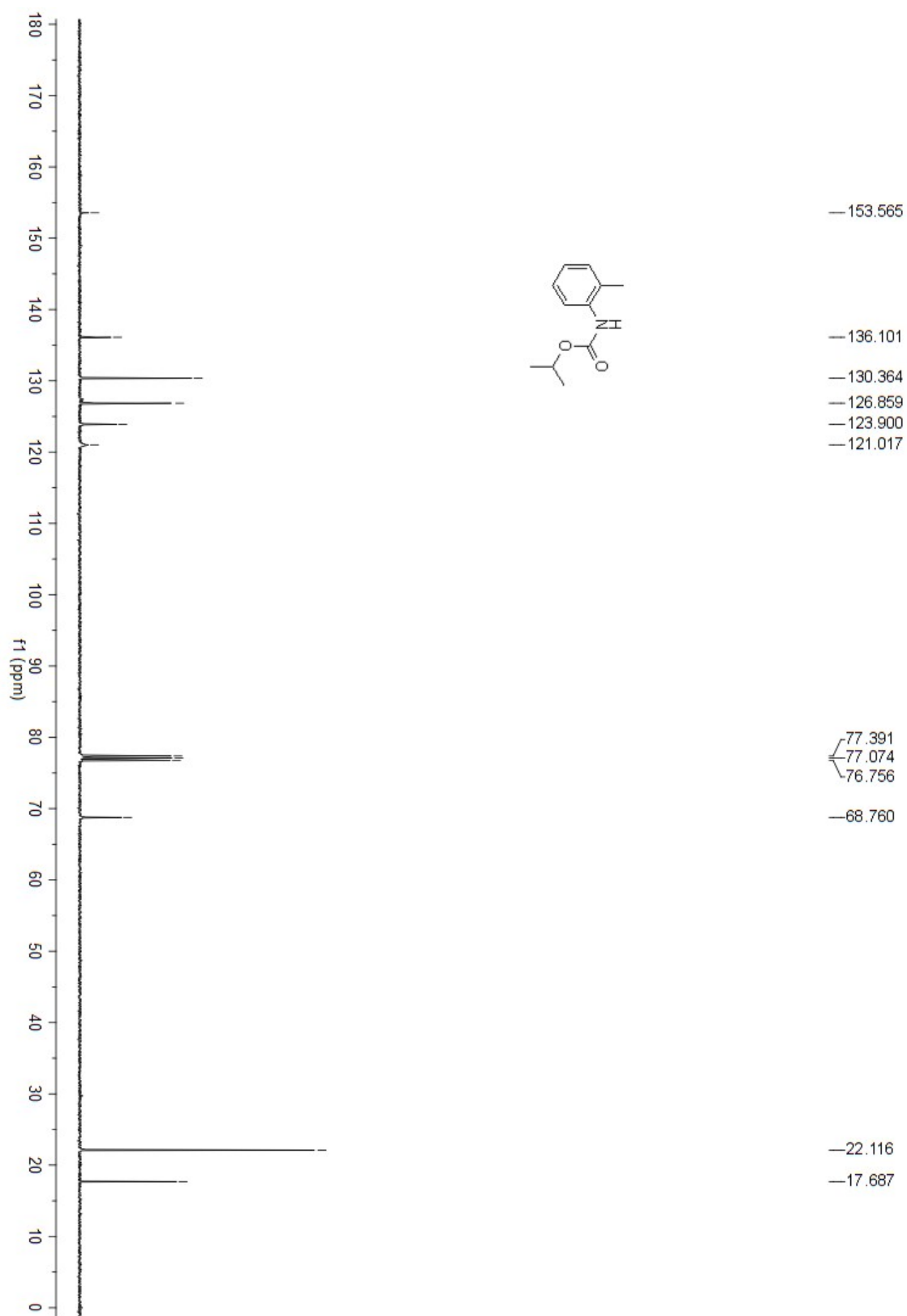
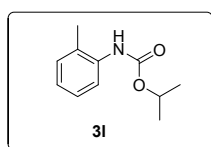


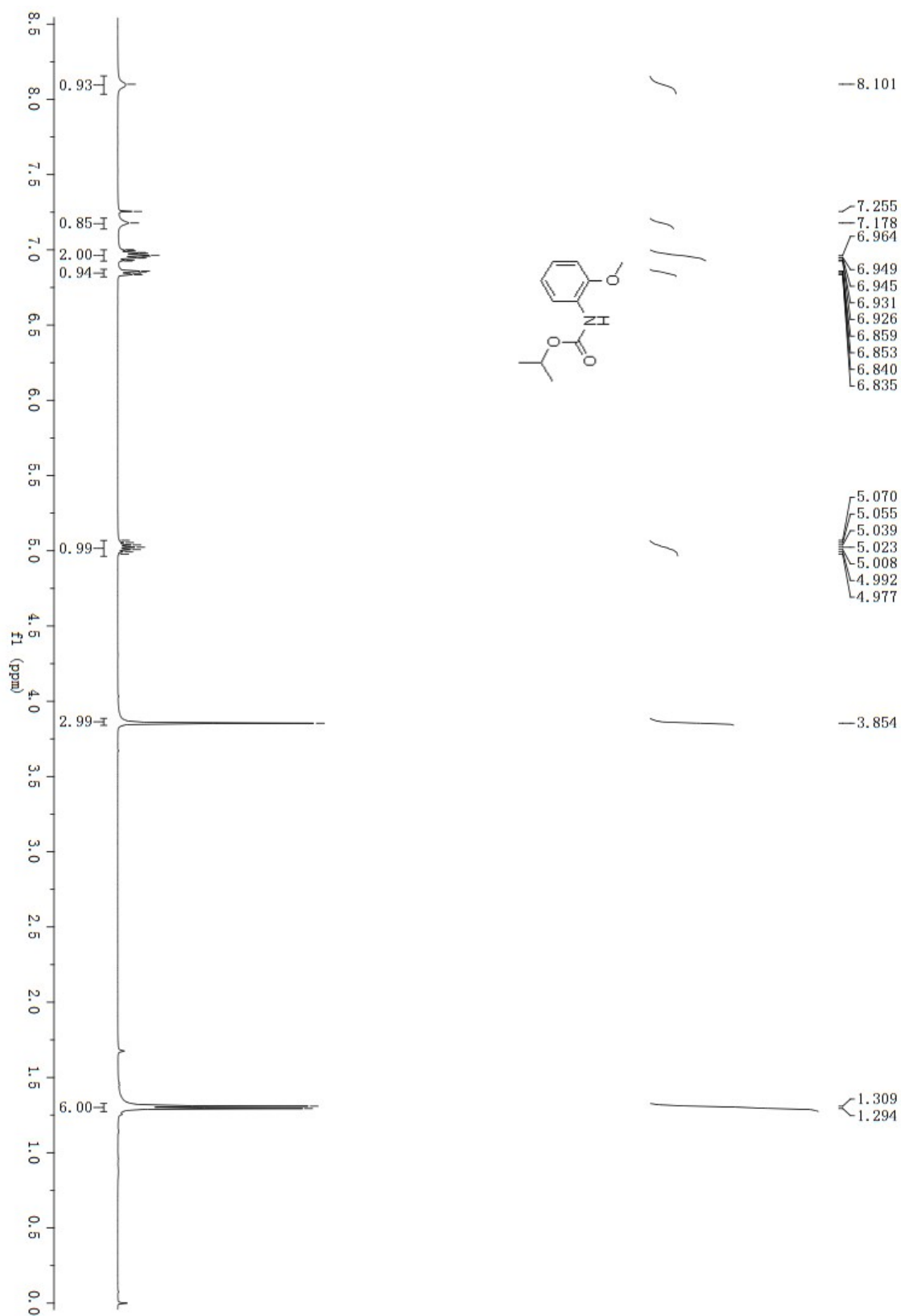
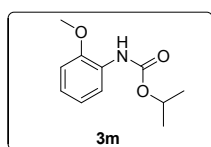


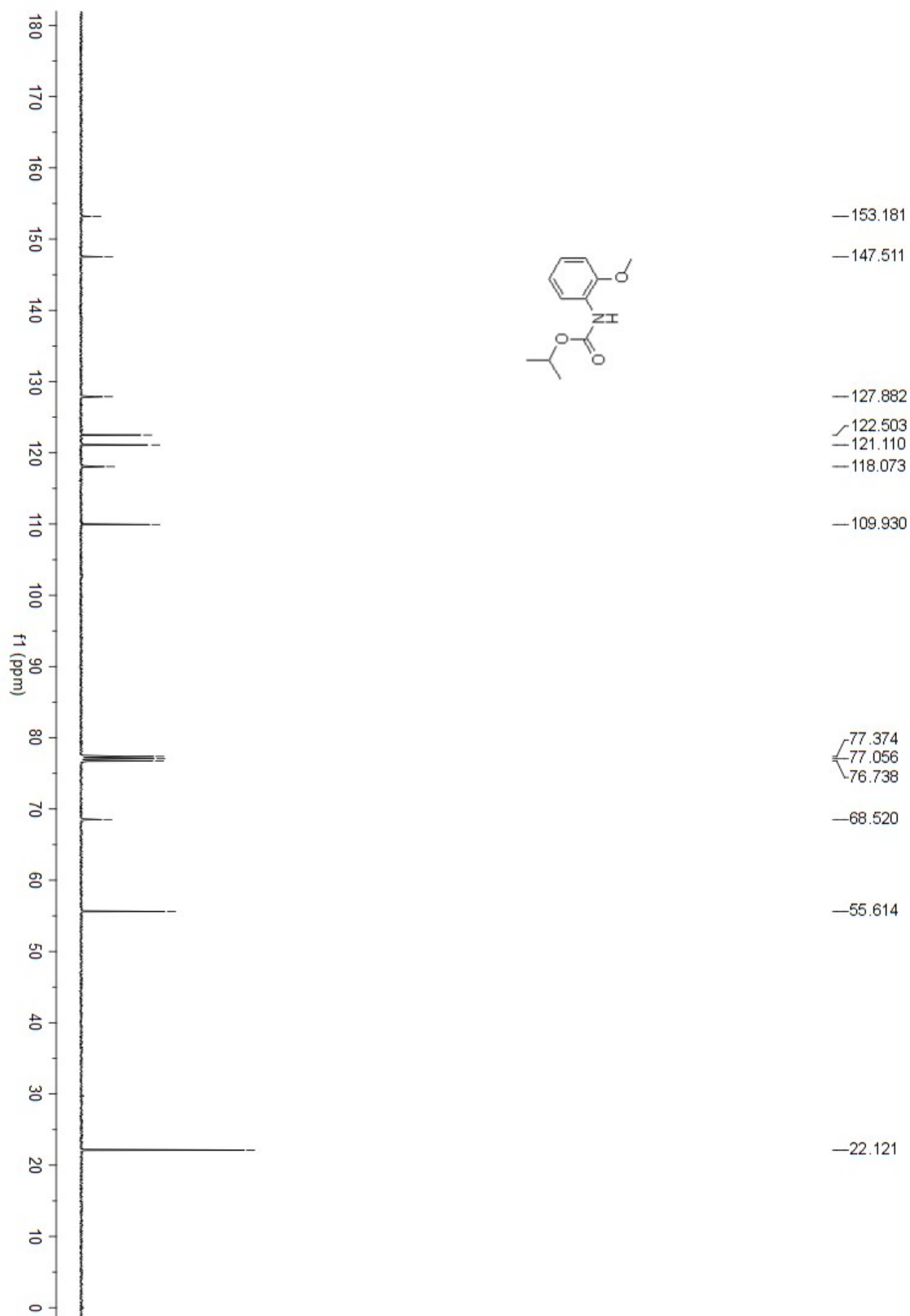
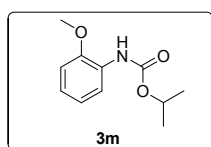


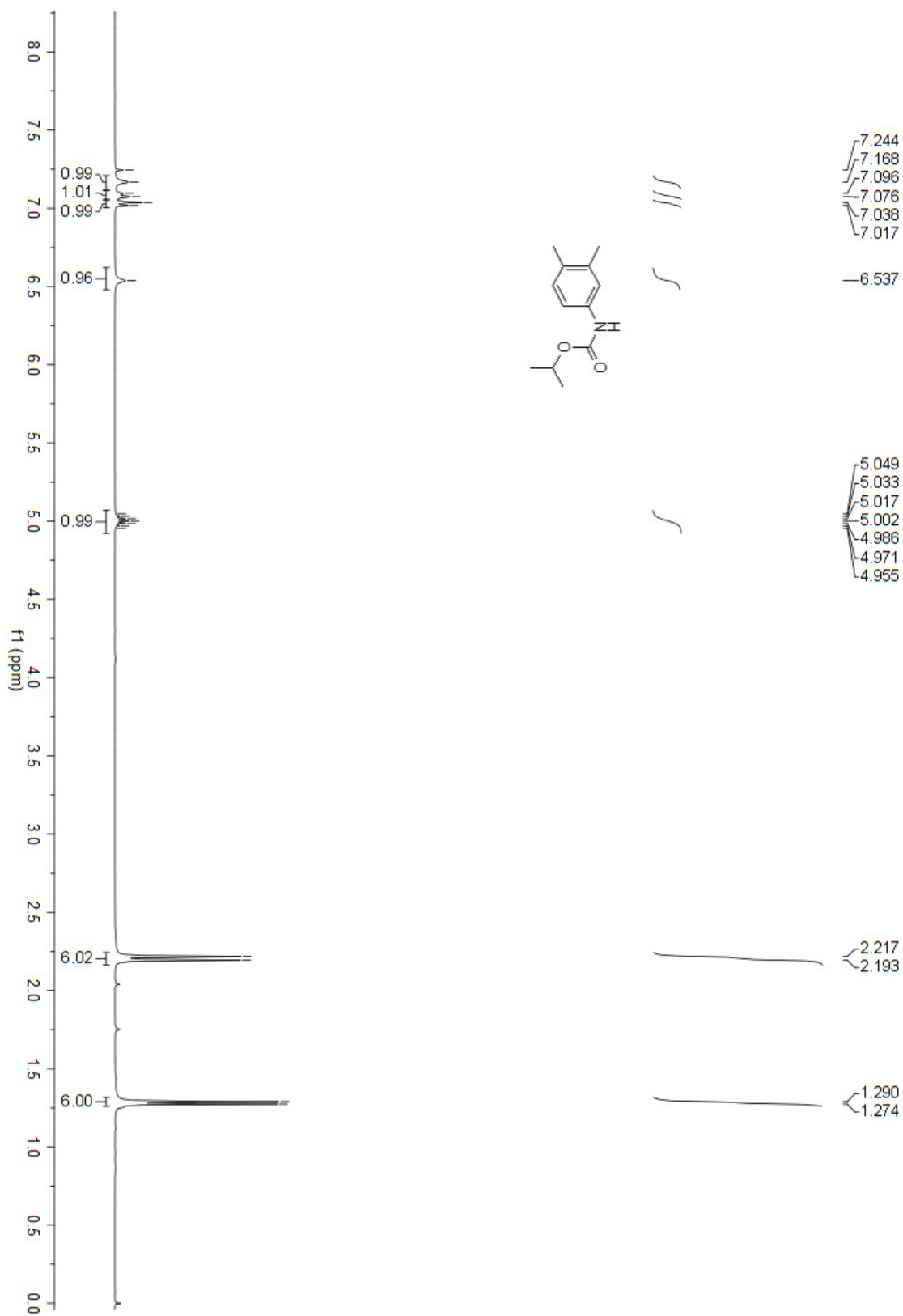
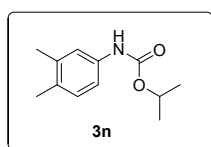


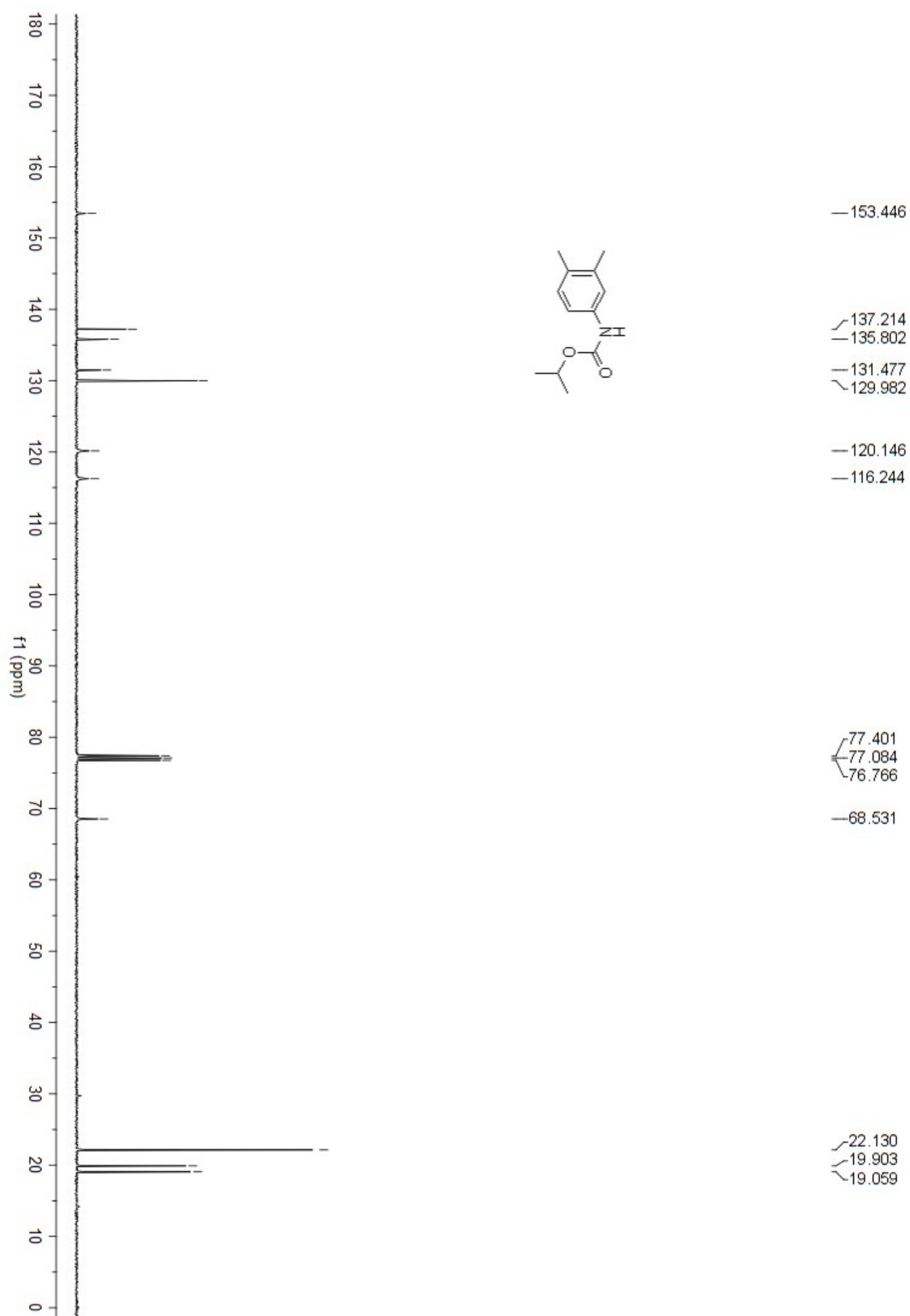
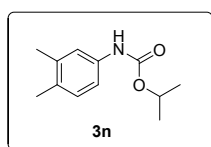


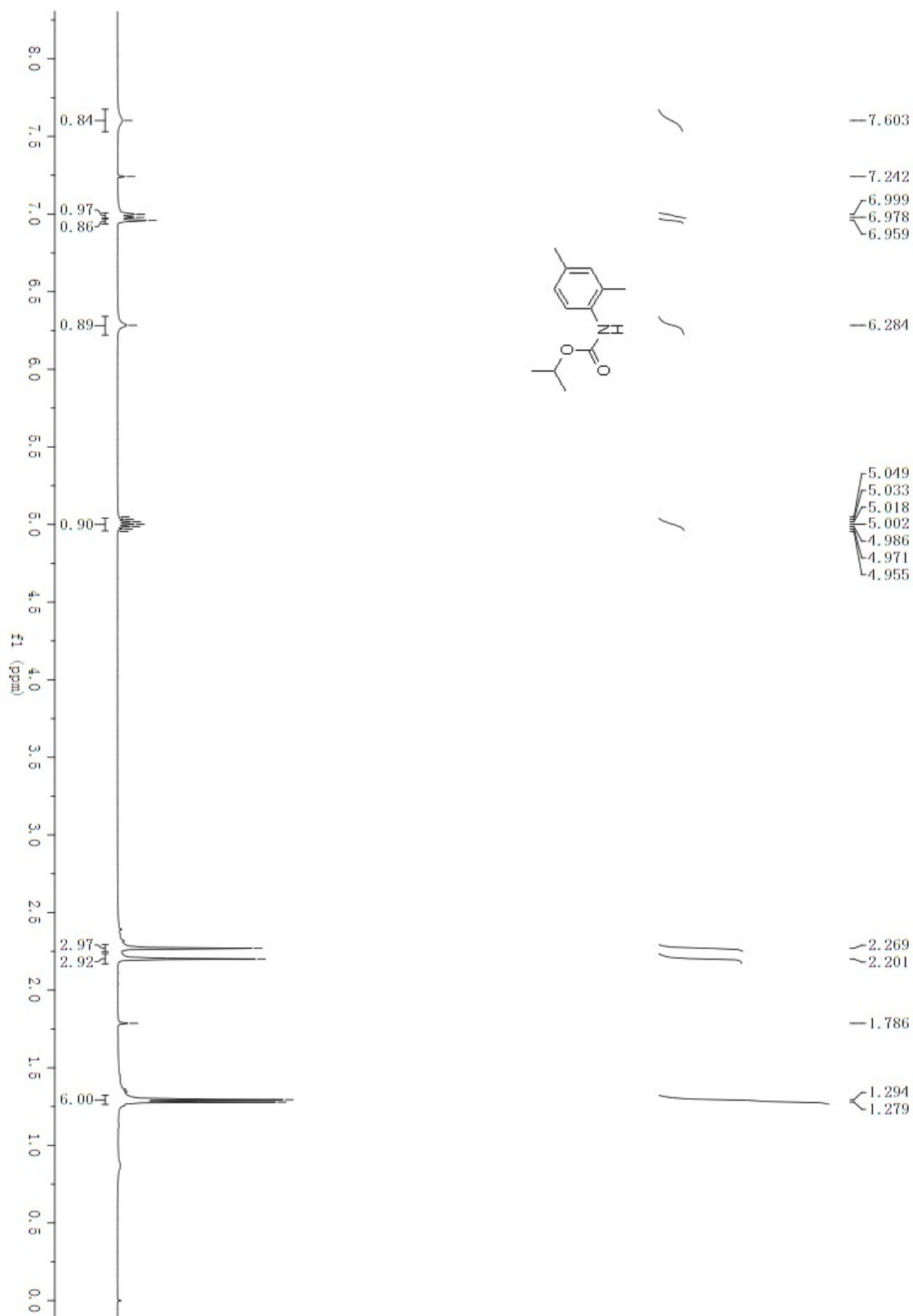
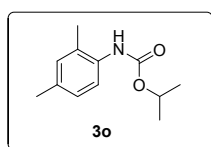


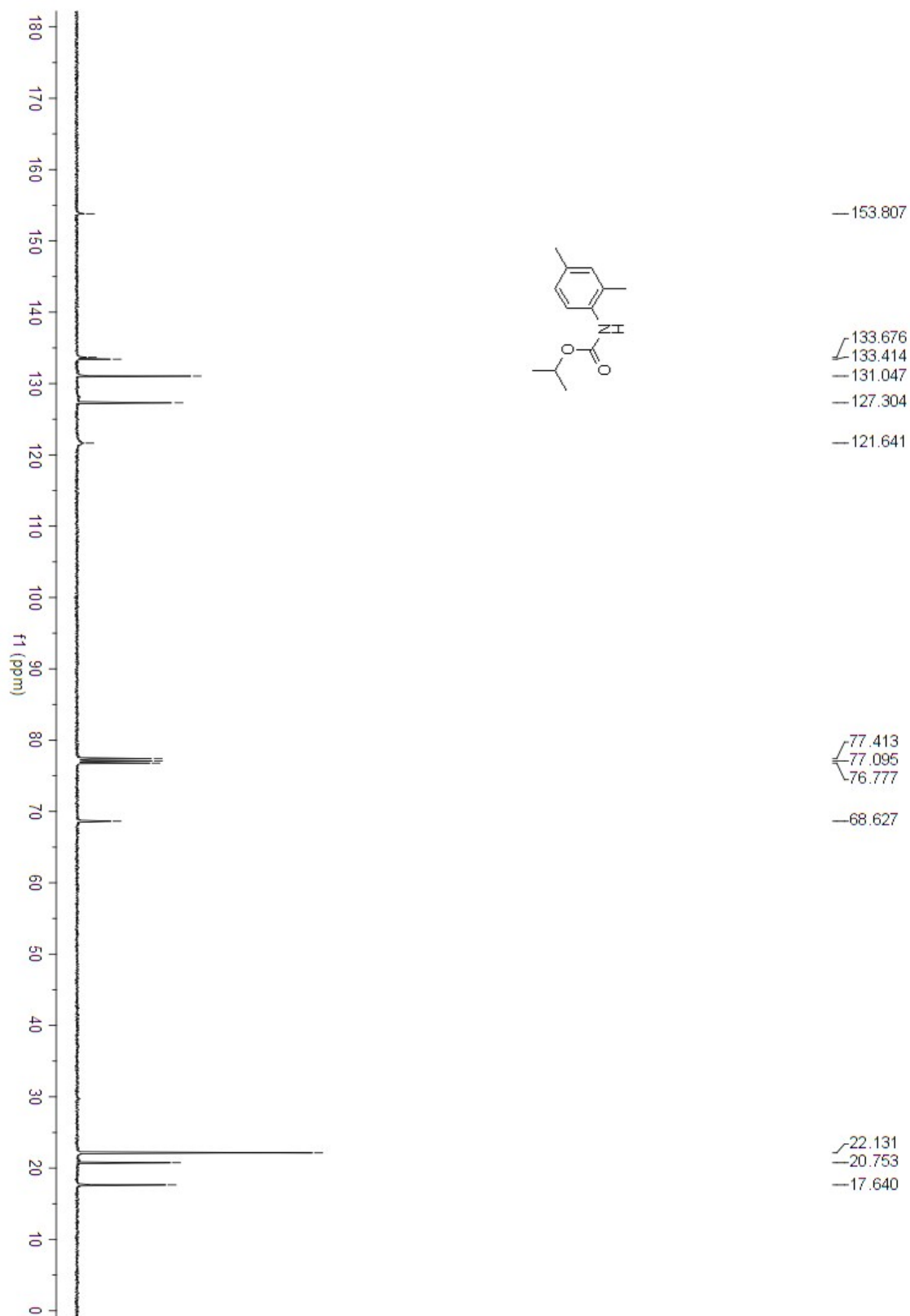
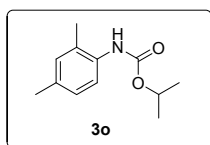


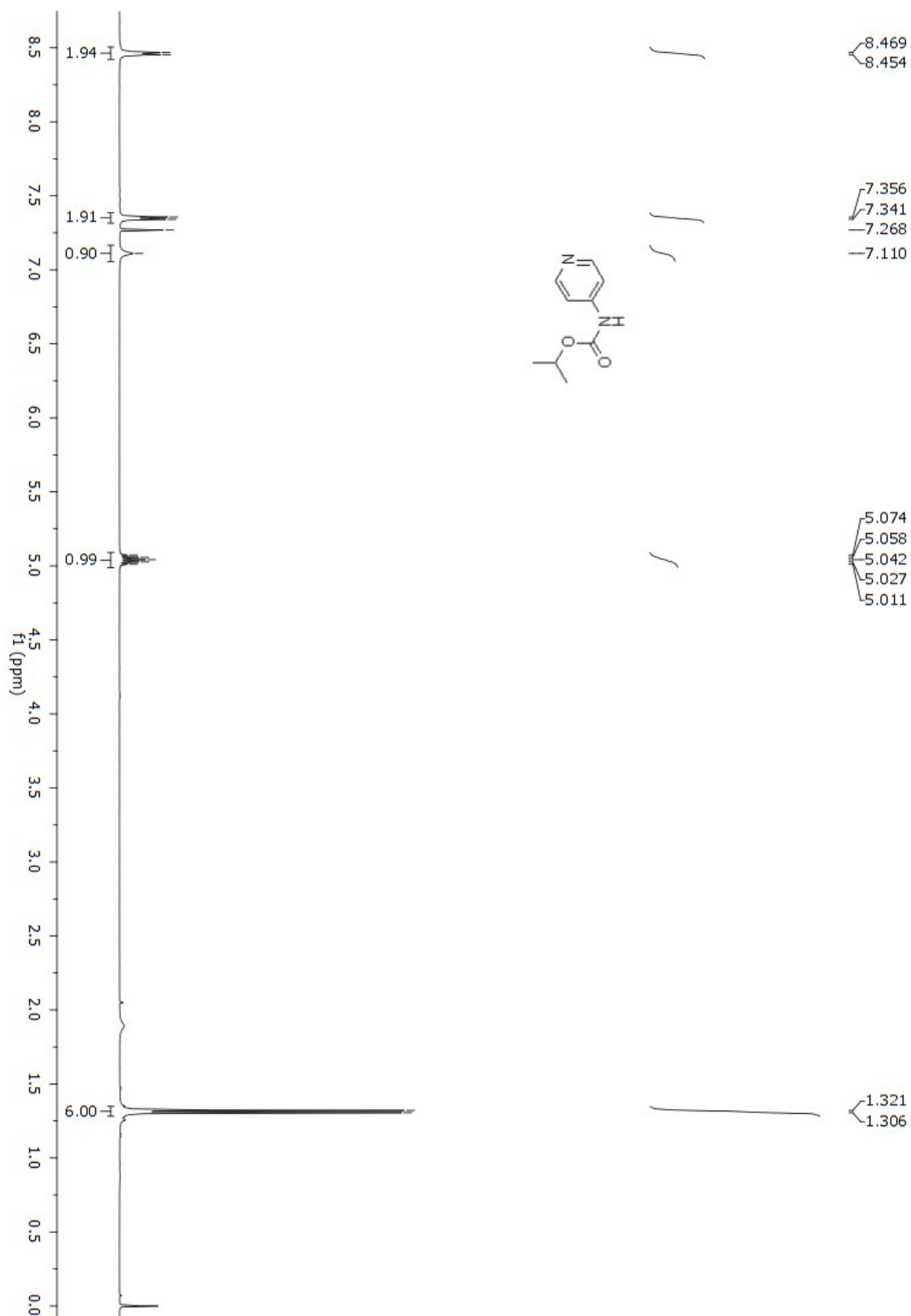
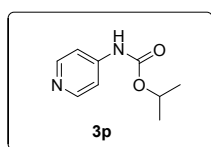


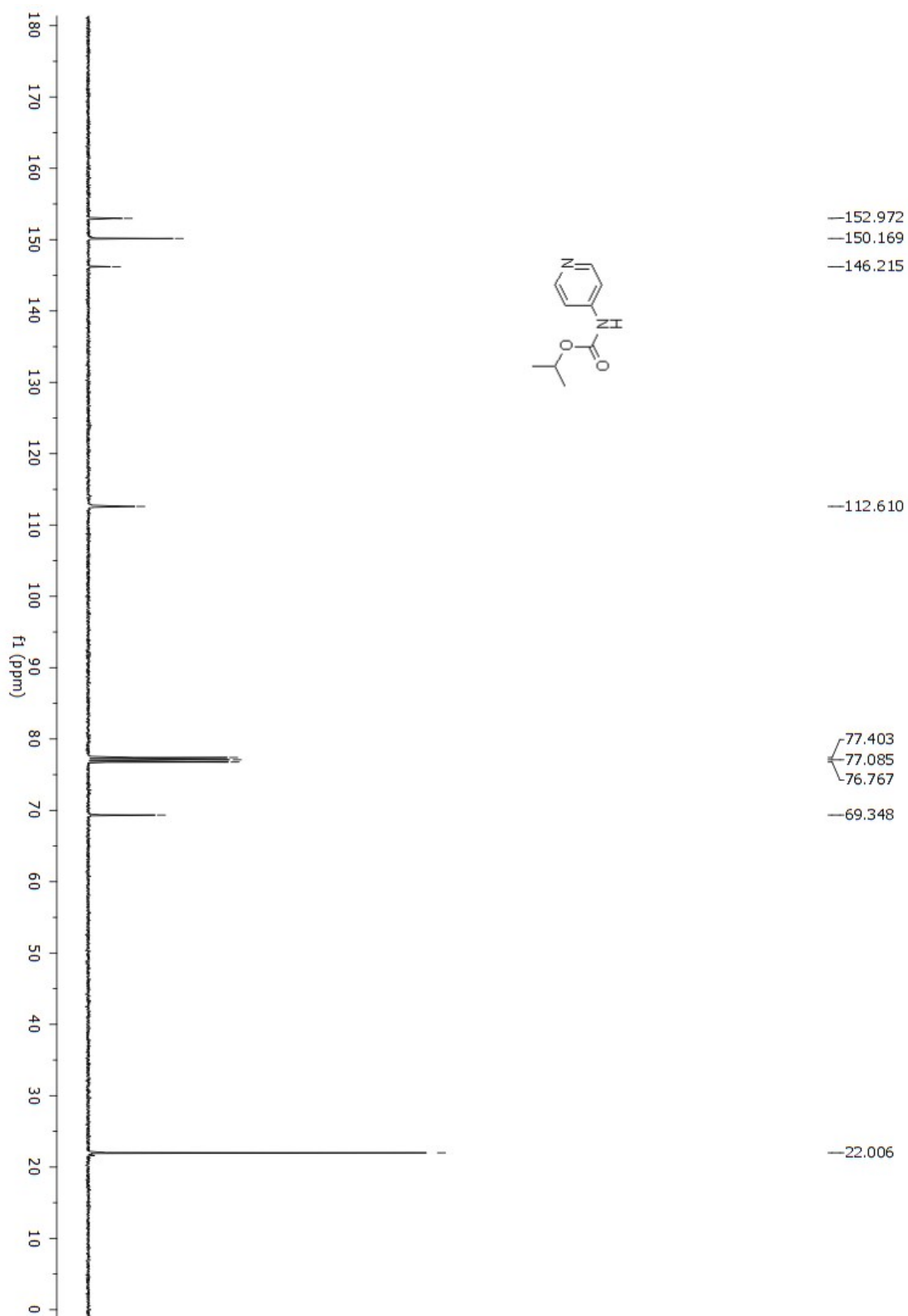
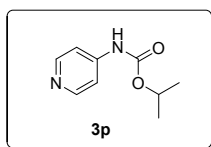


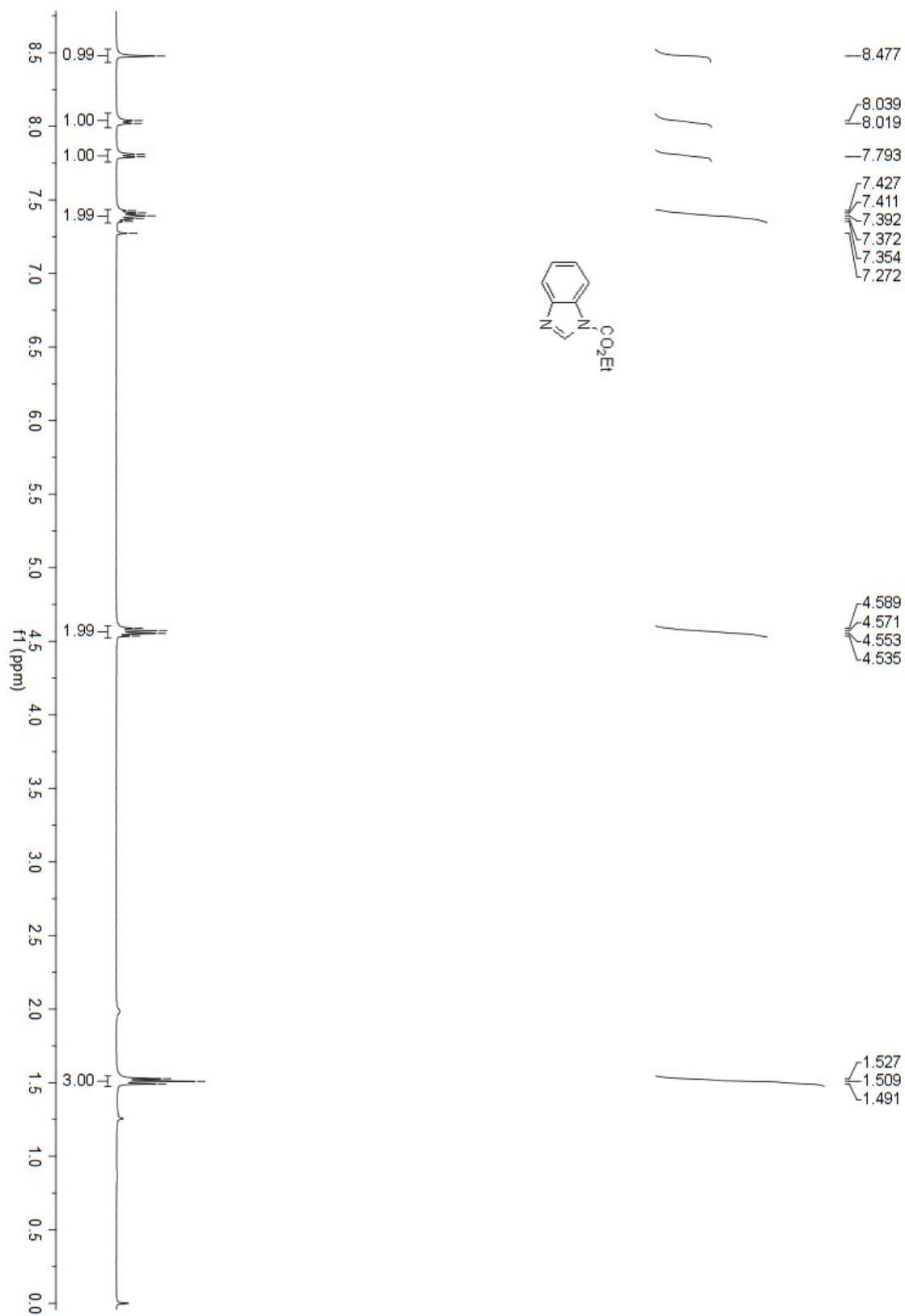
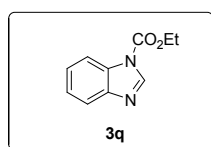


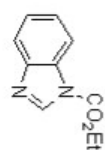
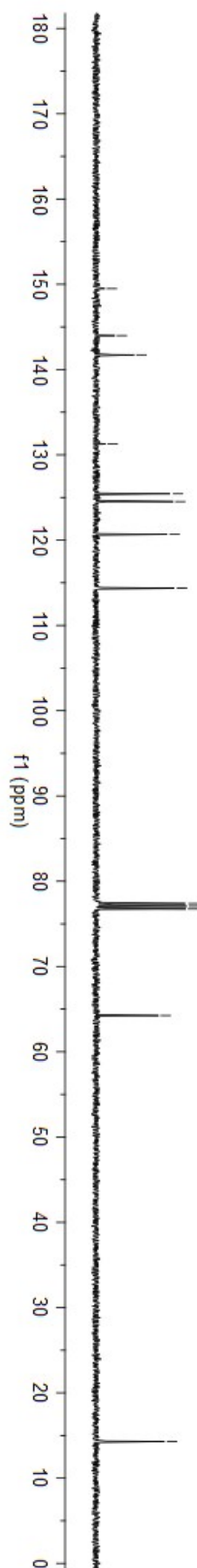
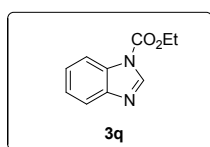












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