

Supporting Information for:

Metal-Free Cascade Cyclization of Alkenes toward Polyfluorinated Oxindoles

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. **Flash** column chromatography was performed using silica gel (200-300 mesh) and a petroleum ether/ethyl acetate combination was used as the eluent. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

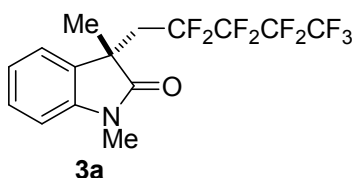
Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury 400 or 500 (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz; ¹H NMR, 500 MHz, ¹³C NMR, 125 MHz,) spectrometer with solvent resonance (¹H NMR, CHCl₃ at 7.26 ppm, and SiMe₄ at 0 ppm; ¹³C NMR, CDCl₃ at 77.0

ppm and SiMe₄ at 0 ppm) as the internal standard. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constants (Hz), and integration. ¹⁹F NMR spectra were obtained by the same NMR spectrometer.

Chemicals. Unless otherwise noted, reagents were commercially available and were used without further purification. Anhydrous THF was distilled from sodium/benzophenone prior to use. Preparation of *N*-arylacrylamides **1** were prepared according to literature procedures.¹

3. General Procedures

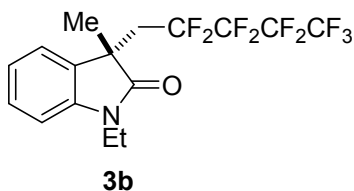
General procedure for the synthesis of perfluorinated oxindoles. To a mixture of *N*-arylacrylamide **1** (0.3 mmol), AIBN (2.0 equiv.), perfluoroalkyl iodide (2 equiv.) in CH₃CN (2.0 mL) was added ^tBuOO^tBu (2.0 equiv.) dropwise, and then the resulting solution was stirred at 105 °C for 12 h. The solvent was evaporated under reduced pressure and the resulted mixture was filtered through a Florisil pad, diluted with Et₂O, and washed with water and then brine. The organic layer was dried over anhydrous MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford the corresponding perfluorinated oxindole in a yield listed in Scheme 1 and 2.



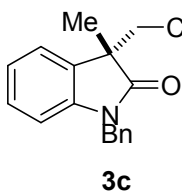
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a).^{1a} ¹H NMR (400 MHz, CDCl₃) δ: 7.36-7.22 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 2.97-2.43 (m, 2H),

1.41 (s, 3H).

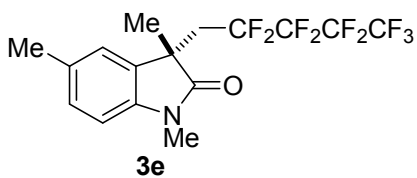
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-



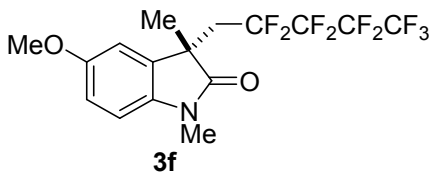
nonafluoropentyl)indolin-2-one (3b). Yellowish oil. ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.23 (m, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 2H), 3.93-3.62 (m, 2H), 2.92-2.43 (m, 2H), 1.41 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 141.7, 131.5, 128.4, 123.7, 122.4, 121.4, 125.0-114.2 (m), 44.1, 36.9 (t, $J = 21$ Hz), 34.7, 26.0, 12.2; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.0 (t, $J = 9.4$ Hz, 3F), -108.8 (AB, m, $J_{F-F} = 268$ Hz, 1F), -114.7 (AB, m, $J_{F-F} = 273$ Hz, 1F), -124.6 (br, 2F), -126.0~ -125.6 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{F}_9\text{NO}$ $[\text{M}+\text{H}]^+$: 408.1005, found: 408.1007.



1-Ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3c). Yellowish oil. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.13 (m, 7H), 7.04 (t, $J = 8.4$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 2H), 4.94 (d, $J = 3.6$ Hz, 2H), 2.93 (dd, $J = 35.6, 14.4$ Hz, 1H), 2.65 (dd, $J = 31.2, 15.2, 8.0$ Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.6, 141.9, 135.7, 131.2, 127.3, 123.6, 122.6, 126.0-114.3 (m), 109.5, 44.3, 44.0, 36.6 (t, $J = 20.4$ Hz), 26.5; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.1 (t, $J = 8.1$ Hz, 3F), -107.6 (d, $J_{F-F} = 264$ Hz, 1F), -114.3 (d, $J_{F-F} = 270$ Hz, 1F), -124.5 (br, 2F), -125.4~ -126.1 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{F}_9\text{NO}$ $[\text{M}+\text{H}]^+$: 470.1161, found: 470.1163.

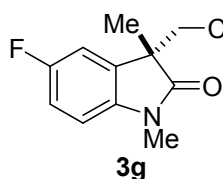


1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e). Yellowish solid. m.p. 62-63 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.05 (m, 2H), 6.76 (d, $J = 8.4$ Hz, 1H), 3.21 (s, 3H), 2.85 (dd, $J = 35.2, 15.6$ Hz, 1H), 2.56 (ddd, $J = 31.2, 15.2, 8.0$ Hz, 1H), 2.34 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.5, 140.4, 132.2, 131.3, 128.8, 124.4, 125.0-114.1 (m), 108.1, 44.2, 36.9 (t, $J = 23$ Hz), 26.5, 25.9, 21.1; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.0 (t, $J = 8.0$ Hz, 3F), -108.9 (d, $J_{F-F} = 272$ Hz, 1F), -114.7 (d, $J_{F-F} = 273$ Hz, 1F), -124.6 (br, 2F), -125.0~ -126.2 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{F}_9\text{NO}$ $[\text{M}+\text{H}]^+$: 408.1005, found: 408.1002.

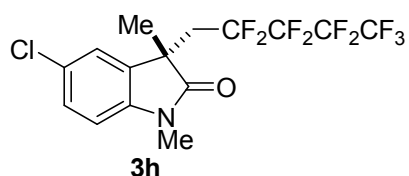


5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).

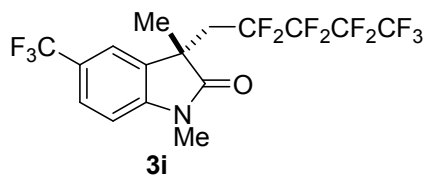
nonafluoropentyl)indolin-2-one (3f). Yellowish oil, ^1H NMR (400 MHz, CDCl_3) δ 6.92-6.74(m, 3H), 3.79 (s, 3H), 3.21 (s, 3H), 2.86 (dd, $J = 35.0, 15.6$ Hz, 1H), 2.56 (ddd, $J = 30.8, 15.6, 8.4$ Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.2, 156.4, 136.3, 132.7, 125.0-114.1 (m), 112.5, 111.3, 108.7, 55.8, 44.6, 36.6 (t, $J = 31.1$ Hz), 26.5, 25.9; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.0 (t, $J = 8.0$ Hz, 3F), -108.8 (d, $J_{F-F} = 268$ Hz, 1F), -114.9 (d, $J_{F-F} = 273$ Hz, 1F), -124.6 (br, 2F), -125.2~ -126.3 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{F}_9\text{NO}_2$ $[\text{M}+\text{H}]^+$: 424.0954, found: 424.0926.



5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g). yellowish solid. m.p. 78-79 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.06-6.95 (m, 2H), 6.93-6.75(m, 1H), 3.22 (s, 3H), 2.87 (dd, $J = 34.8$ Hz, 15.2 Hz, 1H), 2.56 (ddd, $J = 30.8, 15.6, 8.0$ Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.2, 159.3 (d, $J = 241.9$ Hz), 138.8, 132.9, 125.0-114.2 (m). 114.8 (d, $J = 27.6$ Hz), 111.8 (d, $J = 25.5$ Hz), 109.0 (d, $J = 8.2$ Hz), 44.6, 36.9 (t, $J = 20.2$ Hz), 26.6, 25.7; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.0 - 81.0 (t, $J = 8.0$ Hz, 3F), -108.7 (d, $J_{F-F} = 273$ Hz, 1F), -114.6 (d, $J_{F-F} = 266.9$ Hz, 1F), -120.4 (s, 1F), -124.6 (br, 2F), -125.2~ -126.2 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{F}_{10}\text{NO}$ $[\text{M}+\text{H}]^+$ 412.0754, found: 412.0758.

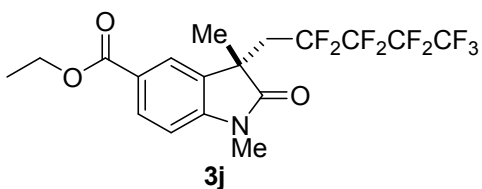


chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h). Yellowish solid. m.p. 73-74 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.21 (m, 2H), 6.79(d, $J = 8.4$ Hz, 1H), 3.20 (s, 3H), 2.87 (dd, $J = 35.2, 15.6$ Hz, 1H), 2.65(ddd, $J = 30.8, 15.6, 8.4$ Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.0, 141.4, 132.9, 128.1, 125.0-114.0 (m). 124.1, 109.5, 44.4, 36.9 (t, $J = 20.2$ Hz), 26.6, 25.8; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.0 (t, $J = 8.0$ Hz, 3F), -108.7 (d, $J_{F-F} = 273$ Hz, 1F), -114.6 (d, $J_{F-F} = 266.9$ Hz, 1F), -124.6 (br, 2F), -125.2~ -126.2 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{11}\text{ClF}_9\text{NO}$ $[\text{M}+\text{H}]^+$ 428.0459, found: 428.0462.



1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-

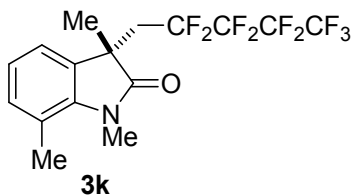
5-(trifluoromethyl)indolin-2-one (3i). Yellowish solid. m.p. 92-93 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.4 Hz), 7.50 (s, 1H), 6.96(d, *J* = 8.4 Hz, 1H), 3.27 (s, 3H), 2.92 (dd, *J* = 35.2 Hz, 15.6 Hz, 1H), 2.63 (ddd, *J* = 30.8, 15.6, 8.4 Hz, 1H), 1.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 178.4, 145.8, 131.7, 126.3 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 32.9 Hz), 124.4 (q, *J* = 272.8 Hz), 124.0-114.0 (m). 109.5, 44.1, 36.9 (t, *J* = 20.1 Hz), 26.6, 25.7; ¹⁹F NMR (282 MHz, CDCl₃) δ: -61.3 (t, *J* = 8.0 Hz, 3F), -81.0 (t, *J* = 8.0 Hz, 3F), -108.5 (d, *J*_{F-F} = 274 Hz, 1F), -114.7 (d, *J*_{F-F} = 272 Hz, 1F), -124.6 (br, 2F), -125.3~ -127.0 (m, 2F); HRMS *m/z* (ESI) calcd for C₁₆H₁₂F₁₂NO [M+H]⁺: 462.0722, found: 462.0726.



Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-

carboxylate (3j). Yellowish oil, ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 8.4, 1.6 Hz, 1H),

7.93 (s, 1H), 6.91(d, *J* = 8.4 Hz, 1H), 3.27 (s, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.91 (dd, *J* = 35.2, 15.6 Hz, 1H), 2.64 (ddd, *J* = 30.8, 15.6, 8.4 Hz, 1H), 1.44 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 178.8, 166.2, 146.8, 131.1, 125.0, 124.8, 125.0-114.0 (m), 108.0, 61.0, 43.9, 36.2 (t, *J* = 20.2 Hz), 26.5, 25.8, 14.4; ¹⁹F NMR (282 MHz, CDCl₃) δ: -81.0 (t, *J* = 8.0 Hz, 3F), -108.7 (d, *J*_{F-F} = 265 Hz, 1F), -114.7 (d, *J*_{F-F} = 268 Hz, 1F), -124.5 (br, 2F), -125.2~ -126.9 (m, 2F); HRMS *m/z* (ESI) calcd for C₁₈H₁₇F₉NO₃ [M+H]⁺: 466.1060, found: 466.1063.

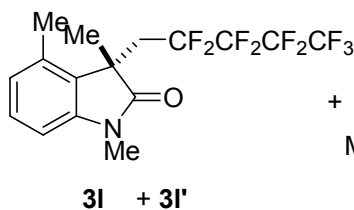


Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k). Yellowish solid.

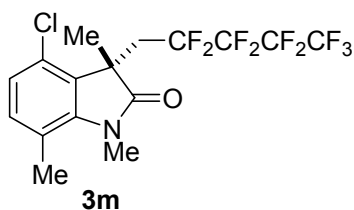
m.p. 115-116 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz,

1H), 3.52 (s, 3H), 2.89 (dd, *J* = 35.2, 15.6 Hz, 1H), 2.65-2.50 (m, 4H), 1.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 179.2, 140.4, 132.0, 131.7, 125.0-114.0 (m), 122.3, 121.3, 119.9, 43.3, 36.0 (t, *J* = 20.3 Hz), 29.7, 26.3, 18.9; ¹⁹F NMR (470 MHz, CDCl₃) δ: -81.1 (t, *J* = 8.0 Hz, 3F), -109.0 (A-B, *J*_{F-F} = 269 Hz, 1F), -114.7 (A-B, *J*_{F-F} = 272 Hz, 1F), -124.6 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS *m/z* (ESI) calcd for C₁₆H₁₅F₉NO [M+H]⁺:

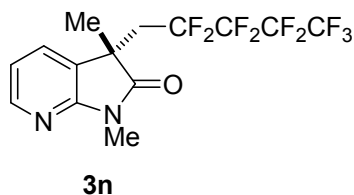
408.1005, found: 408.1001.



Mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I'). 3I:3I' = 0.9:1, ¹H NMR (400 MHz, CDCl₃) δ 7.23-6.68 (m, 3H), 3.21(s, 3H), 3.10-2.48 (m, 2H), 2.36(s, 3H), 1.46(s, 1.6H), 1.40(s, 1.4H); ¹³C NMR (101 MHz, CDCl₃) δ 179.6, 179.3, 143.8, 143.6, 139.4, 135.5, 129.1, 129.0, 125.9, 124.1, 125.0-114.0 (m), 123.9, 122.2, 110.2, 107.0, 45.2, 44.7, 37.7 (t, *J* = 20.4Hz), 36.7 (t, *J* = 20.2Hz), 27.2, 26.6, 24.5, 24.1, 22.5, 18.9; ¹⁹F NMR (282 MHz, CDCl₃) δ: -81.0 (t, *J* = 12.4 Hz, 3F), -107.9—117.9 (m, 2F), -124.7 (br, 2F), -125.1~ -126.7 (m, 2F); HRMS *m/z* (ESI) C₁₆H₁₅F₉NO [M+H]⁺:408.1005, found: 408.1004

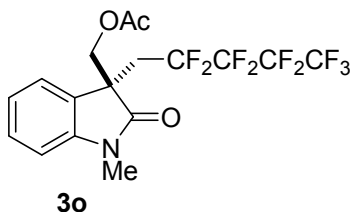


Ethyl 4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m). Yellowish solid. m.p. 98-99 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.97 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.51 (s, 3H), 3.13 (ddd, *J* = 31.2, 15.2, 7.6 Hz, 1H), 2.85 (dd, *J* = 35.2, 15.2 Hz, 1H), 2.56 (s, 3H), 1.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 178.8, 142.2, 133.4, 129.0, 127.9, 114.0-125.0 (m), 123.4, 118.8, 44.5, 36.1, 36.0 (t, *J* = 20.1 Hz), 29.9, 22.9, 16.9; ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.0 (t, *J* = 8.0 Hz, 3F), -112.7 (A-B, *J*_{F-F} = 270 Hz, 1F), -115.6 (A-B, *J*_{F-F} = 272 Hz, 1F), -124.7 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS *m/z* (ESI) calcd for C₁₆H₁₄ClF₉NO [M+H]⁺: 442.0615, found: 442.0618.

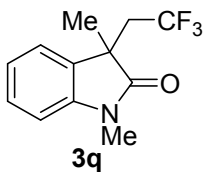


1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n). Yellowish solid. m.p. 83-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.23-7.09 (m, 2H), 3.25(s, 3H), 2.94-2.77 (m, 2H), 1.46 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 152.2, 143.0, 137.9, 114.0-

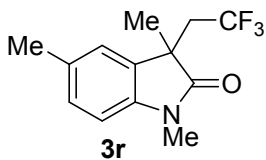
125.0 (m), 123.2, 114.7, 46.2, 36.1 (t, $J = 20.3\text{Hz}$), 26.2, 24.1; ^{19}F NMR (282 MHz, CDCl_3) δ : -81.0 (t, $J = 8.0$ Hz, 3F), -109.8 (A-B, $J_{F-F} = 274$ Hz, 1F), -113..5 (A-B, $J_{F-F} = 261$ Hz, 1F), -124.5 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{F}_9\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 395.0801, found: 395.0798.



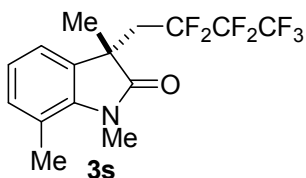
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindolin-3-yl)methyl acetate (3o). Yellowish oil, ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.24 (m, 2H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 4.38 (d, $J = 10.8$ Hz, 1H), 4.07 (d, $J = 10.8$ Hz, 1H), 2.99-2.69 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 175.2, 170.0, 143.5, 129.3, 126.9, 124.8-114.0 (m), 122.7, 108.6, 67.4, 47.9, 33.1 (t, $J = 20.0$ Hz), 36.5, 20.5; ^{19}F NMR (376 MHz, CDCl_3) δ : -81.1 (t, $J = 3.4$ Hz, 3F), -108.1 (A-B, $J_{F-F} = 272$ Hz, 1F), -114.1 (A-B, $J_{F-F} = 276$ Hz, 1F), -124.4 (br, 2F), -125.2~ -126.8 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{F}_9\text{NO}_3$ $[\text{M}+\text{H}]^+$: 452.0903, found: 452.0907.



1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q).^{1a} ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.26 (m, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 7.5$ Hz, 1H), 3.26 (s, 3H), 2.90-2.78(m, 1H), 2.72-2.63 (m, 1H), 1.42 (s, 3H).



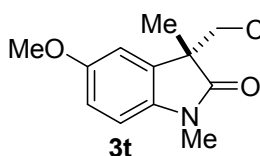
1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3r).^{1b} ^1H NMR (500 MHz, CDCl_3) δ 7.15-7.08 (m, 2H), 6.79(d, $J = 8.0$ Hz, 1H), 3.23 (s, 3H), 2.87-2.77 (m, 1H), 2.70-2.58 (m, 1H), 2.37 (s, 3H), 1.41 (s, 3H).



3-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s). Yellowish solid. m.p. 87-88 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.11 (d, $J = 7.5\text{Hz}$, 2H), 7.07 (d, $J = 7.5$ Hz, 1H), 6.98 (d, $J = 7.5$ Hz, 1H), 3.53 (s, 3H), 2.89 (dd, $J = 35.5$, 15.5 Hz, 1H), 2.65-2.49 (m, 4H), 1.41(s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.3,

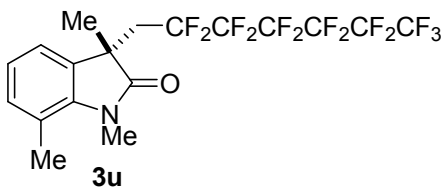
140.6, 132.8, 131.8, 122.5, 125.0-114.0 (m), 121.4, 120.1, 43.5, 36.9 (t, $J=20.5$ Hz), 26.4, 24.8, 19.1; ^{19}F NMR (470 MHz, CDCl_3) δ : -80.3 (t, $J = 8.0$ Hz, 3F), -109.6 (A-B, $J_{F-F} = 270$ Hz, 1F), -115.6 (A-B, $J_{F-F} = 271$ Hz, 1F), -127.2~ -128.6 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{F}_7\text{NO}$ $[\text{M}+\text{H}]^+$: 358.1037, found: 358.1039.

5-Methoxy-1,3-dimethyl-3-



(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t).

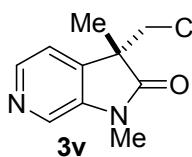
Yellowish solid. m.p. 92-93 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.92-6.75 (m, 3H), 3.78(s, 3H), 3.21(s,3H), 2.86 (dd, $J = 35.2, 14.5$ Hz, 1H), 2.56 (ddd, $J = 29.0, 14.5, 7.5$ Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.3, 136.0, 136.3, 132.7, 125.0-108.0 (m), 121.4, 112.5, 108.7, 55.8, 44.6, 36.9 (t, $J = 20.2$ Hz), 26.5, 25.9; ^{19}F NMR (376 MHz, CDCl_3) δ : -80.8 (t, $J = 8.0$ Hz, 3F), -108.6 (A-B, $J_{F-F} = 268$ Hz, 1F), -114.9 (A-B, $J_{F-F} = 262$ Hz, 1F), -121.7 (br, 2F), -122.9 (br, 2F), -123.7 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$: 524.0890, found: 524.0893.



1,3,7-Trimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3u).

Yellowish solid. m.p. 83-84 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.15-6.90 (m, 3H), 3.51(s, 3H), 2.86 (dd, $J = 35.2, 15.2$ Hz, 1H), 2.6-2.45 (m, 4H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.3, 140.5, 132.1, 131.8, 125.0-107.0 (m), 122.4, 121.3, 120.1, 43.5, 37.2 (t, $J = 20.4$ Hz), 26.3, 25.3, 18.9; ^{19}F NMR (282 MHz, CDCl_3) δ : -80.8 (t, $J = 8.0$ Hz, 3F), -108.6 (A-B, $J_{F-F} = 268$ Hz, 1F), -114.4 (A-B, $J_{F-F} = 262$ Hz, 1F), -121.7 (br, 2F), -122.8 (br, 2F), -123.7 (br, 2F), -125.3~ -126.8 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{F}_{13}\text{NO}$ $[\text{M}+\text{H}]^+$: 508.0941, found: 508.0937.

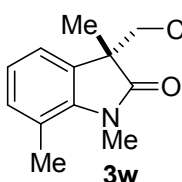
1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-



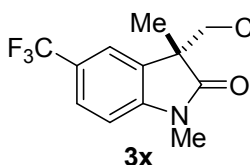
c]pyridin-2(3H)-one (3v). Yellowish oil. ^1H NMR (500 MHz, CDCl_3) δ 8.26 (dd, $J = 5.5, 8.4$ Hz, 1H),

7.55 (d, $J = 7.0$ Hz, 1H), 7.02 (dd, $J = 7.5, 5.0$ Hz, 1H), 3.36 (s, 3H), 2.90 (dd, $J = 35.5, 15.5$ Hz, 1H), 2.63 (ddd, $J = 31.0, 15.5, 8.0$ Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 178.2, 156.2, 147.5, 131.2, 125.7, 125.0-109.0 (m), 118.2.8, 43.9, 36.7 (t, $J = 20.4$ Hz), 25.6, 25.1; ^{19}F NMR (470 MHz, CDCl_3) δ : -80.8 (t, $J = 8.0$ Hz, 3F), -108.3 (A-B, $J_{F-F} = 272$ Hz, 1F), -114.0 (A-B, $J_{F-F} = 270$ Hz, 1F), -121.7 (br, 2F), -122.9 (br, 2F), -123.7 (br, 2F), -125.4~ -126.9 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{F}_{13}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 495.0737, found: 495.0734.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1,3,7-trimethylindolin-2-



one (3w). Yellowish solid. m.p. 101-102 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.15-6.93 (m, 3H), 3.53 (s, 3H), 2.90 (dd, $J = 35.5, 15.5$ Hz, 1H), 2.68-2.50 (m, 4H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.3, 140.6, 132.2, 131.8, 125.0-108.0 (m), 122.4, 121.4, 120.3, 120.1, 120.0-108.0 (m), 43.5, 37.2 (t, $J = 20.2$ Hz), 29.8, 26.4, 19.0; ^{19}F NMR (470 MHz, CDCl_3) δ : -80.9 (t, $J = 8.0$ Hz, 3F), -108.9 (A-B, $J_{F-F} = 269$ Hz, 1F), -114.0 (A-B, $J_{F-F} = 270$ Hz, 1F), -121.8 (br, 2F), -122.1 (br, 4F), -122.9 (br, 2F), -123.8 (br, 2F), -126.1~ -126.8 (m, 2F); HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{F}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$: 608.0877, found: 608.0879.



3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Trifluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x). Yellowish solid. m.p. 121-123 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.63 (dd, $J = 8.0, 6.0$ Hz, 1H), 7.54 (s, 1H), 6.99 (d, $J = 8.5$ Hz), 3.30 (s, 3H), 2.96 (dd, $J = 35.5, 15.5$ Hz, 1H), 2.68 (ddd, $J = 30.5, 15.5, 8.0$ Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 178.4, 145.7, 131.7, 126.3 (q, $J = 4.0$ Hz), 125.1 (q, $J = 32.5$ Hz), 125.0-108.0 (m), 121.4, 120.7, 44.1, 37.1 (t, $J = 20.4$ Hz), 26.6, 25.8; ^{19}F NMR (470 MHz, CDCl_3) δ : -62.0 (s, 3F), -80.7 (t, $J = 8.0$ Hz, 3F), -108.4 (A-B, $J_{F-F} = 270$ Hz, 1F), -114.0 (A-B, $J_{F-F} = 272$ Hz, 1F), -121.6 (br, 2F), 121.6-122.2 (m, 8F),

-122.8 (br, 4F), -123.9 (br, 2F), -126.1~ -126.8 (m, 2F); HRMS m/z (ESI) calcd for $C_{22}H_{12}F_{24}NO$ $[M+H]^+$: 762.0631, found: 762.0628.

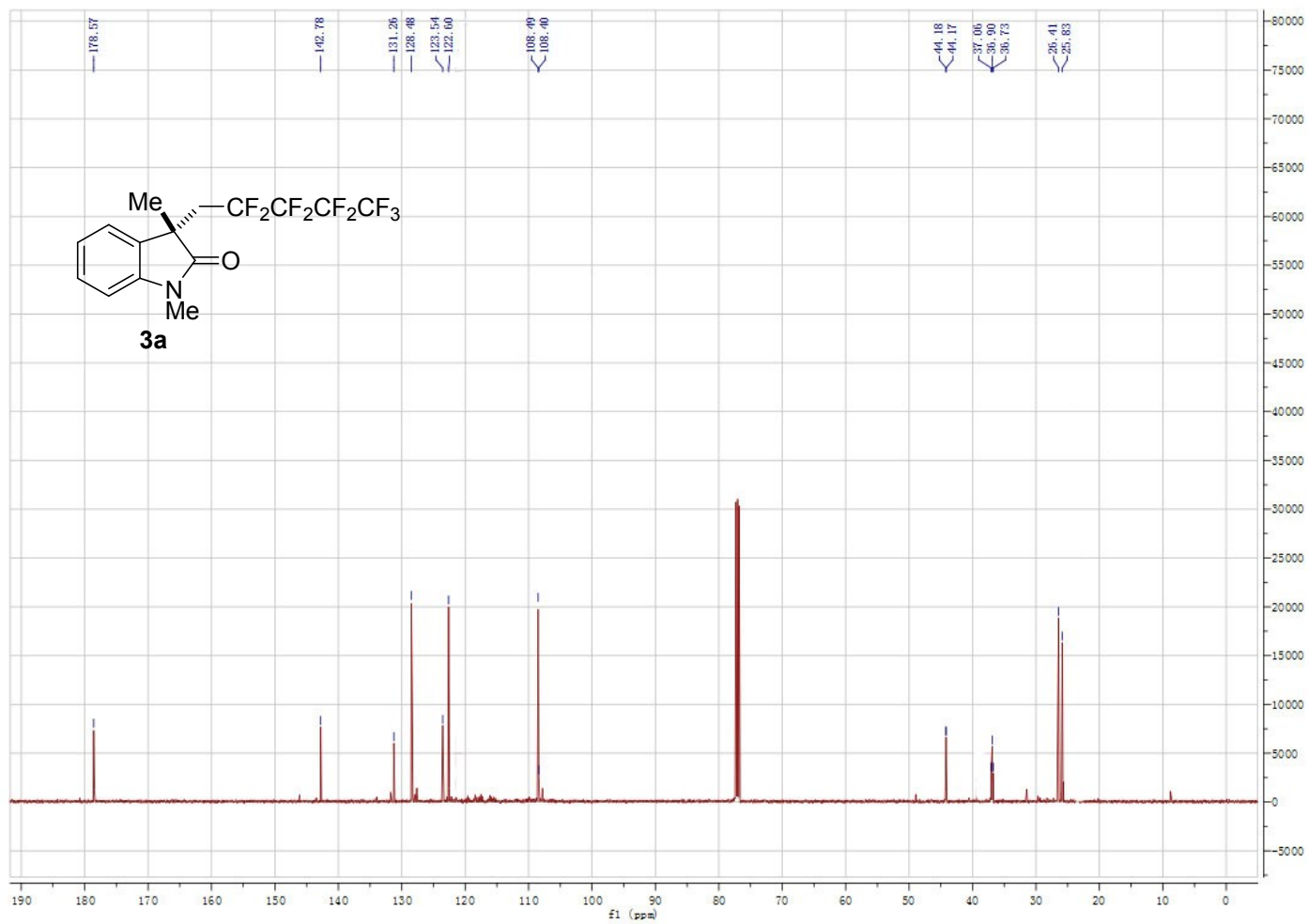
1. (a) Tang, X.-J., Thomason, C. S. and Dolbier Jr., W. R. *Org. Lett.* **2014**, *16*, 4594. (b)
(b) Mu, X.; Wu, T.; Wang, H.; Guo, Y.; Liu, G. *J. Am. Chem. Soc.*, **2012**, *134*, 878.

1 Copies of 1H NMR and ^{13}C NMR spectra

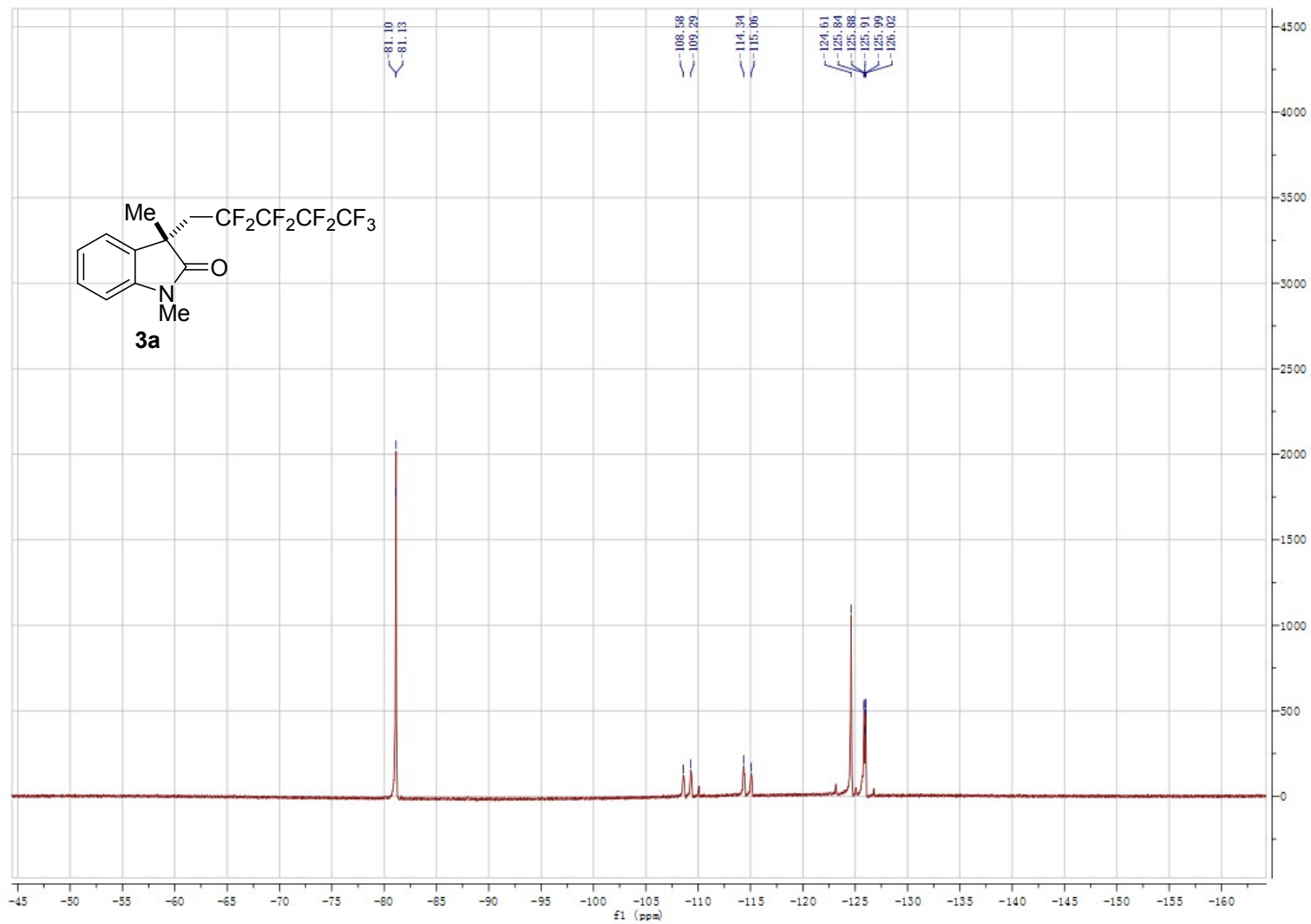
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)



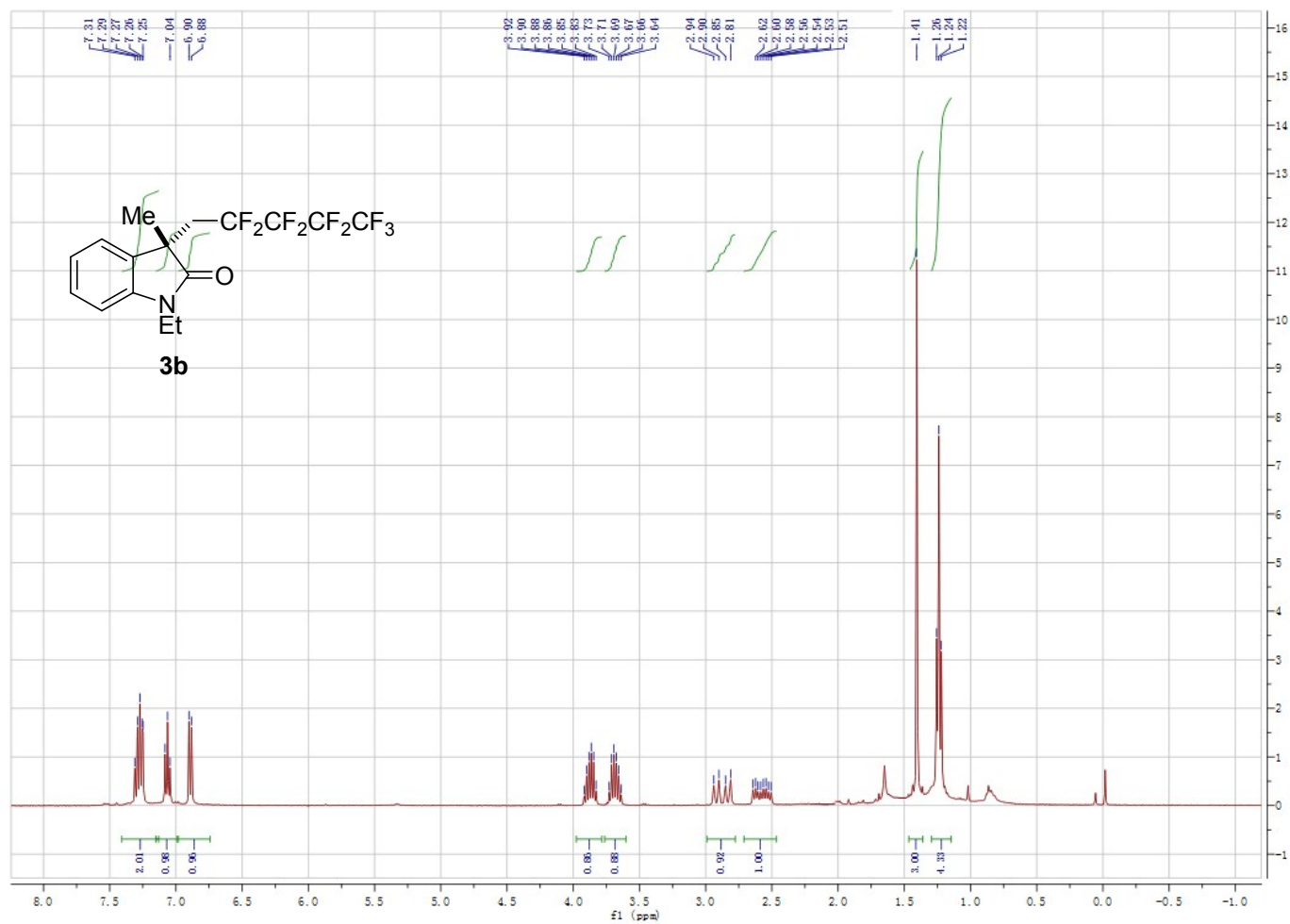
3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)



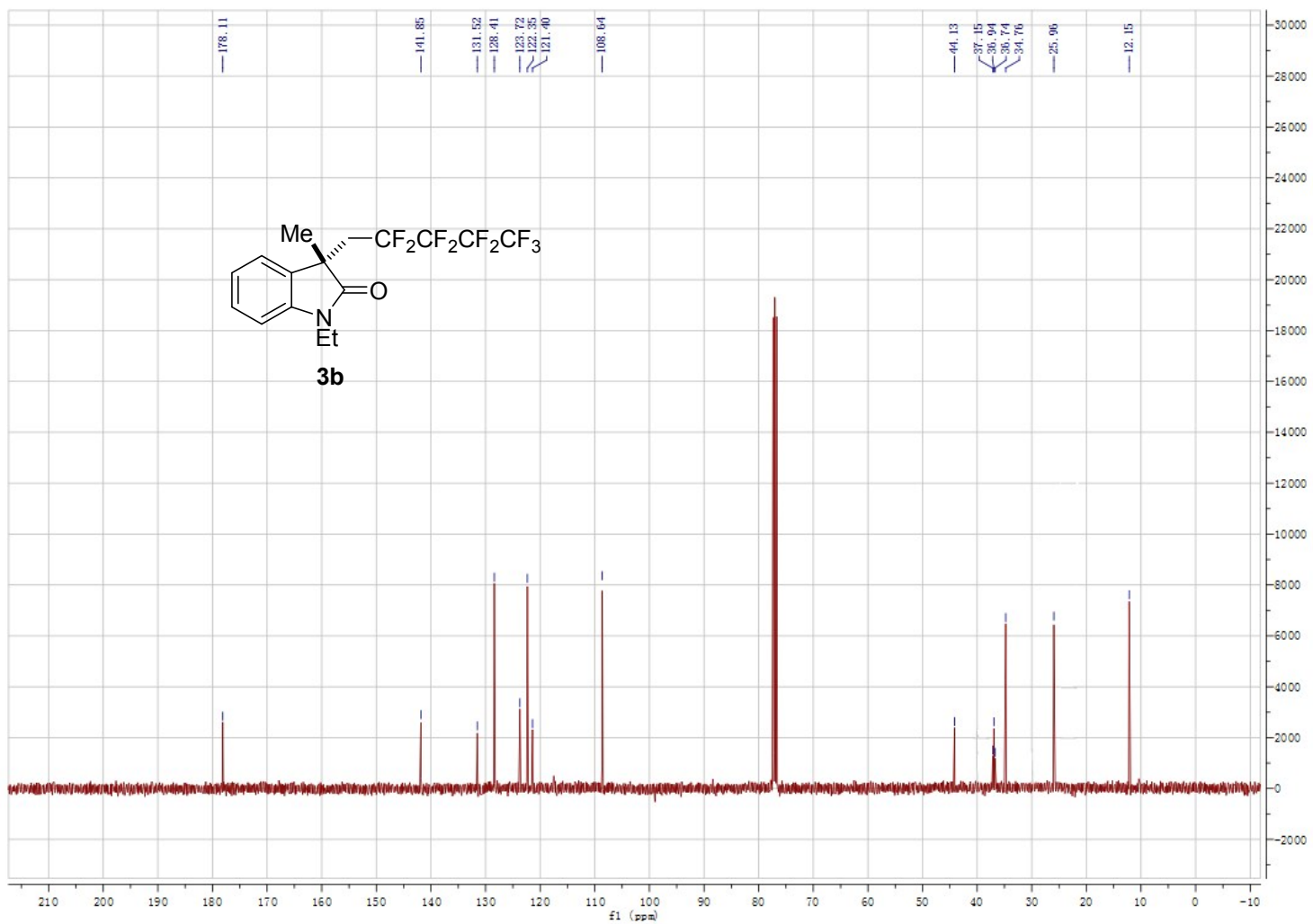
3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)



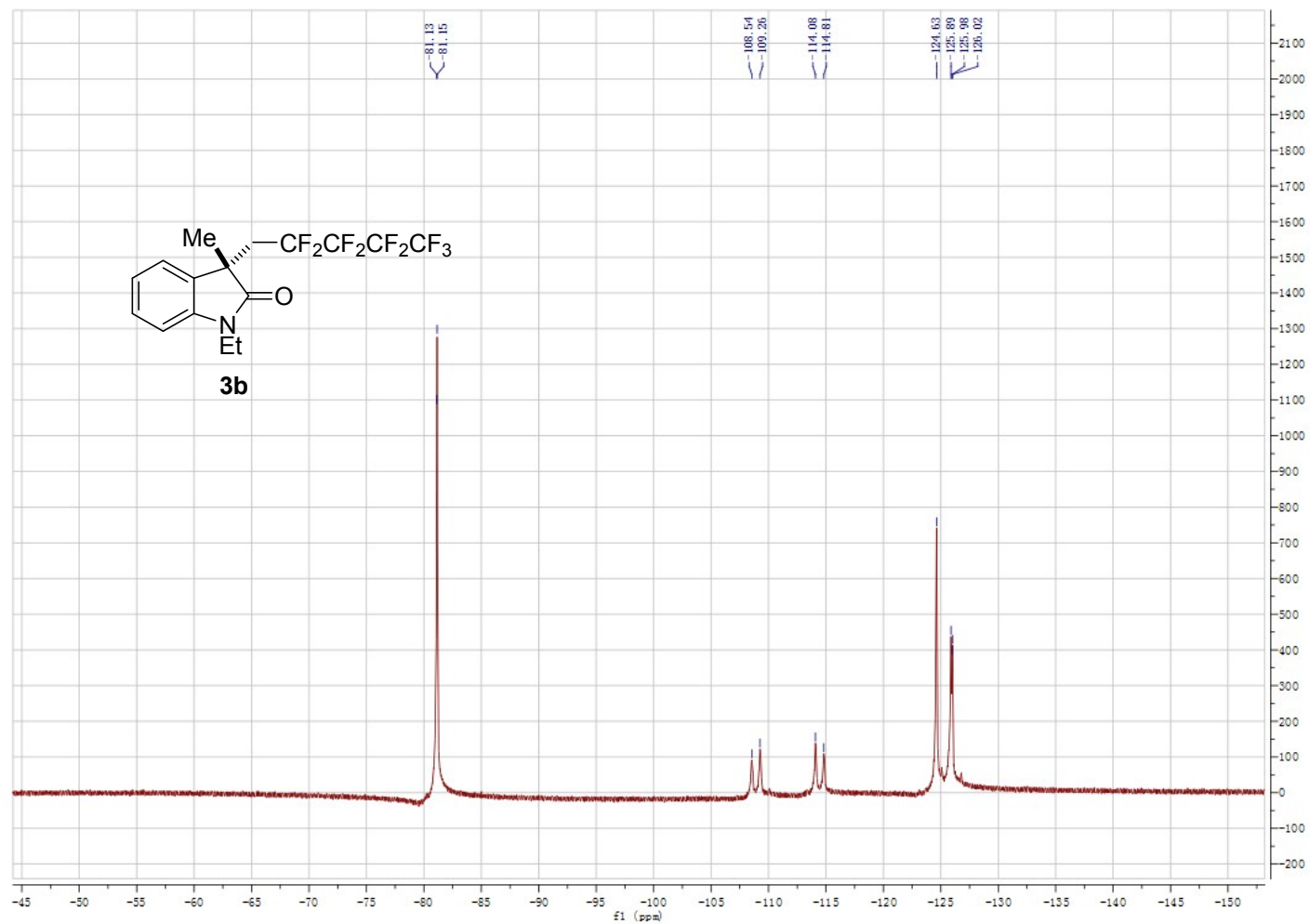
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)



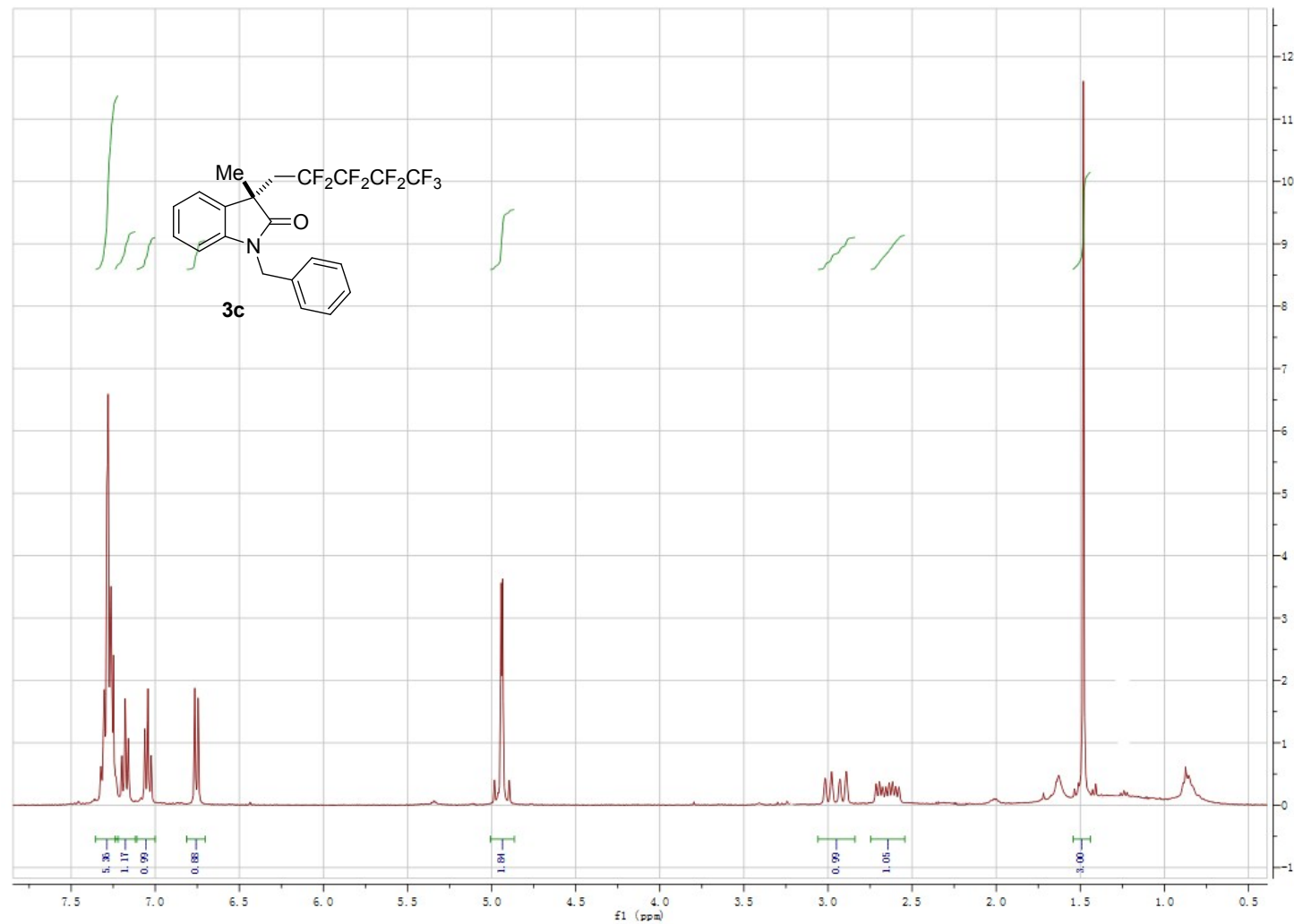
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)



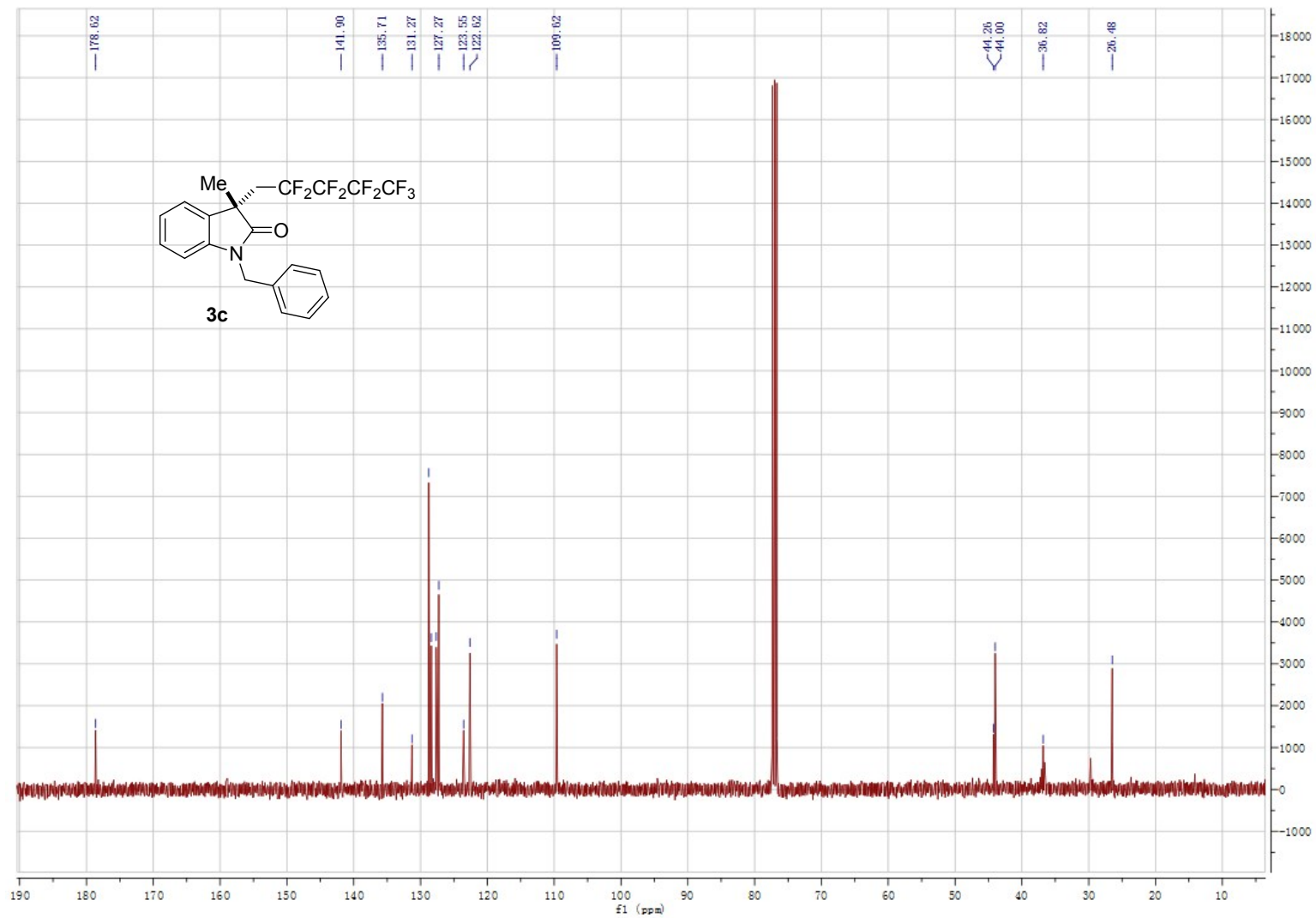
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)



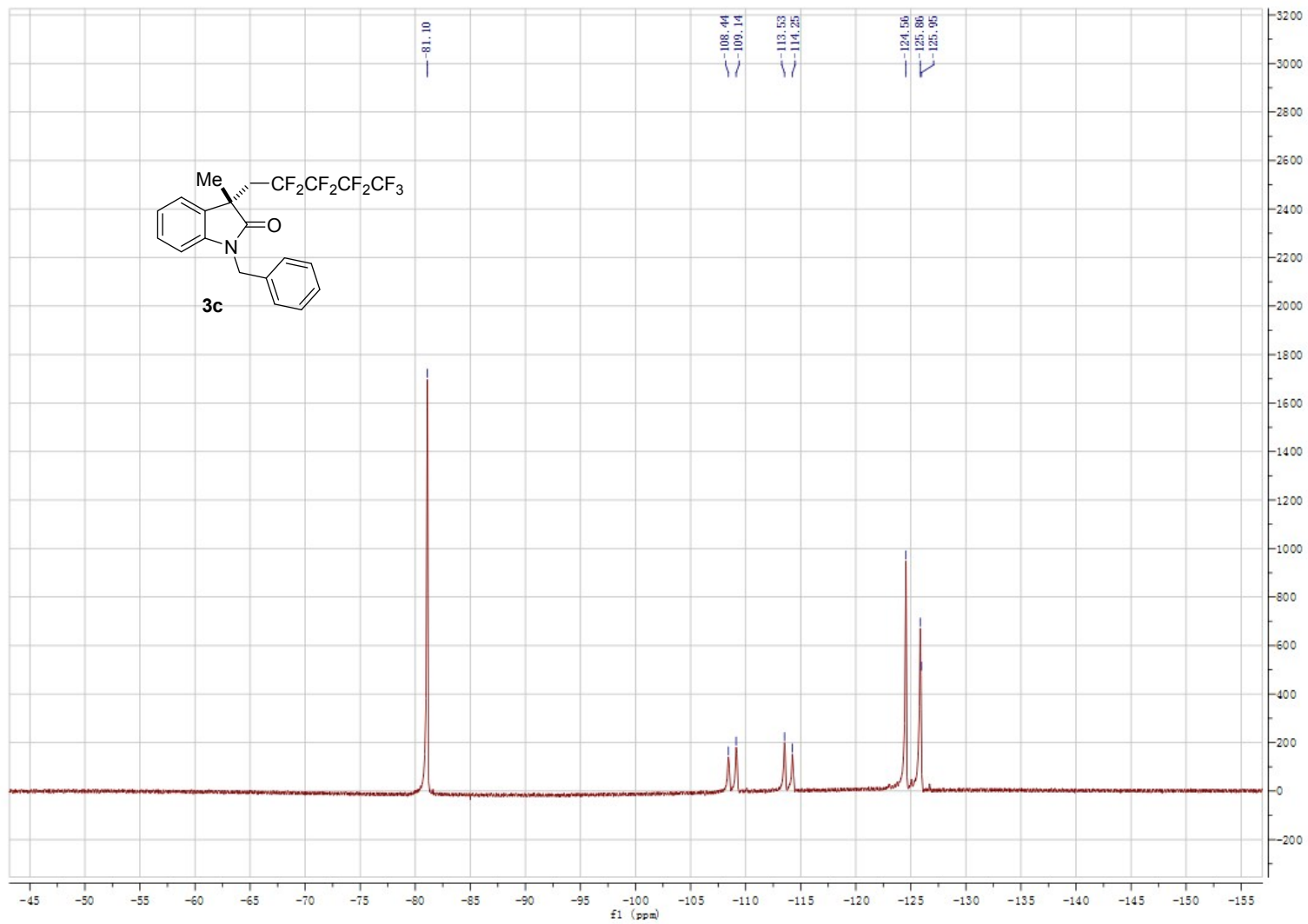
3-(1-Benzyl-3-methyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3c)



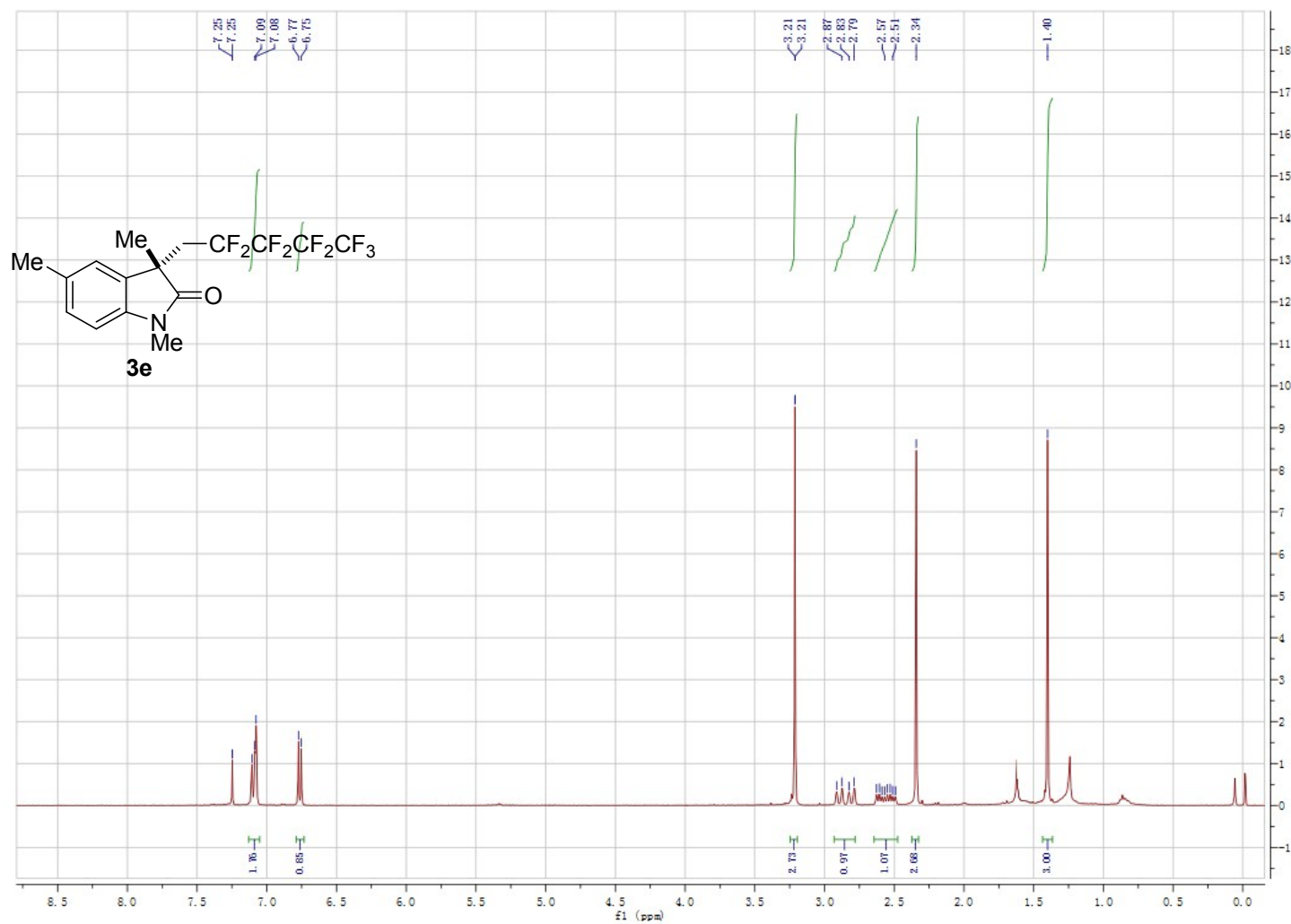
3-(1-Benzyl-3-methyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile(3c)



3-(1-Benzyl-3-methyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile(3c)

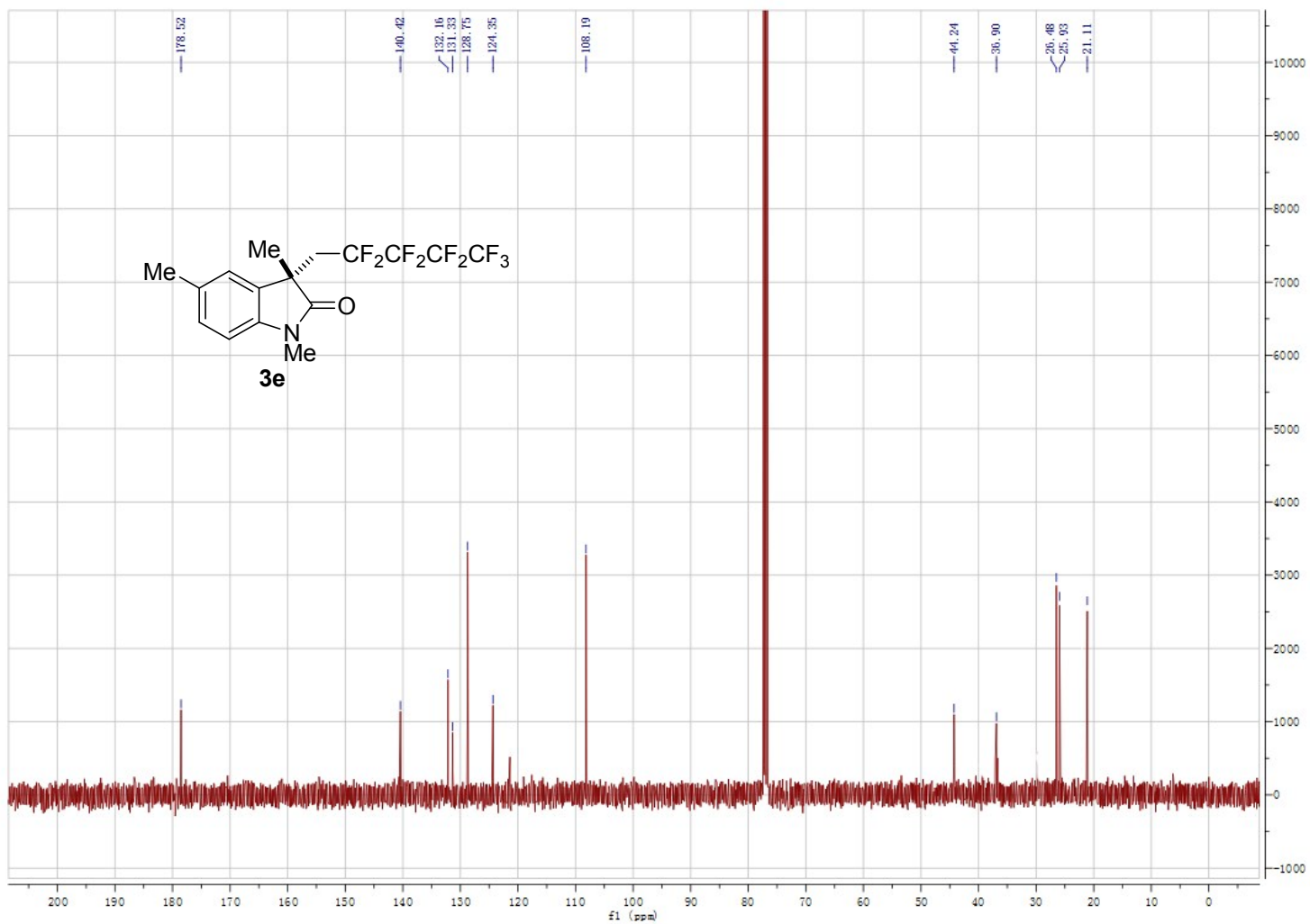


1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)

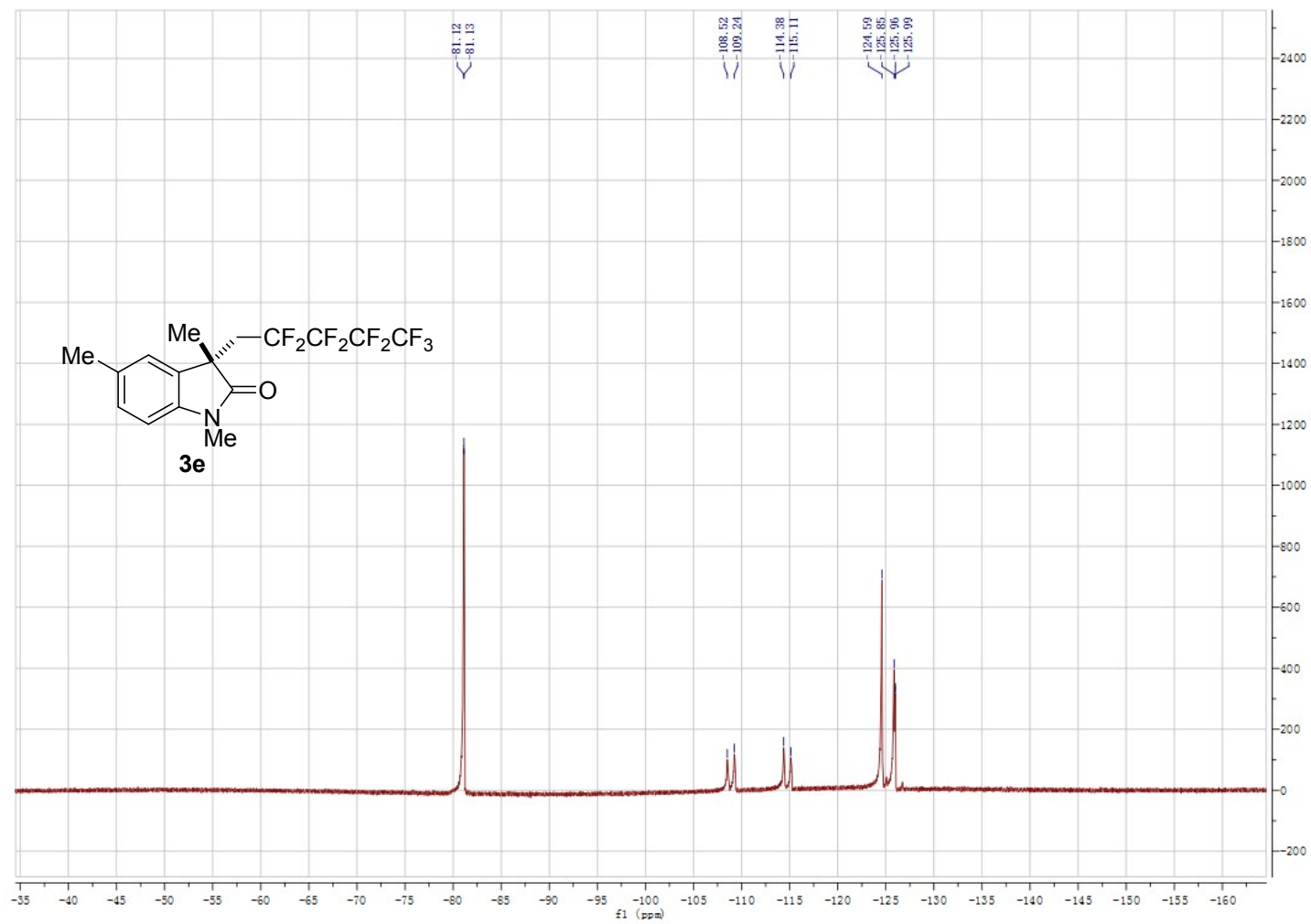


1,3,5-

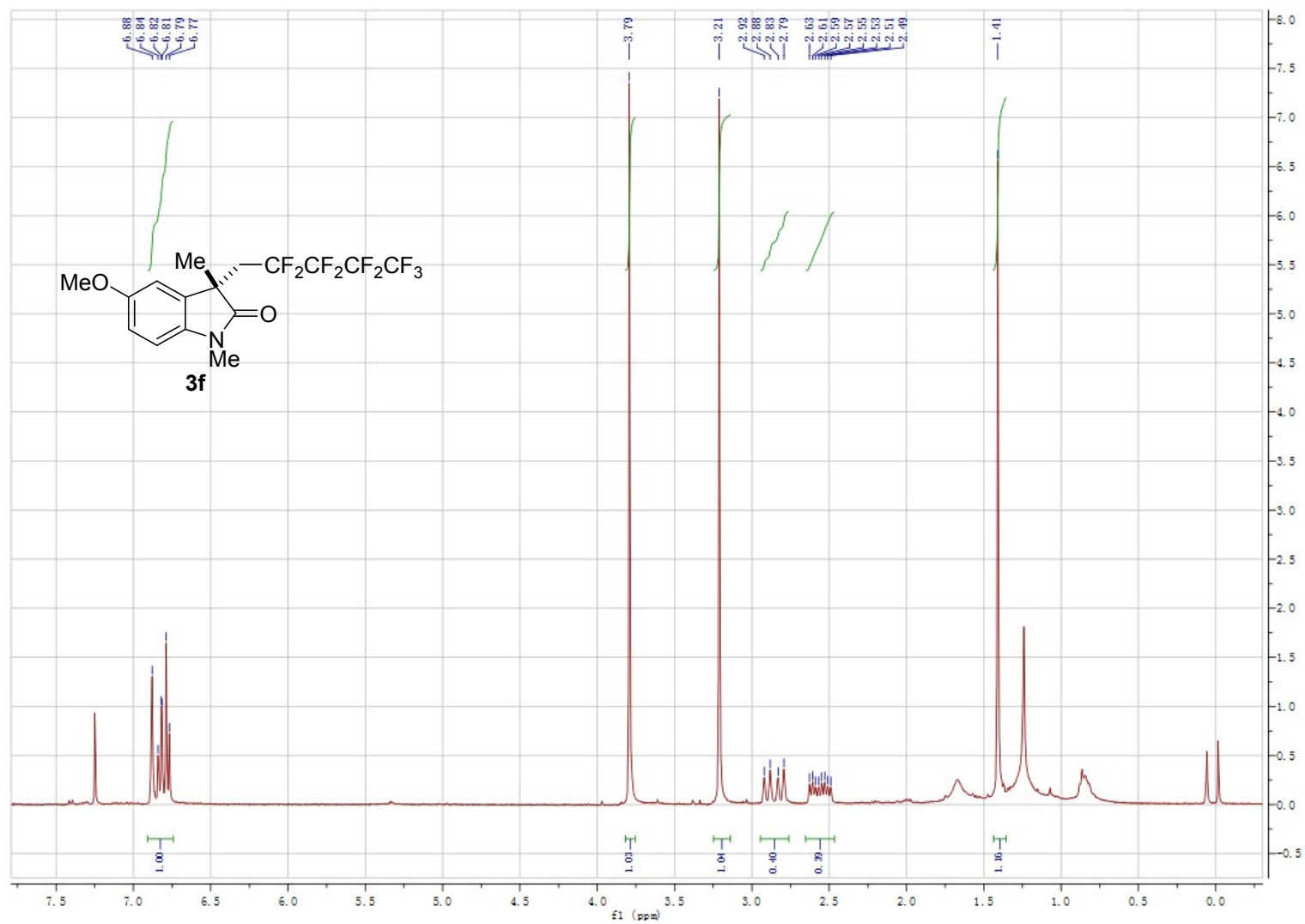
trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)



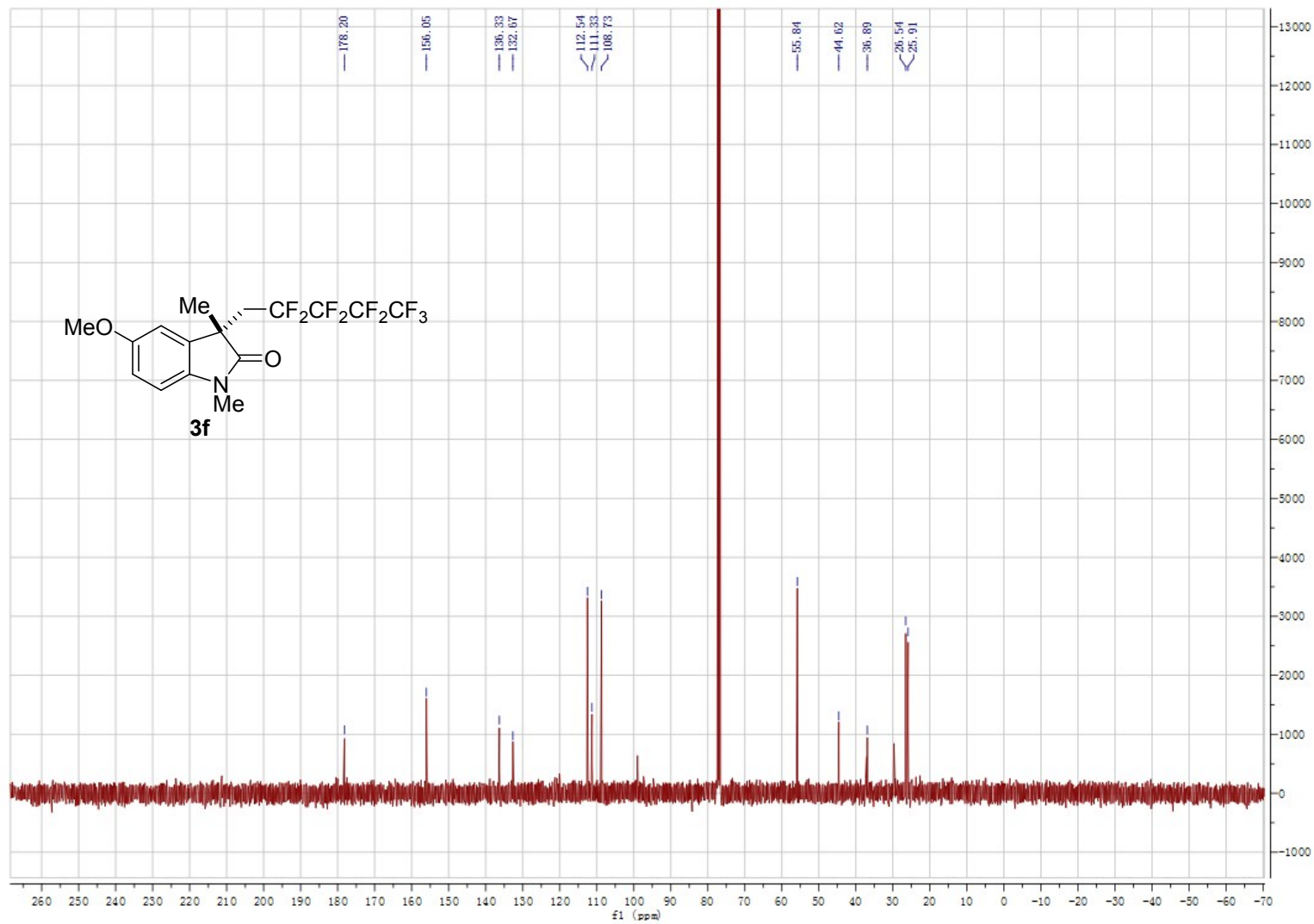
1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)



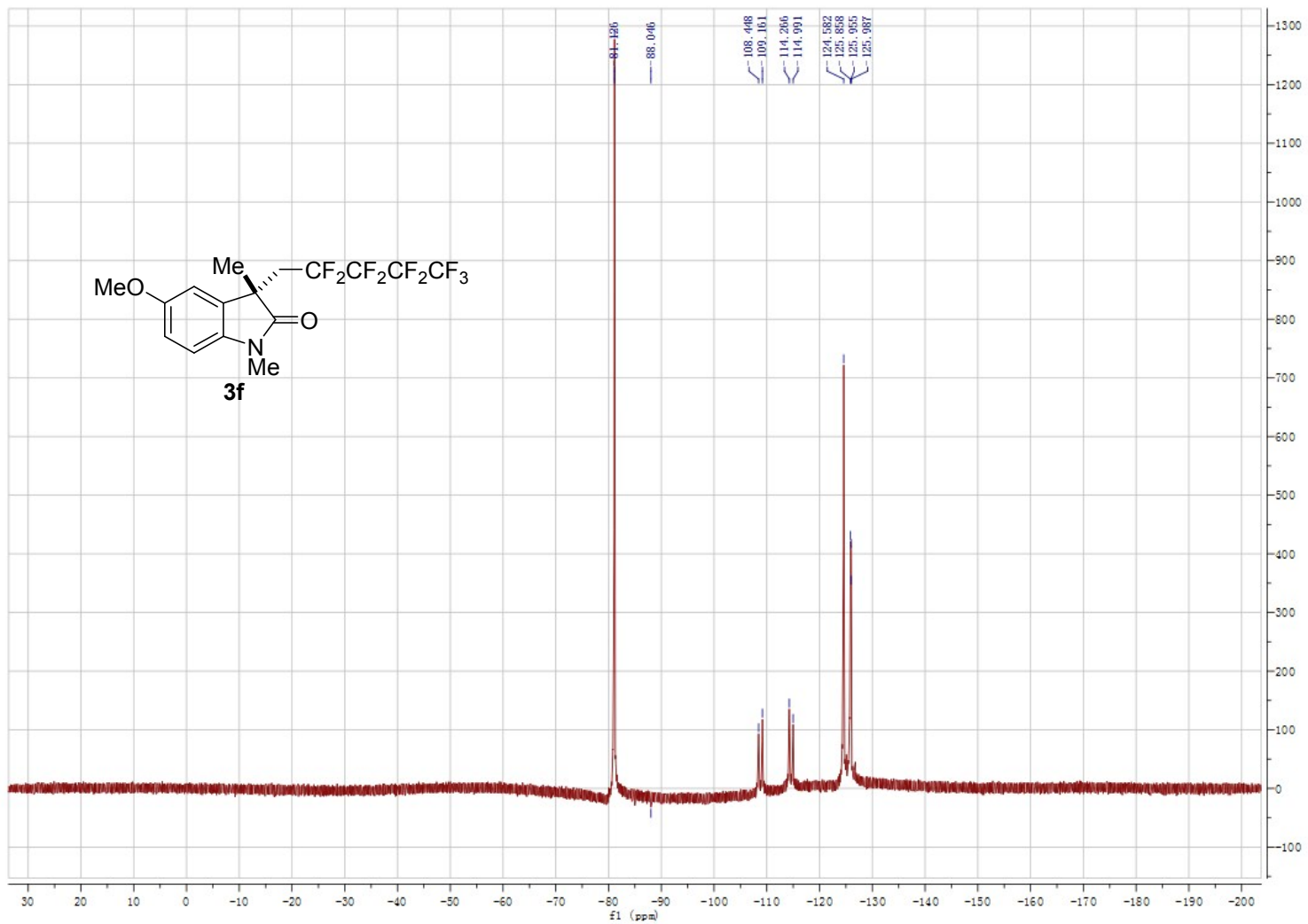
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).



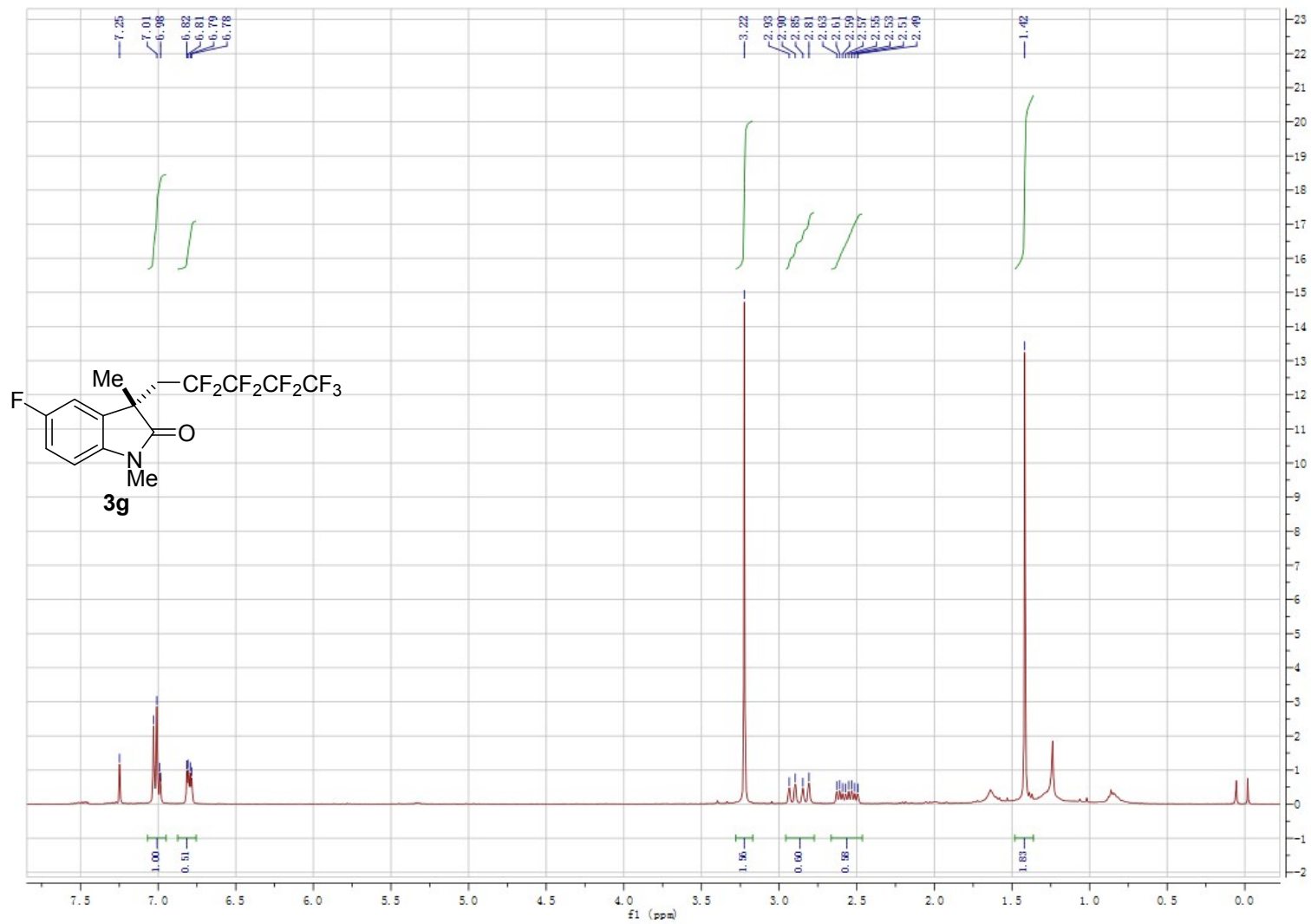
methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).



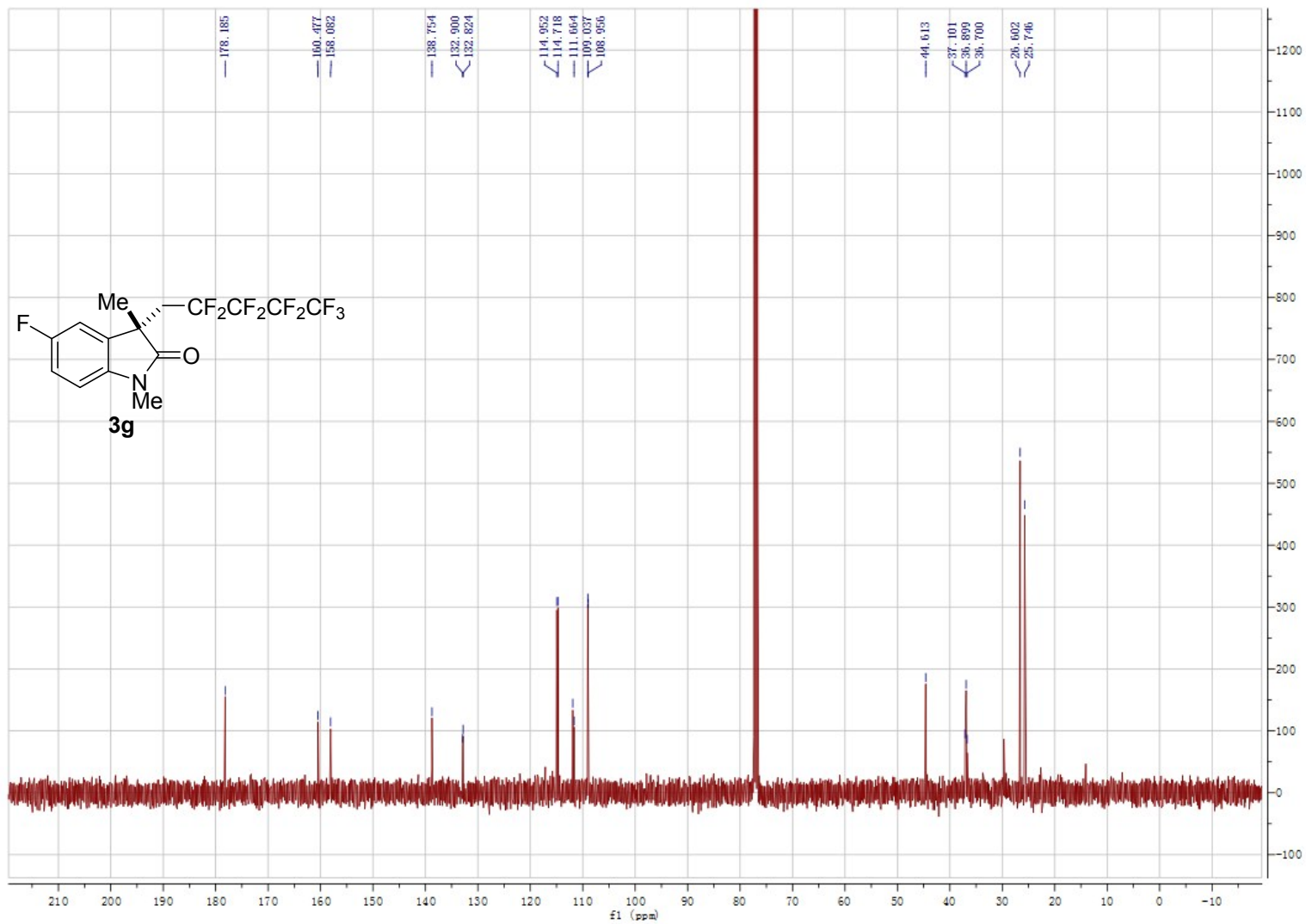
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).



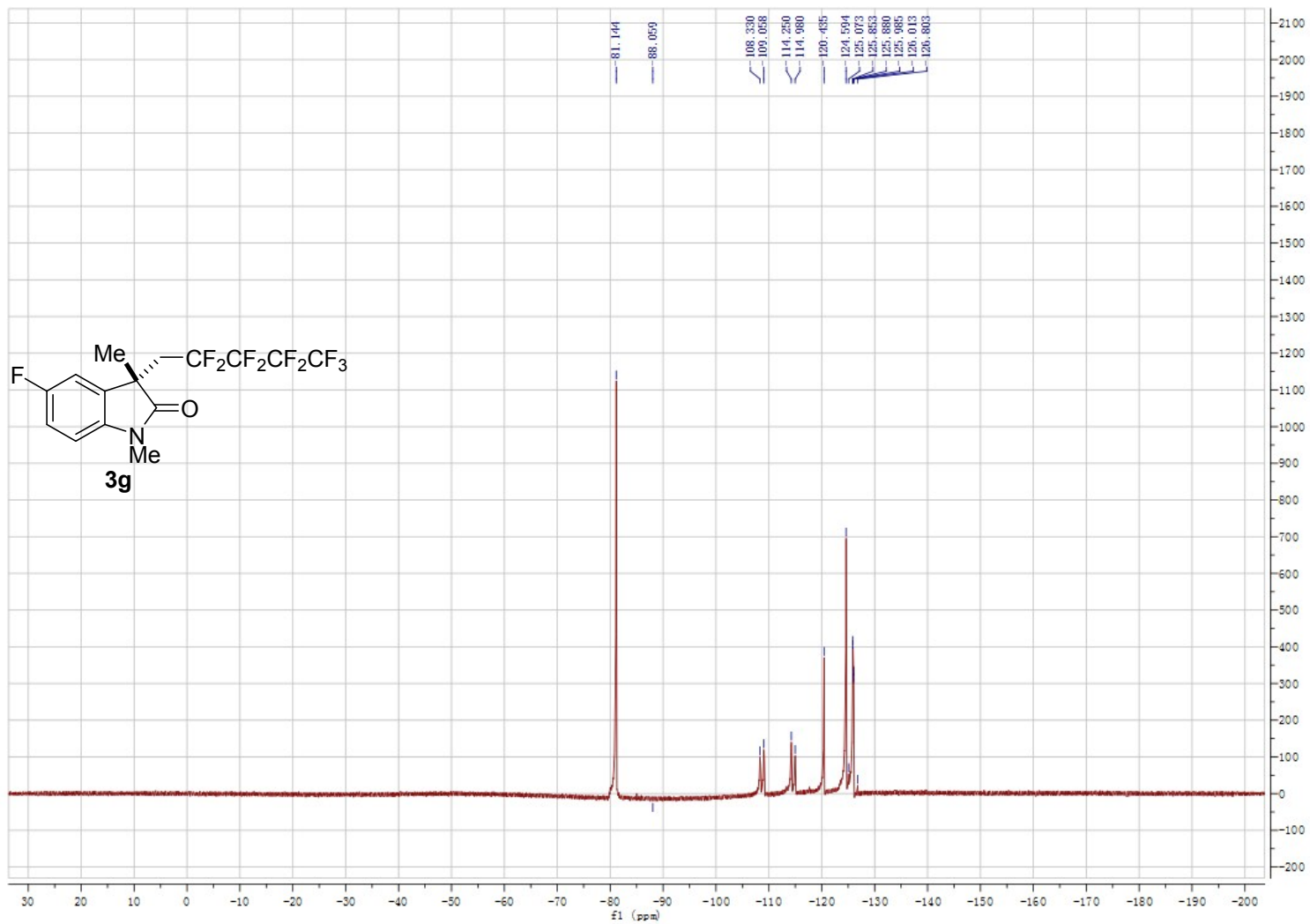
5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)



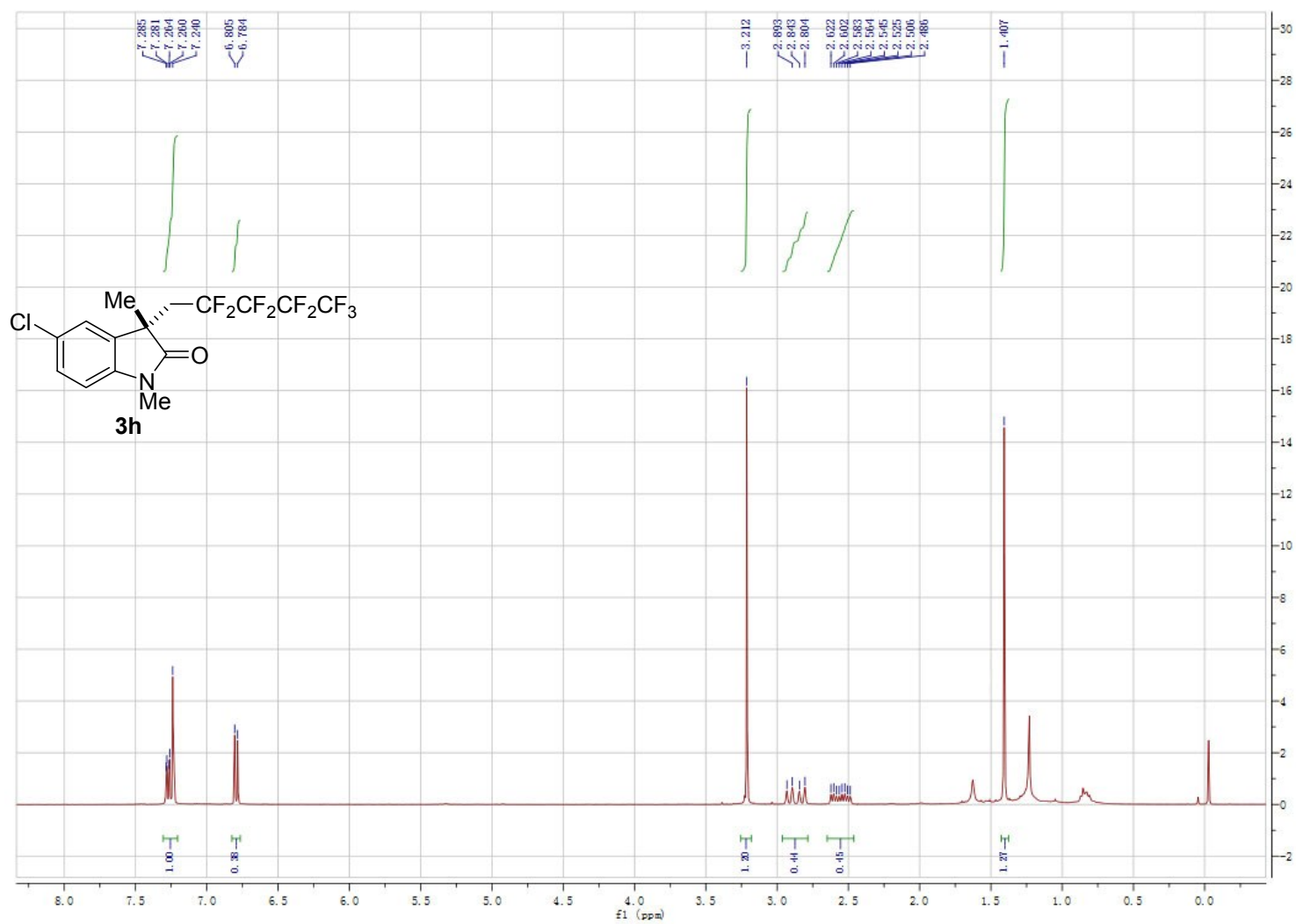
5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)



5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)



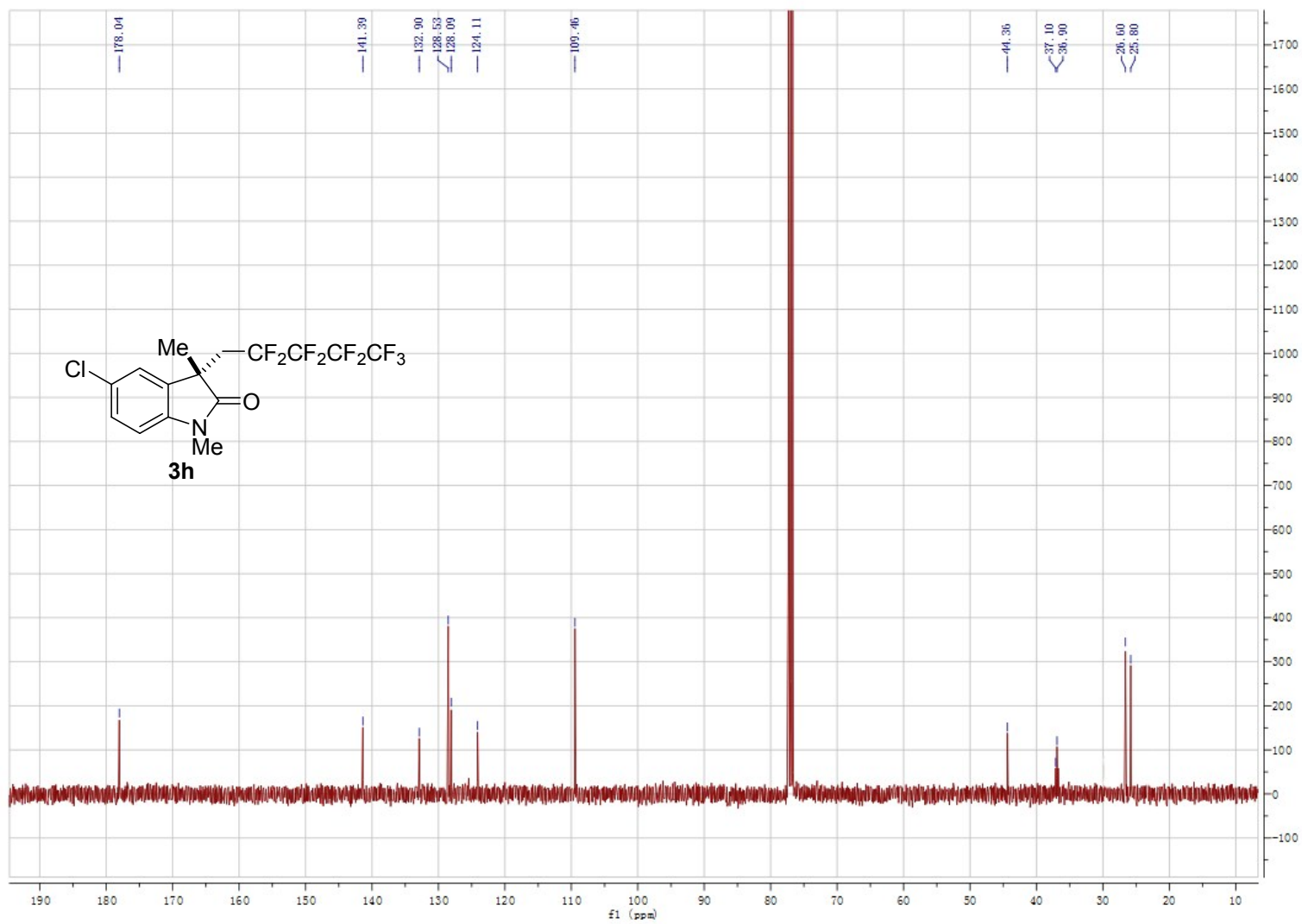
chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)



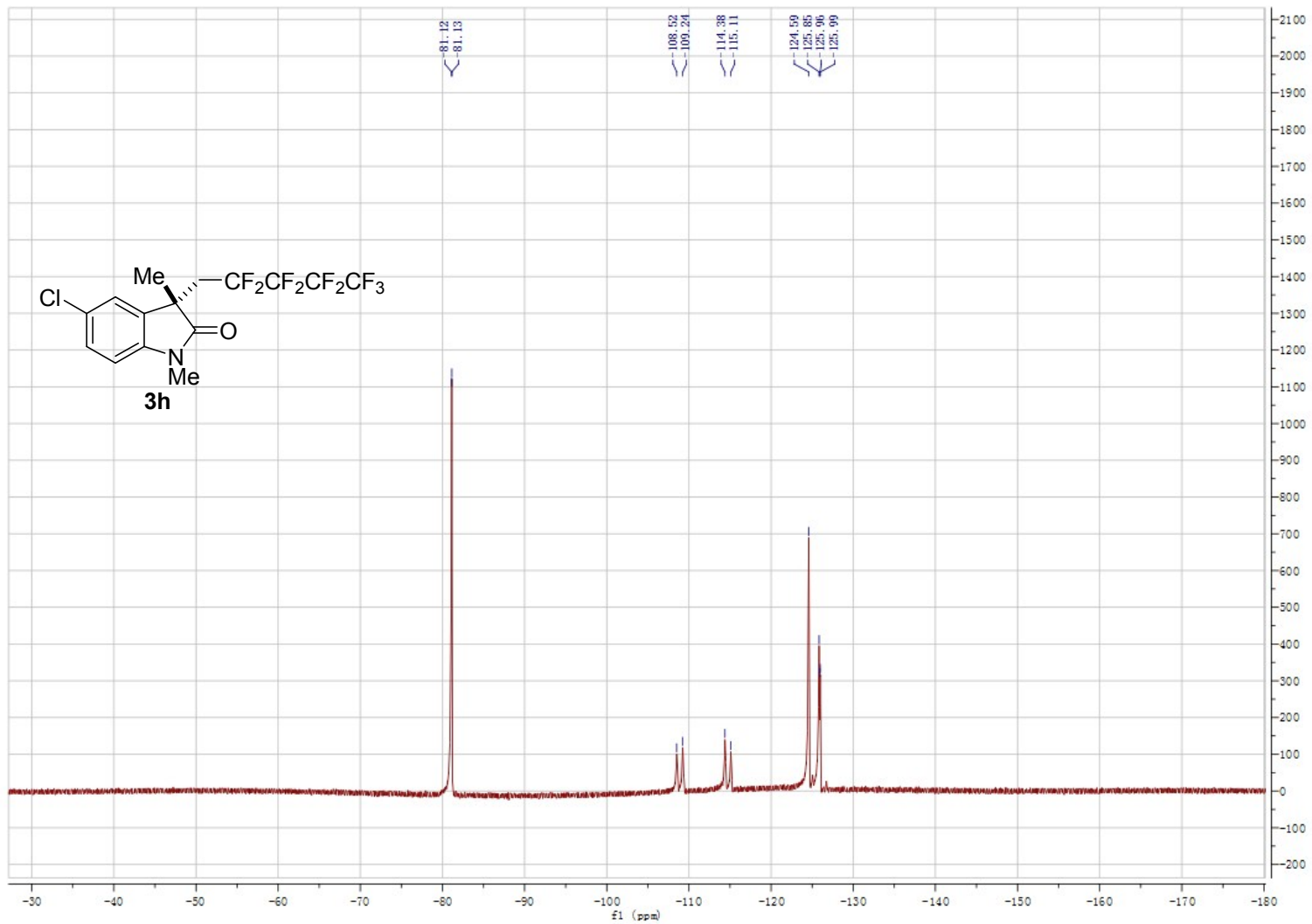
chloro-

1,3-

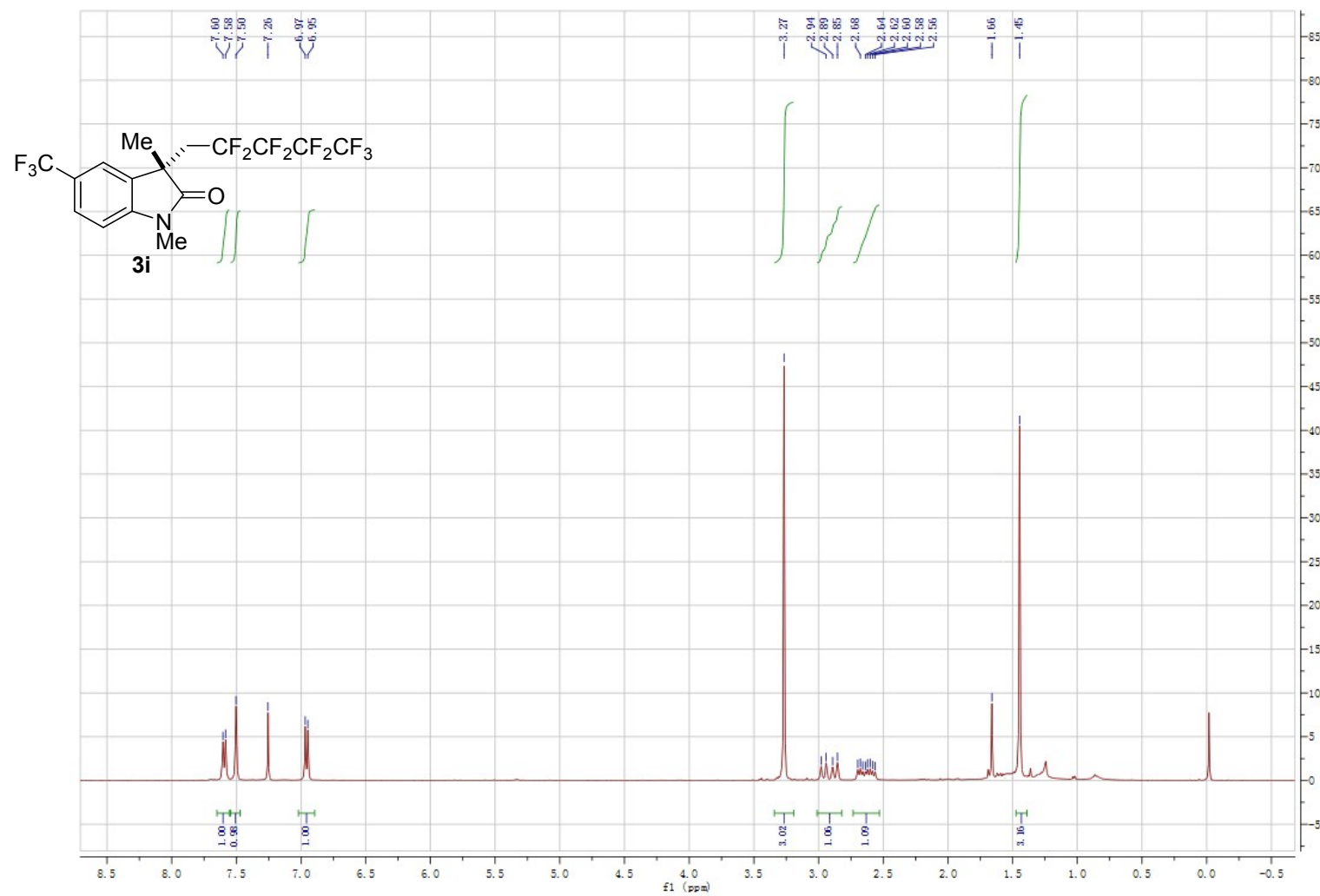
dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)



chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)

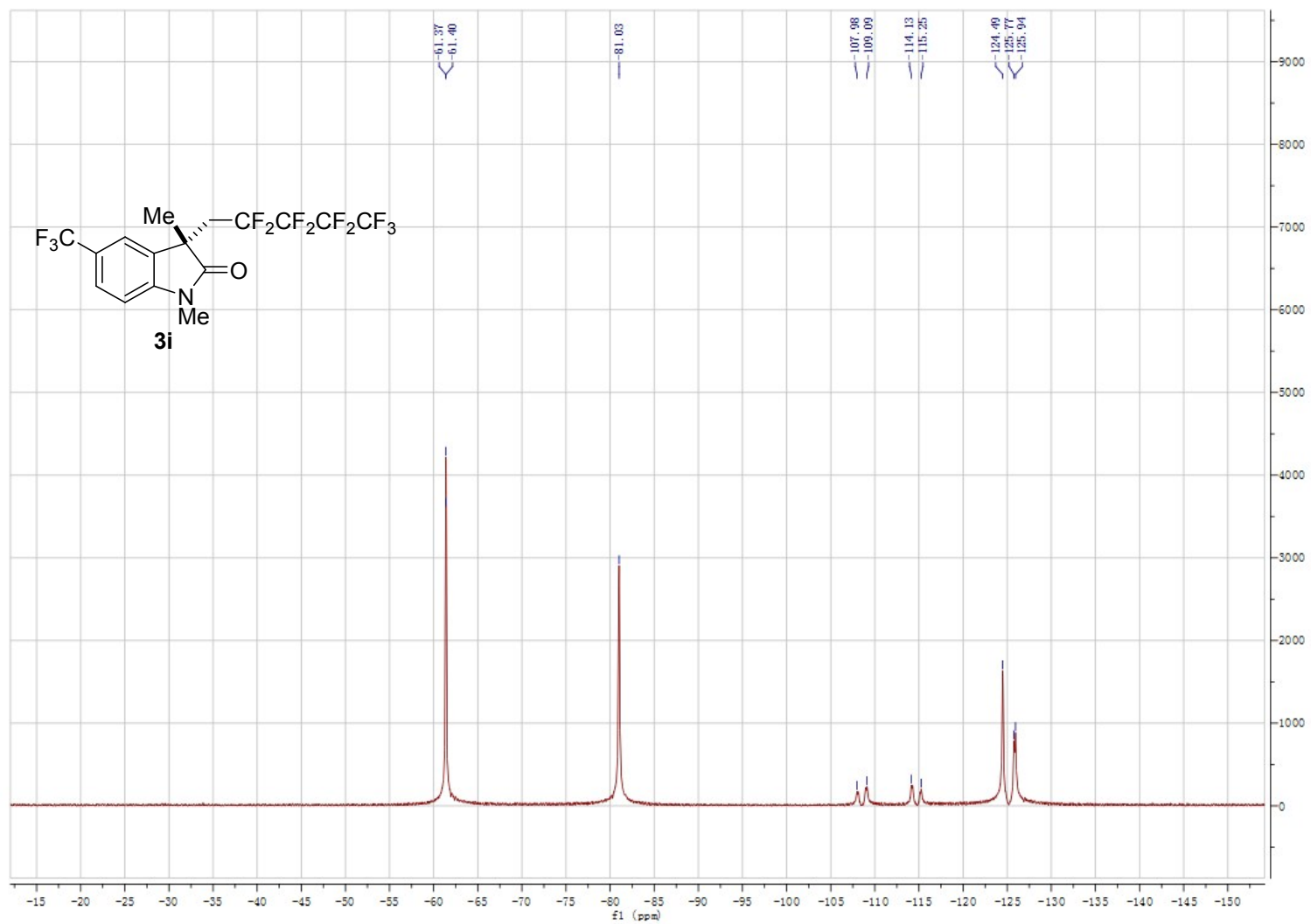


1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (3i)

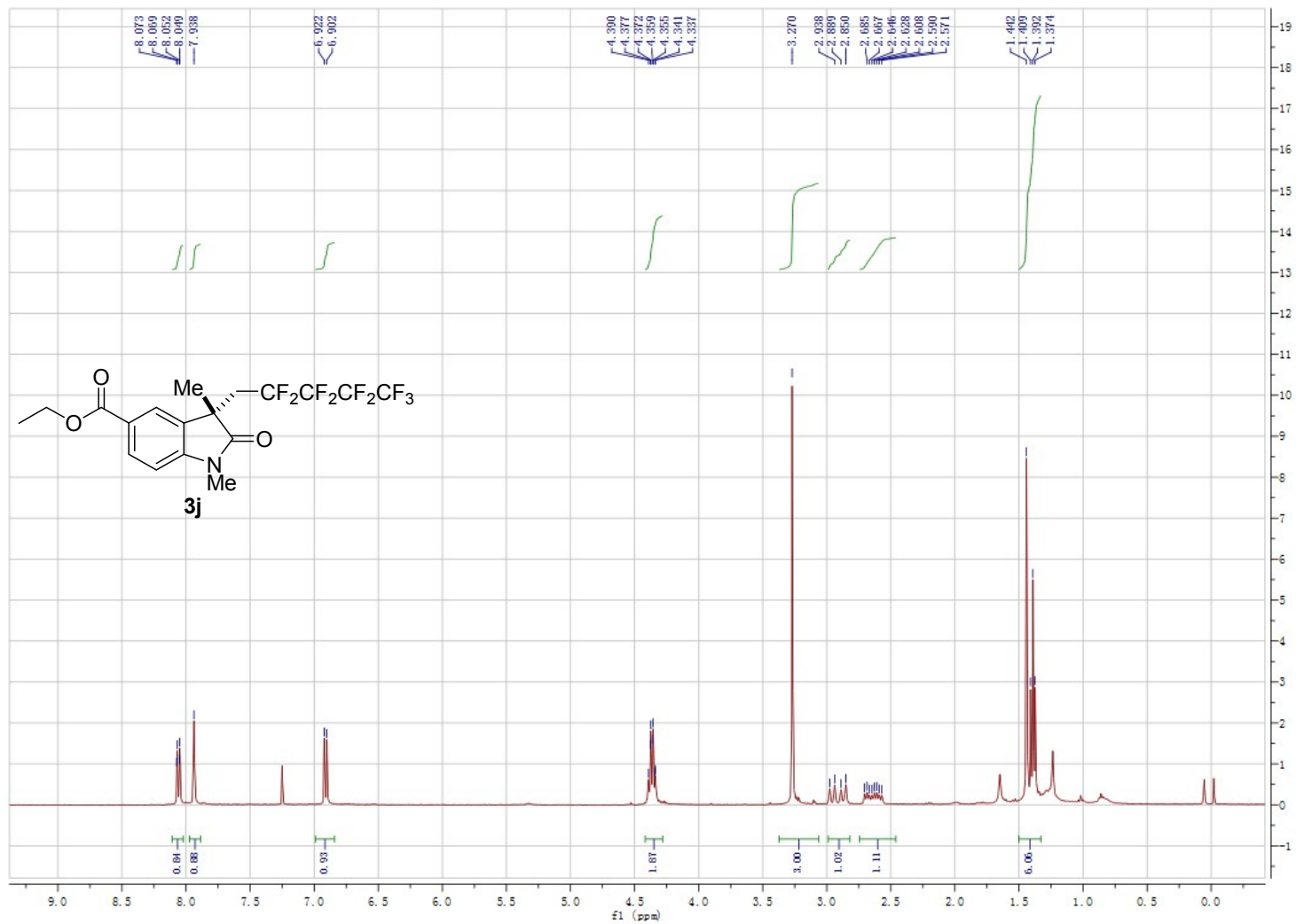


1,3-

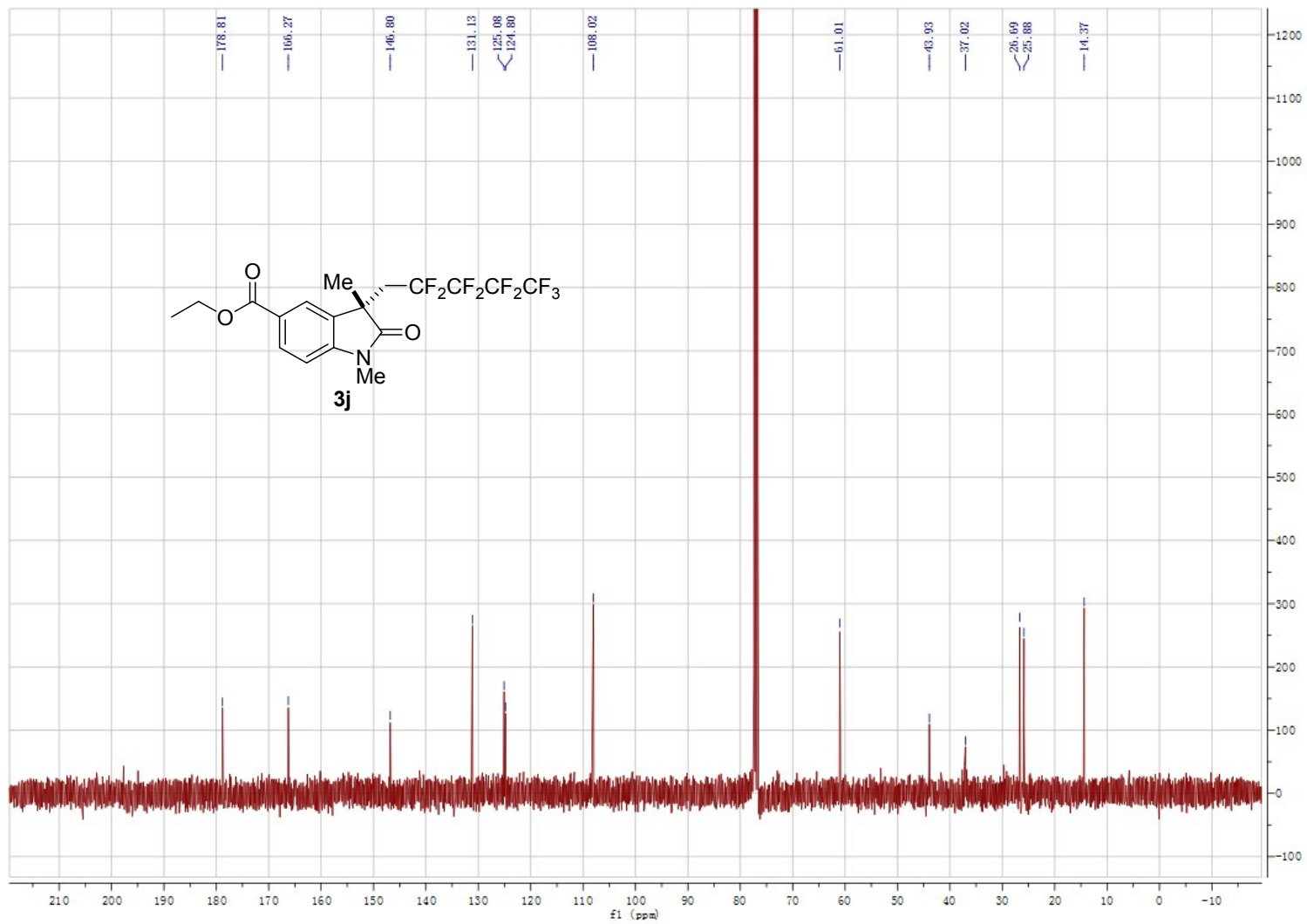
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (3i)



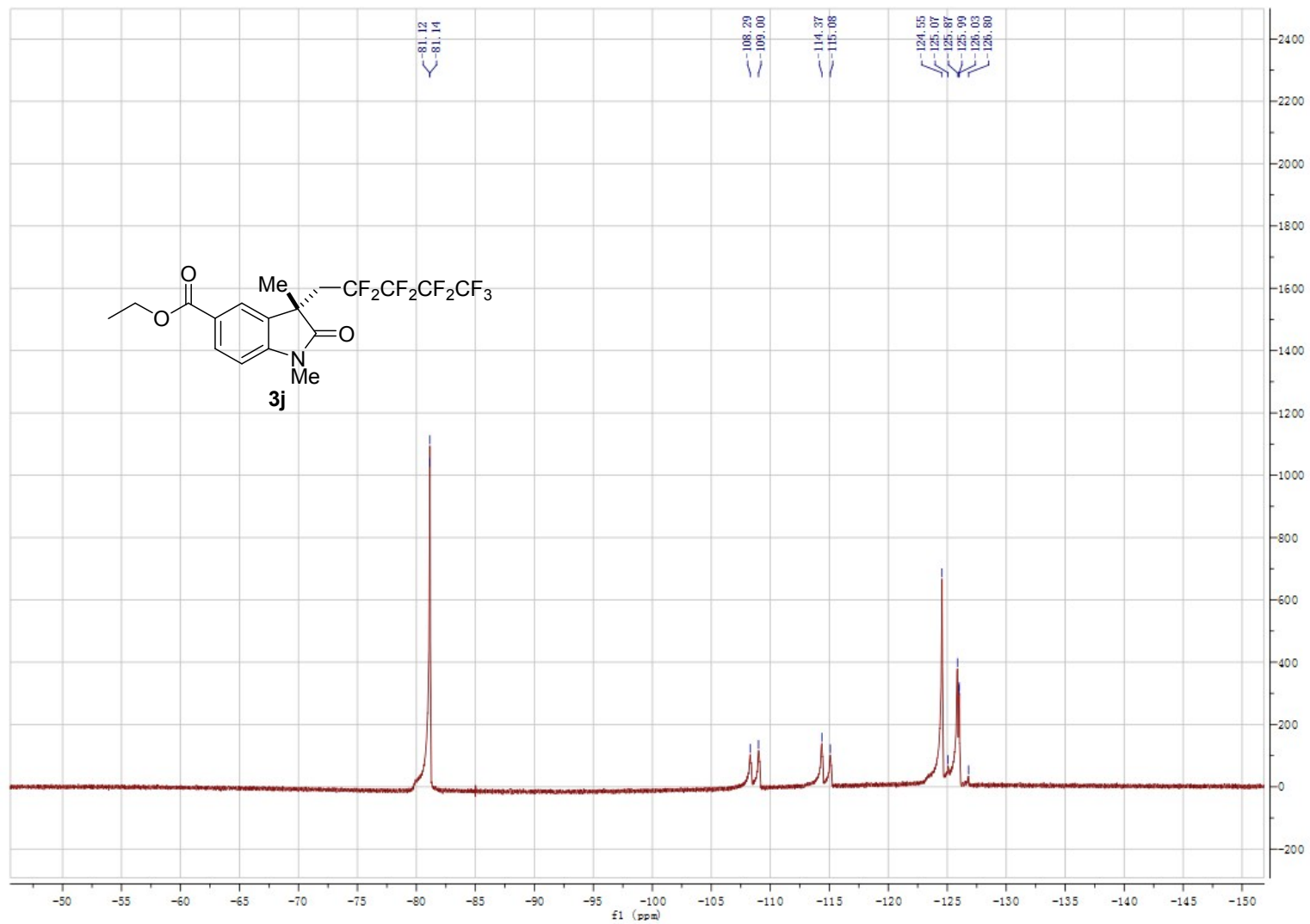
Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindoline-5-carboxylate (3j)



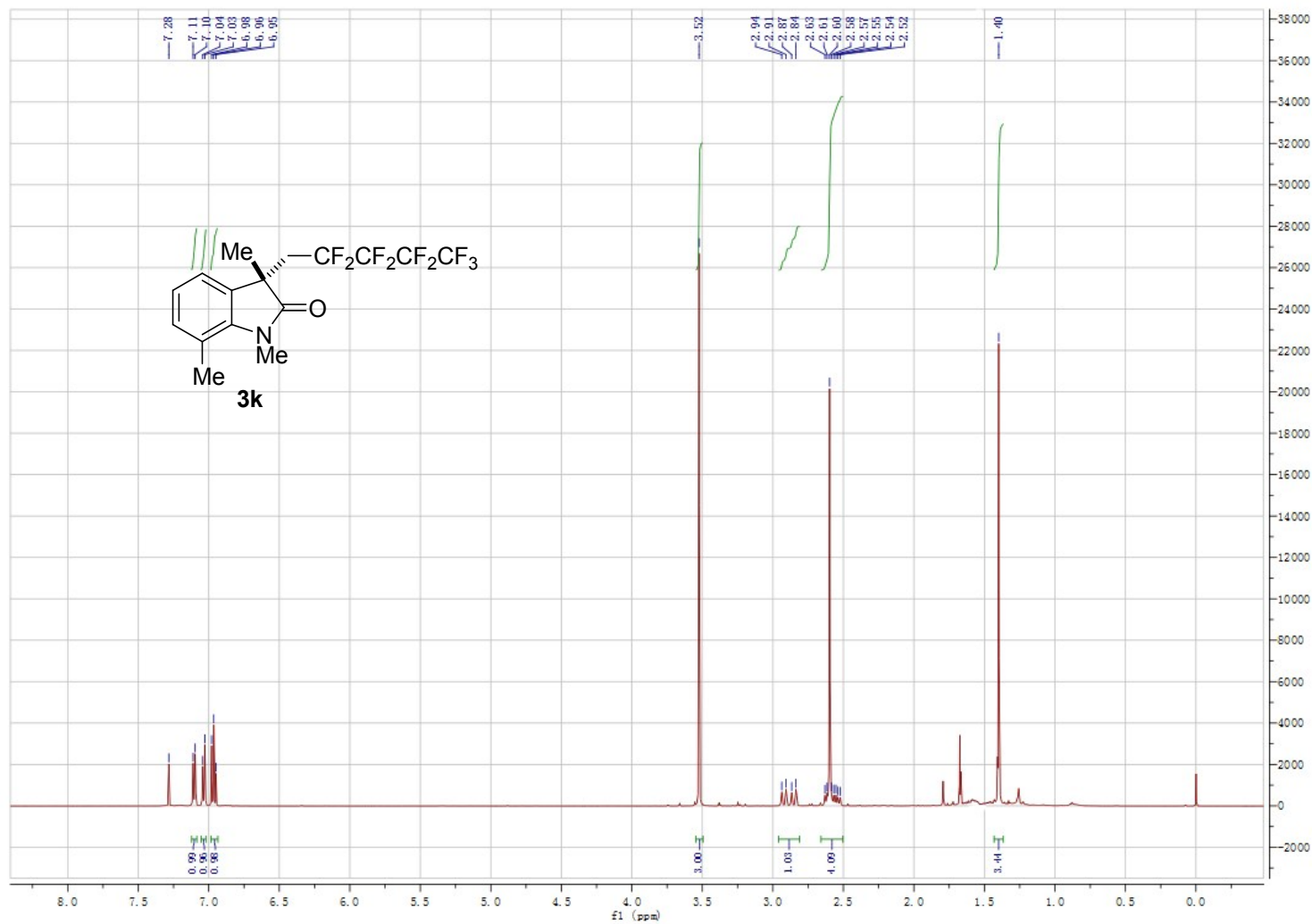
Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindoline-5-carboxylate (**3j**)



Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindoline-5-carboxylate (3j)

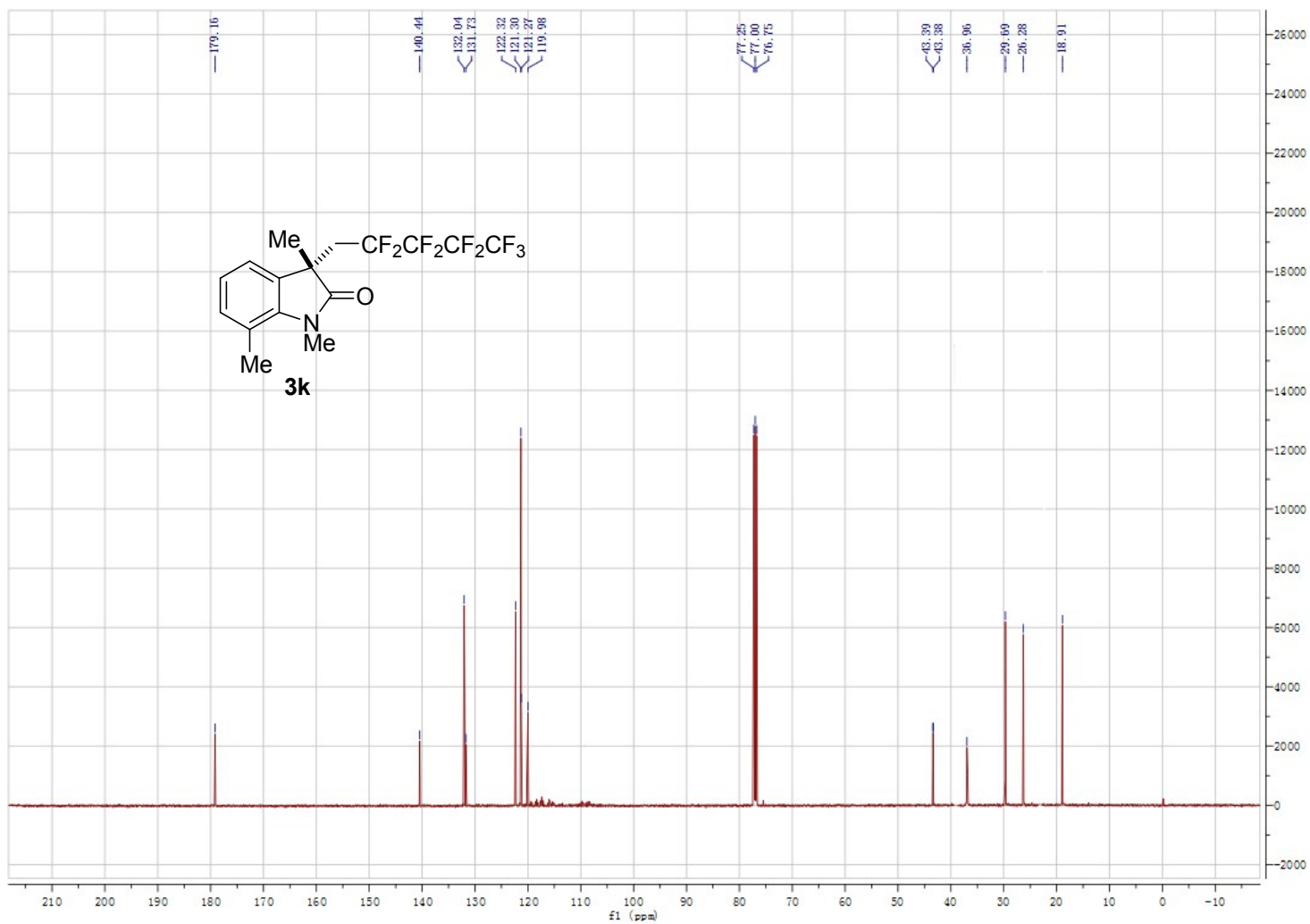


Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).

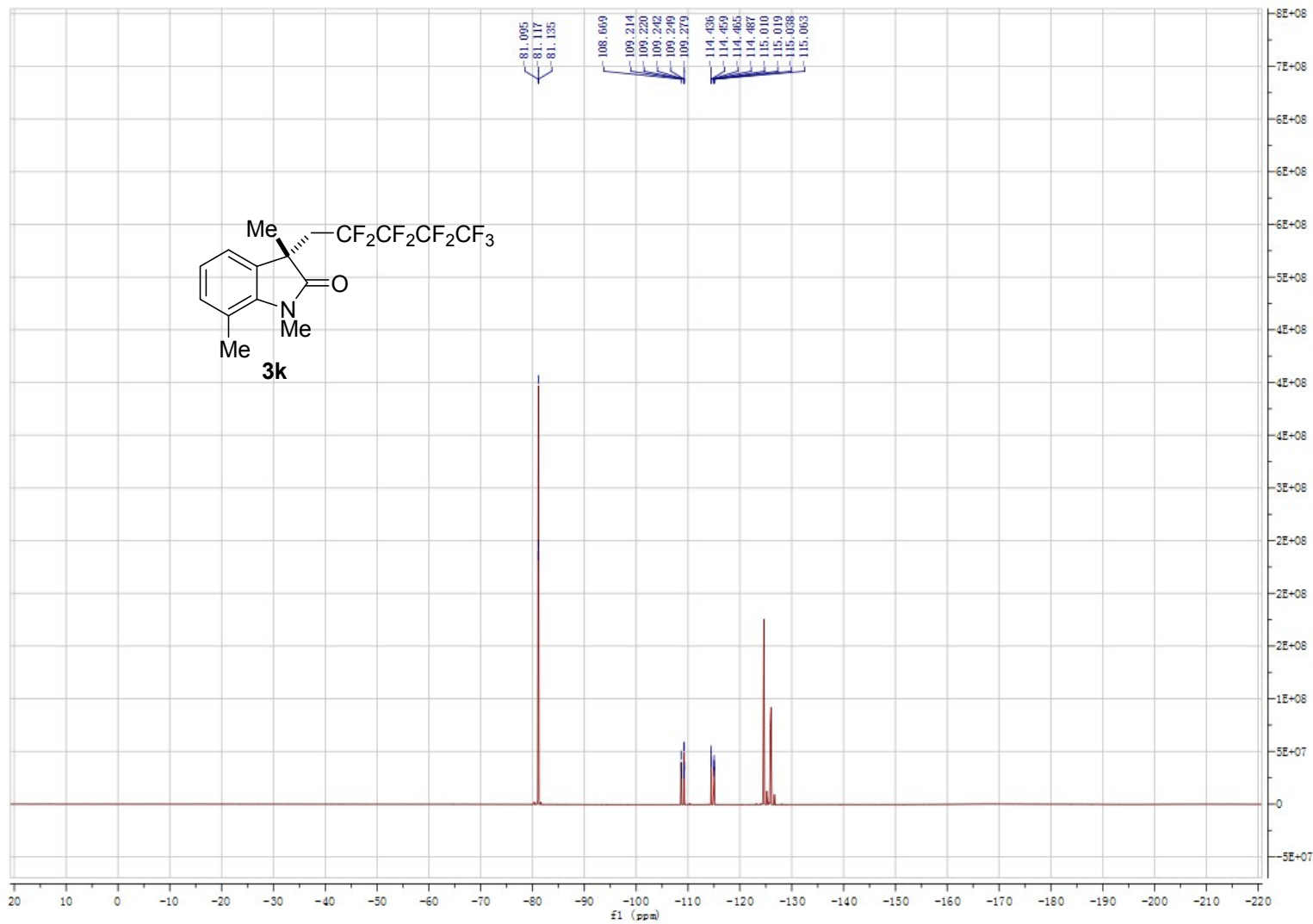


Ethyl

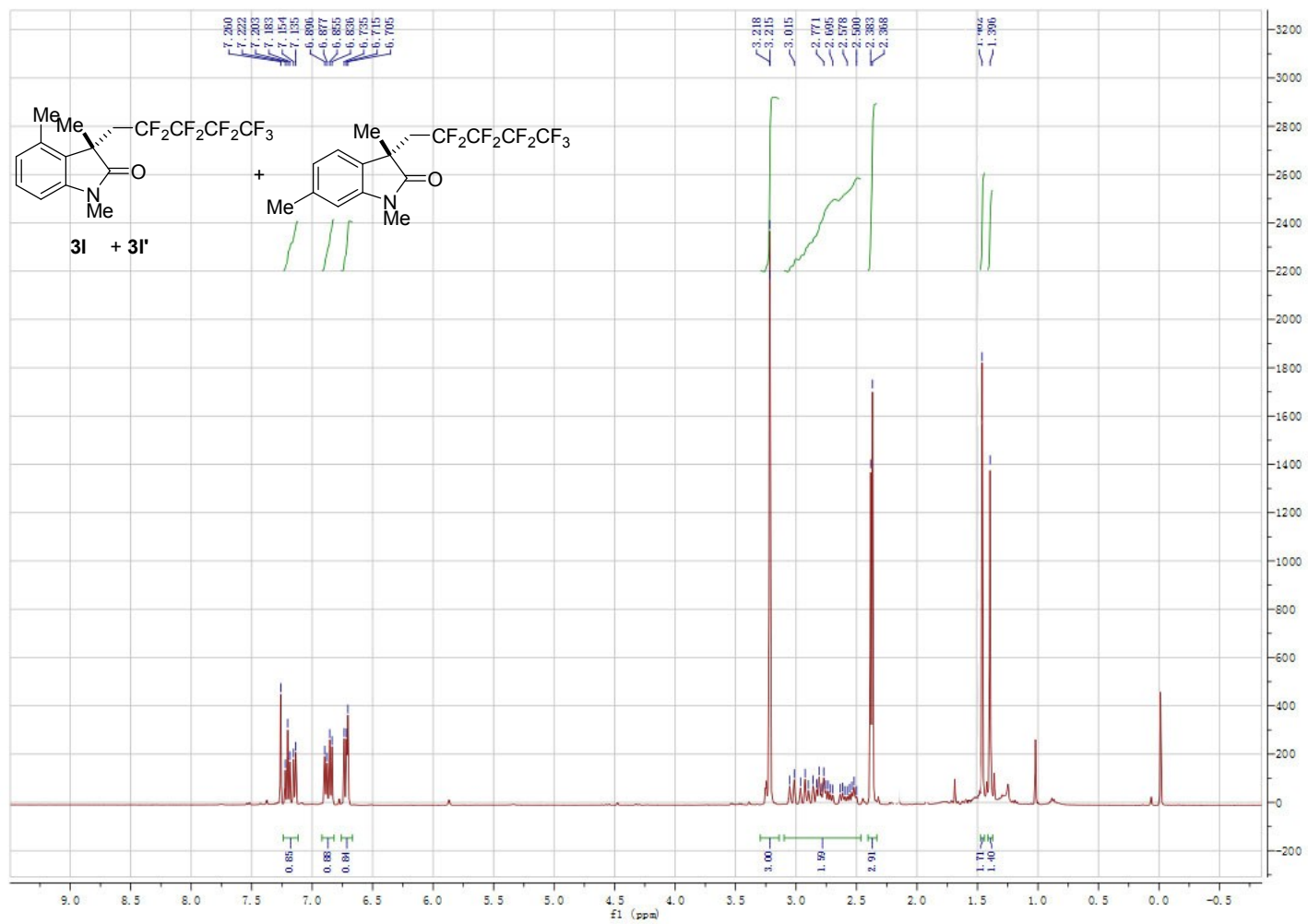
1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).



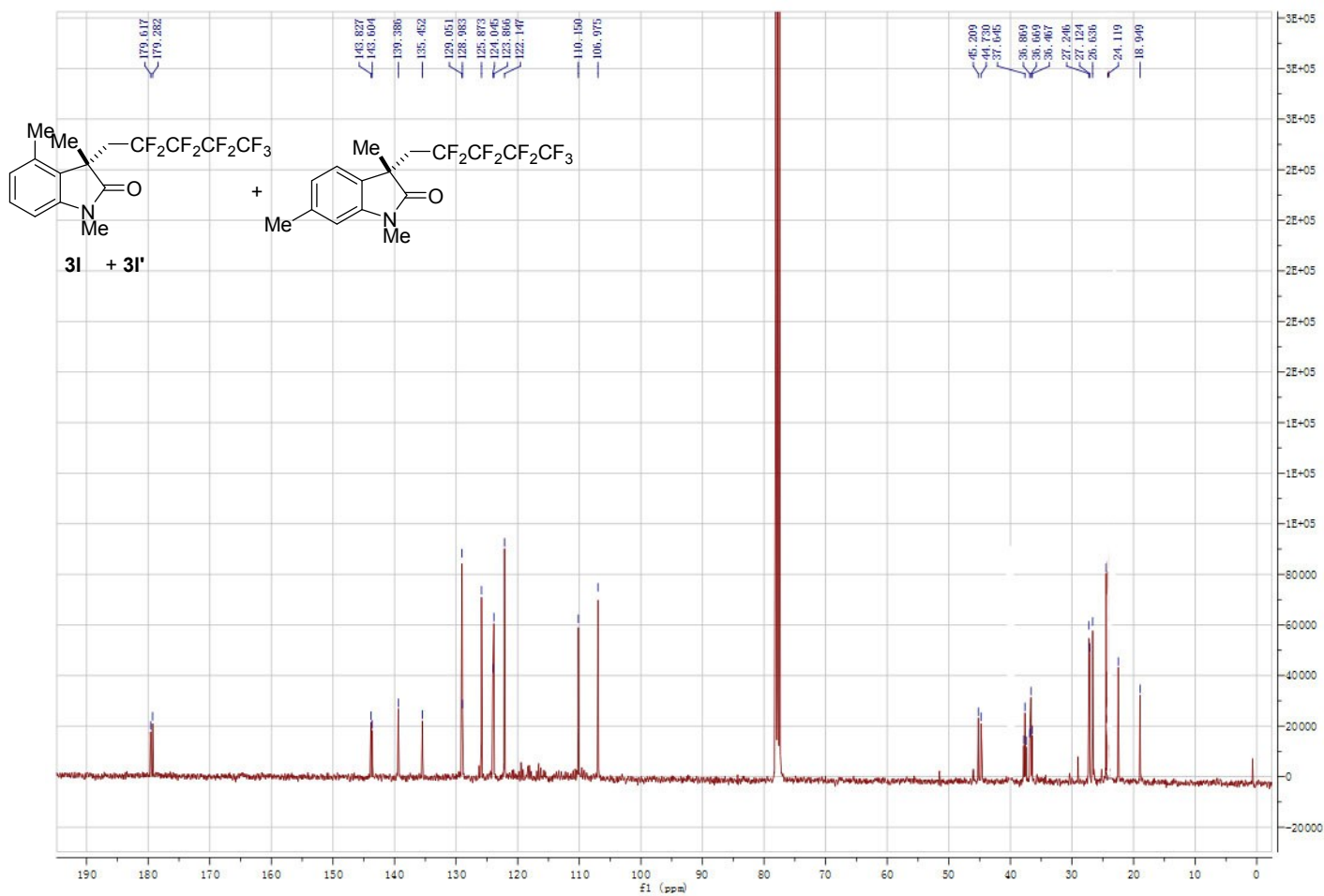
Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).



mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I')

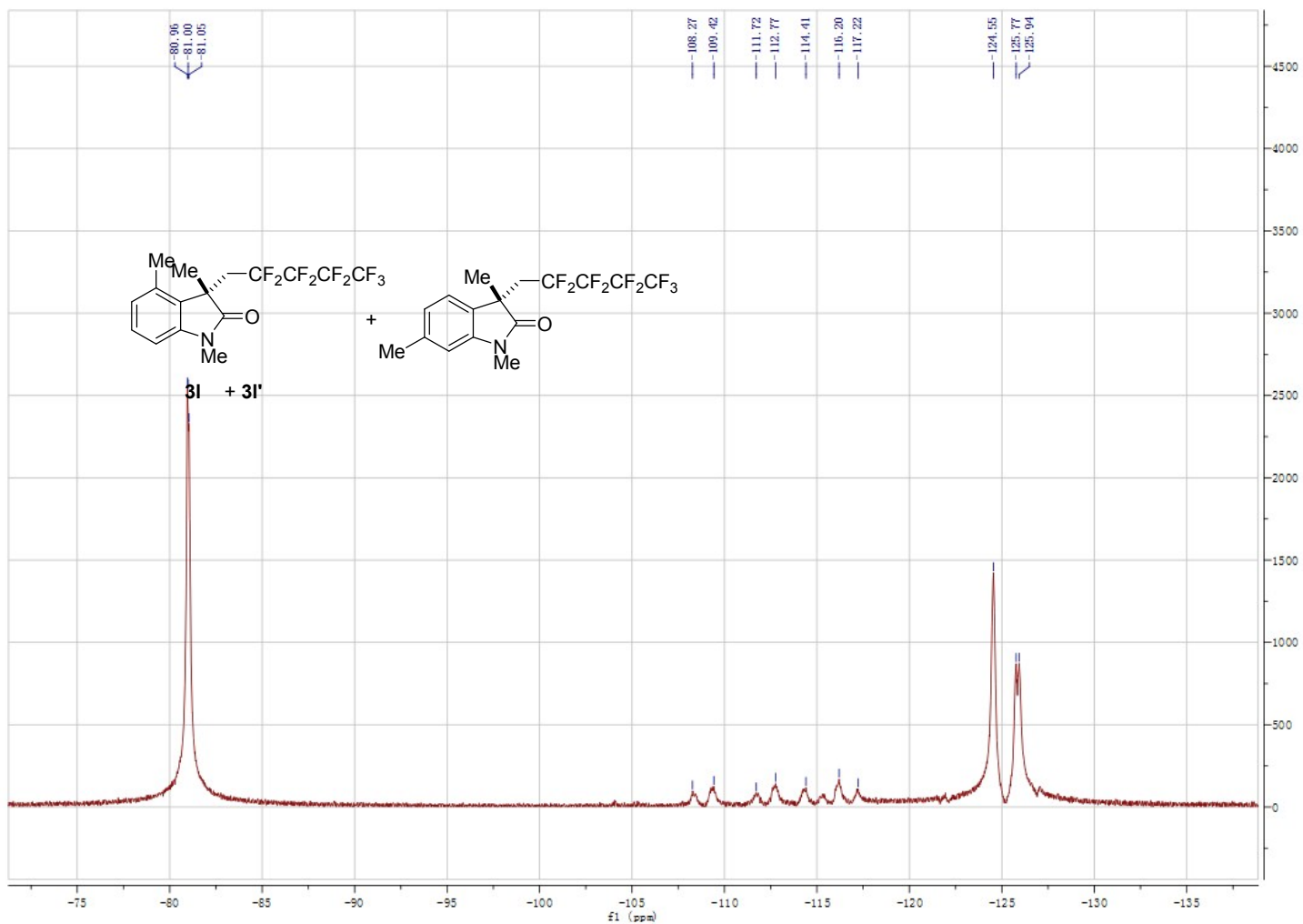


mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I')

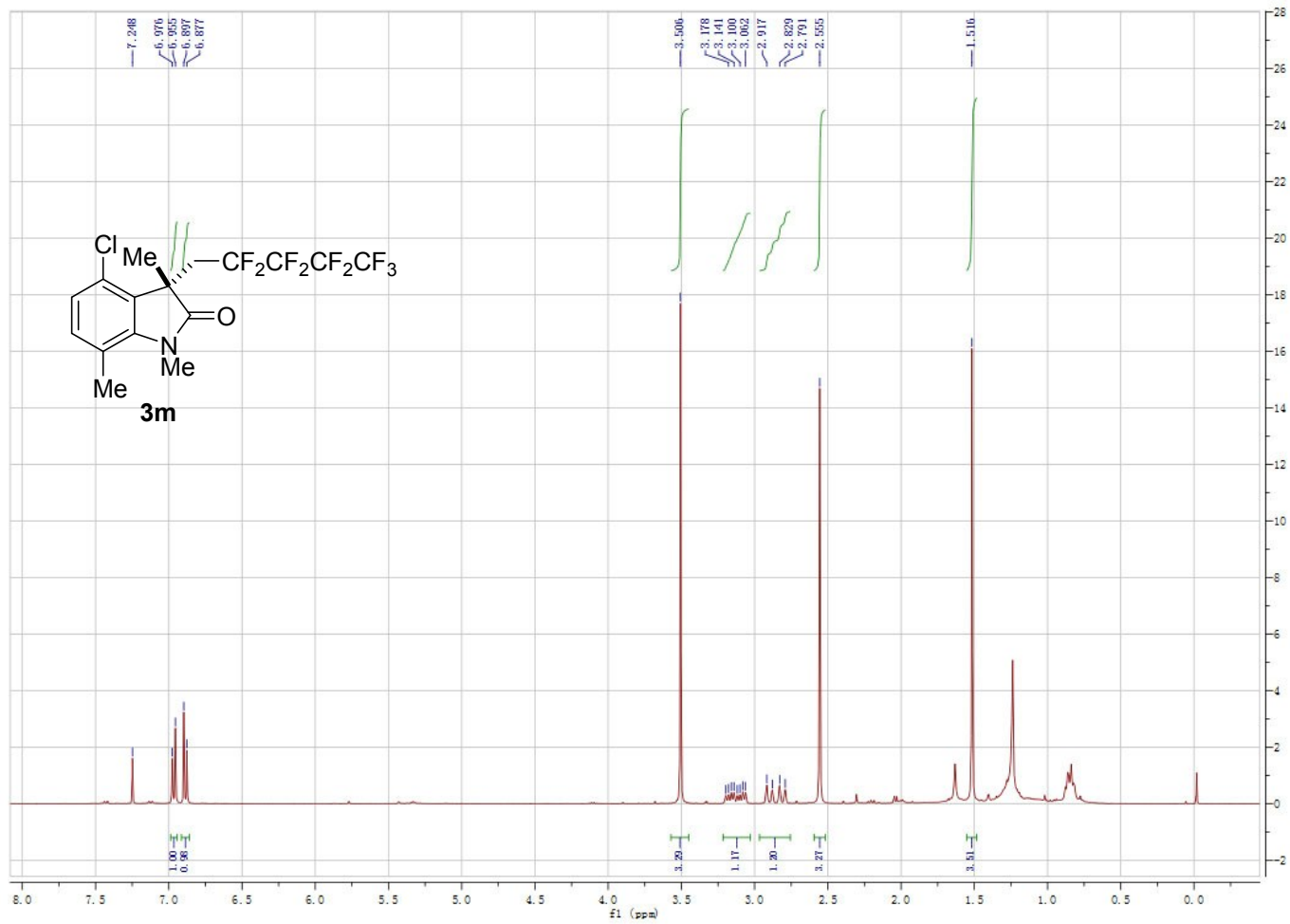


mixture of

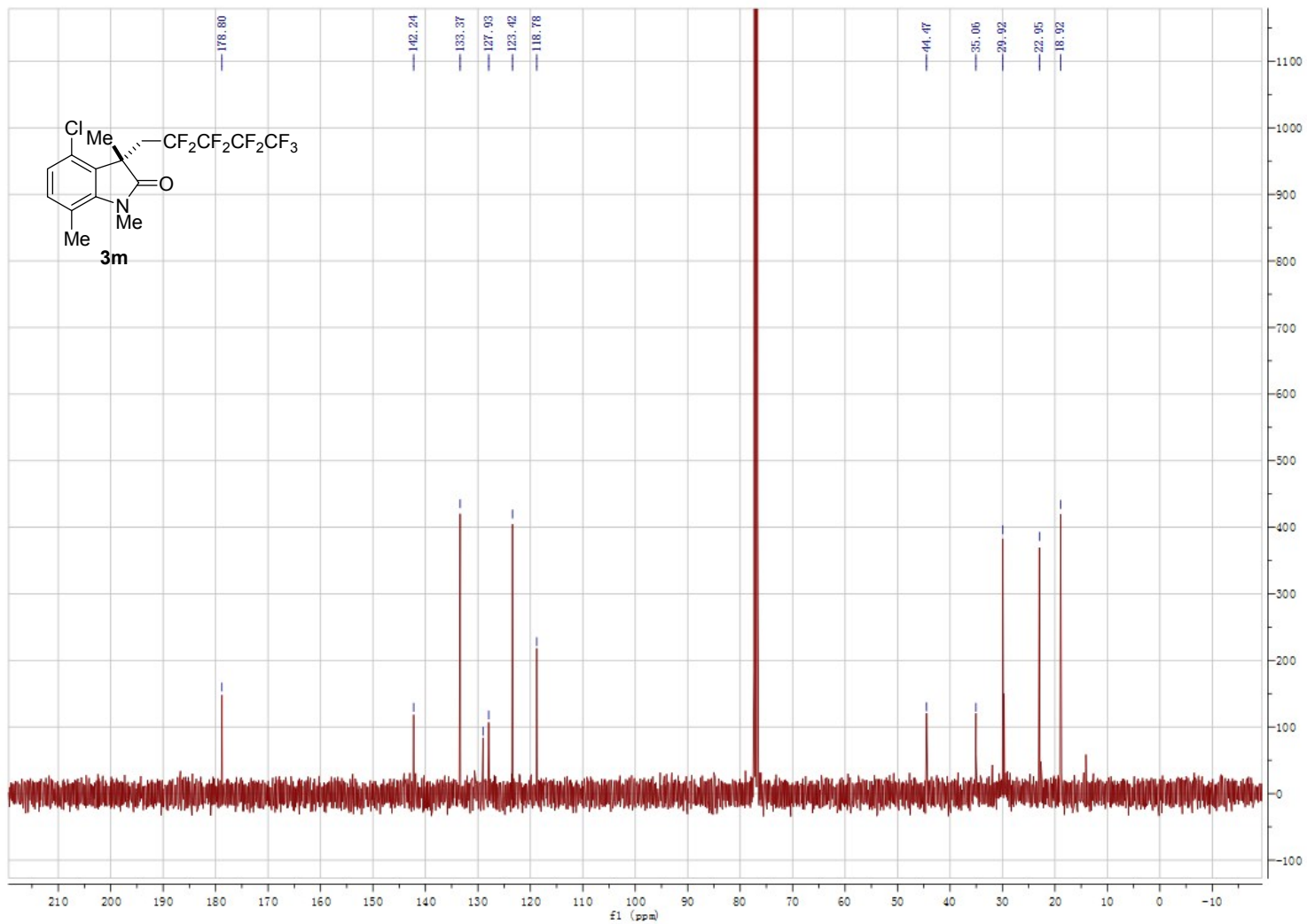
1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3I')



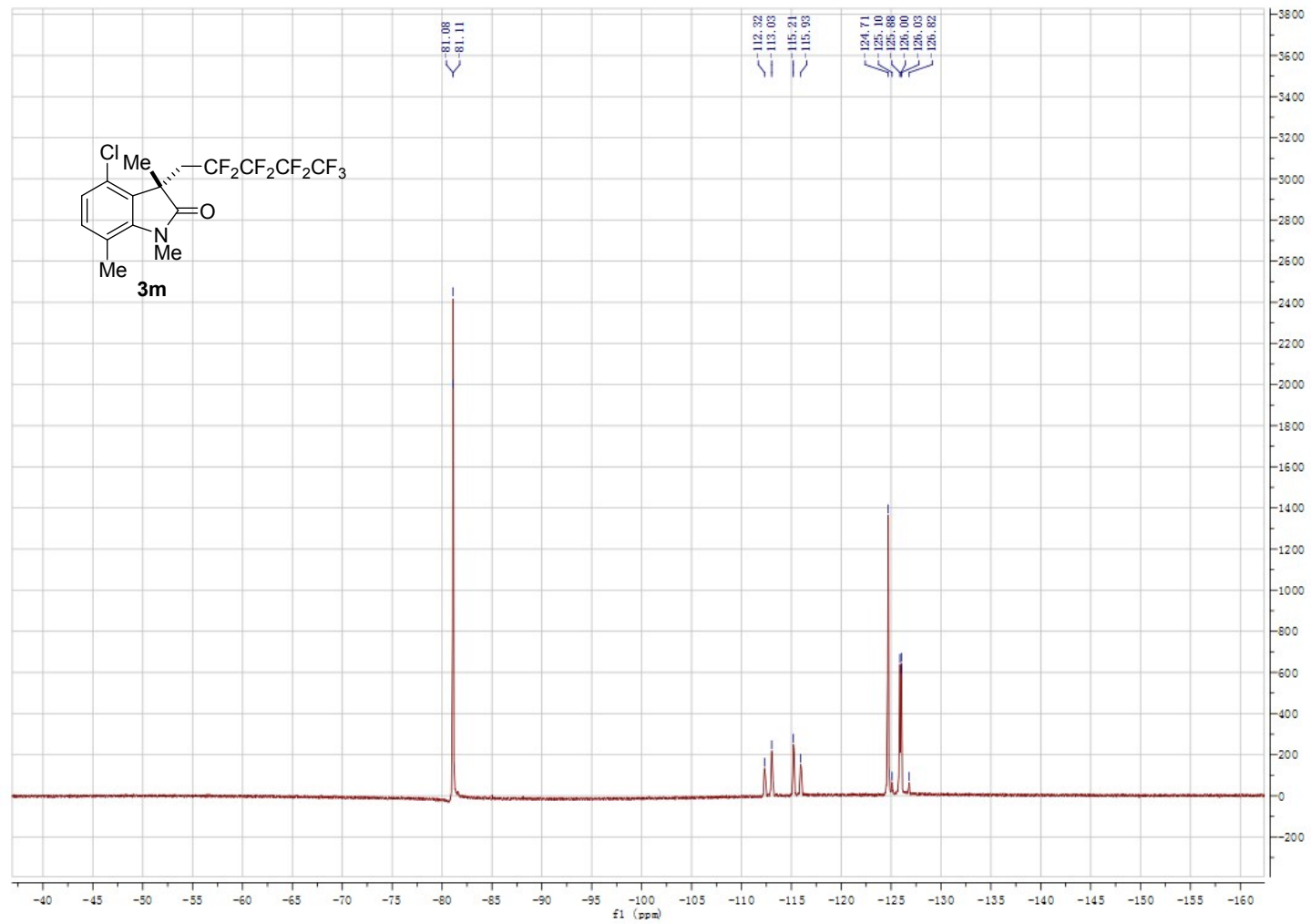
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)



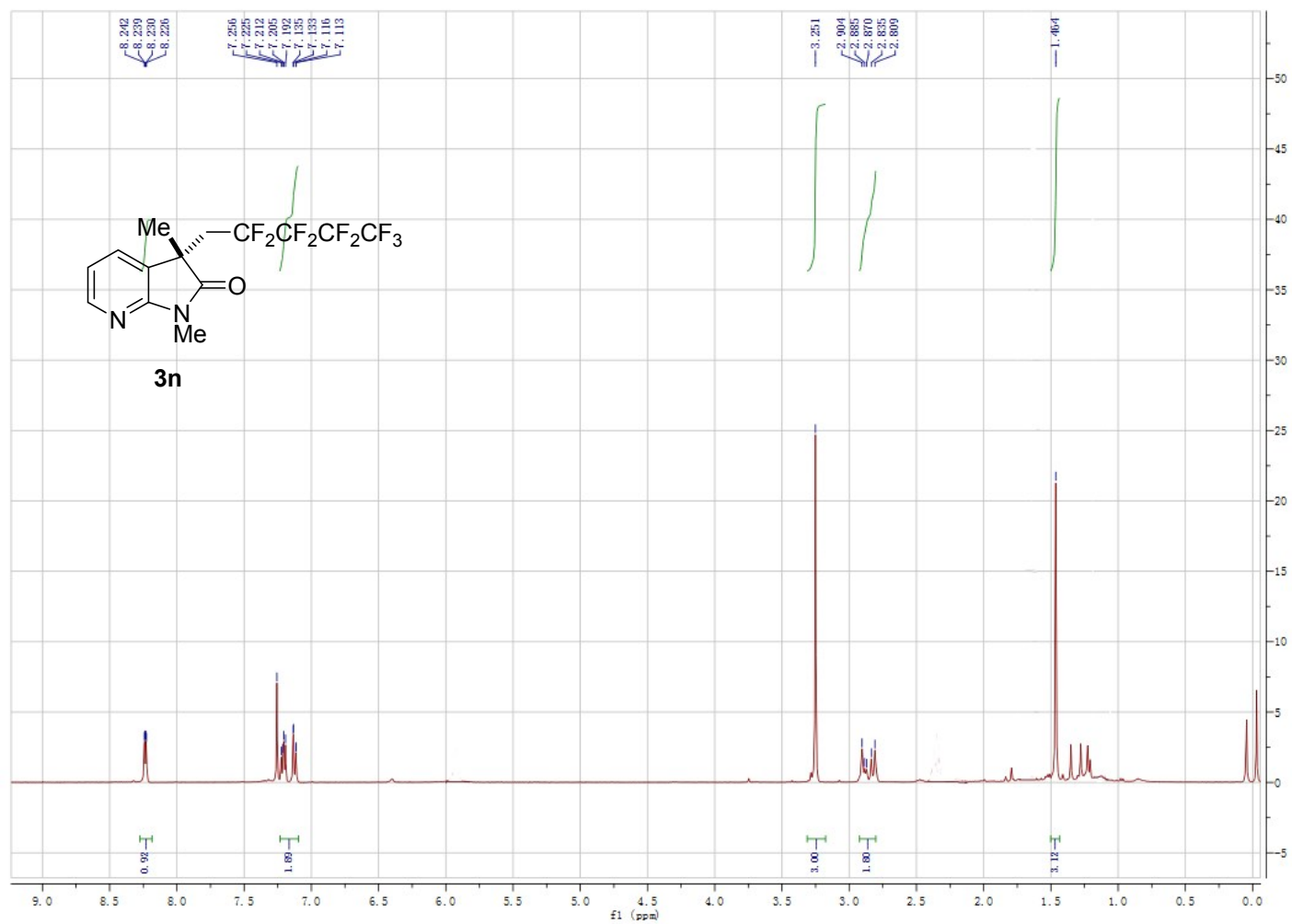
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)



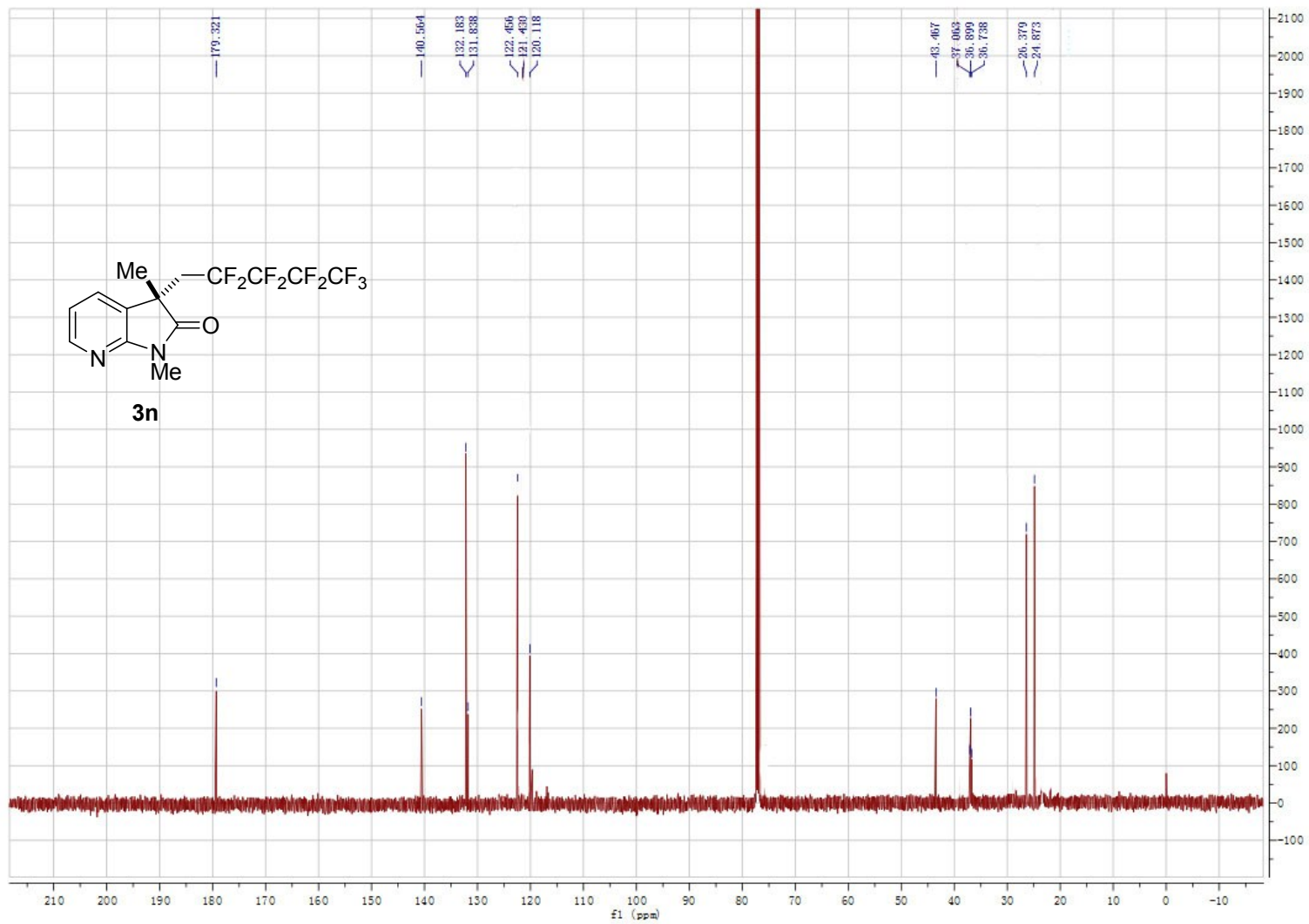
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)



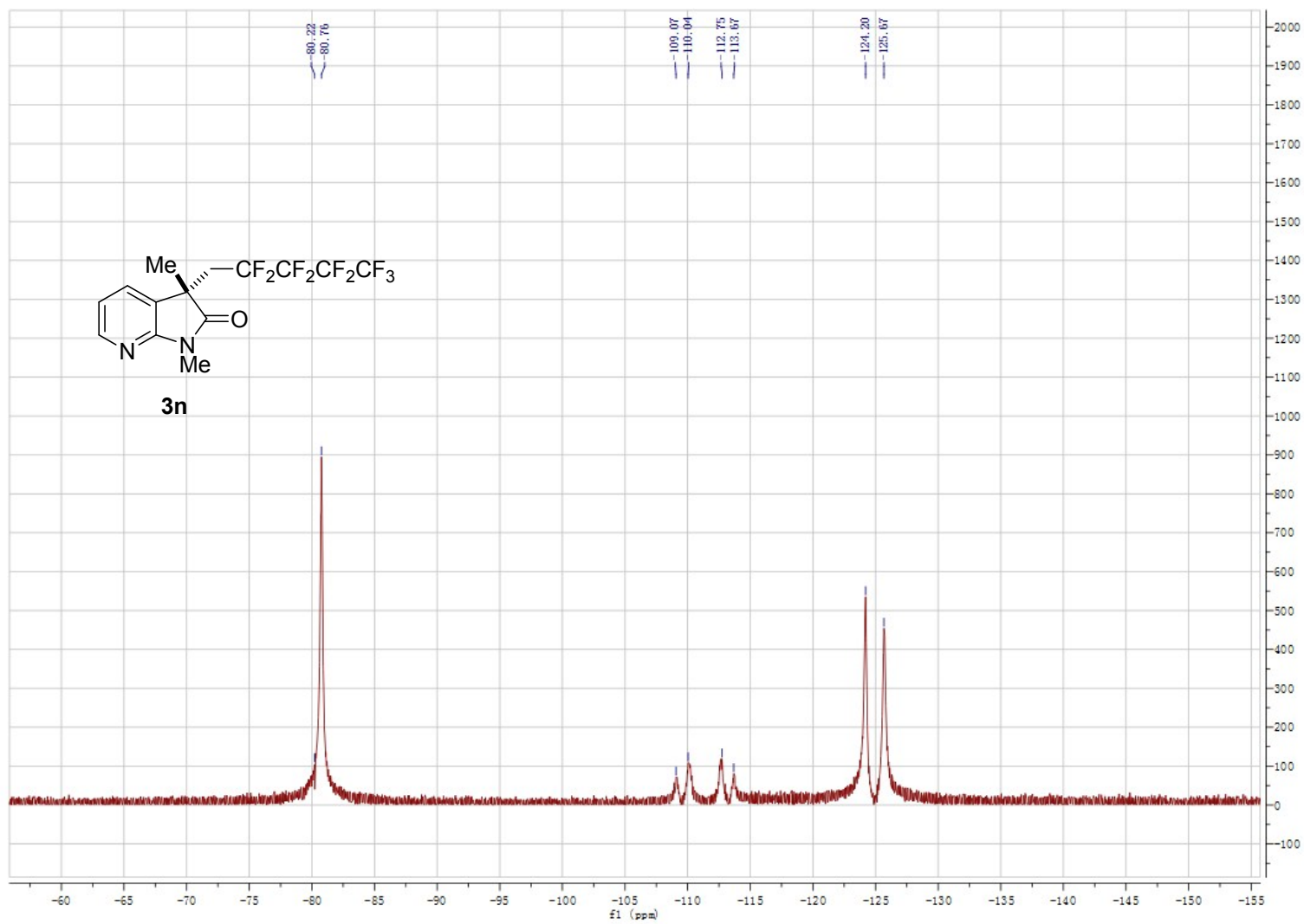
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)



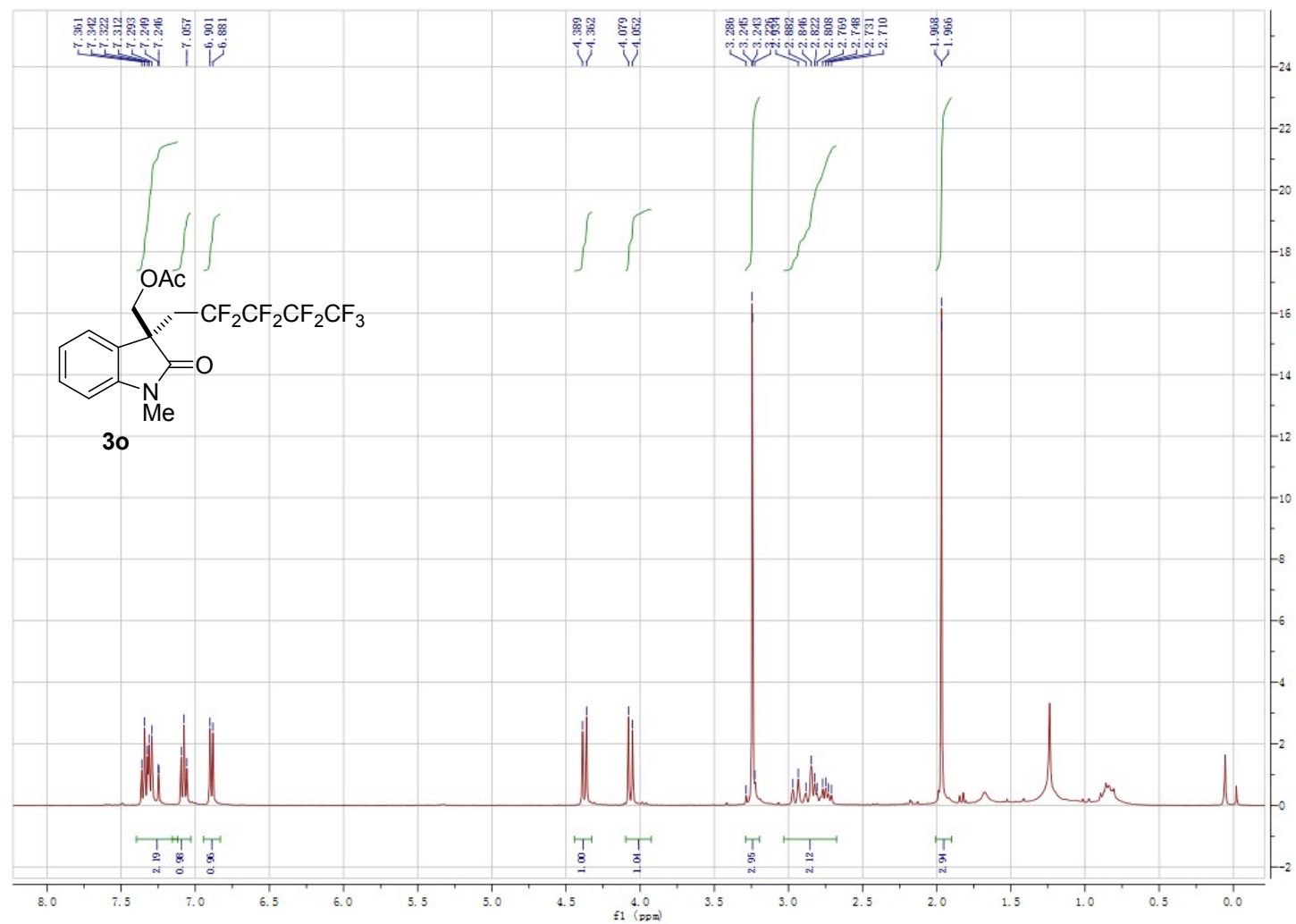
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)



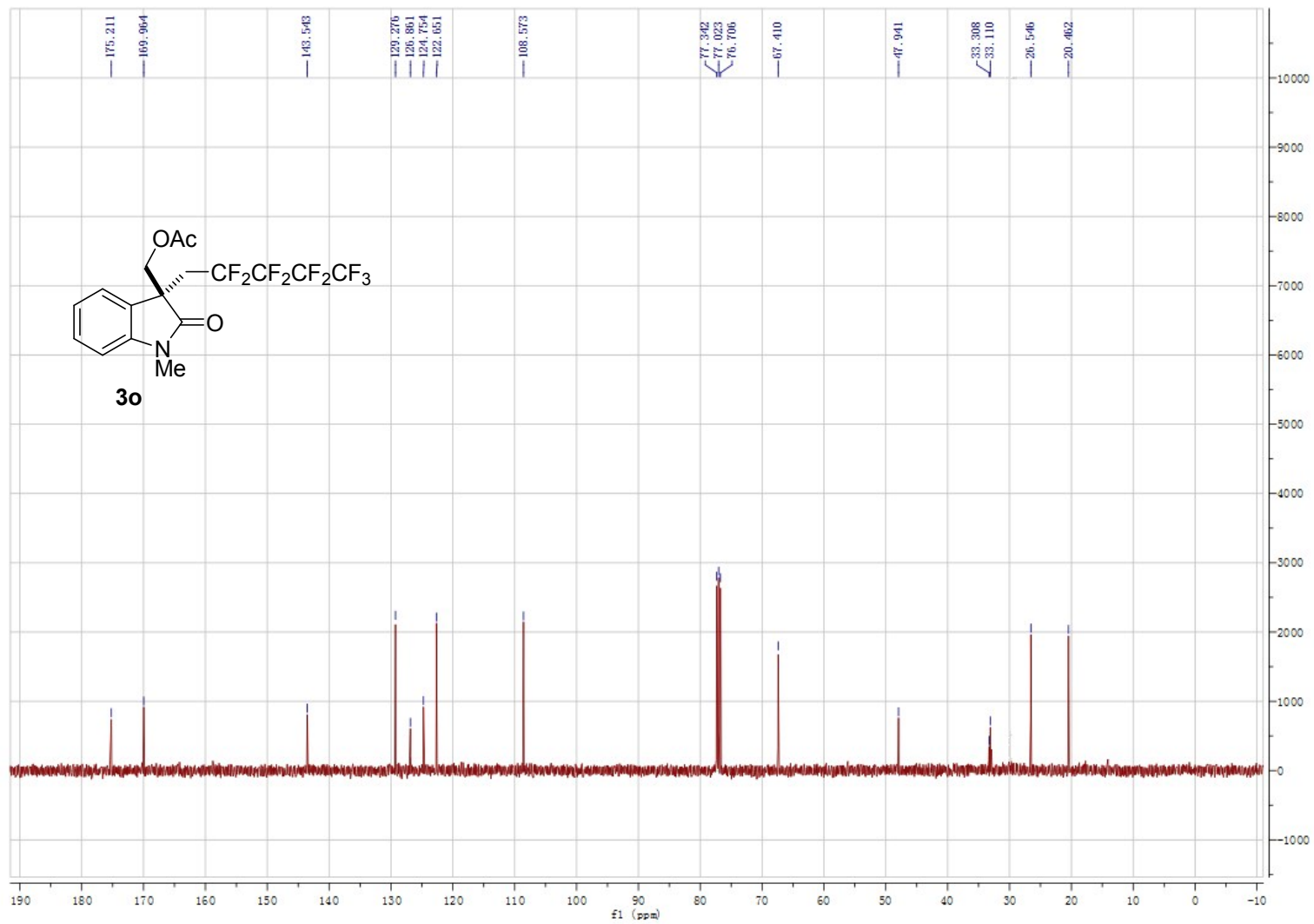
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)



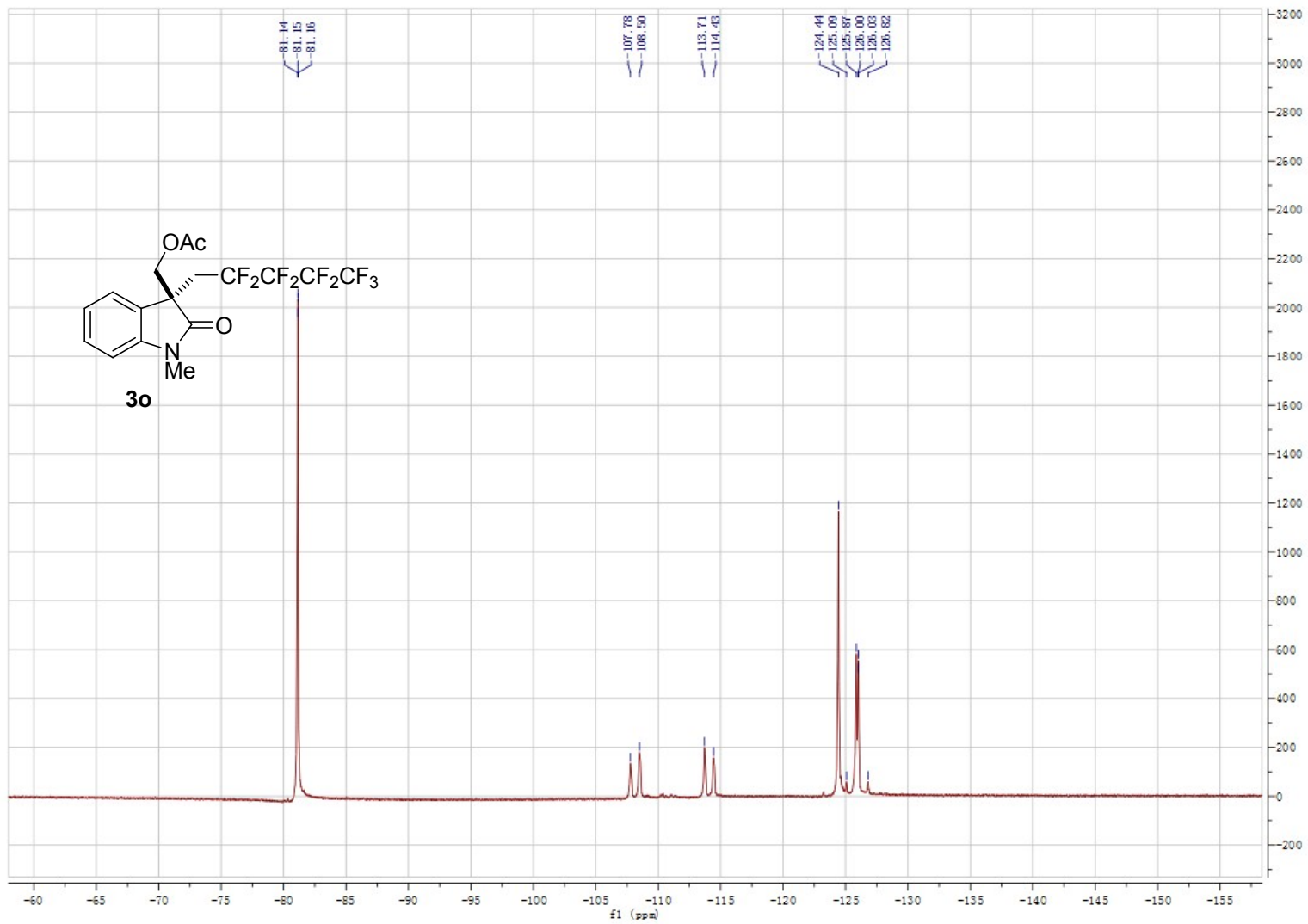
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindolin-3-yl)methyl acetate (3o)



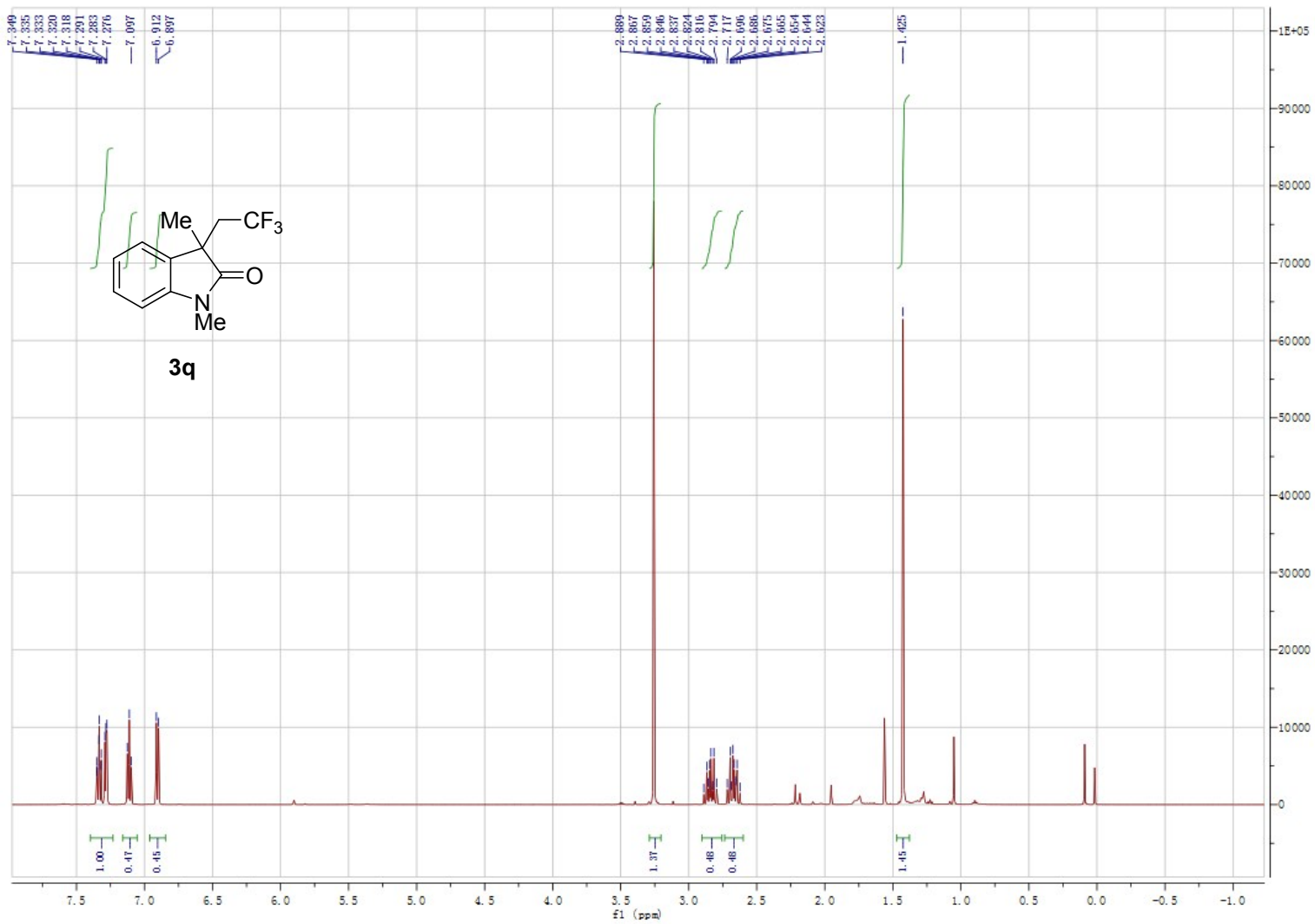
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindolin-3-yl)methyl acetate (3o)



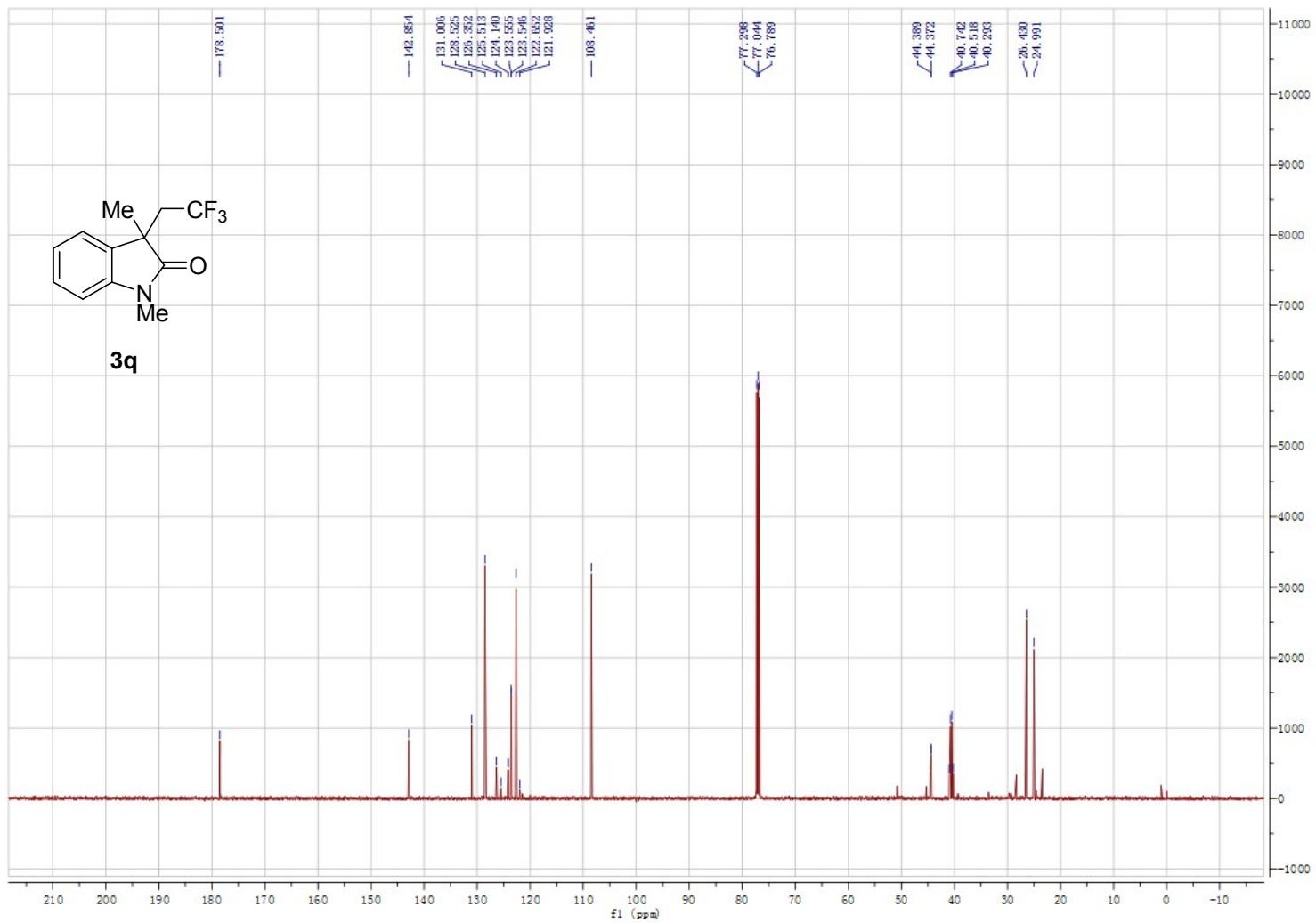
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxindolin-3-yl)methyl acetate (3o)



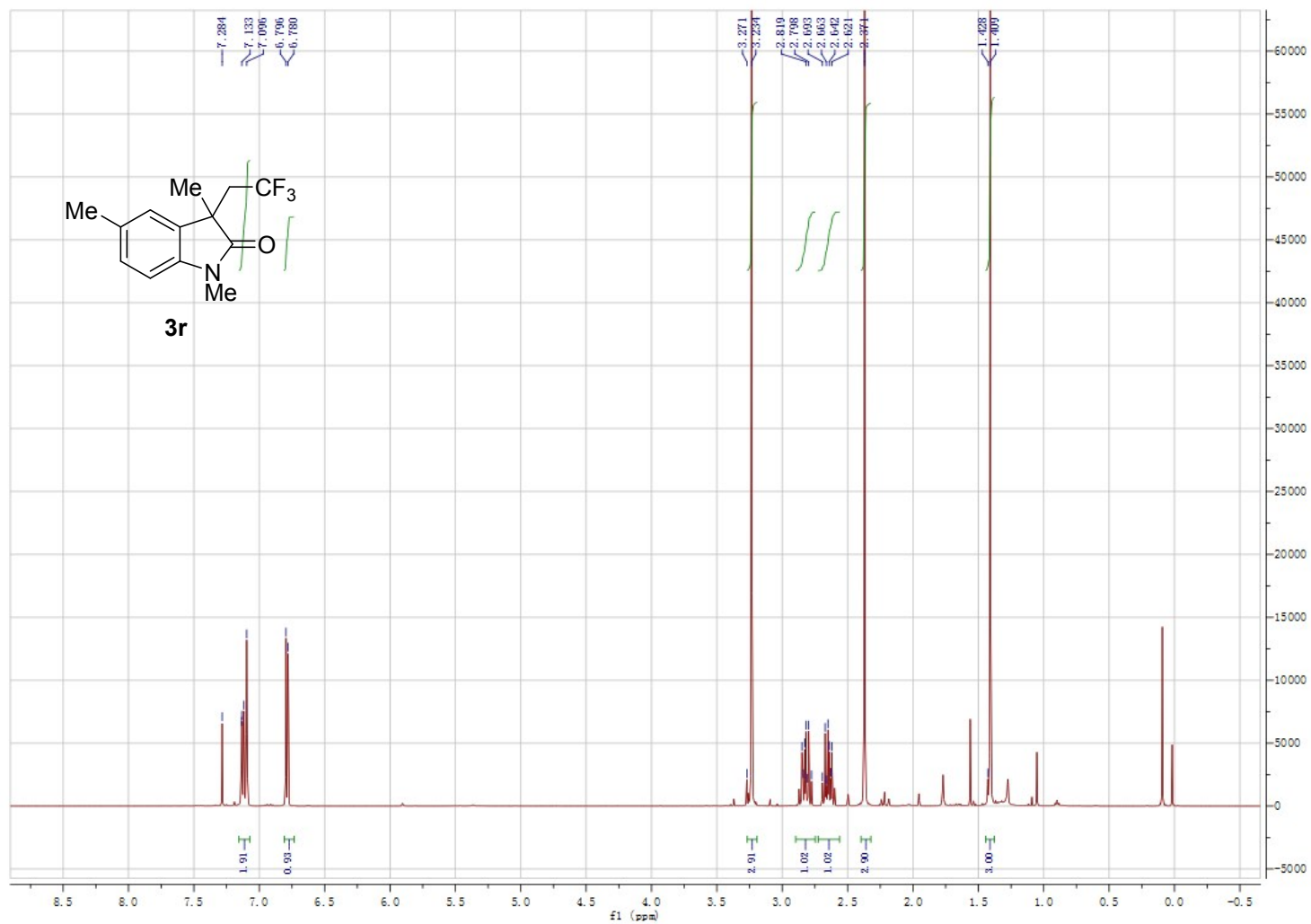
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q)



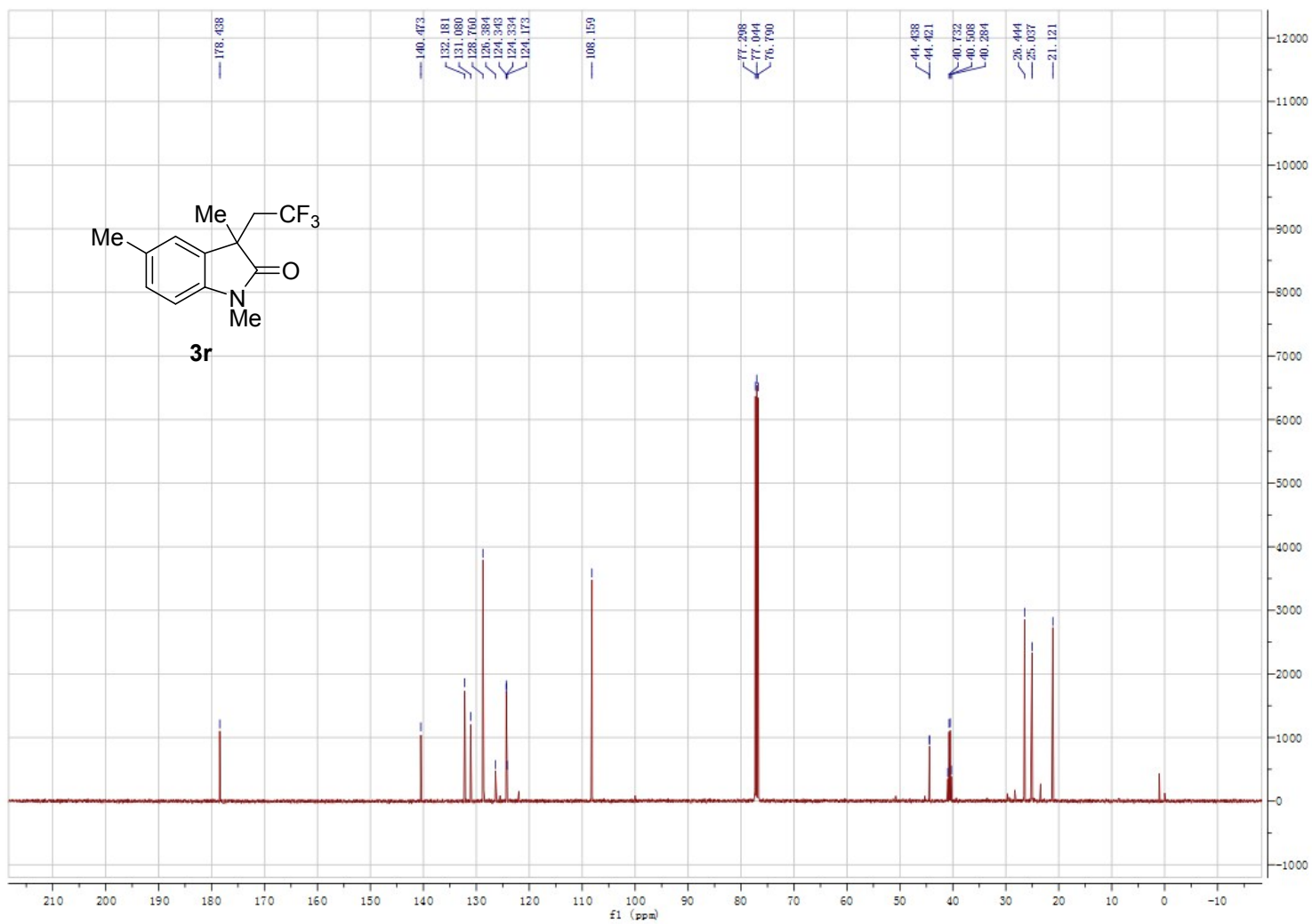
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q)



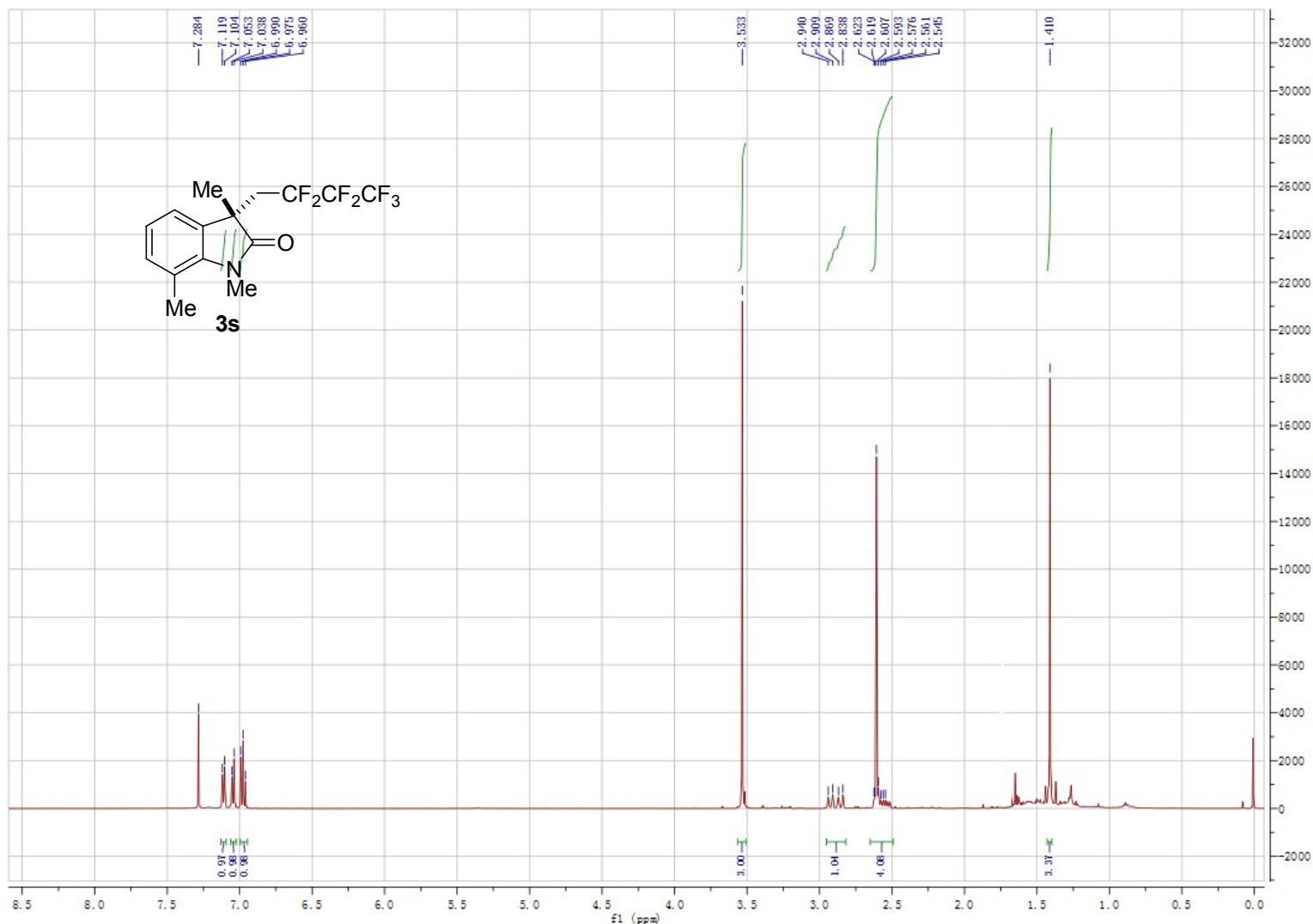
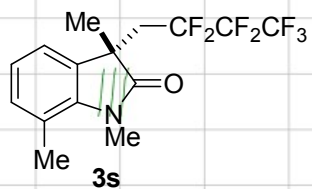
1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3r)



1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3r)

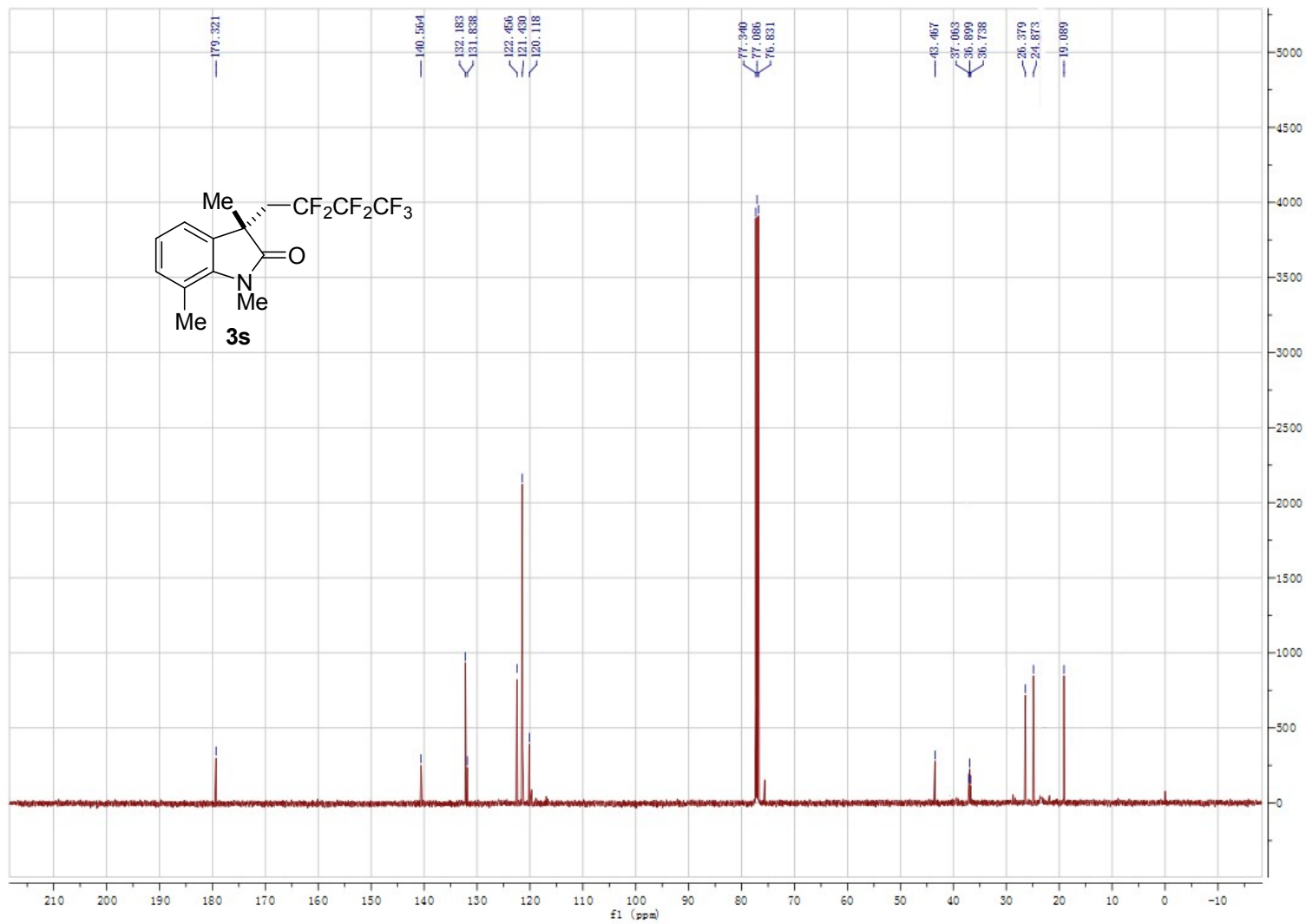


3-(2,2,3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)

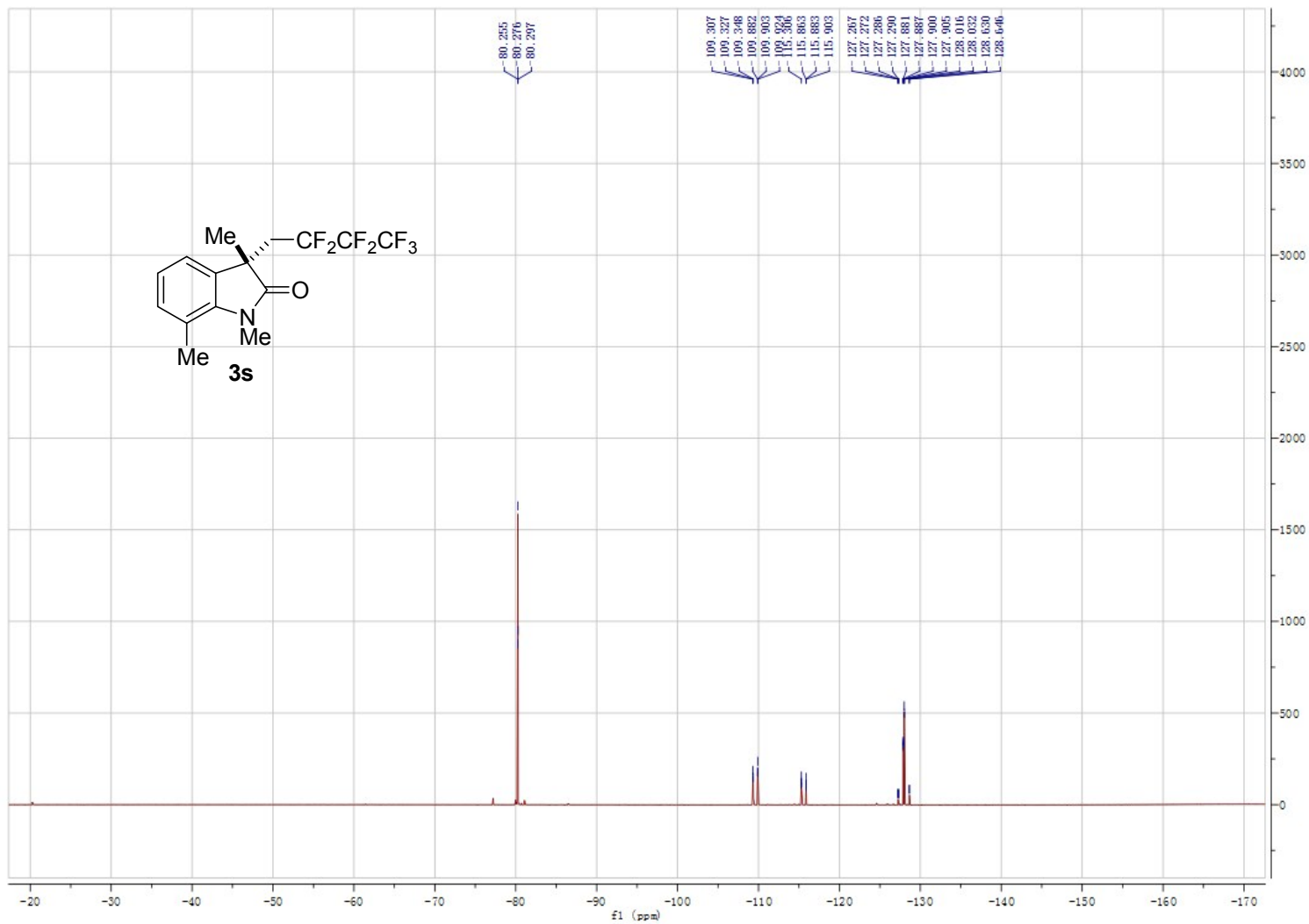


3-
(2,2,

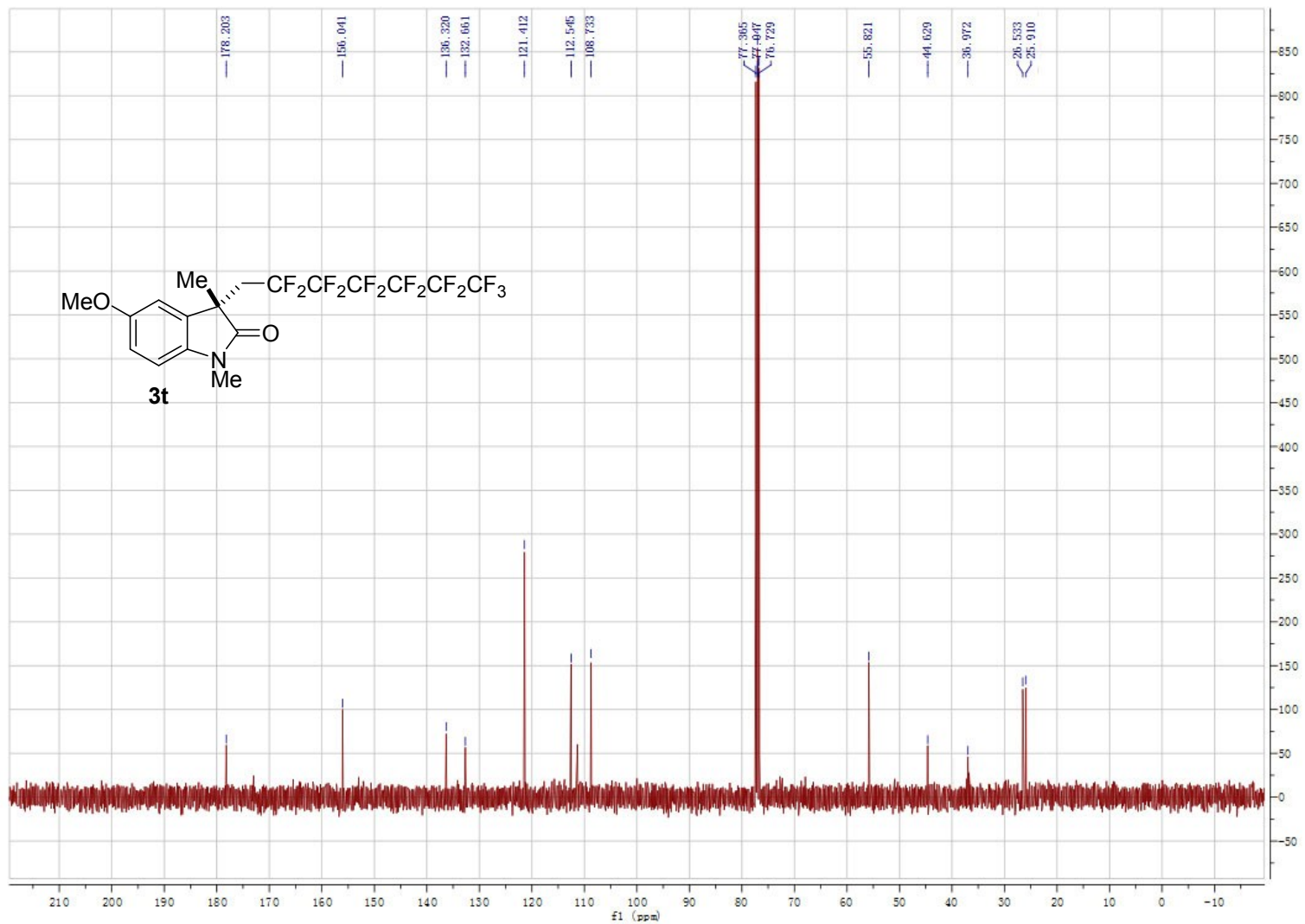
3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)



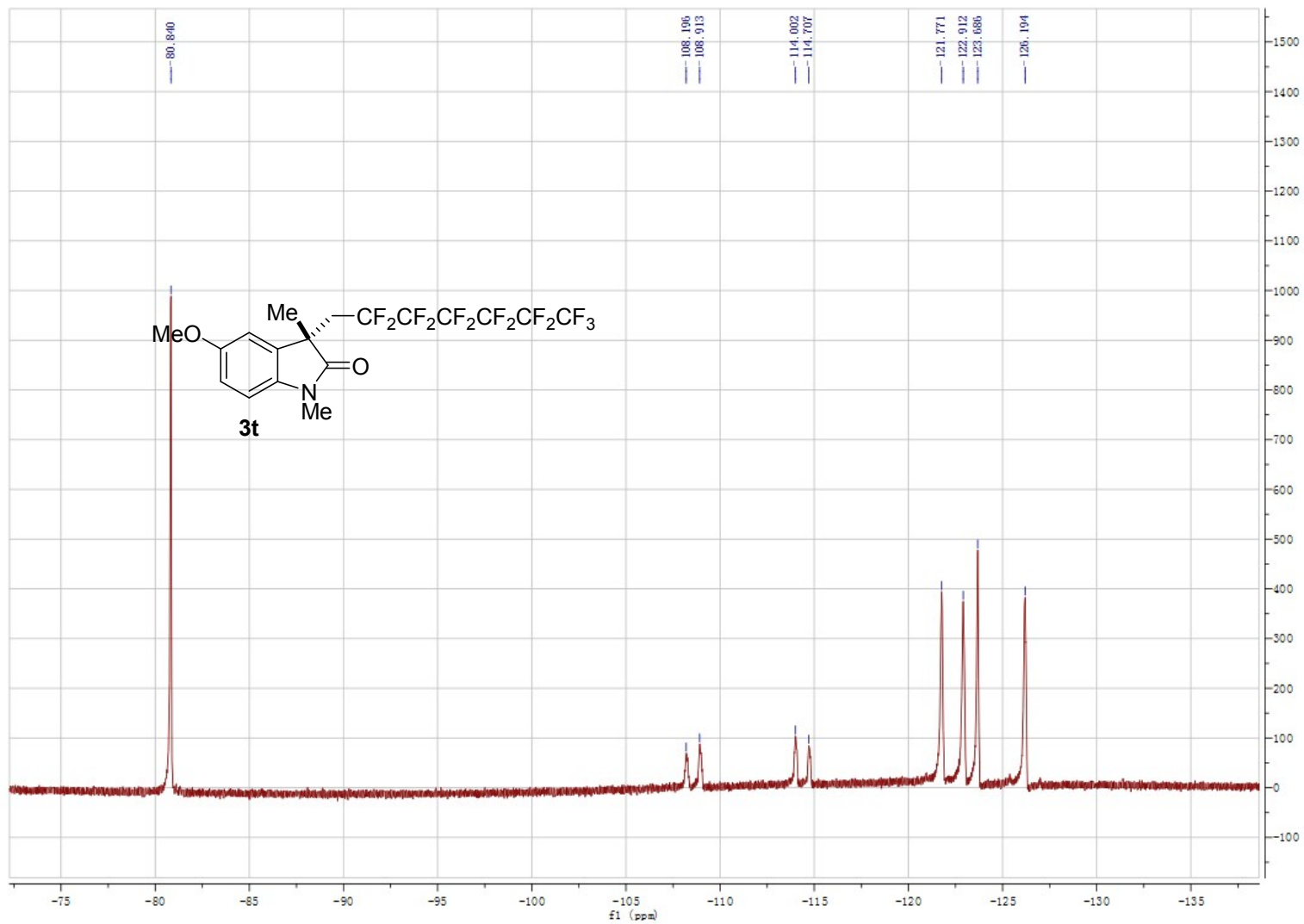
3-(2,2,3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)



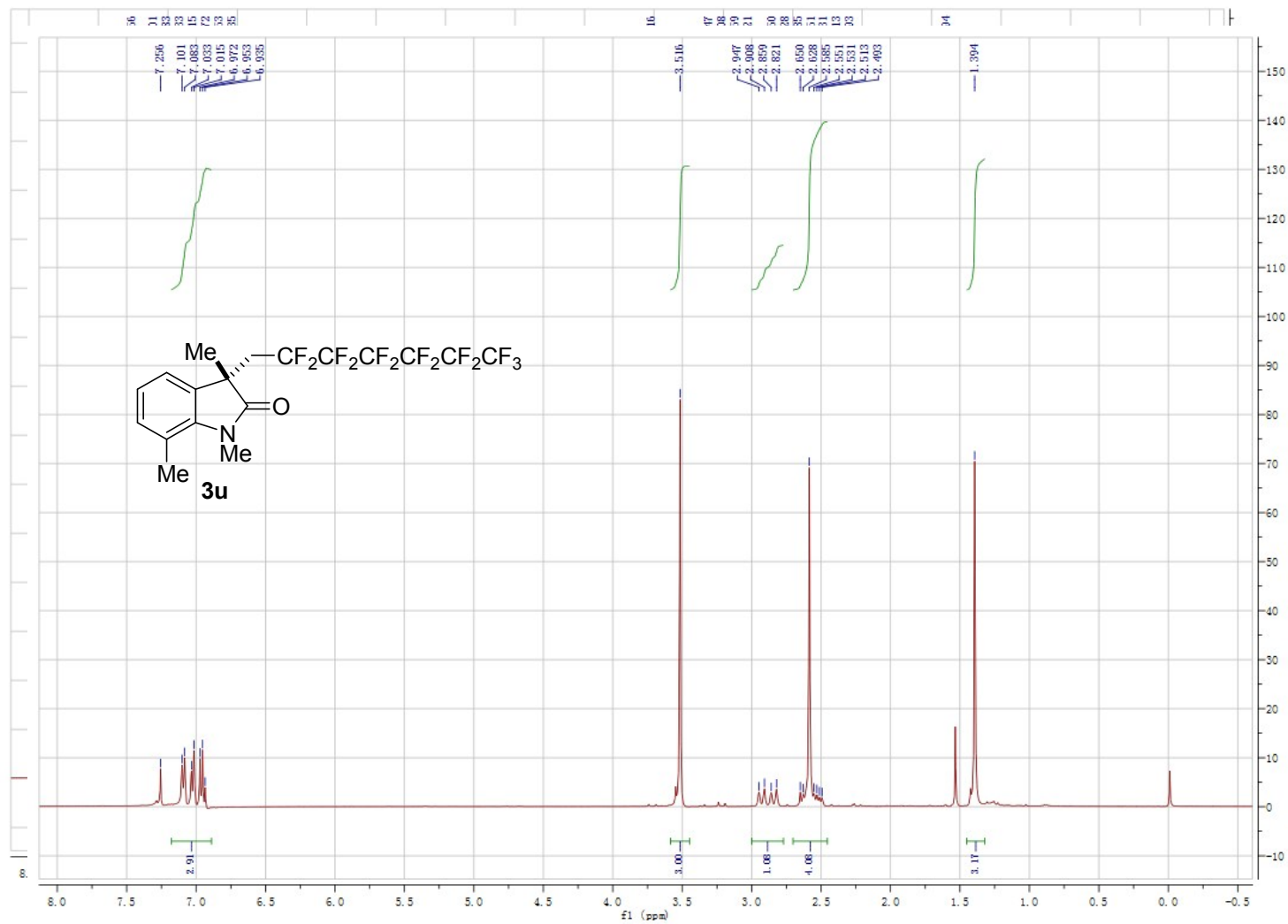
methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t)



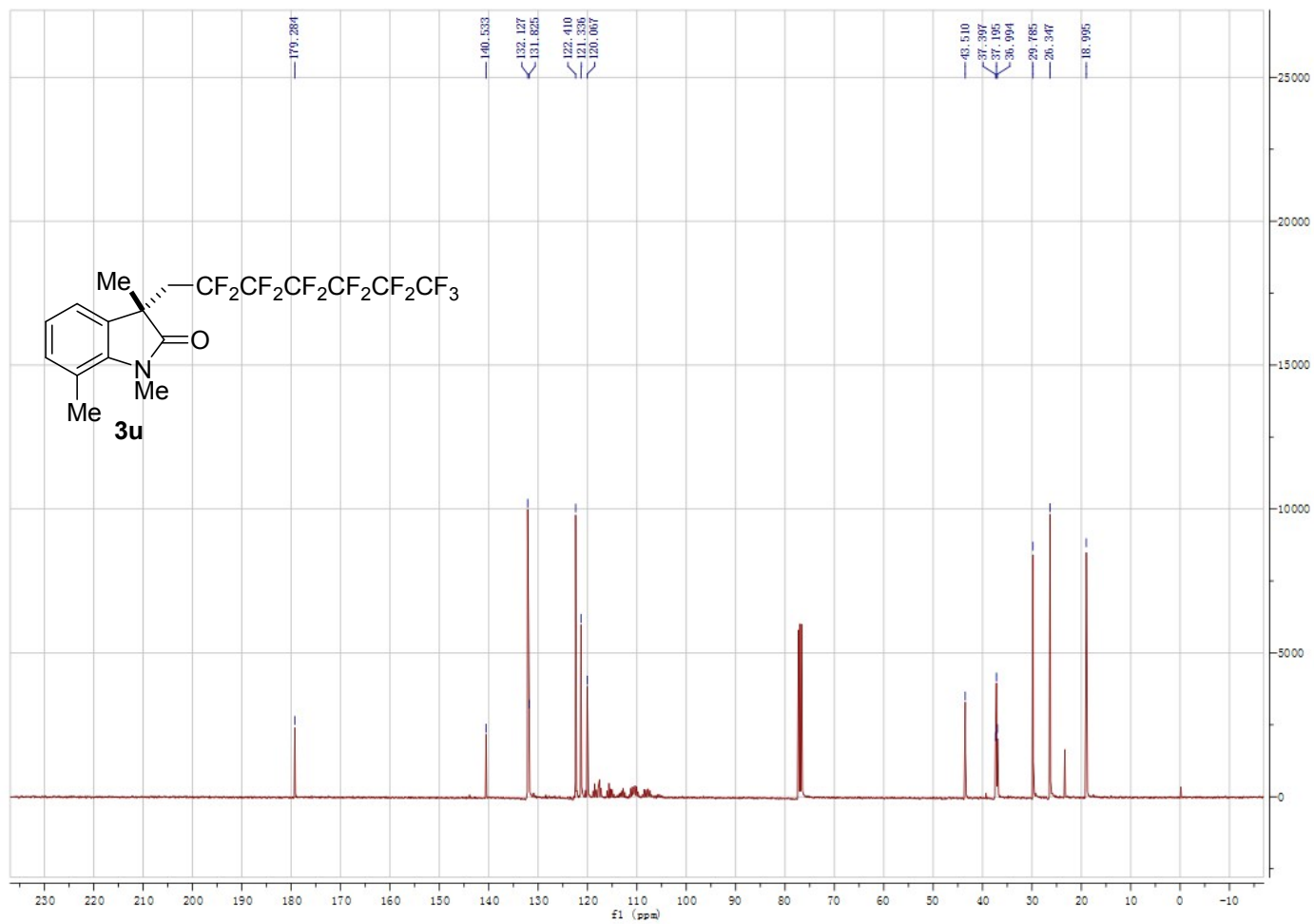
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t)



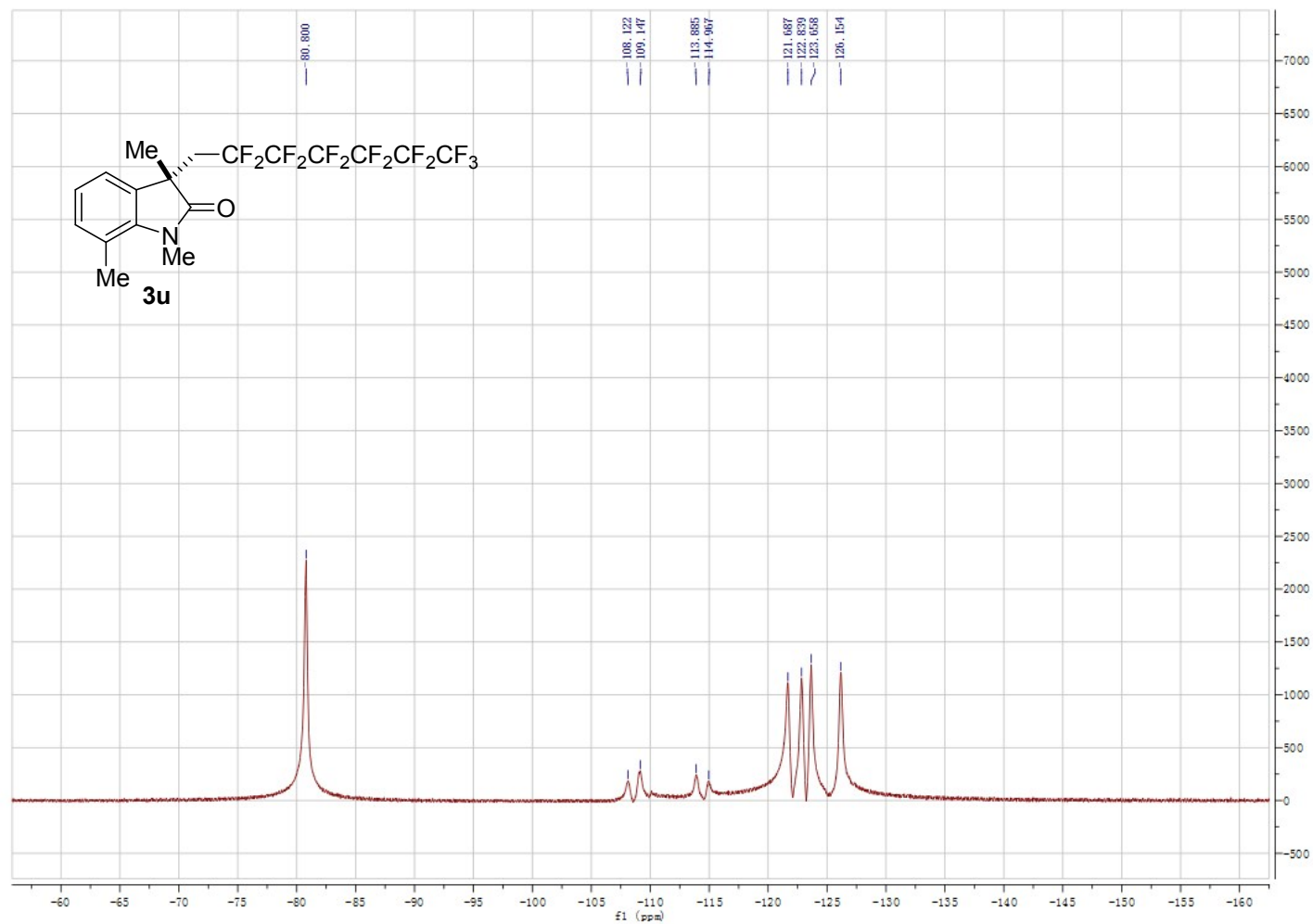
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).



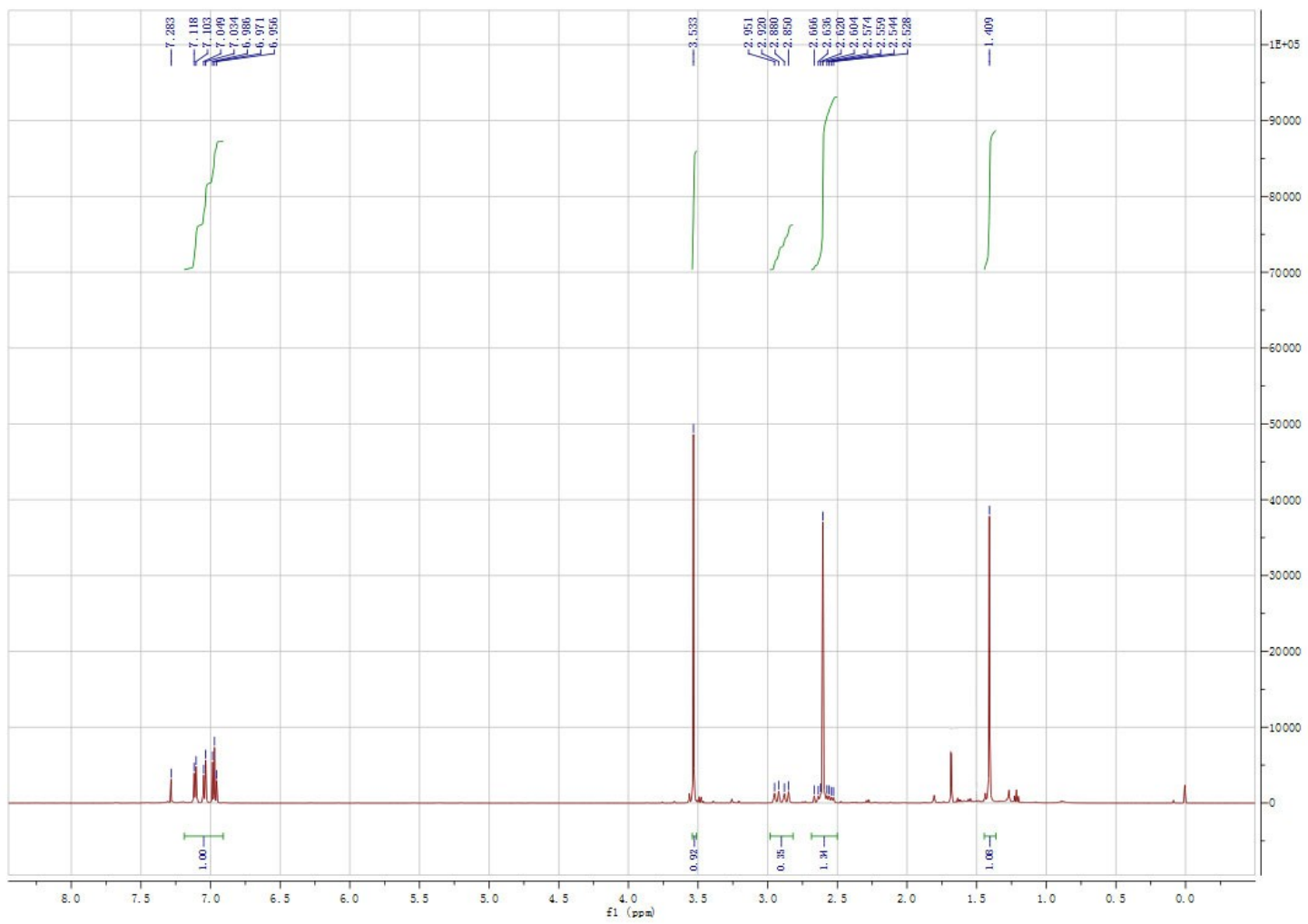
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).



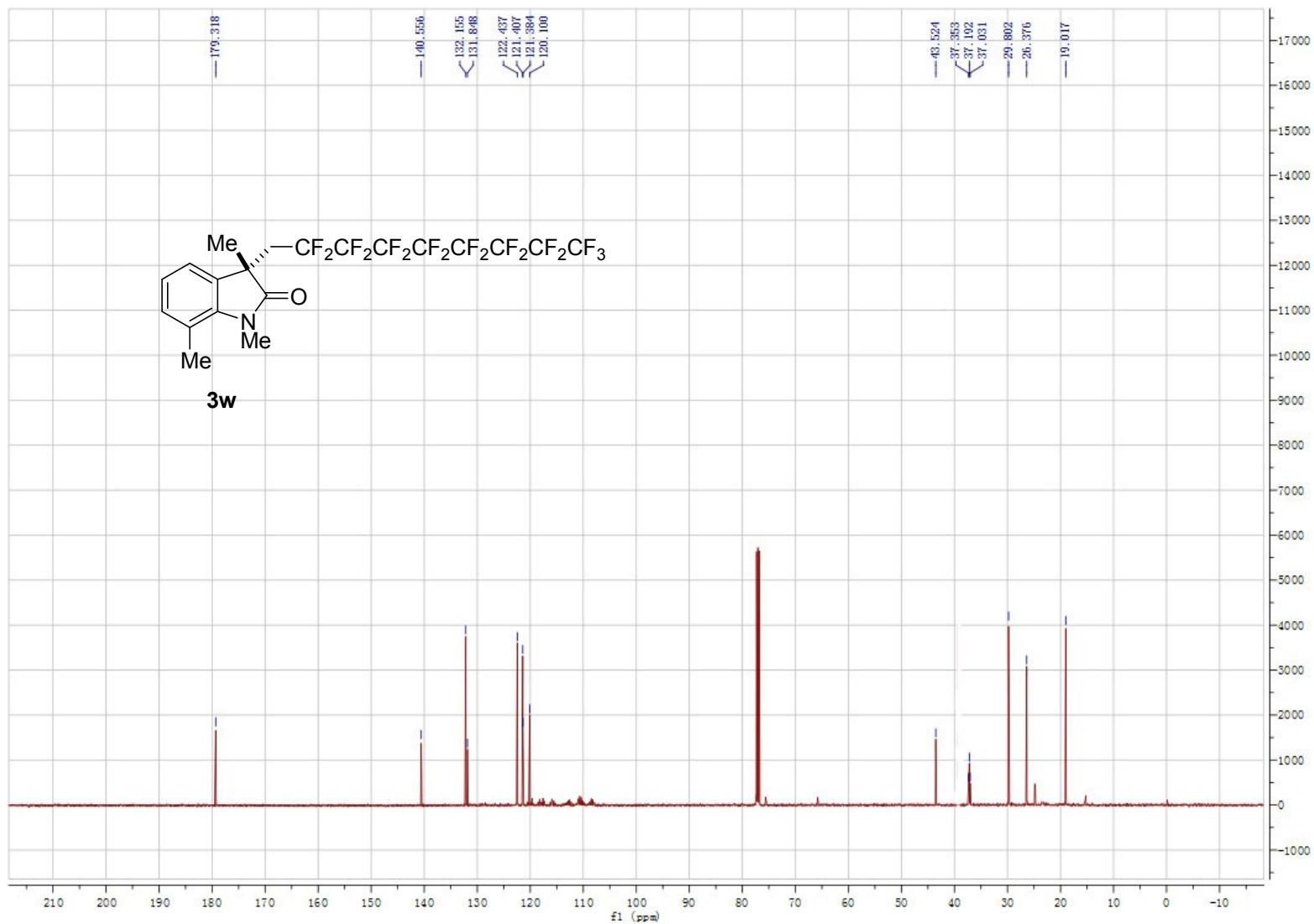
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).



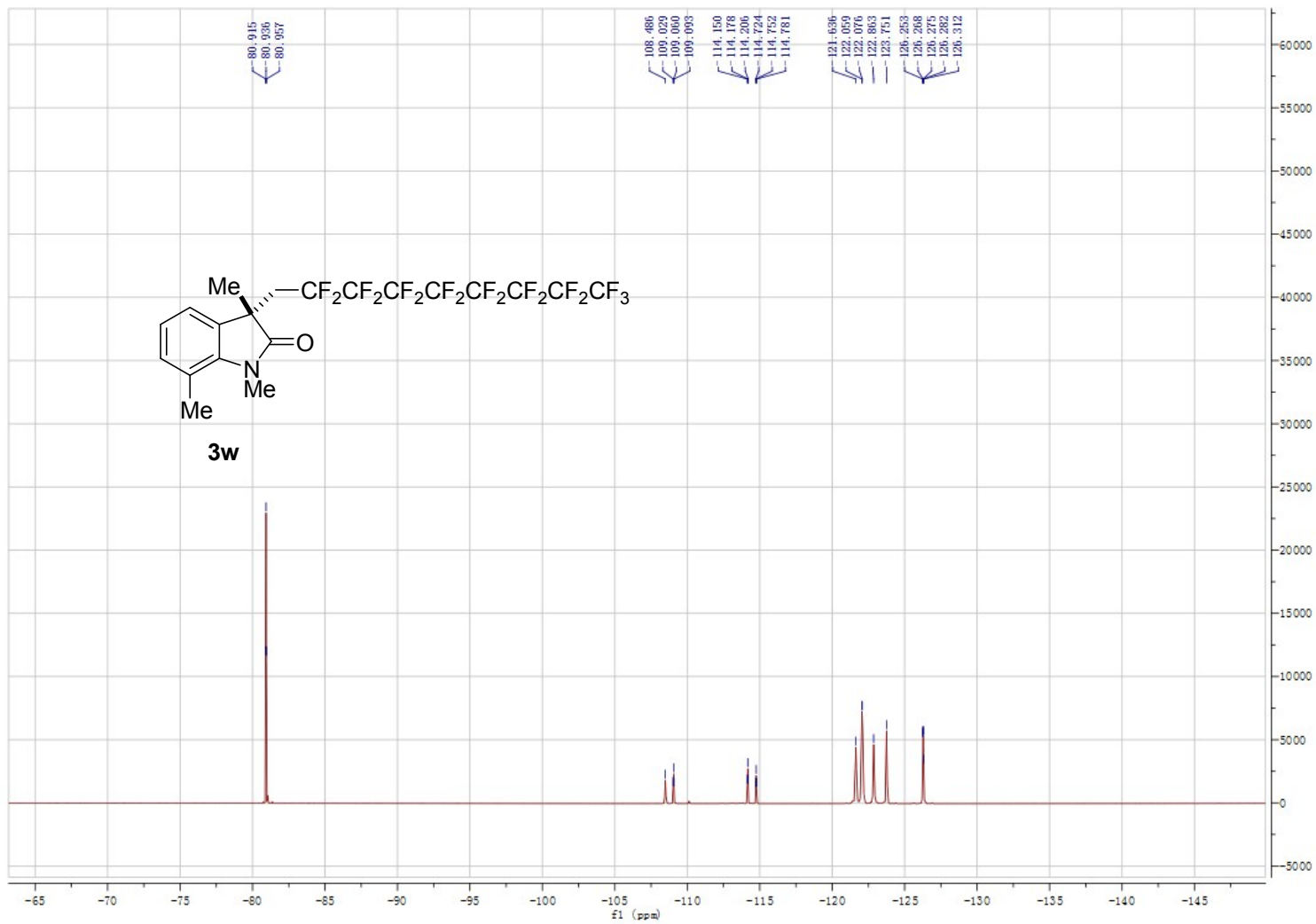
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-1,3,7-trimethylindolin-2-one (3v)



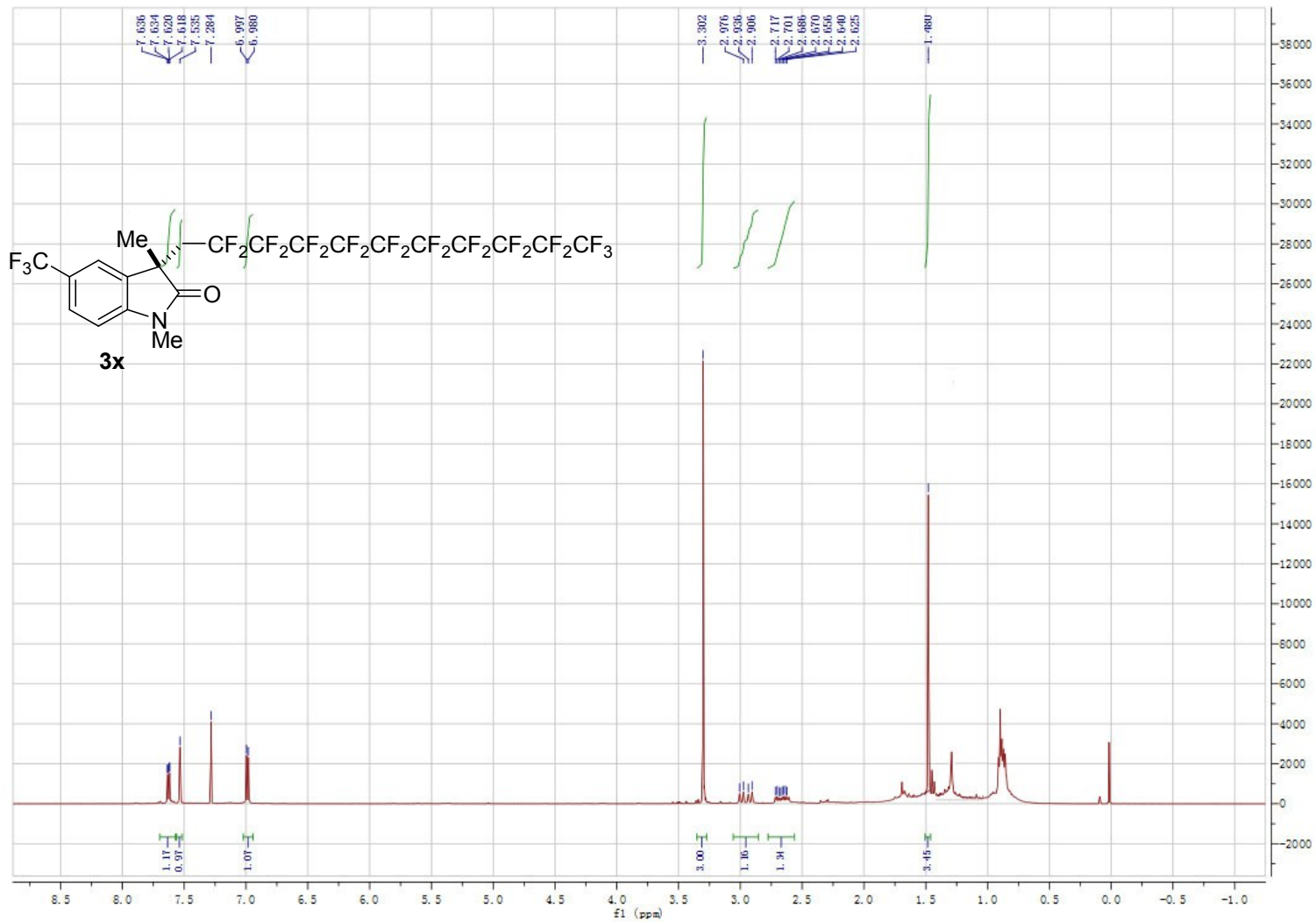
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-1,3,7-trimethylindolin-2-one (3w)



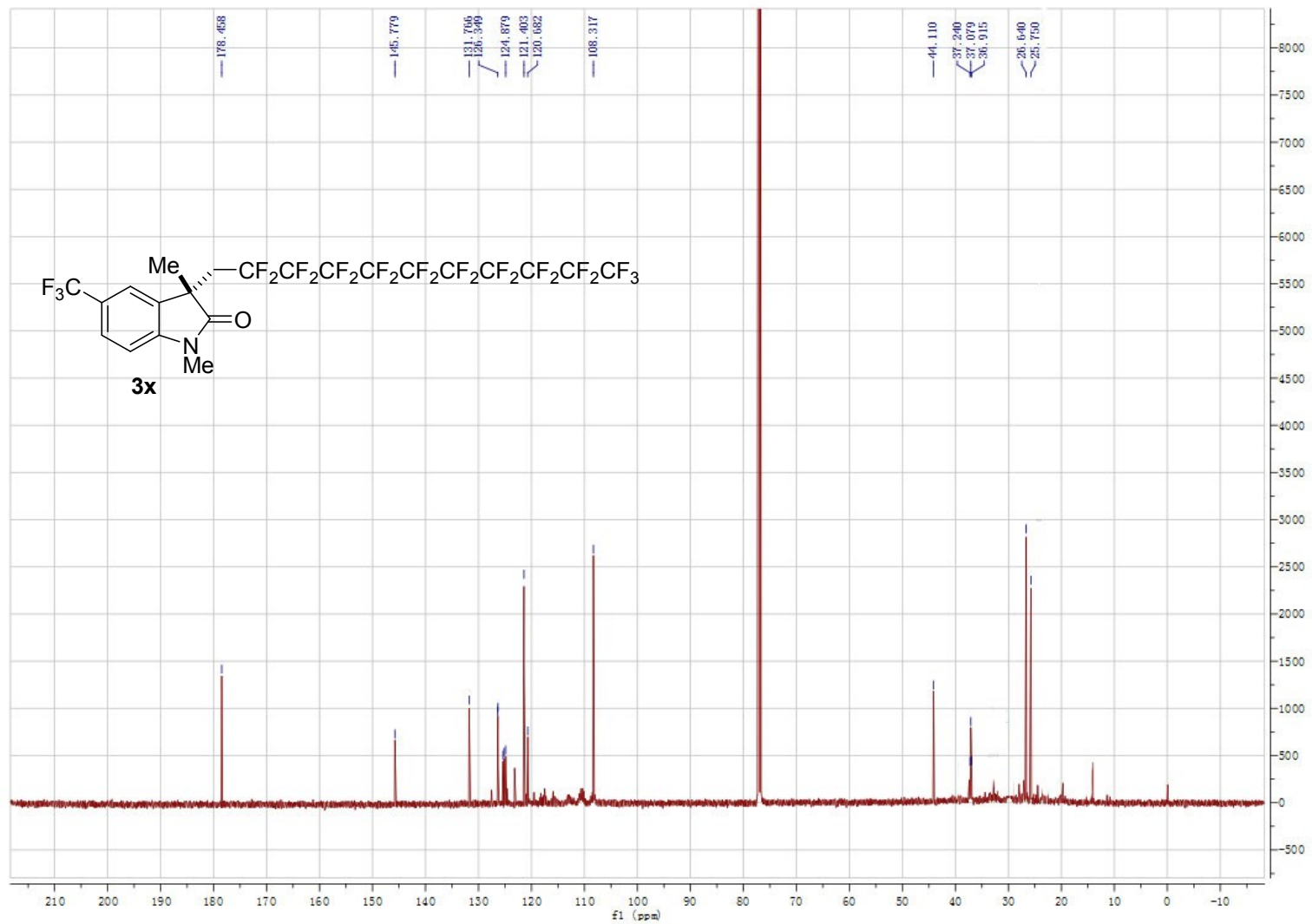
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptafluorononyl)-1,3,7-trimethylindolin-2-one (3w)



3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosafluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)



3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosafuoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)



3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosaflluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)

