Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Solvent- and Additive-free Oxidative Amidation of Aldehydes Using a Recyclable Oxoammonium Salt

Arturo León Sandoval, Katrina E. Doherty, Geoffrey P. Wadey, and Nicholas E. Leadbeater*

Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, Connecticut 06269, USA.
** E-mail: nicholas.leadbeater@uconn.edu*

SUPPORTING INFORMATION

General Considerations

NMR spectra (^{1}H-, ^{13}C-, and ^{19}F-) were performed at 300 K using either a 300 MHz, or 400 MHz spectrometer. ^{1}H-NMR spectra were referenced to residual $CHCl_3$ (7.26 ppm) in $CDCl_3$. ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.16 ppm). ^{19}F-NMR spectra were referenced to hexafluorobenzene (-161.64 ppm).[1] Reactions were monitored by a gas chromatograph attached to a mass spectrometer and / or thin-layer chromatography. High-resolution mass spectra were collected on an Applied Biosystems QSTAR Elite instrument equipped with an electrospray ionization (ESI) source, calibrated using Agilent LC/MS tuning mix. Reactions were monitored by an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer, and/or by TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using UV light.

Chemicals

Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories. 4-Acetamido-TEMPO (ACT, **2**) was prepared using a previously reported protocol.[2] All the starting materials used were purchased from Oakwood Chemicals, Sigma-Aldrich, or Alfa Aesar and distilled before use if required.

Procedure for the Oxidation of Aldehydes to Acyl Pyrazoles

To a 4-dram reaction vial equipped with a stir bar were added the aldehyde (1 mmol, 1 eq), pyrazole (75 mg, 1.1 eq), and 4-acetamido-2,2,6,6-tetramethylpiperidin-1-oxoammonium nitrate, **6** (206 mg, 0.75 eq). The vial was closed tightly and the contents heated at 54 °C for 1 h. Upon completion of the heating step, the reaction mixture was quenched with methanol (1 mL) and the vial contents transferred to a glass separatory funnel, rinsing the reaction vial with diethyl ether (50 mL). Deionized water (10 mL) was added to the separatory funnel and the organic layer washed and separated. The aqueous layer** was then washed with three aliquots of diethyl ether (3 × 30 mL). The organic washes were then combined, placed into a separatory funnel, and washed with 2 M hydrochloric acid (15 mL) followed by saturated aqueous sodium bicarbonate (20 mL). The organic layer was dried over sodium sulfate, and the solvent removed *in vacuo* to afford the product.

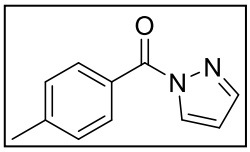
Procedure for Scale-Up of the Reaction

To a 50-mL round-bottom flask, equipped with a stir bar were added **4a** (1.201 g, 10 mmol, 1 eq), pyrazole (0.749 g, 1.1 eq) and 4-acetamido-2,2,6,6-tetramethylpiperidin-1-oxoammonium nitrate, **6** (2.06 g, 0.75 eq). The contents of the flask were heated at 54 °C for 1 h. Upon completion of the heating step, the reaction mixture was quenched with methanol (2 mL) and the vial contents transferred to a glass separatory funnel, rinsing the flask with diethyl ether (50 mL). Deionized water (50 mL) was added to the separatory funnel and the organic layer washed and separated. The aqueous layer was then washed with three aliquots of diethyl ether (3 × 50 mL). The organic washes were then combined, placed into a separatory funnel, and washed with 2 M hydrochloric acid (30 mL) followed by saturated aqueous sodium bicarbonate (40 mL). The organic layer was dried over sodium sulfate, and the solvent removed *in vacuo* to afford the product.

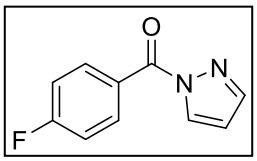
Procedure for the recovery of the spent nitroxide

After performing the workup of an oxidation reaction, the aqueous layer (indicated in the above procedure as **) was taken aside and the water removed by evaporation to leave an orange-brown solid. The solid was dissolved in ethyl acetate (15 mL), the resultant solution transferred to a separatory funnel and this washed with saturated aqueous sodium bicarbonate (3 mL). The organic layer was dried over sodium sulfate, and the solvent removed *in vacuo* to afford 4-Acetamido-TEMPO, **2**.

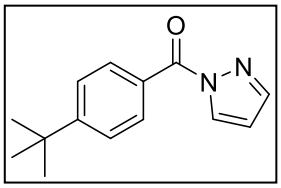
Product characterization



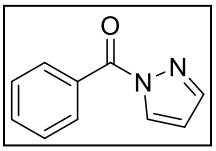
(1*H*-Pyrazol-1-yl)(*p*-tolyl)methanone (7a). Obtained as a white solid (0.153 g, 82%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 8.43 (dd, J = 2.9, 0.7 Hz, 1H), 8.09 – 8.00 (m, 2H), 7.79 (dd, J = 1.5, 0.7 Hz, 1H), 7.35 – 7.26 (m, 2H), 6.51 (dd, J = 2.9, 1.5 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 166.31, 144.33, 143.98, 131.70, 130.44, 128.88, 128.64, 109.28, 21.74. Spectral data for this compound is consistent with that previously reported.[3]



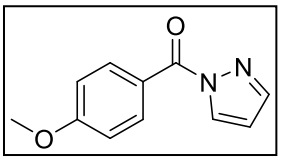
(4-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7b). Obtained as a white solid (0.137 g, 72%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.44 (d, J = 2.9 Hz, 1H), 8.29 – 8.19 (m, 2H), 7.80 (d, J = 1.5 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.53 (dd, J = 2.9, 1.5 Hz, 1H).**^{13}C NMR** (101 MHz, Chloroform-d) δ 165.80 (d, J = 255.4 Hz), 165.15, 144.67, 134.60 (d, J = 9.4 Hz), 130.64, 127.67 (d, J = 3.1 Hz), 115.48 (d, J = 21.9 Hz), 109.61.-**^{19}F NMR** (376 MHz, Chloroform-d) δ -104.61 (tt, J = 8.2, 5.4 Hz). Spectral data for this compound is consistent with that previously reported.[4]



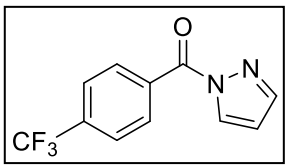
(4-(*tert*-Butyl)phenyl)(1*H*-pyrazol-1-yl)methanone (7c). Obtained as a white solid (0.199 g, 87%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.47 (dd, J = 2.9, 0.7 Hz, 1H), 8.16 – 8.07 (m, 2H), 7.83 (dd, J = 1.5, 0.7 Hz, 1H), 7.61 – 7.52 (m, 2H), 6.54 (dd, J = 2.9, 1.5 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.34, 156.89, 144.41, 131.58, 130.48, 128.64, 125.27, 109.31, 35.23, 31.14. Spectral data for this compound is consistent with that previously reported. [5]



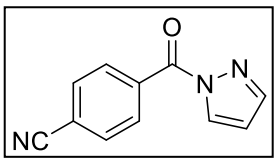
Phenyl(1*H*-pyrazol-1-yl)methanone (7d). Obtained as a clear oil (0.112 g, 65%) was prepared according to general procedure from benzaldehyde ***with the following modifications*** 1) 1.2 equiv of pyrazole was used 2) reaction was run for 20 minutes.**^{1}H NMR** (400 MHz, Chloroform-d) δ 8.44 (d, J = 2.8 Hz, 1H), 8.17 – 8.09 (m, 2H), 7.81 (d, J = 1.5 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.51 (dd, J = 8.4, 7.1 Hz, 2H), 6.52 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.45, 144.55, 133.05, 131.54, 130.47, 128.15, 109.49. Spectral data for this compound is consistent with that previously reported.[6]



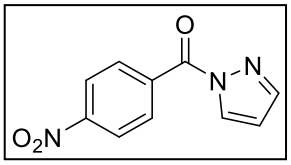
(4-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7e). Obtained as a white solid (0.158 g, 78%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.43 (dd, J = 2.8, 0.7 Hz, 1H), 8.26 – 8.18 (m, 2H), 7.82 – 7.77 (m, 1H), 7.04 – 6.95 (m, 2H), 6.50 (dd, J = 2.8, 1.5 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.43, 163.64, 144.11, 134.22, 130.55, 123.52, 113.55, 108.99, 55.52. Spectral data for this compound is consistent with that previously reported.[3]



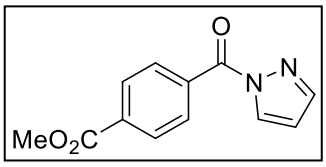
(1*H*-Pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (7f). Obtained as a colorless oil (0.175 g, 73%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.45 (d, J = 2.9 Hz, 1H), 8.23 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 1.5 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 6.55 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.31, 145.03, 134.90, 134.28 (q, J = 32.7 Hz), 131.84, 130.40, 125.09 (q, J = 3.7 Hz), 123.61 (q, J = 272.8 Hz), 110.05. **^{19}F NMR** (376 MHz, Chloroform-d) δ -63.08. Spectral data for this compound is consistent with that previously reported.[3]



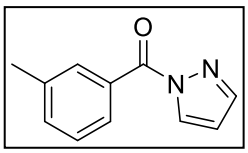
4-(1*H*-Pyrazole-1-carbonyl)benzonitrile (7g). Obtained as a white solid (0.144 g, 73%) **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.46 (dd, J = 2.9, 0.7 Hz, 1H), 8.27 – 8.20 (m, 2H), 7.84 – 7.76 (m, 3H), 6.58 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 164.83, 145.19, 135.45, 131.95, 131.78, 130.40, 117.87, 116.28, 110.26. Spectral data for this compound is consistent with that previously reported.[3]



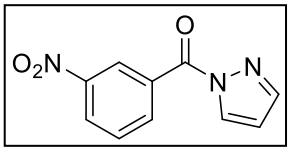
(4-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7h). Obtained as an off white solid (0.178 g, 82%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.47 (d, J = 2.9 Hz, 1H), 8.39 – 8.32 (m, 2H), 8.30 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 1.5 Hz, 1H), 6.59 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 164.65, 150.10, 145.33, 132.55, 130.42, 123.12, 110.41. Spectral data for this compound is consistent with that previously reported.[4]



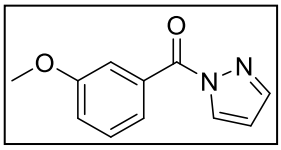
Methyl 4-(1*H*-pyrazole-1-carbonyl)benzoate (7i). Obtained as an yellow solid (0.180 g, 78%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.45 (dd, J = 2.9, 0.8 Hz, 1H), 8.16 (s, 4H), 7.84 – 7.79 (m, 1H), 6.55 (dd, J = 3.0, 1.5 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.27, 165.86, 144.99, 135.50, 133.84, 131.46, 130.47, 129.28, 110.00, 52.61.Spectral data for this compound is consistent with that previously reported.[3]



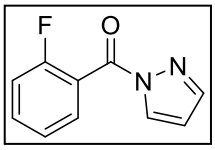
(1*H*-Pyrazol-1-yl)(*m*-tolyl)methanone (7j). Obtained as a colorless oil (0.130 g, 70%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.43 (dd, J = 2.8, 0.7 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.80 (d, J = 1.4 Hz, 1H), 7.46 – 7.32 (m, 2H), 6.52 (dd, J = 2.8, 1.5 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.67, 144.46, 137.97, 133.83, 131.83, 131.52, 130.45, 128.67, 128.02, 109.40, 21.38. Spectral data for this compound is consistent with that previously reported.[5]



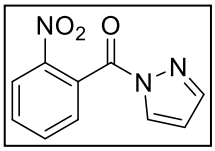
(3-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7k). Obtained as a white solid (0.159 g, 73%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.45 (d, J = 2.8 Hz, 1H), 8.25 (dd, J = 8.2, 1.2 Hz, 1H), 7.81 (td, J = 7.5, 1.2 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.63 (d, J = 1.5 Hz, 1H), 6.53 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.24, 147.14, 145.25, 134.06, 131.53, 129.94, 129.58, 128.97, 124.14, 110.50. Spectral data for this compound is consistent with that previously reported. [5]



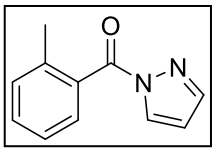
(3-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7l). Obtained as a yellow oil (0.168 g, 83%) was prepared according to general procedure from benzaldehyde ***with the following modification*** reaction was run for 20 minutes. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.43 (d, J = 2.8 Hz, 1H), 7.81 (d, J = 1.5 Hz, 1H), 7.72 (dt, J = 7.7, 1.2 Hz, 1H), 7.65 (dd, J = 2.7, 1.5 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.16 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 6.53 (dd, J = 2.9, 1.4 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 159.24, 144.56, 132.68, 130.55, 129.18, 124.00, 119.37, 116.23, 109.49, 55.51. **HRMS:** (ESI) m/z calculated for C11H11N2O2+ $[M+H]^{+}$ 203.0815, found 203.0858.



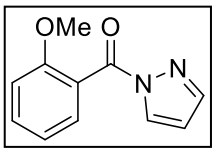
(2-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7m). Obtained as a white solid (0.141 g, 74%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.37 (d, J = 2.9 Hz, 1H), 7.75 (d, J = 1.5 Hz, 1H), 7.65 (ddd, J = 8.1, 6.7, 1.8 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.30 – 7.22 (m, 1H), 7.18 (ddd, J = 9.6, 8.4, 1.0 Hz, 1H), 6.51 (dd, J = 2.9, 1.4 Hz, 1H). **^{13}C NMR** 13C NMR (101 MHz, Chloroform-d) δ 164.19, 160.17 (d, J = 254.5 Hz), 145.01, 133.78 (d, J = 8.6 Hz), 131.00, 129.44, 123.97, 121.51 (d, J = 14.7 Hz), 116.29 (d, J = 21.3 Hz), 110.24. **^{19}F NMR** (376 MHz, Chloroform-d) δ -110.62 (dt, J = 9.9, 5.9 Hz). Spectral data for this compound is consistent with that previously reported.[5]



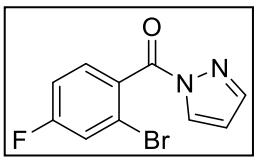
(2-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7n). Obtained as an off yellow powder (0.176 g, 81%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 8.45 (d, J = 2.9 Hz, 1H), 8.25 (dd, J = 8.1, 1.3 Hz, 1H), 7.89 – 7.60 (m, 4H), 6.53 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 165.26, 145.27, 134.08, 131.54, 129.92, 129.57, 128.97, 124.14, 110.52. Spectral data for this compound is consistent with that previously reported.[3]



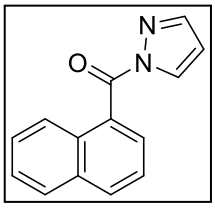
(1*H*-Pyrazol-1-yl)(*o*-tolyl)methanone (7o). Obtained as a yellow oil (0.149 g, 80%).**^{1}H NMR** (400 MHz, Chloroform-d) δ 8.38 (dd, J = 2.8, 0.6 Hz, 1H), 7.76 (d, J = 1.4 Hz, 1H), 7.51 (dd, J = 8.2, 1.3 Hz, 1H), 7.44 (td, J = 7.5, 1.4 Hz, 1H), 7.34 – 7.27 (m, 2H), 6.52 (dt, J = 2.3, 1.1 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 168.16, 144.96, 137.37, 132.64, 131.30, 130.87, 129.72, 129.23, 125.35, 109.95, 19.86. **HRMS:** (ESI) m/z calculated for C11H11N2O+ $[M+H]^+$ 187.0866, found 187.0868.



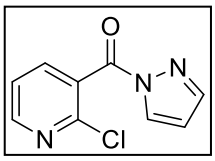
(2-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7p). Obtained as a yellow solid (0.168 g, 83%) was prepared according to general procedure from benzaldehyde ***with the following modification*** reaction was run for 20 minutes. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.33 (dd, J = 2.9, 0.7 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.55 – 7.43 (m, 2H), 7.10 – 6.98 (m, 2H), 6.48 (dd, J = 2.9, 1.4 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.54, 157.53, 144.57, 132.80, 129.87, 129.47, 122.87, 120.31, 111.69, 109.66, 55.93. **HRMS:** (ESI) m/z calculated for C11H11N2O2+ $[M+H]^+$ 203.0815, found 203.0842.



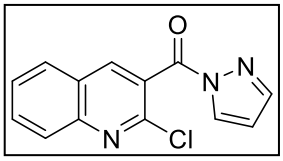
(2-Bromo-4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7q). Obtained as a white solid (0.175 g, 65%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.39 (dd, J = 3.0, 0.7 Hz, 1H), 7.76 (d, J = 1.4 Hz, 1H), 7.52 (dd, J = 8.6, 5.7 Hz, 1H), 7.42 (dd, J = 8.2, 2.5 Hz, 1H), 7.16 (ddd, J = 8.6, 7.9, 2.4 Hz, 1H), 6.55 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.64, 163.56 (d, J = 256.0 Hz), 145.40, 131.61 (d, J = 9.3 Hz), 129.51, 121.62 (d, J = 9.6 Hz), 120.87 (d, J = 24.7 Hz), 114.66 (d, J = 21.8 Hz), 110.70. **^{19}F NMR** (376 MHz, Chloroform-d) δ -106.34 (td, J = 8.1, 5.6 Hz). Spectral data for this compound is consistent with that previously reported.[3]



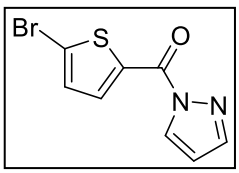
Naphtalen-1-yl(1*H*-pyrazol-1-yl)methanone (7r). Obtained as a yellow solid (0.156 g, 70%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.48 (d, J = 2.8 Hz, 1H), 8.05 (dt, J = 8.3, 1.1 Hz, 1H), 8.05 – 7.96 (m, 1H), 7.96 – 7.88 (m, 1H), 7.82 (dd, J = 7.1, 1.2 Hz, 1H), 7.76 (d, J = 1.4 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.53 (d, J = 3.3 Hz, 1H), 6.55 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.45, 144.94, 133.59, 132.28, 130.96, 130.18, 129.86, 128.97, 128.67, 127.64, 126.63, 125.07, 124.34, 110.05. Spectral data for this compound is consistent with that previously reported.[3]



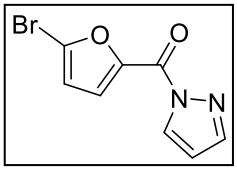
(2-Chloropyridin-3-yl)(1*H*-pyrazol-1-yl)methanone (7s). Obtained as a white solid (0.129 g, 62%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 8.57 (dd, J = 4.9, 1.9 Hz, 1H), 8.42 (dd, J = 2.9, 0.7 Hz, 1H), 7.89 (dd, J = 7.6, 1.9 Hz, 1H), 7.77 (dd, J = 1.4, 0.7 Hz, 1H), 7.40 (dd, J = 7.6, 4.9 Hz, 1H), 6.58 (dd, J = 2.9, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 151.34, 148.32, 145.51, 138.52, 129.83, 129.23, 121.79, 110.92. Spectral data for this compound is consistent with that previously reported.[3]



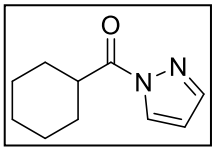
(2-Chloroquinolin-3-yl)(1*H*-pyrazol-1-yl)methanone (7t). Obtained as a yellow solid (0.134 g, 52%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 8.43 (d, J = 3.0 Hz, 1H), 8.36 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.89 – 7.75 (m, 2H), 7.75 – 7.69 (m, 1H), 7.59 (t, J = 7.6 Hz, 1H), 6.56 (dd, J = 2.9, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 164.28, 148.03, 146.27, 145.41, 139.47, 132.27, 129.31, 128.58, 128.29, 127.95, 127.22, 125.52, 110.85. Spectral data for this compound is consistent with that previously reported.[4]



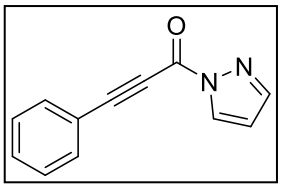
(5-bromothiophen-2-yl)(1*H*-pyrazol-1-yl)methanone (7u). Obtained as a white solid (0.177 g, 69%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.40 (d, J = 2.8 Hz, 1H), 8.13 (d, J = 4.2 Hz, 1H), 7.81 (d, J = 1.5 Hz, 1H), 7.18 (d, J = 4.2 Hz, 1H), 6.52 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.61, 144.02, 138.54, 130.24, 129.55, 127.17, 110.05. Spectral data for this compound is consistent with that previously reported.[3]



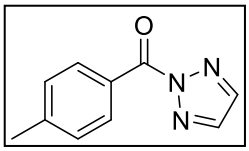
(5-bromofuran-2-yl)(1*H*-pyrazol-1-yl)methanone (7v). Obtained as a yellow solid (0.202 g, 84%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.42 (d, J = 2.8 Hz, 1H), 8.04 (d, J = 3.7 Hz, 1H), 7.78 (d, J = 1.5 Hz, 1H), 6.58 (d, J = 3.7 Hz, 1H), 6.50 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.68, 146.69, 144.68, 130.79, 130.01, 126.96, 114.81, 109.47. Spectral data for this compound is consistent with that previously reported.[3]



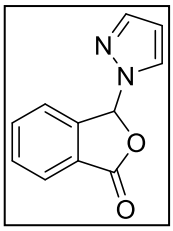
Cyclohexyl(1*H*-pyrazol-1-yl)methanone (7w). Obtained as a clear oil (0.103 g, 58%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 2.7 Hz, 1H), 7.71 (d, *J* = 1.5 Hz, 1H), 6.42 (dd, *J* = 2.9, 1.5 Hz, 1H), 3.64 (tt, *J* = 11.6, 3.5 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.84 (dt, *J* = 12.9, 3.5 Hz, 2H), 1.74 (dddd, *J* = 12.7, 5.1, 3.4, 1.7 Hz, 1H), 1.57 (qd, *J* = 12.3, 3.3 Hz, 2H), 1.42 (qt, *J* = 12.6, 3.3 Hz, 2H), 1.30 (tt, *J* = 12.3, 3.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 174.87, 143.52, 128.17, 109.13, 41.31, 28.86, 25.53, 25.18. Spectral data for this compound is consistent with that previously reported.[3]



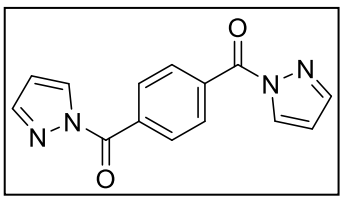
3-phenyl-1-(1*H*-pyrazol-1-yl)prop-2-yn-1-one (7z). Obtained as a orange solid (0.161 g, 82%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.31 (d, J = 2.9 Hz, 1H), 7.85 (d, J = 1.4 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.52 – 7.46 (m, 1H), 7.41 (dd, J = 8.2, 6.7 Hz, 2H), 6.52 (dd, J = 2.9, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 150.79, 145.49, 133.44, 131.38, 129.58, 128.73, 119.38, 110.44, 95.46, 81.28. Spectral data for this compound is consistent with that previously reported.[3]



***p*-Tolyl(2*H*-1,2,3-triazol-2-yl)methanone (7ae).** Obtained as a white solid (0.072 g, 39%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 – 7.99 (m, 2H), 7.97 (s, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.39, 145.04, 138.10, 132.05, 129.12, 127.50, 21.81. Spectral data for this compound is consistent with that previously reported.[5]



3-(1*H*-pyrazol-1-yl)isobenzofuran-1(3*H*)-one (7ai). Obtained as a colorless solid (0.170 g, 85%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.99 (dt, J = 7.5, 1.0 Hz, 1H), 7.73 (dtd, J = 24.9, 7.5, 1.1 Hz, 2H), 7.63 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 7.5, 1.0 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.34 (s, 1H), 6.35 (dd, J = 2.6, 1.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.90, 143.67, 141.93, 135.03, 131.35, 129.09, 126.91, 125.95, 123.79, 108.00, 87.51. Spectral data for this compound is consistent with that previously reported.[7]



1,4-phenylenebis((1*H*-pyrazol-1-yl)methanone) (7aj). Obtained as a white solid (0.152 g, 57%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.38 (d, *J* = 2.9 Hz, 1H), 7.86 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.73 (d, *J* = 1.4 Hz, 1H), 7.37 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.55 (dd, *J* = 3.0, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.69, 145.03, 135.33, 131.14, 130.53, 110.05. Spectral data for this compound is consistent with that previously reported.[8]

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(3) Ovian, J. M.; Kelly, C. B.; Pistritto, V. A.; Leadbeater, N. E. *Org. Lett.* **2017**, *19*, 1286-1289.

(4) Nandi, J.; Ovian, J. M.; Kelly, C. B.; Leadbeater, N. E. *Org. Biomol. Chem.* **2017**, *15*, 8295-8301.

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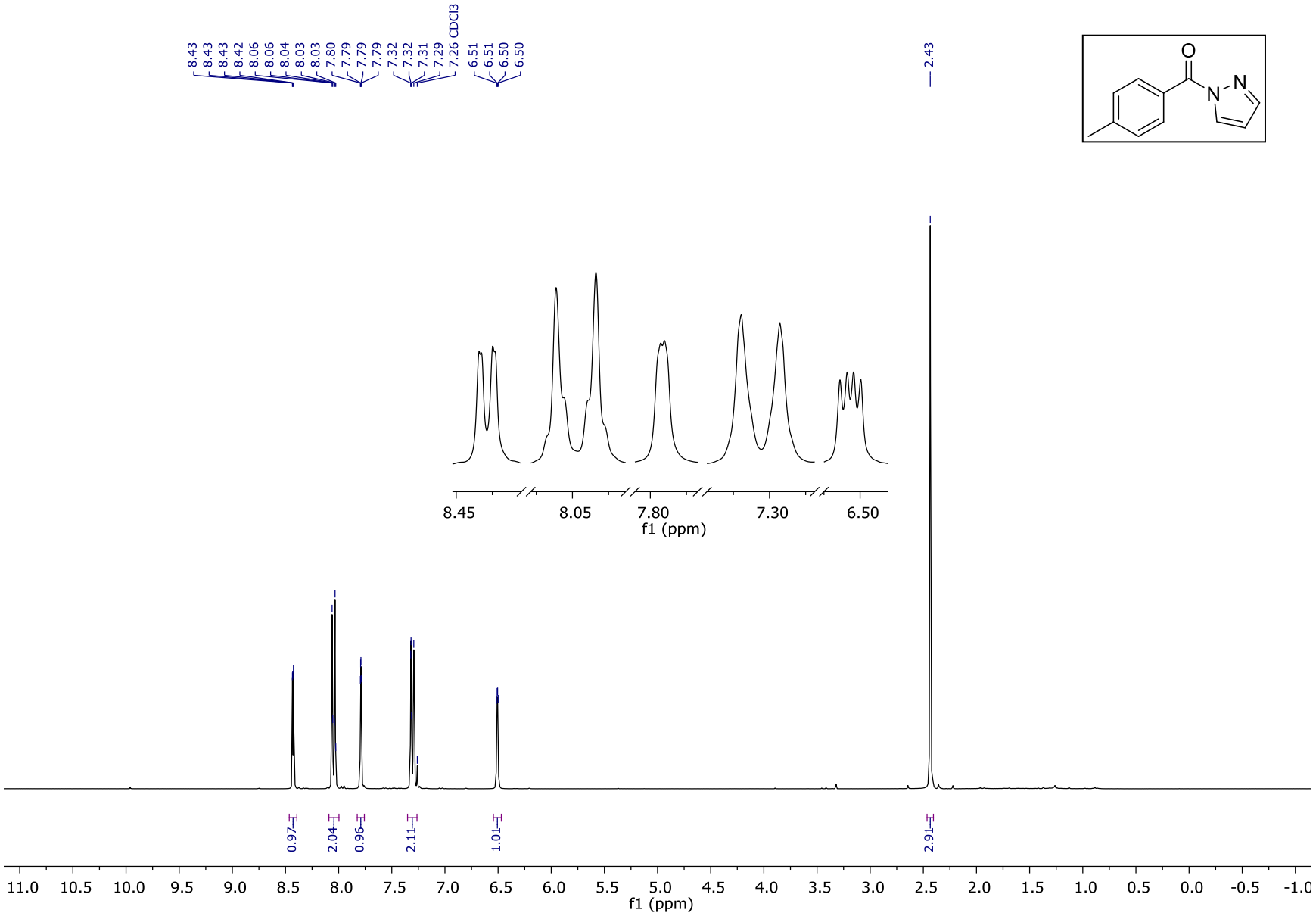
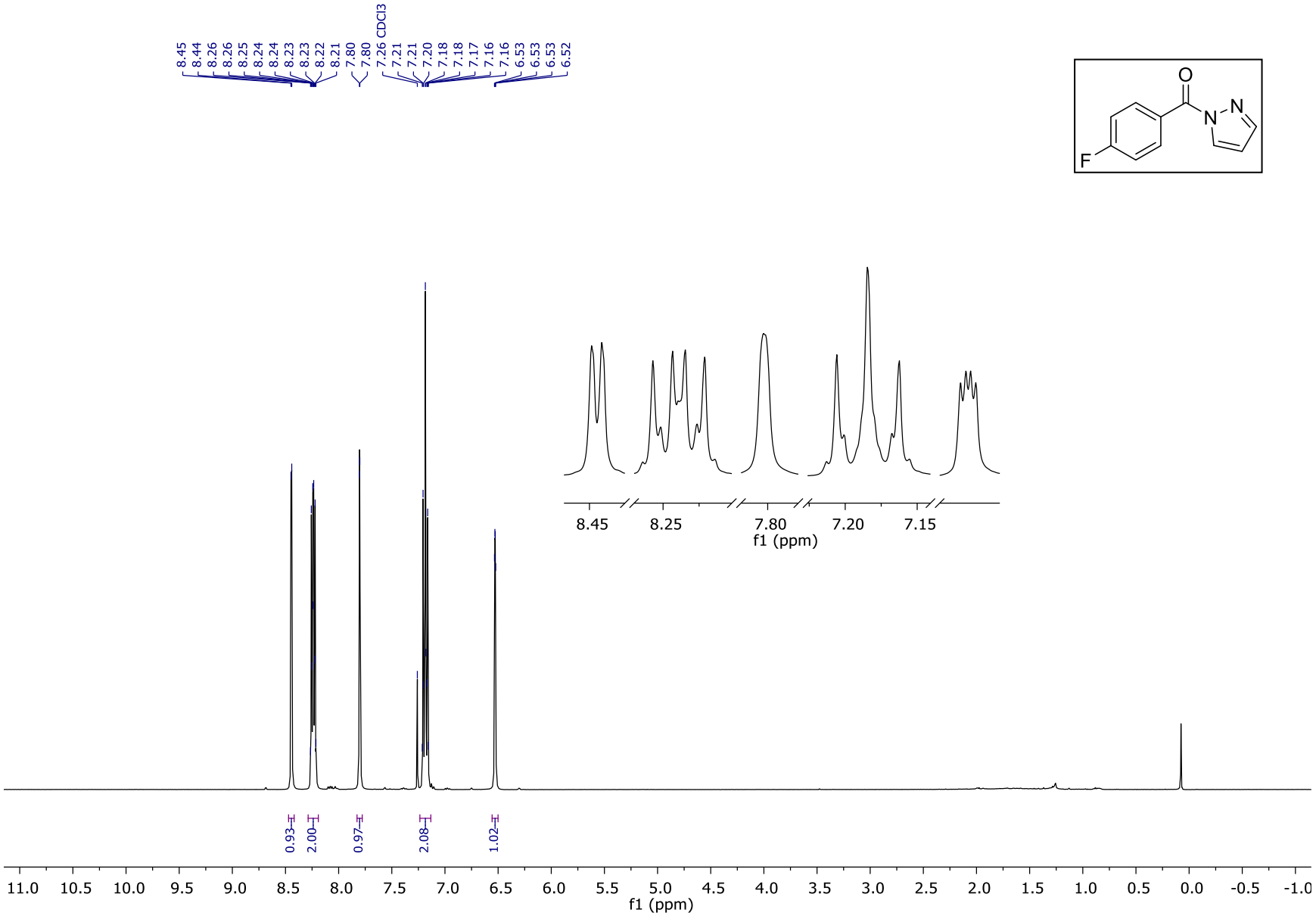
(8) Khan, E.; Khalid, M.; Gul, Z.; Shahzad, A.; Tahir, M. N.; Asif, H. M.; Asim, S.; Braga, A. A. C. *J. Mol. Struct.* **2020**, *1205*, 127633.

^{1}H-, ^{13}C- and ^{19}F-NMR spectra of synthesized compounds

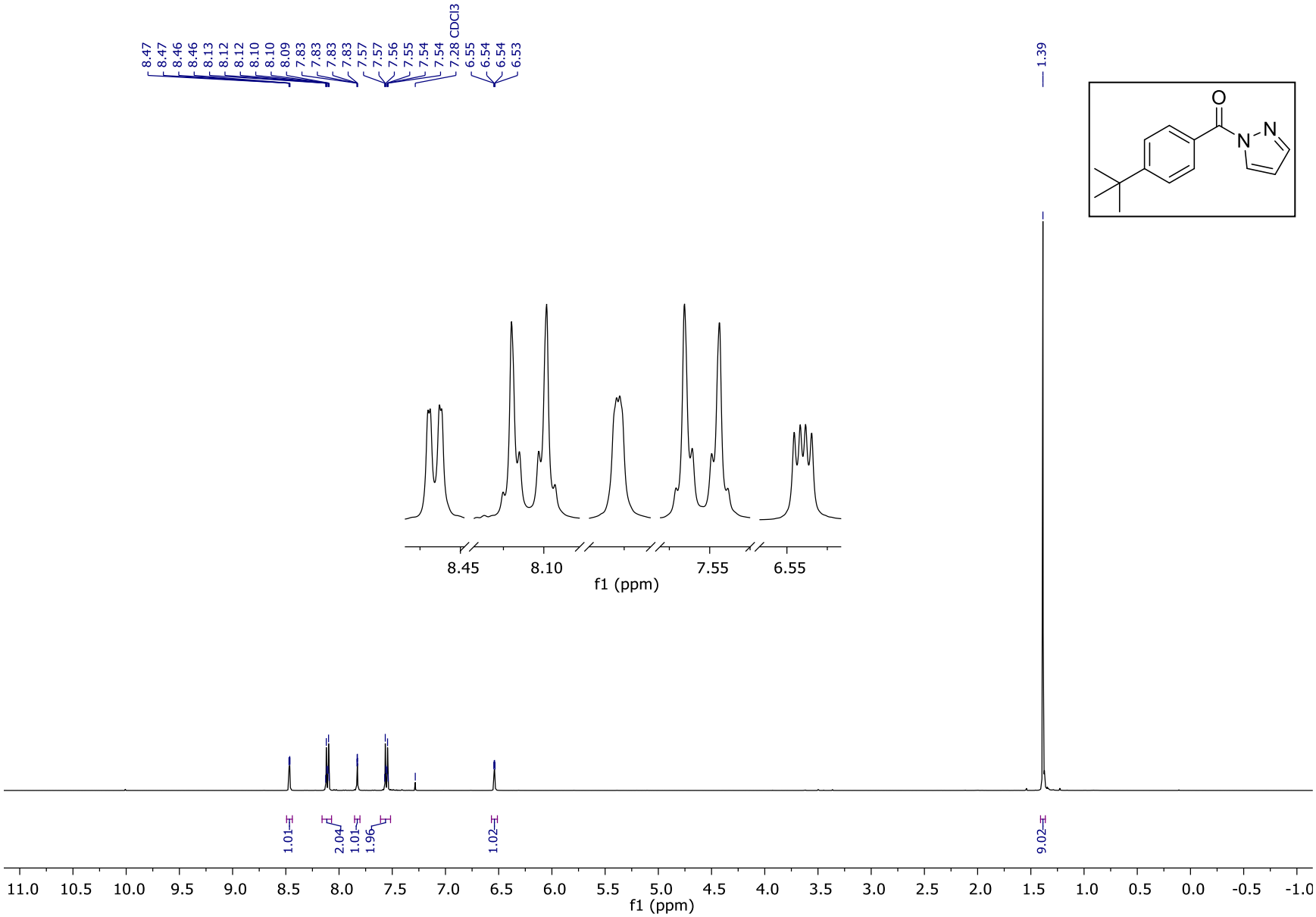
^{1}H-NMR (300 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*p*-tolyl)methanone (7a)



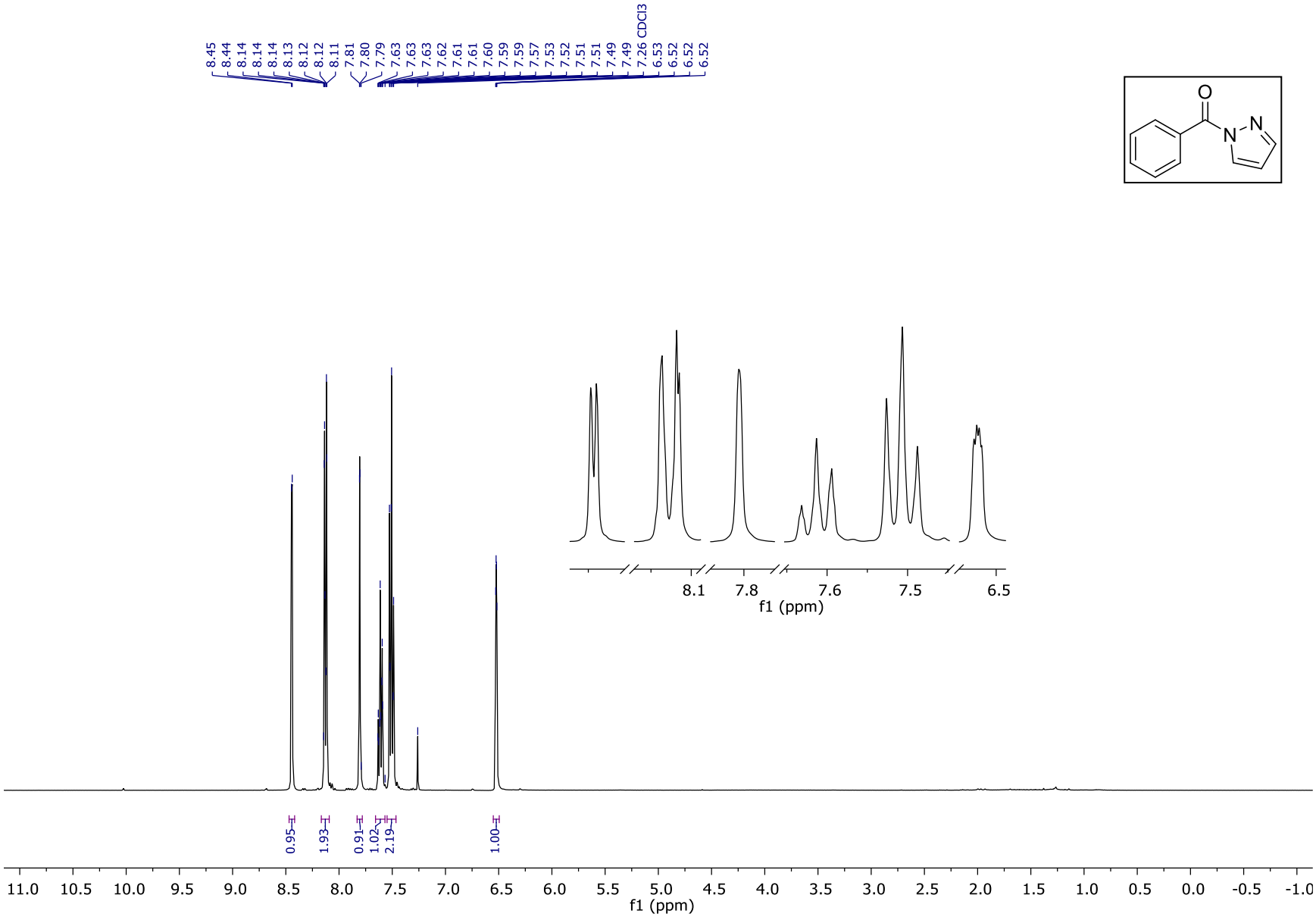
^{1}H-NMR (400 MHz $CDCl_3$) (4-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7b)



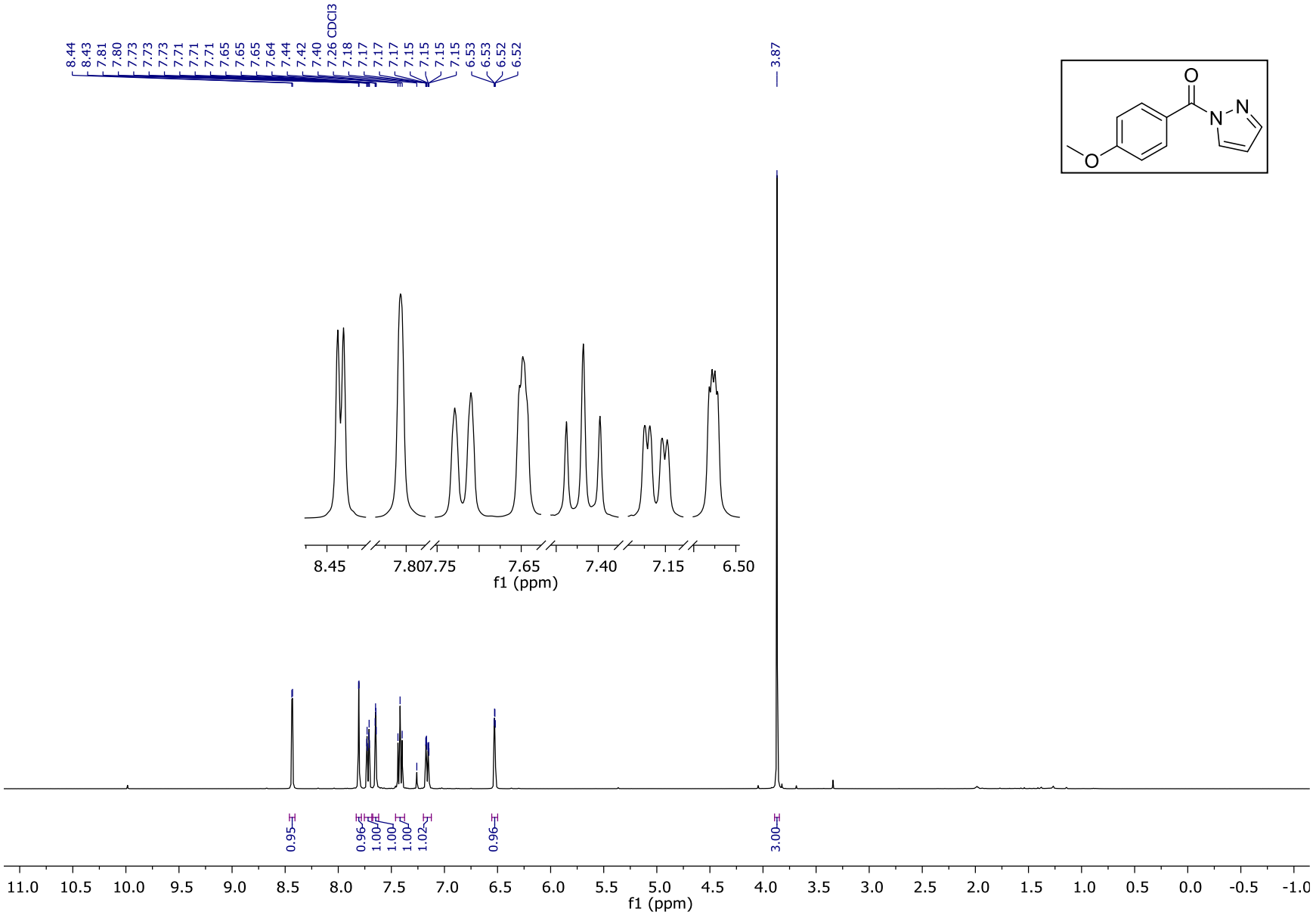
^{1}H-NMR (400 MHz $CDCl_3$) (4-(*tert*-Butyl)phenyl)(1*H*-pyrazol-1-yl)methanone (7c)



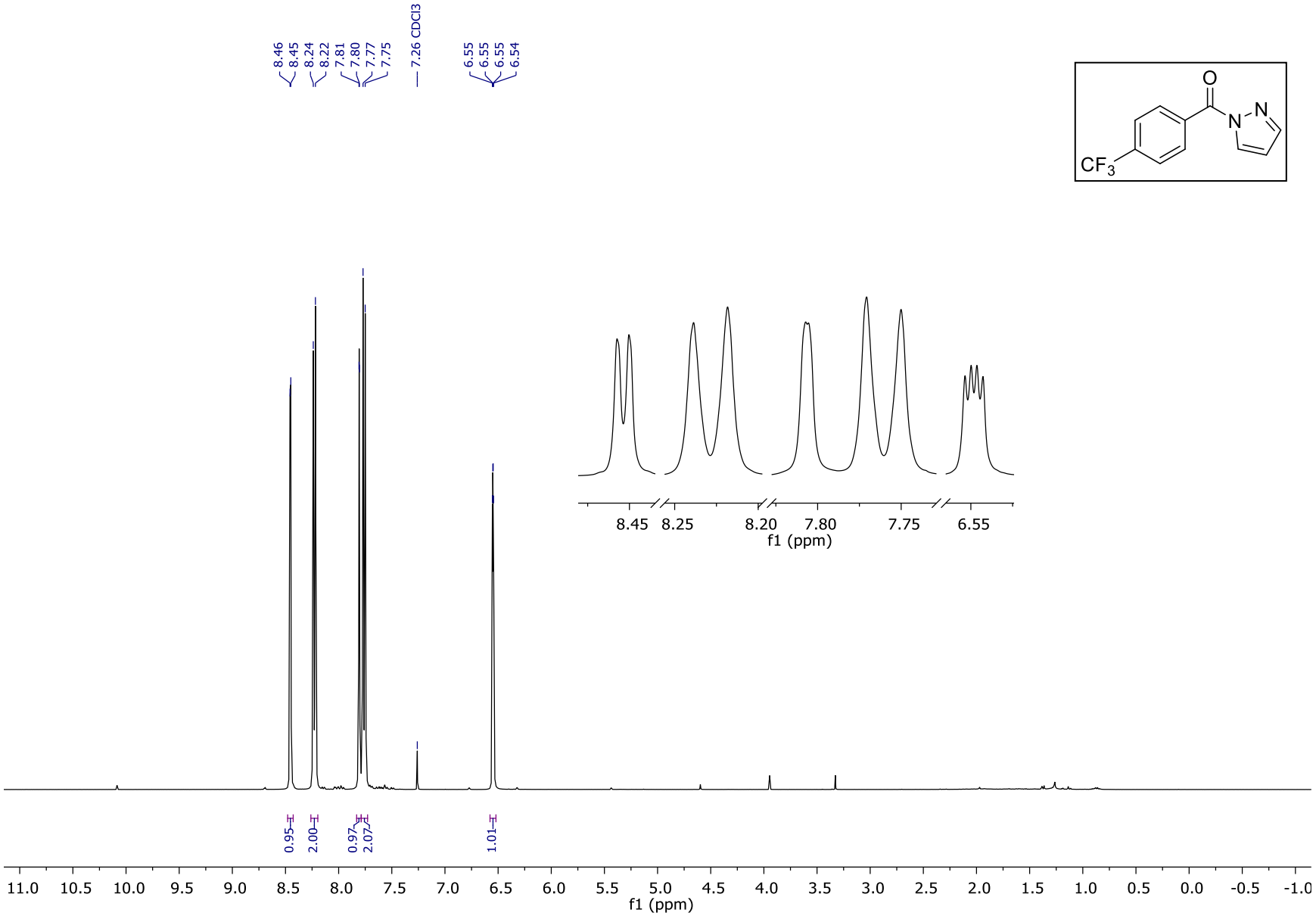
^{1}H-NMR (400 MHz $CDCl_3$) Phenyl(1*H*-pyrazol-1-yl)methanone (7d)



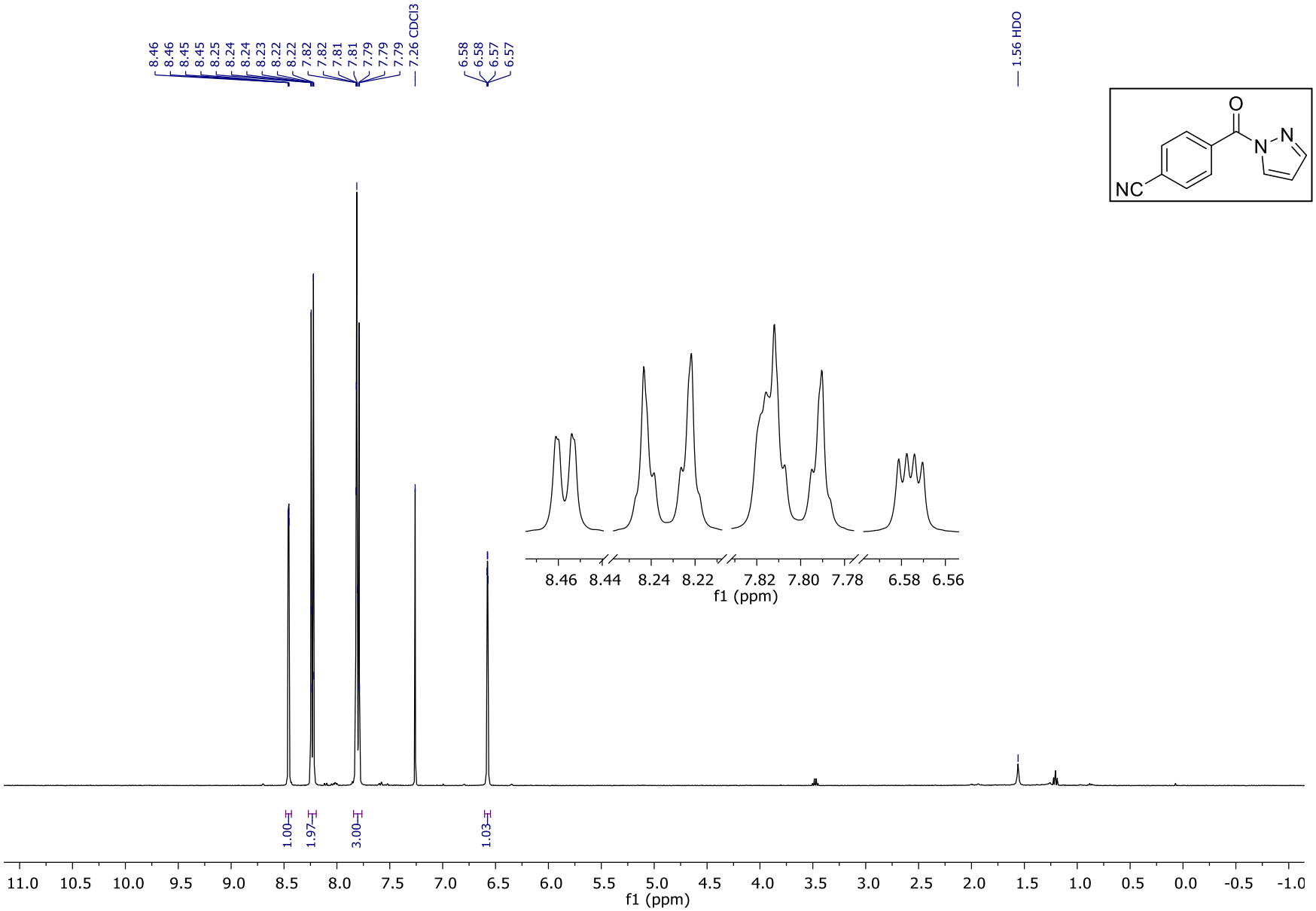
^{1}H-NMR (400 MHz $CDCl_3$) (4-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7e)



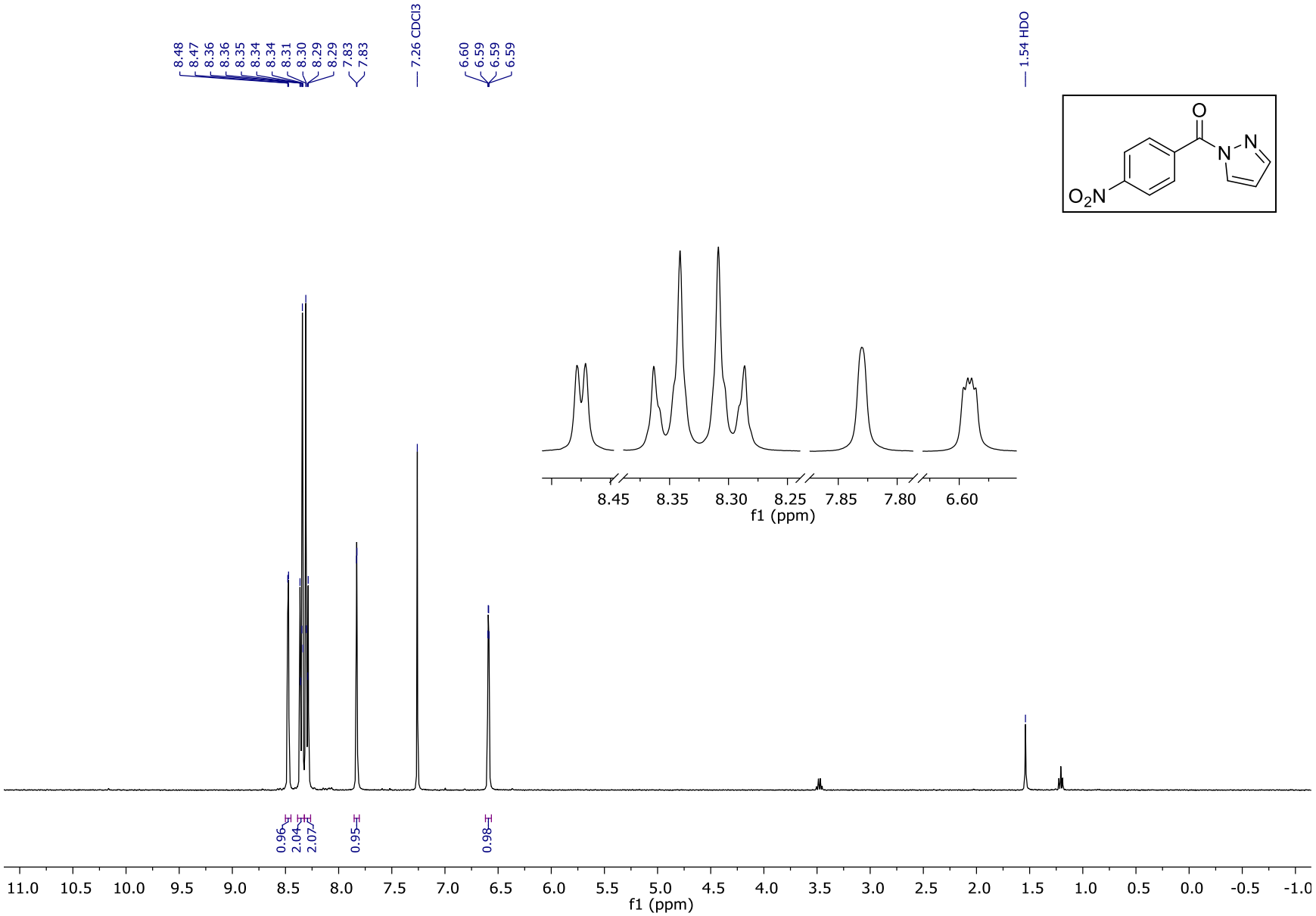
^{1}H-NMR (400 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (7f)



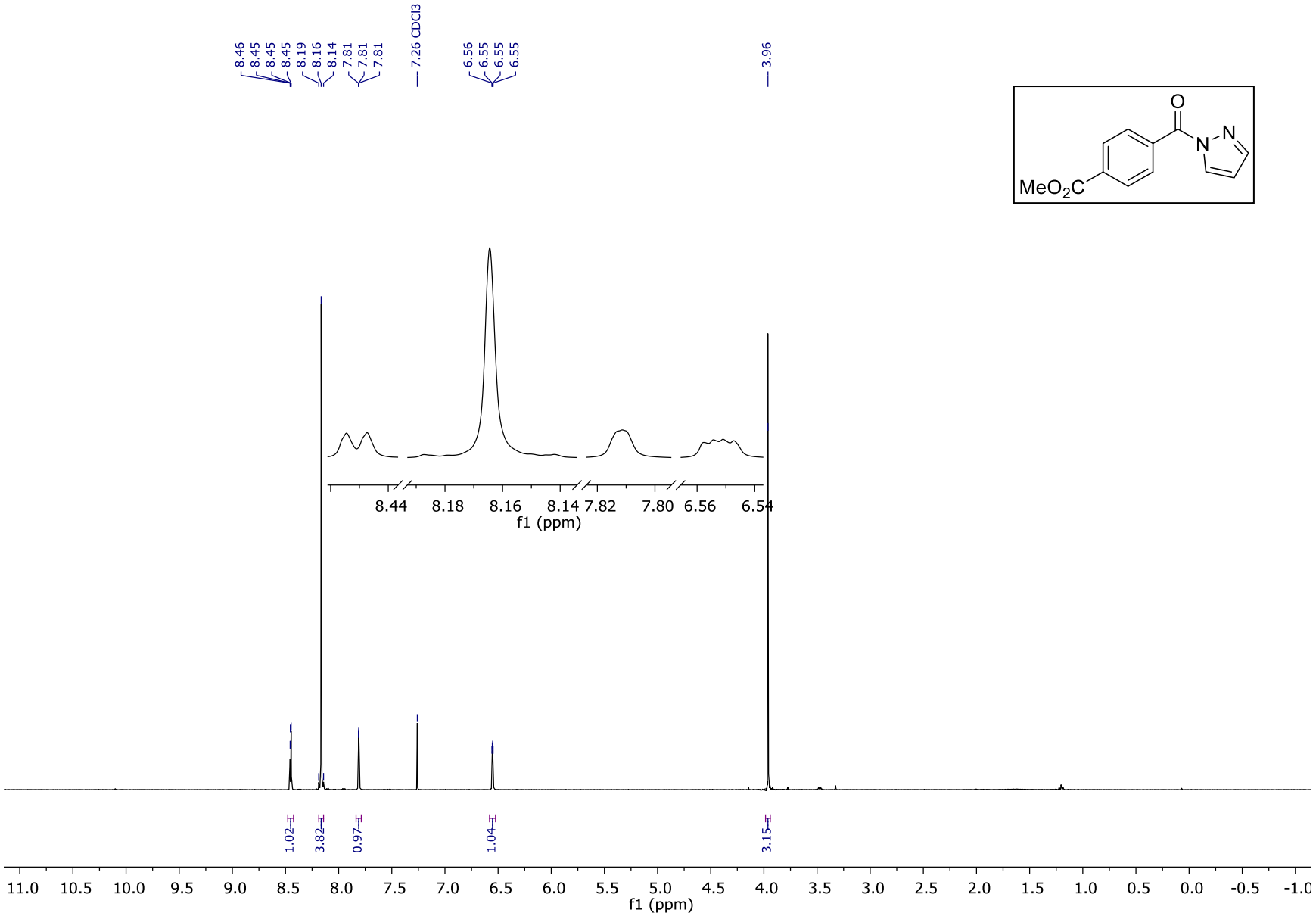
^{1}H-NMR (400 MHz $CDCl_3$) 4-(1*H*-Pyrazole-1-carbonyl)benzonitrile (7g)



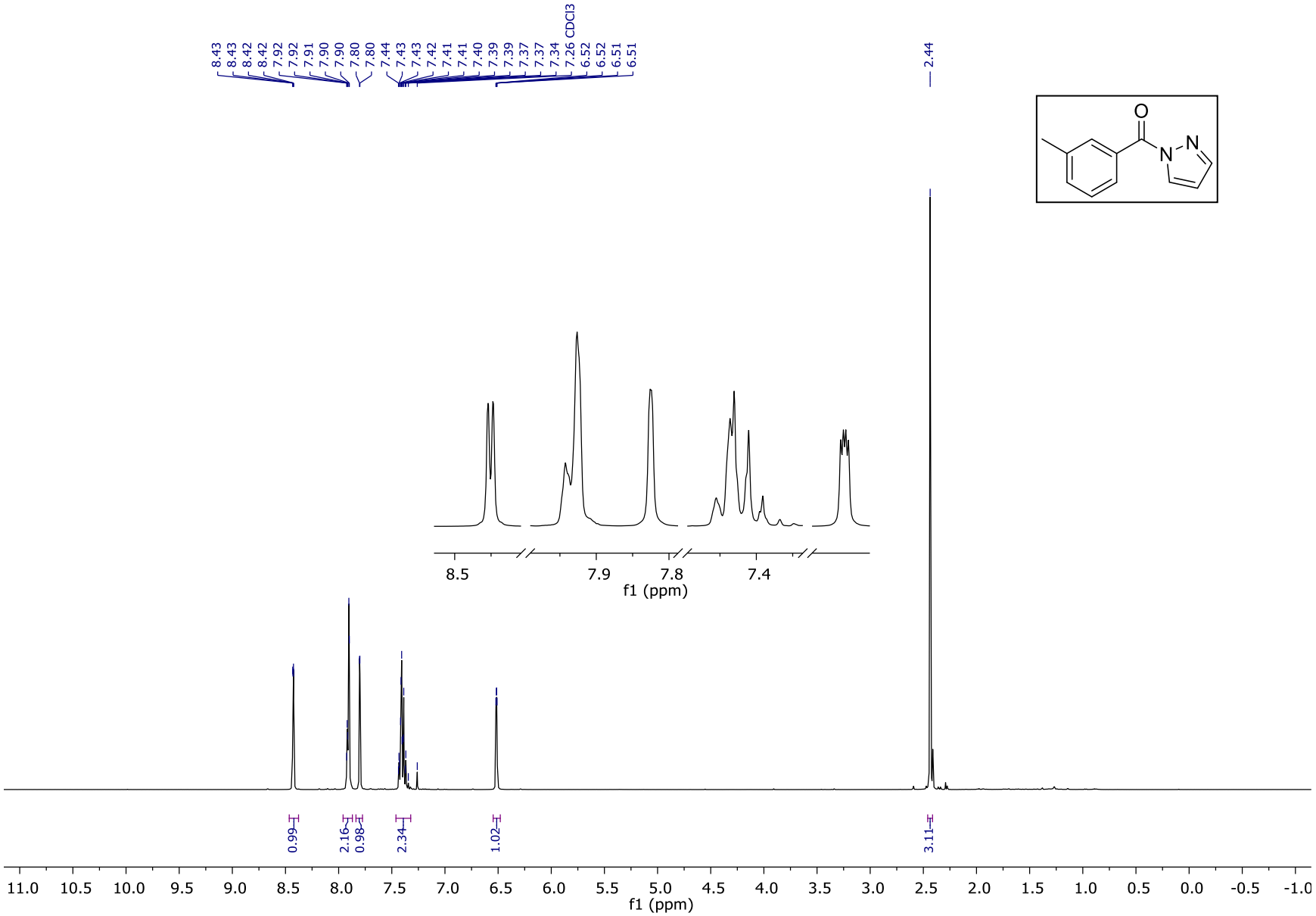
^{1}H-NMR (400 MHz $CDCl_3$) (4-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7h)



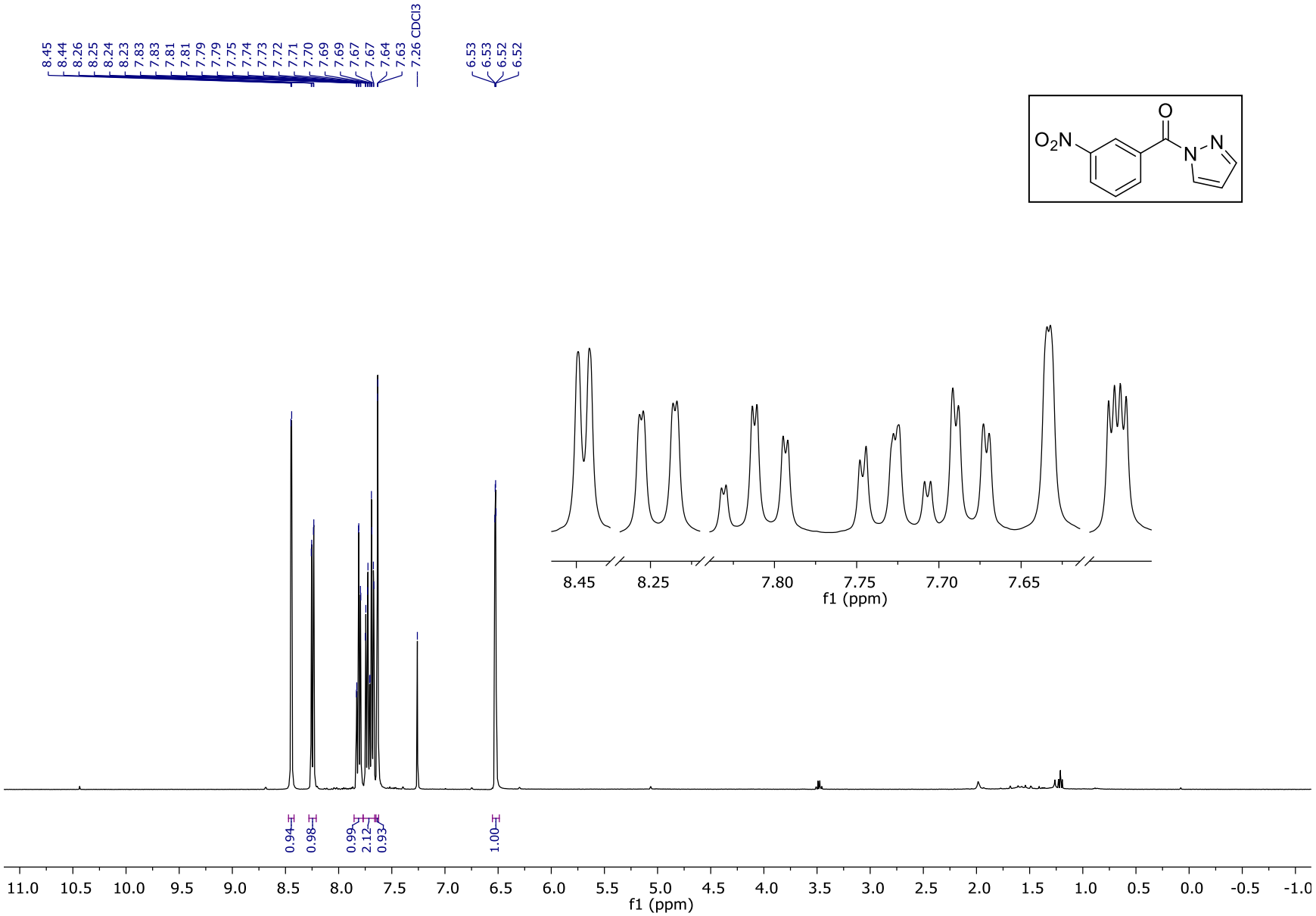
^{1}H-NMR (400 MHz $CDCl_3$) Methyl 4-(1*H*-pyrazole-1-carbonyl)benzoate (7i)



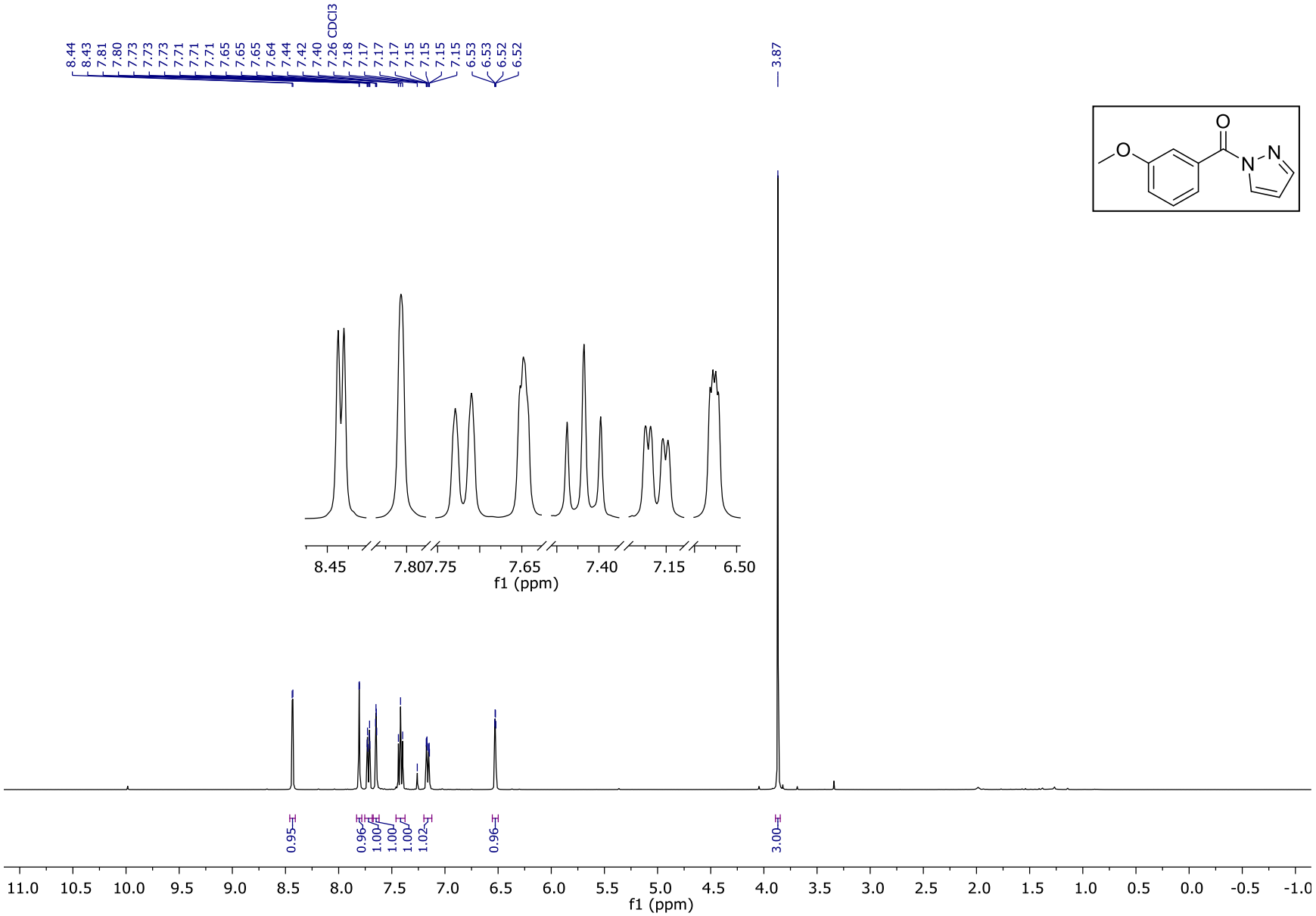
^{1}H-NMR (400 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*m*-tolyl)methanone (7j)



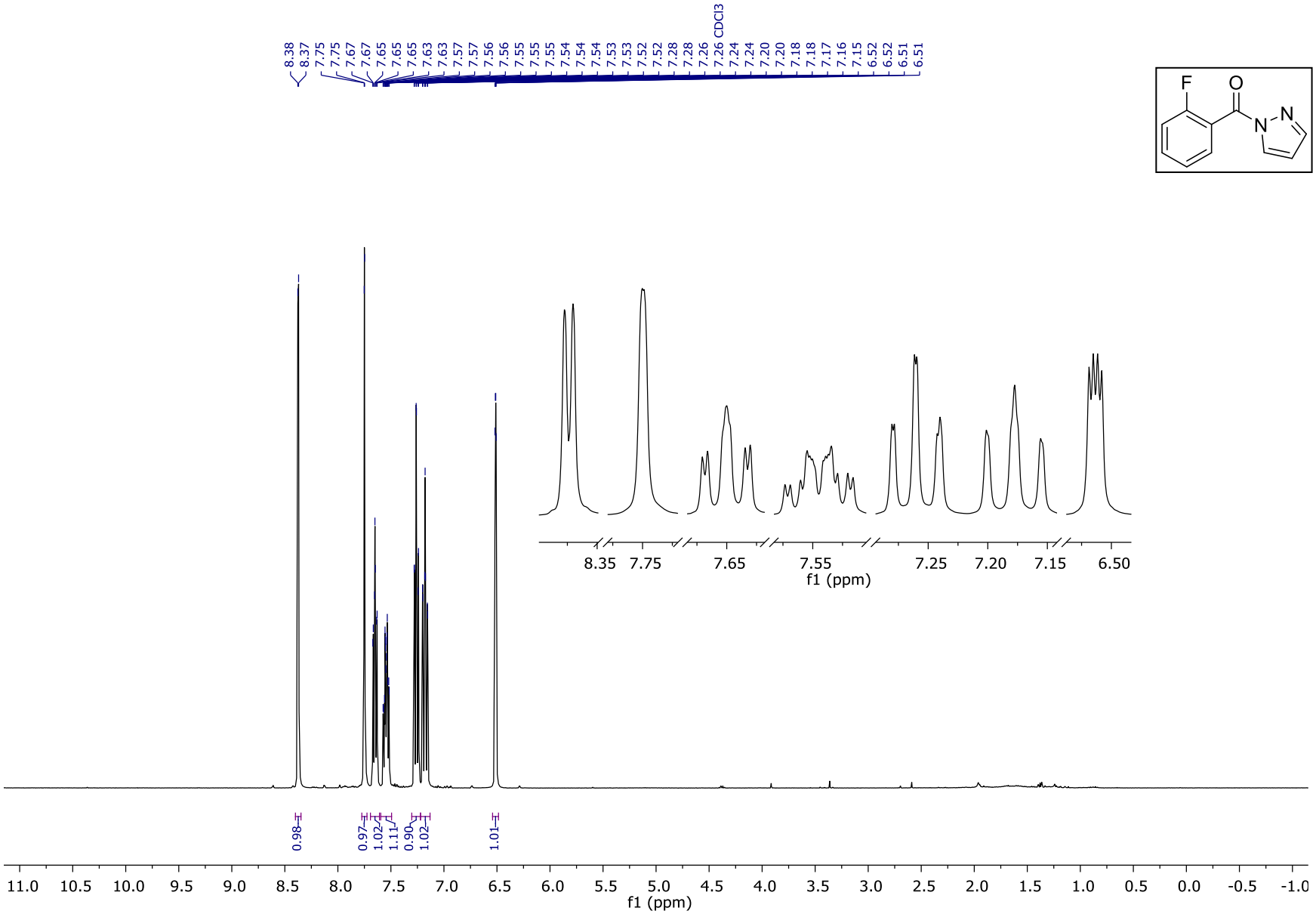
^{1}H-NMR (400 MHz $CDCl_3$) (3-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7k)



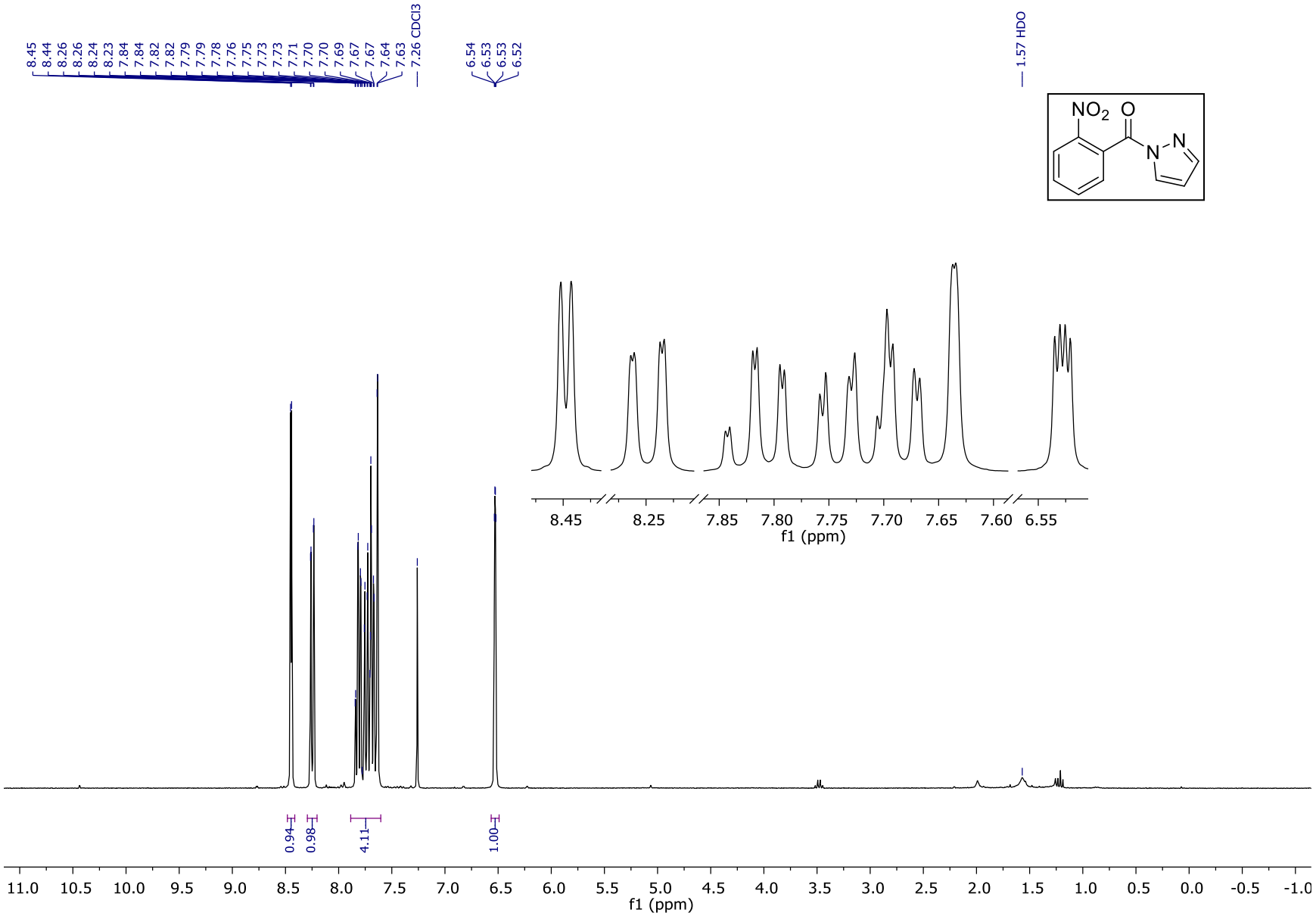
^{1}H-NMR (400 MHz $CDCl_3$) (3-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7l)



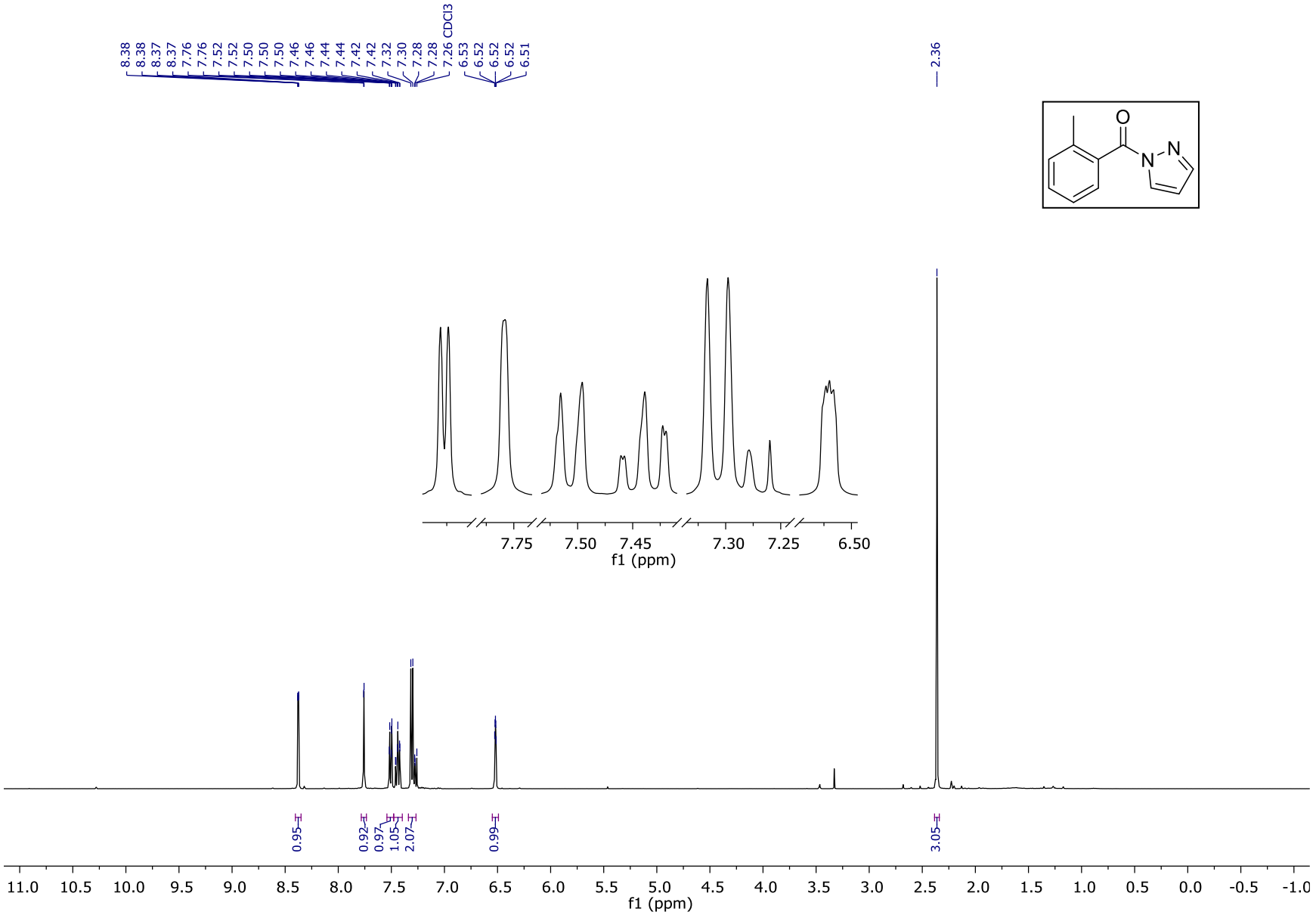
^{1}H-NMR (400 MHz $CDCl_3$) (2-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7m)



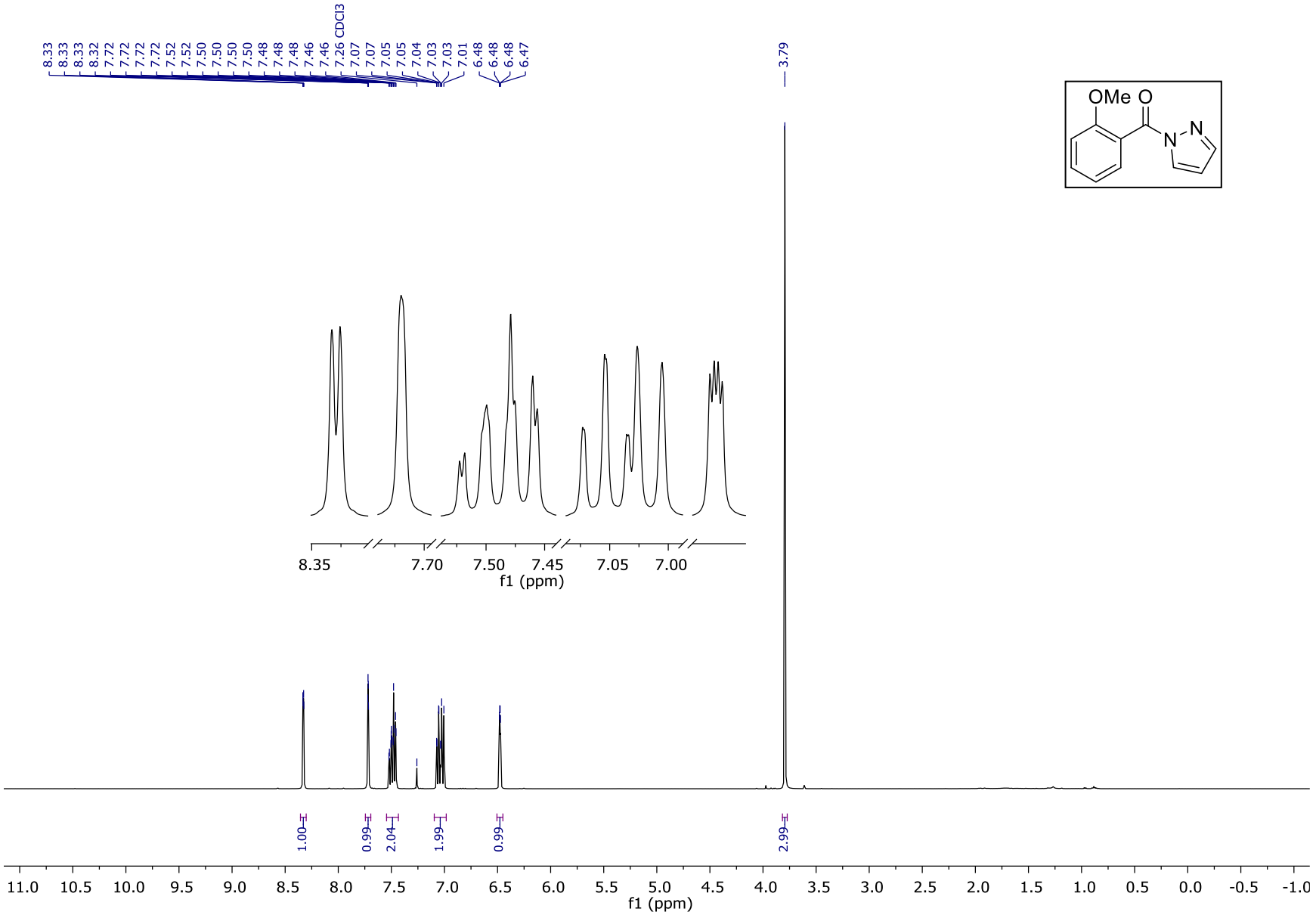
^{1}H-NMR (300 MHz $CDCl_3$) (2-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7n)



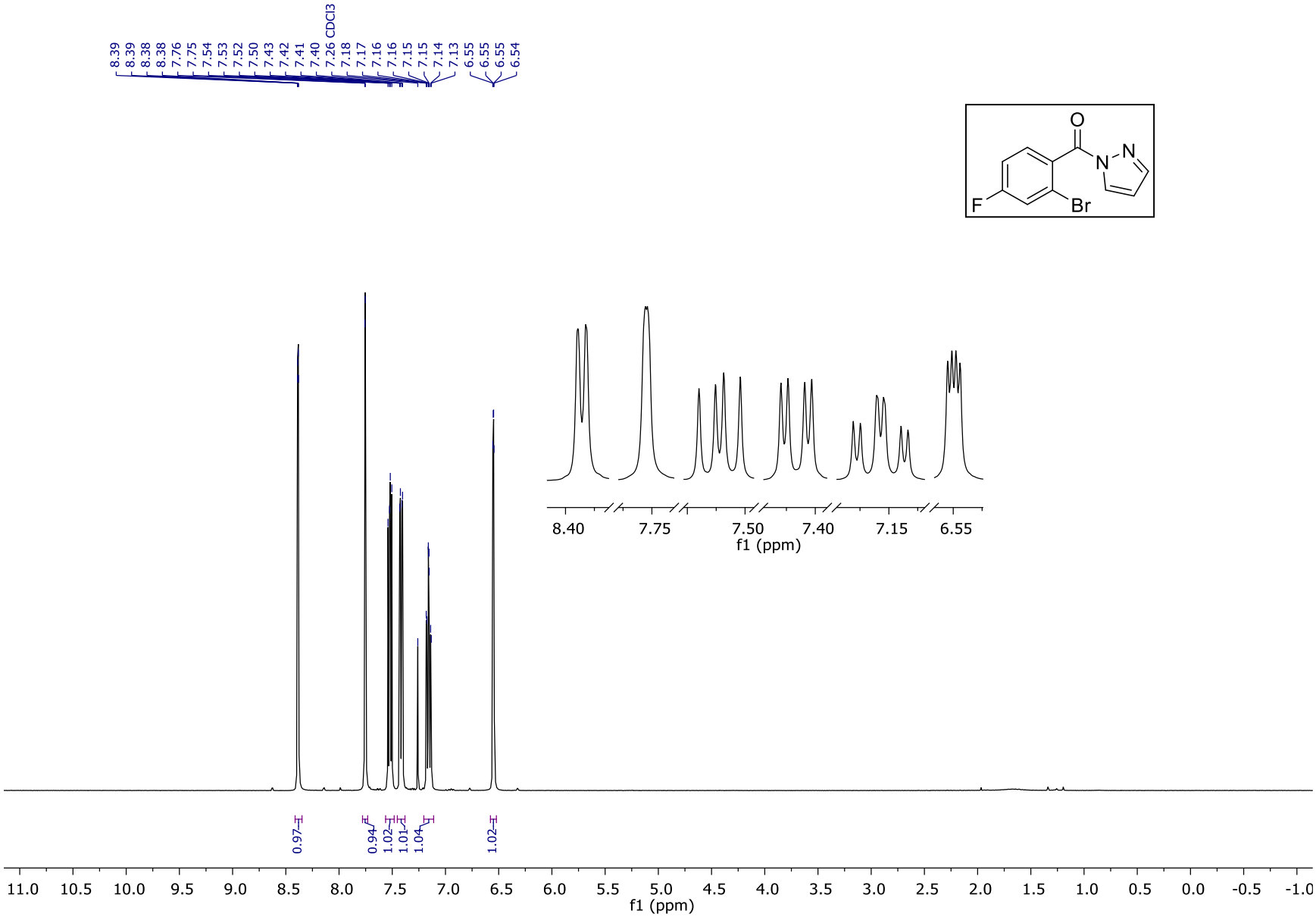
^{1}H-NMR (400 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*o*-tolyl)methanone (7o)



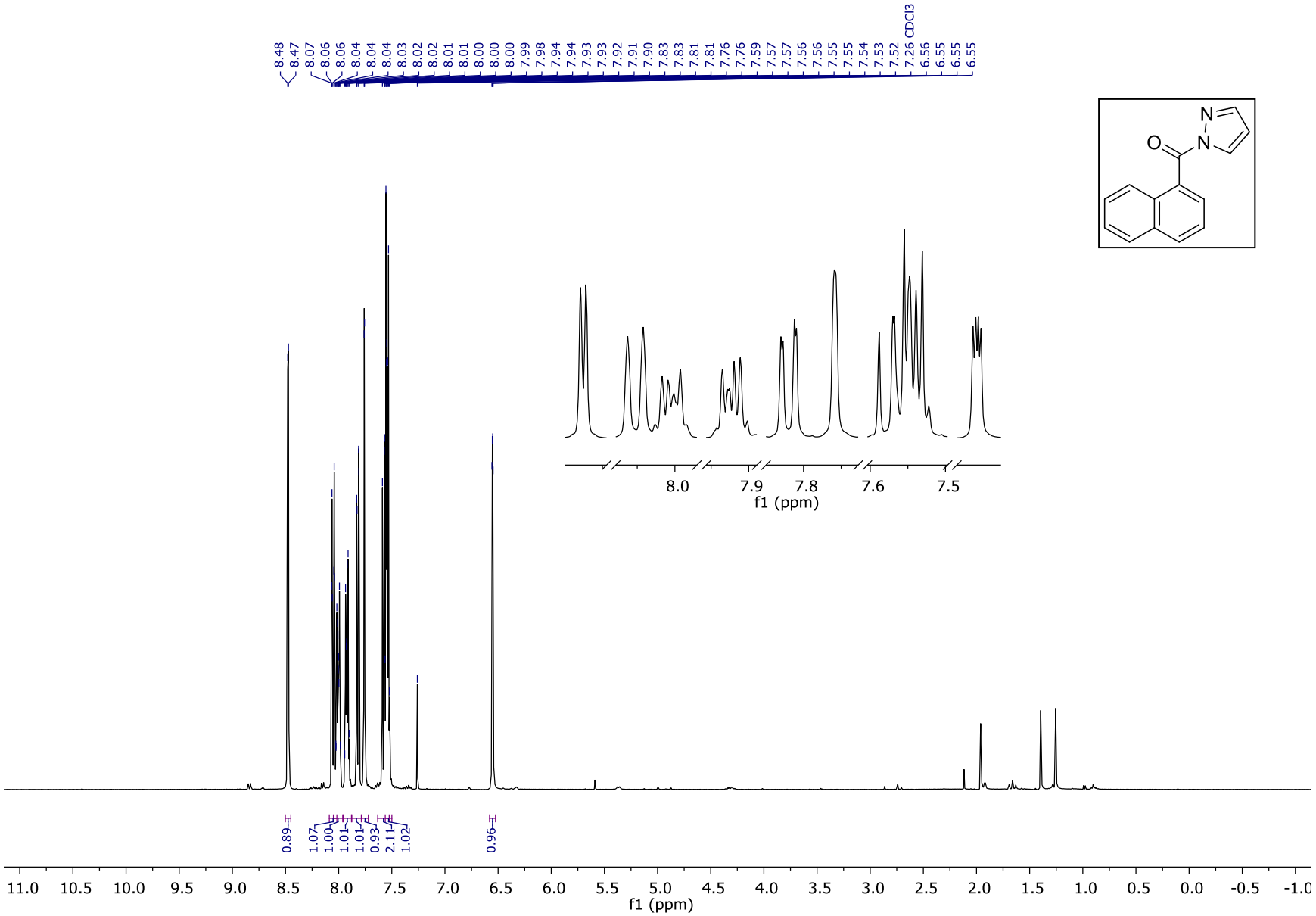
^{1}H-NMR (400 MHz $CDCl_3$) (2-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7p)



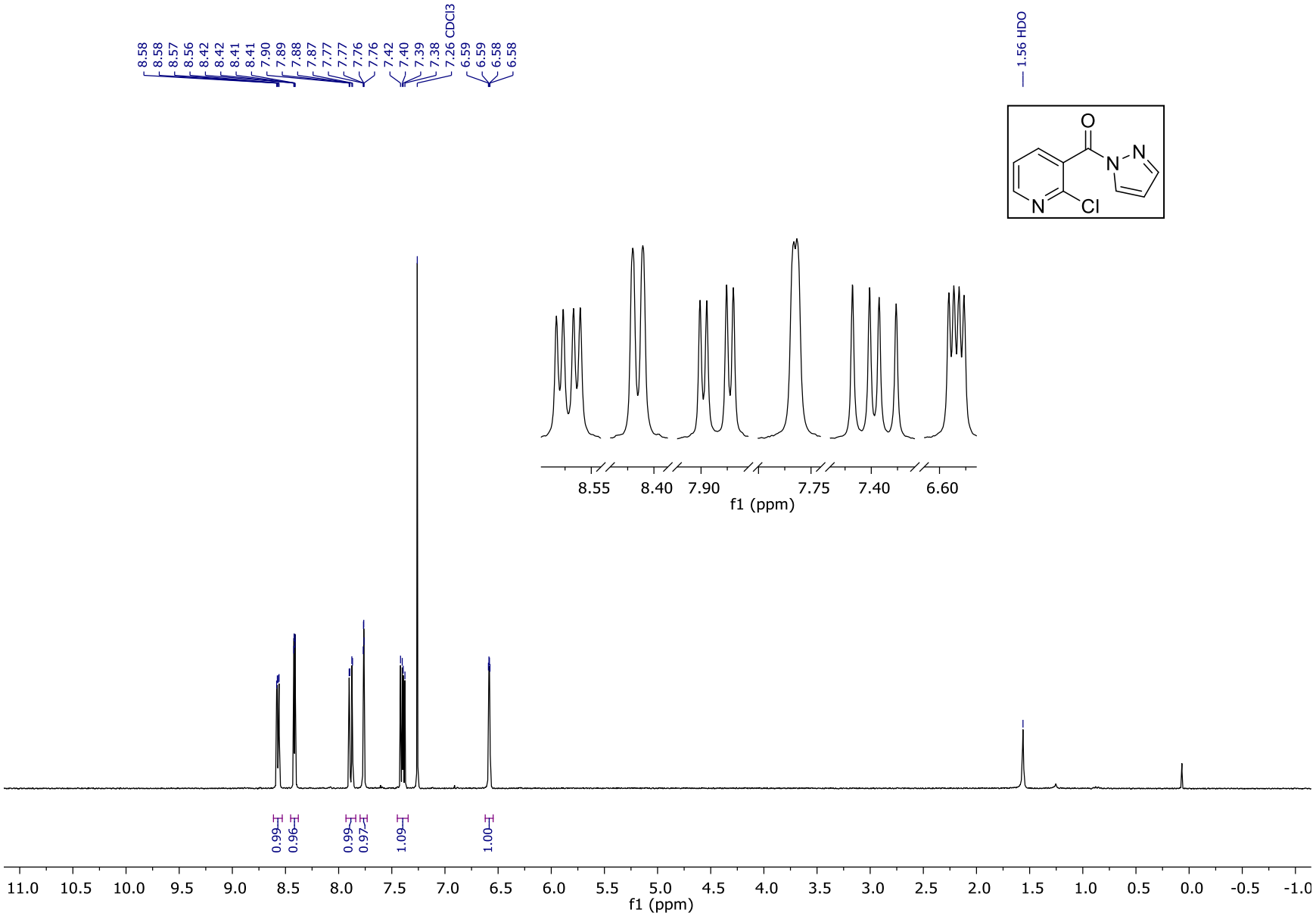
^{1}H-NMR (400 MHz $CDCl_3$) (2-Bromo-4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7q)



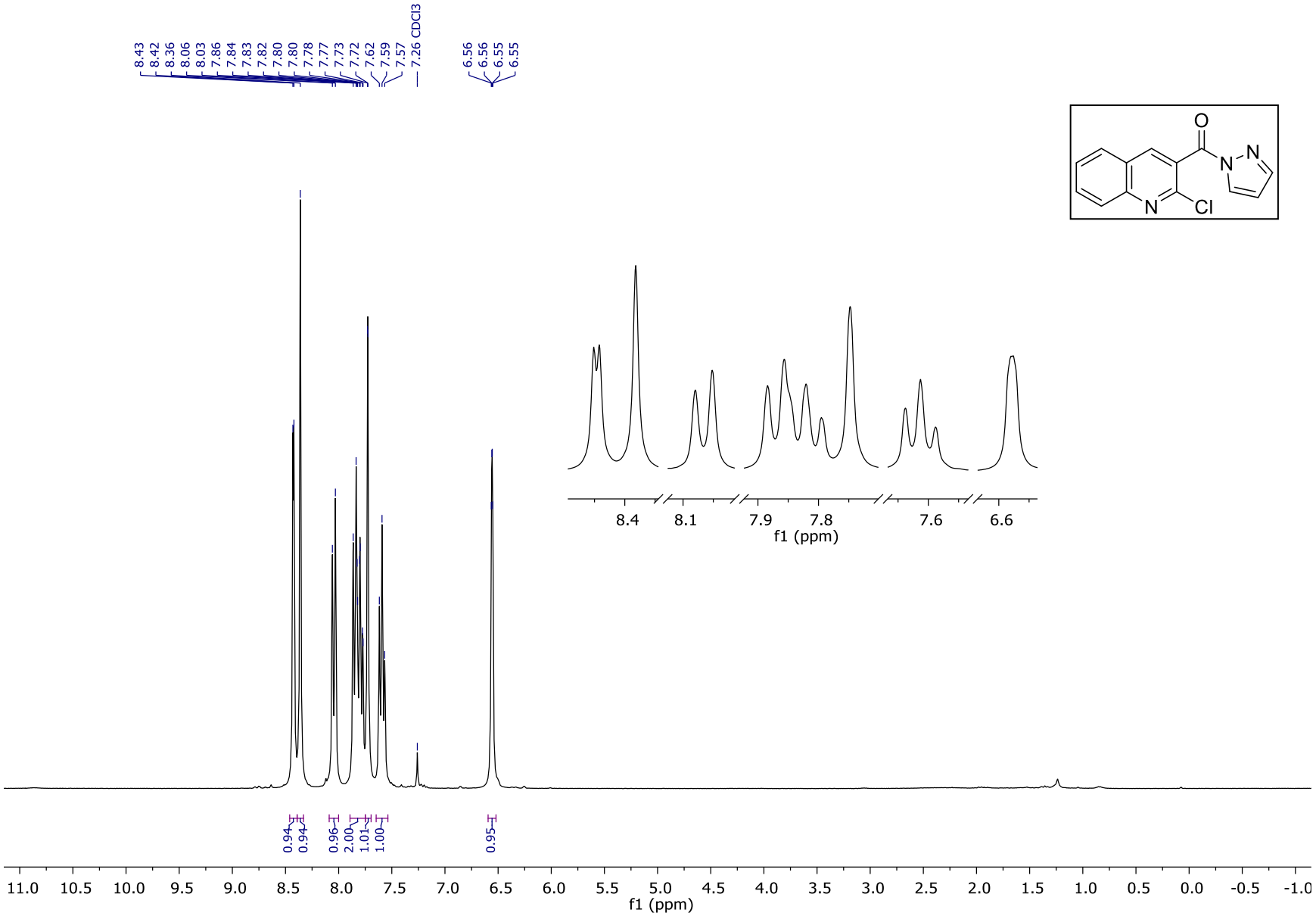
^{1}H-NMR (400 MHz $CDCl_3$) Naphtalen-1-yl(1*H*-pyrazol-1-yl)methanone (7r)



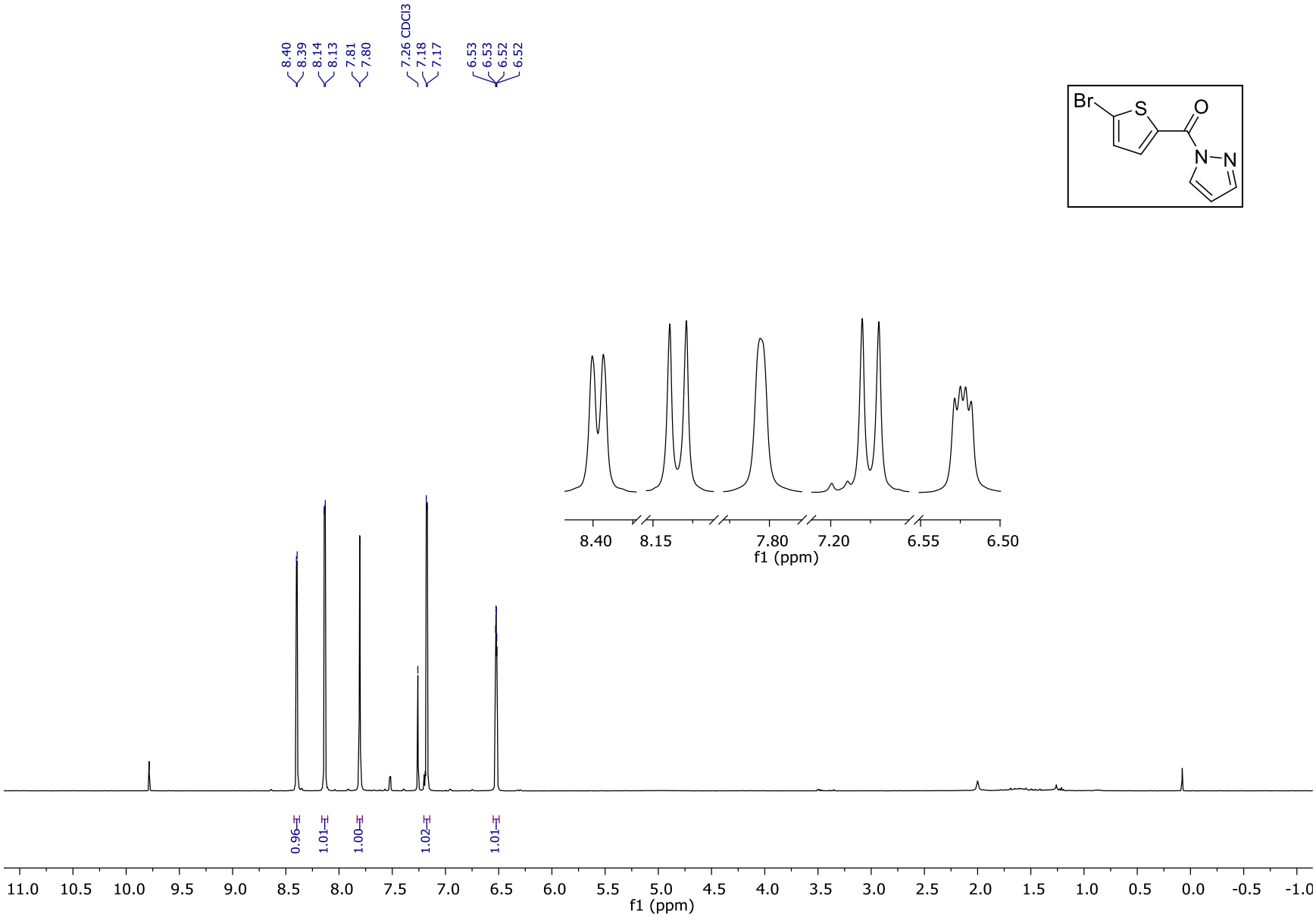
^{1}H-NMR (300 MHz $CDCl_3$) (2-Chloropyridin-3-yl)(1*H*-pyrazol-1-yl)methanone (7s)



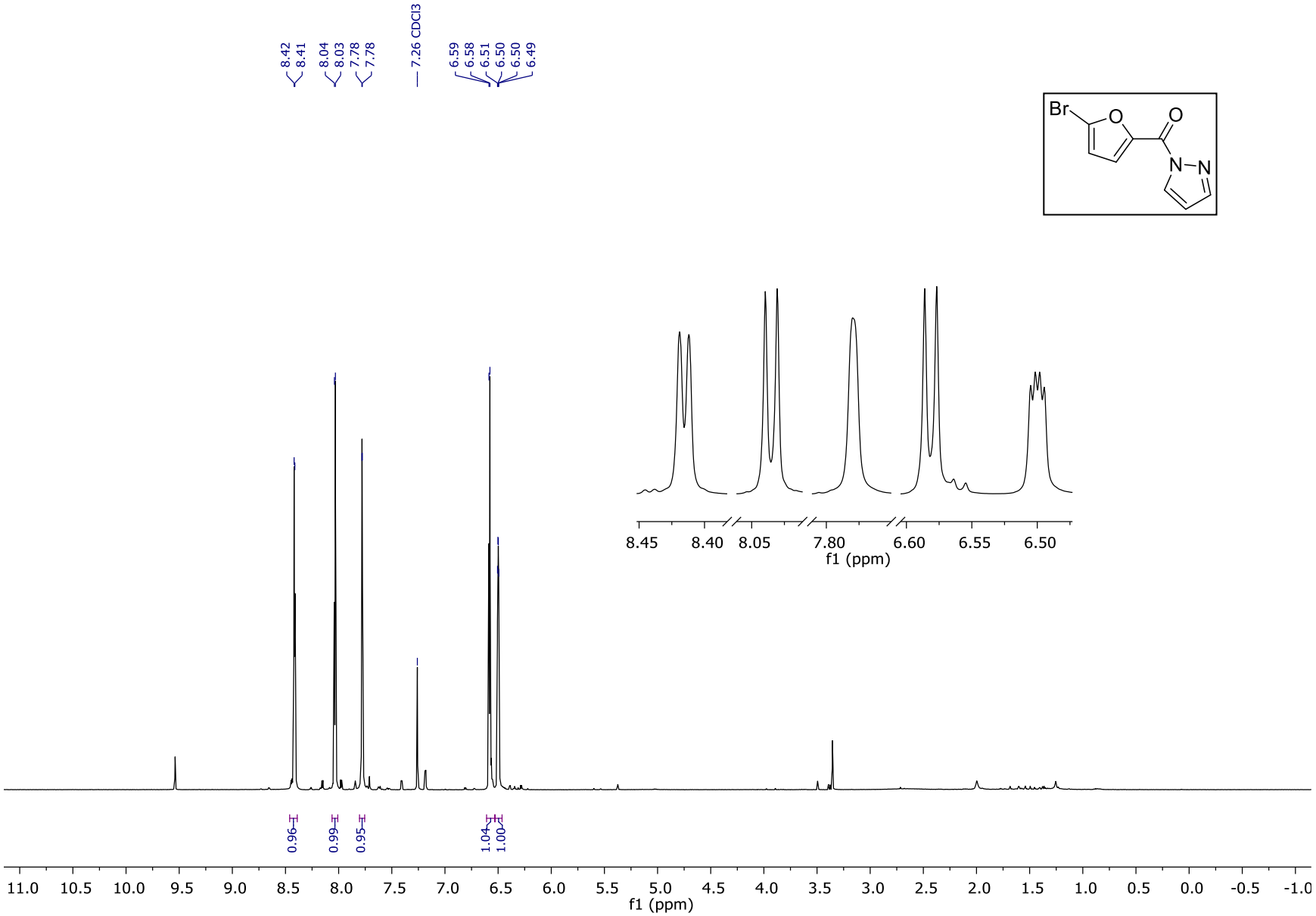
^{1}H-NMR (300 MHz $CDCl_3$) (2-Chloroquinolin-3-yl)(1*H*-pyrazol-1-yl)methanone (7t)



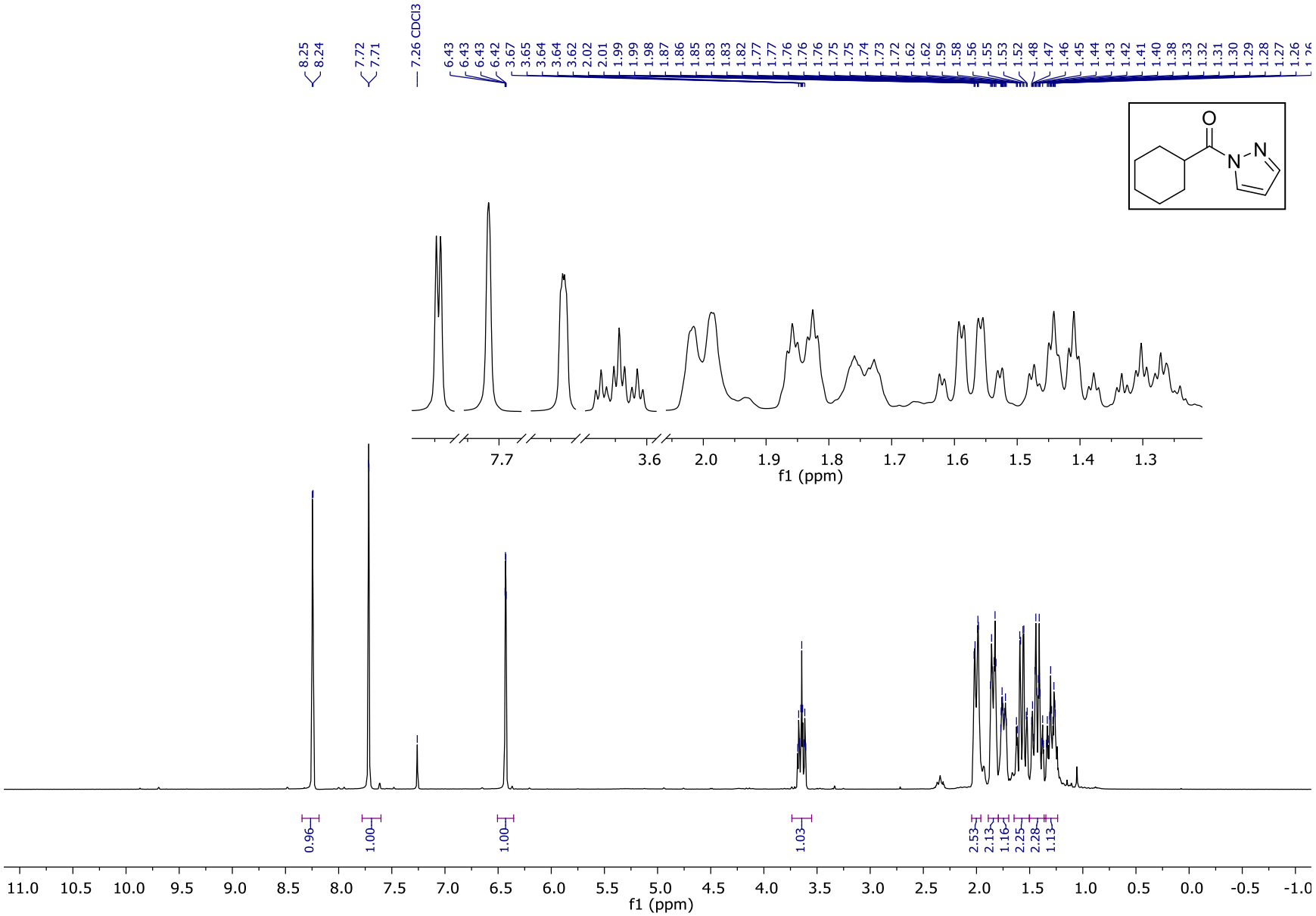
^{1}H-NMR (400 MHz $CDCl_3$) (5-bromothiophen-2-yl)(1*H*-pyrazol-1-yl)methanone (7u)



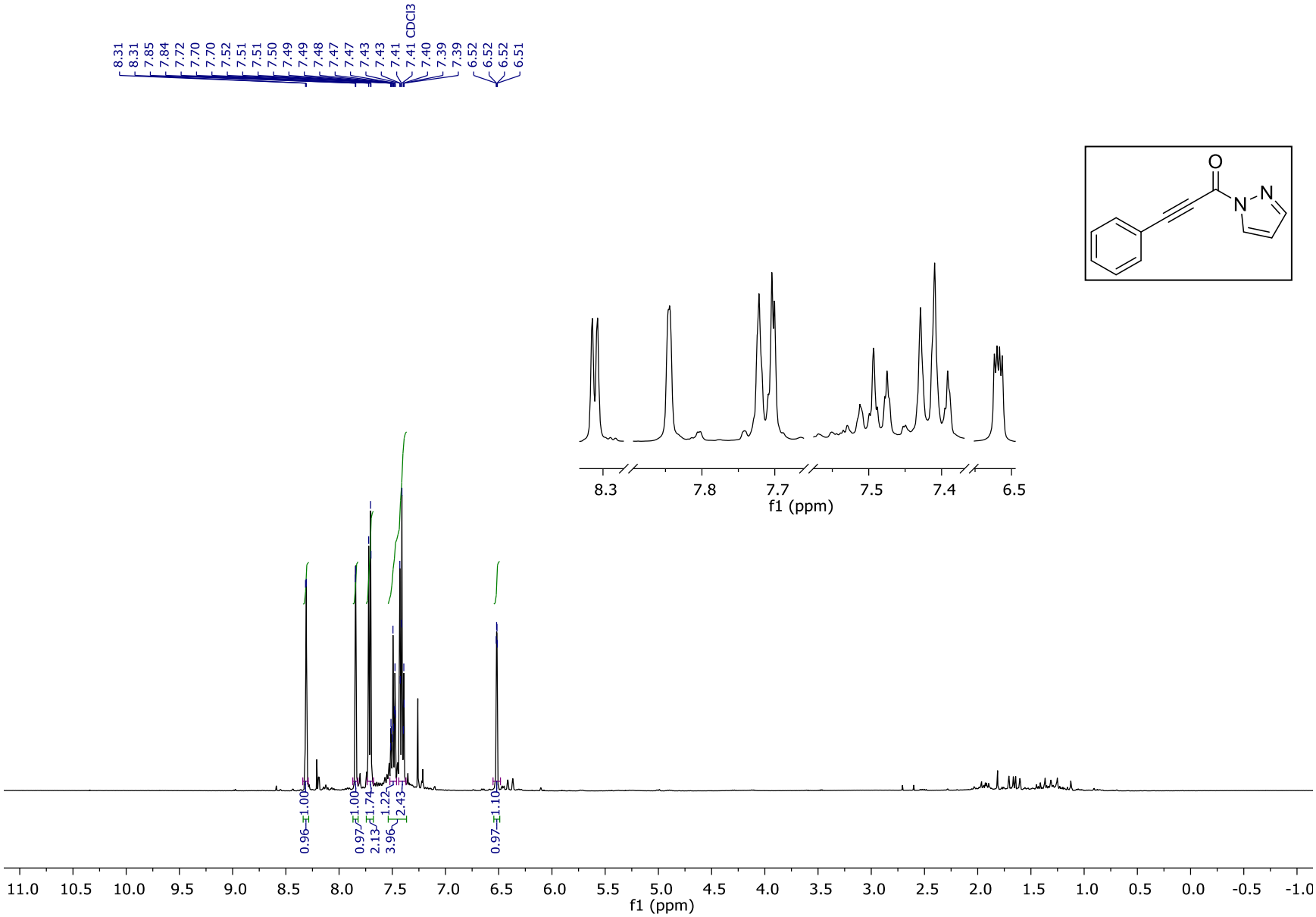
^{1}H-NMR (400 MHz $CDCl_3$) (5-bromofuran-2-yl)(1*H*-pyrazol-1-yl)methanone (7v)



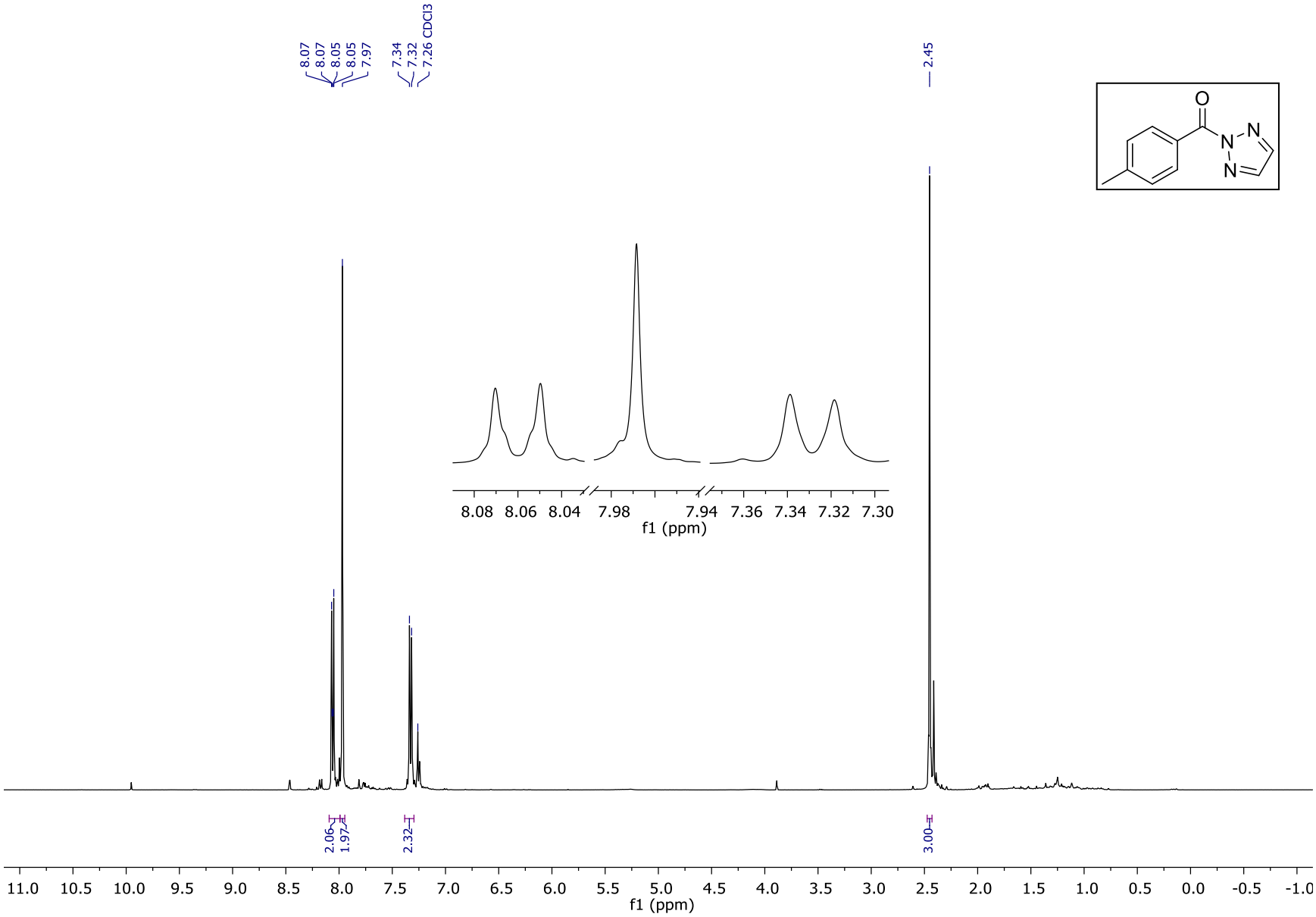
^{1}H-NMR (400 MHz $CDCl_3$) Cyclohexyl(1*H*-pyrazol-1-yl)methanone (7w)



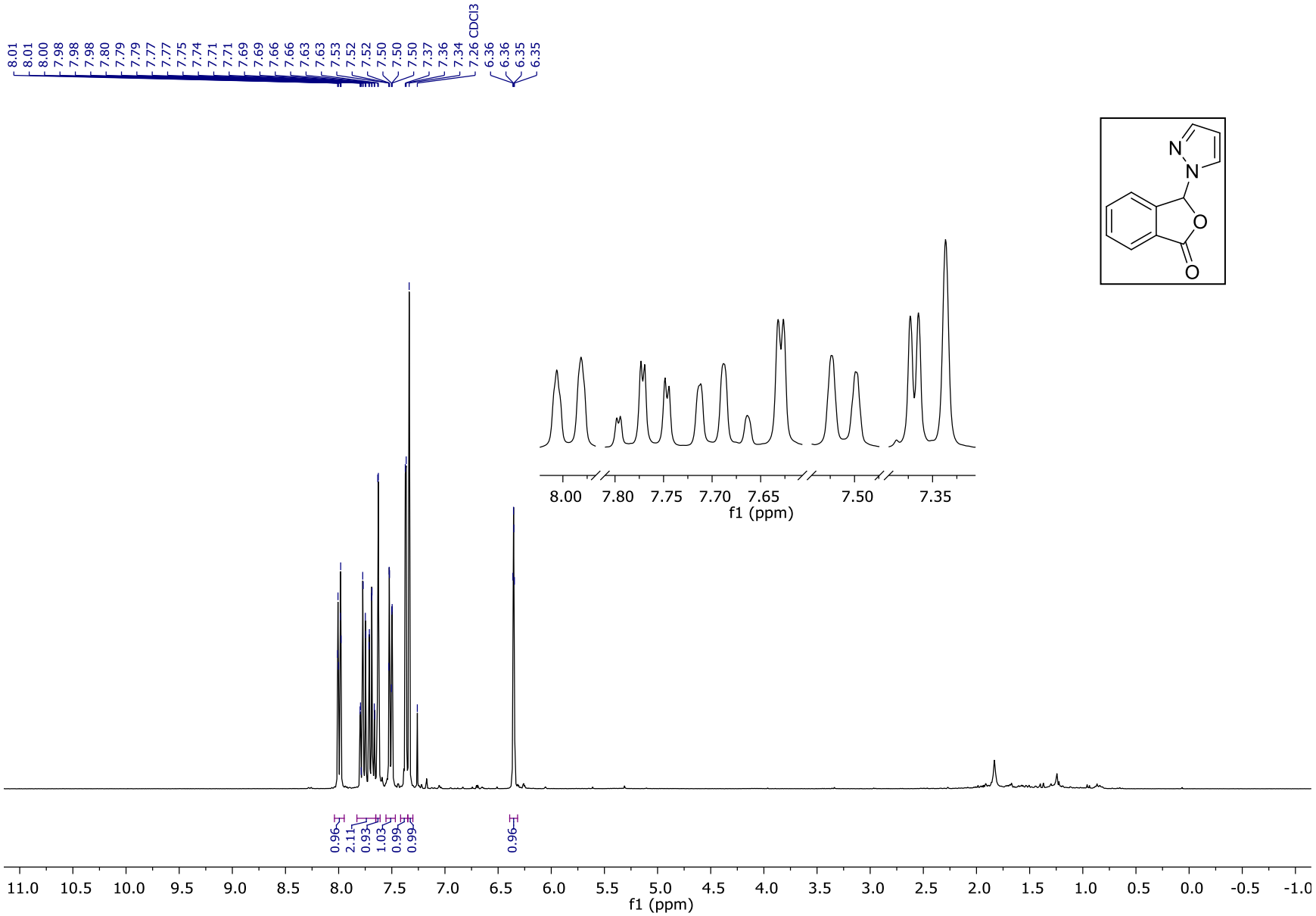
^{1}H-NMR (400 MHz $CDCl_3$) 3-phenyl-1-(1*H*-pyrazol-1-yl)prop-2-yn-1-one (7z)



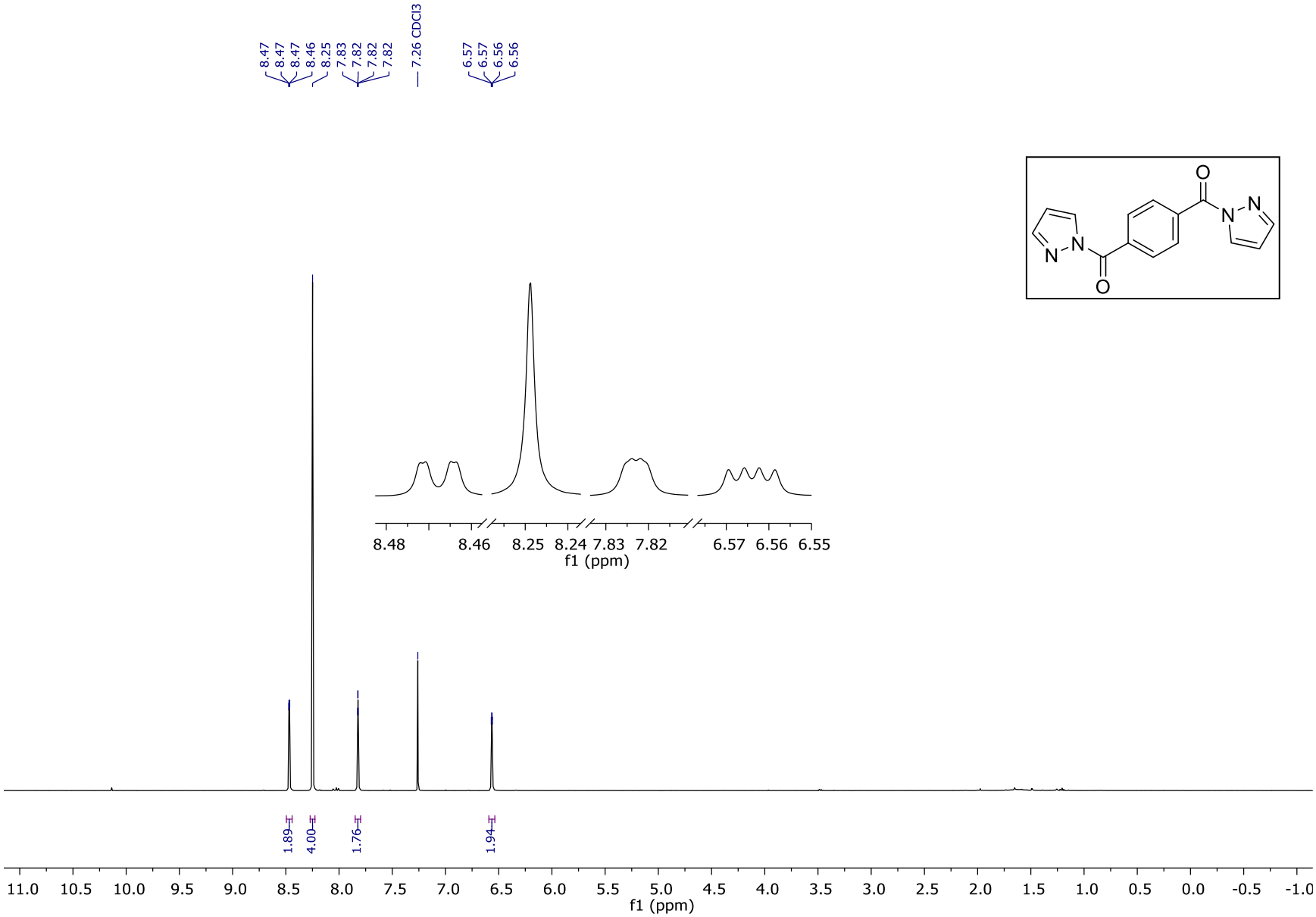
^{1}H-NMR (300 MHz $CDCl_3$) *p*-Tolyl(2*H*-1,2,3-triazol-2-yl)methanone (7ae)



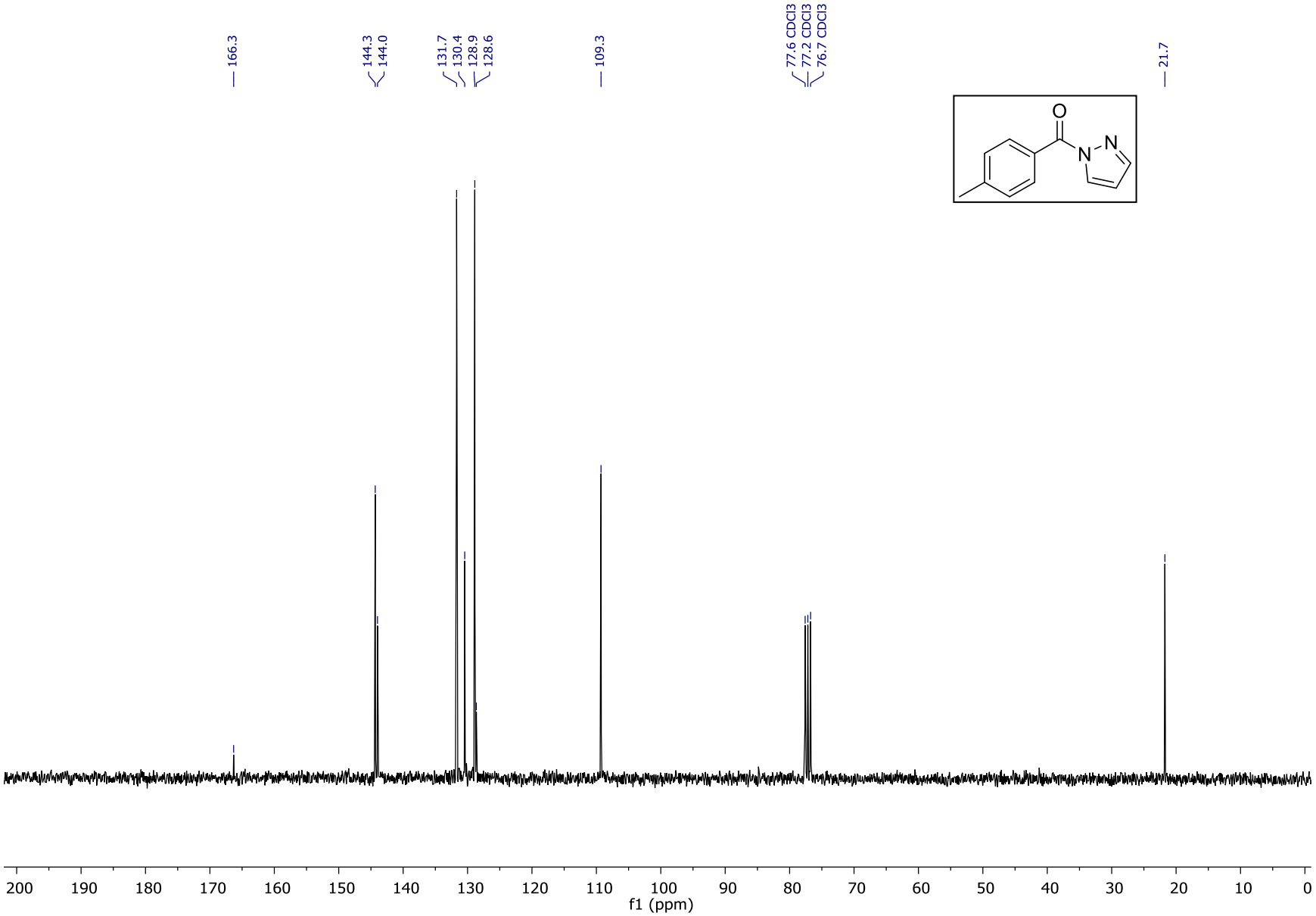
^{1}H-NMR (300 MHz $CDCl_3$) 3-(1H-pyrazol-1-yl)isobenzofuran-1(3*H*)-one (7ai)



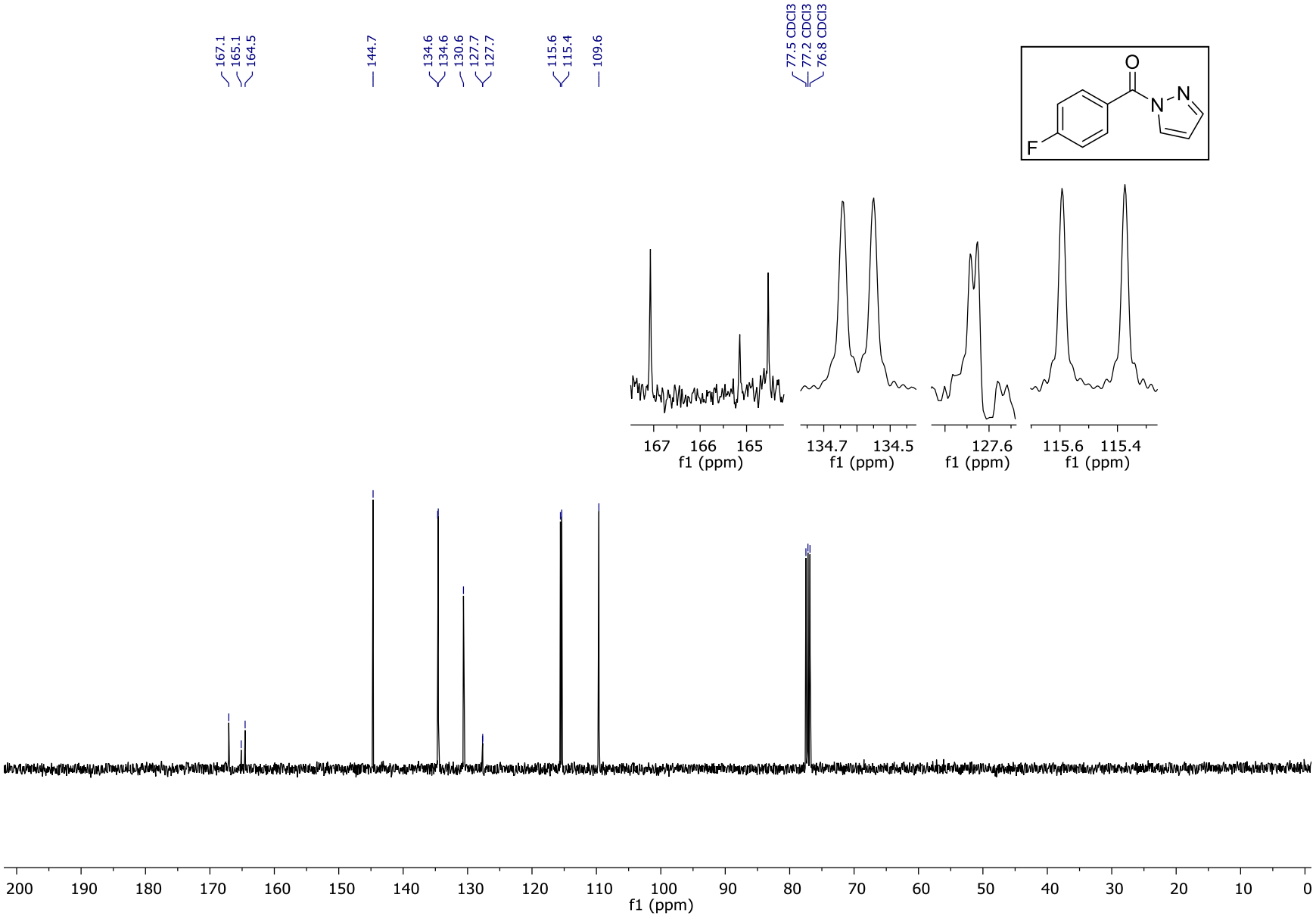
^{1}H-NMR (400 MHz $CDCl_3$) 1,4-phenylenebis((1*H*-pyrazol-1-yl)methanone) (7aj)



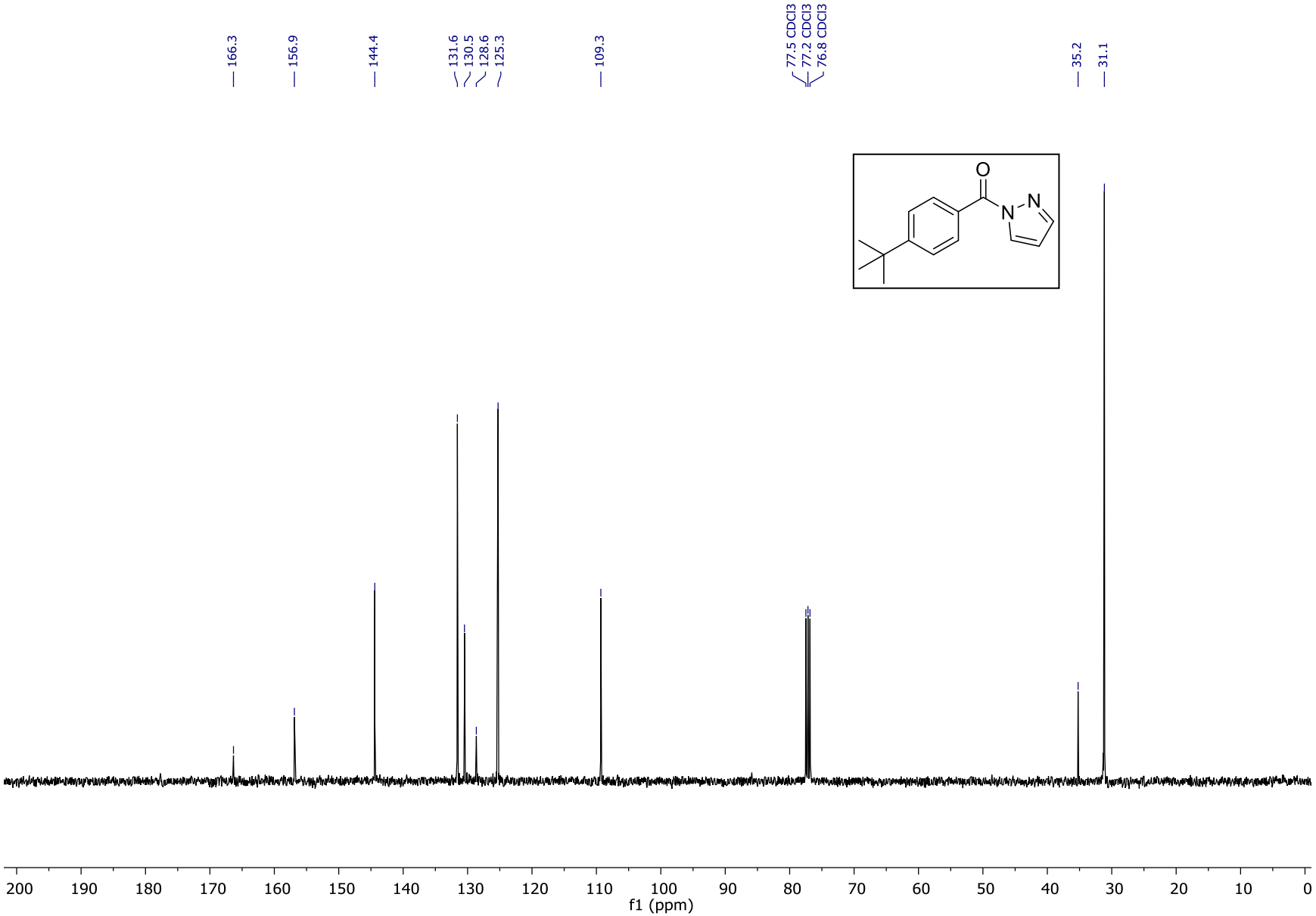
^{13}C-NMR (75 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*p*-tolyl)methanone (7a)



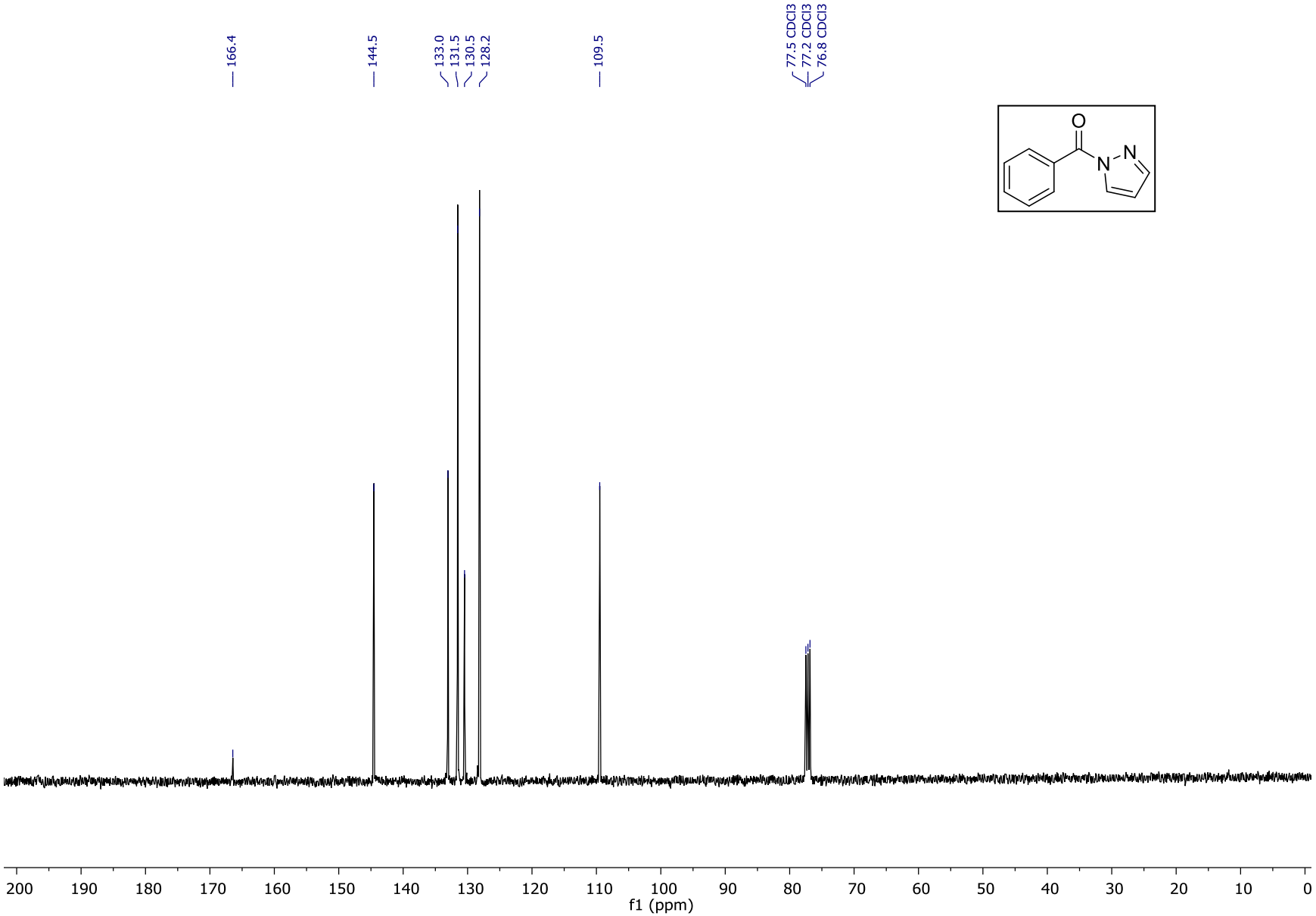
^{13}C-NMR (101 MHz $CDCl_3$) (4-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7b).



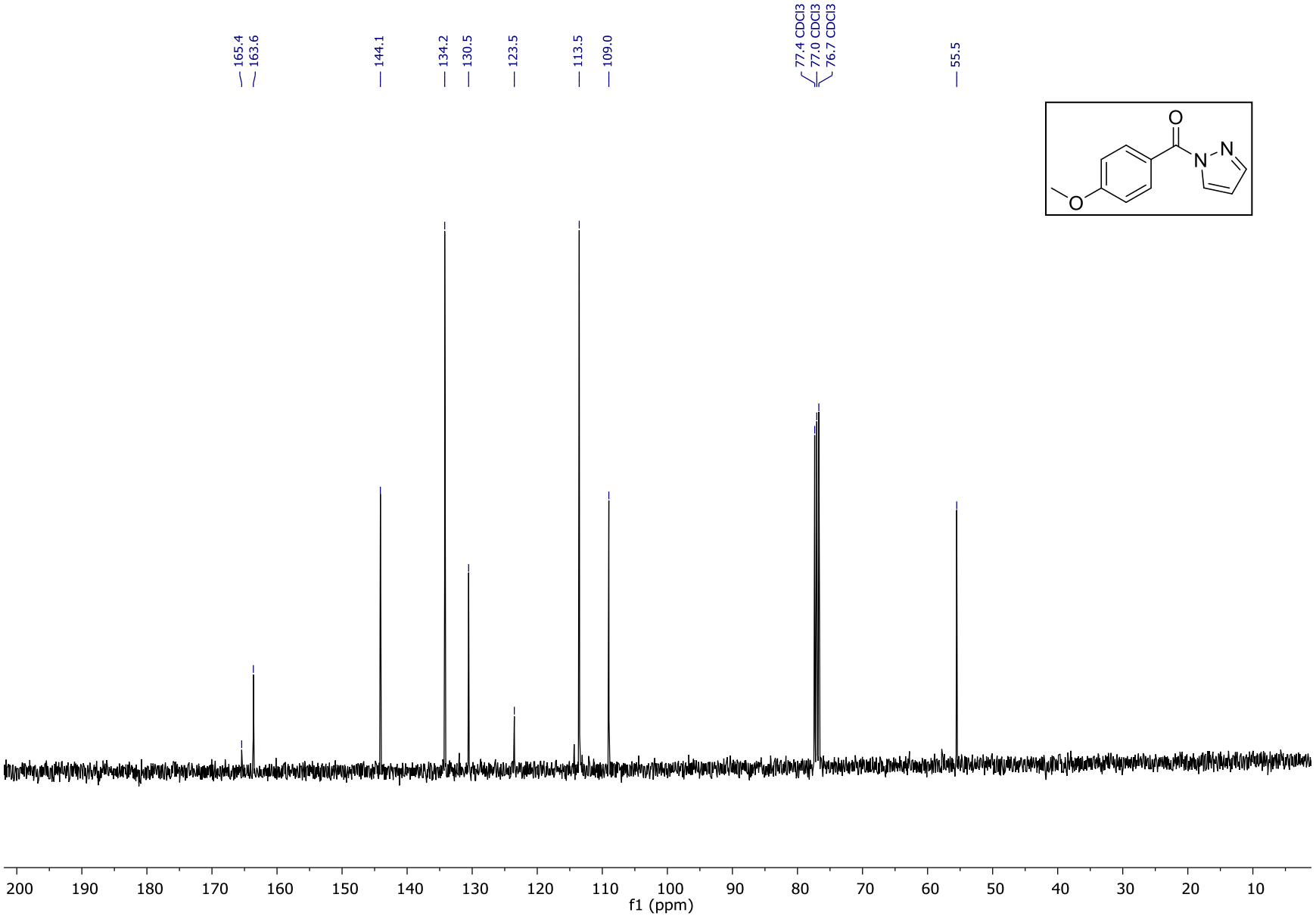
^{13}C-NMR (101 MHz $CDCl_3$) (4-(*tert*-Butyl)phenyl)(1*H*-pyrazol-1-yl)methanone (7c)



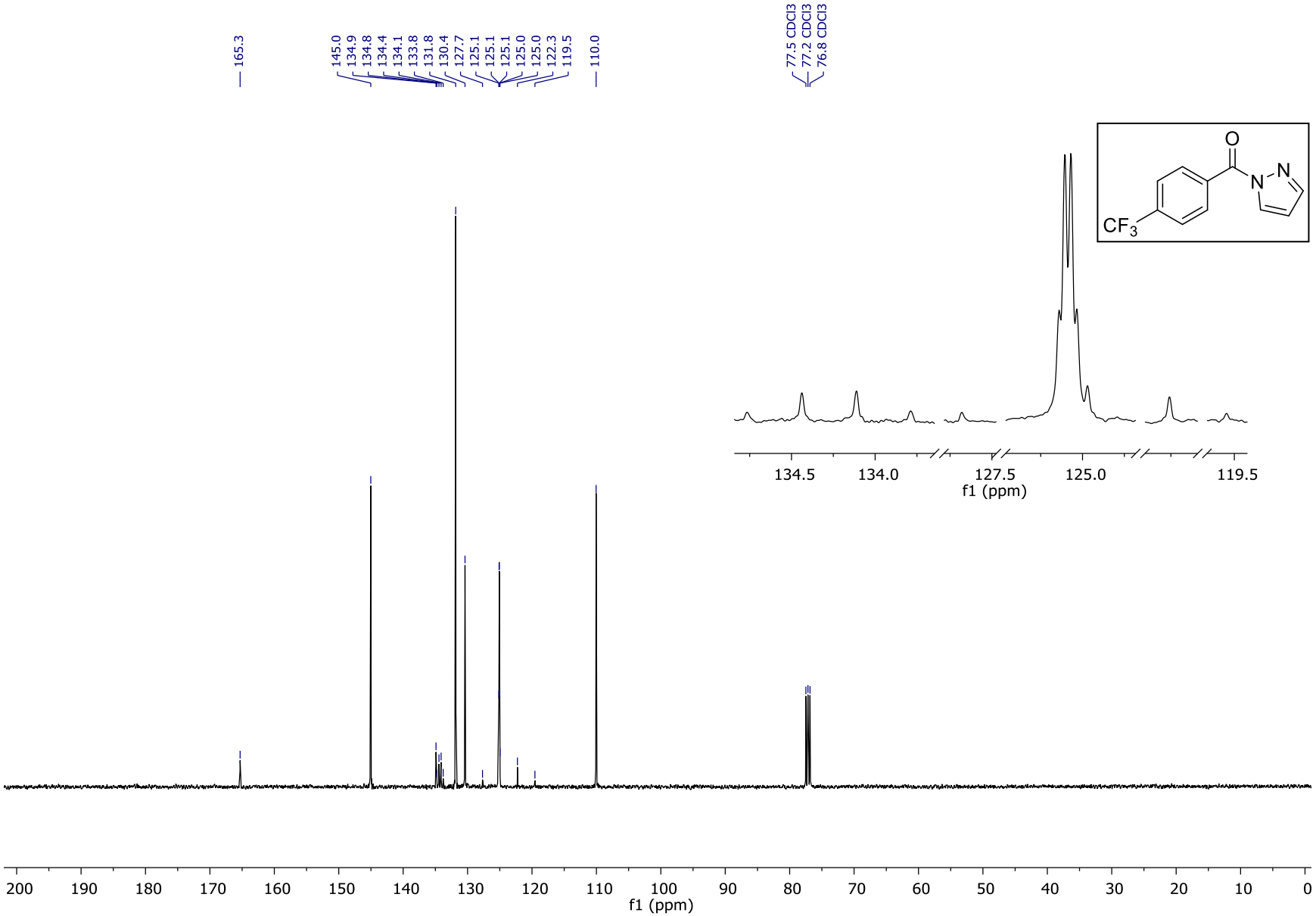
^{13}C-NMR (101 MHz $CDCl_3$) Phenyl(1*H*-pyrazol-1-yl)methanone (7d)



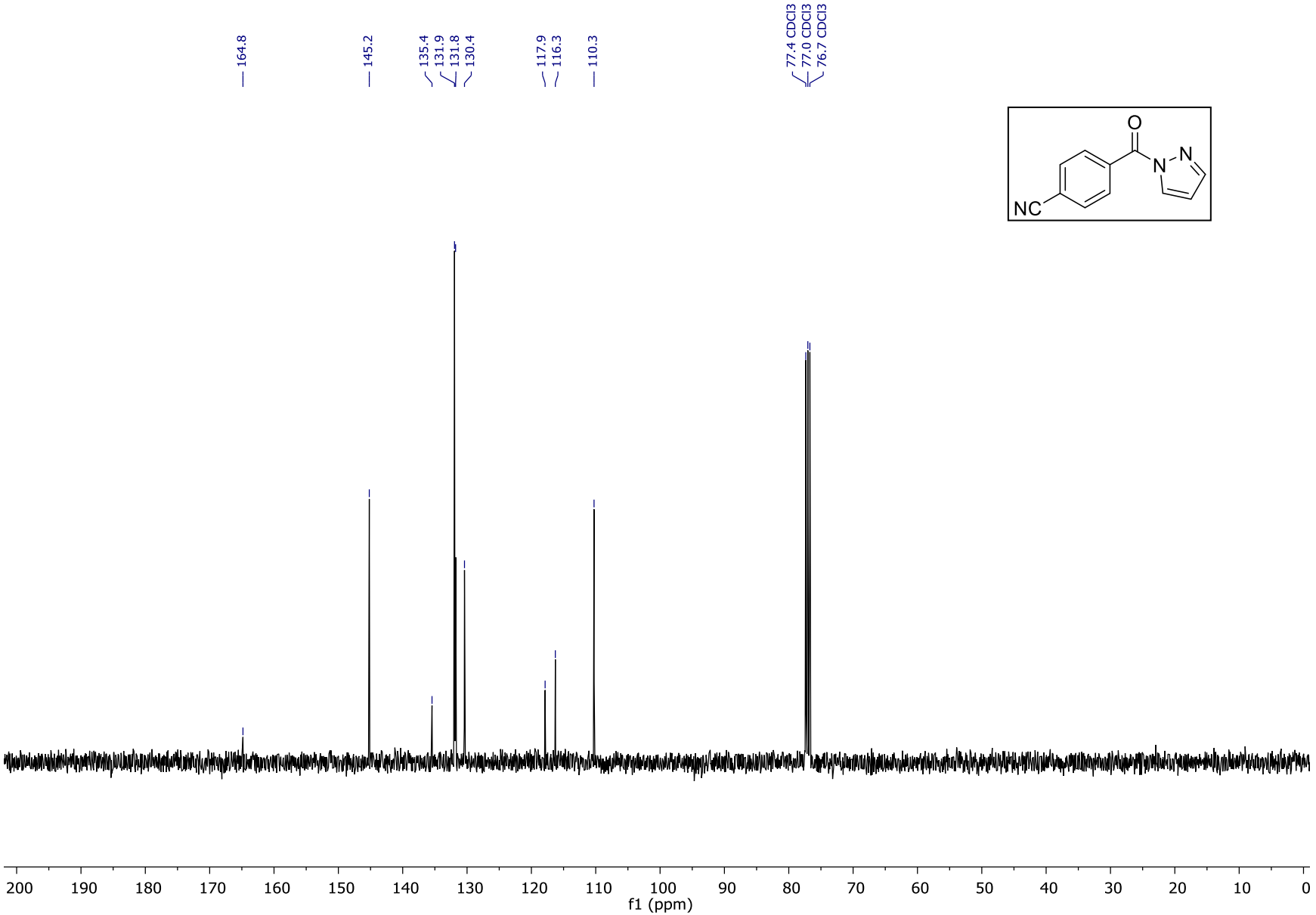
^{13}C-NMR (101 MHz $CDCl_3$) (4-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7e)



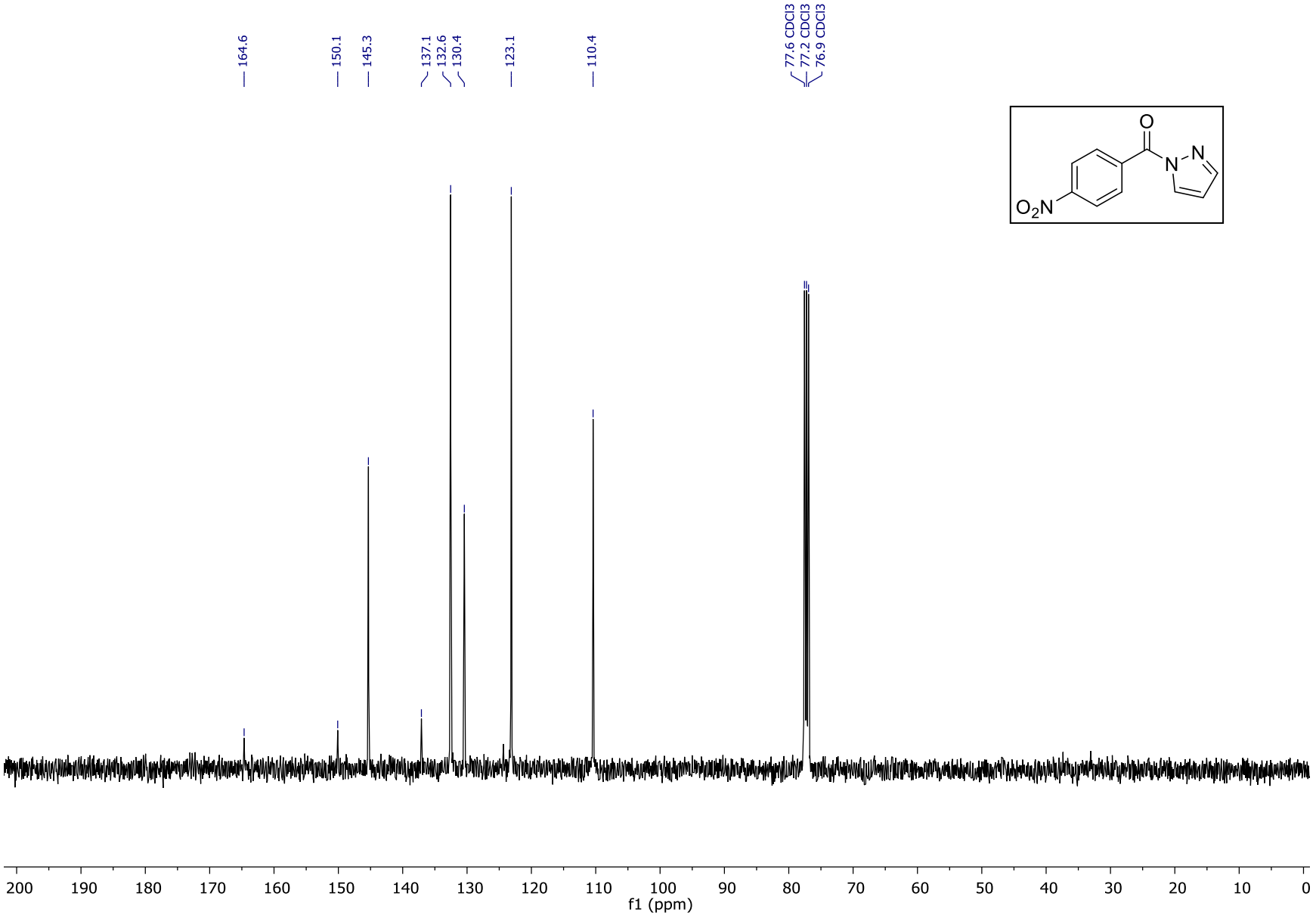
^{13}C-NMR (101 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (7f).



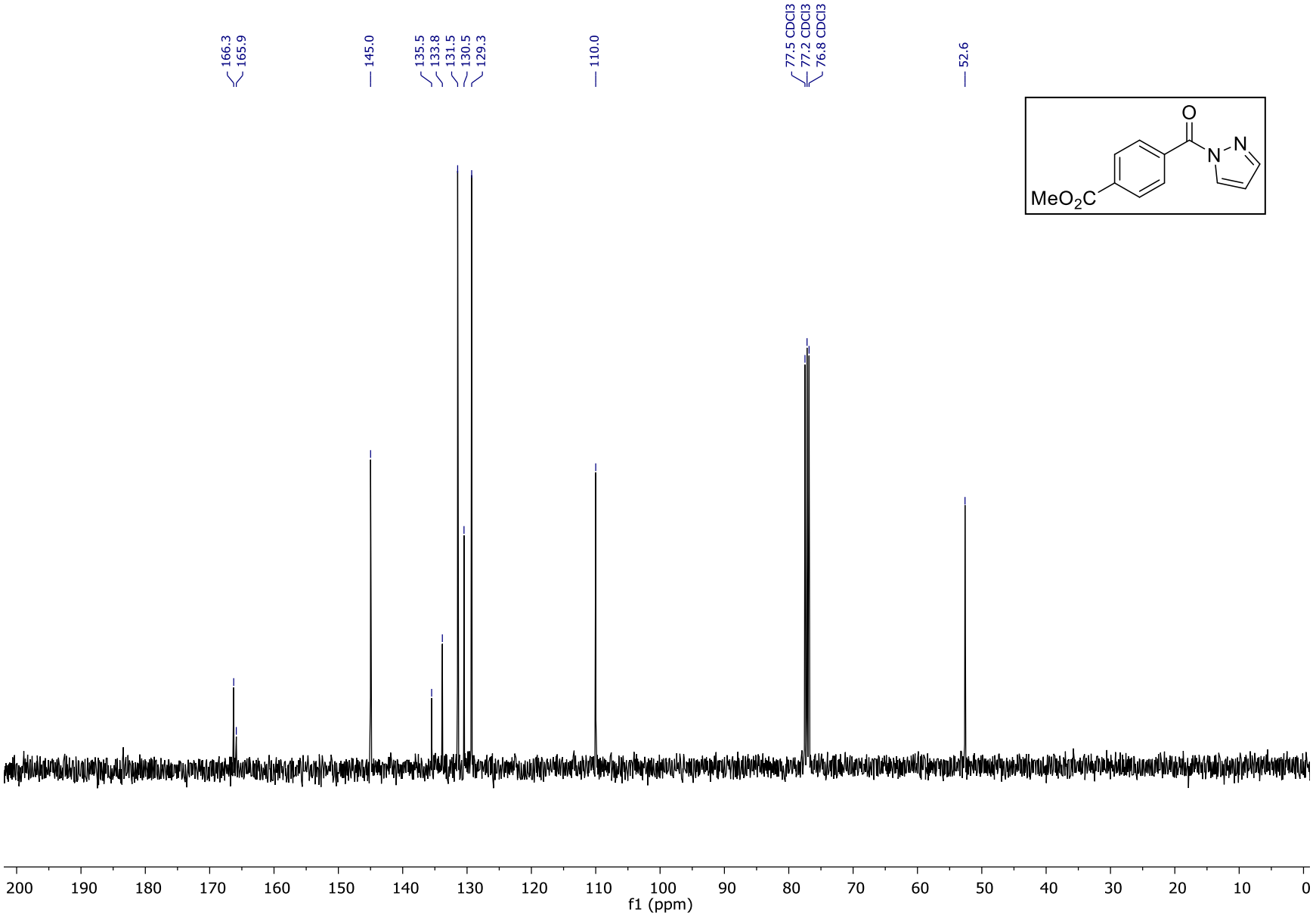
^{13}C-NMR (101 MHz $CDCl_3$) 4-(1*H*-Pyrazole-1-carbonyl)benzonitrile (7g)



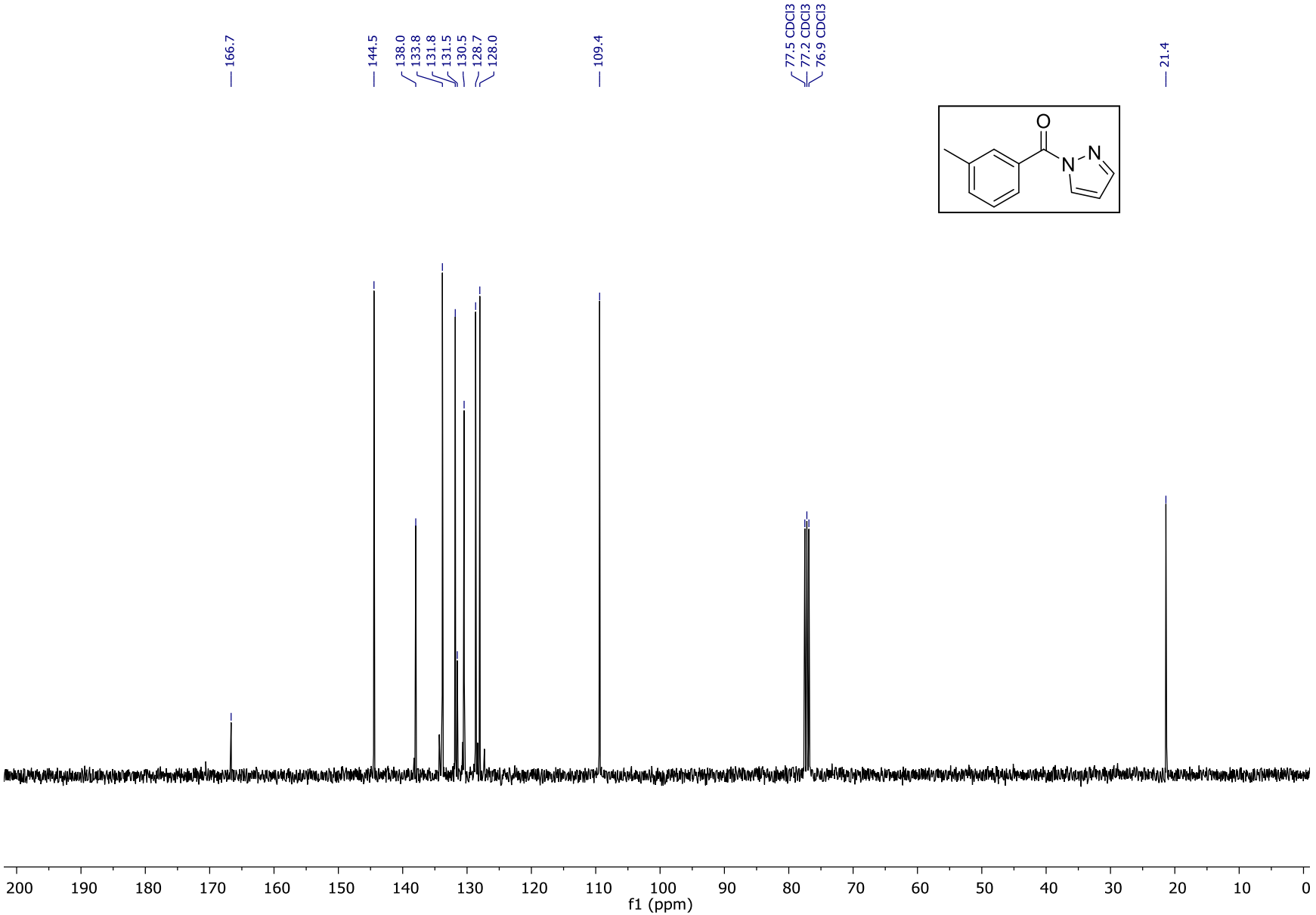
^{13}C-NMR (101 MHz $CDCl_3$) (4-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7h)



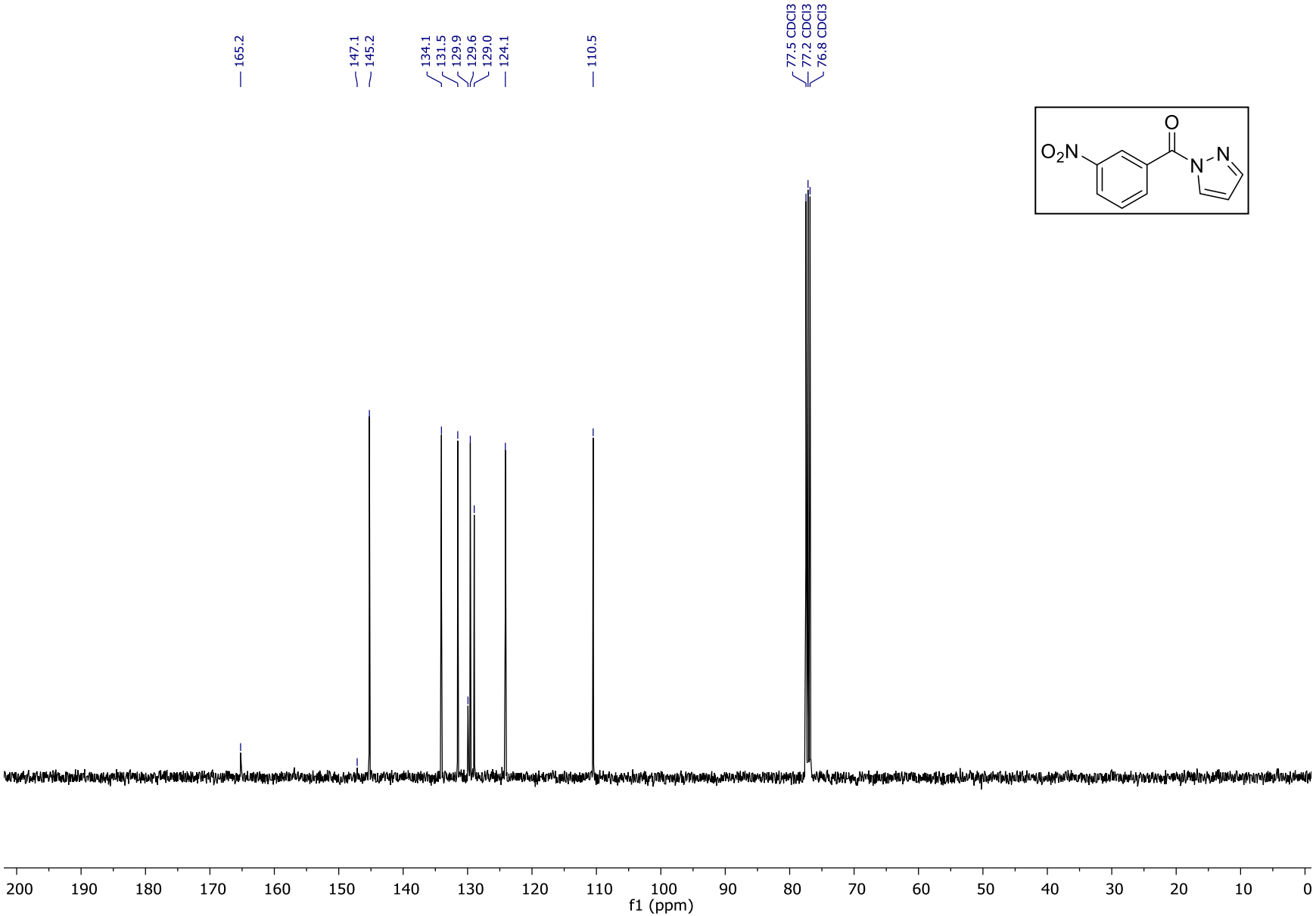
^{13}C-NMR (101 MHz $CDCl_3$) Methyl 4-(1*H*-pyrazole-1-carbonyl)benzoate (7i)



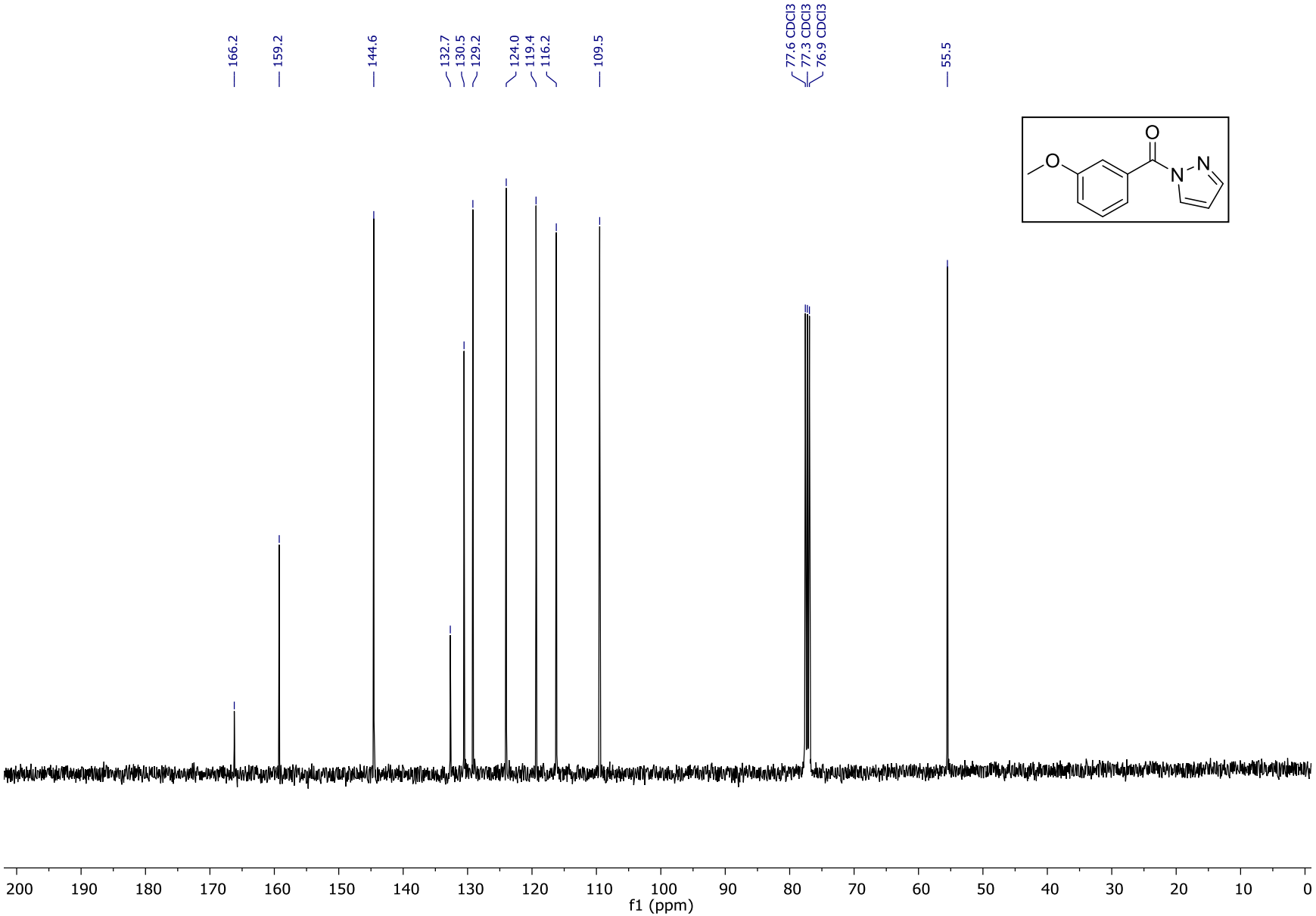
^{13}C-NMR (101 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*m*-tolyl)methanone (7j)



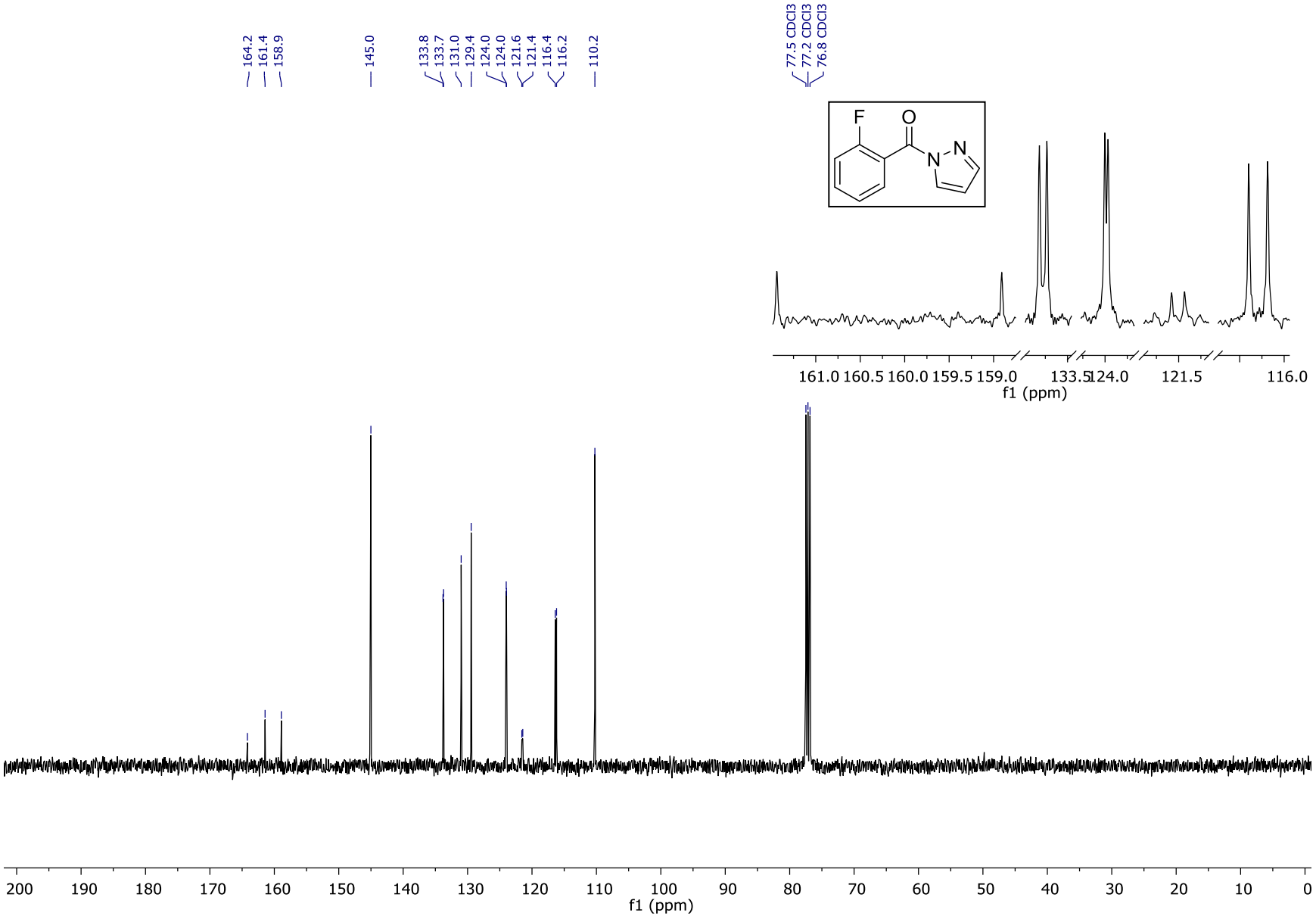
^{13}C-NMR (101 MHz $CDCl_3$) (3-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7k)



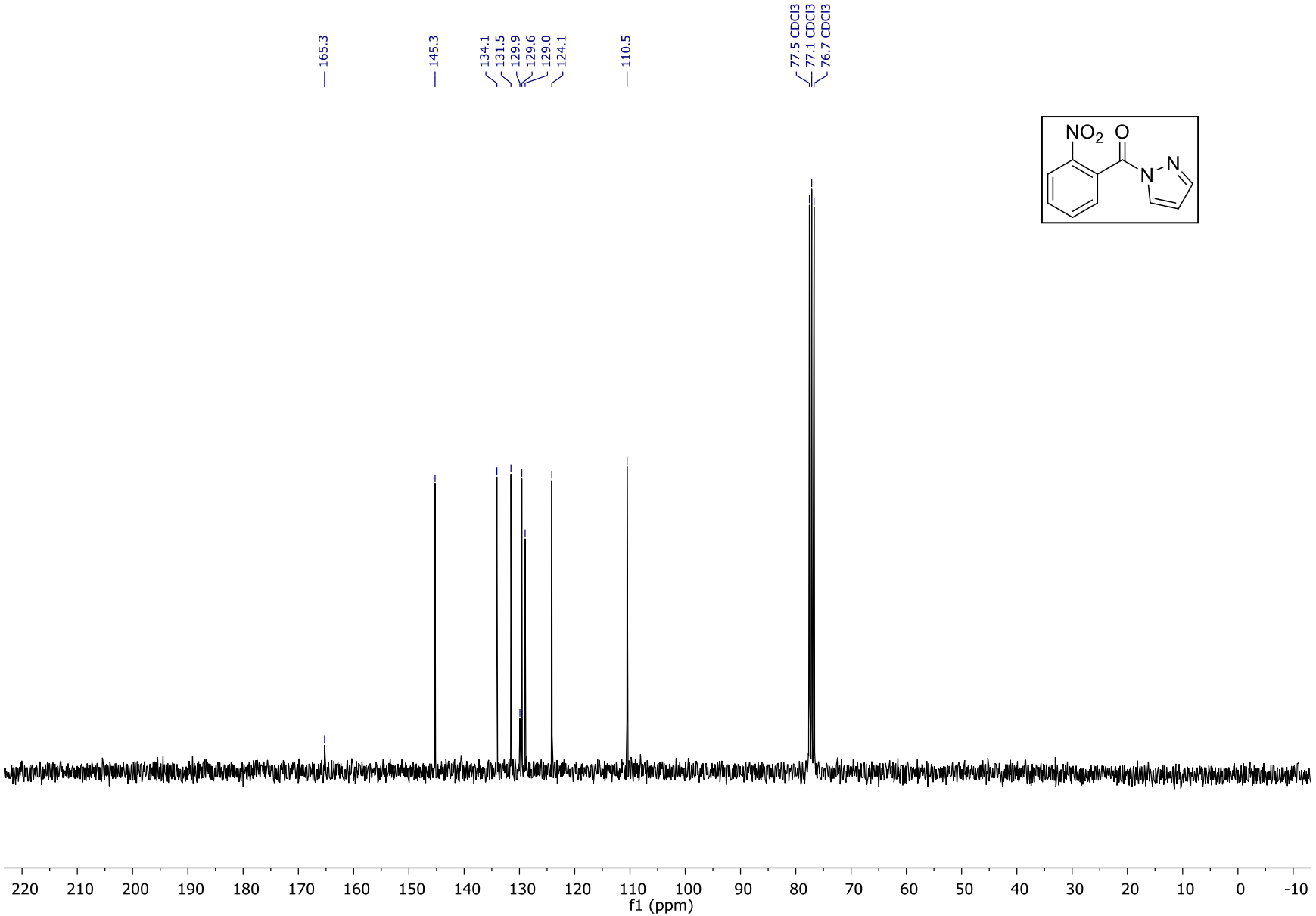
^{13}C-NMR (101 MHz $CDCl_3$) (3-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7l)



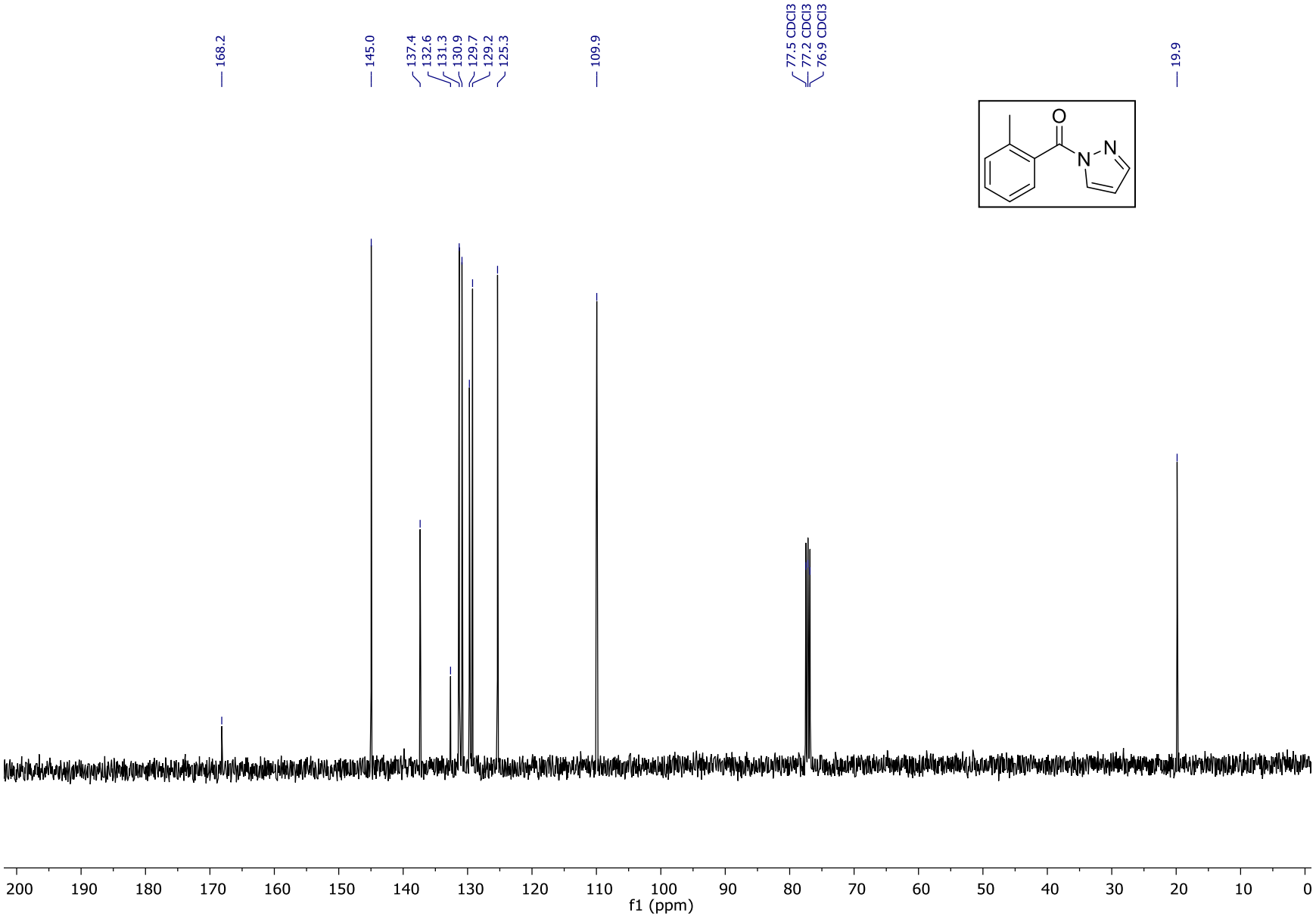
^{13}C-NMR (101 MHz $CDCl_3$) (2-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7m)



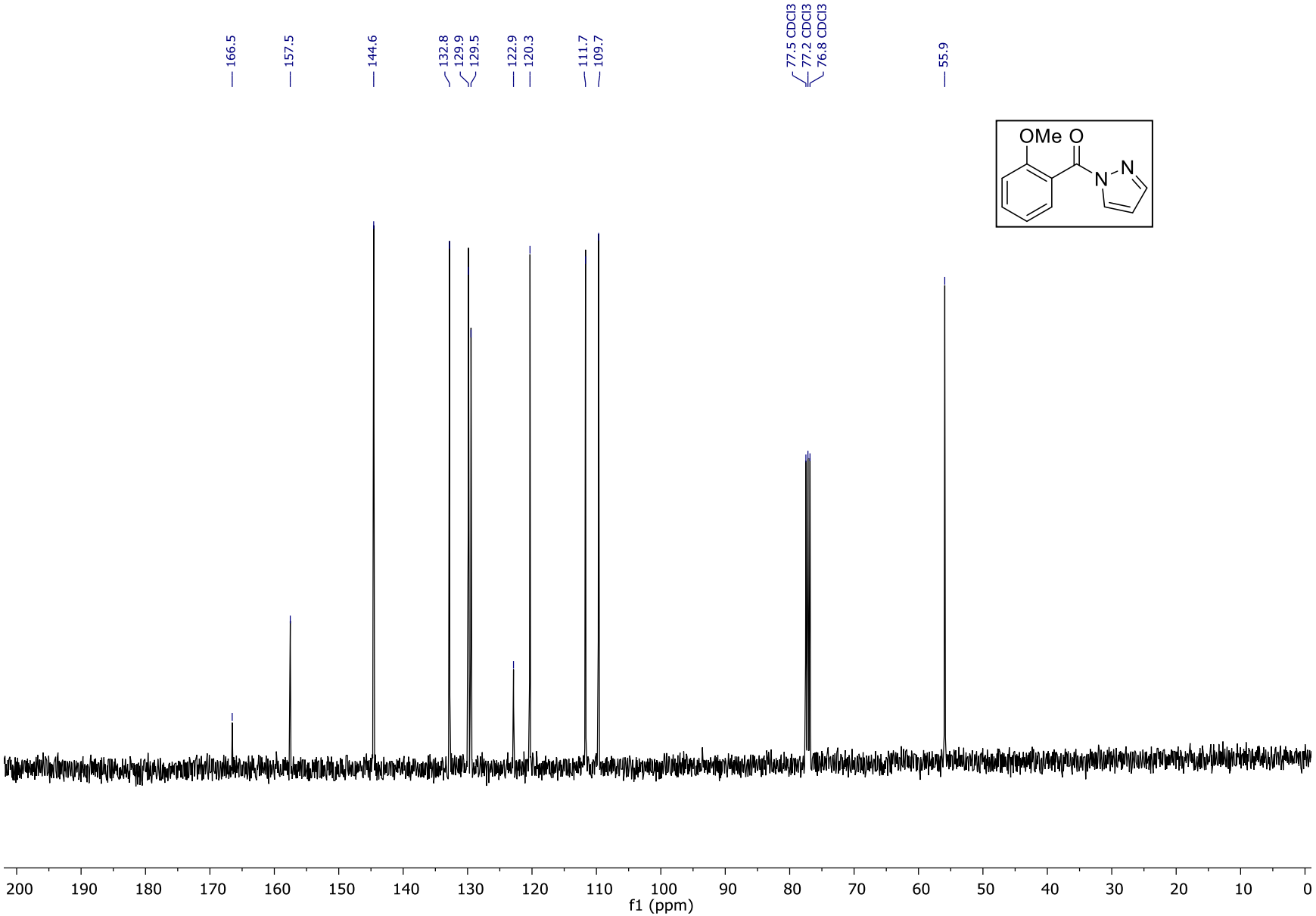
^{13}C-NMR (75 MHz $CDCl_3$) (2-Nitrophenyl)(1*H*-pyrazol-1-yl)methanone (7n)



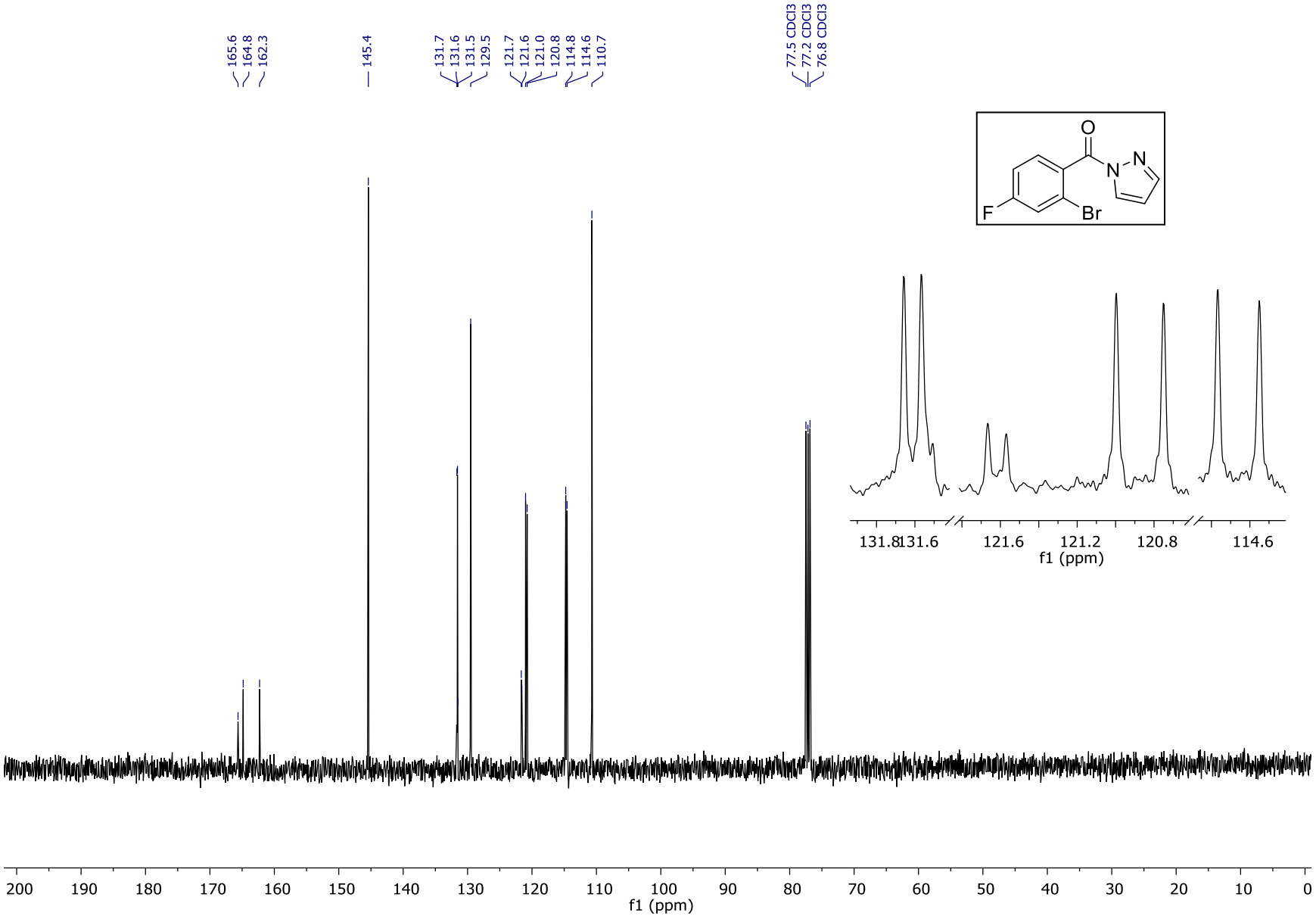
^{13}C-NMR (101 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(*o*-tolyl)methanone (7o)



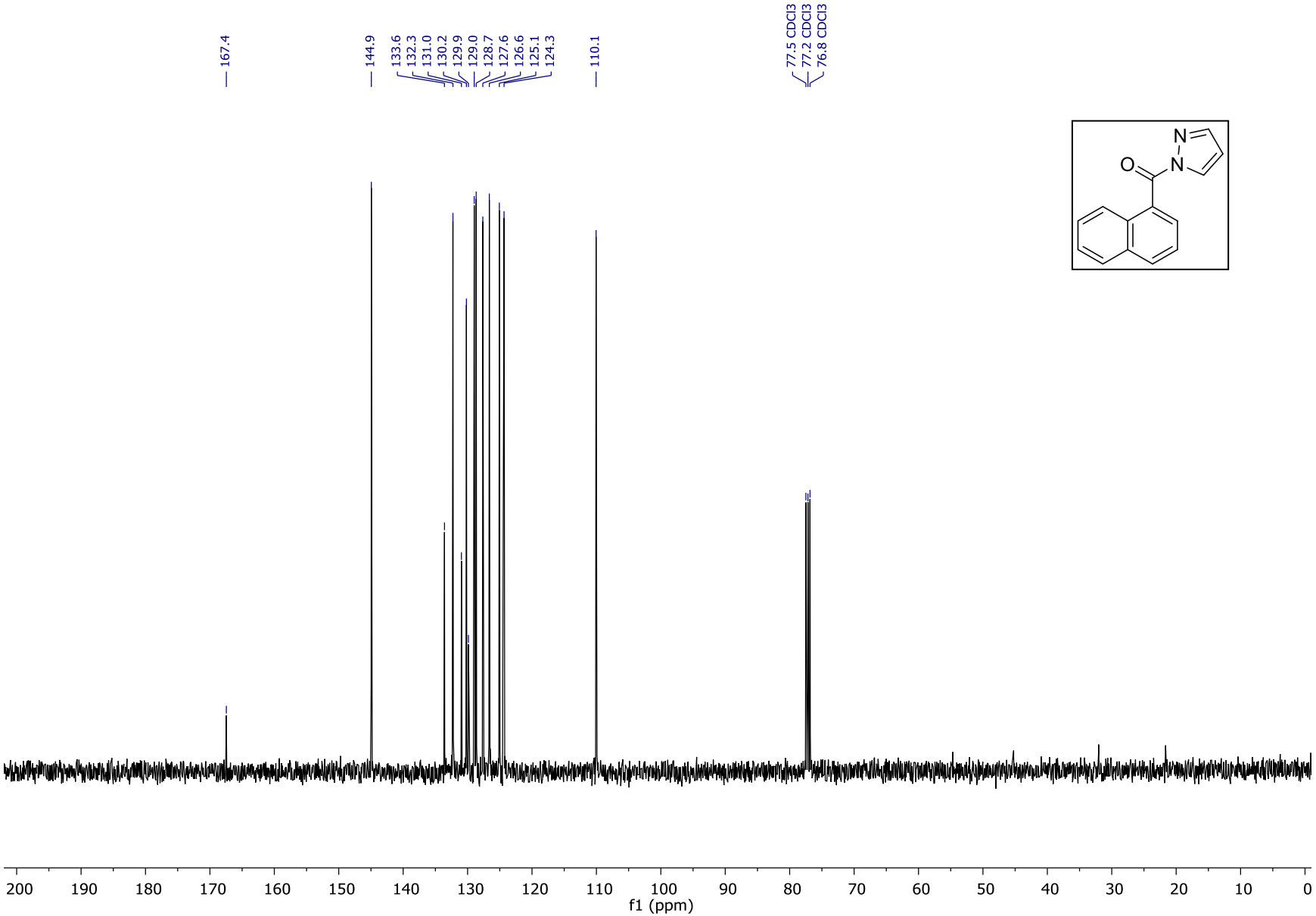
^{13}C-NMR (101 MHz $CDCl_3$) (2-Methoxyphenyl)(1*H*-pyrazol-1-yl)methanone (7p)



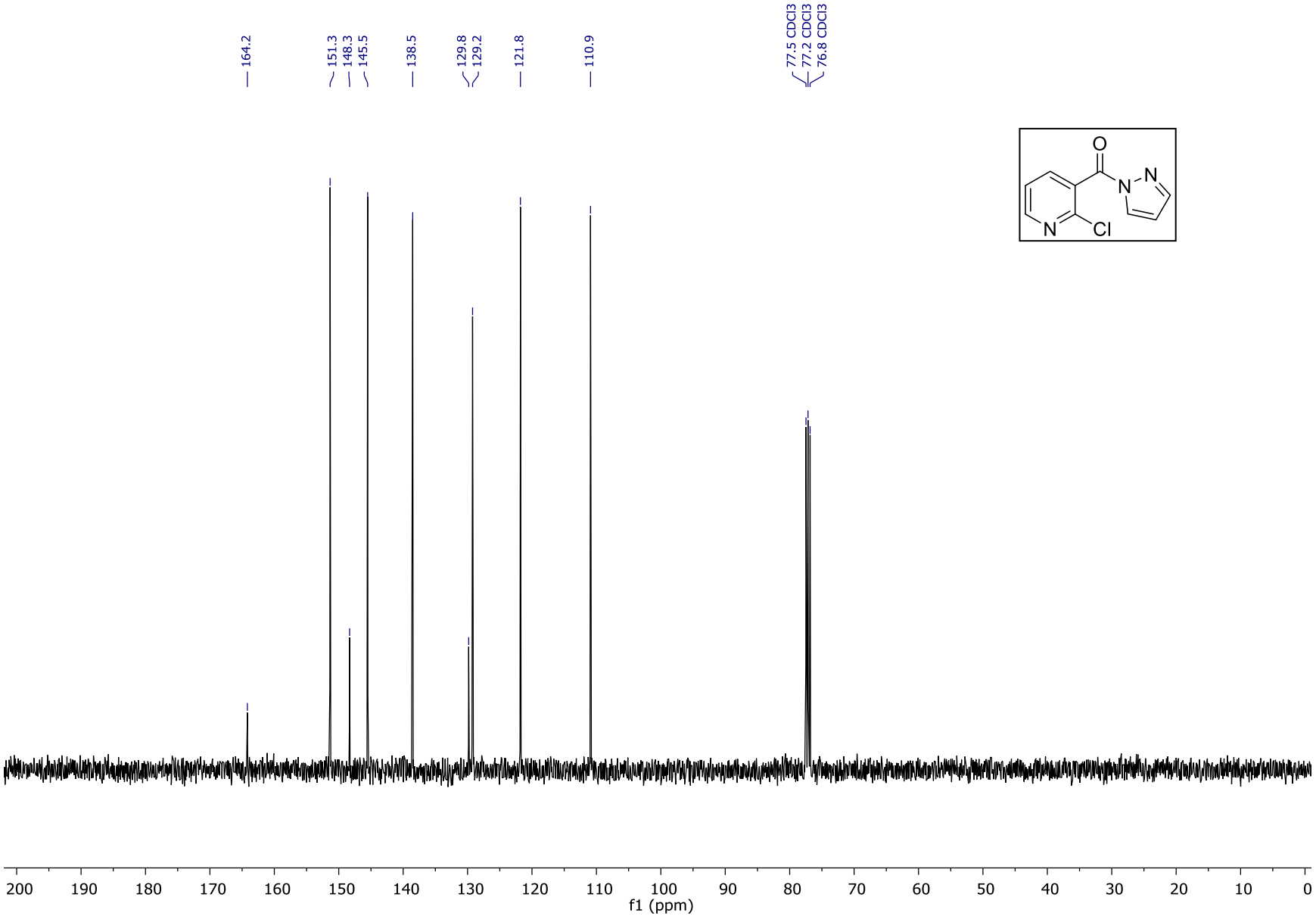
^{13}C-NMR (101 MHz $CDCl_3$) (2-Bromo-4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7q)



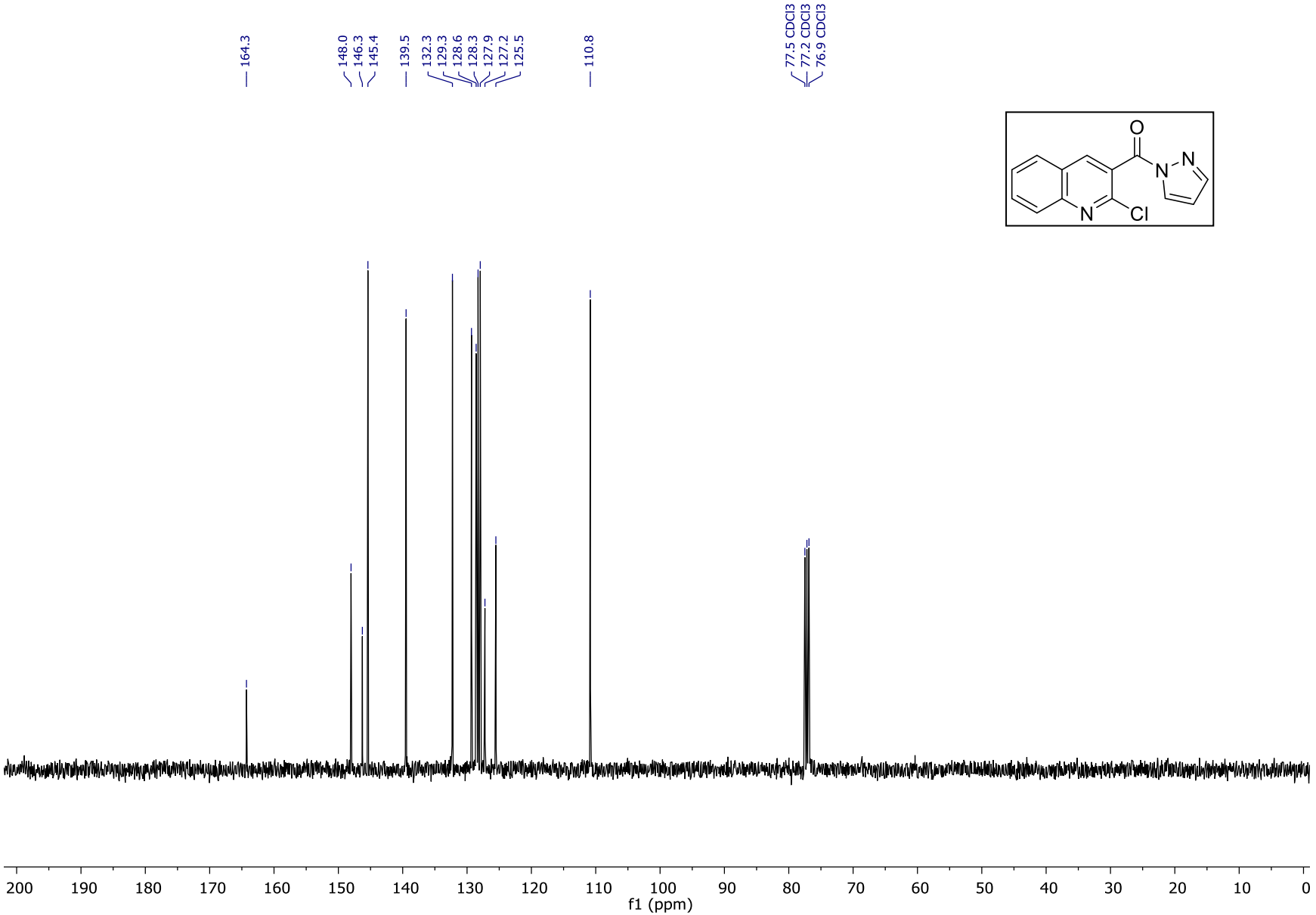
^{13}C-NMR (101 MHz $CDCl_3$) Naphtalen-1-yl(1*H*-pyrazol-1-yl)methanone (7r)



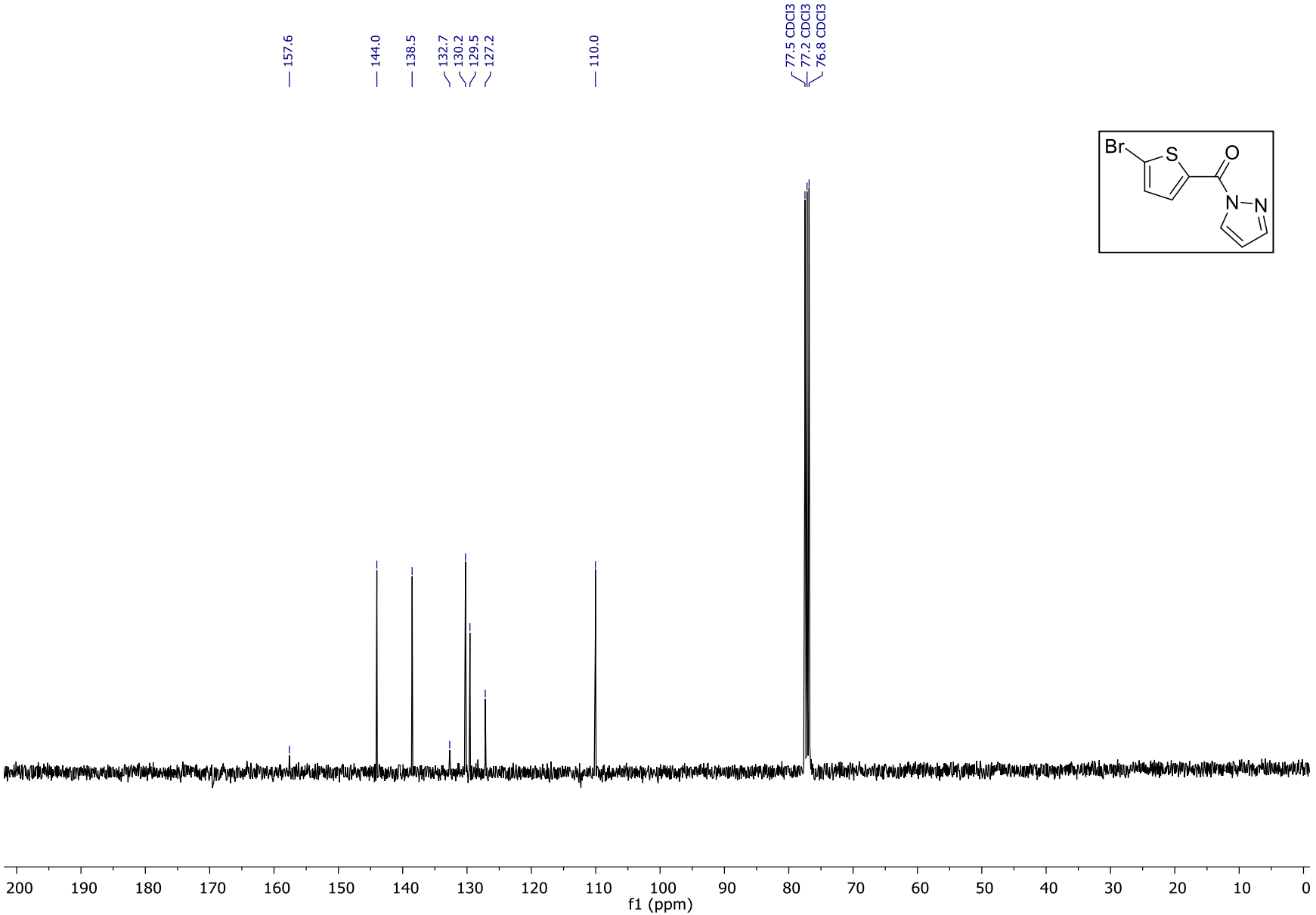
^{13}C-NMR (101 MHz $CDCl_3$) (2-Chloropyridin-3-yl)(1*H*-pyrazol-1-yl)methanone (7s)



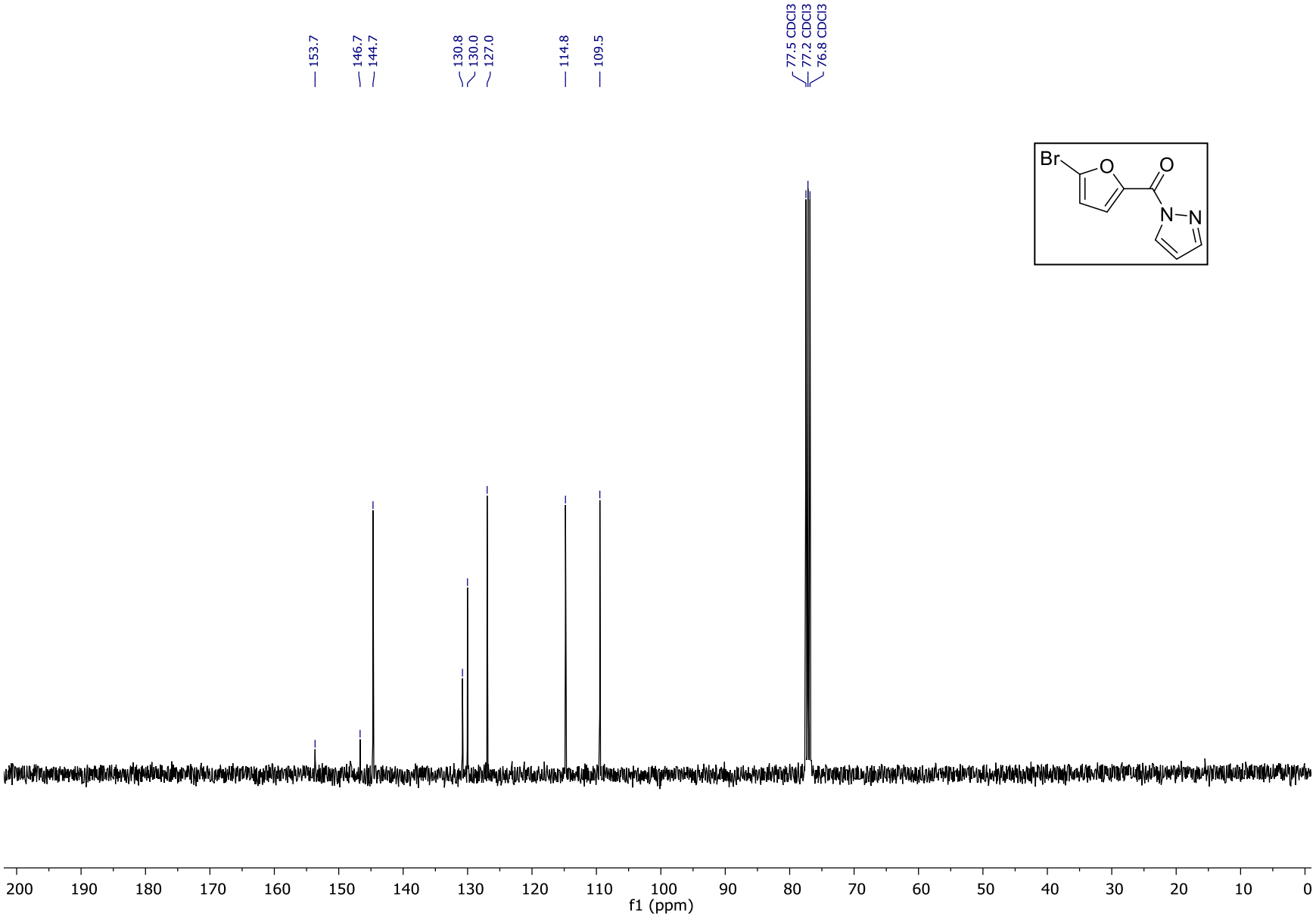
^{13}C-NMR (101 MHz $CDCl_3$) (2-Chloroquinolin-3-yl)(1*H*-pyrazol-1-yl)methanone (7t)



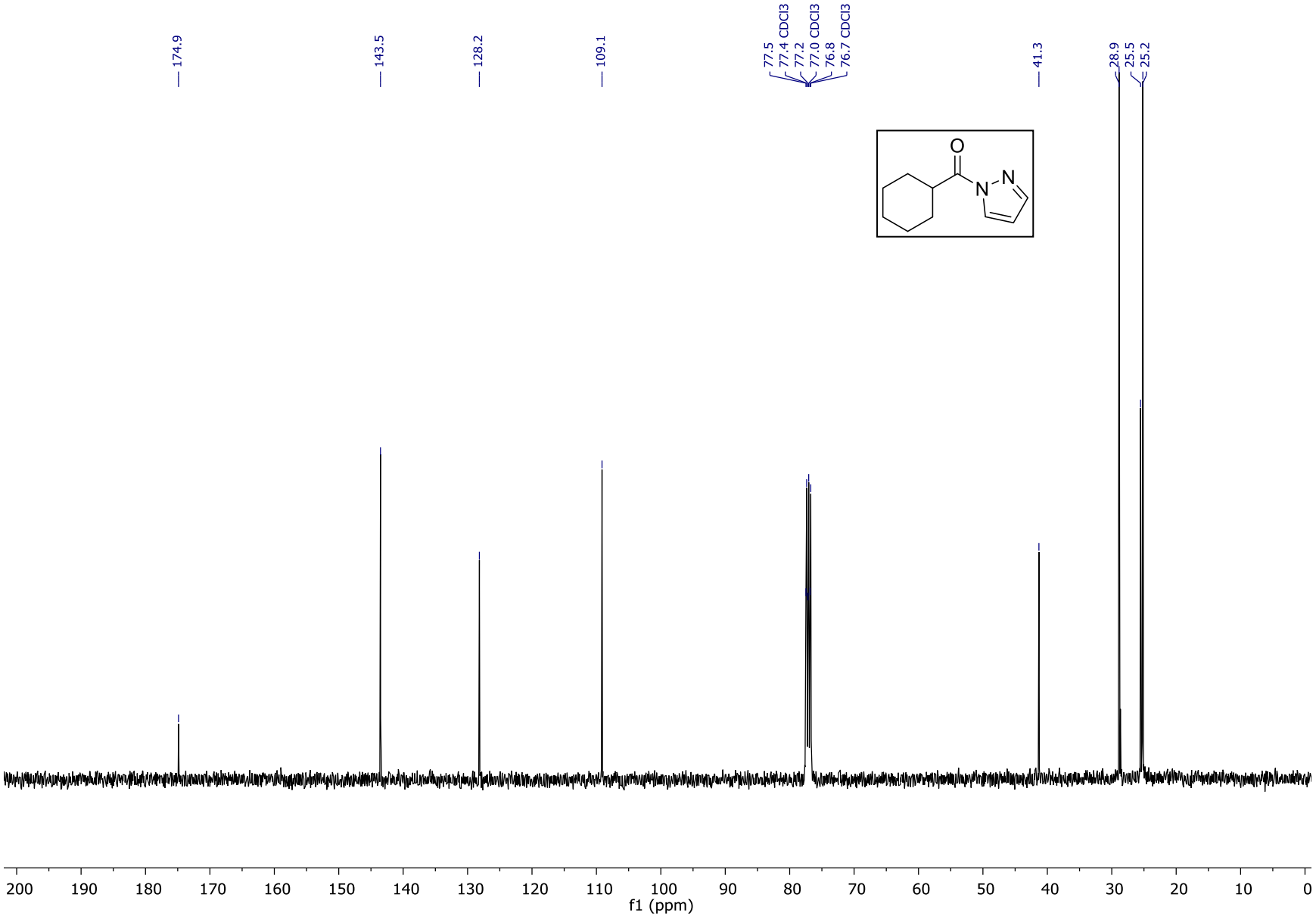
^{13}C-NMR (101 MHz $CDCl_3$) (5-bromothiophen-2-yl)(1*H*-pyrazol-1-yl)methanone (7u)



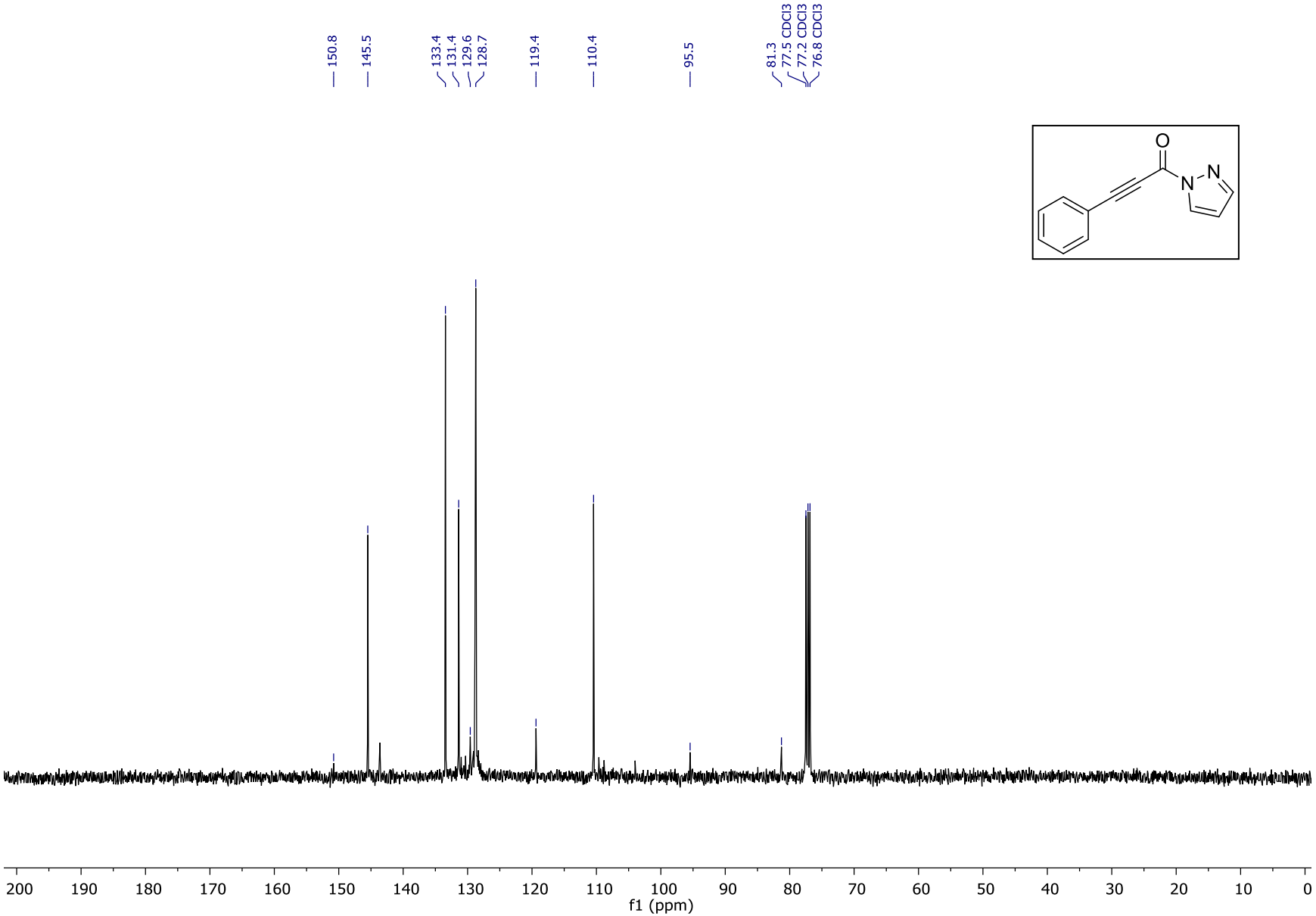
^{13}C-NMR (101 MHz $CDCl_3$) (5-bromofuran-2-yl)(1*H*-pyrazol-1-yl)methanone (7v)



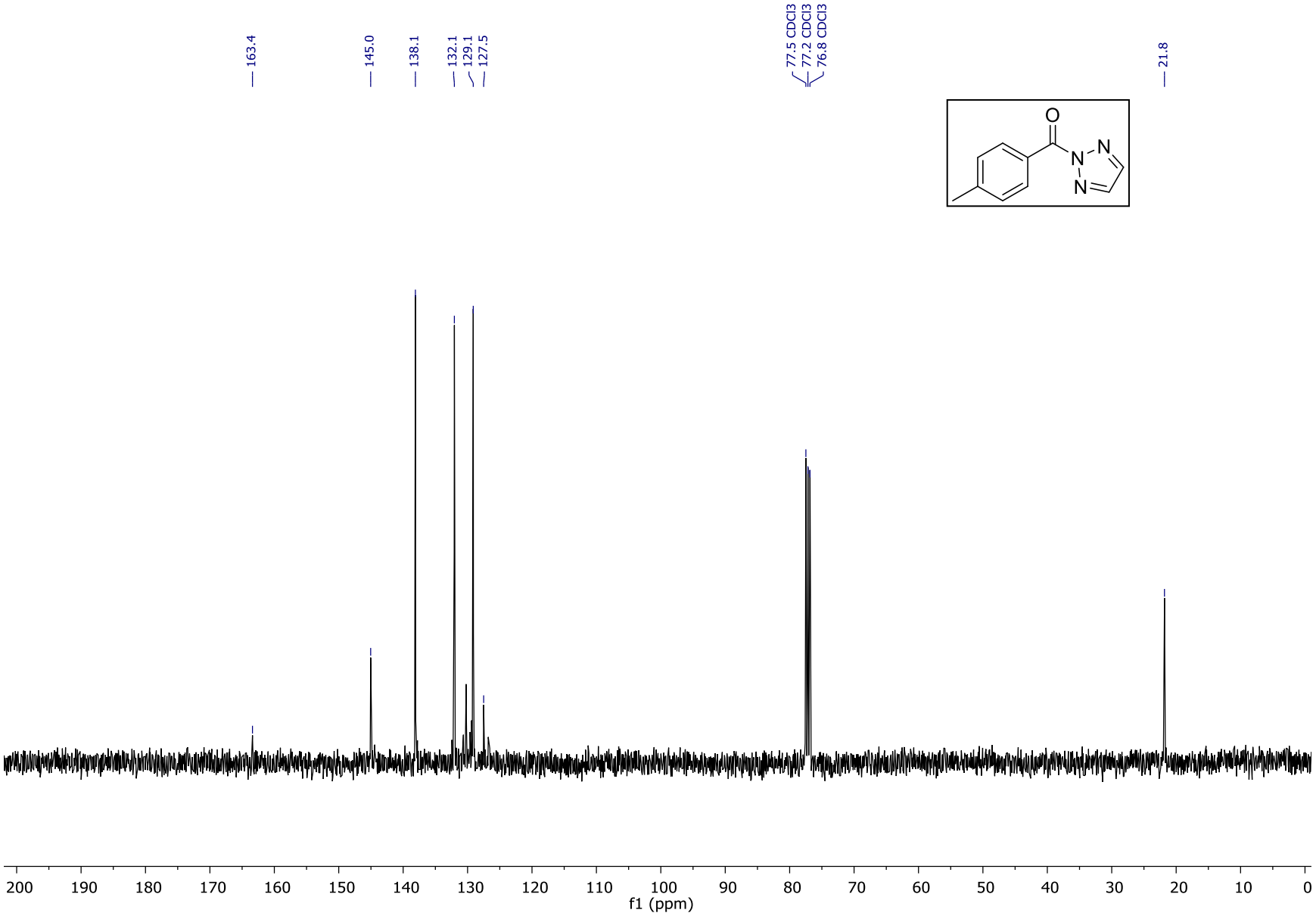
^{13}C-NMR (101 MHz $CDCl_3$) Cyclohexyl(1*H*-pyrazol-1-yl)methanone (7w)



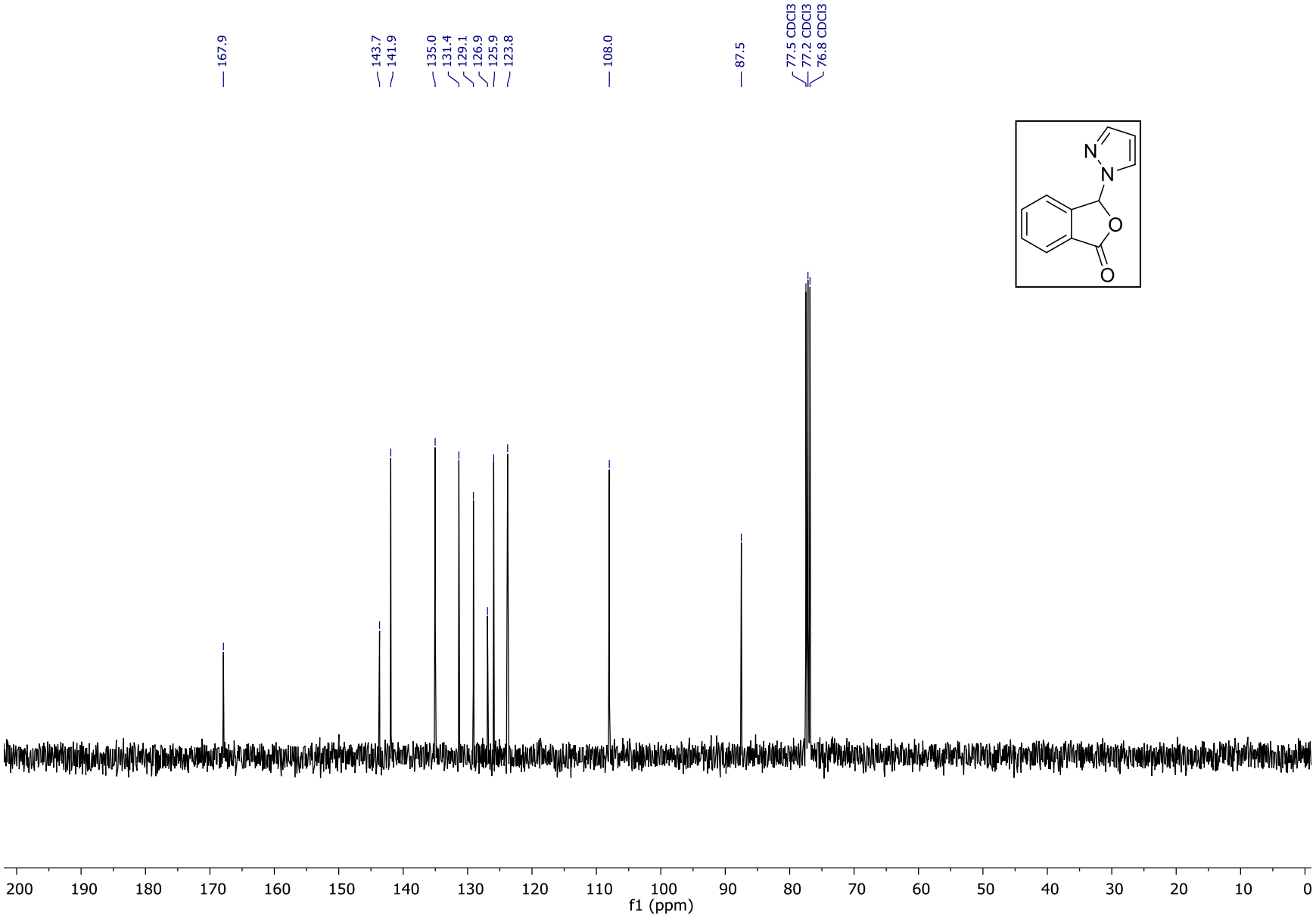
^{13}C-NMR (101 MHz $CDCl_3$) 3-phenyl-1-(1*H*-pyrazol-1-yl)prop-2-yn-1-one (7z)



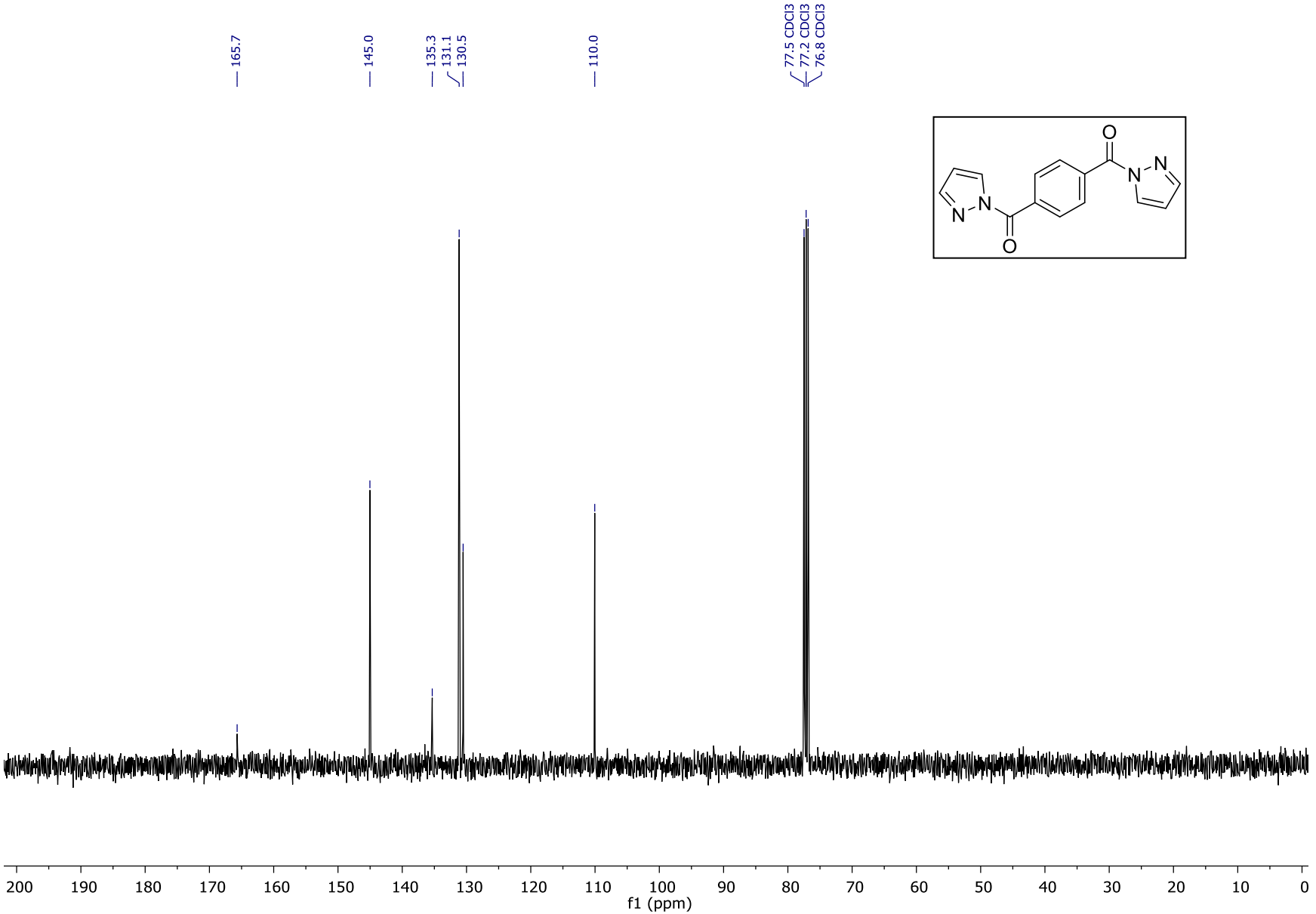
^{13}C-NMR (101 MHz $CDCl_3$) *p*-Tolyl(2*H*-1,2,3-triazol-2-yl)methanone (7ae)



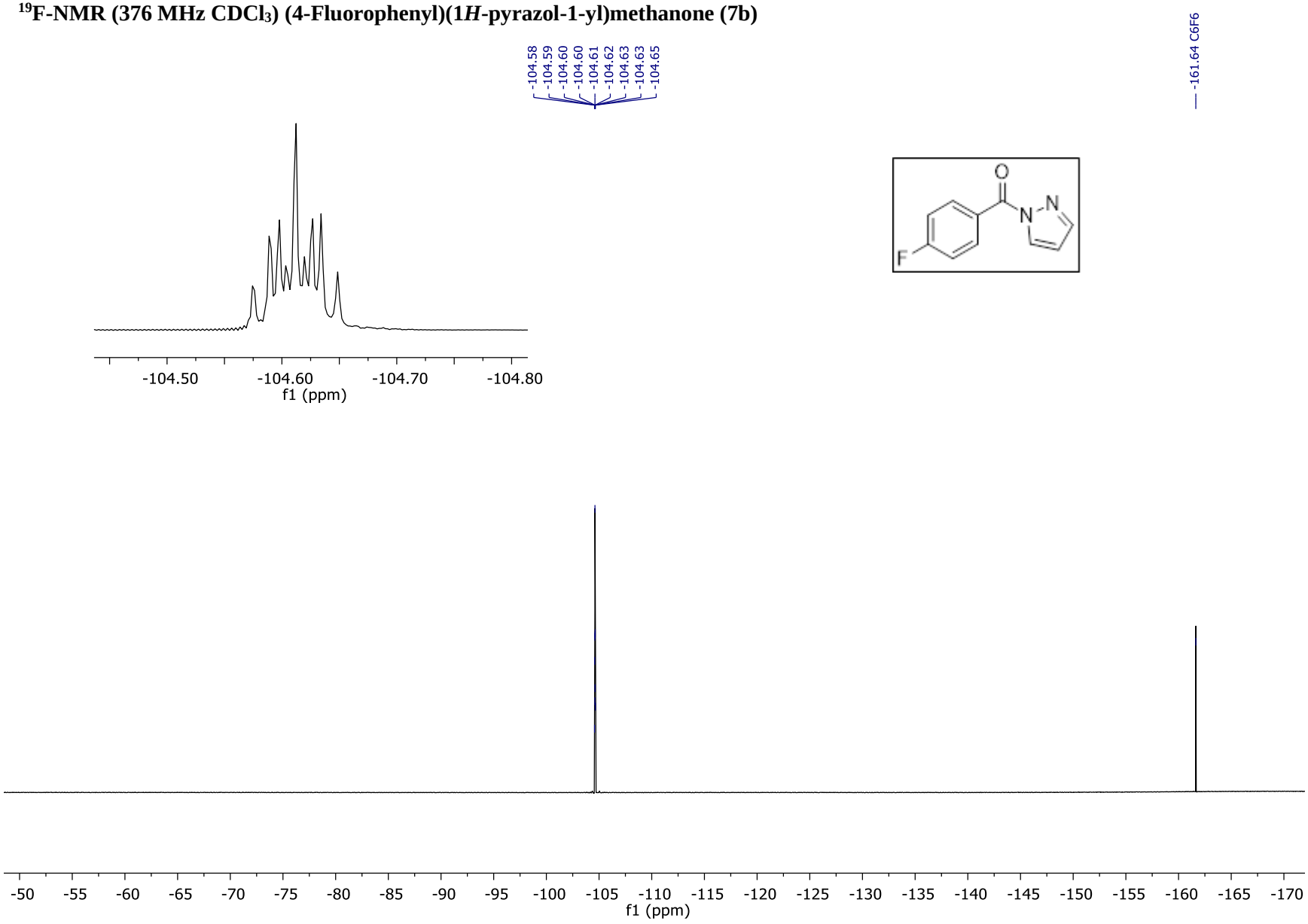
^{13}C-NMR (101 MHz $CDCl_3$) 3-(1*H*-pyrazol-1-yl)isobenzofuran-1(3*H*)-one (7ai)



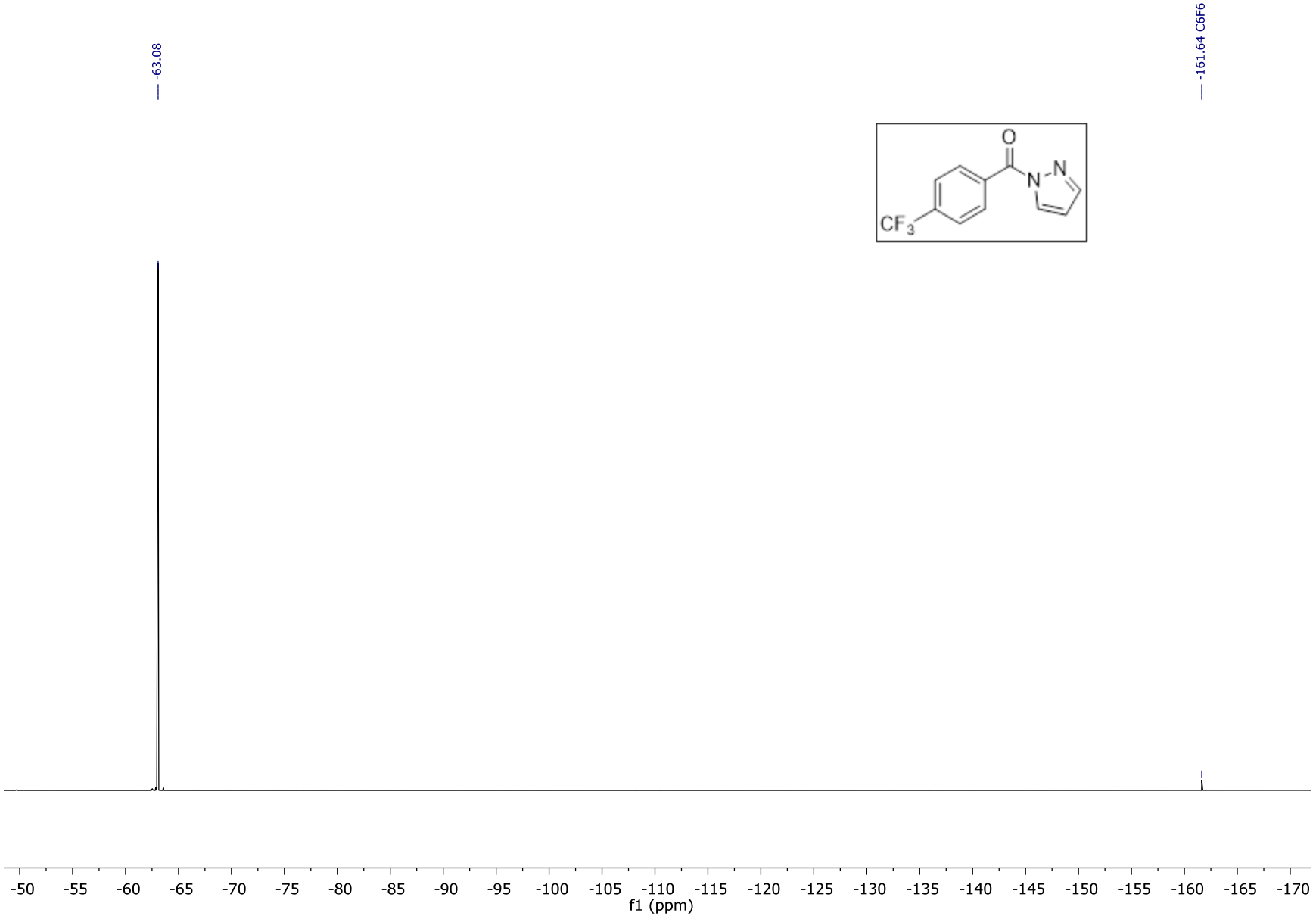
^{13}C-NMR (101 MHz $CDCl_3$) 1,4-phenylenebis((1*H*-pyrazol-1-yl)methanone) (7aj)



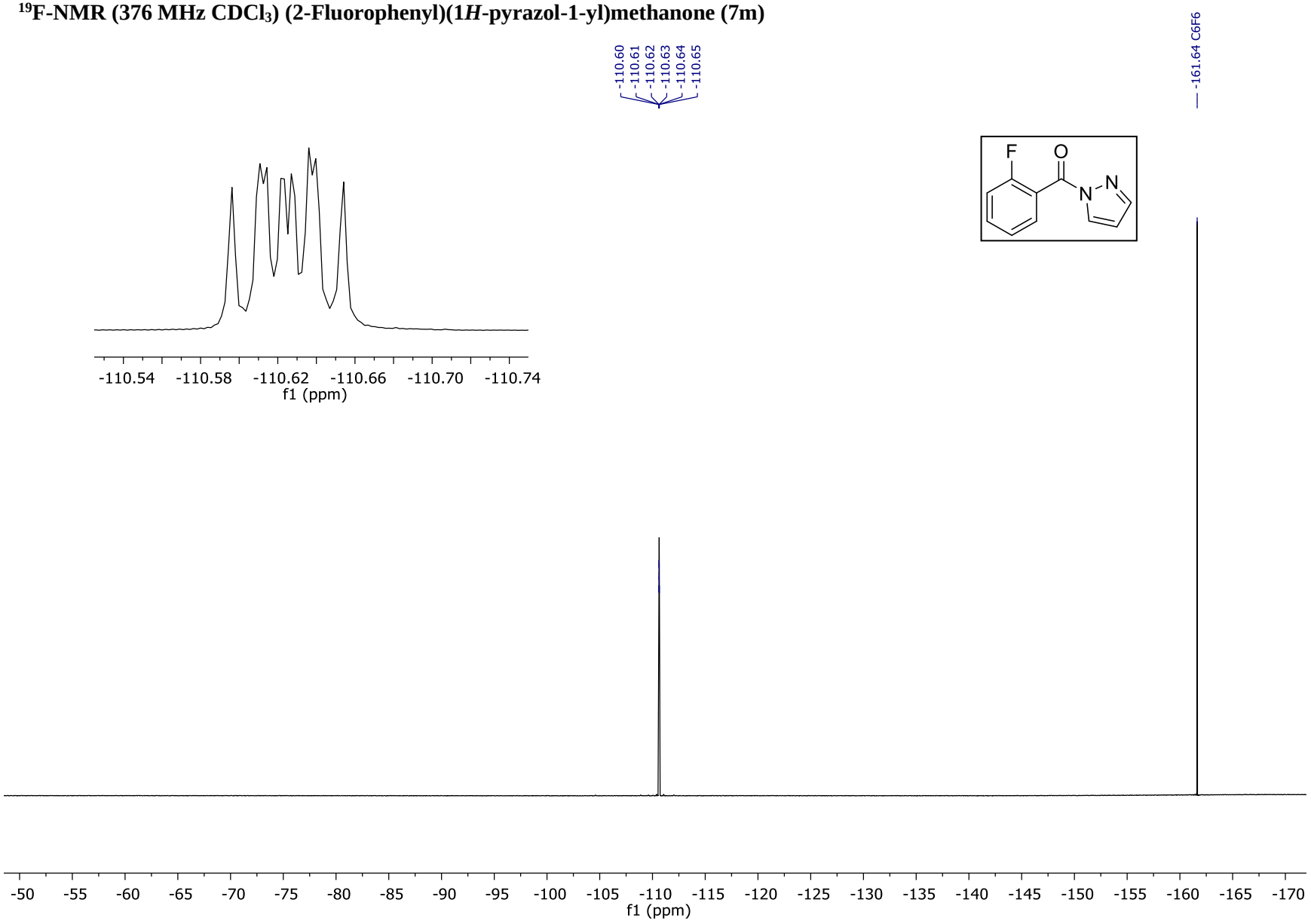
^{19}F-NMR (376 MHz $CDCl_3$) (4-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7b)



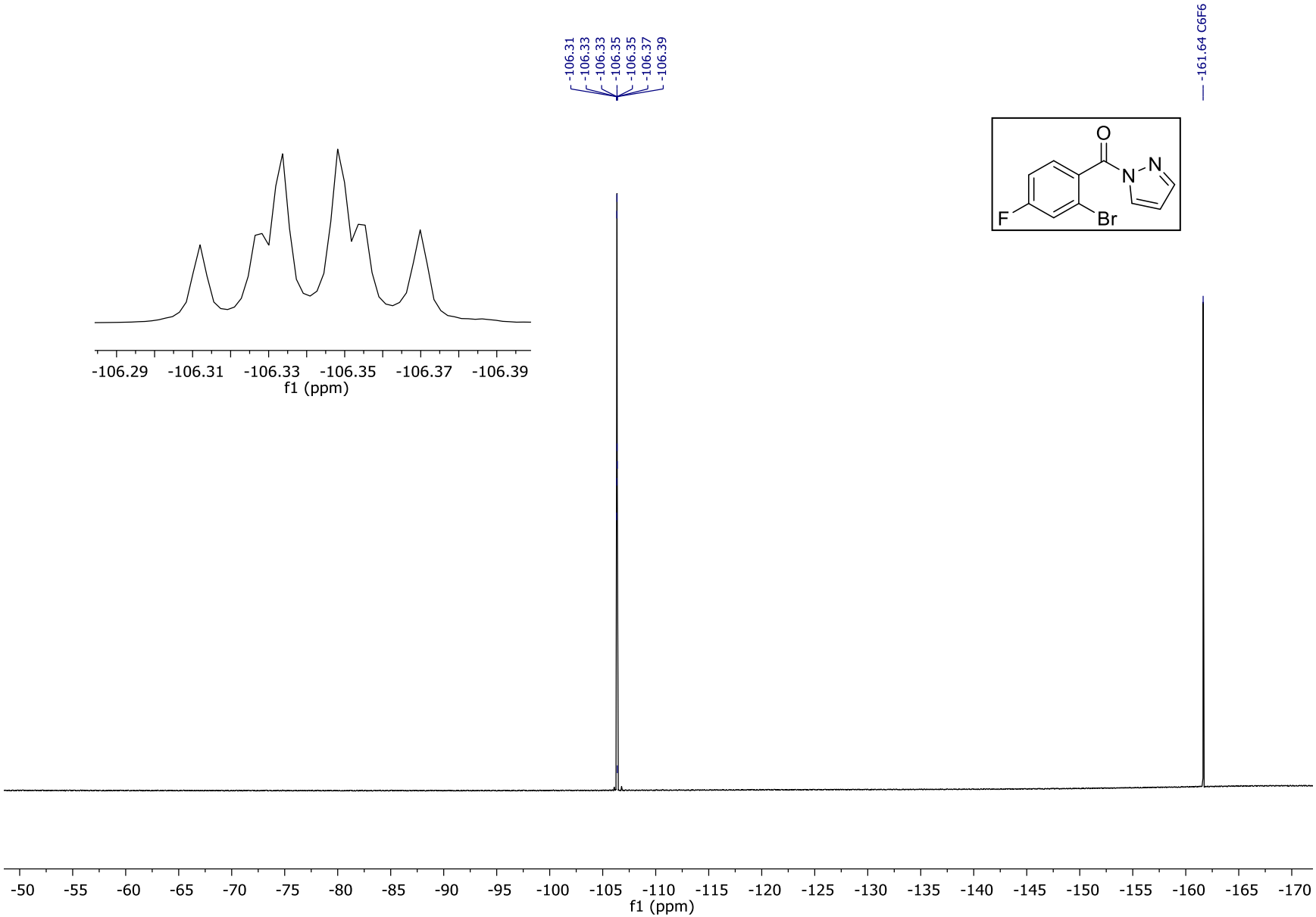
^{19}F-NMR (376 MHz $CDCl_3$) (1*H*-Pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (7f)



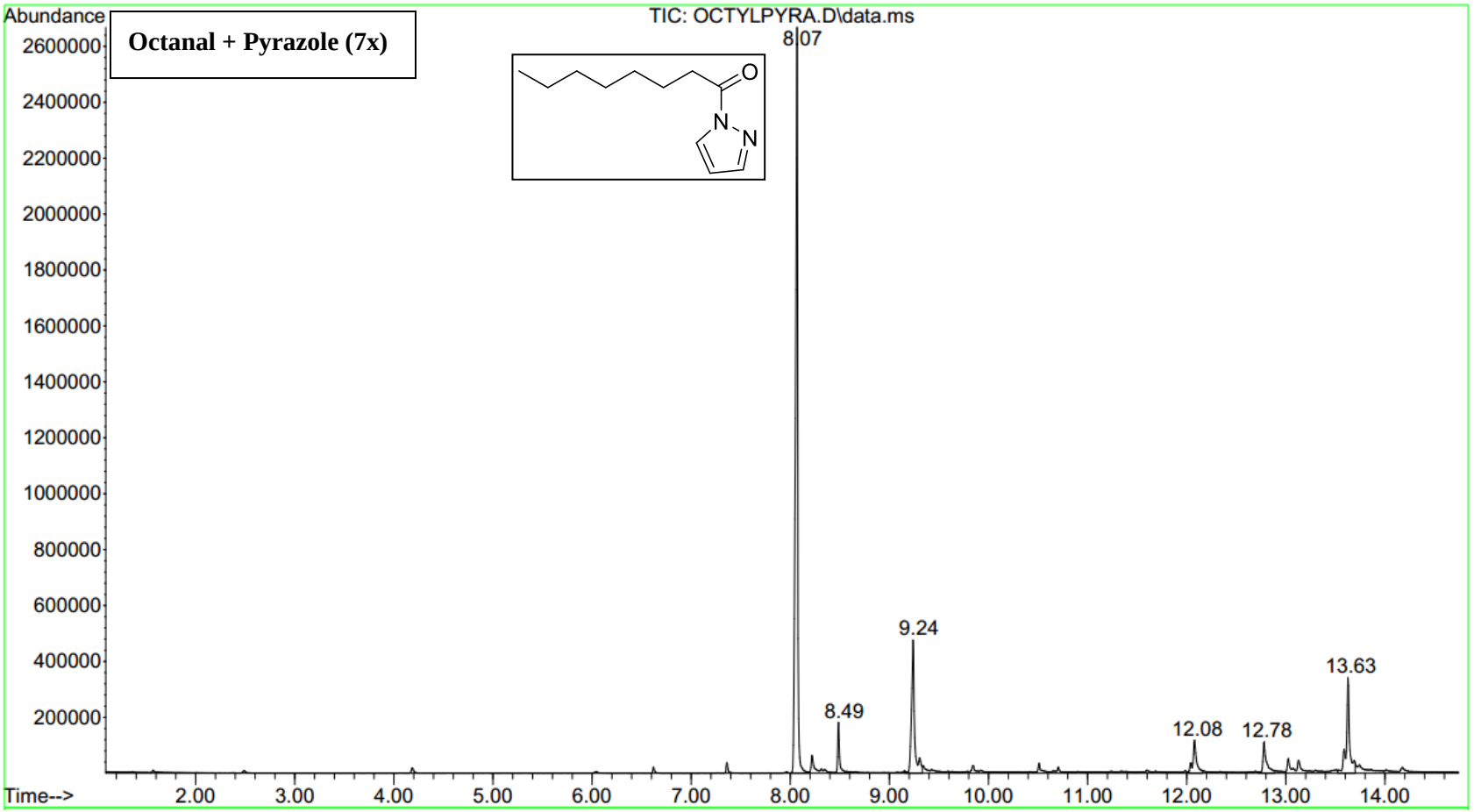
^{19}F-NMR (376 MHz $CDCl_3$) (2-Fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7m)



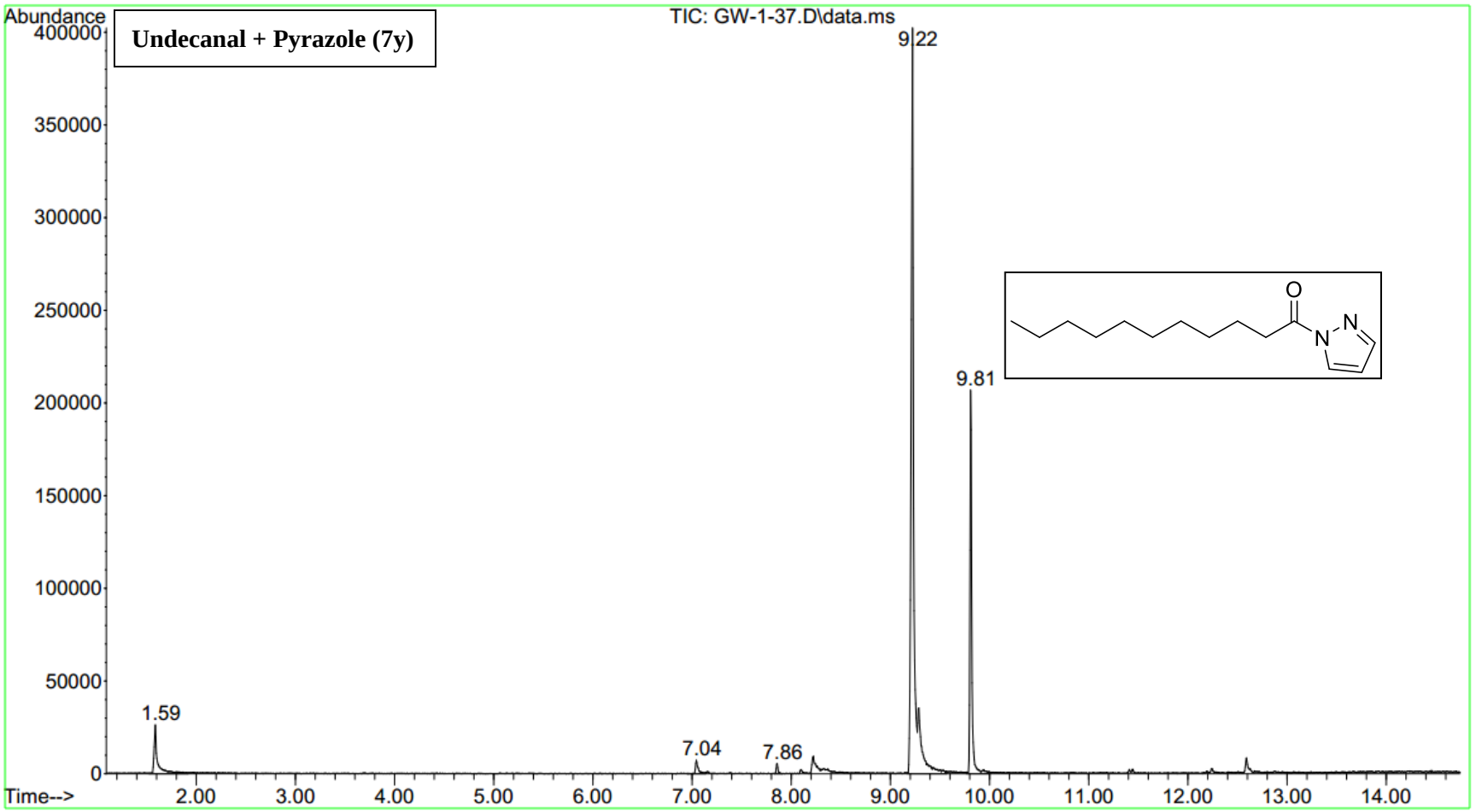
^{19}F-NMR (376 MHz $CDCl_3$) (2-Bromo-4-fluorophenyl)(1*H*-pyrazol-1-yl)methanone (7q)



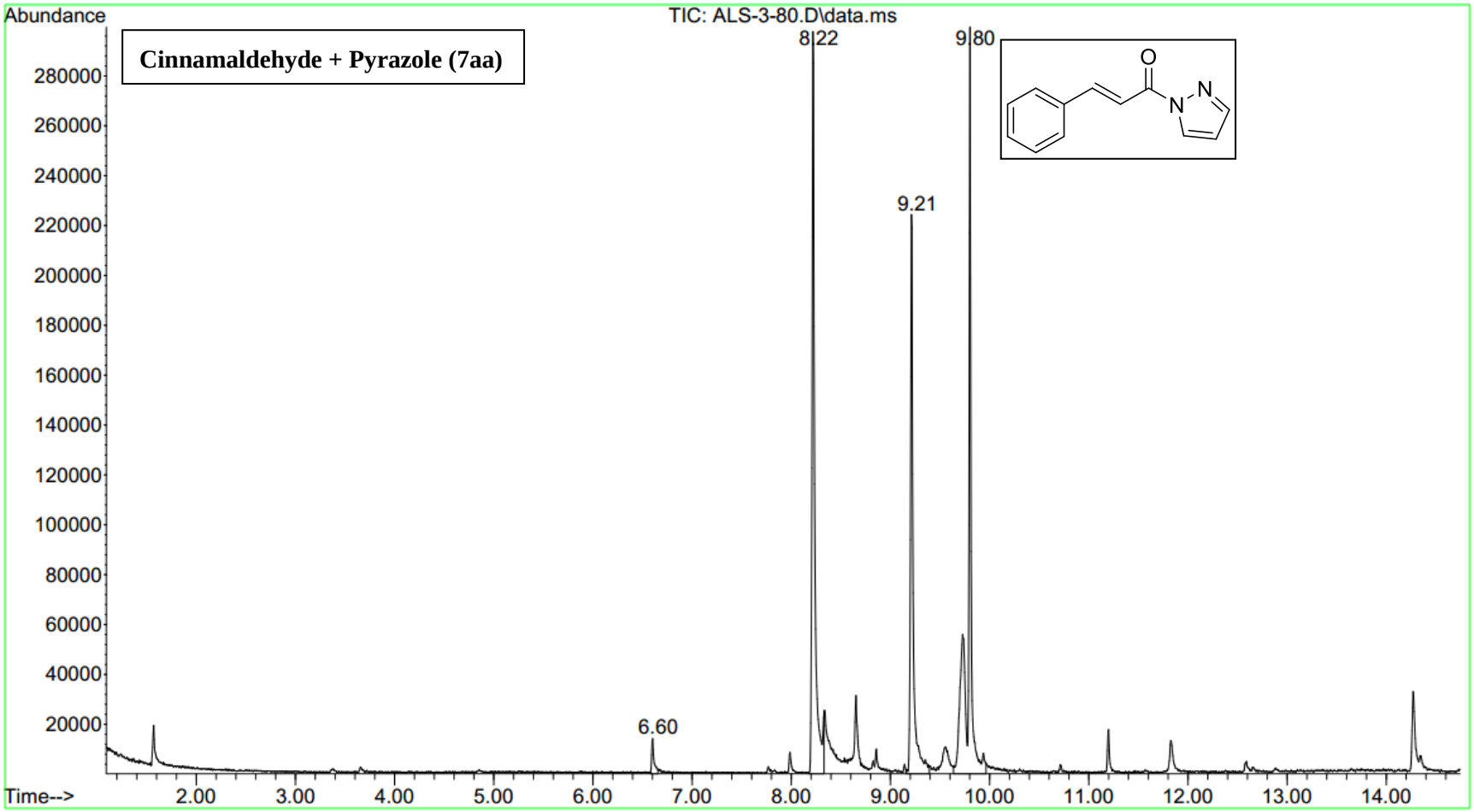
Gas Chromatograms



No.	Peak MW	Ret. time (min)	Area (mAU*min)	Height (mAU)	Identity	% of total
1	194	8.067	40263964	2602505	Product	67.362
2	191	8.486	2090112	171966	Unknown	3.497
3	213	9.241	7694454	443592	ACT	12.873
4	233	12.081	2118774	109562	Unknown	3.545
5	213	12.783	2173858	106036	ACT	3.637
6	283	13.630	5431785	319058	Unknown	9.087



No.	Peak MW	Ret. time (min)	Area (mAU*min)	Height (mAU)	Identity	% of total
1	68	1.586	651866	26372	1*H*-Pyrazole	5.793
2	170	7.043	142359	7331	Starting Material	1.265
3	200	7.856	66929	5653	Methyl Ester from quench	.595
4	213	9.222	7739569	404116	ACT	68.777
5	236	9.809	2652341	211917	Product	23.570



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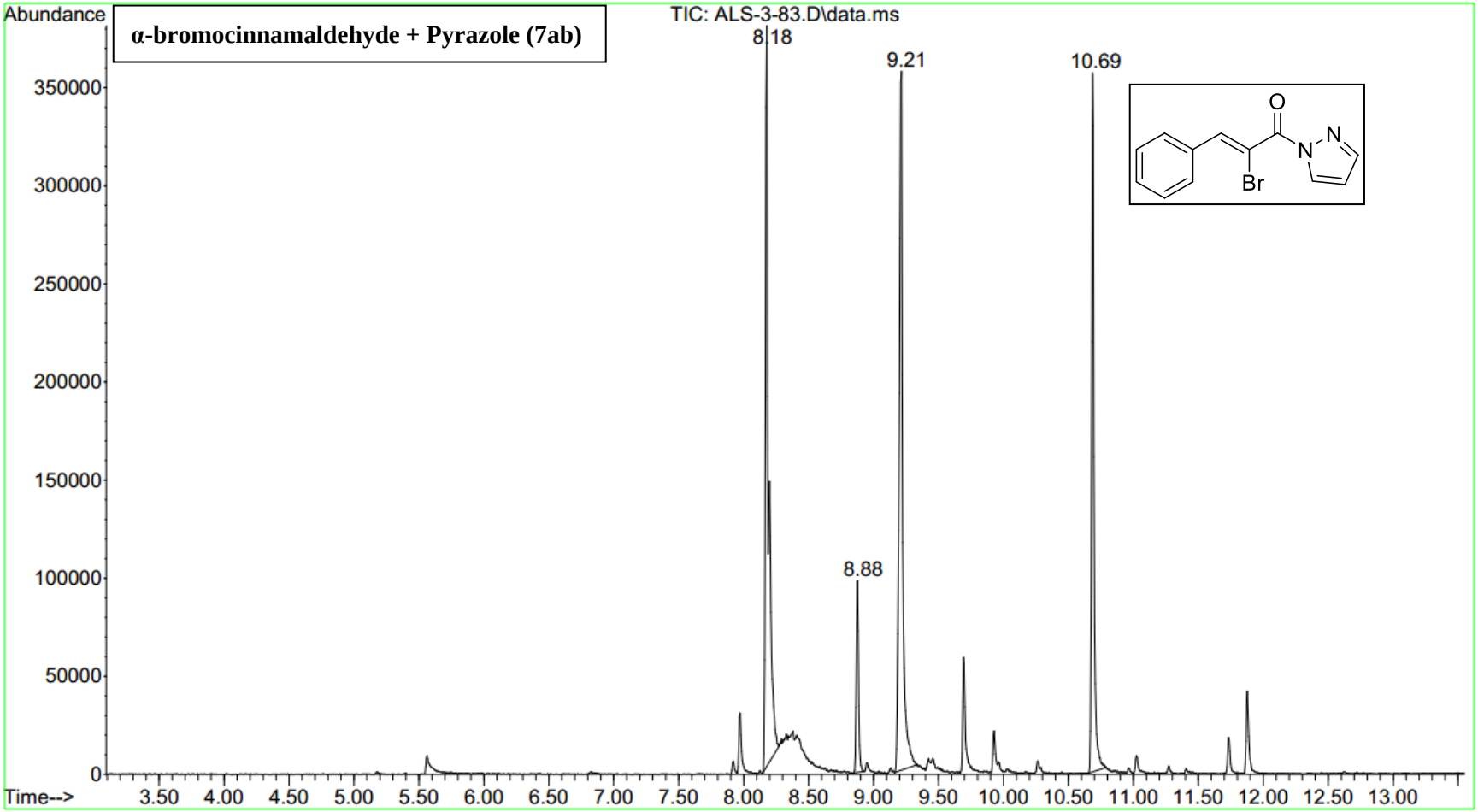
1	132	6.600	232572	14300	Starting Material	1.446
2	198	8.220	5613489	303982	Carboxylic acid byproduct	34.907
3	213	9.214	4115998	230552	ACT	25.595
4	198	9.802	6119442	299670	Product	38.053



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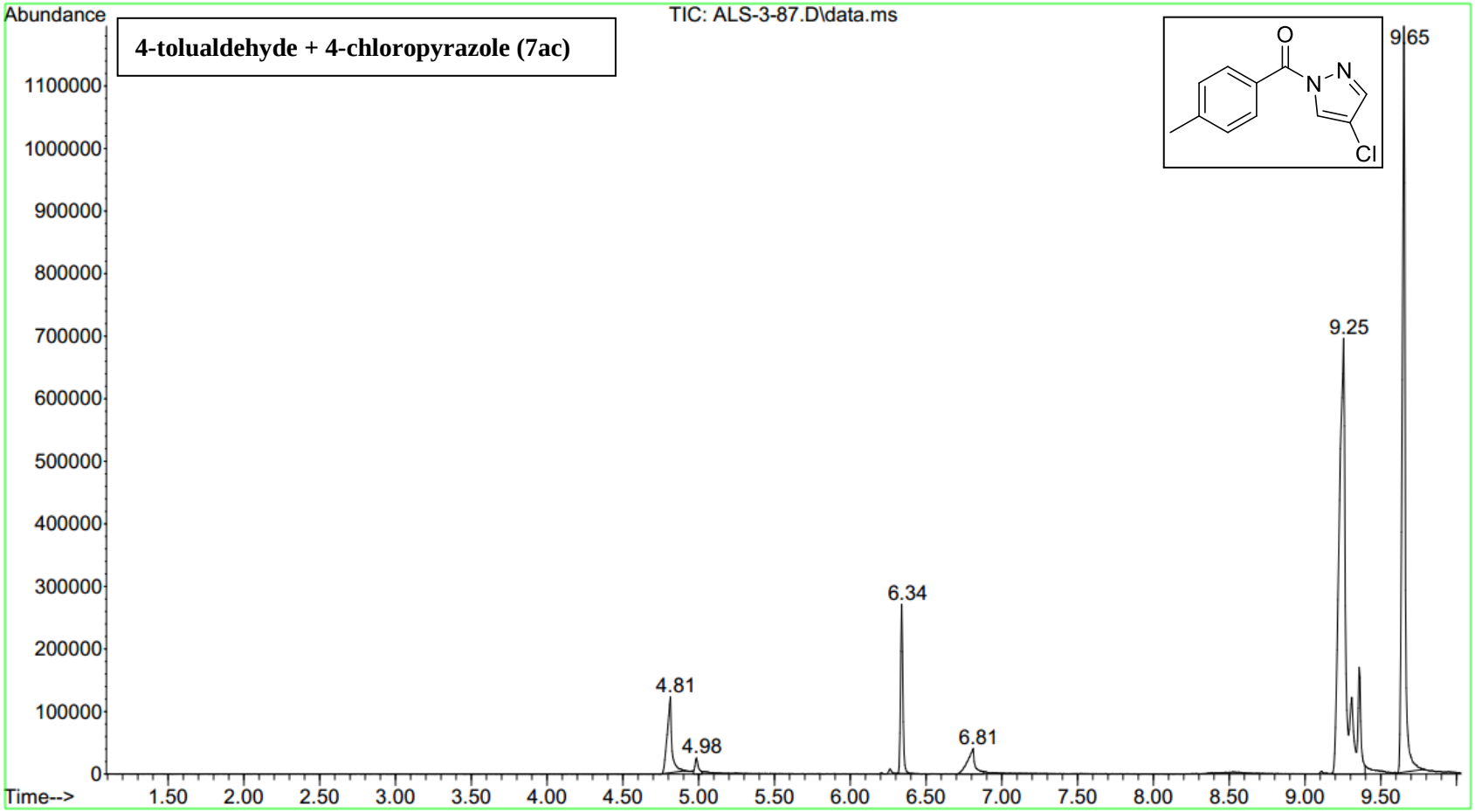
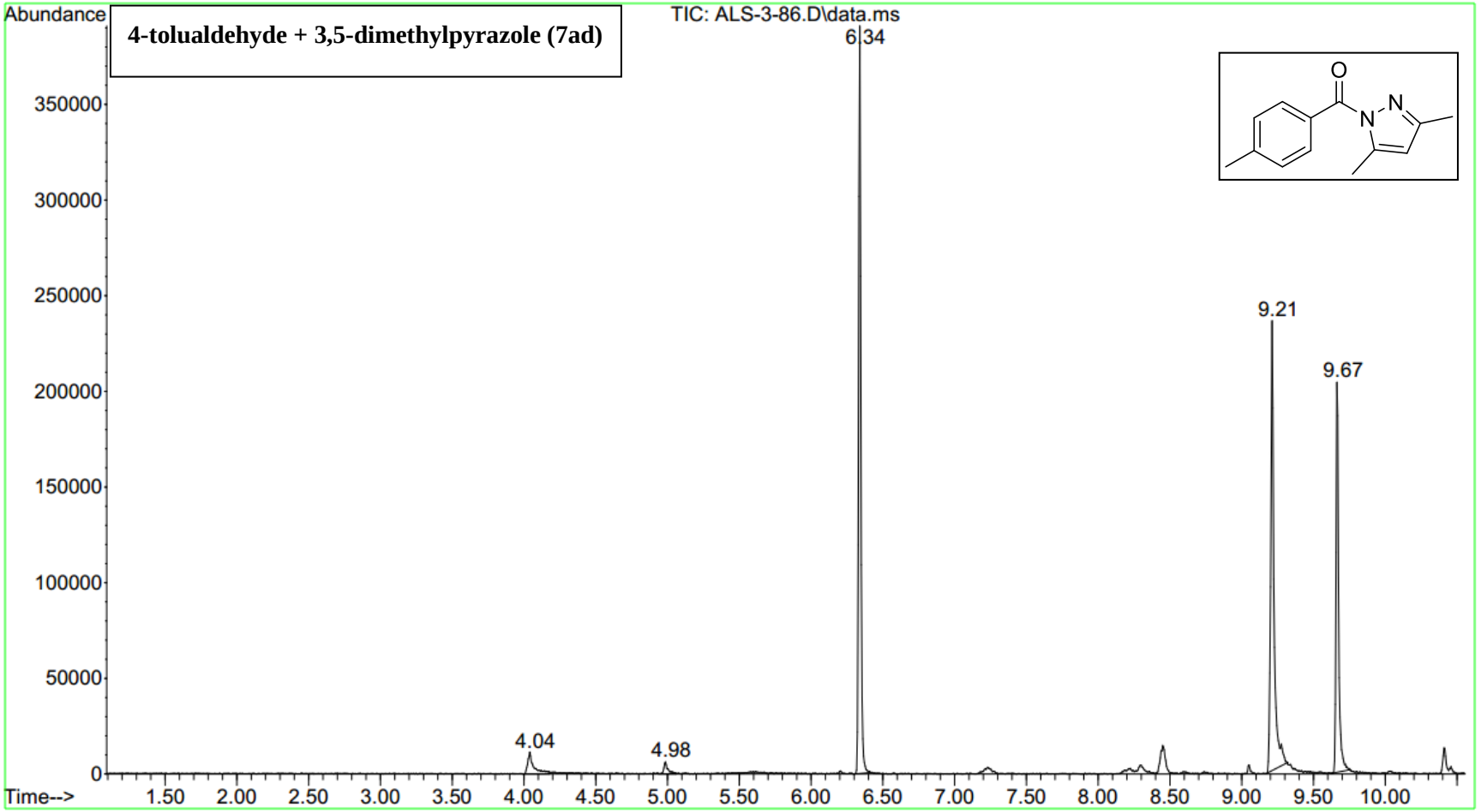
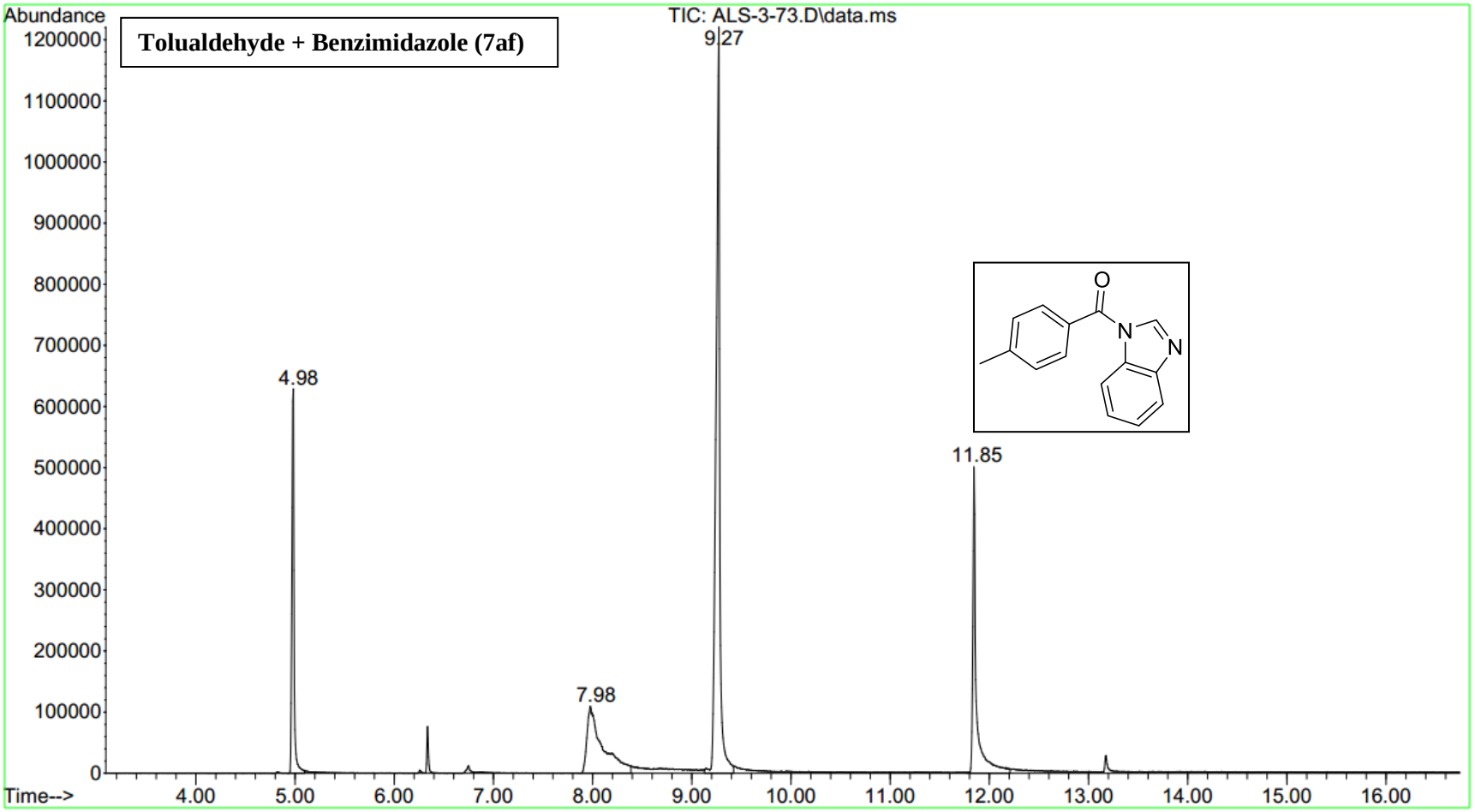
1	210	8.178	6119078	375320	Starting Material	33.365
2	240	8.878	1124105	93093	Carboxylic acid byproduct	6.129
3	213	9.212	6578688	355311	ACT	35.871
4	276	10.689	4518029	349287	Product	24.635



No.	Peak MW	Ret. time (min)	Area (mAU*min)	Height (mAU)	Identity	% of total
1	102	4.812	2560179	116261	4-chloropyrazole	5.469
2	120	4.985	404801	26022	Starting Material	0.865
3	135	6.341	2848335	258018	Unknown	6.085
4	136	6.809	1411865	42764	Carboxylic acid byproduct	3.016
5	213	9.254	23187935	701158	ACT	49.538
6	220	9.654	16395472	1162371	Product	35.027



No.	Peak MW	Ret. time (min)	Area (mAU*min)	Height (mAU)	Identity	% of total
1	96	4.041	335931	11538	3,5-dimethylpyrazole	3.118
2	120	4.985	126524	6392	Starting Material	1.174
3	135	6.341	4146335	374204	Unknown	38.485
4	213	9.214	3621857	223561	ACT	33.617
5	213	9.667	2543207	196597	Product	23.605



No.	Peak MW	Ret. time (min)	Area (mAU*min)	Height (mAU)	Identity	% of total
1	121	4.980	9230360	659123	Starting Material	14.366
2	118	7.976	11851156	110329	Starting Azole	18.445
3	213	9.271	31439683	1261507	ACT	48.933
4	236	11.846	11729566	503408	Product	18.256