Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

POP-Pd(II) catalyzed easy and safe *in-situ* carbonylation towards the synthesis of *α*-ketoamidesfrom secondary cyclic amines utilizing $CHCl_3$ as the carbon monoxide surrogate

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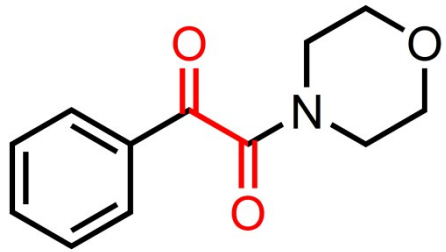
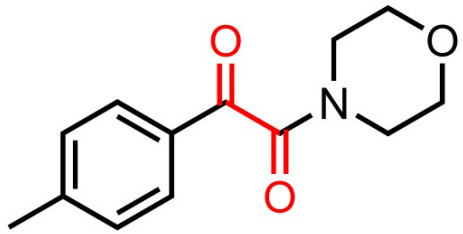
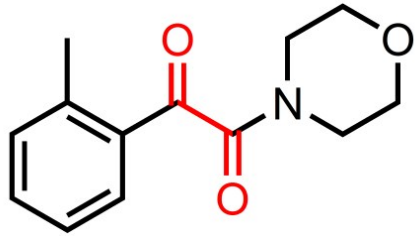
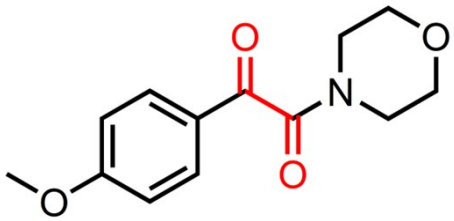
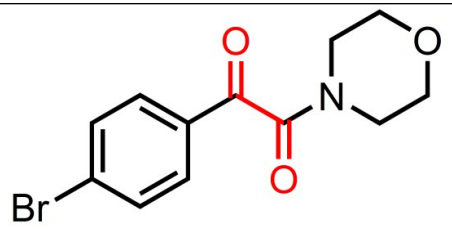
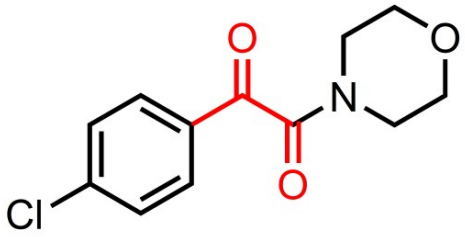
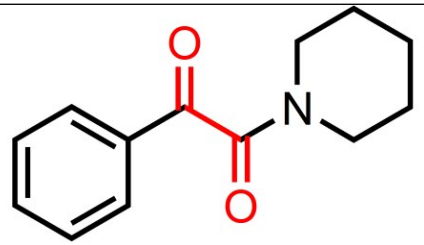
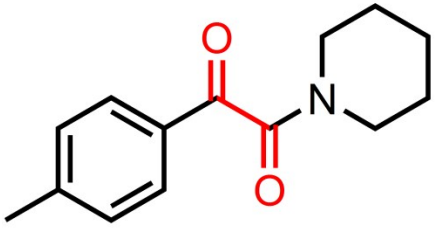
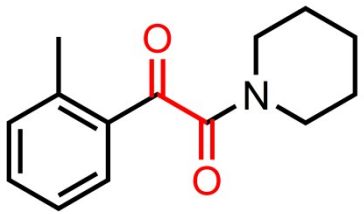
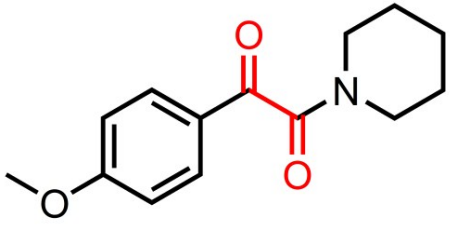
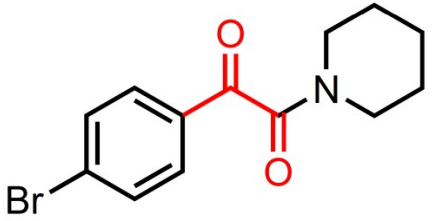
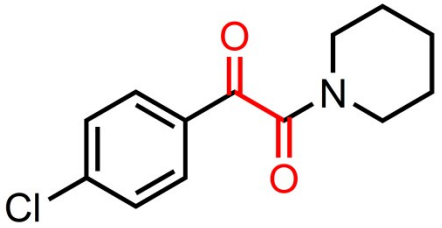
1.General information

Throughout the experiment, distilled and dried solvents and also chemically pure reagents were used. All substrates and reagents were purchased from commercial sources and thus the chemicals used as received. By standardised procedures,the solvents and substrate were distilled and purified. Benzene,benzyl amine,formaldehyde dimethyl acetal and 2-pyridine aldehyde were purchased from USA based Chemical Company Aldrich. From Merck chemical company $Pd(OAc)_2$ was procured and used it without extra purification.On a Perkin–Elmer FTIR 783 spectrophotometer the Fourier transform infrared (FTIR) spectra of the catalysts were recorded from 400 to 4000 cm^{-1} using KBr pellets. Using a Shimadzu, Japan, UV-2401PC doubled beam spectrophotometer with an integrating sphere attachment for solid based samples, UV-Vis spectra was taken. Using a Mettler Toledo TGA/DTA851e instrument, thermogravimetric analysis (TGA) was done. Scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility was used to measure surface morphology of the samples .HR TEM, 5 mg of the Pd@POP-2 catalyst was dispersed into absolute EtOH under the application of sonication for 30 min, followed by the sample coating on a carbon coated copper TEM grid and dried in air.Palladium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). The product mixtures were analyzed using a Varian, USA, 3400 gas chromatograph instrument with a flame ionization detector and a 30 m CP-SIL8CB capillary column. All spectra were taken at 400 MHz for ^1H NMR. Using Bruker DPX-400 in $CDCl_3$ instrument with TMS as internal standard the products was confirmed by ^1H spectroscopy.

2.^{1}H NMR and 13C NMR spectral data of respective products

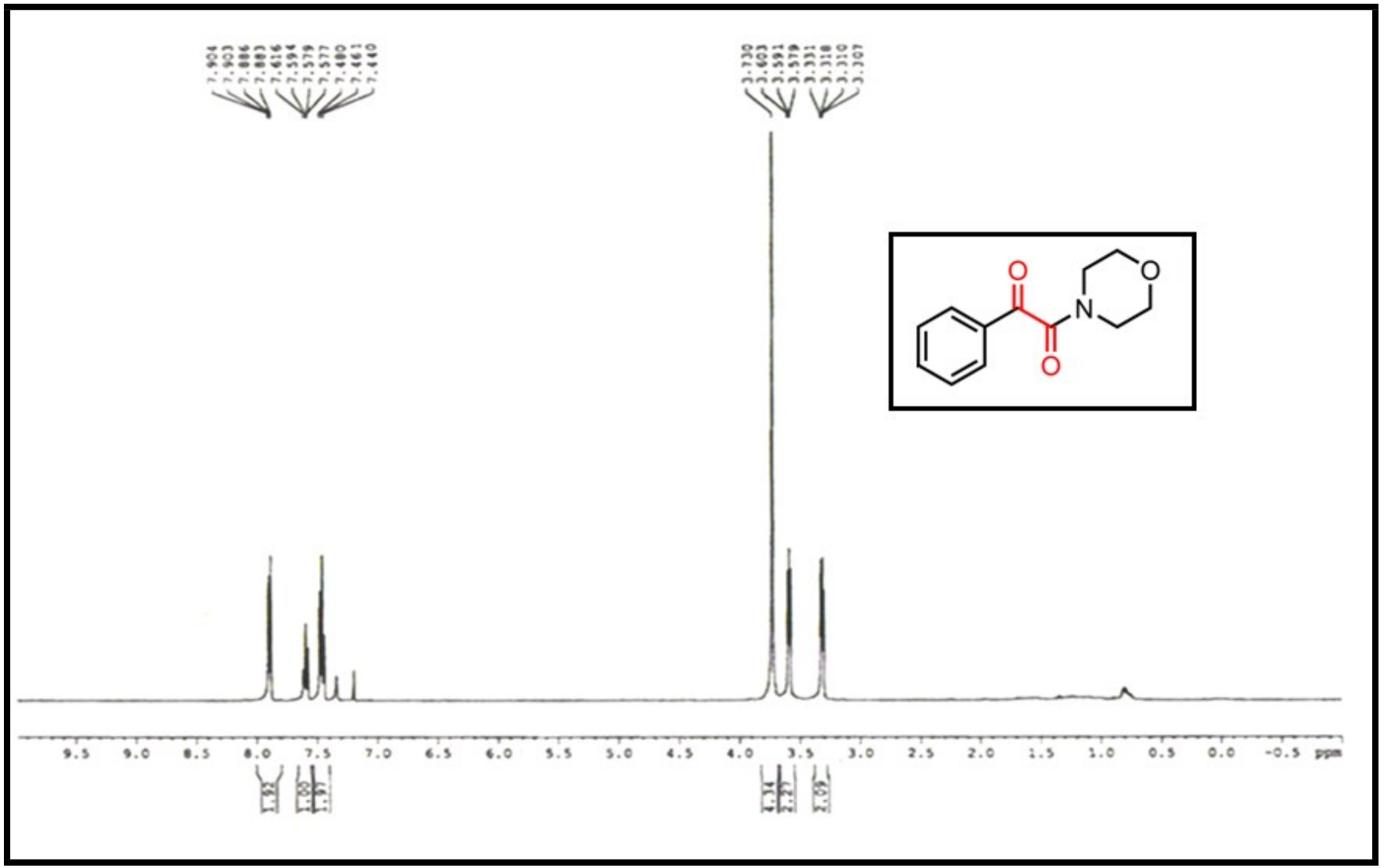
1-Morpholino-2-phenylethane-1,2-dione (1a):White solid;^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.88 (2 H, m), 7.61-7.57 (1 H, m), 7.48-7.44 (2 H, m), 3.73 (4 H, s), 3.60-3.57 (2 H, m), 3.33-3.30 (2 H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 191.47, 165.56, 134.92,133.07,129.66,129.19,66.96,66.75,46.63,41.26.	
1-Morpholino-2-(*p*-tolyl)ethane-1,2-dione(2b): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.84 (2 H, m), 7.33-7.31 (2 H, m), 3.79 (3 H, s),3.66-3.63 (3H, m), 3.38- 3.36 (2 H, m), 2.44 (3 H, s). ^{13}C NMR (400 MHz, CDCl3): δ = 191.02,165.65,146.04,130.02,129.65,129.19,66.78,66.64,46.24,41.52,21.92.	
1-Morpholino-2-(*o*-tolyl)ethane-1,2-dione(3c):Yellowish slurry; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81-7.79 (1 H, m), 7.58-7.52 (1 H, m), 7.27-7.23 (2 H, m), 3.80(4 H, m), 3.57-3.55 (2 H, m), 3.38-3.36 (2 H, m), 2.58 (3 H, s). ^{13}C NMR (400 MHz, CDCl3):δ =193.24,165.99,141.63,133.46,131.74,130.91,129.79,126.32,66.74,66.66,46.21,41.65,21.67.	
1-(4-Methoxyphenyl)-2-morpholinoethane-1,2-dione(4d):White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-7.92 (2 H, m), 7.00-6.97 (2 H, m), 3.90-3.87 (3 H, m), 3.78 (4 H, m), 3.66-3.64 (2 H, m), 3.39-3.37 (2 H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 190.10,165.72,164.97,132.12,126.20,114.41,66.79,66.68,55.67,46.65,41.58.	

1-(4-Bromophenyl)-2-morpholinoethane-1,2-dione(5e): Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.68(2H, m), 7.48-7.46 (2H, m), 3.79 (4H, m), 3.66-3.64 (2H, m), 3.39-3.37(2H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 189.89,165.21,132.61,131.34,129.76,129.19,66.76,66.68,46.27,41.71.	
1-(4-Chlorophenyl)-2-morpholinoethane-1,2-dione(6f):Colorless solid; ^{1}H NMR (400 MHz, CDCl3) δ 7.90-7.88 (2H, m), 7.48-7.44 (2H, m), 3.73 (4H, m), 3.60-3.57 (2H, m), 3.33-3.30 (2H, m) 13C NMR (400 MHz, CDCl3) δ 189.78, 165.14, 141.53, 131.32, 130.98, 129.78, 66.73,66.62,46.26, 41.72	
1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione (7g):White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.88 (2 H, m), 7.61- 7.57 (1 H, m), 7.47- 7.44 (2 H, m) 3.72 (2 H, m), 3.43- 3.31 (2 H, m), 1.66- 1.53 (6 H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 191.71,165.83,145.89,133.79,131.27,130.74,129.06,46.61,42.06,25.80,25.67,24.41.	
1-(Piperidin-1-yl)-2-(*p*-tolyl)ethane-1,2-dione(8h):White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.76 (2 H, m), 7.24- 7.19 (2 H, m), 7.13- 7.11 (1 H, m),3.62 (2 H, s), 3.29-3.19 (2 H, m), 2.36 (3 H, s), 1.62- 1.61 (6 H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 191.75,170.56,145.88,130.87,129.73,128.98,47.06,42.10,26.23,25.46,24.65,21.92.	

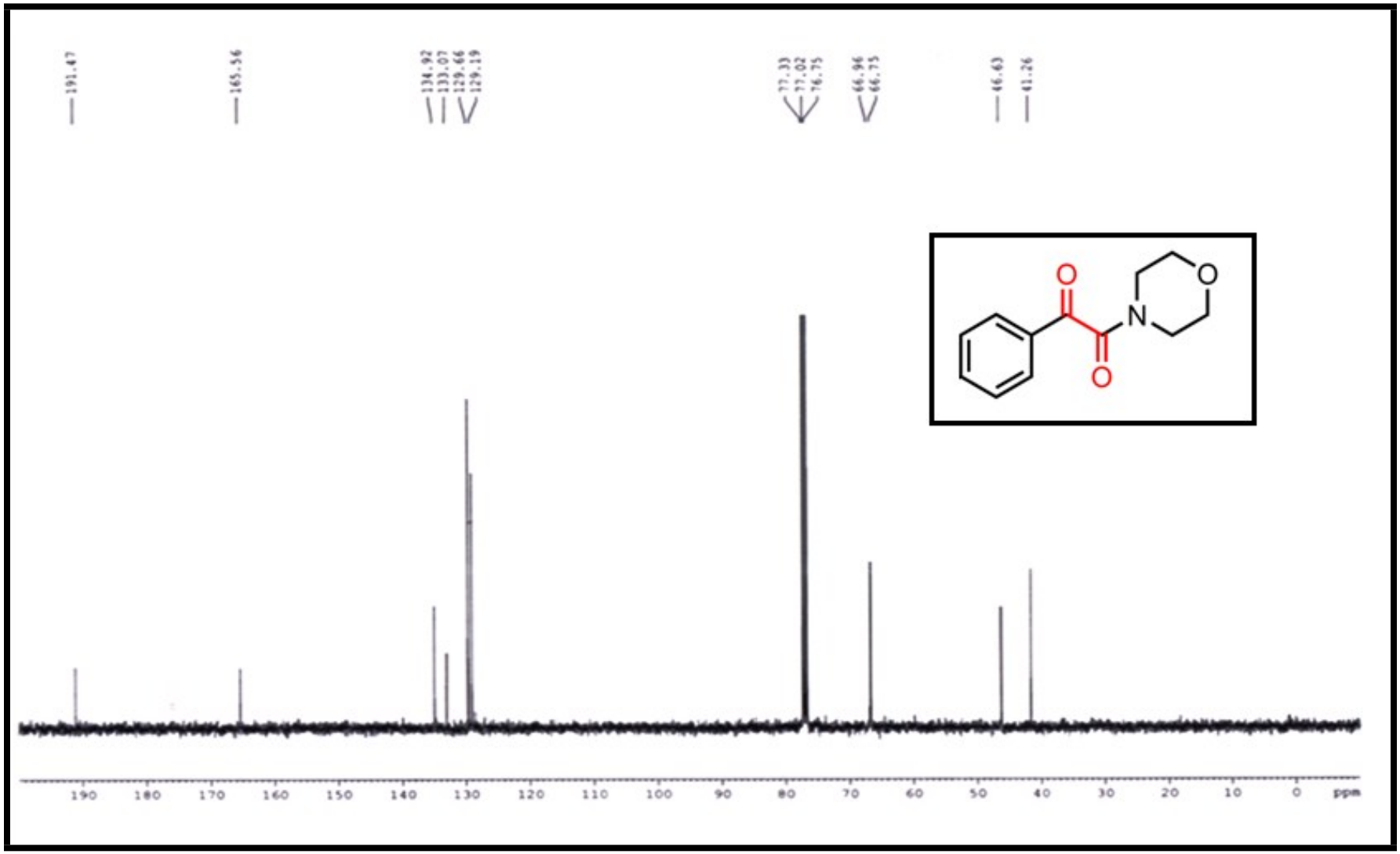
1-(Piperidin-1-yl)-2-(*o*-tolyl)ethane-1,2-dione(9i): Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.76 (1 H, m), 7.24- 7.19 (2 H, m), 7.12- 7.10 (1 H, m) 3.62 (2 H, s), 3.22-3.19 (2 H, m), 2.36 (3 H, s), 1.61- 1.46 (6 H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 191.74,165.83,141.88,133.52,131.27,130.73,129.09,126.93,46.67,42.06,25.82,25.67,24.41,21.73.	
1-(4-Methoxy-phenyl)-2-(piperidin-1-yl)ethane-1,2-dione(10j): Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (2 H, m), 6.98- 6.96(2 H, m), 3.88 (3H, s), 3.69 (2 H, s) 3.30-3.27 (2 H, m), 1.71- 1.68 (4 H, m) 1.55-1.54 (2H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 190.68,165.78,164.77,132.02,126.41,114.32,113.63,55.62,47.06,42.08,26.25,25.46,24.67.	
1-(4-Bromophenyl)-2-(piperidin-1-yl)ethane-1,2-dione(11k):White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.78 (4H,m)3.68(2H, s), 3.31-3.28 (2H, m), 1.67-1.53 (6H, m). ^{13}C NMR (400 MHz, CDCl3): δ = 190.79,164.88,132.05,131.17,130.63,129.77,47.07,41.90,26.28,25.68,24.47.	
1-(4-Chlorophenyl)-2-(piperidin-1-yl)ethane-1,2-dione(12l):off White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.90 (2H, m) δ 7.58-7.56 (2H, m,) 3.69(2H, s), 3.30-3.27 (2H, m), 1.71-1.68 (4H, m),1.55-1.54(2H,m). ^{13}C NMR (400 MHz, CDCl3): δ = 190.59,164.48,141.18,131.13,130.90,129.79,47.16,42.28,26.26,25.65,24.47.	

3.^{1}H NMR and^{13}C NMR copies of respective products

^{1}H NMR for Compound 1a

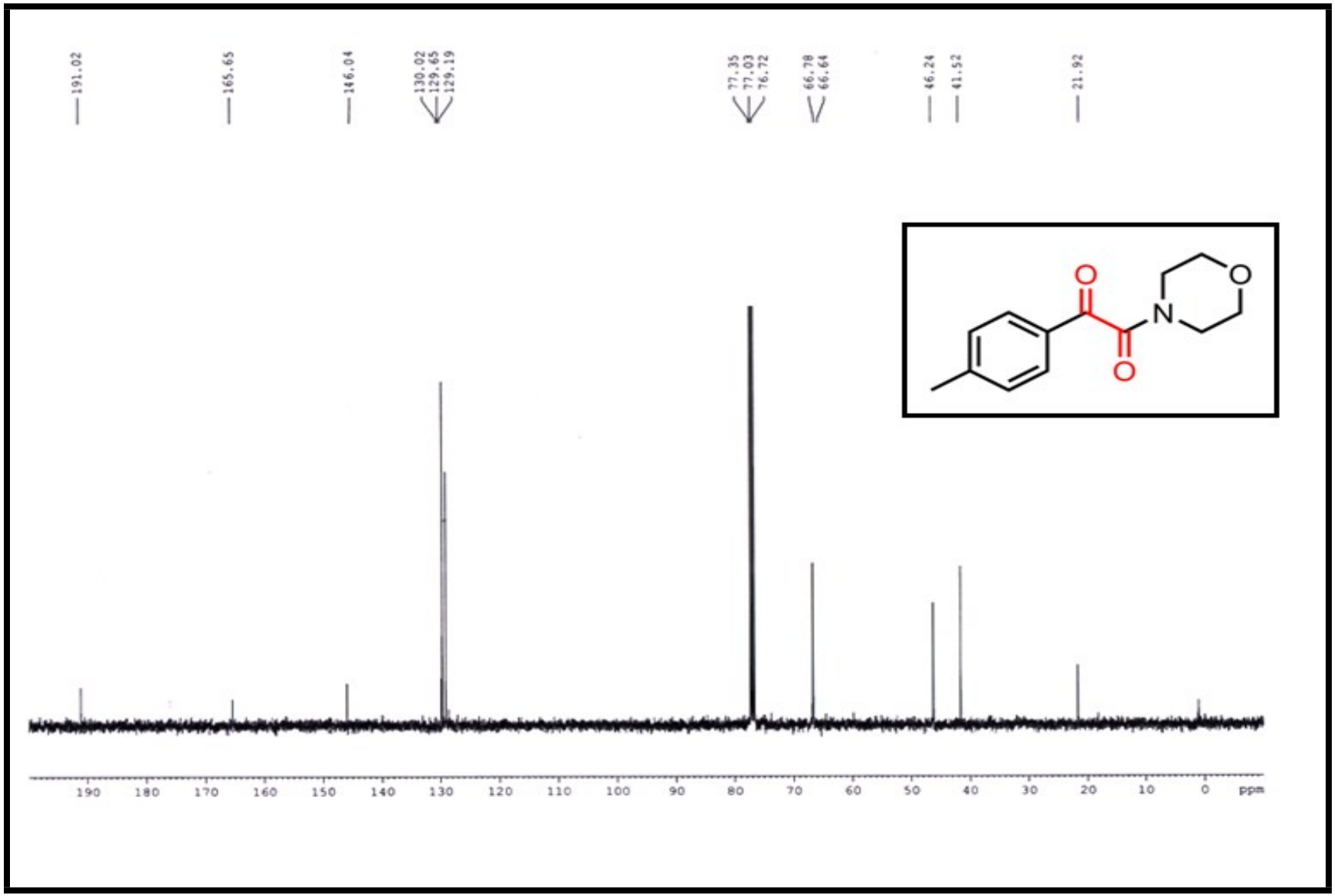


^{13}C NMR for Compound 1a

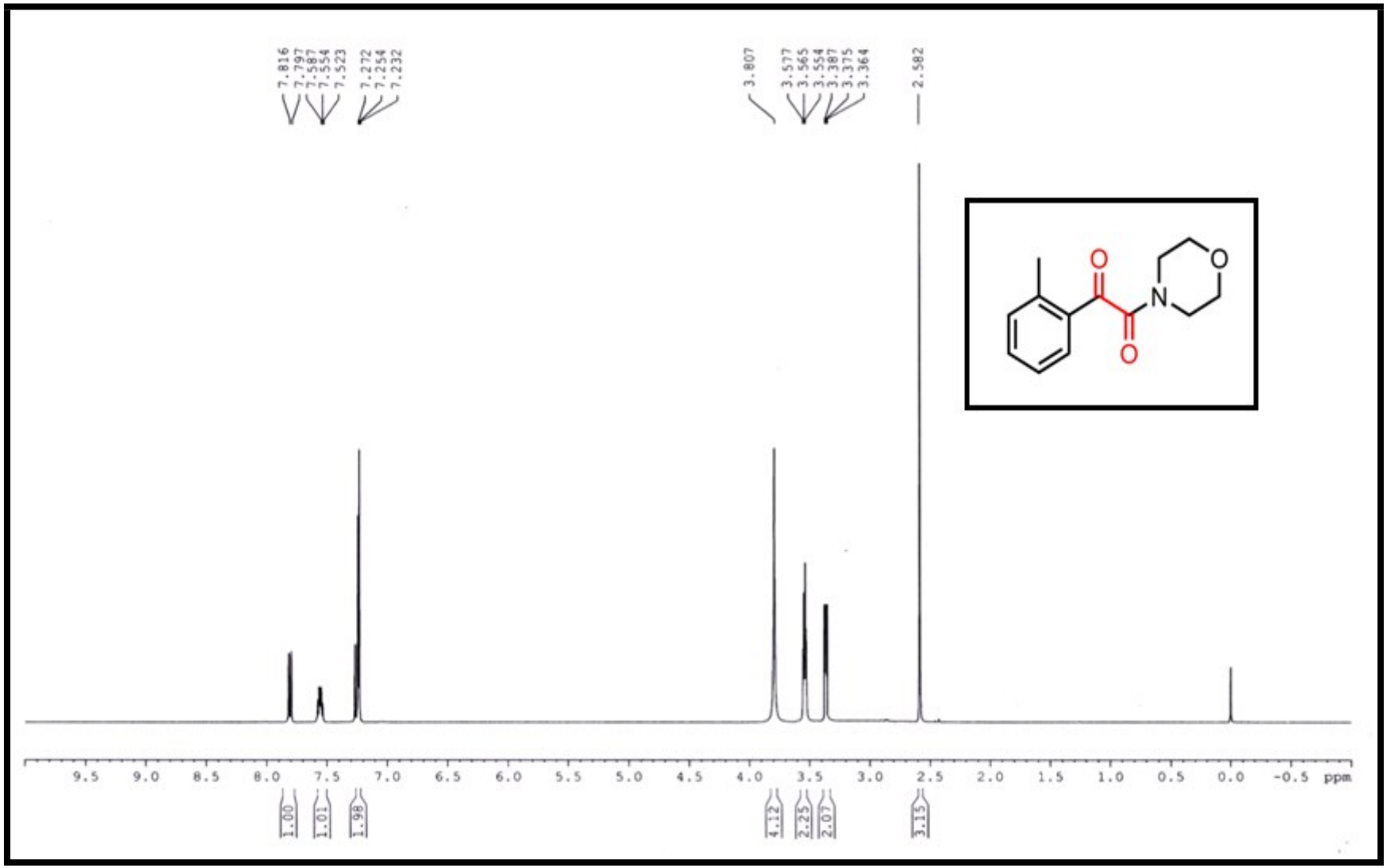


^{1}H NMR for Compound 2b

^{13}C NMR for Compound 2b

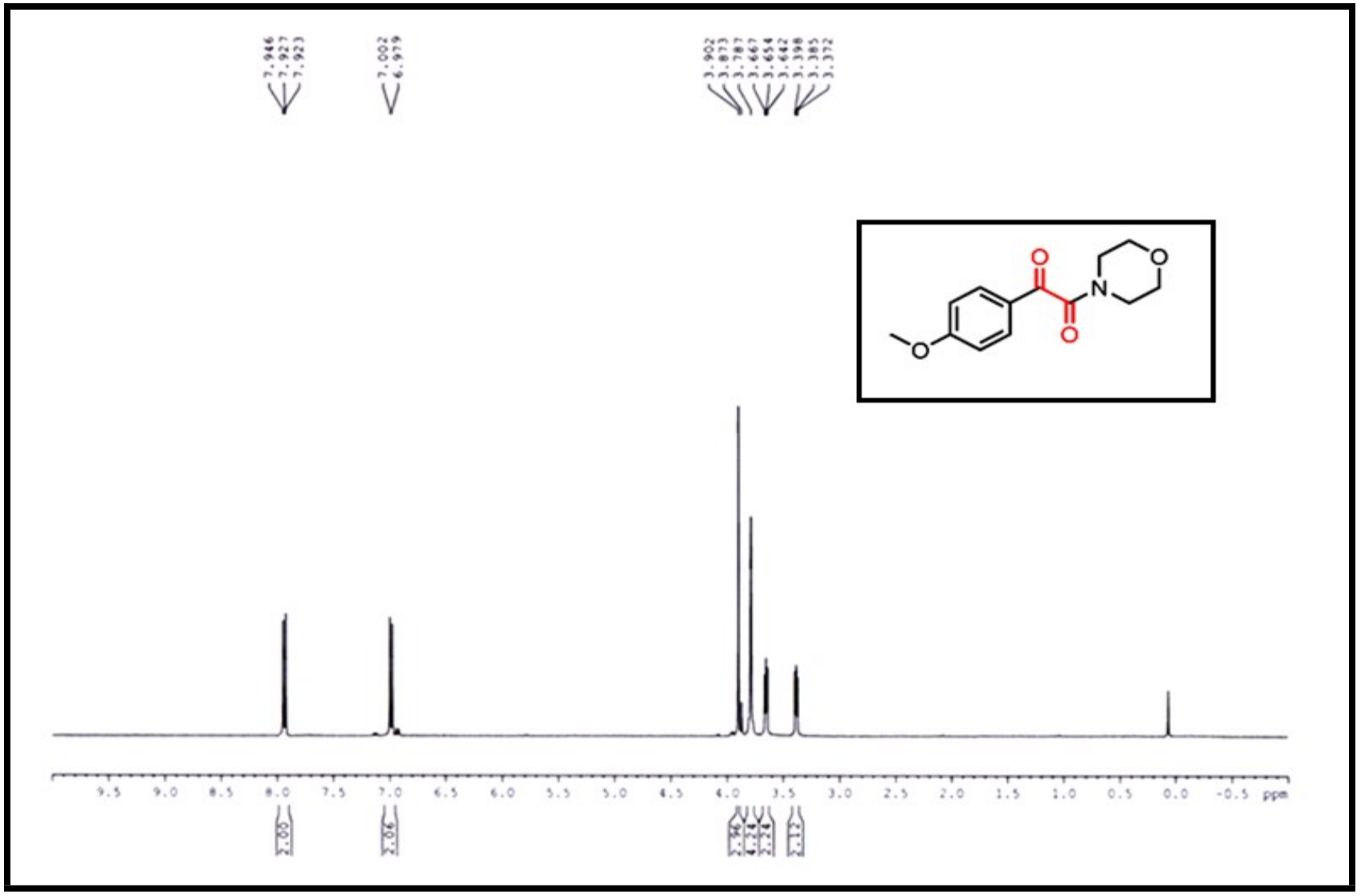


^{1}H NMR for Compound 3c

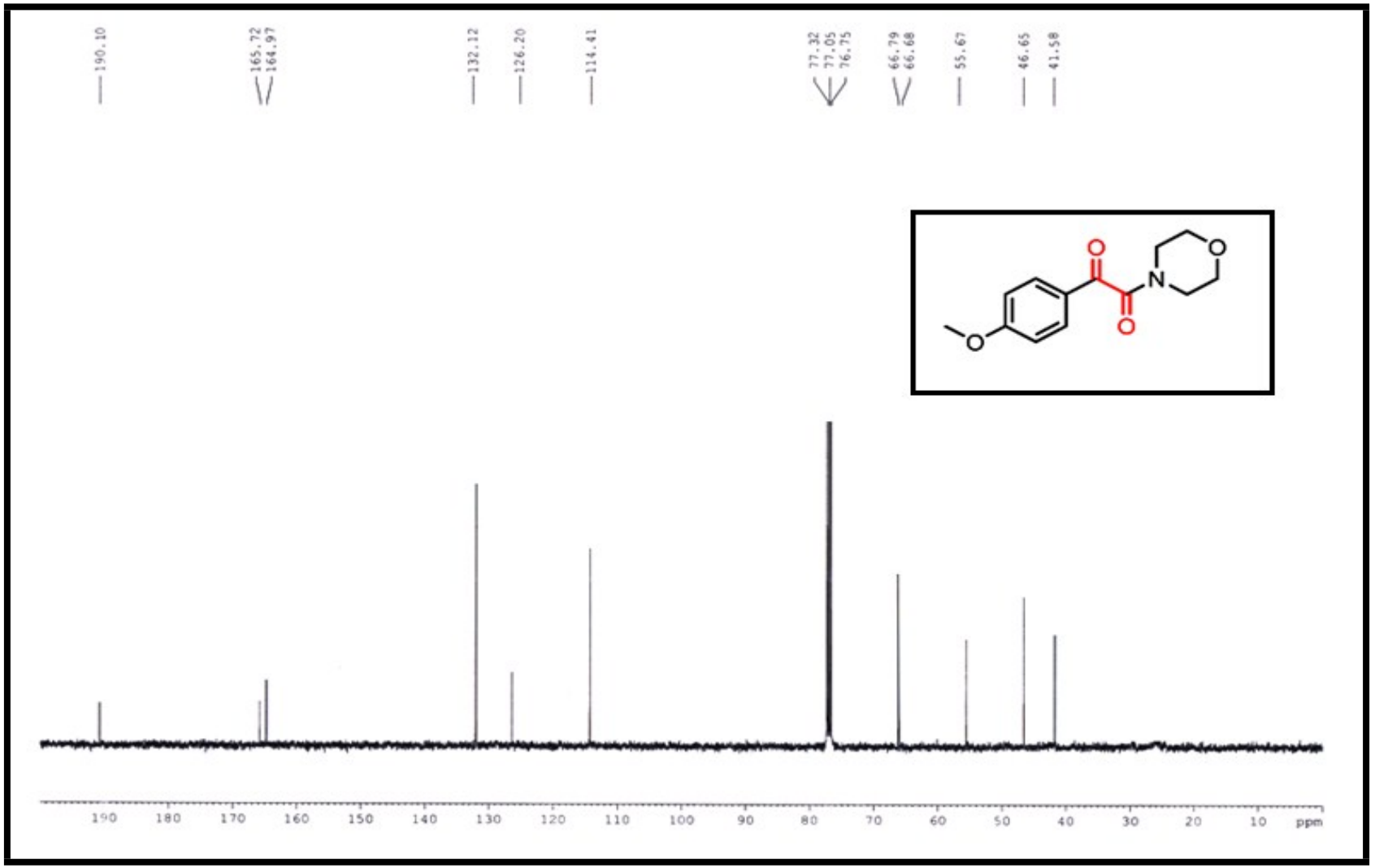


^{13}C NMR for Compound 3c

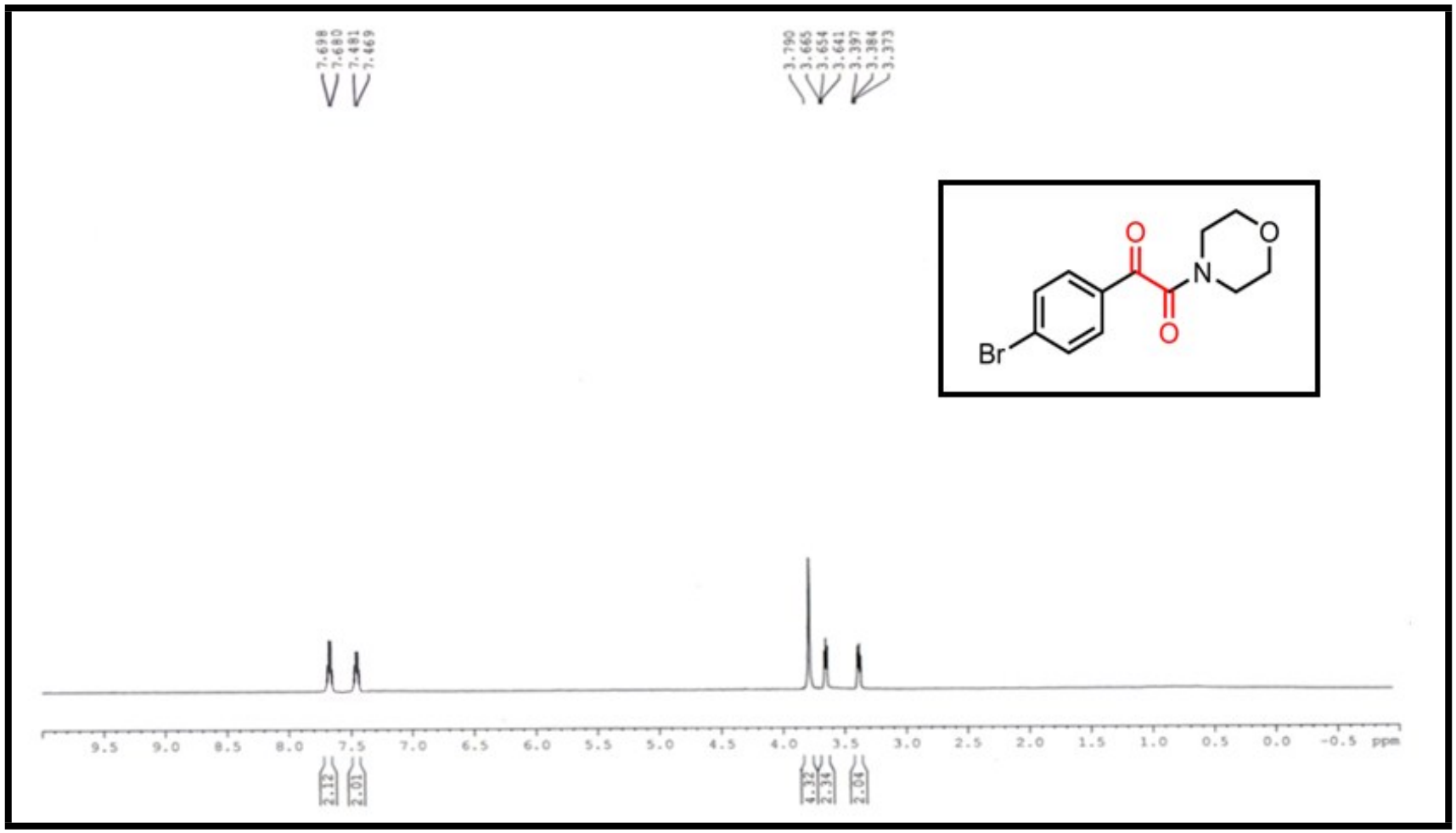
^{1}H NMR for Compound 4d



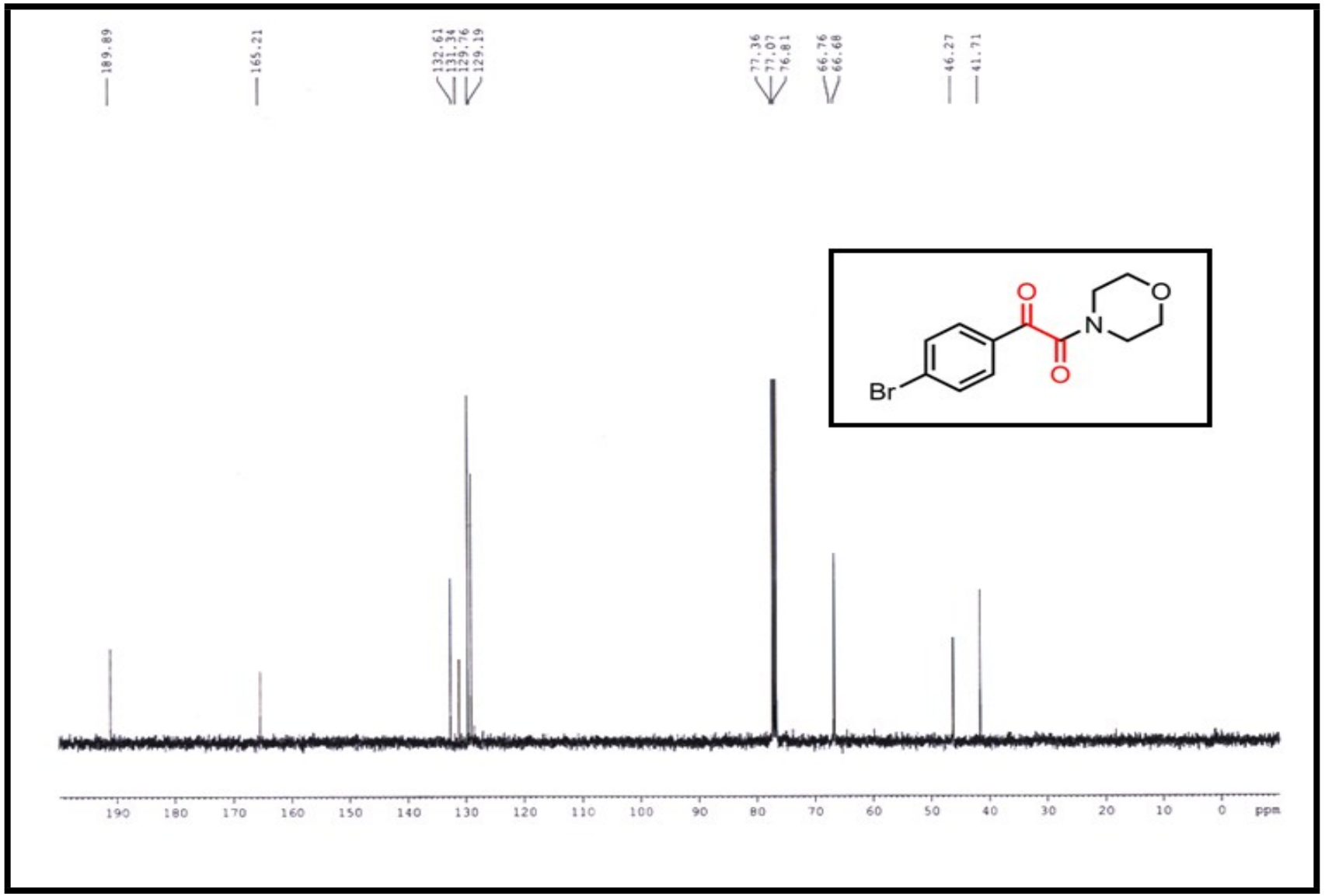
^{13}C NMR for Compound 4d



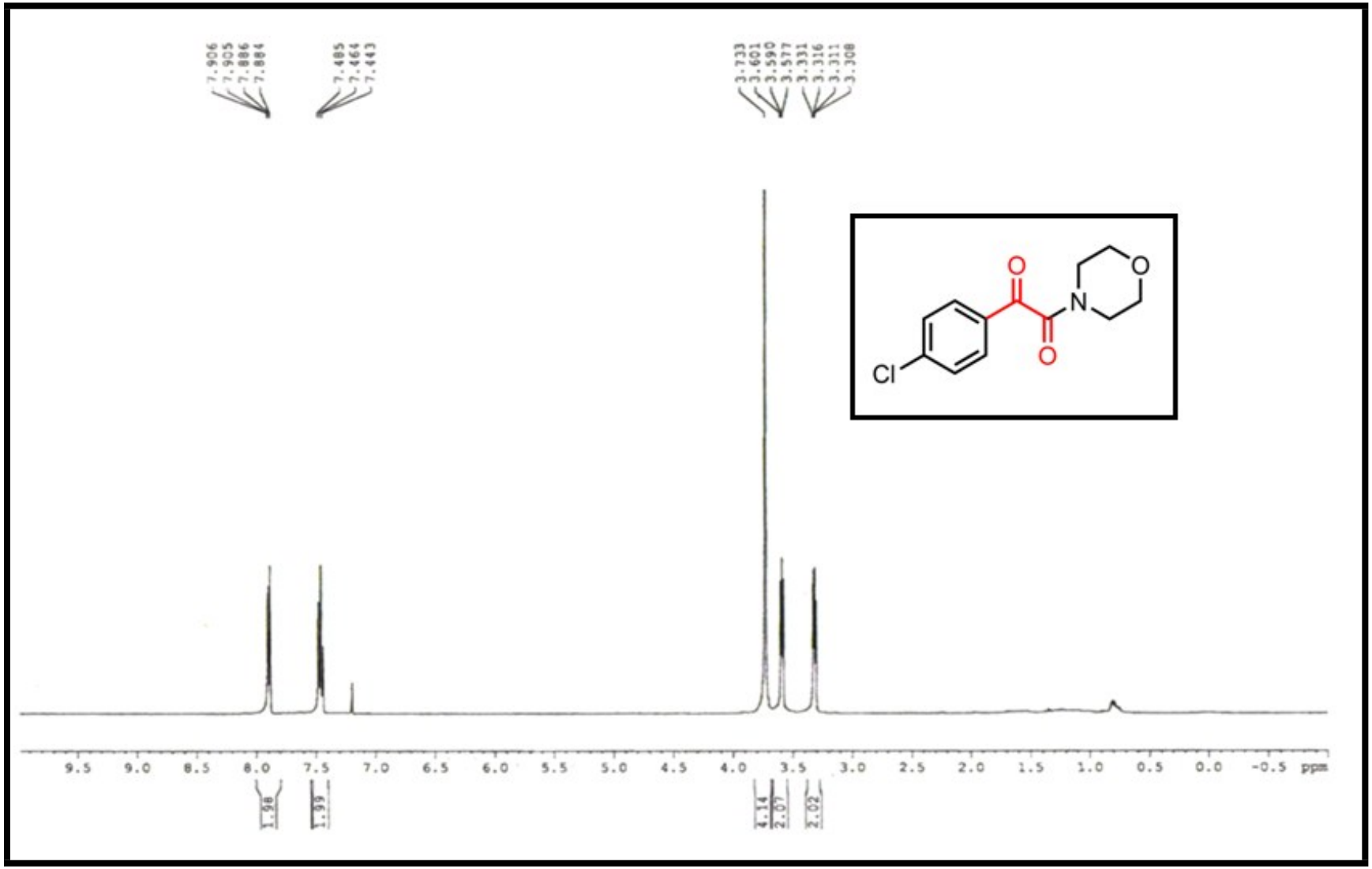
[1]H NMR for Compound 5e



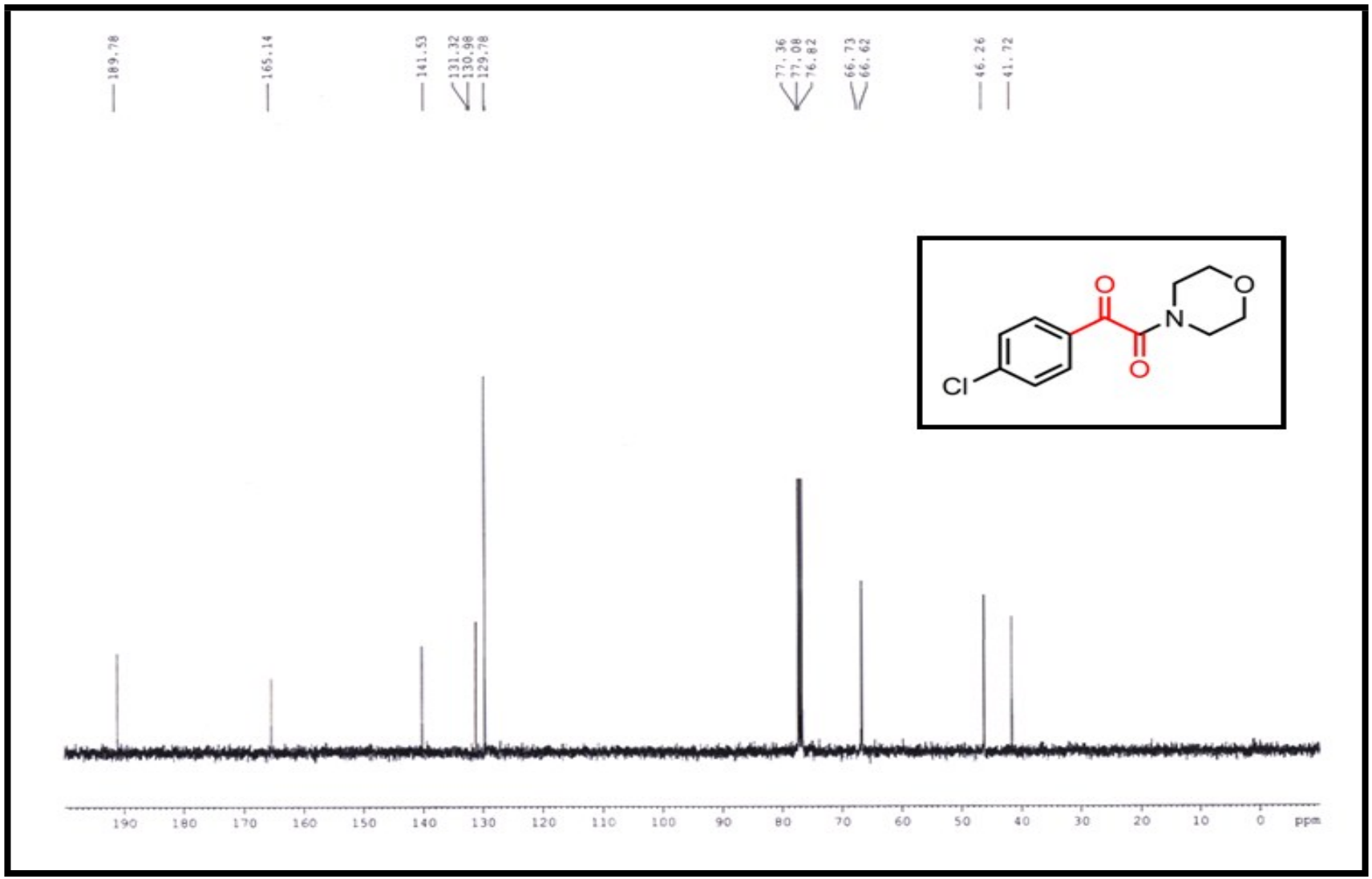
^{13}C NMR for Compound 5e



^{1}H NMR for Compound 6f



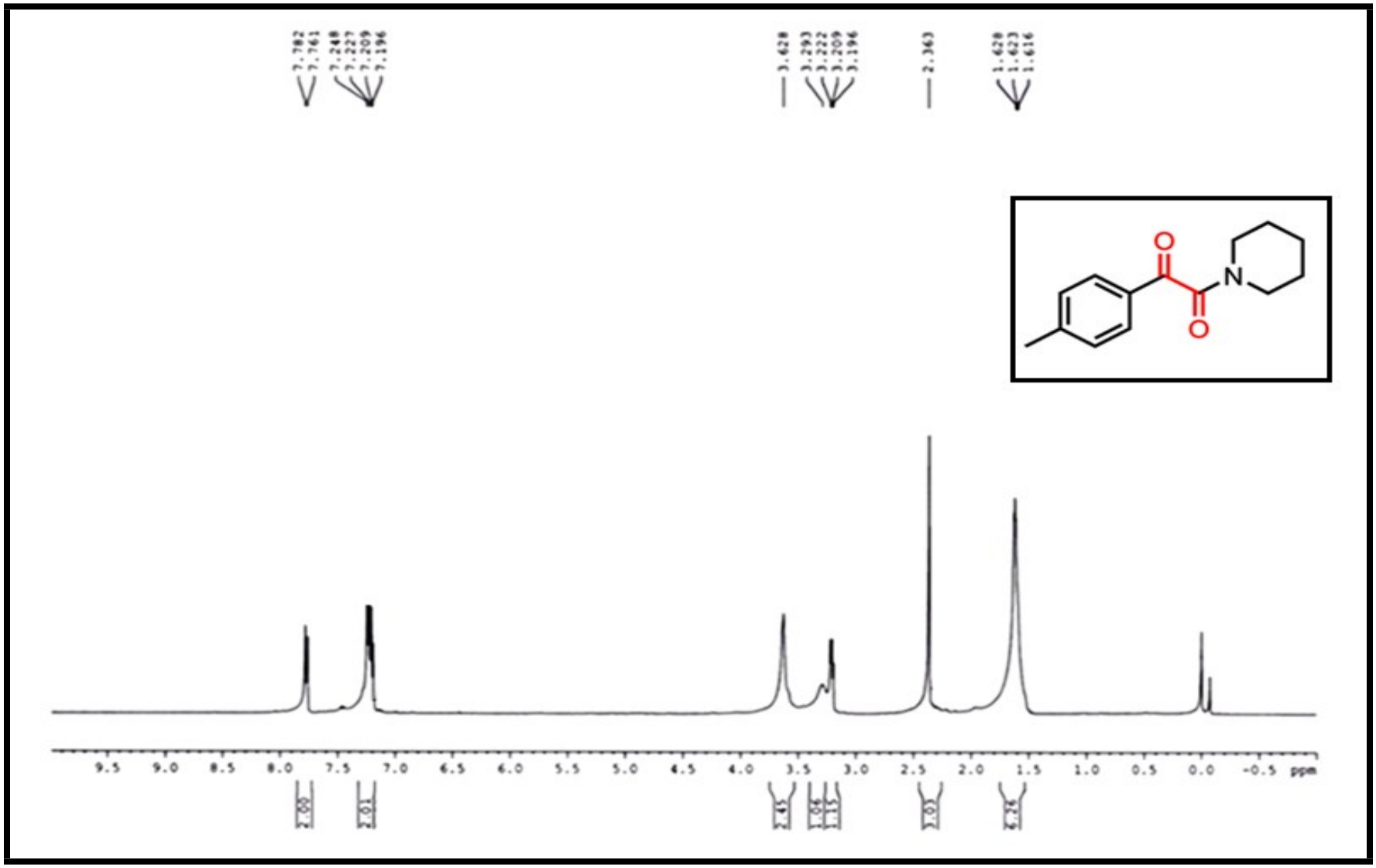
^{13}C NMR for Compound 6f



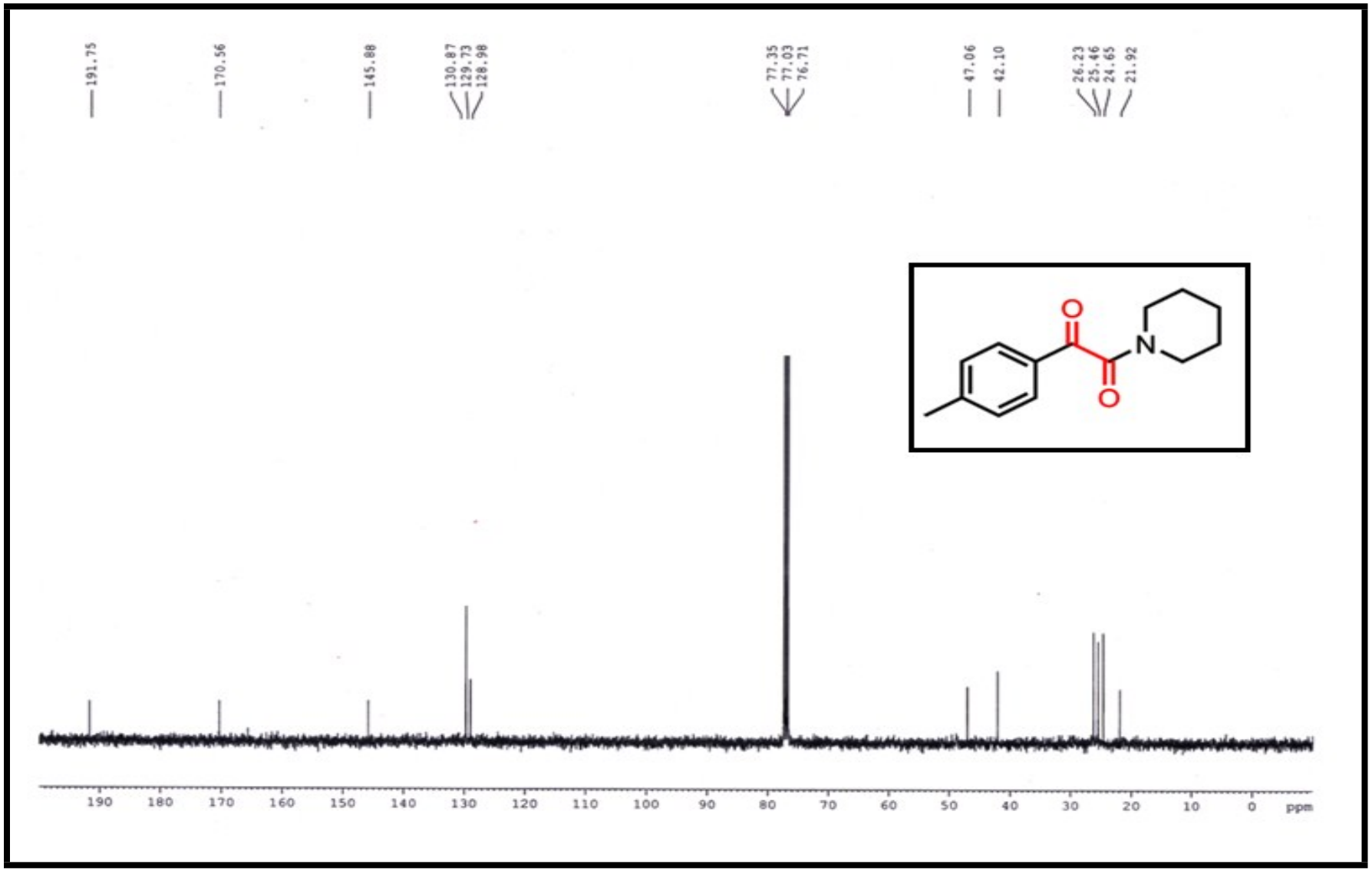
^{1}H NMR for Compound 7g

^{13}C NMR for Compound 7g

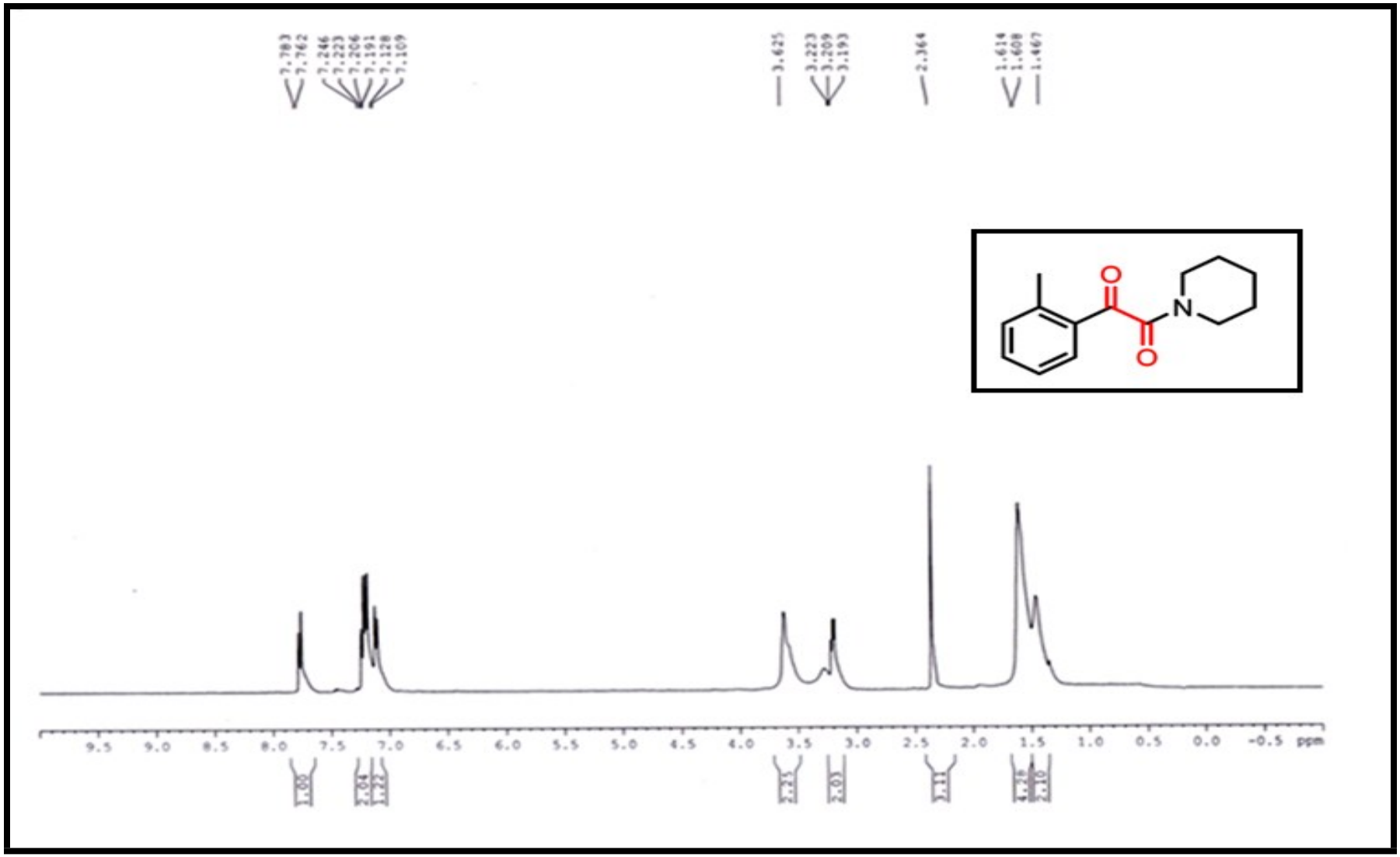
^{1}H NMR for Compound 8h



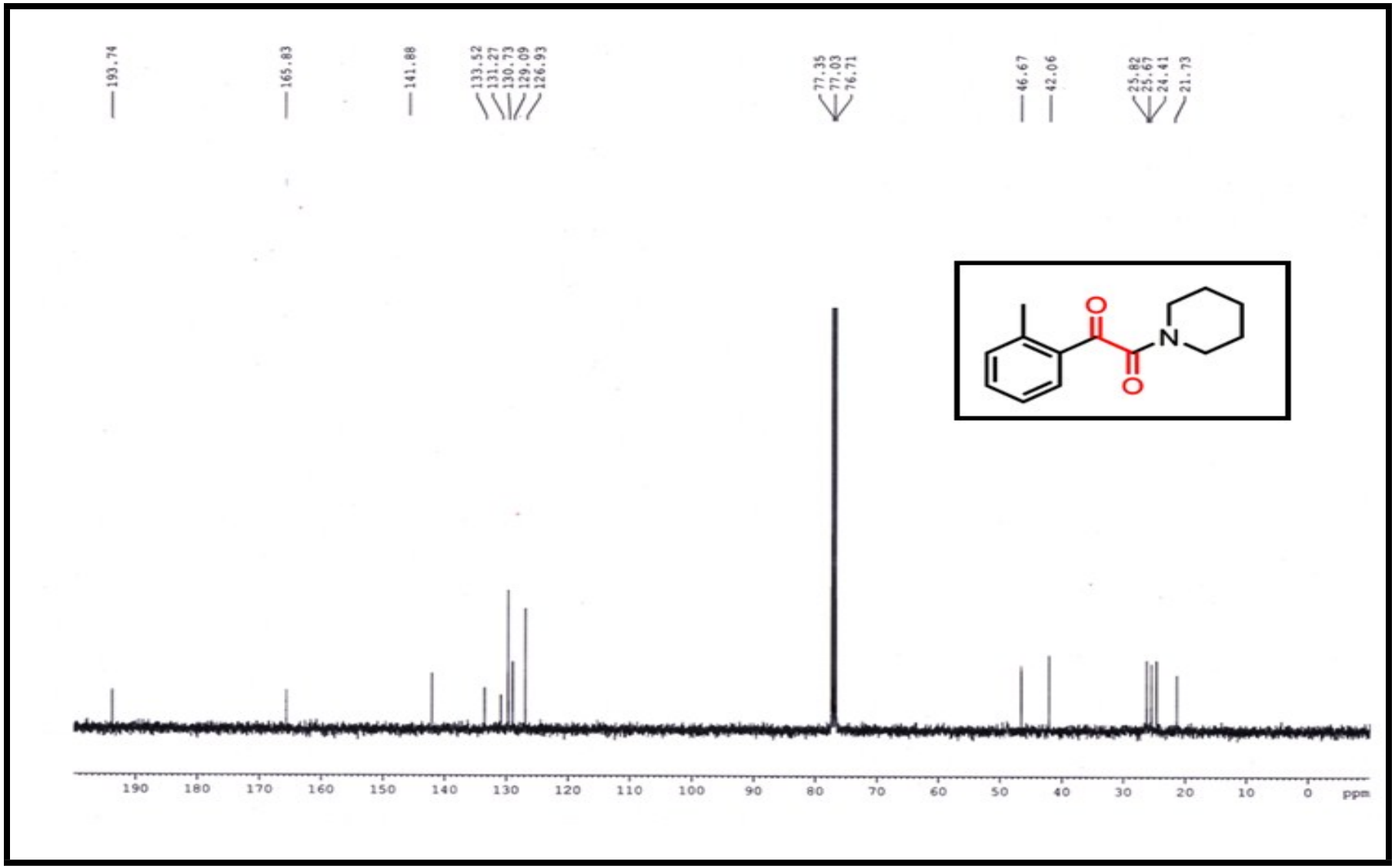
^{13}C NMR for Compound 8h



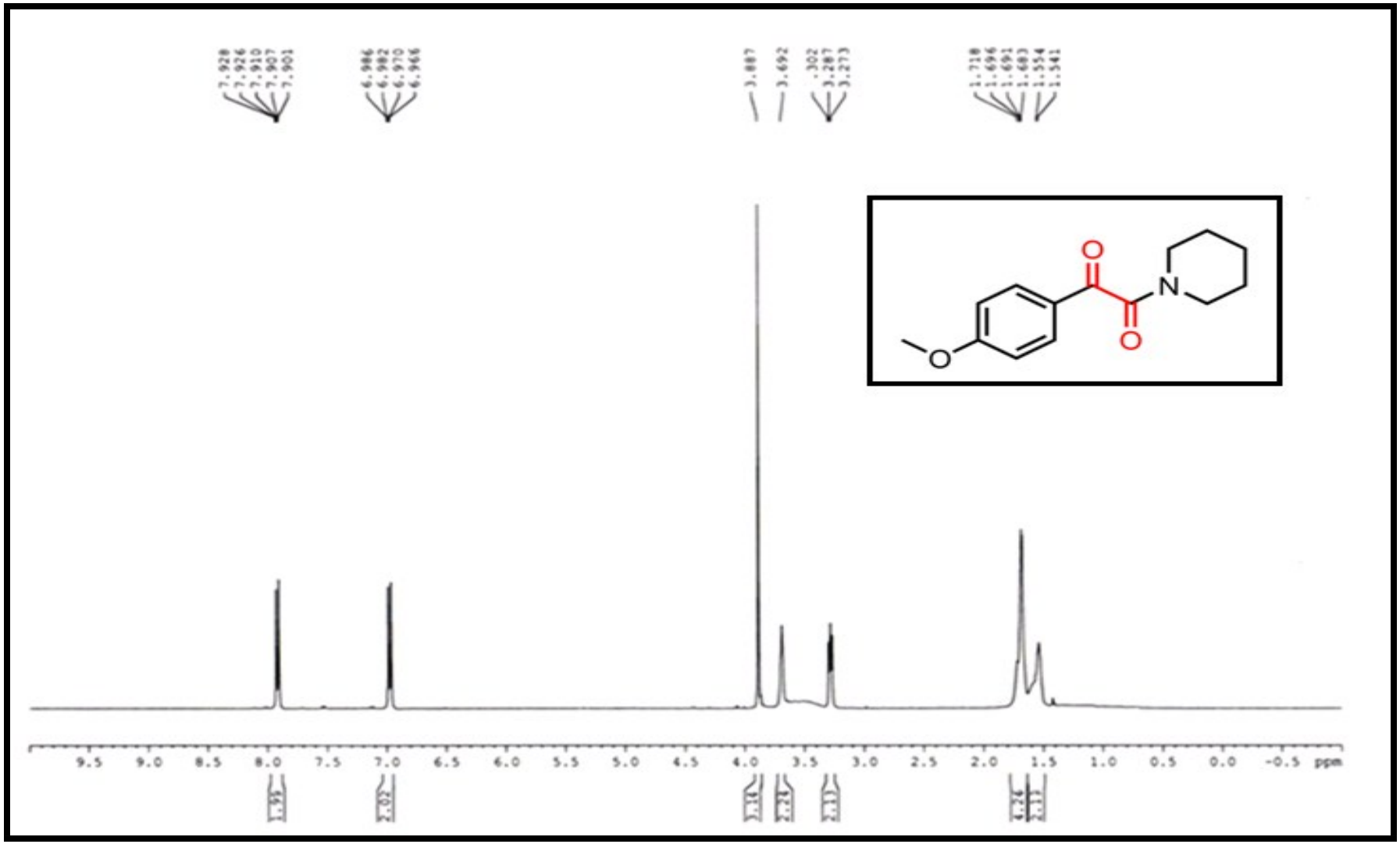
^{1}H NMR for Compound 9i



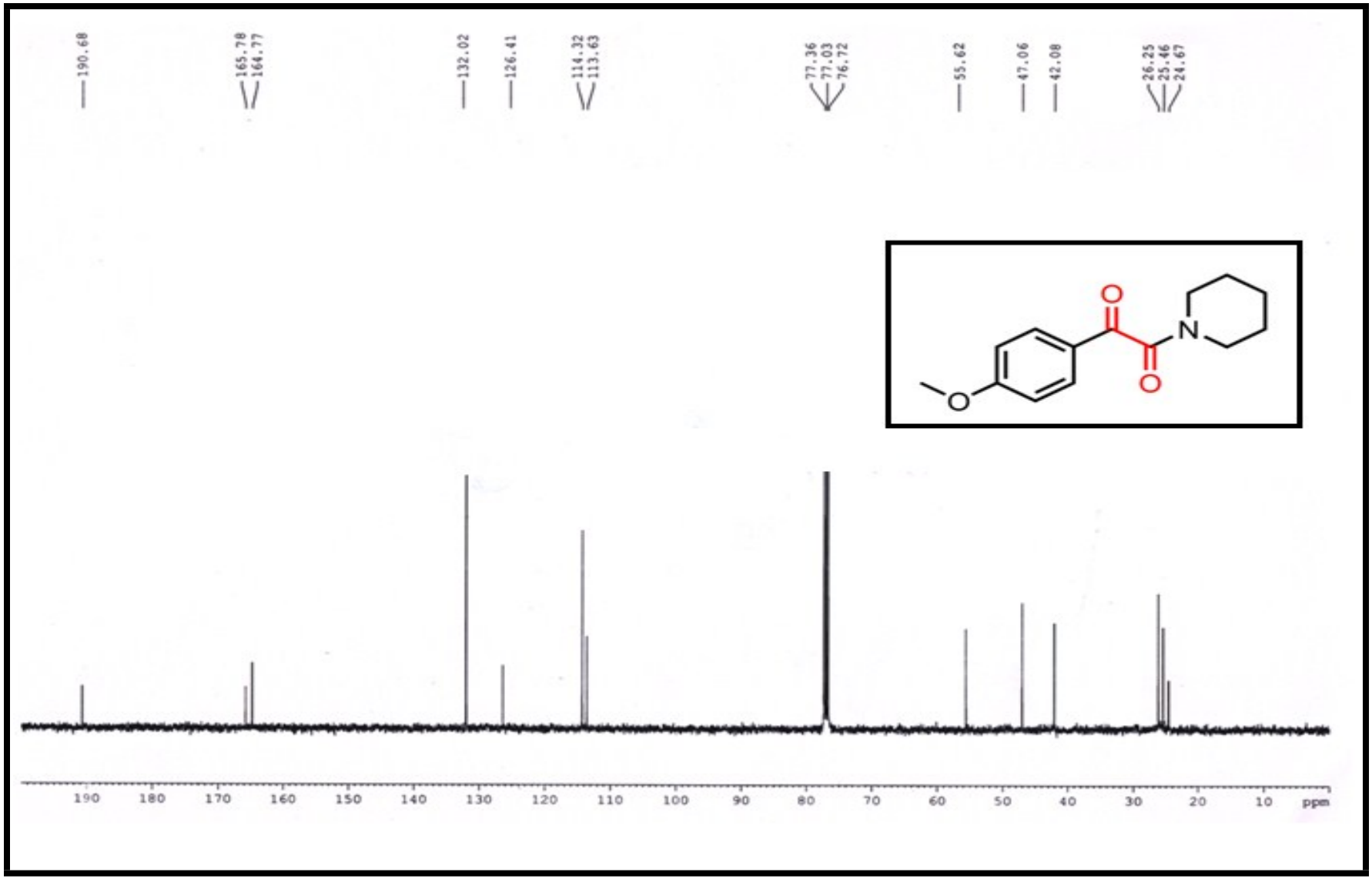
^{13}C NMR for Compound 9i



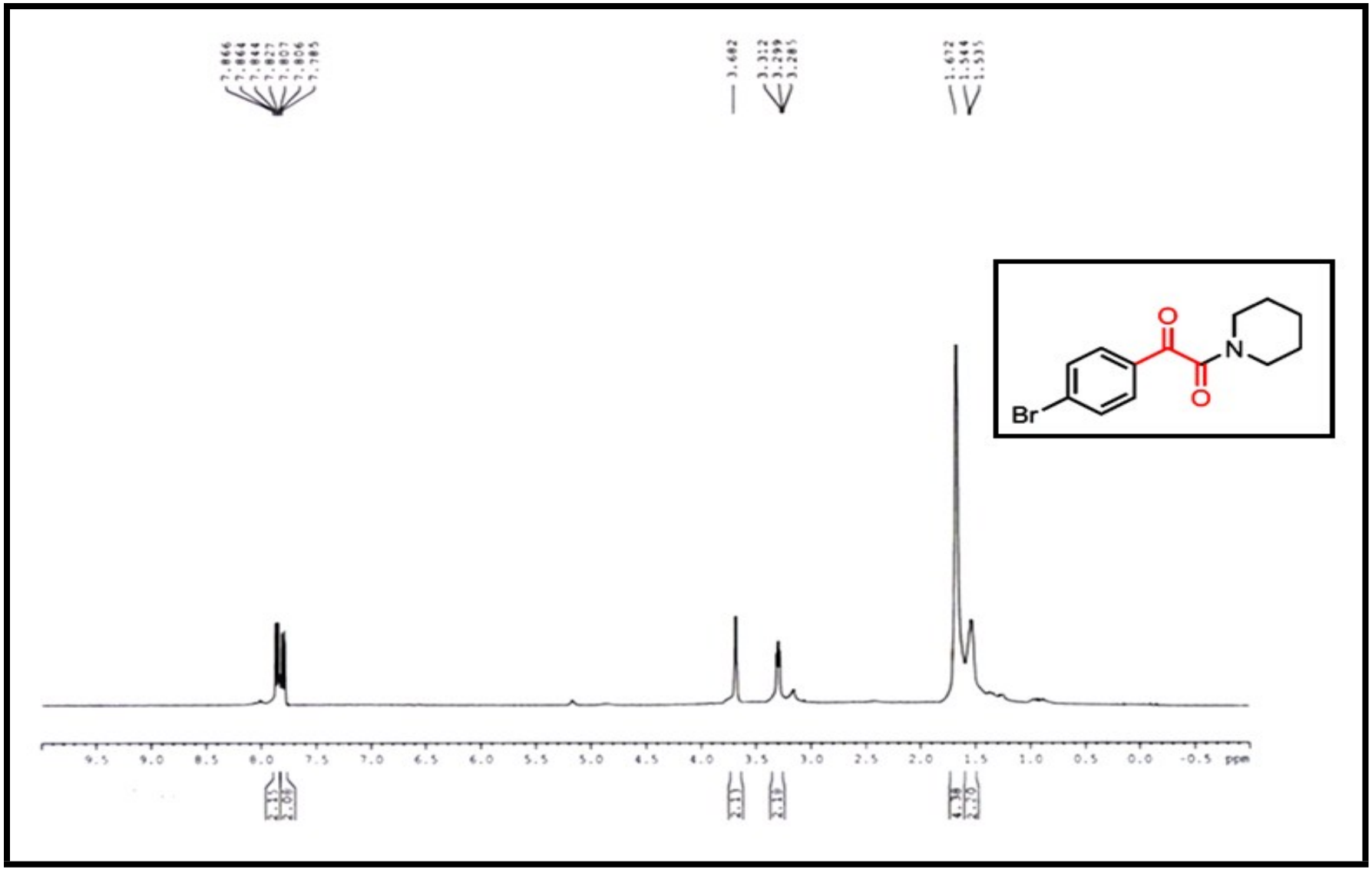
^{1}H NMR for Compound 10j



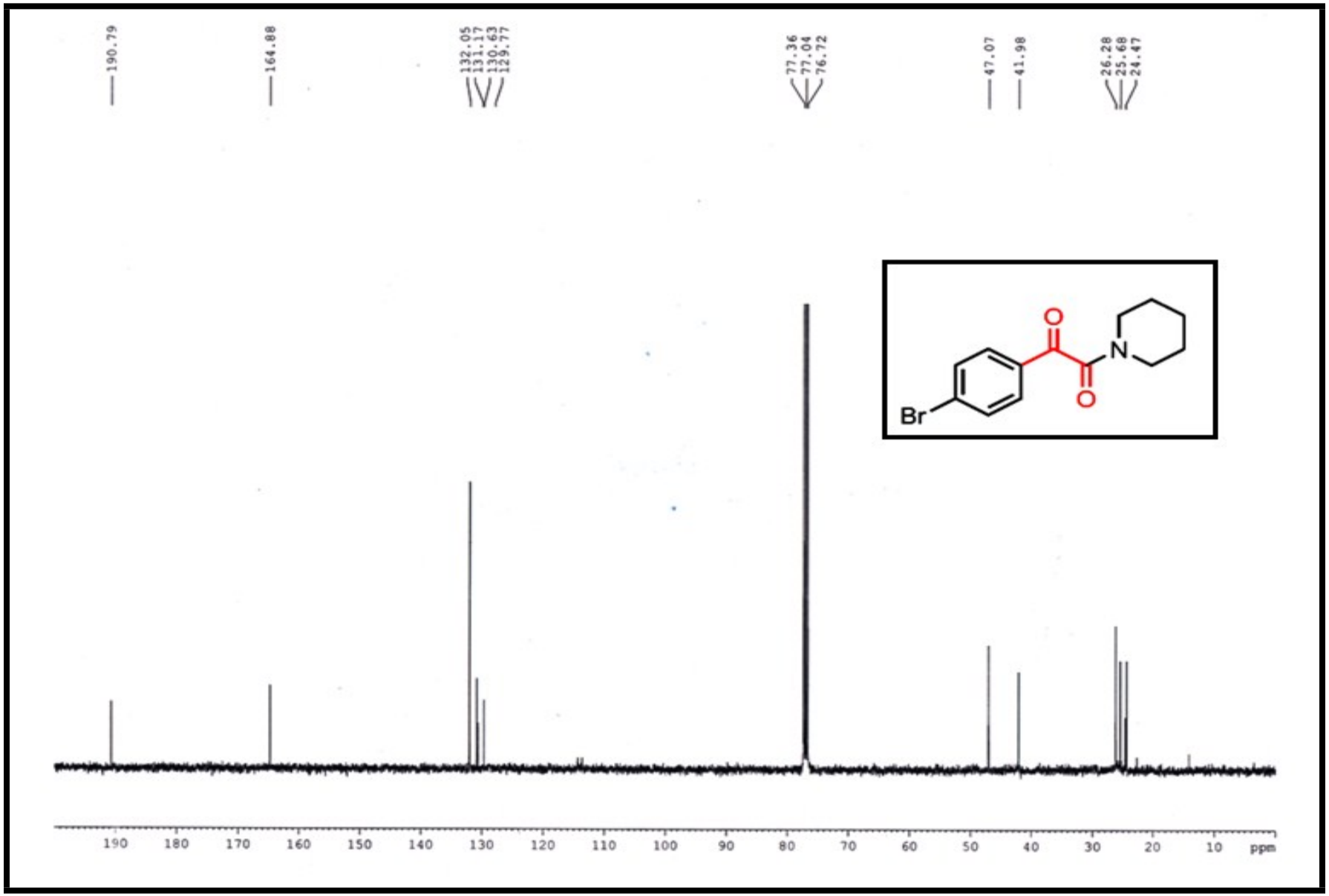
^{13}C NMR for Compound 10j



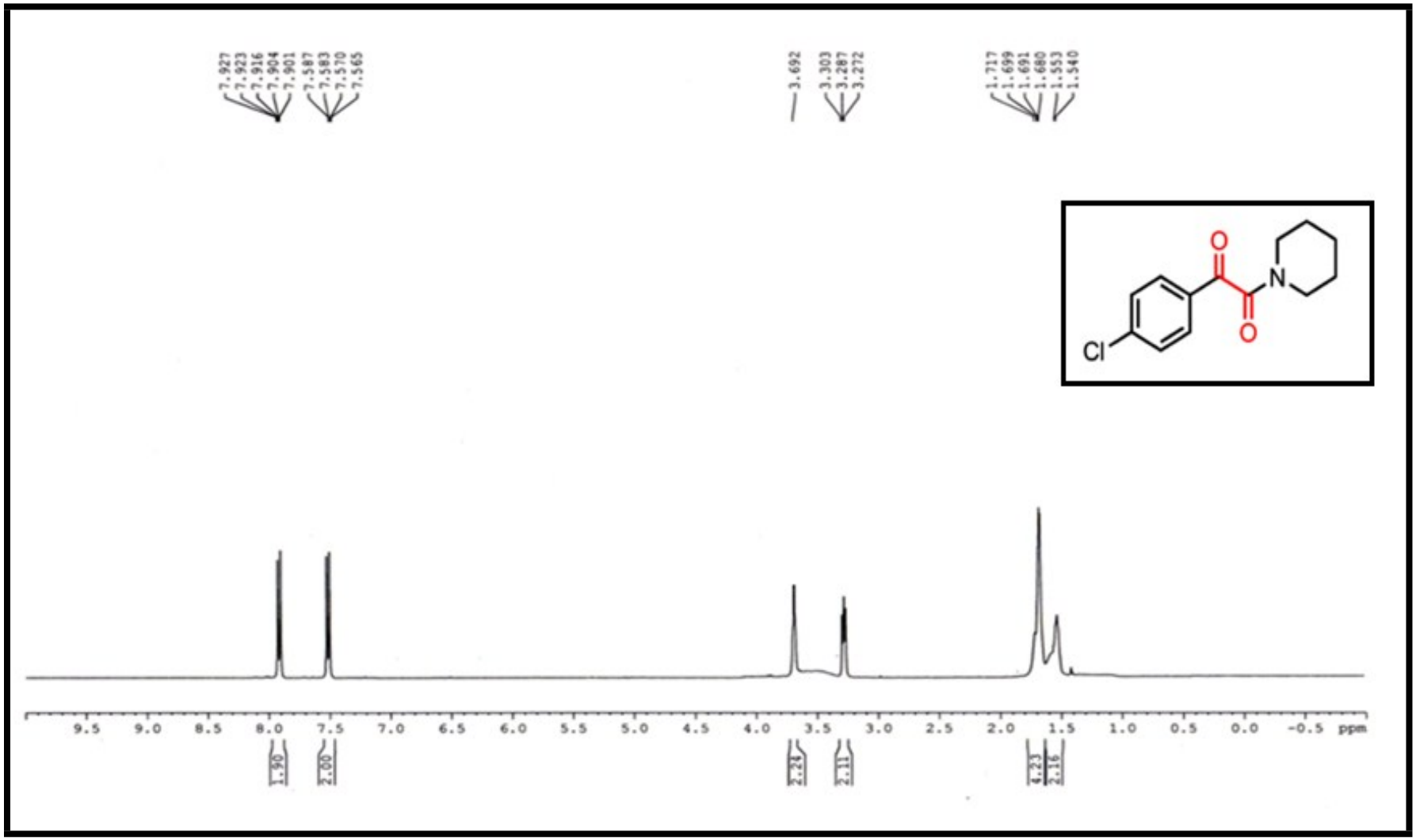
^{1}H NMR for Compound 11k



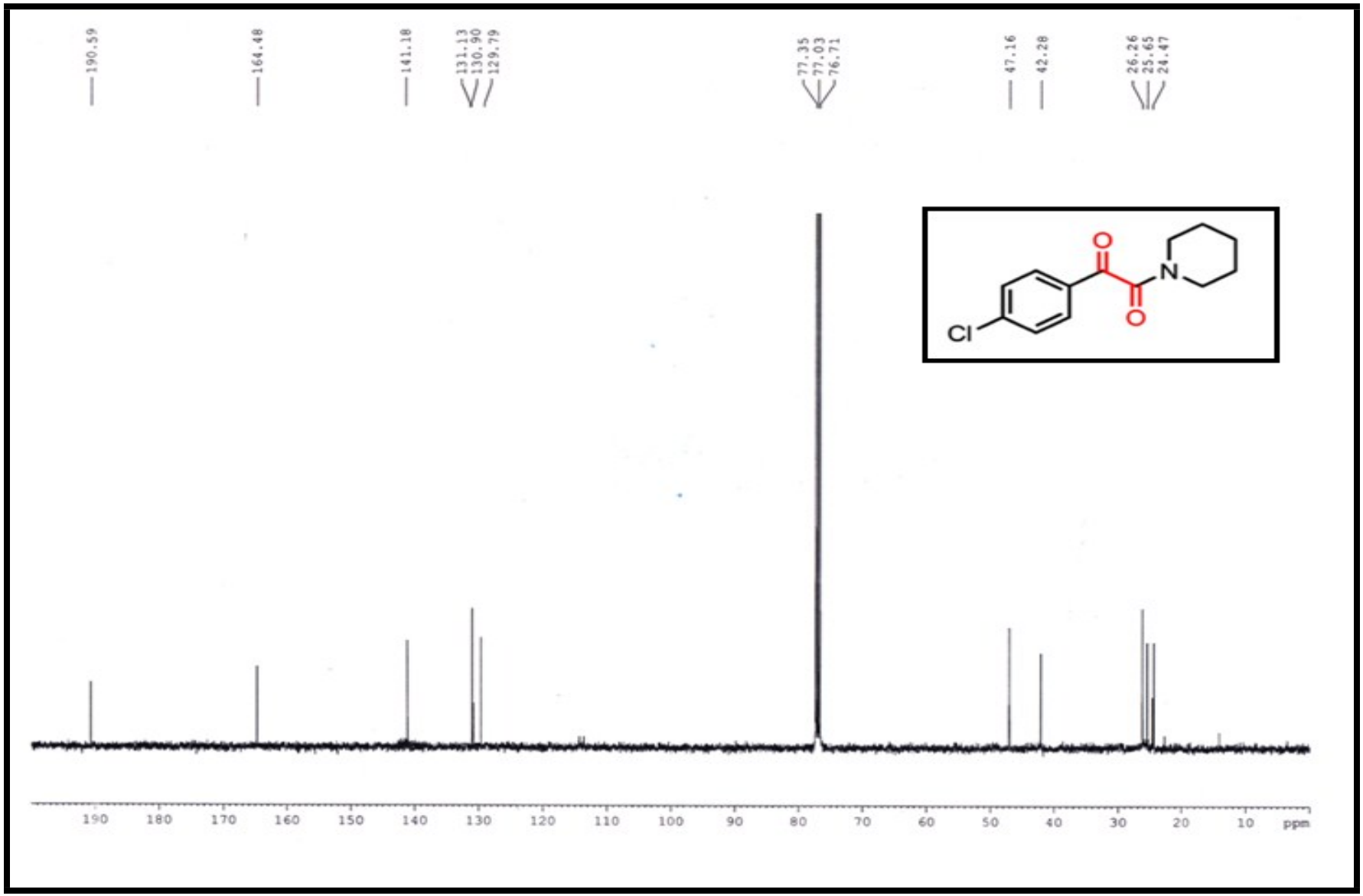
^{13}C NMR for Compound 11k



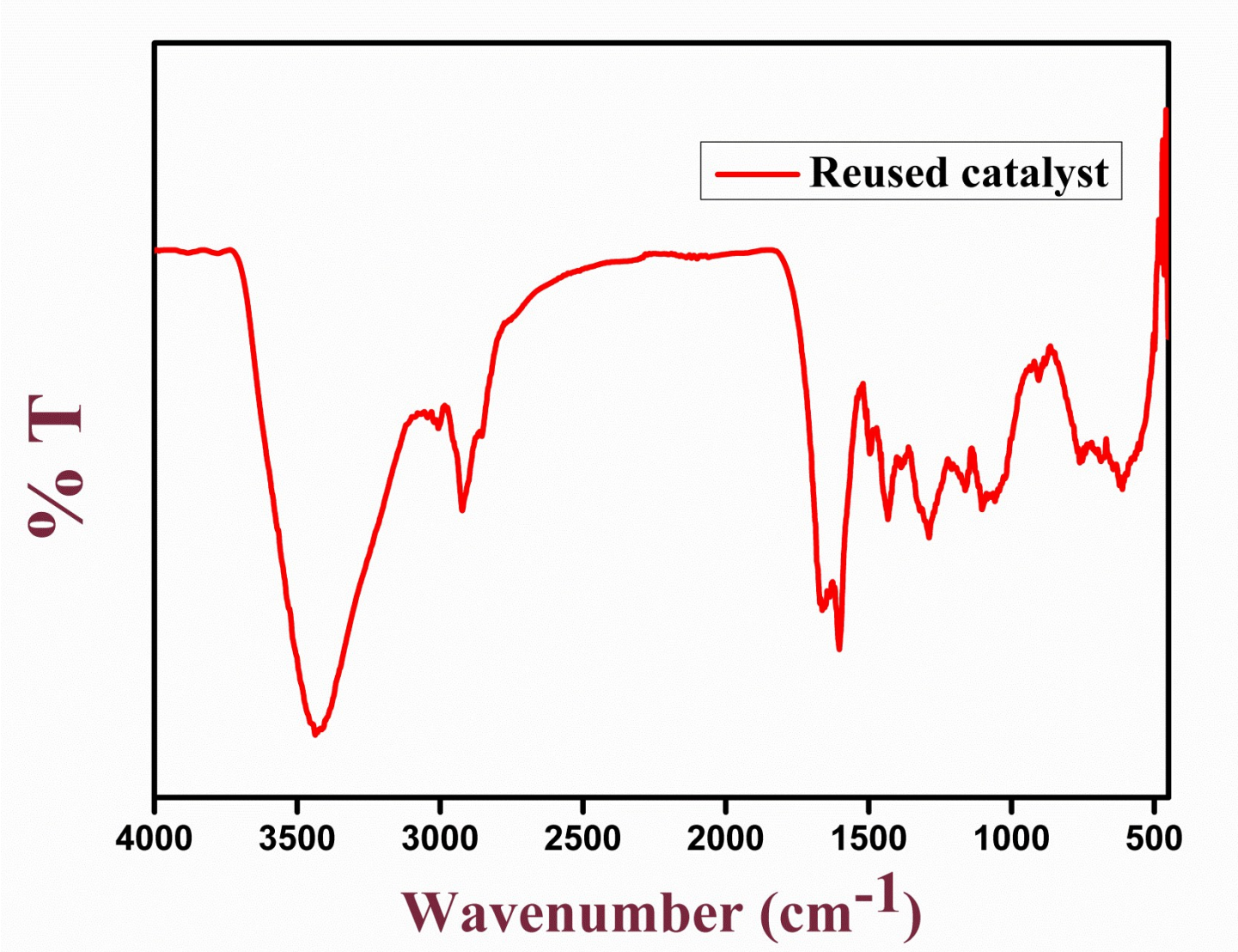
^{1}H NMR for Compound 12l



^{13}C NMR for Compound 12l



4. Reused catalyst IR



5. Reused catalyst TEM images (4th recycled)