Electronic Supplementary Material (ESI) for RSC Advances.

Sustainable synthesis of biomass-derived carbon quantum dots and their catalytic application for the assessment of *α,β*-unsaturated compounds

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Supporting Information

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General

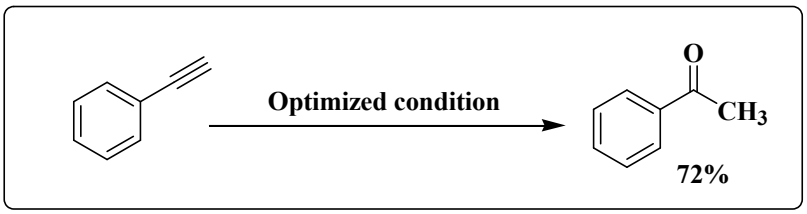
All the chemicals used were of research grade (purchased from Sigma Aldrich, Acros *etc*.) and used without further purification. The mango (Mangifera indica) (Dasheri Mango, India) for experiment was purchased from a local fruit market (Jaipur, Rajasthan). ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ using TMS as an internal standard on a JEOL NMR spectrometer at 400 and 100 MHz respectively. Chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. Mass spectrum of representative compound was recorded on Waters-Xeevo G_2S Q-Tof. X-ray diffraction (XRD) measurements for phase determination were recorded by an X Pert Pro X-ray diffractometer. SEM and EDX measurements were performed using a FEI Quanta 450 FE-SEM. The size and morphology of the synthesized material was observed by transmission electron microscopy (TEM) using a JEOL 1011 at an accelerating voltage of 200kV. (XPS) were measured on a commercial SPECS spectrometer (Germany), equipped with an Al-Kα X-ray source (1486.5eV). UV-Visible spectra analysis was done using a double beam UV-visible spectrometer (Shimadzu). IR spectra were recorded on a Shimadzu FT-IR 8400S spectrophotometer. Raman spectra was performed on a Labram confocal Raman microscope. The melting points of all compounds were determined on a Toshniwal apparatus in capillary and uncorrected. The microwave-assisted reactions were carried out in a MAS-II microwave oven (2450 MHz, Sineo Microwave Chemistry Technology Company, Shanghai, China) with a maximum power output of 1000 W. This system is equipped with a power and temperature feedback control switch.

Catalyst Preparation

Typically, the CQDs were prepared by the hydrothermal process of "Mango (Mangifera indica) kernel". Firstly, we dried the mango kernel part and then put it into a typical ceramic crucible, and carbonized at the temperature of 300 ℃ for 2 h with a heating rate of 10 ℃/min. After cooling down to room temperature, the dark black products were mechanically ground into fine powder. Then, 500 mg of resultant sample was added into 100 mL purified water and ultrasound dispersed to form a black solution. The filtrate was centrifuged (12,000 rpm for 15 min) and after CQDs was collected through filtration with a filtration membrane (0.22 μm of pore size). We got brown yellow colour solution of carbon quantum dots in day light and light greenish colour shown in UV region. The obtained CQDs solution was kept at 4 ℃ for further characterization and use.

Synthesis of *α,β*-unsaturated carbonyl compound

A mixture of benzaldehyde aldehyde (2.0 mmol), phenylacetylene (2.0 mmol) with 10 ml of CQDs aqueous solution (5 mg/ml) were introduced into a 50 mL round-bottom flask. The flask was placed in the microwave cavity and subjected to irradiation for appropriate time at 80 ^{o}C using a maximum power of 400 W. The progress of reaction was monitored with the help of thin layer chromatography (TLC). After completion of the conversion, the target product was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate and evaporation of the solvent under reduced pressure gave the crude product. And the product was purified by recrystallisation from ethanol.



Scheme SI: Control experiment

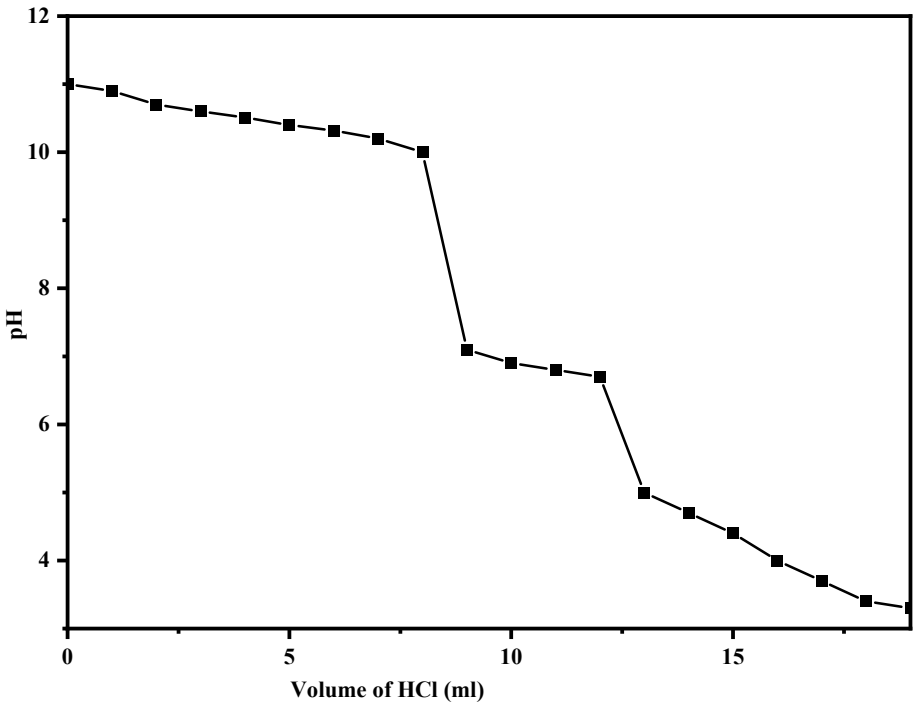


Fig. S1 Back titration curve

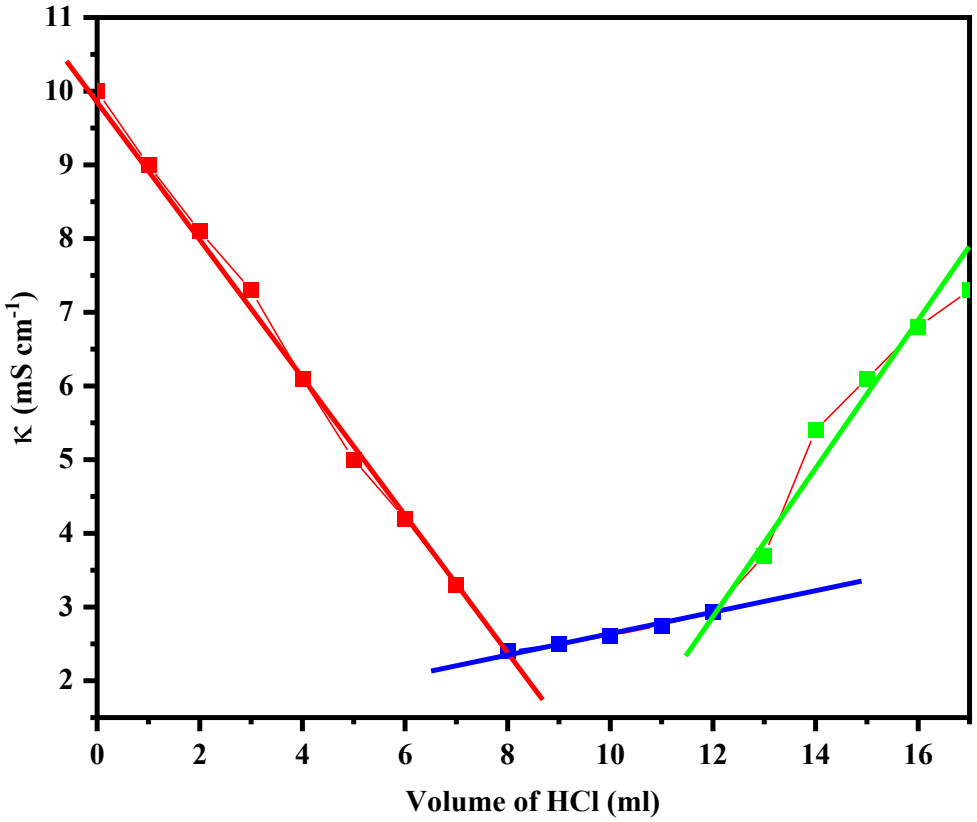


Fig. S2 Conductometric titration curve

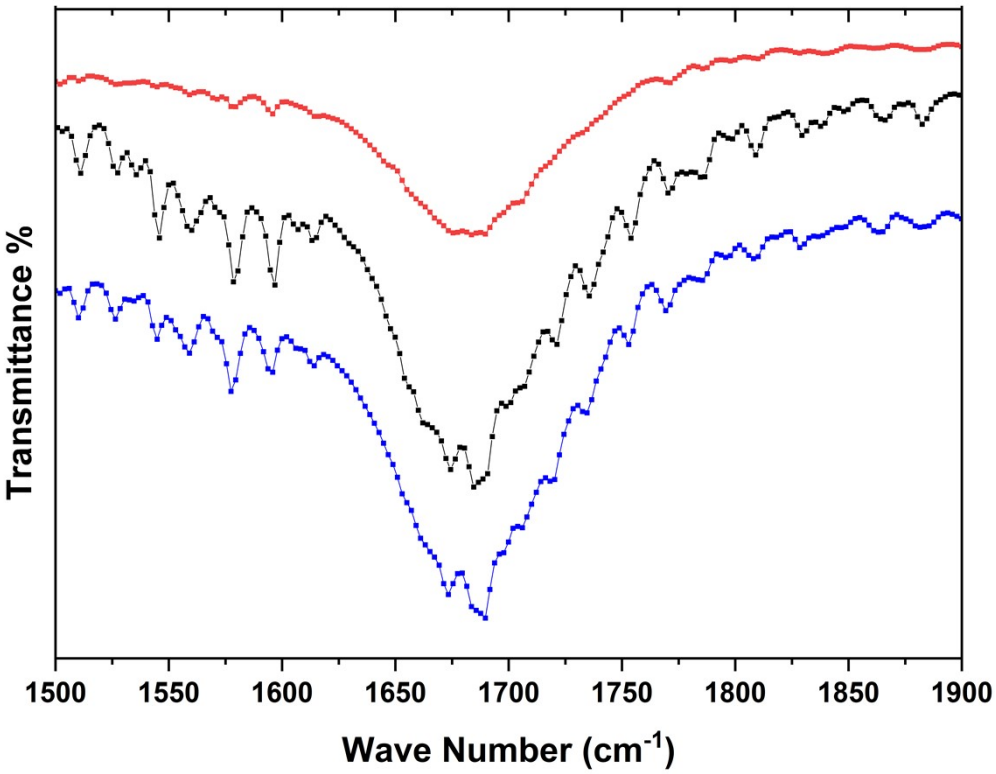


Fig. S3 FT-IR Spectrum of (a) CQDs, (b) Acid base treated CQDs, (c) Base treated CQDs

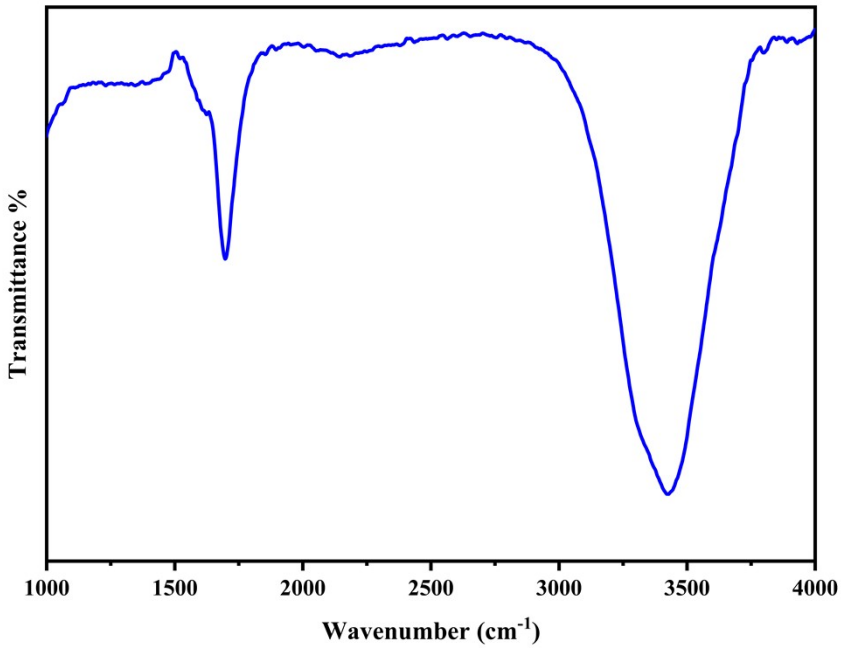


Fig. S4 FT-IR spectra of reused CQDs

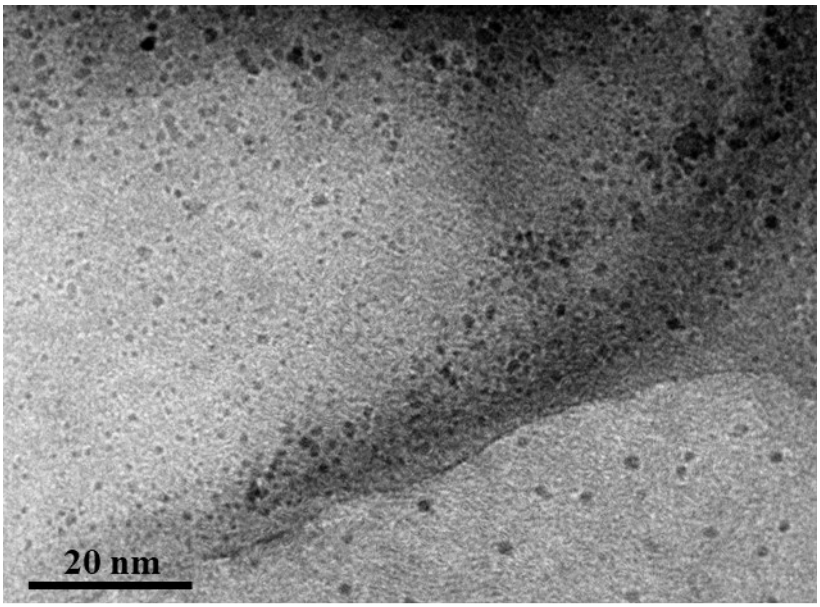
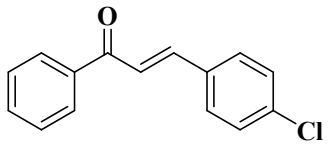


Fig. S5 TEM image of reused CQDs

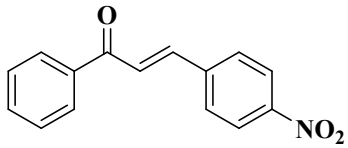
Experimental characterisation data

(E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3a)



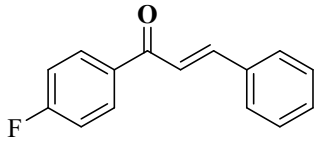
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53-7.51 (m, 2H), 7.29-7.25 (d, J = 15.7 Hz, 1H), 7.23-7.17 (m, 3H), 7.12-7.03 (m, 3H), 6.81-6.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 202.94, 145.47, 137.89, 137.15, 133.11, 132.76, 129.33, 128.59, 128.34, 127.95, 127.73, 127.42, 127.26, 124.76. Mass spectrum (EI, m/z): 243.05 $[M + H]^+$.

(E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (3b)



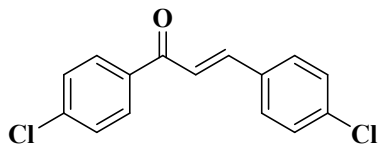
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53-7.50 (d, J = 8.8 Hz, 2H), 7.29-7.17 (m, 4H), 7.14 - 7.05 (m, 3H), 6.99-6.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 202.94, 145.44, 140.94, 138.49, 137.66, 133.10, 131.54, 129.70, 128.35, 124.75, 120.94. Mass spectrum (EI, m/z): 253.07 $[M]^+$.

(E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (3c)



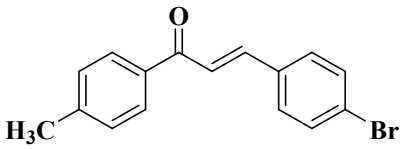
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (m, 2H), 7.83-7.80 (d, J = 15.7 Hz, 1H), 7.65 - 7.63 (m, 2H), 7.52-7.49 (d, J = 15.7 Hz, 1H), 7.44-7.41 (m, 3H), 7.20-7.15 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 188.91, 166.93, 145.14, 134.79, 134.58, 134.55, 131.21, 131.11, 130.74, 129.06, 128.54, 121.60, 115.93, 115.71. Mass spectrum (EI, m/z): 227.08 $[M + H]^+$.

(E)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (3d)



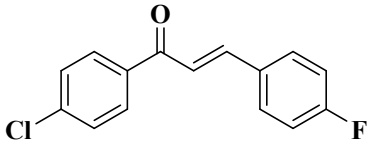
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.90 (d, J = 8.5 Hz, 2H), 7.73-7.69 (d, J = 15.6 Hz, 1H), 7.54-7.52 (d, J = 8.4 Hz, 2H), 7.44-7.42 (d, J = 8.4 Hz, 2H), 7.39-7.34 (t, J = 8.4, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 188.97, 143.91, 139.47, 136.74, 136.36, 133.23, 129.97, 129.72, 129.37, 129.08, 121.89. Mass spectrum (EI, m/z): 277.01$[M + H]^+$.

(E)-3-(4-bromophenyl)-1-(p-tolyl)prop-2-en-1-one (3e)



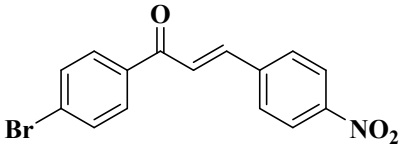
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88-7.86 (d, J = 8.2 Hz, 2H), 7.69-7.65 (d, J = 15.7 Hz, 1H), 7.50-7.47 (d, J = 8.5 Hz, 2H), 7.45-7.44 (d, J = 8.5 Hz, 2H), 7.26-7.20 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 189.77, 143.01, 135.46, 133.95, 132.23, 129.82, 129.45, 128.71, 122.59, 21.77. Mass spectrum (EI, m/z): 300.01 $[M]^+$.

(E)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (3f)



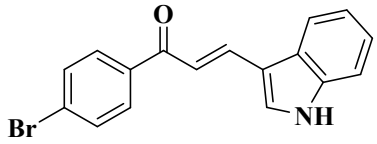
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03-7.98 (dd, J1 = 8.5, J2 = 5.5 Hz, 2H), 7.77-7.71 (d, J = 15.6 Hz, 1H), 7.62-7.56 (d, J = 8.4 Hz, 2H), 7.40-7.35 (d, J = 15.7 Hz, 1H), 7.32-7.13 (d, J = 8.4 Hz, 2H), 7.12-7.04 (t, J = 8.4, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 188.70, 144.59, 143.82, 131.44, 131.19, 131.10, 130.67, 130.50, 130.42, 128.83, 128.73, 128.56, 121.30, 116.15. Mass spectrum (EI, m/z): 260.04 $[M]^+$.

(E)-1-(4-bromophenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3g)



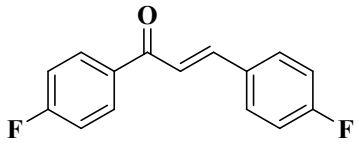
^{1}H NMR (400MHz, $CDCl_3$) δ = 7.75-8.32 (m, 8H, ArH), 7.55 (d, *J* = 16.2 Hz, 1H), 7.71 (d, *J* =16.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 150.6, 147.3, 144.5, 138.2, 134.8, 132.6, 131.9, 130.5, 126.3, 122.3. Mass spectrum (EI, m/z): 331.98 $[M+H]^+$.

(E)-1-(4-bromophenyl)-3-(1H-indol-3-yl)prop-2-en-1-one (3h)



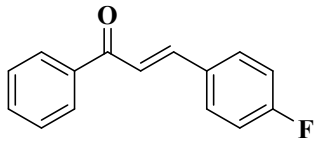
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.15 (s, 1H, NH), 7.70-8.42 (m, 9H), 7.53 (d, *J* = 15.9 Hz, 1H), 7.68 (d, *J* =15.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 188.5, 148.5, 140.5, 136.5, 132.3, 131.1, 130.6, 130.4, 128.2, 127.8, 127.6, 126.0, 124.7, 124.3, 123.7. Mass spectrum (EI, m/z): 326.01 $[M+H]^+$.

(E)-1,3-bis(4-fluorophenyl)prop-2-en-1-one (3i)



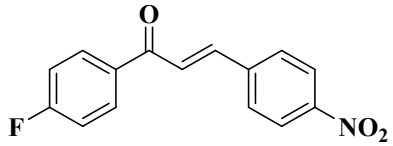
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.87 (m, 8H), 7.56 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* =15.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 186.8, 153.1, 147.5, 138.3, 134.1, 133.9, 132.5, 130.7, 129.8, 117.6, 122.1. Mass spectrum (EI, m/z): 244.07 $[M]^+$.

(E)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3j)



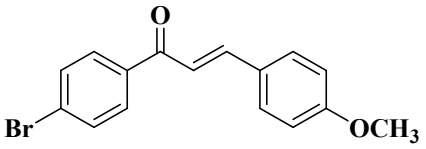
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53-7.51 (m, 2H), 7.29-7.25 (d, J = 15.7 Hz, 1H), 7.23-7.17 (m, 3H), 7.12-7.03 (m, 3H), 6.81-6.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 202.94, 145.47, 137.89, 137.15, 133.11, 132.76, 129.33, 128.59, 128.34, 127.95, 127.73, 127.42, 127.26, 124.76. Mass spectrum (EI, m/z): 226.09 $[M]^+$.

(E)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3k)



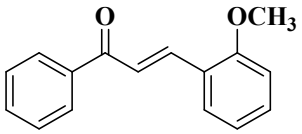
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75-8.32 (m, 8H), 7.55 (d, *J* = 16.2 Hz, 1H), 7.71 (d, *J* =16.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 186.9, 150.6, 147.3, 144.5, 138.2, 134.8, 132.6, 131.9, 130.5, 126.3, 122.3. Mass spectrum (EI, m/z): 333 $[M+H]^+$.

(E)-1-(4-bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (3l)



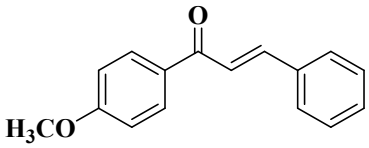
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90-7.89 (m, 8H), 7.52 (d, *J* = 15.9 Hz, 1H), 7.72 (d, *J* =15.9Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 186.4, 160.2, 147.3, 137.6, 133.4, 132.7, 131.2, 129.8, 128.1, 120.9, 118.2, 56.4. Mass spectrum (EI, m/z): 317 $[M+H]^+$.

(E)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one (3m)



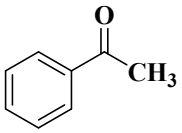
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 15.9 Hz, 1H), 8.05-8.00 (m, 2H), 7.65 (dd, J = 1.7, 7.7 Hz, 1H), 7.64 (d, J = 15.9 Hz, 1H), 7.59-7.54 (m, 1H), 7.51 (t, J = 7.1 Hz, 2H), 7.41-7.35 (m, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 191.08, 158.79, 140.37, 138.51, 132.51, 131.74, 129.20, 128.51, 128.50, 123.90, 122.85, 120.72, 111.23, 55.52. Mass spectrum (EI, m/z): 238 $[M]^+$.

(E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (3n)

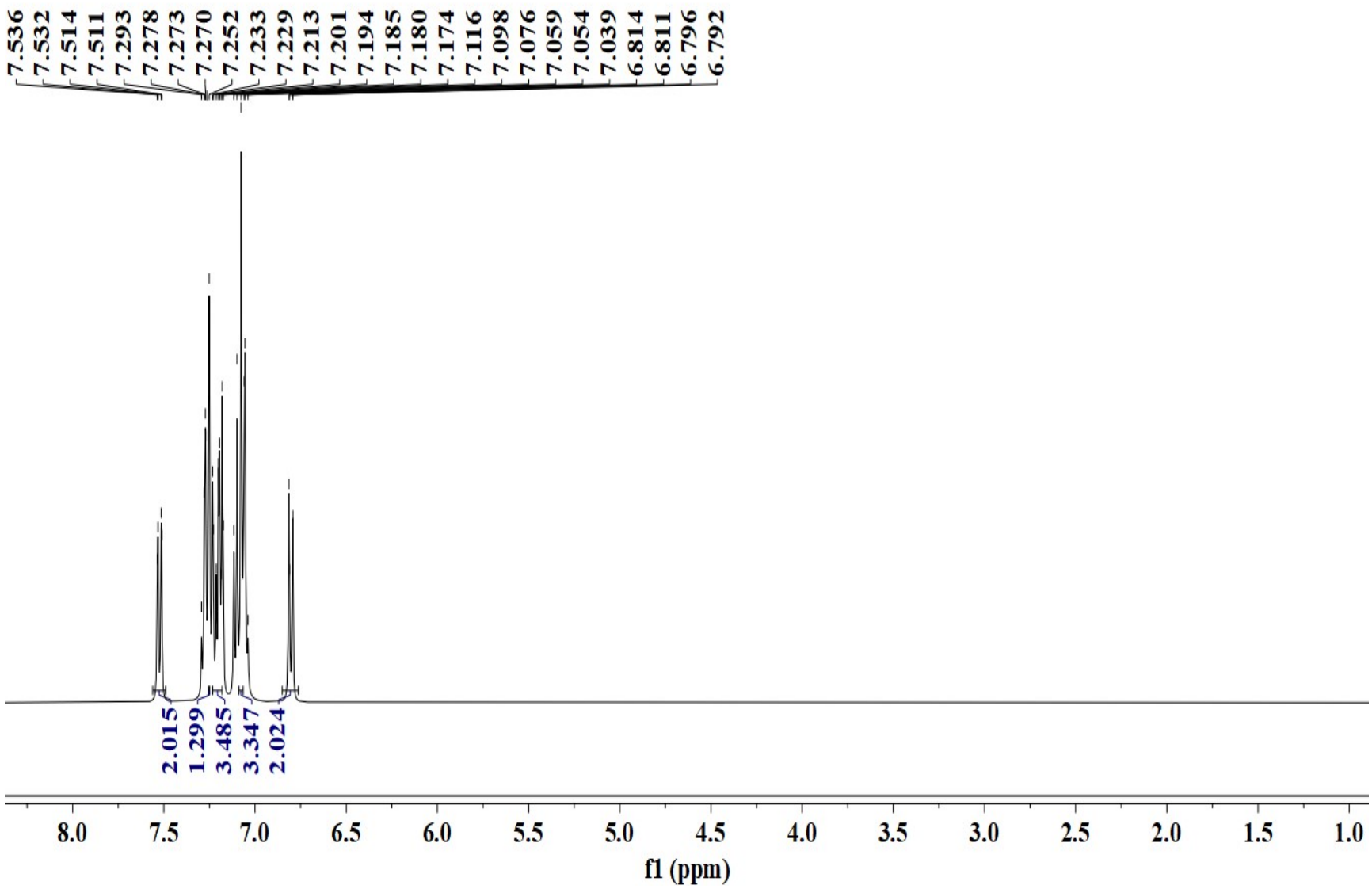


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 15.7 Hz, 1H), 7.69-7.62 (m, 2H), 7.54 (d, J = 15.7 Hz, 1H), 7.46-7.38 (m, 3H), 7.31 (d, J = 8.5 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 190.00, 144.37, 143.62, 135.62, 134.99, 130.39, 129.31, 128.91, 128.64, 128.38, 122.10, 21.67. Mass spectrum (EI, m/): 339 $[M+H]^+$.

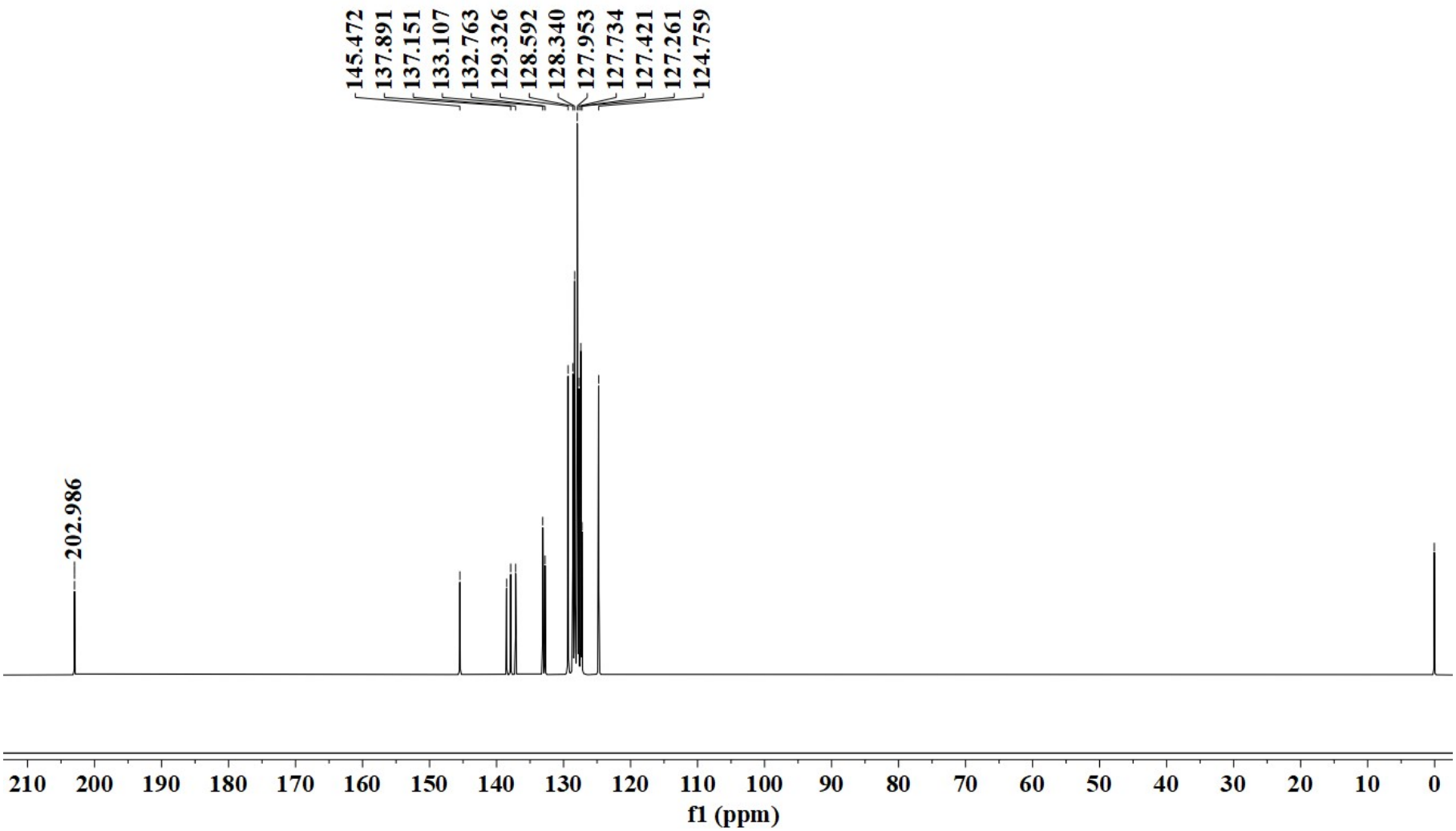
Acetophenone (3o)



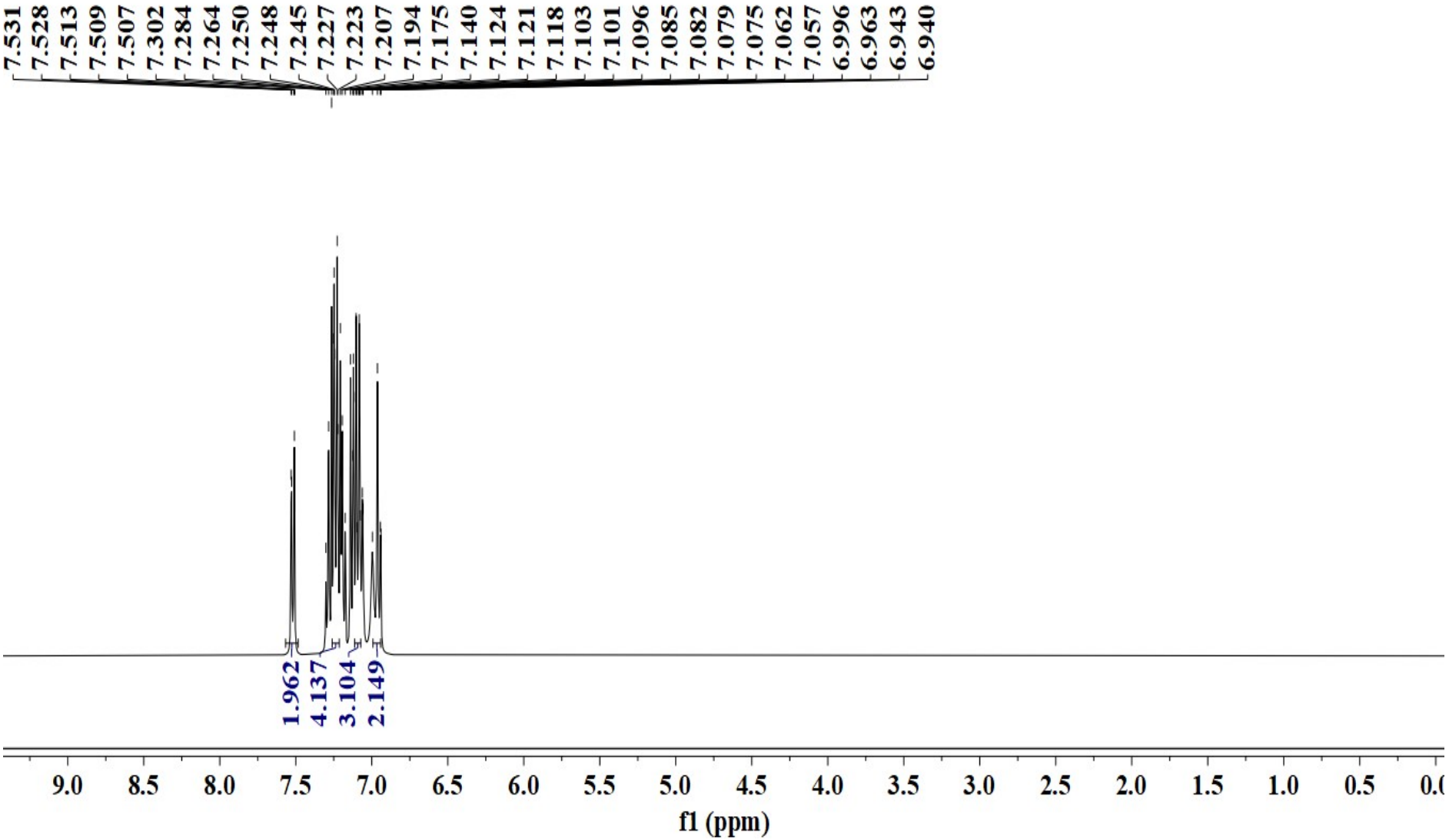
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.949-7.927 (m, 2H), 7.546-7.524 (m, 1H), 7.463-7.424 (m, 2H), 2.589 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 198.324, 137.187, 133.216, 128.664, 128.401, 26.722. Mass spectrum (EI, m/): 121 $[M+H]^+$.



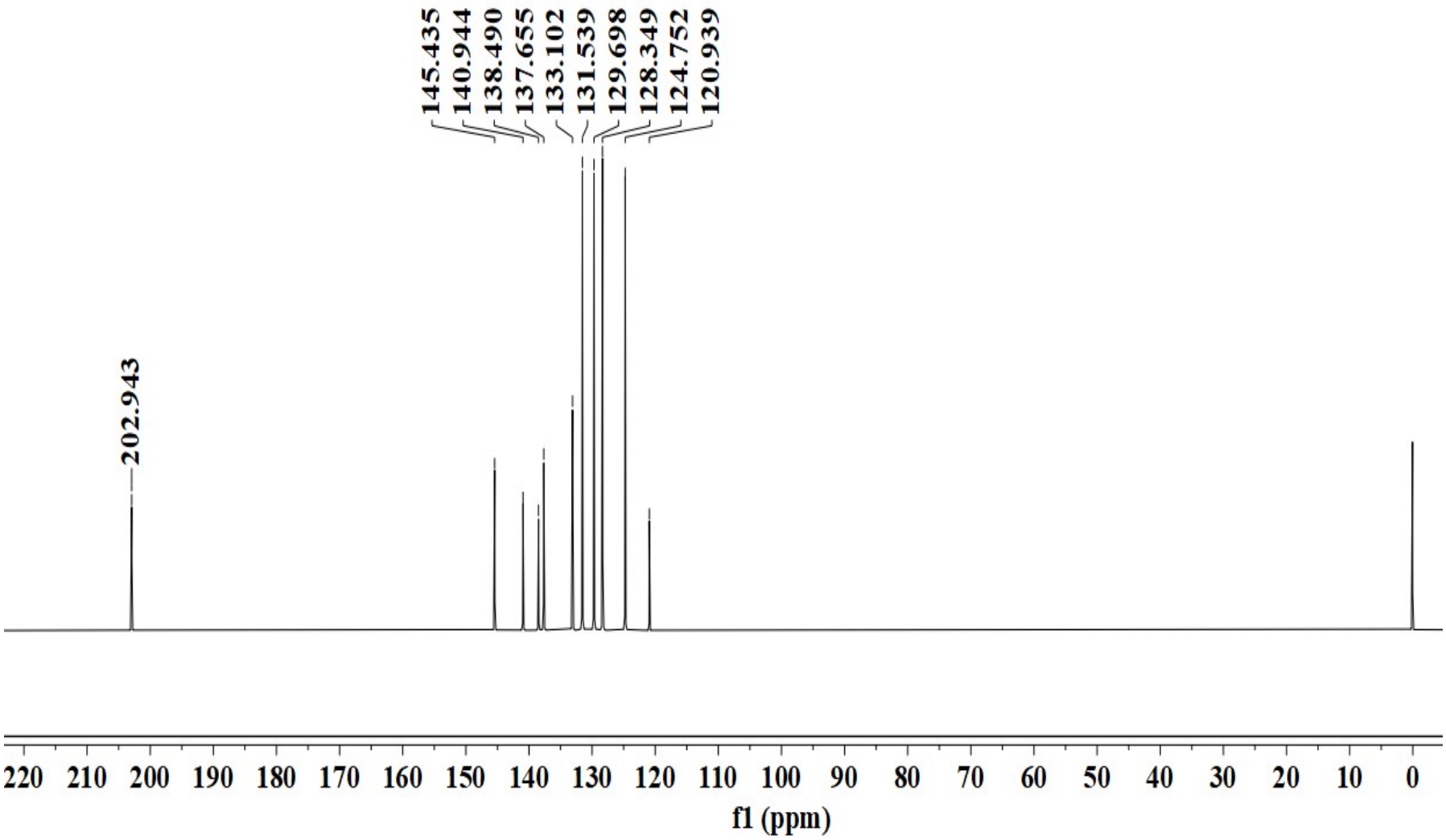
^{1}H NMR of (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3a)



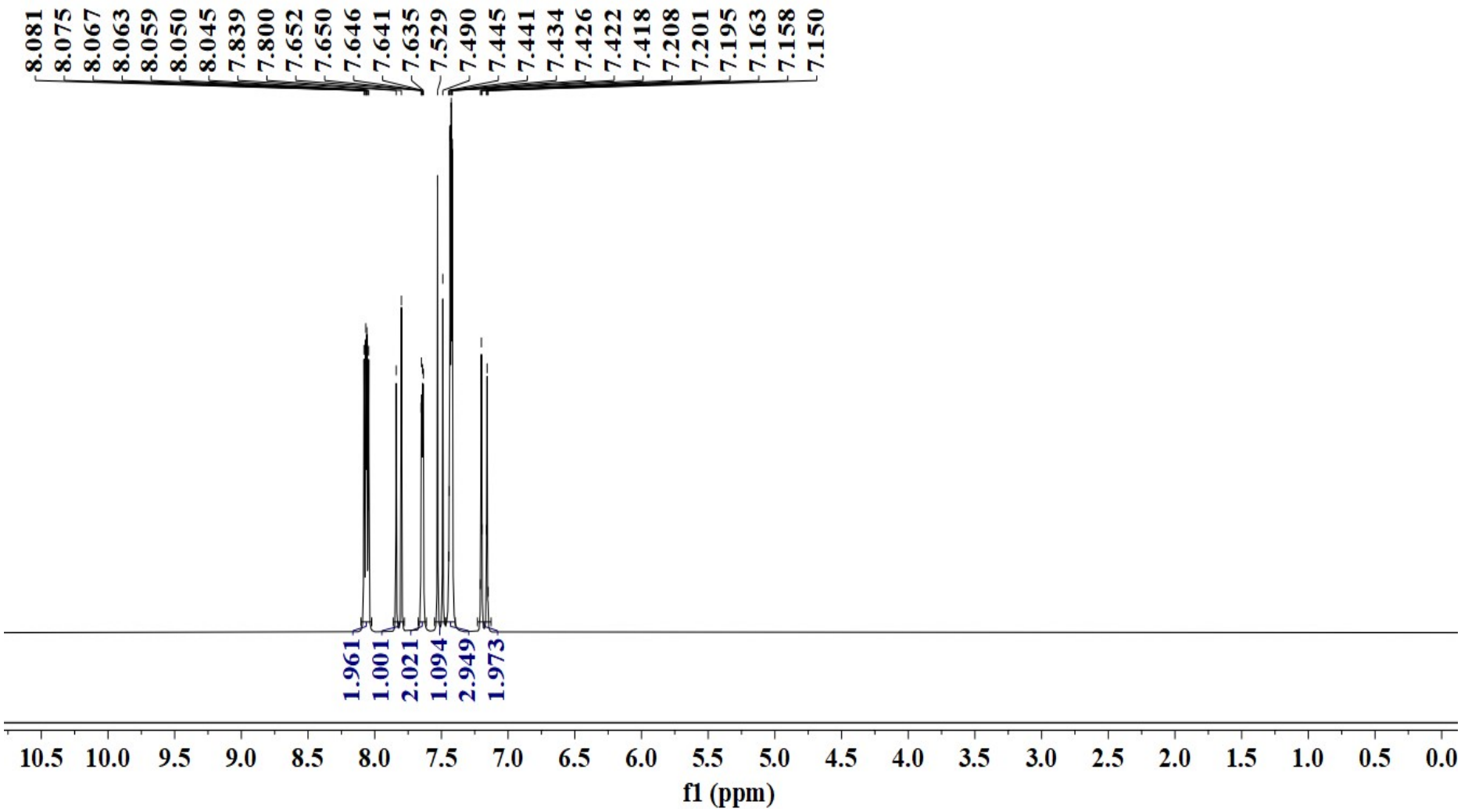
^{13}C NMR of (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3a)



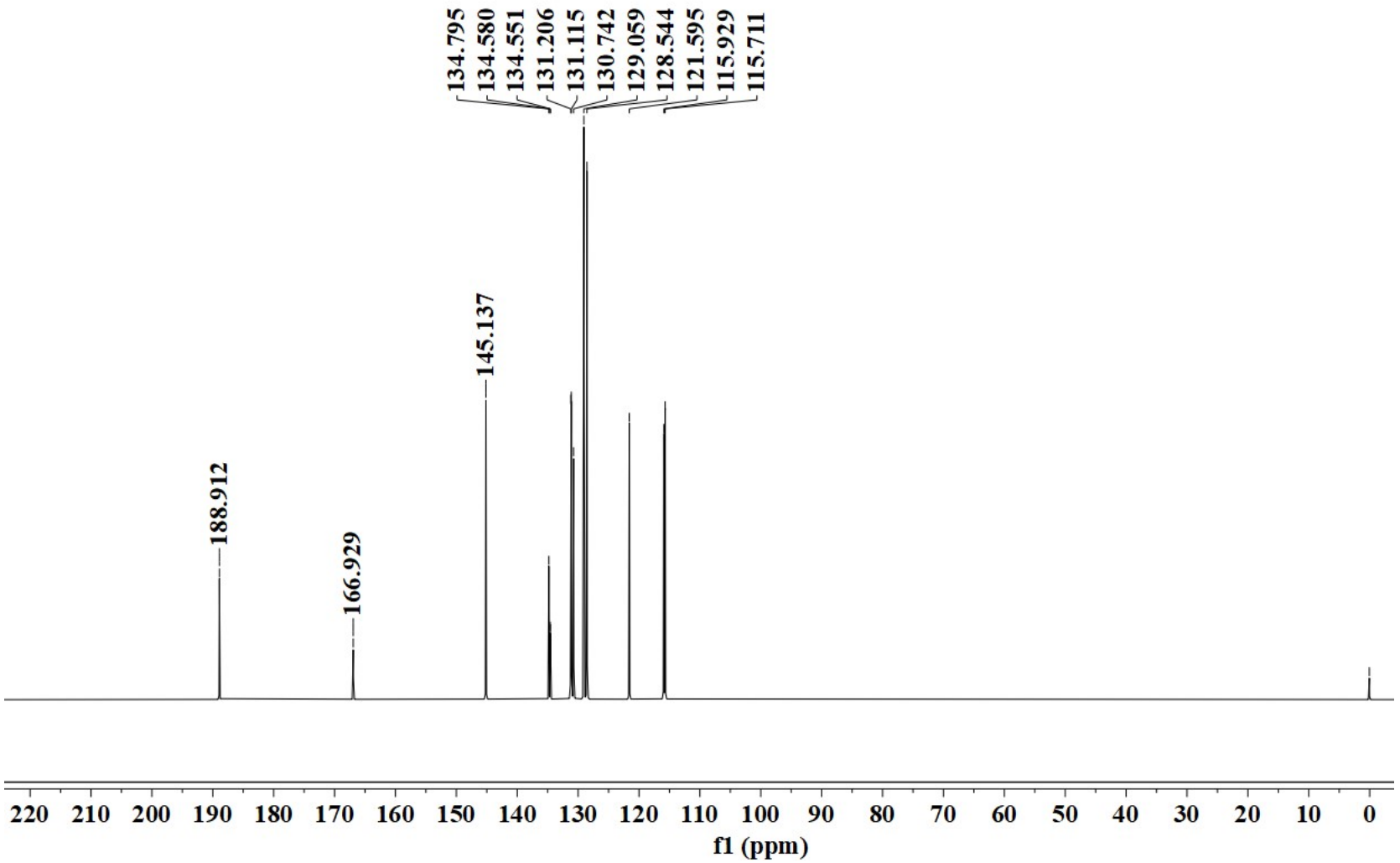
^{1}H NMR of (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (3b)



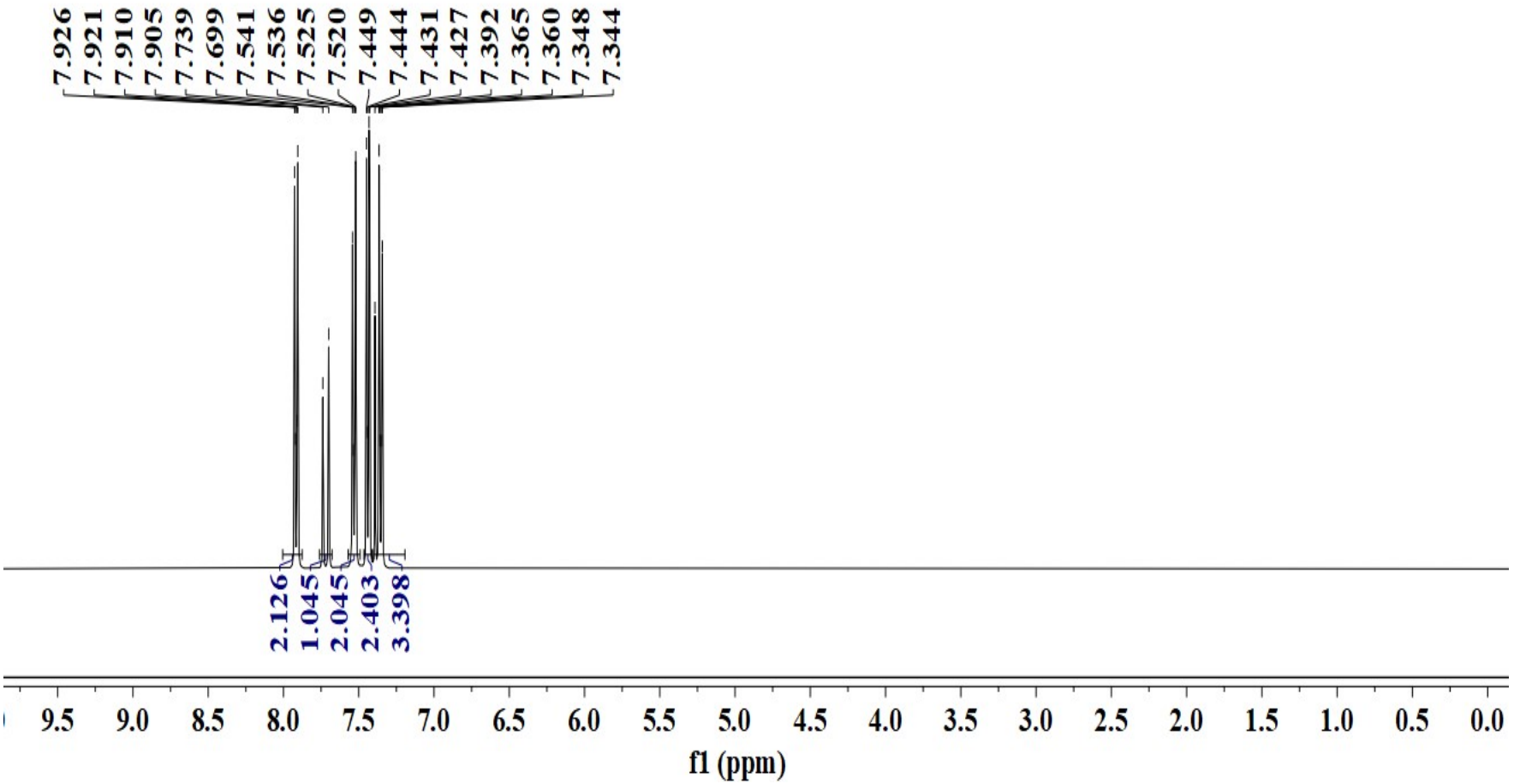
^{13}C NMR of (E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (3b)



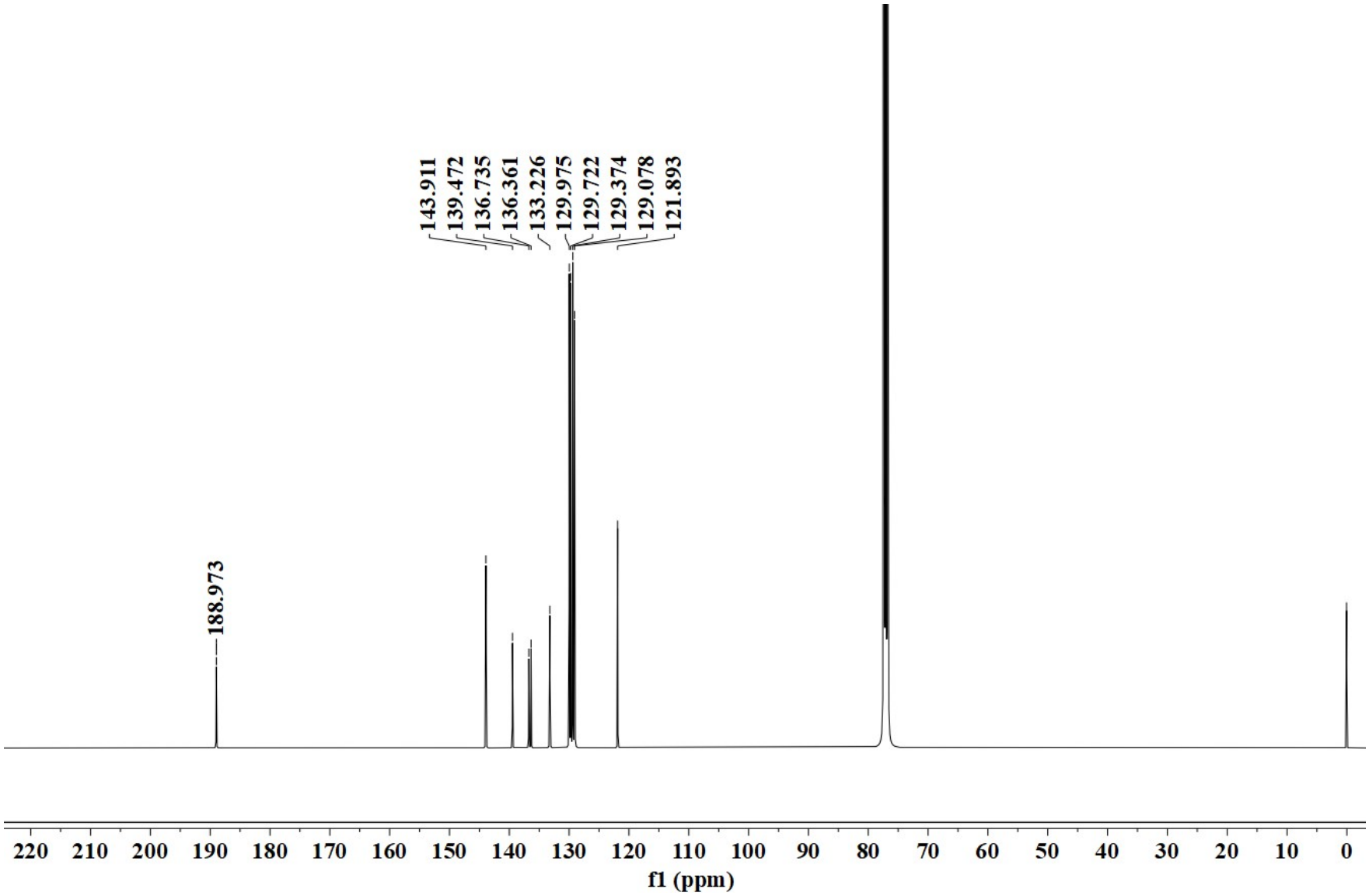
^{1}H NMR of (E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (3c)



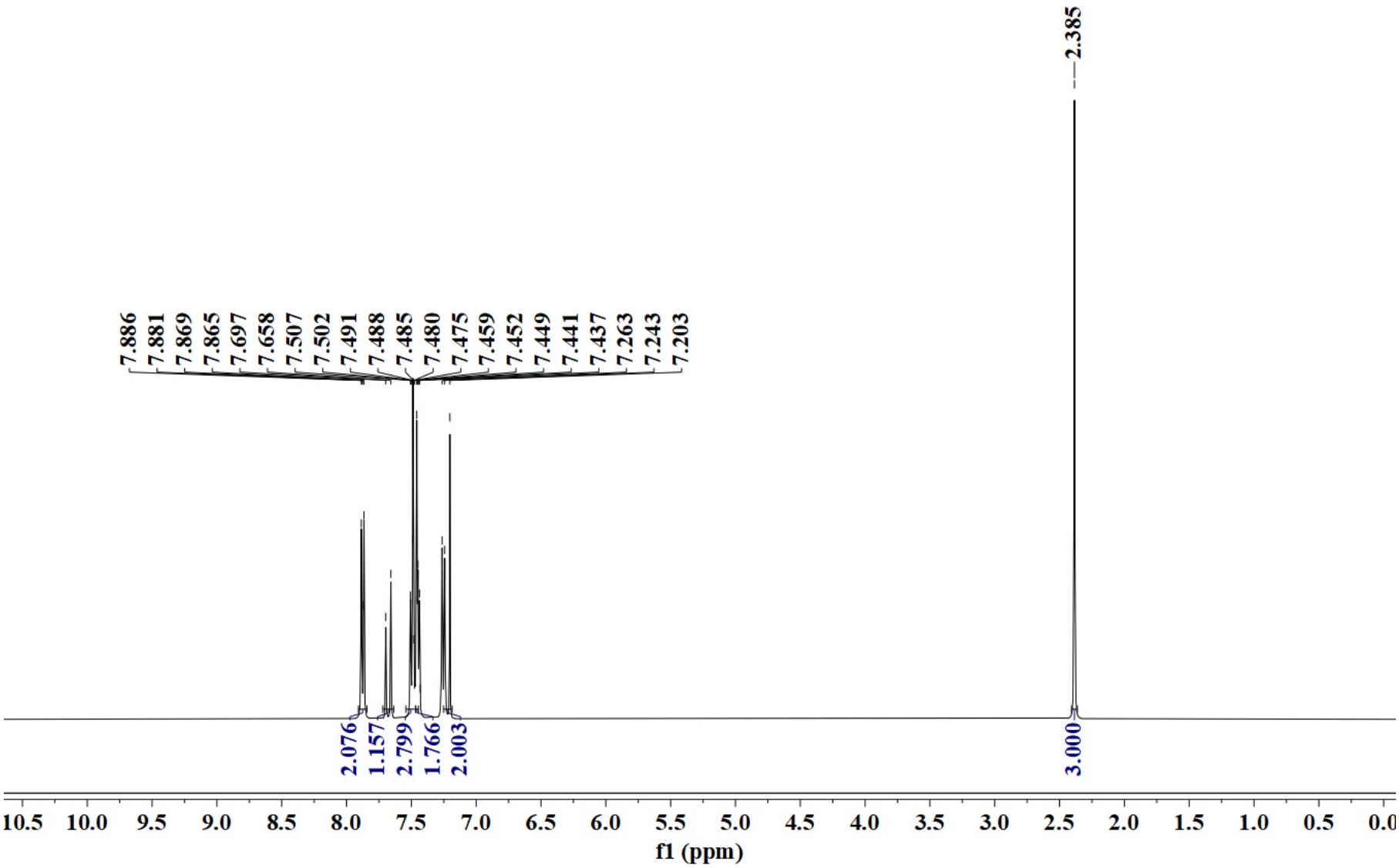
^{13}C NMR of (E)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (3c)



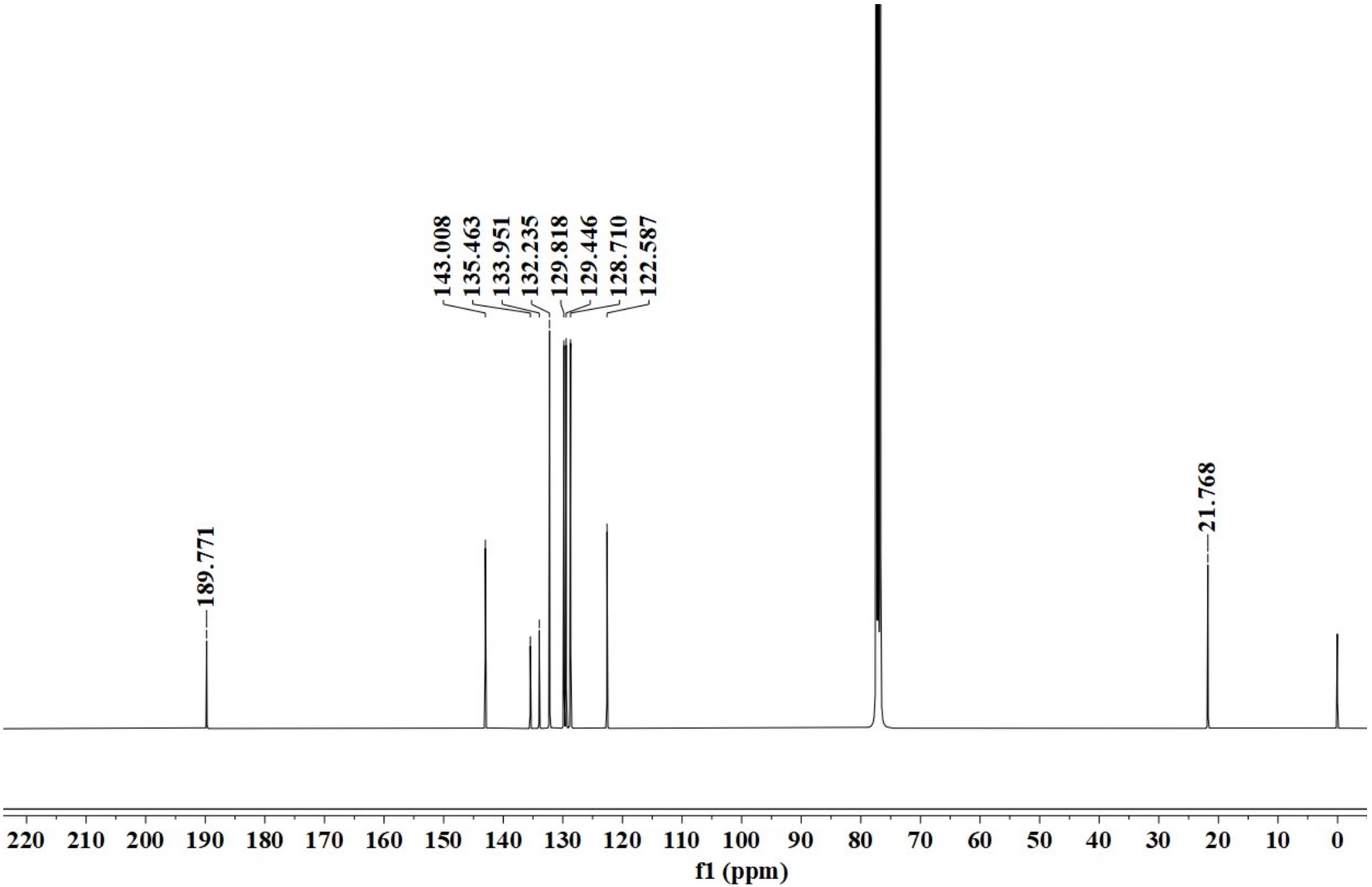
^{1}H NMR of (E)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (3d)



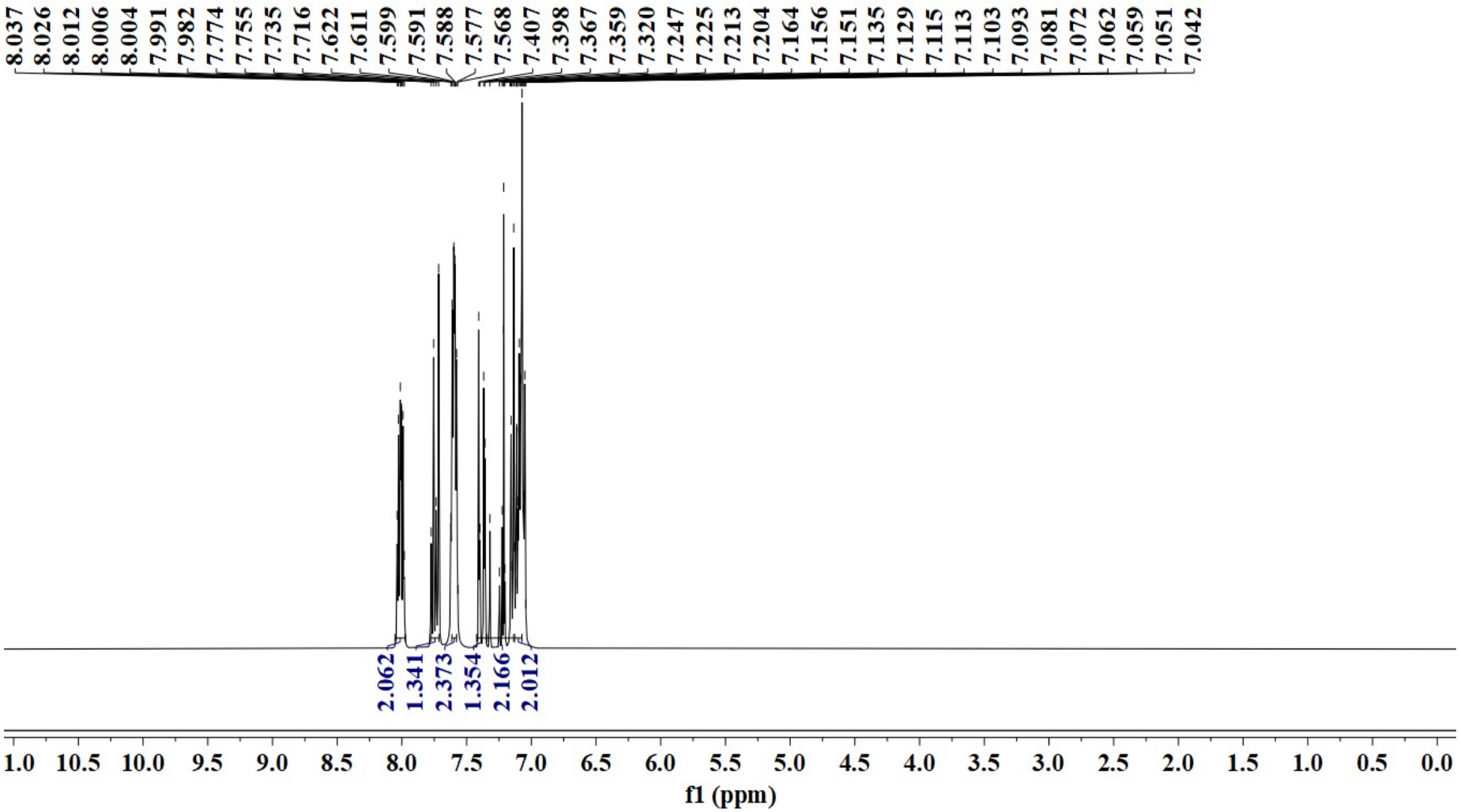
^{13}C NMR of (E)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (3d)



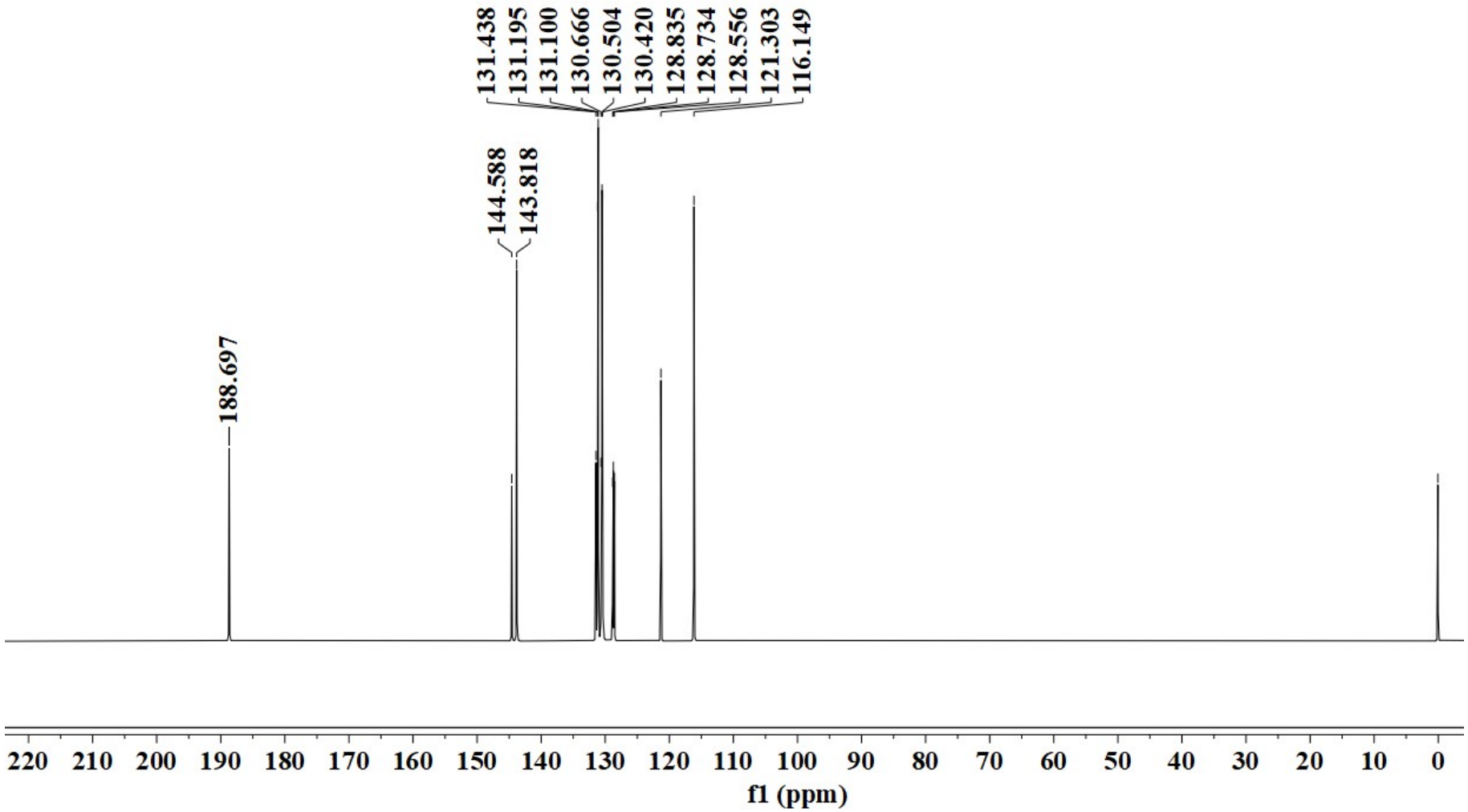
^{1}H NMR of (E)-3-(4-bromophenyl)-1-(p-tolyl)prop-2-en-1-one (3e)



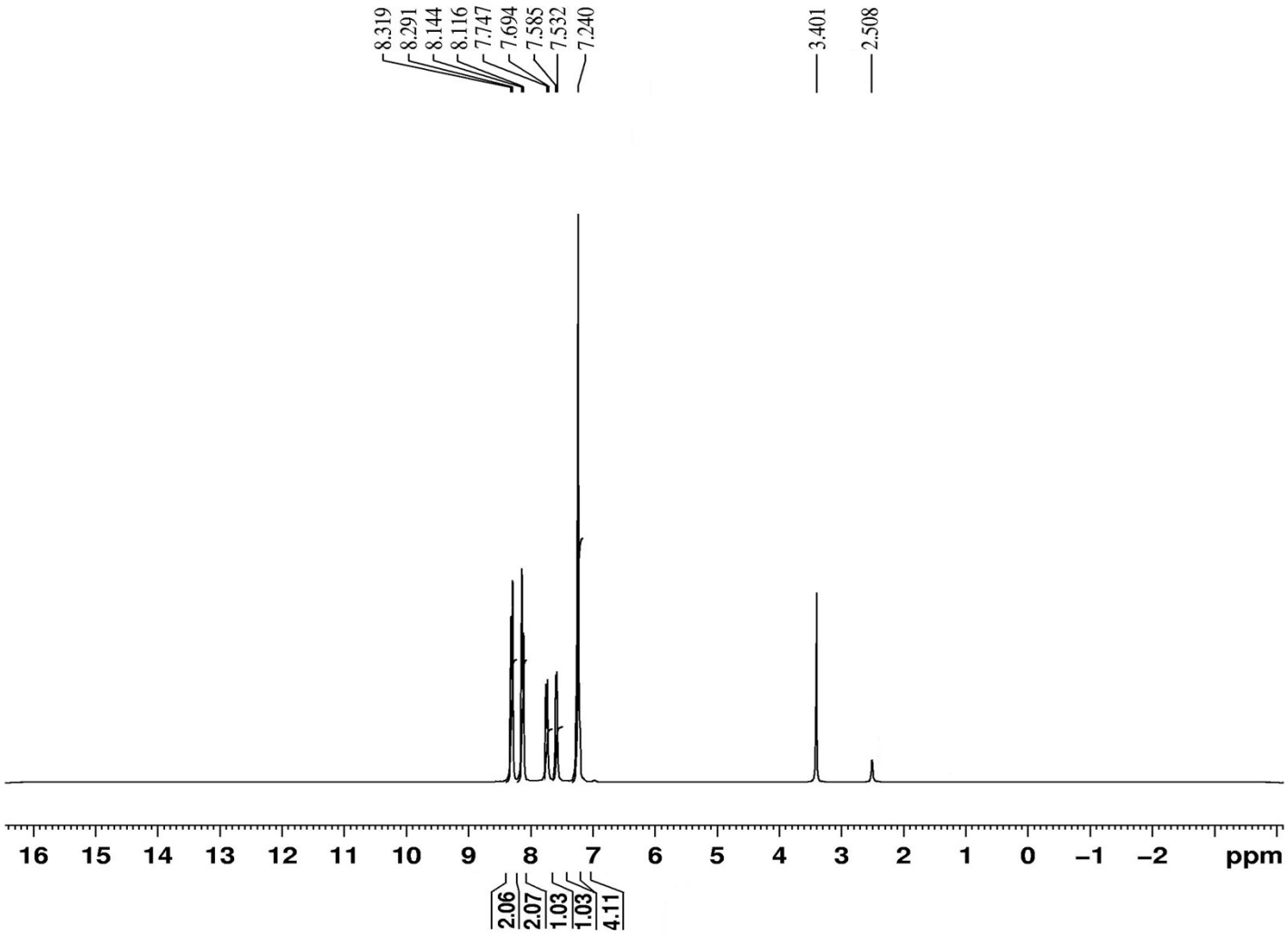
^{13}C NMR of (E)-3-(4-bromophenyl)-1-(p-tolyl)prop-2-en-1-one (3e)



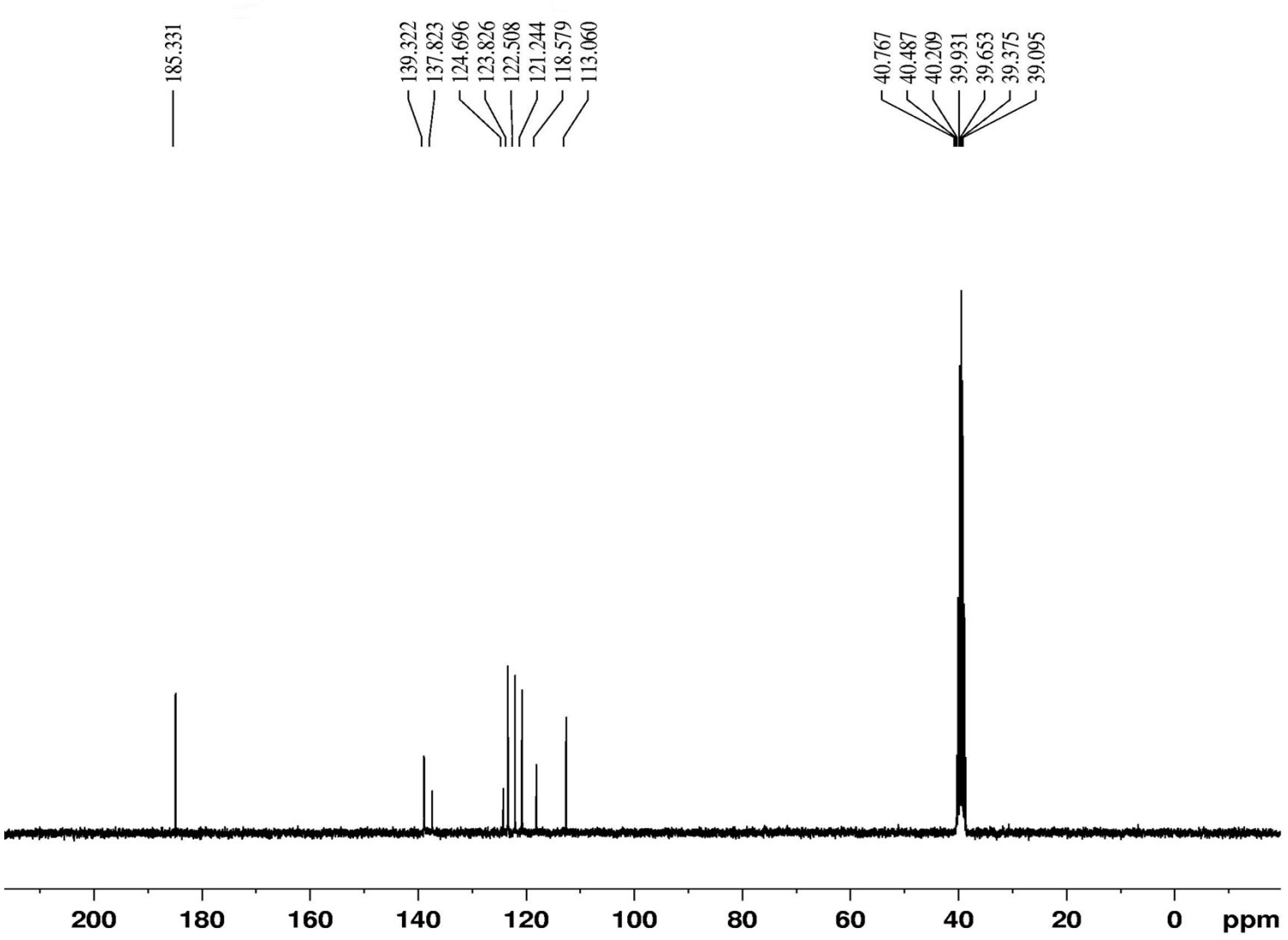
^{1}H NMR of (E)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (3f)



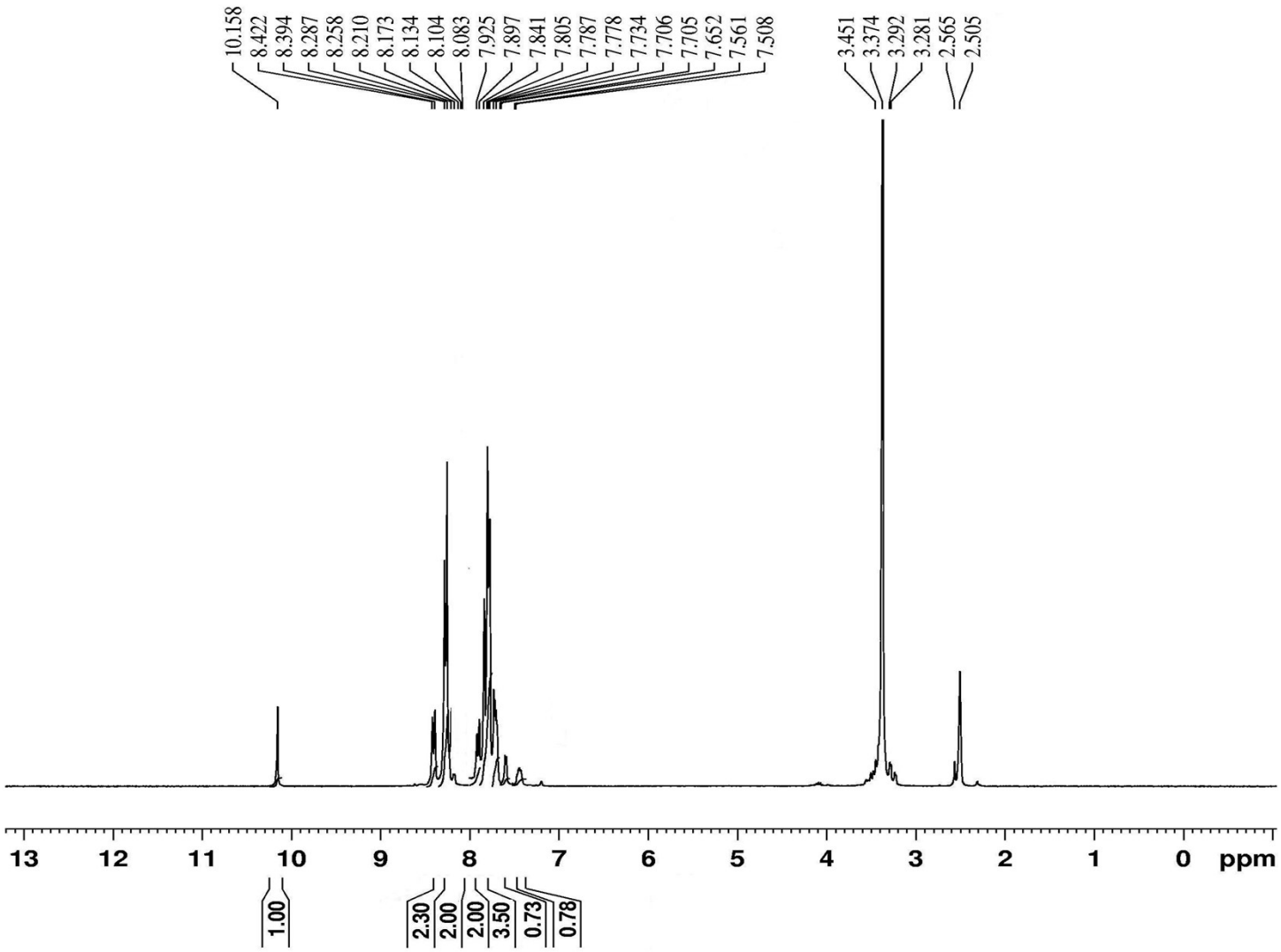
^{13}C NMR of (E)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (3f)



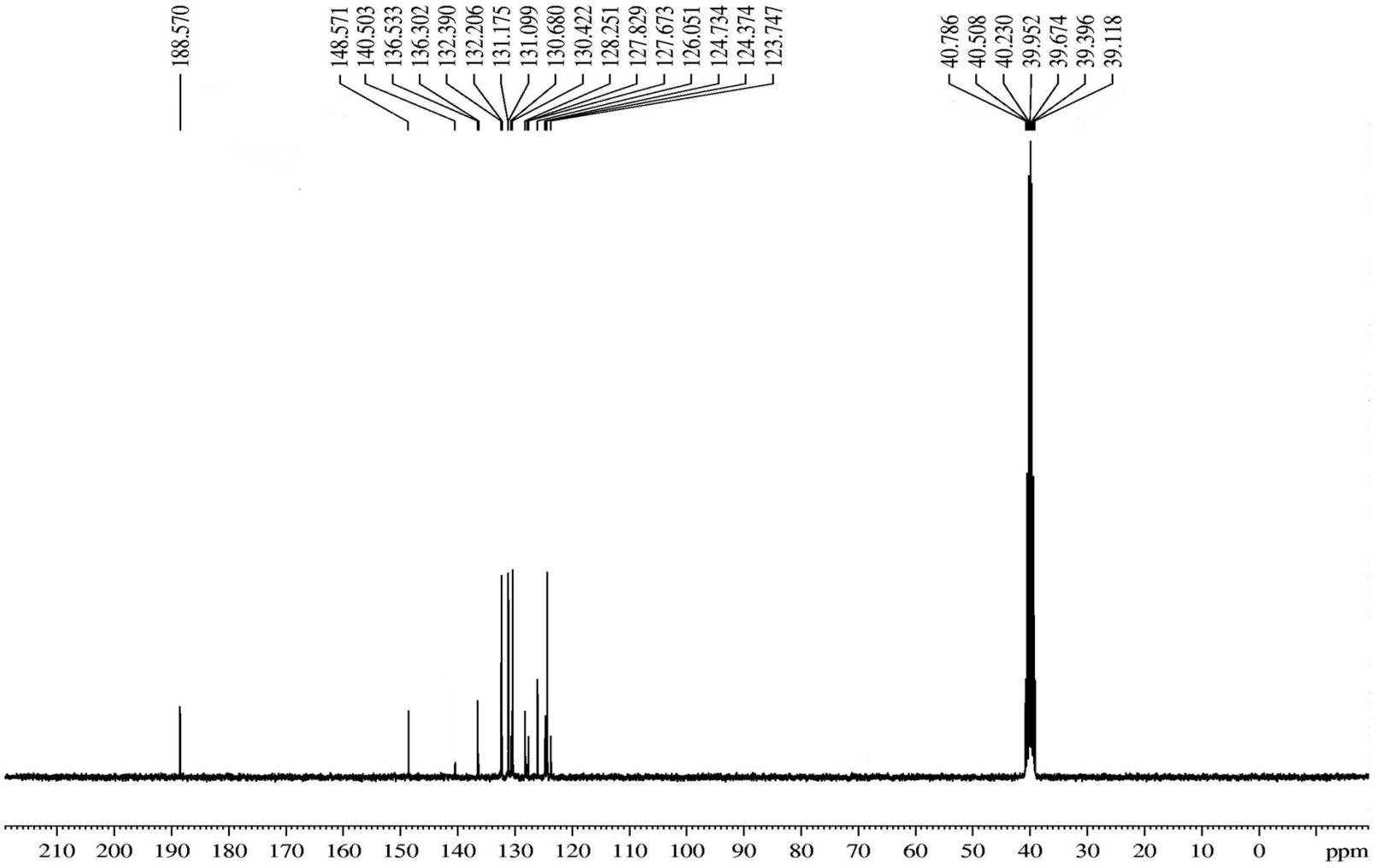
^{1}H NMR of (E)-1-(4-bromophenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3g)



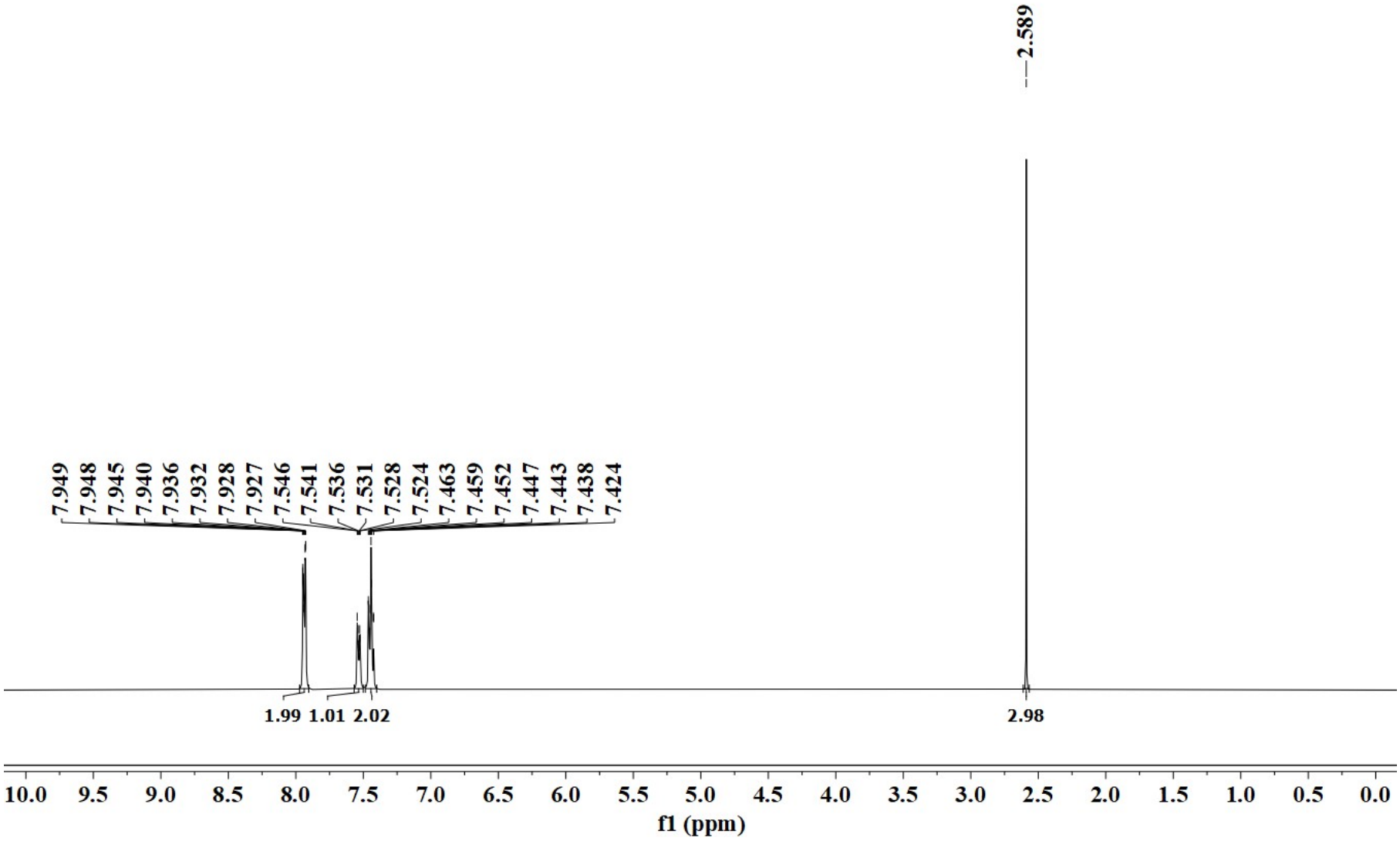
^{13}C NMR of (E)-1-(4-bromophenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3g)



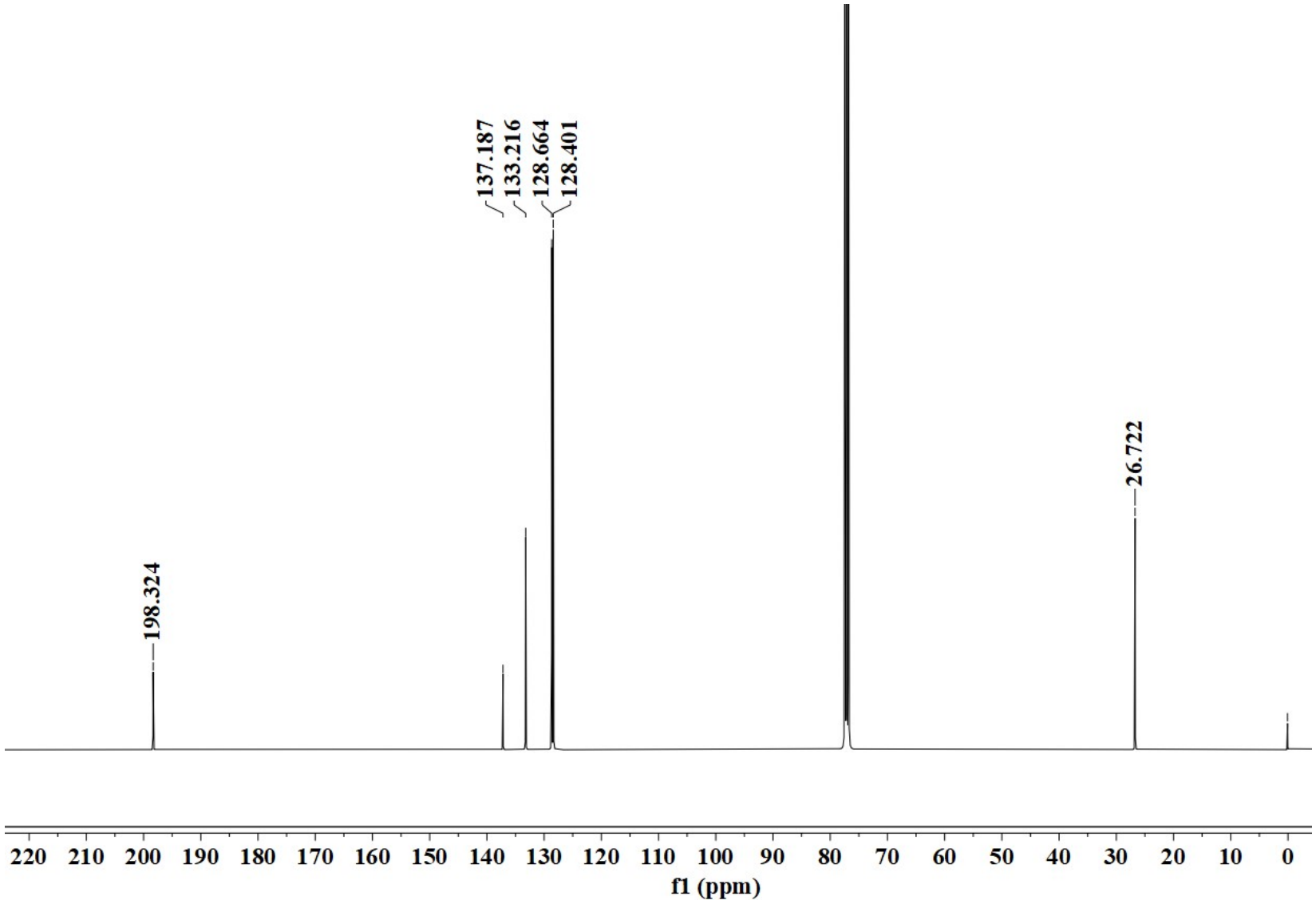
^{1}H NMR of (E)-1-(4-bromophenyl)-3-(1*H*-indol-3-yl)prop-2-en-1-one (3h)



^{13}C NMR of (E)-1-(4-bromophenyl)-3-(1H-indol-3-yl)prop-2-en-1-one (3h)



^{1}H NMR of Acetophenone (3o)



^{13}C NMR of Acetophenone (3o)