Supporting Information

Synthesis of α,β-Unsaturated Ketones from Alkynes and Aldehydes over Hβ Zeolite under Solvent-Free Conditions

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1. Experimental section

i) General information

Aldehydes and alkynes were purchased from Sigma-Aldrich. Hβ (Si/Al = 15) zeolite was obtained from Alfa Aesar, England. All chemicals used were reagent grade and used as received without further purification. All the samples were systematically characterized by different spectroscopic techniques. The XRD patterns of the samples were obtained on a Regaku miniflux X-ray Diffractometer using Ni filtered CuKα radiation at 2θ = 2-80º with a scanning rate of 2º min^{-1} and the beam voltage and currents of 30 kV and 15 mA, respectively. ^{1}H NMR spectra were recorded by using Bruker VX NMR FT-300 or Varian Unity 500 and ^{13}C NMR spectra were recorded by using Bruker VX NMR FT-75 MHz spectrometers instrument in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet). The IR values are reported in reciprocal centimeters (cm^{-1}). Mass spectra were recorded on a time of fight (TOF) mass spectrometer. Column chromatography was carried out using silica gel (100-200 mesh).

ii) General procedure for the tandem hydration/condensation reaction between alkynes and aldehydes

Hβ zeolite (100 mg) was added to the well stirred solution of alkyne (2 mmol), aldehydes (2 mmol) and H_2O (8 mmol) in a 15 mL of sealed vial and the reaction mixture was allowed to stir at 100 °C. After disappearance of the alkyne (monitored by TLC) or after an appropriate time, the reaction mixture was cooled to room temperature, diluted with ethyl acetate. The catalyst was separated by filtration and the removal of solvent in vacuo yielded crude residue. The crude residue was further purified by column chromatography using silica gel (100-200 mesh) to afford pure products. All the products were identified on the basis of ^{1}H and ^{13}C NMR spectral data.

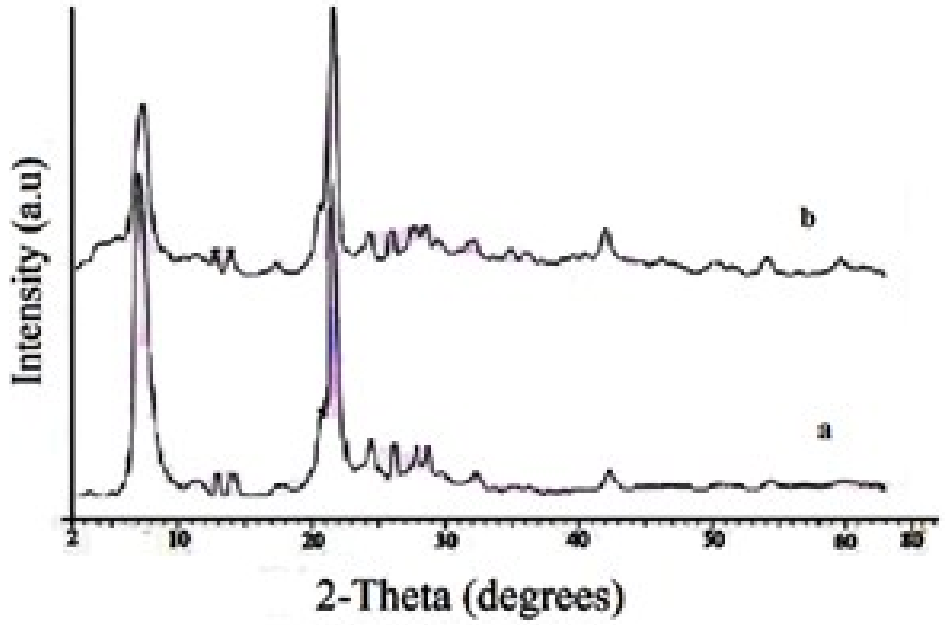
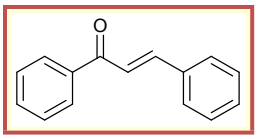


Figure S1. XRD patterns of Hβ zeolite: (a) Before reaction (b) After reaction.

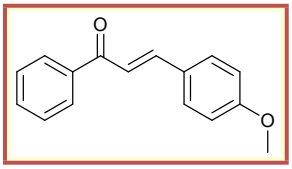
2. Spectral data of all products

(*E*)-Chalcone (Table 2, 4a)[1]



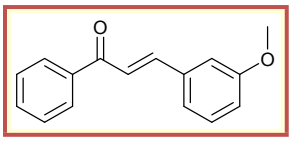
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.81 (d, 1H, J = 15.65 Hz), 7.63-7.66 (m, 2H), 7.48-7.61 (m, 4H), 7.39-7.43 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.50, 144.79, 138.15, 134.83, 132.73, 130.49, 128.90, 128.57, 128.45, 128.40, 122.05.

(*E*)-3-(4-methoxyphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4b)[2]



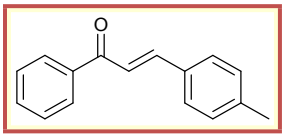
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.79 (d, 1H, J = 15.71 Hz), 7.55-7.62 (m, 3H), 7.48-7.51 (m, 2H), 7.42 (d, 1H, J = 15.56 Hz), 6.94 (d, 2H, J = 8.85 Hz), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.49, 161.61, 144.61, 138.43, 132.48, 130.16, 128.48, 128.34, 127.54, 119.70, 114.35, 55.34.

(*E*)-3-(3-methoxyphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4c) [3]



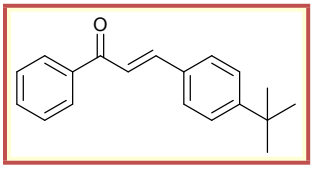
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.77 (d, 1H, J = 15.71 Hz), 7.57-7.61 (m, 1H), 7.50 (t, 3H, J = 7.78 Hz), 7.33 (t, 1H, J = 7.78 Hz), 7.25 (d, 1H, J = 7.62 Hz), 7.15-7.17 (m, 1H), 6.97 (dd, 1H, J = 2.44, 8.69 Hz), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.52, 159.91, 144.72, 138.13, 136.22, 132.75, 129.91, 122.37, 121.05, 116.26, 113.39, 55.31.

(*E*)-3-(4-methylphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4d) [2]



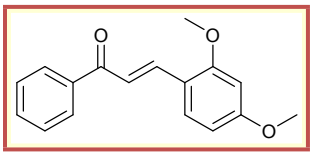
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.02 (m, 2H), 7.80 (d, 1H, J = 15.71 Hz), 7.47-7.59 (m, 6H), 7.23 (d, 2H, J = 7.93 Hz), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.63, 144.91, 141.06, 138.33, 132.62, 132.12, 129.67, 128.55, 128.44, 121.08, 21.51.

(*E*)-3-(4-*tert*-butylphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4e)[4]



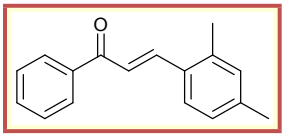
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.80 (d, 1H, J = 15.65 Hz), 7.56-7.60 (m, 3H), 7.43-7.52 (m, 5H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.68, 154.19, 144.83, 138.34, 132.62, 132.10, 128.55, 128.44, 128.29, 125.91, 121.29, 34.92, 31.12.

(*E*)-3-(2,4-dimethoxyphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4f)[5]



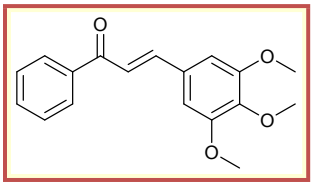
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.06 (d, 1H, J = 15.77 Hz), 7.99-8.01 (m, 2H), 7.46-7.58 (m, 5H), 6.54 (dd, 1H, J = 2.44, 8.55 Hz), 6.48 (d, 1H, J = 15.77 Hz), 3.89 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.93, 162.88, 160.21, 140.33, 138.62, 132.13, 128.29, 120.03, 116.83, 105.28, 98.18, 55.33, 55.27.

(*E*)-3-(2,4-dimethylphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4g)[5]



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.77 (d, 1H, J = 15.65 Hz), 7.55-7.57 (m, 1H), 7.45-7.51 (m, 3H), 7.37-7.41 (m, 2H), 7.17 (d, 1H, J = 7.82 Hz), 2.30 (s, 6H).

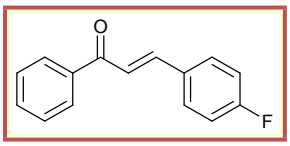
(*E*)-3-(3,4,5-trimethoxyphenyl)-1-phenyl prop-2-en-1-one (Table 2, 4h)[6]



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.02 (m, 2H), 7.72 (d, 1H, J = 15.65 Hz), 7.57-7.61 (m, 1H), 7.49-7.53 (m, 2H), 7.41 (d, 1H, J = 15.65 Hz), 6.87 (s, 2H), 3.92 (s, 6H), 3.90 (s, 3H).

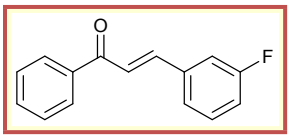
^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.42, 153.32, 144.91, 138.10, 132.63, 130.22, 128.49, 128.36, 121.28, 60.87, 56.07.

(*E*)-3-(4-fluorophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4i)[7]



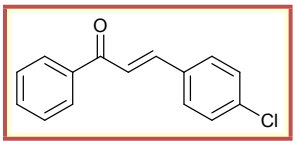
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.78 (d, 1H, J = 15.65 Hz), 7.57-7.66 (m, 3H), 7.44-7.53 (m, 3H), 7.09-7.13 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.18, 163.94 (d, J_{CF} = 251.9 Hz), 143.40, 137.99, 132.77, 130.28 (d, J_{CF} = 8.0 Hz), 128.56, 128.39, 121.61, 116.03 (d, J_{CF} = 21.9 Hz).

(*E*)-3-(3-fluorophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4j)[7]



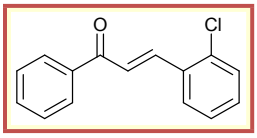
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.76 (d, 1H, J = 15.65 Hz), 7.57-7.65 (m, 1H), 7.44-7.53 (m, 3H), 7.32-7.41 (m, 3H), 7.08-7.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.14, 163.94 (d, J_{CF} = 248.0 Hz), 143.30, 137.92, 137.17 (d, J_{CF} = 6.5 Hz), 133.03, 130.54 (d, J_{CF} = 8.7 Hz), 128.56 (d, J_{CF} = 13.1 Hz), 124.59, 123.17, 117.39 (d, J_{CF} = 21.9 Hz), 114.48 (d, J_{CF} = 21.9 Hz).

(*E*)-3-(4-chlorophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4k)[8]



^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.00-8.02 (m, 2H), 7.76 (d, 1H, J = 15.77 Hz), 7.56-7.61 (m, 3H), 7.48-7.52 (m, 3H), 7.39 (d, 2H, J = 8.43 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.14, 143.23, 137.96, 136.37, 133.32, 132.87, 129.53, 129.19, 128.62, 128.43, 122.41.

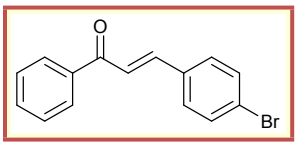
(*E*)-3-(2-chlorophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4l) [8]



^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.18 (d, 1H, J = 15.77 Hz), 8.01-8.03 (m, 2H), 7.74-7.76 (m, 1H), 7.58-7.61 (m, 1H), 7.47-7.52 (m, 3H), 7.43-7.45 (m, 1H), 7.30.7.35 (m, 2H). ^{13}C NMR

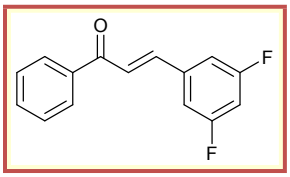
(125 MHz, $CDCl_3$): δ (ppm) = 190.32, 140.52, 137.84, 135.40, 133.17, 132.87, 131.10, 130.22, 128.59, 128.54, 127.70, 127.02, 124.71.

(*E*)-3-(4-bromophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4m) [8]



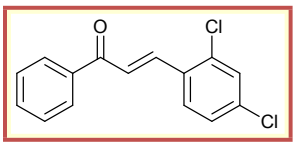
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.00-8.02 (m, 2H), 7.74 (d, 1H, *J* = 15.71 Hz), 7.57-7.61 (m, 1H), 7.49-7.56 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.11, 143.27, 137.91, 133.72, 132.87, 132.12, 129.72, 128.60, 128.42, 124.72, 122.47.

(*E*)-3-(3,5-difluorophenyl)-1-pheyl prop-2-en-1-one (Table 2, 4n)



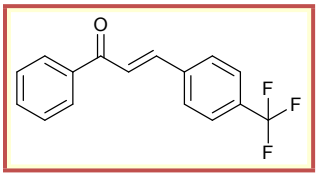
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.00-8.03 (m, 2H), 7.69 (d, 1H, *J* = 15.71 Hz), 7.59-7.63 (m, 1H), 7.49-7.54 (m, 3H), 7.12-7.17 (m, 2H), 6.84-6.88 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 189.71, 164.18 (q, *J* = 12.7 Hz), 141.89, 138.11 (t, *J* = 9.0 Hz), 137.60, 133.16, 128.71, 128.50, 124.19, 111.01, 110.81, 105.52 (t, *J* = 25.43). IR *v* max cm^{-1}: 1657, 1602, 1575, 1484, 1463, 1449, 1332, 1289, 1243, 1205, 1179, 1114, 1058, 1031, 978, 775 cm^{-1}. HRMS (EI): *m/z* calculated for $C_{15}H_{10}F_2O$ $[M]^+$ 244.06997, found: 244.06991.

(*E*)-3-(2,4-dichlorophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4o) [9]



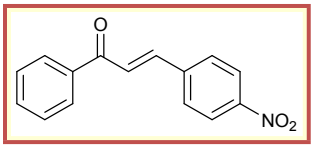
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.10 (d, 1H, *J* = 15.77 Hz), 8.00-8.02 (m, 2H), 7.69 (d, 1H, *J* = 8.43 Hz), 7.58-7.62 (m, 1H), 7.44-7.54 (m, 4H), 7.30 (dd, 1H, *J* = 2.07, 8.06 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 190.11, 139.31, 136.09, 133.12, 130.15, 128.73, 128.61, 124.97.

(*E*)-3-(4-(trifluoromethyl)phenyl)-1-phenyl prop-2-en-1-one (Table 2, 4p)[11]



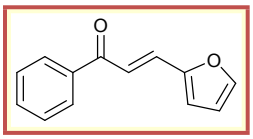
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.02-8.04 (m, 2H), 7.81 (d, 1H, J = 15.71 Hz), 7.75 (d, 2H, J = 8.19 Hz), 7.68 (d, 2H, J = 8.19 Hz), 7.59-7.64 (m, 2H), 7.50-7.58 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.99, 142.67, 138.23, 137.75, 133.09, 131.85 (q, J = 33.0 Hz), 128.70, 128.52, 128.46, 125.87 (d, J = 3.68 Hz), 124.20, 123.78 (q, J = 272.88 Hz).

(*E*)-3-(4-nitrophenyl)-1-phenyl prop-2-en-1-one (Table 2, 4q) [8]



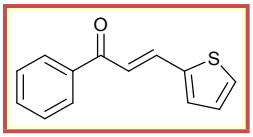
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.27-8.29 (m, 2H), 8.03-8.05 (m, 2H), 7.78-7.84 (m, 3H), 7.61-7.66 (m, 2H), 7.52-7.55 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 188.81, 147.67, 140.66, 140.36, 136.71, 132.60, 128.43, 128.06, 127.84, 125.11, 123.36.

(*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one (Table 2, 4r)[10]



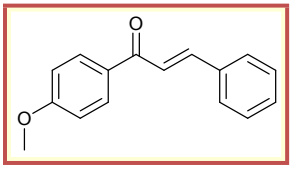
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.00-8.04 (m, 2H), 7.44-7.61 (m, 6H), 6.72 (d, 1H, J = 3.35 Hz), 6.52 (dd, 1H, J = 1.83, 3.35 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.79, 151.62, 144.87, 138.09, 132.70, 130.62, 128.55, 128.36, 119.27, 116.16, 112.62.

(*E*)-3-(thiop-2-yl)-1-phenylprop-2-en-1-one (Table 2, 4s)[10]



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.99-8.01 (m, 2H), 7.95 (d, 1H, J = 15.41Hz), 7.56-7.60 (m, 1H), 7.48-7.52 (m, 2H), 7.43 (d, 1H, J = 5.03 Hz), 7.37 (d, 1H, J = 3.66 Hz), 7.34 (d, 1H, J = 15.41 Hz), 7.10 (dd, 1H, J = 3.50, 5.03 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.80, 140.31, 138.04, 137.15, 132.71, 132.04, 128.78, 128.56, 128.31, 120.70.

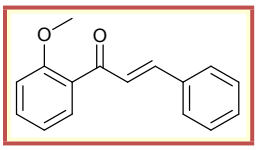
(*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (Table 3, 4aa)[12]



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.03-8.07 (m, 2H), 7.81 (d, 1H, J = 15.65 Hz), 7.64-7.66 (m, 2H), 7.55 (d, 1H, J = 15.65 Hz), 7.41-7.44 (m, 3H), 6.97-7.01 (m, 2H), 3.89 (s, 3H). ^{13}C

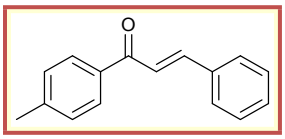
NMR (75 MHz, $CDCl_3$): δ (ppm) = 188.67, 163.38, 143.91, 135.03, 131.05, 130.77, 130.27, 128.86, 128.30, 121.84, 113.80, 55.45.

(*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one (Table 3, 4ab)[16]



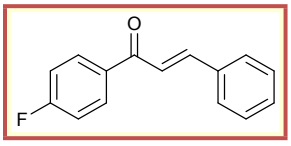
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.57-7.64 (m, 4H), 7.45-7.50 (m, 1H), 7.35-7.40 (m, 4H), 6.99-7.06 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 192.94, 158.04, 143.18, 135.06, 132.80, 130.27, 130.17, 129.21, 128.80, 128.33, 127.02, 120.67, 111.58, 55.69. IR *v* max cm^{-1}: 1665, 1609, 1588, 1449, 1283, 1267, 1229, 1215, 1113, 1038, 1022, 990, 847, 698, 681, 653, 561, 489 cm^{-1}. HRMS (EI): *m/z* calculated for $C_{16}H_{14}O_2$ $[M]^+$ 238.09938, found: 238.09887.

(*E*)-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (Table 3, 4ac)[5]



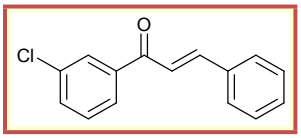
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.92-7.95 (m, 2H), 7.80 (d, 1H, *J* = 15.65 Hz), 7.62-7.65 (m, 2H), 7.53 (d, 1H, *J* = 15.65 Hz), 7.40-7.44 (m, 3H), 7.30 (d, 3H, *J* = 7.94 Hz), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.90, 144.29, 143.55, 135.54, 134.91, 130.33, 129.24, 128.84, 128.57, 128.32, 122.01, 21.60.

(*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (Table 3, 4ad)[12]



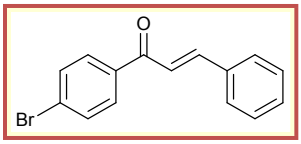
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.04-8.08 (m, 2H), 7.82 (d, 1H, *J* = 15.71 Hz), 7.63-7.66 (m, 2H), 7.50 (d, 1H, *J* = 15.71 Hz), 7.41-7.43 (m, 3H), 7.15-7.19 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 188.80, 165.88 (d, *J* = 254.5 Hz), 145.05, 134.67, 134.55, 131.12 (d, *J* = 8.7 Hz), 130.68, 129.02, 128.49, 121.54, 115.76 (d, *J* = 254.5 Hz).

(*E*)-1-(3-chlorophenyl)-3-phenylprop-2-en-1-one (Table 3, 4ae)[13]



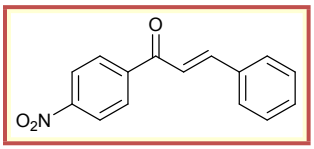
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.98-7.99 (m, 1H), 7.88-7.91 (m, 1H), 7.83 (d, 1H, J = 15.65 Hz), 7.64-7.67 (m, 2H), 7.54-7.57 (m, 1H), 7.42-7.49 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$-): δ (ppm) = 189.01, 145.60, 139.72, 134.86, 134.54, 132.61, 130.76, 129.89, 128.95, 128.50, 126.47, 121.37.

(*E*)-1-(4-bromophenyl)-3-phenylprop-2-en-1-one (Table 3, 4af)[5]



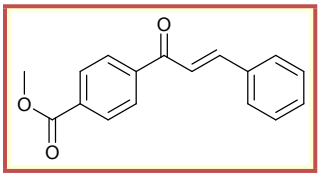
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.87-7.90 (m, 2H), 7.82 (d, 1H, J = 15.56 Hz), 7.63-7.66 (m, 4H), 7.48 (d, 1H, J = 15.56 Hz), 7.42-7.44 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.23, 145.30, 136.82, 134.59, 131.84, 130.67, 129.94, 128.92, 128.44, 127.81, 121.36.

(*E*)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (Table 3, 4ag)[8]



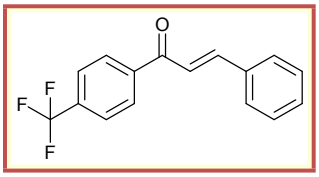
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.34-8.37 (m, 2H), 8.14-8.16 (m, 2H), 7.85 (d, 1H, J = 15.71 Hz), 7.65-7.68 (m, 2H), 7.41-7.47 (m, 4H).

Methyl 4-cinnamoylbenzoate (Table 3, 4ah)[12]



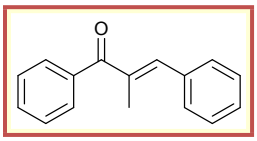
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16-8.18 (m, 2H), 8.04-8.07 (m, 2H), 7.83 (d, 1H, J = 15.65 Hz), 7.64-7.67 (m, 2H), 7.51 (d, 1H, J = 15.65 Hz), 7.43-7.45 (m, 3H), 3.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 189.99, 166.23, 145.72, 134.49, 133.44, 130.79, 129.77, 128.96, 128.52, 128.29, 121.69, 52.39.

(*E*)-1-(4-(trifluoromethyl)phenyl)-3-phenylprop-2-en-1-one (Table 3, 4ai)[10]



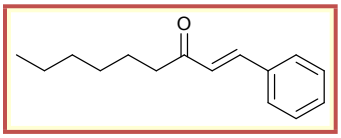
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.10 (d, 2H, J = 8.08 Hz), 7.83 (d, 1H, J = 15.71 Hz), 7.77 (d, 2H, J = 8.08 Hz), 7.64-7.67 (m, 2H), 7.49 (d, 1H, J = 15.71 Hz), 7.43-7.46 (m, 3H).

(*E*)-2-methyl-1,3-diphenylprop-2-en-1-one (Table 3, 4aj)[14]



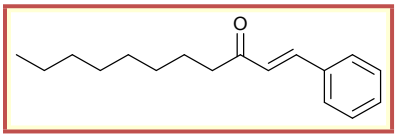
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.73-7.76 (m, 2H), 7.52-7.55 (m, 1H), 7.40.7.47 (m, 6H), 7.31-7.35 (m, 1H), 7.18-7.19 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 199.39, 142.17, 138.37, 136.73, 135.68, 131.68, 131.58, 129.60, 129.40, 128.45, 128.38, 128.12, 14.34.

(*E*)-1-Phenyl-1-nonen-3-one (Table 3, 4ak)[15]



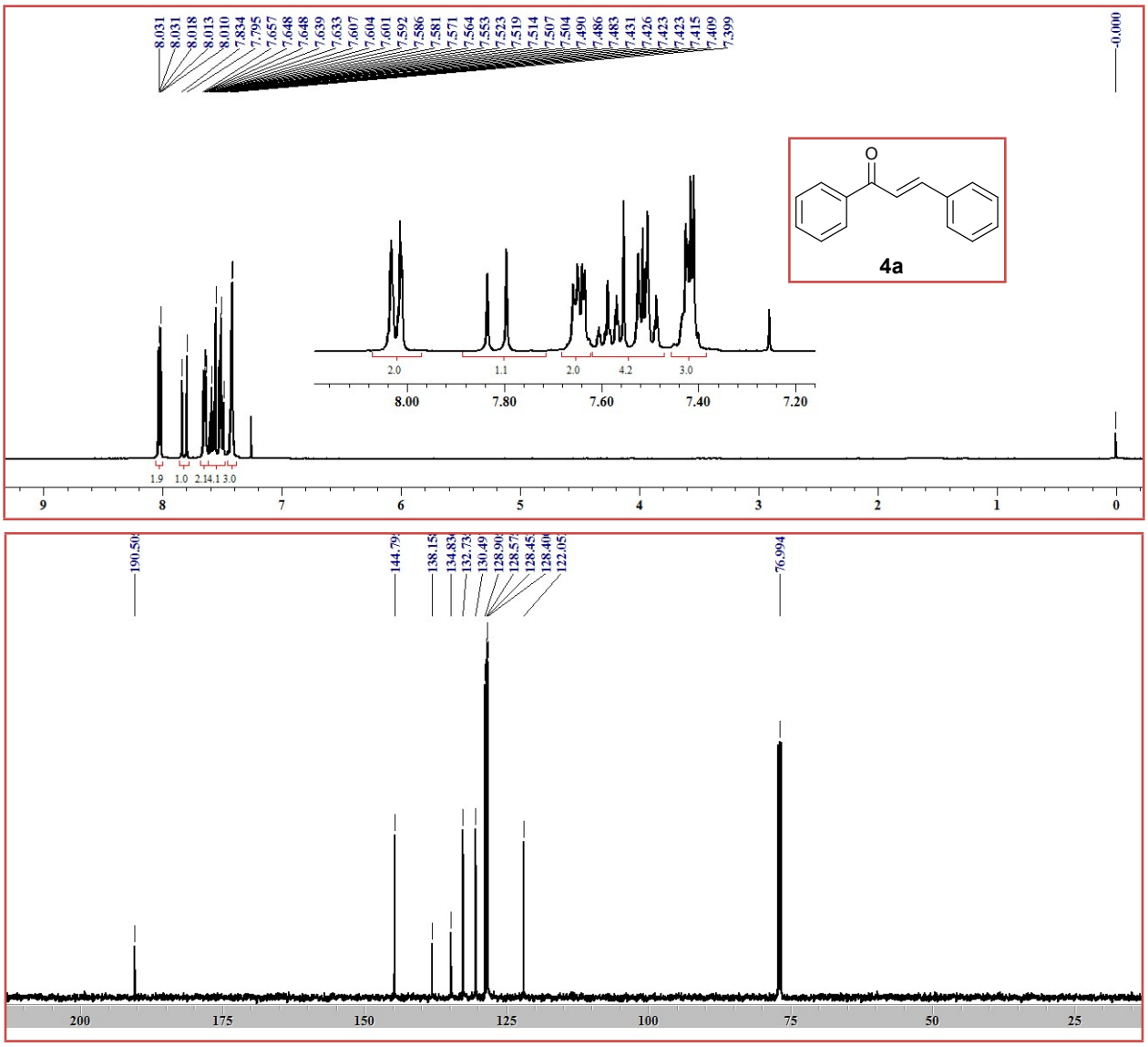
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.53-7.57 (m, 3H), 7.37-7.40 (m, 3H), 6.74 (d, 1H, J = 16.17 Hz), 2.66 (t, 2H, J = 7.47 Hz), 1.64-1.71 (m, 2H), 1.29-1.37 (m, 6H), 0.89 (t, 3H, J = 6.71 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 200.62, 142.21, 134.54, 130.29, 128.85, 128.16, 126.20, 40.91, 31.59, 28.95, 24.29, 22.46, 13.99.

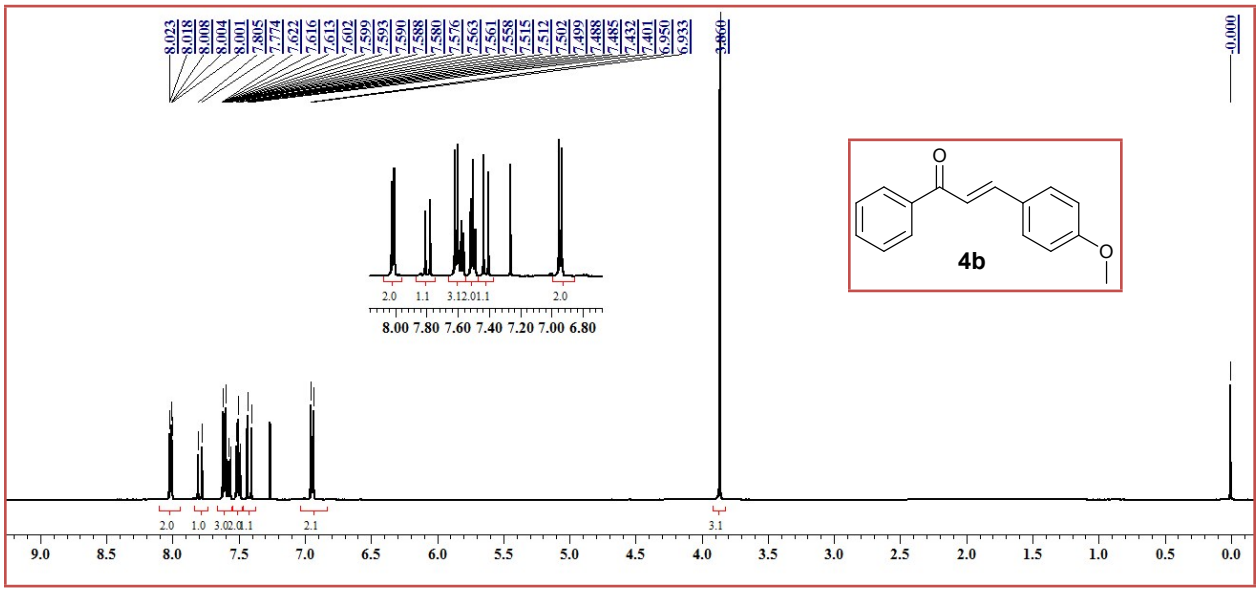
(*E*)-1-phenyl-1-undecen-3-one (Table 3, 4al)[15]



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.53-7.57 (m, 3H), 7.37-7.41 (m, 3H), 6.74 (d, 1H, J = 16.32Hz), 2.66 (t, 2H, J = 7.47 Hz), 1.64-1.70 (m, 2H), 1.26-1.35 (m, 10H), 0.86-0.89 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 200.62, 142.21, 134.54, 130.29, 128.85, 128.17, 126.21, 40.92, 31.65, 29.77, 29.25, 29.07, 24.34, 22.57, 14.02.

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

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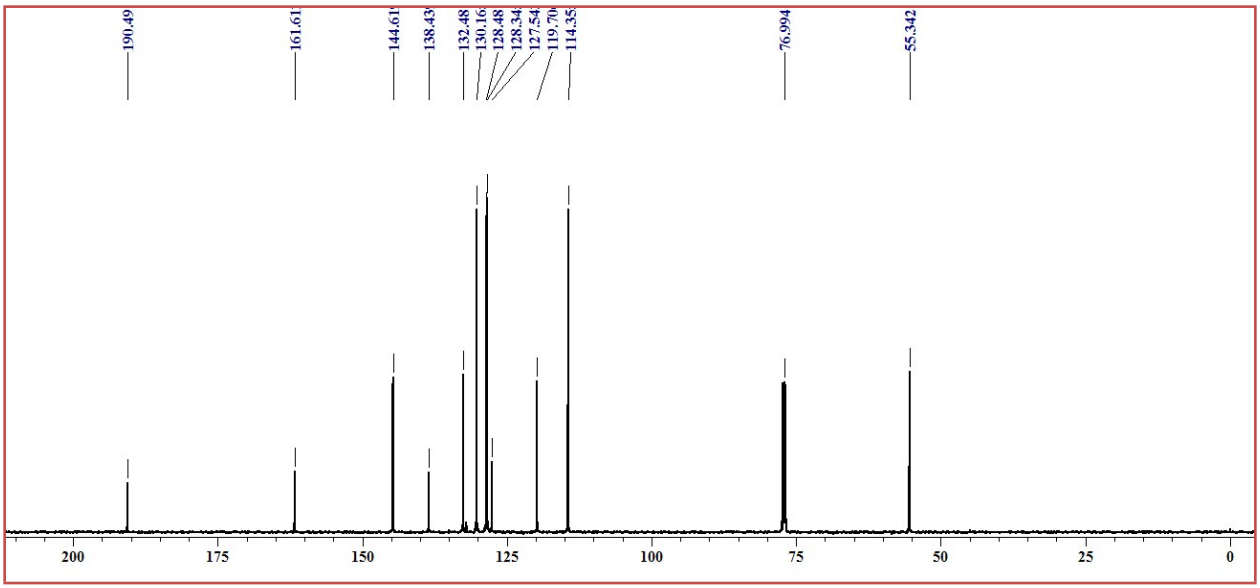
7.593
7.590
7.588
7.580
7.576
7.563
7.561
7.558
7.515
7.512
7.502
7.499
7.488
7.485
7.432
7.401
6.950
6.933
3.860
0.000
2.0 1.1 3.1 2.0 1.1 2.0
8.00 7.80 7.60 7.40 7.20 7.00 6.80
4b
2.0 1.0 3.0 2.0 1.1 2.1 3.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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128.48
128.34
127.54
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114.35
76.994
55.342
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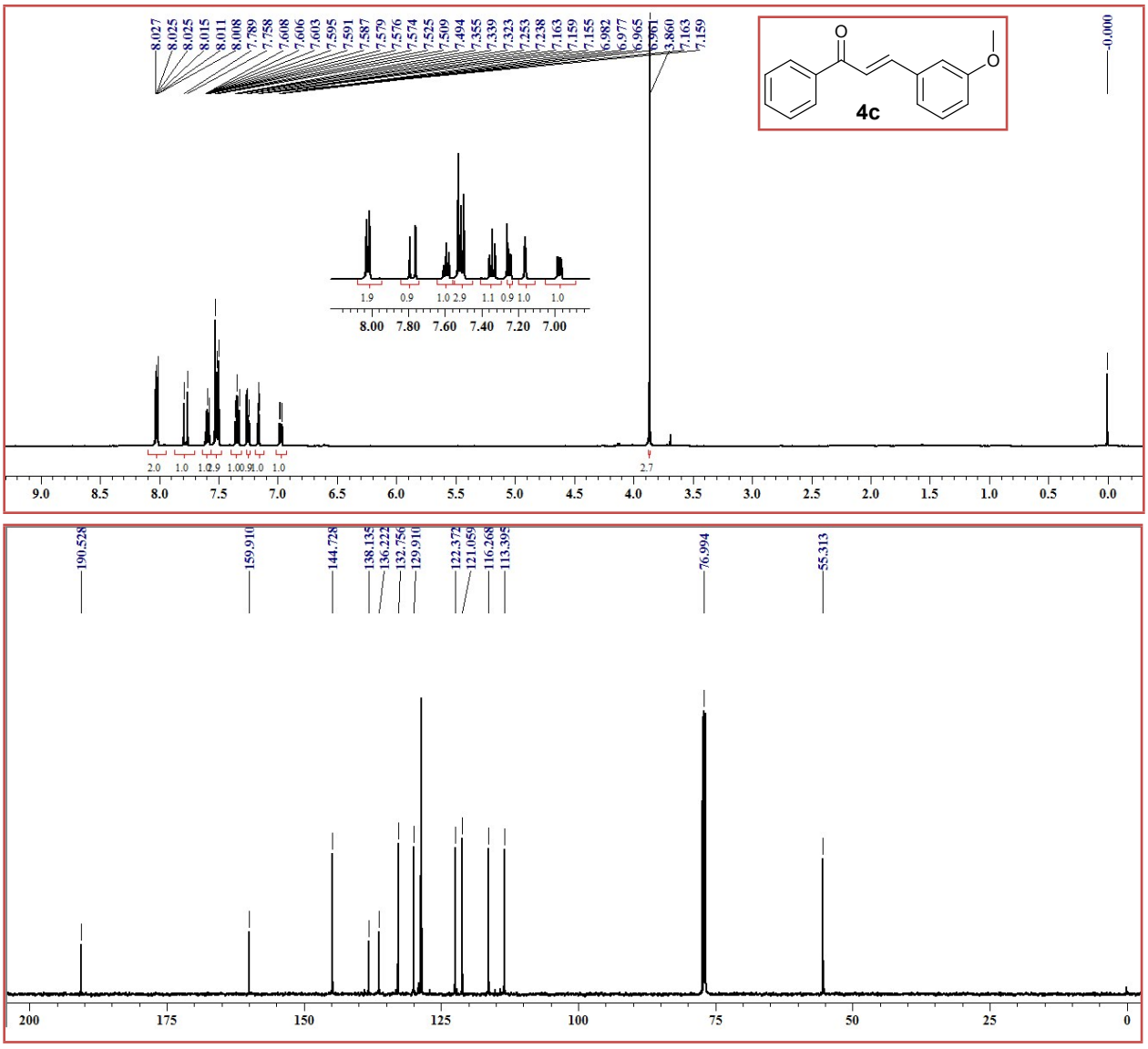
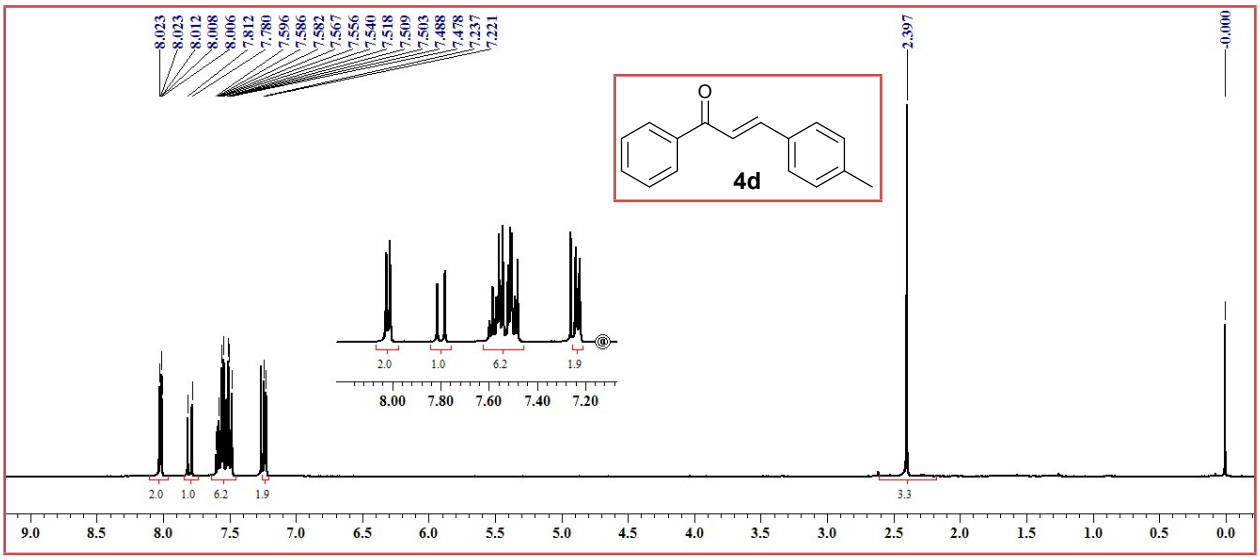
.


4c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7.509
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7.488
7.478
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7.221
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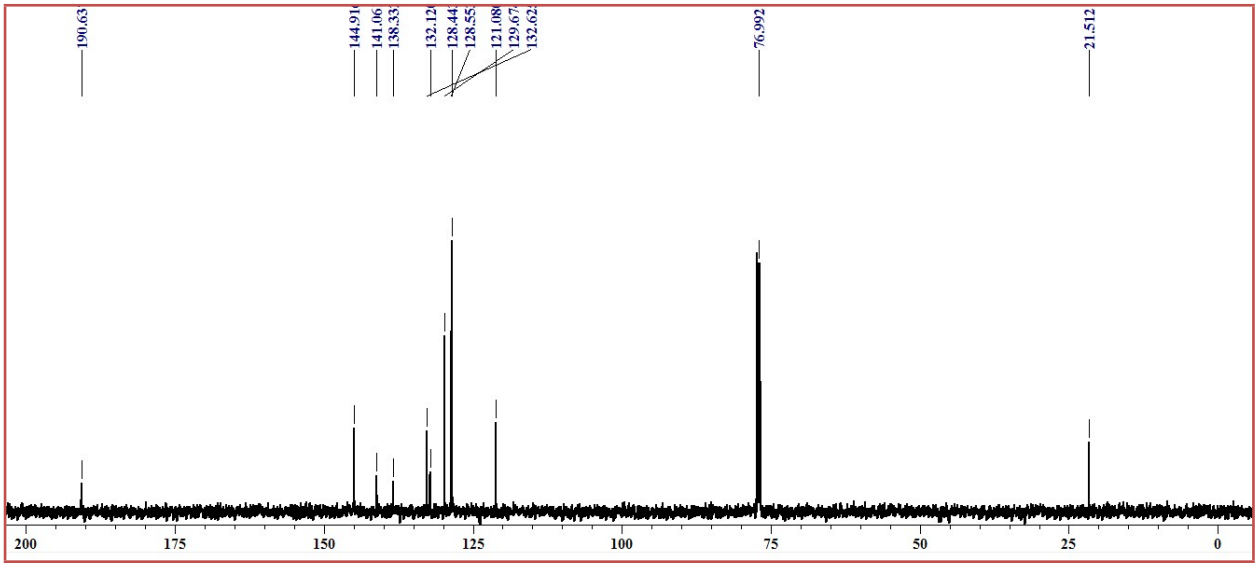
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125
100
75
50
25
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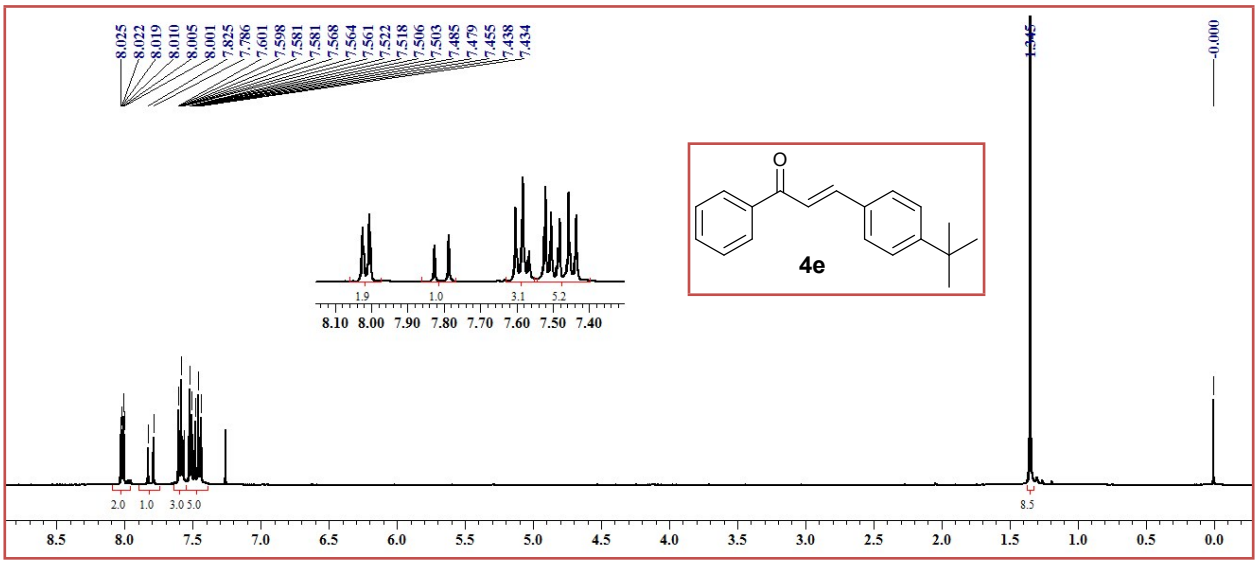
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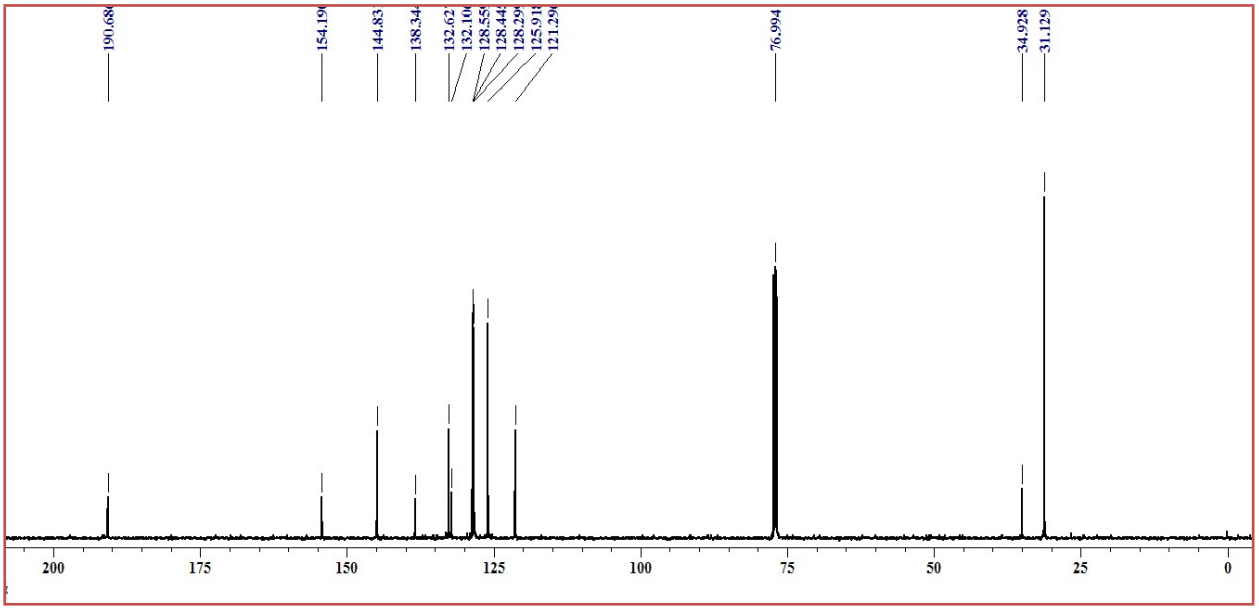
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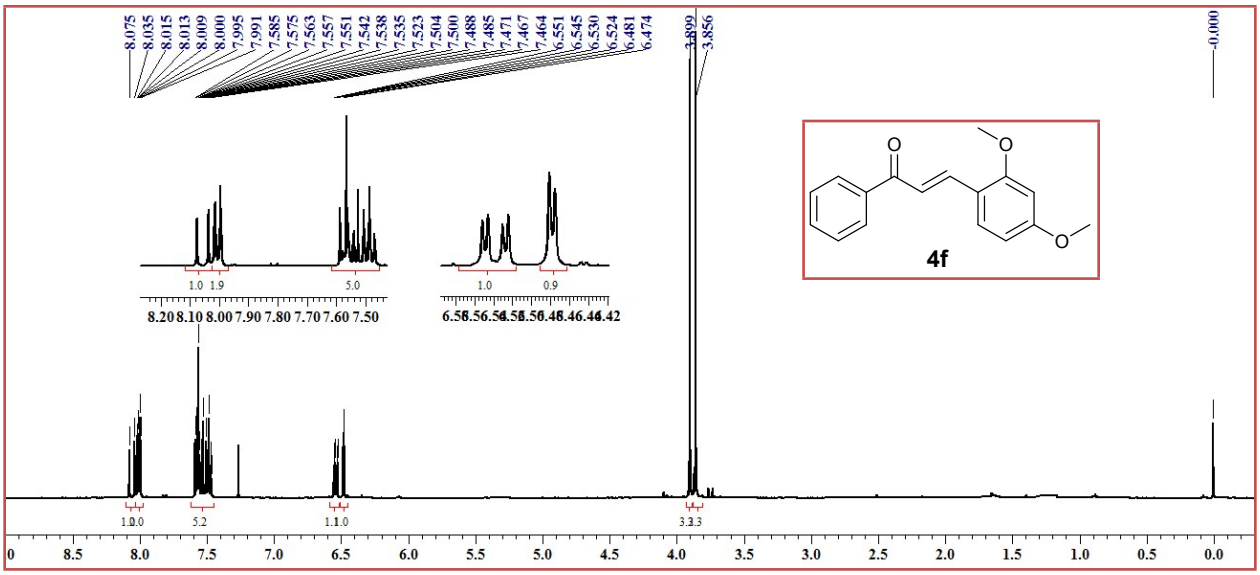
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7.523
7.504
7.500
7.488
7.485
7.471
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7.464
6.551
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1.1.0
3.3.3
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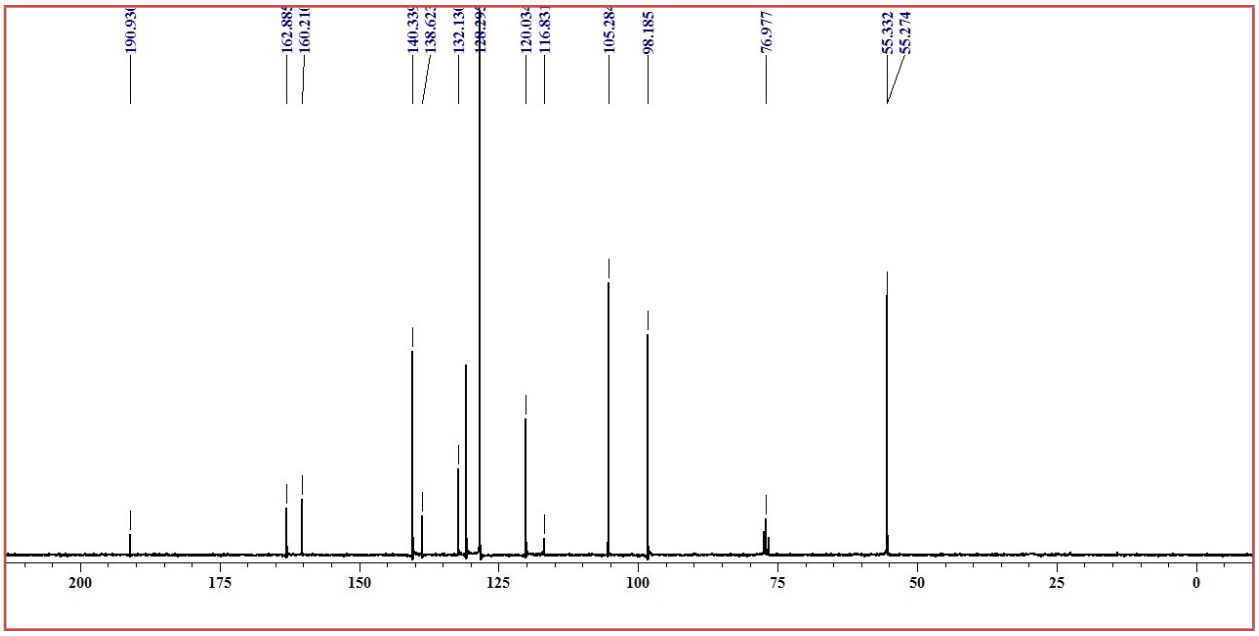
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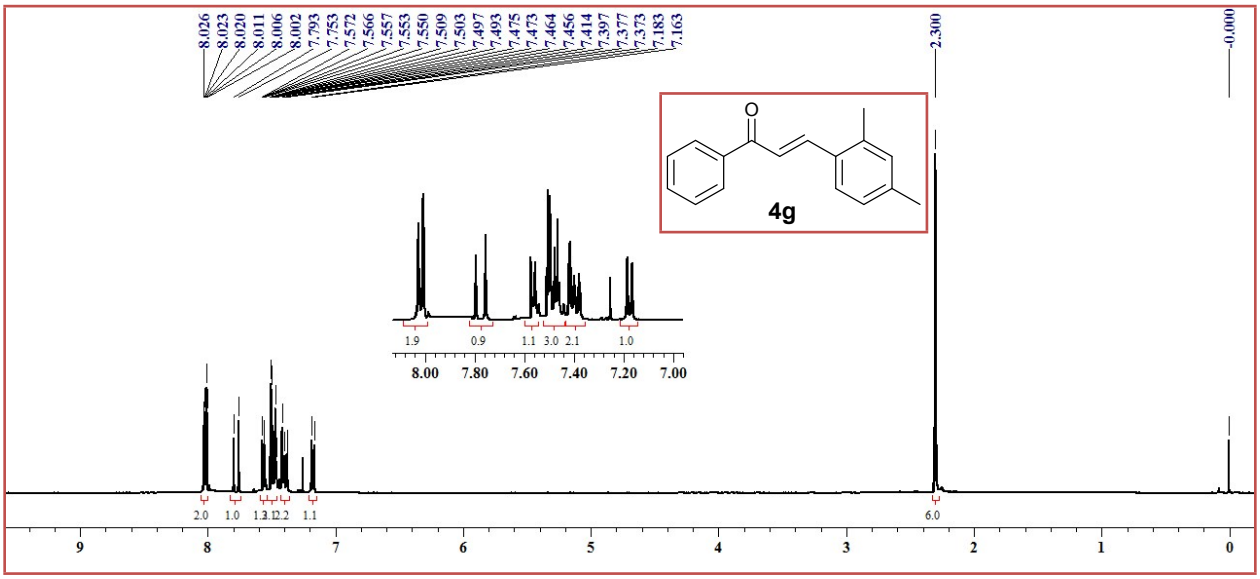
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7.163
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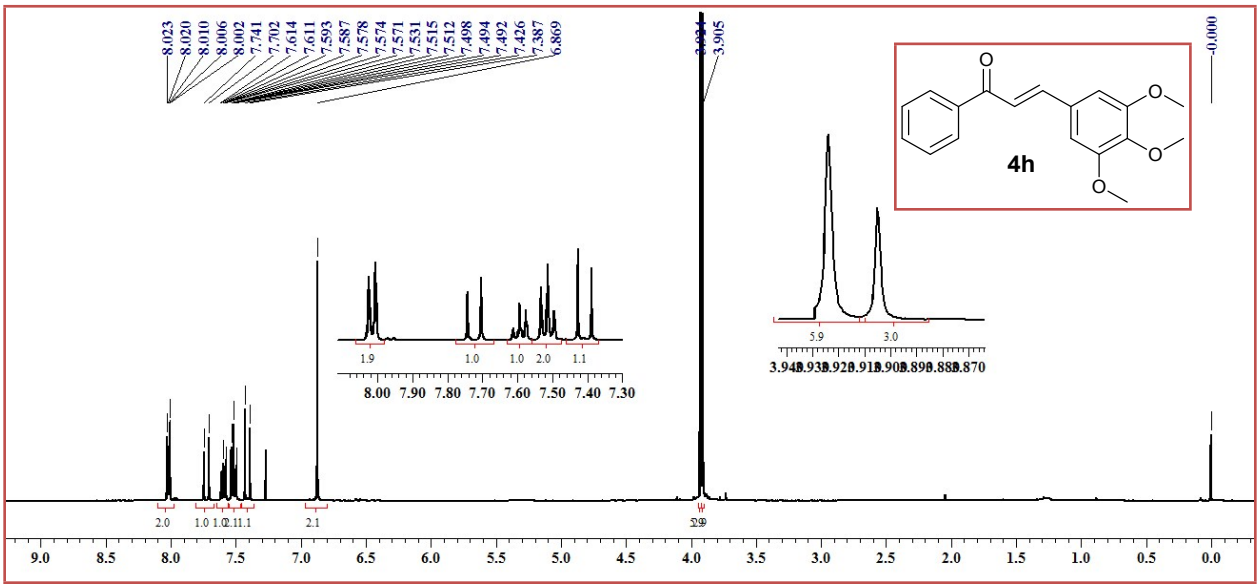
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1.0
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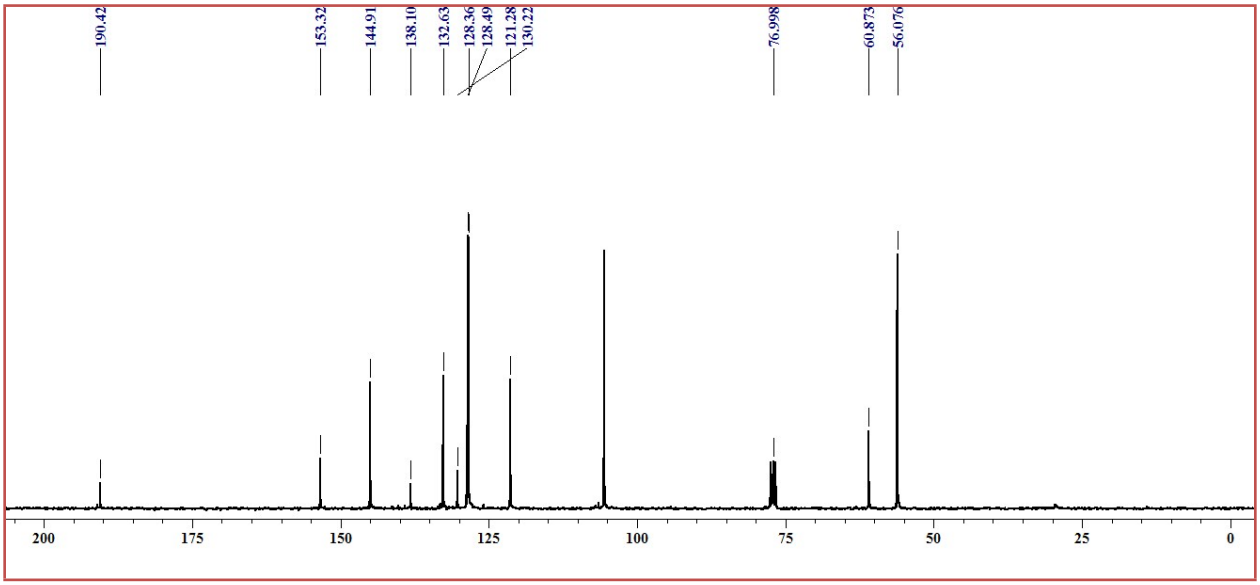
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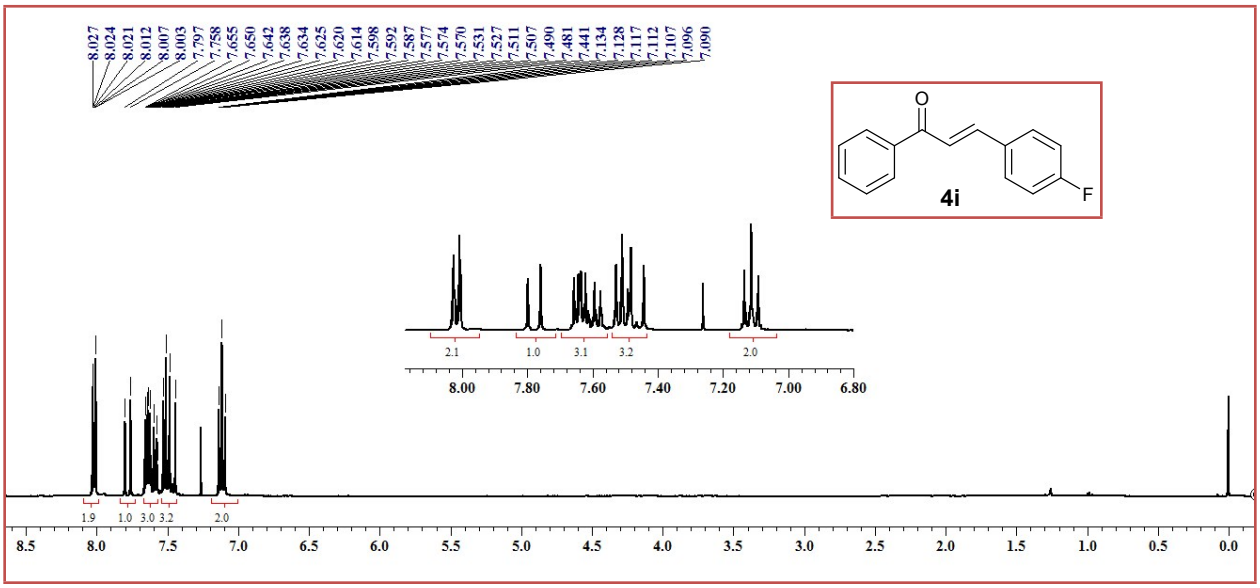
50
25
0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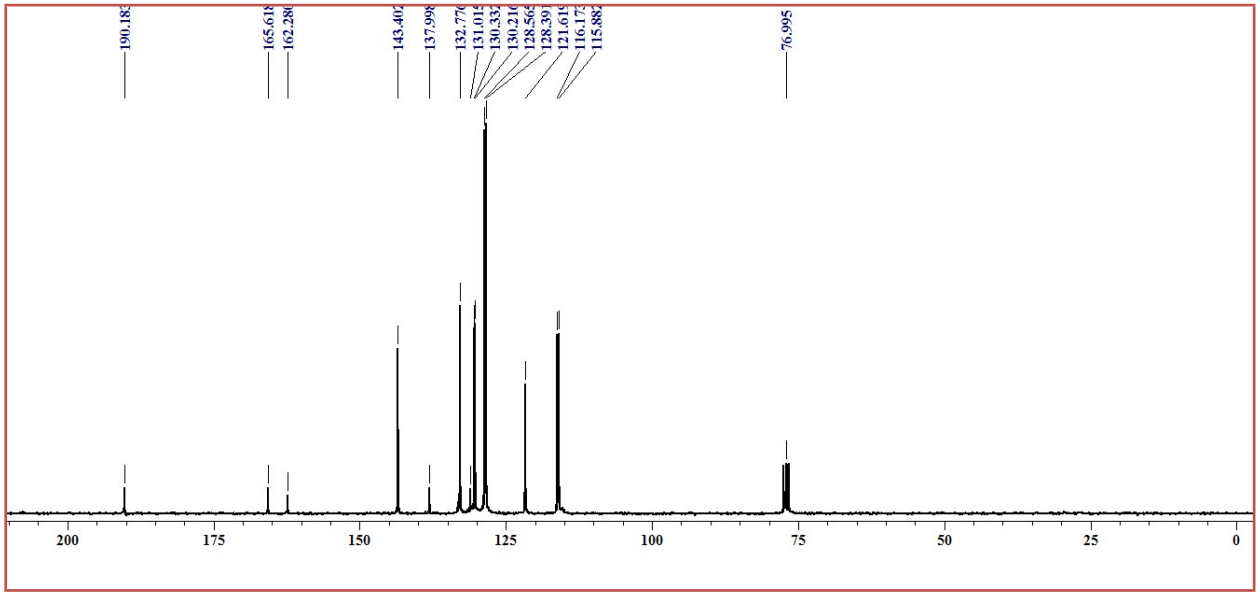
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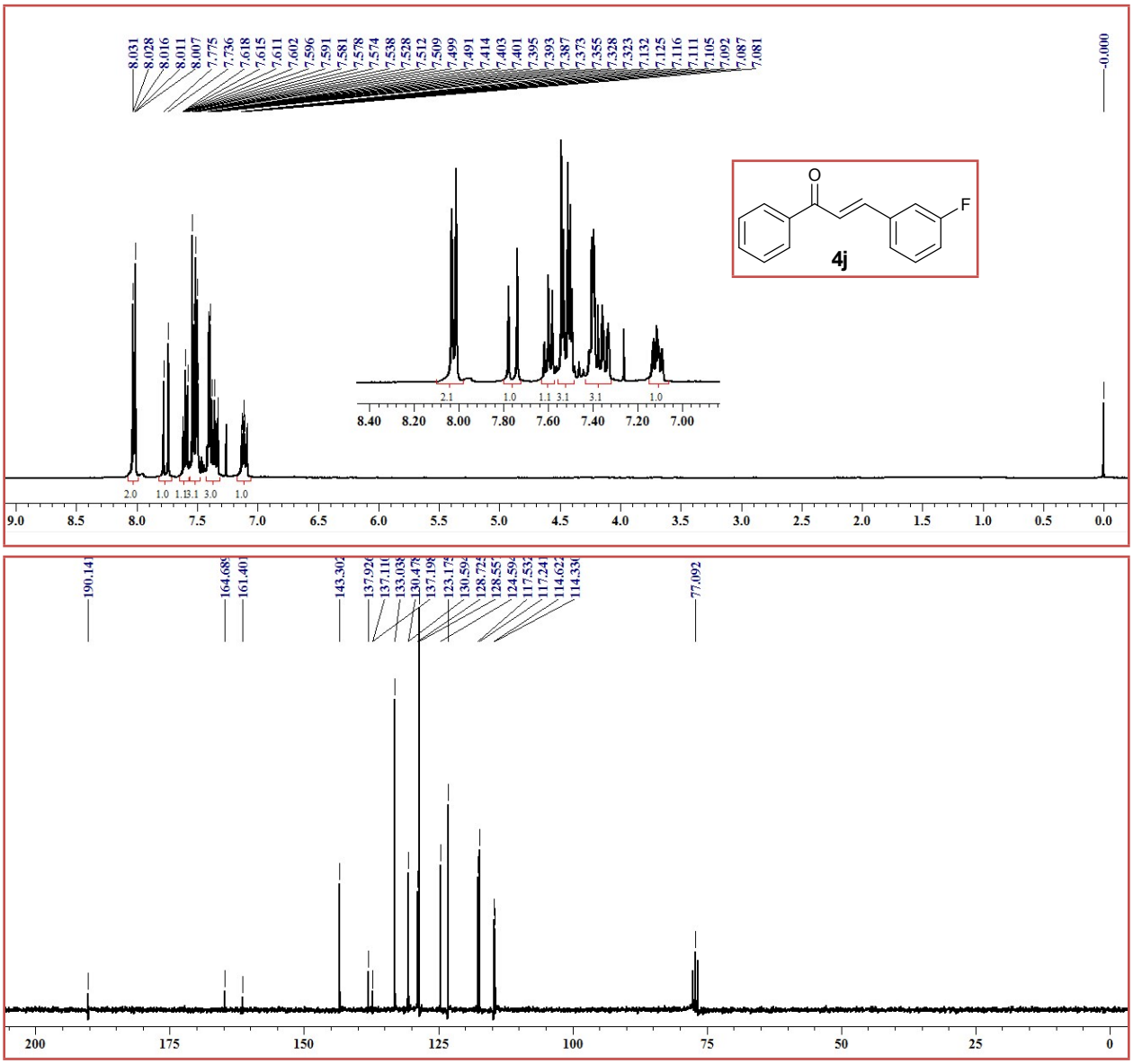
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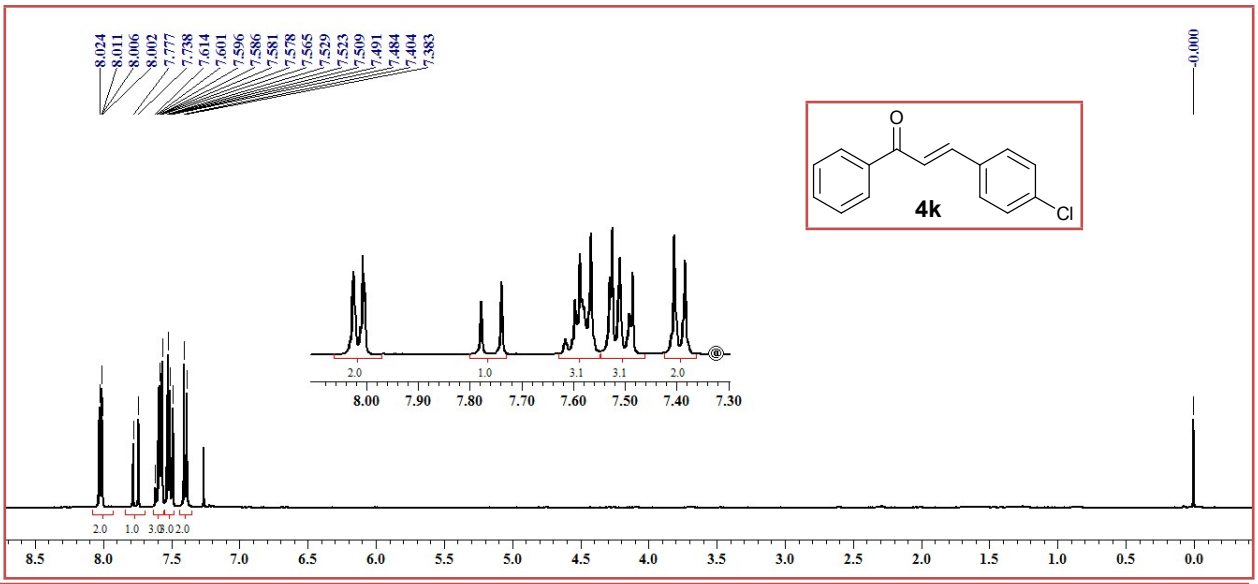
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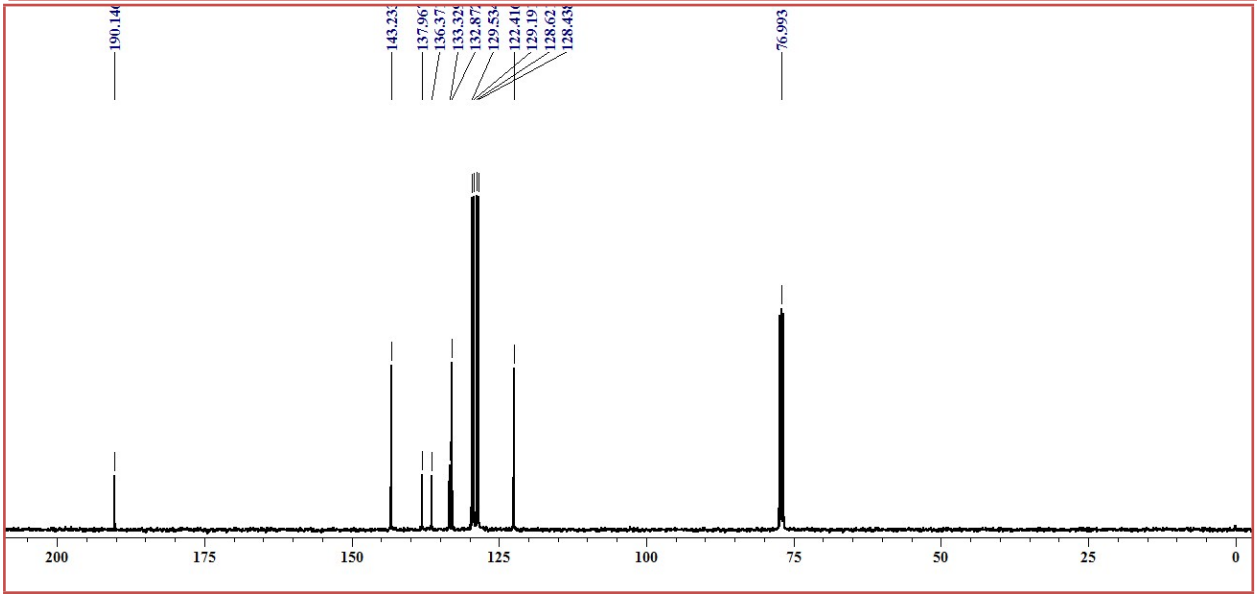
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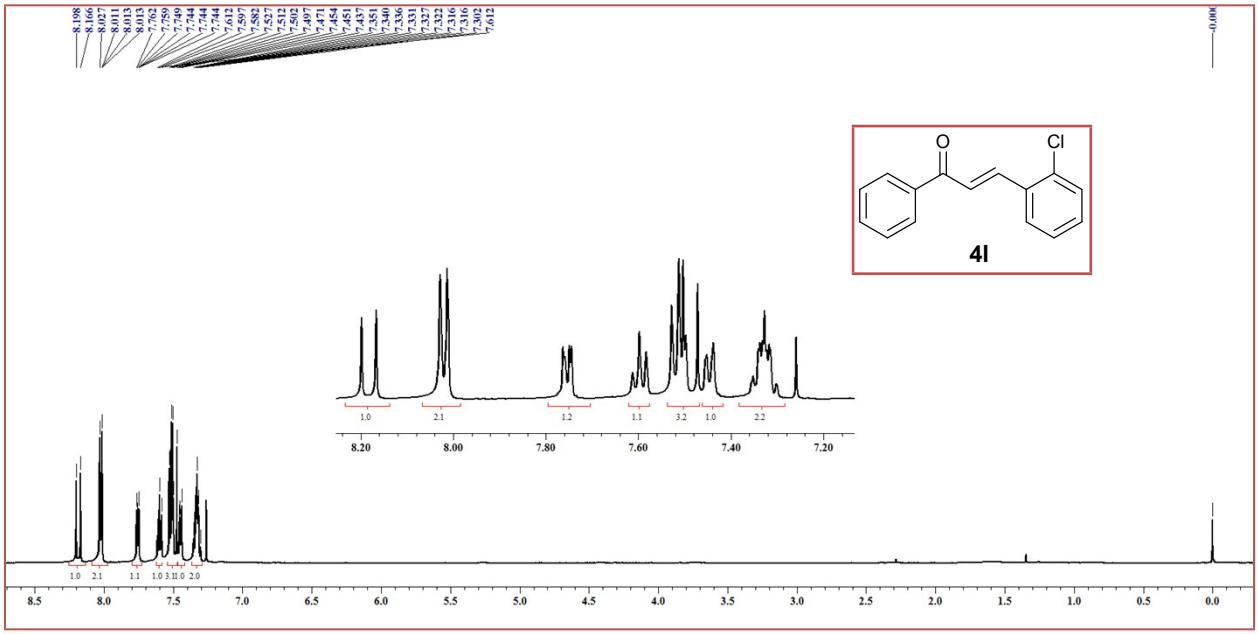
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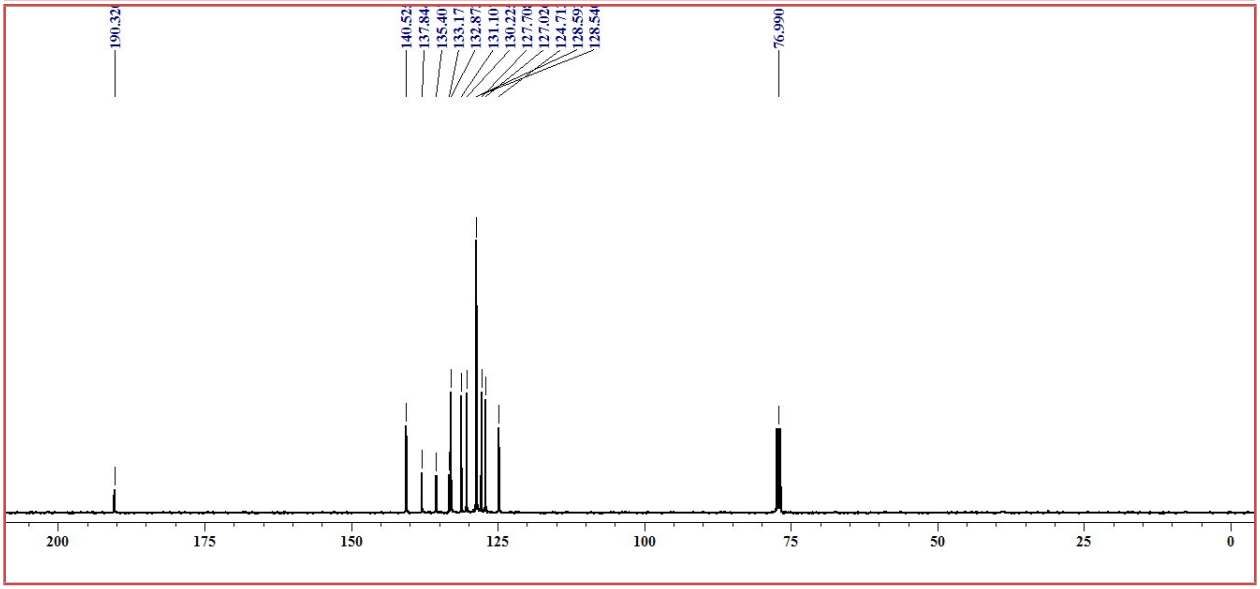

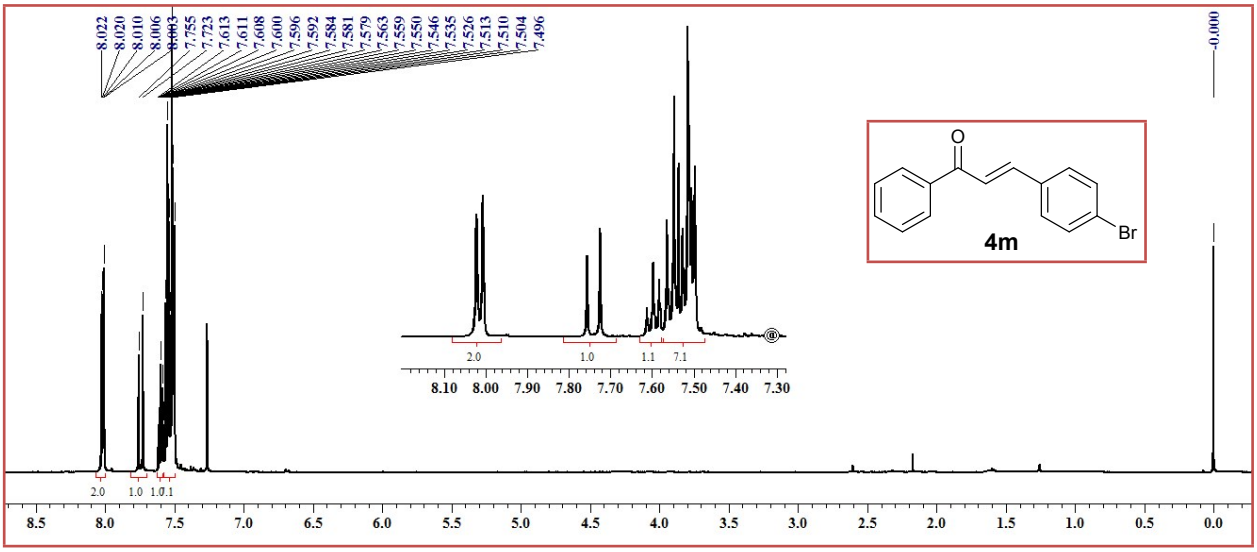
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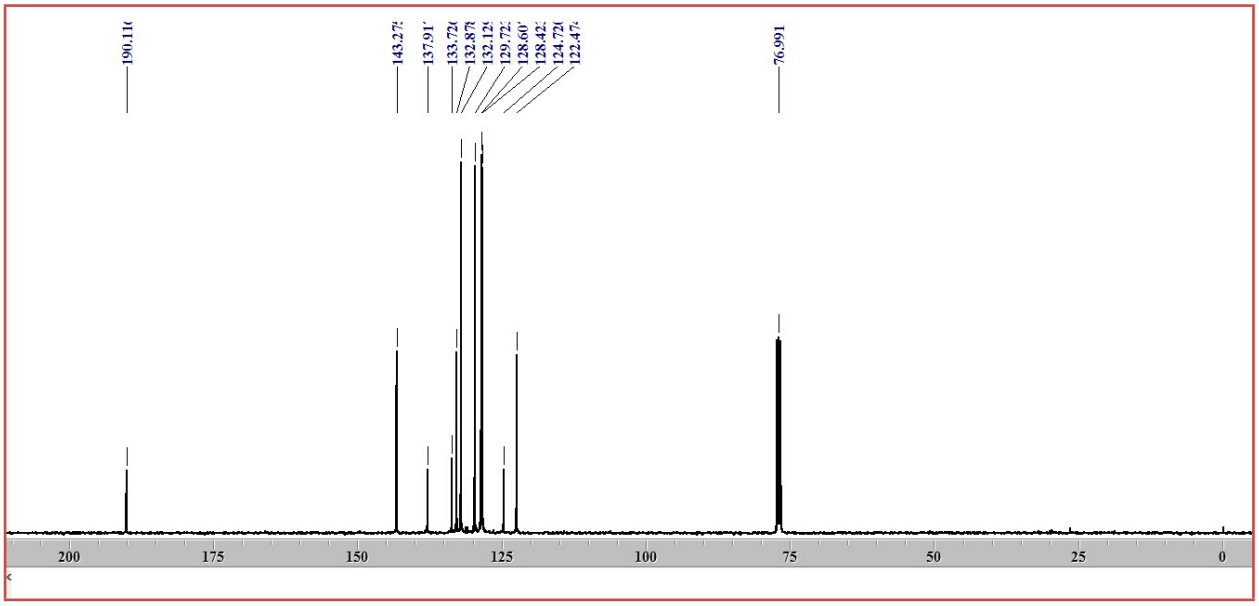
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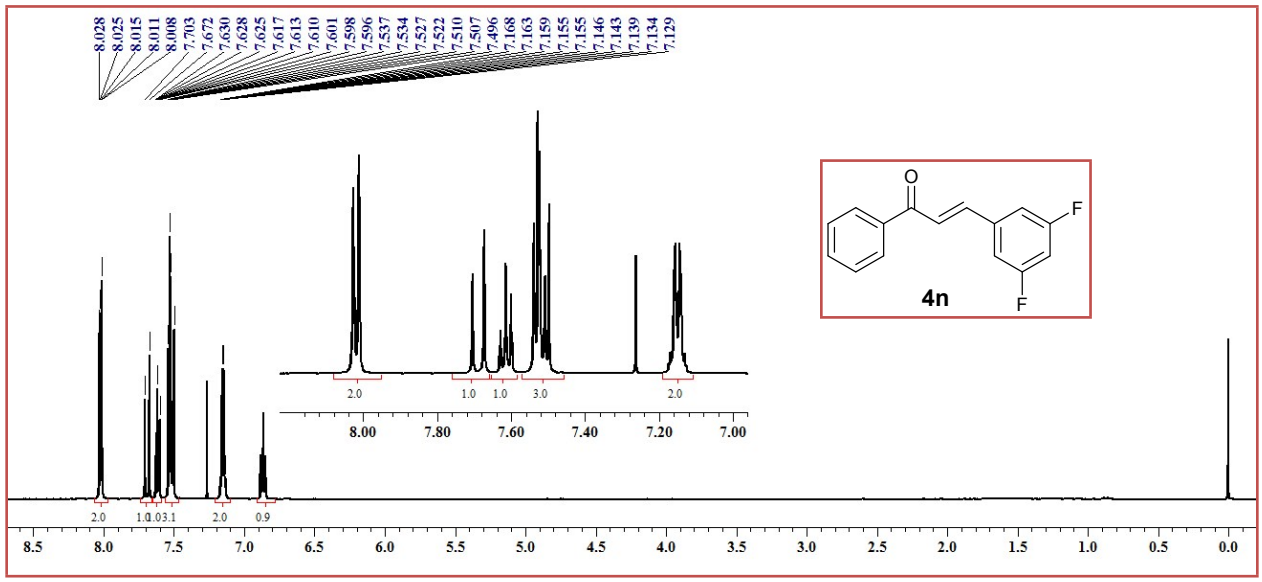
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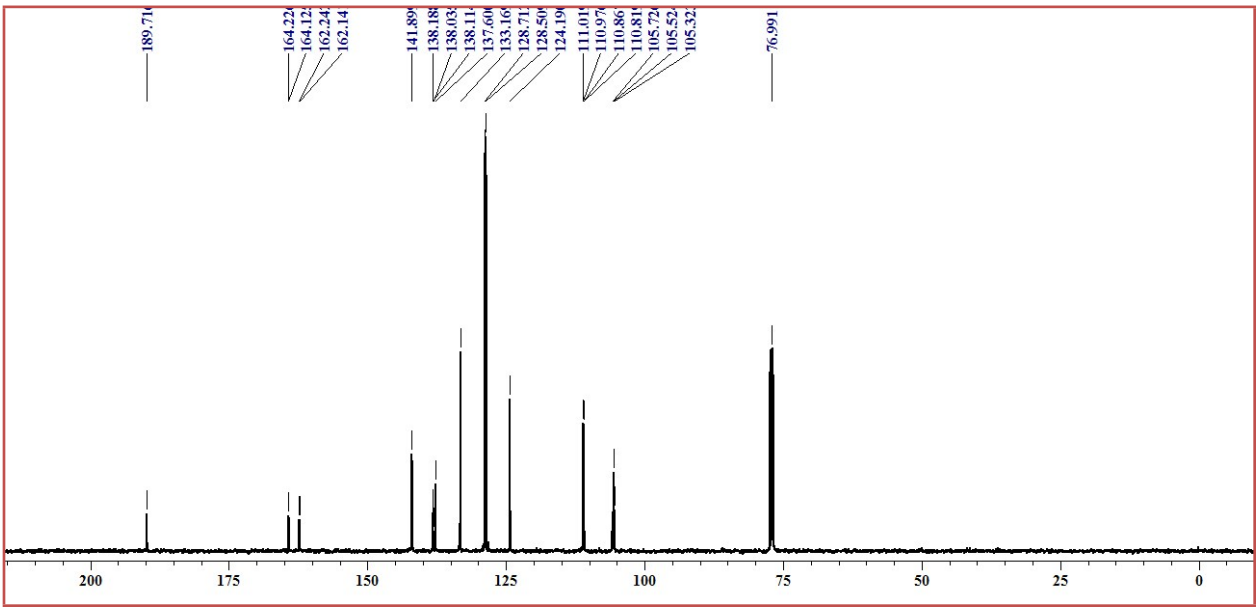
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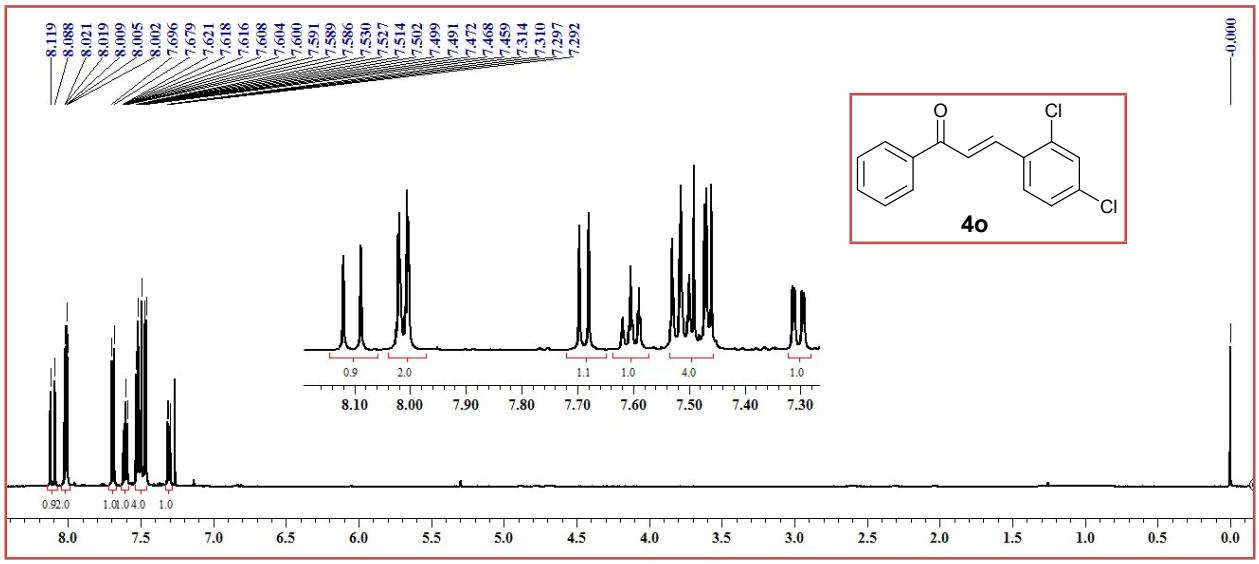
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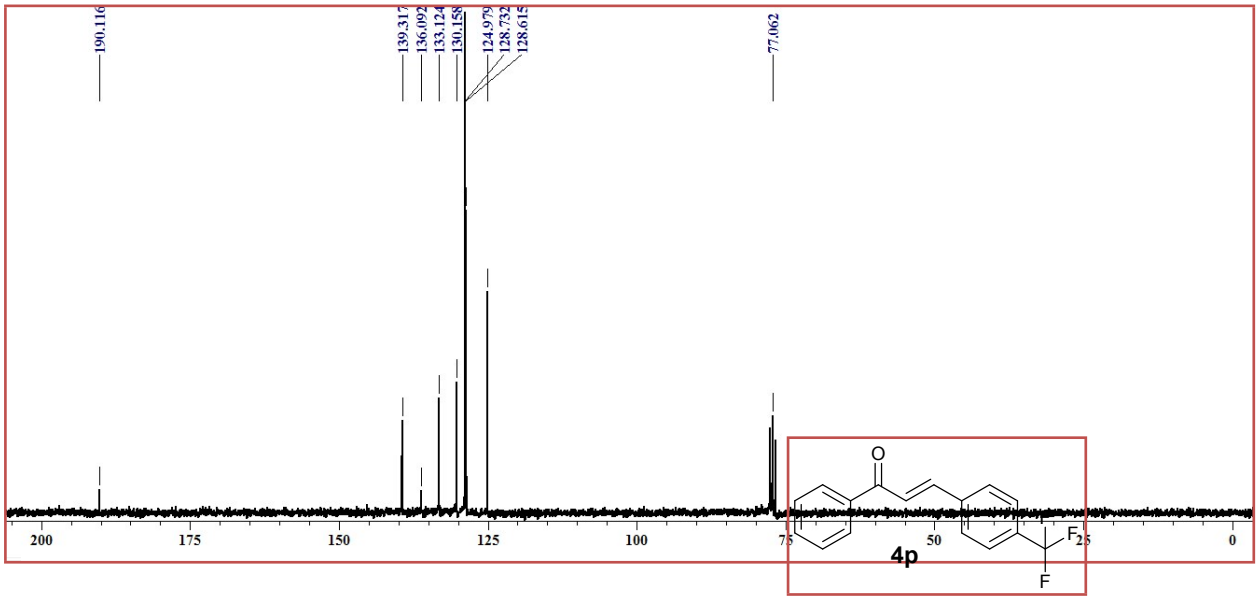
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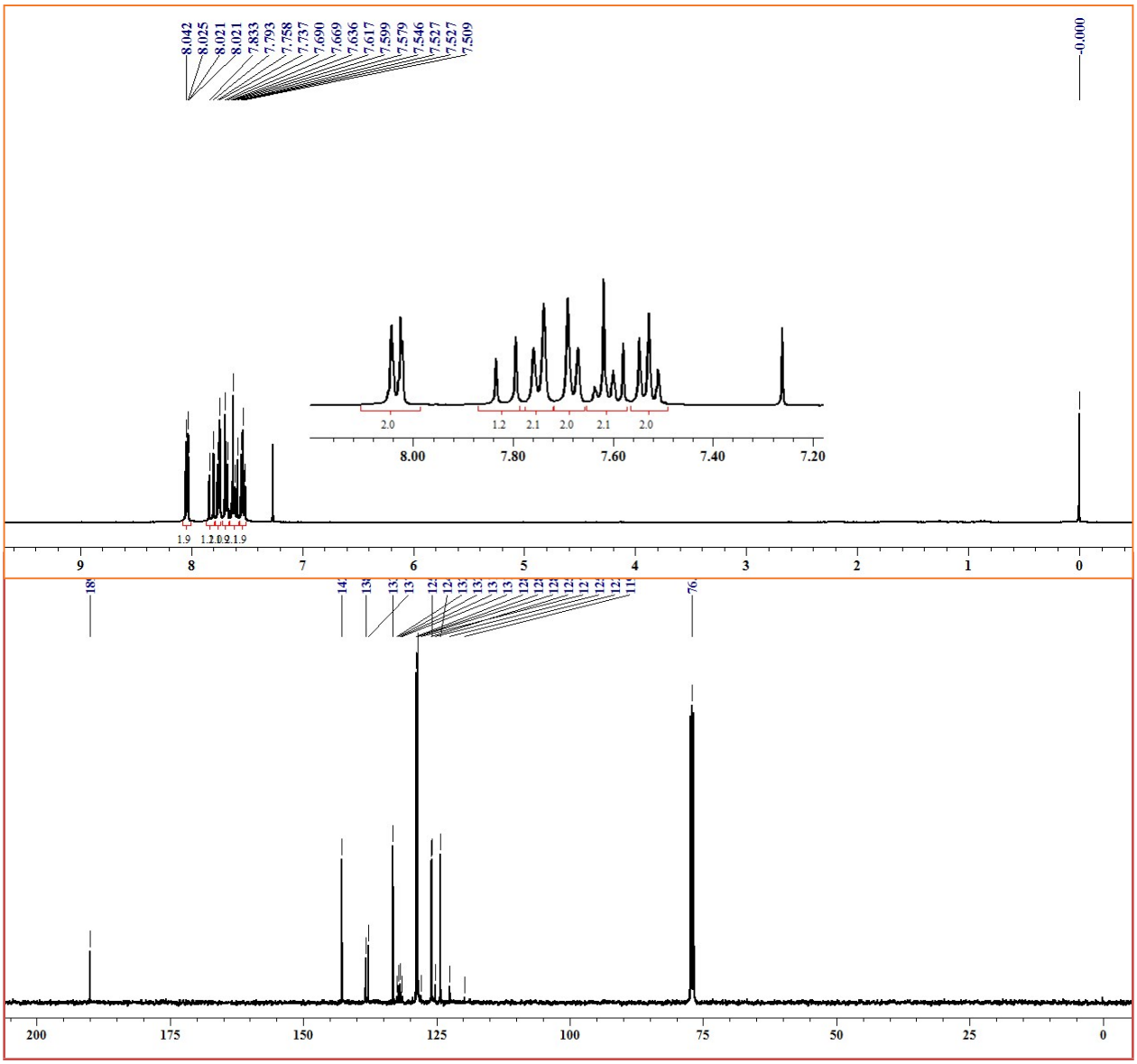
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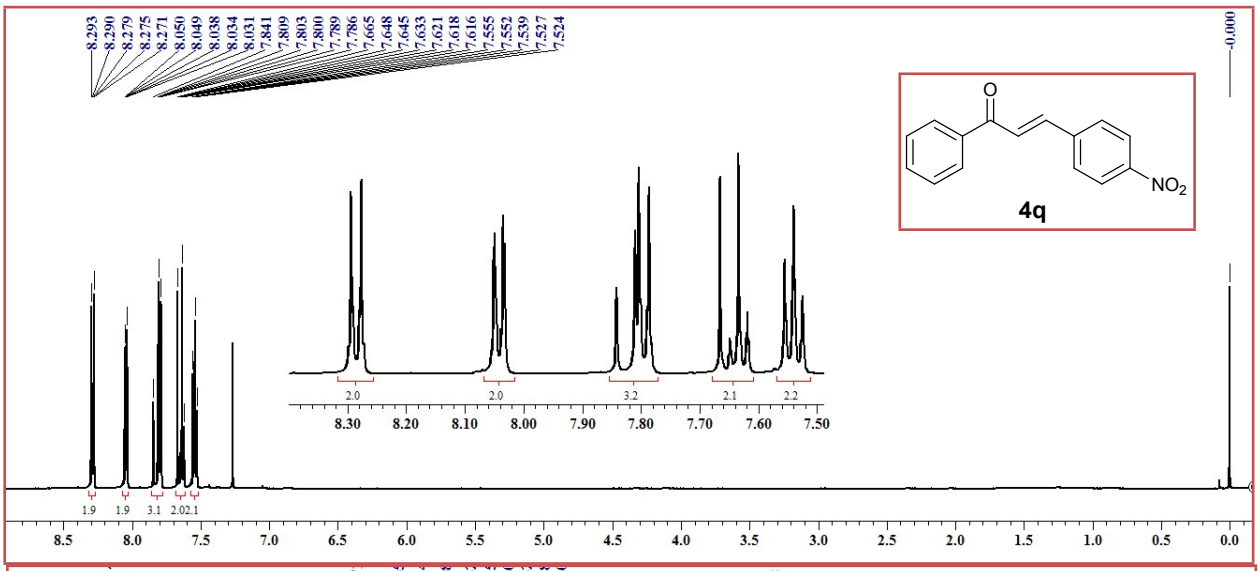
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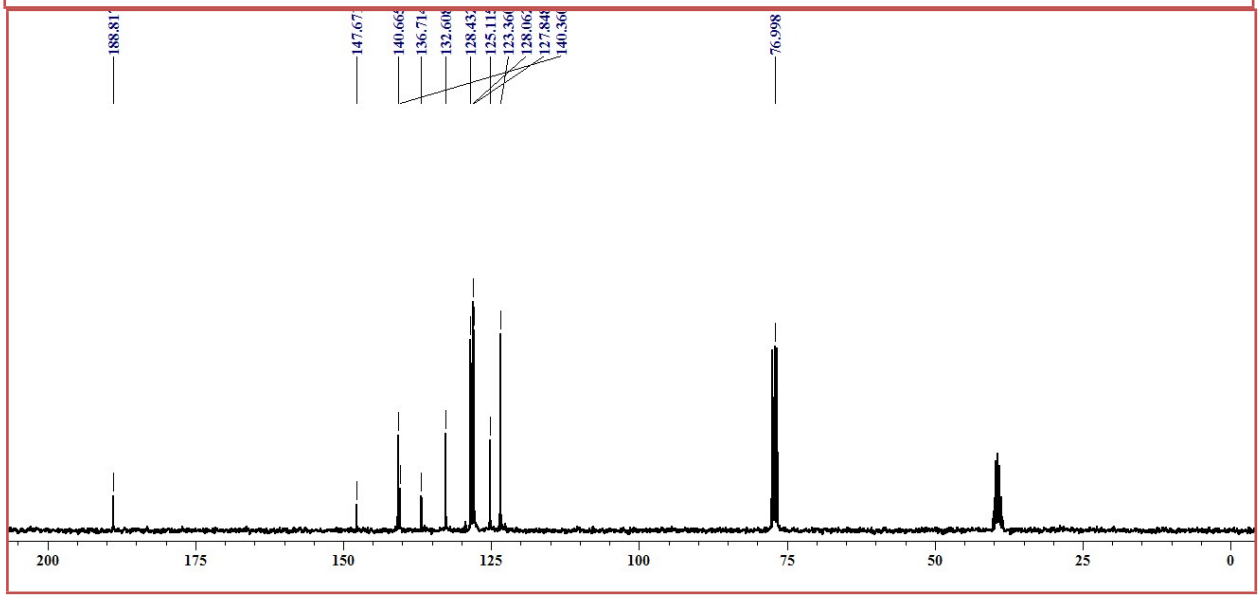
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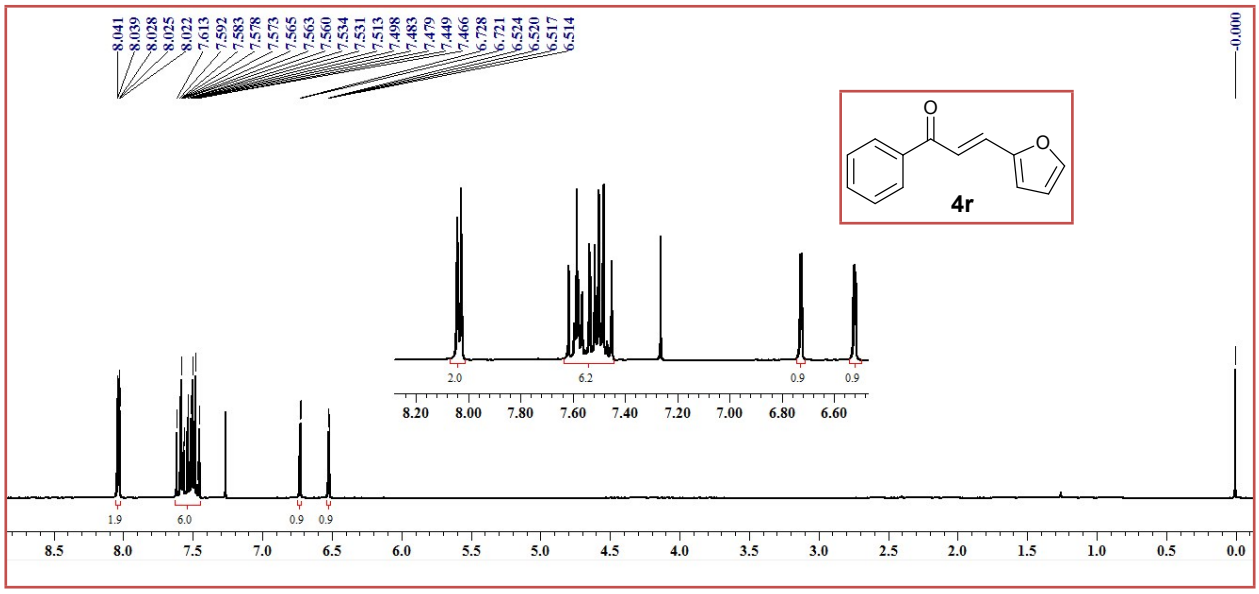
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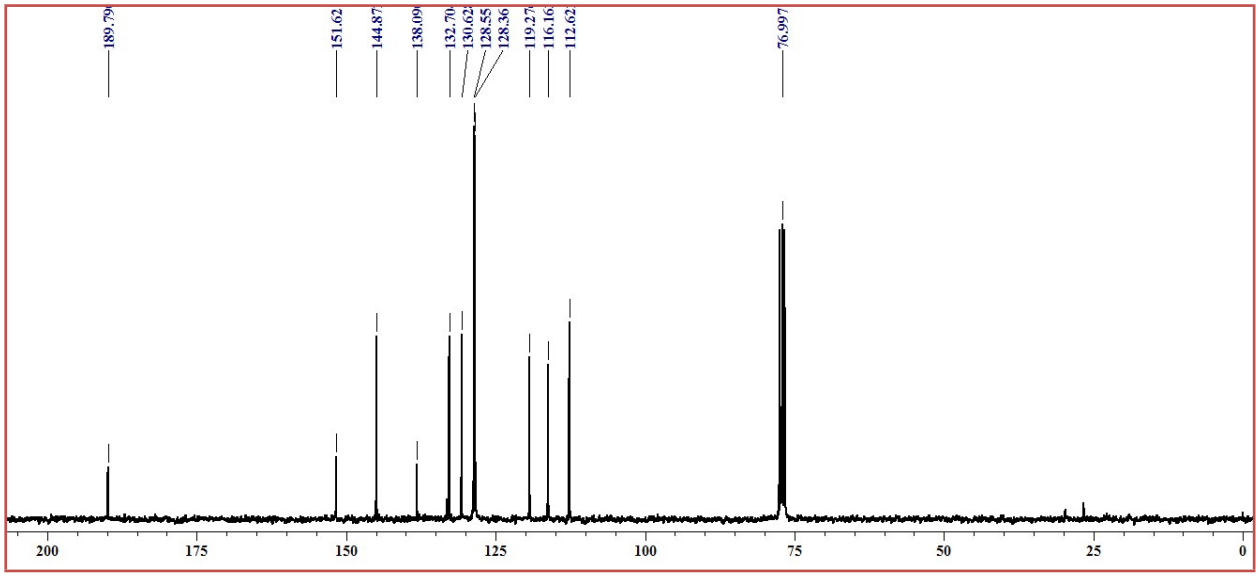
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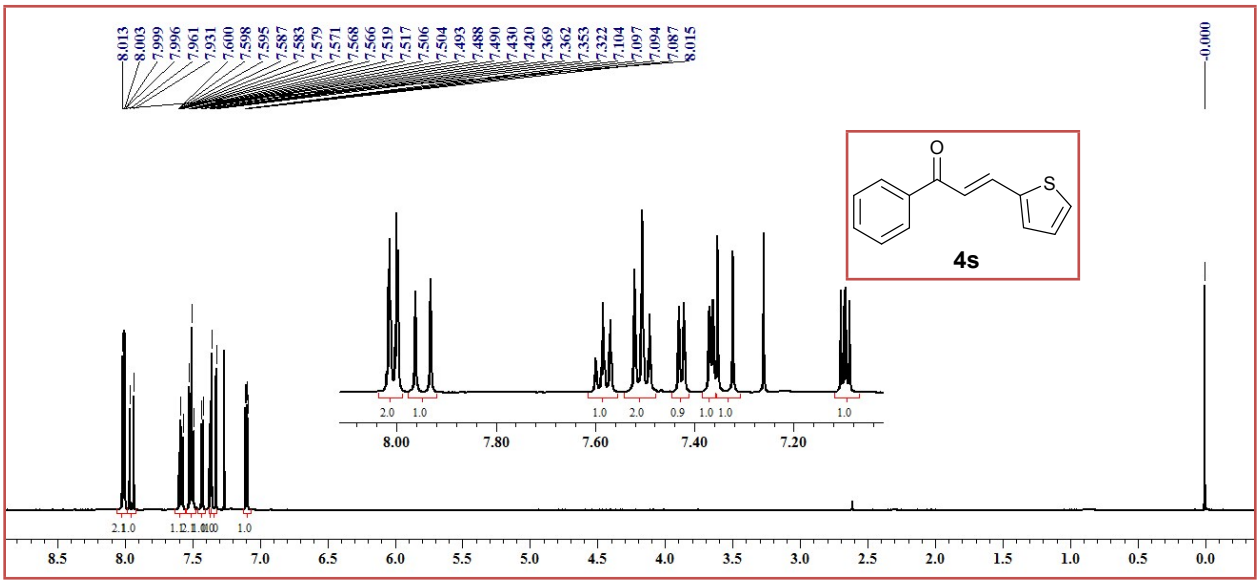
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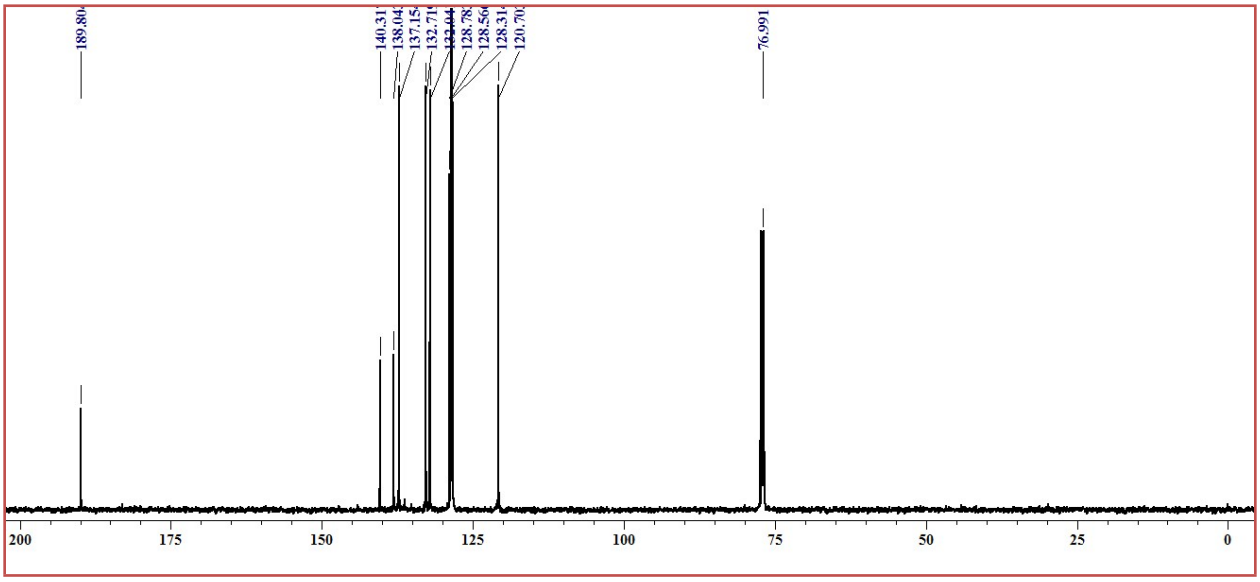
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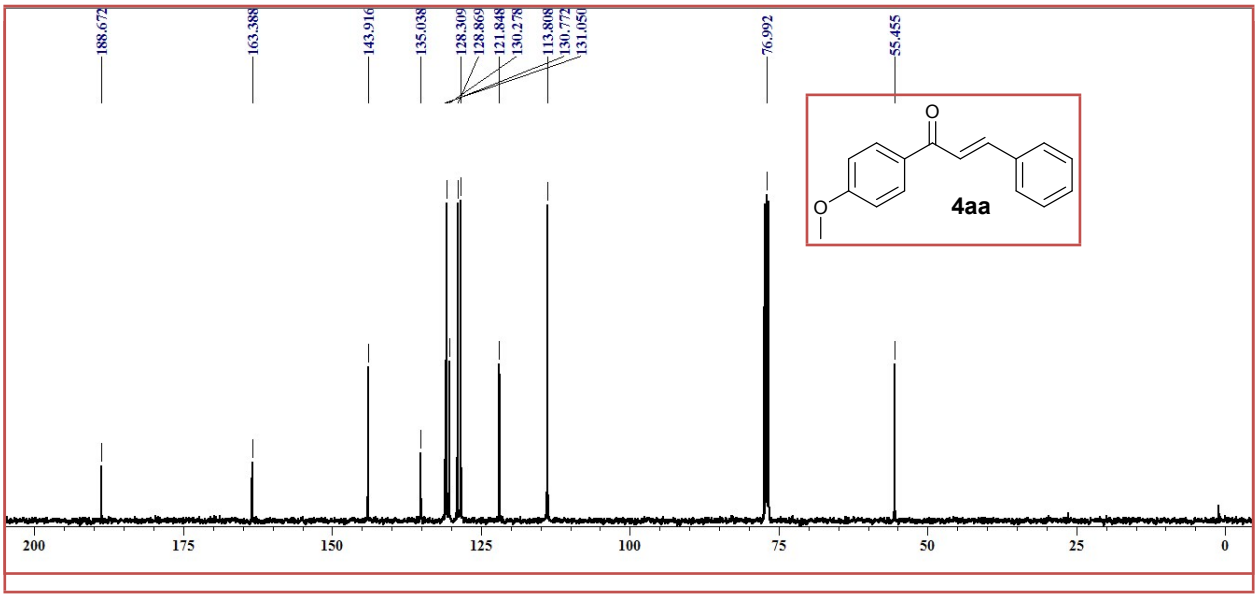
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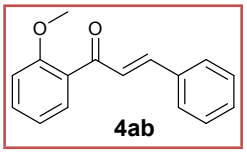
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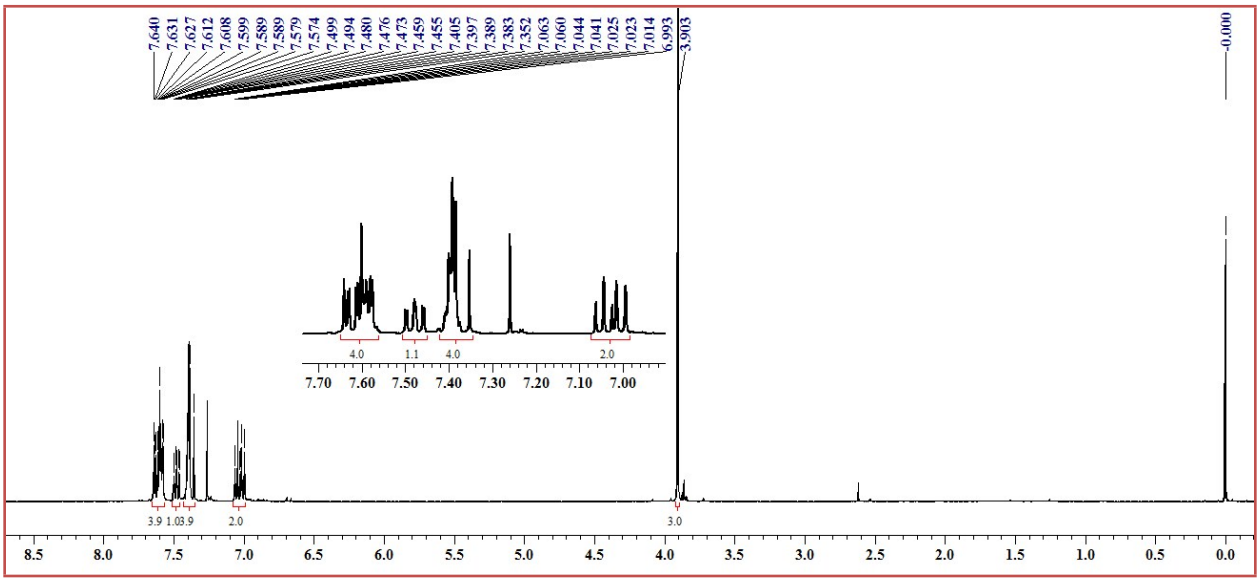
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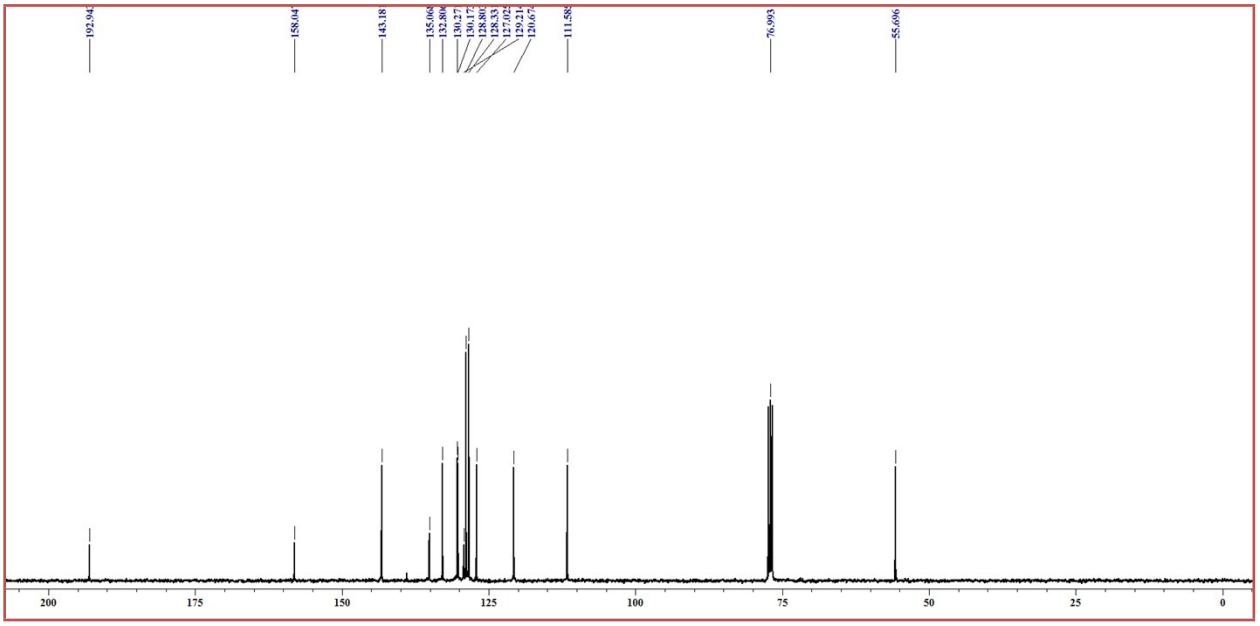
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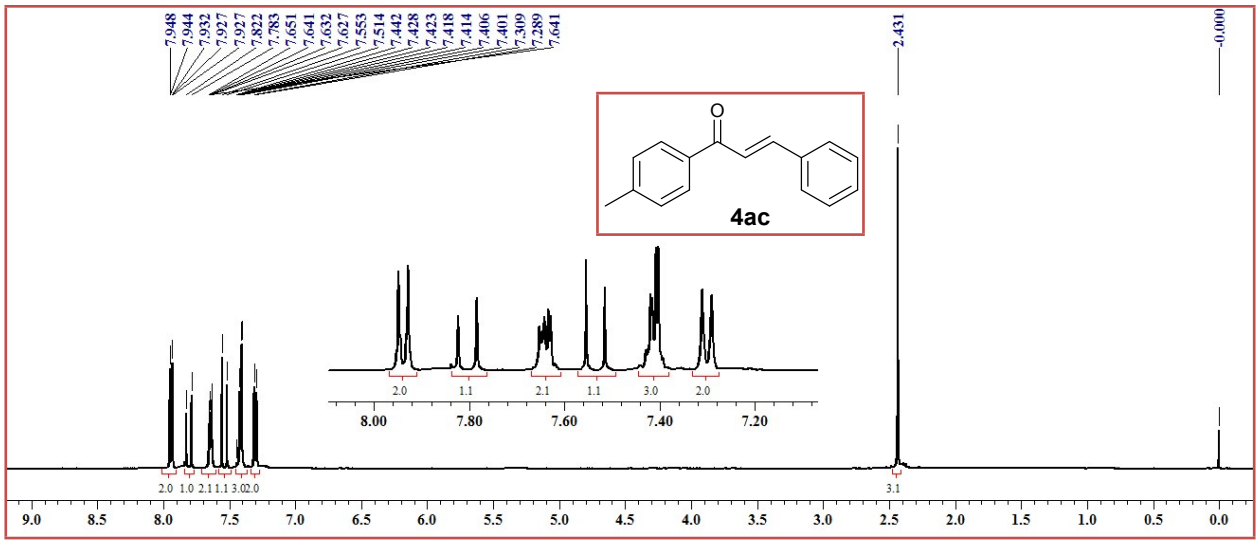
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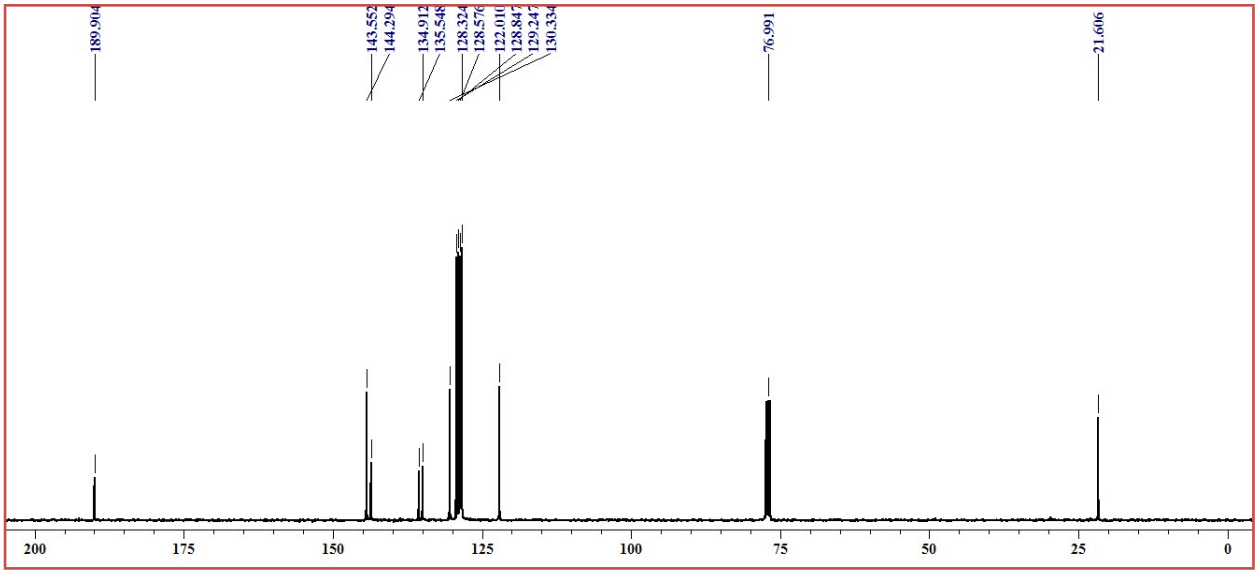
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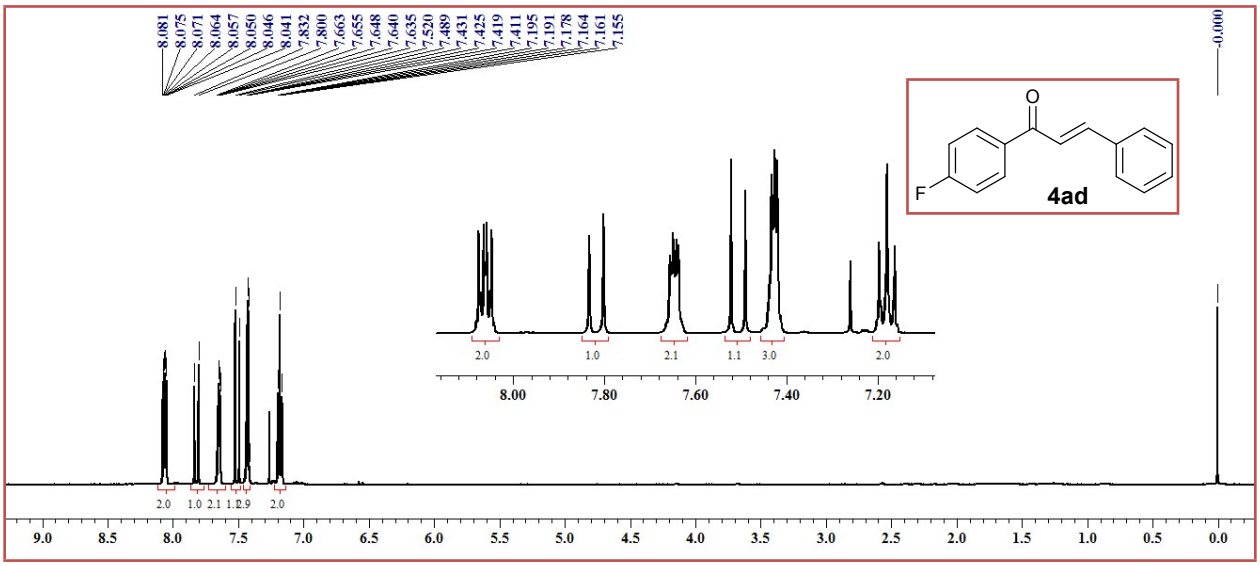
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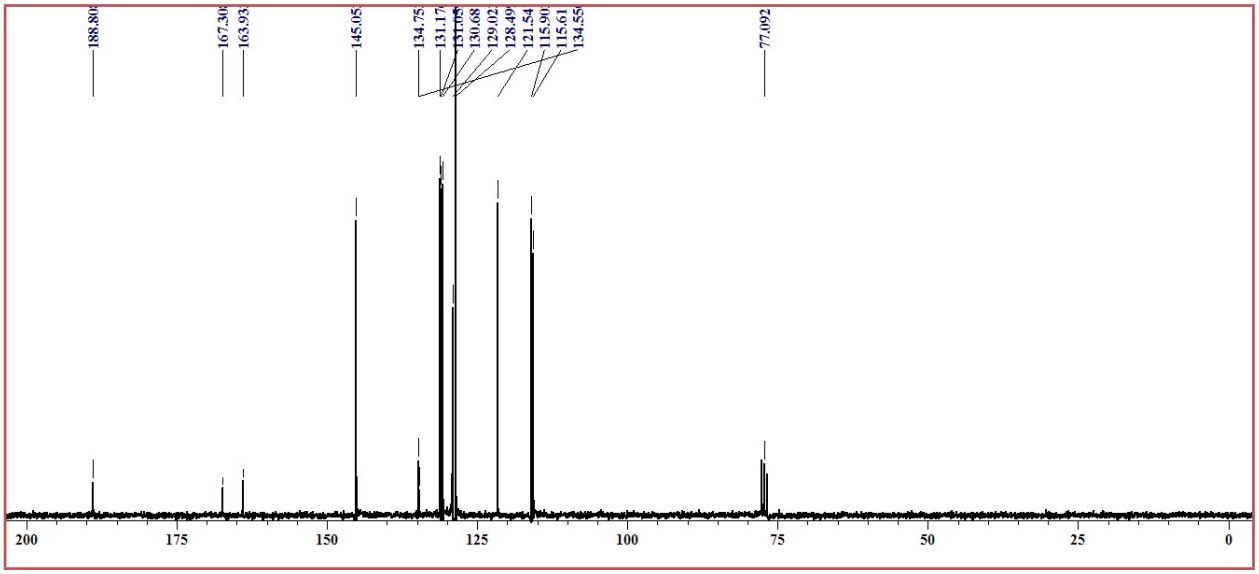
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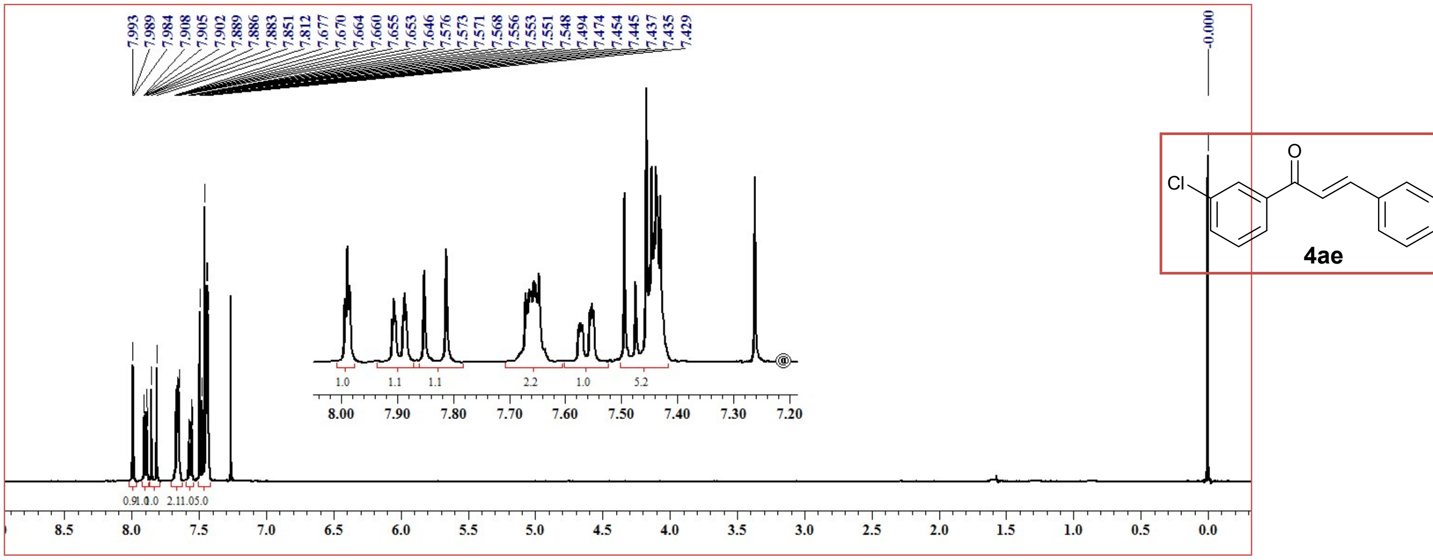
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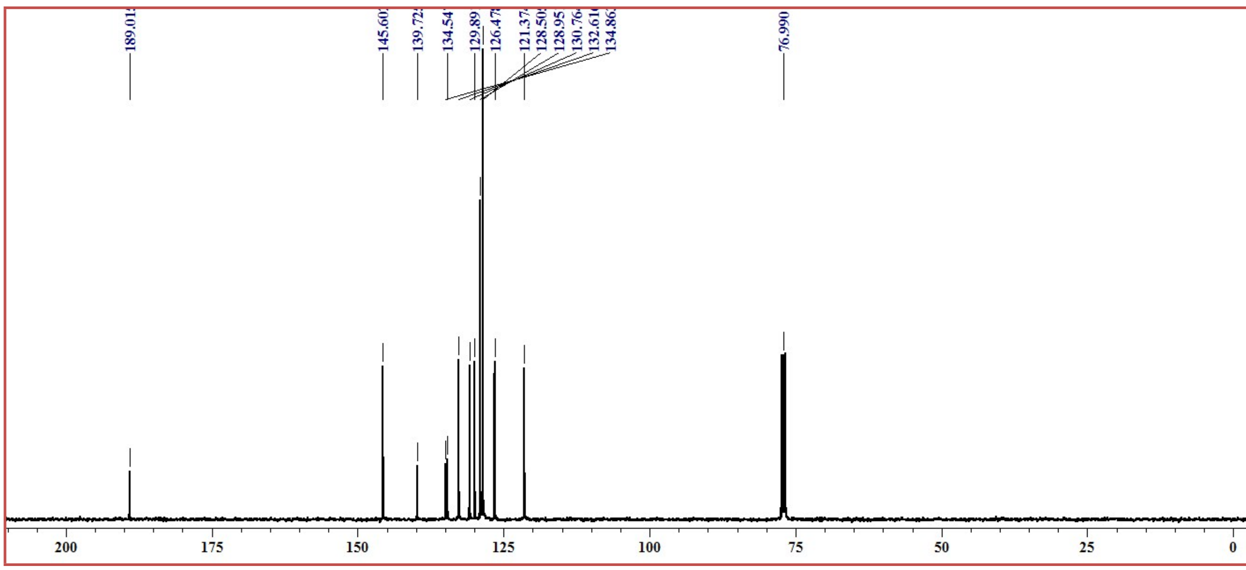
O
4ae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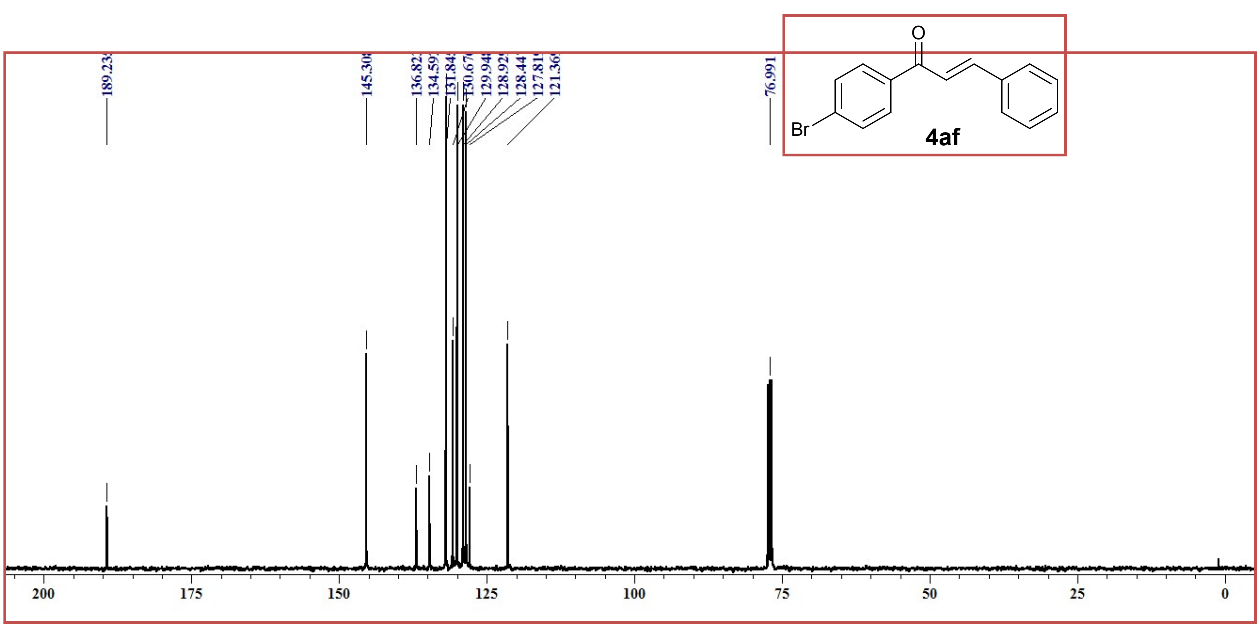
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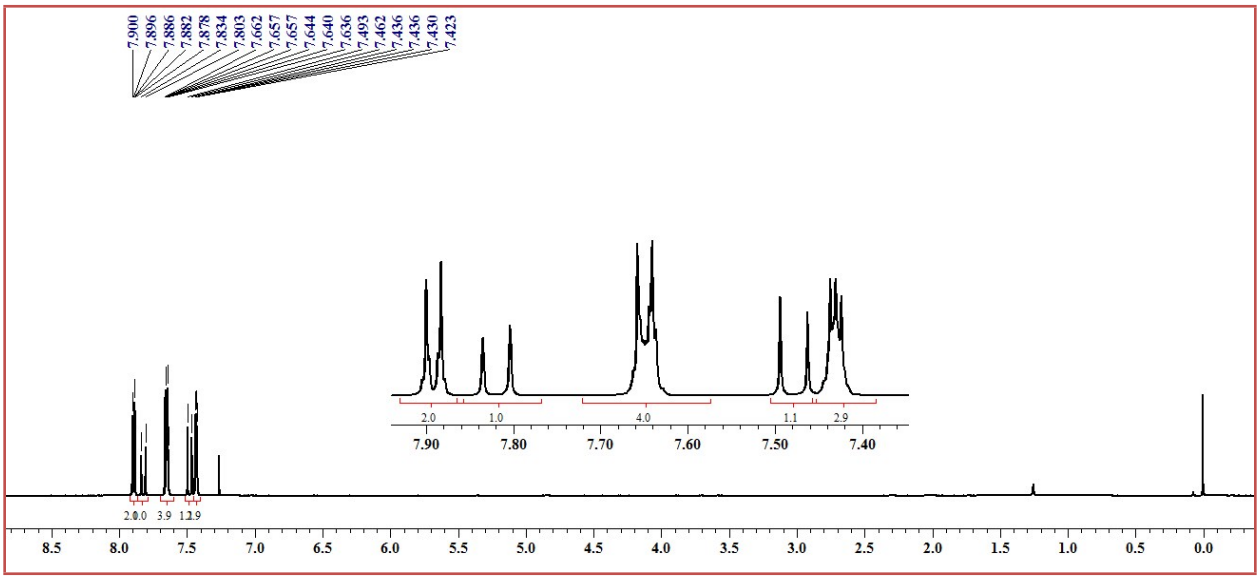
Br
4af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7.636
7.493
7.462
7.436
7.436
7.430
7.423
2.0 1.0 4.0 1.1 2.9
7.90 7.80 7.70 7.60 7.50 7.40
2.0 0.0 3.9 1.2 1.9
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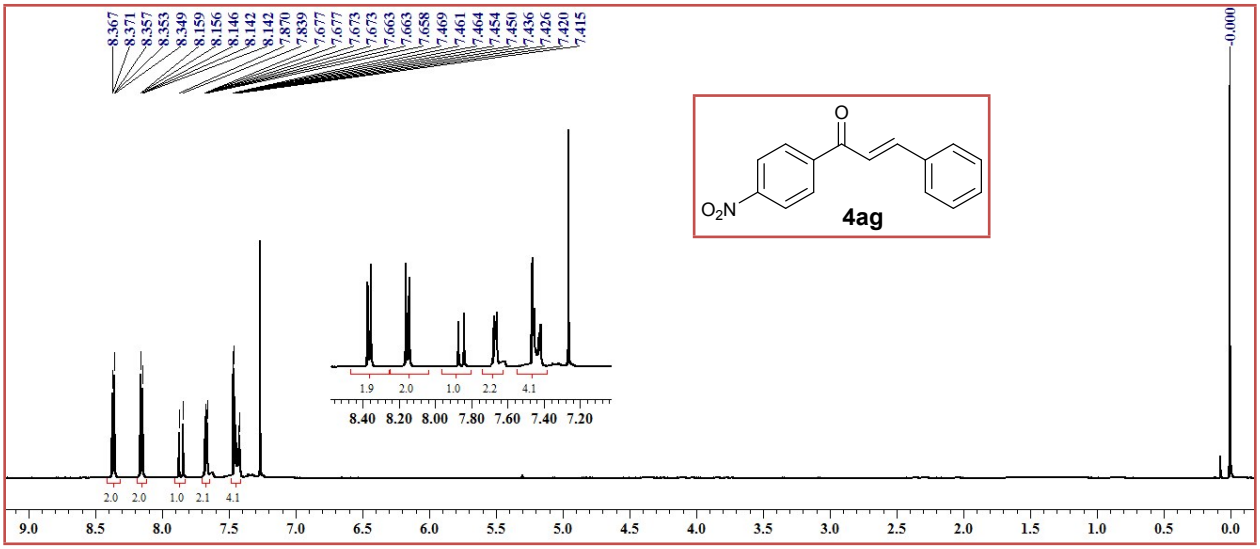
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7.677
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7.663
7.658
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7.464
7.454
7.450
7.436
7.426
7.420
7.415
-0.000
O
O2N
4ag
1.9 2.0 1.0 2.2 4.1
8.40 8.20 8.00 7.80 7.60 7.40 7.20
2.0 2.0 1.0 2.1 4.1
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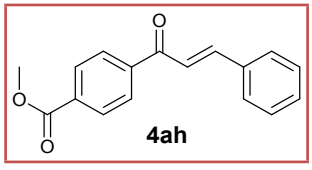

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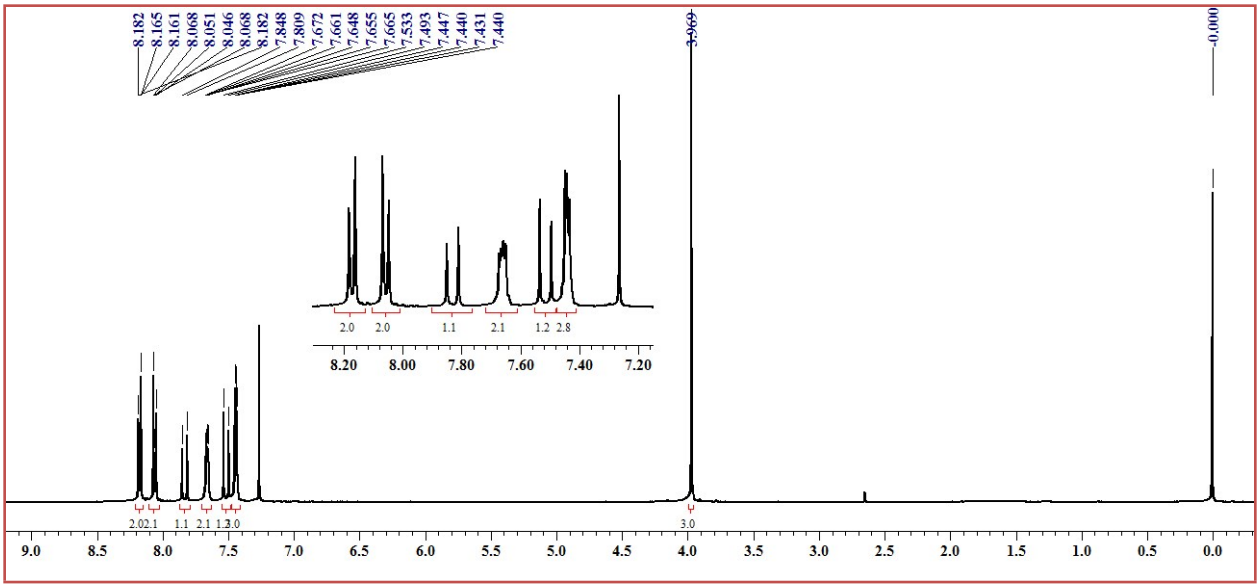
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7.447
7.440
7.431
7.440
3.969
0.000
2.0 2.0 1.1 2.1 1.2 2.8
8.20 8.00 7.80 7.60 7.40 7.20
2.02.1 1.1 2.1 1.3.0 3.0
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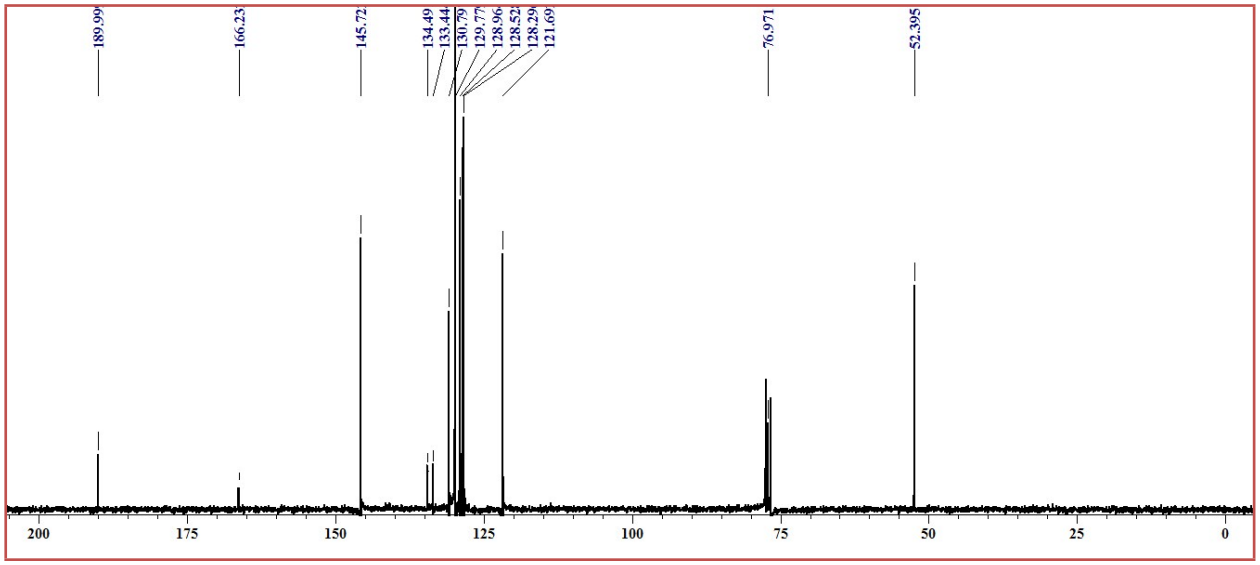
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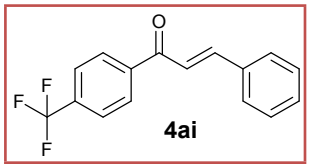
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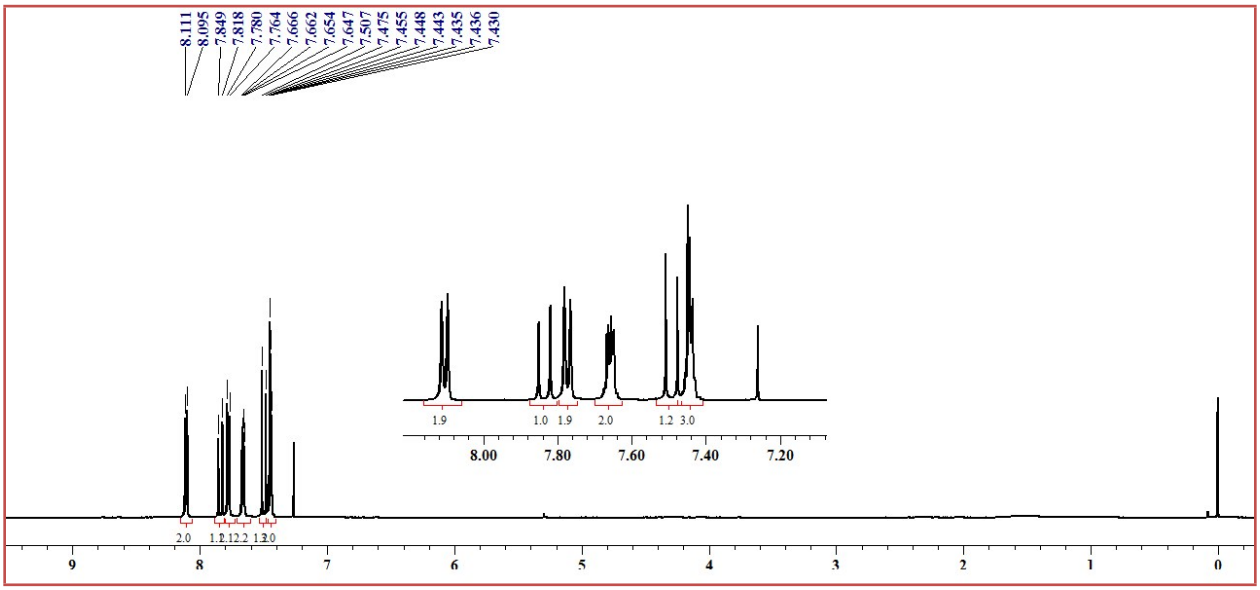
F
F
F
4ai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7.443
7.435
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7.430
1.9
1.0 1.9
2.0
1.2 3.0
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7
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3
2
1
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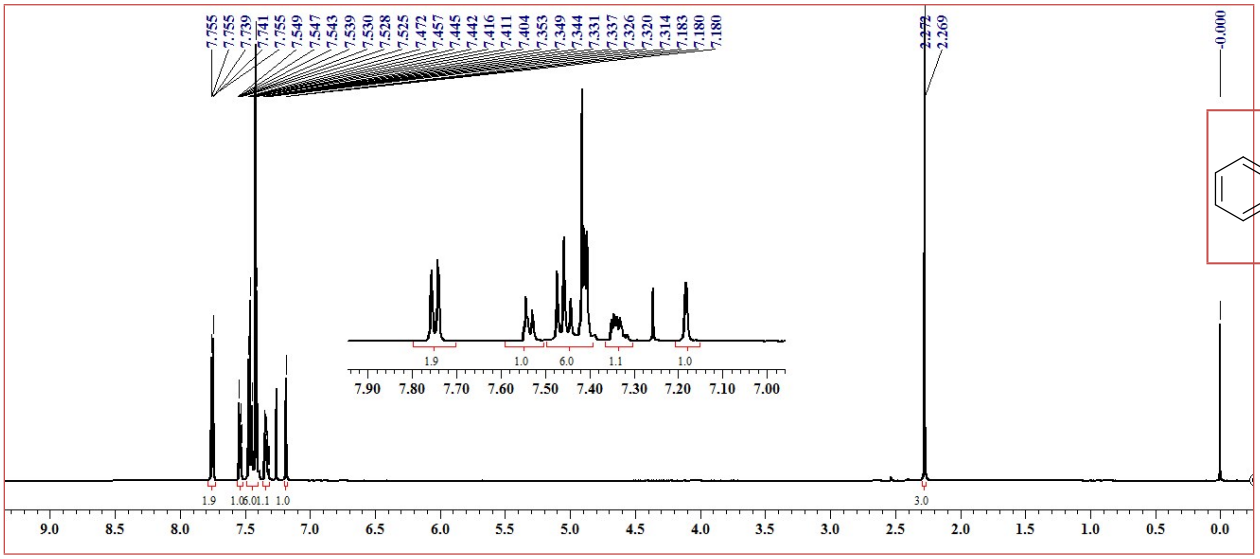
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1.1
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7.70
7.60
7.50
7.40
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7.20
7.10
7.00
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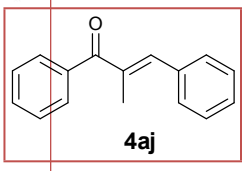
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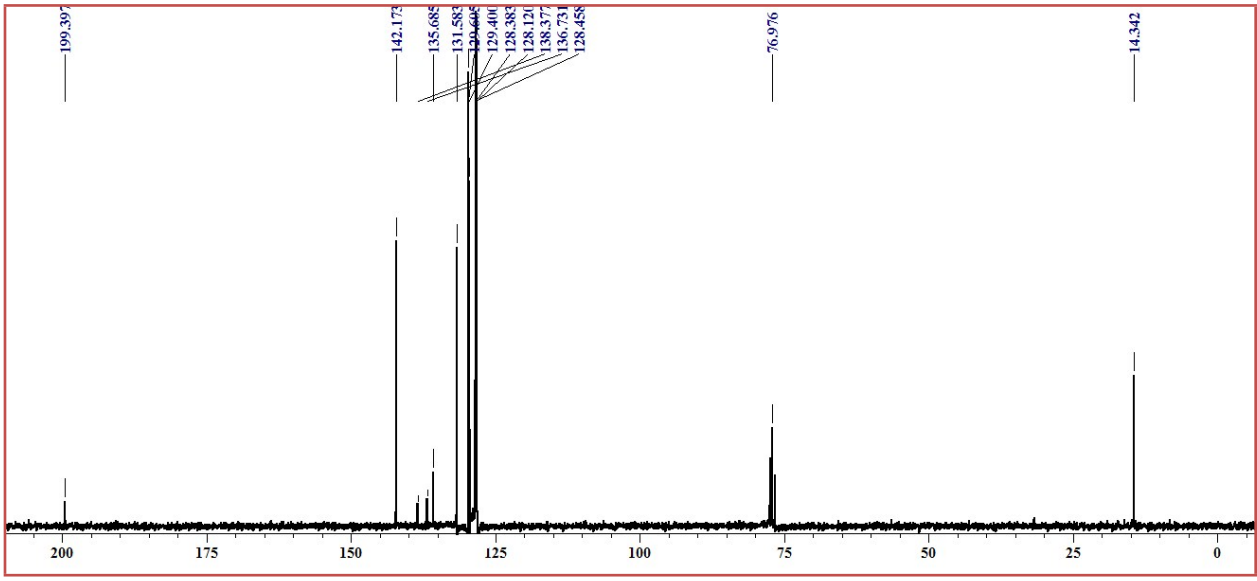
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150
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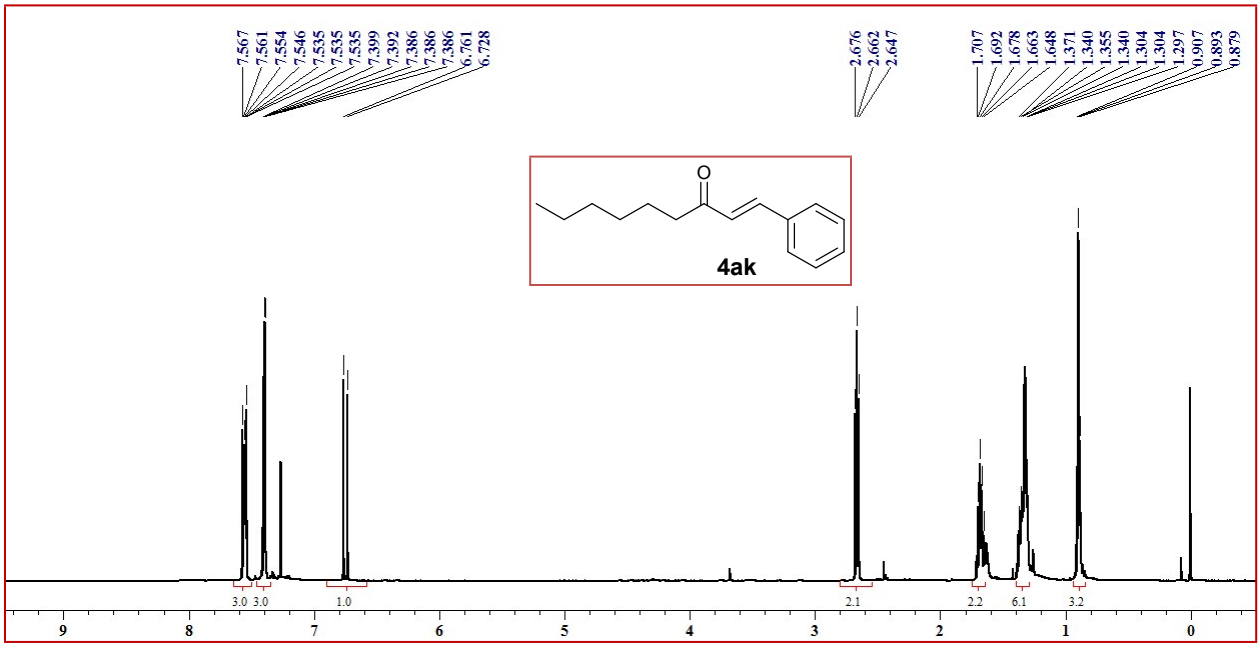
100
75
50
25
0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1.340
1.304
1.304
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0.879
O
4ak
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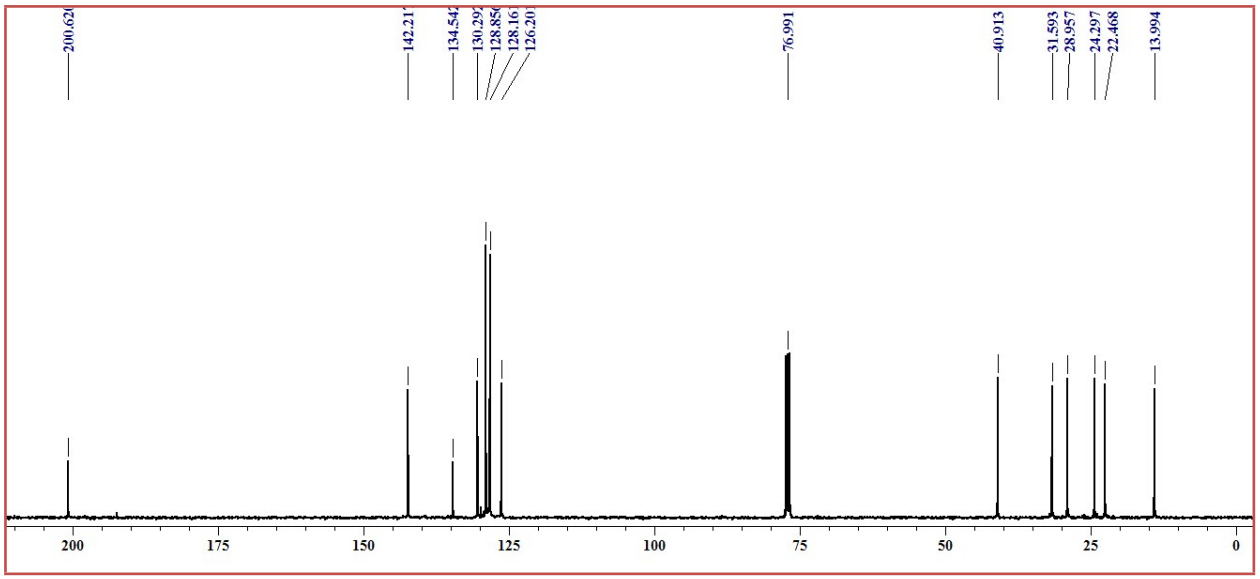
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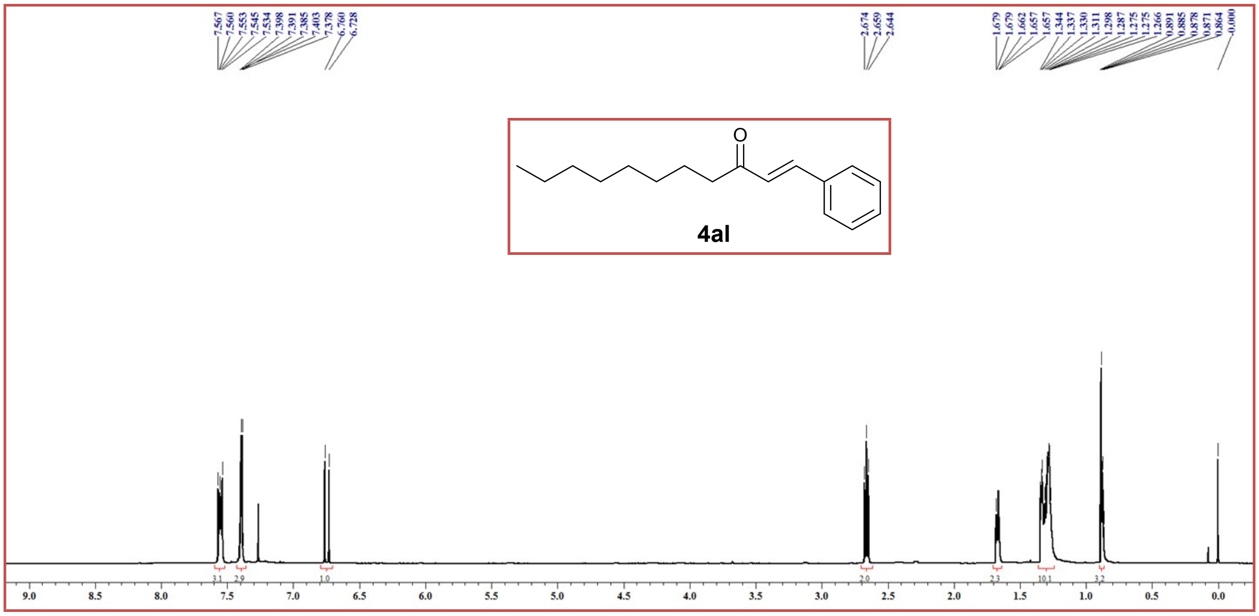
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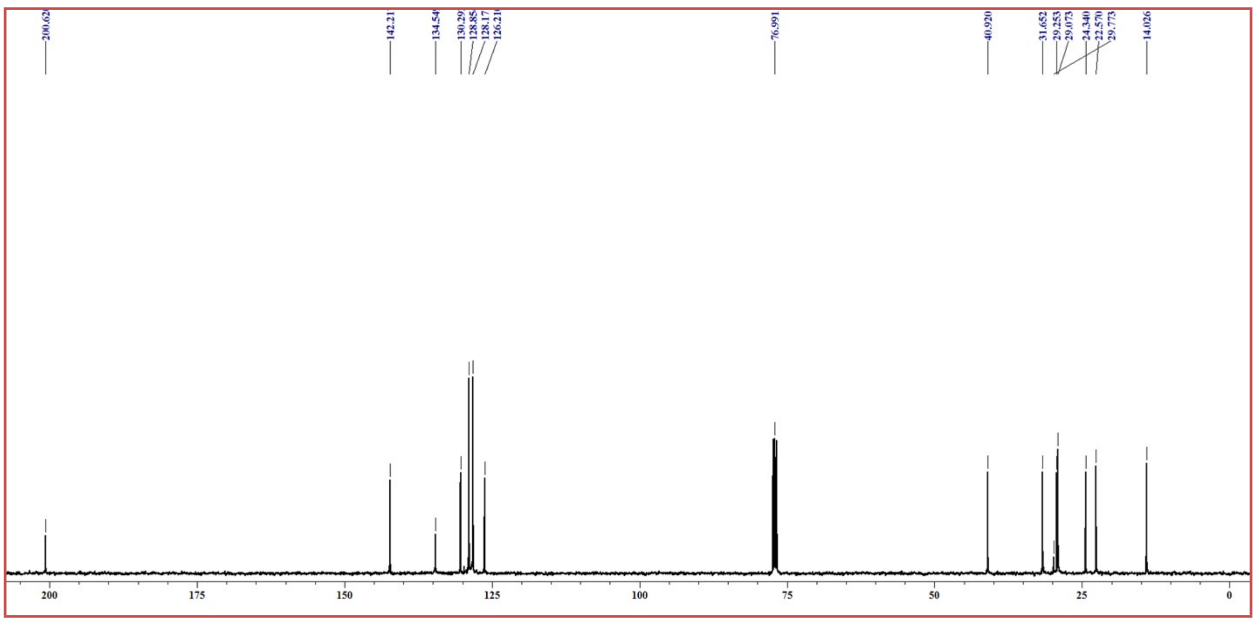

4. References

1. X. F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.,* 2010, **132**, 14596.
2. Y. Kubota, H. Ikeya, Y. Sugi, T. Yamada and T. Tatsumi, *J. Mol. Catal. A: Chem.,* 2006, **249**, 181.
3. Y. Unoh, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.,* 2013, **78**, 5096.
4. C. Matthias, D. Kuck, *Int. J. Mass Spectrom.*, 2002, **217**, 131.
5. M. Rueping, T. Bootwicha, H. Baars and E. Sugiono, *Beilstein J. Org. Chem.,* 2011, **7**, 1680.
6. B. P. Bandgar, S. S. Gawande, R. G. Bodade, J. V. Totre and C. N. Khobragade, *Bioorg. Med. Chem.,* 2010, **18**, 3.
7. J. M. Zhang, W. L. Shang, B. Q. Lu and J. An Jin, *J. Fluorine Chem.,* 2012, 139.
8. D. Rocchi, J. F. González and J. C. Menéndez, *Molecules*, 2014, **19**, 7317.
9. I. Karpaviciene, I. Cikotiene, J. M. Padrón, *Eur. J. Med. Chem.,* 2013, **70***,* 568.
10. Q. Jiang, J. Jia, B. Xu, A. Zhao and C. C. Guo, *J. Org. Chem.,* 2015, **80**, 3586.
11. A. E. Sheshenev, E. V. Boltukhina, A. J. P. White and K. K. Hii *Angew. Chem. Int. Ed.,* 2013, **52**, 6988.
12. X. F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.,* 2010, **132**, 14596.
13. J. Liu, C. Chen, F. Wu and L. Zhao, *Chem. Biol. Drug. Des.,* 2013, **82***,* 39.
14. Y. Wei, J. Tang, X. Cong and X. Zeng, *Green Chem.,* 2013, **15**, 3165.
15. Y. Masuyama, W. Takamura and N. Suzuki, *Eur. J. Org. Chem.,* 2013, 8033.
16. A. Bhunia, A. Patra, V. G. Puranik and A. T. Biju, *Org. Lett*. 2013, **15**, 1756.