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

Supporting Information

Hypervalent Iodine Catalysis for Selective Oxidation of Baylis–Hillman adducts *via* In Situ Generation of o-Iodoxybenzoic Acid (IBX) from 2-Iodosobenzoic acid (IBA) in Presence of Oxone

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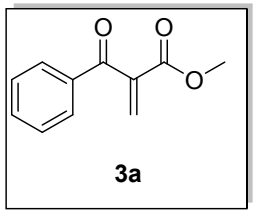
Contents

Experimental Section

General Information: The starting materials and reagents were purchased from various commercial sources and used without further purification. The reactions were performed at room temperature.ACME silica gel (60-120 mesh) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates with silica gel 60-F_{254} plates and visualized by UV-light. ^{1}H NMR and ^{13}C NMR spectra were recorded, using tetramethylsilane (TMS) in the solvent of $CDCl_3$+DMSO as the internal standard on a 300, 500 MHz spectrometer (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO at 39.43). Chemical shifts (δ) were recorded in ppm with respect to TMS as an internal standard and coupling constants are quoted in Hertz (Hz). Mass spectra were recorded on a mass spectrometer by the electron spray ionization (ESI) and the data acquired in positive ionization mode. HRMS spectra were determined on TOF type mass analyzer.

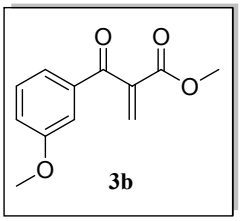
Characterization Data for the Products:

Methyl 2-benzoylacrylate (3a)[1]



Isolated yield: 94%; Colourless liquid. **IR** cm^{-1}: 3063, 2983, 1722, 1672, 1402, 1231, 1021, 983,863, 755,688. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (d, J = 8.3 Hz, 2H), 7.59 (t, *J* = 7.47 Hz, 1H), 7.47 (t, *J* = 7.93 Hz, 2H), 6.72 (s, 1H), 6.05(s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz): δ 192.9, 164.7, 140.8, 136.0, 133.6, 131.5, 129.4, 128.5, 52.4. **MS** (ESI): (m/z) = 191 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{11}H_{11}O_3$ = 191.0698, found = 191.0702.

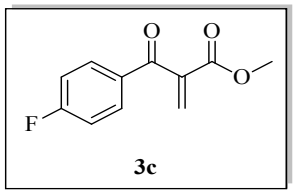
Methyl 2-(3-methoxybenzoyl)acrylate (3b)



Isolated yield: 92%; Colourless Liquid. **IR** cm^{-1}: 3006, 2953, 1723, 1663, 1437, 1316, 1173, 1026, 977, 845, 780,640. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.43 (q, 1H), 7.40-7.35 (m, 2H), 7.15 (dd, *J* = 1.3, *J* = 2.7 Hz,

1H), 6.71 (s, 1H), 6.05 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.7, 164.6, 159.7, 140.7, 137.0, 131.3, 129.4, 122.4, 120.3, 119.0, 55.3, 52.3. **MS** (ESI): (m/z) = 221 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{13}O_4$ = 221.0804, found = 221.0808.

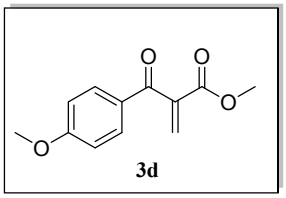
Methyl 2-(4-fluorobenzoyl)acrylate (3c)[2]



3c

Isolated yield: 88%; yellow Liquid. **IR** cm^{-1}: 2954, 2962, 1727, 1697, 1506, 1437, 1329, 1285, 1142, 980, 817, 780. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.95 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 6.72 (s, 1H), 6.05 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.4, 167.3, 140.6, 132.2, 132.1, 131.5, 115.9, 115.7, 52.5. **MS** (ESI): (m/z) = 209 $(M+H)^+$. **HRMS** (ESI) $(M+1)^+$ m/z calcd for $C_{11}H_{10}FO_3$ = 209.0606, found = 209.0608.

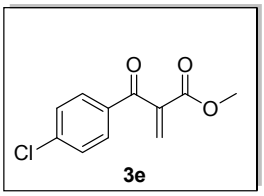
Methyl 2-(4-methoxybenzoyl)acrylate (3d)[3]



3d

Isolated yield: 94%; Pale yellow liquid. **IR** cm^{-1}: 3006, 2953, 1723, 1663, 1437, 1316, 1240, 1173, 1026, 977, 845, 780, 640. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.85 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.68 (s, 1H), 5.99 (s, 1H), 3.88 (s, 3H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.6, 164.0, 140.9, 131.9, 130.6, 129.0, 113.8, 55.5, 52.4. **MS** (ESI): (m/z) = 221 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{13}O_4$ = 221.0803, found = 221.0808.

Methyl 2-(4-chlorobenzoyl)acrylate (3e)[4]

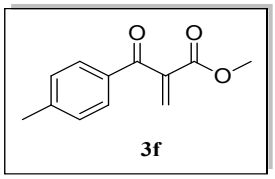


3e

Isolated yield: 89%; yellow liquid. **IR** cm^{-1}: 2955, 2853, 1729, 1679, 1484, 1253, 986, 849, 770, 675. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (d,

J = 8.6 Hz, 2H), 7.43 (d, *J* = 8.69 Hz, 2H), 6.72 (s, 1H), 6.07 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7, 164.5, 140.5, 140.2, 134.4, 131.8, 130.7, 128.9, 52.5. **MS** (ESI): (m/z) = 225 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{11}H_{10}ClO_3$ = 225.0309, found = 225.0313.

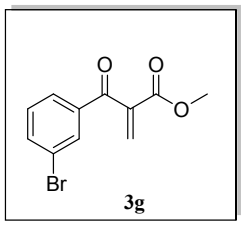
Methyl 2-(4-methylbenzoyl)acrylate (3f)



3f

Isolated yield: 95%; Colourless liquid. **IR** cm^{-1}:3031, 2953, 1724, 1667, 1436 1234, 1138, 974, 837, 766, 607. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.78 Hz, 2H), 7.26 (d, *J* = 7.93 Hz, 2H), 6.68 (s, 1H), 6.01 (s, 1H), 3.75 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5, 164.7, 144.6, 140.9, 133.4, 130.9, 129.5, 126.1, 52.5, 21.5. **MS** (ESI): (m/z) = 205 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{13}O_3$ = 205.0853, found = 205.0859.

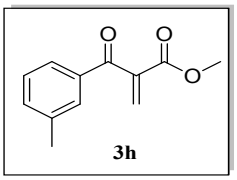
Methyl 2-(3-bromobenzoyl)acrylate (3g)



3g

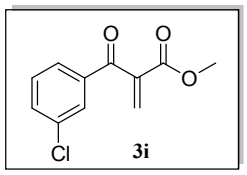
Isolated yield: 85%; yellow Liquid. **IR** cm^{-1}: 2955, 2924, 1722, 1632, 1439, 1282, 1149, 1071, 804, 756,704**^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.74 (dd, *J* = 7.6 Hz, 2H), 7.35 (t, J = 7.9 Hz, 1H), 6.74 (s, 1H), 6.08 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.5, 164.7, 140.2, 137.8, 136.4, 132.2, 132.1, 130.1, 127.9 122.8, 52.5. **MS** (ESI): (m/z) = 271 $(M+H)^+$.

Methyl 2-(3-methylbenzoyl)acrylate (3h)



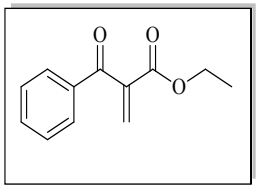
Isolated yield: 91%; White Liquid. **IR** cm^{-1}: 3031, 2953, 1724, 1667, 1436, 1234, 1172, 984, 837, 766, 607. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 7.58 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 6.74 (s, 1H), 6.04 (s, 1H), 3.76 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.1, 164.7, 140.9, 138.4, 136.0, 134.4, 131.2, 129.7, 128.3, 126.7, 52.3, 21.2. **MS** (ESI): (m/z) = 205 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{13}O_3$ = 205.0854, found = 205.0859

Methyl 2-(3-chlorobenzoyl)acrylate (3i)[1]



Isolated yield: 89%; yellow Liquid. **IR** cm^{-1}: 2955, 1729, 1679, 1484, 1326, 1253, 1129,986, 770,650. **^{1}H NMR** (500 MHz, $CDCl_3$+d_6-DMSO): δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 9.3 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.32 – 7.58 (m, 1H), 6.74 (s, 1H), 6.08 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 164.4, 140.5, 132.0, 130.3 130.2, 125.3, 120.8, 120.5, 116.1, 115.8, 52.5. **MS** (ESI): (m/z) = 225 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{11}H_{10}ClO_3$ = 225.0308, found = 225.0313.

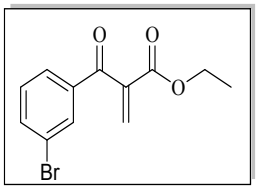
Ethyl 2-benzoylacrylate (3j)[1]



Isolated yield: 95%; Colorless liquid, **IR** cm^{-1}: 3063, 2936, 1722, 1672, 1408, 1231, 1140, 1021, 863, 755, 688. **^{1}H NMR** (500 MHz, $CDCl_3$+): δ 7.84 (d, *J* =7.94 Hz, 2H), 7.58 (t, *J* = 7.58 Hz, 1H), 7.46 (t, J=7.7 Hz, 2H), 6.68 (s, 1H), 6.06 (s, 1H), 4.23 (q, 2H), 1.19 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.0, 164.2, 141.3, 136.1, 133.4, 131.2, 129.2, 128.4, 61.5, 13.8. **MS** (ESI):

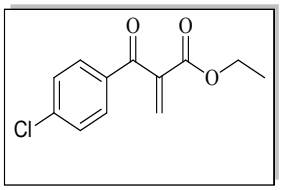
(m/z) = 205 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{12}O_3$ = 205.0854, found = 205.0859.

Ethyl 2-(3-bromobenzoyl)acrylate (3k)[3]



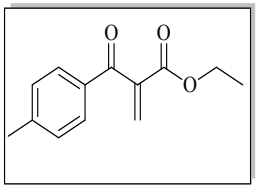
Isolated yield: 85%; yellow Liquid. **IR** cm^{-1}: 2980, 2853, 1725, 1679, 1421, 1281, 1142, 1020, 903,758, 677. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.35(t, J = 7.9 Hz, 1H), 6.7 (s, 1H), 6.1(s, 1H), 4.24 (q, 2H), 1.21(t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.7, 163.9, 140.8, 138.0, 136.3, 132.1, 132.0, 130.1, 127.8, 122.8, 61.6, 13.9. **MS** (ESI): (m/z) = 282 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{12}H_{12}BrO_3$ = 282.9962, found = 282.9964.

Ethyl 2-(4-chlorobenzoyl)acrylate (3l)[3]



Isolated yield: 92%; yellow Liquid. **IR** cm^{-1}: 2955, 1736, 1655, 1490, 1326, 1253, 1129, 982, 849,770, 650. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.6Hz, 2H), 7.44 (d, *J* = 8.6Hz, 2H), 6.69 (s, 1H), 6.07 (s, 1H), 4.23(q, 2H), 1.21(t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.9, 164.0, 141.0, 140.0, 134.6, 131.6, 130.6, 128.8, 61.5, 13.9. **MS** (ESI): (m/z) = 239 $(M+H)^+$.

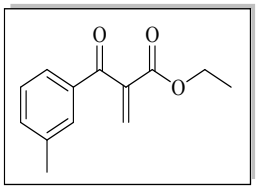
Ethyl 2-(4-methylbenzoyl)acrylate (3m)[3]



Isolated yield: 96%; Colourless liquid. **IR** cm^{-1}: 2983, 1723, 1670, 1447, 1324, 1234, 1022, 981, 839, 768. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, J=8.24Hz, 2H), 7.26 (d, *J* = 7.93Hz, 2H), 6.6 (s, 1H), 6.02 (s, 1H), 4.22(q, 2H), 2.40 (s, 3H), 1.20 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.8,

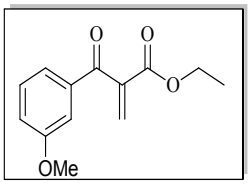
164.4, 144.5, 141.5, 133.7, 130.8, 129.5, 129.2, 61.4, 21.7, 13.9. **MS** (ESI): (m/z) = 219 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{13}H_{15}O_3$ = 219.1010, found = 219.1015.

Ethyl 2-(3-methylbenzoyl)acrylate (3n)[3]



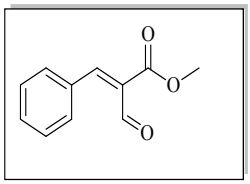
Isolated yield: 94%; Colourless liquid. **IR** cm^{-1}: 2982, 1721, 1670, 1319, 1247, 1197, 1132, 1023, 973, 769, 655. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.62 (d, *J* =7.5 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.34(t, *J* = 7.58Hz, 1H), 6.67(s, 1H), 6.04(s, 1H), 4.23 (q, 2H), 2.40(s, 3H), 1.21(t, 3H) . **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.8, 164.4, 144.5, 141.5, 133.7, 130.8, 129.5, 129.2, 61.4, 21.7, 13.9. **MS** (ESI): (m/z) = 219 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{13}H_{15}O_3$ = 219.10103, found = 219.10157.

Ethyl 2-(3-methoxybenzoyl)acrylate (3o)



Isolated yield: 92%; yellow Liquid. **IR** cm^{-1}: 2981, 1721, 1672, 1429, 1257, 1134, 1010, 865, 766, 655. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42-7.34 (m, 3H), 7.14-7.12 (m, 1H), 6.68 (s, 1H), 6.05 (s, 1H), 4.23(q, 2H), 3.85(s, 3H), 1.20(t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.0, 164.0, 136.1, 133.4, 131.2, 129.2, 128.4, 61.3, 13.8. **MS** (ESI): (m/z) =235 $(M+H)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{13}H_{15}O_4$ = 235.0958, found = 235.0940.

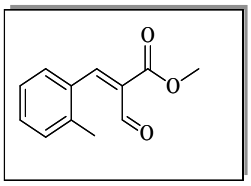
(E)-Methyl 2-formyl-3-phenylacrylate (5a)[5]



Isolated yield: 98%; yellow Liquid. **IR** cm^{-1}: 3221, 1751, 1624, 1480, 1270, 1162, 843, 658, 457. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.53-7.51(m, 2H), 7.47 (s, 1H), 7.46-7.43(m, 3H), 3.88(s, 3H). **^{13}C NMR**

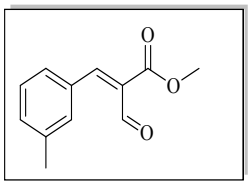
(100 MHz, $CDCl_3$): δ 189.6, 166.2, 152.8, 150.2, 132.2, 131.7, 131.1, 130.0, 129.0, 52.6. **MS** (ESI): (m/z) = 191.03 $(M+1)^+$.

(E)-methyl 2-formyl-3-o-tolylacrylate (5b)



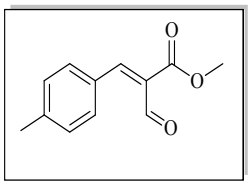
Isolated yield: 90%; yellow Liquid. **IR** cm^{-1}: 2954, 1733, 1689, 1450, 1228, 1141, 755, 687. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.68 (s, 1H), 7.79(s, 1H), 7.37-7.31 (m, 2H), 7.23-7.19(m, 2H), 3.78(s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.3, 166.0, 152.8, 148.8, 138.0, 131.1, 131.1, 130.7, 128.2, 126.2, 52.3, 19.8. **MS** (ESI): (m/z) = 205 $(M+H)^+$.

(E)-methyl 2-formyl-3-m-tolylacrylate (5c)



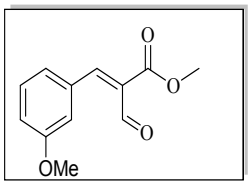
Isolated yield: 92%; yellow Liquid. **IR** cm^{-1}: 2986, 1732, 1679, 1366, 1265, 969,833, 770. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.43 (s, 1H) 7.32.-7.29(m, 4H), 3.87(s, 3H) 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.5, 166.2, 153.1, 150.3, 138.7, 132.5, 130.7, 128.9, 127.1, 52.5, 21.3. **MS** (ESI): (m/z) =205 $(M+H)^+$.

(E)-methyl 2-formyl-3-p-tolylacrylate (5d)[5]



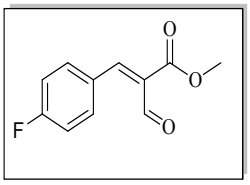
Isolated yield: 95%; yellow Liquid. **IR** cm^{-1}: 2955, 1735, 1679, 1436, 1293, 1154, 969, 833, 770. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.42 (d, J = 8.0Hz, 2H), 7.24(d, J = 7.94Hz, 2H), 7.21 (s, 1H), 3.89(s, 3H) 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.7, 166.4, 153.0, 150.3, 142.7, 141.7, 133.0, 131.5, 130.2, 129.7, 52.5, 21.5. **MS** (ESI): (m/z) = 205 $(M+H)^+$.

(E)-methyl 2-formyl-3-(3-methoxyphenyl)acrylate (5e)



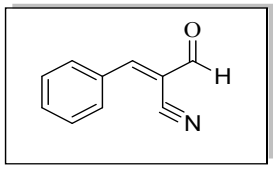
Isolated yield: 93%; yellow Liquid. **IR** cm^{-1}: 2953, 1729, 1605, 1454, 1260, 1076, 1035, 783, 699. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.43 (s, 1H), 7.34 (t, *J* = 7.9Hz, 1H), 7.10(d, *J* = 7.0Hz, 1H), 7.01 (s, 1H), 7.0 (dd, J = 2.4, 8.2Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.5, 166.1, 159.7, 149.9, 134.3, 133.5, 133.0, 122.6, 117.7,114.6, 55.2, 52.6. **MS** (ESI): (m/z) = 221 $(M+H)^+$.

(E)-methyl 3-(4-fluorophenyl)-2-formylacrylate (5f)



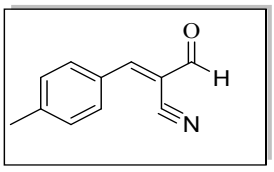
Isolated yield: 85%; yellow Liquid. **IR** cm^{-1}: 2955, 1735, 1684, 1508, 1227, 1157, 967, 835, 768, 611.**^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.58-7.54 (m, 2H), 7.45 (s, 1H), 7.15-7.10 (m, 2H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.3, 166.0, 150.8, 148.6, 132.5, 132.4, 116.4, 116.2, 52.6. **MS** (ESI): (m/z) = 209 $(M+H)^+$.

(E)-2-formyl-3-phenylacrylonitrile (7a)[6]



Isolated yield: 95%; **IR** cm^{-1}: 2224, 1690, 1576, 1464, 1270, 1162, 843, 658. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.86 (s, 1H), 7.38 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 186.7, 159.0, 158.9, 136.1, 134.3, 131.3, 131.2, 129.5, 112.3. **MS** (ESI): (m/z) = 158.17 $(M+H)^+$.

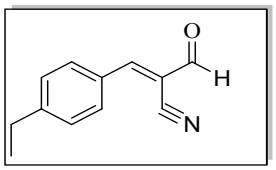
(E)-2-formyl-3-p-tolylacrylonitrile (7b)[6]



Isolated yield: 96%; **IR** cm^{-1}: 2227, 1695, 1480, 1270, 1162, 843, 658, 457. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.95 (d, *J* =

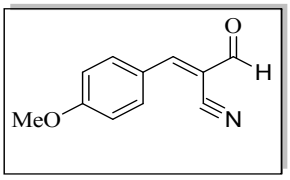
8.2 Hz, 2H), 7.86 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.4(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 186.9, 158.8.0, 146.4, 131.5, 130.3, 128.6, 114.3, 111.1, 22.0. **MS** (ESI): (m/z) = 172.07 $(M+1)^+$.

(E)-3-(4-ethylphenyl)-2-formylacrylonitrile (7c)[7]



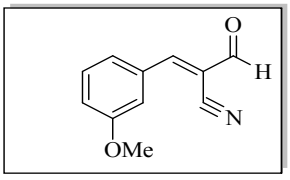
Isolated yield: 95%; White solid, mp 55-57 ^oC. **IR** cm^{-1}: 2226, 1688, 1624, 1456, 1185, 922, 830,738, 601. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.90 (s, 1H), 7.34(d, *J* = 8.1Hz, 2H), 2.75(q, 2H), 1.28(t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.0, 159.3, 159.0, 152.0, 131.6, 129.0, 128.8, 114.3, 111.1, 29.1, 14.8. **MS** (ESI): (m/z) = 186.08 $(M+H)^+$**.**

(E)-2-formyl-3-(4-methoxyphenyl)acrylonitrile (7d)[7]



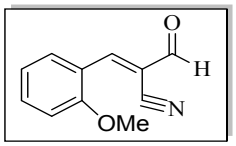
Isolated yield: 95%; **IR** cm^{-1}: 2972, 2223, 1678, 1560, 1431, 1274, 1120, 922, 826, 745. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.54 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.82 (s, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 3.92(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.0, 164.6, 158.2, 134.0, 124.1, 115.0, 114.7, 109.1, 55.7. **MS** (ESI): (m/z) =188.08 $(M+H)^+$.

(E)-2-formyl-3-(3-methoxyphenyl)acrylonitrile (7e)[8]



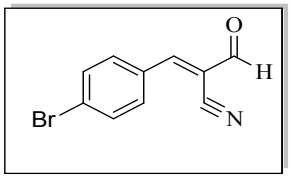
Isolated yield: 92%; **IR** cm^{-1}: 3082, 2920, 2228, 1686, 1573, 1278, 1214,779, 680. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.47(s, 1H), 8.38 (d, *J* = 7.9 Hz, 1H), 7.58(t, 1H), 7.10 (t, 1H), 7.01 (d, *J* = 8.4Hz, 1H), 3.9 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.4, 159.3, 153.4, 136.2, 129.6, 121.2, 120.2, 114.3, 111.6, 111.3, 55.8. **MS** (ESI): (m/z) = 188 $(M+H)^+$.

(E)-2-formyl-3-(2-methoxyphenyl)acrylonitrile (7f)



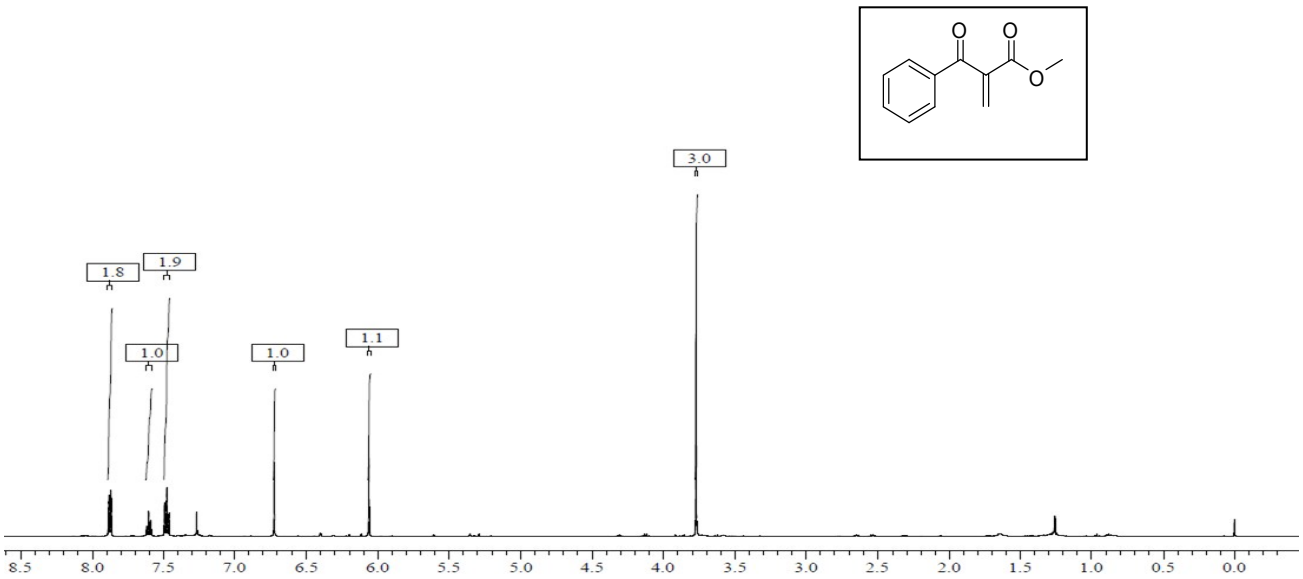
Isolated yield: 91%; **IR** cm^{-1}: 3095, 2920, 2256, 1678, 1556, 1236, 1160, 779, 680. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.47(s, 1H), 8.38 (d, J = 7.9 Hz, 1H), 7.58(t, *J* = 8.5Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.4Hz, 1H), 3.9 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.4, 159.3, 153.4, 136.2, 129.6, 121.2, 120.2, 114.3, 111.6,111.3, 55.8. **MS** (ESI): (m/z) =188 $(M+H)^+$.

(E)-3-(4-bromophenyl)-2-formylacrylonitrile (7g)[7]

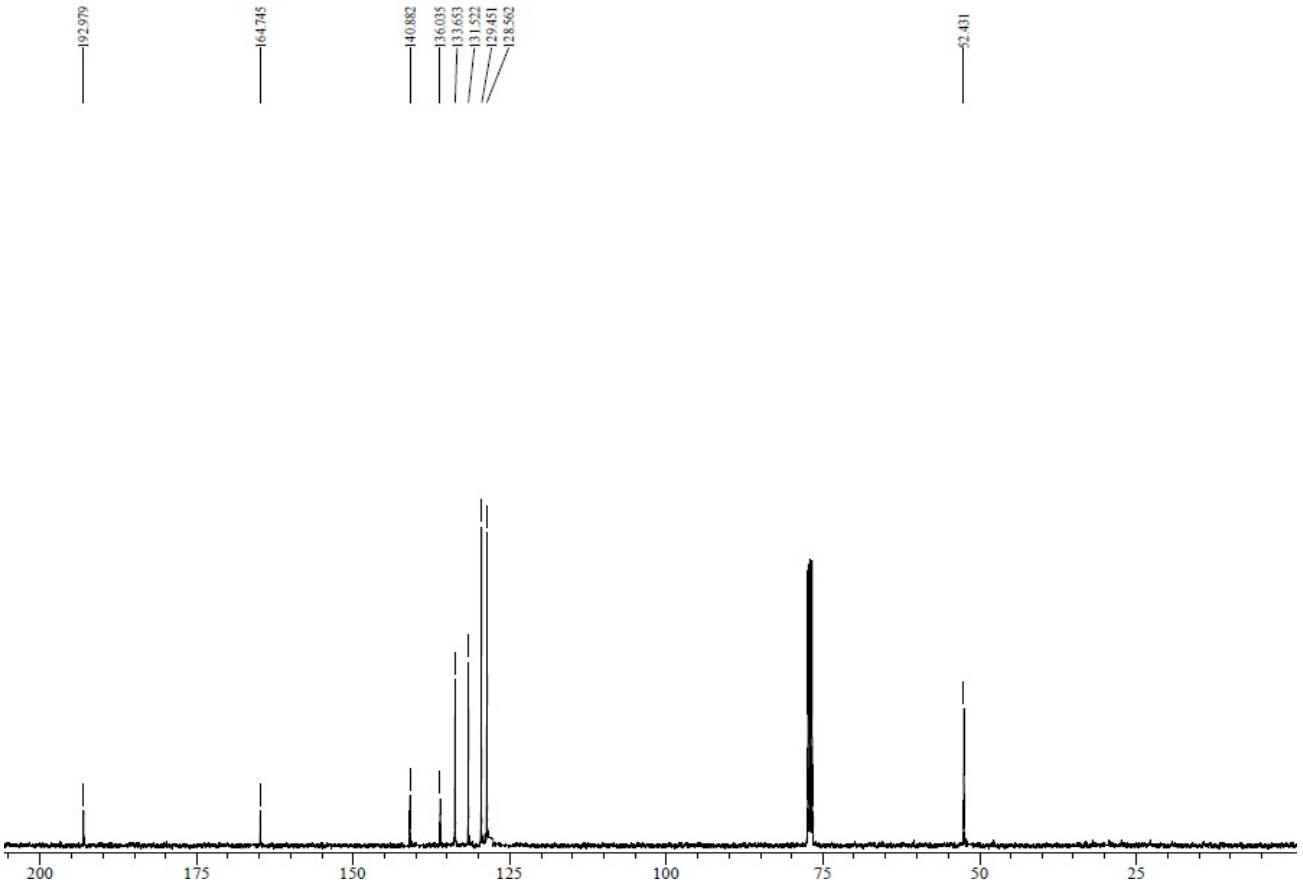


Isolated yield: 88%; **IR** cm^{-1}: 2972, 2224, 1608, 1581, 1399, 1158, 928, 759. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.91(d, J = 8.5 Hz, 2H), 7.86 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 186.3, 157.1, 132.9, 132.4, 129.9, 129.5, 113.9, 112.7. **MS** (ESI): (m/z) = 236.96 $(M+2)^+$.

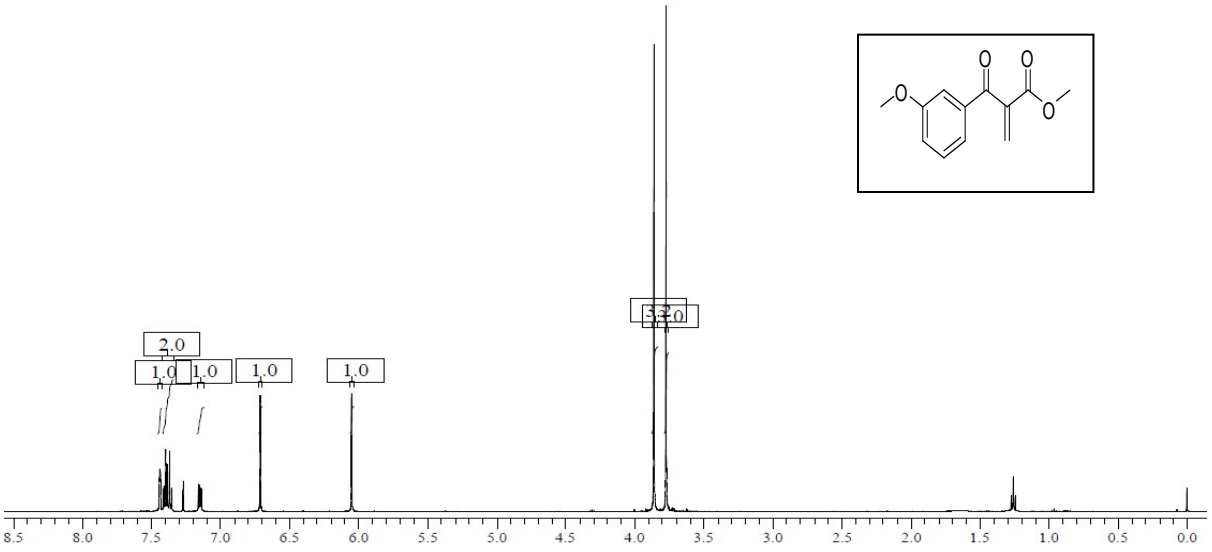
H[1] NMR Spectrum of Methyl 2-benzoylacrylate (**3a**)



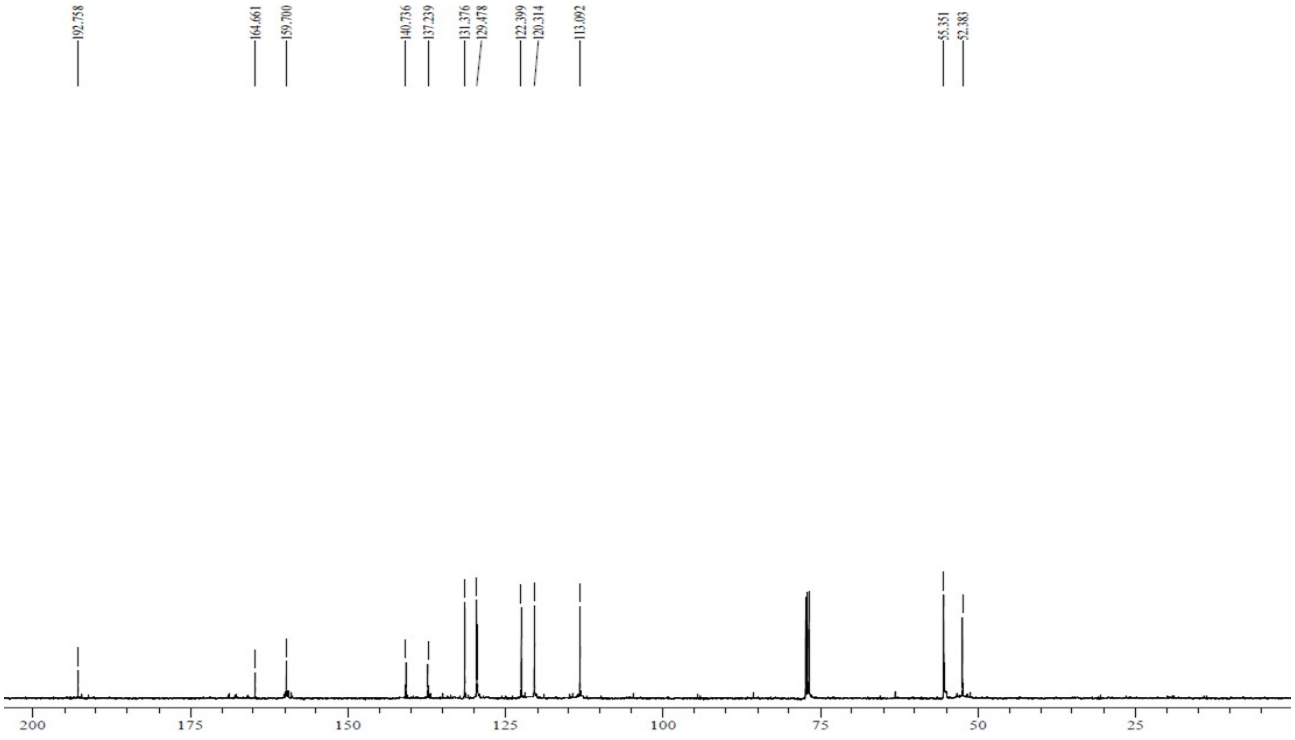
C[13] NMR Spectrum of Methyl 2-benzoylacrylate (**3a**):



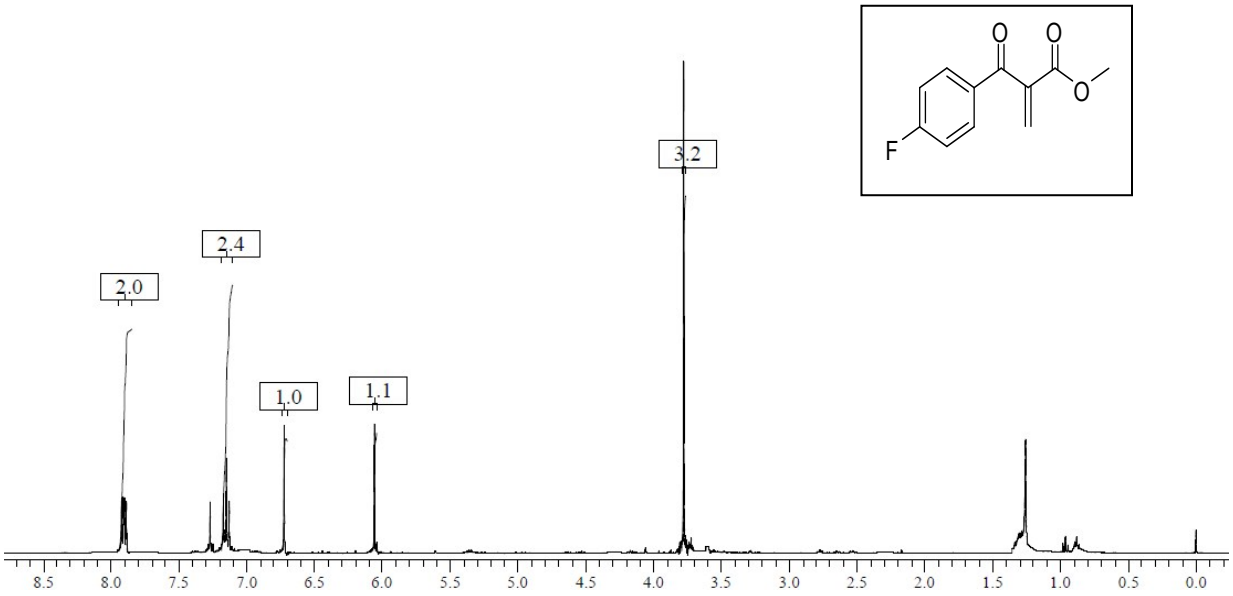
H[1] NMR Spectrum of Methyl 2-(3-methoxybenzoyl)acrylate (**3b**):



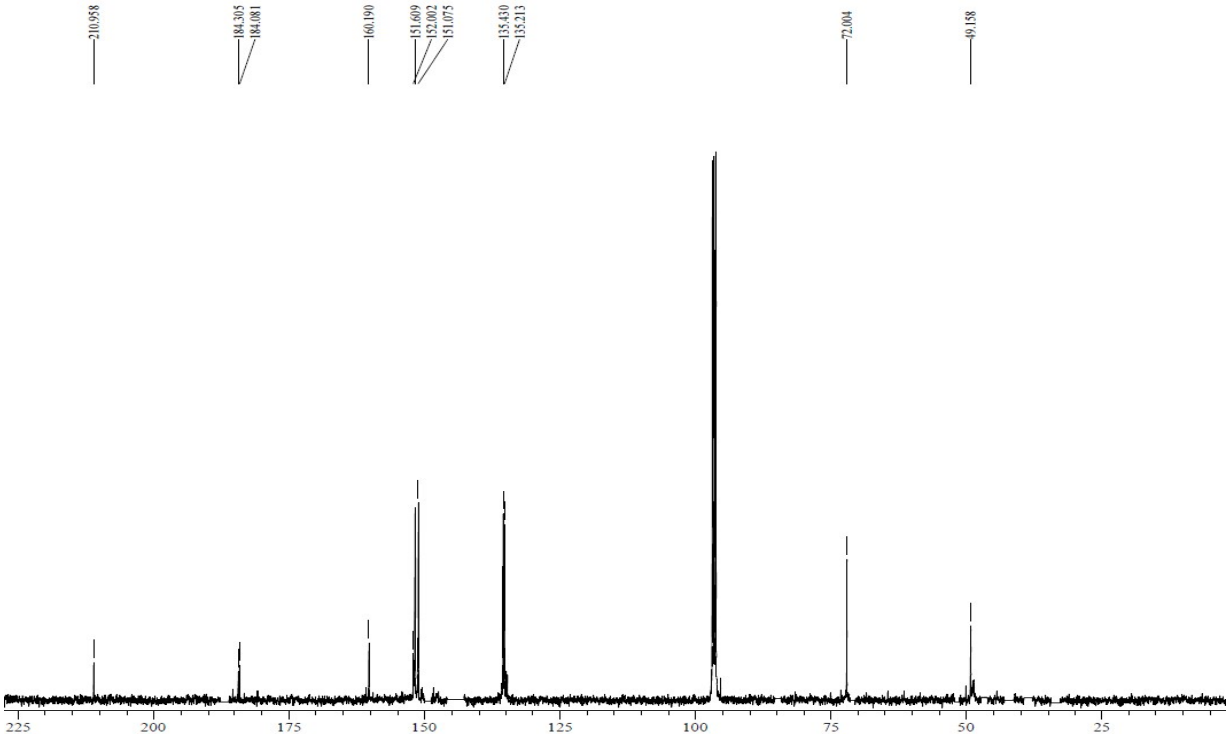
C[13] NMR Spectrum of Methyl 2-(3-methoxybenzoyl)acrylate (**3b**):



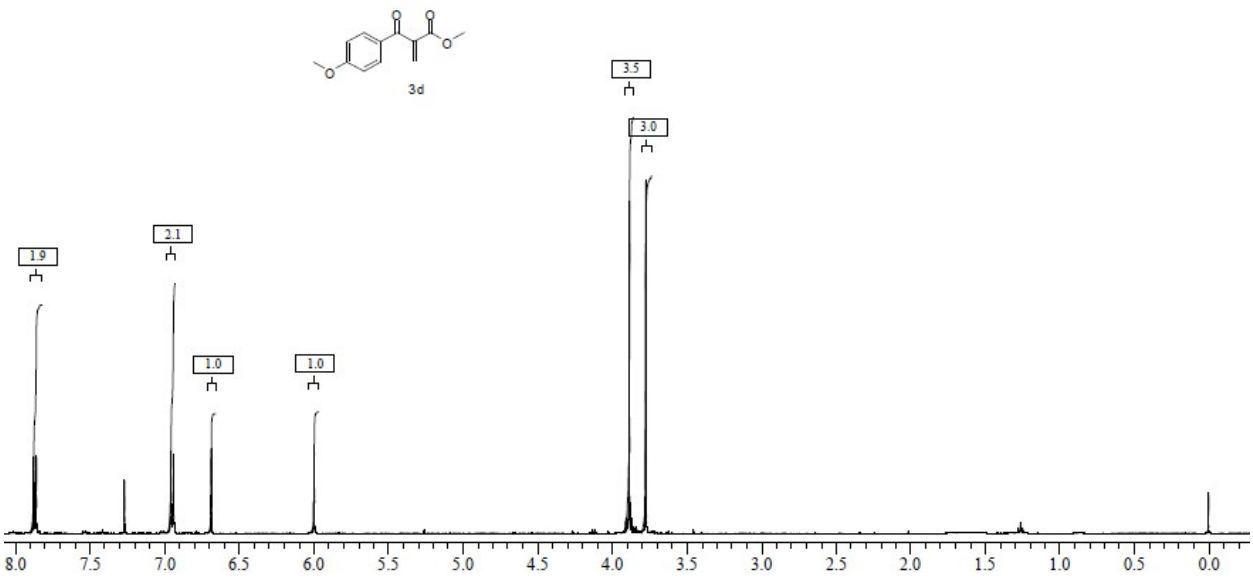
H[1] NMR Spectrum of Methyl 2-(4-fluorobenzoyl)acrylate (**3c**):



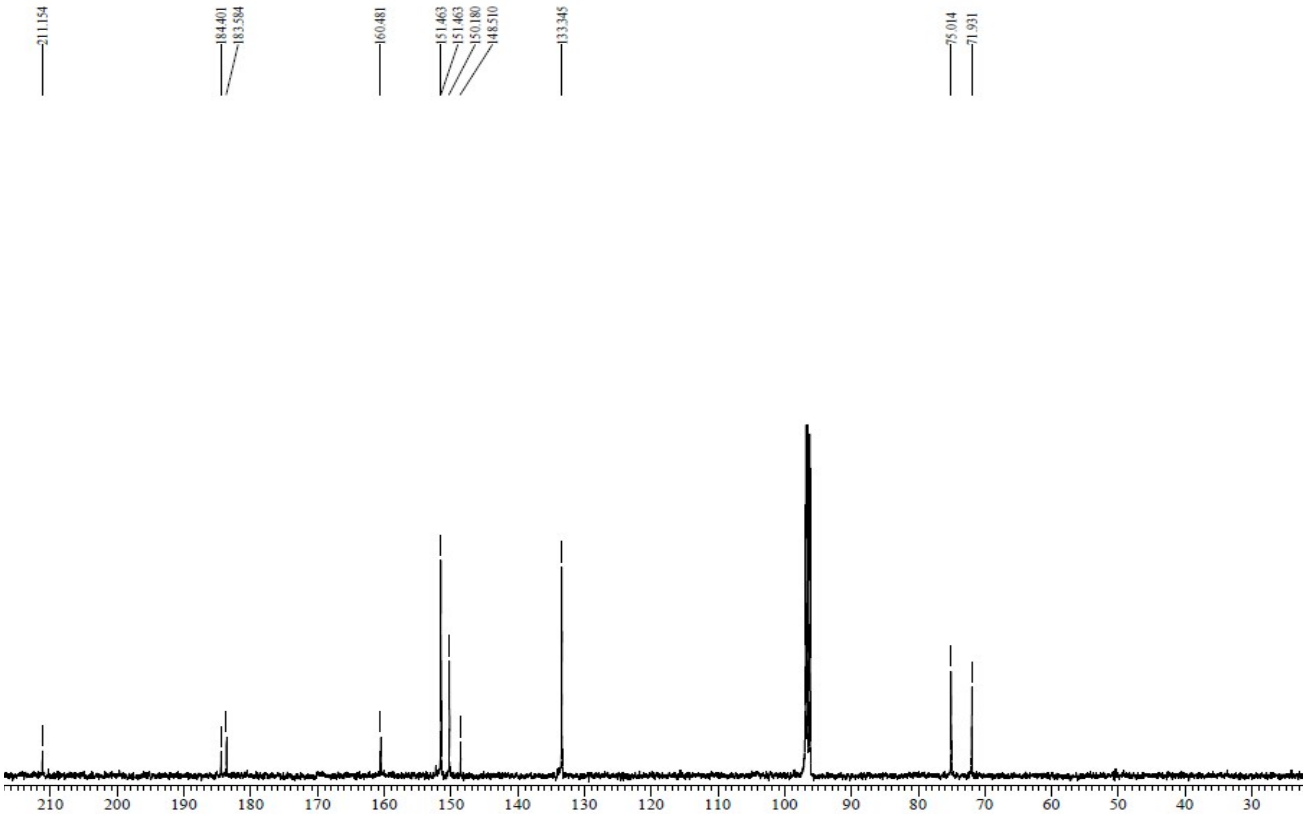
C[13] NMR Spectrum of Methyl 2-(4-fluorobenzoyl)acrylate (**3c**):



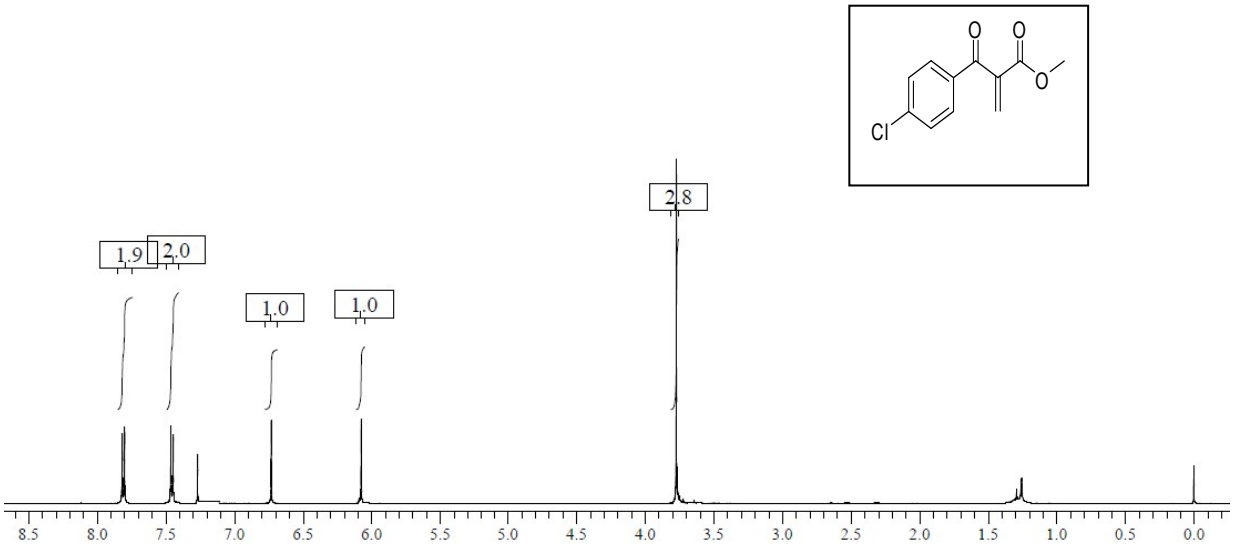
H[1] NMR Spectrum of Methyl 2-(4-methoxybenzoyl)acrylate (**3d**):



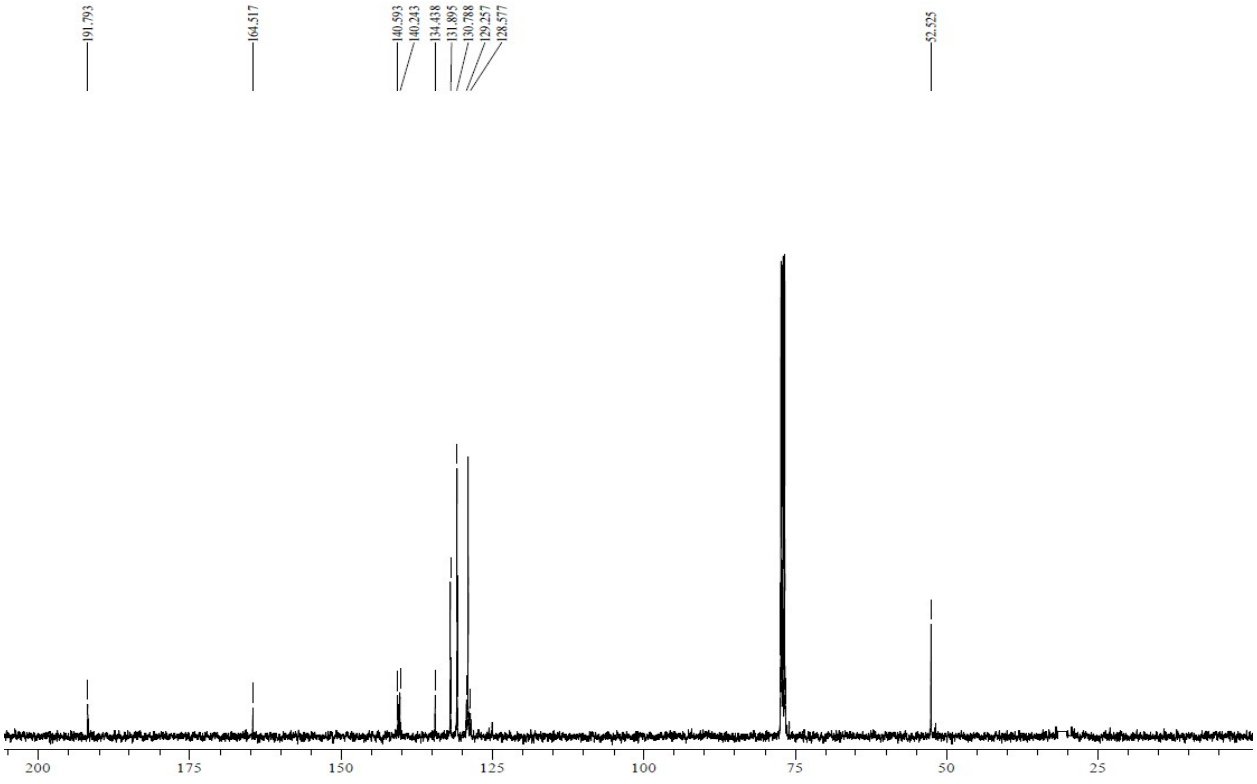
C[13] NMR Spectrum of Methyl 2-(4-methoxybenzoyl)acrylate (**3d**):



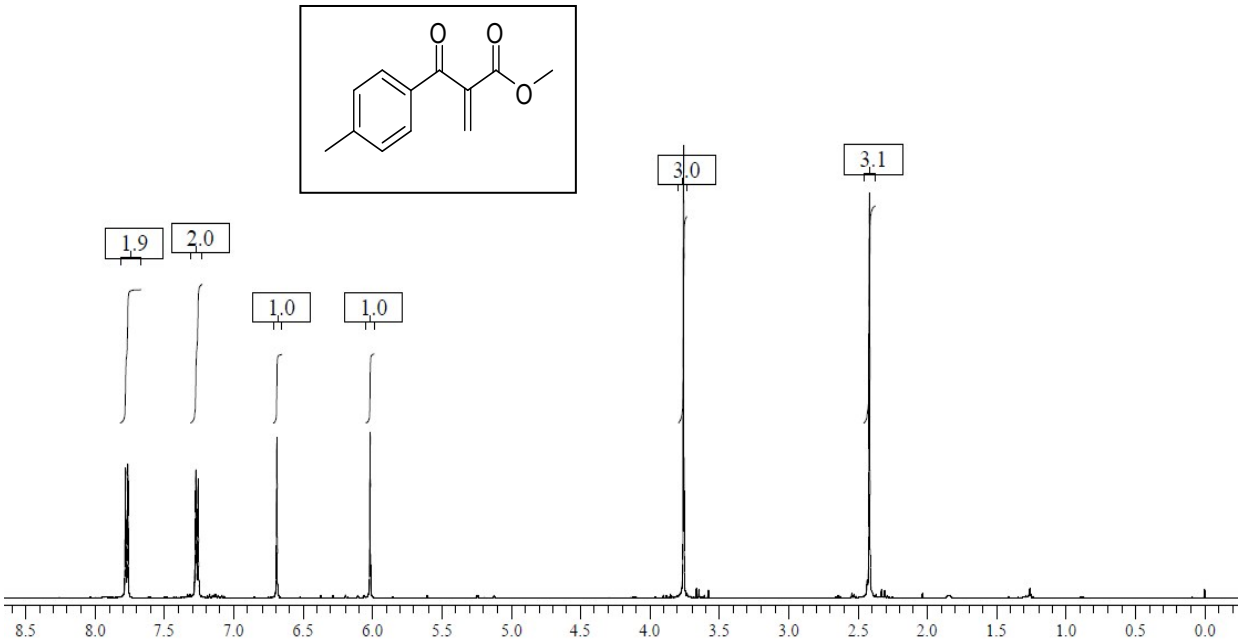
H[1] NMR Spectrum of Methyl 2-(4-chlorobenzoyl)acrylate (**3e**):



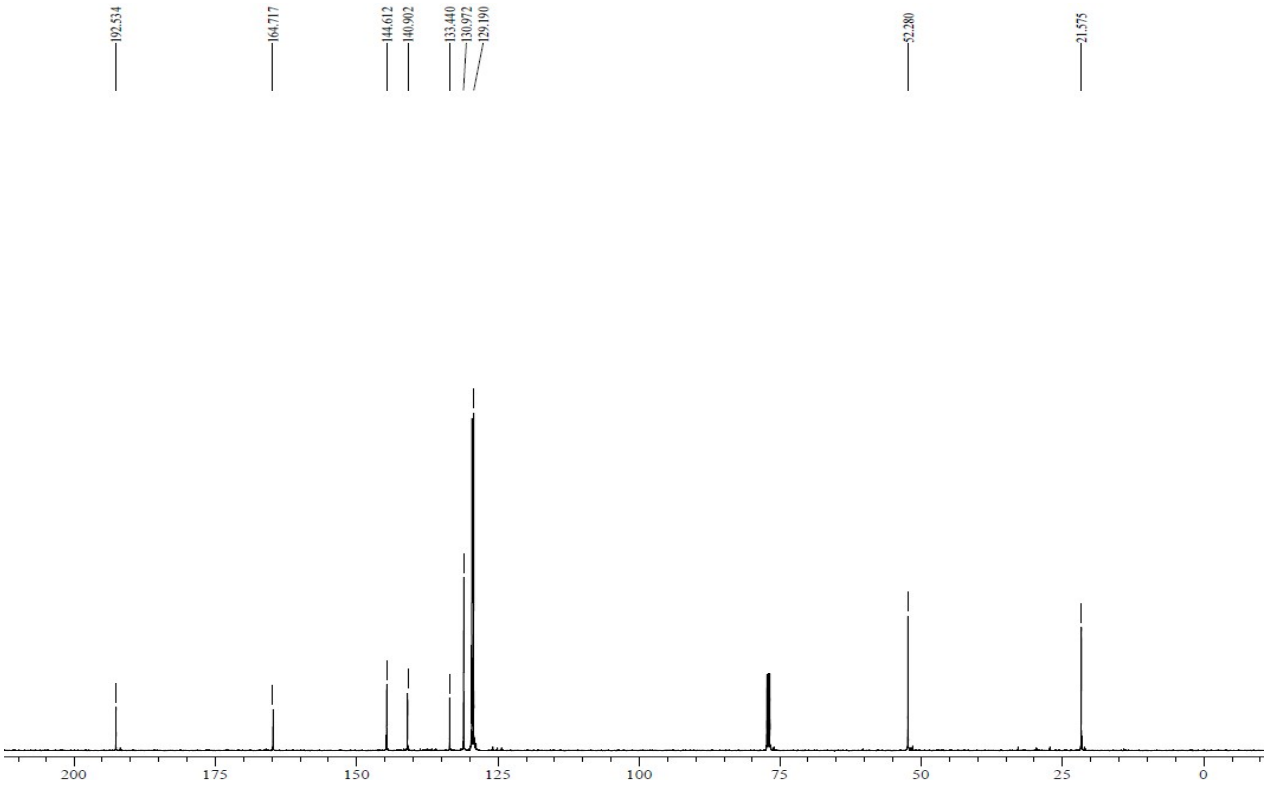
C[13] NMR Spectrum of Methyl 2-(4-chlorobenzoyl)acrylate (**3e**):



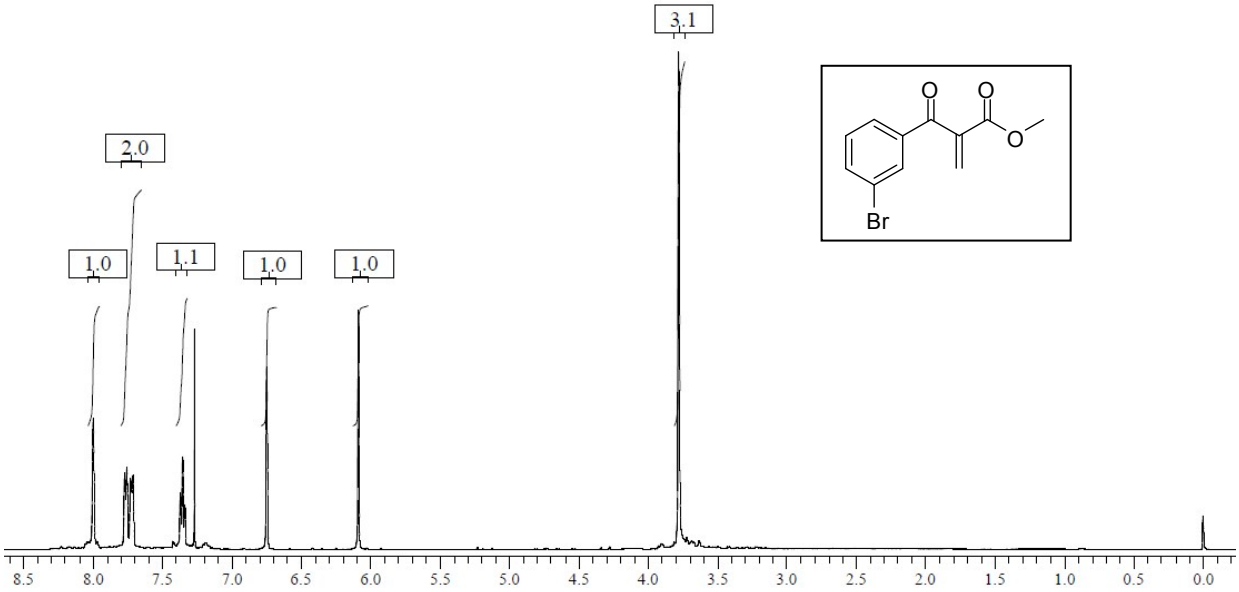
H[1] NMR Spectrum of Methyl 2-(4-methylbenzoyl)acrylate (**3f**):



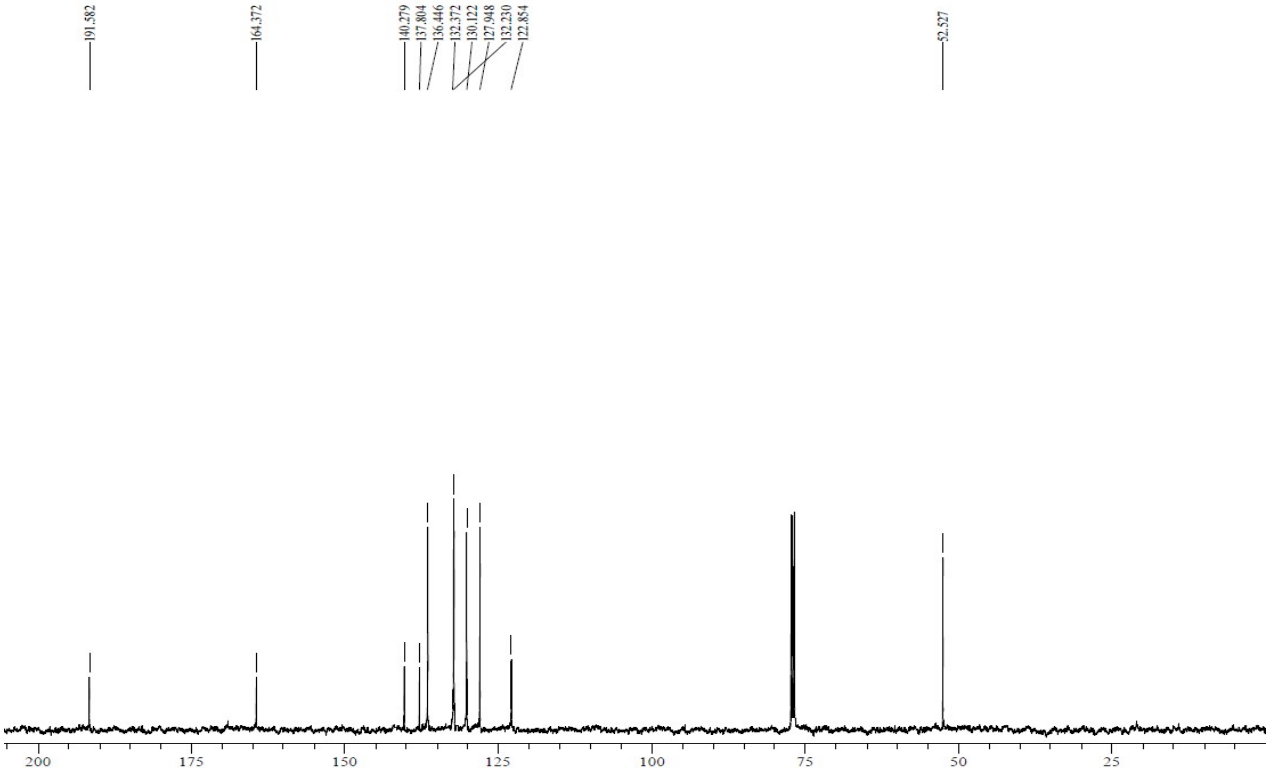
C[13] NMR Spectrum of Methyl 2-(4-methylbenzoyl)acrylate (**3f**):



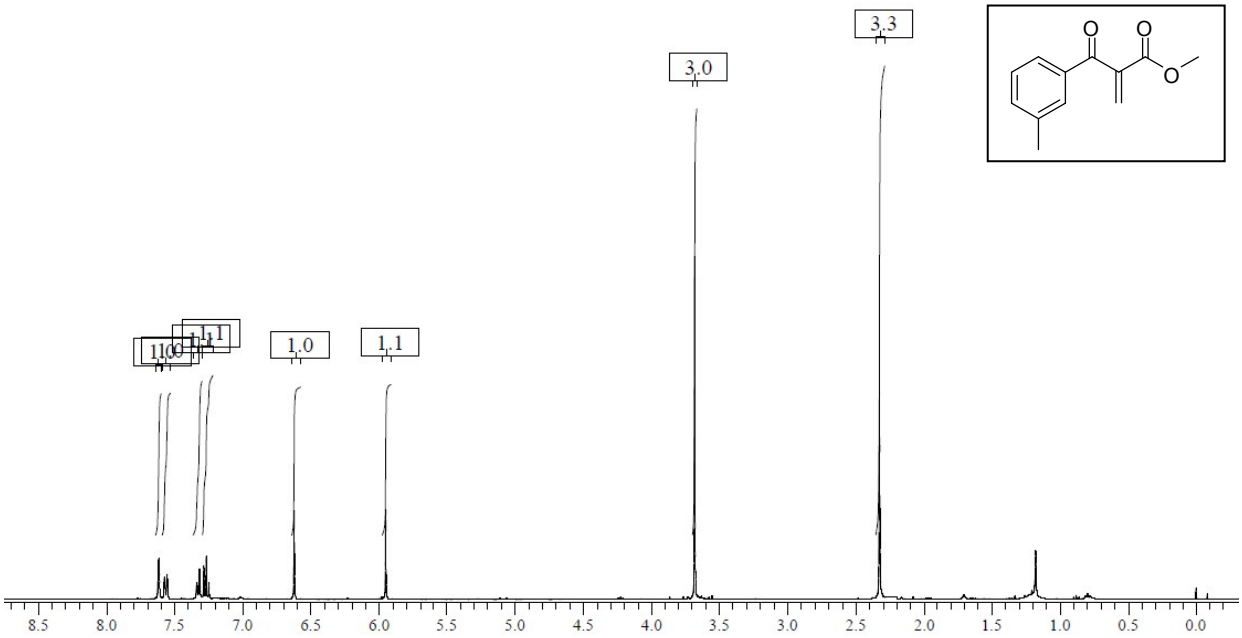
H[1] NMR Spectrum of Methyl 2-(3-bromobenzoyl)acrylate (**3g**):



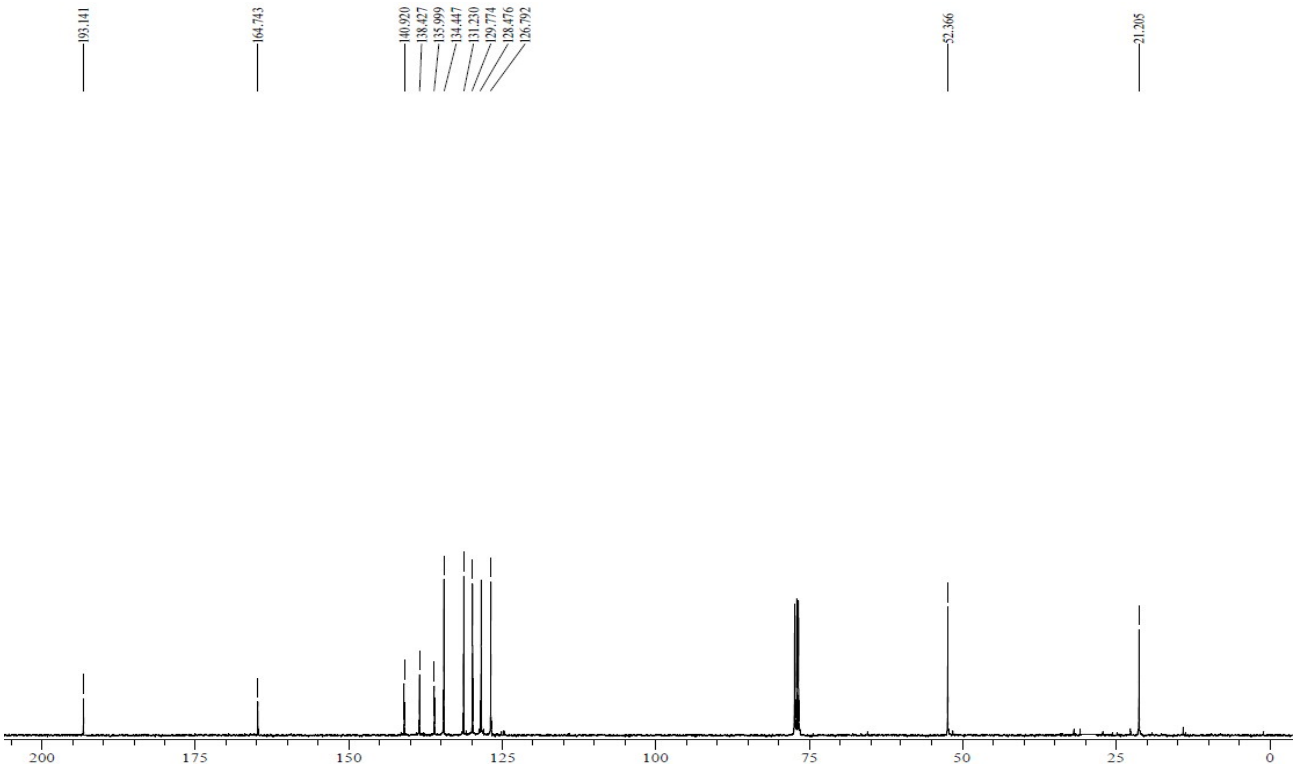
C[13] NMR Spectrum of of Methyl 2-(3-bromobenzoyl)acrylate (**3g**):



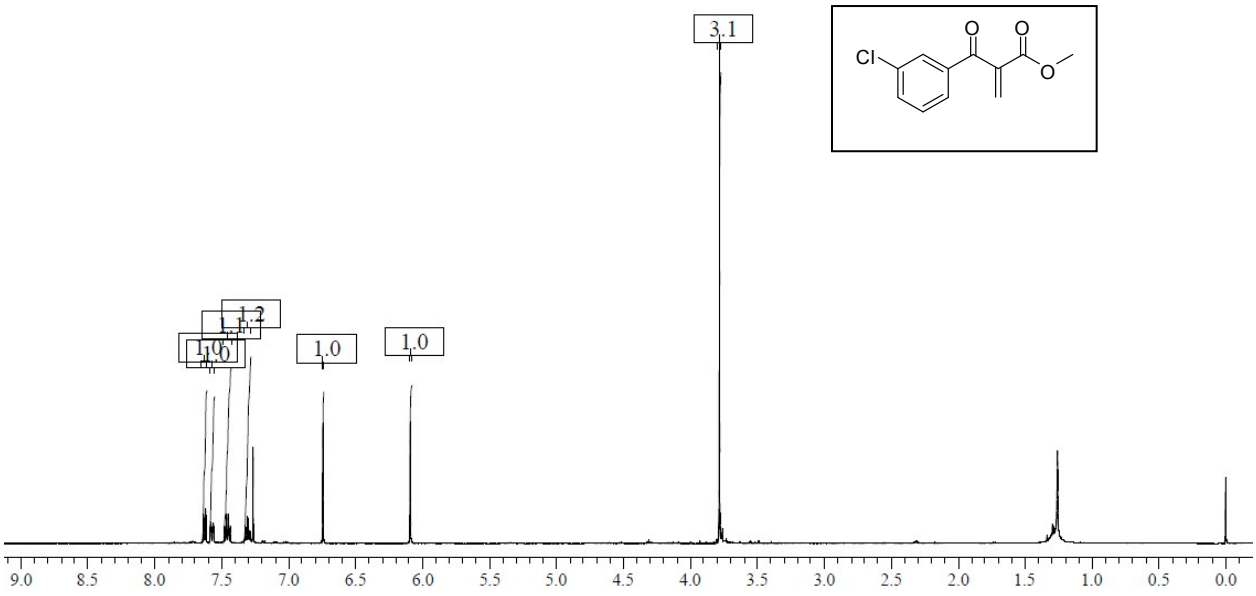
H[1] NMR Spectrum of Methyl 2-(3-methylbenzoyl)acrylate (**3h**):



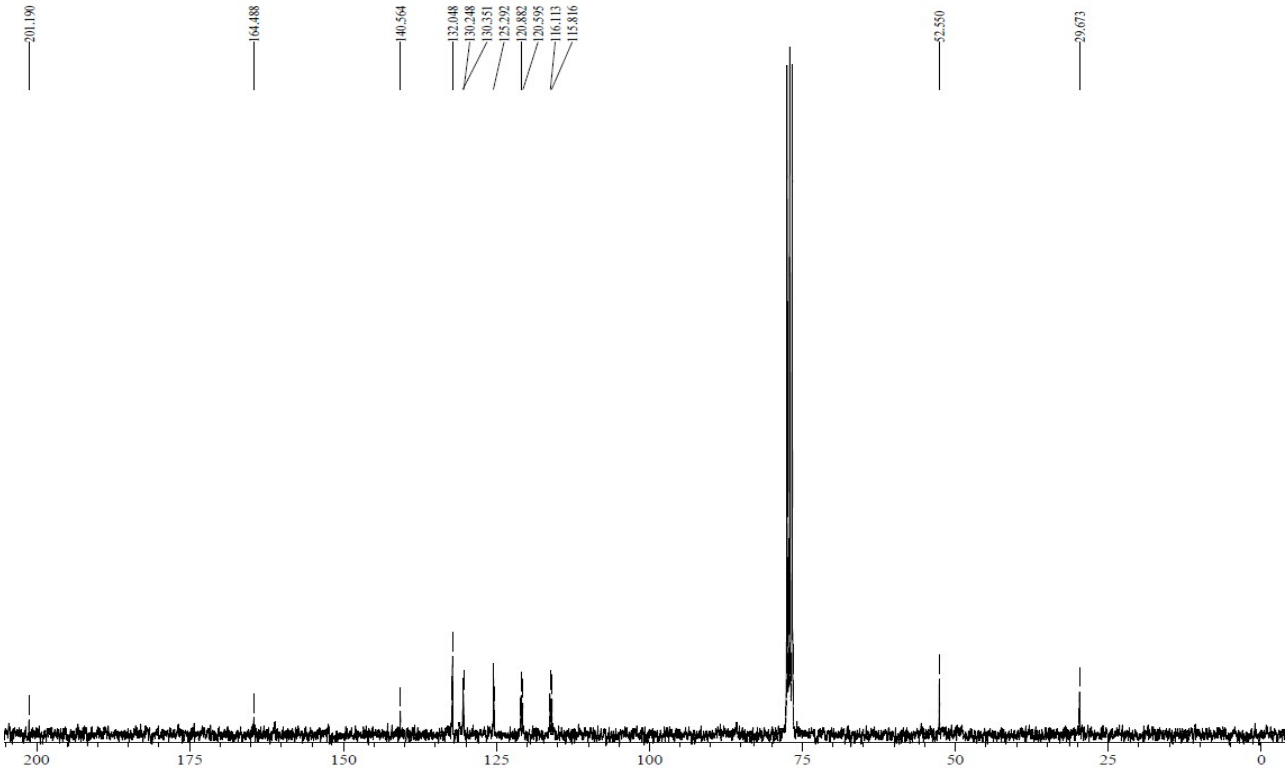
C[13] NMR Spectrum of Methyl 2-(3-methylbenzoyl)acrylate (**3h**):



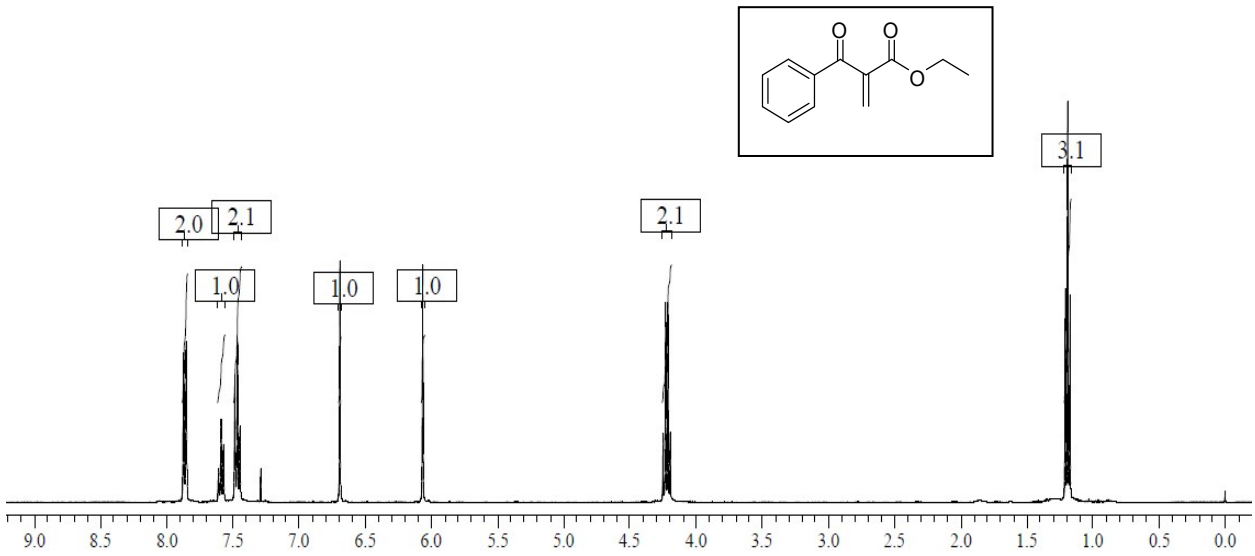
H[1] NMR Spectrum of Methyl 2-(3-chlorobenzoyl)acrylate (**3i**):



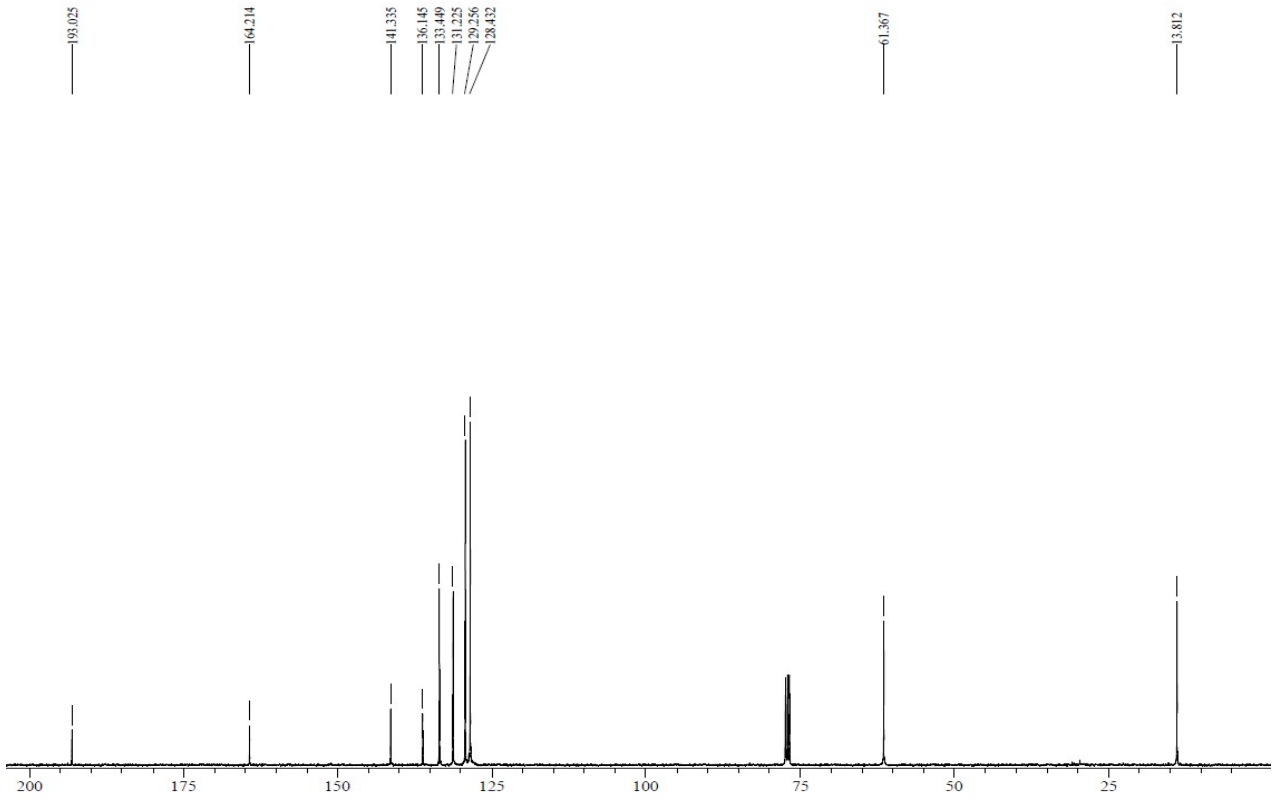
C[13] NMR Spectrum of of Methyl 2-(3-chlorobenzoyl)acrylate (**3i**):



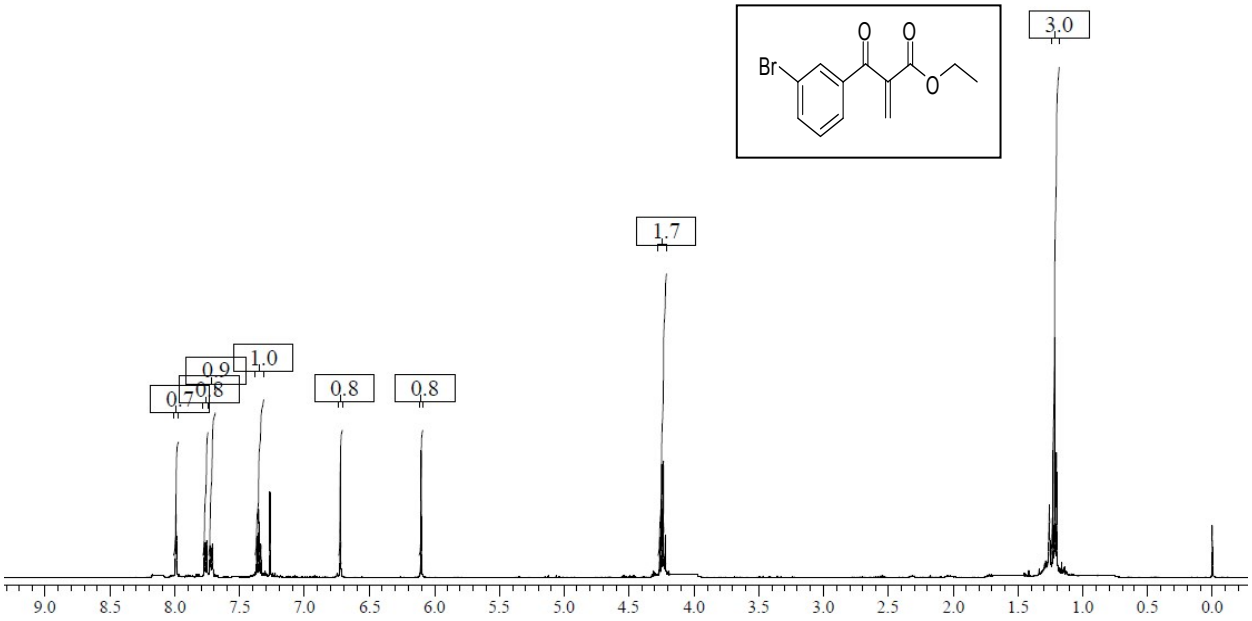
H[1] NMR Spectrum of Ethyl 2-benzoylacrylate (**3j**):



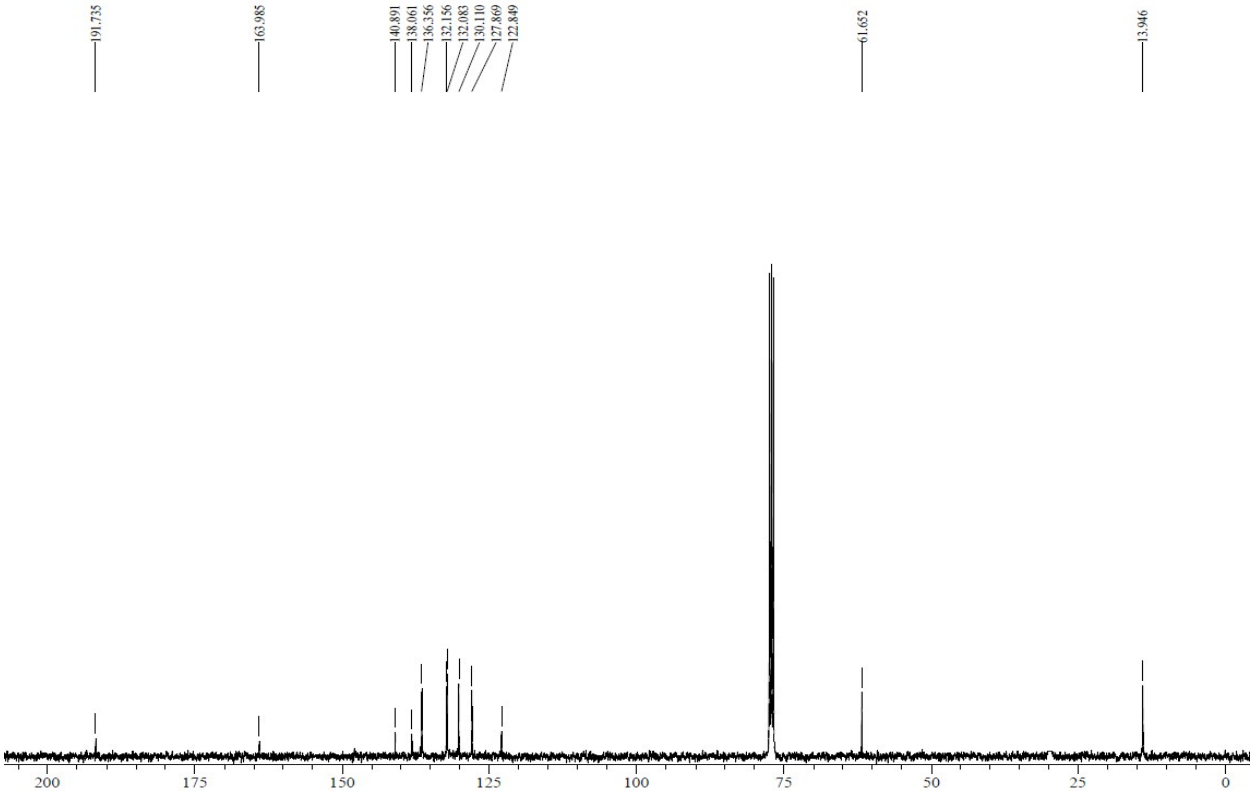
C[13] NMR Spectrum of Ethyl 2-benzoylacrylate (**3j**):



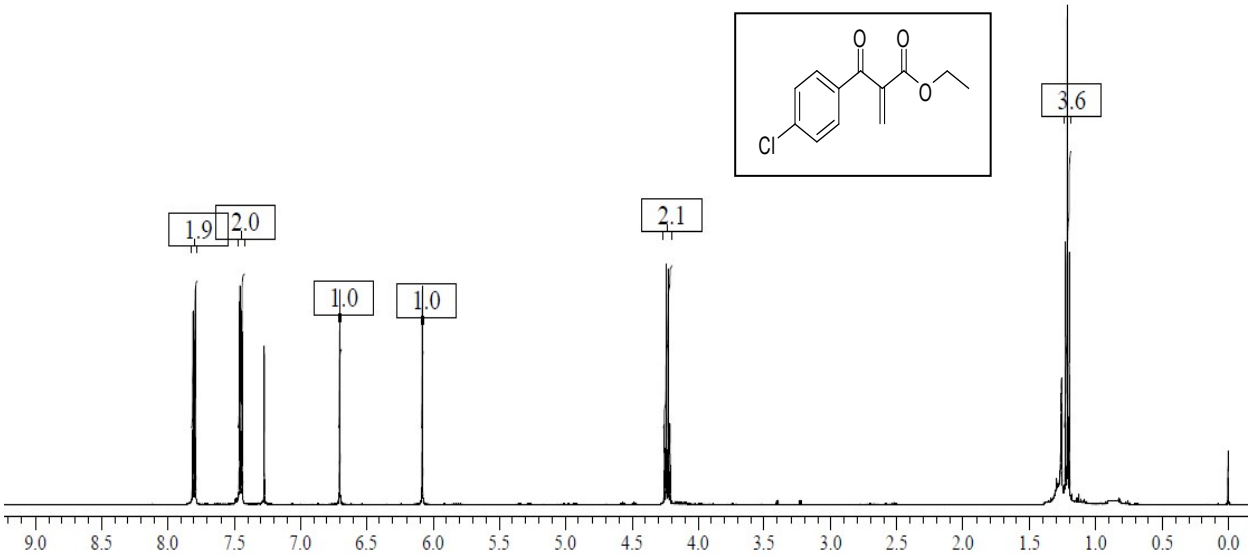
H[1] NMR Spectrum of Ethyl 2-(3-bromobenzoyl)acrylate (**3k**):



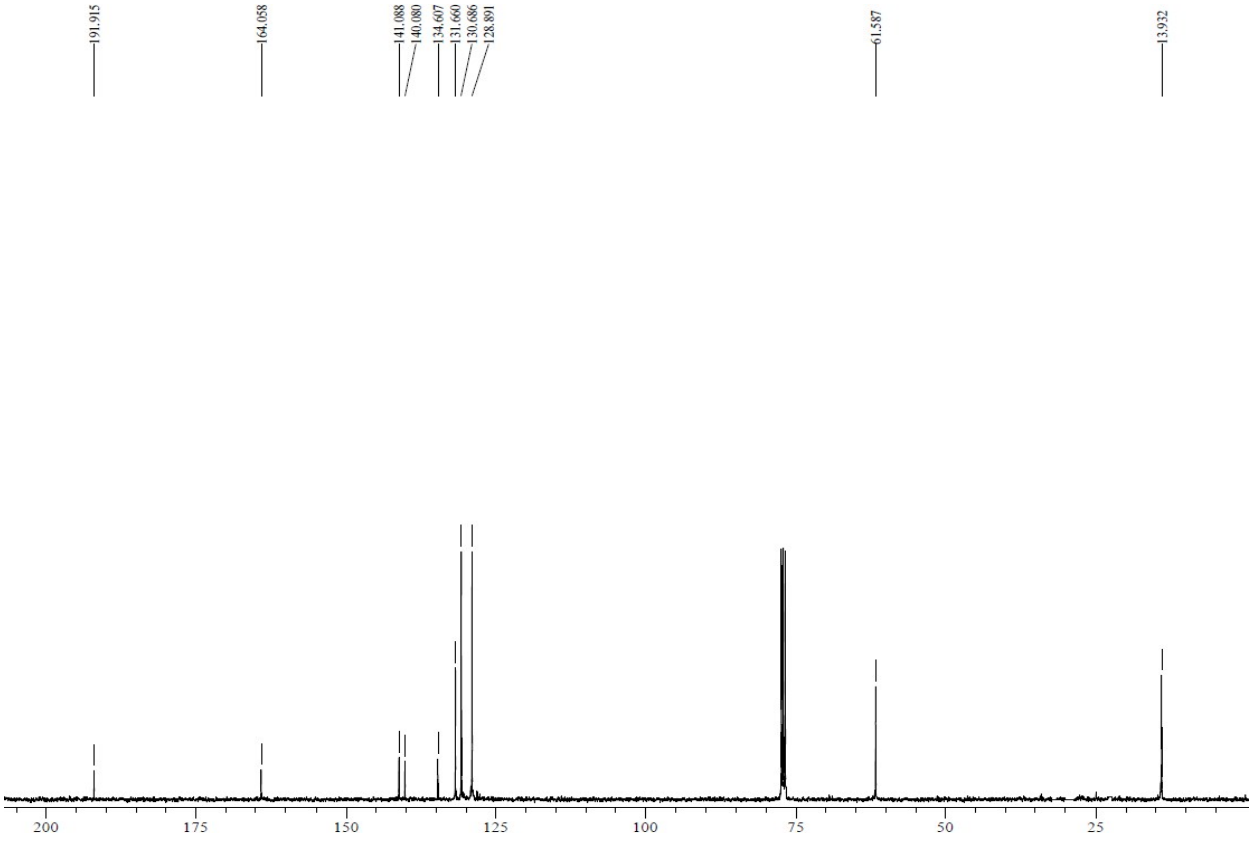
C[13] NMR Spectrum of Ethyl 2-(3-bromobenzoyl)acrylate (**3k**):



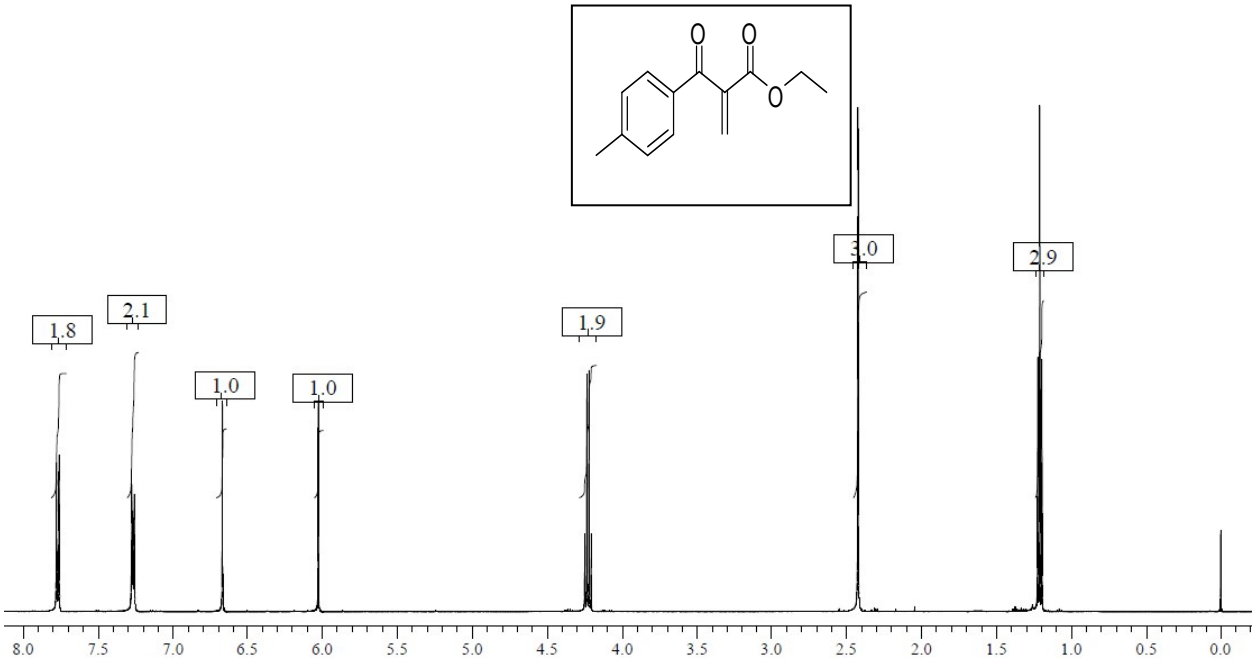
H[1] NMR Spectrum of Ethyl 2-(4-chlorobenzoyl)acrylate (**3l**):



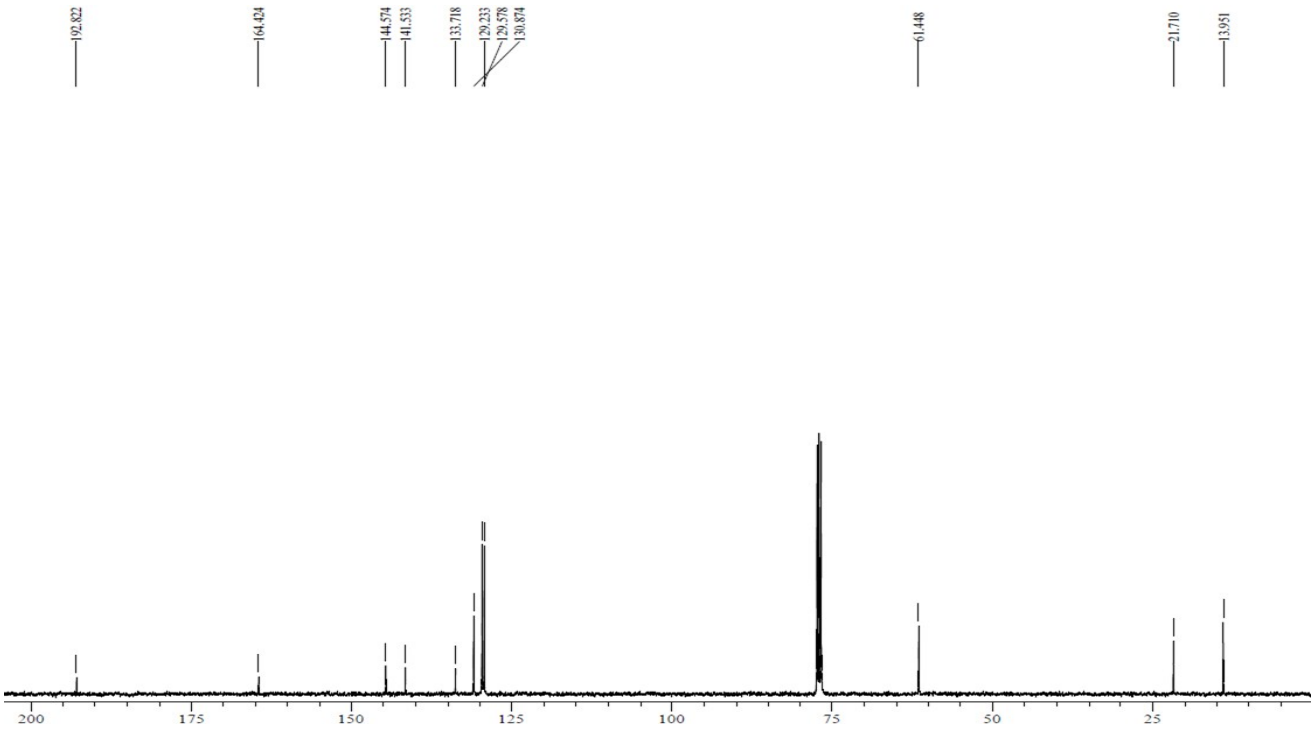
C[13] NMR Spectrum Ethyl 2-(4-chlorobenzoyl)acrylate (**3l**):



H[1] NMR Spectrum of Ethyl 2-(4-methylbenzoyl)acrylate (**3m**):

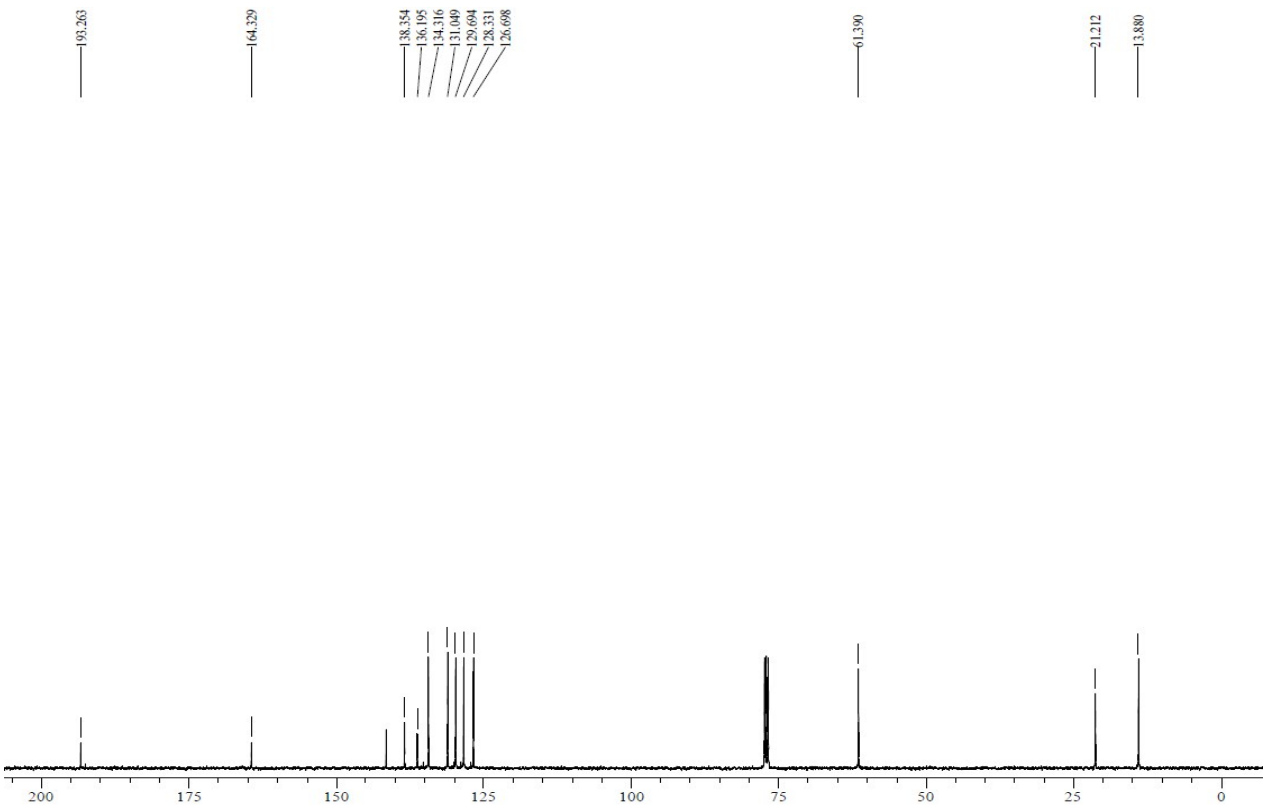


C[13] NMR Spectrum Ethyl 2-(4-methylbenzoyl)acrylate (**3m**):

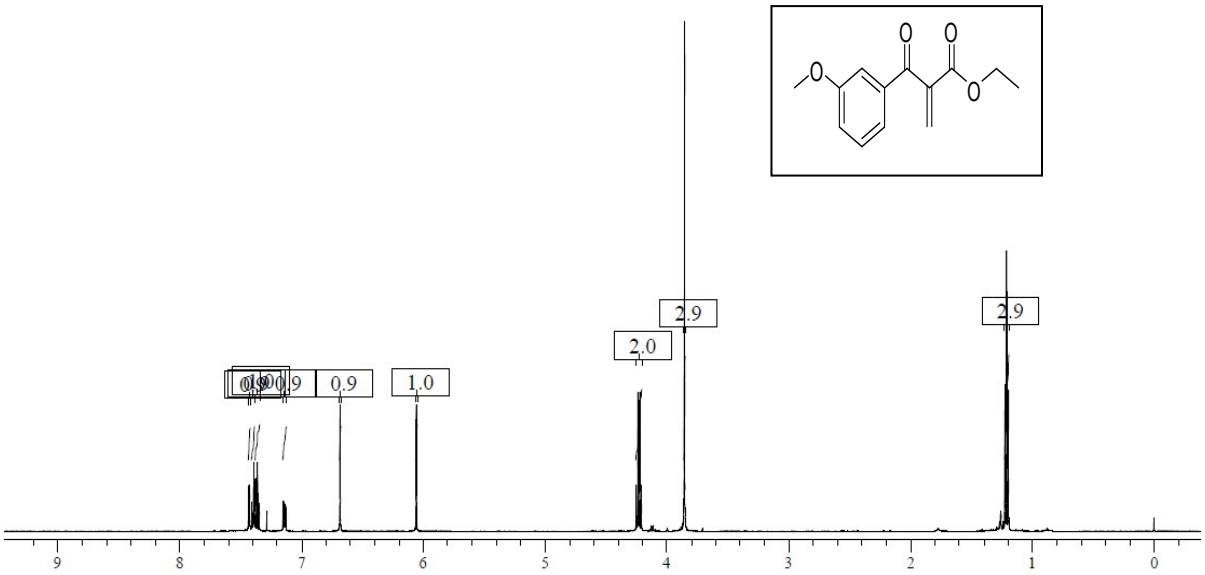


H[1] NMR Spectrum of Ethyl 2-(3-methylbenzoyl)acrylate (**3n**):

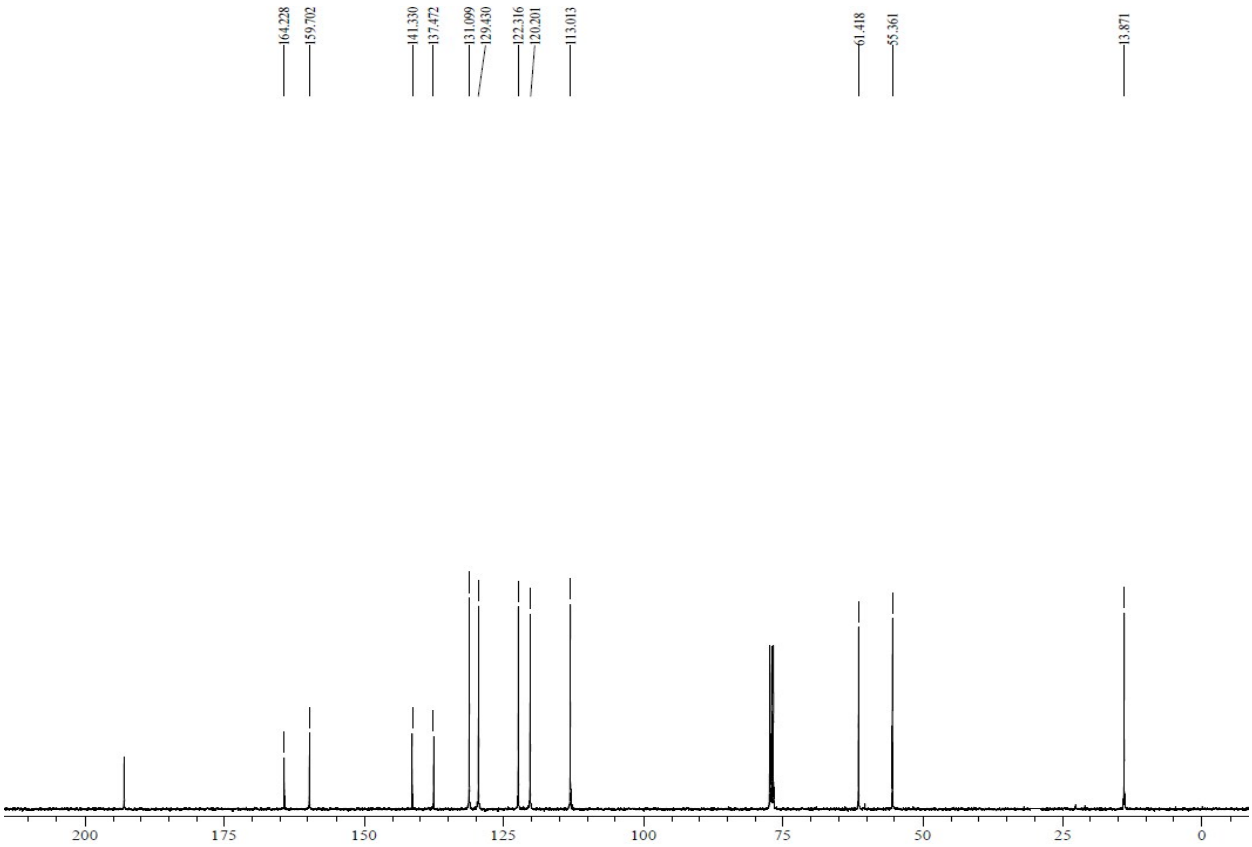
C[13] NMR Spectrum of Ethyl 2-(3-methylbenzoyl)acrylate (**3n**):



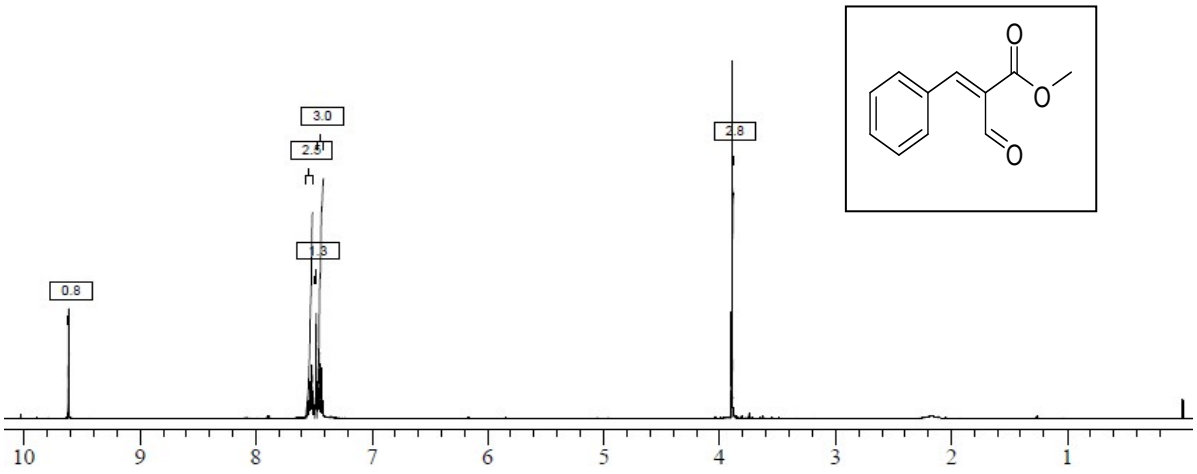
H[1] NMR Spectrum of Ethyl 2-(3-methoxybenzoyl)acrylate (**3o**):



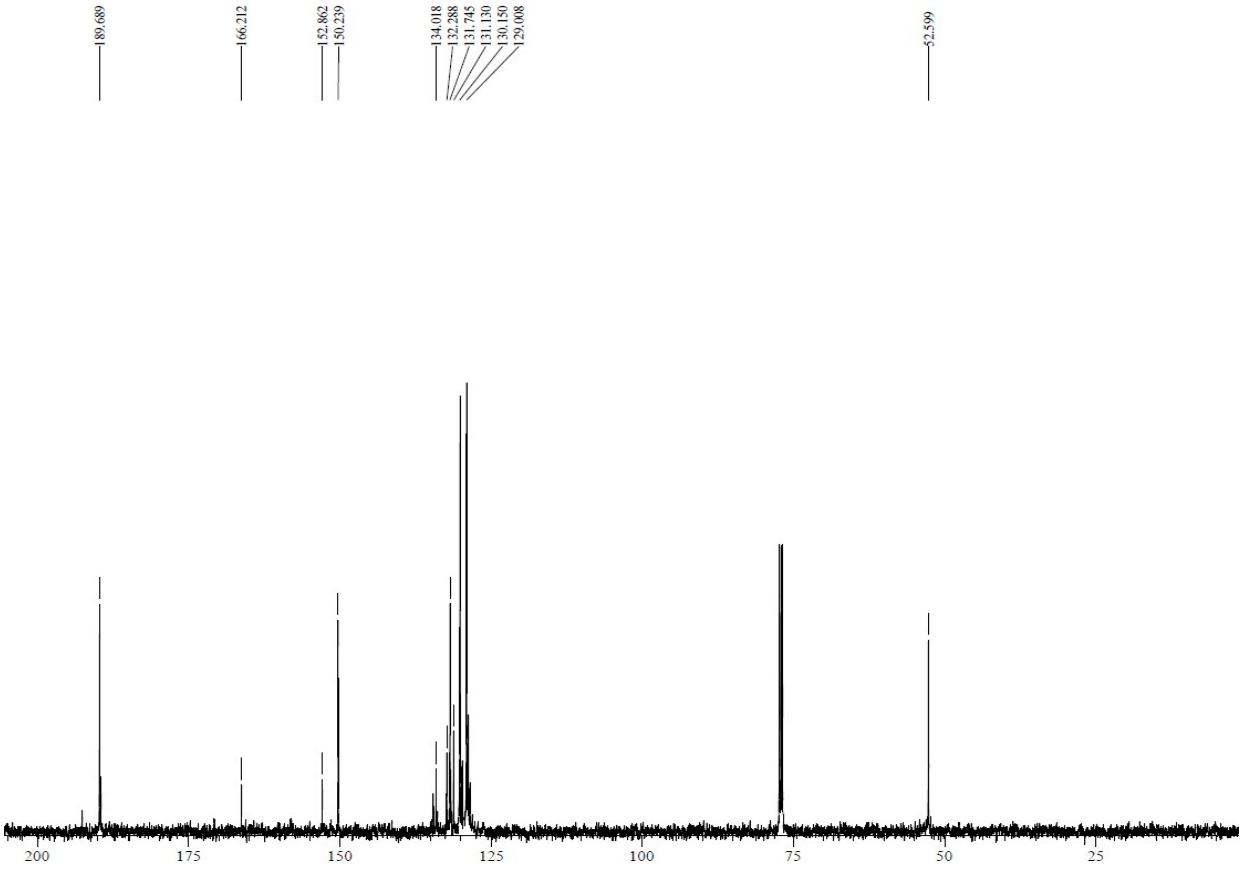
C[13] NMR Spectrum of Ethyl 2-(3-methoxybenzoyl)acrylate (**3o**):



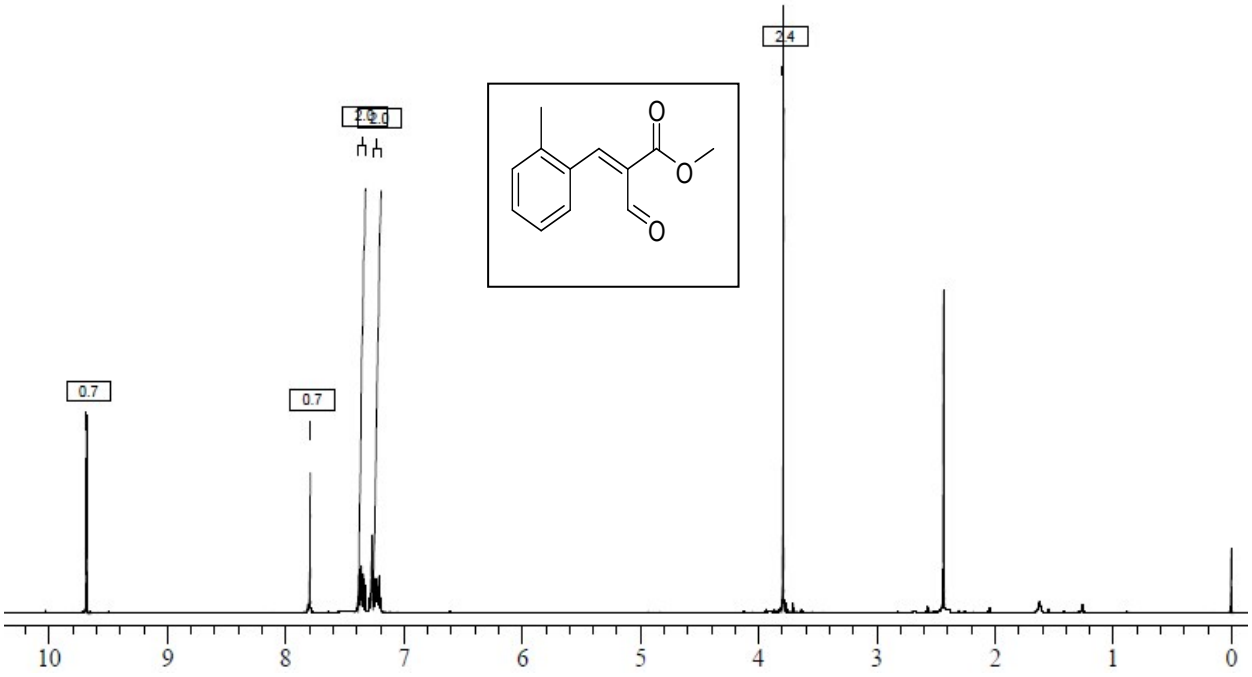
H[1] NMR Spectrum of (E)-Methyl 2-formyl-3-phenylacrylate (**5a**):



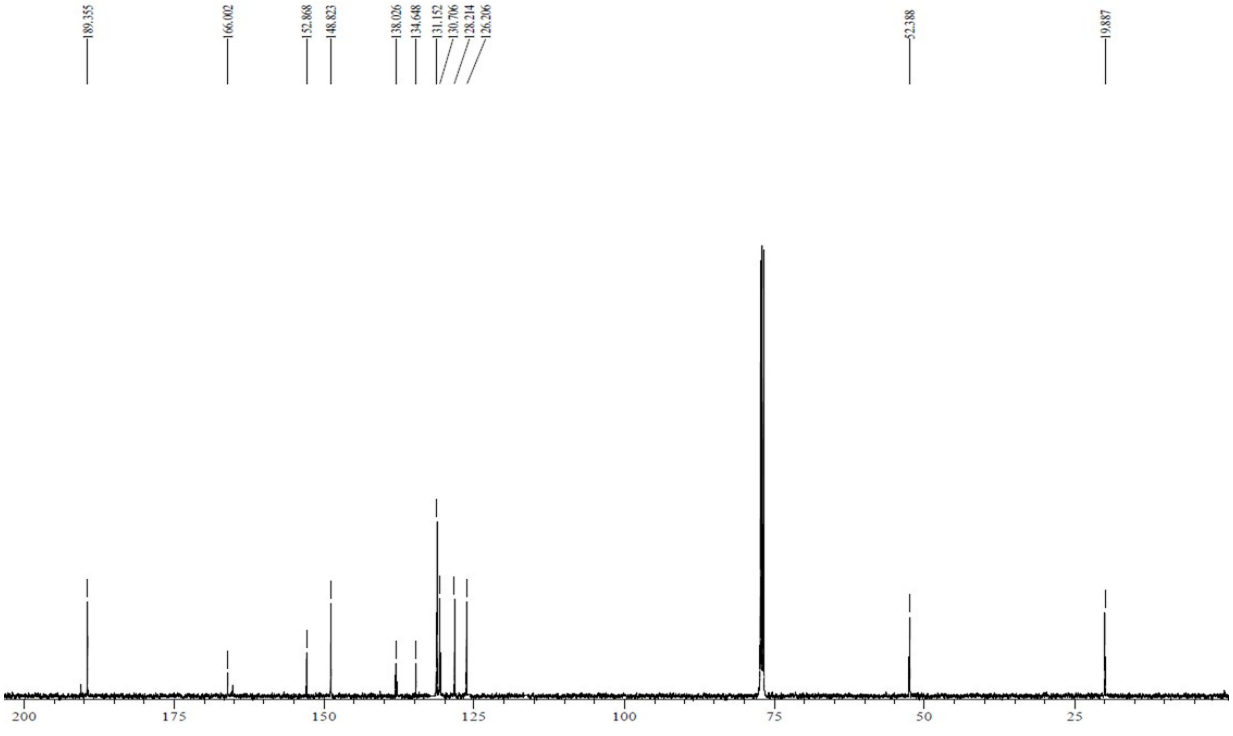
C[13] NMR Spectrum of (E)-Methyl 2-formyl-3-phenylacrylate (**5a**):



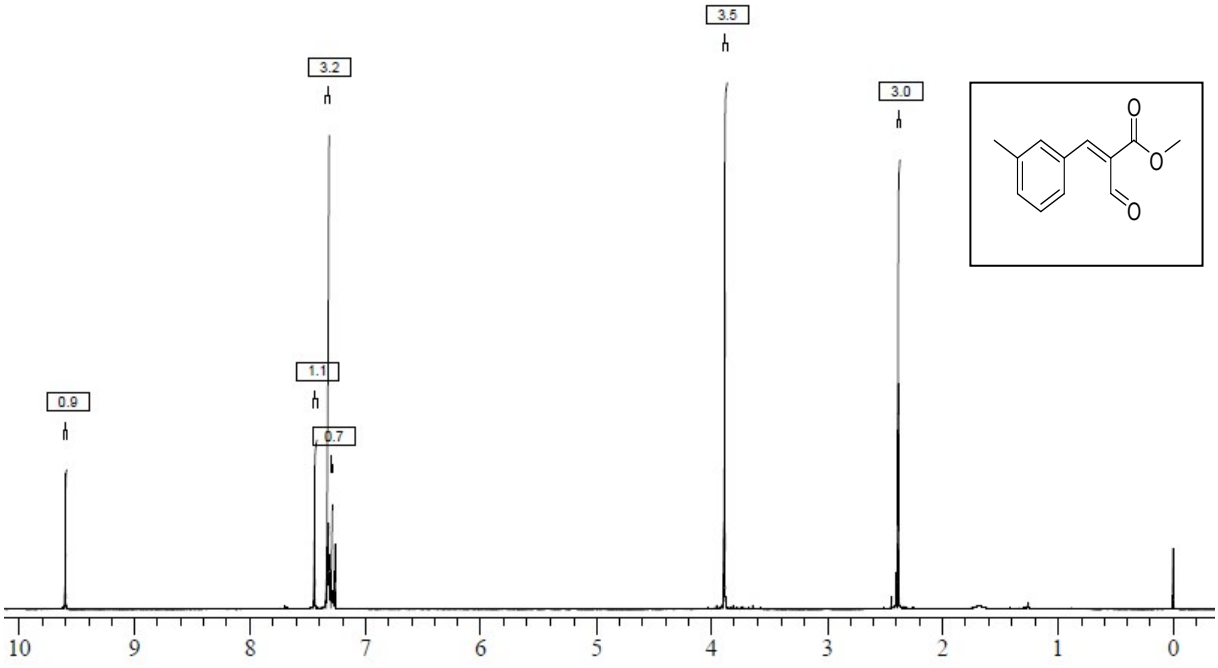
H[1] NMR Spectrum of (E)-Methyl 2-formyl-3-o-tolylacrylate (**5b**):



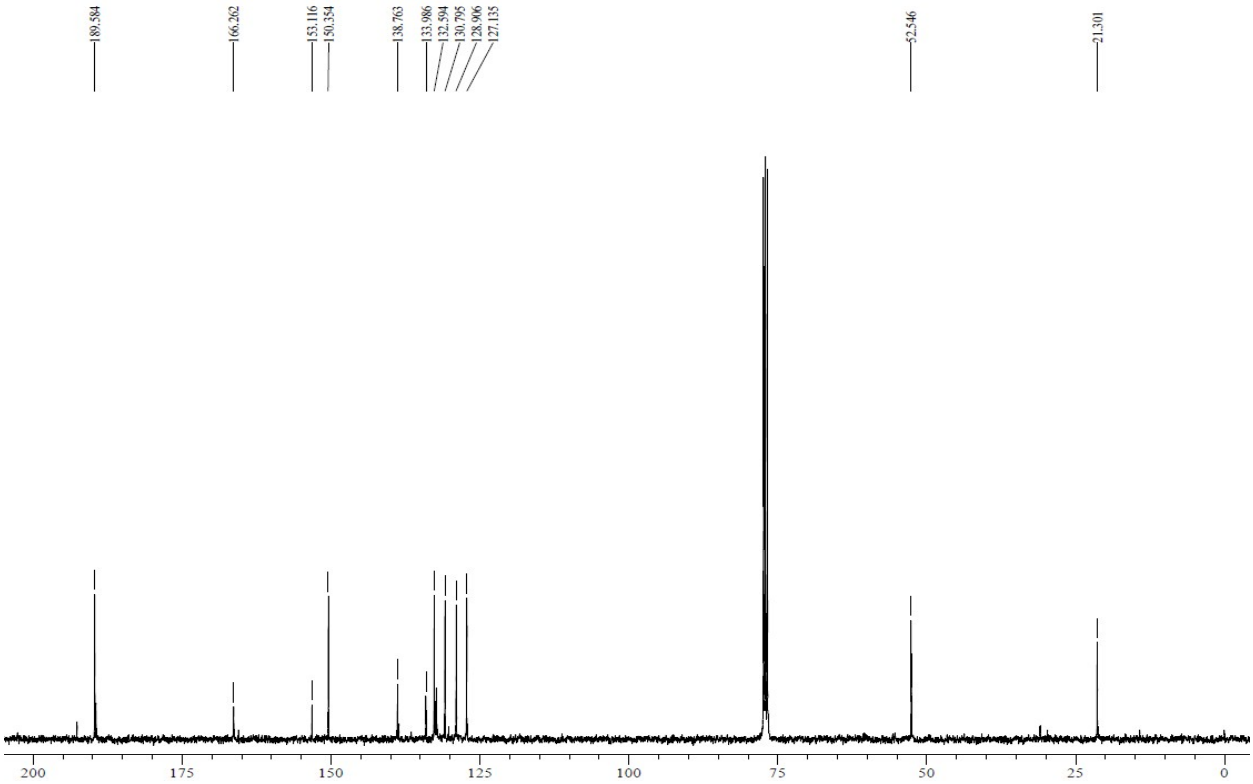
C[13] NMR Spectrum of (E)-Methyl 2-formyl-3-o-tolylacrylate (**5b**):



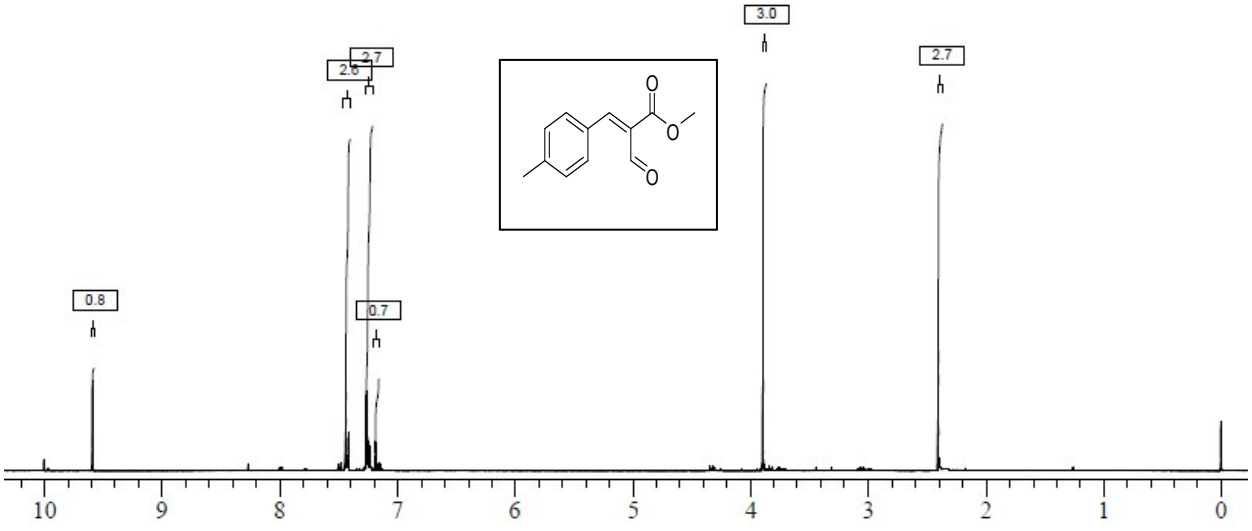
H[1] NMR Spectrum of (E)-Methyl 2-formyl-3-m-tolylacrylate (**5c**):



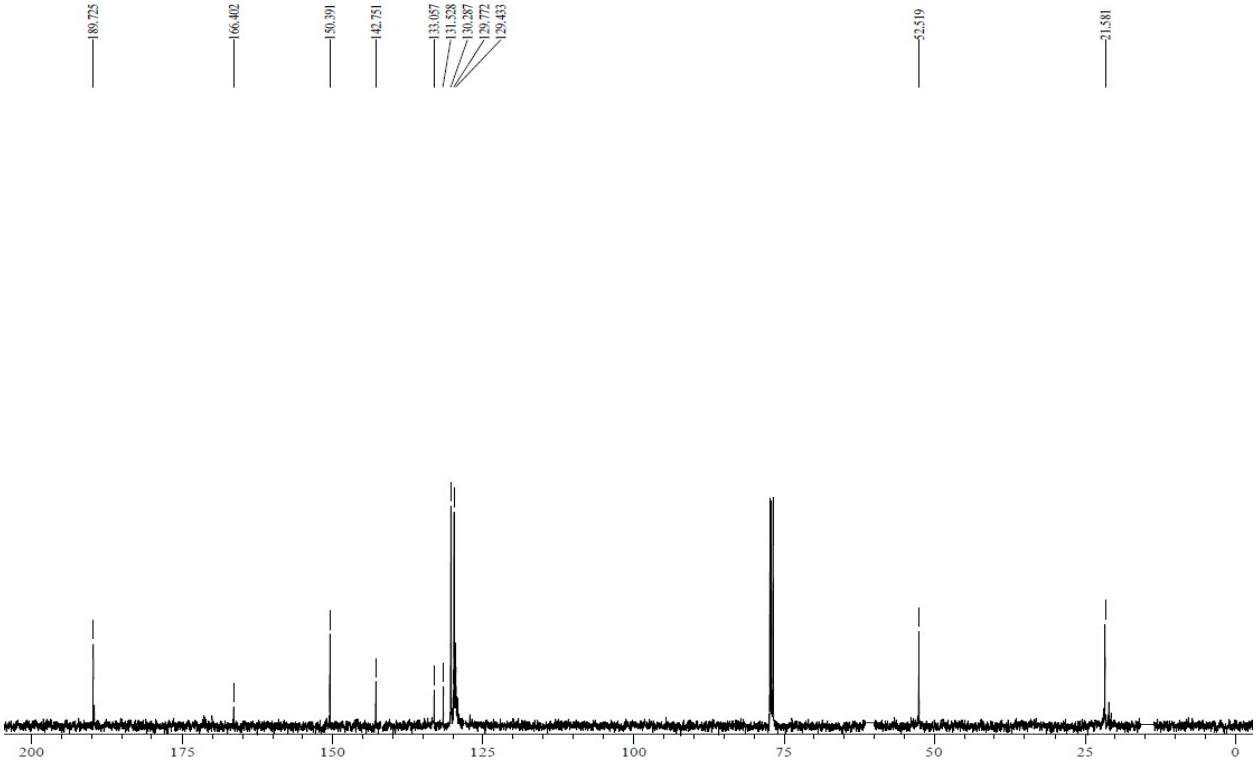
C[13] NMR Spectrum of (E)-Methyl 2-formyl-3-m-tolylacrylate (**5c**):



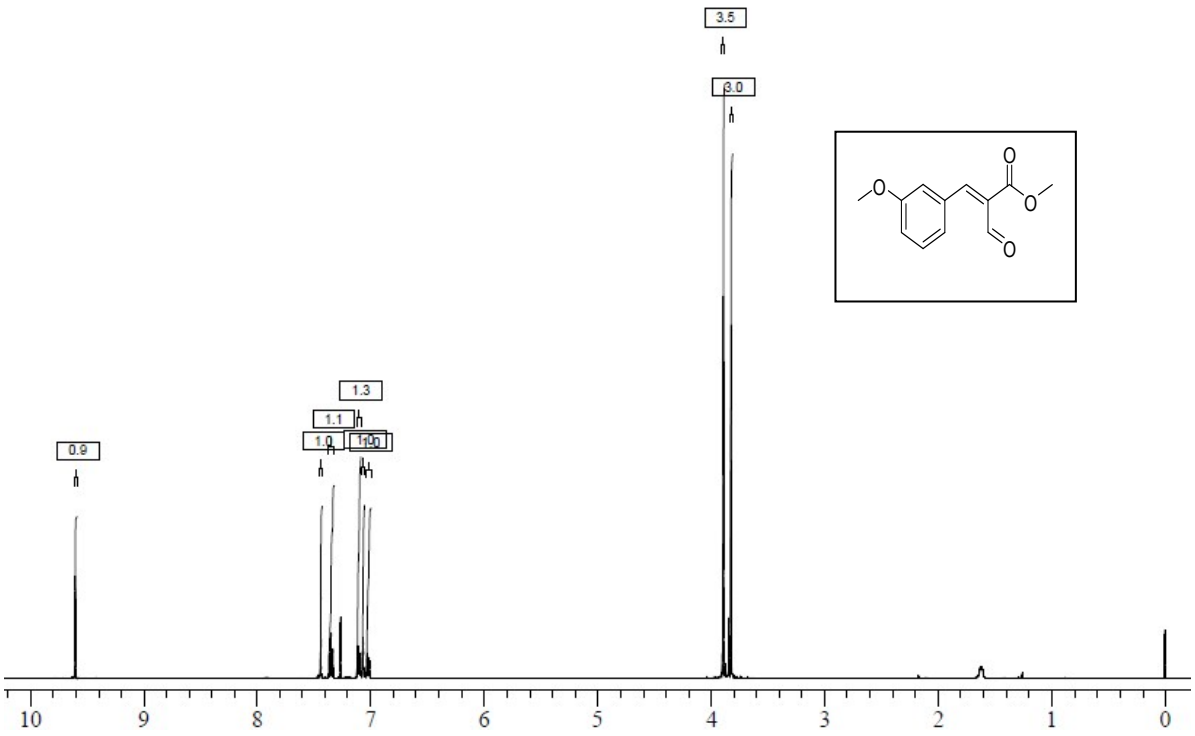
H[1] NMR Spectrum of (E)-Methyl 2-formyl-3-p-tolylacrylate (**5d**):



C[13] NMR Spectrum of (E)-Methyl 2-formyl-3-p-tolylacrylate (**5d**):

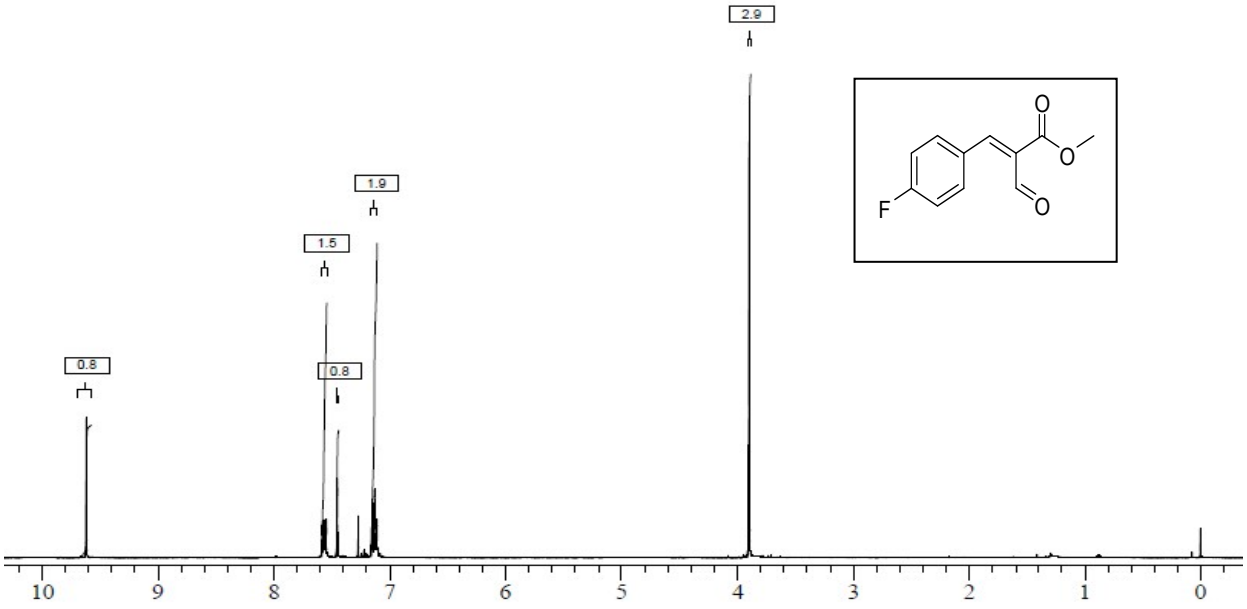


H[1] NMR Spectrum of (E)-Methyl 2-formyl-3-(3-methoxyphenyl)acrylate (**5e**):

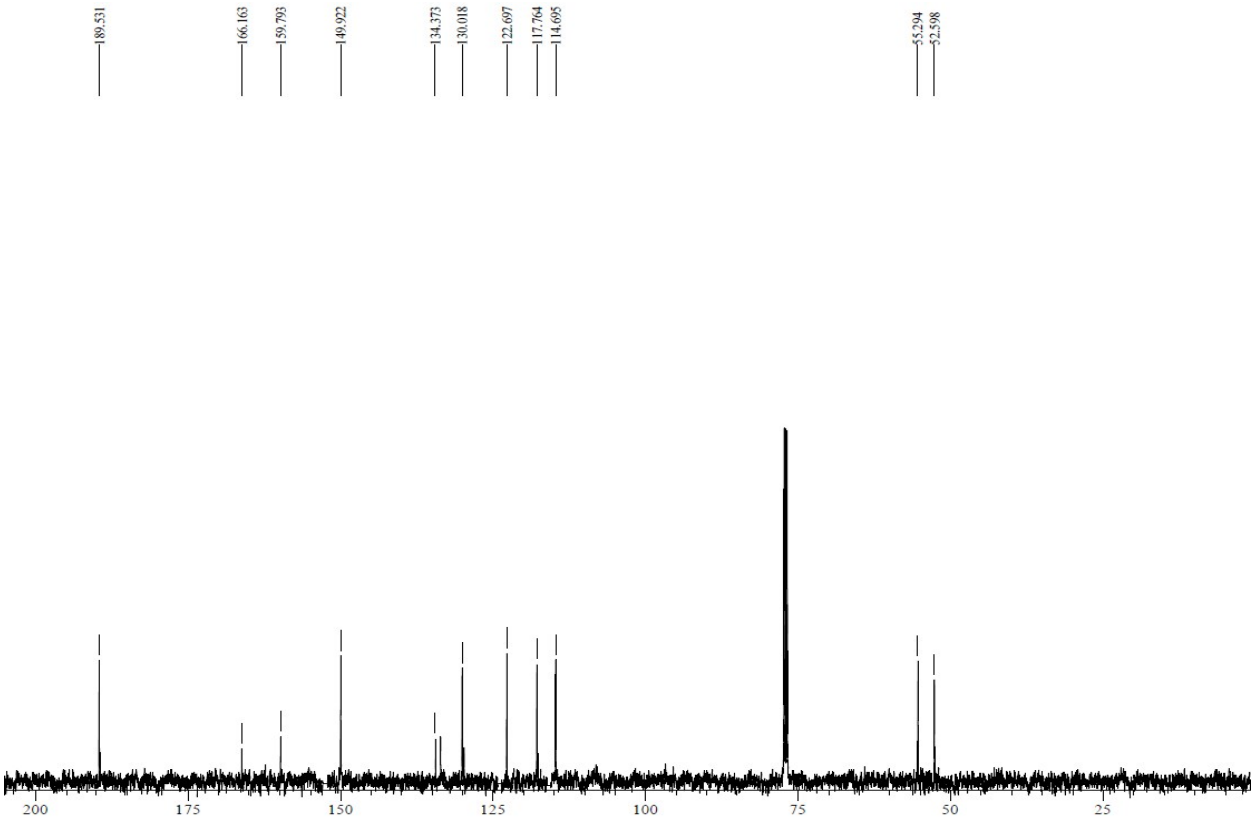


C[13] NMR Spectrum of (E)-Methyl 2-formyl-3-(3-methoxyphenyl)acrylate (**5e**):

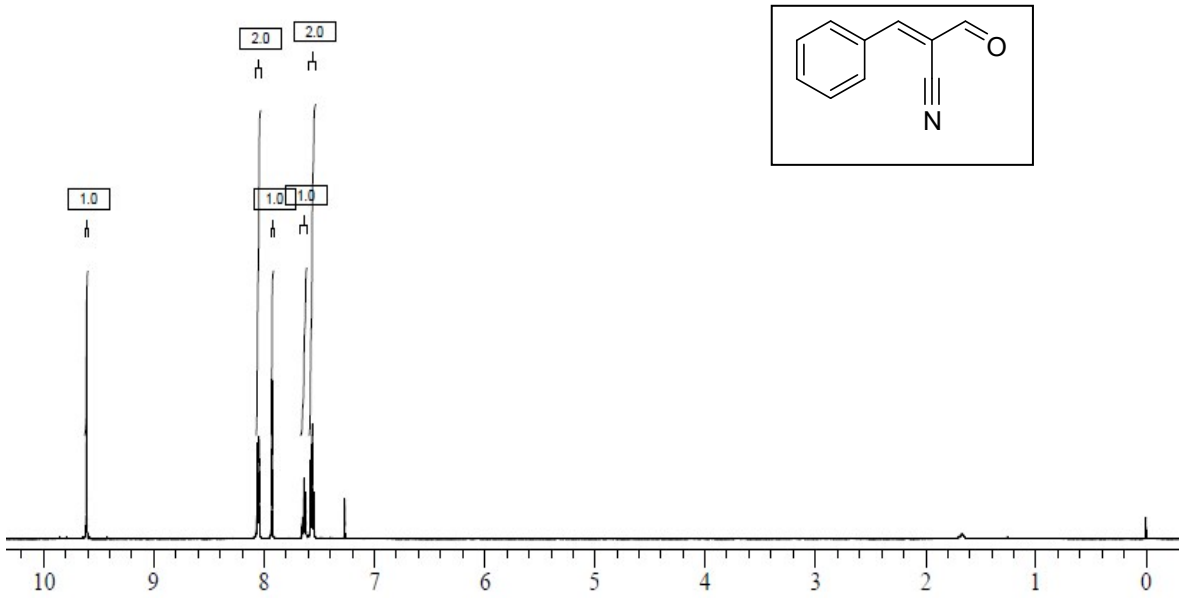
H[1] NMR Spectrum of (E)-Methyl 3-(4-fluorophenyl)-2-formylacrylate (**5f**):



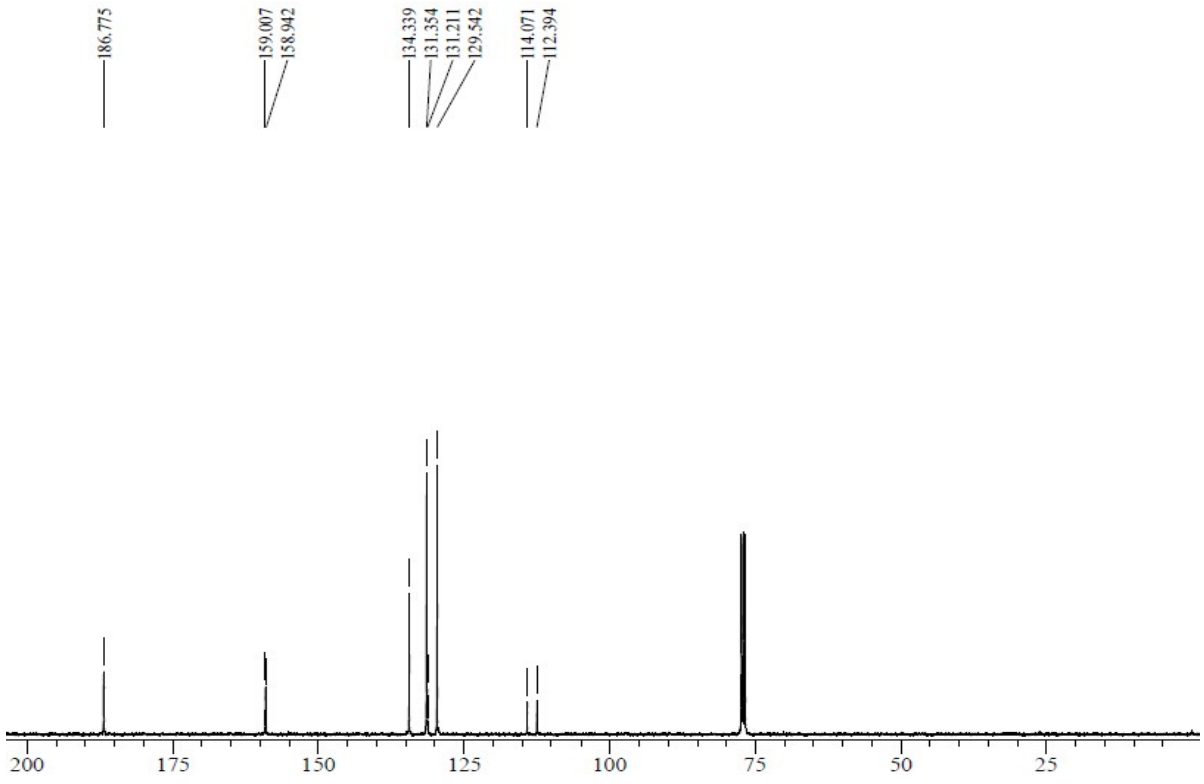
C[13] NMR Spectrum of (E)-Methyl 3-(4-fluorophenyl)-2-formylacrylate (**5f**):



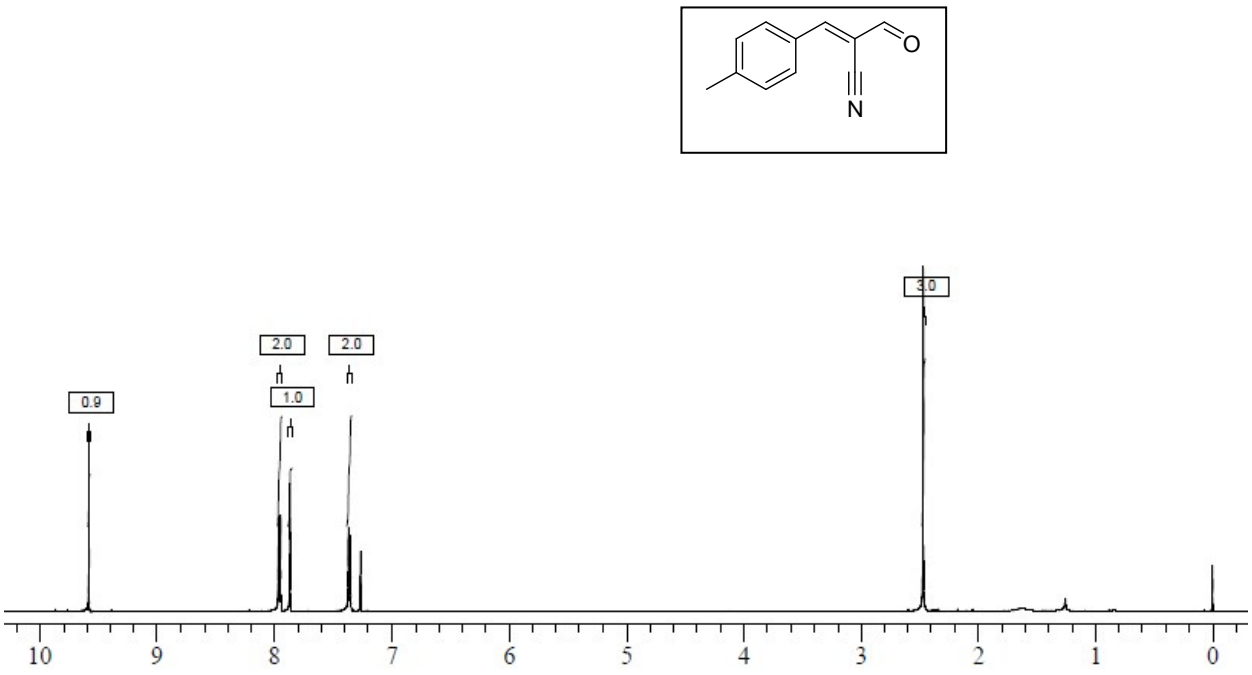
H[1] NMR Spectrum of (E)-2-formyl-3-phenylacrylonitrile (**7a**):



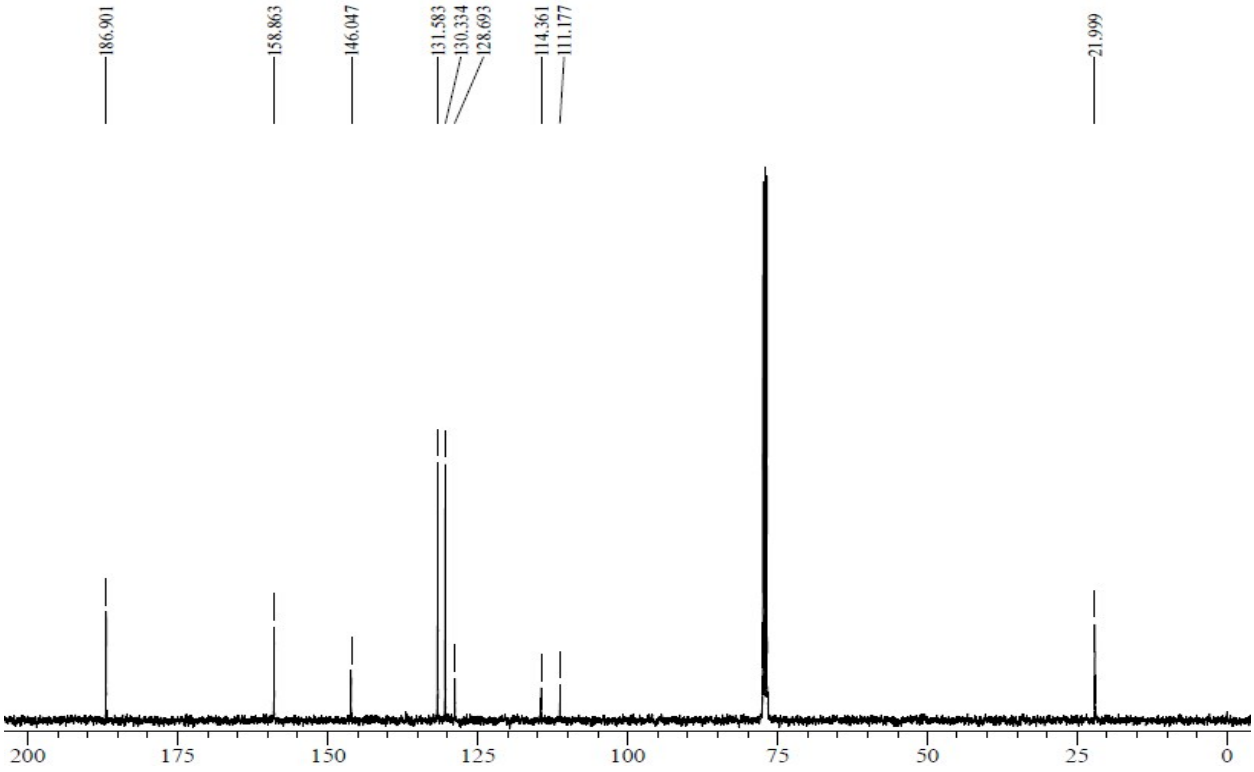
C[13] NMR Spectrum of (E)-2-formyl-3-phenylacrylonitrile (**7a**):



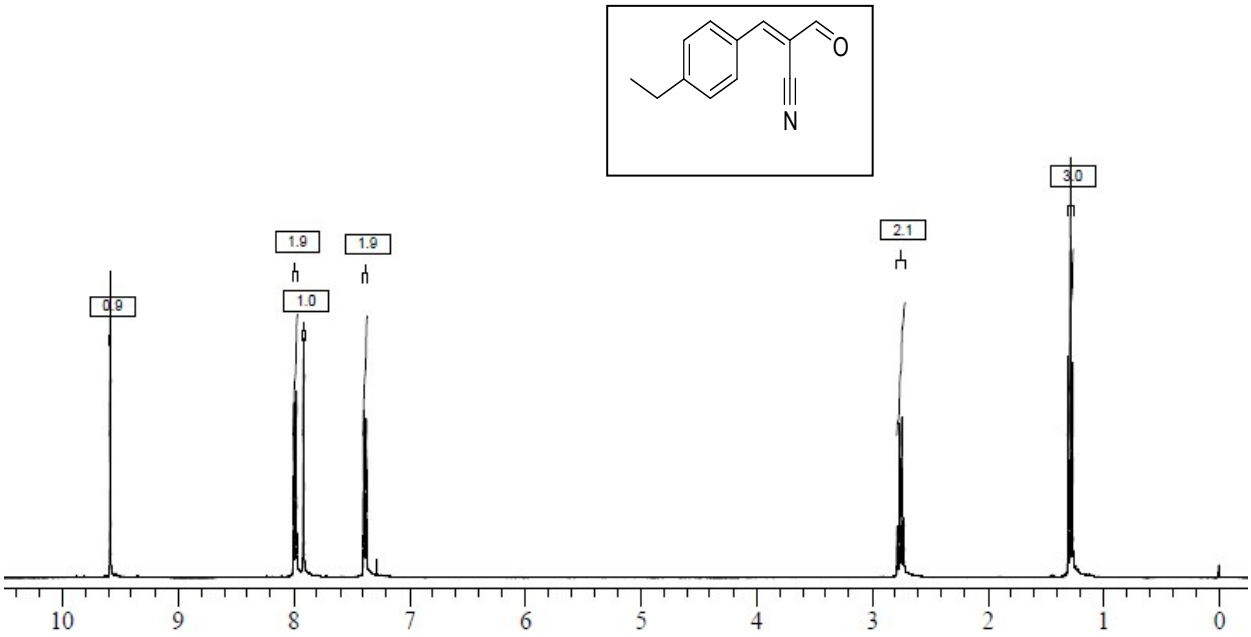
H[1] NMR Spectrum of (E)-2-formyl-3-p-tolylacrylonitrile (**7b**):



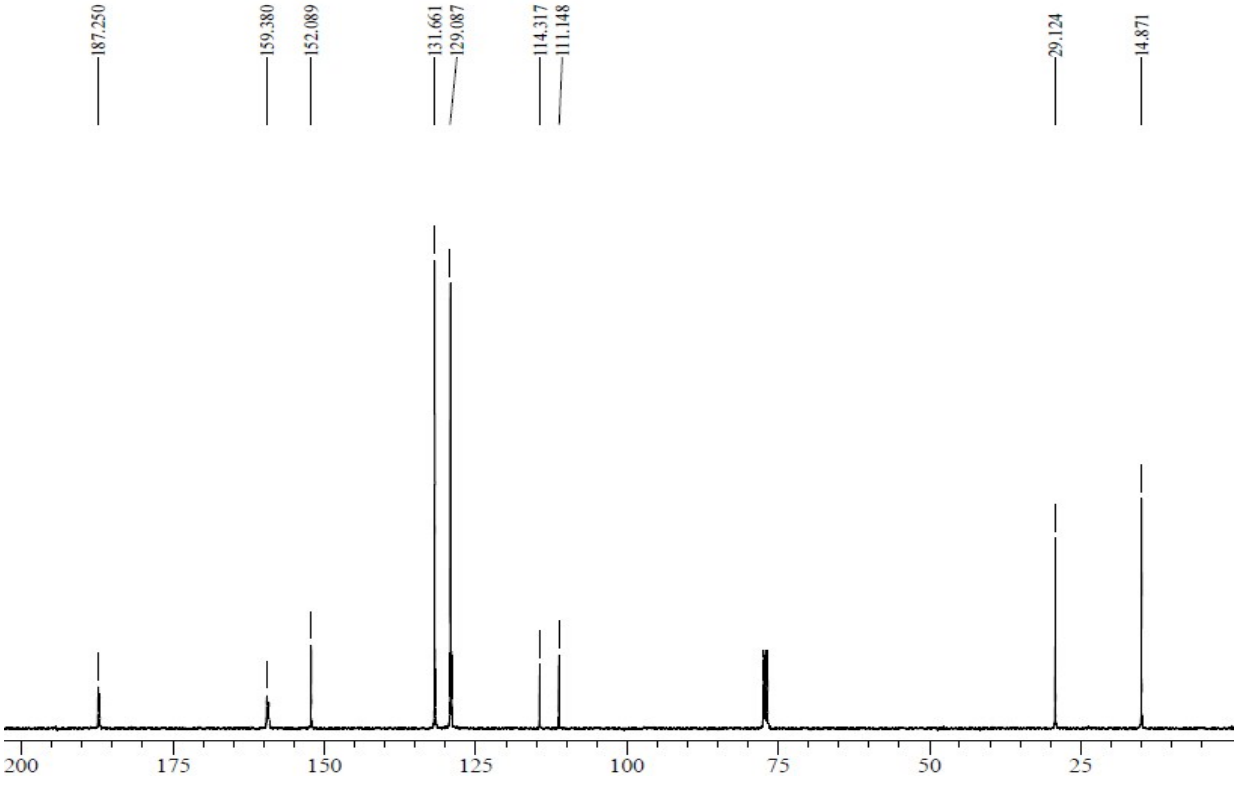
C[13] NMR Spectrum of (E)-2-formyl-3-p-tolylacrylonitrile (**7b**):



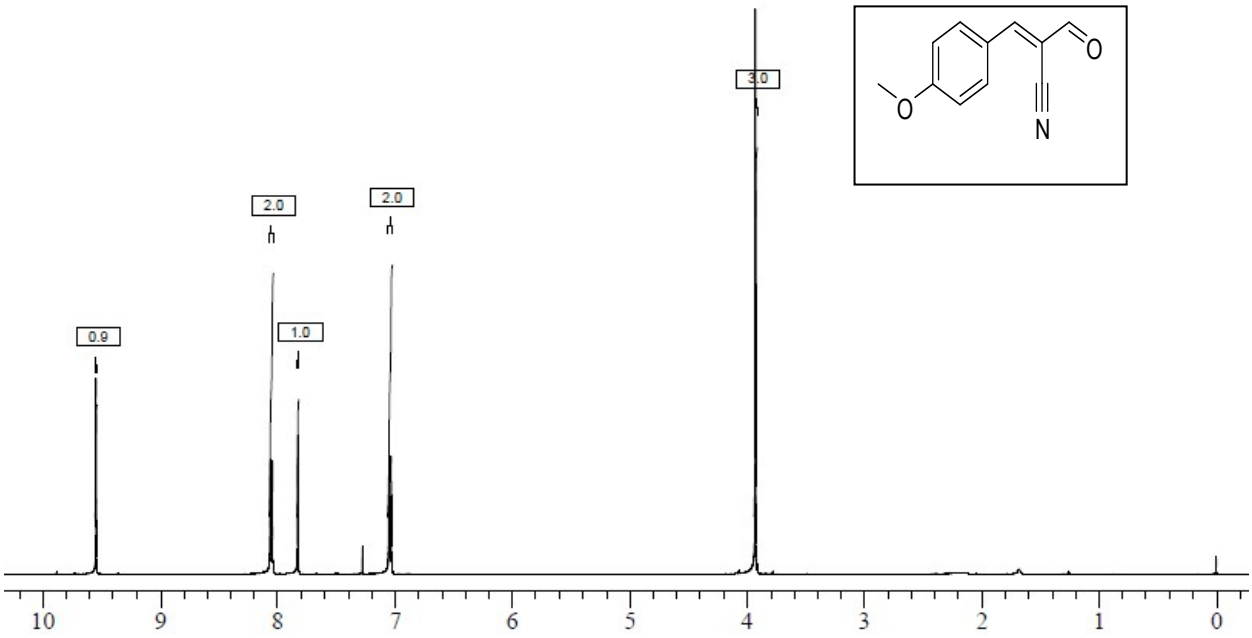
H[1] NMR Spectrum of (E)-3-(4-ethylphenyl)-2-formylacrylonitrile (**7c**):



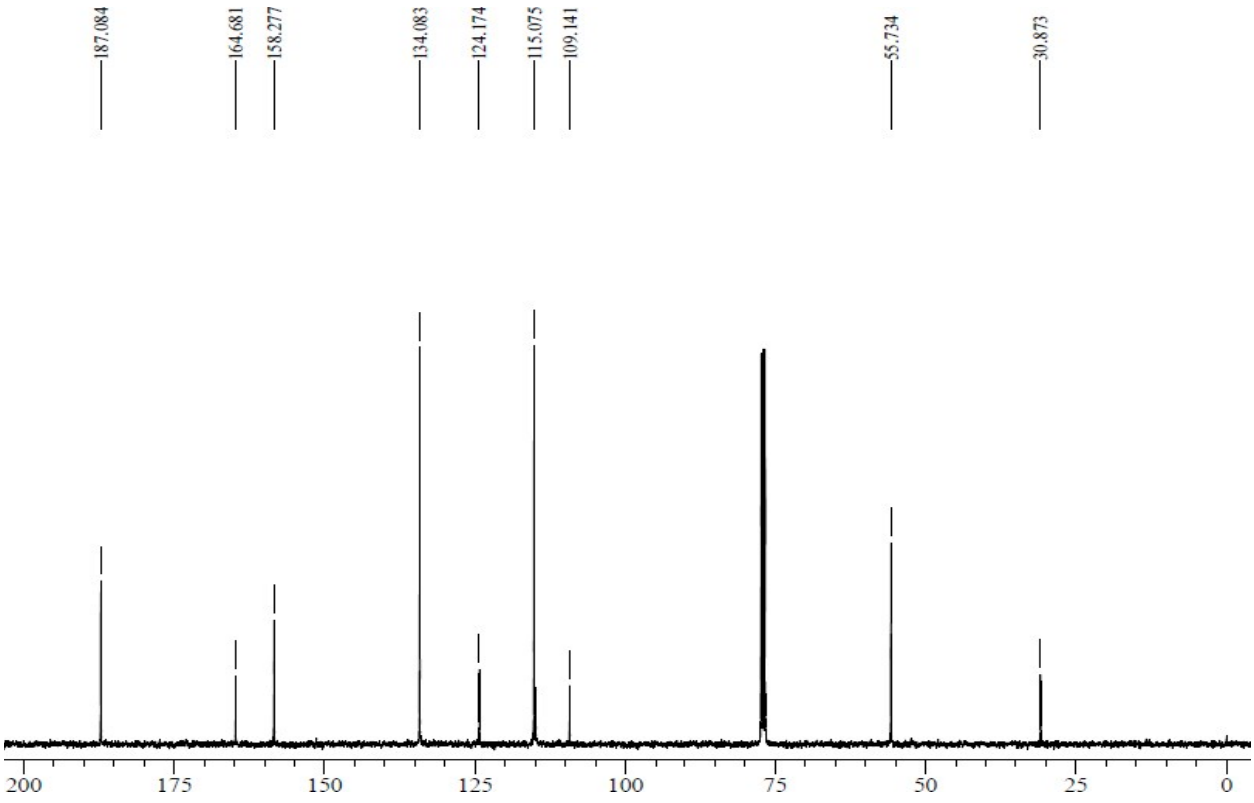
C[13] NMR Spectrum of (E)-3-(4-ethylphenyl)-2-formylacrylonitrile (**7c**):



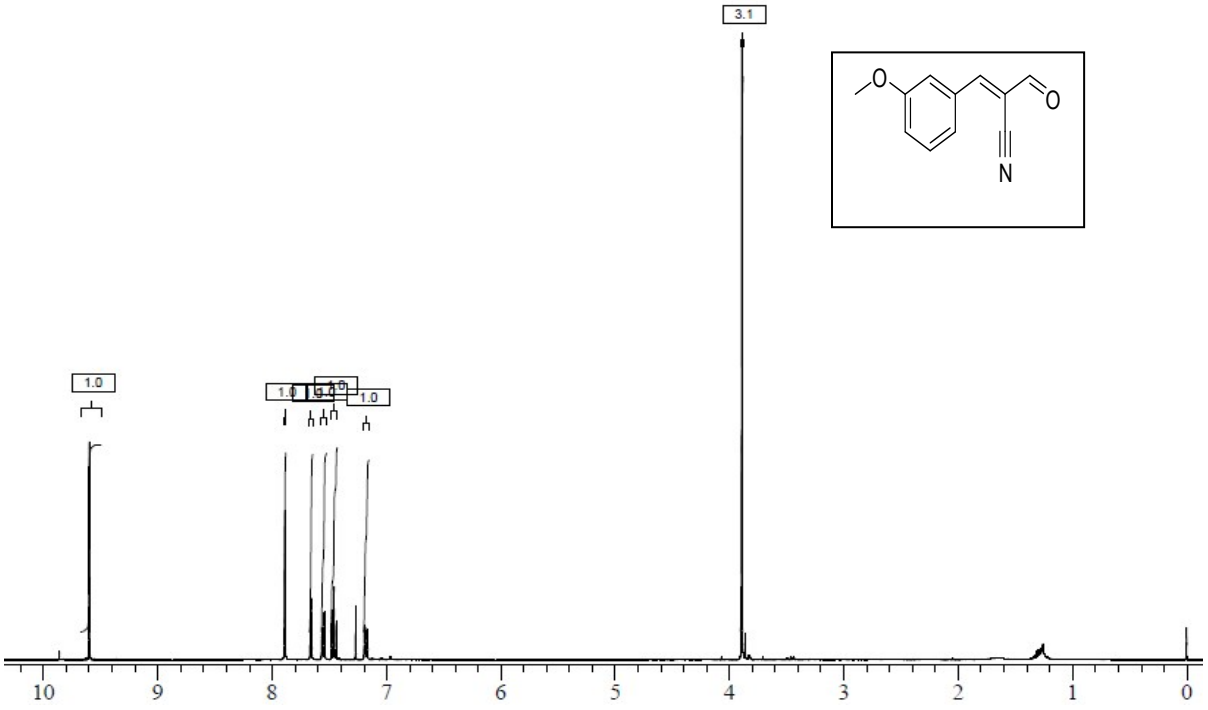
H[1] NMR Spectrum Of (E)-2-formyl-3-(4-methoxyphenyl)acrylonitrile (**7d**):



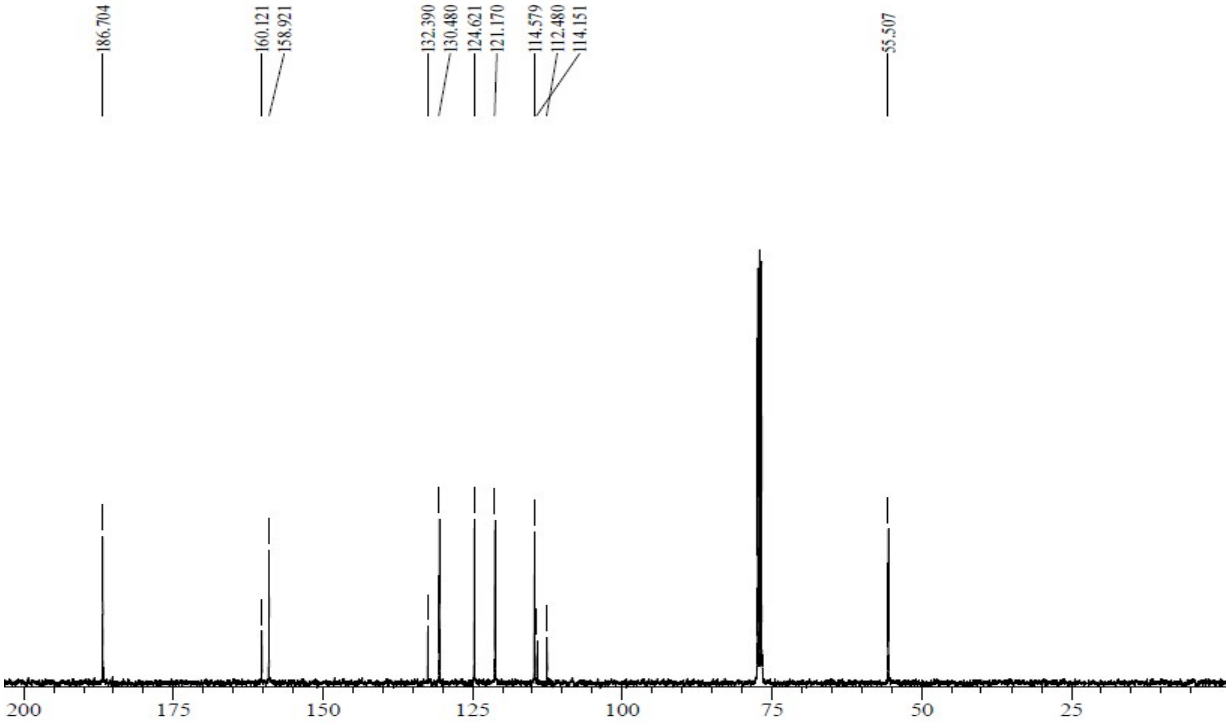
C[13] NMR Spectrum of (E)-2-formyl-3-(4-methoxyphenyl)acrylonitrile (**7d**):



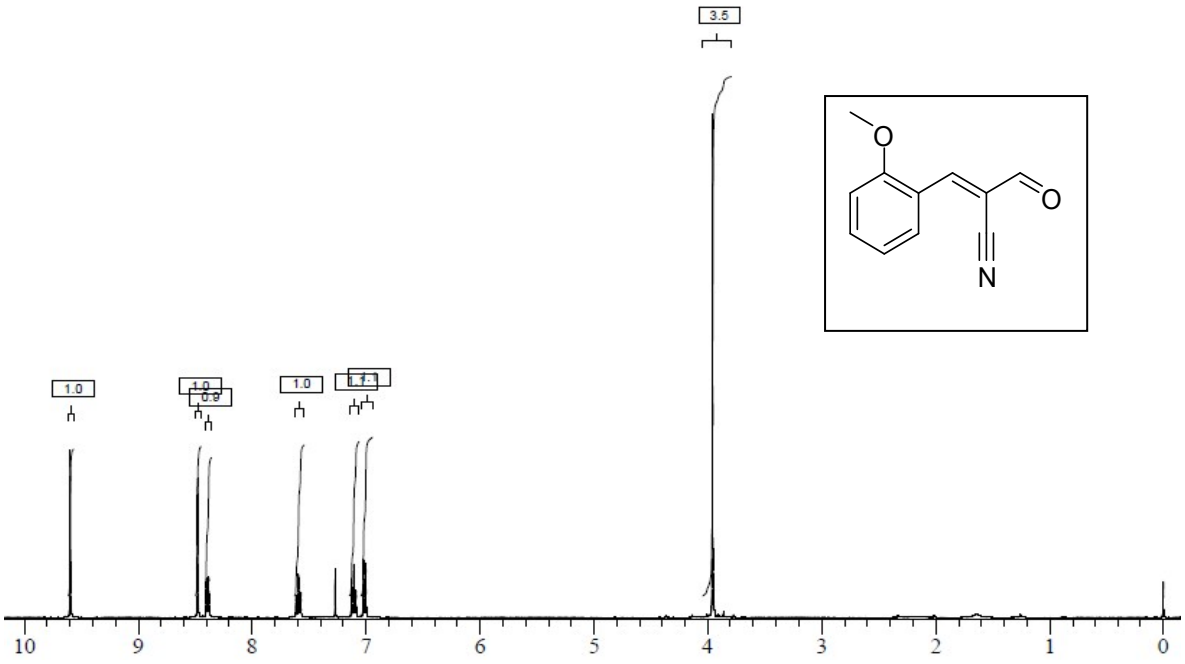
H[1] NMR Spectrum of (E)-2-formyl-3-(3-methoxyphenyl)acrylonitrile (**7e**):



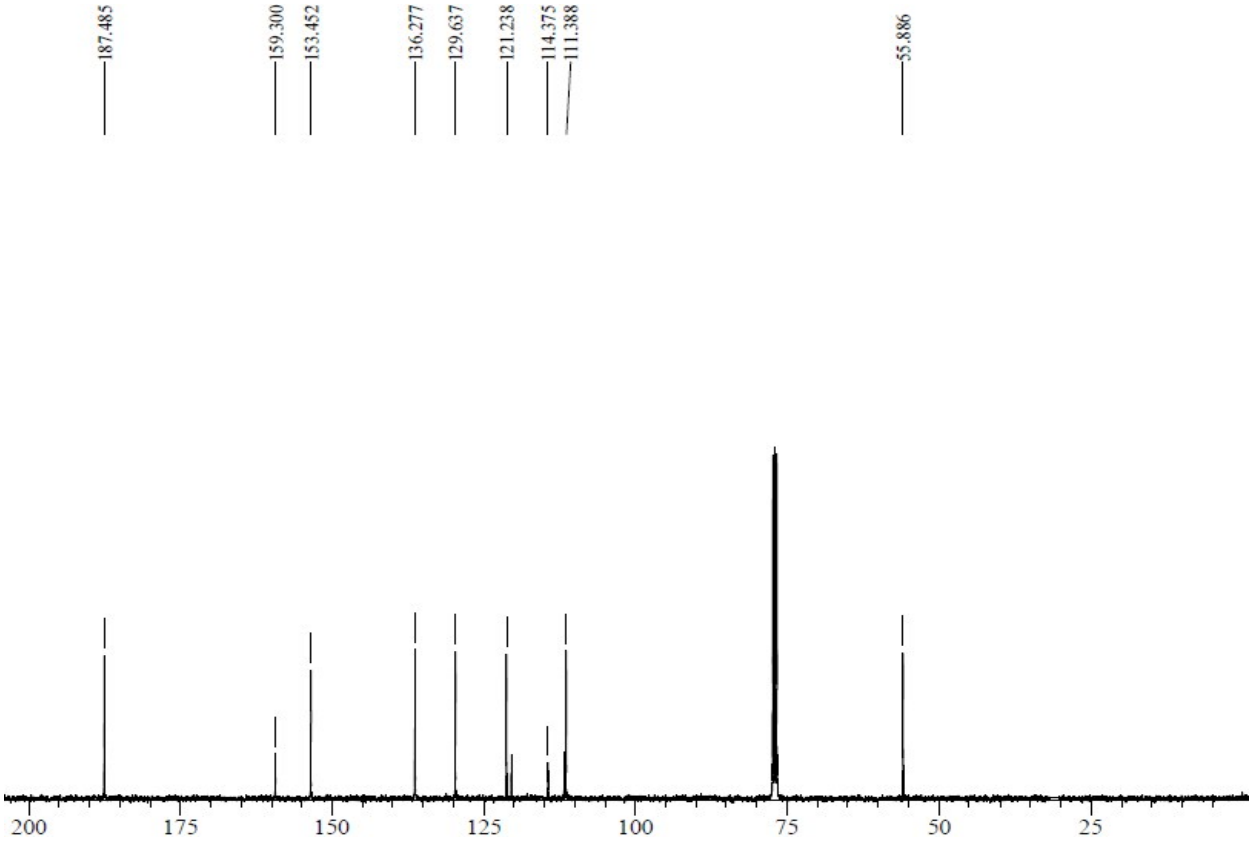
C[13] NMR Spectrum of (E)-2-formyl-3-(3-methoxyphenyl)acrylonitrile (**7e**):



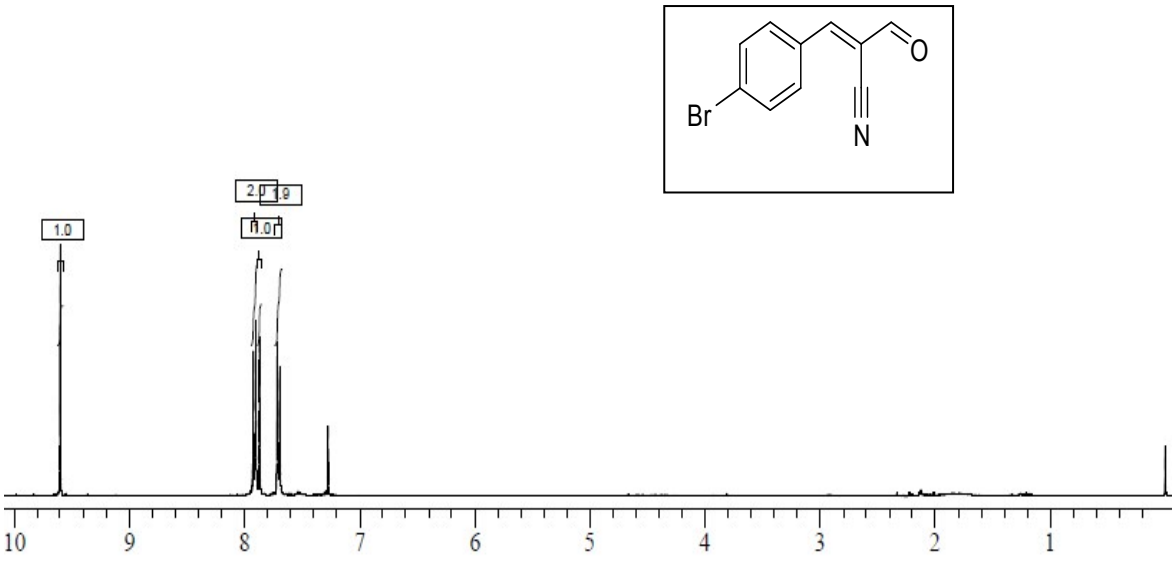
H[1] NMR Spectrum of (E)-2-formyl-3-(2-methoxyphenyl)acrylonitrile (**7f**):



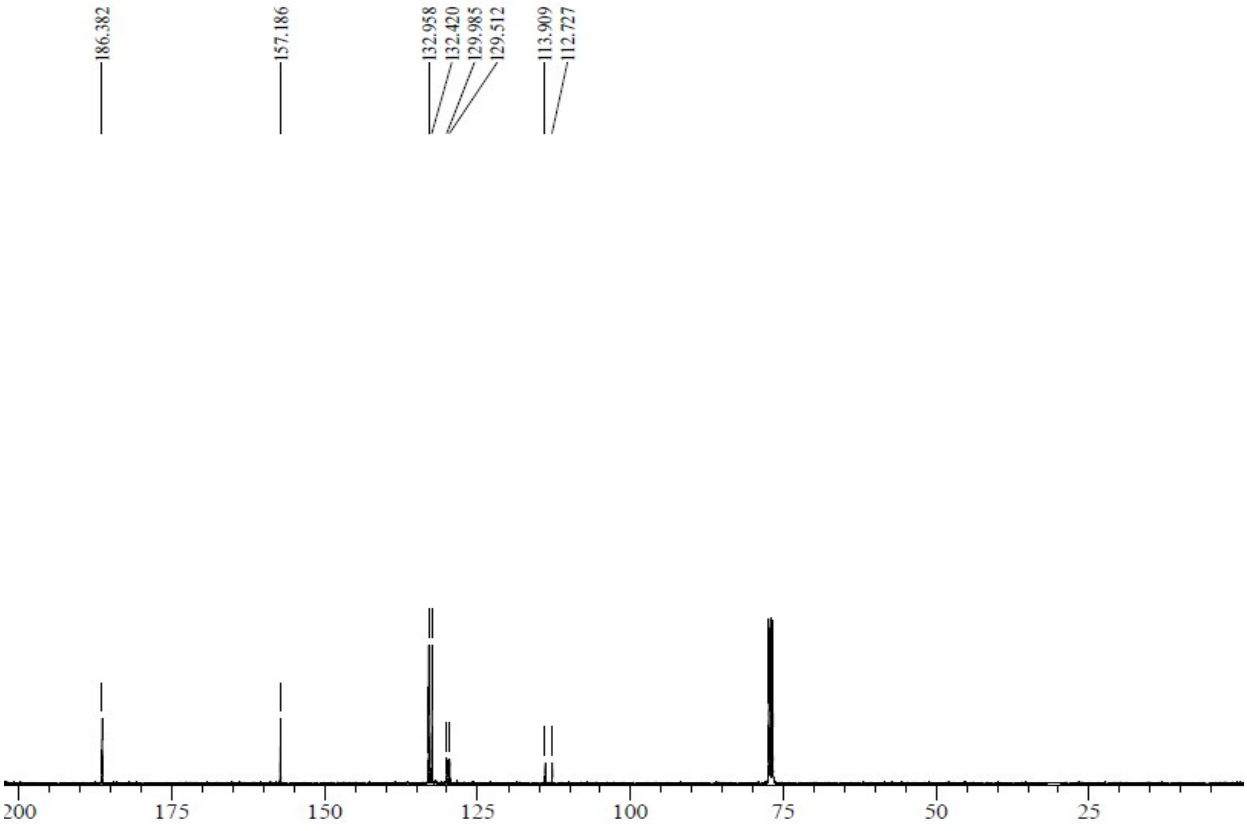
C[13] NMR Spectrum of (E)-2-formyl-3-(2-methoxyphenyl)acrylonitrile (**7f**):



H[1] NMR Spectrum of (E)-3-(4-bromophenyl)-2-formylacrylonitrile (**7g**):



C[13] NMR Spectrum of (E)-3-(4-bromophenyl)-2-formylacrylonitrile (**7g**):



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