

Supporting Information for

Matsuda–Heck reaction with arenediazonium tosylates in water

Ksenia V. Kutonova¹, Marina E. Trusova¹, Andrey V. Stankevich², Pavel S. Postnikov^{3*,§} and Victor D. Filimonov¹

Address: ¹Department of Biotechnology and Organic Chemistry, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia, ²Laboratory of Materials and Technologies of Liquid Crystal Devices, Institute of Chemistry of New Materials NAS Belarus, 220141, Minsk, Belarus and ³Department of General and Inorganic Chemistry, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia

*Corresponding author

Email: Pavel S. Postnikov - postnikov@tpu.ru

[§]Fax +7 (3822)563637

Additional experimental data

1. GENERAL INFORMATION

All starting materials were ACS grade and were employed without further purification. Arenediazonium tosylates **2** were prepared by a previously described method [1]. HPLC analysis was conducted with an Agilent 1200 instrument fitted with an Eclipse Plus C18 column (5 μ m, 4.6 $\times$ 150 mm) and UV detector. GC–MS (EI) measurements were obtained with an Agilent 7890/5975C instrument. ^1H , ^{13}C NMR and IR spectra were recorded on a Bruker Avance 300 and Perkin Elmer BXII instruments, respectively. Melting points were obtained with a melting point system MP50, Mettler Toledo (values are given uncorrected). HPLC–MS measurements were obtained with a Thermo Scientific DFS High Resolution GC–MS. Microwave heating was carried out with a CEM Discover System (model 908010) at 2455 MHz from MATTHEWS, NC (USA).

2. EXPERIMENTAL PROCEDURE

To the solution of ADT (1 mmol) in H_2O (10 mL) at room temperature were added alkene (1.2 mmol) and $\text{Pd}(\text{OAc})_2$ (0.010 mmol; 2.3 mg). The reaction mixture was heated and held at 75 $^\circ\text{C}$ with stirring using a microwave reactor in open-vessel mode with power 50 W. Conversion of ADT was monitored every minute until a negative diazonium test with 2-naphthol. When the diazonium test was negative, the reaction mixture was cooled and in the case of solid methyl cinnamates **3aa–3ac** and **3ae–3ah** the product was filtered, washed with water (25 mL), and dried on air. Otherwise the reaction mixture was extracted twice with dichloromethane (10 mL), the organic layer was filtered through a pad of silica and dried over anhydrous Na_2SO_4 . The solvent was removed in a rotary evaporator under reduced pressure and the crude product was purified by flash chromatography.

3. CHARACTERIZATION FOR PRODUCTS

Methyl (*E*)-3-(4-nitrophenyl)acrylate (**3aa**): Yield 97%, 0.97 mmol, pale yellow solid, mp 138 $^\circ\text{C}$. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 8.24 (d, 2H, J = 8.4 Hz), 7.74–7.65 (m, 3H), 6.56 (d, 1H, J = 16.2 Hz), 3.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 166.5, 148.4, 141.9, 140.4, 128.7, 124.2, 122.0, 52.0; MS (EI): m/z = 207 ($[\text{M}]^+$).

Methyl (*E*)-3-(3-nitrophenyl)acrylate (**3ab**): Yield 92%, 0.92 mmol, pale yellow solid, mp 124 $^\circ\text{C}$. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 8.34 (s, 1H), 8.20 (d, 1H, J = 8.1 Hz), 7.80 (d, 1H, J = 8.1 Hz), 7.69 (d, 1H, J = 15.9 Hz), 7.57 (m, 1H), 6.53 (d, 1H, J = 15.9 Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 166.2, 148.3, 141.6, 135.7, 133.4, 129.8, 124.3, 122.1, 120.6, 51.8; MS (EI): m/z = 207 ($[\text{M}]^+$).

Methyl (*E*)-3-(2-nitrophenyl)acrylate (**3ac**): Yield 92%, 0.92 mmol, pale yellow solid, mp 72 $^\circ\text{C}$. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 8.09 (d, 1H,

$J = 15.6$ Hz), 8.02 (d, 1H, $J = 8.4$ Hz), 7.67-7.60 (m, 2H), 7.56-7.50 (m, 1H), 6.35 (d, 1H, $J = 15.6$ Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 166.1, 148.1, 140.0, 133.5, 130.3, 129.0, 124.8, 122.7, 51.9; MS (EI): $m/z = 207$ ($[\text{M}]^+$).

Methyl (*E*)-cinnamate (**3ad**): Yield 86%, 0.86 mmol, pale yellow oil. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 7.70 (d, 1H, $J = 16.2$ Hz), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 3H), 6.44 (d, 1H, $J = 16.2$ Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 167.4, 144.8, 134.3, 130.3, 128.8, 128.0, 117.7, 51.7; MS (EI): $m/z = 162$ ($[\text{M}]^+$).

Methyl (*E*)-3-(4-methoxyphenyl)acrylate (**3ae**): Yield 96%, 0.96 mmol, white solid, mp 90 °C. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 7.64 (d, 1H, $J = 15.9$ Hz), 7.46 (d, 2H, $J = 8.4$ Hz), 6.88 (d, 2H, $J = 8.4$ Hz), 6.30 (d, 1H, $J = 15.9$ Hz), 3.81 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 167.7, 161.3, 144.5, 129.7, 127.0, 115.2, 114.3, 55.3, 51.6; MS (EI): $m/z = 192$ ($[\text{M}]^+$).

Methyl (*E*)-4-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**3af**): Yield 92%, 0.92 mmol, white solid, mp 125 °C. Analytical data are identical to the reported data [3]. ^1H NMR (300 MHz, CDCl_3) δ : 8.03 (d, 2H, $J = 8.4$ Hz), 7.70 (d, 1H, $J = 16.2$ Hz), 7.57 (d, 2H, $J = 8.4$ Hz), 6.51 (d, 1H, $J = 16.2$ Hz), 3.92 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 167.0, 166.5, 143.5, 138.6, 131.4, 130.1, 128.0, 120.2, 52.4, 52.0; MS (EI): $m/z = 220$ ($[\text{M}]^+$).

Methyl (*E*)-3-(4-cyanophenyl)acrylate (**3ag**): Yield 94%, 0.94 mmol, white solid, mp 138 °C. Analytical data are identical to the reported data [4]. ^1H NMR (300 MHz, CDCl_3) δ : 7.67 (m, 3H), 7.61 (m, 2H), 6.51 (d, 1H, $J = 15.9$ Hz), 3.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 166.6, 142.4, 138.6, 132.7, 128.4, 121.4, 118.4, 113.4, 52.1; MS (EI): $m/z = 187$ ($[\text{M}]^+$).

Methyl (*E*)-3-(4-bromophenyl)acrylate (**3ah**): Yield 88%, 0.88 mmol, white solid, mp 89 °C. Analytical data are identical to the reported data [2]. ^1H NMR (300 MHz, CDCl_3) δ : 7.61 (d, 1H, $J = 16.2$ Hz), 7.50 (d, 2H, $J = 8.1$ Hz), 7.36 (d, 2H, $J = 8.1$ Hz), 6.41 (d, 1H, $J = 16.2$ Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 167.1, 143.4, 133.1, 132.1, 129.4, 124.5, 118.4, 51.8; MS (EI): $m/z = 240$ ($[\text{M}]^+$);

Methyl (*E*)-3-(2-methoxyphenyl)acrylate (**3ai**): Yield 93%, 0.93 mmol, colorless oil. Analytical data are identical to the reported data [5]. ^1H NMR (300 MHz, CDCl_3) δ : 7.99 (d, 1H, $J = 16.2$ Hz), 7.47 (d, 1H, $J = 8.1$ Hz), 7.31 (m, 1H), 6.95-6.86 (m, 2H), 6.97 (m, 1H), 6.51 (d, 1H, $J = 16.2$ Hz), 3.83 (s, 3H), 3.77 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ : 167.6, 158.0, 140.0, 131.3, 128.6, 123.0, 120.4, 117.9, 110.9, 55.2, 51.3; MS (EI): $m/z = 192$ ($[\text{M}]^+$);

3-Chloropropyl (*E*)-3-(4-nitrophenyl)acrylate (**3ba**): Yield 90%, 0.90 mmol, pale yellow solid, mp 86 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ : 8.23 (d, 2H, $J = 8.7$ Hz), 8.00 (d, 2H, $J = 8.7$ Hz), 7.77 (d, 1H, $J = 16.2$ Hz), 6.84 (d, 1H, $J = 16.2$ Hz), 4.28 (t, 2H), 3.76 (t, 2H), 2.11 (m, 2H). ^{13}C

NMR (75 MHz, DMSO-*d*₆) δ : 165.6, 148.0, 142.4, 140.4, 129.5, 123.9, 122.2, 61.4, 41.9, 31.1. MS (EI): *m/z* = 269 ([M]⁺); HR-MS *m/z*: calcd for C₁₂H₁₂NO₄Cl, 269.0449; found, 269.0452.

3-Chloropropyl (*E*)-3-(3-nitrophenyl)acrylate (**3bb**): Yield 72%, 0.72 mmol, pale yellow solid, mp 75 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 8.54 (s, 1H), 8.24-8.17 (m, 2H), 7.80 (d, 1H, *J* = 16.2 Hz), 7.69 (m, 1H), 6.84 (d, 1H, *J* = 16.2 Hz), 4.27 (t, 2H), 3.77 (t, 2H), 2.11 (m, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 165.7, 148.2, 142.2, 135.9, 134.1, 130.4, 124.6, 123.0, 120.9, 61.3, 41.9, 31.2; HR-MS *m/z*: calcd. for C₁₂H₁₂NO₄Cl, 269.0449; found, 269.0456.

3-Chloropropyl (*E*)-3-(4-cyanophenyl)acrylate (**3bg**): Yield 69%, 0.69 mmol, white solid, mp 58 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 7.93-7.85 (m, 4H), 7.74 (d, 1H, *J* = 16.2 Hz), 6.80 (d, 1H, *J* = 16.2 Hz), 4.27 (t, 2H), 3.75 (t, 2H), 2.11 (m, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 165.6, 142.6, 138.5, 132.7, 129.0, 121.4, 118.5, 112.3, 61.3, 41.8, 31.1; HR-MS *m/z*: calcd. for C₁₃H₁₂NO₂Cl, 249.0551; found 249.0548.

(*E*)-1-Nitro-4-styrylbenzene (**3ca**): Yield 67%, 0.67 mmol, pale yellow solid, mp 154 °C. Analytical data are identical to the reported data [6]. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 8.21 (d, 2H, *J* = 7.5 Hz), 7.85 (d, 2H, *J* = 7.4 Hz), 7.66 (d, 2H, *J* = 5.7 Hz), 7.52 (d, 1H, *J* = 16.5 Hz), 7.42 (m, 4H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 146.1, 143.9, 136.2, 133.2, 128.8, 128.7, 127.3, 127.1, 126.3, 124.0.

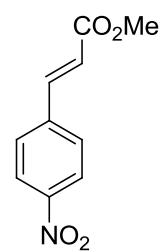
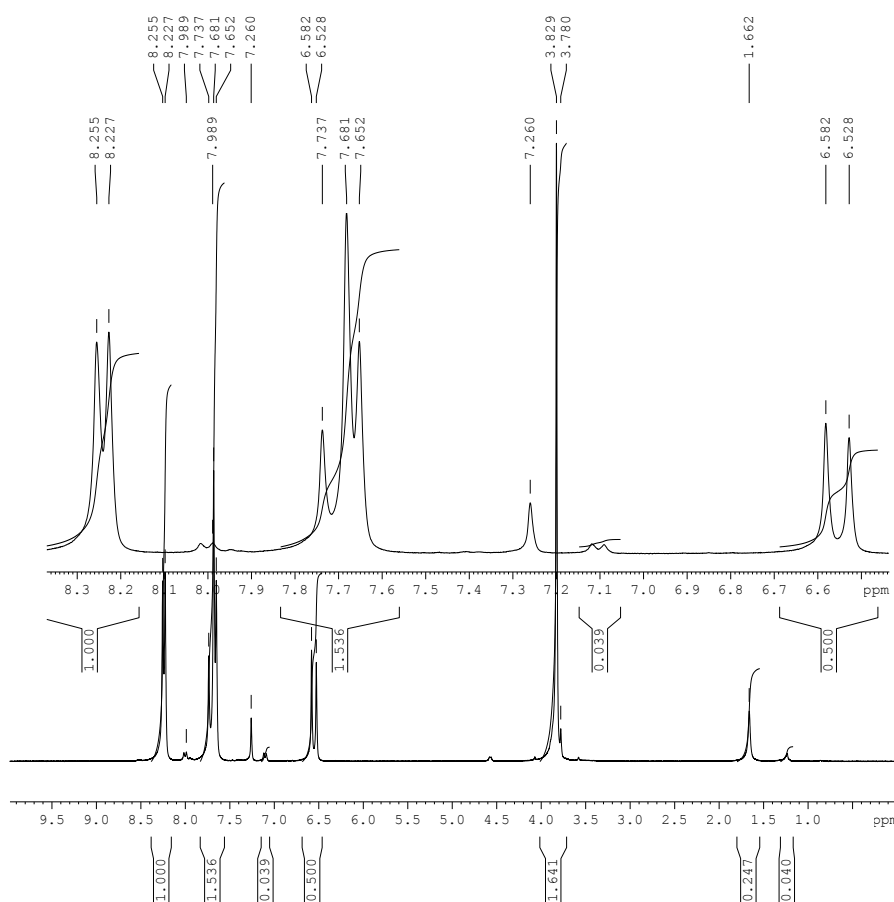
(*E*)-1-Nitro-3-styrylbenzene (**3cb**): Yield 52%, 0.52 mmol, pale yellow solid, mp 93 °C. Analytical data are identical to the reported data [7]. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 8.35 (s, 1H), 8.08 (d, 1H, *J* = 8.1 Hz), 7.78 (d, 1H, *J* = 8.1 Hz), 7.53 (m, 3H), 7.40 (m, 2H), 7.33 (d, 1H, *J* = 6.6 Hz), 7.23 (d, 1H, *J* = 16.5 Hz), 7.11 (d, 1H, *J* = 16.5 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 148.5, 139.0, 136.1, 132.2, 131.6, 129.5, 128.7, 128.4, 126.7, 126.0, 121.9, 120.7.

(*E*)-1-methoxy-4-styrylbenzene (**3ce**): Yield 50%, 0.50 mmol, white solid, mp 140 °C. Analytical data are identical to the reported data [6]. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 7.57-7.53 (m, 4H), 7.38-7.33 (m, 2H), 7.26-7.23 (m, 1H), 7.19 (d, 1H, *J* = 16.5 Hz), 7.08 (d, 1H, *J* = 16.5 Hz), 6.95 (d, 2H, *J* = 8.7 Hz), 3.77 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 158.9, 137.3, 129.6, 128.6, 128.0, 127.8, 127.1, 126.1, 114.1, 55.2.

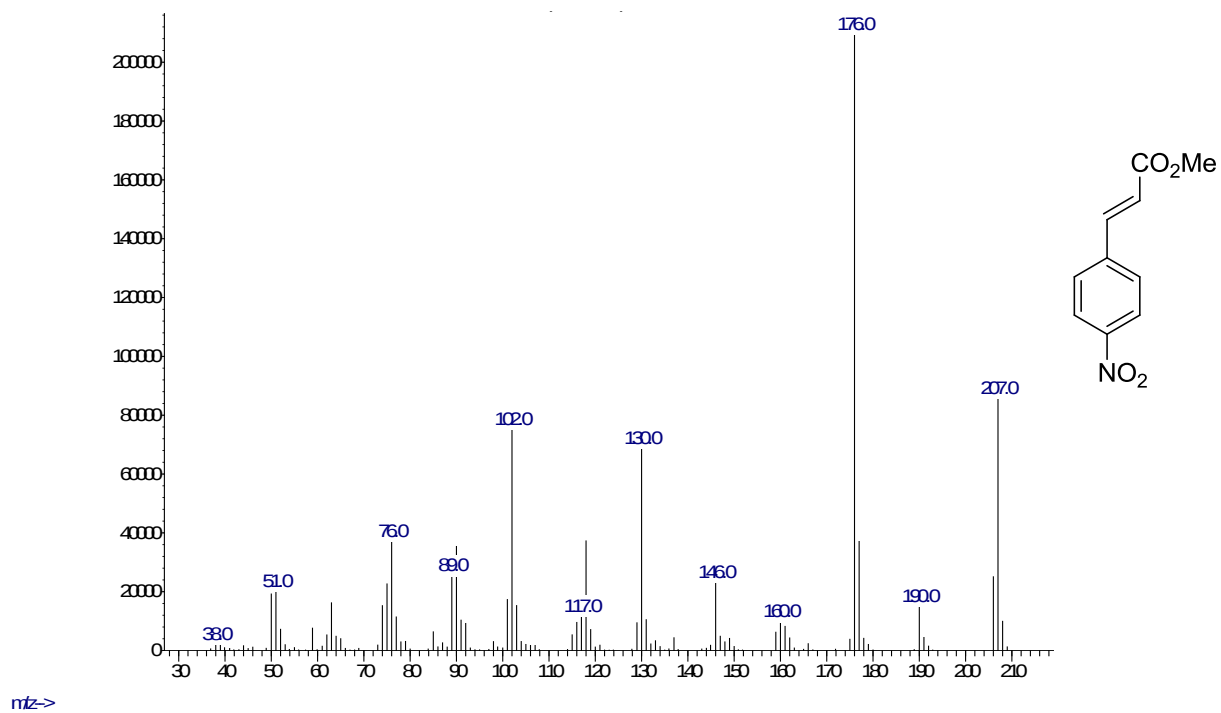
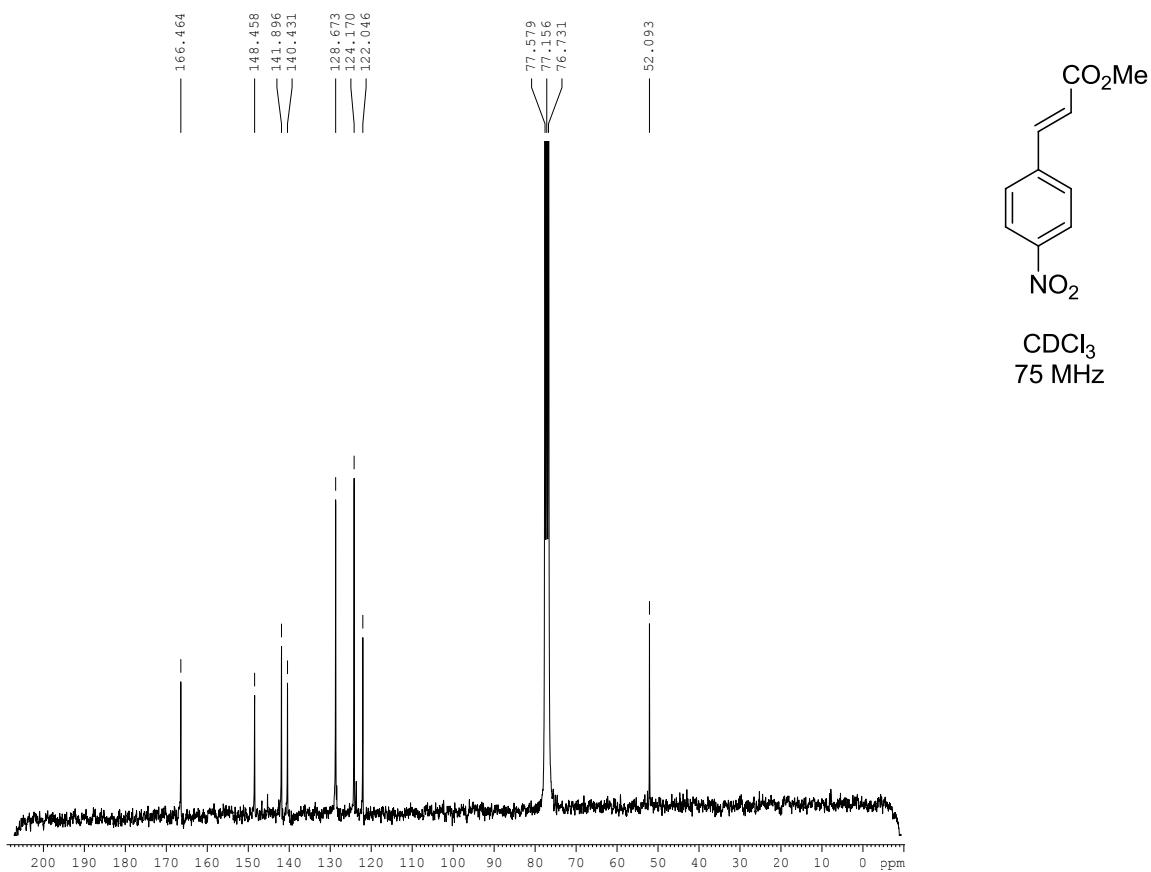
Methyl (*E*)-4-styrylbenzoate (**3cf**): Yield 65%, 0.65 mmol, white solid, mp 158 °C. Analytical data are identical to the reported data [3]. ¹H NMR (300 MHz, DMSO-*d*₆) δ : 8.03 (d, 2H, *J* = 7.8 Hz), 7.55 (m, 4H), 7.39 (m, 2H), 7.30 (m, 1H), 7.22 (d, 1H, *J* = 16.5 Hz), 7.12 (d, 1H, *J* = 16.5 Hz), 3.93 (s, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ : 166.7, 141.6, 136.5, 131.1, 129.9, 128.7, 128.1, 127.4, 126.7, 126.2, 52.0;

4. NMR and MASS SPECTRA COPIES

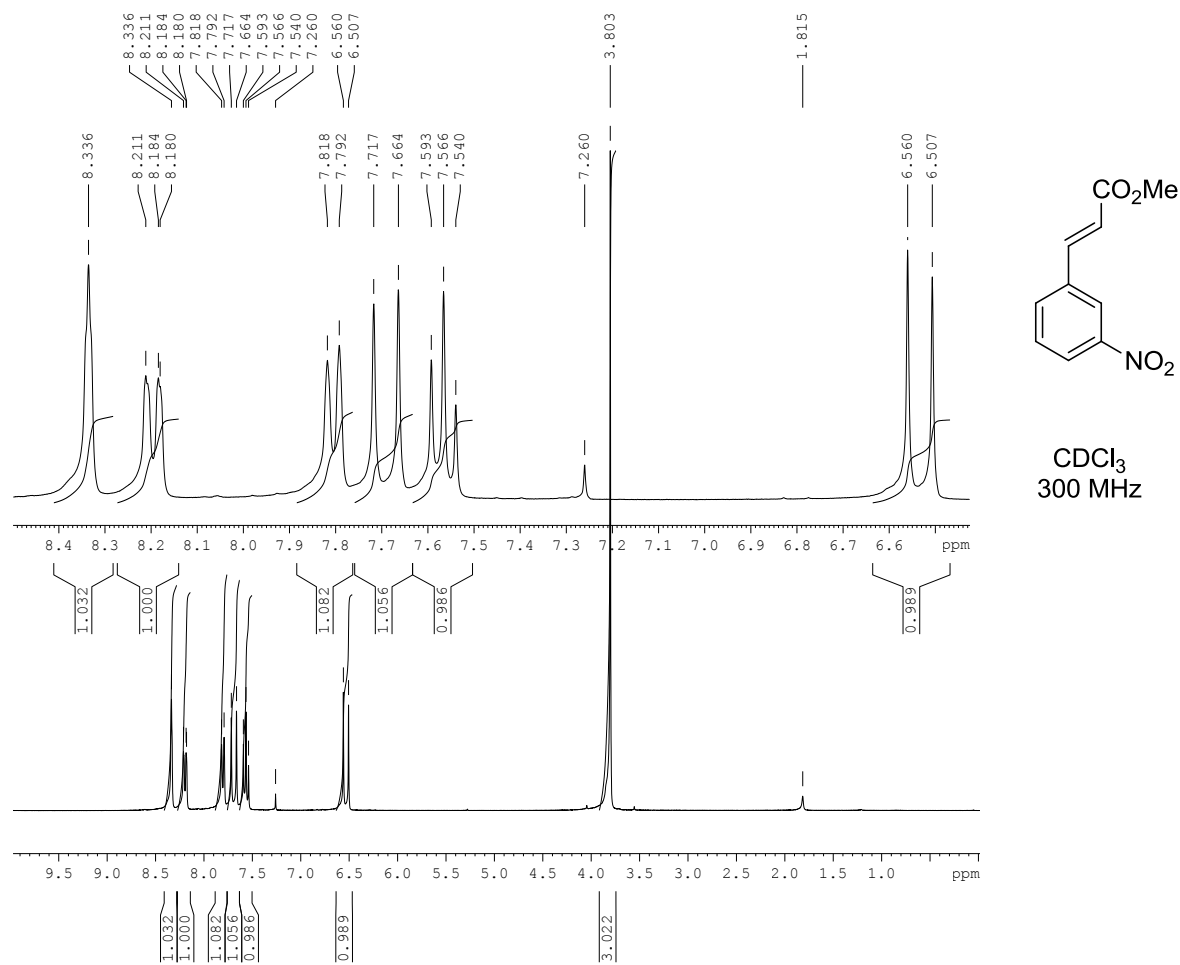
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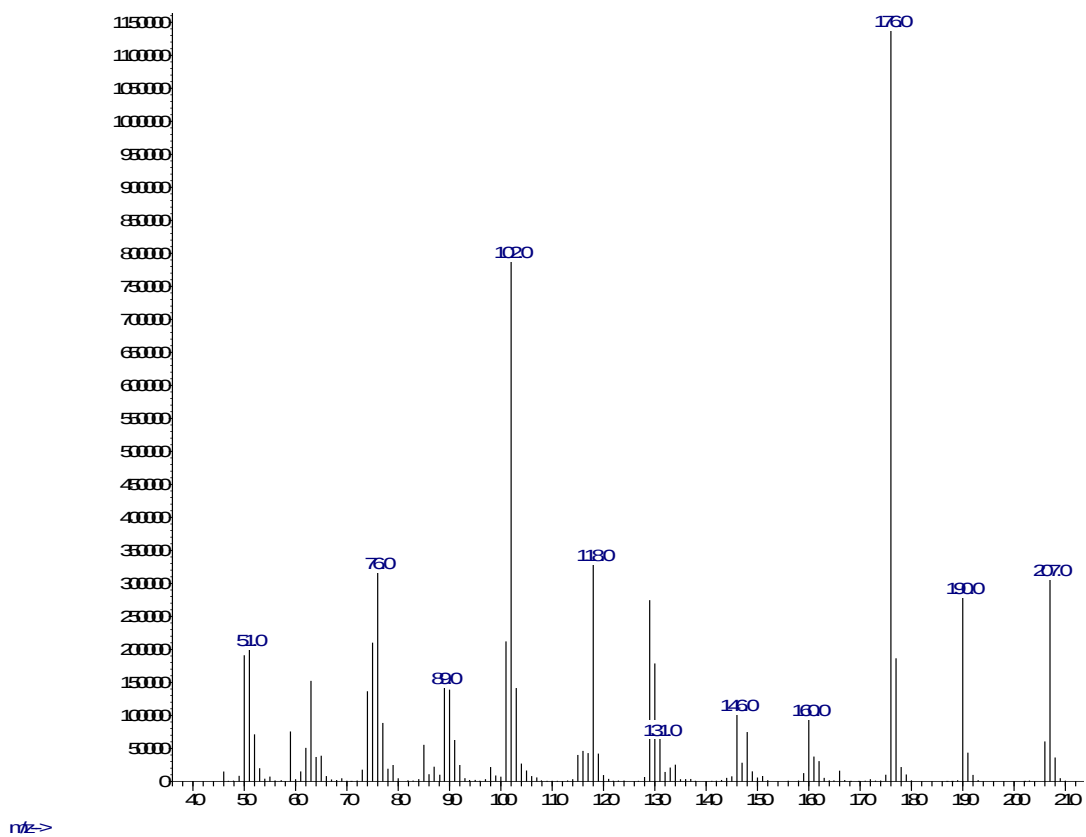
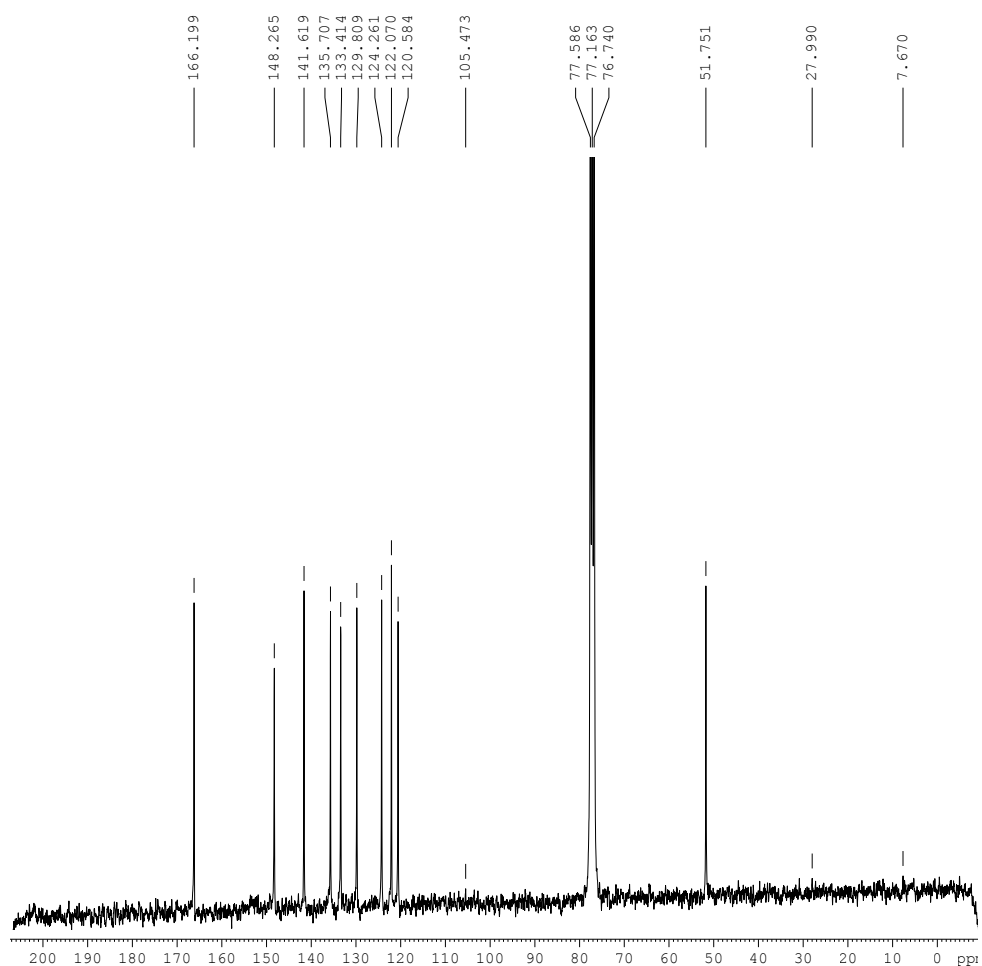


CDCl₃
300 MHz

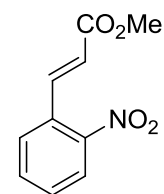
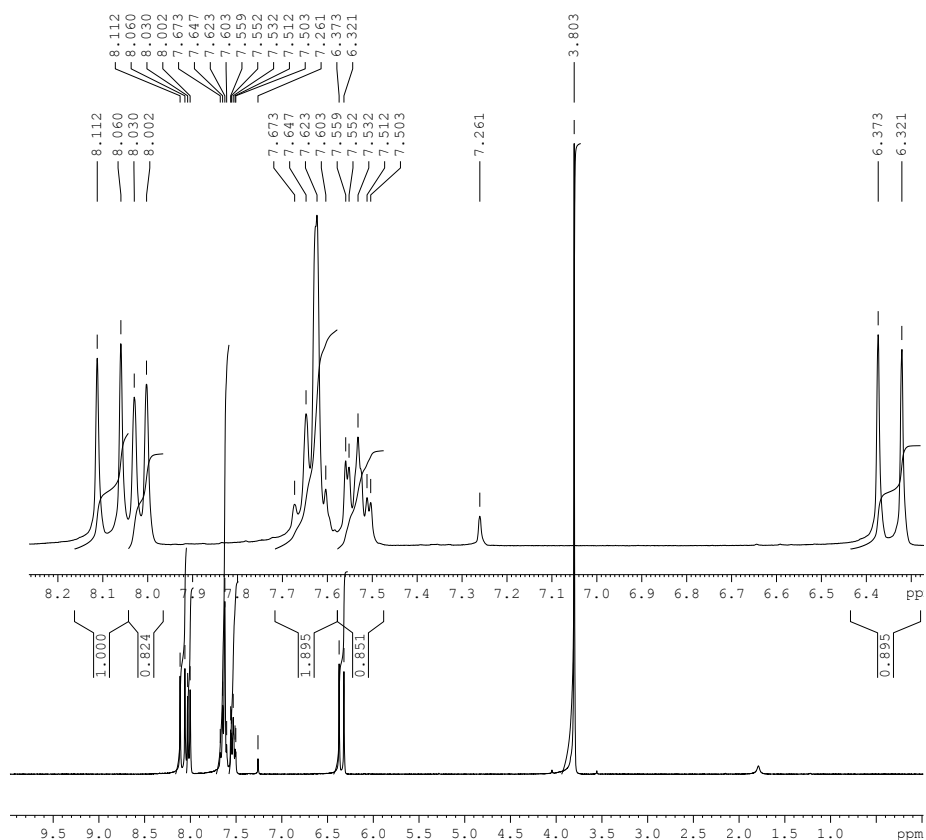


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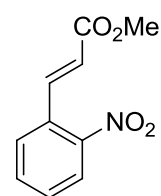
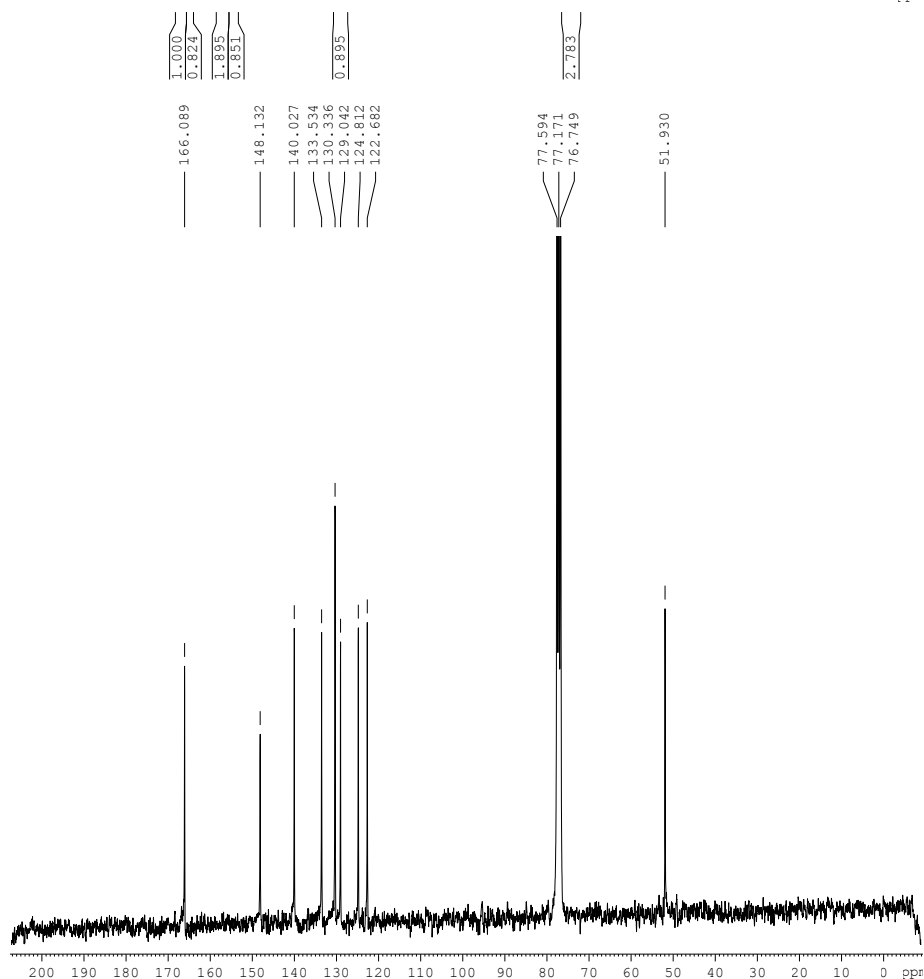




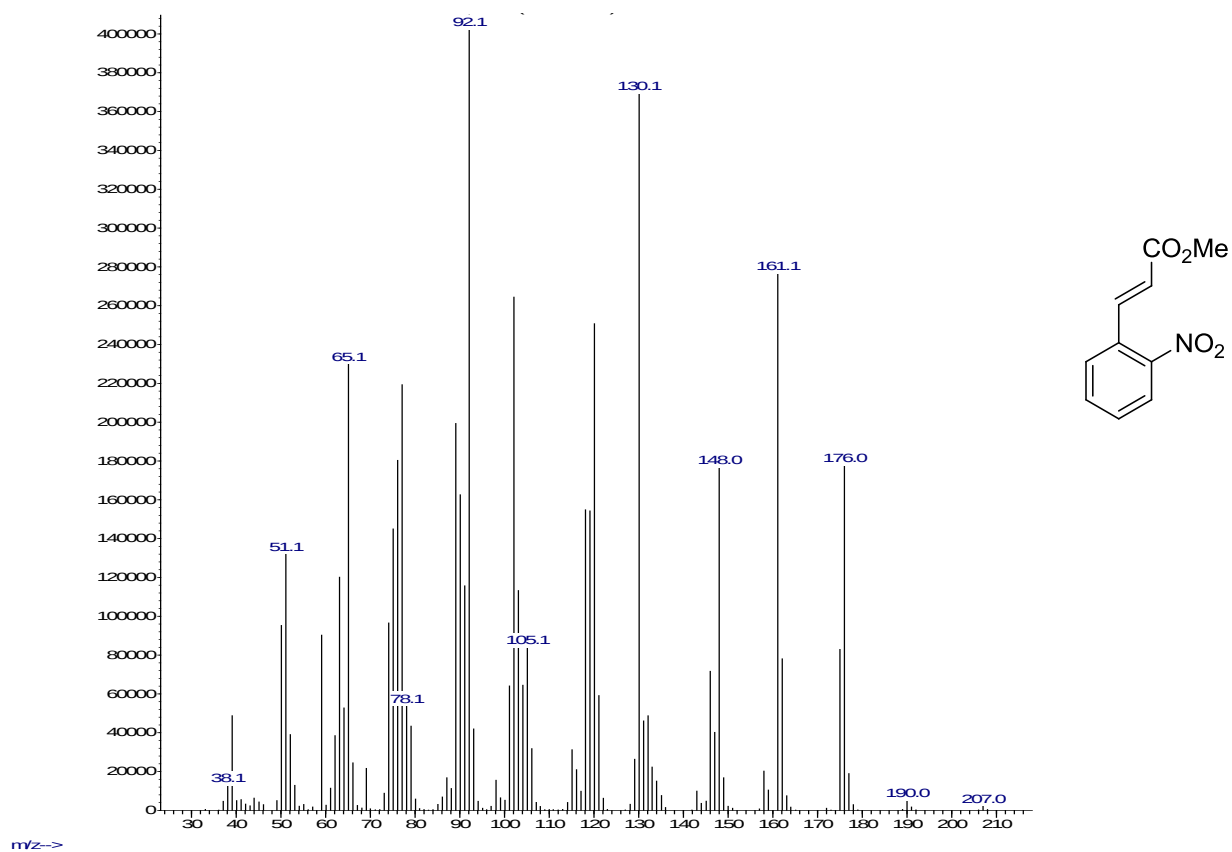
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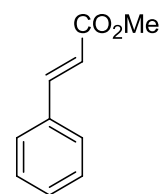
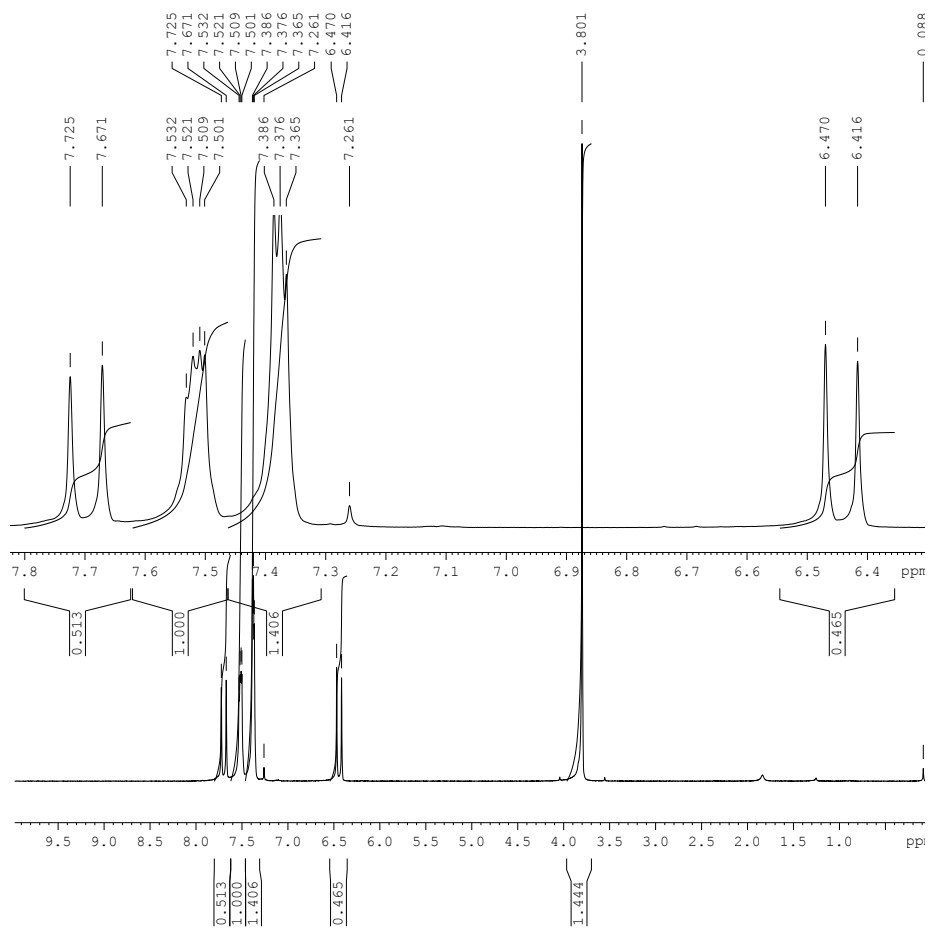
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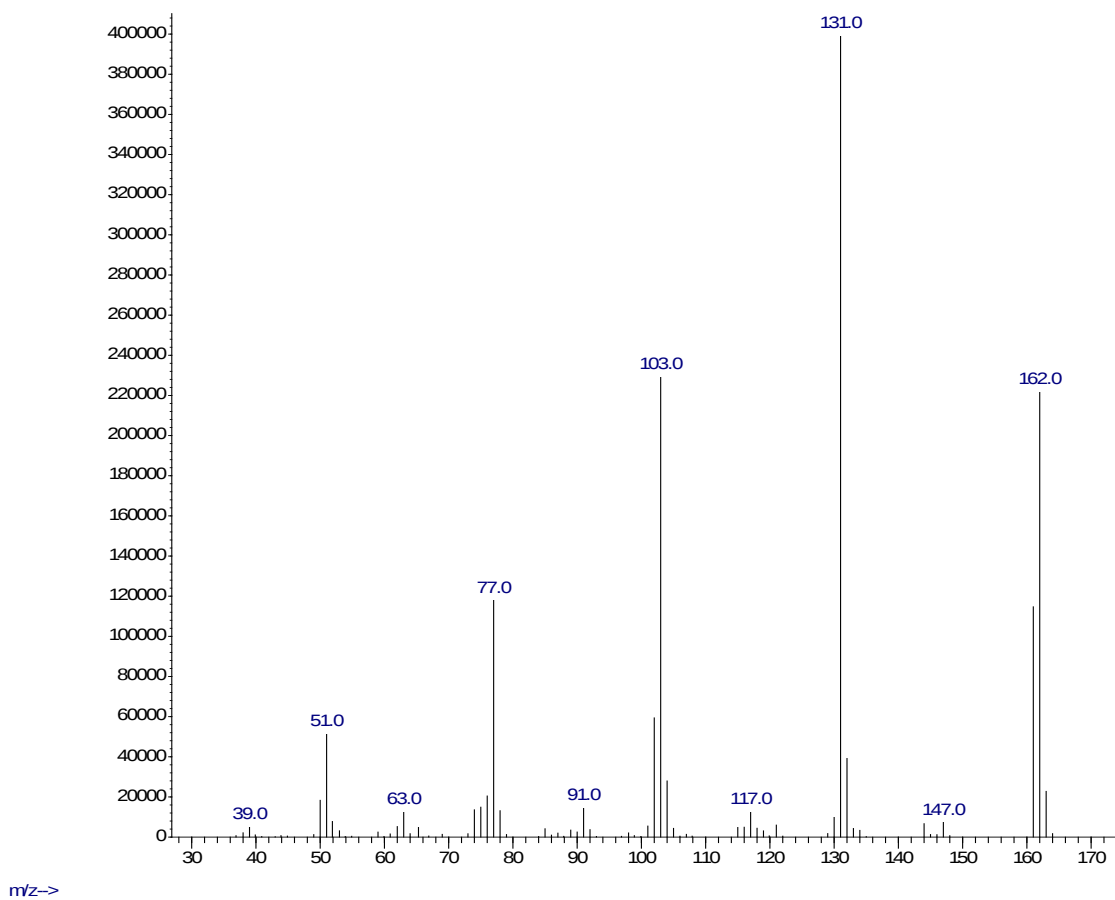
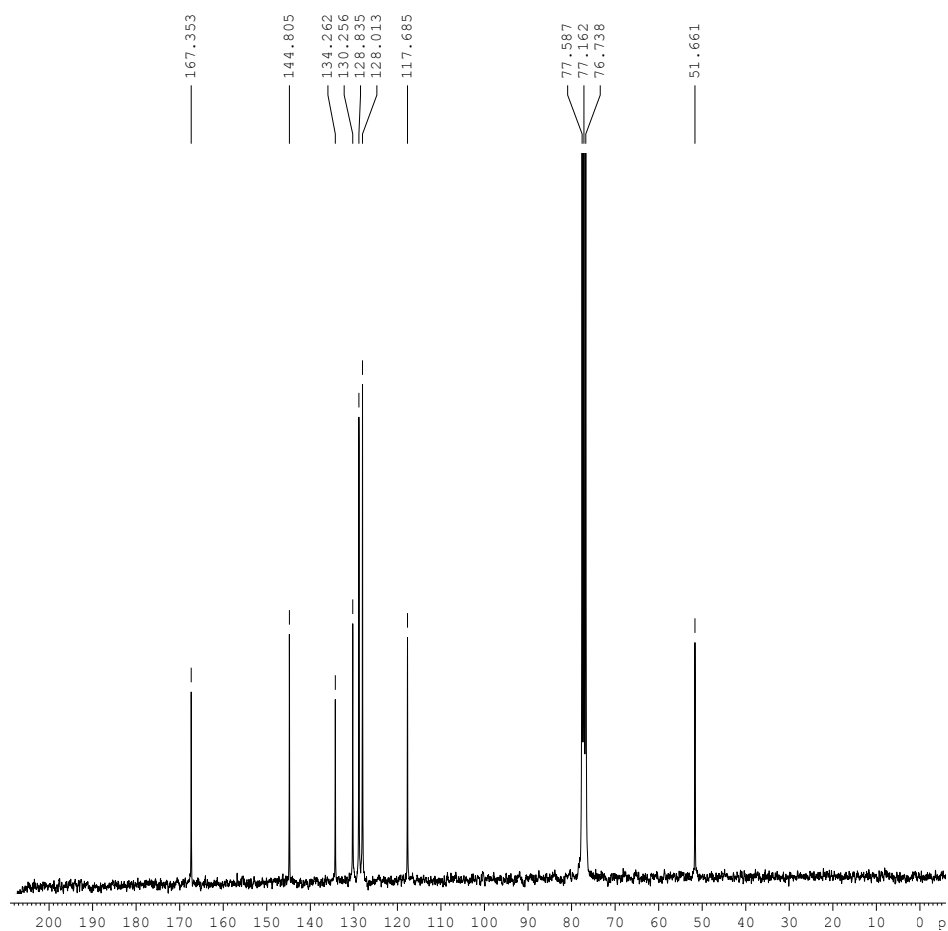
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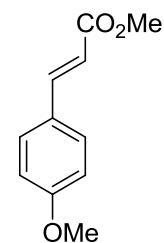
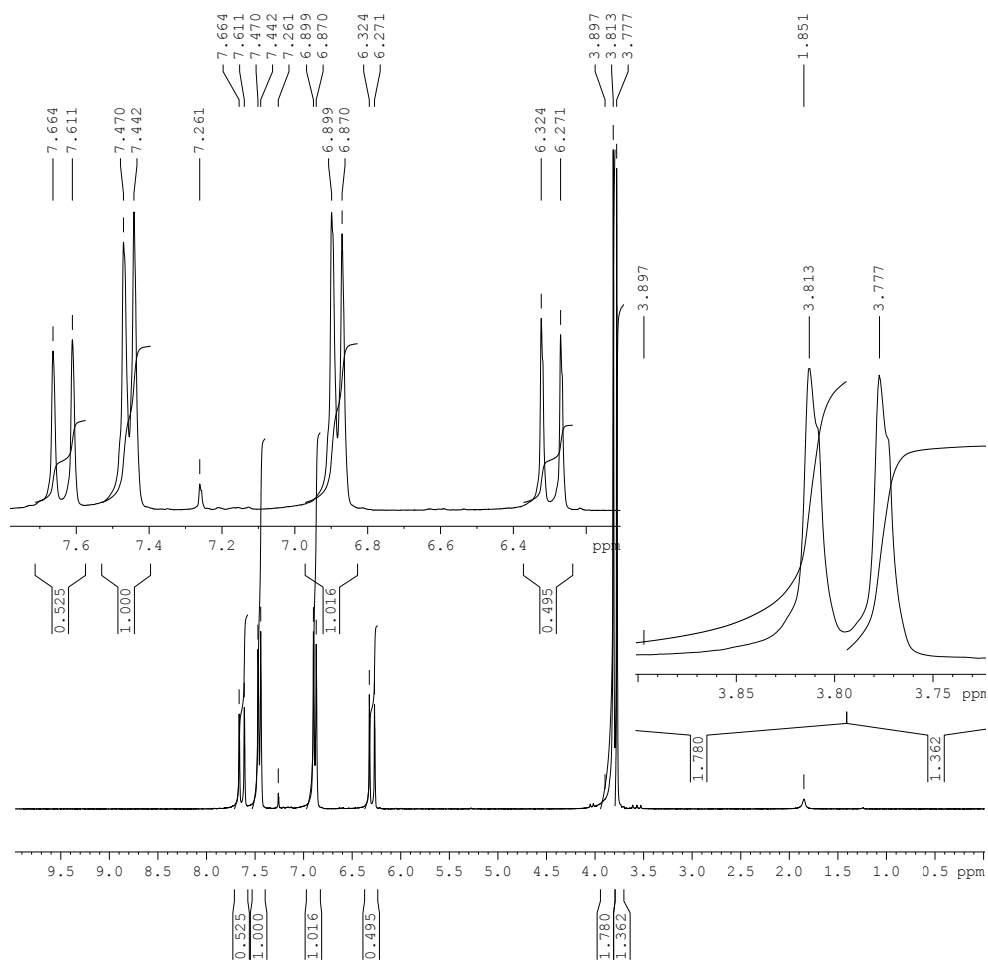
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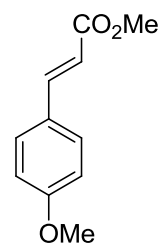
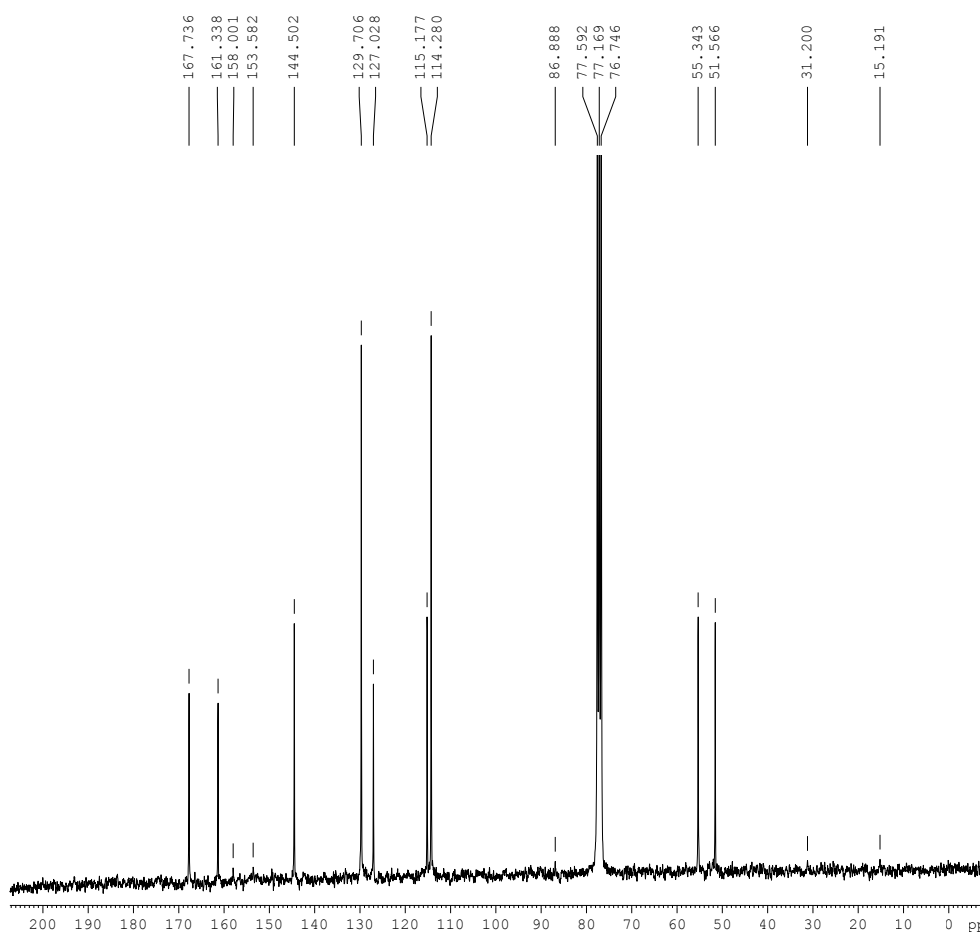
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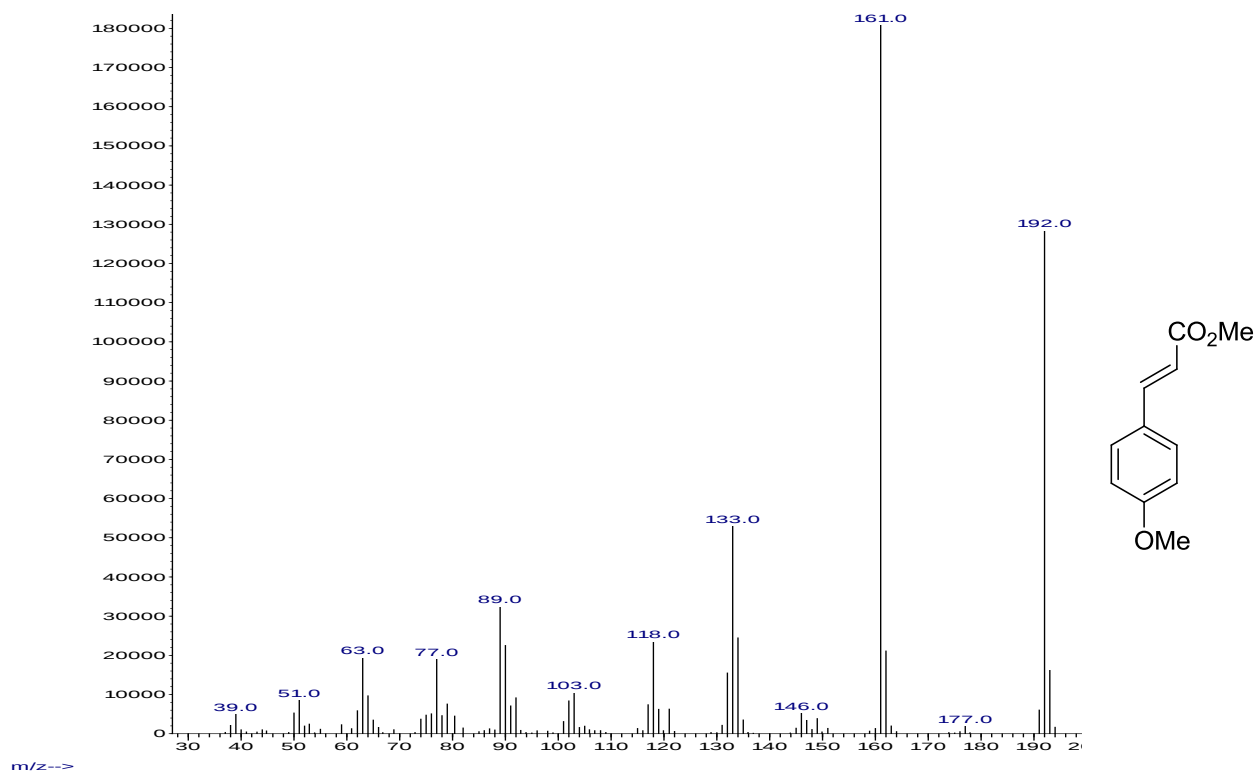
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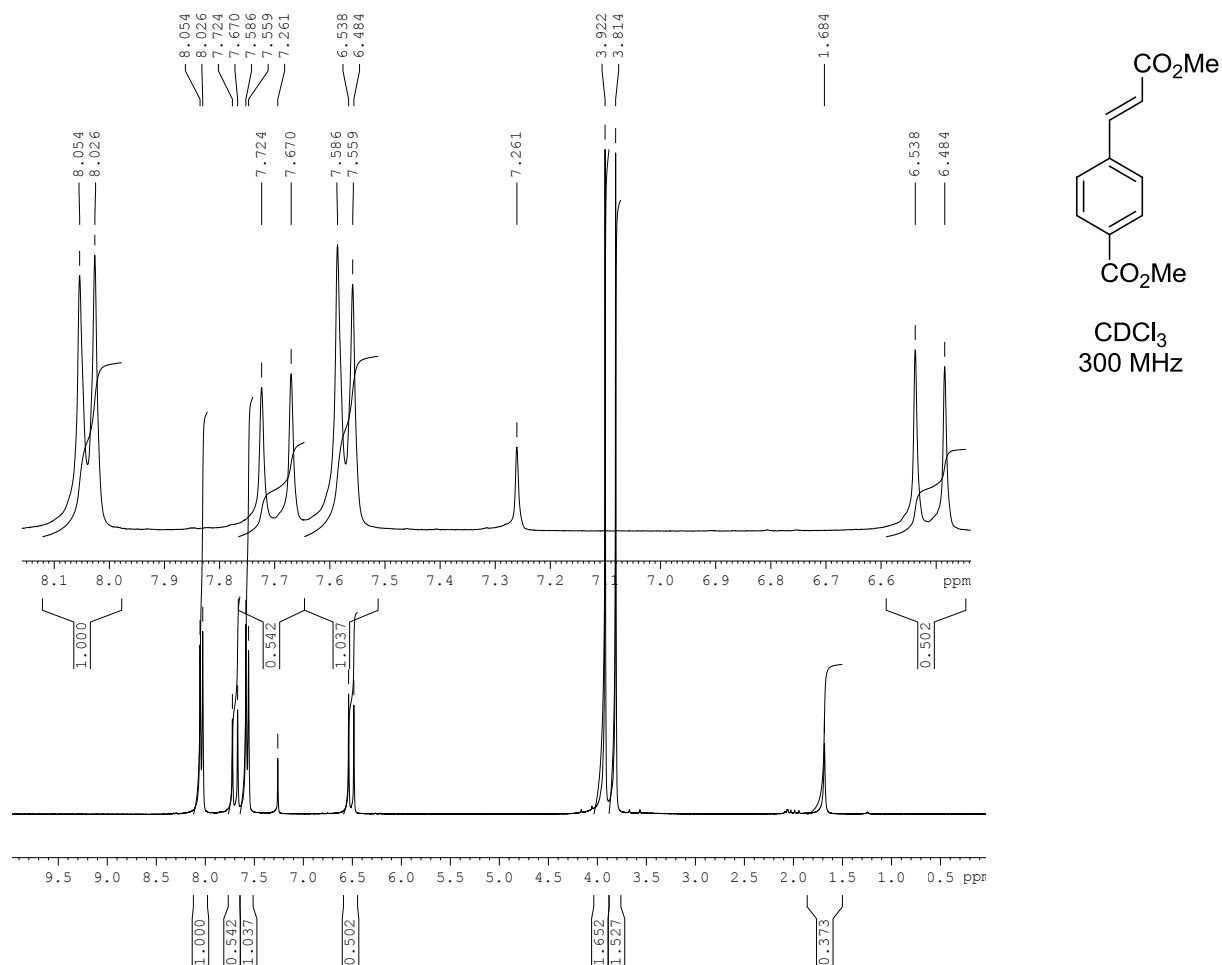
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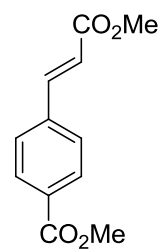
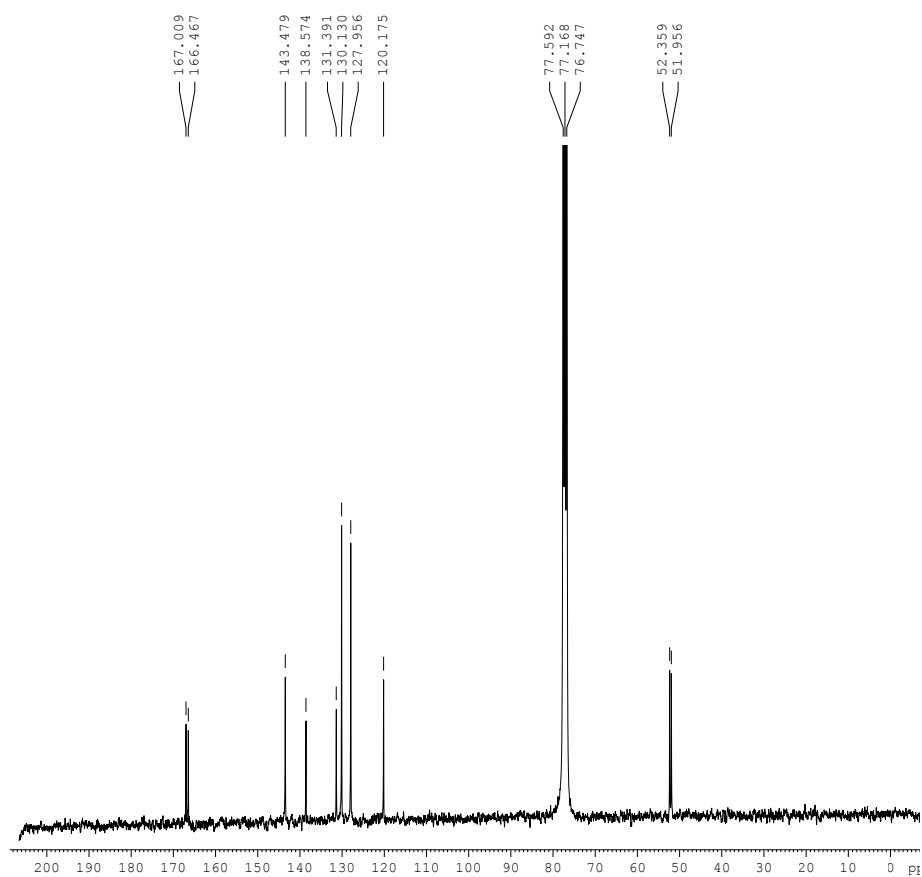


CDCl₃
75 MHz



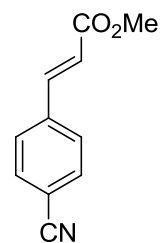
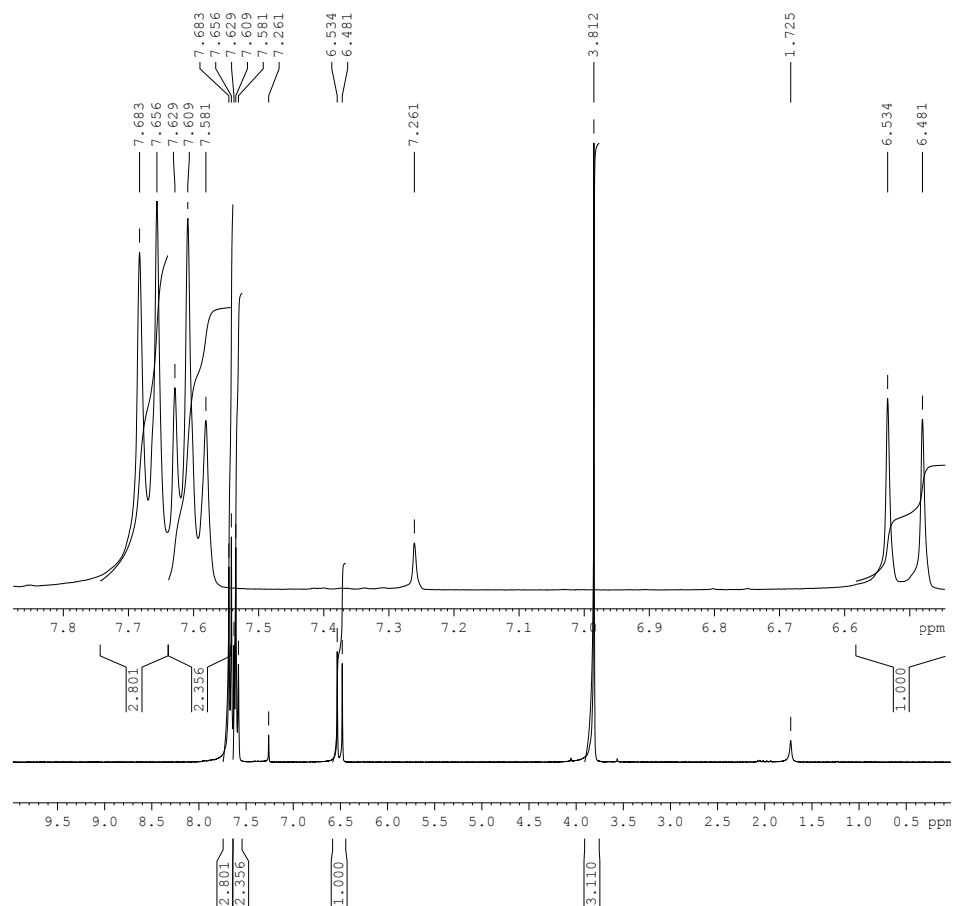
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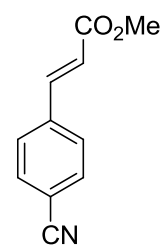
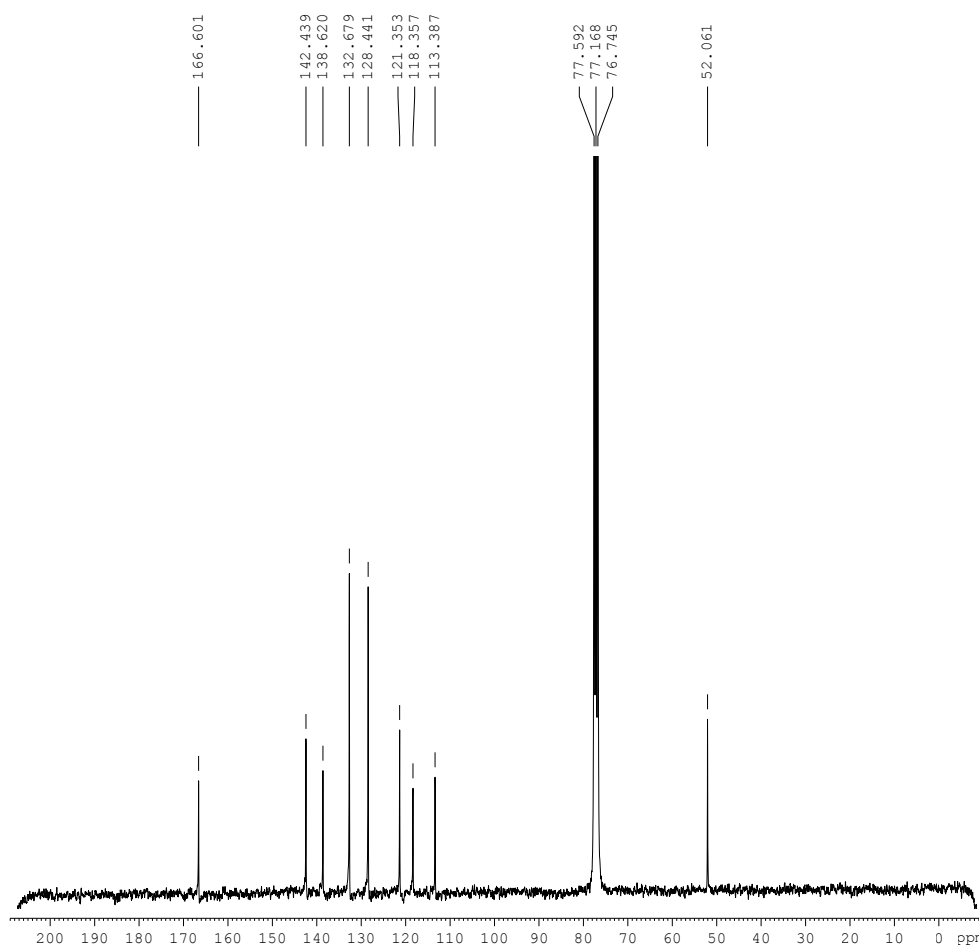


CDCl₃
75 MHz

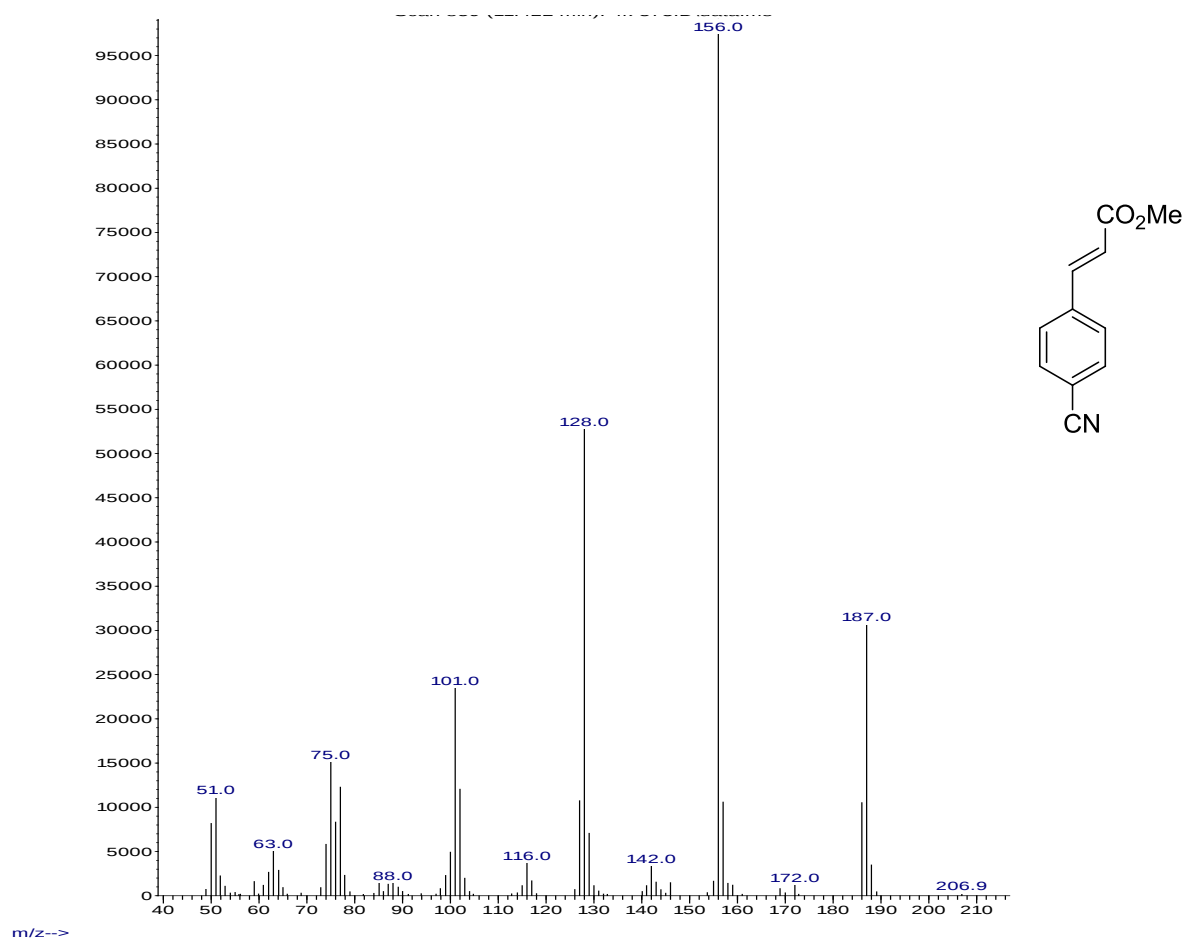
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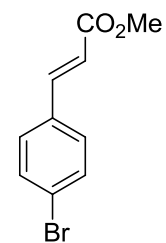
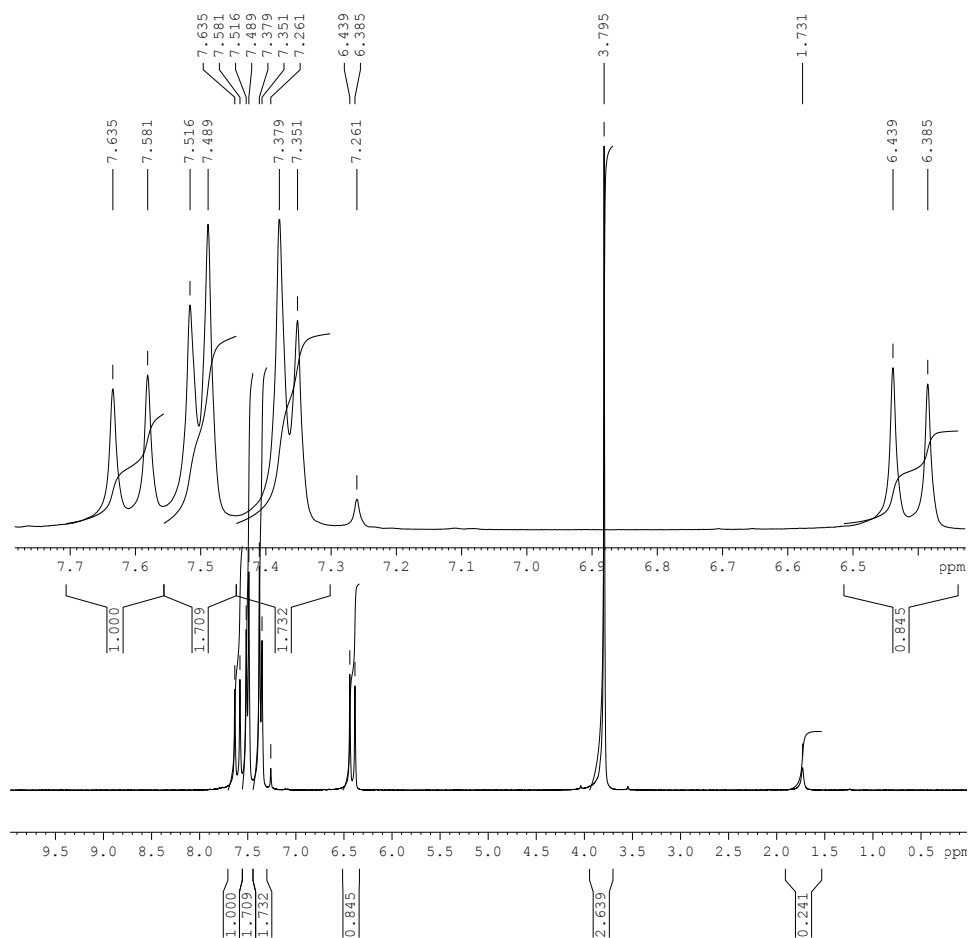
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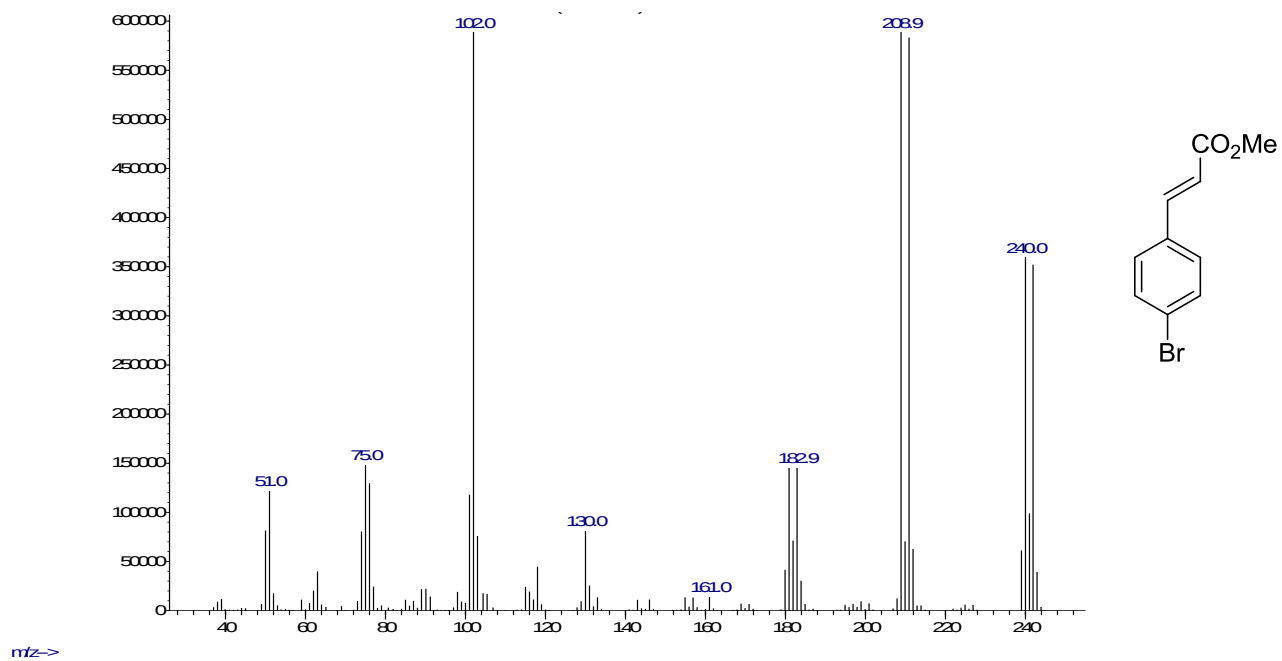
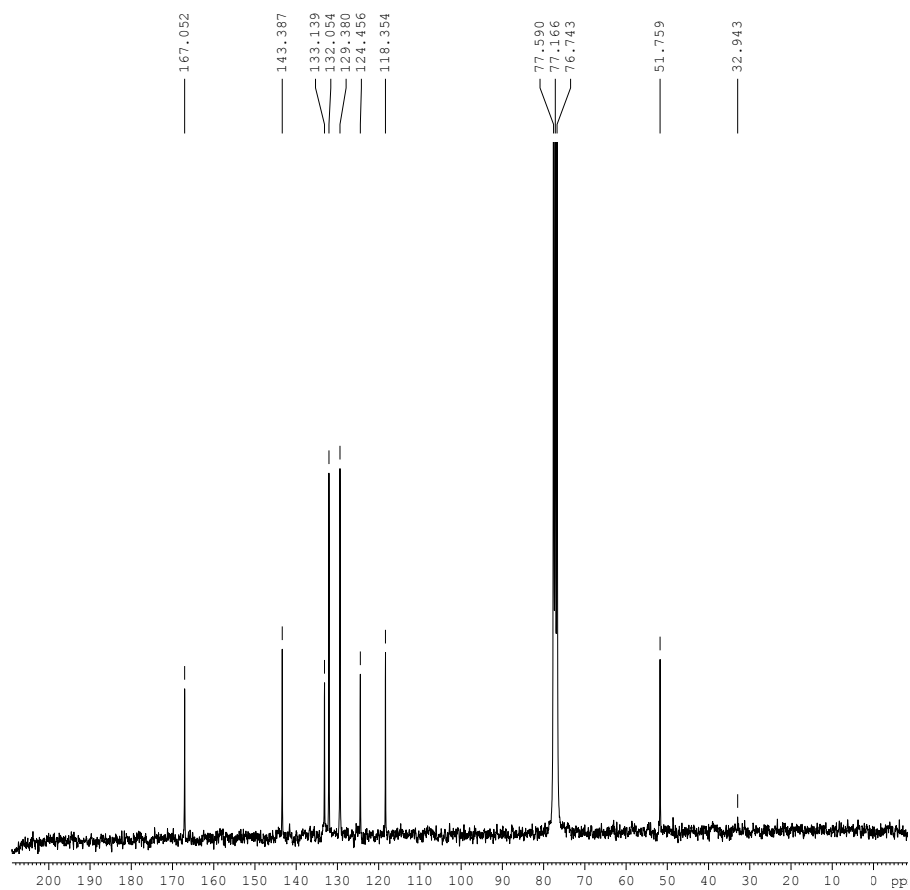
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75 MHz



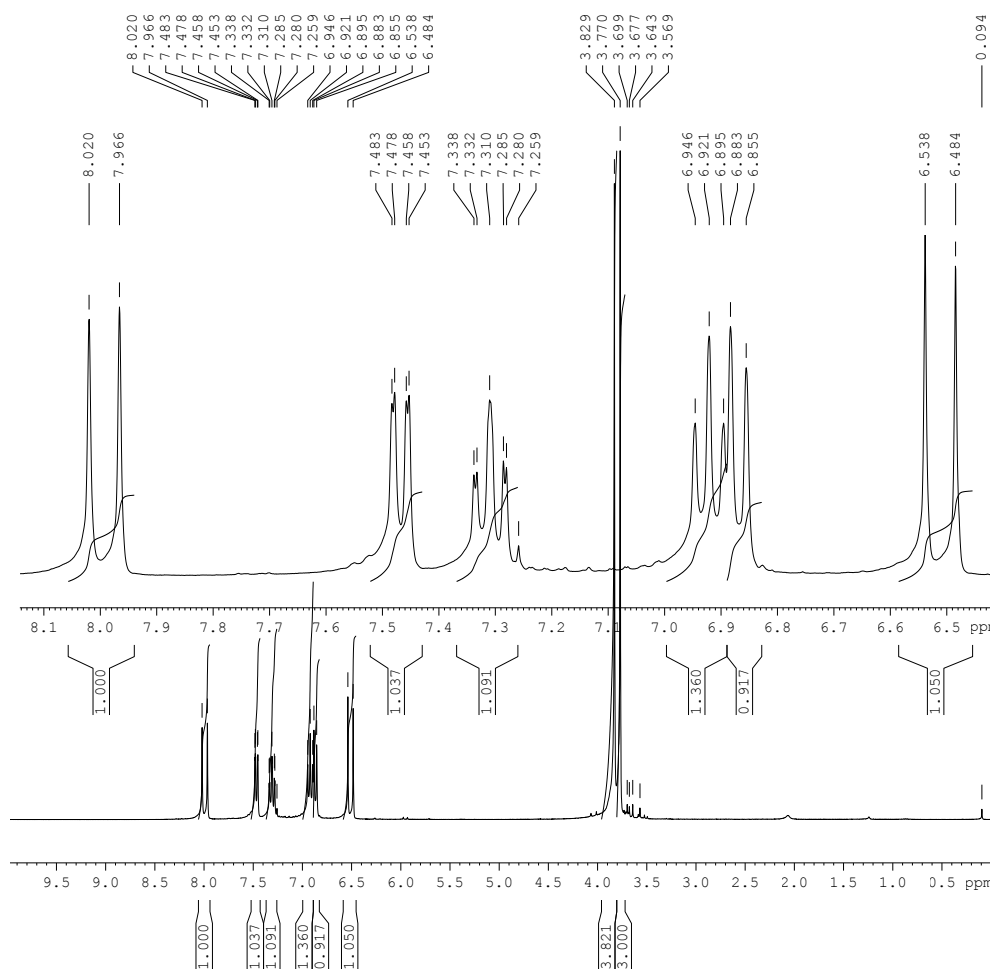
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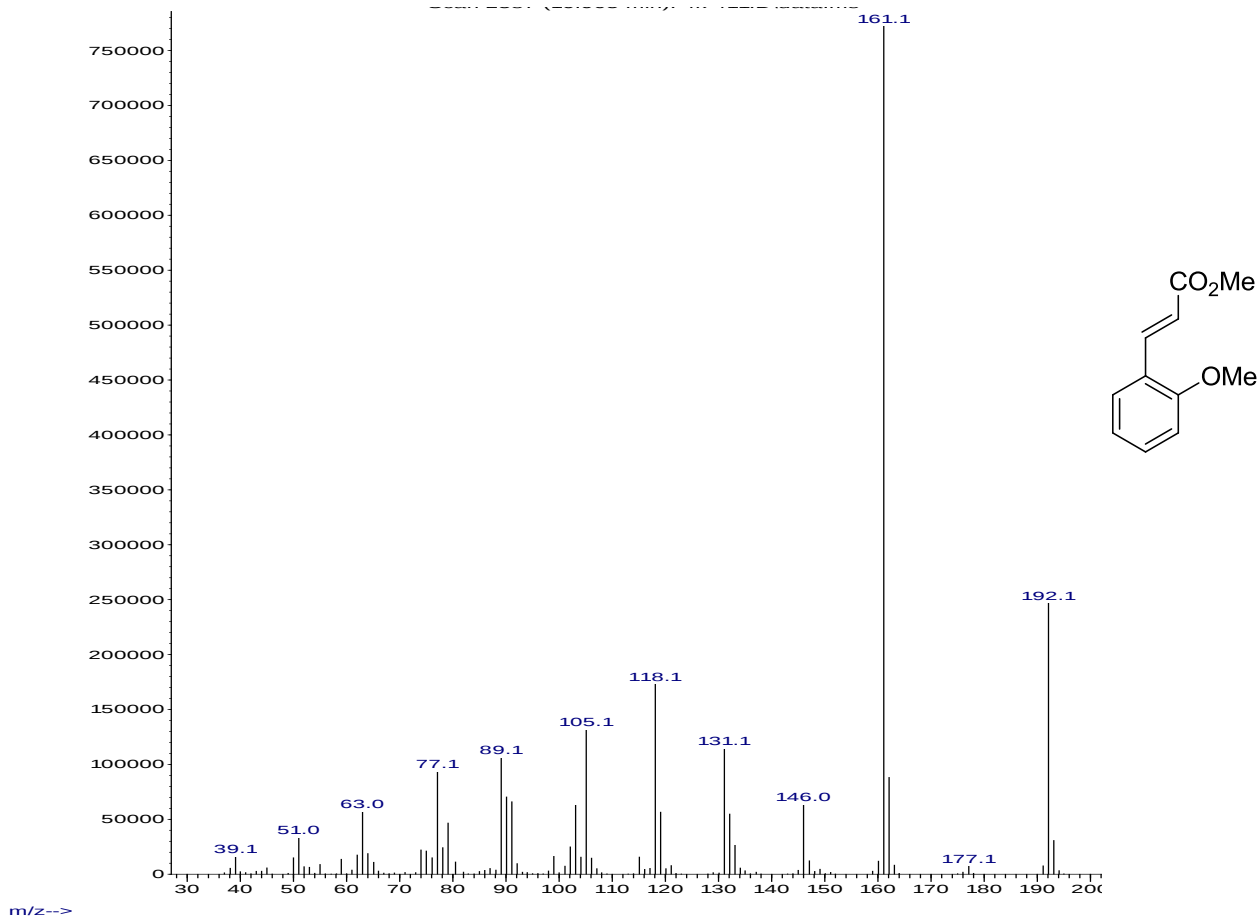
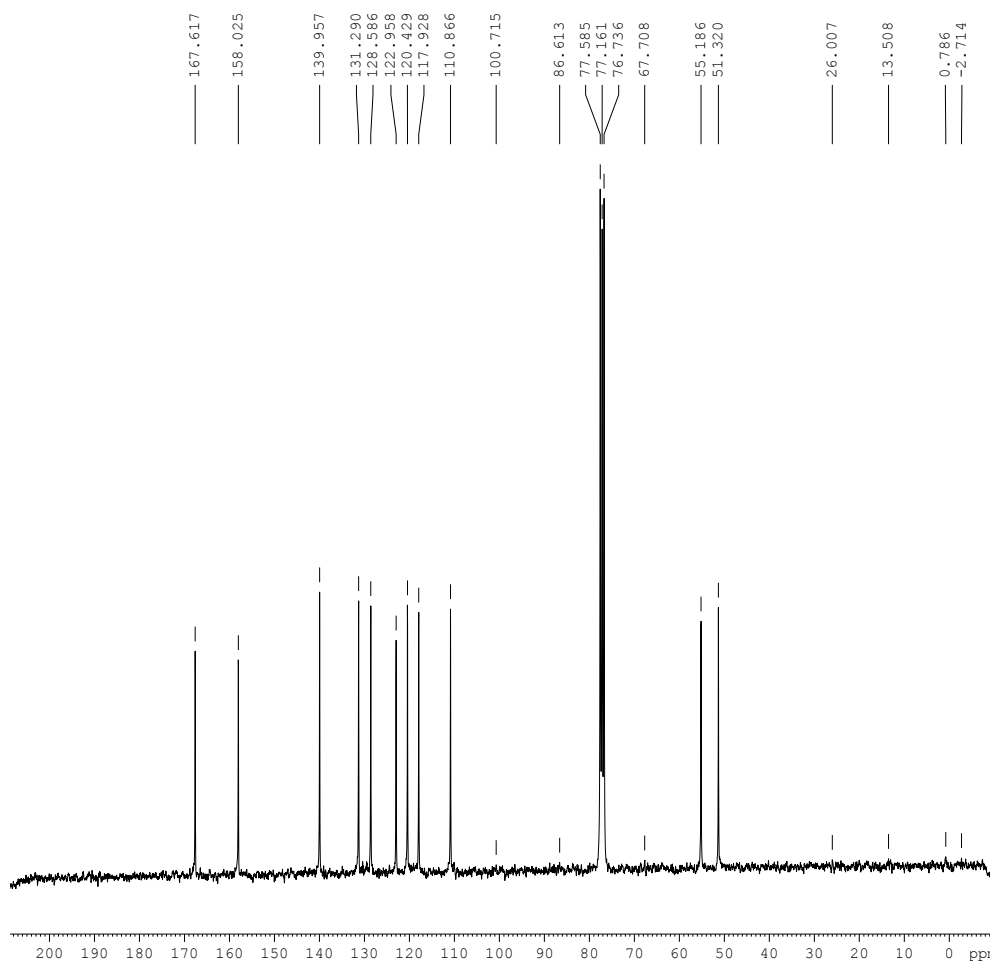


CDCl₃
300 MHz

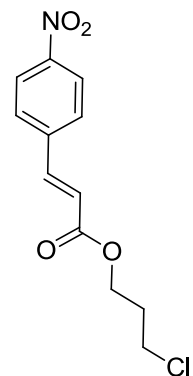
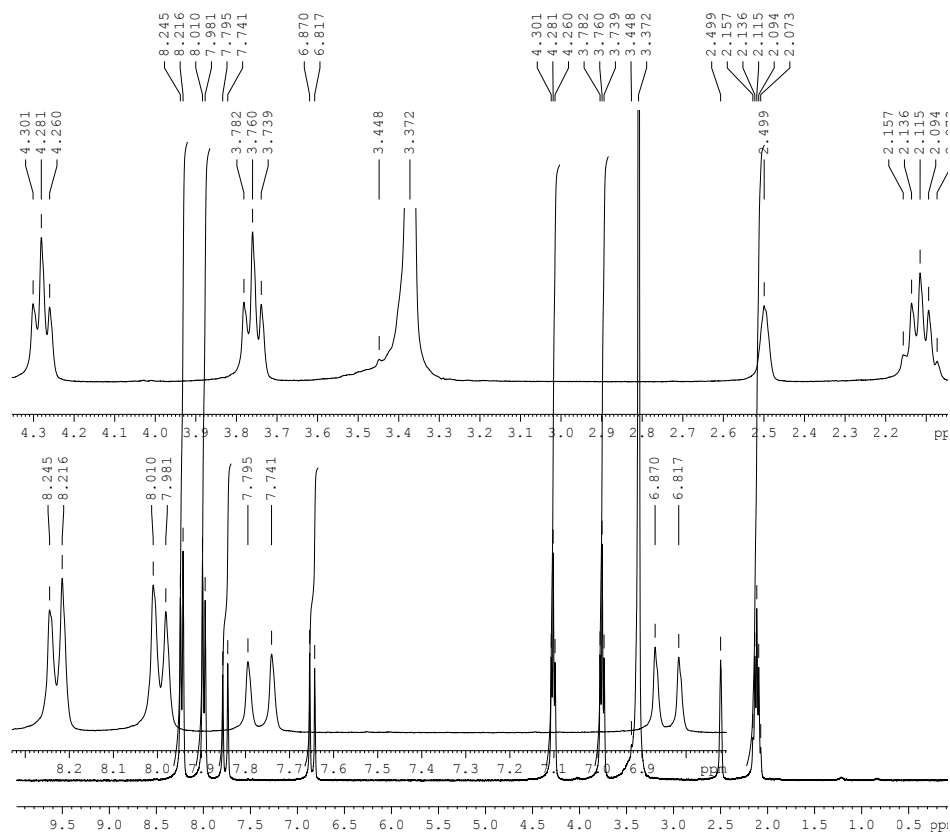


Methyl (*E*)-3-(2-methoxyphenyl)acrylate (**3ai**):

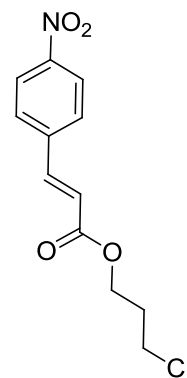
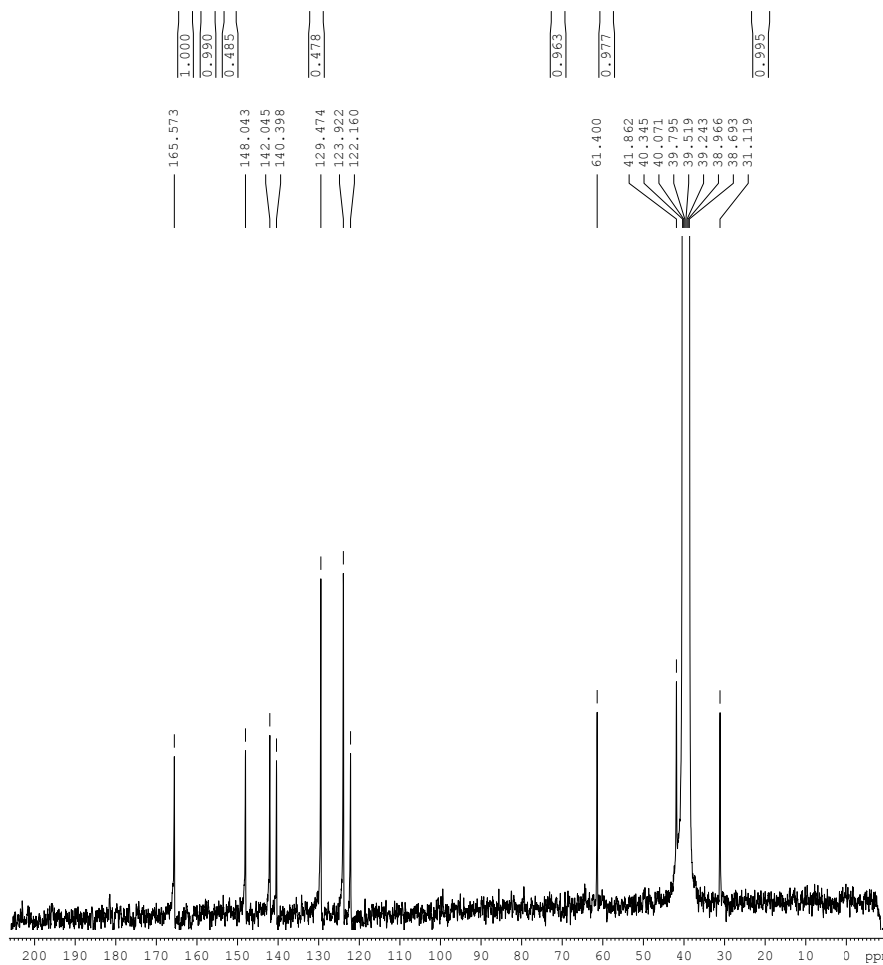




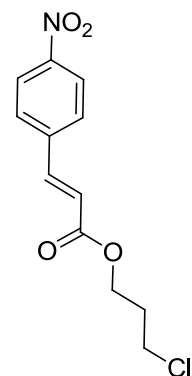
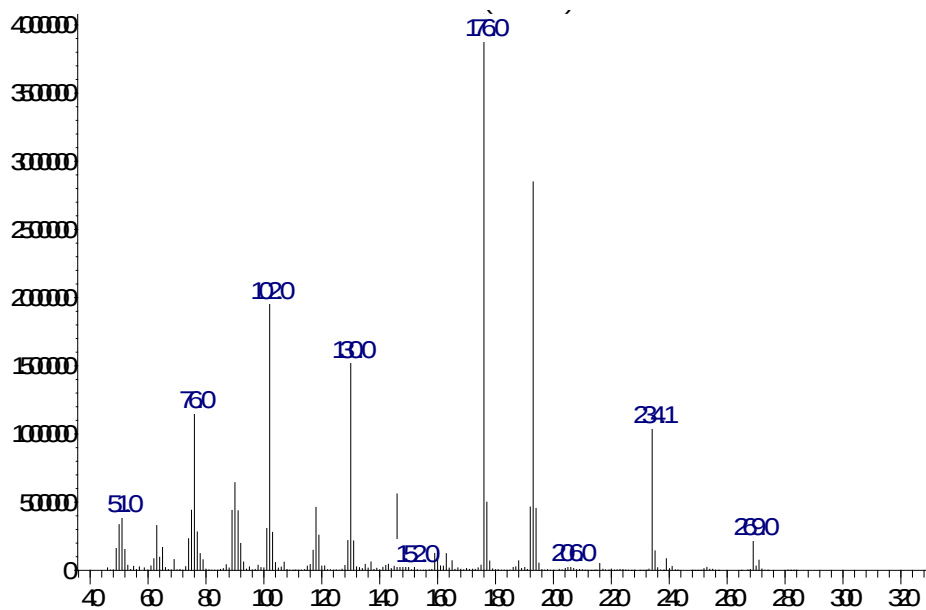
3-Chloropropyl (*E*)-3-(4-nitrophenyl)acrylate (**3ba**):



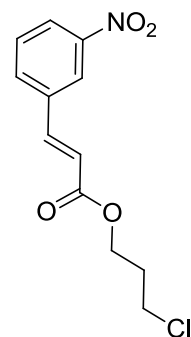
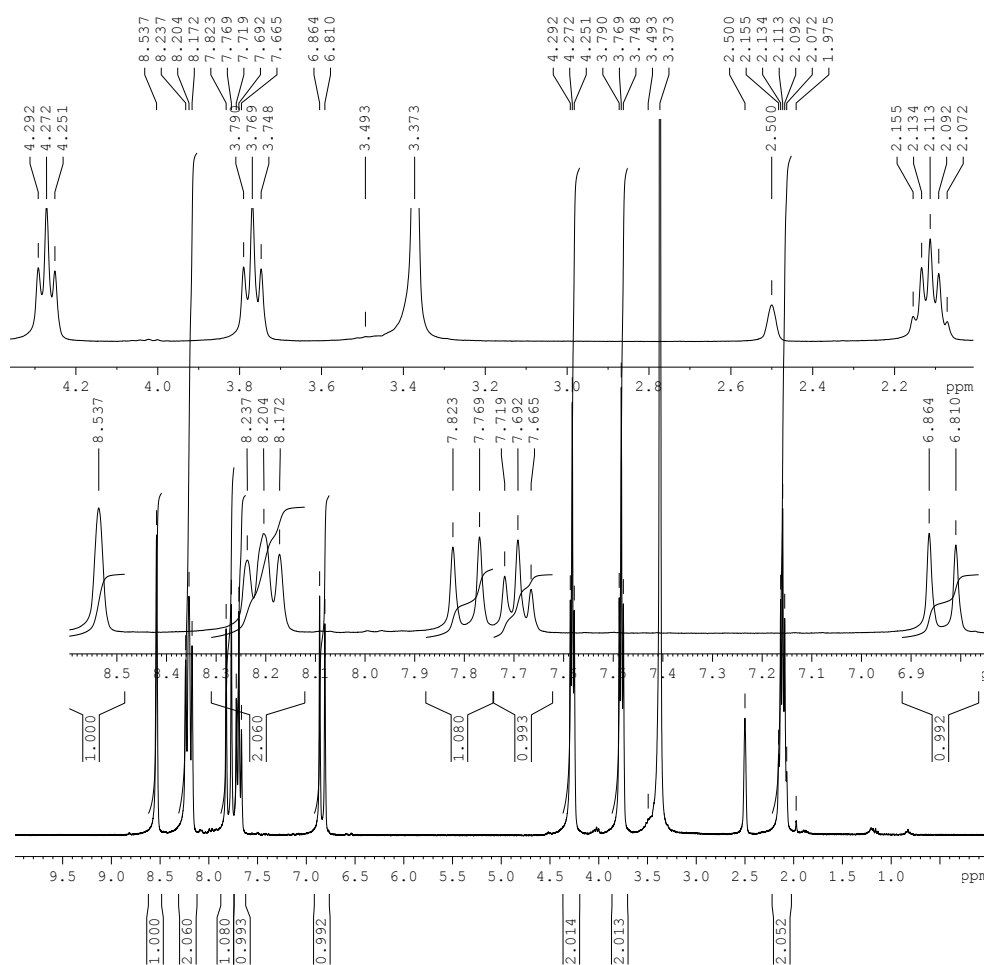
DMSO d₆
300 MHz



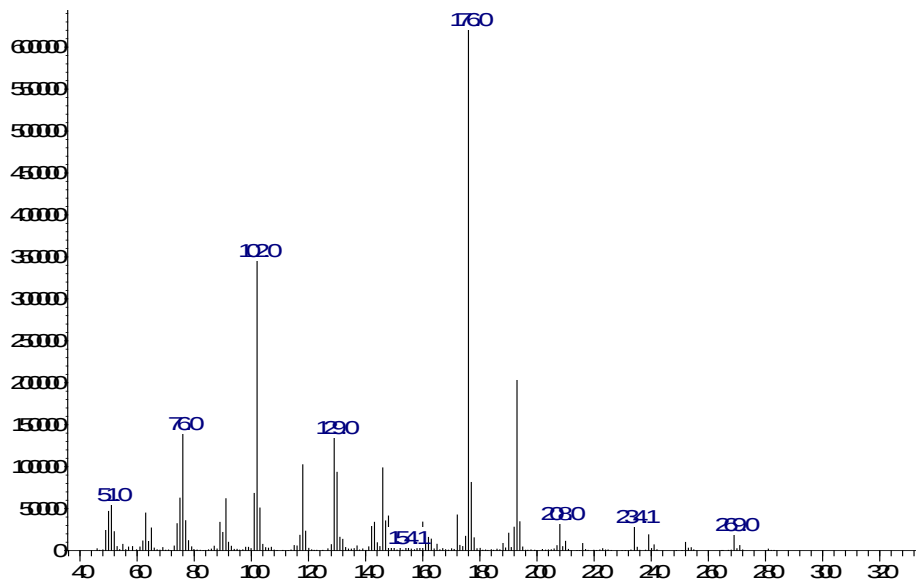
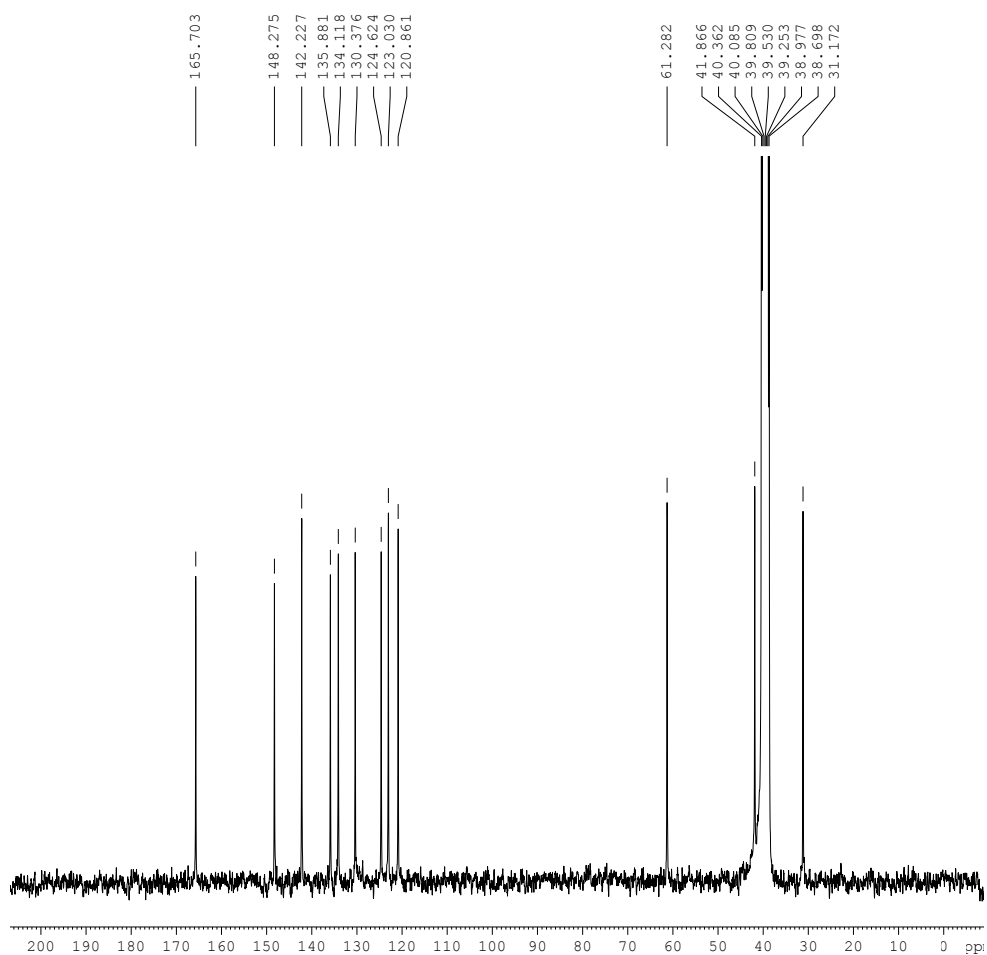
DMSO d₆
75 MHz



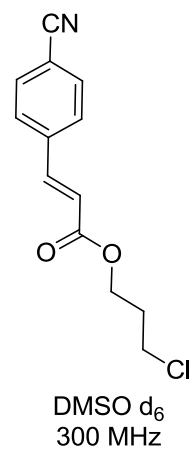
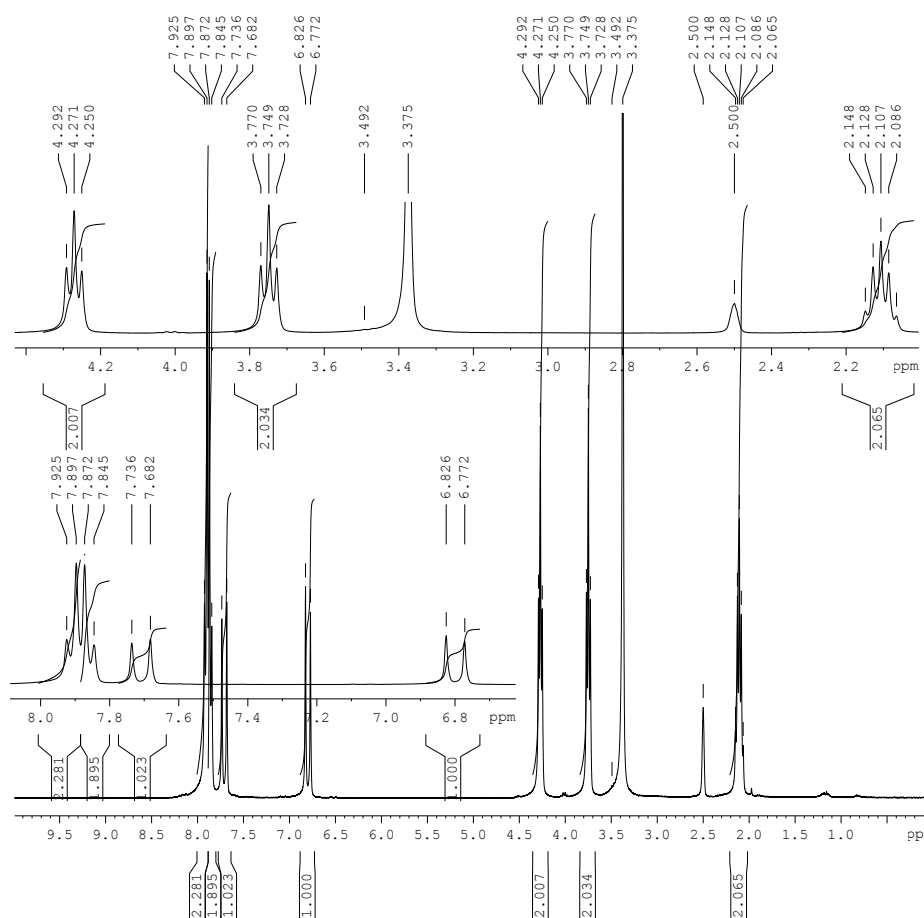
3-Chloropropyl (E)-3-(3-nitrophenyl)acrylate (**3bb**):

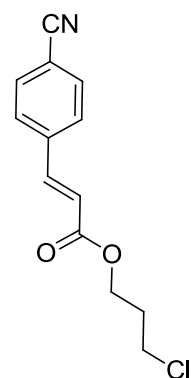
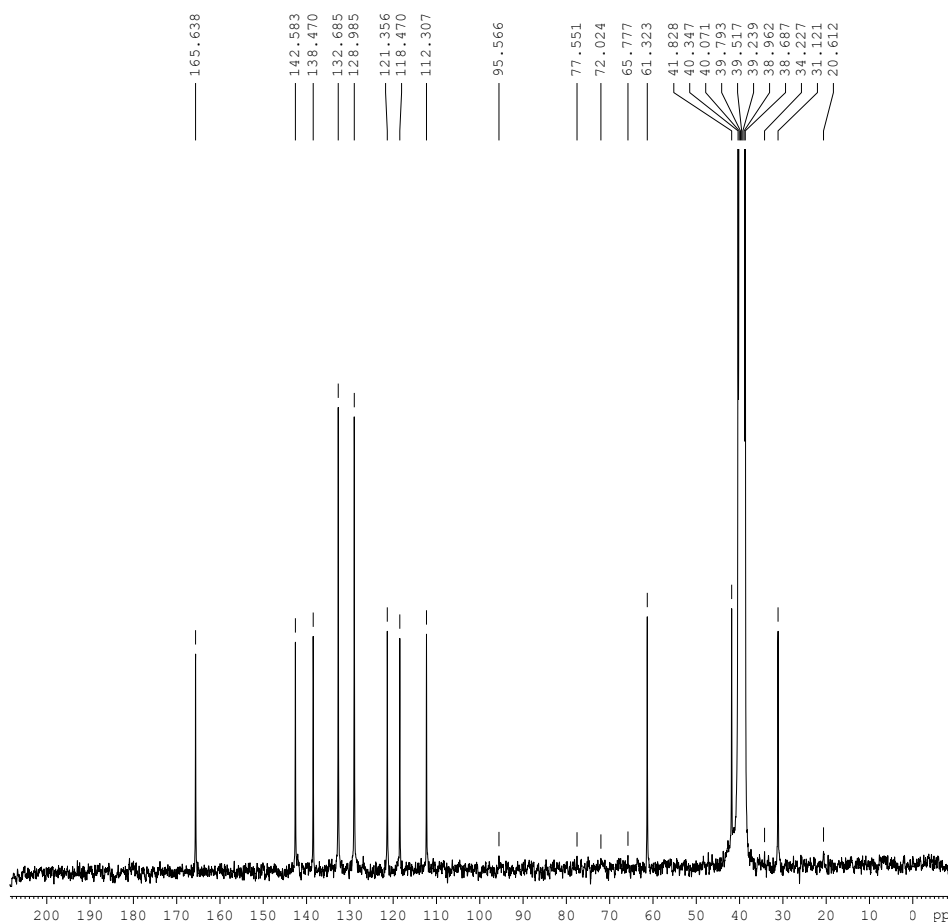


DMSO d₆
300 MHz

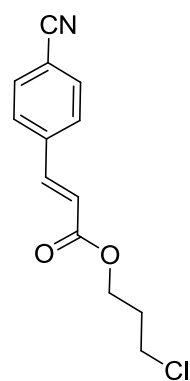
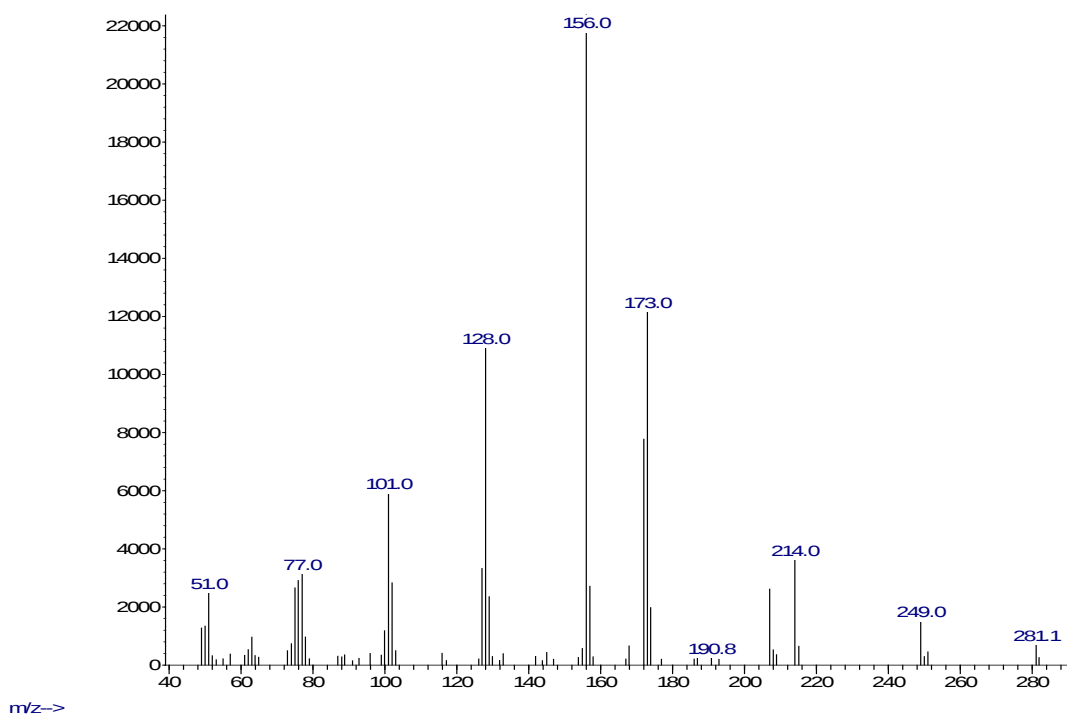


3-Chloropropyl (E)-3-(4-cyanophenyl)acrylate (**3bg**):

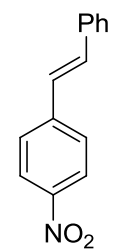
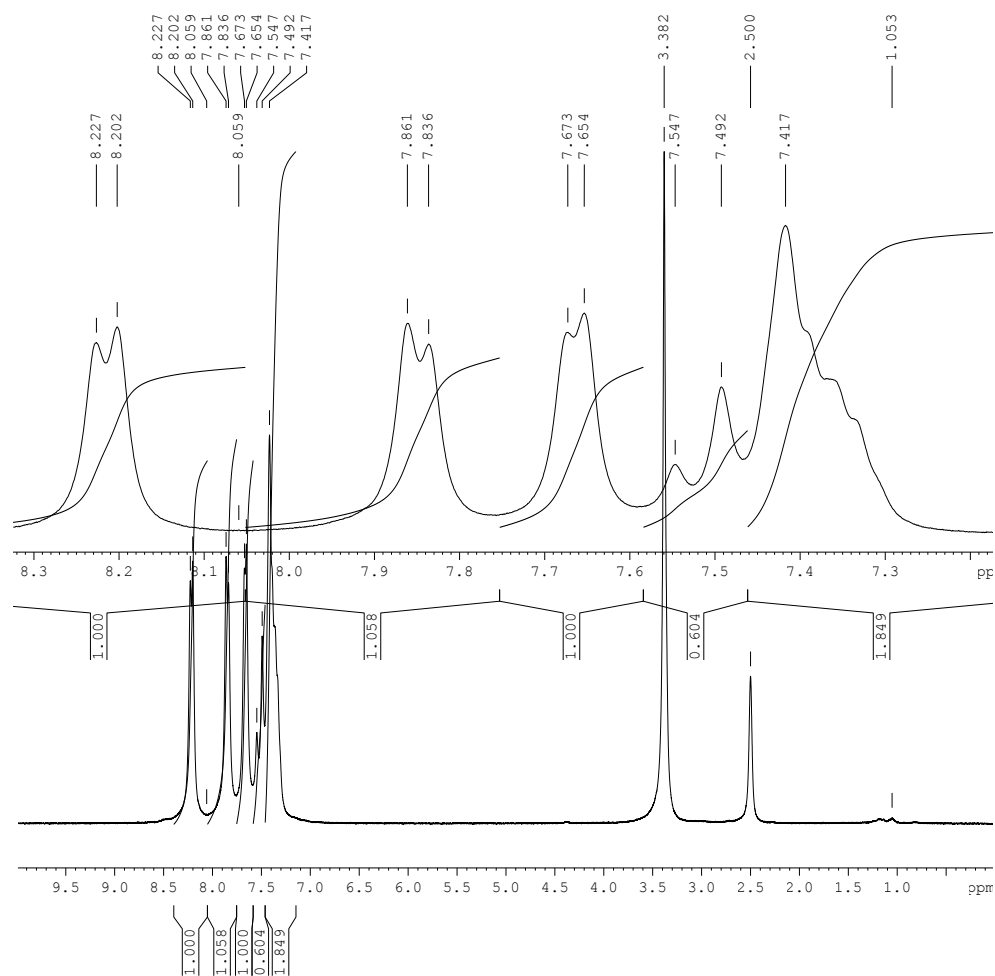




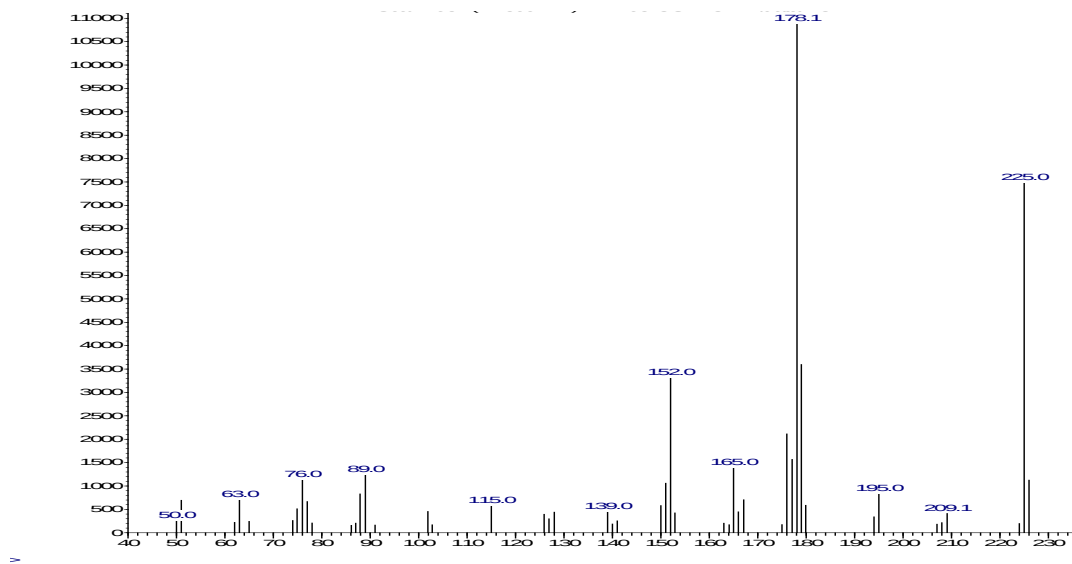
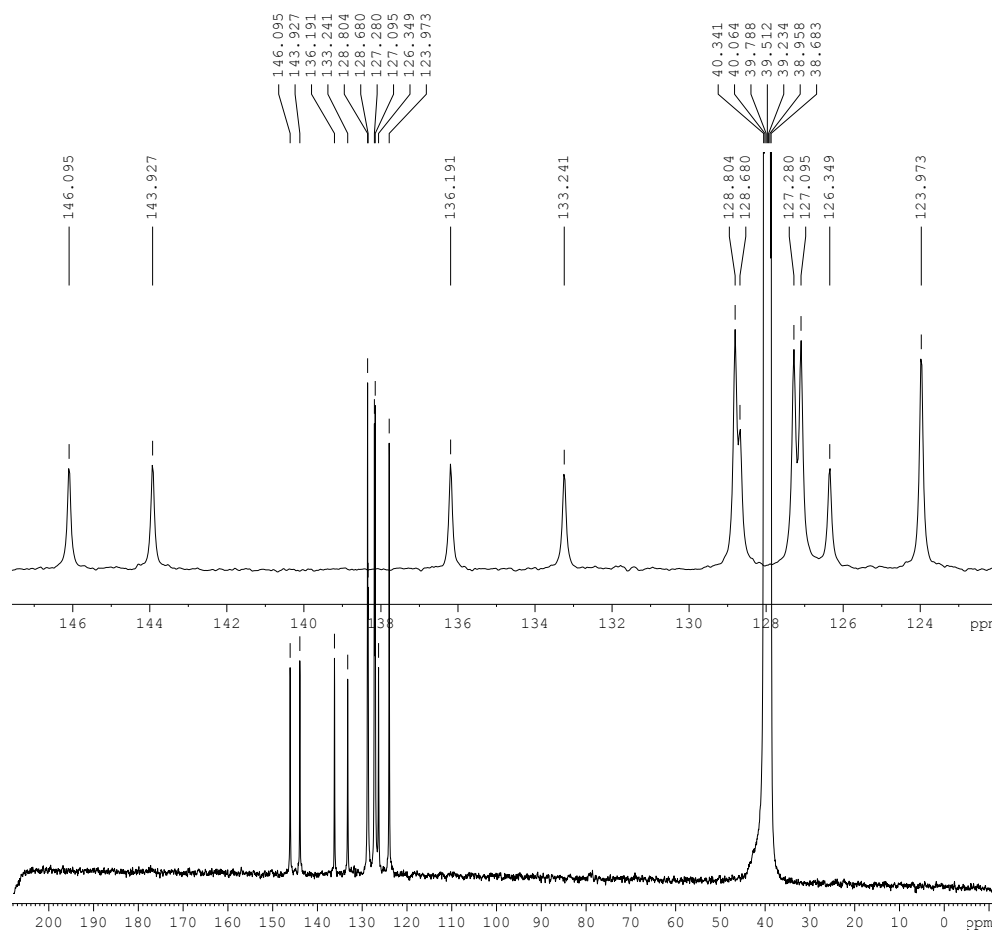
DMSO d_6
75 MHz



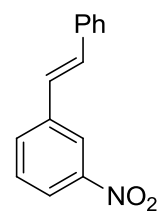
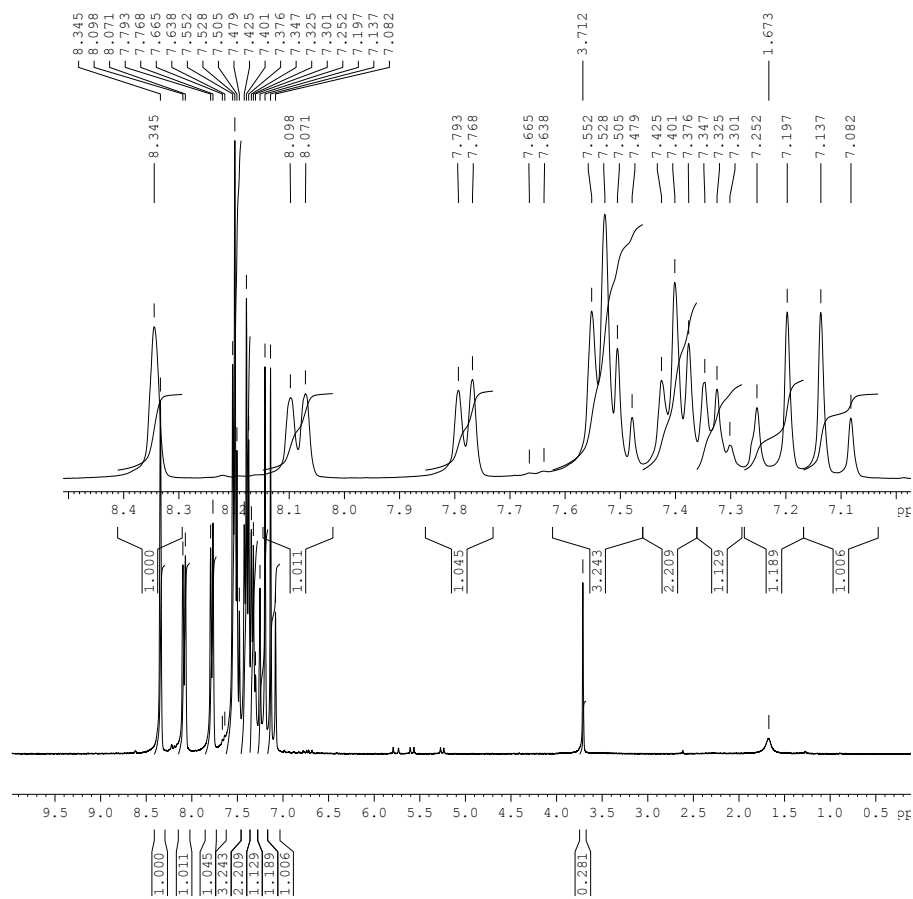
(E)-1-Nitro-4-styrylbenzene (3ca):



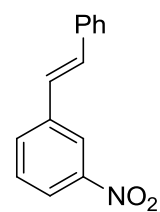
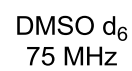
DMSO d₆
300 MHz



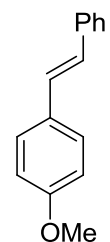
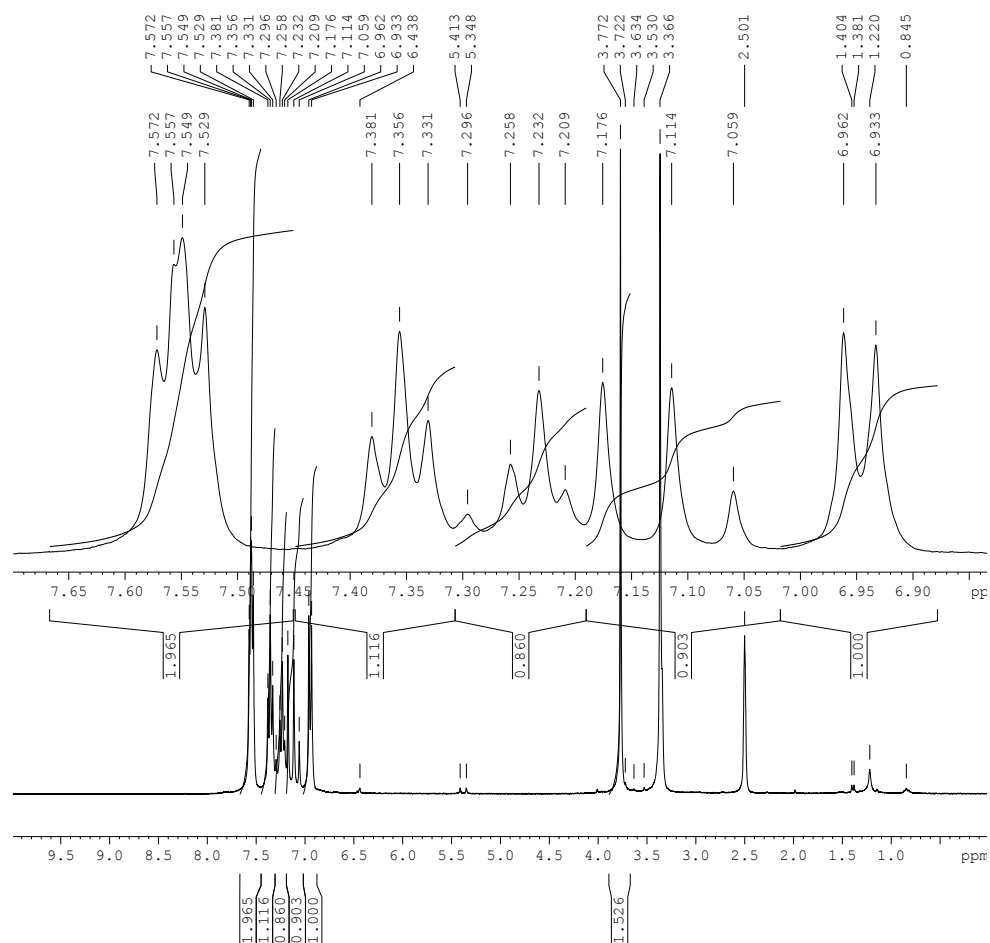
(*E*)-1-Nitro-3-styrylbenzene (3cb):



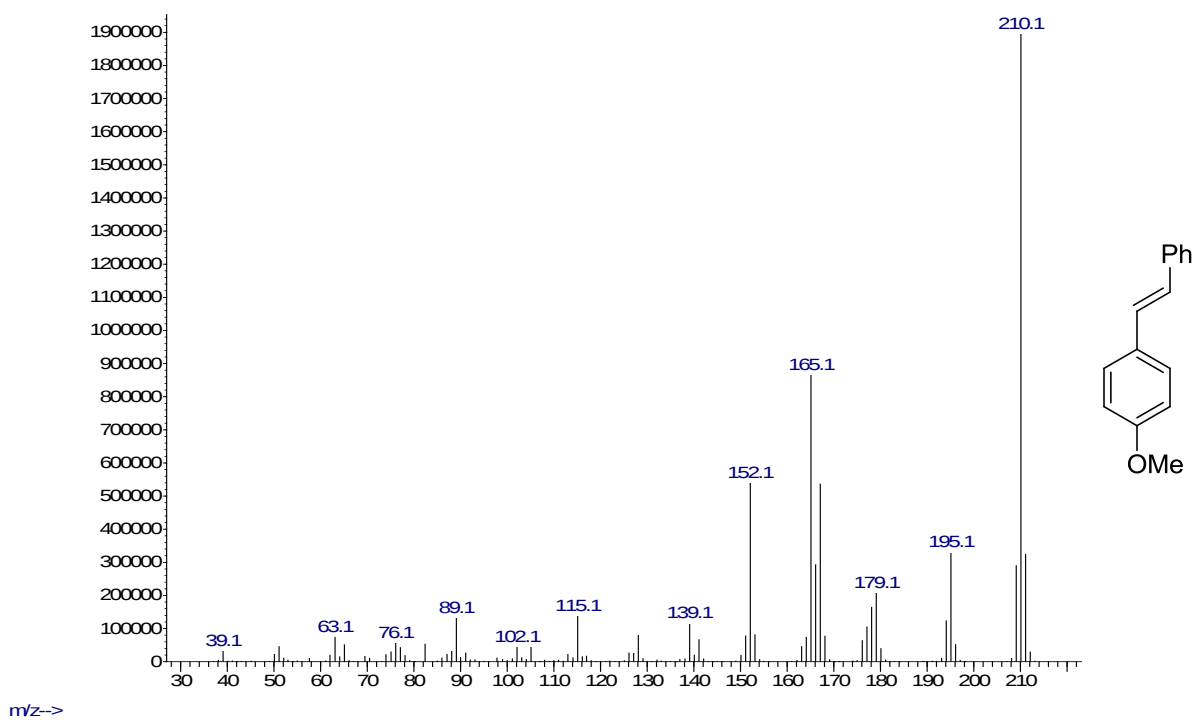
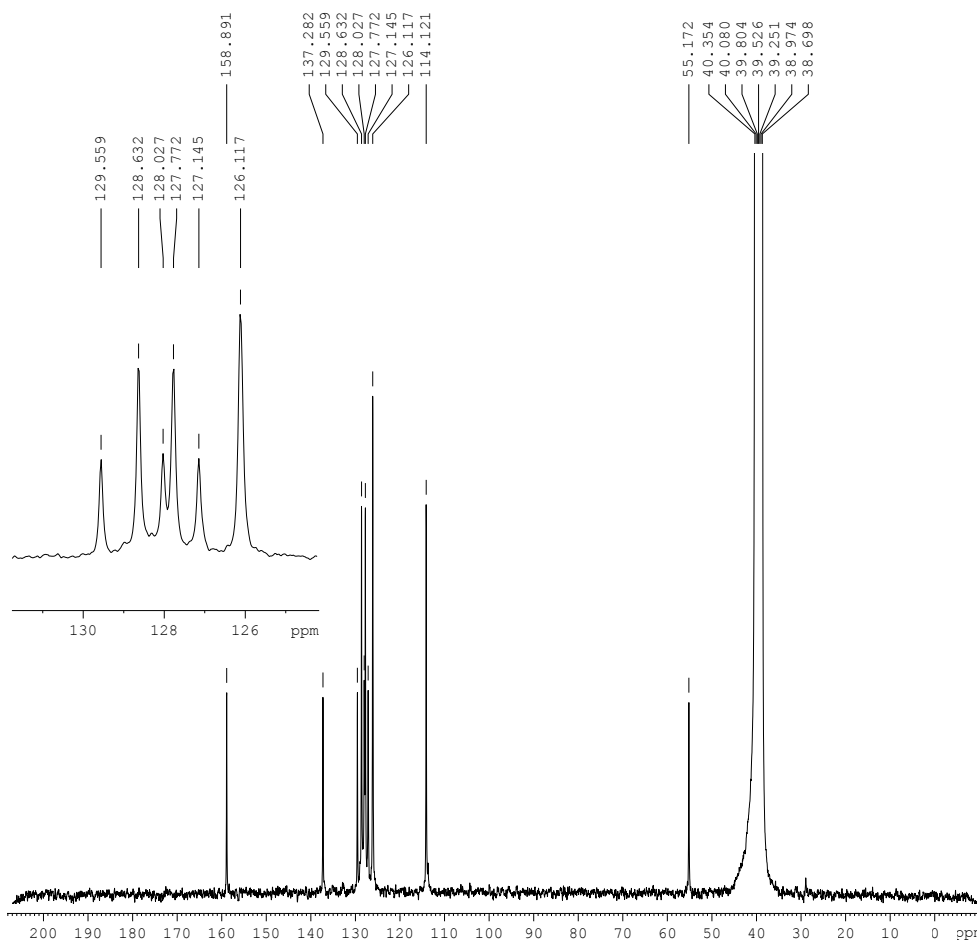
DMSO d₆
300 MHz



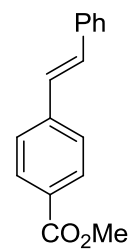
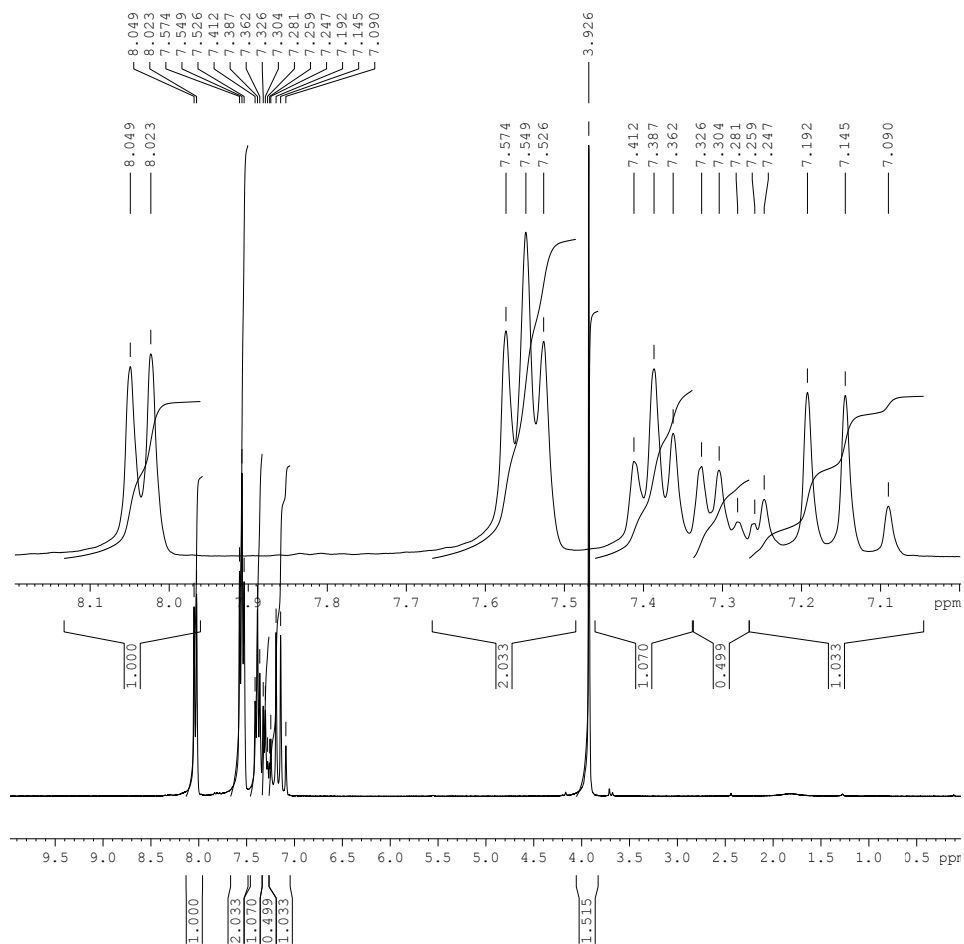
(*E*)-1-methoxy-4-styrylbenzene (**3ce**):



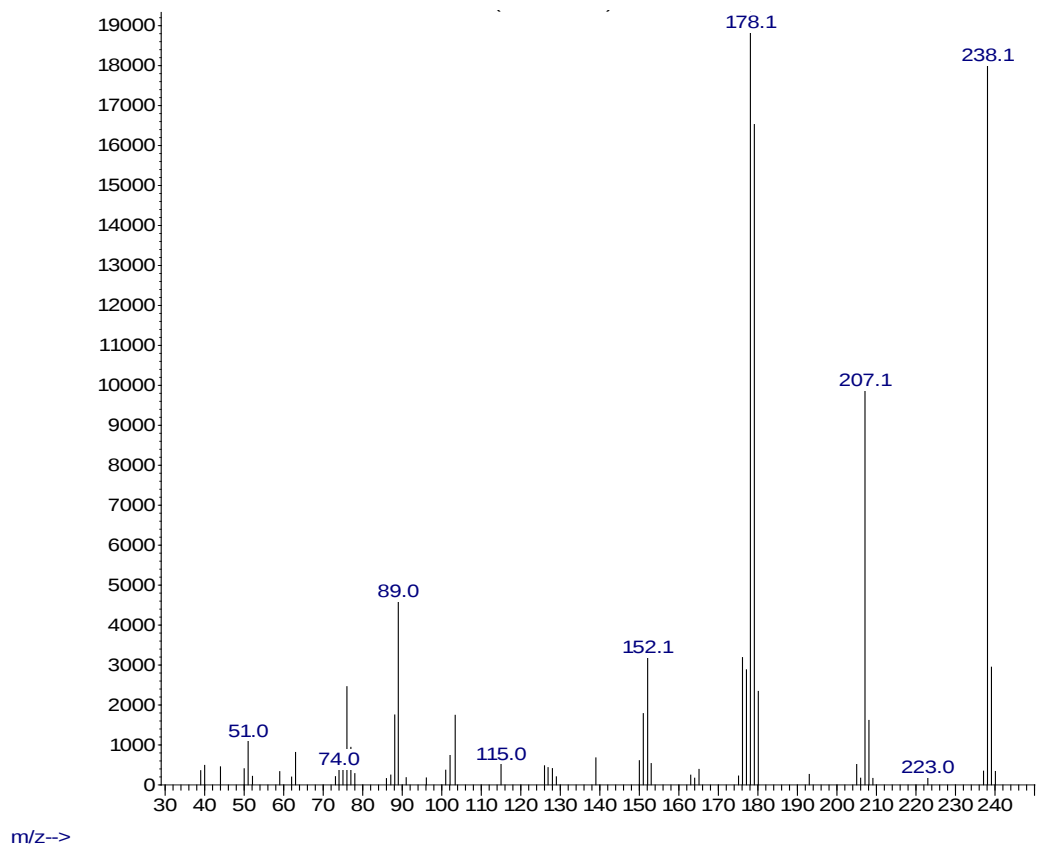
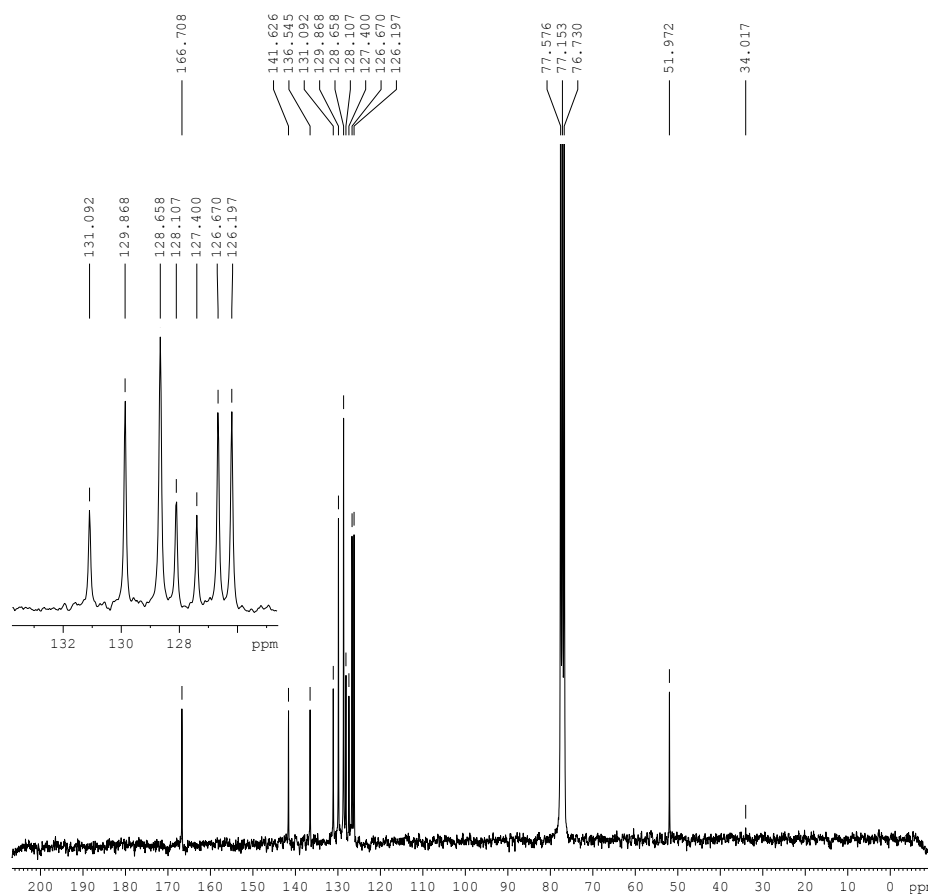
DMSO *d*₆
300 MHz



Methyl (*E*)-4-styrylbenzoate (**3cf**):



DMSO d₆
300 MHz



References

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