Electronic supplementary information for

Visible-light-enabled denitrative carboxylation of β-nitrostyrenes: A direct photocatalytic approach to cinnamic acids†

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I. General Information:

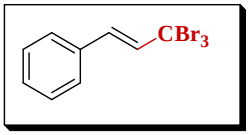
All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware. Organic solutions were concentrated using a Buchi rotary evaporator. Flash chromatography was carried out over silica gel (Merck 200–300 mesh) and TLC was performed using silica gel GF254 (Merck) plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in $CDCl_3$ using TMS as an internal reference with chemical shift values being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer. Luxeon Rebel high power 7 W blue LEDs (λ_{max} = 447.5 nm) were used as visible light source.

II. General procedure for the synthesis of cinnamic acids 2:

A mixture of *β*-nitrostyrene**1** (1 mmol), CBr_4 (1.5 equiv), $Ru(bpy)_3Cl_2$ (**A**, 1 mol%), $^{i}Pr_2NH$ (2 mmol), CH_3CN (3 mL) and H_2O (0.5 mL) was irradiated through the flask's bottom side using 7 W blue LEDs under a nitrogen atmosphere at rt for 10 h. After the completion of reaction (as indicated by TLC), it was quenched with saturated aqueous sodium hydrogen carbonate (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhyd. $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate-hexane to afford an analytically pure sample of **2**. The characterization data and the copies of ^{1}H and ^{13}C NMR spectra of the intermediate **3a** and the products **2** are given below:

Characterization data for the intermediate:

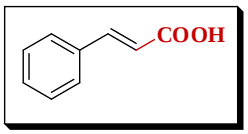
(*E*)-3,3,3-tribromoprop-1-enyl)-benzene (3a)



Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.40 (m, 2H), 6.73 (d, 1H, J = 16 Hz); 7.36-7.33 (m, 3H), 6.40 (d, 1H, J = 16.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 135.8, 130.5, 128.9, 127.6, 123.5, 23.0; HRMS (EI) calcd for $C_9H_7Br_3$: 351.8098; found: 351.8095.

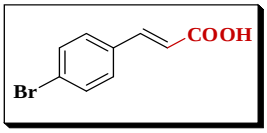
Characterization data for the compounds 2:

(*E*)-Cinnamic acid (2a):



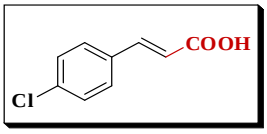
Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.00 (brs, 1H), 7.60-7.56 (m, 2H), 7.45 (d, 1H, J = 16 Hz); 7.44-7.40 (m, 3H), 6.42 (d, 1H, J = 16.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 148.3, 135.8, 131.5, 129.1, 128.9, 118.5; HRMS (EI) calcd for $C_9H_8O_2$: 148.0524; found: 148.0520.

(*E*)-3-(4-bromophenyl)-acrylic acid (2b):



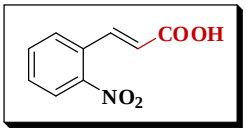
Yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.52 (brs, 1H), 7.54 (d, 2H, J = 8.5 Hz), 7.48 (d, 1H, J = 16 Hz), 7.38 (d, 2H, J = 8.5 Hz), 6.43 (d, 1H, J = 16.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 143.6, 133.5, 132.2, 129.6, 124.6, 118.2; HRMS(EI) calcd for $C_9H_7BrO_2$: 225.9629; found: 225.9631.

(*E*)-3-(4-chlorophenyl)-acrylic acid (2c):



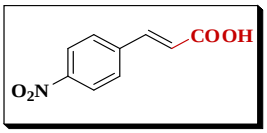
Yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.55 (brs, 1H), 7.49 (d, 1H, J = 16 Hz),7.46 (d, 2H, J = 6.6 Hz), 7.29 (d, 2H, J = 6.6 Hz), 6.43 (d, 1H, J = 16.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 143.5, 136.5, 133.0, 129.2, 128.9, 118.7; HRMS (EI) calcd for $C_9H_7ClO_2$: 196.0291; found: 196.0295.

(*E*)-3-(2-nitrophenyl)-acrylic acid (2d):



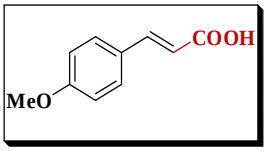
Yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.52 (brs, 1H), 8.32 (d, 1H, J = 15.9 Hz), 8.06 (d, 1H, J = 8.4 Hz), 7.69-7.66 (m, 2H), 7.58-7.52 (m, 1H), 6.35 (d, 1H, J = 15.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 148.1, 140.3, 133.5, 130.5, 130.4, 130.1, 125.2, 122.9; HRMS (EI) calcd for $C_9H_7NO_4$: 193.0375; found: 193.0378.

(*E*)-3-(4-nitrophenyl)-acrylic acid (2e):



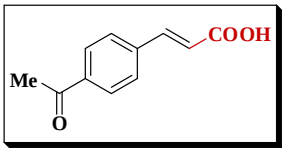
Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.54 (brs, 1H), 8.26 (d, 2H, J = 8.7 Hz), 7.69 (d, 2H, J = 8.7 Hz), 7.64 (d, 1H, J = 16.2 Hz),6.55 (dd, 1H, J = 16.2 Hz, J = 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ171.5, 148.8, 142.3, 140.7, 128.8, 124.5, 122.2; HRMS (EI) calcd for $C_9H_7NO_4$: 193.0375; found: 193.0372.

(*E*)-3-(4-methoxyphenyl)-acrylic acid (2f):



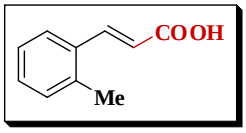
Yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.57 (brs, 1H), 7.49 (m, 2H), 7.46 (d, 1H, J = 16.0 Hz),6.94-6.89 (m, 2H), 6.34 (d, 1H, J = 16.0 Hz), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 161.6, 144.5, 129.7, 127.5, 115.1, 114.6,55.4; HRMS (EI) calcd for $C_{10}H_{10}O_3$: 178.0630; found: 178.0634.

(*E*)-3-(4-acetylphenyl)-acrylic acid (2g):



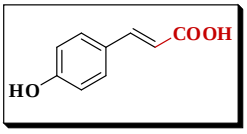
Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.53 (brs, 1H), 7.89 (d, 2H, J = 8.7 Hz), 7.67 (d, 2H, J = 8.7 Hz), 7.45 (d, 1H, J = 16.2 Hz), 6.33 (d, 1H, J = 16.2 Hz), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 172.5, 148.8, 143.2, 140.7, 128.7, 124.5, 122.1, 26.6; HRMS (EI) calcd for$C_{11}H_{10}O_3$: 190.0630; found: 190.0628.

(*E*)-3-*o*-tolyl-acrylic acid (2h):



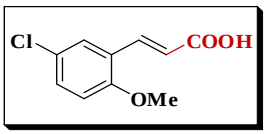
Yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.55 (brs, 1H), 7.98 (d, 1H, J = 16.0 Hz),7.56-7.51 (m, 1H), 7.28-7.20 (m, 3H), 6.15 (d, 1H, J = 16.0 Hz), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 142.6, 137.6, 133.5, 130.9, 130.3, 126.5, 126.3, 118.7, 19.7; HRMS (EI) calcd for $C_{10}H_{10}O_2$: 162.0681; found: 162.0685.

(*E*)-3-(4-hydroxyphenyl)-acrylic acid (2i):



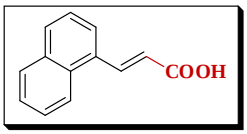
Yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.54 (brs, 1H), 9.40 (brs, 1H), 7.66 (d, 1H, J = 16.0 Hz),7.48 (m, 2H), 6.93-6.89 (m, 2H), 6.30 (d, 1H, J = 16.0 Hz);^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 161.5, 144.5, 129.7, 127.2, 115.3, 114.4; HRMS (EI) calcd for $C_9H_8O_3$: 164.0473; found: 164.0468.

(*E*)-3-(5-chloro-2-methoxyphenyl)-acrylic acid (2j):



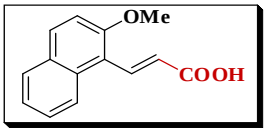
Yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.57 (brs, 1H), 7.94 (d, 1H, J = 16.2 Hz), 7.46 (d, 1H, J = 2.6 Hz), 7.31 (dd, 1H, J = 8.8, J = 2.6 Hz), 6.85 (d, 1H, J = 8.8 Hz), 6.12 (d, 1H, J = 16.2 Hz), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 156.6, 138.4, 130.9, 128.0, 125.5, 124.6, 118.9, 112.5, 55.6; HRMS (EI) calcd for $C_{10}H_9ClO_3$: 212.0240; found: 212.0241.

(*E*)-3-(naphthalen-yl)-acrylic acid (2k):



Yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.52 (brs, 1H), 8.20 (d, 1H, J = 7.5 Hz), 7.91-7.83 (m, 2H), 7.81 (d, 1H, J = 15.8 Hz), 7.77 (d, 1H, J = 7.2 Hz), 7.58-7.46 (m, 3H), 6.33 (d, 1H, J = 15.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 142.2, 133.6, 131.7, 131.4, 130.5, 128.8, 127.0, 126.2, 125.5, 125.1, 123.5, 120.5; HRMS (EI) calcd for $C_{13}H_{10}O_2$: 198.0681; found: 198.0683.

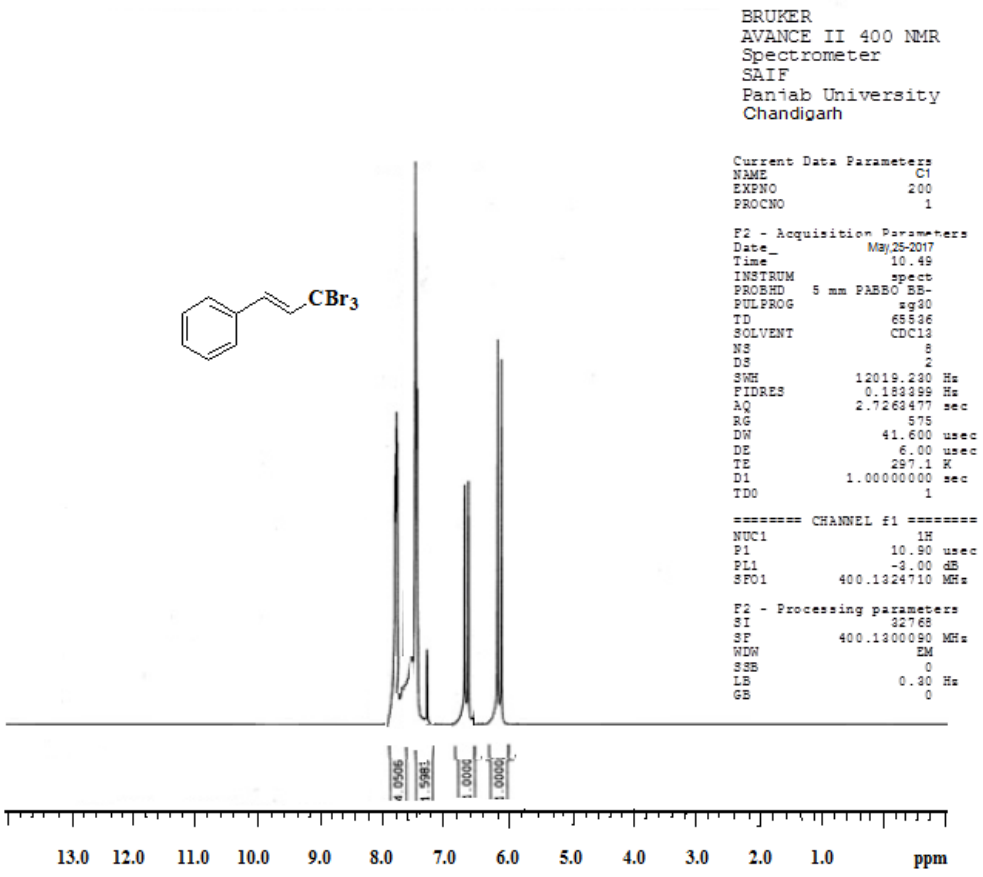
(*E*)-3-(2-methoxynaphthalen-yl)-acrylic acid (2l):



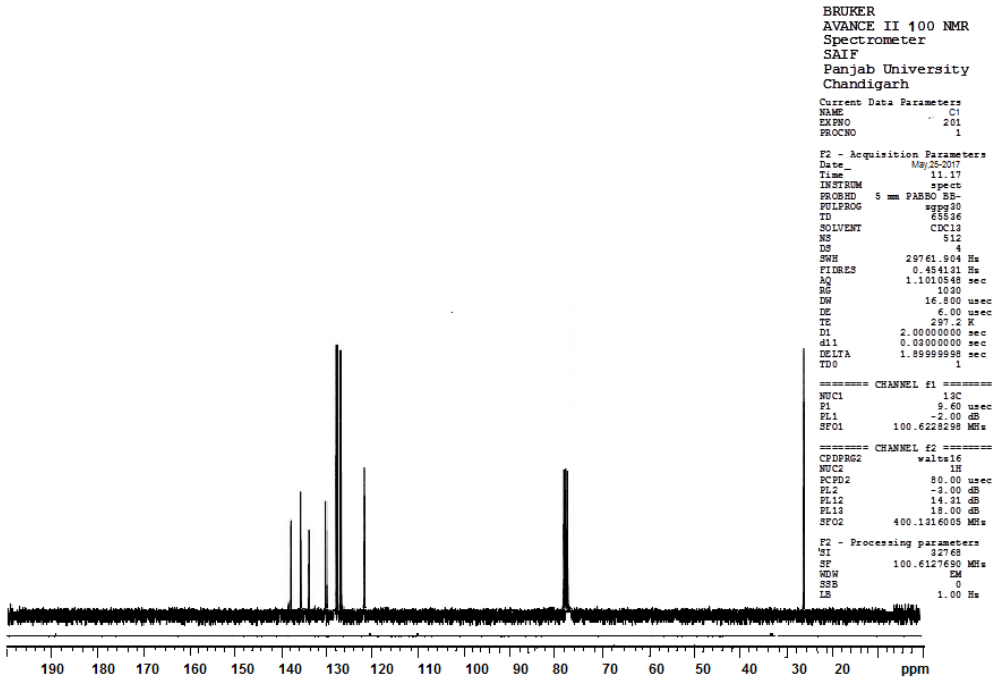
Yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.54 (brs, 1H), 8.21 (d, 1H, *J* = 8.5 Hz), 7.86 (d, 1H, *J* = 9.1 Hz), 7.80 (dd, 1H, *J* = 8.1, *J* = 0.6 Hz), 7.77 (d, 1H, *J* = 16.2 Hz), 7.55-7.49 (m, 1H), 7.42-7.37 (m, 1H), 7.32 (d, 1H, *J* = 9.1 Hz), 6.43 (d, 1H, *J* = 16.2 Hz), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 168.2, 156.9, 137.7, 132.5, 131.7, 128.8, 128.3, 127.3, 123.8, 122.9, 122.4, 116.6, 112.5, 55.8; HRMS (EI) calcd $C_{14}H_{12}O_3$: 228.0786; found: 228.0788.

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

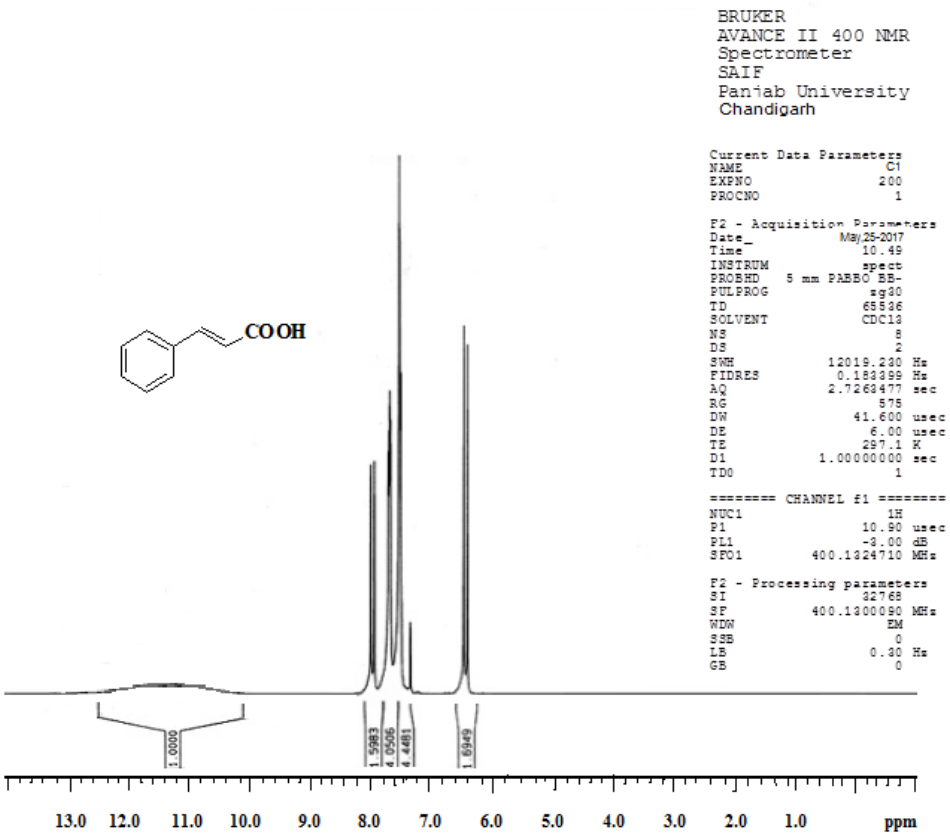
^{1}H NMR spectrum of intermediate 3a



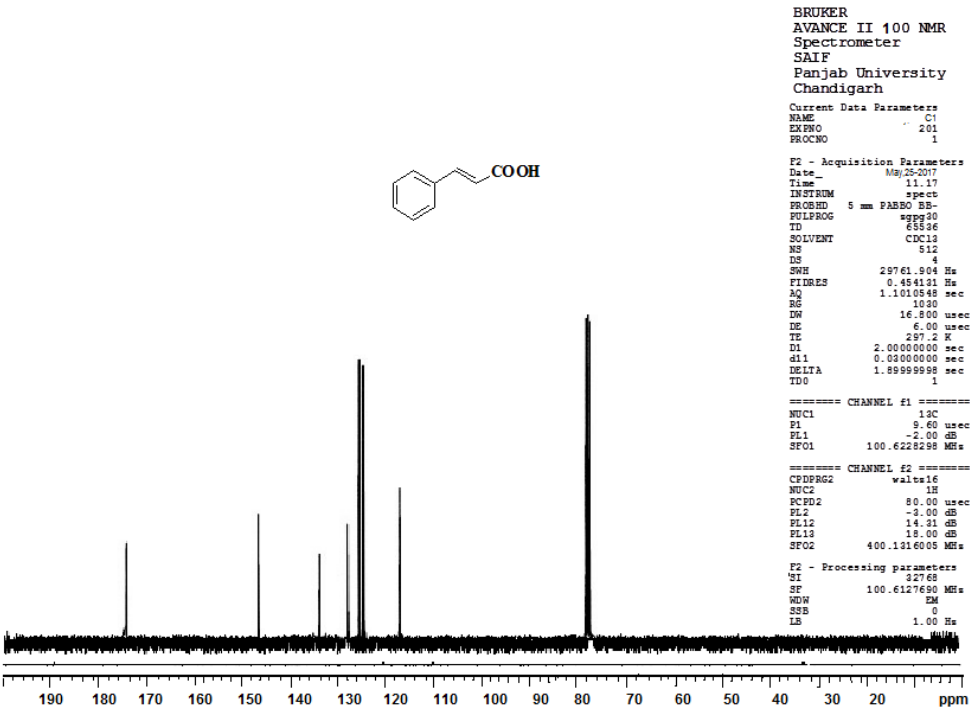
^{13}C NMR spectrum of intermediate3a



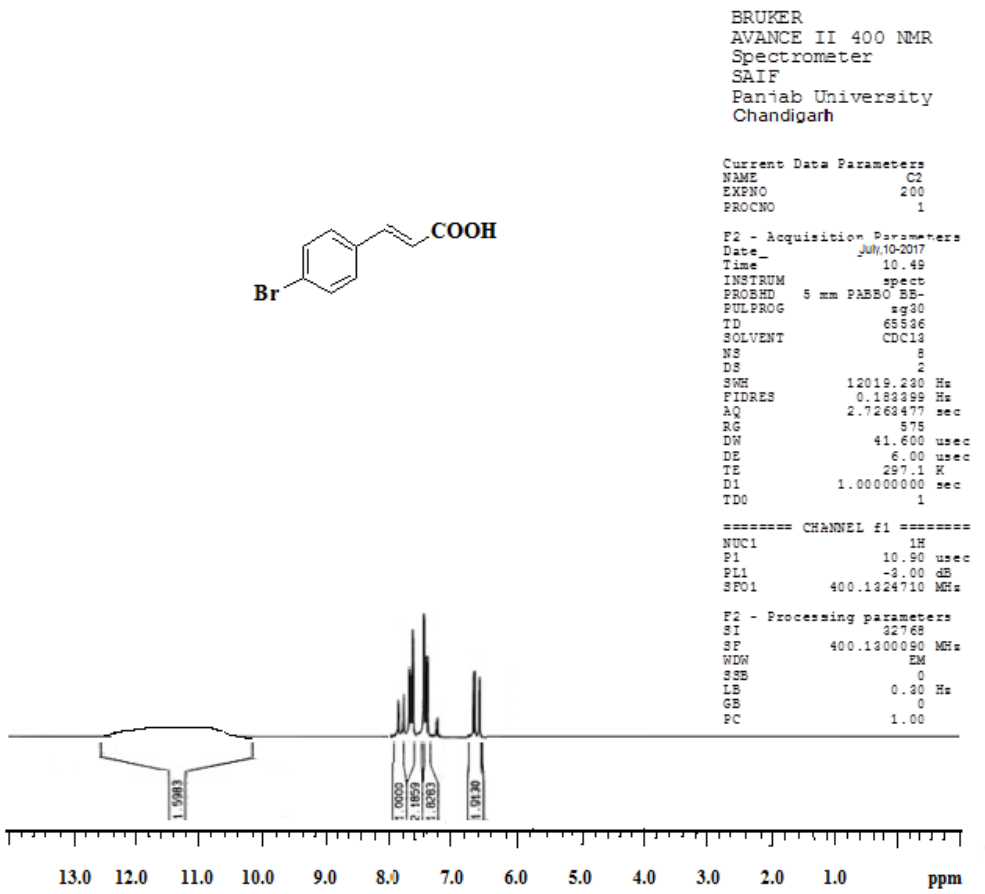
^{1}H NMR spectrum of compound 2a



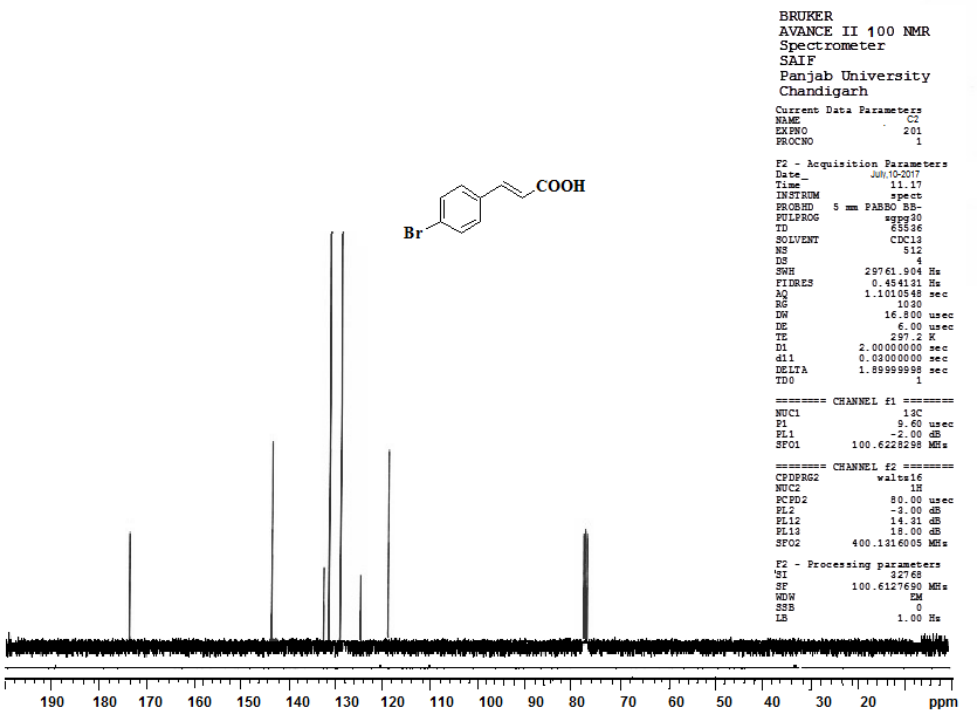
^{13}C NMR spectrum of compound 2a



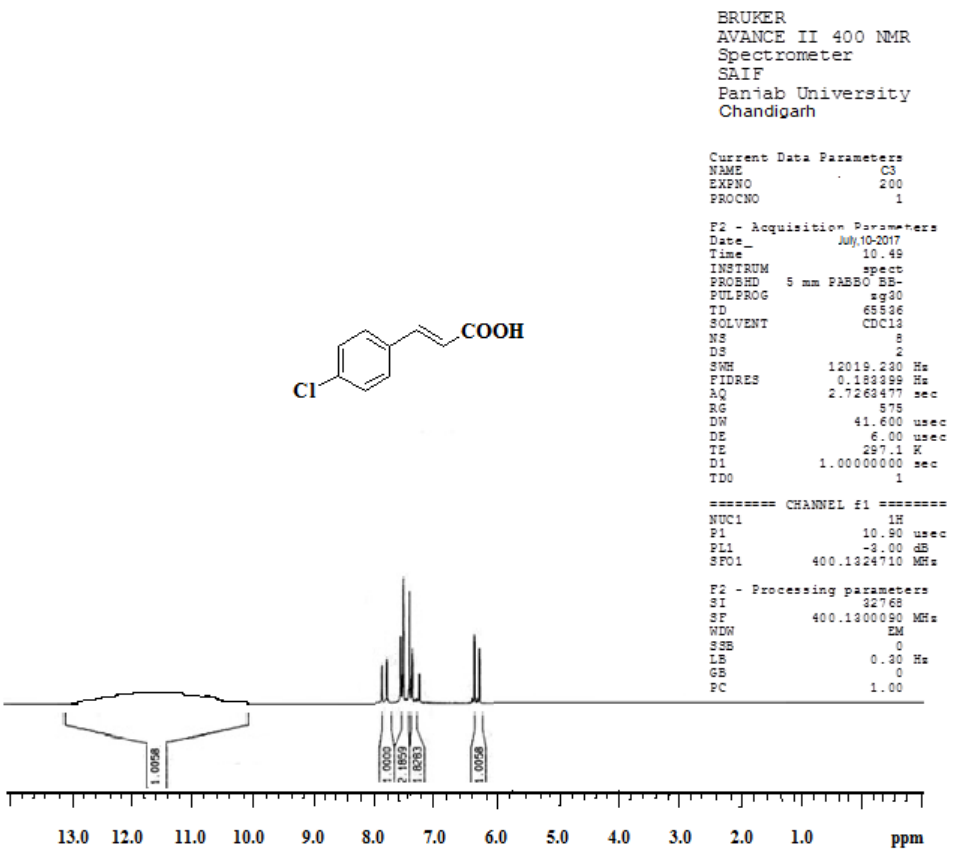
^{1}H NMR spectrum of compound 2b



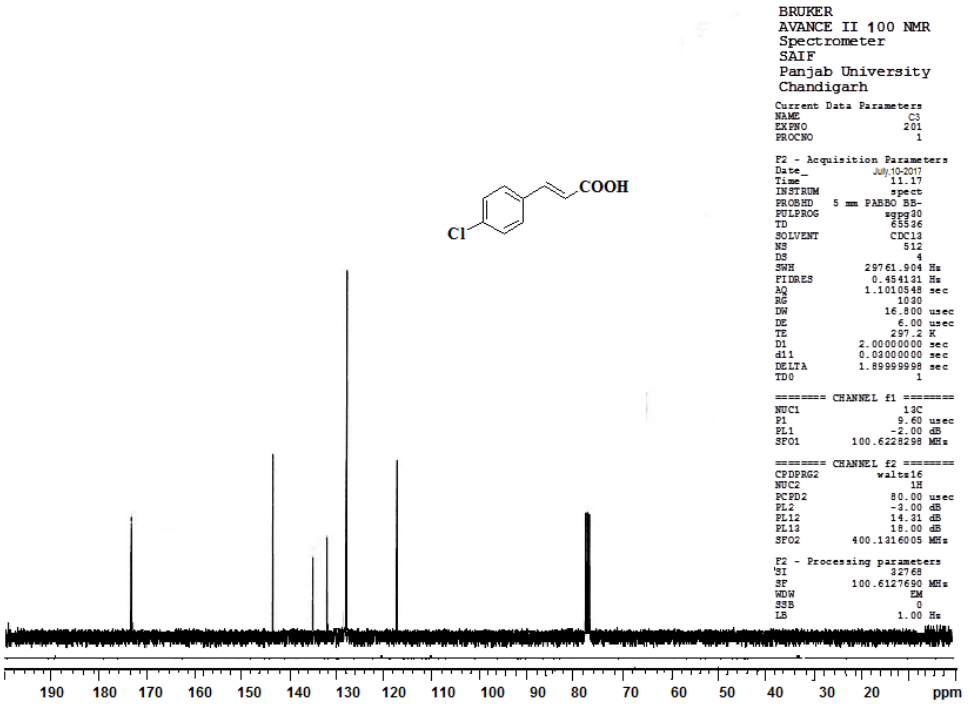
^{13}C NMR spectrum of compound 2b



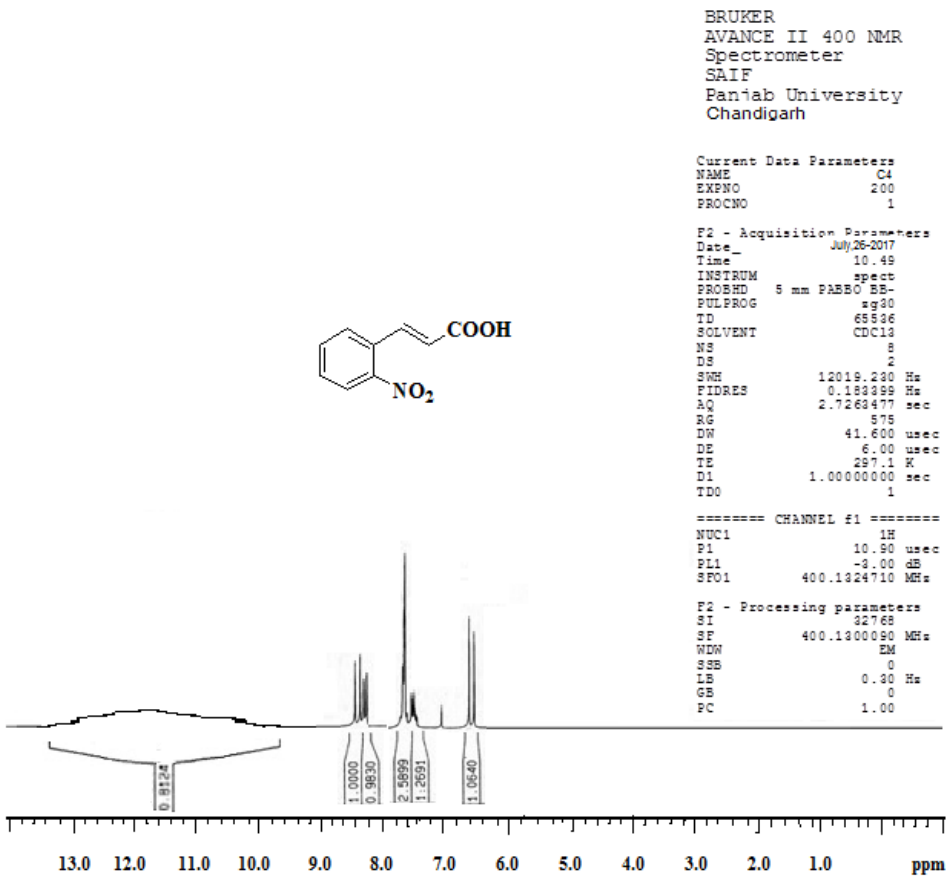
^{1}H NMR spectrum of compound 2c



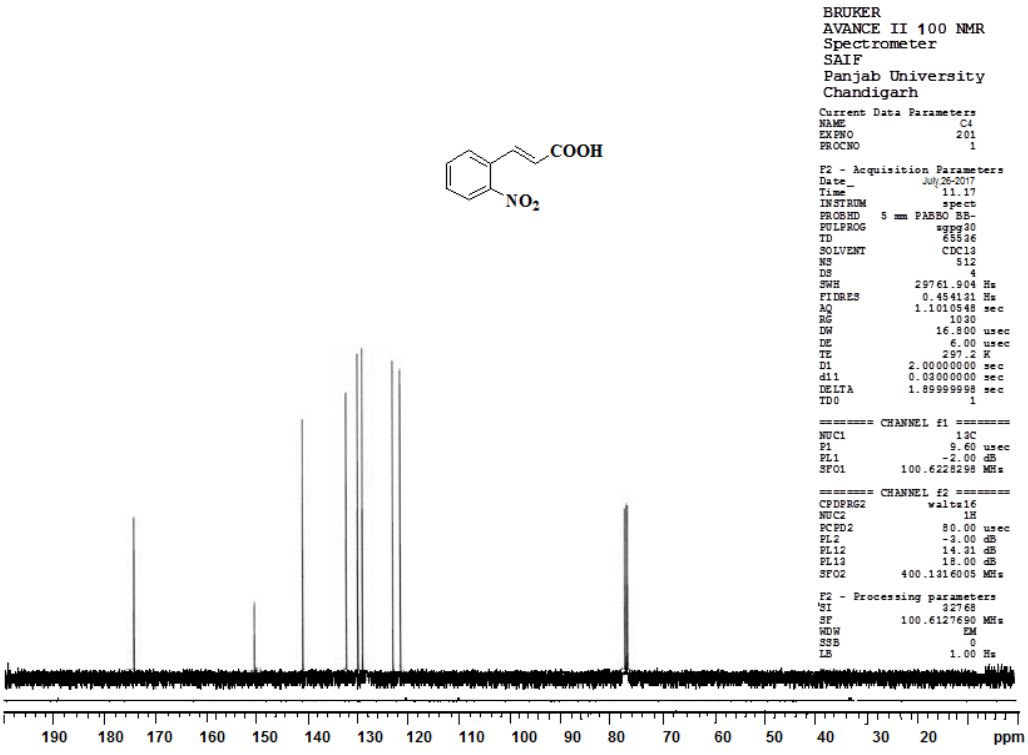
^{13}C NMR spectrum of compound 2c



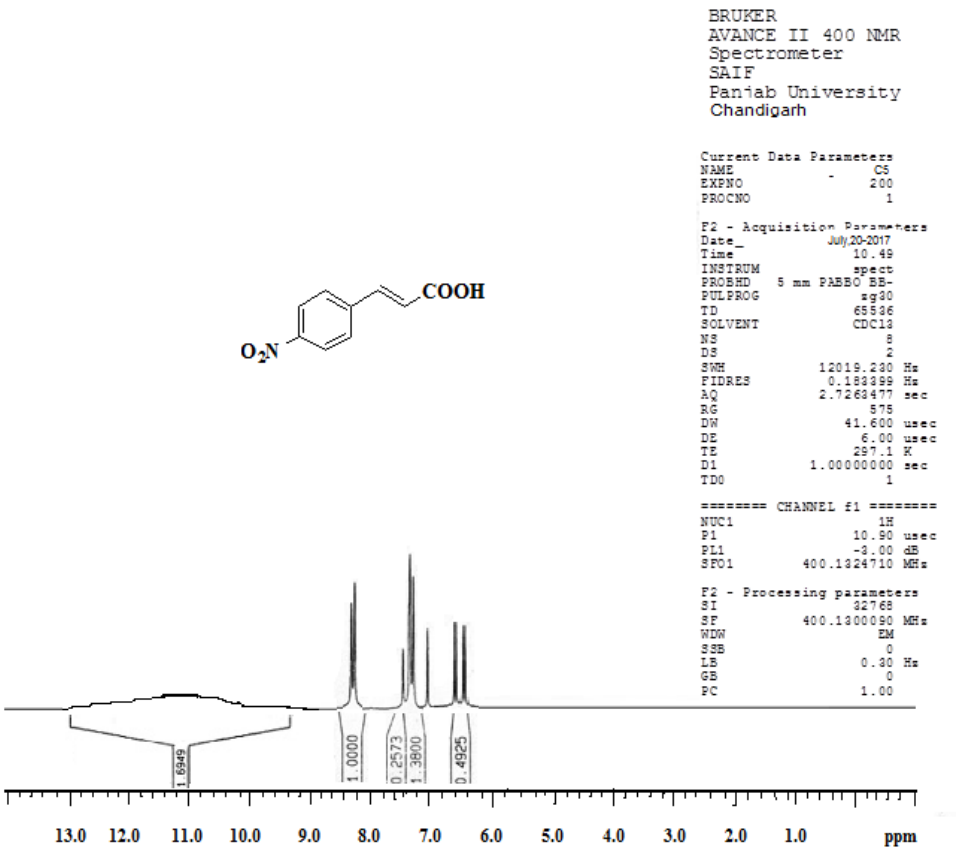
^{1}H NMR spectrum of compound 2d



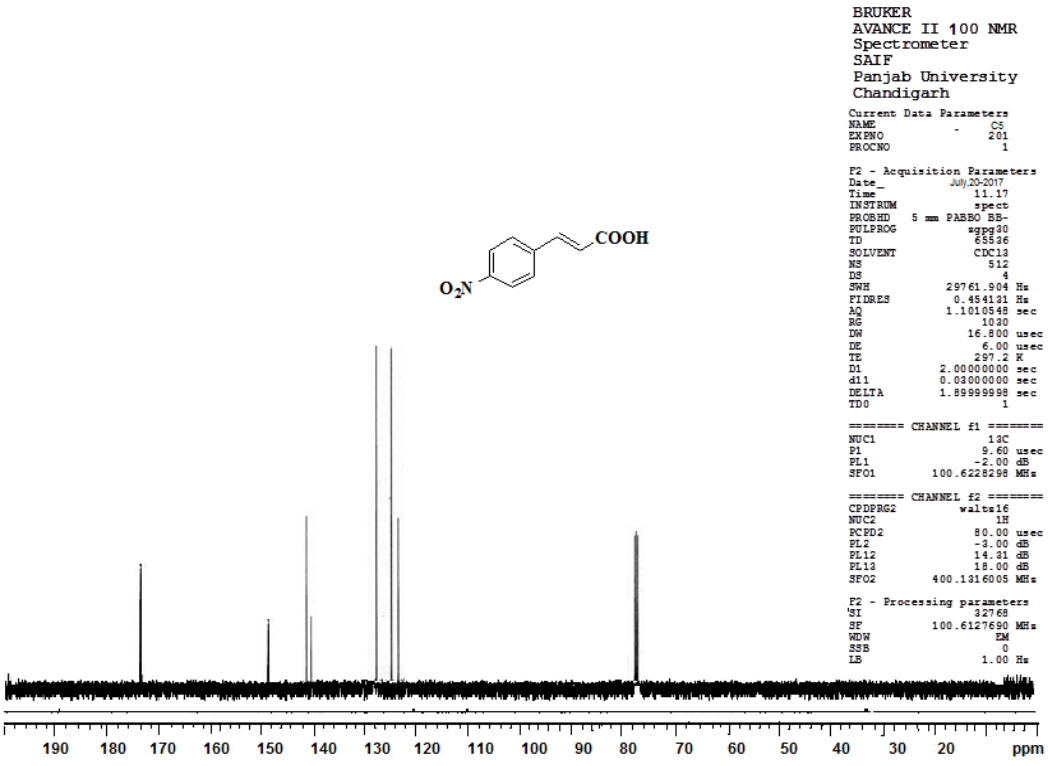
^{13}C NMR spectrum of compound 2d



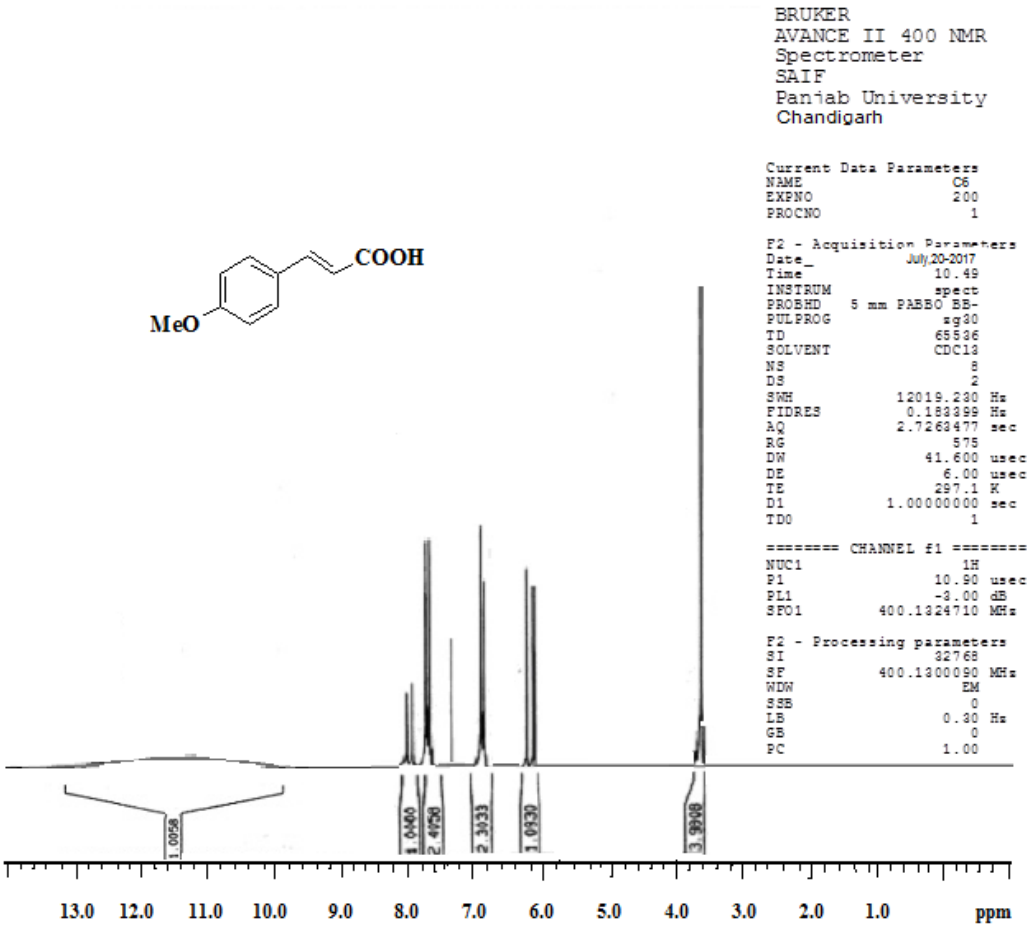
^{1}H NMR spectrum of compound 2e



^{13}C NMR spectrum of compound 2e



^{1}H NMR spectrum of compound 2f



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DE 6.00 usec
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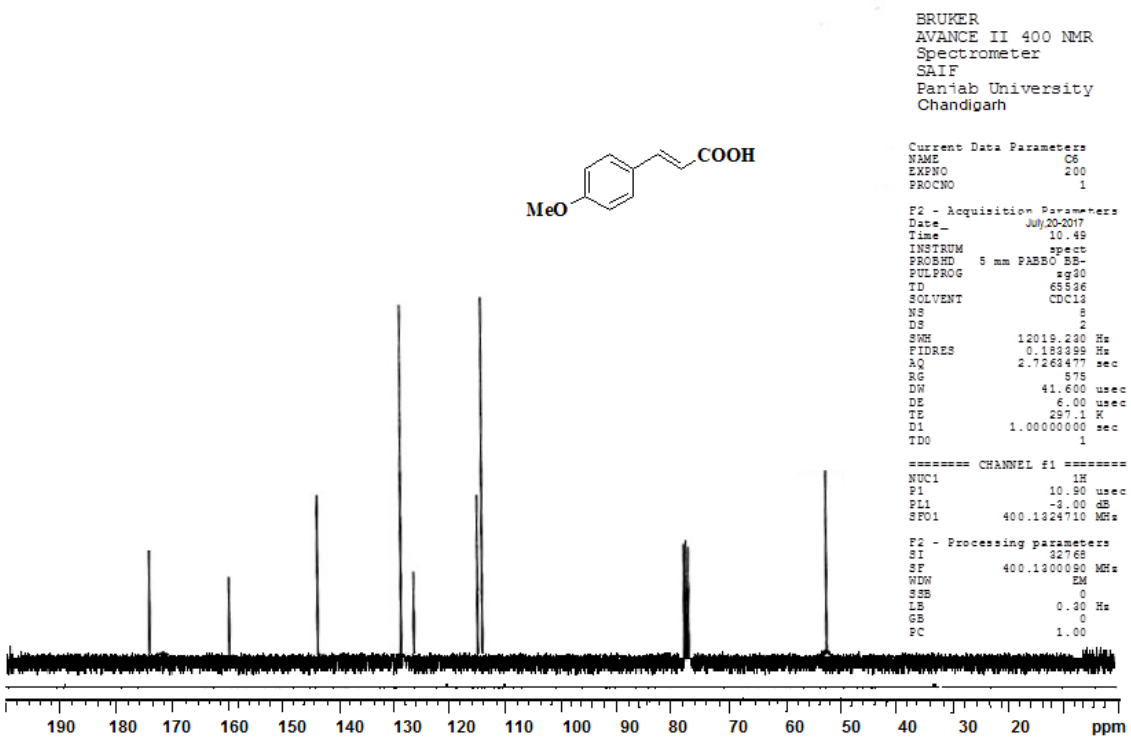
^{13}C NMR spectrum of compound 2f



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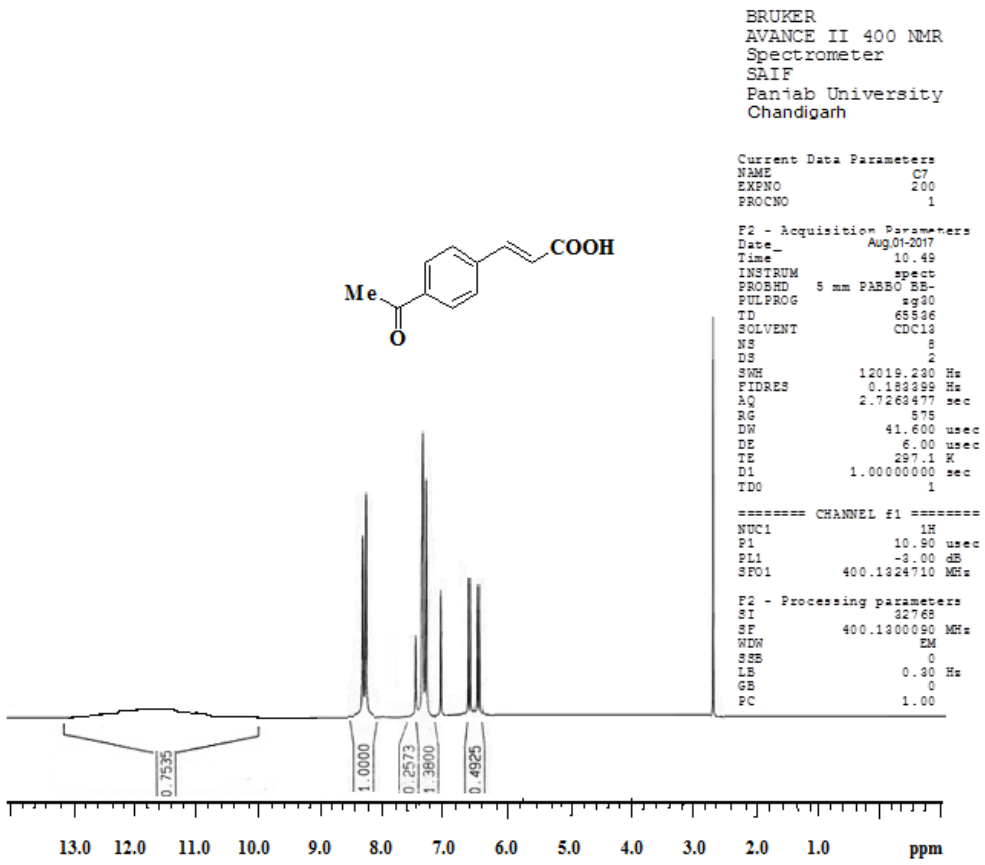
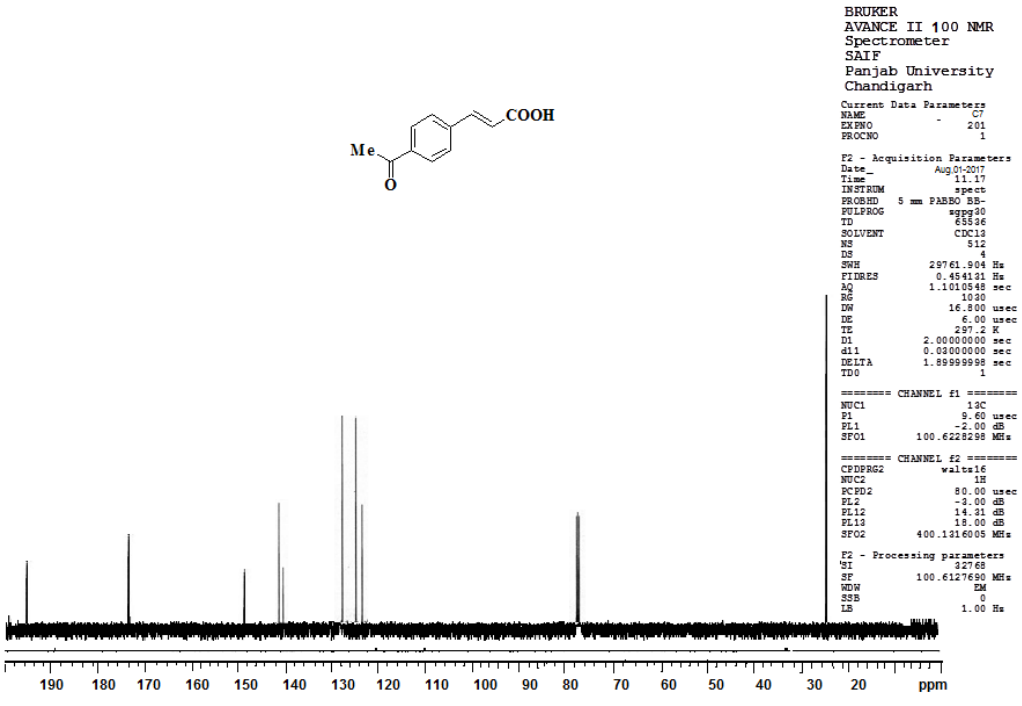
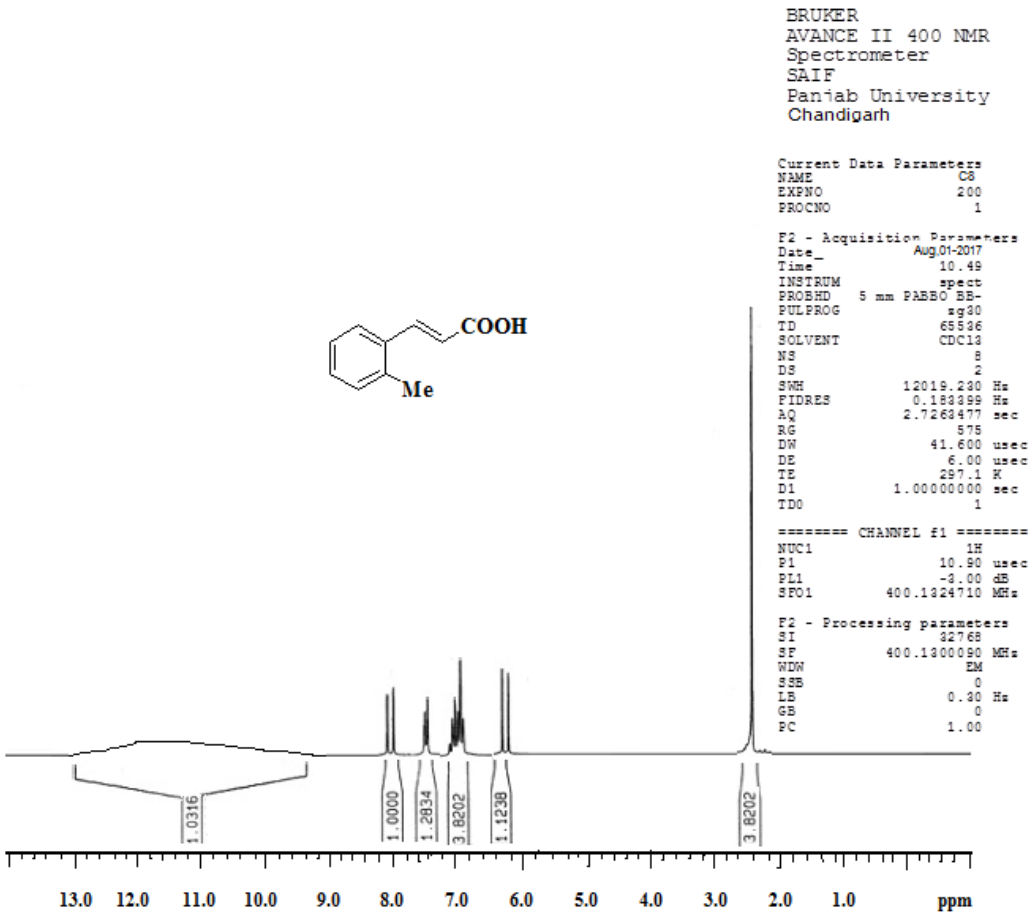
^{1}H NMR spectrum of compound 2g



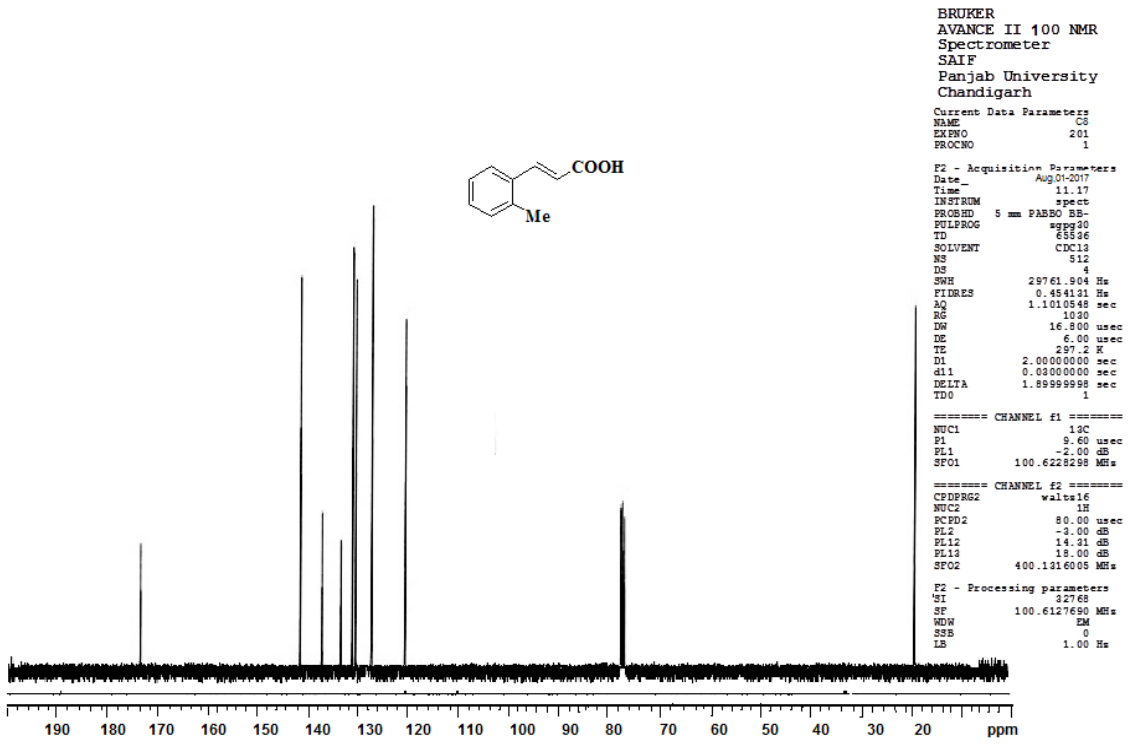
^{13}C NMR spectrum of compound 2g



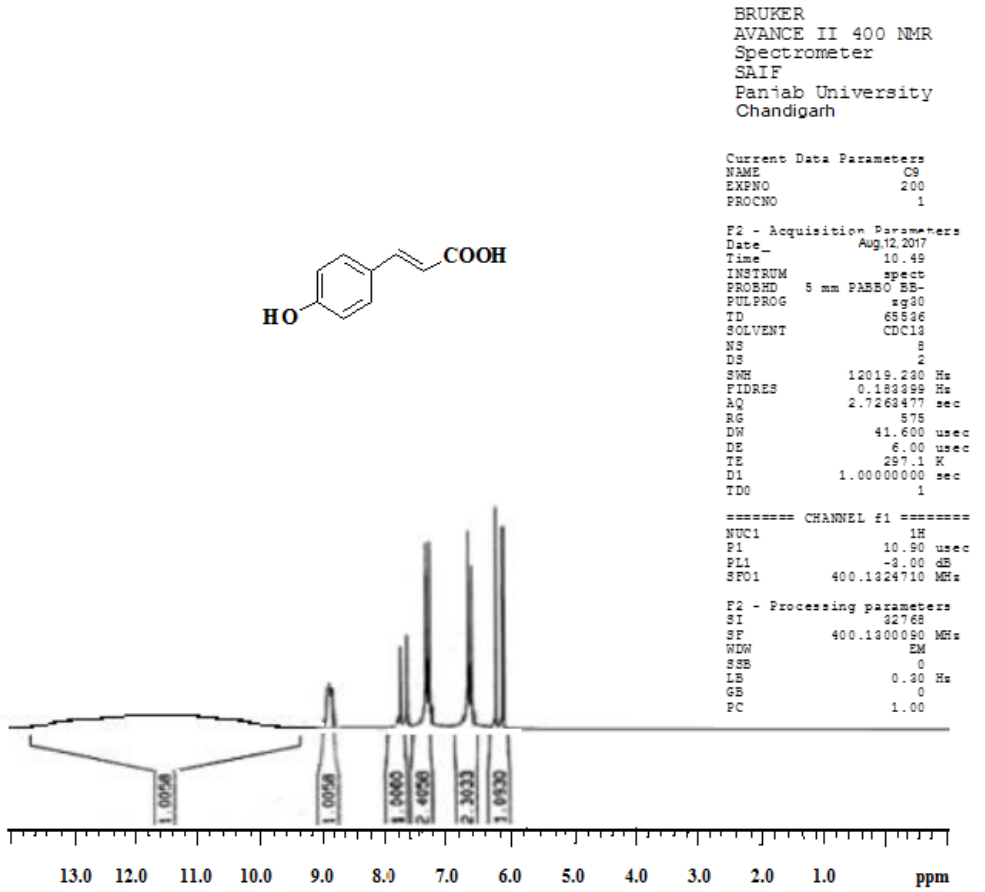
^{1}H NMR spectrum of compound 2h



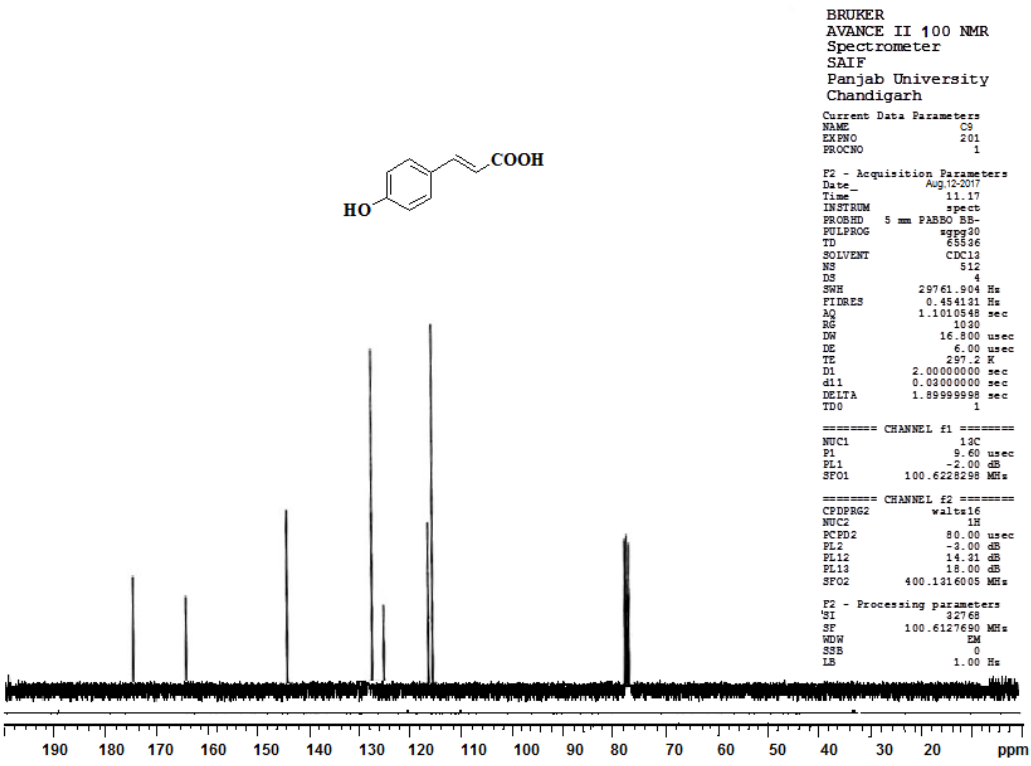
^{13}C NMR spectrum of compound 2h



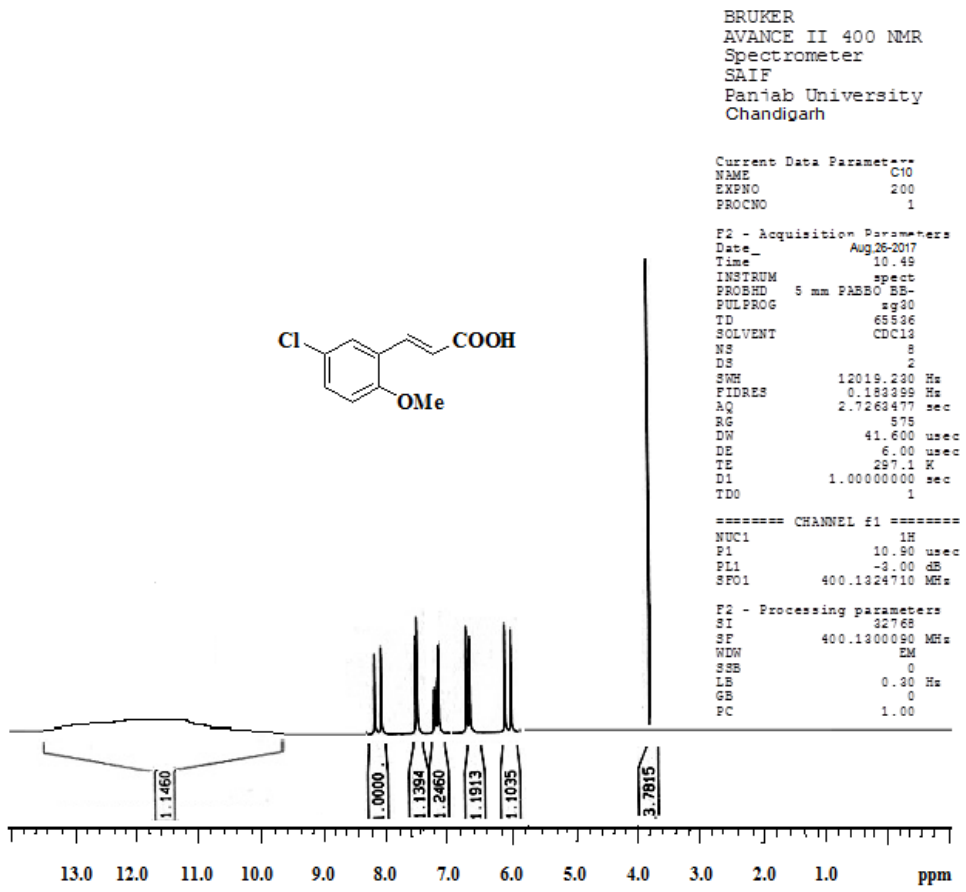
^{1}H NMR spectrum of compound 2i



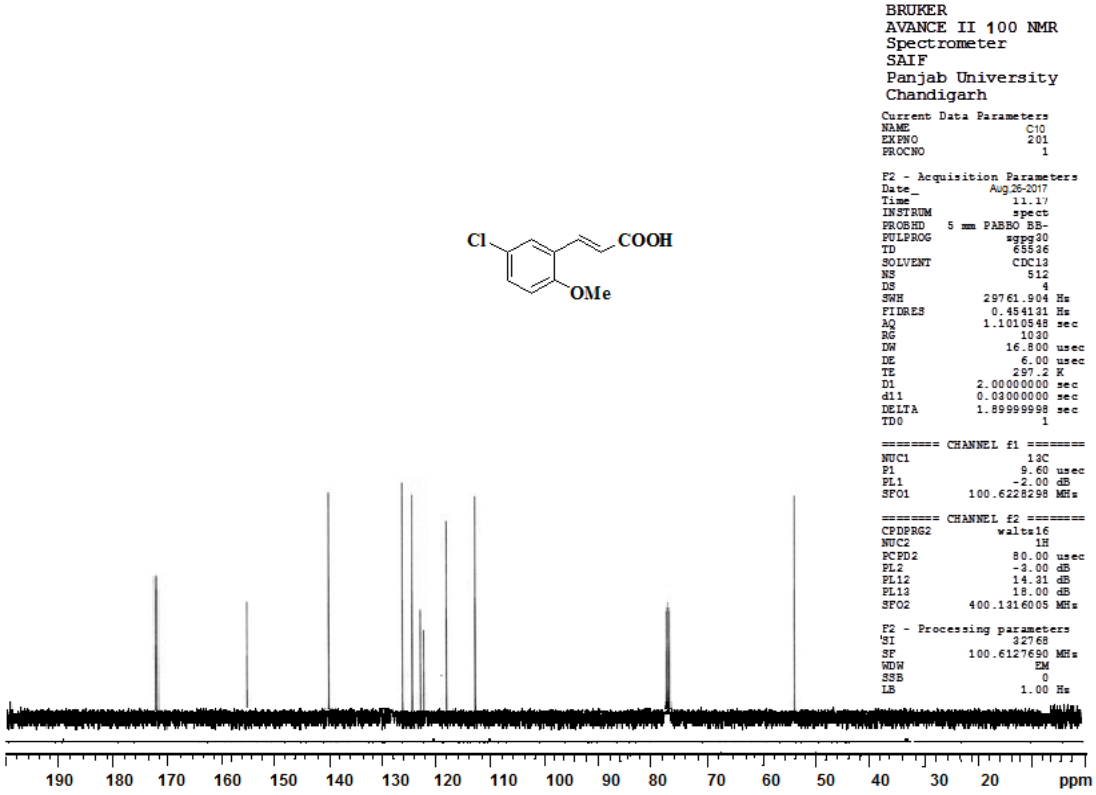
^{13}C NMR spectrum of compound 2i



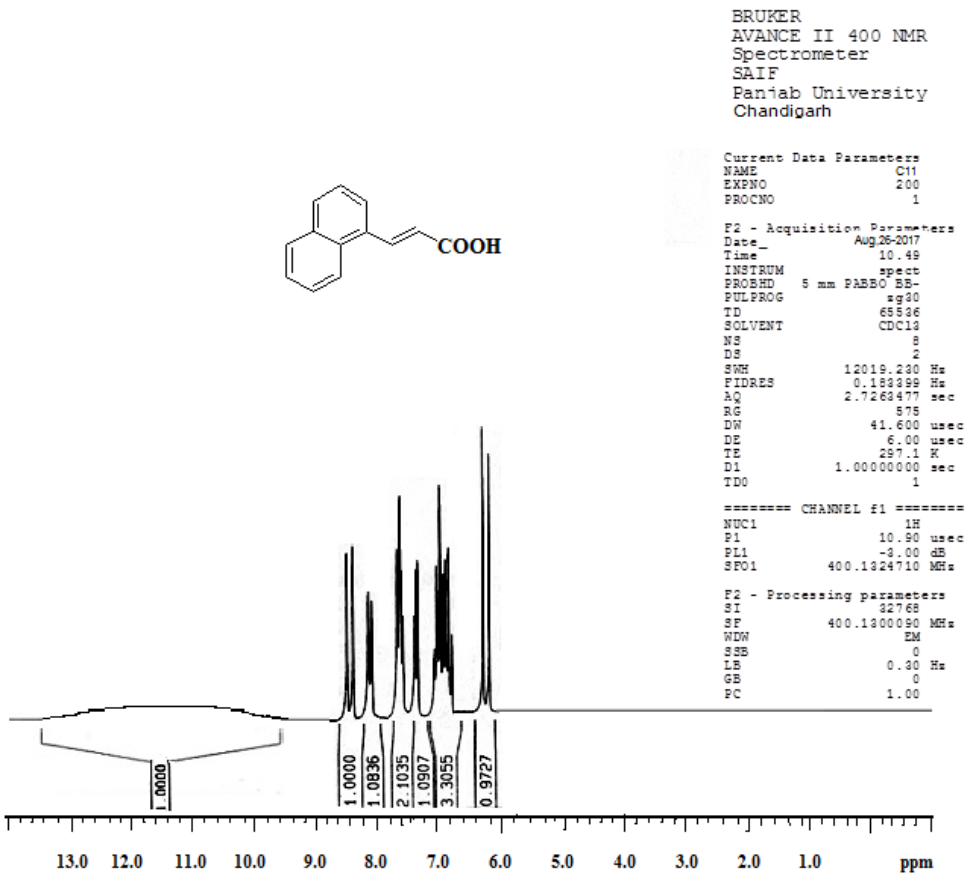
^{1}H NMR spectrum of compound 2j



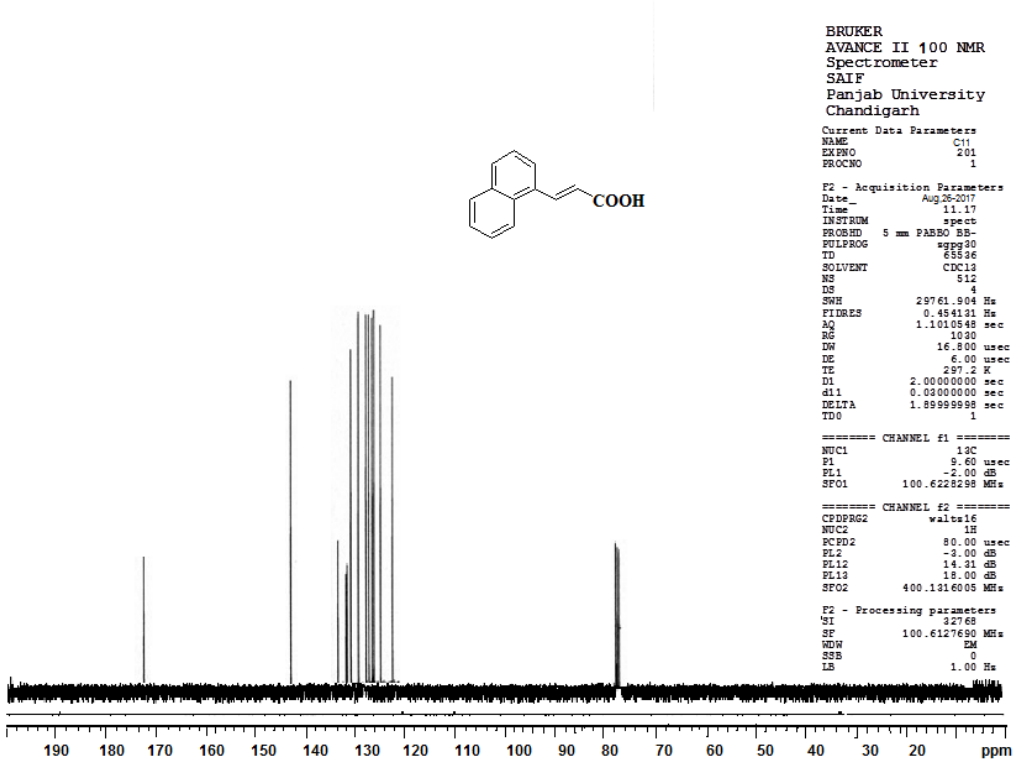
^{13}C NMR spectrum of compound 2j



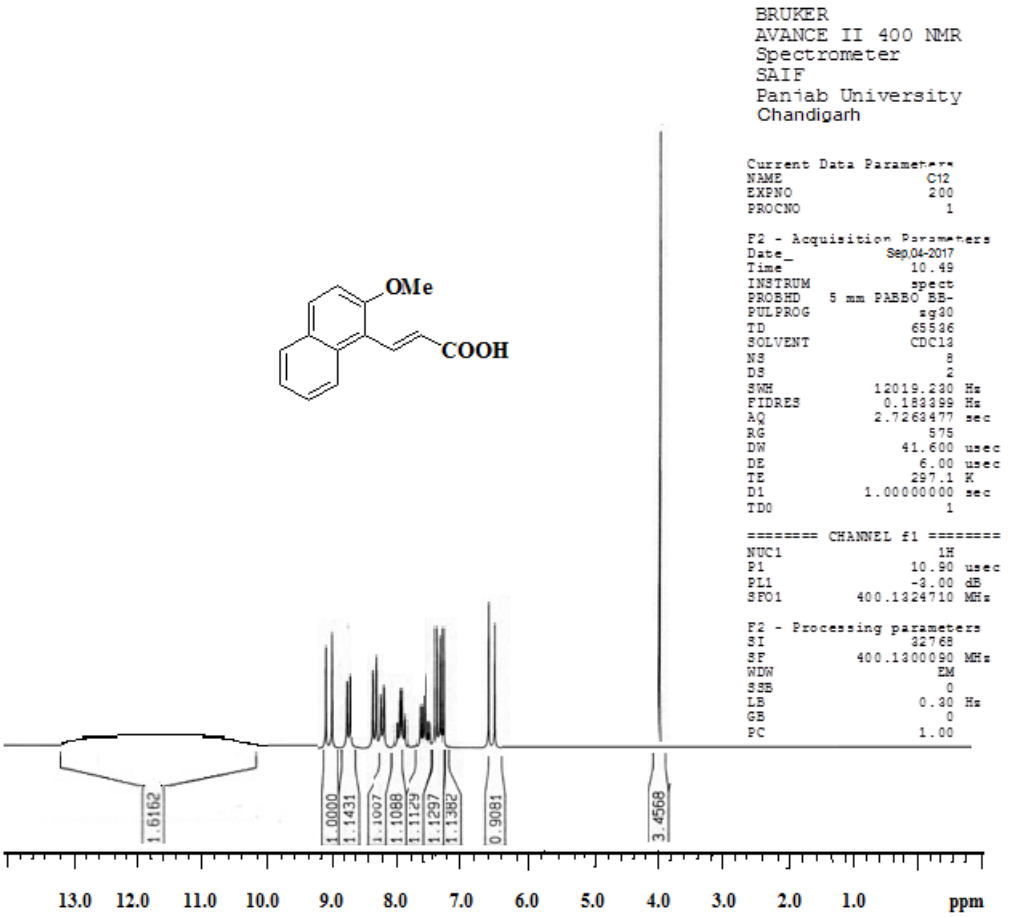
^{1}H NMR spectrum of compound 2k



^{13}C NMR spectrum of compound 2k



^{1}H NMR spectrum of compound 2l



^{13}C NMR spectrum of compound 2l