ELECTRONIC SUPPLEMENTARY INFORMATIO (ESI)

A facile and chemoselective conjugate reduction using polymethylhydrosiloxane (PMHS) and catalytic $B(C_6F_5)_3$

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General Methods: Methylene chloride was distilled over CaH_2 prior to use. Crude products were purified by column chromatography on silica gel of 60-120 mesh. IR spectra were recorded on Perkin-Elmer 683 spectrometer. Optical rotations were obtained on Jasco Dip 360 digital polarimeter. Melting points (uncorrected) were obtained using a Buchi 535 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Gemini 200, Brucker Avance 300 or Varian Unity 400. Chemical shifts were reported in ppm with respect to internal TMS. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL.

General Procedure for chemoselective Reduction: To a solution of the α, β-unsaturated ketone (2 mmol) in anhydrous methylene chloride (5 mL) was added $B(C_6F_5)_3$ (5 mg, 0.01 mmol) and PMHS (4 mmol) and the solution was stirred at room temperature for a period of time (monitored by TLC). Water was added to the reaction mixture and was extracted with methylene chloride (3 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, concentrated under vacuo and the crude product was purified by flash chromatography.

This procedure is followed for the reduction of all the substrates listed in Table 1. Spectroscopic (IR and ^1H and ^{13}C NMR) data for the new compounds are presented below in order of their entries in Table 1.

4-(4-Methoxyphenyl) butan-2-one (entry 1b): ^1H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, *J* = 9.1 Hz, 2H), 6.76, (d, *J* = 8.3 Hz, 2H), 3.76 (s, 3H), 2.83-2.78 (m, 2H), 2.71-2.65

(m, 2H), 2.10 (s, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 207.8, 158.0, 133.0, 129.2 (2C), 113.9 (2C), 55.2, 45.4, 30.0 and 28.9. IR (KBr): 1713, 1615, 1513 and 1246 cm^{-1}. ESI (MS): 179 $[M+H]^+$. HRMS (ESI) Calcd for $C_{11}H_{14}O_2Na$: 201.0891 $[M+Na]^+$, Found: 201.0889 $[M+Na]^+$.

Ethyl 3-(4-chlorophenyl)-2-cyanopropanoate (entry 2b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.18 (m, 4H), 4.23 (q, *J* = 6.8 Hz, 2H), 3.64-3.59 (m, 1H), 3.25-3.11 (m, 2H), 1.29 (t, *J* = 6.8 Hz, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 165.1, 133.7, 133.6, 130.3 (2C), 128.9 (2C), 115.8, 62.9, 39.3, 34.8, and 13.8. IR (KBr): 2984, 2251, 1746, 1493, 1264, 1094 and 1016 cm^{-1}. ESI (MS): 260 $[M+Na]^+$. HRMS (ESI) Calcd for $C_{12}H_{12}NO_2NaCl$: 260.0454 $[M+Na]^+$, Found: 260.0450 $[M+Na]^+$.

Ethyl 3-[3-(allyloxy)-4-methoxyphenyl]-2-cyanopropanoate (entry 3b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79-6.71 (m, 3H), 6.10-5.96 (m, 1H), 5.41-5.23 (m, 2H), 4.54 (d, *J* = 5.3 Hz, 2H), 4.20 (q, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 3.65-3.60 (m, 1H), 3.20-3.06 (m, 2H), 1.28(t, *J* = 6.8 Hz, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 165.4, 149.5, 147.5, 133.2, 128.1, 121.1, 117.7, 116.1, 113.7, 112.7, 69.8, 62.5, 55.8, 39.7, 35.3 and 13.8. IR (KBr): 2939, 2251, 1744, 1515, 1263, 1143, 1032, 931 and 805 cm^{-1}. ESI (MS): 288 $[M-H]^+$. HRMS (ESI) Calcd for $C_{16}H_{20}NO_4$: 290.1392 $[M+H]^+$, Found: 290.1395 $[M+H]^+$.

(E)-Ethyl 2-cyano-5-phenylpent-4-enoate (entry 4b): See reference 1.

1-Nitro-2 - (2-nitroethyl)benzene (entry 5b): ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.10-8.05 (m, 1H), 7.66-7.37 (m, 3H), 4.75 (t, *J* = 6.9 Hz, 2H), 3.59 (t, *J* = 6.9 Hz, 2H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 148.9, 133.8, 132.7, 131.1, 128.9, 125.4, 75.1, and 31.1. IR (KBr): 3414, 1617, 1552, 1524, 1345 and 772 cm^{-1}. ESI (MS): 219 $[M+Na]^+$. HRMS (ESI) Calcd for $C_8H_8N_2O_4Na$ 219.0381 $[M+Na]^+$, Found: 219.0375 $[M+Na]^+$.

(2-Furylmethyl)malononitrile (entry 6b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4 (s, 1H), 6.41-6.38 (m, 2H), 4.00 (t, *J* = 7.5 Hz, 2H), 3.41 (d, *J* = 7.5Hz, 1H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 149.6, 146.4, 143.5, 111.9, 110.9, 110.0, 29.7 and 22.7. IR (KBr): 2920, 2260, 2218, 1504, 1146, 1075 and 1017 cm^{-1}. ESI (MS): 145 $[M-H]^+$. HRMS (ESI) Calcd for $C_8H_5N_2O$ 145.0401 $[M-H]^+$, Found: 145.0407 $[M-H]^+$

4-(2-Furyl)butan-2-one (entry 7b): ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.23 (d, *J* = 2.9 Hz, 1H, Ar), 6.21 (d, *J*= 1.5 Hz, 1H, Ar), 5.92 (d, *J* = 3.7 Hz, 1H), 2.92-2.85 (m, 2H), 2.78-2.70 (m, 2H), 2.13 (s, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 207.1, 141.0, 112.5, 110.5, 105.1, 41.6, 29.8 and 22.1. IR (KBr): 2930, 1713, 1606, 1271 and 775 cm^{-1}. ESI (MS): 139 (M^+).

1-Bromo-4,5-dimethoxy-2-(2-nitroethyl)benzene (entry 8b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 (s, 1H), 6.70 (s, 1H), 4.57 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.35 (t, *J* = 7.2 Hz, 2H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 149.2, 148.2, 126.9, 116.0, 114.1, 113.7, 74.6, 56.2, 56.1, and 33.5. IR (neat): 1619, 1550, 1506, 1258 and 606cm^{-1}. ESI (MS): 288(M^+), 290 $[M+2]^+$. HRMS (ESI) Calcd for $C_{10}H_{16}N_2O_4Br$: 307.0293 $[M+NH_4]^+$, Found: 307.0306 $[M+NH_4]^+$.

(5E)-6-(2-Furyl)hex-5-en-2-one (entry 9b): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, *J* = 1.5 Hz, 1H), 6.34-6.06 (m, 4H), 2.63-2.57 (m, 2H), 2.48-2.41 (m, 2H), 2.16 (s, 3H). ^{13}CNMR (75 MHz, $CDCl_3$): δ 207.5, 152.8, 141.4, 127.7, 119.5, 111.0, 106.5, 43.0, 29.9, and 26.8. IR (KBr): 2927, 1713, 1361, 1164 and 770 cm^{-1}. ESI (MS): 165 $[M+H]^+$. HRMS (ESI) Calcd for $C_{10}H_{13}O_2$ 165.0915 $[M+H]^+$, Found: 165.0913 $[M+H]^+$.

2-Methyl-5-(prop-1-en-2-yl) cyclohexanone (entry 10b): See reference 2.

2-Isopropyl-5-methylcyclohexanone (entry 11b): See reference 3.

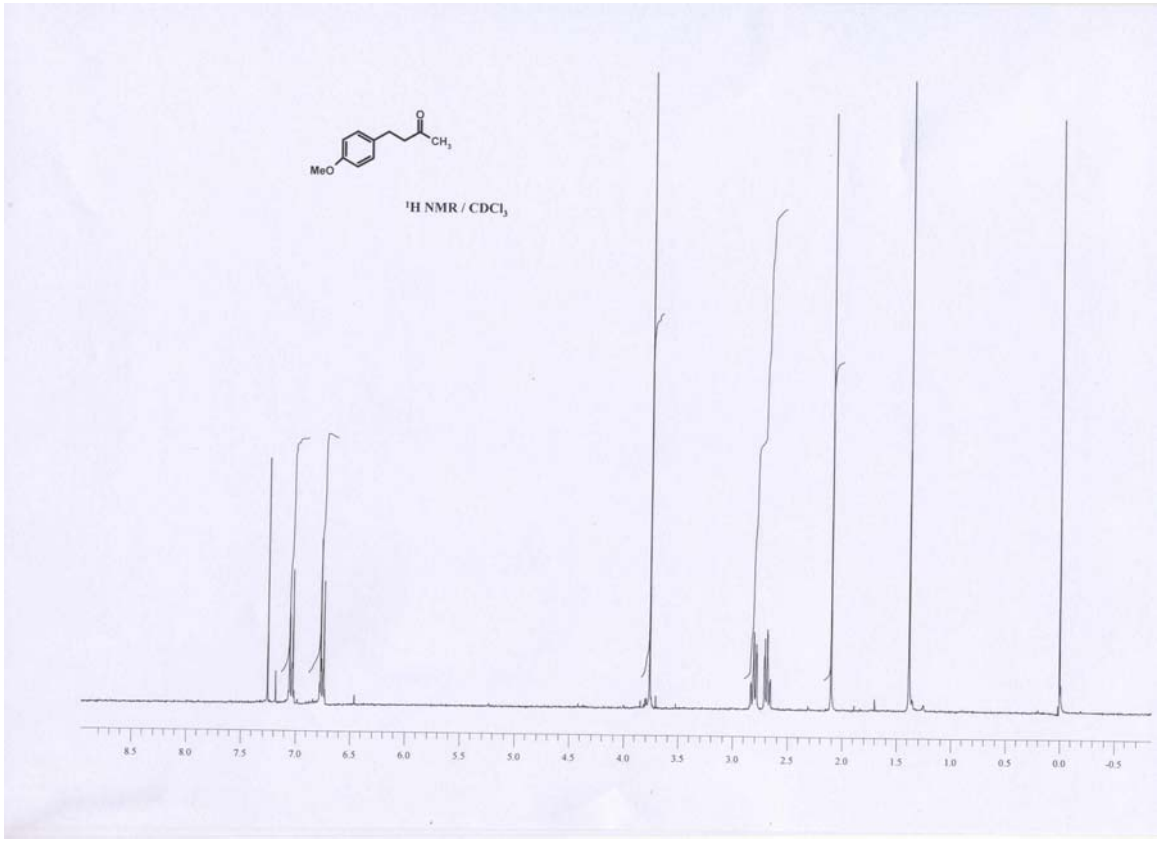
3-Methylcyclohexanone (entry 12b): Product was compared with authentic sample (Aldrich).

References:

(1). B. C. Ranu and S. Samanta, *J. Org. Chem*., 2003, **68**, 7130.

(2). E. Keinan and N. Greenspoon, *J. Am. Chem. Soc*., 1986, **108**, 7314.

(3). E. Keinan and D. Perez, *J. Org. Chem*., 1987, **52**, 2576.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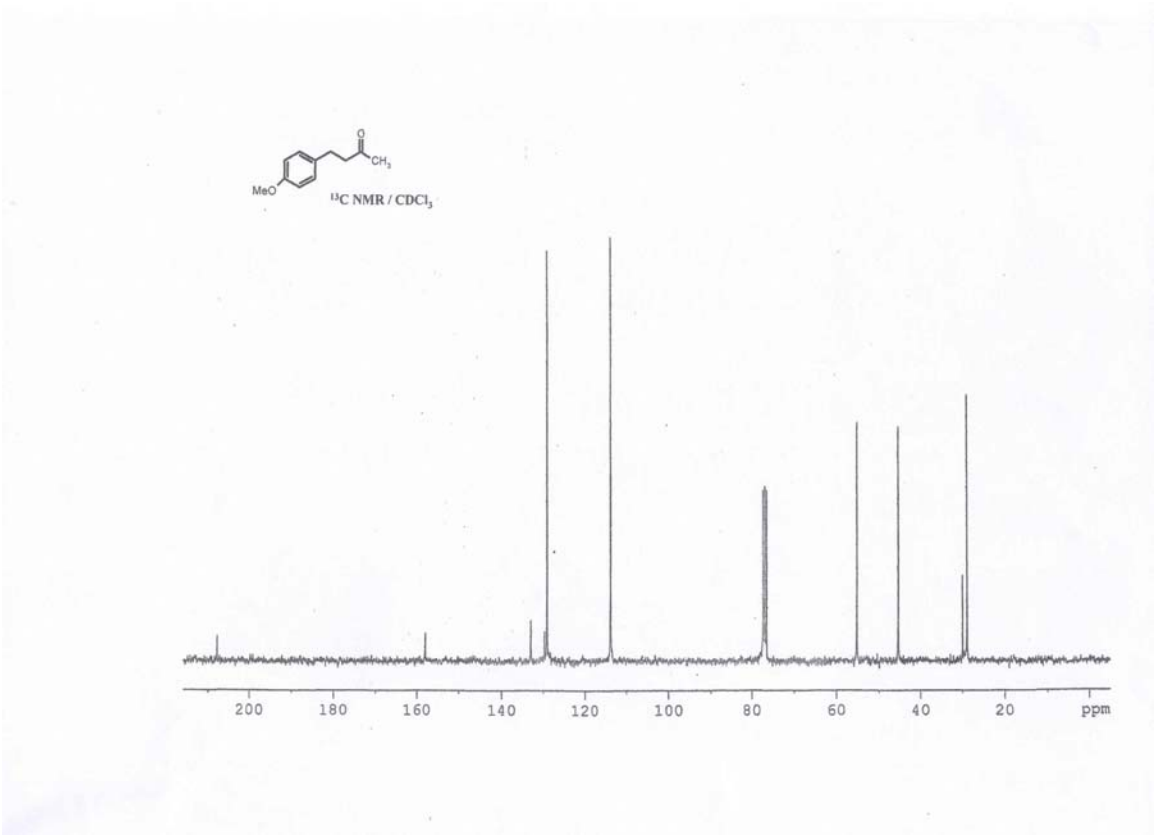
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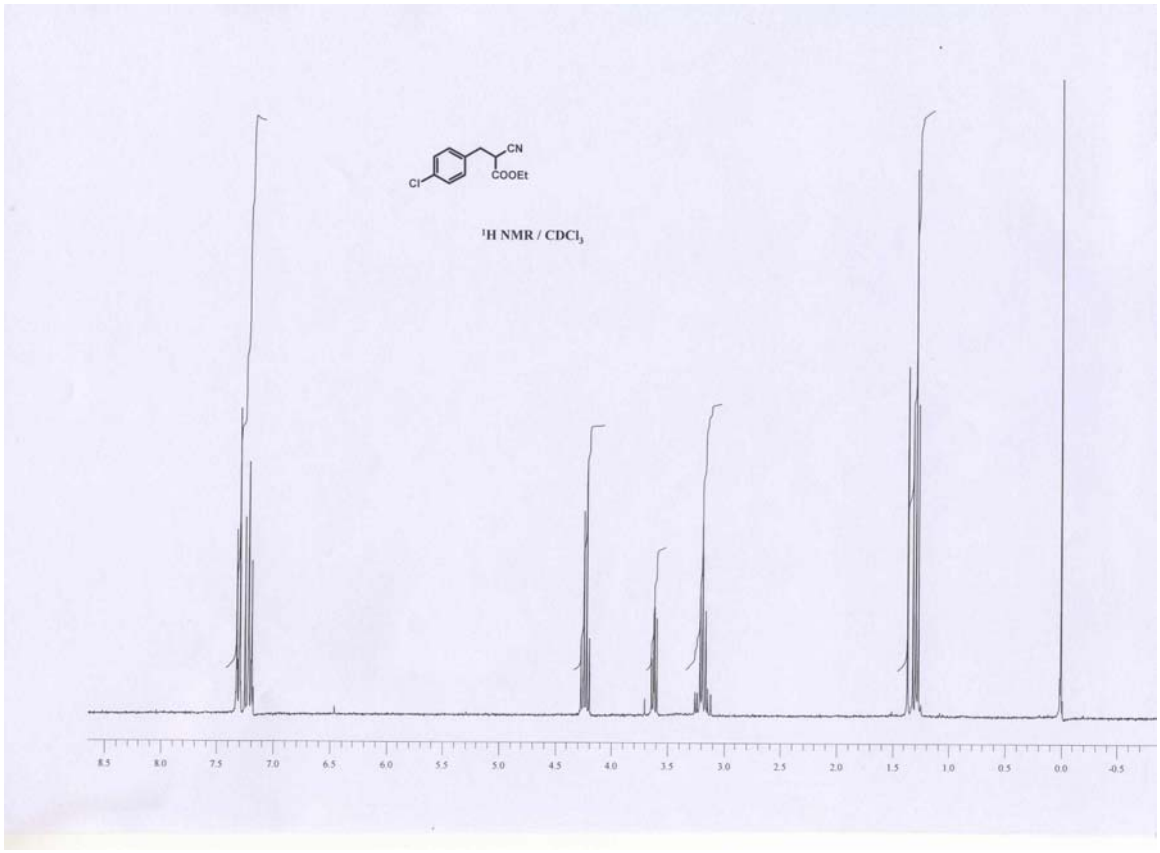
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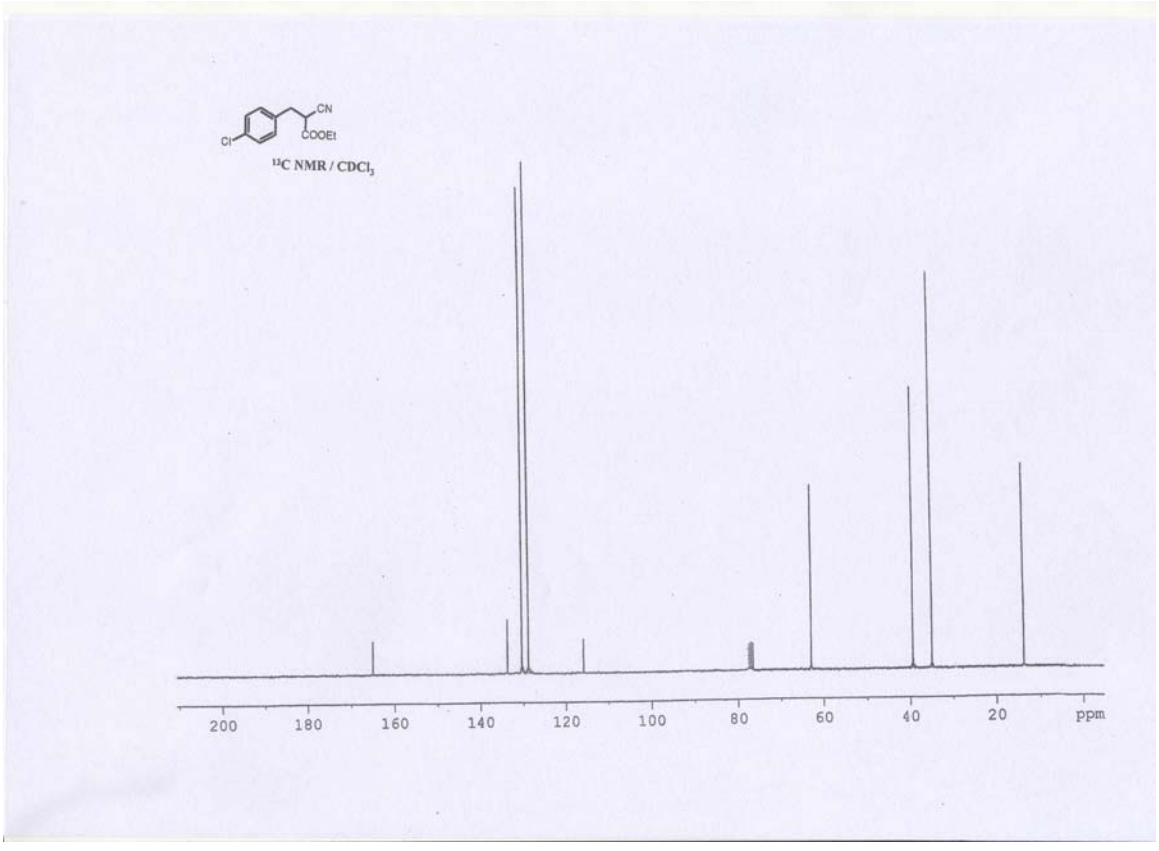
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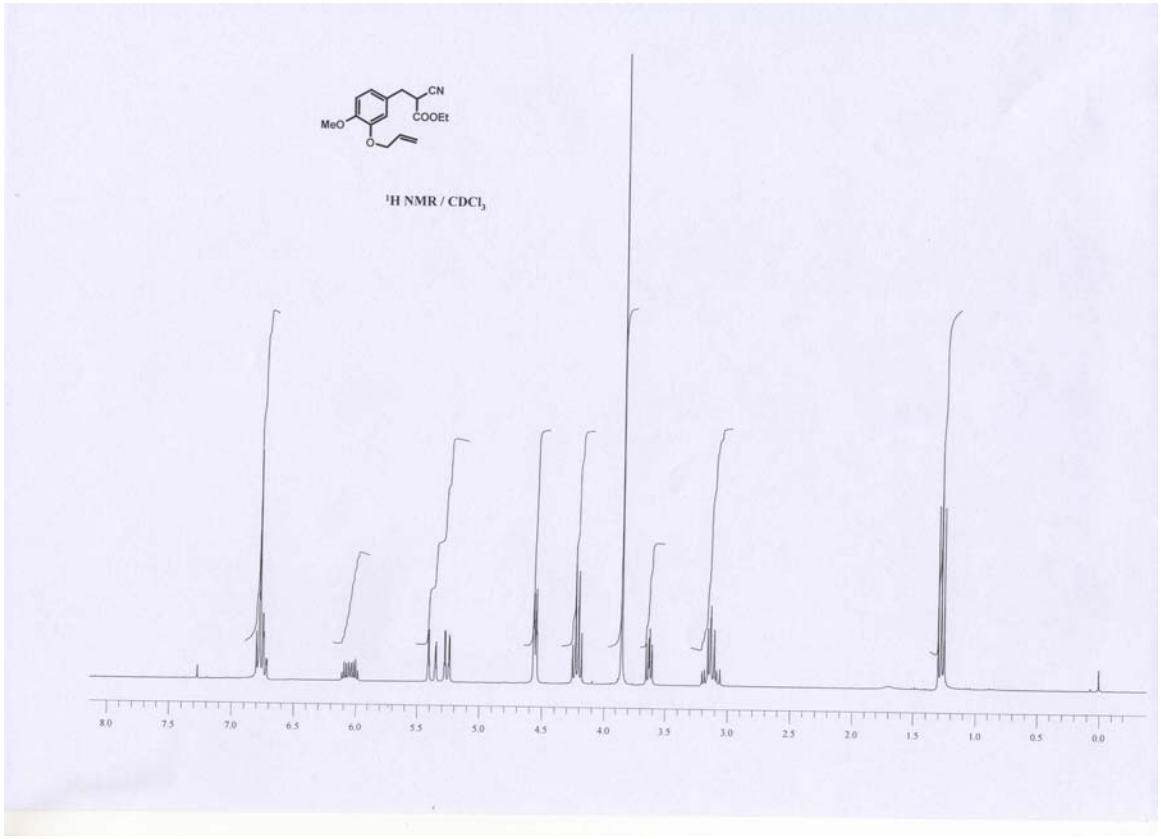
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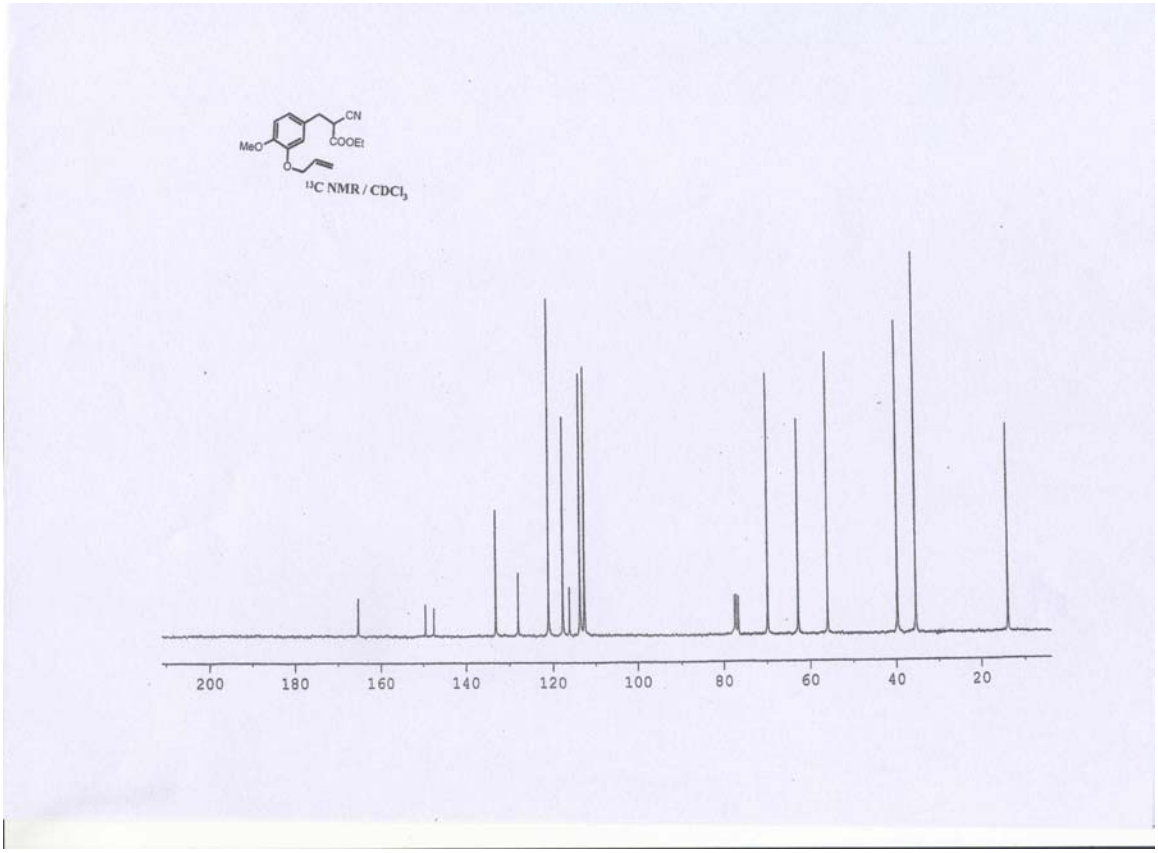
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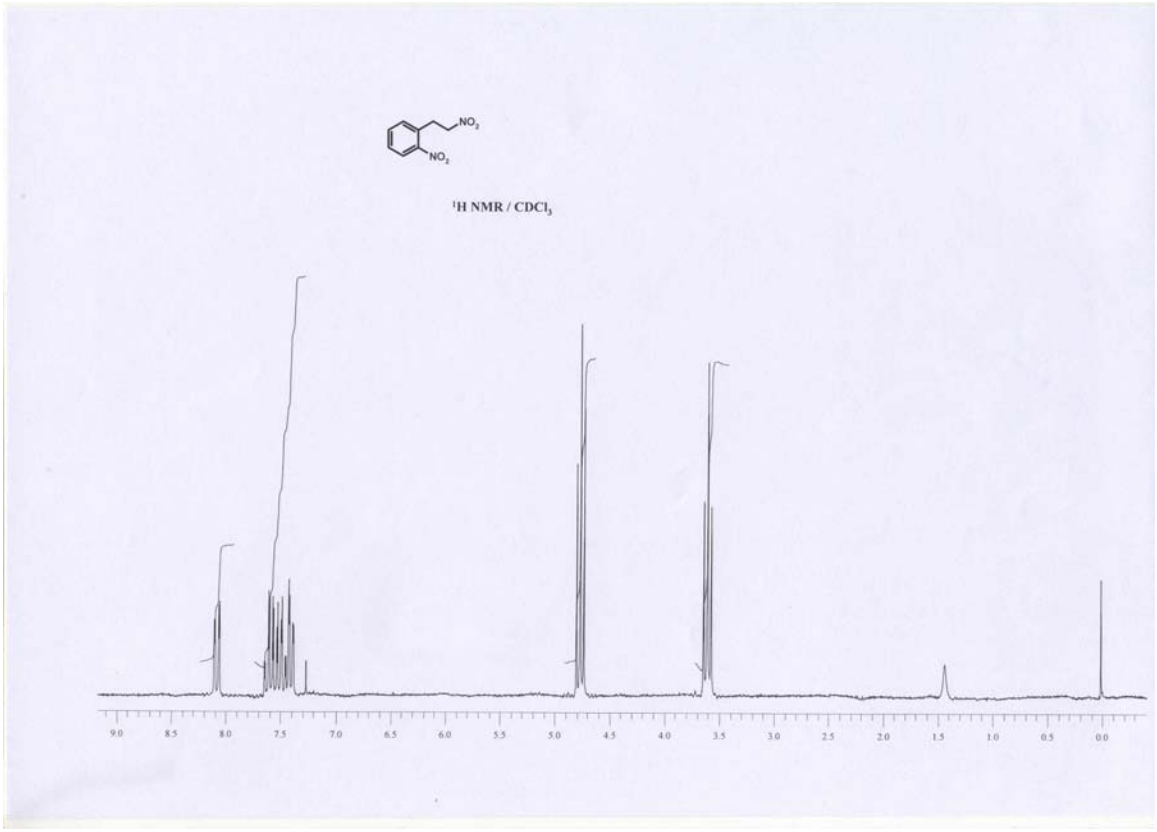
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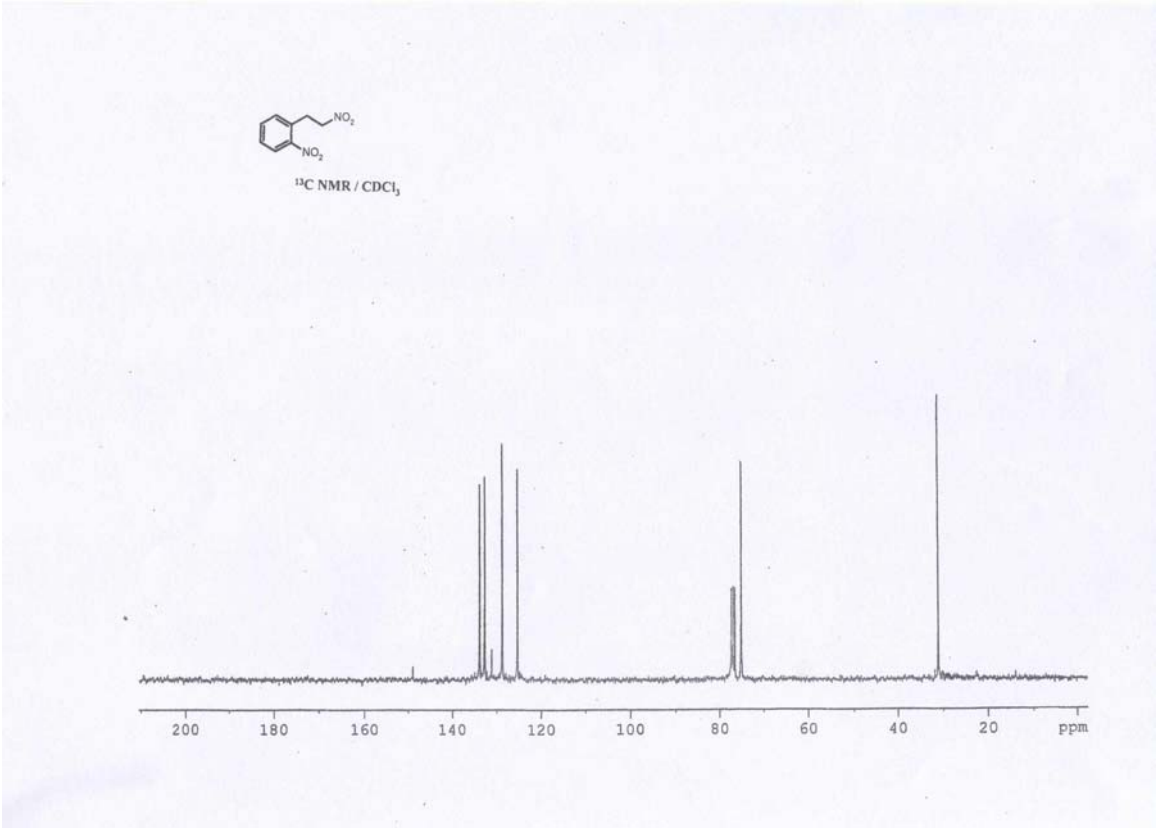
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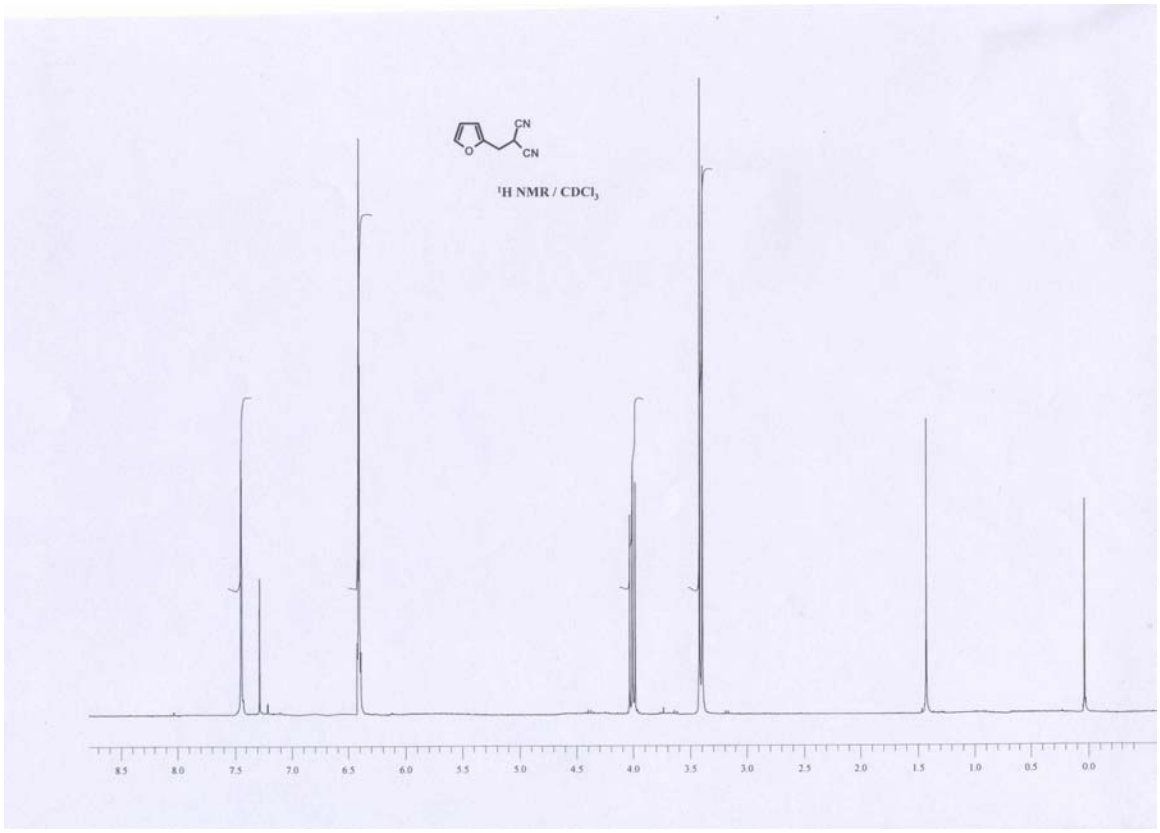
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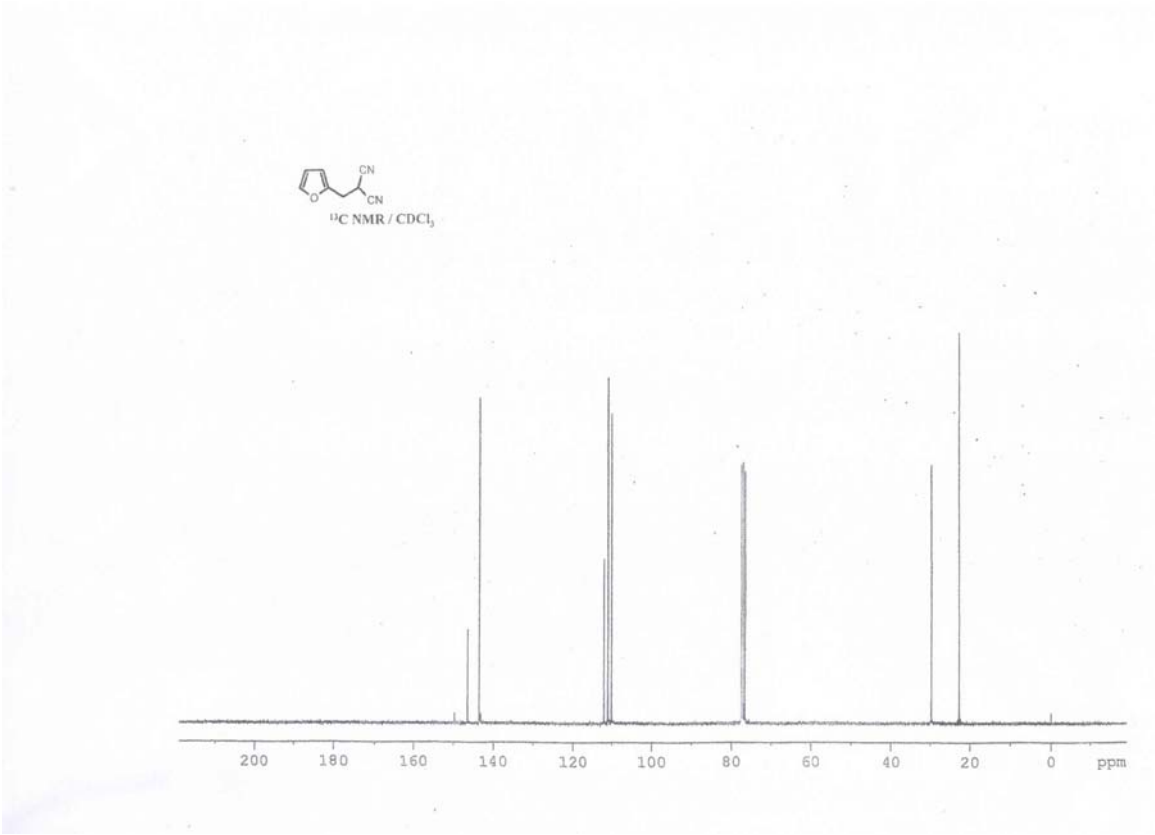
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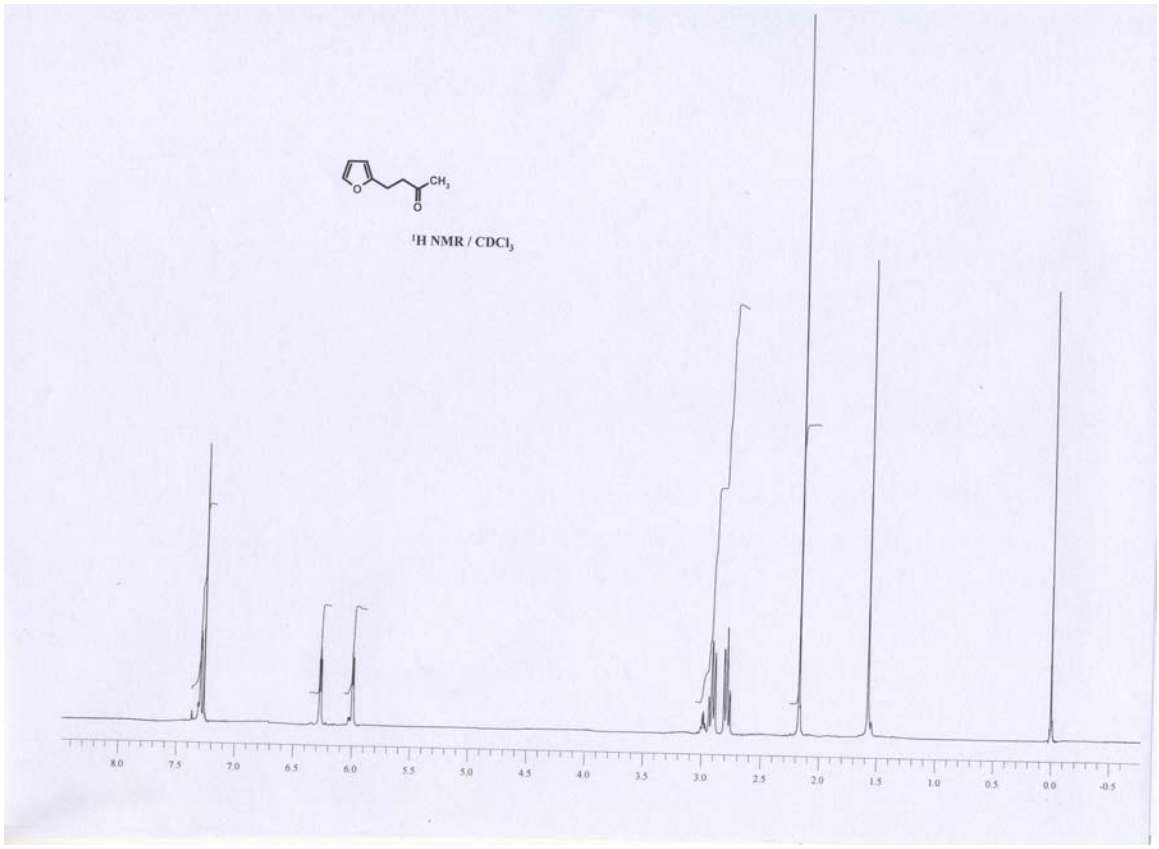
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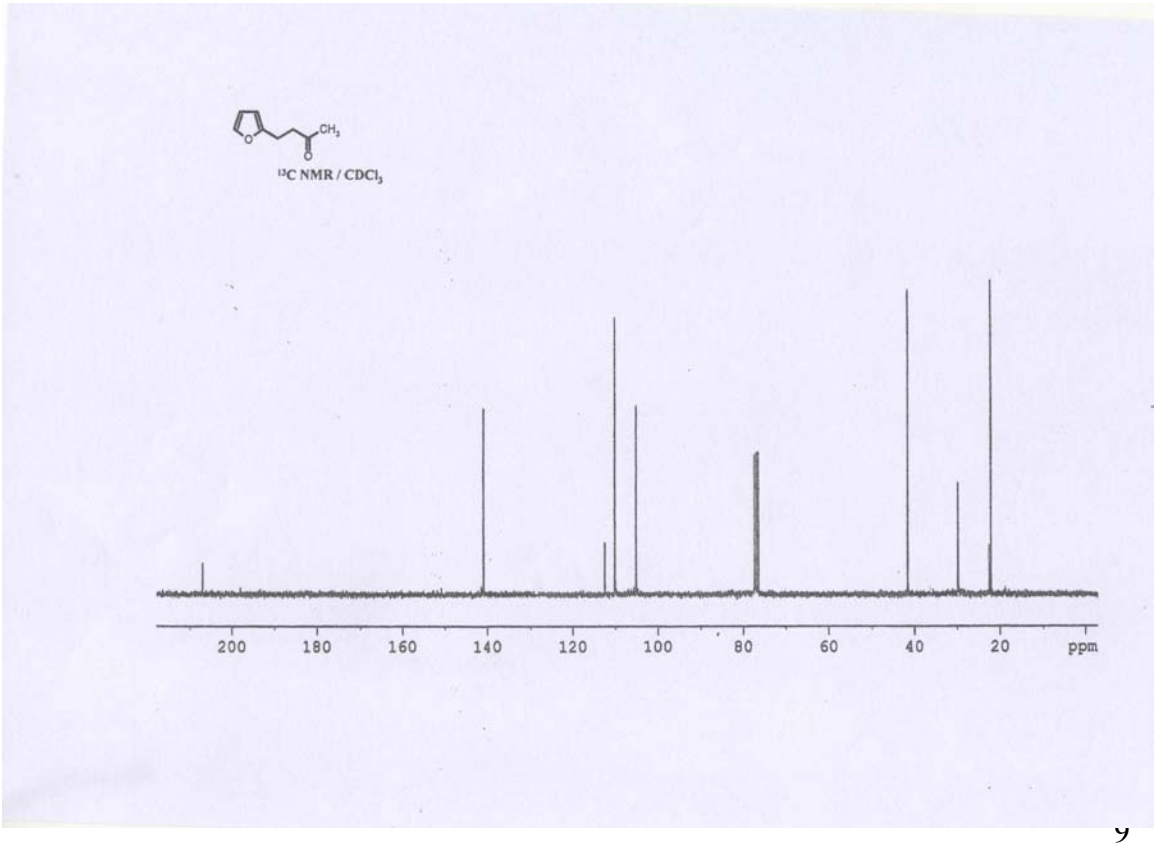
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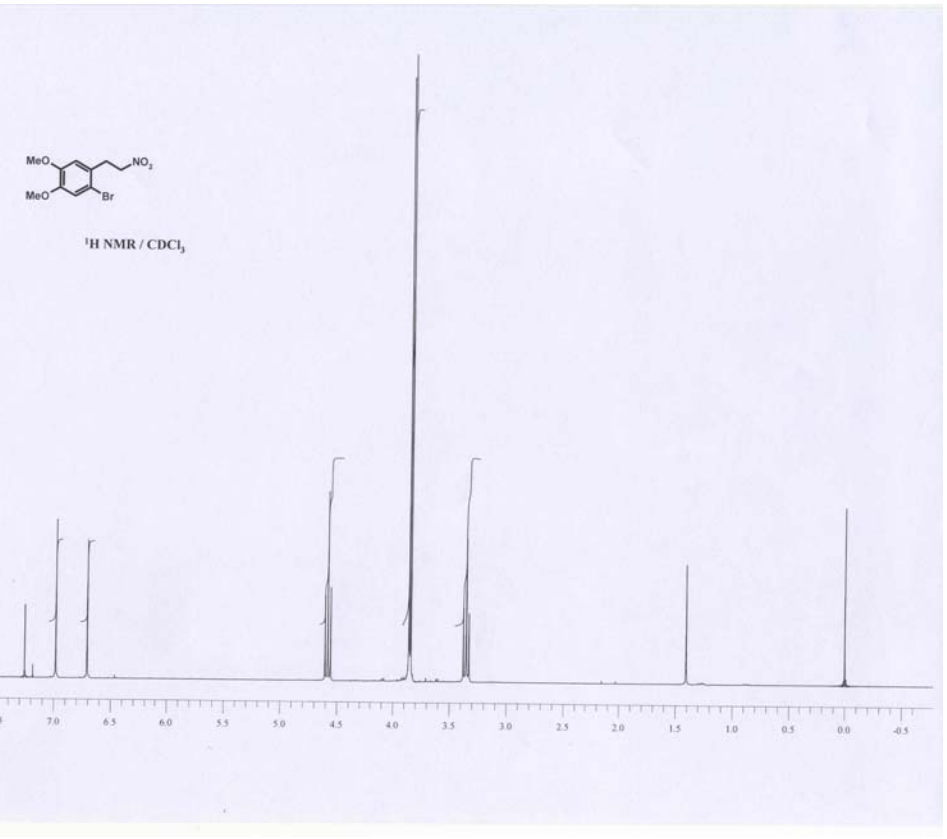
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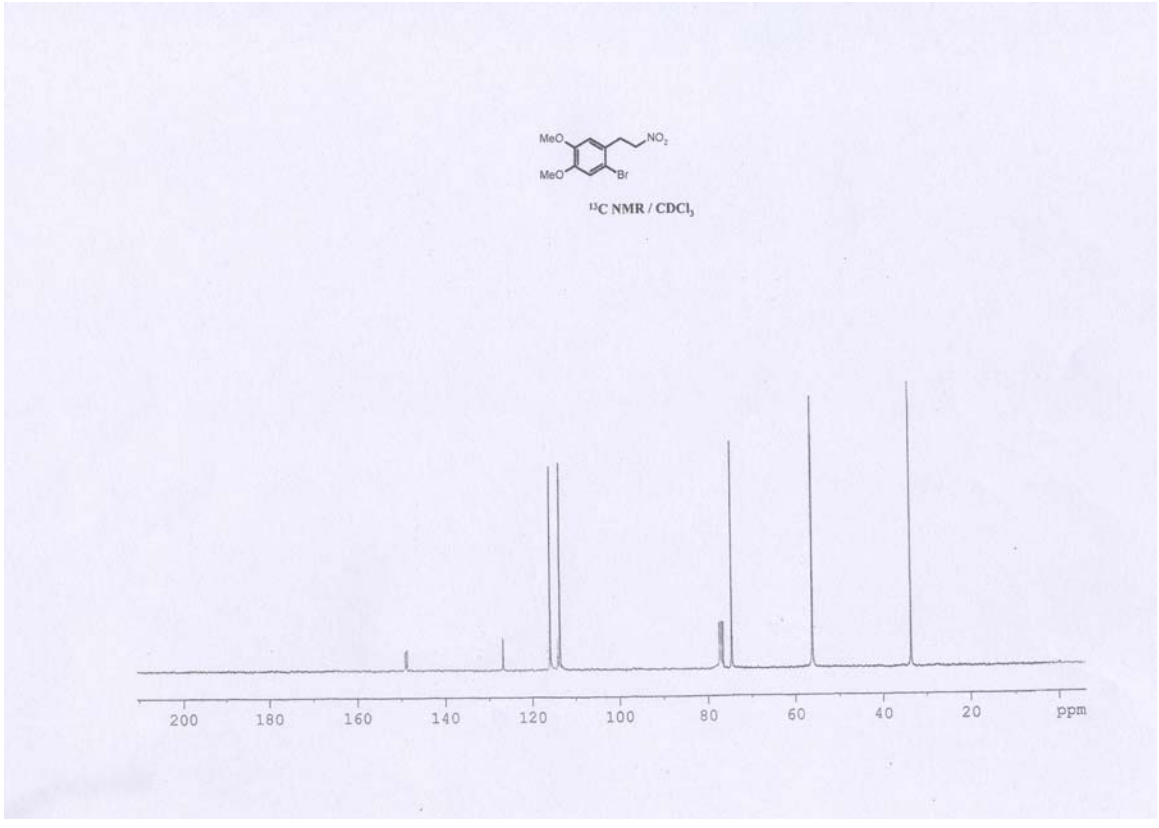
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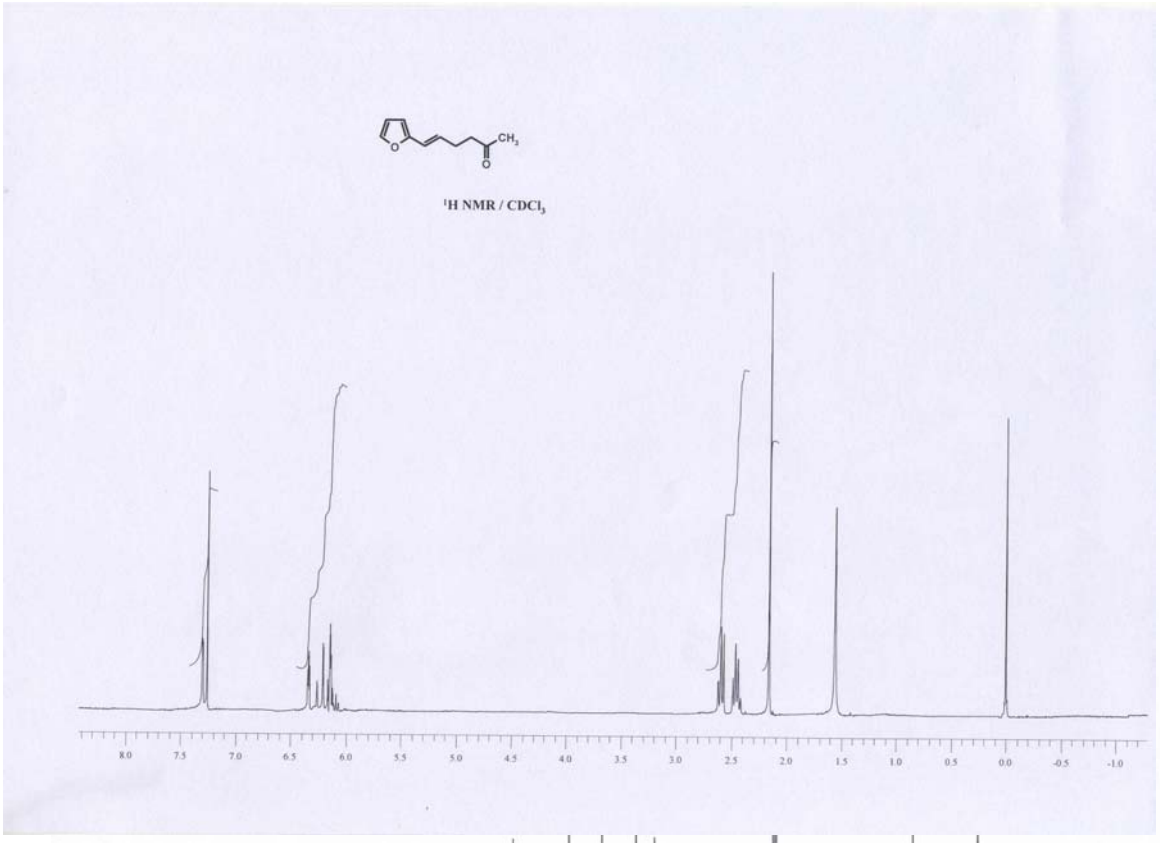

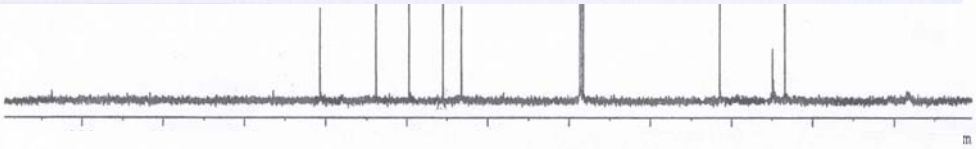

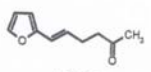

^{13}C NMR / $CDCl_3$