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Supporting Information

Diastereoselective Nitroaldol Reaction Catalyzed by Binuclear Copper(II) Complexes in Aqueous Medium

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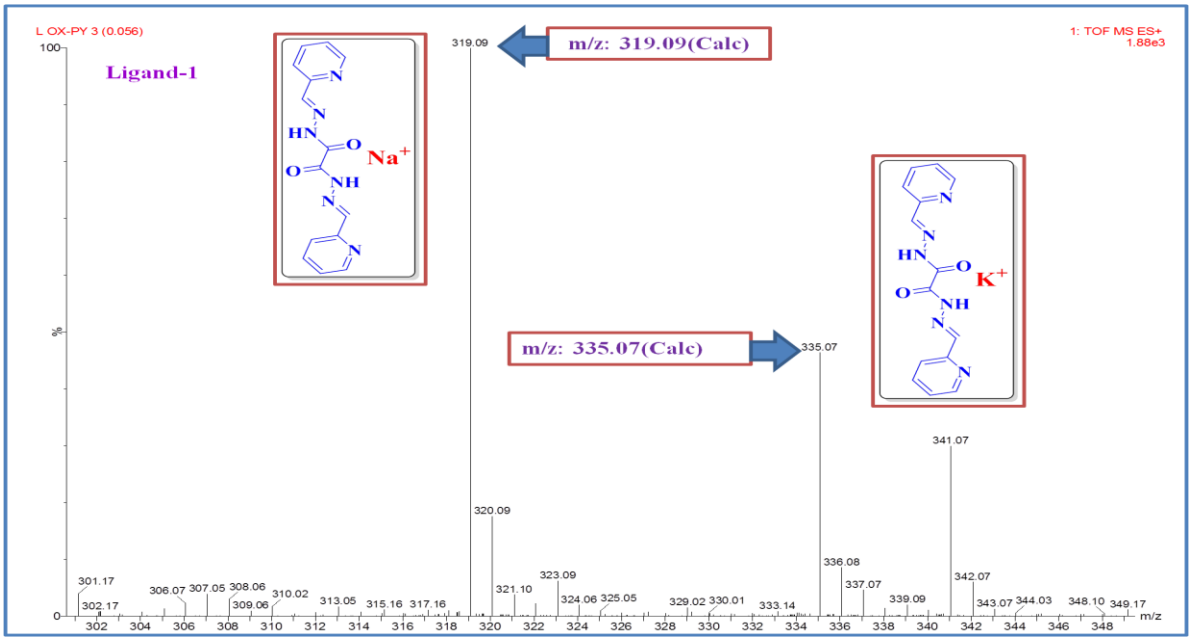
Content

General

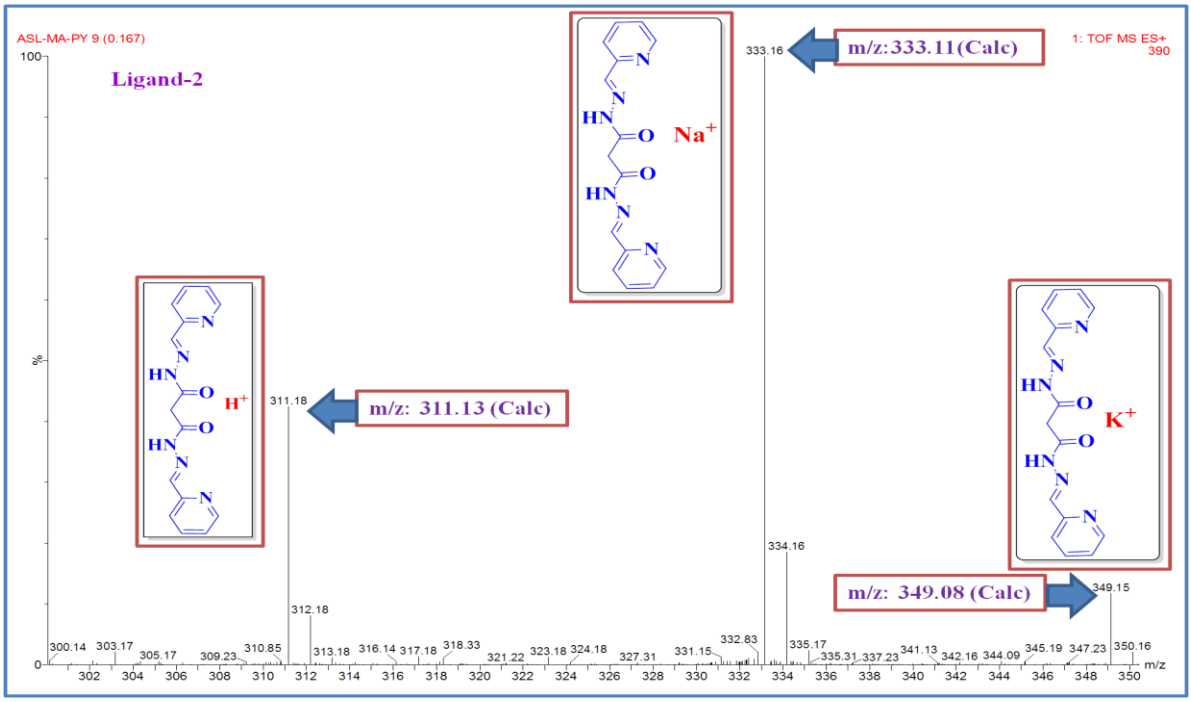
All starting materials and reagents were used as received without any further purification. 200 MHz or 500 MHz spectrometers were used for the ^{1}H and ^{13}C NMR spectra. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$=7.26). Spectra are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment.

Spectral data for Complexes

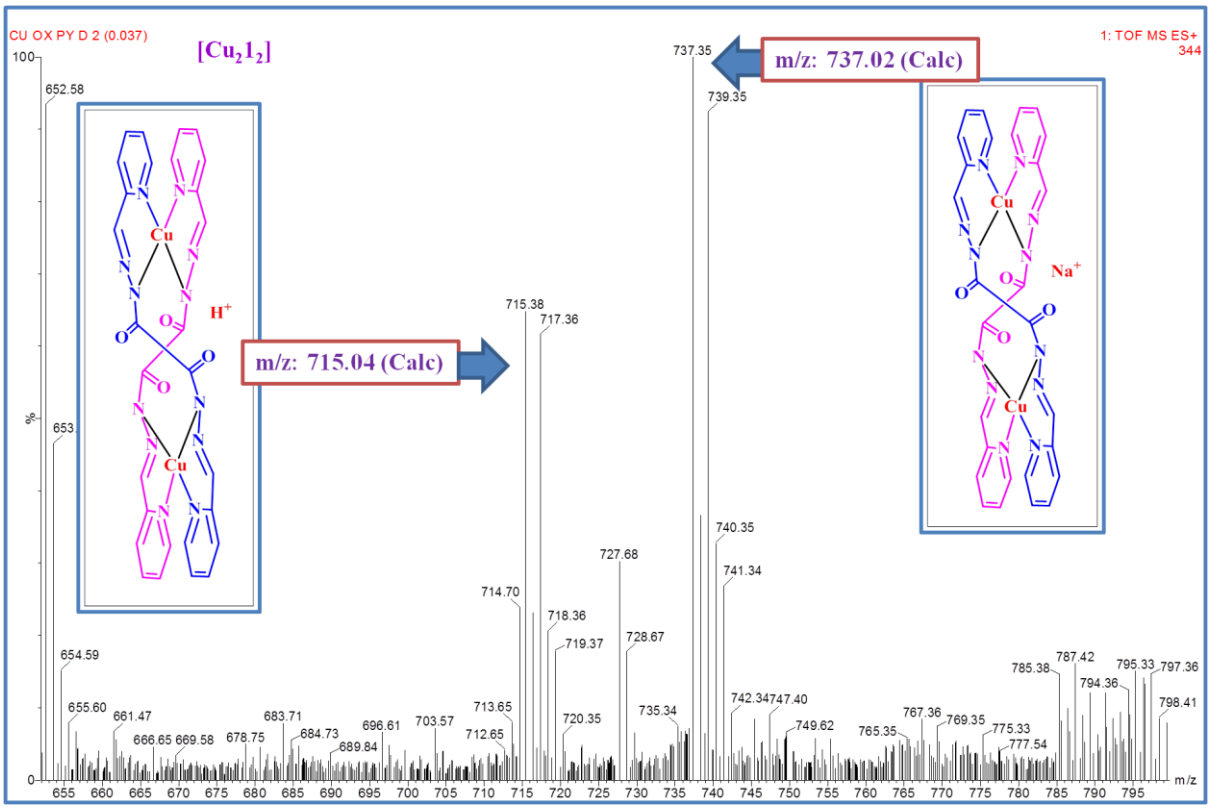
S1. LCMS for Ligand-1



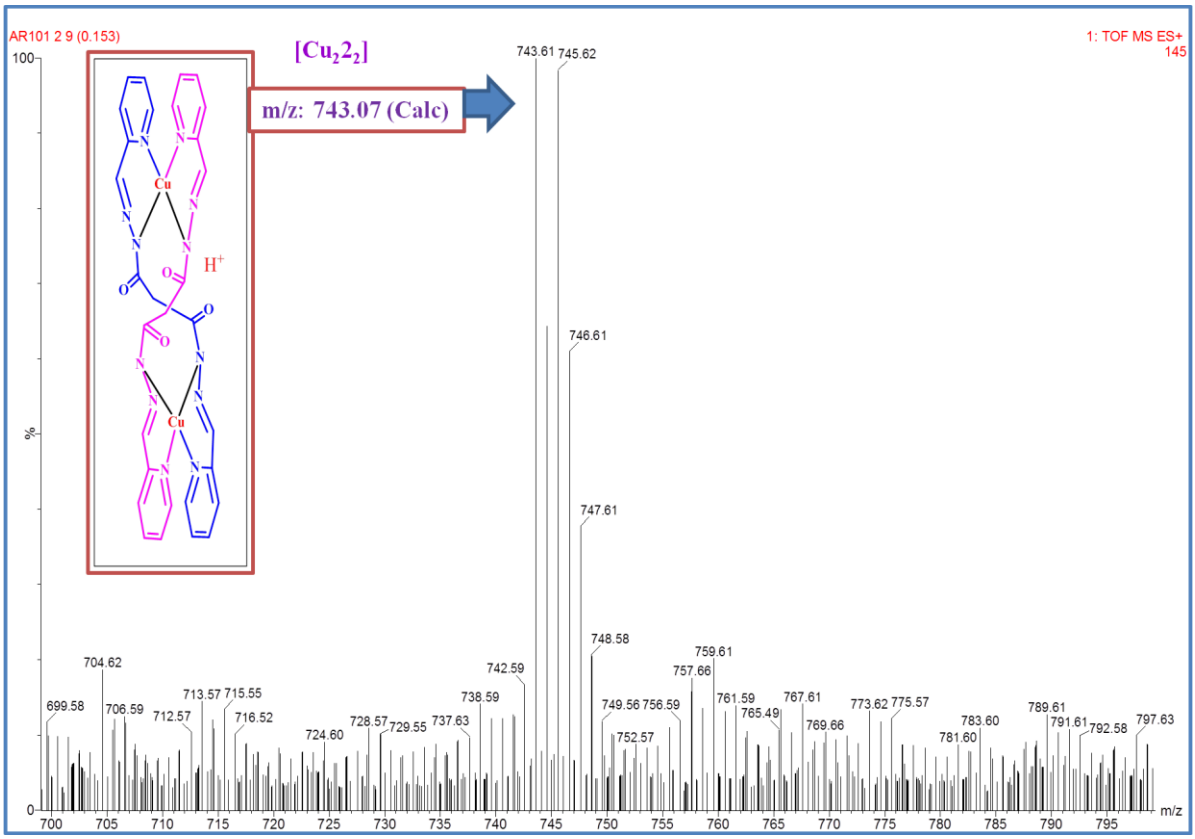
S2. LCMS for Ligand-1



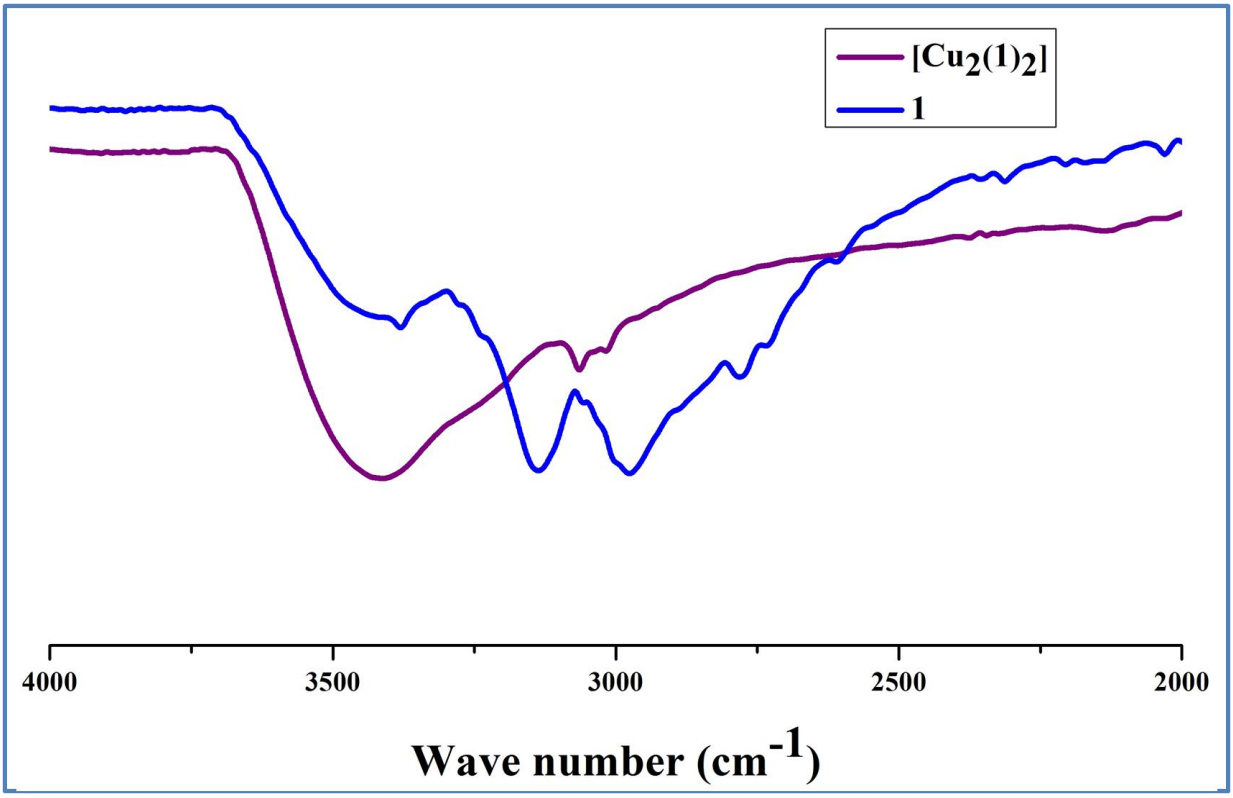
S3. LCMS for [Cu_2L_2]



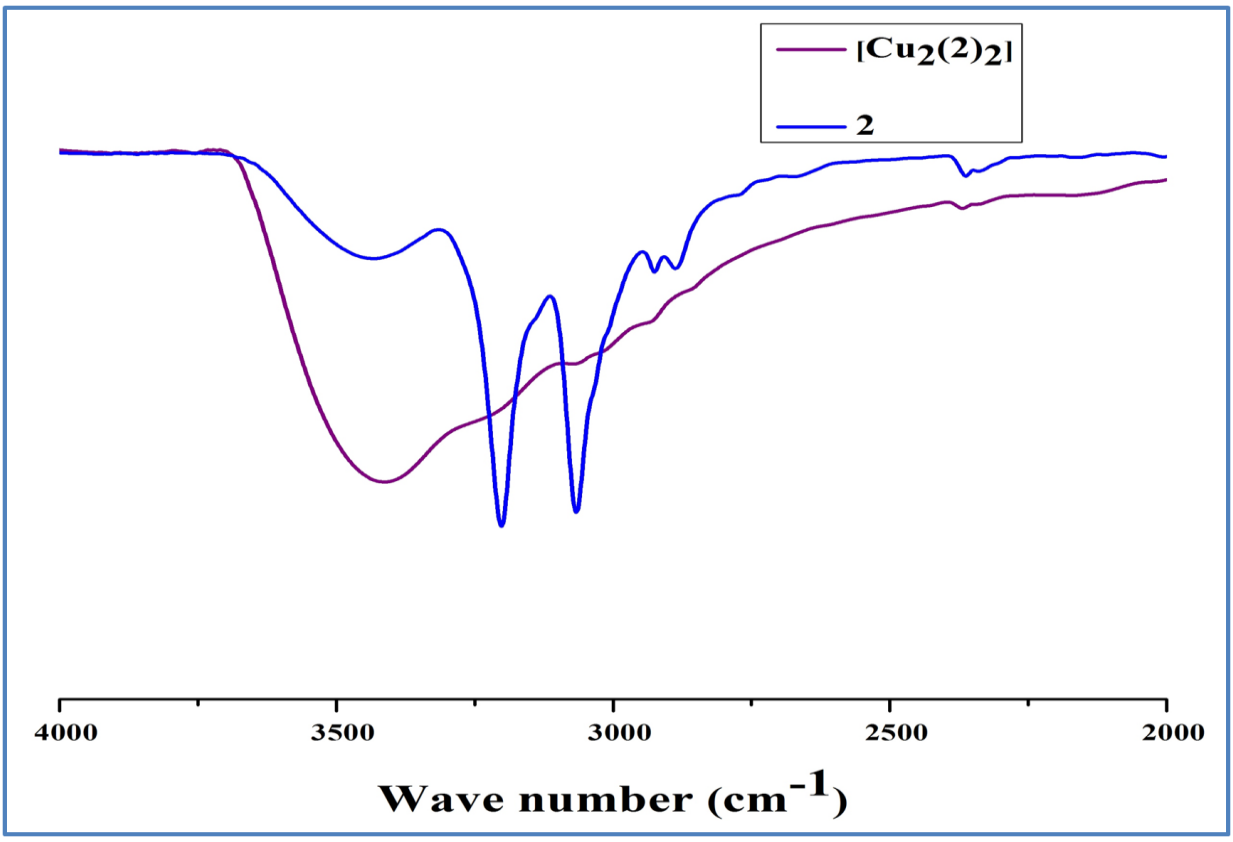
S4. LCMS for [Cu_2L_2]



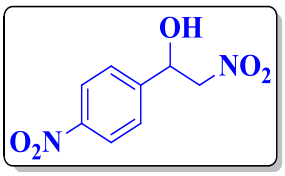
S5. IR for $[Cu_2\mathbf{1}_2]$



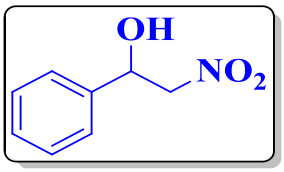
S6. IR for $[Cu_2\mathbf{2}_2]$



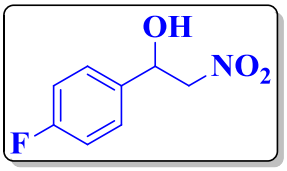
S7. Charterization of Nitroaldol product



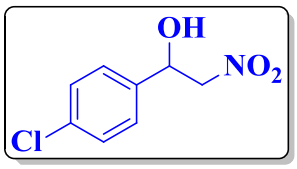
2-nitro-1-(4-nitrophenyl)ethanol: Yellow oil, Yield 92%; ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 8.28-8.24 (d, 2H), 7.65-7.61(d, 2H), 5.65-5.59 (t, 1H), 4.68-4.54 (m, 2H), 3.38 (bs, 1H).



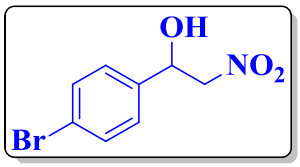
2-nitroethanol-1-phenylethanol: Colorless oil, Yield 83%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.28 (s, 5H), 5.34-4.29 (t, 1H), 4.48-4.39 (m, 2H), 3.12 (bs, 1H).



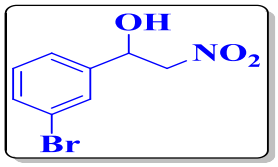
1-(4-fluorophenyl)-2-nitroethanol: Yellow oil, Yield 98%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.43-7.36 (m, 2H), 7.14-7.06 (m, 2H), 5.49-5.43 (m, 1H), 4.58-4.51 (dd, 2H), 2.30 (bs, 1H).



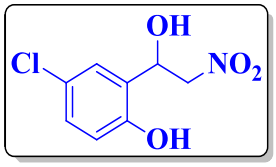
1-(4-chlorophenyl)-2-nitroethanol: Yellow oil, Yield 92%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.44-7.36 (m, 2H), 7.15-7.04 (m, 2H), 5.49-5.43 (m, 1H), 4.58-4.51 (dd, 2H), 1.66 (bs, 1H).



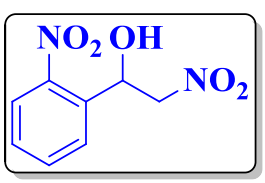
1-(4-bromophenyl)-2-nitroethanol: Yellow oil, Yield 56%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.55-7.51 (d, 2H), 7.30-7.26 (d, 2H), 5.48-5.39 (m, 1H), 4.56-4.50 (t, 2H), 3.09 (bs, 1H).



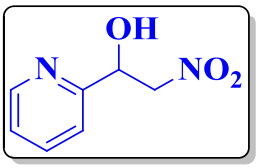
1-(3-bromophenyl)-2-nitroethanol: Colorless oil, Yield 89%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.59-7.48 (t, 2H), 7.30-7.33 (m, 2H), 5.47-5.43 (t, 1H), 4.65-4.53 (m, 2H), 3.00 (bs, 1H).



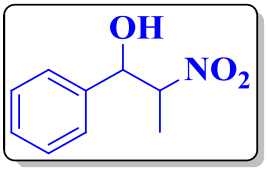
4-chloro-2-(1-hydroxy-2-nitroethyl)phenol: Yellow oil, Yield 26%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.09-8.05 (d, 1H), 7.97-7.94 (d, 1H), 7.79-7.72 (t, 1H), 4.91-4.89 (d, 1H), 4.84-4.82 (d, 1H), 4.61-4.50 (m, 1H), 3.45 (bs, 1H), 1.85 (bs, 1H).



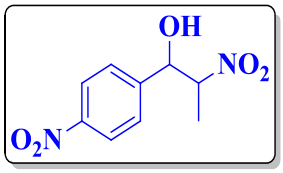
2-nitro-1-(2-nitrophenyl)ethanol: Yellow oil, Yield 90%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 8.03-7.98 (d, 1H), 7.91-7.87 (d, 1H), 7.72- 7.64 (t, 1H),7.52-7.45 (t, 1H), 5.99-5.95 (d, 1H), 4.84-4.76 (dd, 1H), 4.54-4.43 (m, 1H), 3.32 (bs, 1H).



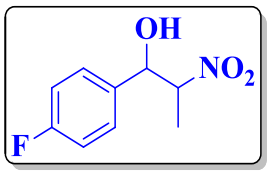
2-nitro-1-(pyridine-2-yl)ethanol: Brown oil, Yield 92%; ^{1}H- NMR**:** (200 MHz, $CDCl_3$) δ = 8.59-8.57 (d, 1H), 7.82-7.73 (t, 1H), 7.46-7.43 (d, 1H), 7.34-7.27 (t, 1H), 5.51-5.45 (dd, 1H), 4.84-4.59 (m, 1H), 1.71 (bs, 1H).



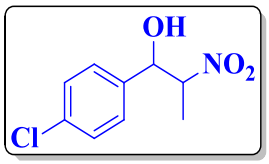
2-nitro-1-phenylpropan-1-ol: Colorless oil, Yield 83%; de 64%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 7.36 (s, 5H), 5.02-4.97 (d, 1H), 4.83-4.72 (m, 1H), 3.00 (bs, 1H), 1.31-1.47 (dd, 3H).



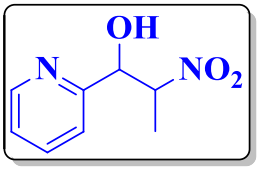
2-nitro-1-(4-nitrophenyl)propan-1-ol: Yellow oil, Yield 93%; de 45 %; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 8.28-8.24 (d, 2H), 7.61-7.57 (d, 2H), 5.22-5.17 (d, 1H), 4.86-4.69 (m, 1H), 3.14 (bs, 1H), 1.51-1.47 (d, 1H), 1.41-1.37 (d, 2H).



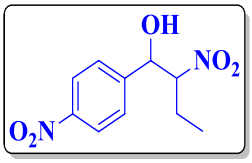
1-(4-fluorophenyl)-2-nitropropan-1-ol: Yellow oil, Yield 94%; de 49%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.31-7.24 (dd, 2H), 7.05-7.01 (d, 2H), 4.97-4.92 (d, 1H), 4.69-4.61 (m, 1H), 2.99 (bs, 1H), 1.24-1.21 (d, 3H).



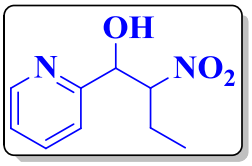
1-(4-chlorophenyl)-2-nitropropan-1-ol: Yellow oil, Yield 85%; de 24%; ^{1}H- NMR (200 MHz, $CDCl_3$) δ = 7.41-7.29 (m, 4H), 5.05-5.01 (d, 1H), 4.79-4.60 (m, 1H), 2.75 (bs, 1H), 1.51-1.48 (d, 1H), 1.35-1.31 (d, 2H).



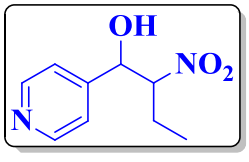
2-nitro-1-(pyridin-2-yl)propan-1-ol: Brown oil, Yield 92%; de 96%; ^{1}H-NMR: (200 MHz, $CDCl_3$) δ = 8.57-8.55 (d, 1H), 7.80-7.72 (t, 1H), 7.37-7.33 (t, 2H), 5.07-5.03 (d, 1H), 4.95-4.85 (m, 1H), 1.44-1.40 (d, 3H).



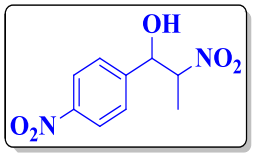
2-nitro-1-(4-nitrophenyl)butan-1-ol: Yellow oil, Yield 91%; de 40%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.29-8.25 (d, 2H), 7.60-7.56 (d, 2H), 5.02-5.16 (d, 1H), 4.67-4.56 (m, 1H), 2.90 (bs, 1H), 1.94-1.89 (m, 1H), 1.56-1.45 (m, 1H), 0.96-0.89 (m, 3H).



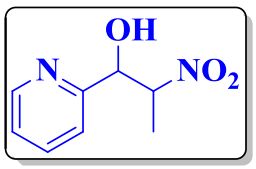
2-nitro-1-(pyridin-2-yl)butan-1-ol: Brown oil, Yield 89%; de 100%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.60-8.58 (d, 1H), 7.76-7.75 (d, 1H), 7.37-7.31 (t, 2H), 5.05-5.02 (d, 1H), 4.81-4.74 (m, 1H), 3.44 (bs, 1H), 2.08-1.99 (m, 1H), 1.08-1.59 (m, 1H), 0.98-0.91(m, 3H).



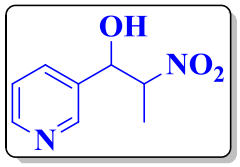
2-nitro-1-(pyridin-4-yl)butan-1-ol. Brown oil, Yield 92%; de 15%; ^{1}H-NMR: (200 MHz, $CDCl_3$) δ = 8.76-8.74 (d, 1H), 7.97-7.94 (d, 1H), 7.76-7.69 (t, 2H), 5.07-5.03 (d, 1H), 4.59-4.54 (m, 1H), 1.83-1.72 (q, 2H), 0.99-0.90(m, 3H).



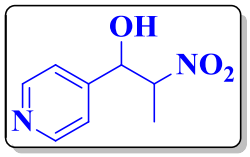
2-nitro-1-(4-nitrophenyl)propan-1-ol: Yellow oil, Yield 94%; de 19%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.29-8.24 (d, 2H), 7.62-7.56 (d, 2H), 5.21-5.17 (d, 1H), 4.81-4.70 (m, 1H), 3.05 (bs, 1H), 1.51-1.48 (d, 1H), 1.41-1.37 (d, 2H).



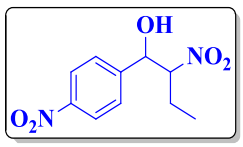
2-nitro-1-(pyridin-2-yl)propan-1-ol: Brown oil, Yield 94%; de 92%;^{1}H-NMR: (200 MHz, $CDCl_3$) δ = 8.51 (s, 1H), 7.72-7.64 (t, 1H), 7.49-7.38 (m, 1H), 7.28-7.19 (t, 1H), 5.00-4.97 (d, 1H), 4.91-4.78 (m, 1H), 1.38-1.35 (d, 3H).



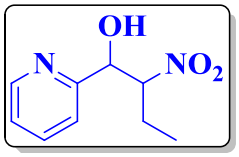
2-nitro-1-(pyridin-3-yl)propan-1-ol: Brown oil, Yield 92%; de 32%; ^{1}H-NMR: (500 MHz, $CDCl_3$) δ = 8.56-8.54 (d, 2H), 7.79-7.77 (d, 1H), 7.38-7.36 (t, 1H), 5.11-5.09 (d, 1H), 4.82-4.76 (m, 1H), 1.53-1.52 (d, 1H), 1.37-1.35 (d, 2H).



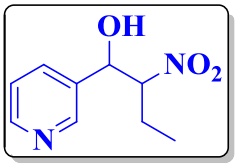
2-nitro-1-(pyridin-4-yl)propan-1-ol: Brown oil, Yield 92%; de 40%; ^{1}H-NMR: (500 MHz, $CDCl_3$) δ = 7.71-7.70 (d, 2H), 7.53-7.52 (d, 2H), 5.15-5.05 (d, 1H), 4.70-4.66 (m, 1H), 1.48-1.46 (d, 3H).



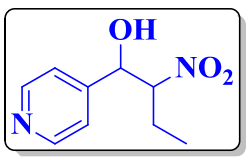
2-nitro-1-(4-nitrophenyl)butan-1-ol: Yellow oil, Yield 95%; de 16%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.23-8.18 (d, 2H), 7.53-7.49 (d, 2H), 5.13-5.09 (d, 1H), 4.60-4.49 (m, 1H), 1.25-1.84 (m, 2H), 0.98-0.82 (t, 3H).



2-nitro-1-(pyridin-2-yl)butan-1-ol: Brown oil, Yield 95%; de 92%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.57-8.55 (d, 1H), 7.77-7.69 (t, 1H), 7.35-7.25 (m, 2H), 5.03-4.99 (d, 1H), 4.79-4.72 (m, 1H), 2.01-1.96 (m, 1H), 1.66-1.59 (m, 1H), 0.95-0.88 (m, 3H).



2-nitro-1-(pyridin-3-yl)butan-1-ol: Brown oil, Yield 92%; de 33%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 8.54-8.50 (d, 2H), 7.79-7.77 (d, 1H), 7.38-7.36 (t, 1H), 5.09-5.07 (d, 1H), 4.64-4.58 (m, 1H), 1.45-1.36 (m, 2H), 0.92-0.89 (d, 3H).



2-nitro-1-(pyridin-4-yl)butan-1-ol: Brown oil, Yield 86%; de 36%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 7.71-7.70 (d, 1H), 7.54-7.53 (d, 1H), 7.33-7.32 (d, 2H), 5.05-5.04 (d, 1H), 4.62-4.54 (m, 1H), 1.36-1.31 (m, 2H), 0.95-0.92 (t, 3H).

^{1}H NMR spectra for nitroaldol product

Table. 1(Entry-17).

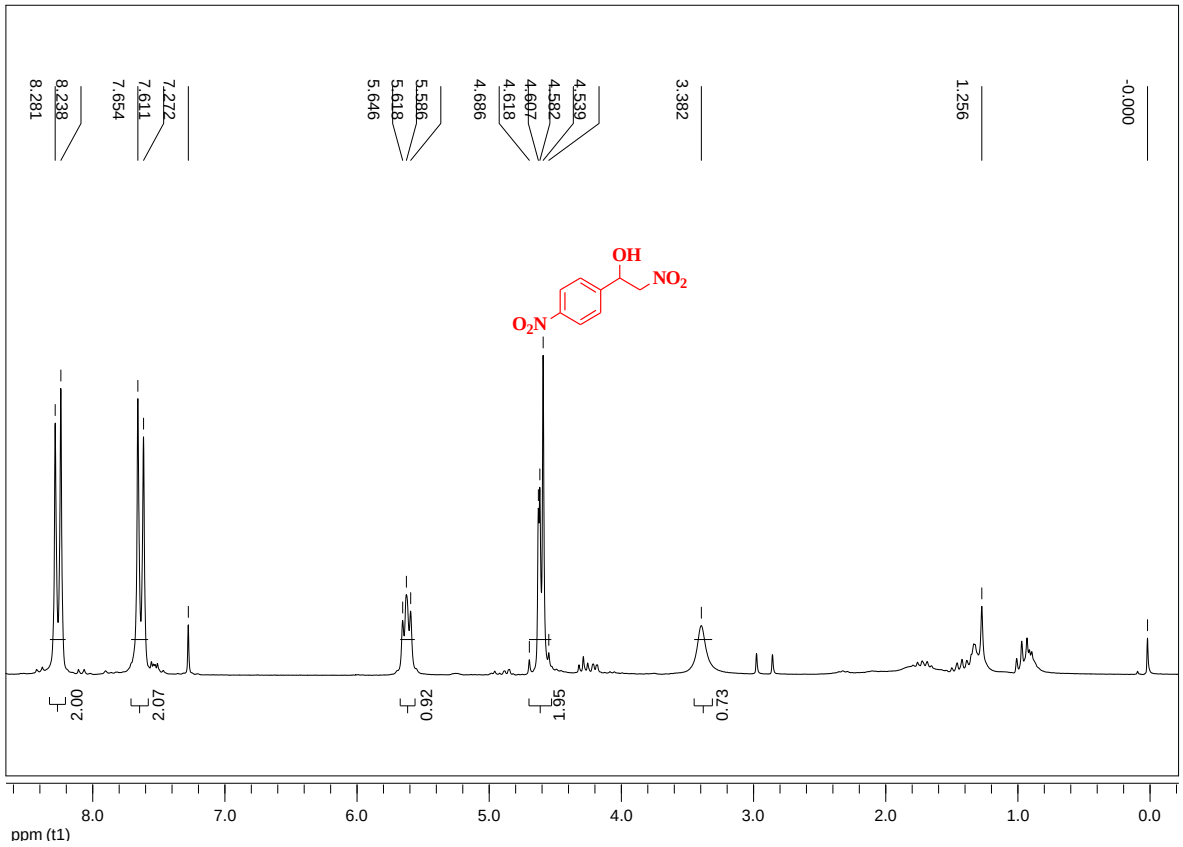


Table. 3(Entry-1)

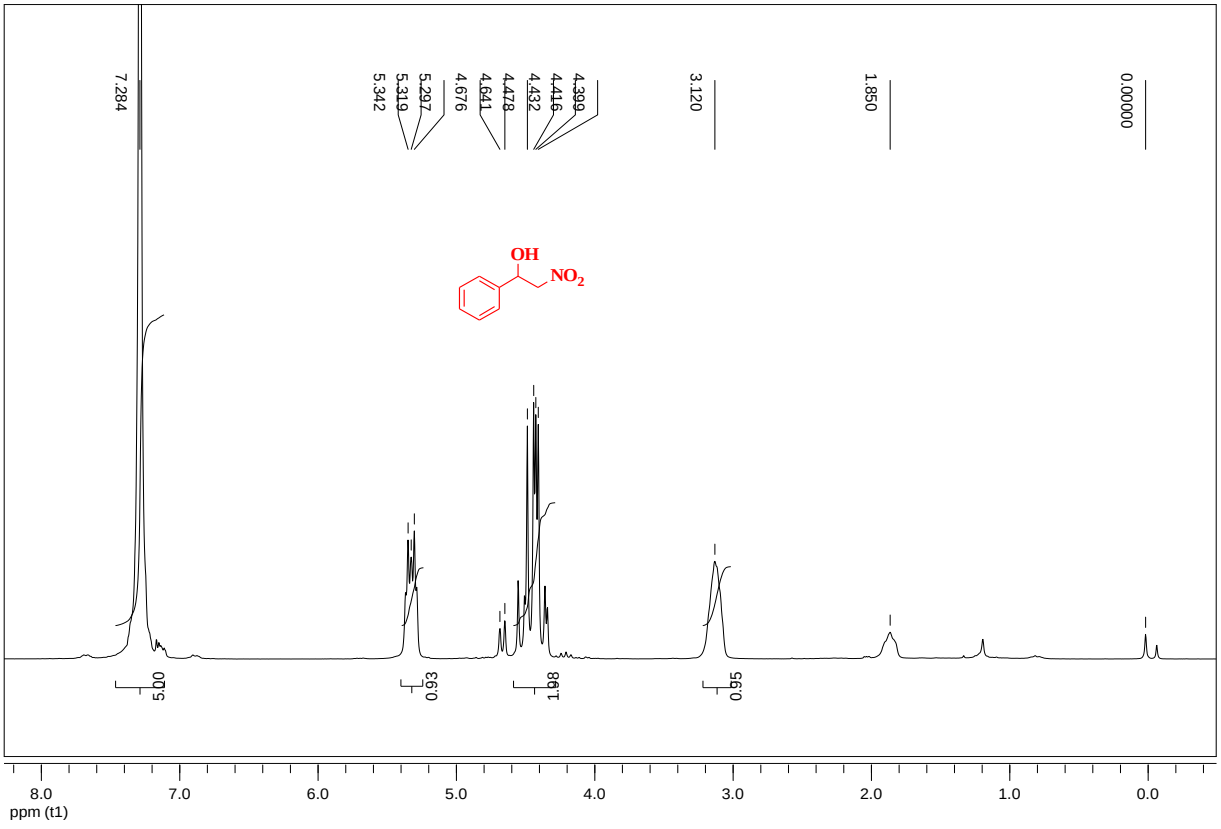


Table. 3(Entry-2).

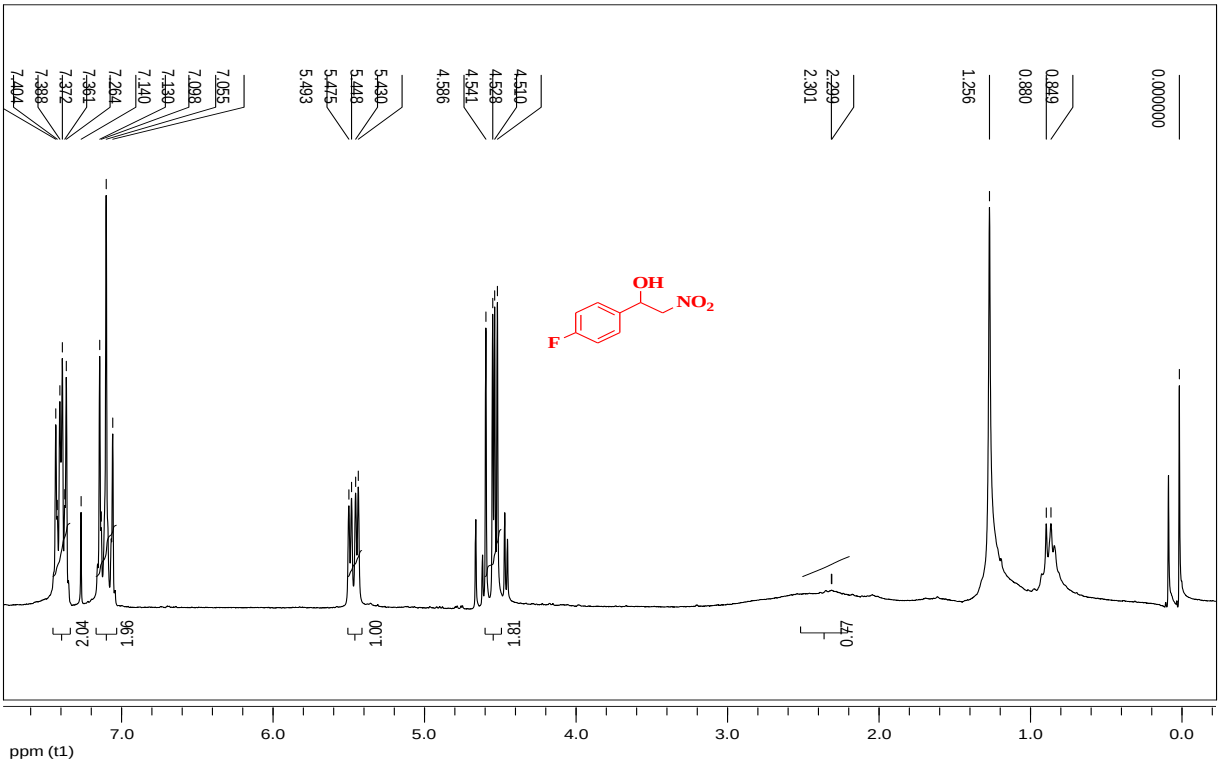


Table. 3(Entry-3)

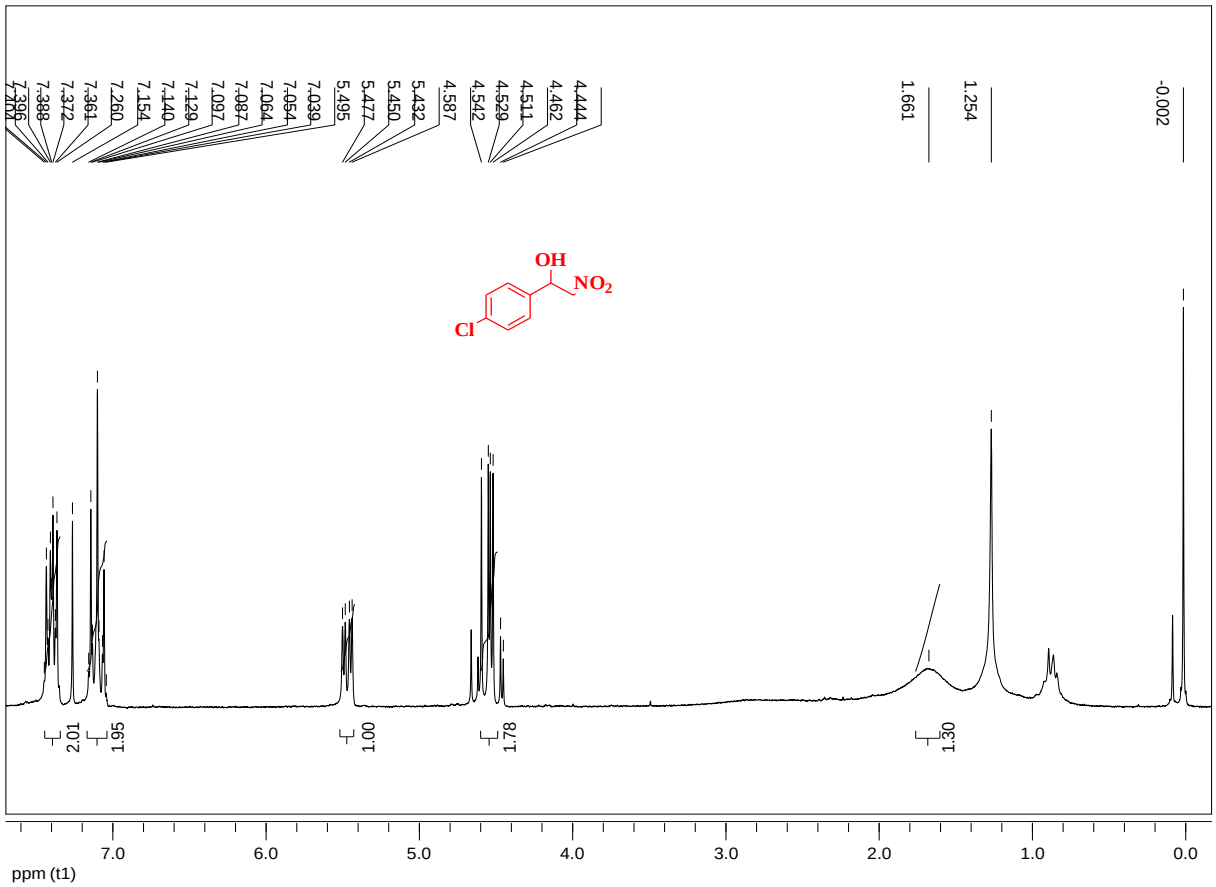


Table. 3(Entry-4).

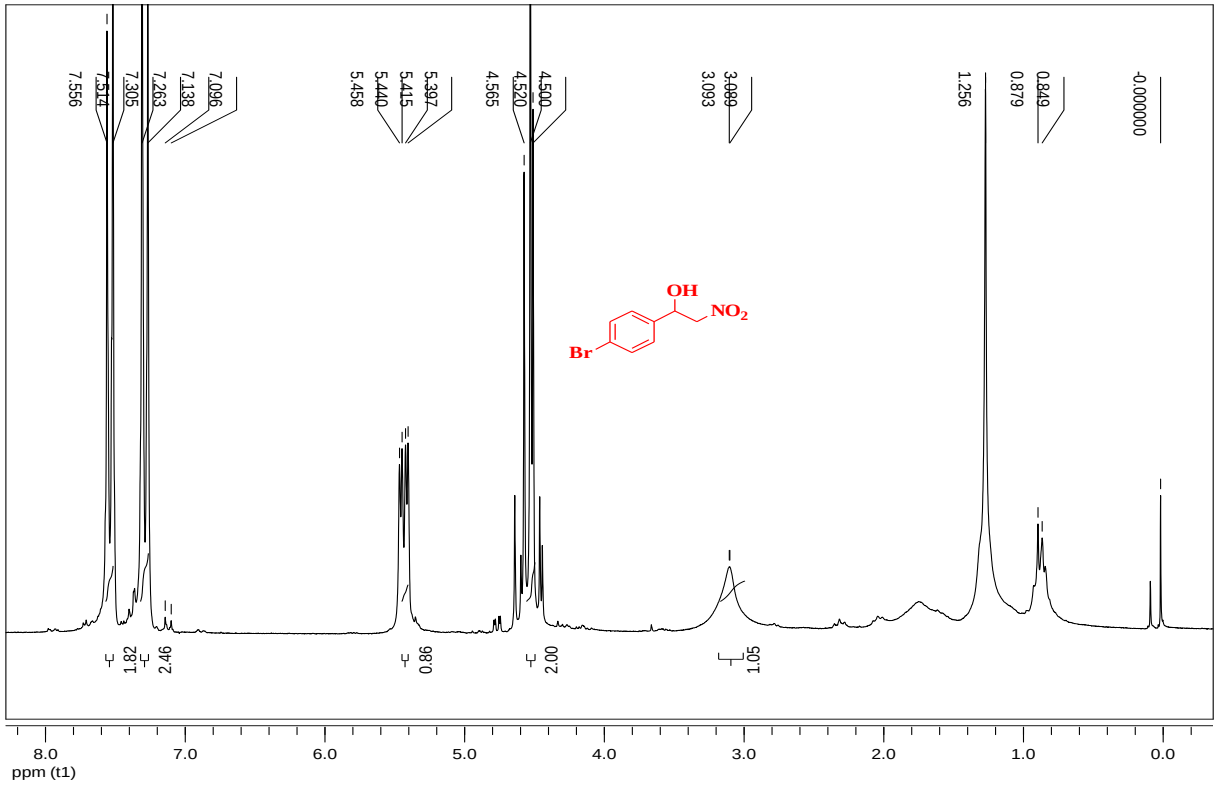


Table. 3(Entry-5).

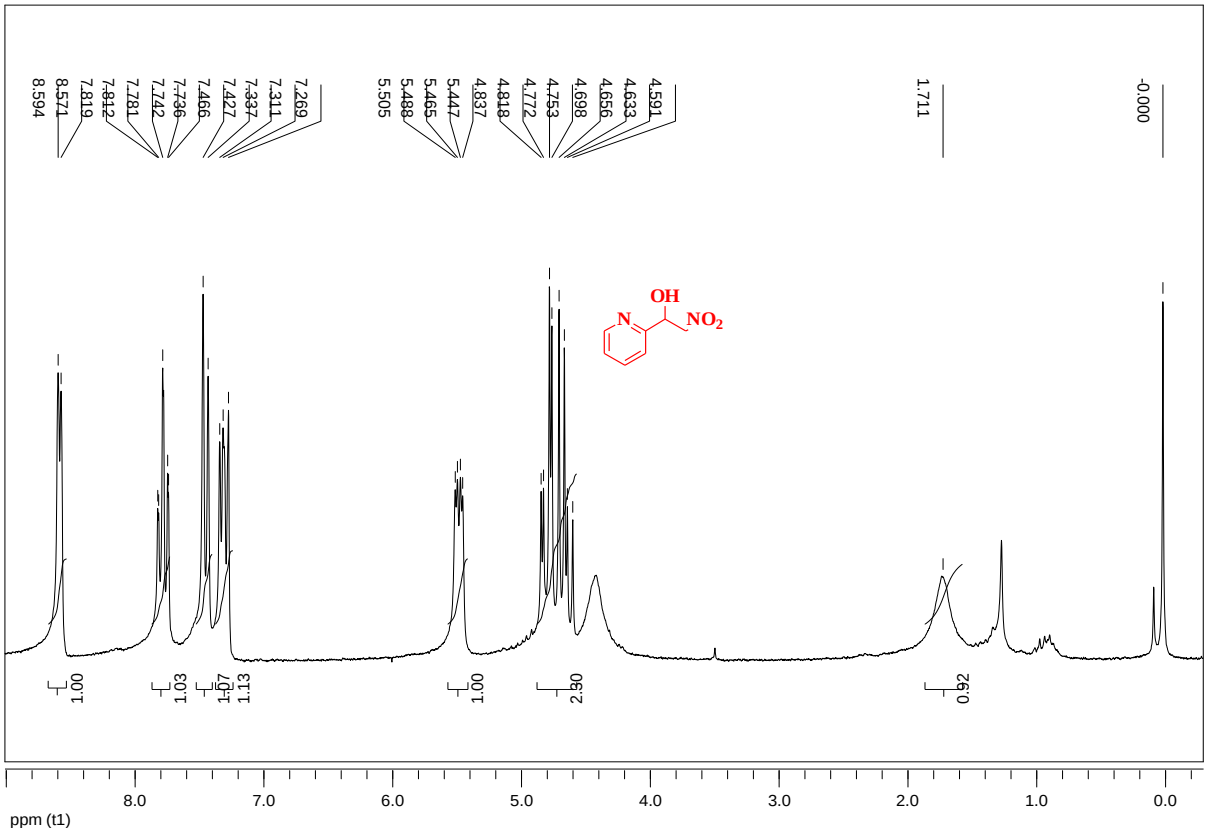


Table. 3(Entry-6).

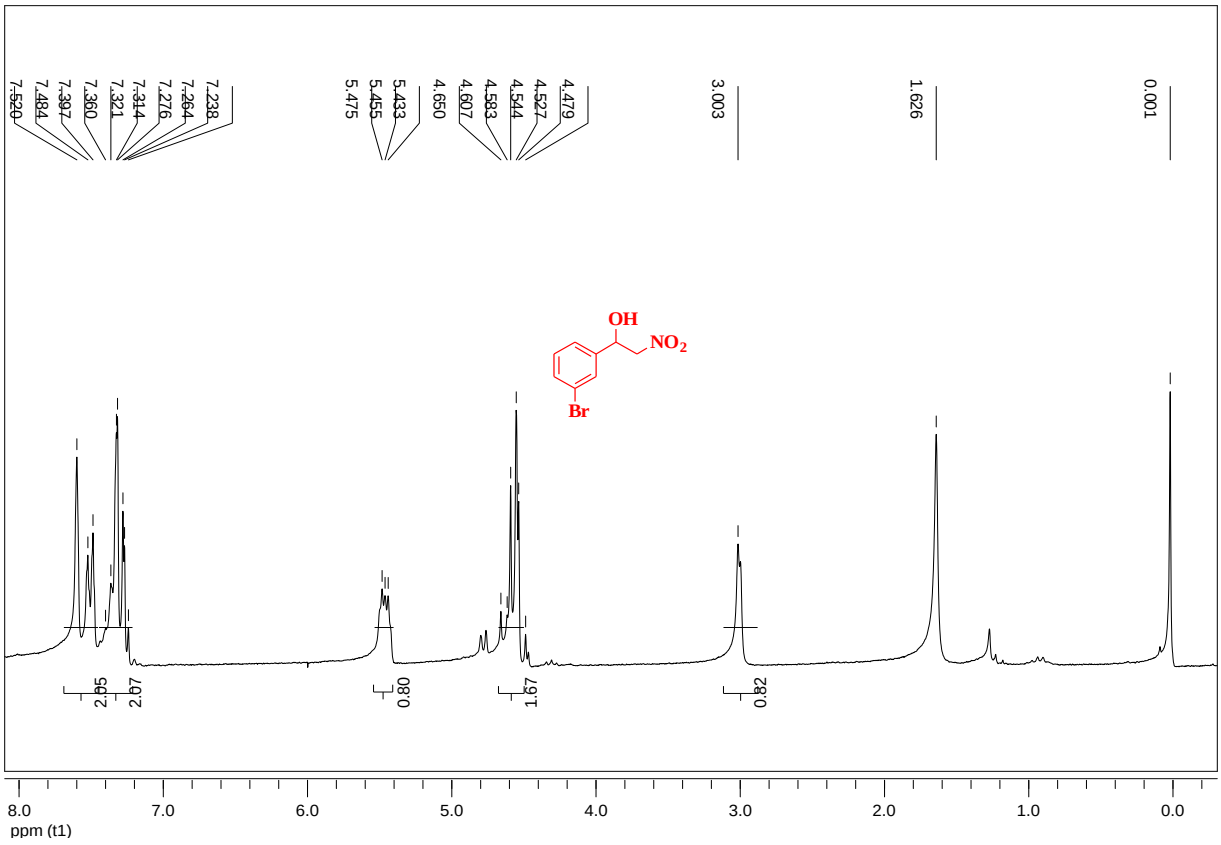


Table. 3(Entry-7).

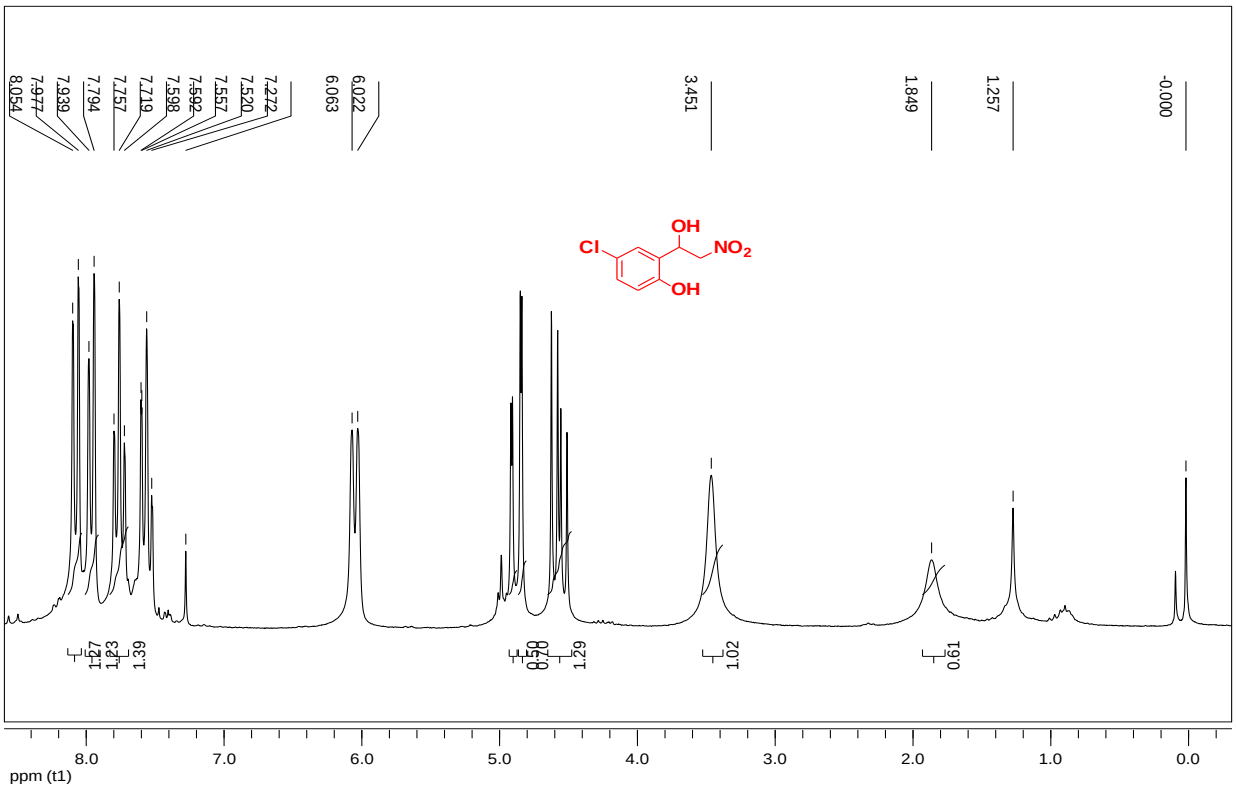


Table. 4(Entry-1).

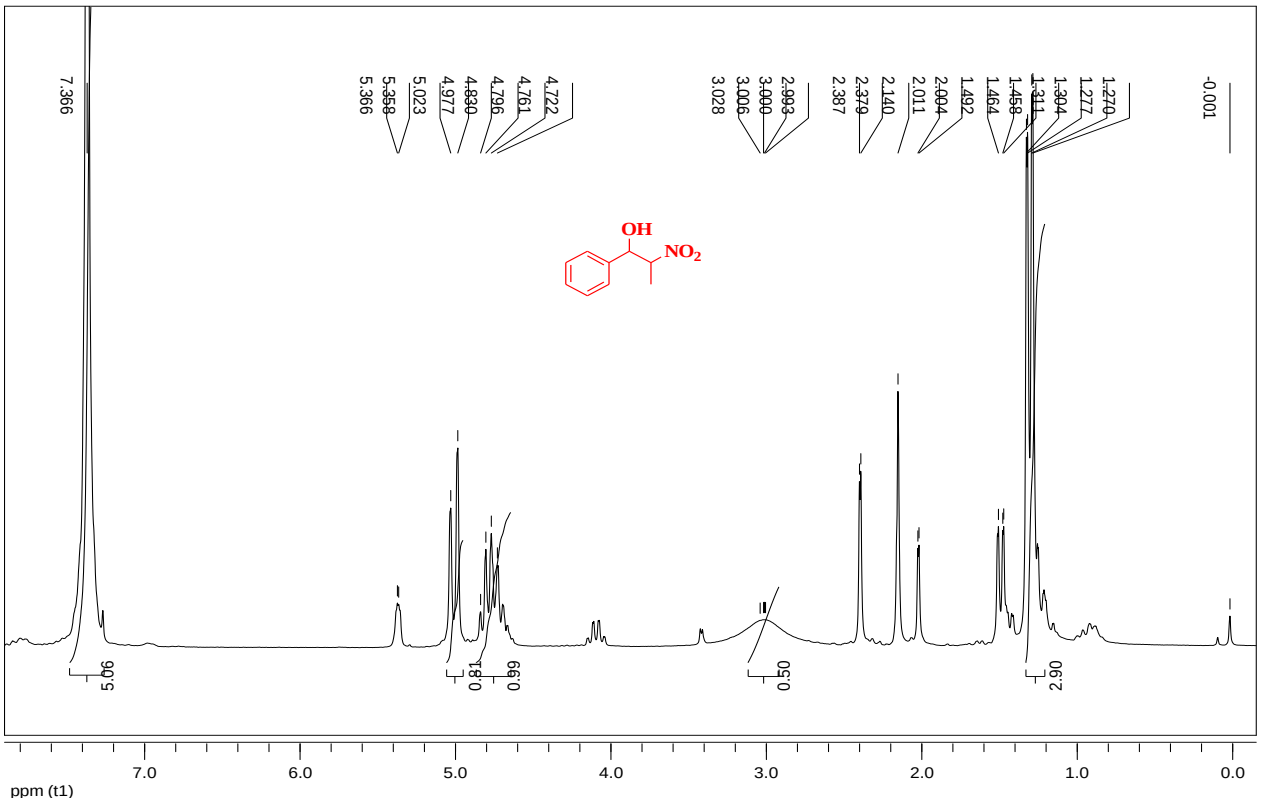


Table. 4(Entry 2).

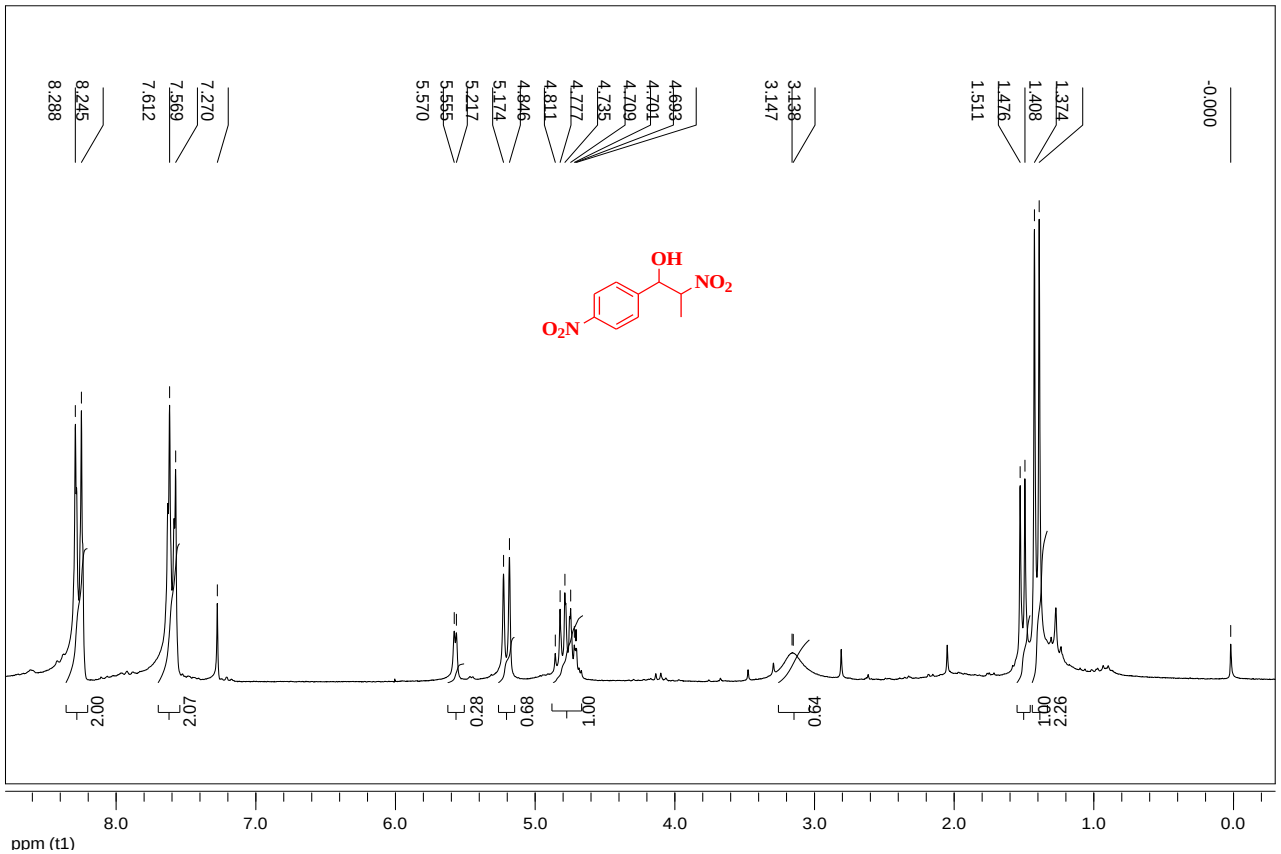


Table. 4(Entry-4).

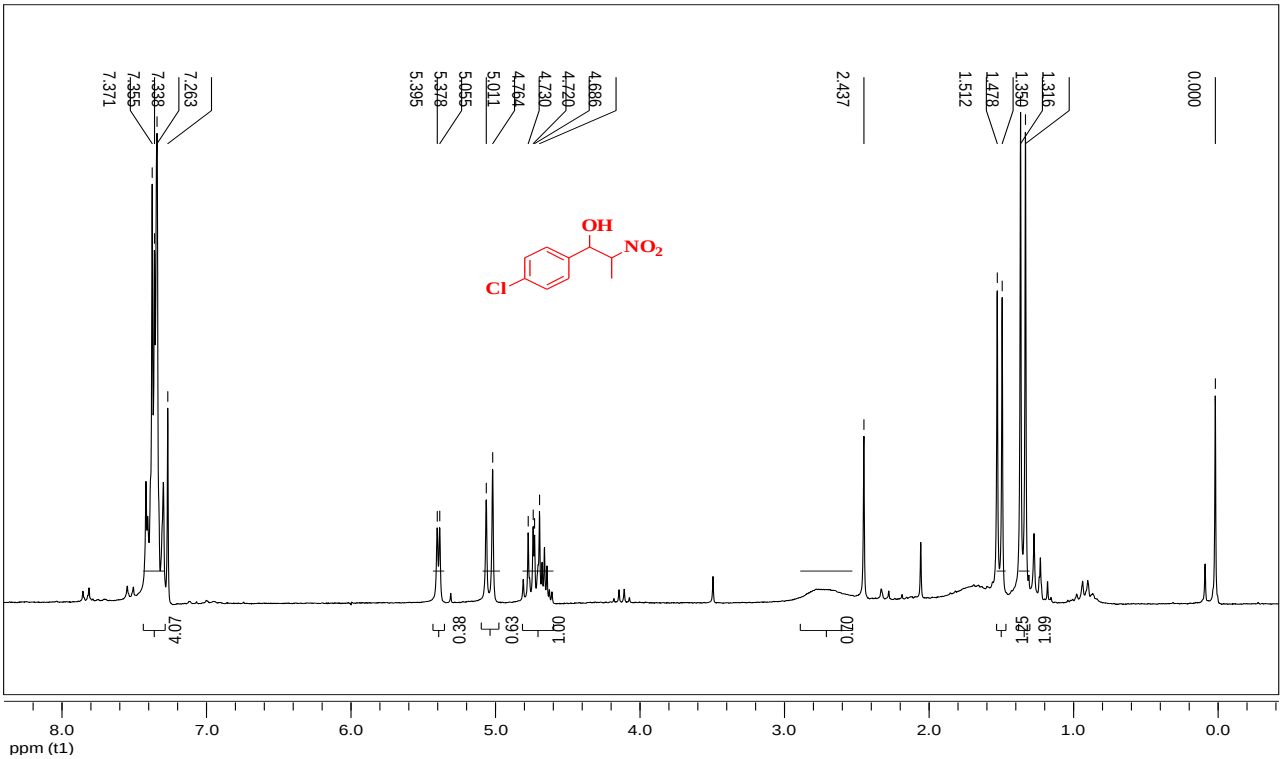
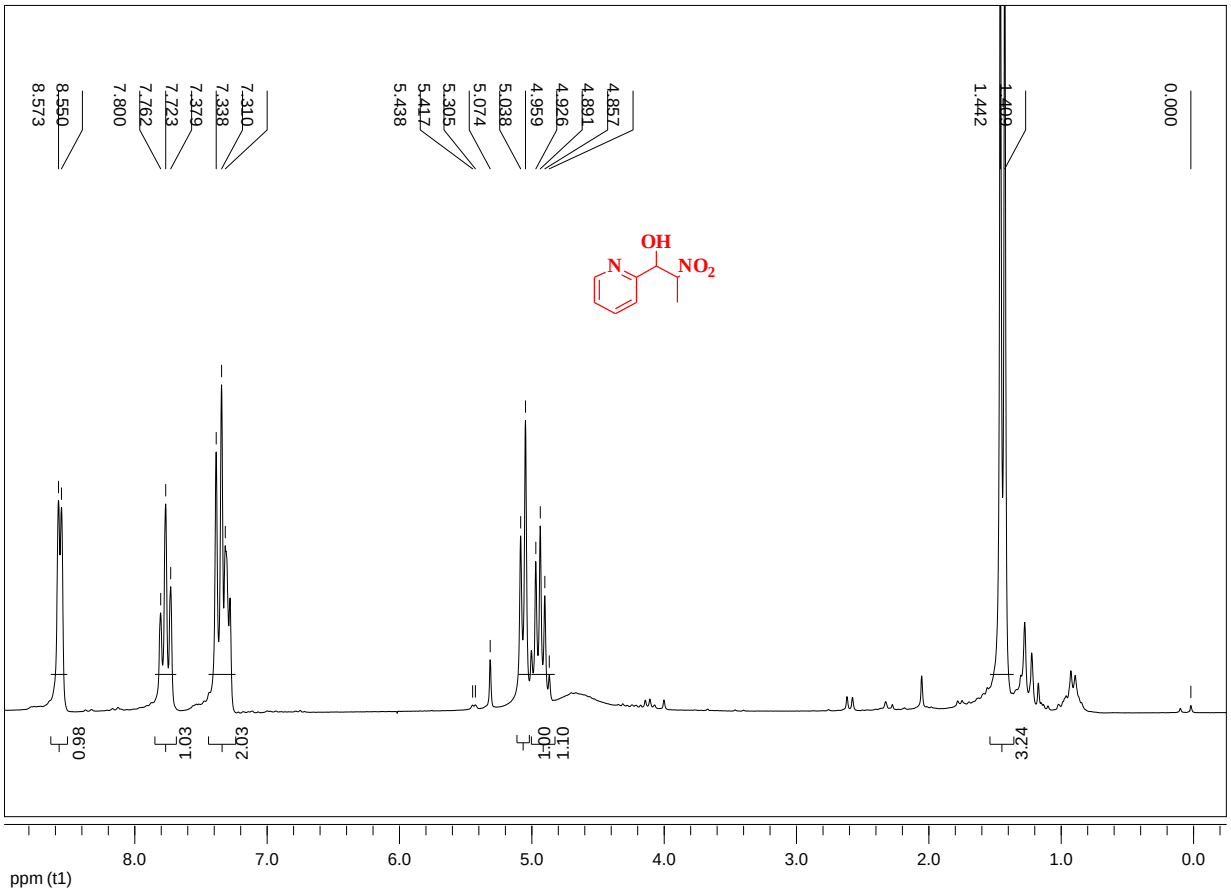


Table. 4(Entry-5).



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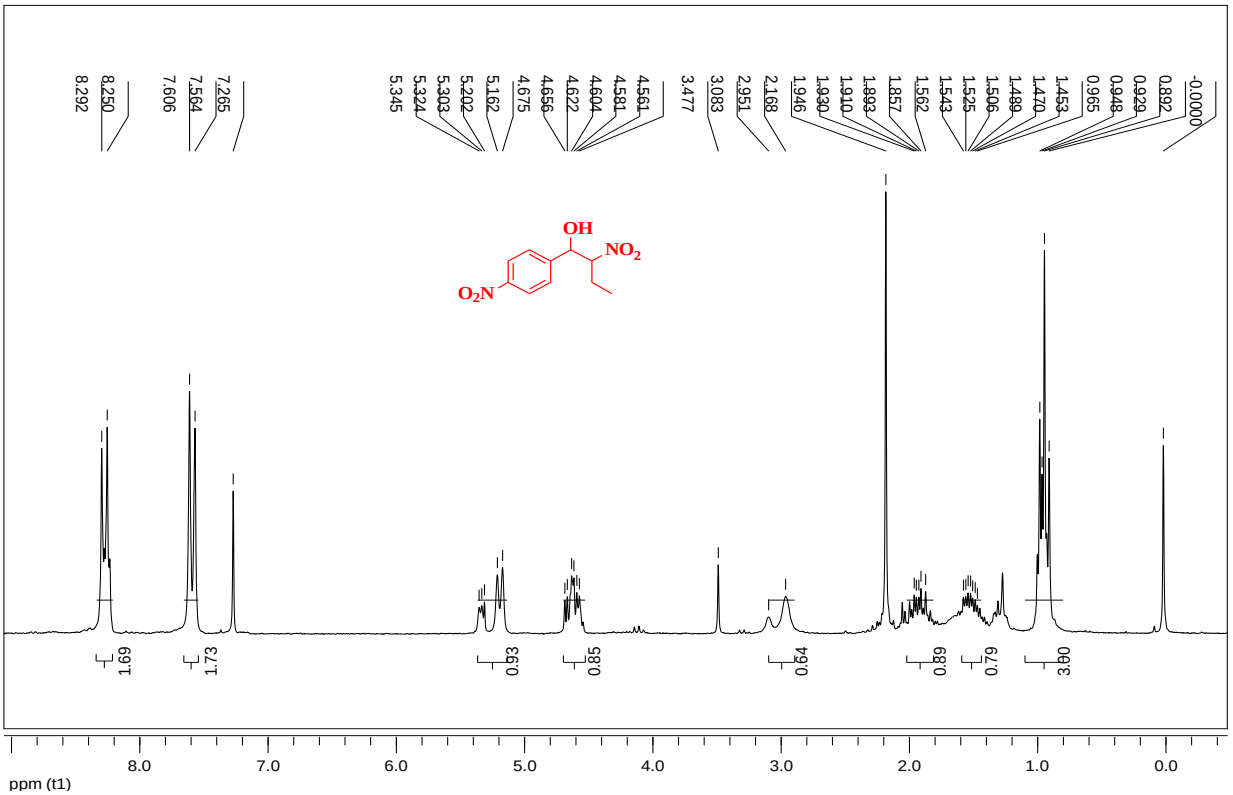

Table. 4(Entry-7).

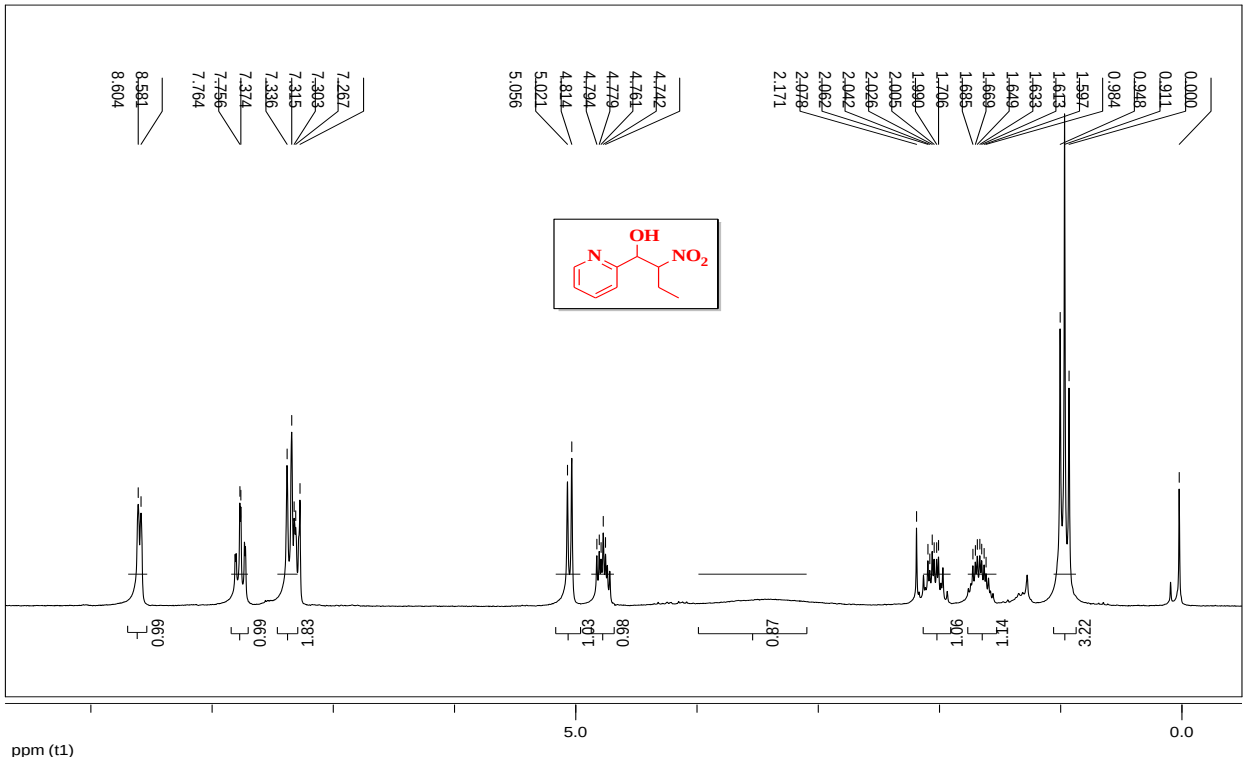

Figure. 3(Entry-2).

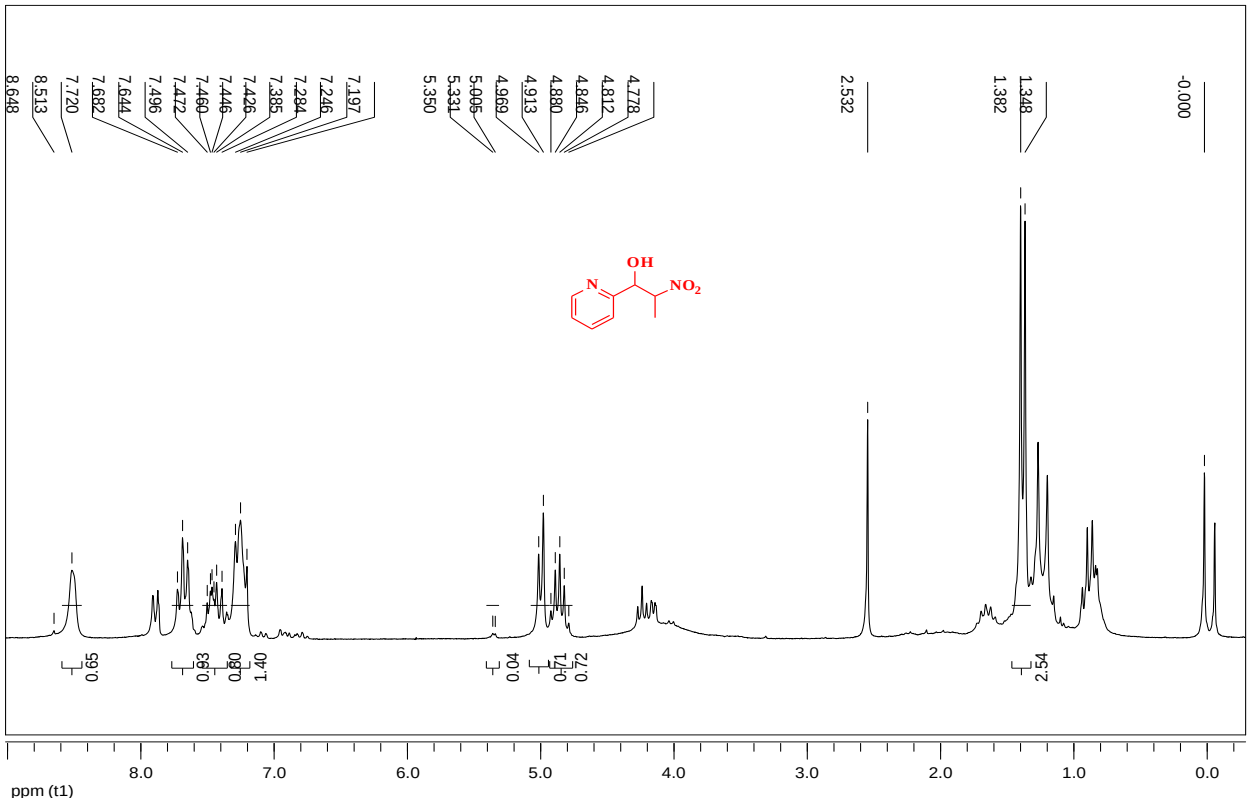

Figure. 3(Entry-3).