Electronic Supplementary Material (ESI) for RSC Advances.


# Combustion synthesized $La_2O_3$ and $La(OH)_3$:Recyclable catalytic activity towards Knoevenagel and Hantzsch reactions

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## Supporting Information

Table S1: Knoevenagel – condensation reaction

| Entry | Reaction with $La_2O_3$ | | Reaction with $La(OH)_3$ | |
|---|---|---|---|---|
| | **Time** | **Yield (%)** | **Time** | **Yield (%)** |
| 1a | 120 | 81 | 125 | 81 |
| 1b | 190 | 76 | 220 | 79 |
| 1c | 140 | 79 | 160 | 80 |
| 1d | 110 | 89 | 130 | 82 |
| 1e | 110 | 80 | 160 | 78 |
| 1f | 150 | 82 | 160 | **75** |
| 1g | 160 | 78 | 170 | 80 |
| 1h | 140 | 80 | 180 | 82 |
| 1i | 160 | 76 | 190 | 81 |

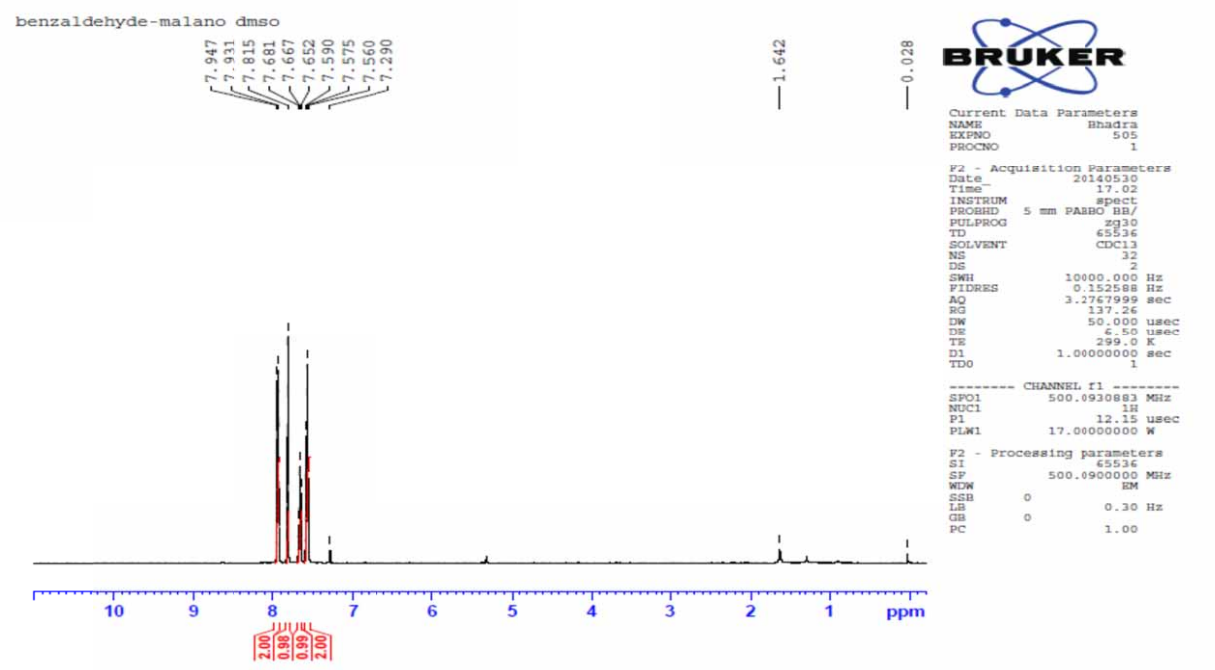
Table S2:Hantzsch Reaction

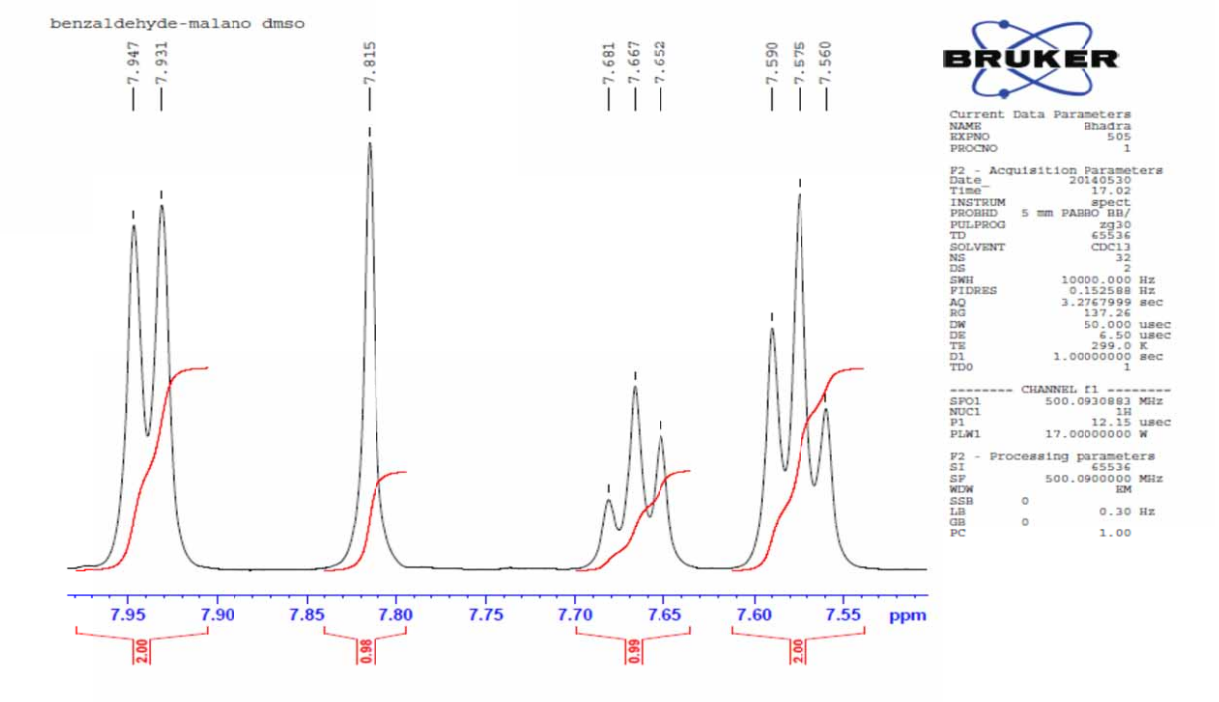
| Entry | Reaction with $La_2O_3$ | | Reaction with $La(OH)_3$ | |
|---|---|---|---|---|
| | **Time** | **Yield (%)** | **Time** | **Yield (%)** |
| 2a | 120 | 81 | 130 | 84 |
| 2b | 140 | 76 | 160 | 79 |
| 2c | 110 | 79 | 130 | 80 |
| 2d | 150 | 89 | 160 | 82 |
| 2e | 160 | 80 | 180 | 83 |
| 2f | 160 | 82 | 190 | 85 |

Table S3: Effect of catalyst loading on the reactivity of substrates in Knoevenagel (1a-Table 1) and Hantzsch (2d, Table-2) reactions in DMSO.

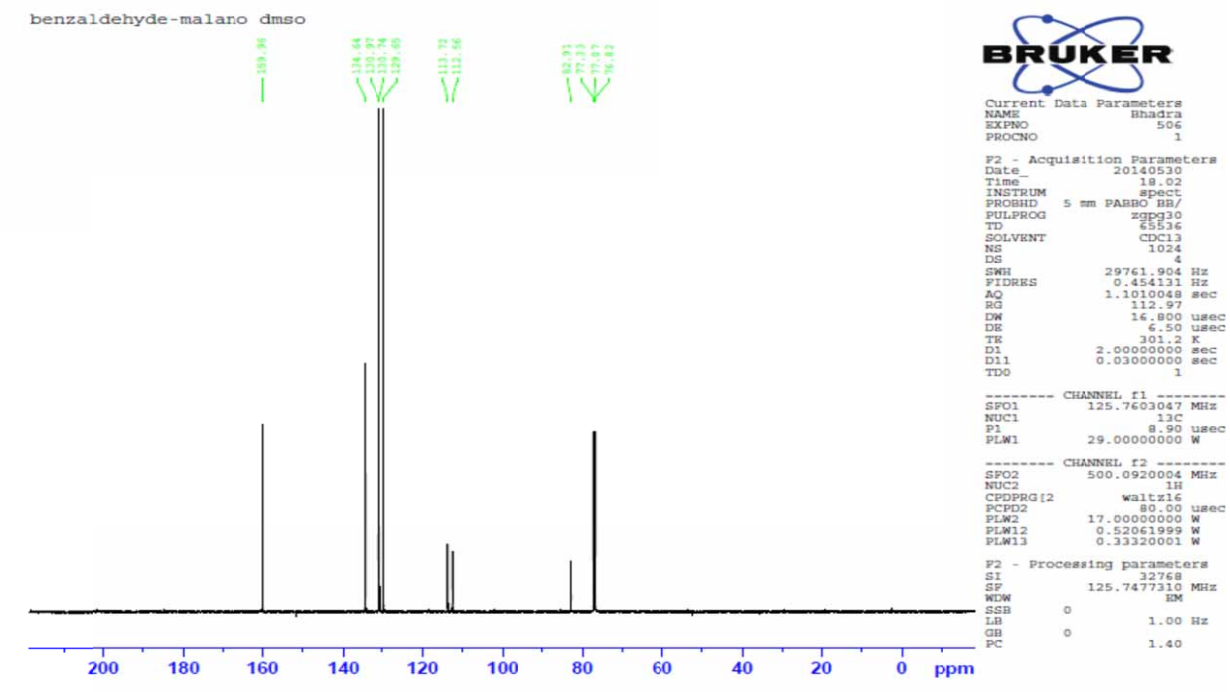
| | Knoevenagel | | Hantzsch | |
|---|---|---|---|---|
| **Loading (equiv)** | **Time (min)** | **Yield (%)** | **Time (min)** | **Yield (%)** |
| 1 | 30 | 85 | 50 | 79 |
| 0.6 | 80 | 85 | 90 | 81 |
| 0.3 | 120 | 81 | 150 | 82 |
| 0.1 | 160 | 83 | 170 | 81 |
| 0.05 | 360 | 81 | 390 | 80 |

$^{1}$H NMR Spectrum of 2-benzylidenemalononitrile(1a)

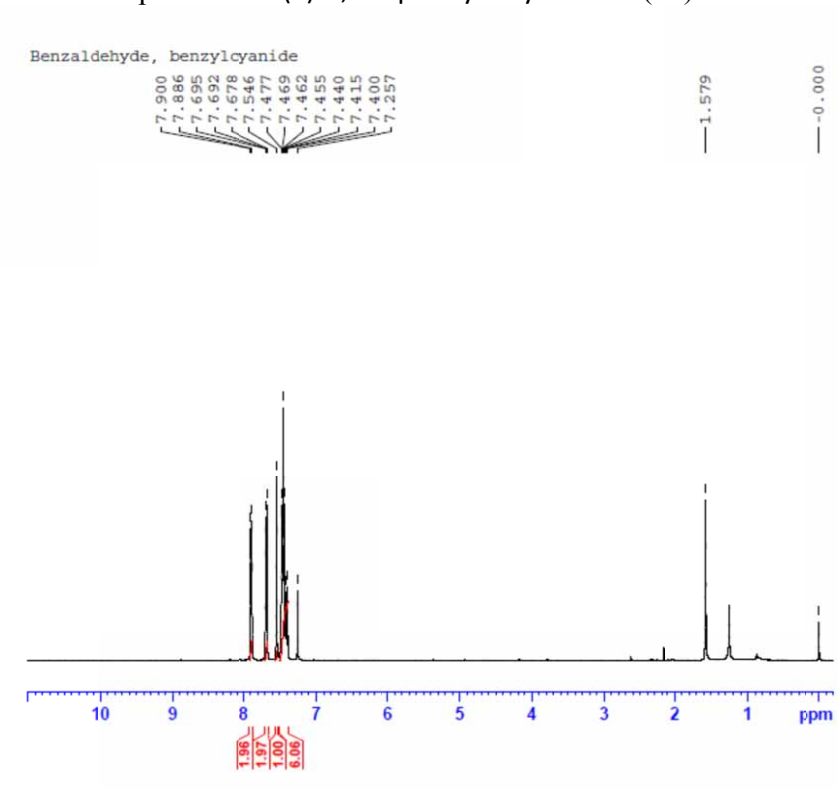


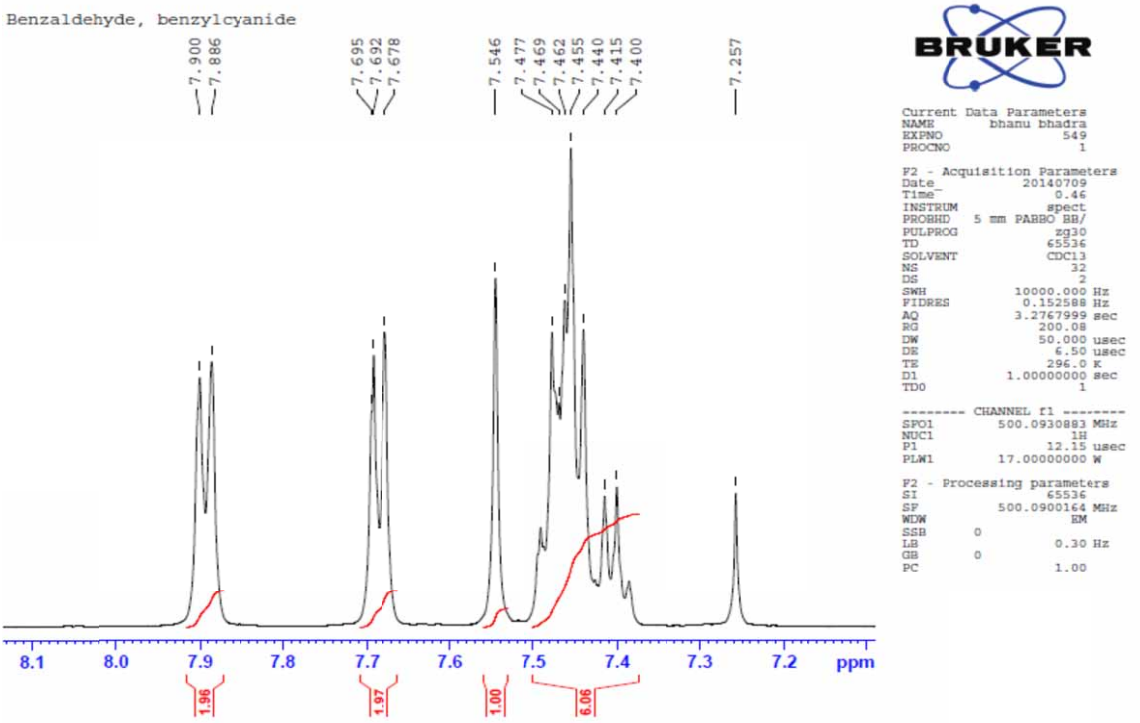



$^{13}$C NMR Spectrum of 2-benzylidenemalononitrile

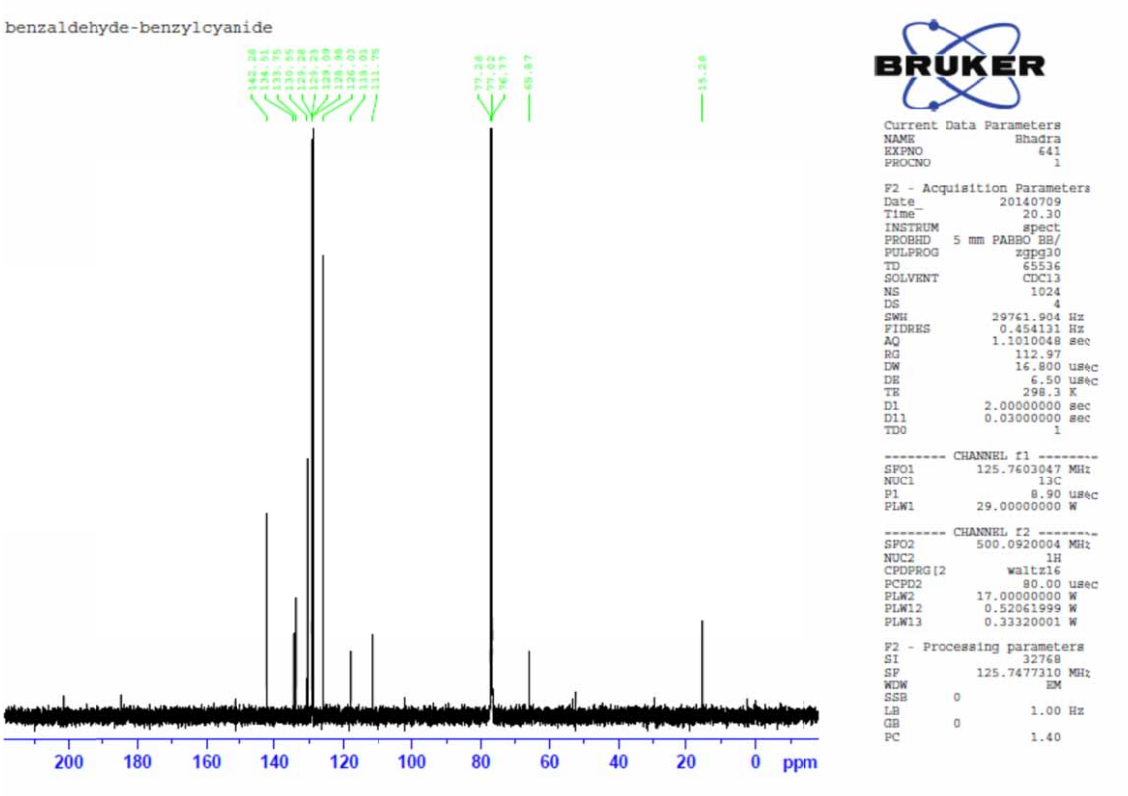


$^{1}$H NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1b)

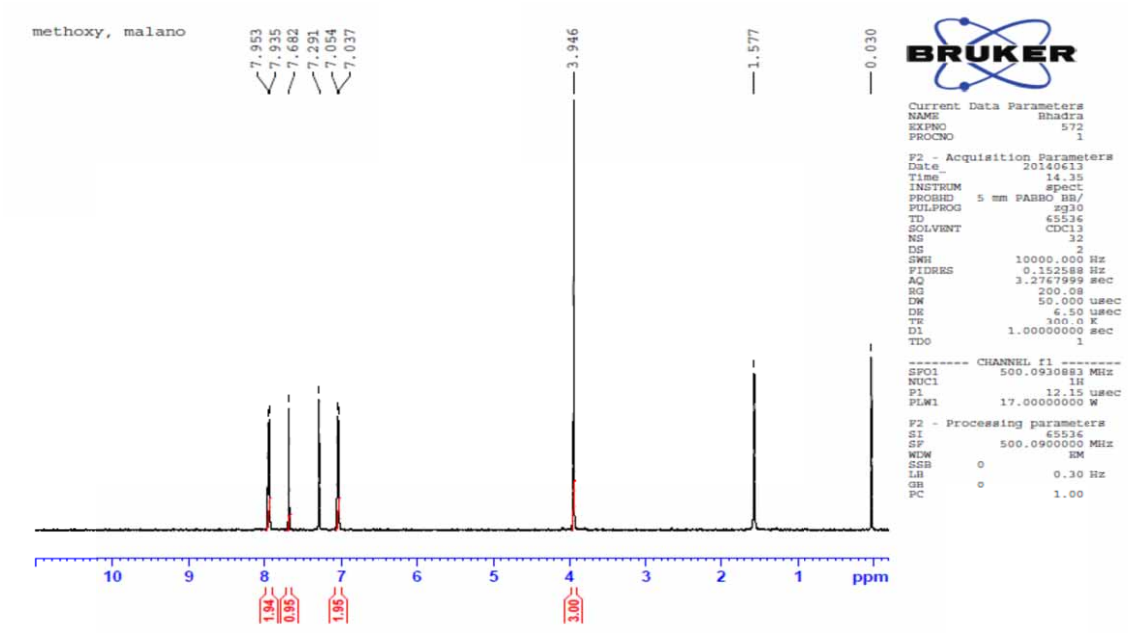


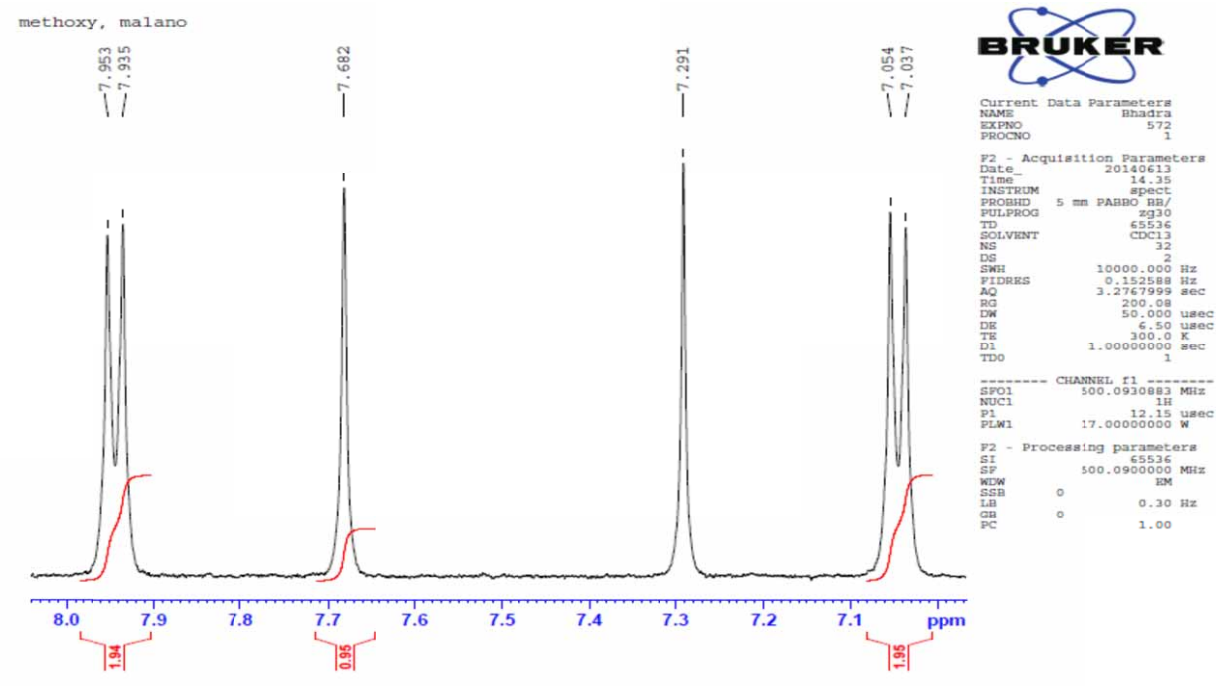



$^{13}$C NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1b)

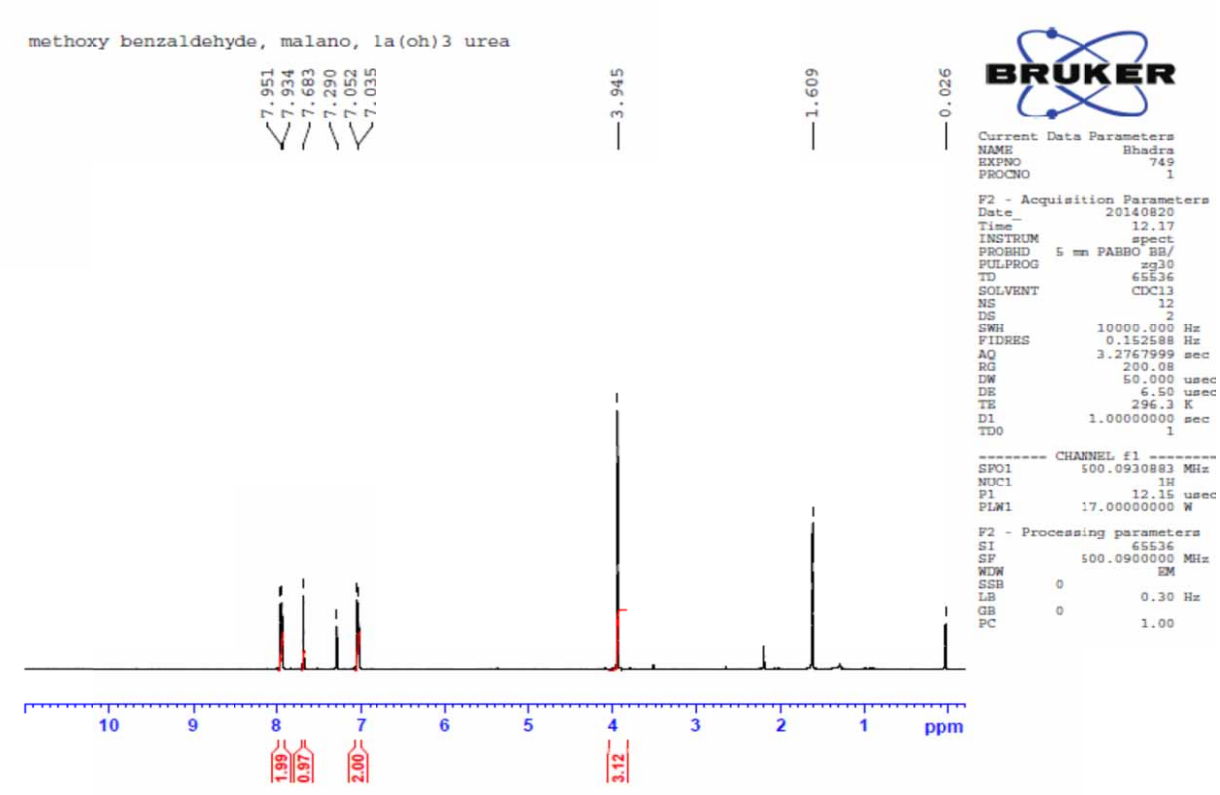


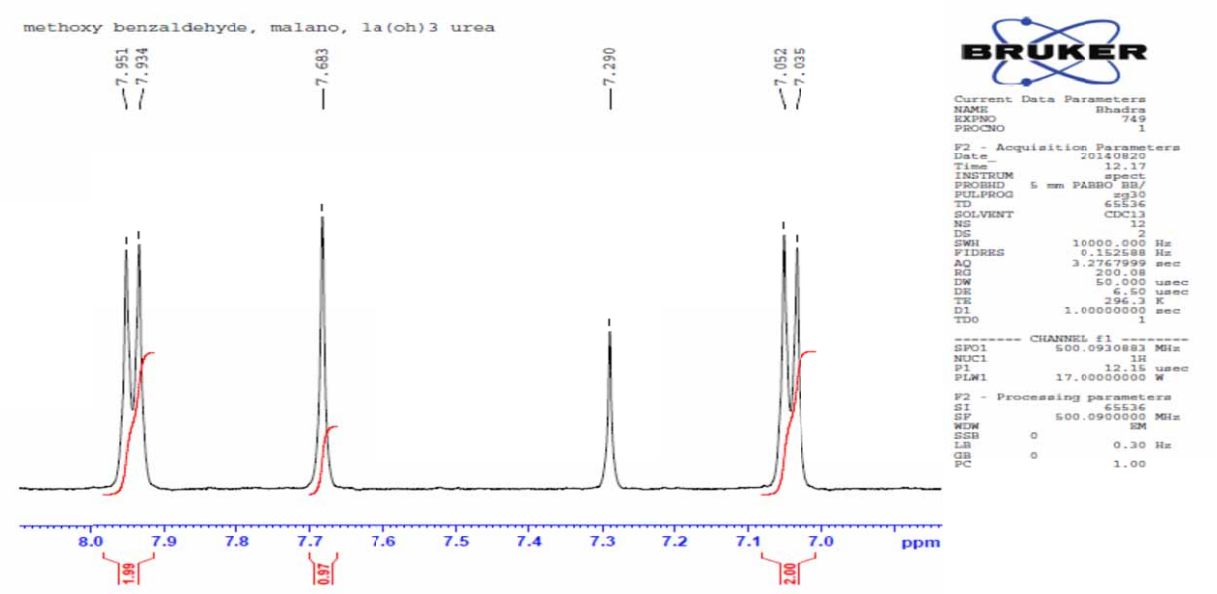

$^{1}$H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile . Reaction was performed with lanthanum oxide prepared by urea as fuel.



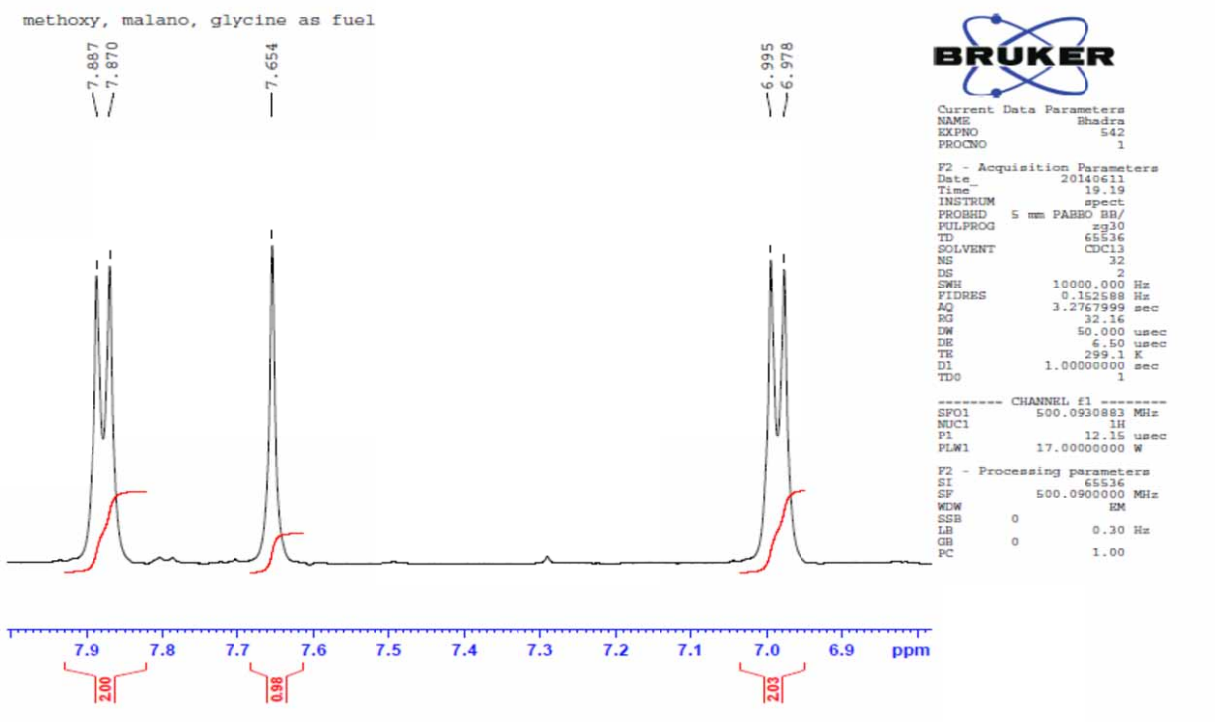



[1]H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile . Reaction was performed with lanthanum hydroxide prepared by urea as fuel.

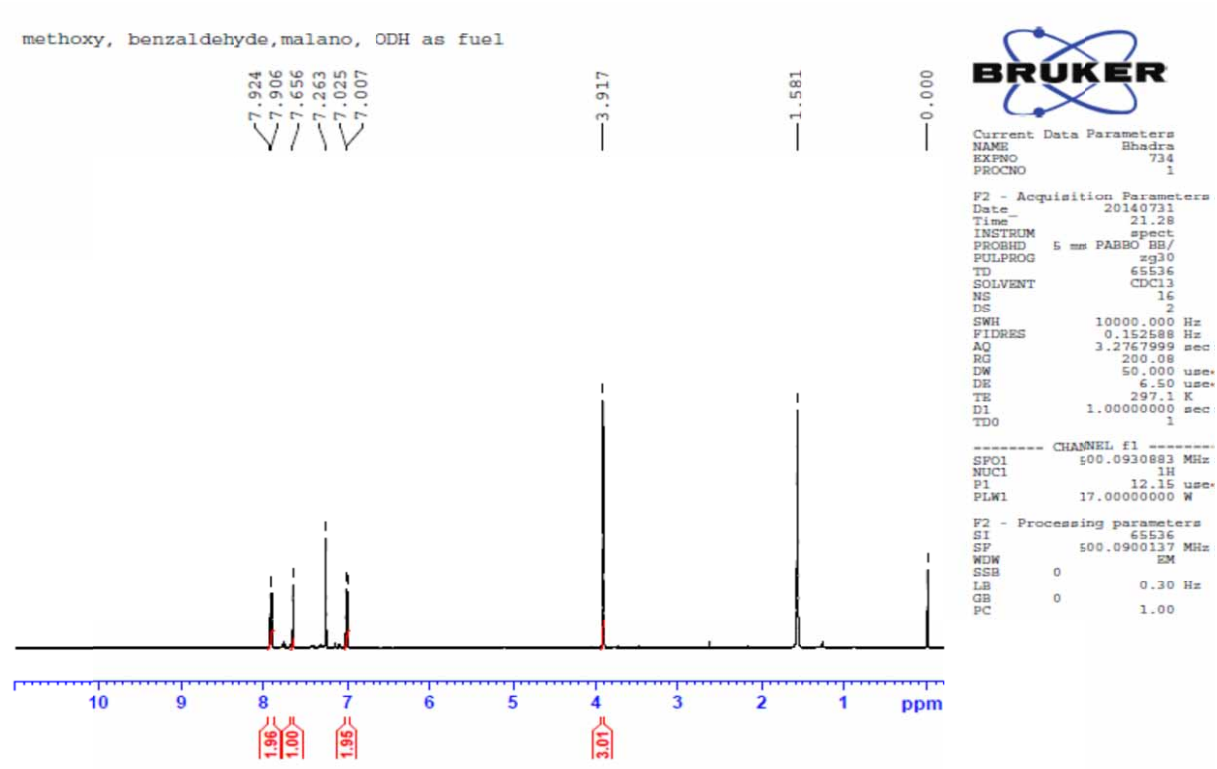


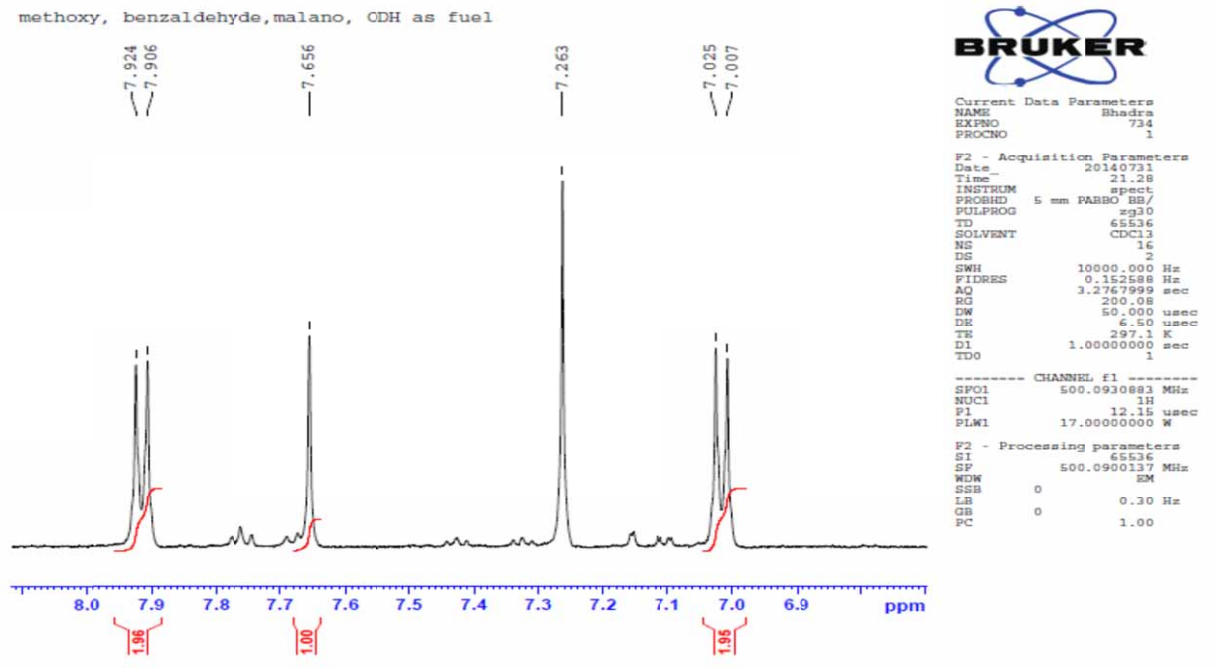



[1]H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile. Reaction was done using glycine as fuel.

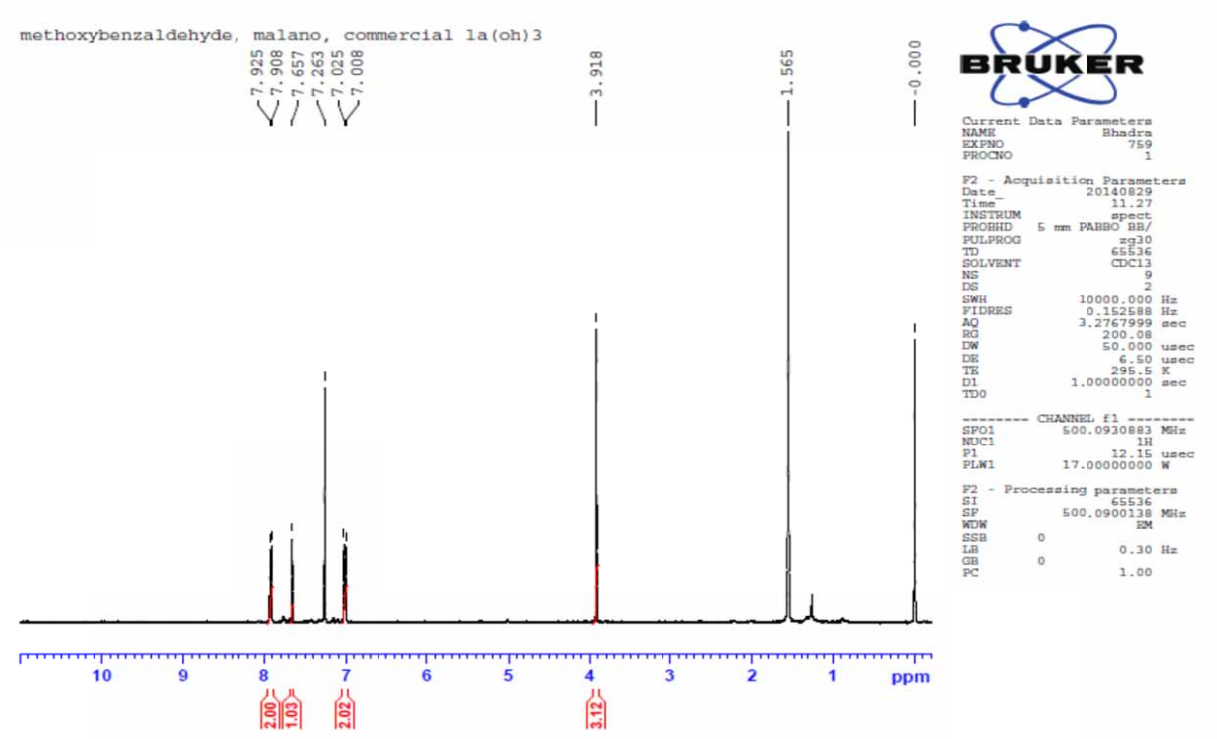


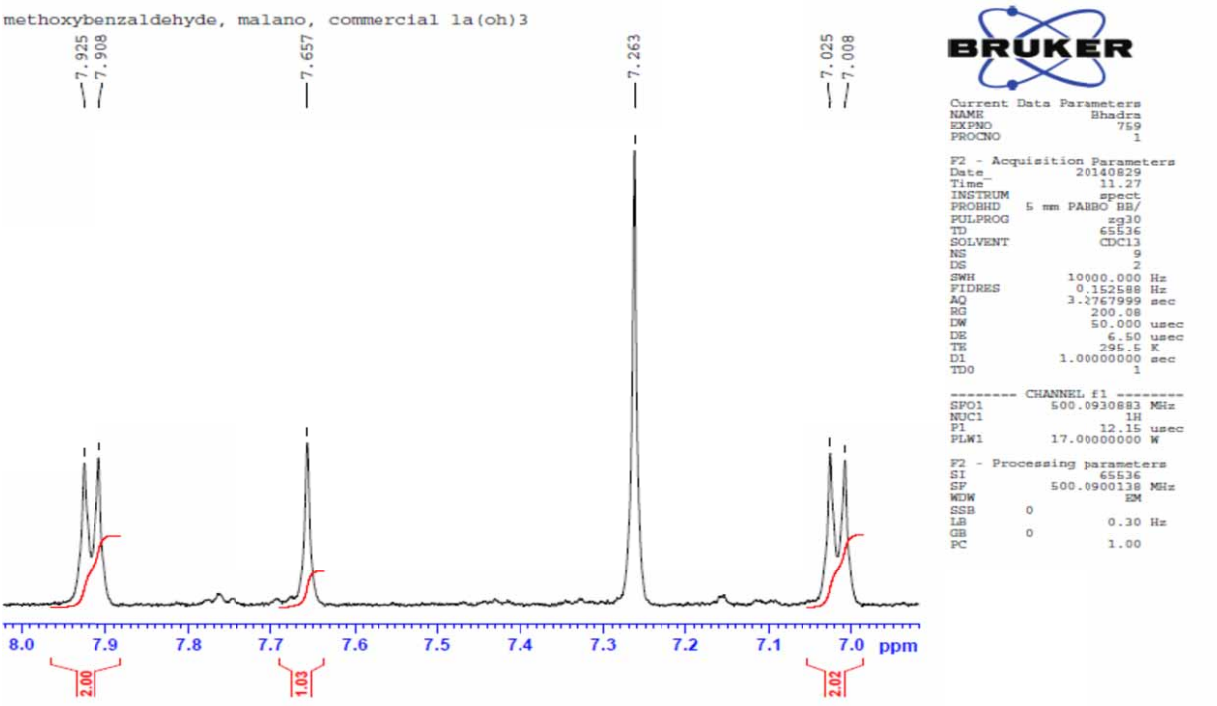
$^{1}$H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile. Reaction was carried out using ODH as fuel



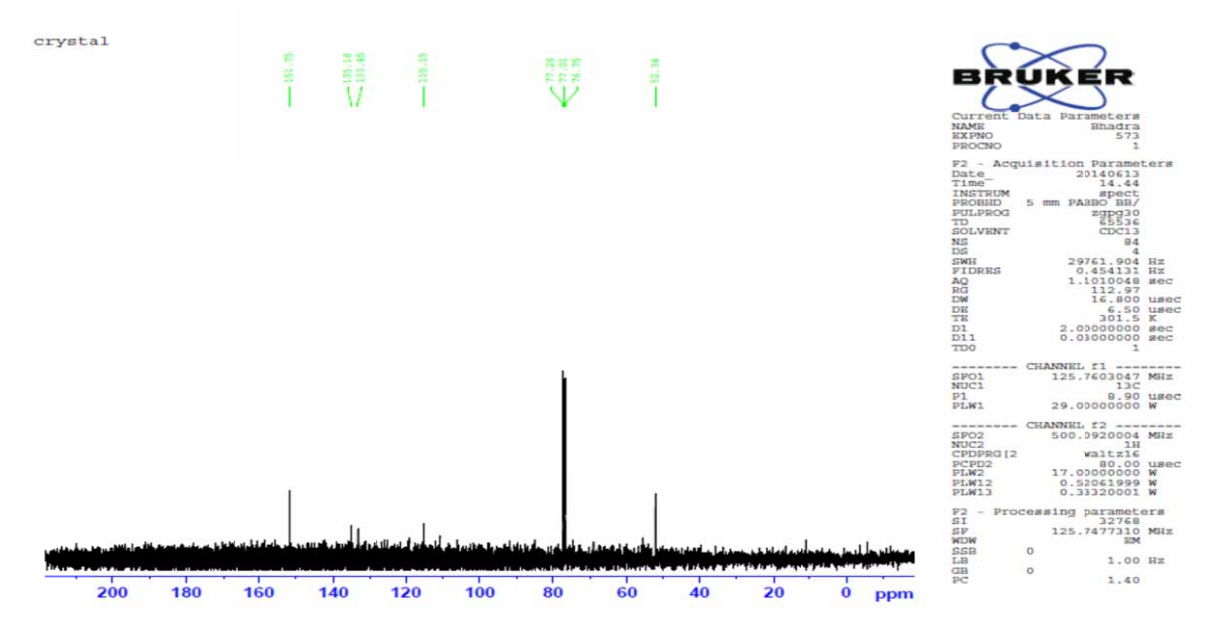



$^{1}$H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile . Reaction was performed by using lanthanum Hyroxide (commercial).

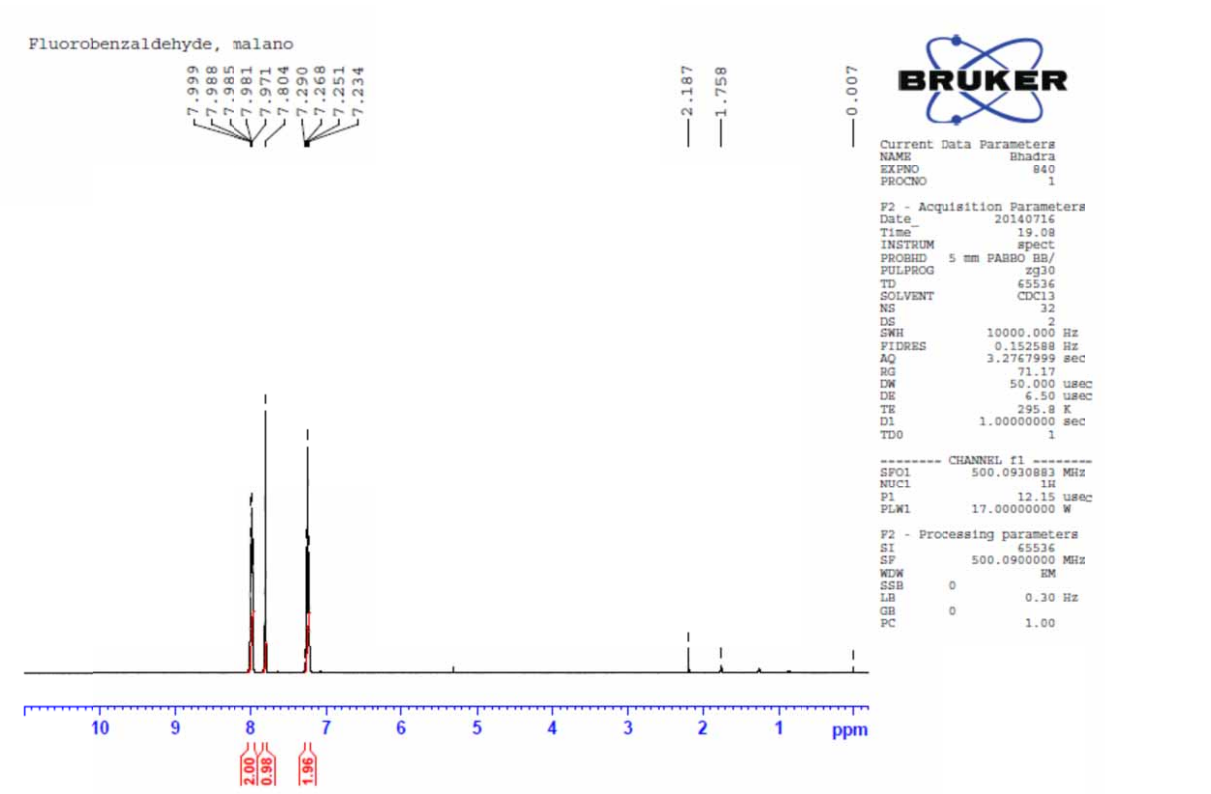


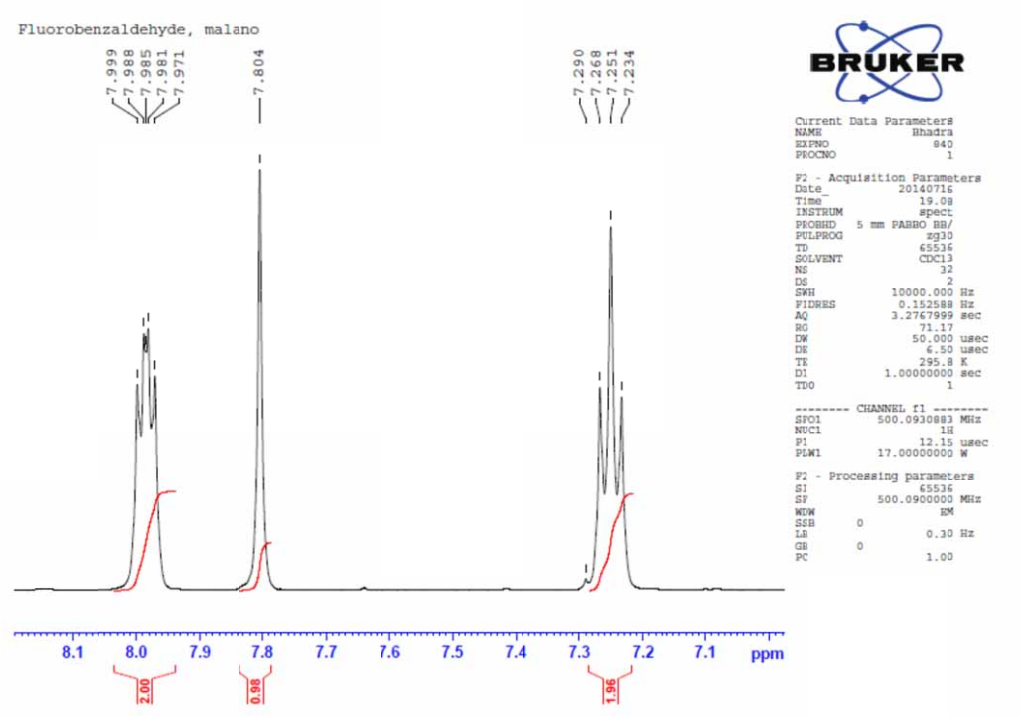



$^{13}$C NMR Spectrum of 2-(4-methoxybenzylidene)malononitrile

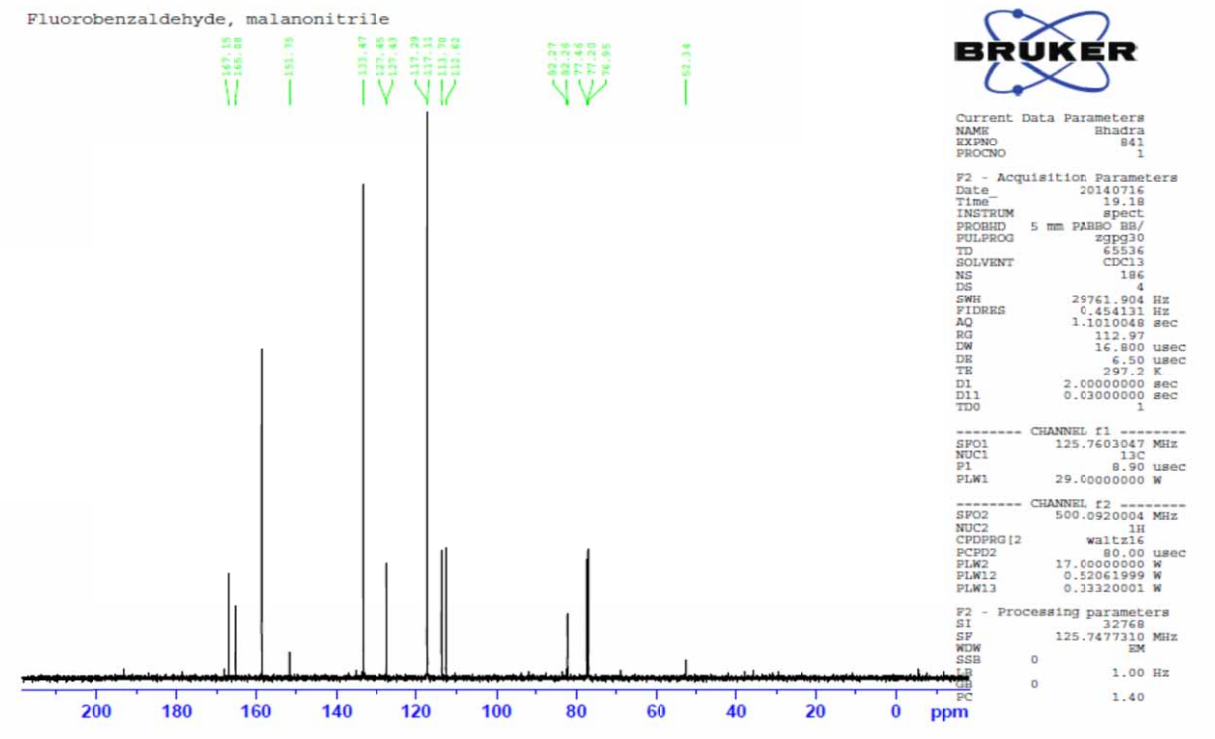



$^{1}$H NMR Spectrum of2-(4-Fluorophenylmethylidene) malononitrile(1d)

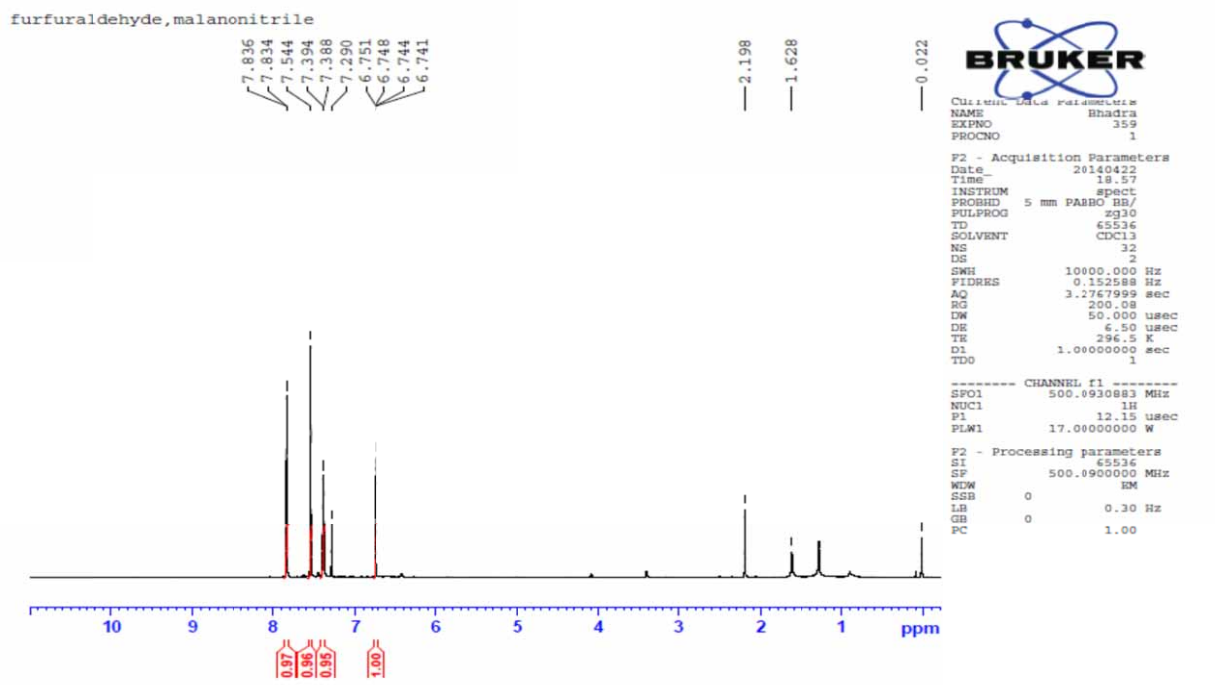


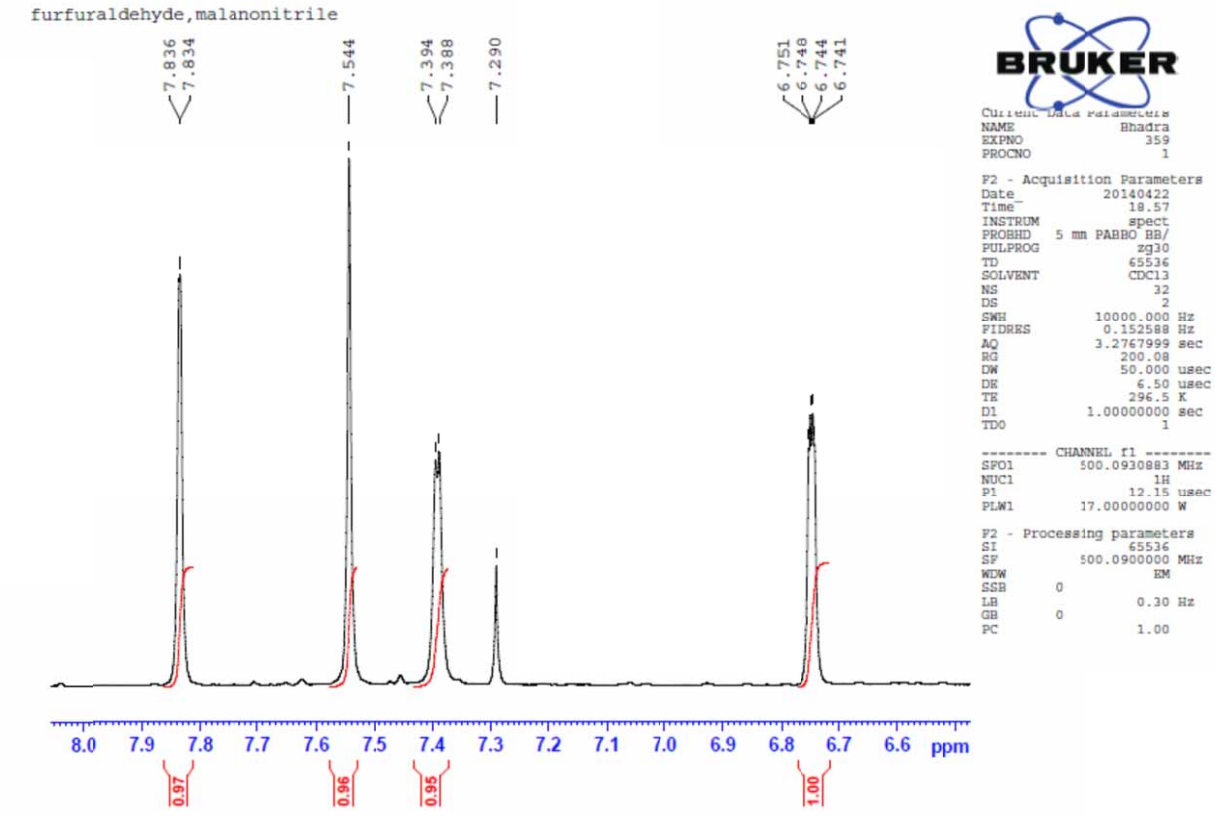



13C Spectra of 2-(4-Fluorophenylmethylidene) malononitrile(1d)

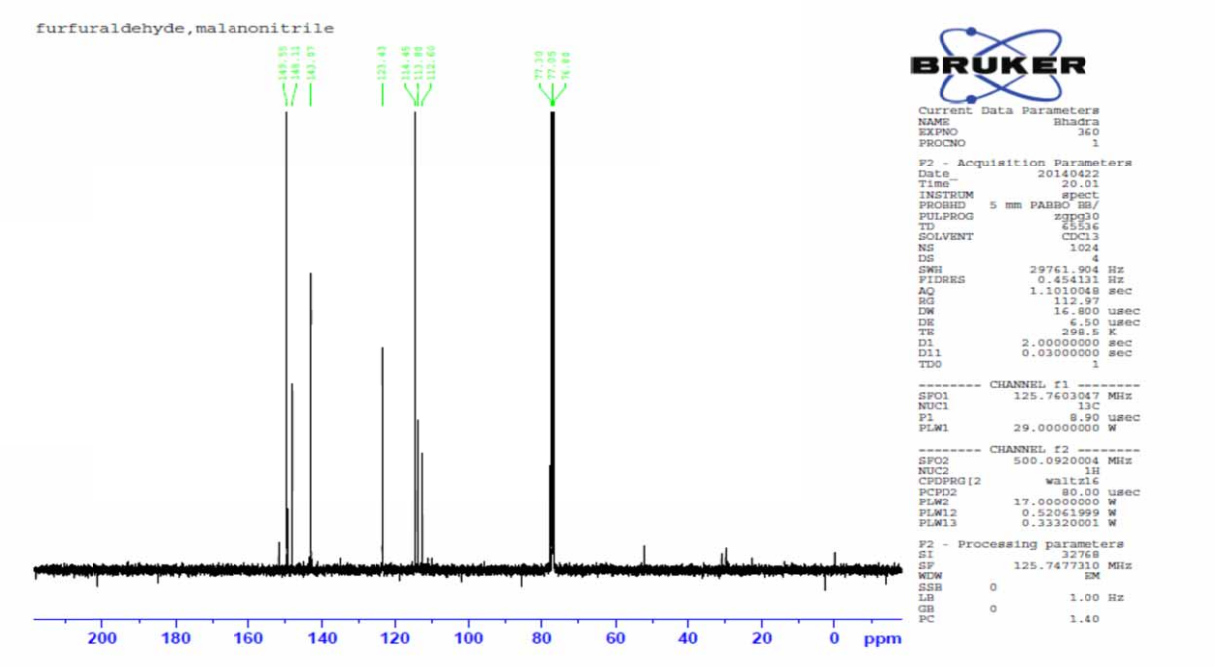


$^{1}$H NMR Spectrum of 2-(furan-2-ylmethylene) malononitrile (1e)

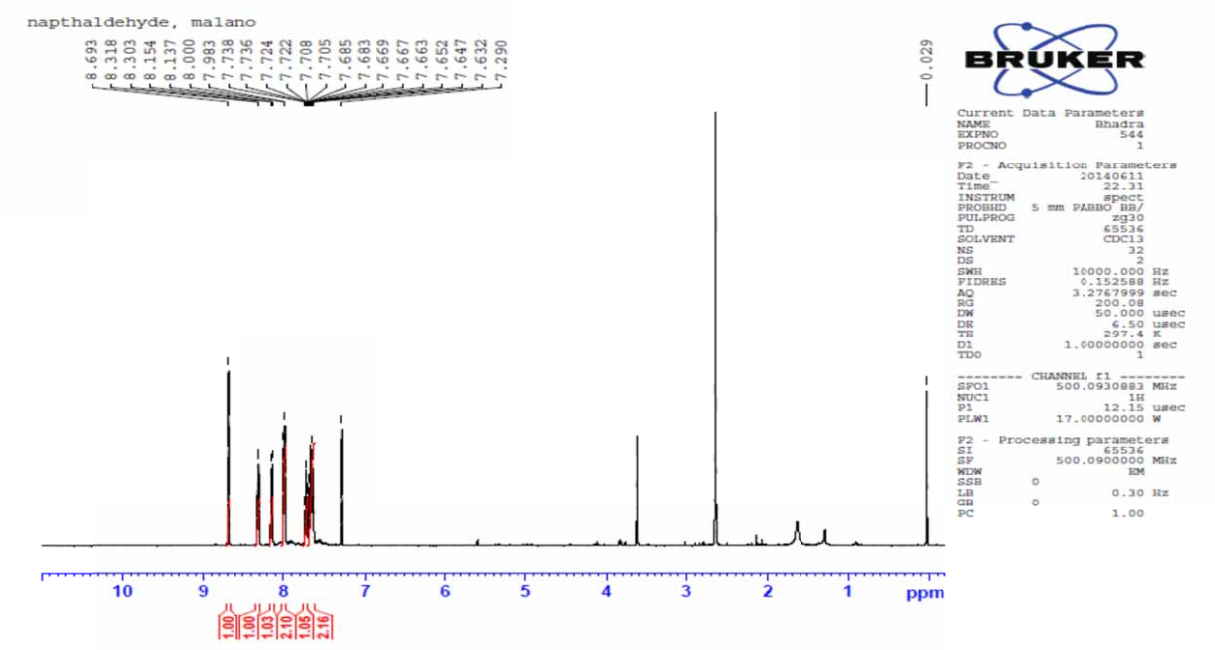


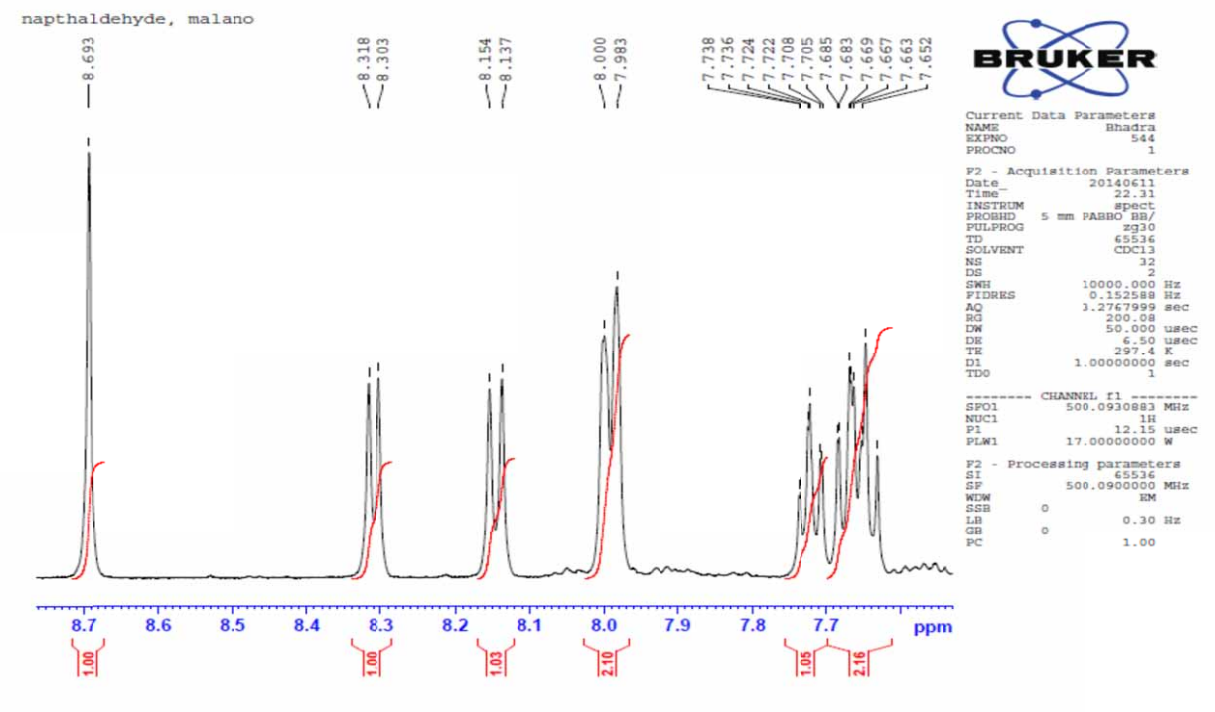



$^{13}$C NMR Spectrum of 2-(furan-2-ylmethylene)malononitrile

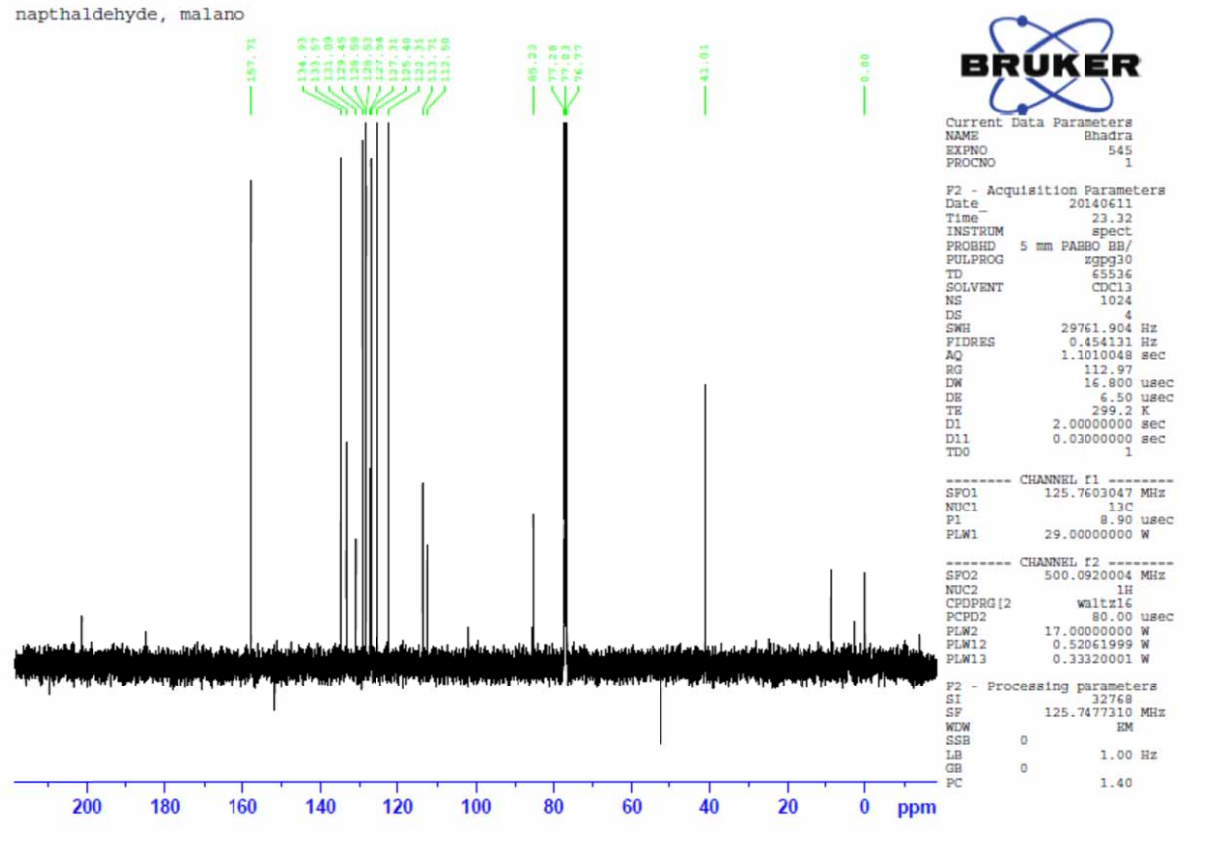



$^{1}$H NMR Spectrum of 2-(naphthalene-1-ylmethylene) malononitrile (1f)

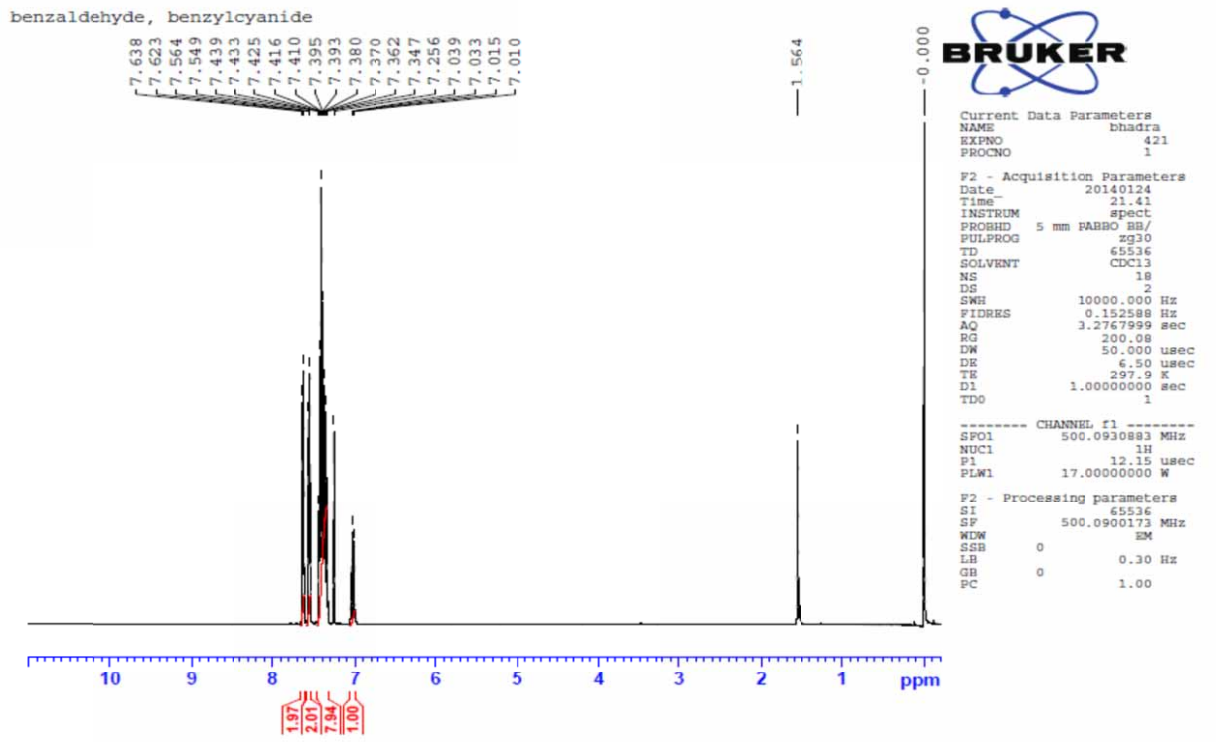


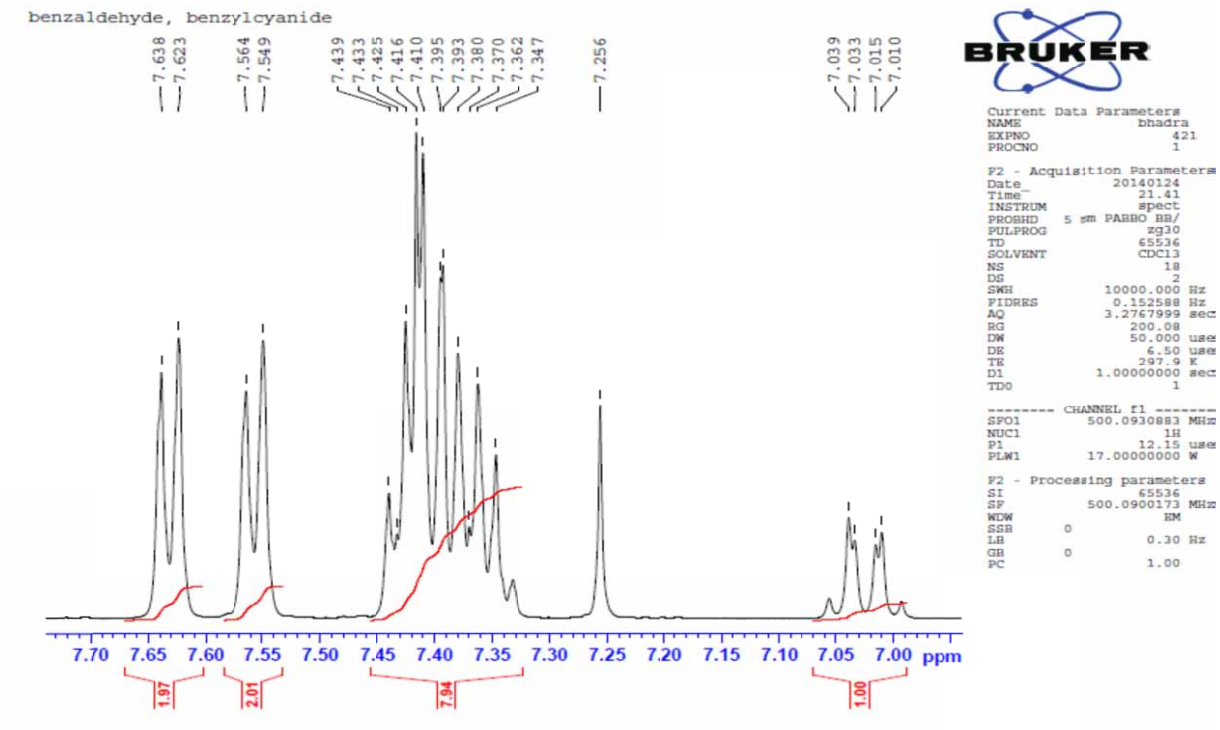



$^{13}$C NMR Spectrum of 2-(naphthalene-1-ylmethylene)malononitrile

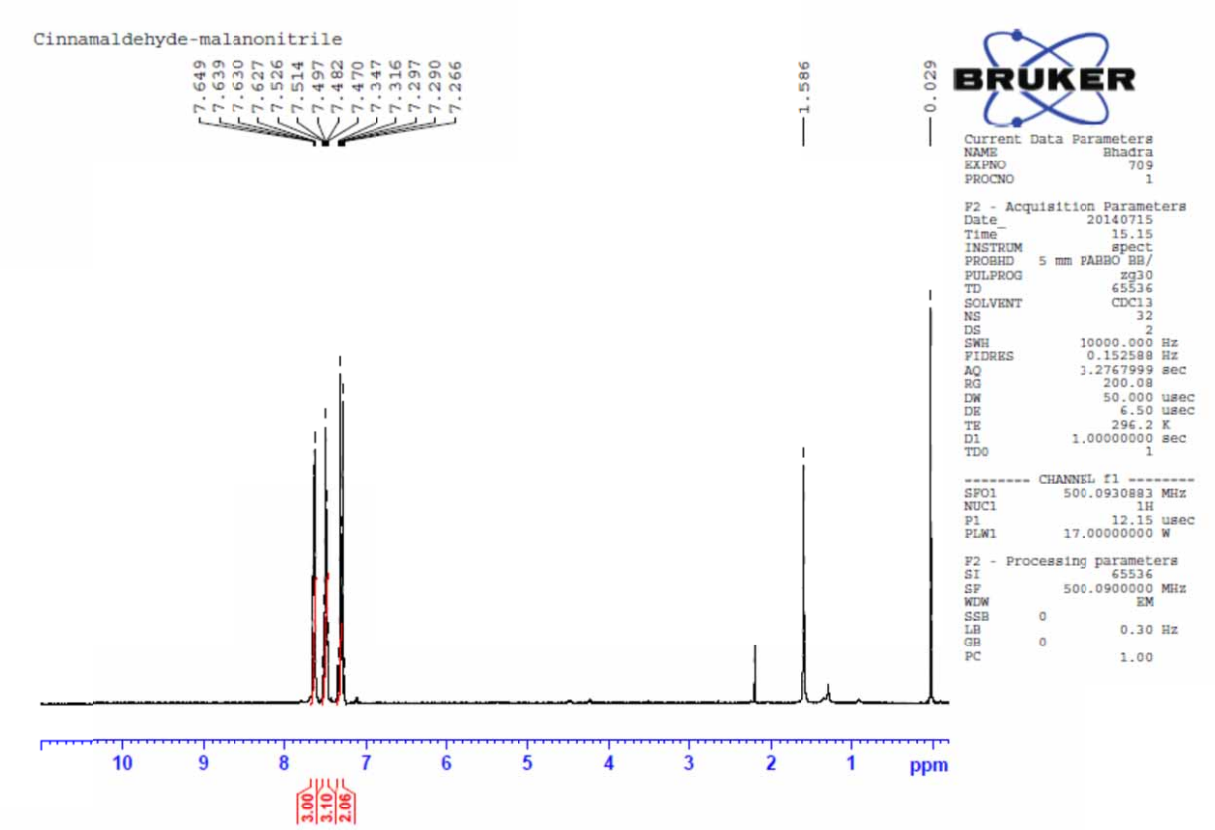


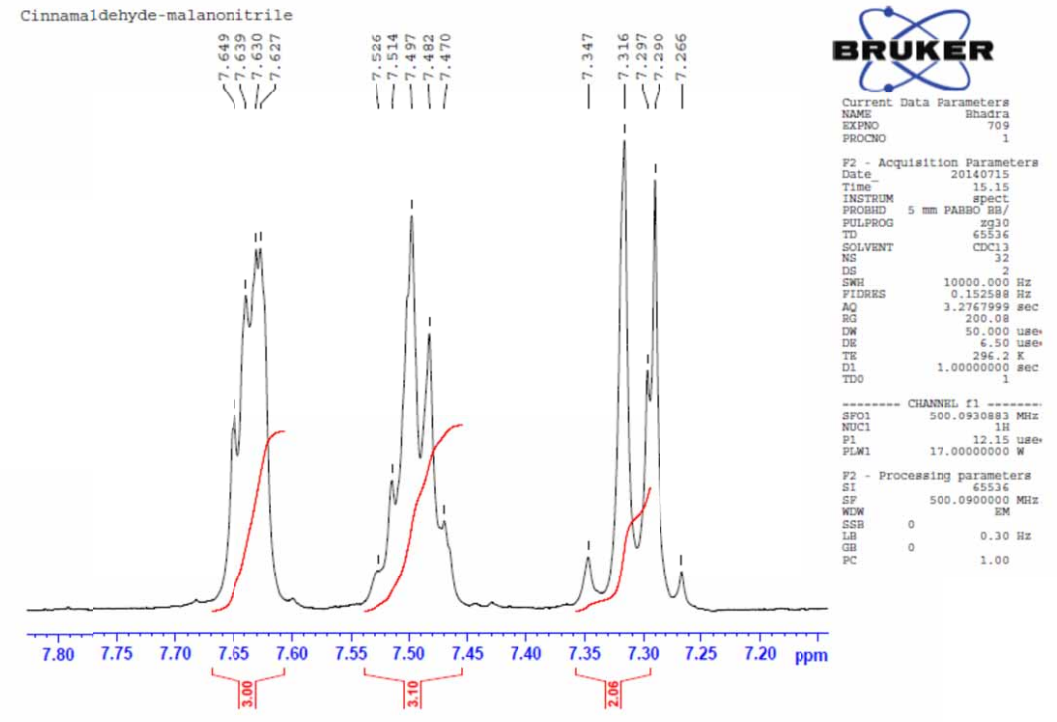
[1]H NMR Spectrum of (2Z,4E)-2,5-diphenylpenta-2,4-dienenitrile(1g)



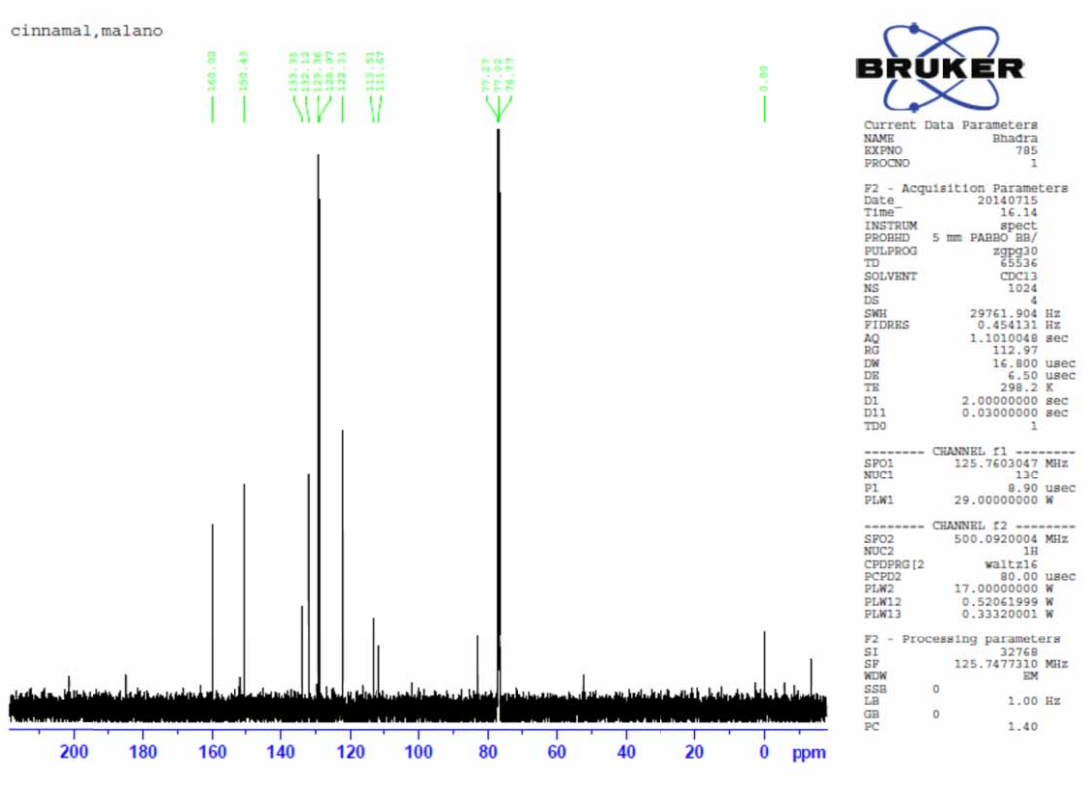



$^{1}$H NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1h)

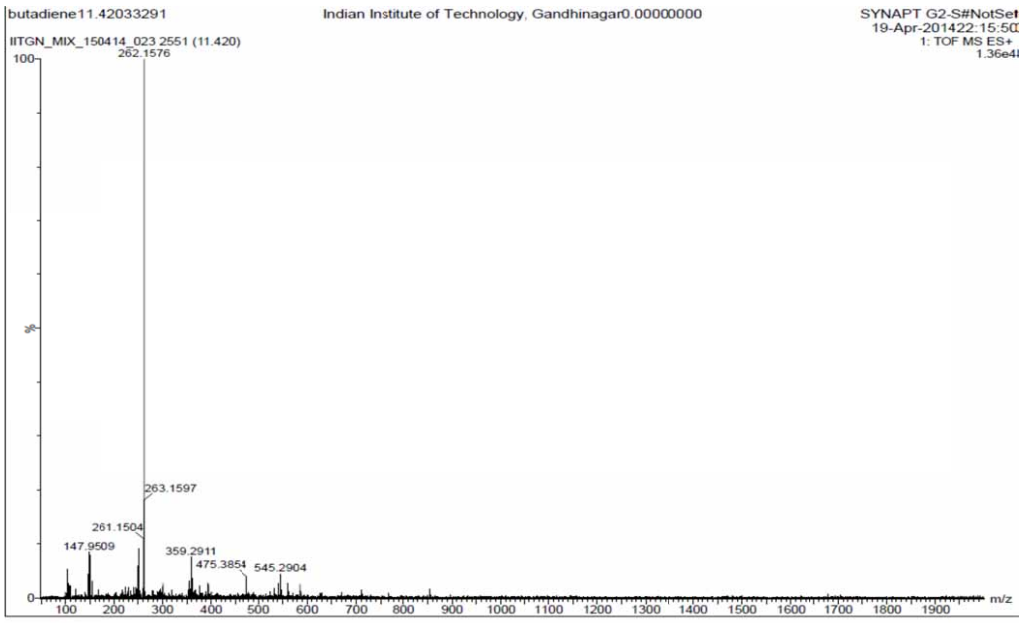


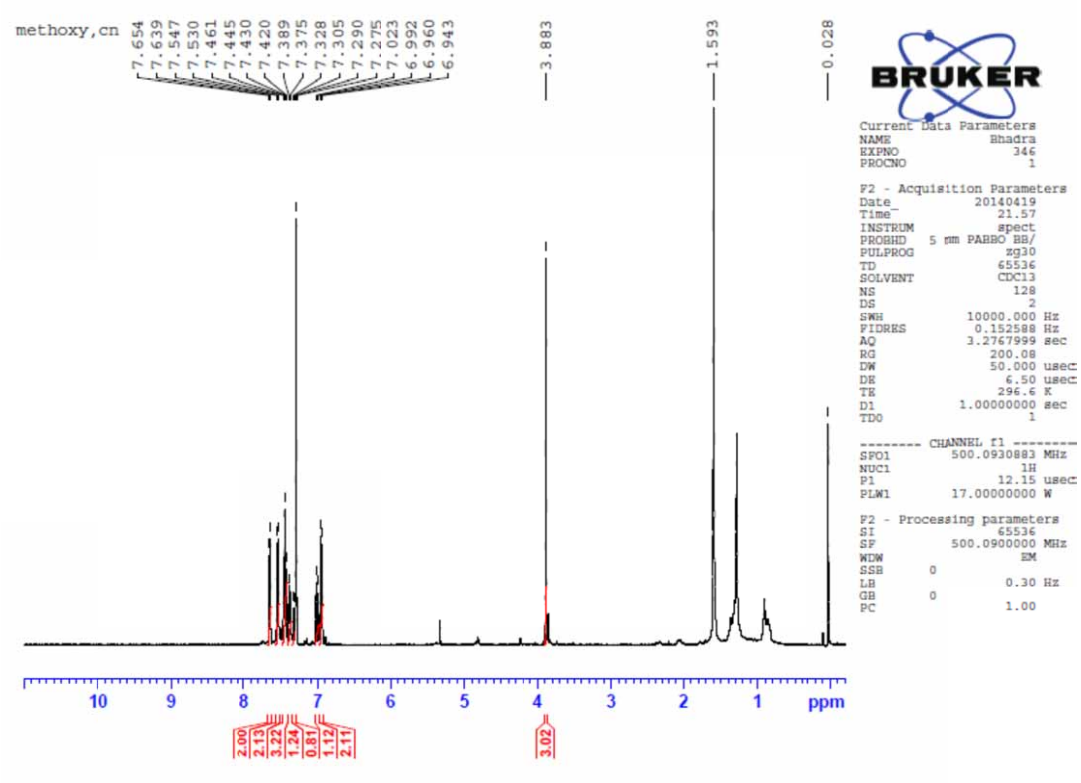
13C Spectra of (Z)-2,3-diphenylacrylonitrile (1h)

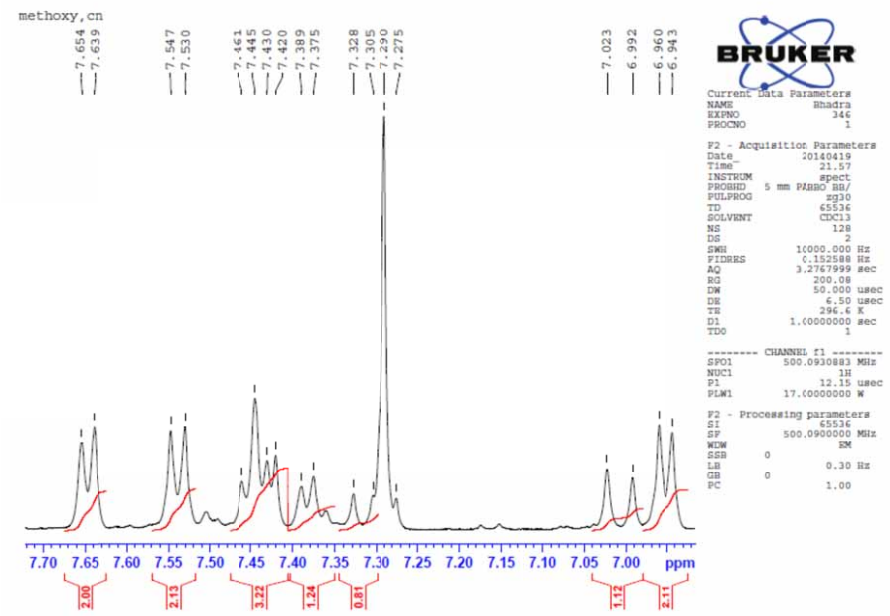



Mass spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienenitrile (1i)
Exact mass: 261.12
Mass obtained in the positive mode: 262.1576
Elemental composition:$C_{18}H_{15}NO$

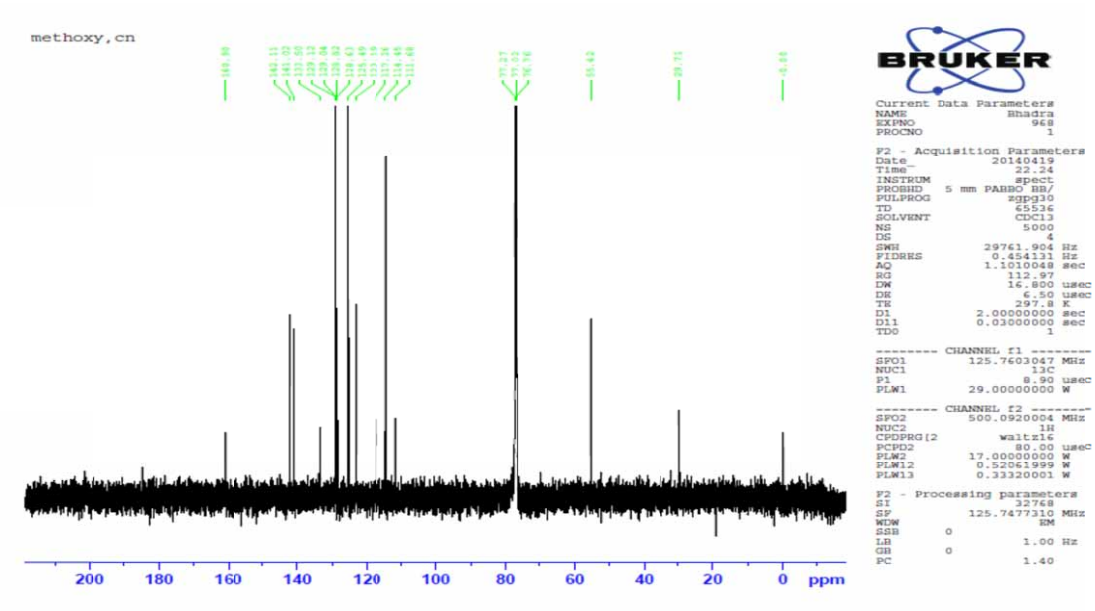


$^{1}$H NMR Spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienenitrile



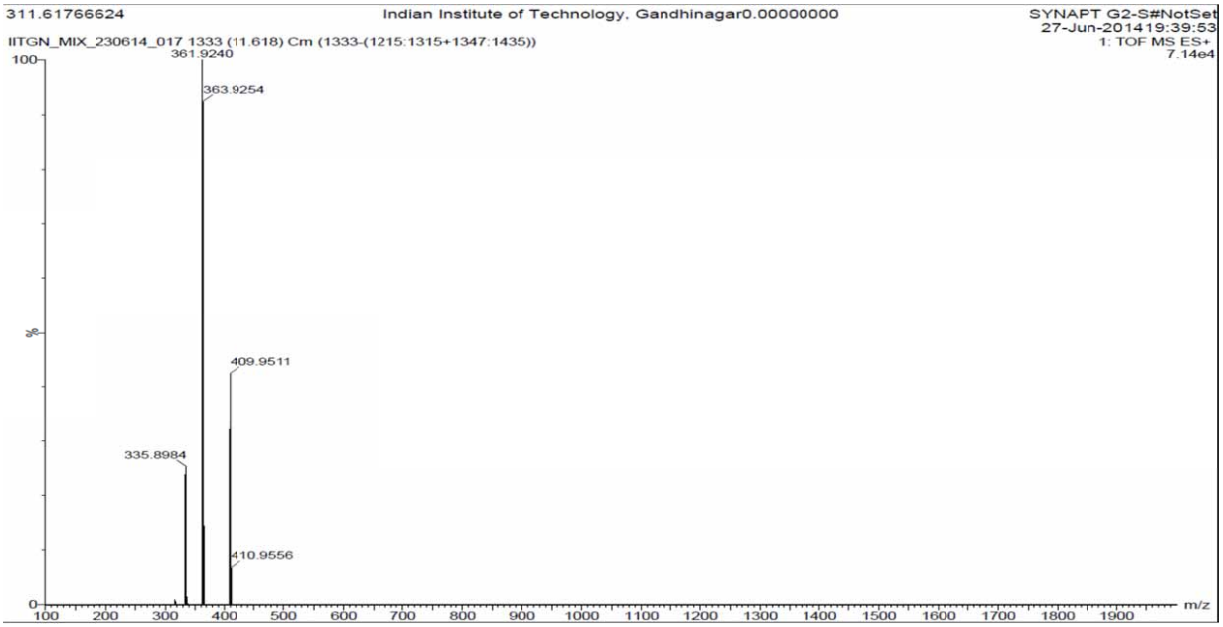



$^{13}$C NMR Spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienenitrile

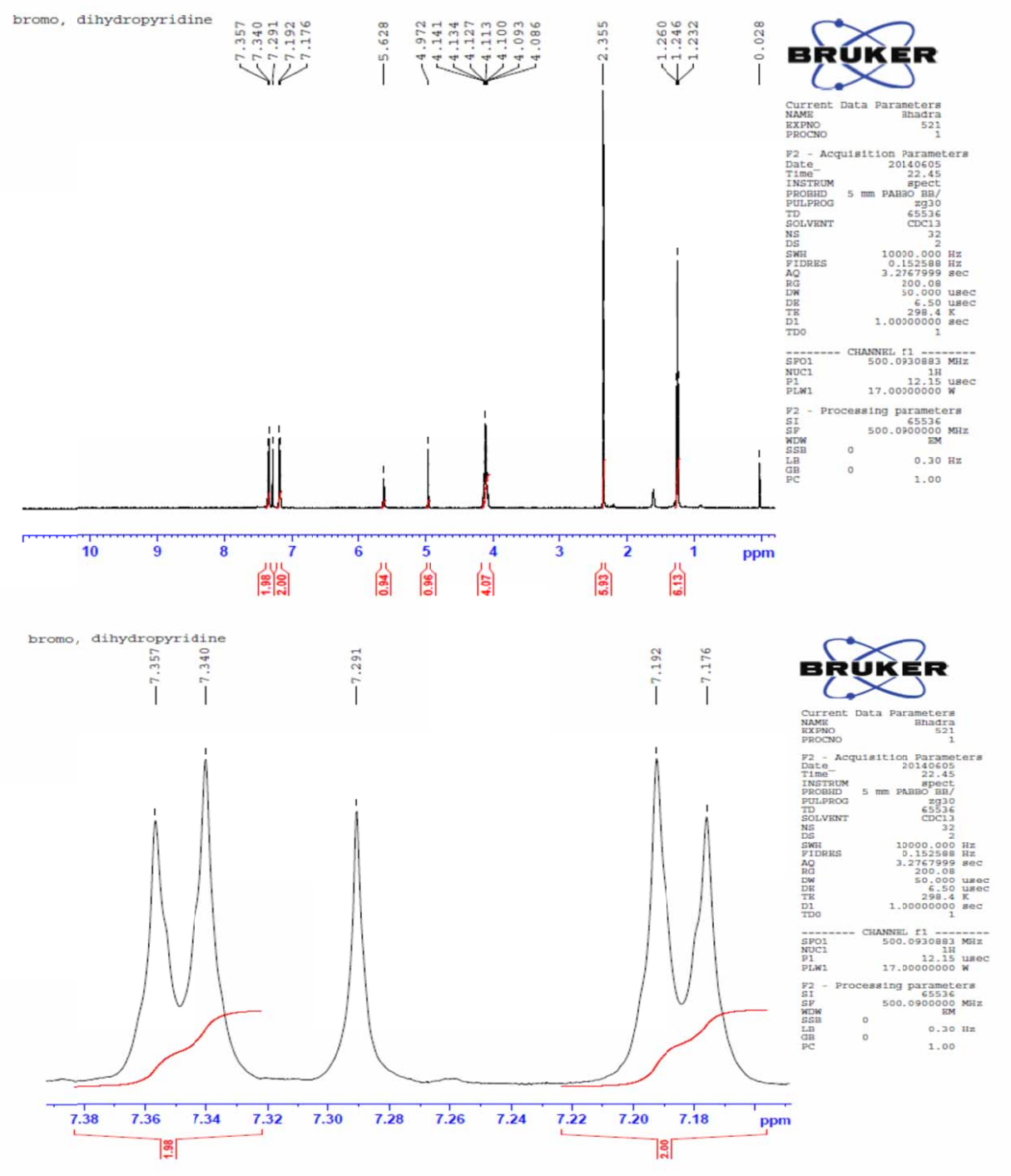



**Hantzsch Reaction**

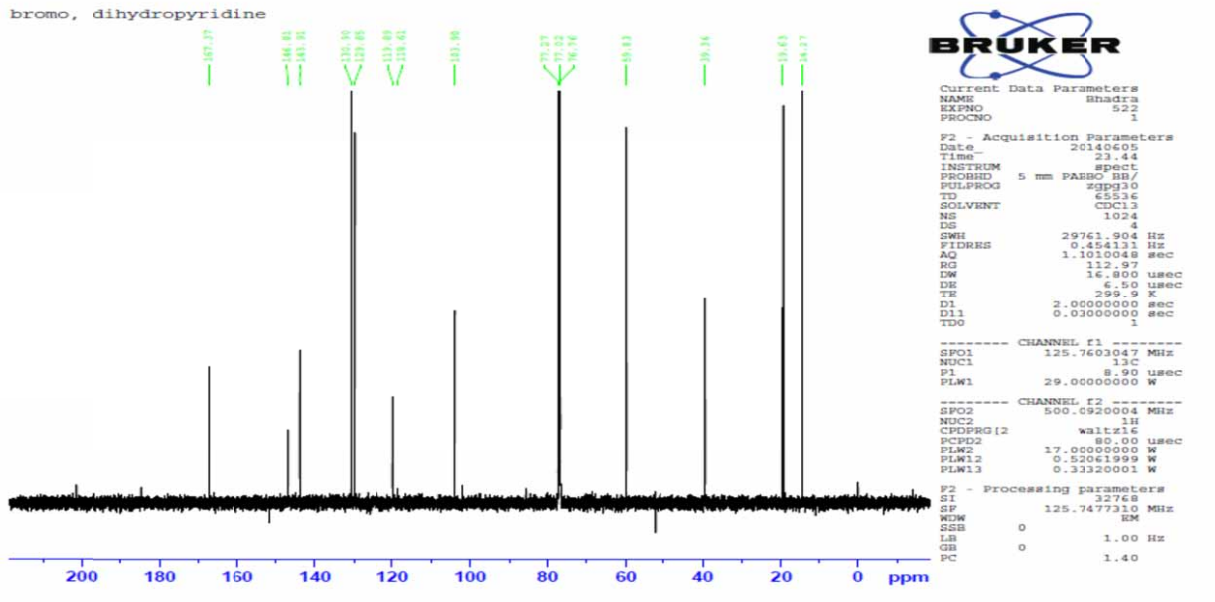
Mass spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate (2a)
Exact mass: 407.07
Mass obtained in the positive mode: 409.9511
Elemental composition:$C_{19}H_{22}BrNO_4$



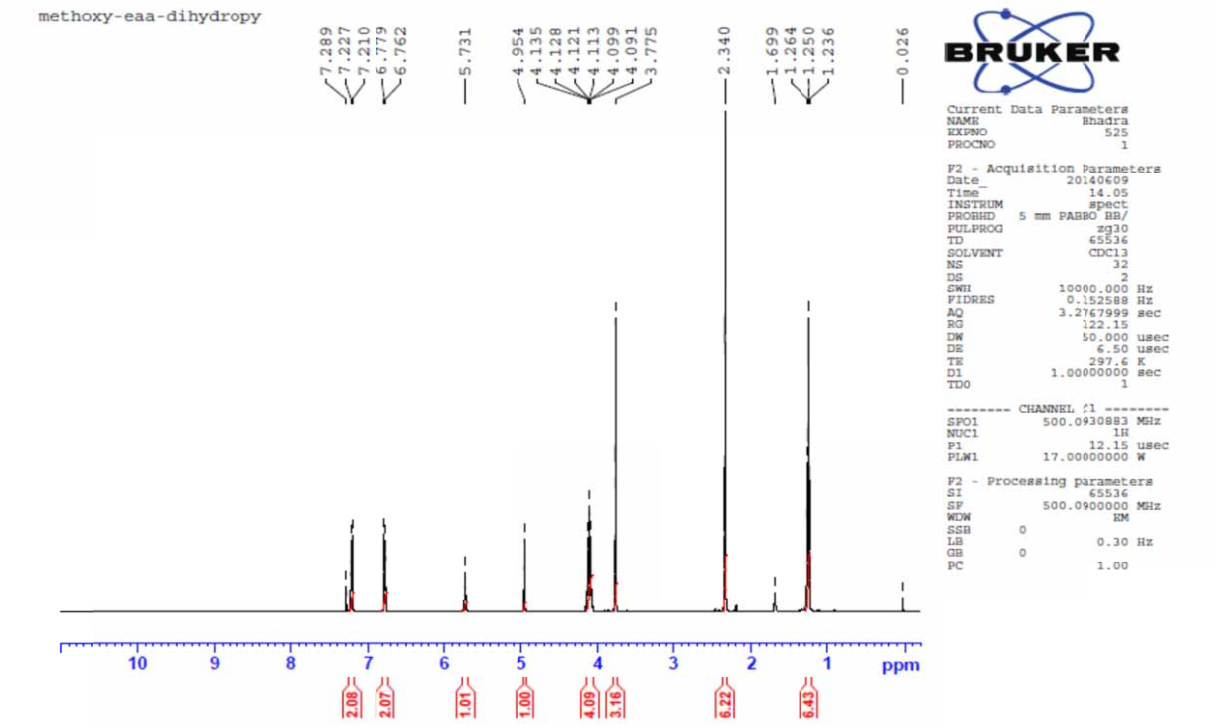
$^{1}$H NMR Spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate

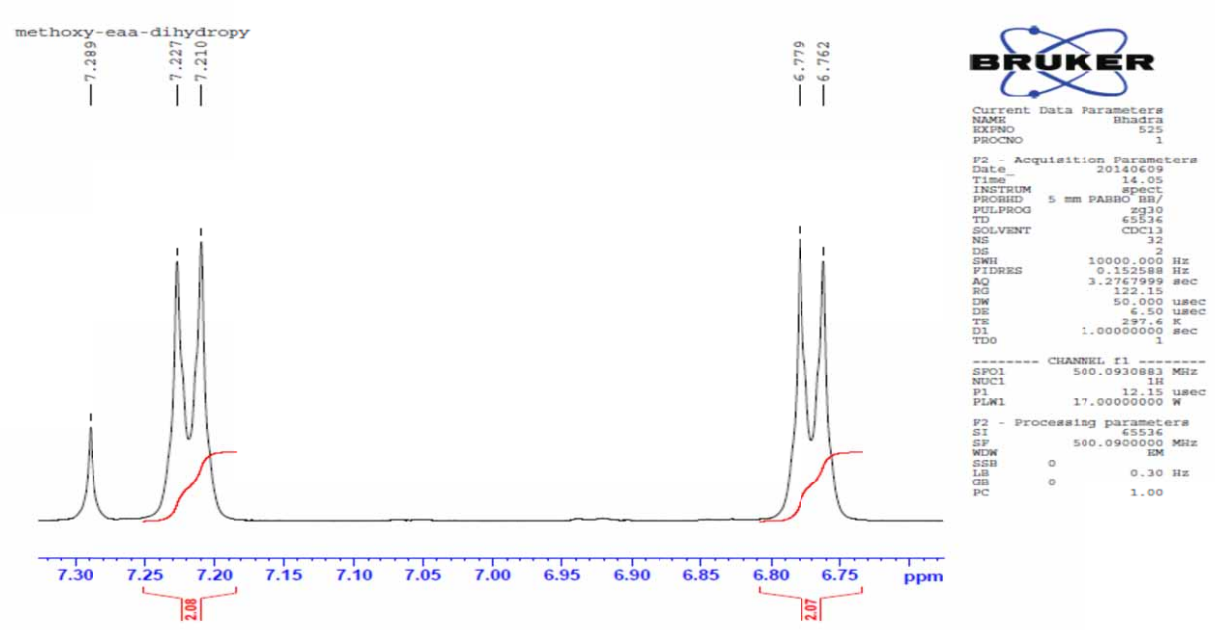


$^{13}$C NMR Spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate

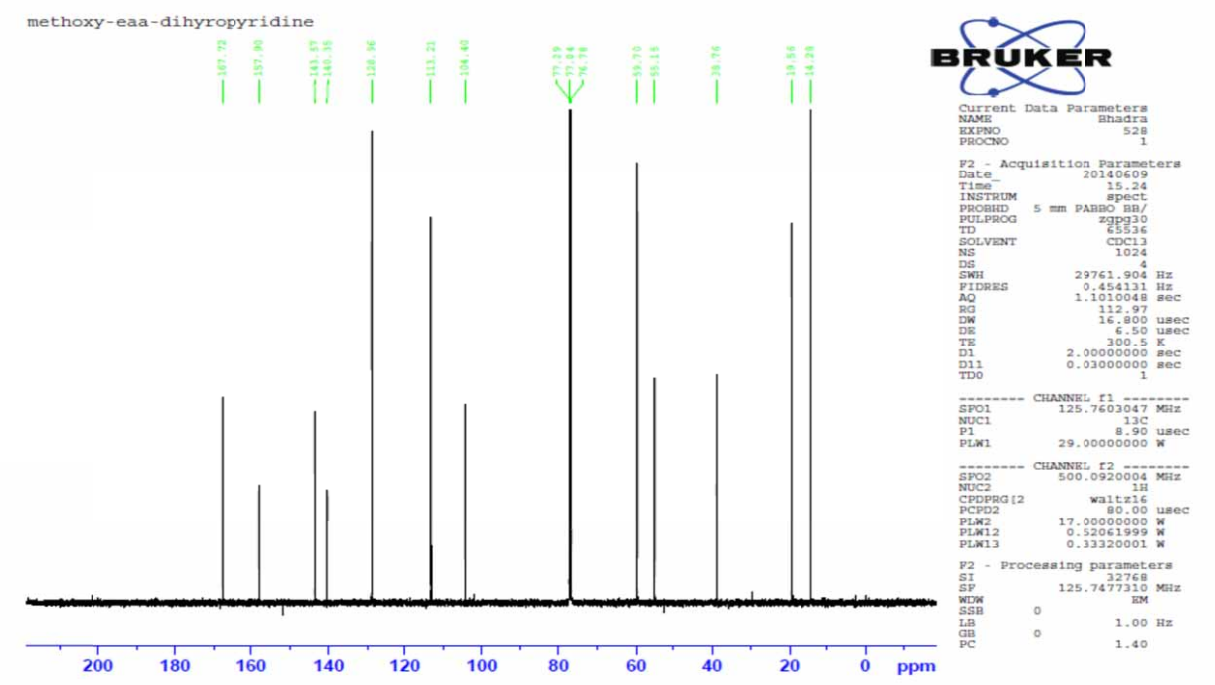



$^{1}$H NMR Spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate(2b)

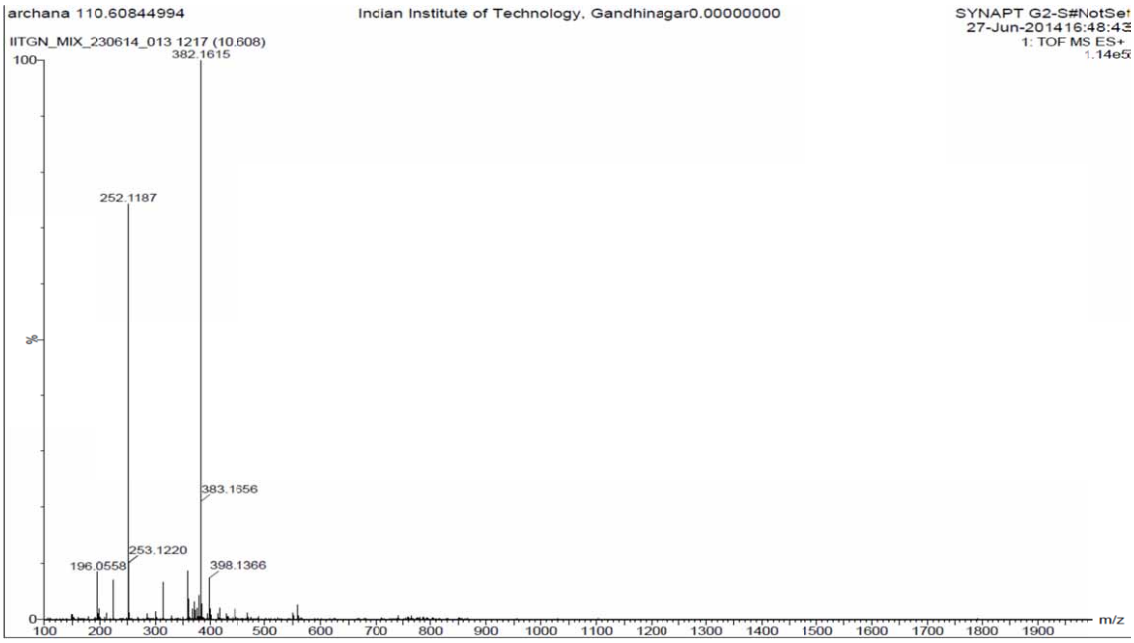




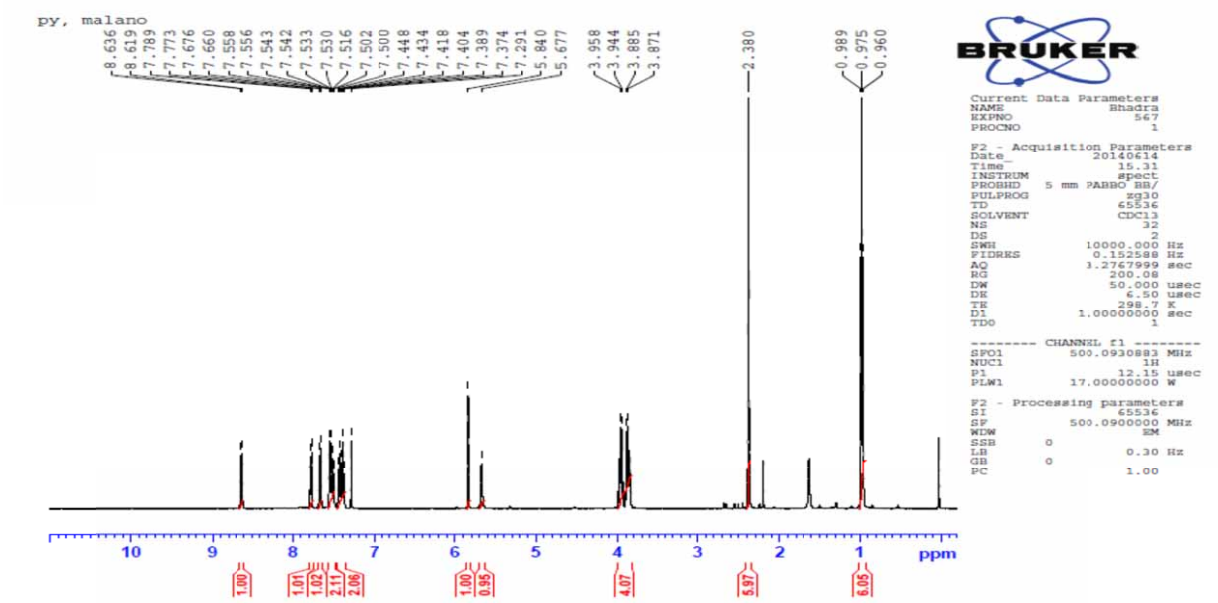

$^{13}$C NMR Spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

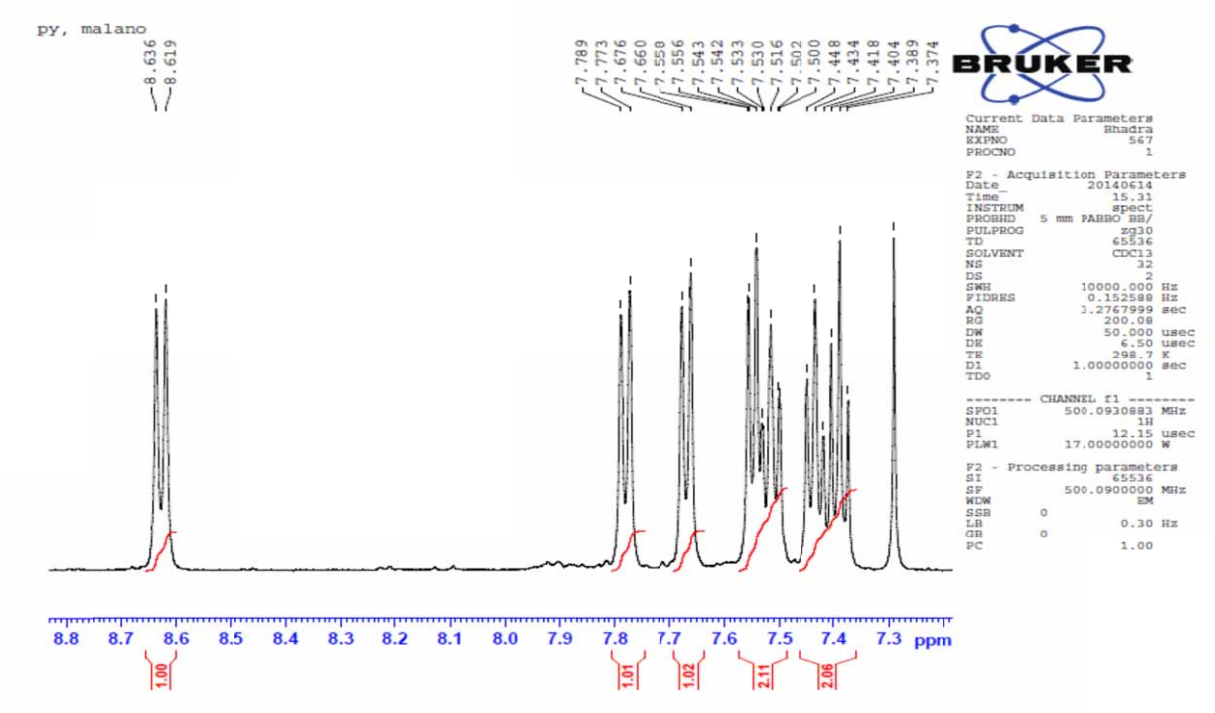


Mass spectrum of diethyl 2, 6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2c)
Exact mass: 379.18
Mass obtained in the positive mode: 382.165
Elemental composition:$C_{23}H_{25}NO_4$

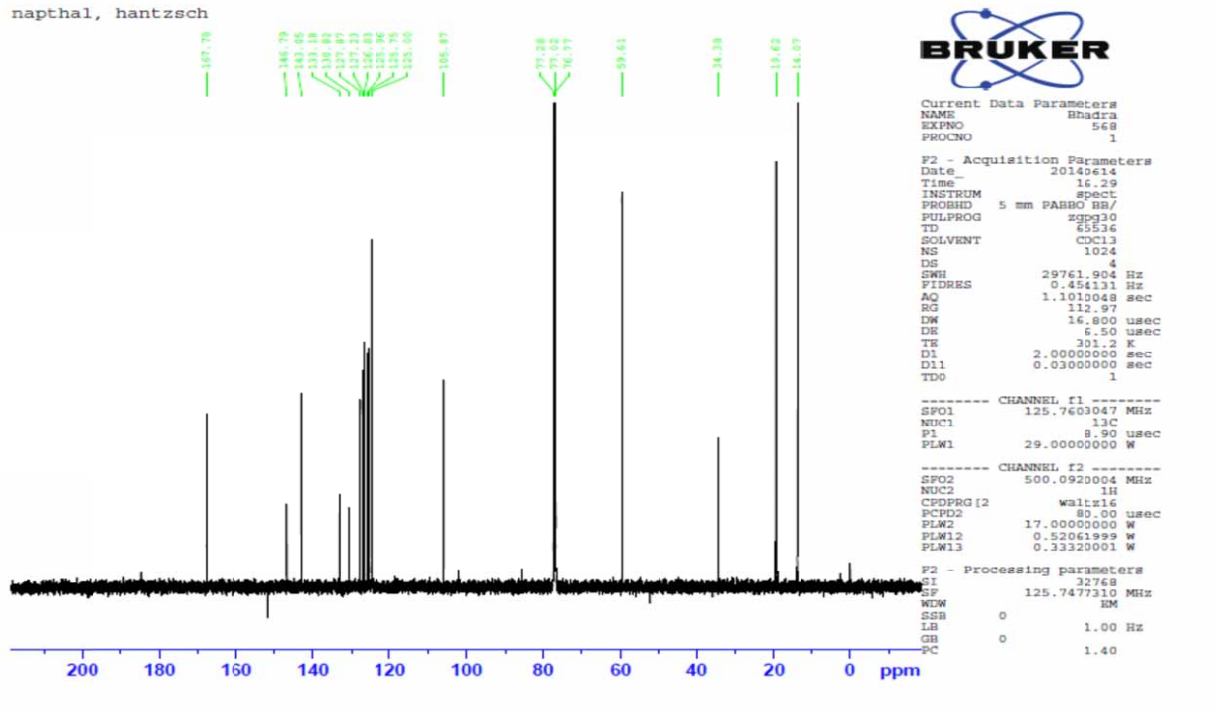



$^1$H NMR Spectrum of diethyl 2,6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate

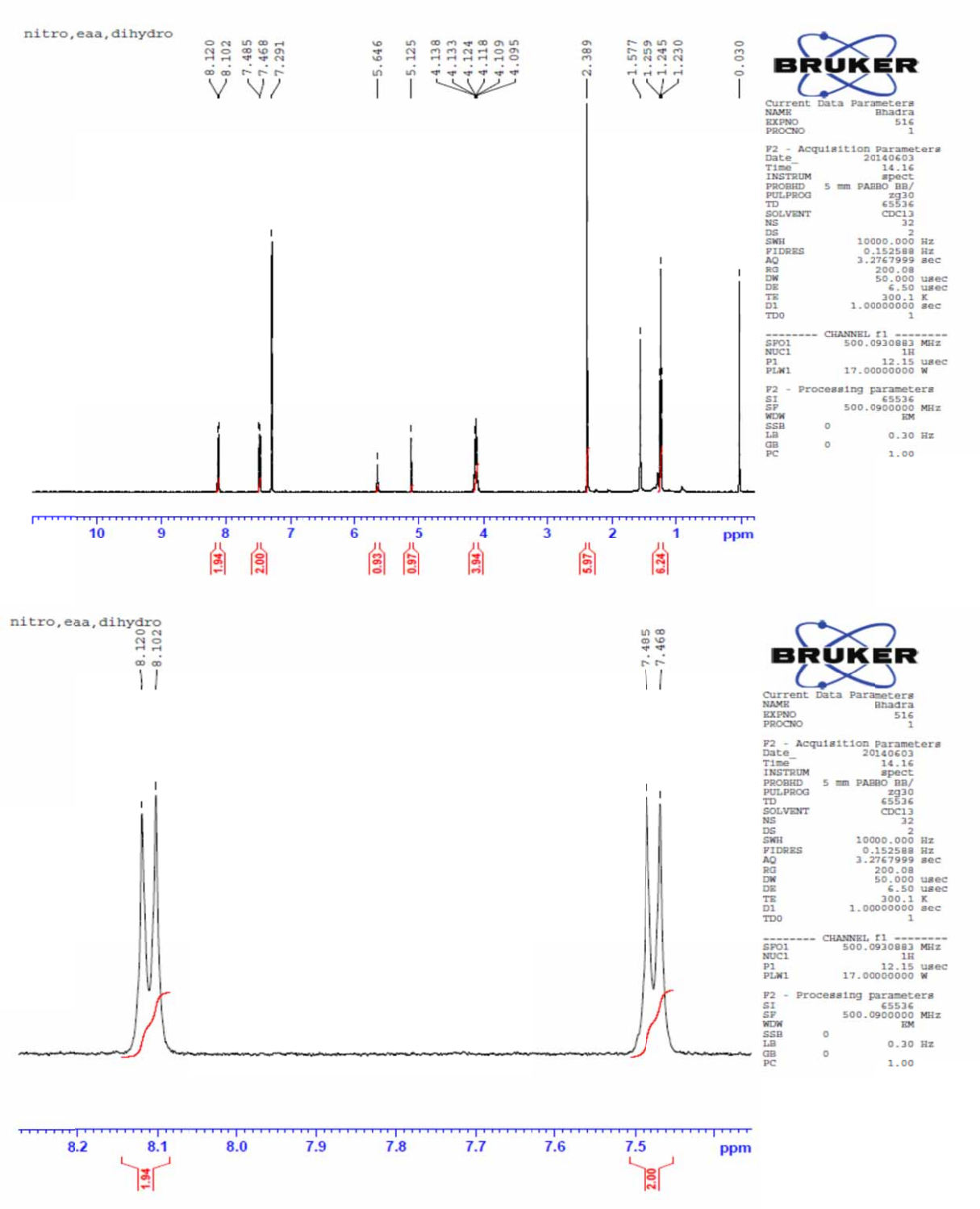




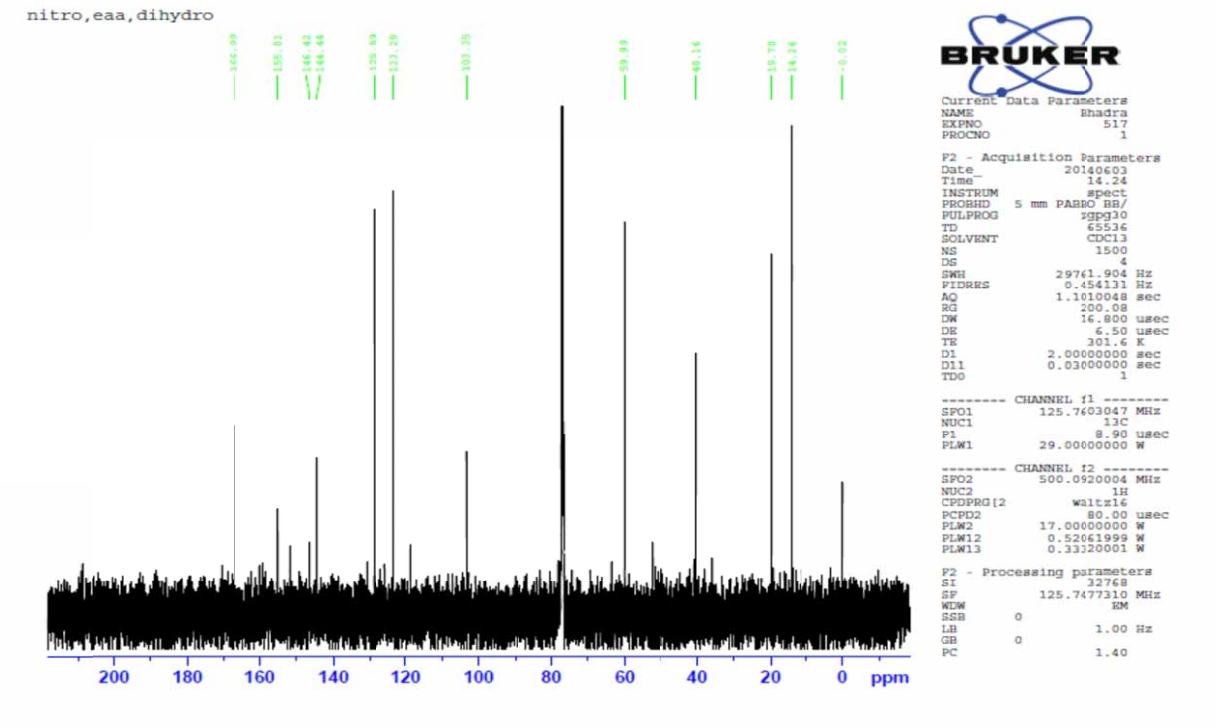

$^{13}$C NMR Spectrum of diethyl 2, 6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate



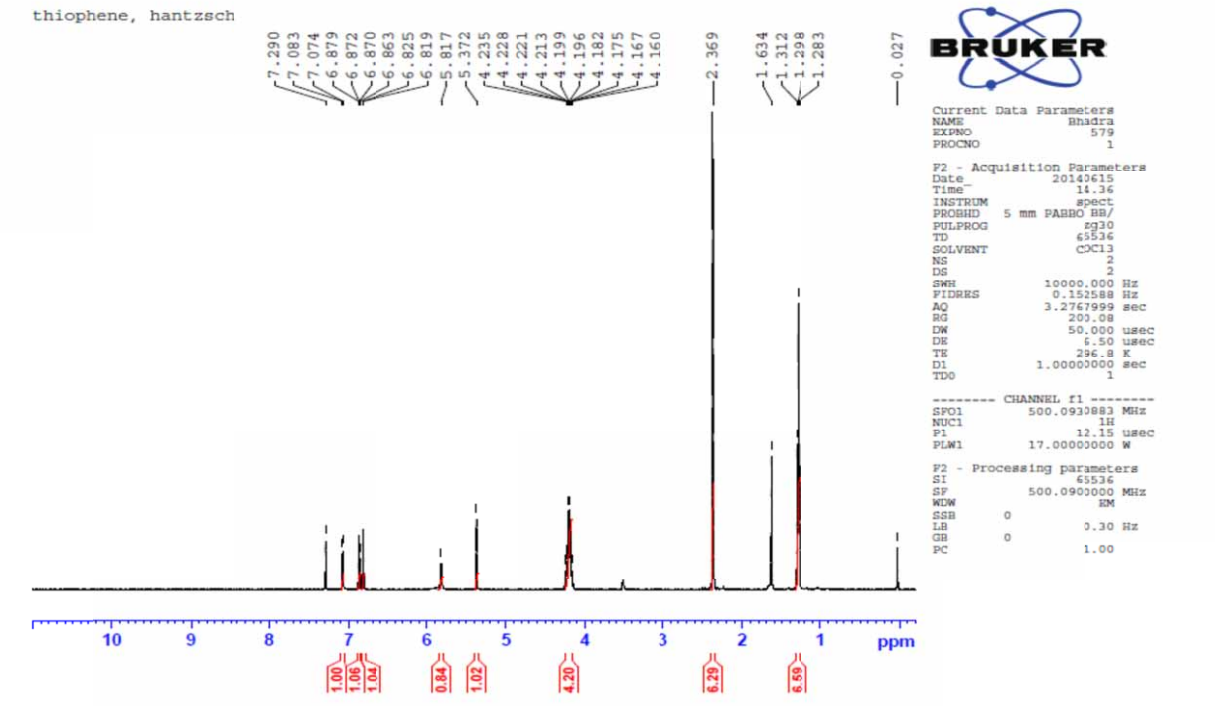
$^{1}$H NMR Spectrum of diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (2d)

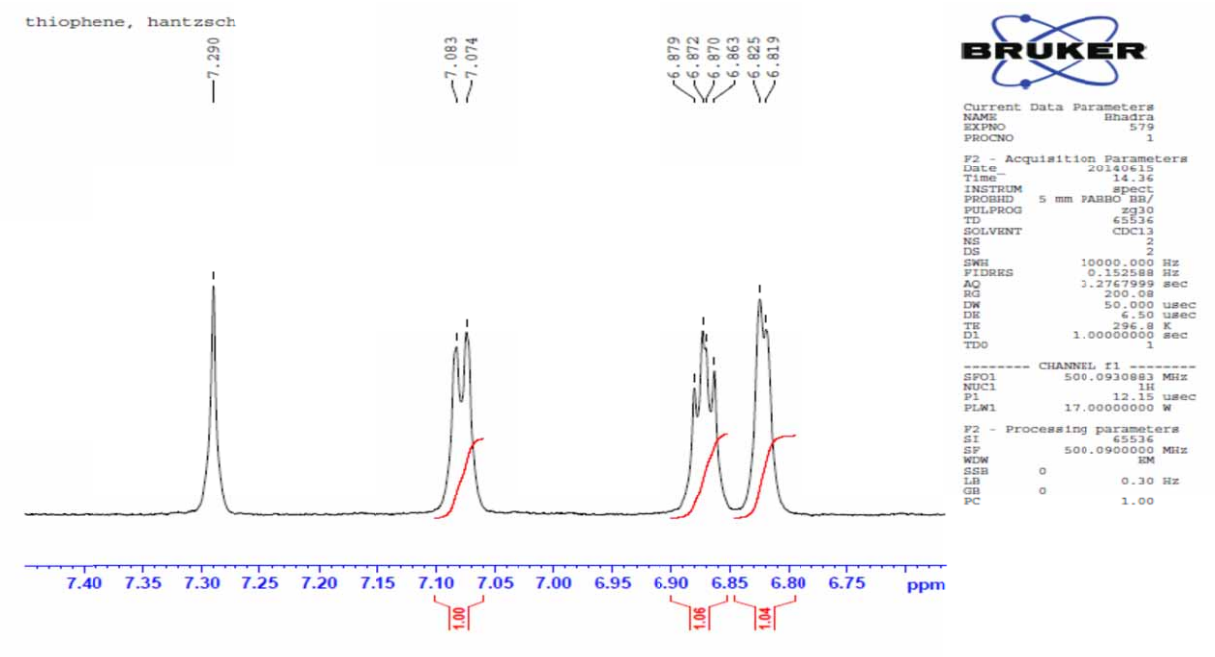


$^{13}$C NMR Spectrum of diethyl 2, 6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

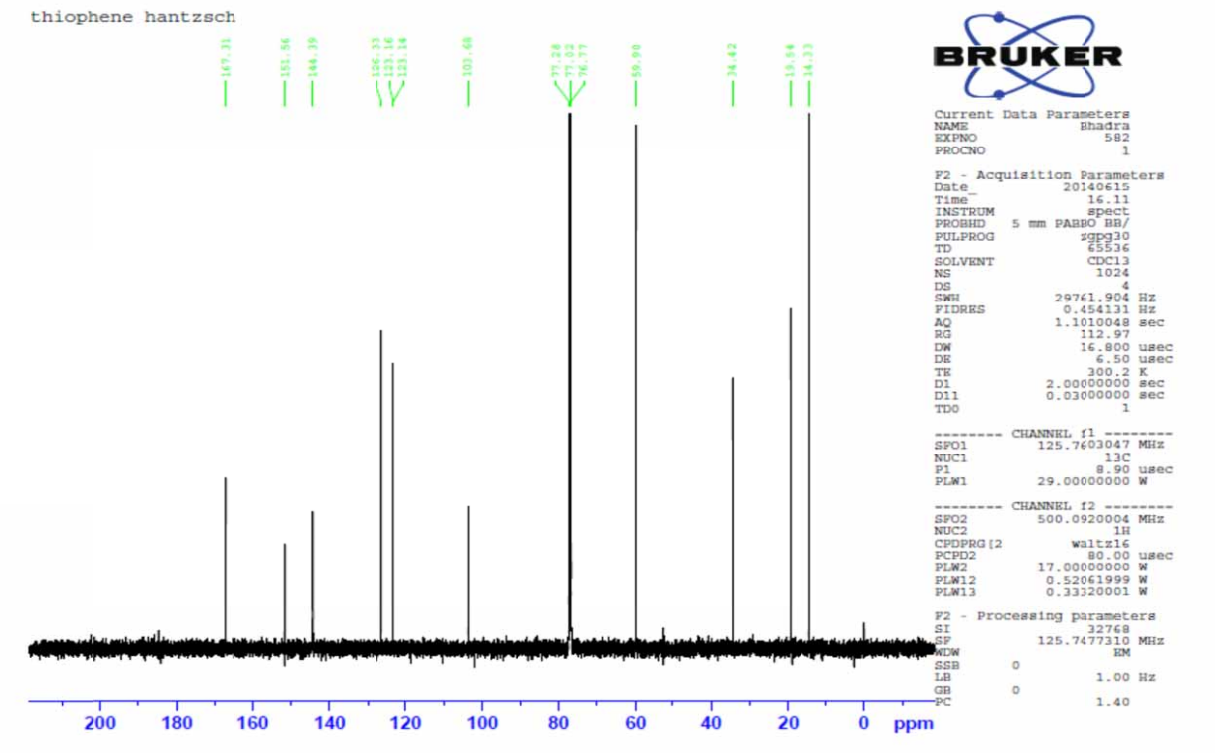



$^{1}$H NMR Spectrum of diethyl 2,6-dimethyl-4-(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2e)

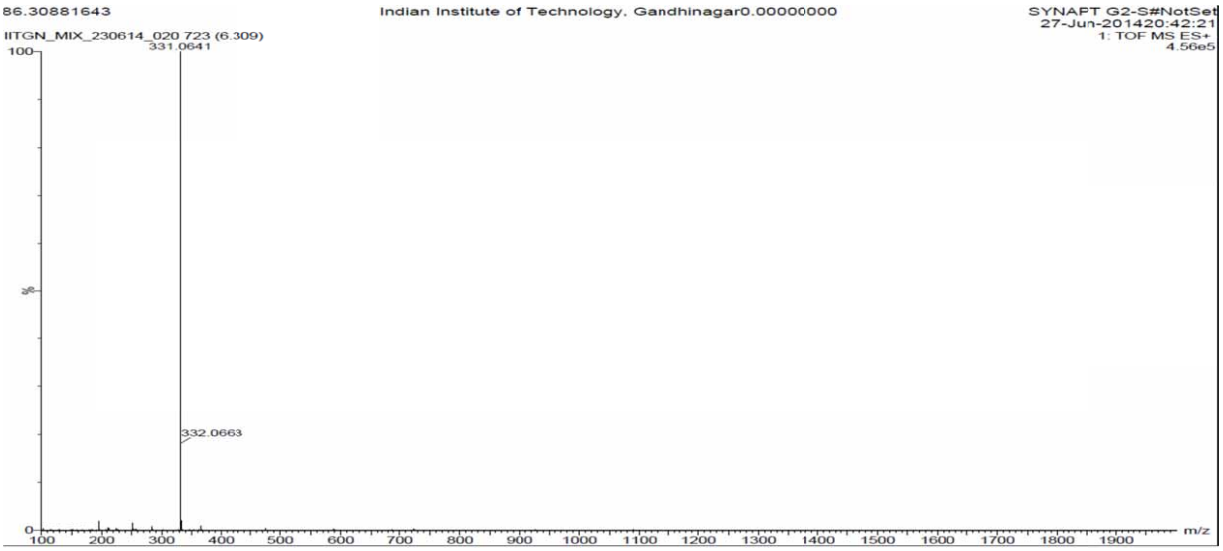




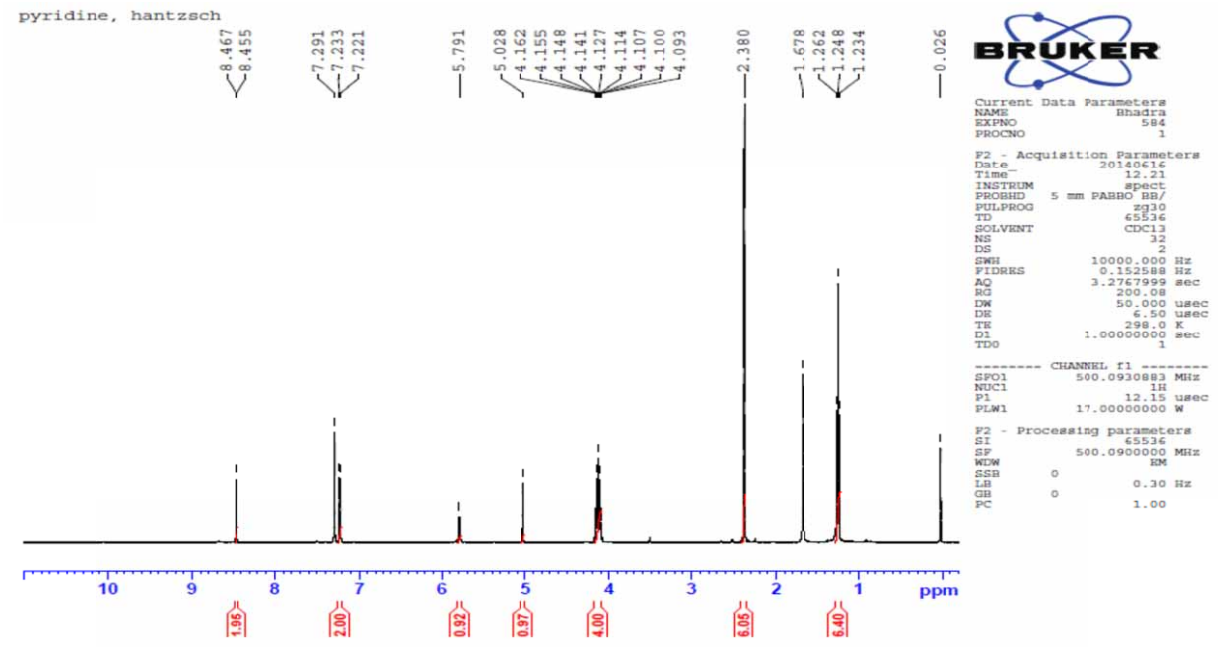

$^{13}$C NMR Spectrum ofdiethyl 2,6-dimethyl-4-(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate

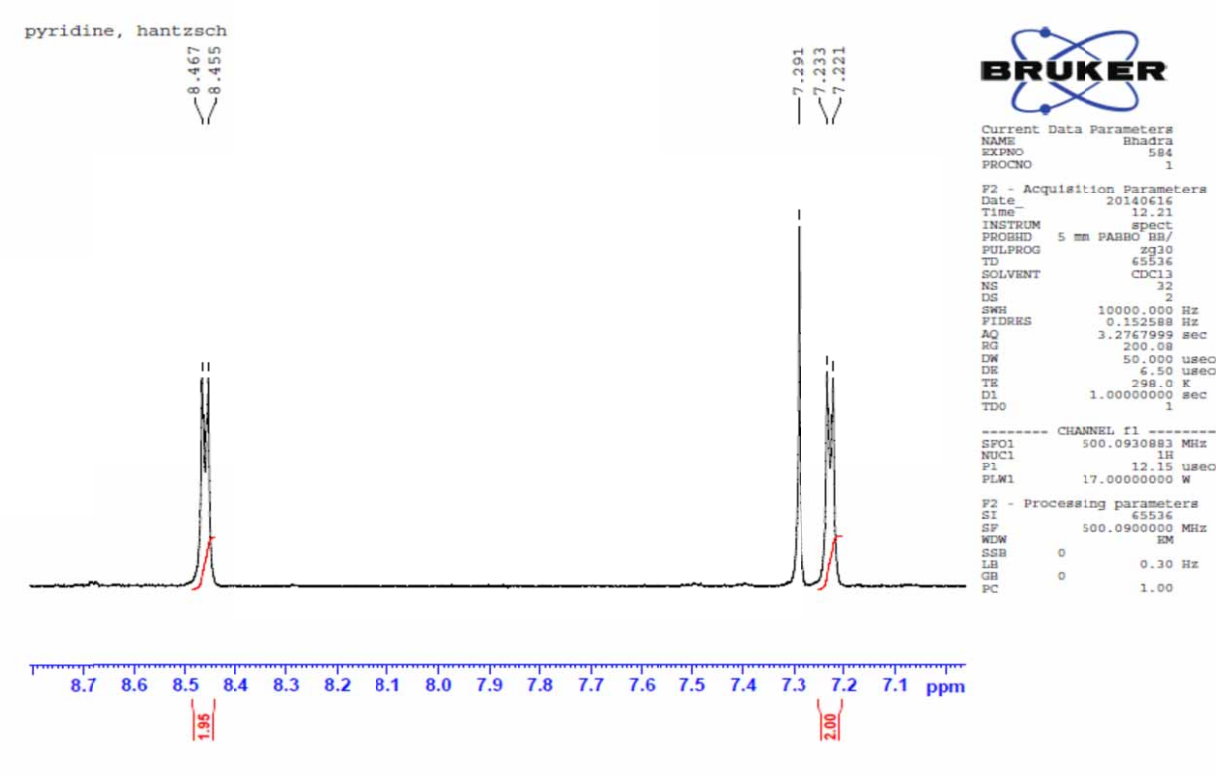


Mass spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2f)
Exact mass: 330.16
Mass obtained in the positive mode: 331.0641
Elemental composition: $C_{18}H_{22}N_2O_4$




$^1$H NMR Spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate






$^{13}$C NMR Spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate