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# Novel Highly Stable Naphthalene Core based Strain Molecule: Influence of Intermolecular H- Bonding Architectures

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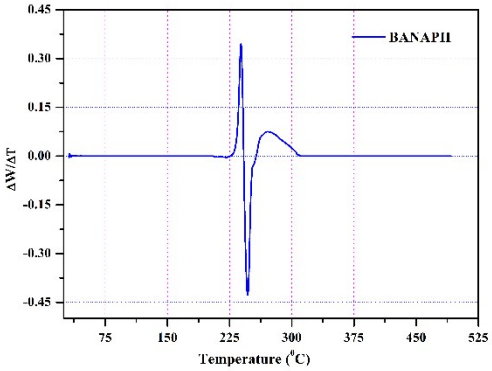



**Figure 1:** DTA plot of BNAP

**FTIR and Raman Spectrum**

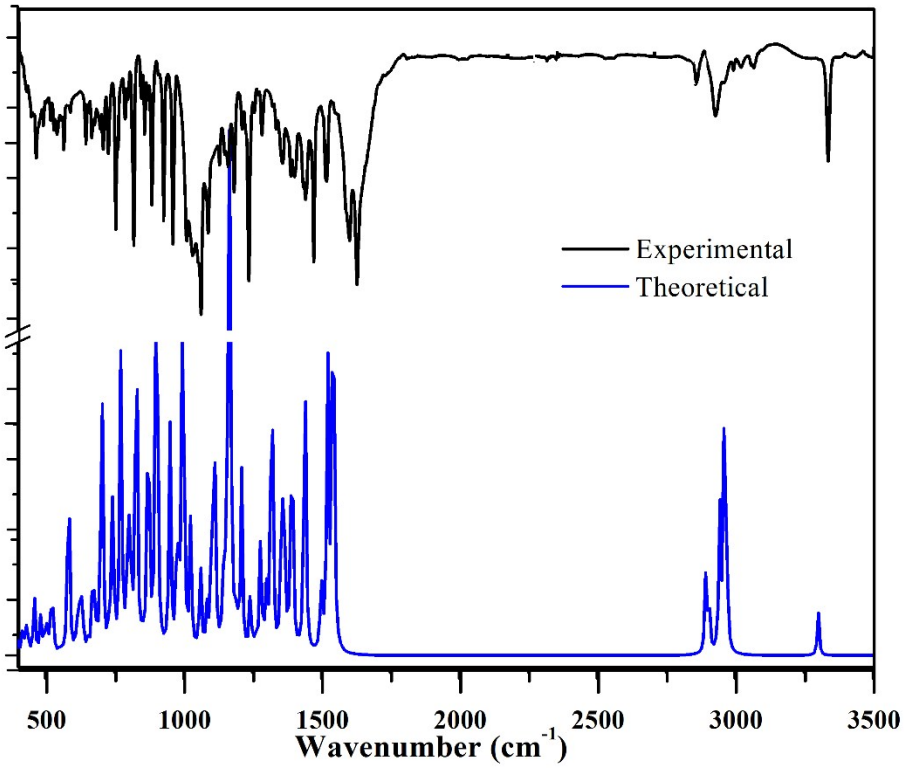



**Figure 2**: Calculated IR spectra of BNAP and compared with experimental result using scaling factor 0.93

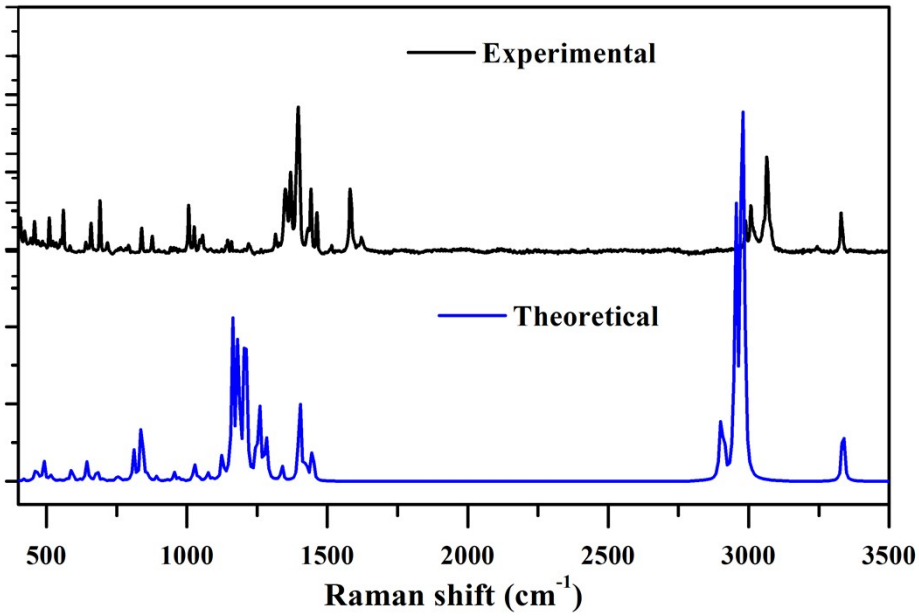



**Figure 3**: Calculated Raman spectra of BNAP and compared with experimental result using scaling factor 0.92

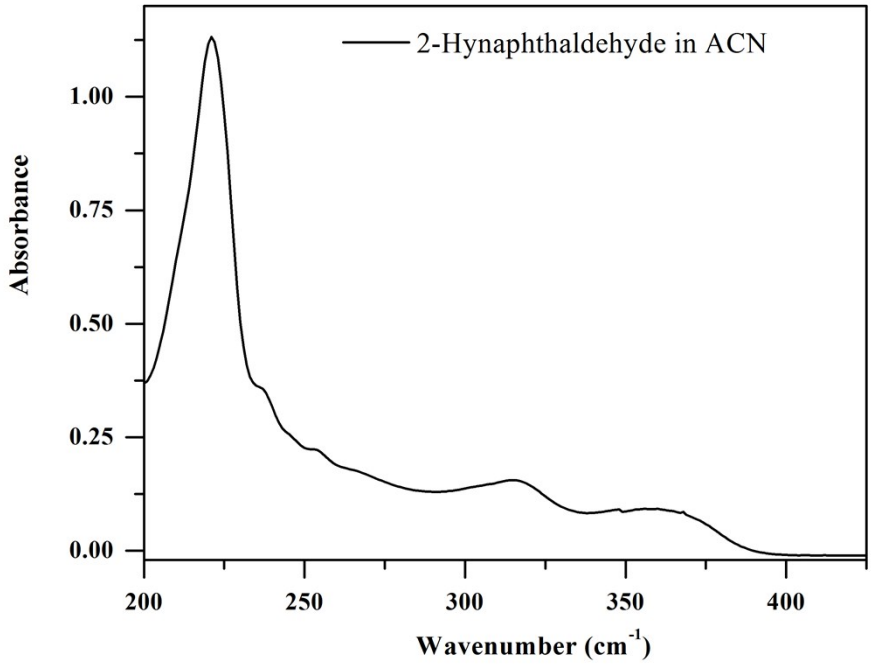



**Figure 4:** UV-Vis spectra of 2-Hydroxynaphthaldehyde in ACN

Further the stability of BNAP is also monitored in basic environment using UV-Vis spectroscopy in ACN. In presence of KOH, new absorbance band is appeared at 614 nm and presented in **Figure 9**. Interesting factor is that the intensity of the new absorption band is gradually decreased with variation of time. Within 24 min, the new absorption band is disappeared and the absorption spectra is similar to original absorption spectra of BNAP (before addition of base). Appearance and disappearance of new absorption band in presence of KOH at 614 nm may due to deprotonation and reformation of N-H bond in basic environment. This new band (614 nm) indicates the electron transfer process in BNAP and it is occurred from deprotonated of N-H form to naphthalene ring in BNAP due to the formation of highly sensitive donor-acceptor system.[1] Interesting factor is that there is no change of UV-Vis spectra of BNAP in acidic environment. Further the time dependent UV-Vis spectral change of BNAP in basic environment is also monitored and shown that the spectral pattern is similar to the initial spectral patter of BNAP in strong base (KOH) after 24 min. In acidic medium, there is no change of spectral patter. Above experimental results suggest that the BNAP is highly stable in acidic and basic condition.

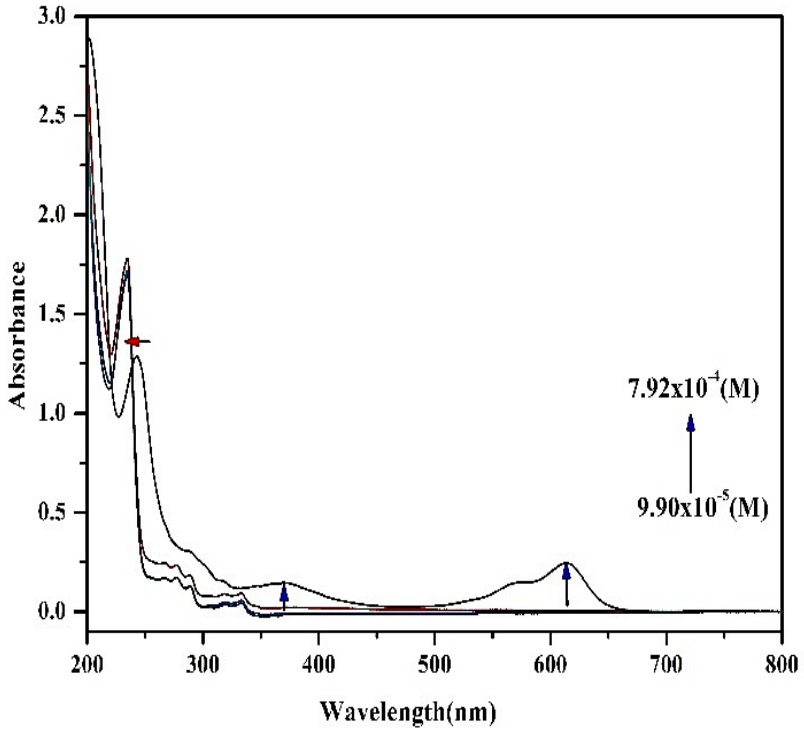



**Figure 5:** UV-Vis spectra of BNAP after addition KOH ($7.92 \times 10^{-4}$ (M)) in ACN

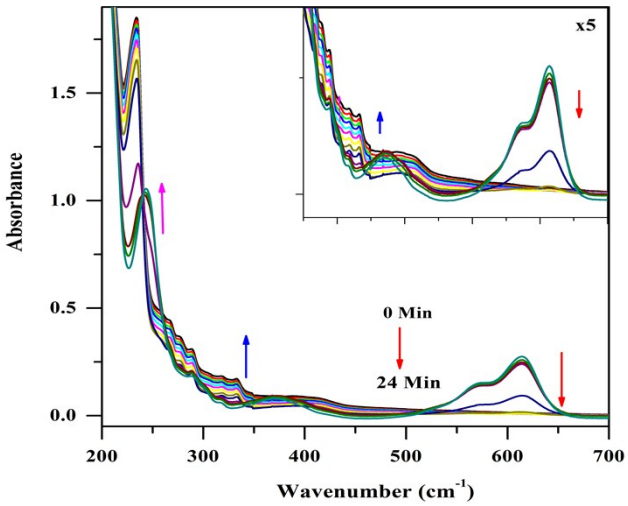



**Figure 6:** Time dependent UV-Vis spectra of BNAP after addition KOH ($7.92x10^{-4}$ (M)) in ACN

## Quantum Chemical Calculation

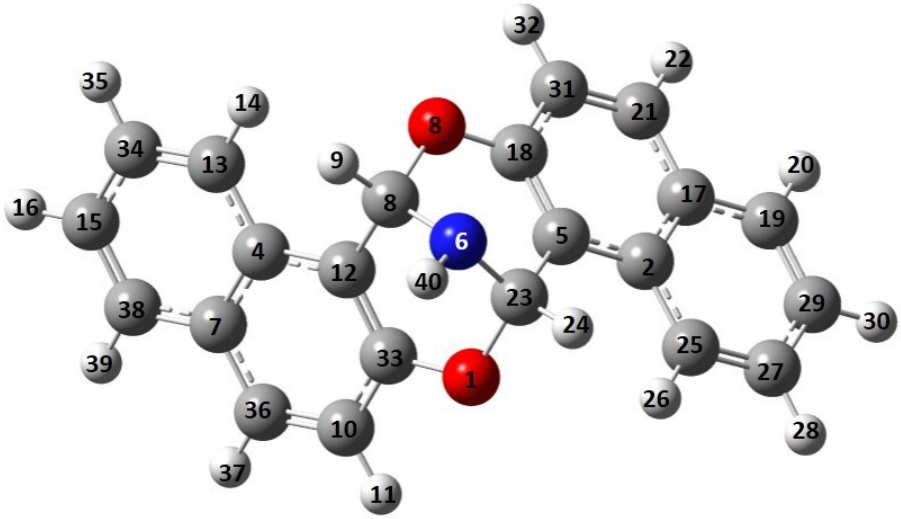



**Figure 7:** Numbering of the BNAPH

## X-ray diffraction study

**Table 1.** Crystallograpphic Information of BNAP

| Compound | BNAPH |
|---|---|
| Formula | $C_{22}\ H_{15}\ NO_2$ |
| Fw | 309.4 |
| *a* (Å) | 9.7948(4) |
| *b* (Å) | 22.5992(7) |
| *c* (Å) | 7.2523(3) |
| α (°) | 90.000(5) |
| β (°) | 105.001(4) |
| γ (°) | 90.000(5) |
| V (Å$^3$) | 1550.61(17) |
| Z | 4 |
| space group | P-121/c1 |
| *T* (ºC) | 298K |
| λ (Å) | 0.71 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.333 |
| $\mu$ (cm$^{-1}$) | 10.1 |
| R ($F_o^2$)[a] | 0.0344 |
| $R_w(F_o^2)$[b] | 0.045 |
| [a]$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [b]$R_w = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w(F_o^4)]^{1/2}$ | |

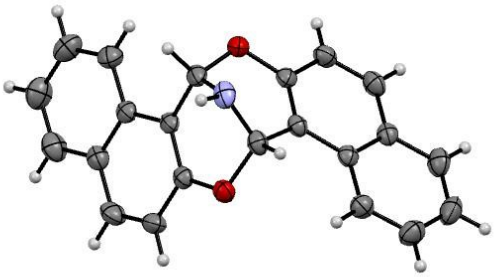


**Figure 8:** ORTEP diagram of BNAP (**CCDC No. 910216**)

**NMR Spectral data of BNAP**

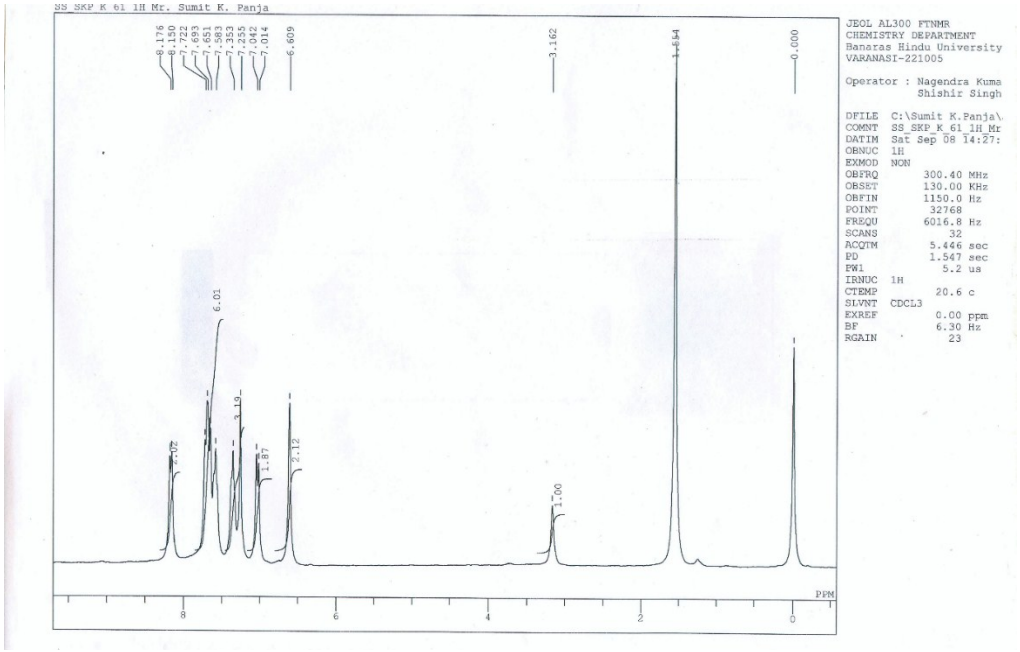
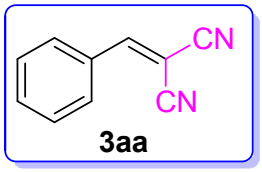



**Figure 9:** $^1$H-NMR of BNAP in $CDCl_3$

## NMR Spectra of Knoevenagel Products

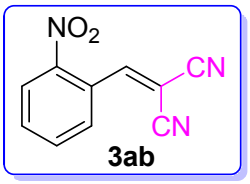
### 2-benzylidenemalononitrile (3aa)




State: Solid; Colour: White; MP.: 83.5 °C (Lit.,[2] 82-83 °C); FTIR (KBr, cm$^{-1}$): 3097, 3075, 3032, 2934, 2223, 1551, 1568, 1490; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.88 (d, *J* = 7.5 Hz, 2H), 7.76 (s, 1H), 7.61 (t, *J* = 5.0 Hz,

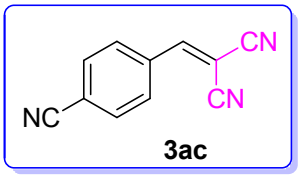
1H), (t, $J$ = 5.0 Hz, 1H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.9, 134.5, 130.9, 129.5, 113.6, 112.5, 82.8.

**2-(2-nitrobenzylidene)malononitrile (3ab)**



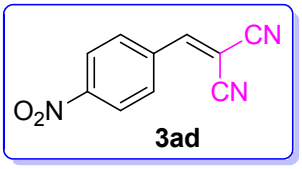

State: Solid; Colour: Gray; MP.: 140.2 °C (Lit.,[3] 136-138 °C); FTIR (KBr, cm$^{-1}$): 3118, 3066, 2996, 2953, 2229, 1723, 1623, 1603, 1569, 1523; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 8.42 (s, 1H), 8.33 (d, $J$ = 7.5 Hz, 1H), 7.88-7.76 (m, 3H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.7, 134.8, 133.3, 130.4, 126.6, 125.7, 112.1, 110.9; 88.5.

**2-(4-cyanobenzylidene)malononitrile (3ac)**



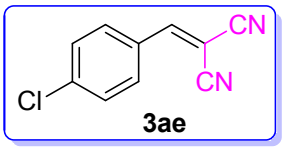

State: Solid; Colour: White; MP.: 155.2 °C (Lit.,[4] 154 °C); FTIR (KBr, cm$^{-1}$): 3110, 3100, 3080, 3043, 2229, 1588, 1550, 1501,1416; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.99 (d, $J$ = 8.4 Hz, 2H), 7.84 (s, 1H), 7.80 (d, $J$ = 2.4 Hz, 2H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 157.2, 134.2, 133.1, 130.6, 117.2, 112.6, 111.6, 86.9.

**2-(4-nitrobenzylidene)malononitrile (3ad)**



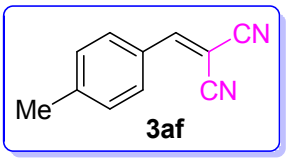

State: Solid; Colour: Light Yellow; MP.: 160.2 °C (Lit.,160-161 °C); FTIR (KBr, cm$^{-1}$): 3110, 3100, 3080, 3043, 2229, 1588, 1550, 1501,1416; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 8.38 (d, $J$ = 8.7 Hz, 2H), 8.71 (d, $J$ = 8.8 Hz, 2H), 7.87 (s, 1H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.2, 137.2, 134.1, 133.6, 117.6, 112.6, 111.6, 87.9.

**2-(4-chlorobenzylidene)malononitrile (3ae)**



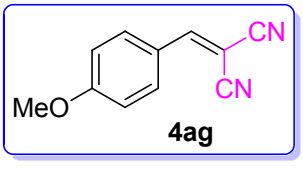

State: Solid; Colour: White; MP.: 163.0 °C (Lit.,[5]162 °C); FTIR (KBr, cm$^{-1}$): 3100, 3080, 3070, 3040, 2235, 1580, 1555, 1505, 1419; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.83 (d, $J$ = 8.4 Hz, 2H), 7.71 (s, 1H), 7.50 (d, $J$ = 8.4 Hz, 2H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.2, 141.1, 131.7, 130.0, 129.2, 117.2, 112.6, 111.6, 86.9.

**2-(4-methylbenzylidene)malononitrile (3af)**




State: Solid; Colour: White; MP., 134.5 °C (lit.,[6] 134-135 °C); FTIR (KBr, cm$^{-1}$): 3034, 2962, 2925, 2223, 1590, 1554, 1509, 1453; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.79 (d, $J$ = 8.3 Hz, 2H), 7.69 (s, 1H), 7.32 (d, $J$ = 8.3 Hz, 2H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.7, 146.3, 130.8, 130.3, 128.3, 113.9, 112.8, 81.1.

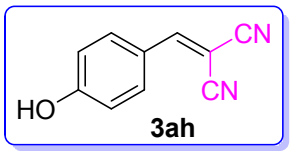
**2-(4-methoxybenzylidene)malononitrile (3ag)**




State: Solid; Colour: White; MP., 115 °C; (Lit.,[7] 114-115 °C) ); FTIR (KBr, cm$^{-1}$): 3030, 2982, 2852, 2220, 1605, 1571, 1557, 1513; $^1$H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.91 (d, $J$ = 10.5 Hz, 2H), 7.65 (s, 1H), 7.01

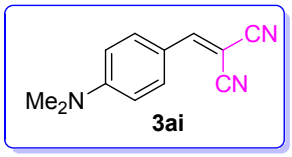
(d, $J$ = 9.0 Hz, 2H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.8, 133.4, 115.10, 114.1, 85.7, 55.7.

**2-(4-hydroxybenzylidene)malononitrile (3ah)**



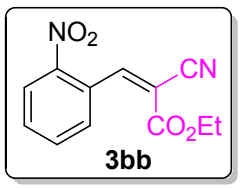

State: Solid; Colour: White; MP.: 190 °C (Lit.,[8] 188-189 °C); FTIR (KBr, $cm^{-1}$): 3350, 3330, 3090, 3070, 3035, 2937, 2228, 1555, 1565, 1495; $^1$H-NMR(300 MHz, $CDCl_3$): δ (ppm) 10.38 (s, 1H), 7.82 (d, $J$ = 8.7 Hz, 2H), 7.65 (s, 1H), 6.95 (d, $J$ = 8.7 Hz, 2H); $^{13}$C-NMR(75MHz, $CDCl_3$): δ (ppm) 163.2, 162.6, 154.6, 133.8, 132.0, 128.6, 122.8, 116.3, 115.8, 97.5, 62.0.

**2-(4-(dimethylamino)benzylidene)malononitrile (3ai)**



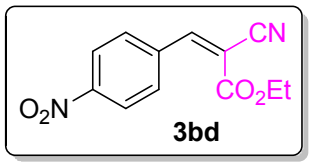

State: Solid; Colour: Brown; MP.: 180.2 °C (lit.,[9] 182-183°C); FTIR (KBr, $cm^{-1}$): 3050, 3030, 2939, 2225, 1545, 1555, 1499; $^1$H-NMR(300MHz, $CDCl_3$): δ(ppm) 7.80 (d, $J$ = 9.0 Hz, 2H), 7.45 (s, 1H), 6.69 (d, $J$ = 8.4 Hz, 2H), 3.16 (s, 6H); $^{13}$C-NMR(75MHz, $CDCl_3$): δ(ppm) 158, 133.7, 131.9, 111.5, 110.9, 40.0.

**(E/Z)-ethyl-2-cyano-3-(2-nitrophenyl)acrylate (3bb)**



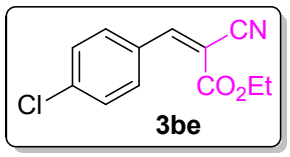

State: Solid; Colour: White; MP.: 105 °C (Lit.,[10] 101-103 °C); FTIR (KBr, cm-1): 3094, 3035, 2987, 2952, 2944, 2905, 2226, 1723, 1610, 1591, 1565, 1491; $^1$H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.69 (s, 1H), 8.25 (d, $J$ = 8.1 Hz, 1H), 7.84-7.76 (dd, $J_1$ = 7.5 Hz, $J_2$ = 7.5 Hz, 2H), 7.69 (t, $J$ = 7.5 Hz, 1H), 3.39 (q, $J$ = 7.0 Hz, 2H), 1.39 (t, $J$ = 7.2 Hz, 3H); $^{13}$C-NMR(75MHz, $CDCl_3$): δ (ppm) 178.4, 160.9, 153.1, 147.3, 134.4, 132.1, 130.5, 128.0, 125.4, 108.6, 72.2, 14.0.

**(E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)**



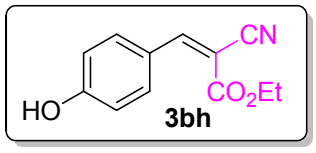

State: Solid; Colour: White; MP.: 172 °C (Lit.,[11] 170 °C); FTIR (KBr, cm-1): 3090, 3045, 2997, 2955, 2946, 2915, 2229, 1720, 1614, 1590, 1560, 1490; $^1$H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.34 (d, $J$ = 9.0 Hz, 2H), 8.29 (s, 1H), 8.12 (d, $J$ = 8.7 Hz, 2H), 4.43 (q, $J$ = 3.6 Hz, 2H), 1.42 (t, $J$ = 7.0 Hz, 3H); $^{13}$C-NMR(75MHz, $CDCl_3$): δ (ppm) 161.3, 151.6, 149.6, 136.8, 131.4, 124.2, 114.4, 107.3, 63.2, 14.0.

**(E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)**




State: Solid; Colour: White; MP. 89 °C (Lit.,[12] 90 °C); FTIR (KBr, cm-1): 3095, 3040, 2997, 2954, 2943, 2910, 2223, 1722, 1610, 1595, 1560, 1491; $^1$H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.16 (s, 1H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 4.35 (q, $J$ = 7.0 Hz, 2H), 1.36 (t, $J$ = 7.0 Hz, 3H); $^{13}$C-NMR(75MHz, $CDCl_3$): δ (ppm) 162.1, 153.3, 139.5, 132.1, 129.8, 115.1, 103.4, 62.8, 14.1.

**(E or Z)-ethyl 2-cyano-3-(4-hydroxyphenyl)acrylate (3bh)**

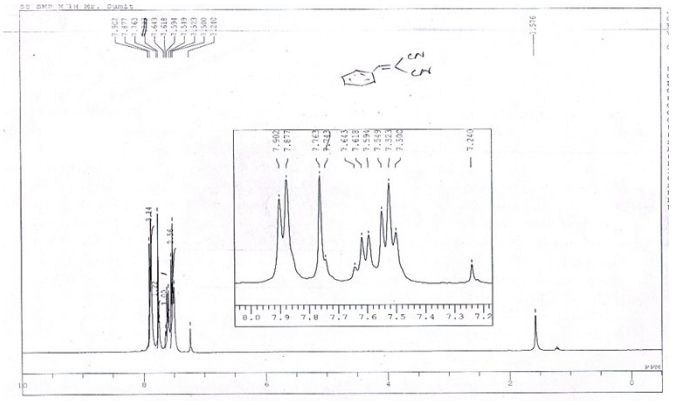



State: Solid; Colour: White; MP.: 168 °C (lit.,[13] 170-171 °C); FTIR (KBr, $cm^{-1}$): 3395, 3340, 3010, 2990, 2952, 2940, 2915, 2222, 1722, 1612, 1590, 1561, 1491; $^1$H-NMR(300MHz, $CDCl_3$): δ (ppm) 8.17 (s, 1H), 7.95 (d, $J$ = 8.7 Hz, 2H), 6.95 (d, $J$ = 8.7 Hz, 2H), 5.96 (s, 1H)4.37 (q, $J$ = 7.1Hz, 2H), 1.39 (t, $J$ = 7.1 Hz,

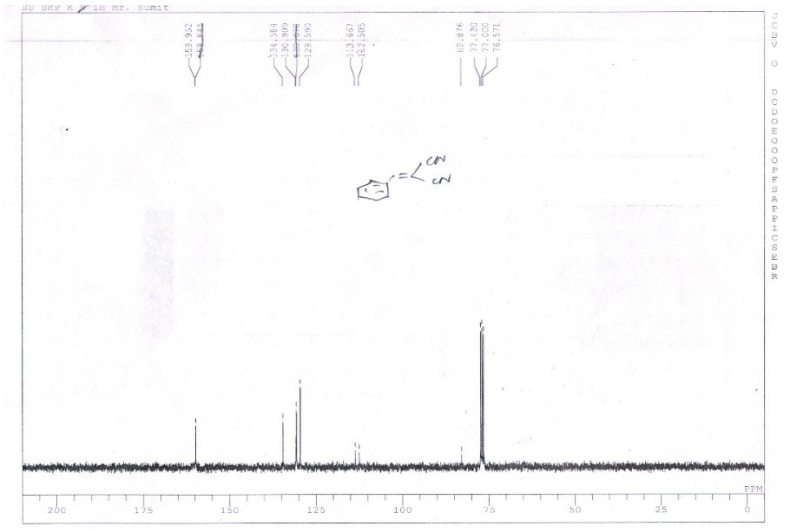
3H); $^{13}$C-NMR (75MHz, $CDCl_3$): δ(ppm) 190.8, 163.2, 162.6, 154.6, 133.8, 132.0, 128.6, 122.8, 166.3, 115.8, 97.5, 62.0, 29.4, 14.0.

## 1. $^{1}$H and $^{13}$C NMR spectra of the selected synthesized derivatives

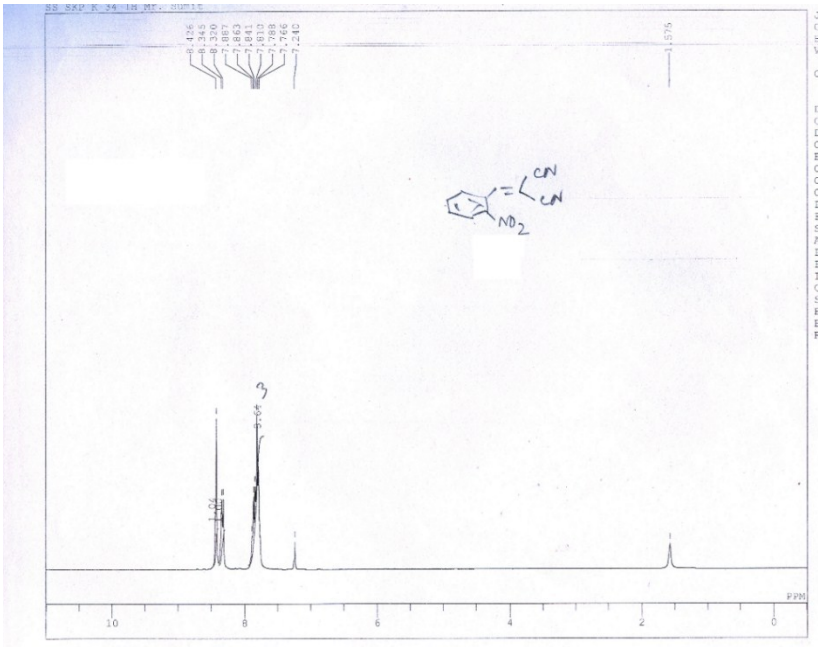
### $^{1}$H-NMR of 2-benzylidenemalononitrile (3aa)



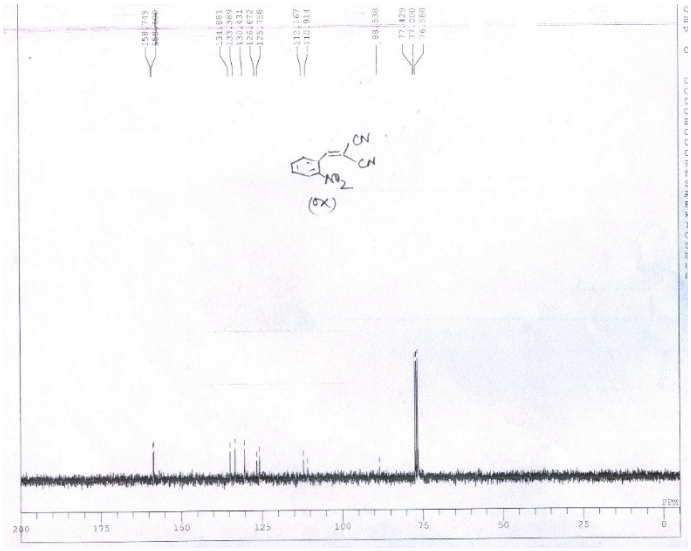
### $^{13}$C-NMR of 2-benzylidenemalononitrile (3aa)



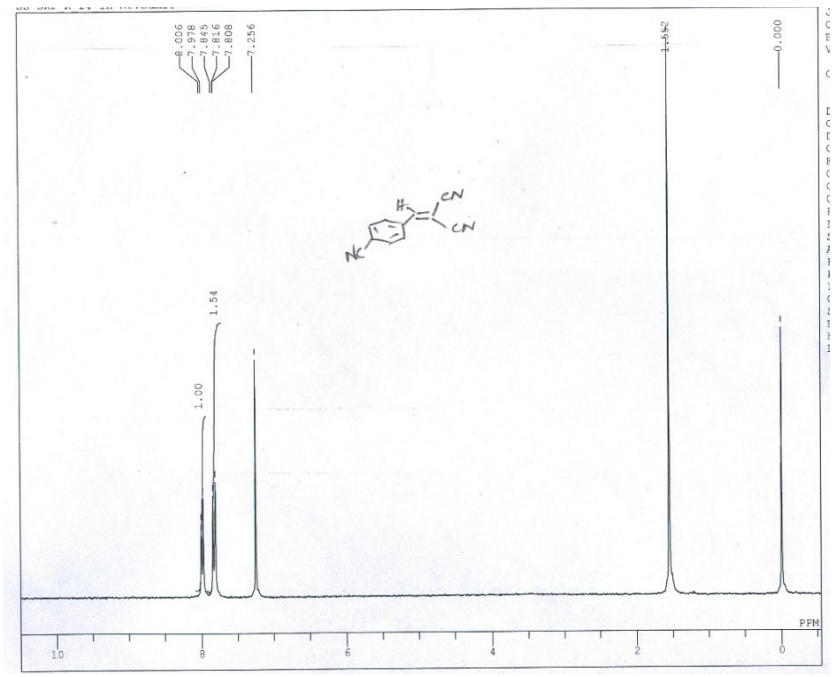
### $^{1}$H-NMR of 2-(2-nitrobenzylidene)malononitrile (3ab)



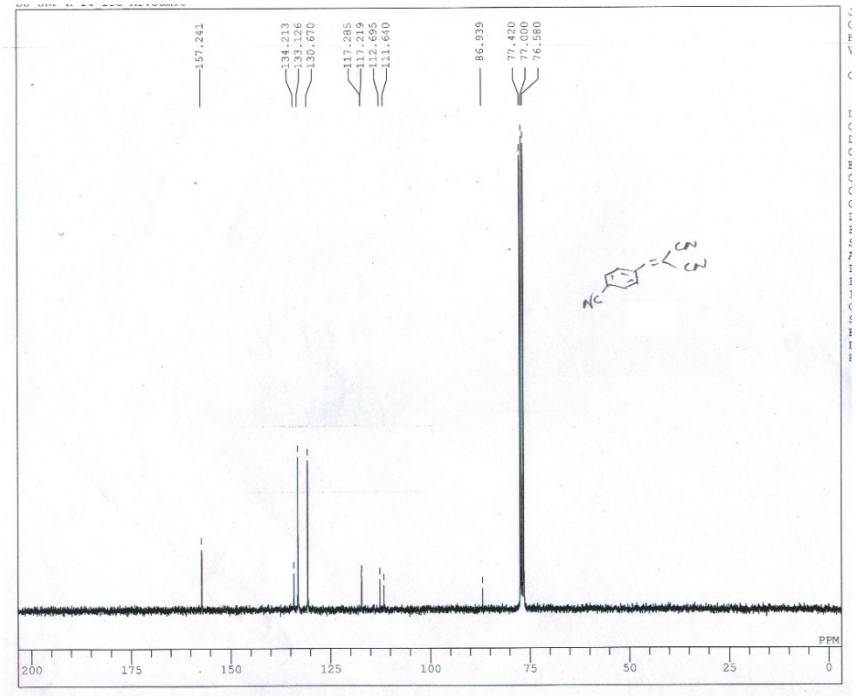
**$^{13}$C-NMR of 2-(2-nitrobenzylidene)malononitrile (3ab)**



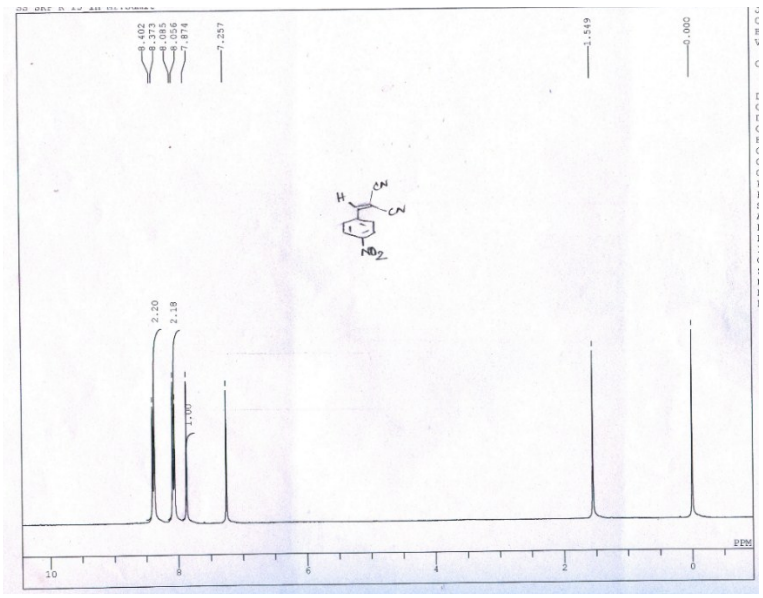
**$^{1}$H-NMR of 2-(4-cyanobenzylidene)malononitrile (3ac)**



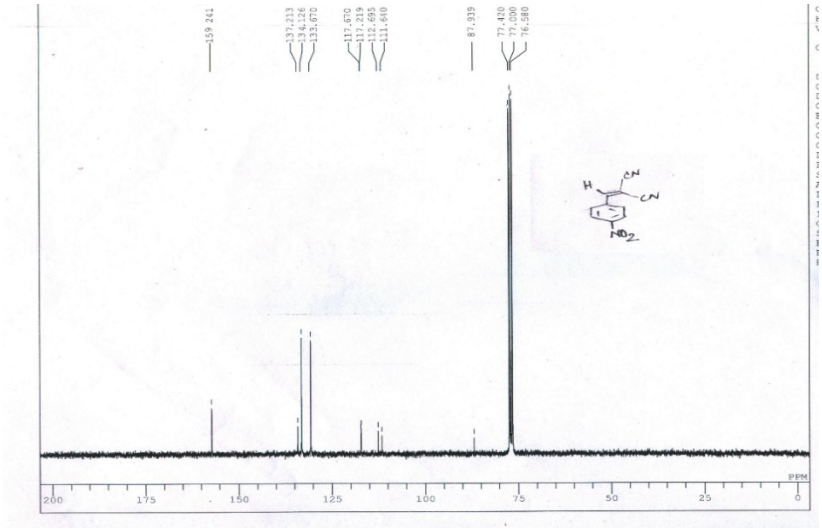

**$^{13}$C-NMR of 2-(4-cyanobenzylidene)malononitrile (3ac)**



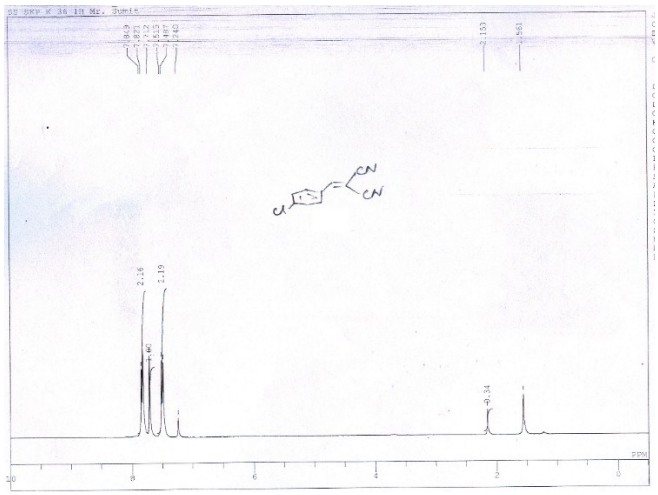

**$^{1}$H-NMR of 2-(4-nitrobenzylidene)malononitrile (3ad)**



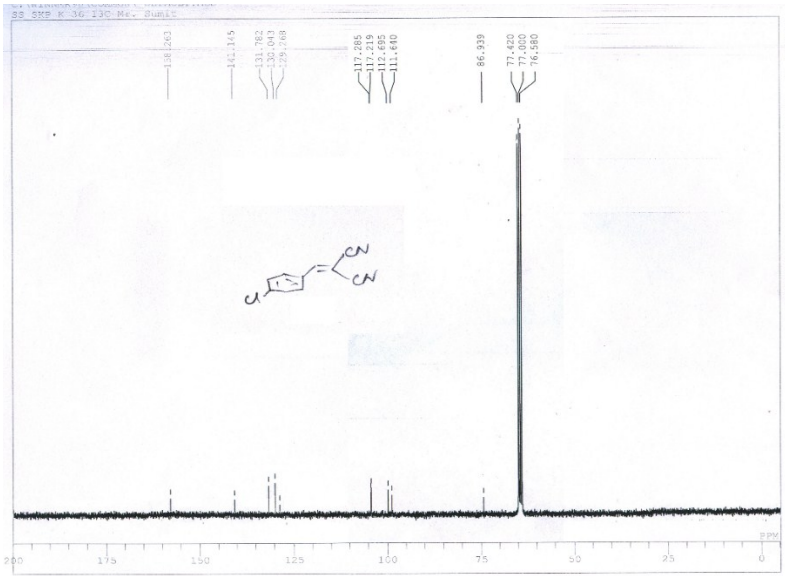
**$^{13}$C-NMR of 2-(4-nitrobenzylidene)malononitrile (3ad)**



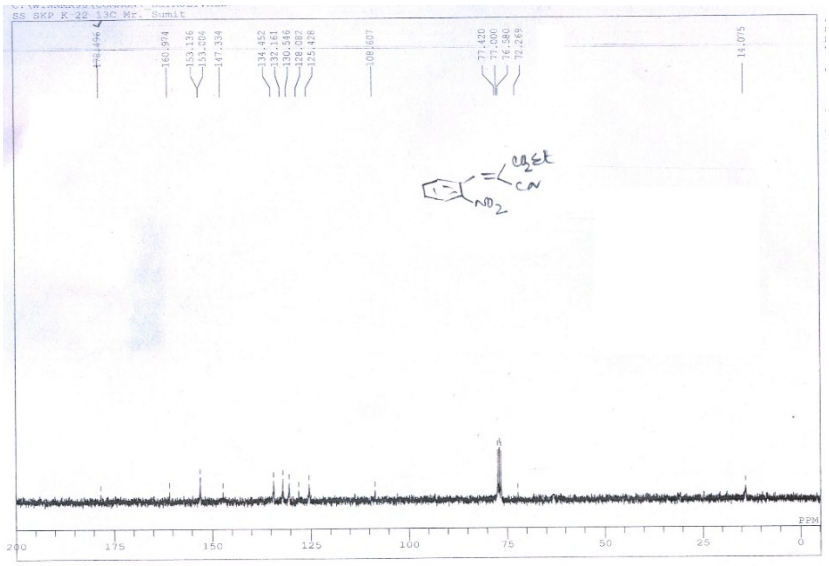
**$^{1}$H-NMR of 2-(4-chlorobenzylidene)malononitrile (3ae)**



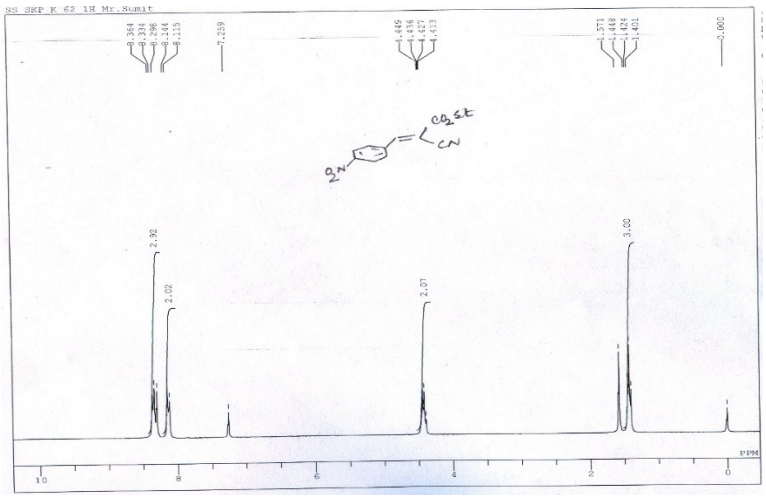
**$^{13}$C-NMR of 2-(4-chlorobenzylidene)malononitrile (3ae)**



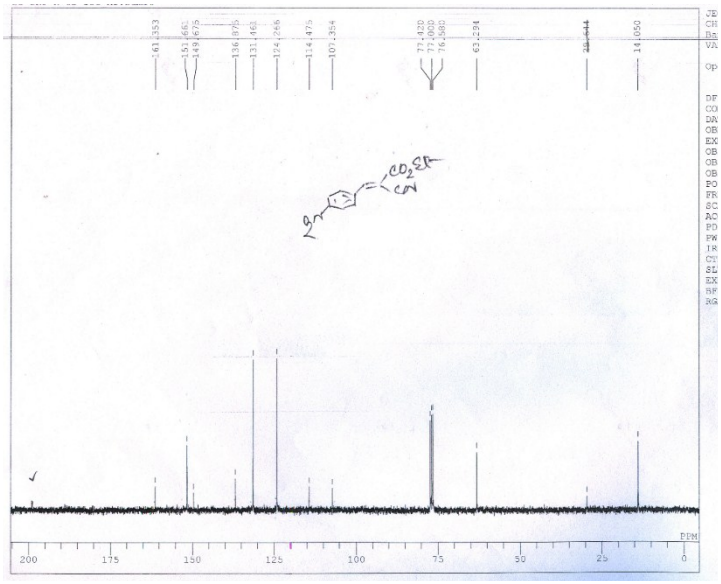
**$^{13}$C-NMR of (E/Z)-ethyl-2-cyano-3-(2-nitrophenyl)acrylate (3bb)**



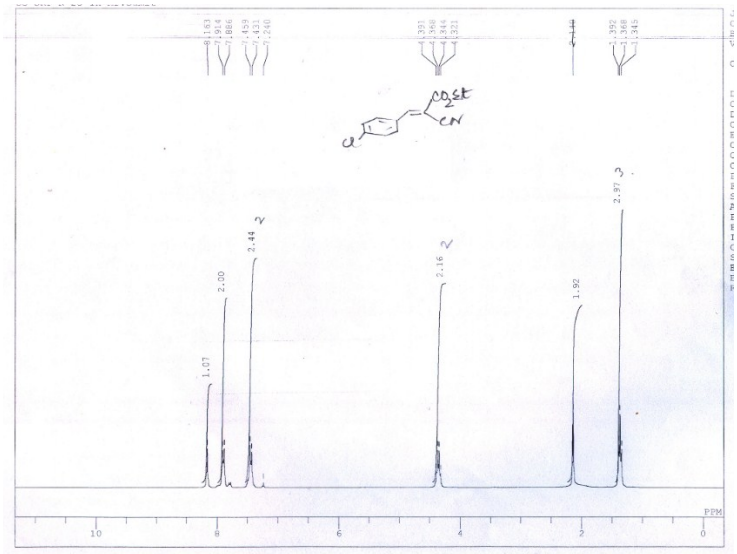
**$^{1}$H-NMR of (E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)**



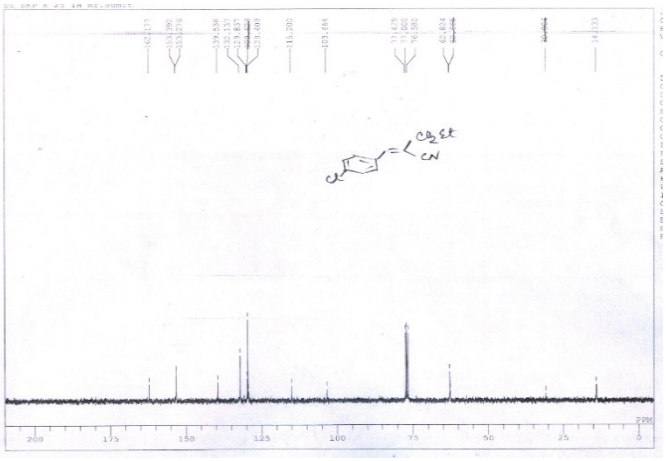
**$^{13}$C-NMR of (E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)**



**$^{1}$H-NMR of (E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)**



**$^{13}$C-NMR of (E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)**



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