Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Successive Oxidation- Condensation Reactions using Multifunctional Gold supported Nanocomposite (Au/MgCe-HDO)

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 # Under Mentorship Program for College Teachers

Supporting Information:

Reaction Procedure for oxidation of benzyl alcohol

For every reaction, Schlenk tube was taken alongwith 0.5 mmol alcohol, 50 mg catalyst and 3mL toluene was taken as solvent. The reaction mixture was then stirred vigorously at 373 K for 2-3 hours. The resulting reaction mixture was then filtered for the removal of catalyst. The filtrate was then dried over anhydrous sodium sulphate. The purification was done using 5% (v/v) ethyl acetate/hexane as eluent to obtain the desired product. The final product was characterized with ^{1}H-NMR and ^{13}C-NMR.

Reaction Procedure for Successive oxidation-condensation reaction with malononitrile/ethyl cyanoacetate/acetophenone.

For every reaction, Schlenk tube was taken along with 0.5 mmol alcohol, 50 mg catalyst and 3mL toluene was taken as solvent. The reaction mixture was then stirred vigorously at 373 K for 4-6 hours. Add 1mmol malononitrile/ethyl cyanoacetate/acetophenone after formation of corresponding aldehyde as suggested by TLC technique. The resulting reaction mixture was then filtered for the removal of catalyst. The filtrate was then dried over anhydrous sodium sulphate. The purification was done using 5% (v/v) ethyl acetate/hexane as eluent to obtain the desired product. The final product was characterized with ^{1}H-NMR and ^{13}C-NMR.

Calculation for yield:

$$\text{Yield (\%)} = \frac{amount\ of\ product\ formed\ (in\ mmol)}{amount\ of\ reactant\ taken\ (in\ mmol)}\ x\ 100$$

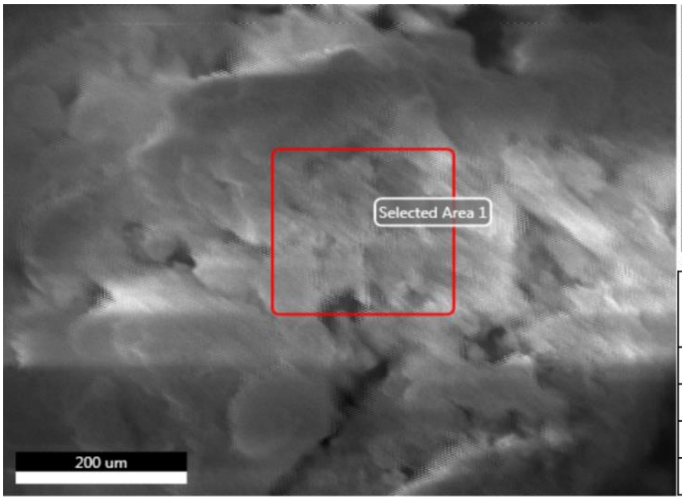
Calculation for metal loading:

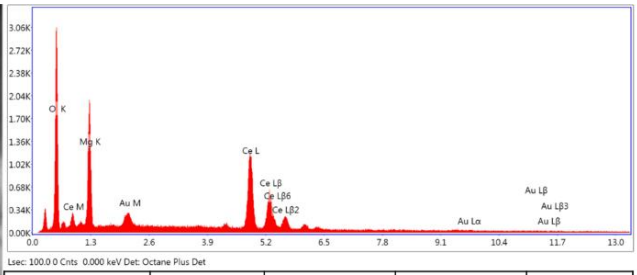
$$\text{Metal loading} = \frac{Concentration\ of\ metal\ (ppm)\ X\ Volume\ of\ extract\ (Litre)}{Weight\ of\ solid\ sample\ taken\ for\ extraction\ (grams)}$$

Calculation for mol% of catalyst:

$$\text{Mol \% of catalyst used} = \frac{no.of\ moles\ of\ catalyst\ used}{(no.\ of\ moles\ of\ catalyst\ used + no.of\ moles\ of\ limiting\ reagent)}\ \text{X } 100$$

SEM-EDX data



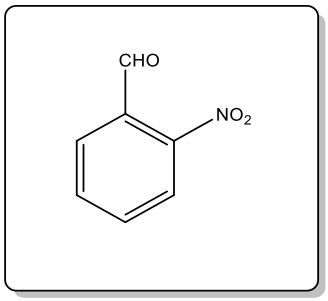


Element	Weight %	Atomic %	Net Int.	Error %
O K	30.83	61.87	227.74	7.33
MgK	20.69	27.32	172.49	9.05
CeL	43.78	10.03	166.44	3.38
AuL	4.71	0.77	3.89	46.87

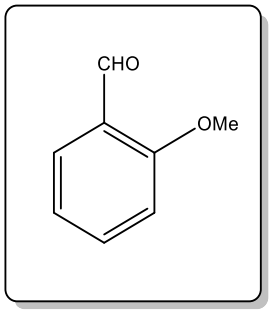
Figure- S1 SEM-EDX of Au/MgCe-HDO nanocomposite., Spectrum, Table of SEM-EDS

NMR spectra:

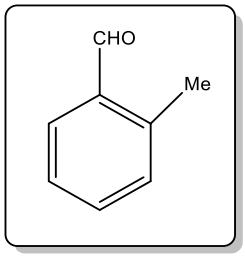
(2a) 2-nitrobenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.43 (s, 1H), 8.13 (dd, J = 7.6, 1.1 Hz, 1H), 7.96 (dd, J = 7.4, 1.6 Hz, 1H), 7.85-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.152, 149.575, 134.081, 133.712, 131.337, 129.626, 124.492



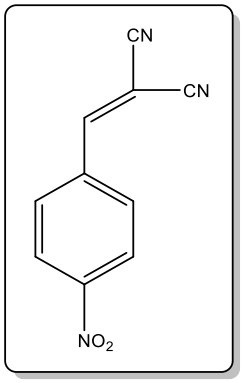
(2d) 2-methoxybenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.88 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.817, 164.607, 131.972, 129.936, 114.409, 55.576



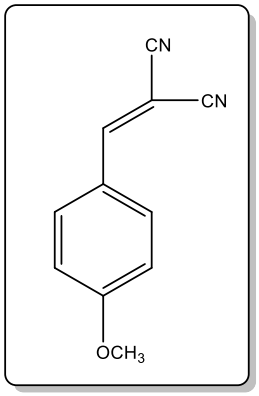
(2g) 2-methylbenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.29 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.50 (td, J = 7.5, 1.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 2.71-2.68 (3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.817, 140.622, 134.153, 133.647, 132.045, 131.770, 126.326, 19.590



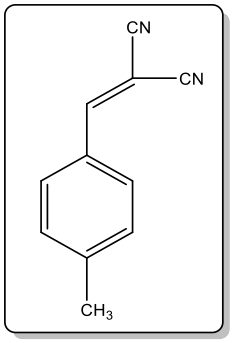
(4b) 2-(4-nitrobenzylidene)malononitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.37 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H), 7.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.021, 150.426, 135.886, 131.419, 124.739, 112.729, 111.703, 87.597



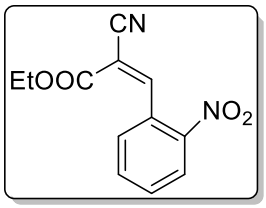
(4e) 2-(4-methoxybenzylidene)malononitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, J = 8.9 Hz, 2H), 7.64 (s, 1H), 7.00 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.928, 159.014, 133.576, 124.106, 115.230, 114.550, 113.467, 78.568, 55.919.



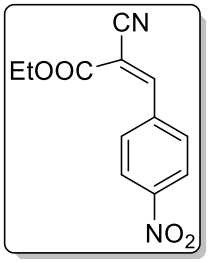
(4h) 2-(4-methylbenzylidene)malononitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, J = 8.0 Hz, 2H), 7.74 (s, 1H), 7.41-7.32 (2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.842, 146.427, 130.940, 130.398, 128.478, 114.059, 112.904, 81.135, 22.038



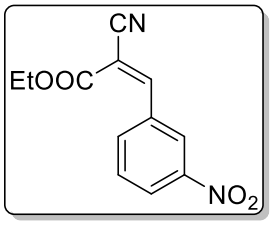
(6a) ethyl (Z)-2-cyano-3-(2-nitrophenyl)acrylate: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.74 (s, 1H), 8.30 (d, J = 8.3 Hz, 1H), 7.92-7.80 (m, 2H), 7.74 (t, J = 7.1 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.034, 153.135, 147.380, 134.521, 132.211, 130.608, 128.131, 125.438, 113.915, 108.644, 63.186, 14.117



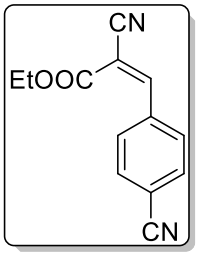
(6b) ethyl (Z)-2-cyano-3-(4-nitrophenyl)acrylate: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.33 (d, J = 8.7 Hz, 2H), 8.29 (s, 1H), 8.12 (d, J = 8.8 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.395, 151.705, 149.727, 136.904, 131.496, 124.312, 114.514, 107.409, 63.345, 14.110



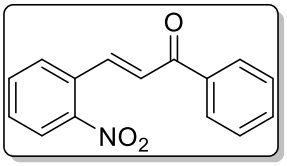
(6c) ethyl (Z)-2-cyano-3-(3-nitrophenyl)acrylate: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.68 (s, 1H), 8.44-8.34 (m, 2H), 8.29 (s, 1H), 7.72 (t, J = 8.0 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.550, 151.948, 148.661, 135.274, 132.955, 130.636, 127.148, 125.988, 114.633, 106.698, 63.356, 14.187



(6d) ethyl (Z)-2-cyano-3-(4-cyanophenyl)acrylate: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) δ 8.23 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.598, 152.341, 135.322, 132.936, 131.086, 117.786, 116.070, 114.700, 106.852, 63.356, 14.187



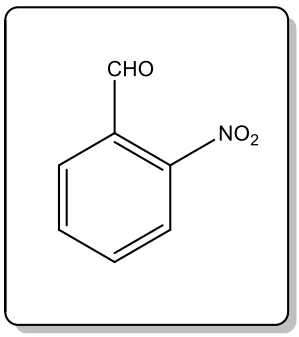
(8a) (E)-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one: ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, J = 15.8 Hz, 1H), 8.06 (dd, J = 8.2, 1.1 Hz, 1H), 8.03-7.98 (m, 2H), 7.73 (dd, J = 7.8, 1.4 Hz, 1H), 7.71-7.65 (m, 1H), 7.62-7.55 (m, 2H), 7.55-7.48 (m, 2H), 7.31 (d, J = 15.8 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.624, 148.623, 140.334, 137.478, 133.693, 133.271, 131.451, 130.464, 129.361, 128.902, 128.834, 127.445, 125.116.

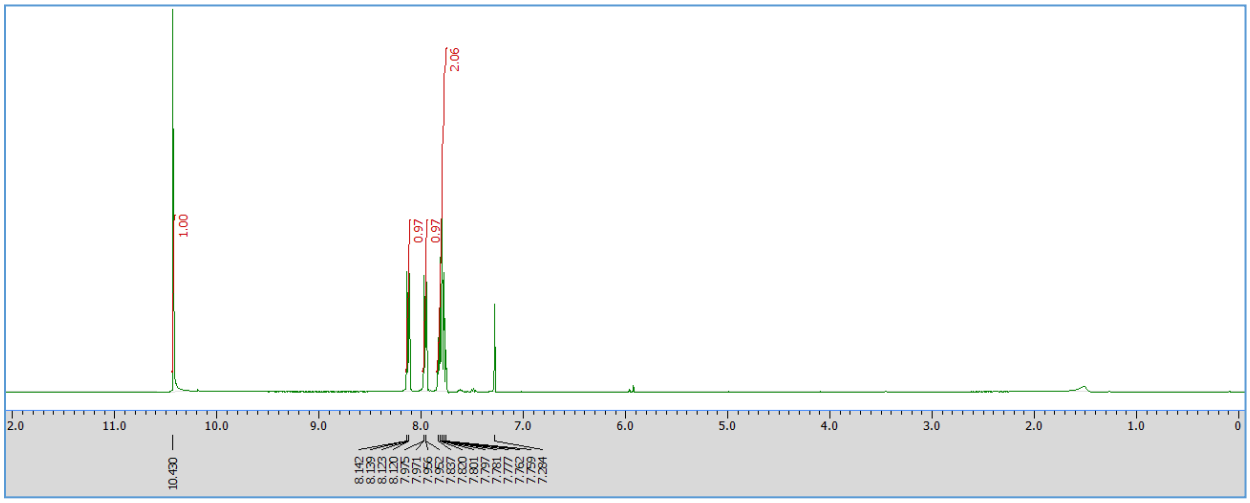


NMR Spectra:

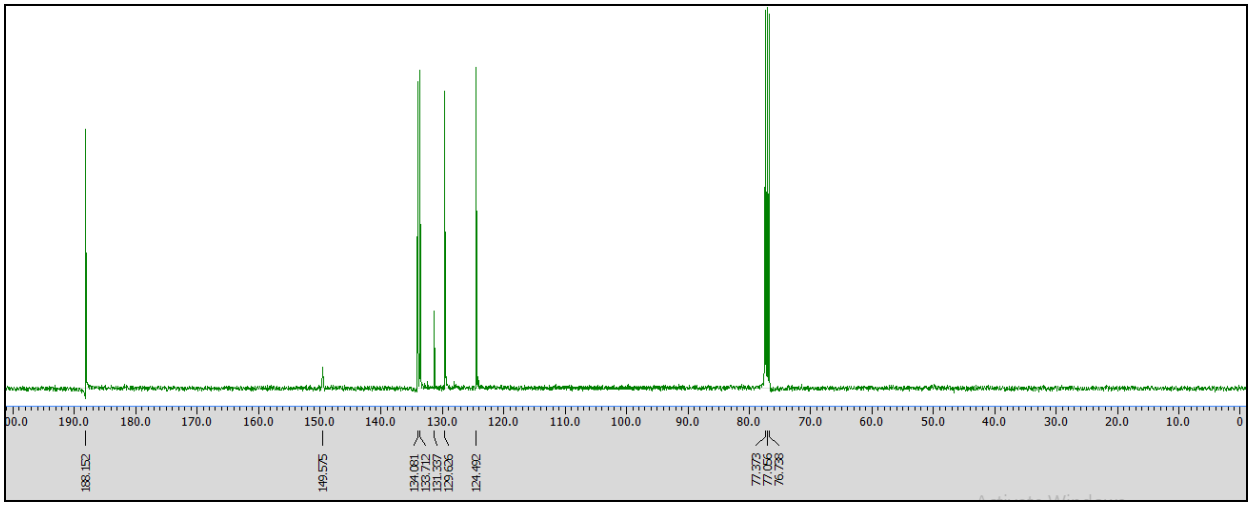
(2a) 2-nitrobenzaldehyde:

^{1}H NMR ($CDCl_3$, 400 MHz)

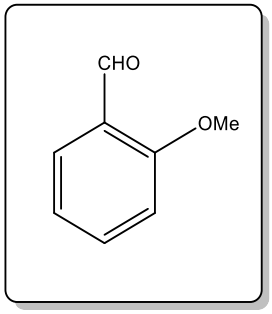




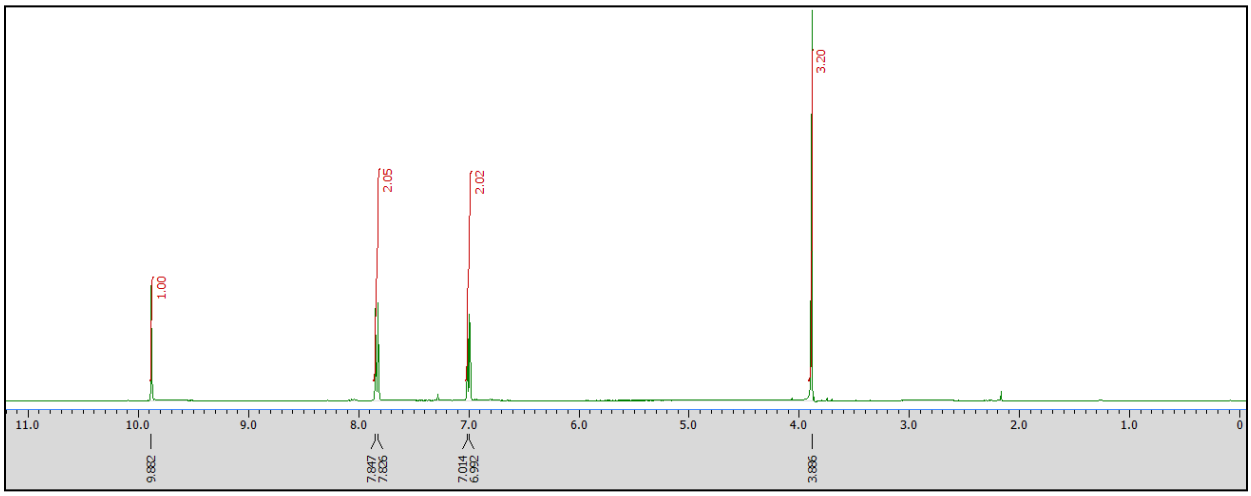
^{13}C NMR ($CDCl_3$, 100 MHz)



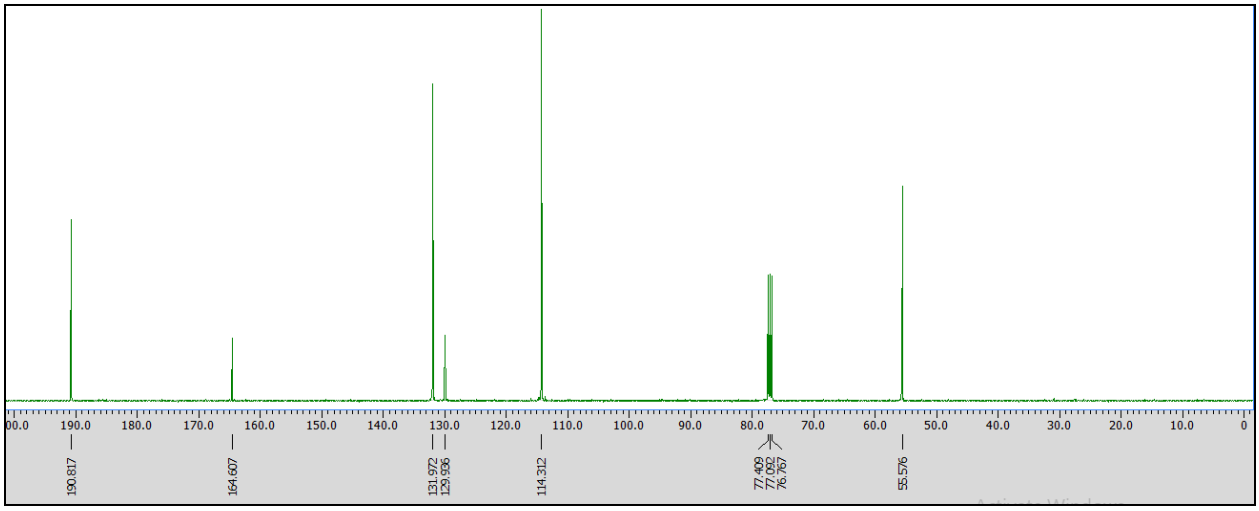
(2d) 2-methoxybenzaldehyde:



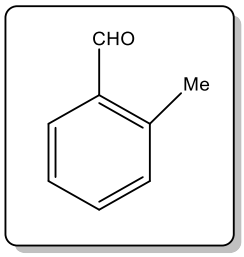
^{1}H NMR ($CDCl_3$, 400 MHz)



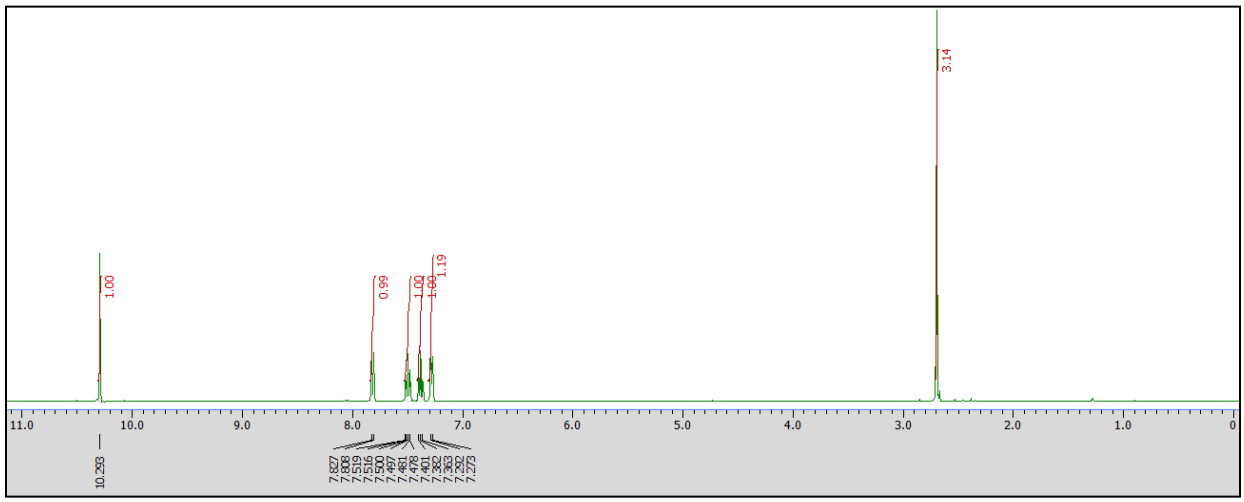
^{13}C NMR ($CDCl_3$, 100 MHz)



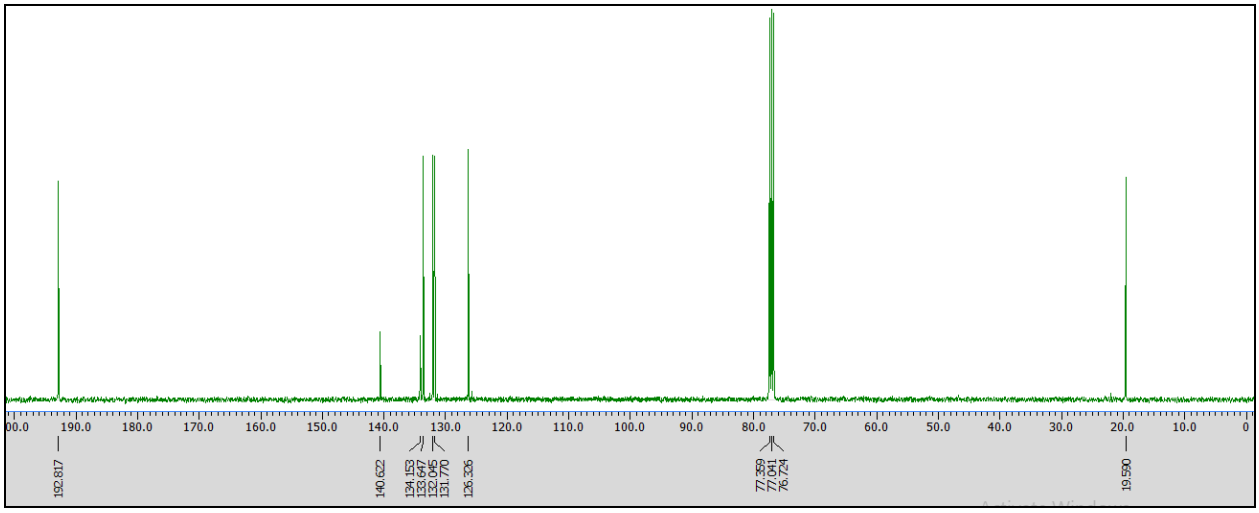
(2g) 2-methylbenzaldehyde:



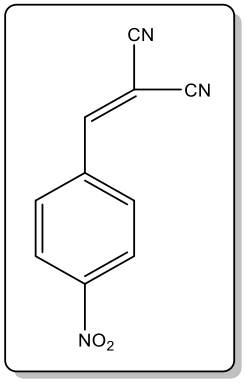
^{1}H NMR ($CDCl_3$, 400 MHz)



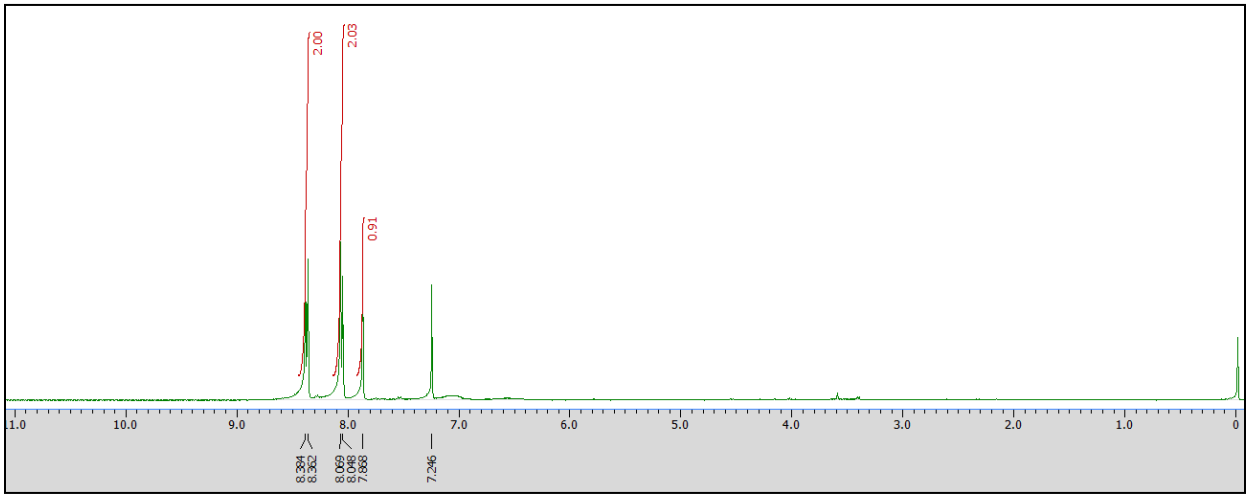
^{13}C NMR ($CDCl_3$, 100 MHz)



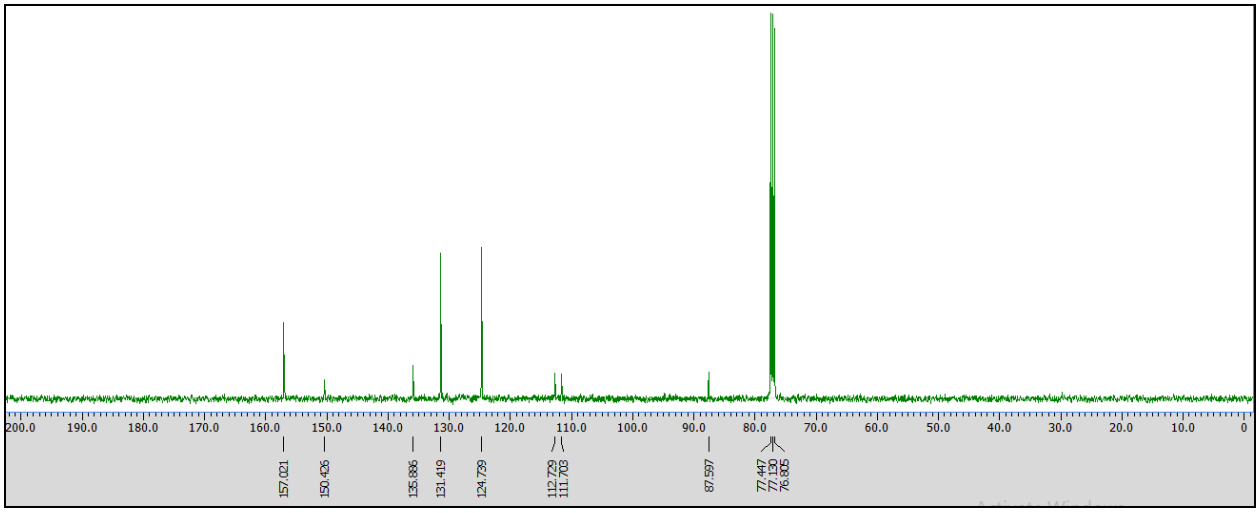
(4b) 2-(4-nitrobenzylidene)malononitrile:



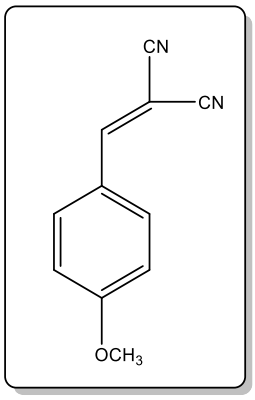
^{1}H NMR ($CDCl_3$, 400 MHz)



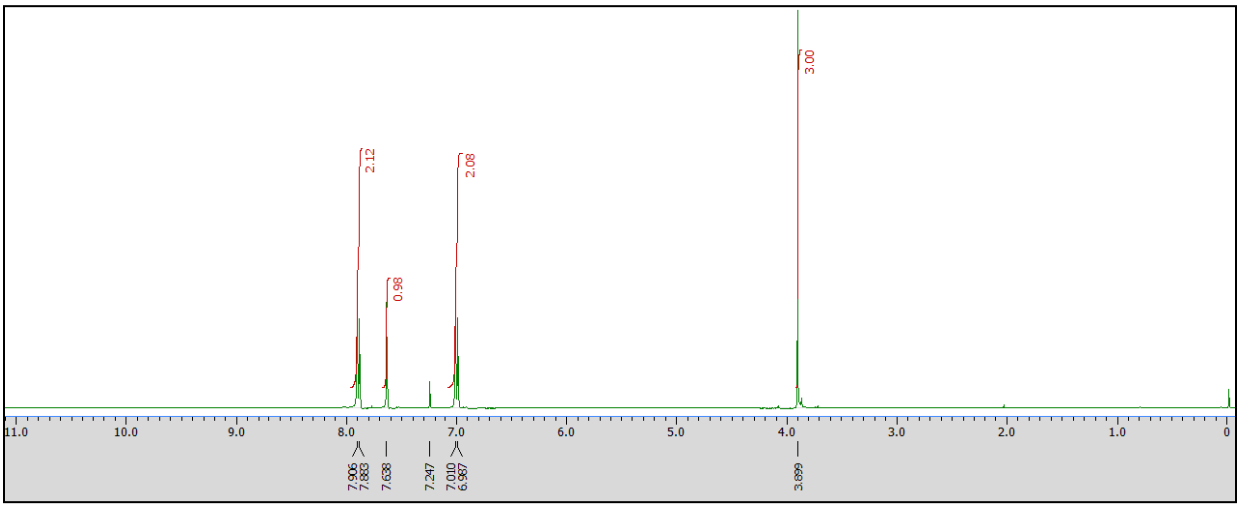
^{13}C NMR ($CDCl_3$, 100 MHz)



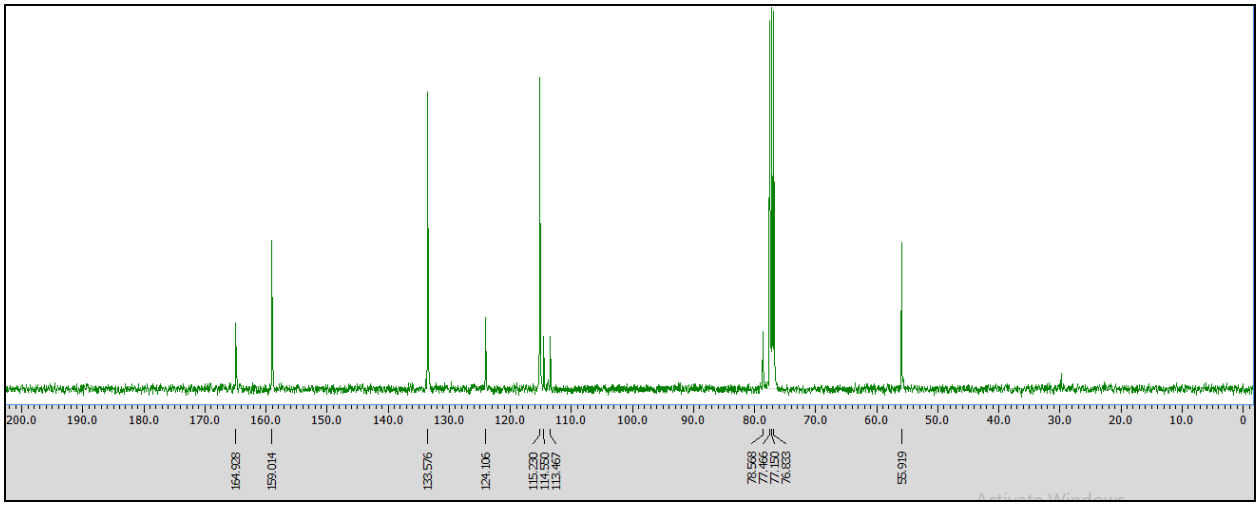
(4e) 2-(4-methoxybenzylidene)malononitrile:



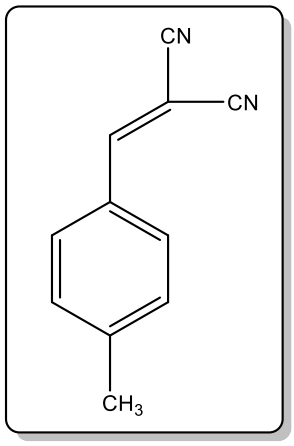
^{1}H NMR ($CDCl_3$, 400 MHz)



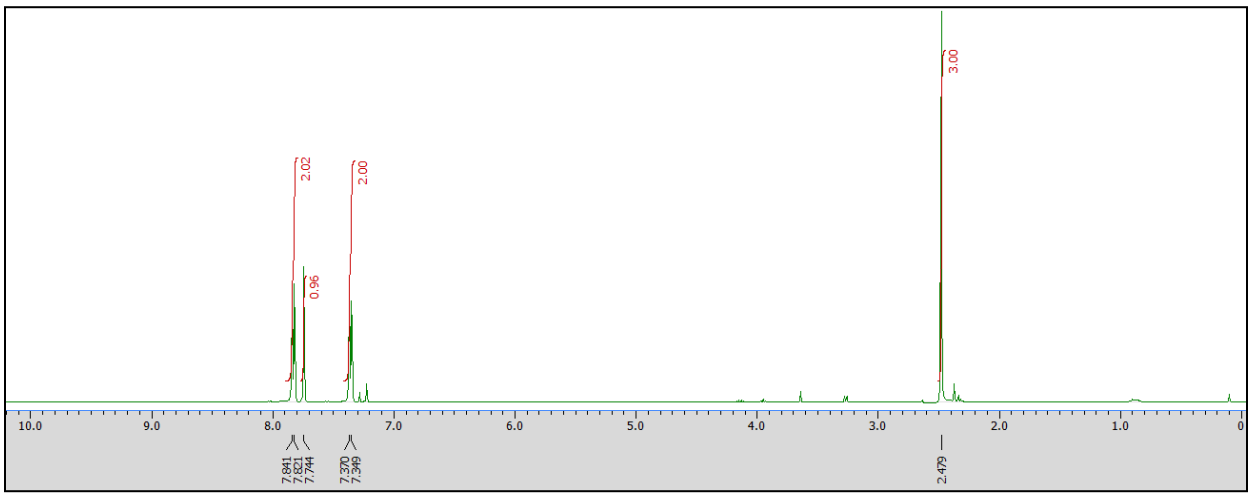
^{13}C NMR ($CDCl_3$, 100 MHz)



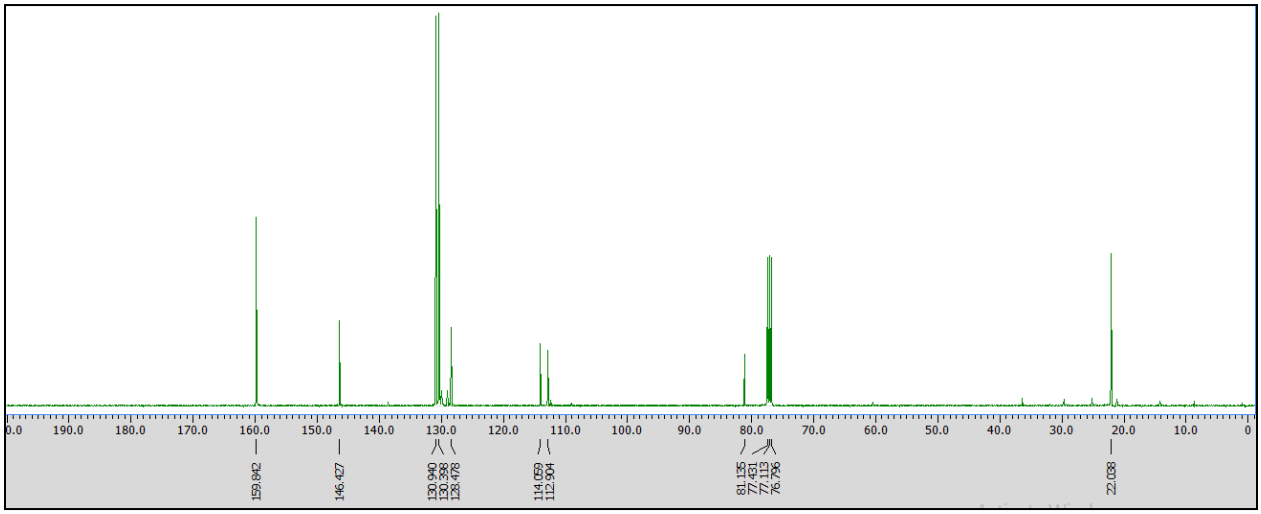
(4h) 2-(4-methylbenzylidene)malononitrile:



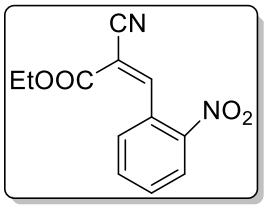
^{1}H NMR ($CDCl_3$, 400 MHz)



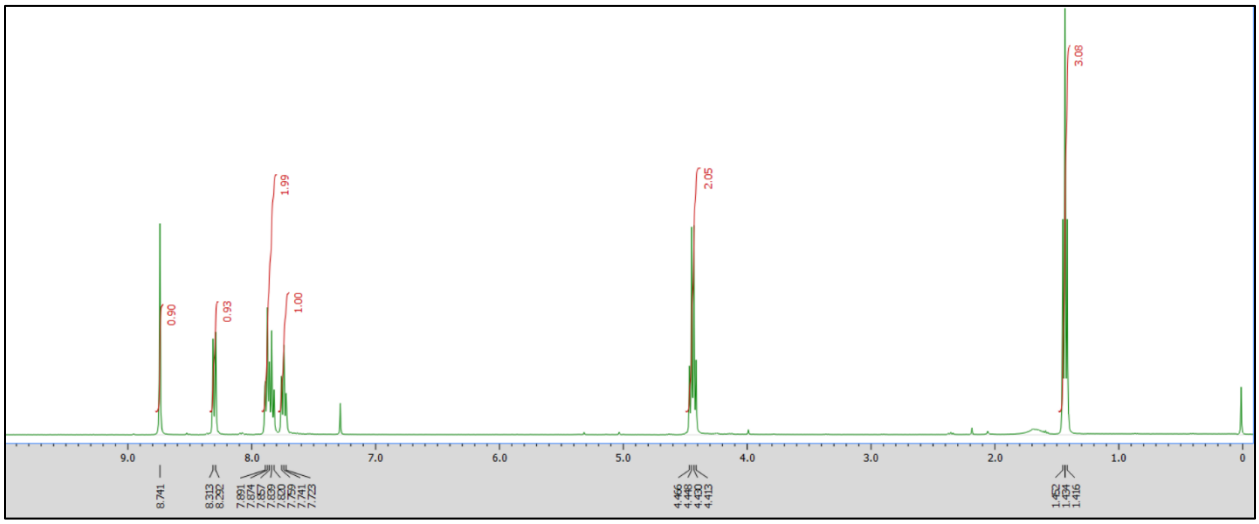
^{13}C NMR ($CDCl_3$, 100 MHz)



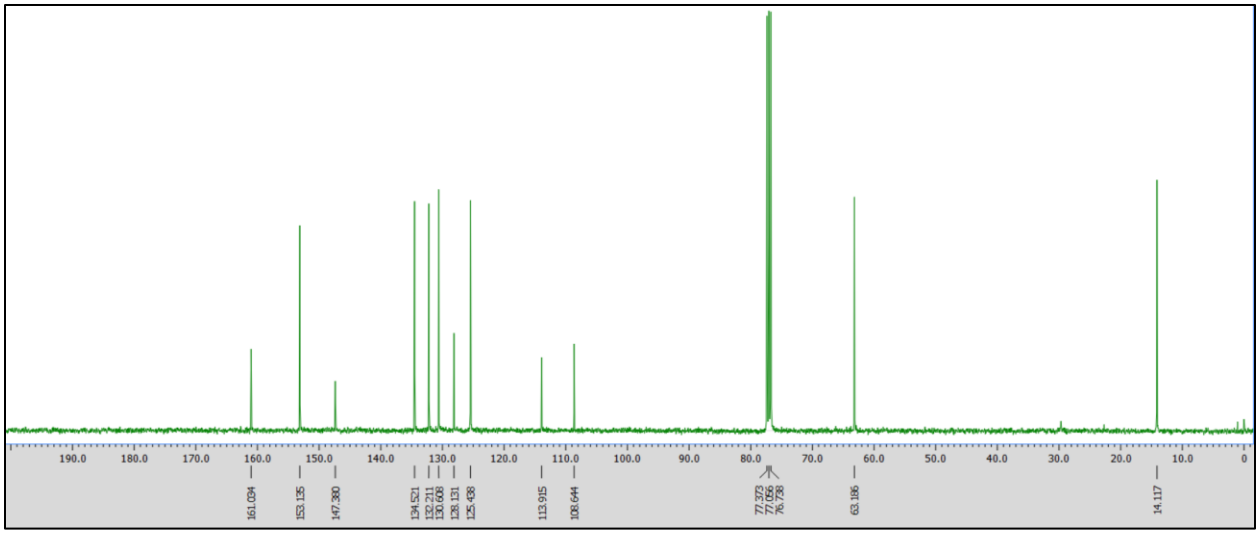
(6a) ethyl (Z)-2-cyano-3-(2-nitrophenyl)acrylate



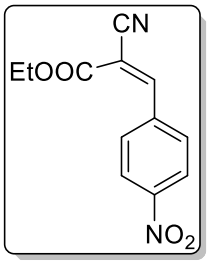
^{1}H NMR ($CDCl_3$, 400 MHz)



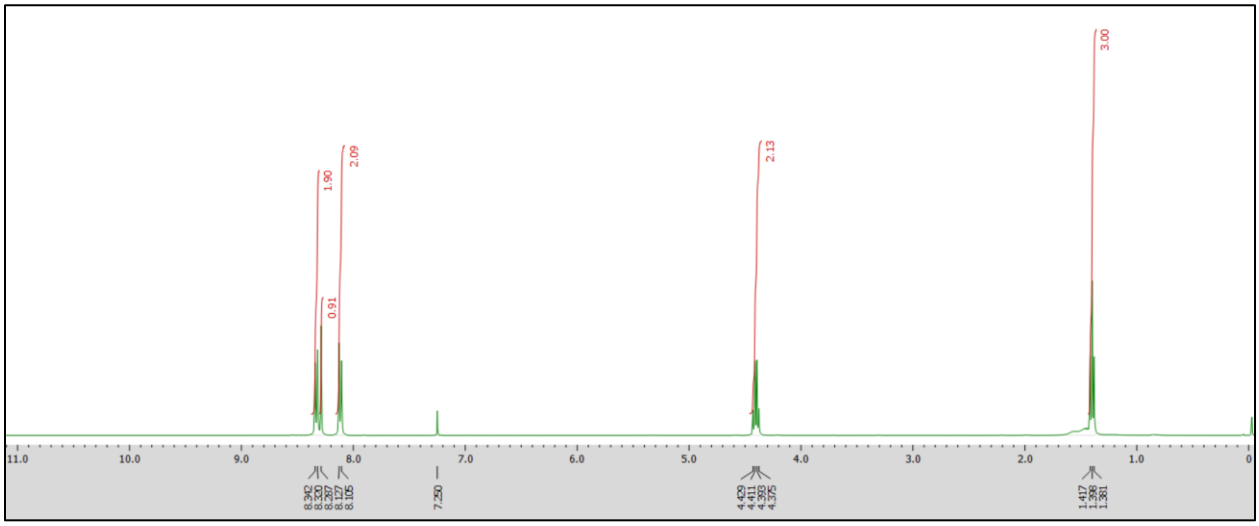
^{13}C NMR ($CDCl_3$, 100 MHz)



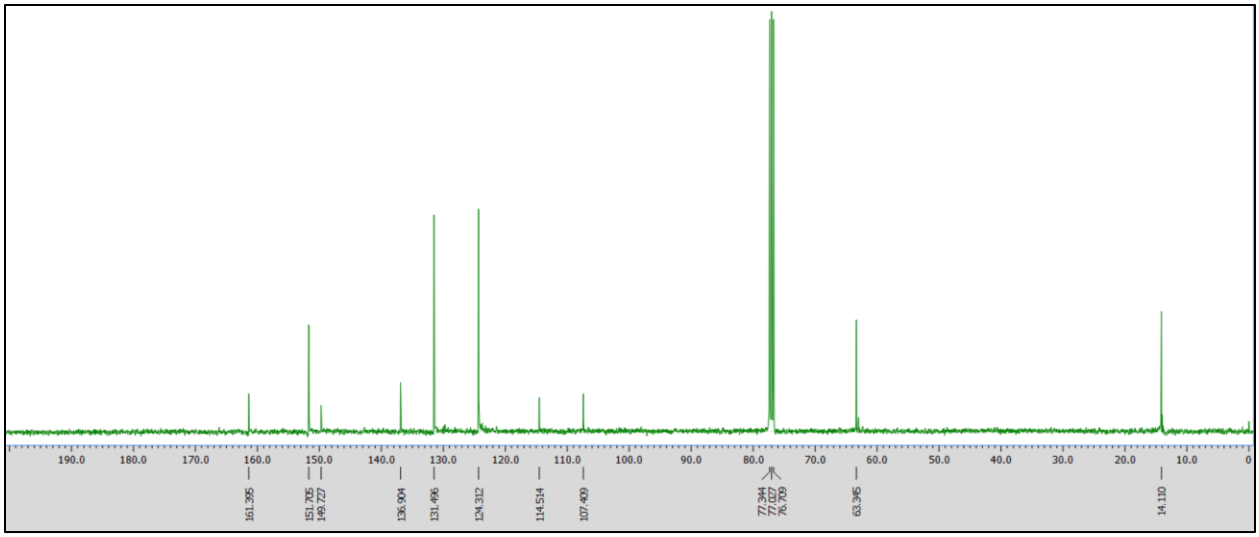
(6b) ethyl (Z)-2-cyano-3-(4-nitrophenyl)acrylate



^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)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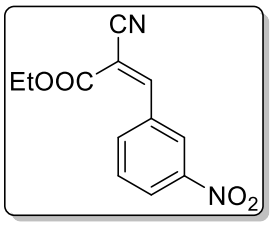
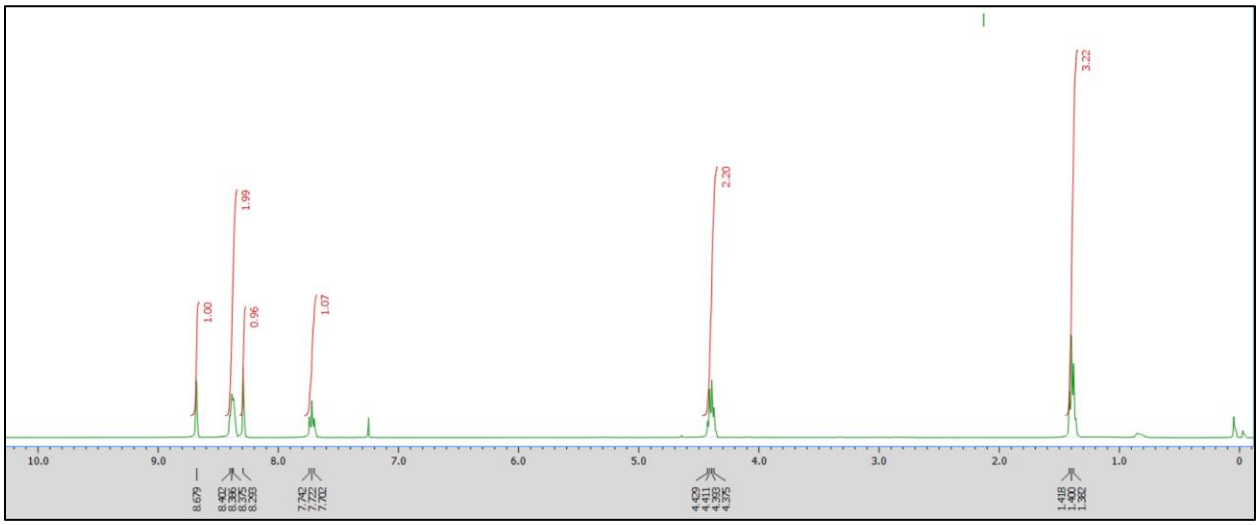
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.395
151.705
149.727
136.904
131.496
124.312
114.514
107.409
77.344
77.027
76.709
63.345
14.110

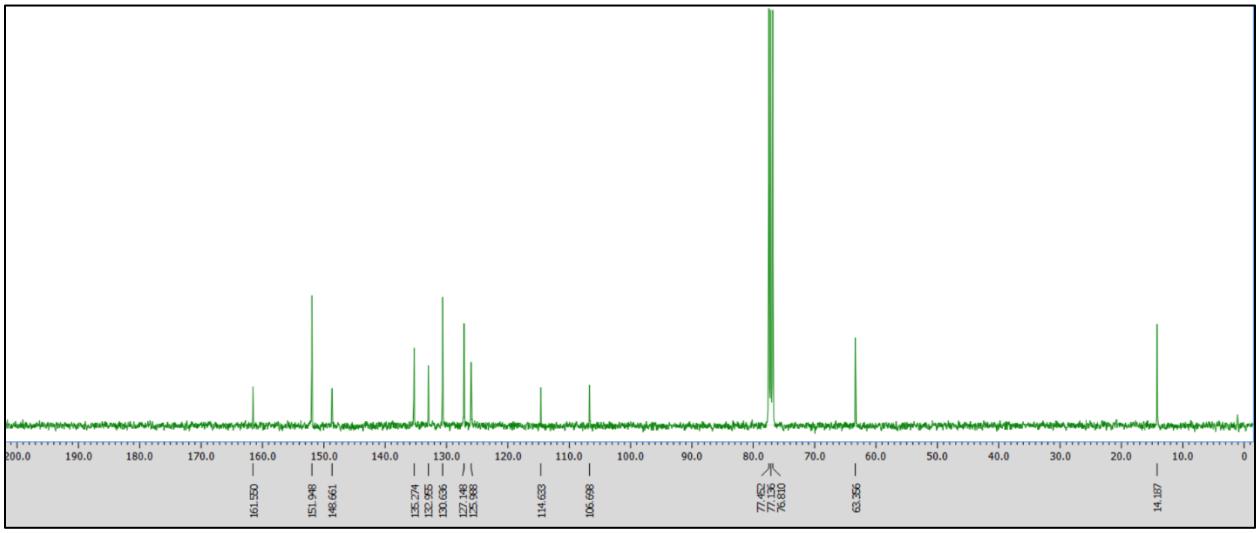
(6c) ethyl (Z)-2-cyano-3-(3-nitrophenyl)acrylate



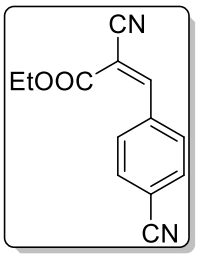
^{1}H NMR ($CDCl_3$, 400 MHz)



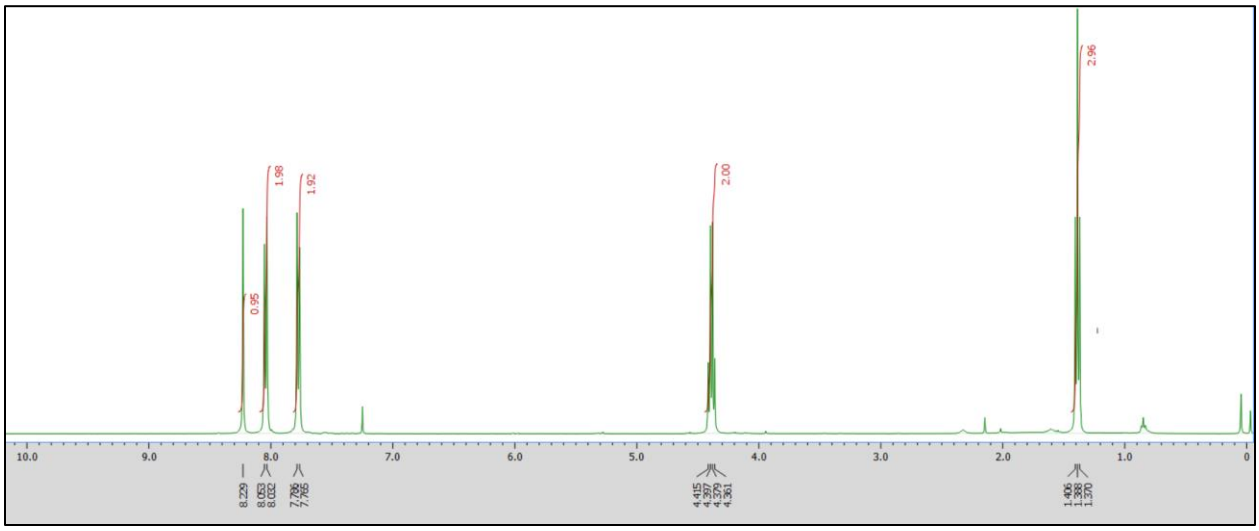
^{13}C NMR ($CDCl_3$, 100 MHz)



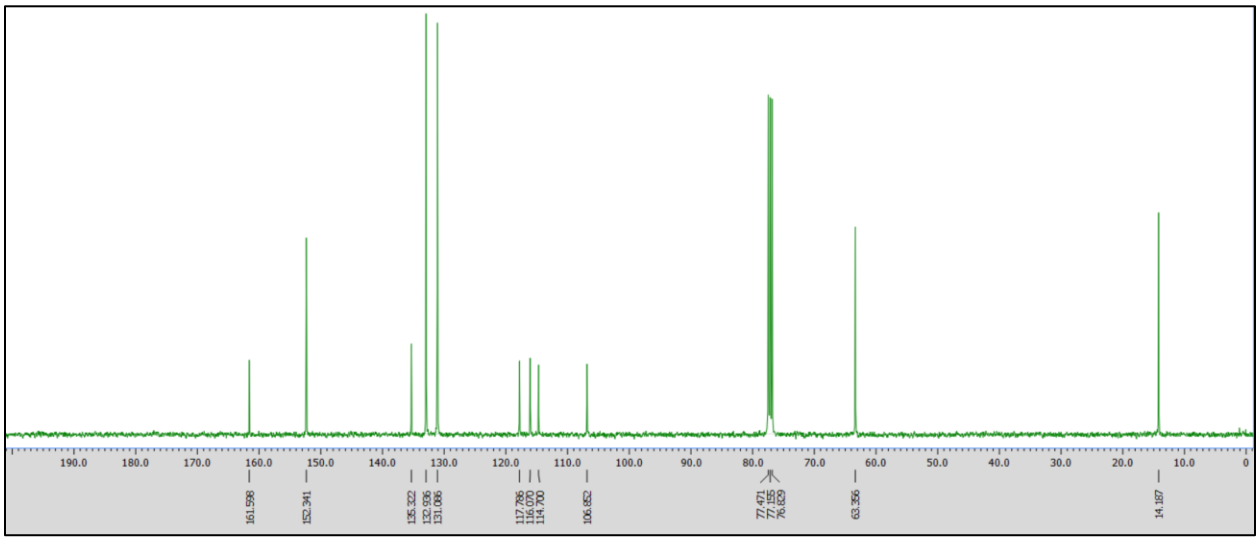
(6d) ethyl (Z)-2-cyano-3-(4-cyanophenyl)acrylate



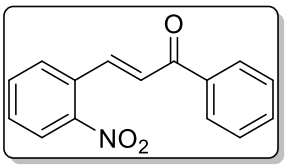
^{1}H NMR ($CDCl_3$, 400 MHz)



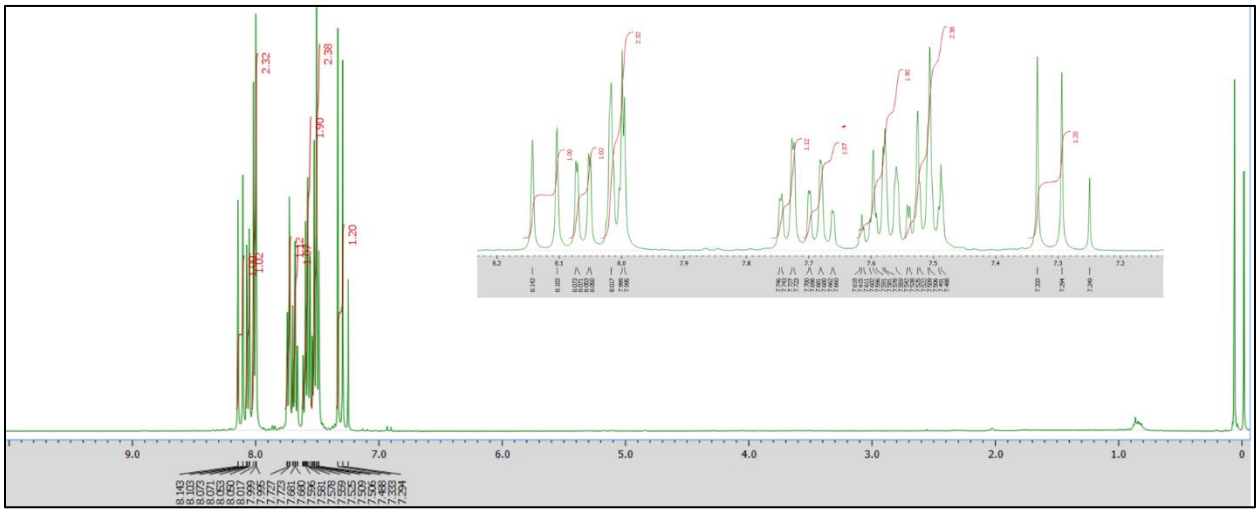
^{13}C NMR ($CDCl_3$, 100 MHz)



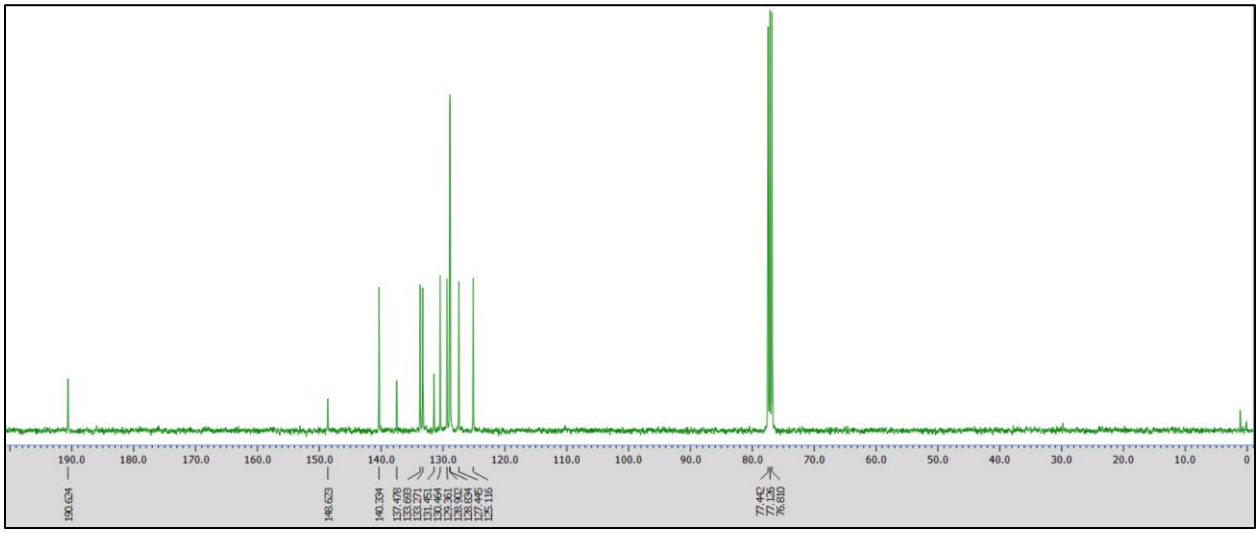
(8a) (E)-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one



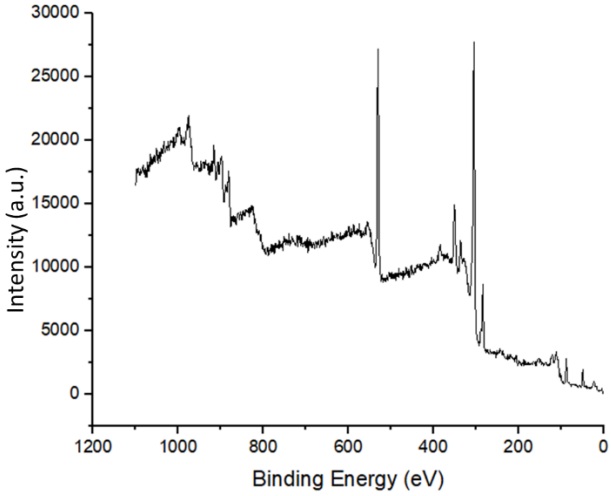
^{1}H NMR ($CDCl_3$, 400 MHz)



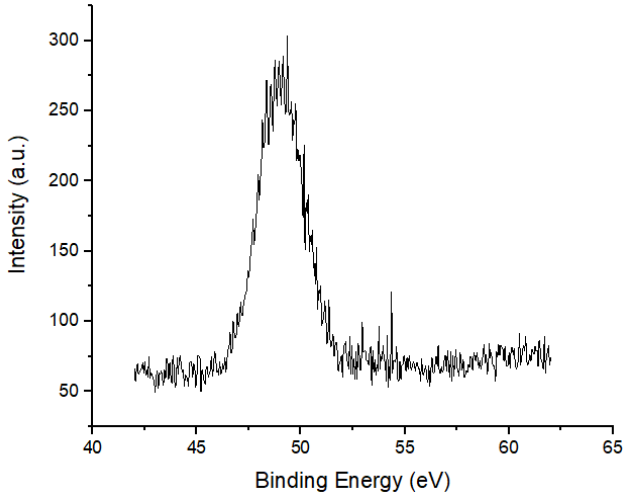
^{13}C NMR ($CDCl_3$, 100 MHz)



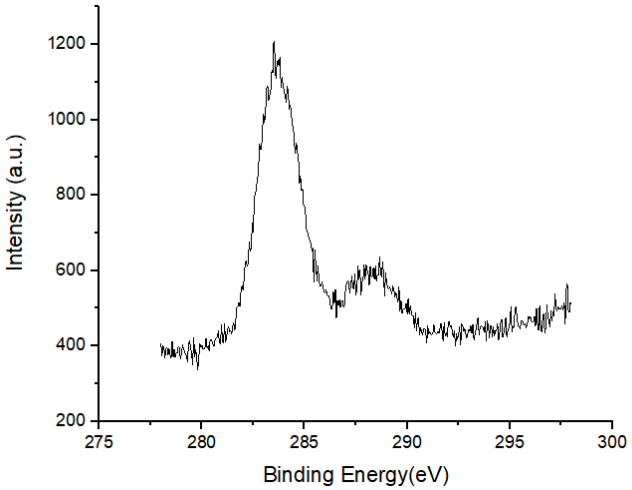
XPS of Au/MgCe-HDO catalyst



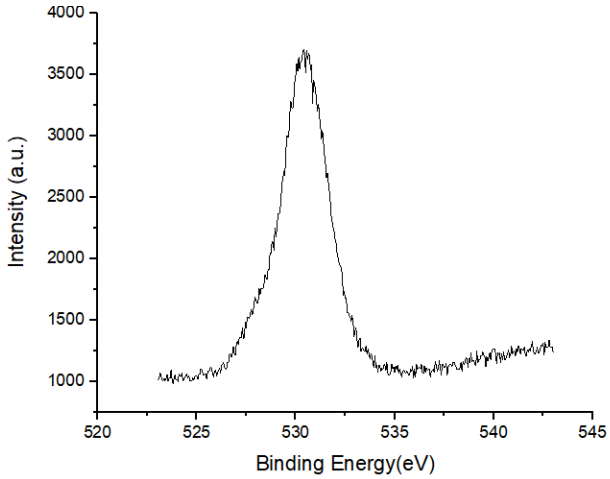
XPS narrow scan of Mg for Au/MgCe-HDO catalyst.



XPS narrow scan of C for Au/MgCe-HDO catalyst



XPS narrow scan of O for Au/MgCe-HDO catalyst



XPS narrow scan of Ce for Au/MgCe-HDO catalyst.