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Supporting Material

Synthesis of a Thermostable Polymer-Supported Strongly

Basic Catalyst and its Catalytic Activity

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1. Determination of chlorine content in solid-supported strong basic catalyst

An accurately weighted 0.2g sample of the resin was placed in the dry crucible and added appropriate amount of KNO₃ and NaOH followed by burning the reagents to melt in the alcohol burner. After the crucible was cooled down to room temperature, it was placed in the beaker containing 200mL of distilled water and heated to make the product dissolve in the solution. The crucible was drawn off the solution and washed with distilled water in which 200mL of distilled water was merged. The pH value of the solution was neutral by the addition of nitric acid using phenolphthalein as indicator. After that, 1N AgNO₃ solution was added quantitatively till the precipitated was no longer produced. The mixture was titrated with KSCN solution by Volhard method. Chlorine content was determined by the following formula:

$$Cl\% = \frac{(V_1C_1 - V_2C_2) \times 35.46}{m \times 1000} \times 100\%$$

Where V_1 and V_2 are the volumes of AgNO₃ and KSCN (mL). C_1 and C_2 are the concentrations of AgNO₃ and KSCN (mol/L); m is the weight of resin (g).

2. Characterization data of the reaction products

2-phenylmethylene-malononitrile (Entry 1, Table 5): White solid; m.p. 82-84°C. IR (KBr, V_{max}/cm^{-1}): 3032(=C-H), 2223 (CN), 1591, 1567, 1450, 1218, 958, 755, 678. ¹H NMR (400MHZ, CDCl₃, ppm): δ_H 7.54 (t, J=7.6Hz, 2H, ArH), 7.63 (t, J=7.6Hz, 1H, ArH), 7.77 (s, 1H, CH=), 7.90 (d, J=8Hz, 2H,

ArH). EI-MS m/z (%): 154.1 (M^+ 100), 127.1 (55), 103.1 (52), 76.0 (14), 50.0 (24), 39.0 (20).

Ethyl-2-cyano-3-phenyl-2-propenoate (Entry 2, Table 5): White solid; m.p. 50-52°C. IR (KBr, V_{max}/cm^{-1}): 3030(=C-H), 2223 (CN), 1726 (C=O), 1607, 1573, 1445, 1255, 1200 (C-O), 768, 684. 1H NMR (400MHZ, $CDCl_3$, ppm): δ_H 1.40 (t, $J=7.1Hz$, 3H, CH_3CH_2O), 4.39 (q, $J=7.1Hz$, 2H, CH_3CH_2O), 7.51-7.56 (m, 3H, ArH), 7.99 (d, $J=7.6Hz$, 2H, ArH), 8.26 (s, 1H, $CH=$). EI-MS m/z (%): 201.0 (M^+ 90), 172.0 (53), 156.0 (100), 102.0 (48), 77.0 (54), 51.0 (40), 29 (57).

Ethyl-2-cyano-3-(4-hydroxyphenyl)-2-propenoate (Entry 3, Table 5): Yellow solid; m.p. 171-172°C. IR (KBr, V_{max}/cm^{-1}): 3287(OH), 2231 (CN), 1714 (C=O), 1587, 1291, 1175 (C-O), 836. 1H NMR (400MHZ, $CDCl_3$, ppm): δ_H 1.39 (t, $J=7.1Hz$, 3H, CH_3CH_2O), 4.37 (q, $J=7.1Hz$, 2H, CH_3CH_2O), 6.10 (s, 1H, OH), 6.97 (d, $J=8.7Hz$ 2H, ArH), 7.96 (d, $J=8.7Hz$, 2H, ArH), 8.19 (s, 1H, $CH=$). EI-MS m/z (%): 217.0 (M^+ 100), 172.0 (83), 144.0 (28), 118.0 (14), 89.0 (27), 39.0 (23), 29.0 (42). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35%; H, 5.10%; N, 6.45%. Found: C, 66.38%; H, 5.29%; N, 6.48%.

Ethyl-2-cyano-3-(4-nitrophenyl)-2-propenoate (Entry 4, Table 5): Yellow solid; m.p. 168-169°C. IR (KBr, V_{max}/cm^{-1}): 2226(CN), 1720 (CO), 1616, 1593, 1514 (NO_2), 1347 (NO_2), 1266, 1202 (C-O), 859, 831. 1H NMR (400MHZ, DMSO- d_6 , ppm): δ_H 1.34 (t, $J=7.2Hz$, 3H, CH_3CH_2O), 4.36 (q, $J=7.2Hz$, 2H, CH_3CH_2O), 8.25 (d, $J=8.9Hz$ 2H, ArH), 8.41 (d, $J=8.9Hz$, 2H, ArH), 8.56 (s, 1H, $CH=$). EI-MS m/z (%): 246.0 (M^+ 36), 218.0 (48), 201.0 (42), 173.0 (12), 155.0 (24), 127.0 (22), 29 (100). Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.54%; H, 4.09%; N, 11.38%. Found: C, 58.57%; H, 4.20%; N, 11.45%.

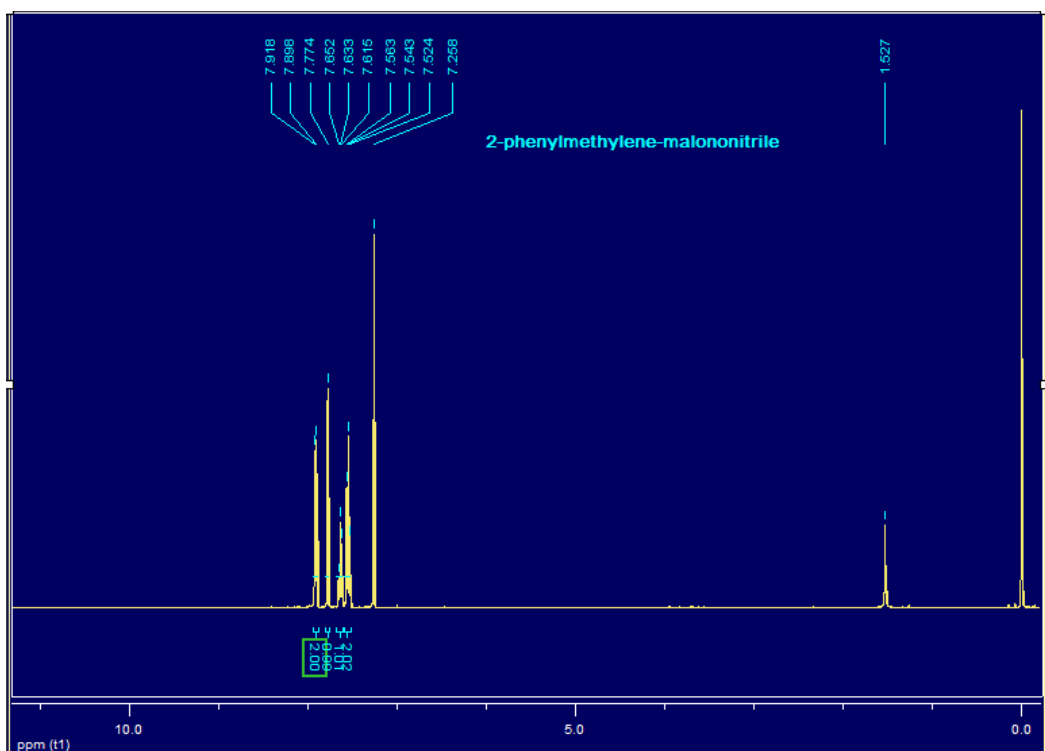
Ethyl-2-benzylideneacetoacetate (Entry 5, Table 5): Light yellow solid; m.p. 45-46°C. IR (KBr, V_{max}/cm^{-1}): 3059(=C-H), 1731 (O-C=O), 1695 (C=O), 1665, 1624, 1397, 1207, 757, 693. 1H NMR (400MHZ, $CDCl_3$, ppm): δ_H 1.27

(t, J=6.8Hz, 3H, CH₃CH₂O), 2.42 (s, 3H, CH₃CO), 4.33 (q, J=6.8Hz, 2H, CH₃CH₂O), 7.26-7.44 (m, 5H, ArH), 7.57 (s, 1H, CH=). EI-MS m/z (%): 218.0 (M⁺ 50), 173.0 (20), 131.0 (43), 103.0 (26), 77.0 (19), 43.0 (100), 29 (50).

2-cyclohexylidenemalononitrile (Entry 6, Table 5): Light yellow oil. IR (KBr, V_{max}/cm^{-1}): 2944 (C-H), 2230 (CN), 1594, 1449, 1352, 1004, 858. ¹H NMR (400MHz, CDCl₃, ppm): δ_H 1.68-1.70 (m, 2H, 2CH₂CH₂CH₂C=), 1.78-1.82 (m, 4H, 2CH₂CH₂C=), 2.66 (t, J=6.1Hz, 4H, 2CH₂C=). EI-MS m/z (%): 146.0 (M⁺ 35), 131.0 (30), 105.0 (28), 81.0 (25), 55.0 (100), 41.0 (71).

Ethyl-2-cyano-2-cyclohexylideneacetate (Entry 7, Table 5): Light yellow oil. IR (KBr, V_{max}/cm^{-1}): 2938, 2224 (CN), 1728 (C=O), 1600, 1447, 1255, 1215 (C-O), 1215, 1098. ¹H NMR (400MHz, CDCl₃, ppm): δ_H 1.35 (t, J=7.2Hz, 3H, CH₃CH₂O), 1.651.81 (m, 6H, 3CH₂), 2.66 (t, J=6.0Hz, 2H, CH₂), 2.97 (t, J=6.0Hz, 2H, CH₂), 4.27 (q, J=7.2Hz, 2H, CH₃CH₂O). EI-MS m/z (%): 193.0 (M⁺ 50), 165.0 (80), 137.0 (95), 121.0 (75), 93.0 (47), 81.0 (45), 29 (100), 27 (76).

3. Figure S-1-Figure S-7



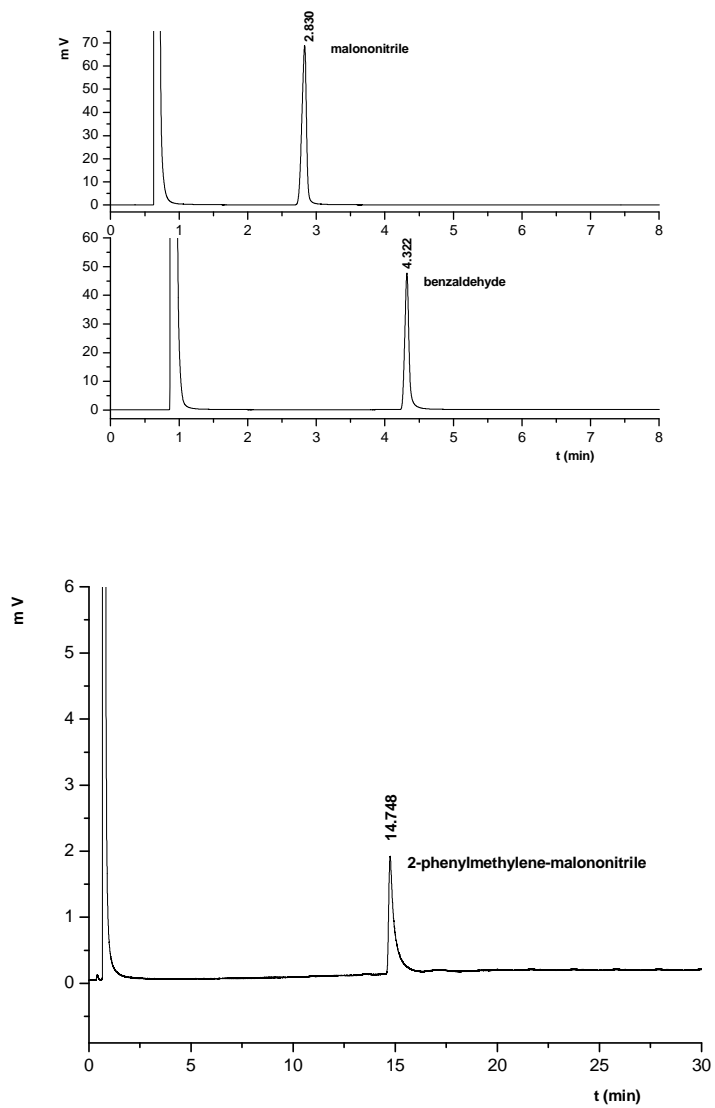
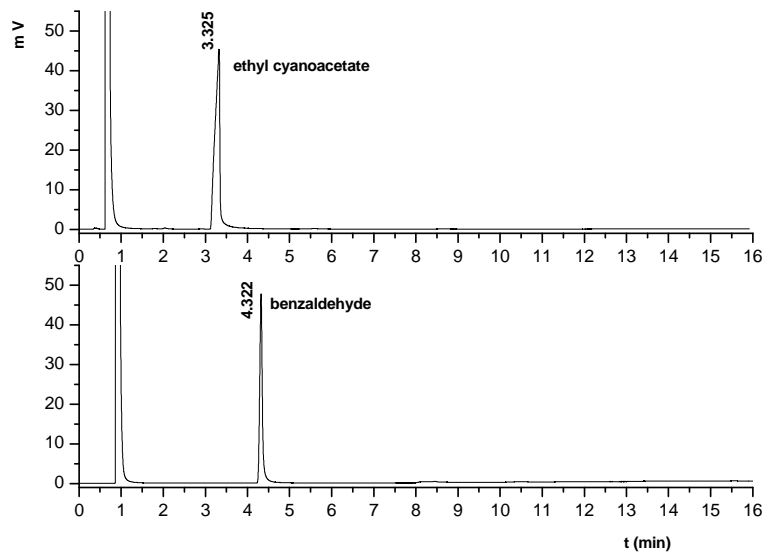
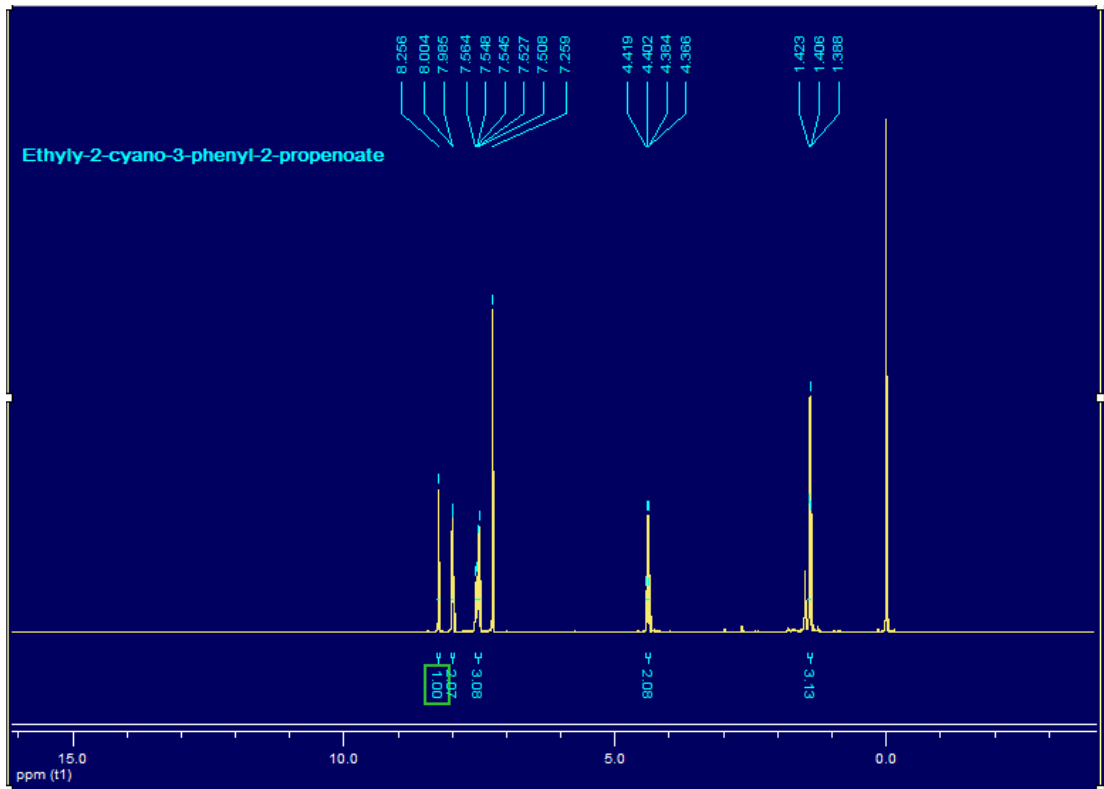


Figure S-1: NMR and gas chromatogram of 2-phenylmethylene-malononitrile



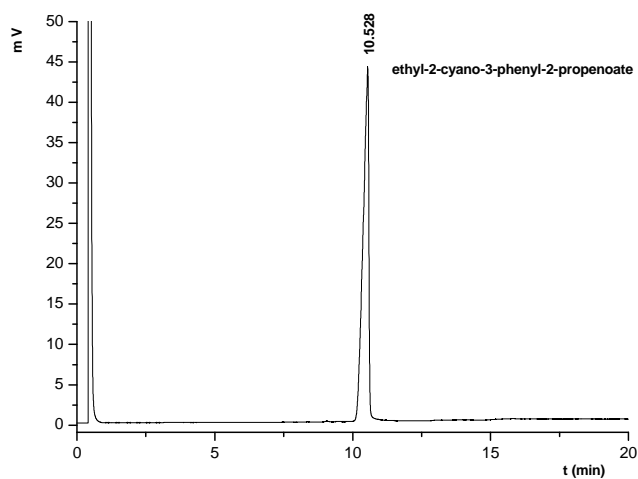


Figure S-2: NMR and gas chromatogram of ethyl-2-cyano-3-phenyl-2-propenoate

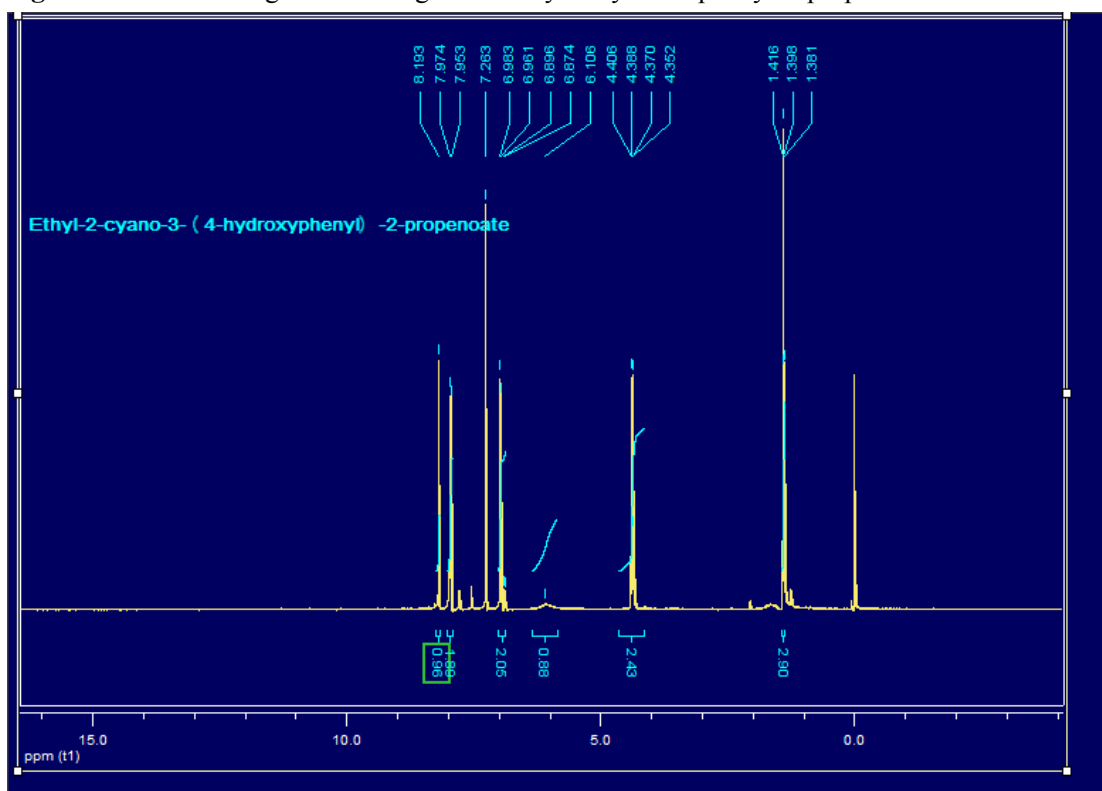


Figure S-3: NMR and gas chromatogram of ethyl-2-cyano-3-phenyl-2-propenoate

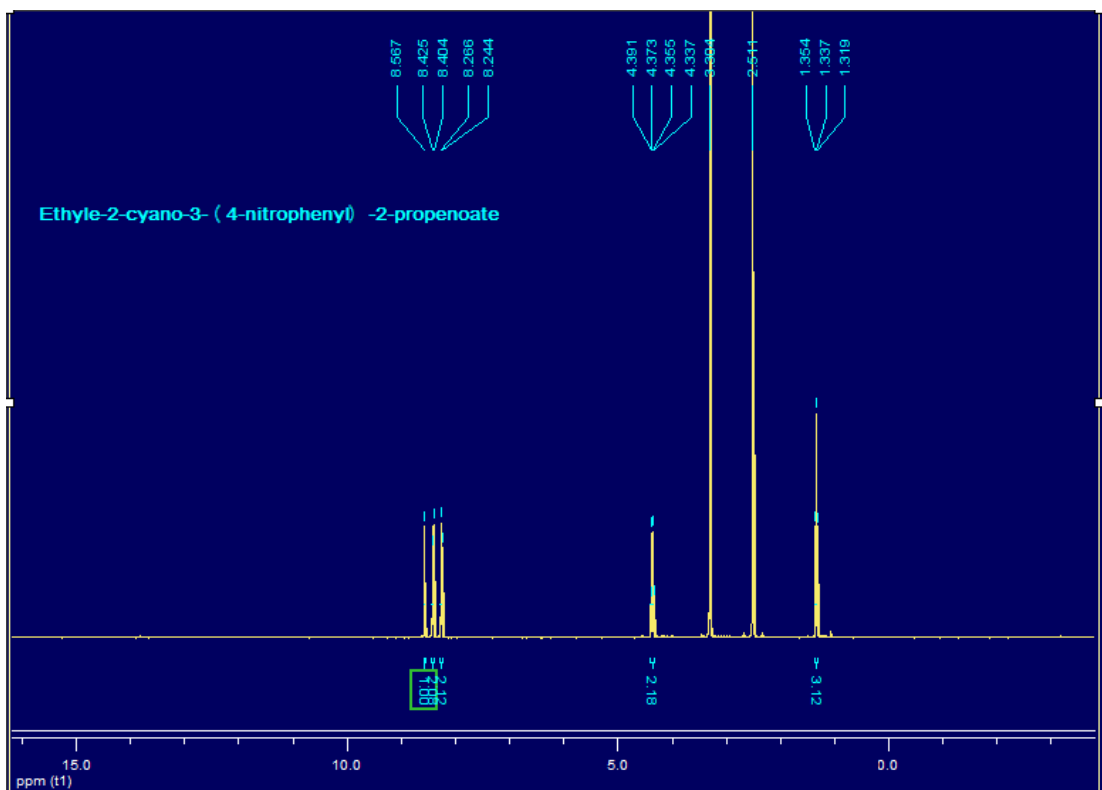
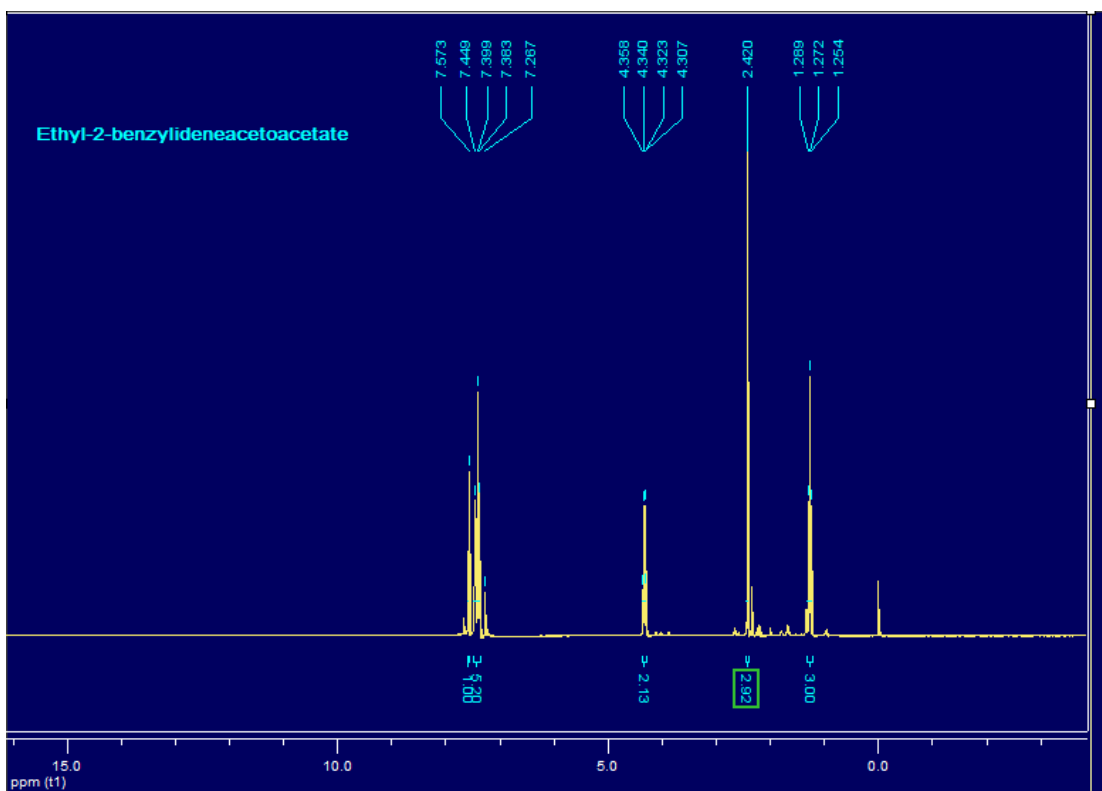


Figure S-4: NMR and gas chromatogram of ethyl-2-cyano-3-phenyl-2-propenoate



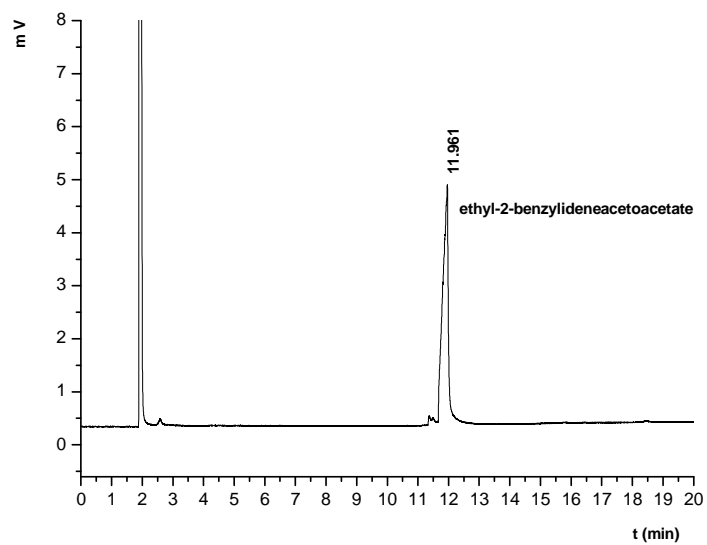
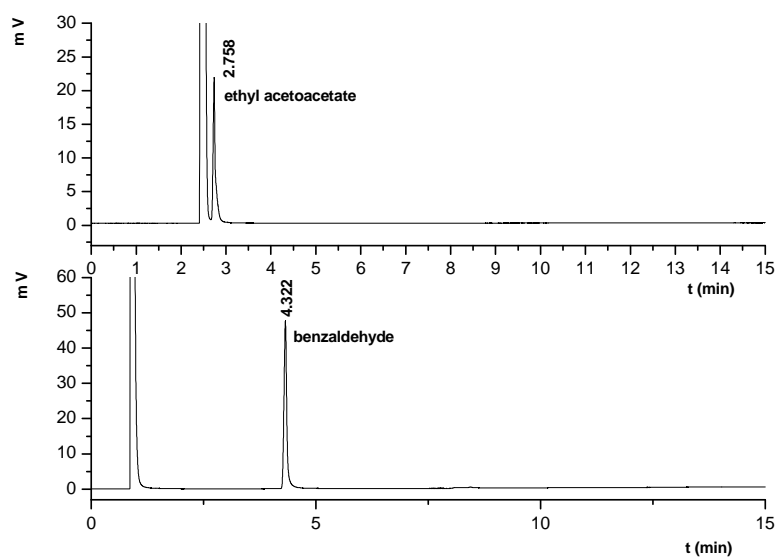
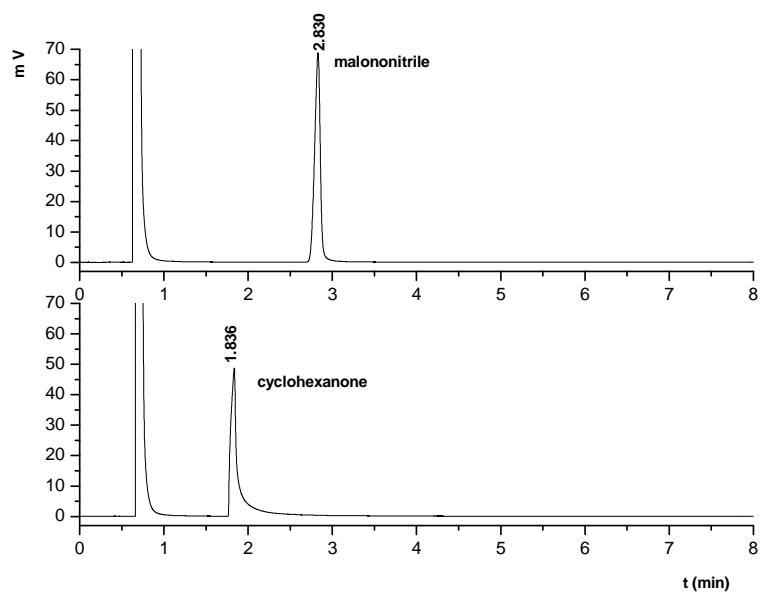
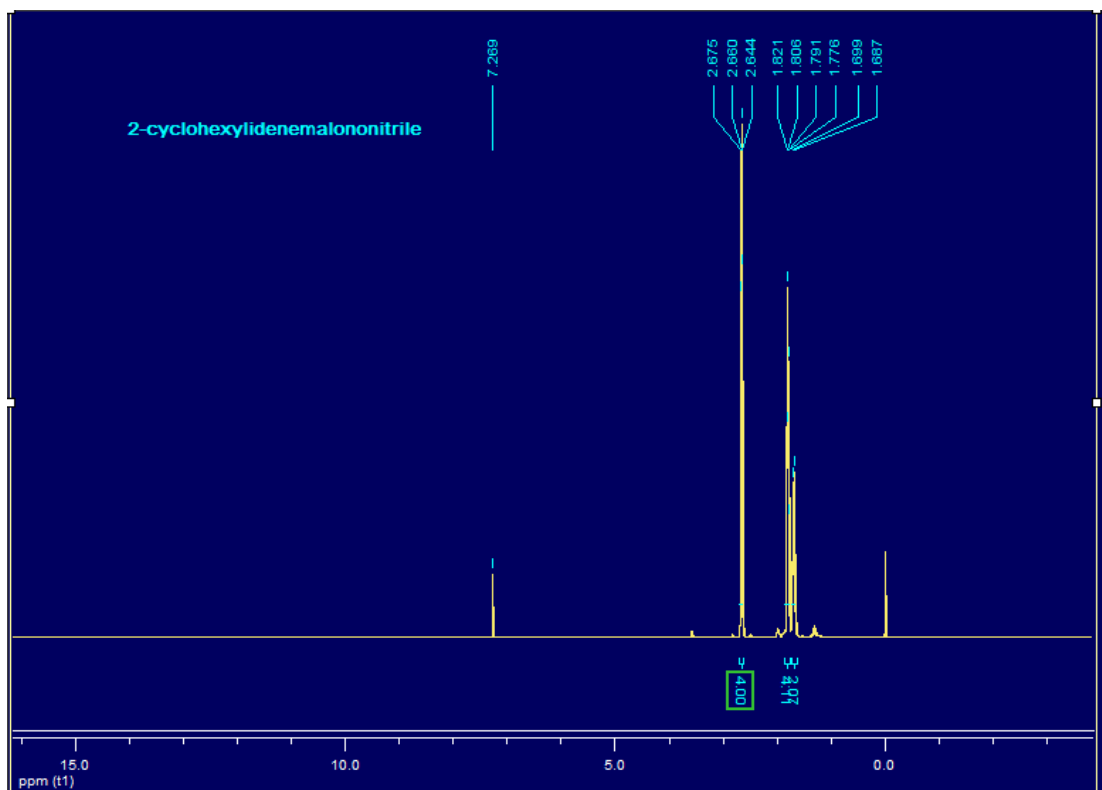


Figure S-5: NMR and gas chromatogram of ethyl-2-benzylideneacetoacetate



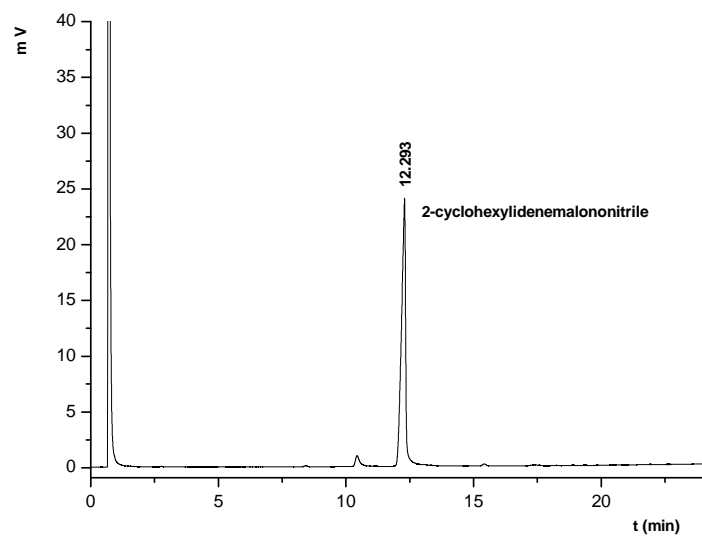
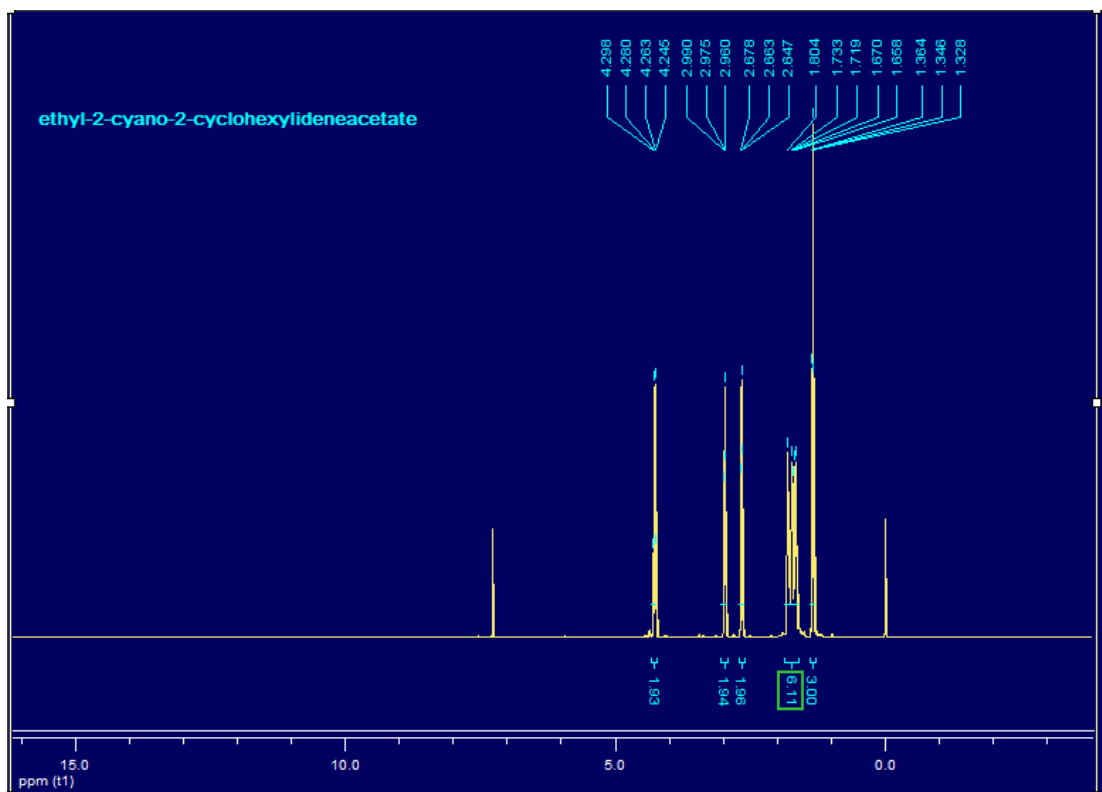


Figure S-6: NMR and gas chromatogram of 2-cyclohexylidenemalononitrile



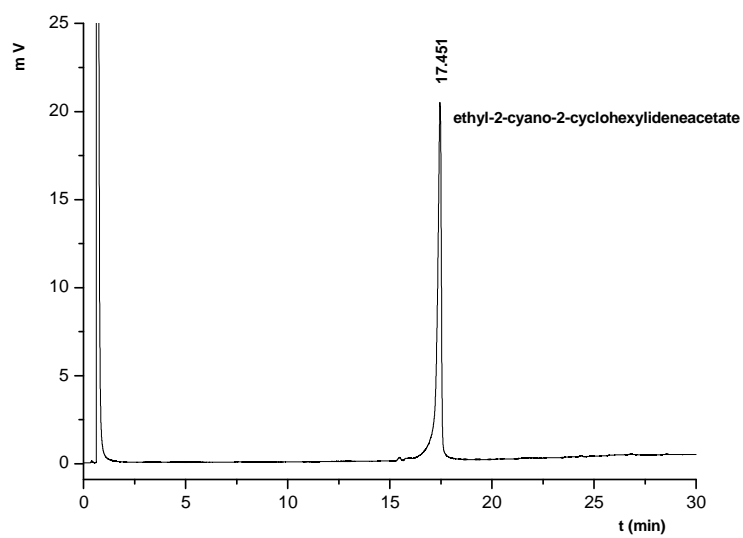
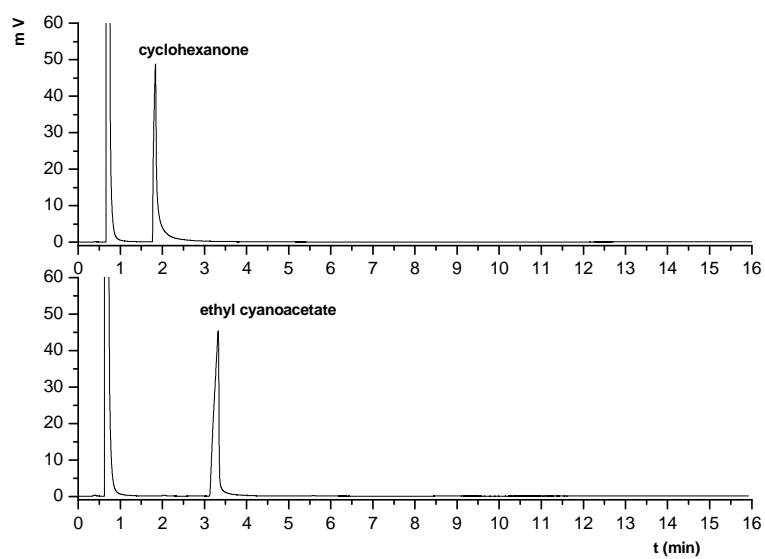


Figure S-7: NMR and gas chromatogram of ethyl-2-cyano-2-cyclohexylideneacetate