Electronic Supporting Information

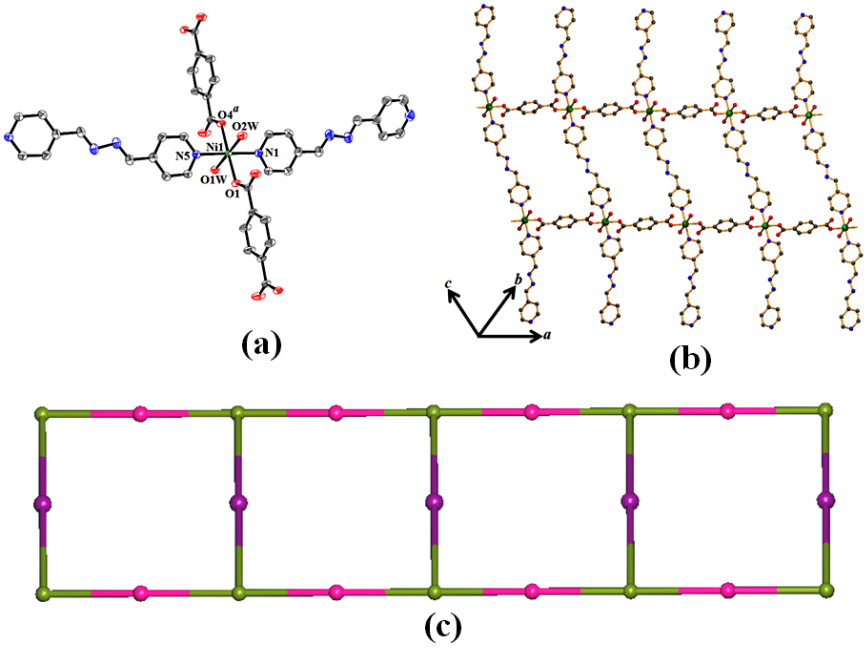

Fig. S1 (a) ORTEP drawing (40% probability ellipsoid) of **2** showing atom labeling scheme. (b) View of extended 1D ladder structure of compound **2** constructed by 1,4-benzenedicarboxylate, *azpy* ligand and Ni(II). (c) Simplified topological representation of 1D ladder in **2**.

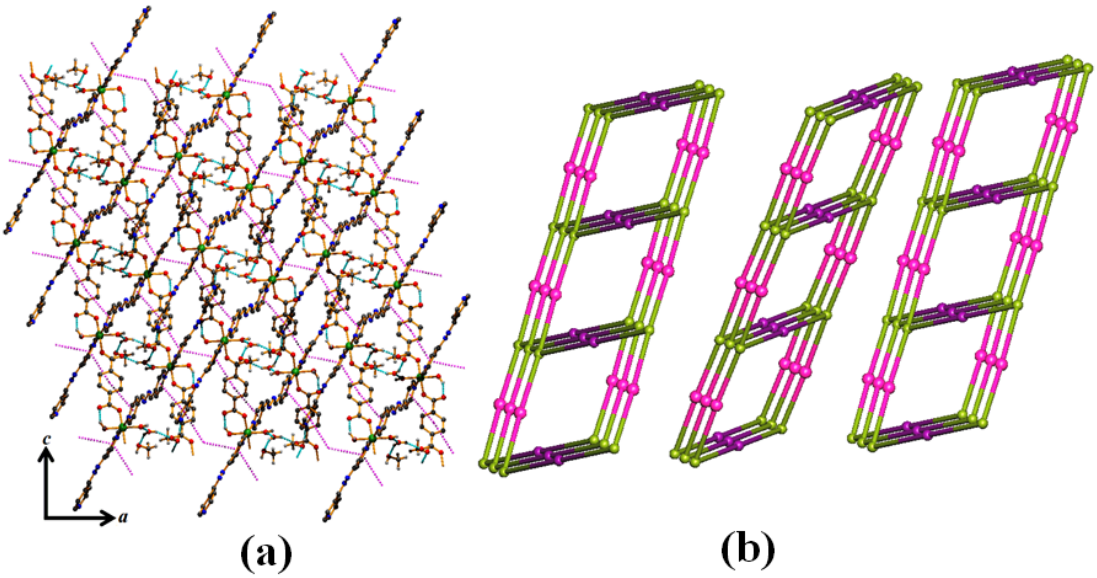

Fig. S2 (a) Supramolecular 3D network in **2** (π-π interaction: pink dotted lines & H-bonding: cyan dotted lines). (b) Simplified topological disposition view of adjacent ladders in **2**.

Table S1 Hydrogen bonding interactions (Å, °) of **1**

D-H…A	D-H	H…A	D…A	<D-H...A
O2W-H2WA...O2	0.8700	1.8400	2.622(3)	147.00
O1S-H1S...N4	0.8200	2.0100	2.807(4)	165.00
O2W-H2WB...O4W	0.8700	1.8700	2.736(4)	170.00
O3W-H3WA...O1S^{i}	0.8500	2.0000	2.844(4)	169.00
O3W-H3WB...O3	0.8500	2.0300	2.819(3)	155.00
O1W-H1WB...O3W^{ii}	0.8700	1.9800	2.800(3)	156.00

Symmetry code: (i) = -1+x, -1-y, -1/2+z; (ii) = 3/2-x, -1/2-y, 1-z.

Table S2 Hydrogen bonding interactions (Å, °) of **2**

D-H…A	D-H	H…A	D…A	<D-H...A
O1S -H1S...N4	0.8200	2.0000	2.801(5)	164.00
O1W-H1WA...O3W^{i}	0.8700	1.9500	2.815(3)	173.00
O2W-H2WA...O2	0.8600	1.8300	2.603(3)	149.00
O2W-H2WB...O4W	0.8600	1.8700	2.714(5)	166.00
O3W-H3WA...O3	0.8500	2.0100	2.818(3)	158.00
O3W-H3WB...O1S^{ii}	0.8500	2.0400	2.852(4)	159.00

Symmetry code: (i) = 3/2-x, -1/2-y, 1-z; (ii) = -1+x, -1-y, -1/2+z.

Table S3 π-π interactions in **1**

ring(i) → ring(j)	distance of centroid(i) from ring(j),(Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids,(Å)
R(1)→ R(1)^{i}	3.825(2)	8	3.6209(9)
R(1)→ R(2)^{ii}	3.866(2)	7.92(12)	3.5217(9)
R(2)→ R(1)^{iii}	3.866(2)	7.92(12)	3.4042(11)
R(2)→ R(3)^{iv}	3.914(2)	15.91(13)	3.4052(11)
R(3)→ R(2)^{v}	3.914(2)	15.91(13)	3.7938(10)

Symmetry code: (i) = 2-x, y, 3/2-z; (ii) = 5/2-x, 1/2+y, 3/2-z; (iii) = 5/2-x, -1/2+y, 3/2-z; (iv) = 2-x, -1+y, 3/2-z; (v) = 2-x, 1+y, 3/2-z.
R(i)/R(j) denotes the ith/jth rings: R(1) = N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2) = N(4)/C(10)/C(9)/ C(8)/C(12)/C(11); R(3) = N(5)/C(13)/C(14)/ C(15)/ C(16)/C(17).

Table S4 π-π interactions in **2**

ring(i) → ring(j)	distance of centroid(i) from ring(j),(Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids,(Å)
R(1)→ R(1)^{i}	3.8406(14)	8	3.6434(10)
R(1)→ R(2)^{ii}	3.8544(17)	8.16(14)	3.5293(10)
R(2)→ R(1)^{iii}	3.8545(17)	8.16(14)	3.4093(13)
R(2)→ R(3)^{iv}	3.9006(17)	14.96(14)	3.3790(13)
R(3)→ R(2)^{v}	3.9006(17)	14.96(14)	3.7578(11)

Symmetry code: (i) = 2-x, y, 3/2-z; (ii) = 5/2-x, 1/2+y, 3/2-z; (iii) = 5/2-x, -1/2+y, 3/2-z; (iv) = 2-x, -1+y, 3/2-z; (v) = 2-x, 1+y, 3/2-z.
R(i)/R(j) denotes the ith/jth rings: R(1) = N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2) = N(4)/C(10)/C(9)/ C(8)/C(12)/C(11); R(3) = N(5)/C(13)/C(14)/ C(15)/ C(16)/C(17).

Physical Data and H[1]-NMR Spectra of All Compounds

2-(Phenylmethylene)malononitrile (Table 4, **entry 1).**White solid; melting point 79–80 °C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.90 (d, J = 7.6 Hz, 2H), 7.79 (s, 1H), 7. 63 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H).

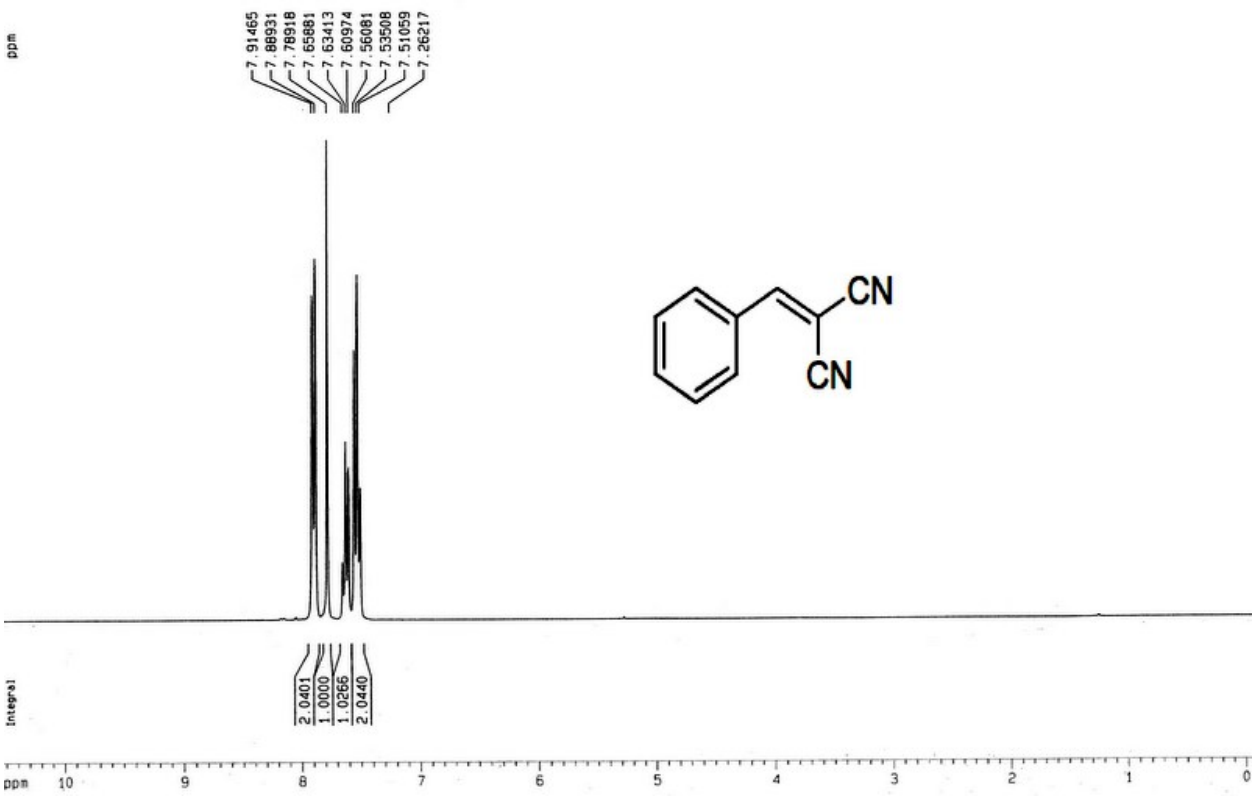

Fig. S3: The ^{1}H-NMR spectrum of 2-(phenylmethylene)malononitrile (Table 4, entry 1).

Ethyl (*E*)-2-cyano-3-phenyl-2-propenoate (Table 4, entry 2). White solid; melting point 49–50 °C, ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.25 (s, 1H, CH), 7.99 (d, J = 7.5 Hz, 2H), 7.56-7.48 (m, 3H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).

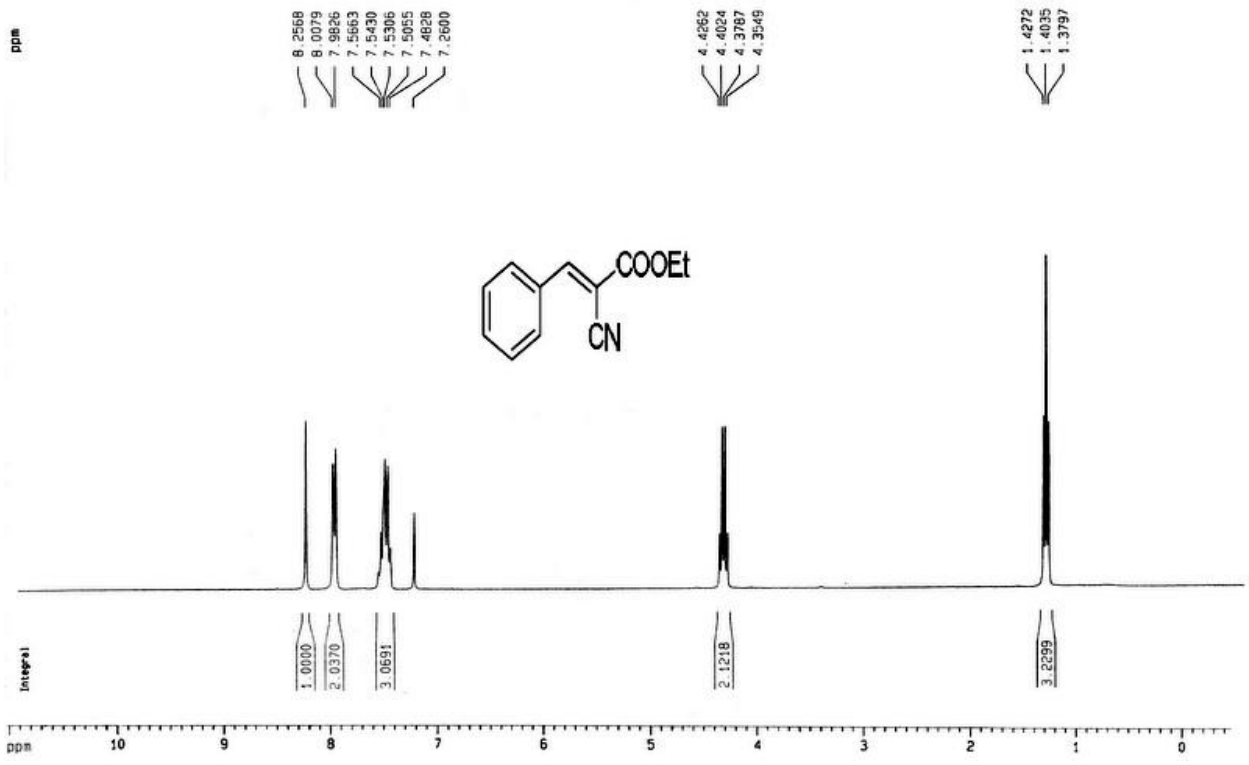

Fig. S4: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-phenyl-2-propenoate (Table 4, entry 2).

2-(4-Bromophenylmethylene)malononitrile (Table 4, entry 3). White solid; melting point 152-153 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.78-7.66 (m, 5H).

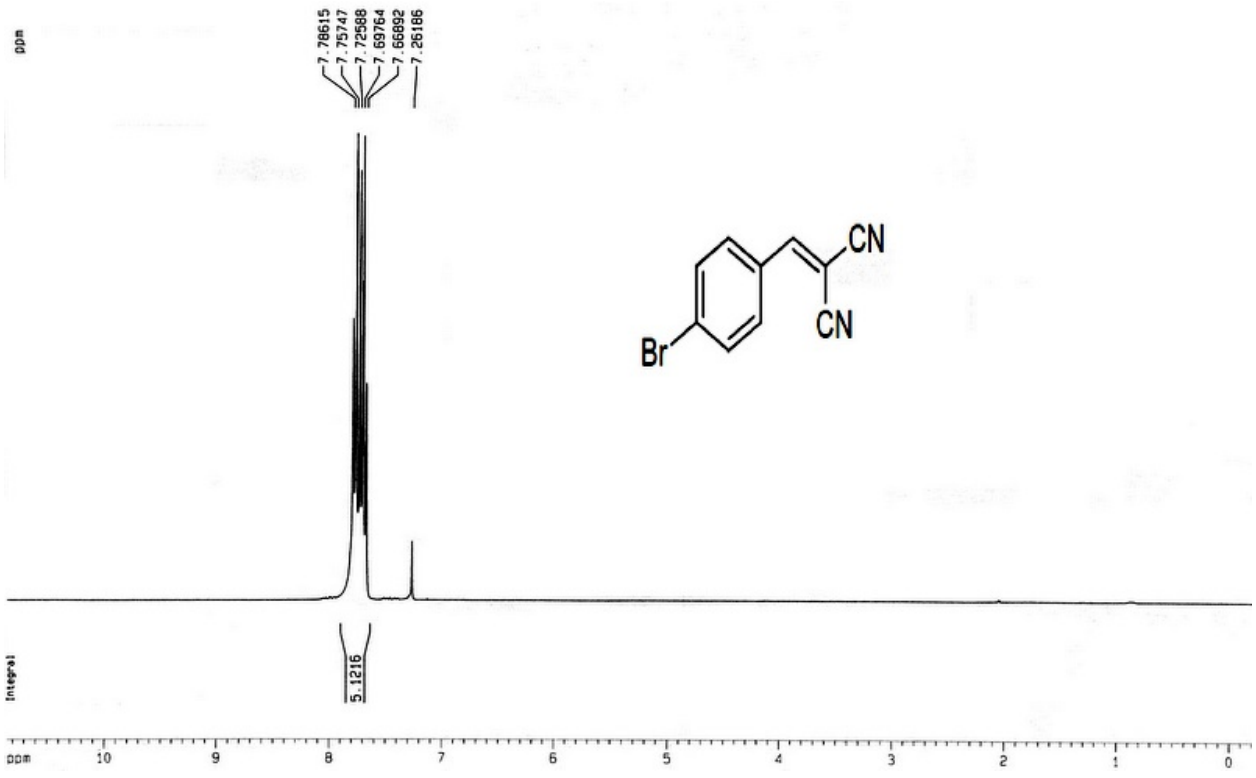

Fig. S5: The ^{1}H-NMR spectrum of 2-(4-bromophenylmethylene)malononitrile (Table 4, entry 3).

Ethyl (*E*)-2-cyano-3-(4-bromophenyl)-2-propenoate (Table 4, entry 4). White solid; melting point 87-88 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.18 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H).

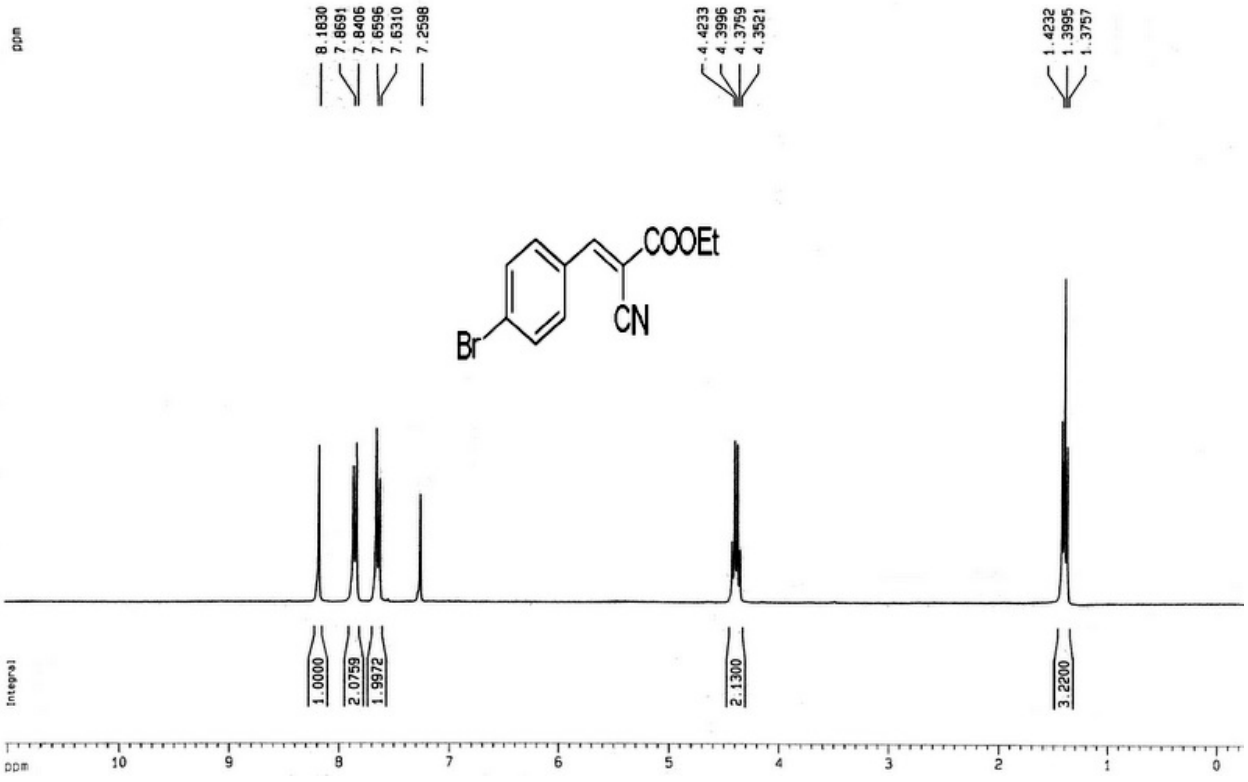

Fig. S6: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(4-bromophenyl)-2-propenoate (Table 4, entry 4).

2-(2-Bromophenylmethylene)malononitrile (Table 4, **entry 5).** White solid; melting point 89-90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.22 (s, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.52–7.43 (m, 2H).

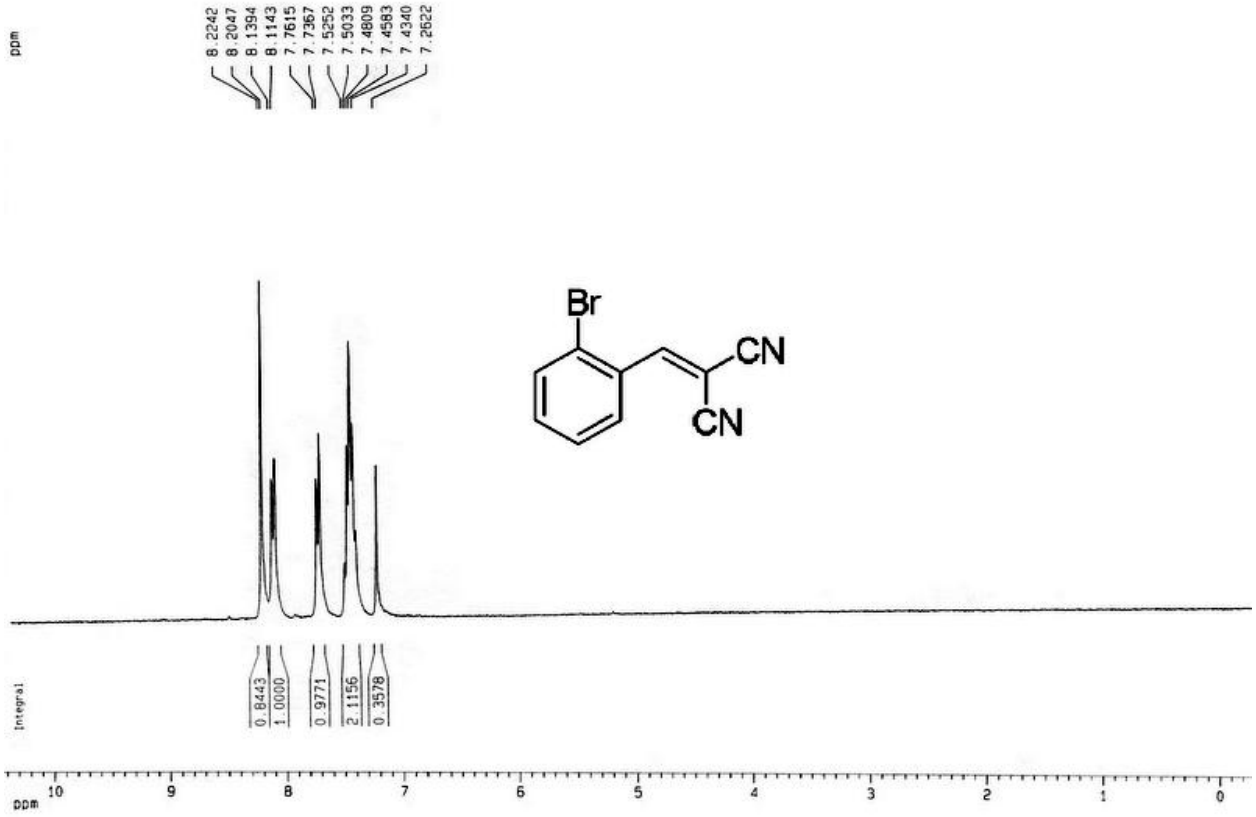

Fig. S7: The ^{1}H-NMR spectrum of 2-(2-bromophenylmethylene)malononitrile (Table 4, entry 5).

Ethyl (*E*)-2-cyano-3-(2-bromophenyl)-2-propenoate (Table 4, entry 6). White solid; melting point 74-75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ (ppm): 8.63 (s, 1H), 8.17 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.40-7.35 (m, 1H), 4.41(q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H).

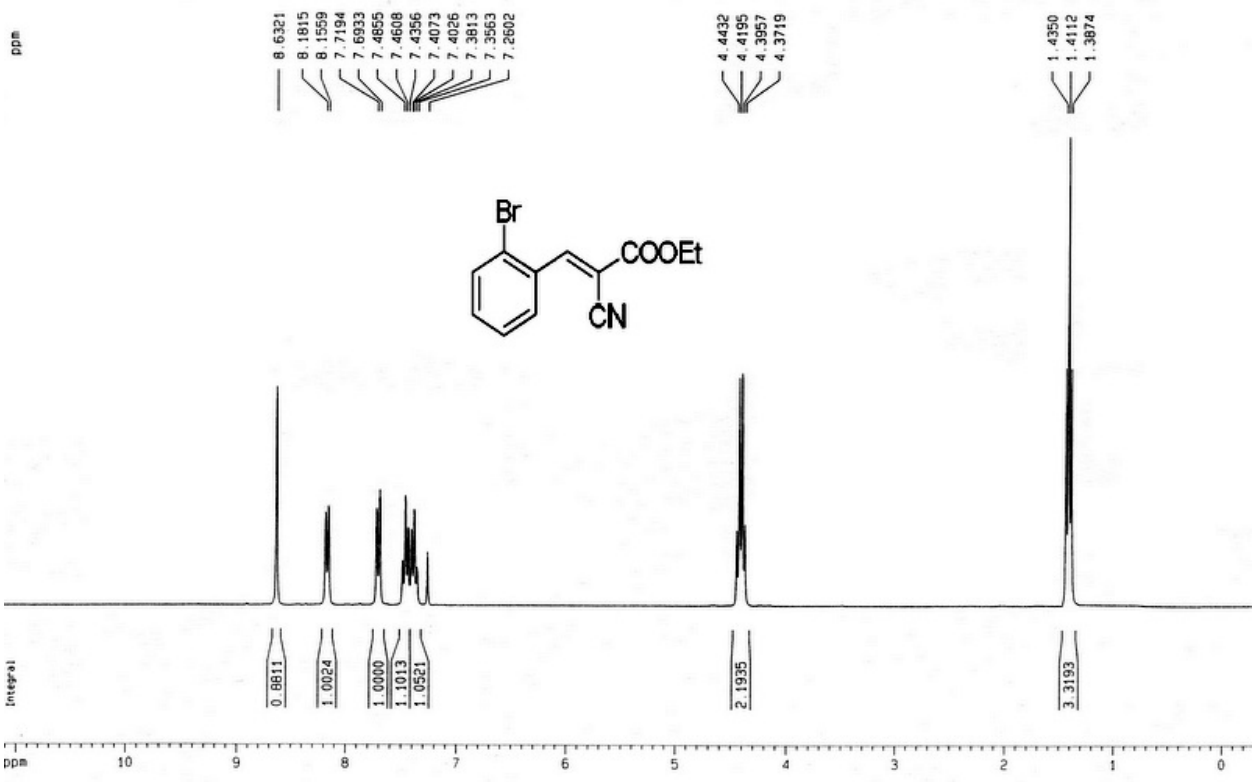

Fig. S8: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(2-bromophenyl)-2-propenoate (Table 4, entry 6).

2-(4-Chlorophenylmethylene)malononitrile (Table 4, entry 7). White solid; melting point 159-160 °C; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ (ppm): 7.85 (d, J = 8.5 Hz, 2H), 7.73 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H).

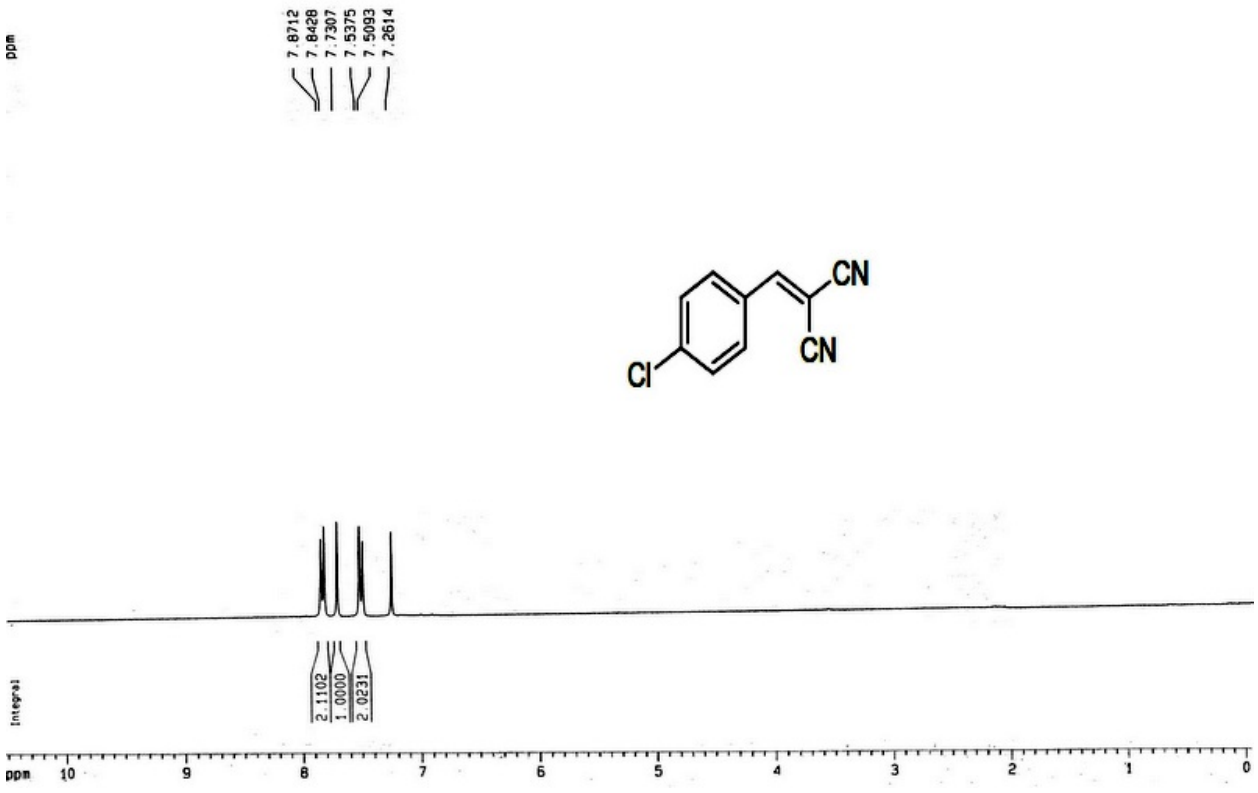

Fig. S9: The ^{1}H-NMR spectrum of 2-(4-chlorophenylmethylene)malononitrile (Table 4, entry 7).

2-(4-Fluorophenylmethylene)malononitrile (Table 4, entry 8). White solid; melting point 123-125 °C; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ (ppm): 8.0-7.95 (m, 2H), 7.76 (s, 1H), 7.28-7.23 (m, 2H).

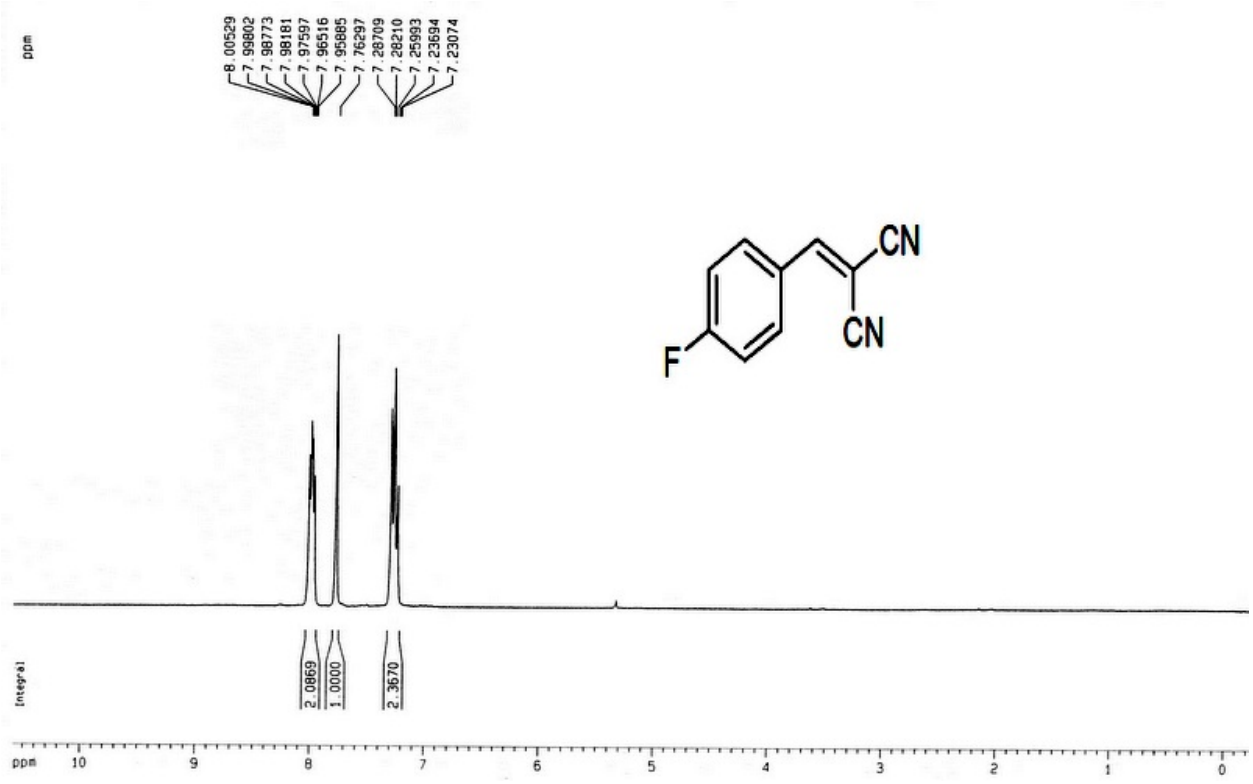

Fig. S10: The ^{1}H-NMR spectrum of 2-(4-fluorophenylmethylene)malononitrile (Table 4, entry 8).

2-(3-Nitrophenylmethylene)malononitrile (Table 4, entry 9). Light yellow solid; melting point 103-104 °C; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ (ppm): 8.66 (s, 1H), 8.47 (d, J = 8.1, 1H), 8.33 (d, J = 7.8, 1H), 7.88 (s, 1H), 7.79 (d, J = 8.0, 1H).

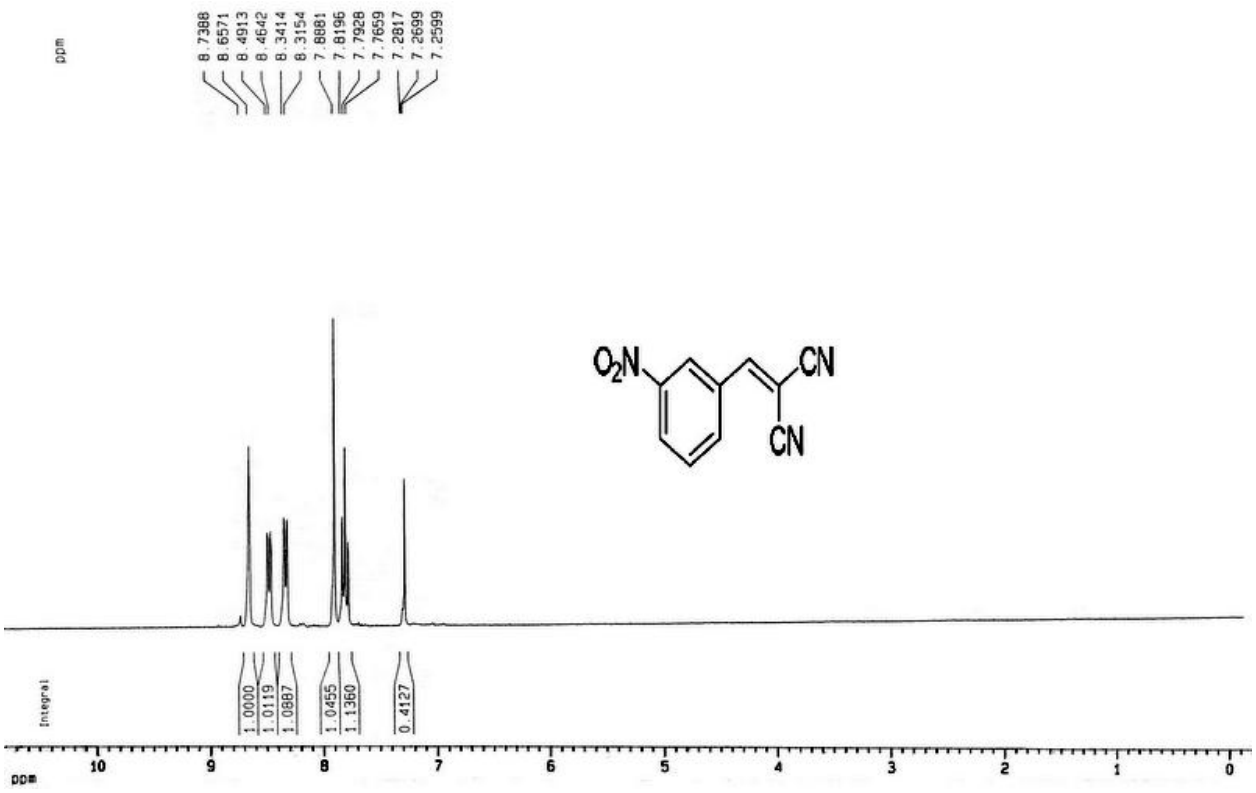

Fig. S11: The ^{1}H-NMR spectrum of 2-(3-nitrophenylmethylene)malononitrile (Table 4, entry 9).

Ethyl (*E*)-2-cyano-3-(3-nitrophenyl)-2-propenoate (Table 4, entry 10). White solid; melting point 130-132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.69 (s, 1H), 8.42-8.40 (m, 2H), 8.30 (s, 1H), 7.74 (t, J = 8.0 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H).

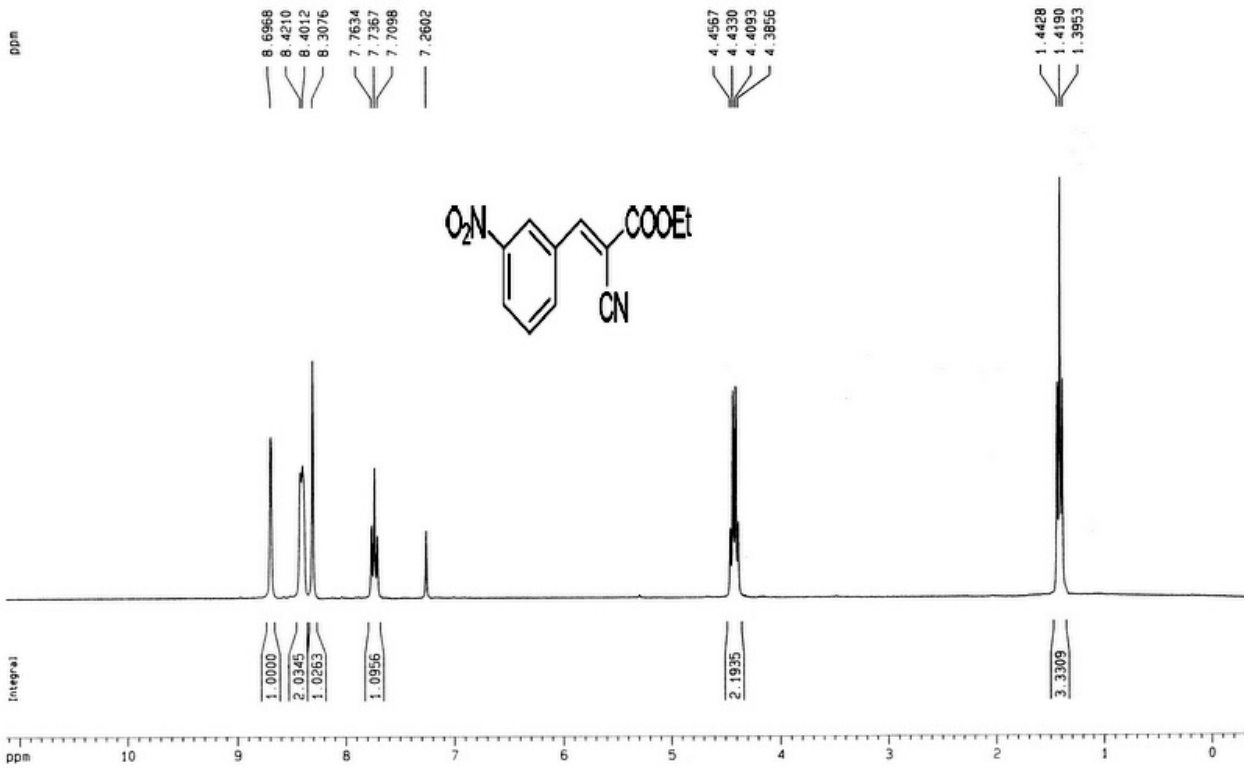

Fig. S12: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(3-nitrophenyl)-2-propenoate (Table 4, entry 10).

2-(4-Cyanophenylmethylene)malononitrile (Table 4, **entry 11).** White solid; melting point 155-156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ (ppm): 8.0 (d, J = 8.3, 2H), 7.85-7.81 (m, 3H).

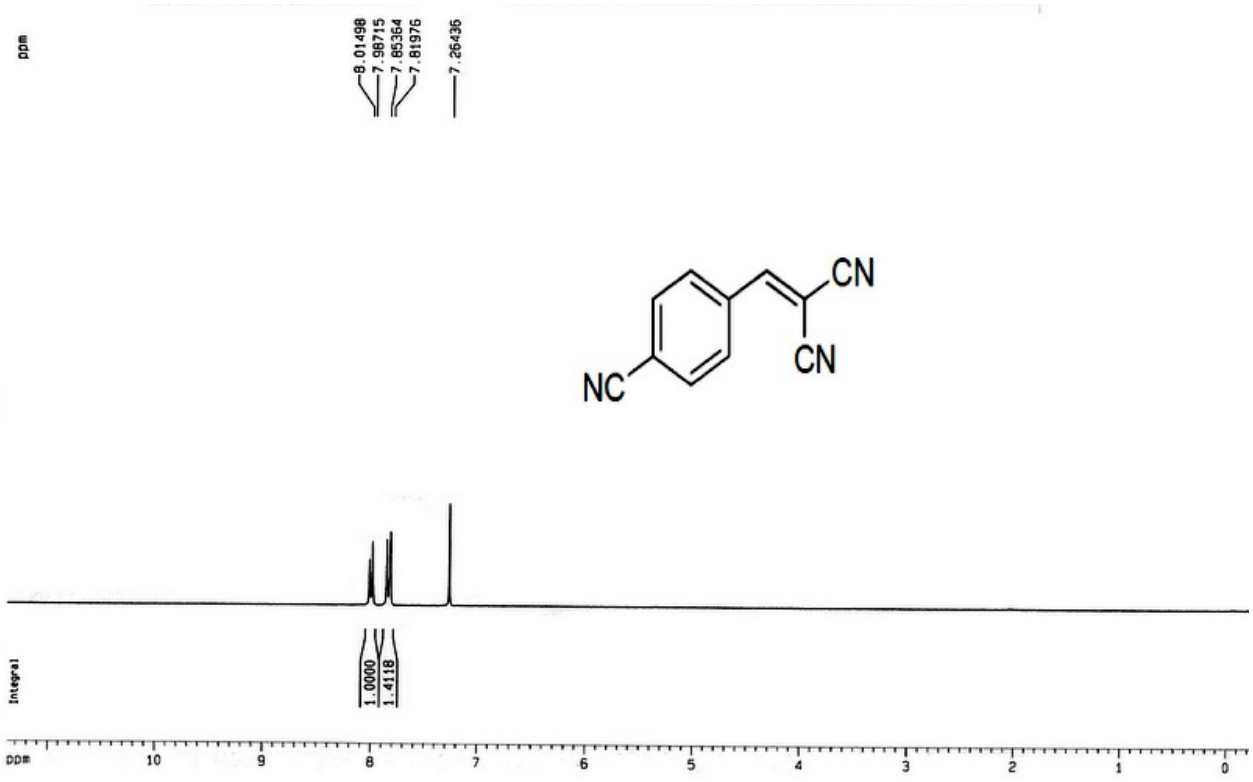

Fig. S13: The ^{1}H-NMR spectrum of 2-(4-cyanophenylmethylene)malononitrile (Table 4, entry 11).

Ethyl (*E*)-2-cyano-3-(4-cyanophenyl)-2-propenoate (Table 4, entry 12). White solid; melting point 170-171 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.26-8.24 (m, 1H), 8.06 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 4.44-4.37 (m, 2H), 1.43-1.38 (m, 3H).

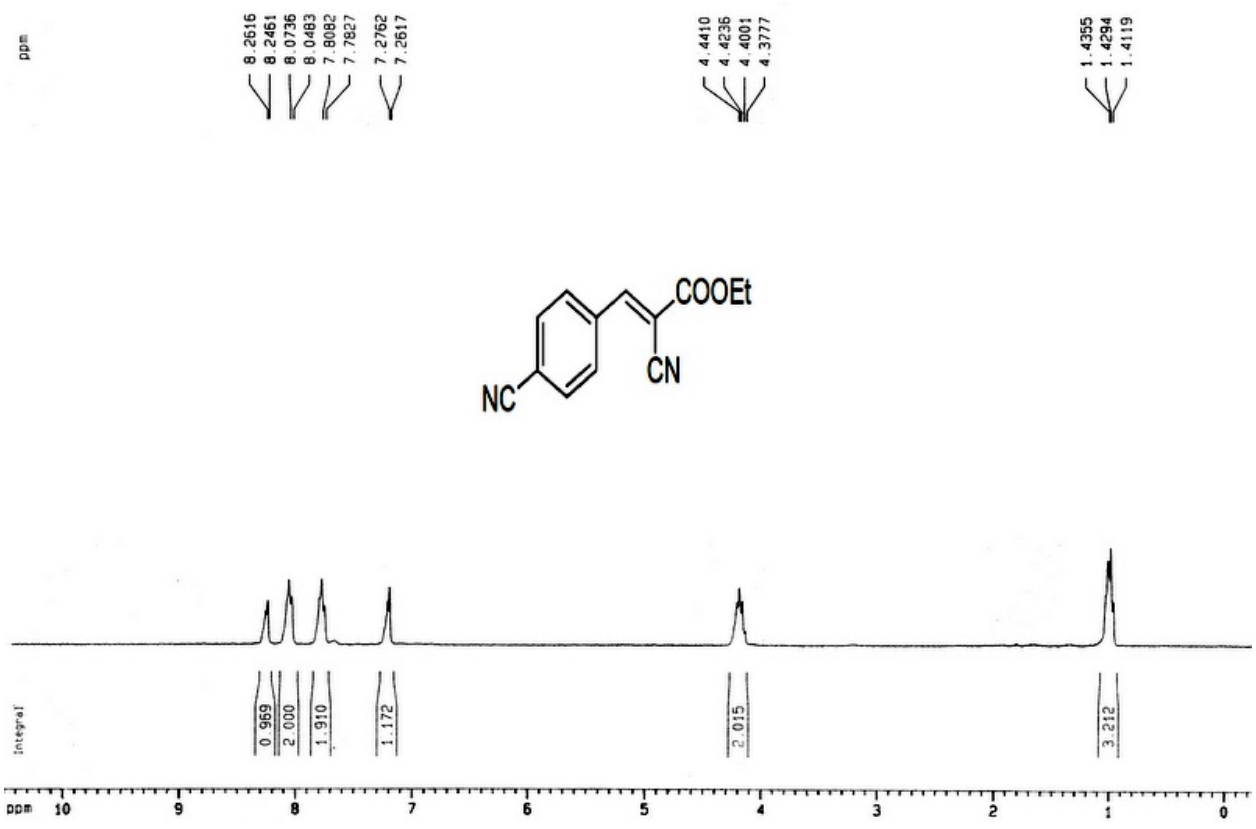

Fig. S14: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(4-cyanophenyl)-2-propenoate (Table 4, entry 12).

2-(4-Nitrophenylmethylene)malononitrile (Table 4, entry 13). Yellow solid; melting point 159-160 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.39 (d, J = 8.8, 2H), 8.07 (d, J = 8.8, 2H), 7.88 (s, 1H).

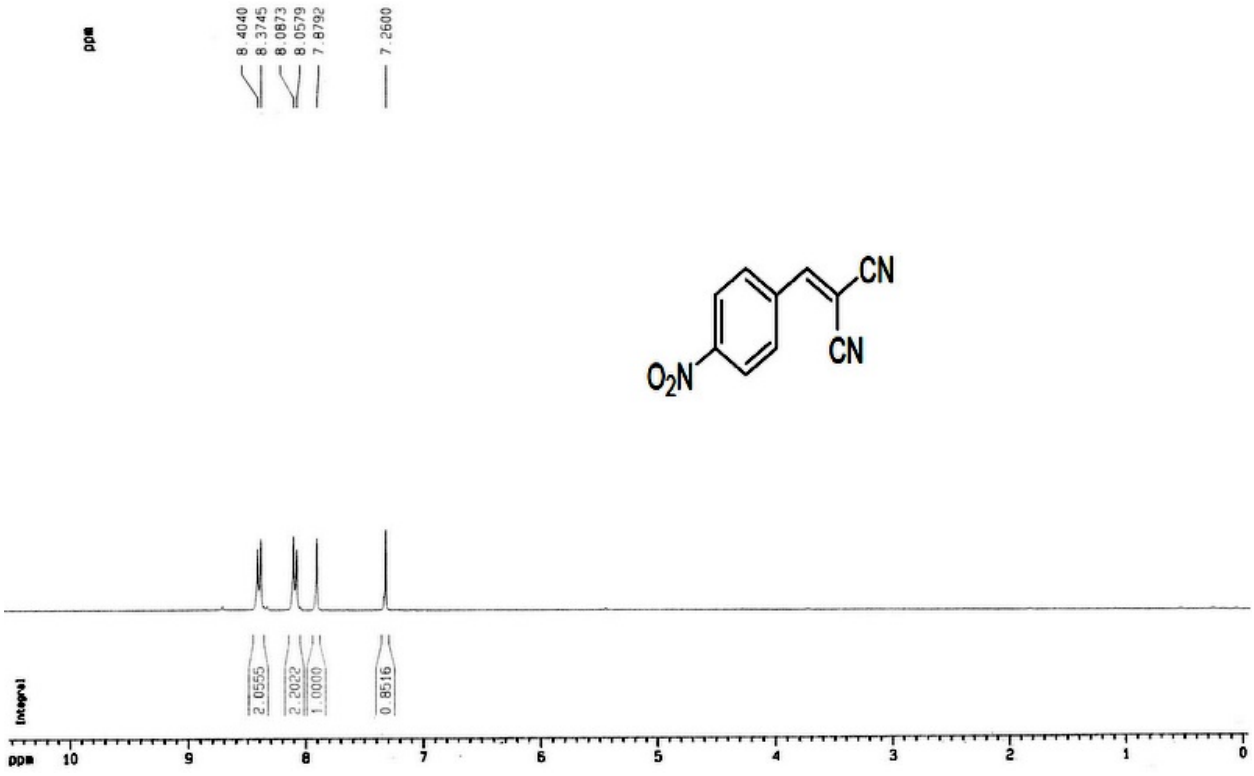

Fig. S15: The ^{1}H-NMR spectrum of 2-(4-nitrophenylmethylene)malononitrile (Table 4, entry 13).

Ethyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate (Table 4, entry 14). Yellow solid; melting point 167-168 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.35 (d, J = 8.8 Hz, 2H), 8.30 (s, 1H), 8.13 (d, J = 8.7 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H).

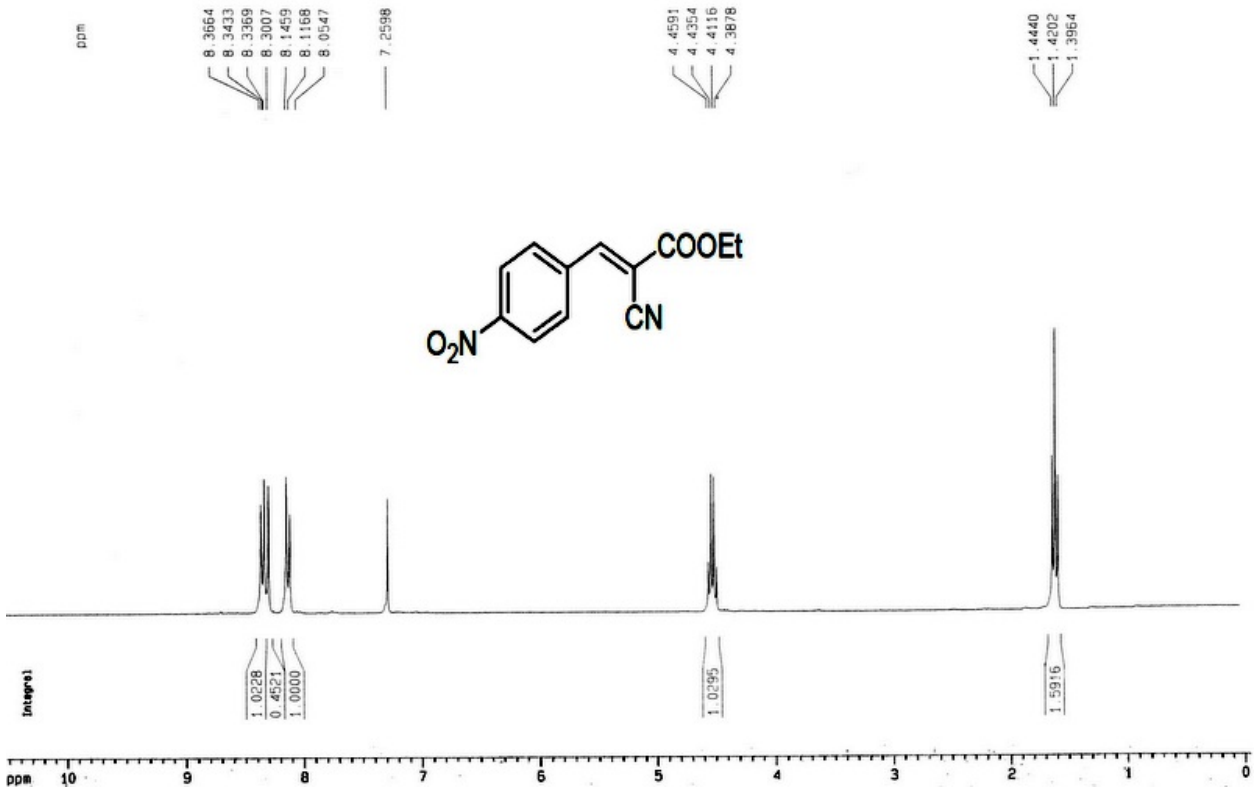

Fig. S16: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate (Table 4, entry 14).

2-(4-Methylphenylmethylene)malononitrile (Table 4, **entry 15).** White solid; melting point 133-134 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.81 (d, J = 8.2, 2H), 7.72 (s, 1H), 7.34 (d, J = 8.1, 2H), 2.46 (s, 3H).

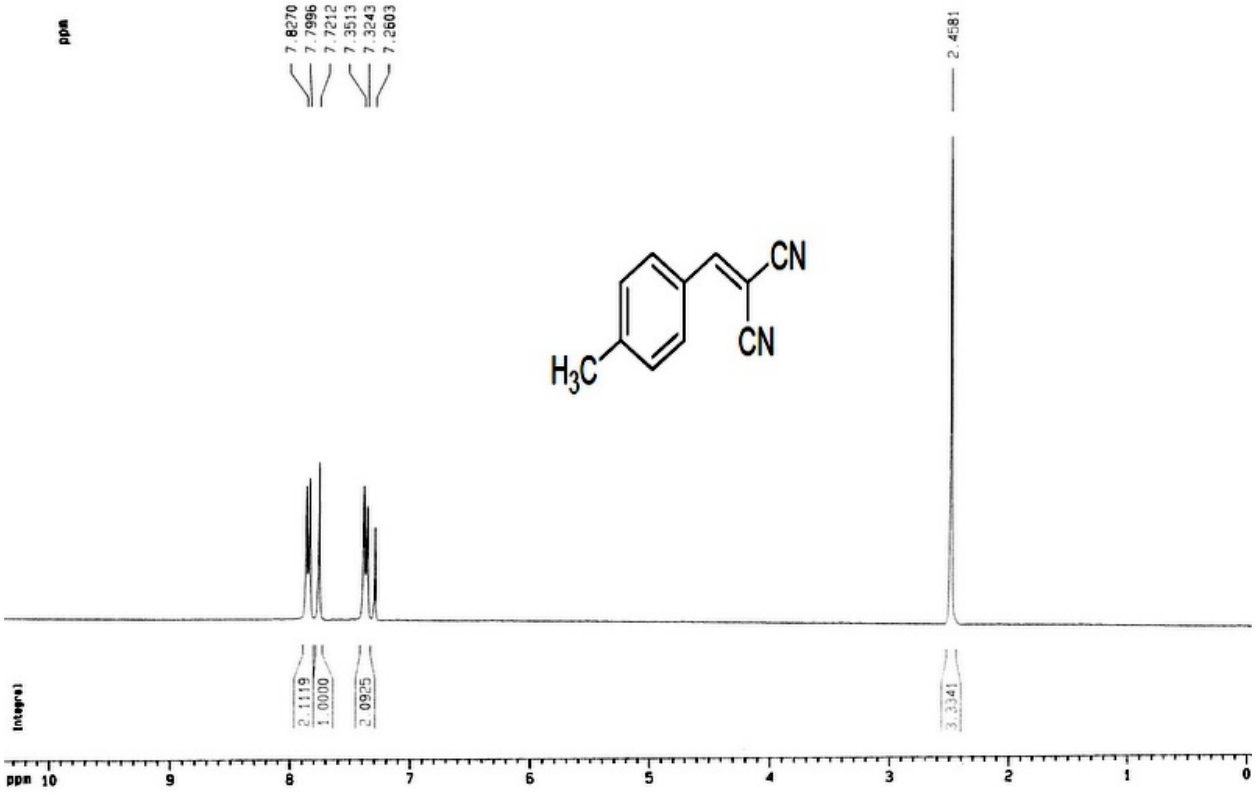

Fig. S17: The ^{1}H-NMR spectrum of 2-(4-methylphenylmethylene)malononitrile (Table 4, entry 15).

2-(4-Methoxyphenylmethylene)malononitrile (Table 4, **entry 16).** Light yellow solid; melting point 111-112 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.91 (d, J = 8.9 Hz, 2H), 7.65 (s, 1H), 7.01 (d, J = 8.9 Hz, 2H), 3.91 (s, 3H).

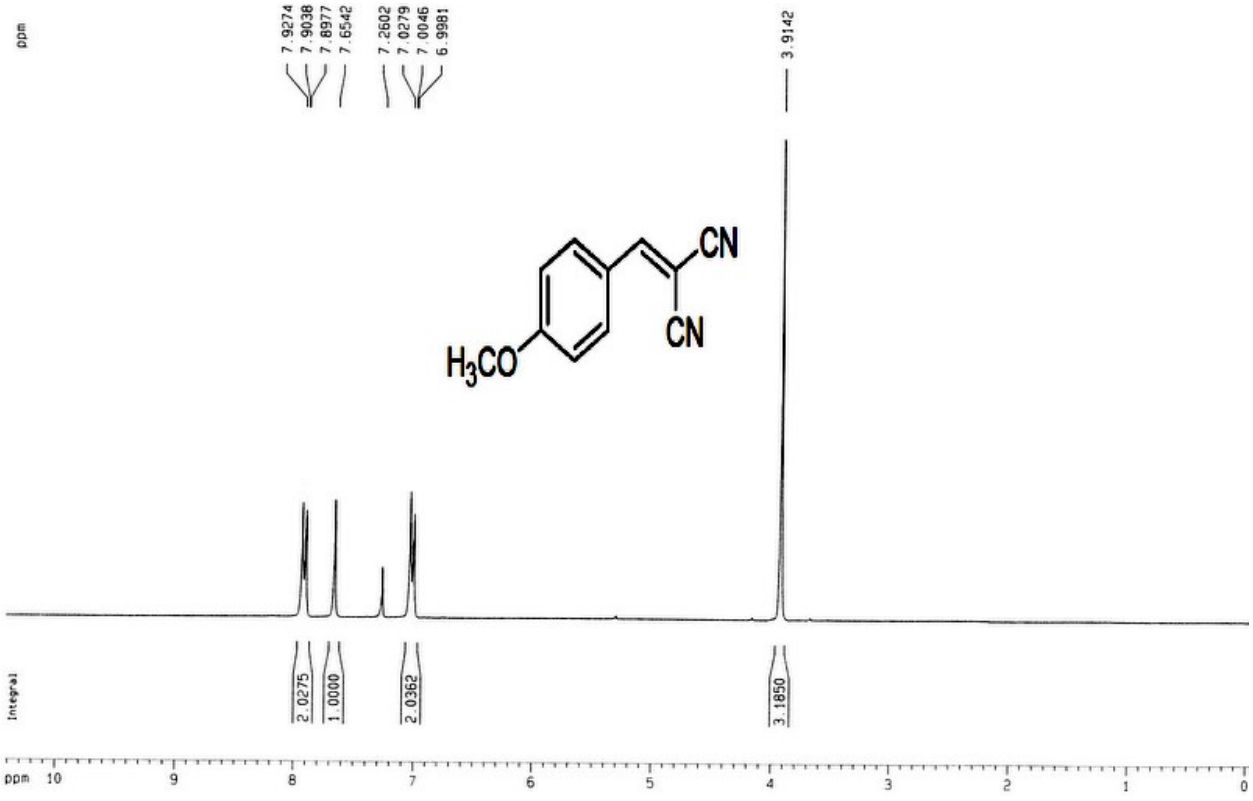

Fig. S18: The ^{1}H-NMR spectrum of 2-(4-methoxyphenylmethylene)malononitrile (Table 4, entry 16).

Ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (Table 4, entry 17). White solid; melting point 80-81 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.17 (s, 1H), 8.00 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).

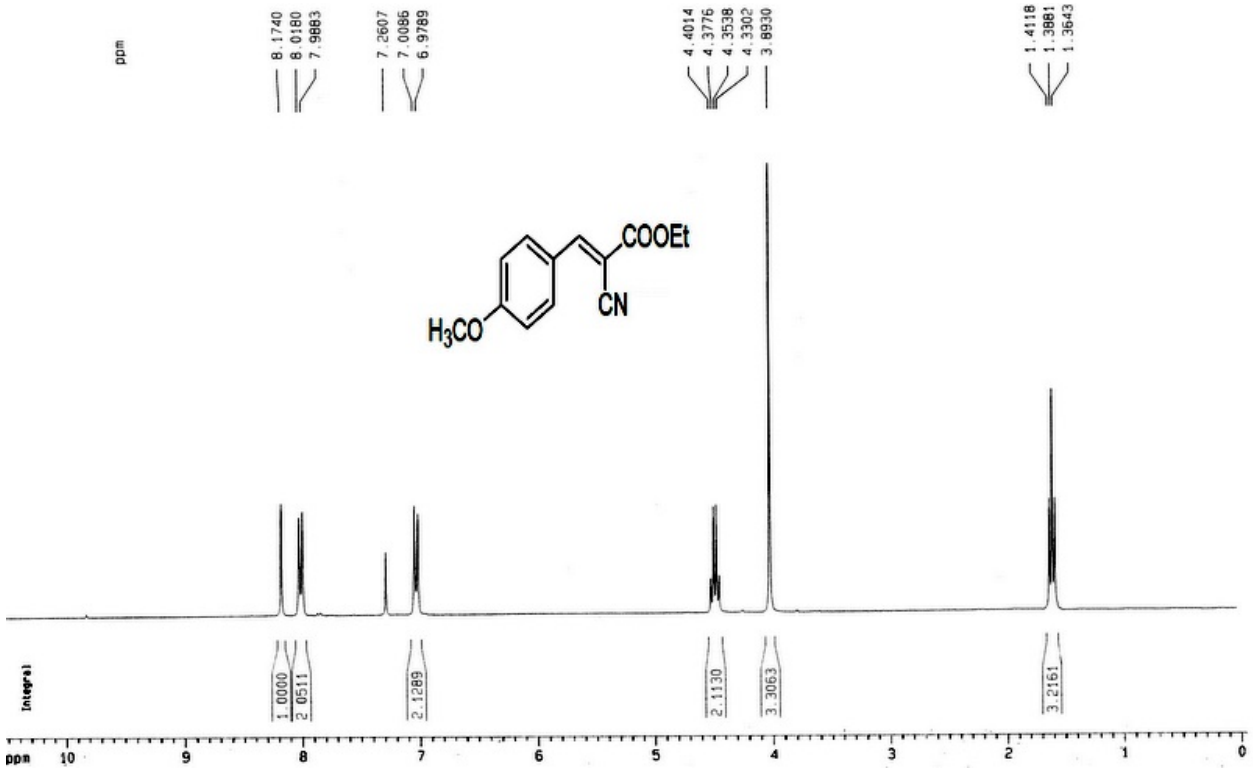

Fig. S19: The ^{1}H-NMR spectrum of ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (Table 4, entry 17).