Supporting Information for
Two Organic-Inorganic Hybrid Polyoxovanadates as Reusable Catalysts for Knoevenagel Condensation

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Table S1. Selected bond distances(Å) and bond angles (º) for compounds **1**-**2**

Compound **1**

Ni(1)-N(3)#1	2.083(13)	Ni(1)-N(3)	2.083(13)
Ni(1)-N(3)#2	2.083(13)	Ni(1)-N(3)#3	2.083(13)
Ni(1)-O(13)	2.164(7)	Ni(1)-N(4)	2.096(13)
Ni(1)-O(13)#2	2.164(7)	Ni(2)-O(2)	2.076(6)
Ni(2)-O(4)	2.056(7)	Ni(2)-O(5)	2.093(5)
Ni(2)-O(3)#3	2.077(5)	Ni(2)-O(5)#3	2.093(5)
V(1)-O(6)	1.610(6)	V(2)-O(9)	1.601(7)
V(1)-O(7)	1.824(4)	V(2)-O(8)#3	1.829(5)
V(3)-O(10)	1.704(5)	V(4)-O(2)	1.642(6)
V(3)-O(10)#5	1.704(5)	V(4)-O(1)#3	1.798(5)
N(3)#1-Ni(1)-N(3)#2	145.0(7)	N(3)-Ni(1)-N(3)#3	145.0(7)
N(3)#1-Ni(1)-N(4)#1	91.8(5)	N(3)#1-Ni(1)-N(4)#3	88.2(5)
O(4)-Ni(2)-O(3)	87.2(2)	O(2)-V(4)-O(1)#3	103.4(2)
O(3)#3-Ni(2)-O(3)	90.5(3)	O(2)-V(4)-O(1)	103.4(2)
O(4)-Ni(2)-O(2)	176.4(3)	O(1)#3-V(4)-O(1)	96.1(3)
O(3)#3-Ni(2)-O(2)	90.3(2)	O(2)-V(4)-O(11)#3	99.4(2)
O(6)-V(1)-O(7)	105.9(3)	O(1)#3-V(4)-O(11)#3	154.3(2)
O(6)-V(1)-O(8)	102.9(3)	O(1)-V(4)-O(11)#3	89.7(2)
O(9)-V(2)-O(8)	103.6(2)	O(10)-V(3)-O(11)	97.3(2)
O(9)-V(2)-O(11)	99.3(2)	O(10)-V(3)-O(11)#5	96.9(2)

Symmetry codes: #1 -x, y,-z+1; #2 -x,-y+1,-z+1; #3 x,-y+1,z; #4 -x+1,-y+1,-z+2; #5 -x+1,y,-z+2.

Compound **2**

V(1)-O(2)	1.615(3)	V(2)-O(6)	1.611(3)
V(1)-O(1)	1.684(2)	V(2)-O(3)#1	1.808(3)
V(1)-O(3)	1.771(3)	V(3)-O(7)	1.607(3)
V(1)-O(4)	1.771(3)	V(3)-O(1)	2.058(3)
V(3)-N(7)	2.109(4)	V(3)-N(3)	2.119(4)
V(3)-N(1)	2.112(4)	V(3)-N(5)	2.120(4)
O(2)-V(1)-O(1)	108.27(14)	O(1)-V(1)-O(4)	110.33(13)
O(5)-V(2)-O(4)	108.02(16)	O(5)-V(2)-O(6)	108.6(2)
O(2)-V(1)-O(4)	108.11(15)	O(5)-V(2)-O(3)#1	109.99(16)
O(7)-V(3)-O(1)	178.09(15)	N(7)-V(3)-N(1)	92.07(14)
O(7)-V(3)-N(5)	93.33(16)	N(1)-V(3)-N(5)	173.46(14)

Symmetry codes: #1 -x+2,-y+2,-z

Table S2. Hydrogen-bonding geometry (Å, °) for compounds **1–2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry codes
compound 1					
O3-H3B... O8	0.847	1.964	2.741	151.93	-x+1/2, y+1/2, -z+2
O3-H3C... O13	0.850	2.363	3.200	168.34	
O4-H4D... O10	0.850	1.870	2.713	171.02	x-1/2, y+1/2, z
O5-H5A... O14	0.850	2.449	3.048	128.14	-x+1/2, -y+3/2, -z+2
O5-H5A... O5	0.850	2.503	2.940	112.92	x, -y+1, z
O5-H5A... O9	0.850	2.599	3.078	116.86	
O5-H5D... O5	0.850	1.996	2.839	171.37	-x+1/2, -y+3/2, -z+2
O5-H5E... O11	0.850	1.876	2.720	171.50	-x+1/2, y+1/2, -z+2
O13-H13... O6	0.850	2.360	3.163	157.72	-x+1/2, -y+1/2, -z+2
O14-H14C... O1	0.850	1.834	2.680	173.43	
O14-H14D... O3	0.850	1.915	2.761	173.25	
compound 2					
O8-H8C... O2	0.850	1.982	2.815	166.14	x, y-1, z
O8-H8D... O5	0.850	2.072	2.905	166.57	-x+2, -y+1, -z

Table S3. Bond valance sum calculations for compounds **1-2**.

1	**V site**	V1	V2	V3	V4
	BVS	4.97	5.03	4.92	4.98
	assigned O.S.	5	5	5	5
2	**V site**	V1	V2	V3	
	BVS	5.22	4.29	4.20	
	assigned O.S.	5	5	4	

The characterization data of Knoevenagel products

Entry 1. 2-benzylidenemalononitrile.

White solid, m.p. 75-77 ℃，(lit.[1] 85 ℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.79 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.06, 134.78, 13 1.08, 130.88, 129.79, 113.84, 112.67, 83.08.

Entry 2. 2-(4-chlorobenzylidene)malononitrile.

White solid, m.p. 166-168 ℃，(lit.[2] 167-168 ℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.72 (s, 1H) ,7.69 (d, *J* = 8.5 Hz 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.44, 133.11, 131.83, 129.96, 12 9.66, 113.46, 112.34, 83.54.

Entry 3. 2-(4-bromobenzylidene)malononitrile.

White solid, m.p. 164-166 ℃, (lit.[2] 162 ℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.74 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.42, 141.30, 131.98, 130.22, 129.40, 113.57, 112.47, 83.49.

Entry 4. 2-(4-nitrobenzylidene)malononitrile.

Yellow solid, m.p. 149-151 ℃, (lit.[1] 159 ℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.98, 150.51, 135.92, 131.45, 124.80, 112.77, 111.73, 87.71.

Entry 5. 2-(4-methylbenzylidene)malononitrile.

White solid, m.p. 136-137 ℃, (lit.[3] 131 ℃); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.96, 159.00, 133.60, 124.17, 115.27, 114.57, 113.48, 78.74, 55.95.

Entry 6. 2-(4-methoxybenzylidene)malononitrile.

White solid, m.p. 114 ℃, (lit.[4] 119 ℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.66 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.84, 158.88, 133.49, 124.05, 115.16, 114.45, 113.37, 78.62, 55.83.

Entry 7. 2-(2-bromobenzylidene)malononitrile.

White solid, m.p. 87-88 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.88, 135.10, 134.15, 130.94, 129.96, 128.50, 126.60, 113.26, 111.94, 86.19.

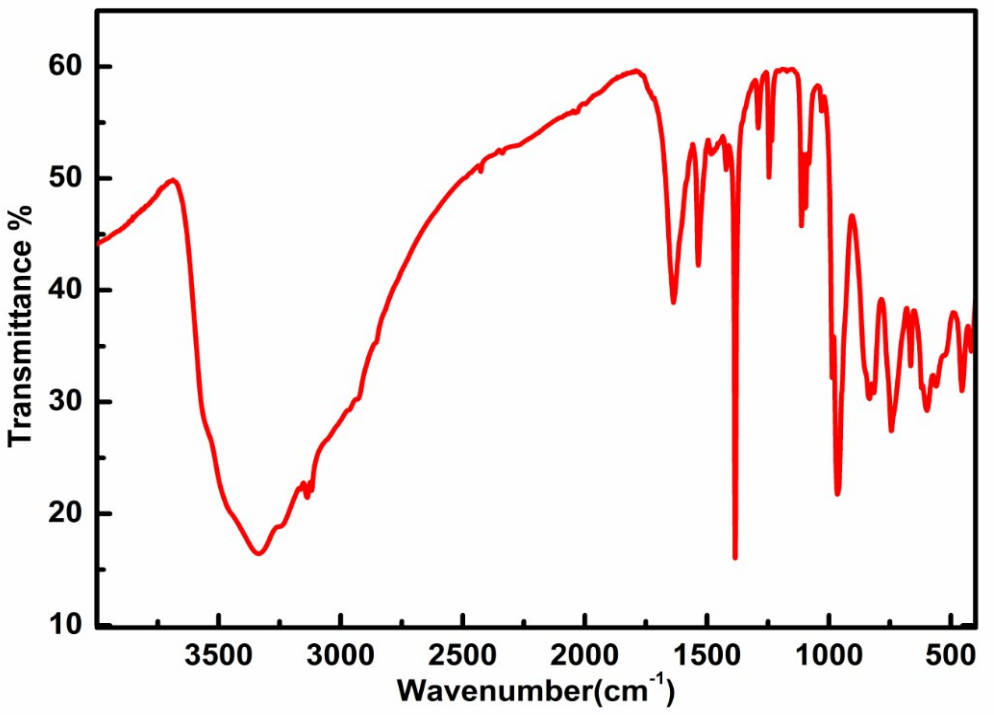

Figure S1. The IR spectrum of compound 1.

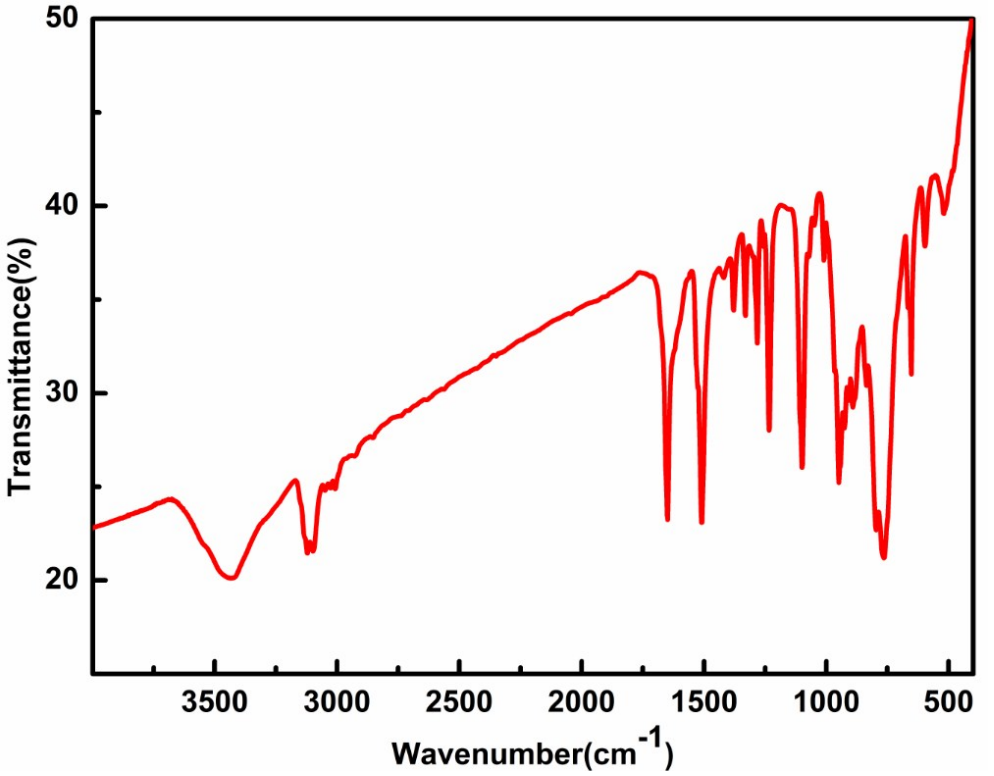

Figure S2. The IR spectrum of compound 2.

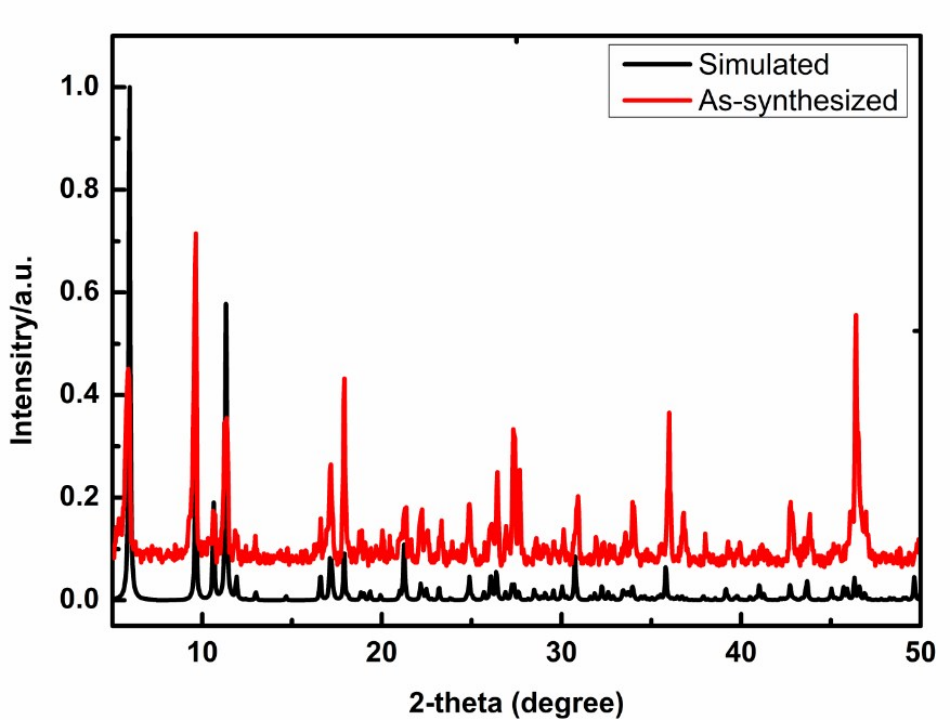

Figure S3. The PXRD spectrum of compound 1

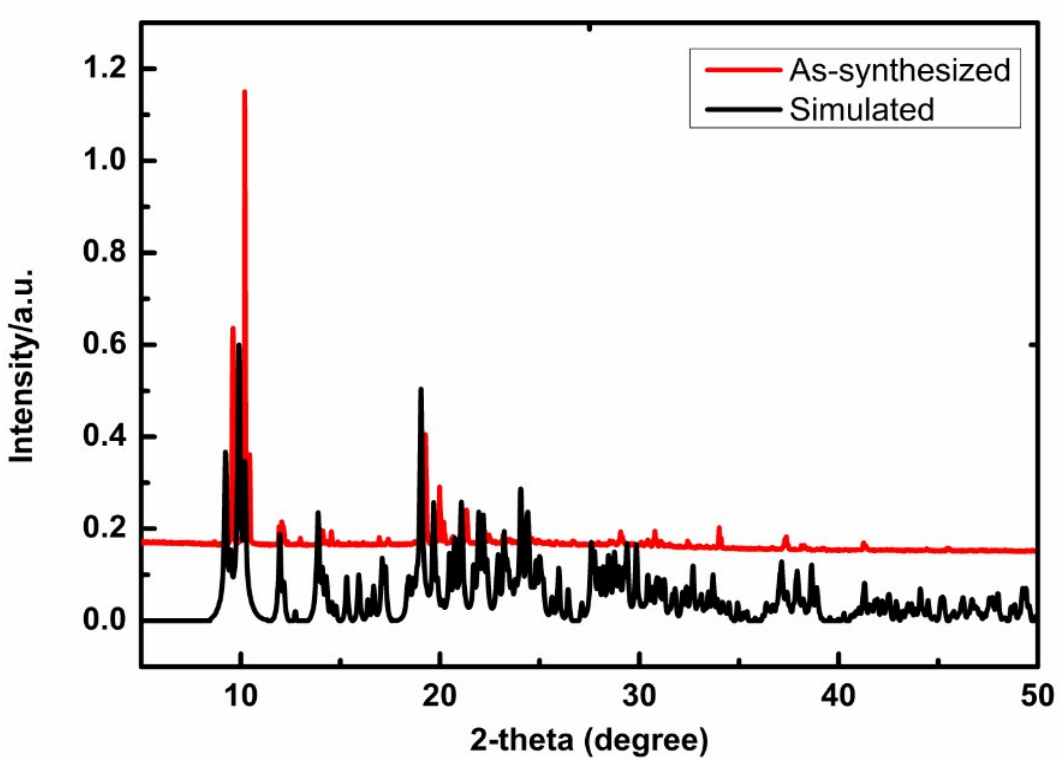

Figure S4. The PXRD spectrum of compound 2.

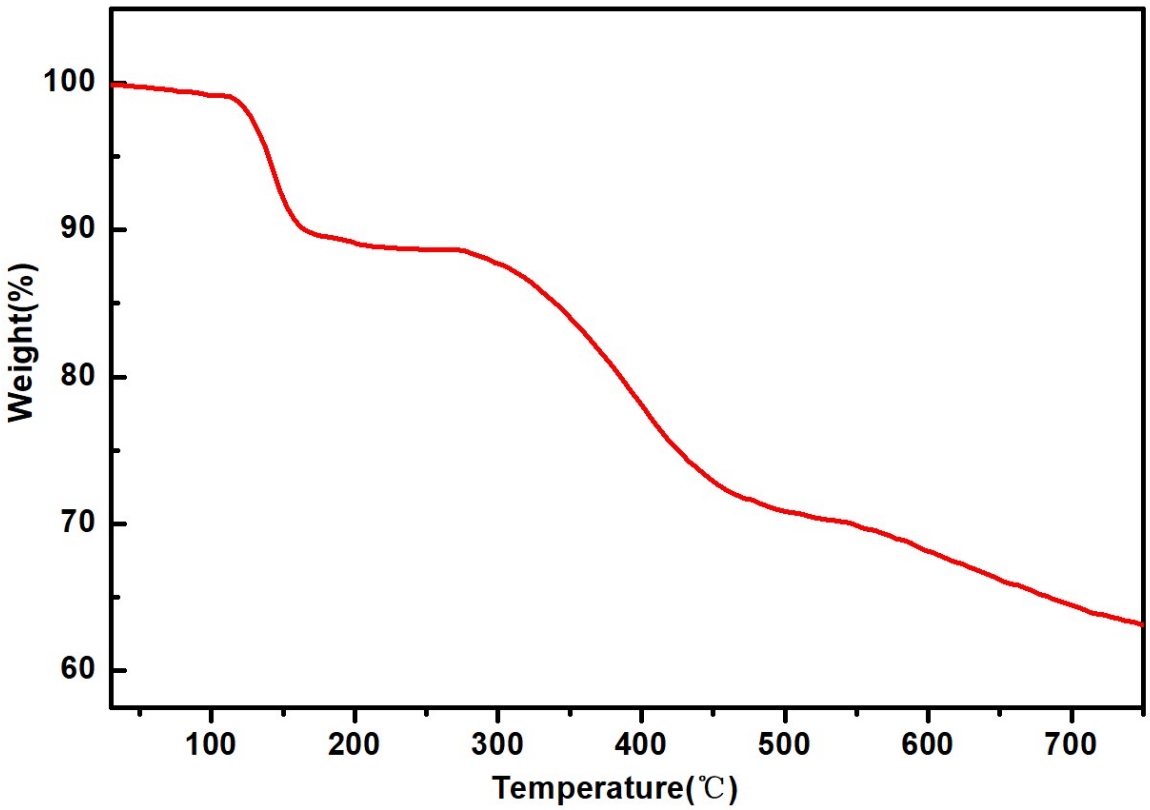

Figure S5 Thermogravimetric analysis curve of compound 1

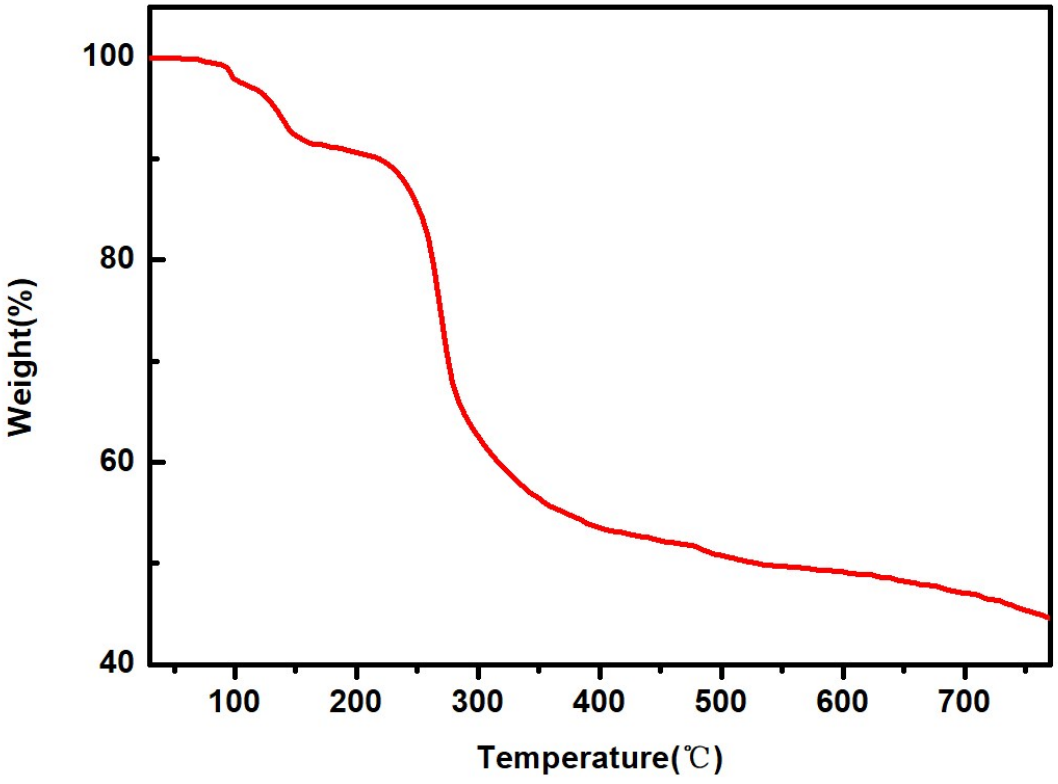

Figure S6 Thermogravimetric analysis curve of compound 2

The NMR spectra

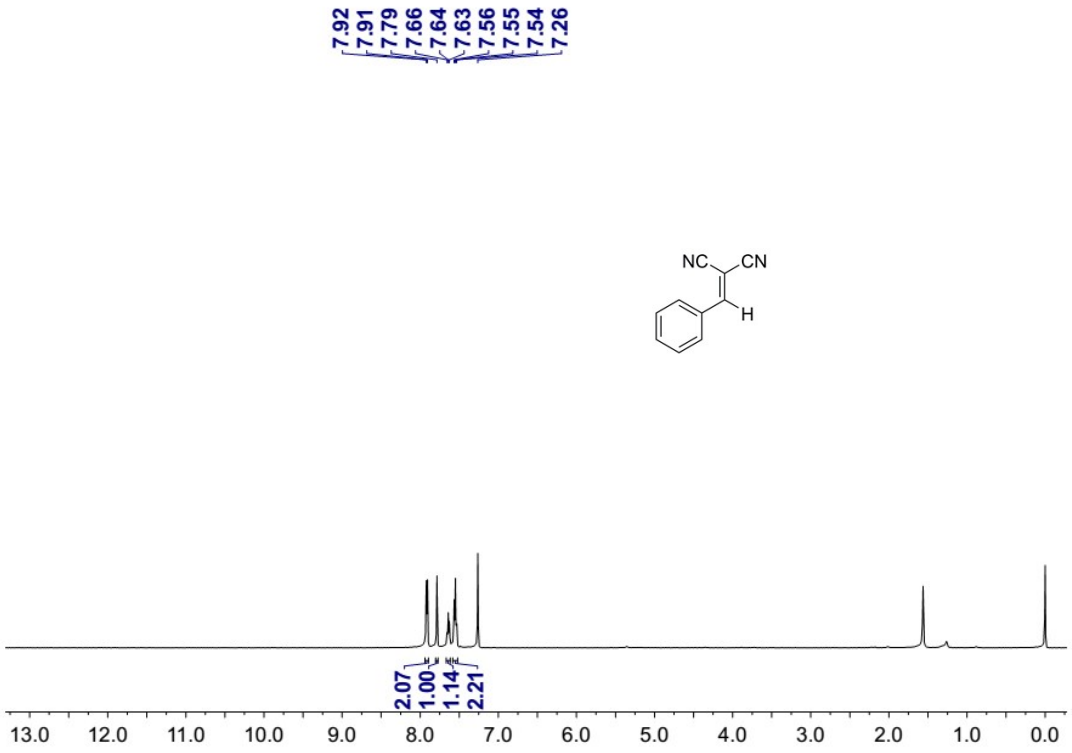

Figure S7. ^{1}H NMR spectrum of 2-benzylidenemalononitrile (entry 1) in $CDCl_3$.

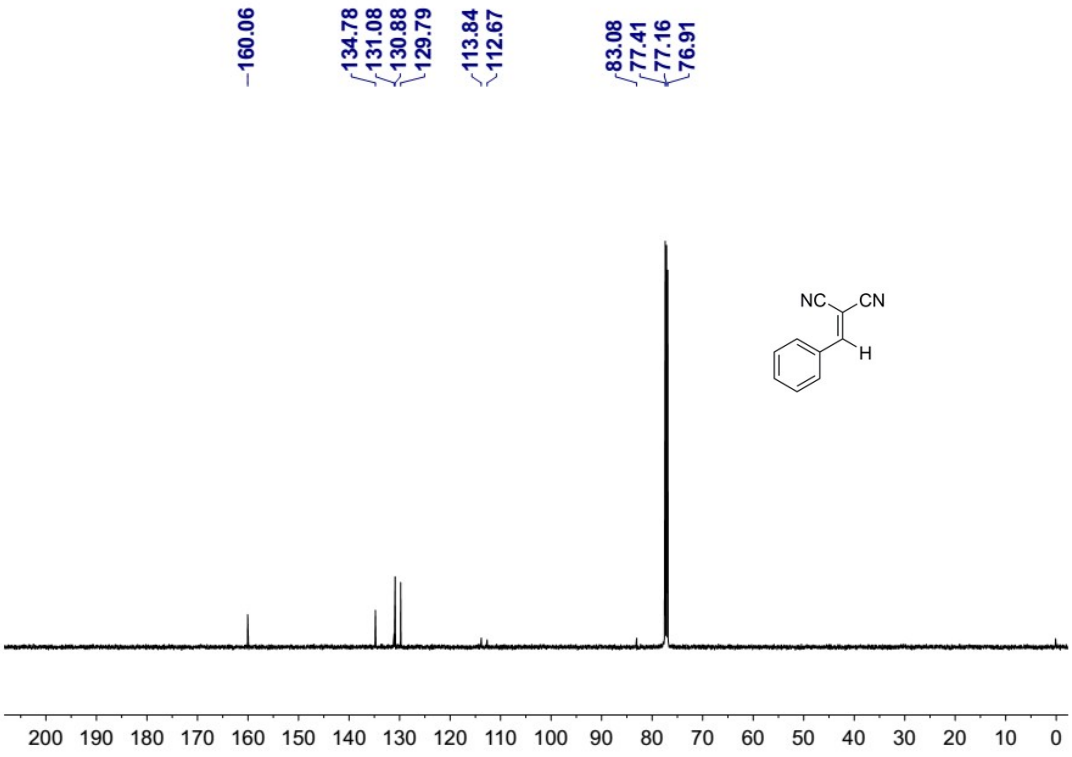

Figure S8. ^{13}C NMR spectrum of 2-benzylidenemalononitrile (entry 1) in $CDCl_3$.

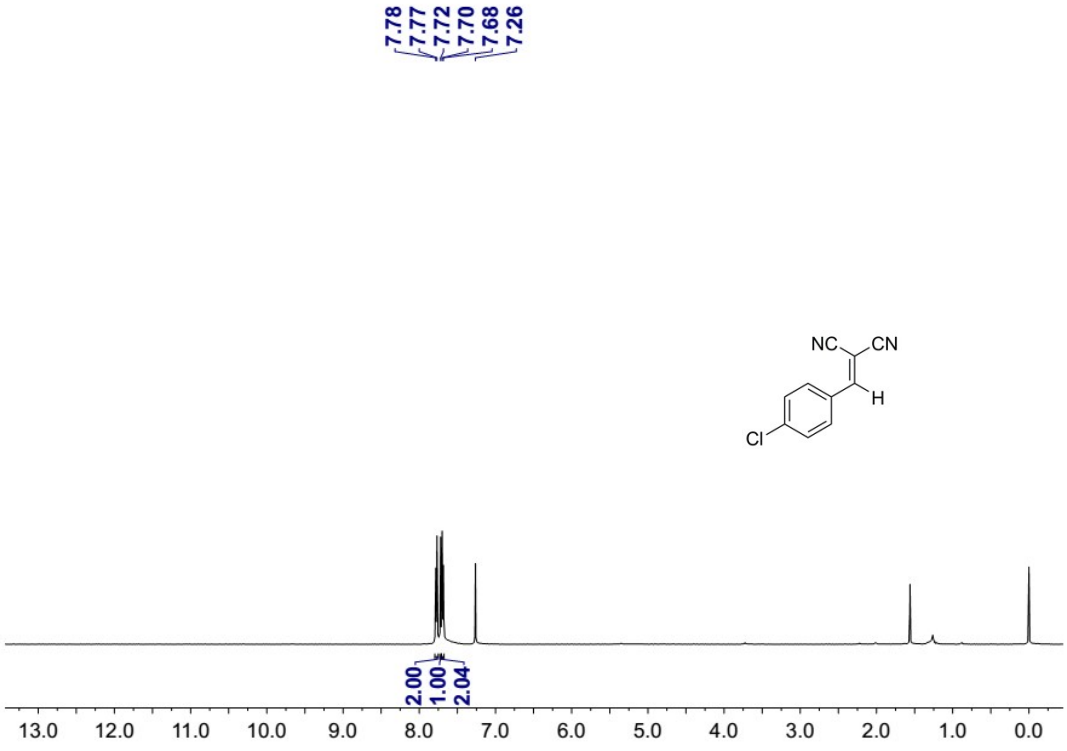

Figure S9. ^{1}H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile. (entry 2) in $CDCl_3$.

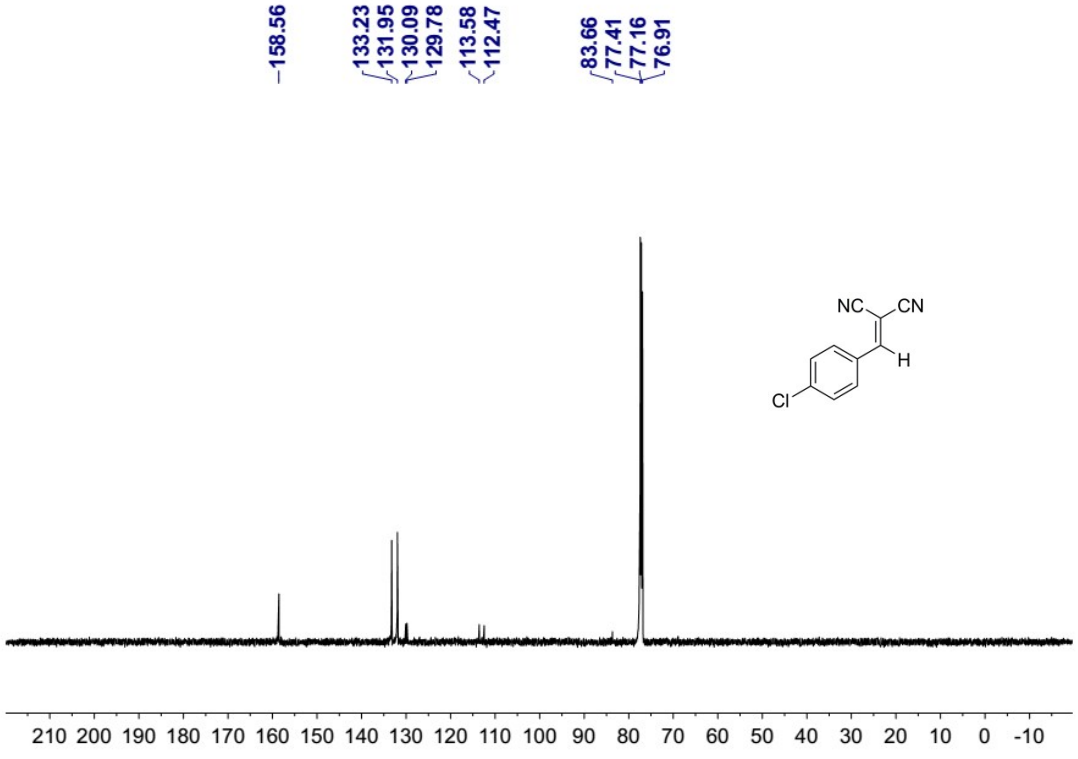

Figure S10. ^{13}C NMR spectrum of 2-(4-chlorobenzylidene)malononitrile (entry 2) in $CDCl_3$.

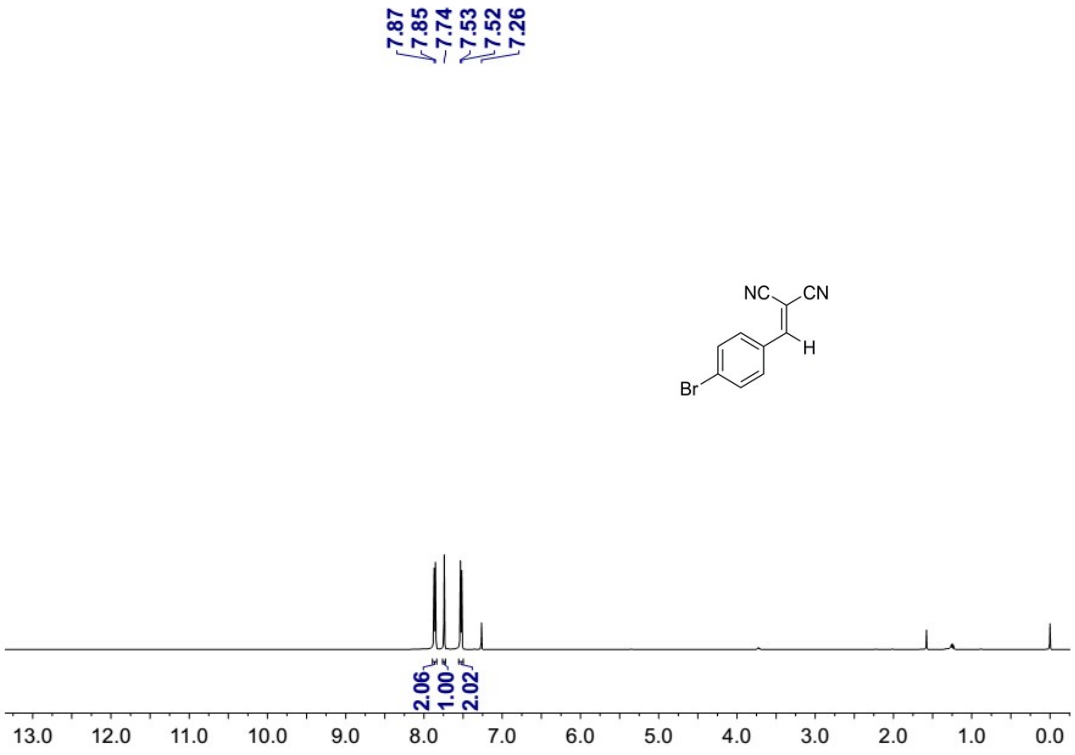

Figure S11. ^{1}H NMR spectrum of 2-(4-bromobenzylidene)malononitrile(entry 2) in $CDCl_3$.

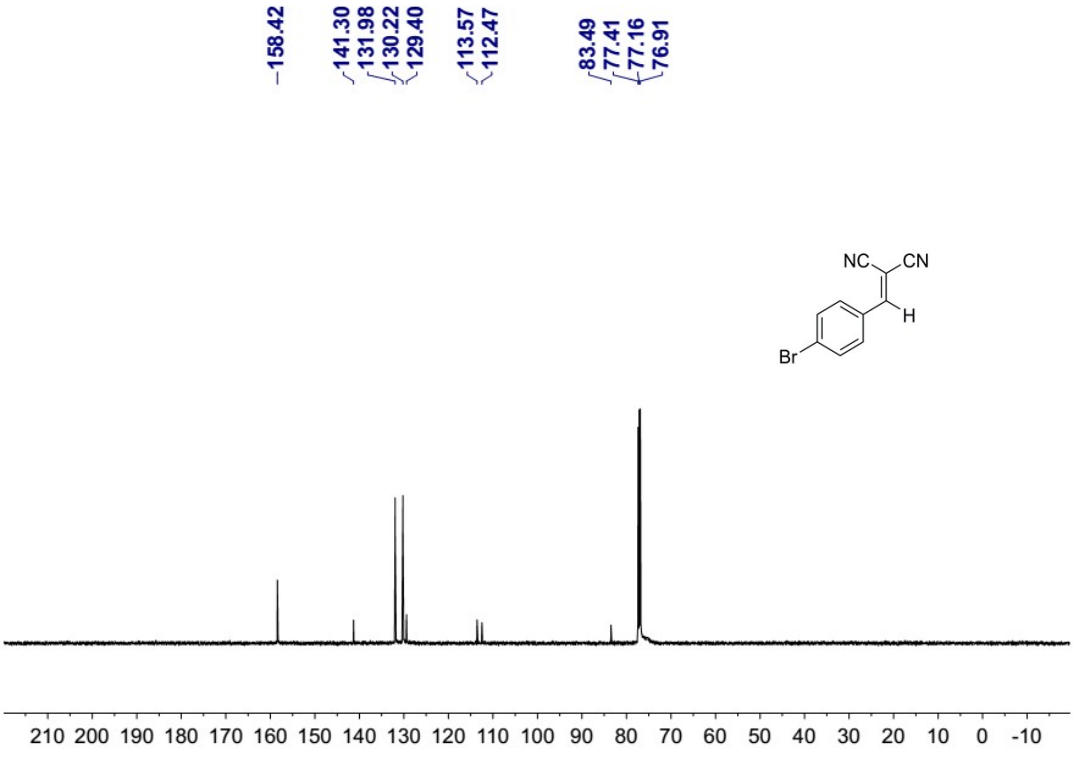

Figure S12. ^{13}C NMR spectrum of 2-(4-bromobenzylidene)malononitrile(entry 3) in $CDCl_3$.

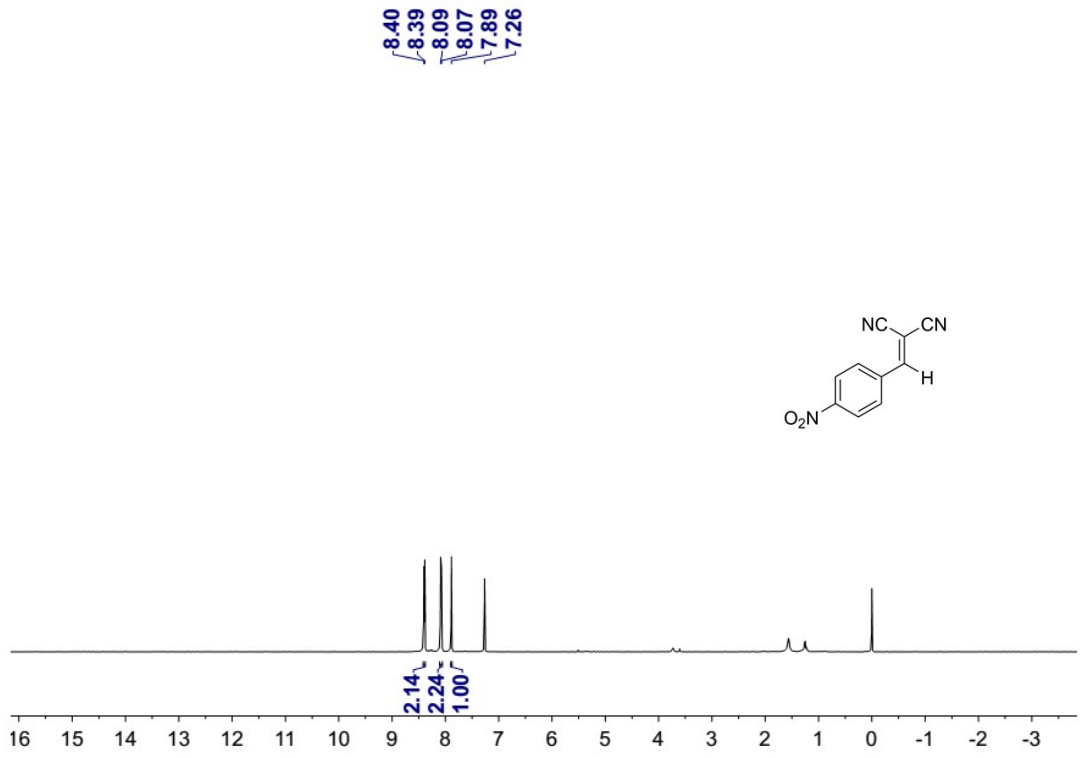

Figure S13. ^{1}H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile (entry 4) in $CDCl_3$.

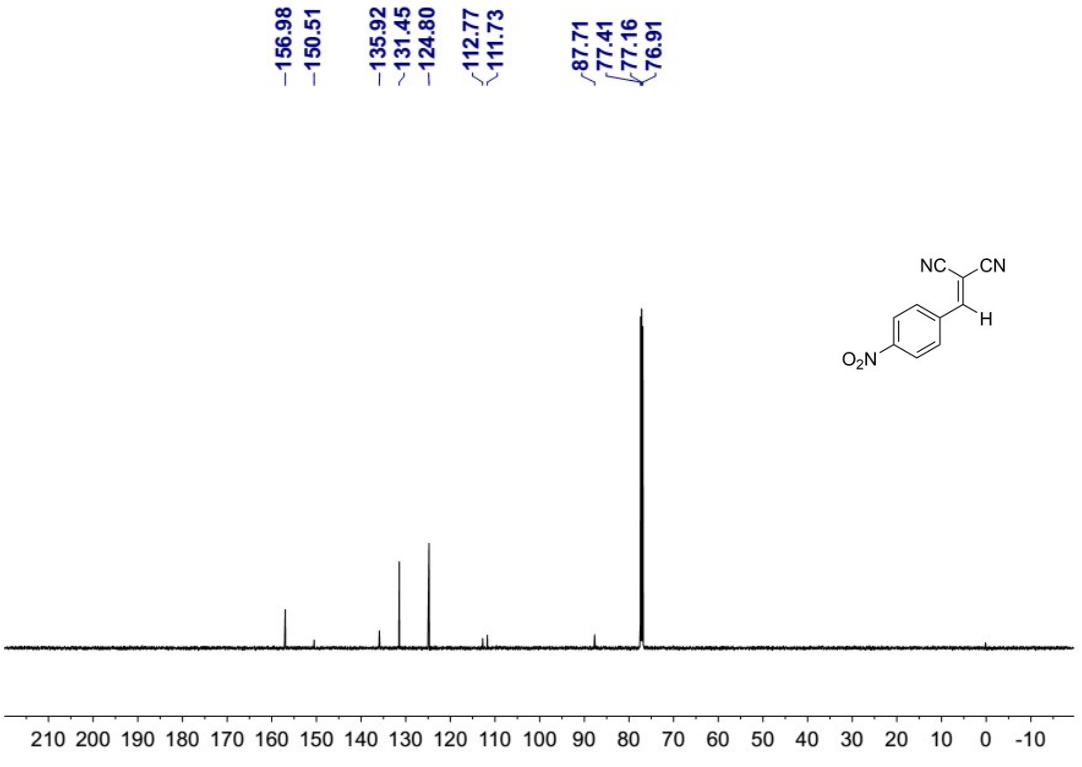

Figure S14. ^{13}C NMR spectrum of 2-(4-nitrobenzylidene)malononitrile (entry 4) in $CDCl_3$.

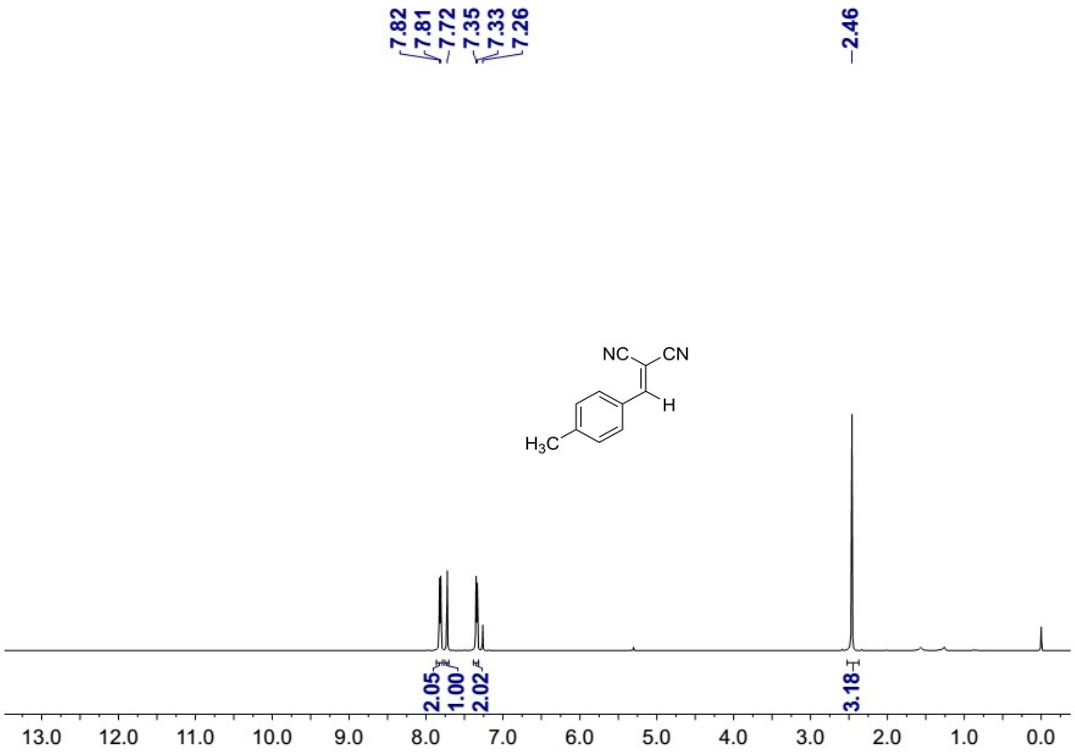

Figure S15. ^{1}H NMR spectrum of 2-(4-methylbenzylidene)malononitrile (entry 5) in $CDCl_3$.

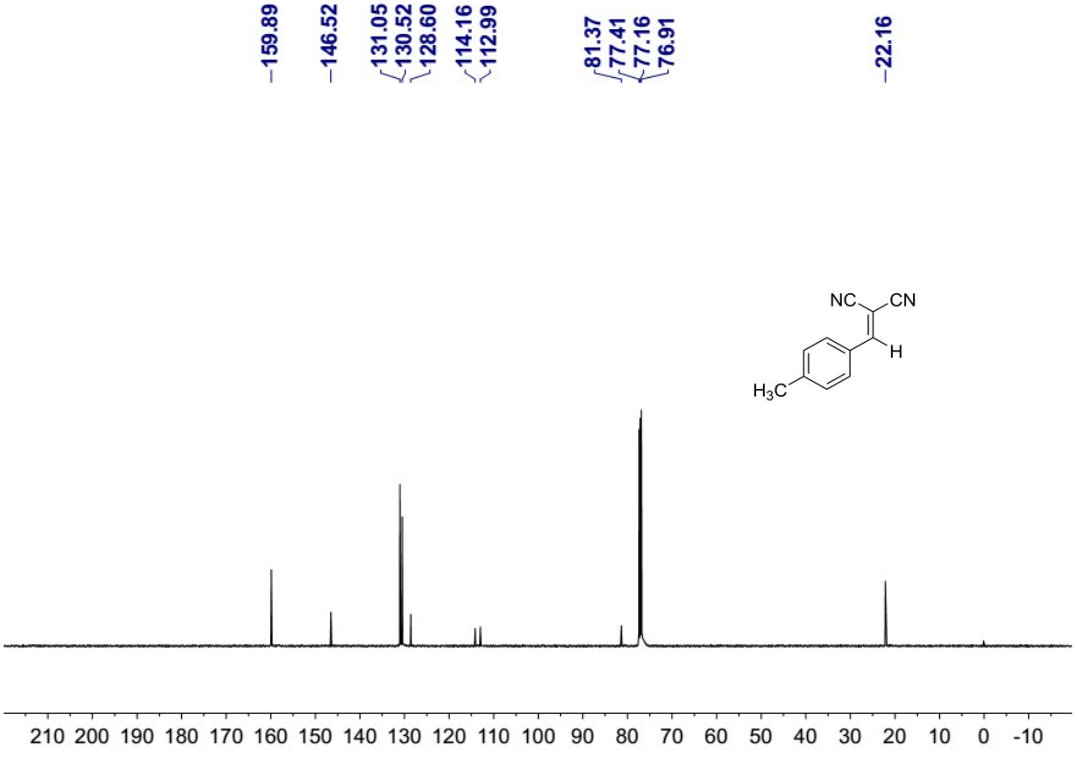

Figure S16. ^{13}C NMR spectrum of Entry 2-(4-methylbenzylidene)malononitrile (entry 5) in $CDCl_3$.

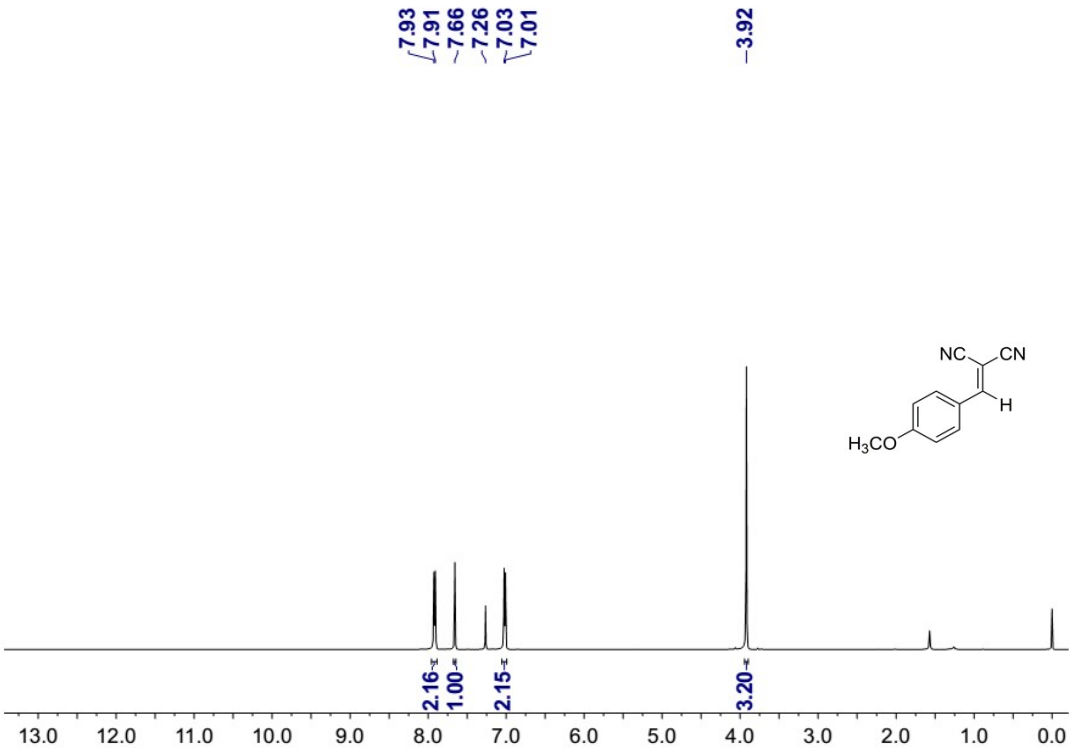

Figure S17. ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile (entry 6) in $CDCl_3$.

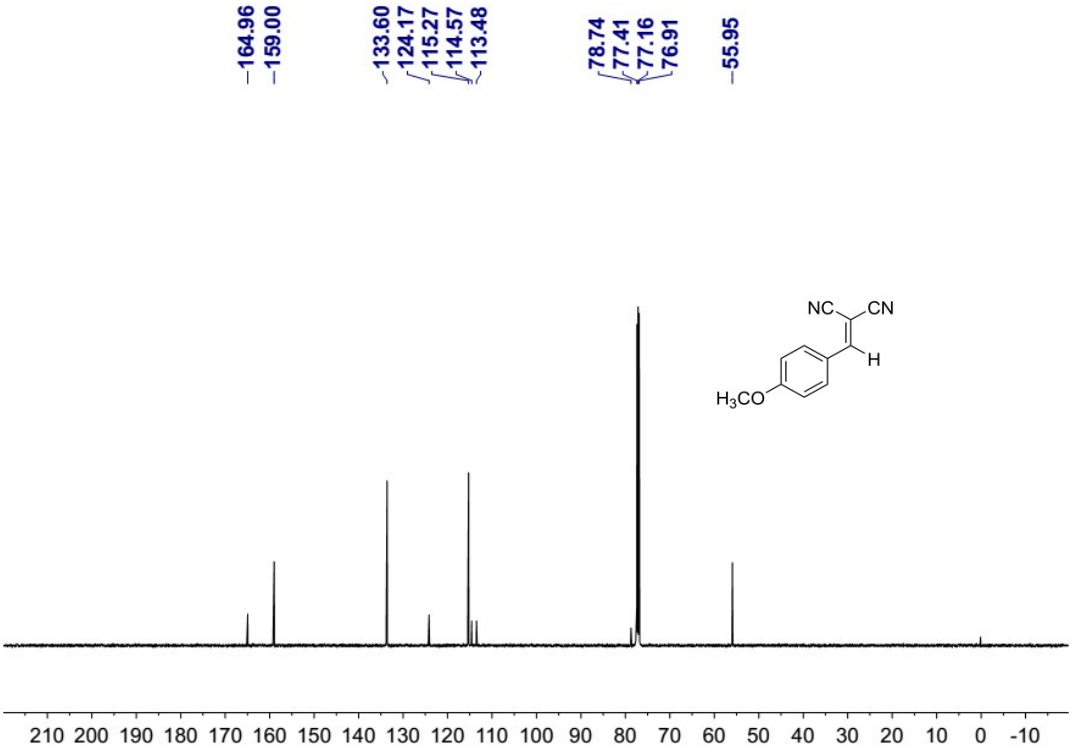

Figure S18. ^{13}C NMR spectrum of 2-(4-methoxybenzylidene)malononitrile (entry 6) in $CDCl_3$.

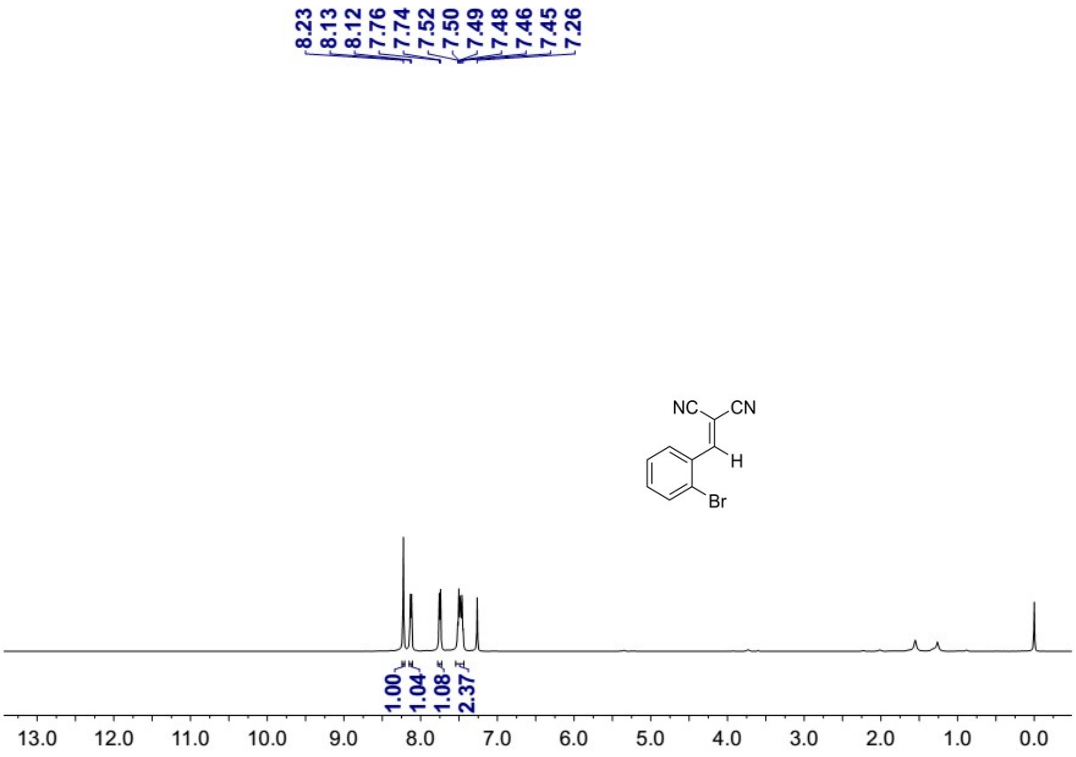

Figure S19. ^{1}H NMR spectrum of 2-(2-bromobenzylidene)malononitrile (entry 7) in $CDCl_3$.

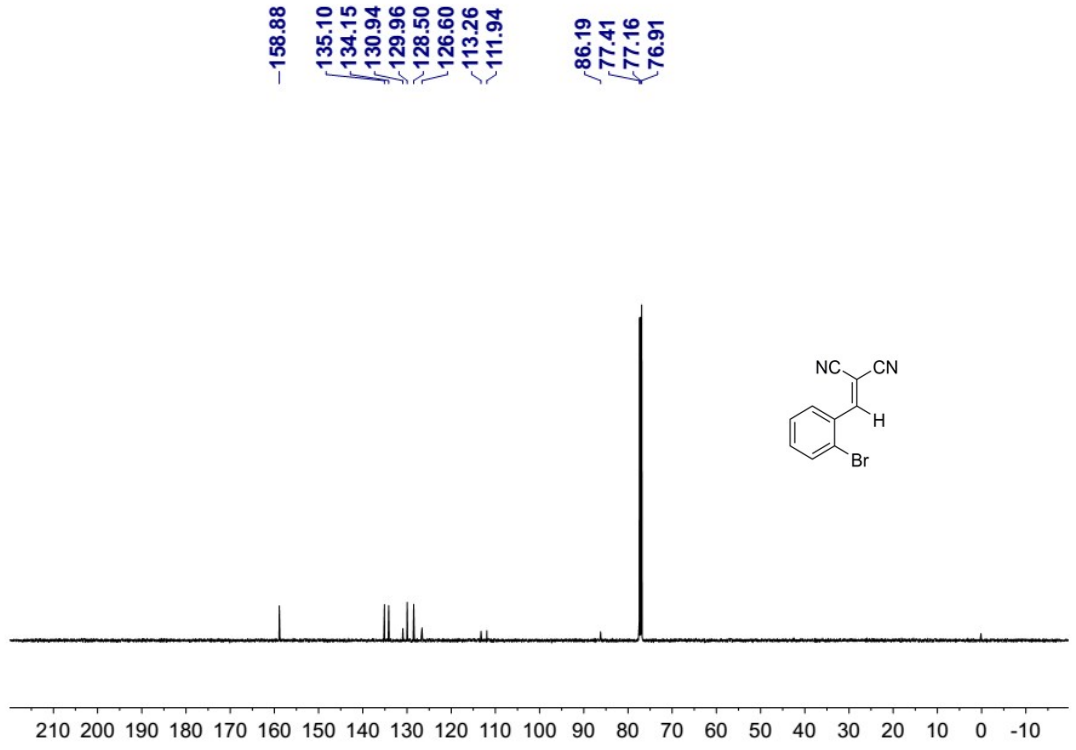

Figure S20. ^{13}C NMR spectrum of 2-(2-bromobenzylidene)malononitrile (entry 7) in $CDCl_3$.

References

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