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Nitrogen enriched polytriazine as metal-free heterogeneous catalyst for the Knoevenagel reaction under mild conditions

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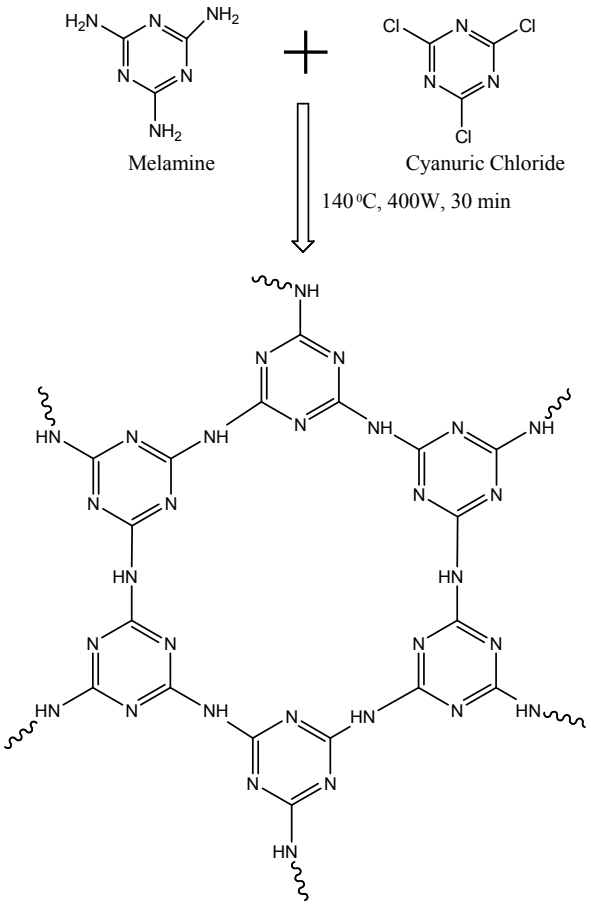


Scheme S1. Reaction scheme for the synthesis of metal-free nitrogen-enriched nanoporous polytriazine (NENP-1) organocatalyst.

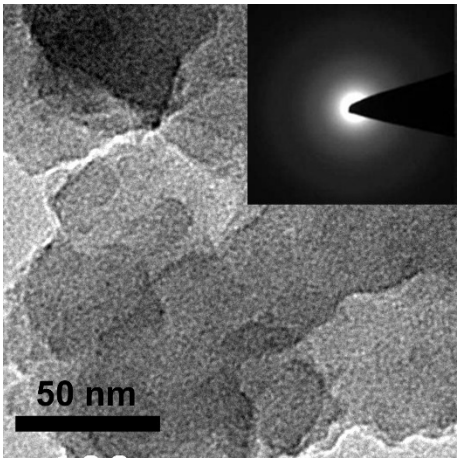


Figure S1. TEM image of NENP-1 (inset: SAED pattern of NENP-1).

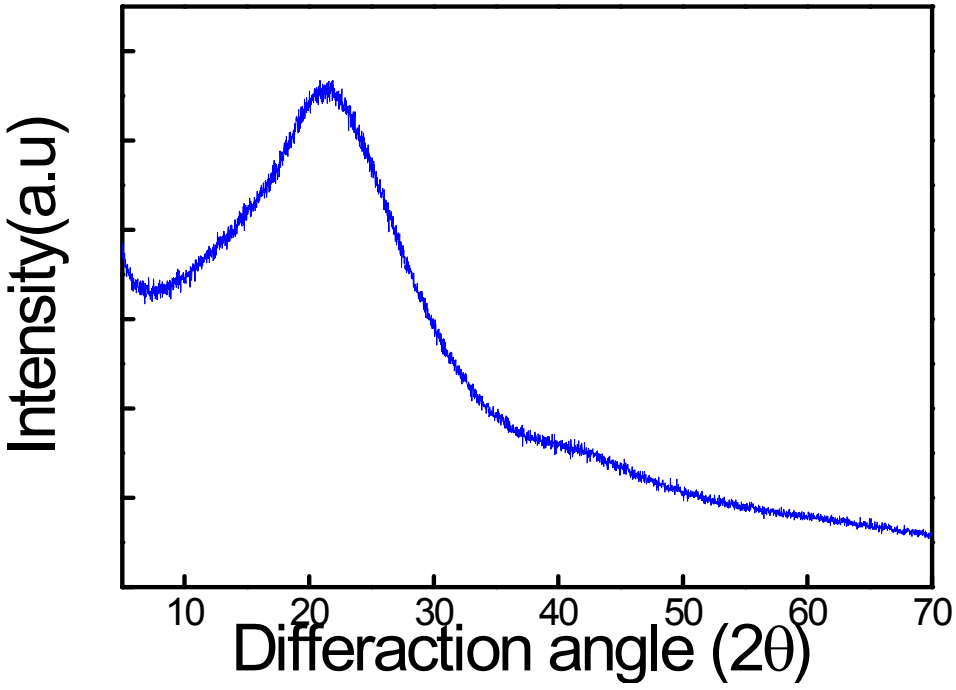


Figure S2. XRD pattern of NENP-1.

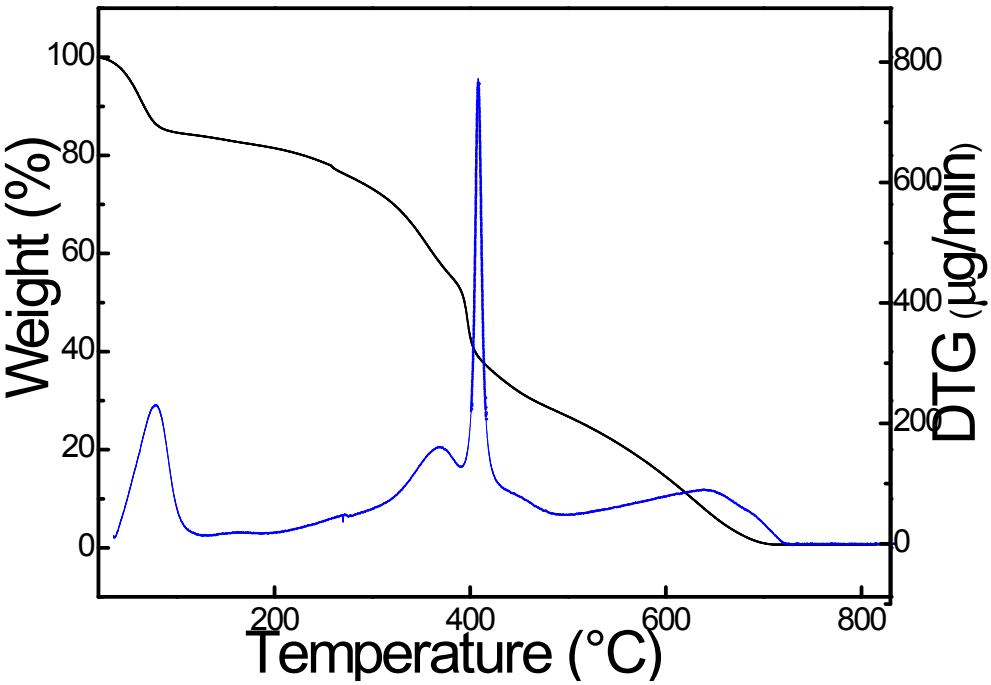


Figure S3. TGA/DTG of NENP-1 in air at a heating rate of 5 °C min^{-1}.

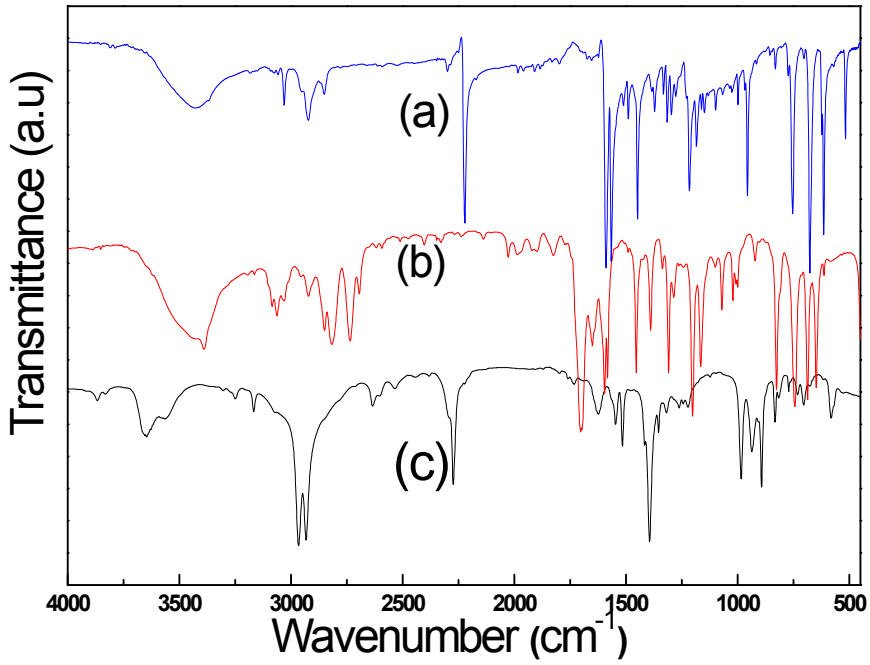


Figure S4. FT-IR spectra of (a) Benzylidinemalononitrile, (b) Benzaldehyde, and (c) Malononitrile.

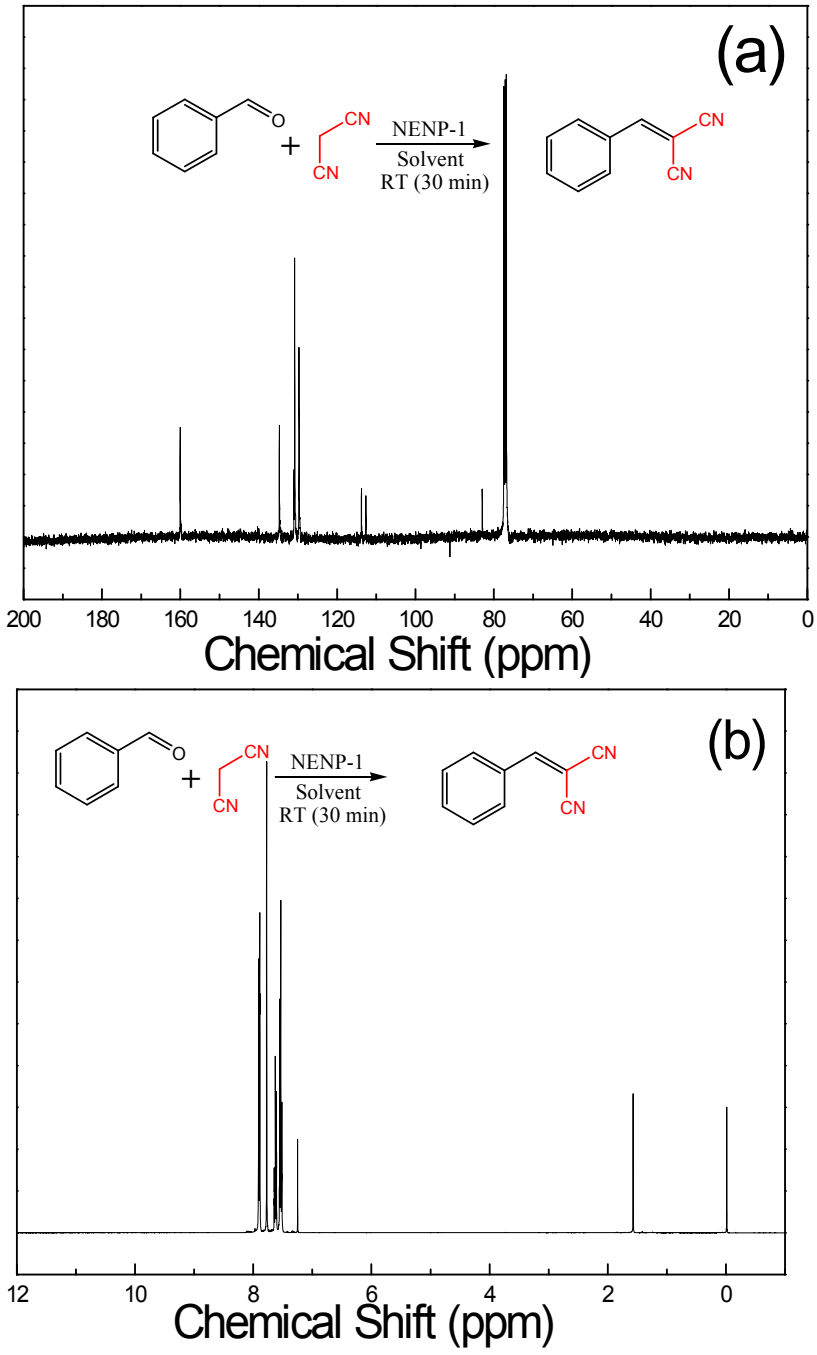


Figure S5. (a) ^{13}C and (b) ^{1}H NMR spectra of benzylidinemalononitrile.

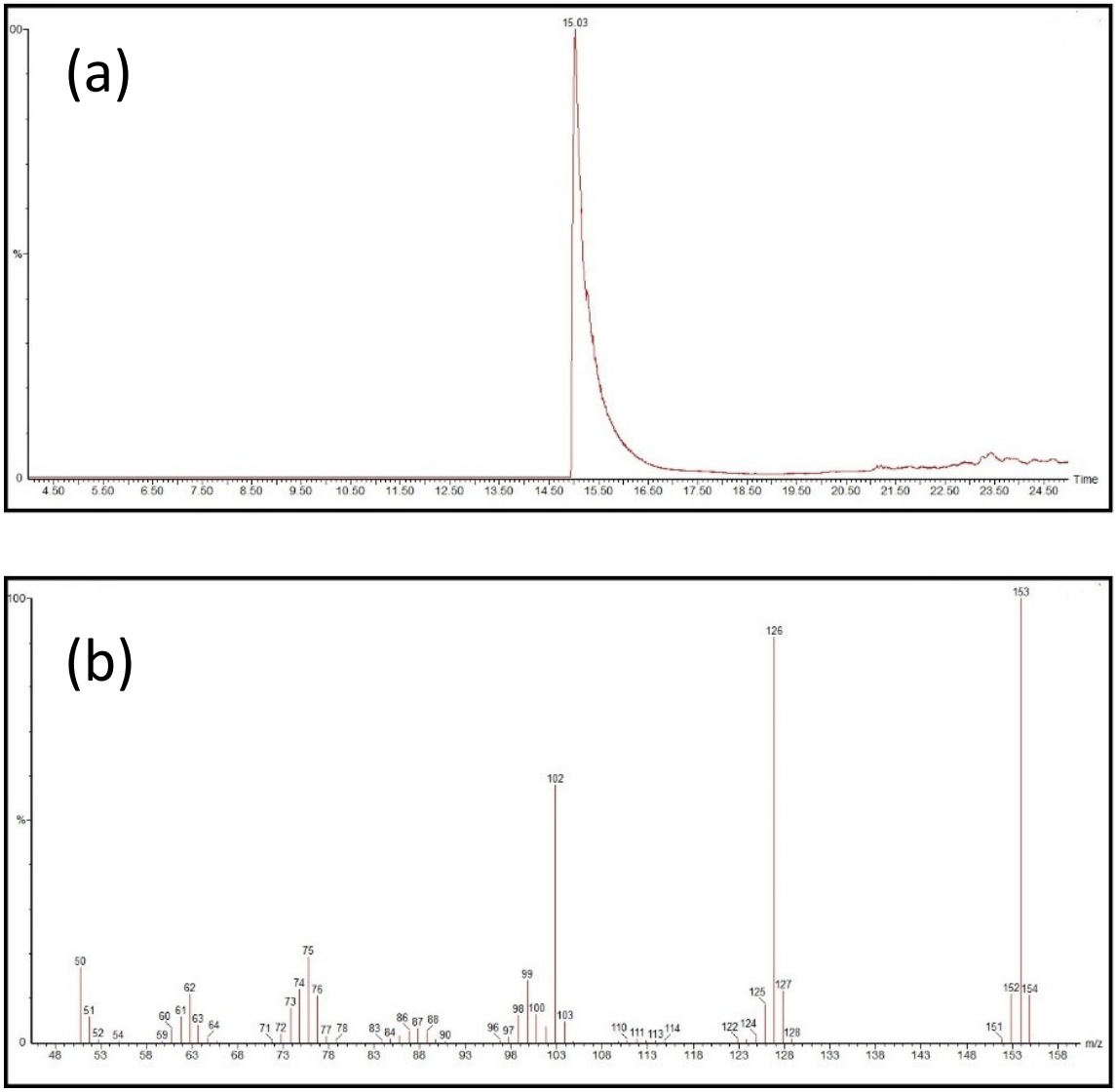
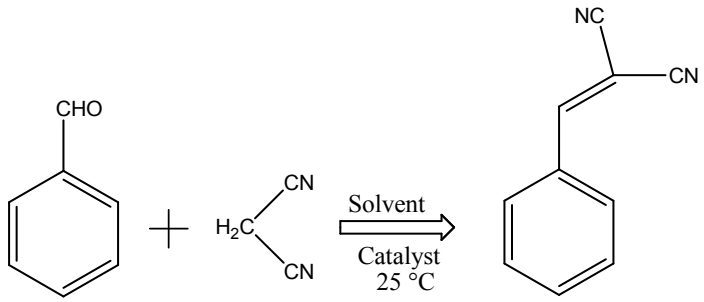


Figure S6. (a) GC and (b) MS spectrum of benzylidinemalononitrile.



Scheme S2. Synthesis of benzylidinemalononitrile from benzaldehyde and malononitrile.

Table S1. Catalytic data of the NENP-1 catalysed model Knoevenagel reaction at various reaction conditions.

Solvent	Volume (mL/mL)	Time (min)	Catalyst amount (wt%)	Yield (%)
THF	1.0/0	30	4.5	37
THF/H_2O	0.5/0.5	30	4.5	95
Methanol	1.0/0	30	4.5	85
Methanol/H_2O	0.5/0.5	30	4.5	94
Ethanol	1.0/0	30	4.5	87
Ethanol/H_2O	0.5/0.5	30	4.5	93
H_2O	1.0/0	30	4.5	48
Dioxane	1.0/0	30	4.5	41
Dioxane/H_2O	0.5/0.5	30	4.5	98
Dioxane/H_2O	0.5/0.5	30	1.9	35
Dioxane/H_2O	0.5/0.5	90	1.9	46
Dioxane/H_2O	0.5/0.5	30	8.6	98
Dioxane/H_2O	0.5/0.5	10	8.6	75
Dioxane/H_2O	0.5/0.5	02	4.5	45
Dioxane/H_2O	0.5/0.5	05	4.5	60
Dioxane/H_2O	0.5/0.5	10	4.5	71

General conditions: Benzaldehyde (1.0 mmol), Malononitrile (1.0 mmol) at 25 °C.

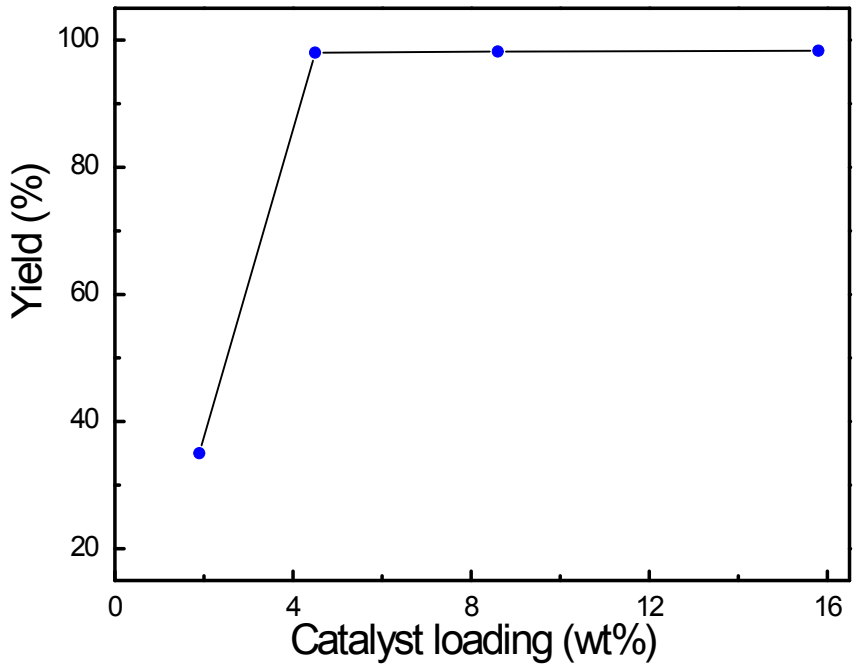
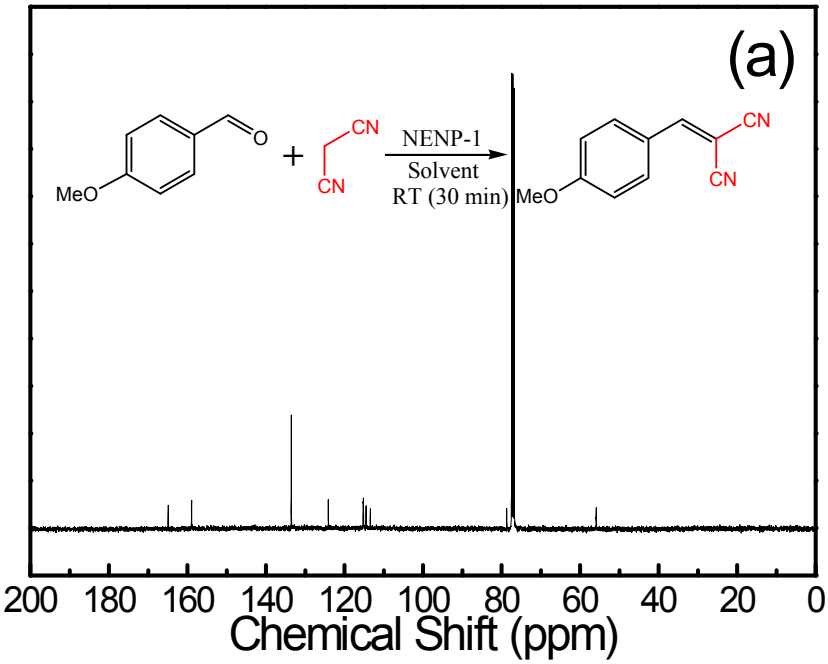


Figure S7. Effect of catalyst loading on yield (%) of benzyldinemalononitrile.



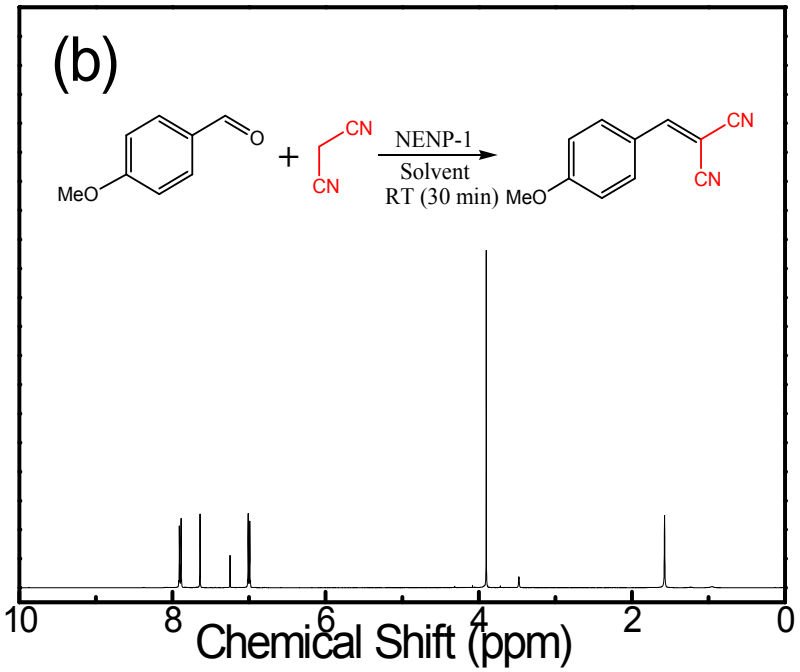


Figure S8. (a) ^{13}C and (b) ^{1}H spectra NMR spectra of 4-methoxy benzylidinemalononitrile.

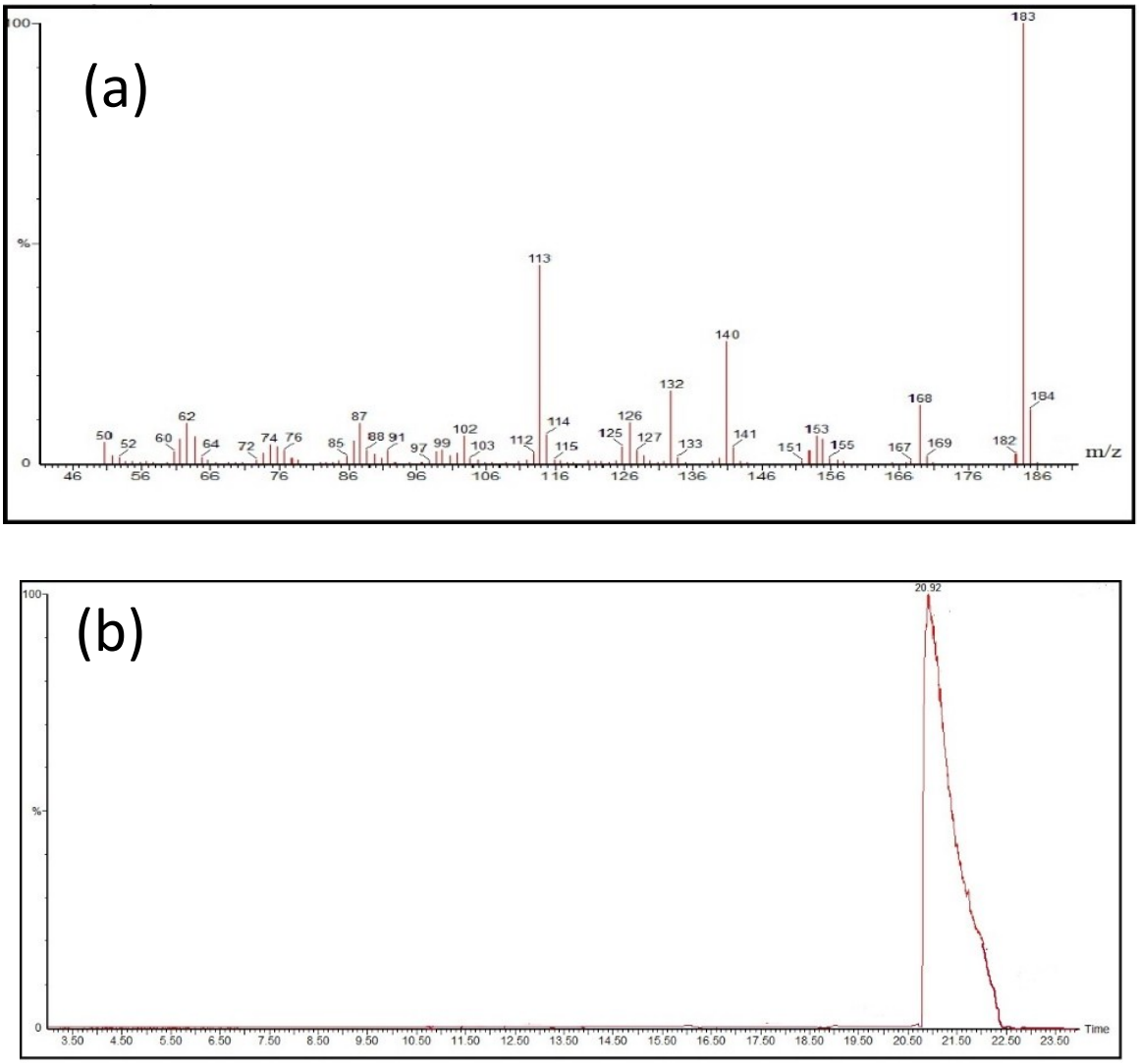


Figure S9. (a) GC and (b) MS spectrum of 4-methoxy benzylidinemalononitrile.

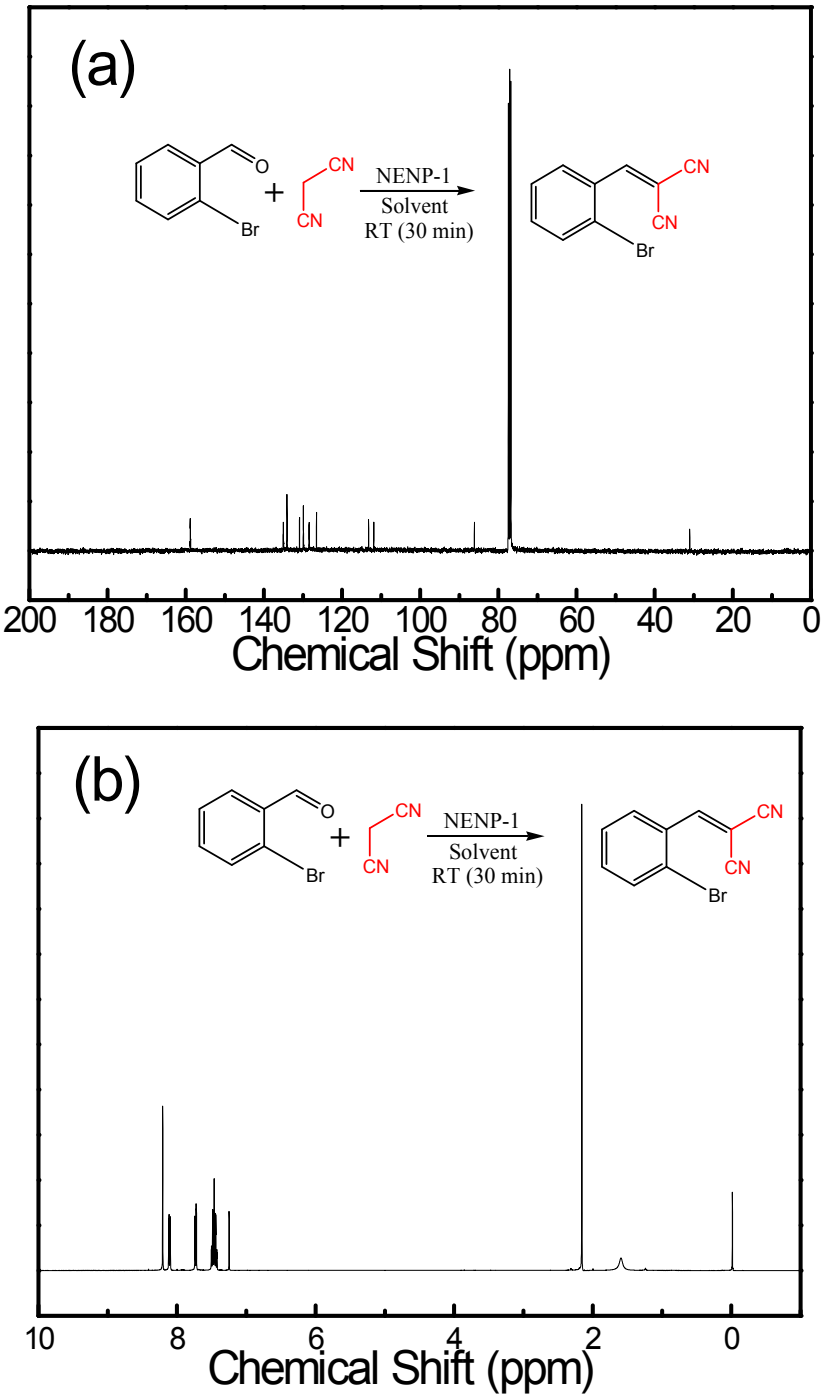


Figure S10. (a) ^{13}C and (b) ^{1}H NMR spectra of 2-bromobenzylidinemalononitrile.

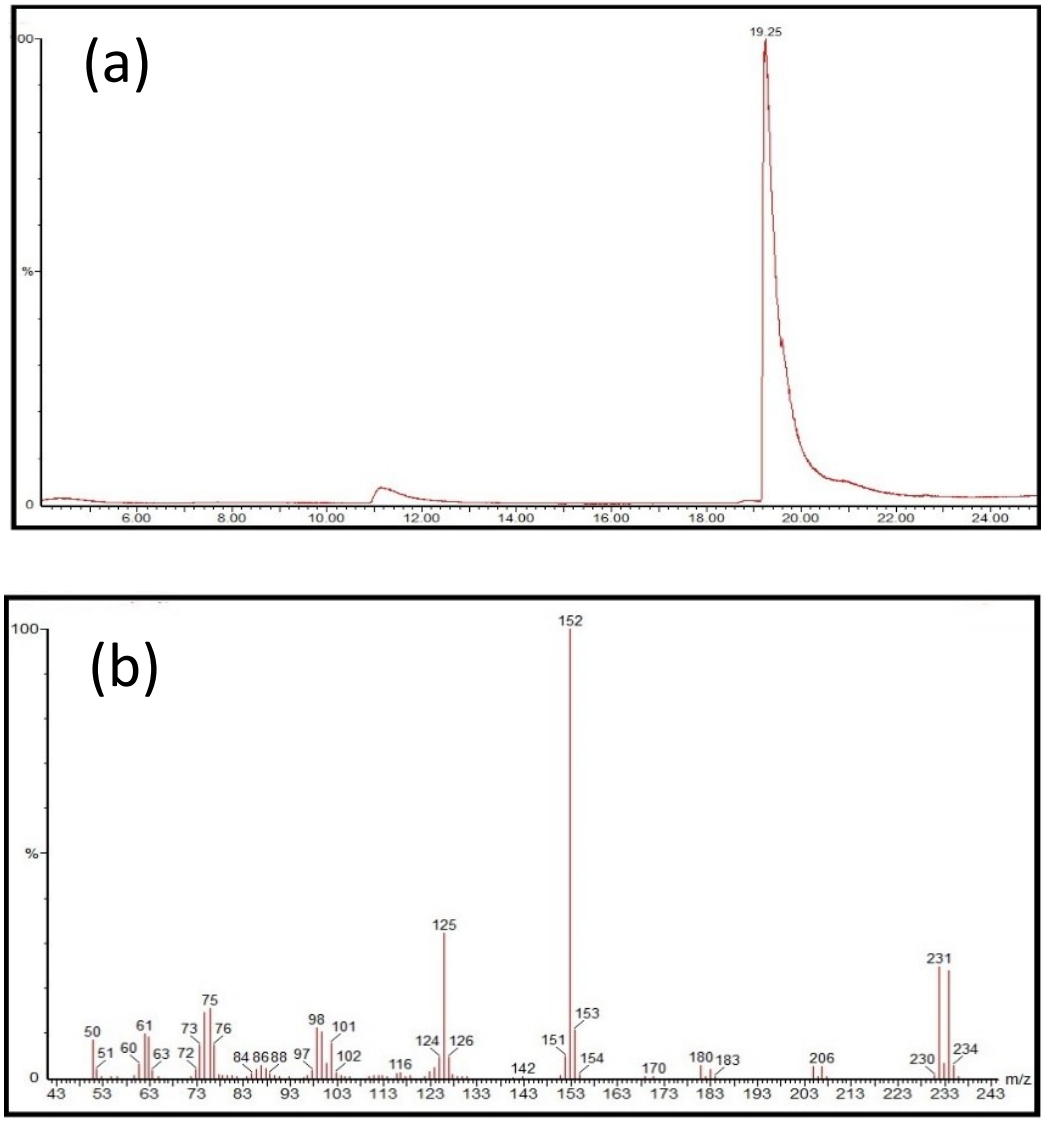


Figure S11. (a) GC and (b) MS spectrum of 2-bromobenzylidinemalononitrile.

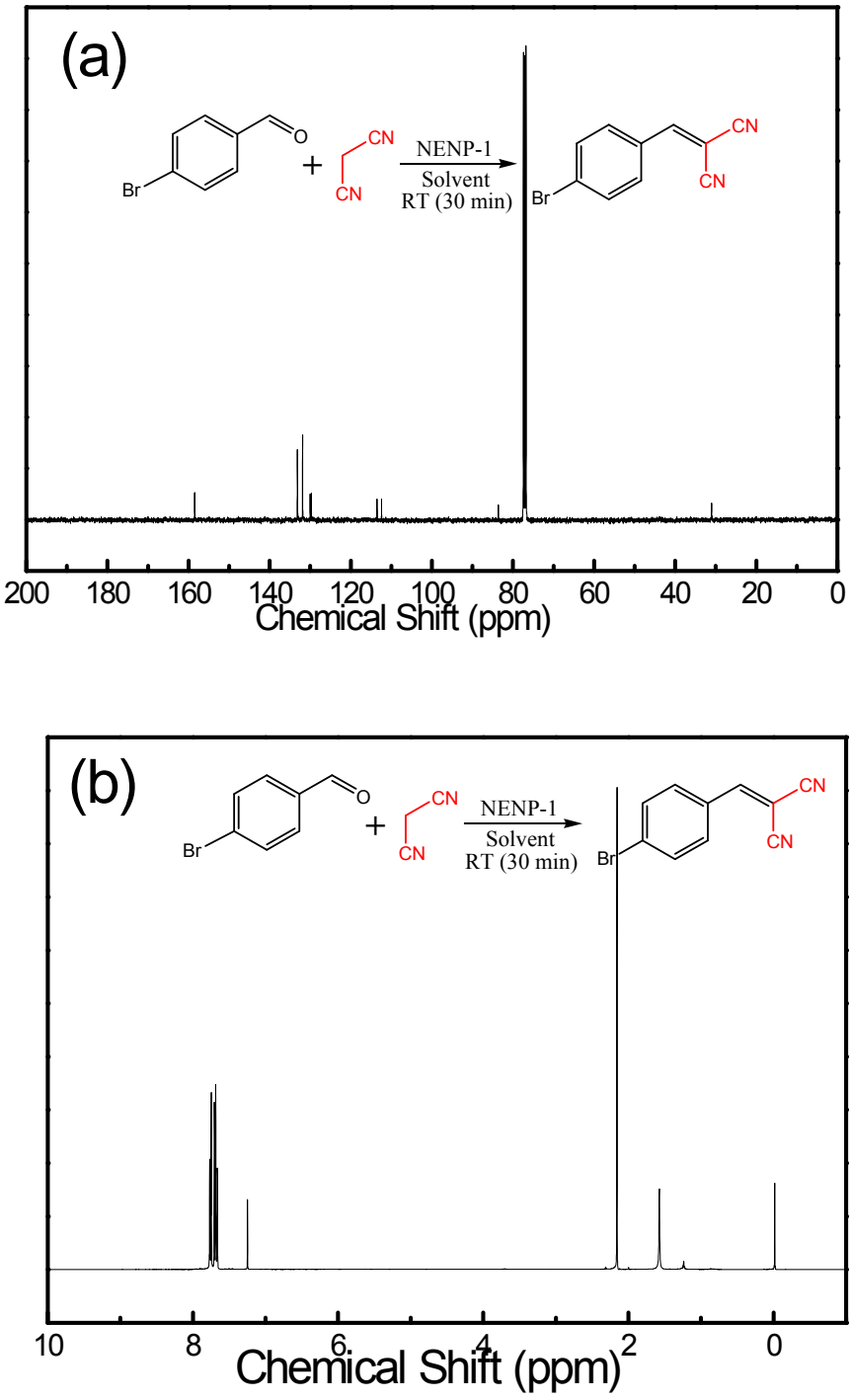


Figure S12. (a) ^{13}C and (b) ^{1}H NMR spectra of 4-bromobenzylidinemalononitrile.

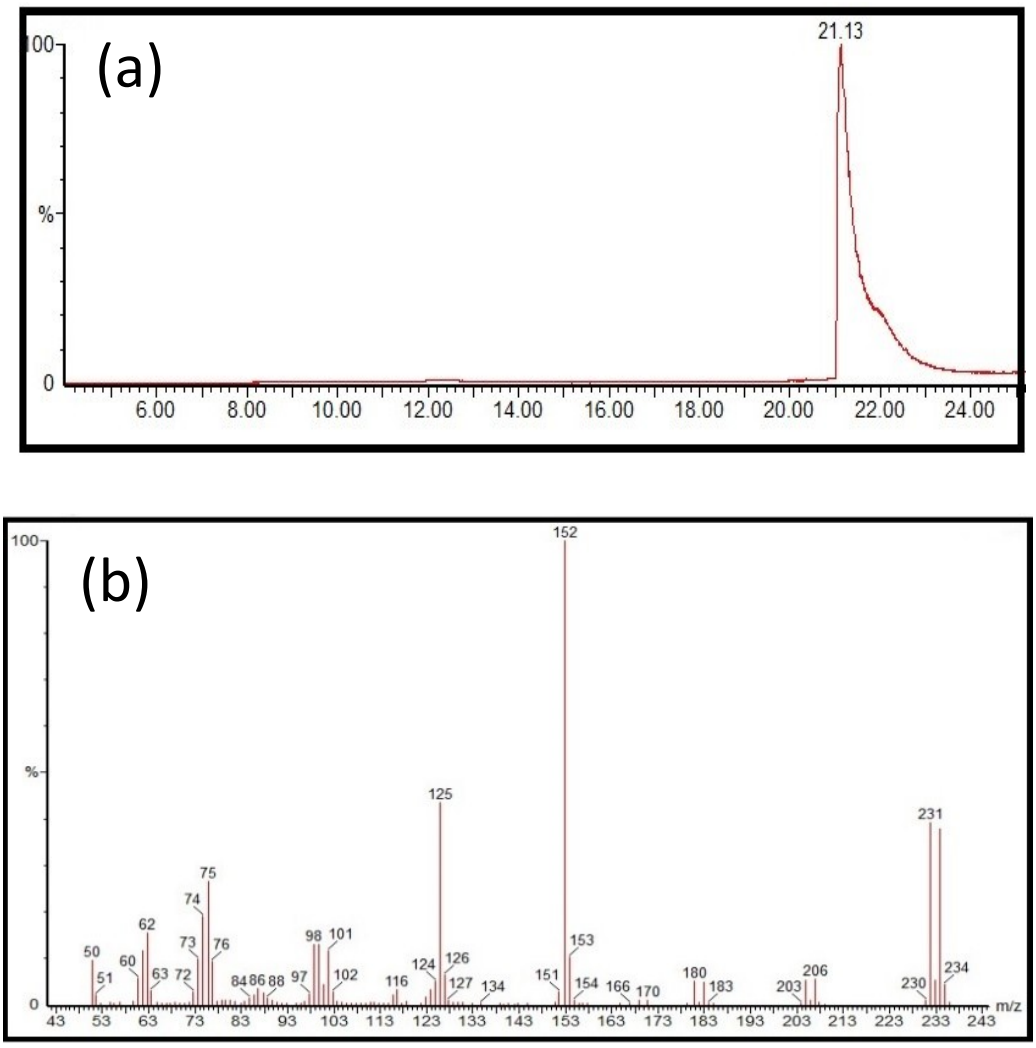


Figure S13. (a) GC (b) MS spectrum of 4-bromobenzylidinemalononitrile.

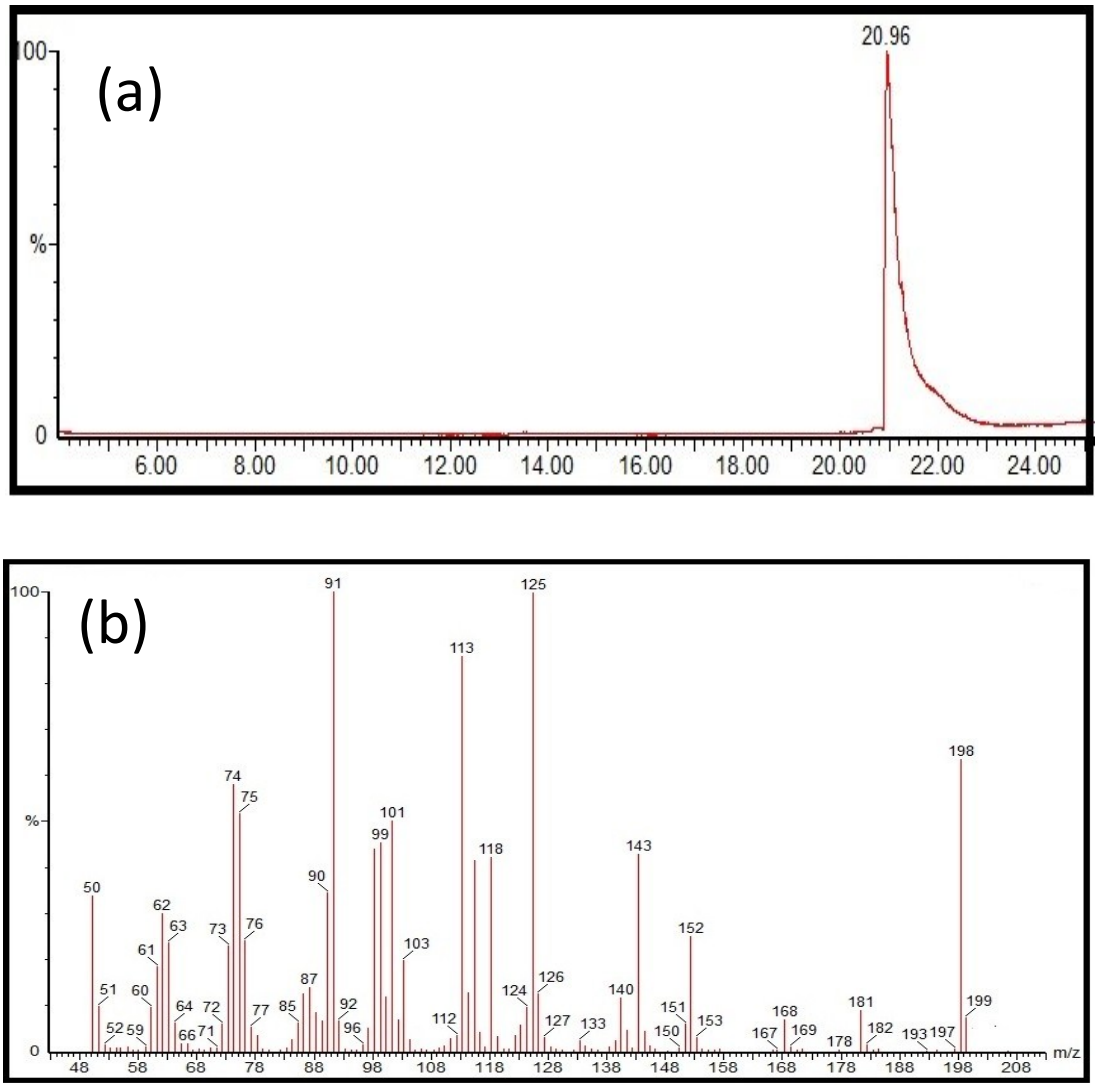


Figure S14. (a) GC and (b) MS spectrum of 2-nitrobenzylidinemalononitrile.

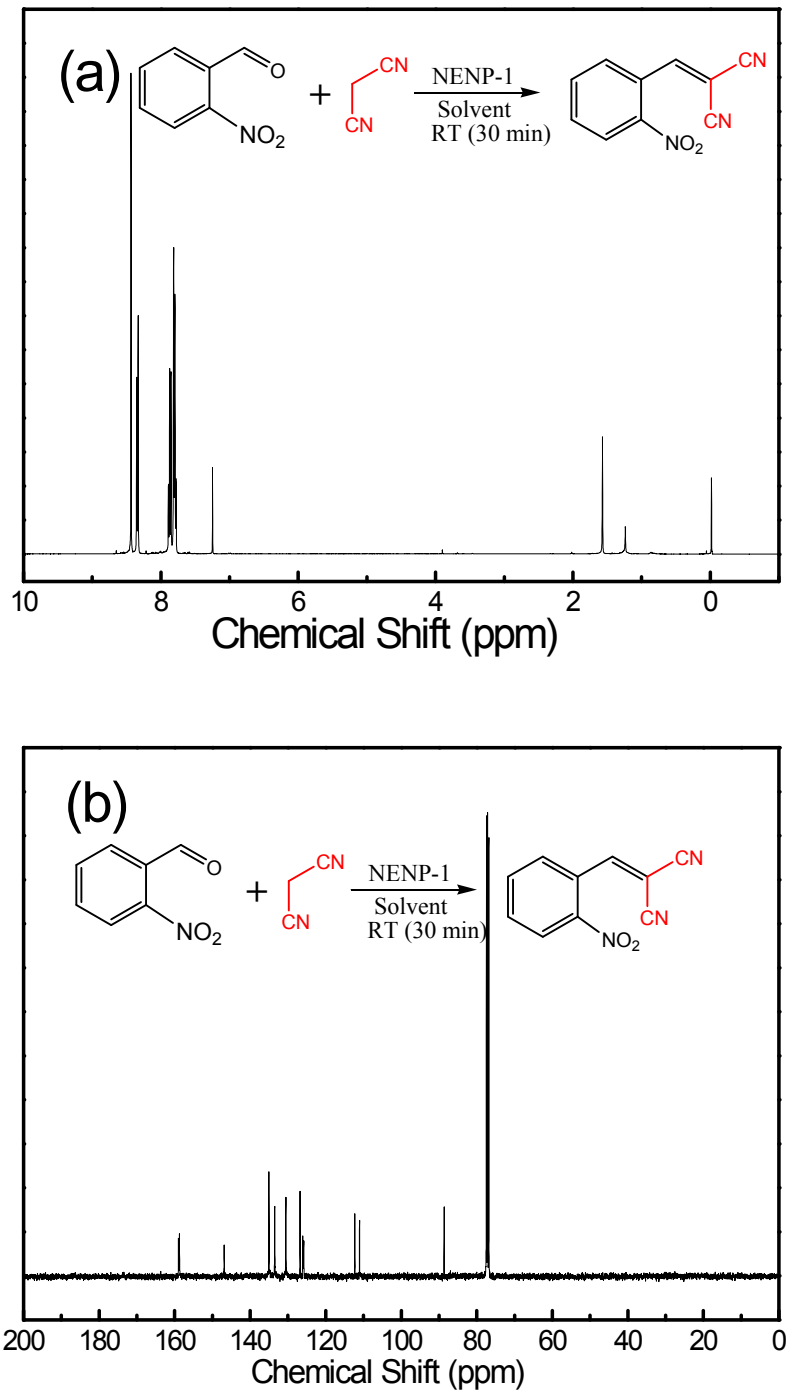


Figure S15. (a) ^{1}H and (b) ^{13}C NMR spectra of 2-nitrobenzylidinemalononitrile.

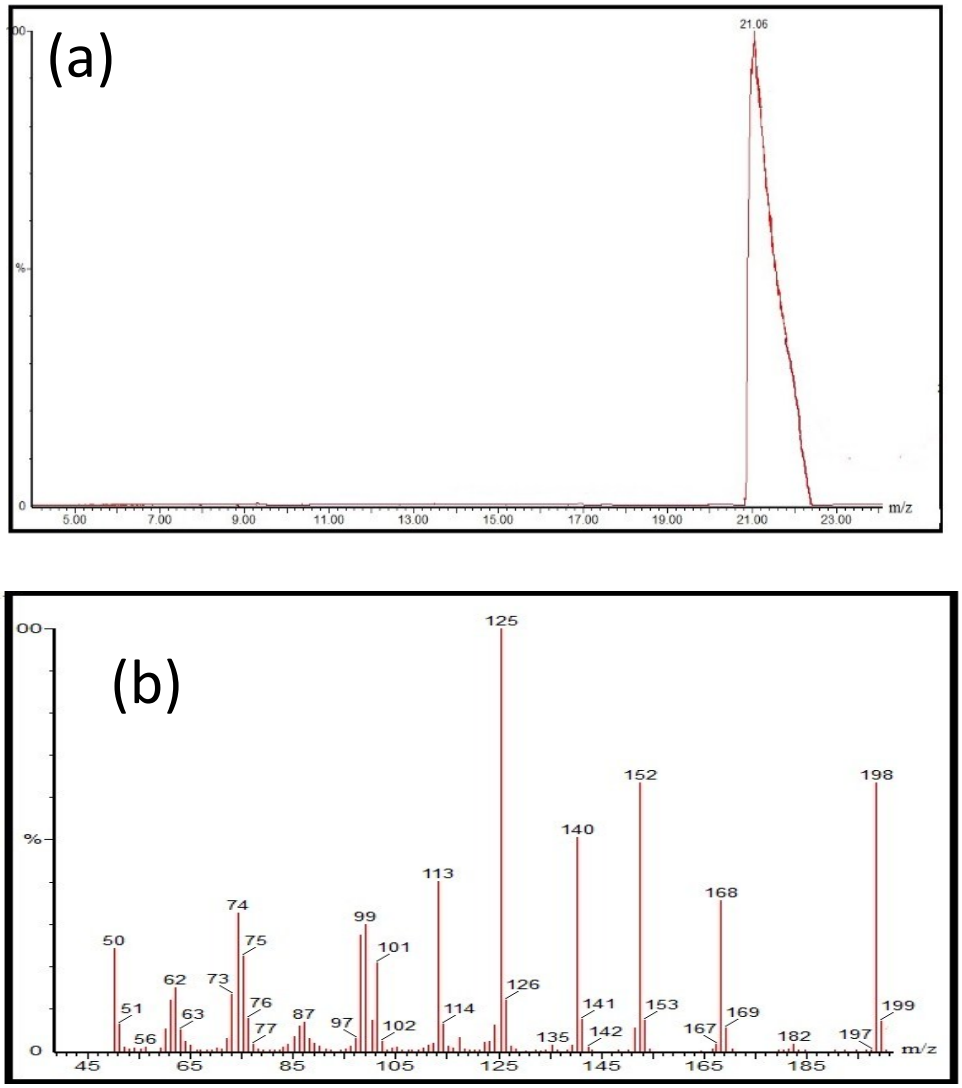


Figure S16. (a) GC and (b) MS spectrum of 4-nitrobenzylidinemalononitrile.

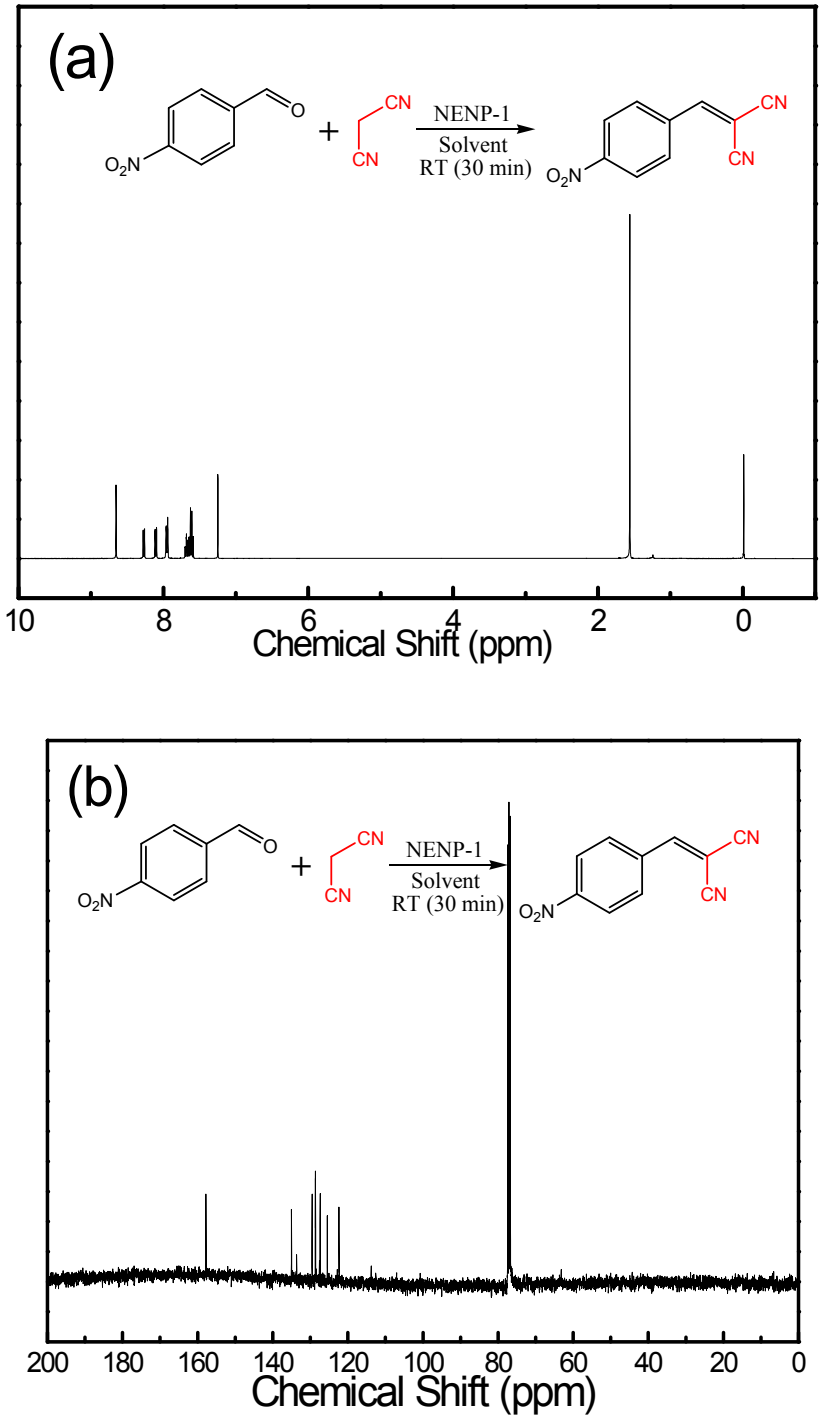


Figure S17. (a) ^{1}H and (b) ^{13}C NMR spectra of 4-nitrobenzylidinemalononitrile.

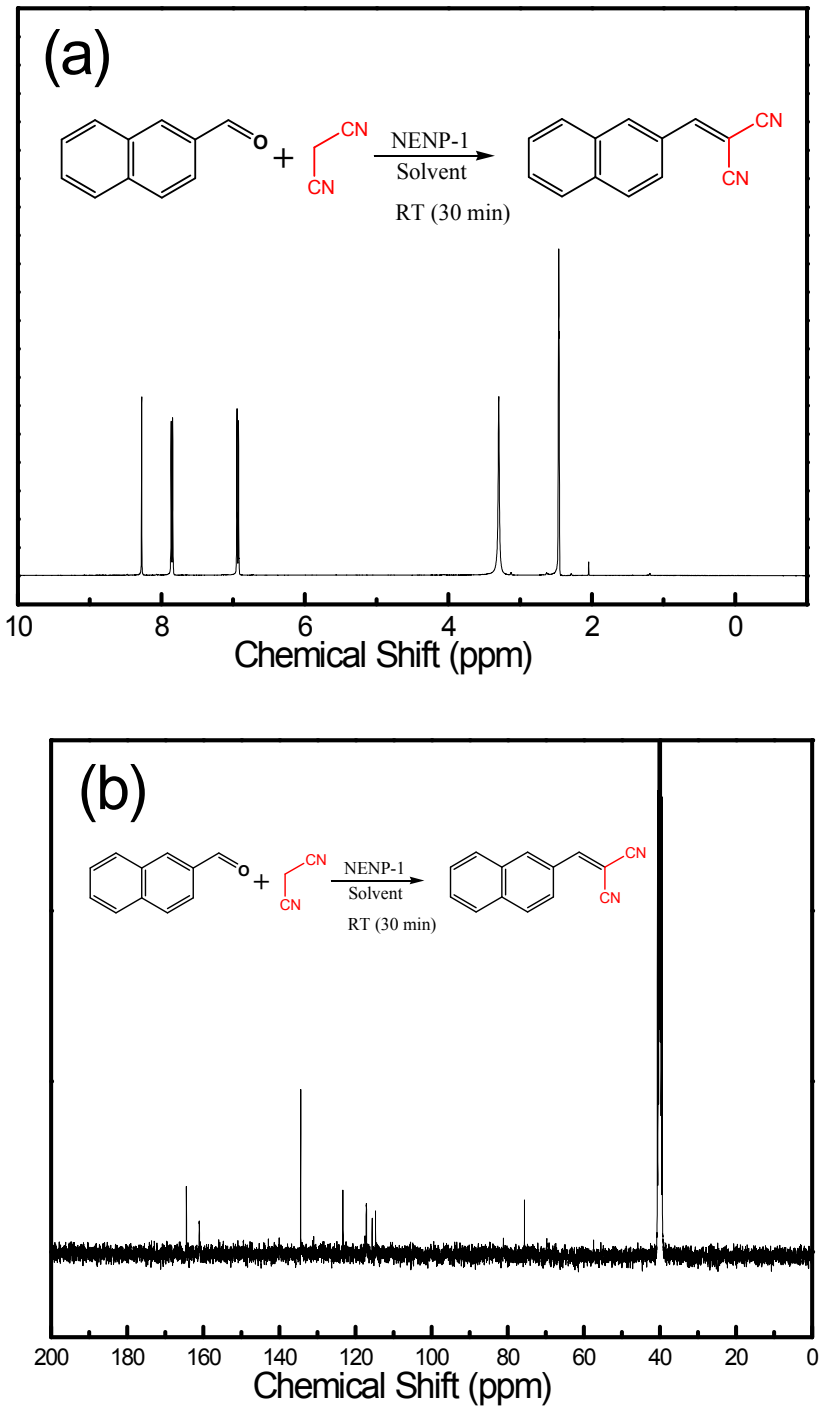


Figure S18. (a) ^{1}H and (b) ^{13}C NMR spectra of α-Napthaldehyde.

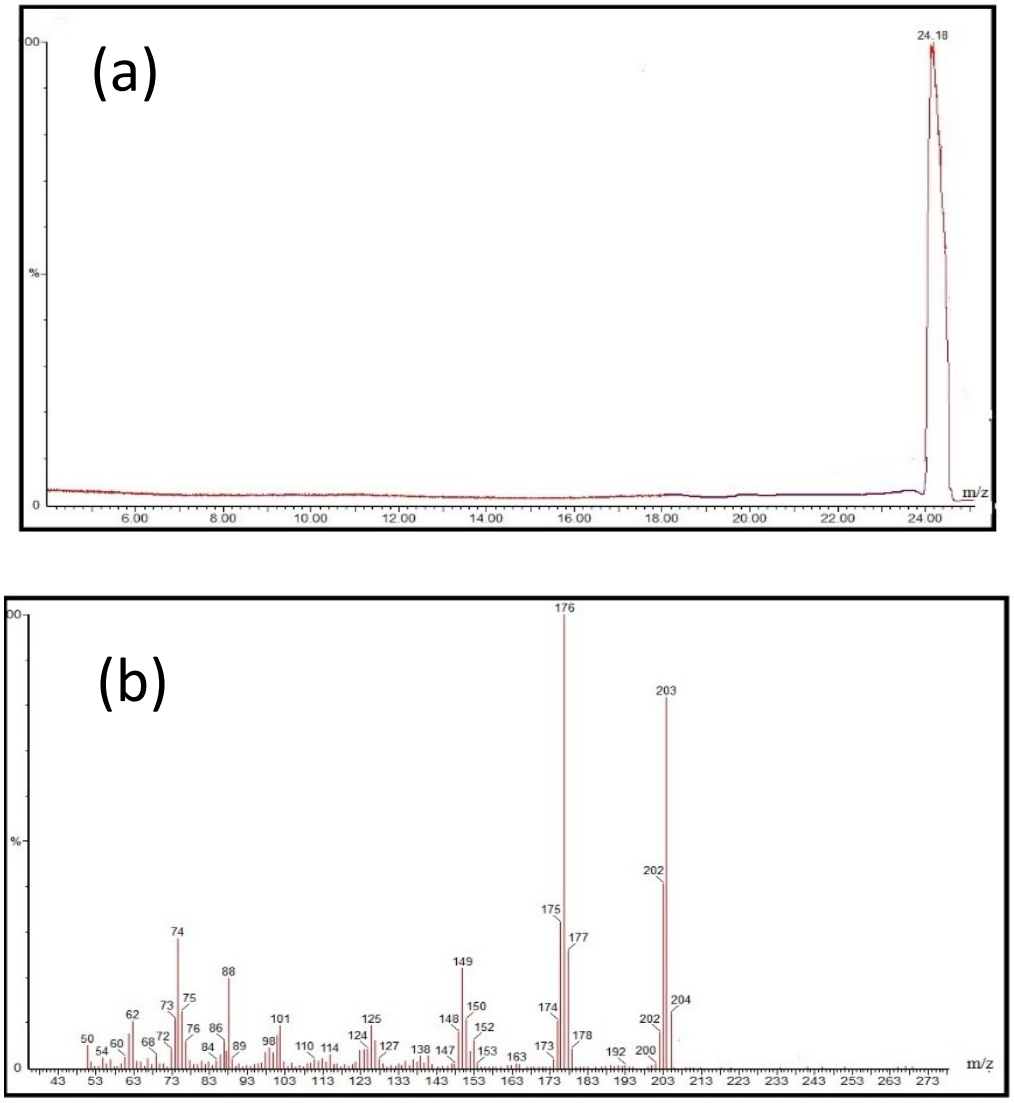


Figure S19. (a) GC and (b) MS spectrum of α-Napthaldehyde.

Table S2. Comparison of experimental conditions for the synthesis of metal-free heterogeneous organocatalysts and their catalytic performance in Knoevenagel reaction.

Organocatalysts	**Synthesis conditions**			**Catalysis**			***References***
	Synthesis method	**Temperature (°C)**	**Time (h)**	**Temperature (°C)**	**Time (min)**	**Yield (%)**	
MFCMP-1	Oxidative coupling polymerization	60	72	25	240	99	S1
JUC-Z12	Oxidative cyclo-dehydrogenation	130	72	25	1440	97	S2
BF-COF-1	Schiff base condensation	120	120	25	600	96	S3
MPU	Solvothermal synthesis	150	72	50	840	98	S4
MCN	Carbonization	550	3	120	12	95	S5
g-C_3N_4	Thermal condensation	550	8	40	120	98	S6
PANF	Thermal condensation	145	6	70	90	97	S7
NENP-1	**Microwave-assisted condensation**	**140**	**0.5**	**25**	**30**	**98**	***Current work***

References

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