Supporting Information

Commercial Zinc Oxide: A Facile, Efficient and Eco-friendly Catalyst for the One-pot Three-component Synthesis of Multi-substituted 2-Aminothiophenes Via Gewald Reaction

Reza Tayebee[1], S. Javad Ahmadi[2], Esmaeil Rezaei Seresht[1], Farzad Javadi[1], Mohammad A. Yasemi[1], Mohsen Hosseinpour[3], Behrouz Maleki[1]

[1]*Department of Chemistry, School of Sciences, Hakim Sabzevary University, Sabzevar, 96179-76487, Iran*

[2]*Atomic energy organization of Iran, Nuclear Science and Technology Research Institute, End of North Karegar Ave., Tehran, 1439951113, Iran*

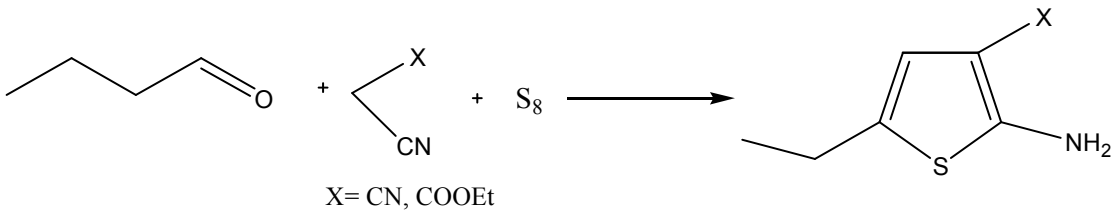
[3]*Department of Energy Engineering, Sharif University of Technology, Azadi Ave. P.O. Box113658639, Tehran, Iran*

Table S2. Effect of Reaction Time on the Condensation of Cyclohexanone, Malonodinitrile, and Elemental Sulfur in the Presence of ZnO (5 mol%).

Entry	**Time (h)**	**Yield (%)**
6	6	66
7	10	70
8	14	72
9	18	73

Reaction conditions is described below Table 1.

Table S3. Comparison of the Catalytic Activity of ZnO with some Reported Catalysts Used for the Synthesis of 2-Aminothiophene Derivatives



X= CN, COOEt

Entry	Catalyst	Mol%	Time (h)	Yield%	Condition	X	Ref.
30	ZnO	5	10	70	Solvent-free	CN	This work
31	Diethylamine	10	10	43	in DMF	CN	12
32	Morpholine	10	11	49	in DMF	CN	12
33	L-Proline	10	10	64	in DMF	CN	12
34	Imidazole	10	10	75	in DMF	CN	12
35	KF-Alumina	0.2 gr	6 min	55	MW	COOEt	15

Copies of NMR Spectra of Multisubstitued 2-Amimothiophenes

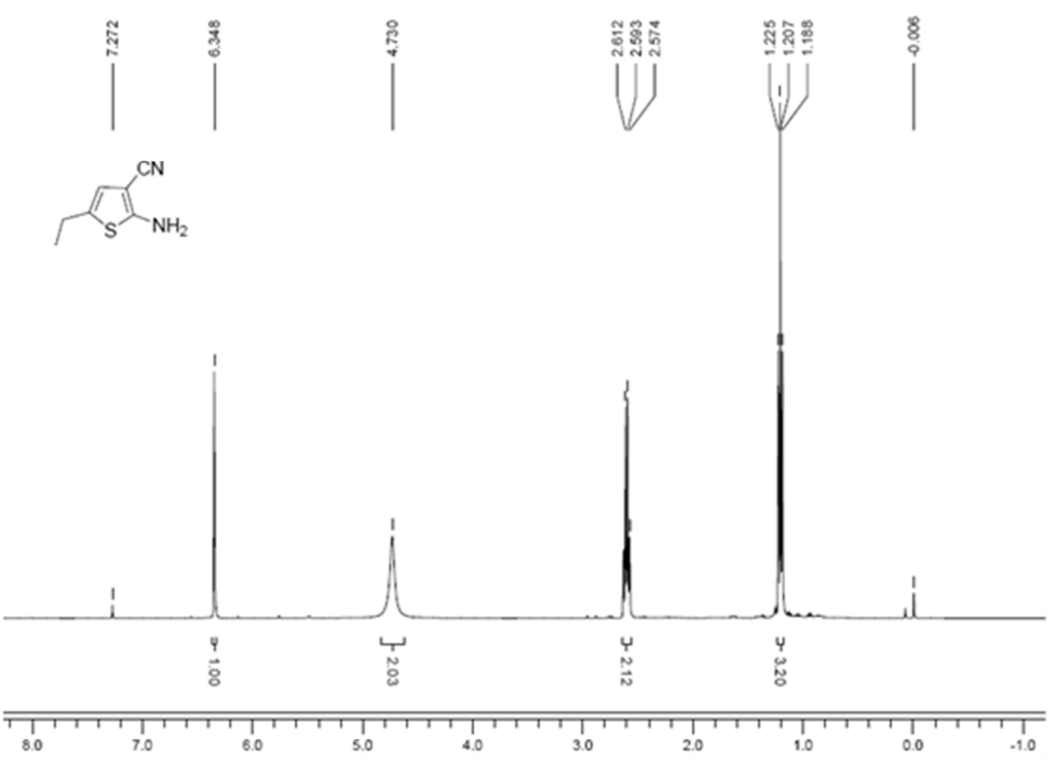


Figure S4: ^{1}H NMR of 2-amino-5-ethylthiophene-3-carbonitrile.

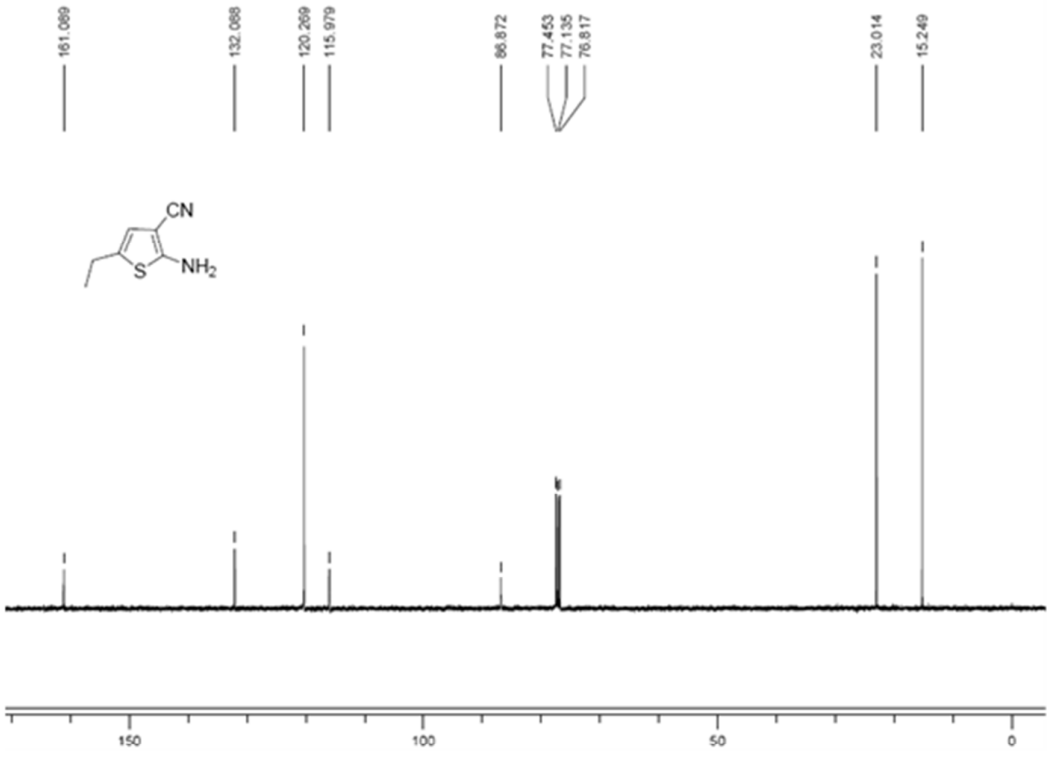


Figure S5: ^{13}C NMR of 2-amino-5-ethylthiophene-3-carbonitrile.

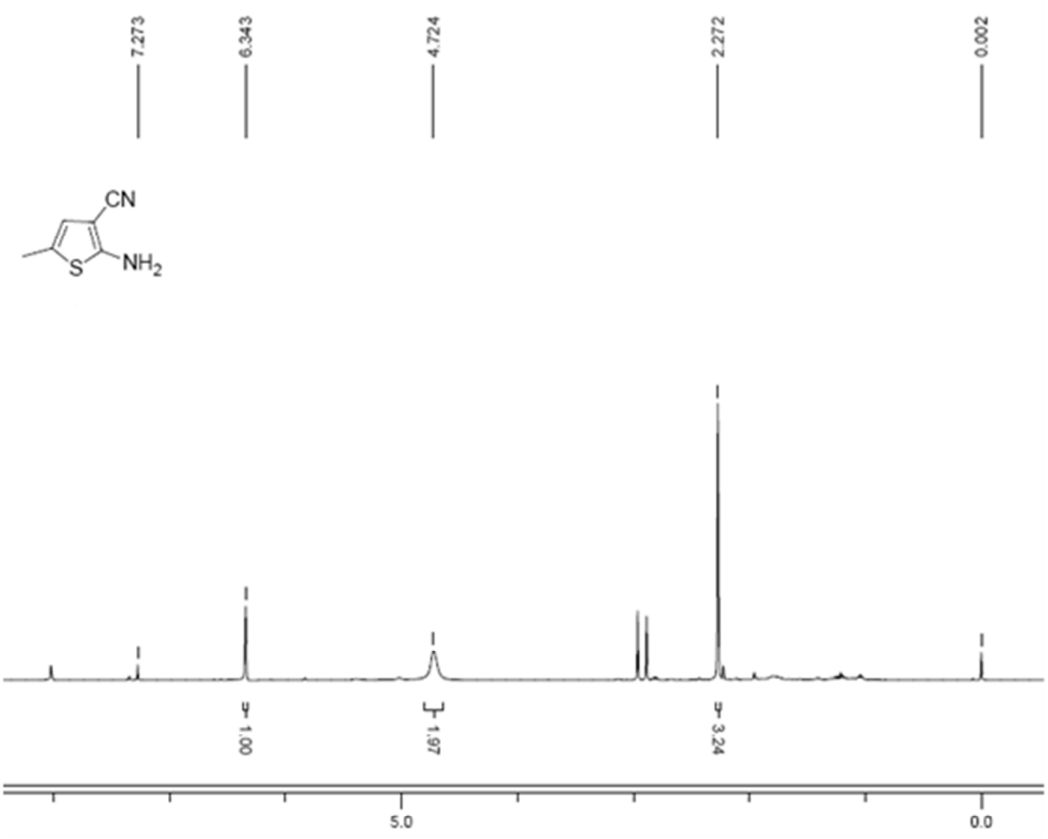


Figure S6: ^{1}H NMR of 2-amino-5-methylthiophene-3-carbonitrile.

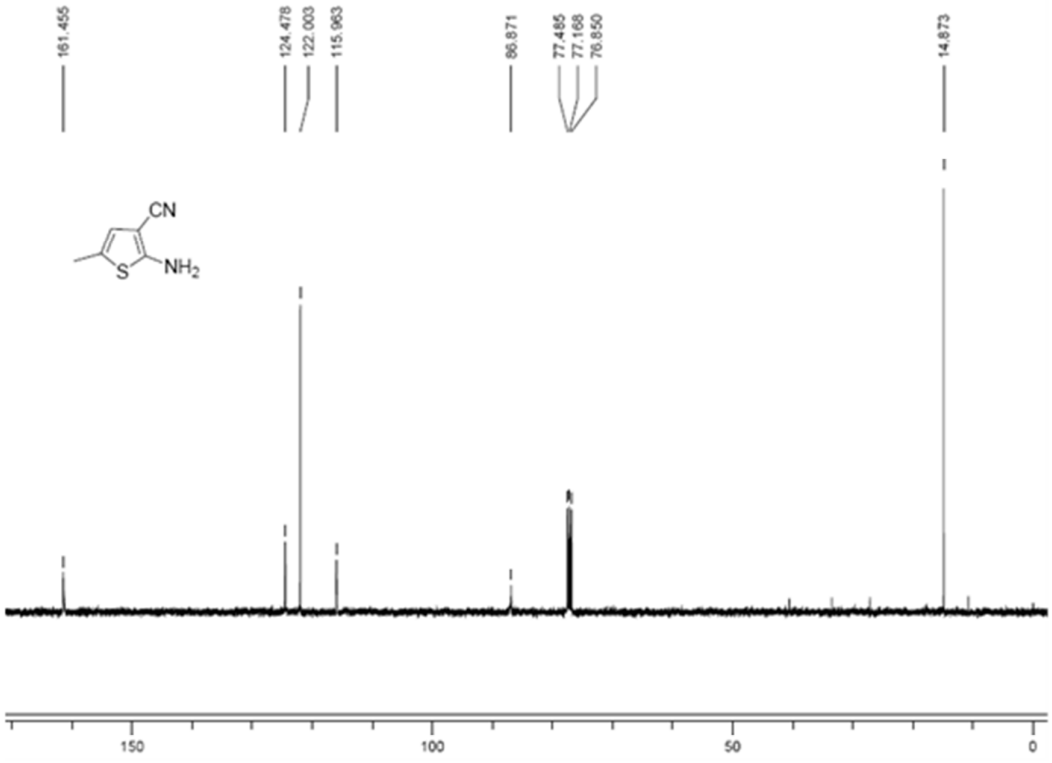


Figure S7: ^{13}C NMR of 2-amino-5-methylthiophene-3-carbonitrile.

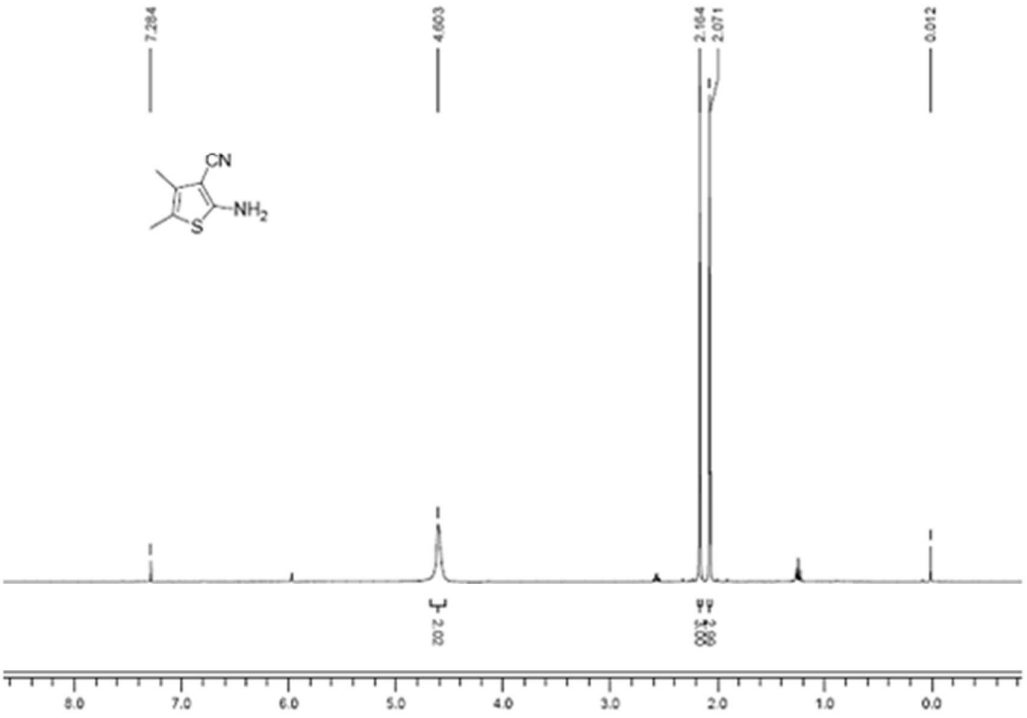


Figure S8: ^{1}H NMR of 2-amino-4,5-methylthiophene-3-carbonitrile.

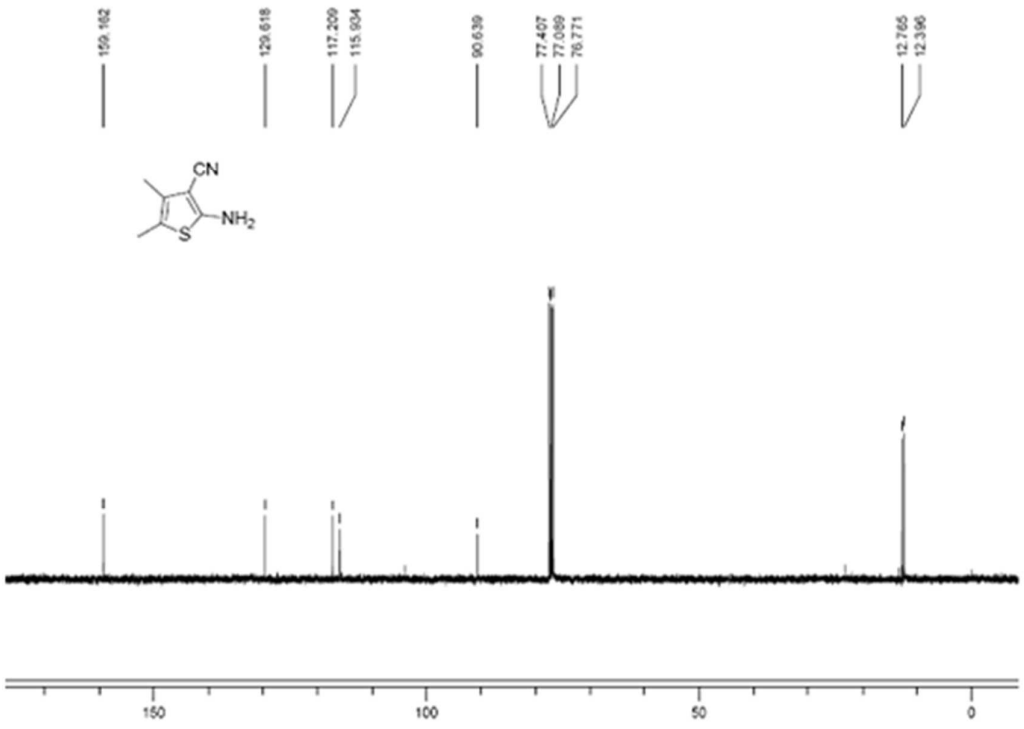


Figure S9: ^{13}C NMR of 2-amino-4,5-methylthiophene-3-carbonitrile.

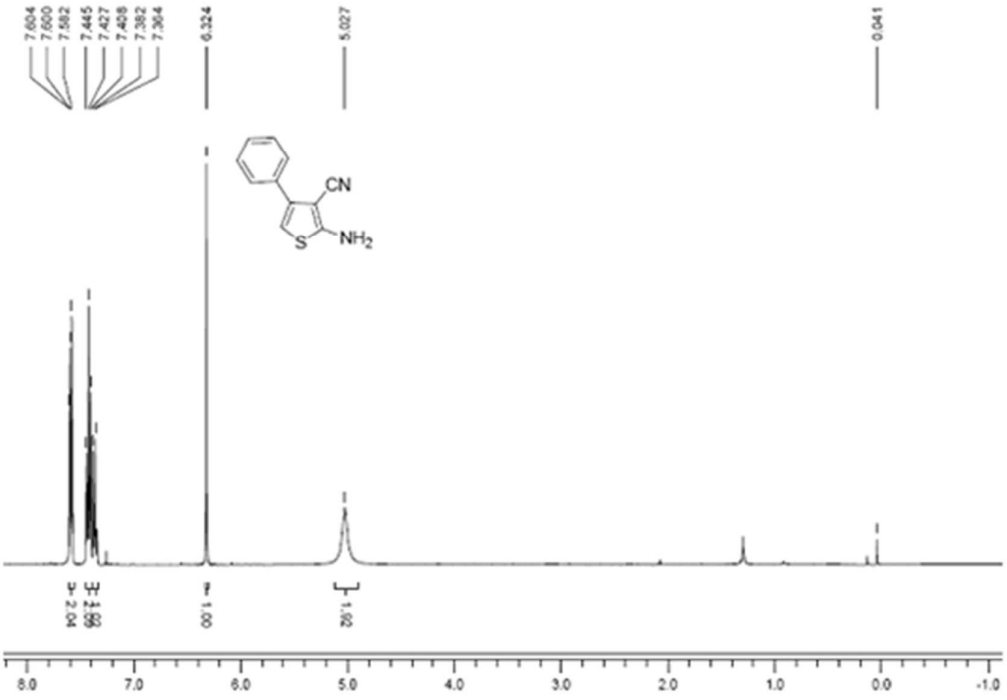


Figure S10: ^{1}H NMR of 2-amino-4-phenylthiophene-3-carbonitrile.

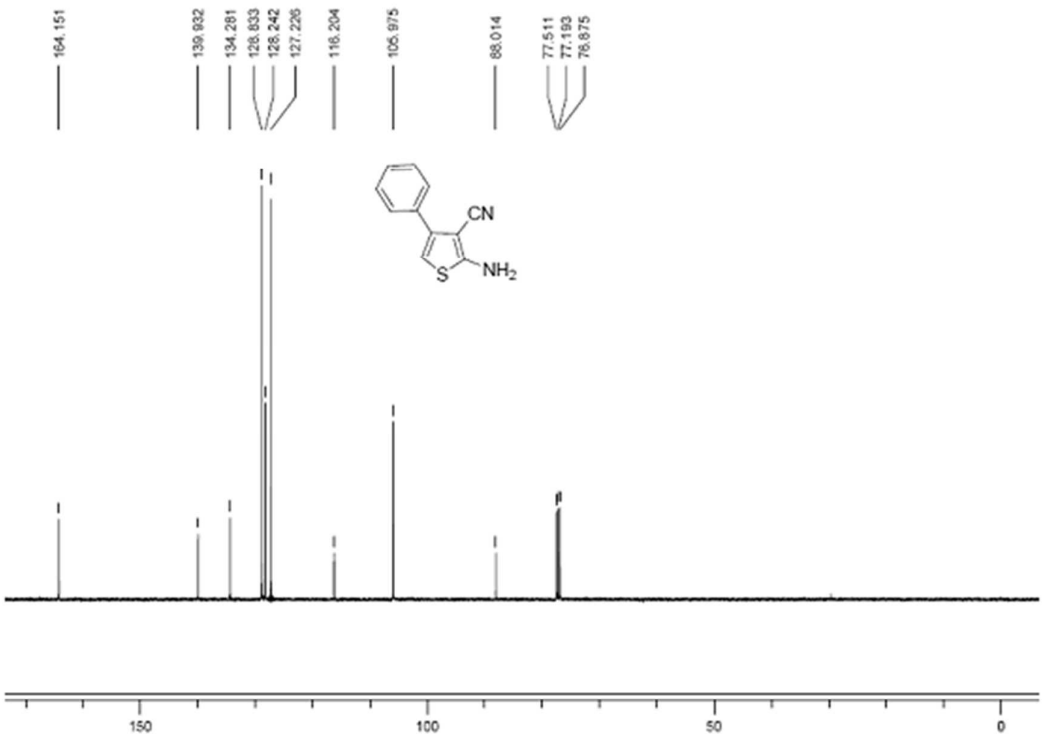


Figure S11: ^{13}C NMR of 2-amino-4-phenylthiophene-3-carbonitrile.

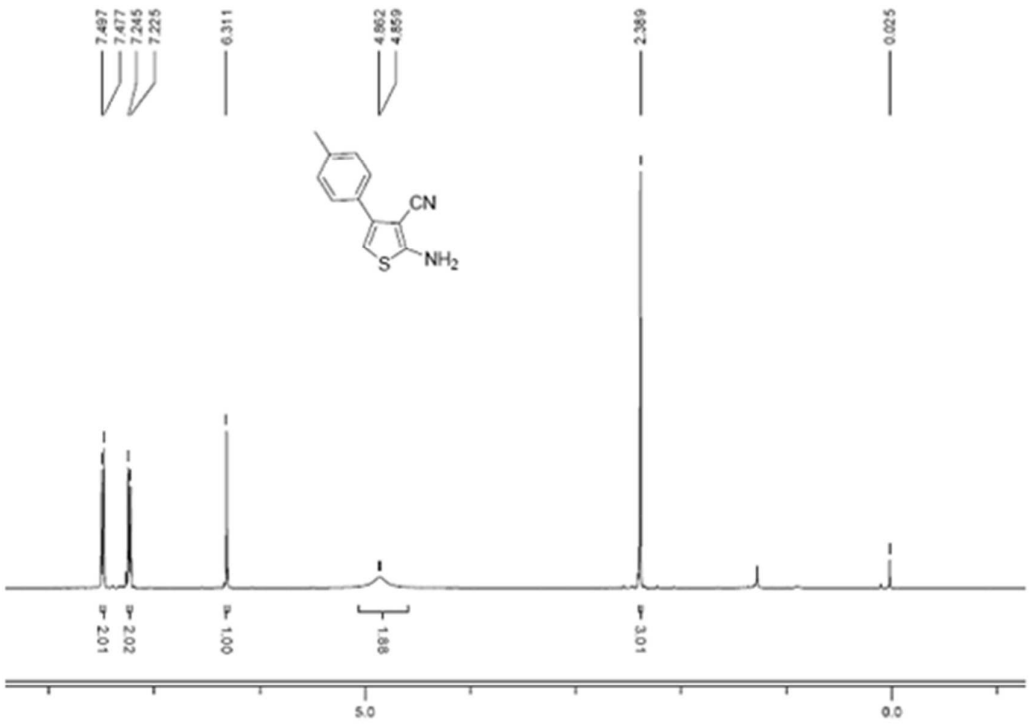


Figure S12: ^{1}H NMR of 2-amino-4-(4-methylphenyl)thiophene-3-carbonitrile.

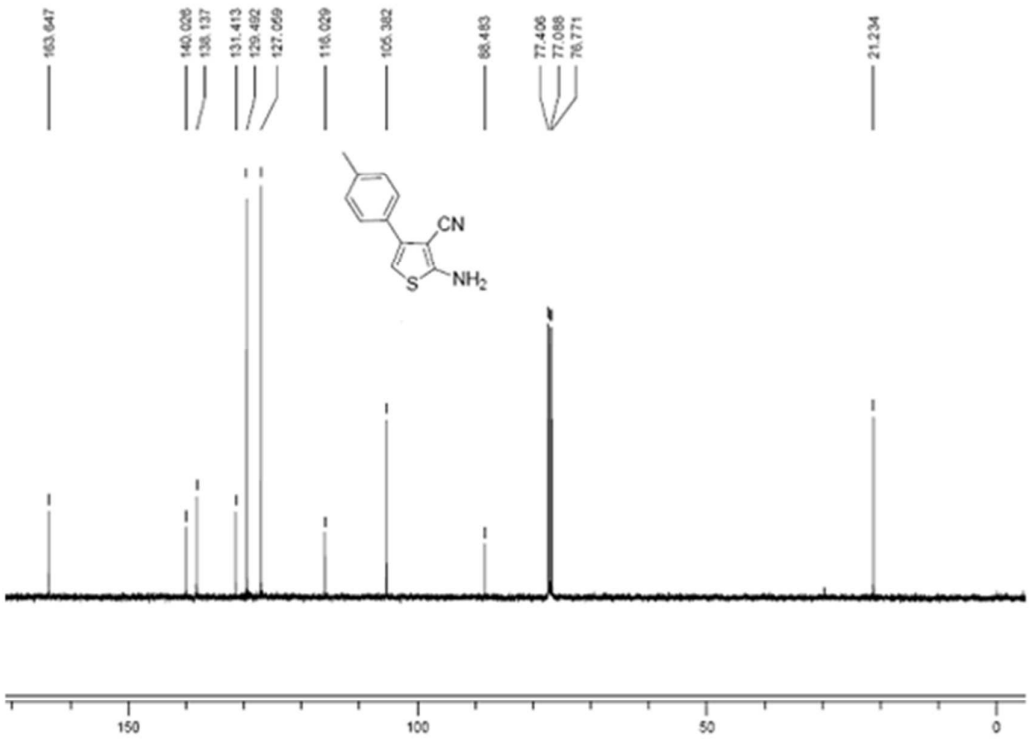


Figure S13: ^{13}C NMR of 2-amino-4-(4-methylphenyl)thiophene-3-carbonitrile.

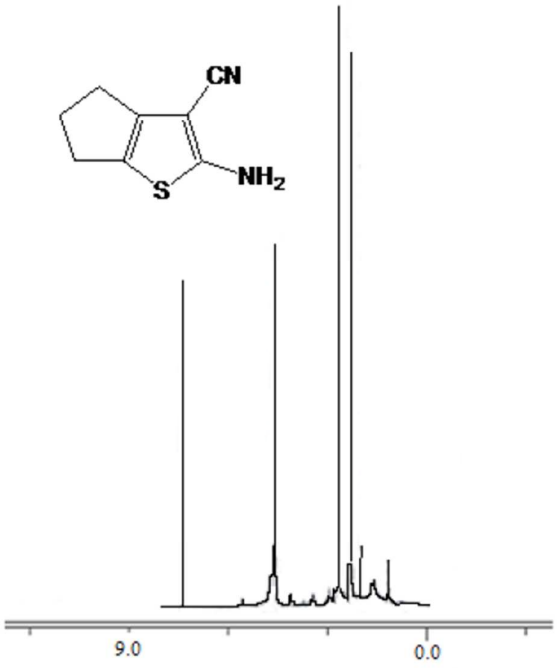
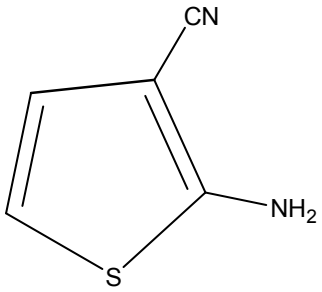
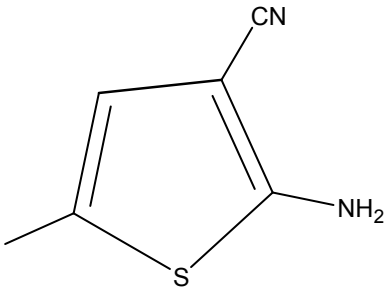


Figure S14: ^{1}H NMR of 2-amino-4H,5H,6H-cyclopenta[b]thiophene-3-carbonitrile.



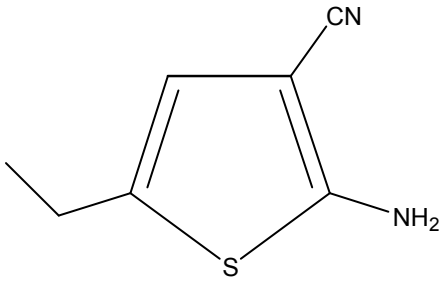
Vibration	NH_2	=C-H	CN	C=C
$\upsilon(cm^{-1})$	3440-3360	3210	2220	1660

Figure S15: FT-IR band assignments of 2-aminothiophene-3-carbonitrile.



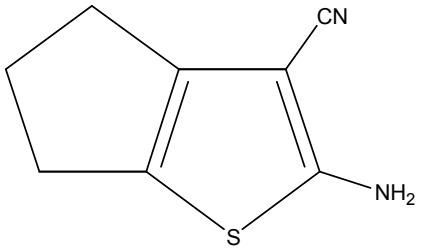
Vibration	NH_2	=C-H	C-H	CN	C=C
$\upsilon(cm^{-1})$	3440-3360	3210	2960	2220	1660

Figure S16: FT-IR band assignments of 2-amino-5-methylthiophene-3-carbonitrile.



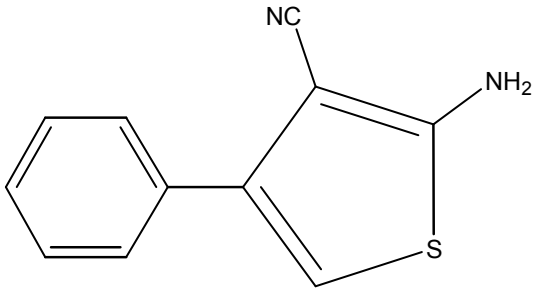
Vibration	NH_2	=C-H	C-H	CN	C=C	$-CH_2$
$\upsilon(cm^{-1})$	3440-3360	3210	2960	2220	1660	1465

Figure S17: FT-IR band assignments of 2-amino-5-ethylthiophene-3-carbonitrile.



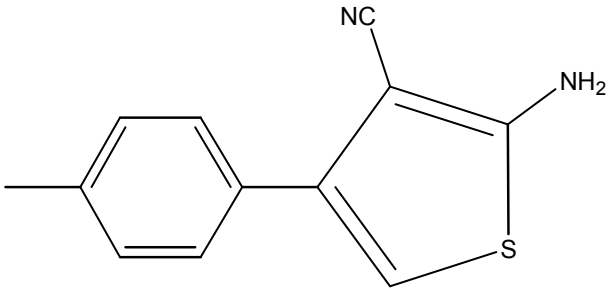
Vibration	NH_2	C-H	CN	C=C
$\upsilon(cm^{-1})$	3440-3340	2840-2920	2220	1630

Figure S18: FT-IR band assignments of 2-amino-4H, 5H, 6H-cyclopenta[b] thiophene-3-carbonitrile.



Vibration	**NH_2**	**=C-H**	**CN**	**C=C**
$\upsilon(cm^{-1})$	3320-3200	3040	2220	1440,1570

Figure S19: FT-IR band assignments of 2-amino-4-phenylthiophene-3-carbonitrile.



Vibration	**NH_2**	**=C-H**	**CN**	**C=C**	**$-CH_2$**
$\upsilon(cm^{-1})$	3320-3200	3040	2220	1440,1560	1375

Figure S20: FT-IR band assignments of 2-amino-4-(4-methylphenyl)thiophene-3-carbonitrile.

References:

[1] Moeinpour, F.; Omidinia, R.; Dorostkar-Ahmadi, N.; Khoshdeli, B. Cesium Carbonate as a *Heterogeneous* Base Catalyst for Synthesis of 2-Aminothiophenes Via Gewald Reaction. *Bull. Kor. Chem. Soc.* **2011***, 32,* 2091.

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[3] Bahrami, K.; Khodaei, M.; Nejati, A. One-Pot Synthesis of 1,2,4,5-Tetrasubstituted and 2,4,5-Trisubstituted Imidazoles by Zinc Oxide as Efficient and Reusable Catalyst. *Chem. Inform*. **2011**, 42.

[4] Chavan, S. S.; Pedgaonkar, Y.Y.; Jadhav, A. J.; Degani, M. S. Microwave Accelerated Synthesis of 2-Aminothiophenes in Ionic Liquid Via Three Component Gewald Reaction. *Ind. J. Chem., Sec. B*, **2012**, *51*, 653.

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[6] Wardakhan, W.W.; Shams, H. Z.; Moustafa, H. E. Synthesis of Polyfunctionally Substituted Thiophene, Thieno[2,3-b]pyridine and Thieno[2,3-d]pyrimidine Derivatives. *Phosphorus, Sulfur Silicon Relat. Elem*. 2005, *180*, 1815.