Electronic Supplementary Information (ESI) for

Hierarchically porous AlPO-5-based microspheres as heterogeneous catalysts for synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition

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Table S1. Unit cell parameters for AlPO-5 and WAlPO-5.

Sample	a=b (Å)	C (Å)	V (Å^3)	ΔV (Å^3)
AlPO-5	13.70	8.41	1367.20	~
WAlPO-5	13.72	8.40	1369.40	2.20

V: unit cell volume, ΔV: unit cell volume change

Table S2. The location of FTIR absorption peaks calcined micropore aluminophosphates.

Sample	1 (cm^{-1})	2 (cm^{-1})	3 (cm^{-1})	4 (cm^{-1})	5 (cm^{-1})
AlPO-5	466.17	635.99	706.52	1128.09	1650.78
WAlPO-5	467.89	637.44	704.53	1113.68	1644.62

Table S3. The molar ratio of P, Al and W calculated from ICP results.

Sample	X[a]	Y[a]	Z[a]
WAlPO-5 (gel)	0.488	0.488	0.024
WAlPO-5 (solid)	0.497	0.502	0.001

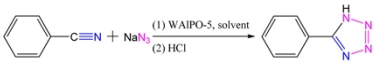
[a] The mole ratio:X=P/(P+Al+W), Y=Al/(P+Al+W), Z=W/(P+Al+W).

Table S4. Nitrogen sorption results of AlPO-5 and WAlPO-5.

Sample	S_{BET} (m^2g^{-1})	V_P (cm^3 g^{-1})	D_P^D (nm)[a]
AlPO-5	229.5	0.20	1.8
WAlPO-5	245.4	0.21	1.7

[a] Pore diameter from desorption branch of isotherms.

Table S5. Formation of 5-phenyltetrazole using various reaction parameters[a].



Entry	Solvent	NaN_3 (mmol)	T (ºC)	Yield (%)
1	DMF	5.3	100	87
2	DMF	2.6	120	19, 34
3	DMF	5.3	120	65[b], 92[c]
4	DMF	5.3	130	40
5	water	5.3	100	2
6	toluene	5.3	120	0
7	DMSO	5.3	120	71
8	NMP	5.3	120	82
9	DMF/H_2O (1/1)	5.3	120	32
10	SC CO_2+DMF	5.3	120	34[d]
11	SC CO_2+DMF	5.3	120	31[e]

[a] *Reaction conditions*: benzonitrile (2.5 mmol), NaN_3 (2.6-5.3 mmol) and catalyst (0.26-0.78 mmol) in DMF (5mL) at 120 ºC for 24 h.

[b] Reaction carried at 120 ºC for 12 h.

[c] Reaction carried at 120 ºC for 24 h.

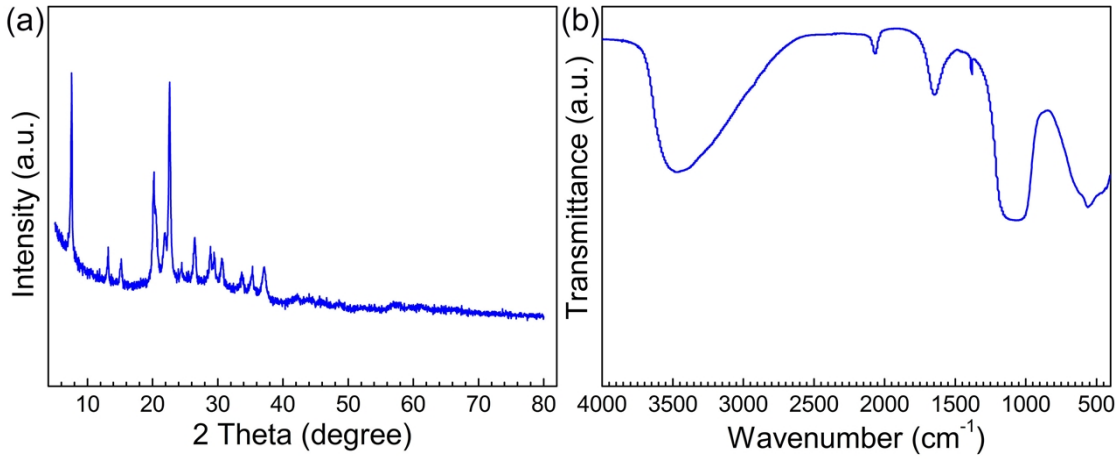


Figure S1. (a) XRD pattern and (b) FTIR spectrum of used WAlPO-5 microspheres.

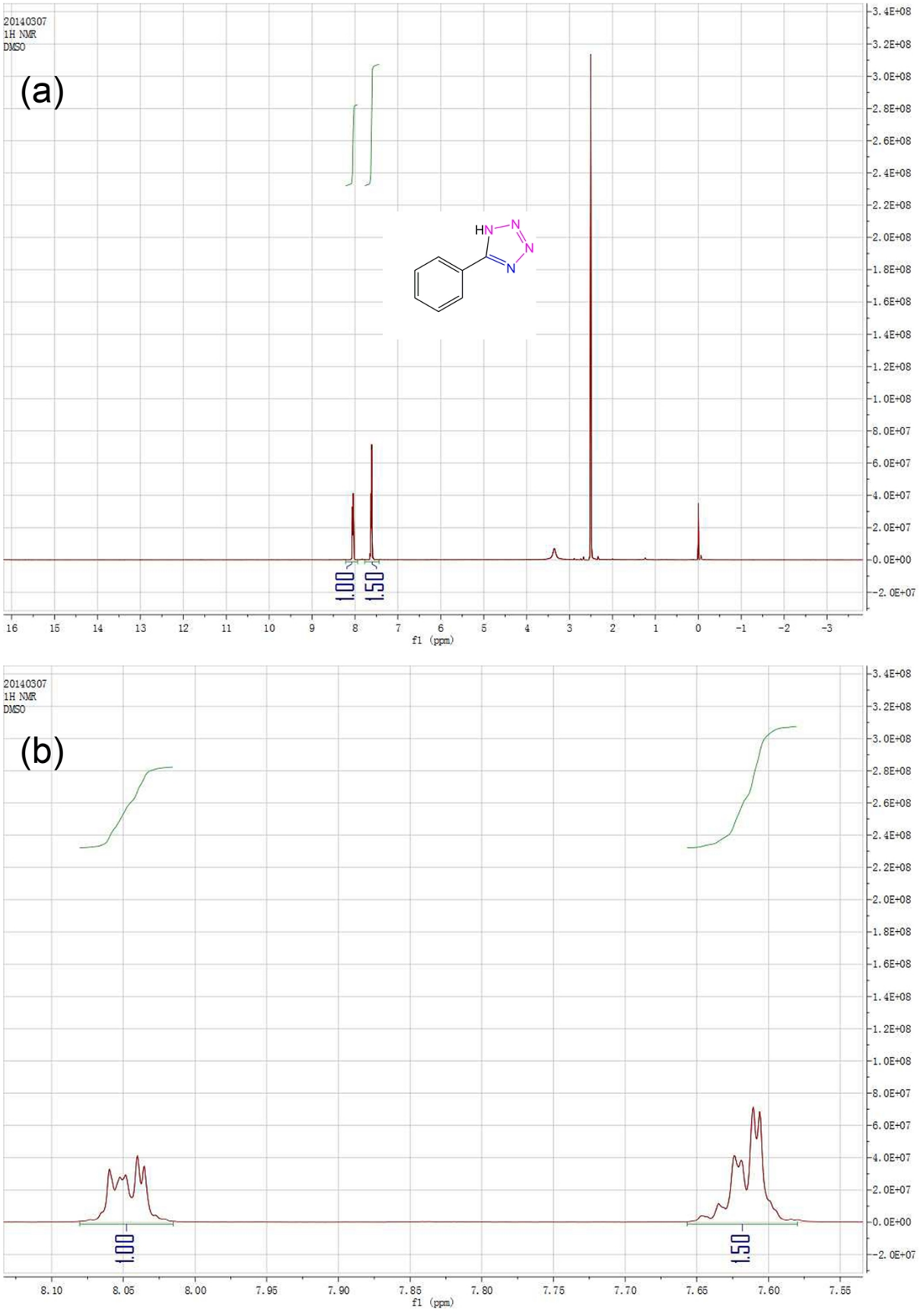


Figure S2. (a) ^{1}H NMR spectrum of 5-phenyltetrazole and (b) the fine structure between 7.56-8.10 ppm.

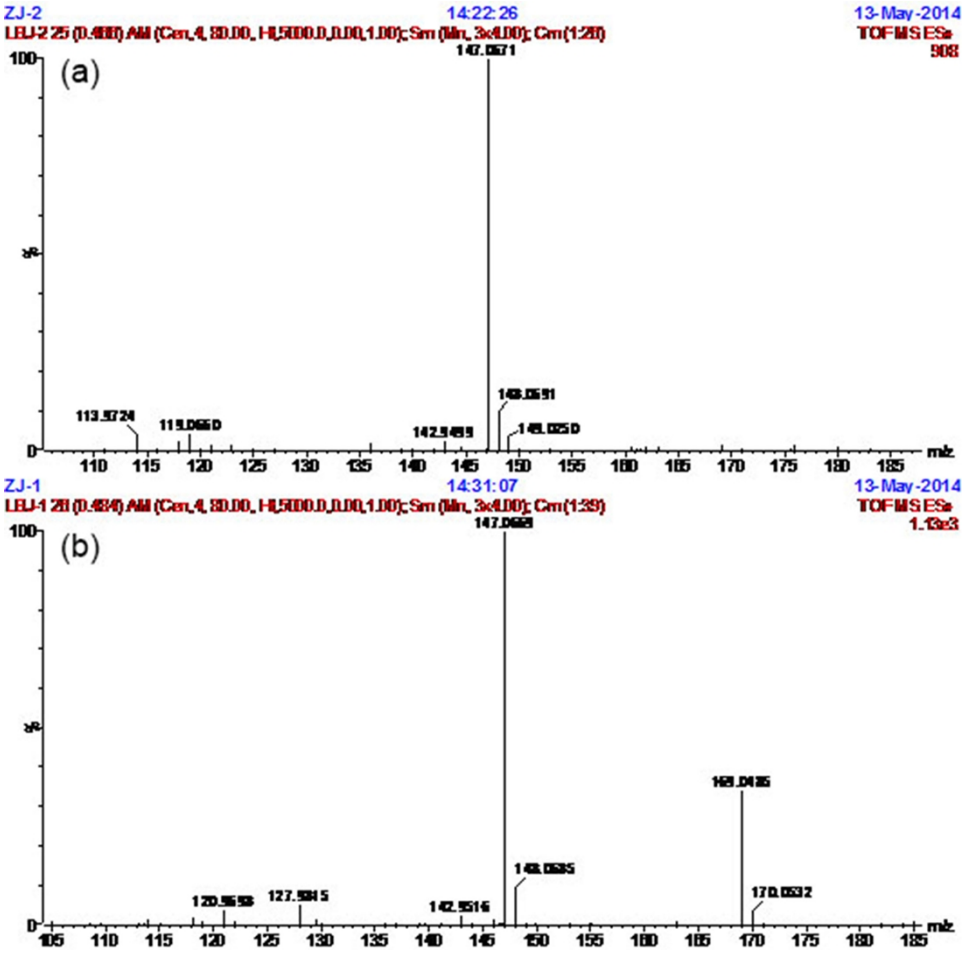


Figure S3. MS spectrum of (a) crude and (b) purified 5-phenyltetrazole synthesized from benzonitrile and sodium azide.