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Eco-friendly heteropoly acid supported on natural clay for the synthesis of calix[4]resorcinarene derivatives

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The catalytic activity of green catalyst heteropoly-11-tungsto-1-vanadophosphoric acid, $H_4[PVW_{11}O_{40}]$ (HPV) supported on activated natural clay (HPVAC) has been tested towards the synthesis of calix[4]resorcinarene under solvent-free condition. It is a one-pot multi-component condensation reaction of four moles of aromatic aldehydes with four moles of resorcinol. The advantages of the protocol, solvent-free heterogeneous reaction condition, simple workup procedure, short reaction time, high yield of products and reusability of the catalyst make this method to declare as green approach for synthesis of calix[4]resorcinarene.

Keywords: Heteropoly acid, Activated Natural Clay, Calix[4]-resorcinarene, Green synthesis, Heterogeneous reaction

The calix[4]resorcinarene, a subclass of calixarenes, has macrocyclic structure of cyclic tetramers. calix[4]resorcinarene and its derivatives as macrocyclic receptors possess a variety of applications as dendrimers in biological systems[1], nanoparticles[2], nano-capsule[3], supramolecular tectons[4], optical chemosensors[5], host molecules[6], components in liquid crystals[7], selective membranes[8,9], HPLC stationary phases[10], surface reforming agents[11], ion channel mimics[12] and metal ion extraction agents[13]. Besides, some calix[4]arenes show metal ion recognition properties[14, 15].

A number of synthetic routes have been reported for the preparation of calix[4]resorcinarene derivatives by employing some Lewis acid catalyst such as $[Yb(H_2O)_9](OTf)_3$[16], $H_3[PW_{12}O_{40}]$ / Conc. HCl[17], Conc. HCl under microwave irradiations[18, 19] and Fe_3O_4 nanoparticle[20]. However, the methods using these catalysts suffer from the drawbacks such as low product yield, cumbersome product isolation and long reaction time. Here is an attempt to synthesize and characterize calix[4]resorcinarene derivatives using a green eco-friendly catalyst ,heteropoly acid supported on activated natural clay minerals (HPVAC) .

Experimental Section

Materials

All commercially available chemicals were obtained from Sigma Aldrich and used without further purification. A series of HPV supported activated natural clay catalysts (HPVAC) were prepared by varying the loading amount of HPV *viz.* 10, 20, and 30% (w/w) on to the activated natural clay and characterized by the reported literature procedure from our laboratory[21]. FT-IR spectra were recorded using Shimadzu IR Affinity-1 FT-IR Spectrophotometer as KBr discs. ^{1}H and ^{13}C-NMR spectra were recorded by Bruker 300 and 100 MHz NMR instrument with DMSO-d_6 as solvent and TMS as internal reference. Elemental analysis was performed on Elementar Vario EL III equipment.

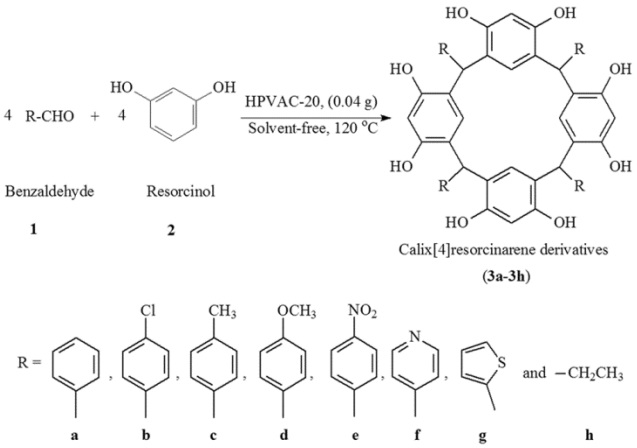
General procedure for the preparation of calix[4]resorcinarene

A mixture of aldehyde (4 mmol), resorcinol (4 mmol) and HPVAC-20 (catalyst) were heated in oil bath at 120°C for 30 min. The completion of reaction was ascertained by TLC (ethyl acetate / n-hexane: 7:3) and after completion, 15 mL of ethanol was added to dissolve the crude product. The catalyst was recovered by simple filtration. And the ethanol solution was poured into cold water to get precipitate. The product was filtered and washed with 30 mL of water. The product was dried in an air oven (Scheme 1). The product was analyzed and identified by melting point, FT-IR, ^{1}H-NMR and ^{13}C-NMR analysis.

Results and Discussion

Optimization of catalytic condition

Condensation of four moles of 4-chloro-benzaldehyde with four moles of resorcinol in the presence of catalyst was taken as a standard reaction for the optimization study in the synthesis of 2,4,6, 8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54,56, 74,76-octaol. This



Scheme 1 — Synthesis of calix[4]resorcinarene using HPVAC-20 as catalyst

Table 1 — Catalyst screening for the synthesis of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56, 74,76-octaol[a]

Catalyst	Catalyst amount (g)	Yield[b] (%)
Activated natural clay (AC)	0.04	44
$H_3[PW_{12}O_{40}]$	0.03	58
$H_4[PVW_{11}O_{40}]$	0.03	67
$H_5[PV_2W_{10}O_{40}]$	0.03	68
10% $H_3[PW_{12}O_{40}]$ / AC	0.04	78
10% $H_4[PVW_{11}O_{40}]$ / AC	0.04	89
10% $H_5[PV_2W_{10}O_{40}]$ / AC	0.04	90

[a]Reaction conditions: 4-chlorobenzaldehyde (4 mmol), resorcinol (4 mmol), Solvent-free condition, 120 °C, 30 min.
[b]Isolated Yields.

condensation reaction was carried out with the different catalytic materials such as activated natural clay (AC), HPAs such as $H_3[PW_{12}O_{40}]$, $H_4[PVW_{11}O_{40}]$ and $H_5[PV_2W_{10}O_{40}]$ and HPA supported on AC such as 10% $H_3[PW_{12}O_{40}]$ over AC, 10% $H_4[PVW_{11}O_{40}]$ over AC (HPVAC-10) and 10% $H_5[PV_2W_{10}O_{40}]$ over AC. The yields obtained for these catalysts are given in Table 1 and it is found that the catalytic ability of $H_4[PVW_{11}O_{40}]$ over AC (HPVAC-10) and 10% $H_5[PV_2W_{10}O_{40}]$ are much higher than other catalytic materials. The reaction was carried out with the different percentage loadings of HPV *viz* HPVAC-10, HPVAC-20 and HPVAC-30 and the results reveal that the usage of HPVAC-20 is a better choice for the conversion (Table 2).

The standard reaction was also examined in various solvent systems such as, ethylene glycol, toluene, dimethyl sulphoxide, 1,2-dichloroethane, *N,N'*-dimethylforamide and dichloromethane. The results (Table 3) indicated that the nature of solvents affects the

Table 2 — Effect of catalyst loading in the synthesis of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56, 74,76-octaol[a]

Catalyst	Catalyst amount (g)	Yield[b] (%)
HPVAC-10	0.04	89
HPVAC-20	0.04	95
HPVAC-30	0.04	96

[a]Reaction conditions: 4-chlorobenzaldehyde (4 mmol), resorcinol (4 mmol), Solvent-free condition, 120 °C, 30 min.
[b]Isolated Yields.

Table 3 — Effect of solvents on the reaction of 4-chlorobenzaldehyde, resorcinol catalyzed by HPVAC-20[a]

Solvent	Time (h)	Yield[b] (%)
Ethylene glycol	4	58
Toluene	4	63
Dimethyl sulfoxide	4	68
1,2-dichloroethane	4	72
N,N'-dimethylforamide	4	70
Dichloromethane	4	74
Solvent free contidion[c]	30 min	95

[a]Reaction conditions: 4-chlorobenzaldehyde (4 mmol), resorcinol (4 mmol), HPVAC-20 (0.04 g), reflux,
[b]Isolated yield,
[c]120 °C.

Table 4 — Effect of reusability of HPVAC-20 catalyst on the of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56, 74,76-octaol yield[a]

Run	Cycle	Yield[b] (%)
1	0	95
2	1	92
3	2	90
4	3	89

[a]Reaction conditions: 4-chlorobenzaldehyde (4 mmol), resorcinol (4 mmol), HPVAC-20 (0.04 g), Solvent-free condition, 120 °C, 30 min.
[b]Isolated yield

efficiency of the reaction in terms of yields. Among the solvents, dichloromethane showed good results. However, the yield of the product under solvent-free condition is much higher than any other solvent system.

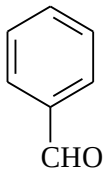
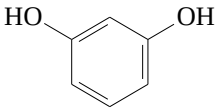
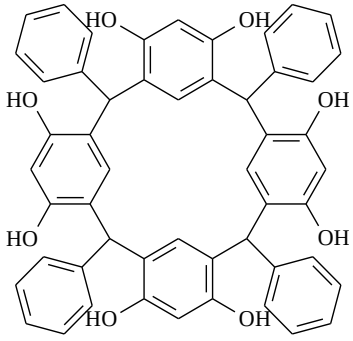
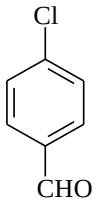
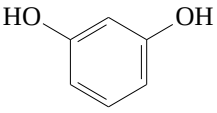
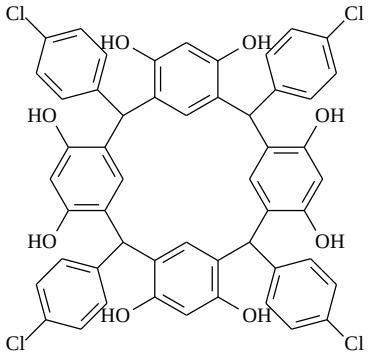
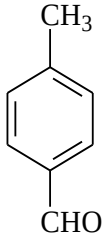
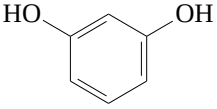
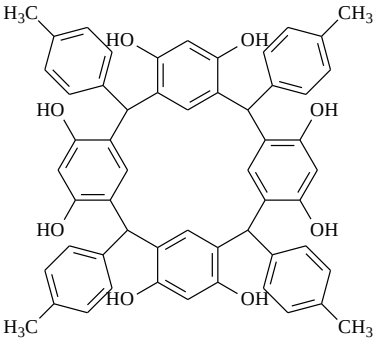
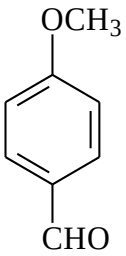
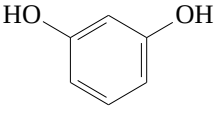
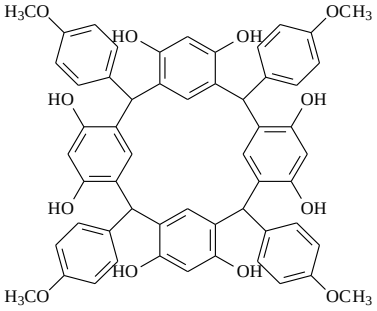
The reusability of the HPVAC-20 catalyst was studied by separating the catalyst from the reaction mixture by simple filtration, washing with hot ethanol and dried in air oven at 120°C for 3h prior to reuse in subsequent reactions. In the reusability experiments, relatively a slight loss in the product yield was observed as given in Table 4. However, the catalytic activity was comparatively maintained at a constant rate until in its fourth time of use.

Based on the optimization study results, eight calix[4]resorcinarene derivatives (3a-3h) were

prepared using resorcinol and various substituted aldehydes (Table 5). The generalized reaction protocol is depicted as Scheme 1. The products were characterized by melting point measurement, FT-IR, ^{1}H and ^{13}C-NMR spectroscopy (Figs. 1, 2 and 3).

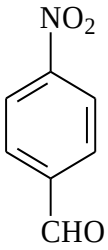
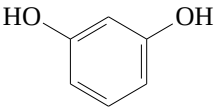
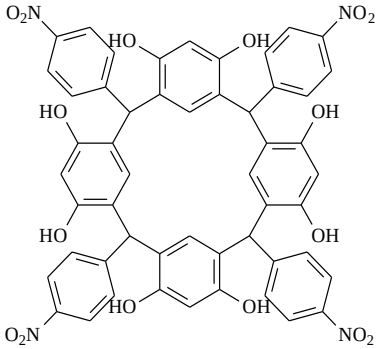
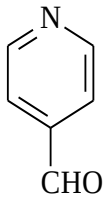
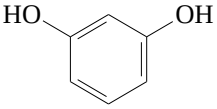
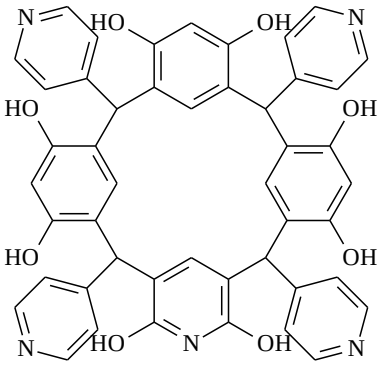
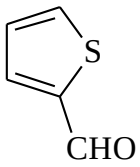
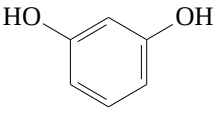
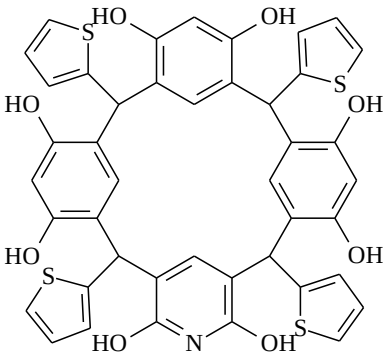
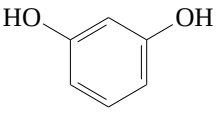
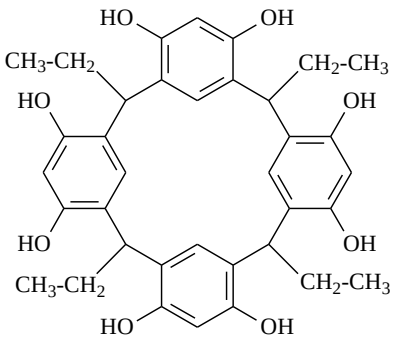
It appears that aromatic aldehydes substituted with electron-withdrawing groups underwent the reaction

Table 5 — The condensation reaction of 4-chlorobenzaldehyde, resorcinol over HPVAC-20 by conventional heating[a].

Entry	Substrates		Product	Yield[b] (%)
	Aldehyde	Resorcinol		
3a				93
3b				95
3c				88
3d				90

(*Contd*.)

Table 5 — The condensation reaction of 4-chlorobenzaldehyde, resorcinol over HPVAC-20 by conventional heating[a]. (*Contd*.)

Entry	Substrates		Product	Yield[b] (%)
	Aldehyde	Resorcinol		
3e				92
3f				93
3g				91
3h	CH_3-CH_2-CHO			85

[a]Reaction conditions: 4-chlorobenzaldehyde (4 mmol), resorcinol (4 mmol), HPVAC-20 (0.04 g), Solvent-free condition, 120°C, 30 min.
[b]Isolated yield

in a slightly faster manner and show higher yield of products in comparison with aromatic aldehydes with electron-donating substituents.

2,4,6,8-Tetraphenyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octaol (3a):

Orange solid; m.p: 292-294°C; FT-IR (KBr disc): 3000-3600, 1614, 1514, 1427, 1282, 1193, 1145, 1074, 929, 839, 700, 553 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.58-8.47 (8H, OH), 6.85-6.83 (20H, aroma), 6.33 (4H, CH), 6.11 (4H, CH), 5.55-5.52 (4H, CH); ^{13}C-NMR (100 MHz): δ 152.9, 152.7, 144.5, 129.2, 128.8, 127.2, 124.6, 121.3, 120.8, 44.8.

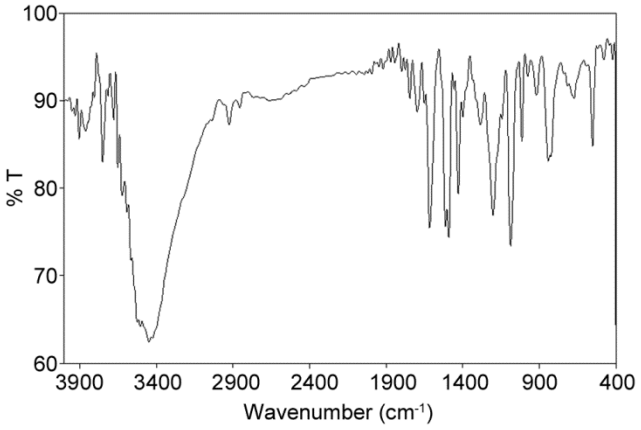


Fig. 1 — FT-IR spectra of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octaol (3b) recorded as KBr pellets.

2,4,6,8-Tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54, 56,74,76-octaol (3b):

Orange solid; mp: 262-264°C; FT-IR (KBr disc): 3600-3000, 1616, 1512, 1490, 1429, 1201, 1087, 1014, 920, 840, 675, 551 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.76-8.65 (8H, OH), 7.09-6.95 (16H, aroma), 6.34 (4H, CH), 6.23-6.16 (4H, CH), 5.50 (4H, CH); ^{13}C-NMR (75 MHz): δ 153.7, 153.6, 144.0, 132.0, 131.3, 130.3, 130.2, 127.7, 121.1, 45.1.

The FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7 (1,3)-tetra-benzenacyclooctaphan-14,16,34,36,54,56,74,76-octaol (3b) recorded in DMSO-*d6* solvent is given as Figs 1–3.

2,4,6,8-Tetrakis(4-methylphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54, 56, 74,76-octaol (3c):

Orange solid; m.p: 256-258°C; FT-IR (KBr disc): 3600-3000, 1621, 1547, 1498, 1432, 1222, 1077,

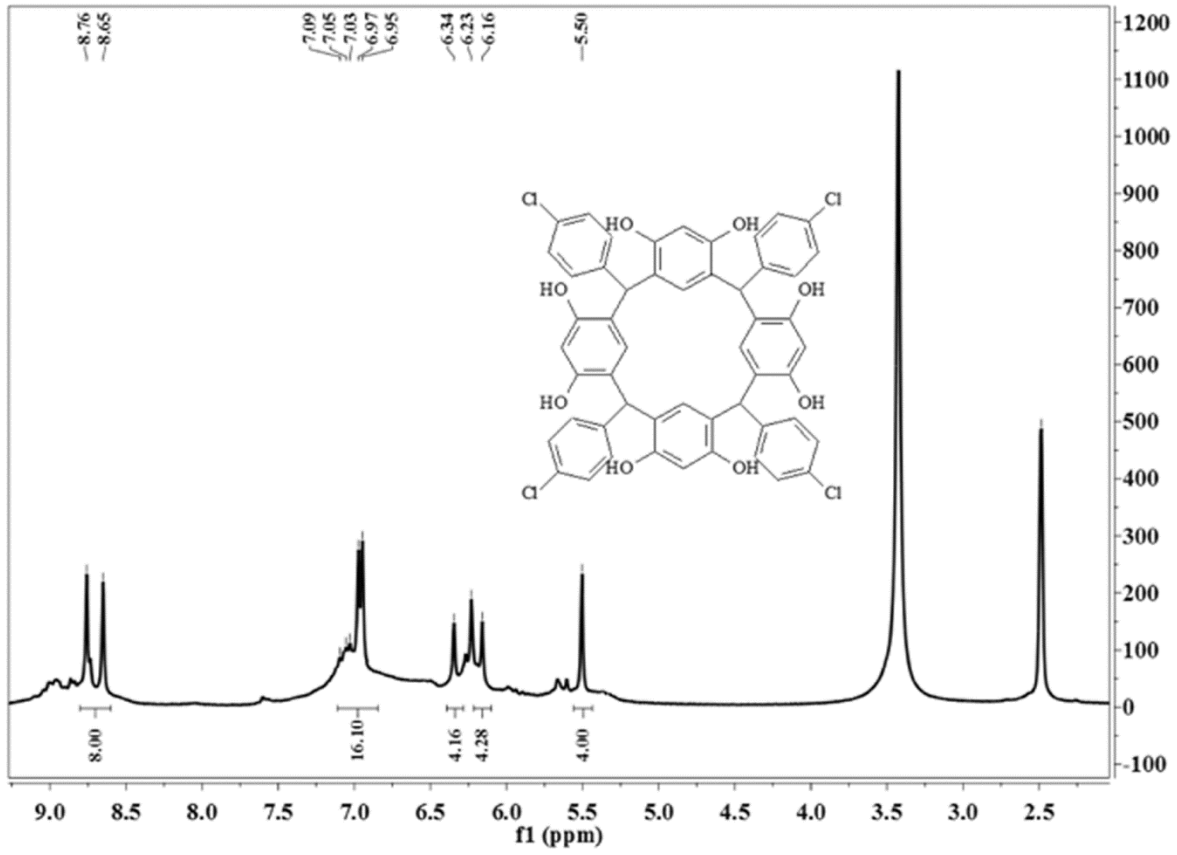


Fig. 2 — The ^{1}H-NMR spectra of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octaol (3b) in DMSO-d_6

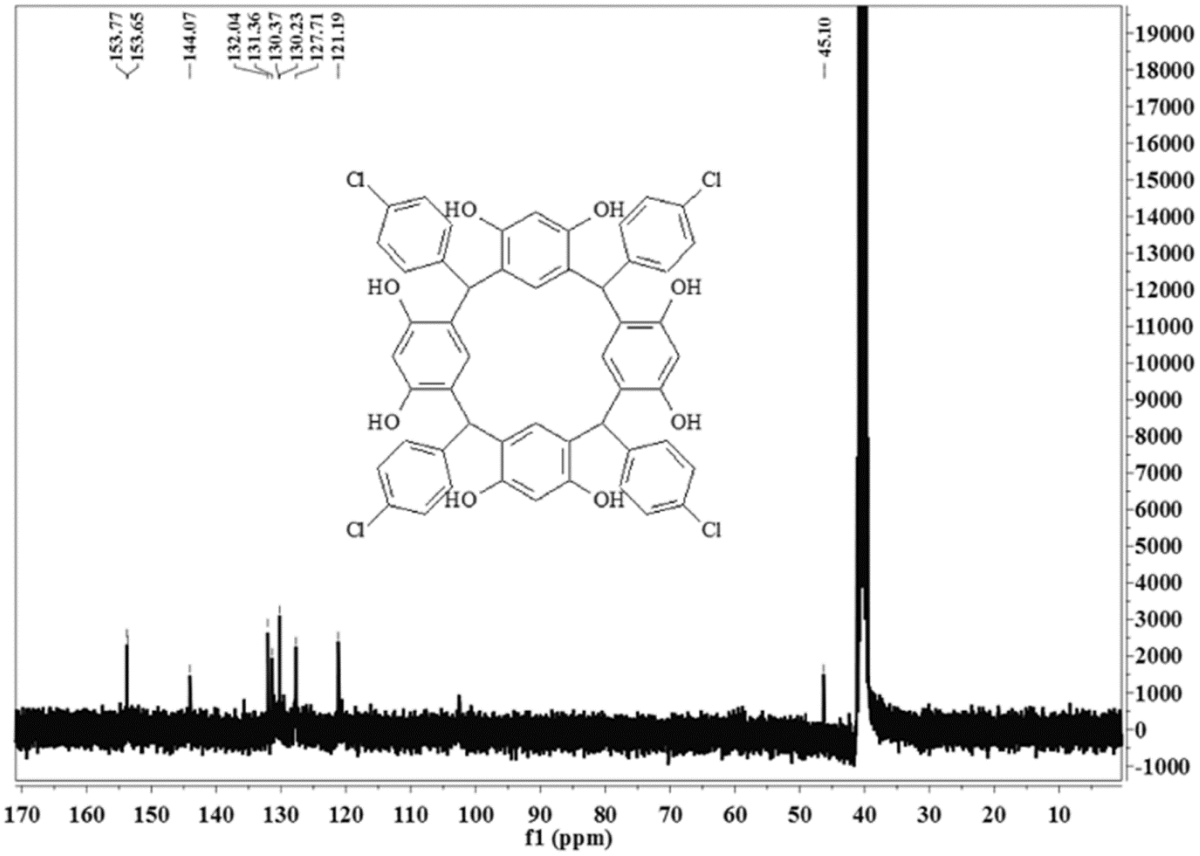


Fig. 3 — The ^{13}C-NMR spectra of 2,4,6,8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octaol (3b) DMSO-d_6

1016, 958, 847, 674, 558 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.63-8.54 (8H, OH), 6.98-6.82 (16H, aroma), 6.27 (4H, CH), 6.14 (4H, CH), 5.53-5.50 (4H, CH), 2.38-2.34 (12H, CH_3); ^{13}C-NMR (75 MHz): δ 153.4, 153.2, 144.1, 132.2, 131.0, 130.3, 127.6, 121.3, 45.6, 21.2.

2,4,6,8-Tetrakis(4-methoxyphenyl)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54, 56, 74,76-octaol (3d):

Orange solid; m.p: 246-248°C; FT-IR (KBr disc): 3600-3000, 1617, 1578, 1514, 1498, 1409, 1204, 1080, 1015, 926, 834, 668, 553 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.68-8.57 (8H, OH), 6.94-6.79 (16H, aroma), 6.27 (4H, CH), 6.19 (4H, CH), 5.46-5.42 (4H, CH), 3.14 (12H, OCH_3); ^{13}C-NMR (75 MHz): δ 154.3, 153.8, 144.7, 132.4, 131.2, 130.6, 127.7, 121.3, 45.2, 32.3.

2,4,6,8-Tetrakis(4-nitrolphenyl)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54, 56, 74,76-octaol (3e):

Orange solid; m.p: 234-236°C; FT-IR (KBr disc): 3600-3000, 2814, 1658, 1547, 1498, 1414, 1265, 1090, 1008, 923, 856, 680 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.82-8.71 (8H, OH), 7.13-7.03 (16H, aroma), 6.32-6.28 (4H, CH), 6.16 (4H, CH), 5.54 (4H, CH); ^{13}C-NMR (75 MHz): δ 154.5, 153.2, 144.6, 132.6, 131.2, 130.1, 129.8, 127.6, 121.4, 45.7.

2,4,6,8-Tetrakis(4-pyridin)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54, 56, 74,76-octaol (3f):

Orange solid; m.p: 243-245°C; FT-IR (KBr disc): 3600-3000, 1622, 1552, 1468, 1361, 1204, 1092, 1018, 928, 848, 673, 554 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.72-8.63 (8H, OH), 7.28-7.19 (16H, aroma), 6.44 (4H, CH), 6.28 (4H, CH), 5.55 (4H, CH); ^{13}C-NMR (75 MHz) : δ 155.8, 154.6, 144.8, 132.6, 131.0, 127.1, 121.4, 45.3.

2,4,6,8-Tetrakis(2-thiophenyl)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54, 56, 74,76-octaol (3g):

Orange solid; m.p: 228-230°C; FT-IR (KBr disc): 3600-3000, 1636, 1510, 1488, 1420, 1211, 1091, 1024, 926, 856, 677, 532 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.63-8.55 (8H, OH), 6.74-6.65 (12H, aroma), 6.28 (4H, CH), 6.18 (4H, CH), 5.45 (4H, CH); ^{13}C-NMR (75 MHz): δ 154.1, 153.6, 144.6, 132.3, 130.6, 130.2, 127.2, 120.8, 43.2.

Table 6 — Comparative account of catalytic ability of HPVAC-20 with other catalysts towards the synthesis of 2,4,6,8-tetraphenyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36, 54, 56,74,76-octaol 3,4-dihydropyrimidin-2(1*H*)-thione

Catalysts	Amount (g)	Condition	Reaction time	Yield (%)	Reference
$[Yb(H_2O)_9](OTf)_3$	0.132	Ethanol solvent and reflux	48 h	89	[16]
$H_3[PW_{12}O_{40}]$ / Conc. HCl	7 mL	Ethanol solvent (80 ^oC)	10 h	75	[17]
Conc. HCl	5 mL	Microwave irradiations (100 ^oC)	5 min	72	[18]
Fe_3O_4 nanoparticle	0.1	Solvent free (120 ^oC)	15 min	92	[20]
HPVAC-20	0.04	Solvent free (120 ^oC)	30 min	93	This work

2,4,6,8-Tetrakis(2-propan)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54,56, 74,76-octaol (3h):

Orange solid; m.p: 214-216°C; FT-IR (KBr disc): 3600-3000, 1605, 1552, 1492, 1432, 1224, 1087, 1012, 998, 926, 842, 668, 553 cm^{-1}; ^{1}H-NMR (300 MHz): δ 8.56-8.48 (8H, OH), 6.42 (4H, CH), 6.36-6.30 (4H, CH), 5.54 (4H, CH), 2.84 (8H, CH_2), 1.92 (12H, CH_3); ^{13}C-NMR (75 MHz): δ 153.6 127.2, 125.3, 121.2, 110.2, 43.2, 20.3.

A comparative account of efficiency of HPVAC-20 with other reported catalysts for the synthesis of 2,4,6, 8-tetraphenyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54, 56,74,76-octaol 3,4-dihydropyrimidin-2(1*H*)-thione is given in Table 6. The data clearly ascertain the versatility of the present protocol using HPVAC-20 as catalyst over the other catalysts.

Conclusion

Keggin-type vanadium (V) substituted heteropoly acids (HPA) have been widely used in numerous acid catalysed homogeneous reactions due to their strong Bronsted acidity. Similarly activated clay minerals are used in organic conversions as heterogeneous catalysts. The catalytic ability of HPV supported on AC (HPVAC) is more efficient than AC and HPA in the condensation of resorcinol and aldehyde under heterogeneous condition. In this practical method one pot procedure for the preparation of calix[4]resorcinarenes has been developed. The work-up procedure is very clear-cut; that is the products were isolated and purified by simple filtration from ethanol / water medium. The molecular structure of calix[4]resorcinarene derivatives were ascertained by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods. This protocol is a green approach for the preparation of calix[4]resorcinarenes using heteropoly acid supported on activated clay mineral as eco-friendly, reusable green heterogeneous catalyst.

References

1 Botta B, Cassani M D I & Misiti D, *Curr Org Chem*, 337 (2005) 9.

2 Gualbert J E, Shahgaldian P & Lazar A, *J Inclusion Phenom Macrocycl Chem*, 37 (2004) 48.

3 Heaven M W, Rastonb C L & Atwood J L, *Chem Commun*, 892 (2005) 7.

4 MacGillivray L R & Atwood J L, *J Solid State Chem*, 199 (2000) 152.

5 Bell T W & Hext N M, *Chem Soc Rev*, 589 (2004) 33.

6 Martinez G M, Teran C R & Tlapanco O A, *Fullerene Sci Technol*, 475 (2000) 8.

7 Yonetake K, Nakayama T & Ueda M, *J Mater Chem*, 761 (2001) 11.

8 Nakayama T, Takhashi D & Takeshi K, *J Photopolym Sci Technol*, 347 (1999) 12.

9 Tbeur N, Rhlalou T & Hlaibi M, *Carbohydr Res*, 409 (2000) 329.

10 Pietraszkiewicz O & Pietraszkiewicz M, *J Inclusion Phenom Macrocycl Chem*, 261 (1999) 35.

11 Ichimura K, Kurita E & Ueda M, *Eur Pat EP*, 67 (1995) 1220.

12 Yoshino N, Satake A & Kobuke Y, *Angew Chem Int Ed*, 457 (2001) 40.

13 Gaunert E, Barnier H & Nicod L, *Sep Sci Technol*, 2309 (1997) 32.

14 Wang H W, Feng, Y Q, Chen C & Xue J Q, *Chin Chem Lett*, 20 (2009) 1271.

15 Peng Q & Tang X H, *Chin Chem Lett*, 20 (2009) 13.

16 Barrett A G M, Christopher Braddock D, Henschke J P & Walker E R, *J Chem Soc Perkin Trans*, 1 (1999) 873.

17 Hedidi M, Hamdi S M, Mazari T, Boutemeur B, Rabia C, Chemat F & Hamdi M, *Tetrahedron*, 62 (2006) 5652.

18 Funck M, Guest D P & Cave G W V, *Tetrahedron Lett*, 51 (2010) 6399.

19 Sardjono R E, Kadarohman A & Mardhiyah A, *Procedia Chem*, 4 (2012) 224.

20 Karami B, Hoseini S J, Nikoseresht S & Khodabakhshi S, *Chin Chem Lett*, 23 (2012) 173.

21 Selvakumar K, Shanmugaprabha T, Annapoorani R, Sami P, *Synth Commun*, 47 (9) (2017) 913