# HETEROPOLYACIDS: AS EFFICIENT CATALYSTS FOR THE NITRATION OF 2,4,6,8,10,12-HEXAACETYL-2,4,6,8,10,12-HEXAAZAISOWURTZITANE

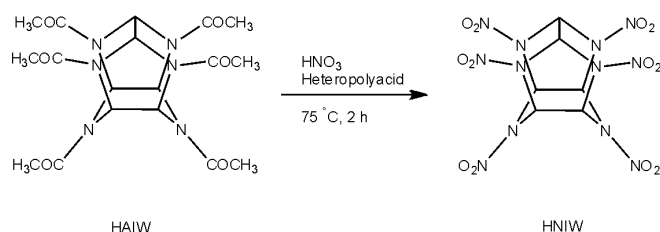Ali RAMAZANI,[a,b,*] Vahid AZIZKHANI[a] and Sang Woo JOO[c,*]

[a] Department of Chemistry, University of Zanjan, P O Box 45195-313, Zanjan, Iran
[b] Research Institute of Modern Biological Techniques, University of Zanjan, P O Box 45195-313, Zanjan, Iran
[c] School of Mechanical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea

2, 4, 6, 8, 10, 12-Hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HNIW) more commonly called CL-20 is a novel high-density cyclic nitramine that is synthesized for the use as an energetic component in propellant formulations. It is usually prepared via nitration of precursors in the presence of concentrated nitric and sulphuric acids. Here in this work, for the first time synthesis of CL-20 from nitration of 2, 4, 6, 8, 10, 12-hexaacetyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HAIW) in the presence of various clean nitrating agents like heteropolyacids has been reported. In the present conditions, the reactions are fairly green, clean and environmentally friendly. Meanwhile, the effects of reaction temperature, time and other factors on the yields were studied. The structure of the synthesized compound was confirmed by using various spectral techniques like IR, $^1$H, $^{13}$C, $^{14}$N-NMR and some of its physical properties.



## INTRODUCTION

Aromatic and aliphatic nitro compounds are of huge industrial importance and are invaluable intermediates in organic syntheses.[1–4a,b] Replacement of amine and amide hydrogen with a nitro group via direct nitration is an important route to *N*-nitro functionality. The energetic nature of the N–NO$_2$ group means that *N*-nitro-based explosives are some of the most powerful explosives available and these have largely superseded aromatic *C*-nitro compounds for military applications. Many nitramines exhibit high brisance and high chemical stability in combination with a favourable low sensitivity to impact and friction compared to nitrate ester explosives of similar power.[5a–5c]

One of the most interesting energetic molecules developed in recent years is the polycyclic nitramine, 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HNIW or CL-20). CL-20 is a new explosive that is 14~20 % more powerful than HMX (tetranitrotetraazacyclooctane)[6,7a,b] Its high detonation velocity and pressure make it a suitable candidate for replacing HMX. The first report on the synthesis of CL-20 has been published by Nielsen *et al*,[8] All known methods of producing 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane based on the same starting material, 2, 4, 6, 8, 10, 12-hexabenzyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane, are first reductively acylated to form 2, 6, 8, 12-tetraacetyl-4, 10-dibenzyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane.[8] Then remaining benzyl groups can be removed either by reductive formylation, with the formation of 2, 6, 8, 12-tetraacetyl-4, 10-diformyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane,[9] or by nitrosation, leading to 2, 6, 8, 12-tetraacetyl- 4, 10-dinitroso-2, 4, 6, 8, 10,

* Corresponding authors: aliramazani@gmail.com ;Tel.: +98 2433052572; fax: +98 2433052477 (Ali Ramazani); swjoo@yu.ac.kr; Tel.: +82 53 810 2568 ; fax: +82 53 810 4627 (Sang Woo Joo)

12-hexaazaisowurtzitane.[8,10] Both are easily converted to 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane by nitration with different nitrating systems.[8, 10]

Synthesis efforts have been made for a number of nitrolysable precursors to CL-20 including isowurtzitane cage substituted with nitroso,[8] formyl,[11] and acetyl,[12] groups. Synthesis of CL-20 from tetraacetylisowurtzitane (TAIW) has appeared as a favorable method, both in terms of process economy and product purity.[12] Sivabalan *et al.* have established a process for the preparation of CL-20 by nitration of HAIW.[13] In several industrially important processes (*e.g.* nitration, nitrosation, etc.) a large excess of sulfuric acid was required because the water byproduct slowed the reaction rate by diluting the acid. At the end of these processes, a large amount of "spent acid" is obtained which in batch reaction, is usually neutralized and disposed. The researcher's interest in the study of the explosive and thermal characteristics of 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane prompted them to develop an acceptable synthetic procedure for this material.

On the other hand, heteropolyacids (HPAs), catalyze a wide variety of reactions in homogeneous or heterogeneous (liquid–solid, gas–solid, or liquid–liquid biphasic) systems, offering strong options for more efficient and cleaner processing compared to conventional mineral acids.[14–19]

Catalysts based on heteropolyacids as Brønsted acids have many advantages over liquid acid catalysts. They are noncorrosive and environmentally benign, presenting fewer disposal problems. Solid heteropolyacids have attracted much attention in organic synthesis owing to easy work-up procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts.[20] Being stronger acids, heteropolyacids will have significantly higher catalytic activity than conventional catalysts such as mineral acids, mixed oxides, zeolites, etc. In particular, in organic media the molar catalytic activity of heteropolyacid is often 100–1000 times higher than that of $H_2SO_4$.[18, 19] This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. As stable, relatively nontoxic crystalline substances, heteropolyacids are also preferable regarding safety and easy of handling. Keggin-type HPAs typically represented by the formula of $[XM_{12}O_{40}]^{n-}$, when X is the heteroatom (most frequently $P^{+5}$ or $Si^{+4}$), and M is the addenda atom (usually $W^{+6}$ or $Mo^{+6}$), are the most important for catalysis.[16–19] They have been widely used as acids and oxidation catalysts for organic synthesis and also have several industrial applications. Among the

Keggin HP. As, transition metal substituted $H_3[PMo_{12}O_{40}]$ compounds have been reported as effective catalysts in organic reactions.[21–28]

In this study, the researchers describe an efficient method for synthesis of CL-20 from HAIW by various nitrating agents such as the heteropolyacids $\alpha$-$H_3[PMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_3[P(W_3O_{10})_4]$, and $H_7SiW_9V_3O_{40}$.

## RESULTS AND DISCUSSION

Reductive *N*-debenzylation of HBIW was achieved by hydrogenation in the presence of palladium catalysts. HBIW can be debenzylated with palladium hydroxide/ carbon catalyst and acetylated with acetic anhydride in a controlled manner to obtain 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10, 12-hexaazaisowurtzitane (TADB). HAIW was prepared by the standard method in reference,[13] after that nitration of HAIW produced CL-20. By the use of this new nitrating agent, the reaction eliminated the use of concentrated sulfuric acid and was environmental friendly.

The performance of CL-20 in propellant and weapon systems is highly dependent upon the crystal polymorph of CL-20. CL-20 may appear in several different crystal polymorphs, the most preferred of which is a high-density phase known in the art and referred to herein as the epsilon-polymorph of CL-20. The epsilon form of CL-20 is preferred because of the high energetic performance and density and lower sensitivity compared to other polymorphs.[32]

In the present study, the ε-CL-20 polymorph was identified and confirmed by comparing FT-IR and Raman spectra with those reported in the literature.[33a–c] Figure S4 (in the Supplemental Materials), shows the Raman spectra (in the regions of 700–900 cm⁻¹) of the ε-CL-20 polymorph.

In a systematic study and also in this work, the effects of the reaction temperature, concentration of nitric acid and catalyst type have been studied.

### Finding an appropriate HPA

Our first goal was finding an appropriate kind of HPAs, so several available HPAs catalysts were used such as: $\alpha$-$H_3[PMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_3[P(W_3O_{10})_4]$, $H_7SiW_9V_3O_{40}$. By decreasing the HPAs acidic strength with PW $\geq$ SiW $\geq$ PMo $\geq$ SiMo order, it was seen that the purity and the yield of CL-20 were decreased (Table 1).[18–28] After investigating data results, $H_3[P(W_3O_{10})_4]$ was selected as the best catalyst. Also it is obviously clear that lack of catalyst leads to poor results.

*Table 1*

Nitration of HAIW by HNO$_3$ in the presence of different heteropolyacids (HPAs)

| Nitrating agent | Ratio of HNO$_3$/HPA (mL/g) | Time (h:min) | Yield (%) |
|---|---|---|---|
| HNO$_3$/H$_2$SO$_4$ | 10/2 | 3 | 65 |
| HNO$_3$/ H$_3$[P(W$_3$O$_{10}$)$_4$] | 10/0.1 | 2 | 95 |
| HNO$_3$/H$_7$SiW$_9$V$_3$O$_{40}$ | 10/0.1 | 2. 20 | 91 |
| HNO$_3$/α-H$_3$PMo$_{12}$O$_{40}$ | 10/0.1 | 2. 40 | 89 |
| HNO$_3$/H$_3$PMo$_{12}$O$_{40}$ | 10/0.1 | 2. 30 | 87 |

## The optimization of catalyst amount

In this work, after selecting an appropriate catalyst, it was tried to find the best ratio of the catalysts for this reaction (Table 2).

Results show that using 10.0 mL of HNO$_3$ and 0.1 g of H$_3$[P(W$_3$O$_{10}$)$_4$] (Table 1) is the best ratio and gives excellent results. The mechanism of formation of nitronium ion and the progress of the reaction were expected to involve the steps shown in Figure 1. In the presence of heteropolyacids, nitric acid underwent ionization to generate nitronium (NO$_2^+$) ions, and HAIW underwent electrophilic substitution reaction at nitrogen atoms by the electrophile NO$_2^+$ ion to give the nitrated product; *i.e.*, CL-20.

## The optimization of reaction temperature

It is essential to know the operating temperature envelope at which the reaction has a maximum yield and optimum heat generation. In order to generate the temperature envelope, nitration was conducted at 20, 30, 45, 55, 65, 75 and 85 °C, in three times for each temperature and the average was taken as a yield result. The process was found safe at a temperature of 75 °C and yield was the highest as well (our results are summarized in Table 3). It was observed that beyond 85 °C, formation of NO$_x$ gases increased significantly, which is not desirable. Thus, the approximate temperature envelope for the reaction is 75 °C. Below 65 °C a reaction takes place but the reaction time is prolonged by almost an additional 2 h.

## The optimization of reaction time

In the other step, the effect of reaction time on the product yield was studied. The results are summarized in Table 4. It seems that increasing reaction time up to 2 h, increases reaction yield but prolonging it beyond 2 h will decrease the HNIW yield.
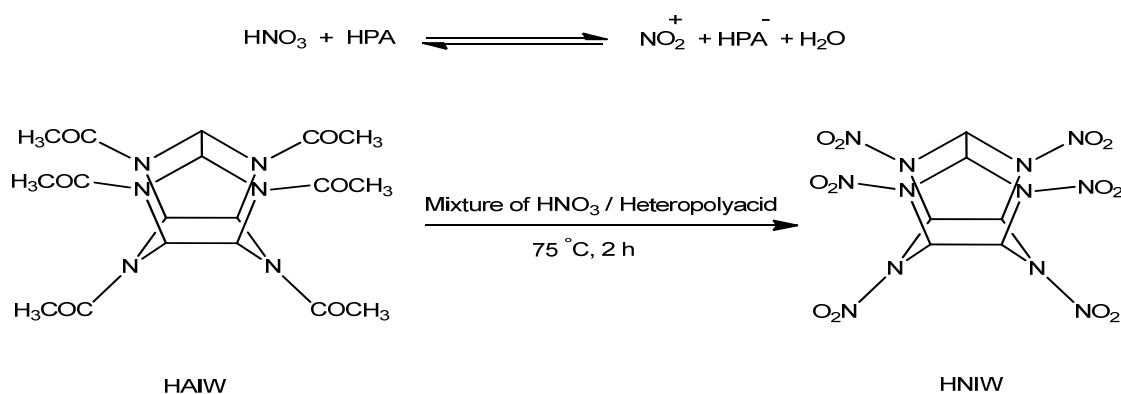


Fig. 1 – Nitration of HAIW with HNO$_3$ in the presence of heteropolyacid (HPA) and its proposed mechanism.

*Table 2*

Effect of catalyst ratio on the reaction yield

| | Catalyst | HNO$_3$ | Heteropolyacid (HPA) Catalyst (g) | Yield (%) |
|---|---|---|---|---|
| 1 | H$_3$[P(W$_3$O$_{10}$)$_4$] | 10 mL | 0.05 | 69 |
| 2 | | | 0.1 | 95 |
| 3 | | | 0.15 | 92 |
| 4 | | | 0.2 | 89 |

*Table 3*

Effect of reaction temperature on the synthesis of HNIW

| | Nitrating agent | T/°C | Yield (%) |
|---|---|---|---|
| 1 | | 20 | 45 |
| 2 | | 30 | 47 |
| 3 | | 45 | 75 |
| 4 | $HNO_3/ H_3[P(W_3O_{10})_4]$ | 55 | 81 |
| 5 | | 65 | 87 |
| 6 | | 75 | 95 |
| 7 | | 85 | 91 |

*Table 4*

Effect of the reaction time on the product yield

| | Nitrating agent | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | | 1 | 68 |
| 2 | | 1. 5 | 79 |
| 3 | | 2 | 95 |
| 4 | $HNO_3/ H_3[P(W_3O_{10})_4]$ | 2. 5 | 89 |
| 5 | | 3 | 73 |
| 6 | | 3. 5 | 59 |
| 7 | | 4 | 45 |

*Table 5*

Effect of Strength and quantity of nitric acid

| Entry | Strength of nitric acid | Volume of acid (mL) | Yields (%) | Purity (%) |
|---|---|---|---|---|
| 1 | 65% | 10 | 73 | 93 |
| 2 | 98% | 2 | 62 | 98 |
| 3 | 98% | 5 | 81 | 97 |
| 4 | 98% | 10 | 95 | 99 |

*Table 6*

Synthesis of CL-20 from nitration of tetraacetylhexzaazaisowurtzitane (TADBIW),
pentaacetylformylazaisowurtzitane (PAFIW), hexzaacetylhehzaazaisowurtzitane (HAIW)

| Compound | Nitration Condition | Yields | Reference |
|---|---|---|---|
| TAIW | $HNO_3/N_2O_4$ | 97 % | [34] |
| TADBIW | Nitration / Sulpholane | 90–97 % | [35] |
| TAIW | $H_3PW_{12}O_{40} / HNO_3$ | 96 % | [36] |
| PAFIW | $HNO_3 / H_2SO_4$ | 97 % | [37] |
| HAIW | $HNO_3 / H_3[P(W_3O_{10})_4]$ | 95 % | This Work |

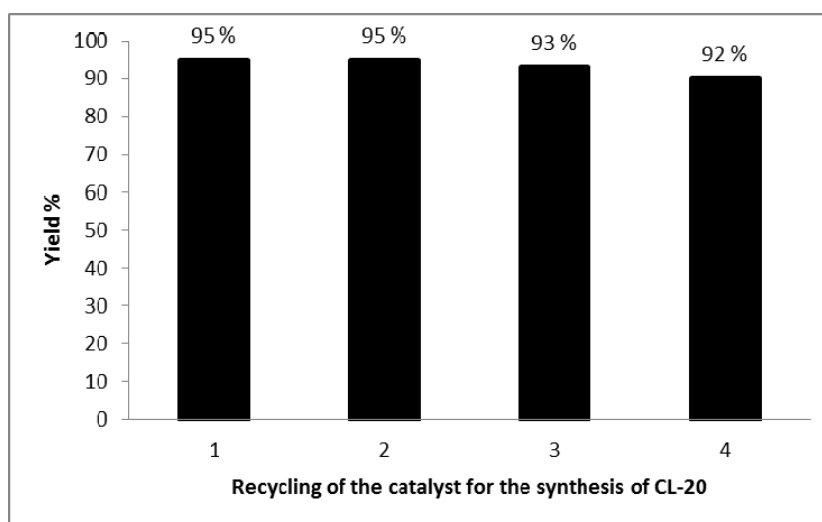

Fig. 2 – Recycling of the catalyst.

## Effect of the nitric acid strength

To study the effect of the strength of the nitric acid on the purity and the product yield, experiments were carried out with nitric acid with strengths of 65 and 98%. As expected, the purity and the yield of the product came down as the strength of the acid was brought down. This is because the nitronium ion concentration and the solubility of partially nitrated products reduced as the water content increased in the nitric acid. Maximum yield and purity of CL-20 was obtained in $HNO_3$ 98% (Table 5).

Various nitration conditions have been reported in literature Bayat, *et al.*[34] introduced $HNO_3/N_2O_4$ for synthesis of CL-20 (Yield of CL-20 = 97%) from nitration of TAIW. In the other work Sikder, *et al.*[35] applied nitration/ sulpholane for nitration and obtained high yield 90–97 %. Bayat, *et al.*[36] reported efficient nitration conditions with 96% yield. Also Chung *et al.*[37] used $HNO_3 / H_2SO_4$ for nitration of PAFIW to produce CL-20 with high yield 96%.

In this work we produced CL-20 from nitration of $HNO_3 / HPAs$ and obtained the product with a yield of 95% (Table 6). High-performance liquid chromatography (HPLC) analysis showed that the purity of the 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane obtained was ≥ 99%. The product was isolated in the hydrated alpha form after drying to a constant weight at 40°C. The structure of the synthesized compound was confirmed by using various spectral techniques like IR, $^1$H-NMR and some of its physical properties were determined.[8]

The catalyst can be reused after a simple work-up (up to four catalytic cycles) without any loss of catalytic activity (Figure 2).

In this work, the effect of the studied parameters for the synthesis of CL-20 from nitration of 2, 4, 6, 8, 10, 12-hexaacetyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HAIW) in the presence of various clean nitrating agents like heteropolyacids such as: (1) Finding an appropriate HPAs; (2) The optimization of catalyst amount; (3) The optimization of reaction temperature; (4) The optimization of reaction time; (5) Effect of the nitric acid strength; was investigated. The results obtained from research done shows that the optimization of studied parameters of the reaction leads to the formation of CL-20 in highest yield and purity.

## EXPERIMENTAL

All chemicals were purchased from Merck (Darmstadt, Germany) and Fluka (Switzerland), and used without further purification. $H_3[P(W_3O_{10})_4]$ was purchased from Sigma-Aldrich. Before use, the catalyst was dried at 50°C. Melting points were determined on open capillary and are not corrected. IR spectra were recorded by Perkin-Elmer infrared spectrometer using matrix KBr at the Zanjan University. $^1$H, $^{13}$C and $^{14}$N-NMR spectra were recorded on Bruker 250 MHz instrument model WG-300 and δ units with reference to tetramethylsilane internal standard at the Zanjan University. Elemental analysis was performed using a Carlo Erba EA-1108 elemental analyzer in the Malek Ashtar University of Technology. High Performance Liquid Chromatography (HPLC) (Microsorb-MV C18 column (4.6 mm × 250 mm, 5 μm; Rainin, Woburn, MA)) was used to confirm further purity of CL-20. Raman spectra of CL-20 were collected at the Spectroscopy Laboratory, Tarbiat Modares University by using a Thermo Nicolet Almega dispersive Raman scattering spectrometer operating by a 532 nm line from the second harmonic of a Nd:YLF laser in a backscattering configuration. Commercially available solvents and reagents were used without further purification. HAIW was prepared according to a published procedure.[13]

### Preparation of Catalyst

**Preparation of $H_3PMo_{12}O_{40}$:** $H_3PMo_{12}O_{40}$ was prepared according to a published procedure [29] as follows: To 420 mL of a 2.85 M aqueous solution of $Na_2Mo_4$ were added successively 6.8 mL of 85% $H_3PO_4$ and 284 mL of 70% $HClO_4$. The disodium salt precipitated from the yellow solution. After filtering the mixture, the obtained powder was airdried. Recrystallization in a mixture of $Et_2O/H_2O$ gave greenish microcrystals. An aqueous solution of the greenish microcrystals was acidified with HCl and extracted by $Et_2O$. To the dense layer water was added water and yellow crystals of $H_3PMo_{12}O_{40}$ precipitated. Before use, the catalyst was dried at 50 °C. IR (cm$^{-1}$): 1067, 975, 963, 870, 810, 785, 593.

**Preparation of α-$H_3PMo_{12}O_{40}$:** α-$H_3PMo_{12}O_{40}$ was prepared according to a published procedure [30] as follows: α-$H_3PMo_{12}O_{40}$ was obtained from an aqueous solution of α-$Na_2HPMo_{12}O_{40}.14H_2O$ (250 g/200 mL), acidified by 50 mL of HCl (12 M), and extracted by $Et_2O$ (400 mL). The dense layer (300 mL), added with half its volume of water, gave yellow crystals after desiccation (190 g). Before use, the catalyst was dried at 50 °C. IR (cm$^{-1}$): 1067, 975, 963, 870, 810, 785, 593, 500, 453, 400, 378, 339.

**Preparation of $H_7SiW_9V_3O_{40}$:** $NaVO_3$ (1.375g, 11.25 mmol) and $Na_{10}[α-SiW_9O_{34}]$ (10g, 3.75 mmol) were mixed as dry powders and added to 100 ml of water at room temperature. The solution was stirred vigorously and HCl (6M) was added dropwise to bring the pH to 1.5. A clear wine red solution was developed and subsequently the solution was passed on an Amberlite IR-120 cation-exchange column in H$^+$ form until pH < 1. Finally the solid HPA had been separated by the cooling method. [31] Before use, the catalyst was dried at 50 °C.

Three prominent peaks at 968, 912, 788 cm$^{-1}$ are assigned to ν (W–Od), ν (Si–O), and ν (W–Oc–W), respectively. The peak positions are coincident to that of $H_4SiW_{12}O_{40}$: 980 cm$^{-1}$ (W–Od), 925 cm$^{-1}$ (Si–O), and 770 cm$^{-1}$ (W–Oc–W).

### Nitration of 2, 4, 6, 8, 10, 12-hexaacetyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane (HAIW)

0.42 g (1mmol) HAIW was added gradually to a cooled mixture of 65 or 98% nitric acid (10 mL) and heteropolyacid 0.1 g. The reaction mixture was heated to 75 °C, maintained at this temperature for 2 h and the mixture was cooled to 35 °C and poured into 10 g ice / water with vigorous stirring. The precipitated product was filtered off and washed with water (four times) to obtained neutral washings. The product was isolated in the hydrated alpha form after drying to a constant weight at 40 °C. The structure of the synthesized compound was confirmed by using various spectral techniques like IR, $^1$H, $^{13}$C, $^{14}$N-NMR and some of its physical properties were determined.[8]

### Purification of CL-20

The crude CL-20 was dissolved in minimum amount of ethyl acetate and *n*-heptane was added drop wise with efficient stirring. CL-20 started precipitating and the addition of *n*-heptane was stopped when there was no further precipitation. The precipitated CL-20 was filtered and air-dried (yield of CL-20 = 95%). High Performance Liquid Chromatography (HPLC) analysis showed that the purity of the 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane obtained was ≥ 99%. A more complete characterization such as: FT-IR and $^1$H NMR spectral data and the HPLC chromatogram of product are presented in the Supplemental Materials (Figures S1-S3).

### Characterization of CL-20

White solid; m.p. 252 °C (dec.);
IR (KBr): 3049, 1650, 1350 cm$^{-1}$;
$^1$H-NMR (acetone-d$_6$): $\delta_H$ 8.35 (4 protons, H-3, H-5, H-9 and H-11) and 8.2 (2 protons, H-1 and H-7);
$^{13}$C-NMR (acetone-d$_6$): $\delta_C$ 75.1 ppm (C-3, C-5, C-9 and C-11, $^1J_{CH}$ = 176.6 Hz) and 72.1 ppm (C-1 and C-7, $^1J_{CH}$ = 175.9 Hz);
$^{14}$N-NMR (acetone-d$_6$): $\delta_N$ (-180.6 ppm, **N**-NO$_2$) and (-41.6 ppm, N-**N**O$_2$).
Elemental analysis calculated for CL-20 (Mol. Wt. 438): C, 16.44 %; H, 1.36 %; N, 38.30 %. Found: C, 17.03 %; H, 1.0 %; N, 37.40 %.

## CONCLUSION

In order to obtain HNIW, HAIW can be nitrated in the presence of HPAs. The present research shows that the H$_3$[P(W$_3$O$_{10}$)$_4$] catalyst leads to the formation of CL-20 in highest yield and purity. The optimized reaction conditions for the nitration is at 75 °C for 2 h and the CL-20 can reach 95 % in yield and high purity. In summary, we found a new, highly efficient and clean method for synthesis of 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane from 2, 4, 6, 8, 10, 12-hexaacetyl-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane in the presence of a mixture of nitric acid and heteropolyacids. HPAs are superior in activity to the conventional acid catalysts such as H$_2$SO$_4$ or zeolites. These catalysts are generally less expensive, and they are more reactive, eco-friendly, and convenient to handle, and they have greater selectivity, simpler workup, and recoverability and more enhanced reaction times than most of the other catalysts.

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