

Combustion Synthesis of Nano CeO₂ and its Application as a Catalytic Agent in Peptidomimetics

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Abstract

An eco-friendly cerium oxide nanoparticle was prepared through a solution combustion system with a novel fuel plant seed source *Albizia richardiana*. The synthetic technique involves the *Albizia richardiana* plant seeds as a fuel and cerium nitrate as an oxidizer (basis of cerium) was added in stoichiometric quantity in a well washed silica crucible and stirred for several minutes until persistent uniform solution was made. Then the mixture was kept in a heat up heating chamber at 500 °C. After dehydration and decomposition of homogeneous solution, the obtained CeO₂ nanoparticles were thoroughly characterized using FT-IR, XRD and SEM morphological analysis. The synthesized nano CeO₂ was a better catalytic agent for the production of N^α-Fmoc/Cbz-keto-1,2,3-triazole equivalents through the three-constituent reaction between amino acyl chloride equivalents of Fmoc/Cbz-protected amino acids, phenyl acetylene and sodium azide. Keto-1,2,3-triazoles were set upon by refluxing amino acyl chlorides with NaN₃ and phenyl acetylene in presence of CeO₂ nano particles in methanol. After a simple workup, the desired products obtained were fully categorized by FTIR, HRMS, proton and ¹³C NMR techniques.

Keywords: Amino Acyl Chlorides, Combustion Method, Fmoc/Cbz-Protected Amino Acids, Sodium Azide, Triazole

1.0 Introduction

In recent times, nanomaterials have acknowledged an outstanding consideration by chemists in industries for improvement of reaction speed, selectivity and green reaction Conditions¹⁻⁵. Considerably, due to their exciting physical and chemical properties matched to their bulk materials nanoparticles have been studied widely^{6,7}. The size and shape of nanomaterials significantly plays a noticeable part in properties like physical, chemical, and electrical⁸. CeO₂ NPs act as a semiconductor which possess a wide band gap of 3.19 eV and larger excitation binding energy⁹. But the usage of nano CeO₂ in broad fields such as solar cells, solid electrolytes, photocatalysis, phosphor fuel cells, cosmetic sunscreens, luminescence,

sensors and due to their strong antioxidant property, it has wide applications in the biomedical industry¹⁰⁻¹⁴.

There are many numbers of biomolecules containing triazole pattern and were prepared well prior to the 'click chemistry' method became widespread. A few examples are shown in Figure 1. They also operate as important synthetic mediates in several industrial uses such as photo stabilizers, agrochemicals, liquid crystals, supramolecular chemistry, additives, dendrimers, polymers, pigments, and metal chelators¹⁵⁻¹⁷. Hence, it is imagined pertinent in the present situation to modernize the medicinal chemistry of this privileged framework.

Plenty of methodologies for the (3+2)-cycloaddition methods have been explored in the literature to produce diversely functionalized triazoles (Scheme 1)¹⁸⁻²⁵. As a

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result, research struggles have been focused to envisage benign protocols to synthesize triazoles.

Many methods are available to prepare nano CeO₂ such as impregnation, sol-gel methods, micro emulsion, co-precipitation, microwave-mediated hydrothermal and hydrothermal²⁶⁻³⁰. Many of these methods may require tough experimental situations and lengthier alert

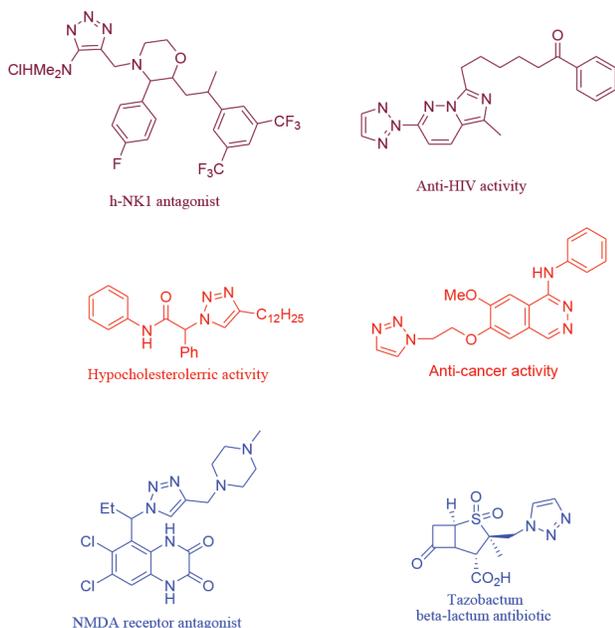


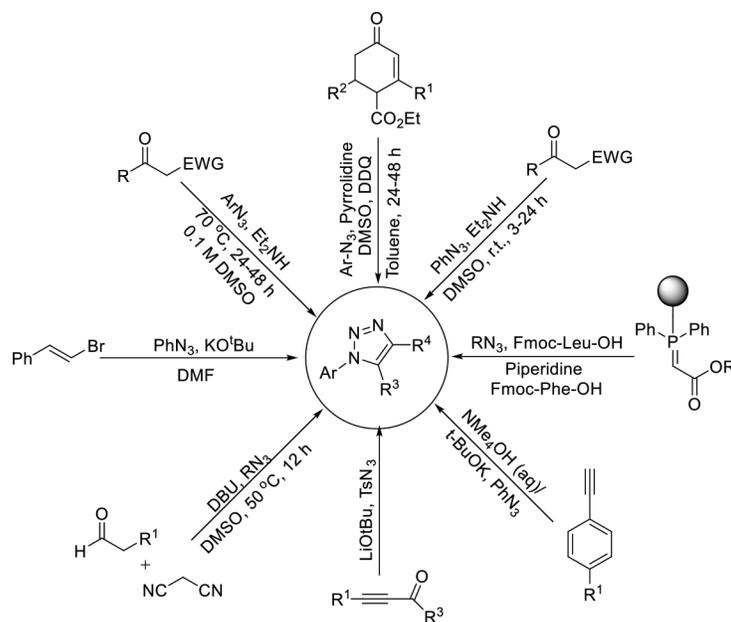
Figure 1. Structures of the triazole comprising commercial drugs.

circumstances. Whereas, a simple solution combustion method, very efficient, multiuse and informal production technique offered with time and energy saving vision is preferred³¹. In view of this, a simple solution combustion system is ideal as it confirms constant supply and atomic level fraternisation of reactants with a combustible material fuel to form uncontaminated product. However, the synthesis of keto-1,2,3-triazoles based peptidomimetics by the application of nano cerium oxide particles has not been reported in peptide chemistry. A convenient, simple, and eco-friendly nano CeO₂ catalysed synthesis of triazoles through the reaction of Fmoc/Cbz-amino acyl chloride derivatives of amino acids with sodium azide and phenyl acetylene in presence of CeO₂ nano particles using methanol as a solvent is presented.

2.0 Materials and Methods

2.1 Experimental Details

The substances used were bought from merck and the solvents were distilled prior to use. The *Albizia richardiana* seeds were collected from Chikkamangaluru state plantation. The seeds were separated and dehydrated, then powdered with mixer and stored in a closed desiccator. X-ray diffraction patterns of equipped yields were categorized by systematic X-ray diffractometer (PXRD-7000). Morphology analysis was studied with the support



Scheme 1: Diversely functionalized triazoles

of well-advanced SEM. TLC analysis was examined with the help of silica plate under UV chamber. ^1H NMR and ^{13}C NMR were recorded on a regular standard instrument. Functional group detection was done by typical FTIR instrument. HRMS were documented with the help of a well-developed Mass Spectrometer.

2.2 Synthesis of CeO_2 Nano Particles (Catalyst)

CeO_2 nanoparticles were prepared by adopting combustion method by the extract obtained from seed of *Albizzia richardiana* commonly known as Hatiamiuki as fuel. Initially, dried seed extract was liquefied in 15 ml of deionized H_2O which was then poured to 2g of cerium nitrate which acts as an oxidizing source. The mixture was stirred well to give rise to a uniform solution. Then, the reaction mixture was meticulously laid on a muffle furnace well maintained at 500°C . First, the homogeneous solution underwent through dehydration followed by liberation of gases. After a while, the formed CeO_2 was preserved in an airtight packet.

2.3 Synthetic Protocol for Fmoc/Cbz-Protected Keto -1,2,3 Triazole

To the stirred solution of the Fmoc/Cbz-protected amino acid solution (1.10 mmol) liquefied in DCM (4 mL), thionyl chloride (1.7 mmol) was added. This blend was subjected to sonication for about 30-50 minutes. The crude product was obtained after the removal of excess DCM by rota evaporator and subsequent addition of solvent hexane. To the obtained solution of acid chloride (0.8 mmol), sodium azide dissolved in methanol, nano CeO_2 (0.5 mmol), phenyl acetylene was added. This was refluxed for around 10-12h. The reaction was tracked by TLC to obtain the desired product. Later, under reduced pressure, methanol was removed, followed by dilution with 30 ml of EtOAc. The product layer was repeatedly washed away with deionized water and brine, finally it was dehydrated with Na_2SO_4 .

3.0 Results and Discussions

3.1 Characterization of Nano- CeO_2

3.1.1 X-Ray Studies

The XRD array of the cerium oxide nanoparticles synthesized using *Albizzia richardiana* seed source as

a fuel and cerium nitrate as basis of cerium. This study confirms the crystalline nature of the particle. X-Ray diffraction arrays visibly indicates the identically produced CeO_2 NPs and could be indexed to the typical CeO_2 with FCC structure (JCPDS NO:4-953). The lattice parameter intended from the (111) reflection of the original CeO_2 nanoparticle sample is 5.412\AA which correlates good by the lattice parameter of substance CeO_2 (a $\frac{1}{4}$ 5:411). No distinctive peaks owing to other impurities were noted in X-ray diffraction arrays, showing that produced CeO_2 NPs were being clean after being submitted to calcination at 500 degrees in absence of air (Figure 2). The crystallite size of CeO_2 NPs was observed to be 36.2 nm calculated from a highly intensive peak employing Debye-Scherrer's formula.

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

3.1.2 FT-IR Spectroscopy

The FTIR spectrum of CeO_2 NPs was made from KBr pellets as shown in Figure 3. The current spectrum has an absorption peak at 3125, 1630, 1400, 544 and 506 cm^{-1} . Peak at 3125 cm^{-1} point out the existence of stretching vibration of hydroxyl bonds in the water molecules. Peak at 506 cm^{-1} specifies Ce-O bond stretching which in shot approves that the obtained product was CeO_2 .

3.1.3 SEM Analysis

Figure 4 reveals that the SEM morphological pictures of CeO_2 NPs which are permeable-spongy and a mass with irregular morphology. This is due to the usage off fuel throughout combustion process releases a large quantity of gases and extracts the voluminous and permeable product.

3.1.4 EDX Analysis

The EDAX spectrum accompanied with SEM can provide the compositional analysis of the compound. The output signals obtained from Energy dispersive X-ray spectroscopy (EDX) is referred as EDX plot. When the particle is beacons with high energy beam of electrons, it gives distinct peaks in the spectra which correlates to the corresponding element. The intensities of X-rays are relatively proportional to the concentration of the specific element. Therefore, it represents the quantitative analysis of the particle. The synthesized nano CeO_2 crystals were

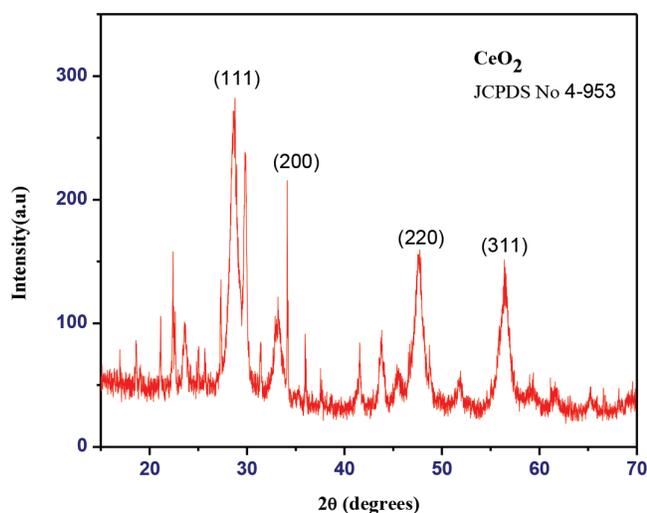


Figure 2. XRD patterns of obtained CeO₂ NPs from *Albizzia richardiana* plant seed extract.

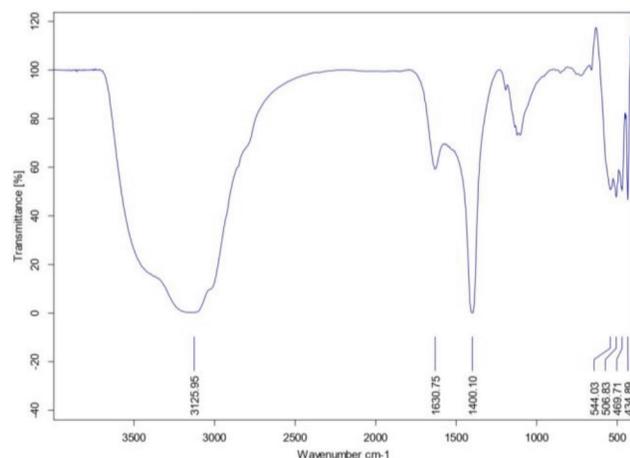


Figure 3. FT-IR spectrum of prepared CeO₂ NPs from *Albizzia richardiana* plant seed extract.

exposed to EDX analysis, significant signals at 0.25-1.25 keV for Ce in M shell, similarly from 4.25-5.75 keV for Ce in L shell represents the existence of CeO₂ and mark no remains of impurities as shown in Figure 5.

3.2 Synthetic Procedure of Fmoc/Cbz-Protected Keto 1,2,3 Triazole using CeO₂ Nanoparticles

Several protocols engaged in the production of 1,2,3-triazoles suffer from lot of obstacles like usage of huge costly compounds, tough circumstances; less percentage of yields, extended synthetic methods and instability of intermediates associated with impurities

and also need extraordinary attention for the desired final yields. Therefore, we conferred the production of Fmoc/Cbz-keto-1,2,3-triazole equivalents as per protocol in Scheme 2. The method includes a two-step approach, addition of chlorine with SOCl₂ followed by cyclization which leads to the final products using CeO₂ NPs. To enhance a reaction for the production of keto-1,2,3-triazole equivalents (1a-1h), our scheme involves reaction of the R-CO-Cl equivalents of Fmoc/Cbz-amino acid, phenylacetylene, and NaN₃ employing CeO₂ as catalytic agent.

Considerably, the procedure which delivered preferred fused keto-1,2,3-triazole equivalents (1a-1h), and the reaction was censored by Thin Layer Chromatography. Methanol was evaporated *in vacuo* after completion of the reaction and the rest was diluted with (EtOAc). The extracted high density organic phase was cleansed with H₂O and saturated solution of NaCl to get unpurified yield and dehydrated with Na₂SO₄. Solvent distance was completed by using rotatory evaporator and purification of the unpurified yield was carried out using CombiFlash NextGen column chromatography. The produced keto-1,2,3-triazole equivalents were categorized by HRMS, ¹H NMR, ¹³C NMR and FTIR methods.

3.3 Spectral Data of the Produced Organic Triazole

3.3.1(1a): IR (KBr, cm⁻¹): 3451, 2059, 1649, 1219. ¹H NMR, (DMSO-d₆, 400 MHz): δ 2.49-2.53 (3H, d, J = 12.0 Hz), 4.20-4.35 (4H, m), 5.33 (1H, br), 7.30-7.70 (13H, m), 8.49 (1H, s) ppm. ¹³C NMR, (DMSO-d₆, 100 MHz): δ 42.11, 43.09, 46.69, 46.73, 125.09, 125.17, 125.20, 127.01, 127.56, 127.60, 140.69, 143.79, 143.87, 143.97, 154.99, 155.55, 156.59 ppm. Mass calculated for C₂₆H₂₂N₄O₃ Na = 461.1590, Observed HR-MS m/z = 461.1593.

3.3.2: (1b) IR (KBr, cm⁻¹): 3469, 2067, 1545, 1240. ¹H NMR, (DMSO-d₆, 400 MHz): δ 2.55 (2H, m), 4.09-4.29 (4H, m), 6.49 (1H, br), 7.29-7.34 (5H, m), 7.40-7.43 (5H, m), 7.70-7.74, (8H, m), 8.30 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 30.59, 46.65, 51.76, 68.01, 120.01, 122.39, 123.19, 124.79, 125.10, 125.17, 126.01, 127.40, 133.0, 139.11, 141.10, 142.19, 144.59, 146.19, 148.39, 155.69, 156.79, 206.40 ppm. Mass calculated for C₃₂H₂₆N₄O₃Na = 537.1903, Observed HR-MS m/z = 537.1990.

3.3.3 (1c): IR (KBr, cm⁻¹): 3435, 2077, 1640, 1216. ¹H NMR, (DMSO-d₆, 400 MHz): δ 1.0-1.19 (6H, m), 1.59-

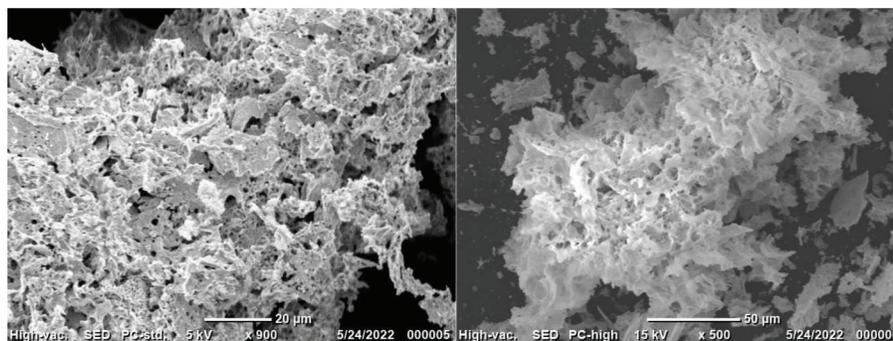


Figure 4. SEM images of synthesized CeO₂ NPs from *Albizzia richardiana* plant seed extract.

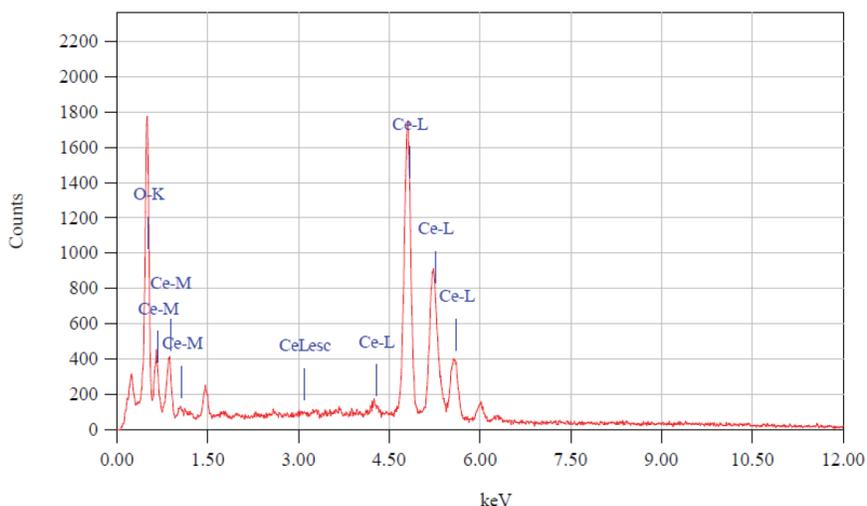


Figure 5. EDX spectrum of synthesized CeO₂ NPs from *Albizzia richardiana* plant seed extract.

1.89 (3H, m), 4.09-4.37 (4H, m), 6.40 (1H, br), 7.11-7.89 (13H, m), 8.19 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 21.69, 37.77, 46.60, 51.59, 53.77, 65.30, 120.0, 125.11, 126.46, 127.01, 127.55, 128.17, 129.10, 136.90, 140.66, 143.79, 154.70, 155.77, 172.80 ppm. Mass calculated for C₂₉H₂₈N₄O₃Na = 503.2059, Observed HR-MS *m/z* = 503.2057.

3.3.4(1d):IR (KBr, cm⁻¹): 3449, 2050, 1645, 1230.¹H NMR, (DMSO-d₆, 400 MHz): δ 0.79-0.83 (3H, m), 1.22-1.40 (5H, m), 2.49 (1H, m), 3.99-4.99 (4H, m), 6.29 (1H, br), 7.29-7.41 (5H, m), 7.59-7.55 (8H, m), 7.99 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 10.79, 15.01, 24.79, 36.89, 47.07, 56.59, 67.19, 126.59, 127.28, 128.07, 128.19, 128.39, 128.79, 129.13, 133.10, 141.09, 143.79, 146.69, 155.48, 156.19, 200.15 ppm. Mass calculated for C₂₉H₂₈N₄O₃Na = 503.2059, Observed HR-MS *m/z* = 503.2010 [M+Na]⁺.

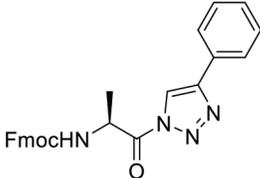
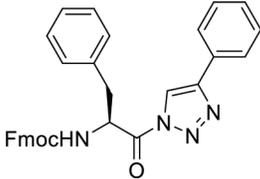
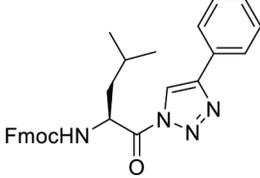
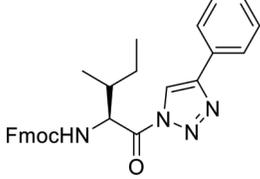
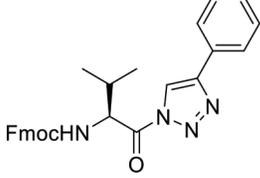
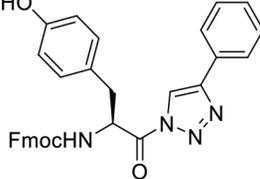
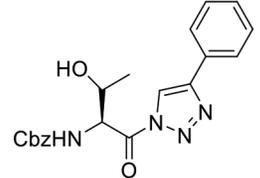
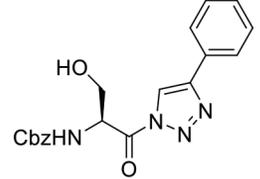
3.3.5(1e):IR (KBr, cm⁻¹): 3455, 2056, 1639, 1215.¹H NMR, (DMSO-d₆, 400 MHz): δ 1.15-1.17 (6H, d, *J* =

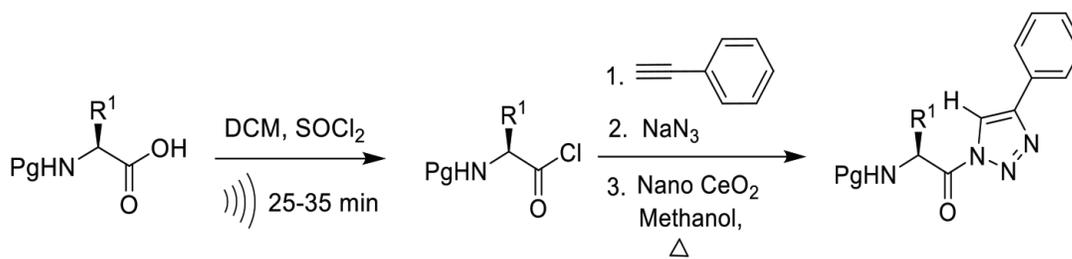
12.0 Hz), 2.56-2.96 (1H, m), 4.02-4.33 (4H, m), 6.49 (1H, br), 7.29-7.87 (13H, m), 8.30 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 21.65, 37.77, 46.60, 51.60, 53.75, 65.22, 120.13, 125.15, 126.49, 127.01, 127.55, 128.19, 129.17, 136.90, 140.66, 143.83, 154.78, 155.76, 172.79 ppm. Mass calculated for C₂₈H₂₆N₄O₃Na = 489.1903, Observed HR-MS *m/z* = 489.1905 [M+Na]⁺.

3.3.6(1e):IR (KBr, cm⁻¹): 3489, 2050, 1655, 1237.¹H NMR, (DMSO-d₆, 400 MHz): δ 3.11-3.36 (2H, d, *J* = 12.0 Hz), 4.66-4.82 (4H, m), 5.49 (1H, br), 5.79-6.13 (2H, d, *J* = 6.0 Hz), 6.49-6.70 (2H, d, *J* = 8.0 Hz), 7.07-7.90 (13H, m), 8.23 (1H, br), 8.49 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 46.60, 46.70, 56.0, 57.09, 119.06, 120.99, 123.66, 124.13, 125.11, 125.29, 127.13, 127.28, 127.66, 127.60, 136.05, 140.70, 143.71, 143.97, 155.15, 156.61 ppm. Mass calculated for C₃₂H₂₆N₄O₄Na = 553.1852, Observed HR-MS *m/z* = 553.1855.

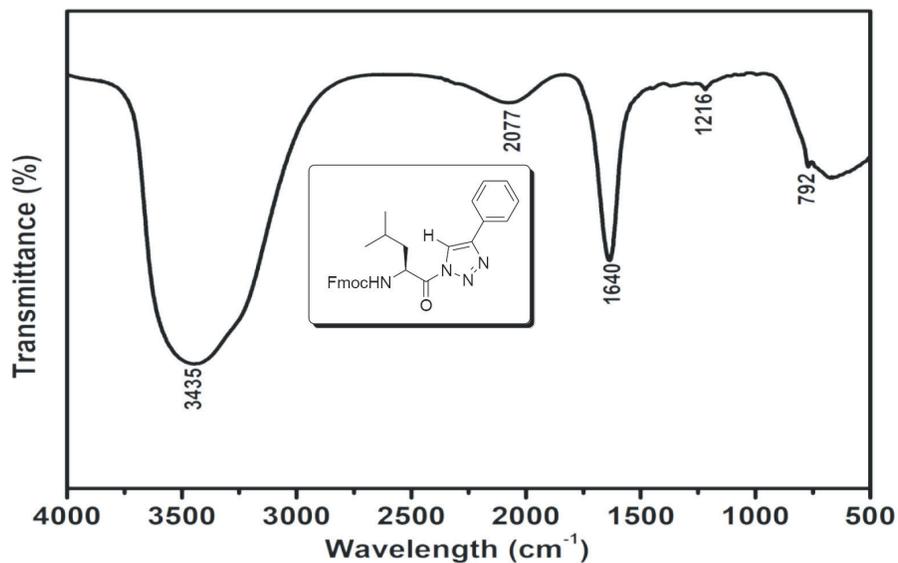
3.3.7(1g):IR (KBr, cm⁻¹): 3460, 2055, 1660, 1238.¹H NMR, (DMSO-d₆, 400 MHz): δ 0.93(3H, s), 2.05 (1H, s),

Table 1. List of synthesized triazoles of Fmoc/Cbz -protected amino acids *via* CeO₂ NPs as catalytic agent

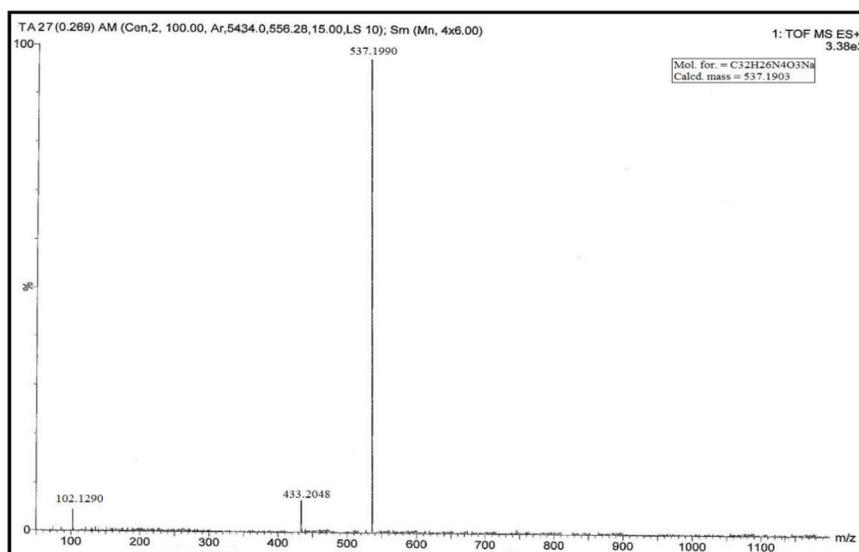
Records	N ^α -protected synthesized keto-1,2,3-triazoles equivalents	Product in (%)
1a		91
1b		92
1c		88
1d		89
1e		94
1f		86
1g		91
1h		79



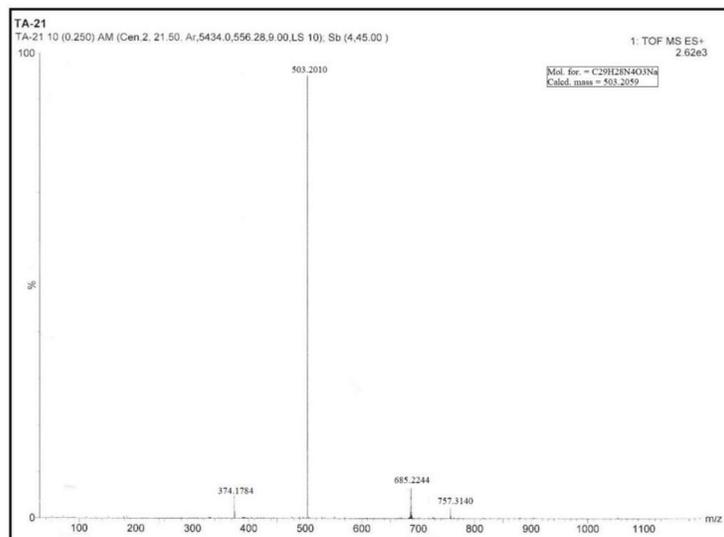
Scheme 2. Production of protected amino keto-1,2,3 triazole equivalents.



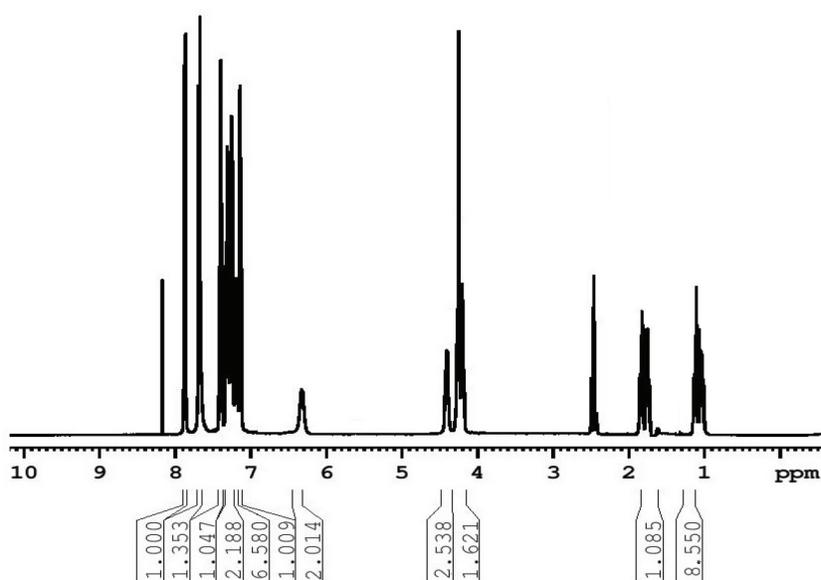
Spectrum 1. IR spectrum of N^{α} -Fmoc-L-Leu-keto-1,2,3-triazole.



Spectrum 2. HRMS of N^{α} -Fmoc-L-Phe-keto-1,2,3-triazole.



Spectrum 3. HRMS of *N*^α-Fmoc-L-Ile-keto-1,2,3-triazole.



Spectrum 4. ¹H NMR of *N*^α-Fmoc-L-Leu-keto-1,2,3-triazole.

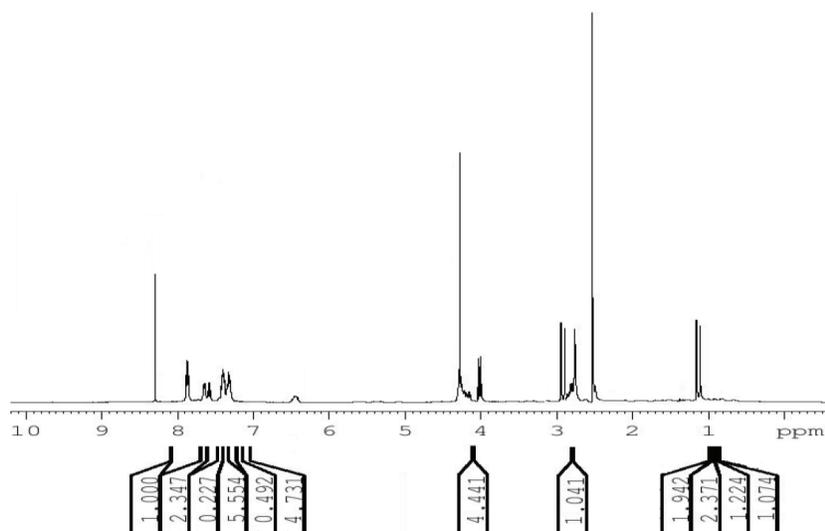
2.30 (1H,t, *J* = 5.0 Hz), 2.99 (1H, t, *J* = 9.2 Hz), 5.29 (1H, s), 5.66 (2H, s), 7.30-7.44 (4H, m), 8.30 (1H,s). ¹³C NMR (DMSO-d₆, 100 MHz): δ 19.17, 51.80, 59.89, 65.88, 120.04, 120.19, 125.44, 127.20, 127.79, 140.80, 143.84, 143.90, 154.11, 155.13, 172.50, 206.95. Mass calculated for C₂₀H₂₀N₄O₄Na = 403.1382, Observed HR-MS *m/z* = 403.1384.

3.3.8(1h):IR (KBr, cm⁻¹): 3450, 2052, 1684, 1242.¹H NMR, (DMSO-d₆, 400 MHz): δ 2.32 (1H, s), 4.06-4.29 (3H, m), 5.40 (2H, s) 6.25 (1H, broad), 7.29-7.89 (10H, m), 8.30 (1H, s) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ 51.81, 65.55, 79.09, 120.10, 121.32, 125.20, 127.11, 127.60,

128.90, 140.70, 143.775, 143.79, 155.80, 156.10, 173.30. Mass calculated for C₁₉H₁₈N₄O₄Na = 389.1226, Observed HR-MS *m/z* = 389.1234.

4.0 Conclusion

A simple, useful and eco-friendly varied nano CeO₂ catalyst was made by plant seed extract *Albizzia richardiana* as a fuel which acts as a lethal agent and categorized by XRD, SEM, EDAX and FTIR methods. The subsequent catalytic agent revealed enriched catalytic action headed for the



Spectrum 5. ^1H NMR of N^α -Fmoc-L-Val-keto-1,2,3-triazole.

production of Fmoc/Cbz-keto-1,2,3-triazole equivalents in a straight from R-CO-Cl, NaN_3 and phenylacetylene. The defined procedure is harmless, healthy systematized for the building of novel ring compounds which contains hetero atoms and also this process has no need of separation of intermediate like acyl azide. Metal nitrates generally used for the synthesis of nano metal oxides are extracted from the earth during the mining process and plant source is used as a fuel for the combustion process.

5.0 Acknowledgement

The author acknowledges the Principal, CEO and as well as director of Siddaganga Institute of Technology for providing research facilities.

6.0 References

1. Astruc D. Transition-metal nanoparticles in catalysis: from historical background to the state-of-the art. *Nanoparticles and Catalysis*. 2008; 1:1-48. <https://doi.org/10.1002/9783527621323.ch1>
2. Xin L, Hu J, Xiang Y, *et al.* Carbon-based nanocomposites as fenton-like catalysts in wastewater treatment applications: a review. *Materials*. 2021; 14:2643. <https://doi.org/10.3390/ma14102643>
3. Yin S, Xu B, Wang S, *et al.* Magnesia-carbon nanotubes (MgO-CNTs) nanocomposite: Novel support of Ru catalyst for the generation of CO x-free hydrogen from ammonia. *Catalysis Letters*. 2004; 96:113-6. <https://doi.org/10.1023/B:CATL.0000030107.64702.74>
4. Wen M, Li G, Liu H, *et al.* Metal-organic framework-based nanomaterials for adsorption and photocatalytic degradation of gaseous pollutants: recent progress and challenges. *Environmental Science: Nano*. 2019; 6:1006-25. <https://doi.org/10.1039/C8EN01167B>
5. Varma R. Solvent-free organic syntheses. using supported reagents and microwave irradiation. *Green Chemistry*. 1999; 1:43-55. <https://doi.org/10.1039/a808223e>
6. Abdel-Karim R, Reda Y, Abdel-Fattah A. Nanostructured materials-based nanosensors. *Journal of the Electrochemical Society*. 2020; 167:037554. <https://doi.org/10.1149/1945-7111/ab67aa>
7. Moghimi SM, Hunter AC and Murray JC. Nanomedicine: current status and future prospects. *The FASEB Journal*. 2005; 19:311-30. <https://doi.org/10.1096/fj.04-2747rev>
8. Tamizhdurai P, Sakthinathan S, Chen S-M, *et al.* Environmentally friendly synthesis of CeO_2 nanoparticles for the catalytic oxidation of benzyl alcohol to benzaldehyde and selective detection of nitrite. *Scientific Reports*. 2017; 7:46372. <https://doi.org/10.1038/srep46372>
9. Miao J-J, Wang H, Li Y-R, *et al.* Ultrasonic-induced synthesis of CeO_2 nanotubes. *Journal of Crystal Growth*. 2005; 281:525-9. <https://doi.org/10.1016/j.jcrysgro.2005.04.058>
10. Khan SA, Ahmad A. Fungus mediated synthesis of biomedically important cerium oxide nanoparticles. *Materials Research Bulletin*. 2013; 48:4134-8. <https://doi.org/10.1016/j.materresbull.2013.06.038>
11. Reddy Yadav L, Manjunath K, Archana B, *et al.* Fruit juice extract mediated synthesis of CeO_2 nanoparticles for antibacterial and photocatalytic activities. *The European Physical Journal Plus*. 2016; 131:1-10. <https://doi.org/10.1140/epjp/i2016-16154-y>

12. Ansari SA, Khan MM, Ansari MO, *et al.* Band gap engineering of CeO₂ nanostructure using an electrochemically active biofilm for visible light applications. *Rsc Advances*. 2014; 4:16782-91. <https://doi.org/10.1039/C4RA00861H>
13. Masui T, Hirai H, Imanaka N, *et al.* Synthesis of cerium oxide nanoparticles by hydrothermal crystallization with citric acid. *Journal of Materials Science Letters*. 2002; 21:489-91. <https://doi.org/10.1023/A:1015342925372>
14. Khan SB, Faisal M, Rahman MM, *et al.* Exploration of CeO₂ nanoparticles as a chemi-sensor and photo-catalyst for environmental applications. *Science of the Total Environment*. 2011; 409:2987-92. <https://doi.org/10.1016/j.scitotenv.2011.04.019>
15. Borgati TF, Alves RB, Teixeira RR, *et al.* Synthesis and phytotoxic activity of 1, 2, 3-triazole derivatives. *Journal of the Brazilian Chemical Society*. 2013; 24:953-61. <https://doi.org/10.5935/0103-5053.20130121>
16. Worthington PA. Synthesis of 1, 2, 4-triazole compounds related to the fungicides flutriafol and hexaconazole. *Pesticide Science*. 1991; 31:457-98. <https://doi.org/10.1002/ps.2780310405>
17. McNeill K, Cancilla D. Detection of triazole deicing additives in soil samples from airports with low, mid, and large volume aircraft deicing activities. *Bulletin of Environmental Contamination and Toxicology*. 2009; 82:265-9. <https://doi.org/10.1007/s00128-008-9626-z>
18. Wu L, Chen Y, Luo J, *et al.* Base-mediated reaction of vinyl bromides with aryl azides: one-pot synthesis of 1, 5-disubstituted 1, 2, 3-triazoles. *Tetrahedron Letters*. 2014; 55:3847-50. <https://doi.org/10.1016/j.tetlet.2014.03.029>
19. Ali A, Corrêa AG, Alves D, *et al.* An efficient one-pot strategy for the highly regioselective metal-free synthesis of 1, 4-disubstituted-1, 2, 3-triazoles. *Chemical Communications*. 2014; 50:11926-9. <https://doi.org/10.1039/C4CC04678A>
20. Cheng G, Zeng X, Shen J, *et al.* A metal-free multicomponent cascade reaction for the regiospecific synthesis of 1, 5-disubstituted 1, 2, 3-triazoles. *Angewandte Chemie*. 2013; 125:13507-10. <https://doi.org/10.1002/ange.201307499>
21. Kwok SW, Fotsing JR, Fraser RJ, *et al.* Transition-metal-free catalytic synthesis of 1, 5-diaryl-1, 2, 3-triazoles. *Organic Letters*. 2010; 12:4217-9. <https://doi.org/10.1021/ol101568d>
22. Ahsanullah, Schmieder P, Kuehne R, *et al.* Metal-free, regioselective triazole ligations that deliver locked cis peptide mimetics. *Angewandte Chemie International Edition*. 2009; 48:5042-5. <https://doi.org/10.1002/anie.200806390>
23. Seus N, Goncalves LC, Deobald AM, *et al.* Synthesis of arylselenanyl-1H-1, 2, 3-triazole-4-carboxylates by organocatalytic cycloaddition of azidophenyl arylselenides with β -keto-esters. *Tetrahedron*. 2012; 68:10456-63. <https://doi.org/10.1016/j.tet.2012.10.007>
24. Ramachary DB, Ramakumar K, Narayana VV. Amino acid-catalyzed cascade [3+ 2]-cycloaddition/hydrolysis reactions based on the push-pull dienamine platform: synthesis of highly functionalized NH-1, 2, 3-triazoles. *Chemistry—A European Journal*. 2008; 14:9143-7. <https://doi.org/10.1002/chem.200801325>
25. Li W, Wang J. Lewis base catalyzed aerobic oxidative intermolecular azide-zwitterion cycloaddition. *Angewandte Chemie International Edition*. 2014; 53:14186-90. <https://doi.org/10.1002/anie.201408265>
26. Panahi-Kalamuei M, Alizadeh S, Mousavi-Kamazani M, *et al.* Synthesis and characterization of CeO₂ nanoparticles via hydrothermal route. *Journal of Industrial and Engineering Chemistry*. 2015; 21:1301-5. <https://doi.org/10.1016/j.jiec.2014.05.046>
27. Wang H, Zhu J-J, Zhu J-M, *et al.* Preparation of nanocrystalline ceria particles by sonochemical and microwave assisted heating methods. *Physical Chemistry Chemical Physics*. 2002; 4:3794-9. <https://doi.org/10.1039/b201394k>
28. Yao S-Y, Xie Z-H. Deagglomeration treatment in the synthesis of doped-ceria nanoparticles via coprecipitation route. *Journal of Materials Processing Technology*. 2007; 186:54-9. <https://doi.org/10.1016/j.jmatprotec.2006.12.006>
29. Ganguli AK, Ganguly A, Vaidya S. Microemulsion-based synthesis of nanocrystalline materials. *Chemical Society Reviews*. 2010; 39:474-85. <https://doi.org/10.1039/B814613F>
30. Periyat P, Laffir F, Tofail S, *et al.* A facile aqueous sol-gel method for high surface area nanocrystalline CeO₂. *RSC Advances*. 2011; 1:1794-8. <https://doi.org/10.1039/c1ra00524c>
31. Bakkiyaraj R, Bharath G, Ramsait KH, *et al.* Solution combustion synthesis and physico-chemical properties of ultrafine CeO₂ nanoparticles and their photocatalytic activity. *RSC Advances*. 2016; 6:51238-45. <https://doi.org/10.1039/C6RA00382F>