



Synthesis of 5-Substituted-1H-Tetrazole Derivatives Using Monodisperse Carbon Black Decorated Pt Nanoparticles as Heterogeneous Nanocatalysts

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A facile and highly efficient protocol for synthesis of new 5-substituted 1H-tetrazoles derivatives has been developed by the assistance of vulcan carbon decorated based on monodisperse platinum nanoparticles (Pt NPs@VC) as superior and recyclable heterogeneous catalyst with excellent catalytic performance. Pt NPs@VC was proved to be an efficient and the durable catalysts with superior catalytic and reusability performance in the synthesis of 5-substituted 1H-tetrazoles.

Keywords: Platinum Nanoparticles, Heterogeneous Catalyst, 5-Substituted 1H-Tetrazoles, Vulcan Carbon.

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1. INTRODUCTION

Tetrazoles are an important class of N-heterocyclic compounds exhibiting widespread applications. Tetrazole derivatives are extensively used in different industries as instance: stabilizers in photography and photo imaging,^{1,2} explosives in rocket propellants,3-5 chelating agents in coordination chemistry,^{6,7} plant growth regulators, herbicides, fungicides in agriculture,^{8,9} and anti-wears and frictions in lubricants. Furthermore, the tetrazole ring is a significant intermediate in the synthesis of other complex heterocycles, through various rearrangements.¹⁰ 5-substituted tetrazoles are also used as activators in oligonucleotide synthesis.¹¹ Besides, Tetrazole is one of the most widely used in pharmaceutical chemistry agent. For instance, the tetrazole ring can be found in variety drugs applicants with anticonvulsants,12 antihypertensive and antibiotic activity, antiallergic, anti-fungal,^{13, 14} in cancer or in AIDS treatments.^{15, 16} Tetrazoles are likewise utilized as a part of agriculture as plant up development controllers, fungicides and herbicides,¹⁷ or photoimaging and in photography as stabilizers.¹⁸ Recently, the synthesis of tetrazole derivatives has attracted considerable attention since broad utilities found for tetrazole and its derivatives.

In this context, different preparative methods have been emerged so far.^{19,20} Most of them are depending upon the addition of the nitrile group of the sodium azide (NaN₃) the trimethylsilyl azide (TMSN₃).^{21(a-f)} There are also various ways for this new type of tetrazole; for illustrate, catalytic methods have been developed through the use of inorganic salts in different proportions.^{22(a-e)} Even though most of these ways at first glance seems to be an effective and suitable protocols for accessing to tetrazole derivatives; however, their practical applications are limited by one or more disadvantages such as harsh reaction conditions, low yields, long reaction times, the use of strong Lewis acids, the in situ generation of highly dangerous volatile HN₃ having the high risk of eruption and toxicity, formation of stable metal-tetrazole complexes, the use of toxic solvents, tedious work-up and failure to do recovery or reusability of the catalyst.

For this reason, heterogeneous catalysts have been the most desirable and attractive. Because of high recovery and reusability performances of the heterogeneous catalyst, nowadays a few heterogeneous catalysts have been designed such as $ZnO_{2^{3(a)}}^{23(a)}$ CSMIL,^{23(b)} ZnO nanoflakes,^{23(c)} CuFe₂O₄ nanoparticles,^{23(d)} Mesoporous ZnS,^{23(e)} CoY zeolite,^{23(f)} Cu₂O,^{23(g)} Fe₃O₄@SiO₂,^{23(h)} nano ZnO/Co₃O₄,²³⁽ⁱ⁾ Graphene^{23(j)} and Graphene oxide/ZnO nanocomposites^{23(k)} as catalysts. Because of

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low reusability performance, low yield and high reflux time in most of those catalytic systems for the synthesis of tetrazole, the discovery of new generation of heterogeneous catalysts is still in demand. Herein we report a facile and one pot synthesis for 5 substituted 1H-tetrazole derivatives by the assistance of Pt NPs@VC as one of the most efficient heterogeneous catalyst. The synthesized molecules have been characterized by ¹H-NMR, ¹³C-NMR, FT-IR and HRMS, respectively.

2. EXPERIMENTAL DETAILS

2.1. Materials and Instrumentation

PtCl₄ (99% Alfa Aesar), tetrahydrofuran (THF) (99.5%, Merck) and ethanol (99.9%) were purchased from Merck, dipropylamine (Sigma Aldrich) were used as received from suppliers. Vulcan XC-72 carbon (VC) was purchased from Cabot Europe Ltd. THF was distilled over sodium under argon atmosphere and stored under inert atmosphere. De-ionized water was filtered by Millipore water purification system (18 M Ω) analytical grade. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by washing with distilled water before drying in an oven.

The chemicals used in the synthesis of tetrazole derivatives were obtained from Merck and Aldrich Chemical Company. All chemicals and solvents used for the synthesis were of spectroscopic reagent grade.

Transmission electron microscopy (TEM) images were obtained on a JEOL 200 kV TEM instrument. Sample preparation for TEM analysis involves placement of a drop of 0.5 mg/mL ethanol solution of the prepared catalysts with a carbon support on a carbon covered 400mesh copper grid; the solvent is then allowed to evaporate. Excess solution was removed with an adsorbent paper and the sample was dried under vacuum at room temperature before analysis. More than 300 particles were calculated to get the integrated information about the overall distribution of Pt-based catalyst sample.

Thermo Scientific spectrometer was used for X-ray photoelectron spectroscopy (XPS) measurements and the X-ray source was K α lines of Mg (1253.6 eV, 10 mA). Samples were prepared by depositing the catalyst on a Cu double-sided tape (3 M Inc.). C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line. A Panalytical Emperian diffractometer with Ultima + theta - theta high resolution goniometer, having an X-ray generator (Cu K ∞ radiation, k = 1.54056 Å) and operating condition of 45 kV and 40 mA, were employed in XRD analysis. An MFP-3D (Asylum Research) was used to carry out tapping-mode atomic force microscopy (AFM) imaging. Samples were directly deposited on a 75 mm 25 mm glass slide (VWR International) and imaged using rectangular silicon tips (Olympus AC240TS) with a nom-

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inal spring constant of 2 Nm⁻¹. Both topographic and height images were recorded during AFM analysis. Height analysis was performed using Igor Pro software. Melting points were measured on a Bibby Scientific Stuart Digital, Advanced, SMP30. Fourier Transform Infrared (FT–IR) spectra were recorded on Bruker Optics, ALPHA FT–IR spectrometer. The ¹H NMR and ¹³C NMR spectra were obtained in DMSO- d_6 with Bruker DPX-300 as solvents with tetramethylsilane as the internal reference. The mass analyses were performed on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/HRMS at the advanced technology research center of Dumlupinar University (ILTEM).

2.2. General Procedure for the Synthesis of Pt NPs@VC

Optimized sonochemical double solvent reduction method has been used for the synthesis of Pt NPs. In this method, $0.25 \text{ mmol of } PtCl_4$ and dipropylamine ligand have been dissolved in tetrahydrofuran in an ultrasonic condition and then the mixture have been reduced by the assistance of ethanol and superhydride until the observation of black color. Lastly, VC has been mixed with the synthesized Pt NPs in a 1:1 ratio by the help of an ultrasonic tip sonicator.²⁴

In a double-necked round bottom flask (100 mL) equipped with a condenser was added a mixture consisting of nitrile (0.005 mol), NaN₃ (0.006 mol), and monodisperse Pt NPs@VC in DMF (1.5 mL). The mixture was heated at reflux until TLC monitoring indicated no further improvement in the conversion. The reaction mixture was then cooled to room temperature, vacuum-filtered using a sintered-glass funnel and the residue was washed with ethyl acetate (3 × 10 mL). The filtrate was treated with 5 mL HCl (4 mol L⁻¹) to reach pH = 3 and it was allowed to stir for 30 minutes. Subsequently, the organic layer was separated, dried over anhydrous Na₂SO₄ and evaporated. The crude product was purified by recrystallization and/or column chromatography on silica gel eluted with proper solvents to get pure 5-Phenyl 1H-tetrazole.

2.4. Characterization of 5-Substituted 1H-Tetrazoles

The disappearance of strong and sharp absorption –CN band, and the appearance of –NH bands in the 2500–3000 cm⁻¹, proved the formation of 5-substituted 1H-tetrazoles. Also the IR spectra of all the products show bands at 1515–1606 cm⁻¹ due to (N=N) and 1233–1293 cm⁻¹ due to (N–N=N–). Analyzing the ¹³C-NMR spectra of all the products, signals at 150–160 ppm is correspond to the quaternary carbon of tetrazole ring (NH–C==N). In addition, analyzing the HRMS spectra of

all the products observation of belonging to the proposed structure $[M-H]^-$ peak and then the loss of 28 units mass that resulted from the loss of N₂ from a tetrazole ring supports the tetrazole formation.

2.4.1. 5-Phenyl 1H-Tetrazole (a)

As a white powder, M.p.: 216–218 °C (lit. 215–216 °C),¹ FT–IR (cm⁻¹): 3053, 2979, 2906, 2833, 2682, 2601, 1607, 1561, 1285, 1254 ¹H NMR (300 MHz, DMSO-*d*₆): $\delta =$ 7.60 – 7.65 (m, 3H, Ar–H), 8.03–8.07 (m, 2H, Ar–H), 16.85 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): $\delta =$ 124.60, 127.40, 129.79, 131.62, 155.77 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₇H₅N₄: 145.0514; found [M–H]⁻: 145.0517.

2.4.2. 4-(1H-Tetrazol-5-yl)Pyridine (b)

As a white powder, M.p.: 255–257 °C (lit. 254–255 °C)¹, FT–IR (cm⁻¹): 3055, 2969, 2885, 2410, 1627, 1526, 1291, 1237, 1041, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 8.05$ (s, 2H, Ar–H), 8.90 (s, 2H, Ar–H), 15.60 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 121.60, 133.91$, 150.51, 155.64 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₆H₅N₅: 146.0467; found [M–H]⁻: 146.0468.

2.4.3. 5-(P-Tolyl) 1H-Tetrazole (c)

As a white powder, M.p.: 247–248 °C (lit. 248–249 °C)², FT–IR (cm⁻¹): 3044, 2979, 2916, 2846, 2767, 2679, 2608, 1612, 1569, 1285, 1256, 1162, 1085, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 2.40$ (s, 3H, –CH₃), 7.42 (d, J = 8.09 Hz, 2H, Ar–H), 7.93 (d, J = 8.17 Hz, 2H, Ar–H), 16.75 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 21.47$, 121.71, 127.34, 130.40, 141.69, 155.53 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₈H₇N₄: 159.0671; found [M–H]⁻: 159.0674.

2.4.4. N-(4-(1H-Tetrazol-5-yl)Phenyl)Acetamide (d)

As a white powder, M.p.: 285–287 °C (lit. 287 °C)³, FT–IR (cm⁻¹): 3264, 3132, 3078, 2325, 2201, 2151, 1600, 1544, 1322, 1290, 1263, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 2.07 (s, 3H, -CH₃), 7.58 (*d*, *J* = 8.21 Hz, 2H, Ar–H), 7.88 (*d*, *J* = 8.26 Hz, 2H, Ar–H), 9.95 (s, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 24.47, 119.40, 126.59, 127.91, 138.74, 155.92, 168.73 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₉H₈N₅O: 202.0729; found [M–H]⁻: 202.0732.

2.4.5. 5-(4-Nitrophenyl) 1H-Tetrazole (f)

As a grey powder, M.p.: 219–220 °C (lit. 219–221 °C)¹, FT–IR (cm⁻¹): 3078, 2913, 2845, 2770, 1605, 1551, 1291, 1222, ¹H NMR (300 MHz, DMSO- d_6): $\delta = 8.31$ (d, J =9.01 Hz, 2H, Ar–H), 8.46 (d, J = 9.00 Hz, 2H, Ar–H), 17.15 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO- d_6): $\delta =$ 125.03, 128.63, 131.10, 149.16, 155.92 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₇H₄N₅O₂: 190.0365; found [M–H]⁻: 190.0367.

2.4.6. 5-(4-Chlorophenyl) 1H-Tetrazole (h)

As a white powder, M.p.: 250–251 °C (lit. 250–252 °C)⁴, FT–IR (cm⁻¹): 3063, 2973, 2902, 2680, 2540, 1606, 1561, 1276, 1255, 1097, ¹H NMR (300 MHz, DMSO- d_6): $\delta =$ 7.70 (d, J = 8.56 Hz, 2H, Ar–H), 8.06 (d, J = 8.57 Hz, 2H, Ar–H), 16.95 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO- d_6): $\delta =$ 123.67, 129.18, 130.03, 136.37, 155.92 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₇H₄ClN₄: 179.0124; found [M–H]⁻: 179.0123.

2.4.7. 4-(1H-Tetrazol-5-yl)Benzaldehyde (i)

As a white powder, M.p.: 185–187 °C (lit. 183–185 °C)⁵, FT–IR (cm⁻¹): 3065, 2978, 2912, 2817, 2686, 2542, 1698, 1565, 1557, 1289, 1255, ¹H NMR (300 MHz, DMSO d_6): $\delta = 8.13$ (d, J = 8.42 Hz, 2H, Ar–H), 8.27 (d, J = 8.22 Hz, 2H, Ar–H), 10.10 (s, 1H, –CHO), 17.15 (br, 1H, –NH) ppm, ¹³C NMR (75 MHz, DMSO- d_6): $\delta = 128.07$, 130.00, 130.82, 138.07, 155.77, 193.13 ppm, HRMS (QTOF-ESI): m/z [M–H]⁻ calcd. for C₈H₆N₄O: 173.0463; found [M–H]⁻: 173.0465.

3. RESULTS AND DISCUSSION

Monodisperse Pt NPs@VC has been synthesized by using optimized sonochemical double solvent reduction protocol as given experimental section. Atomic force microscopy (AFM), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and high resolution electron microscopy (HRTEM) have been used for the characterization of monodisperse Pt NPs@VC.

As shown in Figure 1, Pt NPs@VC exhibit distinct diffraction patterns at $2\theta = 39.82$, 46.22, 67.62, 81.22 and 85.91 which are mainly due to Pt (111), (200), (220), (311), and (320), respectively, planes of the face-centered cubic (fcc) crystal lattice of platinum. The lattice parameter (α Pt) values and average crystallite of the Pt nanoparticles were calculated to be 3.908 Å²⁵ which is in good agreement with 3.923 Å and 3.75 ± 0.41 nm using the



Figure 1. XRD of catalyst monodisperse Pt NPs@VC.

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Figure 2. High resolution transition electron micrograph and particle size histogram of a Pt NPs@VC.

Schrerer equation²⁶ by the assistance of the Pt (220) pattern.

The HRTEM and particle size histogram of the Pt NPs@VC are shown in Figure 2 and it is observed that most of the Pt NPs are in spherical shape and have been distributed uniformly with a very narrow range and the average particle size was found to be 3.82 ± 0.39 nm which is in good agreement with the results from the XRD pattern. The representative atomic lattice fringes obtained by HRTEM have also been analysed and it was observed that Pt (111) spacing of 0.227 nm obtained for Pt NPs@VC is very close to the nominal Pt (111) spacing of 0.228 nm.^{27–29}

In order to reinforce the crystalline particle size obtained by XRD and average particle size found by TEM, AFM was utilized to analyse the height diameter distributions as shown in Figure 3. It was observed that the height values of Pt NPs@VC $(3.85 \pm 0.74 \text{ nm})$ are in good agreement with XRD and TEM results.

XPS has been used to analyse the chemical oxidation state of the Pt in monodisperse Pt NPs@VC as well as to evaluate the interaction between the Pt particles and Vulcan carbon supports. The fittings of all XPS peaks were performed by Gaussian-Lorentzian protocol and the relative intensities of the species were estimated by calculating the integral of each peak, after smoothing, subtraction of the Shirley-shaped background. The peaks at around 70.9 and 74.1 eV (71.75%)^{30, 31} show the zero oxidation state of Pt NPs. Moreover, the other Pt doublet (74.5 and 77.8 eV) as shown in Figure 4 is most probably arised from oxygenated species and/or unreduced Pt precursor.

It is well known that cycloaddition reaction between nitrile and azide is achieved very slow in the absence of a suitable catalyst and thus it is unsuitable for large scale



Figure 3. AFM image and particle height histogram of Pt NPs@VC.

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Figure 4. Pt 4f electron spectra of monodisperse Pt NPs@VC.

synthesis. In this context, the choice of an efficient catalyst is critically significance for the reaction progress. It is worth mentioning that Pt NPs are often used as a catalyst in super-capacitors, hydrogen storage, batteries, sensor, alcohol oxidation and dehydrogenation²⁴⁻³² but its use as a catalyst (Pt NPs@VC) for synthesizing 5-substituted 1H-tetrazoles from nitriles and sodium azide has not been reported before. By the assistance of monodisperse Pt NPs@VC as a heterogeneous catalyst, a new, facile, rapid and efficient procedure has been developed for the synthesis of tetrazole derivatives from different aromatic nitriles and sodium azide (Scheme 1).

In this line of work, we compared the results using Pt NPs@VC in the synthesis of target molecules with those obtained using other catalysts as shown in Table I. Pt NPs@VC are found to be the most efficient catalyst with the highest yield on model reactions. The prepared Pt NPs@VC have been also compared with PtCl₄ which is the precursor material of Pt NPs@VC. When PtCl₄ as a precatalyst and Pt NPs@VC as a catalyst have been used under the same conditions for the preparation of 5substituted 1H-tetrazoles, 72% and 94% yield have been observed, respectively (Table I) most probably due to the weakly coordinating chloride anion which cannot provide enough stabilization for the preparation of 5-substituted 1H-tetrazoles. However, the Pt NPs@VC are found to be very stable towards agglomeration over months by the assistance of dipropylamine and vulcan carbon which are one of the most powerful stabilizing and supporting agent, respectively.

Our model reaction has been standardized by various solvents, amount of catalyst and reaction conditions on the basis of different temperatures.



Scheme 1. Synthesis of 5-substituted 1H-tetrazoles (a-j).

Table I. Comparison of various heterogeneous nanocatalysts.

Entry	Catalyst	Time (h)	Temperature (°C)	TOF (h^{-1})	Yield (%)	Reference [In manuscript]
1	Nanocrystalline ZnO	14	120-130	0.11	72, 66 ^a	15a
2	Nano CSMIL	7	120	\sim	87	15b
3	ZnO nanoflakes	14	125	0.13	87	15c
4	CuFe ₂ O ₄ nanoparticles	12	120	0.17	82, 75 ^b	15d
5	Mesoporous ZnS	36	120	0.06	86	15e
6	CoY zeolite	14	120	2.64	90	15f
7	ZnO/Co ₃ O ₄	12	120-130	0.47	90, 84 ^c	15i
8	Graphene	36	120	\sim	63	15j
9	Graphene oxide/ZnO nanocomposites	30	120	0.14	78	15k
10	Pt NPs@rGO	0.5	75	64.14	96	16
11	$PtCl_4$	12	90	\sim	72	This work
12	Pt NPs@VC	0.7	90	44.86	94, 85 ^d	This work

Notes: ^aYield after third cycle, ^bYield after fifth cycle, ^cYield after fourth cycle, ^dYield after sixth cycle.

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Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	DMF	90	0.7	94
2	DMSO	120	2.5	85
3	Ethanol	80	10	42
4	Toluene	110	15	55
5	Dioxane	100	12	45
6	THF	70	16	37
7	ACN	85	14	35
8	Water	100	48	≤15

 Table II.
 Optimization of reaction conditions for the preparation of 5substituted 1H-tetrazoles

Table IV. The synthesis of 5-substituted 1H-tetrazoles with Pt NPs@VC^a.

For efficient progress of the model reaction, the choice and effect of an appropriate solvent is critically an important task. Among various solvents, DMF (dimethyl formamide), DMSO (dimethyl sulfoxide), ethanol, toluene, dioxane, THF (tetrahydrofuran), ACN (acetonitrile) and water have been used for model reaction as shown in Table II, entry 1–8. However, the corresponding tetrazole compounds were obtained only in poor yields (Table II, entry 3–8). Therefore, these solvents were determined not to be suitable for this model reaction. Even though the phenyl tetrazole was obtained in a moderate yield and a long reaction time in DMSO, the reaction in DMF was performed in a shortest reaction time with the best yield. Therefore, it can be thought that DMF is a superior solvent compared to the others.

Furthermore, the amount of catalyst is likewise another essential parameter in terms of reaction efficiency, the optimum amount of Pt NPs@VC is shown in Table III. As appeared in this table, without catalyst the phenyl tetrazole was acquired 0% yield in 25 °C (36 h), 9% yield in 50 °C and 13% yield in 90 °C (36 h). Expanding the catalyst to 1, 2, 3, 4 and 5 moles% brought about expanding the reaction yields to 74, 82, 94, 94 and 94% the reaction times changed from 0.4 to 36 hours. The phenyl tetrazole product was acquired in the model reaction in the presence of 3 moles% of Pt NPs@VC in DMF in one of the most outstanding yield (94 %) and shortest time (0.7 h). Utilization of only 3 moles% of Pt NPs@VC in DMF is sufficient to manage the efficient synthesis. As a summary, the optimum catalyst amount was determined to be 3 moles% of Pt NPs@VC (Table III, entry 6).



 Table III.
 Optimization of conditions for preparation of 5-substituted

 1H-tetrazoles using Pt NPs@VC as a catalyst in DMF.

Entry	1	2	3	4	5	6	7	8
Catalyst (mol%)	None	None	None	1	2	3	4	5
Time (h)	36	36	36	3.5	2.5	0.7	0.5	0.4
Temperature (°C)	r.t.	50	90	90	90	90	90	90
Yield (%)	-	9	13	74	82	94	94	94

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Entry	Product	Reaction time (h)	Yield $(\%)^b$	TOF TON ^c	$(h^{-1})^d$
a		0.7	94	31.40	44.86
b		0.5	98	32.74	65.48
с	H ₃ C-	4	90	30.07	7.52
d C		5	88	29.34	5.87
e		5	87	29.07	5.81
f v Inaen		1.5	91	30.34	20.23
on, 19 F Seientifi	Br	3.5	95	31.66	9.05
h	ci	3	97	32.34	10.78
i	онс-	2	92	30.66	15.33
j		2.5	89	29.67	11.87

Notes: ^{*a*}Reaction conditions: Benzonitrile (0.5 mmol), NaN₃ (0.6 mmol), Pt NPs@VC (3 mol%), DMF (1.5 mL), reaction time 0.7 h, temperature 90 °C. ^{*b*}Isolated yields. ^{*c*}TON = moles of product formed per mole catalyst. ^{*d*}TOF = TON/time (h) of the reaction.

As a summary, the highest efficiency and shortest reaction time on the model reaction was observed at 90 °C in the presence of 3 moles% of Pt NPs@VC in DMF. To understand the scope and effectiveness of the monodisperse Pt NPs@VC, different substituents of benzonitriles were selected and used in the determined conditions. 5-Substitue 1H-tetrazoles were obtained in a



shorter time with better yields than electron-withdrawing functional groups containing benzonitriles (Table IV, entries f–j) and heteroaromatic nitriles compound such as 4-pyridinecarbonitrile (Table IV, b) while benzonitriles containing electron-donating groups (Table IV, entry c–e) converted to tetrazoles in longer reaction times. The structures of all synthesized compounds were confirmed by melting points, FT-IR, ¹H-NMR, ¹³C-NMR and HRMS analyzes.

Finally, the recovery and reusability of the monodisperse Pt NPs@VC is also important factor from different aspects such as commercial applications and environmental concerns. Thus, the reusability of Pt NPs@VC was investigated for model reaction under optimized reaction condition (Table V). For this purpose, the isolation of the catalyst from the reaction media was carried out using a sintered glass funnel. The catalyst was then washed and dried in a vacuum oven at 90 °C for 20 min. The catalyst was successively reused for 6 runs with excellent yields without the addition of the fresh catalyst to the reaction mixture (Table V). As shown in Table V, the catalyst can be reused for many consecutive times without considerable decline of its catalytic activity. As a conclusion, the reusability performances of the prepared monodisperse Pt NPs@VC have been compared with the others reported in literature and it was found that to our Pt NPs@VC has one of the best reusability performances. It is obvious that the TOF value of monodisperse Pt NPs@VC (44.86 h⁻¹) is higher than the majority of those of other heterogeneous catalysts listed in Table I, except for the prior best heterogeneous $(64.14 h^{-1})^{16}$ catalysts. To determine the amount of leached Pt from catalyst, the Pt content of catalyst was determined using ICP analysis for both fresh and reused catalyst (after 6 runs). Based on the ICP results, the leached Pt was found to be 0.01% which is negligible.

4. CONCLUSIONS

In conclusion, an easy, effective and practical synthetic protocol have been described for the synthesis of a range of new structurally diverse 5-substituated-1H-tetrazoles using Vulcan carbon decorated platinum nanoparticles as the stable, exceptionally reusable, and highly efficient heterogeneous nanocatalyst. This nano sized heterogeneous catalyst was proved to be a useful catalyst for cycloaddition reaction of sodium azide with different nitriles at reflux condition which affords the corresponding tetrazole derivatives in good to excellent yields most likely due to high monodispersity, low crystalline particle size and high % Pt (0) contents of the prepared Pt NPs@VC. The TOF value of monodisperse Pt NPs@VC (44.86 h⁻¹) is higher than the majority of those of other heterogeneous catalysts. Besides, during the presence of dipropylamine and vulcan carbon, the Pt NPs@VC are found to be determined towards agglomeration over months. It shows that dipropylamine and vulcan carbon are powerful stabilizing and supporting agent for the Pt NPs@VC. Furthermore, the use of ecofriendly methodology, the reusability of the catalyst, the simplicity of the process, highest yield with shortest time, and applicability in preparative scale would be a rather attractive synthetic method in near future.

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