RSC Advances

A multicomponent reaction on 'free'KCC-1 catalystat room temperature under solvent free conditions by visible light

Journal:	*RSC Advances*
Manuscript ID	RA-ART-05-2016-011480.R1
Article Type:	Paper
Date Submitted by the Author:	27-May-2016
Complete List of Authors:	Sadeghzadeh, Seyed Mohsen; Department of Chemistry, College of Sciences, Sina Masihabadi Student Research,
Subject area & keyword:	Nanocatalysis - Catalysis < Catalysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A multicomponent reaction on 'free' KCC-1 catalystat room temperature under solvent free conditions by visible light

Seyed Mohsen Sadeghzadeh

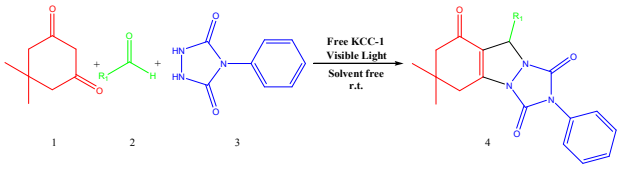
Received (in XXX, XXX) XthXXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A green and efficient method for the synthesis of various triazolo[1,2-*a*]indazole-trione under mildconditions is reported. The reported synthesis includes several advantages like solvent free, operational simplicity, short reaction times, environmentally benign reaction conditions, cost effectiveness, high atom economy, and excellent yields, making it a genuinely green protocol.

Introduction

Synthetic organic chemists pursuit towards new reactions and chemoselective transformations under mild and green conditions is a continuous process. Light, on the other hand, is considered an inexpensive, abundant, and environmentally benign form of energy and the last several years have witnessed a surge in studies exploiting visible light for activating chemical transformations.[1-8] Consequently, an increasing number of chemists are experimenting with visible light driven chemical synthesis as an economically and energetically beneficial, green route for construction of organic molecules.[9-11] The other side, reactions under solvent-free conditions usually need shorter reaction times, simpler reactors and result in simple and efficient work-up procedures. For these reasons, organocatalyzed processes under solvent-free conditions have become a highly pursued goal in green chemistry.[12-15] Green catalysis is a subchapter of green chemistry but probably the most important one. In most cases of organocatalyzed reactions a large amount of the organocatalyst (typically, 10–30 mol%) is needed, which presents a challenge for organic chemists to utilize organocatalysts moreefficiently and economically. In this context, and in view of the environmental and economical reasons, herein an ongoing effort to replace such classical method with a newer method using multicomponent reactions using a Nano catalyst is reported.[16] In general, Nano catalysts offer higher surface area and lower coordinating sites, which are responsible for the higher catalytic activity.[17] Furthermore, Nano catalysis has the advantage of high atom efficiency, easy product purification, and reusability of the catalyst.[18] Clearly, the development of 'free' nanoparticles with tunable catalytic activity is of great significance for both academia and industry.[19] Among the nanoparticle, SiO_2 has been a focus of extensive research due to its chemical stability, large surface area, non-toxicity, cheap, environmentally friendly and abundant. Nano-SiO_2 showed their potential in many fields, such as a catalyst or catalyst support. Fibrous nanosilica (KCC-1)[8] has a high surface area that is due to its fibrous morphology and not to pores, unlike the surface of nano-silica has pores without order. Therefore, most of its surface area is accessible, yielding unusually high activity in catalysis.[20-31] KCC-1 will have several advantages over conventional silica (Nano SiO_2), such as minimum reduction in surface area, and highaccessibility of active sites and hence excellent catalytic performance.

Consequently, in continuation of our ongoing program on the green synthesis of biologically important heterocycles,[32 and 33] we became interested in the development of a new multicomponent, solvent free strategy for the synthesis of triazolo[1,2-*a*]indazole-triones under the greenest conditions (Scheme 1).



Scheme 1 Synthesis of triazolo[1,2-*a*]indazole-triones from dimedone, benzaldehyde, and 4-phenylurazole in the presence of KCC-1.

Experimental

General Procedure for the Preparation of KCC-1 Nanoparticles

In this study, KCC-1was successfully synthesized by a traditional hydrothermalmethod. TEOS (2.5 g) was dissolved in a solution of cyclohexane (30 mL) and 1-pentanol (1.5 mL). A stirred solution of cetylpyridinium bromide (CPB 1 g) and urea (0.6 g) in water (30 mL) was then added. The resulting mixture was continually stirred for 45 min at room temperature and then placed in a teflon-sealed hydrothermal reactor and heated 120 °C for 5 h. The silica formed was isolated by centrifugation, washed with deionized water and acetone, and dried in a drying oven. This material was then calcined at 550 °C for 5 h in air.

General Procedure for the Synthesis of triazolo[1,2-a]indazole-triones

A mixture of dimedone (1 mmol), benzaldehyde (1 mmol), and 4-phenylurazole (1 mmol), and KCC-1 NPs (0.4 mol%) was stirred at room temperature under solvent-free condition under visible light irradiation using a 20 W CFL for the 2 h. Upon completion, the progress of the reaction was monitored by TLC when the reaction was completed, EtOH was added to the reaction mixture and the KCC-1 NPs was separated by filtration. Then the solvent

was removed from solution under reduced pressure and the resulting product purified by recrystallization using ethanol.

Selected spectral data

6,6-Dimethyl-2,9-diphenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.25 (6H, s, $2CH_3$), 2.40 (2H, s, CH_2), 2.95 (2H, AB system, $^2J_{HH}$ = 18.0 Hz, CH_2), 6.22 (1H, s, CH), 7.44-7.50 (10H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 27.9, 28.9, 34.9, 35.5, 51.3, 64.8, 120.3, 125.7, 127.2, 128.5, 128.8, 129.2, 130.8, 131.4, 136.7, 148.9, 150.4, 151.3, 191.8.

9-(4-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.19 (6H, s, $2CH_3$), 2.35 (2H, s, CH_2), 2.89 (2H, AB system, $^2J_{HH}$ = 18.7 Hz, CH_2), 6.19 (1H, s, CH), 7.40–7.51 (9H, m, H–Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.1, 28.9, 34.5, 35.3, 51.4, 63.4, 119.5, 125.8, 128.9, 128.6, 128.9, 129.5, 130.9, 134.7, 135.4, 149.3, 150.9, 151.5, 191.8.

9-(2-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.20 (6H, s, $2CH_3$), 2.34 (2H, AB system, $^2J_{HH}$ = 16.7 Hz, CH_2), 2.95 (2H, AB system, $^2J_{HH}$ = 18.3 Hz, CH_2), 6.32 (1H, s, CH), 7.30–7.44 (9H, m, H-Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.5, 29.2, 34.7, 35.5, 51.1, 63.8, 118.3, 125.9, 127.5, 128.6, 129.2, 130.5, 130.7, 130.8, 131.3, 132.0, 132.9, 148.5, 149.9, 150.8, 192.0.

6,6-Dimethyl-2-phenyl-9-p-tolyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.19 (6H, s, $2CH_3$), 2.35 (5H, s, CH_3 and CH_2), 2.90 (2H, s, CH_2), 6.20 (1H, s, CH), 7.20–7.45 (9H, m, H-Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 21.1, 28.5, 29.0, 34.7, 35.6, 51.5, 63.9, 120.2, 125.5, 126.9, 128.8, 129.4, 129.7, 131.0, 134.1, 138.7, 149.0, 150.3, 151.0, 191.9.

6,6-Dimethyl-9-(4-nitrophenyl)-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.22 (3H, s, $2CH_3$), 2.36 (2H, s, CH_2), 2.90 (2H, AB system, $^2J_{HH}$ = 18.7 Hz, CH_2), 6.28 (1H, s, CH), 7.48–8.30 (9H, m, H-Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.4, 28.9, 34.6, 35.8, 51.4, 63.5, 119.0, 124.3, 125.7, 128.4, 128.9, 129.5, 130.7, 144.0, 147.9, 149.3, 151.7, 192.0.

6,6-Dimethyl-9-(3-nitrophenyl)-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.20 (6H, s, $2CH_3$), 2.34 (2H, s, CH_2), 2.97 (2H, AB system, $^2J_{HH}$ = 18.3 Hz, CH_2), 6.31 (1H, s, CH), 7.47–8.29 (9H, m, H–Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.3, 28.6, 35.0, 35.6, 51.3, 63.1, 119.3, 121.9, 124.0, 125.7, 128.9, 129.5, 130.0, 130.6, 133.8, 139.3, 148.5, 149.3, 151.8, 192.2.

9-(4-Bromophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.19 (6H, s, $2CH_3$), 2.34 (2H, s, CH_2), 2.89 (2H, AB system, $^2J_{HH}$ = 19.6 Hz, CH_2), 6.18 (1H, s, CH), 7.35–7.51 (9H, m, H–Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.2, 28.8, 34.7, 35.4, 51.3, 63.5, 119.8, 123.0, 125.4, 128.9, 129.6, 130.5, 132.2, 136.0, 149.2, 151.0, 151.3, 192.0.

9-(3-Bromophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.20 (3H, s, CH_3), 1.22 (3H, s, CH_3), 2.35 (2H, AB system, $^2J_{HH}$ = 16.4 Hz, CH_2), 2.94 (2H, AB system, $^2J_{HH}$ = 19.7 Hz, CH_2), 6.19 (1H, s, CH), 7.26–7.60 (9H, m, H-Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.4, 28.7, 34.8, 35.6, 51.3, 63.5, 119.7, 123.0, 125.7, 126.2, 129.0, 129.3, 129.9, 130.5, 130.7, 132.0, 139.3, 149.2, 151.2, 151.4, 192.0.

4-(6,6-Dimethyl-1,3,8-trioxo-2-phenyl-1,2,3,5,6,7,8,9-octahydro-[1,2,4]triazolo[1,2-a]indazol-9-yl)benzonitrile
^{1}H NMR (500MHz, $CDCl_3$): δ (ppm) 1.19 (3H, s, CH_3), 1.22 (3H, s, CH_3), 2.34 (2H, AB system, $^2J_{HH}$ = 18.5 Hz, CH_2), 2.41 (2H, AB system, $^2J_{HH}$ = 18.5 Hz, CH_2), 2.89-3.01 (2H, m, CH_2), 6.24 (1H, s, CH), 7.47-7.69 (9H, m, H-Ar). ^{13}C NMR(125 MHz, $CDCl_3$): δ (ppm) 28.5, 28.9, 35.3, 36.0, 51.7, 64.1, 112.9, 118.6, 119.5, 126.0, 128.2, 129.4, 129.7, 131.0, 133.2, 142.5, 149.7, 151.9, 153.0, 192.4.

9-(3-Methoxyphenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.26 (6H, s, CH_3), 2.34 (2H, AB system, $^2J_{HH}$ = 16.5 Hz, CH_2), 2.94 (2H, AB system, $^2J_{HH}$ = 18.5 Hz, CH_2), 3.86 (3H, s, OCH_3), 6.19 (1H, s, CH), 6.90-7.49 (9H, m, H-Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.5, 29.1, 35.0, 35.7, 51.7, 53.3, 64.0, 111.6, 115.8, 116.7, 119.3, 120.6, 123.5, 124.0, 130.8, 130.6, 147.5, 157.3, 157.5, 159.3, 163.5, 196.5.

9-(4-Fluorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.20 (3H, s, CH_3), 1.23 (3H, s, CH_3), 2.34 (2H, AB system, $^2J_{HH}$ = 17.5 Hz, CH_2), 2.94 (2H, AB system, $^2J_{HH}$ = 19.5 Hz, CH_2), 6.20 (1H, s, CH), 7.44–7.60 (9H, m, H–Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 28.3, 28.7, 34.9, 35.6, 51.3, 63.5, 119.8, 123.0, 125.5, 125.9, 129.0, 129.3, 129.9, 130.4, 132.0, 139.2, 149.0, 151.2, 151.5, 192.0.

Results and discussion

First, we examined the effect of solvent on the synthesis of triazolo[1,2-*a*]indazole-trione using the 'free' KCC-1 NPs at heating under reflux. In this study, it was found that conventional heating under solvent-free conditions is more efficient than using organic solvents, with respect to reaction time and yield of the desired triazolo[1,2-*a*]indazole-trione (Table 1). We also investigated the crucial role of temperature in the synthesis of triazolo[1,2-*a*]indazole-trione in the presence of 'free' KCC-1 NPs as a catalyst. Clearly indicated that the catalytic activity is not sensitive to reaction temperature. Due to the high efficiency of the catalysts, the reaction activation energy minimizing and the reaction is carried out at room temperature. Temperatures greater than room temperature does not cause changes in the efficiency of the reaction.

Table 1 Synthesis of triazolo[1,2-*a*]indazole-trione by KCC-1 NPs in different solvents.[a]

Entry	Solvent	Yield (%)[b]
1	EtOH	74
2	H_2O	81
3	CH_3CN	-
4	THF	38

5	CH_2Cl_2	31
6	EtOAc	42
7	DMF	60
8	Toluene	58
9	*n*-Hexane	-
10	$CHCl_3$	42
11	DMSO	88
12	MeOH	59
13	Dioxane	-
14	solvent-free	98

[a]Reaction conditions: dimedone (1mmol), benzaldehyde (1mmol), 4-phenylurazole (1mmol), and KCC-1 (1 mol%) under visible light irradiation using a 32W CFL.
[b] Isolated yields.

We also investigated the crucial role of time in the synthesis of triazolo[1,2-*a*]indazole-trione in the presence of KCC-1 NPs as a catalyst. Results clearly indicated that the catalytic activity is sensitive to reaction time. The best time for this reaction was 2 h. Time more than 2 h does not cause changes in the efficiency of the reaction (Figure 1). Then the reaction progress in the presence of KCC-1 NPs was monitored by GC. In the next step , the amount of catalyst necessary to promote the reaction efficiently was examined. It was observed that the variation for KCC-1 had an effective influence. The best amount of KCC-1 is 0.4 mol% per 1 mmol of reactants which afforded the desired product in 98% yields (Figure 2).

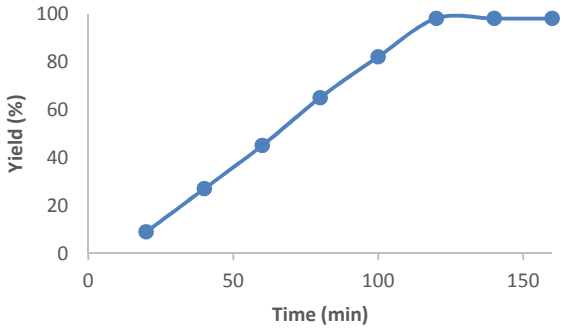


Figure 1 Effect of time on yield of triazolo[1,2-*a*]indazole-trione: dimedone (1mmol), benzaldehyde (1mmol), 4-phenylurazole (1mmol), and KCC-1 (1 mol%) under visible light irradiation using a 32W CFLat room temperature under solvent-free conditions.

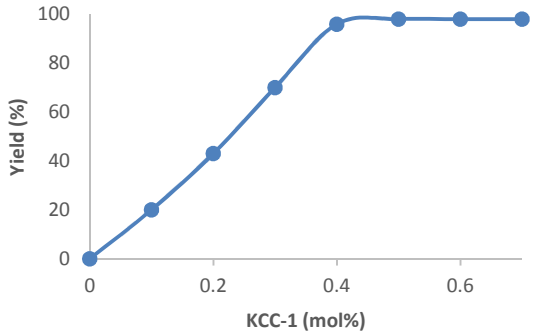


Figure 2 Optimization of the conditions for synthesis of triazolo[1,2-*a*]indazole-trione: dimedone (1mmol), benzaldehyde (1mmol), 4-phenylurazole (1mmol) under visible light irradiation using a 32W CFL at room temperature under solvent-free conditions for 2 h.

We now carried out a series of experiments using light of different intensities in order to identify the optimal intensity of visible light needed for this reaction. The activity was almost noting when 'free' KCC-1 was used as a catalyst without the visible light radiation (Table 2, entries 1). It was observed that the yield was the same when 20W CFL was used. However, when CFL's of lower intensities were used, a marginal decrease in yield and rate of reaction was observed (Table 2, entries 2 and 3). Use of a CFL of higher wattage (22 and 32W) on the other hand did not have any appreciable effect on yield or reaction time.

Table 2 Effect of visible light intensity on course of the reaction.[a]

Entry	Visible Light Intensity (W)	Yield (%)[b]
1	-	-
2	8	70
3	15	89
4	20	98
5	22	98
6	32	98

[a]Reaction conditions: dimedone (1mmol), benzaldehyde (1mmol), 4-phenylurazole (1mmol), and KCC-1 (0.4 mol%) under visible light irradiation at room temperature under solvent-free conditions for 2 h.
[b]Isolated yields.

The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology. To check this, we looked at nano-SiO_2, MCM-41, SBA-15, and KCC-1, which have the same compositions and different structures. When nano-SiO_2, MCM-41 or SBA-15 was used as the catalyst, the yield of the desired product was fair to good, but the yield for KCC-1 was excellent. Non-negligible activity of the silica was attributed to its shape, composition and morphology. Besides, the large space between fibers can significantly increase the accessibility of the active sites of the KCC-1. That is why, the KCC-1 was more effective than nano-SiO_2, MCM-41, and SBA-15 (Table 3, entries 2-4). As a result, KCC-1 NPs were used in the subsequent investigations because of its high reactivity, high selectivity and easy separation(Table 3).

Table 3 Influence of different catalysts for the synthesis of triazolo[1,2-*a*]indazole-trione.[a]

Entry	Catalyst	Yield (%)[b]
1	KCC-1	98
2	Nano-SiO_2	71
3	MCM-41	89
4	SBA-15	83

[a]Reaction condition: dimedone (1mmol), benzaldehyde (1mmol), 4-phenylurazole (1mmol), and catalyst (0.4 mol%) under visible light irradiation using a 20W CFL at room temperature under solvent-free conditions for 2 h.
[b]Isolated yield.

After optimization of the reaction conditions, this methodology was evaluated by using variety of different substituted aromatic aldehydes in the presence of KCC-1 under similar conditions. Aromatic aldehydes, carrying either electron-withdrawing or electron-donating substituents, afforded high yields of products with high purity, the results are presented in table 4. As can be seen from table 4, electronic effects and the nature of substituents on the aromatic ring did not show strongly obvious effects in terms of yields under the reaction conditions. The three-component cyclocondensation reaction proceeded smoothly and was completed in 2 h.

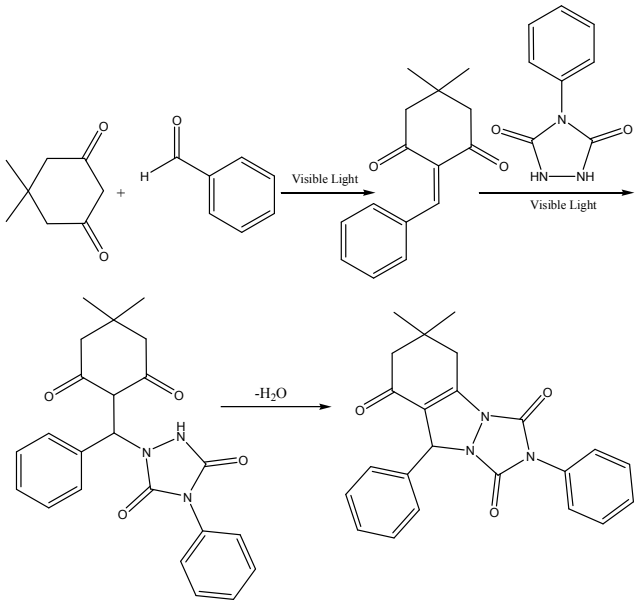
Table 4 Synthesis of triazolo[1,2-*a*]indazole-triones from various aromatic aldehydes, dimedone, and 4-phenylurazole in the presence of

KCC-1 under visible light irradiation using a 20W CFL at room temperature under solvent-free conditions.

Entry	R	Product	Yield (%)[a]	mp (°C)
1	C_6H_5	4a	98	191-193 [34]
2	4-ClC_6H_4	4b	96	170-172 [34]
3	2-ClC_6H_4	4c	95	174-176 [34]
4	4-$CH_3C_6H_4$	4d	96	163-165 [34]
5	4-$O_2NC_6H_4$	4e	96	178-180 [34]
6	3-$O_2NC_6H_4$	4f	93	129-132 [35]
7	4-BrC_6H_4	4g	97	183-186 [34]
8	3-BrC_6H_4	4h	94	173-175 [35]
9	4-NCC_6H_4	4i	95	243-245 [35]
10	3-$CH_3OC_6H_4$	4j	96	103-105 [35]
11	4-FC_6H_4	4k	97	102-105 [35]

[a]Yield refers to isolated product.

In light of the experimental observations and literature reports [36-38] we have proposed a plausible mechanistic pathway for the reaction as depicted in Scheme 2. The formation of triazolo[1,2-*a*]indazole-trione can be rationalized by initial formation of heterodiene by standard Knoevenagel condensation of dimedone and aldehyde . Subsequent Michael-type addition of urazole to heterodyne followed by cyclization afforded the corresponding triazolo[1,2-*a*]indazole-trione. The first step appears to be proceeding through mechanochemical activation although visible light may be imparting it additional energy, speeding up the reaction. Analysis of these results revealed that heterodyne is very much reactive towards the subsequent reaction under multicomponent reaction condition in the presence of visible light and hence could not be detected and evaluated. In the second step photochemical activation seems to have a definite role.



Scheme 2 Plausible Mechanism.

It is important to note that the heterogeneous property of 'free' KCC-1 NPs facilitates its efficient recovery from the reaction mixture during work-up procedure. The activity of the recycled catalyst was also examined under the optimized conditions. After the completion of reaction, the catalyst was separated by filtration, washed with methanol and dried at the pump. The recovered catalyst was reused for eight consecutive cycles without any significant loss in catalytic activity (Figure 3). This lack of reduction in catalyst performance can be attributed to the simple and stability of the catalyst structure. Because no second compound on its surface that by reusing it leaching into the reaction mixture. Comparison of TEM images of used catalyst (Figure 4b) with those of the fresh catalyst (Figure 4a) showed that the morphology and structure of KCC-1NPs remained intact after eight recoveries. Agglomeration of KCC-1NPs can not be seen.

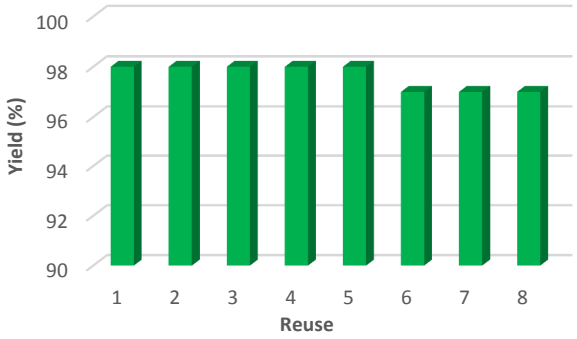


Figure 3 Reuses performance of the catalysts.

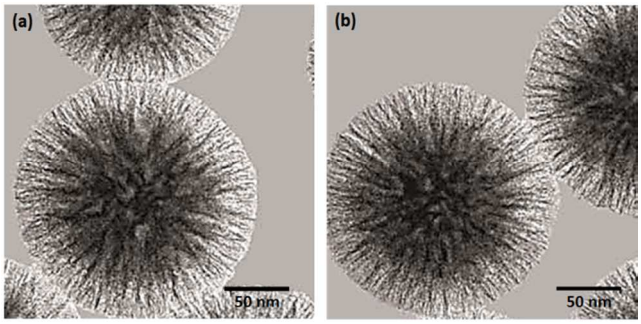


Figure 4 TEM image of KCC-1(a), and KCC-1 NPs after eight runs (d).

Conclusions

In summary, we have developed a simple, yet highly efficient, visible light activated and 'free' KCC-1, green synthetic strategy to obtain highly functionalized triazolo[1,2-*a*]indazole-triones through a one pot, multicomponent reaction. These compound of visible light and KCC-1 provides a simple and direct way to access derivatives of the biologically important heterocycles. These reaction conditions display a wide range of functional group tolerance. Froman environmental point of view, this protocol represents good atom economy, i.e., the expended KCC-1 NPs can be recycled and reused to mediate this reaction. They should be helpful to understand the advantageous combination of the properties of homogeneous and heterogeneous catalysis and the development of simple catalytic systems.

Notes and references

Department of Chemistry, College of Sciences, SinaMasihabadi Student Research, P.O. Box 97175-615, Neishabour, Iran. Fax/Tel: +98 561 2502065; E-mail: seyedmohsen_sadeghzadeh@yahoo.com

1 J. Tiwari, M. Saquib, S. Singh, F. Tufail, M. Singh, J. Singh, J. Singh, *Green Chem.*, 2016, DOI: 10.1039/C5GC02855H, Communication.
2 T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.*, 2010, **2**,527–532.
3 J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.*, 2010, **40**, 102–113.

4 J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 1617–1622.

5 J. Xuan, W.J. Xiao, *Angew. Chem., Int. Ed.*, 2012,**51**, 6828–6838.

6 D. P. Hari, B. Ko¨nig, *Angew. Chem., Int. Ed.*, 2013, **52**, 4734–4743.

7 C. K. Prier, D. A. Rankic, D. W. C. MacMillan,*Chem. Rev.*, 2013, **113**, 5322–5363.

8 D. M. Schultz, T. P. Yoon, *Science*, 2014, **343**, 1239176.

9 M.Y. Cao, X. Ren, Z. Lu, *Tetrahedron Lett.,* 2015, **56**, 3732-3742.

10 I. Ghosh, T.Ghosh, J. I. Bardagi, B. Knig, *Science,* 2014, **346**, 725-728.

11 S. Ghosh, F. Saikh, J. Das, A.K. Pramanik, *Tetrahedron Lett.,* 2013, **54**, 58-62.

12 P. T. Anastas, J. C. Warner, Green Chemistry, Theory and Practice, Oxford University Press, Oxford, 1998.

13 K. Tanaka, Solvent-free Organic Syntesis, WileyVCH, Weinheim, 2003.

14 Special issue on green chemistry: *Chem. Rev.* 2007, **107**, 2167–2820.

15 B. Rodrguez, A. Bruckmann, T. Rantanen, C. Bolm, *Adv. Synth. Catal.* 2007, **349**, 2213–2233.

16 G. Pacchioni, Surf. *Rev. Lett.* 2000, **7**, 277-306.

17 A. Kalor, D. Cox, M. R. Zakin,*Adv. Chem. Phys.* 1988, **70**, 211.

18 M. Hosseini-Sarvari, *Catal. Lett.* 2011, **141**, 347-355.

19 N. Koukabi, E. Kolvari, A. Khazaei, M.A. Zolfigol, B.Shirmardi-Shaghasemi,H.R. Khavasi,*Chem. Commun.* 2011, **47**, 9230-9232.

20 V. Polshettiwar, D. Cha, X. Zhang, J. M. Basset, *Angew. Chem., Int. Ed.* 2010, **49**, 9652−9656.

21 A. S. Lilly Thankamony, C. Lion, F. Pourpoint, B. Singh, A. J. Perez Linde, D. Carnevale, G. Bodenhausen, H. Vezin, O. Lafon, V.Polshettiwar, *Angew. Chem., Int. Ed.* 2015, **54**, 2190−2193.

22 M. Bouhrara, C. Ranga, A. Fihri, R. R. Shaikh, P. Sarawade, A. H. Emwas, M. N. Hedhili, V.Polshettiwar, *ACS Sustainable Chem. Eng.* 2013, **1**, 1192−1199.

23 M. Dhiman, B. Chalke, V. Polshettiwar, *ACS Sustainable Chem. Eng.* 2015, **3**, 3224−3230.

24 A. Fihri, M. Bouhrara, D. Cha, N. Almana, V.Polshettiwar, *ChemSusChem* 2012, **5**, 85−89.

25 A. Fihri, M. Bouhrara, U. Patil, D. Cha, Y. Saih, V.Polshettiwar, *ACS Catal.* 2012, **2**, 1425−1431.

26 V. Polshettiwar, J. Thivolle-Cazat, M. Taoufik, F. Stoffelbach, S. Norsic, J. M. Basset, *Angew. Chem., Int. Ed.* 2011, **50**, 2747−2751.

27 X. Le,Z. Dong, Y. Liu, Z. Jin, T. D. Huy, M, Leb, J. Ma, *J. Mater. Chem. A*, 2014, **2**, 19696-19706.

28 X. Le, Z. Dong, X. Li, W. Zhang, M. Le, J. Ma, *Catalysis Communications* 2015, **59**, 21–25.

29 H. Yang, S. Li, X. Zhang, X. Wang, J. Ma, *J. Mater. Chem. A*, 2014, **2**, 12060–12067.

30 R. Singh, R. Bapat, L. Qin, H. Feng, V. Polshettiwar, *ACS Catal.* 2016, **6**, 2770−2784.

31 Z. Sun, H. Li, D. Guo, J. Sun, G. Cui, Y. Liu, Y. Tian, S. Yan, *J. Mater. Chem. C*, 2015, **3**, 4713-4722.

32 K.C. Joshi, P. Chand, *Pharmazie* 1982, **37**, 1-12.

33 D.R. Chandam, A.G. Mulik, P.P. Patil, S.D. Jagdale, D.R. Patil, M.B. Deshmukh, *Research on Chemical Intermediates,* 2015, **41**, 761-771.

34 A. Bazgir, M. Seyyedhamzeh, Z. Yasaei, P. Mirzaei, *Tetrahedron Lett.* 2007, **48**, 8790-8794.

35 A. Hasaninejad, A. Zare, M. Shekouhy, *Tetrahedron* 2011, **67**, 390-400.

36 S. Ghosh, F. Saikh, J. Das, A.K. Pramanik, *Tetrahedron Lett*., 2013, **54**, 58-62.

37 P.P. Ghosh, S. Paul, A.R. Das, *Tetrahedron Lett*., 2013, **54**, 138–142.

38 Ji-B. Xia, C. Zhu, C. Chen, *J. Am. Chem. Soc*., 2013, **135**, 17494−17500.

Graphical Abstract

A multicomponent reaction on 'free' KCC-1 catalyst at room temperature under solvent free conditions by visible light

A green and efficient method for the synthesis of various triazolo[1,2-*a*]indazoletrione under mild conditions is reported, that includes several advantages like solvent free, operational simplicity, simple catalyst, short reaction times, environmentally benign reaction conditions, cost effectiveness, high atom economy, and excellent yields, making it a genuinely green protocol.