



Original Research Article

Nano particles graphene oxid: A green and effective catalyst for synthesis of pyrazoles

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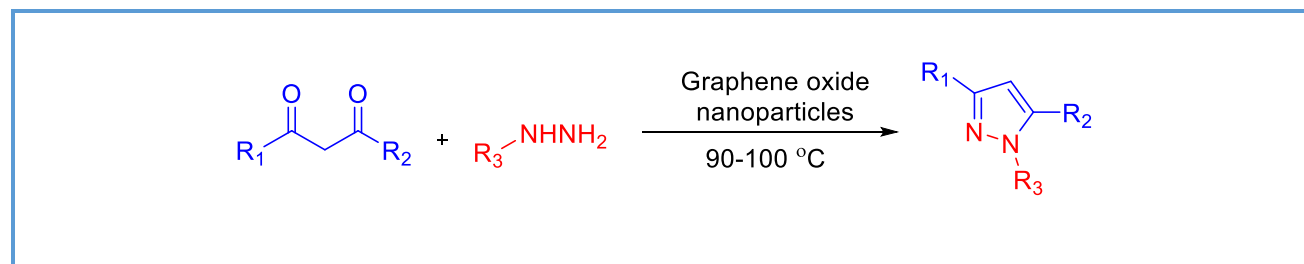
One-Pot Reaction
 Nano graphene oxide
 Pyrazoles
 Green Chemistry

ABSTRACT

In this work, a green and effective method for the synthesis of pyrazole derivatives by the reaction of a pot of various 1,3-dicarbonyl compounds with hydrazine is proposed using graphene oxide nanoparticles as the Lewis base catalyst. Advantages this methods are high yields, perform quick reactions, easy customization, and short-term reaction. The catalyst was recycled several times. The recycled catalyst was reused without any apparent performance drop in subsequent reactions. This process provided not only self-condensation but also cross-condensation by using the hydra-friendly nuclear reaction of hydrazines and high-efficiency, multisubstituted pyrazoles were formed under good and easy conditions.

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Graphical Abstract



Introduction

Pyrazoles are biologically important heterocyclic compounds and are used in major drugs such as Viagra, Lexiscan, Xalkori and Celebrex [1], and ligands for metal catalysts [2]. These are being utilized in dyes [3] medicinally relevant compounds [4, 5], and ligands for metal catalysts [6]. The widespread use of pyrazoles has led to the main artificial candidates, and as a result, newer synthetic pathways have been developed to manipulate the scaffold of pyrazoles derivatives.

In recent years, many methods have been reported for the synthesis of pyrazoles derivatives; however, most of these methods are reactions between 1,3 diketones with hydrazine derivatives [7–9]. The methods without the need for 1 and 3 diketones have been reported for the synthesis of pyrazoles [10–13].

In recent years, pyrazole has been synthesized from the reaction between 1,3-diketones and hydrazine with sophisticated catalyst [14], PSSA [15], saponites [16], $K_2CO_3/[Cp^*IrCl_2]_2$ [17], $Zn[(L)proline]_2$ [18], $Al_2O_3/montmorillonite$ [19], $H_3PW_{12}O_{40}$ [20], Zirconium sulfophenylphosphonate [21], CsF- Al_2O_3 & KOH- Al_2O_3 [22], CsF-Celite [23] and KF- Al_2O_3 [24]. However, these methods suffer from some drawbacks including, low productivity, difficult reaction conditions, expensive catalysts, and long reaction times.

Multicomponent reactions (MCRs) are convergent reactions, in which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product. In MCR, the product is assembled according to the cascade of primary chemical reactions and is widely utilized in the synthesis of organic compounds [25–27].

Nanoparticles have emerged as sustainable alternatives to conventional materials, as

robust, high surface area heterogeneous catalysts and catalyst supports. 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. Recently, for the above reasons, the use of heterogeneous green and nano-catalysts has increased [28–30].

Today, the use of nano particles of Lewis bases and Lewis acids in the synthesis of organic compounds has been considered [31–35]. In this research study we investigated the new method for synthesis of pyrazoles derivatives in the presence of nano particles graphene oxide, as the catalyst at different temperature and solvent. This nano particle is efficient and versatile catalyst which reduces by-products for the synthesis of pyrazoles derivatives. Graphene oxide act as base Lewis.

Experimental

Materials and methods

All the chemicals were purchased from commercial suppliers and were used as received. All products were identified by their spectra and physical data. Melting points were measured using the capillary tube method with an electro thermal 9100 apparatus. The IR spectra were recorded on a Shimadzu spectrometer 883 (KBr pellets, Nujol mulls, $4000-400\text{ cm}^{-1}$). 1H NMR spectra were recorded on a Bruker-Avance DRX 400 spectrometer using TMS as an external standard, UV-Vis absorption spectra were recorded on Optizen 2120 UV-PC spectrophotometer. SEM image was taken with a scanning electron microscopy model Phenom pro X made in Netherlands.

Synthesis of graphene oxide nanoparticles

GO was prepared using a modified Hummer's method [36]. Briefly, 23 mL of 98% H₂SO₄ and 100 mg of NaNO₃ were added to 1 g of graphite, followed by stirring at room temperature over a 24 h period. Subsequently, the mixture was kept below 5 °C by ice bath, and 3 g of KMnO₄ was slowly added into the mixture. After being heated to 35–40 °C, the mixture was stirred for another 30 min. Then 10 mL of 30% H₂O₂ was added into the mixture to stop the reaction. Finally, the unexploited graphite in the resulting mixture was removed by centrifugation.

Synthesis of pyrazoles derivatives

A mixture of phenyl hydrazines (1 mmol), 1,3-diketone (1 mmol) and graphene oxide nanoparticles catalysts (0.045 gr) was stirred at 900-1000 °C temperature for 2 h (Scheme 1). The possible mechanism of the reaction is shown in Scheme 2. The progress of the reaction was monitored using TLC paper (ethyl acetate/n-hexane 1:3). After the reaction was complete, the mixture was dissolved in ethanol, filtered, and washed with 5 mL of acetone to separate the catalyst. The solvent was evaporated at ambient temperature to give a pure product (Entry 1-12).

Selected spectroscopic data

1,3,5-triphenyl-1H-pyrazole (entry 1)

FT-IR: ν_{\max} (KBr)=1597(C=N, C=C), 1492(C=C), 767(CH bend), 689(CH bend)cm⁻¹. ¹HNMR (400MHz, CDCl₃), 6.84(s, 1H), 7.27-7.47 (m, 15H), ¹³CNMR (100 MHz, CDCl₃), 105.6, 125.7, 126.3, 127.8, 128.4, 128.7, 128.9, 129.1, 129.2, 129.3, 131.0, 133.5, 140.6, 144.8, 152.4 ppm.

1-(2,4-dinitrophenyl)-3-5 diphenyl-1H-pyrazole (entry 2)

FT-IR: ν_{\max} (KBr)=1607(C=N, C=C, Stretch), 1458(C=C Stretch), 763(CH bend), 690(CH bend) cm⁻¹. ¹HNMR (400MHz, CDCl₃), 6.92(s, 1H), 7.41(m, 9H), 7.89, 8.37, 8.75(1H), ppm. ¹³CNMR (100 MHz, CDCl₃), 107.1, 126.4, 127.4, 129.1, 129.2, 129.3, 129.5, 129.9, 130.0, 132.2, 138.5, 146.3, 146.4, 155.1 ppm

1-(4-Boromophenyl)-3,5-diphenyl-1H-pyrazole (entry 3)

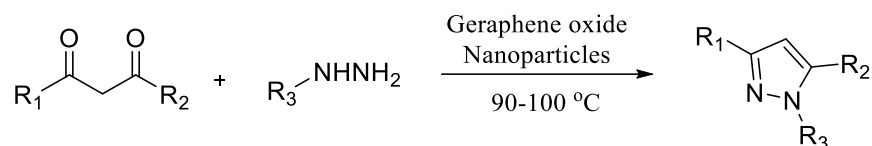
FT-IR: ν_{\max} (ATR, neat) = 1601(C=N, C=C stretch), 465(C=C Stretch), 754(CH bend), 690(CH bend) cm⁻¹. ¹HNMR (400MHz, CDCl₃), 6.93(s, 1H), 7.30-7.60(m, 12H), 7.89(d, 2H), ppm. ¹³CNMR (100 MHz, CDCl₃), 104.5, 123.5, 125.2, 127.5, 128.1, 128.6, 128.8, 129.2, 129.3, 129.4, 131.0, 132.5, 139.9, 143.8, 151.3 ppm

1-(2-chlorophenyl)-3,5-diphenyl-1H-pyrazole (entry 4)

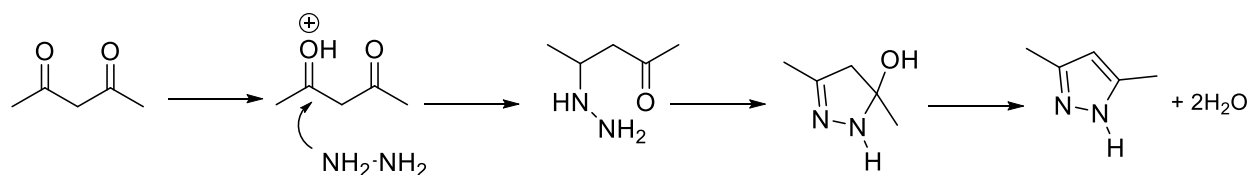
FT-IR: ν_{\max} (ATR, neat) = 1544(C=N, C=C stretch), 488(C=C Stretch), 757(CH bend), 690(CH bend) cm⁻¹. ¹HNMR (400MHz, CDCl₃), 6.90(s, 1H), 7.29-7.55(m, 12H), 7.94(d, 2H), ppm. ¹³CNMR (100 MHz, CDCl₃), 105.6, 125.7, 126.3, 127.8, 128.4, 128.7, 128.9, 129.1, 129.2, 129.3, 131.0, 133.5, 140.6, 144.8, 152.4 ppm

1-(2,4-dinitrophenyl)-3-phenyl-5-methyl-1H pyrazole (entry 5)

FT-IR: ν_{\max} (KBr)=1608(C=C , Stretch), 1537(C=N Stretch), 1505(C=C Stretch), 765(CH bend), 699(CH bend) cm⁻¹. ¹HNMR (400MHz, CDCl₃), 2.38(s, 3H), 6.41(s, 1H), 7.22(2H), 7.27-7.39(m, 3H), 7.44 , 8.60 ppm, ¹³CNMR (100 MHz, CDCl₃), 14.0, 109.8, 121.3, 127.5, 128.9, 129.1, 129.2, 129.5, 129.6, 130.1, 138.7, 145.7, 146.2, 152.1 ppm.



Scheme 1. Synthesis of pyrazoles with graphene oxide nanoparticles



Scheme 2. The possible mechanism of the reaction synthesis of pyrazoles

1-(4-Boromophenyl)-3-phenyl-5-methyl-1H-pyrazole (entry 6)

FT-IR: ν_{\max} (ATR, neat) = 1601(C=N, C=C stretch), 465(C=C Stretch), 754(CH bend), 690(CH bend) cm^{-1} . ^1H NMR (400MHz, CDCl_3), 2.25(s, 3H), 6.93(s, 1H), 7.30-7.60(m, 12H), 7.89(d, 2H), ppm. ^{13}C -NMR (100 MHz, CDCl_3), 104.5, 123.5, 125.2, 127.5, 128.1, 128.6, 128.8, 129.2, 129.3, 129.4, 131.0, 132.5, 139.9, 143.8, 151.3 ppm.

1-(2-chlorophenyl)-3phenyl-5-methyl-1H-pyrazole (entry 7)

FT-IR: ν_{\max} (ATR, neat) = 1544(C=N, C=C stretch), 488(C=C Stretch), 757(CH bend), 690(CH bend) cm^{-1} . ^1H NMR (400MHz, CDCl_3), 2.25(s, 3H), 6.89(s, 1H), 7.33-7.95(m, 12H), 7.94(d, 2H), ppm. ^{13}C NMR (100 MHz, CDCl_3), 104.2, 125.1, 125.9, 126.8, 127.3, 128.4, 128.9, 129.2, 129.3, 129.6, 131.1, 132.4, 140.3, 143.6, 151.8 ppm.

1-phenyl-5-phenyl-3-methyl-1H-pyrazole (entry 8)

FT-IR: ν_{\max} (KBr)=1595 (C=C, C=N Stretch), 1502 (C=C Stretch), 3050 (CH bend aromatic), 2915(CH bend aliphatic) cm^{-1} , ^1H NMR (400MHz, CDCl_3), 2.40(s, 3H), 6.33(s, 1H), 7.23-

7.41 (m, 10H) ppm, ^{13}C NMR (100 MHz, CDCl_3), 13.0, 14.0, 104.8, 108.2, 125.1, 125.4, 125.6, 126.2, 127.4, 127.5, 128.0, 128.2, 128.5, 128.8, 129.0, 129.1, 129.3, 129.5, 131.1, 131.2, 140.6, 144.1, 149.8 ppm.

1-(2,4-dinitrophenyl)-3-5 dimethyl-1H-pyrazole (entry 9)

FT-IR: ν_{\max} (KBr) =1612(C=C, C=N, Stretch), 1531(C=C Stretch), 793(CH bend), cm^{-1} , ^1H NMR (400MHz, CDCl_3), 2.25(s, 3H), 2.28(s, 3H), 7.71(d, 1H), 8.53(1H), 8.63(d, 1H), ppm, ^{13}C NMR (100 MHz, CDCl_3), 12.0, 13.1, 109.3, 121.4, 127.6, 129.8, 138.4, 141.2, 146.6, 152.7 ppm.

1-(4-boromophenyl)-3-5 dimethyl-1H-pyrazole (entry 10)

FT-IR: ν_{\max} (KBr) =1563(C=C, C=N, Stretch), 1585(C=C Stretch), 779(CH bend), cm^{-1} , ^1H NMR (400MHz, CDCl_3), 2.03(s, 3H), 2.17(s, 3H), 7.71(d, 1H), 8.53(1H), 8.81(d, 1H), ppm, ^{13}C -NMR (100 MHz, CDCl_3), 12.1, 13.3, 108.3, 120.5, 126.8, 127.9, 136.3, 140.2, 145.9, 151.8 ppm.

1-(2-chlorophenyl)-3-5 dimethyl-1H-pyrazole (entry 11)

FT-IR: ν_{max} (KBr) = 1548 (C=C, C=N, Stretch), 1572 (C=C Stretch), 780 (CH bend), cm^{-1} , $^1\text{H NMR}$ (400 MHz, CDCl_3), 2.21 (s, 3H), 2.32 (s, 3H), 7.79 (d, 1H), 8.03 (1H), 8.13 (d, 1H), ppm, $^{13}\text{C NMR}$ (100 MHz, CDCl_3), 12.13, 12.31, 109.3, 121.4, 125.9, 128.6, 133.3, 141.2, 143.9, 152.7 ppm.

1-phenyl-3-5 dimethyl-1H-pyrazole (entry 12)

FT-IR: ν_{max} (KBr) = 1623 (C=C, C=N, Stretch), 1592 (C=C Stretch), 782 (CH bend), cm^{-1} , $^1\text{H NMR}$ (400 MHz, CDCl_3), 2.06 (s, 3H), 2.11 (s, 3H), 7.80 (d, 1H), 7.95 (1H), 8.23 (d, 1H), ppm, $^{13}\text{C NMR}$ (100 MHz, CDCl_3), 12.31, 13.14, 108.1, 112.4, 124.8, 127.5, 129.9, 142.3, 143.3, 154.1 ppm.

Results and Discussion

The results of the synthesis of pyrazoles using 1,3-dicarbonyl compounds with hydrazines and graphene oxide catalysts are shown in [Table 1](#).

The reaction of Model 2,4 Dinitro phenyl hydrazine with 1,3-diphenyl-1,3-propanedione ([Scheme 3](#)) was performed in the presence of different catalysts and solvents at different temperatures. The results showed that nano graphene oxide at 90 °C in ethanol promoted the reaction more effectively than other catalysts ([Table 2](#)).

In a systematic study ([Table 2](#)), 2,4 Dinitro Phenyl hydrazine was added to 1,3-diphenyl-1,3-propanedione solution and various amounts of catalyst in ethanol and the reaction mixture was stirred at 90 °C. One reaction was stirred using 0.224 gr of 1,3-diphenyl-1,3-propanedione and 0.198 gr of 2,4-dinitrophenylhydrazine, without the presence of a catalyst at 90 °C. Even after 24 hours, the expected product was not obtained.

To further improve the yield and to optimize the reaction conditions, the same reaction was carried out in the presence of (0.04 gr) of

catalyst under similar conditions. A significant improvement was observed and the yield of product was dramatically increased up to 98% after stirring the mixture for only 2 h.

To minimize the formation of by-products and achieve good performance of the desired product, the reaction was performed by changing the amount of nano graphene oxide catalyst. From 0.004 to 0.04 gr, the yield of the desired product increased to 95% ([Table 2](#), entry 8). Therefore, it was found that the use of 0.04 gr of catalyst is sufficient to enhance the reaction and higher amounts of catalyst do not improve performance.

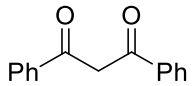
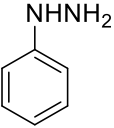
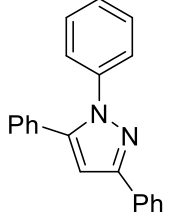
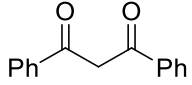
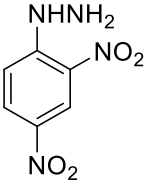
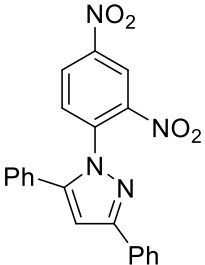
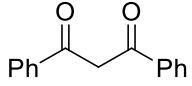
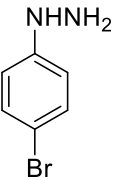
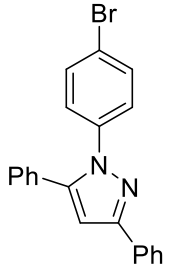
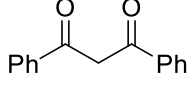
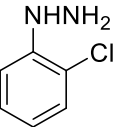
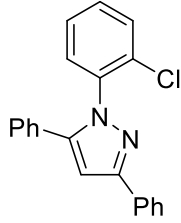
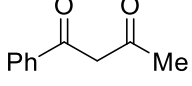
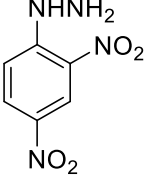
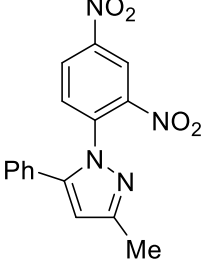
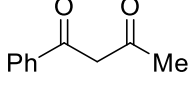
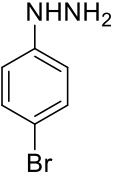
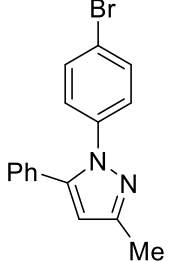
The effect of different solvents on the reaction rate as well as the yield of the products was investigated and the results are presented in [Table 3](#). Ethanol, chloroform, dichloromethane, methanol and water performed well and proved to be the ethanol of choice, while THF and 1,4-dioxane were less yield.

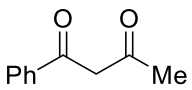
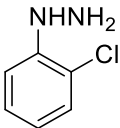
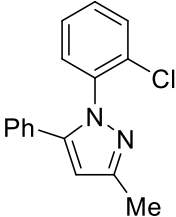
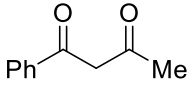
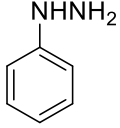
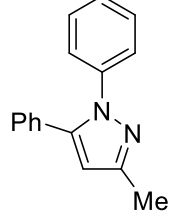
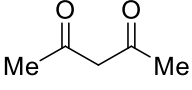
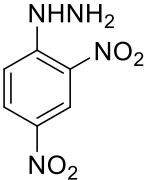
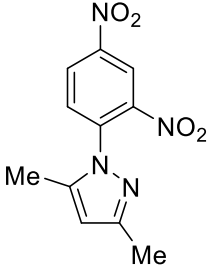
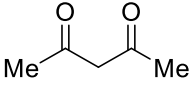
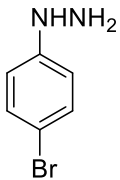
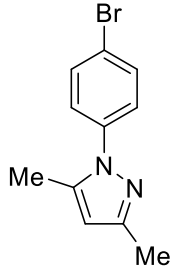
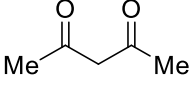
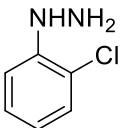
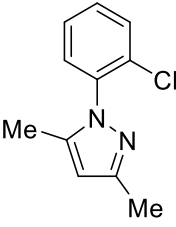
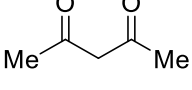
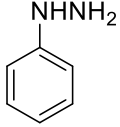
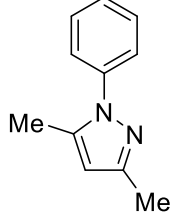
One of the most important advantages of heterogeneous catalysts over homogeneous samples is the possibility of reusing the catalyst with simple filtration, without loss of activity. As a result, the reuse of heterogeneous catalyst in product formation was investigated. After completion of the reaction, the catalyst was removed by filtration, washed 3 times with 5 mL of acetone and then washed several times with distilled water and dried at ambient temperature. The recovered catalyst was used in the next run.

Conclusions

In this research study, we have comprehensively evaluated an efficient, versatile and convenient method for the synthesis of pyrazoles derivatives in reaction of different 1,3-dicarbonyl compounds with hydrazines/hydrazides and graphene oxide nanoparticles as the Lewis base catalyst.

Table 1. Synthesis of pyrazoles derivatives by acid catalyst

Entry	1,3-dicarbonyl	Hydrazine	Product	Time (h)/ %yield	m.p.(°C)
1				2/98	137-139 °C
2				2/85	128-130 °C
3				2/90	179-181 °C
4				2/90	180-182 °C
5				2/80	121-123 °C
6				2/85	120-122 °C

7				2/85	Oil
8				2/90	Oil
9				2/80	170-172 °C
10				2/85	Oil
11				2/85	Oil
12				2/95	Oil

Scheme 3. The reaction of 2,4-dinitro phenyl hydrazine with 1,3-diphenyl-1,3-propanedione

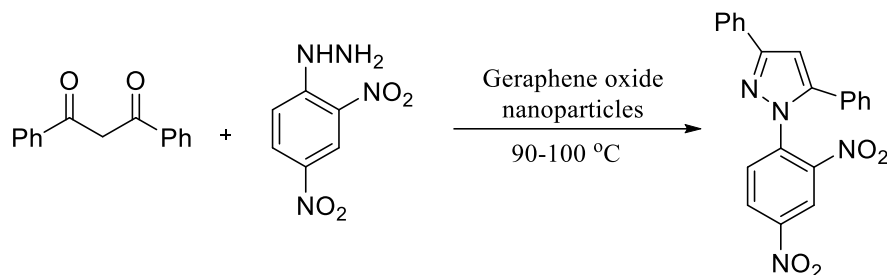


Table 2. Reaction of acetylacetone with 2,4-dinitro Phenyl hydrazine at r.t. in ethanol with different amounts of catalyst

Entry	Catalyst	Catalyst	Time(h)	Yield ^a (%)
1	None	-----	24	No reaction
2	Graphene oxide	0.004 gr	2	50
3	Graphene oxide	0.006 gr	2	60
4	Graphene oxide	0.008 gr	2	65
5	Graphene oxide	0.01 gr	2	70
6	Graphene oxide	0.02 gr	2	80
7	Graphene oxide	0.03 gr	2	85
8	Graphene oxide	0.04 gr	2	95
9	Graphene oxide	0.05 gr	2	95
10	Graphene oxide	0.06 gr	5	95

^aYields after isolation of products

Table 3. Effect of solvent on the reaction yield

Entry	Solvent ^a (Time(2h) ^b /90-100 °C)	Yield(%) ^c
1	EtOH	90
2	Chloroform	85
3	Dichloromethane	80
4	MeOH	80
5	H ₂ O	75
6	1,4-Dioxan	60
7	THF	50

^aReaction was performed with Benzoyl acetone (0.162 g) and 2,4-dinitro Phenyl hydrazine (0.198 g), in the presence of catalyst in various solvents

^bReaction time monitored by TLC

^cIsolated yield

Compared to previously reported methods, the mild reaction conditions, high yields, easy work-up, clean reaction profiles and lower catalyst loading render this approach as an interesting alternative to the existing methods.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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