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Covalent Modification of Organo-Functionalized Graphene Oxide and its Scope as Catalyst for One-Pot Pyrazolo-Pyranopyrimidine Derivatives

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The surface of graphene oxide (GO) was modified using [3-(2-aminoethylamino)propyl]trimethoxysilane (diamine), which exhibited excellent catalytic activity for one-pot multicomponent reactions. The newly synthesized material was fully characterized by various instrumental techniques including Fourier-transfer infrared (FTIR) and Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The instrumental analysis confirmed the successful grafting of organic amine functional groups onto the graphene oxide surface. The diamine-functionalized GO proved to be an excellent catalyst for the synthesis of pyrazolo-pyranopyrimidine derivatives with 93% yield and high selectivity. The catalytic activity almost remained unaltered up to three cycles. The newly synthesized pyrazolo-pyranopyrimidine derivatives have potential use as scaffolds in designing new pharmaceutical products.

In the field of materials science, among different carbon-based materials, graphene oxides (GO) have the prime position due to their honeycomb-like structure, high surface area, and novel electrical properties.[1–9] Graphite oxide is one of the starting materials in the large-scale production of graphene oxide. Monolayer graphene oxide is also prepared by the modified Hummers method followed by sonication. Generally, graphene oxide contains large number of oxygen functional groups such as epoxy, hydroxyl and carboxyl groups, on the basal planes and the edges.[10] Such functional groups can be easily chemically modified to homogeneous colloidal suspensions in various solvents. Thus, graphene-oxide-based materials can be easily functionalized by organoamine through covalent linkage.[11–14] Such stable functionalized materials are used in chemical, as well as pharmaceutical, industries for various applications as catalysts, sensors, and adsorbents.

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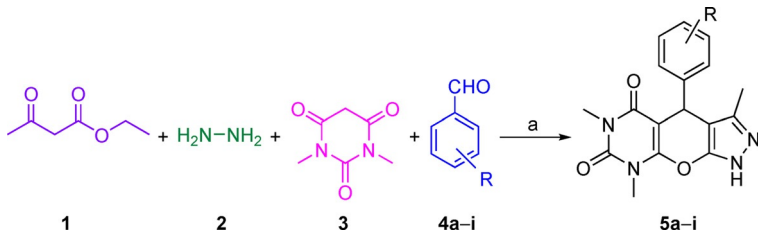
With the growing mandate for 'green chemistry', more environmentally benign forms of catalysts have an overwhelming demand, and some of the leading options and alternatives are environmentally acceptable and biodegradable materials.[15,16] Moreover, simple, effective, globally nonthreatening, and economically viable processes are also in great demand in organic synthesis.[17–19] In the past decade, functionalization of the C–H bond has been one of the most attractive approaches, and environmentally benign processes to build newer chemical bonds have received much attention. Furthermore, multicomponent reactions (MCRs) are considered as vital tools in combinatorial chemistry due to their ability to synthesize novel 'drug-like' small molecules simply in one pot.

Synthesis of novel heterocyclic compounds is most important in the field of organic and medicinal chemistry because of their broad range of applications (e.g. pharmacological). The five and six-membered nitrogen-bearing heterocyclic compounds such as pyrimidine, pyran, and pyrazole are scaffolds are of high interest because these fragments have numerous applications in medical and materials science.[20–23] A large number of molecules bearing the pyran moiety exhibit a broad spectrum of biological activities against hypertension, asthma, urinary diseases, and ischemia, to name a few, and currently, many are in use in the treatment of such diseases.[24–28]

In recent years, heterogeneous catalysts have shown many advantages in synthetic heterocyclic chemistry, for example, recyclability, simple workup procedures, environmental compatibility, low cost, and nontoxic and easy separation of reaction mixtures. Moreover, heterogeneous solid catalysts like GO and other mesoporous high-surface-area support materials have also found significant roles in organic synthesis. Thus, the design of novel, low-cost materials with high catalytic activity to produce substituted pyrazolo-pyranopyrimidine in short reaction times with high yields is highly desired. Herein, we report a protocol for the synthesis of pyrazolo-pyranopyrimidine derivatives by a multicomponent one-pot approach based on the reaction of hydrazine hydrate (1 mol), ethyl acetoacetate (1 mol), 1.3-dimethyl barbaric acid (1 mol), and aldehyde (1 mol) in an ethanol solvent, employing a reusable Diamine@GO heterogeneous catalyst under green conditions, to afford excellent yields (Scheme 1).

In the FTIR spectrum for GO, the 3400 cm^{-1} peak corresponds to O–H stretching, 1385 cm^{-1} to the O–H vibration of the C–OH group, 1740 cm^{-1} to the C=O stretching of –COOH, and 1100 cm^{-1} to epoxy vibration, all agreeing with the litera-



Scheme 1. Diamine@GO-catalyzed one-pot four-component reaction of pyrazolo-pyrano-pyrimidine in EtOH. *Reagents and conditions*: a) diamine-functionalized GO (catalyst), EtOH, reflux, 45 min, yields in Table 1.

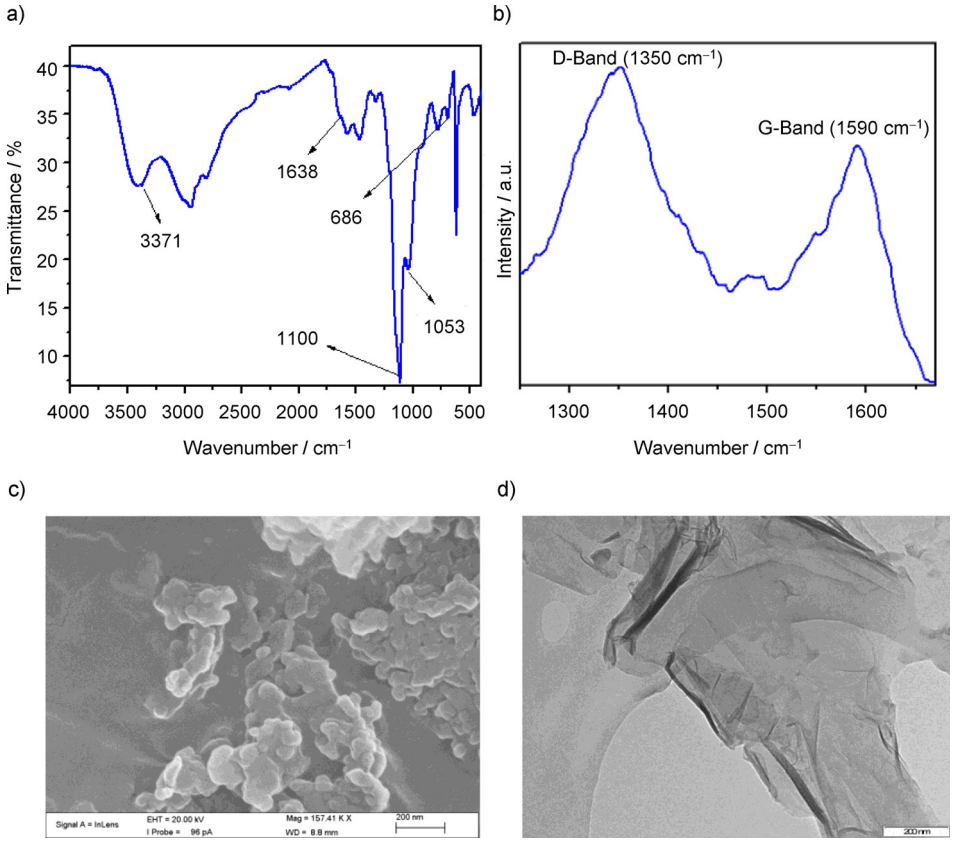


Figure 1. a) FTIR spectrum (4000–400 cm^{-1}), b) Raman spectrum, c) SEM image, scale bar = 200 nm, and d) TEM image, scale bar = 200 nm, of diamine-functionalized GO.

ture reports.[29] The FTIR spectrum corresponding to the Diamine@GO sample is shown in Figure 1 (a). In this spectrum, 3371 cm^{-1}, 1638 cm^{-1}, and 686 cm^{-1} peaks correspond to the N–H stretching and NH_2 bending mode of free NH_2 groups, and the stretching vibration of Si–O–C, respectively. The peaks at 1100 cm^{-1} and 1053 cm^{-1} are due to strong interactions of Si–O bonds. These results confirm that the organic amine group has modified both the surface epoxy and carboxyl groups of the graphene oxide.

Raman spectrum of Diamine@GO sample is shown in Figure 1 (b). Agreeing with the literature, the peak at 1350 cm^{-1} corresponds to sp^2-hybridized carbon atoms in a graphene oxide sheet of D-band and 1578 cm^{-1} to the σ-sp^2-bonded C-atoms of G-band.[30] From the perusal of Figure 1 (b), only the G-band shifted towards a higher wave number, that is, 1590 cm^{-1}, which may be due to the gradually increased compressive local stress caused by molecular intercalation, suggesting that an amine group has modified the functional groups of graphene oxide.

The SEM and TEM images of diamine-functionalized graphene oxide are shown in Figure 1 (c) and (d), respectively. The amine-functionalized graphene consists of randomly aggregated thin sheets forming a disordered network. This could be due to the organic solvent, which softens the normal attack of the amino group on the graphene oxide sheet, which hinders the formation of bigger sheets relative to smaller ones. The advantage in using toluene in maintaining the intrinsic morphology of graphene oxide during the silane functionalization reaction was observed.

In the preliminary experiments, a four-component one-pot reaction between benzaldehyde, hydrazine, 1,3-dimethylbarbituric acid, and ethylacetoacetate was chosen as a model reaction and was investigated under various experimental conditions to optimize the reaction efficiency (Table 1). We compared the efficiencies of Diamine@GO, with other catalysts. No product was obtained in the absence of a catalyst, even after 2 h at room temperature and under reflux conditions (Table 1, entry 1 and 2), which indicates that the catalyst is essential for the reaction. Organic and inorganic weak bases did not facilitate this reaction, although inorganic bases gave some low yields (Table 1, entries 3–7). The results summarized in Table 1 show that the reaction was efficient with Diamine@GO as a catalyst with ethanol as the solvent. Use of 10 mg of Diamine@GO as a catalyst with ethanol afforded the desired products in very small amounts at room temperature within 2 h (Table 1, entry 8). To further investigate the reaction conditions, the same reaction was carried out at reflux for 1 h, which gave the anticipated product in 79% yield (Table 1, entry 9).To optimize the required amount of catalyst, the reaction was performed with varied amounts of Diamine@GO. Increasing the amount of catalyst loading from 10 mg to 50 mg significantly increased the yield and decreased the reaction time (Table 1, entries 9–11). A further increase in the amount of catalyst did not exhibit any advantage on the product yield ((Table 1, entries 12&13). Therefore, using 30 mg

Table 1. Optimization of reaction conditions of the four-component synthesis.[a]

Entry	Product	Catalyst	Amount	Solvent	Temp	Time	Yield [%]
1	**5a**	–	–	EtOH	rt	12 h	[b]
2	**5a**	–	–	EtOH	reflux	6 h	[b]
3	**5a**	NaOH	1 equiv	EtOH	rt	12 h	[b]
4	**5a**	NaOH	1 equiv	EtOH	reflux	6 h	[b]
5	**5a**	Na_2CO_3	1 equiv	EtOH	reflux	6 h	[b]
6	**5a**	Et_3N	1 equiv	EtOH	reflux	6 h	[b]
7	**5a**	Pyridine	1 equiv	EtOH	reflux	6 h	[b]
8	**5a**	Diamine@GO	10 mg	EtOH	rt	2 h	trace
9	**5a**	Diamine@GO	10 mg	EtOH	reflux	60 min	79
10	**5a**	Diamine@GO	20 mg	EtOH	reflux	50 min	88
11	**5a**	Diamine@GO	30 mg	EtOH	reflux	45 min	93
12	**5a**	Diamine@GO	40 mg	EtOH	reflux	45 min	94
13	**5a**	Diamine@GO	50 mg	EtOH	reflux	45 min	94

[a] All products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectral analysis. [b] Products were not found.

of Diamine@GO in ethanol at reflux (Table 1, entry 11) was deemed ideal for the reaction.

The versatility of Diamine@GO as catalyst for the reaction was explored using a wide range of aryl aldehydes possessing different functional groups, including electron-donating and electron-withdrawing substituents. The obtained results summarized in Table 2 indicate that four-component reactions cat-

Table 2. Synthesis of the pyrazolo-pyranopyrimidine (**5a–i**) derivatives catalyzed by Diamine@GO

Entry	R	Product	Time [min]	Yield [%]
1	4-Br	**5a**	45	93
2	4-Cl	**5b**	50	92
3	4-OMe	**5c**	65	87
4	2-Cl	**5d**	55	93
5	2-Br	**5e**	45	92
6	2-OMe	**5f**	70	88
7	2-OH	**5g**	50	91
8	2,3-dimethoxy	**5h**	65	89
9	2,5-dimethoxy	**5i**	60	87

alyzed by Diamine@GO worked in all attempts with varied yields. An examination of the results shows that the electronic nature of the functional groups on the phenyl ring at the *para* position had a significant effect on the yield. Substrates with electron-withdrawing groups (Table 2, entries 1, 2, 4, 5, and 7) reacted rapidly, whereas electron-donating groups (Table 2, entries 3, 6, 8, and 9) displayed decreased reactivity, requiring a longer reaction times. (The proposed reaction mechanism is shown in Scheme II in the Supporting Information.)

We carried out a heterogeneity test for the multicomponent pyrazolo-pyranopyrimidine reaction, which was done at reflux in order to check whether the catalyst was truly behaving heterogeneously or not. The catalyst was separated from the reaction mixture by filtration after 25 min of the reaction, and the filtrate obtained was continuously stirred under the same reaction conditions for another 30 min. No increment in the % conversion was noticed. This suggests that there is no loss of catalyst components during the course of the reaction, which confirmed the heterogeneity of the catalyst.

The scope of recovery and recyclability of the catalyst was examined by carrying out the reaction repeatedly using the recovered catalyst. After the end of the reaction, the catalyst was separated by filtration, washed with distilled water several times, dried at 100 °C overnight, and reused with a fresh reaction mixture. The results for the recycled catalysts are shown in Figure S1 in the Supporting information. By the 4th cycle using the regenerated sample, the yield only decreased by 6%. However, after the 4th cycle, the catalytic activity diminished significantly. This could be probably due to coke formation on the regenerate catalysts.

In conclusion, we report an efficient one-pot multicomponent protocol for the synthesis of pyrazolo[4′,3′:5,6]pyrano[2,3-d]-pyrimidine derivatives using diamine-functionalized graphene oxide as a catalyst with excellent efficiency. The current approach has several advantages such as cost effectiveness, purity of products, good to excellent yields, short reaction times, need for small amounts of catalyst, and simple workup.

Experimental Section

Preparation of GO: Initially, graphite powder (0.5 g) and $NaNO_3$ (0.5 g) were dissolved in concentrated H_2SO_4 (23 mL) with continuous stirring for 20 min, and the mixture was cooled in an ice bath for 2 h. Then, the reaction mixture was heated and stirred at 40 °C, and $KMnO_4$ (6 g) crystalline powder was added slowly with continuous stirring for 70 min. Next, distilled water (50 mL) was added to the mixture and stirred for further 20 min, followed by H_2O_2 (30%) dropwise until the color of the solution changed from dark brown to yellow. Upon the color change, water (50 mL) was added, and the resulting solution was sonicated for 2 h. The solution was centrifuged, separated, filtered, and washed several times with double-distilled water. The product was dried in a vacuum oven at 100 °C overnight to obtain GO.

Preparation of amine-functionalized GO: GO (1 g) was dissolved in toluene (50 mL) in a conical flask and sonicated for 2 h. [3-(2-Aminoethylamino) propyl] trimethoxysilane (diamine) (1.68 mmol) (Aldrich) was added to the solution and sonicated further for 1 h. Then, the solution was centrifuged and dried in a vacuum oven at 100 °C overnight to obtain Diamine@GO.

Characterization of catalysts: FTIR spectra of the samples were recorded using A PerkinElmer FTIR Spectrum 100 series with universal ATR accessory (Waltham, USA). Raman spectra were collected on a DeltaNu advantage 532 Raman Spectrometer (100 mW Nd:YAG laser with an excitation wavelength of 532 nm) (Laramie, USA). The TEM images were viewed on a JEOL JEM-1010 electron microscope (Tokyo, Japan). The images were captured and analyzed by using iTEM software (Soft Imaging System GmbH, 5.0, Build 1089, 1986–2005), and the SEM measurements were carried out using a JEOL JSM-6100 microscope.

General procedure for the synthesis of pyrazolo-pyranopyrimidine derivatives:

To a solution of hydrazine hydrate (55 mg, 1 mol) in EtOH (5 mL) in a two-neck round-bottom flask, ethyl acetoacetate (156 mg, 1 mol)

was added. Then, aldehyde (100 mg, 1 mol) and 1, 3 dimethylbarbaric acid (115 mg, 1 mol) were added to the mixture, followed by the required amount of catalyst (30 mg). Then, the total mixture was heated at reflux for the completion of the reaction. After completion of the reaction (as monitored by thin-layer chromatography), the mixture was cooled to room temperature and filtered. Yields are shown in Table 2. The precipitate was separated and characterized as follows:

3,6,8-Trimethyl-4-(4-bromophenyl)-6,8-dihydropyrazolo[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 a): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.09 (s, 3 H, CH_3), 3.10 (s, 6 H, $N(CH_3)_2$), 5.43 (s, 1 H, CH), 6.99 (d, J = 8.24 Hz, 1 H, ArH), 7.06 (d, J = 8.32 Hz, 1 H, ArH),7.32 (d, J = 8.36 Hz, 1 H, ArH), 7.40 (d, J = 8.36 Hz, 1 H, ArH), 14.57 ppm (s, 1H NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 158.6, 151.3, 137.2, 132.1, 129.1, 128.2, 45.7, 27.68, 8.60 ppm; IR (KBr): $\tilde{\nu}$ = 2952, 2872, 1667, 1582, 1482 cm^{-1}; Anal. calcd for $C_{17}H_{15}BrN_4O_3$: C 50.62, H 3.78, N 13.91, found: C 50.64, H 3.75, N 13.89.

3,6,8-Trimethyl-4-(4-chlorophenyl)-6,8-ihydropyrazolo[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 b): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.25 (s, 3 H, CH_3), 3.12 (s, 6 H, $N(CH_3)_2$), 5.53 (s, 1 H, CH), 7.05 (d, J = 8.12 Hz, 2 H, ArH), 7.24 (d, J = 8.36 Hz, 2 H, ArH), 16.30 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 158.8, 151.5, 141.6 129.8, 128.5, 127.6, 27.6, 9.9 ppm; IR (KBr): $\tilde{\nu}$ = 3436, 2898, 1670, 1556, 1488 cm^{-1}; Anal. calcd for $C_{17}H_{15}ClN_4O_3$: C 56.87, H 4.19, N 15.65, found: C 56.91, H 4.21, N 15.62.

3,6,8-Trimethyl-4-(4-methoxyphenyl)-6,8-dihydropyrazolo-[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione(5 c): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.22 (s, 3H CH_3), 3.10 (s, 3 H, NCH_3), 3.68 (s, 3 H, NCH_3), 3.82 (s, 3 H, OCH_3), 5.48 (s, 1 H, CH), 7.04 (d, J = 8.64 Hz, 2 H, ArH), 7.80 (d, J = 8.64 Hz, 2 H, ArH), 15.99 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 160.4, 159.1, 156.9, 151.6, 129.9, 128.1, 127.6, 126.5, 114.3, 113.2, 113.1, 55.3, 27.6, 9.9 ppm; IR (KBr): $\tilde{\nu}$ = 2939, 2836, 1668, 1508, 1442 cm^{-1}; Anal. calcd for $C_{18}H_{18}N_4O_4$: C 60.97, H 5.17, N 15.83, found: C 61.01, H 5.12, N 15.80.

3,6,8-Trimethyl-4-(2-chlorophenyl)-6,8-dihydropyrazolo[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 d): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.19 (s, 3 H, CH_3), 3.10 (s, 6 H, $N(CH_3)_2$), 5.61 (s, 1 H, CH), 7.20–7.12 (m, 2 H, ArH), 7.26 (d, J = 7.68 Hz, 1 H, ArH), 7.50 (d, J = 7.60 Hz, 1 H, ArH), 12.32 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 159.3, 151.7, 141.1, 140.6, 132.5, 130.5, 129.1, 127, 125.9, 45.7, 27.5, 10.1 ppm; IR (KBr): $\tilde{\nu}$ = 3746, 2954, 1666, 1578, 1439 cm^{-1}; Anal. calcd for $C_{17}H_{15}ClN_4O_3$: C 56.88, H 4.19, N 15.65, found: C 56.91, H 4.21, N 15.62.

3,6,8-Trimethyl-4-(2-bromophenyl)-6,8-dihydropyrazolo[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 e): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.18 (s, 3 H, CH_3), 3.08 (s, 6 H, $N(CH_3)_2$), 5.49 (s, 1 H, CH), 7.04 (t, J = 7.02 Hz, 1 H, ArH), 7.22 (t, J = 7.80 Hz, 1 H, ArH), 7.44 (d, J = 7.72 Hz, 1 H, ArH), 7.50 (d, J = 7.02 Hz, 1 H, ArH), 14.29 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 151.3, 138.4, 132.7, 129.1, 128.9, 127.4, 124.2, 45.7, 27.5, 8.6 ppm; IR (KBr): $\tilde{\nu}$ = 3484, 2948, 1667, 1561, 1430 cm^{-1}; Anal. calcd for $C_{17}H_{15}BrN_4O_3$: C 50.61, H 3.77, N 13.92, found: C 50.64, H 3.75, N 13.88.

3,6,8-Trimethyl-4-(2-methoxyphenyl)-6,8-dihydropyrazolo-[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 f): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.03 (s, 3 H, CH_3), 2.10 (s, 6 H, $N(CH_3)_2$), 3.79 (s, 3 H, OCH_3), 5.11 (s, 1 H, CH), 6.85 (t, J = 7.42 Hz, 1 H, ArH), 6.91 (d, J = 8.00 Hz, 1 H, ArH), 7.13 (t, J = 7.48 Hz, 1 H, ArH), 7.60 (d, J = 7.36 Hz, 1 H, ArH), 11.41 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 155.8, 139.9, 132, 129, 126.5, 11.6, 110.3, 103.7, 55.2, 45.6, 26.8, 11, 10.5 ppm; IR (KBr): $\tilde{\nu}$ = 3215, 2999, 1650, 1568, 1489 cm^{-1}; Anal. calcd for $C_{18}H_{18}N_4O_4$: C 60.98, H 5.16, N 15.84, found: C 61.01, H 5.12, N 15.81.

3,6,8-Trimethyl-4-(2-nitrophenyl)-6,8-dihydropyrazolo[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 g): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.08 (s, 3H CH_3), 3.03 (s, 6 H, $N(CH_3)_2$), 5.81 (s, 1 H. CH), 7.25 (t, J = 7.60 Hz, 1 H, ArH), 7.35 (d, J = 7.68 Hz, 1 H, ArH), 7.41 (t, J = 7.64 Hz, 2H ArH), 10.99 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 157.2, 152.2, 138, 130.3, 125.8, 122.9, 117.5, 114.6, 113.7, 45.7, 27.2, 8.6 ppm; IR (KBr): $\tilde{\nu}$ = 3190, 2980, 1618, 1519, 1431 cm^{-1}; Anal. calcd for $C_{17}H_{15}N_5O_5$: C 55.31, H 4.12, N 18.64, found: C 55.28, H 4.09, N 18.69.

3,6,8-Trimethyl-4-(2,3-dimethoxyphenyl)-6,8-dihydropyrazolo-[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 h): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.19 (s, 3 H, CH_3), 3.11 (s, 6 H, $N(CH_3)_2$), 3.47 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 5.73 (s, 1 H, CH), 6.80 (d, J = 7.25 Hz, 1 H, ArH), 6.86 (t, J = 8.04 Hz, 1 H, ArH), 6.97 (d, J = 7.60 Hz, 1 H, ArH), 15.59 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 152.1, 151.6, 146.1, 128.2, 127.7, 127, 122.3, 59.1, 55.9, 27.6, 18.5, 10.1 ppm; IR (KBr): $\tilde{\nu}$ = 33663, 2963, 1682, 1571, 1431 cm^{-1}; Anal. calcd for $C_{19}H_{20}N_4O_5$: C 59.35, H 5.26, N 14.56, found: C 59.37, H 5.24, N 14.58.

3,6,8-Trimethyl-4-(2,5-dimethoxyphenyl)-6,8-dihydropyrazolo-[4′,3′:5,6] pyrano[2,3-d]-pyrimidine-5,7(1 H,4 H)-dione (5 i): ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.05 (s, 6 H, $N(CH_3)_2$), 3.62 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 5.02 (s, 1 H, CH), 6.77 (d, J = 8.00 Hz, 1 H, ArH), 7.10 (s, 1 H, ArH), 7.18 (d, J = 2.20 Hz, 1 H, ArH), 11.50 ppm (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 153.3, 153.1, 152.6, 150.1, 133.2, 122, 119.4, 116.3, 113.6, 111.1, 110, 109.7, 55.8, 55, 44.4, 27, 10.3 ppm; IR (KBr): $\tilde{\nu}$ = 3333, 2831, 1658, 1588, 1463 cm^{-1}; Anal. calcd for $C_{19}H_{20}N_4O_5$: C 59.35, H 5.27, N 14.56, found: C 59.37, H 5.24, N 14.58.

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Keywords: diamine-functionalized catalysts · graphene oxide · multicomponent reactions · one-pot reactions · pyrazolo-pyranopyrimidine derivatives

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