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FULL PAPER

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Nanomagnetically modified thioglycolic acid (γ-Fe_2O_3@SiO_2-SCH_2CO_2H): Efficient and reusable green catalyst for the one-pot domino synthesis of spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazines

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Superparamagnetic nanoparticles of modified thioglycolic acid (γ-Fe_2O_3@SiO_2-SCH_2CO_2H) represent a new, efficient and green catalyst for the one-pot synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] derivatives via domino Knoevenagel–Michael–cyclization reaction of 2-hydroxynaphthalene-1,4-dione, benzene-1,2-diamines, ninhydrin and isatin. This novel magnetic organocatalyst was easily isolated from the reaction mixture by magnetic decantation using an external magnet and reused at least six times without significant loss in its activity. The catalyst was fully characterized using various techniques. This procedure was also applied successfully for the synthesis of benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazines.

KEYWORDS
encapsulated iron oxide nanoparticles, green chemistry, magnetically recoverable nanocatalyst, modified thioglycolic acid, multi-component domino reactions (MDRs), spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine]

1 | INTRODUCTION

Diversity-oriented synthesis (DOS) has played a critical role at the interface of the fields of organic synthesis and chemical biology.[1–3] At the heart of DOS are the synthetic means needed for the generation of collections of functionally and regiochemically diverse small molecules, particularly those possessing skeletons resembling those found in natural products or drug-like molecules.[4] Multi-component domino reactions (MDRs), in which more than two components are combined in a single synthetic operation, have played an important role in this area due to their atom efficiency, operational simplicity, high selectivity, usually excellent productivity, facile execution, low costs, minimum waste production, structural diversity, shorter reaction times, environmental friendliness and allowing savings of both solvents and reagents.[5–9]

Therefore, the design of novel MDRs for the synthesis of diverse heterocycles has remained an important topic for medicinal and organic chemistry. Heterocycles having phenazine, quinoxaline and chromene moieties are important targets in synthetic organic chemistry. While phenazines,[10–14] quinoxalines[15–18] and chromenes[19–23] have attracted great attention in medicinal chemistry and drug discovery, the preparation of compounds incorporating all of these motifs (Figure 1) has not been reported.

Moreover, spiro heterocycles are found in a number of natural and synthetic molecules.[24,25] A spiro heterocyclic compound in which the spiro carbon is part of the cyclic ring has many unique properties,[26–29] and they are particularly interesting because the conformational restriction associated with the structural rigidity affects considerably their biological activity.[30]

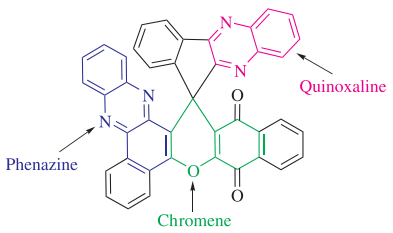


FIGURE 1 Structure of designed compound

Nanomaterial applications as heterogeneous catalysts have expanded in organic synthesis due to high surface area, surface modification ability, excellent thermal and chemical stability, simple work-up procedures, environmentally benign nature, reusability, low cost and ease of synthesis and isolation.[31–35] Among them, organic processes catalysed by non-toxic magnetic nanoparticles (MNPs) such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are often considered to follow the principles of green chemistry, i.e. those catalysed processes that consume a minimum of energy and reagents or auxiliaries and minimize waste.[36,37]

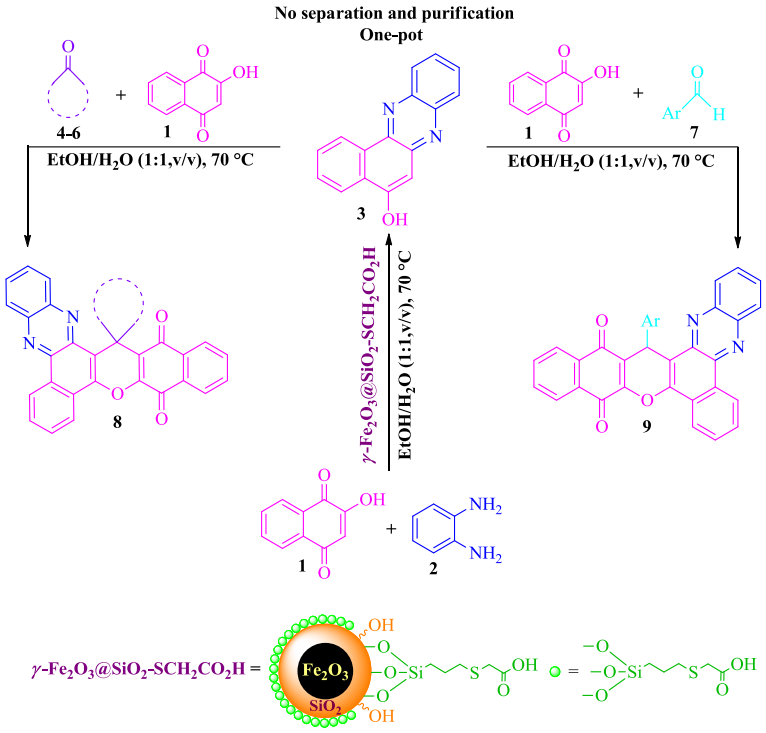
Considering the importance of phenazine, quinoxaline and chromene derivatives and in continuation of our research on multi-component reactions and our ongoing programme for the synthesis of complex organic compounds based on green chemistry protocols,[38–43] herein we report a green synthesis of functionalized spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives catalysed by superparamagnetic nanoparticles of modified thioglycolic acid as a new and efficient catalyst in EtOH–H_2O (1:1) at 70 °C (Scheme 1).

2 | RESULTS AND DISCUSSION

In this work, we report thioglycolic acid-coated MNPs as a new catalyst for the synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives. Initially, superparamagnetic Fe_3O_4 nanoparticles were synthesized using the chemical co-precipitation method from ferric and ferrous ions in ammonia solution with minor modifications.[44] In the next step, the nanoparticles were converted to γ-Fe_2O_3 at 300 °C for 3 h. Subsequently, γ-Fe_2O_3 was encapsulated by tetraethyl orthosilicate (TEOS; $Si(OEt)_4$) as Fe_2O_3@SiO_2.[45] Then, chlorofunctionalized γ-Fe_2O_3@SiO_2 was synthesized.[46] Eventually, the reaction of thioglycolic acid with chlorofunctionalized γ-Fe_2O_3@SiO_2 formed new superparamagnetic silica-encapsulated γ-Fe_2O_3 (γ-Fe_2O_3@SiO_2@thioglycolic acid) as the catalyst (Figure 2).

MNPs-thioglycolic acid was characterized with various techniques and its potential as a catalyst was studied. The structure of the magnetic nanocatalyst was characterized using various techniques such as Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), energy-dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA).

The FT-IR spectrum of γ-Fe_2O_3@SiO_2@thioglycolic acid is shown in Figure 3. The Fe—O stretching vibration near 580 cm^{-1}, the O—H stretching vibration at 3300–3500 cm^{-1}, the Si—O stretching at 1000–1110 cm^{-1}, the C═O vibration at 1600–1750 cm^{-1} and the C—H stretching



SCHEME 1 One-pot, domino, multi-component synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives in the presence of γ-Fe_2O_3@SiO_2-SCH_2CO_2H

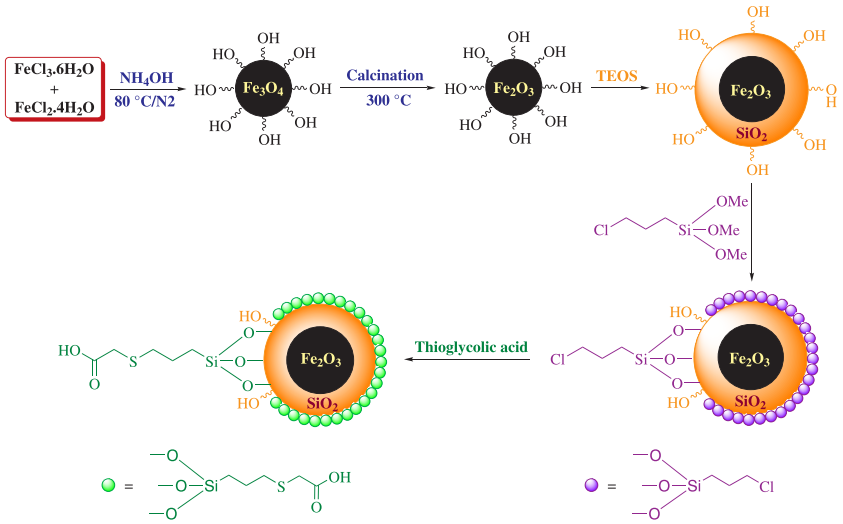


FIGURE 2 Synthesis of MNPs-thioglycolic acid as new heterogeneous catalyst

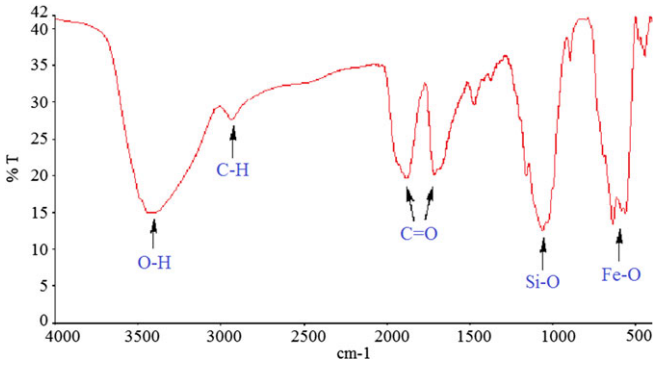


FIGURE 3 FT-IR spectrum of γ-Fe_2O_3@SiO_2@thioglycolic acid

vibration at 2948 cm^{-1} were observed. This spectrum proved that thioglycolic acid was successfully attached on the surface of γ-Fe_2O_3@SiO_2 nanoparticles.

Figure 4 shows the XRD pattern of crystalline structure of γ-Fe_2O_3@SiO_2@thioglycolic acid. Six diffraction peaks

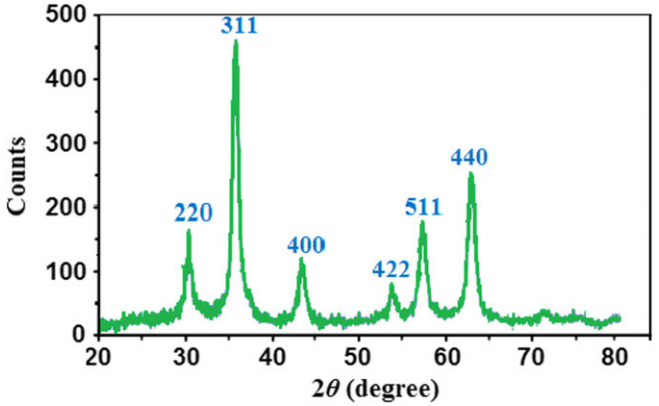


FIGURE 4 XRD pattern of γ-Fe_2O_3@SiO_2@thioglycolic acid

((220), (311), (400), (422), (511) and (440)) were identified in XRD pattern, demonstrating the structure of MNPs. The XRD pattern of γ-Fe_2O_3@SiO_2@thioglycolic acid showed that thioglycolic acid and SiO_2 formed amorphous phase, with the pattern showing only crystalline γ-Fe_2O_3 nanoparticles (JCPDS card no. 39-1346).

The crystalline size and morphology of the prepared catalyst were characterized using SEM. The SEM images of MNPs-thioglycolic acid show spherical morphology and the average size of the nanoparticles is 15.6 nm from the histogram of particle size distribution (Figure 5).

The VSM curves show the magnetic properties of γ-Fe_2O_3 and MNPs-thioglycolic acid and also prove that these nanoparticles are superparamagnetic (Figure 6). Saturation magnetization of MNPs was 63.8 emu g^{-1} and saturation magnetization of MNPs-thioglycolic acid was 50.9 emu g^{-1}. The saturation magnetization of MNPs-thioglycolic acid was obviously decreased as compare with the uncoated γ-Fe_2O_3 nanoparticles. This decrease in magnetization of MNPs-thioglycolic acid is because of the presence of organic material and SiO_2 in the surface of MNPs-thioglycolic acid.

The components of γ-Fe_2O_3@SiO_2@thioglycolic acid were analysed using EDS (Figure 7). The EDS spectrum obviously indicates the presence of Fe, O, Si, C and S atoms in the catalyst.

The thermal stability of MNPs-thioglycolic acid was investigated using TGA (Figure 8). The small weight loss occurring below 100 °C is due to solvent desorption. The second weight loss can be attributed to the decomposition of the organic part. As can be seen from the TGA curve, the amount of organic compound was about 6.5% versus the total heterogeneous catalyst. Considering this weight loss, it was calculated that 0.71 mmol of thioglycolic acid was loaded on 1 g of MNPs-thioglycolic acid catalyst.

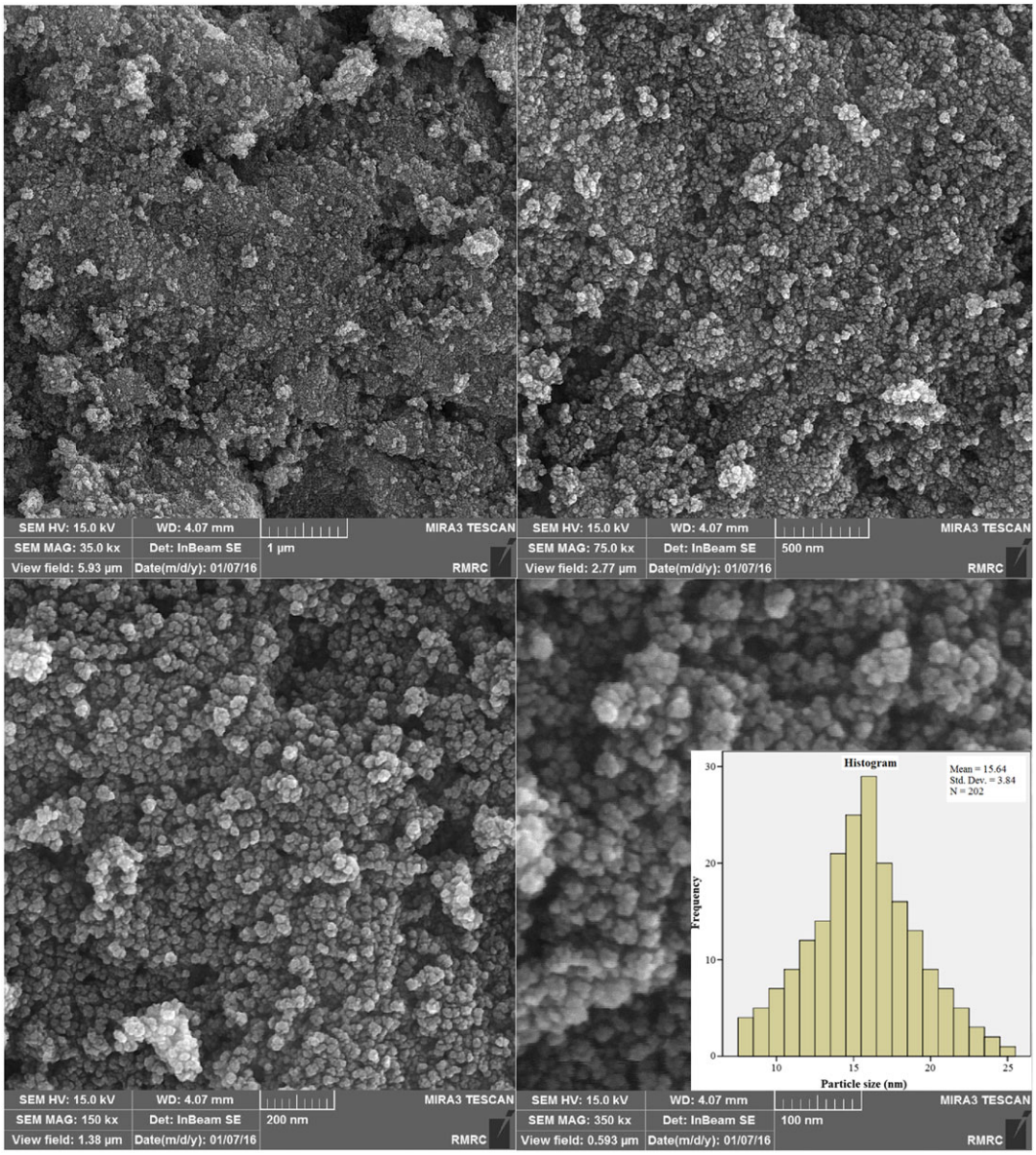


FIGURE 5 SEM images and histogram of particle size distribution of γ-Fe_2O_3@SiO_2@thioglycolic acid

This newly synthesized catalyst consists of economically cost-effective and modified non-toxic MNPs, and its structure convinced us that it could be used as an efficient, green and solid acid catalyst in the synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives. For this purpose, at first, the aromatic ketones **6a–d** were synthesized according to previous work,[47] by means of reaction between ninhydrin (2,2-dihydroxyindane-1,3-dione; **5**) and various aromatic 1,2-diamines, namely benzene-1,2-diamine (**2a**), 4-methylbenzene-1,2-diamine (**2b**), 4-nitrobenzene-1,2-diamine (**2c**) and 2,3-diaminopyridine (**2d**) (Scheme 2). In the cases of **2a** and **2b**, higher yields of the products were obtained in shorter reaction times in comparison with **2c** and **2d**.

In order to investigate the optimal reaction conditions for the synthesis of functionalized spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] derivatives, we carried out the MDR reaction of 2-hydroxynaphthalene-1,4-dione (**1**; 1 mmol), **2a** (1 mmol) and isatin (**4**; 1 mmol) in ethanol as a model (Scheme 3). Initially, to minimize the formation of by-products, **1** and **2a** were refluxed in ethanol until in less than 10 min an orange solid of benzo[*a*]phenazine (**3a**) was formed without using any catalyst. Next, **4** and **1** were added and the mixture was heated in EtOH under reflux conditions. The desired product **8** was not obtained when the reaction was carried out in EtOH for 4 h under reflux and catalyst-free conditions (Table 1, entry 1). However, **8a** was obtained in 83% yield when the reaction was conducted in the presence of thioglycolic acid (0.005 g) in EtOH (Table 1, entry 2).

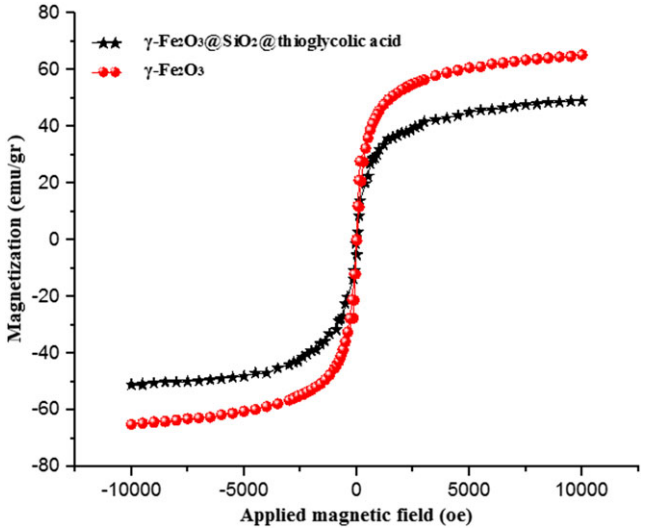


FIGURE 6 VSM curves of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2@thioglycolic acid

Different catalysts were evaluated in the model reaction, including nano-SiO_2, SiO_2-SO_3H, γ-Fe_2O_3, γ-Fe_2O_3@SiO_2 and γ-Fe_2O_3@SiO_2-SCH_2CO_2H; these were all added in sub-stoichiometric amount (0.03 g) and the reactions were carried out in EtOH under reflux conditions. Eventually, we found that γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03 g) showed excellent catalytic activity in terms of reaction time as well as yield of product. Also, to select the best solvent for the reaction, the synthesis of compound **8a** was examined in various solvents (Table 1). The examined solvents were not efficient separately.

Higher yields were obtained in shorter reaction times when the reaction was carried out in EtOH–H_2O (1:1), due to its strong hydrogen bonding ability, hydrophobic effects and high polarity. In this experiment any other organic solvents were not tested because of the green chemistry concept. After extensive screening, we found that the best yields and time profiles were obtained when the reaction was carried out in the presence of 0.03 g of γ-Fe_2O_3@SiO_2-SCH_2CO_2H in EtOH–H_2O (1:1) at 70 °C, which afforded the corresponding spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine-17,3′-indoline]-2′,11,16-trione (**8a**) in 2 h with 92% yield (Table 1, entry 10).

To generate a small library of functionalized spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] derivatives **8**, we next utilized a variety of substrates to explore the synthetic scope and generality of this accelerated one-pot Knoevenagel condensation–Michael addition–cyclization cascade reaction under optimal conditions. Representative results are summarized in Table 2.

The structures of these new compounds were deduced from their satisfactory elemental and spectral (FT-IR, ^{1}H NMR, ^{13}C NMR) analyses. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m*/*z* values.

Then, using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives **9**. An extensive range of substituted and structurally diverse aldehydes (*ortho*-, *meta*- and *para*-substituted) afforded the corresponding products in high to excellent yields using MNPs-thioglycolic acid as an environmentally friendly catalyst. As is evident from Table 3, the reactions

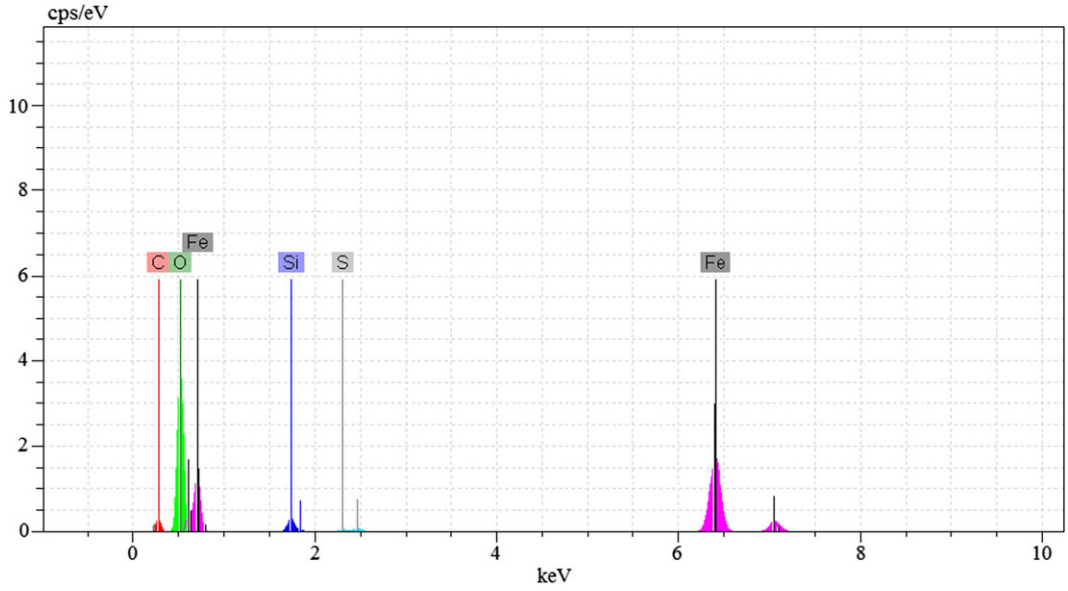


FIGURE 7 EDS spectrum of γ-Fe_2O_3@SiO_2@thioglycolic acid

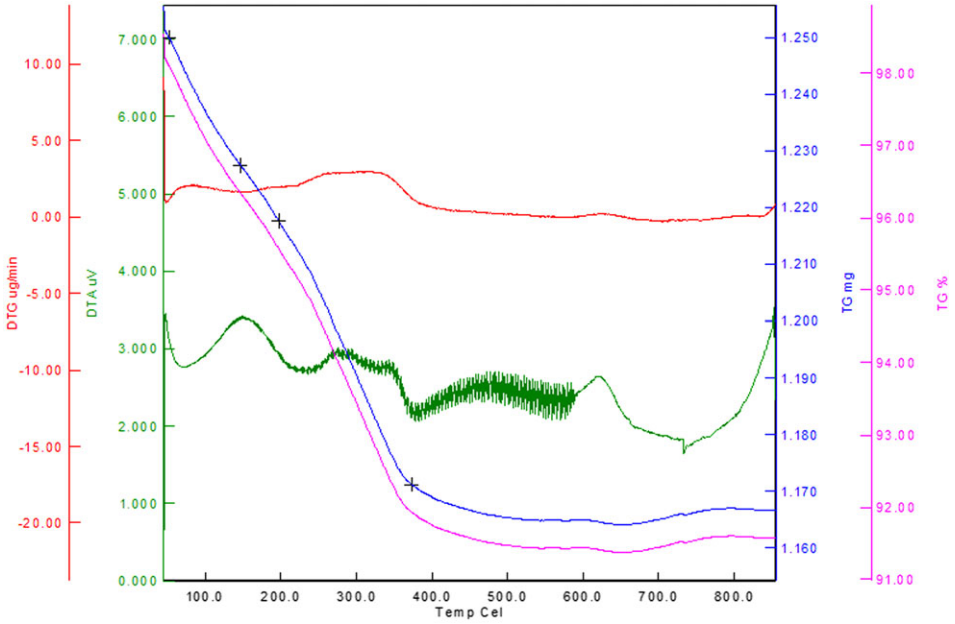
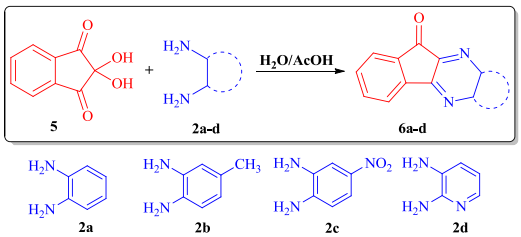


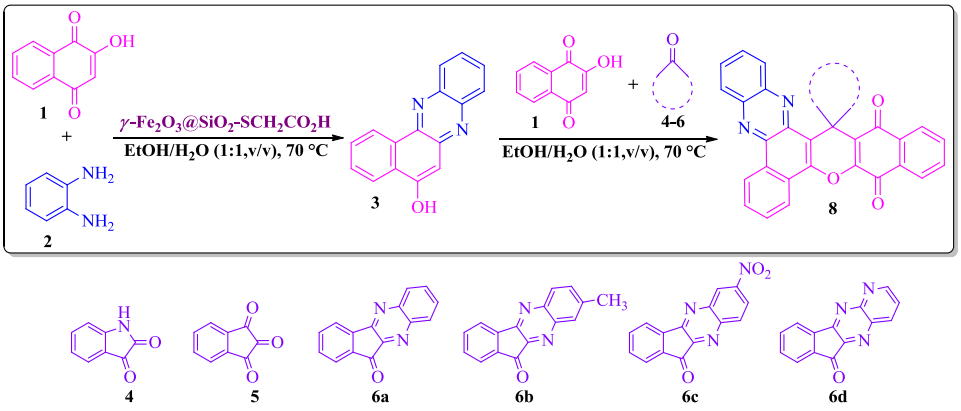
FIGURE 8 TGA and differential TGA of γ-Fe_2O_3@SiO_2@thioglycolic acid



SCHEME 2 Synthesis of 11*H*-indeno[1,2-*b*]quinoxalin-11-one derivatives and 6*H*-indeno[1,2-*b*]pyrido[3,2-*e*]pyrazin-6-one

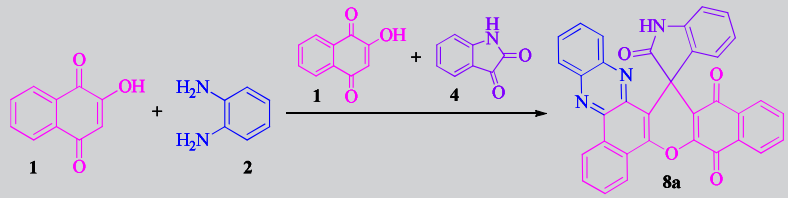
were efficiently promoted using arylaldehydes with electron-withdrawing groups with increased yields and reduced reaction times rather than substitutions of electron-donating groups on the benzene ring. Also, in the presence of aliphatic aldehydes such as *n*-heptanal and *n*-octanal, the expected product was not obtained under these reaction conditions.

The recovery and reuse of catalysts are important advantages in green chemistry and heterogeneous catalysis; and also important from an industrial point of view in large-scale operations and commercial applications. In this regard, we also investigated the recyclability of MNPs-thioglycolic acid in EtOH–H_2O (1:1) at 70 °C using a selected model reaction of **1**, **2** and isatin in the presence of MNPs-thioglycolic acid (Table 2, entry 1). After completion of the reaction, the reaction mixture was diluted with hot ethanol and the catalyst was easily separated from the reaction mixture using an external magnetic field, washed with hot ethanol, dried in air and



SCHEME 3 Synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] derivatives

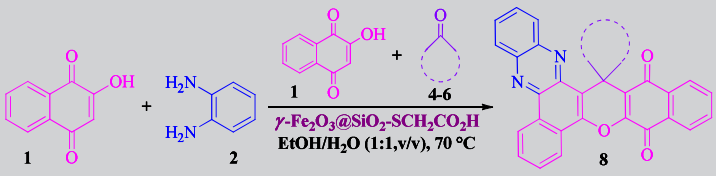
TABLE 1 Optimization of reaction conditions for compound **8a**



Entry	Catalyst (g)	Reaction conditions	Time (h)	Yield (%)[a]
1	—	EtOH, reflux	4	Nil
2	Thioglycolic acid (0.005)	EtOH, reflux	2	83
3	SiO_2-SO_3H (0.03)	EtOH, reflux	2	78
4	Nano-SiO_2 (0.03)	EtOH, reflux	2	42
5	γ-Fe_2O_3 (0.03)	EtOH, reflux	2	64
6	γ-Fe_2O_3@SiO_2 (0.03)	EtOH, reflux	2	71
7	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	EtOH, reflux	2	87
8	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	H_2O, reflux	2	80
9	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	EtOH–H_2O (1:1), reflux	2	91
10	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	EtOH–H_2O (1:1), 70 °C	2	92
11	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	EtOH–H_2O (1:1), 50 °C	3	88
12	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.03)	EtOH–H_2O (1:1), r.t.	6	Trace
13	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.06)	EtOH–H_2O (1:1), 70 °C	2	92
14	γ-Fe_2O_3@SiO_2-SCH_2CO_2H (0.015)	EtOH–H_2O (1:1), 70 °C	2	86

[a]Isolated yield.

TABLE 2 One-pot multi-component domino synthesis of spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] derivatives using MNPs-thioglycolic acid (0.03 g) as catalyst in EtOH–H_2O (1:1) at 70 °C



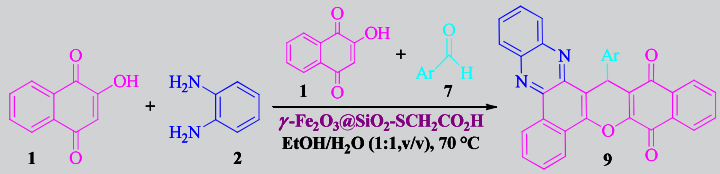
Entry	Cyclic ketone	Product	Time (h)	Yield (%)[a]
1	**4**	**8a**	2	92
2	**5**	**8b**	2	88
3	**6a**	**8c**	3	87
4	**6b**	**8d**	3	85
5	**6c**	**8e**	3	81
6	**6d**	**8f**	3	79

[a]Isolated yield.

reused for a subsequent similar reaction. The recovered catalyst was reused for six consecutive cycles without any significant loss in its catalytic activity (Figure 9).

In order to determine the catalytic behaviour of MNPs-thioglycolic acid, a suggested mechanism for the formation of products is shown in Scheme 4. On the basis

TABLE 3 One-pot multi-component domino synthesis of benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives using MNPs-thioglycolic acid (0.03 g) as catalyst in EtOH–H_2O (1:1) at 70 °C



Entry	Aldehyde	Product	Time (h)	Yield (%)[a]	M.p. (obs.) (°C)	M.p. (lit.) (°C)
1	4-ClC_6H_4	**9a**	2	94	325–327	324–326[42]
2	2-ClC_6H_4	**9b**	2	92	334–336	336–338[42]
3	2,4-$Cl_2C_6H_3$	**9c**	2	92	331–332	330–332[42]
4	4-$NO_2C_6H_4$	**9d**	2	93	273	273–275[42]
5	3-$NO_2C_6H_4$	**9e**	2	91	370–372	368–370[42]
6	2-$NO_2C_6H_4$	**9f**	2	90	294–296	293–295[42]
7	3-CNC_6H_3	**9g**	2	88	286–288	289–291[42]
8	4-$CH_3C_6H_4$	**9h**	3	89	333–335	333–335[42]
9	4-$CH_3OC_6H_4$	**9i**	3	86	342–344	341–342[42]
10	3,4-$(CH_3O)_2C_6H_3$	**9j**	3	85	320–321	Present work
11	4-OHC_6H_4	**9k**	3	83	301–303	Present work
12	2-OH-5-$NO_2C_6H_3$	**9l**	3	89	365	364–366[42]
13	5-Br-2-OHC_6H_3	**9m**	3	85	356–358	359–361[42]
14	*n*-Heptanal	—	4	NR	—	—
15	*n*-Octanal	—	4	NR	—	—

[a]Isolated yield.

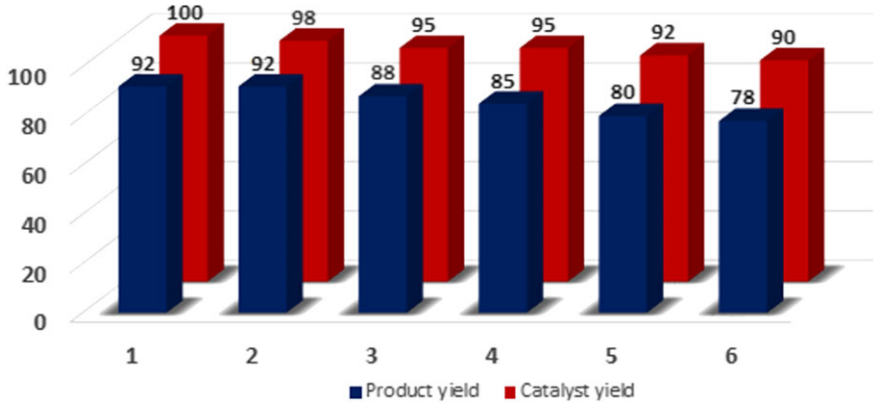
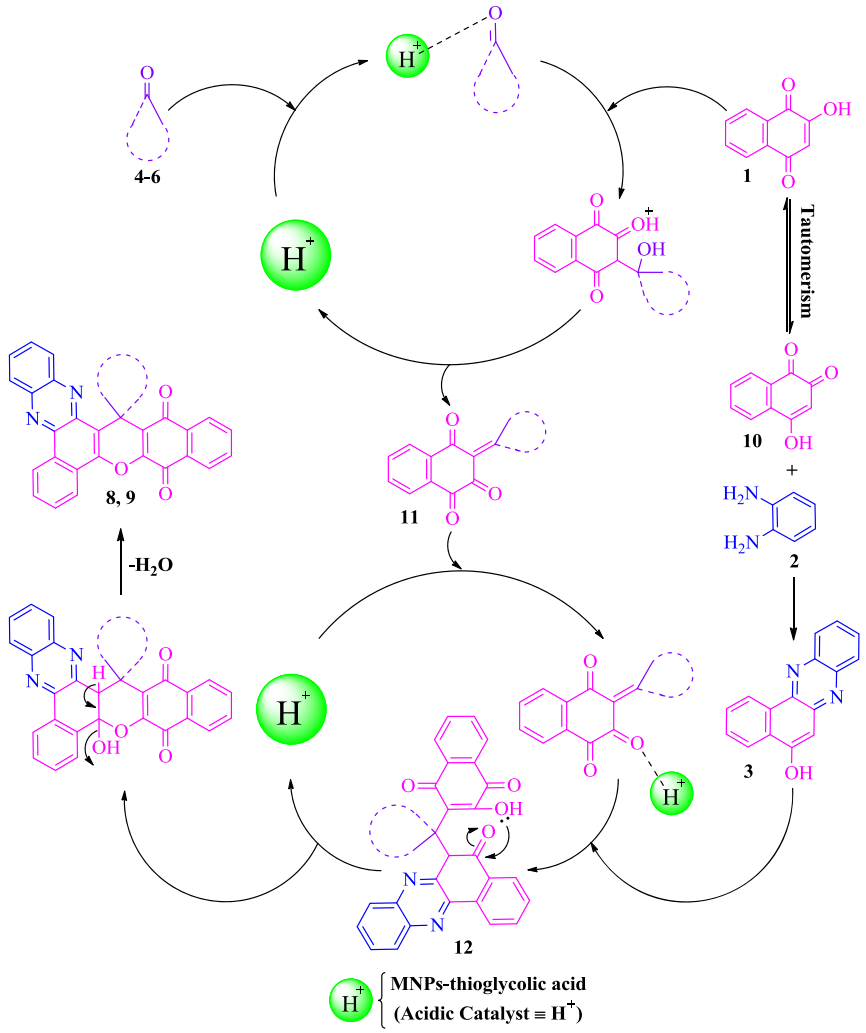


FIGURE 9 Reusability of nanocatalyst

of this mechanism, at first, **1** tautomerizes to intermediate 4-hydroxy-1,2-naphthoquinone (**10**). The primary condensation of **10** with **2** produces 6*H*-benzo[*a*]phenazin-5-ol (**3**). With this mechanism, MNPs-thioglycolic acid is an efficient catalyst for forming the olefin **11**, which is readily prepared *in situ* from Knoevenagel condensation of carbonyl groups of aldehyde or cyclic ketone **4**–**6** with **1**. The Michael addition of **3** with olefin **11** in the presence of MNPs-thioglycolic acid finally gives intermediate **12**, which then makes the inner molecular ring to be formed after a tautomeric proton shift to produce spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives **8** and **9**.



SCHEME 4 Proposed mechanism for the synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives

3 | CONCLUSIONS

In summary, we synthesized superparamagnetic nanoparticles of modified thioglycolic acid (γ-Fe_2O_3@SiO_2-SCH_2CO_2H) as a novel, efficient and reusable catalyst and characterized the catalyst using TGA, FT-IR spectroscopy, SEM, XRD, EDS and VSM. This newly synthesized catalyst was applied as a green heterogeneous organic acid for the efficient synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives through single-pot domino Knoevenagel–Michael–annulation reaction. The environmentally friendly methodology with excellent green chemistry credentials, such as using low loading of reusable, non-toxic, easy-to-handle catalyst, shorter reaction time without any by-product, avoidance of hazardous organic solvents and easy work-up (the catalyst can be easily separated from the reaction mixture using an external magnet), may find a wide range of applications. Furthermore, this attractive atom-economical protocol is expected to produce compounds exhibiting interesting pharmacological activities and may act as potential drug candidates, since phenazine, quinoxaline and chromene motifs have a vast range of biological activities.

4 | EXPERIMENTAL

4.1 | General

All melting points were determined with an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded with a Shimadzu IR-470 spectrometer. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyser at Iranian Central Research of Petroleum Company. Mass spectra were recorded with an Agilent Technology (HP) spectrometer operating at an ionization potential of 70 eV. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker DRX-400 Avance instruments with deuterated dimethylsulfoxide (DMSO-d_6) as solvent. TLC was performed on silica gel Polygram SILG/UV 254 plates. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620

energy dispersive spectrometer presenting a 133 eV resolution at 20 kV. Powder XRD was performed using a Bruker D8-advance X-ray diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation. All reagents and solvents were purchased from Merck and Aldrich and used without further purification.

4.2 | Synthesis of γ-Fe_2O_3

$FeCl_2{\cdot}4H_2O$ (0.802 g) and $FeCl_3{\cdot}6H_2O$ (2.184 g) were dissolved in water (10 ml) separately under argon atmosphere at 25 °C. $NH_3{\cdot}H_2O$ solution (0.7 M, 100 ml) was added dropwise in 5–10 min to the stirring mixture at 25 °C to adjust the reaction pH to 11. MNPs were collected using a powerful external magnet, decanted and, to remove all ions, washed three times with deionized water. Subsequently, tetramethylammonium hydroxide (1–2 ml) was added dropwise to the nanomaterials, stirred rapidly and then the precipitate collected. The dried precipitate of Fe_3O_4 was kept in a furnace for 3 h at 300 °C to afford a reddish-brown powder of γ-Fe_2O_3 nanoparticles.[44,45]

4.3 | Synthesis of γ-Fe_2O_3@SiO_2

A mixture of γ-Fe_2O_3 (2 g) in ethanol (40 ml) was sonicated for 30 min and then heated for 1 h at 40 °C. Then, TEOS (10 ml) was added to the reaction mixture, and continuously stirred for 24 h. The silica-coated nanoparticles were separated using an external magnet, washed three times with EtOH and diethyl ether and then dried in vacuum at 100 °C for 12 h.[45]

4.4 | Synthesis of chloro-functionalized γ-Fe_2O_3@SiO_2

An amount of 2 g of γ-Fe_2O_3@SiO_2 in 40 ml of dry toluene was sonicated for 45 min. Then 1 ml of 3-chloropropyltrimethoxysilane was added to the dispersed γ-Fe_2O_3@SiO_2 in toluene and heated and stirred at 100 °C for 24 h. MNPs were collected using a strong external magnet, washed with EtOH and diethyl ether three times, then dried at 40 °C in an oven for 12 h.[46]

4.5 | Synthesis of γ-Fe_2O_3@SiO_2@thioglycolic acid

A suspension of γ-Fe_2O_3@SiO_2 (1 g) in ethanol (15 ml) in a 50 ml round-bottom flask was sonicated for 30 min, and subsequently thioglycolic acid (1 ml) was added dropwise. Then, the reaction mixture was stirred at 25 °C overnight. Finally, precipitates were collected using an external magnet, washed three times with EtOH and diethyl ether and then dried for 12 h at 40 °C in an oven (Figure 2).

4.6 | General procedure for synthesis of novel spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine] and benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine derivatives (8, 9)

Compounds **1** (1 mmol) and **2a** (1 mmol), MNPs-thioglycolic acid (0.03 g) and 30 ml of EtOH–H_2O (1:1 *v*/v) were placed in a 50 ml round-bottomed flask mounted over a magnetic stirrer. The contents were stirred magnetically in an oil bath maintained at 70 °C until in less than 10 min compound **3** was formed. Then, **1** (1 mmol) and cyclic ketones **4/5/6** or aryl aldehyde **7** (1 mmol) were added to the reaction mixture which was heated further for the times reported in Tables 2 and 3. Upon completion of the reaction, monitored by TLC, the reaction mixture was diluted with hot ethanol and the catalyst was easily separated from the reaction mixture using an external magnet, washed with hot ethanol, dried and reused for a consecutive run under the same reaction conditions. Then, the reaction mixture was cooled to room temperature and the crude product obtained was collected by filtration and recrystallized from hot ethanol to afford the pure solids **8** and **9**.

4.7 | Analytical and spectroscopic data for unknown compounds

4.7.1 | Spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine-17,3′-indoline]-2′,11,16-trione (8a)

Orange solid; yield 92%, 0.489 g; m.p. 297–299 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3305, 2925, 1692, 1614, 1589, 1530, 1497, 1412, 1332, 1247, 1153, 1073, 767. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 6.64 (t, 1H, J = 6.8 Hz, Ar-H), 7.05 (t, 2H, J = 7.2 Hz, Ar-H), 7.13 (t, 1H, J = 7.6 Hz, Ar-H), 7.79 (t, 1H, J = 7.6 Hz, Ar-H), 7.93–8.11 (m, 7H, Ar-H), 8.28–8.30 (m, 1H, Ar-H), 8.60 (d, 1H, J = 7.6 Hz, Ar-H), 8.85 (d, 1H, J = 7.6 Hz, Ar-H), 9.29 (d, 1H, J = 8.0 Hz, Ar-H), 11.55 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 50.5, 108.5, 112.5, 115.8, 120.8, 121.4, 123.0, 125.3, 125.5, 128.0, 128.3, 128.5, 128.9, 129.9, 130.2, 130.8, 131.1, 132.0, 135.4, 140.3, 141.0, 143.6, 144.9, 146.7, 151.8, 153.4, 155.8, 169.5, 176.5, 177.8. MS (*m*/*z*, %): 531 (M^+, 5). Anal. Calcd for $C_{34}H_{17}N_3O_4$ (%): C, 76.83; H, 3.22; N, 7.91. Found (%): C, 76.98; H, 3.36; N, 8.12.

4.7.2 | Spiro[benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine-17,2′-indene]-1′,3′,11,16-tetraone (8b)

Orange solid; yield 88%, 0.479 g; m.p. 210 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3025, 1706, 1660, 1629, 1610, 1590, 1536,

1467, 1315, 1286, 1178, 1079, 758. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.64 (t, 1H, J = 7.2 Hz, Ar-H), 7.74 (d, 1H, J = 7.2 Hz, Ar-H), 7.90–7.99 (m, 6H, Ar-H), 8.11–8.16 (m, 3H, Ar-H), 8.24–8.28 (m, 2H, Ar-H), 8.63 (d, 1H, J = 8.0 Hz, Ar-H), 8.82 (d, 1H, J = 7.6 Hz, Ar-H), 9.20 (d, 1H, J = 6.0 Hz, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 67.5, 112.6, 116.2, 122.6, 122.9, 125.0, 125.4, 128.6, 129.2, 129.3, 129.9, 130.5, 130.6, 131.3, 131.8, 133.6, 134.6, 136.2, 139.1, 139.7, 141.7, 142.0, 145.7, 147.0, 152.2, 154.0, 156.5, 175.8, 177.8, 198.2. MS (*m/z*, %): 544 (M^+, 11). Anal. Calcd for $C_{35}H_{16}N_2O_5$ (%): C, 77.20; H, 2.96; N, 5.14. Found (%): C, 77.44; H, 3.08; N, 5.03.

4.7.3 | Spiro[benzo[*a*]benzo[6,7]chromeno [2,3-*c*]phenazine-17,11′-indeno[1,2-*b*] quinoxaline]-11,16-dione (8c)

Brown solid; yield 87%, 0.536 g; m.p. 163–165 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3035, 1716, 1660, 1587, 1537, 1448, 1327, 1262, 1192, 1038, 757. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.50 (d, 1H, J = 7.6 Hz, Ar-H), 7.70 (t, 2H, J = 7.6 Hz, Ar-H), 7.82–7.93 (m, 7H, Ar-H), 8.08 (d, 1H, J = 7.2 Hz, Ar-H), 8.12–8.18 (m, 3H, Ar-H), 8.20–8.31 (m, 3H, Ar-H), 8.45 (t, 1H, J = 7.2 Hz, Ar-H), 8.61 (d, 1H, J = 7.6 Hz, Ar-H), 9.17–9.29 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 45.3, 112.7, 115.4, 117.0, 122.2, 124.1, 125.3, 125.7, 127.1, 128.4, 129.2, 129.3, 129.4, 129.5, 130.0, 130.3, 130.4, 130.9, 132.4, 132.7, 133.8, 134.1, 136.9, 138.7, 139.1, 139.5, 140.9, 141.6, 142.0, 148.4, 151.7, 153.7, 155.8, 158.4, 177.1, 178.6. MS (*m/z*, %): 616 (M^+, 8). Anal. Calcd for $C_{41}H_{20}N_4O_3$ (%): C, 79.86; H, 3.27; N, 9.09. Found (%): C, 80.09; H, 3.12; N, 9.26.

4.7.4 | 8′-Methylspiro[benzo[*a*]benzo[6,7] chromeno[2,3-*c*]phenazine-17,11′-indeno[1,2-*b*] quinoxaline]-11,16-dione (8d)

Brown solid; yield 85%, 0.536 g; m.p. 182–184 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3045, 1715, 1661, 1589, 1535, 1447, 1326, 1263, 1192, 1005, 756. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.03 (s, 3H, CH_3), 7.47–7.62 (m, 1H, Ar-H), 7.66–7.74 (m, 2H, Ar-H), 7.77–7.93 (m, 7H, Ar-H), 8.03 (d, 1H, J = 8.4 Hz, Ar-H), 8.07–8.12 (m, 2H, Ar-H), 8.16–8.23 (m, 3H, Ar-H), 8.43–8.49 (m, 1H, Ar-H), 8.63 (d, 1H, J = 7.6 Hz, Ar-H), 9.19 (d, 1H, J = 8.4 Hz, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.3, 47.6, 111.7, 112.7, 115.9, 120.9, 121.5, 122.0, 122.9, 124.1, 125.9, 128.3, 128.4, 128.8, 129.2, 129.8, 130.0, 130.2, 130.4, 130.6, 131.5, 132.3, 132.4, 132.6, 134.0, 136.8, 139.0, 140.2, 140.3, 140.6, 141.5, 142.8, 147.6, 150.5, 154.8, 156.1, 158.3, 177.4, 177.6. MS (*m/z*, %): 630 (M^+, 3). Anal. Calcd for $C_{42}H_{22}N_4O_3$ (%): C, 79.99; H, 3.52; N, 8.88. Found (%): C, 79.81; H, 3.74; N, 8.79.

4.7.5 | 7′-Nitrospiro[benzo[*a*]benzo[6,7] chromeno[2,3-*c*]phenazine-17,11′-indeno[1,2-*b*] quinoxaline]-11,16-dione (8e)

Brown solid; yield 81%, 0.535 g; m.p. 220–223 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 2900, 1715, 1657, 1582, 1530, 1503, 1331, 1263, 1188, 1062, 758. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.67–7.69 (m, 2H, Ar-H), 7.74–7.80 (m, 5H, Ar-H), 7.86–7.90 (m, 3H, Ar-H), 7.92–7.95 (m, 1H, Ar-H), 8.00–8.09 (m, 3H, Ar-H), 8.25 (d, 1H, J = 8.8 Hz, Ar-H), 8.44 (d, 1H, J = 7.6 Hz, Ar-H), 8.52 (dd, 1H, J_1 = 9.2 Hz, J_2 = 2.4 Hz, Ar-H), 8.87 (d, 1H, J = 2.4 Hz, Ar-H), 9.39 (d, 1H, J = 8.0 Hz, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 44.7, 110.2, 112.1, 119.4, 120.2, 120.7, 122.9, 124.3, 125.3, 126.2, 126.9, 128.7, 129.3, 130.5, 130.7, 131.2, 131.8, 132.2, 132.7, 133.2, 133.7, 133.9, 136.0, 137.1, 138.9, 139.9, 140.2, 140.7, 141.5, 143.1, 147.7, 152.0, 156.0, 157.0, 177.6, 178.2. MS (*m/z*, %): 661 (M^+, 7). Anal. Calcd for $C_{41}H_{19}N_5O_5$ (%): C, 74.43; H, 2.89; N, 10.59. Found (%): C, 74.68; H, 3.10; N, 10.65.

4.7.6 | Spiro[benzo[*a*]benzo[6,7]chromeno [2,3-*c*]phenazine-17,6′-indeno[1,2-*b*]pyrido[3,2-*e*]pyrazine]-11,16-dione (8f)

Brown solid; yield 79%, 0.487 g; m.p. 269–271 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3015, 1714, 1660, 1583, 1531, 1495, 1327, 1283, 1185, 1038, 758. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.39 (d, 1H, J = 6.4 Hz, Ar-H), 7.63 (t, 1H, J = 8.4 Hz, Ar-H), 7.69–7.80 (m, 3H, Ar-H), 7.85–7.92 (m, 3H, Ar-H), 7.98–8.16 (m, 5H, Ar-H), 8.23 (d, 1H, J = 8.8 Hz, Ar-H), 8.30 (d, 1H, J = 8.4 Hz, Ar-H), 8.36–8.41 (m, 1H, Ar-H), 8.52–8.55 (m, 1H, Ar-H), 8.62 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz, Ar-H), 9.09–9.11 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 48.4, 111.9, 116.0, 117.5, 121.5, 122.4, 122.7, 123.2, 124.1, 124.2, 125.6, 126.1, 127.8, 128.1, 128.3, 128.9, 129.4, 129.6, 130.2, 130.5, 131.1, 131.3, 133.2, 134.0, 135.0, 137.8, 139.1, 139.7, 140.3, 141.1, 147.9, 151.8, 158.5, 159.3, 176.8, 178.2. MS (*m/z*, %): 617 (M^+, 5). Anal. Calcd for $C_{40}H_{19}N_5O_3$ (%): C, 77.79; H, 3.10; N, 11.34. Found (%): C, 78.04; H, 3.38; N, 11.51.

4.7.7 | 17-(3,4-dimethoxyphenyl)-11*H*–benzo [*a*]benzo[6,7]chromeno[2,3-*c*]phenazine-11,16 (17*H*)-dione (9j)

Brown solid; yield 85%, 0.468 g; m.p. 320–321 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 2995, 1682, 1635, 1588, 1509, 1455, 1358, 1264, 1161, 1022, 757. ^{1}H NMR (400 MHz,

DMSO-d_6, δ, ppm): 3.52, 3.71 (s, 6H, $2OCH_3$), 5.95 (s, 1H, CH), 6.64 (d, 1H, J = 8.8 Hz, Ar-H), 6.81 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz, Ar-H), 7.35 (d, 1H, J = 2.0 Hz, Ar-H), 7.76 (t, 1H, J = 7.6 Hz, Ar-H), 7.89–8.00 (m, 5H, Ar-H), 8.06 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz, Ar-H), 8.25 (d, 1H, J = 7.6 Hz, Ar-H), 8.30 (d, 1H, J = 8.0 Hz, Ar-H), 8.44 (d, 1H, J = 7.6 Hz, Ar-H), 8.66 (d, 1H, J = 8.0 Hz, Ar-H), 9.19 (d, 1H, J = 8.0 Hz, Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 33.0, 55.2, 55.4, 111.5, 113.5, 115.3, 120.2, 122.3, 124.6, 124.9, 125.6, 128.7, 129.1, 129.2, 129.8, 129.9, 130.2, 130.5, 130.7, 130.8, 130.9, 131.5, 135.3, 135.9, 140.2, 140.6, 141.5, 145.8, 147.3, 154.5, 156.1, 177.2, 178.1 ppm. MS (*m*/*z*, %): 550 (M^+, 9). Anal. Calcd for $C_{35}H_{22}N_2O_5$ (%): C, 76.35; H, 4.03; N, 5.09. Found (%): C, 76.50; H, 4.19; N, 5.18.

4.7.8 | 17-(4-hydroxyphenyl)-11*H*–benzo[*a*]benzo[6,7]chromeno[2,3-*c*]phenazine-11,16 (17*H*)-dione (9 k)

Yellow solid; yield 83%, 0.420 g; m.p. 301–303 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3030, 1685, 1631, 1571, 1506, 1435, 1364, 1287, 1164, 1084, 760. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 5.82 (s, 1H, CH), 6.50 (d, 2H, J = 8.8 Hz, Ar-H), 7.27 (d, 2H, J = 8.4 Hz, Ar-H), 7.22 (t, 1H, J = 7.6 Hz, Ar-H), 7.82–7.95 (m, 6H, Ar-H), 8.01 (dd, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz, Ar-H), 8.19 (td, 2H, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar-H), 8.34 (d, 1H, J = 7.6 Hz, Ar-H), 8.56 (d, 1H, J = 8.0 Hz, Ar-H), 9.11 (d, 1H, J = 7.6 Hz, Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 32.5, 114.5, 115.4, 116.3, 122.1, 124.5, 124.8, 125.5, 128.7, 128.8, 128.9, 129.0, 129.7, 129.9, 130.1, 130.4, 130.7, 130.8, 131.4, 133.9, 135.3, 139.9, 140.1, 140.5, 141.5, 145.7, 155.7, 155.8, 177.2, 177.9 ppm. MS (*m*/*z*, %): 506 (M^+, 12). Anal. Calcd for $C_{33}H_{18}N_2O_4$ (%): C, 78.25; H, 3.58; N, 5.53. Found (%): C, 78.48; H, 3.64; N, 5.29.

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SUPPORTING INFORMATION

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