Synthesis of Benzenesulfonamide Derivatives via Ring Opening of Aziridines in the Presence of Magnetically Retrievable Graphene Based (CoFe@rGO) Nanohybrid

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Abstract
Graphene based magnetic nanohybrids have engrossed considerable research curiosity because of their exceptional properties and diverse applications associated with green chemistry. In this regard, a practical, facile and regioselective preparation of 1,2-diamines from N-tosylaziridine/(S)-(+-)2-Benzyl-1-(p-tolylsulfonyl)aziridine and aryl amines in the presence of magnetically separable graphene based nanohybrid (CoFe@rGO) has been proposed under mild and solvent free conditions. The FT-IR, FE-SEM, XPS, XRD and TEM spectroscopic analysis confirmed the formation of the CoFe@rGO nanohybrids. For unsymmetrical aziridine, nucleophilic attack of aryl amines was observed to take place selectively at the more substituted carbon atom of aziridine ring. Environmentally benign, efficient, shorter reaction time, solvent-free conditions, low catalyst loading, excellent reaction yields and reusability of the catalyst for six consecutive runs without significant loss in its activity are the key advantages of this protocol.

Graphical Abstract

Keywords Graphene based nanohybrid · Magnetic nanocatalyst · Heterogeneous catalyst · Aziridine ring opening · Benzenesulfonamide derivatives products

Extended author information available on the last page of the article
1 Introduction

Sulfonamides as significant class of heterocyclic compounds have acquired massive pertinence in medicinal as well as in synthetic organic chemistry. Owing to the unique functional groups present in their structure, sulfonamides form the basis of several sulfa drugs and commonly employed as chemotherapeutic and preventive agents against several diseases [1]. Sulfonamides as efficacious pharmacophores display a wide variety of biological activities such as anti-fungal, anti-bacterial, anti-thyroid, anti-inflammatory and anti-viral etc. (Fig. 1) [2]. Besides this, these are also extensively utilized in organic materials, agriculture and dyes [3]. Reflecting their diverse significance, different methodologies have been reported in the literature for the synthesis of sulfonamides [4–6]. However, efficient, environmentally benign, and green approach for the synthesis of sulfonamides from cheap and easily available starting materials is still desirable. One of the most straightforward synthetic approaches for the synthesis of sulfonamides derivatives is via ring opening of aziridines.

Aziridines, a three-membered heterocyclic compound, is an integral component of organic synthesis that possesses proton accepting properties, high rigidity and potential reactivity. Because of these attributes, aziridines act as precursors in the synthesis of organic, pharmaceutical and natural products [7]. Amongst substituted aziridines, N-aryl sulfonyl aziridines have attracted considerable attention owing to their susceptibility towards regio and stereoselective nucleophilic ring opening and ring expansion reactions [8–11]. The nucleophilic ring opening reaction of aziridines with various heteroatomic O-, N- and S-centered molecules such as amines, aldehydes, phenols, alcohols, thiols, silylate yields biologically active compounds such as alkaloids, heterocycles and amino acids [12]. Considering the biological significance of ring opening of aziridines, a variety of catalytic systems are reported in the literature employing a range of homogeneous and heterogeneous catalysts with varying degrees of efficiency. Very recently, Liu et al. [7] employed zinc based catalytic system for the regioselective ring opening of 2, 3-aziridinyl alcohols using aromatic amines and thiophenols as nucleophiles. Ghorai and co-worker, [13] reported an efficient synthesis of biologically important imidazoline and oxazolines via ring opening of the activated aziridines and epoxides with various amines, and a subsequent condensation with aldehydes under mild reaction conditions. Ghosal et al. [14] reported imidazole-based zwitterionic molten salt for the regioselective ring opening of aziridine with indoles, pyrroles, methanol, ethanol, acetic acid and di-iso-propylamine. Similarly, Huang et al. [15] opted green process for synthesis of vicinal diamines via the ring opening of aziridines with amines without the aid of any catalyst and solvent. Despite their specific selectivity and efficiency for ring opening of aziridines, majority of these methodologies experience several drawbacks such as use of expensive and hazardous reagents, non-recyclable catalysts, use of volatile and toxic solvents, extensive reaction time, long reaction times, harsh reaction conditions, tedious workup procedures and low product yields [16, 17]. Therefore, the exploration of such protocol which is energy efficient, environmentally benign, facile, solvent free, and apparently separable are the current need of hour for the ring opening of aziridines.

In this regard, nano catalysis, which involves nanoparticles as heterogeneous catalysts has came to the forefront for carrying out various organic transformations in an environmentally benign manner. For this purpose, a diverse array of nanomaterials such as transition metals, transition metal oxides, composites of metals with organic moieties and carbon based nanostructures have been employed as versatile heterogeneous catalyst due to the several interesting properties such as high surface to volume ratio, great selectivity, high stability, surface modifiability, great biocompatibility etc., [18, 19].

Nowadays, carbon nanomaterials, in particular, the ones based on graphene have acquired enormous attention from material science and catalysis chemists; as a viable catalyst to carry out several organic transformations. Amongst these materials, reduced Graphene oxide (rGO), has emerged as an excellent heterogeneous catalyst, because of its remarkable
characteristics such as large specific surface area, high thermal stability, exceptional structural and electronic properties. Interestingly, rGO possesses several polar functional groups such as hydroxyl, epoxy and carboxyl groups, which imparts hydrophilicity and water solubility to rGO [20–22]. Therefore, rGO has proved to be a competent material for a wide range of catalytic reactions such as Friedel-Craft acylation, hydrogenation, ring opening reaction of epoxides, oxidation-reduction reactions, aerobic oxidation of alcohol etc. [23–25]. However, the separation of rGO from the reaction mixture without causing any secondary pollution has remained a challenge for research community [26]. The recyclability problem can be well addressed by amalgamation of magnetic nanoparticles with rGO, resulting in the fabrication of environmentally benign nanohybrid with simplified isolation of product, facile recovery and recyclability of catalyst [27]. The incorporation of magnetic nanoparticles with rGO not only provides magnetic nature to nanohybrid but also enhances catalytic performance of nanohybrid due to the synergistic interactions between the rGO and magnetic nanoparticles. Based on the same approach, Rouhani et al. synthesized laccase immobilized Fe₃O₄-GO nanocomposite as recyclable nano-biocatalyst for the synthesis of sulfonamide derivatives via oxidative coupling of 2.3 dihydrophthalalazine-1.4-dione with sodium benzene sulfonates [28].

In the present work, graphene based magnetically retrievable (CoFe@rGO) nanohybrid has been synthesized via easy and scalable hydrothermal method. For the first time, CoFe@rGO nanohybrid has been utilized as promising heterogeneous catalyst for the one step construction of benzensulfonamides derivatives via ring opening reaction of N-Tosylaziridine and (S)-(+)-2-Benzyl-1-(p-tolysulfonyl) aziridine with different aromatic amines under solvent free conditions. The catalyst drove the reaction to completion in 9–24 min and afforded good yield (64–92%). As compared to other conventional catalysts, CoFe@rGO nanohybrid exhibited better stability, negligible leaching, good recyclability, and no deactivation of the nanohybrid catalyst.

2 Experimental Section

2.1 Materials Used

Potassium permanganate (KMnO₄), Ferric nitrate nonahydrate [Fe(NO₃)₃-9H₂O, 98%] and Cobalt nitrate hexahydrate [Co(NO₃)₂-6H₂O, 98%] were obtained from Central Drug House (CDH). Hydrogen peroxide (H₂O₂, 30% w/v) and Sodium nitrate (NaNO₃) were purchased from Fisher scientific, and Graphite flakes were purchased from Otto chemicals. Liquor ammonia (Liq. NH₃) and Sulphuric acid (H₂SO₄) and were obtained from Merck. N-Tosylaziridine and (S)-(+)-2-Benzyl-1-(p-tolysulfonyl) were obtained from Sigma Aldrich. All the other mentioned chemicals were of analytical grade and were used as bought without any further refining. All the solutions were prepared in deionized water obtained from an ultrafiltration system (Milli-Q, Millipore).

2.2 Synthesis of Nanocatalysts

2.2.1 Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) was fabricated using graphite flakes as the starting substrate by following modified Hummer’s method [29]. In a typical synthetic procedure, 3 g of graphite powder was mixed with 70 mL of concentrated H₂SO₄ under constant stirring at a temperature below 0 °C in order to avert overheating and explosion. Then, preset amount of KMnO₄ (9 g) and NaNO₃ (1.5 g) were introduced in to the reaction mixture in a duration of 30 min with simultaneous continual stirring while maintaining the temperature of the reaction mixture at −4 °C. The reaction mixture was then magnetically stimulated for an additional 24 h at room temperature. Afterwards, the reaction mixture was diluted by adding deionized water and ultimately 18 mL of H₂O₂ was gradually added to the reaction mixture in anticipation of the change of colour of the reaction mixture from brown to yellow, which stipulated the completion of oxidation of graphite to graphene oxide. The resultant mixture was washed several times with deionized water until the pH of the solution became neutral and the obtained product was then filtered and dried at 80 °C for 10 h.

2.3 Synthesis of CoFe@rGO Nanohybrids

A simplistic hydrothermal methodology was employed for the fabrication of CoFe@rGO nanohybrid as depicted in Scheme 1 [30]. In our previous work [23], cobalt ferrite and rGO based heterogeneous catalysts were examined for their catalytic activity for the ring opening of epoxides and it was inferred that 20 wt% loading of cobalt ferrite in rGO showcased best catalytic performance. So, for the present work, the relative quantity of cobalt ferrite was fixed to 20 wt% to that of GO. To fabricate the nanohybrid, graphene oxide (GO) was initially dispersed in deionized water utilizing ultrasonic technique. Then, stoichiometric amounts of metal nitrates [Fe(NO₃)₃ and Co(NO₃)₂; 0.02 M] were dissolved in slightest amount of water, and pH of the solution was adjusted to 7.5 with liquid ammonia. Subsequently, aqueous graphene oxide (GO) suspension was added to the metal nitrate solution with continuous stirring for 2 h. The resulting solution was then transferred to a Teflon lined autoclave and the autoclave was kept at 160 °C for 15 h in a hot air oven. The obtained precipitates were systematically washed with acetone and deionized water and dried at 60 °C overnight. The obtained nanohybrid was labelled as CoFe@rGO.
2.4 Plausible Mechanism for Formation of CoFe@rGO Nanohybrids

The plausible mechanistic illustration for the formation of CoFe@rGO nanohybrids are depicted in Fig. 2. The surface of GO possesses negative charge due to the presence of abundant oxygen carrying functional groups such as carboxy, epoxy and hydroxyl groups. When the negatively charged GO suspension was mixed with salts solution of cobalt and iron cations, the cations get adsorbed on the surface of GO sheets with high density of negative charges via electrostatic interactions, which leads to the formation of CoFe@rGO nanohybrids [31].

2.5 Physical Characterization Techniques

Several techniques were employed for the characterization of the synthesized CoFe@rGO nanohybrid. The crystallographic structure of the catalyst was examined on a Panalytical’s X’pert Pro X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å), with the range of scanning angle (2θ) varying from 10° to 80°. In order to confirm the functional groups present in the synthesized materials, Fourier Transform Infra-red (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum RX-IIFTIR spectrophotometer in the scan range of 4000–400 cm⁻¹. The samples were prepared with KBr pellets. The surface morphology of the material was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi-SU8010). Transmission electron microscope analysis was performed using FEI TECNAI G2F20 instrument working at 200 keV and 0.2 Å resolution. The specific surface area of the nanohybrid was obtained by using Brunauer–Emmett–Teller (BET) surface area analyser [(11-2370) Gemini, Micromeritics, USA]. The magnetic studies were performed using vibrating sample magnetometer (MicroSense EZ7). The surface states of the CoFe@rGO nanohybrid were obtained by X-ray photoelectron spectroscopy (XPS) using PHI 5000 VersaProbe III spectrometer. Thin layer chromatography (TLC) was performed by using pre-coated silica 60 F254, 0.25 mm aluminium plates (purchased from Merck) and the progress of the reactions was visualized and studied under UV chamber. The efficacious fabrication of desired product was confirmed by nuclear magnetic resonance (NMR) spectrometer (BRUKER AVANCE II 400 MHz) utilizing CDCl₃ as solvent and TMS as an internal standard.
2.6 Catalytic Assessment

Pristine GO as well as CoFe@rGO nanohybrid were employed for the catalytic study of the ring opening of N-Tosylaziridine and (S)-(+)2-Benzyl-1-(p-tolylsulfonyl) aziridine with aromatic amines. The reactions were performed between equimolar amounts of amine (1 mmol) and aziridine (1 mmol) in the presence of GO and CoFe@rGO nanohybrid as catalyst (10 mg) at 80 °C under solvent-free conditions. The progress of the reaction was monitored by thin layer chromatography. After the consumption of the starting materials, the catalysts were separated from the reaction mixture by external magnet, washed with deionized water and acetone to remove the organic or inorganic part from the catalysts. The recovered catalysts were dried and recycled for next cycle. The final isolated products were characterized by 1H NMR.

3 Results and Discussion

3.1 Characterization of the Nanohybrid

3.1.1 FT-IR Spectroscopy

FT-IR spectra aids in the identification of different functional groups existing in the crystal lattice of catalysts by analyzing and examining their particular vibrational modes. FT-IR technique was therefore used to confirm the presence of oxygen containing functionalities in GO and their variations after the formation of nanohybrid. The FT-IR spectra of pure GO and CoFe@rGO nanohybrid are shown in Fig. 3. A broad peak around 3400 cm⁻¹ was observed, which could be ascribed to the stretching vibration of O–H bonds of carboxyl and hydroxyl moieties existing in the structure of GO. Moreover, the characteristic peaks around 1725, 1620, 1415, 1220 and 1088 cm⁻¹ were observed, which could be assigned to stretching modes of C=O, aromatic C–C, carboxyl C–O, epoxy C–O and alkoxy group, respectively [32]. The spectra of CoFe@rGO nanohybrid shows all the characteristic peaks of GO, except the peaks around 1625–1725 and 1150 cm⁻¹ corresponding to the oxygen containing functional groups, which clearly indicates the complete reduction of GO to rGO [34]. Though, the diffraction peak corresponding to rGO was not observed in the XRD pattern of the nanohybrid which could be attributed to the disorder and damage generated in its layered structure by the crystal development of ferrite nanoparticles in its interlayers [35, 36]. The average crystallite size of the synthesized nanohybrid and of pristine GO were evaluated from the broadening of most intense peak i.e. the one corresponding to (311) plane employing Debye–Scherrer equation [37].

\[
D_{hkl} = \frac{k\lambda}{\beta\cos\theta}
\]

where \(D_{hkl}\) is the crystallite size, \(k\) is the Scherrer’s constant with a value of 0.9, \(\lambda\) is the wavelength of radiation used, \(\beta\) is the full width at half maxima of the diffraction peak (FWHM) and \(\theta\) is the angle of diffraction. The values of crystallite size (\(D_{hkl}\)) were observed to lie in the range of 7–12 nm as shown in Table 1. Le Bail refinement method was employed to compute the lattice parameter (a) values of the synthesized materials and results are summarized in Table 1.
3.1.3 Morphological Studies

E-SEM technique was exploited to visualize the morphological details of the synthesized nanohybrid. The typical FE-SEM micrographs of CoFe@rGO nanohybrid at different nanometric resolutions are given in Fig. 5. FE-SEM micrographs display the layered structure of rGO with a random distribution of CoFe₂O₄ nanoparticles on the edges and surface sheets of graphene. Furthermore, FE-SEM micrographs of nanohybrid clearly indicate that CoFe₂O₄ nanoparticles remain adhered to the surface of rGO besides stirring and long period of sonication, signifying strong interaction between CoFe₂O₄ nanoparticles and rGO. Owing to the combined effect of large surface area and layered structure contributed by rGO in the nanohybrid, there occurs an enhancement in the exposure of active sites of nanoferrites, which eventually improves the catalytic efficiency of nanohybrid [38–40].

Additionally, EDX spectra was recorded to confirm the elemental composition of the synthesized nanohybrid as shown in Fig. 5d, which established the existence of desired elements only. The EDS pattern of sample unveiled the presence of Co, Fe, O and C correspondent with the elemental composition of cobalt ferrite and GO. The peak corresponding to C was instigated owing to the basal plane of rGO, and the existence of O could be ascribed to the oxygen present.
in ferrite NPs and oxygen containing functional groups of rGO. No additional peaks corresponding to other elements were observed which further confirmed the purity of the synthesized nanohybrid. The elemental mapping of CoFe@rGO nanohybrid has been illustrated in Fig. 6 which disclosed the uniform distribution of all the essential elements present in the samples.

Furthermore, TEM micrographs was used to provide the detailed structural analysis of CoFe@rGO nanohybrid in terms of morphology, particle size, crystallinity. Figure 7a and b displays the TEM images of CoFe@rGO nanohybrid. The images reveal the rippled structure of rGO sheets which may be prompted by the deformation during the exfoliation and restacking process. Moreover, CoFe$_2$O$_4$ nanoparticles with an average size of around 10 nm were observed to be uniformly distributed on the surface of rGO sheets, without any significant aggregation. The size data acquired from distribution of nanoparticles from TEM image (b) is in close agreement with the D value computed from the Debye–Scherrer equation. SAED analysis was further employed to confirm the crystalline nature of the nanohybrid, which shows concentric light and dark diffraction rings in correspondence to different diffraction planes. The occurrence of concentric diffraction rings in typical SAED pattern (Fig. 7c) ascertains the crystallinity of CoFe@rGO nanohybrid and all the diffraction planes perceived from SAED pattern corresponds to the planes observed in the XRD pattern of the nanohybrid.

3.1.4 Surface Area Investigation

It is eminent that surface area is the most imperative factor for catalysis. Large surface area value of catalyst signifies the presence of more number of active sites for the catalytic reaction. BET analysis was performed for the determination of specific surface area of GO and the fabricated nanohybrid. Before BET analysis, the samples were preheated at 150 °C for 1 h before N$_2$ absorption. Afterwards, the values of total
surface area (S) and specific surface area ($S_{BET}$) were calculated using following equations [24]

$$S = \frac{Q_m N_S}{V} \quad (2)$$

$$S_{BET} = \frac{S}{M} \quad (3)$$

The obtained values of specific surface area of GO and CoFe@rGO were 4.80 and 51.80 m$^2$g$^{-1}$, respectively. It can be clearly seen that the integration of GO and CoFe$_2$O$_4$ resulted in significant enhancement in the specific surface area value. The high specific surface area of the nanohybrid support the augmented catalytically active surface sites resulting in enhancement of catalytic efficacy [41]. The BET plots for GO and CoFe@rGO are shown in supplementary file as Figs. S23 and S24, respectively.

3.1.5 Magnetic Measurements

The magnetic characteristics of the synthesized nanohybrid were examined by recording the room temperature hysteresis loop with the help of vibrating sample magnetometer as shown in Fig. 8. The computed values of saturation magnetization ($M_s$), coercivity ($H_c$), remanence ($M_r$) and squareness ratio ($S_q$) for the synthesized nanohybrid are listed in Table 2. The saturation magnetization value was observed to decrease in comparison to pure CoFe$_2$O$_4$ [42] with addition of rGO but still the sample was sufficiently magnetic to be facely recovered with the help of an external magnet.

3.1.6 X-Ray Photoelectron Spectroscopy (XPS)

To anticipate the presence of desired elements and their corresponding valence states in nanohybrids, high resolution XPS spectra were investigated. The characteristic binding energy peaks corresponding to C 1s, O 1s; and C 1s, O 1s, Fe 2p and Co 2p were examined along with survey scans for GO and CoFe@rGO, respectively, as illustrated in Fig. 9. The survey scan for GO and CoFe@rGO are depicted in Fig. 9a and e, confirming the presence of desired elements at their characteristic binding energy values. The C 1s spectra, as shown in Fig. 9b and f reveals the presence of characteristics peaks around 284.7, 285.2 and 287.0 eV, conforming the presence of several functional groups (C=O, C=C and C–C bonds of aromatic rings). In the XPS spectra of O 1s
Ring opening reactions of aziridine were carried out between aziridine and different aromatic amines using CoFe$_2$O$_4$ GO and CoFe@rGO as heterogeneous catalysts at 80 °C under solvent free conditions. To signify the efficiency of the catalyst, a blank reaction was also performed between Aniline and N-tosylaziridine under similar reaction condition without using any catalyst and 41% yield of 4-Methyl-N-[2-(phenylamino) ethyl] benzene sulfonamide (3a) was observed even after stirring of reaction mixture for 120 min. The reaction mixture was continued to stirring for prolonged time but even then there was no increase in the conversion of reactants. The best results were obtained when CoFe@rGO nanohybrid was used as a catalyst since the reaction was completed in a comparatively shorter time duration as compared to CoFe$_2$O$_4$ and GO nanoparticles.

The scope of the protocol was probed for different aryl amine substrates with N-tosylaziridine as shown in Fig. 10. Distinct aryl amines having electron releasing as well as withdrawing groups on the ring were tested. The desired ring opening products were obtained with good to excellent yields within a very few minutes. The reactions were very quick in case of aryl amines having electron releasing groups such as p–OCH$_3$ and p–CH$_3$ group on the aryl ring (Fig. 10, amines 1h, 1i). Aryl amines having electron withdrawing groups such as p–Cl, p–Br and p–I group on the aryl ring took little longer to undergo ring opening reactions (Fig. 10, amines 1c, 1e, and 1g). In addition, the ring opening of aziridine with hindered aryl amines such as 2-chloroaniline, 2-bromoaniline and 2-iodoaniline were also studied which gave the corresponding products in good to excellent yields (Fig. 10, amines 1b, 1d and 1f). Further, in case of aromatic amines (1j, 1k), the reaction was observed to be really fast which can be credited to increased resonance in these compounds. The list of products (3a–k) obtained from the different aryl amine substrates with N-tosylaziridine are displayed in Table 3. The $^1$H NMR spectra of products 3a–k are given in supplementary file as Figs. S1-S11.

With successful completion of the ring opening of aziridine, similar methodology was applied for the regioselective ring opening of chiral (S)-(+)2-Benzyl-1-(p-tolylsulfonyl) aziridine 4 under solvent free conditions (Fig. 11.) The reaction was also performed between aniline and (S)-(+)2-Benzyl-1-(p-tolylsulfonyl)aziridine without using any catalyst and 33% yield of 4-Methyl-N-(3-phenyl-2-(phenylamino) propyl) benzenesulfonamide (5a) was obtained after stirring reaction mixture for 120 min. However, stirring of the reaction mixture for prolonged time did not increase the conversion of reactants. The best results was achieved using CoFe@rGO nanohybrid as catalyst for the ring opening reaction of chiral (S)-(+)2-Benzyl-1-(p-tolylsulfonyl)aziridine at at 80 °C under solvent free conditions. For unsymmetrical aziridine 4, regioselective nucleophilic substitution of aryl amines occured at the more substituted aziridine site due to

![Graph](image_url)
Fig. 9 The XPS survey scans and typical high resolution (deconvoluted) XPS plots of C (1s), O (1s), Co 2p and Fe 2p for (a–c) GO and (d–h) CoFe@rGO nanohybrid
the presence of electron releasing benzyl group which stabilizes the compound during N–C bond cleavage. The substrate scope of this ring opening reaction was investigated by using unsymmetrical aziridine 4 and various aryl amines (1a–1k) as shown in Fig. 11. Again, different aryl amines having electron releasing as well as withdrawing groups on the ring were tested. It was observed that the reaction time for the ring opening of aziridine was shorter for aryl amines with electron releasing group such as $\text{p-OCH}_3$ and $\text{p-CH}_3$ group on the aryl ring (Fig. 11, amines 1h-1i). Aryl amines with electron withdrawing group such $\text{p-Cl}$, $\text{p-Br}$ and $\text{p-I}$ group on the aryl ring took little longer to undergo ring opening reactions (Fig. 11, amines 1c, 1e, and 1g).

Amongst halogens, the iodine substituted amines possessed least reaction time which was followed by bromine and then chlorine derivatives. Moreover, it was observed that the rate of reaction was not affected by the position at which halogens were attached. Among the different types of aziridine, it was speculated that the time taken was quite less for the reactions of unsymmetrical $N$-tosylaziridine with all aromatic amines. This can be attributed to the presence of electron releasing –$\text{CH}_2$–$\text{Ph}$ group in the unsymmetrical aziridine which stabilizes the carbocation formed during the activation of aziridine by catalyst ring opening and hence, decreases the reaction time. Moreover, it was observed in Figs. 10 and 11. That amine 1k gave product in 65 and 64% yield respectively. This can be understood on the basis of structure of 1-aminoanthraquinone which has three aromatic rings that hinder the completion of the reaction. The list of products (5a–k) obtained from the different aryl amine substrates with (S)-(+) 2-Benzyl-1-(p-tolylsulfonyl)aziridine are displayed in Table 3. The $^1$H NMR spectra of products 5a-k are given in supplementary file as Figs. S12–S22.

The catalytic activity of the synthesized nanohybrid for the ring opening of aziridines was compared with previous reports available in literature. Zhang et al. [46] reported methylquinoline promoted oxidative ring opening of substituted $N$-sulfonyl aziridines with dimethyl sulfoxide (DMSO) to furnish the corresponding $\alpha$-amino aryl ketones with 60–92% yield in 10 h. Similarly, Zhang et al. [47] developed regioselective ring opening of aziridines initiated by aryldiazonium ion at room temperature. The ring opening reaction between 2-phenyl-1-tosylaziridine and methanol in the presence of aryldiazonium tetrafluoroborate and dichloromethane as solvent displayed the formation of ethylamine products with 82–97% yield in 18 h. In context with literature, the present study presented superior results for the ring opening of aziridines in terms of shorter reaction time, solvent free conditions simple work-up, excellent reaction yields and magnetic recyclability of catalyst.

### 3.3 Plausible Mechanistic Pathway

Based on the literature survey [48–50], the plausible reaction mechanism for the ring opening of aziridine upon interaction with amine moieties has been proposed in Figs. 12, 13 and 14. The ring opening of aziridine with aromatic amine was carried out using three different catalysts i.e. spinel ferrites, graphene oxide (GO) and their nanohybrid (CoFe@rGO). The catalytic activity of these...
Table 3  Benzene sulfonamide derivatives product for the ring opening of N-tosylaziridine and (S)-(−)-2-Benzyl-1-(p-tolylsulfonyl)aziridine with aromatic amine (1a–k)

| Product | List of products (3a-k) and (5a-k) |
|---------|----------------------------------|
| 3a      | ![Image of product 3a](image3a)   |
| 3b      | ![Image of product 3b](image3b)   |
| 3c      | ![Image of product 3c](image3c)   |
| 3d      | ![Image of product 3d](image3d)   |
| 3e      | ![Image of product 3e](image3e)   |
| 3f      | ![Image of product 3f](image3f)   |
| 3g      | ![Image of product 3g](image3g)   |
| 3h      | ![Image of product 3h](image3h)   |
| 3i      | ![Image of product 3i](image3i)   |
| 3j      | ![Image of product 3j](image3j)   |
| 3k      | ![Image of product 3k](image3k)   |
| 5a      | ![Image of product 5a](image5a)   |
| 5b      | ![Image of product 5b](image5b)   |
| 5c      | ![Image of product 5c](image5c)   |
| 5d      | ![Image of product 5d](image5d)   |
| 5e      | ![Image of product 5e](image5e)   |
| 5f      | ![Image of product 5f](image5f)   |
| 5g      | ![Image of product 5g](image5g)   |
| 5h      | ![Image of product 5h](image5h)   |
| 5i      | ![Image of product 5i](image5i)   |
| 5j      | ![Image of product 5j](image5j)   |
| 5k      | ![Image of product 5k](image5k)   |
catalysts can be accredited to the presence of acidic sites on their surface. Initially, adsorption of aziridine occurs on the surface of catalysts which leads to an increase in the electrophillicity of one of the cyclic carbon atom in the molecule. Further, aryl amine attacks at the more substituted carbon atom of aziridine to give transition state (I), which transfers proton within the molecule to produce the desired product.

3.4 Stability Studies of CoFe@rGO Nanohybrid

CoFe@rGO nanohybrid possesses great stability when stored in dark place at room temperature. The stability of the synthesized nanohybrid was probed for the ring opening of N-tosylaziridines with aniline consecutively after an interval of 10 days for next 30 days (Fig. 15). It was observed that there was no significant change in the catalytic activity of the nanohybrid which depicts the highly stable nature of CoFe@rGO nanohybrid.

3.5 Recyclability

The stability of the catalyst is of utmost importance to be utilized in large scale industrial synthetic processes. Due to the magnetic nature of the synthesized nanohybrid, the catalyst could be easily recycled and reused for the ring opening of aziridine. Tremendous stability and recyclability are the noteworthy features of the synthesized CoFe@rGO nanohybrid. After completion of the reaction, the catalyst was recovered from the reaction mixture by an external magnet, washed with distilled water and acetone. The obtained material was then dried and subsequently reused for six catalytic cycles. Even after six catalytic cycles, no significant decrease in the percentage yield was observed for ring opening of N-tosylaziridine with aniline indicating excellent reusability of the nanohybrid (Fig. 16). The recovered catalyst was characterized by powder X-ray diffraction and FT-IR, after each catalytic run, no significant change in the nanohybrid was observed signifying high durability of the nanohybrid. The powder XRD pattern and FT-IR spectra of

\[x + y \rightarrow z + w\]

Fig. 11 Reaction completion time and % yield for the ring opening of (S)-(−)-2-Benzyl-1-(p-tolylsulfonyl)aziridine (4) with various aromatic amines (1a–k) in the presence of CoFe₂O₄, GO and CoFe@rGO nanohybrid. Reagents and conditions: aniline derivatives (1 mmol), (S)-(−)-2-Benzyl-1-(p-tolylsulfonyl)aziridine (1 mmol), CoFe₂O₄, GO and CoFe@rGO nanoparticles (10 mg)
the recovered nanohybrid has been provided in supplementary file (Figs. S25, S26).

4 Conclusions

In conclusion, graphene based magnetic nanohybrid (CoFe@rGO) was successfully synthesized through a facile hydrothermal method and was characterized by various standard techniques. The FT-IR, FE-SEM, XPS, XRD and TEM spectroscopic analysis confirmed the proficient fabrication of CoFe@rGO nanohybrid. The formation of single phase cubic structure of CoFe$_2$O$_4$ with Fd-3m space group was confirmed by powder XRD pattern and absence of diffraction peak corresponding to (011) plane specified the complete reduction of GO to rGO in the nanohybrid. It has been demonstrated that CoFe$_2$O$_4$, GO and CoFe@rGO nanohybrid are efficient catalysts for the ring opening of symmetrical and unsymmetrical aziridine with several amines under solvent free conditions. The nanohybrid CoFe@rGO displayed best catalytic activity for the conversion of different aromatic amines to corresponding 1,2-diamines within very short reaction duration. Benzensulfonamides derivatives via ring opening reaction of N-Tosylaziridine
with different aromatic amines were obtained with good to excellent yields within 10–24 min and ring opening of chiral (S)-(+)-2-Benzyl-1-(p-tolylsulfonyl)aziridine with different aromatic amines gave products with 64–92% yields within 9–18 min. Due to the magnetic nature of the nanohybrid, the catalyst could be easily separated from the reaction mixture by an external magnet and reused up to six catalytic runs without significant loss of catalytic activity. This developed methodology exhibits numerous remarkable advantages such as eco-friendly and benign conditions, short reaction times, simple work-up, perfect regioselectivity, excellent yields and the use of recyclable and reusable magnetic nanocatalyst. Thus, in near future, the synthesized magnetic nanohybrid could be potentially utilized as green catalyst for the synthesis of several pharmaceutical and intermediate chemicals.

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**Author Contributions** AS: Experimental work and writing manuscript. K: Experimental work. JK: Writing and Data analysis. PK: Experimental work. JA: review and editing. VK: HRTEM Characterization. SB: XPS Characterization. KBT: HRTEM Characterization. SS: Writing—review & editing.

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Declarations

Conflict of interest There are no conflict of interest to declare.

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