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A Greener Approach for the Chemoselective Boc Protection of Amines Using Sulfonated Reduced Graphene Oxide as a Catalyst in Metal- and Solvent-Free Conditions

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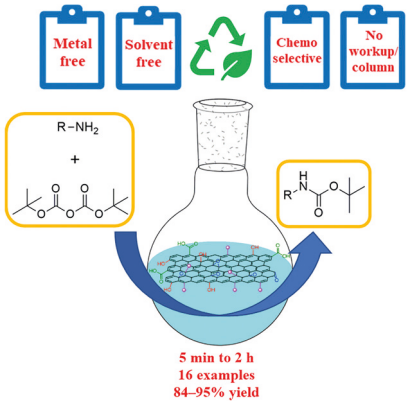
This research article is dedicated to Prof. S. Chandrasekaran, Department of Organic Chemistry, Indian Institute of Science, Bangalore, India on the occasion of his 74th birthday



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Abstract Sulfonated reduced graphene oxide (SrGO) has displayed great potential as a solid acid catalyst due to its efficiency, cost-effectiveness, and reliability. In this study, SrGO was synthesized by the introduction of sulfonic acid-containing aryl radicals onto chemically reduced graphene oxide using ultrasonication. The SrGO catalyst was characterized by Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). Further, SrGO was effectively utilized as a metal-free and reusable solid acid catalyst for the chemoselective *N*-*t*-Boc protection of various aromatic and aliphatic amines under solvent-free conditions. The *N*-*t*-Boc protection of amines was easily achieved under ambient conditions affording high yields (84–95%) in very short reaction times (5 min–2 h). The authenticity of the approach was confirmed by a crystal structure. The catalyst could be easily recovered and was reused up to seven consecutive catalytic cycles without any substantial loss in its activity.

Key words Boc protection, sulfonated reduced graphene oxide, solvent-free, metal-free, heterogeneous catalysis

A wide range of biologically active compounds contain amine groups, which makes their protection and deprotection an attractive and widely used strategy in organic and medicinal chemistry.[1] With the discovery of peptide nucleic acids (PNAs) by Nielsen, protecting groups that are compatible with Fmoc-mediated solid-phase synthesis and which can be removed under acidic or neutral conditions are required.[2] Boc protection strategy fits this criterion perfectly, because it can withstand mild acidic as well as neutral conditions, also it is stable against nucleophiles under basic conditions.[3] It can be further extended to the synthesis of DNA-peptide conjugates.[4] The commercially available $(Boc)_2$ is popularly used for masking amines with *tert*-butoxycarbonyl (Boc) group. Conventionally, several base-mediated strategies like the reaction of amine with $(Boc)_2$ in the presence of DMAP,[5] 2-*tert*-butyloxycarbonyloxyimino-2-phenylacetonitrile in the presence of Et_3N in H_2O–1,4-dioxane,[6] 4-dimethylamino-1-*tert*-butoxycarbonylpyridinium chloride/tetrafluoroborate in aqueous NaOH,[7] *tert*-butyl-2-pyridyl carbonate in the presence of Et_3N in H_2O–DMF,[8] and *tert*-butyl-1-chloroalkyl carbonates in the presence of K_2CO_3 in H_2O–THF[9] have been used. These procedures are associated with several setbacks such as toxicity of DMAP,[10] particular efforts required for the preparation of *tert*-butoxycarbonylation reagents,[6–9] formation of side products like urea,[5d] isocyanates[11] and *N*,*N*-di-Boc derivatives.[12] There have been reports where catalysts like β-cyclodextrin in water[13] and NaI in THF[14] have been used. Also, in the past few years, several Lewis acid mediated procedures[15] have been reported. Lewis acid mediated protocols have a major problem of non-recoverability and non-reusability. Recently, heterogeneous catalysts like sulfonic-acid-functionalized silica,[16] Montmorillonite K10 and Montmorillonite KSF,[17] ZnO nanorods,[18] Amberlyst® A21,[19] V_2O_5/SnO_2,[20] etc. have been used for the *N*-*t*-Boc protection of amines. These catalysts can be easily recovered and recycled. There have also been reports where solvent-free[18–20,21,22] or catalyst-free[23,24] conditions have been employed. Looking at the environmental concerns attached with the use of metals, some metal-free[13,19,25] protocols have been reported in the literature. Interestingly, Chakraborti and co-workers reported organocatalysis by ionic liquids based on 1-alkyl-3-methylimidazolium cation for chemoselective *N*-*tert*-butyloxycarbonylation of amines.[25] Though, these methods have proven to be valuable but keeping in perspective the frequent applications of *N*-*tert*-butyloxycarbo-

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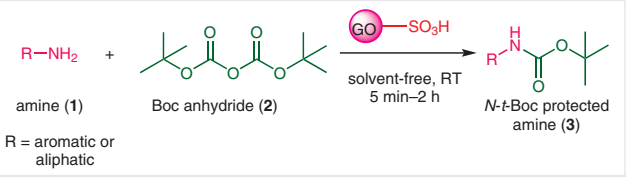
nylation in the preparation of small molecules and peptides, and usefulness in biochemistry, there is still a requirement of new and finer catalytic systems.

Since 2004, articles on graphene research have proliferated indefinitely. Graphene- and graphene oxide (GO)-based materials have displayed interesting mechanical, optical, and physical properties.[26,27] Besides, because of their large specific surface area, high surface-to-volume ratio,[28] thermal and chemical stability, they have been successfully utilized as supports for organic transformations. Over the years, solid acid catalysts have become quite popular environment-friendly replacements for conventional homogeneous liquid acid catalysts.[29] In this regard, sulfonated carbon-based materials have been significantly put to use for many organic syntheses.[30] Thus, the current popularity of GO-based materials inspired us to exploit solid acid potential of sulfonated reduced graphene oxide (SrGO) as a metal-free catalyst for the *N*-*t*-Boc protection of amines. In literature, there is no report that discusses the use of graphene- or GO-based material as a catalyst for the *N*-*t*-Boc protection of amines.

In this article, we report an efficient method for metal- and solvent-free, chemoselective *N*-*tert*-butyloxycarbonylation of amines using sulfonated reduced graphene oxide (SrGO) as a heterogeneous solid acid catalyst at room temperature (Scheme 1).

The sulfonated reduced graphene oxide (SrGO) was synthesized by grafting sulfonic acid-containing aryl radicals onto chemically reduced graphene oxide through ultrasonic irradiation (Figure 1). The detailed synthetic procedures can be found in the experimental section. SrGO catalyst was characterized by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, powder X-ray diffraction



Scheme 1 Boc protection of amines using SrGO as catalyst

(PXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM).

The chemical environment over SrGO was characterized using FTIR spectroscopy. For comparison, Figure 2 (a) depicts FTIR spectra of GO, SrGO, and reused SrGO. The FTIR spectrum of GO shows peaks at 3429, 1729, 1633, and 1084 cm^{-1}, which can be attributed to O–H stretching mode, C=O for carbonyl and carboxylic acid, C=C stretching mode, and C–O (epoxy) stretching mode, respectively. The FTIR spectrum of SrGO suggests chemical changes during the sulfonation process. The increased intensity of O–H peak suggests increase in hydroxyl groups due to SO_3H groups.[31,32] Further, the decreased intensity of carbonyl peak at 1729 cm^{-1} in SrGO depicts partial reduction of GO during sulfonation process.[33] The peak at 1633 cm^{-1} in SrGO indicates partial restoration of aromatic network of GO during chemical modification.[31,32] The emergence of sharp peaks at 1383 and 1204 cm^{-1} due to S=O symmetric and asymmetric stretching modes, respectively, verifies the existence of sulfonic groups on the surface of SrGO. Moreover, the peaks at 630 and 616 cm^{-1} due to S–O and S–C stretching modes, respectively, confirms the presence of covalent sulfonic acid

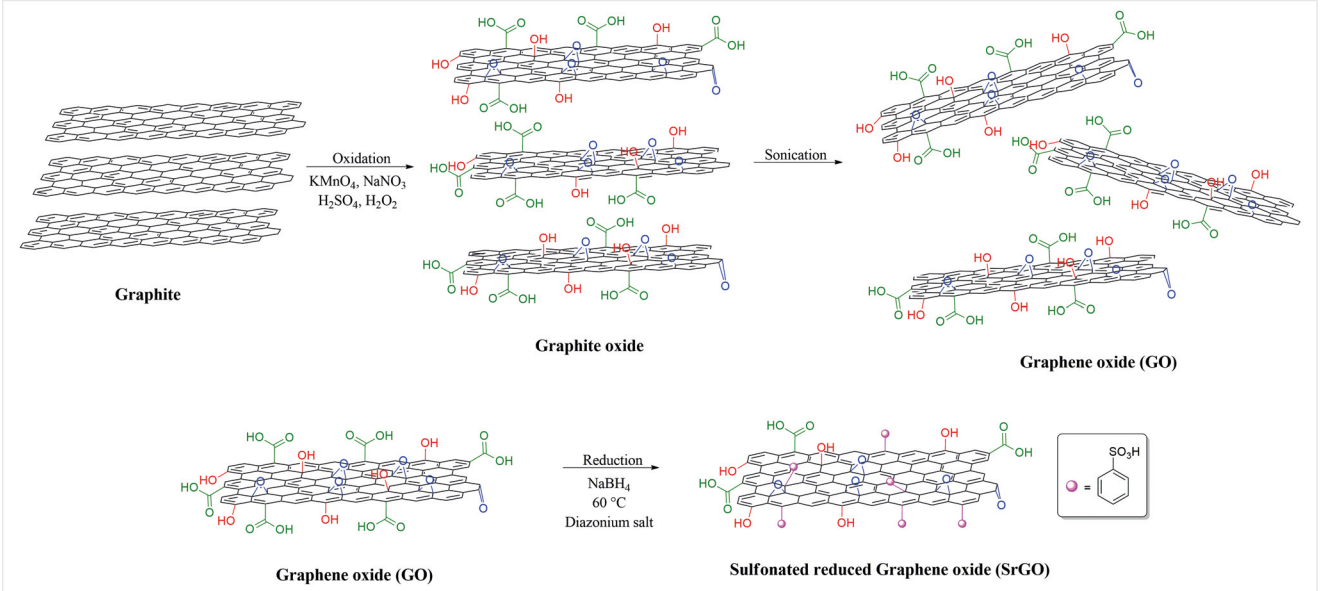


Figure 1 Schematic diagram for the preparation of GO and SrGO

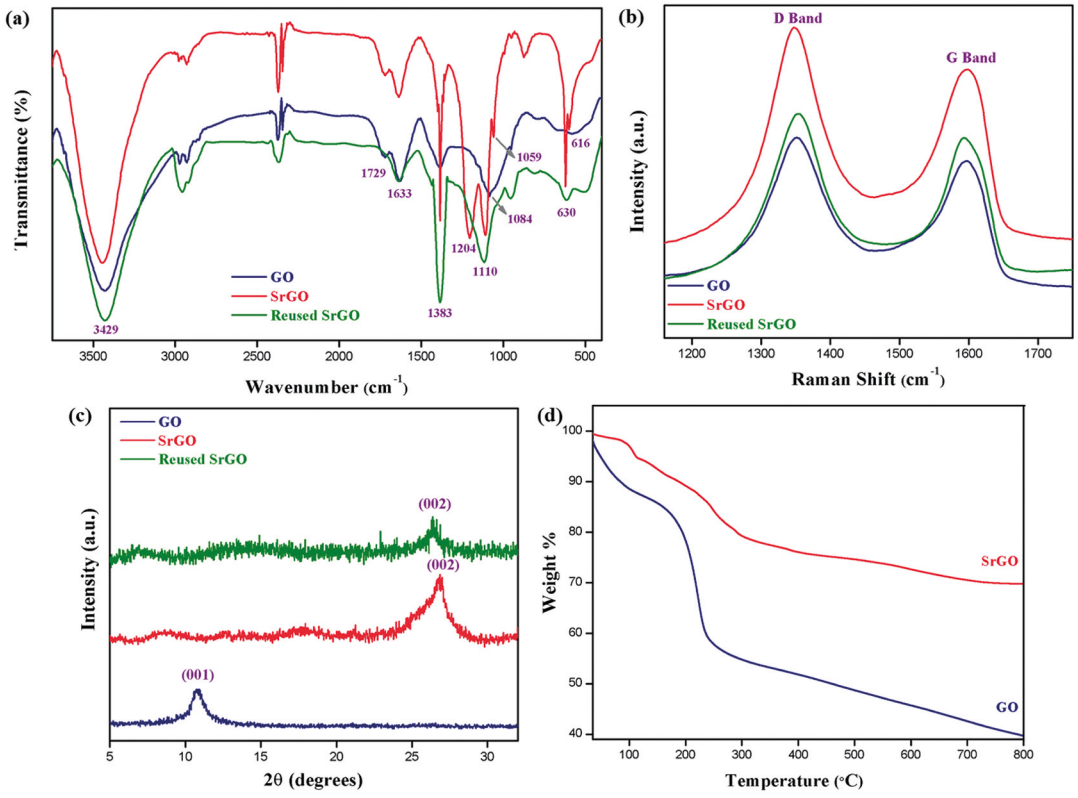


Figure 2 (a) FTIR spectra of GO, SrGO, and reused SrGO; (b) Raman spectra of GO, SrGO, and reused SrGO; (c) XRD pattern of GO, SrGO, and reused SrGO; (d) TGA curves of GO and SrGO.

groups on the SrGO surface.[33] Further, no modifications were observed in the FTIR spectrum of SrGO reused for seven consecutive catalytic cycles.

Raman spectroscopy is one of the most significant characterization for carbon materials. The Raman spectra for GO, SrGO, and reused SrGO is depicted in Figure 2 (b). The two characteristic peaks at 1350 and 1595 cm^{-1} for GO and at 1312 and 1544 cm^{-1} for SrGO correspond to the D and G band, respectively. The D band arises due to the vibration of sp^3 carbon atoms of defects as well as disorder, whereas the G band is a result of the vibration of sp^2 carbon atoms in graphitic hexagonal lattices.[34,35] The I_D/I_G ratio for SrGO (1.18) > GO (1.16), implying that some of the oxygenated groups were removed by $NaBH_4$ during ultrasonication. The I_D/I_G ratio for SrGO reused for seven consecutive catalytic cycles was found to be 1.165.

The XRD patterns acquired for GO, SrGO, and reused SrGO are shown in Figure 2 (c). For GO, single diffraction peak at 2θ = 10.8° corresponding to (001) plane with interlayer spacing of 0.79 nm is observed. This confirms the formation of GO by oxidation of graphite using Hummer's method.[32] After partial reduction of GO with $NaBH_4$ followed by grafting of sulfonic acid containing aryl radicals, the characteristic peak corresponding to (002) plane at 2θ = 26.8° with interlayer spacing of 0.56 nm was observed. The narrower interlayer spacing upon sulfonation implies restacking of GO nanosheets more tightly through π–π interactions.[36] The XRD pattern for SrGO reused for seven consecutive catalytic cycles was similar to that of SrGO, implying no modifications in its crystalline structure.

The thermal stability of both GO and SrGO was explored using thermogravimetric analysis. The obtained thermogravimetric analysis curves for both GO and SrGO are illustrated in Figure 2 (d). For GO, an overall weight loss of 58% is observed in three successive steps. First, due to vaporization of adsorbed water molecules, a steady weight loss of 9% occurs at around 100 °C. Then, due to the decomposition of oxygen-containing groups, a rapid weight loss of 29% occurs in the temperature range of 100–210 °C. Finally, due to pyrolysis of carbon skeleton of GO, a weight loss of 20% occurs in the temperature range of 210–800 °C. For SrGO, in the same temperature range an overall weight loss of ca. 25% occurs in four successive steps. First, a weight loss of 14% occurs at around 280 °C, followed by slower decrease in weight loss of total 11% in three successive steps, over a temperature range of 280–800 °C. The weight loss due to the decomposition of sulfonated groups of SrGO could be observed in the temperature range of 400–600 °C.[31]

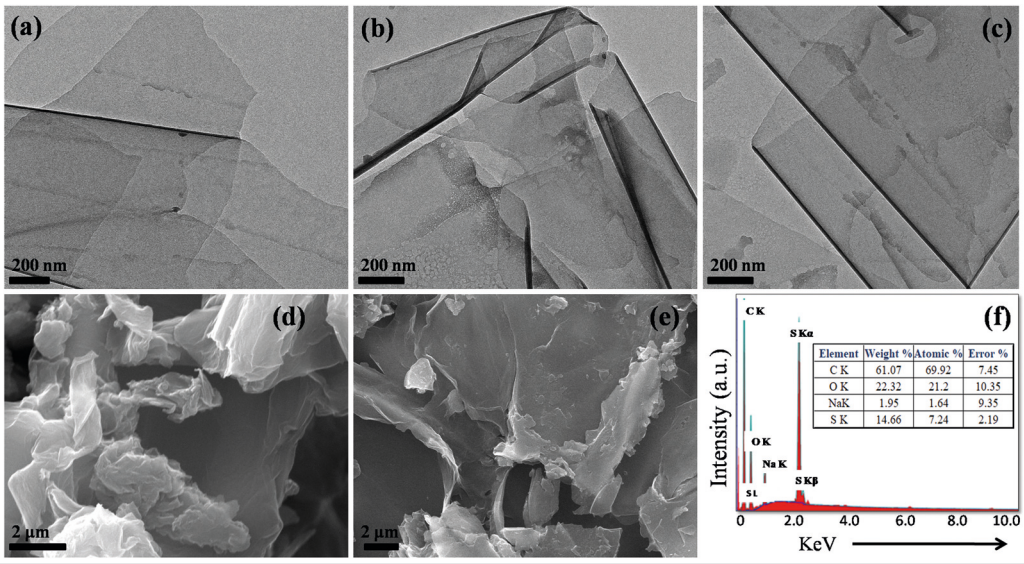


Figure 3 (a), (b), and (c) TEM images of GO, SrGO, and reused SrGO, respectively; (d) and (e) SEM images of GO and SrGO, respectively; (f) EDX analysis spectra of SrGO.

The morphological characteristics of GO and SrGO were tested through TEM and SEM analysis, depicted in Figure 3 (a,b and d,e, respectively). The TEM image of GO illustrated in Figure 3 (a) shows the overlapped sheet-like morphology. The SEM image of GO depicted in Figure 3 (d) shows the wrinkled sheet-like morphology. Both TEM and SEM analysis suggest that the microstructure of GO nanosheets was preserved even after the sulfonation process, depicted in Figure 3 (b and e, respectively). The TEM image of SrGO reused for seven consecutive catalytic cycles depicted in Figure 3 (c) shows no morphological modifications.

The EDS elemental analysis of both GO (Figure S1 in SI) and SrGO [Figure 3 (f)] was performed. The sulfur content of 7.24 atomic% or 14.66 wt% in SrGO suggests the successful grafting of sulfonic acid groups on the surface of GO.

After the successful characterization of GO and SrGO, the catalytic potential of the as synthesized SrGO was evaluated for the Boc protection of amines. Morpholine was selected as the model substrate. To achieve the optimum reaction conditions, influence of different criterions like the amount of catalyst, solvent, temperature, and reaction time were studied for *N*-*t*-Boc protection of morpholine in the presence of SrGO catalyst. The results are summarized in Table 1.

First, the reaction performed between morpholine (1 mmol) and $(Boc)_2O$ (1 mmol) in the absence of catalyst at room temperature under solvent-free condition, in dichloromethane (DCM), in acetonitrile, and under reflux in acetonitrile, could afford the corresponding *N*-*t*-Boc protected morpholine in only 42%, 54%, 45%, and 51% yield after 48 hours, respectively (Table 1, entries 1–4).

To test the role of the catalyst in the *N*-*t*-Boc protection of amines, the reaction was carried out in the presence of GO (5 mg) and SrGO (5 mg) at room temperature under solvent-free condition; the obtained *N*-*t*-Boc protected morpholine was isolated in 72% and 89% yield in 1 hour and 10 minutes, respectively (Table 1, entries 5, 6). The comparison between entries 1, 5, and 6 clearly indicates the vital role of SrGO as a catalyst in *N*-*t*-Boc protection of morpholine be-

Table 1 Optimization of Reaction Conditions[a]

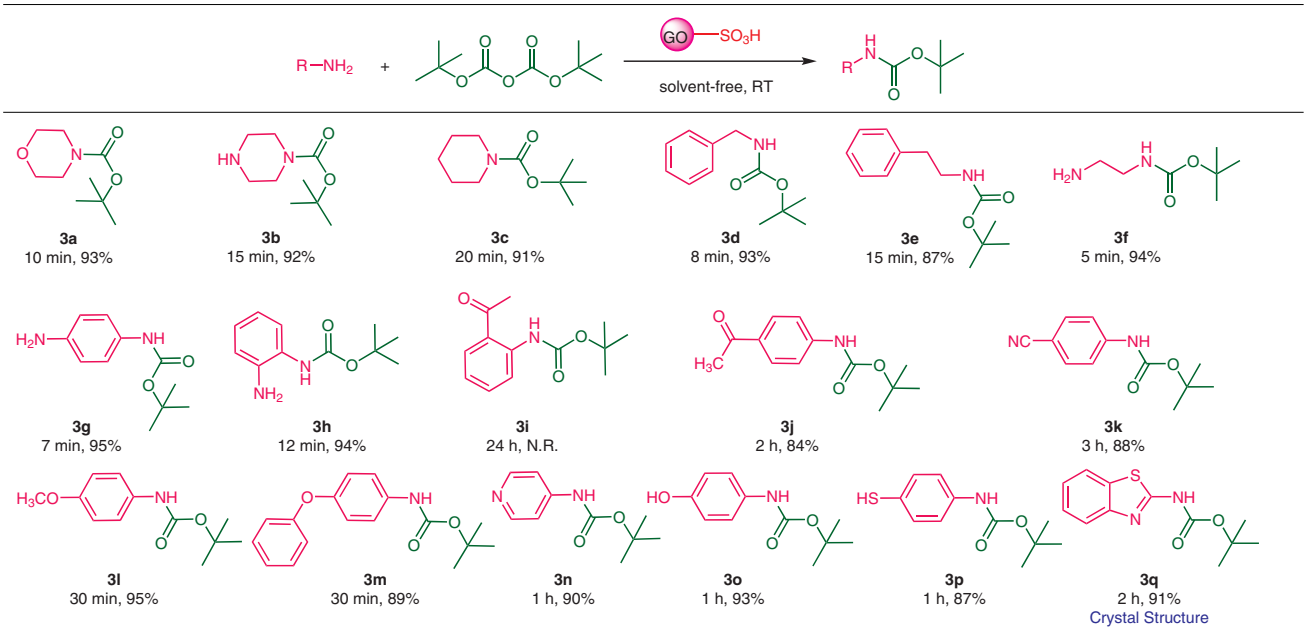
Entry	Catalyst amount (mg)	Conditions	Time	Yield (%)[b]
1	–	Solvent-free, RT	48 h	42
2	–	DCM, RT	48 h	54
3	–	CH_3CN, RT	48 h	45
4	–	CH_3CN, reflux	48 h	51
5	GO (5)	solvent-free, RT	1 h	72
6	SrGO (5)	solvent-free, RT	10 min	89
7	SrGO (5)	DCM, RT	11 min	87
8	SrGO (5)	EtOH, RT	30 min	85
9	SrGO (5)	1,4-dioxane, RT	40 min	79
10	SrGO (5)	CH_3CN, RT	25 min	78
11	SrGO (5)	CH_3CN, reflux	12 min	83
12	SrGO (2.5)	solvent-free, RT	25 min	64
13	**SrGO (7.5)**	**solvent-free, RT**	**10 min**	**93**
14	SrGO (10)	solvent-free, RT	10 min	94

[a] Reaction conditions: morpholine (1 mmol), $(Boc)_2O$ (1 mmol), solvent (2 mL), and catalyst (mg).
[b] Isolated yields.

cause substantial decrease in reaction time with increase in yield was observed. Moreover, better catalytic activity of SrGO over GO was expected because of the enhanced acidic character of SrGO due to the presence of sulfonic acid groups on its surface. Next, the reaction was performed using SrGO (5 mg) at room temperature in DCM, ethanol, 1,4-dioxane, acetonitrile, and under reflux in acetonitrile; *tert*-butyl morpholine-4-carboxylate was obtained in 87%, 85%, 79%, 78%, and 83% yield after 11 minutes, 30 minutes, 40 minutes, 25 minutes, and 12 minutes, respectively (entries 7–11). The comparison between entries 6–11 indicates that the best conditions for the reaction to take place are at room temperature under solvent-free condition. Further, to optimize the amount of catalyst, the reaction was tested using lower amount of SrGO (2.5 mg) at room temperature under solvent-free condition, which gave the desired product in only 64% yield after 25 minutes (entry 12). Next, higher amounts of SrGO (7.5 mg and 10 mg) was tested at room temperature under solvent-free condition, which resulted in 93% and 94% yield after 10 minutes, respectively (entries 13, 14). Increasing the amount of SrGO from 7.5 mg to 10 mg did not have any significant influence on the reaction time and product yield, therefore, it could be concluded that 7.5 mg of SrGO was the required amount of catalyst to yield the best results. Thus, by summing up the above results, 7.5 mg of SrGO catalyst at room temperature under solvent-free condition were found to be the optimal conditions for the *N*-*t*-Boc protection of amines.

In the present study, the scope of the reaction was expanded to aromatic and aliphatic secondary amines (Scheme 1) to produce the corresponding *N*-*t*-Boc protected amines under the optimized reaction conditions (Table 1, entry 13). The results are summarized in Table 2. The substrates readily produced *N*-*t*-Boc protected derivatives with sufficiently high yields in 5 minutes to 2 hours without the formation of any side or waste products. The aromatic substrates with electron-donating groups **3d**,**e**, **3l**–**n** readily attained *N*-*t*-Boc protected derivatives in excellent yields (87–95%) whereas for the aromatic substrates with electron-withdrawing groups **3i**–**k**, the reaction was sluggish and afforded the *N*-*t*-Boc protected derivatives in slightly lower yields (84–88%). This might be because of the introduction of electron-withdrawing group, which rendered amine less nucleophilic. The aliphatic secondary amines **3a**–**c** smoothly produced the corresponding *N*-*t*-Boc protected derivatives in good yields (91–93%). The chemoselectivity was demonstrated by the substrates containing sensitive groups like phenol and thiophenol **3o** and **3p**, which also successfully yielded *N*-*t*-Boc protected derivatives in desirable yield of 93% and 87%, respectively, without the formation of *O*/*S*-*t*-Boc protected products. Further, the substrates containing two primary amine groups **3f**–**h** resulted in *N*-*t*-Boc protection of a single amine group in excellent yields (94–95%). We tested the selectivity of SrGO for mono-*N*-*t*-Boc protection in the case of ethylenediamine by increasing the amount of $(Boc)_2$ to 1.2, 1.5, and 2.0 mmol. Interestingly, in all the cases, mono-*N*-*t*-Boc protected product **3f** was

Table 2 SrGO-Catalyzed *N*-*t*-Boc Protection of Amines[a,b]



[a] Reaction conditions: Amine (1 mmol), $(Boc)_2O$ (1 mmol), SrGO (7.5 mg), RT.
[b] Isolated yields. Products were characterized using ^1H NMR, ^{13}C NMR, mass, and IR spectroscopy.

achieved. It was observed that the reaction between 2′-aminoacetophenone and $(Boc)_2O$ could not afford the corresponding *N*-*t*-Boc protected derivative **3i** even after the reaction time was extended upto 24 hours whereas the reaction between 4′-aminoacetophenone and $(Boc)_2O$ readily produced the corresponding *N*-*t*-Boc protected derivative **3j** with adequate yield (84%) in 2 hours. This is anticipated due to the steric hindrance caused by the bulky acetyl group at the *ortho*-position.

The obtained *N*-*t*-Boc protected derivatives were analyzed by ^1H NMR, ^{13}C NMR, mass, and IR spectroscopy. Moreover, the authenticity of this approach was confirmed by the X-ray analysis of compound **3q**. For the current study, X-ray quality single crystals of compound **3q** were grown in ethyl acetate at room temperature by slow evaporation of solution growth method. Figure 4 shows the ORTEP diagram and unit cell packing of the compound **3q**. The compound **3q** crystallized in monoclinic cell and space group $P2_1/c$ with the following lattice parameters: a = 6.2520 (9) Å, b = 22.958 (4) Å, c = 8.8269 (12) Å, α = 90°, β = 94.667° (14), γ = 90°, V = 1262.8 (3) Å^3, and ρ (calculated) = 1.317 g cm^{-3}.

The role of sulfonated reduced graphene oxide as a catalyst for the *N*-*t*-Boc protection of amines can be explained through the proposed mechanism in Scheme 2. The hydrogen bond formation between the sulfonic acid groups of the SrGO catalyst and oxygen atoms of the carbonyl groups of $(Boc)_2O$ lead to the 'electrophilic activation' of the carbonyl groups. This electrophilic activation makes carbonyl groups more susceptible to the nucleophilic attack by the amine groups. This causes elimination of *tert*-butanol and carbon dioxide gas as by-products, eventually resulting in the formation of desired *N*-*t*-Boc protected amine derivatives.

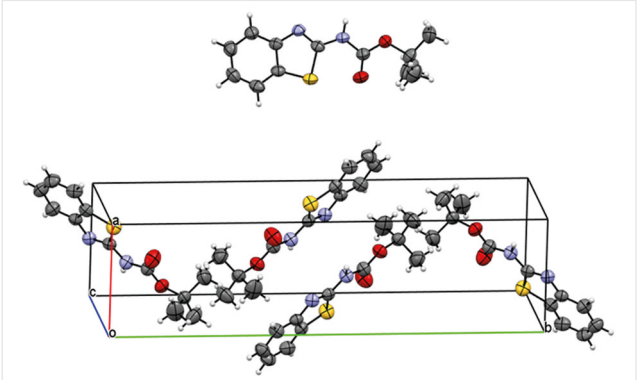
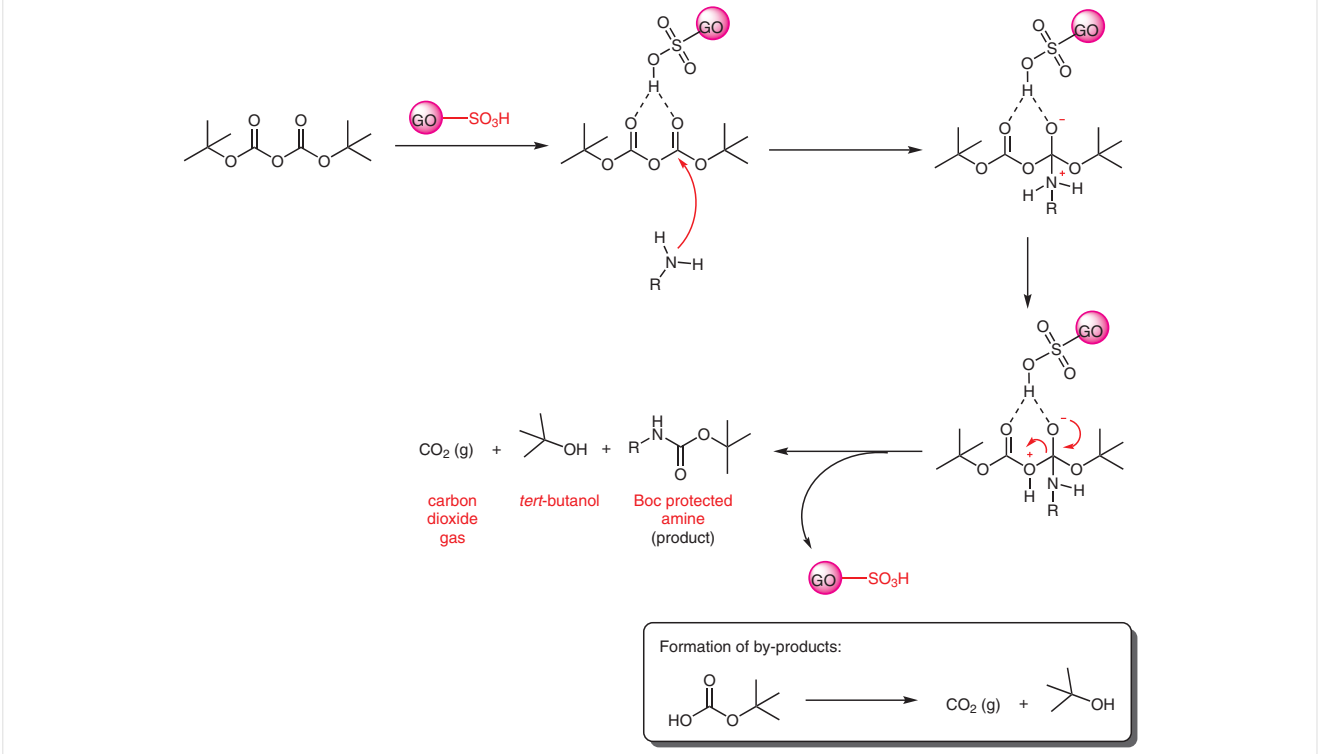


Figure 4 ORTEP diagram and unit cell packing of compound **3q**

Recyclability and reusability of a heterogeneous catalyst determines its feasibility and application. When looking from the industrial application point of view, recyclability and reusability are significant parameters. In the present study, the recyclability of SrGO catalyst was investigated under the optimal reaction conditions (Table 1, entry 13). The catalyst was recovered by vacuum filtration, washed with ethanol (3 × 5 mL) and subsequently dried in an air



Scheme 2 Proposed mechanism for the Boc protection of amines using SrGO

oven at 70 °C for 3 h and reused for further reactions. The isolated yield (%) for 7 cycles is plotted in Figure 5 [the figure has been drawn from 85% to clearly differentiate between the isolated yields (%) for each cycle]. The catalytic activity of SrGO decreased slightly for the first five cycles, eventually becoming constant. The isolated yield (%) was more than 85% even after reusing the catalyst consecutively for 7 cycles. Conclusively, SrGO holds a great potential as a catalyst in organic syntheses because of advantages like the high temperature tolerance, easy recovery, and the reusability without inactiveness.

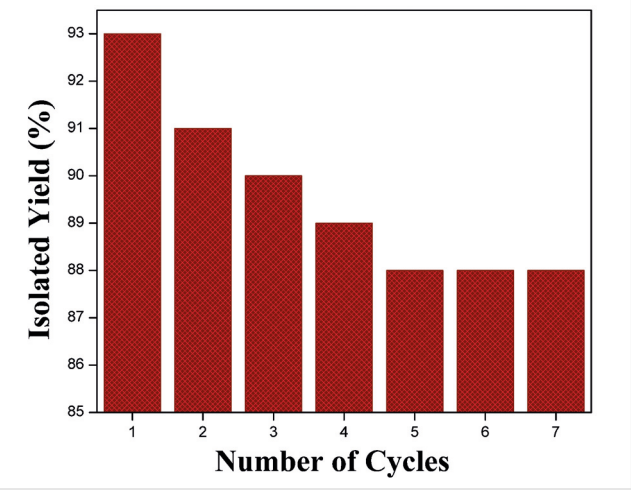


Figure 5 Recyclability test of the SrGO catalyst

The comprehensive literature survey suggests that the use of SrGO as a catalyst for the Boc protection of amines has several advantages over earlier work (Table 3). This is the first report where a graphene- or GO-based heterogeneous catalyst has been employed for the *N*-*t*-Boc protection of amines. The SrGO was found to be superior because most of the earlier methods required purification through column chromatography. Many of the catalysts that have been reported earlier are homogeneous in nature, which means they deteriorate/decompose after the reaction and thus cannot be recovered. Moreover, some of the reported catalysts that could be recovered, showed catalytic activity only up to 4 cycles whereas SrGO is superior in terms of its recyclability and reusability. It could be easily reused up to 7 cycles with excellent catalytic activity. Thus, the present methodology is an interesting alternative for the *N*-*t*-Boc protection of amines.

In conclusion, we have demonstrated a metal-free and chemoselective Boc protection of amines using sulfonated reduced graphene oxide as a catalyst under solvent-free conditions at room temperature. This method has displayed great applicability to a wide range of amine substrates, which could be prepared under two hours at room temperature. Boc protection of amines is a common and important practice in the field of organic and medicinal chemistry. The superior recyclability and reusability of SrGO makes this methodology even more interesting. Besides, looking at the current popularity and easy preparation of graphene-based materials, this protocol is an appealing alternative for the preparation of *N*-*t*-Boc protected amine derivatives. This approach can further be exploited in the natural products and total synthesis.

Table 3 Comparison with Previous Work

Entry	Catalyst	Reusability	Ref.
1	yttria-zirconia	reusable	15a
2	β-cyclodextrin	reusable	13
3	–	–	23
4	$HClO_4$-SiO_2	up to 4 cycles	21
5	molecular I_2	–	22
6	sulfonic acid functionalized silica	up to 3 cycles	16
7	ZnO nanorods	reusable	18
8	1-alkyl-3-methylimidazolium cation-based IL	up to 5 cycles	25
9	–	–	24
10	Amberlyst® A21	reusable	19
11	$MgBr_2$·OEt_2	–	15g,f
12	NaI	–	14
13	V_2O_5/SnO_2	reusable	20
14	**sulfonated reduced graphene oxide**	**up to 7 cycles**	**This work**

All the chemicals were purchased from Sigma–Aldrich or Alfa Aesar. The graphite powder was obtained from Central Drug House (P) Ltd., New Delhi, India. Double-distilled H_2O was used for the preparation of all aqueous solutions. All solvents and reagents were obtained commercially and used as received.

The catalyst was analyzed by various techniques. Fourier Transform IR spectra were recorded on PerkinElmer FTIR spectrophotometer using ATR method with a scanning range of 4000–400 cm^{-1}. The X-ray diffractograms were obtained using Bruker high-resolution X-ray diffractometer with a scan rate of 5° min^{-1} in the 2θ range of 5–40°. The Raman spectra were recorded on Renishaw Laser Raman Spectrometer using a laser of wavelength 514 nm over the wavenumber from 1000–2000 cm^{-1}. The thermal stability of the catalyst was assessed using PerkinElmer, Pyris diamond TGA/DTA by heating the sample under N_2 atmosphere from RT to 800 °C at a constant heating rate of 10 °C/ min and a gas flow of 200 mL/min. The SEM images and Elemental analysis was obtained using Jeol Scanning Electron Microscope with EDX. TEM images were acquired on Technai 200 Kv Transmission Electron Microscope by dispersing nanoparticles in EtOH and casting them onto copper grid coated with an amorphous carbon film.

The synthesized organic compounds were characterized using mass spectra recorded on Agilent LCMS with Quadruple time of flight. ^1H and ^{13}C NMR spectra were obtained on Jeol 400 MHz spectrometer with $CDCl_3$ as solvent and chemical shift is reported in ppm with respect to TMS (internal standard). Fourier Transform IR spectra of the synthesized compounds were recorded on PerkinElmer FTIR spectrophotometer using KBr pellets with a scanning range of 4000-400 cm^{-1}. X-ray analysis results were collected on Crysalis PRO (Oxford Diffraction) with graphite mono75 chromate Mo Kα radiation (λ = 0.71073Å) and the structure was elucidated by direct method using SHELXL-97.

Sulfonated Reduced Graphene Oxide (SrGO)

The reaction scheme for the preparation of graphene oxide (GO) and sulfonated reduced graphene oxide (SrGO) is shown in Figure 1. First, graphene oxide (GO) was synthesized according to the known literature.[36a] Subsequently, sulfonated reduced graphene oxide (SrGO) catalyst was also prepared according to a previously reported procedure.[30g–i,36b] with minor modifications. Initially, GO powder (100 mg) was added to deionized H_2O (100 mL) in a glass flask and mixed uniformly using a magnetic stirrer at RT for 10 min. The resulting dispersion was sonicated in an ultrasonic bath (20 kHz with 100% output) for 1 h. Then, a freshly prepared solution of $NaBH_4$ (0.8 g) in deionized H_2O (20 mL) was added dropwise into the above dispersion while adjusting pH to 10 using 5 wt% Na_2CO_3 solution. The dispersion was then heated at 100 °C for 45 min during which time brown GO dispersion turned black. The dispersion was then centrifuged (8000 rpm for 10 min) and washed with deionized H_2O three times to get partially reduced graphene oxide (rGO). Thus, obtained rGO was dispersed in deionized H_2O (100 mL) using ultrasonic bath for 40 min and then cooled. A diazonium salt was prepared by the reaction of sulfanilic acid (100 mg) and 1 N HCl (1.1 mL) in H_2O (15 mL) at 0 °C, followed by addition of $NaNO_2$ (35 mg) in H_2O (15 mL). This diazonium salt was added into rGO dispersion at 0 °C and stirred overnight at RT. The resulting black precipitate was centrifuged (8000 rpm for 10 min) and washed with deionized H_2O (5 × 3 mL) and with absolute EtOH (1 × 3 mL). Finally, the precipitate was dried in a vacuum oven at 70 °C for 8 h.

Boc Protection of Amines; General Procedure

To a magnetically stirred solution of $(Boc)_2$ (1 mmol, 218.25 mg) and SrGO (7.5 mg), was added the respective amine (1 mmol) and stirred for the appropriate time (Table 2) at RT. The progress of the reaction was monitored by TLC. After the completion of the reaction, DCM (2 mL) was added to the reaction mixture and the catalyst was separated by vacuum filtration. The catalyst was washed with EtOH (3 × 5 mL) and subsequently dried in an air oven at 70 °C for 3 h and reused for further reactions. The solvent was concentrated under reduced pressure to yield *N*-*t*-Boc protected amine derivatives. The products were characterized by ^1H NMR, ^{13}C NMR, MS, and IR spectroscopy.

tert-Butyl Morpholine-4-carboxylate (3a)

White solid; yield: 0.174 g (93%); mp 64–66 °C.

FTIR: 3006, 2967, 2864, 1684, 1454, 1416, 1361, 1273, 1246, 1163, 1112, 1073, 860 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.59–3.61 (4 H, t, *J* = 4.5 Hz), 3.36–3.38 (4 H, t, *J* = 4.9 Hz), 1.43 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.85, 80.01, 66.74, 44.53, 28.44.

HRMS (ESI): *m*/*z* calcd for $C_9H_{17}NO_3$: 187.1208 $[M + H]^+$; found: 188.1290.

tert-Butyl Piperazine-1-carboxylate (3b)

White solid; yield: 0.171 g (92%); mp 44–46 °C.

FTIR: 2979, 1688, 1418, 1366, 1244, 1159, 870 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.60–3.63 (4 H, t, *J* = 4.9 Hz), 3.37–3.40 (4 H, t, *J* = 4.9 Hz), 1.76 (NH, br), 1.44 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.77, 80.11, 50.79, 43.51, 28.45.

HRMS (ESI): *m*/*z* calcd for $C_9H_{18}N_2O_2$: 186.1387 $[M + H]^+$; found: 187.1459.

tert-Butyl Piperidine-1-carboxylate (3c)

Colorless liquid; yield: 0.169 g (91%).

FTIR: 2976, 2933, 2856, 1687, 1416, 1364, 1250, 1120, 1069, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.25–3.28 (4 H, m), 1.40–1.47 (6 H, m), 1.36 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.03, 79.17, 44.89, 27.47, 24.57.

HRMS (ESI): *m*/*z* calcd for $C_{10}H_{19}NO_2$: 185.1418 $[M + H]^+$; found: 186.1491.

tert-Butyl Benzylcarbamate (3d)

Light yellow solid; yield: 0.193 g (93%); mp 57–59 °C.

FTIR: 3461, 3360, 3013, 2978, 1698, 1504, 1453, 1391, 1366, 1245, 1219, 1164, 1027, 745 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.33 (5 H, m), 4.30 (2 H, s), 1.45 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.03, 139.04, 128.67, 127.56, 127.39, 79.53, 44.74, 28.50.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{17}NO_2$: 207.1258 $[M + H]^+$; found: 208.1332.

tert-Butyl Phenethylcarbamate (3e)

Transparent solid; yield: 0.193 g (87%); mp 53–57 °C.

FTIR: 3346, 3027, 2975, 2933, 1691, 1503, 1452, 1391, 1364, 1247, 1163, 1039, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.28 (5 H, m), 3.33–3.35 (2 H, t, *J* = 6.2 Hz), 2.75–2.78 (2 H, t, *J* = 6.9 Hz), 1.42 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.06, 139.17, 128.89, 128.61, 126.43, 79.07, 41.95, 36.31, 28.51.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{19}NO_2$: 221.1427 [M + H]$^+$; found: 222.1500.

tert-Butyl (2-Aminoethyl)carbamate (3f)

Mustard solid; yield: 0.151 g (94%); mp 68–70 °C.

FTIR: 3372, 2979, 2933, 1680, 1518, 1447, 1392, 1365, 1274, 1159, 870 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (NH, br), 5.02 (NH_2), 3.11–3.17 (2 H, m), 2.73–2.76 (2 H, t, *J* = 5.8 Hz), 1.38 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.44, 40.83, 41.88, 79.40, 155.46.

HRMS (ESI): *m*/*z* calcd for $C_7H_{16}N_2O_2$: 160.1209 [M + H]$^+$; found: 161.1282.

tert-Butyl (4-Aminophenyl)carbamate (3g)

Dark brown solid; yield: 0.198 g (95%); mp 114–116 °C.

FTIR: 3364, 2978, 2934, 1690, 1623, 1600, 1515, 1426, 1392, 1366, 1310, 1232, 1155, 1052, 826 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.12 (2 H, d, *J* = 7.7 Hz), 6.60–6.62 (2 H, d, *J* = 8.7 Hz), 6.27 (NH_2), 1.48 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.41, 142.45, 129.79, 120.96, 115.69, 80.11, 28.47.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}N_2O_2$: 208.1219 [M + H]$^+$; found: 209.1292.

tert-Butyl (2-Aminophenyl)carbamate (3h)

Light brown solid; yield: 0.196 g (94%); mp 110–112 °C.

FTIR: 3340, 2978, 1704, 1511, 1451, 1365, 1242, 1156, 1052, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64–7.23 (4 H, m), 6.45 (NH_2), 1.50 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.93, 140.02, 126.23, 124.84, 119.72, 117.70, 80.63, 28.41.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}N_2O_2$: 208.1219 [M + H]$^+$; found: 209.1294.

tert-Butyl (4-Acetylphenyl)carbamate (3j)

White solid; yield: 0.198 g (84%); mp 148–150 °C.

FTIR: 3312, 2980, 1723, 1669, 1594, 1527, 1406, 1362, 1317, 1271, 1234, 1157, 1047, 837 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.90 (2 H, d, *J* = 8.8 Hz), 7.42–7.44 (2 H, d, *J* = 8.7 Hz), 6.71 (NH, br), 2.54 (3 H, s), 1.51 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.01, 152.22, 142.96, 131.92, 129.93, 117.46, 81.40, 28.35, 26.47.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{17}NO_3$: 235.2634 [M + H]$^+$; found: 236.2706.

tert-Butyl (4-Cyanophenyl)carbamate (3k)

White solid; yield: 0.192 g (88%); mp 116–120 °C.

FTIR: 3327, 3019, 2980, 2225, 1721, 1597, 1516, 1405, 1363, 1316, 1225, 1154, 1053, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.52 (4 H, m), 7.11 (NH, br), 1.47 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.28, 142.95, 133.30, 119.25, 118.22, 105.47, 81.63, 28.29.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}N_2O_2$: 218.1059 [M + H]$^+$; found: 219.1131.

tert-Butyl (4-Methoxyphenyl)carbamate (3l)

White solid; yield: 0.212 g (95%); mp 96–98 °C.

FTIR: 3361, 2977, 1692, 1599, 1515, 1367, 1308, 1235, 1156, 1051, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.25 (2 H, m), 6.78–6.82 (2 H, m), 6.56 (NH, br), 3.74 (3 H, s), 1.48 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.69, 153.37, 131.59, 120.67, 114.23, 80.24, 55.55, 28.45.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{17}NO_3$: 223.1221 [M + H]$^+$; found: 224.1293.

tert-Butyl (4-Phenoxyphenyl)carbamate (3m)

Dark brown solid; yield: 0.254 g (89%); mp 107–109 °C.

FTIR: 3377, 2978, 2920, 2850, 1699, 1593, 1514, 1485, 1367, 1311, 1222, 1153, 1049, 1028, 825 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93–7.32 (9 H, m), 6.46 (NH, br), 1.50 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.98, 153.05, 152.46, 134.06, 129.74, 122.86, 120.39, 120.06, 118.15, 80.65, 28.43.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NO_3$: 285.1365 [M + H]$^+$; found: 286.1451.

tert-Butyl Pyridin-4-ylcarbamate (3n)

White solid; yield: 0.175 g (90%); mp 143–147 °C.

FTIR: 1723, 1599, 1525, 1454, 1422, 1394, 1365, 1304, 1257, 1165, 1055, 763 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39–8.41 (2 H, dd, *J* = 4.9, 1.4 Hz), 7.81 (NH, br), 7.34 (2 H, m), 1.48 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.32, 150.31, 146.25, 112.50, 81.54, 28.30.

HRMS (ESI): *m*/*z* calcd for $C_{10}H_{14}N_2O_2$: 194.2349 [M + H]$^+$; found: 195.2422.

tert-Butyl (4-Hydroxyphenyl)carbamate (3o)

Pink solid; yield: 0.195 g (93%); mp 146–148 °C.

FTIR: 3360, 2980, 2929, 1693, 1612, 1519, 1436, 1369, 1226, 1159, 1055, 827 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11–7.13 (2 H, d, *J* = 8.4 Hz), 6.68–6.72 (2 H, m), 6.36 (OH, br), 1.49 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.83, 152.33, 130.76, 121.76, 115.86, 80.61, 28.46.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{15}NO_3$: 209.1052 [M – H]$^-$; found: 208.0977.

tert-Butyl (4-Mercaptophenyl)carbamate (3p)

Light brown solid; yield: 0.196 g (87%); mp 148–152 °C.

FTIR: 3385, 2256, 1651, 1499,.1310, 1235, 1166, 1020, 994, 824, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (NH), 7.15–7.24 (4 H, m), 3.22 (SH), 1.33 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.96, 139.36, 130.97, 129.92, 118.95, 80.16, 28.38.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{15}NO_2S$: 225.0816, [M – H]$^-$; found: 224.0744.

***tert*-Butyl Benzo[*d*]thiazol-2-ylcarbamate (3q)**

White solid; yield: 0.228 g (91%); mp 98–100 °C.

FTIR: 3131, 3056, 2971, 2931, 2801, 1709, 1603, 1558, 1455, 1363, 1280, 1185, 1052, 861, 755, 669 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.76 (NH, br), 7.91–7.93 (1 H, d, *J* = 8.2 Hz), 7.77–7.78 (1 H, d, *J* = 7.8 Hz), 7.36–7.40 (1 H, t, *J* = 7.8 Hz), 7.24–7.28 (1 H, t, *J* = 7.3 Hz), 1.58 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.91, 153.05, 148.73, 131.53, 125.73, 123.45, 121.12, 120.94, 83.32, 28.47.

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{14}N_2O_2S$: 250.0790 [M + H]$^+$; found: 251.0862.

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