Chapter 4

Synthesis and complete characterization of 5-(2-nitro-1-arylbutyl)-4-aryl-1,2,3-selenadiazoles
4.1. Synthetic utility of nitrocompounds

The relatively high electron withdrawing power of the nitro group and its facile transformation into various functionalities have extended the importance of nitro compounds. Nitro compounds have proven to be valuable intermediates for the preparation of complex molecules and to serve as precursors for the compounds extensively used in the agrochemical, pharmaceutical and dyestuff industries. Michael addition of nitroalkanes to α,β-unsaturated ketones in the presence of catalytic amount of bases has been extensively studied. The Michael reaction has attracted much attention as one of the most important carbon–carbon (C–C) bond formation reactions in organic synthesis, this being completely atom-efficient process [1].

Regioselectivity is an important feature that makes nitroalkanes particularly efficient in conjugate additions with α,β-unsaturated carbonyl derivatives. Indeed, while other activating groups give variable amounts of 1,2-addition products when reacted with enones or enals [2], nitroalkanes afford exclusively 1,4-addition products with α,β-unsaturated ketones as reactive acceptors [3].

Conjugate additions using highly stabilized carbanions are still of interest since a growing number of these procedures can be carried out even at room temperature using easily available substrates and suitable base/solvent combinations. Nitroalkanes are valuable sources of stabilized carbanions since the high electron-withdrawing power of the nitro group provides an outstanding enhancement of the hydrogen acidity at the α-position [4-8]. Base treatment of the nitroalkanes 1 produces the corresponding nitronate anions 2 which can be used as carbon nucleophiles in reactions with haloalkanes [5], aldehydes [6,7], and Michael acceptors leading to adducts 3–5 (Scheme 4.1) [9].
Nitroalkanes 6 are versatile intermediates since their reduction provides a straightforward entry to amino derivatives 7. Furthermore, the conversion of nitro to carbonyl group conversion, known as the Nef reaction, allows the introduction of the hydroxyl group by means of nucleophilic addition or reduction processes (Scheme 4.2). Hence heterocyclic derivatives like lactones and spiroketaels can be constructed by exploiting Nef conversion. Pyrrolidines, lactams and other nitrogenated derivatives can be prepared by reduction of the nitro group.

Scheme 4.2

Michael reaction of 2,2-pentamethylene-5-nitro-1,3-dioxane 10 with methyl 2-bromo acrylate 11, generated in situ from methyl 2,3-dibromopropanoate and triethylamine, afforded 2-bromo-4-nitroester 12, which was readily converted into various 5,5-bis (hydroxymethyl)pyrrolidine analogues of nucleosides [10].

A convenient solvent-free synthesis of γ-nitroketones and γ-nitroesters based on the reaction of nitroalkanes with α,β-unsaturated carbonyl compounds in the ultrasonically activated heterogeneous catalytic system 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄])/ K₂CO₃ was developed [11].

4.2 Biological importance nitro compounds

Nitro groups are found to be responsible for potential biological activity in several molecules. Naturally occurring nitro compounds like chloramphenicol 13 and aureothin exhibit a broad antibiotic activity and certain alkyl nitro compounds exhibit
antitumor activity. The antibiotic azomycin 14, a 2-nitroimidazole, isolated from a streptomycete, was the first active nitroimidazole to be discovered [12], which acted as the main impetus for the systematic search for drugs with activity against anaerobic protozoa. The other 2-nitroimidazoles tested for their efficiency are misonidazole 15 and etanidazole 16.

The use of nitrofurans in antibacterial chemotherapy was recognized by Dodd and Stillman, who discovered that the addition of a single nitro group in C5 of the furan ring imparted bacteriostatic properties to the molecule [13].

Furazolidone 17, hydrazone formed from 5-nitro-2-furaldehyde and 3-amino-2-oxazolidinone, has a broad spectrum of bacterial activity against intestinal pathogens, including various species of *Salmonella, Shigella, Proteus* and *E. Coli*. It is useful for the treatment of bacterial or protozoal diarrhoea [14]. The treatment of urinary infections with nitrofurantoin 18 was reported by Salvaris [15].
The nitro group has been found to be a pharmacophore in nitro imidazole PA-824 19 [16], which has shown to be active against MDR-TB strains. An advantage with PA-824 is that it shows no significant inhibition of cytochrome P450 isozymes suggesting that it could be used with HIV medications, being useful in the TB/HIV treatment.
4.3. Synthesis of 5-(2-nitro-1-arylbutyl)-4-aryl-1,2,3-selenadiazoles 23 -The present work

One of the most useful methods to produce a large variety of nitroalkanes is the formation of ČC bonds by conjugate addition of nitroalkanes to enones (Michael addition). Besides, the 1,4-addition is a highly atom-efficient reaction, in agreement with the second principle of green chemistry, which says that the synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. The 1,4-addition of primary nitroalkanes to functionalized α,β-unsaturated ketones was considered as an appropriate method to prepare multifunctional γ-nitro ketones. The adducts are found to be versatile intermediates as they contain the α-keto methylene functionality. The potential biological activity of several molecules containing nitro groups prompted us to synthesize selenadiazoles having nitro group in the side chain by exploiting the synthetic utility of α-ketomethylene functionality obtained by the Michael addition of chalcones to 1-nitropropane followed by oxidative ring closure of semicarbazone of the adduct with selenium dioxide.

Various diversely substituted novel 1,2,3-selenadiazole derivatives have been synthesized using Lalezari’s procedure. The adducts, 4-nitro-1,3-diarylhexan-1-one 21 have all been synthesized by stirring chalcone 20, 1-nitropropane and aqueous potassium hydroxide in DMF. No significant double Michael addition was observed under the present reaction condition and the desired monoadduct was obtained in excellent yields. The reaction was typically complete within 2h. The semicarbazone derivatives 22 of the adducts were prepared and converted in good yield into the corresponding selenadiazoles 23 by refluxing the semicarbazones with selenium dioxide in tetrahydrofuran (Scheme 4.3). The reaction started immediately with the precipitation of red selenium and was complete within 2 h.

Although it was difficult to characterize the semicarbazone intermediates using NMR data due to their poor solubility in NMR solvents, the formation of products was established from the IR data. The IR spectra of semicarbazones 22 showed the characteristic peaks at 3500-3400 cm\(^{-1}\) due to -NH\(_2\), at 3400-3470 cm\(^{-1}\) due to -NH, at 1700-1680 cm\(^{-1}\) due to amide C=O, at 1560-1420 cm\(^{-1}\) due to -C=N and at 1120-1100 cm\(^{-1}\) due to –CN showing the formation of the product. The peaks at 1550-1535
cm\(^{-1}\) and 1350-1370 cm\(^{-1}\) were also observed indicating the presence of NO\(_2\) group in the product.

![Diagram of chemical structures and reactions](image)

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**Scheme 4.3** Synthesis of 4-aryl-5-(2-nitro-1-arylbutyl)-1,2,3-selenadiazoles

The formation of selenadiazole ring is evident from the appearance of bands corresponding to N=N and C-Se around 1580 cm\(^{-1}\) and 700 cm\(^{-1}\) respectively in the IR spectra of 23. Structures of selenadiazoles 23, were further confirmed by \(^1\)H NMR and \(^{13}\)C NMR. The disappearance of methylene signals of the adducts around δ 3.5 ppm arising due to the cyclization forming 1,2,3-selenadiazole rings confirmed the cyclization of semicarbazones. Structures of the selenadiazoles were further supported by the \(^{13}\)C NMR spectra. Disappearance of the ketonic carbon (C=O) signal of the adducts around 197.0 ppm confirmed the formation of selenadiazole derivatives. The appearance of characteristic signals for C-4 and C-5 carbon atoms also clearly indicated the formation of 1,2,3-selenadiazole rings in all compounds.
The structures of the 1,2,3-selenadiazoles 23 were established from $^1$H, $^{13}$C and two dimensional NMR spectroscopic data as illustrated for a representative example, 23b (Figure 4.1). $^1$H, $^{13}$C, 2D NMR, IR and mass spectra of compound 23b are presented in Figures 4.2 - 4.13.

In the $^1$H NMR spectrum of 23b, the terminal methyl protons of the carbethoxy group appears as a triplet at 0.86 ppm ($J = 7.3$ Hz) and shows C,H-COSY correlation with the signal at 10.3 ppm assignable to methyl carbon. This also shows HMBC contours with carbons at 26.2 and 96.5 ppm which are assignable to the methylene carbon C-8 and methine carbon attached to nitro group C-7. The methylene protons appear as a multiplet in the range 1.64-1.77. The methylene protons being diastereotopic, become non-equivalent and show two multiplets in the range 1.64-1.69 ppm and 1.72-1.77 ppm assignable to H-8 and H-8' and show H,H-COSY correlation with the triplet of methyl protons. These protons show HMBC contour with carbons at 10.3 and 96.5 ppm corresponding to C-9 and C-7 respectively.

Figure 4.1 Selected HMBCs and $^1$H and $^{13}$C chemical shifts in compound 23b
There is a three proton singlet at 3.80 ppm due to the methoxy protons. This signal has a C,H- COSY contour with the signal at 55.3 ppm and hence is assigned to C-10. As the signal at 3.80 ppm also shows HMBC contour with the signal at 159.5 ppm, the latter is assigned to C-4'. The H-7 proton appears as a triplet of doublet at 4.9 ppm ( $J = 10.5, 3.0 \text{ Hz}$). This shows H,H-COSY correlation with the multiplet of methylene protons in the range 1.64-1.77 ppm, C,H-COSY correlation with the signal at 96.5 ppm assignable to C-7 and HMBC contour with the carbon at 49.3 ppm assignable to C-6.

The H-6 methine proton appears as a doublet at 4.97 ppm ( $J = 10.5 \text{ Hz}$). This shows C,H-COSY correlation with the signal at 49.3 ppm assignable to C-6. This proton shows four HMBC contours, of which the signals at 26.2 and 96.5 ppm have already been assigned and now the signals at 159.7 and 128.9 ppm are assigned to the carbons C-5 and C-2' respectively. From the C,H- COSY spectrum also the signal at 128.9 is assigned to C-2'. The signals for C-4 and C-5 are distinguished by the fact that C-4 shows only one HMBC contour with the Ar-H signal in the range 7.50-7.62 ppm, while C-5 makes contour with signals at 6.83 and 4.97 ppm. The Ar-H protons at 6.84 ppm appear as a doublet with a $J$ value of 8.5 Hz corresponding to two protons. These protons show C,H-COSY correlation with the signal at 114.9 ppm and H,H-COSY correlation with the doublet of Ar-H protons at 7.12 ppm ( $J = 9.0 \text{ Hz}$) which accounts for two protons.

The results of single crystal X-ray crystallographic study of 5-(1-(4-methoxyphenyl)-2-nitrobutyl)-4-phenyl-1,2,3-selenadiazole 23b [15] are presented in Table 4.1. The ORTEP diagram is shown in Figure 4.16. The bond lengths [Se1—N1] 1.879 Å and [Se1—C8] 1.844 Å are comparable with the values reported in the literature. The selenadiazole ring system and the methoxyphenyl group are oriented at an angle of 76.3° with respect to each other. The crystal packing of the molecules is shown in Figure 4.17. The crystal structure of 23a [17] (Figure 4.18) has also been solved.
**Figure 4.2.** $^1$H NMR Spectrum of 23b (CDCl$_3$)

**Figure 4.3.** $^1$H NMR Spectrum of 23b (expanded)
Figure 4.4. $^{13}$C NMR Spectrum of 23b (CDCl$_3$)

Figure 4.5. $^{13}$C NMR Spectrum of 23b (expanded)
Figure 4.6. DEPT 135 Spectrum of 23b (CDCl₃)

Figure 4.7. DEPT 135 Spectrum of 23b (expanded)
Figure 4.8. H,H-COSY Spectrum of 23b (CDCl$_3$)

Figure 4.9. H,H-COSY Spectrum of 23b (expanded)
Figure 4.10. C,H-COSY Spectrum of 23b (CDCl₃)

Figure 4.11. C,H-COSY Spectrum of 23b (expanded)
Figure 4.12. HMBC Spectrum of 23b (CDCl$_3$)

Figure 4.13. HMBC Spectrum of 23b (expanded)
Figure 4.14. IR Spectrum of 23b (CDCl₃)

Figure 4.15. Mass Spectrum of 23b
Figure 4.16. ORTEP diagram of 23b

Figure 4.17. The crystal packing of 23b
Chapter 4

Results and discussion

Figure 4.18. ORTEP diagram of 23a

Table 4.1. Crystal data and structural refinement for 23b

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4.4. Conclusion

In conclusion, an efficient procedure for the synthesis of new sets of 4-aryl-5-(2-nitro-1-arylbutyl)-1,2,3-selenadiazoles in excellent yields has been developed using Lalezari’s procedure. All the synthesized compounds were characterized by NMR and crystal analysis. Facile transformation of nitro group into various functionalities have extended the importance of nitro compounds. 1,2,3-selenadiazoles can be transformed into various new heterocycles and selenium-containing compounds. Therefore the synthesised compounds are promising materials for the investigation of the mechanism of some reactions and for the synthesis of many interesting compounds of practical importance.
4.5. Experimental section

4.5.1. General method

Solid chemicals were used as such without further purification. Liquid chemicals were purified by distillation before use. Standard methods were used for purification of solvents. The melting points were determined through Ajay melting point apparatus using open capillaries and were uncorrected. The TLC method was used to monitor the progress of the reaction and to check the purity of the compounds with a mixture of petroleum ether (60-80 °C) and ethyl acetate as eluent. Hand drawn silica gel plates of 0.5-0.7mm thickness were used for TLC.

The NMR spectra were recorded on a JEOL GX 500 Spectrometer or Bruker (Avance) 300 MHz NMR instrument using TMS as internal standard and CDCl₃ as solvent. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. IR spectra were recorded on a Bruker IFS-66V FT-IR spectrometer or FT-IR Shimadzu instrument (KBr pellet). The vibrational frequencies are reported in reciprocal centimeter. Mass spectra were recorded on a JEOL GC mate instrument. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyzer. The single crystal X-ray data were collected on a Bruker SMART APEX CCD detector diffractometer. The structure was solved by direct methods from SHELXS-97 and refined by full matrix least squares on F2 by SHELXL-97.

4.5.2. General procedure for the preparation of 4-nitro-1,3-diarylmethylhexan-1-ones (21)

Potassium hydroxide (1.0 M, 10 mL) was added to a solution of chalcone (1 mmol) and 1-nitropropane (1 mmol) at room temperature in DMF (10 mL) and the resulting mixture was stirred until the reaction was complete (monitored by TLC). The product obtained was poured into crushed ice, filtered and dried.

4.5.3. General procedure for the preparation of 4-aryl-5-(2-nitro-1-arylbutyl)-1,2,3-selenadiazoles (23)

A mixture of 4-nitro-1,3-diarylmethylhexan-1-one (1 mmol), semicarbazide hydrochloride (2 mmol) and anhydrous sodium acetate (3 mmol) in ethanol (10 mL) was refluxed for 4h. After completion of the reaction as monitored by TLC, the mixture was poured into crushed ice and the resulting semicarbazone was filtered off and dried. Then,
a mixture of semicarbazone (1 mmol) and selenium dioxide (2 mmol) in tetrahydrofuran (10 mL) were refluxed on a water bath for 1h. The selenium deposited on cooling was removed by filtration, and the filtrate was poured into crushed ice, extracted with dichloromethane, and purified by column chromatography using silica gel (60–120 mesh) with 97:3 petroleum ether:ethyl acetate(v/v) as eluent to afford the pure product 23. The analytical data for all the compounds are given below:

4.5.3.1. 5-(2-nitro-1-phenylbutyl)-4-phenyl-1,2,3-selenadiazole (23a). Pale green solid; Yield 70%; m.p. 134-135 °C; IR (KBr): 2922 (C-H), 1556 (NO2 asy), 1337 (NO2 sym), 1587, (N=N), 700 (C-Se) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_{H}: 0.87\) (t, \(J = 7.3\) Hz, 3H, CH\(_3\)), 1.69-1.76 (m, 2H, CH\(_2\)), 4.95 (dt, \(J = 10.7, 3.1\) Hz, 1H, H-7), 5.03 (d, \(J = 11.5\) Hz, 1H, H-6), 7.22-7.34 (m, 5H, Ar-H), 7.59 (s, 5H, Ar-H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_{C}: 10.4, 26.3, 50.0, 96.3, 127.8, 128.7, 129.3, 129.6, 129.7, 130.1, 131.3, 137.4, 159.3, 161.2. MS: m/z 388.00 (M+1); Anal. Calcd. for C\(_{18}\)H\(_{17}\)N\(_3\)O\(_2\)Se: C, 55.96; H, 4.44; N, 10.88%. Found: C, 55.99; H, 4.46; N, 10.91%.

4.5.3.2. 5-(1-(4-methoxyphenyl)-2-nitrobutyl)-4-phenyl-1,2,3-selenadiazole (23b). Pale green solid; Yield 65%; m.p. 142-143 °C; IR (KBr): 2934 (C-H), 1556 (NO2 asy), 1336 (NO2 sym), 1584, (N=N), 703 (C-Se) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_{H}: 0.86\) (t, \(J = 7.3\) Hz, 3H, CH\(_3\)), 1.64-1.69 (m, 1H, H-8), 1.72-1.77 (m, 1H, H-8'), 3.80 (s, 3H, Ar-OCH\(_3\)), 4.90 (dt, \(J = 10.5\) Hz, 3.0 Hz, 1H, H-7), 4.97 (d, \(J = 10.5\) Hz, 1H, H-6), 6.84 (d, \(J = 8.8\) Hz, 2H, Ar-H), 7.12 (d, \(J = 8.8\) Hz, 2H, Ar-H), 7.56 (s, 5H, Ar-H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_{C}: 10.3, 26.2, 49.3, 55.3, 96.5, 114.9, 128.9, 129.2*, 129.5, 130.0, 131.3, 159.5, 159.7, 160.8. MS: m/z 418.13 (M+1); Anal. Calcd. for C\(_{19}\)H\(_{19}\)N\(_3\)O\(_2\)Se: C, 54.81; H, 4.60; N, 10.09%. Found: C, 54.75; H, 4.52; N, 10.14%

* One carbon merged with other.

4.5.3.3. 4-(4-chlorophenyl)-5-(2-nitro-1-p-tolylbutyl)-1,2,3-selenadiazole (23c). Pale green solid; Yield 72%; m.p. 152-153 °C; IR (KBr): 2932 (C-H), 1555 (NO2 asy), 1338 (NO2 sym), 1580, (N=N), 701 (C-Se) cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_{H}: 0.87\) (t, \(J = 7.3\) Hz, 3H, CH\(_3\)), 1.64-1.69 (m, 1H, H-8), 1.76-1.80 (m, 1H, H-8'), 2.32 (s, 3H, Ar-CH\(_3\)), 4.91 (dt, \(J = 9.5\) Hz, 3.0 Hz, 1H, H-7), 4.96 (d, \(J = 9.5\) Hz, 1H, H-6), 7.00-7.19 (m, 4H, Ar-H), 7.51-7.62 (m, 4H, Ar-H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_{C}: 10.3, 21.1,
4.5.3.4. 5-(1-(4-chlorophenyl)-2-nitrobutyl)-4-phenyl-1,2,3-selenadiazole (23c). Pale green solid; Yield- 65%; m.p. 142-143 °C; IR (KBr): 2940 (C-H), 1555 (NO₂ asy), 1325 (NO₂ sym), 1578, (N=N), 701 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ_H: 0.87 (t, J = 7.3 Hz, 3H, CH₃), 1.63-1.69 (m, 1H, H-8), 1.72-1.78 (m, 1H, H-8'), 4.93 (td, J = 10.5, 3.1 Hz, 1H, H-7), 5.02 (d, J=10.5 Hz, 1H, H-6), 7.24-7.37 (m, 4H, Ar-H), 7.57-7.62 (m, 5H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ_C: 10.4, 26.3, 50.0, 96.1, 127.9, 128.7, 128.8, 129.6, 130.1, 131.6, 133.6, 136.9, 159.3, 160.8. MS: 422.02 (M+1); Anal. Calcd. for C₁₈H₁₆ClN₃O₂Se: C, 51.38; H, 3.83; N, 9.99%. Found: C, 51.30; H, 3.80; N, 10.03%.

4.5.3.5. 5-(2-nitro-1-p-tolylbutyl)-4-phenyl-1,2,3-selenadiazole (23d). Pale green solid; Yield- 75%; m.p. 125-126 °C; IR (KBr): 2933 (C-H), 1556 (NO₂ asy), 1341 (NO₂ sym), 1580, (N=N), 703 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ_H: 0.86 (t, J = 7.3 Hz, 3H, CH₃), 1.62-1.69 (m, 1H, H-8), 1.70-1.78 (m, 1H, H-8'), 2.29 s, 3H, Ar-CH₃, 4.92 (td, J = 10.0 Hz, 3.1 Hz, 1H, H-7), 4.98 (d, J = 10.7 Hz, 1H, H-6), 7.09 (d, J = 8.4 Hz, 2H, Ar-H), 7.13 (d, J = 8.4 Hz, 2H, Ar-H), 7.56-7.62 (m, 5H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ_C: 10.4, 21.2, 26.3, 49.7, 96.4, 127.6, 129.3, 129.6, 130.1, 130.3, 131.4, 134.4, 138.6, 159.6, 160.5. M S: m/z 402.07 (M+1); Anal. Calcd. for C₁₉H₁₉N₃O₂Se: C, 57.00; H, 4.78; N, 10.50%. Found: C, 56.93; H, 4.71; N, 10.55%.

4.5.3.6. 4-(4-chlorophenyl)-5-(2-nitro-1-phenylbutyl)-1,2,3-selenadiazole (23e). Pale green solid; Yield- 70%; m.p. 129-130 °C; IR (KBr): 2930 (C-H), 1554 (NO₂ asy), 1343 (NO₂ sym), 1581, (N=N), 701 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ_H: 0.89 (t, J =7.5 Hz, 3H, CH₃), 1.61-1.71 (m, 1H, H-8), 1.77-1.81 (m, 1H, H-8'), 4.90-4.96 (m, 1H, H-7), 4.97 -4.99 (m, 1H, H-6), 7.20-7.86 (m, 9H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ_C: 10.3, 26.2, 50.1, 96.2, 127.7, 128.5, 129.2, 129.7, 129.9, 131.4, 135.5, 137.0, 159.4, 159.5. MS: m/z 422.03 (M+1); Anal. Calcd. for C₁₉H₁₆ClN₃O₂Se: C, 51.38; H, 3.83; N, 9.99%. Found: C, 51.32; H, 3.76; N, 10.03%. 

26.2, 49.7, 96.3, 127.6, 129.0, 129.2, 129.8, 130.5, 131.4, 135.5, 138.7, 159.8, 159.9. MS: m/z 436.08 (M+1); Anal. Calcd. for C₁₉H₁₆ClN₃O₂Se: C, 52.49; H, 4.17; N, 9.66%. Found: C, 52.43; H, 4.12; N, 9.69%.
4.5.3.7. 5-(1-(4-chlorophenyl)-2-nitrobutyl)-4-(4-methoxyphenyl)-1,2,3-selenadiazole (23f). Pale green solid; Yield: 62%; m.p. 121-122 °C; IR (KBr): 2929 (C-H), 1555 (NO₂ asym), 1340 (NO₂ sym), 1578, (N=N), 703 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDC₁₃) δH: 0.89 (t, J = 7.3 Hz, 3H, CH₃), 1.52-1.57 (m, 1H, H-8), 1.84-1.91 (m, 1H, H-8'), 3.87 (s, 3H, Ar-OCH₃), 4.79-4.88 (m, 1H, H-7), 5.01-5.05 (m, 1H, H-6), 6.85-7.91 (m, 8H, Ar-H). ¹³C NMR (75 MHz, CDC₁₃) δC: 10.3, 26.1, 50.0, 55.5, 96.5, 114.0, 128.8, 129.5, 129.8, 130.4, 133.5, 137.4, 159.0, 160.2, 163.7. MS: m/z 451.02 (M+1); 452.08. Anal. Calcd. for C₁₉H₁₈ClN₃O₃Se: C, 50.62; H, 4.02; N, 9.32%. Found: C, 50.56; H, 3.96; N, 9.35%.

4.5.3.8. 4-(4-methoxyphenyl)-5-(2-nitro-1-p-tolybutyl)-1,2,3-selenadiazole (23g). Green solid; Yield: 66%; m.p. 143-144 °C; IR (KBr): 2933 (C-H), 1554 (NO₂ asym), 1340 (NO₂ sym), 1597 (N=N), 701(C-Se) cm⁻¹; ¹H NMR (300 MHz, CDC₁₃) δH: ¹H NMR (300 MHz, CDC₁₃) δH: 0.88 (t, J = 7.3 Hz, 3H, CH₃), 1.52-1.70 (m, 1H, H-8), 1.71-1.92 (m, 1H, H-8'), 2.30 (s, 3H, Ar-CH₃), 3.8 (s, 3H, Ar-OCH₃), 4.90 (td, J = 10.0 Hz, 3.0 Hz, 1H, H-7), 4.98 (d, J = 10.7 Hz, 1H, H-6), 6.89-8.06 (m, 8H, Ar-H); ¹³C NMR (75 MHz, CDC₁₃) δC: 10.3, 21.1, 26.2, 49.7, 55.5, 96.4, 114.3, 127.6, 128.4, 129.7, 130.2, 133.5, 138.4, 160.0, 160.5, 163.6. MS: m/z 432.02 (M+1); Anal. Calcd. for C₂₀H₂₁N₃O₃Se: C, 55.82; H, 4.92; N, 9.76%. Found: C, 55.76; H, 4.87; N, 9.80%.

4.5.3.9. 4-(4-chlorophenyl)-5-(1-(4-methoxyphenyl)-2-nitrobutyl)-1,2,3-selenadiazole (23h). Green solid; Yield: 63%; m.p. 126-128 °C; IR (KBr): 2983 (C-H), 1555 (NO₂ asym), 1340 (NO₂ sym), 1595 (N=N), 701 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDC₁₃) δH: 0.87 (t, J = 7.5 Hz, 3H, CH₃), 1.63-1.70 (m, 1H, H-8), 1.75-1.82 (m, 1H, H-8'), 3.79 (s, 3H, Ar-OCH₃), 4.84-4.89 (m, 1H, H-7), 4.91-4.95 (m, 1H, H-6), 7.02 (d, J = 9.0 Hz, 2H, Ar-H), 7.13 (d, J = 9.0 Hz, 2H, Ar-H), 7.49-7.61 (m, 4H, Ar-H). ¹³C NMR (75 MHz, CDC₁₃) δC: 10.3, 26.2, 49.4, 55.3, 96.5, 114.9, 128.8, 129.1, 129.2, 131.3, 132.9, 135.7, 159.1, 159.5, 160.0. MS: m/z 452.15 (M+1); Anal. Calcd. for C₁₉H₁₈ClN₃O₃Se: C, 50.62; H, 4.02; N, 9.32%. Found: C, 50.56; H, 3.96; N, 9.37%.
4.5.3.10. 4-(4-chlorophenyl)-5-(1-(4-chlorophenyl)-2-nitrobutyl)-1,2,3-selenadiazole (23i). Green solid; Yield- 69%; m.p. 138-139 °C; IR (KBr): 2983 (C-H), 1557 (NO₂ Asy), 1342 (NO₂ sym), 1592 (N=N), 702 (C-Se) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δH: 0.87 (t, J = 7.2 Hz, 3H, CH₃), 1.51-1.60 (m, 2H, CH₂), 4.64-4.71 (m, 1H, H-7), 4.89-4.94 (m, 1H, H-6), 7.09-7.95, (m, 8H, Ar-H). ¹³C NMR (75 MHz, CDCl₃) δC: 10.1, 26.0, 48.1, 95.3, 128.8, 129.1, 129.2, 129.4, 133.5, 134.5, 136.9, 139.8, 159.1, 160.1. MS: m/z 455.22 (M+1) Anal. Calcd. for C₁₈H₁₅Cl₂N₃O₂Se: C, 47.49; H, 3.32; N, 9.23%. Found: C, 47.36 ; H, 3.26; N, 9.26%. 