Synthesis of 4-Imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide through Cycloaddition Reaction of N-Sulphinylanilines and N-(α-Cyano-α-aryl)-methylanilines

Manpreet Kaur and Baldev Singh*

Department of Chemistry, Punjabi University, Patiala 147002, Punjab, India
*E-mail: singhbaldev1981@gmail.com

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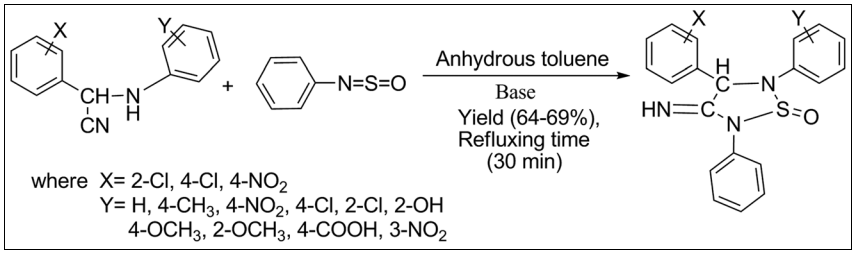

Through the normal mode of cycloaddition reaction of N-(α-cyano-α-aryl)-methylanilines (II) onto N-sulphinylanilines (III) has provided 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxides (IV). The present protocol has advantage of convenient operation to synthesize heterocyclics in good yield.

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INTRODUCTION

N-Sulphinylanilines because of the presence of cumulative double bonds and suitable polarity in bonds have been known for the synthesis of new heterocyclic compounds [1]. The 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide has been synthesized successfully by the cycloaddition reaction of N-sulphinylanilines acting as diene with substituted benzalanilines [2,3] (Scheme 1). In an earlier report from these laboratories, the Diels–Alder cycloaddition reaction of N-sulphinylanilines acting as dienophiles with conjugated open chain azomethines acting as diene has been reported [4].

RESULT AND DISCUSSION

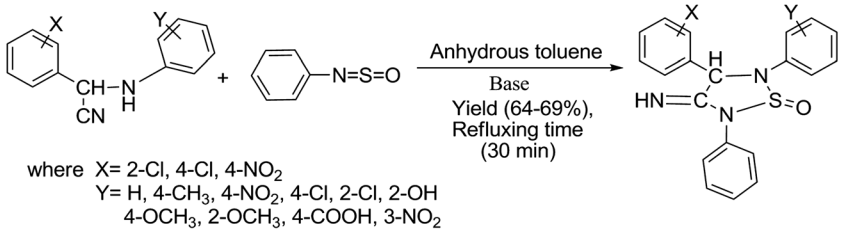
Presently, the cycloaddition reaction of N-sulphinylanilines with N-(α-cyano-α-aryl)-methylanilines have been successfully carried out. The N-(α-cyano-α-aryl)-methylanilines needed for the reaction have been synthesized through hydrocyanation of azomethines employing potassium cyanide in aqueous ethanolic solution under acidic condition [5], whereas the azomethines required for hydrocyanation were synthesized by condensing aromatic aldehyde and aromatic amines having both electron withdrawing and electron-donating substituents on C-phenyl and N-phenyl moiety [6].

N-Sulphinylaniline used for cycloaddition reaction has been synthesized by the reaction of thionyl chloride with aniline [7,8]. In these dipolar cycloaddition, N-(α-cyano-α-aryl)-methylanilines (II) act as a "dipole" and sulphinylanilines (III) act as "dipolarophiles." This cycloaddition reaction has been carried out by the refluxing of N-(α-cyano-α-aryl)-methylanilines with an excess of sulphinylanilines in anhydrous toluene in the presence of catalytic amount of anhydrous pyridine. The usual work-up of the reaction mixture provided the crude product, which on recrystallization gave pure product in good yield. These have been characterized as 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IV) through their melting point, elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectra (Scheme 2). The reaction seems to proceed by the initial attack of the lone pair of electrons on the nitrogen atom of secondary amine on the electron-deficient sulfur atom of N-sulphinylaniline, and cyclization is completed by the subsequent attack of the heterocumulene double bond at the carbon atom of the nitrile function, followed by the loss of proton from the ammonium ion to pyridine base. The iminium anion in turn takes up this proton from the protonated base to give the cycloadduct (IV) (Scheme 2).

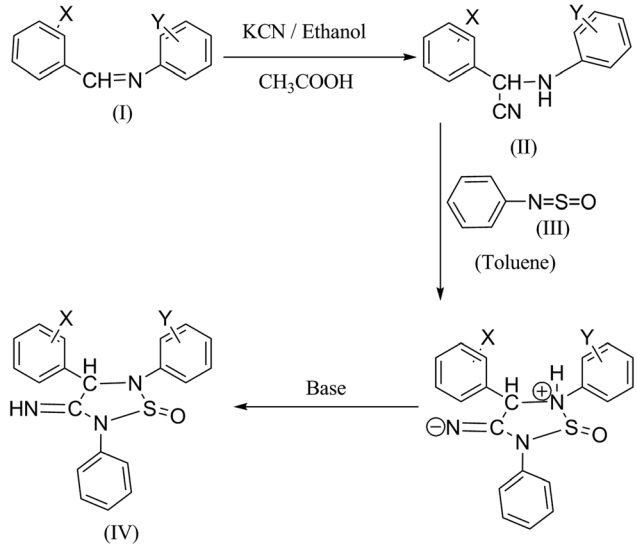
The infrared spectra of cycloadduct (IV) show absorption band at 3379 (>N–H), 1660–1616 (>C=N–), 1021 (>S=O), and 1632–1597 (aromatic >C=C) cm^{-1} in addition to absorption bands because of other functions present. These spectra lack the absorption band at 2236–2230 cm^{-1} because of nitrile function, indicating that nitrile group has enter into the cycloaddition reaction.

In the 400 MHz ^{1}H NMR spectra of 3-(2-chlorophenyl)-4-imino-5-phenyl-2-(2-methoxyphenyl)-2H,3H,5H-[1,2,5] thiadiazolidin-1-oxide display a multiplet signal in the region at δ 7.8–6.7 (13H, Ar) has been assigned to aromatic proton, a singlet in the region at δ 4.6 (1H, >N–H) assigned to imino proton. A singlet in the region at δ 5.7 (1H, CH–) assigned to the benzylic proton, this proton disappears on deuterium exchange, whereas a sharp singlet in the region at δ 3.8 (3H, –OCH$_3$) assigned to methoxy proton.

Scheme 1. Classical Synthesis of 4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide.



Scheme 2. Mechanistic pathway of 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide.



In their ^{13}C NMR spectra, compound 3-(2′-chlorophenyl)-4-imino-5-phenyl-2-(2″-methoxyphenyl)-2H,3H,5H-[1,2,5] thiadiazolidin-1-oxide displays the signal at δ 147.5 has been assigned to imino carbon, signal at δ 134.4 has been assigned to etheric aromatic carbon, whereas carbon bearing chlorine appears at δ 133.5. The signals at δ 130.9 and δ 130.4 have been assigned to aromatic carbon attached to nitrogen atom and other signals at δ 110.1–111.7, 117.8–119.8, and 121.2–128.8 have been assigned to carbon atom of aromatic ring. The signal at δ 47.5 has been assigned to carbon atom of benzylic group, whereas the signal at δ 55.5 assigned to carbon atom of methoxy group. In the high resolution mass spectra, 3-(2′-chlorophenyl)-4-imino-5-phenyl-2-(2″-methoxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide display molecular ion peak at *m/z* 411 and others prominent peaks are at *m/z* 271, 246 and, 212.

These cycloaddition reactions are regiospecific in nature as all the cycloaddition reactions lead to the formation of only one isomer in each case. It may be concluded that the azomethines having electron donating as well as electron withdrawing groups in the N-phenyl ring and C-phenyl ring undergo these cycloaddition reaction effectively.

EXPERIMENTAL

I. General procedure for the preparation of azomethines. Variously substituted azomethines were prepared by following an identical procedure as described in the literature [5]. Synthesis of *o*-chlorobenzylidene-*o*-anisidine is described as a representative case. Orthochlorobenzaldehyde 1.40 g (0.01 mol) was mixed with 1.23 g (0.01 mol) of *o*-anisidine in 10 cm^3 of ethyl alcohol. The reaction mixture after gentle warming provided the required azomethines. Mp 78–80°C.

II. General procedure for the preparation of N-(α-cyano-α-aryl)-methylanilines. To the aqueous ethanolic solution of azomethines 2.45 g (0.01 mol) taken in conical flask, an equimolar quantity of sodium cyanide 1.06 g (0.01 mol) was added along with the addition of glacial acetic acid (3–5 mL), in a good ventilated hood. The flask was tightly corked and shaken intermitantly for half an hour. The reaction mixture was kept for overnight period. Usual work-up of reaction mixture provided the crystalline product that was recrystallized from petroleum ether. Mp 94–96°C.

III. General procedure for the preparation of 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide. To N-(α-cyano-α-aryl)-methylanilines (0.01 mol, 2.08 g), in anhydrous toluene taken in a 100 mL round bottom flask, were added a few drops of anhydrous pyridine and N-sulphinylanilines (0.015 mol, 2.34 g) at

room temperature. The reaction mixture was refluxed for 30–40 min and was allowed to stand overnight. This, on addition of solvent ether, gave a white product. The crude product was washed with anhydrous ether and was recrystallized from alcohol–ether (1:1) mixture to yield 3-(2′-chlorophenyl)-4-imino-5-phenyl-2-(2″-methoxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide in 67% yield. Mp 85–87°C. These thiadiazolidin-1-oxides have been characterized through elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and high resolution mass spectral data. All the thiadiazolidin-1-oxides (IIa to IIs) were prepared by following an identical procedure (Tables 1 and 2).

3-(2-Chlorophenyl)-4-imino-2,5-diphenyl-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIa). Mp 85–87°C; Yield: 69%; IR (Potassium bromide): 3332 (>N–H), 1656 (>C═N–), 1632–1575 (aromatic >C═C<), 1023 (>S═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.7–6.8 (14H, m, Ar), 4.2 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 46.7, 111.3, 116.7, 118.2, 119.3, 121.7, 127.3, 129.2, 129.4, 130.3, 131.7, 133.2, 143.7; MS: Molecular ion peak *m/z* 381; *Anal*. Calcd for $C_{20}H_{16}ClN_3OS$: C, 62.90; H, 4.22; N, 11.00. Found: C, 62.83; H, 4.10; N, 11.02.

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(4-tolyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIb). Mp 112–114°C; Yield 67%; IR (Potassium bromide): 3338 (>N–H), 1024 (>S═O), 1630–1585 (aromatic >C═C), 1675 (>C═N–) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.8–6.9 (13H, m, Ar), 4.3 (1H, S, >N–H), 5.5 (1H, S, CH–), 2.5 (3H, S, –CH_3); ^{13}C NMR ($CDCl_3$) δ: 43.2, 46.5, 110.2, 111.6, 117.7, 119.6, 121.4, 127.6, 128.3, 129.2, 130.2, 130.7, 131.7, 133.4, 134.2, 148.3; MS: Molecular ion peak *m/z* 395; *Anal*. Calcd for $C_{21}H_{18}ClN_3OS$: C, 63.71; H, 4.58; N, 10.61. Found: C, 63.07; H, 4.36; N, 10.22.

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(4-nitrophenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIc). Mp 155–157°C; Yield: 63%; IR (Potassium bromide): 3334 (>N–H), 1021 (>S═O), 1632–1573 (aromatic >C═C<), 1665 (>C═N–) cm^{-1}; H NMR (400 MHz, $CDCl_3$) δ: 7.9–6.8 (13H, m, Ar), 4.4 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ 47.3, 109.2, 111.3, 117.3, 119.4, 121.7, 127.3, 128.3, 128.8, 129.2, 130.3, 131.4, 133.5, 134.3, 147.5; MS: Molecular ion peak *m/z* 426; *Anal*. Calcd for $C_{20}H_{15}ClN_4O_3S$: C, 56.27; H, 3.54; N, 13.12. Found: C, 56.12; H, 3.17; N, 13.12.

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(4-chlorophenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IId). Mp 102–104°C; Yield: 64%; IR (Potassium bromide): 3344 (>N–H), 1035–1050 (S═O), 1635–1598 (aromatic >C═C<), 1686–1612 (>C═N–) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.4–6.7 (13H, m, Ar), 4.1 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}CNMR ($CDCl_3$) δ: 48.1, 115.5, 117.4, 125.3, 127.8, 129.0, 129.5, 129.8, 130.5, 131.2, 131.8, 133.5, 143.1; MS: Molecular ion peak *m/z* 415; *Anal*. Calcd for $C_{20}H_{15}Cl_2N_3OS$: C, 57.70; H, 3.63; N, 10.09. Found: C, 57.23; H, 3.17; N, 10.02.

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(4-methoxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolodin-1-oxide (IIe). Mp 95–97°C; Yield: 68%; IR (Potassium bromide): 3337– (>N–H), 1024 (>S═O), 1630–1580 (aromatic >C═C<), 1665 (>C═N–) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.9–6.8 (13H, m, Ar), 4.4 (1H, s, >N–H), 5.6 (1H, s, CH–), 3.6 (3H, s, –OCH_3); ^{13}C NMR ($CDCl_3$) δ: 46.0, 56.3, 110.2, 111.3, 116.4, 117.7, 119.6, 121.0, 126.7, 128.8, 129.0, 130.3, 130.7, 131.6, 133.3, 134.5, 147.7; MS: Molecular ion peak *m/z* 411; *Anal*. Calcd for $C_{21}H_{18}ClN_3O_2S$: C, 61.23; H, 4.40; N, 10.20. Found: C, 61.03; H, 4.14; N, 10.03.

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(2-chlorophenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIf). Mp 115–117°C; Yield: 67%; IR (Potassium bromide): 3365 (>N–H), 1021 (>S═O), 1630–1595 (aromatic >C═C), 1683 (>C═N–) cm^{-1}; H NMR (400 MHz, $CDCl_3$) δ7.8–6.9 (13H, m, Ar), 4.6 (1H, s, >N–H), 5.4 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 46.8, 109.8, 110.2, 111.4, 117.3, 119.8, 121.7, 126.6, 127.3, 128.6, 129.3, 130.7, 131.8, 133.4, 134.3, 146.7; MS: Molecular ion peak *m/z* 416; *Anal*. Calcd for $C_{20}H_{15}Cl_2N_3OS$: C, 57.70; H, 3.63; N, 10.09. Found: C, 57.22; H, 3.12; N, 10.09

3-(2-Chlorophenyl)-4-imino-5-phenyl-2-(2-methoxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIg). Mp 85–87°C; Yield: 66%; IR (Potassium bromide): 3379 (>N–H), 1660–1616

Table 1

Characterization data of azomethines and N-(α-Cyano-α-aryl)-methylanilines.

Entry	X	Y	Mp of azomethines (°C)	Mp of N-(α-Cyano-α-aryl)-methylanilines (°C)
II (a)	2-Cl	H	45–47	68–70
II (b)	2-Cl	4-CH_3	52–54	90–92
II (c)	2-Cl	4-NO_2	122–23	185–87
II (d)	2-Cl	4-Cl	64–66	110–12
II (e)	2-Cl	4-OCH_3	60–62	87–89
II (f)	2-Cl	2-Cl	112–14	132–34
II (g)	2-Cl	2-OCH_3	78–80	94–96
II (h)	4-Cl	H	65–63	108–10
II (i)	4-Cl	4-CH_3	125–27	92–94
II (j)	4-Cl	4-OCH_3	120–23	78–80
II (k)	4-Cl	4-Cl	110–12	121–23
II (l)	4-Cl	4-COOH	257–59	207–210
II (m)	4-Cl	3-NO_2	121–23	93–95
II (n)	4-Cl	2-OH	112–13	108–10
II (o)	4-NO_2	H	88–90	116–18
II (p)	4-NO_2	4-CH_3	116–18	202–04
II (q)	4-NO_2	4-NO_2	198–200	138–40
II (r)	4-NO_2	4-Cl	126–28	252–54
II (s)	4-NO_2	2-OCH_3	98–100	122–23

Table 2

Characterization data of 2,3,5-triaryl-4-imino-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxides.

Entry	X	Y	Mp of thiadiazolidin-1-oxide (°C)	Refluxing time (min)	Yield (%)
II (a)	2-Cl	H	85–87	25	69
II (b)	2-Cl	4-CH_3	112–14	30	67
II (c)	2-Cl	4-NO_2	155–57	60	63
II (d)	2-Cl	4-Cl	102–04	40	64
II (e)	2-Cl	4-OCH_3	95–97	15	68
II (f)	2-Cl	2-Cl	115–17	55	67
II (g)	2-Cl	2-OCH_3	85–87	20	67
II (h)	4-Cl	H	83–85	28	67
II (i)	4-Cl	4-CH_3	68–70	32	62
II (j)	4-Cl	4-OCH_3	92–94	22	64
II (k)	4-Cl	4-Cl	105–07	38	66
II (l)	4-Cl	4-COOH	170–72	39	65
II (m)	4-Cl	3-NO_2	155–57	58	64
II (n)	4-Cl	2-OH	115–17	45	67
II (o)	4-NO_2	H	122–24	30	69
II (p)	4-NO_2	4-CH_3	228–30	28	67
II (q)	4-NO_2	4-NO_2	158–160	57	64
II (r)	4-NO_2	4-Cl	297–99	38	67
II (s)	4-NO_2	2-OCH_3	172–73	18	63

(>C=N–), 1021 (>S=O), 1632–1597 and 1536–1500 (aromatic >C=C<) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.8–6.7 (13H, m, Ar), 4.6 (1H, s, >N–H–), 5.7 (1H, s, CH–), 3.8 (3H, s, –OCH_3); ^{13}C NMR ($CDCl_3$) δ: 47.5, 55.5, 110.1, 111.7, 117.8, 119.8, 121.2, 127.8, 128.8, 129.0, 130.4, 130.9, 131.9, 133.5, 134.4, 147.5; MS: Molecular ion peak *m/z* 411 and others prominent peak are at *m/z* 271, 246, 212; *Anal*. Calcd for $C_{21}H_{18}ClN_3O_2S$: C, 61.23; H, 4.40; N, 10.20. Found: C, 61.12; H, 4.17; N, 10.08.

3-(4-Chlorophenyl)-4-imino-2,5-diphenyl-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIh). Mp 83–85°C; Yield: 67%; IR (Potassium bromide): 3345 (>N–H), 1645 (>C=N–), 1632–1580 (aromatic >C=C<), 1021 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2–6.8 (14H, s, CH–), 4.2 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 48.3, 115.4, 117.6, 125.3, 125.8, 126.7, 127.3, 128.3, 128.8, 129.5, 130.5, 131.3, 131.7, 133.7, 144.2; MS: Molecular ion peak *m/z* 383; *Anal*. Calcd for $C_{20}H_{16}ClN_3OS$: C, 62.57; H, 4.73; N, 10.95.. Found: C, 62.27; H, 4.23; N, 10.12.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(4-tolyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIi). Mp 68–70°C; Yield: 62%; IR (Potassium bromide): 3342–3312 (>N–H), 1667 (>C=N–), 1640–1575 (aromatic >C=C<), 1024 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.1–7.1 (13H, m, Ar), 4.3 (1H, s, >N–H), 5.5 (1H, S, CH–), 2.4 (3H, s, –CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 43.6, 48.7, 110.2, 111.6, 117.3, 119.7, 121.3, 127.6, 128.7, 129.3, 130.6, 131.8, 132.3, 132.9, 133.3, 134.5, 147.2; MS: Molecular ion peak *m/z* 395; *Anal*. Calcd for $C_{21}H_{18}ClN_3OS$: C, 63.3; H, 5.07; N, 10.56. Found: C, 62.9; H, 4.89; N, 10.12.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(4-methoxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIj). Mp 92–94°C; Yield: 64%; IR (Potassium bromide): 3342 (>N–H), 1672 (>C=N–), 1638–1573 (aromatic >C=C<), 1024 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.0–6.9 (13H, m, Ar), 4.5 (1H, s, >N–H), 5.4 (1H, s, CH–), 3.4 (3H, s, –OCH_3); ^{13}C NMR ($CDCl_3$) δ: 46.7, 57.3, 110.3, 111.7, 116.6, 117.4, 119.5, 121.2, 126.4, 128.3, 129.2, 130.4, 130.7, 131.6, 133.7, 134.7, 147.7; MS: Molecular ion peak *m/z* 410; *Anal*. Calcd for $C_{21}H_{18}ClN_3O_2S$: C, 60.94; H, 4.87; N, 10.15. Found: C, 60.23; H, 4.12; N, 10.02.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(4-chlorophenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIk). Mp 105–107°C; Yield: 66%; IR (Potassium bromide): 3338 (>N–H), 1673 (>C=N–), 1630–1590 (aromatic >C=C<), 1023 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.2–6.8 (13H, m, Ar), 4.6 (1H, s, >N–H), 5.5 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 47.8, 114.7, 115.3, 117.7, 125.4, 127.7, 128.3, 128.9, 129.7, 130.4, 131.5, 131.9, 133.6, 144.6; MS: Molecular ion peak *m/z* 416; *Anal*. Calcd for $C_{20}H_{15}Cl_2N_3OS$: C, 57.42; H, 4.10; N, 10.04. Found: C, 57.12; H, 3.92; N, 9.93.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(4-carboxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIl). Mp 170–72°C; Yield 66%; IR (Potassium bromide): 3379 (>N–H), 1665 (>C=N), 1630–1590 (aromatic >C=C), 1023 (>S=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.1–6.7 (13H, m, Ar), 4.3 (1H, s, >N–H), 5.7 (1H, s, –CH), 11.9 (1H, s, COOH); ^{13}C NMR ($CDCl_3$) δ: 48.3, 110.4, 111.3, 111.9, 121.7, 127.6, 128.3, 128.7, 129.6, 130.5, 130.7, 131.3, 131.7, 133.6, 134.7, 147.7, 150.7; MS: Molecular ion peak *m/z* 425; *Anal*. Calcd for $C_{21}H_{16}ClN_3O_3S$: C, 58.94; H, 4.24; N, 9.82. Found: C, 58.14; H, 4.03; N, 9.12.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(3-nitrophenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIm). Mp 155–157°C; Yield: 64%; IR (Potassium bromide): 3345 (>N–H), 1645 (>C=N–), 1638–1587 (aromatic >C=C<), 1021 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.1–6.8 (13H, m, Ar), 4.4 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 44.6, 110.7, 111.4, 117.8, 119.3, 121.3, 127.4, 128.5, 129.2, 130.4, 130.8, 131.4, 133.3, 134.7, 148.3; MS: Molecular ion peak *m/z* 426; *Anal*. Calcd for $C_{20}H_{15}ClN_4O_3S$: C, 56.01; H, 4.00; N, 13.06. Found: C, 55.93; H, 3.97; N, 13.02.

3-(4-Chlorophenyl)-4-imino-5-phenyl-2-(2-hydroxyphenyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIn). Mp 115–117°C; Yield: 67%; IR (Potassium bromide): 3342 (>N–H), 1665 (>C=N–), 1630–1585, 1545–1515 (aromatic >C=C<), 1024 (>S=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.9–6.7 (13H,

m, Ar), 4.6 (1H, s, >N–H), 5.4 (1H, s, CH–), 9.2 (1H, s, –OH); ^{13}C NMR ($CDCl_3$) δ: 47.3, 111.7, 115.8, 116.8, 118.3, 119.5, 121.3, 127.4, 129.4, 130.4, 131.6, 132.3, 143.3; MS: Molecular ion peak *m/z* 399; *Anal*. Calcd for $C_{20}H_{16}ClN_3O_2S$: C, 60.07; H, 4.54; N, 10.51. Found: C, 60.02; H, 4.23; N, 10.28.

3-(4-Nitrophenyl)-4-imino-2,5-diphenyl-2H,3H,5H-[1,2,5] thiadiazolidin-1-oxide (IIo). Mp 122–124°C; Yield: 69%; IR (Potassium bromide): 3373 (>N–H), 1665 (>C═N–), 1024 (>S═0), 1630–1585 and 1545–1515 (aromatic >C═C<) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.0–6.8 (14H, m, Ar), 4.4 (1H, s, >N–H), 5.5 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 46.3, 112.2, 114.4, 117.3, 119.7, 126.3, 127.4, 128.3, 128.8, 130.7, 130.9, 131.5, 133.4, 134.3, 148.2; Ms: Molecular ion peak *m/z* 392; *Anal*. Calcd for $C_{20}H_{16}N_4O_3S$: C, 61.21; H, 4.11; N, 14.28. Found: C, 61.12; H, 4.02; N, 14.12.

3-(4-Nitrophenyl)-4-imino-5-phenyl-2-(4-tolyl)-2H,3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIp). Mp 228–230°C; Yield: 67%; IR (Potassium bromide): 3375 (>N–H), 1675 (>C═N–), 1021 (>S═O), 1635–1590 (aromatic >C═C<) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.9–6.9 (13H, m, Ar), 2.5 (3H, s, $–CH_3$), 4.5 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 44.7, 48.3, 110.2, 111.4, 117.7, 119.3, 121.4, 127.7, 128.6, 129.3, 129.7, 130.6, 131.7, 133.4, 134.4, 147.5; MS: Molecular ion peak *m/z* 406; *Anal*. Calcd for $C_{21}H_{18}N_4O_3S$: C, 62.05; H, 4.46; N, 13.78. Found: C, 61.93; H, 4.12; N, 13.27.

3-(4-Nitrophenyl)-4-imino-5-phenyl-2-(4-nirophenyl)-2H,3H, 5H-[1,2,5]thiadiazolidin-1-oxide (IIq). Mp 158–160°C; Yield: 64%; IR (Potassium bromide): 3360 (>N–H), 1673 (>C═N–), 1024 (>S═O), 1632–1593 (aromatic >C═C<) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.1–6.8 (13H, m, Ar), 4.6 (1H, s, >N–H), 5.5 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 47.8, 111.2, 111.8, 116.3, 117.8, 119.2, 121.4, 126.4, 127.2, 127.9, 128.8, 129.3, 130.4, 130.9, 131.3, 133.2, 134.7, 146.4; MS: Molecular ion peak *m/z* 437. *Anal*. Calcd for $C_{20}H_{15}N_5O_5S$: C, 54.91; H, 3.46; N, 16.01. Found: C, 54.17; H, 3.11; N, 16.00.

3-(4-Nitrophenyl)-4-imino-5-phenyl-2-(4-chlorophenyl)-2H, 3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIr). Mp above 300°C; Yield: 67%; IR (Potassium bromide): 3365 (>N–H), 1665 (>C═N–), 1023 (>S═O), 1635–1585 (aromatic >C═C<) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 8.2–6.9 (13H, m, Ar), 4.5 (1H, s, >N–H), 5.6 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 47.3, 110.1, 111.7, 119.8, 121.2, 127.4, 128.3, 128.8, 129.2, 130.2, 130.7, 131.7, 133.4, 134.2, 147.8; MS: Molecular ion peak *m/z* 426; *Anal*. Calcd for $C_{20}H_{15}Cl\ N_4O_3S$: C, 56.27; H, 3.54; N, 13.12. Found: C, 56.12; H, 3.12; N, 13.02.

3-(4-Nitrophenyl)-4-imino-5-phenyl-2-(2-methoxyphenyl)-2H, 3H,5H-[1,2,5]thiadiazolidin-1-oxide (IIs). Mp 172–173°C; Yield: 63%; IR (Potassium bromide): 3375 (>N–H), 1668 (>C═N–), 1024 (>S═O), 1630–1590 (aromatic >C═C<) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.0–6.9 (13H, m, Ar), 3.6 (3H, s, $–OCH_3$), 4.6 (1H, s, >N–H), 5.5 (1H, s, CH–); ^{13}C NMR ($CDCl_3$) δ: 46.7, 55.2, 110.1, 111.3, 117.3, 119.3, 121.7, 127.4, 127.9, 128.8, 129.0, 130.7, 131.3, 133.4, 134.2, 143.7; MS: Molecular ion peak *m/z* 422; *Anal*. Calcd for $C_{21}H_{18}N_4O_4S$: C, 59.42; H, 4.75; N, 13.20. Found: C, 59.12; H, 4.27; N, 13.00.

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