SUBSTITUENT EFFECTS USING ^{13}C CHEMCIAL SHIFTS FOR A SERIES OF SUBSTITUTED 2-PHENYL-3-(PYRIDIN-2-YL)-1,3-THIAZOLIDIN-4-ONES WITH A COMPARISON TO SIMILARLY SUBSTITUTED 1,3-THIAZOLIDIN-4-ONES

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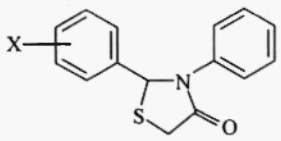
Abstract: Substituted 2,3-diphenyl-1,3-thiazolidin-4-ones and substituted 3-benzyl-2-phenyl-1,3-thiazolidin-4-ones have been shown to exhibit good correlations using ^{13}C chemical shift measurements (substituents chemical shifts or scs) for substituents placed on the phenyl and benzyl moieties versus Hammett σ constants; the chemical shifts for C(2), C(4) and C(5) in the thiazolidinone ring have been the focus of interest. In some instances the correlations can be further improved by using dual substituent parameters. In this study the effects of substituents on ^{13}C chemical shifts in the thiazolidinone ring at C(2), C(4) and C(5) were measured for a series of substituted 2-phenyl-3-pyridin-2-yl-1,3-thiazolidin-4-ones. The chemical shift changes were compared to the two aforementioned series of thiazolidin-4-ones.

Introduction

Thiazolidin-4-ones have a long history of exhibiting biological activity, and the earliest compilation was completed by Brown.[1] Further, thiazolidin-4-ones have also been used as ligands where their metal complexes also exhibit biological activity;[2] for these reasons synthesizing and investigating the properties of additional novel series is of interest.

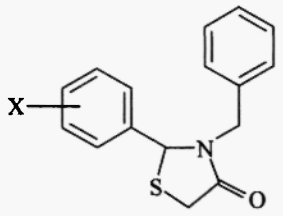
Previously, we have described[3-6] the substituent effects on C(2), C(4) and C(5) sites in the heterocyclic ring, from the phenyl ring at C(2), Figure-1 (Series1), using ^{13}C data for a series of substituted 2,3-diphenyl-1,3-



Series 1: X = *p*-NO_2, *m*-NO_2, *p*-F, *m*-F, *p*-Cl, *p*-Br, *m*-Br, H, *p*-CH_3, *m*-CH_3, *p*-OCH_3, *m*-OCH_3

Figure-1

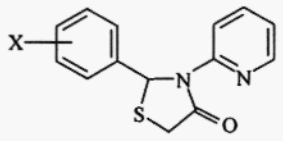
thiazolidin-4-ones. Also,for the same series of compounds the effects of the substituents on the methine proton and the protons at C(5) utilizing ^1H NMR have been shown. Woolston *et al*[7] have also reported similar substituent effects with a number of different substituent groups in the 2-phenyl ring. In addition, we have observed[8] similar substituent effects in a series of substituted 3-benzyl-2-phenyl-1,3-thiazolidin-4-ones (Series 2) shown in Figure-2. Series 2 has a more limited range of substituents than Series 1, and we have taken the unusual stance of including as many halogens in the series as possible in order to test the robustness of the Hammett and Swain-Lupton correlations; normally only the fluoro group and either the chloro or bromo substituents are used, but not all three halogens due to anomalous outcomes.[9]



Series 2: X = *p*-F, *p*-Cl, *p*-Br, H, *p*-CH_3, *p*-OCH_3,

Figure-2

With this background in mind we synthesized a series of substituted 2-phenyl-3-pyridin-2-yl-1,3-thiazolidin-4-ones shown in Figure-3 (Series 3). For this series we followed the same substituent pattern used in Series 1. In concert with the previous studies our focus was on the transmission of substituent effects from the C(2) phenyl ring to the C(2), C(4) and C(5) carbons.



Series 3: X = *p*-NO_2, *m*-NO_2, *p*-F, *m*-F, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, H, *p*-CH_3, *m*-CH_3, *p*-OCH_3, *m*-OCH

Figure-3

Results and Discussion

The ^{13}C chemical shift values for C(2), C(4) and C(5) are shown in Table 1 for all three series of thiazolidin-4-ones. The most obvious effect of having a phenyl group at N(3) (Series1) is that there is a marked upfield shift for the ^{13}C chemical shifts at C(2) when a benzyl group (Series 2) or pyridyl group (Series 3) is attached to N(3). The ^{13}C chemical shifts at C(4) are shifted slightly downfield for the Series 2 and 3 compared to Series 1. At C(5) the ^{13}C chemical shifts, when compared to Series 1, are shifted upfield for Series 2 and downfield for Series 3.

A plot of the chemical shifts at C(2) for Series 1 versus Series 3 is shown in Figure 4. It can be seen that there is a significant amount of scatter in the data. However, if the plot is made excluding the *meta* substituted compounds in both series, the result is shown in Figure 5. It appears that the transmission of effects from substituent to C(2) are more effective via resonance from the *para* position on the C(2) phenyl ring than via inductance from the meta-position. Less dramatic improvements in correlations for the *para*-substituted compounds were noted at C(4) and C(5).

Table-1. ^{13}C NMR chemical shifts (ppm) for Series1, Series 2 and Series 3

substituent X ↓ site →	C(2)			C(4)			C(5)		
Series →	1	2	3	1	2	3	1	2	3
p-NO_2	64.06	-	62.02	170.60	-	171.00	33.21	-	34.04
m-NO_2	64.52	-	62.07	170.73	-	171.02	33.39	-	34.08
p-F	64.92	62.01	62.48	170.82	170.99	171.25	33.43	32.93	34.22
m-F	64.88	-	62.33	170.88	-	171.28	33.29	-	34.10
p-Cl	64.73	62.06	62.39	170.65	171.08	171.23	33.32	32.96	34.15
m-Cl	64.88	-	62.93	170.80	-	171.26	33.31	-	34.11
p-Br	64.85	62.06	62.45	170.69	171.01	171.26	33.35	32.91	34.18
m-Br	64.72	-	62.46	170.92	-	171.27	33.41	-	34.16
H	65.57	62.67	63.01	170.92	171.15	171.50	33.41	32.97	34.24
p-CH_3	65.57	62.51	62.92	170.92	171.08	171.51	33.43	32.99	34.26
m-CH_3	65.50	-	62.84	170.94	-	171.56	33.39	-	34.19
p-OCH_3	65.41	62.44	62.82	170.93	171.00	171.33	33.54	33.06	34.26
m-OCH_3	65.37	-	62.94	170.95	-	171.49	33.35	-	34.19

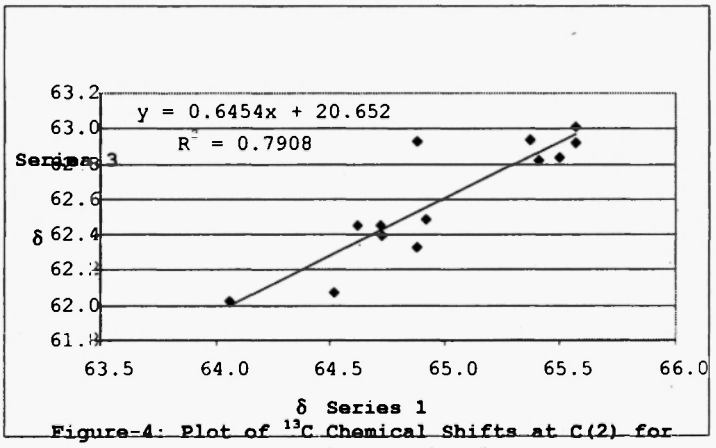


Figure-4: Plot of ^{13}C Chemical Shifts at C(2) for Series 1 *vs* Series 3

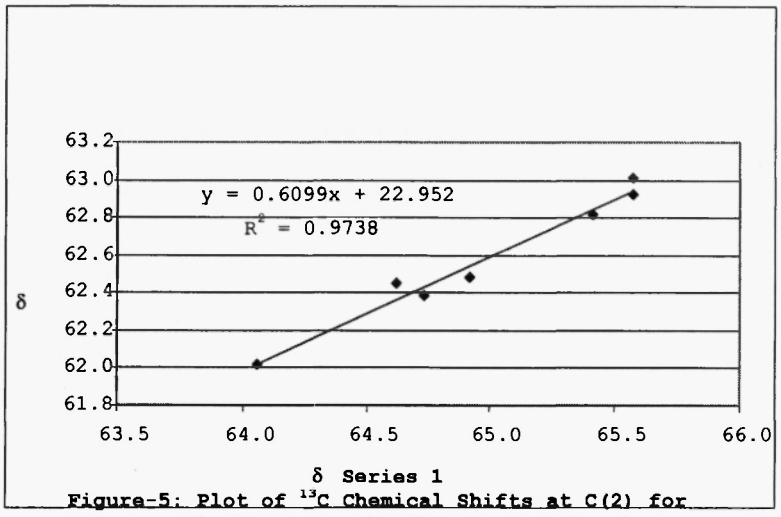


Figure-5: Plot of ^{13}C Chemical Shifts at C(2) for *parasubstituted* Series 1 *versus* Series 3

Typically, we have used Hammett correlations as an initial indicator for the level of effectiveness of the trans of substituent effects (3-6) from the substituent location to site using the relationship shown in Equation 1, w δ_0 is defined as the substituent chemical shift or SCS, σ is the Hammett constant, and ρ is the susceptibility factor for substituent effects in a series. It should be pointed out that the complexity of the

$$\delta - \delta_0 = \rho\sigma \qquad (1)$$

thiazolidinone systems under investigation is much greater than the substituted benzoic acids used originally to determine the Hammett σ constants (10). It is for this reason that we also take a more flexible approach by also using Swain-Lupton dual substituent parameters. This relationship is shown in Equation 2, where F and R are field and Resonance constants, respectively.

$$\delta - \delta_0 = fF + rR \qquad (2)$$

It has already been shown in Figure 5 that there is a reasonably good, direct correlation between the substituents on the C(2) phenyl at the *para* position and the ^{13}C chemical shift at C(2) for Series 1 and 3, when the chemical shift values for Series 1 and Series 3 are plotted against each other. The mode of transmission for the substituents on the phenyl rings at C(2) to the sites in the thiazolidin-4-one ring would be expected to be similar in nature, if not the same. The slope of 0.61 indicates that the presence of the pyridyl group at N(3), in place of the phenyl group, causes a consistent upfield shift for ^{13}C resonance at C(2). Also, the pyridyl nitrogen is contributing significantly to this upfield shift in place of the carbon at the same position in the ring at N(3).

The results for Hammett correlations for the ^{13}C substituent chemical shifts at C(2), C(4) and C(5) centers for Series 3 are shown in Table 2. Even though the trends in the absolute chemical shifts at C(2) for Series 1 and Series 3 appear to show concurrence, and the previously reported[3,7] Hammett correlation for Series 1 was reasonably good, the data in Table-2 show mixed results. Hammett correlations for the *para* substituted compounds have always been better than when considering both *meta* and *para* data for these types of compounds. However, for Series 3 the only relatively good correlation is at C(5), the site furthest from the substituents on the C(2) phenyl and the pyridyl group. This observation prompts the earlier assertion[3,4,6,8] that nitrogen atoms, which have the ability to conjugate with substituents in the system, can attenuate electronic effects, and may, in addition, distort substituent effects as described by the Hammett Equation.

Table-2 : Hammett Correlations for ^{13}C Substituent Chemical Shifts for Series 3.			
site	**Equation**	**Correlation Coefficient**	**Comments**
C(2)	SCS = - 0.85σ - 0.24 SCS = - 0.90σ - 0.32	$R^2 = 0.616$ $R^2 = 0.788$	*meta* and *para* substituents *para* substituents only
C(4)	SCS = - 0.46σ - 0.10 SCS = - 0.43x – 0.15	$R^2 = 0.686$ $R^2 = 0.702$	*meta* and *para* substituents *para* substituents only
C(5)	SCS = - 0.21σ - 0.03 SCS = - 0.22σ - 0.02	$R^2 = 0.885$ $R^2 = 0.960$	*meta* and *para* substituents *para* substituents only

Table-3 shows the results for the Swain-Lupton Dual Substituent Parameter Correlations for sites C(2), C(4) and C(5) in Series 3. The sensitivity of the transmission of electronic effects from substituents in the C(2) phenyl ring to the sites C(2), C(4) are shown best by the Swain-Lupton approach. The data shows that for these sites, the transmission of electronic effects by substituents is more effective from the *para* position on the C(2) phenyl ring than the *meta* position. A small improvement can be seen in the correlation coefficient for the Hammett correlation at C(2), using all the data points, and the correlation coefficient for Swain-Lupton Correlation. There is a dramatic increase in the correlation coefficient for the transmission of electronic effects from substituents at the *para* position, on the phenyl ring at C(2), to the C(2) site. The Swain-Lupton data indicates that there is only a 13% resonance contribution for substituents at the *para* position, significantly less than the contribution predicted by Hammett constants. For the transmission of electronic effects to C(4) there is a marked improvement in the Swain-Lupton correlation over the Hammett correlation for all the data points. There is even further improvement in the Swain-Lupton correlation if only the *para* substituted compounds are considered. The data for effects at C(4) for both *para* and *meta* substituted compounds show a 21% resonance contribution, and the *para* substituted compounds

Table-3 : Swain-Lupton Dual Substituent Parameter Correlations for ^{13}C Substituent Chemical Shifts for Series 3.			
site	**Equation**	**Correlation Coefficient**	**Comments**
C(2)	SCS = - 1.35F - 0.16R + 0.02 SCS = - 1.42F - 0.21R + 0.01	$R^2 = 0.781$ $R^2 = 0.936$	*meta* and *para* substituents *para* substituents only
C(4)	SCS = - 0.74F - 0.20R + 0.03 SCS = - 0.71F - 0.20R	$R^2 = 0.935$ $R^2 = 0.987$	*meta* and *para* substituents *para* substituents only
C(5)	SCS = - 0.24F - 0.08R SCS = - 0.27F - 0.21R+ 001	$R^2 = 0.642$ $R^2 = 0.867$	*meta* and *para* substituents *para* substituents only

alone exhibit a 22% resonance contribution. The data for the C(5) site shows a relatively good Hammett correlation for the para substituted compounds. The negative ρ value indicates that C(5) prefers a positive charge buildup. Utilizing even the poor Hammett correlations at C(2) and C(4), each center prefers a decreasing positive charge character in the order C(2) > C(4) > C(5).

The data for C(5) also produces a dilemma. It is the first time that the Swain-Lupton approach has produced a slightly weaker correlation than the Hammett correlation for all the similar systems that have been investigated. The system is quite complex and the direction of electronic effects from substituents to site can occur via a number of different routes. For example in Figure 6, route A passes the electronic effects through a sulfur atom, route B goes via a nitrogen atom and a carbonyl carbon, and route C passes through the pyridyl ring and then follows route B. For Series 1 and series 2 the pathways are more limited, and there is symmetry through the phenyl and benzyl groups,

respectively, at N(3). The major difference with Series 3 is the presence of the pyridyl group at N(3). The presence of the pyridyl nitrogen could significantly perturb the effects of substituents on the C(2) phenyl to the sites in the thiazolidinone ring. The pyridyl nitrogen introduces an additional asymmetry into the system which could be a reason for the inability to reproducibly quantify the electron density effects at C(5); complicated further by three potential routes for field and resonance effects to flow through.

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The data for C(5) also produces a dilemma. It is the first time that the Swain-Lupton approach has produced a slightly weaker correlation than the Hammett correlation for all the similar systems that have been investigated. The system is quite complex and the direction of electronic effects from substituents to site can occur via a number of different routes. For example in Figure-6, route A passes the electronic effects from X through S(1), route B_1 goes via N(3) in the thiazolidinone ring and a carbonyl carbon, and route B_2 passes through the pyridyl ring via N(3) twice *en route* to C(5). For Series 1 and series 2 the pathways are more limited, and there is symmetry through the phenyl and benzyl groups, respectively, at N(3). The major difference with Series 3 is the presence of the pyridyl group at N(3). The presence of the pyridyl nitrogen could significantly perturb the effects of substituents on the C(2) phenyl to the sites in the thiazolidinone ring. The pyridinyl nitrogen introduces an additional asymmetry into the system which could be a reason for the inability to reproducibly quantify the electron density effects at C(5); complicated further by three potential routes for field and resonance effects to follow.

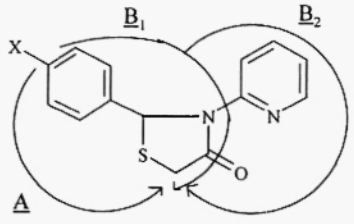

Figure-6

Conclusions

The introduction of a pyridyl group at the N(3) position of the thiazolidinone ring shifts the ^{13}C NMR resonances downfield for C(4) and C(5) when compared to substituted 2,3-diphenyl-1,3-thiazolid-in-4-ones and upfield for the substituted 2-phenyl-3-benzyl-1,3-thiazolidin-4-ones. When the electronic effects, due to substituents in the phenyl group at C(2) of the substituted 2-phenyl-3-pyridin-2-yl-1,3-thiazolidin-4-ones, are quantified using Hammett and Swain-Lupton correlations similar trends are noted when compared to N(3)- phenyl and N(3)-benzyl series with one notable exception for the ^{13}C chemical shifts at C(4). The presence of the pyridyl group at N(3) appears to complicate the transmission of electronic effects for substituents on the C(2)-phenyl ring into the thiazolidinone ring causing a decrease in the ability to reliably predict electronic density effects at the more remote C(5) position. Further study of the system with substituents in the N(3)-pyridyl ring may help to throw further light on the role of the pyridyl nitrogen's involvement in the electronic transmission of substituent effects.

Experimental

The thiazolidine-4-ones were prepared using a previously described procedure.[3] Melting points are uncorrected; a Mel-Temp apparatus was used. All spectra were recorded on a GE QE-300 at 298K observing ^1H and ^{13}C at 300.15 and 75.48 MHz, respectively. All samples were dissolved in $CDCl_3$ at a concentration of 100 mg/mL using precision bore 5 mm nmr tubes supplied by Norell, Inc.

^1H spectra were collected into 32K data sets over a spectral width of 3.012 kHz using a 30° pulse; pulse width, 3.0 μs; acquisition time, 2.72 s; relaxation delay, 1.0 s; number of scans, 16. ^{13}C spectra were collected into 16K data sets over a spectral width of 20 kHz using a 60° observed pulse using Waltz-16 decoupling; pulse width, 6.0 μs; acquisition time 409.60 ms; relaxation delay, 2.00 s; number of scans 1492. The spectrometer was locked to the deuterium resonance of the solvent ($CDCl_3$) and all chemical shifts were referenced to internal TMS (δ = 0.00 ppm). Mass spectra were recorded on a Varian 2100 G ion trap mass spectrometer, fitted with a Varian 3900 gas chromatograph: column - Factor 4 VF-5ms 0.25 mm id, 30 m, 0.25 μm film thickness, He carrier gas, 1.0 mL/min flow, 80°C for 1 minute isothermal 15°C/min to 275°C then 275°C for 3 minutes isothermal, injector temp 250°C, 0 min ,1:50 split. Yields are based on starting amounts for the imines (amine is the limiting reactant) and it was assumed that 100% of the imine was produced *in situ*. No attempt was made to maximize the yields. Hammett and Swain-Lupton correlations were obtained using Excel in Microsoft Office.

2-(4-Nitrophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1a**) (75%); b.p. red oil decomposes at 100 °C (753 mm Hg). IR: ν cm^{-1} 1705 (C=O). ^1H NMR ($CDCl_3$): 8.42-7.01 (8H, m, aromatics), 6.90 (1H, s, CH), 4.06, 4.00 (2H, d of d, CH_2, J = 16.5 Hz), 3.88, 3.83 (2H, d of d, CH_2, J = 16.2 Hz). ^{13}C NMR: 171.00 (C-4), 150.39, 148.54, 147.27, 143.76, 138.11, 132.25, 129.66, 123.18, 120.87, 116.58 (Ar), 62.02 (C-2), 34.04 (C-5). MS: (m/z) 301 (M^+, 99 %), $C_{14}H_{11}N_3O_3S$ (301.32)

2-(3-Nitrophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1b**) (12%); m.p. 155-157 °C. IR: ν cm^{-1} 1687 (C=O). ^1H NMR: 8.12-6.92 (8H, m, aromatics), 6.84 (1H, s, CH), 4.01, 3.96 (2H, d of d, CH_2, J = 16.2 Hz), 3.81 and 3.76 (2H, d of d, CH_2, J = 16.2 Hz). ^{13}C NMR: 171.02 (C-4), 150.35, 148.44, 147.07, 143.87, 138.10, 132.14, 129.73, 123.15, 120.98, 116.73 (Ar), 62.07 (C-2), 34.08 (C-5). MS: (m/z) 301 (M^+, 100%), $C_{14}H_{11}N_3O_3S$ (301.32).

2-(4-Fluorophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1c**) (39 %); m.p. 91-92 °C. IR: ν cm^{-1}1693 (C=O). ^1H [illegible] 8.30-6.92 (8H, m, aromatics), 6.85, (1H), 4.04, 3.99 (2H, d of d, CH_2, J = 15.9 Hz), 3.85 and 3.80 (2H, d of [illegible], J = 16.2). ^{13}C NMR, 171.25 (C-4), 150.64, 147.83, 137.89, 136.87, 128.17, 128.06, 120.93, 117.51, 115.81, 115.52 (Ar), 62.48 (C-2), 34.22 (C-5). MS: (m/z) 274 (M^+, 15%), $C_{14}H_{11}N_2OSF$ (274.31).

2-(3-Fluorophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1d**) (51%); m.p. 104.5-106 °C. IR: ν cm^{-1}1693 (C=O). ^1H NMR, 8.29-7.04 (8H, m, aromatics), 6.93 (1H, s, CH), 4.11, 4.06 (2H, d of d, CH_2, J = 15.9 Hz), 3.88 and 3.83 (2H, d of d, CH_2, J = 15.9 Hz). ^{13}C NMR, 171.28 (C-4), 164.54, 161.29, 150.62, 147.79, 144.099, 144.009, 137.939, 130.39, 130.29, 121.65, 121.62, 120.85, 116.94, 115.27, 114.99, 113.21 (Ar), 62.33 (C-2), 34.10 (C-5). MS: (m/z) 274 (M^+, 70%), $C_{14}H_{11}N_2OSF$ (274.31).

2-(4-Chlorophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1e**) (60%); m.p. 93-94 °C. IR: ν cm^{-1}1695 (C=O). ^1H NMR, 8.28-7.03 (8H, m, aromatics), 6.88 (1H, s, CH), 4.075, 4.02 (2H, d of d, CH_2, J = 15.9 Hz), 3.88 and 3.82 (2H, d of d, CH_2, J = 16.2 Hz). ^{13}C NMR, 171.23 (C-4), 150.58, 147.79, 139.80, 137.90, 133.84, 128.90, 127.66, 120.88, 117.15 (Ar), 62.39 (C-2), 34.15 (C-5). MS: (m/z) 290 (M^+, 100%, M+2, 38%), $C_{14}H_{11}N_2OSCl$ (290.77).

2-(3-Chlorophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1f**) (63%); m.p. 83-83.5 °C. IR: ν cm^{-1}1705 (C=O). ^1H NMR, 8.28-6.99 (8H, m, aromatics), 6.89 (1H, s, CH), 4.10, 4.08 (2H, d of d, CH_2, J = 16.2 Hz), 3.87 and 3.82 (2H, d of d, CH_2, J = 15.9 Hz). ^{13}C NMR, 171.26 (C-4), 150.53, 147.79, 143.51, 137.95, 134.57, 130.02, 128.33, 126.20, 124.16, 120.87, 116.898 (Ar), 62.93 (C-2), 34.11 (C-5). MS: (m/z) 290 (M^+, 100%, M+2, 35%), $C_{14}H_{11}N_2OSCl$ (290.77).

2-(4-Bromophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1g**) (13%); m.p. 107-109 °C. IR: ν cm^{-1}1697 (C=O). ^1H NMR, 8.13-6.88 (8H, m, aromatics), 6.73 (1H, s, CH), 3.93, 3.88 (2H, d of d, CH_2, J = 15.9 Hz), 3.73 and 3.68 (2H, d of d. CH_2, J = 15.9 Hz). ^{13}C NMR, 171.26 (C-4), 150.59, 147.82, 140.41, 137.94, 132.12, 131.88, 128.23, 127.89, 122.02, 120.91, 117.11 (Ar), 62.46 (C-2), 34.18 (C-5). MS: (m/z) 334 (M^+, 100%, M+2, 100%), 335.98 (M+2, 98.8%) $C_{14}H_{11}N_2OSBr$ (335.22).

2-(3-Bromophenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1h**) (51%); m.p. 99-100 °C.IR: ν cm^{-1} 1690 (C=O). ^1H NMR, 8.29-7.08 (8H, m, aromatics), 6.88 (1H, s, CH), 4.10, 4.05 (2H, d of d, CH_2, J = 15.9 Hz), 3.908, 3.849 (2H, d of d, CH_2, J = 16.2 Hz). ^{13}C NMR, 171.27 (C-4), 150.57, 147.81, 140.34, 137.93, 131.84, 127.88, 122.02, 120.92, 117.16 (Ar), 62.46 (C-2), 34.16 (C-5). MS: (m/z) 334 (M^+, 100%, M+2, 100%), $C_{14}H_{11}N_2OSBr$ (335.22).

2-Phenyl-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1i**) (82%); m.p. 98-99 °C. IR: ν cm^{-1}1684 (C=O). IR: 1683 cm^{-1} (C=O); ^{1}H NMR, 8.31-7.02 (9H, m, aromatics), 6.98 (1H, s, CH), 4.13, 4.02 (2H, d of d, CH_2, J = 16.2 Hz), 3.89, 3.84 (2H, d of d, CH_2, J = 15.9 Hz). ^{13}C NMR, 171.50 (C-4), 150.81, 147.87, 141.25, 137.85, 128.77, 128.19, 126.06, 120.80, 117.27 (Ar), 63.01 (C-2), 34.24 (C-5). MS: (m/z) 256 (M^+, 54%), $C_{14}H_{12}N_2OS$ (256.32).

2-(4-Methylphenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1j**) (63%); m.p. 132-133 °C. IR: ν cm^{-1}1688 (C=O). ^{1}H NMR, 8.33-7.03 (8H, m, aromatics), 6.97 (1H, s, CH), 4.14, 4.10 (2H, d of d, CH_2, J = 15.9 Hz), 3.90, 3.85 (2H, d of d, CH_2, J = 16.2 Hz), 2.35 (3H, Me). ^{13}C NMR, 171.51 (C-4), 150.87, 147.89, 138.25, 138.02, 137.82, 129.47, 126.02, 120.79, 117.41 (Ar), 62.92 (C-2), 34.26 (C-5), 21.25 (Me). MS: (m/z) 270 (M^+, 100%), $C_{15}H_{14}N_2OS$ (270.35).

2-(3-Methylphenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1k**) (30%); m.p. 79-80 °C.IR: ν cm^{-1}1693 (C=O). ^{1}H NMR, 8.32-6.98 (8H, m, aromatics), 6.80 (1H, s, CH), 4.11, 4.05 (2H, d of d, CH_2, J = 16.2 Hz), 3.86, 3.80 (2H, d of d, CH_2, J = 16.2 Hz), 2.329 (3H, Me). ^{13}C NMR, 171.48 (C-4), 150.81, 147.85, 141.20, 138.95, 137.81, 129.00, 128.63, 126.56, 122.75, 117.19 (Ar), 62.83 (C-2), 34.19 (C-5), 21.51 (Me). MS: (m/z) 270 (M^+, 100%), $C_{15}H_{14}N_2OS$ (270.35).

2-(4-Methoxyphenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1m**) (28%); m.p. 113-114.5 °C. IR: ν cm^{-1}1693 (C=O).^{1}H NMR, 8.29-6.99 (8H, m, aromatics), 6.88 (1H, s, CH), 4.04, 4.03 (2H, d of d, CH_2, J = 15.9 Hz), 3.87, 3.82 (2H, d of d, CH_2, J = 15.9 Hz), 3.76 (3H, OMe). ^{13}C NMR, 171.33 (C-4), 159.31, 150.78, 147.87, 137.75, 132.86, 127.65, 120.84, 117.79, 114.01 (Ar), 62.82 (C-2), 34.26 (C-5), 55.25 (O-Me). MS: (m/z) 286 (M^+, 100%), $C_{15}H_{14}N_2O_2S$ (286.35).

2-(3-Methoxyphenyl)-3-(pyridin-2-yl)-1,3-thiazolidin-4-one (**1c**) (28%); m.p. 72-73 °C. IR: ν cm^{-1}1697 (C=O). ^{1}H NMR, 8.26-6.99 (8H, m, aromatics), 6.92 (1H, s, CH), 4.12, 4.07 (2H, d of d, CH_2, J = 16.2 Hz), 3.95, 3.85 (2H, d of d, CH_2, J = 16.2 Hz), 3.81 (3H, OMe). ^{13}C NMR, 171.56 (C-4), 159.83, 147.87, 142.87, 137.86, 129.84, 120.83, 118.13, 117.23, 113.38, 111.74 (Ar), 62.93 (C-2), 34.19 (C-5), 55.28 (O-Me). MS: (m/z) 286 (M^+, 100%) $C_{15}H_{14}N_2O_2S$ (286.35).

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