A PRELIMINARY STUDY ON PREDICTING THE ¹³C CHEMICAL SHIFTS FOR A SERIES OF DISUBSTITUTED 2,3-DIPHENYL-1,3-THIAZOLIDIN-4-ONES

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Abstract: A successful attempt has been made to predict ¹³C chemical shifts for a series of disubstituted 2,3-diphenyl-1,3thiazolidin-4-ones. Prior work has shown that substituents placed on either phenyl ring of the 2,3-diphenyl-1,3-thiazolidin-4-one system affect the electron density surrounding the C-2, C-4 and C-5 a toms. These changes are reflected in the different nmr chemical shifts for these carbon atoms relative to the unsubstituted compound. The ¹³C chemical shifts for the C-2, C-4 and C-5 carbons of these compounds have previously been shown to correlate with Hammett σ constants and Swain Lupton dual substituent parameters. Because of these correlations we decided to investigate the potential for predicting ¹³C chemical shifts for C-2, C4 and C-5 in the thiazolidinone ring based on the known shifts for the two monosubstituted series of compounds. The effect of the substituents on the ¹³C chemical shifts for the C-2, C-4 and C-5 carbons in the disubstituted 2,3-diphenylthiazolidinones are discussed relative to the two *mono*-substituted 2,3diphenylthiazolidinone series. The data is then used to predict the ¹³C chemical shift values at C-2, C-4 and C-5 in the thiazolidinone ring with all possible substituents combinations in the 2-phenyl and 3-phenyl rings.

Introduction

The reasons for our interest in thiazolidinones have been discussed extensively in previous publications.¹⁻⁵ It should be pointed out that the most popular method of synthesizing the substituted diphenyl-1,3-thiazolidin-4-ones, shown in Scheme 1, is by the reaction of the appropriately substituted imine with thioglycollic acid.^{6,7} However, this method does not always result in the desired product.



Brought to you by | Purdue University Libraries Authenticated Download Date | 5/30/15 7:29 AM When the formation of the imine is attempted by the reaction of chloral hydrate with an amine, the reaction can result in two outcomes depending on whether the amine is a liphatic or a romatic. The reaction of a n a romatic a mine y ields a n unstable imine⁸ that can be trapped with thioglycolic acid to form a thiazolidinone,⁴ and the reaction with an aliphatic amine produces formamides.⁹ Recently, evidence of oxazolidione formation has been shown as a side reaction in the process.⁶ Attempts to use hydroxylated aldehydes for imine formation by treatment with substituted anilines result in polymeric products.¹⁰ Having a method for predicting the C-2, C-4 and C-5 resonances, in advance of synthesis, would aid in a quick confirmation of the desired product.

Results and Discussion.

We previously reported an investigation of the relationship between substituent chemical shift values for two series of monosubstituted 2,3-diphenyl-1,3-thiazolidin-4-ones, with both Hammett and Swain Lupton substituent constants.² A similar study utilizing differently substituted diphenyl thiazolidinones has also been reported.¹¹

Based on these previous studies^{2,11} we became interested in seeing if the same substituent, placed at the same position in both rings would give predictable ¹³C chemical shift values at C-2, C-4 and C-5. This should be the case in light of the Hammett correlations previously observed for the two monosubstituted Series 1 and 2 (Figure 1). Three additional monosubstituted diphenyl-1,3-thiazolidinones, **1k**, **1m** and **2m** (Figure 1) that were not included in the original work ² were synthesized. Their addition to the sequence of monosubstituted compounds did not change the correlations determined in the original work; their synthesis did complete the full comparison with the disubstituted diphenyl-1,3-thiazolidinones in Series 3. We report in Table 1, the high resolution ¹³C nmr results for the two mono-substituted series of 2,3-diphenyl-1,3-thiazolidin-4-ones (Series 1 and 2).



Series 1: $X = p-NO_2$, $m-NO_2$, p-F, m-F, p-Cl, p-Br, m-Br, H, $p-CH_3$, $m-CH_3$, $p-OCH_3$, $m-OCH_3$; Y = HSeries 2: $Y = p-NO_2$, $m-NO_2$, p-F, m-F, p-Cl, p-Br, m-Br, H, $p-CH_3$, $m-CH_3$, $p-OCH_3$, $m-OCH_3$; X = HSeries 3: $X = Y = p-NO_2$, $m-NO_2$, p-F, m-F, p-Cl, p-Br, m-Br, $p-CH_3$, $m-CH_3$, $p-OCH_3$, $m-OCH_3$

Figure 1

Also shown in Figure I are the disubstituted diphenylthiazolidinones of Series 3. The experimental ¹³C chemical shift values at C-2, C-4 and C-5 are presented Table 2. The values in parentheses below for each of the experimental values are calculated chemical shift values, derived from the values for the two monosubstituted series. Equation 1 was used to calculate the values given in Table 2. The calculated chemical shift value for C-2, C-4 or C-5 in Series 3 compounds is denoted as δ_{XY} . Similarly, δ_H is the chemical shift value for the unsubstituted compound, δ_X is the chemical shift value observed for Series 1 compounds, and δ_Y is the chemical shift value observed for Series 2 compounds.

$\delta_{XY} = \delta_{H} + (\delta_{X} - \delta_{H}) + (\delta_{Y} - \delta_{H})$

(1)

The largest deviations between experimental and predicted ¹³C chemical shifts for the Series 3 compounds occurs at C-2, in particular, for the *para*-nitro **3a**, *meta*-nitro **3b**, *meta*-fluoro **3d** and *meta*-methoxy **3m** substituents. All the other predicted chemical shifts are within 0.1 ppm of the respective experimental values for C-2, C-4 and C-5.

An additional resonance effect between the two nitro groups in 3a is probably in play accounting for the difference in experimental and predicted chemical shifts. The transmission of effects from substituents on the phenyl rings at C-2 and N-3 are not equal. We previously noted an attenuation of effects from substituents to sites, C-2, C-4 and C-5, in the thiazolidinone ring, from the phenyl ring via the N-3 atom. The *para*-nitro group on the N-3 phenyl is probably exhibiting an increased attenuation with the *para*-nitro group on the C-2 phenyl, hence the 0.35 ppm difference between experimental and predicted values; this discrepancy is not predicted from the linear combination of the individual monosubstituted Series 1 and 2. Also, additional inductive effects must play a role in order to account for the discrepancies between experimental and predicted ¹³C chemical shifts at C-2 for 3b, 3d and 3m, respectively.

Table-1: ¹³ C Chemical Shift Data for the Two Series of Monosubstituted 2,3-Diphenylthiazolidin-4-ones in ppm relative										
to TMS.										
Compound	substituent X	substituent	C(2)	C(4)	C(5)					
		Ŷ								
1a	p-NO ₂	Н	64.06	170.60	33.21					
2a	Н	<i>p</i> -NO ₂	64.53	170.67	33.37					
1b	m-NO ₂	Н	64.52	170.73	33.39					
2 b	н	m-NO ₂	64.94	171.10	33.35					
1c	p-F	Н	64.92	170.82	33.43					
2c	Н	<i>p-</i> F	65.59	170.98	33.23					
1d	<i>m</i> -F	Н	64.88	170.88	33.29					
2d	Н	<i>m</i> -F	65.33	170.97	33.38					
1e	p-Cl	Н	64.73	170.65	33.32					
2e	Н	p-Cl	65.31	170.90	33.35					
1f	m-Cl	Н	64.88	170.80	33.31					
2f	Н	m-Cl	65.34	170.98	33.35					
1g	p-Br	Н	64.85	170.69	33.35					
2g	Н	<i>p</i> -Br	65.24	170.88	33.35					
1h	<i>m</i> -Br	Н	64.72	170.92	33.41					
2Կ	Н	<i>m</i> -Br	65.16	170.78	33.24					
1i	Н	Н	65.51	170.99	33.47					
1j	p-CH ₃	Н	65.57	170.92	33.43					
2j	н	<i>p</i> -CH ₃	65.68	170.98	33.41					
1k	m-CH ₃	Н	65.50	171.04	33.39					
2k	н	m-CH ₃	65.68	170.93	33.41					
11	p-OCH ₃	Н	65.41	170.93	33.54					
21	Н	p-OCH ₃	65.91	171.10	33.36					
1m	m-OCH ₃	Н	65.37	170.95	33.35					
2m	Н	m-OCH ₃	66.29	171.70	34.14					

At this point we have chosen not to make any additional corrections for the discrepancies between the experimental and predicated values already mentioned. This method of predicting the chemical shift values by using experimental data does appear to show a reasonable degree of sensitivity to the substituents used in this study.

Further, using Equation 1, we can predict the ¹³C chemical shift values at C-2, C-4 and C-5 for the disubstitued thiazolidinones where the substituents are different on both rings. The predicted values for the ¹³C chemical shifts for C-2 are shown in Table 3 and the values for C-4 and C-5 are shown in Tables 4 and 5, respectively.

Table-2: Exper Diphe	imental and Calculated (i nylthiazolidin-4-ones in	in parenthesis) ¹³ C Chemi ppm relative to TMS.	cal Shift Data for a Series o	f Disubstituted 2,3-		
compound	Substituent X = Y	C(2)	C(4)	C(5)		
3a	p-NO ₂	63.43 (63.08)	170.76 (170.28)	33.14 (33.11)		
3b	m-NO ₂	63.79 (63.95)	170.79 (170.84)	33.27 (33.27)		
3c	<i>p</i> -F	65.07 (65.00)	170.84 (170.81)	33.31 (33.19)		
3d	<i>m</i> -F	64.51 (64.70)	170.80 (170.86)	33.22 (33.20)		
3e	p-Cl	64.59 (64.53)	170.74 (170.56)	33.29 (33.20)		
3f	<i>m</i> -Cl	64.51 (64.71)	170.81 (170.79)	33.23 (33.19)		
3g	<i>p</i> -Br	64.64 (64.58)	170.78 (170.58)	33.34 (33.23)		
3h	<i>m</i> -Br	64.44 (64.37)	170.76 (170.71)	33.17 (33.18)		
Зј	p-CH3	65.54 (65.74)	171.04 (170.92)	33.47 (33.37)		
3k	m-CH ₃	65.59 (65.67)	171.03 (170.98)	33.37 (33.33)		
31	p-OCH3	65.71 (65.81)	171.02 (171.04)	33.42 (33.43)		
3m	m-OCH ₃	65.39 (66.15)	170.93 (171.66)	33.33 (34.02)		

Conclusions

The chemical shifts at C-2, C-4 and C-5 for a series of *bis*-disubstituted thiazolidin-4-ones were measured experimentally. The ¹³C chemical shifts for the same sites were predicted from two mono-substituted series of thiazolidones using an additive formula (Equation 1). The predicted ¹³C chemical shift values were in good agreement with the experimental values to within 0.1 ppm. There were four compounds outside this range, the 3a, 3b, 3d and 3m; however, the upfield or downfield shift for these values was in the same direction that would generally be predicted by the substituents.

With the 23 monosubstituted diphenylthiazolidinones and the corresponding 12 disubstituted diphenylthiazolidinones it is possible to predict the ¹³C chemical shift values for the other 134 compounds in the 13 x 13 matrix of potential derivatives.

	3-phenyl	•											
2-phenyl- 1	p-nitro	m-nitro	p-F	m-F	p-Cl	m-Cl	p-Br	m-Br	Н	p-Me	m-Me	p-MeO	m-MeO
p-nitro	63.02	63.43	64.08	63.82	63.80	63.83	63.73	63.65	64.06	64.17	64.17	64.40	64.78
m-nitro	63.48	63.89	64.54	64.28	64.26	64.29	64.19	64.11	64.52	64.63	64.63	64.86	65.24
p-F	63.88	64.29	64.94	64.68	64.66	64.69	64.59	64.51	64.92	65.03	65.03	65.26	65.64
m-F	63.84	64.25	64.90	64.64	64.62	64.65	64.55	64.47	64.88	64.99	64.99	65.22	65.60
p-Cl	63.69	64.10	64.75	64.49	64.47	64.50	64.40	64.32	64.73	64.84	64.84	65.07	65.45
m-Cl	63.84	64.25	64.90	64.64	64.62	64.65	64.55	64.47	64.88	64.99	64.99	65.22	65.60
p-Br	63.81	64.22	64.87	64.61	64.59	64.62	64.52	64.44	64.85	64.96	64.96	65.19	65.57
m-Br	63.68	64.09	64.74	64.48	64.46	64.49	64.39	64.31	64.72	64.83	64.83	65.06	65.44
Н	64.53	64.94	65.59	65.33	65.31	65.34	65.24	65.16	65.57	65.68	65.68	65.91	66.29
p-Me	64.53	64.94	65.59	65.33	65.31	65.34	65.24	65.16	65.57	65.68	65.68	65.91	66.29
m-Me	64.46	64.87	65.52	65.26	65.24	65.27	65.17	65.09	65.50	65.61	65.61	65.84	66.22
p-MeO	64.37	64.78	65.43	65.17	65.15	65.18	65.08	65.00	65.41	65.52	65.52	65.75	66.13
m-MeO	64.33	64.74	65.39	65.13	65.11	65.14	65.04	64.96	65.37	65.48	65.48	65.71	66.09

Table-3: Calculated ¹³C Chemical Shifts for C-2

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Table-4: Calculated ¹³C Chemical Shifts for C-4

3-phenylm-Me p-MeO m-MeO 2-phenyl p-nitro m-nitro p-F m-F p-Cl m-Cl p-Br m-Br Н p-Me T 170.35 170.78 170.66 170.65 170.58 170.66 170.56 170.46 170.60 170.66 170.61 170.78 171.38 p-nitro 170.48 170.91 170.79 170.78 170.71 170.79 170.69 170.59 170.73 170.79 170.74 170.91 171.51 m-nitro 170.57 171.00 170.88 170.87 170.80 170.88 170.78 170.68 170.82 170.88 170.83 171.00 171.60 p-F m-F 170.63 171.06 170.94 170.93 170.86 170.94 170.84 170.74 170.88 170.94 170.89 171.06 171.66 170.71 170.70 170.63 170.71 170.61 170.51 170.65 170.71 170.66 170.83 171.43 p-Cl 170.40 170.83 170.98 170.86 170.85 170.78 170.86 170.76 170.66 170.80 170.86 170.81 170.98 171.58 m-Cl 170.55 p-Br 170.44 170.87 170.75 170.74 170.67 170.75 170.65 170.55 170.69 170.75 170.70 170.87 171.47 m-Br 170.67 171.10 170.98 170.97 170.90 170.98 170.88 170.78 170.92 170.98 170.93 171.10 171.70 170.67 171.10 170.98 170.97 170.90 170.98 170.88 170.78 170.92 170.98 170.93 171.10 171.70 Н 170.67 171.10 170.98 170.97 170.90 170.98 170.88 170.78 170.92 170.98 170.93 171.10 171.70 p-Me 171.22 171.10 171.09 171.02 171.10 171.00 170.90 171.04 171.10 171.05 171.22 171.82 m-Me 170.79 171.11 170.99 170.98 170.91 170.99 170.89 170.79 170.93 170.99 170.94 171.11 171.71 170.68 p-MeO m-MeO 170.70 171.13 171.01 171.00 170.93 171.01 170.91 170.81 170.95 171.01 170.96 171.13 171.73

	3-phenyl-												
2-phenyl-	→ p-nitro	m-nitro	p-F	m-F	p-Cl	m-Cl	p-Br	m-Br	н	p-Me	m-Me	p-Me 0	m-McO
1	22.17	22.16	22.02	22.10	22.16	22.16	22.16	22.04	22.21	22.21	22.21	22.16	22.04
p-nitro	33.17	33.15	33.03	33.18	33.15	35.15	33.15	33.04	33.21	33.21	33.21	33.10	33.94
m-nitro	33.35	33.33	33.21	33.36	33.33	33.33	33.33	33.22	33.39	33.39	33.39	33.34	34.12
p-F	33.39	33.37	33.25	33.40	33.37	33.37	33.37	33.26	33.43	33.43	33.43	33.38	34.16
m-F	33.25	33.23	33.11	33.26	33.23	33.23	33.23	33.12	33.29	33.29	33.29	33.24	34.02
p-Cl	33.28	33.26	33.14	33.29	33.26	33.26	33.26	33.15	33.32	33.32	33.32	33.27	34.05
m-Cl	33.27	33.25	33.13	33.28	33.25	33.25	33.25	33.14	33.31	33.31	33.31	33.26	34.04
p-Br	33.31	33.29	33.17	33.32	33.29	33.29	33.29	33.18	33.35	33.35	33.35	33.30	34.08
m-Br	33.37	33.35	33.23	33.38	33.35	33.35	33.35	33.24	33.41	33.41	33.41	33.36	34.14
н	33.37	33.35	33.23	33.38	33.35	33.35	33.35	33.24	33.41	33.41	33.41	33.36	34.14
p-Me	33.39	33.37	33.25	33.40	33.37	33.37	33.37	33.26	33.43	33.43	33.43	33.38	34.16
m-Me	33.35	33.33	33.21	33.36	33.33	33.33	33.33	33.22	33.39	33.39	33.39	33.34	34.12
p-MeO	33.50	33.48	33.36	33.51	33.48	33.48	33.48	33.37	33.54	33.54	33.54	33.49	34.27
m-MeO	33.31	33.29	33.17	33.32	33.29	33.29	33.29	33.18	33.35	33.35	33.35	33.30	34.08

Table-5: Calculated ¹³C Chemical Shifts for C-5

Experimental

The thiazolidine-4-ones were prepared, with one exception, using the procedure previously described² by adapting a method originally utilized by Surrey.¹² Compound **3a** was prepared by forming the imine *in situ* in refluxing ethanol for 3 hours. After cooling, the thioglycolic acid was added to the ethanol solution and the solution was further heated under reflux for 48 hours. On cooling the product crystallized out. The compounds **1a-j**, **11**, and **2a-l** have all been previously reported.² Melting points are uncorrected; a Mel-Temp apparatus was used. All spectra were recorded on a Bruker 300 at 298K observing ¹H and ¹³C at 300.15 and 75.48 MHz, respectively. All samples were dissolved in CDCl₃ 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 3012.0 Hz using a 30° pulse; pulse width, 3.0 μ s; acquisition time, 2.72 s; relaxation delay, 1.0 s; number of scans, 16. ¹³C spectra were collected into 16K data sets over a spectral width of ±10.000 Hz with a 60° observed pulse using Waltz-16 decoupling; pulse width, 6.0 μ s; acquisition time 4 09.6 m s; relaxation delay, 2.00 s; number of scans, 512. Elemental analyses on all samples were performed by Galbraith Laboratories, Inc., 2323 Sycamore Drive, Knoxville, TN 37921-1750 USA

2,3-Diphenylthiazolidin-4-one (1i): yield 60%; m.p. 131-132 °C, (lit. m.p.130-131 °C)^{2,13}; ¹H NMR: δ 7.30-7.14 (9H, m), 6.09 (1H, s,), 4.01-3.82 (2H, dd, J = 15.9 Hz); ¹³C NMR: δ 170.99, 139.51, 137.51, 129.05, 128.85, 126.91, 125.54, 65.57, 33.41.

2-(3-Methylphenyl)-3-phenyl-1,3-thiazolidin-4-one (1k): yield 74%; m.p. 111-112 °C; Anal. Found: C, 71.55; H, 5.87. Calc. for C₁₆H₁₅ NOS: C, 71.35; H, 5.61; ¹H NMR: δ 7.31-7.05 (9H, m), 6.07 (1H, s,), 4.03, 3.98, 3.87, 3.82 (2H, dd, J = 15.6 Hz), 2.29 (3H, s); ¹³C NMR: δ 171.04, 139.62, 138.61, 137.62, 129.62, 129.00, 128.73, 127.30, 126.90, 125.41, 123.81, 65.50, 33.39, 21.37.

2-(4-Methoxyphenyl)-3-phenyl-1,3-thiazolidin-4-one (1m): yield 68%; m.p. 117-118 °C; Anal. Found: C, 67.71; H, 5.48. Calc. for C₁₆H₁₅ NO₂S: C, 67.34; H, 5.30; ¹H NMR: δ 7.29-6.76 (9H, m), 6.07 (1H, s), 4.01, 3.95, 3.86, 3.81 (2H, dd, J = 15.9 Hz), 3.73 (3H, s); ¹³C NMR: δ 170.95, 159.91, 141.22, 137.58, 129.89, 129.00, 126.91, 125.36, 118.98, 114.18, 112.37, 65.37, 55.19, 33.35. 2-Phenyl-3-(3-methoxyphenyl)-1,3-thiazolidin-4-one (**2m**): yield 57%; m.p. 98-99 °C; Anal. Found: C, 67.41; H, 5.68. Calc. for C₁₆H₁₅ NO₂S: C, 67.34; H, 5.30; ¹H NMR: δ 7.35-6.73 (9H, m), 6.13 (1H, s), 4.05, 3.99, 3.98, 3.86 (2H, dd, , J = 15.9 Hz), 3.71 (3H, s); ¹³C NMR: δ 170.93, 159.89, 139.57, 138.58, 129.64, 128.82, 126.84, 117.66, 112.66, 111.55, 65.57, 55.20, 33.21.

2-(4-Nitrophenyl)-3-(4-nitrophenyl)-1,3-thiazolidin-4-one (**3a**): yield 26%; m.p. 168-169 °C; Anal. Found: C, 51.94; H, 3.32, Calc. for $C_{15}H_{11}N_3O_5S$: C, 52.17; H, 3.21; ¹H NMR: δ 8.19-7.46 (8H, m), 6.34 (1H, s, CH), 4.01, 3.97, 3.93, 3.90 (2H, dd, J = 16.2 Hz); ¹³C NMR: δ 170.76, 148.21, 145.69, 145.29, 142.69, 127.27, 124.57, 123.87, 63.43, 33.14.

2-(3-Nitrophenyl)-3-(3-nitrophenyl)-1,3-thiazolidin-4-one (**3b**): yield 56 %; m.p. 1 33-134 °C; A nal. Found: C, 52.06; H, 3.22, Calc. for $C_{15}H_{11}N_3O_5S$: C, 52.17; H, 3.21; ¹H NMR: δ 8.84-7.32 (8H, m), 6.29 (1H, s), 4.02, 3.97, 3.93, 3.87 (2H, dd, J = 16.2 Hz); ¹³C NMR: δ 170.79, 151.95, 148.99, 148.53, 140.36, 137.05, 127.62, 126.32, 124.30, 121.96, 121.52, 119.69, 115.37, 63.79, 33.27.

2,-(4-Fluorophenyl)-3-(4-fluorophenyl)-1,3-thiazolidin-4-one (**3c**): yield 70 %; m.p. 119-120 °C; Anal. Found: C, 61.95; H, 3.84, Calc. for C₁₅H₁₁NOSF₂: C, 61.84; H, 3.81; ¹H NMR: δ 7.47-6.82 (8H, m), 5.97 (1H, s), 3.94, 3.89, 3.85, 3.80 (2H, dd, , J = 15.9 Hz); ¹³C NMR: δ 170.84, 164.50, 162.85, 161.19, 159.51, 134.79, 133.18, 129.13, 127.81, 116.08, 65.07, 33.31.

2-(3-Fluorophenyl)-3-(3-fluorophenyl)-1,3-thiazolidin-4-one (**3d**): yield 61%; m.p. 88-89 °C; Anal. Found: C, 66.67; H, 3.77, Calc. for C₁₅H₁₁NOSF₂: C, 61.84; H, 3.81; ¹H NMR: δ 7.39-6.77 (8H, m), 6.03 (1H, s), 3.95, 3.90, 3.82, 3.77 (2H, dd, J = 15.0 Hz); ¹³C NMR: δ 170.80, 164.44, 161.16, 141.87, 138.79, 130.67, 130.20, 122.34, 120.43, 116.09, 113.81, 112.53, 64.51, 33.22.

2-(4-Chlorophenyl)-3-(4-chlorophenyl)-1,3-thiazolidin-4-one (**3e**): yield 56%; m.p. 143-144 °C; Anal. Found: C, 55.69; H, 3.59, Calc. for C₁₅H₁₁ NOSCl₂: C, 55.57; H, 3.42; ¹H NMR: δ 7.43-7.03 (8H, m), 5.99 (1H, s, CH), 3.92, 3.87, 3.83, 3.77 (2H, dd, J = 15.9 Hz); ¹³C NMR: δ 170.74, 137.52, 135.74, 134.87, 132.70, 129.25, 128.32, 126.65, 64.59, 33.27.

2-(3-Chlorophenyl)-3-(3-chlorophenyl)-1,3-thiazolidin-4-one (**3f**): yield 36%; m.p.129-131 °C; Anal. Found: C, 55.66; H, 3.53, Calc. for $C_{15}H_{11}$ NOSCl₂: C, 55.57; H, 3.42; ¹H NMR: δ 7.38-6.94 (8H, m), 5.98 (1H, s,), 3.95, 3.90, 3.82, 3.77 (2H, dd, J = 15.0 Hz); ¹³C NMR: δ 170.81, 141.29, 138.43, 134.84, 130.21, 129.28, 127.10, 125.15, 123.28, 64.51, 33.23.

2-(4-Bromophenyl)-3-(4-bromophenyl)-1,3-thiazolidin-4-one (**3g**): yield 54%; m.p. 180-182 °C; Anal. Found: C, 43.35; H, 2.64. Calc. for $C_{15}H_{11}$ NOSBr₂: C, 43.61; H, 2.68; ¹H NMR: δ 7.40-6.92 (8H, m), 5.98 (1H, s), 3.93, 3.88, 3.83, 3.78 (2H, dd, , J = 15.9 Hz); ¹³C NMR: δ 170.78, 138.07, 136.28, 132.34, 128.58, 126.90, 123.13, 120.75, 64.64, 33.34.

2-(3-Bromophenyl)-3-(3-bromophenyl)-1,3-thiazolidin-4-one (3h): yield 49%; m.p. 140-142 °C; Anal. Found: C, 43.43; H, 2.72. Calc. for C₁₅H₁₁ NOSBr₂: C, 43.61; H, 2.68; ¹H NMR: δ 7.42-7.03 (8H, m), 5.96 (1H, s), 3.95, 3.90, 3.83, 3.78 (2H, dd, J = 15.0 Hz); ¹³C NMR: δ 170.76, 141.40, 138.44, 132.19, 130.32, 129.79, 128.29, 125.31, 123.81, 122.96, 122.51, 64.44, 33.17.

2-(4Methylphenyl)-3-(4-methylphenyl)-1,3-thiazolidin-4-one (**3j**): yield 52%; m.p. 119-120 °C; Anal. Found: C, 71.92; H, 5.87. Calc. for C₁₇H₁₇NOS: C, 72.05; H, 5.97; ¹H NMR: δ 7.33-6.96 (8H, m), 5.97 (1H, s), 3.96, 3.91, 3.83,

3.78 (2H, dd, J = 15.9 Hz), 2.24 (3H, d), 2.22 (3H, d); ¹³C NMR: δ 171.04, 138.74, 136.79, 134.95, 129.62, 126.92, 125.65, 65.53, 33.47, 21.10.

2-(3-Methylphenyl)-3-(3-methylphenyl)-1,3-thiazolidin-4-one (**3k**): yield 55%; m.p. 97-98 °C; Anal. Found: C, 71.85; H, 6.14. Calc. for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; ¹H NMR: δ 7.21-6.95 (8H, m), 6.05 (1H, s), 4.02, 3.97, 3.86, 3.81 (2H, dd, J = 15.6 Hz), 2.28 (3H, s), 2.23 (3H, s₃); ¹³C NMR: δ 171.03, 139.77, 138.74, 138.52, 137.55, 129.56, 128.72, 127.83, 127.34, 126.28, 123.85, 122.50, 65.89, 33.37, 21.32.

2-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-1,3-thiazolidin-4-one (**3**l): yield 54%; m.p. 119-120 °C, (lit. m.p.119-120 °C) (13); ¹H NMR: δ 7.85-6.76 (8H, m, aromatics), 5.95 (1H, s), 3.99, 3.94, 3.80, 3.76 (2H, dd, , J = 15.0 Hz), 3.72 (3H, d), 3.66 (3H, d); ¹³C NMR: δ 171.02, 159.89, 145.27, 130.23, 128.69, 127.62, 122.05, 114.24, 65.71, 55.46, 33.43. 2-(3-Methoxyphenyl)-3-(3-methoxyphenyl)-1,3-thiazolidin-4-one (**3m**): yield 44%; m.p. 87-88 °C; Anal. Found: C, 64.50; H, 5.54. Calc. for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; ¹H NMR: δ 7.21-6.61 (8H, m), 6.04 (1H, s, CH), 3.99, 3.94, 3.84, 3.80 (2H, dd, J = 15.6 Hz), 3.72 (3H, s), 3.67 (3H, s); ¹³C NMR: δ 170.93, 159.91, 144.27, 138.66, 129.85, 129.61, 118.93, 117.49, 114.17, 112.58, 112.33, 111.43, 65.39, 55.19, 33.33.

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