



## Application of Hammett equation on IR and NMR spectral data of (5-bromothiophen-2-yl) (3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones

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### ABSTRACT

More than 60% yield of the titled compounds, (5-bromothiophen-2-yl)(3-substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones were prepared and examined their purities by literature method. The characteristic infrared spectral frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) and NMR chemical shifts ( $\delta$ , ppm) of these ketones were assigned. These spectral data were applied to Hammett equation with Hammett substituent constants for prediction of effects substituent using single and multi-regression analysis. From the results of statistical analysis, the electronic effect of substituents on the spectral data has been studied.

**Keywords:** (5-bromothiophen-2-yl)(3-substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones; IR and NMR spectra; Hammett equation; Hammett substituent constants; Regression analysis; Electronic effects

## 1. INTRODUCTION

Hammett equation is useful for studying the comparative chemical characteristic properties such as reaction velocity, free energy, entropy, enthalpy, kinetic and spectral QSAR, QSPR, QSR, QPR, SAR and the electrochemical and biochemical potential correlations [1]. The spectroscopic data were useful for the studying the ground state configurations of organic molecules [2]. The *s-cis* and *s-trans* conformers of unsaturated aldehydes, ketones, acids, esters and its chlorides were predicted by infrared spectroscopy [2-6]. The *E* and *Z* configuration of unsaturated systems of organic molecules and spatial arrangement of gem and vicinal protons in ring system was predicted by NMR spectroscopy [7-10]. The correlation analysis is useful for the study of stability of reaction intermediates [11], HPLC-pharmaceutical quality [12], normal co-ordinate analysis [13], Diels-Alder reaction [14],  $\beta$ -sheet structure elucidation of oligopeptides [15], enone-dienol tautomerism [16], cancer activity-density functional theory [17] and rotational barriers in selenomide derivatives [18]. Alkyl-alkyl, aryl-alkyl or aryl-aryl methanone derivatives are important bioorganic substrates [19]. These are due to the presence of carbonyl, unsaturation and polar substituents in their moieties and are origin for the biological potentials. Existence of substituents enhances the structural activity relationships (SAR) of organic compounds [20]. Norbornyl type methanone possess antimicrobial, antioxidant and insect antifeedant activities [21]. Thirunarayanan have studied the effect of substituents and evaluation of biological activities of some aryl-aryl bicyclo methanones [22-24]. The effect of substituents and the biological activities of some pyrazoline based chalcones was reported by Senbgam et al., [25]. Recently, the QSAR study of formamide products was reported by Thirunarayanan et al., [26]. Vijayakumar et al., [27] have reported the synthesis, spectral correlation and effect of substituents on some hydraone derivatives. The effect of substituents and evaluation of antimicrobial activities of some imine compounds were reported in literature [28]. Balaji et al., have reported the study of effect of substituents on some (*E*)-1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one compounds [29]. Within this view there is no information available in the literature for the study of effect of substituents through Hammett equation on (5-bromothiophen-2-yl)(3-substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl methanones. Therefore the author taken effort to synthesize some titled compounds and recorded their IR and NMR spectra for studying the spectral QSAR.

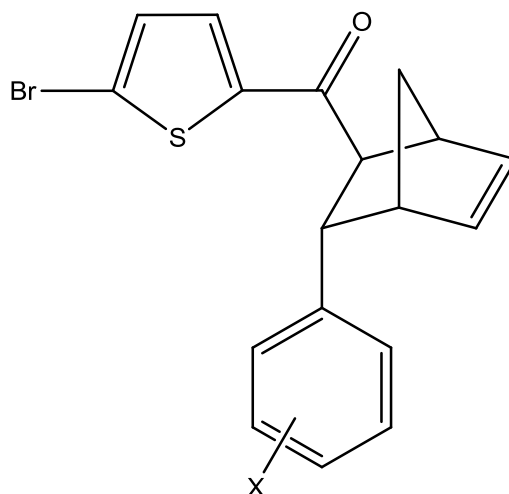
## 2. EXPERIMENTAL

### 2. 1. Material and methods

IR spectra (KBr, 4000-400  $\text{cm}^{-1}$ ) of all methanones have been recorded on SHIMADZU-2010 Fourier transform spectrophotometer. The NMR spectra of all methanones have been recorded in BRUKER 400 spectrometer operating at 400 MHz for  $^1\text{H}$  NMR spectra and 100 MHz for  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  solvent using TMS as internal standard.

### 2. 2. Synthesis of (5-bromothiophen-2-yl)(3-substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl methanones

The titled compounds were synthesized and examined their purities by literature method [21]. The general structure of the synthesized methanones was shown in Figure 1.



No.	1	2	3	4	5	6	7	8	9
X	H	4-Br	2-Cl	4-Cl	4-OH	4-I	4-OCH <sub>3</sub>	4-CH <sub>3</sub>	4-NO <sub>2</sub>

**Figure 1.** The general structure of (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones

### 3. RESULTS AND DISCUSSION

#### 3. 1. Infrared spectral study

In the present investigation, the author has studied the effect of substituents on the infrared spectral frequencies on the synthesized methanones as shown in Figure 1. The characteristic infrared spectral frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) of CO and CH=CH were assigned and tabulated in Table 1.

**Table 1.** The IR and NMR spectral data of (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones.

No.	X	IR( $\nu$ , $\text{cm}^{-1}$ )		<sup>1</sup> H NMR ( $\delta$ , ppm)		<sup>13</sup> C NMR ( $\delta$ , ppm)				
		CO	CH=CH <sub>op</sub>	H <sub>5</sub>	H <sub>6</sub>	CO	C <sub>5</sub>	C <sub>6</sub>	C-Br	C <sub>ipso</sub>
1	H	1655	1038	6.376	6.417	195.64	133.38	136.11	117.22	124.38
2	4-Br	1673	1081	6.317	6.422	196.63	133.45	136.06	117.36	121.32
3	2-Cl	1667	1074	6.307	6.431	198.73	133.26	136.27	117.24	132.26
4	4-Cl	1663	1029	6.341	6.463	196.72	134.72	136.21	117.38	131.47
5	4-OH	1673	1058	6.301	6.392	195.74	134.67	135.38	117.31	155.73

6	4-I	1625	1010	6.293	6.317	194.66	134.52	135.46	117.16	102.71
7	4-OCH <sub>3</sub>	1676	1092	6.27	6.308	195.74	134.26	135.38	117.08	158.72
8	4-CH <sub>3</sub>	1638	1057	6.274	6.317	194.92	134.66	136.47	117.11	135.28
9	4-NO <sub>2</sub>	1654	1054	6.372	6.407	196.73	134.92	136.89	117.62	145.71

The assigned CO and CH=CH spectral frequencies ( $\nu$ , cm<sup>-1</sup>) of (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones have been correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis through Hammett equation. In this infrared spectral correlation the Hammett equation was taken in form as in (1).

$$\nu = \rho\sigma + \nu_0 \quad \dots (4)$$

where  $\nu_0$  is the carbonyl frequencies of unsubstituted system.

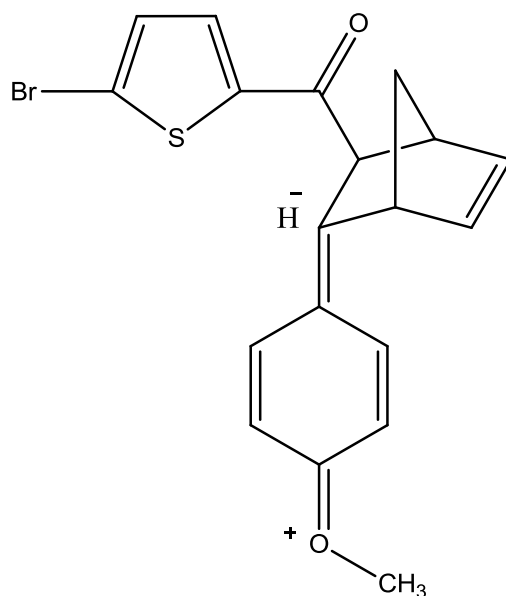
The statistical single regression analysis of these assigned CO and CH=CH spectral frequencies ( $\nu$ , cm<sup>-1</sup>) of (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones are presented in Table 2. From the Table 2, the Hammett  $\sigma_R$  constant and R parameters gave satisfactory correlation with the carbonyl stretches ( $\nu$ , cm<sup>-1</sup>) of methanones excluding 4-I and 4-CH<sub>3</sub> substituents. When inclusion of these substituents in the correlation, the reduced the correlation coefficient considerably. All correlation gave negative  $\rho$  values except F parameter. This may mean that the electron donating substituents may be predicting the reactivity on the reaction center. The remaining Hammett substituent constants and F parameters were fails in correlation. This is due to the inability of effect of substituents for prediction of reactivity and associated with the resonance-conjugative structure as shown in Figure 2.

**Table 2.** The single regression-statistical analysis results of IR frequencies ( $\nu$ , cm<sup>-1</sup>) and NMR chemical shifts ( $\delta$ , ppm) of substituted (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo [2.2.1]hept-5-en-2-yl)methanones with Hammett substituent constants ( $\sigma$ ,  $\sigma^+$ ,  $\sigma_I$  &  $\sigma_R$ ) and F and R parameters.

Frequency	Constant	r	I	$\rho$	s	n	Correlated derivatives
CO	$\sigma$	0.820	1659.15	-10.366	18.08	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.823	1658.12	-7.276	17.95	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.821	1652.84	16.414	18.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.904	1650.51	-44.492	16.23	7	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.818	1653.08	15.496	18.16	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>

	R	0.904	1650.94	-29.928	16.61	7	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
<b>CH=CH<sub>op</sub></b>	$\sigma$	0.822	1056.31	-17.082	27.06	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.819	1054.66	-8.996	27.25	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.804	1053.27	4.600	27.77	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.837	1045.80	-51.755	25.82	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.803	1053.26	4.561	27.78	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.833	1046.20	-35.236	26.10	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>H<sub>5</sub></b>	$\sigma$	0.906	6.310	0.071	0.03	8	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.905	6.317	0.040	0.03	8	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.902	6.302	0.042	0.04	8	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.907	6.342	0.149	0.02	8	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.901	6.304	0.038	0.04	8	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.907	6.342	0.107	0.02	8	H, 4-Br, 2-Cl, 4-Cl, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>H<sub>6</sub></b>	$\sigma$	0.843	6.378	0.072	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.848	6.386	0.049	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.840	6.352	0.102	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.825	6.399	0.077	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.831	6.357	0.086	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.832	6.404	0.074	0.05	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>CO</b>	$\sigma$	0.841	196.03	1.454	1.18	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.849	196.18	1.068	1.12	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.905	195.18	3.018	1.07	7	H, 4-Br, 4-Cl, 4-OH, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.801	196.18	0.077	1.32	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.847	195.25	2.741	1.14	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.816	196.35	0.781	1.28	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>C<sub>5</sub></b>	$\sigma$	0.806	134.19	0.116	0.70	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>

	$\sigma^+$	0.822	134.20	-0.238	0.68	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.812	134.08	0.366	0.69	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.803	134.22	0.126	0.70	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.822	133.6	0.712	0.68	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.810	134.14	-0.264	0.69	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>C<sub>6</sub></b>	$\sigma$	0.916	135.93	1.056	0.40	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.917	136.03	0.666	0.39	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.819	135.87	0.444	0.55	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.928	136.41	2.261	0.33	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.814	135.90	0.562	0.55	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.924	136.44	1.711	0.31	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>C-Br</b>	$\sigma$	0.958	117.39	0.490	0.41	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.906	116.96	1.282	0.39	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.906	117.67	1.645	0.38	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.906	116.90	1.446	0.38	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.905	117.63	1.030	0.42	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.928	117.28	1.099	0.50	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
<b>C<sub>ipso</sub></b>	$\sigma$	0.904	133.52	-16.788	17.42	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.803	134.64	-2.798	19.74	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_I$	0.837	127.28	-37.188	18.30	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	$\sigma_R$	0.801	133.31	1.262	19.74	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	F	0.843	126.07	-31.477	17.80	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
	R	0.903	135.19	-16.788	18.80	9	H, 4-Br, 2-Cl, 4-Cl, 4-OH, 4-I, 4-OCH <sub>3</sub> , 4-CH <sub>3</sub> , 4-NO <sub>2</sub>
r = correlation co-efficient; $\rho$ = slope; I = intercept; s = standard deviation; n = number of substituents							



**Figure 2.** The resonance-conjugative structure of (5-bromothiophen-2-yl)-(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones.

All correlation of  $\text{CH}=\text{CH}_{op}$  frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) of (5-bromothiophen-2-yl)-(3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones gave poor correlation coefficient. All correlation gave negative  $\rho$  values except F parameter. This may mean that the electron donating substituents may be predicting the reactivity on the reaction center. The remaining Hammett substituent constants and F parameters were fails in correlation. This is due to the reasons stated earlier as the inability of effect of substituents for prediction of reactivity and associated with the resonance-conjugative structure as shown in Figure 2. Some of single regression plots are shown in Figure 3-6.

Some of the correlation of carbonyl carbons and all correlation of  $\text{CH}=\text{CH}$  stretches were failed for production of satisfactory correlations. They are worth full when they in multi-regression analysis with Swain-Lupton's constants [30]. The obtained multi-regression analysis equations are given in (2-5).

$$\nu\text{CO}(\text{cm}^{-1}) = 1642.74(\pm 12.087) + 21.758(\pm 2.595)\sigma_I - 48.216(\pm 3.180)\sigma_R \quad \dots(2)$$

(R = 0.955, n = 9, P > 95%)

$$\nu\text{CO}(\text{cm}^{-1}) = 1644.23(\pm 13.187) + 19.081(\pm 2.982)F - 31.435(\pm 2.427)R \quad \dots(3)$$

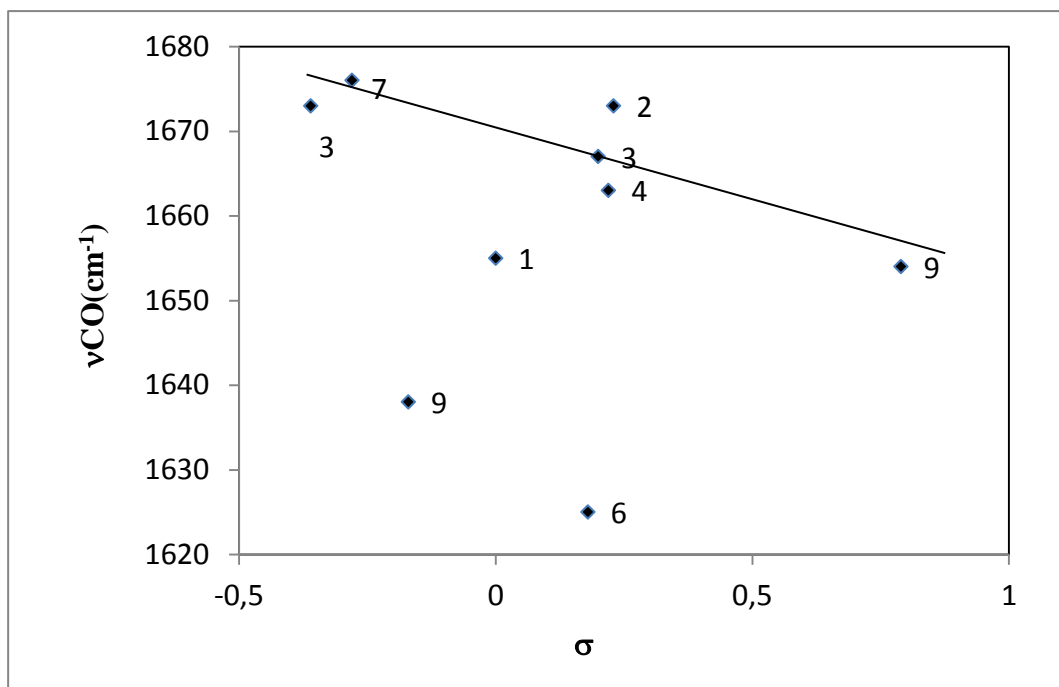
(R = 0.949, n = 9, P > 90%)

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1042.04(\pm 20.220) + 10.543(\pm 4.341)\sigma_I - 53.514(\pm 5.320)\sigma_R \quad \dots(4)$$

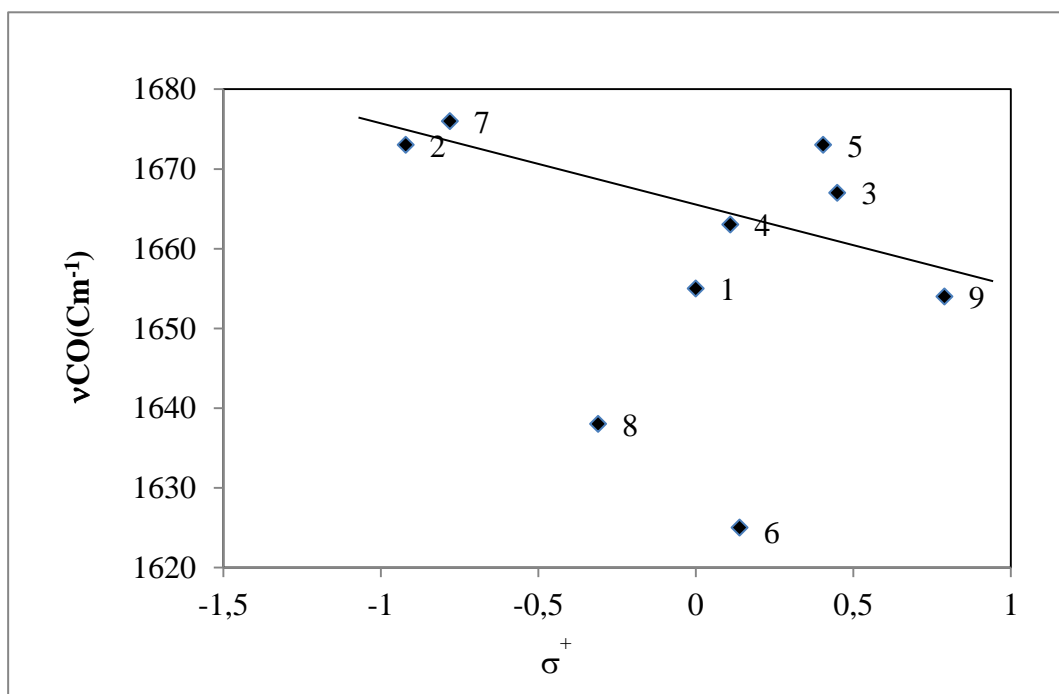
(R = 0.938, n = 9, P > 90%)

$$\nu\text{CH}=\text{CH}_{op}(\text{cm}^{-1}) = 1043.15(\pm 21.380) + 8.688(\pm 4.747)F - 35.922(\pm 3.396)R \quad \dots(5)$$

(R = 0.935, n = 9, P > 90%)

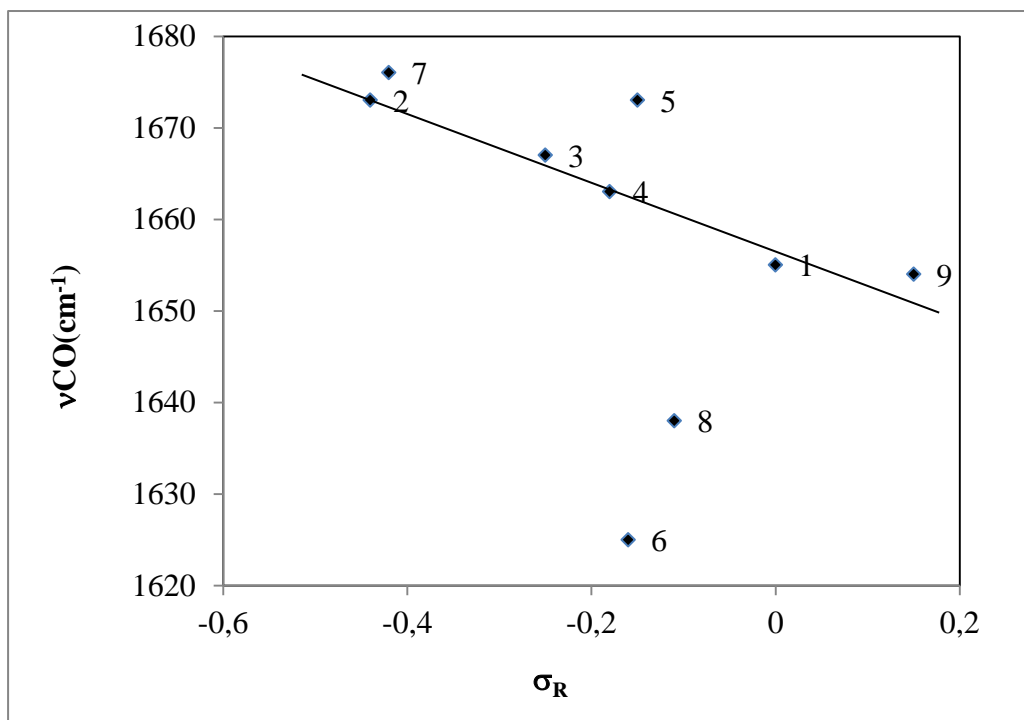


**Figure 3.** The plot of CO( $\nu$ ,  $cm^{-1}$ ) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .

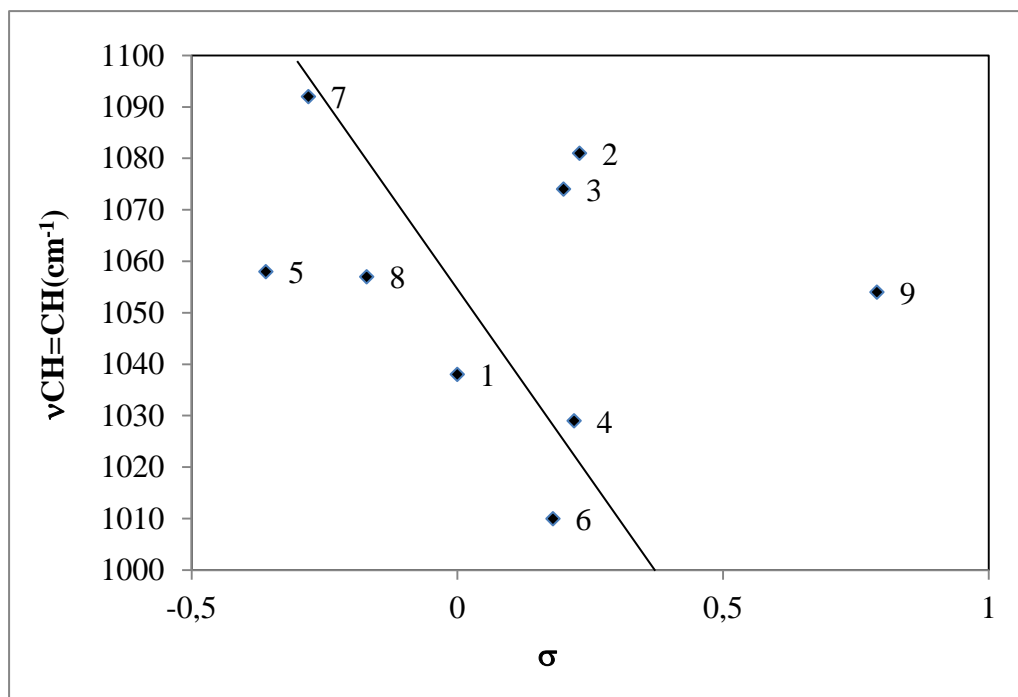


**Figure 4.** The plot of CO( $\nu$ ,  $cm^{-1}$ ) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma^+$ .





**Figure 5.** The plot of CO( $\nu$ ,  $\text{cm}^{-1}$ ) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo [2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma_R$ .



**Figure 6.** The plot of CH=CH( $\nu$ ,  $\text{cm}^{-1}$ ) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .

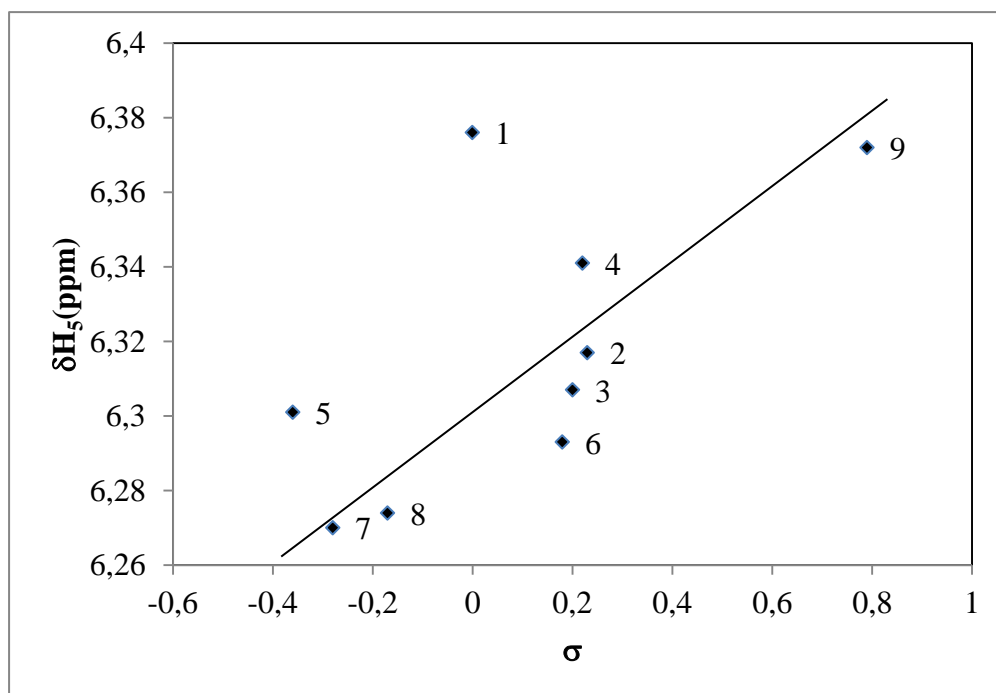
### 3. 2. $^1\text{H}$ NMR spectral correlation

In NMR spectral correlations, the Hammett equation was employed as

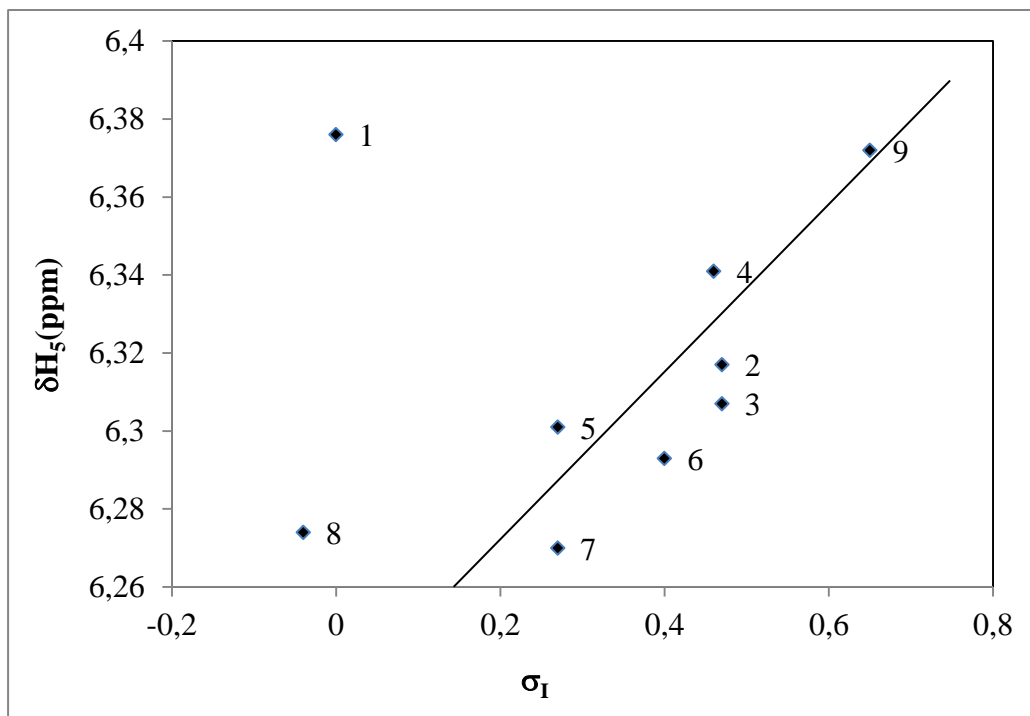
$$\delta = \rho\sigma + \delta_0 \quad \dots(6)$$

where  $\delta_0$  is the chemical shifts (ppm) of particular nuclei of unsubstituted system.

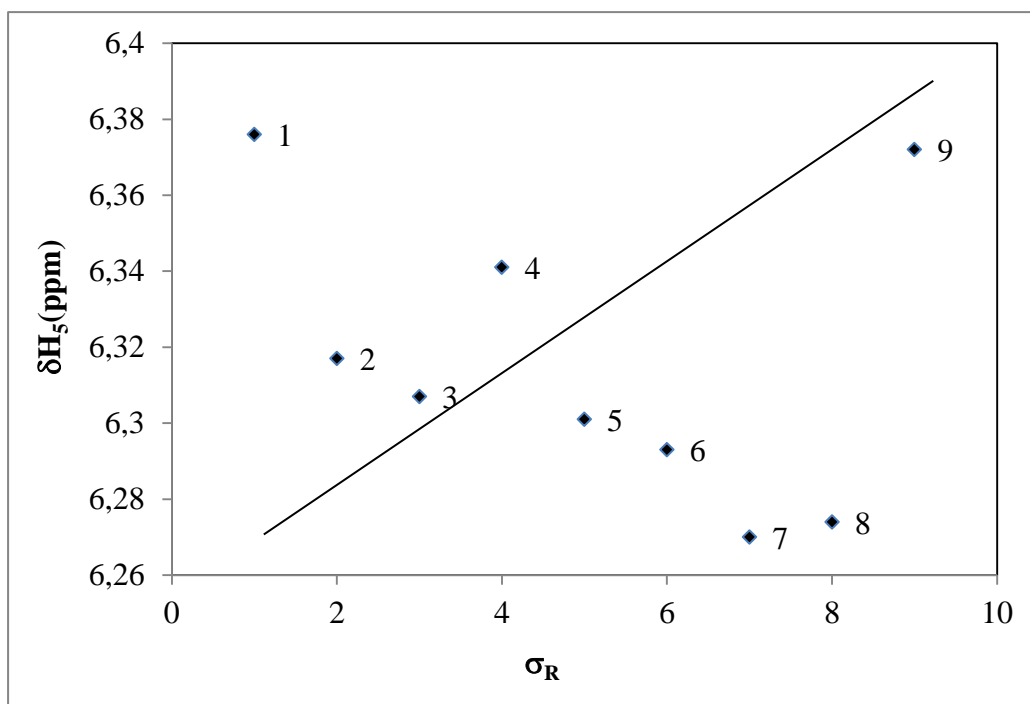
The assigned  $\text{H}_5$  and  $\text{H}_6$  proton chemical shifts ( $\delta$ , ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones are tabulated in Table 1. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. The results of statistical analysis were presented in Table 2. From Table 2, the  $\text{H}_5$  proton chemical shifts ( $\delta$ , ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones were correlated satisfactorily with hammett substituent constants, F and R parameters. While the correlation of  $\text{H}_6$  proton chemical shifts ( $\delta$ , ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones seems unsatisfactory. The polar and inductive effect of the substituents seems slightly better than the resonance effects. Here the inductive effect was influences the  $\text{H}_6$  proton chemical shifts from more than six carbon lengths. While the resonance effects was not effectively no longer with the same number of carbon atoms. The field and resonance effects of the substituents act very least in individually. All correlations gave positive  $\rho$  values except  $\sigma^+$  and R parameters. This may mean that the normal substituent effect operates in all systems. The failure in correlation was due to the reason stated earlier and associated with resonance-conjugated structure as shown in Figure 2. Some of the single parameter correlation plots are shown in Figures 7-11.



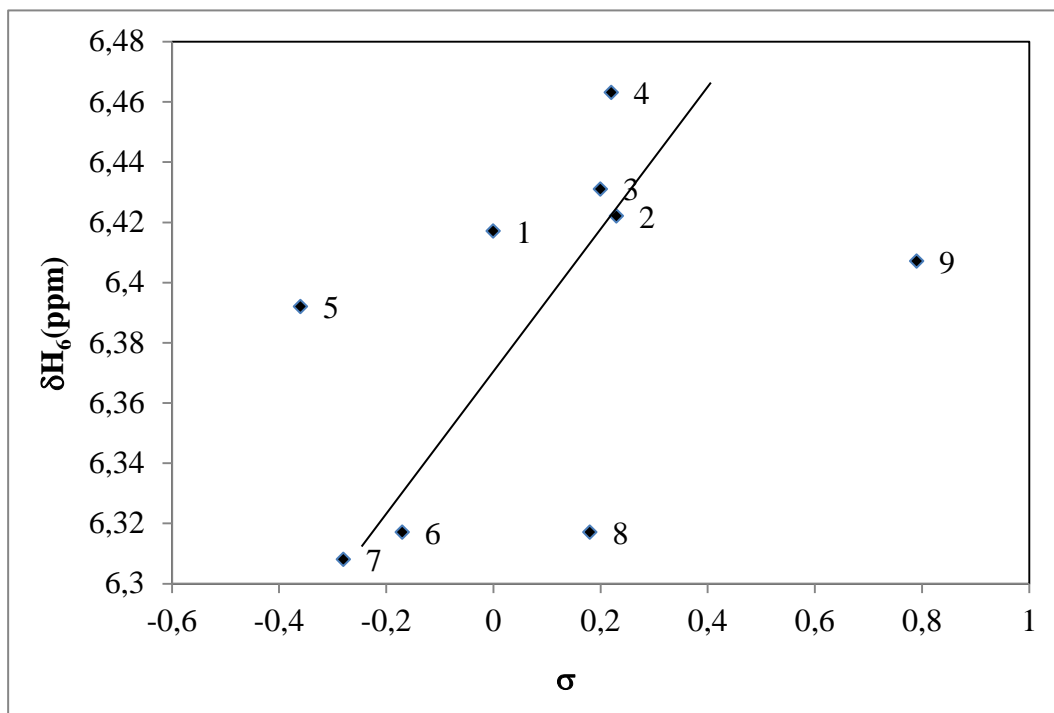
**Figure 7.** The plot of  $\delta\text{H}_5(\text{ppm})$  of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



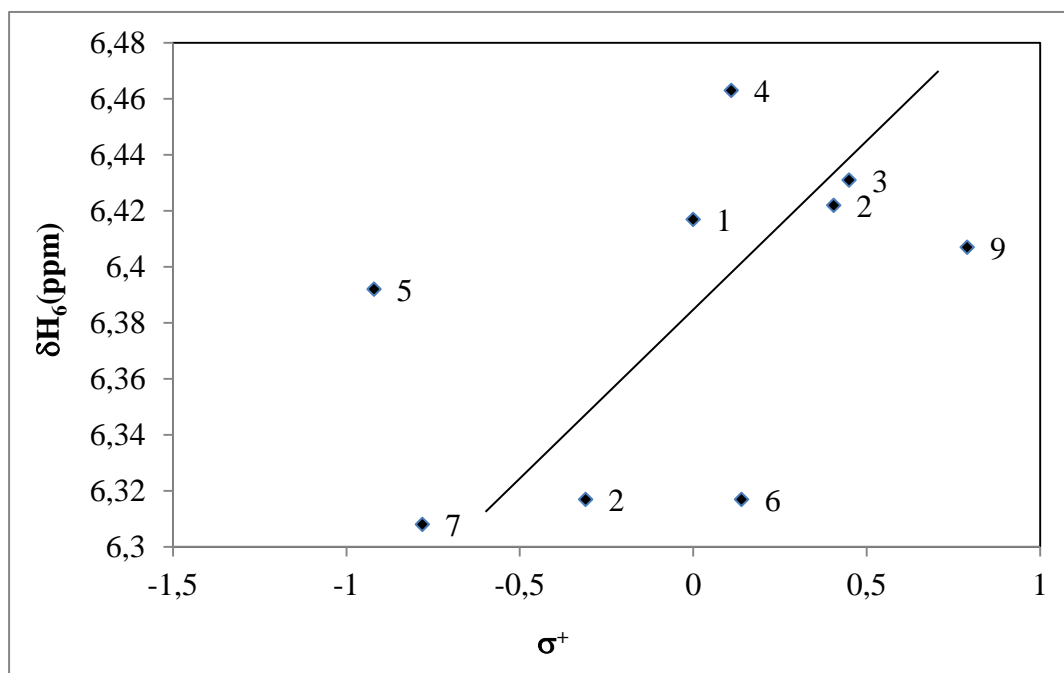
**Figure 8.** The plot of  $\delta H_5$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma_I$ .



**Figure 9.** The plot of  $\delta H_5$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma_R$ .



**Figure 10.** The plot of  $\delta H_6$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



**Figure 11.** The plot of  $\delta H_6$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma^+$ .

The correlation of H<sub>6</sub> proton chemical shifts (δ, ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones gave poor correlations in single regression analysis. While seeking these proton chemical shifts with multi-regression analysis using Swain-Lupton's [30] and σ<sub>I</sub> and σ<sub>R</sub> constants gave satisfactory correlation coefficients. The obtained multi-regression analysis equations are given in (7-10)

$$\delta H_5(\text{ppm}) = 6.333(\pm 0.022) + 0.026(\pm 0.004) \sigma_I + 0.145(\pm 0.058) \sigma_R$$

(R = 0.973, n = 9, P > 95%) ...(7)

$$\delta H_5(\text{ppm}) = 6.334(\pm 0.023) + 0.024(\pm 0.005) F + 0.105(\pm 0.014) R$$

(R = 0.971, n = 9, P > 95%) ...(8)

$$\delta H_6(\text{ppm}) = 6.365(\pm 0.042) + 0.096(\pm 0.092) \sigma_I + 0.061(\pm 0.011) \sigma_R$$

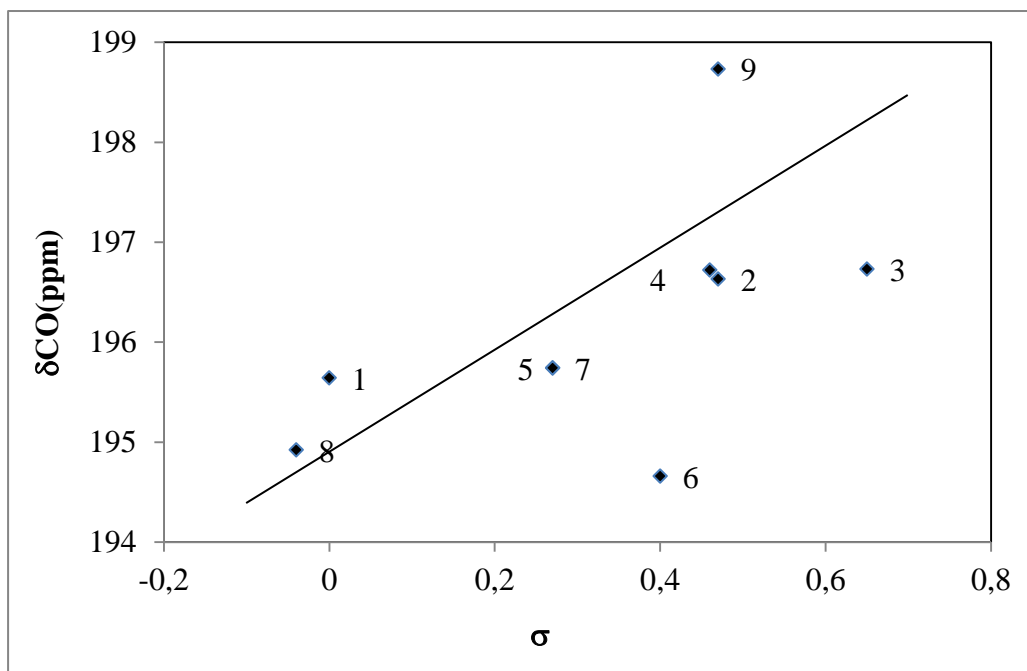
(R = 0.945, n = 9, P > 90%) ...(9)

$$\delta H_6(\text{ppm}) = 6.366(\pm 0.045) + 0.079(\pm 0.010) F + 0.068(\pm 0.008) R$$

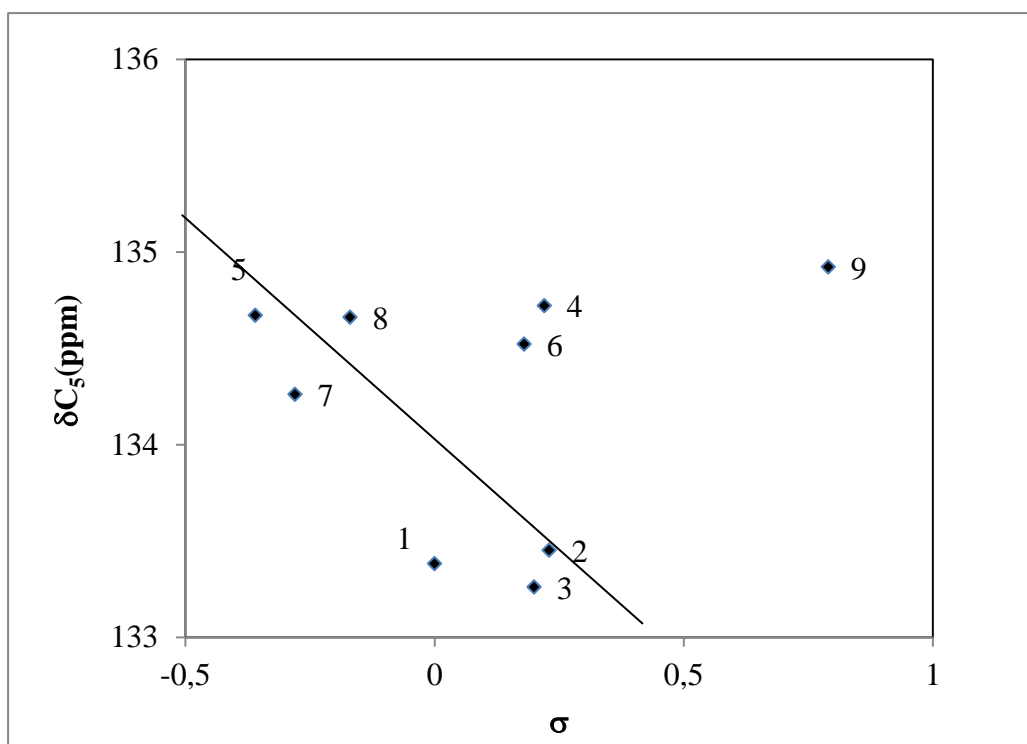
(R = 0.943, n = 9, P > 90%) ...(10)

### 3. 3. <sup>13</sup>C NMR spectral correlations

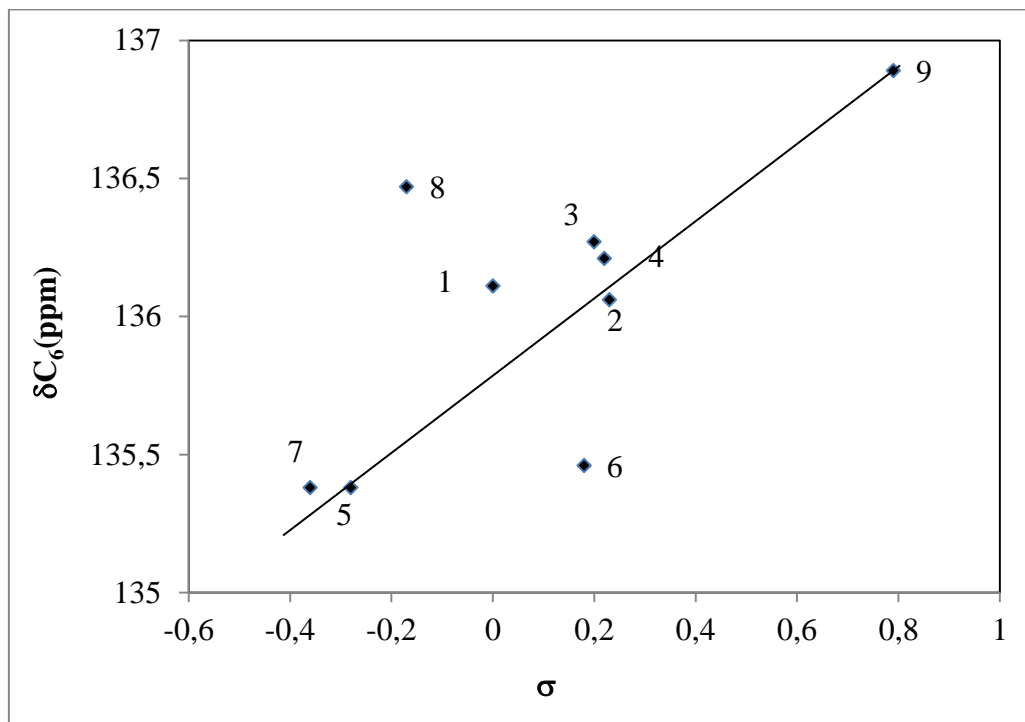
The assigned CO, C<sub>5</sub>, C<sub>6</sub>, C-Br and ipso carbon chemical shifts (δ, ppm) of prepared (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones were presented in Table 1. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. The results of statistical analysis are shown in Table 2. From the table, the correlation of carbonyl chemical shifts (δ, ppm) of prepared (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones gave satisfactorily correlation coefficient t with Hammett σ<sub>I</sub> constants. The polar, resonance and field effects of the substituents were failed for prediction of the correlation. All correlations gave positive ρ values. The failure in correlation is due to the reasons stated earlier and associated with resonance-conjugative structure as shown in Figure 2. The correlation of C<sub>5</sub>, C<sub>6</sub>, carbon chemical shifts (δ, ppm) of prepared (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones seems, the C<sub>5</sub> carbon chemical shifts(δ, ppm) were fail in correlations. The C<sub>6</sub>, carbon chemical shifts(δ, ppm) of ketones gave satisfactory correlations with Hammett σ, σ<sup>+</sup>, σ<sub>R</sub> and R parameters. The Inductive and field effects of the substituents are completely inactive. All correlations gave positive ρ values. This may mean that the normal substituent effects operate in all systems. The correlation of C-Br, carbon chemical shifts (δ, ppm) of prepared (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones gave satisfactory correlation coefficients with Hammett substituent constants, F and R parameters. The correlation of ipso carbon chemical shifts (δ, ppm) of prepared (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones gave satisfactory correlation coefficients with Hammett σ substituent constant and R parameters. The remaining substituent constants were failed in correlations. The polar, inductive and field effects of the substituents are completely inactive. All correlations gave negative ρ values except σ<sub>R</sub> constant. This may mean that the electro donating substituents try to predict the substituent effects in all systems. Some of the single parameter correlation plots are shown in Figures 12-15.



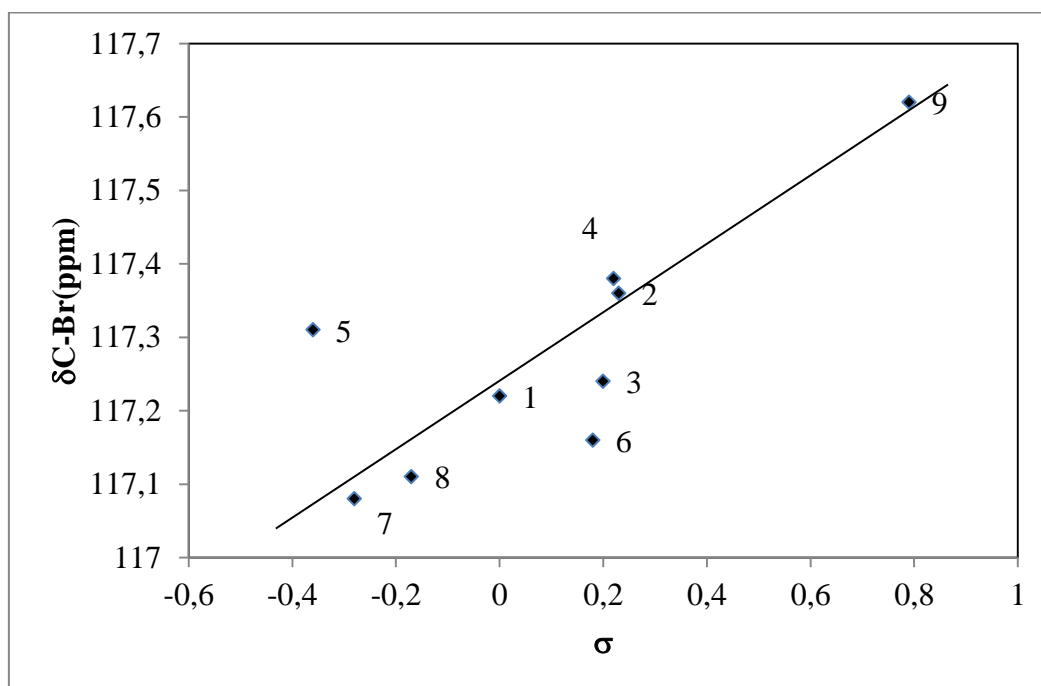
**Figure 12.** The plot of  $\delta\text{CO}(\text{ppm})$  of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



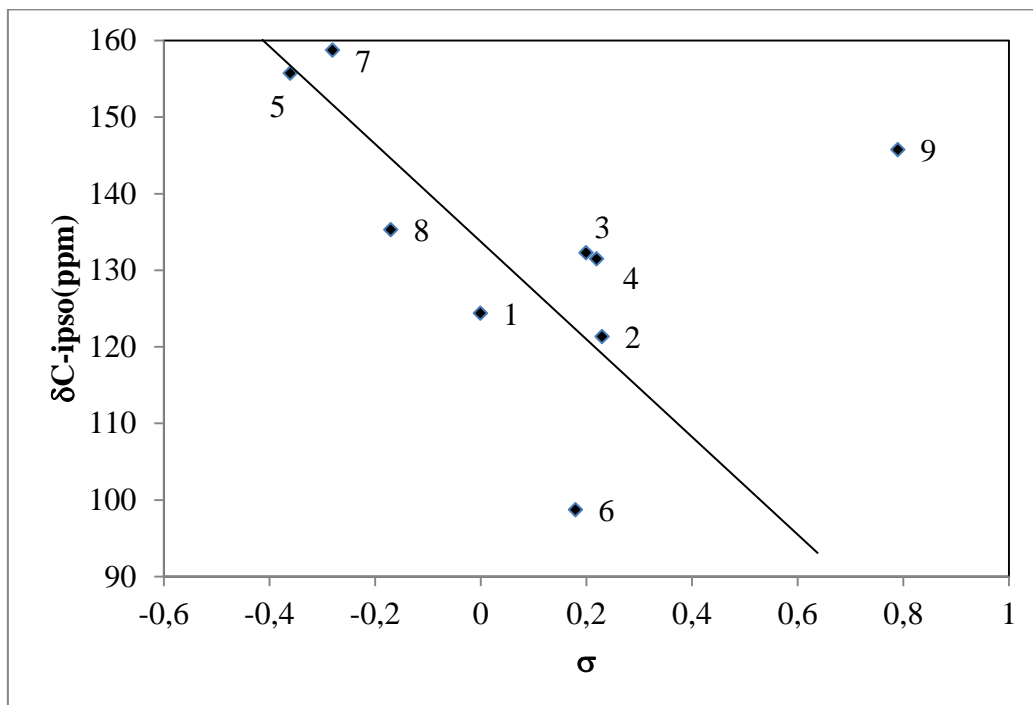
**Figure 13.** The plot of  $\delta\text{C}_5(\text{ppm})$  of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



**Figure 13.** The plot of  $\delta C_6$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



**Figure 14.** The plot of  $\delta C-Br$ (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl) bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .



**Figure 15.** The plot of  $\delta C\text{-ipso (ppm)}$  of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones Vs  $\sigma$ .

Some of the correlations involving carbon-13 NMR chemical shifts (ppm) of (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanones gave poor correlations. These data were worth full when seeking in multi-regressions with Swain-Lupton's parameters [30]. They gave satisfactory correlations and the obtained multi-regression equations are given in (11-20).

$$\delta CO(\text{ppm}) = 195.08(\pm 0.842) + 3.066(\pm 1.802) \sigma_I - 0.434(\pm 0.022) \sigma_R \quad \dots(11)$$

(R = 0.956, n = 9, P > 95%)

$$\delta CO(\text{ppm}) = 195.41(\pm 0.933) + 2.676(\pm 0.207)F + 0.570(\pm 0.171)R \quad \dots(12)$$

(R = 0.948, n = 9, P > 90%)

$$\delta C_5(\text{ppm}) = 134.09(\pm 0.547) + 0.358(\pm 0.115) \sigma_I + 0.066(\pm 0.001) \sigma_R \quad \dots(13)$$

(R = 0.912, n = 9, P > 90%)

$$\delta C_5(\text{ppm}) = 133.87(\pm 0.556) + 0.750(\pm 0.123)F + 0.320(\pm 0.120)R \quad \dots(14)$$

(R = 0.926, n = 9, P > 90%)

$$\delta C_6(\text{ppm}) = 136.36(\pm 0.272) + 2.244(\pm 0.686) \sigma_I + 0.145(\pm 0.060) \sigma_R \quad \dots(15)$$

(R = 0.980, n = 9, P > 95%)



$$\delta C_6(\text{ppm}) = 136.34(\pm 0.260) + 0.197(\pm 0.055)F + 2.228(\pm 0.687)R$$

(R = 0.980, n = 9, P > 95%)

...(16)

$$\delta C\text{-Br}(\text{ppm}) = 117.27(\pm 0.217) + 1.120(\pm 0.461)\sigma_I + 1.458(\pm 0.5722)\sigma_R$$

(R = 0.983, n = 9, P > 95%)

...(17)

$$\delta C\text{-Br}(\text{ppm}) = 117.16(\pm 0.244) + 1.343(\pm 0.542)F + 0.997(\pm 0.042)R$$

(R = 0.980, n = 9, P > 95%)

...(18)

$$\delta C_{\text{ipso}}(\text{ppm}) = 126.79(\pm 14.109) + 1.363(\pm 0.309)\sigma_I - 37.415(\pm 3.716)\sigma_R$$

(R = 0.937, n = 9, P > 90%)

...(19)

$$\delta C_{\text{ipso}}(\text{ppm}) = 124.34(\pm 14.598) + 4.923(\pm 1.327)F - 31.866(\pm 2.687)R$$

(R = 0.943, n = 9, P > 90%)

...(20)

#### 4. CONCLUSIONS

About nine (5-bromothiophen-2-yl)(3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl) methanones were prepared and assigned the infrared and nuclear magnetic resonance spectral data. These data were correlated with Hammett substituent constants, F and R parameters. In infrared spectral correlations, the carbonyl frequencies only gave satisfactory correlation coefficients with resonance components. In <sup>1</sup>H NMR spectral correlations, the H<sub>5</sub> chemical shifts (δ, ppm) gave satisfactory correlation coefficients with Hammett substituent constants, F and R parameters. In <sup>13</sup>C NMR spectral correlations, the carbonyl carbon chemical shifts (δ, ppm) gave satisfactory correlations with inductive effect of the substituents. The C<sub>6</sub> carbon chemical shifts (δ, ppm) gave satisfactory correlations with Hammett σ, σ<sup>+</sup>, σ<sub>R</sub> and R parameters. The C-Br carbon chemical shifts (δ, ppm) gave satisfactory correlations with Hammett substituent constants, F and R parameters. The ipso carbon chemical shifts (δ, ppm) gave the satisfactory correlations with sigma constant and R parameters.

#### ACKNOWLEDGEMENT

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