



Spectral Quantitative Structure activity relationships in 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives

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ABSTRACT

About nine titled compounds were synthesized by greener method and the purities of these methanones have been examined using their analytical and spectral data reported in literature. The infrared and NMR spectral data of these methanones were assigned and correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. From the results of statistical analyses, the effects of substituents in terms of spectral quantitative structure activity on the spectral frequencies were studied.

Keywords: 2,3-Diarylbicyclo[2.2.1]-hept-5-ene-2-yl methanones; Greener synthesis, IR and NMR spectra, QSAR study, Hammett equation, Correlation analysis

1. INTRODUCTION

The QSAR, QSPR, QSR and QPR studies were important and play for assessing and predicting the ground state molecular equilibration of *s-cis* and *s-trans* conformers of unsaturated ketones [1], aldehydes [2], acids [3], alkenes [4], alkynes [5], polyenes [6], acid chlorides [7], esters [8], pyrazolines [9], sulphonamides [10], phenazine derivatives [11], pyrimidines [12], oxazines [13], imines [14], trifluoro methyl imines [15], carboxamides [16], Trogers bases [17], oxypropyl diazenyl [18], acyl chlorides [19], quinoxalines [20], keto oxiranes [21], isoxazoles [22], triazolylthiones [23], sydnones [24], methacrylates [25], N-phenyl formamides [26] and norbornyl methanones [27] in physic-chemical systems. In medicinal field, these studies were useful for prediction of its effectiveness of drug activity of biologically active molecules [28].

Infrared spectral technique is one of the tools for studying quantitative and qualitative study of chemical substrates [29]. The correlation analysis is useful for the study of transition states of reaction mechanisms [30], biological activities [31], and normal co-ordinate [32] analysis, long range interactions in the β -sheet structure [33] of oligopeptides, enone–dienol tautomerism [34],

Qsar study of substituted benzo[α]phenazines [35] cancer agents, density functional theory [36], Diels–Alder reactions [37], rotational barriers in selenomides [38], gas phase reactivity of alkyl allyl sulphides [39], linear-relationships in α , β -unsaturated carbonyl compounds between the half wave reduction potential [40], the frontier orbital energy and the Hammett σ_p values [40], Chemometric potential analysis [41], toxicological analysis [42], Leishmaniasis-Trypanosomiasis [43] and vector regression for agricultural fields. Manikandan and Thirunarayanan have studied the HPLC method for the simultaneous estimation of olmesartan medoxomil and chlorthalidone in dosage forms, validation of dissolution method for levocetirizine dihydrochloride by isocratic reverse phase HPLC with help of correlation analysis [44,45].

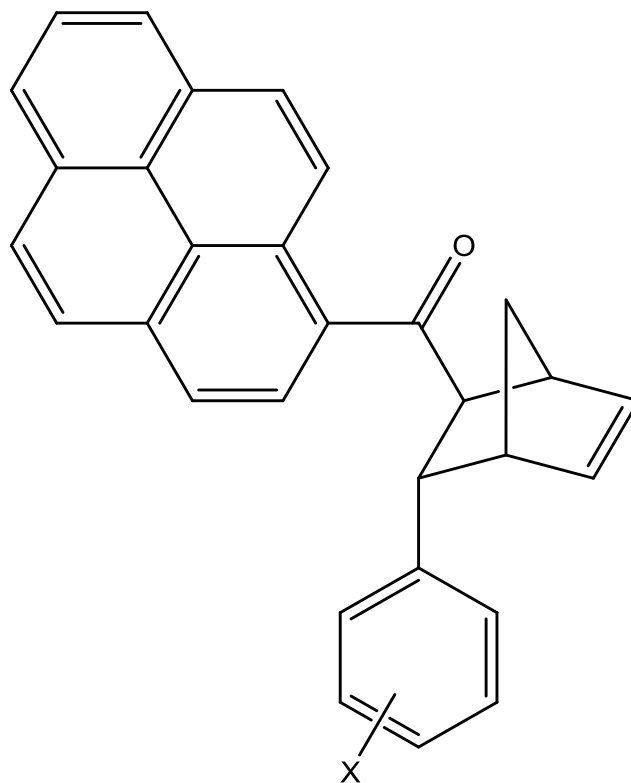
Senbagam et. al., have studied the effects of substituent on spectral frequencies of pyrazoline based imines [46]. Methanones possess valuable biological activities such as antimicrobial [47], antioxidant [48], insect antifeedant activities [49]. Recently, Thirunarayanan have studied the substituent effects on the infrared and nuclear magnetic resonance spectral data and biological activities of norbornyl methanones [50].

Literature review shows no report on the study of spectral QSAR study of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives. Therefore the author has taken effort to synthesis and study the spectral QSAR study on the above norbornyl methanones with their infrared and NMR spectra.

2. EXPERIMENTAL

All 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives have been synthesized and their purities were examined by literature method [51].

The general structure of the present investigation compounds are shown in Figure 1.



Entry	1	2	3	4	5	6	7	8	9
X	H	3-Br	2-Cl	3-Cl	4-Cl	4-F	4-CH ₃	3-NO ₂	4-NO ₂

Figure 1. General structure of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives

3. RESULTS AND DISCUSSION

3. 1. Infrared spectral study

The assigned infrared spectral group frequencies of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives were presented in TABLE 1. These frequencies were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. In infrared spectral correlation, the Hammett equation was employed in the form as equation (1)

$$\nu = \rho\sigma + \nu_0 \quad \dots (1)$$

where ν_0 is the frequency for the parent member of the series.

Table 1. The infrared spectral frequencies (ν , cm^{-1}) of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives.

Entry	X	CO	C=C
1	H	1672.57	1076.12
2	3-Br	1657.26	1073.25
3	2-Cl	1673.18	1036.01
4	3-Cl	1668.25	1062.38
5	4-Cl	1615.59	1065.28
6	4-F	1669.35	1085.29
7	4-CH ₃	1675.26	1085.24
8	3-NO ₂	1687.36	1136.16
9	4-NO ₂	1689.36	1173.96

Table 2. The results of statistical analysis of infrared spectral frequencies (ν , cm^{-1}) of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives with Hammett substituent constants, F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
CO	σ	0.829	1661.84	19.895	22.25	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.834	1661.99	20.048	21.88	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.804	1666.11	3.599	23.26	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.904	1672.73	44.220	21.30	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.809	1664.12	8.549	23.16	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.903	1672.74	34.455	21.78	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH=CH	σ	0.906	1062.87	83.914	32.96	6	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 3-NO ₂ , 4-NO ₂

	σ^+	0.904	1072.61	35.411	38.71	6	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 3-NO ₂ , 4-NO ₂
	σ_I	0.903	1063.27	61.285	41.44	7	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_R	0.916	1105.17	45.581	32.26	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.904	1067.27	64.25	40.81	6	3-Br, 2-Cl, 3-Cl, 4-Cl, 3-NO ₂ , 4-NO ₂
	R	0.915	1059.35	36.59	32.29	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

r = correlation coefficient; I = intercept; ρ = slope; s = standard deviation; n = number of correlated derivatives.

The result of statistical analysis was presented in Table 2. From the Table 2, a satisfactory correlation obtained for the Hammett σ_R constant and R parameters with the carbonyl stretches (ν , cm⁻¹) of the methanones. The Hammett σ , σ^+ , σ_I constants and F parameters were failing in correlations. The -I effect of halogens, nitro groups, +I effect of methyl substituents, polar, field and hyper conjugation effects of substituents were completely absent. Therefore they unable to predicted the substituent effects on the carbonyl frequencies. Also this is associated with the resonance-conjugative structure as shown in Figure 2.

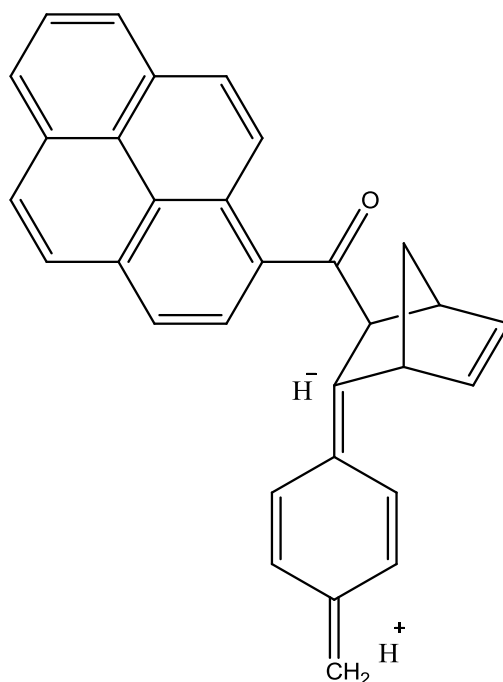


Figure 2. The resonance – conjugative structure of 3-(4-methyl phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone.

The correlation of CH=CH_{op} vibrations (ν, cm⁻¹) With Hammett substituent constants, F and R parameters were shown satisfactory correlation coefficients except 4-F, H, and 4-CH₃ substituents. When they will include the correlation, these substituents reduced the correlation coefficients considerably.

The correlation of σ_R constant seems slightly better comparatively other constants, F and R parameters. The inductive, polar, inductive and resonance and field effects of 4-F, H, and 4-CH₃ substituents disturbed the linear effects in Hammett correlations. The hyper conjugation of 4-CH₃ substituent also influenced the correlation considerably and these are associated with resonance-conjugative structure as illustrated in Figure 2. All correlations of both CO and CH=CH_{op} vibrations (ν, cm⁻¹) gave positive ρ values. This may mean that the normal substituent effects operate in all systems.

In the infrared spectral single parameter correlations, some of the Hammett substituent constants and F parameters were failed with CO stretches (ν, cm⁻¹). While seeking these are worthwhile when they are in the multi-linear regression analysis with Swain-Lupton's[51] constants.

All multi-regression of the infrared spectral frequencies of 3-(4-methyl phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives gave satisfactory correlations. The generated multi-regression analysis equations are presented in (2-6)

$$\text{CO } (\nu, \text{ cm}^{-1}) = 1671.73(\pm 16.004) + 2.434(\pm 0.320)\sigma_1 + 4.411(\pm 0.410)\sigma_R \quad \dots(2)$$

(R = 0.940, n = 9, P > 90%)

$$\text{CO } (\nu, \text{ cm}^{-1}) = 1667.74(\pm 15.099) + 12.758(\pm 3.185)F + 3.666(\pm 0.371)R \quad \dots(3)$$

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

$$\text{CH=CH } (\nu, \text{ cm}^{-1}) = 1081.58(\pm 21.228) + 57.473(\pm 4.225)\sigma_1 + 143.104(\pm 5.413)\sigma_R \quad \dots(4)$$

(R = 0.977, n = 9, P > 95%)

$$\text{CH=CH } (\nu, \text{ cm}^{-1}) = 1081.58(\pm 20.509) + 79.772(\pm 4.199)F + 124.933(\pm 4.895)R \quad \dots(5)$$

(R = 0.977, n = 9, P > 95%)

3. 2. NMR Spectral study

3. 2. 1. ¹H NMR spectral study

The assigned proton chemical shifts (δ, ppm) of norbornyl protons of synthesized of 3-(4-methyl phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives were presented in Table 3. These chemical shifts are correlated with Hammett substituent constants, F and R parameters. In this NMR spectral correlation the Hammett equation was employed as in the form of (6)

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

where δ₀ is the chemical shift of the corresponding parent compound.

Table 3. The ¹H NMR chemical shifts (δ , ppm) of norbornyl protons 3-(4-methyl phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives.

Entry	X	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H _{7'}
1	H	2.935	3.285	3.468	2.795	5.560	5.961	2.009	1.622
2	3-Br	2.295	3.426	3.223	2.179	4.125	5.319	2.050	1.421
3	2-Cl	3.227	4.316	3.496	2.929	4.944	1.015	2.174	1.603
4	3-Cl	2.829	3.763	3.582	2.850	5.393	5.965	2.160	1.621
5	4-Cl	2.839	3.615	3.588	2.710	5.437	5.861	2.035	1.963
6	4-F	2.256	3.573	3.873	2.356	5.678	5.798	2.346	1.789
7	4-CH ₃	2.391	4.967	3.217	2.798	5.970	5.976	2.174	1.973
8	3-NO ₂	3.967	4.687	3.214	2.787	5.991	5.998	2.215	1.723
9	4-NO ₂	3.213	4.798	3.629	2.901	5.592	5.957	2.110	1.623

The results of statistical analysis were presented in TABLE 4. From the table 4, the Hammett substituent constants, F and R parameters were shown satisfactory correlations with H₁ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones.

Table 4. The results of statistical analysis of H₁ proton chemical shifts (δ , ppm) with 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives with Hammett substituent constants, F and R parameters.

Chem. shift	Constt.	r	I	ρ	s	n	Correlated derivatives
H ₁	σ	0.964	2.566	1.102	0.44	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.907	2.598	1.002	0.41	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.903	2.531	0.854	0.53	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.906	3.101	1.866	0.42	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	F	0.902	2.661	0.518	0.56	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.917	3.154	1.813	0.39	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₂	σ	0.902	3.878	0.589	0.66	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ^+	0.902	3.917	0.468	0.66	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_I	0.908	3.651	0.220	0.64	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	σ_R	0.904	4.229	1.558	0.60	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.806	3.977	1.167	0.69	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.904	4.240	1.287	0.62	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₃	σ	0.866	3.489	-0.041	0.24	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.808	3.491	-0.052	0.23	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.831	3.364	0.279	0.22	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.905	3.408	-0.587	0.20	8	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂
	F	0.904	3.322	0.368	0.21	7	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂
	R	0.904	3.402	-0.478	0.21	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₄	σ	0.812	2.672	0.101	0.27	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.851	2.658	0.152	0.26	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.813	2.754	-0.135	0.27	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.846	2.770	0.604	0.24	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.825	2.805	-0.252	0.28	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.905	2.798	0.650	0.22	8	H, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₅	σ	0.907	5.440	-0.130	0.61	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃
	σ^+	0.821	5.501	-0.326	0.60	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.817	5.568	-0.388	0.60	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_R	0.825	5.458	0.735	0.59	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.805	5.462	-0.126	0.61	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.821	5.495	0.567	0.59	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₆	σ	0.807	5.447	0.134	0.61	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.821	5.500	0.326	0.60	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.817	5.568	-0.388	0.60	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.825	5.495	0.735	0.59	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.805	5.126	0.136	0.61	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.821	5.459	0.567	0.59	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
H₇	σ	0.803	2.145	0.120	0.11	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.907	2.147	0.111	0.11	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 3-NO ₂ , 4-NO ₂
	σ_I	0.831	2.081	0.132	0.10	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.904	2.114	-0.238	0.10	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-NO ₂
	F	0.905	2.025	0.207	0.09	7	3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 3-NO ₂ , 4-NO ₂
	R	0.905	2.106	-0.231	0.09	7	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-NO ₂
H₇	σ	0.842	1.772	-0.238	0.17	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	7.781	-0.277	0.15	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.828	1.788	-0.204	0.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.815	0.768	-0.137	0.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.818	0.708	-0.128	0.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.817	1.683	-0.138	0.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

r = correlation coefficient; I = intercept; ρ = slope; s = standard deviation;
n = number of correlated derivatives.

The correlation of H₂ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones gave satisfactory correlations coefficients with Hammett σ , σ^+ and σ_I substituent constants excluding 4-CH₃ substituent. When this methyl group will be included in the correlations, the hyper conjugative and +I effect of methyl substituent was insufficient for predicting the reactivity on H₂ proton chemical shifts (δ , ppm). Hammett σ_R substituent constant and R parameters were satisfactorily correlated with H₂ proton chemical shifts (δ , ppm). The Field effects of substituents were failed in correlations. This is due the reasons stated earlier and it is associated with resonance-conjugative structure as illustrated in Figure 2. The positive ρ values were obtained for all correlations and it implies that the normal substituent effect operates in all systems.

A satisfactory correlation were observed for of H₃ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones with Hammett σ_R substituent constant, F and R parameters excluding 3-Br and 3-NO₂ substituents. The -I effect of these substituents were incapable for predicting the reactivity and reduced the correlation when they will included in the regression. The Hammett σ_R substituent constant R parameters gave negative ρ values it implies that the electron donating substituents predicts the reactivity by means of obtaining satisfactory correlations. The unsatisfactory correlations observed for the Hammett σ , σ^+ and σ_I substituent constants with H₃ proton chemical shifts(δ , ppm) along with negative ρ values. The failure in correlation was already stated the reason and associated with the resonance conjugative structure as illustrated in Figure 2.

The R parameter only produce satisfactory correlation with H₄ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones excluding 3-Br substituent. If this substituent will included in the correlations, it reduces the correlation coefficient considerably. The -I effect of this substituent was not sufficient for predicting the correlation. The Hammett σ , σ^+ , σ_I and σ_R substituents and F parameters were failed in correlations. The inductive effect and field effects of the substituents were gave negative ρ values. The reason for failure in correlation was already stated and associated with resonance-conjugative structure as illustrated in Figure 2.

Hammett σ constant only produced the satisfactory correlation with H₅ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones excluding nitro substituents. These substituents reduced the correlation considerably when these are included in the regression. The -I effect of these substituents were not sufficiently supported for the predicting the reactivity. The remaining Hammett σ^+ , σ_I , σ_R substituents, F and R parameters were failed in correlations. The polar, inductive, hyper conjugation, resonance and field effects of the substituents were insufficient for predicting the reactivity through the correlation. In this correlation, the Hammett σ , σ^+ , σ_I and F parameters were produced negative ρ values. This is due to the reason stated earlier and associated with resonance-conjugative structure as illustrated in Figure 2.

A poor correlation was observed for the correlation of H₆ proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones with Hammett substituent constants, F and R parameters. Many of the correlation gave positive ρ values. This means that the normal substituent effect operates in all systems. The reason for failure in correlation was already stated and associated with the resonance conjugative structure as shown in Figure 2.

The Hammett σ^+ , σ_R substituent constants, F and R parameters produced satisfactory correlation with H_7 proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones. The resonance components gave negative ρ values. This may mean that the electro donating substituents responded for the prediction of substituent effect on the proton chemical shifts. The H_7 proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones were unsatisfactorily correlated with Hammett σ , σ^+ and σ_I constants along with positive ρ values. This may mean that the normal substituent effect operates in all systems. The reason for failure in correlation was already stated and associated with the resonance-conjugative structure as illustrated in Figure 2.

The H_7 proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones were satisfactorily correlated with Hammett σ^+ constant. Remaining all Hammett σ^+ , σ_I and σ_R constants, F and R parameters were produced unsatisfactory correlations. Here the -I effect of electron withdrawing halogen, nitro substituents and +I and hyper conjugative effect of methyl group, resonance and field effects of substituents were incapable for predicting the reactivity and it leads to poor correlation. All correlations produced with negative ρ values. This may mean that the electron donating substituents dominated in the correlation. The failure in correlation was already stated the reason and associated with the resonance-conjugative structure as shown in Figure 2.

Some of the single parameter correlations were fail for production of correlation coefficients for the proton chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones. When they are worthwhile in multi-parameter correlation [51] and they produced satisfactory correlation coefficients. he generated multi-regression analysis equations are shown in (7-22).

$$H_1(\delta, \text{ppm}) = 2.770(\pm 0.278) + 0.803(\pm 0.058)\sigma_I + 1.831(\pm 0.712)\sigma_R \quad \dots(7)$$

($R = 0.977$, $n = 9$, $P > 95\%$)

$$H_1(\delta, \text{ppm}) = 2.865(\pm 0.248) + 0.756(\pm 0.049)F + 1.937(\pm 0.579)R \quad \dots(8)$$

($R = 0.982$, $n = 9$, $P > 95\%$)

$$H_2(\delta, \text{ppm}) = 4.155(\pm 0.455) + 0.179(\pm 0.091)\sigma_I + 1.550(\pm 0.116)\sigma_R \quad \dots(9)$$

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

$$H_2(\delta, \text{ppm}) = 4.110(\pm 0.448) + 0.332(\pm 0.089)F + 1.344(\pm 0.106)R \quad \dots(10)$$

($R = 0.946$, $n = 9$, $P > 90\%$)

$$H_3(\delta, \text{ppm}) = 3.288(\pm 0.143) + 0.292(\pm 0.026)\sigma_I - 0.397(\pm 0.036)\sigma_R \quad \dots(11)$$

($R = 0.961$, $n = 9$, $P > 95\%$)

$$H_3(\delta, \text{ppm}) = 3.279(\pm 0.138) + 0.314(\pm 0.028)F - 0.437(\pm 0.033)R \quad \dots(12)$$

($R = 0.960$, $n = 9$, $P > 95\%$)

$$H_4(\delta, \text{ppm}) = 2.832(\pm 0.180) + 0.185(\pm 0.036)\sigma_I + 0.610(\pm 0.046)\sigma_R \quad \dots(13)$$

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

$$H_4(\delta, \text{ppm}) = 2.897(\pm 0.161) - 0.175(\pm 0.032)F + 0.620(\pm 0.038)R$$

($R = 0.959$, $n = 9$, $P > 95\%$)

...(14)

$$H_5(\delta, \text{ppm}) = 5.664(\pm 0.432) + 0.408(\pm 0.085)\sigma_I + 0.753(\pm 0.112)\sigma_R$$

($R = 0.931$, $n = 9$, $P > 90\%$)

...(15)

$$H_5(\delta, \text{ppm}) = 5.517(\pm 0.435) - 0.051(\pm 0.008)F + 0.558(\pm 0.013)R$$

($R = 0.922$, $n = 9$, $P > 90\%$)

...(16)

$$H_6(\delta, \text{ppm}) = 5.926(\pm 1.239) + 0.801(\pm 0.021)\sigma_I + 2.438(\pm 0.031)\sigma_R$$

($R = 0.931$, $n = 9$, $P > 90\%$)

...(17)

$$H_6(\delta, \text{ppm}) = 5.718(\pm 1.243) + 0.913(\pm 0.021)F + 1.328(\pm 0.241)R$$

($R = 0.918$, $n = 9$, $P > 90\%$)

...(18)

$$H_7(\delta, \text{ppm}) = 2.056(\pm 0.069) + 0.139(\pm 0.140)\sigma_I + 0.241(\pm 0.147)\sigma_R$$

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

...(19)

$$H_7(\delta, \text{ppm}) = 2.034(\pm 0.067) + 0.181(\pm 0.012)F - 0.204(\pm 0.014)R$$

($R = 0.967$, $n = 9$, $P > 95\%$)

...(20)

$$H_{7'}(\delta, \text{ppm}) = 1.771(\pm 0.069) - 0.201(\pm 0.021)\sigma_I - 0.129(\pm 0.034)\sigma_R$$

($R = 0.932$, $n = 9$, $P > 90\%$)

...(21)

$$H_{7'}(\delta, \text{ppm}) = 1.741(\pm 0.133) - 0.149(\pm 0.027)F - 0.164(\pm 0.031)R$$

($R = 0.927$, $n = 9$, $P > 90\%$)

...(22)

3. 2. 2. ¹³C NMR spectral study

The assigned characteristic ¹³C NMR spectral chemical shifts (δ , ppm) such as CO and norbornyl carbons of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones were presented in TABLE 5. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. The result of single parameter regression analysis was presented in TABLE 6.

Table 5. The ¹³C NMR spectral chemical shifts (δ , ppm) such as CO and norbornyl carbons of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones

Entry	X	CO	C ₁	C ₂	C ₃	C ₄	C _{5,6}	C ₇
1	H	192.72	47.24	37.12	31.95	32.77	136.72	30.06
2	3-Br	202.22	41.35	54.18	46.17	51.85	134.05	46.92
3	2-Cl	195.56	42.03	51.12	49.06	51.95	135.54	48.32

4	3-Cl	189.89	28.34	28.64	32.80	30.91	135.34	41.28
5	4-Cl	194.56	28.67	30.90	32.82	45.16	135.89	48.37
6	4-F	198.23	41.56	53.97	46.36	51.24	135.98	45.84
7	4-CH ₃	196.31	29.73	41.74	31.96	30.96	134.09	29.40
8	3-NO ₂	205.12	33.72	45.48	41.54	51.36	136.57	49.57
9	4-NO ₂	204.19	42.72	51.48	43.54	51.38	137.57	42.57

From the table, the carbonyl carbon chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones gave satisfactory correlations with Hammett σ , σ^+ , σ_I , σ_R constants, F and R parameters excluding 3-Br, 3-Cl and 4-F substituents along with positive ρ values.

Table 1. The results of single parameter regression analysis of ¹³C NMR spectral chemical shifts (δ , ppm) CO and norbornyl carbons of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones.

Chem. shift	Constt.	r	I	ρ	s	n	Correlated derivatives
CO	σ	0.916	194.59	10.604	4.26	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.915	195.49	7.708	4.70	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.953	193.16	11.010	4.70	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.945	199.03	11.972	5.00	7	3-Br, 2-Cl, 3-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.951	192.99	11.130	4.67	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.903	198.88	8.163	5.28	7	H, 2-Cl, 3-Cl, 4-Cl, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C₁	σ	0.803	37.04	0.759	7.57	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.814	36.49	02.977	7.65	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.800	37.28	-0.874	7.64	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_R	0.803	37.41	1.272	7.64	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.805	36.63	1.510	7.64	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.802	37.39	1.917	7.64	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C₂	σ	0.820	42.02	6.331	10.27	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.824	42.04	6.472	10.18	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.834	38.40	13.393	9.85	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.809	43.27	-4.881	10.44	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.904	36.77	16.923	9.35	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.817	42.68	-7.763	10.33	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C₃	σ	0.836	37.21	8.206	7.08	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.846	37.06	9.033	6.72	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.903	32.35	17.767	5.90	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.821	38.66	-7.781	7.44	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.906	31.98	18.169	5.65	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.823	38.44	-7.512	7.40	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C₄	σ	0.905	39.45	16.392	8.73	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	40.31	14.505	8.64	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.907	32.08	29.735	6.53	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.804	43.92	-2.105	10.30	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.907	32.09	28.92	6.45	8	H, 3-Br, 2-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.806	43.74	-2.851	10.35	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C_{5,6}	σ	0.905	135.32	1.831	1.07	7	2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ^+	0.904	135.34	1.452	1.10	7	2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.831	135.05	1.718	1.15	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.844	136.05	2.618	1.11	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.836	135.06	1.631	1.15	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.847	136.11	2.461	1.09	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
C₇	σ	0.905	38.14	13.908	6.74	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.905	39.02	12.422	6.62	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.918	31.43	27.147	3.71	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.816	41.75	-6.563	8.13	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.928	32.32	24.775	4.63	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.814	41.74	-4.878	8.17	9	H, 3-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

r = correlation coefficient; I = intercept; ρ = slope; s = standard deviation; n = number of correlated derivatives.

The correlation of C₁ carbonyl carbon chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones gave poor correlations with Hammett σ , σ^+ , σ_I , σ_R constants, F and R parameters along with positive ρ values. Here the polar, inductive, resonance and hyper conjugation effects of all substituents were incapable for determining the reactivity on the carbon through substituent effect. The reason for failure in correlation was already stated along with the Figure 2.

The F parameter only correlated satisfactorily with C₂ carbonyl carbon chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones. The remaining Hammett substituent constants and R parameters were gave poor correlation. Here all electronic effects i.e. polar, +I, -I, resonance excluding field effect of substituents were absent for predicting the reactivity through the nmr shielding and is associated with the resonance-conjugative structure as shown in Figure 2.

The C₃ carbonyl carbon chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones were satisfactorily correlated with Hammett σ_I constant and F parameters along with positive ρ values. The remaining substituent constants and R parameters were failed in correlation. The resonance components gave negative ρ values. Here the inductive effect only dominates for the prediction of reactivity through nmr shielding's than other electronic effects including hyper conjugation.

The observation of poor correlation was due to the reasons stated earlier and associated with resonance-conjugative structure as illustrated in Figure. 2.

The C₄ carbon chemical shifts (δ, ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones gave satisfactory correlations with Hammett σ, σ⁺, σ_I, σ_R constants and F parameters excluding 3-Cl substituents along with positive ρ values. The resonance parameters of the substituents were failed in correlation along with negative ρ values. This is due to the reasons stated earlier and it is associated with resonance-conjugative structure as illustrated in Figure 2.

Hammett σ and σ⁺ constants only gave satisfactory correlation with C_{5 and 6} carbon chemical shifts (δ, ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones excluding 3-Br substituent. The remaining Hammett σ_I, σ_R constants, F and R parameters produced poor correlation with the C_{5and 6} carbon chemical shifts (δ, ppm). All correlation produced positive ρ values. Here the normal substituent effect operates in all systems. The reason for obtaining the poor correlation was already stated and associated with the resonance-conjugative structure as shown in Figure 2.

The correlation of C₇ carbon chemical shifts (δ, ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones gave satisfactory correlations correlation coefficients with Hammett σ, σ⁺, σ_I constants and F parameters along with positive ρ values. The resonance parameters of the substituents were failed in correlation along with negative ρ values. This is due to the reasons stated earlier and it is associated with resonance-conjugative structure as illustrated in Figure 2.

Some of the single parameter correlations gave poor correlation coefficients. When this is worthwhile to seek the multi-parameter correlations with Swain-Lupton's [51] parameters.

The generated correlation equations are given in (23- 36)

$$\text{CO}(\delta, \text{ppm}) = 194.62(\pm 3.062) + 10.707(\pm 6.139)\sigma_I + 11.465(\pm 7.850)\sigma_R \\ (R = 0.968, n = 9, P > 95\%) \quad \dots(23)$$

$$\text{CO}(\delta, \text{ppm}) = 194.00(\pm 2.879) + 12.400(\pm 5.924)F + 10.289(\pm 1.672)R \\ (R = 0.970, n = 9, P > 95\%) \quad \dots(24)$$

$$C_1(\delta, \text{ppm}) = 37.44(\pm 35.747) + 0.886(\pm 0.111)\sigma_I + 1.275(\pm 0.147)\sigma_R \\ (R = 0.903, n = 9, P > 90\%) \quad \dots(25)$$

$$C_1(\delta, \text{ppm}) = 36.74(\pm 5.541) + 1.665(\pm 0.125)F + 1.184(\pm 0.135)R \\ (R = 0.906, n = 9, P > 90\%) \quad \dots(26)$$

$$C_2(\delta, \text{ppm}) = 37.70(\pm 7.350) + 13.537(\pm 1.147)\sigma_I - 5.467(\pm 1.845)\sigma_R \\ (R = 0.936, n = 9, P > 90\%) \quad \dots(27)$$

$$C_2(\delta, \text{ppm}) = 36.28(\pm 6.738) + 16.315(\pm 1.317)F - 4.975(\pm 1.608)R \\ (R = 0.946, n = 9, P > 90\%) \quad \dots(28)$$

$$C_3(\delta, \text{ppm}) = 31.26(\pm 4.223) + 17.993(\pm 8.499)\sigma_I - 8.565(\pm 1.082)\sigma_R \\ (R = 0.967, n = 9, P > 95\%) \quad \dots(29)$$

$$C_3(\delta, \text{ppm}) = 31.31(\pm 4.032) + 17.615(\pm 8.013)F - 4.505(\pm 1.902)R \\ (R = 0.968, n = 9, P > 95\%) \quad \dots(30)$$

$$C_4(\delta, \text{ppm}) = 31.65(\pm 4.883) + 29.825(\pm 9.788)\sigma_I - 3.394(\pm 1.275)\sigma_R \\ (R = 0.977, n = 9, P > 95\%) \quad \dots(31)$$

$$C_4(\delta, \text{ppm}) = 32.30(\pm 4.668) + 29.183(\pm 9.438)F + 2.145(\pm 1.114)R \\ (R = 0.978, n = 9, P > 95\%) \quad \dots(32)$$

$$C_{5,6}(\delta, \text{ppm}) = 135.37(\pm 0.767) + 1.651(\pm 0.155)\sigma_I + 2.571(\pm 1.961)\sigma_R \\ (R = 0.957, n = 9, P > 95\%) \quad \dots(33)$$

$$C_{5,6}(\delta, \text{ppm}) = 135.34(\pm 0.699) + 1.975(\pm 0.139)F + 2.799(\pm 0.164)R \\ (R = 0.964, n = 9, P > 95\%) \quad \dots(34)$$

$$C_7(\delta, \text{ppm}) = 30.44(\pm 2.505) + 27.379(\pm 5.504)\sigma_I - 7.754(\pm 0.643)\sigma_R \\ (R = 0.997, n = 9, P > 95\%) \quad \dots(35)$$

$$C_7(\delta, \text{ppm}) = 32.26(\pm 3.363) + 24.187(\pm 6.800)F - 0.737(\pm 0.0024)R \\ (R = 0.982, n = 9, P > 95\%) \quad \dots(36)$$

4. CONCLUSIONS

A series about nine 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones were synthesized by greener method and the purities of these methanones have been examined using their analytical and spectral data reported in literature. The infrared CO, CH=CH out of plane vibration's (ν , cm^{-1}), and NMR chemical shifts (δ , ppm) of all norbornyl protons, carbonyl and norbornyl carbons of these methanones were assigned and correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. The carbonyl stretches (ν , cm^{-1}) satisfactorily correlated with resonance components only.

The CH=CH out of plane vibration's (ν , cm^{-1}) correlated satisfactorily correlated with Hammett substituent constants, F and R parameters. In ^1H NMR spectral correlations, the H_1 chemical shift (δ , ppm) of the prepared methanones correlates satisfactorily with Hammett substituent constants, F and R parameters. The H_2 chemical shift (δ , ppm) of the prepared methanones correlates satisfactorily with Hammett substituent constants and R parameters. Resonance and field components of the substituents gave satisfactory correlation coefficient with the H_3 chemical shifts (δ , ppm) of the synthesized methanones.

The R parameter only correlated satisfactorily with the H_4 chemical shifts (δ , ppm). Hammett σ constant only gave satisfactory correlations with H_5 chemical shifts (δ , ppm). The H_6 chemical shift (δ , ppm) of the prepared methanones gave poor correlation with Hammett substituent constants, F and R parameters. The polar and resonance components were satisfactorily correlates with H_7 chemical shifts (δ , ppm) of the prepared methanones. The H_7 chemical shifts (δ , ppm) of the methanones satisfactory correlated with Hammett σ^+ constant only.

In ^{13}C NMR correlation study, the carbonyl carbon chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones correlated satisfactorily with Hammett substituent constants, F and R parameters. There is no correlation obtained for C_1 chemical shifts (δ , ppm) of the prepared methanones. The F parameter only produced satisfactory correlation with C_2 chemical shifts (δ , ppm). The inductive and field components were satisfactorily correlated with C_3 chemical shifts (δ , ppm). The Hammett σ , σ^+ , σ_1 constants and F parameters correlated satisfactorily with C_4 chemical shifts (δ , ppm). Satisfactory correlation obtained for Hammett σ and σ^+ substituent constants with C_5 and C_6 chemical shifts (δ , ppm). The correlation pattern of C_7 chemical shifts (δ , ppm) was resemblance with C_4 chemical shifts (δ , ppm) of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones.

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