IR & NMR spectral studies of some 7-substituted 9*H*-fluorenacyl bromides: Assessment of substituent effects

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ABSTRACT

A series of some 2-bromo-1-(2-substituted 9*H*-fluorene-7-yl)ethanones have been prepared. The purities of these ethanones have been checked by their physical constants and spectroscopic data. The spectral group frequencies of these enones have been assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses, the effects of substituent have been discussed.

Keywords: 9*H*-Fluorenacyl bromides; IR and NMR spectra; Hammett substituent constants; Correlation analysis

1. INTRODUCTION

Spectroscopic data are useful for prediction of ground state equilibration of organic molecules such as aryl ketones, alkenes, unsaturated carbonyl compounds, acyl chlorides and their esters [1-5]. The quantitative structure activity relationship and quantitative structure property relationships were used for finding the structure of molecule, quantitative and qualitative analysis [6,7]. Their use in structure parameter correlations becomes popular for studying biological activities [8], normal co-ordinate analysis [9] and transition states of reaction mechanisms [10]. Infrared spectroscopy is a powerful tool technique for the qualitative and quantitative study of natural and synthetic molecules [11]. IR spectroscopy can provide information about the nature, concentration and structure of samples at the molecular level [12]. A great deal of work has been devoted to the reactivity of α,β-carbonyl compounds particularly, the theoretical study of substituent effects has been studied on long range interactions in the β-sheet structure [13] of oligopeptides, enone-dienol tautomerism [14]. Literature study reveals QSAR study of substituted benzo[α] phenazines [15] cancer agents, Diels-Alder reactions [16], density functional theory [17], gas phase reactivity of alkyl allyl sulphides [18] rotational barriers in selenomides [19]. Ananthakrishna Nadar et al., [20] have studied the synthesis and spectral properties of some ω-bromo-1-naphthyl ketones. Thirunarayanan et al., [21] have studied the solvent free synthesis, spectral correlations and antioxidant activities of some ω-bromo-2-naphthacyl bromide and its esters. In their study they observed the *cis-* and *gauche-* form of the naphthones from infrared spectra.

Similarly they assigned the chemical shifts (δ, ppm) of methylene proton, carbon and carbonyl carbons. Also these chemical shifts (δ, ppm) were correlated with Hammett substituent constants. Recently, Thirunarayanan [22] have studied the insect antifeedant activities of some 6-substituted ω-bromo-2-naphthyl ketones. With the above view, there is no report available for spectral correlation study of substituted 9*H*-fluorenacyl bromides in literature in the past. Therefore the author have taken efforts to synthesize some 2-bromo-1-(2-substituted 9*H*-fluorene-7-yl)ethanones and recorded their infrared and NMR spectra for investigate the effect of substituents on the functional group frequencies using Hammett linear correlation analysis.

## 2. EXPERIMENTAL

2. 1. Materials and methods

The fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu, India. All chemicals used were purchased from Sigma-Aldrich and E-Merck Chemical Company. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected.

Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on Avatar-300 Fourier transform spectrophotometer. Instrum AV300 NMR spectrometer was used and operating at 500 MHz for ^{1}H NMR spectra and 125.46 MHz for ^{13}C NMR spectra in CDCl$_3$ solvent using TMS as internal standard. Electron impact (EI, 70 eV) and chemical ionization mode FAB$^+$ mass spectra were recorded with a Varian 500 spectrometer.

2. 2. General procedure for bromination of 2-acetyl 9*H*-fluorene

In a 100 mL flask, 7-substituted 2-acetyl 9*H*-fluorene (4.16 mmol) in aqueous ethanol (20 ml), 0.5 g of fly ash and 10 ml of water were taken. To this mixture Winkler's solution (bromate-bromide solution) 10 ml was added drop wise with stirring for 45 min. until a decoloration of orange solution took place (Scheme 1) [23].

The completion of reaction was monitored by TLC. After completion of the reaction, the brominated products were separated   by column chromatography using ethyl acetate-dichloromethane (6:4) to obtain the pale yellow products of ω-bromo-9*H*-fluorones with more than 60 % yield. The analytical and spectroscopic data are presented in Table 1.

R= H, NH$_2$, Br, Cl, Et, OH, OMe, Me, NO$_2$
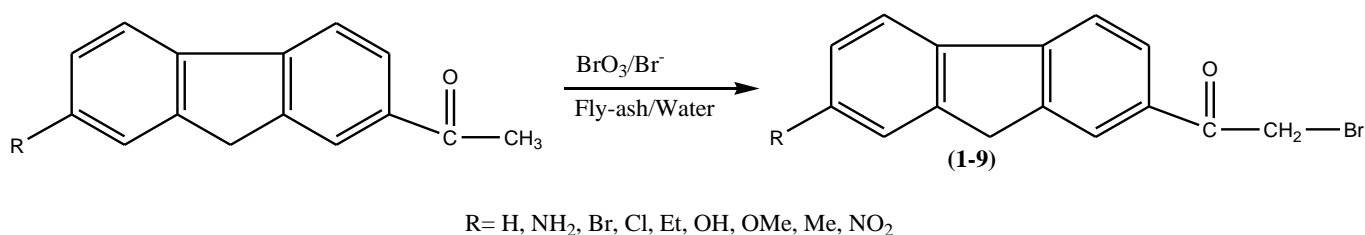
Scheme 1. Synthesis of 7-substituted 9*H*-fluorenacyl bromides.

3. RESULTS AND DISCUSSION

3. 1. Infrared spectral study

The introduction of an $\propto$- halogen atom into any open chain structure, -CH$_2$-CO-, results in a raise in the carbonyl frequency. As rotation is possible about the C-C- bond, one would expect infinite number of conformations in $\propto$- halogeno ketones. One would expect a

second carbonyl absorption arising from a rotational isomer in which the chlorine atom is twisted away from the oxygen and the carbonyl frequencies should therefore be unaffected. Hence compounds such as bromoacetic and fluoroacetic esters are clearly marked and they do in fact exhibit a second C=O absorption in the solution state which is very close to the acid itself.

The ∝-haloacetophenone [24] have been shown to exhibit rotational isomerism which give raise to two carbonyl frequencies and the higher of these has been assigned to the form in which the halogen atom is *cis* with respect to the carbonyl oxygen and therefore nearer to it in space. The same trend was observed in the substituted 9*H*-fluorenacyl bromides, the CO*cis* and CO*gauche* conformers are shown in Figure 1 and the corresponding frequencies were tabulated in Table 1.
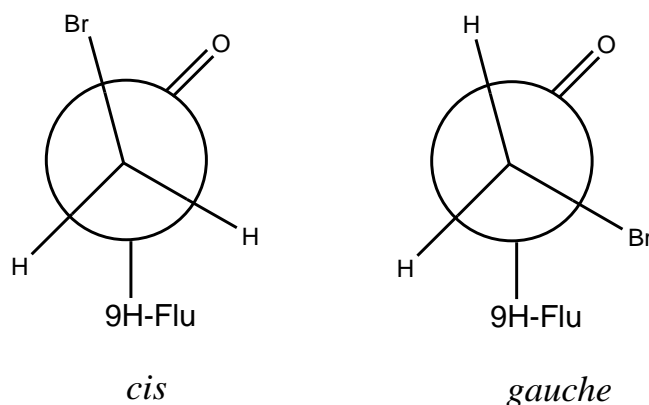

cis   *gauche*

Fig. 1. The *cis-* and *gauche* rotomers of 7-substituted 9H-fluorenacyl bromides.

The assigned CO*cis* and CO*gauche* stretches (v, cm^{-1}) form of 9*H*-fluorenacyl bromides have been correlated with Hammett substituent constants, F and R parameters using linear regression analysis. The results of statistical analyses are presented in Table 2. From Table 2, satisfactory correlation was found to be Hammett σ, σ^+, σ_R constants and R parameters for CO*cis* conformers.

The remaining inductive polar effects of the substituents were fail in correlation. All correlation gave positive ρ values. This shows that there is a normal substituent effect operates in all systems. The Hammett σ_R constants only produce satisfactory correlation for CO*gauche* conformers. The remaining Hammett substituent constants, F and R parameters were fail in correlation. This is due to the incapable for predicting the reactivity on the carbonyl absorptions and is associated with the resonance-conjugated structure shown in Figure 2.
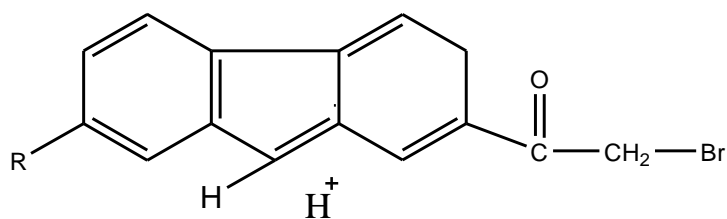

Figure 2. The resonance-conjugative structure.

Table 1. Analytical, physical constants and spectroscopic data of 2-Bromo-1-(2-substitued 9*H*-Fluorene-7-yl) ethanones.

Entry	X	M. F.	M. W.	M. P. (°C)	IR ν(cm^{-1})			^{1}HNMR (δ, ppm)	^{13}CNMR (δ, ppm)		Mass (m/z)
					CO_{cis}	CO_{gauche}	C-Br	CH$_2$ (s, 2H)	CO	C-Br	
1	H	C$_{15}$H$_{11}$BrO	287	97-98 (97-98)[23]	1674.43	1644.82	1278.11	4.25	188.28	32.83	287[M$^+$], 289[M^{+2}]
2	NH$_2$	C$_{15}$H$_{12}$BrNO	302	107-108 (107-108) [23]	1668.21	1638.41	1223.28	4.87	187.23	31.45	302[M$^+$], 304[M^{+2}]
3	Br	C$_{15}$H$_{11}$Br$_2$NO	366	86-87 (86-87) [23]	1671.23	1648.21	1245.18	4.45	188.18	33.58	366[M$^+$], 368[M^{+2}], 370[M^{+4}]
4	Cl	C$_{15}$H$_{11}$BrClO	321	78-79 (78-79) [23]	1673.41	1652.32	1238.15	4.01	186.38	33.78	321[M$^+$], 323[M^{+2}], 325[M+4]
5	OH	C$_{15}$H$_{11}$BrO$_2$	303	102-103 (102-103) [23]	1663.51	1648.06	1234.38	3.97	189.78	33.74	303[M$^+$], 305[M^{+2}]
6	CH$_2$CH$_3$	C$_{17}$H$_{15}$BrO	317	112-113 (112-113) [23]	1667.62	1651.38	1253.24	4.32	188.01	33.63	317[M$^+$], 319[M^{+2}]
7	OCH$_3$	C$_{16}$H$_{13}$BrO$_2$	317	98-99 (98-99) [23]	1668.25	1649.35	1249.35	3.02	186.3	33.32	317[M$^+$], 319[M^{+2}]
8	CH$_3$	C$_{16}$H$_{13}$BrO	301	118-119 (118-119) [23]	1670.36	1656.65	1254.28	3.76	189.96	33.34	301[M$^+$], 303[M^{+2}]
9	NO$_2$	C$_{14}$H$_{10}$BrNO$_2$	304	103-104 (103-104) [23]	1679.23	1652.34	1258.53	3.86	191.52	33.82	304[M$^+$], 306[M^{+2}]

The observed the C-Br stretches (v, cm^{-1}) of all synthesized fluorenacyl bromides were presented in Table 1. These stretches (v, cm^{-1}) were correlated with Hammett substituent constants and F and R parameters.

The results of statistical analysis are presented in Table 2. From Table 2, the C-Br stretches (v, cm^{-1}) satisfactorily correlated with Hammett σ_R constant and F parameters. The remaining Hammett substituent constants and R parameters were fail in correlation. This is due to reasons stated earlier and it is associated with the resonance conjugative structure shown in Figure 2.

Some of the single parameter correlations of carbonyl and C-Br absorptions (v, cm^{-1}) were fail and it is worthful while seeking in the multi-regression analysis with Swain-Lupton's [25] constants. The multi-regression analysis has shown satisfactory correlations and the regression equations are given in (1) to (6).

$$vCO_{cis}(cm^{-1}) = 7.499(\pm 2.861)\,\sigma_I + 18.555(\pm 3.497)\sigma_R + 1672.37(\pm 1.754) \qquad \ldots(1)$$
$$(R = 0.918, P > 90\%, n = 9)$$

$$vCO_{cis}(cm^{-1}) = 6.232(\pm 4.787)F + 6.783(\pm 2.321)R + 1671.16(\pm 2.049) \qquad \ldots(2)$$
$$(R = 0.972, P > 95\%, n = 9)$$

$$vCO_{gauche}(cm^{-1}) = -4.653(\pm 0.781)\sigma_I + 10.765(\pm 4.231)\sigma_R + 1652.64(\pm 3.098) \qquad \ldots(3)$$
$$(R = 0.951, P > 95\%, n = 9)$$

$$vCO_{gauche}(cm^{-1}) = -6.666(\pm 2.272)F + 1.165(\pm 0.411)R + 1651.82(\pm 3.081) \qquad \ldots(4)$$
$$(R = 0.941, P > 90\%, n = 9)$$

$$vC\text{-}Br(cm^{-1}) = -26.535(\pm 11.182)\sigma_I + 54.611(\pm 13.621)\sigma_R + 1267.32(\pm 4.899) \qquad \ldots(5)$$
$$(R = 0.989, P > 95\%, n = 9)$$

$$vC\text{-}Br(cm^{-1}) = -29.172(\pm 18.210)F + 7.518(\pm 1.024)R + 1261.30(\pm 7.812) \qquad \ldots(6)$$
$$(R = 0.964, P > 95\%, n = 9)$$

Table 2. Results of statistical analysis of infrared absorptions (v, cm^{-1}) and NMR chemical shifts (δ, ppm) of 2-Bromo-1-(9*H*-Fluorene-7-yl) ethanones with Hammett σ, σ^+, σ_I, σ_R, F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
$vCO_{s\text{-}cis}$ (cm^{-1})	σ	0.908	1669.90	10.874	2.85	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ^+	0.900	1671.89	8.032	2.12	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_I	0.833	1668.98	5.907	4.61	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_R	0.933	1674.31	17.599	2.08	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	F	0.791	1669.88	2.336	4.84	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$

	R	0.906	1672.88	5.655	3.82	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
νCO$_{gauche}$ (cm^{-1})	σ	0.813	1648.91	1.981	5.52	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ^+	0.781	1649.15	0.643	5.56	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_I	0.827	1650.67	-5571	5.35	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_R	0.904	1651.42	11.360	4.94	7	NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$
	F	0.830	1651.60	-7.331	5.11	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	R	0.823	1649.98	2.372	5.42	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
νC-Br (cm^{-1})	σ	0.818	1247.65	8.575	16.55	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ^+	0.825	1249.44	7.834	16.28	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_I	0.851	1251.33	-31.221	14.45	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_R	0.907	1260.32	50.001	10.50	8	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$
	F	0.906	1259.88	-33.49	13.42	8	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$
	R	0.841	1253.24	12.083	15.35	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
$\delta_{H\alpha}$ (ppm)	σ	0.826	4.028	0.395	0.53	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ^+	0.831	4.107	0.342	0.51	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_I	0.816	3.961	0.328	0.54	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ_R	0.801	4.051	-0.027	0.55	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	F	0.804	4.031	0.073	0.55	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	R	0.851	4.260	0.525	0.47	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
δCO (ppm)	σ	0.834	188.27	1.736	1.74	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$
	σ^+	0.831	188.56	1.056	1.76	9	H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$,

		R	I	ρ	s	n	
							NO_2
	σ_I	0.802	188.36	0.150	1.50	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	σ_R	0.908	189.40	4.821	1.50	8	H, NH_2, Br, Cl, CH_2CH_3, OCH_3, CH_3, NO_2
	F	0.811	188.65	-0.732	1.84	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	R	0.850	189.071	1.721	1.60	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
δC-Br (ppm)	σ	0.817	33.24	0.390	0.79	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	σ^+	0.802	33.28	0.036	0.80	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	σ_I	0.808	33.34	-0.235	0.80	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	σ_R	0.839	33.56	1.383	0.73	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	F	0.827	33.52	-0.714	0.77	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2
	R	0.816	33.37	0.251	0.79	9	H, NH_2, Br, Cl, OH, CH_2CH_3, OCH_3, CH_3, NO_2

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

$$\nu CO_{gauche}(cm^{-1}) = -4.653(\pm0.781)\sigma_I + 10.765(\pm4.231)\sigma_R + 1652.64(\pm3.098) \qquad \ldots(3)$$
$$(R = 0.951, P > 95\,\%, n = 9)$$
$$\nu CO_{gauche}(cm^{-1}) = -6.666(\pm2.272)F + 1.165(\pm0.411)R + 1651.82(\pm3.081) \qquad \ldots(4)$$
$$(R = 0.941, P > 90\,\%, n = 9)$$
$$\nu C\text{-}Br(cm^{-1}) = -26.535(\pm11.182)\sigma_I + 54.611(\pm13.621)\sigma_R + 1267.32(\pm4.899) \qquad \ldots(5)$$
$$(R = 0.989, P > 95\,\%, n = 9)$$
$$\nu C\text{-}Br(cm^{-1}) = -29.172(\pm18.210)F + 7.518(\pm1.024)R + 1261.30(\pm7.812) \qquad \ldots(6)$$
$$(R = 0.964, P > 95\,\%, n = 9)$$

3. 2. NMR spectral study

3. 2. 1. ^{1}H NMR study

From the ^{1}H NMR spectra of all substituted 9*H*-fluorenacyl bromides, the methylene proton signals obtained as singlet. The assigned methylene proton chemical shifts (δ, ppm) of all substituted 9*H*-fluorenacyl bromides were presented in Table 1, and these values are correlated with Hammett substituent constants, F and R parameters.

The results of statistical analysis are shown in Table 2. From the table 2, there is poor correlation was observed for these methylene proton chemical shifts (δ, ppm) of all fluorenacyl bromides.

These is due the reasons stated earlier and is associated with the resonance-conjugative structure shown in Figure 1. The multi-regression analysis shows satisfactory correlation for these chemical shifts with Swain-Lupton's [25] constants and the generated equations are given in (7) and (8)

$$\delta CH_2(ppm) = 0.329(\pm 0.081)\ \sigma_I + 0.015(\pm 0.001)\ \sigma_R + 3.964(\pm 0.357) \qquad \ldots(7)$$
$$(R = 0.916,\ P > 90\ \%,\ n = 9)$$

$$\delta CH_2(ppm) = 0.418(\pm 0.062)F + 0.601(\pm 0.031)R + 4.144(\pm 0.278) \qquad \ldots(8)$$
$$(R = 0.955,\ P > 95\ \%,\ n = 9)$$

3. 2. 3. ^{13}C NMR spectral study

The observed carbonyl and methylene carbon chemical shifts (δ, ppm) of all synthesized substituted 9*H*-fluorenacyl bromides were presented in Table 1. These chemical shifts (δ, ppm) were correlated with Hammett substituent constants, F and R parameters.

The results of statistical analysis are shown in Table 2. From the table 2, Hammett σ_R constant gave satisfactory correlation for carbonyl carbon chemical shifts (δ, ppm) of fluorenacyl bromides. The remaining Hammett substituent constants, F and R parameters were failing in the correlation.

The methylene carbon chemical shifts (δ, ppm) of all fluorenacyl bromides were shown poor correlations with Hammett substituent constants, F and R parameters. This is due to the reasons stated earlier and is associated with the resonance-conjugative structure shown in Figure 2. Some of the single parameter correlations of carbonyl and methylene carbon chemical shifts(δ, ppm) were fail and it is worthful while seeking in the multi-regression analysis with Swain - Lupton's [25] constants.

The multi-regression analysis has shown satisfactory correlations and the regression equations are given in (9) to (12).

$$\delta CO(ppm) = 0.579(\pm 0.221)\ \sigma_I + 4.894(\pm 2.691)\ \sigma_R + 189.25(\pm 0.968) \qquad \ldots(9)$$
$$(R = 0.959,\ P > 95\ \%,\ n = 9)$$
$$\delta CO(ppm) = 0.285(\pm 0.022)F + 1.772(\pm 0.127)R + 188.99(\pm 0.974) \qquad \ldots(10)$$
$$(R = 0.950,\ P > 95\ \%,\ n = 9)$$
$$\delta CH_2(ppm) = -0.117(\pm 0.001)\ \sigma_I + 1.362(\pm 0.013)\ \sigma_R + 33.59(\pm 0.479) \qquad \ldots(11)$$
$$(R = 0.939,\ P > 90\ \%,\ n = 9)$$
$$\delta CH_2(ppm) = -0.674(\pm 0.109)F + 0.134(\pm 0.061)R + 33.55(\pm 0.462) \qquad \ldots(12)$$
$$(R = 0.928,\ P > 90\ \%,\ n = 9)$$

4. CONCLUSIONS

Some substituted 9H-fluorenacyl bromides have been prepared by bromination of 7-X-9H-fluorene-2-methyl ketones. The purities of these ethanones have been checked by their physical constants and spectroscopic data.

The spectral group frequencies of these substituted 9H-fluorenacyl bromides have been assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses, the effects of substituent have been discussed.

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