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

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ABSTRACT
A series of some 2-bromo-1-(2-substituted 9H-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: 9H-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 9H-fluorenacyl bromides in literature in the past. Therefore the author have taken efforts to synthesize some 2-bromo-1-(2-substituted 9H-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 ¹H NMR spectra and 125.46 MHz for ¹³C NMR spectra in CDCl₃ 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 9H-fluorene

In a 100 mL flask, 7-substituted 2-acetyl 9H-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-9H-fluorones with more than 60 % yield. The analytical and spectroscopic data are presented in Table 1.


3. RESULTS AND DISCUSSION

3.1. Infrared spectral study

The introduction of an ω- halogen atom into any open chain structure, -CH₂-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 ω- 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 \( \alpha \)-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 9H-fluorenacly bromides, the COcis and COgauche conformers are shown in Figure 1 and the corresponding frequencies were tabulated in Table 1.

\[
\begin{align*}
\text{Br} & \quad \text{H} & \quad \text{H}
\end{align*}
\]
\[
\begin{align*}
\text{H} & \quad \text{O} & \quad \text{9H-Flu}
\end{align*}
\]
\[
\begin{align*}
\text{cis}
\end{align*}
\]
\[
\begin{align*}
\text{gauche}
\end{align*}
\]

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

The assigned COcis and COgauche stretches (\( \nu, \text{ cm}^{-1} \)) form of 9H-fluorenacly 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 \( \sigma, \sigma^+, \sigma_R \) constants and R parameters for COcis conformers.

The remaining inductive polar effects of the substituents were fail in correlation. All correlation gave positive \( \rho \) values. This shows that there is a normal substituent effect operates in all systems. The Hammett \( \sigma_R \) constants only produce satisfactory correlation for COgauche 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.

\[
\begin{align*}
\text{R} & \quad \text{C} & \quad \text{O}
\end{align*}
\]
\[
\begin{align*}
\text{CH}_2 & \quad \text{Br}
\end{align*}
\]

Figure 2. The resonance-conjugative structure.
Table 1. Analytical, physical constants and spectroscopic data of 2-Bromo-1-(2-substituted 9H-Fluorene-7-yl) ethanones.

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>M. F.</th>
<th>M. W.</th>
<th>M. P. (°C)</th>
<th>IR ν(cm⁻¹)</th>
<th>¹HNMR (δ, ppm)</th>
<th>¹³CNMR (δ, ppm)</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO₂ cis</td>
<td>CO₂ gauche</td>
<td>C-Br</td>
<td>CH₂ (s, 2H)</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>C₁₃H₁₅BrO</td>
<td>287</td>
<td>97.98 (97-98) [23]</td>
<td>1674.43</td>
<td>1644.82</td>
<td>1278.11</td>
<td>4.25</td>
</tr>
<tr>
<td>2</td>
<td>NH₂</td>
<td>C₁₃H₁₅BrNO</td>
<td>302</td>
<td>107-108 (107-108) [23]</td>
<td>1668.21</td>
<td>1638.41</td>
<td>1223.28</td>
<td>4.87</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>C₁₃H₁₅BrNO</td>
<td>366</td>
<td>86-87 (86-87) [23]</td>
<td>1671.23</td>
<td>1648.21</td>
<td>1245.18</td>
<td>4.45</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>C₁₃H₁₅BrClO</td>
<td>321</td>
<td>78-79 (78-79) [23]</td>
<td>1673.41</td>
<td>1652.32</td>
<td>1238.15</td>
<td>4.01</td>
</tr>
<tr>
<td>5</td>
<td>OH</td>
<td>C₁₃H₁₅BrO₂</td>
<td>303</td>
<td>102-103 (102-103) [23]</td>
<td>1663.51</td>
<td>1648.06</td>
<td>1234.38</td>
<td>3.97</td>
</tr>
<tr>
<td>6</td>
<td>CH₂CH₃</td>
<td>C₁₃H₁₅BrO</td>
<td>317</td>
<td>112-113 (112-113) [23]</td>
<td>1667.62</td>
<td>1651.38</td>
<td>1253.24</td>
<td>4.32</td>
</tr>
<tr>
<td>7</td>
<td>OCH₃</td>
<td>C₁₃H₁₅BrO₂</td>
<td>317</td>
<td>98-99 (98-99) [23]</td>
<td>1668.25</td>
<td>1649.35</td>
<td>1249.35</td>
<td>3.02</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>C₁₃H₁₅BrO</td>
<td>301</td>
<td>118-119 (118-119) [23]</td>
<td>1670.36</td>
<td>1656.65</td>
<td>1254.28</td>
<td>3.76</td>
</tr>
<tr>
<td>9</td>
<td>NO₂</td>
<td>C₁₃H₁₅BrNO₂</td>
<td>304</td>
<td>103-104 (103-104) [23]</td>
<td>1679.23</td>
<td>1652.34</td>
<td>1258.53</td>
<td>3.86</td>
</tr>
</tbody>
</table>
The observed the C-Br stretches (ν, cm$^{-1}$) of all synthesized fluorenacyl bromides were presented in Table 1. These stretches (ν, 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 (ν, 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 (ν, 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).

\[
v_{CO}^{cis}(\text{cm}^{-1}) = 7.499(\pm 2.861) \sigma_I + 18.555(\pm 3.497)\sigma_R + 1672.37(\pm 1.754)
\]

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

\[
v_{CO}^{cis}(\text{cm}^{-1}) = 6.232(\pm 4.787)F + 6.783(\pm 2.321)R + 1671.16(\pm 2.049)
\]

\[
(R = 0.972, P > 95 \%, n = 9)
\]

\[
v_{CO}^{gauche}(\text{cm}^{-1}) = -4.653(\pm 0.781)\sigma_I + 10.765(\pm 4.231)\sigma_R + 1652.64(\pm 3.098)
\]

\[
(R = 0.951, P > 95 \%, n = 9)
\]

\[
v_{CO}^{gauche}(\text{cm}^{-1}) = -6.666(\pm 2.272)F + 1.165(\pm 0.411)R + 1651.82(\pm 3.081)
\]

\[
(R = 0.941, P > 90 \%, n = 9)
\]

\[
v_{C-Br}(\text{cm}^{-1}) = -26.535(\pm 11.182)\sigma_I + 54.611(\pm 13.621)\sigma_R + 1267.32(\pm 4.899)
\]

\[
(R = 0.989, P > 95 \%, n = 9)
\]

\[
v_{C-Br}(\text{cm}^{-1}) = -29.172(\pm 18.210)F + 7.518(\pm 1.024)R + 1261.30(\pm 7.812)
\]

\[
(R = 0.964, P > 95 \%, n = 9)
\]

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

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Constants</th>
<th>r</th>
<th>I</th>
<th>ρ</th>
<th>s</th>
<th>n</th>
<th>Correlated derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>v$CO_{cis}$ (cm$^{-1}$)</td>
<td>σ</td>
<td>0.908</td>
<td>1669.90</td>
<td>10.874</td>
<td>2.85</td>
<td>9</td>
<td>H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$</td>
</tr>
<tr>
<td></td>
<td>σ$^+$</td>
<td>0.900</td>
<td>1671.89</td>
<td>8.032</td>
<td>2.12</td>
<td>9</td>
<td>H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$</td>
</tr>
<tr>
<td></td>
<td>σ$^I$</td>
<td>0.833</td>
<td>1668.98</td>
<td>5.907</td>
<td>4.61</td>
<td>9</td>
<td>H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$</td>
</tr>
<tr>
<td></td>
<td>σ$^R$</td>
<td>0.933</td>
<td>1674.31</td>
<td>17.599</td>
<td>2.08</td>
<td>9</td>
<td>H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.791</td>
<td>1669.88</td>
<td>2.336</td>
<td>4.84</td>
<td>9</td>
<td>H, NH$_2$, Br, Cl, OH, CH$_2$CH$_3$, OCH$_3$, CH$_3$, NO$_2$</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>1672.88</td>
<td>5.655</td>
<td>3.82</td>
<td>9</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>vCO\textsubscript{gauche} (cm\textsuperscript{-1})</td>
<td>σ</td>
<td>0.813</td>
<td>1.981</td>
<td>5.52</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>σ\textsuperscript{+}</td>
<td>0.781</td>
<td>0.643</td>
<td>5.56</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>σ\textsubscript{I}</td>
<td>0.827</td>
<td>-5571</td>
<td>5.35</td>
<td>9</td>
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</tr>
<tr>
<td></td>
<td>σ\textsubscript{R}</td>
<td>0.904</td>
<td>11.360</td>
<td>4.94</td>
<td>7</td>
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<td></td>
</tr>
<tr>
<td>vC-Br (cm\textsuperscript{-1})</td>
<td>σ</td>
<td>0.818</td>
<td>8.575</td>
<td>16.55</td>
<td>9</td>
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<tr>
<td></td>
<td>σ\textsuperscript{+}</td>
<td>0.825</td>
<td>7.834</td>
<td>16.28</td>
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<tr>
<td></td>
<td>σ\textsubscript{I}</td>
<td>0.851</td>
<td>-31.221</td>
<td>14.45</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>σ\textsubscript{R}</td>
<td>0.907</td>
<td>50.001</td>
<td>10.50</td>
<td>8</td>
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</tr>
<tr>
<td>δ\textsubscript{Hα} (ppm)</td>
<td>σ</td>
<td>0.826</td>
<td>4.028</td>
<td>0.395</td>
<td>0.53</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>σ\textsuperscript{+}</td>
<td>0.831</td>
<td>4.107</td>
<td>0.342</td>
<td>0.51</td>
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</tr>
<tr>
<td></td>
<td>σ\textsubscript{I}</td>
<td>0.816</td>
<td>3.961</td>
<td>0.328</td>
<td>0.54</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>σ\textsubscript{R}</td>
<td>0.801</td>
<td>4.051</td>
<td>-0.027</td>
<td>0.55</td>
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</tr>
<tr>
<td></td>
<td>F</td>
<td>0.804</td>
<td>4.031</td>
<td>0.073</td>
<td>0.55</td>
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</tr>
<tr>
<td>δCO (ppm)</td>
<td>σ</td>
<td>0.834</td>
<td>188.27</td>
<td>1.736</td>
<td>1.74</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>σ\textsuperscript{+}</td>
<td>0.831</td>
<td>188.56</td>
<td>1.056</td>
<td>1.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \sigma_I )</td>
<td>( \sigma_R )</td>
<td>( F )</td>
<td>( R )</td>
<td>( \delta C-\text{Br} (\text{ppm}) )</td>
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<td>188.36</td>
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<td>1.50</td>
<td>1.50</td>
<td>1.84</td>
<td>1.60</td>
<td>0.79</td>
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</tr>
<tr>
<td></td>
<td>H, NH(_2), Br, Cl, OH, CH(_2)CH(_3), OCH(_3), CH(_3), NO(_2)</td>
<td>H, NH(_2), Br, Cl, CH(_2)CH(_3), OCH(_3), CH(_3), NO(_2)</td>
<td>H, NH(_2), Br, Cl, OH, CH(_2)CH(_3), OCH(_3), CH(_3), NO(_2)</td>
<td>H, NH(_2), Br, Cl, OH, CH(_2)CH(_3), OCH(_3), CH(_3), NO(_2)</td>
<td>H, NH(_2), Br, Cl, OH, CH(_2)CH(_3), OCH(_3), CH(_3), NO(_2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \nu_{\text{CO gauche}} (\text{cm}^{-1}) = -4.653(\pm 0.781)\sigma_I + 10.765(\pm 4.231)\sigma_R + 1652.64(\pm 3.098) \]
\[ (R = 0.951, P > 95\%, n = 9) \] …(3)

\[ \nu_{\text{CO gauche}} (\text{cm}^{-1}) = -6.666(\pm 2.272)F + 1.165(\pm 0.411)R + 1651.82(\pm 3.081) \]
\[ (R = 0.941, P > 90\%, n = 9) \] …(4)

\[ \nu_{\text{C-Br}} (\text{cm}^{-1}) = -26.535(\pm 11.182)\sigma_I + 54.611(\pm 13.621)\sigma_R + 1267.32(\pm 4.899) \]
\[ (R = 0.989, P > 95\%, n = 9) \] …(5)

\[ \nu_{\text{C-Br}} (\text{cm}^{-1}) = -29.172(\pm 18.210)F + 7.518(\pm 1.024)R + 1261.30(\pm 7.812) \]
\[ (R = 0.964, P > 95\%, n = 9) \] …(6)

3. 2. NMR spectral study

3. 2. 1. \(^1\text{H}\) NMR study

From the \(^1\text{H}\) NMR spectra of all substituted 9\(H\)-fluorenacyl bromides, the methylene proton signals obtained as singlet. The assigned methylene proton chemical shifts (\(\delta\), 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 (\(\delta\), 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)

\[
\delta \text{CH}_2(\text{ppm}) = 0.329(\pm 0.081) \sigma_I + 0.015(\pm 0.001) \sigma_R + 3.964(\pm 0.357) \\
(R = 0.916, P > 90 \%, n = 9)
\]

\[
\delta \text{CH}_2(\text{ppm}) = 0.418(\pm 0.062)F + 0.601(\pm 0.031)R + 4.144(\pm 0.278) \\
(R = 0.955, P > 95 \%, n = 9)
\]

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

The observed carbonyl and methylene carbon chemical shifts (δ, ppm) of all synthesized substituted 9H-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 σR 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 worthwhile 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).

\[
\delta \text{CO}(\text{ppm}) = 0.579(\pm 0.221)\sigma_I + 4.894(\pm 2.691)\sigma_R + 189.25(\pm 0.968) \\
(R = 0.959, P > 95 \%, n = 9)
\]

\[
\delta \text{CO}(\text{ppm}) = 0.285(\pm 0.022)F + 1.772(\pm 0.127)R + 188.99(\pm 0.974) \\
(R = 0.950, P > 95 \%, n = 9)
\]

\[
\delta \text{CH}_2(\text{ppm}) = -0.117(\pm 0.001)\sigma_I + 1.362(\pm 0.013)\sigma_R + 33.59(\pm 0.479) \\
(R = 0.939, P > 90 \%, n = 9)
\]

\[
\delta \text{CH}_2(\text{ppm}) = -0.674(\pm 0.109)F + 0.134(\pm 0.061)R + 33.55(\pm 0.462) \\
(R = 0.928, P > 90 \%, n = 9)
\]

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.
References


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