

## Styryl-6-Methoxy-2-Naphthyl Ketone 유도체의 합성 및 특성 분석

G. Thirunarayanan\*

Department of Chemistry, Annamalai University, Annamalainagar-608 002, India

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## Synthesis, Characterization and Correlation Analysis in Styryl 6-Methoxy-2-Naphthyl Ketones

G. Thirunarayanan\*

Department of Chemistry, Annamalai University, Annamalainagar-608 002, India

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**요 약.**  $\alpha$ ,  $\beta$ -불포화 케톤 유도체를 실리카-황산 촉매 하에서 비용매 교차 알돌 응축 반응법을 이용하여 합성하였다. 합성 수율은 90% 이상이었으며, 사용된 촉매는 회수 가능하였다. 합성된 화합물들의 물리화학적인 특성은 IR, NMR, Mass 등의 분광학적 분석 방법을 이용하여 결정하였다. 케톤 생성물에 미치는 치환기 효과는 측정된 분광 데이터와 Hammett 치환기 상수간의 상관관계로 표현되는 다중 상관계수 방정식에 의하여 잘 설명될 수 있었다.

**주제어:** 비용매 합성, 교차 알돌 응축 반응, 환경 친화적 화학반응, 상관계수 분석법, 적외선, 핵자기 공명, 질량 분석법

**ABSTRACT.** A series of  $\alpha$ ,  $\beta$ -unsaturated ketones are synthesized by Crossed – Aldol condensation reaction, from eco-friendly 6-methoxy-2-naphthyl ketones and substituted benzaldehydes under solvent free conditions using silica-sulfuric acid as a catalytic reagent. The yields of ketones are more than 90% and the catalyst was reusable for further run. There is no appreciable decrease in the yield of product and the activity of catalyst. These chalcones were characterized by their physical constants and spectral data (IR,  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and Mass). These spectral data are subjected to correlate various Hammett substituent constants with single and multiparameter correlation equations. From the results of statistical analysis the influence of electronic effects of substituents on the spectral data of the ketones were explained.

**Keywords:** Solvent Free Synthesis, Crossed-Aldol Condensation, Environmentally Eco-friendly Benign Reaction, 6-Methoxy-2-naphthyl Chalcones, IR, NMR and Mass Spectra, Correlation Analysis, Electronic Effects

### INTRODUCTION

Since 1990's chemists are paying much more interest in the application of solvent free synthetic methods<sup>1</sup> in organic reactions like Claisen<sup>2</sup>-Schmidt, Knoevenagel<sup>3</sup>, Aldol<sup>4</sup> and Crossed-aldol<sup>5</sup> employed for synthesis of carbonyl compounds due to the operational simplicity, easier work-up, better yield and eco-friendly nature. Among these reactions aldol

condensation is useful for the formation of carbon-carbon bond in many kinds of carbonyl compounds.<sup>6</sup> The basic skeleton of chalcones and antibiotics are widely figured in natural products, are known to have multipronged activity.<sup>7,8</sup> Many of the chalcones are used as agrochemicals and drugs.<sup>9</sup> Condensation of ketones with aldehydes is special interest and crossed-aldol condensation is an effective pathway for those preparations. But traditional

acid-base catalyzed reactions suffer from the reverse reaction<sup>10</sup> and self condensation of starting molecules.<sup>11</sup>

Many reagents and Co-ordination complexes of Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) ions with various ligands have been employed for aldol condensation.<sup>12</sup> Metal salts of  $Cp_2ZrH_2$  are used for condensation of cycloalkanones.<sup>13</sup>  $KF \cdot Al_2O_3$  and bis (*p*-methoxy phenyl) tellurides have been used for crossed condensation under microwave irradiation.<sup>14</sup> Anhydrous  $RuCl_3$  and  $TiCl_3(SO_2CF_3)$  have also been applied for aldol condensation reactions under solvent free conditions.<sup>15</sup> Now more attention has been paid to synthesis of acyclic and cyclic chalcones by chemists and scientists.<sup>16</sup> Balakrishna Kalluraya<sup>17</sup> *et al.* reported to obtain 60-70% yield of sydnone chalcones under solvent free condition by aldol condensation reaction by grinding of ketones and aldehydes with sodium hydroxide. Mohamed A. Hassan *et al.*<sup>18</sup> synthesized various *2E-3-aryl-1-hetarylprop-2-en-1-ones* by eco-friendly condensation reaction in sodium hydroxide-water heterogeneous phase reaction medium. Silica-sulphuric acid is used as a versatile and stable solid acid catalyst for organic synthesis. The author wish to report an efficient and selective method for condensation of 6-methoxy-2-naphthyl ketones with various *m*- and *p*-substituted benzaldehydes under solvent free conditions using silica-sulphuric acid as a reagent in an oven to yields the respective *E-2-propen-1-ones*. The promoting effect of silica – sulphuric acid in their reaction was shown good performance and it is proved by obtaining higher percentage of yields. The product was isolated and the remaining catalyst was washed and reused with fresh substrate for further reactions. No decrease in the yield was observed, demonstrating that silica-sulphuric acid can be reused in crossed-aldol condensation reaction without environmental discharge.

## EXPERIMENTAL

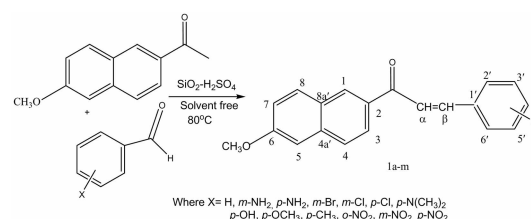
### Materials and Methods

All chemicals and Analytical Grade solvents were purchased from 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 ( $KBr$ ,  $4000-400\text{ cm}^{-1}$ ) were recorded on Perkin Elmer-Fourier transform spectrophotometer. The nuclear magnetic resonance spectra both  $^1H$  and  $^{13}C$  of chalcones were recorded using UNITYPI.US-300 “KIBSIPS” 300MHz spectrometer. Electron impact (EI) (70 eV) and chemical ionization (CI) were recorded with a Finnigan MAT 95S spectrometer. Micro analyses of all chalcones were performed in Perkin Elmer 240C Analyzer.

### General procedure for synthesis of substituted styryl 6-methoxy-2-naphthyl ketones

6-Methoxy-2-naphthyl ketones (2 mmol), *m*- and *p*-substituted benzaldehydes (4.2 mmol) and silica-sulphuric acid (1.5 g equal to 4 mmol of  $H^+$ ) were mixed thoroughly, placed in a glass tube and capped (Scheme 1). The mixture was heated in an oven at  $80\text{ }^\circ\text{C}$  for 2-3.5 h. After complete conversion of the ketones as monitored by TLC, the mixture was cooled to room temperature. Dichloromethane (20-30 ml) was added and heated for 3-5 minutes. The reagent was removed by filtration. The filtrate was concentrated and the solid residue was recrystallised from ethanol to afford the pure products as pale yellow glittering solid<sup>19</sup> (1a-m). The catalyst was recycled by washing the solid reagent remained on the filter by ethyl acetate (20 ml) followed by drying in an oven at  $50\text{ }^\circ\text{C}$  for 2 h and it can be reusable for another reaction run. Based on Hays and Timmons<sup>20,21</sup> infrared carbonyl stretching frequencies of *s-cis* and *s-trans* conformers are assigned. The NMR chemical shifts (ppm) of ethylene  $\alpha$ ,  $\beta$  protons and carbons are assigned based on reported in earlier literature values.<sup>22-27</sup> The characterization data of all chalcones are summarized.



Scheme 1

**1a. (2E)-1-(6-Methoxy-2-naphthyl)-3-phenyl-2-propen-1-one.** Yield: 96%; m.p. 67-69(69-70<sup>20</sup>)°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1665 (CO *s-cis*), 1626 (CO *s-trans*), 993 (CH=CH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.612(d, 1H,  $\alpha$ ), 7.766(d, 1H,  $\beta$ ), 6.711-7.482(m, 11H Ar-H), 3.821(s, 3H -OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =119.460(C $\alpha$ ), 144.628(C $\beta$ ), 182.105(CO), 128.420(C<sub>1</sub>), 132.760(C<sub>2</sub>), 124.711(C<sub>3</sub>), 127.110(C<sub>4</sub>), 104.992(C<sub>5</sub>), 159.320(C<sub>6</sub>), 119.553(C<sub>7</sub>), 130.993(C<sub>8</sub>), 133.499(C<sub>9</sub>), 131.299(C<sub>10</sub>), 56.235(-OCH<sub>3</sub>), 135.934(C<sub>11</sub>), 126.421(C<sub>2,6</sub>), 127.989(C<sub>3,5</sub>), 128.101(C<sub>6</sub>). C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>. MS: m/z=288[M<sup>+</sup>], 185, 158, 136, 131, 128, 103, 91, 77, 65.

**1b. (2E)-1-(6-Methoxy-1-naphthyl)-3-(3-aminophenyl)-2-propen-1-one.** Yield: 94%; m.p. 97-98°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1667 (CO *s-cis*), 1622 (CO *s-trans*), 985 (CH=CH), 3533(-NH<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.554(d, 1H,  $\alpha$ ), 7.823(d, 1H,  $\beta$ ), 6.811-7.342(m, 10H, Ar-H), 4.570(s, 2H -NH<sub>2</sub>), 3.633(s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =119.240(C $\alpha$ ), 144.527(C $\beta$ ), 187.220(CO), 128.423(C<sub>1</sub>), 132.763(C<sub>2</sub>), 124.698(C<sub>3</sub>), 127.320(C<sub>4</sub>), 104.902(C<sub>5</sub>), 159.243(C<sub>6</sub>), 119.583(C<sub>7</sub>), 130.932(C<sub>8</sub>), 133.475(C<sub>9</sub>), 131.309(C<sub>10</sub>), 56.993(-OCH<sub>3</sub>), 136.091(C<sub>11</sub>), 111.421(C<sub>12</sub>), 148.279(C<sub>13</sub>), 116.010(C<sub>14</sub>), 129.498(C<sub>15</sub>), 116.412(C<sub>16</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.13; H, 5.46; N, 4.60. MS: m/z=303[M<sup>+</sup>], 287, 272, 185, 158, 136, 128, 118, 102, 93.

**1c. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-aminophenyl)-2-propen-1-one.** Yield: 96%; m.p. 86-87°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1660 (CO *s-cis*), 1627 (CO *s-trans*), 985 (CH=CH), 3528(-NH<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.234(d, 1H,  $\alpha$ ), 7.672(d, 1H,  $\beta$ ), 6.767-7.201(m, 10H, Ar-H), 4.671(s, 2H -NH<sub>2</sub>), 3.479(-OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =118.770(C $\alpha$ ), 144.224(C $\beta$ ), 185.340(CO), 127.994(C<sub>1</sub>), 132.653(C<sub>2</sub>), 124.721(C<sub>3</sub>), 127.381(C<sub>4</sub>), 106.002(C<sub>5</sub>), 159.497(C<sub>6</sub>), 119.498(C<sub>7</sub>), 130.995(C<sub>8</sub>), 133.963(C<sub>9</sub>), 132.003(C<sub>10</sub>), 56.064(-OCH<sub>3</sub>), 125.043(C<sub>11</sub>), 126.995(C<sub>12</sub>), 117.009(C<sub>13</sub>), 146.994(C<sub>14</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.16; H, 5.59; N, 5.57. MS: m/z=303[M<sup>+</sup>], 185, 158, 136, 128, 118, 102, 77, 93.

**1d. (2E)-1-(6-Methoxy-2-naphthyl)-3-(3-bromophenyl)-2-propen-1-one.** Yield: 95%; m.p. 114-115°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1674 (CO *s-cis*), 1633 (CO *s-trans*), 978 (CH=CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.727

(d, 1H,  $\alpha$ ), 7.891(d, 1H,  $\beta$ ), 7.041-7.644(m, 10H Ar-H), 3.595(s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =119.642(C $\alpha$ ), 144.748(C $\beta$ ), 188.796(CO), 128.475(C<sub>1</sub>), 133.201(C<sub>2</sub>), 124.021(C<sub>3</sub>), 127.098(C<sub>4</sub>), 106.490(C<sub>5</sub>), 159.782(C<sub>6</sub>), 120.991(C<sub>7</sub>), 130.995(C<sub>8</sub>), 133.453(C<sub>9</sub>), 131.396(C<sub>10</sub>), 56.632(-OCH<sub>3</sub>), 136.994(C<sub>11</sub>), 129.899(C<sub>12</sub>), 123.643(C<sub>13</sub>), 131.010(C<sub>14</sub>), 129.996(C<sub>15</sub>), 125.949(C<sub>16</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>BrO<sub>2</sub>: C, 65.41; H, 4.12. Found: C, 65.36; H, 4.09. MS m/z=367 [M<sup>+</sup>, Br<sup>80,9</sup>], 365 [M<sup>+</sup>, Br<sup>79,9</sup>], 287, 285, 188, 186, 182, 180, 169, 167, 156, 154, 136, 89, 91, 77, 65.

**1e. (2E)-1-(6-Methoxy-2-naphthyl)-3-(3-chlorophenyl)-2-propen-1-one.** Yield: 92%; m.p. 101-102°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1671 (CO *s-cis*), 1628 (CO *s-trans*), 965 (CH=CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.981(d, 1H,  $\alpha$ ), 8.112(d, 1H,  $\beta$ ), 7.261-7.924(m, 10H, Ar-H), 3.328 (s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =119.527(C $\alpha$ ), 144.664(C $\beta$ ), 190.193(CO), 127.979(C<sub>1</sub>), 133.342(C<sub>2</sub>), 124.443(C<sub>3</sub>), 127.954(C<sub>4</sub>), 105.996(C<sub>5</sub>), 159.236(C<sub>6</sub>), 120.191(C<sub>7</sub>), 131.099(C<sub>8</sub>), 133.634(C<sub>9</sub>), 131.702(C<sub>10</sub>), 54.247(-OCH<sub>3</sub>), 136.798(C<sub>11</sub>), 126.955(C<sub>12</sub>), 134.199(C<sub>13</sub>), 127.997(C<sub>14</sub>), 129.996(C<sub>15</sub>), 124.549(C<sub>16</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>ClO<sub>2</sub>: C, 74.42; H, 4.68. Found: C, 74.38; H, 4.61. MS: m/z=324[M<sup>+</sup>, Cl<sup>37</sup>], 322[M<sup>+</sup>, Cl<sup>35</sup>], 289, 287, 187, 185, 139, 138, 137, 136, 113, 111, 93, 91, 79, 77, 67, 65, 53, 51.

**1f. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one.** Yield: 93%; m.p. 122-123°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1664 (CO *s-cis*), 1634 (CO *s-trans*), 1015 (CH=CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.905(d, 1H,  $\alpha$ ), 7.992(d, 1H,  $\beta$ ), 7.143-7.870(m, 10H, Ar-H), 3.543 (-OCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =119.401(C $\alpha$ ), 141.822(C $\beta$ ), 188.230(CO), 127.644(C<sub>1</sub>), 132.843(C<sub>2</sub>), 124.3831(C<sub>3</sub>), 127.942(C<sub>4</sub>), 106.502(C<sub>5</sub>), 159.721(C<sub>6</sub>), 119.128(C<sub>7</sub>), 130.931(C<sub>8</sub>), 133.932(C<sub>9</sub>), 132.732(C<sub>10</sub>), 55.648(-OCH<sub>3</sub>), 133.399(C<sub>11</sub>), 127.992(C<sub>12</sub>), 128.964(C<sub>13</sub>), 134.974(C<sub>14</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>ClO<sub>2</sub>: C, 74.42; H, 4.68. Found: C, 74.40; H, 4.64. MS m/z=324[M<sup>+</sup>, Cl<sup>37</sup>], 322[M<sup>+</sup>, Cl<sup>35</sup>], 289, 287, 187, 160, 158, 139, 138, 136, 113, 93, 91, 79, 67, 65.

**1g. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-dimethylaminophenyl)-2-propen-1-one.** Yield: 95%; m.p. 142-143°C; IR (KBr, cm<sup>-1</sup>):  $\nu$ =1655 (CO *s-cis*), 1624 (CO *s-trans*), 1008 (CH=C=NH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$ =7.167(d, 1H,  $\alpha$ ), 7.737(d, 1H,  $\beta$ ), 6.803-7.081(m,

101I, Ar-H), 3.874(s, 3H -OCH<sub>3</sub>), 2.878(s, 6H -(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=118.475(C<sub>2</sub>), 144.059(C<sub>1</sub>), 187.021(CO), 127.979(C<sub>1</sub>), 132.498(C<sub>2</sub>), 124.967(C<sub>3</sub>), 127.064(C<sub>4</sub>), 106.764(C<sub>5</sub>), 159.543(C<sub>6</sub>), 119.398(C<sub>7</sub>), 132.012(C<sub>8</sub>), 133.643(C<sub>9</sub>), 132.298(C<sub>10</sub>), 56.023(-OCH<sub>3</sub>), 124.699(C<sub>1</sub>), 127.339(C<sub>2,6</sub>), 115.227(C<sub>3,5</sub>), 148.997(C<sub>4</sub>), 41.043(-(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd. for C<sub>22</sub>H<sub>21</sub>NO<sub>2</sub>: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.68; H, 6.27; N, 4.19. MS: m/z=331[M<sup>+</sup>], 316, 287, 185, 158, 146, 136, 134, 120, 91, 65.

**1h. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-hydroxyphenyl)-2-propen-1-one.** Yield: 91%; m.p. 117-118°C; IR (KBr, cm<sup>-1</sup>): ν=1657 (CO *s-cis*), 1633 (CO *s-trans*), 983(CH=CH), 3498(-OH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ=7.197(d, 1H, α), 7.737(d, 1H, β), 6.269-7.013(m, 10H, Ar-H), 4.788(s, 1H -OH), 3.576(-OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=118.927(C<sub>2</sub>), 144.246(C<sub>1</sub>), 190.242(CO), 128.326(C<sub>1</sub>), 132.496(C<sub>2</sub>), 124.653(C<sub>3</sub>), 127.091(C<sub>4</sub>), 105.555(C<sub>5</sub>), 159.608(C<sub>6</sub>), 119.604(C<sub>7</sub>), 131.852(C<sub>8</sub>), 133.591(C<sub>9</sub>), 132.091(C<sub>10</sub>), 56.601(-OCH<sub>3</sub>), 127.003(C<sub>1</sub>), 127.890(C<sub>2,6</sub>), 115.974(C<sub>3,5</sub>), 158.004(C<sub>4</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>16</sub>O<sub>3</sub>: C, 78.93; H, 5.30. Found: C, 78.19; H, 5.25. MS: m/z=294[M<sup>+</sup>], 277, 258, 185, 168, 140, 128, 124, 107, 102, 91, 77, 65.

**1i. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-methoxyphenyl)-2-propen-1-one.** Yield: 94%; m.p. 107-108 °C; IR(KBr, cm<sup>-1</sup>): ν=1655 (CO *s-cis*), 1628 (CO *s-trans*), 995(CH=CH); <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm): δ=7.197(d, 1H, α), 7.822(d, 1H, β), 6.910-7.034(m, 10H, Ar-H), 3.6726(s, 6H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=119.442(C<sub>2</sub>), 144.246(C<sub>1</sub>), 192.203(CO), 127.998(C<sub>1</sub>), 132.967(C<sub>2</sub>), 124.704(C<sub>3</sub>), 127.096(C<sub>4</sub>), 105.504(C<sub>5</sub>), 159.623(C<sub>6</sub>), 119.479(C<sub>7</sub>), 131.443(C<sub>8</sub>), 133.864(C<sub>9</sub>), 132.442(C<sub>10</sub>), 54.758(-OCH<sub>3</sub>), 127.596(C<sub>1</sub>), 127.339(C<sub>2,6</sub>), 114.099(C<sub>3,5</sub>), 158.996(C<sub>4</sub>), 55.993(-OCH<sub>3</sub>, Ph). Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>3</sub>: Anal. C, 81.79; H, 6.10. Found: C, 81.74; H, 5.98. MS: m/z=317[M<sup>+</sup>], 185, 158, 136, 131, 128, 93, 91, 77, 65.

**1j. (2E)-1-(6-Methoxy-2-naphthyl)-3-(4-methylphenyl)-2-propen-1-one.** Yield: 95%; m.p. 87-88°C; IR (KBr, cm<sup>-1</sup>): ν=1662 (CO *s-cis*), 1621 (CO *s-trans*), 998(CH=CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ=7.511(d, 1H, α), 7.763(d, 1H, β), 6.327-7.354(m, 10H, Ar-H), 3.394(s, 3H -OCH<sub>3</sub>), 2.424(s, 3H -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=119.199(C<sub>2</sub>), 144.362(C<sub>1</sub>), 187.902(CO),

128.546(C<sub>1</sub>), 132.465(C<sub>2</sub>), 125.096(C<sub>3</sub>), 127.433(C<sub>4</sub>), 105.843(C<sub>5</sub>), 159.965(C<sub>6</sub>), 119.597(C<sub>7</sub>), 131.009(C<sub>8</sub>), 133.663(C<sub>9</sub>), 132.006(C<sub>10</sub>), 54.421(-OCH<sub>3</sub>), 132.922(C<sub>1</sub>), 127.001(C<sub>2,6</sub>), 129.111(C<sub>3,5</sub>), 138.956(C<sub>4</sub>), 25.901(CH<sub>3</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>: C, 87.06; H, 6.49. Found: C, 86.98; H, 6.39. MS: m/z=301[M<sup>+</sup>], 286, 185, 158, 136, 128, 118, 102, 91, 65.

**1k. (2E)-1-(6-Methoxy-2-naphthyl)-3-(2-nitrophenyl)-2-propen-1-one.** Yield: 94%; m.p. 92-93°C; IR(KBr, cm<sup>-1</sup>): ν=1679(CO *s-cis*), 1646 (CO *s-trans*), 1015(CH=CII); <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm): δ=8.062(d, 1H, α), 8.142(d, 1H, β), 6.440-7.869(m, 10H, Ar-H), 3.295(s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR(CDCl<sub>3</sub>, ppm): δ=119.934(C<sub>2</sub>), 145.242(C<sub>1</sub>), 186.458(CO), 128.936(C<sub>1</sub>), 132.382(C<sub>2</sub>), 124.674(C<sub>3</sub>), 127.632(C<sub>4</sub>), 105.361(C<sub>5</sub>), 159.654(C<sub>6</sub>), 119.009(C<sub>7</sub>), 131.996(C<sub>8</sub>), 133.487(C<sub>9</sub>), 131.921(C<sub>10</sub>), 54.247(-OCH<sub>3</sub>), 130.098(C<sub>1</sub>), 146.095(C<sub>2</sub>), 120.909(C<sub>3</sub>), 128.899(C<sub>4</sub>), 134.799(C<sub>5</sub>), 127.338(C<sub>6</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>NO<sub>3</sub>: C, 87.06; H, 6.49; N, 4.34. Found: C, 86.92; H, 6.42; N, 4.29. MS: m/z=333[M<sup>+</sup>], 287, 158, 148, 136, 77, 65.

**1l. (2E)-1-(6-methoxy-2-naphthyl)-3-(3-nitrophenyl)-2-propen-1-one** Yield: 95%; m.p. 133-134°C; IR(KBr, cm<sup>-1</sup>): ν=1675 (CO *s-cis*), 1642 (CO *s-trans*), 1013(CH=CII); <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm): δ=8.114(d, 1H, α), 8.154(d, 1H, β), 7.051-8.021(m, 10H, Ar-H), 3.803(s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=119.843(C<sub>2</sub>), 145.314(C<sub>1</sub>), 191.025(CO), 128.091(C<sub>1</sub>), 133.455(C<sub>2</sub>), 124.761(C<sub>3</sub>), 127.091(C<sub>4</sub>), 105.601(C<sub>5</sub>), 159.765(C<sub>6</sub>), 120.009(C<sub>7</sub>), 131.109(C<sub>8</sub>), 133.554(C<sub>9</sub>), 131.334(C<sub>10</sub>), 56.297(-OCH<sub>3</sub>), 136.117(C<sub>1</sub>), 121.295(C<sub>2</sub>), 148.419(C<sub>3</sub>), 120.932(C<sub>4</sub>), 129.765(C<sub>5</sub>), 132.245(C<sub>6</sub>). Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>NO<sub>3</sub>: C, 87.06; H, 6.49; N, 4.34. Found: C, 86.90; H, 6.42; N, 4.25. MS: m/z=333[M<sup>+</sup>], 185, 287, 158, 148, 136, 128, 91, 77, 65.

**1m. (2E)-1-(6-methoxy-2-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one.** Yield: 95%; m.p. 148-149°C; IR(KBr, cm<sup>-1</sup>): ν=1677 (CO *s-cis*), 1640 (CO *s-trans*), 1018(CH=CH). <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm): δ=8.157(d, 1H, α), 8.206(d, 1H, β), 7.461-8.044(m, 10H, Ar-H), 3.630(s, 3H -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ=119.927(C<sub>2</sub>), 144.942(C<sub>1</sub>), 191.843(CO), 128.499(C<sub>1</sub>), 132.621(C<sub>2</sub>), 124.895(C<sub>3</sub>), 127.461(C<sub>4</sub>), 105.551(C<sub>5</sub>), 159.698(C<sub>6</sub>), 119.553(C<sub>7</sub>), 131.101(C<sub>8</sub>), 133.509(C<sub>9</sub>), 131.309(C<sub>10</sub>), 55.720(-OCH<sub>3</sub>), 141.397(C<sub>1</sub>), 127.309

( $C_{21.6}$ ), 120.832( $C_{3.7}$ ), 148.009( $C_{17}$ ), Anal. Calcd. for  $C_{20}H_{15}NO$ : C, 87.06; H, 6.49; N, 4.34 Found: C, 87.01; H, 6.45; 4.31. MS:  $m/z$ -333[M<sup>+</sup>], 185,287, 158, 148, 136, 131, 128, 91, 77, 65.

### CORRELATION ANALYSIS

Previous investigations of substituted styryl 4-methoxy 1-naphthyl chalcones includes the synthesis and identification of new compounds,<sup>28</sup> and the study of new catalysts for obtaining the chalcones. The spectral data of these types of chalcones have been investigated. Other investigators studied the tautomerism of some substituted carbonyl compounds by spectral data.<sup>29</sup> These papers and other communications were reported in earlier and recent publication.

It is well known from the literature that the chalcones of structure similar to those investigated here have a broad spectrum of biological activity<sup>30</sup> and to mentions only a few exhibited vasodilatory, antioxidant, antidiabetic, antimicrobial and antiviral activity. Therefore we considered it worthwhile to investigate the effects of substituents in this title of the compounds in *Scheme 1*. On the spectral features of the groups in investigated molecules which might be either directly or indirectly in molecular interactions in living organisms.

A large number of spectral data relating to substituted styryl naphthyl chalcones accumulated in the previous investigations, were correlated in the present work using a variety of LFER models, conventionally used for the study of structure – reactivity and structure-property relationships. It was assumed that it should be possible to find an adequate approach to study the transmission of substituent effects in the multi-substituted chalcones, considering that their aromaticity has been established. It was always initially attempted to use a simple Hammett Equations as presented in Eq. 1.a., but it was frequently more appropriate to use other approaches, like the Hammett-Taft (Extended Hammett Equation) DSP model, Eq. 1.b., and Swain-Lupton Eq. 1.c., which are usually given in the literature in their general form.<sup>31</sup>

$$\text{a. } s = \rho\sigma + s_0; \text{ b. } s = \rho_I\sigma_I + \rho_R\sigma_R + s_0; \text{ c. } s = fF + rR + s_0 \quad (1)$$

In these models, the author applied Eq. 1. a. and c. only for evaluation of electronic effects in this aromatic system and  $s$  is the measured spectral characteristics,  $\sigma_{\text{avg}}$ ,  $\sigma_I$ ,  $\sigma_R$ ,  $F$  and  $R$ <sup>32</sup> are substituent constants,  $\rho$ ,  $\rho_I$ ,  $\rho_R$ ,  $f$  and  $r$  are the corresponding calculated proportionality constants, which in a broad sense reflect the sensitivity of the spectral characteristics to substituent effects and  $s_0$  is the intercept. On certain occasions, when other model failed, combined multiparameter equations were applied, the method known to be used before and with the same precision as obtained here.

### Correlation analysis from infrared spectral data

From infrared spectra of all chalcones the carbonyl stretching frequencies ( $\text{cm}^{-1}$ ) of *s-cis* and *s-trans* conformers are assigned are presented in *Table 1* and the corresponding isomers are shown in (I). The infrared spectra were all recorded on the KBr disc in order to avoid the shoulder formation<sup>33</sup> on carbonyl doublets. The *s-cis* conformers exhibit higher frequencies than the *s-trans* conformers due

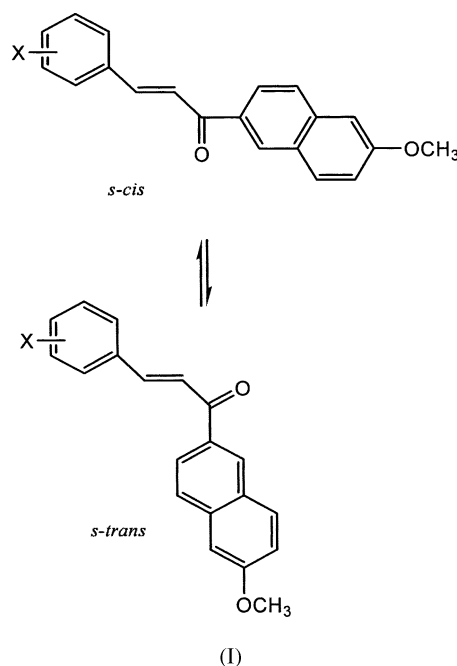


Table I. Infra red  $\nu\text{C}=\text{O}$  ( $\text{cm}^{-1}$ ) frequencies of *s-cis* and *s-trans* conformers,  $^1\text{H}$  chemical shifts (ppm) of  $\text{H}_\alpha$  and  $\text{H}_\beta$  protons and  $^{13}\text{C}$  chemical shifts (ppm) of  $\text{C}_\alpha$  and  $\text{C}_\beta$  carbons of in substituted styryl 6-methoxy 2-naphthyl ketones

No	$\nu\text{C}=\text{O}$ ( <i>s-cis</i> )	$\nu\text{C}=\text{O}$ ( <i>s-trans</i> )	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{C}_\alpha$	$\text{C}_\beta$
1a	1665	1626	7.612	7.766	119.460	144.628
1b	1667	1622	7.554	7.832	119.240	144.527
1c	1660	1627	7.234	7.672	118.770	144.224
1d	1674	1633	7.727	7.891	119.642	144.748
1e	1671	1628	7.981	8.112	119.527	144.664
1f	1664	1634	7.905	7.992	119.401	144.822
1g	1655	1624	7.167	7.737	118.475	144.059
1h	1657	1633	7.197	7.822	118.927	144.246
1i	1655	1628	7.511	7.974	119.442	144.362
1j	1662	1621	7.511	7.763	119.199	144.519
1k	1679	1646	8.062	8.142	119.934	145.242
1l	1675	1642	8.114	8.154	119.843	145.314
1m	1677	1640	8.157	8.209	119.927	144.942

to the bulkier naphthalene group causes greater strain and they enhance the higher absorption of carbonyl group of *s-cis* isomer than the *s-trans* isomer. These frequencies are separately analyzed through various Hammett sigma constants.

From the statistical analysis<sup>34</sup>, there is a fair correlation ( $r=0.917$ ) obtained with Hammett  $\sigma$  constants. And no significant correlation obtained with Hammett  $\sigma^+$ ,  $\sigma_p$ , and  $\sigma_R$  constants in *s-cis* isomers. The poor correlation is due to hindered rotation between styryl and the naphthyl moiety. In *s-trans* isomers  $\sigma_1$  constants gave a fair correlation ( $r=0.915$ ) with the carbonyl frequencies of the chalcones and other constants are failure for production of correlation. Because, the expected conjugation between the  $-\text{C}=\text{C}-$  and the  $\text{C}=\text{O}$  groups is missing in the *s-trans* isomers and the restriction of free rotation of the bulkier naphthyl group affects hyper conjugational resonance interaction shown in (II). Single parameter correlation is shown in Fig. 1 and 2. The generated correlation equations (2, 3) are;

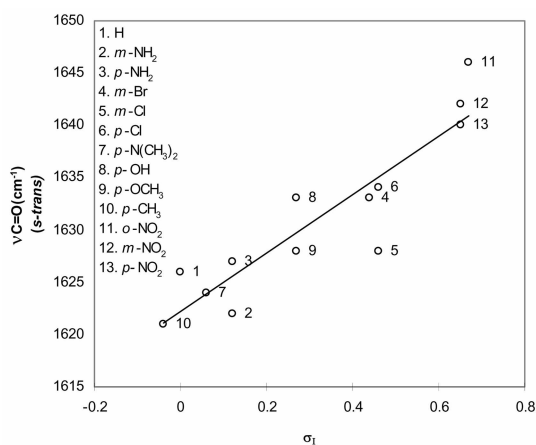
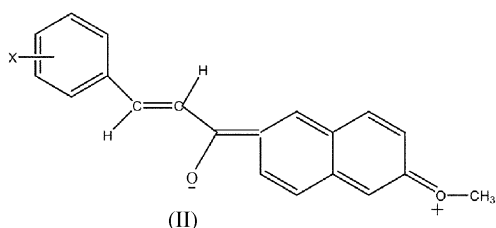


Fig. 1. Plot of  $\nu\text{C}=\text{O}$  (*s-cis*) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma_1$ .

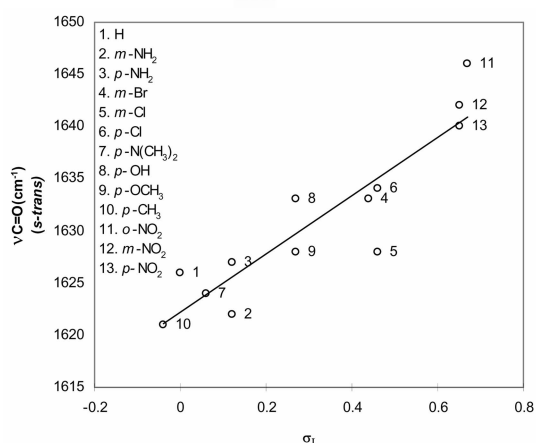


Fig. 2. Plot of  $\nu\text{C}=\text{O}$  (*s-trans*) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma_1$ .

$$\nu\text{C=O (s-cis) (cm}^{-1}\text{)} = (1665.42 \pm 0.13) + 1.69 \pm 0.10) \sigma_{\text{m}^{\text{r}}} \text{ (r = 0.917, n=13, s = 0.61) (2)}$$

$$\nu\text{C=O (s-trans) (cm}^{-1}\text{)} = 1624.22 \pm 0.10) + 2.17 \pm 0.31) \sigma_{\text{1,m}^{\text{r}}} \text{ (r = 0.915, n = 13, s = 0.20) (3)}$$

Similarly the collective correlation of  $\sigma_1$ ,  $\sigma_R$ , or F and R constants with these frequencies are failed to produce the correlation in *s-cis* carbonyl frequencies of these chalcones. But the correlation was also performed  $\sigma_1$  and  $\sigma_R$  constants with *s-trans* carbonyl frequencies of the all chalcones generated the correlation equation (4) is,

$$\nu\text{C=O(s-trans)(cm}^{-1}\text{)} = (1622.60 \pm 5.95) + (24.47 \pm 3.14) \sigma_{\text{1,m}^{\text{r}}} - 4.862 \pm 1.14) \sigma_{\text{R,m}^{\text{r}}} \text{ (R = 0.917, n = 13, P > 92\%)} \text{ (4)}$$

#### Correlation analysis from NMR spectral data <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectral signals of ethylenic protons in all chalcones investigated are assigned.<sup>35</sup> The ethylenic protons near the carbonyl group in Scheme 1 are termed as H<sub>α</sub> and those next to H<sub>α</sub> are termed as H<sub>β</sub>. The chemical shifts of H<sub>α</sub> protons are at higher field than those of H<sub>β</sub> protons in all chal-

cones. The ethylenic proton signals give an AB pattern and the β protons doublet in most cases is well separated from the signals of the aromatic protons. The chemical shifts of α, β protons are given in Table 1. The observation that H<sub>α</sub> protons appear at higher field than that of H<sub>β</sub> protons makes the subject very interesting. This may possibly due to the polarization of C=C double bond in the system being predominantly caused by the carbonyl group so as to make electron density greater at the α position than that of β position.

The results of statistical analysis are presented in Table 2. All the attempted correlations involving substituent parameters gave only positive ρ values. This shows normal substituent effects is operates in all the chalcones. The Chemical shifts observed for H<sub>α</sub> protons in the present investigation are correlated well (r=990) with Hammett sigma constants. The other constants σ<sup>-</sup>, σ<sub>1</sub>, and σ<sub>R</sub> of this proton chemical shifts and H<sub>β</sub> were satisfactorily. The correlation with σ<sub>R</sub> parameters is very poor in both the cases. This is due to these values are incapable of predicting chemical shifts individually due to the domination of cross conjugation between carbonyl group and methoxy group in naphthyl ring(II). The

Table 2. Results of statistical analysis of chemical shifts (ppm) of H<sub>α</sub> and H<sub>β</sub> protons and C<sub>α</sub> and C<sub>β</sub> carbons of in substituted styryl 6-methoxy 2-naphthyl ketones

Chemical shift correlated	Constants for correlation	r	I	ρ	s	n	Substituent in styryl part
H <sub>α</sub>	σ	0.990	7.614	0.655	0.10	13	H
	σ	0.971	7.734	0.408	0.12	13	m-NH <sub>2</sub>
σ <sub>1</sub>		0.901	7.314	1.125	0.21	13	p-NM <sub>2</sub>
	σ <sub>R</sub>	0.786	7.773	0.724	0.29	13	m-Br
H <sub>β</sub>	σ	0.935	7.091	0.307	0.09	13	m-Cl
	σ	0.900	7.955	0.176	0.15	13	p-Cl
	σ <sub>1</sub>	0.957	7.721	0.651	0.07	13	p-N(CH <sub>3</sub> ) <sub>2</sub>
	σ <sub>R</sub>	0.805	7.983	0.393	0.14	13	p-OH
C <sub>α</sub>	σ	0.971	119.296	0.814	0.15	13	p-OCH <sub>3</sub>
	σ	0.974	119.447	0.519	0.14	13	p-CH <sub>3</sub>
	σ <sub>1</sub>	0.869	118.949	1.318	0.32	13	o-NO <sub>2</sub>
	σ <sub>R</sub>	0.861	119.526	1.129	0.95	13	m-NO <sub>2</sub>
C <sub>β</sub>	σ	0.973	144.577	0.699	0.09	13	p-NO <sub>2</sub>
	σ <sup>-</sup>	0.962	144.902	0.432	0.15	13	
	σ <sub>1</sub>	0.887	144.265	1.172	0.23	13	
	σ <sub>R</sub>	0.762	144.741	0.738	0.32	13	

Where r = Correlation coefficient, I = Intercept, ρ = Slope, s = Standard deviation and n = Number of substituents correlated.

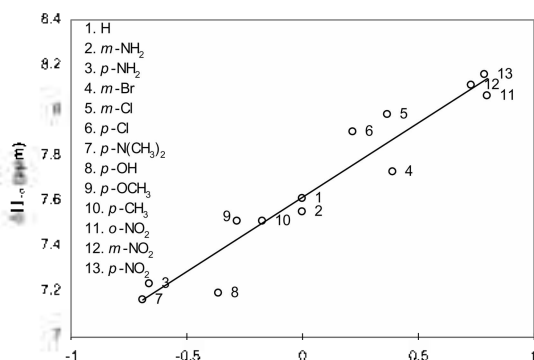


Fig. 3. Plot of  $\delta H-\alpha$  (ppm) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma$ .

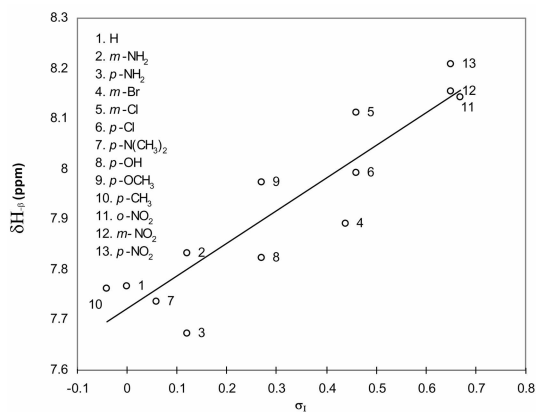


Fig. 4. Plot of  $\delta H-\beta$  (ppm) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma$ .

multiple correlations involving either  $\sigma$  and  $\sigma_R$  or  $F$  and  $R$  values for these ketones are satisfactory that in most cases the multiple correlations are successful through the equations (5-8). Some of the single parameter correlations are shown in Fig. 3 and 4.

$$H_{\alpha(\text{ppm})} = (7.423 \pm 0.11) + (0.038 \pm 0.01) \sigma_{1, \text{avg}} + (0.052 \pm 0.001) \sigma_{R, m, i} \quad (R=0.926, n=13, P>90\%) \quad (5)$$

$$H_{\alpha(\text{ppm})} = (7.679 \pm 0.10) + (0.559 \pm 0.20) F + (0.593 \pm 0.131) R \quad (R=0.939, n=13, P>90\%) \quad (6)$$

$$H_{\beta(\text{ppm})} = (7.423 \pm 0.3) + (0.558 \pm 0.08) \sigma_{1, m, p} + (0.116 \pm 0.07) \sigma_{R, m, i} \quad (R=0.973, n=13, P>90\%) \quad (7)$$

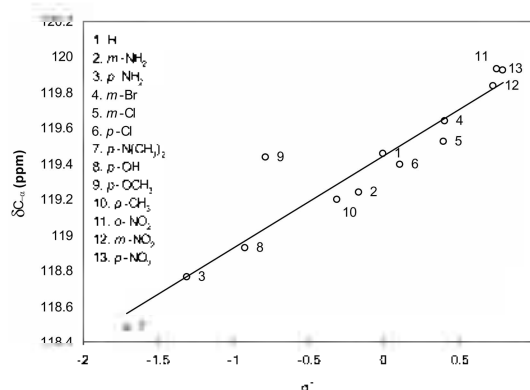


Fig. 5. Plot of  $\delta C-\alpha$  (ppm) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma$ .

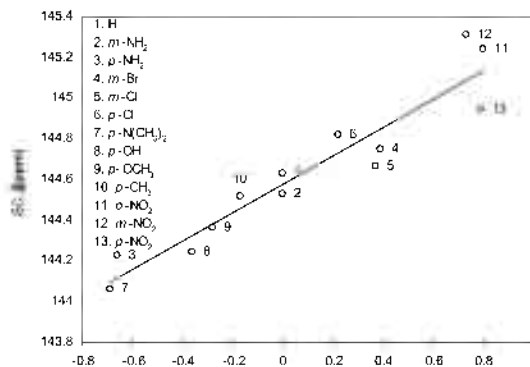


Fig. 6. Plot of  $\delta C-\beta$  (ppm) of substituted styryl 6-methoxy-2-naphthyl ketones versus  $\sigma$ .

$$H_{\beta(\text{ppm})} = (7.786 \pm 0.05) + (0.559 \pm 0.11) F + (0.121 \pm 0.07) R \quad (R=0.961, n=13, P>90\%) \quad (8)$$

### $^{13}\text{C}$ NMR Spectra:

From  $^{13}\text{C}$  NMR spectra the observed  $^{13}\text{C}$  Chemical shifts of  $C_{\alpha}$  and the  $C_{\beta}$  carbons are presented in Table 1. The ethylenic carbons near the carbonyl group in Scheme 1 are termed as  $C_{\alpha}$  and those next to  $C_{\alpha}$  are termed as  $C_{\beta}$ . These chemical shifts are correlated<sup>16</sup> with various Hammett substituent constants. The statistical analysis results are presented in Table 2. There is a fair degree of correlation obtained for  $C_{\alpha}$  and the  $C_{\beta}$  carbon chemical shifts with Hammett  $\sigma$  and  $\sigma^1$  constants. The degree of transmission of electronic effects is found to be higher with  $C_{\alpha}$  carbon ( $r=0.974$ ) than  $C_{\beta}$  carbon.



The good linear fitness are shown in Fig. 5 and 6. Correlations of  $\sigma_i$  and  $\sigma_R$  constants with these carbon chemical shifts are failed. The resonance and inductive effects of substituents are not capable for predicting the substituent effects individually on the  $\pi$  system of all chalcones. Uniformly  $\sigma_i$  and  $\sigma_R$  parameters or F and R values are adequately explain the substituent effects in all chalcones are evidenced from the correlation Eqs. (9-12) are,

$$C_{\alpha(ppm)} = (119.193 \pm 0.131) + (0.888 \pm 0.296) \sigma_{1,meta} + (0.768 \pm 0.252) \sigma_{R,ortho} \quad (R=0.941, n=13, P>90\%) \quad (9)$$

$$C_{\alpha(ppm)} = (119.460 \pm 0.139) + (5.342 \pm 0.276) F + (0.834 \pm 0.174) R \quad (R=0.960, n=13, P>90\%) \quad (10)$$

$$C_{\beta(ppm)} = (144.373 \pm 0.135) + (0.982 \pm 0.304) \sigma_{1,meta} + (0.339 \pm 0.260) \sigma_{R,ortho} \quad (R=0.906, n=13, P>90\%) \quad (11)$$

$$C_{\beta(ppm)} = (144.678 \pm 0.118) + (0.541 \pm 0.11) F + (0.677 \pm 0.141) R \quad (R=0.965, n=13, P>90\%) \quad (12)$$

## CONCLUSIONS

This synthetic methodology is very efficient and selective protocol for crossed-aldol condensation of 6-methoxy-2-naphthyl ketones and aldehydes to produced high yield of 6-methoxy-2-naphthyl chalcones in the presence of a reusable and environmentally beginning catalyst silica-sulphuric acid. Operative simplicity, easy procedure, better yield including washing the mixture followed by evaporation of the solvent are another advantages of this method. In correlation analyses infrared spectral data, the  $\sigma$  constants produce a fair correlation with carbonyl absorption frequencies in both conformers of all chalcones. Nuclear magnetic resonance spectral data correlation,  $H_\alpha$  chemical shifts were correlated with  $\sigma$  constants significant than  $H_\beta$ . Other Hammett constants produce a fair correlation except  $\sigma_R$  constant. There is satisfactory correlation obtained in the correlation of  $C_\alpha$  and  $C_\beta$  chemical shifts with Hammett  $\sigma$  and  $\sigma^-$  substituent constants.

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