

# **APPENDICES**

**APPENDIX 1: TABLES A1 – A11**

**Table A-1: Values of Kinetic Parameter  $k_{\text{obs}}$ ,  $\epsilon_{\text{app}}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of  $\text{CH}_3\text{NH}_2$  buffer.<sup>a</sup>**

$\text{pH} = 9.80 \pm 0.40$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^2 k_{\text{obs}}^{\text{c}}$<br>( $\text{s}^{-1}$ ) | $\epsilon_{\text{app}}^{\text{d}}$<br>( $\text{M}^{-1}\text{cm}^{-1}$ ) | $A_o^{\text{e}}$  | $10^2 k_{\text{obscald}}^{\text{f}}$<br>( $\text{s}^{-1}$ ) | $10^2 k_{\text{obscald}}^{\text{g}}$<br>( $\text{s}^{-1}$ ) |
|--------------------------|-----------------|---------------------------------------------------------|-------------------------------------------------------------------------|-------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| 0.02                     | 8.79            | $3.18 \pm 0.008$                                        | $18488 \pm 24$                                                          | $0.134 \pm 0.002$ | 3.14                                                        | 3.04                                                        |
| 0.03                     | 9.85            | $4.96 \pm 0.07$                                         | $18612 \pm 134$                                                         | $0.132 \pm 0.009$ | 5.01                                                        | 4.98                                                        |
| 0.04                     | 9.95            | $6.96 \pm 0.06$                                         | $18132 \pm 114$                                                         | $0.156 \pm 0.007$ | 6.90                                                        | 6.92                                                        |
| 0.05                     | 9.92            | $8.37 \pm 0.9$                                          | $17267 \pm 133$                                                         | $0.208 \pm 0.008$ | 8.81                                                        | 8.87                                                        |
| 0.06                     | 9.95            | $11.2 \pm 0.1$                                          | $18477 \pm 211$                                                         | $0.119 \pm 0.013$ | 10.7                                                        | 10.8                                                        |
| 0.07                     | 9.96            | $13.0 \pm 0.2$                                          | $18677 \pm 329$                                                         | $0.119 \pm 0.020$ | 12.7                                                        | 12.8                                                        |
| 0.08                     | 9.97            | $14.2 \pm 0.2$                                          | $18277 \pm 392$                                                         | $0.143 \pm 0.024$ | 14.7                                                        | 14.7                                                        |
| 0.10                     | 9.97            | $18.8 \pm 0.1$                                          | $18228 \pm 177$                                                         | $0.152 \pm 0.011$ | 18.7                                                        | 18.6                                                        |

$\text{pH} = 10.15 \pm 0.05$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^2 k_{\text{obs}}^{\text{c}}$<br>( $\text{s}^{-1}$ ) | $\epsilon_{\text{app}}^{\text{d}}$<br>( $\text{M}^{-1}\text{cm}^{-1}$ ) | $A_o^{\text{e}}$  | $10^2 k_{\text{obscald}}^{\text{f}}$<br>( $\text{s}^{-1}$ ) | $10^2 k_{\text{obscald}}^{\text{g}}$<br>( $\text{s}^{-1}$ ) |
|--------------------------|-----------------|---------------------------------------------------------|-------------------------------------------------------------------------|-------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| 0.02                     | 10.03           | $4.08 \pm 0.04$                                         | $18232 \pm 97$                                                          | $0.155 \pm 0.006$ | 4.52                                                        | 4.04                                                        |
| 0.03                     | 10.12           | $6.50 \pm 0.05$                                         | $18411 \pm 97$                                                          | $0.153 \pm 0.006$ | 6.77                                                        | 6.5                                                         |
| 0.04                     | 10.15           | $8.84 \pm 0.08$                                         | $17691 \pm 138$                                                         | $0.176 \pm 0.009$ | 9.03                                                        | 8.95                                                        |
| 0.05                     | 10.17           | $11.3 \pm 0.04$                                         | $18880 \pm 61$                                                          | $0.127 \pm 0.004$ | 11.3                                                        | 11.4                                                        |
| 0.06                     | 10.17           | $13.9 \pm 0.08$                                         | $17751 \pm 119$                                                         | $0.198 \pm 0.008$ | 13.5                                                        | 13.9                                                        |
| 0.07                     | 10.17           | $16.4 \pm 0.1$                                          | $18519 \pm 238$                                                         | $0.156 \pm 0.015$ | 15.8                                                        | 16.3                                                        |
| 0.08                     | 10.18           | $19.0 \pm 0.09$                                         | $18929 \pm 145$                                                         | $0.133 \pm 0.009$ | 18.1                                                        | 18.8                                                        |
| 0.10                     | 10.19           | $23.5 \pm 0.2$                                          | $18300 \pm 355$                                                         | $0.170 \pm 0.022$ | 22.6                                                        | 23.7                                                        |

$\text{pH} = 10.35 \pm 0.05$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^2 k_{\text{obs}}^{\text{c}}$<br>( $\text{s}^{-1}$ ) | $\epsilon_{\text{app}}^{\text{d}}$<br>( $\text{M}^{-1}\text{cm}^{-1}$ ) | $A_o^{\text{e}}$  | $10^2 k_{\text{obscald}}^{\text{f}}$<br>( $\text{s}^{-1}$ ) | $10^2 k_{\text{obscald}}^{\text{g}}$<br>( $\text{s}^{-1}$ ) |
|--------------------------|-----------------|---------------------------------------------------------|-------------------------------------------------------------------------|-------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| 0.02                     | 10.25           | $5.55 \pm 0.06$                                         | $17500 \pm 116$                                                         | $0.197 \pm 0.007$ | 6.11                                                        | 5.08                                                        |
| 0.03                     | 10.32           | $8.47 \pm 0.07$                                         | $17188 \pm 114$                                                         | $0.226 \pm 0.007$ | 9.17                                                        | 8.61                                                        |
| 0.04                     | 10.35           | $12.0 \pm 0.05$                                         | $17961 \pm 84$                                                          | $0.195 \pm 0.005$ | 12.2                                                        | 12.1                                                        |
| 0.05                     | 10.36           | $15.2 \pm 0.08$                                         | $18095 \pm 132$                                                         | $0.178 \pm 0.008$ | 15.3                                                        | 15.7                                                        |
| 0.06                     | 10.38           | $19.0 \pm 0.2$                                          | $19152 \pm 438$                                                         | $0.114 \pm 0.027$ | 18.3                                                        | 19.2                                                        |
| 0.07                     | 10.38           | $23.4 \pm 0.4$                                          | $17446 \pm 662$                                                         | $0.226 \pm 0.040$ | 21.4                                                        | 22.8                                                        |
| 0.08                     | 10.39           | $26.2 \pm 0.5$                                          | $16641 \pm 725$                                                         | $0.297 \pm 0.044$ | 24.5                                                        | 26.3                                                        |

Table A1, Continued

pH = 10.56 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>2</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>2</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) | 10 <sup>2</sup> k <sub>obscald</sub> <sup>g</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 0.020                    | 10.45           | 7.18 ± 0.2                                                          | 18113 ± 343                                                          | 0.174 ± 0.023               | 7.70                                                                    | 6.78                                                                    |
| 0.025                    | 10.53           | 9.25 ± 0.03                                                         | 17716 ± 53                                                           | 0.185 ± 0.003               | 9.62                                                                    | 8.96                                                                    |
| 0.030                    | 10.54           | 11.2 ± 0.06                                                         | 17304 ± 91                                                           | 0.218 ± 0.006               | 11.5                                                                    | 11.1                                                                    |
| 0.035                    | 10.56           | 13.3 ± 0.06                                                         | 17380 ± 87                                                           | 0.214 ± 0.006               | 13.5                                                                    | 13.3                                                                    |
| 0.040                    | 10.56           | 15.1 ± 0.06                                                         | 17267 ± 86                                                           | 0.209 ± 0.005               | 14.4                                                                    | 15.5                                                                    |
| 0.044                    | 10.57           | 17.1 ± 0.1                                                          | 16336 ± 122                                                          | 0.281 ± 0.008               | 16.9                                                                    | 17.2                                                                    |
| 0.049                    | 10.58           | 19.3 ± 0.2                                                          | 17113 ± 211                                                          | 0.248 ± 0.013               | 18.9                                                                    | 19.4                                                                    |
| 0.054                    | 10.57           | 20.2 ± 0.3                                                          | 15292 ± 519                                                          | 0.362 ± 0.032               | 20.8                                                                    | 21.6                                                                    |
| 0.060                    | 10.60           | 24.8 ± 0.5                                                          | 17100 ± 693                                                          | 0.236 ± 0.042               | 23.1                                                                    | 24.2                                                                    |
| 0.700                    | 10.61           | 29.3 ± 0.7                                                          | 18014 ± 1025                                                         | 0.180 ± 0.062               | 26.9                                                                    | 28.6                                                                    |

<sup>a</sup> [26<sub>0</sub>] = 6 x 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = methylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>g</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub> with k<sub>o</sub> = 0

**Table A-2 : Values of Kinetic Parameter k<sub>obs</sub>, ɛ<sub>app</sub> and A<sub>o</sub> Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> buffer.<sup>a</sup>**

pH = 8.28 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) | 10 <sup>3</sup> k <sub>obscald</sub> <sup>g</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.35            | 2.70 ± 0.04                                                         | 15291 ± 76                                                           | 0.089 ± 0.004               | 2.69                                                                    | 2.76                                                                    |
| 0.10                     | 8.34            | 5.58 ± 0.07                                                         | 15225 ± 66                                                           | 0.105 ± 0.003               | 5.49                                                                    | 5.52                                                                    |
| 0.20                     | 8.30            | 11.0 ± 0.2                                                          | 14836 ± 76                                                           | 0.145 ± 0.004               | 11.0                                                                    | 11.0                                                                    |
| 0.30                     | 8.23            | 16.5 ± 0.02                                                         | 14871 ± 67                                                           | 0.181 ± 0.004               | 16.7                                                                    | 16.6                                                                    |
| 0.35                     | 8.20            | 19.7 ± 0.8                                                          | 14994 ± 251                                                          | 0.177 ± 0.016               | 19.5                                                                    | 19.3                                                                    |

Table A2, Continued

pH = 8.51 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.57            | 3.84 ± 0.03                                                         | 16236 ± 40                                                           | 0.099 ± 0.002               | 4.12                                                                    |
| 0.10                     | 8.56            | 7.57 ± 0.1                                                          | 16327 ± 64                                                           | 0.106 ± 0.004               | 7.59                                                                    |
| 0.20                     | 8.50            | 15.1 ± 0.2                                                          | 16161 ± 78                                                           | 0.122 ± 0.005               | 14.50                                                                   |
| 0.30                     | 8.46            | 21.6 ± 0.2                                                          | 16044 ± 76                                                           | 0.170 ± 0.005               | 21.5                                                                    |
| 0.35                     | 8.44            | 24.6 ± 0.3                                                          | 16004 ± 94                                                           | 0.188 ± 0.006               | 25.0                                                                    |

pH = 8.72 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.77            | 5.21 ± 0.07                                                         | 17364 ± 58                                                           | 0.095 ± 0.003               | 5.42                                                                    |
| 0.10                     | 8.77            | 10.2 ± 0.1                                                          | 17255 ± 74                                                           | 0.119 ± 0.004               | 10.1                                                                    |
| 0.20                     | 8.73            | 19.6 ± 0.2                                                          | 16816 ± 92                                                           | 0.131 ± 0.006               | 19.4                                                                    |
| 0.30                     | 8.68            | 28.5 ± 0.3                                                          | 17063 ± 76                                                           | 0.173 ± 0.005               | 28.7                                                                    |
| 0.35                     | 8.64            | 33.3 ± 0.3                                                          | 16840 ± 97                                                           | 0.195 ± 0.006               | 33.3                                                                    |

pH = 8.91 ± 0.03

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.92            | 6.67 ± 0.07                                                         | 18293 ± 62                                                           | 0.100 ± 0.003               | 7.03                                                                    |
| 0.10                     | 8.94            | 13.3 ± 0.1                                                          | 18238 ± 69                                                           | 0.111 ± 0.004               | 13.00                                                                   |
| 0.20                     | 8.91            | 25.2 ± 0.3                                                          | 17820 ± 111                                                          | 0.163 ± 0.007               | 24.9                                                                    |
| 0.30                     | 8.91            | 36.7 ± 0.3                                                          | 17574 ± 73                                                           | 0.196 ± 0.005               | 37.0                                                                    |
| 0.35                     | 8.86            | 42.8 ± 0.4                                                          | 17234 ± 114                                                          | 0.193 ± 0.008               | 42.8                                                                    |

pH = 9.31 ± 0.01

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.29            | 7.42 ± 0.2                                                          | 19380 ± 165                                                          | 0.083 ± 0.009               | 7.69                                                                    |
| 0.08                     | 9.32            | 14.3 ± 0.1                                                          | 19125 ± 63                                                           | 0.081 ± 0.004               | 14.3                                                                    |
| 0.12                     | 9.31            | 21.3 ± 0.2                                                          | 19123 ± 67                                                           | 0.089 ± 0.004               | 20.9                                                                    |
| 0.16                     | 9.31            | 27.7 ± 0.4                                                          | 18896 ± 120                                                          | 0.094 ± 0.008               | 27.5                                                                    |
| 0.20                     | 9.31            | 33.7 ± 0.6                                                          | 18431 ± 159                                                          | 0.110 ± 0.010               | 34.1                                                                    |

<sup>a</sup> [26]<sub>0</sub> = 6 x 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = benzylamine buffer concentration.<sup>b</sup> pH at t = ∞ (reaction finished)<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub><sup>d</sup> ɛ apparent<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from  $k_{obs} = k_o + k_{1obs}$  [Buf]<sub>T</sub>

<sup>g</sup> Calculated from  $k_{obs} = k_o + k_{1obs}$  [Buf]<sub>T</sub> with  $k_o = 0$

**Table A-3: Values of Kinetic Parameter  $k_{obs}$ ,  $\epsilon_{app}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of  $C_6H_5CH_2NH_2$  buffer.<sup>a</sup>**

pH = 8.37 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|
| 0.05                     | 8.46            | $3.31 \pm 0.03$                        | $16277 \pm 50$                                            | $0.021 \pm 0.003$ | 3.09                                       |
| 0.10                     | 8.42            | $5.84 \pm 0.2$                         | $16088 \pm 197$                                           | $0.042 \pm 0.010$ | 6.09                                       |
| 0.20                     | 8.39            | $12.1 \pm 0.7$                         | $16672 \pm 361$                                           | $0.052 \pm 0.021$ | 12.1                                       |
| 0.30                     | 8.31            | $17.9 \pm 0.7$                         | $15781 \pm 279$                                           | $0.050 \pm 0.017$ | 18.1                                       |
| 0.35                     | 8.29            | $21.2 \pm 0.3$                         | $15645 \pm 93$                                            | $0.059 \pm 0.006$ | 21.0                                       |

pH = 8.46 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|
| 0.05                     | 8.63            | $3.81 \pm 0.03$                        | $16399 \pm 42$                                            | $0.029 \pm 0.002$ | 3.76                                       |
| 0.10                     | 8.52            | $6.64 \pm 0.4$                         | $16684 \pm 268$                                           | $0.049 \pm 0.015$ | 7.31                                       |
| 0.20                     | 8.45            | $15.5 \pm 0.4$                         | $16645 \pm 201$                                           | $0.018 \pm 0.012$ | 14.4                                       |
| 0.30                     | 8.40            | $21.2 \pm 0.4$                         | $16274 \pm 142$                                           | $0.053 \pm 0.009$ | 21.5                                       |
| 0.35                     | 8.37            | $24.8 \pm 0.4$                         | $16187 \pm 131$                                           | $0.059 \pm 0.008$ | 25.0                                       |

pH = 8.65 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{obscald}^f$<br>(s <sup>-1</sup> ) | $10^3 k_{obscald}^g$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|--------------------------------------------|
| 0.05                     | 8.73            | $4.88 \pm 0.07$                        | $17388 \pm 73$                                            | $0.079 \pm 0.004$ | 4.64                                       | 4.72                                       |
| 0.10                     | 8.71            | $8.54 \pm 0.5$                         | $18003 \pm 363$                                           | $0.092 \pm 0.019$ | 9.41                                       | 9.43                                       |
| 0.20                     | 8.648           | $19.9 \pm 0.2$                         | $17286 \pm 64$                                            | $0.076 \pm 0.004$ | 18.9                                       | 18.9                                       |
| 0.30                     | 8.59            | $28.5 \pm 0.2$                         | $17038 \pm 65$                                            | $0.091 \pm 0.004$ | 28.5                                       | 28.3                                       |
| 0.35                     | 8.59            | $32.9 \pm 0.4$                         | $17254 \pm 103$                                           | $0.093 \pm 0.007$ | 33.2                                       | 33.0                                       |

Table A3, Continued

pH = 8.86 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.91            | 6.53 ± 0.05                                                         | 18361 ± 45                                                           | 0.076 ± 0.003               | 7.01                                                                    |
| 0.10                     | 8.90            | 13.4 ± 0.1                                                          | 18414 ± 58                                                           | 0.078 ± 0.004               | 13.0                                                                    |
| 0.20                     | 8.88            | 24.8 ± 0.5                                                          | 18042 ± 201                                                          | 0.105 ± 0.012               | 24.9                                                                    |
| 0.25                     | 8.83            | 37.9 ± 0.8                                                          | 18305 ± 203                                                          | 0.079 ± 0.014               | 36.8                                                                    |
| 0.30                     | 8.80            | 41.9 ± 0.4                                                          | 17783 ± 101                                                          | 0.112 ± 0.007               | 42.8                                                                    |

pH = 9.25 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.24            | 7.39 ± 0.06                                                         | 19435 ± 58                                                           | 0.080 ± 0.003               | 7.71                                                                    |
| 0.08                     | 9.28            | 14.9 ± 0.1                                                          | 19469 ± 61                                                           | 0.969 ± 0.004               | 14.90                                                                   |
| 0.12                     | 9.26            | 22.3 ± 0.3                                                          | 19705 ± 125                                                          | 0.065 ± 0.008               | 22.1                                                                    |
| 0.16                     | 9.24            | 30.0 ± 0.2                                                          | 19113 ± 59                                                           | 0.101 ± 0.004               | 29.2                                                                    |
| 0.20                     | 9.24            | 35.7 ± 0.2                                                          | 18925 ± 67                                                           | 0.104 ± 0.004               | 36.4                                                                    |

<sup>a</sup> [26]<sub>0</sub> = 6 x 10<sup>-5</sup> M, μ = 0.3 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = benzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>g</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub> with k<sub>o</sub> = 0

**Table A-4 : Values of Kinetic Parameter k<sub>obs</sub>, ɛ<sub>app</sub> and A<sub>o</sub> Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub> buffer.<sup>a</sup>**

pH = 10.05 ± 0.10

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) | 10 <sup>3</sup> k <sub>obscald</sub> <sup>g</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 0.010                    | 8.93            | 1.84 ± 0.03                                                         | 19938 ± 127                                                          | 0.048 ± 0.007               | 2.14                                                                    | 1.76                                                                    |
| 0.015                    | 9.95            | 2.86 ± 0.03                                                         | 19694 ± 95                                                           | 0.090 ± 0.006               | 3.21                                                                    | 3                                                                       |
| 0.020                    | 10.03           | 4.18 ± 0.03                                                         | 19854 ± 88                                                           | 0.068 ± 0.006               | 4.28                                                                    | 4.22                                                                    |
| 0.025                    | 10.11           | 5.48 ± 0.05                                                         | 19476 ± 124                                                          | 0.044 ± 0.008               | 5.36                                                                    | 5.45                                                                    |
| 0.030                    | 10.10           | 6.73 ± 0.07                                                         | 19779 ± 136                                                          | 0.077 ± 0.009               | 6.43                                                                    | 6.68                                                                    |
| 0.035                    | 10.12           | 8.09 ± 0.05                                                         | 20108 ± 107                                                          | 0.032 ± 0.007               | 7.50                                                                    | 7.91                                                                    |
| 0.040                    | 10.12           | 9.06 ± 0.08                                                         | 19611 ± 136                                                          | 0.075 ± 0.009               | 8.57                                                                    | 9.14                                                                    |
| 0.045                    | 10.12           | 10.3 ± 0.09                                                         | 19141 ± 157                                                          | 0.091 ± 0.010               | 9.64                                                                    | 10.4                                                                    |

Table A4, Continued

 $\text{pH} = 10.20 \pm 0.08$ 

| $[\text{Am}]_T$<br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}$ <sup>c</sup><br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}$ <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o$ <sup>e</sup> | $10^3 k_{\text{obscald}}$ <sup>f</sup><br>(s <sup>-1</sup> ) | $10^3 k_{\text{obscald}}$ <sup>g</sup><br>(s <sup>-1</sup> ) |
|------------------------|-----------------|----------------------------------------------------------|-----------------------------------------------------------------------------|--------------------|--------------------------------------------------------------|--------------------------------------------------------------|
| 0.010                  | 10.04           | $2.66 \pm 0.04$                                          | $19683 \pm 100$                                                             | $0.094 \pm 0.006$  | 2.67                                                         | 2.31                                                         |
| 0.015                  | 10.14           | $3.51 \pm 0.1$                                           | $19592 \pm 294$                                                             | $0.081 \pm 0.019$  | 4.00                                                         | 3.78                                                         |
| 0.020                  | 10.17           | $5.12 \pm 0.03$                                          | $20024 \pm 68$                                                              | $0.059 \pm 0.04$   | 5.33                                                         | 5.25                                                         |
| 0.250                  | 10.221          | $6.69 \pm 0.06$                                          | $20161 \pm 100$                                                             | $0.064 \pm 0.007$  | 6.67                                                         | 6.72                                                         |
| 0.030                  | 0.251           | $8.18 \pm 0.06$                                          | $19706 \pm 122$                                                             | $0.070 \pm 0.008$  | 8.00                                                         | 8.19                                                         |
| 0.035                  | 0.24            | $9.61 \pm 0.1$                                           | $19659 \pm 201$                                                             | $0.104 \pm 0.013$  | 9.33                                                         | 9.66                                                         |
| 0.040                  | 10.26           | $11.3 \pm 0.2$                                           | $19363 \pm 291$                                                             | $0.111 \pm 0.018$  | 10.7                                                         | 11.3                                                         |
| 0.045                  | 10.28           | $12.6 \pm 0.2$                                           | $20429 \pm 309$                                                             | $0.017 \pm 0.019$  | 12.0                                                         | 12.6                                                         |

 $\text{pH} = 10.32 \pm 0.10$ 

| $[\text{Am}]_T$<br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}$ <sup>c</sup><br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}$ <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o$ <sup>e</sup> | $10^3 k_{\text{obscald}}$ <sup>f</sup><br>(s <sup>-1</sup> ) | $10^3 k_{\text{obscald}}$ <sup>g</sup><br>(s <sup>-1</sup> ) |
|------------------------|-----------------|----------------------------------------------------------|-----------------------------------------------------------------------------|--------------------|--------------------------------------------------------------|--------------------------------------------------------------|
| 0.010                  | 10.15           | $3.11 \pm 0.03$                                          | $20036 \pm 81$                                                              | $0.069 \pm 0.005$  | 3.51                                                         | 3.04                                                         |
| 0.015                  | 10.25           | $5.00 \pm 0.04$                                          | $20036 \pm 99$                                                              | $0.067 \pm 0.006$  | 5.27                                                         | 5.06                                                         |
| 0.020                  | 10.37           | $7.20 \pm 0.1$                                           | $20023 \pm 221$                                                             | $0.074 \pm 0.014$  | 7.02                                                         | 7.08                                                         |
| 0.025                  | 10.39           | $8.91 \pm 0.08$                                          | $19307 \pm 161$                                                             | $0.093 \pm 0.010$  | 8.78                                                         | 9.10                                                         |
| 0.030                  | 10.33           | $11.0 \pm 0.1$                                           | $19654 \pm 206$                                                             | $0.074 \pm 0.013$  | 10.5                                                         | 11.1                                                         |
| 0.035                  | 10.43           | $13.3 \pm 0.2$                                           | $20540 \pm 313$                                                             | $0.024 \pm 0.020$  | 12.3                                                         | 13.1                                                         |

 $\text{pH} = 10.66 \pm 0.08$ 

| $[\text{Am}]_T$<br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}$ <sup>c</sup><br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}$ <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o$ <sup>e</sup> | $10^3 k_{\text{obscald}}$ <sup>f</sup><br>(s <sup>-1</sup> ) | $10^3 k_{\text{obscald}}$ <sup>g</sup><br>(s <sup>-1</sup> ) |
|------------------------|-----------------|----------------------------------------------------------|-----------------------------------------------------------------------------|--------------------|--------------------------------------------------------------|--------------------------------------------------------------|
| 0.010                  | 10.55           | $4.85 \pm 0.06$                                          | $19926 \pm 155$                                                             | $0.045 \pm 0.010$  | 5.24                                                         | 4.79                                                         |
| 0.150                  | 10.57           | $7.95 \pm 0.06$                                          | $19841 \pm 108$                                                             | $0.048 \pm 0.007$  | 7.87                                                         | 7.66                                                         |
| 0.020                  | 10.72           | $10.3 \pm 0.09$                                          | $19411 \pm 158$                                                             | $0.073 \pm 0.010$  | 10.5                                                         | 10.5                                                         |
| 0.025                  | 10.72           | $13.1 \pm 0.1$                                           | $20183 \pm 277$                                                             | $0.024 \pm 0.017$  | 13.1                                                         | 13.4                                                         |
| 0.030                  | 10.72           | $16.1 \pm 0.1$                                           | $19219 \pm 163$                                                             | $0.089 \pm 0.010$  | 15.7                                                         | 16.3                                                         |
| 0.035                  | 10.68           | $19.5 \pm 0.2$                                           | $19175 \pm 245$                                                             | $0.102 \pm 0.015$  | 18.4                                                         | 19.1                                                         |

<sup>a</sup>  $[26_0] = 6 \times 10^{-5}$  M,  $\mu = 0.4$  M, T = 30°C,  $\lambda = 400$  nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and  $[\text{Am}]_T = N,N$ -dimethylamine buffer concentration.

<sup>b</sup> pH at t =  $\infty$  (reaction finished)

<sup>c</sup>  $k_{\text{obs}} = k_o + k_{\text{1obs}} [\text{Buf}]_T$

<sup>d</sup>  $\epsilon$  apparent

<sup>e</sup>  $A_o$  = initial absorbance

<sup>f</sup> Calculated from  $k_{\text{obs}} = k_o + k_{\text{1obs}} [\text{Buf}]_T$

<sup>g</sup> Calculated from  $k_{\text{obs}} = k_o + k_{\text{1obs}} [\text{Buf}]_T$  with  $k_o = 0$

**Table A-5: Values of Kinetic Parameter  $k_{\text{obs}}$ ,  $\epsilon_{\text{app}}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2$  buffer.<sup>a</sup>**

pH = 10.34 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^{\text{c}}$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^{\text{d}}$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^{\text{e}}$ | $10^3 k_{\text{obs} \text{calcd}}^{\text{f}}$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|--------------------------------------------------------|---------------------------------------------------------------------------|------------------|---------------------------------------------------------------------|
| 0.05                     | 10.39           | 1.02 ± 0.02                                            | 20224 ± 96                                                                | 0.074 ± 0.005    | 1.07                                                                |
| 0.10                     | 10.38           | 2.06 ± 0.03                                            | 20091 ± 86                                                                | 0.067 ± 0.005    | 2.05                                                                |
| 0.20                     | 10.36           | 4.01 ± 0.05                                            | 19956 ± 71                                                                | 0.082 ± 0.004    | 4.02                                                                |
| 0.30                     | 10.35           | 6.09 ± 0.04                                            | 19948 ± 47                                                                | 0.076 ± 0.003    | 5.99                                                                |
| 0.40                     | 10.31           | 8.01 ± 0.06                                            | 19853 ± 83                                                                | 0.103 ± 0.003    | 7.96                                                                |
| 0.45                     | 10.27           | 8.84 ± 0.07                                            | 19707 ± 51                                                                | 0.114 ± 0.003    | 8.94                                                                |

pH = 10.44 ± 0.04

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^{\text{c}}$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^{\text{d}}$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^{\text{e}}$ | $10^3 k_{\text{obs} \text{calcd}}^{\text{f}}$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|--------------------------------------------------------|---------------------------------------------------------------------------|------------------|---------------------------------------------------------------------|
| 0.05                     | 10.46           | 1.28 ± 0.01                                            | 20028 ± 67                                                                | 0.079 ± 0.003    | 1.32                                                                |
| 0.10                     | 10.47           | 2.54 ± 0.03                                            | 19823 ± 73                                                                | 0.073 ± 0.004    | 2.49                                                                |
| 0.20                     | 10.39           | 4.80 ± 0.04                                            | 19505 ± 53                                                                | 0.088 ± 0.003    | 4.83                                                                |
| 0.30                     | 10.42           | 7.22 ± 0.06                                            | 19435 ± 55                                                                | 0.093 ± 0.003    | 7.16                                                                |
| 0.40                     | 10.41           | 9.43 ± 0.07                                            | 19577 ± 48                                                                | 0.105 ± 0.003    | 9.50                                                                |
| 0.45                     | 10.39           | 10.7 ± 0.07                                            | 19314 ± 45                                                                | 0.110 ± 0.003    | 10.67                                                               |

pH = 10.77 ± 0.04

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^{\text{c}}$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^{\text{d}}$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^{\text{e}}$ | $10^3 k_{\text{obs} \text{calcd}}^{\text{f}}$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|--------------------------------------------------------|---------------------------------------------------------------------------|------------------|---------------------------------------------------------------------|
| 0.05                     | 10.79           | 2.04 ± 0.02                                            | 20225 ± 80                                                                | 0.065 ± 0.004    | 2.08                                                                |
| 0.10                     | 10.81           | 3.58 ± 0.2                                             | 19804 ± 288                                                               | 0.083 ± 0.015    | 3.57                                                                |
| 0.20                     | 10.79           | 6.60 ± 0.08                                            | 20106 ± 82                                                                | 0.099 ± 0.005    | 6.55                                                                |
| 0.35                     | 10.72           | 11.0 ± 0.2                                             | 20095 ± 123                                                               | 0.107 ± 0.007    | 11.0                                                                |
| 0.40                     | 10.74           | 12.5 ± 0.1                                             | 19611 ± 71                                                                | 0.104 ± 0.004    | 12.5                                                                |

pH = 11.10 ± 0.04

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^{\text{c}}$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^{\text{d}}$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^{\text{e}}$ | $10^3 k_{\text{obs} \text{calcd}}^{\text{f}}$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|--------------------------------------------------------|---------------------------------------------------------------------------|------------------|---------------------------------------------------------------------|
| 0.05                     | 11.12           | 3.01 ± 0.03                                            | 19979 ± 69                                                                | 0.079 ± 0.004    | 3.39                                                                |
| 0.10                     | 11.14           | 5.46 ± 0.04                                            | 20048 ± 50                                                                | 0.089 ± 0.003    | 5.3                                                                 |
| 0.20                     | 11.15           | 9.57 ± 0.09                                            | 19980 ± 67                                                                | 0.106 ± 0.004    | 9.06                                                                |
| 0.35                     | 11.09           | 12.7 ± 0.1                                             | 20527 ± 65                                                                | 0.127 ± 0.004    | 12.8                                                                |
| 0.35                     | 11.07           | 14.6 ± 0.2                                             | 20176 ± 84                                                                | 0.156 ± 0.005    | 14.7                                                                |
| 0.40                     | 11.05           | 16.6 ± 0.2                                             | 19999 ± 77                                                                | 0.177 ± 0.005    | 16.6                                                                |

<sup>a</sup>  $[26_0] = 6 \times 10^{-5}$  M,  $\mu = 0.4$  M,  $T = 30^\circ\text{C}$ ,  $\lambda = 400$  nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N,N-diEthylamine buffer concentration.

<sup>b</sup> pH at  $t = \infty$  (reaction finished)

<sup>c</sup>  $k_{\text{obs}} = k_o + k_{1\text{obs}} [\text{Buf}]_T$

<sup>d</sup>  $\epsilon$  apparent

<sup>e</sup>  $A_o$  = initial absorbance

<sup>f</sup> Calculated from  $k_{\text{obs}} = k_o + k_{1\text{obs}} [\text{Buf}]_T$

**Table A-6 : Values of Kinetic Parameter  $k_{\text{obs}}$ ,  $\epsilon_{\text{app}}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NHCH<sub>3</sub> buffer.<sup>a</sup>**

$$\text{pH} = 8.64 \pm 0.07$$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{\text{obs} \text{calcd}}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|-----------------------------------------------|------------------------------------------------------------------|-------------------|------------------------------------------------------------|
| 0.05                     | 8.73            | $1.92 \pm 0.06$                               | $18247 \pm 143$                                                  | $0.071 \pm 0.007$ | 2.06                                                       |
| 0.10                     | 8.72            | $3.49 \pm 0.06$                               | $18154 \pm 87$                                                   | $0.088 \pm 0.004$ | 3.55                                                       |
| 0.20                     | 8.65            | $6.99 \pm 0.08$                               | $17262 \pm 62$                                                   | $0.100 \pm 0.003$ | 6.53                                                       |
| 0.30                     | 8.59            | $9.39 \pm 0.2$                                | $17689 \pm 104$                                                  | $0.144 \pm 0.006$ | 9.52                                                       |
| 0.35                     | 8.55            | $10.9 \pm 0.1$                                | $17284 \pm 81$                                                   | $0.153 \pm 0.004$ | 11.0                                                       |

$$\text{pH} = 8.79 \pm 0.07$$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{\text{obs} \text{calcd}}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|-----------------------------------------------|------------------------------------------------------------------|-------------------|------------------------------------------------------------|
| 0.05                     | 8.88            | $2.38 \pm 0.03$                               | $18599 \pm 62$                                                   | $0.079 \pm 0.003$ | 2.67                                                       |
| 0.10                     | 8.85            | $4.61 \pm 0.05$                               | $18476 \pm 64$                                                   | $0.089 \pm 0.004$ | 4.50                                                       |
| 0.20                     | 8.79            | $8.64 \pm 0.1$                                | $18242 \pm 72$                                                   | $0.127 \pm 0.004$ | 8.15                                                       |
| 0.30                     | 8.74            | $11.5 \pm 0.1$                                | $18435 \pm 88$                                                   | $0.147 \pm 0.005$ | 11.8                                                       |
| 0.35                     | 8.71            | $13.6 \pm 0.1$                                | $18456 \pm 66$                                                   | $0.158 \pm 0.004$ | 13.6                                                       |

$$\text{pH} = 9.00 \pm 0.06$$

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{\text{obs}}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{\text{app}}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{\text{obs} \text{calcd}}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|-----------------------------------------------|------------------------------------------------------------------|-------------------|------------------------------------------------------------|
| 0.05                     | 9.06            | $3.36 \pm 0.02$                               | $18676 \pm 36$                                                   | $0.069 \pm 0.002$ | 3.44                                                       |
| 0.10                     | 9.06            | $6.21 \pm 0.07$                               | $18553 \pm 77$                                                   | $0.088 \pm 0.004$ | 5.95                                                       |
| 0.20                     | 9.00            | $10.8 \pm 0.2$                                | $18868 \pm 139$                                                  | $0.127 \pm 0.008$ | 11.0                                                       |
| 0.30                     | 8.94            | $15.6 \pm 0.3$                                | $18308 \pm 162$                                                  | $0.174 \pm 0.010$ | 16.0                                                       |
| 0.35                     | 8.95            | $18.8 \pm 0.1$                                | $18220 \pm 60$                                                   | $0.176 \pm 0.004$ | 18.5                                                       |

Table A6, Continued

pH = 9.22 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 9.28            | 4.31 ± 0.05                                                         | 19500 ± 67                                                           | 0.078 ± 0.004               | 4.97                                                                    |
| 0.10                     | 9.26            | 8.35 ± 0.07                                                         | 19148 ± 62                                                           | 0.089 ± 0.004               | 8.10                                                                    |
| 0.20                     | 9.23            | 15.1 ± 0.2                                                          | 19318 ± 84                                                           | 0.147 ± 0.005               | 14.4                                                                    |
| 0.30                     | 9.18            | 20.8 ± 0.3                                                          | 19364 ± 88                                                           | 0.140 ± 0.006               | 20.6                                                                    |
| 0.35                     | 9.16            | 23.1 ± 0.3                                                          | 18343 ± 106                                                          | 0.180 ± 0.007               | 23.7                                                                    |

pH = 9.63 ± 0.01

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.64            | 5.32 ± 0.07                                                         | 20446 ± 95                                                           | 0.067 ± 0.005               | 5.40                                                                    |
| 0.08                     | 9.63            | 9.26 ± 0.2                                                          | 20071 ± 150                                                          | 0.111 ± 0.008               | 9.51                                                                    |
| 0.12                     | 9.63            | 13.8 ± 0.1                                                          | 19723 ± 91                                                           | 0.112 ± 0.005               | 13.6                                                                    |
| 0.16                     | 9.63            | 18.2 ± 0.2                                                          | 19655 ± 99                                                           | 0.119 ± 0.006               | 17.7                                                                    |
| 0.20                     | 9.61            | 21.3 ± 0.3                                                          | 19319 ± 128                                                          | 0.167 ± 0.008               | 21.8                                                                    |

<sup>a</sup> [26<sub>0</sub>] = 6 x 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N-methylbenzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

**Table A-7 : Values of Kinetic Parameter k<sub>obs</sub>, ɛ<sub>app</sub> and A<sub>o</sub> Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NHCH<sub>3</sub> buffer.<sup>a</sup>**

pH = 8.60 ± 0.10

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.70            | 1.75 ± 0.03                                                         | 18721 ± 108                                                          | 0.078 ± 0.004               | 2.11                                                                    |
| 0.10                     | 8.69            | 3.80 ± 0.03                                                         | 17800 ± 53                                                           | 0.077 ± 0.003               | 3.69                                                                    |
| 0.20                     | 8.60            | 7.45 ± 0.06                                                         | 18931 ± 62                                                           | 0.104 ± 0.004               | 6.86                                                                    |
| 0.30                     | 8.53            | 9.89 ± 0.1                                                          | 17732 ± 70                                                           | 0.139 ± 0.004               | 10.0                                                                    |
| 0.35                     | 8.48            | 11.4 ± 0.2                                                          | 17042 ± 94                                                           | 0.154 ± 0.005               | 11.6                                                                    |

Table A7, Continued

pH = 8.71 ± 0.09

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.82            | 2.15 ± 0.05                                                         | 18841 ± 148                                                          | 0.065 ± 0.008               | 2.43                                                                    |
| 0.10                     | 8.80            | 4.53 ± 0.04                                                         | 18438 ± 55                                                           | 0.085 ± 0.003               | 4.33                                                                    |
| 0.20                     | 8.70            | 8.28 ± 0.05                                                         | 18058 ± 37                                                           | 0.108 ± 0.002               | 8.13                                                                    |
| 0.30                     | 8.64            | 12.2 ± 0.09                                                         | 18174 ± 46                                                           | 0.134 ± 0.003               | 11.9                                                                    |
| 0.35                     | 8.61            | 13.5 ± 0.1                                                          | 17692 ± 54                                                           | 0.157 ± 0.003               | 13.8                                                                    |

pH = 8.97 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 9.01            | 3.33 ± 0.04                                                         | 19057 ± 90                                                           | 0.078 ± 0.005               | 3.31                                                                    |
| 0.10                     | 9.05            | 6.06 ± 0.08                                                         | 18777 ± 86                                                           | 0.085 ± 0.005               | 5.84                                                                    |
| 0.20                     | 8.98            | 10.5 ± 0.2                                                          | 18633 ± 173                                                          | 0.135 ± 0.010               | 10.9                                                                    |
| 0.30                     | 8.92            | 15.9 ± 0.3                                                          | 18294 ± 153                                                          | 0.172 ± 0.009               | 16.0                                                                    |
| 0.35                     | 8.88            | 18.7 ± 0.2                                                          | 18040 ± 74                                                           | 0.194 ± 0.005               | 18.5                                                                    |

pH = 9.16 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 9.23            | 4.21 ± 0.03                                                         | 19858 ± 56                                                           | 0.064 ± 0.003               | 4.46                                                                    |
| 0.10                     | 9.20            | 7.84 ± 0.09                                                         | 19390 ± 68                                                           | 0.092 ± 0.004               | 7.69                                                                    |
| 0.20                     | 9.18            | 14.6 ± 0.1                                                          | 18712 ± 80                                                           | 0.128 ± 0.005               | 14.2                                                                    |
| 0.25                     | 9.12            | 20.0 ± 0.2                                                          | 19588 ± 89                                                           | 0.141 ± 0.006               | 20.6                                                                    |
| 0.30                     | 9.07            | 24.1 ± 0.3                                                          | 18617 ± 102                                                          | 0.192 ± 0.006               | 23.8                                                                    |

pH = 9.60 ± 0.02

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>3</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>3</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.62            | 4.79 ± 0.06                                                         | 20415 ± 84                                                           | 0.071 ± 0.005               | 5.28                                                                    |
| 0.08                     | 9.62            | 9.62 ± 0.1                                                          | 19905 ± 118                                                          | 0.105 ± 0.007               | 9.30                                                                    |
| 0.12                     | 9.60            | 13.3 ± 0.2                                                          | 19748 ± 121                                                          | 0.126 ± 0.007               | 13.3                                                                    |
| 0.16                     | 9.60            | 18.4 ± 0.2                                                          | 19802 ± 120                                                          | 0.130 ± 0.007               | 17.3                                                                    |
| 0.20                     | 9.57            | 20.5 ± 0.4                                                          | 19319 ± 127                                                          | 0.165 ± 0.008               | 21.4                                                                    |

<sup>a</sup> [26]<sub>0</sub> = 6 × 10<sup>-5</sup> M, μ = 0.3 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N-methylbenzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

**Table A-8: Values of Kinetic Parameter  $k_{obs}$ ,  $\epsilon_{app}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of  $C_6H_5CH_2NCH_2CH_3$  buffer.<sup>a</sup>**

pH = 8.28 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^3 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^3 k_{obscald}^f$<br>(s <sup>-1</sup> ) | $10^3 k_{obscald}^g$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|--------------------------------------------|
| 0.05                     | 8.35            | $2.70 \pm 0.04$                        | $15291 \pm 76$                                            | $0.089 \pm 0.004$ | 2.69                                       | 2.76                                       |
| 0.10                     | 8.34            | $5.58 \pm 0.07$                        | $15225 \pm 66$                                            | $0.105 \pm 0.003$ | 5.49                                       | 5.52                                       |
| 0.20                     | 8.30            | $11.0 \pm 0.2$                         | $14836 \pm 76$                                            | $0.145 \pm 0.004$ | 11.0                                       | 11.0                                       |
| 0.30                     | 8.23            | $16.5 \pm 0.02$                        | $14871 \pm 67$                                            | $0.181 \pm 0.004$ | 16.7                                       | 16.6                                       |
| 0.35                     | 8.20            | $19.7 \pm 0.8$                         | $14994 \pm 251$                                           | $0.177 \pm 0.016$ | 19.5                                       | 19.3                                       |

pH = 8.81 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^5 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^5 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|
| 0.05                     | 8.86            | $9.29 \pm 0.1$                         | $18539 \pm 104$                                           | $0.077 \pm 0.004$ | 9.64                                       |
| 0.10                     | 8.87            | $18.2 \pm 0.4$                         | $18932 \pm 131$                                           | $0.078 \pm 0.005$ | 18.20                                      |
| 0.20                     | 8.83            | $35.9 \pm 0.5$                         | $18995 \pm 96$                                            | $0.072 \pm 0.005$ | 35.40                                      |
| 0.30                     | 8.76            | $53.4 \pm 1.1$                         | $18225 \pm 113$                                           | $0.093 \pm 0.006$ | 52.6                                       |
| 0.35                     | 8.73            | $60.3 \pm 1.3$                         | $18469 \pm 114$                                           | $0.104 \pm 0.006$ | 61.2                                       |

pH = 9.11 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^4 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^4 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|
| 0.05                     | 9.19            | $1.36 \pm 0.03$                        | $20172 \pm 140$                                           | $0.075 \pm 0.004$ | 1.53                                       |
| 0.10                     | 9.17            | $2.73 \pm 0.1$                         | $19156 \pm 45$                                            | $0.075 \pm 0.002$ | 2.67                                       |
| 0.20                     | 9.13            | $5.12 \pm 0.08$                        | $18926 \pm 103$                                           | $0.079 \pm 0.006$ | 4.96                                       |
| 0.30                     | 9.05            | $7.47 \pm 0.1$                         | $18779 \pm 80$                                            | $0.125 \pm 0.004$ | 7.24                                       |
| 0.35                     | 9.03            | $8.11 \pm 0.2$                         | $19082 \pm 160$                                           | $0.139 \pm 0.008$ | 8.39                                       |

pH = 9.31 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^4 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$           | $10^4 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|-------------------|--------------------------------------------|
| 0.05                     | 9.36            | $1.78 \pm 0.03$                        | $20315 \pm 108$                                           | $0.083 \pm 0.005$ | 1.76                                       |
| 0.10                     | 9.36            | $3.29 \pm 0.03$                        | $20222 \pm 53$                                            | $0.088 \pm 0.003$ | 3.33                                       |
| 0.20                     | 9.32            | $6.48 \pm 0.09$                        | $19304 \pm 75$                                            | $0.086 \pm 0.004$ | 6.47                                       |
| 0.30                     | 9.25            | $9.70 \pm 0.09$                        | $19820 \pm 51$                                            | $0.131 \pm 0.003$ | 9.6                                        |
| 0.35                     | 9.24            | $11.1 \pm 0.1$                         | $18843 \pm 65$                                            | $0.142 \pm 0.003$ | 11.2                                       |

Table A8, Continued

pH = 9.71 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.75            | 2.86 ± 0.02                                                         | 19524 ± 53                                                           | 0.120 ± 0.002               | 2.98                                                                    |
| 0.08                     | 9.74            | 5.57 ± 0.02                                                         | 20240 ± 50                                                           | 0.145 ± 0.002               | 5.39                                                                    |
| 0.12                     | 9.73            | 7.56 ± 0.02                                                         | 19258 ± 73                                                           | 0.141 ± 0.004               | 7.80                                                                    |
| 0.16                     | 9.74            | 10.6 ± 0.02                                                         | 19979 ± 62                                                           | 0.137 ± 0.003               | 10.20                                                                   |
| 0.20                     | 9.71            | 12.4 ± 0.07                                                         | 19063 ± 40                                                           | 0.137 ± 0.002               | 12.60                                                                   |

<sup>a</sup> [26]<sub>0</sub> = 6 × 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N-ethylbenzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>g</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub> with k<sub>o</sub> = 0

**Table A-9 : Values of Kinetic Parameter k<sub>obs</sub>, ɛ<sub>app</sub> and A<sub>o</sub> Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NCH<sub>2</sub>CH<sub>3</sub> buffer.<sup>a</sup>**

pH = 8.65 ± 0.09

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.75            | 7.76 ± 0.09                                                         | 17938 ± 79                                                           | 0.083 ± 0.003               | 7.37                                                                    |
| 0.10                     | 8.73            | 15.1 ± 0.3                                                          | 18032 ± 113                                                          | 0.078 ± 0.005               | 14.7                                                                    |
| 0.20                     | 8.66            | 27.8 ± 1.2                                                          | 19102 ± 275                                                          | 0.100 ± 0.014               | 29.4                                                                    |
| 0.30                     | 8.57            | 44.7 ± 1.2                                                          | 17224 ± 148                                                          | 0.092 ± 0.008               | 44.2                                                                    |
| 0.33                     | 8.54            | 48.9 ± 0.8                                                          | 17685 ± 99                                                           | 0.094 ± 0.005               | 48.6                                                                    |

pH = 8.77 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.86            | 9.42 ± 0.1                                                          | 18891 ± 91                                                           | 0.080 ± 0.004               | 9.85                                                                    |
| 0.10                     | 8.85            | 18.6 ± 0.3                                                          | 19331 ± 107                                                          | 0.077 ± 0.005               | 18.2                                                                    |
| 0.20                     | 8.74            | 35.2 ± 1.0                                                          | 18786 ± 175                                                          | 0.085 ± 0.008               | 35.0                                                                    |
| 0.30                     | 8.71            | 51.8 ± 1.3                                                          | 18398 ± 144                                                          | 0.120 ± 0.007               | 51.7                                                                    |
| 0.35                     | 8.68            | 59.9 ± 1.7                                                          | 18312 ± 156                                                          | 0.123 ± 0.008               | 60.1                                                                    |

Table A9, Continued

pH = 8.97 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>obscald</sub> <sup>g</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 0.05                     | 9.05            | 1.28 ± 0.04                                                         | 20367 ± 215                                                          | 0.074 ± 0.007               | 1.06                                                                    | 1.16                                                                    |
| 0.10                     | 9.05            | 2.12 ± 0.03                                                         | 21527 ± 104                                                          | 0.092 ± 0.004               | 2.24                                                                    | 2.31                                                                    |
| 0.20                     | 8.89            | 4.26 ± 0.1                                                          | 20034 ± 184                                                          | 0.091 ± 0.009               | 4.61                                                                    | 4.62                                                                    |
| 0.30                     | 8.90            | 7.30 ± 0.06                                                         | 18523 ± 54                                                           | 0.077 ± 0.003               | 6.97                                                                    | 6.93                                                                    |
| 0.35                     | 8.89            | 8.08 ± 0.06                                                         | 18607 ± 47                                                           | 0.080 ± 0.002               | 8.16                                                                    | 8.09                                                                    |

pH = 9.21 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 9.31            | 1.81 ± 0.01                                                         | 20373 ± 52                                                           | 0.075 ± 0.002               | 1.80                                                                    |
| 0.10                     | 9.28            | 3.22 ± 0.02                                                         | 20708 ± 37                                                           | 0.081 ± 0.002               | 3.38                                                                    |
| 0.20                     | 9.20            | 6.79 ± 0.04                                                         | 19196 ± 36                                                           | 0.070 ± 0.002               | 6.56                                                                    |
| 0.25                     | 9.15            | 9.80 ± 0.07                                                         | 19273 ± 44                                                           | 0.076 ± 0.002               | 9.74                                                                    |
| 0.30                     | 9.12            | 11.2 ± 0.09                                                         | 19261 ± 46                                                           | 0.082 ± 0.002               | 11.3                                                                    |

pH = 9.61 ± 0.02

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 9.60            | 1.99 ± 0.03                                                         | 21020 ± 113                                                          | 0.083 ± 0.004               | 2.06                                                                    |
| 0.08                     | 9.64            | 3.92 ± 0.05                                                         | 20684 ± 88                                                           | 0.079 ± 0.004               | 3.85                                                                    |
| 0.12                     | 9.63            | 5.66 ± 0.08                                                         | 20397 ± 83                                                           | 0.087 ± 0.004               | 5.63                                                                    |
| 0.16                     | 9.61            | 7.41 ± 0.1                                                          | 20018 ± 109                                                          | 0.083 ± 0.005               | 7.41                                                                    |
| 0.20                     | 9.59            | 9.16 ± 0.1                                                          | 19809 ± 110                                                          | 0.079 ± 0.006               | 9.19                                                                    |

<sup>a</sup> [26]<sub>0</sub> = 6 × 10<sup>-5</sup> M, μ = 0.3 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N-ethylbenzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

**Table A-10 : Values of Kinetic Parameter  $k_{obs}$ ,  $\epsilon_{app}$  and  $A_o$  Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of  $C_6H_5CH_2N(CH_3)_2$  buffer.<sup>a</sup>**

pH = 8.07 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^5 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$       | $10^5 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|---------------|--------------------------------------------|
| 0.05                     | 8.14            | 0.513 ± 0.01                           | 14430 ± 111                                               | 0.089 ± 0.004 | 0.533                                      |
| 0.10                     | 8.11            | 1.02 ± 0.03                            | 13966 ± 147                                               | 0.081 ± 0.006 | 0.95                                       |
| 0.20                     | 8.10            | 1.70 ± 0.1                             | 14431 ± 273                                               | 0.093 ± 0.001 | 1.78                                       |
| 0.30                     | 8.01            | 2.61 ± 0.08                            | 12372 ± 112                                               | 0.066 ± 0.005 | 2.61                                       |
| 0.35                     | 7.97            | 3.05 ± 0.1                             | 12032 ± 127                                               | 0.051 ± 0.006 | 3.02                                       |

pH = 8.16 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^5 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$        | $10^5 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|----------------|--------------------------------------------|
| 0.05                     | 8.16            | 0.907 ± 0.01                           | 15053 ± 78                                                | 0.085 ± 0.002  | 0.797                                      |
| 0.10                     | 8.21            | 1.12 ± 0.04                            | 145766 ± 159                                              | 0.0979 ± 0.005 | 1.34                                       |
| 0.20                     | 8.17            | 2.60 ± 0.05                            | 13721 ± 79                                                | 0.089 ± 0.004  | 2.43                                       |
| 0.30                     | 8.09            | 3.46 ± 0.7                             | 13245 ± 74                                                | 0.090 ± 0.003  | 3.52                                       |
| 0.35                     | 8.80            | 4.07 ± 0.08                            | 12702 ± 79                                                | 0.084 ± 0.004  | 4.07                                       |

pH = 8.20 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^5 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$       | $10^5 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|---------------|--------------------------------------------|
| 0.05                     | 8.27            | 0.613 ± 0.01                           | 15957 ± 128                                               | 0.100 ± 0.005 | 0.75                                       |
| 0.10                     | 8.26            | 1.35 ± 0.04                            | 15085 ± 119                                               | 0.090 ± 0.005 | 1.24                                       |
| 0.20                     | 8.21            | 2.31 ± 0.03                            | 13776 ± 62                                                | 0.093 ± 0.003 | 2.30                                       |
| 0.30                     | 8.17            | 3.32 ± 0.08                            | 13233 ± 103                                               | 0.080 ± 0.005 | 3.36                                       |
| 0.35                     | 8.11            | 3.91 ± 0.06                            | 12904 ± 77                                                | 0.086 ± 0.004 | 3.90                                       |

pH = 8.34 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | $10^5 k_{obs}^c$<br>(s <sup>-1</sup> ) | $\epsilon_{app}^d$<br>(M <sup>-1</sup> cm <sup>-1</sup> ) | $A_o^e$       | $10^5 k_{obscald}^f$<br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|----------------------------------------|-----------------------------------------------------------|---------------|--------------------------------------------|
| 0.05                     | 8.42            | 0.573 ± 0.01                           | 16896 ± 163                                               | 0.037 ± 0.004 | 0.643                                      |
| 0.10                     | 8.39            | 1.23 ± 0.03                            | 14441 ± 110                                               | 0.038 ± 0.004 | 1.17                                       |
| 0.20                     | 8.38            | 2.28 ± 0.2                             | 14763 ± 292                                               | 0.041 ± 0.010 | 2.24                                       |
| 0.30                     | 8.27            | 3.31 ± 0.2                             | 13525 ± 211                                               | 0.033 ± 0.010 | 3.30                                       |
| 0.35                     | 8.23            | 3.79 ± 0.2                             | 12652 ± 188                                               | 0.039 ± 0.009 | 3.83                                       |

Table A10, Continued

pH = 8.35 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.41            | 1.04 ± 0.02                                                         | 15799 ± 105                                                          | 0.111 ± 0.004               | 1.04                                                                    |
| 0.10                     | 8.42            | 1.94 ± 0.07                                                         | 16106 ± 171                                                          | 0.113 ± 0.008               | 1.94                                                                    |
| 0.20                     | 8.37            | 3.58 ± 0.08                                                         | 15643 ± 130                                                          | 0.102 ± 0.006               | 3.58                                                                    |
| 0.30                     | 8.31            | 5.13 ± 0.1                                                          | 14839 ± 117                                                          | 0.078 ± 0.005               | 5.13                                                                    |
| 0.35                     | 8.24            | 5.55 ± 0.04                                                         | 13825 ± 45                                                           | 0.103 ± 0.002               | 5.55                                                                    |

pH = 8.45 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.54            | 0.948 ± 0.05                                                        | 19372 ± 333                                                          | 0.037 ± 0.008               | 0.994                                                                   |
| 0.10                     | 8.51            | 1.79 ± 0.1                                                          | 17116 ± 276                                                          | 0.037 ± 0.010               | 1.83                                                                    |
| 0.20                     | 8.46            | 3.61 ± 0.14                                                         | 15497 ± 176                                                          | 0.033 ± 0.007               | 3.51                                                                    |
| 0.30                     | 8.38            | 5.39 ± 0.17                                                         | 15454 ± 152                                                          | 0.033 ± 0.006               | 5.19                                                                    |
| 0.35                     | 8.35            | 5.82 ± 0.15                                                         | 14976 ± 124                                                          | 0.032 ± 0.005               | 6.0                                                                     |

pH = 8.50 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.57            | 1.48 ± 0.02                                                         | 17241 ± 85                                                           | 0.119 ± 0.003               | 1.67                                                                    |
| 0.10                     | 8.57            | 2.59 ± 0.02                                                         | 16469 ± 54                                                           | 0.113 ± 0.002               | 2.51                                                                    |
| 0.20                     | 8.51            | 4.43 ± 0.07                                                         | 16045 ± 97                                                           | 0.120 ± 0.004               | 4.19                                                                    |
| 0.30                     | 8.46            | 5.90 ± 0.08                                                         | 15965 ± 91                                                           | 0.103 ± 0.004               | 5.86                                                                    |
| 0.35                     | 8.41            | 6.53 ± 0.2                                                          | 15156 ± 164                                                          | 0.126 ± 0.008               | 6.70                                                                    |

pH = 8.65 ± 0.06

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.71            | 2.11 ± 0.04                                                         | 17690 ± 99                                                           | 0.087 ± 0.004               | 2.26                                                                    |
| 0.10                     | 8.69            | 3.63 ± 0.05                                                         | 17766 ± 67                                                           | 0.087 ± 0.003               | 3.59                                                                    |
| 0.20                     | 8.66            | 6.57 ± 0.09                                                         | 17148 ± 93                                                           | 0.084 ± 0.004               | 6.24                                                                    |
| 0.30                     | 8.62            | 8.59 ± 0.4                                                          | 16233 ± 268                                                          | 0.068 ± 0.010               | 8.89                                                                    |
| 0.35                     | 8.57            | 10.3 ± 0.4                                                          | 15645 ± 260                                                          | 0.078 ± 0.010               | 10.20                                                                   |

Table A10, Continued

pH = 8.76 ± 0.02

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>5</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>5</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.78            | 1.47 ± 0.3                                                          | 18043 ± 119                                                          | 0.086 ± 0.005               | 1.34                                                                    |
| 0.10                     | 8.77            | 2.32 ± 0.2                                                          | 17831 ± 310                                                          | 0.088 ± 0.014               | 2.60                                                                    |
| 0.20                     | 8.78            | 5.26 ± 0.13                                                         | 15220 ± 120                                                          | 0.143 ± 0.005               | 5.11                                                                    |
| 0.30                     | 8.75            | 7.81 ± 0.2                                                          | 15088 ± 129                                                          | 0.145 ± 0.006               | 7.63                                                                    |
| 0.35                     | 8.74            | 8.71 ± 0.2                                                          | 14971 ± 122                                                          | 0.144 ± 0.006               | 8.89                                                                    |

<sup>a</sup> [26<sub>0</sub>] = 6 × 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N,N-dimethylbenzylamine buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

**Table A-11 : Values of Kinetic Parameter k<sub>obs</sub>, ɛ<sub>app</sub> and A<sub>o</sub> Calculated from Eq. (3-13) for the Cleavage of 26 in the Presence of o-HOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> buffer.<sup>a</sup>**

pH = 7.99 ± 0.07

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.06            | 1.09 ± 0.03                                                         | 12540 ± 119                                                          | 0.043 ± 0.005               | 1.10                                                                    |
| 0.10                     | 8.04            | 1.96 ± 0.05                                                         | 11778 ± 113                                                          | 0.039 ± 0.005               | 1.89                                                                    |
| 0.15                     | 7.99            | 2.56 ± 0.03                                                         | 12455 ± 58                                                           | 0.014 ± 0.003               | 2.69                                                                    |
| 0.20                     | 7.95            | 3.57 ± 0.1                                                          | 10778 ± 99                                                           | 0.033 ± 0.005               | 3.48                                                                    |
| 0.25                     | 7.90            | 4.25 ± 0.2                                                          | 10316 ± 139                                                          | 0.026 ± 0.007               | 4.27                                                                    |

pH = 7.91 ± 0.09

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.73            | 0.92 ± 0.02                                                         | 11218 ± 87                                                           | 0.034 ± 0.004               | 1.01                                                                    |
| 0.10                     | 8.72            | 1.51 ± 0.1                                                          | 11503 ± 287                                                          | 0.068 ± 0.012               | 1.55                                                                    |
| 0.15                     | 7.91            | 2.28 ± 0.07                                                         | 10954 ± 138                                                          | 0.101 ± 0.006               | 2.09                                                                    |
| 0.20                     | 7.86            | 2.73 ± 0.1                                                          | 11339 ± 186                                                          | 0.131 ± 0.009               | 2.62                                                                    |
| 0.25                     | 7.80            | 2.99 ± 0.2                                                          | 10706 ± 296                                                          | 0.204 ± 0.015               | 3.20                                                                    |

Table A11, Continued

pH = 8.21 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.29            | 1.18 ± 0.02                                                         | 13767 ± 89                                                           | 0.064 ± 0.004               | 1.20                                                                    |
| 0.08                     | 8.22            | 2.09 ± 0.03                                                         | 13419 ± 80                                                           | 0.077 ± 0.003               | 2.08                                                                    |
| 0.12                     | 8.19            | 3.01 ± 0.07                                                         | 13399 ± 107                                                          | 0.092 ± 0.004               | 2.97                                                                    |
| 0.14                     | 8.18            | 3.37 ± 0.04                                                         | 10652 ± 40                                                           | 0.086 ± 0.002               | 3.40                                                                    |
| 0.16                     | 8.17            | 3.84 ± 0.09                                                         | 12853 ± 97                                                           | 0.109 ± 0.004               | 3.90                                                                    |

pH = 8.22 ± 0.08

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.05                     | 8.29            | 1.42 ± 0.02                                                         | 14070 ± 88                                                           | 0.053 ± 0.004               | 1.55                                                                    |
| 0.10                     | 8.25            | 2.65 ± 0.06                                                         | 13515 ± 101                                                          | 0.106 ± 0.005               | 2.55                                                                    |
| 0.15                     | 8.22            | 3.66 ± 0.08                                                         | 13897 ± 106                                                          | 0.145 ± 0.005               | 3.55                                                                    |
| 0.24                     | 8.10            | 5.27 ± 0.2                                                          | 12157 ± 181                                                          | 0.274 ± 0.009               | 5.35                                                                    |

pH = 8.27 ± 0.03

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.23            | 0.822 ± 0.009                                                       | 11712 ± 468                                                          | 0.033 ± 0.002               | 0.92                                                                    |
| 0.08                     | 8.29            | 1.89 ± 0.02                                                         | 13620 ± 65                                                           | 0.031 ± 0.003               | 2.01                                                                    |
| 0.12                     | 8.30            | 3.45 ± 0.04                                                         | 14328 ± 54                                                           | 0.043 ± 0.003               | 3.11                                                                    |
| 0.16                     | 8.29            | 4.25 ± 0.1                                                          | 13914 ± 94                                                           | 0.033 ± 0.005               | 4.20                                                                    |
| 0.20                     | 8.25            | 5.12 ± 0.1                                                          | 13254 ± 123                                                          | 0.045 ± 0.006               | 5.30                                                                    |

pH = 8.56 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.62            | 1.76 ± 0.03                                                         | 116743 ± 90                                                          | 0.079 ± 0.004               | 1.82                                                                    |
| 0.08                     | 8.60            | 3.07 ± 0.06                                                         | 16684 ± 115                                                          | 0.093 ± 0.004               | 3.07                                                                    |
| 0.12                     | 8.58            | 4.50 ± 0.02                                                         | 15611 ± 27                                                           | 0.106 ± 0.001               | 4.31                                                                    |
| 0.16                     | 8.53            | 5.43 ± 0.1                                                          | 15427 ± 94                                                           | 0.114 ± 0.005               | 5.56                                                                    |
| 0.20                     | 8.49            | 6.80 ± 0.1                                                          | 14753 ± 83                                                           | 0.111 ± 0.004               | 6.80                                                                    |

Table A11, Continued

pH = 8.68 ± 0.05

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.71            | 1.84 ± 0.02                                                         | 17503 ± 87                                                           | 0.033 ± 0.004               | 1.99                                                                    |
| 0.08                     | 8.72            | 3.53 ± 0.07                                                         | 17141 ± 116                                                          | 0.060 ± 0.005               | 3.21                                                                    |
| 0.12                     | 8.69            | 4.30 ± 0.1                                                          | 16721 ± 170                                                          | 0.088 ± 0.008               | 4.44                                                                    |
| 0.16                     | 8.65            | 5.57 ± 0.3                                                          | 16555 ± 296                                                          | 0.141 ± 0.015               | 5.66                                                                    |
| 0.20                     | 8.61            | 6.94 ± 0.2                                                          | 16127 ± 136                                                          | 0.164 ± 0.007               | 6.88                                                                    |

pH = 8.85 ± 0.04

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.87            | 2.03 ± 0.02                                                         | 17416 ± 59                                                           | 0.116 ± 0.003               | 2.28                                                                    |
| 0.08                     | 8.89            | 3.69 ± 0.03                                                         | 17210 ± 51                                                           | 0.130 ± 0.002               | 3.58                                                                    |
| 0.12                     | 8.85            | 5.20 ± 0.05                                                         | 17123 ± 49                                                           | 0.145 ± 0.002               | 4.88                                                                    |
| 0.16                     | 8.82            | 6.23 ± 0.07                                                         | 16698 ± 61                                                           | 0.160 ± 0.003               | 6.18                                                                    |
| 0.20                     | 8.80            | 7.26 ± 0.08                                                         | 16775 ± 60                                                           | 0.173 ± 0.003               | 7.48                                                                    |

pH = 8.93 ± 0.03

| [Am] <sub>T</sub><br>(M) | pH <sup>b</sup> | 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup><br>(s <sup>-1</sup> ) | ɛ <sub>app</sub> <sup>d</sup><br>(M <sup>-1</sup> cm <sup>-1</sup> ) | A <sub>o</sub> <sup>e</sup> | 10 <sup>4</sup> k <sub>obscald</sub> <sup>f</sup><br>(s <sup>-1</sup> ) |
|--------------------------|-----------------|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------|
| 0.04                     | 8.96            | 2.23 ± 0.03                                                         | 18536 ± 100                                                          | 0.028 ± 0.005               | 2.46                                                                    |
| 0.08                     | 8.96            | 4.17 ± 0.1                                                          | 17826 ± 215                                                          | 0.061 ± 0.010               | 3.94                                                                    |
| 0.20                     | 8.94            | 5.48 ± 0.07                                                         | 17842 ± 80                                                           | 0.084 ± 0.003               | 5.41                                                                    |
| 0.12                     | 8.89            | 7.00 ± 0.10                                                         | 17674 ± 88                                                           | 0.120 ± 0.005               | 6.89                                                                    |
| 0.16                     | 8.92            | 8.19 ± 0.2                                                          | 17620 ± 115                                                          | 0.138 ± 0.006               | 8.36                                                                    |

<sup>a</sup> [26<sub>0</sub>] = 6 × 10<sup>-5</sup> M, μ = 0.4 M, T = 30°C, λ = 400 nm, 50 % v/v CH<sub>3</sub>CN in mixed aqueous reaction mixture and [Am]<sub>T</sub> = N,N-(diethylmethylamino)benzyl alcohol buffer concentration.

<sup>b</sup> pH at t = ∞ (reaction finished)

<sup>c</sup> k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

<sup>d</sup> ɛ apparent

<sup>e</sup> A<sub>o</sub> = initial absorbance

<sup>f</sup> Calculated from k<sub>obs</sub> = k<sub>o</sub> + k<sub>1obs</sub> [Buf]<sub>T</sub>

**Table A-12 : Values of pH and  $[NaOH]_T/M$  for The Plot of pH Versus  $[NaOH]_T/M$** 

| $10^5 [NaOH]_T$<br>(M) | pH <sup>a</sup> | pH <sup>b</sup> |
|------------------------|-----------------|-----------------|
| 5                      | 7.20            | 7.15            |
| 6                      | 7.38            | 7.17            |
| 7                      | 7.52            | 7.36            |
| 9                      | 8.04            | 8.04            |
| 10                     | 8.05            | 8.24            |
| 13                     | - <sup>c</sup>  | 9.04            |
| 15                     | 9.38            | 9.38            |
| 20                     | 10.30           | 10.10           |
| 25                     | 10.42           | 10.29           |
| 30                     | 10.61           | 10.51           |
| 40                     | 11.04           | 10.95           |

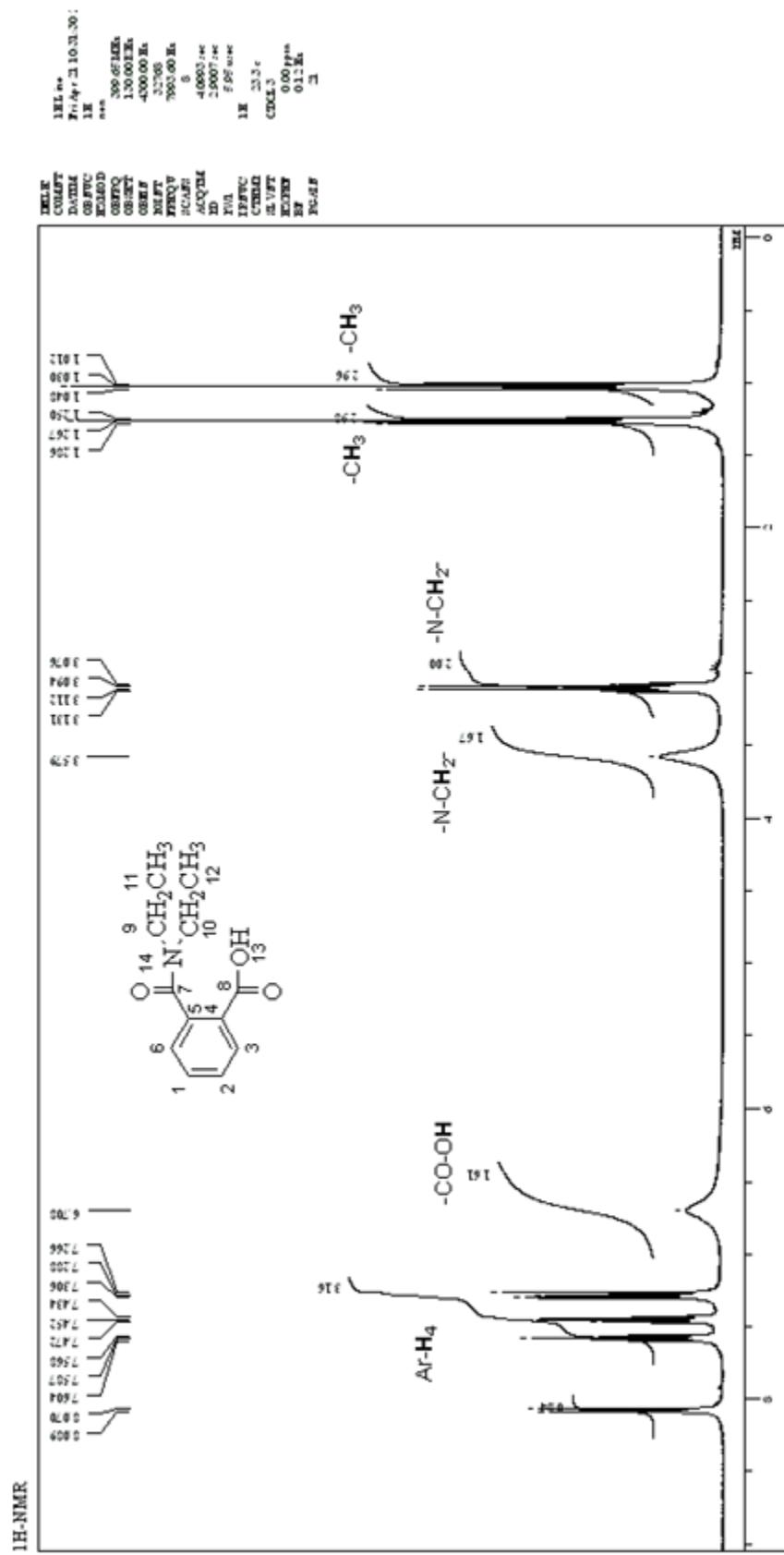
<sup>a</sup>  $\mu = 0.3$  M, revealed Eq. (4-6).

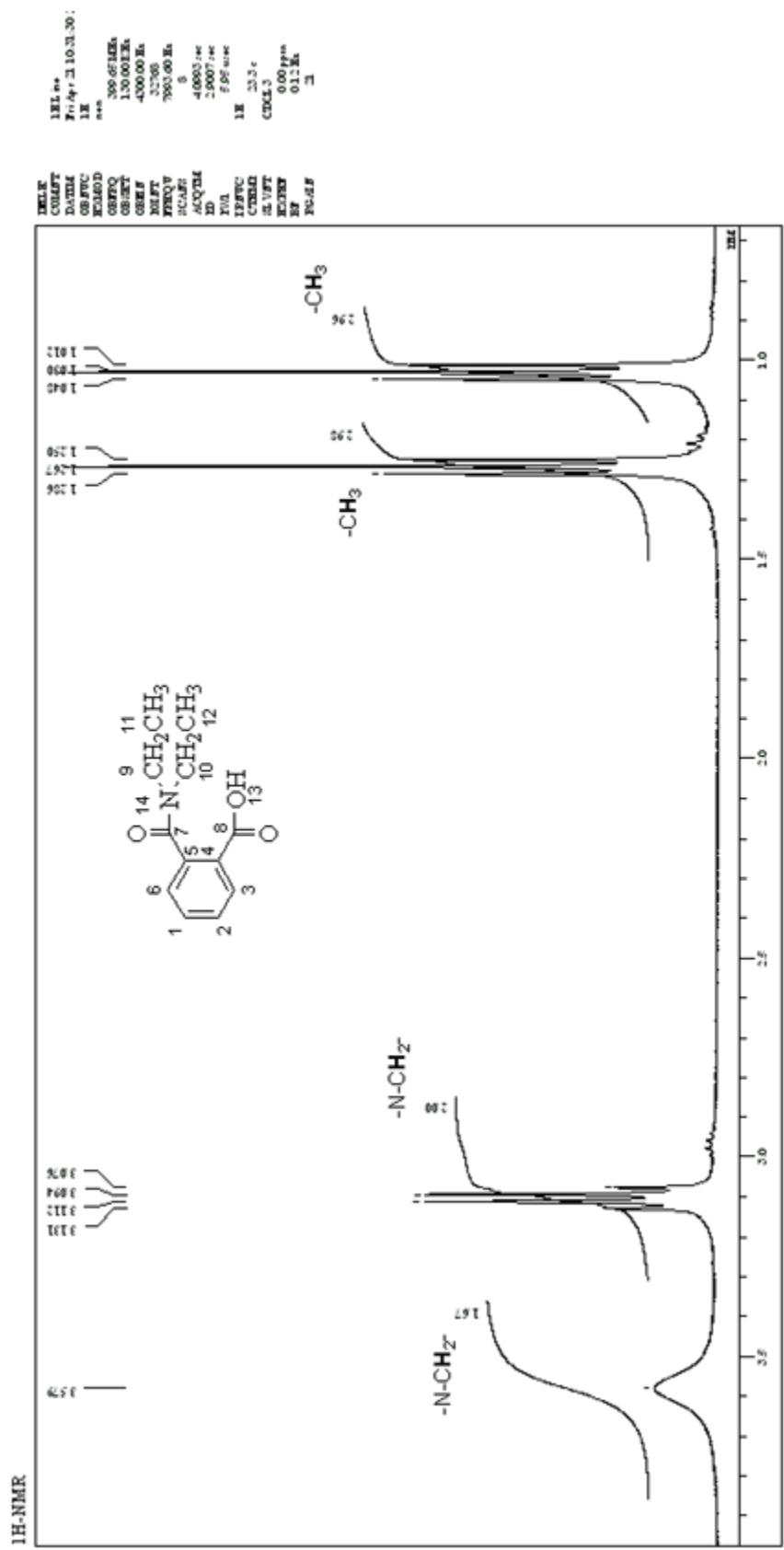
<sup>a</sup>  $\mu = 0.4$  M, revealed Eq. (4-7).

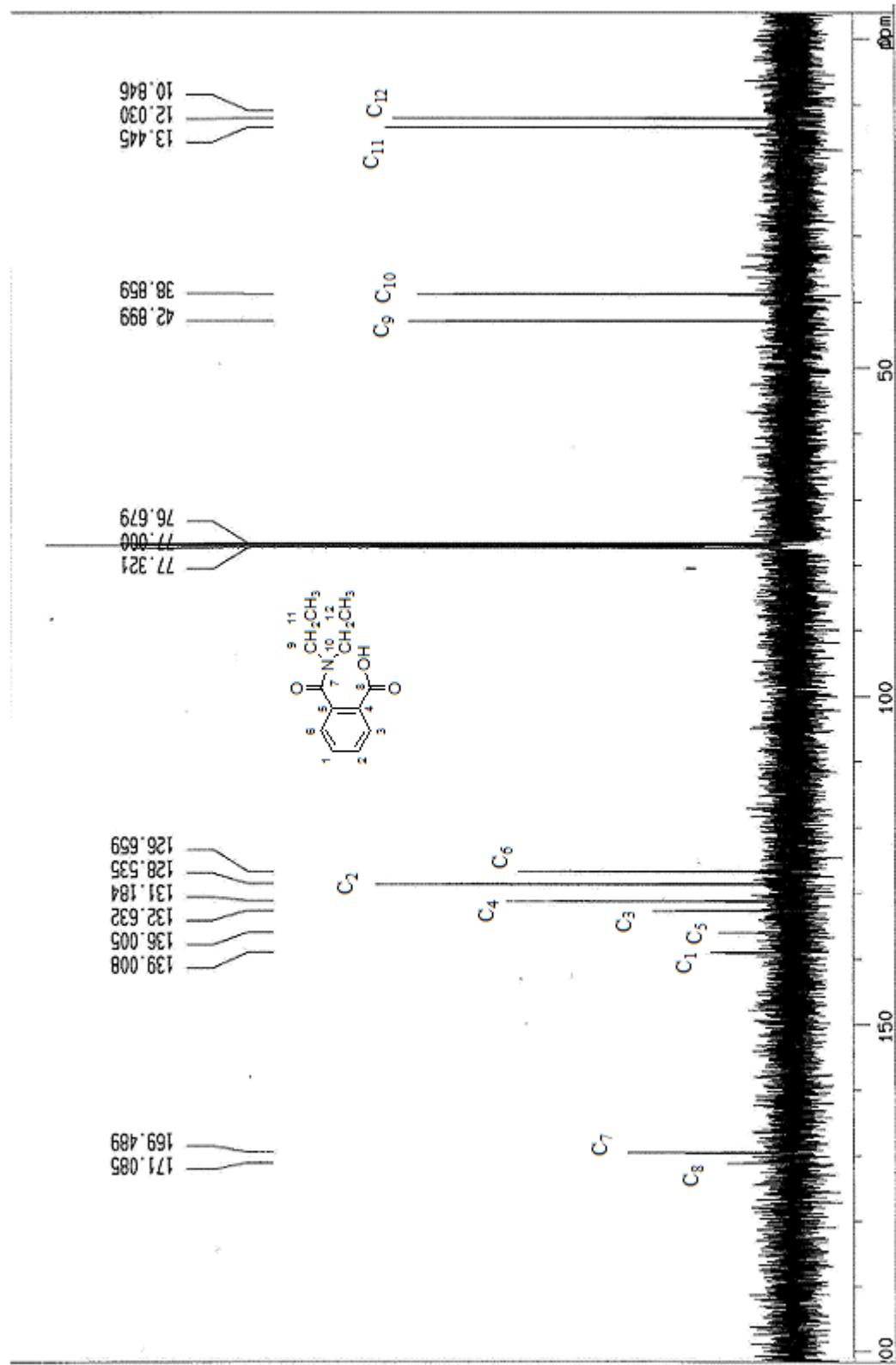
<sup>c</sup> data was not taken.

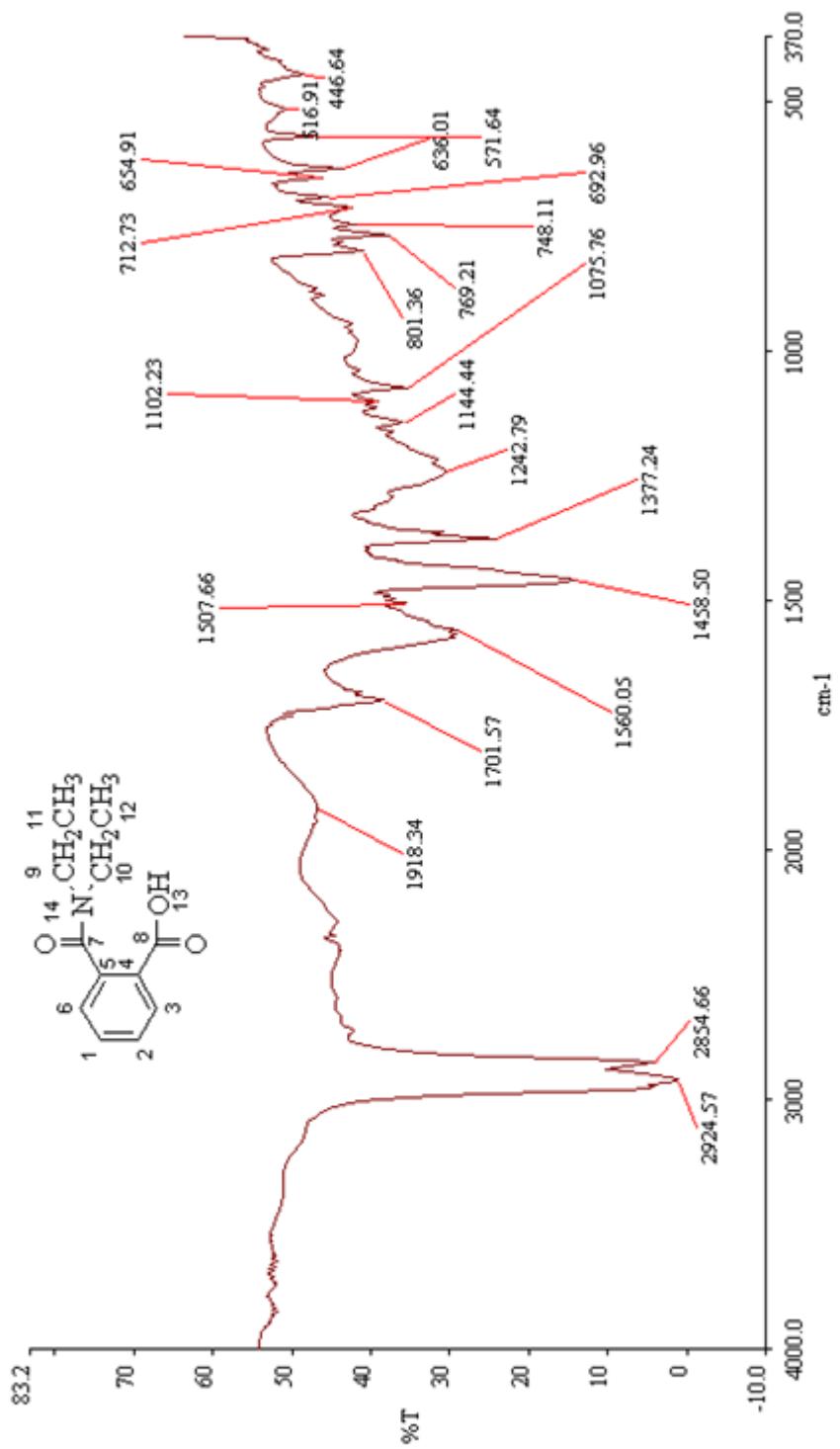
**APPENDIX 2: 1H-NMR, 13C-NMR, COSY AND IR SPECTRUMS.**

**1. N,N-Diethylphthalamic Acid**

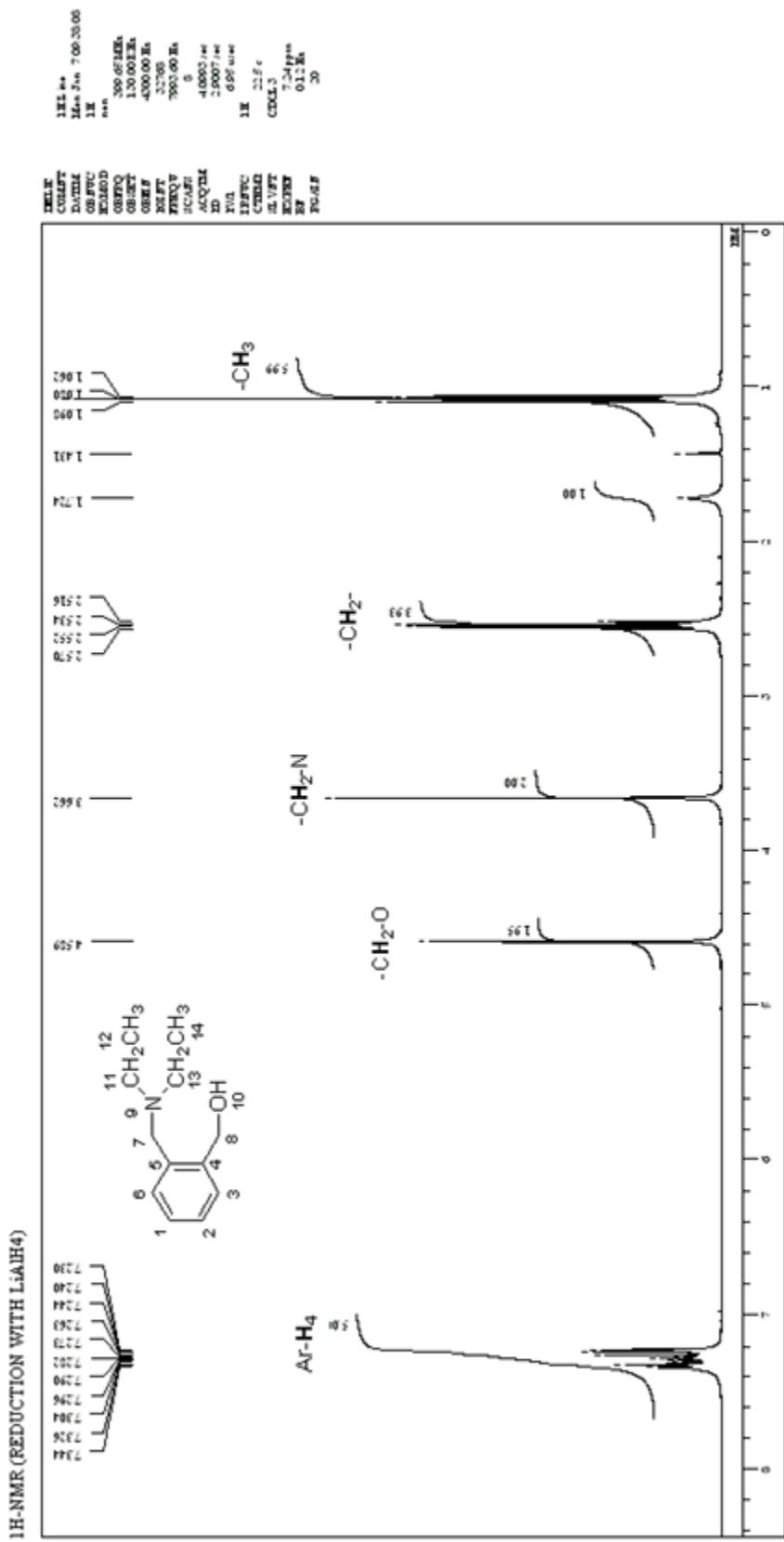




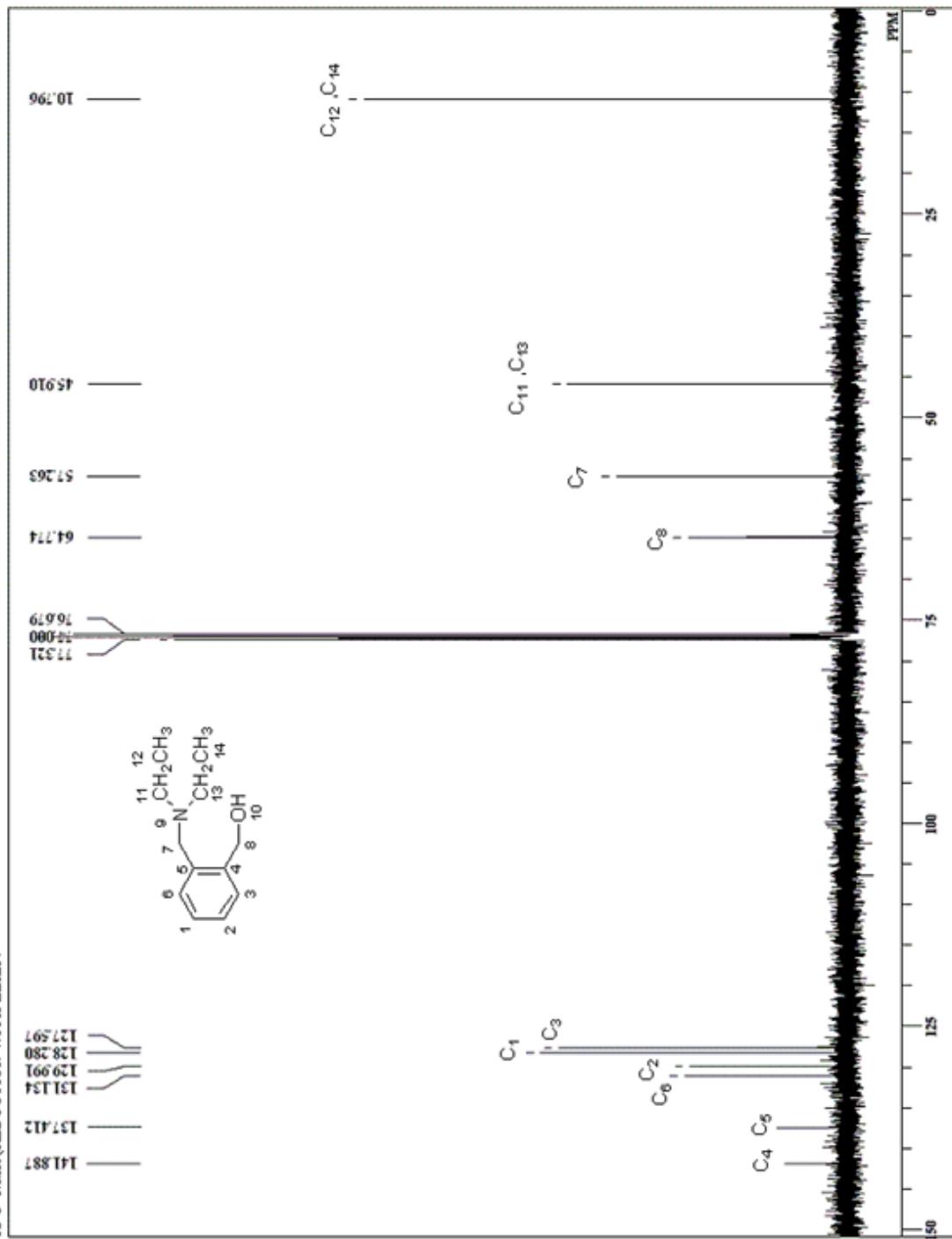


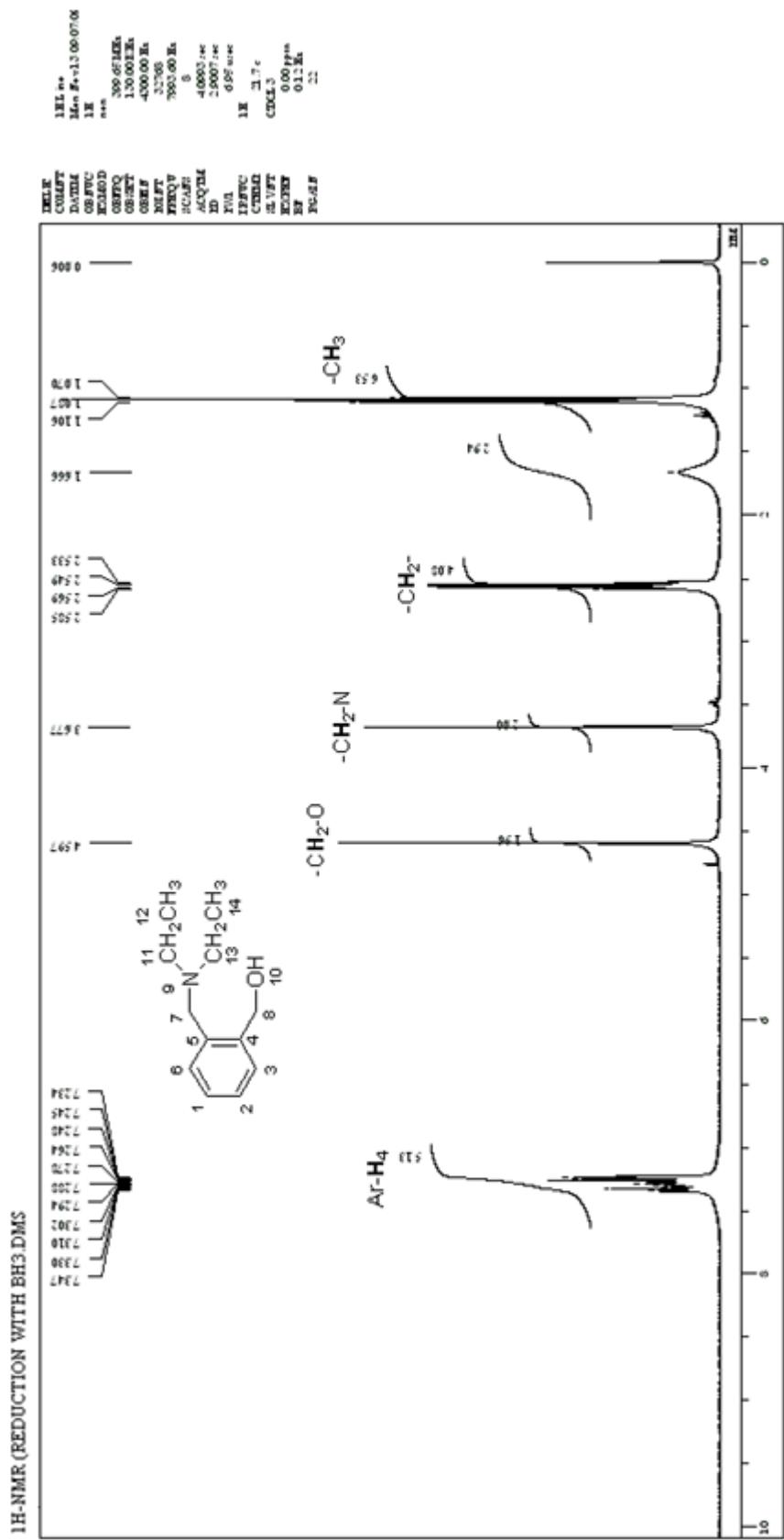


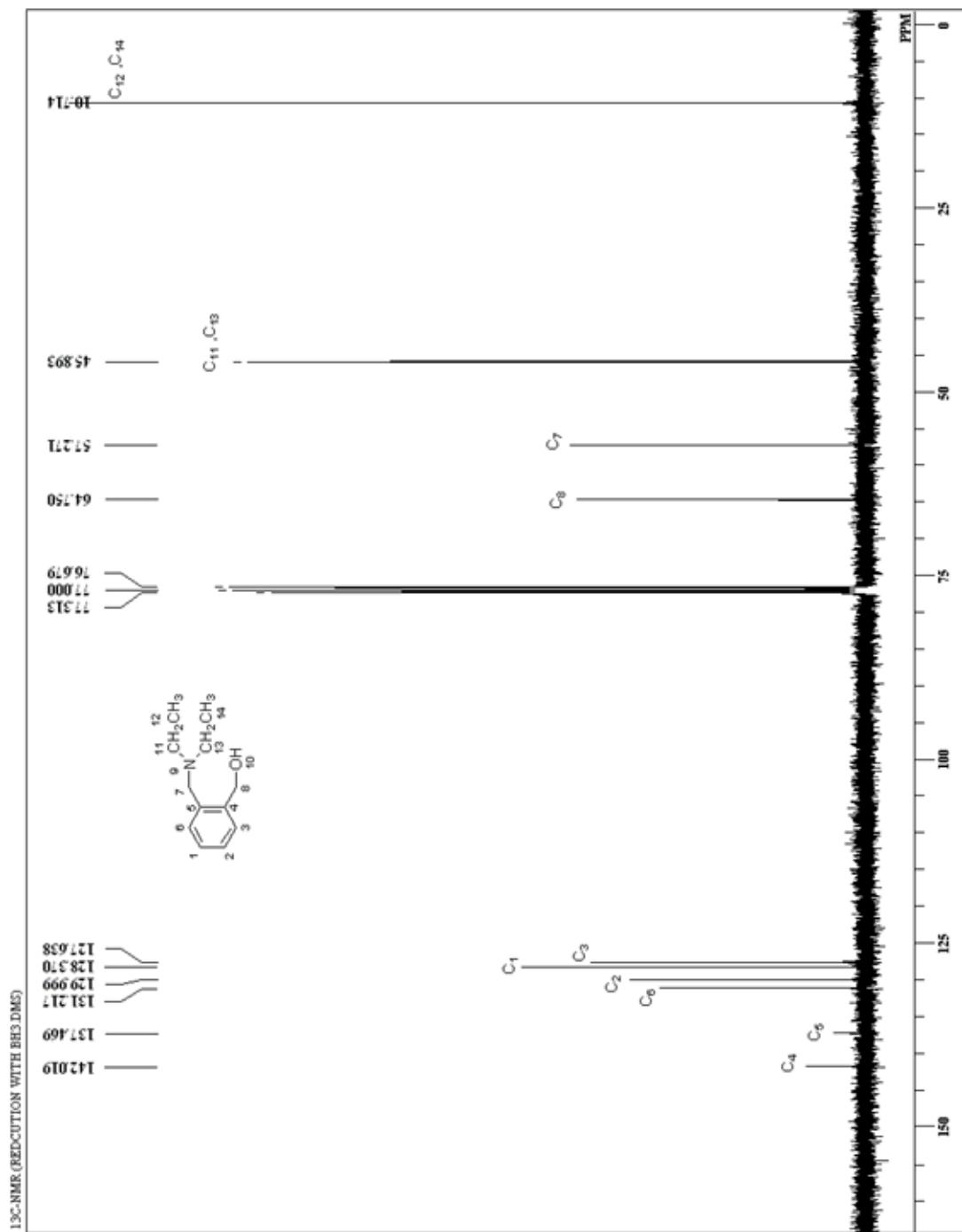
## 2. N,N-(Diethylmethylamino)benzyl Alcohol

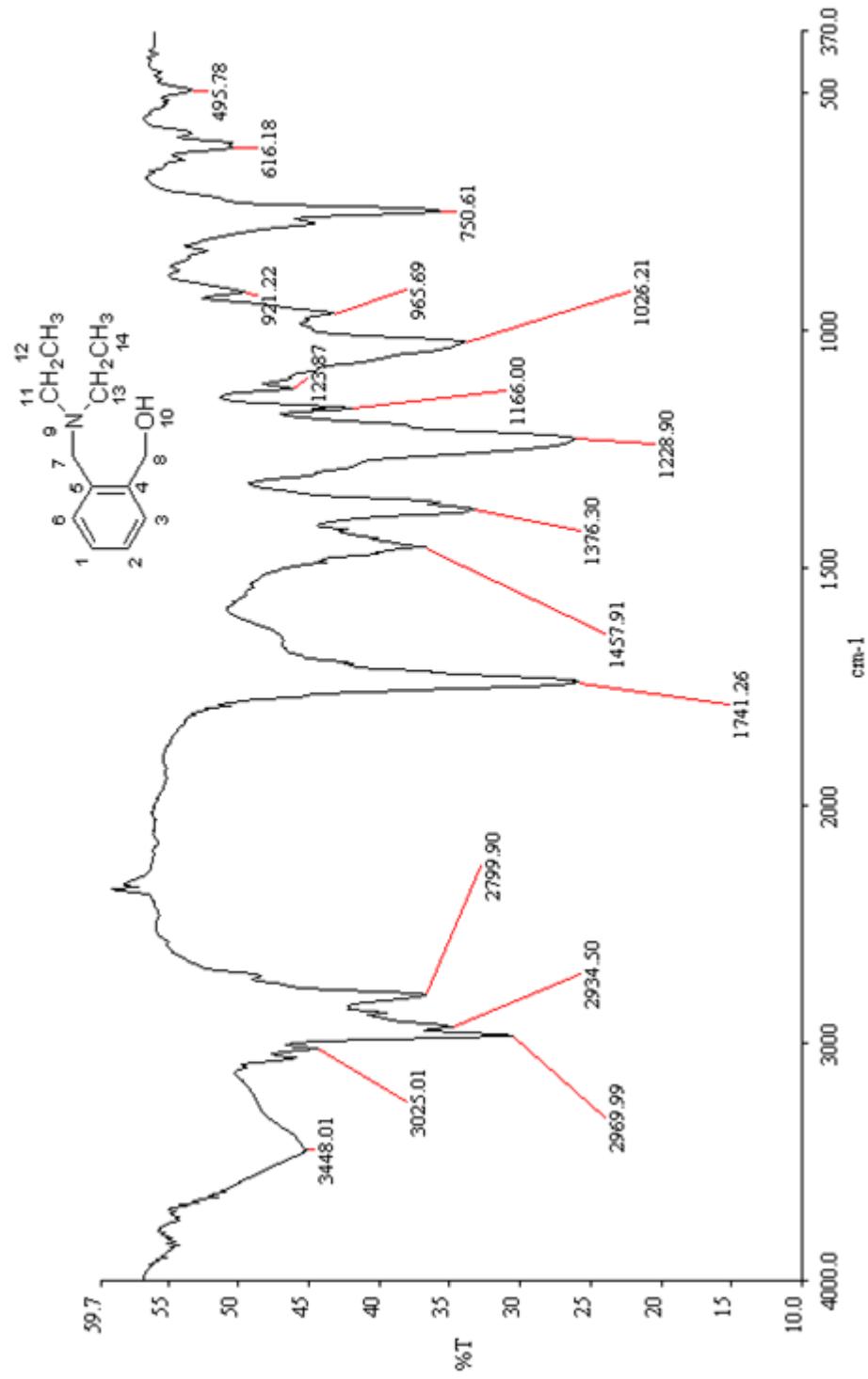


<sup>13</sup>C-NMR (REDUCTION WITH LiAlH<sub>4</sub>)

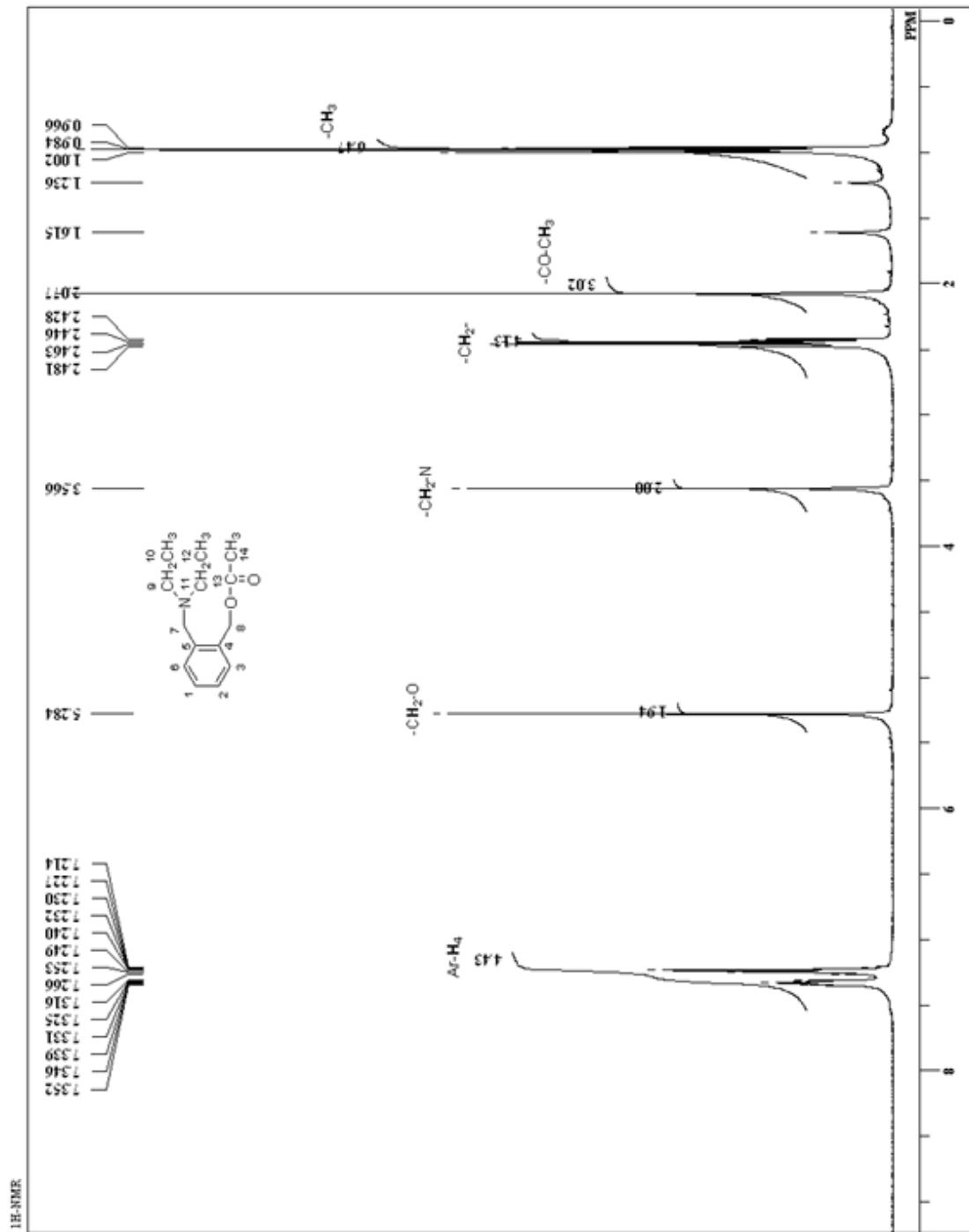


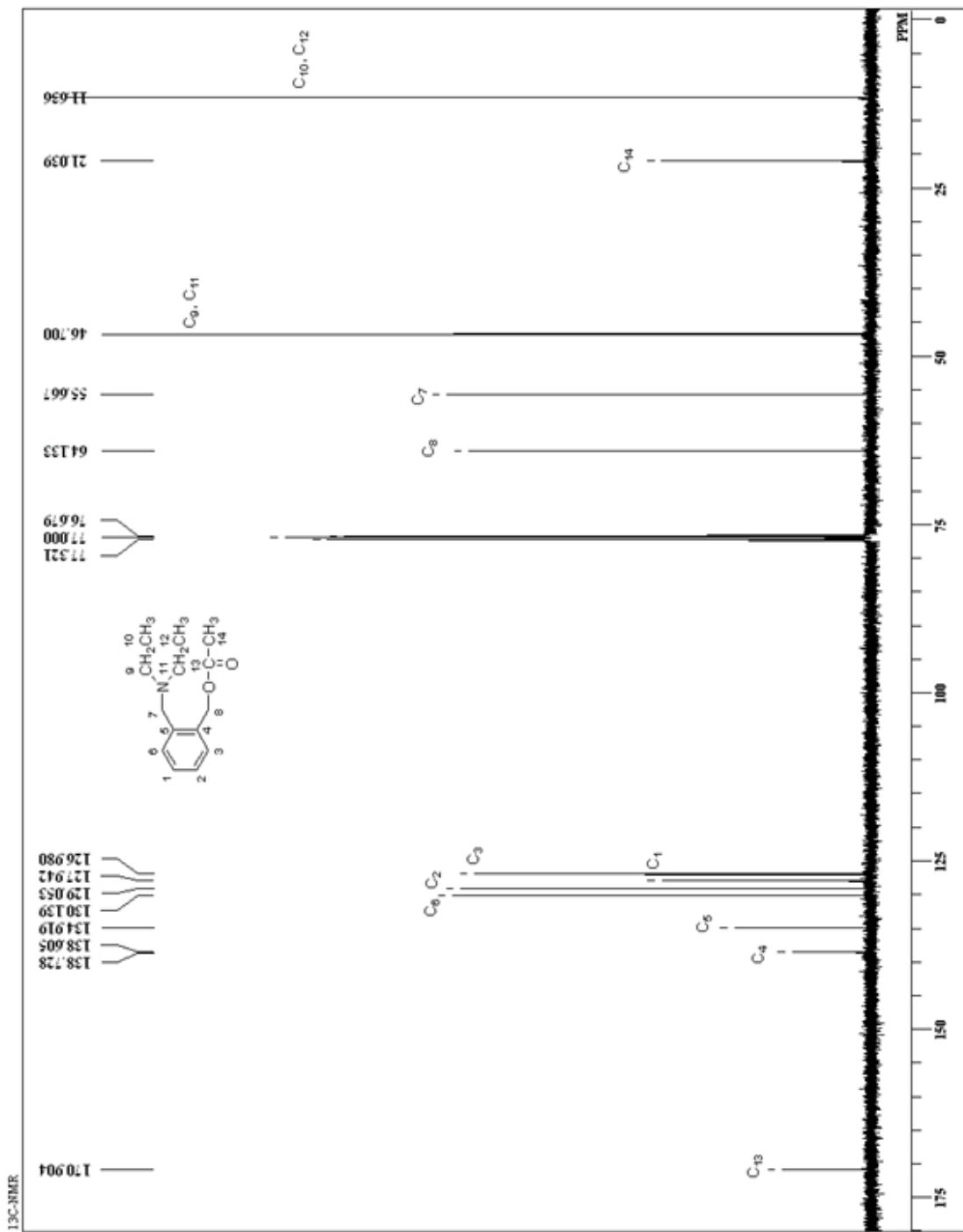


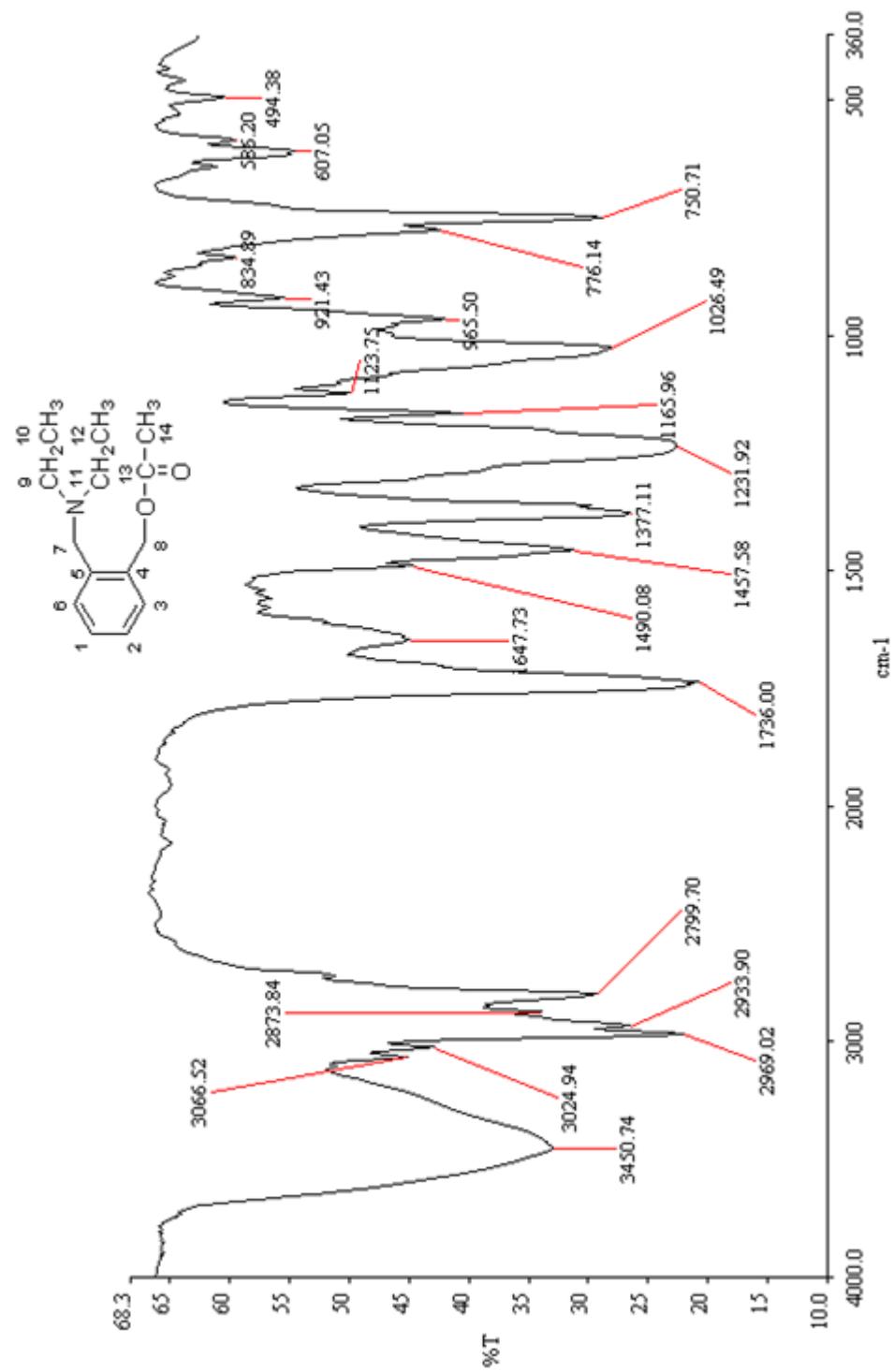




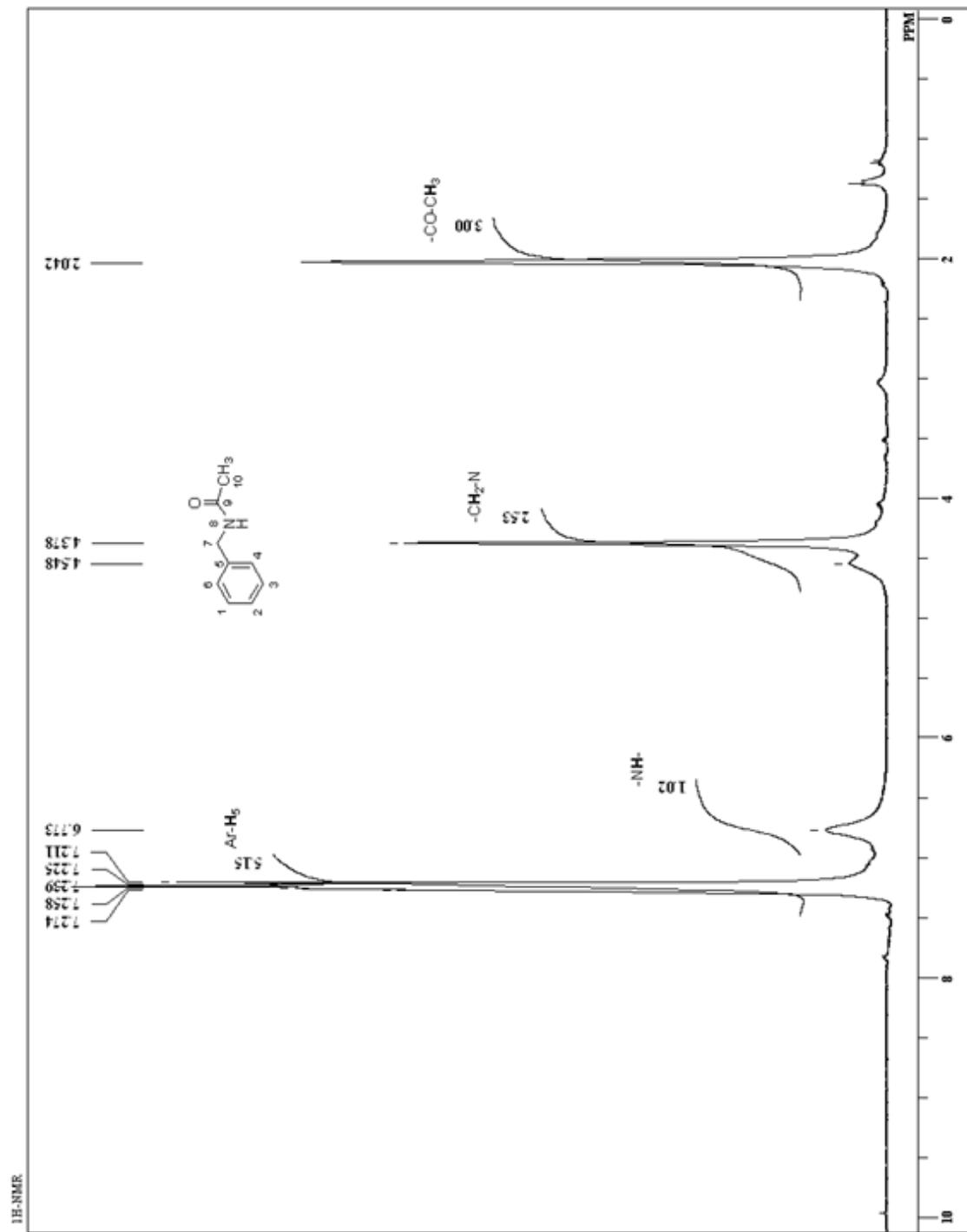
### 3. 2 – ((Diethylamino)methyl)benzyl Acetate

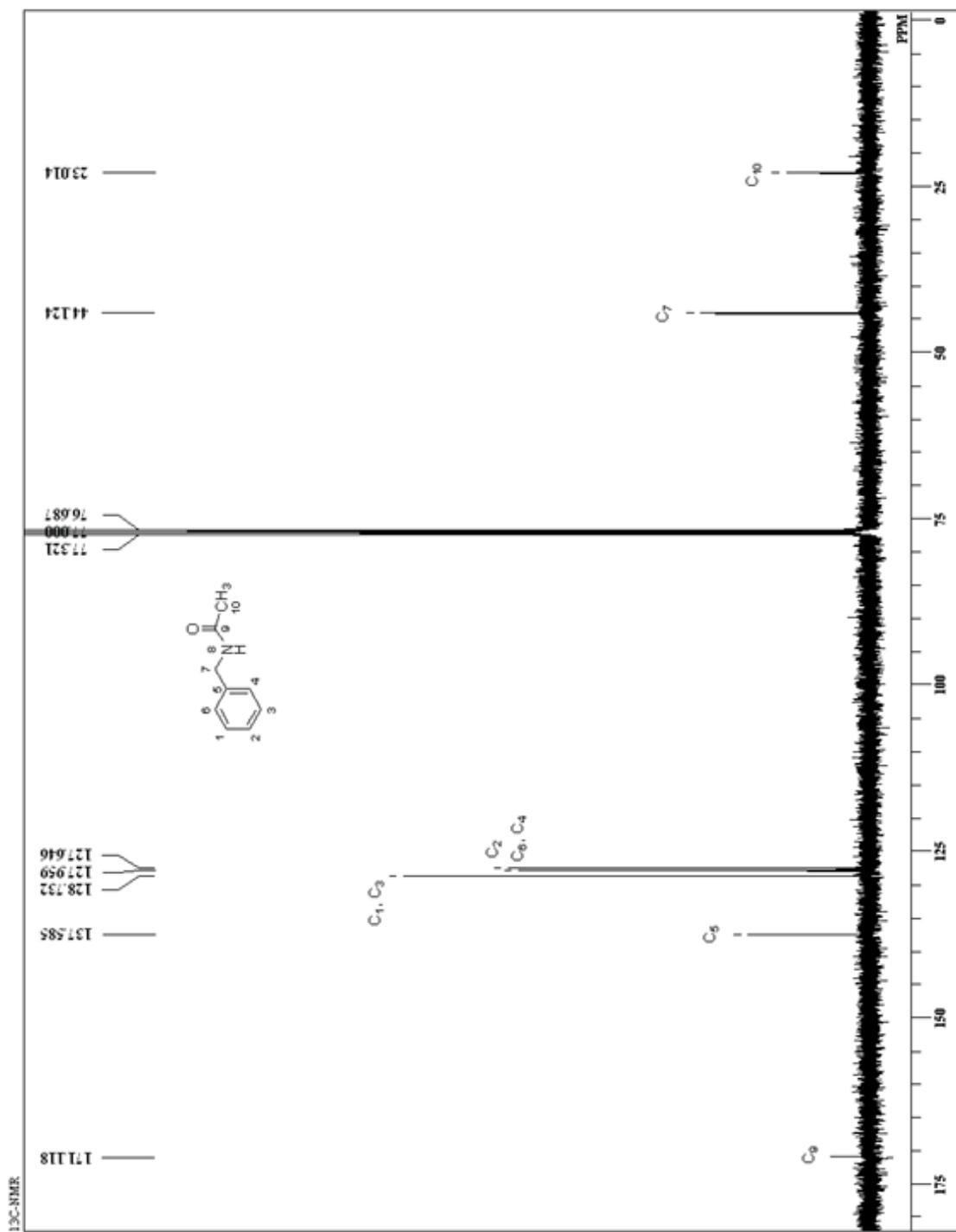


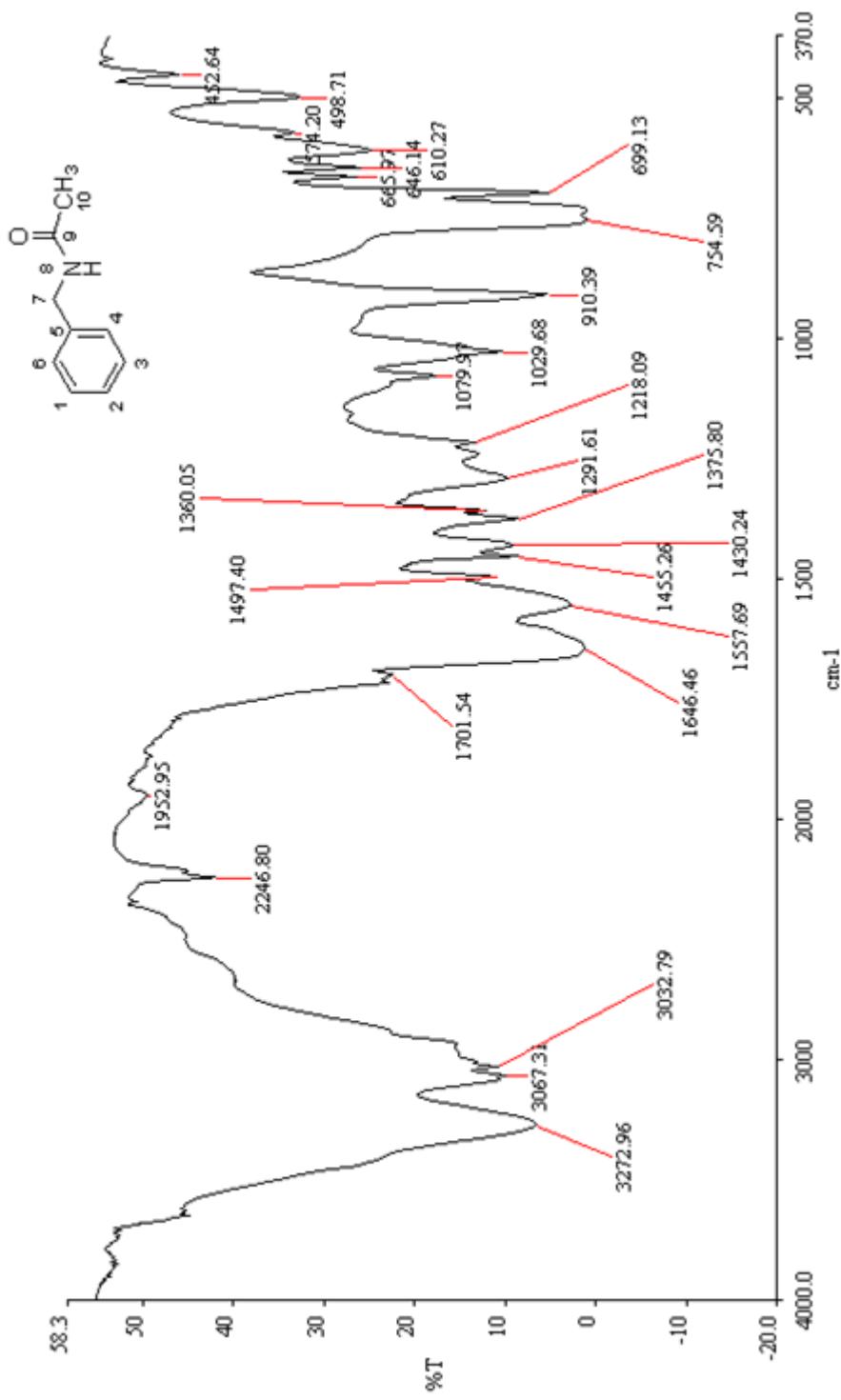




#### 4. N-Benzylacetamide







## 5. N,N-Diethylacetamide

