

## Supporting information

### Experimental and theoretical study of $\alpha$ - acetoxylation of ketones by (diacetoxy)iodobenzene

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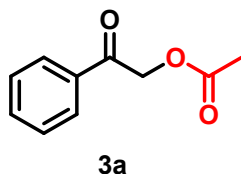
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## General Information

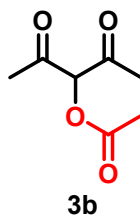
All reagents were purchased from Sigma-Aldrich and used without previous purification. The NMR spectra were recorded using a JEOL ECA-500 spectrometer with a magnetic field of 11.75 T ( $^1\text{H}$ , 500.160 MHz;  $^{13}\text{C}$ , 125.765 MHz). The unified scale was used with TMS as reference diluted (volume fraction  $\varphi < 1\%$ ) in chloroform for  $^1\text{H}$  resonance ( $(\text{CH}_3)_4\text{Si}$   $^1\text{H}$ ,  $^{13}\text{C} = 0$ ).<sup>1</sup> The UV/Vis absorption spectra were recorded with a Perkin Elmer Lambda 2S UV-VIS spectrophotometer. Low resolution mass spectra were acquired with HPLC/coupled mass Agilent Technologies (ESI).

## Synthesis of $\alpha$ -acetoxyketones

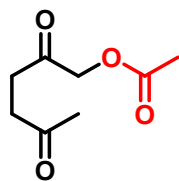
**General procedure:** In a flask, 1 equivalent of the corresponding ketone and 2.5 equivalents of  $\text{PhI}(\text{OAc})_2$  were dissolved in the appropriate solvent, and 10 equivalents of acetic acid were added. The reaction mixture was stirred for 3 days at  $70^\circ\text{C}$ . The solvent was evaporated, and the samples were purified by column chromatography using silica gel (60 Å, 200-240 mesh) and hexane/ethyl acetate 8:2 as the eluent.



**2-Oxo-2-phenylethyl acetate (3a):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.93 (2H, d,  $J = 7.4$  Hz), 7.62 (1H, t,  $J = 7.4$  Hz), 7.50 (2H, t,  $J = 7.4$  Hz), 5.35 (2H, s), 2.25 (3H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  192.27, 170.58, 134.29, 134.04, 128.99, 127.89, 66.15, 20.71. MS ES-API  $m/z$ :  $M^+$  179.1. The spectral data are in accordance with previous reports.<sup>2-4</sup>

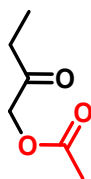


**2,4-Dioxopentan-3-yl, acetate (3b):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.42 (1H, s), 2.22 (6H, s), 2.18 (3H, s); enol tautomer 14.4 (br, 1H), 2.20 (s, 3H), 2.19 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  199.14, 169.32, 85.12, 27.33, 20.48; enol tautomer 184.78, 169.40, 128.20. ES-API  $m/z$ :  $M^+$  159.1. The spectral data are in accordance with previous reports.<sup>5</sup>



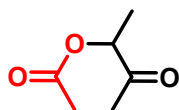
3d-1

**2,5-Dioxohexyl, acetate (3d-1):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.66 (2H, s), 2.73 (2H, t,  $J = 6.7$  Hz), 2.60 (2H, t,  $J = 6.7$  Hz), 2.12 (3H, s), 2.10 (3H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  206.82, 202.29, 170.35, 68.06, 36.65, 32.29, 29.77, 20.49. ES-API  $m/z$ :  $M^+$  173.1. The spectral data are in agreement with previous reports.<sup>6</sup>



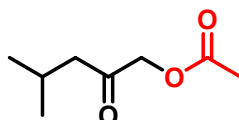
3e-1

**2-Oxobutyl, acetate (3e-1):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.43 (1H, s), 2.43 (2H, q,  $J = 7.4$  Hz), 2.15 (3H, s), 1.08 (3H, t,  $J = 7.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  204.53, 170.40, 67.82, 32.14, 20.58, 7.22. ES-API  $m/z$ :  $M^+$  131.0. The spectral data are in agreement with previous reports.<sup>7</sup>



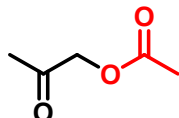
3e-3

**2-Oxobutyl-3-acetate (3e-3):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.19 (1H, q,  $J = 7.1$  Hz), 2.15 (3H, s), 2.12 (3H, s), 1.43 (3H, d,  $J = 7.1$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  205.73, 170.46, 74.98, 25.73, 20.81, 16.04. ES-API  $m/z$ :  $M^+$  131.0. The spectral data are in agreement with previous reports.<sup>7</sup>



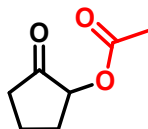
3f

**4-Methyl-2-oxopentyl, acetate (3f):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.60 (2H, s), 2.26 (2H, d,  $J = 6.7$  Hz), 2.14 (1H, m), 2.14 (3H, s), 0.92 (6H, d,  $J = 6.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  203.60, 170.38, 68.43, 47.66, 24.58, 22.60, 20.58. ES-API  $m/z$ :  $M^+$  159.1. The spectral data are in agreement with previous reports.<sup>8</sup>



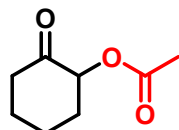
**3g**

**2-Oxopropyl, acetate (3g):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.64 (2H, s), 2.16 (3H, s), 2.15 (3H, s).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  201.64, 170.18, 68.39, 26.15, 20.57. ES-API  $m/z$ :  $M^+$  117.5. The spectral data are in agreement with previous reports.<sup>9</sup>



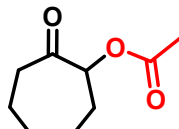
**3h**

**2-Oxocyclopentyl, acetate (3h):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.04 (1H, dt,  $J = 1.4$ , 10.2 Hz), 2.40 (1H, m), 2.33 (1H, m), 2.23 (1H, quint,  $J = 9.5$ ), 2.11 (3H, s), 2.08 (1H, m), 1.83 (2H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  212.62, 170.31, 75.80, 34.92, 28.47, 20.85, 17.18. ES-API  $m/z$ :  $M^+$  143.1. The spectral data are in agreement with previous reports.<sup>7,10-13</sup>



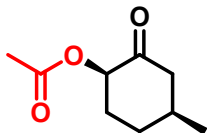
**3i**

**2-Oxocyclohexyl, acetate (3i):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.09 (1H, dd,  $J = 6.3$ , 12.0 Hz), 2.43 (1H, ddt,  $J = 2.4$ , 4.5, 13.7 Hz), 2.33 (1H, dt,  $J = 6.0$ , 13.7 Hz), 2.23 (1H, m), 2.08 (3H, s), 2.03 (1H, dq,  $J = 2.8$ , 6.0, 13.0 Hz), 1.91 (1H, m), 1.70 (2H, m), 1.56 (1H, tq,  $J = 3.8$ , 13.0 Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  204.67, 170.06, 76.61, 40.73, 33.10, 27.21, 23.79, 20.78. ES-API  $m/z$ :  $M^+$  157.1. The spectral data are in agreement with previous reports.<sup>10,12,14</sup>



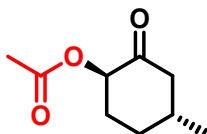
**3j**

**2-Oxocycloheptyl, acetate (3j):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.19 (1H, dd,  $J = 3.5$ , 9.8 Hz), 2.60 (1H, dt,  $J = 5.6$ , 16.6 Hz), 2.38 (1H, ddd,  $J = 4.5$ , 10.9, 15.8 Hz), 2.08 (3H, s), 1.95 (1H, dq,  $J = 3.1$ , 13.7 Hz), 1.80 (3H, m), 1.70 (2H, m), 1.59 (1H, qd,  $J = 2.4$ , 10.6 Hz), 1.31 (1H, m).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  207.75, 170.30, 78.21, 40.74, 30.34 (2C), 28.52, 26.51, 23.06, 20.80. ES-API  $m/z$ :  $M^+$  171.1. The spectral data are in agreement with previous reports.<sup>15,16</sup>



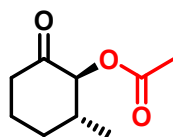
*cis*-3n-5

**Cis-4-methyl-2-oxocyclohexyl, acetate (*cis*-3n-5):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.01 (1H, dd,  $J = 6.3, 10.9$  Hz), 2.48 (1H, dd,  $J = 5.3, 12.7$  Hz), 2.20 (1H, m), 2.17 (1H, m), 2.05 (3H, s), 1.95 (1H, m), 1.92 (1H, m), 1.67 (1H, m), 1.52 (1H, dd,  $J = 2.8, 13.4$  Hz), 0.95 (3H, d,  $J = 6.3$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  204.97, 170.10, 76.46, 46.77, 34.33, 31.63, 24.42, 22.21, 20.73. ES-API  $m/z$ :  $M^+$  171.1.



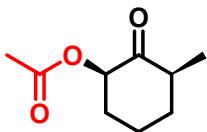
*trans*-3n-5

**Trans-4-methyl-2-oxocyclohexyl, acetate (*trans*-3n-5):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.05 (1H, ddd,  $J = 1.0, 6.7, 12.7$  Hz), 2.35 (1H, ddd,  $J = 2.8, 3.8, 13.4$  Hz), 2.16 (1H, m), 2.05, (3H, s), 2.05 (1H, m), 1.84 (1H, m), 1.77 (1H, m), 1.66 (1H, qd,  $J = 3.5, 13.4$  Hz), 1.42 (1H, qd,  $J = 3.5, 13.4$  Hz), 0.95 (3H, d,  $J = 6.3$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  203.99, 170.00, 76.26, 48.61, 35.03, 32.16, 31.63, 22.11, 20.73. ES-API  $m/z$ :  $M^+$  171.1.



*trans*-3n-2

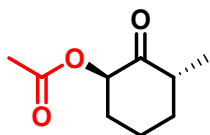
**Trans-(3-methyl-2-oxocyclohexyl) acetate (*trans*-3n-2):** The mixture of isomers could not be separated by chromatography over silica gel, however, **15b** was also present in the reaction mixture as evidenced by the signal at 5.15 ppm  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz).



*cis*-3o-2

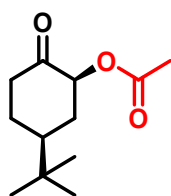
**Cis-3-methyl-2-oxocyclohexyl, acetate (*cis*-3o-2):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.12 (1H, ddd,  $J = 1.0, 6.3, 12.3$  Hz), 2.48, (1H, septd,  $J = 1.06, 6.36$  Hz), 2.28 (1H, m), 2.13 (3H, s), 2.11 (1H, m), 2.05, (1H, m), 1.82 (1H, m), 1.72 (1H, m), 1.32 (1H, ddd,  $J = 3.8, 13.0$  Hz) 1.03 (3H, d,  $J = 6.3$  Hz).  $^{13}\text{C}$  $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$

206.13, 170.05, 76.79, 44.34, 36.13, 33.49, 28.00, 20.82, 13.94. ES-API  $m/z$ :  $M^+$  171.1.



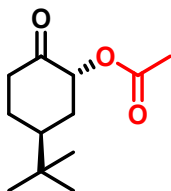
*trans-3o-2*

**Trans-3-methyl-2-oxocyclohexyl, acetate (*trans-3o-2*):** The mixture of isomers could not be separated by chromatography over silica gel. However, ***trans-3o-2*** was also present in the reaction mixture as evidenced by the signal at 5.13 ppm and 2.65 ppm correspondingly  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz).



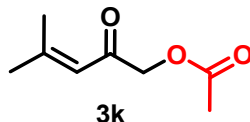
*cis-3p*

**Cis-4-tert-butyl-2-oxocyclohexyl, acetate (*cis-3p*):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  5.17 (1H, ddd, ,  $J = 1.0, 6.3, 13.0$  Hz), 2.45 (1H, dq, ,  $J = 2.4, 4.2, 13.7$  Hz), 2.37 (1H, ddd, ,  $J = 1.0, 6.0, 13.7$  Hz), 2.27 (1H, dq, ,  $J = 2.18, 12.01$  Hz) 2.11 (3H, s), 2.07 (2H, m), 1.66 (1H, tt, ,  $J = 2.8, 12.3$  Hz) 1.53 (1H, q,  $J = 12.3$  Hz), 1.39 (1H, qd,  $J = 4.5, 13.4$  Hz), 0.89 (9H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  205.01, 170.08, 76.22, 45.83, 39.56, 34.25, 32.51, 27.65, 20.82. ES-API  $m/z$ :  $M^+$  213.1. The spectral data are in agreement with previous reports.<sup>17</sup>

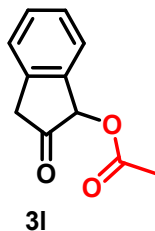


*trans-3p*

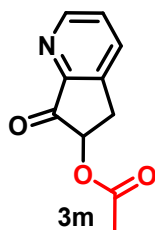
**Trans-4-tert-butyl-2-oxocyclohexyl, acetate (*trans-3p*):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.15992 MHz):  $\delta$  5.05 (1H, t,  $J = 5.6$  Hz), 2.54 (1H, ddd,  $J = 2.4, 6.0, 15.1$  Hz), 2.40 (1H, m), 2.15 (3H, s), 2.01 (2H, m), 1.80 (2H, m), 1.59 (1H, m), 0.90 (9H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125.7653 MHz):  $\delta$  208.30, 170.01, 75.56, 41.72, 41.36, 31.71, 29.75, 27.76, 20.99. ES-API  $m/z$ :  $M^+$  213.1. The spectral data are in agreement with previous reports<sup>17</sup> and it was determined as mixture with compound ***cis-3p***.



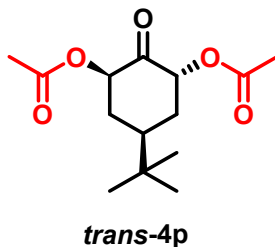
**4-Methyl-2-oxopent-3-enyl, acetate (3k):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  6.00 (1H, septet,  $J = 1.0$  Hz), 4.61 (2H, s), 2.13 (3H, d,  $J = 1.0$  Hz), 2.12 (3H, s), 1.88 (3H, d,  $J = 1.0$  Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  203.60, 170.38, 159.41, 118.93, 68.79, 23.01, 21.31, 20.62. ES-API  $m/z$ :  $M^+$  157.1. The spectral data are in agreement with previous reports.<sup>18</sup>



**2-Oxo-1,3-dihydroinden-1-yl, acetate (3l):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.36 (4H, m), 5.97 (1H, s), 3.60 (1H, d,  $J = 22.0$  Hz), 3.67 (1H, d,  $J = 22.0$  Hz), 2.17 (3H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  209.53, 170.33, 137.18, 136.95, 129.71, 128.10, 125.31, 125.27, 75.38, 41.40, 20.69. ES-API  $m/z$ :  $M^+$  192.1. The spectral data are in agreement with previous reports.<sup>19</sup>



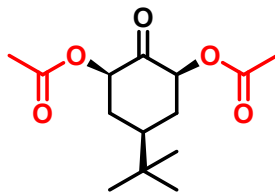
**7-Oxo-5,6-dihydrocyclopenta[b]pyridin-6-yl, acetate (3m):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.81 (1H, d,  $J = 4.2$  Hz), 7.85 (1H, d,  $J = 7.7$  Hz), 7.50 (1H, dd,  $J = 4.5, 8.1$  Hz), 5.41 (1H, dd,  $J = 4.9, 8.1$  Hz), 3.68 (1H, dd,  $J = 8.12, 17.3$  Hz), 3.08 (1H, dd,  $J = 4.9, 17.31$  Hz), 2.18 (3H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  199.55, 170.38, 151.80, 151.64, 146.05, 135.36, 128.56, 72.77, 31.65, 20.75. ES-API  $m/z$ :  $M^+$  192.0.



**Trans,Cis-5-(tert-butyl)-2-oxocyclohexane-1,3-diyl, diacetate (trans-4p):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.15992 MHz):  $\delta$  5.54 (1H, dd,  $J = 6.3, 12.7$  Hz), 5.12 (1H, t,  $J = 2.8$



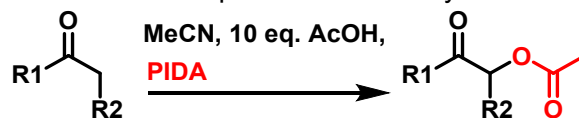
Hz), 2.33 (1H, m), 2.29 (1H, m), 2.14 (3H, s), 2.13 (3H, s), 1.97 (1H, tt,  $J = 3.5, 12.7$  Hz), 1.55 (1H, m), 1.54 (1H, q,  $J = 12.7$  Hz), 0.91 (9H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125.7653 MHz):  $\delta$  201.26, 169.74, 169.39, 76.18, 73.82, 39.78, 34.62, 33.56, 27.66, 27.55, 20.96, 20.74. ES-API  $m/z$ :  $M^+$  271.1.



***cis-4p***

***Cis, Cis-5-(tert-butyl)-2-oxocyclohexane-1,3-diyloxy diacetate (cis-4p)***: ES-API  $m/z$ :  $M^+$  271.1. The mixture of isomers could not be separated by chromatography over silica gel. However, ***cis-4p*** was also present in the reaction mixture as evidenced by the signal at 5.27 ppm correspondingly  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.15992 MHz).

**Table S1.** Scope of the  $\alpha$ -acetoxy ketones.

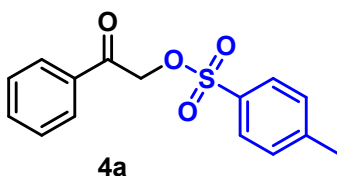


Entry	Product	Temp. (°C)	Conversion (%) <sup>a</sup>
1	<b>3a</b>	70	67 (60)
2	<b>3b</b>	70	98 (73)
3	<b>3c</b>	70	0
4	<b>3d-1 : 3d-3</b>	70	75 <sup>b</sup> [ <b>3d-1 : 3d-3</b> 2.57:1]
5	<b>3e-1 : 3e-3</b>	70	95 <sup>b</sup> [ <b>3e-1 : 3e-3</b> 3.50:1]
6	<b>3f</b>	60	80 (65)
7	<b>3g</b>	60	50 <sup>d</sup> (25)
8	<b>3h</b>	70	75 (70)
9	<b>3i</b>	70	91 (85)
10	<b>3j</b>	70	77 (72)
11	<b>3k</b>	60	72 (60)
12	<b>3l</b>	40	60 (55)
13	<b>3m</b>	40	70 (68)
	<b><i>cis</i>-3n-5 : <i>trans</i>-3n-5 : <i>cis</i>-3n-2 : <i>trans</i>-3n-2</b>	70	93 <sup>c</sup> [ <b><i>cis</i>-3n-5 : <i>trans</i>-3n-5 : <i>cis</i>-3n-2 : <i>trans</i>-3n-2</b> 1.15:2.85:0:1]
14	<b><i>cis</i>-3o-2 : <i>trans</i>-3o-2</b>	70	73 <sup>c</sup> [ <b><i>cis</i>-3o-2 : <i>trans</i>-3o-2</b> 1:1.63]
15	<b><i>cis</i>-3p : <i>trans</i>-3p</b>	70	90 <sup>c</sup> [ <b><i>cis</i>-3p : <i>trans</i>-3p</b> 7.33:1]

a) The percent conversion was determined from the crude reaction mixture by <sup>1</sup>H NMR spectroscopy. The yield % is in parenthesis and the selectivity ratio in brackets. b) Conversion calculated in the mixture. c) Direct determination from the crude reaction in order to prevent the loss due to the evaporation of the solvent.

## Cross-over acid experiment

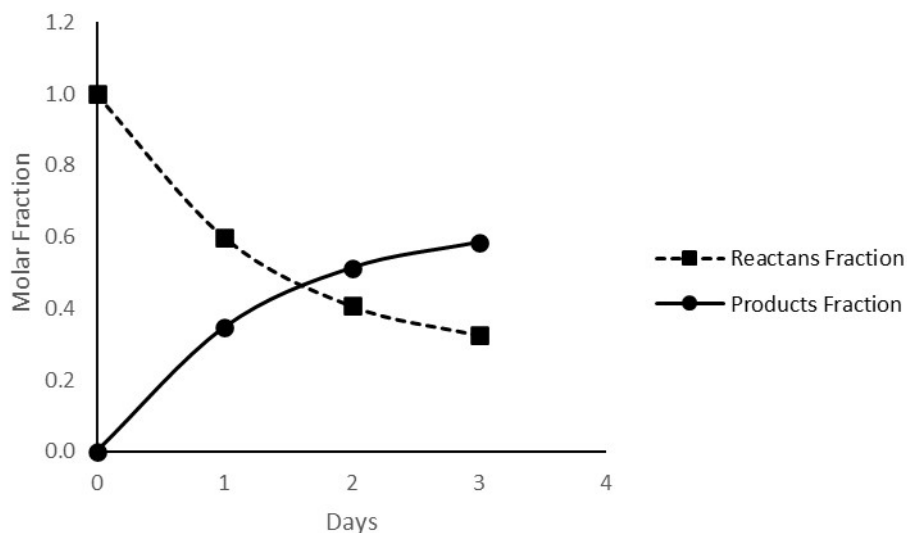
**General procedure:** In a round-bottom flask, 0.17 mL (1.46 mmol) of acetophenone, 0.96 g (2.98 mmol) of  $\text{PhI}(\text{OAc})_2$ , and the corresponding equivalents of *p*-TsOH monohydrate and acetic acid were added in 3 mL of acetonitrile. The reaction mixture was stirred for 3 d at 70°C and allowed to cool to room temperature. After work-up, the solvent was removed under vacuum and the crude reaction mixture was analyzed by  $^1\text{H}$  NMR.



**2-Oxo-2-phenylethyl 4-methylbenzenesulfonate (4a):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.82 (2H, d,  $J = 8.5$  Hz), 7.81 (2H, dd,  $J = 8.1, 1.1$  Hz), 7.58 (1H, tt,  $J = 7.4, 1.1$  Hz), 7.44 (2H, dd,  $J = 8.1, 7.4$  Hz), 7.31 (2H, d,  $J = 8.5$  Hz), 5.25 (2H, s), 2.41 (3H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  190.44, 145.44, 134.31, 133.81, 132.68, 130.03, 129.01, 128.21, 128.06, 70.10, 21.76. The spectral data are in agreement with previous reports.<sup>20,21</sup>

## Kinetic determination of 3a the obtention

**Procedure:** In a round-bottom flask, 0.17 mL (1.46 mmol) of acetophenone and 0.72 g (2.24 mmol) of  $\text{PhI}(\text{OAc})_2$  were dissolved in 3 mL of acetonitrile, and 0.85 mL (14.85 mmol) of acetic acid were added. The reaction mixture was stirred and monitored for 3 d at 70°C; each aliquot was taken per day. For the analysis of the aliquots, the solvent was removed under vacuum and the crude reaction mixture was analyzed by  $^1\text{H}$  NMR.



**Figure S1.** Kinetic  $\alpha$ -acetoxylation of acetophenone.

## Kinetic study of the 4-*tert*-butylcyclohexanone

Equation for kinetic determination.

The equations and methodology for the management of the kinetic data were consulted in the bibliography.<sup>22</sup>

[A] = Concentration of reactant 1.

[A]<sub>0</sub> = The initial concentration of reactant 1.

[B] = Concentration of reactant 2.

[B]<sub>0</sub> = The initial concentration of reactant 2.

[P] = Total product.

$k$  = rate constant of the reaction.

$k'$  = Observable constant rate of the reaction.

$t$  = time.

$$rate = k[A]$$

(Eq 1)

Estimated product equation:

$$[P] = rate * t$$

(Eq 2)

Zero order equation:

$$[A]_0 - [A] = kt$$

(Eq 3)

First order equation:

$$\ln\left(\frac{[A]_0}{[A]_0 - [P]}\right) = kt$$

(Eq 4)

Second order equation:

$$\left(\frac{1}{[B]_0 - [A]_0}\right) \ln\left(\frac{[A]_0[B]}{[B]_0[A]}\right) = kt$$

(Eq 5)

Pseudo first order equation:

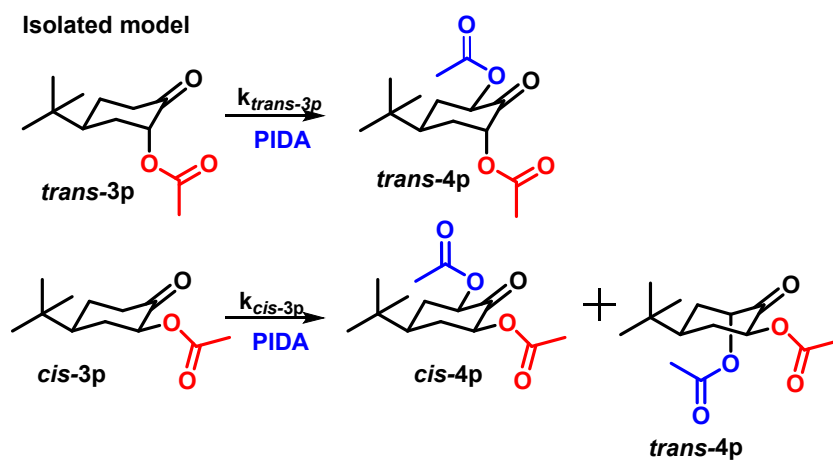
$$\ln\left(\frac{[A]_0}{[A]_0 - [P]}\right) = k't$$

(Eq 6)

$$k[A][B]_0 = k'[A]$$

(Eq 7)

Approximation for isolate model:



$$\ln [PIDA] = k'_{PIDA} t \quad (\text{Eq 8})$$

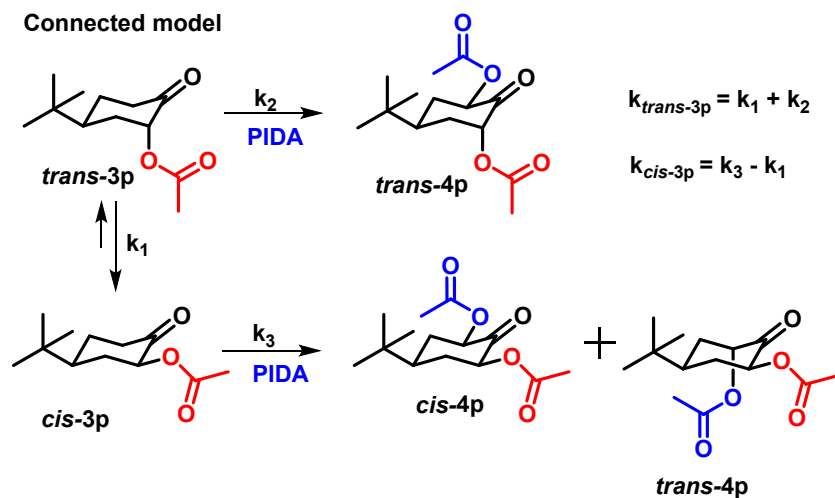
$$k'_{PIDA} ([trans - 3P]_0 + ([cis - 3P]_0)) = k_{PIDA} = k_{trans - 3p} + k_{cis - 3p} \quad (\text{Eq 9})$$

$$-k_{PIDA} \cong k_{P \text{ total}} = k_{trans - 4p} + k_{cis - 4p} \quad (\text{Eq 10})$$

$$\ln \left( \frac{([trans - 3P]_0 + ([cis - 3P]_0))}{([trans - 3P]_0 + ([cis - 3P]_0) - [trans - 4P])} \right) = k_{trans - 4P} t \quad (\text{Eq 11})$$

$$\ln \left( \frac{[cis - 3P]_0}{[cis - 3P]_0 - [trans - 4P]} \right) = k_{cis - 4P} t \quad (\text{Eq 12})$$

Approximation for connect model:



$$k'_{cis - 3p} \llll k'_{trans - 3P} \quad (\text{Eq 13})$$

$$k' \cong k'_{trans-3P}$$

(Eq 14)

$$\ln([trans-3P]) = k' t$$

(Eq 15)

$$k' [PIDA] = k = k_{trans-3P} + k_{cis-3P}$$

(Eq 16)

$$k_{trans-3P} = k_1 + k_2$$

(Eq 17)

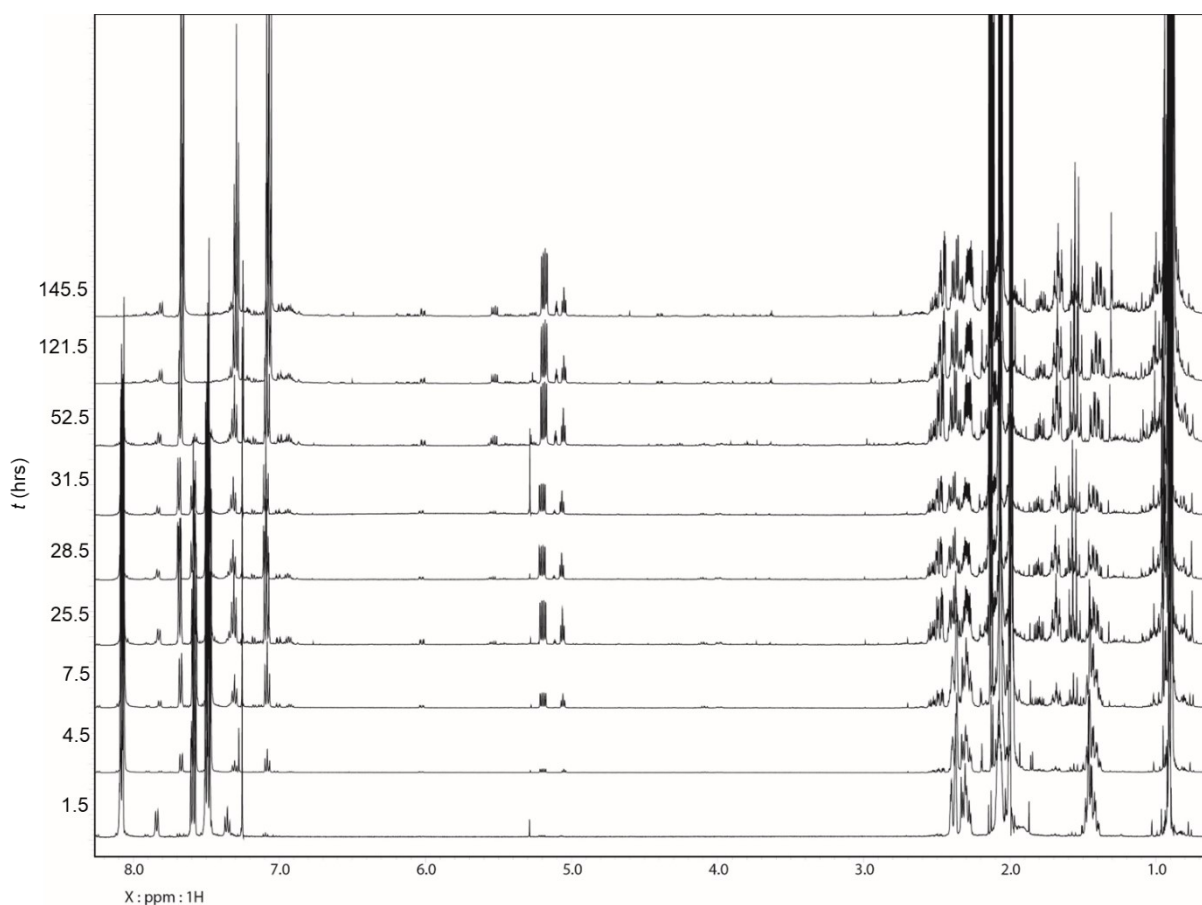
$$k_{cis-3P} = k_3 - k_1$$

(Eq 18)

## Experimental part for kinetic determination.

First- $\alpha$ -acetoxylation.

**Procedure:** In a round-bottom flask, 0.23 g (1.49 mmol) of 4-*tert*-butylcyclohexanone and 0.96 g (2.98 mmol) of  $\text{PhI}(\text{OAc})_2$  were dissolved in 3mL of acetonitrile, and 0.85mL (14.85 mmol) of acetic acid were added. The reaction mixture was stirred and monitored for 6 d at 70°C; each aliquot was taken per period showed in the table S1. For the analysis of the aliquots, the solvent was removed under vacuum and the crude reaction mixture was analyzed by  $^1\text{H}$  NMR.



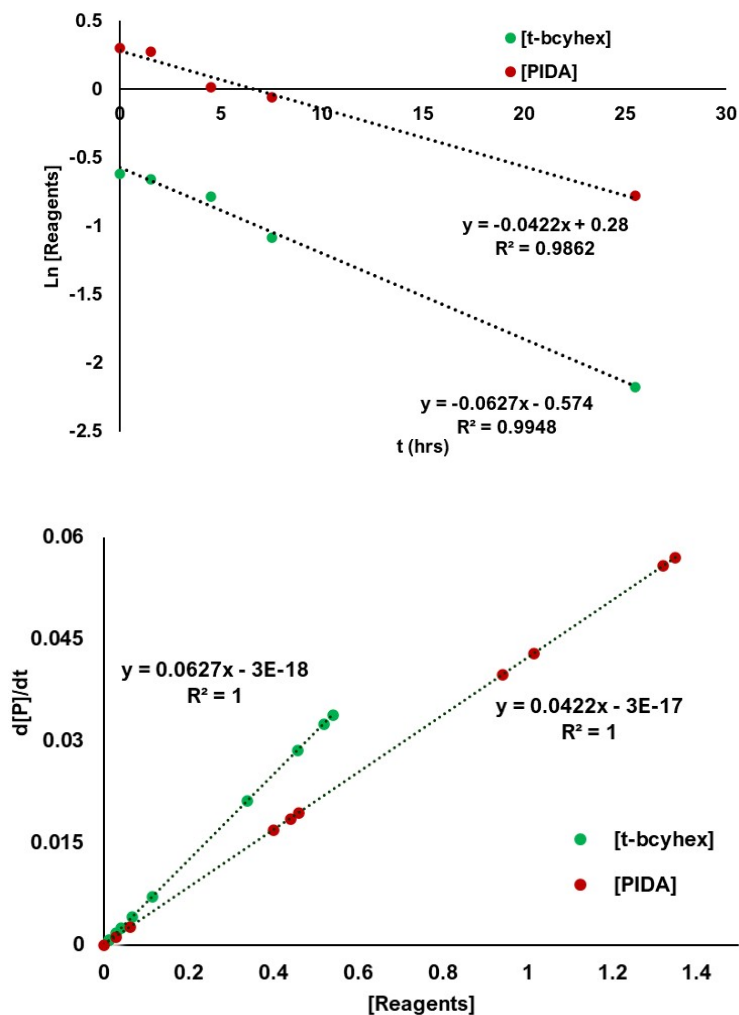
**Figure S2.** Kinetic  $\alpha$ -acetoxylation of 4-*tert*-butylcyclohexanone.



Table S1. Concentration of the reactants and products in the kinetic experiment of 4-*tert*-butylcyclohexanone.

Time (hrs)	[PIDA] (M)	[ <i>t</i> -bcyhex] (M)	[ <i>cis</i> -3p] (M)	[ <i>trans</i> -3p] (M)	[ <i>trans</i> -4p] (M)	[ <i>cis</i> -4p] (M)	[P] (M)
0	1.3506	0.5402	0	0	0	0	0
1.5	1.3203	0.5186	0.0144	0.0073	0	0	0.0217
4.5	1.0155	0.4566	0.0494	0.0254	0	0	0.0749
7.5	0.9421	0.3381	0.1243	0.0594	0	0	0.1838
25.5	0.4590	0.1138	0.2831	0.1197	0.0162	0.0072	0.4028
28.5	0.4405	0.0661	0.3036	0.1268	0.0177	0.0102	0.4305
31.5	0.4007	0.0397	0.3253	0.1245	0.0287	0.0216	0.4499
52.5	0.0625	0.0109	0.3432	0.1073	0.0376	0.0160	0.4506
121.5	0.0295	0.0292	0.3356	0.0848	0.0343	0.0155	0.4205
145.5	0	0.0127	0.3695	0.0881	0.0393	0.0089	0.4576

Pseudo-first order reaction method.



**Figure S3.** Top: Graphic of time VS natural logarithm (Ln) on the reagent concentrations in the mono  $\alpha$ -acetoxilation. Bottom: Graphic of the reagent concentration VS the reaction rates in the mono  $\alpha$ -acetoxilation

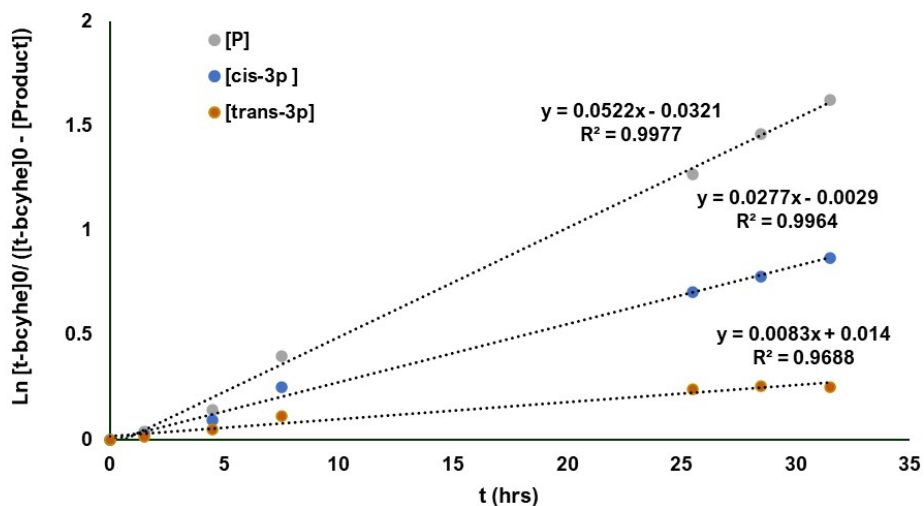
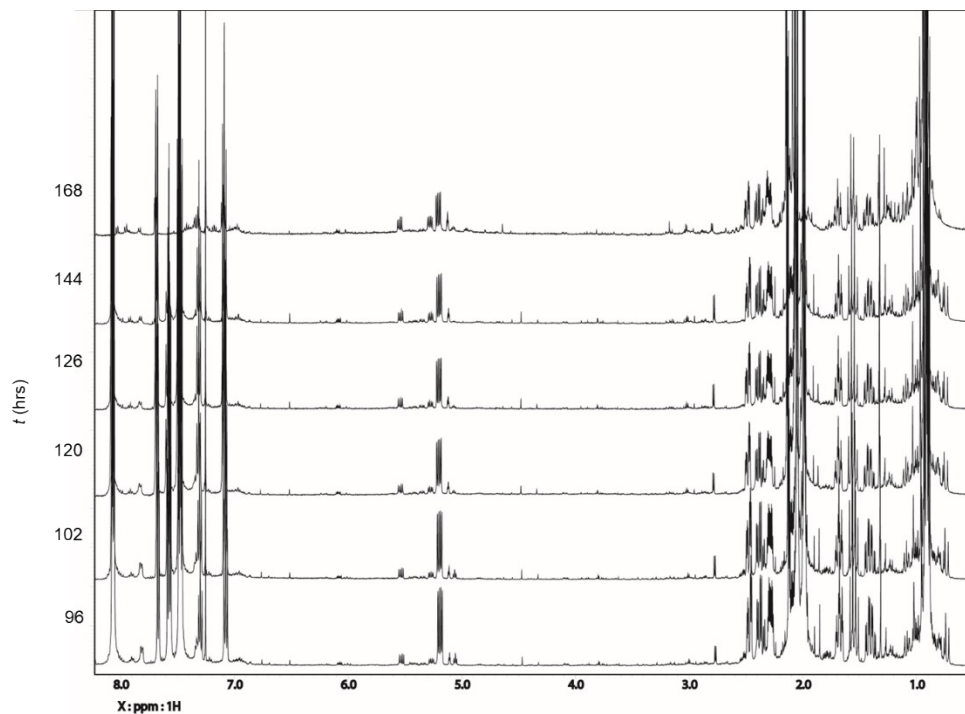


Table S2. Calculated rates and products with estimated constants rates.

Time (hrs)	Calculated rates		Calculated products		
	$d[\text{cis-3}]/dt$	$d[\text{trans-3p}]/dt$	$[\text{cis-3p}]$ (M)	$[\text{cis-3p}]$ (M)	$[\text{P}]$ (M)
0	0	0	0	0	0
1.5	0.0335	0.0095	0.0503	0.0142	0.0835
4.5	0.0258	0.0073	0.1162	0.0329	0.1928
7.5	0.0239	0.0067	0.1797	0.0508	0.2982
25.5	0.0116	0.0033	0.2977	0.0842	0.4939
28.5	0.0112	0.0031	0.3194	0.0904	0.5299
31.5	0.0101	0.0028	0.3211	0.0908	0.5326
		Error:	73.35%	37.52%	94.57%

Second- $\alpha$ -acetoxylation.

**Procedure:** In a round-bottom flask, 0.0885 g (0.41 mmol) of the mixture of **cis-3n-6** and **trans-3n-6** (9:1) and 0.375 g (1.16 mmol) of  $\text{PhI}(\text{OAc})_2$  were dissolved in 1.2 mL of acetonitrile, and 0.32 mL (5.59 mmol) of acetic acid were added. The reaction mixture was stirred and monitored for 7 d at 70°C; each aliquot was taken per period showed in the table S3. For the analysis of the aliquots, the solvent was removed under vacuum and the crude reaction mixture was analyzed by  $^1\text{H}$  NMR.

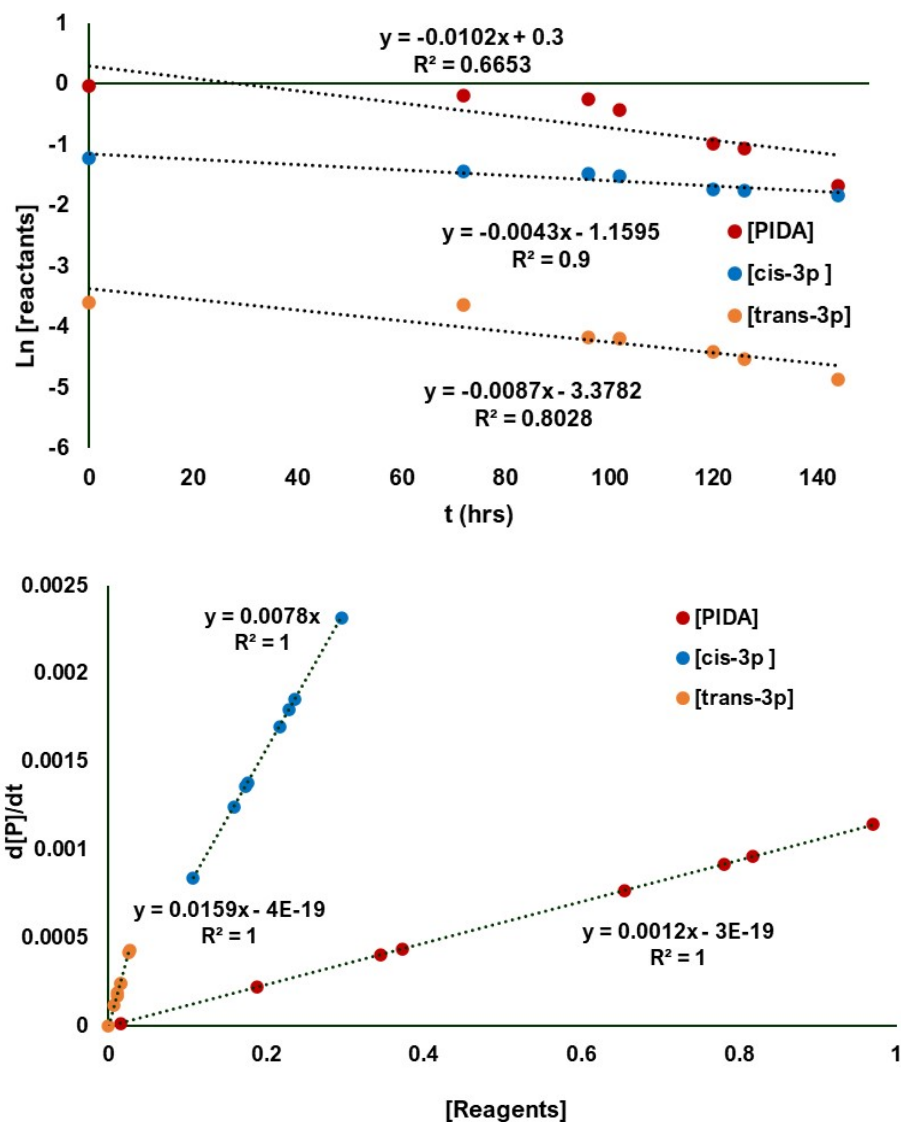


**Figure S4.** Kinetic  $\alpha$ -acetoxylation of **3p**.

Table S3. Concentration of the reactants and products in the kinetic experiment of 4-*tert*-butylcyclohexanon.

Time (hrs)	[PIDA] (M)	[ <i>cis</i> -3p] (M)	[ <i>trans</i> -3p] (M)	[ <i>trans</i> -4p] (M)	[ <i>cis</i> -4p] (M)
0	0.9701	0.2959	0.0273	0	0
72	0.8180	0.2369	0.0263	0.0176	0.0194
96	0.7807	0.2292	0.0155	0.0193	0.0197
102	0.6543	0.2170	0.0152	0.0205	0.0225
120	0.3723	0.1765	0.0121	0.0267	0.0343
126	0.3459	0.1736	0.0107	0.0269	0.0346
144	0.1887	0.1588	0.0076	0.0289	0.0422
168	0.0155	0.1073	0	0.0349	0.0612

Pseudo-first order reaction method.



**Figure S5.** Top: graphic of the time VS mono and di  $\alpha$ -acetoxylation products of t-bcyhex. Bottom: graphic of the reagent concentration VS the reaction rates in the di  $\alpha$ -acetoxylation.

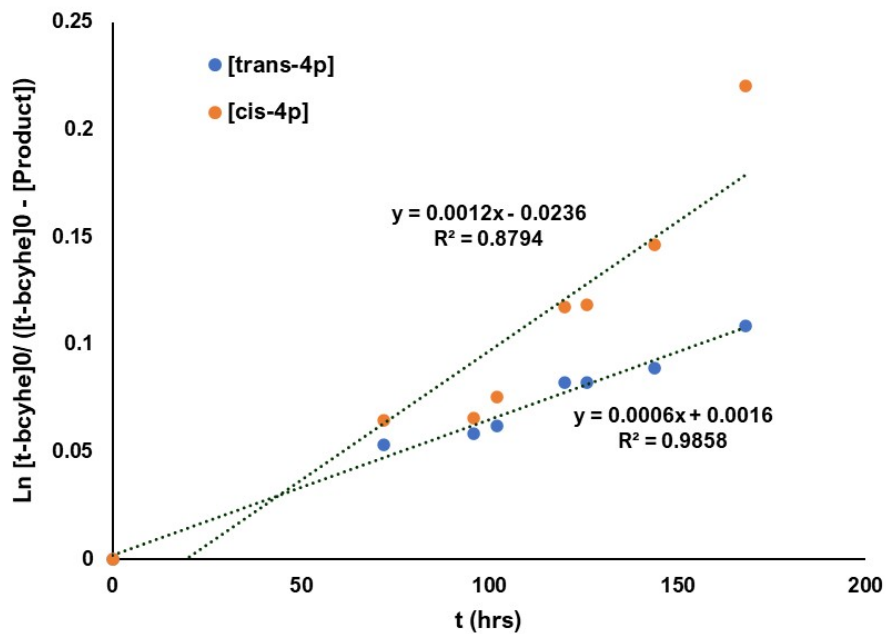
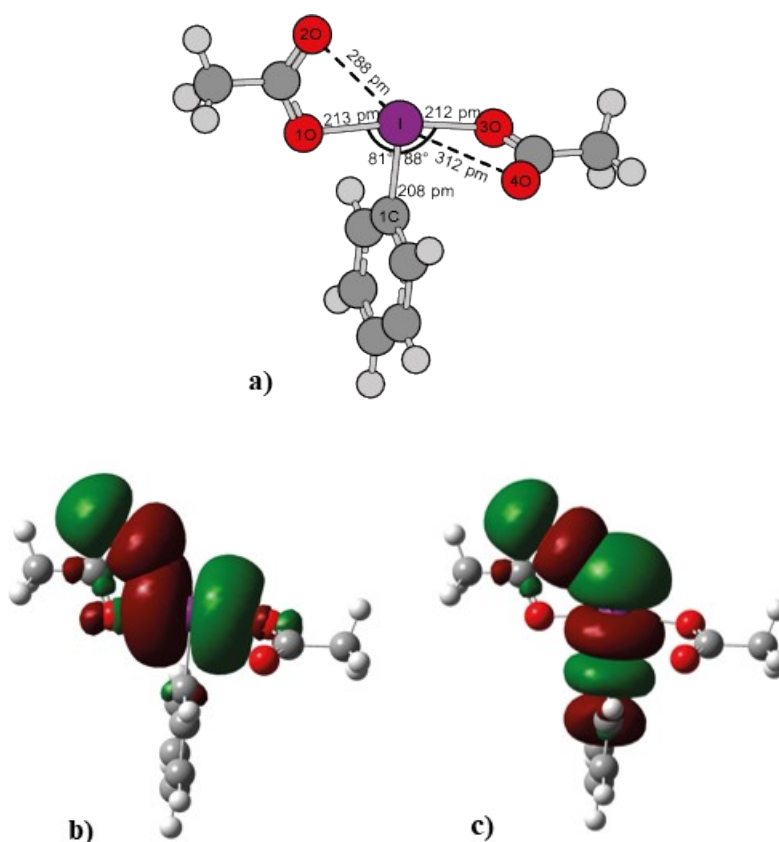


Table S4. Calculated rates and products of the two models with estimated constants rates.

Time (hrs)	Calculated rates					Calculated products			
	Isolated model		Connected model			Isolated model		Connected model	
	$\frac{d[\text{trans-4p}]}{dt}$	$\frac{d[\text{cis-4p}]}{dt}$	$\frac{d[\text{trans-4p}]}{dt}$	$\frac{d[\text{trans-4p}]}{dt}$	$\frac{d[\text{cis-4p}]}{dt}$	$[\text{trans-4p}]$ (M)	$[\text{cis-4p}]$ (M)	$[\text{trans-4p}]$ (M)	$[\text{cis-4p}]$ (M)
0	0.0003	0.0007	0.0003	0.00004	0.0003	0.0000	0.0000	0.0000	0.0000
72	0.0002	0.0005	0.0003	0.00004	0.0002	0.0148	0.0379	0.0243	0.0174
96	0.0002	0.0005	0.0002	0.00002	0.0002	0.0183	0.0488	0.0191	0.0224
102	0.0002	0.0005	0.0002	0.00002	0.0002	0.0185	0.0491	0.0199	0.0226
120	0.0001	0.0004	0.0001	0.00002	0.0002	0.0177	0.0470	0.0186	0.0216
126	0.0001	0.0004	0.0001	0.00002	0.0002	0.0181	0.0486	0.0174	0.0223
144	0.0001	0.0004	0.0001	0.00001	0.0002	0.0187	0.0508	0.0142	0.0233
					Error:	22.59%	76.30%	26.53%	23.65%

## Computational details

The optimization of the geometries and calculation of the frequencies were carried using functional  $\omega$ B97X-D<sup>23</sup> with the basis set Def2TZVP<sup>24</sup> for C, H and O, and LANL2DZ for iodine atoms, with effective core potential and the addition of polarization (P) and diffuse (D) functions.<sup>25,26</sup> The addition of P and D functions to the LANL2DZ leads to geometries closer to those obtained by experimental methods as described previously by Cerioni and coworkers.<sup>27</sup> The free energy data was obtained with thermal correction in the frequency calculations. The NBO analysis was carried out with the basis set AUG-cc-pVTZ for C, H, and O atoms and AUG-cc-pVDZ-PP for I with effective core potential as described by Peterson.<sup>28</sup> The basis sets were obtained from Basis Set Exchange data base.<sup>29</sup> The NBO analysis included a solvation model (SMD) on acetonitrile. All the calculations were carried out using the Gaussian 09 suite.<sup>30</sup>



**Figure S6.** a) PIDA structure optimized by theoretical calculations. b) Orbital Interaction of the orbitals LP 2O to I LP\* of PIDA. c) Interaction of the orbitals 2O LP to I-1C  $\sigma^*$  (Iodine  $\sigma$ -hole) of PIDA.

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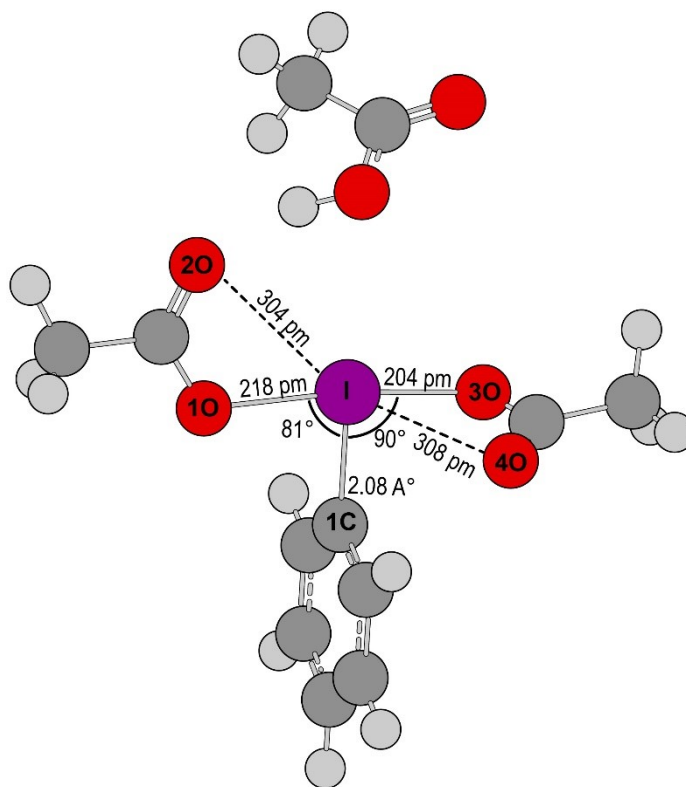
**PIDA**

Zero-point correction= 0.194314 Hartree  
Thermal correction to Energy= 0.211129 Hartree  
Thermal correction to Enthalpy= 0.212073 Hartree  
Thermal correction to Gibbs Free Energy= 0.145779 Hartree  
Sum of electronic and zero-point Energies= -699.783163 Hartree  
Sum of electronic and thermal Energies= -699.766348 Hartree  
Sum of electronic and thermal Enthalpies= -699.765404  
Hartree  
Sum of electronic and thermal Free Energies= -699.831698  
Hartree

Label	Symbol	X	Y	Z
1	C	-0.5774439	1.1340211	-0.0833819
2	C	-0.5407416	1.9916287	-1.1695529
3	C	-1.2028173	3.2055033	-1.0784005
4	C	-1.8842839	3.5411160	0.0819434
5	C	-1.9082303	2.6663412	1.1569215
6	C	-1.2494231	1.4479419	1.0844582
7	H	-0.0061657	1.7256336	-2.0708955
8	H	-1.1844836	3.8876358	-1.9182461
9	H	-2.4011273	4.4899532	0.1473860
10	H	-2.4421997	2.9273921	2.0611580
11	H	-1.2806599	0.7494808	1.9079283
12	I	0.4289667	-0.6907538	-0.2186670
13	O	2.1153612	0.5542135	0.1875642
14	O	-1.4182086	-1.5915426	-0.7398084
15	C	-2.2721369	-1.8578683	0.2319494
16	O	-2.1043230	-1.5508124	1.3902832
17	C	3.2141983	-0.1626968	0.2138144
18	O	3.2203067	-1.3624263	0.0191728
19	C	4.4512945	0.6435040	0.5078315
20	H	5.3232825	-0.0046183	0.5020098
21	H	4.5624575	1.4304786	-0.2383283
22	H	4.3488515	1.1250999	1.4805976
23	C	-3.4956001	-2.5837716	-0.2677958
24	H	-4.1530583	-2.8153035	0.5657613
25	H	-4.0172711	-1.9569590	-0.9918343
26	H	-3.1988473	-3.4986184	-0.7806024

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**Figure S7.** Activated PIDA with acetic acid structure optimized by theoretical calculations.

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**PIDA-Acetic Acid**

Zero-point correction= 0.257737 Hartree  
 Thermal correction to Energy= 0.281003 Hartree  
 Thermal correction to Enthalpy= 0.281947 Hartree  
 Thermal correction to Gibbs Free Energy= 0.196523 Hartree  
 Sum of electronic and zero-point Energies= -928.841352 Hartree  
 Sum of electronic and thermal Energies= -928.818087 Hartree  
 Sum of electronic and thermal Enthalpies= -928.817143 Hartree  
 Sum of electronic and thermal Free Energies= -928.902566 Hartree

Label	Symbol	X	Y	Z
1	C	2.0616060	-0.2834320	-0.2415730
2	C	2.5121750	-0.8607700	-1.4164290
3	C	3.8756940	-1.0395310	-1.5852950
4	C	4.7580980	-0.6422010	-0.5916480
5	C	4.2839050	-0.0648000	0.5758740
6	C	2.9221180	0.1186420	0.7645340
7	H	1.8194260	-1.1691210	-2.1870810
8	H	4.2460980	-1.4885900	-2.4974590

9	H	5.8224780	-0.7820480	-0.7299940
10	H	4.9730330	0.2468120	1.3497220
11	H	2.5420690	0.5851200	1.6621410
12	I	0.0083220	-0.0167550	0.0199520
13	O	0.0877990	-2.1713280	0.3531890
14	O	0.1971990	1.9867120	-0.4829370
15	C	0.5576230	2.8315330	0.4783700
16	O	0.9660650	2.4849180	1.5599070
17	C	-1.0652870	-2.7258170	0.5513990
18	O	-2.1298490	-2.1162050	0.5554700
19	C	-0.9997210	-4.2116390	0.7882870
20	H	-2.0025480	-4.6244530	0.8545110
21	H	-0.4422540	-4.6910060	-0.0159060
22	H	-0.4606600	-4.3992160	1.7176710
23	C	0.3876040	4.2642690	0.0536130
24	H	0.7797690	4.9244100	0.8221870
25	H	0.8967220	4.4363650	-0.8943190
26	H	-0.6740030	4.4605140	-0.1020080
27	O	-3.1011680	0.4371940	0.5759280
28	H	-2.9389830	-0.5242820	0.6308970
29	C	-3.9617050	0.7416950	-0.4098610
30	C	-4.5599260	-0.4444600	-1.1258430
31	H	-5.1398880	-1.0465090	-0.4240960
32	H	-5.2021760	-0.0966900	-1.9294740
33	H	-3.7707970	-1.0841740	-1.5244800
34	O	-4.2103570	1.8837020	-0.6663470

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**2p-Ax**

Zero-point correction= 0.397524 Hartree  
Thermal correction to Energy= 0.421939 Hartree  
Thermal correction to Enthalpy= 0.422883 Hartree  
Thermal correction to Gibbs Free Energy= 0.340053 Hartree  
Sum of electronic and zero-point Energies= -937.646044 Hartree  
Sum of electronic and thermal Energies= -937.621629 Hartree  
Sum of electronic and thermal Enthalpies= -937.620684  
Hartree  
Sum of electronic and thermal Free Energies= -937.703514  
Hartree

Label	Symbol	X	Y	Z
1	C	1.9022720	0.0946240	0.8612080
2	C	2.4322970	-0.4302350	-0.4754760
3	C	2.9650470	-1.8483820	-0.2508960
4	C	1.8813750	-2.7843970	0.2894150
5	H	3.3491440	-2.2732200	-1.1773320
6	H	1.5834240	-0.5133570	-1.1670320
7	H	2.7266270	0.1193130	1.5826060
8	H	1.5460540	1.1207760	0.7769150
9	H	1.1276350	-2.9461540	-0.4918020
10	H	2.2790840	-3.7639460	0.5513900
11	H	3.8015940	-1.8192340	0.4541570
12	C	3.4307600	0.5416350	-1.1640640
13	C	4.6094100	0.9007750	-0.2540860
14	H	5.3246300	1.5220140	-0.7974260
15	H	4.2887970	1.4645180	0.6236180
16	H	5.1422920	0.0112980	0.0879880
17	C	3.9735850	-0.0948780	-2.4491570
18	H	3.1616370	-0.4664340	-3.0797600
19	H	4.5328100	0.6439160	-3.0266120
20	H	4.6504290	-0.9246200	-2.2423600
21	C	2.6940230	1.8280520	-1.5590160
22	H	3.3681290	2.4999060	-2.0944420
23	H	1.8504840	1.6070150	-2.2180680
24	H	2.3105460	2.3728060	-0.6954950
25	C	1.1413620	-2.2433710	1.4919710
26	O	0.7949760	-2.9485200	2.4087290
27	C	0.8080710	-0.7751060	1.4653590
28	H	0.5472150	-0.4666420	2.4756070
29	I	-1.1284170	-0.6395120	0.3405930
30	C	-1.0278340	1.4441450	0.5562420
31	C	-0.9062580	2.2257940	-0.5775930
32	C	-1.0516900	1.9938220	1.8248610
33	C	-0.7893090	3.5989620	-0.4291950
34	H	-0.9173410	1.7765490	-1.5601730
35	C	-0.9319370	3.3692190	1.9586970
36	H	-1.1641640	1.3697340	2.7013510
37	C	-0.7966790	4.1692380	0.8347150
38	H	-0.6918220	4.2224020	-1.3083520
39	H	-0.9517560	3.8124820	2.9457240
40	H	-0.7037720	5.2419750	0.9438550
41	O	-3.0433130	0.0398000	-0.7889270
42	C	-3.5908690	-1.0033480	-1.3206380
43	C	-4.8662950	-0.7229240	-2.0872910
44	H	-5.6157900	-0.3202650	-1.4045470
45	H	-4.6803880	0.0337580	-2.8502370
46	H	-5.2383690	-1.6354400	-2.5468090

47 O -3.1372910 -2.1383760 -1.2228650

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### 2p-Eq

Zero-point correction= 0.396980 Hartree  
Thermal correction to Energy= 0.421554 Hartree  
Thermal correction to Enthalpy= 0.422498 Hartree  
Thermal correction to Gibbs Free Energy= 0.338097 Hartree  
Sum of electronic and zero-point Energies= -937.632434 Hartree  
Sum of electronic and thermal Energies= -937.607860 Hartree  
Sum of electronic and thermal Enthalpies= -937.606916 Hartree  
Sum of electronic and thermal Free Energies= -937.691316 Hartree

Label	Symbol	X	Y	Z
1	C	1.7412510	0.0363630	0.1572990
2	C	3.2361810	-0.0335240	-0.1833150
3	C	3.7211660	-1.4722820	0.0157220
4	C	2.9246930	-2.4694280	-0.8334130
5	C	0.9194330	-0.9090030	-0.7135090
6	H	4.7739510	-1.5692780	-0.2455380
7	H	3.3370430	0.1968300	-1.2529940
8	H	1.5946300	-0.2283360	1.2091970
9	H	1.3680400	1.0491940	0.0260330
10	H	3.1226550	-2.2751040	-1.8937070
11	H	3.2061790	-3.5004360	-0.6235530
12	H	0.9728920	-0.5850850	-1.7570420
13	H	3.6295850	-1.7504350	1.0696890
14	C	4.0814070	1.0401360	0.5601100
15	C	3.9554940	0.9233870	2.0823780
16	H	4.6011770	1.6591250	2.5661850
17	H	2.9359590	1.1127590	2.4226260
18	H	4.2574690	-0.0619220	2.4421830
19	C	5.5580920	0.8931660	0.1727240
20	H	5.6821620	0.8738210	-0.9132120
21	H	6.1330070	1.7372540	0.5581760
22	H	6.0024820	-0.0145050	0.5825780
23	C	3.6235630	2.4399300	0.1299110
24	H	4.2717610	3.1991750	0.5717140
25	H	3.6705350	2.5529310	-0.9561010
26	H	2.6042360	2.6617240	0.4489040
27	C	1.4391340	-2.3241010	-0.6282120
28	O	0.7102420	-3.2584730	-0.3955460
29	I	-1.2270100	-1.0346060	-0.2336330
30	C	-1.3869270	1.0343560	-0.5084150
31	C	-1.8568470	1.5102960	-1.7199550
32	C	-1.0493780	1.8900860	0.5267600
33	C	-1.9742620	2.8798320	-1.8989960
34	H	-2.1558960	0.8282250	-2.5035050
35	C	-1.1724680	3.2579670	0.3338820
36	H	-0.7006990	1.5043390	1.4750660
37	C	-1.6305740	3.7517520	-0.8772020
38	H	-2.3491170	3.2626900	-2.8390860
39	H	-0.9173840	3.9349800	1.1387560
40	H	-1.7319390	4.8194850	-1.0213700
41	O	-3.4954610	-0.7890010	-0.0147340
42	C	-4.2270490	-0.4347050	1.0009780
43	O	-5.4152090	-0.2025280	0.9203050
44	C	-3.5145790	-0.3088530	2.3454230
45	H	-2.9264910	-1.2018940	2.5667960

46	H	-2.8327450	0.5454300	2.3226900
47	H	-4.2445210	-0.1490910	3.1348680

### 2p-OI

Zero-point correction= 0.397213 Hartree  
 Thermal correction to Energy= 0.421389 Hartree  
 Thermal correction to Enthalpy= 0.422333 Hartree  
 Thermal correction to Gibbs Free Energy= 0.339195 Hartree  
 Sum of electronic and zero-point Energies= -937.626731 Hartree  
 Sum of electronic and thermal Energies= -937.602555 Hartree  
 Sum of electronic and thermal Enthalpies= -937.601610 Hartree  
 Sum of electronic and thermal Free Energies= -937.684749 Hartree

Label	Symbol	X	Y	Z
1	C	-3.2644720	-0.1653240	-1.2867530
2	C	-3.4136630	-0.3298090	0.2286900
3	C	-2.6992160	-1.6179090	0.6433070
4	C	-1.2036570	-1.5261910	0.3648100
5	C	-1.8621320	-0.4164640	-1.7570390
6	H	-2.8557810	-1.8390460	1.6998190
7	H	-2.8683890	0.5055680	0.6890780
8	H	-3.9598210	-0.8324030	-1.8111360
9	H	-3.5460000	0.8485590	-1.5803190
10	H	-0.7317130	-0.8683570	1.1053970
11	H	-0.7320240	-2.5066020	0.4763990
12	H	-1.5939550	-0.0899610	-2.7555720
13	H	-3.1131690	-2.4571090	0.0769370
14	C	-4.8761080	-0.2244610	0.7406310
15	C	-5.6992140	-1.4662230	0.3836370
16	H	-6.7377780	-1.3302160	0.6939150
17	H	-5.6996940	-1.6572390	-0.6913560
18	H	-5.3203900	-2.3584690	0.8848500
19	C	-4.8701780	-0.0559730	2.2648100
20	H	-4.3139030	0.8386530	2.5557600
21	H	-5.8906600	0.0478310	2.6404850
22	H	-4.4222440	-0.9116150	2.7719850
23	C	-5.5545590	1.0109370	0.1377620
24	H	-6.5285340	1.1729450	0.6048750
25	H	-4.9519760	1.9087440	0.2998390
26	H	-5.7189790	0.9025060	-0.9352040
27	C	-0.9280840	-1.0104010	-1.0188480
28	O	0.3183080	-1.2019600	-1.5277860
29	I	1.9818000	-0.6692190	-0.4327910
30	C	1.1780910	1.2632420	-0.2575870
31	C	0.6352790	1.8443070	-1.3878260
32	C	1.1413340	1.8825990	0.9787070
33	C	0.0420760	3.0925420	-1.2729540
34	H	0.6548740	1.3271650	-2.3367770
35	C	0.5469910	3.1308870	1.0764690
36	H	1.5793660	1.4118690	1.8471940
37	C	-0.0016350	3.7341640	-0.0456560
38	H	-0.3873990	3.5598150	-2.1494150
39	H	0.5131940	3.6304200	2.0359330
40	H	-0.4667780	4.7078960	0.0384440
41	O	3.6115350	0.2588240	0.6451650
42	C	4.5532140	-0.6162020	0.8934840
43	O	4.4837740	-1.7810950	0.5495190

44	C	5.7289830	-0.0424290	1.6423450
45	H	6.1669830	0.7721030	1.0649040
46	H	5.3917860	0.3732180	2.5923420
47	H	6.4703680	-0.8175620	1.8164220

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**2p-AxAx**

Zero-point correction= 0.398045 Hartree  
 Thermal correction to Energy= 0.422199 Hartree  
 Thermal correction to Enthalpy= 0.423143 Hartree  
 Thermal correction to Gibbs Free Energy= 0.341078 Hartree  
 Sum of electronic and zero-point Energies= -937.634553 Hartree  
 Sum of electronic and thermal Energies= -937.610399 Hartree  
 Sum of electronic and thermal Enthalpies= -937.609455 Hartree  
 Sum of electronic and thermal Free Energies= -937.691520 Hartree

Label	Symbol	X	Y	Z
1	C	1.8038700	-1.4137470	-0.5343220
2	C	2.9884450	-0.8504720	0.2807950
3	C	3.8360640	0.0543770	-0.6263930
4	C	3.0487460	1.1269120	-1.3840340
5	H	4.6325530	0.5345340	-0.0560190
6	H	2.2343310	-2.1809770	-1.1873300
7	H	1.1044170	-1.9538820	0.1042650
8	H	2.6449260	1.8691990	-0.6895040
9	H	3.6853850	1.6651060	-2.0854940
10	H	4.3374090	-0.5785350	-1.3647900
11	C	1.8739860	0.5816360	-2.1534560
12	O	1.5760610	0.9878330	-3.2517730
13	C	1.0463360	-0.4758380	-1.4725600
14	H	0.5563930	-1.0423360	-2.2611910
15	I	-0.6864090	0.5993930	-0.5558560
16	C	-1.5950430	-1.2672030	-0.2283570
17	C	-1.9280760	-1.6264320	1.0648670
18	C	-1.8455980	-2.0987650	-1.3044600
19	C	-2.5070330	-2.8669110	1.2826510
20	H	-1.7638490	-0.9439230	1.8860280
21	C	-2.4247500	-3.3374250	-1.0716140
22	H	-1.6099230	-1.7933200	-2.3151040
23	C	-2.7498310	-3.7228820	0.2192910
24	H	-2.7723820	-3.1595290	2.2901350
25	H	-2.6292190	-3.9948820	-1.9064980
26	H	-3.2029800	-4.6896760	0.3961630
27	O	-2.6609190	1.2360930	0.5018560
28	C	-2.5903560	2.5030920	0.7456910
29	C	-3.8133230	3.0828640	1.4249980
30	H	-4.6744820	2.9788730	0.7633750
31	H	-4.0321850	2.5239120	2.3353530
32	H	-3.6531200	4.1328230	1.6578710
33	O	-1.6261420	3.2037710	0.4556500
34	H	3.6013920	-1.7371050	0.4698800
35	C	2.7351990	-0.2941030	1.7225620
36	C	2.3729700	1.1923240	1.7975030
37	H	1.4641220	1.4373610	1.2501940
38	H	2.1992640	1.4721700	2.8386700
39	H	3.1822290	1.8242470	1.4279530
40	C	4.0363370	-0.4888890	2.5174990
41	H	4.2873980	-1.5484070	2.6072920
42	H	4.8807170	0.0181860	2.0466110

43	H	3.9317360	-0.0825650	3.5255010
44	C	1.6413780	-1.1022170	2.4253010
45	H	1.6011910	-0.8353800	3.4832620
46	H	0.6554270	-0.9065790	2.0027540
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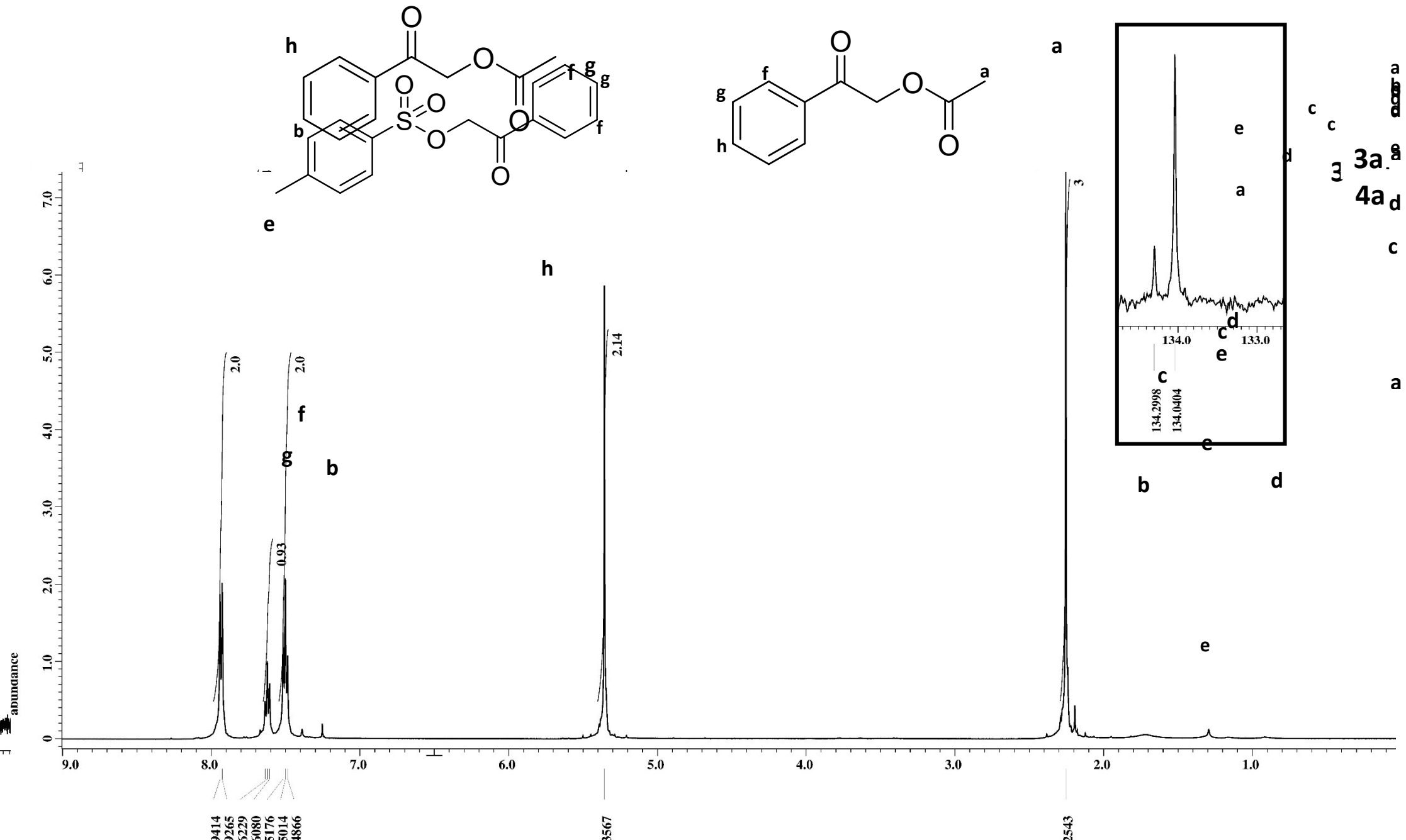
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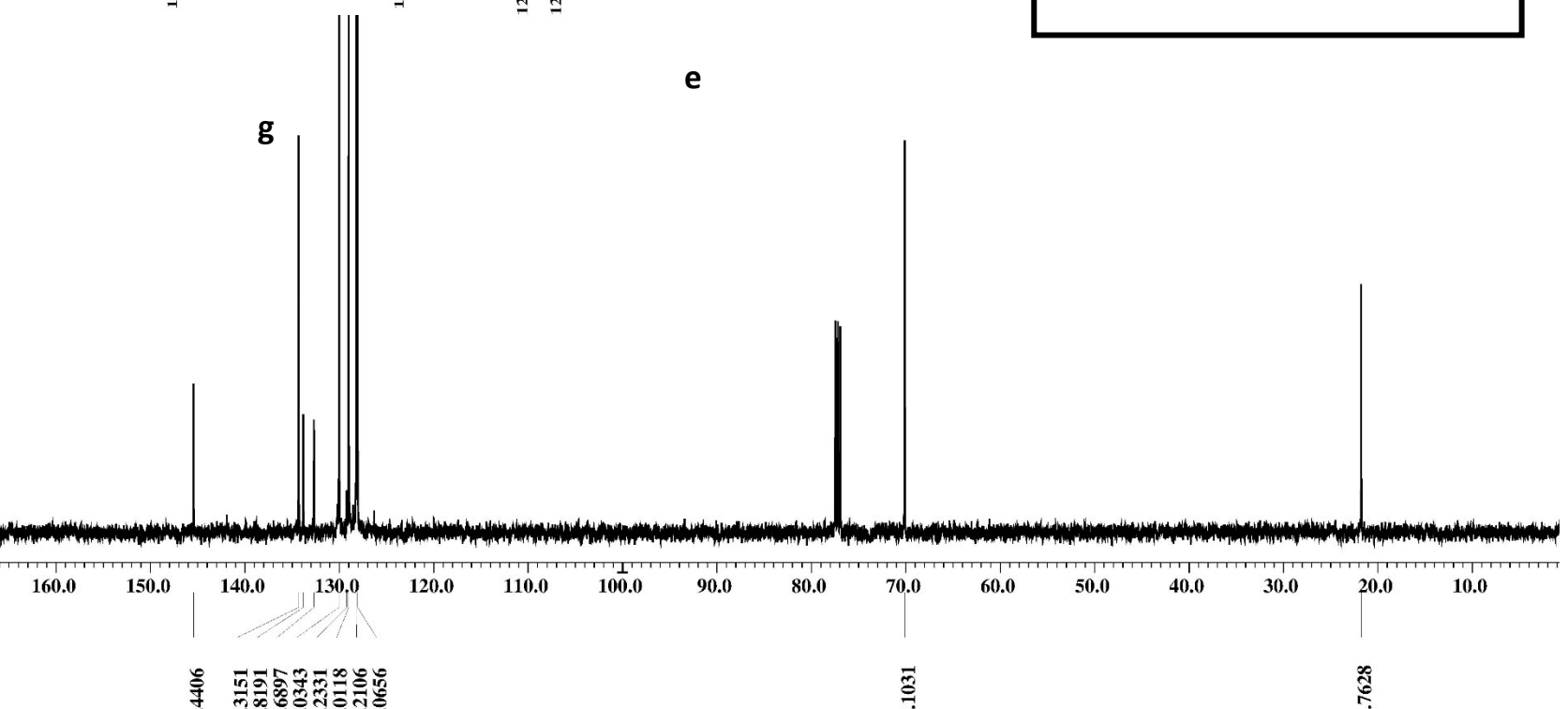
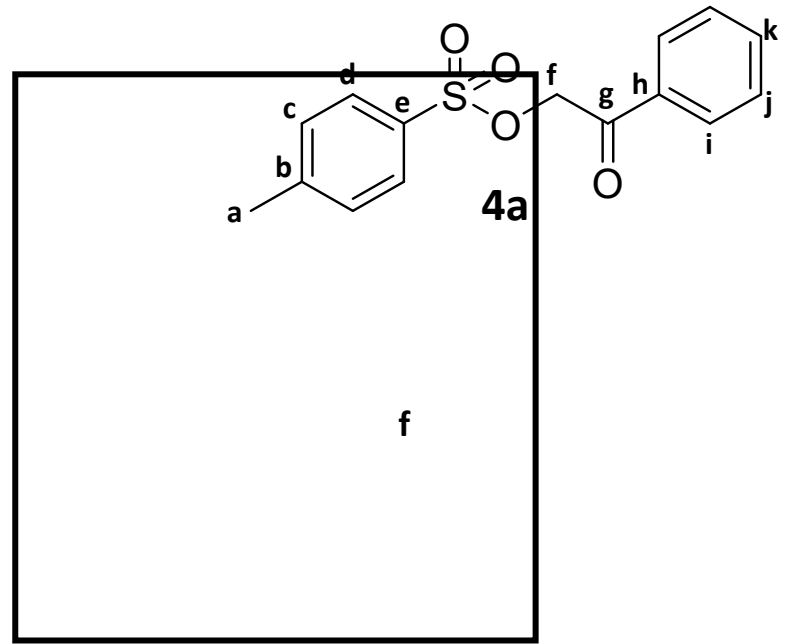
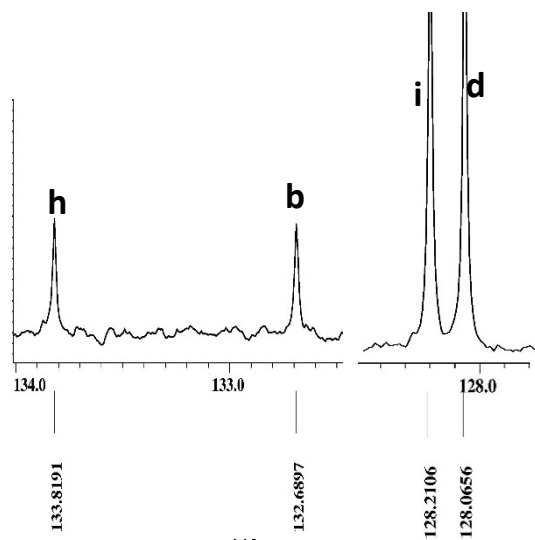
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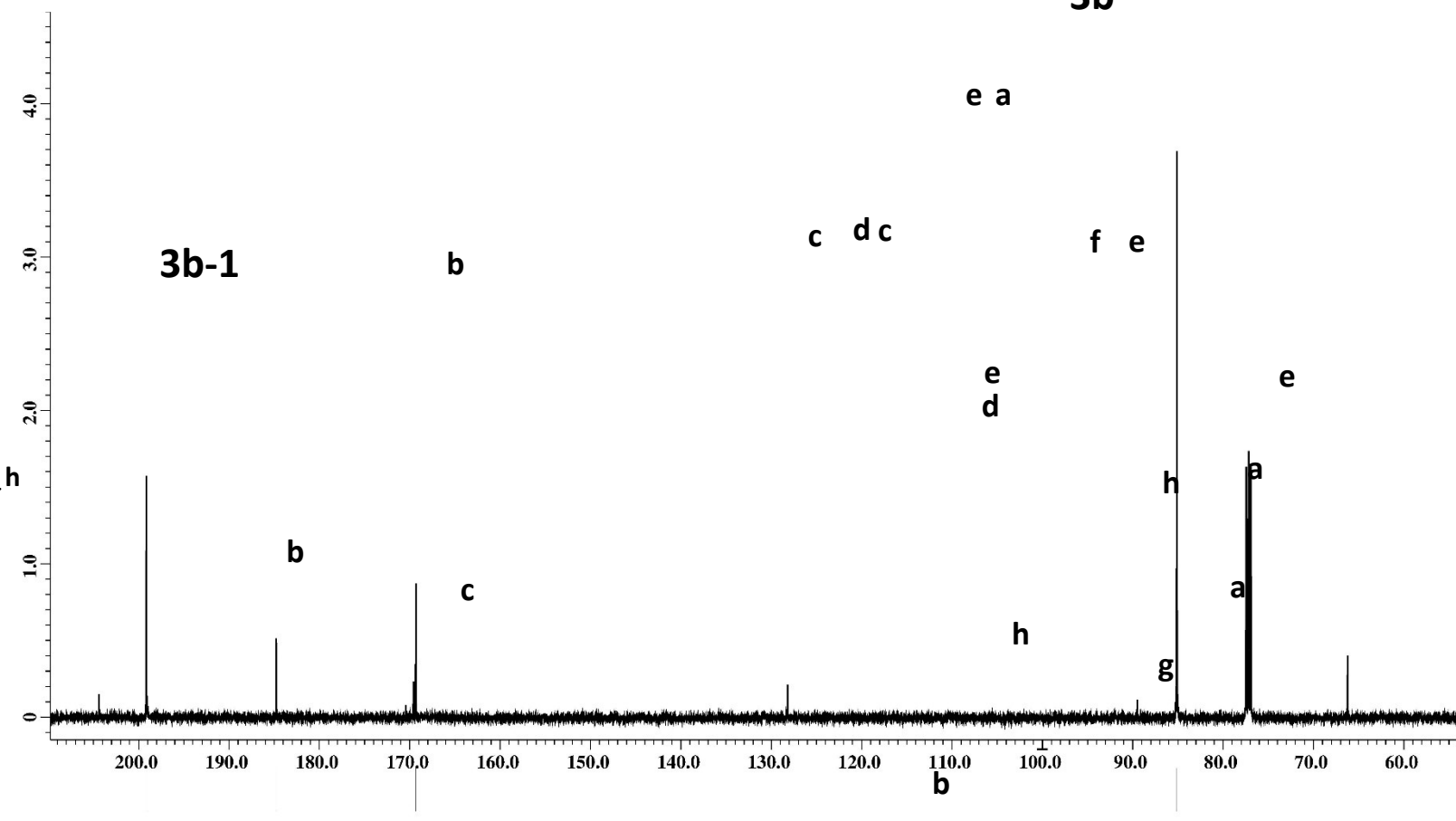
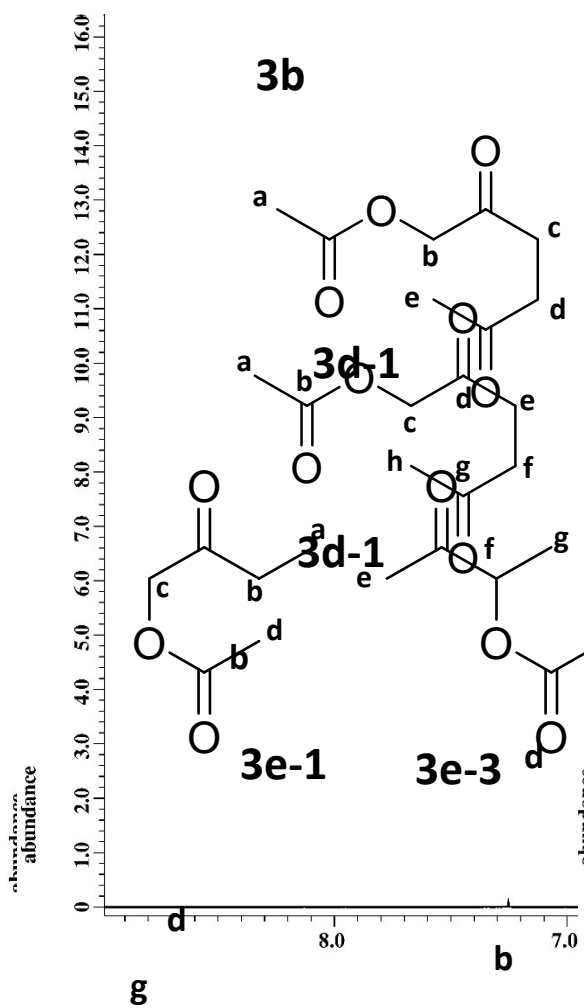
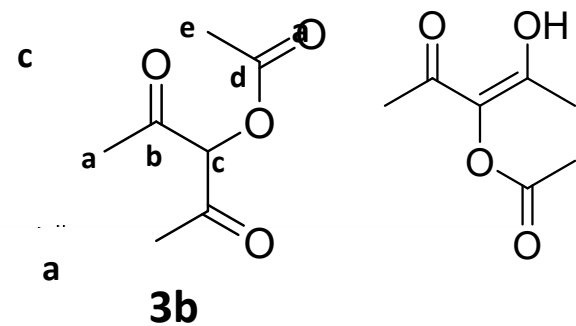
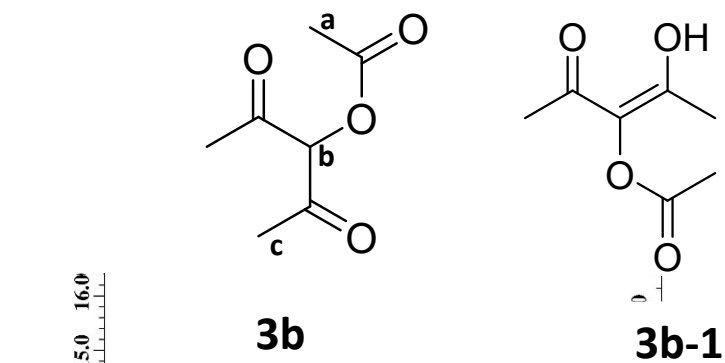




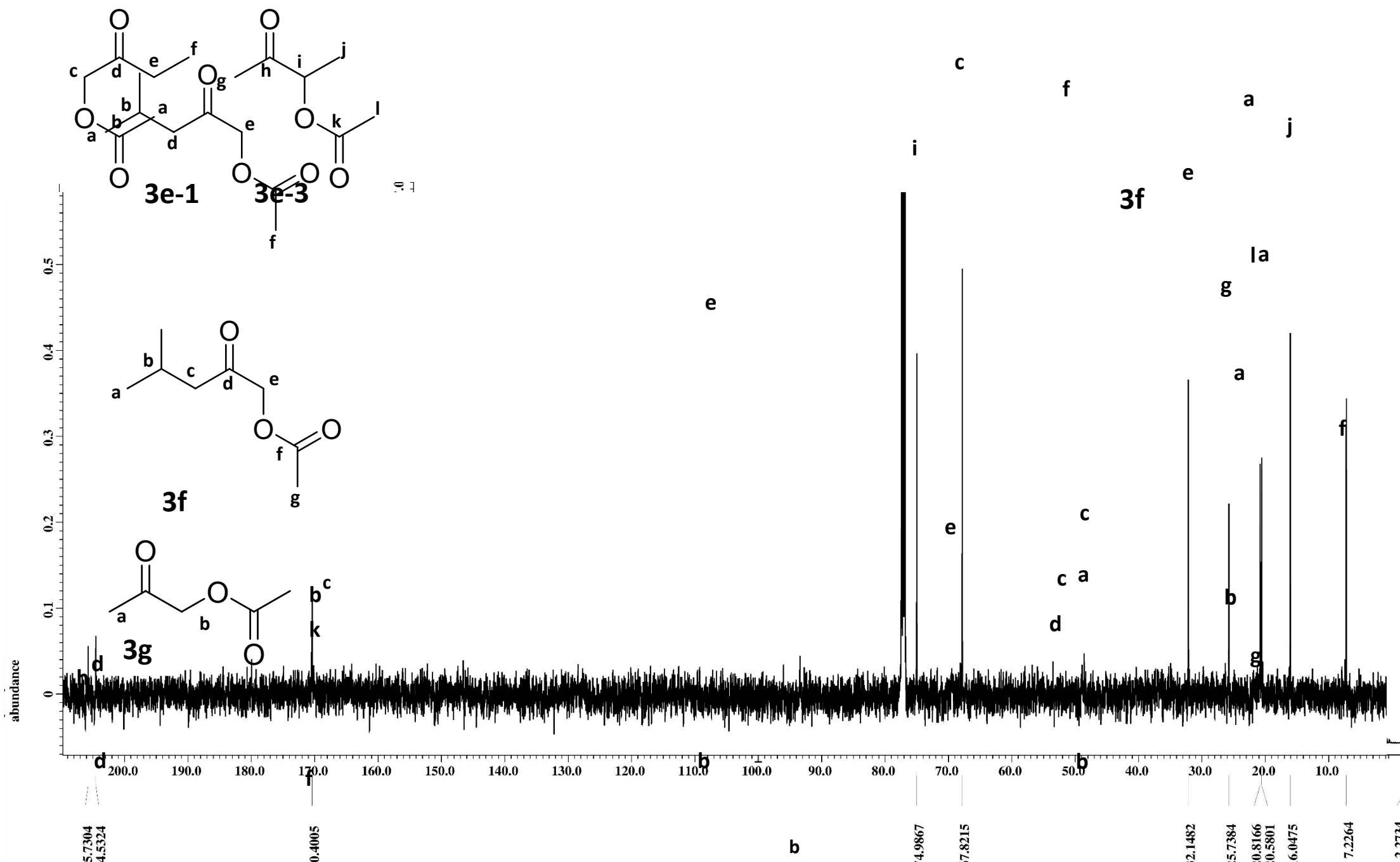
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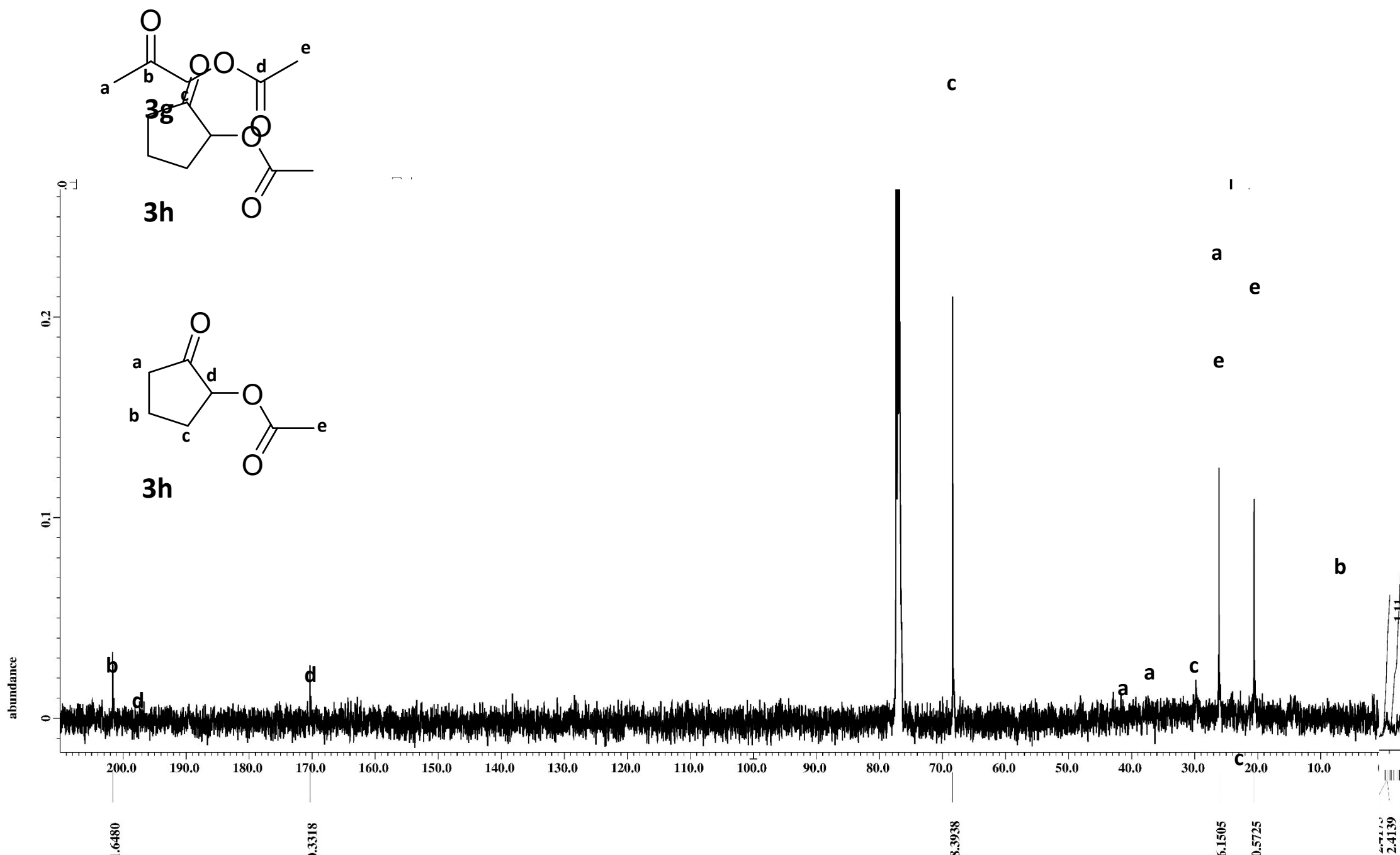


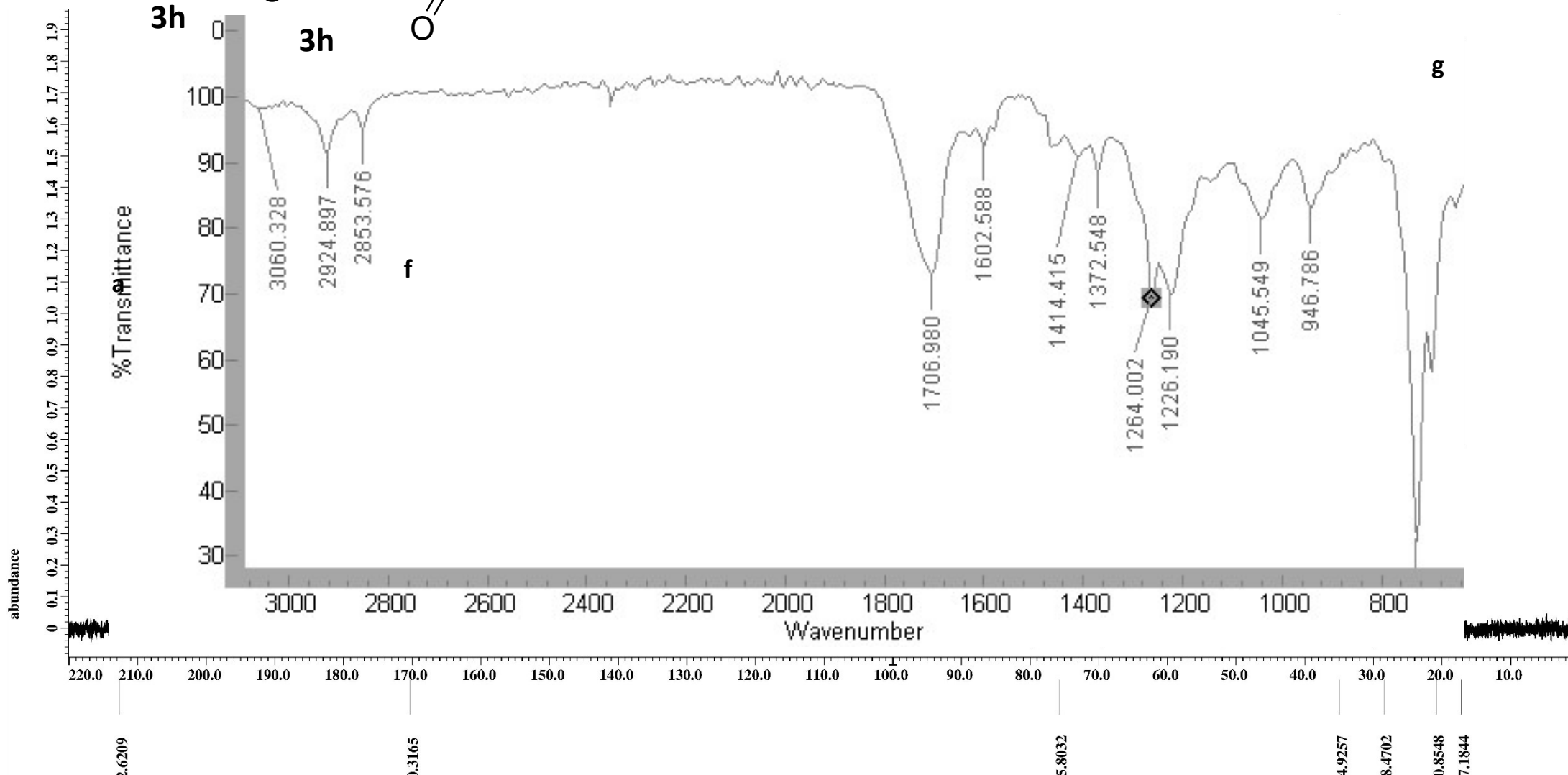
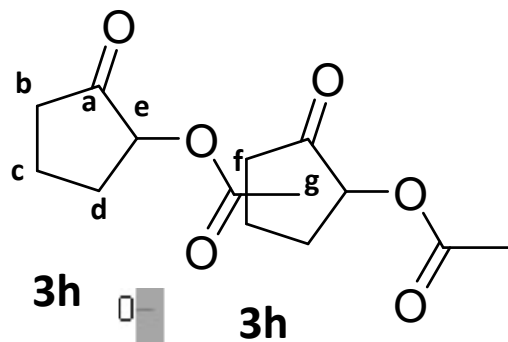


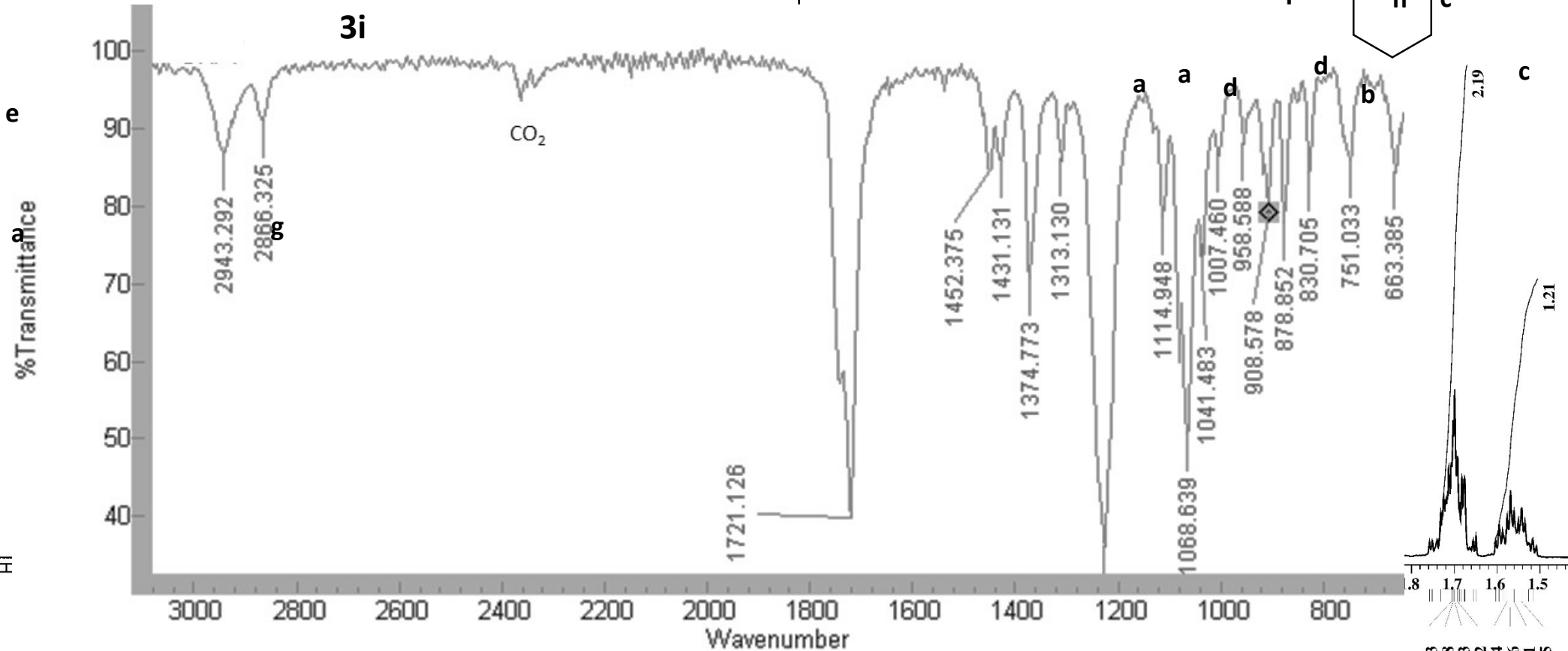
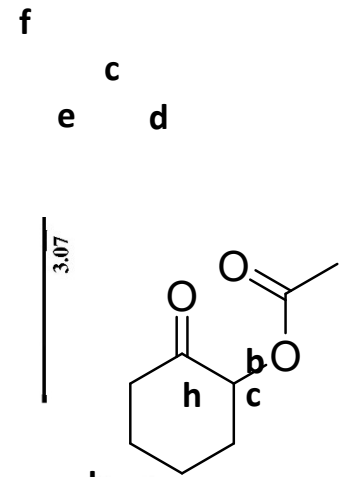
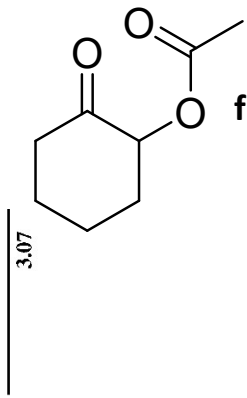
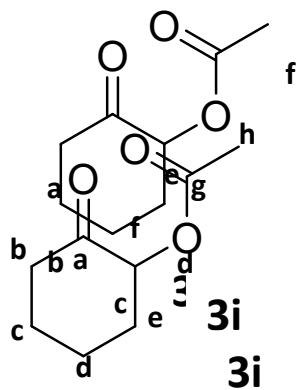


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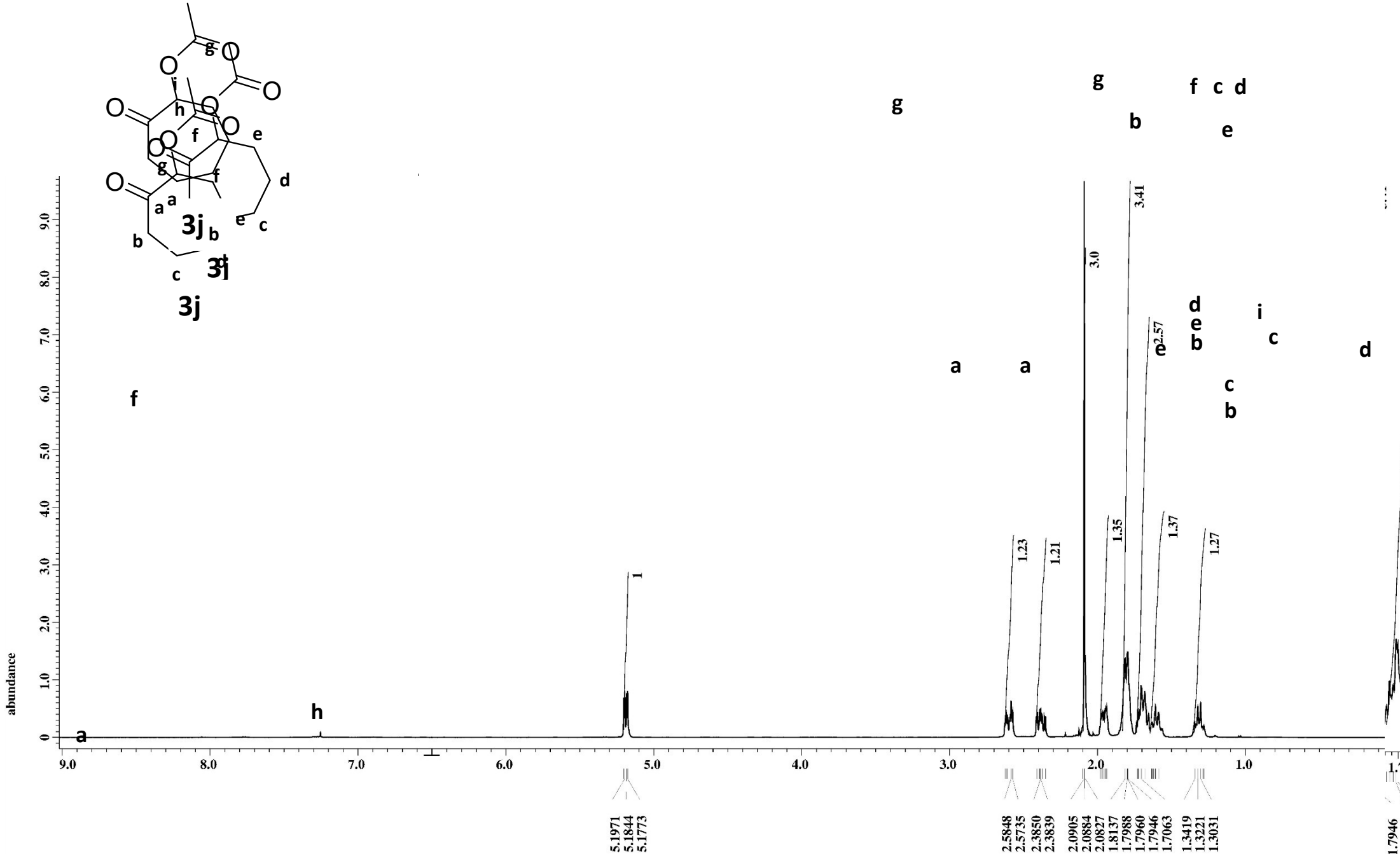


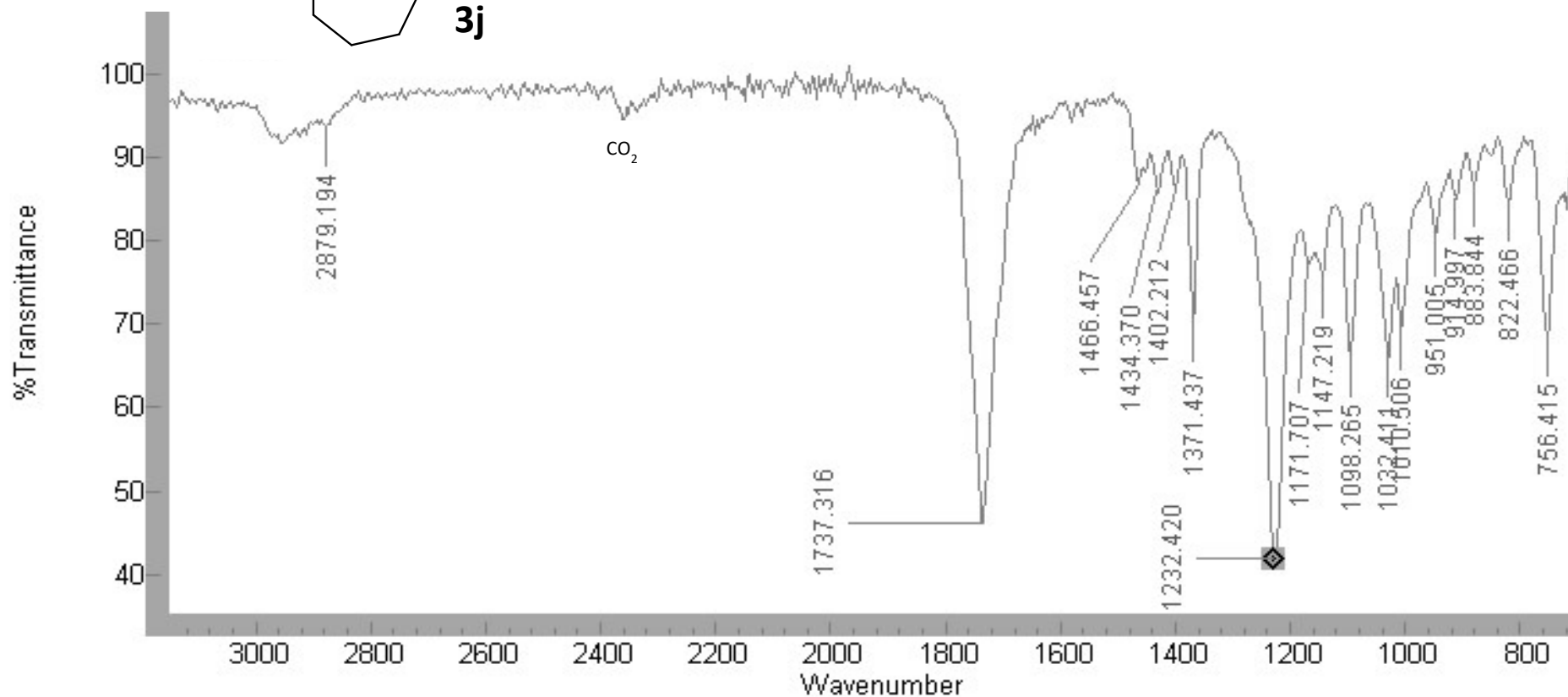
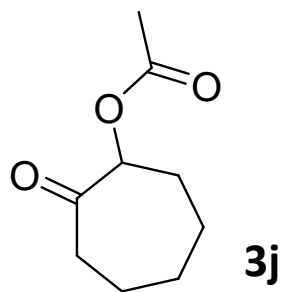


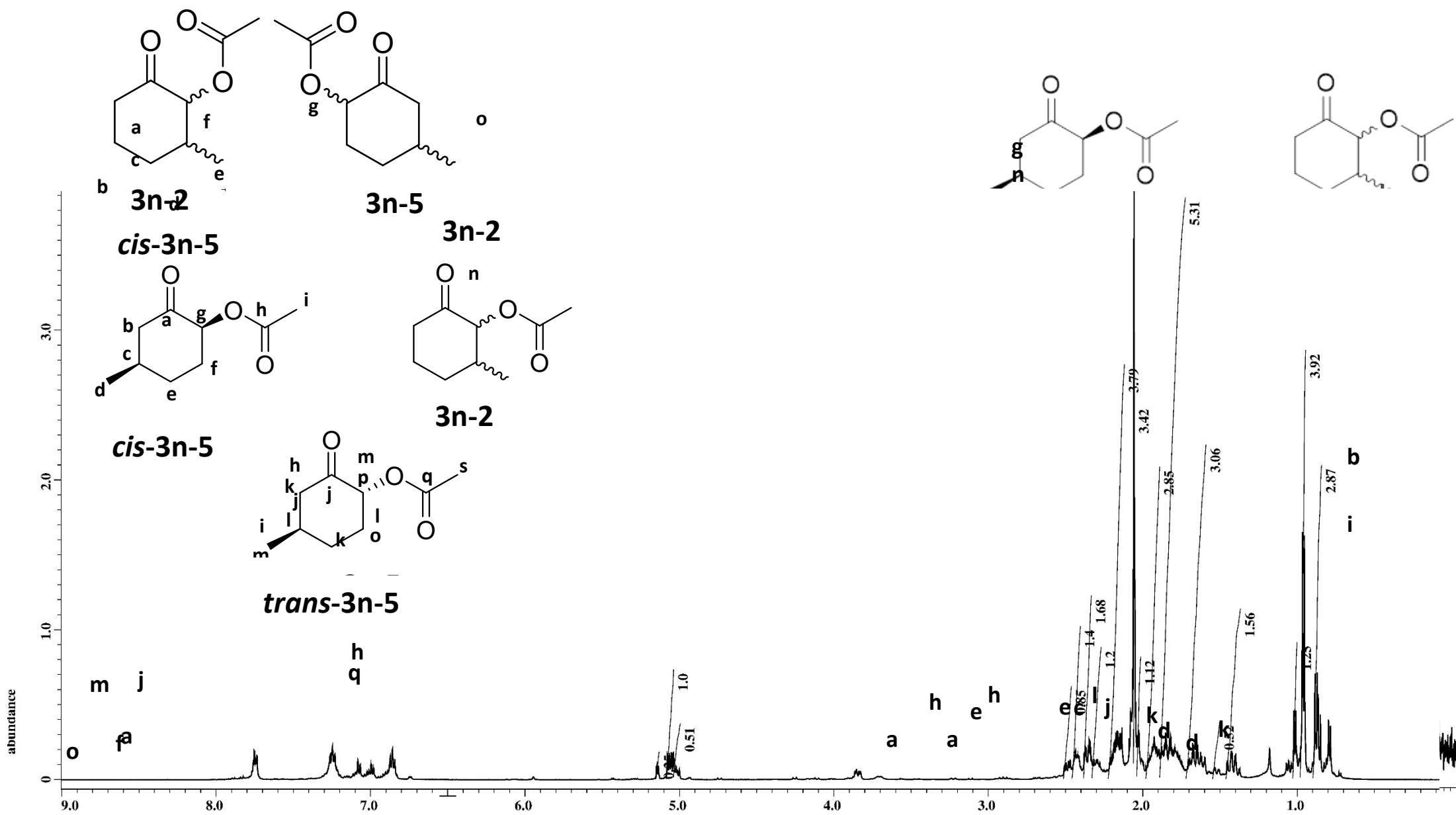


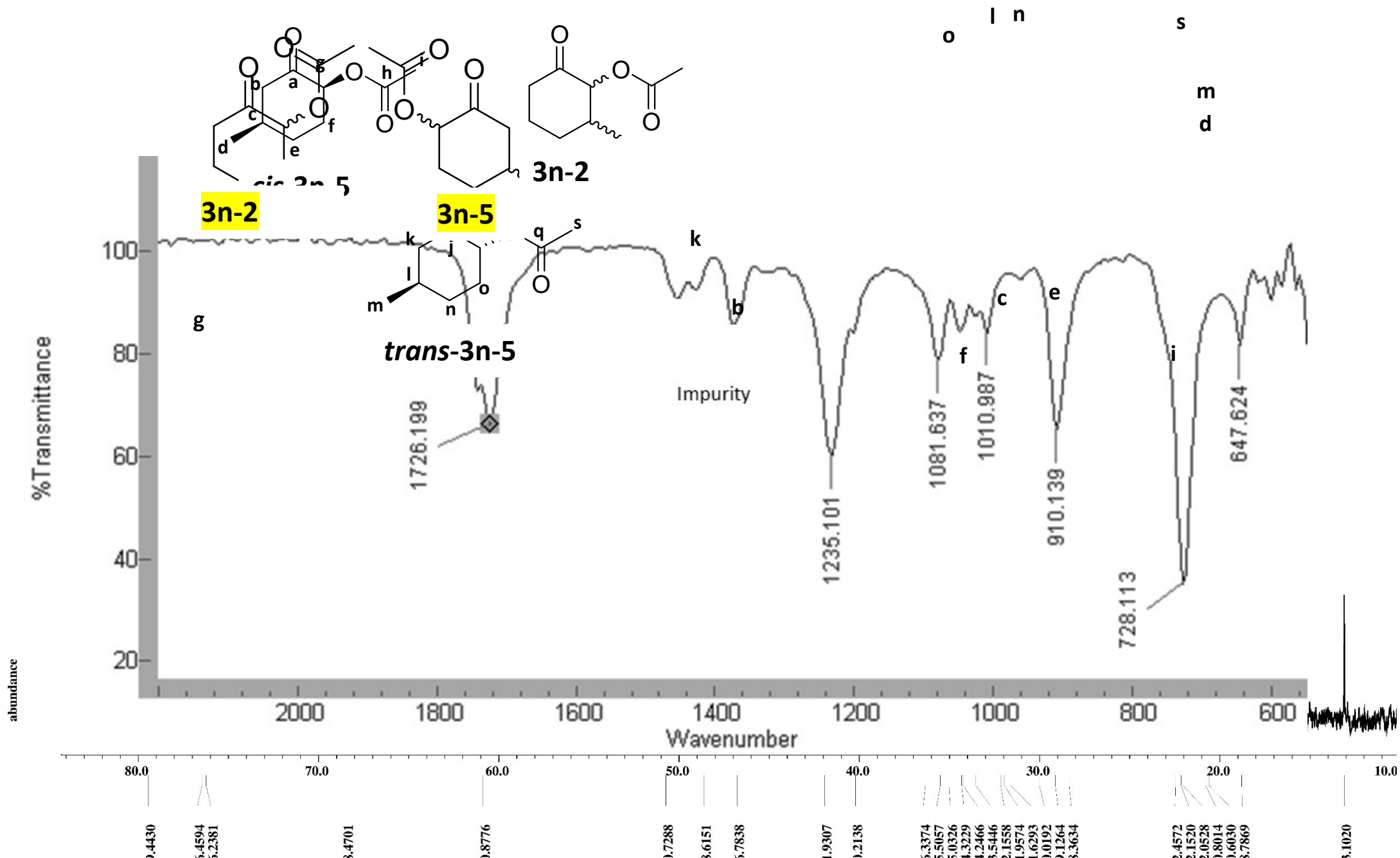


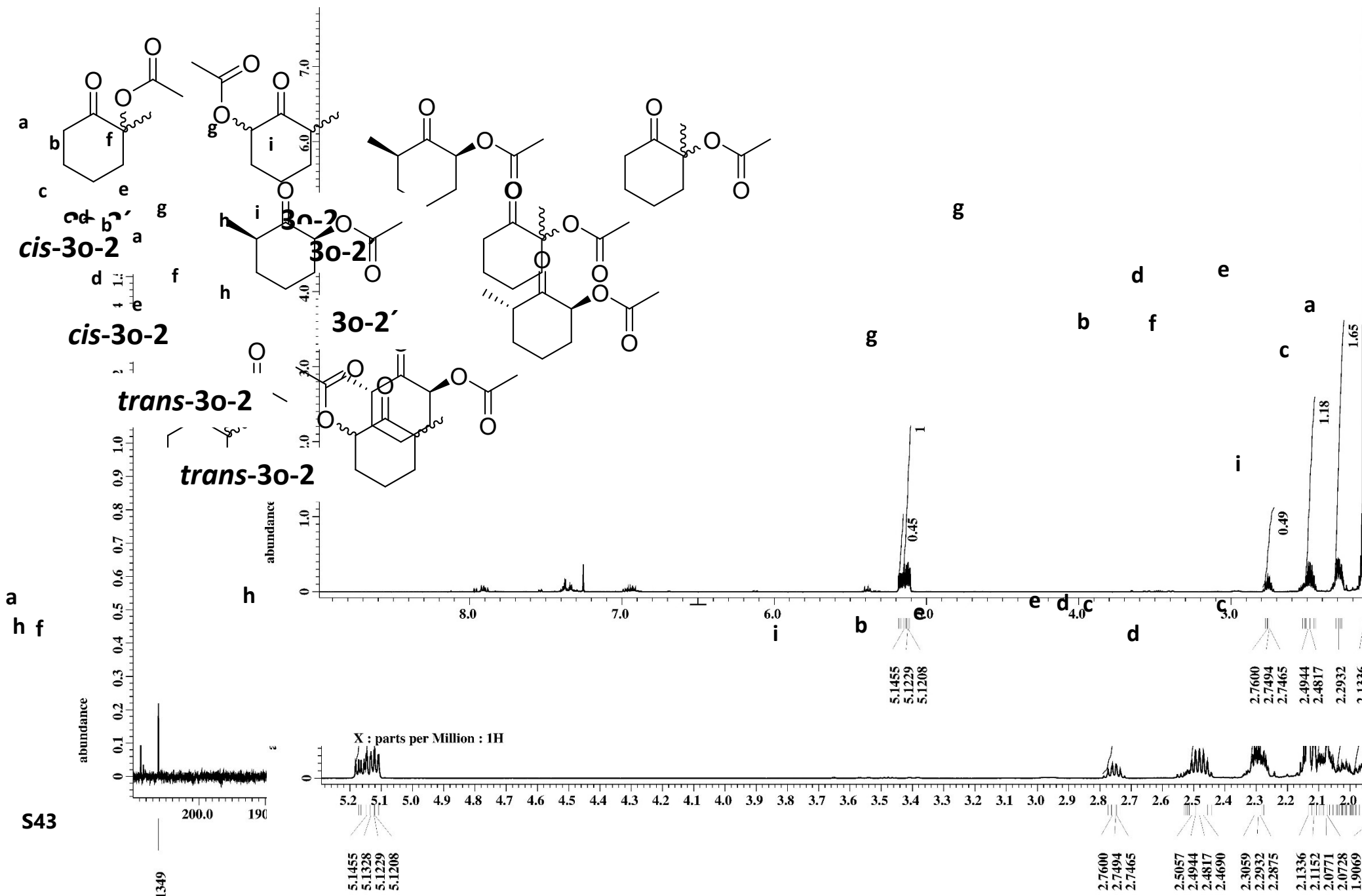


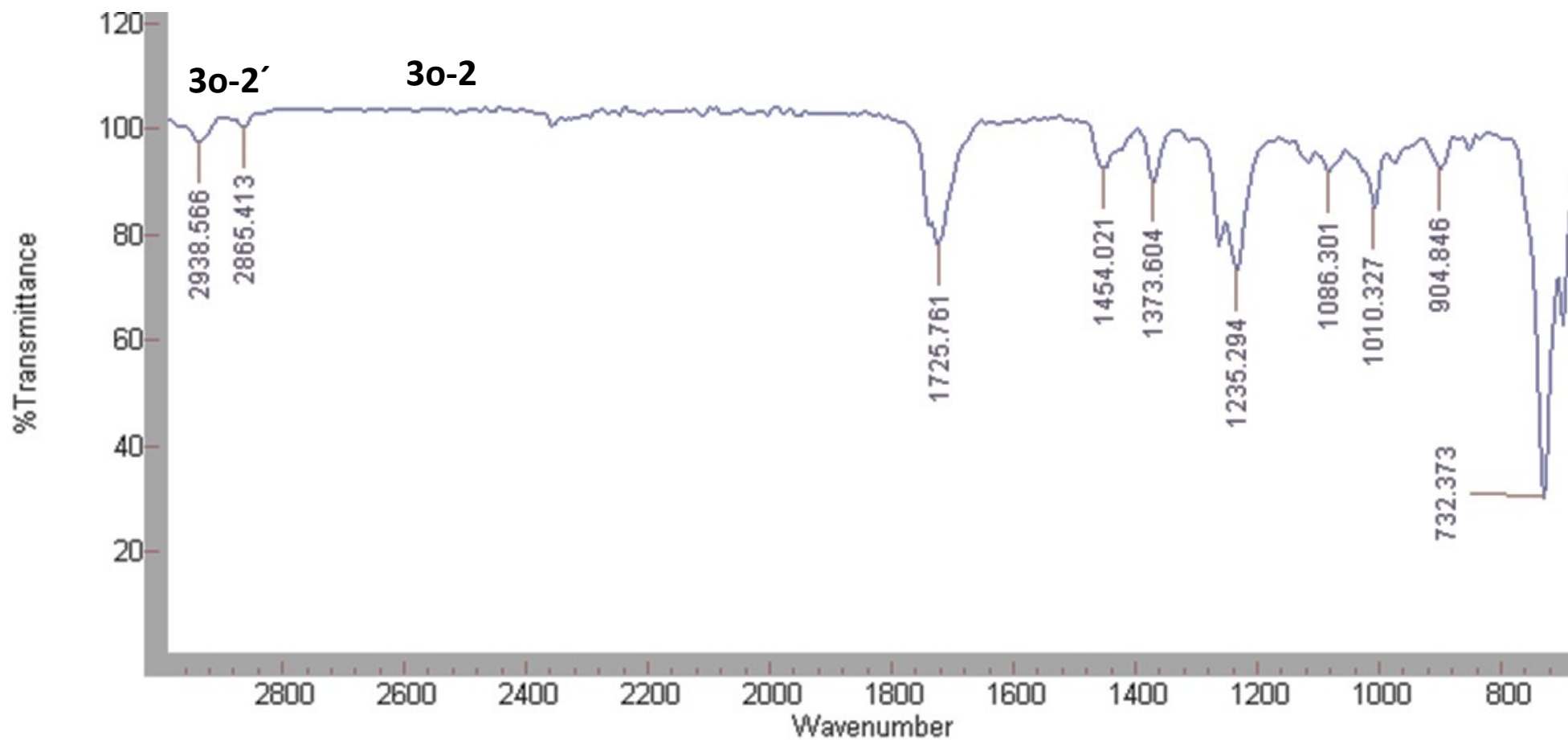


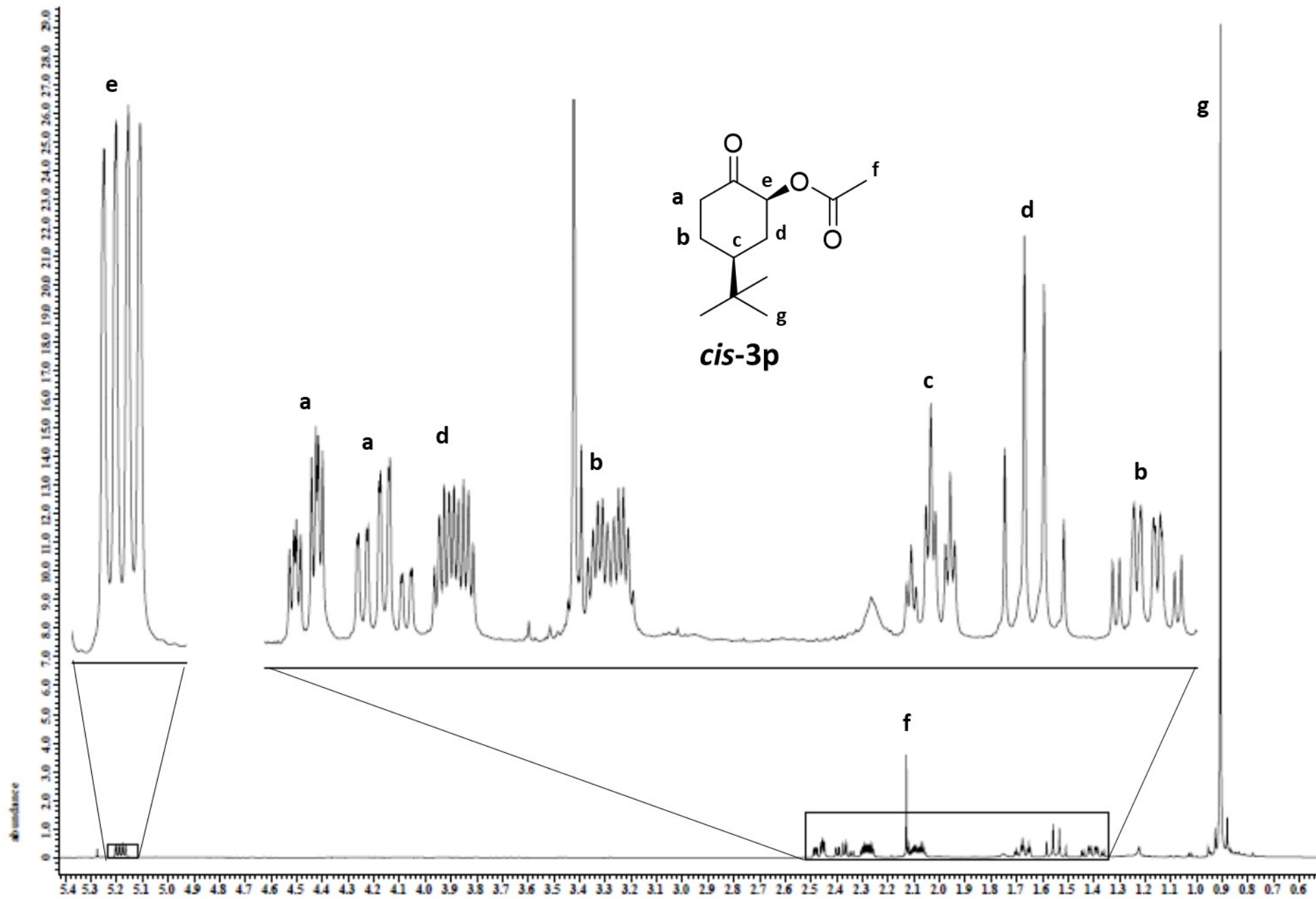




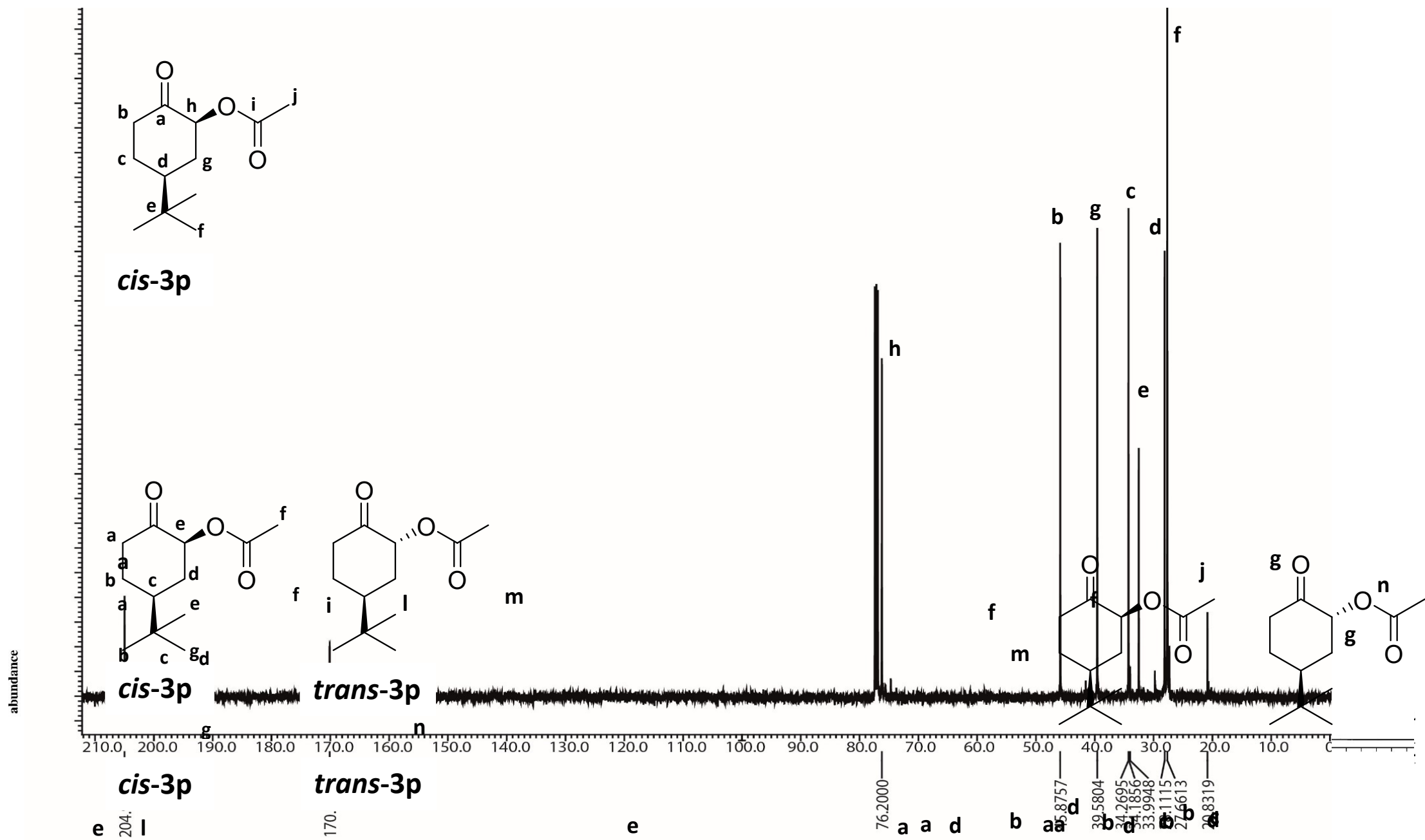




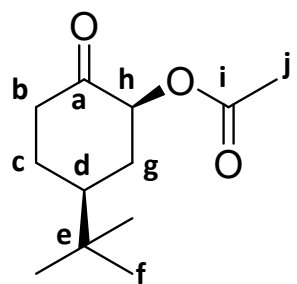




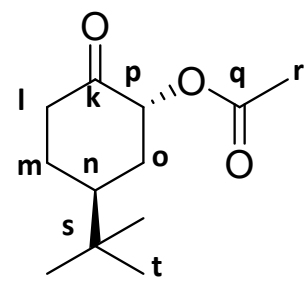
X : parts per Million : 1H



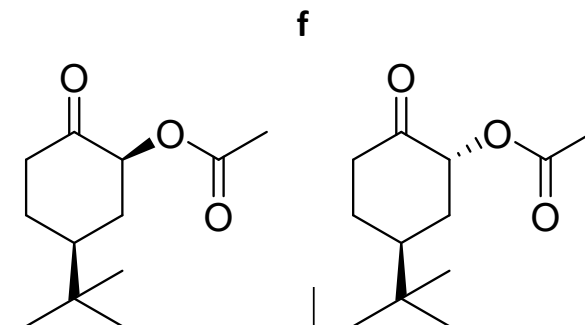




***cis-3p***



***trans-3p***



**f**

