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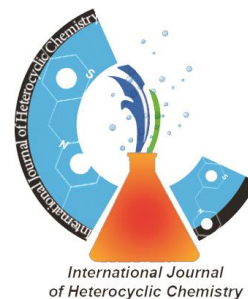
## Research article

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### A hybrid density functional theory (DFT) and ab initio study of $\alpha$ -Acyloxycarboxamides Derived from Indane-1, 2, 3-trione

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**Abstract-**  $\alpha$ -acyloxycarboxamides are synthesized from three component Passerini reaction between indane-1,2,3-trione, isocyanides, and thiophenecarboxylic acids in quantitative yields. The structures of the final products were confirmed by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis. The B3LYP/HF calculations for computation of <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts have been carried out for the title compounds at the 6-311+G\*\* and 6-311++G\*\* basis set levels within GIAO and CSGT approaches by DFT and HF methods. Predicted <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts have been assigned and compared with experimental <sup>1</sup>H and <sup>13</sup>C NMR spectra and they are supported each other.

**Keywords:** DFT, HF, NMR spectra, Passerini reaction, isocyanide.

#### Introduction

According to definition a multicomponent reaction (MCR) comprises reactions with more than two starting materials participating in the reaction and, at the same time, the atoms of these educts contribute the majority of the novel skeleton of the product. In recent years, multicomponent reactions (MCRs) have become important tools in modern preparative synthetic

chemistry because these reactions increase the efficiency by combining several operational steps without isolation of intermediates or changes of the conditions. [1-3] among the known multicomponent reactions to date, the most valuable reactions are those based on isocyanides. Isocyanide-based multicomponent reactions (abbreviated to IMCRs by Ugi and Dömling) are particularly interesting because they are more versatile and diverse than the remaining MCRs. [4-9] Today most IMCR chemistry relates to the classical reactions of Passerini and Ugi. Passerini reactions involve an oxo component, an isocyanide, and a nucleophile in a single step, and it was first discovered by Passerini about 90 years ago. [10] The Passerini reaction has developed in organic synthesis, the total synthesis of natural products, polycyclics and macrocycles, and pharmaceutical industry for the synthesis of druglike compounds. [11,12]

In recent years computational chemistry has become an important tool for chemists and a well-accepted partner for experimental chemistry. [13-19] Density functional theory (DFT) and Hartree-Fock (HF) method have become a major tool in the methodological arsenal of computational organic chemists. Density functional theory methods are increasingly applied to representative pharmacological compounds aiming to elucidate their molecular structures, electronic properties and bonds, the establishment of electronic and structural factors of selected reactions and their mechanisms. [20-24] There is an increasing demand for a reliable theoretical treatment for gaining the spectroscopic parameters. In the view of the wide use of NMR spectroscopy and the ready availability of NMR chemical shift information in many areas of chemistry, biology and material science, it is nevertheless mandatory that one attempts to extract all possible relevant information about molecular and electronic structure from nuclear shieldings. Various methods for the calculation of the nuclear magnetic shielding have been developed and applied since the fundamental formulation of the theory by Ramsey. [25] Calculations of NMR chemical shifts at various levels of theory have become a standard tool in chemistry. [26-32] Recently the GIAO (gauge including atomic orbitals) and CSGT (continuous set of gauge transformation) methods for calculation of NMR chemical shifts has been implemented in major quantum chemistry packages. [33-38] The GIAO approach facilitates accurate NMR shift calculations via electron-correlated methods. In this paper we will discuss the accuracy of the calculation of  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts performed at both the Hartree-Fock and density functional theory (B3LYP) frameworks using GIAO and CSGT techniques at the 6-

311+G\*\*, and 6-311++G\*\* basis set levels. Dependence on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts on the choice of method and basis set have been investigated.

### Computational details

The *ab initio* calculations were calculated using the Gaussian 98 software package on a Pentium IV personal computer by HF and DFT methods. The DFT technique employed the Becke3 (B3) (Becke 1992) exchange functional which supplement with Lee, Yang, Parr (LYP) (Lee et al., 1988) correlation functional. Geometry optimizations and calculation of chemical shifts were performed with HF/6-311+G\*\*, HF/6-311++G\*\*, B3LYP/6-311+G\*\*, and B3LYP/6-311++G\*\*. The NMR chemical shifts were calculated using GIAO and CSGT approaches.

### Experimental

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Jasco FT-IR 6300 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured ( $\text{CDCl}_3$  solution) with a BRUKER DRX-250 AVANCE spectrometer at 250.0 and 62.5 MHz, respectively. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values.

#### *General procedure*

To a magnetically stirred solution of indane-1,2,3-trione (**1**) (0.2 mmol) and thiophenecarboxylic acids (**3**) (0.2 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 ml) was added dropwise a solution of isocyanides (**2**) (0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) at room temperature over 10 min. The mixture was stirred at room temperature. After completion of the reaction, the solvent was removed under reduced pressure and pure products (**4a-g**) were obtained. The characterization data of the compounds are given below.

#### **The characterization data of the compounds (4a-f)**

2-[(Cyclohexylamino)carbonyl]-1,3-dioxo-2,3-dihydro-1H-inden-2-yl 2-thiophenecarboxylate (**4a**): Yield 95%, light yellow powder, mp 183.8-185.4° (dec). IR (KBr): 3327, 3108, 2934, 1725, 1648, 1524, 1262  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.28-1.95 (*m*, 10 H, 5 $\text{CH}_2$  of cyclohexyl), 3.76 (*m*, 1H, N-CH), 6.56 (*d*,  $^3J = 7.25$  Hz, 1H, NH), 7.14-8.06 (*m*, 7H, arom CH).  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>):  $\delta$  24.46, 25.35 and 32.51 (CH<sub>2</sub> of cyclohexyl), 48.83 (NCH), 83.96 (C-O), 124.09, 128.45, 129.61, 134.67, 135.80, 136.09 and 141.55 (aromatic carbons), 159.01 (CO of ester), 161.26 (CO of amide), 191.32 (CO of ketone). MS (EI): 397 (6, [M]<sup>+</sup>), 269 (4), 111 (100, [C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup>), 83 (6, [C<sub>6</sub>H<sub>11</sub>]<sup>+</sup>), 55 (8), 41 (5). Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>NO<sub>5</sub>S (397.45): C 63.46, H 4.82, N 3.52. Found: C 63.37, H 4.73, N 3.59.

*2-[(tert-butylamino)carbonyl]-1,3-dioxo-2,3-dihydro-1H-inden-2-yl 2-thiophenecarboxylate (4b)*: Yield 94%, light yellow powder, mp 188.3-190.4° (dec). IR (KBr): 3408, 3106, 3091, 2968, 1722, 1678, 1526, 1257 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.40 (s, 9H, *t*-Bu); 6.52 (s, 1H, NH); 7.15-8.08 (m, 7H, arom CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  28.51 (CMe<sub>3</sub>), 52.62 (N-C), 83.94 (C-O), 124.06, 128.45, 129.59, 134.63, 135.77, 136.06 and 141.70 (aromatic carbons), 158.86 (CO of ester), 161.36 (CO of amide), 191.55 (CO of ketone). MS (EI): 371 (5, [M]<sup>+</sup>), 299 (4, [M - NHR]<sup>+</sup>), 243 (5), 111 (100, [C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup>), 76 (6), 57 (14, [*t*-Bu]<sup>+</sup>), 41 (5). Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>5</sub>S (371.42): C 61.44, H 4.61, N 3.77. Found: C 61.33, H 4.53, N 3.83.

*1,3-dioxo-2-[(1,1,3,3-tetramethylbutyl)amino]carbonyl-2,3-dihydro-1H-inden-2-yl 2-thiophenecarboxylate (4c)*: Yield 98%, white powder, mp 167.3-169.0° (dec). IR (KBr): 3404, 3120, 2951, 1725, 1677, 1521, 1261 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.07 (s, 9H, CMe<sub>3</sub>), 1.45 (s, 6H, CMe<sub>2</sub>), 1.74 (s, 2H, CH<sub>2</sub>), 6.58 (s, 1H, NH), 7.15-8.07 (m, 7H, arom CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  28.86 (2Me), 31.56 (CMe<sub>3</sub>), 31.71 (CMe<sub>3</sub>), 51.87 (CH<sub>2</sub>), 56.61 (N-C), 84.12 (C-O), 124.05, 128.44, 129.62, 134.56, 135.80, 136.01 and 141.68 (aromatic carbons), 158.96 (CO of ester), 160.96 (CO of amide), 191.48 (CO of ketone). MS (EI): 356 (19, [M - CH<sub>2</sub>-*t*-Bu]<sup>+</sup>), 299 (45, [M - NHR]<sup>+</sup>), 111 (100, [C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup>), 104 (33), 76 (41), 57 (64, [*t*-Bu]<sup>+</sup>), 41 (29). Anal. Calcd. for C<sub>23</sub>H<sub>25</sub>NO<sub>5</sub>S (427.52): C 64.62, H 5.89, N 3.28. Found: C 64.75, H 5.80, N 3.34.

*2-[(Cyclohexylamino)carbonyl]-1,3-dioxo-2,3-dihydro-1H-inden-2-yl 3-thiophenecarboxylate (4d)*: Yield 94%, white powder, mp 207.1-208.2° (dec). IR (KBr): 3317, 3117, 2935, 1722, 1645, 1529, 1266 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.22-1.96 (m, 10H, 5CH<sub>2</sub> of cyclohexyl), 3.76 (m, 1H, N-CH), 6.53 (d, <sup>3</sup>J = 7.5 Hz, 1H, NH), 7.26-8.20 (m, 7H, arom CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  24.64, 25.32 and 32.62 (CH<sub>2</sub> of cyclohexyl), 48.98 (NCH), 83.91 (C-O), 124.08, 127.07, 127.78,

129.82, 135.29, 136.11 and 141.45 (aromatic carbons), 159.57 (CO of ester), 161.42 (CO of amide), 191.62 (CO of ketone). MS (EI): 149 (3), 91 (4), 71 (5), 69 (6), 58 (30), 43 (100), 41 (12). Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>NO<sub>5</sub>S (397.45): C 63.46, H 4.82, N 3.52. Found: C 63.59, H 4.79, N 3.45.

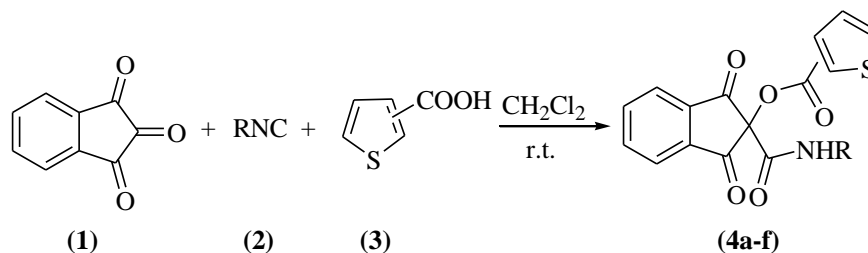
*2-[(tert-butylamino)carbonyl]-1,3-dioxo-2,3-dihydro-1H-inden-2-yl 3-thiophenecarboxylate (4e)*: Yield 98%, light yellow powder, mp 199.9-200.4° (dec). IR (KBr): 3401, 3103, 2969, 1721, 1681, 1529, 1251 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.40 (s, 9H, *t*-Bu), 6.50 (s, 1H, NH), 7.26-8.19 (m, 7H, arom CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.54 (CMe<sub>3</sub>), 52.64 (N-C), 83.91 (C-O), 124.04, 127.08, 127.72, 129.85, 135.19, 136.05 and 141.61 (aromatic carbons), 159.43 (CO of ester), 161.53 (CO of amide), 191.82 (CO of ketone). MS (EI): 371(3, [M]<sup>+</sup>), 299 (3, [M - NHR]<sup>+</sup>), 243 (4), 111 (100, [C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup>), 83 (6), 76 (4), 57 (11, [*t*-Bu]<sup>+</sup>), 41 (6). Anal. Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>5</sub>S (371.42): C 61.44, H 4.61, N 3.77. Found: C 61.38, H 4.65, N 3.82,.

*1,3-dioxo-2-[(1,1,3,3-tetramethylbutyl)amino]carbonyl-2,3-dihydro-1H-inden-2-yl 3-thiophenecarboxylate (4f)*: Yield 94%, white powder, mp 171.1-172.8° (dec). IR (KBr): 3409, 3132, 2950, 1724, 1675, 1519, 1254 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.06 (s, 9H, CMe<sub>3</sub>), 1.45 (s, 6H, CMe<sub>2</sub>), 1.74 (s, 2H, CH<sub>2</sub>), 6.54 (s, 1 H, NH), 7.26-8.18 (m, 7 H, arom CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.88 (2Me), 31.55 (CMe<sub>3</sub>), 31.72 (CMe<sub>3</sub>), 51.87 (CH<sub>2</sub>), 56.62 (N-C), 84.09 (C-O), 124.02, 127.06, 127.68, 129.97, 135.01, 136.00 and 141.58 (aromatic carbons), 159.55 (CO of ester), 161.12 (CO of amide), 191.73 (CO of ketone). MS (EI): 427 ([M]<sup>+</sup>, 1), 412 ([M]<sup>+</sup>-15, 1), 356 (25), 299 (58), 111 ([C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup>, 100), 57 (*t*-Bu)<sup>+</sup>, 24), 43 (5). Anal. Calcd. for C<sub>23</sub>H<sub>25</sub>NO<sub>5</sub>S (427.52): C 64.62, H 5.89, N 3.28. Found: C 64.55, H 5.93, N 3.33.

## Results and discussion

The indane-trione (1), isocyanides (2) and thiophenecarboxylic acids (3) in dichloromethane react together in a 1:1:1 ratio at room temperature to produce α-acyloxycarboxamides (4a-f) (Scheme 1). The reaction proceeds smoothly and cleanly under mild conditions and no side reactions were observed. The structures of the products were deduced from their IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analyses and mass spectroscopy. In the present work we have calculated the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts using HF/B3LYP methods at the 6-311+G\*\*, and 6-311++G\*\* basis set levels within GIAO and CSGT approaches for the title compounds (4a-f). In

the literature, not any theoretical computation of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts on the  $\alpha$ -acyloxycarboxamides were found. The schematic drawing with the theoretical geometric structure of **4a** is shown in Figure 1. The observed  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts and the calculated amounts are given in Tables 2 to 25. On the basis of our calculations and experimental  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts, we made a reliable one-to-one correspondence between observed chemical shifts and any of our chemical shifts calculated by the HF and B3LYP methods. In order to compare this agreement, the correlation graphic based on the theoretical and experimental data has been investigated. The correlation value ( $R^2$ ) for calculated  $^{13}\text{C}$  chemical shifts of **4a** by the HF/B3LYP methods at the 6-311+G\*\*, and 6-311++G\*\* basis set levels within GIAO and CSGT approaches is shown in Table 14. The correlation graphic for **4a** by the HF/B3LYP methods at 6-311++G\*\* basis set levels within GIAO and CSGT approaches is depicted in Fig. 2 to Fig. 5. There is an excellent agreement between experimental and theoretical results.

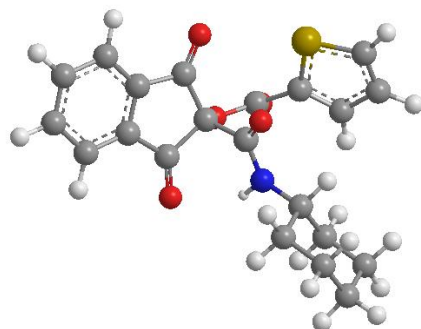


**Scheme 1.** Passerini multi-component reaction of indane-1,2,3-trione (see Table 1).

**Table 1:** Synthesis of  $\alpha$ -acyloxycarboxamide derivatives (**4a-f**) (Scheme 1)

Products	R	Carboxylic acid	Time of reaction (h)	Yield(%)
<b>4a</b>	cyclohexyl	2-thiophenecarboxylic acid	1	95
<b>4b</b>	<i>t</i> -Bu	2-thiophenecarboxylic acid	1	94
<b>4c</b>	1,1,3,3-tetramethylbutyl	2-thiophenecarboxylic acid	1	98
<b>4d</b>	cyclohexyl	3-thiophenecarboxylic acid	1	94

<b>4e</b>	<i>t</i> -Bu	3-thiophenecarboxylic acid	1	98
<b>4f</b>	1,1,3,3-tetramethylbutyl	3-thiophenecarboxylic acid	1	94



**Figure 1.** Theoretical geometric structure of **4a**

**Table 2.** Experimentally measured and calculated  $^1\text{H}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4a**)

H atom	$\delta_{\text{H}}$ (CDCl <sub>3</sub> )	HF/6-311+G** GIAO		HF/6-311++G**		B3LYP/6-311+G**		B3LYP/6-311++G**	
10H,	1.28-	1.34-	1.22-	1.29-	1.37-	1.18-	1.26-	1.27-	1.18-
1H, N-	3.76	3.70	3.09	3.72	3.49	3.70	3.65	3.60	2.83
1H, NH	6.56	6.61	6.21	6.52	6.56	6.60	6.83	5.90	6.55
7H, arom	7.14-	7.16-	7.01-	7.27-	7.32-	7.24-	7.31-	7.10-	7.16-

**Table 3.** Experimentally measured and calculated  $^{13}\text{C}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4a**)

C atom	$\delta_{\text{C}}$	HF/6-311+G**		HF/6-311++G**		B3LYP /6-311+G**		B3LYP /6-311++G**	
CH <sub>2</sub> of	24.46	24.5	24.97	24.44	24.21	24.36	24.65	24.94	24.54
	25.35	25.3	25.63	25.98	25.31	25.31	23.56	24.43	24.31
	32.51	33.1	34.73	33.39	34.24	32.65	32.76	31.98	32.22
NCH	48.83	48.7	47.81	48.81	47.22	47.63	47.98	48.02	48.56
C-O	83.96	82.2	82.31	82.07	82.72	82.21	82.94	82.38	83.05
aromatic	124.09	122.	121.98	122.3	121.26	123.32	124.7	124.82	124.21
	128.45	127.	128.22	127.5	128.83	127.21	127.7	127.95	128.01
	129.61	129.	129.31	129.0	129.28	128.98	129.0	129.06	129.56

		134.67	134.	133.01	134.4	133.88	133.98	133.4	133.97	133.45
		135.80	135.	134.98	135.7	134.21	135.86	134.4	135.81	137.43
		136.09	137.	136.49	137.1	136.39	136.67	137.0	137.56	136.21
		141.55	141.	140.33	141.0	140.63	140.76	140.3	142.98	141.66
CO	of	159.01	156.	158.65	156.7	158.31	157.33	157.3	157.75	158.23
CO	of	161.26	161.	160.37	161.9	160.88	160.36	161.9	161.91	161.54
CO	of	191.32	191.	190.44	191.8	190.18	191.75	190.1	190.95	190.11

**Table 4.** Experimentally measured and calculated  $^1\text{H}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4b**)

H atom	$\delta_{\text{H}}$ (CDCl <sub>3</sub> )	HF/6-311+G** GIAO	HF/6-311++G**	B3LYP 311+G**	/6- 311+G**	B3LYP 311++G**	/6- 311+G**		
9 H, <i>t</i> -Bu	1.40	1.42	1.44	1.41	1.40	1.47	1.41	1.41	1.40
1H, NH	6.52	6.76	6.39	6.41	6.50	6.86	5.99	6.37	6.22
7H, arom CH	7.15- 8.08	7.1726- 8.05	6.99- 8.25	7.31 8.14	- 8.27	7.02- 8.00	7.01- 8.56	7.15- 8.24	7.20- 8.16

**Table 5.** Experimentally measured and calculated  $^{13}\text{C}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4b**)

	$\delta_{\text{C}}$	HF/6-311+G** GIAO	HF/6-311++G**	B3LYP 311+G**	/6- 311+G**	B3LYP 311++G**	/6- 311+G**			
CMe <sub>3</sub>	28.51	28.98	28.33	27.42	27.86	26.97	26.03	26.3	27.67	
N-C	52.62	50.22	51.68	54.31	57.05	51.66	51.52	51.8	51.79	
C-O	83.94	84.34	88.19	85.37	84.29	80.51	80.66	83.4	83.98	
aromati	124.0	124.5	123.79	124.8	124.31	124.07	124.22	124.	124.91	
	128.4	127.1	127.90	128.5	128.24	128.55	128.37	128.	128.39	
	129.5	128.7	130.71	131.3	129.21	128.86	128.99	129.	129.11	
	134.6	132.3	131.51	133.4	133.69	134.11	134.97	135.	135.21	
	135.7	134.6	135.92	135.8	134.57	135.51	135.66	135.	135.90	
	136.0	137.3	137.87	137.1	135.91	136.14	136.01	136.	136.17	
	141.7	141.2	141.76	141.8	141.72	141.98	141.81	141.	141.33	
CO	of	158.8	155.9	155.31	156.7	156.31	156.31	157.11	157.	157.84
CO	of	161.3	160.6	161.50	161.3	161.99	163.86	163.97	163.	163.39
CO	of	191.5	197.9	197.07	197.2	197.44	191.71	191.32	191.	191.72

**Table 6.** Experimentally measured and calculated  $^1\text{H}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4c**)



H atom	$\delta_H$	HF/6-311+G**		HF/6-311++G**		B3LYP /6-311+G**		B3LYP /6-311++G**	
	(CDC)	GIAO							
9H,	1.07	1.13	1.02	1.04	1.07	1.22	1.21	1.07	1.03
6H,	1.45	1.56	1.44	1.45	1.49	1.56	1.47	1.40	1.41
2H, CH <sub>2</sub>	1.74	1.91	1.84	1.80	1.81	1.76	1.71	1.79	1.71
1H, NH	6.58	6.53	6.59	6.54	6.49	6.87	6.08	6.41	6.34
7H,	7.15-	7.29-	7.39-	7.11-	7.16-	7.32-	7.27-	7.01-	7.11-

**Table 7.** Experimentally measured and calculated <sup>13</sup>C chemical shifts  $\delta$  (ppm, vs TMS) for (4c)

A C atom	$\delta_C$	HF/6-311+G**		HF/6-311++G**		B3LYP /6-311+G**		B3LYP /6-311++G**	
	(CDCl <sub>3</sub> )								
2Me	28.86	27.01	27.76	27.11	27.41	27.17	28.6	28.21	28.49
CMe <sub>3</sub>	31.56	30.32	31.76	31.42	31.56	31.47	31.5	31.22	31.97
CMe <sub>3</sub>	31.71	40.03	40.37	40.46	40.99	35.90	35.7	35.89	35.02
CH <sub>2</sub>	51.87	52.33	53.76	52.41	52.66	51.62	51.5	51.32	51.79
N-C	56.61	56.43	56.11	54.71	56.18	57.32	58.5	58.11	58.32
C-O	84.12	83.71	83.55	86.33	84.97	80.54	80.3	80.76	80.21
aromat	124.05	122.8	120.0	120.66	121.01	123.31	124.	123.34	123.42
	128.44	127.3	127.0	126.11	126.92	128.11	128.	128.32	128.11
	129.62	128.0	129.1	128.45	128.63	130.52	130.	130.47	130.01
	134.56	130.7	133.6	134.63	134.6	133.41	133.	134.07	134.77
	135.80	134.8	134.9	135.11	135.27	135.67	135.	135.81	135.66
	136.01	136.4	135.0	136.51	135.94	136.56	136.	136.09	136.03
	141.68	141.7	140.9	140.96	141.99	141.71	141.	141.98	140.66
CO of	158.96	154.3	157.9	158.13	158.31	158.11	158.	158.92	158.16
CO of	160.96	160.3	160.1	161.01	161.23	160.32	160.	160.51	160.59
CO of	191.48	190.2	190.8	190.39	190.57	196.86	196.	196.16	196.32

**Table 8.** Experimentally measured and calculated <sup>1</sup>H chemical shifts  $\delta$  (ppm, vs TMS) for (4d)

H atom	$\delta_{\text{H}}$ (CDCl <sub>3</sub> )	HF /6-311+G** GIAO	HF 311++G**	/6- 311+G**	B3LYP /6- 311+G**	B3LYP /6- 311++G**	B3LYP /6- 311+G**	B3LYP /6- 311++G**	
10H,5C	1.22-	1.16-	1.29-	1.18-	1.20-	1.22-	1.29-	1.12-	1.15-
1 H, N-	3.76	3.74	3.80	3.81	3.72	3.89	3.76	3.91	3.74
1H, NH	6.53	6.51	6.50	6.54	6.57	6.65	6.31	6.51	6.32
7H,	7.26-	7.16-	7.10-	7.18	7.16-	7.38-	7.10-	7.47-	7.29-

**Table 9.** Experimentally measured and calculated <sup>13</sup>C chemical shifts  $\delta$  (ppm, vs TMS) for (4d)

C atom	$\delta_{\text{C}}$	HF/6- 311+G**	HF/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**
CH <sub>2</sub> of	24.64	21.37	21.87	21.39	21.77	23.87	23.98	23.88	23.99
	25.32	25.45	25.01	25.98	25.31	26.77	26.98	27.99	27.78
	32.62	30.54	30.66	30.32	31.02	32.55	32.62	32.71	32.60
	48.98	45.66	45.87	45.99	45.32	45.88	45.87	45.88	45.66
	83.91	83.76	83.62	83.08	83.39	81.77	81.76	81.87	83.90
	124.0	124.5	124.89	124.1	124.22	124.09	124.7	124.87	124.29
	127.0	127.9	127.34	126.8	127.39	127.13	127.2	127.15	127.16
	127.7	127.2	128.61	127.8	127.98	127.98	128.3	128.65	127.89
129.8	129.9	129.51	129.9	130.06	130.65	130.3	129.56	128.98	
135.2	135.6	135.11	135.1	135.21	135.98	135.8	135.98	135.01	
136.1	138.0	136.27	136.0	136.90	138.98	137.7	138.06	137.51	
141.4	141.3	141.59	141.1	141.82	143.98	143.9	142.72	142.31	
CO of	159.5	158.3	158.02	158.3	159.05	159.61	159.6	159.87	159.19
CO of	161.4	165.9	161.87	161.9	164.41	161.20	161.8	161.89	161.02
CO of	191.6	191.2	191.55	191.8	191.77	193.76	194.7	193.43	192.98

**Table 10.** Experimentally measured and calculated <sup>1</sup>H chemical shifts  $\delta$  (ppm, vs TMS) for (4e)

H atom	$\delta_{\text{H}}$	HF/6- 311+G**	HF/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**
9 H, <i>t</i> -Bu	1.40	1.47	1.45	1.44	1.40	1.48	1.43	1.40	1.42
1H, NH	6.50	6.16	6.37	6.38	6.40	6.49	6.38	6.65	6.48
7H, arom	7.26-	7.45-	7.49-	7.11-	7.13-	7.39-	7.29-	7.32-	7.21-8.20

**Table 11.** Experimentally measured and calculated  $^{13}\text{C}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4e**)

C atom	$\delta_{\text{C}}$ (CDCl <sub>3</sub> )	HF/6- 311+G**	HF/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**				
CMe <sub>3</sub>	28.54	26.5	25.32	25.21	25.79	28.03	27.9	28.81	28.41
N-C	52.64	45.8	40.54	46.76	45.31	52.61	52.7	52.60	52.54
C-O	83.91	83.3	83.11	83.62	82.41	83.22	80.7	82.61	83.12
aromatic	124.04	123.	124.91	122.7	121.2	123.12	123.	124.78	124.66
	127.08	127.	125.81	124.3	125.3	126.91	126.	126.99	126.21
	127.72	128.	127.42	127.3	127.5	127.08	127.	127.06	127.90
	129.85	133.	130.52	129.9	129.8	129.98	131.	129.26	129.72
	135.19	135.	135.81	135.4	135.7	135.76	135.	135.87	135.08
	136.05	136.	136.56	136.4	136.1	136.18	136.	136.09	136.87
	141.61	141.	141.28	140.7	140.3	141.98	141.	141.87	141.16
CO of	159.43	158.	157.33	158.5	158.3	159.98	159.	158.96	159.52
CO of	161.53	160.	160.30	160.1	160.2	160.87	161.	161.56	161.78
CO of	191.82	186.	186.54	186.7	187.8	185.41	183.	184.76	184.11

**Table 12.** Experimentally measured and calculated  $^1\text{H}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4f**)

H atom	$\delta_{\text{H}}$ (CDCl <sub>3</sub> )	HF 311+G**	/6- HF/6- 311++G**	B3LYP 311+G**	/6- B3LYP 311++G**				
9H,	1.06	1.09	1.09	1.26	1.05	1.11	1.09	1.15	1.10
6H,	1.45	1.51	1.40	1.41	1.45	1.48	1.40	1.50	1.52
2H, CH <sub>2</sub>	1.74	1.72	1.79	1.80	1.70	1.80	1.89	1.78	1.79
1H, NH	6.54	6.51	6.60	6.53	6.54	6.49	6.37	6.71	6.59
7H, arom	7.26-	7.39-	7.41-	6.89-	7.19-	7.61-	7.13-	6.99-	7.22-

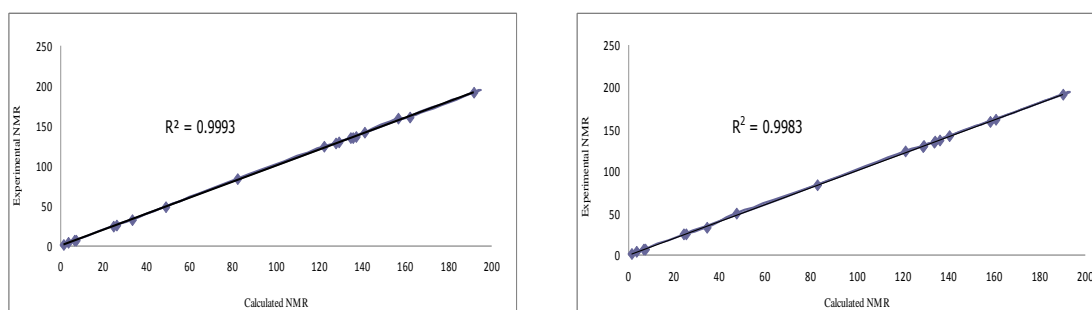
**Table 13.** Experimentally measured and calculated  $^{13}\text{C}$  chemical shifts  $\delta$  (ppm, vs TMS) for (**4f**)

C	$\delta_{\text{C}}$ (CDCl <sub>3</sub> )	HF/6- 311+G**	HF/6- 311++G**	B3LYP/6- 311+G**	B3LYP/6- 311++G**				
2Me	28.88	28.54	28.72	28.96	27.32	26.37	26.4	26.98	26.22
CMe <sub>3</sub>	31.55	30.86	30.69	30.65	30.11	30.97	30.9	30.14	30.86
CMe <sub>3</sub>	31.72	32.76	31.87	33.23	32.67	31.22	31.9	31.67	31.93

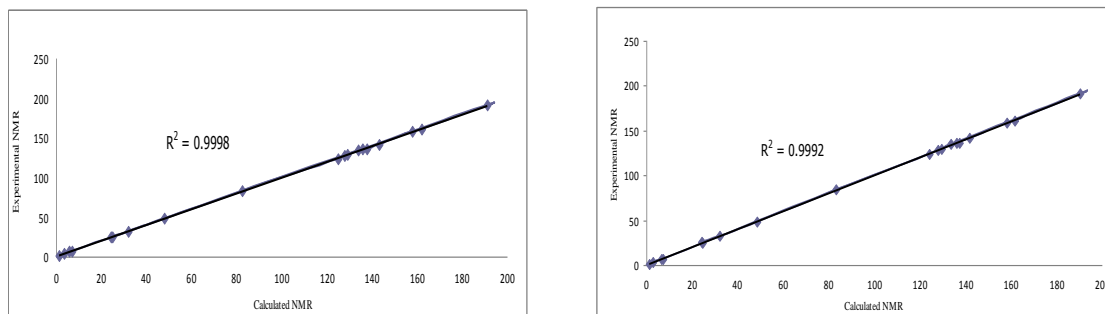
CH <sub>2</sub>	51.87	50.21	51.87	51.49	50.98	50.98	50.6	50.65	50.58
N-C	56.62	56.98	56.32	56.93	56.01	56.76	56.7	56.11	56.92
C-O	84.09	84.34	81.98	84.09	84.31	82.65	82.9	82.48	82.56
aromat	124.02	122.30	122.9	123.31	123.8	124.76	124.	124.98	124.54
	127.06	127.06	127.2	127.22	127.2	126.85	126.	126.93	126.97
	127.68	127.15	127.9	128.13	128.2	127.67	127.	127.11	127.34
	129.97	129.54	130.1	131.08	129.9	129.47	129.	128.51	128.17
	135.01	136.34	134.9	134.89	134.9	135.32	135.	135.37	135.51
	136.00	138.80	137.7	137.88	137.1	137.89	137.	137.45	137.02
	141.58	141.77	141.5	140.36	140.5	141.87	141.	140.87	140.93
CO of	159.55	156.39	153.0	158.54	154.3	159.66	159.	159.76	158.01
CO of	161.12	163.75	164.0	163.71	163.3	162.99	162.	162.06	162.87
CO of	191.73	197.43	191.7	191.54	191.3	191.87	191.	191.23	191.18

**Table 14.** The correlation value ( $R^2$ ) for calculated  $^{13}\text{C}$  chemical shifts of **4a** by the HF/B3LYP.

Basis	HF		B3LYP	
	6-311+G**	0.9991	0.9986	0.9991
6-311++G**	0.9993	0.9983	0.9998	0.9992



**Fig. 2.** Correlation graphic of calculated and experimental  $^{13}\text{C}$  chemical shifts for **4a** at HF/6-311++G\*\* using GIAO and CSGT approach.



**Fig. 3.** Correlation graphic of calculated and experimental  $^{13}\text{C}$  chemical shifts for 4a at B3LYP/6-311++G\*\* using GIAO and CSGT approach.

In summary, there are a good agreement between experimental and calculated  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts for  $\alpha$ -acyloxycarboxamides and they are supported each other.

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