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The '*Baylis - Hillman* Reaction' Mechanism and Applications Revisited

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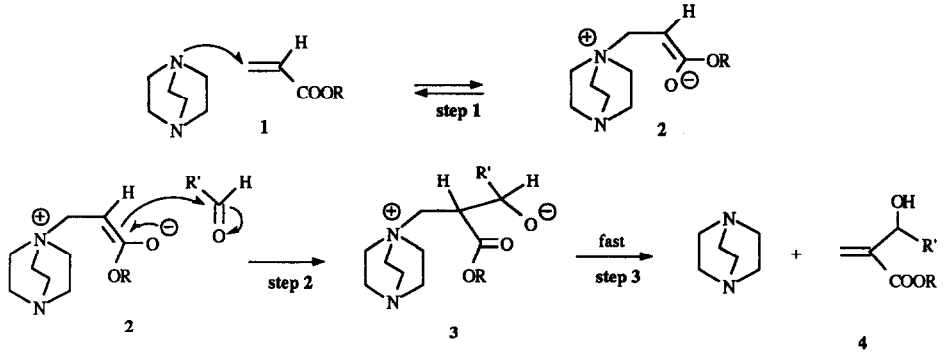
Abstract: It is shown that reaction of aryl, benzyl, alkyl and functionalised alkyl acrylic esters with benzaldehyde, in the presence of 1,4-diazabicyclo[2.2.2] octane, strongly depends upon the electronic and steric effects of the ester part. This influence is also observed in condensation of furfuraldehyde. Moreover, for the first time, it is shown that the overall condensation is equilibrated.

As part of a program aiming at the synthesis of new acrylic monomers for the preparation of new polymers,[1] we considered the possibility offered by the α-hydroxyalkylation of acrylic esters (well known as the *Baylis-Hillman* Reaction[2]) symbolized in Scheme 1 according to the mechanism proposed by Hill and Isaacs.[3]



Scheme 1

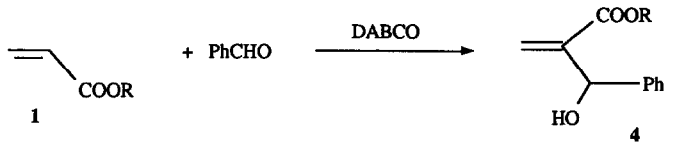
From a practical point of view, examination of the literature shows that the yields of a large number of these condensations have to be improved, and their fields of applications extended.[2,4] Thus, it is now well accepted that aldehydes may be condensed under atmospheric pressure (while ketones necessitate high pressure[5]) but in numerous cases, yields are not very high, and reaction times are rather long.[6] Considering the mechanism reported in Scheme 1, we thought that the nature of R would play a significant role in the reactivity of the acrylic esters.

Indeed R with electron-withdrawing properties would increase the impoverishment of the unsaturation and favour the formation of **2**. On the other hand step 2 which has been found to be the rate-determining step[3] must be favoured by electron-rich betaine **2**. So if our hypothesis is right, the result of such condensations would strongly depend on the electronic effects of R. When we started this work the influence of R had never been studied. However recently, and independently of our work, Bode and Kaye found that varying R from Me to Et or *i*-Pr led to a variation of the kinetics of the reaction.[7]

In the present paper we will show that the nature of R is a very important factor, particularly when R is not a simple alkyl group. Moreover, as we shall see this study led us to conclude that many of these reactions, if not all, must actually be completely equilibrated.

Results and Discussion

Taking account of the literature data and after exploratory experiments the conditions summarized in Scheme 2 were used with benzaldehyde as substrate.



Reagents and conditions : **1** /PhCHO/DABCO = 1.3/1/0.13, room temp.

Scheme 2

In the present study, we were interested in the knowledge of the complete evolution of the condensation when the structure of the starting acrylate was varied for the following reasons: i) to know the synthetic possibilities offered by these condensations, in other words the yield of isolated product, ii) to have some informations about the possible further evolution of the products as well as the importance taken by the side-reactions. Thus, we decided to determine the time after which the reaction no longer evolved and the corresponding isolated yield of hydroxyalkylated acrylate.

Condensation of aryl and benzylacrylates with benzaldehyde

We first studied arylacrylates *meta* and *para* substituted by electron-releasing or withdrawing groups on the benzene ring. The results obtained are reported in Table 1 together with the corresponding σ values. We verified that during the isolation of the monomers no destruction took place and that isolated yields exactly reflected the nature of the reaction performed. Besides the hydroxyalkylation we were able to identify a number of side reactions. Benzaldehyde was oxidized into benzoïc acid by the air contained in the reagents. Note that oxygen must not be removed from the reaction medium. Indeed stabilization of (meth)acrylic monomers by EMHQ necessitates the presence of oxygen in order to prevent side polymerizations. In such condensations, we observed the formation

of by-products isolated and identified (by comparison of their spectral data with those described in the literature[8,9]) as compounds due to Michael condensation[8] and dimerization.[9] Of course, we have verified the purity of the reactants and the absence of these by-products at the start of the reaction. Moreover 10 to 20 % of the substituted phenols resulting from the cleavage of the starting acrylate were characterized; they come from transesterification.

Table 1: Condensation of Arylacrylates with Benzaldehyde in the Presence of 1,4-Diazabicyclo[2.2.2] Octane.[a]

Entry	Compound	R	σ	time[b] (h)	Product	yield (%) [c]
1	**1a**	*p*-Me_2N-C_6H_4	-0.63	84	**4a**	62 (77)
2	**1b**	*p*-MeO-C_6H_4	-0.28	8	**4b**	54 (60)
3	**1c**	*p*-Me-C_6H_4	-0.14	36	**4c**	55 (61)
4	**1d**	*m*-Me_2N-C_6H_4	-0.10	20	**4d**	61 (77)
5	**1e**	*m*-Me-C_6H_4	-0.06	36	**4e**	54 (60)
6	**1f**	C_6H_5	0	5	**4f**	55 (81)
7	**1g**	*m*-MeO-C_6H_4	0.10	24	**4g**	43 (48)
8	**1h**	*p*-F-C_6H_4	0.15	72	**4h**	39 (51)
9	**1i**	*p*-Cl-C_6H_4	0.24	72	**4i**	42 (53)
10	**1j**	*m*-F-C_6H_4	0.34	5	**4j**	43 (54)
11	**1k**	*p*-MeOOC-C_6H_4	0.44	20	**4k**	37 (48)
12	**1l**	*m*-CF_3-C_6H_4	0.46	24	**4l**	22 (37)
13	**1m**	*p*-CF_3-C_6H_4	0.53	24	d	-
14	**1n**	*m*-NC-C_6H_4	0.62	24	d	-
15	**1o**	*p*-NC-C_6H_4	0.70	24	d	-
16	**1p**	*p*-O_2N-C_6H_4	0.81	24	d	-

[a] All reactions were run without solvent with ratio of (1) : PhCHO : DABCO = 1.3 : 1 : 0.13 at room temperature. [b] Time after which the reaction mixture no longer evolved. [c] Isolated yield based on benzaldehyde. In parenthesis, isolated yield based on converted benzaldehyde. [d] No product was detected.

Taking into account the above observations as well as the mechanism reported in Scheme 1, it is not surprising that no simple relation between yields and σ values may be obtained. However some interesting points emerge. After 5 hours, one equivalent of phenylacrylate (entry 6) has disappeared from the reaction medium (in other words 30-40% were destroyed). During this short reaction time only a small amount of benzaldehyde led to by-products and a good yield relative to the consumed benzaldehyde was obtained. Electron-donating groups decreased both the condensation and the destruction of the acrylic ester. Comparison of conversion yields shows that the presence of a dimethylamino group (entries 1 and 4) decreases the destruction of PhCHO but correlatively increases the destruction of the corresponding acrylate which seems to play the role of an antioxidizing agent. This could be related to the antioxidizing properties of aminophenols which may be formed during the reaction. It is not easy to interpret the effect of electron-withdrawing groups. However it appears that generally speaking they disfavour the condensation. This could be due to a decrease of the

nucleophilicity of **2**. Interestingly with the very strong electron-withdrawing groups only traces of the expected products were observed even after a much longer time (240 h) than reported in Table 1. Curiously after 24 h, 80 to 90 % of the starting acrylate as well as of benzaldehyde was recovered. Of course, the very low reactivity of the acrylate may be explained, as above, by the weak nucleophilic character of **2**. However, it was striking that the monomers and above all PhCHO were apparently slowly destroyed. A possible hypothesis could be that in the presence of a strong electron-withdrawing group the last "fast step" could be reversible thus regenerating PhCHO as well as the starting **1**. We were able to verify this hypothesis in a few cases (*vide infra*).

In order to confirm the important role played by the electronic effects of R we decided to study some substituted benzyl acrylates. The results obtained are reported in Table 2.

Table 2. Condensation of Benzylacrylates with Benzaldehyde in the Presence of 1,4-Diazabicyclo [2.2.2] Octane.[a]

Entry	Compound	R	time[b] (h)	Product	yield (%) [c]
1	**1q**	C_6H_5-CH_2-	40	**4q**	88 (93)
2	**1r**	*p*-F-$C_6H_4CH_2$-	92	**4r**	85 (94)
3	**1s**	*p*-CF_3-$C_6H_4CH_2$-	67	**4s**	88 (98)
4	**1t**	*p*-CH_3O-$C_6H_4CH_2$-	192	**4t**	86 (91)
5	**1u**	*p*-CH_3-$C_6H_4CH_2$-	120	**4u**	76 (95)
6	**1v**	*m*-F-$C_6H_4CH_2$-	90	**4v**	77 (91)
7	**1w**	*m*-CF_3-$C_6H_4CH_2$-	67	**4w**	83 (92)
8	**1x**	*m*-CH_3O-$C_6H_4CH_2$-	120	**4x**	86 (91)
9	**1y**	*m*-CH_3-$C_6H_4CH_2$-	120	**4y**	83 (92)

[a] All reactions were run without solvent with ratio of (1) : PhCHO : DABCO = 1.3 : 1 : 0.13 at room temperature. [b] Time after which the reaction mixture no longer evolved. [c] Isolated yield based on benzaldehyde. In parenthesis, isolated yield based on converted benzaldehyde.

From the comparison with the data of Table 1, it appears as expected that the attenuation of electronic effects lowered the condensation rates. However the side reactions were also considerably attenuated leading to good to excellent condensation yields. Interestingly most of these reactions were faster than condensation of methylacrylate.

Condensation of simple alkylacrylates with benzaldehyde

We wondered if electronic effects were the only ones influencing the results of these reactions. So we studied the condensation of a number of selected alkylacrylates on PhCHO. The results obtained are reported in Table 3. It clearly appears that increasing the length of R decreases the reactivity (entries 1 to 6). These results are in accordance with the recent results of Bode and Kaye.[7]

Table 3. Condensation of Alkylacrylates with Benzaldehyde in the Presence of 1,4-Diaza bicyclo[2.2.2] Octane.[a]

Entry	Compounds	R	time[b] (days)	Product	yield (%) [c]
1	**1z**	CH_3	6	**4z**	89 (94)
2	**1aa**	C_2H_5	7	**4aa**	79 (83)
3	**1ab**	*n*-C_4H_9	4	**4ab**	85 (94)
4	**1ac**	*n*-C_6H_{13}	9	**4ac**	82 (86)
5	**1ad**	*n*-C_8H_{17}	12	**4ad**	78 (82)
6	**1ae**	*n*-$C_{10}H_{21}$	14	**4ae**	75 (79)
7	**1af**	*i*-C_4H_9	16	**4af**	85 (89)
8	**1ag**	*t*-C_4H_9	28	**4ag**	65 (93)
9	**1ah**	CH_2-$CH(C_2H_5)$-C_4H_9	20	**4ah**	82 (91)
10	**1z**	CH_3 [d]	33	**4z**	73 (91)
11	**1ai**	2-adamentyl [d]	62	**4ai**	40 (80)

[a] All reactions were run without solvent with ratio of (**1**) : PhCHO : DABCO = 1.3 : 1 : 0.13 at room temperature. [b] Time after which the reaction mixture no longer evolved. [c] Isolated yield based on benzaldehyde. In parenthesis, isolated yield based on converted benzaldehyde. [d] Reaction performed in the presence of dioxane (5ml).

On the other hand and with few exceptions an increase in the steric hindrance also strongly decreases the rate of condensation (entries 3 to 9). This is confirmed by comparison of runs 10 and 11. In passing it may be noted that solvents considerably lower the reaction rates (compare entries 1 and 10). We concluded that steric hindrance must impede the approach of the reagents. With linear alkyl lipophilic interactions, the chain could fold in on itself forming clusters which could increase the steric hindrance. However variation of the polarity of the reaction medium with the chain length could also intervene.[10]

Condensation of functionalised alkyl acrylates with benzaldehyde

With these results in hand we turned toward the hydroxyalkylation of a number of representative functionalised alkylacrylates. The results obtained are gathered in Table 4.

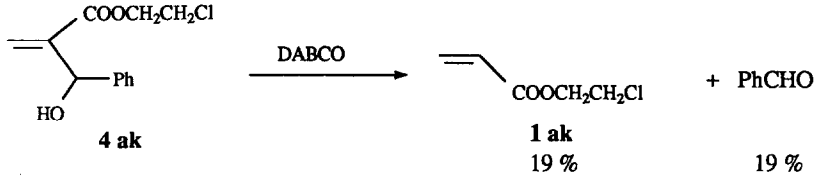
Interpretation of these results is much more difficult than with aryl or benzyl esters. It seems that the electron-withdrawing group in the β position relative to the oxygen favours condensation (compare entries 1 to 8). However electronic effects are not the only factors since, for example, 2-bromoethyl-acrylate (**1al**) did not condense. Steric hindrance, as described above, also played an important role. Thus it could be responsible for the extremely low reactivity of acrylates containing long chain alkyl halides (entries 13 to 15) which could be due to cluster aggregation around the reaction sites. Why such aggregation did not take place with 6-thiocyanohexyl acrylate (entry 16) is not clear. Finally the above tentative explanation may not be complete if, as we suggested, the overall condensation is equilibrated.

Table 4. Condensation of Functional Alkylacrylates with Benzaldehyde in the Presence of 1,4-Diazabicyclo[2.2.2] Octane.[a]

Entry	Compound	R	t [b]	Product	Yield (%) [c]
1	**1aj**	$-CH_2-CH_2-F$	3 d	**4aj**	81 (85)
2	**1ak**	$-CH_2-CH_2-Cl$	3 d	**4ak**	61 (81)
3	**1al**	$-CH_2-CH_2-Br$	2 d	e	
4	**1am**	$-CH_2-CF_3$	15 h	**4am**	58 (77)
5	**1an**	$-CH_2-CCl_3$	36 h	**4an**	64 (85)
6	**1ao**	$-CH_2-CH_2-OH$ [d]	2 d	**4ao**	29 (34)
7	**1ap**	$-CH_2-CH_2-OCH_3$	4 d	**4ap**	89 (93)
8	**1aq**	$-CH_2-CH_2-N(CH_3)_2$	8 d	**4aq**	82 (91)
9	**1ar**	$-CH_2-CH_2-SCN$	2 d	**4ar**	66 (88)
10	**1as**	$-CH_2-CH_2-C_6H_5$	4 d	**4as**	84 (88)
11	**1at**	$-CH_2-CH=CH_2$	3 d	**4at**	75 (88)
12	**1au**	$-CH_2COCH_3$	2 d	**4au**	65 (93)
13	**1av**	$-(CH_2)_3Cl$	15 d	e	
14	**1aw**	$-(CH_2)_6Cl$	15 d	e	
15	**1ax**	$-(CH_2)_6Br$	15 d	e	
16	**1ay**	$-(CH_2)_6SCN$	6 d	**4ay**	68 (86)

[a] All reactions were run without solvent with ratio of (1) : PhCHO : DABCO = 1.3 : 1 : 0.13 at room temperature. [b] Time after which the reaction mixture no longer evolved. [c] Isolated yield based on benzaldehyde. In parenthesis, isolated yield based on converted benzaldehyde. [d] 35 % of diacrylate were formed. This result was expected considering ref 9. [e] No reaction was observed.

To study this possible retrogradation we chose to work with 3-phenyl-3-hydroxy-2-methylene propanoic acid, 2-chloroethyl ester (**4ak**). Exploratory experiments showed that they reacted with DABCO to give back 2-chloroethyl acrylate (**1ak**) and benzaldehyde. We then performed the reactions reported in Scheme 3.



4 ak **1 ak** 19 % 19 %

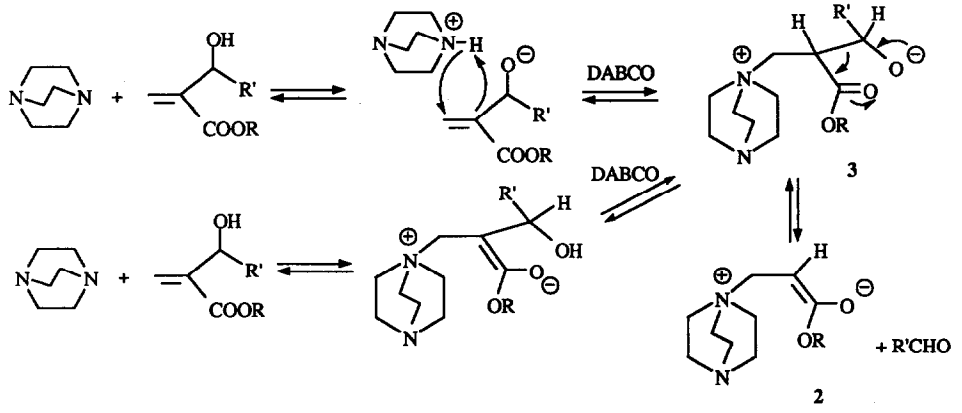
Reagents and conditions : **4 ak** /DABCO = 1/0.13 ; room temp. ; 12 h.

Scheme 3

It clearly appears that, contrary to the mechanism proposed by Hill and Isaacs,[3] the overall reaction is equilibrated. This conclusion has been confirmed with **4am** and **4an**. In these cases, and under the conditions of scheme 3, the retrogradation rise to 25 % and 20% respectively. Note that,

with very sensitive acrylates such as **4b-f**, we were unable to see an retrogradation because a strong degradation took place.

So a mechanistic interpretation, which in fact should complete the Hill and Isaacs's mechanism, could be done as follow: every time the structure of the hydroxyalkylated acrylate is appropriate to proton abstraction from the hydroxy group with concomitant elimination of benzaldehyde to give an enolate esters, the condensation will be reversible. So steps 2 and 3 of scheme 1 could be tentatively written as in scheme 4.



Scheme 4

As expected from an equilibrated reaction, displacement may be obtained by increasing the amount of one of the starting materials. The results reported in table 5 confirme this point. Note that the same kind of reaction was observed with 2,2,2-trifluoroethyl-acrylate (**1am**) and 2-thiocyanatoethyl-acrylate (**1an**).

Table 5. Condensation of 2-Chloroethylacrylate (**1ak**) with Benzaldehyde in Presence of 1,4-Diaza bicyclo[2.2.2] Octane at Room Temperature.

Entry	(**1ak**) : PhCHO : DABCO[a]	time	(**1ak**) : PhCHO : (**4ak**) [b]
1	1 : 1 : 0.1	3 d	0.17 : 0.17 : 0.83
2	1 : 2 : 0.1	3 d	0.13 : 1.13 : 0.87
		5 d	0.10 : 1.10 : 0.90
3	1 : 3 : 0.1	3 d	0.05 : 2.05 : 0.95
4	2 : 1 : 0.1	3 d	1.17 : 0.17 : 0.83
		5 d	1.12 : 0.12 : 0.88
5	3 : 1 : 0.1	3 d	2.3 : 0.3 : 0.7
		5 d	2.1 : 0.1 : 0.9

[a] Initial ratio of (**1ak**) : PhCHO : DABCO. [b] Ratio of (**1ak**) : PhCHO : (**4ak**) determined by ^{1}H NMR.

Finally, the results obtained in the present work have been confirmed in a few examples performed with furfuraldehyde instead of benzaldehyde (Table 6).

Table 6. Condensation of Various Alkylacrylates with Furfuraldehyde in the Presence of 1,4-Diaza bicyclo[2.2.2] Octane.[a]

Entry	Compound	R	t ime[b] (h)	Product	yield (%) [c]
1	**1z**	CH_3	24	**5a**	76 (80)
2	**1ab**	*n*-C_4H_9	72	**5b**	88 (95)
3	**1ah**	CH_2-$CH(C_2H_5)$-C_4H_9	154	**5c**	86 (95)
4	**1ak**	CH_2-CH_2-Cl	17	**5d**	70 (87)
5	**1am**	CH_2-CF_3	2	**5e**	54 (63)
6	**1ap**	CH_2-CH_2-OCH_3	36	**5f**	90 (95)
7	**1ar**	CH_2-CH_2-$N(CH_3)_2$	72	**5g**	86 (95)

[a] All reactions were run without solvent with ratio of (**1**) : furfural : DABCO = 1.3 : 1 : 0.13 at room temperature. [b] Time after which the reaction mixture no longer evolved. [c] Isolated yield based on furfural. In parenthesis, isolated yield based on converted furfural.

Conclusion

From this work the following important conclusions may be drawn : i) The result of the condensation of acrylic esters with benzaldehyde, in the presence of 1,4-diazabicyclo[2.2.2] octane, strongly depends upon the nature of the ester part of the acrylic ester. ii) Electronic as well as steric effects are important. The electronic effects broadly agree with the mechanism proposed by Hill and Isaacs. iii) It is difficult to accurately determine the exact mechanism of these reactions since a number of side reactions may intervene the extent to which depends on the nature of the acrylic ester. iv) Last but not least, the overall reaction must be considered as equilibrated.

Experimental Section

Gas chromatography analyses were performed using a Shimadzu GC-8A apparatus, equipped with a Merck D-2500 data processor, with a column of silicone OV-101 (10 %) - chromosorb W (3 m) (N_2 as carrier gas). ^1H and ^{13}C NMR spectra were measured for $CDCl_3$ or CCl_4 solutions containing tetramethylsilane (as an internal standard) on a Jeol PMX 60 or Bruker AM 400 spectrometer respectively. IR spectra were recorded on a 580B Perkin Elmer spectrophotometer. High resolution mass spectra were conducted on a Finnigan MAT 95 Q mass spectrometer at the Centre de Recherches Lorraine of Elf-Atochem (Marienau, France). Exact mass were determined by ESCAN method. T.l.c. analyses were performed with hexane - ethyl acetate mixtures (100:0 to 80:20). Products were purified by silica flash chromatography on Kieselgel 60 (230-400 mesh) with petroleum ether - ethyl acetate mixtures as eluent (90:10 to 80:20). All acrylic esters used as substrate were prepared by esterification of acryloyl chloride with the corresponding alcohol (1.1 equiv) in the presence of triethylamine (3 equiv) at 10 °C in $CHCl_3$ for 12H. Pure products (GC analysis) were obtained after usual workup and flash chromatography. All spectroscopic data (IR, ^1H and ^{13}C NMR) were in agreement with the expected formulas and the literature data. Acrylic esters were used under air atmosphere after stabilization with 100 ppm hydroquinone monomethylether to avoid polymerisation.

General procedure for the condensation of acrylic esters with benzaldehyde or furfuraldehyde.

At room temperature, benzaldehyde or furfuraldehyde (distilled prior to use) (13.5 mmol, 1 equiv.) was added to a stirred mixture of acrylic ester (20 mmol, 1.3 equiv.) and DABCO (2 mmol, 0.13 equiv.) under air atmosphere. If necessary (as specified in tables), 5 ml of dioxan was added to the reaction mixture. Disappearance of benzaldehyde and the apparition of **4** or **5** was monitored by gc analysis (each hour at the start of the reaction and each 12 hours after 12 hours of reaction) of small aliquots (internal standard : dodecan). Methylene chloride (30 ml) and the solution was washed first with a solution of HCl (10%) and then with water. The solvent was removed under vacuum. Alpha-hydroxylated acrylic esters were isolated by flash chromatography and their purity were controlled by GC analysis. They were identified by comparison of their physical and spectroscopic properties with those of samples prepared according to known procedures.[2-4]

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-N,N-dimethylamino-phenyl ester (**4a**): IR (neat) 3460 (OH), 3064-2804 (C-H), 1738 (C=O), 1633 (C=C, vinyl) and 1611, 1569, 1511, 1454 (C=C, aromatic) cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.32 (m, 5 H , aromatic), 6.33-6.95 (m, 4 H, aromatic), 6.46 (s, 1 H, CH_2 vinyl), 5.95 (s, 1 H, CH_2 vinyl), 5.51 (s, 1 H, CHOH), 3.47 (m, 1 H, OH) and 2.78 ppm (s, 6 H, CH_3); ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.81 (CO), 148.22 (C=), 142.02 (C=), 141.243 (C=), 140.98 (C=), 127.95 (CH=), 127.34 (CH=), 126.53 (CH=), 125.95 (C=), 121.27 (CH=), 112.81 (CH=), 72.14 (CH) and 40.45 ppm (CH_3).

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-methoxy-phenyl ester (**4b**): IR (neat) 3451, 1729, 1638, 1609, 1598, 1504, 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.19 (m, 5 H), 6.68 (m, 4 H), 6.37 (s, 1 H), 5.87 (s, 1 H), 5.45 (s, 1 H), 3.63 (s, 3H), 3.33 ppm (m, 1 H, OH); ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.73, 156.91, 143.50, 141.80, 141.13, 128.13, 127.59, 126.62, 126.55, 121.93, 114.08, 72.24 and 55.16 ppm. High-resolution MS for $C_{12}H_{13}FO_3$ (M^+) : Calcd m/z: 224.0848 ; Found : 224.0850.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-methyl-phenyl ester (**4c**): IR (neat) 3443, 3063-2925, 1732 ,1633 and 1508 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.37 (m, 5 H), 6.68-7.33 (m, 4 H), 6.52 (s,1 H), 6.03 (s, 1 H), 5.56 (s, 1 H), 3.50 (m, 1H , OH) and 2.27 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.41, 147.78, 141.79, 141.02, 135.03, 129.47, 128.02, 127.47, 126.56, 126.37, 120.74, 72.05 and 20.35 ppm. High-resolution MS for $C_{17}H_{16}O_4$ (M^+) : Calcd m/z: 284.1049 ; Found : 284.1053.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-N,N-dimethylamino-phenyl ester (**4d**): IR (neat) 3494, 3064-2808, 1733,1633, 1616, 1576, 1504, 1455 cm^{-1}; ^{1}H-NMR (CCl_4 , 60 MHz) 6.2-7.45 (m, 9 H), 6.12 (s, 1 H), 5.85 (s,1 H), 5.42 (s, 1 H), 3.31 (m, 1 H, OH) and 2.73 ppm (s, 6 H).^{13}C-NMR ($CDCl_3$; 75 MHz) 164.49, 151.24, 151.12, 141.94, 141.13, 129.25, 128.06, 127.49, 126.60, 126.39, 107.79, 108.91, 105.06, 72.32 and 40.00 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-methyl-phenyl ester (**4e**): IR (neat) 3459, 3033-2921, 1740, 1636, 1616, 1589, 1489, 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.33 (m, 5 H), 6.54-7.73 (m, 4 H), 6.47 (s, 1 H), 5.99 (s, 1 H), 5.52 (s, 1 H), 3.41 (m, 1 H OH) and 2.26 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.25, 149.92, 141.77, 141.02, 139.05, 128.66, 127.99, 127.43, 126.53, 126.36, 116.24, 121.61, 118.01, 71.99 and 20.71 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, phenyl ester (**4f**): IR (neat) 3453, 3064-2915, 1736, 1632, 1592, 1492, 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.71-7.50 (m, 10 H), 6.40 (s, 1 H), 5.87 (s, 1 H), 5.46 (s, 1 H) and 2.82 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.67, 150.35, 141.88, 141.14, 129.34, 128.47, 127.95, 127.27, 126.69, 125.90 , 121.40 and 73.01 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-methoxy-phenyl ester (**4g**): IR (neat) 3496, 3065-2838, 1739,1632, 1610, 1592, 1454 and 1450 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.34 (m, 5 H), 6.35-7.28 (m, 5 H, 4 H + 1 H vinyl), 5.99 (s, 1 H), 5.54 (s, 1 H), 3.68 (s, 3 H,) and 3.14 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.18, 160.01, 150.99, 141.74, 141.05, 129.44, 128.11, 127.57, 126.62, 126.42, 113.36, 111.45, 107.13, 72.13 and 54.90 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-fluoro-phenyl ester (**4h**): IR (neat) 3450, 3065-2921, 1739,1634, 1600, 1504, 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.23 (m, 5 H), 6.64-7.06

(m, 4 H), 6.41 (s, 1 H) . 5.93 (s, 1 H), 5.47 (s, 1 H) and 3.23 (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.55, 160.08 (d, J=243 Hz), 145.96, 141.50, 140.93, 128.38, 127.91, 127.34, 126.66, 122.74 (d, J= 9 Hz), 115.83 (d, J =24 Hz), 72.57 and 40.45 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-chloro-phenyl ester (**4i**): IR (neat) 3451, 3065-2916, 1738,1633, 1590, 1510, 1487 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.19 (m, 5 H), 6.63-7.27 (m, 4 H), 6.40 (s, 1 H), 5.90 (s, 1 H), 5.46 (s, 1 H) and 2.97 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.34, 148.78, 141.5, 140.95, 131.27, 129.38, 128.50, 128.04, 127.57, 126.67, 122.80 and 72.84 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-fluoro-phenyl ester (**4j**): IR (neat) 3460, 3067-2903, 1739, 1631, 1602, 1512, 1488 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.23-7.63 (m, 9 H), 6.40 (s, 1 H), 5.96 (s, 1 H), 5.48 (s, 1 H,) and 3.12 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 169.17, 162.52 (=C-F, d, J = 245 Hz), 150.98 (d, J= 10 Hz), 141.44, 140.92, 129.91 (d, J= 10 Hz), 128.27, 127.80, 127.21, 126.65, 117.10, 112.64 (d, J=24 Hz), 109.32 (d, J=24 Hz) and 72.34 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-carbomethoxy-phenyl ester (**4k**): IR (neat) 3493, 3064-2953, 1725, 1633, 1604, 1504 and 1437 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.79-8.1 (m, 4 H), 7.23 (m, 5 H), 6.43 (s, 1 H), 5.99 (s, 1 H), 5.51 (s, 1 H), 3.78 (s, 3 H) and 3.27 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.24, 163.94, 153.92, 141.56, 140.99, 131.09, 128.46, 128.00, 127.73, 127.62, 126.68, 121.47, 72.70 and 52.09 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-trifluoromethyl-phenyl ester (**4l**): IR (neat) 3434, 3068-2919, 1737, 1634, 1598, 1513, 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.82-7.63 (m, 9 H), 6.39 (s, 1 H), 5.93 (s, 1 H), 5.44 (s, 1 H) and 3.35 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.12, 150.31, 141.38, 140.90, 131.79 (=C-CF_3, q, J = 33 Hz), 129.91, 128.52, 128.09, 127.85, 126.72, 125.09, 123.39 (CF_3, q, J= 271 Hz), 122.71, 118.79 and 72.67 ppm. High-resolution MS for $C_{17}H_{15}F_3NO_3$ ($M^+ + NH_4$) : Calcd m/z: 340.1160 ; Found : 340.1161.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, benzyl ester (**4m**): IR (neat) 3456, 3089-2895, 1713, 1630, 1588, 1495 and 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.11 (m, 10 H), 6.18 (s, 1 H), 5.70 (s, 1 H), 5.35 (s, 1 H), 4.93 (s, 2 H) and 3.25 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.76, 141.89, 141.16, 135.29, 128.27, 128.17, 127.98, 127.78, 127.57, 126.58, 125.84, 72.58 and 66.32 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-fluoro-benzyl ester (**4r**): IR (neat) 3466, 3065-2958, 1717,1631, 1607, 1514, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.14 (m, 5 H), 6.62-7.23 (m, 4 H), 6.20 (s, 1 H), 5.73 (s, 1 H), 5.38 (m, 1 H), 4.96 (s, 2 H) and 3.19 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.57, 162.19 (=C-F, d, J = 245 Hz, 141.80, 141.09, 131.08 , 129.68 (CH=, d, J = 8 Hz), 128.05, 127.47, 126.51, 125.66, 115.03 (CH=, d, J= 22 Hz), 72.37 and 65.44 ppm. High-resolution MS for $C_{17}H_{17}FNO_2$ (M^+-H_2O + NH_4) : Calcd m/z: 286.1243 ; Found : 286.1241.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-trifluoromethyl-benzyl ester (**4s**): IR (neat) 3588, 3056-2988, 1723, 1624, 1550 and 1494 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.97-7.70 (m, 4 H), 7.21 (m, 5 H), 6.30 (s, 1 H), 5.84 (s, 1 H), 5.47 (m, 1 H), 5.08 (s, 2 H) and 2.94 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.70, 141.70, 141.12, 139.42, 130.16 (=C-CF_3, q, J = 32 Hz), 128.39, 127.79, 126.65, 126.39, 125.33, 123.89 (CF_3, q, J = 270 Hz), 72.84 and 65.43 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-methoxy-benzyl ester (**4t**): IR (neat) 3492, 3062-2838, 1711, 1636, 1615, 1515 and 1494 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.13 (m, 5 H), 6.43-7.07 (m, 4 H), 6.13 (s, 1 H), 5.65 (s, 1 H), 5.32 (s, 1 H), 4.86 (s, 2 H), 3.62 (s, 3 H) and 3.23 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.54, 159.07, 142.02, 141.17, 129.44, 127.88, 127.26, 127.12, 126.48, 125.14, 113.40, 72.07, 65.89 and 54.60 ppm. High-resolution MS for $C_{18}H_{18}O_4$ (M^+) : Calcd m/z: 298.1206 ; Found : 298.1205.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *p*-methyl-benzyl ester (**4u**): IR (neat) 3463, 3032-2962, 1717, 1630, 1520, 1494 and 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.28 (m 5 H), 7.10 (m, 4 H), 6.27 (s, 1 H), 5.80 (s, 1 H), 5.42 (m, 1 H), 4.97 (s, 2 H), 3.42 (m, 1 H, OH) and 2.29 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.67, 141.99, 141.18, 137.56, 132.22, 128.82, 127.98, 127.82, 127.37, 126.53, 125.43, 72.28 , 66.13 and 20.78 ppm. High-resolution MS for $C_{18}H_{22}NO_3$ ($M^+ + NH_4$) : Calcd m/z: 300.1600 ; Found : 300.1603.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-fluoro-benzyl ester (**4v**): IR (neat) 3452, 3065-2896, 1721, 1632, 1619, 1594, 1492 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.10 (m, 5H), 6.52-7.3 (m, 4 H), 6.17 (s, 1 H), 5.71 (s, 1 H), 5.32 (m, 1 H), 4.89 (s, 2 H) and 3.20 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.44, 162.39 (=C-F, d, J = 245 Hz), 141.76, 141.11, 137.77 (C=, d, J = 8 Hz), 129.73 (CH=, d, J = 8 Hz), 128.02, 127.55, 126.59, 125.75, 122.99, 114.67 (CH=, d, J = 22 Hz), 114.27 (CH=, d, J = 22 Hz), 72.28 and 65.23 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-trifluoromethyl-benzyl ester (**4w**): IR (neat) 3445, 3065-3033, 1723, 1631, 1602, 1513, 1494 and 1452 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.13 (m, 5 H), 6.95-7.8 (m, 4 H), 6.21 (s, 1H), 5.78 (s, 1 H), 5.36 (m, 1 H), 4.95 (s, 2 H) and 3.42 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.79, 141.90, 141.31, 136.56, 131.25, 130.79 (=C-CF_3, q, J = 32 Hz), 129.04, 128.44, 127.91, 126.83, 126.27, 124.99, 124.60, 123.98 (CF_3, q, J = 271 Hz), 72.70 and 65.60 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-methoxy-benzyl ester (**4x**): IR (neat) 3480, 3063-2837, 1721, 1630, 1589, 1492 and 1459 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.17 (m, 5 H), 6.58-7.20 (m, 4 H), 6.23 (s, 1 H), 5.71 (s, 1 H), 5.40 (m, 1 H), 4.96 (s, 2 H), 3.65 (m, 3H) and 3.05 ppm (m, 1H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.44, 159.13, 141.88, 141.10, 136.65, 129.11, 127.91, 127.31, 126.50, 125.32, 119.72, 113.22, 113.01, 72.05, 65.90 and 54.56 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *m*-methyl-benzyl ester (**4y**): IR (neat) 3464, 3063-2922, 1717, 1631, 1613, 1595, 1493 and 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.30 (m, 5 H), 6.84-7.33 (m, 4 H), 6.32 (s, 1 H), 5.82 (s, 1 H,), 5.47 (m, 1 H), 5.04 (s, 2 H,), 3.15 (s, 1 H, OH) and 2.3 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.80, 142.22, 141.44, 137.28, 135.36, 128.79, 128.56, 128.23, 127.59, 126.82, 125.59 , 124.95, 72.41, 66.39 and 21.13 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, methyl ester (**4z**): IR (neat) 3481, 3088-2903, 1722, 1631, 1604, 1494 and 1441 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.23 (m, 5H), 6.17 (s, 1H), 5.69 (s, 1H), 5.38 (s, 1H), 3.63 (s, 3H) and 3.16 ppm (s, 1H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.80, 142.17, 141.43, 128.44, 127.84, 126.69, 125.97, 73.13 and 51.94 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, ethyl ester (**4aa**): IR (neat) 3473, 3088-2907, 1712, 1630, 1603, 1587, 1493 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.08 (m, 5 H), 6.08 (s, 1 H), 5.65 (1 H, s), 5.32 (1 H, m), 3.97 (2 H, q, J = 7 Hz), 3.50 (m, 1 H, OH) and 1.13 ppm (3 H, t, J = 7 Hz). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.03, 142.25, 141.35, 128.07, 127.45, 126.51, 125.16, 72.61 and 60.60 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, butyl ester (**4ab**): IR (neat) 3468, 3087-2874, 1713, 1630 , 1603, 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.23 (m, 5 H), 6.30 (s, 1 H), 5.80 (s, 1 H), 5.52 (s, 1 H), 4.07 (t, 2 H, J = 7 Hz), 3.13 (m, 1 H,OH) and 0.67-1.87 ppm (m, 7 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.27, 142.18, 141.33, 128.07, 127.63, 126.70, 125.68, 73.09, 64.64. 30.37. 18.95 and 13.46 ppm. High-resolution MS for $C_{14}H_{18}O_3$ (M^+) : Calcd m/z: 234.1256; Found : 234.1261.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, hexyl ester (**4ac**): IR (neat) 3468, 3064-2860 , 1713, 1628 , 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.10 (m, 5 H), 6.09 (s, 1 H), 5.65 (s, 1H), 5.30 (m, 1 H), 3.73-4.15 (m, 2 H), 3.37 (m, 1 H, OH) and 0.44-1.77 ppm (m, 8 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.21, 142.20, 141.36, 128.21, 127.50, 126.51, 125.48, 72.96, 64.89, 31.23, 28.27, 25.37, 22.33 and 13.84 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, octyl ester (**4ad**): IR (neat) 3475, 3087-2857, 1717, 1630, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz)7.37 (m, 5 H), 6.36 (s, 1 H), 5.87 (s, 1 H), 5.57 (m, 1 H), 4.12 (t, 2 H, J = 7 Hz), 3.03 (m, 1 H, OH) and 0.63-1.93 ppm (m, 12 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.25, 142.12, 141.32, 128.25, 127.63, 126.68, 125.65, 73.04, 65.95, 31.65, 29.03, 28.34, 25.74, 22.52 and13.98 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, decyl ester (**4ae**): IR (neat) 3470, 3064-2856, 1717, 1629, 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz)7.13 (m, 5 H), 6.11 (s, 1 H) 5.67 (s, 1 H), 5.53 (m, 1 H), 3.96 (t, 2 H, J = 7 Hz), 3.33 (m, 1 H, OH) and 0.62-1.77 ppm (m, 16 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.46, 141.36, 140.53, 127.46, 126.84, 125.72, 124.81, 72.35, 64.24, 30.97, 28.59, 28.38, 28.29, 27.73, 27.56, 24.95, 21.77 and 13.17 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *i*-butyl ester (**4af**): IR (neat) 3458, 3087-2964, 1722 , 1630, 1603, 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.10 (m, 5 H), 6.13 (s, 1 H), 5.63 (s, 1 H), 5.33 (s, 1 H), 3.77 (d, 2 H, J = 7 Hz), 3.15 (m, 1 H, OH), 1.3-2.27 (m, 1 H) and 0.83 ppm (d, 6 H, J = 7 Hz). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.86, 142.10, 141.24, 127.93, 127.31, 126.49, 124.96, 72.23 , 70.45 , 27.34, 27.22 and 18.59 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, *t*-butyl ester (**4ag**): IR (neat) 3456, 3064-2934 , 1714, 1633 and 1494, 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz)7.13 (m, 5 H), 6.05 (s, 1 H), 5.63 (s, 1 H), 5.27 (s, 1 H), 3.55 (m, 1 H, OH) and 1.3 ppm (s, 9 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.3, 143.40, 141.54, 128.05, 127.38 , 126.49 , 124.63 , 81.21 , 72.90 and 27.67 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-ethylhexyl ester (**4ah**): IR (neat) 3467, 3088-2862, 1703, 1630, 1604, 1494 and 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.16 (m, 5 H), 6.16 (s, 1 H), 5.68 (s, 1 H), 5.34 (s, 1 H), 3.94 (d, 2 H, J = 5 Hz), 3.18 (m, 1 H, OH) and 0.47-1.75 ppm (m, 15 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.28, 142.07, 141.26, 128.23, 127.60, 126.53, 125.57, 72.9, 67.01, 38.53, 30.19, 28.71, 23.59, 22.76, 13.86 and 10.81 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-adamentyl ester (**4ai**): IR (neat) 3471, 3088-2857, 1715, 1630, 1513, 1494 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.17 (m, 5 H), 6.23 (s, 1 H), 5.65 (s, 1 H), 5.38 (m, 1 H), 4.80 (m, 1 H), 3.40 (m, 1 H, OH) and 1.13-2.32 ppm (m, 14 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.33, 142.47, 141.36, 128.11, 127.48, 126.48, 125.34, 77.56, 72.82, 37.05, 35.90, 31.55, 31.51, 31.45, 26.90 and 26.68 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-fluoro-ethyl ester (**4aj**): IR (neat) 3436, 3064-2894, 1720, 1629, 1512, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.16 (m, 5 H), 6.25 (s, 1 H), 5.75 (s, 1 H), 5.37 (m, 1 H), 3.88-4.92 (m, 4 H) and 2.89 ppm (m, 1 H, OH);. ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.78, 141.77, 141.22, 128.31, 127.76, 126.59, 126.35, 80.95 (CH_2-F, d, J = 170 Hz), 72.78 and 63.54 ppm (d, J = 20 Hz). High-resolution MS for $C_{12}H_{13}FO_3$ (M^+) : Calcd m/z: 224.0848 ; Found : 224.850.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-chloro-ethyl ester (**4ak**): IR (neat) 3472, 3087-2962, 1721, 1630, 1603, 1493, 1455 and 723 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.28 (m, 5 H), 6.30 (s, 1 H), 5.80 (s, 1 H), 5.46 (m, 1 H), 4.24 (t, 2 H, J = 6 Hz), 3.51 (t, 2 H, J = 6 Hz) and 2.97 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.60, 141.73, 141.16, 128.61, 128.37, 127.81, 126.56, 72.39, 64.21 and 41.22 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2,2,2-trifluoro-ethyl ester (**4am**): IR (neat) 3449, 3066-2900, 1738, 1633, 1512, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.14 (m, 5 H), 6.17 (s, 1 H), 5.89 (s, 1 H), 5.33 (s, 1 H) 4.27 (q, 2 H, J = 8 Hz) and 3.38 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.17, 140.78, 140.76, 128.38, 127.98, 127.37, 126.54, 122.76 (CF_3, q, J = 275 Hz), 72.28 and 60.37 ppm (q, J = 36 Hz). High-resolution MS for $C_{12}H_{11}F_3O_3$ (M^+) : Calcd m/z: 260.0660 ; Found : 260.0665.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2,2,2-trichloro-ethyl ester (**4an**): IR (neat) 3431 , 3064-2956, 1732, 1632, 1494 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.10 (m, 5 H), 6.28 (s, 1 H), 5.84 (s, 1 H), 5.32 (m, 1 H), 4.53 (s, 2 H) and 3.45 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.24, 141.06, 140.86, 128.44, 128.01, 127.73, 126.74, 76.12 and 12.45 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-hydroxy-ethyl ester (**4ao**): IR (neat) 3412, 3064-2953, 1713, 1629, 1493 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.33 (m, 5 H), 6.37 (s, 1 H), 5.80 (s, 1 H), 5.57 (m, 1 H, OH), 3.96-4.37 (m, 2 H), 3.78 (m, 1 H), 3.44-3.76 (m, 2 H) and 3.40-3.93 ppm (m, 1 OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.25, 141.95, 141.24, 128.44, 127.87, 126.75, 126.52, 72.91, 66.29 and 60.70 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-methoxy-ethyl ester (**4ap**): IR (neat) 3440, 3064-2894, 1718, 1630, 1513, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.21 (m, 5 H), 6.23 (s, 1 H), 5.75 (s, 1 H), 5.40 (m, 1 H), 4.10 (t, 2 H, J = 6 Hz), 3.57 (m, 1 H, OH), 3.37 (t, 2 H, J = 6 Hz) and 3.18 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.88, 142.32, 141.60, 128.14, 127.52, 126.76, 125.58, 72.27, 69.99, 63.50 and 58.58 ppm. High-resolution MS for $C_{13}H_{18}NO_3$ (M^+ - H_2O+ NH_4) : Calcd m/z: 236.1287 ; Found : 236.1286.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-N,N-dimethylamino-ethyl ester (**4aq**): IR (neat) 3267, 3061-2824, 1718, 1630 , 1511, 1492 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.23 (m, 5 H), 6.22 (s, 1 H), 5.95 (s, 1 H), 5.49 (s, 1 H), 5.11 (m, 1 H, OH), 4.07 (t, 2 H, J = 6 Hz), 2.40 (t, 2 H, J = 6 Hz) and 2.08 ppm (m, 6 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.37, 142.79, 141.78, 127.61, 126.90, 126.40, 124.45, 71.36, 61.35, 56.57 and 44.57 ppm .

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-thiocyano-ethyl ester (**4ar**): IR (neat) 3484, 3087-2953, 2157 (SCN), 1721, 1630, 1603, 1493 and 1455 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.24 (m, 5 H), 6.34 (s, 1 H), 5.87 (s, 1 H), 5.48 (m, 1 H), 4.32 (t, 2 H, J = 6 Hz), 3.04 (t, 2H , CH2-S, J = 6 Hz)and 2.89-3.2 (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.48, 141.44, 141.15, 128.44, 127.92, 127.16, 126.63, 111.24 (SCN), 72.77, 62.29 and 32.50 ($\underline{CH_2}$SCN) ppm .

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-pheny-ethyl ester (**4as**): IR (neat) 3465, 3087-2899,1713 , 1630, 1605, 1512, 1496 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 6.62-7.46 (m, 10 H), 6.06 (s, 1 H), 5.63 (s, 1 H), 5.30 (m, 1 H), 4.10 (t, 2 H, J = 6 Hz), 3.35 (m, 1 H, OH) and 2.72 ppm (t, 2 H, J = 6 Hz). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.15, 142.30, 141.50, 137.68, 128.88, 128.58, 128.40, 127.79, 126.62, 126.64, 125.82, 72.77, 65.36 and 34.87 ppm. High-resolution MS for $C_{18}H_{22}NO_3$ (M^+ + NH_4) : Calcd m/z: 300.1600 ; Found : 300.1602. High-resolution MS for $C_{17}H_{20}NO_2$ (M^+ - H_2O+ NH_4) : Calcd m/z: 282.1494 ; Found : 282.1495.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-vinyl-ethyl ester (**4at**): IR (neat) 3446, 3087-2944, 1722, 1631, 1494 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4, 60 MHz) 7.23 (m, 5 H), 6.26 (s, 1 H), 5.74 (s, 1 H), 5.15-5.68 (m, 3 H vinylic), 5.07 (m, 1 H), 4.54 (d, 2 H, J = 6 Hz) and 3.01 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.34, 141.92, 141.12, 131.36, 127.90, 127.30, 126.47, 125.17, 117.70, 72.06 and 64.87 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 2-oxo-propyl ester (**4au**): IR (neat) 3461, 3031-2934, 1723,1633, 1512, 1493 and 1453 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.17 (m, 5 H), 6.27 (s, 1 H), 5.75 (s, 1 H), 5.42 (m, 1 H), 4.46 (s, 2 H), 3.27 (m, 1H, OH) and 1.91 ppm (s, 3 H_s). ^{13}C-NMR ($CDCl_3$; 75 MHz) 201.74, 165.10, 141.44, 140.97, 128.17, 127.63, 126.88 , 126.59, 72.31, 68.18 and 25.70 ppm.

3-phenyl-3-hydroxy-2-methylene-propanoic acid, 6-thiocyano-hexyl ester (**4ay**): IR (neat) 3487, 3063-2861, 2153 (SCN), 1715 , 1630, 1511, 1493 and 1454 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.22 (m, 5 H), 6.16 (s, 1 H), 5.74 (s, 1 H), 5.35 (m, 1 H), 3.96 (t, 2 H, J = 7 hz), 2.37 (m, 1 H, OH), 2.78 (t, 2 H, CH_2-S, J = 7 Hz) and 0.53-1.37 ppm (m, 8 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.12, 142.31, 141.58, 128.27, 127.66, 126.72, 125.48, 112.37 (SCN), 72.67, 64.45, 33.73, 29.61, 28.14, 27.34 and 25.06 ppm.

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, methyl ester (**5a**): IR (neat) 3452 (OH), 2955 (C-H), 1723 (C=O) and 1633 cm^{-1} (C=C, vinyl). ^{1}H-NMR (CCl_4 , 60 MHz) 7.33 (s, 1 H furyl), 6.06-6.43 (m, 3 H, 1 H vinyl + 2 H furyl), 5.97 (s, 1 H, CH_2 vinyl), 5.53 (m, 1 H, C<u>H</u>OH), 3.80 (m, 1 H, OH) and 3.69 ppm (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$; 75 MHz) 166.28 (CO), 154.04 (C=), 139.42 (C=), 126.49 (C=), 110.20 (CH=), 107.01 (CH=), 66.61 (CH) and 51.84 ppm (CH_3).

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, butyl ester (**5b**): IR (neat) 3460, 2963-2876, 1720 and 1635 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.36 (s, 1 H, furyl), 6.03-6.50 (m, 1 H acrylic + 2 H furyl), 5.98 (s, 1 H), 5.55 (d, 1 H, J = 6 Hz), 4.13 (t, 2 H, J = 7 Hz), 3.78 (d, 1 H, OH, J = 6 Hz) and 0.50-1.85 ppm (m, 7 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.61, 154.12, 139.69, 125.59, 109.87, 106.63, 65.94, 64.29, 30.03, 18.58 and 13.14 ppm. High-resolution MS for $C_{12}H_{16}O_4$ (M^+) : Calcd m/z: 224.1049 ; Found : 224.1050.

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, 2-ethyl-hexyl ester (**5c**): IR (neat) 3462, 2961-2862, 1720 and 1634 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.37 (s, 1 H, furyl), 6.08-6.60 (m, 3 H, 1 H vinyl + 2 H furyl), 5.99 (s, 1 H), 5.56 (d, 1 H, J = 6 Hz), 3.60-4.42 (m, 2 H + 1 H, OH) and 0.43-2.0 ppm (m, 15 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.87, 154.27, 141.96, 139.77, 125.89, 110.10, 106.85, 66.90, 66.31, 38.47, 30.08, 28.60, 23.51, 22.66, 13.75 and 10.72 ppm.

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, 2-chloro-ethyl ester (**5d**): IR (neat) 3463, 2965, 1723 and 1635 cm^{-1}. ^{1}H-NMR (CCl_4 , 60 MHz) 7.36 (s, 1 H furyl), 6.08-6.64 (m, 3 H, 1 H vinyl + 2 H furyl), 6.02 (s, 1 H), 5.55 (s, 1 H), 4.33 (t, 2H, J = 7 Hz), 3.93 (m, 1 H, OH) and 3.61 ppm (t, 2H, J = 7 Hz). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.07, 153.76, 139.05, 126.82, 110.34, 100.96, 65.75, 64.03 and 41.12 (CH_2-Cl) ppm.

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, 2,2,2-trifluoro-ethyl ester (**5e**): IR (neat) 3419, 2977, 1739 and 1638 cm^{-1}. ^{1}H-NMR (CCl_4, 60 MHz) 7.21 (s, 1 H furyl), 5.81-6.47 (m, 2 H vinyl + 2 H furyl), 5.45 (m, 1 H), 4.37 (q, 2 H, J = 8 Hz) and 4.00 ppm (m, 1 H, OH). ^{13}C-NMR ($CDCl_3$; 75 MHz) 164.00, 153.53, 138.32, 128.48, 124.61 (CF_3, q, J = 275 Hz), 110.36, 107.46, 66.18 and 60.73 ppm ($\underline{C}H_2$-CF_3, q, J = 37 Hz).

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, 2-methoxy-ethyl ester (**5f**): IR (neat) 3431, 2935-2894, 1722 and 1633cm^{-1}. ^{1}H-NMR (CCl_4, 60 MHz) 7.33 (s, 1 H furyl), 6.04-6.43 (3 H, m, 1 H acrylic + 2 H furyl), 5.95 (s, 1 H), 5.53 (d, 1 H, J = 6 Hz), 4.22 (d, 1 H, OH, J = 7 Hz), 4.12 (t, 2H, J = 7 Hz), 3.47 (t, 2H, J = 7 Hz) and 3.27 ppm (s, 3 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.36, 154.06, 139.50, 126.14, 109.90, 106.70, 69.72, 65.60, 63.32 and 58.28 ppm. High-resolution MS for $C_{11}H_{14}O_5$ (M^+) : Calcd m/z: 226.0842; Found : 226.0843.

3-(2-furyl)-3-hydroxy-2-methylene-propanoic acid, 2-N,N-dimethylamino-ethyl ester (**5g**): IR (neat) 3435, 2950, 1722 and 1634 cm^{-1}. ^{1}H-NMR (CCl_4, 60 MHz) 7.47 (s, 1 H, furyl), 6.20-6.51 (m, 3 H, 1 H vinyl + 2 H furyl), 5.88-6.08 (m, 1 H), 5.69 (s, 1 H), 5.19 (m, 1 H, OH), 4.32 (t, 2H, J = 7 Hz), 2.63 (t, 2H, J = 7 Hz) and 2.27 ppm (s, 6 H). ^{13}C-NMR ($CDCl_3$; 75 MHz) 165.12, 154.43, 139.69, 125.62, 108.42, 107.10, 68.71, 57.21, 56.33 and 44.32 ppm.

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