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Isomerization of oxazolinyl allylic alcohols: synthesis of 3-alkylidene-2-iminooxetanes

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Abstract—Oxazolinyl allylic alcohols **2** convert smoothly into 3-alkylidene-2-iminooxetanes **3** and dienic carboxylic acids **7** simply upon treatment with aqueous HCl.

Alkylideneoxetanes **1** (Chart 1) do not occur so frequently in the organic chemistry literature. Just few papers dealing with their preparation and reactions have been reported.[1] These involve either photochemical transformations[2,3] or are restricted to few specific substitution patterns.[4,5] The alkylideneoxetane ring system contains a number of elements of potential reactivity (ring strain, an exocyclic double bond, an electron-rich enol ether and a latent enolate leaving group) which would suggest a high level of, as yet, under-exploited utility. Indeed, 2-methyleneoxetanes undergo useful ring opening,[6,7] alkene addition reactions[8,9] and serve as biologically active β-lactones isosters.[10] 3-Alkylidene-2-iminooxetanes of the kind of **3**, which are even rarer than alkylidene oxetanes **1** (Chart 1),[11] are expected to possess a more varied reactivity due to the presence in their structure of the aza group. Indeed, they look like good Michael acceptors, Diels–Alder reagents, masked α,β-unsaturated carboxamides. It is also worth stressing that 3-alkylidene-2-iminooxetanes of the kind of **3** are masked forms of α-methylene-β-lactones which have quite recently been reported to act as good precursors of 2,3-dialkylideneoxetanes and compounds derived from.[12]

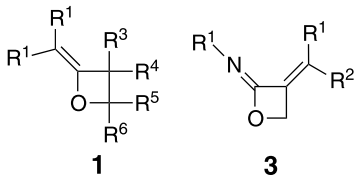

Chart 1.

In this paper we report an unprecedented simple synthesis of certain 3-alkylidene-2-iminooxetanes substantially based on the isomerization reaction of oxazolinyl allylic alcohols. The alcohols **2a–h** to be isomerized were synthesized by a base-induced isomerization of oxazolinyl oxiranes as recently reported from our laboratory.[13]

Treatment of the allylic alcohol **2a** with aqueous HCl at reflux for 2 h resulted in the formation of a new compound which was assigned the structure of **3a** on the basis of spectroscopic evidence (^{1}H and fully-coupled ^{13}C NMR, ^{1}H–^{13}C HETCOR, FT-IR, GC–MS and microanalysis, see Ref. 14). A likely explanation for the formation of **3a** considers that the allylic alcohol **2a**, under the acidic conditions created by HCl, undergoes ring opening of the oxazolinyl moiety to give the amide **4a** (Scheme 1) and an E_1 dehydration reaction to generate the stable carbocation **5a**. Cyclization of the amide function on the carbocation would terminate with the formation of the 3-benzhydrylidene-2-iminooxetane **3a**.

The acid-promoted isomerization above was not restricted to the alcohol **2a** as it takes place with other oxazolinyl allylic alcohols such as **2b–f** to give 2-iminooxetanes **3b–f**. The *Z* or *E* configuration to alkylideneiminooxetanes **3d–f** was assigned by comparing the oxetane **3a** CH_2 protons chemical shifts (4.5 δ), which feel the effect of the close phenyl ring, with those of the above-mentioned diastereomers. In the case of the *E* isomers these protons were always downfield shifted of

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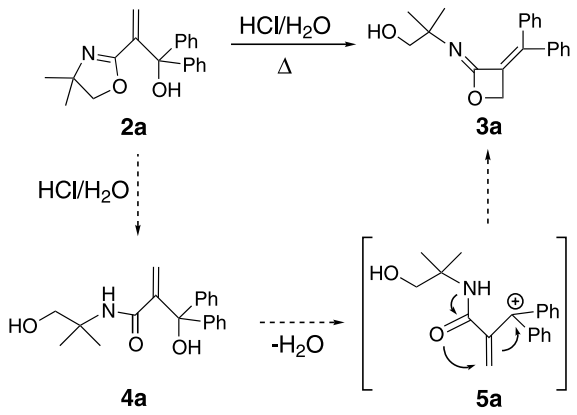
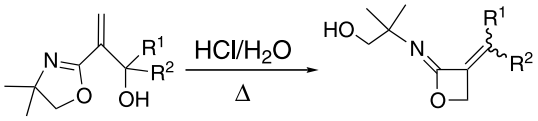


Scheme 1.

Table 1. Synthesis of 3-alkylidene-2-iminooxetanes **3**



Compound	R^1	R^2	Yield (%)[a]	E/Z ratio[b]
a	Ph	Ph	80	–
b	*p*-MeC_6H_4	*p*-MeC_6H_4	82	–
c	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	89	–
d	Ph (*n*-Pr)	*n*-Pr (Ph)	62[c]	81/19[d,e]
e	Ph (Et)	Et (Ph)	62[c]	82/18[d,e]
f	Ph (*t*-Bu)	*t*-Bu (Ph)	63[c]	60/40[d,f]
g	Et	Et	–[g]	–
h	-$(CH_2)_5$-	-$(CH_2)_5$-	–[g]	–

[a] Isolated yield.
[b] Diastereomeric ratio determined by ^1H NMR on the crude reaction mixture.
[c] Combined isolated yields in both *E* and *Z* isomers.
[d] Isomers *E* and *Z* could be separated by column chromatography (silica gel, Et_2O).
[e] In the case of compounds **2d**,**e**, a diastereomeric mixture of the dienic carboxylic acids **7d** (30% yield, *Z*/*E* ratio 85/15) and **7e** (20% yields, *Z*/*E* ratio 80/20) separable by column chromatography (both on silica gel, Et_2O/acetone 9/1) also formed, respectively (see Chart 2).
[f] In this case the α-methylenelactone **10** (30% yield, see Chart 2) also formed.
[g] A mixture of unidentified products formed.

about 0.5 ppm by the anisotropic ring current of the vinylic phenyl ring and fall at ca. 4.5 δ as in **3a**.

The rearrangement of α-phenyl allylic alcohols **2d**,**e** furnished mixtures of separable 3-alkykidene-2-iminooxetanes **3d**,**e** and dienic carboxylic acids **7d**,**e** (see Table 1 and typical procedure) (Chart 2). The configur-

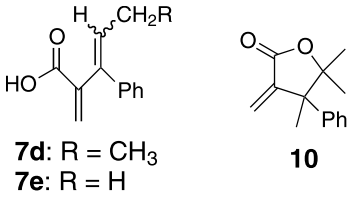


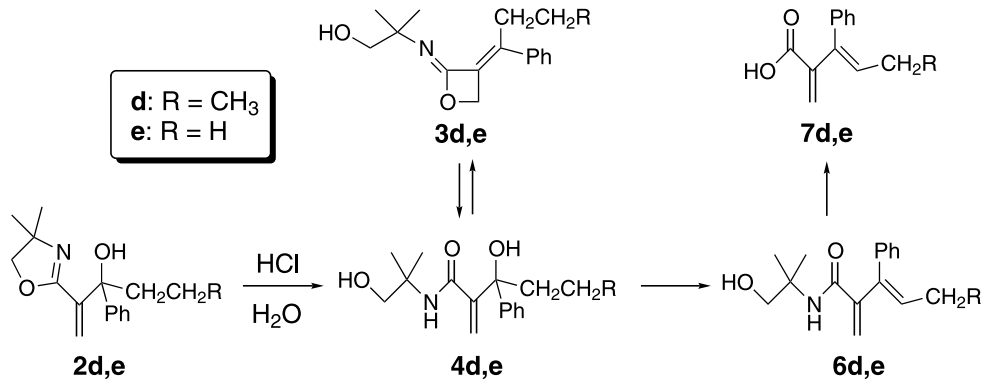
Chart 2.

ation to the dienic carboxylic acids **7d**,**e** was assigned on the basis of the chemical shifts of the terminal olefinic protons in conjunction with a 2D-NOESY phase-sensitive experiment in the case of **7d**. Strong NOE interactions between the olefinic C-4 proton and the *ortho* hydrogens of the phenyl ring and between Ph and the CH_2 were diagnostic of a *Z* and *E* stereochemistry for the two isomers of **7d**, respectively. The *Z* isomer in both cases resulted to be that having the terminal olefinic protons more deshielded of about 0.3–0.5 ppm. As shown in Scheme 2, the dihydroxycarboxamides **4d**,**e**, once formed from **2d**,**e**, might cyclize straithforwardly to the 2-iminooxetanes **3d**,**e** or dehydrate to give the dienic carboxamides **6d**,**e** and then hydrolize to the acids **7d**,**e**, which is reasonable considering the reaction conditions (refluxing HCl).[14] In support of the above mechanism, 2-iminooxetanes **3d**,**e** could be also cleanly converted into acids **7d**,**e** when heated under reflux with HCl/H_2O for several hours (60% yield).

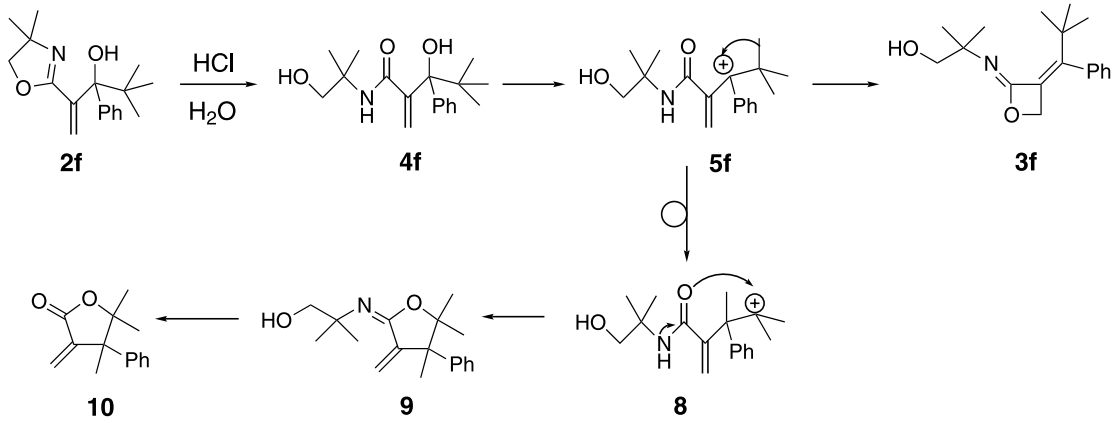
Allylic alcohols **2g**,**h** did not rearrange to the expected 3-alkylidene-2-iminooxetanes. Prolonged treatment with 4% w/w HCl produced mixtures of products that we could not identify. A possible explanation could be that carbocations derived from **2g**,**h** are not sufficiently stable.

Interestingly, treatment of the allylic alcohol **2f** with HCl afforded the 3-alkylidene-2-iminooxetane **3f** (through **4f** and the carbocation **5f**) as a mixture of two separable isomers (see Table 1 and typical procedure) together with the α-methylenelactone **10** (Scheme 3) that probably results from the rearrangement of the carbocation **5f** to **8** followed by its cyclization to compound **9** (not isolated) and hydrolysis to the lactone **10**, as shown in Scheme 3. In contrast to the above-cited oxetanes **3d**,**e**, compound **3f** was found to be chemically stable under reaction conditions and did not tend to transform into the lactone **10** once subjected to reflux under acidic conditions.

In conclusion, this work shows that 2-iminooxetanes of the kind of **3** and dienic carboxylic acids **7**, which are susceptible of synthetic elaboration in view of their multifaceted reactivity, can be simply obtained by an acidic isomerization of the oxazolinyl allyl alcohols **2**. Work is in progress in our laboratory to exploit the reactional features of these 2-iminooxetanes **3** and the dienic carboxylic acids **7**.



Scheme 2.



Scheme 3.

Acknowledgements

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14. *Typical procedure for the synthesis of 2-(3-benzhydrylideneoxetan-2-ylideneamino)-2-methylpropan-1-ol* ***3a***: A solution of the oxazolinyl allylic alcohol **2a** (0.5 mmol, 0.154 g) in 5 mL HCl 4% w/w was heated under reflux for 1 h. After this time, the mixture was extracted with Et_2O (3×10 mL), the aqueous layer treated with NaOH 4% w/w until the pH reached 8–9 and then re-extracted with Et_2O (3×10 mL). The resulting organic layer was dried

(Na_2SO_4) and volatiles were removed under reduced pressure. The crude oxetane **3a** was purified by crystallization (Et_2O) (0.122 g, 80% yield): white solid, mp 119–120°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 6H, 2×CH_3), 2.96 (br. s, exchanges with D_2O, OH), 3.73 (s, 2H, CH_2O oxetane), 4.39 (s, 2H, CH_2OH), 7.12–7.20 (m, 4H, Ar-H), 7.27–7.38 (m, 6H, Ar-H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.8 (2×CH$_3$), 62.4 (t, $^1J_{CH}$=144.9 Hz, CH$_2$O oxetane), 6.4 [C(CH$_3$)$_2$], 78.9 (triplet of septets, $^1J_{CH}$=149.7 Hz, $^3J_{CH}$=4.7 Hz, CH$_2$OH), 125.3, 127.7, 128.1, 128.2, 128.4, 129.1, 129.7, 140.1, 141.8, 151.4, 164.8 (C=N). GC–MS (70 eV) m/z (%) 307 (M^+, 25), 306 (100), 290 (9, M$^+$–OH$^\bullet$), 234 (14, M$^+$–C$_4$H$_9$O$^\bullet$), 191 (5, Ph$_2$C=C=CH$^+$), 178 (14). FT-IR (film, cm^{-1}): 3374 (br., OH), 2925, 1647 (C=N), 1444, 1362, 1099, 760, 701. Anal. calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.23; H, 6.96; N, 4.45. It is interesting to point out that in the case of methylene β-lactam isomers, exocyclic C=O stretching always falls in the range 1710–1740 cm^{-1} (see: Mori, M.; Ban, Y. *Heterocycles* **1985**, *23*, 317–323). The same procedure was followed for the preparation of oxetanes **3b**,**c** from **2b**,**c**. In the case of allylic alcohols **2d**–**f**, the two diastereomeric oxetanes **3d**–**f** (see Table 1 for ratios and yields) were separated by flash chromatography on silica gel (Et_2O as the eluent) whereas dienic carboxylic acids **7d**,**e** (see Table 1) or the lactone **10** were recovered from the first organic extract, as above described. The two diastereomers of **7d**,**e** were separated by flash chromatography on silica gel (Et_2O/acetone 9/1) while the lactone **10** was purified by crystallization (Et_2O). All these new compounds showed the following data: **3b**: white solid, mp 121–122°C (Et_2O), 84%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 6H), 2.30 (s, 3H), 2.32 (s, 3H), 3.65 (s, 2H), 4.33 (s, 2H), 4.42 (br. s, exchanges with D_2O, OH), 6.98–7.09 (m, 8H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.1, 21.2, 27.9, 62.8, 66.7, 77.2, 124.7, 128.3, 128.7, 129.2, 129.7, 137.6, 137.7, 138.1, 139.2, 150.3, 164.2. GC–MS (70 eV) m/z (%) 335 (M^+, 26), 334 (100), 318 (6), 262 (10), 244 (6), 115 (3). FT-IR (film, cm^{-1}): 3378 (br., OH), 2957, 2924, 1621 (C=N), 1463, 1104, 822. Anal. calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 79.01; H, 7.19; N, 4.16. **3c**: white solid, mp 123–124°C (Et_2O), 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 6H), 3.70 (s, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 4.37 (s, 2H), 6.78–6.86 (m, 4H), 7.05–7.12 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9, 55.2, 62.8, 66.6, 78.5, 112.9, 113.4, 123.8, 130.8, 131.4, 132.6, 134.4, 149.9, 159.5, 159.7, 164.6. GC–MS (70 eV) m/z (%) 367 (M^+, 26), 366 (100), 350 (8), 294 (8), 260 (3), 188 (2), 135 (3). FT-IR (film, cm^{-1}): 3380 (br., OH), 2964, 1605 (C=N), 1510, 1248, 1175, 1032, 835. Anal. calcd for $C_{22}H_{25}NO_4$: C, 71.91; H, 6.86; N, 3.81. Found: C, 72.07; H, 6.98; N, 3.55. **3d**: colorless oil, overall yield 62% (dr E/Z=85/15). (E): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J=7.4 Hz, 3H), 1.16 (s, 6H), 1.31–1.40 (m, 2H), 2.48–2.53 (m, 2H), 3.54 (s, 2H), 4.04 (br. s, exchanges with D_2O, OH), 4.45 (s, 2H), 7.15–7.20 (m, 2H), 7.26–7.37 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 21.5, 28.0, 36.8, 60.8, 66.7, 78.4, 125.2, 127.3, 127.5, 127.8, 142.3, 150.0, 163.8. GC–MS (70 eV) m/z (%) 273 (M^+, 20), 272 (100), 240 (16), 128 (10), 115 (14), 72 (27), 58 (39). FT-IR (film, cm^{-1}): 3377 (br., OH), 2963, 2927, 1725, 1660 (C=N), 1462, 1365, 1017, 766, 701. (Z): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, J=7.4 Hz, 3H), 1.06 (s, 6H), 1.26–1.35 (m, 2H), 2.58–2.63 (m, 2H), 3.48 (s, 2H), 3.98 (s, 2H), 4.00 (br. s, exchanges with D_2O, OH), 7.13–7.21 (m, 2H), 7.26–7.39 (m, 3H). GC–MS (70 eV) m/z (%) 273 (M^+, 37), 272 (100), 242 (72), 240 (56), 154 (20), 128 (25), 115 (32), 77 (14), 55 (12). FT-IR (film, cm^{-1}): 3385 (br., OH), 2965, 2927, 1655 (C=N), 1364, 1016, 754, 701. **3e**: colorless oil, overall yield 62% (dr E/Z=85/15). (E): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.14 (s 6H), 2.49–2.55 (m, 2H), 3.53 (s, 2H), 4.00 (br. s, exchanges with D_2O, OH), 4.43 (s, 2H), 7.15–7.20 (m, 2H), 7.26–7.37 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.0, 28.0, 28.5, 60.6, 66.5, 78.4, 124.5, 127.2, 127.5, 127.7, 142.0, 151.5, 163.8. GC–MS (70 eV) m/z (%) 259 (M^+, 21), 258 (100), 240 (16), 186 (18), 128 (17), 72 (23), 58 (30). FT-IR (film, cm^{-1}): 3364 (br., OH), 2965, 2927, 1660 (C=N), 1462, 1365, 1019, 701. (Z): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, J=7.4 Hz, 3H), 1.07 (s, 6H), 2.58–2.63 (m, 2H), 3.48 (s, 2H), 3.98 (s, 2H), 7.13–7.21 (m, 2H), 7.26–7.39 (m, 3H). GC–MS (70 eV) m/z (%) 259 (M^+, 38), 258 (100), 240 (57), 186 (38), 128 (29), 115 (25), 55 (12). FT-IR (film, cm^{-1}): 3373 (br., OH), 2965, 2925, 1654 (C=N), 1366, 1017, 761, 699. **3f**: colorless oil, overall yield 63% (dr E/Z=60/40). (E): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 6H), 1.12 (s, 9H), 2.78 (br. s, exchanges with D_2O, OH), 3.39 (s, 2H), 4.51 (s, 2H), 6.95–6.99 (m, 2H), 7.11–7.20 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.1, 27.6, 40.1, 64.2, 66.7, 78.8, 125.5, 126.8, 127.9, 128.1, 140.3, 155.5, 163.2. GC–MS (70 eV) m/z (%) 287 (M^+, 26), 286 (100), 256 (82), 244 (54), 230 (60), 200 (31), 129 (27), 77 (15). FT-IR (film, cm^{-1}): 3382 (br., OH), 2966, 2928, 1660 (C=N), 1365, 1016, 701. (Z): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.24 (s, 6H), 3.72 (s, 2H), 4.04 (s, 2H), 6.96–7.03 (m, 2H), 7.19–7.25 (m, 3H). GC–MS (70 eV) m/z (%) 287 (M^+, 24), 286 (100), 256 (82), 244 (61), 230 (52), 200 (37), 129 (34), 115 (822). FT-IR (film, cm^{-1}): 3347 (br., OH), 2961, 2926, 1660 (C=N), 1463, 1365, 1084, 704. **7d**: colorless oil, overall yield 30% (dr Z/E=85/15). (Z): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J=7.5 Hz, 3H), 2.07–2.13 (m, 2H), 5.71 (d, J=1.8 Hz, 1H), 6.00 (t, J=7.5 Hz, 1H), 6.61 (d, J=1.8 Hz, 1H), 7.04–7.26 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.1, 23.3, 126.0, 127.1, 128.3, 131.6, 133.9, 136.0, 138.2, 140.3, 171.5 (COOH). GC–MS (70 eV) m/z (%) 202 (M^+, 67), 201 (27), 187 (24), 169 (76), 157 (35, M$^+$–CO$_2$H), 141 (100), 129 (66), 115 (78), 91 (32), 77 (26). FT-IR (film, cm^{-1}): 3500–2400 (br., OH), 2964, 2926, 1695 (C=O), 1613, 1439, 1252, 764, 699. (E): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J=7.5 Hz, 3H), 1.79–2.06 (m, 2H), 5.47 (d, J=1.8 Hz, 1H), 5.91 (t, J=7.5 Hz, 1H), 6.07 (d, J=1.8 Hz, 1H), 7.08–7.29 (m, 5H). GC–MS (70 eV) m/z (%) 202 (M^+, 61), 201 (25), 187 (21), 169 (76), 157 (32, M$^+$–CO$_2$H), 141 (100), 129 (70), 115 (83), 91 (37), 77 (28). FT-IR (film, cm^{-1}): 3500–2400 (br., OH), 2964, 2928, 1692 (C=O), 1610, 1252, 764, 699. **7e**: colorless oil, overall yield 20% (dr Z/E=80/20). (Z): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (d, J=7.3 Hz, 3H), 5.75 (d, J=1.2 Hz, 1H), 6.14 (q, J=7.3 Hz, 1H), 6.80 (d, J=1.2 Hz, 1H), 7.21–7.42 (m, 5H). GC–MS (70 eV) m/z (%) 188 (M^+, 56), 170 (16), 143 (100, M$^+$–CO$_2$H), 141 (62), 128 (90), 115 (61), 91 (20), 77 2 (15). FT-IR (film, cm^{-1}): 3500–2400 (br., OH), 2964, 2924, 1729 (C=O), 1689, 1448, 1379, 765, 701. (E): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (d, J=7.3 Hz, 3H), 5.62 (d, J=1.2 Hz,

1H), 6.10 (q, $J=7.3$ Hz, 1H), 6.54 (d, $J=1.2$ Hz, 1H), 7.21–7.42 (m, 5H). GC–MS (70 eV) m/z (%) 188 (M^+, 57), 170 (17), 143 (100, M^+-CO_2H), 141 (68), 128 (85), 115 (57), 77 (20). FT-IR (film, cm^{-1}): 3500–2400 (br., OH), 2964, 2928, 1692 (C=O), 1360, 764, 699. **10**: colorless oil, 30%, ^1H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.66 (s, 3H), 1.84 (s, 3H), 5.83 (s, 1H), 6.7 (s, 1H), 7.51–7.57 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 23.5, 23.6, 26.6, 52.8, 87.7, 123.0, 127.1, 127.2, 127.3, 128.2, 141.3, 145.5, 170.0 (C=O). GC–MS (70 eV) m/z (%) 217 (M^++1, 1), 158 (82), 130 (100), 129 (56), 115 (58), 77 (10). FT-IR (film, cm^{-1}): 3059, 2977, 2933, 1761 (C=O), 1601, 1254, 1083, 758, 702.