One-Pot Ester Synthesis from Allyl and Benzyl Halides and Alcohols by Palladium-Catalyzed Carbonylation

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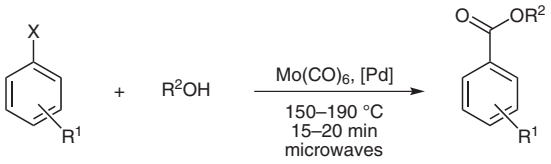
Abstract: A mild and efficient one-pot synthesis of esters based on the Pd-catalyzed alkoxy- and aryloxycarbonylation of allylic and benzylic halides is described. The methodology has been applied to primary, secondary, and tertiary alcohols as well as to phenol derivatives. The O-protection of some biologically relevant molecules is also reported.

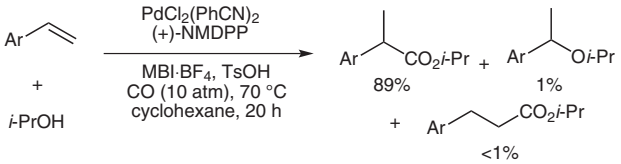
Key words: alcohols, allyl halides, benzyl halides, esterification, Pd-catalysis

Esters are widely found among all naturally occurring compounds, and they are also significantly important intermediates in organic synthesis.[1] The ester bond is one of the most common linkages in organic chemistry and could be formed by different strategies using acids,[2] anhydrides,[3] or acyl chlorides[4] with alcohols as starting substrates. The reactions proceed with or without the help of a base or an acid and also with[5] or without[6] a metallic catalysis. Palladium is one of the most common metals used as a catalyst in these reactions. A rapid palladium-catalyzed synthesis of esters from aryl halides utilizing $Mo(CO)_6$ as a solid carbon monoxide source has been reported (Scheme 1).[7]



Scheme 1

According to Zim et al., a regioselective synthesis of 2-arylpropionic esters can be achieved by palladium-catalyzed hydroesterification of styrene derivatives in ionic liquid (MBI·BF_4)[8] (Scheme 2).



Scheme 2

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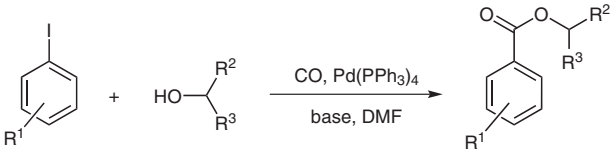
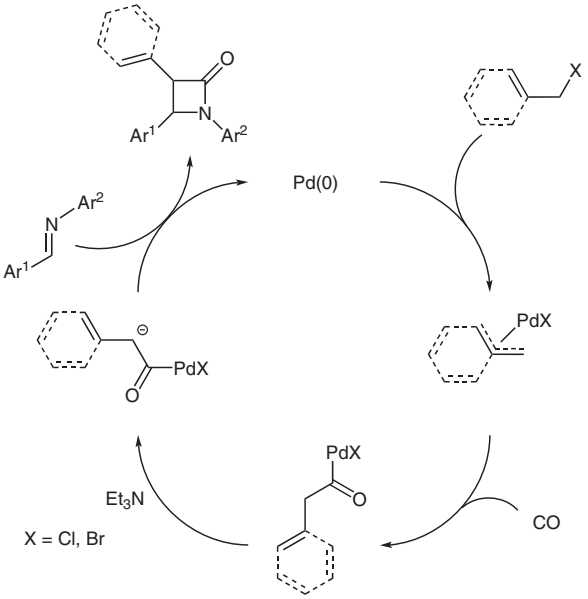
Palladium(0)-catalyzed carbonylation using carbon monoxide and various aryl iodides with polymer-supported primary and secondary alcohols is also known[9] (Scheme 3).



Scheme 3

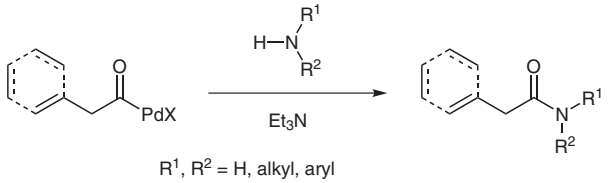
As reported in our previous work,[10] an allyl or a benzyl halide, in THF, under the pressure of CO and in the presence of Pd(0), produces an acylpalladium halide, which can be deprotonated in the α-position by a tertiary amine, and in the presence of imines incurs a [2+2] cycloaddition (Scheme 4).



Scheme 4

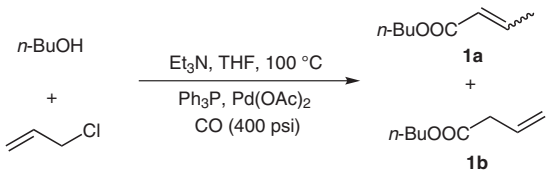
The reaction occurs with a variety of different allyl and benzyl halides, and gives the possibility to produce many differently substituted and functionalized β-lactams.[10] The production of the acylpalladium halide in this catalytic system prompted us to investigate about the possibility of using it in the acylation of functions such as NH, OH,

SH, and ≡CH. Surely protection of one of this group is often relevant in the success of a more complex synthesis of an organic compound. Thus, it became possible to transform aliphatic or aromatic, primary or secondary amines into amides of different structure using appropriate allyl or benzyl halides (Scheme 5).[11]



Scheme 5

We envisaged that the same methodology of reaction could be applied to other compounds such as alcohols and the results of this investigation are reported in this article. In order to investigate such a hypothesis, the following experiment was carried out: *n*-butanol (1.0 mmol), allyl chloride (1.2 mmol), $Pd(OAc)_2$ (0.02 mmol), Ph_3P (0.08 mmol), and Et_3N (2.0 mmol) were dissolved in THF (15 mL); the mixture was placed in an autoclave, pressurized with CO (400 psi), and heated to 100 °C under magnetic stirring for about 10 hours. After this time, more than 90% of the alcohol had reacted and then the solvent was evaporated under reduced pressure. Products were isolated by column chromatography on silica gel and fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and GC-MS analysis (Scheme 6).



Scheme 6

It was found that *n*-butanol had been transformed to the expected ester **1b** beside two other isomeric esters *trans*-**1a** and *cis*-**1a**. The origin of such products could be attributed to the migration of C=C bond to the position conjugated with the carbonyl group. The undesired isomerization could be due to the increased stability of conjugated alkenes *cis*- and *trans*-**1a** with respect to the terminal alkene **1b** (Table 1, entry 1). The isomer distribution is influenced by the heating time; in fact, if the reaction mixture was heated for 20 hours a major percentage of the conjugated esters *trans*-**1a** and *cis*-**1a** was obtained (Table 1, entry 2). The same trend was observed for *sec*-butyl alcohol and *tert*-butyl alcohol in forming *trans*-**2a**, *cis*-**2a**, **2b** and *trans*-**3a**, *cis*-**3a**, **3b**, respectively (Table 1, entries 3–6), with the *trans*/*cis* ratio being nearly to 7:1 at longer reaction times.

The applicability of this method has been verified on more complex alcoholic substrates of biological interest. Our attention was directed toward the synthesis of cholesteryl esters as interesting targets for their structural and biochemical connection with membrane phospholipids and their potential roles in cardiovascular health.[12] Significant results were obtained in the acylation of cholesterol that, in the same reaction conditions, was transformed into esters *trans*-**4a**, *cis*-**4a** and **4b**, with a consequent increase in lipophilicity; the isomeric distribution, after 15 hours, was found to be slightly in favor of the γ,δ-unsaturated ester **4b** (Table 1, entry 7).

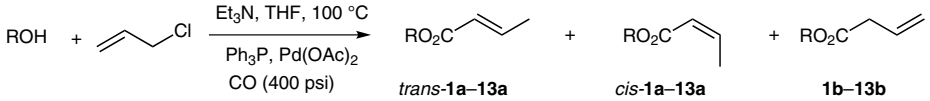
When the reaction was carried out on 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in the same time (15 h) and reaction conditions mentioned above, only the isomers with the conjugate C=C bond *trans*- and *cis*-**5a** (ratio 55:45) were formed (Table 1, entry 8). After examining the reactivity of aliphatic alcohols, we next turned our attention to the reactions of phenols and polyhydroxylated aromatic compounds. By performing the reaction under the already mentioned conditions, phenol too was smoothly acylated; interestingly, only the isomerized products, *trans*-**6a** and *cis*-**6a** were formed in 12 hours and in high yields (99%) (*trans*/*cis* ratio: 75:25, Table 1, entry 9). Phenoxy function favors the migration of the C=C bond to the α-position, even more than alkoxy group, probably because of the favorable formation of highly conjugated products.

Therefore, the methodology was applied to phenolic substrates of biological interest. 4-Methylcatechol, in the same reaction conditions underwent acylation at both oxygens producing compounds *trans*- and *cis*-**7a**, and regioisomeric compounds *trans*- and *cis*-**8a** to a similar extent. For all isomers, the double bonds are located in conjugated position and the ratio *trans*/*cis* was found to be about 70:30 in both cases (Table 1, entry 10). Traces of doubly acylated product were also observed by GC-MS analysis. However, when an excess of allyl chloride was used (3.0 mmol) the double acylation was complete and a mixture of *trans*,*trans*-**9a**, *trans*,*cis*-**9a**, *cis*,*trans*-**9a**, and *cis*,*cis*-**9a**, resolved by column chromatography on silica gel, was obtained (Table 1, entry 11).

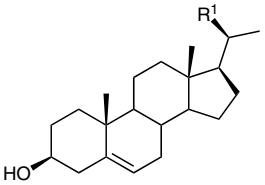
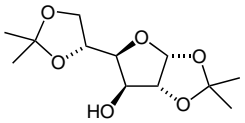
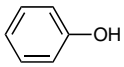
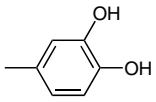
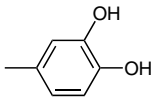
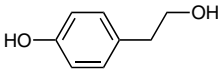
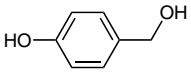
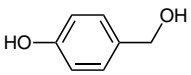
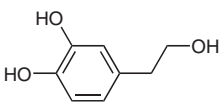
Phenolic group seems to be more reactive than alcoholic one; thus, when tyrosol was treated with allyl chloride (1.2 mmol) for 12 hours acylation occurred only at the phenolic oxygen and the ratio **10a**/**10b** was near to 95:5, while the ratio *trans*-**10a**/*cis*-**10a** was 82:13 (Table 1, entry 12). Even in this case, traces of double acylation were visible by GC-MS. A very similar behavior occurred with 4-hydroxybenzyl alcohol: when allyl chloride was used in slight excess (1.2 mmol) mainly the isomers *trans*-**11a** and *cis*-**11a** were obtained, 78% and 19%, respectively, and **11b** only in 3% (Table 1, entry 13). In contrast, when allyl chloride was used in large quantities (3.0 mmol), only the isomers *trans*-**12a** and *cis*-**12a**, with both hydroxy groups functionalized, were formed (Table 1, entry 14). It is worth mentioning that the double bond shift has been noticed only for the acylic moiety bonded to the phenolic oxygen and never on the other unsaturated chain bonded to the aliphatic hydroxy group. The ratio *trans*-

12a/*cis*-**12a** (doubly acetylated product) is slightly influenced by the excess of allyl chloride. Finally, hydroxytyrosol was subjected to acylation using an excess of allyl chloride (5.0 mmol): the three OH functions were all acylated and GC-MS analysis showed the presence of 12 isomeric products, all having the same molecular weight (Table 1, entry 15). Unfortunately, the mixture was very difficult to separate by column chromatography on silica

Table 1 Ester Synthesis by Pd-Catalyzed Alkoxy- and Aryloxycarbonylation of Allyl Chloride

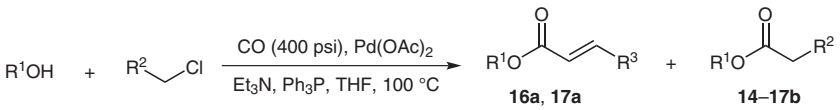


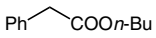
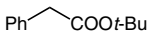
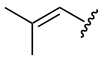
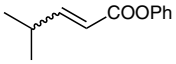
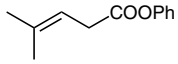
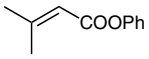
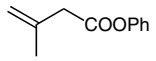
trans-**1a**–**13a** *cis*-**1a**–**13a** **1b**–**13b**

Entry	ROH	Allyl chloride (equiv)	Time (h)	Total yield (%)[a]	Conjugated alkene **1a**-**13a** (%)[b]	Non-conjugated alkene **1b**-**13b** (%)[b]
1	*n*-BuOH	1.2	10	75	*trans*-**1a** (10)/*cis*-**1a** (2)	**1b** (88)
2	*n*-BuOH	1.2	20	77	*trans*-**1a** (70)/*cis*-**1a** (10)	**1b** (20)
3	*s*-BuOH	1.2	10	68	*trans*-**2a** (12)/*cis*-**2a** (4)	**2b** (84)
4	*s*-BuOH	1.2	20	68	*trans*-**2a** (75)/*cis*-**2a** (8)	**2b** (17)
5	*t*-BuOH	1.2	10	60	*trans*-**3a** (8)/*cis*-**3a** (4)	**3b** (88)
6	*t*-BuOH	1.2	20	58	*trans*-**3a** (65)/*cis*-**3a** (8)	**3b** (27)
7[c]		1.2	15	56	*trans*-**4a** (33)/*cis*-**4a** (12)	**4b** (55)
8		1.2	15	58	*trans*-**5a** (55)/*cis*-**5a** (45)	–
9		1.2	12	99	*trans*-**6a** (75)/*cis*-**6a** (25)	–
10		1.2	15	99	*trans*-**7a** (36)/*cis*-**7a** (14) *trans*-**8a** (34)/*cis*-**8a** (16)	–
11		3.0	17	99[d]	*trans*,*trans*-**9a** (45) *trans*,*cis*-**9a** (21) *cis*,*trans*-**9a** (24) *cis*,*cis*-**9a** (10)	–
12		1.2	12	99	*trans*-**10a** (82)/*cis*-**10a** (13)[e]	**10b** (5)[f]
13		1.2	12	99	*trans*-**11a** (78)/*cis*-**11a** (19)[e]	**11b** (3)[f]
14		3.0	15	99	*trans*-**12a** (88)/*cis*-**12a** (12)[d]	–
15		5.0	17	99[g]	**13a**	**13b** (10)

[a] Isolated yields after column chromatography.
[b] Calculated by GC-MS analysis of the crude reaction mixture.
[c] R^1 = isohexyl.
[d] Mixture of doubly acylated isomeric products.
[e] *cis*/*trans* stereochemistry refers to the but-2-enoyl moiety bonded to phenolic oxygen.
[f] Not isolated.
[g] Mixture of 12 isomeric products.

Table 2 Esters Synthesis by Pd-Catalyzed Alkoxy- and Aryloxycarbonylation of Benzylic and Allylic Chlorides



Entry	R^1	R^2	Time (h)	Yield (%)[a]	Conjugated alkenes **16a**, **17a** (%)[b]	Nonconjugated alkenes **14–17b** (%)[b]
1	*n*-Bu	Ph	20	68	–	 **14**
2	*t*-Bu	Ph	20	55	–	 **15**
3	Ph		10	95	 **16a** (*trans*/*cis* = 25:12)	 **16b** (63)
4	Ph		10	90	 **17a** (55)	 **17b** (45)

[a] Isolated yields after column chromatography.
[b] Calculated by GC analysis of the crude reaction mixture.

gel and only the triester **13b**, with all the C=C double bonds not conjugated with the carbonyl moiety, was isolated. This result is very important because the polyester **13b**, easily obtained with the described methodology, is a rather stable molecule in contrast to the parent substrate that, according to Gambacorta et al., is very susceptible to degradation, because of an intrinsic instability to air and silica.[13] In contrast, the ester **13b** can be stored, unaffected, at room temperature for months.

On the basis of the data reported here and by considering our previous knowledge, the probable reaction mechanism for the palladium-catalyzed alkoxycarboylation of alcohols and phenols could be similar to that one reported for amines (Scheme 4).

Various allylic and benzylic chlorides have been also used for the acylation reaction (Table 2). In particular, benzyl chloride reacting with *n*-butanol and *tert*-butyl alcohol produced esters **14** and **15**, respectively (Table 2, entries 1, 2); while phenol, reacting with 1-chloro-3-methylbut-2-ene and 3-chloro-2-methylpropene gave, in good yields, compounds *trans*-**16a**, *cis*-**16a**, **16b** and **17a**, **17b**, respectively (Table 2, entries 3, 4).

Moreover, we verified that all reactions reported here proceed in a very similar manner by starting from allyl and benzyl bromide; because of negligible differences it was considered unnecessary to report these data. Instead, we proved that the methodology is not effective when alkyl or aryl halides are used in the reaction with alcohols or phenols.

In conclusion, our methodology represents a useful way of protection of alcoholic and phenolic functions by using several allyl and benzyl halides (bromides and chlorides). The simple method of operation and good yields of this new strategy for the Pd-catalyzed acylation, could lead to its use in substitution of other less advantageous reactions, especially on substrates particularly sensible to more drastic conditions.

Et_3N, $Pd(OAc)_2$, Ph_3P, and all other chemicals used are commercially available and were used without further purification. THF was purified by distillation from sodium/benzophenone, under N_2 atmosphere, before use. Petroleum ether (PE) refers to the fraction boiling at 40–60 °C. The ^1H and the ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer (400.13 and 100.62 MHz, for ^1H and ^{13}C, respectively) with $CDCl_3$ as the solvent and TMS as an internal standard (δ = 7.26 ppm for ^1H spectra; δ = 77.0 ppm for ^{13}C spectra). The IR spectra were recorded with an FT-IR spectrophotometer Digilab Scimitar Series FTS 2000. GC-MS analyses were performed with an Agilent Technologies 6850 series II gas chromatograph (5% phenylpolymethylsiloxane capillary column, 30 m, 0.25 mm i.d.), equipped with a 5973 Network mass-selective detector operating at 70 eV. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. TLC was performed on Merck silica gel plates with F-254 indicator; viewing was by UV light (254 nm). Column chromatography was performed on silica gel (63–200 mm) using PE–Et_2O mixture as eluent. All reactions involving air-sensitive reagents were performed under an atmosphere of N_2 in oven-dried glassware by using syringe/septum cap techniques. Spectroscopic data of compounds *trans*- and *cis*-**1a**,[14] **1b**,[15] *trans*- and *cis*-**2a**,[16] **2b**,[17] *trans*-**3a**,[18] *cis*-**3a**,[19] **3b**,[15] *trans*-**6a**,[20] *cis*-**6a**,[21] **14**,[22] **15**,[23] **17a**,[20] and **17b**[24] have been reported.

Palladium-Catalyzed Synthesis of Esters; General Procedure

A solution of alcohol (1.0 mmol), allylic or benzylic halide (1.2 mmol or an excess when required, see Table 1), $Pd(AcO)_2$ (4 mg, 2% mmol), Ph_3P (21 mg, 0.08 mmol), and Et_3N (202 mg, 2.0 mmol) in THF (10 mL) was placed in a 45 mL autoclave. The autoclave was purged, pressurized with CO (400 psi), and then heated at 100 °C, under magnetic stirring, for 10–20 h. After this time, the solution was cooled to r.t. and the solvent was removed under reduced pressure to give the crude material. The crude mixture was then purified by chromatography on silica gel (PE–Et_2O, 90:10–97:3) to afford the corresponding ester (Tables 1 and 2).

***trans*-3β-Cholest-5-en-3-yl But-3-enoate (*trans*-4a)**
Yield: 79 mg (18%); white solid; mp 108–111 °C (hexane).

IR ($CHCl_3$): 3030, 2949, 2867, 1707 (C=O), 1457, 1378, 1276, 1190, 1103, 1014 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.96 (dq, *J* = 6.9, 15.5 Hz, 1 H, CH_3CH=CH), 5.82 (dd, *J* = 15.5, 1.7 Hz, 1 H, CH_3CH=C*H*), 5.37 (dd, *J* = 4.4, 2.0 Hz, 1 H, C=C*H*CH_2), 4.63–4.68 (m, 1 H, OCH), 2.34 (d, *J* = 7.2 Hz, 2 H, OCHCH_2), 2.02–0.85 (m, 41 H, aliphatic CH, CH_2, CH_3), 0.68 (s, 3 H, CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 17.9, 18.7, 19.3, 21.1, 22.6, 22.8, 23.8, 24.3, 27.9, 28.0, 28.3, 31.9, 35.8, 36.2, 36.6, 37.0, 38.2, 39.5, 39.8, 42.3, 50.1, 56.2, 56.7, 73.7 (C–O), 122.6, 123.3, 139.8, 144.1, 166.0 (C=O).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{49}O_2$: 441.3732; found: 441.3733.

***cis*-3β-Cholest-5-en-3-yl But-3-enoate (*cis*-4a)**
Yield: 30 mg (7%); white solid; mp 98–100 °C (hexane).

IR ($CHCl_3$): 3030, 2940, 2867, 1710 (C=O), 1466, 1378, 1260, 1190, 1006 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.27–6.31 (m, 1 H, CH_3CH=CH), 5.77 (dd, *J* = 11.5, 1.7 Hz, 1 H, CH_3CH=C*H*), 5.37 (br s, 1 H, C=C*H*CH_2), 4.63–4.67 (m, 1 H, OCH), 2.36–0.85 (m, 43 H, aliphatic CH, CH_2, CH_3), 0.68 (s, 3 H, CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 18.7, 19.3, 21.1, 22.6, 22.8, 23.8, 24.3, 28.0, 28.2, 29.7, 31.9, 35.8, 36.2, 36.6, 37.1, 38.1, 38.3, 39.5, 39.8, 42.3, 50.1, 56.2, 56.7, 73.4 (C–O), 121.2, 122.6, 139.8, 144.6, 166.0 (C=O).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{49}O_2$: 441.3732; found: 441.3734.

3β-Cholest-5-en-3-yl But-3-enoate (4b)
Yield: 137 mg (31%); white solid; mp 81–83 °C (hexane).

IR ($CHCl_3$): 3030, 2949, 2878, 1724 (C=O), 1642, 1467, 1379, 1329, 1260, 1182, 1000 cm^{-1}.

^1H NMR (400 MHz, $CDC1_3$): δ = 6.00–5.85 (m, 1 H, CH_2=C*H*), 5.37 (dd, *J* = 4.4, 2.0 Hz, 1 H, C=C*H*CH_2), 5.18–5.14 (m, 2 H, CH_2=C), 4.60–4.64 (m, 1 H, OCH), 3.06 (d, *J* = 6.9 Hz, 2 H, CH_2CO), 2.32 (d, *J* = 7.7 Hz, 2 H, C=CHCH_2), 1.99–0.85 (m, 38 H, aliphatic CH, CH_2, CH_3), 0.67 (s, 3 H, CHCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 18.7, 19.3, 21.0, 22.6, 22.8, 24.3, 27.7, 28.0, 28.2, 31.9, 35.8, 36.2, 36.6, 37.0, 38.1, 39.5, 39.7, 42.3, 50.0, 56.2, 56.7, 118.3, 122.7, 130.6, 139.6, 170.9 (C=O).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{49}O_2$ $[M + H]^+$: 441.3732; found: 441.3732.

***trans*-1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-yl But-2-enoate (*trans*-5a)**
Yield: 110 mg (32%); colorless oil.

IR ($CHCl_3$): 3030, 2987, 2870, 1723 (C=O), 1655, 1377, 1213, 1165, 1076, 1023 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.03 (dq, *J* = 17.0, 6.9 Hz, 1 H, CH_3CH=CH), 5.89–5.83 (m, 2 H, CH_3CH=C*H*, OCHO), 5.30 (d, *J* = 2.2 Hz, 1 H, OCH), 4.52 (d, *J* = 3.7 Hz, 1 H, OCH), 4.26–4.22 (m, 2 H, 2 × OCH), 4.09–4.01 (m, 2 H, OCH_2), 1.90 (dd, *J* = 1.7, 6.9 Hz, 3 H, CH_3CH=C), 1.53 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2, 18.1, 25.3, 26.2, 26.8, 67.0, 72.5, 75.9, 79.8, 83.4, 105.0, 109.3, 112.3, 121.9, 146.2, 165.0 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 328 ($[M^+]$, 1), 313 (40), 255 (8), 195 (10), 169 (20), 101 (80), 69 (100).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{25}O_7$: 329.1590; found: 329.1591.

***cis*-1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-yl But-2-enoate (*cis*-5a)**
Yield: 90 mg (26%); colorless oil.

IR ($CHCl_3$): 3030, 2990, 2870, 1723 (C=O), 1646, 1377, 1224, 1162, 1076, 1022 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.42 (dq, *J* = 11.7, 7.2 Hz, 1 H, CH_3CH=CH), 5.88 (d, *J* = 3.7 Hz, 1 H, OC*H*O), 5.80 (dq, *J* = 11.7, 1.7 Hz, 1 H, CH_3CH=C*H*), 5.29 (d, *J* = 2.5 Hz, 1 H, OCH), 4.52 (d, *J* = 3.7 Hz, 1 H, OCH), 4.27–4.21 (m, 2 H, 2 × OCH), 4.09–4.01 (m, 2 H, OCH_2), 2.17 (dd, *J* = 7.2, 1.7 Hz, 3 H, CH_3CH=CH), 1.53 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 17.9, 25.2, 26.2, 26.8, 67.0, 72.5, 75.6, 79.7, 83.4, 105.0, 109.3, 112.2, 119.7, 147.0, 164.8 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 328 ($[M^+]$, 1), 313 (45), 255 (10), 195 (11), 169 (18), 101 (82), 69 (100).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{25}O_7$: 329.1590; found: 329.1590.

***trans*-2-Hydroxy-5-methylphenyl But-2-enoate (*trans*-7a) and *trans*-2-Hydroxy-4-methylphenyl But-2-enoate (*trans*-8a)**
Inseparable mixture of regioisomers; yield: 135 mg (70%); colorless oil.

IR ($CHCl_3$): 3576 (OH, free), 3374 (OH, br), 3026, 2923, 2850, 1736 (C=O), 1655, 1506, 1442, 1296, 1178, 1149, 1110, 969 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (br s, 2 H, OH), 7.25–7.18 (m, 2 H, CH_3CH=CH), 6.94 (d, *J* = 8.1 Hz, 2 H_{arom}), 6.76 (br s, 2 H_{arom}), 6.71–6.68 (m, 2 H_{arom}), 6.06 (dq, *J* = 1.4, 15.5 Hz, 2 H, CH_3CH=C*H*), 2.25 (br s, 6 H, ArCH_3), 1.97–1.94 (2 m, 6 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 18.2, 20.4, 20.9, 117.6, 118.3, 121.4, 122.0, 122.7, 127.4, 130.5, 136.3, 136.9, 138.2, 144.8, 146.8, 148.1, 165.0 (C=O), 165.1 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 192 ($[M^+]$, 10), 124 (12), 69 (100).

***cis*-2-Hydroxy-5-methylphenyl But-2-enoate (*cis*-7a) and *cis*-2-Hydroxy-4-methylphenyl But-2-enoate (*cis*-8a)**
Inseparable mixture of regioisomers; yield: 58 mg (30%); colorless oil.

IR ($CHCl_3$): 3574 (OH, free), 3339 (OH, br), 3033, 2925, 2855, 1738 (C=O), 1643, 1507, 1439, 1296, 1178, 1147 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.60 (br s, 2 H, OH), 6.98 (d, *J* = 8.1 Hz, 2 H_{arom}), 6.83 (d, *J* = 1.4 Hz, 2 H_{arom}), 6.72 (dd, *J* = 1.4, 8.1 Hz, 2 H_{arom}), 6.62–6.55 (m, 2 H, CH_3CH=CH), 6.09–6.05 (m, 2 H, CH_3CH=C*H*), 2.28 (s, 3 H, ArCH_3), 2.40 (s, 3 H, ArCH_3), 2.23–2.21 (2 m, 6 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 20.5, 20.9, 22.7, 117.6, 118.3, 119.1, 121.6, 122.0, 122.8, 127.4, 130.7, 136.1, 137.0, 138.1, 144.7, 146.7, 149.1, 164.5 (C=O), 164.6 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 192 ($[M^+]$, 9), 124 (14), 69 (100).

***trans*,*trans*-4-Methyl-1,2-phenylene Dibut-2-enoate (*trans*,*trans*-9a)**
Yield: 117 mg (45%); colorless oil.

IR ($CHCl_3$): 3022, 2924, 2854, 1743 (C=O), 1656, 1505, 1442, 1256, 1212, 1155, 1110, 970 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.01 (m, 5 H, 3 H_{arom}, 2 × CH_3CH=CH), 6.00 (d, *J* = 15.7 Hz, 2 H, 2 × CH_3CH=C*H*), 2.34 (s, 3 H, ArCH_3), 1.93 (d, *J* = 6.9 Hz, 6 H, 2 × CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 18.1 (2 C), 20.9, 121.4, 122.9, 123.8, 127.0, 136.5, 139.9, 141.9, 147.2, 147.3, 163.9 (C=O), 164.0 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 ([M$^+$], 11), 129 (26), 124 (10), 69 (100).

cis,_trans_-4-Methyl-1,2-phenylene Dibut-2-enoate (_cis_,_trans_-9a) and _trans_,_cis_-4-Methyl-1,2-phenylene Dibut-2-enoate (_trans_,_cis_-9a)

Inseparable mixture of stereoisomers (1:1 ratio); yield: 117 mg (45%); colorless oil.

IR ($CHCl_3$): 3026, 2926, 2854, 1743 (C=O), 1654, 1504, 1442, 1259, 1133, 969 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–6.97 (m, 4 H, 3 H_{arom}, CH_3CH=CH), 6.52–6.46 (m, 1 H, CH_3CH=CH), 6.01–5.96 (m, 2 H, CH_3CH=C*H*), 2.31 (s, 3 H, ArCH_3), 2.18–2.15 (m, 3 H, CH_3CH=CH), 1.95–1.91 (m, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 18.1, 20.9, 119.2, 121.4, 123.0, 123.9, 125.5, 127.0, 136.5, 139.7, 139.9, 141.7, 141.9, 147.1, 147.9, 148.0, 163.8 (C=O), 163.9 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 ([M$^+$], 13), 129 (24), 124 (9), 69 (100).

cis,_cis_-4-Methyl-1,2-phenylene Dibut-2-enoate (_cis_,_cis_-9a)

Yield: 23 mg (9% mg); colorless oil.

IR ($CHCl_3$): 3022, 2926, 2855, 1743 (C=O), 1645, 1504, 1413, 1261, 1214, 1128 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11–7.03 (m, 3 H_{arom}), 6.53–6.46 (m, 2 H, CH_3CH=CH), 6.00–5.97 (m, 2 H, CH_3CH=C*H*), 2.35 (s, 3 H, ArCH_3), 2.20–2.15 (m, 6 H, 2 × CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 20.9, 25.6, 119.3, 123.1, 123.9, 127.0, 129.4, 136.6, 139.8, 141.7, 147.9, 148.0, 163.7 (C=O), 163.8 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 ([M$^+$], 12), 129 (24), 124 (8), 69 (100).

trans-4-(2-Hydroxyethyl)phenyl But-2-enoate (_trans_-10a)

Yield: 169 mg (82% mg); colorless oil.

IR ($CHCl_3$): 3580 (OH, free), 3430 (OH, br), 3010, 2930, 2850, 1730 (C=O), 1655, 1502, 1440 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.3 Hz, 2 H_{arom}), 7.15 (dq, *J* = 15.6, 6.9 Hz, 1 H, CH_3CH=CH), 6.98 (d, *J* = 8.3 Hz, 2 H_{arom}), 6.00 (dq, *J* = 1.7, 15.6 Hz, 1 H, CH_3CH=C*H*), 4.26 (t, *J* = 7.1 Hz, 2 H, CH_2CH_2O), 2.86 (t, *J* = 7.1 Hz, 2 H, PhCH_2CH_2O), 1.93 (dd, *J* = 1.7, 6.9 Hz, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6, 38.5, 65.1, 120.8, 121.5, 128.1, 137.0, 144.1, 150.3, 163.1 (C=O).

GC-MS (70 eV): *m*/*z* (%) = 206 ([M$^+$], <1), 188 (10), 120 (100), 107 (19), 91 (16), 69 (10).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{15}O_3$: 207.1021; found: 207.1022.

cis-4-(2-Hydroxyethyl)phenyl But-2-enoate (_cis_-10a)

Yield: 27 mg (13%); colorless oil.

IR ($CHCl_3$): 3580 (OH, free), 3435 (OH, br), 3015, 2930, 2850, 1727 (C=O), 1650, 1500, 1440 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (br s, OH), 7.23 (d, *J* = 8.4 Hz, 2 H_{arom}), 7.05 (d, *J* = 8.4 Hz, 2 H_{arom}), 6.53 (dq, *J* = 7.4, 11.5 Hz, 1 H, CH_3CH=CH), 6.03 (dd, *J* = 1.7, 11.5 Hz, 1 H, CH_3CH=C*H*), 4.30 (t, *J* = 7.0 Hz, 2 H, CH_2CH_2O), 2.94 (t, *J* = 7.0 Hz, 2 H, CH_2CH_2O), 2.21 (dd, *J* = 1.7, 7.4 Hz, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 39.1, 65.0, 121.6, 122.0, 129.8, 135.1, 146.9, 149.4, 164.9 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 206 ([M$^+$], 1), 188 (12), 120 (100), 91 (15).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{15}O_3$: 207.1021; found: 207.1023.

trans-4-(Hydroxymethyl)phenyl But-2-enoate (_trans_-11a)

Yield: 150 mg (78%); colorless oil.

IR ($CHCl_3$): 3604 (OH, free), 3431 (OH, br), 3011, 2930, 2855, 1735 (C=O), 1654, 1507, 1442 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.4 Hz, 2 H_{arom}), 7.18 (dq, *J* = 15.6, 6.9 Hz, 1 H, CH_3CH=CH), 7.06 (d, *J* = 8.4 Hz, 2 H_{arom}), 6.03 (dq, *J* = 1.7, 15.6 Hz, 1 H, CH_3CH=C*H*), 4.62 (s, 2 H, CH_2O), 1.96 (dd, *J* = 1.7, 6.9 Hz, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 64.2, 121.4, 121.7, 127.9, 138.2, 147.2, 149.8, 165.1 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 192 ([M$^+$], 10), 174 (2), 124 (8), 107 (13), 69 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}O_3$: 193.0865; found: 193.0864.

cis-4-(Hydroxymethyl)phenyl But-2-enoate (_cis_-11a)

Yield: 35 mg (18%); colorless oil.

IR ($CHCl_3$): 3604 (OH, free), 3431 (OH, br), 3017, 2927, 2854, 1735 (C=O), 1644, 1509, 1142, 1013, 954 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.09 (d, *J* = 8.5, 2 H_{arom}), 6.57–6.50 (m, 1 H, CH_3CH=CH), 6.03 (dd, *J* = 1.8, 11.2 Hz, 1 H, CH_3CH=C*H*), 4.67 (s, 2 H, CH_2O), 2.20 (dd, *J* = 1.8 Hz, *J* = 7.2 Hz, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 64.7, 119.7, 121.8, 128.1, 138.3, 148.0, 149.9, 164.8 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 192 ([M$^+$], 12), 174 (5), 124 (13), 107 (58), 69 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}O_3$: 193.0865; found: 193.0864.

trans-4-[(But-3-enoyloxy)methyl]phenyl But-2-enoate (_trans_-12a)

Yield: 221 mg (85%); colorless oil.

IR ($CHCl_3$): 3025, 2950, 2855, 1735 (C=O), 1655, 1510, 1443, 1163, 1010, 979 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.23–7.14 (m, 1 H, CH_3CH=CH), 7.10 (d, *J* = 8.5 Hz, 2 H_{arom}), 6.04 (dd, *J* = 1.7, 15.6 Hz, 1 H, CH_3CH=C*H*), 5.97–5.86 (m, 1 H, CH_2=C*H*CH_2), 5.19–5.15 (m, 2 H, CH_2=$CHCH_2$), 5.12 (s, 2 H, CH_2O), 3.15–3.12 (m, 2 H, CH_2=$CHCH_2$), 1.97 (dd, *J* = 1.6, 6.9 Hz, 3 H, CH_3CH=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 39.0, 65.8, 118.7, 121.7, 121.9, 129.4, 130.0, 133.2, 147.1, 150.6, 164.7 (C=O), 171.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 ([M$^+$], 4), 192 (4), 69 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{17}O_4$: 261.1127; found: 261.1126.

cis-4-[(But-3-enoyloxy)methyl]phenyl But-2-enoate (_cis_-12a)

Yield: 36 mg (14%); colorless oil.

IR ($CHCl_3$): 3025, 2956, 2861, 1734 (C=O), 1644, 1509, 1415, 1218, 1142, 1014 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.11 (d, *J* = 8.5 Hz, 2 H_{arom}), 6.56–6.50 (m, 1 H, CH_3CH=CH), 6.03 (d, *J* = 11.5 Hz, 1 H, CH_3CH=C*H*), 5.98–5.92 (m, 1 H, CH_2=C*H*CH_2), 5.19–5.15 (m, 2 H, CH_2=CHCH_2), 5.12 (s, 2 H, CH_2O), 3.14 (d, *J* = 7.0 Hz, 2 H, CH_2=CHCH_2), 2.20 (dd, *J* = 1.7, 7.3 Hz, 3 H, CH_3CH=CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 39.0, 65.8, 118.7, 119.6, 121.8, 129.4, 130.0, 133.2, 148.0, 150.4, 164.5 (C=O), 171.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 ([M^+], 5), 192 (5), 69 (100).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{17}O_4$: 261.1127; found: 261.1128.

4-[2-(But-3-enoyloxy)ethyl]-1,2-phenylene Dibut-3-enoate (13b)
Yield: 36 mg (10%); colorless oil.

IR ($CHCl_3$): 3025, 2927, 2850, 1762 (C=O), 1733 (C=O), 1643, 1505, 1142, 1023 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.00 (m, 3 H_{arom}), 6.00–5.80 (m, 3 H, CH_2=C*H*CH_2), 5.29–5.13 (m, 6 H, CH_2=CHCH_2), 4.30 (t, *J* = 6.8 Hz, 2 H, CH_2O), 3.62–3.55 (m, 2 H, CH_2=CHCH_2), 3.31–3.27 (m, 2 H, CH_2=CHCH_2), 3.08 (d, *J* = 6.9 Hz, 2 H, CH_2=CHCH_2), 2.93 (t, *J* = 6.8 Hz, 2 H, ArCH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5, 34.4, 38.8, 39.1, 64.5, 118.6, 119.1, 119.3, 123.2, 123.8, 127.0, 129.4, 130.1, 136.7, 140.6, 141.8, 148.5, 168.8 (C=O), 168.9 (C=O), 171.4 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 358 ([M^+], 1), 272 (3), 204 (21), 136 (100), 69 (23).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{22}O_6$: 358.1416; found: 358.1417.

***trans*-Phenyl 4-Methylpent-2-enoate (*trans*-16a)**
Yield: 44 mg (24%); colorless oil.

IR ($CHCl_3$): 3030, 2949, 2875, 1702 (C=O), 1650, 1450, 1265 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (t, *J* = 8.1 Hz, 2 H, H_{arom}), 7.15 (t, *J* = 8.1 Hz, 1 H, H_{arom}), 7.07 (d, *J* = 8.1 Hz, 2 H, H_{arom}), 6.84 (dd, *J* = 16.0, 7.0 Hz, 1 H, CHC*H*=CH), 5.81 (d, *J* = 16.0 Hz, 1 H, CHCH=C*H*), 2.50–2.53 (m, 1 H, C*H*CH=CH), 1.10 (d, *J* = 6.5 Hz, 6 H, 2 × CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 30.7, 116.1, 121.3, 125.3, 128.7, 150.1, 153.2, 161.9 (C=O).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{15}O_2$: 191.1072; found: 191.1073.

***cis*-Phenyl 4-Methylpent-2-enoate (*cis*-16a)**
Yield: 21 mg (11%); colorless oil.

IR ($CHCl_3$): 3031, 2953, 2880, 1700 (C=O), 1650, 1450, 1265 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 8.2 Hz, 2 H, H_{arom}), 7.16 (t, *J* = 8.2 Hz, 1 H, H_{arom}), 7.07 (d, *J* = 8.2 Hz, 2 H, H_{arom}), 6.12 (dd, *J* = 11.1, 7.1 Hz, 1 H, CHC*H*=CH), 5.74 (d, *J* = 11.1 Hz, 1 H, CHCH=C*H*), 2.49 (m, 1 H, C*H*CH=CH), 1.12 (d, *J* = 6.5 Hz, 6 H, 2 × CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 30.1, 115.9, 121.6, 124.9, 128.6, 151.1, 152.8, 161.9 (C=O).

HRMS (ESI): *m*/z [M + H]$^+$ calcd for $C_{12}H_{15}O_2$: 191.1072; found: 191.1073.

Phenyl 4-Methylpent-3-enoate (16b)
Yield: 114 mg (60%); colorless oil.

IR ($CHCl_3$): 3032, 2950, 2878, 1724 (C=O), 1640, 1450, 1260 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 8.3 Hz, 2 H, H_{arom}), 7.13 (t, *J* = 8.3 Hz, 1 H, H_{arom}), 7.07 (d, *J* = 8.3 Hz, 2 H, H_{arom}), 5.50 (t, *J* = 7.5 Hz, 1 H, C=C*H*CH_2), 2.95 (d, *J* = 7.5 Hz, 2 H, C=CHCH_2), 1.91 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 24.5, 30.1, 116.8, 122.0, 125.6, 128.7, 133.1, 152.0, 168,1 (C=O).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{15}O_2$: 191.1072; found: 191.1072.

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