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A general route for the stereoselective synthesis of (*E*)-(1-propenyl)phenyl esters by catalytic C═C bond isomerization

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Dedicated to Dr. Hubert Le Bozec on the occasion of his 60th birthday

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ABSTRACT

A general and efficient procedure for the stereoselective synthesis of (*E*)-(1-propenyl)phenyl esters from readily accessible allylphenols has been developed. The process involves a two-step sequence consisting of the initial acylation of the allylphenols with an acid chloride, followed by catalytic C═C bond isomerization in the resulting allylphenyl esters. The latter step was performed in methanol at 80 °C using catalytic amounts (0.5 mol %) of the commercially available bis(allyl)-ruthenium(IV) dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$=2,7-dimethylocta-2,6-diene-1,8-diyl). Reactions proceeded in high yields (68–93%) and short times (4–9 h) with complete *E*-selectivity.

1. Introduction

The catalytic isomerization of olefins is a fundamental reaction in organic chemistry with widespread academic and industrial applications.[1] Transformation of allylbenzenes into the corresponding 1-propenyl derivatives is a clear example of the synthetic utility of this textbook reaction since the latter are common starting materials in the flavour and fragrance industries,[2] as well as advanced intermediates for the preparation of a large variety of biologically active compounds.[3] Traditionally, these isomerization reactions have been performed with alkali hydroxides in alcoholic media under high temperature regimes.[4] However, these methods usually suffer from drawbacks like long reactions times, low conversions, limited tolerance to functional groups and tedious post-synthetic work-up. During the last years, more convenient approaches based on the use of heterogeneous and homogeneous catalysts have been developed.[5,6] In particular, since the pioneering works by Shimizu and Blum on the isomerization of allylbenzene using Natta-type[7] and Ru-, Rh-, and Ir-based catalysts,[8] respectively, a wide array of transition metal complexes has proven effective for the C═C bond migration of allyl-aromatic compounds.[9] However, despite these advances, there is still a high request for readily available and efficient systems providing the desired 1-propenyl products in a stereoselective manner under mild conditions. Indeed, stereoselectivity is a key issue in the industrial isomerization of several allylbenzene derivatives, such as estragole, eugenol or safrole, where only the *E*-products are marketed due to the toxic character and unpleasant organoleptic properties of the corresponding *Z*-isomers.[9t]

Recently, in the context of our studies on the catalytic isomerization of functionalized allylic compounds,[10] we have brought to light different organometallic ruthenium complexes able to isomerize estragole into anethole with *E*-selectivities ≥99%.[11] Among them, the bis(allyl)-ruthenium(IV) dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$=2,7-dimethylocta-2,6-diene-1,8-diyl)[12] deserves to be highlighted due to its outstanding activity and accessibility (Scheme 1).[11b] In fact, it can be purchased from commercial suppliers (Sigma–Aldrich or Strem Chemicals) or easily prepared by simple reaction of $RuCl_3 \cdot nH_2O$ with isoprene.[13]

The remarkable *E*-selectivity shown by complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] in this industrially relevant transformation prompted us to undertake a systematic evaluation of its catalytic behaviour towards related allylbenzene derivatives. As a first result of these studies, herein we disclose a general and efficient procedure for the stereoselective synthesis of (*E*)-(1-propenyl)phenyl esters **C** starting from readily available allylphenols **A**, via initial acylation of the OH unit of **A** with an acid chloride and subsequent

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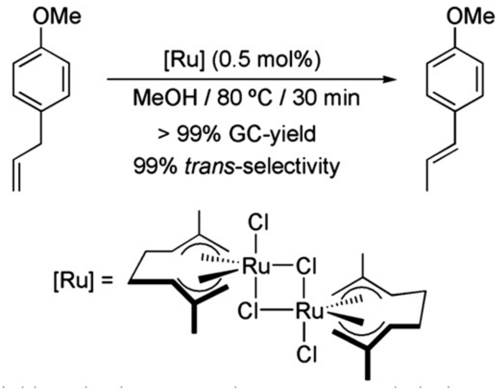
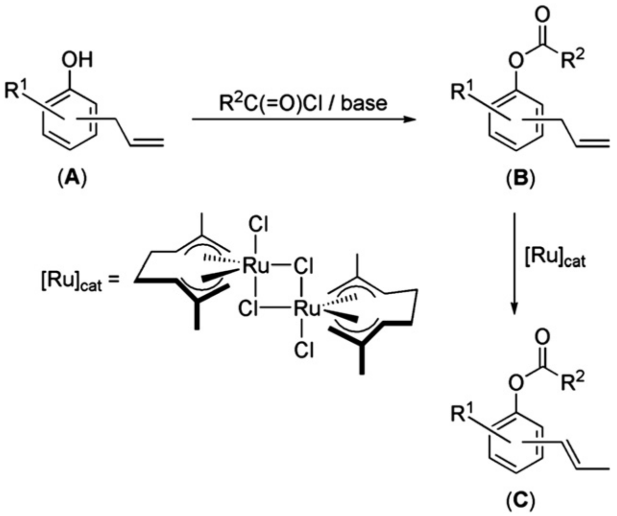


Scheme 1. Highly selective estragole to *trans*-anethole isomerization using complex $[\{RuCl(\mu-Cl)(\eta^3:\eta^3-C_{10}H_{16})\}_2]$ as catalyst.

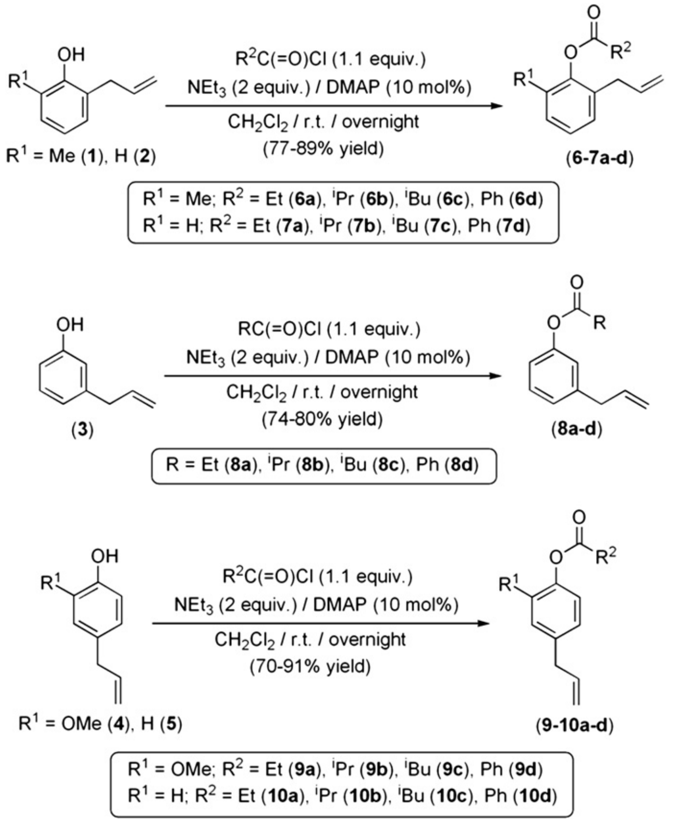
stereoselective C═C bond isomerization in the resulting allylphenyl esters **B** (Scheme 2). Note that, although compounds of type **C** widely occur in nature and present interesting biological activities,[14] to date no convenient routes of access have been described in the literature.[15] In fact, some representatives of this family of compounds have shown relevant anti-inflammatory,[14q] antimalarial,[14p,r] anti-bacterial[14p,r] and anti-fungal[14p,r] properties, as well as insecticidal[14n] and oestrogenic activities.[14k]



Scheme 2. General route for the stereoselective synthesis of (*E*)-(1-propenyl)phenyl esters **C**.

2. Results and discussion

Our investigations started with the preparation of a varied family of allylphenyl esters **6**–**10**(**a**–**d**) showing a mutual 1,2-, 1,3- or 1,4-disposition of the ester and allyl functional groups (Scheme 3). These species were generated by acylation of the commercially available, or readily accessible, allylphenols **1**–**5** with propionyl chloride, isobutyryl chloride, 3-methyl-butyryl chloride and benzoyl chloride. Reactions, which were routinely performed in dichloromethane at rt in the presence of catalytic amounts of 4-dimethylaminopyridine (DMAP) and triethylamine as HCl scavenger, delivered the desired allylphenyl esters **6**–**10**(**a**–**d**) in 70–91% isolated yield after appropriate chromatographic purification. Characterization of compounds **6**–**10**(**a**–**d**) was straightforward following their HRMS, IR and ^1H and $^{13}C\{^1H\}$ NMR data (details are given in Experimental section). In particular, selective acylation of the alcohol units was readily evidenced by the appearance of a low-field carbon resonance at 164.5–176.1 ppm, and a strong absorption band at 1733–1761 cm^{-1}, in the $^{13}C\{^1H\}$ NMR and IR spectra, respectively, characteristic of ester RCO_2-moieties.

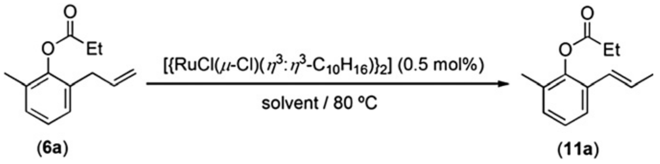


Scheme 3. Synthesis of the allylphenyl esters **6**–**10**(**a**–**d**).

Once synthesized, the ability of complex $[\{RuCl(\mu-Cl)(\eta^3:\eta^3-C_{10}H_{16})\}_2]$ to promote the isomerization of the allyl unit in these compounds was then evaluated. Optimization of the reaction conditions was carried out using 2-allyl-6-methylphenyl propionate (**6a**) as model compound. In our previous studies on the estragole to anethole isomerization (Scheme 1), dependence of the activity of complex $[\{RuCl(\mu-Cl)(\eta^3:\eta^3-C_{10}H_{16})\}_2]$ with the solvent was evidenced.[11b] Consequently, our initial efforts focused on finding the optimal solvent for the process. To this end, we conducted a series of experiments in different reaction media. They were performed at 80 °C with 2 mmol of **6a**, a ruthenium loading of 1 mol % and 0.5 mL of the appropriate solvent (4 M solutions of **6a**), monitoring the course of the reactions by GC analyses of aliquots. The results obtained are collected in Table 1.

As a general trend, the efficiency of the process increased with the polarity of the solvent due to the easier chloride bridge cleavage and ruthenium-chloride bond dissociation in $[\{RuCl(\mu-Cl)(\eta^3:\eta^3-C_{10}H_{16})\}_2]$, key processes to generate the required vacant sites on the metal. However, we must note that, although acetonitrile was one of the most polar solvents used, the conversion obtained in this medium was particularly low (28% after 4 h, entry 7). This is probably due to its capacity to coordinate on the active species, competing then with the substrate. In particular, the best results were obtained in methanol and ethanol where 95–96% conversions of **6a** into its 1-propenyl isomer **11a** were reached after 4 h of heating (>90% after only 1 h; entries 1 and 2). The higher activities observed in these solvents versus water or THF (69–83% yield after 4 h; entries 4 and 5) can be attributed to their ability to generate

Table 1
Isomerization of the allylphenyl ester **6a** into the (*E*)-(1-propenyl)phenyl ester **11a** catalyzed by complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] in different solvents[a]

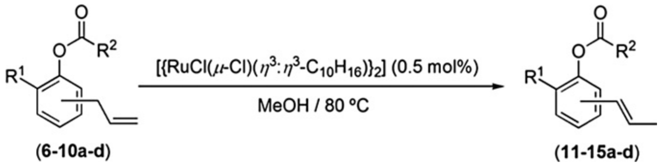


Entry	Solvent	Yield after 1 h[b] (%)	Yield after 4 h[b] (%)
1	MeOH	91	96
2	EtOH	90	95
3	Glycerol	70	77
4	Water	78	83
5	THF	61	69
6	Toluene	30	57
7	Acetonitrile	10	28
8	1,2-Dichloroethane	12	43

[a] Reactions performed under N_2 atmosphere at 80 °C using 2 mmol of **6a** (4 M solutions). [Substrate]/[Ru] ratio=100:1.

[b] Determined by GC. Formation of the corresponding *Z*-isomer not observed.

Table 2
Isomerization of the allylphenyl esters **6**–**10**(**a**–**d**) into the (*E*)-(1-propenyl)phenyl ester **11**–**15**(**a**–**d**) catalyzed by complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] in methanol[a]



Entry	Solvent	Time (h)	Product	Yield[b] (%)
1	**6a**	4	**11a**	96 (85)
2	**6b**	4	**11b**	88 (76)
3	**6c**	4	**11c**	94 (84)
4	**6d**	7	**11d**	83 (70)
5	**7a**	4	**12a**	99 (87)
6	**7b**	4	**12b**	96 (84)
7	**7c**	4	**12c**	97 (88)
8	**7d**	4	**12d**	97 (90)
9	**8a**	4	**13a**	87 (74)
10	**8b**	4	**13b**	92 (86)
11	**8c**	4	**13c**	88 (79)
12	**8d**	4	**13d**	94 (87)
13	**9a**	9	**14a**	86 (79)
14	**9b**	4	**14b**	88 (78)
15	**9c**	7	**14c**	97 (84)
16	**9d**	4	**14d**	99 (88)
17	**10a**	4	**15a**	91 (83)
18	**10b**	4	**15b**	95 (87)
19	**10c**	4	**15c**	98 (89)
20	**10d**	4	**15d**	94 (80)

[a] Reactions performed in methanol under N_2 atmosphere at 80 °C using 2 mmol of the corresponding allylphenyl ester **6**–**10**(**a**–**d**) (4 M solutions). [Substrate]/[Ru] ratio=100:1.

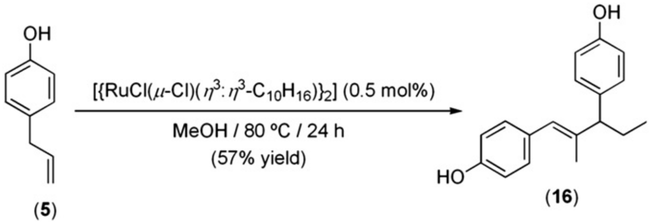
[b] Determined by GC. Isolated yields after appropriate chromatographic work-up are given in parentheses. Formation of the corresponding *Z*-isomers not observed.

catalytically active ruthenium-hydride species, via a β-hydride elimination process on the corresponding Ru-alkoxide intermediates, thus suggesting that the C=C bond migration process proceeds through a classical 'hydride mechanism'. Although Ru–H species can also be easily formed from glycerol, the use of this emerging green solvent led to a poorer conversion (77% after 4 h; entry 3).[16] The high viscosity of glycerol, which provokes poor substrate diffusion in the medium, could be responsible of this disappointing result.

Remarkably, regardless of the solvent employed, formation of a single reaction product was in all cases observed by GC, suggesting that the migration of the C=C bond in **6a** proceeds in a complete stereoselective manner. This point was unambiguously confirmed by running a ^1H NMR spectrum of one reaction crude after solvent removal (entry 1), which showed a unique set of signals for the 1-propenyl product **11a**. The mutual coupling constant observed for the olefinic –CH=CHMe protons (15.7 Hz) clearly indicated the formation of the thermodynamically more stable *E*-isomer.[17] In order to improve the efficiency of the process, some experiments were also performed in methanol at different concentrations of the substrate (from 1 M to 5 M). However, while no marked differences in activity were observed under more concentrated conditions (5 M), the use of more diluted solutions of **6a** slowed the reaction considerably (e.g., only 43% of conversion after 4 h was observed with a 1 M solution). Much poorer results were also obtained lowering the reaction temperature (e.g., at 50 °C only 8% of conversion was observed after 4 h) or the ruthenium loadings (e.g., using 0.1 mol % of [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] only 57% of conversion was observed after 4 h of heating at 80 °C). However, we must note that, in all these reactions, the *E*-isomer was again exclusively formed.

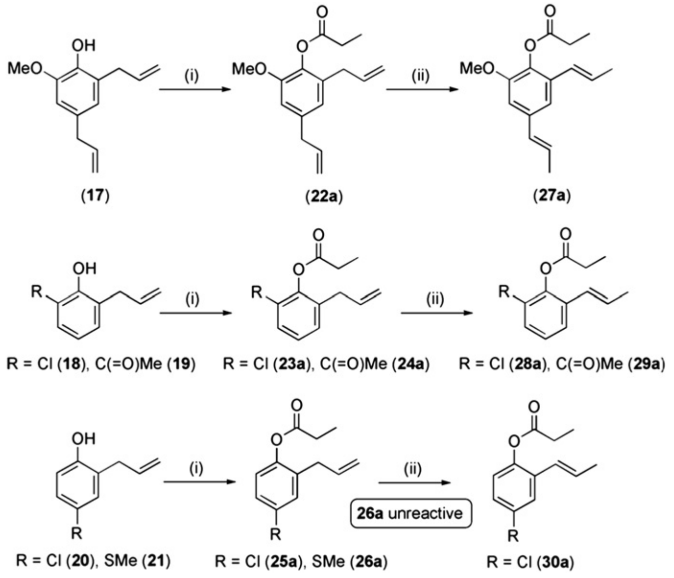
Gratifyingly, as observed for **6a**, isomerization of the other allylphenyl esters synthesized **6b**–**10d** with complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.5 mol %) also proceeded with complete *E*-selectivity, thus proving the wide scope of this new synthetic methodology (Table 2). Reactions, which were performed in methanol at 80 °C, led to the corresponding (*E*)-(1-propenyl)phenyl esters **11b**–**15d** in more than 83% yield by GC (formation of *Z*-isomers not observed by GC). No notable influence of the substitution pattern of the arene ring on the reaction rates was noticed, most of the reactions being completed within 4 h. Solvent removal and appropriate chromatographic work-up on silica gel provided analytically pure samples of all these compounds in high isolated yields (70–90%), which were fully characterized by means of high-resolution mass spectrometry and standard IR and multinuclear NMR spectroscopic techniques (details are given in Experimental section; copies of the ^1H and $^{13}C\{^1H\}$ are included in Supplementary data). A characteristic AB system of quartets for the olefinic protons of the –CH=CHMe units was found in their ^1H NMR spectra, the mutual coupling constants observed (ca. 15.7 Hz) being in complete accord with the proposed *E*-alkene geometry.

At this point, we must notice that an alternative route to (*E*)-(1-propenyl)phenyl esters **11**–**15**(**a**–**d**) involving the reverse reactions sequence, i.e., initial C=C bond migration in allylphenols **1**–**5** followed by acylation of the resulting (1-propenyl)phenols, proved inoperative using complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$]. Formation of complicated mixtures of products was observed upon treatment of **1**–**5** with [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.5 mol %) in methanol at 80 °C. Only in the case of chavicol (**5**) one major reaction product could be isolated in pure form, and identified as the known (*E*)-diphenol **16** (Scheme 4).[18] Compound **16** formally results from the self-coupling of two molecules of the isomerized 4-(1-propenyl) phenol, a process with precedents in acid media.[18,19] The high Lewis-acid character of the ruthenium(IV) centres in [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] may be therefore responsible of this unexpected result.



Scheme 4. Synthesis of the diphenol **16** from chavicol.

Finally, to further demonstrate the synthetic utility of our route to (*E*)-(1-propenyl)phenyl esters, a series of allylphenols **17**–**21** containing different functionalities on the aromatic ring were synthesized, through a Claisen rearrangement of the corresponding allylphenyl ethers,[22] and subsequently transformed into the esters **22a**–**26a** by treatment with propionyl chloride (synthetic details and characterization data for these new compounds are given in Experimental section). As shown in Scheme 5, with the exception of 2-allyl-4-methylsulfanylphenyl propionate (**26a**), which remained unaltered,[23] all these substrates underwent a clean and *E*-selective isomerization of their C=C bonds in the presence of complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.5 mol %) under the standard reaction conditions (MeOH, 80 °C), leading to the novel (*E*)-(1-propenyl)phenyl esters **27a**–**30a** in 68–93% isolated yield. The selective *E*-isomerization of the two allylic units of **22a** clearly reflects outstanding potential of [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$].



Scheme 5. Synthesis and isomerization of the allylphenyl esters **22a**–**26a**. Reagents and conditions: (i) EtC(=O)Cl (1.1 equiv), Et_3N (2 equiv), DMAP (10 mol %), CH_2Cl_2, rt, overnight, 73–88% yield; (ii) [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (0.5 mol %), MeOH, 80 °C, 9 h, 68–93% yield.

3. Conclusions

In summary, a general and efficient method of synthesis of (*E*)-(1-propenyl)phenyl esters starting from readily accessible allylphenols has been developed. The process involves the initial acylation of the allylphenols, followed by catalytic C=C bond isomerization in the resulting allylphenyl esters. The key isomerization step proceeded with complete *E*-selectivity in the presence of catalytic amounts of the commercially available dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$=2,7-dimethylocta-2,6-diene-1,8-diyl). Following this route, a large number of (*E*)-(1-propenyl)phenyl esters, including the naturally occurring ones **14b** and **15a**–**c**,[14a,c,h,r] could be selectively synthesized in high yields. Overall, the results reported herein represent a new example of the utility of the bis(allyl)-ruthenium(IV) complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] in synthetic organic chemistry.[12]

4. Experimental section

4.1. General

Synthetic procedures were performed under an atmosphere of dry nitrogen. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of compounds [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$],[13] 3-allylphenol (**3**),[20] 4-allylphenol (chavicol; **5**),[21] 2,4-diallyl-6-methoxyphenol (**17**),[24] 2-allyl-6-chlorophenol (**18**),[25] 2-acetyl-6-allylphenol (**19**),[26] 2-allyl-4-chlorophenol (**20**)[25] and 2-allyl-4-methylsulfanylphenol (**21**),[27] which were prepared by following the methods reported in the literature. GC measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex™ 120 column (30 m length; 250 μm diameter). Flash chromatography was performed using Merck silica gel 60 (230–400 mesh). Melting points were determined in a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX-300 (300/75 MHz) or Bruker AV-400 (400/100 MHz) instruments. The chemical shift values (δ) are given in parts per million and are referred to the residual peak of the deuterated solvent used ($CDCl_3$). DEPT experiments have been carried out for all the compounds reported. High-resolution mass spectra (HRMS) were provided by the Mass Spectrometry Service of Instituto de Investigaciones Químicas (IIQ-CSIC, Seville).

4.2. General procedure for the synthesis of allylphenyl esters 6–10(a–d) and 22a–26a

To a solution of the corresponding allylphenol **1**–**5** or **18**–**21** (10 mmol) in 20 mL of CH_2Cl_2, NEt_3 (20 mmol), dimethylaminopyridine (DMAP) (1 mmol) and the appropriate acid chloride (11 mmol) were added at 0 °C. The reaction mixture was allowed to reach the rt and stirred overnight at this temperature. The volatiles were then removed under reduced pressure, and the resulting oily residue dissolved in water and extracted with Et_2O (4×30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated to dryness under reduced pressure. Final purification by column chromatography over SiO_2, using a mixture hexanes/Et_2O (85:15) as eluent, afforded the desired allylphenyl esters **6**–**10**(**a**–**d**) and **22a**–**26a**. Characterization data for these compounds are as follows (copies of the ^1H and $^{13}C\{^1H\}$ spectra are included in Supplementary data):

*4.2.1. 2-Allyl-6-methylphenyl propionate (**6a**).* Colourless oil. Yield: 84% (1.716 g). IR (neat): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.34 (t, *J*=7.6 Hz, 3H, CH_2CH_3), 2.18 (s, 3H, CH_3), 2.65 (q, *J*=7.6 Hz, 2H, CH_2CH_3), 3.30 (d, *J*=6.6 Hz, 2H, CH_2CH=CH_2), 5.06–5.14 (m, 2H, CH_2CH=CH_2), 5.86–6.00 (m, 1H, CH_2CH=CH_2), 7.10–7.14 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.4 and 16.4 (s, CH_3), 27.5 (s, CH_2CH_3), 34.8 (s, CH_2CH=CH_2), 116.1 (s, CH_2CH=CH_2), 125.9, 127.8 and 129.1 (s, CH_{arom}), 130.5, 132.1 and 147.8 (s, C_{arom}), 136.1 (s, CH_2CH=CH_2), 172.2 (s, C=O). HRMS (EI): *m*/*z*=204.1154, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.2.2. 2-Allyl-6-methylphenyl isobutyrate (**6b**).* Pale yellow oil. Yield: 80% (1.746 g). IR (neat): ν=1639 (m, C=C), 1755 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.41 (d, *J*=7.0 Hz, 6H, $CH(CH_3)_2$), 2.20 (s, 3H, CH_3), 2.91 (sept, *J*=7.0 Hz, 1H, $CH(CH_3)_2$), 3.30 (d, *J*=6.5 Hz, 2H, CH_2CH=CH_2), 5.08–5.14 (m, 2H, CH_2CH=CH_2), 5.89–6.03 (m, 1H, CH_2CH=CH_2), 7.11–7.15 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=16.4 (s, CH_3), 19.1 (s, $CH(CH_3)_2$), 34.2 (s, $CH(CH_3)_2$), 34.6 (s, CH_2CH=CH_2), 116.1 (s, CH_2CH=CH_2), 125.9, 127.8 and 129.1 (s, CH_{arom}), 130.5, 132.1 and 147.8 (s, C_{arom}), 136.1 (s, CH_2CH=CH_2), 174.7 (s, C=O). HRMS (EI): *m*/*z*=218.1302, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.2.3. 2-Allyl-6-methylphenyl-3-methyl butanoate (**6c**).* Colourless oil. Yield: 77% (1.788 g). IR (neat): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.11 (d, *J*=6.9 Hz, 6H, $CH(CH_3)_2$), 2.19 (s, 3H, CH_3), 2.19–2.40 (m, 1H, $CH(CH_3)_2$), 2.51 (d, *J*=7.0 Hz, 2H,

$CH_2CH(CH_3)_2$), 3.29 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.06–5.13 (m, 2H, $CH_2CH{=}CH_2$), 5.86–6.00 (m, 1H, $CH_2CH{=}CH_2$), 7.09–7.14 (m, 3H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=17.0 (s, CH_3), 23.0 (s, $CH(CH_3)_2$), 26.0 (s, $CH(CH_3)_2$), 35.2 (s, $CH_2CH{=}CH_2$), 43.5 (s, $CH_2CH(CH_3)_2$), 116.2 (s, $CH_2CH{=}CH_2$), 126.3, 128.2 and 129.5 (s, CH_{arom}), 130.9, 132.5 and 142.3 (s, C_{arom}), 136.5 (s, $CH_2CH{=}CH_2$), 171.2 (s, C=O). HRMS (EI): m/z=232.1465, calcd for $C_{15}H_{20}O_2$: 232.1463.

*4.2.4. 2-Allyl-6-methylphenyl benzoate (**6d**).* Yellow oil. Yield: 82% (2.069 g). IR (neat): ν=1639 (m, C=C), 1737 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.25 (s, 3H, CH_3), 3.36 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.02–5.89 (m, 2H, $CH_2CH{=}CH_2$), 5.90–6.03 (m, 1H, $CH_2CH{=}CH_2$), 7.17–8.30 (m, 8H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=16.5 (s, CH_3), 34.9 (s, $CH_2CH{=}CH_2$), 116.2 (s, $CH_2CH{=}CH_2$), 126.7, 127.9, 128.7, 129.2, 130.2 and 133.6 (s, CH_{arom}), 129.3, 130.8, 132.3 and 148.0 (s, C_{arom}), 136.1 (s, $CH_2CH{=}CH_2$), 164.5 (s, C=O). HRMS (EI): m/z=252.1158, calcd for $C_{17}H_{16}O_2$: 252.1150.

*4.2.5. 2-Allylphenyl propionate (**7a**).* Colourless oil. Yield: 78% (1.483 g). IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.31 (t, J=7.6 Hz, 3H, CH_3), 2.63 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.32 (d, J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 5.05–5.12 (m, 2H, $CH_2CH{=}CH_2$), 5.87–6.00 (m, 1H, $CH_2CH{=}CH_2$), 7.05–7.28 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=9.6 (s, CH_3), 28.1 (s, CH_2CH_3), 35.0 (s, $CH_2CH{=}CH_2$), 116.2 (s, $CH_2CH{=}CH_2$), 122.8, 126.5, 127.8 and 130.7 (s, CH_{arom}), 132.3 and 149.4 (s, C_{arom}), 136.3 (s, $CH_2CH{=}CH_2$), 173.2 (s, C=O). HRMS (EI): m/z=190.0992, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.2.6. 2-Allylphenyl isobutyrate (**7b**).* Colourless oil. Yield: 89% (1.818 g). IR (neat): ν=1639 (m, C=C), 1756 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.37 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 2.86 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 3.33 (d, J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 5.05–5.13 (m, 2H, $CH_2CH{=}CH_2$), 5.87–6.00 (m, 1H, $CH_2CH{=}CH_2$), 7.04–7.31 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=19.0 (s, $CH(CH_3)_2$), 34.2 (s, $CH(CH_3)_2$), 34.4 (s, $CH_2CH{=}CH_2$), 116.2 (s, $CH_2CH{=}CH_2$), 122.3, 126.0, 127.4 and 130.4 (s, CH_{arom}), 131.9 and 149.0 (s, C_{arom}), 135.9 (s, $CH_2CH{=}CH_2$), 175.4 (s, C=O). HRMS (EI): m/z=204.1149, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.2.7. 2-Allylphenyl-3-methyl butanoate (**7c**).* Colourless oil. Yield: 81% (1.768 g). IR (neat): ν=1639 (m, C=C), 1760 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.12 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 2.28 (m, 1H, $CH(CH_3)_2$), 2.49 (d, J=7.2 Hz, 2H, $CH_2CH(CH_3)_2$), 3.36 (d, J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 5.05–5.12 (m, 2H, $CH_2CH{=}CH_2$), 5.89–5.98 (m, 1H, $CH_2CH{=}CH_2$), 7.07–7.22 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=22.9 (s, $CH(CH_3)_2$), 26.2 (s, $CH(CH_3)_2$), 35.0 (s, $CH_2CH{=}CH_2$), 43.7 (s, $CH_2CH(CH_3)_2$), 116.7 (s, $CH_2CH{=}CH_2$), 122.8, 126.5, 127.8 and 130.8 (s, CH_{arom}), 132.3 and 149.4 (s, C_{arom}), 136.3 (s, $CH_2CH{=}CH_2$), 171.8 (s, C=O). HRMS (EI): m/z=218.1310, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.2.8. 2-Allylphenyl benzoate (**7d**).*[28] Colourless oil. Yield: 84% (2.001 g). IR (neat): ν=1639 (m, C=C), 1736 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.41 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.03–5.10 (m, 2H, $CH_2CH{=}CH_2$), 5.90–6.04 (m, 1H, $CH_2CH{=}CH_2$), 7.23–7.34 (m, 4H, CH_{arom}), 7.53–7.70 (m, 3H, CH_{arom}), 8.26 (m, 2H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=35.1 (s, $CH_2CH{=}CH_2$), 116.7 (s, $CH_2CH{=}CH_2$), 122.9, 126.7, 127.9, 129.0, 130.6, 130.8 and 134.0 (s, CH_{arom}), 129.9, 132.6 and 149.6 (s, C_{arom}), 136.2 (s, $CH_2CH{=}CH_2$), 165.4 (s, C=O). HRMS (EI): m/z=238.0995, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.2.9. 3-Allylphenyl propionate (**8a**).* Colourless oil. Yield: 76% (1.445 g). IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.30 (t, J=7.5 Hz, 3H, CH_3), 2.63 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.43 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.10–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.95–6.04 (m, 1H, $CH_2CH{=}CH_2$), 6.96–7.33 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=9.1 (s, CH_3), 27.8 (s, CH_2CH_3), 39.9 (s, $CH_2CH{=}CH_2$), 116.4 (s, $CH_2CH{=}CH_2$), 119.3, 121.7, 126.0 and 129.3 (s, CH_{arom}), 136.8 (s, $CH_2CH{=}CH_2$), 141.8 and 150.9 (s, C_{arom}), 173.0 (s, C=O). HRMS (EI): m/z=190.0995, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.2.10. 3-Allylphenyl isobutyrate (**8b**).* Colourless oil. Yield: 80% (1.634 g). IR (neat): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.36 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 2.83 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 3.43 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.11–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.93–6.07 (m, 1H, $CH_2CH{=}CH_2$), 6.95–7.33 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=18.9 (s, $CH(CH_3)_2$), 34.2 (s, $CH(CH_3)_2$), 39.9 (s, $CH_2CH{=}CH_2$), 116.3 (s, $CH_2CH{=}CH_2$), 119.2, 121.6, 125.9 and 129.2 (s, CH_{arom}), 136.8 (s, $CH_2CH{=}CH_2$), 141.7 and 151.0 (s, C_{arom}), 175.6 (s, C=O). HRMS (EI): m/z=204.1148, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.2.11. 3-Allylphenyl-3-methyl butanoate (**8c**).* Colourless oil. Yield: 79% (1.724 g). IR (neat): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.10 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 2.21–2.35 (m, 1H, $CH(CH_3)_2$), 2.47 (d, J=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 3.44 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.10–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.95–6.04 (m, 1H, $CH_2CH{=}CH_2$), 6.95–7.36 (m, 4H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=22.4 (s, $CH(CH_3)_2$), 25.9 (s, $CH(CH_3)_2$), 39.9 (s, $CH_2CH{=}CH_2$), 43.4 (s, $CH_2CH(CH_3)_2$), 116.3 (s, $CH_2CH{=}CH_2$), 119.3, 121.7, 126.0 and 129.3 (s, CH_{arom}), 136.8 (s, $CH_2CH{=}CH_2$), 141.8 and 150.8 (s, C_{arom}), 171.6 (s, C=O). HRMS (EI): m/z=218.1311, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.2.12. 3-Allylphenyl benzoate (**8d**).* Colourless oil. Yield: 74% (1.763 g). IR (neat): ν=1638 (m, C=C), 1738 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.47 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.13–5.19 (m, 2H, $CH_2CH{=}CH_2$), 5.96–6.07 (m, 1H, $CH_2CH{=}CH_2$), 7.10–7.70 (m, 7H, CH_{arom}), 8.23 (m, 2H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=40.0 (s, $CH_2CH{=}CH_2$), 116.4 (s, $CH_2CH{=}CH_2$), 119.4, 121.8, 126.2, 128.6, 129.4, 130.2 and 133.6 (s, CH_{arom}), 129.7, 141.9 and 151.1 (s, C_{arom}), 136.8 (s, $CH_2CH{=}CH_2$), 165.2 (s, C=O). HRMS (EI): m/z=238.0998, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.2.13. 4-Allyl-2-methoxyphenyl propionate (**9a**).*[29] White solid. Yield: 85% (1.872 g). Mp: 44–45 °C. IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.30 (t, J=7.6 Hz, 3H, CH_3), 2.63 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.40 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 3.83 (s, 3H, OCH_3), 5.11–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.93–6.04 (m, 1H, $CH_2CH{=}CH_2$), 6.79–6.99 (m, 3H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=9.6 (s, CH_3), 27.8 (s, CH_2CH_3), 40.5 (s, $CH_2CH{=}CH_2$), 56.2 (s, OCH_3), 113.1, 121.1 and 122.9 (s, CH_{arom}), 116.5 (s, $CH_2CH{=}CH_2$), 137.5 (s, $CH_2CH{=}CH_2$), 138.5, 149.4 and 151.3 (s, C_{arom}), 173.1 (s, C=O). HRMS (EI): m/z=220.1093, calcd for $C_{13}H_{16}O_3$: 220.1099.

*4.2.14. 4-Allyl-2-methoxyphenyl isobutyrate (**9b**).*[30] Colourless oil. Yield: 84% (1.968 g). IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.35 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 2.86 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 3.41 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 3.83 (s, 3H, OCH_3), 5.10–5.16 (m, 2H, $CH_2CH{=}CH_2$), 5.95–6.04 (m, 1H, $CH_2CH{=}CH_2$), 6.77–6.97 (m, 3H, CH_{arom}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ=19.1 (s, $CH(CH_3)_2$), 34.0 (s, $CH(CH_3)_2$), 40.1 (s, $CH_2CH{=}CH_2$), 55.8 (s, OCH_3), 112.8, 120.7 and 122.5 (s, CH_{arom}), 116.1 (s, $CH_2CH{=}CH_2$), 137.1 (s, $CH_2CH{=}CH_2$), 138.2, 138.7 and 151.0 (s, C_{arom}), 175.4 (s, C=O). HRMS (EI): m/z=234.1257, calcd for $C_{14}H_{18}O_3$: 234.1256.

*4.2.15. 4-Allyl-2-methoxyphenyl-3-methyl butanoate (**9c**).*[31] Colourless oil. Yield: 87% (2.160 g). IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.09 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 2.22–2.33 (m, 1H, $CH(CH_3)_2$), 2.47 (d, J=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 3.40 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 3.82 (s, 3H, OCH_3), 5.10–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.92–6.05 (m, 1H, $CH_2CH{=}CH_2$), 6.78–7.01 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=22.8 (s, $CH(CH_3)_2$), 26.4 (s, $CH(CH_3)_2$), 40.5 (s, $CH_2CH{=}CH_2$), 43.5 (s, $CH_2CH(CH_3)_2$), 56.1 (s, OCH_3), 113.1, 121.0 and 122.9 (s, CH_{arom}), 116.5 (s, $CH_2CH{=}CH_2$), 137.5 (s, $CH_2CH{=}CH_2$), 138.4, 139.3 and 151.3 (s, C_{arom}), 171.7 (s, C=O). HRMS (EI): m/z=248.1415, calcd for $C_{15}H_{20}O_3$: 248.1412.

*4.2.16. 4-Allyl-2-methoxyphenyl benzoate (**9d**).*[32] White solid. Yield: 91% (2.441 g). Mp: 66–67 °C. IR (neat): ν=1638 (m, C=C), 1738 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.43 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 3.83 (s, 3H, OCH_3), 5.11–5.18 (m, 2H, $CH_2CH{=}CH_2$), 6.00–6.14 (m, 1H, $CH_2CH{=}CH_2$), 6.83–8.25 (m, 8H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=40.2 (s, $CH_2CH{=}CH_2$), 55.9 (s, OCH_3), 112.9, 120.8, 127.9, 128.6, 130.3 and 133.5 (s, CH_{arom}), 116.2 (s, $CH_2CH{=}CH_2$), 129.6, 138.3, 139.1 and 151.2 (s, C_{arom}), 137.2 (s, $CH_2CH{=}CH_2$), 164.9 (s, C=O). HRMS (EI): m/z=268.1099, calcd for $C_{17}H_{16}O_3$: 268.1099.

*4.2.17. 4-Allylphenyl propionate (**10a**).* Colourless oil. Yield: 73% (1.388 g). IR (neat): ν=1639 (m, C=C), 1761 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.29 (t, J=7.6 Hz, 3H, CH_3), 2.60 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.41 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.08–5.14 (m, 2H, $CH_2CH{=}CH_2$), 5.90–6.05 (m, 1H, $CH_2CH{=}CH_2$), 7.01–7.23 (m, 4H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.5 (s, CH_3), 28.1 (s, CH_2CH_3), 40.0 (s, $CH_2CH{=}CH_2$), 116.4 (s, $CH_2CH{=}CH_2$), 121.8 and 129.9 (s, CH_{arom}), 137.6 (s, $CH_2CH{=}CH_2$), 137.9 and 149.5 (s, C_{arom}), 173.5 (s, C=O). HRMS (EI): m/z=190.0990, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.2.18. 4-Allylphenyl isobutyrate (**10b**).* Colourless oil. Yield: 78% (1.593 g). IR (neat): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.36 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 2.83 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 3.42 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.10–5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.94–6.07 (m, 1H, $CH_2CH{=}CH_2$), 7.04 (d, J=8.6 Hz, 2H, CH_{arom}), 7.23 (d, J=8.6 Hz, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=19.4 (s, $CH(CH_3)_2$), 34.6 (s, $CH(CH_3)_2$), 40.0 (s, $CH_2CH{=}CH_2$), 116.4 (s, $CH_2CH{=}CH_2$), 121.8 and 129.9 (s, CH_{arom}), 137.6 (s, $CH_2CH{=}CH_2$), 137.8 and 149.6 (s, C_{arom}), 176.1 (s, C=O). HRMS (EI): m/z=204.1150, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.2.19. 4-Allylphenyl-3-methyl butanoate (**10c**).* Pale yellow oil. Yield: 75% (1.637 g). IR (neat): ν=1639 (m, C=C), 1759 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.09 (d, J=6.7 Hz, 6H, $CH(CH_3)_2$), 2.21–2.34 (m, 1H, $CH(CH_3)_2$), 2.46 (d, J=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 3.41 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.09–5.15 (m, 2H, $CH_2CH{=}CH_2$), 5.92–6.05 (m, 1H, $CH_2CH{=}CH_2$), 7.03 (d, J=8.4 Hz, 2H, CH_{arom}), 7.23 (d, J=8.4 Hz, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=22.8 (s, $CH(CH_3)_2$), 26.3 (s, $CH(CH_3)_2$), 40.0 (s, $CH_2CH{=}CH_2$), 43.7 (s, $CH_2CH(CH_3)_2$), 116.4 (s, $CH_2CH{=}CH_2$), 121.9 and 129.9 (s, CH_{arom}), 137.6 (s, $CH_2CH{=}CH_2$), 137.9 and 149.4 (s, C_{arom}), 172.1 (s, C=O). HRMS (EI): m/z=218.1302, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.2.20. 4-Allylphenyl benzoate (**10d**).*[33] White solid. Yield: 70% (1.668 g). Mp: 61–62 °C. IR (Nujol): ν=1641 (m, C=C), 1733 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.45 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 5.11–5.18 (m, 2H, $CH_2CH{=}CH_2$), 5.95–6.09 (m, 1H, $CH_2CH{=}CH_2$), 7.18 (d, J=8.4 Hz, 2H, CH_{arom}), 7.28 (d, J=8.4 Hz, 2H, CH_{arom}), 7.51–7.66 (m, 3H, CH_{arom}), 8.22 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=40.0 (s, $CH_2CH{=}CH_2$), 116.5 (s, $CH_2CH{=}CH_2$), 122.0, 129.0 and 130.0, 130.3 and 133.9 (s, CH_{arom}), 130.1, 138.1 and 149.7 (s, C_{arom}), 137.6 (s, $CH_2CH{=}CH_2$), 165.7 (s, C=O). HRMS (EI): m/z=238.0997, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.2.21. 2,4-Diallyl-6-methoxyphenyl propionate (**22a**).* Colourless oil. Yield: 73% (1.900 g). IR (Nujol): ν=1638 (m, C=C), 1763 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.32 (t, J=7.5 Hz, 3H, CH_3), 2.64 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.30 (d, J=7.9 Hz, 2H, $CH_2CH{=}CH_2$), 3.39 (d, J=6.7 Hz, 2H, $CH_2CH{=}CH_2$), 3.82 (s, 3H, OCH_3), 5.07–5.19 (m, 4H, $CH_2CH{=}CH_2$), 5.86–6.07 (m, 2H, $CH_2CH{=}CH_2$), 6.69 (s, 1H, CH_{arom}), 6.70 (s, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.7 (s, CH_3), 27.7 (s, CH_2CH_3), 35.0 and 40.6 (s, $CH_2CH{=}CH_2$), 56.3 (s, OCH_3), 111.1 and 122.1 (s, CH_{arom}), 116.4 and 116.5 (s, $CH_2CH{=}CH_2$), 133.4, 136.9, 138.6 and 151.6 (s, C_{arom}), 136.5 and 137.6 (s, $CH_2CH{=}CH_2$), 172.6 (s, C=O). HRMS (EI): m/z=260.1416, calcd for $C_{16}H_{20}O_3$: 260.1412.

*4.2.22. 2-Allyl-6-chlorophenyl propionate (**23a**).* Pale yellow oil. Yield: 81% (1.819 g). IR (Nujol): ν=1639 (m, C=C), 1771 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.34 (t, J=6.4 Hz, 3H, CH_3), 2.67 (q, J=6.4 Hz, 2H, CH_2CH_3), 3.33 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.08–5.15 (m, 2H, $CH_2CH{=}CH_2$), 5.83–5.97 (m, 1H, $CH_2CH{=}CH_2$), 7.14–7.39 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.6 (s, CH_3), 27.8 (s, CH_2CH_3), 35.3 (s, $CH_2CH{=}CH_2$), 116.7 (s, $CH_2CH{=}CH_2$), 127.1, 128.6 and 129.0 (s, CH_{arom}), 127.8, 135.0 and 145.9 (s, C_{arom}), 135.7 (s, $CH_2CH{=}CH_2$), 171.9 (s, C=O). HRMS (EI): m/z=224.0611, calcd for $C_{12}H_{13}O_2Cl$: 224.0604.

*4.2.23. 2-Acetyl-6-allylphenyl propionate (**24a**).* Colourless oil. Yield: 88% (2.042 g). IR (Nujol): ν=1639 (m, C=C), 1693 and 1760 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.30 (t, J=7.6 Hz, 3H, CH_2CH_3), 2.55 (s, 3H, $COCH_3$), 2.66 (q, J=7.6 Hz, 2H, CH_2CH_3), 3.34 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.05–5.12 (m, 2H, $CH_2CH{=}CH_2$), 5.83–5.96 (m, 1H, $CH_2CH{=}CH_2$), 7.27 (dd, J=7.7 and 7.4 Hz, 1H, CH_{arom}), 7.43 (d, J=7.7 Hz, 1H, CH_{arom}), 7.66 (d, J=7.4 Hz, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.2 (s, CH_2CH_3), 28.1 (s, CH_2CH_3), 29.5 (s, $COCH_3$), 34.8 (s, $CH_2CH{=}CH_2$), 117.1 (s, $CH_2CH{=}CH_2$), 126.1, 128.8 and 134.6 (s, CH_{arom}), 131.5, 134.4 and 147.5 (s, C_{arom}), 135.8 (s, $CH_2CH{=}CH_2$), 173.1 (s, OC=O), 198.5 (s, $COCH_3$). HRMS (EI): m/z=232.1098, calcd for $C_{14}H_{16}O_3$: 232.1099.

*4.2.24. 2-Allyl-4-chlorophenyl propionate (**25a**).* Pale yellow oil. Yield: 77% (1.730 g). IR (Nujol): ν=1635 (m, C=C), 1762 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.29 (t, J=7.5 Hz, 3H, CH_3), 2.61 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.28 (d, J=6.6 Hz, 2H, $CH_2CH{=}CH_2$), 5.06–5.15 (m, 2H, $CH_2CH{=}CH_2$), 5.82–5.95 (m, 1H, $CH_2CH{=}CH_2$), 7.00 (d, J=8.2 Hz, 1H, CH_{arom}), 7.20–7.25 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.5 (s, CH_3), 28.0 (s, CH_2CH_3), 34.7 (s, $CH_2CH{=}CH_2$), 117.4 (s, $CH_2CH{=}CH_2$), 124.1, 127.8 and 130.6 (s, CH_{arom}), 131.6, 134.2 and 147.9 (s, C_{arom}), 135.4 (s, $CH_2CH{=}CH_2$), 172.9 (s, C=O). HRMS (EI): m/z=224.0602, calcd for $C_{12}H_{13}O_2Cl$: 224.0604.

*4.2.25. 2-Allyl-4-methylsulfanylphenyl propionate (**26a**).* Yellow oil. Yield: 75% (1.772 g). IR (Nujol): ν=1639 (m, C=C), 1757 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.29 (t, J=7.3 Hz, 3H, CH_2CH_3), 2.48 (s, 3H, SCH_3), 2.60 (q, J=7.3 Hz, 2H, CH_2CH_3), 3.28 (d, J=6.5 Hz, 2H, $CH_2CH{=}CH_2$), 5.06–5.12 (m, 2H, $CH_2CH{=}CH_2$), 5.83–5.97 (m, 1H, $CH_2CH{=}CH_2$), 6.98 (d, J=8.4 Hz, 1H, CH_{arom}), 7.15 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.5 (s, CH_2CH_3), 16.9 (s, SCH_3), 28.0 (s, CH_2CH_3), 35.0 (s, $CH_2CH{=}CH_2$), 116.9 (s, $CH_2CH{=}CH_2$), 123.2, 126.3 and 129.3 (s, CH_{arom}), 132.8, 136.1 and 147.2 (s, C_{arom}), 135.9 (s, $CH_2CH{=}CH_2$), 173.2 (s, C=O). HRMS (EI): m/z=236.0867, calcd for $C_{13}H_{16}O_2S$: 236.0871.

4.3. General procedure for the synthesis of (*E*)-(1-propenyl) phenyl esters 11–15(a–d) and 27a–30a

Under nitrogen atmosphere, the corresponding allylphenyl ester **6**–**10**(**a**–**d**) or **22a**–**25a** (2 mmol), the ruthenium(IV) catalyst precursor $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (6 mg, 0.01 mmol; 1 mol % of Ru) and methanol (0.5 mL) were introduced into a Teflon-capped sealed tube. Then, the mixture was heated at 80 °C in an oil-bath for the indicated time. The course of the reaction was monitored by taking regularly samples of ca. 10 μL, which after dilution were analyzed by GC. Solvent removal under reduced pressure, followed by purification of the resulting oily residue by column chromatography over SiO_2, using a mixture hexanes/Et_2O (85:15) as eluent, afforded the (*E*)-propenylphenyl esters **11**–**15**(**a**–**d**) and **27**–**30a**. Characterization data for these compounds are as follows (copies of the ^{1}H and $^{13}C\{^{1}H\}$ spectra are included in Supplementary data):

*4.3.1. (E)-2-Methyl-6-(1-propenyl)phenyl propionate (**11a**).* Yellow oil. Yield: 85% (0.347 g). IR (neat): ν=1653 (w, C=C), 1759 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.38 (t, *J*=7.6 Hz, 3H, CH_2CH_3), 1.93 (dd, *J*=6.4 and 1.5 Hz, 3H, HC=$CHCH_3$), 2.20 (s, 3H, CH_3), 2.70 (q, *J*=7.6 Hz, 2H, CH_2CH_3), 6.26 (part A of AB system of q, *J*=15.7 and 6.4 Hz, 1H, HC=$CHCH_3$), 6.42 (part B of AB system of q, *J*=15.7 and 1.5 Hz, 1H, *H*C=$CHCH_3$), 7.12–7.40 (m, 3H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=9.8, 16.8 and 19.3 (s, CH_3), 27.9 (s, CH_2), 124.5, 125.0, 126.3, 128.6 and 129.8 (s, CH_{arom} and =CH), 130.9, 131.1 and 146.9 (s, C_{arom}), 172.7 (s, C=O). HRMS (EI): *m*/*z*=204.1155, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.3.2. (E)-2-Methyl-6-(1-propenyl)phenyl isobutyrate (**11b**).* Yellow oil. Yield: 76% (0.331 g). IR (neat): ν=1657 (w, C=C), 1757 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.44 (d, *J*=7.0 Hz, 6H, $CH(CH_3)_2$), 1.93 (dd, *J*=6.4 and 1.6 Hz, 3H, HC=$CHCH_3$), 2.20 (s, 3H, CH_3), 2.95 (sept, *J*=7.0 Hz, 1H, $CH(CH_3)_2$), 6.25 (part A of AB system of q, *J*=15.7 and 6.4 Hz, 1H, HC=$CHCH_3$), 6.43 (part B of AB system of q, *J*=15.7 and 1.6 Hz, 1H, *H*C=$CHCH_3$), 7.36–7.42 (m, 3H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=16.4 and 18.9 (s, CH_3), 19.2 (s, $CH(CH_3)_2$), 34.3 (s, $CH(CH_3)_2$), 124.1, 124.6, 125.8, 128.2 and 129.4 (s, CH_{arom} and =CH), 130.5, 130.7 and 146.4 (s, C_{arom}), 174.7 (s, C=O). HRMS (EI): *m*/*z*=218.1306, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.3.3. (E)-2-Methyl-6-(1-propenyl)phenyl-3-methyl butanoate (**11c**).* Yellow oil. Yield: 84% (0.390 g). IR (neat): ν=1653 (w, C=C), 1759 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.14 (d, *J*=6.6 Hz, 6H, $CH(CH_3)_2$), 1.91 (dd, *J*=6.5 and 1.6 Hz, 3H, HC=$CHCH_3$), 2.20 (s, 3H, CH_3), 2.30–2.41 (m, 1H, $CH(CH_3)_2$), 2.56 (d, *J*=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 6.25 (part A of AB system of q, *J*=15.7 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.43 (part B of AB system of q, *J*=15.7 and 1.6 Hz, 1H, *H*C=$CHCH_3$), 7.12–7.39 (m, 3H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=16.9 and 19.3 (s, CH_3), 23.0 (s, $CH(CH_3)_2$), 26.1 (s, $CH(CH_3)_2$), 43.5 (s, CH_2), 124.5, 125.3, 126.3, 128.6 and 129.8 (s, CH_{arom} and =CH), 130.9, 131.2 and 146.9 (s, C_{arom}), 171.3 (s, C=O). HRMS (EI): *m*/*z*=232.1466, calcd for $C_{15}H_{20}O_2$: 232.1463.

*4.3.4. (E)-2-Methyl-6-(1-propenyl)phenyl benzoate (**11d**).* Yellow oil. Yield: 70% (0.353 g). IR (neat): ν=1639 (w, C=C), 1737 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.86 (dd, *J*=6.5 and 1.5 Hz, 3H, HC=$CHCH_3$), 2.25 (s, 3H, CH_3), 6.34 (part A of AB system of q, *J*=15.7 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.52 (part B of AB system of q, *J*=15.7 and 1.5 Hz, 1H, *H*C=$CHCH_3$), 7.19–7.70 (m, 6H, CH_{arom}), 8.32–8.39 (m, 2H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=16.9 and 19.3, (s, CH_3), 124.5, 124.9, 126.5, 128.8, 129.1, 129.8, 130.7 and 134.1 (s, CH_{arom} and =CH), 129.7, 131.2, 131.3 and 147.0 (s, C_{arom}), 165.0 (s, C=O). HRMS (EI): *m*/*z*=252.1157, calcd for $C_{17}H_{16}O_2$: 252.1150.

*4.3.5. (E)-2-(1-Propenyl)phenyl propionate (**12a**).* Yellow oil. Yield: 87% (0.331 g). IR (neat): ν=1657 (w, C=C), 1763 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.34 (t, *J*=7.6 Hz, 3H, CH_2CH_3), 1.93 (dd, *J*=6.5 and 1.5 Hz, 3H, HC=$CHCH_3$), 2.67 (q, *J*=7.6 Hz, 2H, CH_2CH_3), 6.28 (part A of AB system of q, *J*=15.8 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.46 (part B of AB system of q, *J*=15.8 and 1.5 Hz, 1H, *H*C=$CHCH_3$), 7.04–7.26 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=9.6 and 19.3 (s, CH_3), 28.1 (s, CH_2), 122.9, 124.8, 126.4, 126.9, 128.0 and 128.7 (s, CH_{arom} and =CH), 130.9 and 147.9 (s, C_{arom}), 173.2 (s, C=O). HRMS (EI): *m*/*z*=190.0992, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.3.6. (E)-2-(1-Propenyl)phenyl isobutyrate (**12b**).* Yellow oil. Yield: 84% (0.343 g). IR (neat): ν=1657 (w, C=C), 1758 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.40 (d, *J*=7.0 Hz, 6H, $CH(CH_3)_2$), 1.92 (dd, *J*=6.5 and 1.6 Hz, 3H, HC=$CHCH_3$), 2.90 (sept, *J*=7.0 Hz, 1H, $CH(CH_3)_2$), 6.26 (part A of AB system of q, *J*=15.7 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.46 (part B of AB system of q, *J*=15.7 and 1.6 Hz, 1H, *H*C=$CHCH_3$), 7.01–7.57 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=19.3 (CH=$CHCH_3$), 19.5 (s, $CH(CH_3)_2$), 34.6 (s, $CH(CH_3)_2$), 122.8, 124.7, 126.4, 126.9, 128.0 and 128.6 (s, CH_{arom} and =CH), 131.0 and 148.0 (s, C_{arom}), 175.8 (s, C=O). HRMS (EI): *m*/*z*=204.1153, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.3.7. (E)-2-(1-Propenyl)phenyl-3-methyl butanoate (**12c**).* Yellow oil. Yield: 88% (0.384 g). IR (neat): ν=1653 (w, C=C), 1759 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.13 (d, *J*=6.6 Hz, 6H, $CH(CH_3)_2$), 1.92 (dd, *J*=6.5 and 1.6 Hz, 3H, HC=$CHCH_3$), 2.31–2.35 (m, 1H, $CH(CH_3)_2$), 2.52 (d, *J*=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 6.27 (part A of AB system of q, *J*=15.8 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.47 (part B of AB system of q, *J*=15.8 and 1.6 Hz, 1H, *H*C=$CHCH_3$), 7.05–7.55 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=18.9 (s, CH=$CHCH_3$), 22.5 (s, $CH(CH_3)_2$), 25.9 (s, $CH(CH_3)_2$), 43.3 (s, CH_2), 122.5, 124.5, 126.0, 126.5, 127.6 and 128.3 (s, CH_{arom} and =CH), 130.6 and 147.6 (s, C_{arom}), 171.4 (s, C=O). HRMS (EI): *m*/*z*=218.1307, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.3.8. (E)-2-(1-Propenyl)phenyl benzoate (**12d**).* Colourless oil. Yield: 90% (0.429 g). IR (neat): ν=1656 (w, C=C), 1735 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.89 (dd, *J*=6.6 and 1.6 Hz, 3H, HC=$CHCH_3$), 6.35 (part A of AB system of q, *J*=15.8 and 6.6 Hz, 1H, HC=$CHCH_3$), 6.56 (part B of AB system of q, *J*=15.8 and 1.6 Hz, 1H, *H*C=$CHCH_3$), 7.18–7.33 (m, 3H, CH_{arom}), 7.56–7.74 (m, 4H, CH_{arom}), 8.31 (m, 2H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=19.3 (s, CH_3), 123.1, 124.7, 126.7, 126.9, 128.2, 128.9, 129.1, 130.7 and 134.1 (s, CH_{arom} and =CH), 129.9, 131.1 and 148.1 (s, C_{arom}), 165.5 (s, C=O). HRMS (EI): *m*/*z*=238.1001, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.3.9. (E)-3-(1-Propenyl)phenyl propionate (**13a**).* Yellow oil. Yield: 74% (0.281 g). IR (neat): ν=1657 (w, C=C), 1761 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.30 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 1.90 (dd, *J*=6.4 and 1.3 Hz, 3H, HC=$CHCH_3$), 2.62 (q, *J*=7.5 Hz, 2H, CH_2CH_3), 6.24 (part A of AB system of q, *J*=15.7 and 6.4 Hz, 1H, HC=$CHCH_3$), 6.41 (part B of AB system of q, *J*=15.7 and 1.3 Hz, 1H, *H*C=$CHCH_3$), 6.93–7.09 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=9.1 and 18.5 (s, CH_3), 27.8 (s, CH_2), 118.7, 119.8, 123.4, 126.9, 129.3 and 130.4 (s, CH_{arom} and =CH), 139.6 and 151.1 (s, C_{arom}), 173.0 (s, C=O). HRMS (EI): *m*/*z*=190.0992, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.3.10. (E)-3-(1-Propenyl)phenyl isobutyrate (**13b**).* Colourless oil. Yield: 86% (0.351 g). IR (neat): ν=1657 (w, C=C), 1760 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.35 (d, *J*=7.0 Hz, 6H, $CH(CH_3)_2$), 1.91 (dd, *J*=6.4 and 1.3 Hz, 3H, HC=$CHCH_3$), 2.83 (sept, *J*=7.0 Hz, 1H, $CH(CH_3)_2$), 6.28 (part A of AB system of q, *J*=15.7 and 6.4 Hz, 1H, HC=$CHCH_3$), 6.41 (part B of AB system of q, *J*=15.7 and 1.3 Hz, 1H, *H*C=$CHCH_3$), 7.07–7.31 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=18.4 (s, CH_3), 18.9 (s, $CH(CH_3)_2$), 34.2 (s, $CH(CH_3)_2$), 118.6, 119.7, 123.3, 126.8, 129.3 and 130.2 (s, CH_{arom} and =CH), 139.6 and 151.2 (s, C_{arom}), 175.6 (s, C=O). HRMS (EI): *m*/*z*=204.1145, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.3.11. (E)-3-(1-Propenyl)phenyl-3-methyl butanoate (**13c**).* Pale yellow oil. Yield: 79% (0.345 g). IR (neat): ν=1657 (w, C=C), 1757 (s, C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.11 (d, *J*=6.6 Hz, 6H, $CH(CH_3)_2$), 1.91 (dd, *J*=6.5 and 1.3 Hz, 3H, HC=$CHCH_3$), 2.23–2.36 (m, 1H, $CH(CH_3)_2$), 2.47 (d, *J*=7.0 Hz, 2H, $CH_2CH(CH_3)_2$), 6.28 (part A of AB system of q, *J*=15.7 and 6.5 Hz, 1H, HC=$CHCH_3$), 6.42 (part B of AB system of q, *J*=15.7 and 1.3 Hz, 1H, *H*C=$CHCH_3$), 6.94–7.10 (m, 4H, CH_{arom}). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=18.5 (s, CH_3), 22.4 (s, $CH(CH_3)_2$), 25.9 (s, $CH(CH_3)_2$), 43.4 (s, CH_2), 118.8, 119.9, 123.4, 126.8, 129.3 and

130.3 (s, CH_{arom} and $=CH$), 139.6 and 151.0 (s, C_{arom}), 171.5 (s, $C{=}O$). HRMS (EI): m/z=218.1306, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.3.12. (E)-3-(1-Propenyl)phenyl benzoate (**13d**).* White solid. Yield: 87% (0.414 g). Mp: 58–59 °C. IR (Nujol): ν=1655 (w, $C{=}C$), 1745 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.94 (dd, J=6.4 and 1.4 Hz, 3H, $HC{=}CHCH_3$), 6.33 (part A of AB system of q, J=15.7 and 6.4 Hz, 1H, $HC{=}CHCH_3$), 6.47 (part B of AB system of q, J=15.7 and 1.4 Hz, 1H, $HC{=}CHCH_3$), 7.10–7.71 (m, 7H, CH_{arom}), 8.26 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.5 (s, CH_3), 118.9, 120.0, 123.6, 127.0, 128.6, 129.5, 130.2, 130.3 and 133.6 (s, CH_{arom} and $=CH$), 129.7, 139.8 and 151.3 (s, C_{arom}), 165.2 (s, $C{=}O$). HRMS (EI): m/z=238.0999, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.3.13. (E)-2-Methoxy-4-(1-propenyl)phenyl propionate (**14a**).*[34] Colourless oil. Yield: 79% (0.348 g). IR (neat): ν=1645 (w, $C{=}C$), 1763 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.30 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.90 (dd, J=6.5 and 1.6 Hz, 3H, $HC{=}CHCH_3$), 2.63 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.85 (s, 3H, OCH_3), 6.21 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.40 (part B of AB system of q, J=15.7 and 1.6 Hz, 1H, $HC{=}CHCH_3$), 6.80–7.28 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.2 and 18.4 (s, CH_3), 27.4 (s, CH_2), 55.8 (s, OCH_3), 109.6, 118.4, 122.7, 125.9 and 130.5 (s, CH_{arom} and $=CH$), 136.9, 138.7 and 151.0 (s, C_{arom}), 172.7 (s, $C{=}O$). HRMS (EI): m/z=220.1099, calcd for $C_{13}H_{16}O_3$: 220.1099.

*4.3.14. (E)-2-Methoxy-4-(1-propenyl)phenyl isobutyrate (**14b**).*[14h] Colourless oil. Yield: 78% (0.365 g). IR (neat): ν=1656 (w, $C{=}C$), 1760 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.36 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 1.90 (dd, J=6.5 and 1.5 Hz, 3H, $HC{=}CHCH_3$), 2.87 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 3.82 (s, 3H, OCH_3), 6.20 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.40 (part B of AB system of q, J=15.7 and 1.5 Hz, 1H, $HC{=}CHCH_3$), 6.90–6.98 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.8 (s, CH_3), 19.4 (s, $CH(CH_3)_2$), 34.4 (s, $CH(CH_3)_2$), 56.2 (s, OCH_3), 110.1, 118.7, 123.0, 126.2 and 131.0 (s, CH_{arom} and $=CH$), 137.2, 139.3 and 151.5 (s, C_{arom}), 175.7 (s, $C{=}O$). HRMS (EI): m/z=234.1255, calcd for $C_{14}H_{18}O_3$: 234.1256.

*4.3.15. (E)-2-Methoxy-4-(1-propenyl)phenyl-3-methyl butanoate (**14c**).*[35] White solid. Yield: 84% (0.417 g). Mp: 41–42 °C. IR (Nujol): ν=1656 (w, $C{=}C$), 1761 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.11 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 1.91 (dd, J=6.5 and 1.6 Hz, 3H, $HC{=}CHCH_3$), 2.23–2.37 (m, 1H, $CH(CH_3)_2$), 2.48 (d, J=7.1 Hz, 2H, $CH_2CH(CH_3)_2$), 3.83 (s, 3H, OCH_3), 6.22 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.40 (part B of AB system of q, J=15.7 and 1.6 Hz, 1H, $HC{=}CHCH_3$), 6.90–6.99 (m, 3H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.8 (s, CH_3), 22.8 (s, $CH(CH_3)_2$), 26.3 (s, $CH(CH_3)_2$), 43.5 (s, CH_2), 56.1 (s, OCH_3), 110.0, 118.8, 123.1, 126.3 and 131.0 (s, CH_{arom} and $=CH$), 137.3, 139.1 and 151.5 (s, C_{arom}), 171.5 (s, $C{=}O$). HRMS (EI): m/z=248.1407, calcd for $C_{15}H_{20}O_3$: 248.1412.

*4.3.16. (E)-2-Methoxy-4-(1-propenyl)phenyl benzoate (**14d**).*[36] White solid. Yield: 88% (0.472 g). Mp: 49–50 °C. IR (Nujol): ν=1651 (w, $C{=}C$), 1732 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.92 (dd, J=6.5 and 1.5 Hz, 3H, $HC{=}CHCH_3$), 3.85 (s, 3H, OCH_3), 6.26 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.43 (part B of AB system of q, J=15.7 and 1.5 Hz, 1H, $HC{=}CHCH_3$), 6.95–7.11 (s, 3H, CH_{arom}), 7.28–7.63 (m, 3H, CH_{arom}), 8.24 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.8 (s, CH_3), 56.3 (s, OCH_3), 110.2, 118.8, 123.2, 126.5, 128.9, 130.7, 130.9 and 133.8 (s, CH_{arom} and $=CH$), 129.9, 137.5, 139.2 and 151.6 (s, C_{arom}), 165.2 (s, $C{=}O$). HRMS (EI): m/z=268.1103, calcd for $C_{17}H_{16}O_3$: 268.1099.

*4.3.17. (E)-4-(1-Propenyl)phenyl propionate (**15a**).*[14r] Colourless oil. Yield: 83% (0.316 g). IR (neat): ν=1645 (w, $C{=}C$), 1755 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.29 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.99 (dd, J=6.5 and 1.6 Hz, 3H, $HC{=}CHCH_3$), 2.60 (q, J=7.5 Hz, 2H, CH_2CH_3), 6.20 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.41 (part B of AB system of q, J=15.7 and 1.6 Hz, 1H, $HC{=}CHCH_3$), 7.02 (d, J=8.6 Hz, 2H, CH_{arom}), 7.34 (d, J=8.6 Hz, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.5 and 18.9 (s, CH_3), 28.2 (s, CH_2), 121.9 and 127.1 (s, CH_{arom}), 126.3 and 130.5 (s, $=CH$), 136.0 and 149.9 (s, C_{arom}), 173.4 (s, $C{=}O$). HRMS (EI): m/z=190.0999, calcd for $C_{12}H_{14}O_2$: 190.0994.

*4.3.18. (E)-4-(1-Propenyl)phenyl isobutyrate (**15b**).*[14r] Pale yellow solid. Yield: 87% (0.355 g). Mp: 43–44 °C. IR (Nujol): ν=1658 (w, $C{=}C$), 1757 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.35 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 1.91 (dd, J=6.5 and 1.6 Hz, 3H, $HC{=}CHCH_3$), 2.83 (sept, J=7.0 Hz, 1H, $CH(CH_3)_2$), 6.22 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.42 (part B of AB system of q, J=15.7 and 1.6 Hz, 1H, $HC{=}CHCH_3$), 7.03 (d, J=8.6 Hz, 2H, CH_{arom}), 7.35 (d, J=8.6 Hz, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.9 (s, CH_3), 19.3 (s, $CH(CH_3)_2$), 34.6 (s, $CH(CH_3)_2$), 121.9 and 127.1 (s, CH_{arom}), 126.2 and 130.6 (s, $=CH$), 136.0 and 150.1 (s, C_{arom}), 176.0 (s, $C{=}O$). HRMS (EI): m/z=204.1158, calcd for $C_{13}H_{16}O_2$: 204.1150.

*4.3.19. (E)-4-(1-Propenyl)phenyl-3-methyl butanoate (**15c**).*[14a,c] Pale yellow oil. Yield: 89% (0.388 g). IR (neat): ν=1657 (w, $C{=}C$), 1761 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.09 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 1.90 (dd, J=6.5 and 1.5 Hz, 3H, $HC{=}CHCH_3$), 2.25–2.34 (m, 1H, $CH(CH_3)_2$), 2.46 (d, J=7.1 Hz, 2H, $CH_2CH(CH_3)_2$), 6.21 (part A of AB system of q, J=15.8 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.40 (part B of AB system of q, J=15.8 and 1.5 Hz, 1H, $HC{=}CHCH_3$), 7.05 (d, J=8.6 Hz, 2H, CH_{arom}), 7.37 (d, J=8.6 Hz, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.9 (s, CH_3), 22.8 (s, $CH(CH_3)_2$), 26.3 (s, $CH(CH_3)_2$), 43.8 (s, CH_2), 122.0 and 127.1 (s, CH_{arom}), 126.2 and 130.5 (s, $=CH$), 136.1 and 149.9 (s, C_{arom}), 172.0 (s, $C{=}O$). HRMS (EI): m/z=218.1304, calcd for $C_{14}H_{18}O_2$: 218.1307.

*4.3.20. (E)-4-(1-Propenyl)phenyl benzoate (**15d**).* White solid. Yield: 80% (0.381 g). Mp: 53–54 °C. IR (Nujol): ν=1652 (w, $C{=}C$), 1745 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.93 (dd, J=6.5 and 1.5 Hz, 3H, $HC{=}CHCH_3$), 6.25 (part A of AB system of q, J=15.7 and 6.5 Hz, 1H, $HC{=}CHCH_3$), 6.45 (part B of AB system of q, J=15.7 and 1.5 Hz, 1H, $HC{=}CHCH_3$), 7.15 (d, J=8.6 Hz, 2H, CH_{arom}), 7.41 (d, J=8.6 Hz, 2H, CH_{arom}), 7.64–7.70 (m, 3H, CH_{arom}), 8.23 (m, 2H, CH of CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=18.5 (s, CH_3), 121.7, 126.8, 128.6, 129.6 and 130.2 (s, CH_{arom}), 126.2 and 133.6 (s, $=CH$), 135.8 and 149.7 (s, C_{arom}), 165.2 (s, $C{=}O$). HRMS (EI): m/z=238.0987, calcd for $C_{16}H_{14}O_2$: 238.0994.

*4.3.21. (E,E)-2-Methoxy-4,6-di(1-propenyl)phenyl propionate (**27a**).* Colourless oil. Yield: 68% (0.354 g). IR (Nujol): ν=1656 (m, $C{=}C$), 1760 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.33 (t, J=7.5 Hz, 3H, CH_3), 1.90 (dd, J=6.4 and 1.3 Hz, 6H, $HC{=}CHCH_3$), 2.67 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.83 (s, 3H, OCH_3), 6.16–6.33 (m, 2H, $HC{=}CHCH_3$), 6.41 (part B of AB system of q, J=15.8 and 1.3 Hz, 1H, $HC{=}CHCH_3$), 6.52 (part B of AB system of q, J=15.7 and 1.3 Hz, 1H, $HC{=}CHCH_3$), 6.82 (d, J=1.6 Hz, 1H, CH_{arom}), 7.05 (d, J=1.6 Hz, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.7 (s, CH_2CH_3), 18.4 and 18.9 (s, $=CHCH_3$), 27.3 (s, CH_2CH_3), 55.9 (s, OCH_3), 107.6 and 115.8 (s, CH_{arom}), 124.3, 125.8, 128.5 and 130.7 (s, $=CH$), 131.4, 135.9, 136.1 and 151.3 (s, C_{arom}), 172.4 (s, $C{=}O$). HRMS (EI): m/z=260.1417, calcd for $C_{16}H_{20}O_3$: 260.1412.

*4.3.22. (E)-2-Chloro-6-(1-propenyl)phenyl propionate (**28a**).* Pale yellow oil. Yield: 93% (0.417 g). IR (Nujol): ν=1654 (m, $C{=}C$), 1769 (s, $C{=}O$) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.36 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.91 (dd, J=6.1 and 1.1 Hz, 3H, $HC{=}CHCH_3$), 2.71 (q, J=7.5 Hz, 2H, CH_2CH_3), 6.25 (part A of AB system of q, J=15.8 and 6.1 Hz, 1H, $HC{=}CHCH_3$), 6.37 (part B of AB system of q, J=15.8 and 1.1 Hz, 1H, $HC{=}$

$CHCH_3$), 7.13 (dd, J=8.0 and 7.8 Hz, 1H, CH_{arom}), 7.30 (d, J=8.0 Hz, 1H, CH_{arom}), 7.39 (d, J=7.8 Hz, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.6 (s, CH_2CH_3), 19.3 (s, $=CHCH_3$), 27.8 (s, CH_2CH_3), 124.3, 125.2, 127.0, 128.6 and 130.2 (s, CH_{arom} and $=CH$), 128.0, 133.4 and 144.4 (s, C_{arom}), 172.1 (s, C=O). HRMS (EI): m/z=224.0607, calcd for $C_{12}H_{13}O_2Cl$: 224.0604.

*4.3.23. (E)-2-Acetyl-6-(1-propenyl)phenyl propionate (**29a**).* Colourless oil. Yield: 82% (0.381 g). IR (Nujol): ν=1652 (w, C=C), 1689 and 1762 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.31 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.89 (dd, J=6.5 and 1.5 Hz, 3H, $HC=CHCH_3$), 2.52 (s, 3H, $COCH_3$), 2.69 (q, J=7.5 Hz, 2H, CH_2CH_3), 6.25 (part A of AB system of q, J=15.8 and 6.5 Hz, 1H, $HC=CHCH_3$), 6.43 (part B of AB system of q, J=15.8 and 1.5 Hz, 1H, $HC=CHCH_3$), 7.23 (dd, J=7.8 and 7.2 Hz, 1H, CH_{arom}), 7.63 (m, 2H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=8.9 (s, CH_2CH_3), 18.9 (s, $=CHCH_3$), 27.6 (s, CH_2CH_3), 29.2 (s, $COCH_3$), 123.7, 125.7, 128.5, 129.7 and 130.3 (s, CH_{arom} and $=CH$), 131.2, 132.5 and 145.5 (s, C_{arom}), 172.7 (s, OC=O), 198.0 (s, $COCH_3$). HRMS (EI): m/z=232.1098, calcd for $C_{14}H_{16}O_3$: 232.1099.

*4.3.24. (E)-4-Chloro-2-(1-propenyl)phenyl propionate (**30a**).* Pale yellow oil. Yield: 86% (0.386 g). IR (Nujol): ν=1653 (w, C=C), 1762 (s, C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.32 (t, J=7.6 Hz, 3H, CH_2CH_3), 1.92 (dd, J=6.0 and 1.0 Hz, 3H, $HC=CHCH_3$), 2.65 (q, J=7.6 Hz, 2H, CH_2CH_3), 6.27 (part A of AB system of q, J=16.0 and 6.0 Hz, 1H, $HC=CHCH_3$), 6.35 (part B of AB system of q, J=16.0 and 1.0 Hz, 1H, $HC=CHCH_3$), 6.98 (d, J=8.6 Hz, 1H, CH_{arom}), 7.19 (dd, J=8.6 and 2.5 Hz, 1H, CH_{arom}), 7.99 (d, J=2.5 Hz, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=9.2 (s, CH_2CH_3), 18.9 (s, $=CHCH_3$), 27.6 (s, CH_2CH_3), 123.3, 123.9, 126.3, 127.4 and 129.8 (s, CH_{arom} and $=CH$), 131.4, 132.1 and 145.9 (s, C_{arom}), 172.6 (s, C=O). HRMS (EI): m/z=224.0600, calcd for $C_{12}H_{13}O_2Cl$: 224.0604.

4.4. Synthesis of (*E*)-1,3-di(4-hydroxyphenyl)-2-methyl-1-pentene (16)[18]

Under nitrogen atmosphere, 4-allylphenol (**5**) (0.268 g, 2 mmol), the ruthenium(IV) catalyst precursor $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (6 mg, 0.01 mmol; 1 mol % of Ru) and methanol (0.5 mL) were introduced into a Teflon-capped sealed tube. Then, the mixture was heated at 80 °C in an oil-bath for 24 h. Solvent removal under reduced pressure, followed by purification of the resulting oily residue by column chromatography over SiO_2, using a mixture hexanes/Et_2O (85:15) as eluent, afforded diphenol **16** in 57% yield (0.153 g) as a yellow oil. Characterization data for this compound are as follows (copies of the ^1H and $^{13}C\{^1H\}$ spectra are included in Supplementary data): IR (Nujol): ν=1651 (w, C=C), 3324 (s, O–H) cm^{-1}. ^1H NMR ($CDCl_3$): δ=0.93 (t, J=7.3 Hz, 3H, CH_2CH_3), 1.65 (d, J=1.2 Hz, 3H, CH_3), 1.79–1.92 (m, 2H, CH_2), 3.19 (t, J=7.6 Hz, 1H, CH), 5.37 (br, 1H, OH), 5.47 (br, 1H, OH), 6.41 (br, 1H, $=CH$), 6.79–6.85 (m, 4H, CH_{arom}), 7.14–7.16 (m, 4H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=13.0 and 16.1 (s, CH_3), 25.8 (s, CH_2), 56.2 (s, CH), 115.3, 115.4, 129.5 and 130.7 (s, CH_{arom}), 124.9 (s, $=CH$), 131.7, 136.5, 154.0 and 154.1 (s, C_{arom}), 140.3 (s, $=C$). HRMS (EI): m/z=268.1459, calcd for $C_{18}H_{20}O_2$: 268.1463.

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Supplementary data

Copies of the ^1H and $^{13}C\{^1H\}$ NMR spectra of all compounds synthesized in this work. Supplementary data related to this article can be found in the online version, at doi:10.1016/j.tet.2012.01.083.

References and notes

1. See, for example: (a) *Metal-Catalysis in Industrial Organic Processes*; Chiusoli, G. P., Maitlis, P. M., Eds.; RSC Publishing: Cambridge, 2008; (b) van Leeuwen, P. W. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic: Dordrecht, 2004; (c) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; John Wiley & Sons: New York, NY, 1992.
2. See, for example: (a) Reineccius, G. *Flavor Chemistry and Technology*; CRC: Boca Raton, FL, 2006; (b) Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavour Materials*; Wiley-VCH: Weinheim, 2001; (c) Ashurst, P. R. *Food Flavorings*; Aspen: Maryland, 1999; (d) Chalk, A. J. In *Flavors and Fragrances: A World Perspective*; Lawrence, B. M., Mookherjee, B. D., Willis, B. J., Eds.; Elsevier Science: Amsterdam, 1988.
3. See, for example: (a) Arenas, D. R. M.; Ruíz, F. A. R.; Kouznetsov, V. V. *Tetrahedron Lett.* **2011**, *52*, 1388–1391; (b) Kouznetsov, V. V.; Arenas, D. R. M. *Tetrahedron Lett.* **2009**, *50*, 1546–1549; (c) Kouznetsov, V. V.; Forero, J. S. B.; Torres, D. F. A. *Tetrahedron Lett.* **2008**, *49*, 5855–5857; (d) Alvarez, H. M.; de Andrade, J. L.; Pereira, N., Jr.; Muri, E. M. F.; Horn, A., Jr.; Barbosa, D. P.; Antunes, O. A. C. *Catal. Commun.* **2007**, *8*, 1336–1340; (e) Fujita, K.-I.; Fujita, T.; Kubo, I. *Phytother. Res.* **2007**, *21*, 47–51; (f) Soares, P. M. G.; Lima, R. F.; de Freitas Pires, A.; Souza, E. P.; Assreuy, A. M. S.; Criddle, D. N. *Life Sci.* **2007**, *81*, 1085–1093; (g) Gross, J. L. *Tetrahedron Lett.* **2003**, *44*, 8563–8565; (h) de Lima, M. E. F.; Gabriel, A. J. A.; Castro, R. N. *J. Braz. Chem. Soc.* **2000**, *11*, 371–374; (i) Amano, T.; Yoshikawa, K.; Ogawa, T.; Sano, T.; Ohuchi, Y.; Tanami, T.; Ota, T.; Hatayama, K.; Higuchi, S.; Amanuma, F.; Sota, K. *Chem. Pharm. Bull.* **1986**, *34*, 4653–4662.
4. For a review, see: Pines, H.; Stalick, W. M. *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*; Academic: New York, NY, 1977.
5. The heterogeneous ones rely mainly on the use of solid bases. Selected examples can be found in: (a) Kishore, D.; Kannan, S. *Green Chem.* **2002**, *4*, 607–610; (b) Srivastava, V. K.; Bajaj, H. C.; Jasra, R. V. *Catal. Commun.* **2003**, *4*, 543–548; (c) Kishore, D.; Kannan, S. *J. Mol. Catal. A: Chem.* **2004**, *223*, 225–230; (d) Kishore, D.; Kannan, S. *Appl. Catal., A: Gen.* **2004**, *270*, 227–235; (e) Kishore, D.; Kannan, S. *J. Mol. Catal. A: Chem.* **2006**, *244*, 83–92; (f) Jinesh, C. M.; Antonyraj, C. A.; Kannan, S. *Catal. Today* **2009**, *141*, 176–181; (g) Sharma, S. K.; Parikh, P. A.; Jasra, R. V. *J. Mol. Catal. A: Chem.* **2010**, *317*, 27–33.
6. Efficient approaches to isomerize allylaromatics using catalytic amounts of strong non-ionic bases, such as phosphazenes and proazaphosphatranes, have also been described: (a) Wu, W.; Verkade, J. G. *Arkivoc* **2004**, *9*, 88–95; (b) Yu, Z.; Yan, S.; Zhang, G.; He, W.; Wang, L.; Li, Y.; Zeng, F. *Adv. Synth. Catal.* **2006**, *348*, 111–117.
7. Shimizu, A.; Otsu, T.; Imoto, M. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 953–959.
8. Blum, J.; Pickholtz, Y. *Isr. J. Chem.* **1969**, *7*, 723–733.
9. For selected examples, see: (a) Tooley, P. A.; Arndt, L. W.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2422–2427; (b) Satyanarayana, N.; Periasamy, M. *J. Organomet. Chem.* **1987**, *319*, 113–117; (c) Rao, S. A.; Periasamy, M. *J. Organomet. Chem.* **1988**, *342*, 15–20; (d) Reddy, M. R.; Periasamy, M. *J. Organomet. Chem.* **1995**, *491*, 263–266; (e) Blum, J.; Rosenfeld, A.; Polak, N.; Israelson, O.; Schumann, H.; Avnir, D. *J. Mol. Catal. A: Chem.* **1996**, *107*, 217–223; (f) Bricout, H.; Mortreux, A.; Monflier, E. *J. Organomet. Chem.* **1998**, *553*, 469–471; (g) Sato, T.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **1999**, 441–442; (h) Averbuj, C.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 8755–8759; (i) Baxendale, I. R.; Lee, A.-L.; Ley, S. V. *Synlett* **2002**, 516–518; (j) Baxendale, I. R.; Lee, A.-L.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1850–1857; (k) Arisawa, M.; Terada, Y.; Nakagawa, N.; Nishida, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4732–4734; (l) Shaviv, E.; Botoshansky, M.; Eisen, M. S. *J. Organomet. Chem.* **2003**, *683*, 165–180; (m) Lee, H. S.; Lee, G. Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 461–462; (n) Hanessian, S.; Giroux, S.; Larsson, A. *Org. Lett.* **2006**, *8*, 5481–5484; (o) Sharma, S. K.; Srivastava, V. K.; Jasra, R. V. *J. Mol. Catal. A: Chem.* **2006**, *245*, 200–209; (p) Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424–5426; (q) Erdogan, G.; Grotjahn, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 10354–10355; (r) Donohoe, T. J.; O'Riordan, T. J. C.; Rosa, C. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1014–1017; (s) Ding, F.; Sun, Y.; Verpoort, F. *Eur. J. Inorg. Chem.* **2010**, 1536–1543; (t) Scarso, A.; Colladon, M.; Sgarbossa, P.; Santo, C.; Michelin, R. A.; Strukul, G. *Organometallics* **2010**, *29*, 1487–1497; (u) Nishiwaki, N.; Kamimura, R.; Shono, K.; Kawakami, T.; Nakayama, K.; Nishino, K.; Nakayama, T.; Takahashi, K.; Nakamura, A.; Hosokawa, T. *Tetrahedron Lett.* **2010**, *51*, 3590–3592; (v) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998–8009; (w) Meltzer, D.; Avnir, D.; Fanun, M.; Gutkin, V.; Popov, I.; Schomäcker, R.; Schwarze, M.; Blum, J. *J. Mol. Catal. A: Chem.* **2011**, *335*, 8–13; (x) Mayer, M.; Welther, A.; von Wangelin, A. J. *ChemCatChem* **2011**, *3*, 1567–1571.
10. (a) Cadierno, V.; Crochet, P.; García-Garrido, S. E.; Gimeno, J. *Dalton Trans.* **2004**, 3635–3641; (b) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *Chem. Commun.* **2004**, 232–233; (c) Cadierno, V.; García-Garrido, S. E.; Gimeno, J.; Nebra, N. *Chem. Commun.* **2005**, 4086–4088; (d) Cadierno, V.; García-Garrido, S. E.; Gimeno, J.; Varela-Álvarez, A.; Sordo, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 1360–1370; (e) Crochet, P.; Díez, J.; Fernández-Zúmel, M. A.; Gimeno, J. *Adv. Synth. Catal.* **2006**, *348*, 93–100; (f) Díaz-Álvarez, A. E.; Crochet, P.; Zablocka, M.; Duhayon, C.; Cadierno, V.; Gimeno, J.; Majoral, J. P. *Adv. Synth. Catal.* **2006**, *348*, 1671–1679; (g) Crochet, P.; Fernández-Zúmel, M. A.; Gimeno, J.; Scheele, M. *Organometallics* **2006**, *25*, 4846–4849; (h) Cadierno, V.; Gimeno, J.; Nebra, N. *Chem.—Eur. J.* **2007**, *13*, 6590–6594; (i) Cadierno, V.; Crochet, P.; Gimeno, J. *Synlett* **2008**, 1105–1124; (j) Lastra-Barreira, B.; Díez, J.; Crochet, P. *Green Chem.* **2009**, *11*, 1681–1686; (k) Fernández-Zúmel, M. A.; Lastra-Barreira, B.; Scheele, M.; Díez, J.; Crochet, P.; Gimeno, J. *Dalton Trans.* **2010**, *39*, 7780–7785; (l) García-Garrido, S. E.; Francos, J.; Cadierno, V.; Basset, J.-M.; Polshettiwar, V.

ChemSusChem **2011**, *4*, 104–111; (m) Varela-Álvarez, A.; Sordo, J. A.; Piedra, E.; Nebra, N.; Cadierno, V.; Gimeno, J. *Chem.—Eur. J.* **2011**, *17*, 10583–10599.

11. (a) Lastra-Barreira, B.; Crochet, P. *Green Chem.* **2010**, *12*, 1311–1314; (b) Lastra-Barreira, B.; Francos, J.; Crochet, P.; Cadierno, V. *Green Chem.* **2011**, *13*, 307–313.
12. For a review on the chemistry and catalytic applications of complex $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ and its derivatives, see: Cadierno, V.; Crochet, P.; García-Garrido, S. E.; Gimeno, J. *Curr. Org. Chem.* **2006**, *10*, 165–183.
13. (a) Porri, L.; Gallazzi, M. C.; Colombo, A.; Allegra, G. *Tetrahedron Lett.* **1965**, *47*, 4187–4189; (b) Salzer, A.; Bauer, A.; Podewils, F. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme: Stuttgart, 2000; Vol. 9, pp 36–38; (c) Salzer, A.; Bauer, A.; Geyser, S.; Podewils, F.; Turpin, G. C.; Ernst, R. D. *Inorg. Synth.* **2004**, *34*, 59–65.
14. See, for example: (a) Sörensen, J. S.; Sörensen, N. A. *Acta Chem. Scand.* **1966**, *20*, 992–1002; (b) D'Albuquerque, I. L.; Monache, F. D.; Ferrari, F.; Marini-Bettolo, G. B. *Gazz. Chim. Ital.* **1968**, *98*, 1189–1196; (c) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1969**, *102*, 1691–1697; (d) Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 145–147; (e) Kleiman, R.; Plattner, R. D.; Weisleder, D. *J. Nat. Prod.* **1988**, *51*, 249–256; (f) Ahmed, M.; Gunatilaka, A. A. L. *Pharmazie* **1988**, *43*, 372–373; (g) Merkel, B.; Reichling, J. *Z. Naturforsch.* **1990**, *45c*, 602–606; (h) Reichling, J.; Merkel, B.; Hofmeister, P. *J. Nat. Prod.* **1991**, *54*, 1416–1418; (i) Bos, R.; Woerdenbag, H. J.; Hendriks, H.; Sidik; Wikström, H. V.; Scheffer, J. J. C. *Flavour Fragrance J.* **1996**, *11*, 321–326; (j) Santos, P. M.; Figueiredo, A. C.; Oliveira, M. M.; Barroso, J. G.; Pedro, L. G.; Deans, S. G.; Younus, A. K. M.; Scheffer, J. J. C. *Phytochemistry* **1998**, *48*, 455–460; (k) Tabanca, N.; Khan, S. I.; Bedir, E.; Annavarapu, S.; Willett, K.; Khan, I. A.; Kirimer, N.; Baser, K. H. C. *Planta Med.* **2004**, *70*, 728–735; (l) Tabanca, N.; Bedir, E.; Ferreira, D.; Slade, D.; Wedge, D. E.; Jacob, M. R.; Khan, S. I.; Kirimer, N.; Baser, K. H. C.; Khan, I. A. *Chem. Biodivers.* **2005**, *2*, 221–232; (m) Tabanca, N.; Demerci, B.; Kirimer, N.; Baser, K. H. C.; Bedir, E.; Khan, I. A.; Wedge, D. E. *J. Chromatogr., A* **2005**, *1097*, 192–198; (n) Sampson, B. J.; Tabanca, N.; Kirimer, N.; Demerci, B.; Baser, K. H. C.; Khan, I. A.; Spiers, J. M.; Wedge, D. E. *Pest Manag. Sci.* **2005**, *61*, 1122–1128; (o) Tabanca, N.; Demerci, B.; Ozek, T.; Kirimer, N.; Baser, K. H. C.; Bedir, E.; Khan, I. A.; Wedge, D. E. *J. Chromatogr., A* **2006**, *1117*, 194–205; (p) Baser, K. H. C.; Tabanca, N.; Kirimer, N.; Bedir, E.; Khan, I. A.; Wedge, D. E. *Pure Appl. Chem.* **2007**, *79*, 539–556; (q) Tabanca, N.; Ma, G.; Pasco, D. S.; Bedir, E.; Kirimer, N.; Baser, K. H. C.; Khan, I. A.; Khan, S. I. *Phytother. Res.* **2007**, *21*, 741–745; (r) Lanfranchi, D.-A.; Laouer, H.; Kolli, M. E.; Prado, S.; Maulay-Bailly, C.; Baldovini, N. *J. Agric. Food Chem.* **2010**, *58*, 2174–2179.
15. (a) Compounds of type C are generated by plants through a biosynthetic pathway involving the enzymatic acylation of the corresponding (E)-(1-propenyl)phenol with carboxylic acids: Tabanca, N.; Douglas, A. W.; Bedir, E.; Dayan, F. E.; Kirimer, N.; Baser, K. H. C.; Aytac, Z.; Khan, I. A.; Scheffler, B. E. *Plant Genet. Res.* **2005**, *3*, 149–169 and references cited therein; (b) Extraction from essential oils of *Pimpinella* species is the main route of access to these compounds (see Ref. 14).
16. The utilization of glycerol as a green reaction solvent for synthetic organic chemistry is currently a highly active research field that has as main objective the valorization of a waste generated by the biodiesel industry. For recent reviews on this topic, see: (a) Gu, Y.; Jérôme, F. *Green Chem.* **2010**, *12*, 1127–1138; (b) Díaz-Álvarez, A. E.; Francos, J.; Lastra-Barreira, B.; Crochet, P.; Cadierno, V. *Chem. Commun.* **2011**, 6208–6227.
17. Although, in general, the catalytic isomerization of allylbenzenes results in products with predominantly the *trans* alkene geometry (see Ref. 9) no previous data for the particular case of allylphenyl esters are available. However, we must note that the use of complexes $[RuCl_2(PPh_3)_3]$, $[RuCl_2(DMSO)_4]$, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$, $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ or $[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})]$ ($C_{12}H_{18}$=dodeca-2,6,10-triene-1,12-diyl) as catalysts also resulted in the exclusive formation of (*E*)-**11a**, suggesting that this isomer is particularly favoured with respect to the *Z* one. We must also note that the activity of all these complexes was comparatively lower to that shown by $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$. The most active, i.e., the indenyl-ruthenium(II) complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (1 mol %), led to **11a** in 82% GC-yield after 4 h of heating at 80 °C in methanol (to be compared with the entry 1 of Table 1). The stronger Lewis-acid character of the ruthenium centres in $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$, which facilitates the generation of the catalytically active Ru–H species from methanol through β-hydride elimination in the in situ formed Ru–OMe intermediates, could explain the higher reactivity observed. In addition, coordination of the allylic C=C bond of the substrate to the metal should also be favoured in Ru(IV) versus Ru(II) species.
18. (a) Smirnova, L. S.; Abduazimov, K. A. *Khim. Prir. Soedin.* **1992**, 564–567; (b) Maksomov, V. I.; Yartseva, N. G.; Zalesskaya, T. E.; Madaeva, O. S. *Zh. Obshch. Khim.* **1950**, *20*, 2194–2201.
19. For related acid-promoted dimerizations of styrenes, see: Fornés, V.; García, H.; Martí, V.; Fernández, L. *Tetrahedron* **1998**, *54*, 3827–3832.
20. Okano, K.; Okuyama, K.-I.; Fukuyama, T.; Tokuyama, H. *Synlett* **2008**, 1977–1980.
21. Gu, W.; She, X.; Pan, X.; Yang, T.-K. *Tetrahedron: Asymmetry* **1998**, *9*, 1377–1380.
22. For reviews on the Claisen rearrangement, see: (a) Castro, A. M. M. *Chem. Rev.* **2004**, *104*, 2939–3002; (b) *Claisen Rearrangement*; Hiersemann, M., Nubbemeyer, U., Eds.; Wiley-VCH: Weinheim, 2007.
23. This negative result is not surprising since sulphur species are well-known poisons for homogeneous catalysts due to the formation of strong metal–sulphur bonds. See, for example: Dunleavy, J. *Platinum Metals Rev.* **2006**, *50*, 110.
24. Mal, D.; Pahari, P.; Senapati, B. K. *Tetrahedron Lett.* **2005**, *46*, 2097–2100.
25. Lin, Y.-L.; Cheng, J.-Y.; Chu, Y.-H. *Tetrahedron* **2007**, *63*, 10949–10957.
26. Adibi, H.; Mojarrad, J. S.; Asgharloo, H.; Zarrini, G. *Med. Chem. Res.* **2011**, *20*, 1318–1324.
27. Goruin, J. H.; Harfenist, M. Ger. Pat. DE2921824, 1979.
28. Takahashi, T.; Kai, K.; Uchida, H. Jpn. Pat. JP07-206941, 1995.
29. Kazuno, K.; Yamazaki, Y. Jpn. Pat. JP07-010727, 1995.
30. Priestap, H. A.; Bennett, B. C.; Quirke, J. M. E. *J. Essent. Oil Res.* **2008**, *20*, 396–402.
31. Hendriks, H.; Smith, D.; Hazelhoff, B. *Phytochemistry* **1977**, *16*, 1853–1854.
32. Sadeghian, H.; Seyedi, S. M.; Saberi, M. R.; Arghiani, Z.; Riazi, M. *Bioorg. Med. Chem.* **2008**, *16*, 890–901.
33. Seyedi, S. M.; Jafari, Z.; Attaran, N.; Sadeghian, H.; Saberi, M. R.; Riazi, M. M. *Bioorg. Med. Chem.* **2009**, *17*, 1614–1622.
34. Furuhata, A.; Takagi, K.; Kojo, K. Jpn. Pat. JP59-065035, 1984.
35. von Massow, F.; Smith, M. A. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 977–980.
36. Tho, F. C.; Natova, L.; Ruschev, D. *J. Therm. Anal.* **1991**, *37*, 2723–2727.