

Palladium catalyzed hydroesterification of substituted alkenes under microwave conditions

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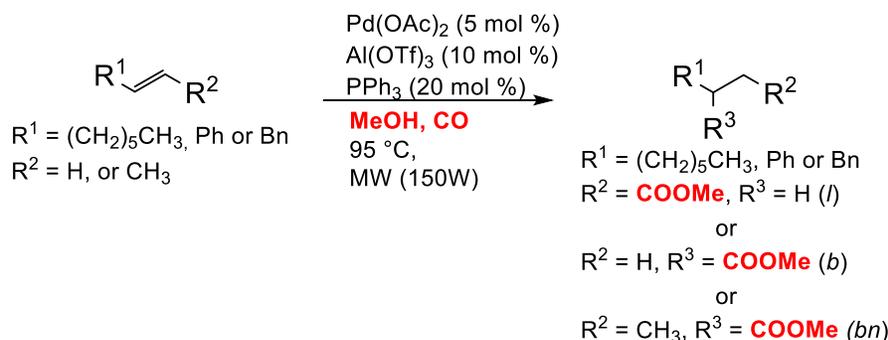
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Abstract

While several catalyst systems have been utilized in the hydroesterification or methoxycarbonylation of alkenes or equivalent substrates, these reactions are conventionally performed in autoclave reactor systems under high CO pressure (20 - 70 bar) and thermal heating (70 – 110 °C). In this paper, the first methoxycarbonylation reactions performed in a microwave reactor fitted with a gas-addition accessory system are reported on and compared to the same reactions performed under conventional heating in an autoclave reactor. Thus 1-octene, styrene, allylbenzene, *o*- and *p*-methoxyallylbenzene and β -methylstyrene were subjected to methoxycarbonylation over a palladium acetate–aluminum triflate catalyst system at 12 bar and 95 °C. Results obtained indicated the methoxycarbonylation of these alkenes to be much faster under microwave conditions when compared to conventional heating and improvements in conversion ranged between 3 and 5% for the more reactive substrates (1-octene and styrene) and 6 – 20% for the allylbenzenes and β -methylstyrene.



Keywords: Alkoxy carbonylation, hydroesterification, palladium catalyst, aluminum triflate, alkenes, microwave heating.

Introduction

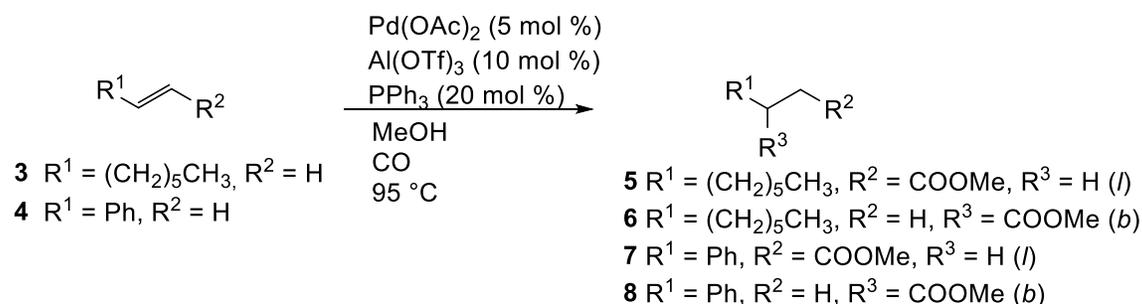
While the palladium catalyzed alkoxy carbonylation or hydroesterification of alkenes or equivalent substrates has been well documented for a plethora of catalyst systems,¹⁻¹⁶ these reactions are usually performed in autoclave reactors at CO pressures ranging from ca. 1-70 bar and temperatures of ca. 70 – 110°C. During an investigation into the electronic factors governing the regioselectivity (ratio of linear to branched to benzylic products) of the addition of the ester entity to aromatic substituted alkenes over a palladium catalyst system,¹⁷ it was found that the reactivity of the substituted allylbenzene (**1**) and β -methylstyrene (**2**) reactants were rather low [Turn-over frequencies (TOF) of 7 – 30 h⁻¹], so prolonged reactions times (up to 3 h) were required to obtain decent yields (50 – 90%).



Since it is generally known that microwave heating has the ability to accelerate some chemical reactions¹⁸ and the hydroesterification reaction was found to be rather slow, it was decided to evaluate the effect of microwave heating on the rate of the alkoxy carbonylation of substituted alkenes over a palladium acetate catalyst system.

Results and Discussion

In order to be in a position to compare the results of the microwave mediated reactions with the results obtained under conditions of ordinary heating at 95 °C and the optimum pressure of 35 bar, as reported earlier,⁵ the same Pd(II)/Al(OTf)₃/PPh₃ catalyst system, developed by Williams et al.,^{19,20} was utilized during the current investigation. Furthermore, since the glass vessels of the microwave reactor are rated at 12 bar only, the reactions in an autoclave reactor were also performed at 12 bar CO pressure (95 °C), while the investigation was started with the very reactive general hydroesterification substrates, 1-octene (**3**) and styrene (**4**) (Scheme 1) for possible comparison with literature results.



Scheme 1. Methoxycarbonylation of 1-octene (**3**) and styrene (**4**). *l* and *b* refers to the 'linear' and 'branched' isomers, respectively.

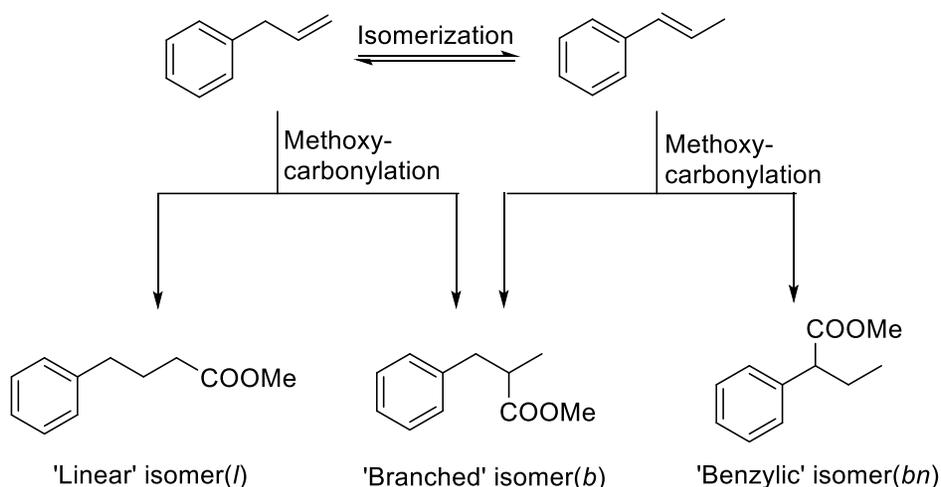
As indicated in Table 1, both substrates, 1-octene (**3**) and styrene (**4**) showed a substantial increase in conversion of ca. 20% and 30%, respectively, even after only 10 minutes of reaction time for the microwave reaction when compared to the autoclave reaction at the same pressure (12 bar). Furthermore, virtually complete conversion of the starting material (99%) was observed after 30 minutes under microwave irradiation, while the reactions under conventional heating conditions at the same pressure (12 bar) were not fully completed (Table 1, entries 2 vs. 3 and 5 vs. 6). Even when compared to the reactions at 35 bar, the microwave equivalents showed a slight improvement over those performed with conventional heating (Table 1, entries 1 vs. 3 and 4 vs. 6). The fact that the final yields for the microwave reactions are somewhat lower than those of the reactions in the autoclave reactor under the same conditions (82% vs. 91% and 72% vs. 92%, respectively) is probably explicable in terms of unwanted side-reactions. These could include reactions like polymerization in the case of styrene (**4**), and/or subsequent hydrolysis of the ester products, **5**, **6**, **7** and **8**, by water present in the methanol, due to the extended exposure to the microwave heating conditions, since the MW reactions were already 99% and 89% completed after only 10 minutes (Table 1, entries 3 and 6).

Table 1. Methoxycarbonylation of 1-octene (**3**) and styrene (**4**)

Entry	Substrate	CO Pressure (bar)	Temp. (°C)	Conversion ^c (%)		Products	Yield ^d (%)		Ratio (<i>l</i> : <i>b</i>)
				10 min	30 min		10 min	30 min	
1	3	35	95 ^a	85	95	5 & 6	76	92	4:1
2	3	12	95 ^a	80	94	5 & 6	70	91	4:1
3	3	12	95 (MW) ^b	99	99	5 & 6	82	82	4:1
4	4	35	95 ^a	77	96	7 & 8	64	93	4:1
5	4	12	95 ^a	58	96	7 & 8	53	92	4:1
6	4	12	95 (MW) ^b	89	99	7 & 8	71	72	4:1

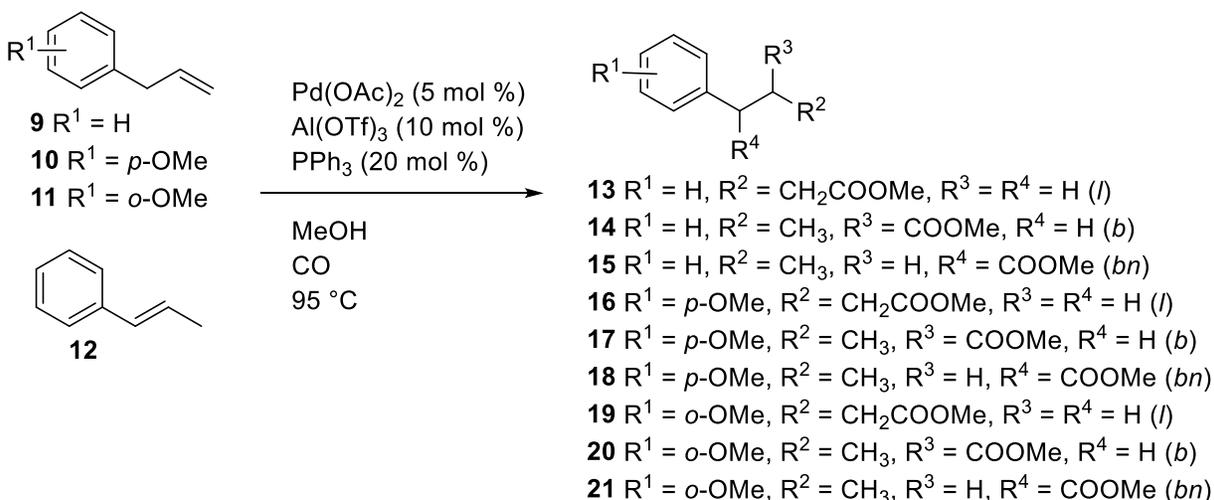
^aConventional heating in an autoclave reactor. ^bMicrowave irradiation (150 W). ^cDetermined by GC analysis with xylene as internal standard. ^dCombined yield determined by GC analysis (with xylene as internal standard).

When subjecting the aryl substituted alkenes, allylbenzene (**9**), 4-allylanisole (**10**), 2-allylanisole (**11**) and *trans*- β -methylstyrene (**12**) to the methoxycarbonylation reaction, it should be kept in mind that these substrates are prone to palladium catalyzed isomerization of the double bond between the internal and terminal positions, so the same products, i.e. 'linear', 'branched' and 'benzylic' isomers, could be formed from both the similarly substituted allylbenzene and β -methylstyrene derivatives (Scheme 2).



Scheme 2. Methoxycarbonylation and isomerization of allylbenzene (**9**) and β -methylstyrene (**12**).

When the 1- and 2-propenylaryl substrates (Scheme 3) were subjected to the methoxycarbonylation reaction under microwave heating (150 W) over the standard catalyst system, Pd(OAc)₂/Al(OTf)₃/PPh₃, it was found that all the substrates reacted much slower than 1-octene (**3**) and styrene (**4**), so reaction times of up to three hours were required to reach completion in both the MW and autoclave reactions at 35 bar. *p*-Methoxyallylbenzene (**10**) proved to be even less reactive and gave conversions of only 40-60% after the 3 hours, with the better conversion (60%) observed for the autoclave reaction at 35 bar. When comparing the reactions at 12 bar for this substrate (**10**), however, the MW method gave a better conversion (28% vs. 20%) even after only 1 hour (Table 2, entry 5 vs. 6).



Scheme 3. Methoxycarbonylation of allylbenzenes (**9** – **11**) and β -methylstyrene (**12**).

A substantial improvement in conversion (70% vs. 86% and 29% vs. 65%, respectively) was also obtained for the *o*-methoxy substituted allylbenzene analogue, **11** and β -methylstyrene (**12**), during conditions of MW irradiation over conventional heating after 1 hour at the same pressure (Table 2, entries 8 vs. 9 and 11 vs 12). After 3 hours at 12 bar (at nearly full conversion), improved conversion rates were obtained for all substrates

(**9** - **12**), with the more profound improvements (ca. 20%) for the less reactive substrates, *p*-methoxyallylbenzene (**10**) and β -methylstyrene (**12**), (Table 2, entries 2 vs 3, 5 vs. 6, 8 vs 9 and 11 vs 12 respectively).

Table 2. Methoxycarbonylation of allylbenzenes (**9** - **11**) and β -methylstyrene (**12**)

Entry	Substrate	CO Pressure (bar)	Temp. (°C)	Conversion ^c (%)		Products	Yield ^d (%)	Ratio (<i>l:b:bn</i>)
				1 h	3 h			
1	9	35	95 ^a	72	97	13, 14, 15	80	7:2:1
2	9	12	95 ^a	57	87	13, 14, 15	80	12:2:1
3	9	12	95 (MW) ^b	57	90	13, 14, 15	81	9:2:1
4	10	35	95 ^a	38	60	16, 17, 18	51	5:2:1
5	10	12	95 ^a	20	21	16, 17, 18	20	15:2:1
6	10	12	95 (MW) ^b	28	40	16, 17, 18	37	6:1:1
7	11	35	95 ^a	88	96	19, 20, 21	75	26:5:1
8	11	12	95 ^a	70	90	19, 20, 21	73	28:6:1
9	11	12	95 (MW) ^b	86	96	19, 20, 21	89	27:5:1
10	12	35	95 ^a	47	95	13, 14, 15	76	5:2:1
11	12	12	95 ^a	29	74	13, 14, 15	66	10:2:1
12	12	12	95 (MW) ^b	65	94	13, 14, 15	82	8:2:1

^aConventional heating in an autoclave reactor. ^bMicrowave irradiation (150 W). ^cDetermined by GC analysis with xylene as internal standard. ^dCombined yield determined by GC analysis (with xylene as internal standard) after 3 hours.

A comparison of the final product yields revealed that, apart from allylbenzene (**9**), MW irradiation resulted in substantial increases (ca. 16%) for all substrates when compared to the conventional thermal reactions at the same pressure (12 bar) (table 2, entries 5 vs 6, 8 vs 9 and 11 vs 12, respectively).

With regard to the regioselectivity of the reactions, a general decrease in selectivity was evident in the microwave reactions when compared to the conventional heating experiments at the same CO pressure (Table 2, entry 2 vs. 3, 5 vs. 6, 8 vs. 9 and 11 vs. 12). Though still the major products, the lower selectivity towards the linear products is probably explicable in terms of a more facile isomerization to the corresponding internal olefins for the allylbenzene substrates under the microwave conditions, while isomerization of the β -methylstyrene to the sterically less hindered allylbenzene isomer may be slower than the secondary terminal to internal isomerization.

Conclusions

Finally, for 1-octene (**3**) and styrene (**4**), a definite reaction rate increasing effect was observed with the conversion after 10 minutes under microwave conditions at 12 bar being almost the same or better than what was obtained after 30 minutes at 35 bar with conventional heating in an autoclave reactor. Although no dramatic reaction rate enhancing effect was observed for the other substrates, both the substituted allylbenzene analogues (**10** and **11**) and β -methylstyrene (**12**) showed improvements in conversion and yield under microwave conditions when compared to conventional heating at the same pressure. The fact that only

a very slight improvement in conversion and yield could be detected for allylbenzene (**9**) is currently inexplicable.

Experimental Section

General. All the chemicals used were purchased from Sigma-Aldrich and used as received. Reactions were performed in a 4590 Parr autoclave reactor (25 ml vessel) with mechanical stirring (500 rpm) and a CEM Discover SP Microwave Reactor, equipped with a gas addition accessory and an internal IR temperature sensor, in a sealed tube (10 ml tube) and stirred by a magnetic stirrer bar. ^1H and ^{13}C NMR as well as 2D experiments were done on a 600 MHz Bruker AM FT spectrometer at 20 °C at 600 MHz for ^1H NMR and 151 MHz for ^{13}C in CDCl_3 as solvent. ^1H NMR chemical shifts are given relative to the TMS signal at 0 ppm and ^{13}C NMR shifts are given relative to the CDCl_3 peak at 77.16 ppm, coupling constants are measured in Hz and chemical shifts in ppm. Mass spectrometry was performed on a Shimadzu GCMS QP-2010 instrument using electron-impact (EI) ionization. Conversions, yields and product ratios were determined on a Shimadzu 2010 GC instrument with xylene as the internal standard. Methyl nonanoate (**5**) and methyl 2-methyloctanoate (**6**) were purified by passing the reaction mixture through a pad of silica gel, while all the other products were purified using flash column chromatography with silica gel 60 as stationary phase and obtained as mixtures of linear, branched and, in the case of the allylbenzenes, benzylic isomers.

Autoclave procedure. $\text{Pd}(\text{OAc})_2$ (5 mol%), $\text{Al}(\text{OTf})_3$ (10 mol%), PPh_3 (20 mol%), xylene (0.5 g) and the alkene (4 mmol) were added together in the Parr autoclave reactor and dissolved in MeOH (8 ml). The mechanical stirrer was activated, the reactor purged with CO (purified by passing the gas through a CrO_3 column) and allowed to heat up to 95 °C, where after it was pressurized to 12 bar with CO.

Microwave procedure. $\text{Pd}(\text{OAc})_2$ (5 mol%), $\text{Al}(\text{OTf})_3$ (10 mol%), PPh_3 (20 mol%), xylene (0.25 g) and the alkene (2 mmol) were added together in a microwave vial (10 ml) and dissolved in MeOH (4 ml). The magnetic stirrer was started and the reactor purged with CO (purified by passing the gas through a CrO_3 column) and the CO pressure set to 12 bar, where after irradiation at 150 W was initiated and the temperature kept at 95 °C by utilizing the fixed power method.

Methyl nonanoate (5**) and methyl 2-methyloctanoate (**6**).**²¹ δ_{H} (600 MHz; CDCl_3 ; Me_4Si) 3.67 [0.7H, s, OMe, (**6**)], 3.66 [3H, s, OMe, (**5**)], 2.44-2.41 [0.2H, m, H-2, (**6**)], 2.29 [2H, t, J 7.57 Hz, H-2, (**5**)], 1.64-1.59 [2H, m, H-3, (**5**)], 1.32-1.22 [10H, m, H-4, H-5, H-6, H-7, H-8 (**5**)], 1.32-1.22 [2.2H, m, H-3, H-4, H-5, H-6, H-7, (**6**)], 1.13 [0.7H, d, J 7.02 Hz, 2- CH_3 , (**6**)], 0.87 [0.7H, t, J 7.02 Hz, H-8, (**6**)], 0.87 [3H, t, J 7.02 Hz, H-9, (**5**)]; δ_{C} (151 MHz; CDCl_3) 177.5 [C-1 (**6**)], 174.4 [C-1 (**5**)], 51.5 [OMe (**5**)], 51.3 [OMe (**6**)], 39.6 [C-2 (**6**)], 34.19 [C-2 (**5**)], 33.9 (**6**), 32.0 (**5**), 31.8, (**6**), 29.3 (**5**), 29.3 (**6**), 29.3 (**5**), 29.2 (**5**), 27.3 (**6**), 25.1 [C-3, (**5**)], 22.7 (**5**), 22.7 (**6**), 17.2 [2- CH_3 , (**6**)], 14.2 [C-9, (**5**)], 14.1 [C-8, (**6**)]; MS (EI) m/z 172 [M^+ , 2%, (**5**)], 172 [M^+ , 1%, (**6**)].

Methyl 3-phenylpropanoate²² (7**) and methyl 2-phenylpropanoate²³ (**8**).** R_f = 0.595 (petroleum ether:ether 7:3); δ_{H} (600 MHz; CDCl_3 ; Me_4Si) 7.34-7.26 [2.7H, m, H-Ar, (**7**) and (**8**)], 7.22-7.19 [2.9H, m, CH aromatic, (**7**) and (**8**)], 3.72 [0.2H, q, J 7.17 Hz, H-2, (**8**)], 3.67 [3H, s, OMe, (**7**)], 3.65 [0.5H, s, OMe, (**8**)], 2.95 [2H, t, J 7.89 Hz, H-3, (**7**)], 2.63 [2H, t, J 7.89 Hz, H-2, (**7**)], 1.50 [0.5H, d, J 7.17 Hz, H-3, (**8**)]; δ_{C} (151 MHz; CDCl_3) 175.1 [C-1, (**8**)], 173.5 [C-1, (**7**)], 140.7 [C-1', (**8**)], 140.6 [C-1', (**7**)], 128.8 [C-4', (**8**)], 128.6 [CH aromatic, (**7**)], 128.4 [CH aromatic, (**7**)], 127.6 [CH aromatic, (**8**)], 127.3 [CH aromatic, (**8**)], 126.4 [C-4' (**7**)], 52.2 [-OMe, (**8**)], 51.7 [-OMe (**7**)], 45.6 [C-2, (**8**)], 35.8 [C-2, (**7**)], 31.1 [C-3 (**7**)], 18.7 [C-3, (**8**)]; MS (EI) m/z 164 [M^+ , 35%, (**7**)], 164 [M^+ , 23%, (**8**)].

Methyl 4-phenylbutanoate¹² (**13**), **methyl 2-methyl-3-phenylpropanoate**²⁴ (**14**) and **methyl 2-phenylbutanoate**²⁵ (**15**). $R_f = 0.784$ (hexane:toluene:acetone 4:4:2); δ_H (600 MHz; CDCl₃; Me₄Si) 7.33-7.24 [4.8H, m, CH aromatic, (**13**), (**14**) and (**15**)], 7.22-7.15 [4.5H, m, CH aromatic, (**13**), (**14**) and (**15**)], 3.66 [3H, s, OMe (**13**)], 3.65 [1H, s, OMe (**15**)], 3.64 [1.7H, s, OMe (**14**)], 3.46 [0.3H, t, J 7.71 Hz, H-2, (**15**)], 3.03 [0.6H, dd, J 6.83 and 13.37 Hz, H-3a/b, (**14**)], 2.77-2.71 [0.6H, m, H-2, (**14**)], 2.66 [0.6H, dd, J 7.83 and 13.37 Hz, H-3a/b, (**14**)], 2.65 [2H, t, J 7.56 Hz, H-4, (**13**)], 2.33 [2H, t, J 7.56 Hz, H-2, (**13**)], 2.14-2.06 [0.3H, m, H-3a/b, (**15**)], 1.96 [2H, p, J 7.56 Hz, H-3, (**13**)], 1.83-1.76 [0.3H, m, H3a/b, (**15**)], 1.15 [1.7H, d, J 6.92 Hz, 2-CH₃, (**14**)], 0.94 [1H, t, J 7.37 Hz, H-4, (**15**)]; δ_C (151 MHz; CDCl₃) 176.7 [C-1, (**14**)], 174.7 [C-1, (**15**)], 174.1 [C-1, (**13**)], 141.5 [C-1', (**13**)], 139.5 [C-1', (**14**)], 139.2 [C-1', (**15**)], 129.1, 128.7, 128.6, 128.51, 128.48, 128.1, 127.3, 126.4, 126.1, 53.5 [C-2, (**15**)], 52.0 [OMe, (**15**)], 51.72 [OMe, (**14**)], 51.65 [OMe (**13**)], 41.6 [C-2, (**14**)], 39.8 [C-3 (**14**)], 35.2 [C-4, (**13**)], 33.5 [C-2, (**13**)], 26.9 [C-3 (**15**)], 26.6 [C-3, (**13**)], 16.9 [2-CH₃ (**14**)], 12.3 [C-4, (**15**)]; MS (EI) m/z 178 [M⁺, 37%, (**13**)], 178 [M⁺, 18%, (**14**)], 178 [M⁺, 18%, (**15**)].

Methyl 4-(4'-methoxyphenyl)butanoate¹² (**16**), **methyl 3-(4'-methoxyphenyl)-2-methylpropanoate**²⁴ (**17**) and **methyl 2-(4'-methoxyphenyl)butanoate**²⁶ (**18**). R_f 0.639 (petroleum ether:ether 7:3); δ_H (600 MHz; CDCl₃; Me₄Si) 7.25 [0.2H, d, J 8.7 Hz, H-3' and H-5', (**18**)], 7.11 [2H, d, J 8.66 Hz, H-3' and H-5', (**16**)], 7.10 [0.4H, d, J 8.64 Hz, H-3' and H-5', (**17**)], 6.88 [0.2H, d, J 8.7 Hz, H-2' and H-6', (**18**)], 6.86-6.83 [0.4H, m, H-2' and H-6', (**17**)], 6.85 [2H, d, J 8.66 Hz, H-2' and H-6', (**16**)], 3.81-3.80 [3.9H, s, 4'-OMe, (**16**), (**17**) and (**18**)], 3.68 [3H, s, COOMe, (**16**)], 3.67 [0.3H, s, COOMe, (**18**)], 3.66 [0.6H, s, COOMe (**17**)], 3.43 [0.1H, t, J 7.73 Hz, H-2, (**18**)], 2.98 [0.2H, dd, J 6.94 and 13.53 Hz, H-3a/b, (**17**)], 2.75-2.69 [0.2H, m, H-2, (**17**)], 2.65-2.63 [0.2H, m, H-3a/b, (**17**)], 2.61 [2H, t, J 7.54 Hz, H-4, (**16**)], 2.34 [2H, t, J 7.54 Hz, H-2, (**16**)], 2.11-2.07 [0.1H, m, H-3a/b, (**18**)], 1.94 [2H, p, J 7.54 Hz, H-3, (**16**)], 1.81-1.76 [0.1H, m, H-3a/b, (**18**)], 1.16 [0.6H, d, J 6.92 Hz, 2-CH₃, (**17**)], 0.90 [0.3H, t, J 7.34 Hz, H-4, (**18**)]; δ_C (151 MHz, CDCl₃) 176.7 [C-1, (**17**)], 174.8 [C-1, (**18**)], 174.0 [C-1, (**16**)], 158.7 [C-4', (**18**)], 158.1 [C-4', (**17**)], 157.9 [C-4', (**16**)], 133.4 [C-1', (**16**)], 131.4 [C-1', (**17**)], 131.2 [C-1', (**18**)], 129.9 [C-2' and C-6', (**17**)], 129.4 [C-2' and C-6', (**16**)], 128.9 [C-2' and C-6', (**18**)], 113.9 [C-3' and C-5', (**18**)], 113.8 [C-3' and C-5', (**16**)], 113.7 [C-3' and C-5', (**17**)], 55.2 [4'-OMe, (**16**), (**17**) and (**18**)], 52.5 [C-2, (**18**)], 51.9 [COOMe, (**18**)], 51.6 [COOMe, (**17**)], 51.5 [COOMe (**16**)], 41.7 [C-2, (**17**)], 38.9 [C-3 (**17**)], 34.2 [C-4, (**16**)], 33.3 [C-2, (**16**)], 26.8 [C-3 (**18**)], 26.7 [C-3, (**16**)], 16.7 [2-CH₃ (**17**)], 12.2 [C-4, (**18**)]; MS (EI) m/z 208 [M⁺, 39%, (**16**)], 208 [M⁺, 13%, (**17**)], 208 [M⁺, 21%, (**18**)].

Methyl 4-(2'-methoxyphenyl)butanoate²⁷ (**19**), **methyl 3-(2'-methoxyphenyl)-2-methylpropanoate**²⁴ (**20**) and **methyl 2-(2'-methoxyphenyl)butanoate**¹⁷ (**21**). R_f 0.583 (petroleum ether:ether 7:3); δ_H (600 MHz; CDCl₃; Me₄Si) 7.25-7.23 [0.04H, m, H-4', (**21**)], 7.20-7.15 [1.2H, m, H-4', (**19**) and (**20**)], 7.11-7.07 [1.25H, m, H-6', (**19**), (**20**) and (**21**)], 6.94-6.91 [0.04H, m, H-5', (**21**)], 6.88-6.84 [1.2H, m, H-5', (**19**) and (**20**)], 6.83-6.81 [1.25H, m, H-3', (**19**), (**20**) and (**21**)], 3.80 [0.12H, s, 4'-OMe, (**21**)], 3.79 [0.6H, s, 4'-OMe, (**20**)], 3.78 [3H, s, 4'-OMe, (**19**)], 3.76-3.75 [0.04H, m, H-2, (**21**)], 3.64 [3H, s, COOMe, (**19**)], 3.63 [0.12H, s, COOMe, (**21**)], 3.61 [0.6H, s, COOMe (**20**)], 2.98 [0.2H, dd, J 7.10 and 13.22 Hz, H-3a/b, (**20**)], 2.86-2.80 [0.2H, m, H-2, (**20**)], 2.70 [0.2H, dd, J 7.59 and 13.22 Hz, H-3a/b, (**20**)], 2.65 [2H, t, J 7.56 Hz, H-4, (**19**)], 2.32 [2H, t, J 7.56 Hz, H-2, (**19**)], 2.08-2.03 [0.04H, m, H-3a/b, (**21**)], 1.92 [2H, p, J 7.56 Hz, H-3, (**19**)], 1.78-1.73 [0.04H, m, H-3a/b, (**21**)], 1.13 [0.6H, d, J 7.0 Hz, 2-CH₃, (**20**)], 0.89 [0.12H, t, J 7.39 Hz, H-4, (**21**)]; δ_C (151 MHz, CDCl₃) 177.1 [C-1, (**20**)], 175.0 [C-1, (**21**)], 174.2 [C-1, (**19**)], 157.6 [C-2', (**20**)], 157.5 [C-2', (**19**)], 156.9 [C-2', (**21**)], 130.8 [C-6', (**20**)], 131.0 [C-6', (**19**)], 129.7 [C-1', (**19**)], 129.4, 128.4, 128.1, 127.72, 127.69 [C-4', (**20**)], 127.3 [C-4' (**19**)], 120.7 [C-5', (**21**)], 120.4 [C-5', (**19**)], 120.3 [C-5', (**20**)], 110.7 [C-3', (**21**)], 110.2 [C-3', (**19**) and (**20**)], 55.7 [2'-OMe, (**21**)], 55.2 [2'-OMe, (**19**) and (**20**)], 51.8 [COOMe, (**21**)], 51.47 [COOMe, (**20**)], 51.45 [COOMe (**19**)], 45.7 [C-2, (**21**)], 39.5 [C-2, (**20**)], 34.6 [C-3 (**20**)], 33.6 [C-2, (**19**)], 29.5 [C-4, (**19**)], 25.7 [C-3 (**21**)], 25.0 [C-3, (**19**)], 17.0 [2-CH₃ (**20**)], 12.2 [C-4, (**21**)]; MS (EI) m/z 208 [M⁺, 40%, (**19**)], 208 [M⁺, 22%, (**20**)], 208 [M⁺, 34%, (**21**)].

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Supplementary Material

Quantities of reagents for the methoxycarbonylation of substrates under microwave conditions and ^1H and ^{13}C NMR spectra of mixtures of linear, branched products.

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