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Efficient C–H Activation of Alkylbenzenes and Methylcyclohexenes to Benzyl Esters by $Pd(OAc)_2/Sn(OAc)_2$ Catalyst System

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Selective activation of the side-chain C–H bond of alkylbenzenes and methylcyclohexenes is achieved by a $Pd(OAc)_2/Sn(OAc)_2$ catalyst system. Under an oxygen atmosphere, various benzyl esters were obtained from the substrates and carboxylic anhydrides. The esters were obtained in more than 100% yield based on the amount of benzoic anhydride, and consumption of oxygen was observed. This suggests that oxygen may be incorporated to produce two moles of the benzoxyl group from one mole of benzoic anhydride. It is interesting that either 1-, 3- or 4-methylcyclohexene reacted with benzoic anhydride to give benzyl benzoate. These carboxylations proceeded at the side-chain alkyl group with high selectivity and no ring-carboxylated product or coupling product was detected. From these results, a mechanism involving the formation of a η^3-benzylpalladium complex was proposed. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The activation of aromatic and aliphatic C–H bonds by transition metals leading to the selective functionalization of hydrocarbons is one of the most challenging problems in organometallic chemistry, and many examples have appeared over the past few years, offering attractive new routes to organometallic species.[1–8]

As for the carboxylation of the C–H bond, Bryant *et al.* have reported that selective side-chain acetoxylation of toluene and xylene proceeded in acetic acid by using a $Pd(OAc)_2/Sn(OAc)_2$/charcoal catalyst system.[9, 10] Recently, we also found that the methoxy group of anisole was activated to give phenoxymethyl benzoate by using a $Pd(OAc)_2/Sn(OAc)_2$ catalyst.[11] However, we are unaware of any report of a catalytic selective side-chain carboxylation of alkylbenzenes, apart from acetoxylation. In this paper, we report our results on the carboxylation of alkylbenzenes and 1-, 3- or 4-methylcyclohexene catalyzed by a $Pd(OAc)_2/Sn(OAc)_2$ system, and discuss the reaction mechanism.

RESULTS AND DISCUSSION

At first, toluene was treated with benzoic acid in the presence of $Pd(OAc)_2$ alone as a catalyst, but no benzyl benzoate (**1**) was obtained. When the reaction was carried out under on oxygen atmosphere using benzoic anhydride instead of benzoic acid, a trace amount of **1** was obtained. Therefore several co-catalysts were examined. As a result, addition of $Sn(OAc)_2$ and potassium acetate or benzoate increased the yield of **1** drastically (Table 1). Although a long reaction time was required, phosphine ligands gave equally good results in place of $Sn(OAc)_2$. As a base, triethylamine also gave good results, but many unidentified by-products were formed. The addition of charcoal had no effect on the yield. From these results, the benzoxylation reaction

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Table 1 Effect of co-catalysts and base on the benzoxylation of toluene at 100 °C[a]

Run	Co-catalyst	Base	Time (h)	Yield (%)[c,d]
1	None	PB[b]	96	Trace
2	$(EtO)_3P$	KAOc	168	29.2
3	$(EtO)_3P$	PB	48	24.0
4	$(n\text{-}Bu)_3P$	KOAc	144	116.6
5	Ph_3P	PB	144	31.2
6	AgOAc	PB	72	—
7	$Cu(OAc)_2$	PB	46	—
8	$SnCl_2$	KOAc	144	5.6
9	$SnCl_2$	PB	288	11.6
10	$Sn(OAc)_2$	None	168	44.6
11	$Sn(OAc)_2$	Pyridine	72	—
12	$Sn(OAc)_2$	Na_2CO_3	1[e]	—
13	$Sn(OAc)_2$	K_2CO_3	23.5[e]	14.7
14	$Sn(OAc)_2$	Et_3N	44	116.5
15	$Sn(OAc)_2$	KOAc	35	151.7
16	$Sn(OAc)_2$	PB	47	111.8

[a] All experiments were carried out in solution of 50 mmol of toluene, 0.32 mmol of $Pd(OAc)_2$, 1.2 mmol of co-catalyst, 4 mmol of base and 10 mmol of benzoic anhydride under an oxygen atmosphere.

[b] PB, potassium benzoate.

[c] Yields were determined by GC.

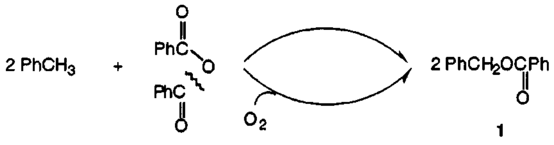
[d] Based on the amunt of benzoic anhydride.

[e] The reaction mixture became a tarry material in this reaction time, and it was impoosible to continue.

using a $Pd(OAc)_2/Sn(OAc)_2/KOAc$ catalyst system was found to proceed in good yield with high regioselectivity. Only benzyl acetate (**2**) was obtained as a by-product, and no ring benzoxylation products, dibenzoxylation products or coupling products were detected. Needless to say, $Pd(OAc)_2$ is essential in this reaction, and $Sn(OAc)_2$ alone and/or KOAc did not catalyze the reaction.

It is interesting that the ester **1** was obtained in more than 100% yield based on the amount of benzoic anhydride, and consumption of oxygen was observed. In reactions such as the Friedel–Crafts acylation with anhydrides, the anhydride produces an acyl group and a carboxyl group. However, in this reaction, although the detailed mechanism is unknown, oxygen may be incorporated to produce two moles of benzoxyl group from one mole of benzoic anhydride (Scheme 1).

These phenomena were also detected using other carboxylic anhydrides, such as pentanoic and hexanoic anhydrides (see Table 2). However, in the absence of oxygen (under an argon or carbon monoxide atmosphere) the reaction did not occur, and only starting materials were recovered. These results show that two moles of benzoxyl group were generated in the process of formation of the active palladium species.



Scheme 1.

Table 2 presents the investigation of the catalytic activity of $Pd(OAc)_2$ for benzoxylation of toluene. In all cases, **1** was obtained in good yield and the maximum turnover number was 300. With decreasing amounts of $Pd(OAc)_2$, the production of by-product **2** was reduced, but a longer reaction time was required.

From these investigations, $Pd(OAc)_2/Sn(OAc)_2$/KOAc/benzoic anhydride/toluene in a molar ratio of 0.16 : 0.6 : 2 : 5 : 25 was found to be the best choice for increasing the yield of **1**.

Next, for the application of this reaction, various benzyl esters were synthesized from various anhydrides and toluene (Table 3). All the anhydrides employed reacted with toluene to give the corresponding benzyl esters and a trace amount of **2** as a by-product. It is worth noting that all cases except acetic and propionic anhydrides gave the esters in more than 100% yield based on the molar amount of anhydride.

The reactions of several alkylbenzenes and benzoic anhydride were also examined (Table 4). *o*-, *m*- and *p*-xylene reacted with benzoic anhydride to give the corresponding esters in good yields. Mesitylene also reacted with benzoic anhydride to give the ester, but the yield was quite low compared with that of xylene, presumably due to steric effects. In all these reactions, only monobenzoxylation proceeded selectively, and no dibenzoxylation product (such as the α,α-/α,α'-dibenzoxylation products which were formed in the acetoxylation of xylene[9, 10] was obtained. When ethylbenzene was treated with benzoic anhydride, 1-phenylethyl benzoate (**15**) was expected to be formed, but the major product was styryl benzoate (**14**) (*cis*/*trans* = 3 : 1). Moreover, it is interesting that *p*-methylanisole gave not only *p*-methoxybenzyl benzoate (**16**) but also phenoxymethyl benzoate. This C–H activation of the methoxy group of anisole has been discussed in detail in a separate paper.[11]

In the course of our continuing investigation

Table 2 Benzoxylation of toluene with $Pd(OAc)_2$ at 100 °C[a]

Run	Toluene/$Pd(OAc)_2$ molar ratio	Time 0h)	Yield (mmol)[b]		Turnover number[c]
			1	**2**	
1	1250	168	12.02	0.89	300
2	625	120	14.78	1.63	185
3	312.5	72	14.16	2.48	89
4	156.25	35	15.17	2.31	47

[a] The reaction conditions were the same as those given in Table 1, with the exception of certain reaction times and the amount of $Pd(OAc)_2$.
[b] Yields were determined by GC.
[c] Based on the amount of $Pd(OAc)_2$.

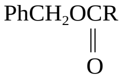
of this palladium-catalyzed carboxylation, we found that the selective side-chain benzoxylation of methylcyclohexenes also proceeded in the presence of this catalyst system (Table 5). It is surprising that both benzoxylation and aromatization occurred, to give the ester **1**. Moreover, all isomers of methylcyclohexene(1-, 3-, 4-) gave **1**, but benzoxylation of methylcyclohexane did not proceed (Scheme 2).

GC–MS analysis of the reaction mixture revealed the formation of benzoxylation products **17**–**19**, so it is considered that benzoxylation of the methyl group of methylcyclohexenes took place first, and then aromatization of cyclohexene ring might have occurred.

The present work does not permit the proposal of a definite mechanism, but some comments are made on the reaction mechanism. On the basis of the results reported here, it seems that the reaction mechanism of our carboxylation differs from the benzylic acetoxylation reported by Bryant *et al.* as follows:[9, 10, 12] (1) the corresponding esters were obtained in good yields regardless of the presence or absence of charcoal; (2) the carboxylation of methylcyclohexene also proceeded; (3) the esters were obtained in more than 100% yield based on the amount of carboxylic anhydrides.

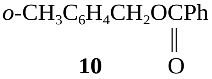
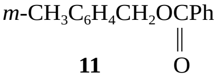
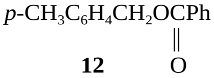
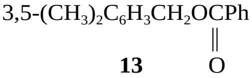
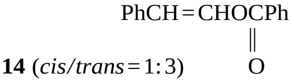
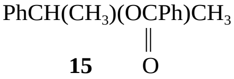
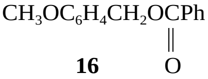
Since benzylic acetoxylation catalyzed by $Pd(OAc)_2$ under their conditions was inhibited by oxygen, Davidson and Triggs have proposed a radical-based mechanism involving palladium(I)

Table 3 Carboxylation of toluene with $Pd(OAc)_2$ and anhydrides[a]

Run	Anhydride	Time (h)	 $PhCH_2OC(=O)R$ product	Yield (%)[b, c]
1	Acetic	72	**2**: R = methyl	72.1
2	Propionic	144	**3**: R = ethyl	94.6
3	Butyric	29.5	**4**: R = propyl	119.9
4	Pentanoic	32.5	**5**: R = n-butyl	135.2
5	Hexanoic	96	**6**: R = pentyl	159.0
6	Octanoic	62.5	**7**: R = hexyl	153.5
7	2,2-Dimethylpropanoic	23	**8**: R = t-butyl	172.0
8	2-Methylpropanoic	62.5	**9**: R = isopropyl	132.6
9	1,8-Naphthalic	24	Many unidentified products	—
10	Crotonic	44		—
11	Phthalic	48		—

[a] The reaction conditions were the same as those given in Table 1, with the exception of certain reaction times.
[b] Yields were determined by GC.
[c] Based on the amount of anhydride.

Table 4 Benzoxylation of various aromatics with $Pd(OAc)_2$[a]

Run	Aromatic	Time (h)	Product	Yield (%)[b,c]
1[d, f]	*o*-Xylene	72	 $o\text{-}CH_3C_6H_4CH_2O\underset{\underset{O}{\Vert}}{C}Ph$ **10**	99.1
2[d,f]	*m*-Xylene	120	 $m\text{-}CH_3C_6H_4CH_2O\underset{\underset{O}{\Vert}}{C}Ph$ **11**	135.1
3[d,f]	*p*-Xylene	144	 $p\text{-}CH_3C_6H_4CH_2O\underset{\underset{O}{\Vert}}{C}Ph$ **12**	118.5
4[f]	Mesitylene	94	 $3,5\text{-}(CH_3)_2C_6H_3CH_2O\underset{\underset{O}{\Vert}}{C}Ph$ **13**	10.3[g]
			 $PhCH{=}CHO\underset{\underset{O}{\Vert}}{C}Ph$ **14** (*cis/trans* = 1:3)	15.9[g]
5[e,f]	Ethylbenzene	94	 $PhCH(CH_3)(O\underset{\underset{O}{\Vert}}{C}Ph)CH_3$ **15**	4.3[g]
6	*p*-Methylanisole	288	 $CH_3OC_6H_4CH_2O\underset{\underset{O}{\Vert}}{C}Ph$ **16**	17.5
7	*p-Bromotoluene*	90	—	—
8	*p*-Chlorotoluene	96	—	—
9	Benzene	48	—	—

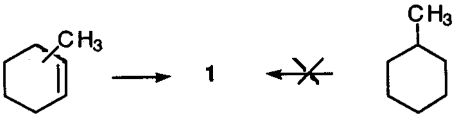
[a] The reaction conditions were the same as those given in Table 1, with the excepton of certain reaction times.
[b] Yields were determined by DGC.
[c] Based on the amount of anhydride.
[d] Carried out on a half-scale.
[e] Carried out on a triple scale.
[f] Carried out at 130 °C.
[g] Isolated yield.

Table 5 Benzoxylation of methylcyclohexene with $Pd(OAc)_2$[a]

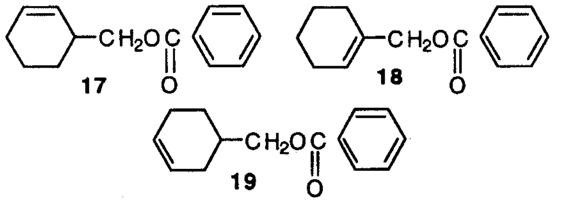
Run	Cyclohexene	Time (h)	Yield (%)[b]
1	1-Methylcyclohexene	122	121.8
2[c]	3-Methylcyclohexene	168	64.9
3	4-Methylcyclohexene	122	91.9

[a] All experiments were carried out in a solution of 25 mmol of methylcyclohexene, 0.16 mmol of $Pd(OAc)_2$, 0.6 mmol of $Sn(OAc)_2$ and 5 mmol of benzoic anhydride under an O_2 atmosphere at 100 °C.
[b] Yields were determined by GC.
[c] 2 mmol of KOAc was added.

species.[13] In the presence of $Pb(OAc)_4$, benzylic acetoxylation also proceeded in acetic acid, and it is known that this reaction is a radical chain process.[14] However, the radical nature of $Pd(OAc)_2$-catalyzed benzylic acetoxylation was later disputed, and more recently, Starchevskii *et al.* have concluded that this is not a radical reaction.[15–17] We considered that our benzylic carboxylation also is not a radical reaction, on



Scheme 2.



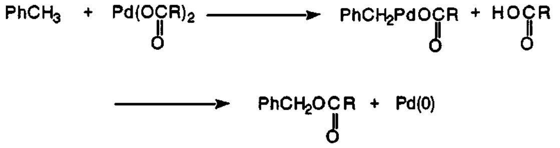
Structures 17–19.

the basis of these two results: (1) oxygen did not inhibit the reaction; (2) no coupling product was detected.

A possible mechanism involving the formation of a σ-benzylpalladium complex is shown in Scheme 3. Electrophilic metallation of mercury(II),[18] thallium(II)[19, 20] or lead(IV),[20] salts to aromatic rings is well known and several examples of metallation of aliphatic carbons are also reported.[22–24] The attack could be either on the aromatic ring followed by rearrangement or directly on the benzylic carbon. However, the side-chain selectivity, the formation of **14** from ethylbenzene and the difference in reactivity between methylcyclohexene and methylcyclohexane could not be explained by this mechanism.

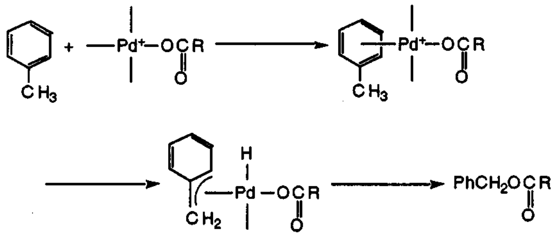
Another possible mechanism involving the formation of a π-aromatic palladium complex was proposed by Ichikawa *et al.* in benzylic acetoxylation;[25] however, this mechanism is also in conflict with the results for methylcyclohexene. We therefore propose a mechanism as follows (Scheme 4). First, palladium cation attacks the aromatic ring electrophilically to form a π-aromatic palladium complex, which rearranges into a η^3-benzylpalladium complex;[26, 27] then, the carboxylate anion attacks the benzyl position to produce the corresponding benzyl esters. In the case of methylcyclohexene, a η-allylpalladium complex was considered as an intermediate, although the mechanism of aromatization of the cyclohexene ring is uncertain. $Sn(OAc)_2$ was proposed to increase the electrophilicity of palladium in the form of $Sn(OAc)_2(OOCR)^-$.

The formation of **14** in the reaction of ethylbenzene and benzoic anhydride is understood by the following reaction mechanism: (1) the elimination of acetic acid from η^3-benzylpalladium complex **A**; (2) the formation of η^3-benzylpalladium complex **B**; (3) β-elimination (Scheme 5).



$$PhCH_3 + Pd(O\underset{\underset{O}{\|}}{C}R)_2 \longrightarrow PhCH_2PdO\underset{\underset{O}{\|}}{C}R + HO\underset{\underset{O}{\|}}{C}R \longrightarrow PhCH_2O\underset{\underset{O}{\|}}{C}R + Pd(0)$$

Scheme 3.

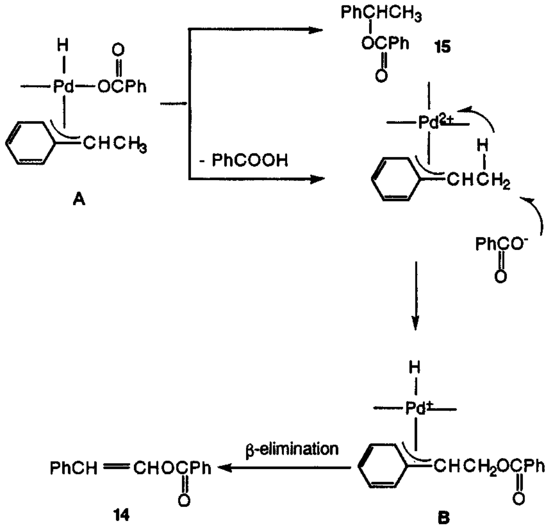


Scheme 4.

EXPERIMENTAL

General comments

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Hitachi R-600 FT-NMR spectrometer operating at 60 MHz or a JEOL GX-400 FT-NMR spectrometer operating at 400 MHz. Peak positions are reported in parts per million relative to the tetramethylsilane internal standard. Spectra which were recorded with off-resonance decoupling have peaks reported as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Infrared spectra were



Scheme 5.

recorded on a Hitachi 260-10 spectrometer as Nujol (for solids) or liquid films (for liquids). Mass spectra were recorded on a Hitachi M-80B or Shimadzu GCMS-QP2000A instrument. Gas chromatography was performed on a Shimadzu GC-14A model equipped with a capillary column (CBP 1-W12-100, 0.53 mm i.d. × 12 m) using helium as carrier gas. All melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was done with E. Merk regent silica gel 60 (230–400 mesh). Analytical thin-layer chromatography (TLC) was performed with E. Merk reagent silica gel 60 F-254, 0.25 mm thick.

All alkylbenzenes were dehydrated over an appropriate drying agent and distilled before use. Other reagents were all commercial products and were used without further purification.

General procedure for the synthesis of esters

A flask equipped with an oxygen-filled balloon was charged with $Pd(OAc)_2$ (0.035 g, 0.16 mmol), $Sn(OAc)_2$ (0.142 g, 0.6 mmol), KOAc (0.197 g, 2 mmol), carboxylic anhydride (5 mmol) and toluene (2.26 ml, 25 mmol). The reaction mixture was stirred at 100 °C for a given reaction time (Table 1), and then quenched with aqueous saturated $NaHCO_3$. After work-up, the crude product was purified by silica-gel column chromatography. The ester thus obtained was identified by means of its spectral data (IR, NMR, MS) and by comparison of the retention time of the GLC with those of authentic samples. The yields were determined by GLC using biphenyl as an internal standard.

Benzyl benzoate (1)
IR (liquid film): ν 3050, 1730, 1460, 1280, 1120, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.34 (s, 2H), 7.08–8.18 (m, 10 H); GC/MS: *m*/*z* (relative intensity) 121 (M^+, 23), 105 (100), 91 (56), 77 (40), 51 (25).

Benzyl acetate (2)
IR (liquid film): ν 3100, 1760, 1250, 1050, 760, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H), 5.09 (s, 2H), 7.60 (s, 5H); GC/MS: *m*/*z* (relative intensity) 150 (M^+, 17), 108 (26), 91 (39), 77 (24), 43 (100).

Benzyl propionate (3)
IR (liquid film): ν 3000, 1750, 1200, 1100, 1040, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.16 (t, 3H, $J = 7.32$ Hz), 2.38 (q, 2H, $J = 7.32$ Hz), 5.12 (s, 2H), 7.31–7.38 (m, 5H); GC/MS: *m*/*z* (relative intensity) 164 (M^+, 41), 108 (100), 91 (73), 79 (9), 57 (39), 29 (13).

Benzyl butyrate (4)
IR (Liquid film) ν 3000, 1750, 1190, 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.95 (t, 3H, $J = 7.32$ Hz), 1.63–1.73 (m, 2H), 2.34 (t, 2H, $J = 7.32$ Hz), 5.12 (s, 2H), 7.32–7.37 (m, 5H); GC/MS: *m*/*z* (relative intensity) 178 (M^+, 21), 108 (98), 91 (100), 71 (40).

Benzyl pentanoate (5)
IR (liquid film): ν 2995, 1750, 1180, 760 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, $J = 7.32$ Hz), 1.35 (m, 2H), 1.63 (m, 2H), 2.36 (t, 2H, $J = 7.32$ Hz), 5.11 (s, 2H), 7.32–7.37 (m, 5H); GC/MS: *m*/*z* (relative intensity) 192 (M^+, 7), 174 (3), 108 (79), 91 (100), 57 (40).

Benzyl hexanoate (6)
IR (liquid film): ν 2950, 1740, 1170, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J = 7.32$ Hz), 1.26–1.34 (m, 4H), 1.59–1.69 (m, 2H), 2.35 (t, 2H, $J = 7.32$ Hz), 5.11 (s, 2H), 7.32–7.38 (m, 5H); GC/MS: *m*/*z* (relative intensity) 206 (M^+, 6), 188 (2), 188 (2), 108 (80), 91 (100).

Benzyl octanoate (7)
IR (liquid film): ν 2960, 1760, 1180, 710 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, $J = 7.32$ Hz), 1.26–1.31 (m, 8H), 1.61–1.68 (m, 2H), 2.35 (t, 2H, $J = 7.32$ Hz), 5.11 (s, 2H), 7.31–7.36 (m, 5H); GC/MS: *m*/*z* (relative intensity) 234 (M^+, 3), 108 (66), 91 (100), 57 (34).

Benzyl 2,2-dimethylpropionate (8)
IR (liquid film): ν 3000, 1740, 1160, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.22 (s, 9H), 5.10 (s, 2H), 7.40 (s, 5H); GC/MS: *m*/*z* (relative intensity) 192 (M^+, 7), 91 (60), 57 (100).

Benzyl 2-methylpropionate (9)
IR (liquid film): ν 3000, 1740, 1160, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.19 (d, 9H, $J = 7.10$ Hz), 2.25–2.90 (m, 1H), 5.10 (s, 2H), 7.31 (s, 5H); GC/MS: *m*/*z* (relative intensity) 178 (M^+, 2), 108 (30), 91 (100).

***o*-Methylbenzyl benzoate (10)**
IR (liquid film): ν 2950, 1720, 1280, 1110, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.40 (s, 3H), 5.35 (s, 2H), 7.10–8.25 (m, 9H); GC/MS: *m*/*z*

(relative intensity) 105 ($M^+ - CH_3PhCh_2$, 66), 104 (100), 77 (34), 41 (10).

m-Methylbenzyl benzoate (11)

IR (liquid film): ν 2950, 1750, 1720, 1110, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.47 (s, 3H), 5.30 (s, 2H), 7.10–8.30 (m, 9H); GC/MS: m/z (relative intensity) 226 (M^+, 13), 105 (100), 77 (29).

p-Methylbenzyl benzoate (12)

IR (liquid film): ν 3000, 1740, 1280, 1120, 820, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.35 (s, 3H), 5.30 (s, 2H), 7.10–8.20 (m, 9H); GC/MS: m/z (relative intensity) 226 (M^+, 16), 105 (100), 77 (25).

3,5-Dimethylbenzyl benzoate (13)

IR (liquid film): ν 2940, 1720, 1270, 1120, 720 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.30 (s, 6H), 5.29 (s, 2H), 6.90–8.20 (m, 8H); GC/MS: m/z (relative intensity) 240 (M^+, 15), 105 (100), 77 (27).

Styryl benzoate (14)

IR (liquid film): ν 3000, 1740, 1280, 1130, 950, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.86 (d, 1H, $J = 7.32$ Hz, CHO *cis*), 6.59 (d, 1H, $J = 12.82$ Hz, CHO *trans*), 7.23–8.18 (m, 12H, Ar and PhCH *cis*, *trans*); GC/MS: m/z (relative intensity) *cis*-**16** 224 (M^+, 6), 105 (100), 77 (71), 51 (55) and *trans*-**16** 224 (M^+, 8), 105 (100), 77 (85), 51 (27).

1-Phenylethyl benzoate (15)

IR (liquid film): ν 2930, 1720, 1270, 1110, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.65 (d, 3H, $J = 6.70$ Hz), 6.12 (q, 1H, $J = 6.70$ Hz), 7.15–8.20 (m, 12H); GC/MS: m/z (relative intensity) 226 (M^+, 8), 105 (100), 77 (37), 51 (21).

p-Methoxybenzyl benzoate (16)

IR (Nujol): ν 3000, 1740, 1620, 1280, 1180, 1120, 1040, 780 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.80 (s, 3H), 5.30 (s, 2H), 6.75–8.15 (m, 9H); GC/MS: m/z (relative intensity) 242 (M^+, 10), 197 (2), 135 (100), 91 (48).

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