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A Catalytic Process Based on Sequential *ortho*-Alkylation and Vinylation of *ortho*-Alkylaryl Iodides *via* Palladacycles

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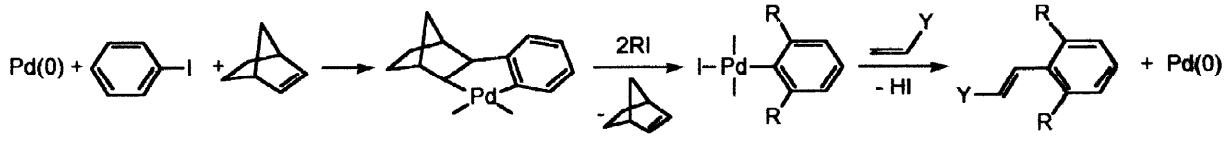
Abstract: A new synthesis of vinylarenes selectively substituted in both their *ortho* positions with different alkyl groups is reported. The reaction occurs starting from *ortho*-alkyl substituted iodoarenes which are caused to react with aliphatic iodides, terminal olefins, K_2CO_3, AcOK and $Pd(OAc)_2$ in a one-pot reaction consisting of a series of elementary steps controlled by palladium in its oxidation states 0, II and IV. A correct balance of all the steps involved is required to obtain a catalytic reaction.

Keywords: Palladium; Catalysis; Arenes

Introduction

Selective aromatic substitution is a long-standing goal of chemistry [1,2]. Aromatic molecules substituted by different groups in their *ortho* positions and free *para* position are rather unusual, yet in some cases they have been employed as part of biologically active compounds such as the largely used herbicide metolachlor [3]. We recently described a new methodology, consisting of the temporary construction of an alkylaromatic palladacycle from palladium(0), an aromatic iodide and a strained olefin [4]. The palladacycle is able to direct organic groups from aliphatic iodide towards the *ortho*-positions of the aromatic moiety and is subsequently dismantled to generate an *o,o*-disubstituted arylpalladium complex, which is caused to react with a terminal olefin to regenerate palladium(0). As depicted in the simplified Scheme 1 a catalytic cycle thus results from the multistep sequence. In the present paper we report further progress in the palladacycle-based methodology, consisting of the synthesis of vinylaromatics containing two different alkyl groups in the *ortho*-positions.



Scheme 1. Reagents and conditions. K_2CO_3, DMA, under N_2, 20°C, 30h.

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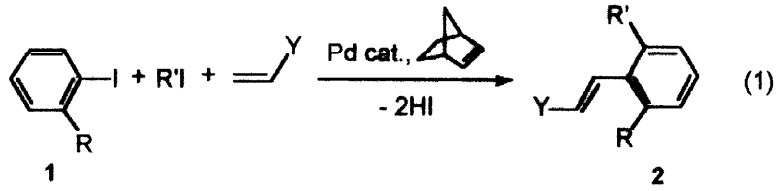
Results

The overall reaction which is the subject of this paper is represented by eq. 1.



This is a one-pot multistep reaction occurring at mild temperature (55 °C) in dimethylformamide (DMF) as solvent under the catalytic action of palladium acetate and norbornene.

Originally we regarded reaction 1 as an extension of the aromatic dialkylation process reported in Scheme 1 [4] which utilizes aromatic iodides with free *o*-positions. In spite of the similarity, however, the reaction reported in Scheme 1 cannot be utilized for dialkylation with a mixture of different alkyl groups because the system is not able to discriminate between them efficiently. We thus resorted to an *ortho*-substituted aryl iodide as the starting material. The *ortho* substituent, however, exerted negative effects and no reaction occurred under the conditions of Scheme 1. A satisfactory reaction could only be obtained by increasing the temperature to 55 °C and adding potassium acetate to the reaction mixture, containing an *o*-substituted aromatic iodide, an aliphatic iodide, norbornene, a terminal olefin, K_2CO_3 and $Pd(OAc)_2$. Additional alkyl iodide and terminal olefin had to be introduced gradually to the reaction mixture by a syringe pump.

The by-product of the reaction with norbornene is the substituted benzocyclobutene derivative depicted in eq. 2 [5].

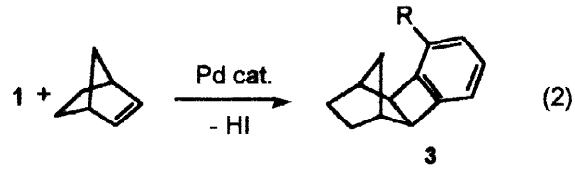


Table 1 reports significant results.

Satisfactory yields could be obtained with Y = CO_2Me or electron-withdrawing substituents. However, care must be taken to prevent secondary reactions of the terminal olefin by controlling its excess. Unsubstituted terminal olefins reacted too sluggishly and are not reported.

Conversions are positively influenced not only by electron-withdrawing substituents in the olefin (compare runs 1-5 with 11-13) but also by *o*-alkyl substituents R exerting low steric hindrance (compare runs 1-5 and 7, 8) and by linear alkyl iodides (compare runs 1-5 with 6).

On the other hand selectivity towards compound **2** is adversely affected by the steric hindrance exerted by *o*-substituents R in aryl iodides and R' in alkyl iodides, which favor reductive elimination to hexahydromethanobiphenylenes **3** (compare 1-5 and 6-8) as previously reported [5].

The low selectivity towards **2** observed with styrene (run 11) and 4-methylstyrene (run 12) parallels the low reactivity of these olefins with palladium. Accordingly selectivity improves with the more reactive 4-fluorostyrene (run 13). With acrylonitrile (run 10) results are similar to those obtained with styrene although selectivity is lower owing to the formation of heavy products which have not been identified.

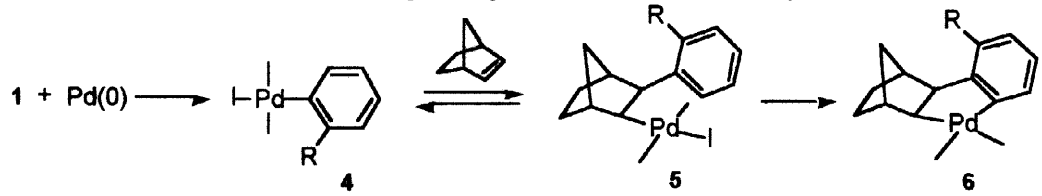
Table 1. Reaction of aliphatic iodides and *o*-substituted aromatic iodides with terminal olefins in the presence of K_2CO_3, AcOK, norbornene and $Pd(OAc)_2$[a].

Run	R in aryl iodide	R' in alkyl iodide	Y in olefin	Conversion[b] (%)	Selectivity[b] (%)
1	Me	*n*-Pr	CO_2Me	88	**2a** 84 **3a** 16
2	Me	*n*-Bu	CO_2Me	72	**2b** 81 **3a** 19
3	Et	*n*-Pr	CO_2Me	76	**2c** 93 **3b** 7
4	*n*-Bu	*n*-Pr	CO_2Me	100	**2d** 76 **3c** 24
5	*n*-Bu	*n*-Oct	CO_2Me	62	**2e** 73 **3c** 27
6	*n*-Bu	*i*-Pr	CO_2Me	31	**2f** 25 **3c** 75
7	*i*-Pr	*n*-Bu	CO_2Me	59	**2f** 60 **3d** 40
8	*t*-Bu	*n*-Pr	CO_2Me	20	**2g** 42 **3e** 58
9[c]	*n*-Bu	*n*-Pr	COMe	43	**2h** 71 **3c** 29
10[c]	*n*-Bu	*n*-Pr	CN	47	**2i** 43 **3c** 46
11	*n*-Bu	*n*-Pr	C_6H_5	22	**2j** 46 **3c** 54
12	*n*-Bu	*n*-Pr	4-MeC_6H_4	21	**2k** 50 **3c** 50
13	*n*-Bu	*n*-Pr	4-FC_6H_4	43	**2l** 67 **3c** 23

[a] Molar ratio of the reagents in the order reported in the title (in brackets after addition of alkyl iodide and terminal olefin by syringe pump): 33 (66): 5: 5 (10): 26: 26: 10:1 (55 °C, 72h, DMF as solvent; N_2 atmosphere). [b] On the aryl iodide by GLC. [c] Terminal olefin to palladium ratio = 6 instead of 10.

Discussion

Since we had previously isolated and characterized the intermediates involved in the single steps of the dialkylation process of Scheme 1 we could easily observe the different course of the present one. For mechanistic aspects not discussed here the reader is referred to our previous work [4,6]. The first step consisting of the oxidative addition of the aryl iodide to palladium(0) to give **4** and the subsequent norbornene insertion to **5** (Scheme 2) are much slower than the corresponding ones on unsubstituted aryl iodides.



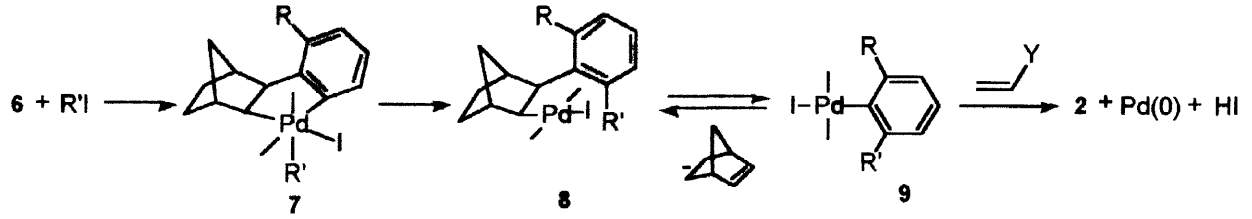
Scheme 2

To promote these steps the increase of temperature and the addition of potassium acetate were required. The positive action of carboxylate anions to the insertion of norbornene was previously reported [7].

Under the conditions chosen the subsequent step leads to the formation of the palladacycle **6** (Scheme 2). At this point ring closure to *exo*-hexahydromethanobiphenylene, which, as noted above, is favored by the bulkiness of R (eq. 2) readily occurs. To minimise this undesired reaction we added a large excess of the alkyl iodide (preferably a linear one to minimise the negative effects due to steric hindrance), which attacks the metallacyclic palladium to form a palladium(IV) complex [4,6,8-10].

As shown in Scheme 3 the reaction then proceeds through oxidative addition of the alkyl iodide to the palladacycle to form **7**, migration of the R' group to the *ortho* aryl site via reductive elimination to **8** and norbornene deinsertion to **9**. *ortho*-Alkylation thus triggers norbornene deinsertion by steric effect and in its turn the deinsertion process generates a palladium(II) species (**9**) able to undergo a Heck-type reaction with olefin

CH_2=CHY. This last step leads to the final product and at the same time liberates the palladium(0) necessary for starting a new catalytic cycle. Palladium(0) therefore must be present in sufficient concentration to allow oxidative addition and the following steps to proceed readily.



Scheme 3

The addition of alkyl iodide in excess, however, is not without negative consequences on the reaction course: although it favors aromatic alkylation, at 55 °C it gives rise to an undesired oxidative addition to palladium(0), followed by reductive elimination, which forms the olefin and iodide ions by neutralization of the resulting HI with K_2CO_3 (eq. 3).

$$RCH_2CH_2I + Pd(0) \longrightarrow RCH_2CH_2\text{-}Pd\text{-}I \longrightarrow RCH{=}CH_2 + HI \qquad (3)$$

Since iodide ions tend to stabilize palladium(II) the overall reaction slows down [11] and the advantage of using the excess of alkyl iodides vanishes. The gradual addition of these reagents with a syringe pump improves the reaction, however, especially as far as the number of catalytic cycles is concerned. The latter can reach 3.5-3.8 cycles which is very low as an absolute number, yet rather satisfactory in view of the complexity of the reaction. It is worth noting that the final reaction solution contains dissolved palladium and no separation of the latter occurs.

Summing up we have shown that vinylation and selective *o*-alkylation of *o*-alkyl-substituted iodoarenes is feasible and provides a simple and direct way to gain access to a class of compounds which would be difficult to obtain by conventional means.

Experimental

Most starting material were commercial products. 2-Ethyliodobenzene, 2-*i*-propyliodobenzene, 2-*n*-butyliodobenzene and 2-*t*-butyliodobenzene were prepared by iodination of the corresponding diazonium salt according to the literature [12-13]. DMF was distilled at reduced pressure and stored over 4 Å molecular sieves under dinitrogen. Products **3a** (Ar = 2-MeC_6H_4) [5] and **3e** (Ar = 2-*t*-BuC_6H_4) [14] were compared with those described in the literature. Reactions were carried out under dinitrogen by use of conventional Schlenk techniques. Products were isolated by flash chromarography on silica gel (32-63 μm 60 ICN Biomedicals) using hexane or mixtures of hexane-ethyl acetate as eluent. A syringe pump from Sage Instruments (Orion Research) was used. Gas chromatography (GC) was carried out with a Carlo Erba HRGC 5300 instrument equipped with a 30 m SE-30 gas capillary column and a Helwett-Packard 3394 integrator. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC300 spectrometer operating at 300 and 75 MHz, respectively. All spectra were recorded at 20 °C in $CDCl_3$ using the solvent as internal reference (7.26 and 77.00 ppm respectively for ^1H and ^{13}C). ^{13}C NMR spectra were run using 64K of memory. Assignments are based on decoupling and 2D experiments. * indicates interchangeable assignments. IR spectra were obtained with a Perkin-Elmer 298 FT spectrophotometer. Electron impact mass spectra (*m/z*, relative intensity (%)) were registered with a Finnigan

Mat SSQ 710 instrument working at 70 eV ionization energy. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

Reaction of 2-substituted aryl iodides, alkyl iodides and a terminal olefin. General procedure

A DMF solution (4 ml) of the aryl iodide (0.3 mmol), the alkyl iodide (2 mmol), the terminal olefin (0.3 mmol) and norbornene (0.6 mmol) was introduced under dinitrogen into a Schlenk-type flask containing $Pd(OAc)_2$ (0.06 mmol), K_2CO_3 (1.6 mmol), AcOK (1.6 mmol). To the resulting mixture a solution of the alkyl iodide (2 mmol) and the terminal olefin (0.3 mmol) in DMF (8 ml) was added at 55 °C during 64 h by a syringe pump. The reaction was prolonged for an additional 8 h. The mixture was then cooled, treated with $NaBH_4$ in excess, diluted with Et_2O and extracted four times with H_2O. The organic layer was dried over Na_2SO_4. The solvent was evaporated and the products were isolated by flash chromatography using hexane or a mixture of hexane and ethyl acetate as eluent. Yields are based on the aryl iodide. GC analysis of the volatile products removed under vacuum and trapped at -196 °C showed that most of the norbornene was recovered. The alkyl iodide was mostly converted into the corresponding olefin (50-55%) and to dialkyl carbonate (10-15%). In the case of run 9 and 10 (Table 1) only 0.36 mmol of the terminal olefin were used; 0.06 mmol were introduced at the beginning of the reaction and the remaining 0.30 mmol by syringe pump.

Methyl (*E*)-6-methyl-2-*n*-propylcinnamate (**2a**, Ar = 2-MeC_6H_4, R' = *n*-Pr, Y = CO_2Me) was obtained following the general procedure in 74% yield as a colourless oil (b.p. 165-169°C/7 mm Hg). ^{1}H NMR: δ 7.87 (1H, d, J = 16.3 Hz, =C*H*Ar), 7.15, 7.06 (3H, AB_2 system, J = 7.5 Hz, H4, H5, H6), 6.04 (1H, d, J = 16.3 Hz, =C*H*CO_2CH_3), 3.82 (3H, s, CO_2CH_3), 2.61 (2H, m, CH_2Ar), 2.33 (3H, s, CH_3Ar), 1.57 (2H, m, CH_2CH_3), 0.94 (3H, t, J = 7.3 Hz, CH_3). ^{13}C NMR: δ 167.11 (CO), 143.85 (=CHAr), 141.22 (C2), 136.24 (C6), 133.79 (C1), 128.17 (C4, C3), 127.13 (C5), 123.70 (=*C*HCO_2CH_3), 51.69 (CO_2CH_3), 35.81 (CH_2Ar), 24.20 (CH_2CH_3), 21.20 (CH_3Ar), 14.03 (CH_3). IR (neat): ν = 1724, 1646, 988 cm^{-1}. MS: 218 (5), 175 (16), 129 (100), 128 (49), 115 (69), 59 (48). Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C,76.92, H 8.35.

Methyl (*E*)-2-*n*-butyl-6-methylcinnamate (**2b**, Ar = 2-MeC_6H_4, R' = *n*-Bu, Y = CO_2Me) was obtained following the general procedure in 58% yield as a colourless oil (b.p. 169-173°C/7 mm Hg). ^{1}H NMR: δ 7.88 (1H, d, J = 16.3 Hz, =C*H*Ar), 7.16, 7.06 (3H, AB_2 system, J = 7.5 Hz, H4, H3, H5), 6.05 (1H, d, J = 16.3 Hz, =C*H*CO_2CH_3), 3.83 (3H, s, CO_2CH_3), 2.63 (2H, m, CH_2Ar), 2.33 (3H, s, CH_3Ar), 1.53 (2H, m, CH_2CH_2Ar), 1.35 (2H, m, CH_2CH_3), 0.92 (3H, t , J = 7.2 Hz, CH_3). ^{13}C NMR: δ 167.11 (CO), 143.84 (=CHAr), 141.46 (C2), 136.26 (C6), 133.75 (C1), 128.20 (C4), 128.14 (C3), 127.10 (C5), 123.68 (=*C*HCO_2CH_3), 51.70 (CO_2CH_3), 33.44 (CH_2Ar), 33.28 (CH_2CH_2Ar), 22.55 (CH_2CH_3), 21.22 (CH_3 Ar), 13.91 (CH_3). IR (neat): ν = 1718, 1645, 990 cm^{-1}. MS: 232 (5), 175 (18), 147 (38), 129 (100), 128 (61), 115 (68), 59 (47), 41 (47). Anal. Calcd. for $C_{15}H_{20}O_2$: C 77.55, H 8.68. Found: C 77.09, H 8.69.

Methyl (*E*)-6-ethyl-2-*n*-propylcinnamate (**2c**, Ar = 2-EtC_6H_4, R' = *n*-Pr, Y = CO_2Me) was obtained following the general procedure in 71% yield as a colourless oil (b.p. 168-171°C/7 mm Hg). ^{1}H NMR: δ 7.90 (1H, d, J = 16.3 Hz, =C*H*Ar), 7.21 (1H, t, J = 7.5 Hz, H4), 7.09, 7.07 (2H, 2 partly overlapping dd, H3, H5), 6.02 (1H, d, J = 16.3 Hz, =C*H*CO_2CH_3), 3.83 (3H, s, CO_2CH_3), 2.65 (2H, q, J = 7.5 Hz, CH_2Ar (Et)), 2.59 (2H, m, CH_2Ar (Pr)), 1.57 (2H, m, CH_2CH_3 (Pr)), 1.18 (3H, t, J = 7.5 Hz, CH_3 (Et)), 0.94 (3H, t , J = 7.3 Hz, CH_3 (Pr)). ^{13}C NMR: δ 166.95 (CO), 144.03 (=CHAr), 142.26 (C6), 140.79 (C2), 133.56 (C1), 128.23 (C4), 126.96 (C3*), 126.20 (C5*), 123.77 (=*C*HCO_2CH_3), 51.71 (CO_2CH_3), 35.81 (CH_2Ar (Pr)), 26.79 (CH_2Ar (Et)), 24.22 (CH_2CH_3 (Pr)), 15.37 (CH_3 (Et)), 14.07 (CH_3 (Pr)). IR (neat): ν = 1723, 1641, 983 cm^{-1}. MS: 232 (27), 203 (37), 172 (62), 143 (100), 129 (88), 128 (74), 115 (51). Anal. Calcd. for $C_{15}H_{20}O_2$: C 77.55, H 8.68. Found: C 77.78, H 8.64.

Methyl (*E*)-2-*n*-butyl-6-*n*-propylcinnamate (**2d**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = CO_2Me) was obtained following the general procedure in 76% yield as a colourless oil (b.p. 180-183°C/7 mm Hg). ^{1}H NMR: δ 7.90 (1H, d, *J* = 16.3 Hz, =C*H*Ar), 7.18, 7.06 (3H, AB_2 system, *J* = 7.5 Hz, H4, H3, H5), 6.01 (1H, d, *J* = 16.3 Hz, =C*H*CO_2CH_3), 3.83 (3H, s, CO_2CH_3), 2.60 (4H, m, $2CH_2$Ar), 1.56 (4H, m, $2CH_2CH_2$Ar), 1.35 (2H, sext., *J* = 7.7 Hz, CH_2CH_3 (Bu)), 0.94, 0.92 (6H, 2 partly overlapping t, CH_3(Pr), CH_3(Bu)). ^{13}C NMR: δ 166.94 (CO), 144.17 (=*C*HAr), 140.99 (C2), 140.77 (C6), 133.70 (C1), 128.03 (C4), 126.94 (C3), 126.91 (C5), 123.71 (=*C*HCO_2CH_3), 51.68 (CO_2CH_3), 35.82 (CH_2Ar (Pr)), 33.43 (CH_2Ar (Bu)), 33.28 (CH_2CH_2Ar (Bu)), 24.21 (CH_2CH_3 (Pr)), 22.56 (CH_2CH_3 (Bu)), 14.05 (CH_3 (Pr)), 13.90 (CH_3 (Bu)). IR (neat): ν = 1721, 1641, 990 cm^{-1}. MS: 260 (16), 217 (26), 203 (20), 157 (50), 129 (100), 128 (87), 115 (57). Anal. Calcd. for $C_{17}H_{24}O_2$: C 78.42, H 9.29. Found: C 78.50, H 9.23.

Methyl (*E*)-6-*n*-butyl-2-*n*-octylcinnamate (**2e**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Oct, Y = CO_2Me) was obtained following the general procedure in 45% yield as a colourless oil (b.p. 203-205°C/7 mm Hg). ^{1}H NMR: δ 7.89 (1H, d, *J* = 16.3 Hz, =C*H*Ar), 7.17, 7.06 (3H, AB_2 system, *J* = 7.5 Hz, H4, H3, H5), 6.01 (1H, d, *J* = 16.3 Hz, =C*H*CO_2CH_3), 3.83 (3H, s, CO_2CH_3), 2.60 (4H, m, $2CH_2$Ar), 1.56, 1.24 (16H, m, $8CH_2$), 0.91 (3H, t, *J* = 7.2 Hz, CH_3 (Bu)), 0.88 (3H, t, *J* = 7.1 Hz, CH_3(Oct)). ^{13}C NMR: δ 166.94 (CO), 144.16 (=*C*H Ar), 141.02 (C2, C6), 133.68 (C1), 128.05 (C4), 126.89 (C3, C5), 123.74 (=*C*HCO_2CH_3), 51.67 (CO_2CH_3), 33.77 (CH_2Ar (Oct)), 33.45 (CH_2Ar (Bu)), 33.29 (CH_2CH_2Ar (Bu)), 31.85 (CH_2 (Oct)), 31.12 (CH_2CH_2Ar (Oct)), 29.52 (CH_2 (Oct)), 29.37 (CH_2 (Oct)), 29.21 (CH_2 (Oct)), 22.64 ($2CH_2CH_3$), 14.09 (CH_3 (Oct)), 13.90 (CH_3 (Bu)). IR (neat): ν = 1726, 1646, 989 cm^{-1}. MS: 330 (5), 217 (37), 143 (41), 129 (100), 128 (49), 115 (28). Anal. Calcd. for $C_{22}H_{34}O_2$: C 79.95, H 10.37. Found: C 79.23, H 10.48.

Methyl (*E*)-6-*n*-butyl-2-*i*-propylcinnamate (**2f**, Ar = 2-*n*-BuC_6H_4, R' = *i*-Pr or Ar = 2-*i*-PrC_6H_4, R' = *n*-Bu, Y = CO_2Me) was obtained following the general procedure in 8% (run 6) and 35% (run 7) yield respectively, as a colourless oil (b.p. 177-181°C/7 mm Hg). ^{1}H NMR: δ 7.93 (1H, d, *J* = 16.3 Hz, =C*H*Ar), 7.24 (1H, t, *J* = 7.7 Hz, H4), 7.17 (2H, dd, *J* = 7.7, 1.5 Hz, H3, H5), 5.99 (1H, d, *J* = 16.3 Hz, =C*H*CO_2CH_3), 3.84 (3H, s, CO_2CH_3), 3.13 (1H, hept., *J* = 6.8 Hz, C*H*$(CH_3)_2$), 2.59 (2H, m, CH_2Ar), 1.52 (2H, m, CH_2CH_2Ar), 1.34 (2H, sext., *J* = 7.2 Hz, CH_2CH_3), 1.19 (6H, d, *J* = 6.8 Hz, $(CH_3)_2$(CH)), 0.91 (3H, t, *J* = 7.2 Hz, CH_3). ^{13}C NMR: δ 166.79 (CO), 146.81 (C2), 144.44 (=*C*HAr), 140.55 (C6), 133.16 (C1), 128.24 (C4), 126.65 (C5), 124.09 (=*C*HCO_2CH_3), 122.83 (C3), 51.69 (CO_2CH_3), 33.54 (CH_2Ar), 33.23 (CH_2CH_2Ar), 29.96 (*C*H$(CH_3)_2$), 23.87 ($(CH_3)_2$CH), 22.59 (CH_2CH_3), 13.89 (CH_3). IR (neat): ν = 1726, 1642, 986 cm^{-1}. MS: 260 (9), 217 (37), 157 (37), 143 (90), 131 (59), 129 (71), 128 (75), 115 (67), 43 (88), 41 (100). Anal. Calcd. for $C_{17}H_{24}O_2$: C 78.42, H 9.29. Found: C 78.33, H 9.25.

Methyl (*E*)-2-*t*-butyl-6-*n*-propylcinnamate (**2g**, Ar = 2-*t*-BuC_6H_4, R' = *n*-Pr, Y = CO_2Me) was obtained following the general procedure in 8% yield as a colourless oil (b.p. 175-177°C/7 mm Hg). ^{1}H NMR: δ 8.12 (1H, d, *J* = 16.4 Hz, =C*H*Ar), 7.30 (1H, dd, *J* = 8.0, 1.4 Hz, H3), 7.19 (1H, dd, *J* = 8.0, 7.5 Hz, H4), 7.10 (1H, dd, *J* = 7.5, 1.4 Hz, H5), 5.89 (1H, d, *J* = 16.4 Hz, =C*H*CO_2CH_3), 3.83 (3H, s, CO_2CH_3), 2.52 (2H, m, CH_2Ar), 1.53 (2H, m, CH_2CH_2Ar), 1.36 (9H, s, $3CH_3$), 0.91 (3H, t, *J* = 7.3 Hz, CH_3). ^{13}C NMR: δ 166.76 (CO), 148.04 (C2), 147.72 (=*C*HAr), 140.59 (C6), 134.53 (C1), 127.56 (C4), 127.15 (C5), 123.71 (C3), 123.68 (=*C*HCO_2CH_3), 51.73 (CO_2CH_3), 36.25 (Cq), 36.22 (CH_2Ar), 31.58 ($3CH_3$), 24.30 (CH_2CH_3), 14.15 (CH_3). IR (neat): ν = 1724, 1639, 990 cm^{-1}. MS: 260 (6), 203 (100), 185 (19), 143 (19), 129 (9), 128 (10), 115 (8), 57 (6). Anal. Calcd. for $C_{17}H_{24}O_2$: C 78.42, H 9.29. Found: C 78.32, H 9.33.

Methyl (*E*)-2-*n*-butyl-6-*n*-propylstyryl ketone (**2h**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = COMe) was obtained following the general procedure in 30% yield as a colourless oil (b.p. 180-184°C/7 mm Hg). ^{1}H NMR: δ 7.22 (1H, d, *J* = 16.6 Hz, =C*H*Ar), 7.19 (1H, t, *J* = 7.6 Hz, H4), 7.07 (2H, d, *J* = 7.6 Hz, H3, H5), 6.27 (1H, d, *J* = 16.6 Hz, =C*H*$COCH_3$), 2.59 (4H, m, $2CH_2$Ar), 2.40 (3H, s, $COCH_3$), 1.52 (4H, m, $2CH_2CH_2$Ar), 1.34 (2H, sext., *J* = 7.3 Hz, CH_2CH_3 (Bu)), 0.93, 0.91 (6H, 2 partly overlapping t, CH_3 (Pr), CH_3 (Bu)). ^{13}C NMR: δ 198.18 (CO), 142.66 (=*C*HAr), 140.72 (C2, C6), 133.66 (C1), 133.33 (=*C*H$COCH_3$), 128.18 (C4), 127.05 (C3*), 127.02 (C5*), 35.91 (CH_2Ar (Pr)), 33.52 (CH_2Ar (Bu)), 33.31 (CH_2CH_2Ar (Bu)), 27.46 ($COCH_3$), 24.23 (CH_2CH_3 (Pr)),

22.60 (CH_2CH_3 (Bu)), 14.09 (CH_3 (Pr)), 13.92 (CH_3 (Bu)). IR (neat): ν = 1676, 1616, 985 cm^{-1}. MS: 244 (4), 201 (87), 187 (100), 129 (34), 128 (35), 115 (20), 43 (36). Anal. Calcd. for $C_{17}H_{24}O$: C 83.55, H 9.90. Found: C 83.48, H 9.92.

(*E*)-2-*n*-Butyl-6-*n*-propylcinnamonitrile (**2i**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = CN) was obtained following the general procedure in 20% yield as a colourless oil (b.p. 175-177°C/7 mm Hg). ^{1}H NMR: δ 7.63 (1H, d, *J* = 17.0 Hz, =C*H*Ar), 7.21 (1H, t, *J* = 7.6 Hz, H4), 7.07 (2H, d, *J* = 7.6 Hz, H3, H5), 5.51 (1H, d, *J* = 17.0 Hz, =C*H*CN), 2.57 (4H, m, 2CH_2Ar), 1.51 (4H, m, 2C$H_2$$CH_2$Ar), 1.37 (2H, sext., *J* = 7.2 Hz, C$H_2$$CH_3$ (Bu)), 0.95, 0.93 (6H, 2 partly overlapping t, CH_3 (Pr), CH_3 (Bu)). ^{13}C NMR: δ 150.59 (=*C*HAr), 140.86 (C2*), 140.65 (C6*), 132.69 (C1), 128.93 (C4), 127.23 (C3**), 127.21 (C5**), 117.64 (CN), 102.71 (=*C*HCN), 35.78 (*C*H_2Ar (Pr)), 33.44 (*C*H_2Ar (Bu)), 33.37 (*C*$H_2$$CH_2$Ar (Bu)), 24.29 (*C*$H_2$$CH_3$ (Pr)), 22.59 (*C*$H_2$$CH_3$ (Bu)), 14.03 (CH_3 (Pr)), 13.92 (CH_3 (Bu)). IR (neat): ν = 2220 cm^{-1}. MS: 227 (15), 199 (22), 185 (43), 157 (37), 156 (100), 142 (29), 129 (35), 128 (33), 127 (24), 115 (43). Anal. Calcd. for $C_{16}H_{21}N$: C 84.53, H 9.31. Found: C 84.58, H 9.29.

(*E*)-2-*n*-Butyl-6-*n*-propylstilbene (**2j**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = C_6H_5) was obtained following the general procedure in 10% yield as a colourless oil (b.p. 203-206°C/7 mm Hg). ^{1}H NMR: δ 7.50 (2H, m, H2', H6'), 7.39 (2H, m, H3', H5'), 7.29 (1H, tt, *J* = 7.3, 1.4 Hz, H4'), 7.19-7.04 (4H, m, H3, H4, H5, =C*H*Ph centred at 7.15), 6.54 (1H, d, *J* = 16.6 Hz, =C*H*Ar), 2.67, 2.65 (4H, 2 partly overlapping t, *J* = 7.3 Hz, 2CH_2Ar), 1.59 (4H, m, 2C$H_2$$CH_2$Ar (Bu+Pr)), 1.33 (2H, sext., *J* = 7.4 Hz, C$H_2$$CH_3$ (Bu)), 0.93 (3H, t, *J* = 7.3 Hz, CH_3 (Pr)), 0.89 (3H, t, *J* = 7.4 Hz, CH_3 (Bu)). ^{13}C NMR: δ 141.18 (C2), 140.98 (C6), 137.66 (C1*), 136.61 (C1'*), 133.73 (=*C*HAr), 128.66 (C3', C5'), 127.46 (C4'), 126.84 (=*C*HPh), 126.75, 126.70, 126.67 (C3, C4, C5), 126.28 (C2', C6'), 36.02 (CH_2Ar (Pr)), 33.58 (CH_2Ar (Bu)), 33.33 (*C*$H_2$$CH_2$Ar (Bu)), 24.21 (*C*$H_2$$CH_3$ (Pr)), 22.68 (*C*$H_2$$CH_3$ (Bu)), 14.21 (CH_3 (Pr)), 14.01 (CH_3 (Bu)). MS: 278 (60), 249 (53), 235 (98), 193 (62), 145 (65), 129 (53), 115 (95), 91 (100). IR (neat): ν = 968, 755 cm^{-1}. Anal. Calcd. for $C_{21}H_{26}$: C 90.59, H 9.41. Found: C 90.67, H 9.33.

(*E*)-2-*n*-Butyl-6-*n*-propyl-4'-methylstilbene (**2k**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = 4-MeC_6H_4) was obtained following the general procedure in 11% yield as a colourless oil (b.p. 206-211°C/7 mm Hg). ^{1}H NMR: δ 7.39 (2H, m, H2', H6'), 7.19 (2H, m, H3', H5'), 7.15-7.03 (4H, m, H3, H4, H5, =C*H*(4-MeC_6H_4) centred at 7.10), 6.50 (1H, d, *J* = 16.6 Hz, =C*H*Ar), 2.65 (4H, m, 2CH_2Ar), 2.38 (3H, s, CH_3Ar), 1.56 (4H, m, 2C$H_2$$CH_2$Ar (Bu+Pr)), 1.32 (2H, m, C$H_2$$CH_3$ (Bu)), 0.92 (3H, t, *J* = 7.3 Hz, CH_3 (Pr)), 0.88 (3H, t, *J* = 7.3 Hz, CH_3 (Bu)). ^{13}C NMR: δ 141.21 (C2, C6), 141.01 (C4'), 137.32 (C1), 134.90 (C1'), 133.56 (=*C*HAr), 129.35 (C3', C5'), 126.67 (C4*), 126.65 (C3*, C5*), 126.18 (C2', C6'), 125.82 (=*C*H(4-MeC_6H_4)), 36.05 (CH_2Ar (Pr)), 33.59 (CH_2Ar (Bu)), 33.34 (*C*$H_2$$CH_2$Ar (Bu)), 24.21 (*C*$H_2$$CH_3$ (Pr)), 22.69 (*C*$H_2$$CH_3$ (Bu)), 21.21 (CH_3Ar), 14.22 (CH_3 (Pr)), 14.01 (CH_3 (Bu)); MS: 292 (56), 263 (53), 249 (100), 207 (51), 145 (66), 129 (82), 115 (62), 105 (90), 91 (35). IR (neat): ν = 971, 799 cm^{-1}. Anal. Calcd. for $C_{22}H_{28}$: C 90.35, H 9.65. Found: C 90.31, H 9.69.

(*E*)-2-*n*-Butyl-6-*n*-propyl-4'-fluorostilbene (**2l**, Ar = 2-*n*-BuC_6H_4, R' = *n*-Pr, Y = 4-FC_6H_4) was obtained following the general procedure in 29% yield as a colourless oil (b.p. 199-202°C/7 mm Hg). ^{1}H NMR: δ 7.45 (2H, m, H2', H6'), 7.18-7.01 (6H, m, H3', H5', H3, H4, H5, =C*H*(4-FC_6H_4)), 6.49 (1H, d, *J* = 16.6 Hz, =C*H*Ar), 2.64 (4H, m, 2 CH_2Ar), 1.56 (4H, m, 2 C$H_2$$CH_2$Ar (Bu+Pr)), 1.33 (2H, sext., *J* = 7.3 Hz, C$H_2$$CH_3$ (Bu)), 0.92 (3H, t, *J* = 7.3 Hz, CH_3 (Pr)), 0.89 (3H, t, *J* = 7.3 Hz, CH_3 (Bu)). MS: 296 (10), 253 (18), 145 (29), 129 (29), 115 (40), 109 (71), 57 (36), 43 (87), 41 (100). IR (neat): ν = 965, 802 cm^{-1}. Anal. Calcd. for $C_{21}H_{25}F$: C 85.09, H 8.50. Found: C 85.00, H 8.51.

cis,exo 5-Ethyl-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**3b**) was obtained following the general procedure in 5% yield as a colourless oil (b.p. 112-115°C/760 mm Hg). ^{1}H NMR: δ 7.16 (1H, t, *J* = 7.5 Hz, H7), 7.02 (1H, d further split, *J* = 7.8 Hz, H6), 6.85 (1H, br d, *J* = 7.1 Hz, H8), 3.21 (1H, d, *J* = 3.9 Hz, H8b), 3.16 (1H, d, *J* = 3.9 Hz, H4a), 2.58, 2.57 (2H, 2 partly overlapping q, *J* = 7.6 Hz, CH_2Ar), 2.33 (1H, m, H1), 2.28 (1H, m, H4), 1.71-1.56 (2H, m, H2 *exo*, H3 *exo*), 1.25 (3H, t, *J* = 7.6 Hz, CH_3), 1.25-1.16 (2H, m, H2 *endo*, H3 *endo*), 0.99 (1H, d quint., *J* = 10.1, 1.4 Hz, H9 *anti*), 0.90 (1H, d quint., *J* = 10.1, 1.8 Hz, H9 *syn*). ^{13}C NMR: δ 146.32, 144.27, 138.47, (quaternary C), 127.58 (C7), 126.42 (C6), 119.13 (C8), 49.90 (C4a*), 49.89 (C8b*), 36.48 (C4),

36.35 (C1), 31.94 (C9), 27.88 (C2**) 27.84 (C3**), 24.90 (CH_2CH_3), 14.85 (CH_3). MS: 198 (11), 157 (100), 141 (37), 129 (50), 128 (31), 115 (31). IR (neat): ν = 1609, 779 cm^{-1}. Anal. Calcd. for $C_{15}H_{18}$: C 90.85, H 9.15. Found: C 90.90, H 9.10.

cis,exo 5-*n*-Butyl-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**3c**) was obtained following the general procedure in 24% yield (run 4) as a colourless oil (b.p. 122-125°C/760 mm Hg). ^{1}H NMR: δ 7.18 (1H, t, *J* = 7.5 Hz, H7), 7.03 (1H, d, further split, H6), 6.87 (1H, d, *J* = 7.4 Hz, H8), 3.23 (1H, d, *J* = 3.9 Hz, H4a*), 3.19 (1H, d, *J* = 3.9 Hz, H8b*), 2.57 (2H, ABX_2 system, CH_2Ar), 2.35 (1H, m, H4**), 2.31 (1H, m, H1**), 1.72-1.60 (4H, m, CH_2CH_2Ar, H2 *exo*, H3 *exo*), 1.42 (2H, m, CH_2CH_3), 1.29-1.20 (2H, m, H2 *endo*, H3 *endo*), 1.02 (1H, d quint. partly overlapping with CH_3, H9), 1.00 (3H, t, *J* = 7.3 Hz, CH_3), 0.94 (1H, d quint., *J* = 10.1, 1.8 Hz, H9). ^{13}C NMR: δ 146.20, 144.50, 137.15, (quaternary C), 127.48 (C7), 127.05 (C6), 119.06 (C8), 49.91 (C4a*), 49.81 (C8b*), 36.51 (C4**), 36.32 (C1**), 32.71 (CH_2CH_2Ar), 31.95 (C9), 31.45 (CH_2Ar), 27.89 (C2, C3), 22.54 (CH_2CH_3), 13.97 (CH_3). MS: 226 (11), 185 (100), 143 (31), 141 (39), 129 (33), 128 (28), 115 (24). IR (neat): ν = 1609, 775 cm^{-1}. Anal. Calcd. for $C_{17}H_{22}$: C 90.20, H 9.80. Found: C 90.16, H 9.84.

cis,exo 5-*i*-Propyl-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**3d**) was obtained following the general procedure in 24% yield as a colourless oil (b.p. 112-116°C/760 mm Hg). ^{1}H NMR: δ 7.22 (1H, t, *J* = 7.5 Hz, H7), 7.09 (1H, d, *J* = 7.5 Hz, H6), 6.90 (1H, d, *J* = 7.5 Hz, H8), 3.30 (1H, d, *J* = 3.8 Hz, H4a), 3.21 (1H, d, *J* = 3.8 Hz, H8b), 2.95 (1H, hept., *J* = 6.9 Hz, $CH(CH_3)_2$), 2.42 (1H, m, H4), 2.34 (1H, m, H1), 1.78-1.60 (2H, m, H2 *exo*, H3 *exo*), 1.34, 1.33 (6H, 2 d, *J* = 6.9 Hz, 2 CH_3), 1.30-1.25 (2H, m, H2 *endo*, H3 *endo*), 1.06, 0.99 (2H, AB system, 2 H9). ^{13}C NMR: δ 146.54, 143.32, 143.29 (quaternary C), 127.58 (C7), 124.94 (C6), 119.12 (C8), 50.68 (C4a), 49.94 (C8b), 36.89 (C4), 36.57 (C1), 31.84 (C9), 31.54 ($CH(CH_3)_2$), 27.91 (C2, C3), 23.82 (CH_3), 22.99 (CH_3). MS: 212 (7), 171 (100), 141 (36), 129 (63), 128 (27), 115 (26), 43 (55), 41 (48). IR (neat): ν = 1609, 776 cm^{-1}. Anal. Calcd. for $C_{16}H_{20}$: C 90.51, H 9.49. Found: C 90.47, H 9.53.

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