Palladium-catalysed synthesis of nonsymmetrically disubstituted-1,1′-biphenyls from *o*-substituted aryl iodides through aryl coupling and delayed hydrogenolysis[1]

Sara Deledda, Elena Motti, and Marta Catellani

Abstract: In the presence of $Pd(OAc)_2$ and norbornene as catalysts, two molecules of an ortho-substituted aryl iodide undergo aryl–aryl coupling to a palladium-bonded biphenylyl intermediate, which is hydrogenolyzed by benzyl alcohol to give 2,3′-disubstituted biaryl derivatives in satisfactory yields. A curious behaviour was observed with *o*-chloroiodobenzene, which gave activation of the C—Cl bond with four-membered ring formation.

Key words: biphenyls, aryl–aryl coupling, multistep reactions, palladium, palladacycles, C-H activation, catalysis.

Résumé : En présence de $Pd(OAc)_2$ et de norbornène agissant comme catalyseurs, deux molécules d'iodure d'aryle substituées en ortho subissent une réaction de couplage aryle–aryle conduisant à un intermédiaire biphénylyle lié au palladium qui peut subir une réaction d'hydrogénolyse sous l'action de l'alcool benzylique pour conduire à la formation de dérivés biaryles 2,3′-disubstitués, avec des rendements satisfaisants. On a observé un comportement bizarre avec l'*o*-chloroiodobenzène donne lieu à une activation de la liaison C—Cl avec formation d'un cycle à quatre membres.

Mots clés : biphényles, couplage aryle–aryle, réactions en plusieurs étapes, palladium, palladacyles, activation C-H, catalyse.

[Traduit par la Rédaction]

Introduction

Biphenyls are an important class of organic compounds, the biphenyl unit being the building block of several types of structures of current interest, including natural products, polymers, advanced materials, liquid crystals, ligands, and drugs (1).

The most successful catalytic methods in biphenyl synthesis are based on palladium catalysis (2–7). We used a catalytic system involving palladacycles (8–13). Different types of the latter have been extensively studied by several groups (14–17).

According to our methodology, aryl–aryl coupling through palladacycles occurs regioselectively. As shown in the simplified Scheme 1 (L = solvent or coordinating molecule), these palladacycles are formed by the reaction of an aryl iodide with palladium(0) and norbornene. In the presence of an *ortho*-R substituent (alkyl, aryl, and other functional groups), the palladacycle reacts selectively with the aryl iodide to form an sp^2–sp^2 carbon–carbon bond at the aryl site (pathway a), while the remaining norbornylpalladium bond readily deinserts norbornene to afford a biphenylylpalladium complex (18). By contrast, when the R substituent is H or a small group like F, the aryl group preferentially migrates on the norbornyl site of the palladacycle (pathway b) (18).

Causing the biphenylylpalladium complex to undergo a reaction able to liberate the organic product and palladium(0) renders the process catalytic. In this way the synthesis of a variety of interesting classes of organic compounds such as selectively substituted phenanthrenes (19), terphenyls (20), and biphenyl derivatives containing an oxoalkyl (21) or a vinyl (22) chain has been achieved.

We now report a catalytic synthesis of 2,3′-disubstituted-1,1′-biphenyls, based on the combination of the stoichiometric sequence leading to the biphenylylpalladium species with a delayed hydrogenolysis reaction.

Results and discussion

As shown in Scheme 2, two molecules of an ortho-substituted aryl iodide and one of a hydrogen donor react in the presence of $Pd(OAc)_2$ and norbornene as catalysts, and K_2CO_3 as a base in a dipolar aprotic solvent such as 1-methyl-2-pyrrolidinone (NMP) at 105 °C for 24 h to give 2,3′-disubstituted-1,1′-biphenyls (**1**).

The main difficulty for the achievement of this synthesis laid in obtaining an efficient hydrogenolysis of the

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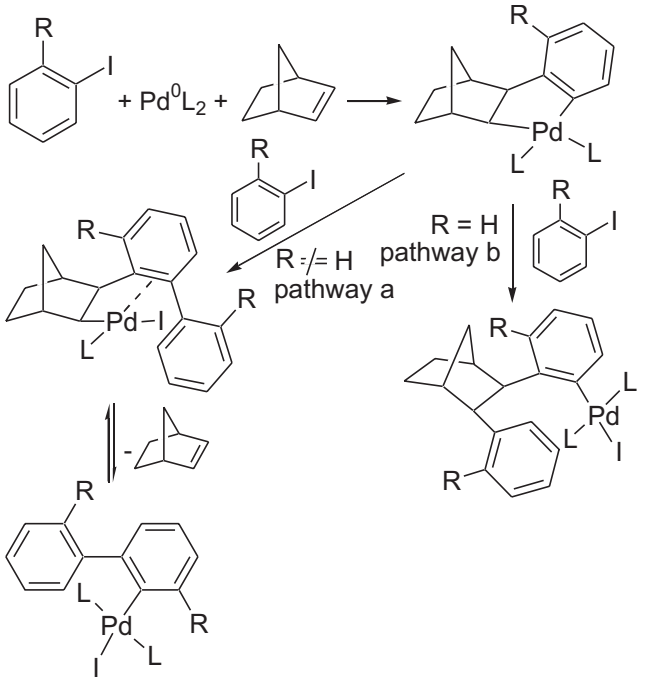
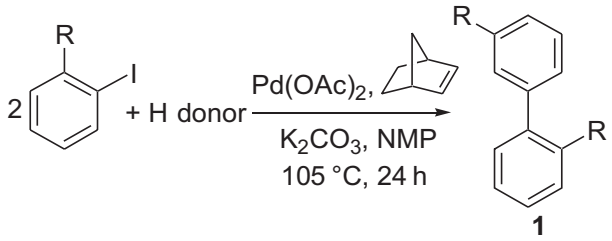
Scheme 1.



Scheme 2.



biphenylylpalladium species without interfering with the previous steps. To effect hydrogenolysis, two main methods were available: hydrogenation of the C-Pd-I bond with dihydrogen and hydrogen transfer from suitable sources. In principle, with both methods a selectivity problem could be expected since hydrogenolysis can occur at any step of the sequence. However, while hydrogenation with dihydrogen at atmospheric pressure gave a nonselective outcome, the appropriate use of the hydrogen transfer methodology led to delayed hydrogenolysis to the end of the catalytic sequence with good selectivity.

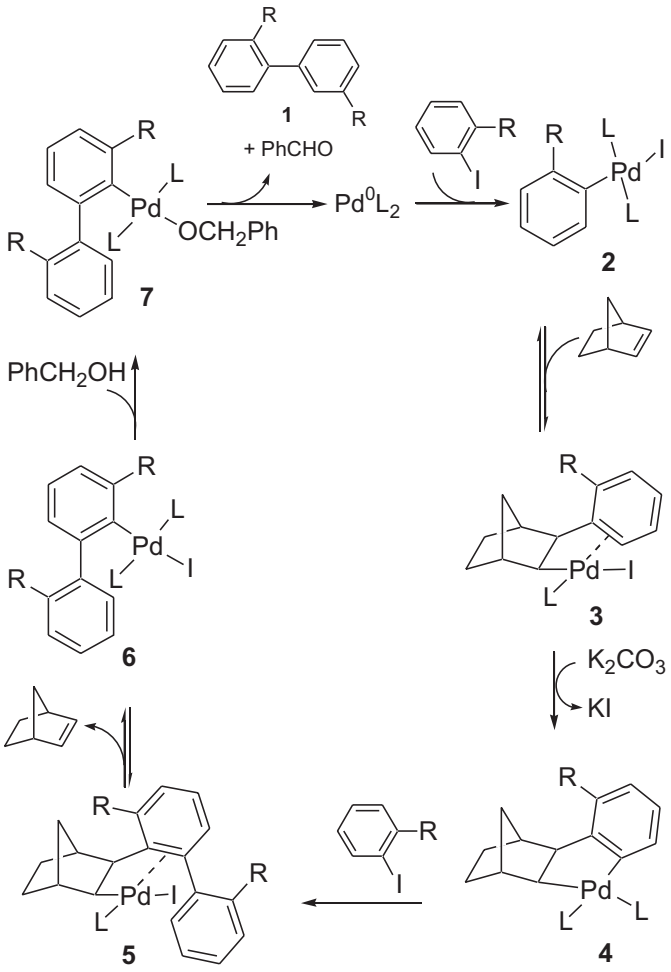
Among the combination of palladium sources, solvents, and bases examined, $Pd(OAc)_2$, NMP, and K_2CO_3 proved to be the most effective. The norbornene to aryl iodide molar ratio was found to play an important role, better results being obtained when using a ratio as low as 0.25 equiv. The reaction of *o*-isopropyliodobenzene (80 equiv.) with different hydrogen donors (80 equiv.) was thus carried out in the presence of $Pd(OAc)_2$ (1 equiv.), K_2CO_3 (160 equiv.), norbornene (20 equiv.) in NMP at 105 °C for 24 h under nitrogen. Various hydrogen donors were tested in a 1:1 molar ratio to *o*-isopropyliodobenzene as the substrate. Table 1 reports the yield of the biphenyl **1** (Scheme 2, R = *i*-Pr) obtained. Among the examined hydrogen sources, benzyl

Table 1. Reaction of *o*-*i*-propyliodobenzene and a H donor in the presence of K_2CO_3, norbornene, and $Pd(OAc)_2$.[a]

Run	Hydrogen donor	Biphenyl **1** yield (%)[b]
1	Benzyl alcohol	86
2	Benzydrol	84
3	Butanol	75
4	Isobutyl formate	72
5	Sodium formate	21
6	Water	37, 77[c]

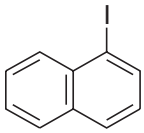
[a]Molar ratio of the reagents *o*-*i*-propyliodobenzene : H donor : K_2CO_3 : norbornene : $Pd(OAc)_2$ = 80:80:160:20:1 at 105 °C for 24 h in NMP under nitrogen; 2×10^{-3} mmol $Pd(OAc)_2$/mL NMP.
[b]GC yield on the charged amount of the aryl iodide.
[c]Water to palladium molar ratio: 2.5×10^2.

Scheme 3.



alcohol and benzhydrol appear the most effective ones (Table 1, runs 1 and 2). Butanol (Table 1, run 3) and isobutyl formate (Table 1, run 4) behave analogously affording satisfactory results, while sodium formate (23) (Table 1, run 5) gives a low yield because of the formation of products resulting from Pd-C hydrogenolysis of the intermediate complexes **3** and **4** reported in Scheme 3. Water also is effective (Table 1, run 6) but only if used in large excess (2.5×10^2 molar ratio to palladium) otherwise the reaction leads to

Table 2. Reaction of ortho-substituted aryl iodides and benzyl alcohol in the presence of K_2CO_3, norbornene, and $Pd(OAc)_2$.[a]

Run	Aryl iodide	Biphenyl **1** yield (%)[b]
1	*o*-MeC_6H_4I	72
2	*o*-EtC_6H_4I	84
3	*o*-*n*-BuC_6H_4I	79
4	*o*-*i*-PrC_6H_4I	83
5	*o*-$MeO_2CC_6H_4I$	87
6	*o*-$MeOC_6H_4I$	48
7		78

[a]Molar ratio of the reagents in the order reported in the title: 80:80:160:20:1 at 105 °C for 24 h in NMP, N_2 atmosphere; 2×10^{-3} mmol $Pd(OAc)_2$/mL NMP.
[b]Isolated yield on the charged aryl iodide. Conversion was complete.

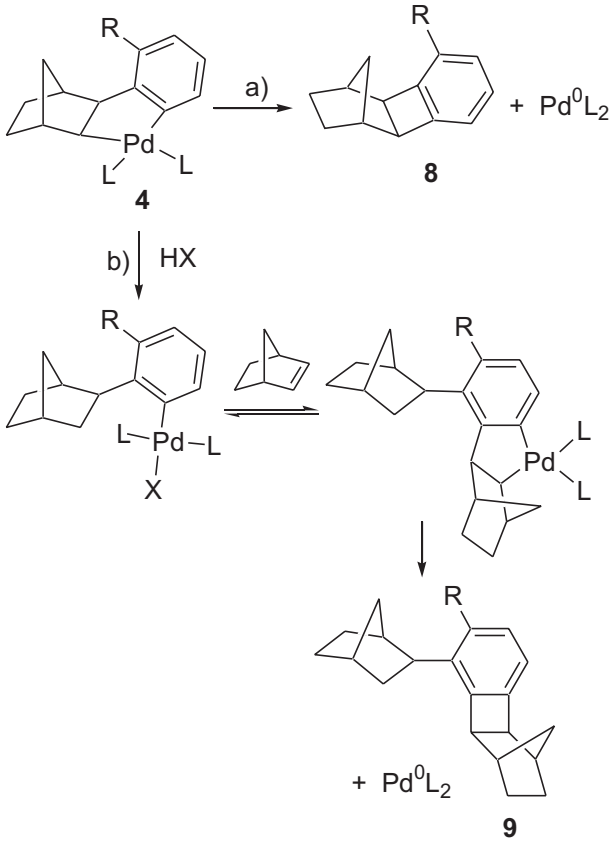
poor results. An aryl iodide to benzyl alcohol molar ratio of 1:1 was found to be optimal, an excess of benzyl alcohol being detrimental.

Scheme 3 shows the proposed reaction pathway. The catalytic cycle is initiated by the oxidative addition of the *o*-substituted aryl iodide to palladium(0) formed in situ by $Pd(OAc)_2$ reduction. Norbornene insertion into the resulting arylpalladium complex **2** occurs stereoselectively leading to the *cis*,*exo* arylnorbornylpalladium species **3** (24–28). In the presence of a base such as K_2CO_3, the open precursor undergoes ring closure to **4** (10–13) through an electrophilic aromatic substitution (11) facilitated by an η^2-interaction of palladium with one double bond of the aromatic ring (25, 28). Palladacycle formation implies activation of an usually inert aromatic C—H bond (29–31). Because of the presence of the ortho substituent in the aromatic ring of palladacycle **4**, a second molecule of aryl iodide selectively attacks the aromatic moiety of the same palladacycle **4** affording complex **5**, which deinserts norbornene with formation of the biphenylylpalladium species **6** (18). At this stage, complex **6** reacts with benzyl alcohol to give **7**, which promotes hydrogen transfer via a Pd-H intermediate to form biphenyl **1** together with palladium(0) and benzaldehyde.

Table 2 reports the results obtained carrying out the reaction with an *o*-substituted aryl iodide (80 equiv.), benzyl alcohol (80 equiv.), palladium acetate (1 equiv.), norbornene (20 equiv.), and potassium carbonate (160 equiv.) in NMP under nitrogen at 105 °C for 24 h. Satisfactory results were obtained with different primary and secondary alkyl groups as well as with electron-withdrawing substituents (Table 2, runs 1–5) while the presence of an electron-releasing group such as the methoxy one (Table 2, run 6) led only to poor results. 1-Iodonaphthalene (Table 2, run 7) behaved as an ortho-substituted arene, which is a requirement for the aryl coupling to occur, and gave acceptable yields.

By-products result from hydrogen transfer to intermediate complexes. The hydrogen donor mostly reacts with the species containing a norbornyl– rather than an aryl–palladium bond. In particular, arylnorbornylpalladium iodide **3** is readily hydrogenolysed to the corresponding arylnorbornane and

Scheme 4.



palladacycle **4**, after hydrogenolysis of the norbornylpalladium bond, inserts a new molecule of norbornene in the resulting Pd–aryl bond to form **9** according to pathway b of Scheme 4. Compound **8** also derives from palladacycle **4** as shown in Scheme 4. The steric effect of the ortho substituent favours reductive elimination to compound **8**, containing a four-membered ring (pathway a) (32), in place of the reaction with a second molecule of aryl iodide. By-products **8** and **9** were usually formed with a yield from 1% to 5%.

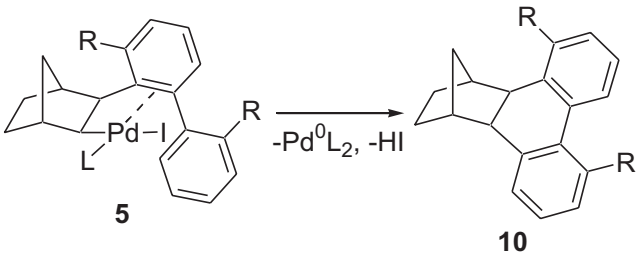
A 5,9-disubstituted 1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene derivative of type **10** (33, 34), was usually formed to a large extent when the hydrogen donor became deficient owing to secondary reactions. As shown in Scheme 5, **10** derives from complex **5**, which, in the absence of an efficient terminating agent, prefers to undergo reductive elimination by ring closure instead of norbornene deinsertion.

As previously reported, if R is a methyl group, two additional by-products resulting from activation of the benzylic C-H (35) were formed to a small extent (5%).

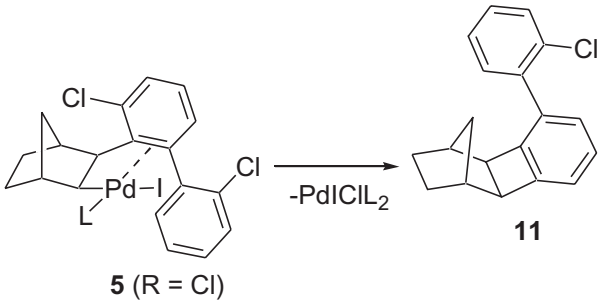
Anomalous behaviours were observed with *o*-chloro- and *o*-fluoroiodobenzene.

o-Chloroiodobenzene, used in a 40:1 molar ratio to palladium, gave poor conversion (28%) and only a small amount (6%) of **1** was formed. The main product was the hexahydromethanobiphenylene derivative **11** (15%), which derives from C—Cl bond activation (Scheme 6). This result is surprising not only because it implies activation of an usually inert C—Cl bond, but also because it should be regarded as involving the C—Cl bond of the norbornyl-bonded *o*-

Scheme 5.



Scheme 6.



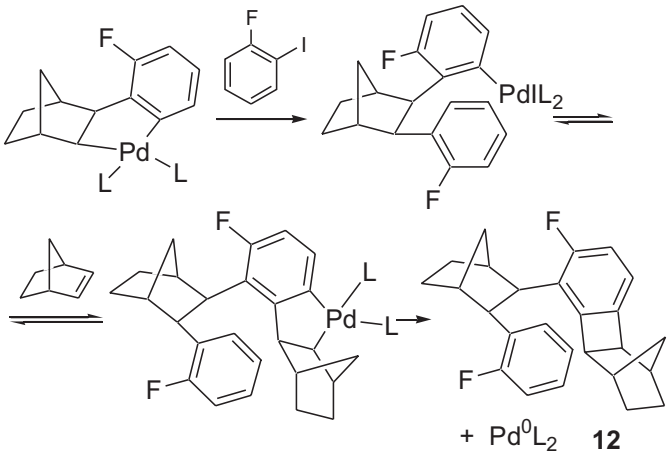
chloroaryl group of complex **5** (Scheme 6), C—Cl bond activation occurring only in the presence of a second *o*-chloroaryl unit. The alternative formation of a type **10** compound does not occur. The origin of this behaviour is probably to be attributed to a Pd-Cl interaction that favours C-Cl activation, thus preventing not only formation of a type **10** compound but also norbornene deinsertion.

As previously reported (22), the different reactivity of the F group is likely to be ascribed to the small size of the fluorine atom. The latter is not large enough to give "the ortho effect", which would cause the formation of the aryl–aryl bond of intermediate **5** by reaction of palladacycle **4** with *o*-fluoroiodobenzene (Scheme 3, R = F), and so the *ortho*-fluorophenyl group migrates to the norbornyl site of the palladacycle. Ring closure to hexahydromethanotriphenylene does not occur, however, because of the deactivation of the aromatic nucleus towards the arylpalladium electrophilic attack and norbornene is instead inserted. The reaction thus terminates with the formation of the hexahydromethanobiphenylene **12** in 67% yield, as reported in Scheme 7.

Conclusion

In conclusion, the catalytic method we have worked out offers a ready access to nonsymmetrically disubstituted biphenyls starting from two molecules of an *o*-substituted aryl iodide and represents a useful alternative to the Suzuki reaction and to other organometallic processes. The failure of *o*-fluoroiodobenzene to give the expected reaction confirms the need for a sufficiently bulky group ortho to iodobenzene, while the observation that the usually unreactive arene C—Cl bond is readily cleaved shows that competitive steps readily occur in sequential reactions when usually inert bonds are forced into the appropriate position for the interaction with the metal.

Scheme 7.



Experimental

General

All reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Most chemicals were obtained commercially and used as received. Compounds **1** (R = Me (36), Et (37), OMe (38), CO_2Me (39), -$(CH)_4$- (40), Cl (41)), **8** (R = Me, OMe (32), Et, *n*-Bu, *i*-Pr (42), -$(CH)_4$- (43)), **9** (R = Me, Et, *n*-Bu, *i*-Pr (20), -$(CH)_4$- (43)), and **12** (22) were previously reported. ^{1}H and ^{13}C NMR spectra were carried out in $CDCl_3$ at 20 °C using Bruker AC300 and AVANCE300 spectrometers at 300.1 and 75.4 MHz, respectively. Chemical shifts are reported in ppm using the solvent as the internal reference. The assignments of NMR resonances are based on decoupling and 2D experiments; one or more asterisks indicates interchangeable assignments. Mass spectra (EI) were recorded using a Finnigan Mat SSQ 710 spectrometer operating at 70 eV and are reported as *m*/*z* (relative intensity). IR spectra were run on a PerkinElmer 298 FT-IR spectrophotometer and are reported as wavenumbers (cm^{-1}). GC analyses were performed with a Carlo Erba HRGC 5300 instrument using a 30 m long SE-30 capillary column and a Hewlett-Packard 3394 integrator. Flash column chromatography was performed on Merck Kieselgel 60 and analytical TLC on Merck 60F_{254} plates. Melting points were determined on an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108 elemental analyser.

Reaction of *o*-substituted aryl iodides with benzyl alcohol

General procedure

A mixture of $Pd(OAc)_2$ (5 mg, 0.022 mmol), K_2CO_3 (498 mg, 3.6 mmol), the desired aryl iodide (1.8 mmol), norbornene (42 mg, 0.45 mmol), and benzyl alcohol (195 mg, 1.8 mmol) in NMP (10 mL) under nitrogen was heated at 105 °C with stirring for 24 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2 (20 mL), and extracted twice with a 5% solution of H_2SO_4 (2 × 15 mL). The organic layer was washed with water (20 mL) and dried over anhydr. Na_2SO_4. The crude product was ana-

lysed by GC, GC–MS, and TLC. Products were isolated by flash column chromatography using hexane or mixtures of hexane–EtOAc as the eluents. By-product yields were determined by GC analysis.

2,3′-Dimethyl-1,1′-biphenyl (1, R = Me)

The reaction was carried out following the general procedure using 393 mg (1.8 mmol) of *o*-iodotoluene. Compound **1** (R = Me) (36) was isolated as a colourless oil in 72% yield (118 mg) by column chromatography, using hexane as the eluent. Compounds **8** (R = Me) (32) and **9** (R = Me) (20) were formed in 2% and 3% yield, respectively, together with two by-products resulting from the activation of the benzylic C—H bond (35) (2% yield each) and *exo*,*o*-tolylnorbornane (4%) (44) resulting from hydrogenolysis of complex **3** (R = Me).

2,3′-Diethyl-1,1′-biphenyl (1, R = Et)

The reaction was carried out following the general procedure using 418 mg (1.8 mmol) of *o*-ethyliodobenzene. Compound **1** (R = Et) (37) was isolated as a colourless oil in 84% yield (159 mg) by column chromatography, using hexane as the eluent. Compounds **8** (R = Et) (42) and **9** (R = Et) (20) were formed in 4% and 5% yield, respectively.

2,3′-Di*-i-*propyl-1,1′-biphenyl (1, R = i-Pr)

The reaction was carried out following the general procedure using 443 mg (1.8 mmol) of *o*-*i*-propyliodobenzene. Compound **1** (R = *i*-Pr) was isolated as a white solid in 83% yield (178 mg) by column chromatography, using hexane as the eluent. Compounds **8** (R = *i*-Pr) (42), **9** (R = *i*-Pr) (20), and **10** (R = *i*-Pr) were formed in 5%, 3%, and 2% yield, respectively.

***1** (R = i-Pr)*

^{1}H NMR δ: 7.44–7.30 (3H, m), 7.27–7.16 (4H, m), 7.13 (1H, dt, *J* = 7.4, 1.4 Hz), 3.07, 2.96 (2H, 2 hept. partly overlapping, *J* = 6.9 Hz), 1.30 (6H, d, *J* = 6.9 Hz), 1.18 (6H, d, *J* = 6.9 Hz). ^{13}C NMR δ: 148.45, 146.38, 141.98, 141.40, 129.91, 127.82, 127.52, 126.66, 125.53, 125.22, 124.82, 34.06, 29.37, 24.34, 24.02. MS *m*/*z* (%): 238 (M^+, 61), 223 (33), 195 (81), 181 (100), 179 (21), 165 (29). Anal. calcd. for $C_{18}H_{22}$: C 90.70, H 9.30; found: C 90.82, H 9.18.

5,9-Di-i-*propyl-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene (**10**, R = i-Pr)*

^{1}H NMR δ: 7.29–7.24 (1H, m, H8), 7.23–7.17 (3H, m, H10, H6, H7), 7.14 (1H, t, *J* = 7.5 Hz, H11), 7.03 (1H, d further split, *J* = 7.3 Hz, H12), 3.76 (1H, hept., *J* = 6.8 Hz, CH(C9)), 3.34 (1H, d, *J* = 9.4 Hz, H12b), 3.20 (1H, hept., *J* = 6.8 Hz, CH(C5)), 3.06 (1H, d, *J* = 9.4 Hz, H4a), 2.30 (1H, m, H4), 2.21 (1H, m, H1), 1.81–1.56 (4H, m, H2 exo, H3 exo, H2 endo, H3 endo), 1.53 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH(C9)), 1.36 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH(C5)), 1.24–1.17 (4H, m, H13 syn, C*H*$_3$CH(C5) centred at 1.21), 1.06 (3H, d, *J* = 6.8 Hz, C*H*$_3$CH(C9)), 0.96 (1H, d quintets, *J* = 10.0, 1.5 Hz, H13 anti). ^{13}C NMR δ: 147.45, 145.26, 140.04, 135.73, 133.94, 132.69, 126.99 (C8), 126.67 (C11), 125.64 (C7*), 125.19 (C12), 124.87 (C10), 124.27 (C6*), 48.57 (C1), 47.63 (C4, C12b), 42.82 (C4a), 33.77 (C13), 32.10 (C3), 30.52 (CH(C9)), 28.64 (CH(C5)), 28.28 (C2), 26.71 (*C*H$_3$CH(C9)), 24.65 (*C*H$_3$CH(C5)), 24.03 (*C*H$_3$CH(C9)), 23.57 (*C*H$_3$CH(C5)). MS *m*/*z* (%): 330 (M^+, 63), 262 (25), 245 (26), 205 (76), 203 (39), 202 (37), 179 (100). Anal. calcd. for $C_{25}H_{30}$: C 90.85, H 9.15; found: C 90.98, H 9.02.

2,3′-Di*-n-*butyl-1,1′-biphenyl (1, R = n-Bu)

The reaction was carried out following the general procedure using 469 mg (1.8 mmol) of *o*-*n*-butyliodobenzene. Compound **1** (R = *n*-Bu) was isolated as a colourless oil in 79% yield (190 mg) by column chromatography, using hexane as the eluent. Compounds **8** (R = *n*-Bu) (42) and **9** (R = *n*-Bu) (20) were formed in 4% and 3% yield, respectively.

***1** (R = n-Bu)*

^{1}H NMR δ: 7.35–7.27 (3H, m), 7.24–7.20 (2H, m), 7.19–7.09 (3H, m), 2.66 (2H, t, *J* = 7.6 Hz), 2.61–2.54 (2H, m), 1.70–1.57 (2H, m), 1.57–1.30 (6H, m), 1.30–1.09 (2H, m), 0.94 (3H, t, *J* = 7.3 Hz), 0.80 (3H, t, *J* = 7.3 Hz). ^{13}C NMR δ: 142.44, 142.03, 141.85, 140.35, 129.94, 129.40, 129.18, 127.79, 127.14, 126.77, 126.46, 125.42, 35.61, 33.65, 32.74, 22.53, 22.29, 13.96, 13.83. MS *m*/*z* (%): 266 (M^+, 39), 223 (20), 209 (22), 180 (16), 178 (16), 167 (100), 152 (10). Anal. calcd. for $C_{20}H_{26}$: C 90.19, H 9.84; found: C 90.28, H 9.75.

2,3′-Dimethoxycarbonyl-1,1′-biphenyl (1, R = CO$_2$Me)

The reaction was carried out following the general procedure using 472 mg (1.8 mmol) of methyl *o*-iodobenzoate. Compound **1** (R = CO_2Me) (39) was isolated as a solid in 87% yield (212 mg) by flash chromatography, using hexane – CH_2Cl_2 – ethyl acetate (7:2.5:0.5) as the eluent. Compounds **8** (R = CO_2Me) and **10** (R = CO_2Me) were formed in 5% and 4% yield, respectively.

***1** (R = CO$_2$Me)*

^{1}H NMR δ: 8.07–8.00 (2H, m, H4′, H2′), 7.89 (1H, dd, *J* = 7.7, 1.5 Hz, H3), 7.55 (1H, td, *J* = 7.5, 1.5 Hz, H5), 7.52–7.45 (2H, m, H5′, H6′), 7.44 (1H, td, *J* = 7.6, 1.4 Hz, H4), 7.37 (1H, dt, *J* = 7.6, 1.4 Hz, H6), 3.92 (3H, s, CO_2CH_3), 3.64 (3H, s, CO_2CH_3). ^{13}C NMR δ: 168.49 (q), 166.95 (q), 141.67 (q), 132.88 (C6′), 131.52 (C5), 130.79 (C6), 130.40 (q), 130.11 (C3), 129.99 (q), 129.43 (C2′), 128.39 (C4′), 128.00 (C5′), 127.61 (C4), 52.15 (CO_2CH_3), 51.98 (CO_2CH_3). MS *m*/*z* (%): 270 (M^+, 83), 239 (71), 207 (100), 181 (29), 180 (23), 152 (44), 151 (43), 76 (29). Anal. calcd. for $C_{16}H_{14}O_4$: C 71.10, H 5.22; found: C 71.37, H 5.19.

*5-Methoxycarbonyl-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**8**, R = CO$_2$Me)*

^{1}H NMR δ: 7.78 (1H, dd, *J* = 7.8 Hz), 7.27 (1H, dd, *J* = 7.8, 7.4 Hz), 7.15 (1H, d, *J* = 7.4 Hz), 3.39 (1H, d, *J* = 3.7 Hz), 3.20 (1H, d, *J* = 3.8 Hz), 2.48–2.43 (1H, m), 2.31–2.25 (1H, m), 1.65–1.55 (2H, m), 1.29–1.18 (1H, m), 0.97 (1H, d quintets, *J* = 10.2, 1.4 Hz), 0.78 (1H, d quintets, *J* = 10.2, 1.7 Hz). MS *m*/*z* (%): 228 (M^+, 7), 187 (100), 155 (89), 141 (26), 128 (38), 115 (22).

*5,9-Dimethoxycarbonyl-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene (**10**, R = CO$_2$Me)*

Mp (hexane–CH_2Cl_2, 1:1) 142 to 143 °C. IR (KBr) ν: 1735, 1712. ^{1}H NMR δ: 7.71 (1H, dd, *J* = 7.8, 1.2 Hz, H6), 7.42 (1H, dd, *J* = 7.5, 1.5 Hz, H10), 7.37–7.31 (2H, m, H8, H12), 7.25 (1H, t, *J* = 7.5 Hz, H11), 7.17 (1H, t, *J* = 7.8 Hz,

H7), 3.92 (3H, s, CH_3O_2C(C5)), 3.90 (1H, d, J = 9.9 Hz, H4a), 3.76 (3H, s, CH_3O_2C(C9)), 3.30 (1H, d, J = 9.9 Hz, H12b), 2.29 (1H, br s, H4), 2.26 (1H, br s, H1), 1.79–1.55 (4H, m, H2 exo, H3 exo, H2 endo, H3 endo), 1.29 (1H, d quintets, J = 10.2, 1.8 Hz, H13 syn), 1.02 (1H, d quintets, J = 10.2, 1.2 Hz, H13 anti). ^{13}C NMR δ: 172.13 (CO), 168.77 (CO), 140.48 (q), 139.47 (q), 132.27 (q), 132.14 (q), 131.42 (C12), 131.17 (C8), 130.96 (q), 130.32 (C6), 129.92 (q), 128.15 (C10), 127.32 (C11), 125.29 (C7), 52.30 (CH_3CO_2(C9)), 52.14 (CH_3CO_2(C5)), 49.45 (C4), 49.12 (C1), 46.60 (C12b), 42.76 (C4a), 33.57 (C13), 31.15 (C2*), 29.25 (C3*). MS *m/z* (%): 362 (M^+, 29), 295 (29), 294 (100), 293 (22), 263 (72), 204 (15), 203 (17), 176 (18). Anal. calcd. for $C_{23}H_{22}O_4$: C 76.22, H 6.12; found: C 76.02, H 6.07.

2,3′-Dimethoxy-1,1′-biphenyl (1, R = OMe)

The reaction was carried out following the general procedure using 421 mg (1.8 mmol) of 2-iodoanisole. Compound **1** (R = OMe) (38) was isolated as a colourless oil in 48% yield (93 mg) by column chromatography, using hexane – ethyl acetate (9:1) as the eluent. Compound **8** (R = OMe) (32) was formed in 2% yield. Various by-products were also isolated but not further investigated.

1,2′-Binaphthyl (1, R = -(CH)$_4$-)

The reaction was carried out following the general procedure using 457 mg (1.8 mmol) of 1-iodonaphthalene. Compound **1** (R = -$(CH)_4$-) (40) was isolated as a white solid in 78% yield (179 mg) by column chromatography, using hexane as the eluent. Compounds **8** (R = -$(CH)_4$-) and **9** (R = -$(CH)_4$-)) (43) were formed in 2% yield each.

2,3′-Dichloro-1,1′-biphenyl (1, R = Cl)

The reaction was carried out following the general procedure using 215 mg (0.9 mmol) of *o*-chloroiodobenzene. Compound **1** (R = Cl) (41) was isolated as a colourless oil in 6% yield (6 mg) by column chromatography, using hexane as the eluent together with 72% of unconverted *o*-chloroiodobenzene (155 mg) and 15% yield (19 mg) of compound **11**.

*5-(2′-Chlorophenyl)-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**11**)*

^{1}H NMR δ: 7.50–7.42 (1H, m), 7.35–7.24 (5H, m), 7.21 (1H, br d, J = 7.1 Hz), 7.01 (1H, dd, J = 7.1, 1.0 Hz), 3.26–3.19 (2H, m), 2.32–2.28 (1H, m), 2.10–2.07 (1H, m), 1.65–1.44 (2H, m), 1.28–1.05 (2H, m), 1.00–0.89 (2H, m). ^{13}C NMR δ: 146.50, 144.91, 137.89, 133.92, 132.65, 131.13, 129.72, 128.42, 128.03, 127.17, 126.44, 121.30, 50.69, 49.97, 36.61, 36.31, 32.05, 27.85, 27.67. MS *m/z* (%): 280 (M^+, 11), 241 (32), 240 (18), 239 (100), 215 (19), 204 (19), 203 (209), 202 (33). Anal. calcd. for $C_{19}H_{17}Cl$: C 81.27, H 6.10; found: C 81.42, H 6.17.

Reaction of* o-*fluoroiodobenzene

The reaction was carried out following the general procedure using 200 mg (0.9 mmol) of *o*-fluoroiodobenzene. Compound **12** (22) was isolated in 67% yield (based on norbornene, 57 mg) by column chromatography, using hexane as the eluent. Other products were isolated but not further investigated.

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