Chemistry of alkylaromatic metallacycles. Regiochemistry of C–C coupling in ring opening or enlargement reactions of a palladacycle with alkynes

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Abstract

A phenylnorbornylpalladacycle containing methyl isonicotinate ligands was shown to undergo either ring opening or ring enlargement by reaction with acetylenic compounds to give norbornylalkynes regioselectively and ring-enlarged tetracyclic compounds non-regioselectively. However, in the case of ethyl propiolate regioselective ring enlargement takes place.

Keywords: Palladium; Metallacycle; Alkyne

1. Introduction

It is well known that metallacyclic complexes are more resistant towards β-hydrogen elimination than the acyclic analogues [1], and in particular that alkylaromatic metallacycles of type **1** are especially stable owing to the absence of any β-hydrogen atoms with appropriate geometric requirements for elimination [2]. We previously described their isolation as phenanthroline complexes [3] and their oxidative addition reactions to afford palladium(IV) metallacycles [4]. They have also been shown to be the intermediates in many catalytic reactions [5]. Their reactivity towards small molecules is thus of special interest, and we report here the preparation and characterization of complex **1** and its reactions with alkynes.

2. Results and discussion

A complex similar to **1**, but containing the bidentate ligand phenanthroline (L–L) was found not to react with alkynes at room temperature and so a new complex containing two monodentate methyl isonicotinate ligands was prepared. Treatment of the phenylnorbornylpalladium chloride dimer in CH_2Cl_2 with potassium phenoxide in the presence of methyl isonicotinate at room temperature gave **1** (L = methyl isonicotinate, *cis, exo*) in good yield. The reaction of this species with alkynes proceeded readily at room temperature and gave the alkyne products **2** formed by ring opening or the six-membered organic ring species **3** and **4** (Eq. (1)) formed by ring enlargement. In all compounds the norbornyl unit was *cis, exo* substituted.

While our work was in progress, an analogous complex prepared from norbornadiene and containing L = triphenylphosphine was found to show similar behaviour towards phenylacetylene and dimethyl acetylenedicarboxylate [6].

We obtained further insight into the regiochemistry of the reaction, however, by exploring the behaviour of other unsymmetrical alkynes. The reactions were carried out in anisole at room temperature by treatment of **1** with 10 molar equivalents of the alkyne. After stirring for 24 h the reaction mixture was treated with $NaBH_4$ to decompose any remaining **1**, with formation of palladium black and 2-phenylnorbornane. After filtration, the resulting clear solution was analysed quantitatively by GC using internal standards. The pure products were obtained by flash chromatography. Table 1 reports the results of the experiments with various substrates.

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(1)
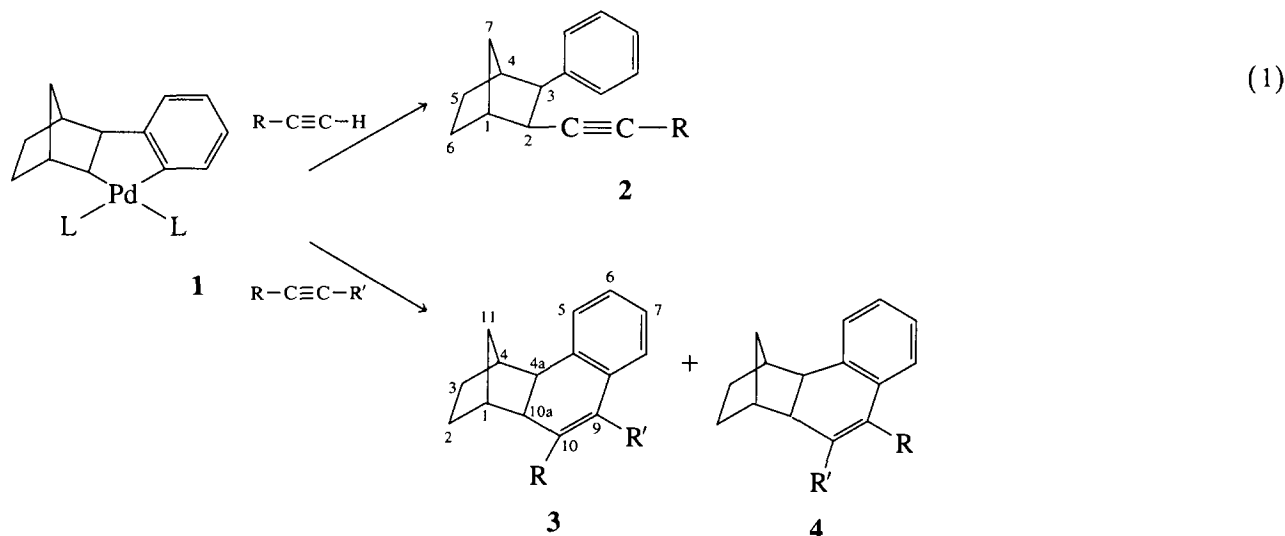
All compounds were fully characterized by NMR, IR and mass spectrometry. Assignments of the structure of 1,2,3,4,4a,10a-hexahydro-1,4-methanophenanthrene derivatives to compounds **3** and **4** are based on COSY, relay COSY, 1D-, 2D-TOCSY and decoupling experiments. The regiochemistry of products was established from the NOESY spectra, which also allowed us to discriminate between the two bridgehead protons (H1 and H4) of the hydrogenated unit (because of the presence of H4–H5 and H4a–H5 dipolar interactions) and to confirm the *exo*, *endo* assignments of H2 and H3.

For **3** (R = CO_2Et, R' = H, run 5), the strong NOE effect between the vinyl proton and H8 clearly indicates that the former is located on the same side of the aromatic ring. Although NMR data were in agreement with the proposed structure, the possibility remained that a fluorene derivative had been formed according to

Eq. (2). This was ruled out by ozonolysis, which confirmed the assignment of structure **3**.

$$1 + EtO_2C—C≡C—H \;\longrightarrow\!\!\!\!\times\!\!\!\longrightarrow$$

(2)
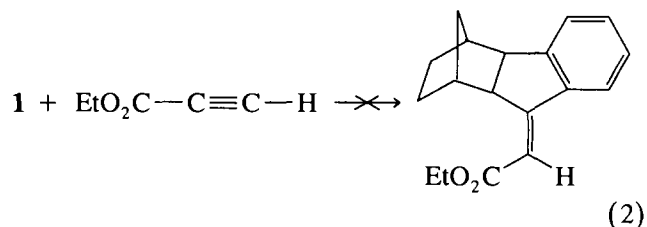
With $PhC≡CCO_2Me$, two isomers (**3** and **4**, R = CO_2Me, R' = Ph, run 6) were obtained in 59 and 20% yield, respectively. The free phenyl ring was shown to be on the side of the aromatic moiety of the hexahydrophenanthrene derivative **3** (R = CO_2Me, R' = Ph) by the presence of an NOE interaction between H8 and the protons of the aromatic free ring. Compound **4** (R =

Table 1
Reaction of complex **1** (L = methyl isonicotinate) with RC≡CR' in anisole at room temperature for 24 h

Run No.	R in the alkyne	R' in the alkyne	Conversion (%) [a]	Selectivity (%)		
				2	3	4
1	Ph	H	96	86 [b]		
2	p-MeOC$_6$H$_4$	H	94	53 [b,c]		
3	p-NO$_2$C$_6$H$_4$	H	91	35 [b,c]		
4	C$_6$H$_{13}$	H	58	46		
5	EtOCO	H	100		62 [c,d]	
6	MeOCO	Ph	89		59	20 [d]
7	MeOCO	MeOCO	67		97	
8	Me	Ph	38		13	54
9	Ph	Ph	2	–		

[a] Of complex **1**. The degrees of conversion was based on the amount of phenylnorbornane obtained after treatment of the reaction mixture with NaBH$_4$.
[b] Small amounts (2–5%) of two other isomers were detected by GC–MS; they are probably cyclic compounds, their mass spectra after hydrogenation corresponding to the presence of M$^+$ + 2.
[c] Heavy products, not detectable by GC, were also formed.
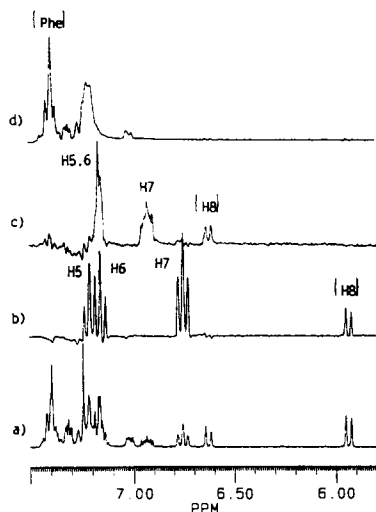[d] GC-detectable heavier products were present in less than 5% yield.

Fig. 1. 300 MHz ^{1}H NMR spectra of a mixture of isomers 3 and 4 (R = CO_2Me, R' = Ph) from run 6: (a) standard 1D spectrum; (b), (c) and (d) 1D-TOCSY spectra obtained by selective irradiation of H8 (3), H8 (4) and free phenyl rings, respectively. 1D-TOCSY spectra were performed by a selective inversion obtained by a soft DANTE pulse of about 39.2 ms followed by a MLEV17 for spin-lock used as mixing time (70 ms) [7].

CO_2Me, R' = Ph) was characterized in a mixture of isomers 3 and 4 using 1D-TOCSY experiments, which allowed the isolation of a full spin system from the crowded standard spectrum (Fig. 1).

Discrimination between the two regioisomers 3 and 4 (R = Me, R' = Ph) of run 8 was possible because of the presence in the case of 4 of various dipolar interactions between the high-field aromatic protons and the aliphatic protons of the norbornane unit. Moreover, the correlations of the methyl group with H8 and H10a indicate that the methyl lies on the aromatic side of the hexahydrophenanthrene derivative and that there is an interaction with the *endo* proton H10a, owing to the nonplanarity of the internal six-membered ring.

As shown in Table 1, terminal alkynes caused ring opening to give 2 (except in the case of ethyl propiolate) whereas internal alkynes caused ring enlargement to give 3 and 4. Both aryl and alkylacetylenes reacted. Good selectivity towards 2 was obtained with phenylacetylene, while the presence of either electron-releasing or electron-withdrawing substituents on the aromatic ring led to lower selectivities because of the formation of heavy products not detected by GC. Low conversion and selectivity towards the formation of 2 were observed for 1-octyne. With internal alkynes the cyclic compounds 3 and 4 were selectively formed, with the former predominant. The extent of conversion to 3 and 4 decreased with increasing steric hindrance of the substituents, but the positive effect of electron-withdrawing substituents counterbalanced the steric effect. (cf. runs 6 and 8)

When the reaction of complex 1 with phenylacetylene was carried out in solvents such as DMF or quinoline, no formation of compound 2 (R = Ph) was observed; phenylnorbornane was obtained after decomposition with $NaBH_4$. Use of more weakly coordinating solvents such as acetone, THF, chlorobenzene, CH_2Cl_2, $CHCl_3$ and toluene led to a less selective reaction. The marked solvent effect must be associated with coordination pre-equilibria, with coordinating solvents competing with alkynes for coordination. Other less polar solvents exert subtle effects on the regioselectivity, which cannot be rationalized at present.

The different behaviour of terminal and internal alkynes with respect to the formation of compounds 2 and 3 is attributable to the fact that terminal alkynes can react through oxidative addition [8] and reductive elimination (Eq. (3)), whereas internal alkynes can only insert into a Pd–C bond before undergoing ring closure.

$$1 + R-C\equiv C-H \longrightarrow \quad \longrightarrow 2 \qquad (3)$$
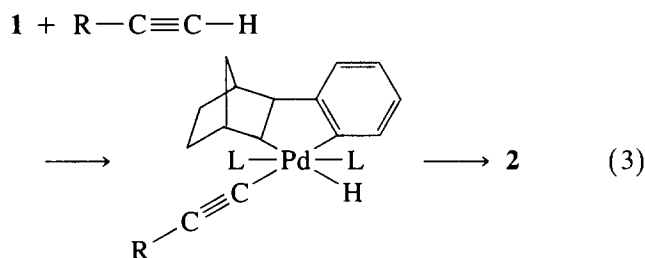
It is noteworthy that the formation of the ring-opened product is regioselective, only the cycloaliphatic carbon being involved, while the ring enlargement leads to two regioisomers if R and R' are different. This can be explained by assuming that norbornyl–alkynyl coupling on palladium is sensitive to electronic effects, the carbon atom of the norbornyl–palladium bond being relatively less negatively polarized than that of the alkynyl–palladium bond. In contrast, the incorporation of a neutral molecule into the metallacycle is less sensitive to electronic effects and is substantially affected by steric factors (as shown, for example, by the unreactivity of diphenylacetylene).

In contrast to other terminal alkynes, ethyl propiolate did not give compound 2, forming compound 3 (R = CO_2Et, R' = H) exclusively. Since the latter cannot be derived from 2 (R = CO_2Et), which shows the opposite regiochemistry with respect to the norbornyl group, we must conclude that ethyl propiolate behaves like the internal alkynes, from which it differs, however, in showing complete regioselectivity. The reason why it gives a type 3 compound rather than 2 probably lies in its good coordination ability, which would render the insertion process easier than oxidative addition. The preferred regiochemistry is to be attributed to steric factors. In view of previous work by Huggins and Bergman [9], who showed that migration of a carbon group occurs at the less sterically hindered site of an alkyne, and that by Carmona and co-workers [10], who

proposed aryl rather than alkyl attack as the key step in the incorporation of alkynes into a benzonickelacyclopentene complex (because of the higher ligand lability *trans* to the aliphatic group), it is likely that the site at which the alkyne inserts is the Pd to aryl bond (route a, Scheme 1) and not the Pd to norbornyl bond (route b).

This might not be consistent with the difference between the arylpalladium and the alkylpalladium bond energies (at present not clearly established [11]), and it is likely that kinetic factor control the process.

3. Experimental section

All reagents were commercial products (Carlo Erba, Merck and Fluka) and were used without further purification. Reactions were carried out under dinitrogen by use of conventional Schlenk techniques. Solvents were dried and degassed before use. ^{1}H NMR spectra were recorded on Bruker AC-300 and AMX-400 spectrometers in $CDCl_3$ with TMS as internal standard. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Electron impact mass spectra (m/z, relative intensity (%)) were obtained with a Finnigan Mat SSQ 710 instrument working at 70 eV ionization energy. 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. The ozone source was an Elbe Ozo/B laboratory ozonizer, with pure, dry oxygen as the feed gas.

3.1. Preparation of complex 1 (L = methyl isonicotinate)

This complex was prepared as described previously for the phenanthroline complex [3] using 2.4 molar equivalents of methyl isonicotinate in place of phenanthroline. The compound was obtained as a yellow powder in 80% yield after recrystallization at − 10°C from a mixture of methylene chloride and diethyl ether. ^{1}H NMR (300 MHz, 25°C): δ 8.81 (4H, br signal, protons *ortho* to nitrogen), 7.89–7.83 (4H, m, protons *meta* to nitrogen), 6.99 (1H, d, $J = 7.4$ Hz, H8), 6.88 (1H, t, $J = 7.3$ Hz, H9), 6.65 (1H, t, $J = 7.2$ Hz, H10), 6.24 (1H, brd, $J = 6.8$ Hz, H11), 3.96 (6H, s, Me), 2.94 (1H, brd, $J = 7.0$ Hz, H3) 2.79 (1H, brd, $J = 6.9$ Hz, H2), 2.23 (1H, brs, H4), 2.11 (1H, d, $J = 8.0$ Hz, H7 *syn*), 1.77 (1H, brs, H1), 1.52-1.45 (1H, m, H5 *exo*), 1.40-1.20 (2H, m, H6 *exo*, H5 *endo*), 1.05–0.90 (2H, m, H6 *endo*, H7 *anti*).
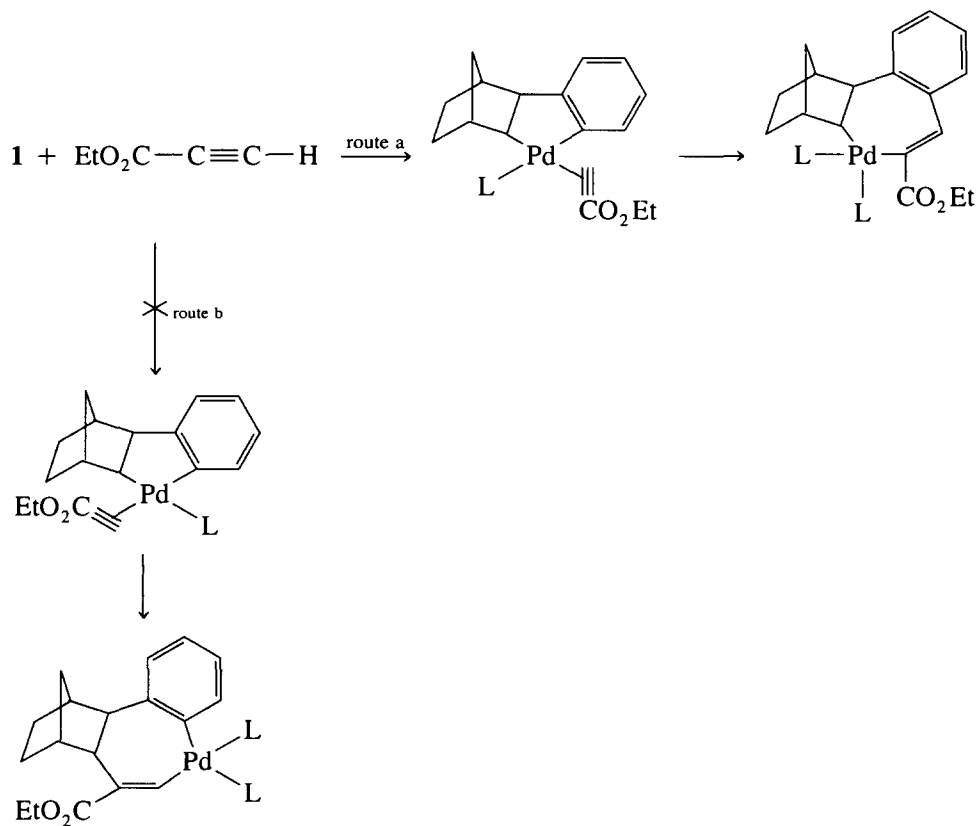
Scheme 1. Reaction pathways for ethyl propiolate.

3.2. Reaction of 1 with alkynes

General procedure: complex **1** (L = methyl isonicotinate, 0.2 mmol) was dissolved under dinitrogen in anisole (8 ml) in a Schlenk vessel, the alkyne (2 mmol) was added and the mixture was stirred at room temperature for 24 h. After addition of 0.2 ml of methanol, the solution was treated with an excess of $NaBH_4$, causing the almost instantaneous formation of palladium black. Water was then added and the mixture extracted twice with methylene chloride. The combined extracts were dried over Na_2SO_4 and filtered. The methylene chloride was removed in a rotary-evaporator and anisole under vacuum. The amount of 2-phenylnorbornane, formed by decomposition with $NaBH_4$ of the unchanged **1** (L = methyl isonicotinate), was determined by quantitative GC analysis with n-hexadecane as internal standard. The products were isolated by flash chromatography on a silica gel column with hexane–ethyl acetate as eluent, and were characterized by ^1H NMR (1D and 2D experiments), IR and mass spectrometry.

3.3. Ozonolysis of product 3 (R = CO_2Et, R' = H) [12]

A solution of **3** (R = CO_2Et, R' = H) (55 mg, 0.2 mmol) in 8 ml of methylene chloride was cooled to −65°C and a stream of ozonized oxygen was passed through the solution for 1 h. The system was then swept with dinitrogen and allowed to reach room temperature. Water (4 ml) was added and the mixture was stirred for 1 h at room temperature, heated under reflux for a further 1 h, then allowed to cool. The organic layer was separated and treated with aqueous Na_2CO_3. The product of ozonolysis was present in the neutral fraction and was analysed by GC–MS. It corresponded to the product of lactonization of the expected keto acid (M^+ 316, two diastereoisomers). The highest peak was at m/z 298 (316 − 18), and was accompanied by peaks at m/z 271, 243 and 225. No peak from the ketonic compound that could be derived from a five-membered ring was observed.

3.4. Spectroscopic data

Compound **2** (R = C_6H_5) was reported previously [13].

2 (R = p-C_6H_4OMe): m.p. (CH_2Cl_2) 95–96°C. ^1H NMR: δ 7.37–7.21 (4H, m, *meta* and *ortho* protons of the unsubstituted phenyl ring), 7.16 (1H, pstt, *para* proton of the unsubstituted phenyl ring), 6.74, 6.63 (2H + 2H, parts AA' and BB' of an AA'BB' system, protons *ortho* and *meta* to OMe), 3.72 (3H, s, Me), 3.05, 3.01 (2H, AB system, H2, H3), 2.59 (1H, brs, H4 or H1), 2.53 (1H, brs, H1 or H4), 2.11 (1H, d quintets, J = 10.0, 1.6 Hz, H7 *syn*), 1.70–1.60 (2H, m, H5 *exo*,

H6 *exo*), 1.43–1.33 (3H, m, H7 *anti*, H5 *endo*, H6 *endo*) ppm. MS: M^+ 302 (100), m/z 273 (22), 235 (30), 234 (29), 222 (26), 202 (21), 189 (26), 171 (24), 165 (30), 128 (27), 115 (30), 91 (36), 84 (27).

2 (R = p-$C_6H_4NO_2$): ^1H NMR: δ 7.94 (2H, part AA' of an AA'BB' system, protons *ortho* to NO_2), 7.31–7.16 (5H, m, protons of the unsubstituted phenyl ring), 6.86 (2H, part BB' of an AA'BB' system, protons *meta* to NO_2), 3.05 (2H, AB system, H2, H3), 2.61 (1H, brs, H4 or H1), 2.53 (1H, brs, H1 or H4), 2.04 (1H, d quintets, J = 10.1, 1.9 Hz, H7 *syn*), 1.74–1.60 (2H, m, H5 *exo*, H6 *exo*), 1.42 (1H, d quintets partly overlapping with H5 *endo*, H6 *endo*, J = 10.1, 1.6 Hz, H7 *anti*), 1.40–1.32 (2H, m, H5 *endo*, H6 *endo*) ppm. IR (film, cm^{-1}): 2235 (C≡C). MS: M^+ 317 (30), m/z 289 (25), 207 (20), 165 (20), 115 (25), 91 (39), 86 (60), 84 (91), 51 (35), 49 (100), 47 (20).

2 (R = C_6H_{13}): ^1H NMR: δ 7.21 (2H, part BB' of an AA'BB'C system, *meta* protons of the aromatic ring), 7.15 (2H, part AA' of an AA'BB'C system, *ortho* protons of the aromatic ring), 7.09 (1H, pstt, *para* proton of the aromatic ring), 2.87 (1H, brd, J = 9.1 Hz, H3), 2.78 (1H, d quartets, J = 9.0, 2.1 Hz, H2), 2.48 (1H, brs, H4), 2.35 (1H, brs, H1), 2.01 (1H, d quintets, J = 9.9, 2.0 Hz, H7 *syn*), 1.74 (2H, 2td partly overlapped, J = 6.8, 1.1 Hz, ≡CCH_2), 1.61–1.54 (2H, m, H5 *exo*, H6 *exo*), 1.31 (1H, d quintets partly overlapping with H5 *endo*, H6 *endo*, J = 9.8, 1.6 Hz, H7 *anti*), 1.30–1.25 (2H, m, H5 *endo*, H6 *endo*), 1.24–1.16 (2H, m, CH_2Me), 1.08–0.96 (6H, m, 3CH_2), 0.84 (3H, t, J = 7.2 Hz, Me) ppm. MS: M^+ 280 (10) m/z 210 (10), 195 (10), 167 (10), 141 (14), 115 (10), 91 (25), 86 (66), 84 (100), 51 (43).

3 (R = CO_2Et, R' = H): ^1H NMR: δ 7.30 (1H, brs, H9), 7.23 (1H, td, J = 7.4, 1.5 Hz, H6), 7.15 (1H, d with long-range couplings, J = 7.6 Hz, H5), 7.10 (1H, t with long-range couplings, J = 7.6 Hz, H7), 7.06 (1H, dd, J = 7.5, 1.4 Hz, H8), 4.26 (2H, m, OCH_2), 3.21 (1H, brd, J = 10.6 Hz, H4a), 2.97 (1H, brd, J = 10.5 Hz, H10a), 2.34 (1H, brs, H4), 2.31 (1H, brs, H1), 1.75–1.52 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.43 (1H, d quintets, J = 9.9, 1.7 Hz, H11 *syn*), 1.34 (3H, t, J = 7.1 Hz, Me), 1.12 (1H, d quintets, J = 10.0, 1.4 Hz, H11 *anti*) ppm. IR (film, cm^{-1}): 1707 (s), COO; 1643 (w) C=C. MS: M^+ 268 (41), m/z 223 (12), 201 (15), 200 (62), 195 (20), 172 (16), 155 (45), 129 (17), 128 (13), 127 (24), 86 (59), 84 (100), 51 (31).

3 (R = CO_2Me, R' = Ph): ^1H NMR: δ 7.46–7.31 (5H, m, Ph), 7.21 (1H, brd, H5), 7.15 (1H, ddd partly overlapping with the previous multiplet, J = 7.6, 7.2, 1.0 Hz, H6), 6.75 (1H, dd, J = 8.1, 7.6 Hz, H7), 5.95 (1H, d, J = 8.1 Hz, H8), 3.71 (1H, brd, J = 6.7 Hz, H10a), 3.69 (3H, s, Me), 3.11 (1H, brd, J = 6.6 Hz, H4a), 2.40 (1H, brs, H1), 2.28 (1H, brs, H4), 1.75–1.42 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 0.92 (2H, brs, H11 *syn*, H11 *anti*). IR (KBr, cm^{-1}): 1710

(s), COO; 1615 (w) C=C. MS: M^+ 330 (100), m/z 231 (33), 229 (19), 204 (27), 203 (88), 68 (18).

4 (R = CO_2Me, R' = Ph): ^{1}H NMR: δ 7.40, 7.31, 7.04 (5H, m, Ph), 7.15 (2H, m, H5, H6), 6.93 (1H, m, H7), 6.63 (1H, brd, J = 7.7 Hz, H8), 3.35 (3H, s, Me), 3.25 (1H, d, J = 10.7 Hz, H4a), 3.16 (1H, d, J = 10.7 Hz, H10a), 2.41 (1H, brs, H4), 2.22 (1H, brs, H1), 1.74–1.57 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.70 (1H, d, H11 *syn*), 1.20 (1H, d quintets, J = 9.9 Hz, H11 *anti*) ppm. GC–MS: M^+ 330 (82), m/z 271 (30), 262 (61), 231 (98), 202 (100), 68 (31).

3 (R = R' = CO_2Me): m.p. (CH_2Cl_2) 94–95°C. ^{1}H NMR: δ 7.26 (1H, td, J = 7.6, 1.3 Hz, H6), 7.17 (1H, d with long-range couplings, J = 7.6 Hz, H5), 7.11 (1H, t with long-range couplings, J = 7.7 Hz, H7), 6.95 (1H, dd, J = 7.7, 1.4 Hz, H8), 3.93 (3H, s, Me), 3.79 (3H, s, Me), 3.21 (1H, brd, J = 10.8 Hz, H4a), 3.03 (1H, brd, J = 10.7 Hz, H10a), 2.34 (1H, brs, H4), 2.28 (1H, brs, H1), 1.74–1.53 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.49 (1H, d quintets, J = 10.2, 1.7 Hz, H11 *syn*), 1.15 (1H, d quintets, J = 10.2, 1.5 Hz, H11 *anti*) ppm. IR (KBr, cm^{-1}): 1710 (s), 1735 (s), COO; 1630 (w) C=C. MS: M^+ 312 (25), m/z 244 (47), 214 (21), 213 (100), 177 (12), 127 (11), 67 (13).

3 (R = Me, R' = Ph): ^{1}H NMR: δ 7.15 (1H, d, J = 7.6 Hz, H5), 7.06 (1H, t, J = 7.6 Hz, H6), 6.90 (1H, t, J = 7.7 Hz, H7), 6.40 (1H, d, J = 7.7 Hz, H8), 3.21 (1H, brd, J = 10.2 Hz, H4a), 2.59 (1H, brd, J = 10.2 Hz, H10a), 2.47 (1H, m, H4), 2.08 (1H, m, H1), 1.72–1.50 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.68 (1H, d, H11 *syn*), 1.16 (1H, d quintets, J = 9.8 Hz, H11 *anti*) ppm. GC–MS: M^+ 286 (82), m/z 271 (20), 220 (19), 218 (100), 217 (32), 203 (19), 202 (59), 68 (21).

4 (R = Me, R' = Ph): ^{1}H NMR: δ 7.37 (2H, part BB' of an AA'BB' system, H3', H5'), 7.25–7.20 (1H, m, H4'), 7.27 (1H, d, H8), 7.17–7.08 (5H, m, H2', H6', H5, H6, H7), 3.21 (1H, brd, J = 10.2 Hz, H4a), 2.85 (1H, brd, J = 10.2 Hz, H10a), 2.40 (1H, m, H4), 2.08 (1H, m, H1), 1.83 (3H, d, J = 1.8 Hz, Me), 1.60–1.50 (3H, m, H11 *syn*, H3 *exo*, H3 *endo*), 1.45 (1H, tt, J = 12.0, 4.4 Hz, H2 *exo*), 1.25 (1H, m, H2 *endo*), 1.07 (1H, d quintets, J = 9.7, 1.4 Hz, H11 *anti*) ppm. IR (film, cm^{-1}): 1630 (w) C=C. MS: M^+ 286 (100), m/z 271 (21), 229 (23), 218 (92), 217 (42), 202 (50), 68 (24).

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