New route to *o*-terphenyls: application to the synthesis of 6,7,10,11-tetramethoxy-2-(methoxycarbonyl)triphenylene

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The hydroxy-*o*-terphenylcarboxylic acid esters 6a–f have been prepared by benzannulation of the 5,6-diaryl-3-methoxycarbonylhexa-3,5-dienoic acids 5a–f using triethylamine–ethyl chloroformate. The application of this new synthesis of triphenylenes is illustrated through the synthesis of 2-methoxycarbonyl-6,7,10,11-tetramethoxytriphenylene 9.

Introduction

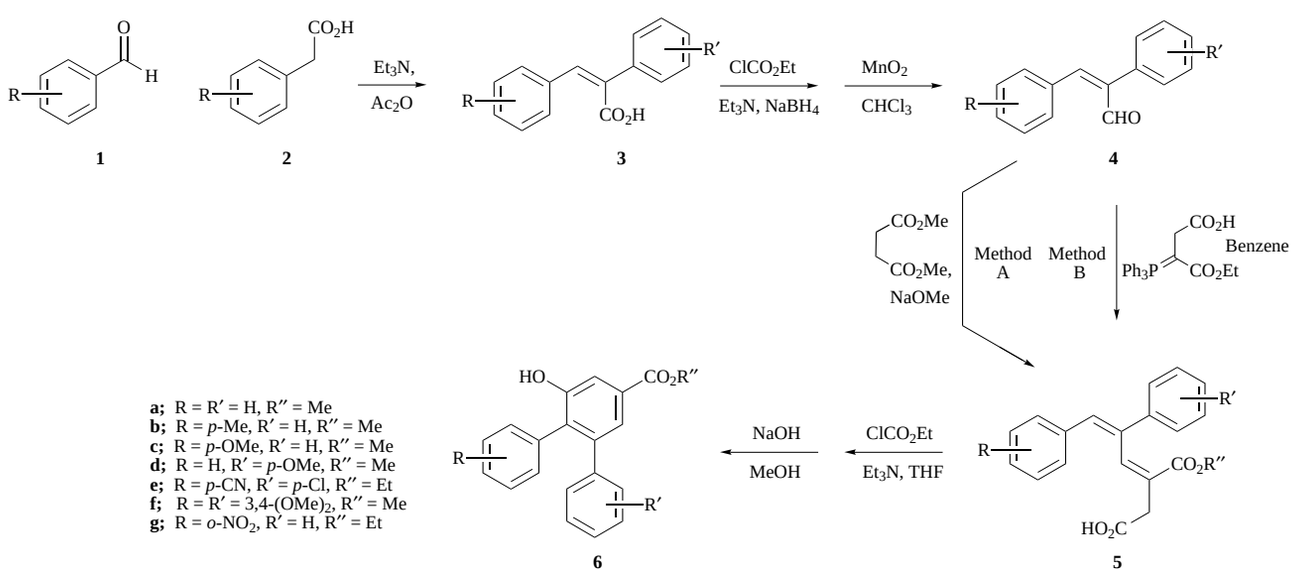
The chemistry of triphenylenes is receiving current interest due to the relevant physical properties of these disc-shaped molecules.[1,2] Whereas hexaalkoxytriphenylenes can be easily obtained through oxidative trimerization of an *ortho*-dialkoxybenzene derivative,[3] the preparation of unsymmetrically substituted derivatives best proceeds from biphenyl[4] or *o*-terphenyl derivatives,[5] respectively, by iron(III) chloride oxidative coupling. Alternatively, the cyclization can be achieved by photolysis.[6] Moreover, unsymmetrically substituted triphenylenes can be obtained by stepwise palladium-catalyzed cross-coupling reactions, involving arylboronic acids as intermediates.[7] A major problem in the synthesis of unsymmetrical triphenylenes through intramolecular C–C bond formation is the obtainment of the *o*-terphenyls useful as substrates for the ring closure. Amongst the proposed methods, the Pd^0-catalyzed coupling of arylzinc halides with 1,2-diahalogenobenzenes seems to be the most effective.[5]

In this context we report now on a novel, flexible approach to 3-hydroxy-4,5-diphenylbenzoic acid esters and on the obtainment, from one of the materials prepared by these means, of 6,7,10,11-tetramethoxy-2-methoxycarbonyltriphenylene **9**. The present synthetic method is compatible with the presence, in the B and C rings, of a variety of substituents.

Results and discussion

The synthesis of *o*-terphenylcarboxylic acid derivatives **6a**–**g** involves the stepwise construction of the C_{18}–C_1 carbon framework of the target molecules from three components, *i.e.* C_6–C_1 aromatic aldehydes **1**, C_6–C_2 phenylacetic acids **2** and C_4 dimethyl succinate, respectively (Scheme 1). Key step in the synthesis is the benzannulation of the C_{19} acid **5**, bearing two aromatic rings, through a variation[8] of a procedure reported a few years ago by Ramage and co-workers.[9] The cyclization process, supposedly involving a ketene intermediate, consists of a base-catalyzed elimination of ethanol and carbon dioxide from the mixed anhydride formed from ethyl chloroformate and the carboxylic acid. As in the case of the synthesis of 3-hydroxy biphenyls and *p*-terphenyl systems,[8] high yields of annulated products **6** are indeed obtained also in the treatment of the carboxylic acid **5**, in dry tetrahydrofuran (THF) and below 25 °C, with ~2 mol equiv. of ethyl chloroformate, followed by dropwise addition of 3 mol equiv. of triethylamine.

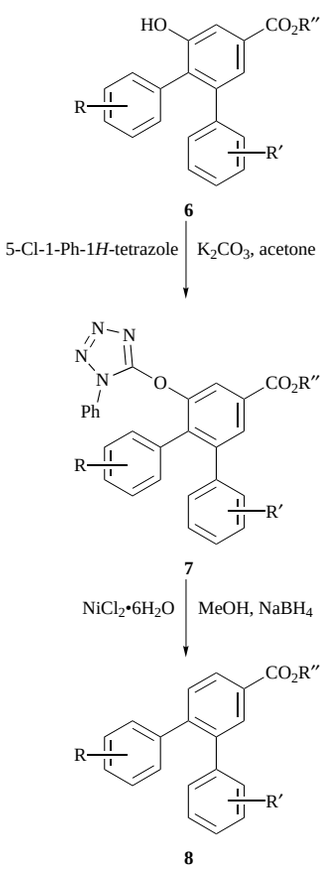
A further advantage of the present synthesis of *o*-terphenyl derivatives is represented by the simple preparation of the substrates. Indeed, products **5a**–**g** are obtained through unexceptional steps from commercially available products. First, C_{15} α-arylcinnamic acids **3a**–**g** are obtained by Perkin condensation[10] of benzaldehydes **1** with phenylacetic acids **2**. Sub-



Scheme 1

sequently, the C_{15} carboxylic acids are converted into the corresponding aldehydes **4a**–**g** in two steps. The corresponding alcohols are first prepared upon reduction, with $NaBH_4$, of the mixed anhydride formed by treatment of the acids in THF with ethyl chloroformate–Et_3N.[11] Subsequently, the alcohols are converted into the aldehydes upon MnO_2 oxidation. The C_{15} aldehydes obtained by these means are homologated to the desired C_{19} acids **5a**–**d**, **5f**, by Stobbe condensation (Method A).[12] In the case of the aldehydes **4e**, **4g**, bearing base-sensitive substituent(s), homologation to the acids **5e**, **5g** is achieved by reaction with [β-carboxy-α-(ethoxycarbonyl)ethyl]triphenylphosphonium betaine[13] (Method B) in ~50% yield, comparable with those observed in the other instances under the Stobbe conditions.

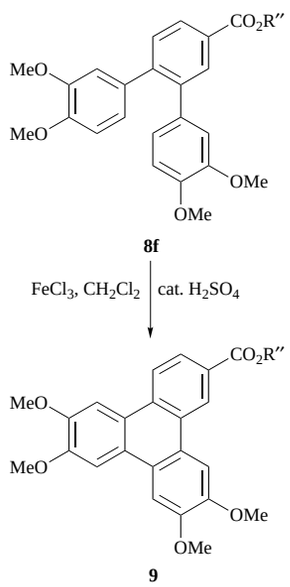
The benzannulation of the acids **5a**–**g** to the *o*-terphenyl derivatives **6a**–**g** proceeds, under the conditions mentioned above, in ~80–90% isolated yield. The utility of this new entry to *o*-terphenyls in the synthesis of unsymmetrically substituted triphenylene derivatives is demonstrated by the following experiments. The esters **6a** and **6f** are deoxygenated to products **8a** and **8f**, respectively, upon treatment of the corresponding 5-phenyltetrazolyl derivatives[14] with $NaBH_4$ in the presence of $NiCl_2{\cdot}6H_2O$ in methanol (Scheme 2). We had to rely on this



Scheme 2

new method for the cleavage of the oxygen–carbon bond of the phenyltetrazolyl derivatives at position 3 of the above 4,5-aryl-substituted benzoate esters, since catalytic hydrogenation failed under the experimental conditions found to be effective in the removal of the oxygen functionality in positions 'out of the bay' of triphenylene systems.[15] Finally, the ester **8f**, bearing oxygen-substituted aromatic rings, was cleanly converted into the desired triphenylene derivative **9** by iron(III) chloride oxidation.[5] The photochemical cyclization of unsubstituted terphenylcarboxylate **8a** to the methyl ester of triphenylene-2-carboxylic acid is under study.

Thus, these experiments demonstrate the utility in the synthesis of *o*-terphenyl derivatives of the benzannulation procedure *via* activation of the carboxy group of β-methoxycarbonyl-β,δ-dienic acids by formation of the mixed anhydride with ethyl chloroformate, followed by triethylamine treatment.[8] By this procedure a whole set of 3-hydroxy-4,5-aryl-substituted benzoic acid esters become accessible. The conditions of the synthesis are compatible with the presence, in the aromatic B and C rings, of a variety of functionalities. The hydroxy group necessarily formed in position 3 of the annulated products can be reductively removed, thus widening the scope of the synthesis. The claimed utility of the proposed new access to *o*-terphenyls in the chemistry of triphenylenes is now demonstrated only by the conversion of the *o*-terphenyl **8f** into triphenylene product **9**, but the results of ongoing experiments



on the synthesis of a whole set of unsymmetrically substituted triphenylenes from *o*-terphenyls produced by this method will be presented in due course.

Experimental

Mps were measured on a Reichert melting point apparatus, equipped with a Reichert microscope and are uncorrected. IR spectra were measured on a Perkin Elmer 2000 FTIR spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solutions at room temp. unless otherwise stated, on a Bruker AC-250 spectrometer (250 MHz ^1H). The chemical-shift scale is based on internal tetramethylsilane. *J*-Values are given in Hz. Mass spectra were measured on a FINNIGAN–MAT TSQ 70 spectrometer. TLC analyses were performed on Merck Kieselgel 60 F_{254} plates.

General procedure for aldehyde 4

Ethyl chloroformate (15.9 g, 0.147 mol) was added to a solution of acid **3a** (30 g, 0.134 mol) in THF (200 ml) at 0 °C. Then a solution of triethylamine (14.8 g, 0.147 mol) in THF (30 ml) was dropped and the mixture was stirred for 30 min. The precipitate (triethylammonium chloride) was filtered off, and washed with THF (50 ml). The combined filtrate and washings were then added in a few portions to aq. $NaBH_4$ (12.7 g, 0.335 mol in 100 ml), while the reaction mixture was kept below 20 °C. After 15 min, diethyl ether (250 ml) and 5% HCl (200 ml) were added; the organic phase was separated, dried over sodium sulfate, and concentrated under reduced pressure. The crude alcohol was dissolved in $CHCl_3$ (150 ml), treated with MnO_2 (58 g, 0.67 mol), and the mixture was heated under reflux for 5 h. Filtration and evaporation of the mixture provided an oil, which was crystallized from ethanol to give pure aldehyde **4a** (17 g, 61%).

Procedure for method A

1-Methyl hydrogen 2-(2,3-diphenylprop-2-enylidene)succinate 5a. A 2.0 M solution of sodium methylate (34.5 ml, 68.8 mmol) in methanol was added to a mixture of aldehyde **4a** (13 g, 62.5 mmol) and dimethyl succinate (10 g, 68.8 mmol). The homogeneous solution was concentrated under reduced pressure in 30 min at 40 °C. The residue was treated with 5% HCl (100 ml) and extracted with diethyl ether (200 ml). The organic phase was dried over sodium sulfate and concentrated under reduced pressure to give a crude product, which was crystallized from diisopropyl ether as a *solid* (11 g, 54%), mp 136–137 °C (Found: C, 74.46; H, 5.65. $C_{20}H_{18}O_4$ requires C, 74.52; H, 5.63%); ν_{max}(Nujol)/cm^{-1} 1610, 1712 (CO_2Me); δ_H 3.1 (s, 2 H, CH_2CO$_2$H), 3.8 (s, 3 H, OMe), 6.9–7.4 (3 m, 11 H, C*H*C-CO_2Me + 10 × ArH) and 7.68 (s, 1 H, ArC*H*CAr); *m*/*z* (EI) 322 (M$^+$, 100%), 305 (M$^+$ − OH, 11), 290 (M$^+$ − MeOH, 18), 276 (15), 262 (25), 215 (93), 202 (64), 189 (41) and 165 (17).

1-Methyl hydrogen 2-[3-(4-methylphenyl)-2-phenylprop-2-enylidene]succinate 5b. Yield 51%; *solid*, mp 105–107 °C (Found: C, 75.08; H, 5.97. $C_{21}H_{20}O_4$ requires C, 74.98; H, 5.99%); ν_{max}(Nujol)/cm^{-1} 1582, 1600 and 1710 (CO_2Me); δ_H 2.25 (s, 3 H, Ar*Me*), 3.06 (s, 2 H, CH_2CO$_2$H), 3.78 (s, 3 H, CO_2Me), 6.8–7.4 (m, 10 H, C*H*CCO_2Me + 9 × ArH) and 7.68 (s, 1 H, ArC*H*CAr); *m*/*z* (EI) 336 (M$^+$, 23%), 304 (M$^+$ − MeOH, 7), 276 (M$^+$ − HCO_2Me, 43), 258 (25), 245 (36), 231 (100), 215 (76), 202 (33) and 115 (41).

1-Methyl hydrogen 2-[3-(4-methoxyphenyl)-2-phenylprop-2-enylidene]succinate 5c. Yield 56%; *solid*, mp 125–126 °C (Found: C, 71.70; H, 5.66. $C_{21}H_{20}O_5$ requires C, 71.58; H, 5.72%); ν_{max}(Nujol)/cm^{-1} 1583, 1600 and 1703 (CO_2Me); δ_H 3.02 (s, 2 H, CH_2CO$_2$H), 3.73 (s, 3 H, OMe), 3.79 (s, 3 H, CO_2Me), 6.6–7.4 (m, 10 H, C*H*CCO_2Me + 9 × ArH) and 7.65 (s, 1 H, ArC*H*CAr); *m*/*z* (EI) 352 (M$^+$, 61%), 321 (M$^+$ − OMe, 6), 292 (M$^+$ − HCO_2Me, 67), 261 (38), 247 (100), 233 (31), 202 (49), 189 (27), 165 (37) and 121 (46).

1-Methyl hydrogen 2-[2-(4-methoxyphenyl)-3-phenylprop-2-enylidene]succinate 5d. Yield 60%; amorphous *solid* obtained as a pure compound by column chromatography with hexane–ethyl acetate (3:1–1:1) as eluent (Found: C, 71.74; H, 5.72%); ν_{max}(Nujol)/cm^{-1} 1610 and 1699 (CO_2Me); δ_H 3.15 (s, 2 H, CH_2CO$_2$H), 3.76 (s, 3 H, OMe), 3.81 (s, 3 H, CO_2Me), 6.8–7.2 (m, 10 H, C*H*CCO_2Me + 9 × ArH) and 7.66 (s, 1 H, ArC*H*-CAr); *m*/*z* (EI) 353 (M$^+$ + 1, 52%), 352 (M$^+$, 100), 320 (M$^+$ − MeOH, 25), 292 (M$^+$ − HCO_2Me, 88), 261 (51), 247 (98), 233 (56), 215 (69), 189 (43), 165 (57) and 135 (40).

1-Methyl hydrogen 2-[2,3-bis-(3,4-dimethoxyphenyl)prop-2-enylidene]succinate 5f. Yield 66%; *solid*, mp 125–126 °C (from AcOEt) (Found: C, 65.04; H, 5.87. $C_{24}H_{26}O_8$ requires C, 65.15; H, 5.92%); ν_{max}(Nujol)/cm^{-1} 1587, 1620, 1690 and 1715; δ_H 3.08 (s, 2 H, CH_2CO$_2$H), 3.47 (s, 3 H, CO_2Me), 3.76 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 3.89 (s, 3 H, OMe), 6.43 (s, 1 H, C*H*CCO_2Me), 6.65–6.95 (m, 6 H, 6 × ArH) and 7.68 (s, 1 H, ArC*H*CAr); *m*/*z* (EI) 442 (M$^+$, 100%), 410 (M$^+$ − MeOH, 10), 382 (M$^+$ − HCO_2Me, 41), 337 (63), 323 (38), 306 (35), 292 (29) and 151 (46).

Procedure for method B

1-Ethyl hydrogen 2-[2-(4-chlorophenyl)-3-(4-cyanophenyl)-prop-2-enylidene]succinate 5e. [β-Carboxy-α-(ethoxycarbonyl)-ethyl]triphenylphosphonium betaine (4.05 g, 10 mmol) was added in one portion to a solution of aldehyde **4e** (2.1 g, 8 mmol) in dry benzene (20 ml). After stirring of the mixture at 40 °C for 48 h, the reaction mixture was treated with water (40 ml) and extracted with ethyl acetate (100 ml). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was chromatographed on a silica gel column and eluted with hexane–ethyl acetate (5:1–1:1) to give the *monoester monoacid* **5e** (1.8 g, 56%) as an oil (Found: C, 66.84; H, 4.63; Cl, 8.79; N, 3.67. $C_{22}H_{18}ClNO_4$ requires C, 66.75; H, 4.58; Cl, 8.96; N, 3.54%); ν_{max}(Nujol)/cm^{-1} 1600, 1710 (CO_2Et) and 2228 (C≡N); δ_H 1.30 (t, *J* 7, 3 H, CO_2CH_2*Me*), 3.23 (s, 2 H, CH_2CO$_2$H), 4.25 (q, *J* 7, 2 H, CO_2CH_2Me), 6.85–7.50 (m, 9 H, C*H*CCO_2Me + 8 × ArH) and 7.60 (s, 1 H, ArC*H*CAr); *m*/*z* (EI) 395 (M$^+$, 19%), 349 (M$^+$ − EtOH, 22), 321 (M$^+$ − HCO_2Et, 40), 277 (76), 240 (100), 227 (57), 201 (26), 183 (24), 139 (29) and 116 (44).

1-Ethyl hydrogen 2-[3-(2-nitrophenyl)-2-phenylprop-2-enylidene]succinate 5g. Yield 53%; amorphous *solid* obtained as a pure compound by column chromatography with hexane–ethyl acetate (2:1–1:1) as eluent (Found: C, 66.01; H, 4.97; N, 3.73. $C_{21}H_{19}NO_6$ requires C, 66.14; H, 5.02; N, 3.67%); ν_{max}(Nujol)/cm^{-1} 1527 and 1712 (CO_2Et); δ_H 1.3 (t, *J* 7.2, 3 H, CO_2CH_2*Me*), 3.36 (s, 2 H, CH_2CO$_2$H), 4.37 (q, *J* 7.2, 2 H, CO_2CH_2Me), 6.90–7.30 (m, 8 H, 7 × ArH + ArC*H*CO_2Et), 7.70 (s, 1 H, ArC*H*CAr) and 7.99 (m, 1 H, ArH); *m*/*z* (EI) 381 (M$^+$, 9%), 353 (M$^+$ − CO, 20), 279 (18), 246 (58), 217 (40), 155 (27), 149 (100), 141 (64), 105 (60), 99 (68) and 91 (61).

Procedure for the cyclization

3′-Hydroxy-5′-methoxycarbonyl-1,1′:2′,1″-terphenyl 6a. Ethyl chloroformate (6.65 g, 61.5 mmol) was added to a solution of the monoacid monoester **5a** (9 g, 28 mmol) in dry THF (80 ml); then, triethylamine (8.5 g, 84 mmol) was added dropwise, with the temperature kept under 25 °C. The reaction mixture was stirred for 15 min, then was treated with 5% HCl (80 ml) and extracted with diethyl ether. The organic phase was concentrated under reduced pressure and the residue was stirred at room temp. with NaOH (2 g, 50 mmol) in methanol for 10 min. The mixture was treated with 5% HCl (100 ml), extracted with diethyl ether, and the organic phase was concentrated under reduced pressure. The residue was crystallized from diisopropyl ether to give the *phenol derivative* **6a** (7.1 g, 83%) as a solid, mp 155–157 °C (Found: C, 79.01; H, 5.35. $C_{20}H_{16}O_3$ requires C, 78.93; H, 5.30%); ν_{max}(Nujol)/cm^{-1} 1565, 1706 (CO_2Me) and 3463 (OH); δ_H 3.92 (s, 3 H, CO_2Me), 5.40 (br s, 1 H, OH), 7.0–7.4 (m, 10 H, 10 × ArH) and 7.70 (br s, 2 H, 2 × ArH); *m*/*z* (EI) 304 (M$^+$, 48%), 273 (M$^+$ − OMe, 87), 245 (M$^+$ − CO_2Me, 92), 227 (M$^+$ − Ph, 81), 215 (100), 202 (93), 189 (67), 139 (42) and 115 (13).

3′-Hydroxy-5′-methoxycarbonyl-4″-methyl-1,1′:2′,1″-terphenyl 6b. Yield 94%; a *solid*, mp 211–212 °C (Found: C, 79.11; H, 5.66. $C_{21}H_{18}O_3$ requires C, 79.23; H, 5.70%); ν_{max}(Nujol)/cm^{-1} 1585, 1698 (CO_2Me) and 3434 (OH); δ_H 2.32 (s, 3 H, Ar*Me*), 3.90 (s, 3 H, CO_2Me), 4.80 (br s, 1 H, OH), 7.00–7.20 (m, 9 H, 9 × ArH) and 7.68 (m, 2 H, 2 × ArH); *m*/*z* (EI) 319 (M$^+$ + 1, 20%), 318 (M$^+$, 100), 303 (M$^+$ − Me, 18), 287 (M$^+$ − OMe, 23), 259 (M$^+$ − CO_2Me, 19), 226 (16), 215 (41), 202 (15), 189 (18), 139 (13) and 115 (12).

3′-Hydroxy-4″-methoxy-5′-methoxycarbonyl-1,1′:2′,1″-terphenyl 6c. Yield 88%; a *solid*, mp 208–209 °C (Found: C, 75.61; H, 5.35. $C_{21}H_{18}O_4$ requires C, 75.43; H, 5.43%); ν_{max}(Nujol)/cm^{-1} 1609, 1694 (CO_2Me) and 3436 (OH); δ_H 3.78 (s, 3 H, OMe), 3.92 (s, 3 H, CO_2Me), 5.34 (s, 1 H), 6.8–7.2 (m, 9 H, 9 × ArH) and 7.67 (m, 2 H, 2 × ArH); *m*/*z* (EI) 334 (M$^+$, 39%), 303 (M$^+$ − OMe, 9), 301 (10), 275 (M$^+$ − CO_2Me, 94), 215 (38), 202 (100), 189 (29), 176 (21) and 152 (12).

3′-Hydroxy-4-methoxy-5′-methoxycarbonyl-1,1′:2′,1″-terphenyl 6d. Yield 81%; a *solid*, mp 158–159 °C (Found: C, 75.38; H, 5.51%); ν_{max}(Nujol)/cm^{-1} 1609, 1690 (CO_2Me) and 3374 (OH); δ_H 3.78 (s, 3 H, OMe), 3.93 (s, 3 H, CO_2Me), 5.3 (s, 1 H, OH), 6.60–7.05 (m, 4 H, 4 × ArH *p*-substituted), 7.10–7.40 (m, 5 H, 5 × ArH) and 7.66 (m, 2 H, 2 × ArH); *m*/*z* (EI) 334 (M$^+$, 36%), 303 (M$^+$ − OMe, 12), 301 (10), 275 (M$^+$ − CO_2Me, 60), 242 (34), 213 (76), 202 (100), 189 (28), 176 (21) and 152 (14).

4-Chloro-4″-cyano-5′-ethoxycarbonyl-3′-hydroxy-1,1′:2′,1″-terphenyl 6e. Yield 77%; a *solid*, mp 164–165 °C (Found: C, 70.10; H, 4.31; Cl, 9.21; N, 3.59. $C_{22}H_{16}ClNO_3$ requires C, 69.94; H, 4.27; Cl, 9.38; N, 3.71%); ν_{max}(Nujol)/cm^{-1} 1610, 1719 (CO_2Et), 2236 (C≡N) and 3341 (OH); δ_H 1.40 (t, *J* 7.5, 3 H,

CO_2CH_2*Me*), 4.40 (q, *J* 7.5, 2 H, CO_2CH_2Me), 5.56 (br s, 1 H) and 6.90–7.70 (m, 10 H, 10 × ArH); *m*/*z* (EI) 379 (M^+ + 2, 21%), 377 (M^+, 62), 332 (M^+ − OEt, 44), 304 (M^+ − CO_2Et, 8), 269 (61), 240 (100), 213 (23), 201 (13) and 187 (8).

3′-Hydroxy-3,3″,4,4″-tetramethoxy-5′-methoxycarbonyl-1,1′:2′,1″-terphenyl 6f. Yield 84%; a *solid*, mp 175–176 °C (from AcOEt) (Found: C, 68.04; H, 5.63. $C_{24}H_{24}O_7$ requires C, 67.92; H, 5.70%); ν_{max}(Nujol)/cm^{-1} 1702 (CO_2Me) and 3425 (OH); δ_H 3.60 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 3.96 (s, 3 H, CO_2Me), 4.75 (br s, 1 H, OH), 6.5–6.9 (m, 6 H, 6 × ArH) and 7.63–7.72 (m, 2 H, 2 × ArH); *m*/*z* (EI) 424 (M^+, 100%), 393 (M^+ − OMe, 8), 377 (11), 247 (5), 189 (10) and 91 (18).

5′-Ethoxycarbonyl-3′-hydroxy-2″-nitro-1,1′:2′,1″-terphenyl 6g. Yield 78%; amorphous *solid* obtained as a pure compound by column chromatography and elution with hexane–ethyl acetate (3:1–2:1) (Found: C, 69.28; H, 4.66; N, 3.75. $C_{21}H_{17}NO_5$ requires C, 69.41; H, 4.72; N, 3.85%); ν_{max}(Nujol)/cm^{-1} 1708 (CO_2Et) and 3380 (OH); δ_H 1.35 (t, *J* 6.7, 3 H, CO_2CH_2*Me*), 4.40 (q, *J* 6.7, 2 H, CO_2CH_2Me), 6.90–7.40 (m, 8 H, 8 × ArH), 7.63 (d, *J* 1.5, 1 H, ArH), 7.72 (d, *J* 1.5, 1 H, ArH) and 7.92–8.00 (m, 1 H, ArH); *m*/*z* (EI) 363 (M^+, 100%), 318 (M^+ − OEt, 47), 274 (34), 246 (62), 215 (69), 119 (67), 105 (81) and 77 (36).

Procedure for deoxygenation of derivative 6

4′-Methoxycarbonyl-1,1′:2′,1″-terphenyl 8a. A mixture of compound **6a** (2 g, 6.6 mmol), potassium carbonate (4.8 g, 33 mmol), and 5-chloro-1-phenyl-1*H*-tetrazole (1.8 g, 10 mmol) in acetone (80 ml) was refluxed for 12 h. The solvent was removed under reduced pressure; the residue was treated with water (100 ml), and extracted with methylene dichloride. The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was chromatographed on a silica gel column, with hexane–ethyl acetate (2:1) as eluent, to give derivative **7a** (2.8 g, 94%).

This derivative was added to a solution of $NiCl_2$·$6H_2O$ (7.8 g, 33 mmol) in methanol (100 ml) and the mixture was stirred until it became homogeneous. The resulting solution was cooled at 0 °C and $NaBH_4$ (0.75 g, 20 mmol) in methanol (20 ml) was added dropwise. After being stirred for 30 min the black mixture was treated with 1% HCl (100 ml) and extracted with diethyl ether (150 ml). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The residue was chromatographed on a silica gel column, and eluted with hexane–acetate (9:1), to give recovered intermediate **7a** (1.0 g) and the o-*terphenyl* **8a** as an oil (0.93 g, 51%) (Found: C, 83.47; H, 5.51. $C_{20}H_{16}O_2$ requires C, 83.31; H, 5.59%); ν_{max}(film)/cm^{-1} 1600 and 1721 (CO_2Me); δ_H 3.93 (s, 3 H, CO_2Me), 7.05–7.3 (m, 11 H) and 8.04–8.12 (m, 2 H); *m*/*z* (EI) 288 (M^+, 100%), 274 (15), 257 (M^+ − OMe, 43), 229 (M^+ − CO_2Me, 65), 202 (24), 165 (8), 152 (11), 128 (9) and 113 (13).

3,3″,4,4″-Tetramethoxy-4′-methoxycarbonyl-1,1′:2′,1″-terphenyl 8f. Yield 55%; an *oil* obtained as a pure compound by column chromatography with hexane–ethyl acetate (2:1–1:1) as eluent (Found: C, 70.79; H, 6.01. $C_{24}H_{24}O_6$ requires C, 70.58; H, 5.92%); ν_{max}(film)/cm^{-1} 1600 and 1716 (CO_2Me); δ_H 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.86 (br s, 6 H, 2 × OMe), 3.95 (s, 3 H, CO_2Me), 6.55–6.85 (m, 6 H, 6 × ArH) and 7.9–8.1 (m, 3 H, ArH); *m*/*z* (EI) 408 (M^+, 52%), 376 (M^+ − MeOH, 7), 349 (M^+ − CO_2Me, 100), 318 (24), 202 (30) and 189 (54).

Preparation of the triphenylene

Methyl 6,7,10,11-tetramethoxytriphenylene-2-carboxylate 9. The *o*-terphenyl **8f** (0.9 g, 2.2 mmol) as a solution in CH_2Cl_2 (5 ml) was added dropwise at room temp. to a stirred solution of $FeCl_3$ (1.1 g, 6.7 mmol) in CH_2Cl_2 (20 ml). A catalytic quantity (few mg) of conc. H_2SO_4 was added and the stirring was continued for 15 min; then the mixture was quenched with MeOH (5 ml), diluted with diethyl ether (80 ml), and washed with water (80 ml). The organic phase was dried over sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on a silica gel column, and eluted with hexane–ethyl acetate (2:1–1:3), to give *derivative* **9** (0.5 g, 56%) as an amorphous solid (Found: C, 70.86; H, 5.40. $C_{24}H_{22}O_6$ requires C, 70.93; H, 5.46%); ν_{max}(Nujol)/cm^{-1} 1518, 1614 and 1720 (CO_2Me); δ_H 4.05 (s, 3 H, CO_2Me), 4.12 (s, 9 H, 3 × OMe), 4.14 (s, 3 H, OMe), 7.65 (br s, 2 H, 2 × ArH), 7.86 (s, 1 H, ArH), 7.93 (s, 1 H, ArH), 8.15 (d, *J* 8, 1 H, ArH), 8.42 (d, *J* 8, 1 H, ArH) and 9.10 (s, 1 H, ArH); *m*/*z* (EI) 406 (M^+, 100%), 363 (18), 348 (10), 304 (17), 203 (22) and 188 (19).

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