Thermal oxidation of tetracyclones (2,3,4,5-tetraarylcyclopentadienones)

Thies Thiemann[a]*, Jesus Iniesta[b] and David J. Walton[c]

[a]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816-8580, Japan*

[b]*Department of Physical Chemistry, Institute of Electrochemistry, University of Alicante, E-03080 Alicante, Spain*

[c]*School of Science and the Environment, Coventry University, Priory Street, Coventry CV1 5FB, UK*

Tetracyclones are transformed to a mixture of diacylstilbenes and α-pyrones, when they are heated in diphenylether saturated with oxygen.

Keywords: tetracyclones, tetraarylcyclopentadienones, oxidation, diacylstilbenes, α-pyrones, Diels–Alder reaction

Tetracyclones[1] (2,3,4,5-tetrarylcyclopentadienones) are valuable dienes for Diels–Alder reactions and can be used as substrates for the preparation of branched oligoarenes.[2-5] Due to the aryl groups at C2 and C5, the molecules often necessitate high temperatures[3] for the cycloaddition reactions to be successful. The corresponding tetraarylthiophene *S*-oxide show a much better reactivity in Diels–Alder reactions under normal electron demand. They are thermally less stable, however.[6] Typical solvents used in the transformations are dichlorobenzene and diphenyl ether.[7-9] The authors have noted that when tetracyclones are treated with poorly reactive enes, such as with estra-1,3,5(10),16-tetraenes (unpublished results), in diphenyl ether at higher temperatures and under a normal atmosphere, products can be isolated stemming from an oxidation of the tetracyclones. That tetracyclones can be oxidised easily in diphenyl ether at elevated temperatures can also be seen in the Diels–Alder reaction with benzo[*b*]thiophene *S*,*S*-dioxide, where the primary cycloadduct sulfone oxidises excess tetracyclone.[10] In the following contribution, the authors report on the composition of these products.

The redox behaviour of tetracyclones has been studied in some detail, although the reductive behaviour of the molecules leading to its radical anion is much better known than the oxidative behaviour. In particular, while there are numerous reports on the electrochemical reduction of the systems, there is no report on the direct preparative electrooxidation of tetracyclones. Analytically, the electrochemical redox behaviour of tetracyclone has been studied to some degree, but no product analysis has been undertaken for the electrooxidative process.[11,12] Our interest in an electrochemical oxidation of these compounds, especially in view of a comparative analysis to the electrooxidative behaviour of the related tetraarylthiophene *S*-oxides,[13,14] led us to a preliminary study of the behaviour of tetracyclones towards oxygen under non-photolytic conditions. These experiments found further encouragement by our identification of oxidation products of tetracyclone (tetraphenylcyclopentadienone) itself, when the molecule was reacted with sterically hindered steroidal dienophiles in Diels–Alder reactions at high temperatures (unpublished results and ref.15).

The reactions of tetracyclone (**1a**) and its derivatives with a number of oxidants have been reported, such as with peroxides, especially with hydrogen peroxide (in pyridine[16] or acetic acid/acetic anhydride[17] reaction systems),[16,17] with peracids,[18] and with nitric acid.[19] Also, tetracyclone (**1a**) has been reacted with iodosylbenzene (PhIO) and catalytic tetraphenylporphinato manganese (III) chloride (TPPMnCl),[20] with bis(trimethylsilyl) monoperoxysulfate,[21] and with chromium pentoxide etherate as well as with chromium trioxide (see ref. 22 and refs cited therein). Furthermore, tetracyclone (**1a**) has been reacted with superoxide anion.[23-26]

Also, the reaction of tetracyclone (**1a**) with photochemically[27-32] and chemically[33,34] generated singlet oxygen has been studied in some detail.

The oxidation of tetracyclone (**1a**) and of similar cyclopentadienones can follow a number of pathways, depending on the oxidant. The most important routes, though, are an initial epoxidation of the tetracyclone as is witnessed in the case of the reaction of tetracyclone with H_2O_2 [16,17] and with PhIO and catalytic TPPMnCl.[20] The epoxide **2** has been isolated, but it has also been shown that there are routes

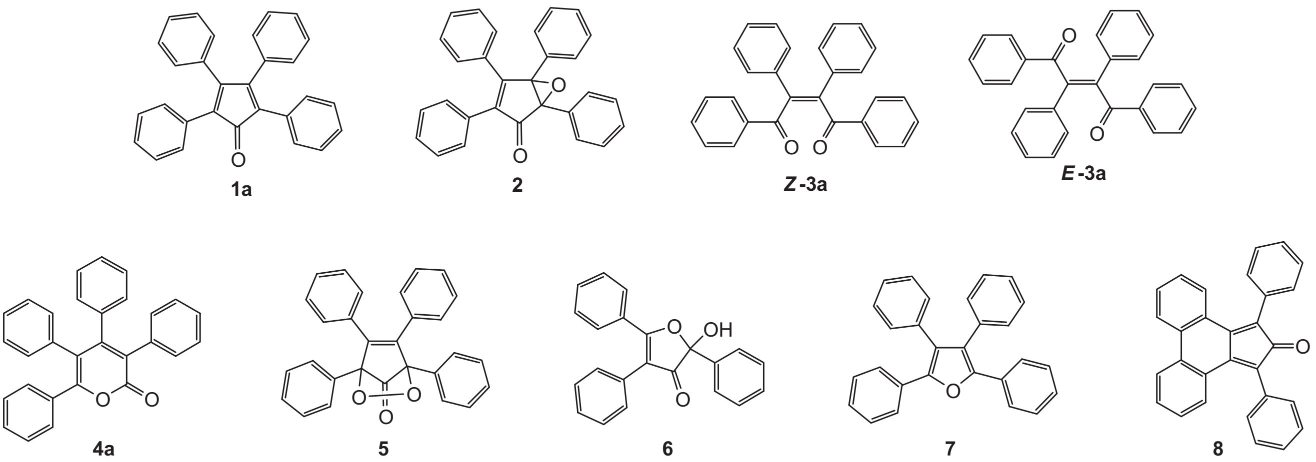


Fig. 1 Tetracyclone (**1a**) and some of its known oxidation products **2–7** and phencyclone **8.**

---

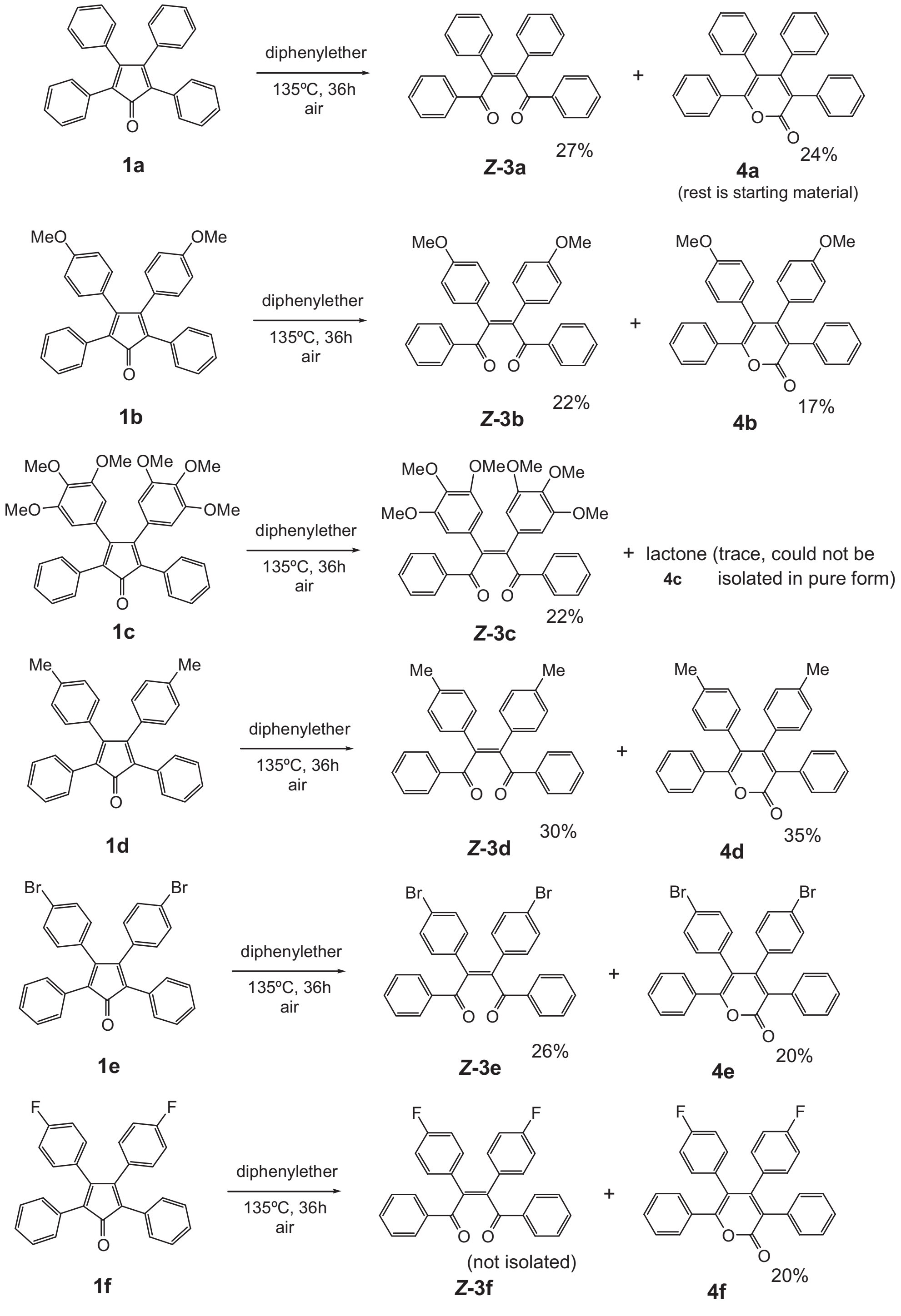
* Correspondent. E-mail: thies@cm.kyushu-u.ac.jp

from the epoxide to the tetraphenyl-α-pyrone. A Baeyer Villiger type rearrangement leading from the tetracyclone (**1a**) to the α-pyrone **4a** has been observed in the reaction with bis(trimethylsilyl) monoperoxysulfate.[21] Also, the oxidation of tetraarylcyclopentadienones with cerium ammonium nitrate (CAN)[35] in aqueous 75% THF has been reported to yield the lactones directly and to give tetraphenyl-α-pyrones **4a** and derivatives in fair yield.

Different products, namely 2-hydroxyfuran-3-one **6** and tetraphenylfuran (**7**), are obtained by the reaction of tetracyclone with superoxide, where the reaction is thought to be initiated by a one-electron transfer from the superoxide to tetracyclone (**1a**) with subsequent addition of oxygen to the tetracyclone radical anion and follow-up reactions.[23-26]

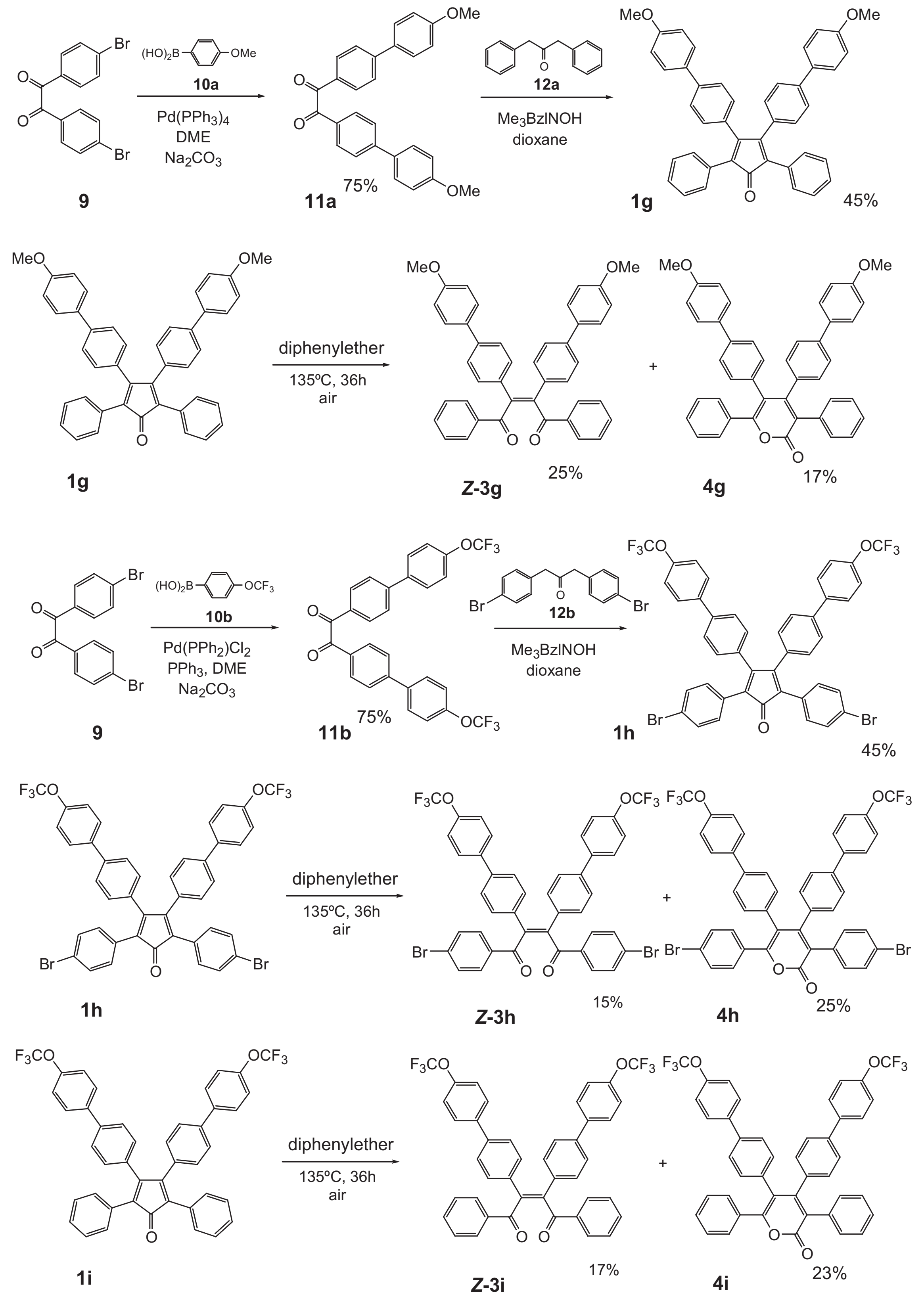
The photoirradiation of tetracyclone in the presence of oxygen is thought to proceed via an epidioxide **5**, stemming from a 1,4-cycloaddition of singlet oxygen to the tetracyclone (**1a**). The epidioxide **5** then loses carbon monoxide to form (*Z*)-diacylstilbenes, ***Z*-3a**, which under the photolytic conditions can partly isomerise to the (*E*)-diacylstilbenes, ***E*-3a**. Also, the photoreaction of other substituted tetracyclones in diethyl ether is known to give (*Z*)-α,α'-diacylstilbenes **3**. Often, tetraphenyl substituted α-pyrone **4a** is also formed in the reaction.

We have found that both (*Z*)-diacylstilbenes **3** as well as α-pyrones **4**, being products of most of the oxidation reactions of tetracyclone (**1a**) mentioned above, are formed in significant amounts, when tetracyclone or its derivatives

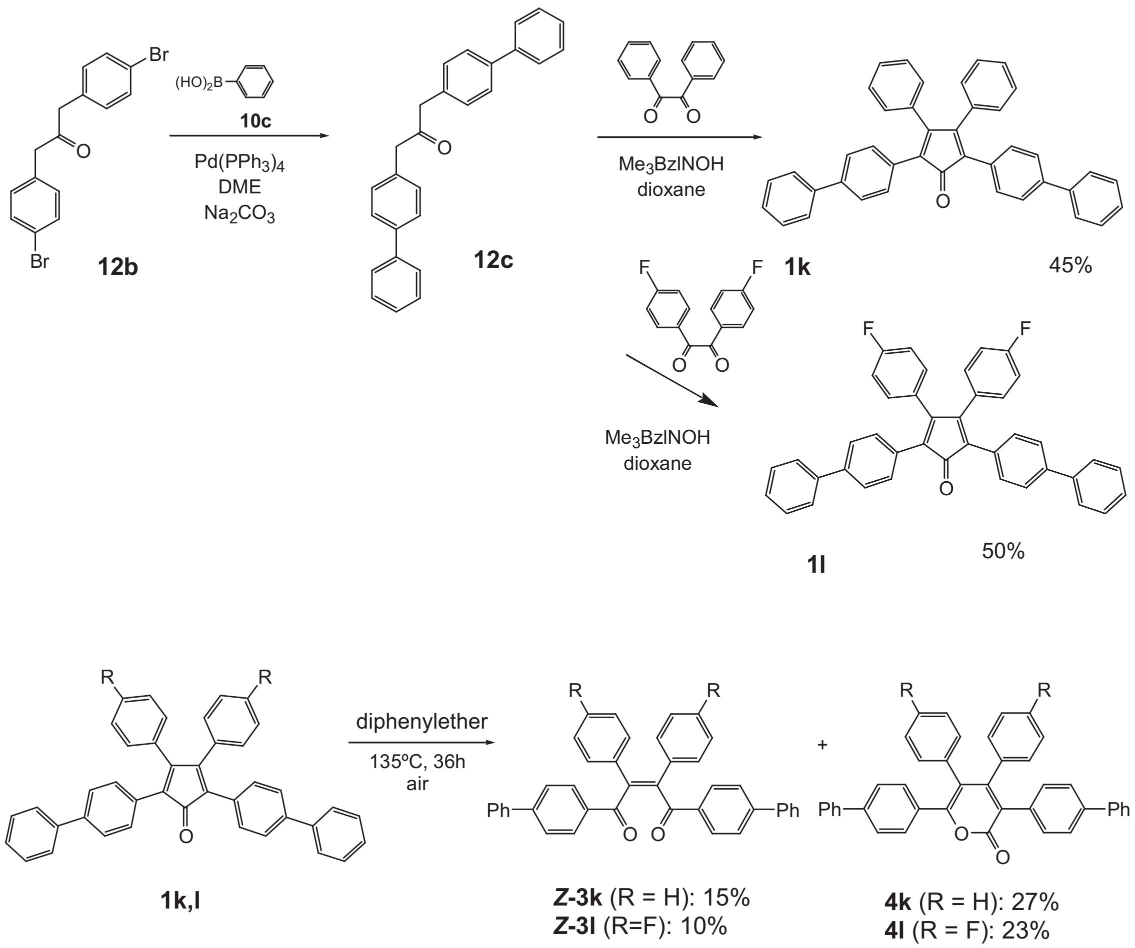


Scheme 1 Thermal oxidation of tetracyclones **1** in diphenyl ether in the presence of oxygen.

are heated in a solvent that contains oxygen. Thus, when tetracyclone (**1a**) in diphenylether is heated at 135°C for 35 h (under non-photolytic conditions), (*Z*)-1,2-dibenzoyl-1,2-diphenylethene (***Z*-3a**) and tetraphenyl α-pyrone (**4a**) can be isolated in 27% and 24%, respectively, the remainder being unreacted starting material. A number of substituted tetraarylcyclopentadienones were subjected to the same procedure yielding the corresponding (*Z*)-diacylstilbenes and α-pyrones, where (*Z*)-diacylstilbene and α-pyrone are formed in varying amounts (Schemes 2 and 3). The reaction of **1c** with electron rich and sterically exacting methyl substituents led to reduced formation of the α-pyrone, while in the case of **1f**, a tetracyclone with flurosubstituents, no (*Z*)-diacylstilbenes could be isolated.



Scheme 2 Synthesis and reaction of expanded tetracyclones **1g** – **1i**.



Scheme 3 Synthesis and reaction of expanded tetracyclones **1k,1l.**

To our knowledge, this thermal oxidative reaction of cyclopentadienones with oxygen under non-photolytic conditions has only been commented upon once, namely in the work of Dilthey *et al.*,[36] who have studied the non-photolytic oxidation of phencyclone (**8**) in toluene and in pyridine. Thus, the authors reported that passing oxygen through a solution of phencyclone [1,3-diphenyl-2*H*-cyclopenta-[1]phenanthren-2-one] in pyridine gives 9,10-dibenzoylphenanthrene.

As the high reaction temperatures preclude the isolation of reaction intermediates, the mechanism of the reaction could not yet be ascertained. We feel, however, that this oxidative 'degradation' of cyclopentadienones is important to take into account when subjecting the molecules to cycloaddition reactions with sluggish dienophiles or to other reactions at higher temperatures in the presence of oxygen.

Within this context, it may be noted that solventless cycloaddition of tetracyclones with relatively low melting or liquid dienophiles can lead to a significant lowering of reaction temperature at which the cycloaddition reactions are successful (for further examples of solventless cycloaddition of tetracyclone see refs 37 and 38). Thus, reaction of tetracyclone (**1a**) itself with phenylacetylene (**13a**) can be performed at 135°C within 10 min., with diphenylacetylene [tolane] (**13b**) at 175°C within 5 h (Scheme 4). Otherwise, the reaction solutions need to be deaerated with care.

Experimental

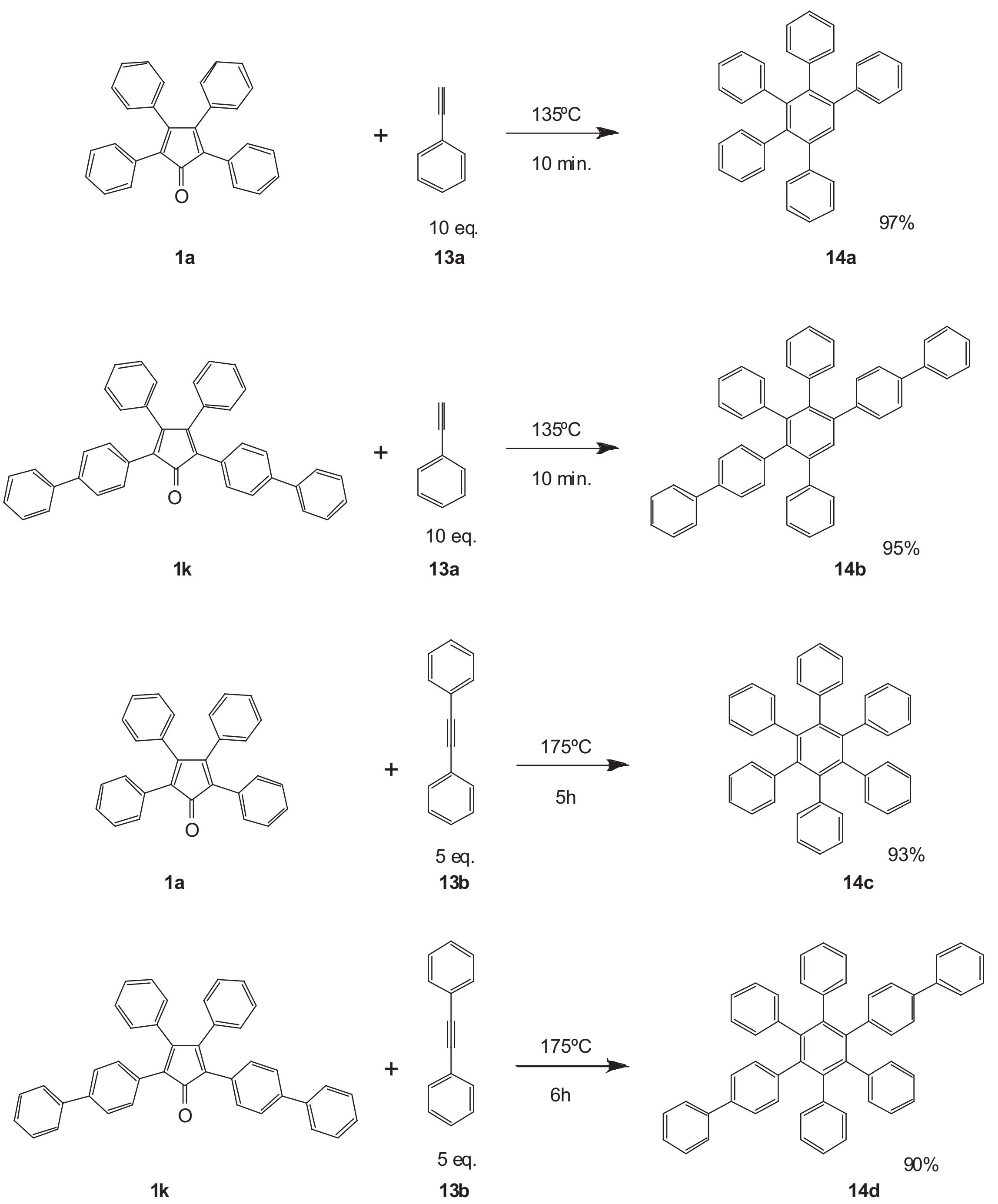
General

Tetracyclone (**1a**) was obtained commercially (TCI) as well as by known synthesis.[39] Hexamethoxytetracyclone (**1c**) was prepared according to a procedure by Müllen *et al.*,[40] which was slightly modified (dioxane, trimethylbenzylammonium hydroxide, 1 h, reflux, 25% yield). **1b**,[41] **1d**,[42] **1e**[43] and **1f**[44] were synthesised accordingly from the respective 4,4'-substituted benzils and diphenylacetone. 4,4'-Dibromodiphenylacetone (**12b**) was obtained from 4-bromophenylacetic acid (DCC, DMP, CH_2Cl_2).[45]

Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^1H- and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). J^* = denotes the coupling constant of an AA'XX' system, in the present case for *p*-substituted arenes as listed below, where the apparent J value is $J^* = J_{23} + J_{25}$. Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV). Column chromatography was carried out on Wakogel 300. All experiments leading to the preparation of the tetracyclones were purged with argon at the start.

Tetracyclone **1f** was prepared from the commercially available *p,p*'-dibromobenzil (**9**) (Acros) which was transformed to bis (*p*-methoxybiphenyl)benzil (**10**) by Suzuki coupling (Scheme 2). The subsequent reaction of the benzil **10** with diphenylacetone was carried out by the usual procedure.

Preparation of tetracyclone derivative **1g**: A deaerated mixture of commercially available *p,p*'-dibromobenzil (**9**) (700 mg, 1.90 mmol), *p*-methoxyphenylboronic acid (1.0 g, 6.58 mmol) and $Pd(PPh_3)_4$ (30 mg, 2.6×10^{-5} mol) in DME (6.0 ml) and 2M Na_2CO_3 (2.6 ml) was held at 70°C for 12 h. Thereafter, the cooled reaction solution was diluted with water (10 ml) and extracted with chloroform (3 × 20 ml). The organic phase was dried and concentrated under reduced pressure. Column chromatography of the residue on silica gel gave *p,p*'-bis(*p*-methoxyphenyl)benzil (**11a**) (see ref. 46) (600 mg, 75%) as pale yellow needles m.p. 208°C; [Found: MH^+, 423.1595. $C_{28}H_{23}O_4$ requires (MH^+) 423.1596; FAB mode]; ν_{max} (KBr/cm^{-1}) 1660, 1597, 1525, 1495, 1297, 1249, 1172, 1038, 883, 852, 818, 694; δ_H (270 MHz, $CDCl_3$) δ 3.85 (6H, s, 2 OCH_3), 6.99 (4H, m, J^* = 8.6 Hz), 7.58 (4H, m, J^* = 8.6 Hz), 7.69 (4H, m, J^* = 8.2 Hz), 8.03 (4H, m, J^* = 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 55.4 (OCH_3), 114.5 (CH), 126.9 (CH), 128.5 (CH), 130.6 (CH), 131.2 (C_{quat}), 131.8 (C_{quat}), 147.1



Scheme 4 Solventless cycloaddition of tetracyclones to phenyl-substituted alkynes.

(C_{quat}), 160.2 (C_{quat}), 194,2 (C_{quat}, C=O); MS (FAB, 3-nitrobenyl alcohol) *m/z* (%) 423 (MH^+, 4), 211 ($MeO\text{-}C_6H_4\text{-}C_6H_4CO^+$, 43).

To **11a** (575 mg, 1.36 mmol) in a mixed solution of dioxane (2 ml) and trimethylbenzylammonium hydroxide (40%aq., 1.2 ml) was added diphenylacetone (295 mg, 1.40 mmol). The reaction mixture was held at 65°C for 6 h. Then the reaction mixture was diluted with chloroform (20 ml) and washed with water (2 × 10 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated. Column chromatography of the residue on silica gel (chloroform/ether/hexane 1: 1: 1 eluting two smaller fractions, then changed to chloroform to elute **1g**) gave 3,4-bis(*p*-methoxybiphenyl)-2,5-diphenylcyclopentadienone (**1g**) (363 mg, 0.61 mmol, 45%) as purple-brownish crystals, m.p. 199°C; (Found: MH^+ 597.2432. $C_{43}H_{33}O_3$ requires M[H], 597.2430); ν_{max} (KBr/cm^{-1}) 2956, 2832, 1703, 1601, 1495, 1248, 1175, 1116, 1039, 828; δ_H (270 MHz, $CDCl_3$) 3.84 (6H, s, 2 OCH_3), 6.95 (4H, m, J^* = 8.6 Hz), 7.01 (4H, m, J^* = 8.3 Hz), 7.24–7.29 (10H, m), 7.40 (4H, m, J^* = 8.3 Hz), 7.52 (4H, m, J^* = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 55.4 (OCH_3), 114.3 (CH), 125.4 (C_{quat}), 125.9 (CH), 127.4 (CH), 128.0 (CH), 128.1 (CH), 130.1 (CH), 130.2 (CH), 131.0 (C_{quat}), 131.3 (C_{quat}), 132.6 (C_{quat}), 140.6 (C_{quat}), 154.1 (C_{quat}), 159.5 (C_{quat}), 200.2 (C_{quat}, C=O). MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 597 (MH^+, 9).

Preparation of tetracyclone derivative **1h**: A mixture of *p,p'*-dibromobenzil (**9**, 2.38 g, 6.4 mmol), *p*-trifluoromethoxyphenylboronic acid (**10b**, 4.26 g, 20.7 mmol), $Pd(PPh_3)_2Cl_2$ (110 mg, 0.16 mmol) and PPh_3 (84 mg, 0.32 mmol) in DME (15 ml) and aq. Na_2CO_3 (2.3 g Na_2CO_3 in 15 ml H_2O) was kept at 70°C for 14 h. The cooled reaction mixture was poured into water (100 ml) and extracted with chloroform (3 × 25 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was submitted to column chromatography on silica gel (hexane/$CHCl_3$ 2:3) to give 1,2-bis-(4'-trifluoromethoxybiphenyl-4-yl)ethane-1,2-dione (**11b**) as pale yellow needles, m.p. 215°C; [Found: MH^+, 531.1025. $C_{28}H_{17}F_6O_4$ requires (MH^+), 531.1025]; ν_{max} (KBr/cm^{-1}) 1653, 1603, 1563, 1530, 1493, 1408, 1282, 1004, 923, 890, 855, 830, 775, 751, 731, 698, 640, 626, 543, 514 cm; δ_H (270 MHz, $CDCl_3$)

7.32 (4H, m), 7.65 (4H, m, J^* = 8.9 Hz), 7.70 (4H, m, J^* = 8.9 Hz), 8.09 (4H, m, J^* = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 120.5 (2C, q, $^1J_{C-F}$ = –257 Hz), 121.4 (4C), 127.6 (4C), 128.8 (4C), 130.6 (4C), 132.1 (2C), 138.2 (2C), 146.1 (2C), 149.6 (2C, q, J = 1.7 Hz), 193.7 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 531 (MH^+, 9.4), 423 (5.9), 265 (100). (Found: C, 63.3; H, 3.1. $C_{28}H_{16}F_6O_4$ requires C, 63.40; H, 3.04).

To **11b**, column chromatography on silica gel (hexane/$CHCl_3$ 4:1) provided **1h** as a deep 'metallic' purple solid; m.p. 269°C; (Found: M^+, 861.9996. $C_{43}H_{24}O_3$ requires M, $^{79}Br^{81}BrF_6$: 861.9981); ν_{max} (KBr/cm^{-1}) 1704, 1488, 1263, 1211, 1165, 1072, 1007, 845, 809, 771; δ_H (270 MHz, $CDCl_3$) 7.02 (4H, m, J^* = 7.6 Hz), 7.14 (4H, m, J^* = 7.8 Hz), 7.27 (4H, m, J^* = 7.6 Hz), 7.37–7.45 (8H, m), 7.59 (4H, m, J^* = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) 118.1 (2C, q, ^2J = –251 Hz), 121.3 (4C), 122.2 (2C), 124.2 (2C), 126.7 (4C), 128.3 (4C), 129.4 (2C), 129.9 (4C), 131.5 (4C), 131.6 (4C), 131.9 (2C), 138.6 (2C), 140.1 (2C), 149.0 (2C, q, J = 2.2 Hz), 199.1 (CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 864 ($^{81}Br_2$)M^+, 25), 862 ([$^{79}Br^{81}Br$]M^+, 36), 860 ([$^{79}Br_2$]M^+, 17), 498 (14).

Further tetracyclones

Hexamethoxytetracyclone (**1c**): Red-brown needles, m.p. 175°C; [Found: MH^+ 565.2228. $C_{35}H_{33}O_7$ requires (MH^+), 565.2226]; ν_{max} (KBr/cm^{-1}) 3070, 2996, 2926, 1712, 1579, 1411, 1351, 1240, 1128, 1004, 852; δ_H (270 MHz, $CDCl_3$) 3.45 (12H, s, 4 OCH_3), 3.84 (6H, s, 2 OCH_3), 6.17 (4H, s), 7.24–7.28 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 55.9, 61.0, 107.2, 125.3, 127.6, 128.1, 130.1, 130.8, 138.3, 152.6 (two sets of isochronous nuclei), 153.6, 199.9; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 565 (MH^+, 36), 564 (M^+, 32). (Found: C, 74.1; H, 5.7. $C_{35}H_{32}O_7$ requires C, 74.45; H, 5.71).

3,4-Bis(4-trifluoromethoxybiphenyl)-2,5-diphenylcyclopentadienone (**1i**): Deep-purple solid, m.p. 208°C; (Found: MH^+ 705.1862. $C_{43}H_{27}O_3F_6$ requires: MH^+, 705.1864); ν_{max} (KBr/cm^{-1}) 1704, 1490, 1267, 1219, 1164, 1005, 920, 841, 738, 693; δ_H (270 MHz, $CDCl_3$) 7.04 (4H, d, ^3J = 8.6 Hz), 7.24–7.29 (14H, m), 7.41 (4H, m, J^* = 8.6 Hz), 7.58 (4H, m, J^* = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 120.5 (q, 2C, $^1J_{CF}$ = –256 Hz), 121.3 (4C), 125.8 (2C), 126.5 (4C), 127.6 (2C), 128.1 (4C), 128.3 (4C), 130.1 (4C), 130.2 (4C), 130.7 (2C), 132.4 (2C), 138.8 (2C), 139.7 (2C), 148.9 (q, J = 1.7 Hz), 153.6 (2C), 200.0 (CO); MS FAB, 3-nitrobenzyl alcohol) *m/z* (%) 705 (MH^+, 100), 676 (9.2), 587 (11), 498 (14), 338 (40), 265 (30).

2,5-Bis(biphenyl)-3,4-diphenylcyclopentadienone (**1k**):[47] Brown-black solid; m.p. 282°C; ν_{max} (KBr/cm^{-1}) 1709, 1485, 1301, 1115, 1084, 1026, 1006, 915, 850, 798, 761, 738, 708 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.98 (4H, m, J^* = 8.4 Hz), 7.17–7.35 (12H, m), 7.41 (4H, m), 7.49 (4H, m, J^* = 8.1 Hz), 7.58 (4H, m, J^* = 7.8 Hz); δ_C (67.8 MHz, $CDCl_3$) 124.9 (2C), 126.7 (4C), 127.0 (4C), 127.3 (2C), 128.1 (4C), 128.6 (2C), 128.7 (4C), 129.3 (4C), 129.7 (2C), 130.5 (4C), 133.2 (2C), 140.0 (2C), 140.7 (2C), 154.6 (2C), 200.5; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 536 (M^+, 0.5).

2,5-Bis(biphenyl)-3,4-bis(4-fluorophenyl)cyclopentadienone (**1l**): Brown-black solid; 235°C; (Found: M^+ 572.1941. $C_{41}H_{26}OF_2$ requires: 572.1952); ν_{max} (KBr/cm^{-1}) 1702, 1540, 1531, 1529, 1507, 1223, 1158, 1122, 1006, 859, 843, 755, 700, 585, 569, 536, 516, 496; δ_H (270 MHz, $CDCl_3$) 6.89–6.96 (8H, m), 7.24–7.60 (18H, m); δ_C (67.8 MHz, $CDCl_3$) 115.5 (4C, d, J_{CF} = 20.7 Hz), 125.2 (2C), 126.8 (4C), 127.0 (4C), 127.5 (2C), 128.8 (4C), 128.9 (2C), 129.4 (2C), 130.4 (4C), 131.3 (4C, d, J_{CF} = 11 Hz), 140.3 (2C), 140.5 (2C), 153.1 (2C), 164.0 (2C, d, J_{CF} = –232 Hz), 200.1; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 572 (M^+, 1.1).

Thermal reaction of tetracyclone (**1a**) with oxygen: Tetracyclone (**1a**) (450 mg, 1.17 mmol) in diphenylether (2.0 ml) was heated at 135°C for 36 h. Thereafter, the solution was subjected directly to column chromatography on silica gel with hexane as an initial eluant (to separate off diphenyl ether), thereafter with a solvent mixture of hexane/$CHCl_3$/ether (10:1:1) to give ***Z*-3a** (124 mg, 27%) and **4a** (112 mg, 24%).

Selected spectroscopic and analytical data of (Z)-1,2-diaroyl-1,2-diarylethenes **3** *and α-pyrones* **4**

(Z)-1,2-Dibenzoyl-1,2-bis(4-methoxyphenyl)ethene (***Z*-3b**): Pale yellow needles; m.p. 189°C; (Found: MH^+ 449.1756. $C_{30}H_{25}O_4$ requires: MH^+, 449.1753); ν_{max} (KBr/cm^{-1}) 3058, 2926, 1657, 1605, 1509, 1250, 1175, 1031, 835, 692; δ_H (270 MHz, $CDCl_3$) 3.74 (6H, s, 2 OCH_3), 6.71 (4H, m, J^* = 8.6 Hz), 7.08 (4H, m, J^* = 8.6 Hz), 7.41 (2H, m), 7.28 (4H, m), 7.83 (4H, m, J^* = 7.3 Hz); δ_C (67.8 MHz, $CDCl_3$) 55.1, 114.1, 127.7, 128.2, 130.0, 131.3, 132.7, 136.6, 143.5, 159.4, 197.4; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 449 (MH^+, 100). (Found: C, 80.5; H, 5.4. $C_{30}H_{24}O$ requires C, 80.33; H, 5.39).

(Z)-1,2-Dibenzoyl-1,2-bis(3,4,5-trimethoxyphenyl)ethene (***Z*-3c**): Slowly crystallising colourless solid; (Found: MH^+, 569.2174. $C_{34}H_{33}O_8$ requires 569.2175); ν_{max} (KBr/cm^{-1}) 3056, 2928, 1581, 1504, 1450, 1413, 1341, 1243, 1128, 1006, 750; δ_H (270 MHz, $CDCl_3$) 3.59 (12H, s, 4 OCH_3), 3.79 (6H, s, 2 OCH_3), 6.40 (4H, s), 7.26–7.48 (6H, m), 7.87 (4H, m, J^* = 7.3 Hz); δ_C (67.8 MHz, $CDCl_3$) 56.1, 60.9, 107.0, 128.4, 129.8, 130.5, 133.2, 136.4, 138.2, 144.3, 153.3, 197.4; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 569 (57, MH^+).

(Z)-1,2-Dibenzoyl-1,2-bis(4-bromophenyl)ethene (***Z*-3e**) (for ***Z*-3d**, see also refs 49,50; ***Z*-3e** had been reported previously[51,52]): Colourless solid; m.p. 228°C (Found: MH^+, 558.9738. $C_{29}H_{19}O_2{}^{79}Br^{81}Br$ requires MH, 558.9734); ν_{max} (KBr/cm^{-1}) 2924, 1663, 1593, 1484, 1273, 1012, 829, 713; δ_H (270 MHz, $CDCl_3$) 7.03 (4H, m, J^* = 8.2 Hz), 7.29–7.37 (8H, m), 7.43 (2H, m), 7.80 (4H, m, J^* = 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 123.1, 128.4, 130.0, 131.2, 132.2, 133.3, 133.8, 135.9, 143.8, 196.2 (C=O); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 559 ([$^{81}Br^{79}Br$]MH^+, 12).

(Z)-1,2-Dibenzoyl-1,2-bis(4-methoxybiphenyl)ethene (***Z*-3g**): Colourless solid; m.p. 233°C; (Found: MH^+, 601.2377. $C_{42}H_{33}O_4$ requires MH, 601.2379); ν_{max} (KBr/cm^{-1}) 3032, 2924, 1653, 1602, 1495, 1289, 1246, 1178, 1037, 826, 809; δ_H (270 MHz, $CDCl_3$) 3.82 (6H, s, 2 OCH_3), 6.92 (4H, m, J^* = 8.9 Hz), 7.23–7.49 (18H, m), 7.88 (4H, m, J^* = 7.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 55.4 (OCH_3), 114.3 (CH), 126.7 (CH), 128.0 (CH), 128.4 (CH), 130.1 (CH), 130.3 (CH), 132.5 (C_{quat}), 133.0 (CH), 133.6 (C_{quat}), 136.5 (C_{quat}), 140.5 (C_{quat}), 144.1 (C_{quat}), 159.5 (C_{quat}), 197.1 (C_{quat}, C=O). MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 601 (MH^+, 38).

(Z)-1,2-Bis(-4-bromobenzoyl)-1,2-bis(4-trifluoromethoxybiphenyl)ethene (***Z*-3h**):Slowly crystallising colourless solid; (Found: MH^+, 867.0005. $C_{42}H_{25}O_4{}^{79}Br^{81}BrF_6$ requires MH, 867.0008). ν_{max} (KBr/cm^{-1}) 1654, 1584, 1494, 1397, 1259, 1165, 1068, 1003, 828; δ_H (270 MHz, $CDCl_3$) 7.24 (4H, m, J^* = 7.0 Hz), 7.38–7.57 (16H, m), 7.72 (4H, d, J^* = 8.4 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 867 ($^{79}Br^{81}BrMH^+$, 13).

(Z)-1,2-Dibenzoyl-1,2-bis(4-trifluoromethoxybiphenyl)ethene (***Z*-3i**): Slowly crystallising colourless solid; (Found: MH^+, 709.1808. $C_{42}H_{27}O_4F_6$ requires MH, 709.1814); ν_{max} (neat/cm^{-1}) 3028, 2926, 2866, 1655, 1611, 1510, 1453, 1251, 1173, 1089, 1034, 1004, 838, 809, 755, 671; δ_H (270 MHz, $CDCl_3$) 7.22–7.47 (14H, m), 7.35 (4H, m, J^* = 7.8 Hz), 7.53 (4H, m, J^* = 8.6 Hz), 7.88 (4H, m, J^* = 7.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 120.5 (2C, $^1J_{CF}$ -256 Hz), 121.2 (4C), 127.3 (4C), 128.3 (4C), 128.4 (4C), 130.1 (4C), 130.4 (4C), 133.1 (2C), 134.6 (2C), 136.3 (2C), 138.7 (2C), 139.6 (2C), 144.1 (2C), 148.9 (q, 2C, J 1.7 Hz), 196.7 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 709 (MH^+, 24), 265 (29), 105 (100).

(Z)-1,2-Bis(biphenylcarbonyl-1,2-bis(phenyl)ethene (***Z*-3k**): Colourless needles; m.p. 234°C; (Found: MH^+, 541.2159. $C_{40}H_{29}O_2$ requires MH^+, 541.2168); ν_{max} (neat/cm^{-1}) 1663, 1603, 1486, 1442, 1404, 1263, 1178, 1072, 1029, 1004, 849, 768, 728, 695, 579; δ_H (270 MHz, $CDCl_3$) 7.22 (10H, m), 7.33–7.43 (6H, m), 7.52–7.60 (8H, m), 7.93 (4H, m, J^* = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) 127.02 (4C), 127.26 (4C), 128.10 (2C), 128.41 (2C), 128.71 (4C), 128.83 (4C), 129.85 (4C), 130.63 (4C), 135.17 (2C), 135.31 (2C), 139.99 (2C), 144.48 (2C), 145.66 (2C), 196.48 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 541 (MH^+, 4.6). (Found: C, 88.9; H, 5.15. $C_{40}H_{28}O_2$ requires C, 88.86; H, 5.22).

(Z)-1,2-Bis(biphenylcarbonyl-1,2-bis(4-fluorophenyl)ethene (***Z*-3l**): Colourless needles; m.p. 227°C; (Found: MH^+, 577.1984. $C_{40}H_{27}O_2F_2$ requires 577.1979); ν_{max} (neat/cm^{-1}) 1651, 1599, 1504, 1404, 1236, 1006, 847, 818, 760, 690; δ_H (270 MHz, $CDCl_3$) 6.90–6.96 (4H, m), 7.17–7.44 (10H, m), 7.52–7.60 (8H, m), 7.89 (4H, m, J^* = 7.8 Hz); δ_C 116.1 (4C, J_{CF} 21.2 Hz), 127.1 (4C), 127.3 (4C), 128.2 (2C), 128.9 (4C), 130.6 (4C), 131.2 (2C, d, J_{CF} 3.4 Hz), 131.7 (4C, d, J_{CF} 7.9 Hz), 134.9 (2C), 139.9 (2C), 143.6 (2C), 145.9 (2C), 162.6 (2C, d, J_{CF} -250 Hz), 196.1 (2C, CO); MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 577 (MH^+, 8.5).

4,5-Bis-(4-methoxyphenyl)-3,6-diphenyl-α-pyrone (**4b**):[18] Colourless solid; m.p. 246°C (Lit[18] 234°C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.66 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 6.49 (2H, m, J^* = 8.6 Hz), 6.61 (2H, m, J^* = 8.6 Hz), 6.63 (2H, m, J^* = 8.6 Hz), 6.75 (2H, m, J^* = 8.6 Hz), 7.11–7.34 (10H, m).

4,5-Bis-(4-methylphenyl)-3,6-diphenyl-α-pyrone (**4d**):[18] Colourless solid; m.p. 198°C; [HRMS Found: 429.1852. Calcd. for $C_{31}H_{25}O_2$: 429.1855 (MH^+, FAB)]; ^1H NMR (270 MHz, $CDCl_3$) δ 2.13 (3H, s, CH_3), 2.21 (3H, s, CH_3), 6.59 (2H, m, J^* = 8.1 Hz), 6.72 (2H, m, J^* = 8.1 Hz), 6.74 (2H, m, J^* = 8.1 Hz), 6.85 (2H, m, J^* = 8.1 Hz), 7.10–7.33 (10H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.1 (CH_3), 21.1 (CH_3), 119.7 (C_{quat}), 124.9 (C_{quat}), 127.1 (CH), 127.6 (2C, CH), 127.8 (2C, CH), 128.0 (2C, CH), 128.8 (2C, CH), 129.2 (CH), 129.3 (4C,

CH), 130.6 (2C, CH), 131.1 (2C, CH), 131.9 (C_{quat}), 132.9 (C_{quat}), 133.1 (C_{quat}), 134.5 (C_{quat}), 136.7 (C_{quat}), 136.8 (C_{quat}), 155.6 (C_{quat}), 156.4 (C_{quat}), 162.4 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 429 (MH$^+$, 100), 400 (36), 295 (33), 105 (20).

4,5-Bis(4-bromophenyl)-3,6-diphenyl-α-pyrone (**4e**):[14] Slowly crystallising colourless solid; (Found: M$^+$, 545.9658. $C_{28}H_{18}O_2{}^{79}Br^{81}Br$ requires M, 545.9655); ν_{max} (KBr/cm^{-1}) 1717, 1485, 1072, 1011, 696; δ_H (270 MHz, $CDCl_3$) 6.59 (2H, m, *J** = 8.6 Hz), 6.73 (2H, m, *J** = 8.5 Hz), 7.07–7.36 (14H, m); δ_C (67.8 MHz, $CDCl_3$) 118.0, 121.8, 121.9, 125.5, 127.7, 128.0, 128.1, 128.3, 129.3, 129.8, 130.5, 130.9, 131.6, 132.2, 133.0, 133.6, 133.8, 134.8, 153.4, 157.5, 162.2; MS (70 eV) *m/z* (%) 548 ([$^{81}Br_2$]M$^+$, 6), 546 ([$^{79}Br^{81}Br$]M$^+$, 12), 544 ([$^{79}Br_2$]M$^+$, 6), 105 (100).

4,5-Bis(4-fluorophenyl)-3,6-diphenyl-α-pyrone (**4f**): Colourless solid, m.p. 193°C; (Found: M$^+$, 436.1277. $C_{29}H_{18}O_2F_2$ requires M, 436.1275); ν_{max} (KBr/cm^{-1}) 1715, 1647, 1506, 1440, 1223, 1157, 929, 836, 759, 697; δ_H (270 MHz, $CDCl_3$) 6.67–6.70 (4H, m), 6.78–6.82 (4H, m), 7.09–7.32 (10H, m); δ_C (67.8 MHz, $CDCl_3$) 114.7 (2C, d, J_{CF} = 21.7 Hz), 115.4 (2C, d, J_{CF} = 21.7 Hz), 118.4, 125.5, 127.5, 127.9 (2C), 128.0 (2C), 129.3 (2C), 129.6, 130.5 (2C), 130.8 (d, J_{CF} = 3.9 Hz), 131.2 (2C, d, J_{CF} = 8.4 Hz), 132.0 (d, J_{CF} = 3.3 Hz), 132.4, 133.0 (2C, d, J_{CF} = 8.4 Hz), 133.9, 154.0, 157.0, 161.7 (d, J_{CF} = –248 Hz), 161.8 (d, J_{CF} = –248 Hz), 161.9; MS (EI, 70 eV) *m/z* (%) 436 (M$^+$, 1.2), 199 (100).

3,6-Diphenyl-4,5-bis(4-methoxybiphenyl)-α-pyrone (**4g**): Slowly crystallising colourless solid; (Found: MH$^+$, 613.2390. $C_{43}H_{33}O_4$ requires MH 613.2379); ν_{max} (KBr/cm^{-1}) 2924, 1713, 1607, 1495, 1246, 826; δ_H (270 MHz, $CDCl_3$) 3.80 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.78 (2H, m, *J** = 8.4 Hz), 6.86–6.94 (6H, m), 7.15–7.45 (18H, m); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 613 (MH$^+$, 84), 584 (15), 479 (15).

3,6-Bis(p-bromophenyl)-4,5-bis(4-trifluoromethoxybiphenyl)-α-pyrone (**4h**)*:* Slowly solidifying colourless oil, (Found: MH$^+$, 879.0002. $C_{43}H_{25}O_4{}^{79}Br^{81}BrF_6$ requires MH, 879.0008); ν_{max} 1710, 1500, 735, 707; δ_H (270 MHz, $CDCl_3$) 6.82 (2H, m, *J** = 7.3 Hz), 6.95 (2H, m, *J** = 7.3 Hz), 7.00–7.37 (16H, m), 7.46 (2H, m, *J** = 8.9 Hz), 7.51 (2H, m, *J** = 8.6 Hz).

3,6-Diphenyl-4,5-bis(4-trifluoromethoxybiphenyl)-α-pyrone (**4i**)*:* Colourless solid, m.p. 204°C; (Found: MH$^+$, 721.1814. $C_{43}H_{27}O_4F_6$ requires MH, 721.1814); ν_{max} (KBr/cm^{-1}) 1712, 1497, 1273, 1005, 928, 832, 808, 780, 751, 696; δ_H (270 MHz, $CDCl_3$) 6.84 (2H, m, *J** = 8.4 Hz), 6.97 (2H, m, *J** = 8.4 Hz), 7.17–7.27 (14H, m), 7.29 (2H, m, *J** = 8.1 Hz), 7.37 (2H, m), 7.43 (2H, m, *J** = 8.6 Hz), 7.49 (2H, m, *J** = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 118.9, 120.0 (q, $^1J_{CF}$ -258 Hz), 120.6 (q, $^1J_{CF}$ -255 Hz), 121.2 (2C), 121.3, 125.9 (2C), 126.6 (2C), 127.5, 127.8 (2C), 128.0 (2C), 128.1 (4C), 129.4 (2C), 129.6, 130.2 (2C), 130.6 (2C), 132.0 (2C), 132.6, 134.1, 134.5, 135.6, 138.4, 138.4, 138.6, 138.8 (d, *J* 1.7 Hz), 148.8, 154.5, 157.0, 162.1, 168.4; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 721 (MH$^+$, 100), 692 (42), 587 (43), 265 (28), 105 (95).

3,6-Bis(biphenyl)-4,5-diphenyl)-α-pyrone (**4k**)*:* Pale yellow solid, m.p. > 300°C; ν_{max} (KBr/cm^{-1}) 1704, 1485, 926, 848, 829, 764, 731, 700; δ_H (270 MHz, $CDCl_3$) 6.70 – 6.80 (2H, m), 6.91–6.99 (6H, m), 7.08–7.11 (3H, m), 7.20–7.25 (2H, m), 7.27–7.56 (15H, m); δ_C (67.8 MHz, $CDCl_3$) 119.7, 124.6, 126.3 (2C), 126.4 (2C), 126.9 (2C), 127.0 (2C), 127.2, 127.3 (2C), 127.4 (2C), 127.8, 128.2 (2C), 128.6 (2C), 128.8 (2C), 129.5 (2C), 129.8 (2C), 131.1 (2C), 131.4 (2C), 131.5, 133.2, 135.1, 136.2, 139.8, 139.9, 140.6, 142.0, 155.3, 156.2, 162.3; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 553 (MH$^+$, 1.5).

3,6-Bis(biphenyl)-4,5-bis(4-fluorophenyl)-α-pyrone (**4l**)*:* Grey-greenish solid, m.p. 323°C; (Found M$^+$, 589.1976. $C_{41}H_{27}O_2F_2$ requires M, 589.1979); ν_{max} (KBr/cm^{-1}) 1712, 1603, 1510, 1230, 1163, 923, 835, 768, 752, 696, 568; δ_H (270 MHz, $CDCl_3$) 6.71 – 6.74 (4H, m), 6.83–6.89 (4H, m), 7.19 (2H, m, *J** = 7.6 Hz), 7.31–7.58 (16H, m); δ_C (67.8 MHz, $CDCl_3$) 114.9 (2C, d, J_{CF} 21.2 Hz), 115.6 (2C, d, J_{CF} 21.3 Hz), 118.5, 125.1, 126.5 (2C), 126.6 (2C), 127.0 (2C), 127.1 (2C), 127.4, 127.9, 128.7 (2C), 128.9 (2C), 129.7 (2C), 130.9, 131.0, 131.1 (2C), 131.2, 131.3 (2C, d, J_{CF} 7.9 Hz), 132.0, 133.1 (2C, d, J_{CF} 8.1 Hz), 139.8, 140.3, 140.5, 142.3, 154.1, 156.6, 161.7 (d, J_{CF} -246 Hz), 161.9, 162.0 (d, J_{CF} -249 Hz); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 589 (MH$^+$, 8.1), 588 (M$^+$, 4.1).

Diacylstilbenes ***Z*-3a**,[53] ***Z*-3d**[49] and ***Z*-3f**[49] are known compounds.

Cycloaddition of tetracyclone **1a** *to phenylacetylene* (**13a**): A mixture of **1a** (113 mg, 0.29 mmol) and phenylacetylene (**13a**, 1.39 g, 13.6 mmol) was heated at 135°C for 10 min. Thereafter, the colourless solution was cooled and the mixture was subjected directly to column chromatography on silica gel (initially hexane to remove excess phenylacetylene, then hexane/chloroform/ether 2:1:1) to give pentaphenylbenzene (**14a**) (129 mg, 97%), colourless solid; m.p. 248°C;[29] δ_H (270 MHz, $CDCl_3$) 6.76–6.93 (15H, m), 7.17 (10H, bs), 7.60 (1H, s); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 458 (M$^+$, 15).

Analogously, tetracyclone **1k** was reacted with phenylacetylene (**13a**) to give 2,3,5-triphenyl-*p*-quinquephenyl (**14b**): Colourless solid, m.p. 277°C;[30] (Found M$^+$, 610.2658. $C_{48}H_{34}$ requires M, 610.2661); ν_{max} (KBr/cm^{-1}) 1490, 1440, 1118, 1073, 1006, 908, 841, 763, 734, 697; δ_H (270 MHz, $CDCl_3$) 6.84–6.94 (12H, m), 7.15–7.45 (21 H, m), 7.64 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 125.4, 125.5 (2C), 125.7, 126.2 (2C), 126.3, 126.7 (5C), 126.9 (2C), 127.0, 127.1 (2C), 127.2, 127.7 (2C), 128.6 (2C), 128.7 (2C), 130.0 (2C), 130.4 (2C), 131.5 (2C), 131.6 (2C), 132.0 (2C), 137.9, 138.9, 139.0, 139.1, 139.4, 140.0, 140.3, 140.4, 140.7 (2C), 140.8, 140.9, 141.7, 141.9; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 610 (M$^+$, 2.6).

Cycloaddition of tetracyclone **1a** *to diphenylacetylene (tolane,* **13b**): A mixture of tetracyclone **7a** (384 mg, 1.0 mmol) and tolane (**13b**) (890 mg, 5.0 mmol) was heated at 175°C for 6 h. Thereafter a mixture of ether-hexane (1:1, 5 ml) was added to the cooled reaction solution. The formed precipitate was filtered off and washed with cold ether-hexane to give hexaphenylbenzene[56] (**14c**) (497 mg, 93%) as a colourless solid; m.p. > 300°C (Lit.[55] > 300°C); ν_{max} (KBr/cm^{-1}) 1600, 1494, 1440, 1401, 1072, 1027, 906, 780, 728, 697, 554; δ_H (270 MHz, $CDCl_3$) 6.82–6.86 (30H, m); δ_C (67.8 MHz, $CDCl_3$) 125.2 (6C), 126.5 (12C), 131.4 (12C), 140.3 (6C), 140.6 (6C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 534 (M$^+$, 0.2).

Analogously, tetracyclone **1k** was reacted with tolane (**13b**) to give 2,3,5,6-tetraphenyl-*p*-quinquephenyl (**14d**) as a beige coloured solid, m.p. > 300°C, ν_{max} (KBr/cm^{-1}) 1486, 1440, 1398, 1070, 1025, 1006, 911, 843, 740, 697, 566; δ_H (270 MHz, $CDCl_3$) 6.85–6.89 (22H, m), 7.12 (4H, m, *J** = 8.4 Hz), 7.20–7.32 (8H, m), 7.43 (4H, m, *J** = 7.3 Hz); δ_C (67.8 MHz, $CDCl_3$) 125.1 (4C), 125.2 (4C), 126.6 (8C), 126.7 (4C), 126.9 (2C), 128.5 (4C), 131.5 (8C), 131.8 (4C), 137.4 (2C), 139.8 (2C), 140.0 (2C), 140.5 (4C), 140.6 (4C), 140.8 (2C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 686 (M$^+$, 12), 307 (22).

The authors thank Ms. Y. Tanaka for the mass spectroscopic measurements. Elemental analysis was carried out at the Centre of Analysis, Kyushu University, Hakozaki Campus. This work was supported in part by EPSRC project, UK (Grant No. GR/S41982/01). J. I. wishes to thank both EPSRC and the Ministry of Science and Technology (Ramon y Cajal programme), Spain, for their financial support.

Received 17 March 2008; accepted 28 March 2008
Paper 08/5162 doi: 10.3184/030823408X310792

References

1 M.A. Ogliaruso, M.G. Romanelli and E.I. Becker, *Chem. Rev.,* 1965, **65**, 261.
2 D. Wasserfallen, G. Mattersteig, V. Enkelmann and K. Müllen, *Tetrahedron*, 2006, **62**, 5417.
3 K. Dinakaran, S.-M. Hsiao, C.-H. Chou, S.-L. Shu and K.-H. Wei, *Macromolecules*, 2005, **38**, 10429.
4 K.-Y. Kay, J.H. Kim, H.N. Cho and J.W. Park, *Mol. Cryst. Liq. Cryst.*, 2004, **424**, 167.
5 J.K. Stille, *J. Macromol. Sci.*, *Chem.*, 1969, **3**, 1043.
6 T. Thiemann, H. Fujii, D. Ohira, K. Arima, Y.Q. Li and S. Mataka, *New J. Chem.,* 2003, **27**, 1377.
7 Q. Song, C.W. Lebeis, X. Shen, D.M. Ho and R.A. Pascal, Jr., *J. Am. Chem. Soc.*, 2005, **127**, 13732.
8 X.-Y. Cao, H. Zi, W. Zhang, H. Lu and J. Pei, *J. Org. Chem.*, 2005, **70**, 3645.
9 R.G. Potter and T.S. Hughes, *Org. Lett.*, 2007, **9**, 1187.
10 J. Iniesta, T. Matsumoto and T. Thiemann, *J. Chem. Res.*, 2008, 109.
11 M.A. Fox, K. Campbell, G. Maier and L.H. Franz, *J. Org. Chem.*, 1983, **48**, 1762.
12 T. Kawase, S. Ohsawa, T. Enomoto and M. Oda, *Chem. Lett.*, 1994, 1333.
13 D.J. Walton, J. Iniesta, M. Plattes, T.J. Mason, J.P. Lorimer, S. Ryley, S.S. Phull, A. Chyla, J. Heptinstall, T. Thiemann, H. Fujii, S. Mataka and Y. Tanaka, *Ultrasonics Sonochemistry*, 2003, **10**, 209.
14 J. Iniesta, H. Alcock, D.J. Walton, M. Watanabe, S. Mataka and T. Thiemann, *Electrochim. Acta*, 2006, **51**, 5682.
15 M. Imai, MSc-thesis, Kyushu University, 2002.
16 J.M. Dunston and P. Yates, *Tetrahedron Lett.*, 1964, 505.
17 R. Pütter and W. Dilthey, *J. Prakt. Chem.*, 1937, **149**, 183.
18 D.C. Neckers and G. Hauck, *J. Org. Chem.*, 1983, **48**, 4691.
19 P. Yates and G.H. Stout, *J. Am. Chem. Soc.*, 1954, **76**, 5510.
20 T. Takata, R. Tajima and W. Ando, *Chem. Lett.*, 1985, 665.
21 W. Adam and A. Rodriguez, *J. Org. Chem.*, 1979, **44**, 4969.

22 J.E. Baldwin, J.L. Swallow and H.W.S. Chan, *J. Chem. Soc., Chem. Commun.*, 1971, 1407

23 A.A. Frimer, G. Strul and H.E. Gottlieb, *J. Org. Chem.*, 1995, **60**, 4521.

24 I. Rosenthal and A.A. Frimer, *Tetrahedron Lett.*, 1975, 3731.

25 I. Rosenthal and A.A. Frimer, *Tetrahedron Lett.*, 1976, 2805.

26 B. Pandey, M.P. Mahajan, R.K. Tikare, M. Muneer, N.P. Rath, P.V. Kamat and M.V. George, *Res. Chem. Intermed.*, 1991, **15**, 271.

27 N.M. Bikales and E.I. Becker, *J. Org. Chem.*, 1956, **21**, 1405.

28 C. Dufraisse, A. Etienne and J.-M. Aubry, *Compt. Rend.*, 1954, **239**, 1170.

29 C. Dufraisse, A. Etienne and J.-M. Aubry, *Bull. Soc. Chim.*, 1954, **21**, 1201.

30 G.O. Schenck, *Z. Elektrochem.*, 1952, **56**, 855.

31 C.F.H. Allen and J. VanAllan, *J. Org. Chem.*, 1953, **18**, 882.

32 J. Rigaudy, K. Cuong Nguyen, J. Baranne-Lafont, P. Duminy and C. Chassagnard, *Tetrahedron*, 1986, **42**, 1345.

33 J.-M. Aubry and S. Bouttemy, *J. Am. Chem. Soc.*, 1997, **119**, 5286.

34 F. El Khatib, C. Tachon, A.M. Caminade and M. Koenig, *Tetrahedron Lett.*, 1985, **26**, 3007.

35 T.L. Ho, T.W. Hall and C.M. Wong, *Synth. Commun.*, 1973, **3**, 79.

36 W. Dilthey, S. Henkels and M. Leonhard, *J. Prakt. Chem.,* 1938, **151**, 97.

37 A. Khazaei, M.A. Zolfigol and A.A. Manesh, *J. Chin. Chem. Soc.* (Taiwan), 2005, **52**, 515.

38 W. Broser, J. Reusch, H. Kurreck and P. Siegle, *Chem. Ber.*, 1969, **102**, 1715.

39 J.R. Johnson and O. Grummitt, *Org. Synth.*, 1943, **23**, 92.

40 F. Dötz, J.D. Brand, S. Ito, L. Gherghel and K. Müllen, *J. Am. Chem. Soc.,* 2000, **122**, 7707.

41 F.A. Amer, A.A. Khalaf and Y.M. Darwish, *Ind. J. Chem.*, *Sect. B*, 1979, **17**, 575.

42 L.D. Field, K.M. Ho, C.M. Lindall, A.F. Masters and A.G. Webb, *Austr. J. Chem.*, 1990, **43**, 281.

43 K. Chmil and U. Scherf, *Makromol. Chem.*, 1993, **194**, 1377.

44 E. Elce and A.S. Hay, *J. Polymer Sci.*, *Part A*, 1995, **33**, 1143.

45 H. Sauriat-Dorizon, T. Maris, J.P. Wuest and G.D. Enright, *J. Org. Chem.*, 2003, **68**, 240.

46 S. Mataka and T. Hatta, P.C.T. Appl., 2005, W02005085208.

47 W. Broser, P. Siegle and H. Kurreck, *Chem. Ber.*, 1968, **101**, 69.

48 A.V. Vasil‘ev and A.P. Rudenko, *Russ. J. Org. Chem.*, 1997, **33**, 1555.

49 W. Ried and R. Lantzsch, *Chem. Ber.*, 1971, **104**, 679.

50 J. Smidt and R. Sieber, *Angew. Chem.*, 1959, **71**, 626.

51 M. Koral and E.I. Becker, *J. Org. Chem.*, 1962, **27**, 1038.

52 A.M. Caminade, F. El Khatib, M. Koenig and J.-M. Aubry, *Can. J. Chem.*, 1985, **63**, 3203.

53 G.R. Evanega, W. Bergmann and J. English, Jr., *J. Org. Chem.*, 1962, **27**, 13.

54 W. Dilthey, W. Schommer and O. Troshen, *Ber.*, 1933, **66B**, 1627.

55 J.K. Stille and G.K. Noren, *Macromolecules*, 1972, **5**, 49.

56 A. Borrini, P. Diversi, G. Ingrosso, A. Lucherini and G. Serra, *J. Mol. Cat.,* 1985, **30**, 181.