ipso-Acylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane with acid anhydrides: through-space electronic interaction among the two benzene rings

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Acylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane with acid anhydrides led to mono-*ipso*-acylation at the *tert*-butyl group to give 5-acyl-13-*tert*-butyl-8,16-dimethyl[2.2]metacyclophanes, from which the second electrophilic substitition with acid anhydrides can be strongly suppressed because of deactivation of the second aromatic ring by acyl group introduced by the through-space electronic interaction.

Keywords: cyclophanes, [2.2]metacyclophanes, *ipso*-acylation, Clemmensen reduction

For many years various research groups have been attracted by the chemistry and spectral properties of the [2.2]MCP ([2.2]MCP = [2.2]metacyclophane) skeleton.[1-3] Its conformation, which was elucidated by X-ray measurements,[4] is apparently frozen into a chair-like non-planar form. The two halves of the molecule form a stepped system. The benzene rings are not planar, but have a boat conformation, with the result that the molecule avoids the steric interaction of the central carbon atoms C-8 and C-16 and of the attached hydrogen atoms. The C(8)–C(16) distance is 2.689 Å. The increased strain in the molecule 8,16-dimethyl[2.2]MCP as compared with that in the parent hydrocarbon can be seen, in particular, in the distance between C-1 and C-2 (1.573 Å).[5]

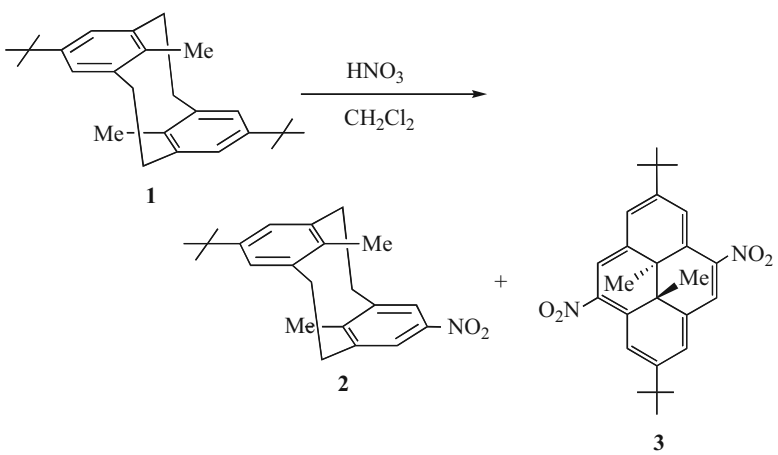
Previously, we reported that[6–8] nitration of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **1** with fuming HNO_3 afforded 13-*tert*-butyl-5-nitro-8,16-dimethyl[2.2]MCP **2** along with the transannular reaction product, 2,7-di-*tert*-butyl-4,9-dinitro-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **3**.

Although the replacement of a *tert*-butyl group by a nitro group in electrophilic aromatic substitutions has frequently been described,[9–16] generally the yields are modest because of the accompanying side reactions.[17] Only in activated compounds are better yields obtained. However, the mechanistic aspects for *ipso*-attack in electrophilic aromatic substitutions having more than two aromatic rings are still not clear in spite of the possibility of through space electronic interactions among the other benzene rings.[18] Thus there is substantial interest in investigating the acylation of the internally substituted [2.2]MCPs, which might afford single mono- and di-acylated products. We report here on the through-space electronic interaction among the two benzene rings during the acylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP **1** with various acid anhydrides. Further Clemmensen reduction of the acylation products to prepare 8,16-dimethyl[2.2]benzonapthaleno- and benzoanthracenoMCPs by Friedel–Crafts intramolecular cyclisation was also described.

Results and discussion

When acetylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (**1**)[19] with acetic anhydride in the presence of $TiCl_4$ as a catalyst was carried out at 0 °C for 2 h, 5-acetyl-13-*tert*-butyl-8,16-dimethyl[2.2]MCP (**5a**) and 2,7-di-*tert*-butyl-*trans*-10b,10-dimethyl-10b,10c-dihydropyrene (**7**)[20] were obtained in 83% and 17% yield, respectively. Interestingly, acetylation of **1** with acetic anhydride in the presence of $AlCl_3$–$MeNO_2$ as a catalyst was carried out at 0 °C for 2 h led to the two-fold *ipso*-acetylation to give 5,13-diacetyl-8,16-dimethyl[2.2]MCP (**6a**) in 90% yield along with the monoacylation product **5a** in 10% yield.

$TiCl_4$ catalysed acylation of **1** with benzoic anhydride carried out at 0 °C for 2 h afforded 5-benzoyl-13-*tert*-butyl-8,16-dimethyl[2.2]MCP (**5b**) in 95% yield along with a small amount of **7**. A similar reaction was carried out in the presence of $AlCl_3$–$MeNO_2$ that led to *ipso*-acylation at just one *tert*-butyl group to give **5b** in quantitative yield. However, attempted further acylation of **1** with benzoic anhydride failed. In spite of increasing the amount of benzoic anhydride and $AlCl_3$–$MeNO_2$ or increasing the reaction temperature to 50 °C and prolonging the reaction time, no formation of two-fold *ipso*-acylation product **6b** was observed. Only the mono-*ipso*-acylation product **5b** was obtained in good yields.



Scheme 1

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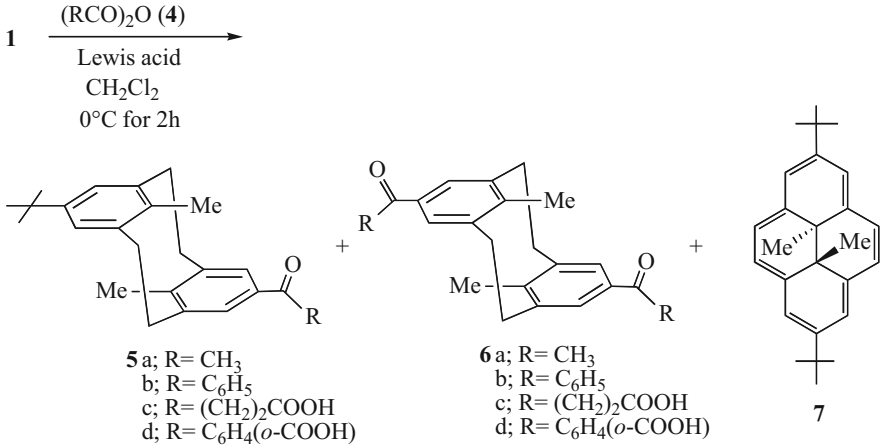


Scheme 2

Similar treatment of **1** with 3.0 equiv. of succinic anhydride or phthalic anhydride in the presence of $AlCl_3$–$MeNO_2$ under the same conditions afforded the corresponding mono-acylation product **5c** and **5d** in 90 and 95% yields, respectively. Thus, the number of *ipso*-acylation of **1** was strongly affected by the acid anhydrides and the reaction conditions used.

The present acylation behaviour of [2.2]MCP **1** can be explained by the stability of the cationic intermediates, which could arise from the through-space electronic interaction with the benzene ring located on the opposite side. Thus, a first σ-complex intermediate (**A**) would be stabilised by the through-space electronic intraannular interaction through 8,16-positions with the opposing benzene ring, thus accelerating the reaction.

However, the second electrophilic substitition with acyl group can be strongly suppressed in the intermediate (**B**) because of deactivation of the second aromatic ring by acyl group like nitration of 8,16-dimethyl[2.2]MCP, which only afforded mono-nitration product even in the drastic nitration conditions.[8] This effect seems to be increased for benzoyl, 3-(carboxyl)propionyl and (2-carboxyl)benzoyl group in comparison with that of acetyl group.

Similarly, 5-*tert*-butyl-1,2,3-trimethylbenzene (**8**)[21] with excess succinic anhydride in the presence of $AlCl_3$-$MeNO_2$ at room temperature only gave a quantitative recovery of the starting compound. Raising the reaction temperature to 50 °C and prolonging the reaction time resulted only the recovery of the starting compound. No formation of the *ipso*-acylation at the *tert*-butyl group was observed. In contrast with **8**, acylation of [2.2]MCP **1** with excess succinic anhydride in the presence of $AlCl_3$–$MeNO_2$ led to *ipso*-acylation only at one of the *tert*-butyl groups to give **5c** in good yield. This result seems to indicate that the metacyclophane structure in **1** plays an important role in the present *ipso*-acylation reaction. The *ipso*-acylation of **1** is attributed to the highly activated character of the aryl ring and the increased stabilisation of σ-complex intermediate **A** arising from the through-space electronic. Recently, Cacace *et al.* reported[22] that the intramolecular proton shift, namely, ring-to-ring proton migration in (β-phenylethyl)arenium ions from the higher cationic alkylation rate of 1,2-diphenylethane than that of toluene in the gas-phase. Thus in the present system, σ-complex intermediate **A** would be stabilised by a through-space electronic interaction through intraannular 8,16-positions

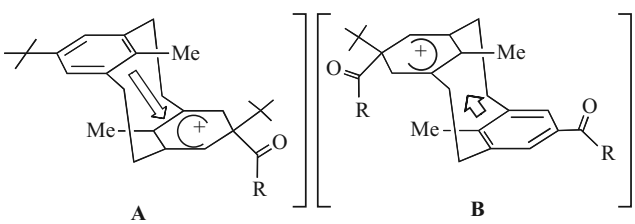
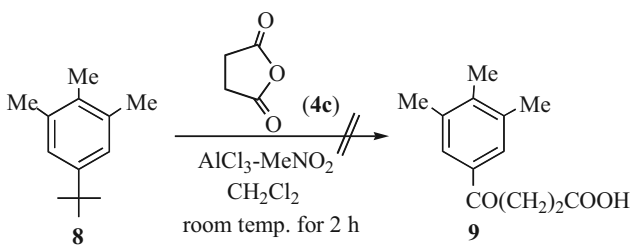


Fig. 1 The through-space electronic interaction of σ-complex intermediates

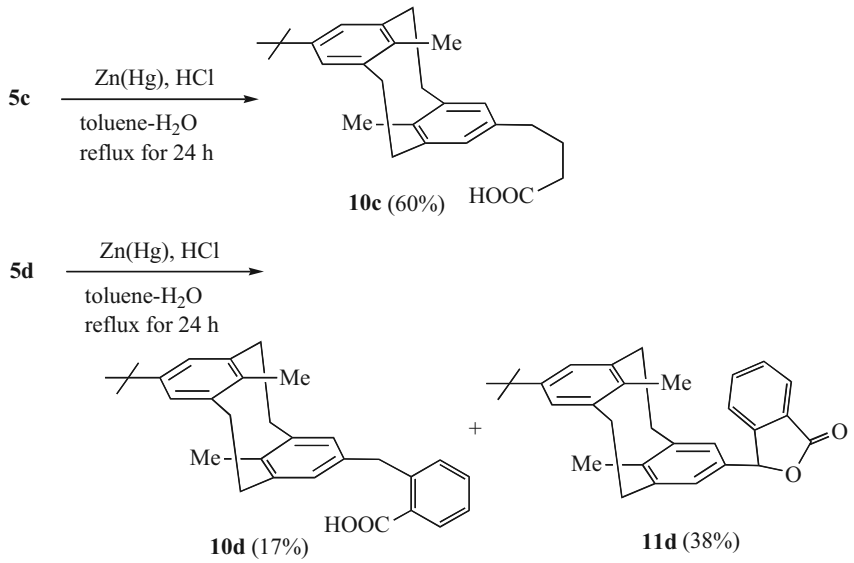


Scheme 3

Table 1 Lewis acid catalysed acylation of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]MCP (**1**) with acid anhydrides (**4**)

Run	Reagent (**4**)	Lewis acid[a]	**4**/**1** (mol mol^{-1})	Product/%[b,c]	
1	Acetic anhydride (**4a**)	A	3.0	**5a** (83) [70][d]	**6a** (0)
2	Acetic anhydride (**4a**)	B	3.0	**5a** (10) [5]	**6a** (90) [85]
3	Benzoic anhydride (**4b**)	A	3.0	**5b** (95) [90][d]	**6b** (0)
4	Benzoic anhydride (**4b**)	B	3.0	**5b** (100) [95]	**6b** (0)
5	Succinic anhydride (**4b**)	A	1.5	**5c** (0)	**6c** (0)
6	Succinic anhydride (**4b**)	B	1.5	**5c** (85) [73]	**6c** (0)
7	Succinic anhydride (**4b**)	B	3.0	**5c** (90) [80]	**6c** (0)
8	Phthalic anhydride (**4c**)	A	1.5	**5d** (0)	**6d** (0)
9	Phthalic anhydride (**4c**)	B	3.0	**5d** (95) [89]	**6d** (0)

[a]A: $TiCl_4$, Catalyst/reagent (**4**) = 7.0 (mol/mol); B: $AlCl_3$–$MeNO_2$, Catalyst/reagent (**4**) = 3.0 (mol/mol). [b]Yields were determined by G.L.C. analyses. [c]Isolated yields are shown in square brackets. [d]2,7-Di-*tert*-butyl-*trans*-10b,10-dimethyl-10b,10c-dihydropyrene (**7**) was also obtained in 17 and 3% yields, respectively.



Scheme 4

with the opposing benzene ring, therefore accelerating the reaction like the formylation of *tert*-butyl[*n*.2]MCPs.[23,24] However, only one *tert*-butyl group is *ipso*-acylated because of deactivation of the second aromatic ring by the acyl group introduced (intermediate **B**).

Clemmensen reduction of **5c** with Zn–Hg afforded the desired **10c** in 60% yield. In contrast, in the case of **5d** the desired product **10d** was obtained only in 17% yield along with 5-*tert*-butyl-13-(3-oxo-1,3-dihydroisobenzofuran-1-yl)-8,16-dimethyl[2.2]metacyclophane **11d** was obtained in 38% yield.

The structure of **11d** was assigned on the basis of elemental analyses and spectral data. The ^{1}H NMR spectrum of **11d** shows two kinds of methyl protons, each as a singlet and the methyl protons shifted strongly up-field at δ –0.26 and 0.35 ppm in comparison with those of **10d** (δ 0.54 and 0.58 ppm). In contrast, the cyclophane aromatic protons of **11d** are observed as four sets of doublet (J = 1.8 Hz) at much lower fields (δ 7.00, 7.02, 7.24 and 7.45 ppm) than those of **10d** at δ 6.85 and 7.08 ppm as a singlet. The methine proton was also observed at δ 7.32 ppm as a singlet. The above data show that the structure of **11d** is the 8,16-dimethyl[2.2.MCP having the isobenzofuran group at the 13-position in which benzene ring cause one of the methyl protons to the upper field shift at δ –0.26 ppm due to the ring current effect.

We conclude that the *ipso*-acylation reactions of **1** lead to the first-reported direct introduction of one acyl group. The selective *ipso*-acylation of **1** is attributed to the highly activated character of the aryl ring and the increased stabilisation of σ-complex intermediate. Also we have deduced that a first σ-complex intermediate, (β-phenylethyl)arenium ion is stabilised by the through-space electronic interaction with the other benzene ring in acylation like the electrophilic aromatic substitution of MCPs. Further studies on *ipso*-acylation and Friedel–Crafts intramolecular cyclisation of **10c** and **10d** to prepare 8,16-dimethyl[2.2]benzonapthaleno- and benzoanthracenoMCPs are currently in progress in our laboratory.

Experiment

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A ultrahigh performance mass spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Materials

The preparations of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane **1**[19], and 5-*tert*-butyl-1,2,3-trimethylbenzene **8**[21] have been previously described.

Titanium tetrachloride catalysed acylation of 5,13-di-tert-butyl-8,16-dimethyl [2.2]metacyclophane (**1**); *typical procedure*

A solution of $TiCl_4$ (1.2 ml, 10.92 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added to a solution of 5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophane (**1**) (181 mg, 0.52 mmol) and acetic anhydride (0.16 mL, 1.56 mmol) in CH_2Cl_2 (4 mL). After the reaction mixture was stirred at 0 °C for 2 h, it was poured into ice-water (10 mL). The organic layer was extracted with CH_2Cl_2 (10 mL × 2). The extract was washed with water (5 mL), dried (Na_2SO_4), and concentrated. The residue was column chromatographed over silica gel with hexane, hexane: benzene 1:1, and benzene as eluent to give 30 mg (17%) of **7** and 144 mg (70%) of **5a**, respectively.

5-Acetyl-13-tert-butyl-8,16-dimethyl[2.2]metacyclophane (**5a**): Colourless prisms (hexane), m.p. 157–161 °C; ν_{max}/cm^{-1} (KBr) 1665 (C=O); δ_H ($CDCl_3$) 0.50 (3H, s, *Me*), 0.63 (3H, s, *Me*), 1.30 (9H, s, *tBu*), 2.55 (3H, s, *Me*), 2.73–3.04 (8H, m, *CH*$_2$), 7.13 (2H, s, Ar*H*) and 7.73 (2H, s, Ar*H*); *m*/*z* 334 (M^+) (Found: C, 86.65; H, 8.98. $C_{24}H_{30}O$ (334.51) requires C, 86.18; H, 9.04%).

2,7-Di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (**7**): Deep green prisms (hexane), m.p. 203–204 °C (lit.[20] m.p. 203–204 °C).

Compound **5b** was obtained by the acylation of **1** with benzoic anhydride in the same manner described above. The yields are compiled in Table 1.

5-Benzoyl-13-tert-butyl-8,16-dimethyl[2.2]metacyclophane (**5b**): Colourless prisms (hexane), m.p. 179–182 °C; ν_{max}/cm^{-1} (KBr) 1648 (C=O); δ_H ($CDCl_3$) 0.58 (3H, s, *Me*), 0.67 (3H, s, *Me*), 1.30 (9H, s, *tBu*), 2.74–3.03 (8H, m, *CH*$_2$), 7.14 (2H, s, Ar*H*), 7.45–7.78 (5H, m, Ar*H*) and 7.65 (2H, s, Ar*H*); *m*/*z* 396 (M^+) (Found: C, 87.74; H, 8.22. $C_{29}H_{32}O$ (396.58) requires C, 87.83; H, 8.13%).

Acylation of **1** *with acid anhydrides in the presence of $AlCl_3$-$MeNO_2$; typical procedure*

To a solution of **1** (1.0 g, 2.87 mmol) and succinic anhydride (432 mg, 4.31 mmol) in CH_2Cl_2 (17 mL) was added a solution of aluminum chloride (1.73 g, 12.9 mmol) in nitromethane (3 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 2 h, it was poured into a large amount of water. The organic layer was extracted with diethyl ether (20 mL × 3). The extract was washed with 10% hydrochloric acid (10 mL × 2) and water (10 mL × 2), dried with Na_2SO_4, and evaporated *in vacuo*. The residue was recrystallised from benzene to afford 13-*tert*-butyl-5-(3-carboxylpropionyl)-8,16-dimethyl[2.2]metacyclophane (**5c**) (821 mg, 73%) as *colourless prisms*, m.p. 176–178 °C; ν_{max}/cm^{-1} (KBr) 1712, 1676 (C=O); δ_H ($CDCl_3$) 0.50 (3H, s, *Me*), 0.63 (3H, s, *Me*), 1.30 (9 H, s, *tBu*), 2.69–2.86 (6H, m, *CH*$_2$), 2.90–3.07 (4H, m, *CH*$_2$), 3.27–3.33 (2H, m, *CH*$_2$), 7.13 (2H, s, Ar*H*) and 7.69 (2H, s, Ar*H*); *m*/*z* 392 (M^+) (Found: C, 79.89; H, 8.13. $C_{26}H_{32}O_3$ (392.56) requires C, 79.56; H, 8.22%).

Acylation of **1** with acetic anhydride carried out as described above afforded 5,13-diacetyl-8,16-dimethyl[2.2]metacyclophane **6a** in 85% yield as colourless prisms (hexane), m.p. 284–285 °C; ν_{max}/cm^{-1} (KBr) 1666 (C=O); δ_H ($CDCl_3$) 0.59 (6H, s, *Me*), 2.58 (6H, s, *Me*), 2.79–3.10 (8H, m, CH_2), 7.76 (4H, s, Ar*H*); *m*/*z* 320 (M^+) (Found: C, 82.56; H, 7.56. $C_{22}H_{24}O_2$ (320.44) requires C, 82.46; H, 7.55%).

Acylation of **1** with phthalic anhydride carried out as described above afforded 13-*tert*-butyl-5-[(2-carboxyl)benzoyl]-8,16-dimethyl [2.2]metacyclophane **5d** in 89% yield as colourless prisms, m.p. 257 °C; ν_{max}/cm^{-1} (KBr) 1690, 1649 (C=O); δ_H ($CDCl_3$) 0.49 (3H, s, *Me*), 0.57 (3H, s, *Me*), 1.29 (9H, s, *tBu*), 2.65–2.78 (4H, m, CH_2), 2.83–2.93 (4H, m, CH_2), 7.10 (2H, s, Ar*H*), 7.27–7.30 (1H, m, Ar*H*), 7.46 (2H, s, Ar*H*), 7.50–7.57 (1H, m, Ar*H*), 7.60–7.68 (1H, m, Ar*H*) and 8.06–8.10 (1 H, m, Ar*H*); *m*/*z* 440 (M^+) (Found: C, 81.67; H, 7.26. $C_{30}H_{32}O_3$ (440.57) requires C, 81.78; H, 7.32%).

Reduction of **5c** *with Zn-Hg*

To a solution of $HgCl_2$ (206 mg, 0.76 mmol) in conc. HCl (0.1 mL) and water (3.44 mL) was added zinc powder (2.06 g, 31.5 mmol) and a mixture was stirred for 5 min. at room temperature. A suspension was decantated to leave the residue to which conc. HCl (3.1 mL), water (1.3 mL) was added. To the reaction mixture was added a solution of **5c** (500 mg, 1.28 mmol) in toluene (1.7 mL) and refluxed for 6 h. After the fresh conc. HCl (2 mL) was added three times every 6 h, the reaction mixture was cooled to room temperature. The organic layer was extracted with ether (10 mL × 3). The extract was washed with water (10 mL × 2), dried with Na_2SO_4, and evaporated *in vacuo*. The residue was recrystallised from hexane–benzene (1 : 2) to afford **10c** (290 mg, 60%) as colourless prisms, m.p. 150–156 °C; ν_{max}/cm^{-1} (KBr) 1700 (C=O); δ_H ($CDCl_3$) 0.56 (3H, s, *Me*), 0.59 (3H, s, *Me*), 1.29 (9H, s, *tB*u), 1.90–1.99 (2H, m, CH_2), 2.35–2.41 (2H, m, CH_2), 2.52–2.58 (2H, m, CH_2), 2.74–2.93 (8H, m, CH_2), 6.92 (2H, s, Ar*H*) and 7.11 (2H, s, Ar*H*); *m*/*z* 378 (M^+) (Found: C, 82.22; H, 9.05. $C_{26}H_{34}O_2$ (378.56) requires C, 82.49; H, 9.05%).

Reduction of **5d** *with Zn-Hg*

Zinc powder (1.84 g, 28.2 mmol) was added to a solution of $HgCl_2$ (184 mg, 0.68 mmol) in conc. HCl (0.1 mL) and water (3.1 mL) and the mixture was stirred for 5 min. at room temperature. The suspension was decantated to leave the residue to which conc. HCl (2.8 mL), water (1.2 mL) was added. A solution of **5d** (500 mg, 1.14 mmol) in toluene (1.5 mL) was added to the reaction mixture and refluxed for 6 h. After the fresh conc. HCl (2 mL) was added three times every 6 h, the reaction mixture was cooled to room temperature. The organic layer was extracted with ether (10 cm^3 × 3). The extract was washed with water (10 mL × 2), dried with Na_2SO_4, and evaporated *in vacuo*. The residue was recrystallised from hexane–benzene (1 : 2) to afford **10d** (83 mg, 17%) as colourless prisms. Chromatography on silica gel (Wako, C-300; 100 g) eluting with hexane–benzene (1 : 3) afforded **11d** (178 mg, 38%) as colourless solid.

Compound **10d** was obtained as prisms [hexane–benzene (1 : 2)]; m.p. 215 °C; ν_{max}/cm^{-1} (KBr) 1695 (C=O); δ_H ($CDCl_3$) 0.54 (3H, s, *Me*), 0.58 (3H, s, *Me*), 1.27 (9H, s, *tBu*), 2.69–2.88 (8H, m, CH_2), 4.33 (2H, s, CH_2), 6.85 (2H, s, Ar*H*), 7.08 (2H, s, Ar*H*), 7.22 (1H, d, *J* = 7.3 Hz, Ar*H*), 7.31 (1H, t, *J* = 7.3 Hz, Ar*H*), 7.46 (1H, t, *J* = 7.3 Hz, Ar*H*) and 8.05 (1H, d, *J* = 7.3 Hz, Ar*H*); *m*/*z* 426 (M^+) (Found: C, 84.33; H, 8.05. $C_{30}H_{34}O_2$ (426.6) requires C, 84.47; H, 8.03%).

Compound **11d** was obtained as prisms [hexane–benzene (1 : 2)]; m.p. 235–237 °C; ν_{max}/cm^{-1} 1775 (C=O); δ_H ($CDCl_3$) –0.26 (3H, s, *Me*), 0.35 (3H, s, *Me*), 1.23 (9H, s, *tBu*), 2.59–2.85 (8H, m, CH_2), 7.00 (1H, d, *J* = 1.8 Hz, Ar*H*), 7.02 (1H, d, *J* = 1.8 Hz, Ar*H*), 7.24 (1H, d, *J* = 1.8 Hz, Ar*H*), 7.32 (1H, s, *CH*), 7.35 (1H, t, *J* = 7.9 Hz, Ar*H*), 7.45 (1H, d, *J* = 1.8 Hz, Ar*H*), 7.56 (1H, d, *J* = 7.9 Hz, Ar*H*), 7.74 (1H, t, *J* = 7.9 Hz, Ar*H*) and 8.41 (1H, d, *J* = 7.9 Hz, Ar*H*); *m*/*z* 424 (M^+) (Found: C, 84.63; H, 7.75. $C_{30}H_{32}O_2$ (424.59) requires C, 84.87; H, 7.6%).

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