

A 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane derivative: a novel bisdiene molecule that produces a Dewar benzene skeleton upon two successive Diels–Alder reactions with dienophiles

Masakazu Ohkita, Kieko Sano, Sotoyuki Dohba, Yuko Fujita, Takanori Suzuki and Takashi Tsuji*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

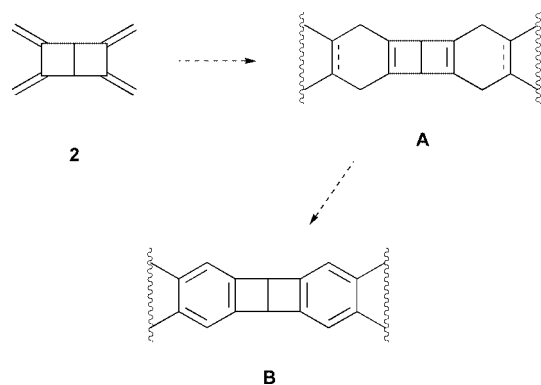
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A new bisdiene molecule **1**, the 1,4-acetal-bridged derivative of the hitherto unknown 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane, is synthesized in four steps from dimethyl acetylenedicarboxylate and (*E*)-1,4-dichlorobut-2-ene. Reaction of **1** with dimethyl acetylenedicarboxylate or benzyne leads to the formation of the Dewar benzene derivatives **6** and **7**, respectively, through two successive Diels–Alder additions of the dienophiles to **1**. Dehydrogenation of the adducts **6** and **7** affords the corresponding 9,10-Dewar anthracene derivative **10** and 6,13-Dewar pentacene derivative **11**, respectively. Compound **11** is characterized crystallographically. Reactions of 1,4-benzoquinone and *N*-phenylmaleimide with **1** are also reported.

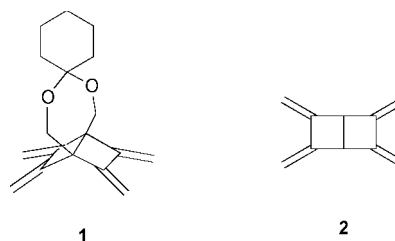
Introduction

Awareness of the power of the Diels–Alder reaction in organic synthesis continues to stimulate the search for novel dienes and dienophiles.¹ Of a wide range of dienes taking part in the Diels–Alder reaction, bisdiene molecules have attracted considerable recent attention owing to their potential use in the construction of belt-type molecular frameworks through repetitive Diels–Alder reactions with dienophiles.² We were interested in developing a new bisdiene molecule, possessing a hitherto unknown 2,3,5,6-tetramethylenebicyclo[2.2.0]hexane skeleton **2**,³ because its two successive Diels–Alder reactions with dienophiles formally produce a Dewar benzene structure **A** and subsequent dehydrogenation of the two six-membered rings thus formed would give the corresponding Dewar polyacene skeleton **B** (Scheme 1). We designed 1,4-acetal-



Scheme 1

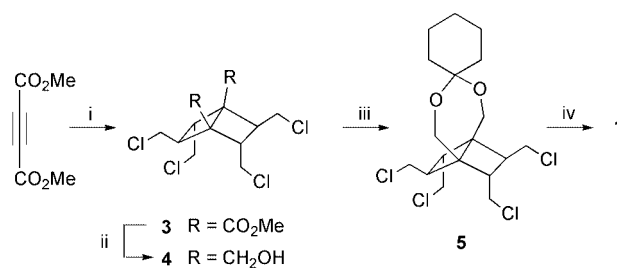
bridged derivative **1** to prevent an undesired aromatization of the Dewar benzene product under thermal cycloaddition conditions and found, in fact, that the reaction sequence illustrated in Scheme 1 could be realized with it.⁴ In this paper we describe the preparation of **1** and its Diels–Alder reaction with some dienophiles.



Results and discussion

Preparation of **1**

The synthesis of **1** is simple and straightforward (Scheme 2).



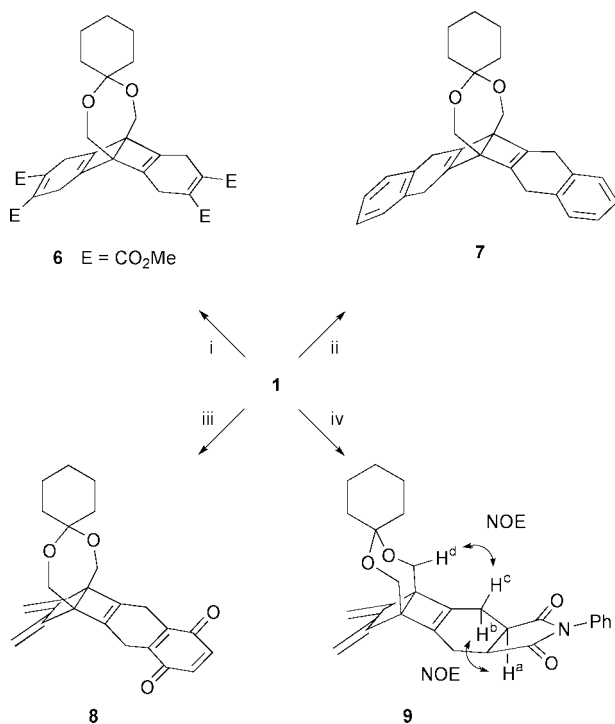
Scheme 2 Reagents and conditions: i, *hv*, (*E*)-1,4-dichlorobut-2-ene, 12 °C, 20%; ii, LiAlH₄, Et₂O, 90%; iii, 1,1-dimethoxycyclohexane, TsOH, benzene, 68%; iv, *t*-BuOK, 18-crown-6, THF, room temp., 78%.

Thus, irradiation of dimethyl acetylenedicarboxylate (DMAD) in (*E*)-1,4-dichlorobut-2-ene with a high-pressure mercury lamp at 12 °C afforded bicyclo[2.2.0]hexanes as a mixture of stereoisomers after purification by chromatography and distillation.⁵ A major isomer **3** was then isolated (yield 20%) from the mixture by crystallization from ether, identified as a *trans-anti-trans* isomer by X-ray crystallography and used for the following transformations. LiAlH₄ reduction of **3** followed by treatment of the resulting diol **4** with 1,1-dimethoxycyclohexane under the influence of a catalytic amount of TsOH

provided cyclohexylidene acetal **5** in 68% yield. Quadruple dehydrochlorination of **5** was achieved with *t*-BuOK in THF in the presence of 18-crown-6 at room temperature to afford the desired **1** in 78% yield as a colorless oil. The elimination reaction conditions described above were found to be essential for the efficient generation of **1**; only a trace amount of **1** was produced when the reaction was carried out in THF in the absence of 18-crown-6 or in DMSO. Compound **1** is prone to polymerization, as has been observed in other bisdiene systems,^{2,6} but shows stability adequate to allow its chromatographic purification and spectroscopic characterization.

Diels–Alder reaction of **1** with dienophiles

The Diels–Alder reactivity of 1,2-dimethylenecycloalkanes has been discussed in relation to the distance between the methylene carbon atoms (1,4-distance),⁷ and the long 1,4-distance in 1,2-dimethylenecyclobutanes obstructs the Diels–Alder addition of dienophiles.⁸ Accordingly, reaction of **1** with highly activated dienophiles was initially examined and was found to proceed smoothly. Thus, when a mixture of **1** and DMAD in benzene was heated at 65 °C for 20 h, the 1:2 adduct **6** was obtained in 65% yield (Scheme 3). Similarly, reaction of **1** with benzyne,

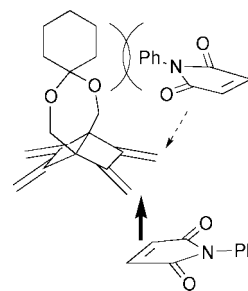


Scheme 3 Reagents and conditions: i, DMAD, benzene, 65 °C, 20 h, 65%; ii, 1,2-dibromobenzene, *n*-BuLi, toluene, room temp., 20 h, 35%; iii, 1,4-benzoquinone, benzene, 65 °C, 44 h, then DDQ, room temp., 4 h, 55%; iv, *N*-phenylmaleimide, benzene, 65 °C, 4 h, 75%.

generated from 1,2-dibromobenzene and *n*-BuLi, in toluene at room temperature afforded the 1:2 adduct **7** in 35% yield. It should be pointed out that the formation of **6** and **7** represents a novel preparation of Dewar benzene derivatives.⁹

The addition of the first equivalent of dienophile to **1** was faster than that of the second one,⁶ so that the 1:1 adducts could also be isolated in reasonable yields from the reaction of **1** with certain dienophiles. Thus, reaction of **1** with 1,4-benzoquinone in benzene at 65 °C followed by treatment of the mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the 1:1 adduct **8** in 55% yield as the major product. Similarly, reaction of **1** with *N*-phenylmaleimide (65 °C, 4 h) gave the 1:1 adduct **9** in 75% yield. The stereochemistry of **9** was determined by examining the NOESY spectrum; the methylene proton H^c which is *trans* to the angular

proton H^a exhibits a NOE with the acetal methylene proton H^d. The selective formation of **9** would be most reasonably explained by the *exo*-orientation approach of the dienophile from the *endo*-face of the diene moiety in **1** (Scheme 4). There-

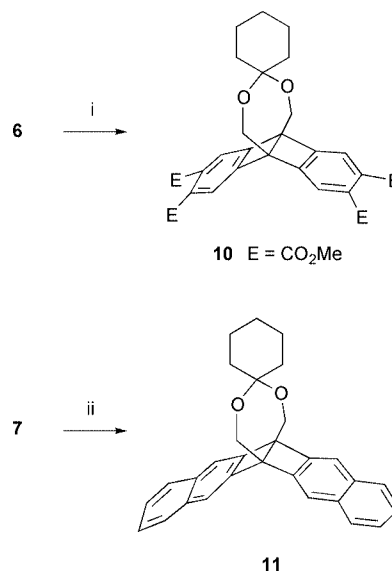


Scheme 4

fore, the cyclohexylidene acetal moiety in **1** would confer not only the thermal stability of the adducts but also the π -facial selectivity for the addition owing to the steric hindrance.

9,10-Dewar anthracene and 6,13-Dewar pentacene derivatives

To explore the scope of the Diels–Alder reaction of **1** with dienophiles, further chemical transformations of the adducts were also examined. A salient feature of the present methodology is the formation of a Dewar benzene structure fused with cyclohexa-1,4-diene moieties, and this provides a simple and versatile route to the Dewar forms of polyacenes.^{10–12} Thus, the dehydrogenation of **6** with activated MnO₂ in benzene at room temperature gave the 9,10-Dewar anthracene derivative **10** in 84% yield while the dehydrogenation of **7** with DDQ in benzene at room temperature gave 6,13-Dewar pentacene derivative **11** in 41% yield (Scheme 5). Compound **11** repre-



Scheme 5 Reagents and conditions: i, activated MnO₂, benzene, room temp., 6 days, 84%; ii, DDQ, benzene, room temp., 1 h, 41%.

sents, to the best of our knowledge, the first example of the Dewar form of pentacenes, so that its structure was determined by X-ray crystallography (Fig. 1). The remarkably long C–C bond length [1.614(3) Å] found for the central bond of the Dewar structure is noteworthy.¹³

Conclusions

We have successfully developed a new bisdiene molecule **1** which produces a Dewar benzene skeleton upon two successive

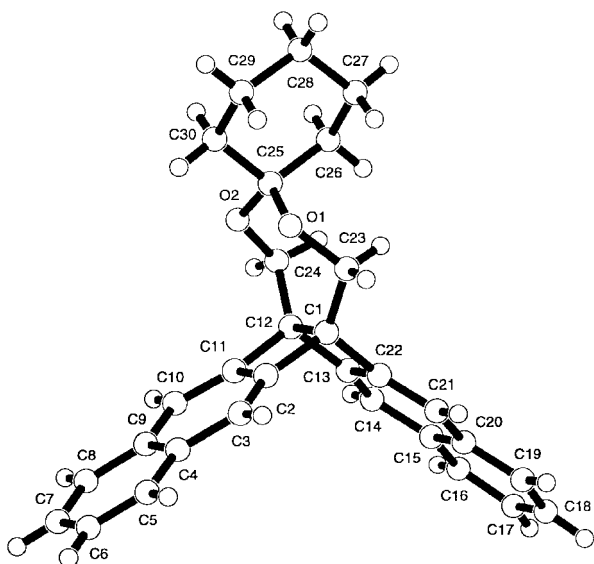


Fig. 1 X-Ray molecular structure of **11**. Selected bond length (Å) and torsion angles (°) (standard deviation in parentheses): C1–C2 1.531(3), C2–C3 1.353(3), C3–C4 1.427(3), C4–C5 1.418(3), C5–C6 1.361(4), C6–C7 1.401(4), C7–C8 1.360(4), C8–C9 1.421(3), C9–C10 1.417(3), C10–C11 1.368(3), C11–C12 1.533(3), C12–C13 1.535(3), C13–C14 1.355(3), C14–C15 1.428(3), C15–C16 1.408(3), C16–C17 1.367(3), C17–C18 1.392(4), C18–C19 1.363(3), C19–C20 1.416(3), C20–C21 1.429(3), C21–C22 1.355(3), C1–C22 1.530(3), C1–C12 1.614(3), C2–C11 1.411(3), C4–C9 1.436(3), C13–C22 1.414(3), C15–C20 1.436(3); C2–C1–C12–C13 112.6(2), C11–C12–C1–C22 112.2(2).

Diels–Alder reactions with activated dienophiles. Dehydrogenation of the 1:2 adducts provides the corresponding Dewar form of polyacenes. Similar bisdiene systems possessing other 1,4-bridging units may also be available based on the synthetic scheme for **1**. Therefore, the present results open a unique and versatile route to Dewar derivatives which, in turn, would be regarded as potential precursors for novel cyclophanes as well as belt-type molecules.

Experimental

General methods

Melting points are uncorrected. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. IR spectra were taken on a Hitachi 270-30 infrared spectrometer. ¹H NMR spectra were recorded on Hitachi R-1900 and JEOL EX-400 spectrometers at 90 and 400 MHz, respectively; chemical shifts are given in ppm using tetramethylsilane as a reference, and *J* values are given Hz. ¹³C NMR spectra were recorded on a JEOL EX-400 spectrometer in CDCl₃ at 100 MHz; chemical shifts are given in ppm using solvent peak as a reference. Electronic absorption spectra were measured on a Hitachi U-3500 spectrophotometer in hexane. Mass spectra were recorded on a JEOL JMS-SX102A spectrometer. GLC work was done on Hitachi 163 gas chromatographs. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). The light source for photochemistry was a Halos (Eiko-sha, Japan) 450 W high-pressure Hg lamp. Reagents and solvents were obtained from commercial sources and purified prior to use. Ether refers to diethyl ether.

(2*R**,3*R**,5*S**,6*S**)-1,4-Bis(methoxycarbonyl)-2,3,5,6-tetrakis(chloromethyl)bicyclo[2.2.0]hexane (**3**)

A solution of DMAD (23.1 g, 0.16 mol) in (*E*)-1,4-dichlorobut-2-ene (350 mL) was bubbled with argon for 10 min, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction

was monitored by GLC (10% Silicon SE30, 0.5 m, 100–270 °C) and the irradiation was terminated after 14 h (46% GC conversion). The mixture was concentrated *in vacuo* to recover the unreacted DMAD and (*E*)-1,4-dichlorobut-2-ene. The residue was purified by chromatography (hexane 90%, ether 5%, chloroform 5%) to give **3** as a mixture of stereoisomers (22.2 g, 35%), from which the *trans-anti-trans* isomer **3** was isolated by crystallization from ether (12.7 g, 20%), mp 132–133 °C (ether) (Found: C, 42.74; H, 4.60; Cl, 36.18. C₁₄H₁₈O₄Cl₄ requires C, 42.88; H, 4.63; Cl, 36.17%); ν_{\max} (KBr)/cm⁻¹ 2956, 1712, 1440, 1312, 1284 and 1216; δ_{H} (400 MHz, CDCl₃) 2.96 (2 H, ddd, *J* 11.2, 9.8 and 4.9), 3.17 (2 H, ddd, *J* 10.8, 9.8 and 5.4), 3.69 (2 H, dd, *J* 11.2 and 10.8), 3.70 (2 H, t, *J* 11.2), 3.72–3.78 (2 H, m), 3.75 (6 H, s) and 3.92 (2 H, dd, *J* 11.2 and 4.9); δ_{C} (100 MHz, CDCl₃) 42.23, 42.30, 43.44, 45.01, 49.64, 52.41 and 169.82; *m/z* (FD) 396 (M⁺ + 6, 16%), 394 (M⁺ + 4, 64), 392 (M⁺ + 2, 100) and 390 (M⁺, 75).

(2*R**,3*R**,5*S**,6*S**)-1,4-Bis(hydroxymethyl)-2,3,5,6-tetrakis(chloromethyl)bicyclo[2.2.0]hexane (**4**)

To a stirred suspension of lithium aluminium hydride (5.3 g, 140 mmol) in dry ether (830 mL) was added dropwise a solution of **3** (27.4 g, 70 mmol) in dry ether (400 mL) over 2 h under ice-cooling. The mixture was stirred at room temperature for 12 h and then treated successively with water (5.3 mL), 15% aqueous NaOH (5.3 mL), and water (15.9 mL) under ice-cooling. The precipitate was filtered off and the ethereal filtrate was washed successively with water (2 × 300 mL) and brine (200 mL), dried with Na₂SO₄ and concentrated to give **4** as crystals (17.6 g, 90%), mp 123–124 °C (ether); ν_{\max} (KBr)/cm⁻¹ 3396, 2952, 2856, 1448, 1280, 1040 and 712; δ_{H} (400 MHz, CDCl₃) 2.66 (2 H, ddd, *J* 9.2, 7.8 and 7.3), 2.77 (2 H, ddd, *J* 9.7, 9.2 and 6.3), 2.97 (2 H, s), 3.63 (2 H, dd, *J* 11.2 and 9.7), 3.77 (2 H, dd, *J* 11.3 and 7.3), 3.78 (2 H, dd, *J* 11.2 and 6.3), 3.85 (2 H, d, *J* 11.7), 3.86 (2 H, dd, *J* 11.3 and 7.8) and 4.00 (2 H, *J* 11.7).

(8'*R**,9'*R**,10'*S**,11'*S**)-Spiro[cyclohexane-1,4'-3',5'-dioxo-8',9',10',11'-tetrakis(chloromethyl)tricyclo[5.2.2.0^{1,7}]-undecane] (**5**)

A mixture of **4** (5.7 g, 17 mmol), 1,1-dimethoxycyclohexane (4.9 g, 34 mmol), and TsOH (0.15 g, 0.8 mmol) in benzene (300 mL) was heated to boiling and MeOH generated was azeotropically distilled off through a Vigreux column (30 cm). After 2 h, the mixture was cooled to room temperature, diluted with ether (500 mL), washed successively with 5% aqueous NaHCO₃ (300 mL) and brine (300 mL), dried with Na₂CO₃–Na₂SO₄ (1:1), concentrated and purified by chromatography (CH₂Cl₂) to give **5** (4.77 g, 68%) as an oil (Found: M⁺, 414.0696. C₁₈H₂₆O₂Cl₄ requires *M*, 414.0687); ν_{\max} (KBr)/cm⁻¹ 2936, 2856, 1450, 1290, 1158, 1100, 1036 and 734; δ_{H} (400 MHz, CDCl₃) 1.42–1.71 (10 H, m), 2.49–2.86 (4 H, m) and 3.58–3.96 (12 H, m); δ_{C} (100 MHz, CDCl₃) 22.75, 25.68, 33.69, 42.34, 42.48, 43.69, 44.35, 46.11, 58.05 and 103.57; *m/z* (FD) 420 (M⁺ + 6, 11%), 418 (M⁺ + 4, 52), 416 (M⁺ + 2, 100) and 414 (M⁺, 78).

Spiro[cyclohexane-1,4'-3',5'-dioxo-8',9',10',11'-tetramethylene-tricyclo[5.2.2.0^{1,7}]-undecane] (**1**)

To a mixture of *t*-BuOK (739 mg, 6.6 mmol) and 18-crown-6 (917 mg, 4.5 mmol) in THF (45 mL) was added dropwise a solution of **5** (445 mg, 1.1 mmol) in THF (30 mL) over 1 h at 0 °C under argon. After the addition, the mixture was stirred at room temperature for 3 h, poured into water (100 mL) and extracted with pentane (2 × 100 mL). The combined extracts were washed with brine (2 × 50 mL), dried with Na₂CO₃–Na₂SO₄ (1:1), concentrated and purified by chromatography (hexane 90%, ether 10%) to give **1** (225 mg, 78%) as an oil; ν_{\max} (neat)/cm⁻¹ 2932, 2860, 1100 and 882; λ_{\max} (hexane)/nm

231 ($\epsilon/\text{mL mol}^{-1} \text{ cm}^{-1}$ 17800), 238 (16700) and 255sh (6900); δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 4.02 (4 H, s), 4.89 (4 H, s) and 5.28 (4 H, s); δ_{C} (100 MHz, CDCl_3) 22.79, 25.71, 33.27, 60.99, 62.14, 103.62, 104.10 and 150.46; m/z (EI) 270 (M^+ , 0.5%) and 172 ($\text{M}^+ - 98$, 100).

Reaction of 1 with DMAD

A mixture of **1** (350 mg, 1.3 mmol) and DMAD (1.81 g, 12.8 mmol) in benzene (15 mL) was heated at 65 °C for 20 h. After the solvent was evaporated, the unreacted DMAD was recovered by distillation *in vacuo*. The residue was purified by chromatography (CH_2Cl_2 50%, ether 50%) followed by crystallization from ether to give **6** (468 mg, 65%) as crystals, mp 167.5–169 °C (ether) (Found: M^+ , 554.2148. $\text{C}_{30}\text{H}_{34}\text{O}_{10}$ requires M , 554.2152); ν_{max} (KBr)/ cm^{-1} 2944, 1720, 1630, 1434, 1272, 1096 and 1052; δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 2.90 (4 H, d, J 16.0), 3.14 (4 H, d, J 16.0), 3.78 (12 H, s) and 3.93 (4 H, s); δ_{C} (100 MHz, CDCl_3) 22.79, 25.73, 27.45, 33.03, 52.38, 58.19, 65.07, 103.47, 133.67, 143.25 and 168.60; m/z (FD) 554 (M^+ , 23%) and 524 ($\text{M}^+ - 30$, 100).

Reaction of 1 with benzyne

To a mixture of **1** (119 mg, 0.44 mmol) and 1,2-dibromobenzene (360 mg, 1.5 mmol) in toluene (10 mL) was added *n*-BuLi (1.0 mL of a 1.5 M solution in hexane, 1.5 mmol) over 10 min under ice-cooling. After the reaction was stirred at room temperature for 20 h, the mixture was diluted with ether (50 mL), washed successively with water (30 mL) and brine (30 mL), dried with Na_2SO_4 , concentrated and purified by chromatography (benzene 50%, hexane 50%) followed by crystallization from ether to give **7** (92 mg, 35%) as an amorphous solid (Found: M^+ , 422.2271. $\text{C}_{30}\text{H}_{30}\text{O}_2$ requires M , 422.2246); ν_{max} (KBr)/ cm^{-1} 2932, 2860, 1098 and 744; δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 3.33 (4 H, d, J 16.1), 3.54 (4 H, d, J 16.1), 4.08 (4 H, s) and 7.13 (8 H, s); δ_{C} (100 MHz, CDCl_3) 22.89, 25.85, 29.25, 33.46, 58.97, 65.21, 103.28, 125.94, 129.88, 134.35 and 145.31; m/z (FD) 422 (M^+ , 100%) and 324 ($\text{M}^+ - 98$, 64).

Reaction of 1 with benzo-1,4-quinone

A mixture of **1** (220 mg, 0.8 mmol) and 1,4-benzoquinone (300 mg, 2.7 mmol) in benzene (20 mL) was heated at 65 °C for 44 h. DDQ (362 mg, 1.6 mmol) was added to the cooled mixture and the reaction was stirred at room temperature for 4 h. After the solvent was evaporated, the residue was purified by chromatography (hexane 80%, EtOAc 20%) followed by crystallization from ether to give **8** (165 mg, 55%) as an amorphous solid (Found: M^+ , 376.1694. $\text{C}_{24}\text{H}_{24}\text{O}_4$ requires M , 376.1674); ν_{max} (KBr)/ cm^{-1} 2932, 1656, 1308 and 1092; δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 2.89–3.32 (10 H, m), 4.00 (4 H, s), 4.92 (2 H, s), 5.29 (2 H, s) and 6.74 (2 H, s); δ_{C} (100 MHz, CDCl_3) 22.66, 22.82, 25.71, 32.66, 59.29, 64.47, 103.66, 105.05, 136.36, 140.71, 141.42 and 147.68; m/z (FD) 378 (M^+ , 100%).

Reaction of 1 with *N*-phenylmaleimide

A mixture of **1** (82 mg, 0.3 mmol) and *N*-phenylmaleimide (320 mg, 18 mmol) in benzene (5 mL) was heated at 65 °C for 4 h. After the solvent was evaporated, the residue was purified by chromatography (ether) followed by preparative TLC (CH_2Cl_2 50%, ether 50%) to give **9** (99 mg, 75%) as an amorphous solid (Found: M^+ , 443.2070. $\text{C}_{28}\text{H}_{25}\text{O}_4\text{N}$ requires M , 443.2096); ν_{max} (KBr)/ cm^{-1} 2936, 1710 and 1100; δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 2.44 (2 H, dd, J 16.6 and 6.8), 2.63 (2 H, d, J 16.6), 3.30 (2 H, d, J 6.8), 3.94 (4 H, s), 4.91 (2 H, s), 5.30 (2 H, s) and 7.30–7.50 (5 H, m); δ_{C} (100 MHz, CDCl_3) 20.92, 22.78, 25.73, 37.71, 38.30, 59.13, 64.10, 103.51, 104.79, 126.50, 128.58, 129.15, 132.04, 142.78, 148.50 and 178.71; m/z (FD) 443 (M^+ , 31%) and 345 ($\text{M}^+ - 98$, 100).

Dehydrogenation of 6

A mixture of **6** (211 mg, 0.4 mmol), activated MnO_2 (3.8 g, 43.7 mmol) and NaHCO_3 (50 mg) in benzene (55 mL) was stirred at room temperature for 6 days under argon. The mixture was filtered through a short pad of Celite and the filtrate was concentrated *in vacuo*. Crystallization of the residue from ether afforded **10** as crystals (176 mg, 84%), mp 140–142 °C (ether) (Found: M^+ , 550.1838. $\text{C}_{30}\text{H}_{30}\text{O}_{10}$ requires M , 550.1839); ν_{max} (KBr)/ cm^{-1} 2952, 1732, 1272 and 1106; δ_{H} (90 MHz, CDCl_3) 1.40–1.71 (10 H, m), 3.88 (12 H, s), 4.42 (4 H, s) and 7.56 (4 H, s); δ_{C} (100 MHz, CDCl_3) 22.64, 25.56, 33.15, 52.70, 59.34, 66.72, 104.33, 123.44, 128.46, 132.37 and 167.97; m/z (FD) 550 (M^+ , 100%).

Dehydrogenation of 7

To a solution of **7** (157 mg, 0.37 mmol) in benzene (30 mL) was added DDQ (211 mg, 0.93 mmol) in portions and the reaction was stirred at room temperature for 1 h. The mixture was diluted with ether (30 mL), washed successively with 10% aqueous NaOH (30 mL) and brine (30 mL), dried with Na_2SO_4 , concentrated and purified by chromatography (dichloromethane) followed by crystallization from ether to give **11** as crystals (63 mg, 41%), mp 152.5–153.5 °C (ether) (Found: M^+ , 418.1929. $\text{C}_{30}\text{H}_{26}\text{O}_2$ requires M , 418.1933); ν_{max} (KBr)/ cm^{-1} 2936, 2856 and 1098; δ_{H} (400 MHz, CDCl_3) 1.40–1.71 (10 H, m), 4.60 (4 H, s), 7.37 (4 H, AA'BB'), 7.65 (4 H, s) and 7.75 (4 H, AA'BB'); δ_{C} (100 MHz, CDCl_3) 22.76, 25.70, 33.20, 61.00, 66.97, 104.08, 120.74, 125.27, 128.40, 134.15 and 145.05; m/z (FD) 418 (M^+ , 100%).

X-Ray structure determinations†

Crystal data for 3. Colorless block (0.2 × 0.2 × 0.2 mm), $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Cl}_4$, $M = 392.1$, orthorhombic, space group $Pbca$, $a = 15.857(3)$, $b = 17.205(2)$, $c = 13.287(2)$ Å, $V = 3624(1)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.437$ g cm⁻³, $T = 296$ K, $\mu = 6.67$ cm⁻¹, $F(000) = 1616$. Measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). A total of 4455 unique reflections ($2\theta_{\text{max}} = 55^\circ$) were collected, of which 1102 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 199 parameters) to give final $R = 0.043$ and $wR = 0.055$. Residual electron density is 0.22 e Å⁻³.

Crystal data for 11. Colorless rod (0.4 × 0.2 × 0.1 mm), $\text{C}_{30}\text{H}_{26}\text{O}_2$, $M = 418.5$, monoclinic, space group $P2_1/c$, $a = 11.4190(8)$, $b = 11.0908(5)$, $c = 17.519(2)$ Å, $\beta = 90.025(3)^\circ$, $V = 2218.7(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.253$ g cm⁻³, $T = 203$ K, $\mu = 0.77$ cm⁻¹, $F(000) = 888$. Measurements were made on a Rigaku CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). A total of 5601 unique reflections ($2\theta_{\text{max}} = 55^\circ$) were collected, of which 3346 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 289 parameters) to give final $R = 0.062$ and $wR = 0.077$. Residual electron density is 0.16 e Å⁻³.

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† CCDC reference number 207/432. See <http://www.rsc.org/suppdata/p1/b0/b000569j/> for crystallographic files in .cif format.

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