A 1,3-$sp^2$,sp$^3$-hybridized dilithio intermediate by direct lithiation of cyclopropylidene diphenylmethane

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This paper is dedicated to Professor Benito Alcaide on occasion of his 60th birthday

Abstract
The reaction of cyclopropylidene diphenylmethane 1 with an excess of lithium and a catalytic amount of naphthalene (5 mol %) at -20 ºC, followed by addition of an electrophile [E = H2O, D2O, t-BuCHO, Me2CO, Et2CO, n-Pr2CO, i-Pr2CO, (c-C3H5)2CO, (CH2)5CO] at -78 ºC and final hydrolysis with water at -78 ºC to rt gives the corresponding products 5, which in some case are contaminated with the corresponding by-products 6, resulting from the incorporation of only one electrophilic moiety at the intermediate dianion of type 2. The separation of both reaction products is easy by simple column chromatography.

Keywords: Lithium, naphthalene, alkylidene cyclopropane, ring opening, electrophilic substitution, diols

Introduction
Dilithium synths are interesting intermediates in synthetic organic chemistry because by reaction with electrophiles they are able to introduce two electrophilic fragments in only one synthetic step, thus giving directly polyfunctionalized molecules.¹ The main problem when one wants to generate these intermediates by standard methods (including deprotonation, halogen-lithium exchange or transmetallation methodologies)² is that they are usually very unstable and tend to decompose through (a) elimination reactions, (b) hydrogen abstractions from the reaction medium, and (c) rearrangement processes.¹ In the last few years we have been applying the arenecatalyzed lithiation technology³-⁵ for the addition of activated lithium to carbon-carbon double bond containing compounds⁶ or cyclopropyl derivatives⁷ in order to generate directly dilithium species that react with electrophiles to afford polyfunctionalized molecules, this procedure being of great interest from an atom-economy point of view.⁸ Namely, the lithiation of cyclopropylidene diphenylmethane (1) with lithium in ether was studied years ago by
Maercker et al\(^9\) who found that after obtaining of the expected dilithium intermediate 2 at -20 °C it is converted at room temperature into the undesired new ortho-lithiated species 3, which reacted with different electrophiles to give the final products 4. Actually, only the hydrolysis and the reaction of intermediate 2 with dimethyl sulphate were described to give compounds 5. In this paper we report the application of the above mentioned methodology (the arene-catalyzed lithiation) to lithiate the starting material 1 under very mild reaction conditions for the generation of the \(\text{sp}^2,\text{sp}^3\)-hybridized dilithium synthon 2\(^{10-12}\) as the only intermediate and its reaction with different electrophiles to give different functionalized products of type 5 (Scheme 1).

![Scheme 1](image)

**Scheme 1.** Reagents and conditions: (i) Li, ether, -20 °C; (ii) rt; (iii) \(E = \text{H}_2\text{O}, \text{D}_2\text{O}, \text{Me}_2\text{SO}_4, \text{RMeSiCl}_2, \text{CO}_2\); (iv) \(\text{H}_2\text{O}\); (v) \(E = \text{H}_2\text{O}, \text{Me}_2\text{SO}_4\).

**Results and Discussion**

The reaction of cyclopropane 1 [prepared from benzophenone and 3-(bromopropyl)triphenylphosphonium bromide through a Wittig reaction]\(^13\) with an excess of lithium powder (1:7 molar ratio) and a catalytic amount of naphthalene (5 mol %) in ether at -20 °C for 5 h, followed by addition of different electrophiles \(E = \text{H}_2\text{O}, \text{D}_2\text{O}, t\)-BuCHO, Me\(_2\)CO, Et\(_2\)CO, \(n\)-Pr\(_2\)CO, \(i\)-Pr\(_2\)CO, (\(c\)-C\(_3\)H\(_5\))\(_2\)CO, (CH\(_2\))\(_3\)CO] at -78 °C and final hydrolysis with water, allowing the reaction to reach the ambient temperature, gave the corresponding products 5 as the main compounds (Scheme 2 and Table 1). In the case of using enolizable ketones (except for dicyclopropylketone), variable amounts (<31%; Table 1, entries 4-7 and 9, and footnote b) of the
corresponding mono-reduced compounds of type 6 were also obtained, the separation of both products being easy by column chromatography. This product 6 is produced by partial proton abstraction of intermediate 2 from the reaction medium.\(^\text{14}\)

![Diagram of reaction and products](image)

**Scheme 2.** Reagents and conditions: (i) Li, C\(_{10}\)H\(_8\) cat. (5 mol %), ether, -20 °C; (ii) E = H\(_2\)O, D\(_2\)O, t-BuCHO, Me\(_2\)CO, Et\(_2\)CO, n-Pr\(_2\)CO, i-Pr\(_2\)CO, (c-C\(_3\)H\(_5\))\(_2\)CO, (CH\(_2\))\(_2\)CO, -78 °C; (iii) H\(_2\)O, -78 to 20 °C.

**Table 1.** Lithiation of compound 1 and reaction with electrophiles. Preparation of products 5

<table>
<thead>
<tr>
<th>Entry</th>
<th>E</th>
<th>No.</th>
<th>X</th>
<th>Yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_2)O</td>
<td>5a</td>
<td>H</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>D(_2)O</td>
<td>5b</td>
<td>D</td>
<td>68(^c)</td>
</tr>
<tr>
<td>3</td>
<td>t-BuCHO</td>
<td>5c</td>
<td>t-BuCHOH</td>
<td>56(^d,e)</td>
</tr>
<tr>
<td>4</td>
<td>Me(_2)CO</td>
<td>5d</td>
<td>Me(_2)COH</td>
<td>41 [20]</td>
</tr>
<tr>
<td>5</td>
<td>Et(_2)CO</td>
<td>5e</td>
<td>Et(_2)COH</td>
<td>33 [30]</td>
</tr>
<tr>
<td>6</td>
<td>n-Pr(_2)CO</td>
<td>5f</td>
<td>n-Pr(_2)CO</td>
<td>39 [29]</td>
</tr>
<tr>
<td>7</td>
<td>i-Pr(_2)CO</td>
<td>5g</td>
<td>i-Pr(_2)CO</td>
<td>26 [31](^f)</td>
</tr>
<tr>
<td>8</td>
<td>(c-C(_3)H(_5))(_2)CO</td>
<td>5h</td>
<td>(c-C(_3)H(_5))(_2)CO</td>
<td>55(^d)</td>
</tr>
<tr>
<td>9</td>
<td>(CH(_2))(_2)CO</td>
<td>5i</td>
<td>(CH(_2))(_2)CO</td>
<td>39 [27]</td>
</tr>
</tbody>
</table>

\(^a\) All products 5 (and 6) were >95% pure by 300 MHz \(^1\)H NMR and/or GLC.

\(^b\) Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting material 1. In brackets isolated yield of the corresponding product 6.

\(^c\) 85% deuterium content from 300 MHz \(^1\)H NMR.

\(^d\) <10% of the alcohol resulting from the reduction of the carbonyl compound used as electrophile was detected by GLC/MS and not isolated.

\(^e\) A ca. 1:1 mixture of diastereomers (GLC) were obtained and separated by column chromatography (silica gel, hexane/ethyl acetate).
Compounds 5g and 6g could not be separated by column chromatography.

The structure of compounds 5 was unequivocally assigned not only through their analytical and spectroscopic data but also thanks to the X-ray structure determination for compound 5d (see Experimental Part and Figure 1).

![Figure 1. X-ray structure of compound 5d.](image)

Concerning the possible mechanism for the reaction shown in Scheme 2, after one electron transfer from the lithiating mixture a lithium radical-anion of type 7 is generated that can get a second electron to give the dilithium dianion 8, which upon rearrangement suffers ring opening to yield the more stable dilithium intermediate 2 able to react with two molecules of the electrophile to yield, after final hydrolysis, compounds 5. Depending on its stability it can abstract a proton from the reaction medium to yield the monolithiated species 9, precursor of by-products 6 (Chart 1).

![Chart 1. Intermediates 7-9.](image)
Some light to the proposed mechanism was brought in the 4,4'-di-tert-butylbiphenyl (DTBB)-catalyzed lithiation of the starting material 1 in THF at -78 °C for 1 h: after hydrolysis with water or deuterium oxide, the dimeric products 10a,b were isolated, the saturated cyclopropyl derivative 11a being the other detected (<10%; GLC-MS) by-product (Scheme 3). On the other hand, performing the same reaction but under Barbier type conditions (in the presence of the electrophile: E = PhNH₂, Et₂CO), the monosubstituted species 11 were isolated (Scheme 3). It seems that the initially formed radical anion of type 7a can dimerize to give a dilithioderivative of type 10c, the precursor of compounds 10a,b, after final quenching with the electrophile. Under Barbier conditions either the intermediate 7b reacts with the electrophile present in the reaction medium (before being converted in the anion and final abstraction of a proton) or probably via a sequential process takes two protons (through intermediates 7 or 8) to yield compound 11a.

$$\text{Scheme 3. Reagents and conditions: (i) Li, DTBB cat. (5 mol %), THF, -78 °C, 2 h; (ii) H}_2\text{O, -78 °C to rt, 1 h; (iii) Li, DTBB cat. (5 mol %), Electrophile [E = PhNH}_2\text{ (for 11a), Et}_2\text{CO (for 11b)]}, -78 \text{ to } -50 \text{ °C, 2 h (slow addition).}$$

In the final part of this study we tried to extend the chemistry described above to the corresponding four-membered ring starting material 12. When this compound was submitted to the lithiation under the same reaction conditions shown in Scheme 2, only the expected reaction products 13 coming from the use of water and deuterium oxide were obtained (Scheme 4). The use of other electrophiles, such as t-BuCHO, Et₂CO or Me₃SiCl, even under Barbier-type reaction conditions (or using DTBB as the arene catalyst) failed, the main reaction product
being the corresponding reduced material 13a. This result could indicate us that the real cyclobutane opening (in the formation of compounds 13) takes place during the work-up between H$_2$O or D$_2$O and the lithium present in the reaction mixture. Anyhow, for the formation of compounds 13, intermediates 14 and/or 15 could be involved in the process.

![Scheme 4](image)

**Scheme 4.** Reagents and conditions: (i)-(iii) as in Scheme 2.

In conclusion, we report here the selective naphthalene-catalyzed lithiation of cyclopropylidene diphenylmethane (1), which by a ring opening allowed the generation of a dilithium intermediate 2 with both lithium atoms attached to a two differently hybridized (sp$^2$, sp$^3$) carbon atom. This species react with two molecules of several electrophiles to give, after final hydrolysis, the expected polyfunctionalized products in one only synthetic operation, this procedure being very productive from an atom-economy point of view.

**Experimental Section**

**General Procedures.** All lithiation reactions were carried out under argon atmosphere in oven-dried glassware. All commercially available reagents (Acros, Aldrich, Fluka) were used without further purification. Commercially available anhydrous THF (99.5%, water content ≤0.005%, Fluka) and ether (99.8%, water content ≤0.005%, Fluka) were used as solvents in all the lithiation reactions. Elemental analyses were performed by the Microanalyses Service at the University of Alicante. The IR spectra were measured (film) with a Nicolet Impact 400 D-FT Spectrometer. NMR spectra were recorded in the Technical Services of the University of
Alicante with a Bruker AC-300 or Bruker AC-400 spectrometer using CDCl₃ as solvent and TMS as internal standard; chemical shifts are given in parts per million and coupling constants (J) are given in hertz. ¹³C NMR assignments were made on the basis of DEPT experiments. LRMS were measured with a Hewlett-Packard EM/CG-5973N spectrometers, and HRMS were measured in the Technical Services of the University of Alicante with a Finnigan MAT95 S spectrometer, fragment ions in m/z with relative intensities (%) in parentheses. The purity of volatile products and the chromatographic analyses (GLC) were determined with a Hewlett-Packard HP-6890 instrument equipped with a flame ionisation detector and a 30 m HP-5 capillary column (0.32 mm diam., 0.25 µm film thickness), using nitrogen (2 mL/min) as carrier gas, TInjector=275 °C, TDetector=300 °C, TColumn=60 °C (3 min) and 60–270 °C (15 °C/min), P=40 kPa; retention times (tR) are given under these conditions. Thin layer chromatography (TLC) was carried out on Merck plastic sheets coated with silica gel 60 F₂₅₄. Melting points were obtained with a Reichert Thermovar apparatus. Lithium powder, which can be prepared from commercially available lithium granules (99%, high sodium content, Aldrich) as it was already reported by us,¹⁷ was supplied by Medalchemy S.L. and Chemetall GmbH.

Naphthalene-catalyzed lithiation of cyclopropylidene diphenylmethane (1) and reaction with electrophiles. Isolation of compounds 5 and byproducts 6. General procedure
To a purple suspension of lithium (49 mg, 7 mmol) and naphthalene (13 mg, 0.10 mmol) in ether (1 mL) cooled at –20 ºC was added dropwise a solution of cyclopropylidene diphenylmethane (206 mg, 1 mmol) in ether (2 mL). The resulting mixture was stirred for 5 h at the same temperature then the suspension was cooled at -78 ºC and the corresponding electrophile (2.2 mmol) was added dropwise. The resulting mixture was stirred for 0.5 h at the same temperature and then it was hydrolyzed with water (5 mL), allowing the temperature to rise to rt. The resulting mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous MgSO₄ and the solvents were evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding product(s). Isolated yields for compounds 5 are given in Table 1. Yields for compounds not included in Table 1, physical and spectroscopic data, as well as literature references for known compounds, follow.

1,1-Diphenyl-1-butene (5a).⁹ Colourless liquid; tR = 13.1 min; Rf (hexane) = 0.53; ν (film) 3078, 3054 (=CH) cm⁻¹; δH (300 MHz) 1.03 (3H, t, J = 7.3, CH₃), 2.12 (2H, dq, J = 7.3, CH₂), 6.07 (1H, t, J = 7.3, CH), 7.03-7.46 (10H, m, 10×ArH); m/z 208 (M⁺, 87), 207 (22), 194 (11), 193 (67), 191 (13), 189 (11), 179 (32), 178 (49), 165 (46), 152 (16), 131 (11), 130 (49), 129 (32), 128 (19), 116 (12), 115 (100), 91 (33), 89 (13), 78 (15), 77 (17), 63 (10), 51 (17).

2,4-Dideutero-1,1-diphenyl-1-butene (5b). Colourless liquid; tR = 13.1 min; Rf (hexane) = 0.53; ν (film) 3077, 3054 (=CH) cm⁻¹; δH (300 MHz) 1.01 (2H, t, J = 7.3, CH₂D), 2.11 (2H, t, J = 7.3, CH₂CH₂D), 7.16-7.38 (10H, m, 10×ArH); δC (75 MHz) 14.2 (t, J = 19, CH₂D), 23.0 (CH₂CH₂D), 126.7, 126.8, 127.2, 128.0, 128.1, 129.9 (ArCH), 131.3 (t, J = 23, C=CD), 140.2, 140.8, 142.8 (ArC, C=CD); m/z 210 (M⁺, 100%), 209 (48), 208 (23), 207 (10), 195 (16), 194 (83), 193 (29),
192 (18), 191 (13), 190 (13), 180 (28), 179 (58), 178 (34), 167 (12), 166 (24), 165 (39), 152 (13), 133 (11), 132 (38), 131 (36), 130 (25), 129 (15), 117 (13), 116 (72), 115 (47), 92 (23), 91 (23), 89 (11), 77 (13), 51 (11); HRMS: M⁺, found 210.1339. C₁₆H₄₄D₂ requires 210.1378.

4-Diphenylmethylen-2,2,8,8-tetramethyl-3,7-nonanediol (5c'). White solid, 29% yield; mp 114 °C (diethyl ether); tᵣ = 19.9 min; Rᵣ (hexane/ethyl acetate 8/2) = 0.44; ν (KBr) 3354 (OH), 3077, 3056 (ν(CH)) cm⁻¹; δH (300 MHz) 0.76 (9H, s, 3×CH₃), 0.87 (9H, s, 3×CH₃), 0.91-1.26 (2H, m, CH₂CHOH), 1.60 (1H, br, OH), 2.37-2.49 (1H, m, CHH₂CH₂), 2.62-2.71 (1H, m, CHH₂CH₂CH), 2.92 (1H, br, OH), 3.32-3.37 (1H, m, CH₂CHOH), 4.49 (1H, s, C=CH₂CHOH), 7.09-7.30 (10H, m, 10×ArH); δC (75 MHz) 23.2 (CH₂CH₂CH₂), 26.0, 27.0 (CH₃), 29.7 (CH₂CHOH), 34.4, 37.8 [C(CH₃)₃], 76.4, 79.9 (CH₂OH), 126.4, 126.8, 128.2, 128.3, 128.9, 129.7 (ArCH), 137.6, 143.2, 143.6, 143.9 (ArC, C=C); m/z 344 (M⁺-2H₂O, 2%), 324 (14), 323 (50), 306 (14), 305 (60), 287 (18), 261 (29), 247 (49), 245 (17), 232 (11), 231 (53), 221 (28), 219 (19), 218 (28), 217 (37), 216 (18), 215 (30), 207 (10), 206 (17), 205 (100), 204 (48), 203 (67), 202 (52), 193 (26), 192 (27), 191 (40), 190 (16), 189 (19), 179 (15), 178 (38), 169 (18), 167 (25), 165 (33), 143 (16), 129 (15), 128 (12), 115 (58), 105 (20), 91 (41), 77 (10), 69 (14), 57 (99), 56 (10), 55 (23); HRMS: M⁺-H₂O, found 362.2573. C₂₂H₄₆O requires 362.2610.

4-Diphenylmethylen-2,2,8,8-tetramethyl-3,7-nonanediol (5c**). Colourless crystals, 27% yield; mp 147 °C (diethyl ether); tᵣ = 19.9 min; Rᵣ (hexane/ethyl acetate 8/2) = 0.15; ν (KBr) 3386 (OH), 3077, 3054 (ν(CH)) cm⁻¹; δH (300 MHz) 0.73 (9H, s, 3×CH₃), 0.87 (9H, s, 3×CH₃), 1.15-1.25 (1H, m, CHHCHOH), 1.34-1.42 (1H, m, CHHCHOH), 1.60 (2H, br, 2×OH), 2.35-2.46 (1H, m, CHH₂CH₂), 2.52-2.63 (1H, m, CHH₂CH₂CH), 3.00-3.06 (1H, m, CH₂CHOH), 4.49 (1H, s, C=CH₂CHOH), 7.10-7.31 (10H, m, 10×ArH); δC (75 MHz) 25.5 (CH₃), 26.0 (CH₂), 27.2 (CH₃), 31.2 (CH₂), 34.8, 37.4 [C(CH₃)₃], 79.3, 81.7 (CH₂OH), 126.2, 126.5, 128.2, 128.3, 129.1, 129.5 (ArCH), 140.5, 142.2, 143.6, 143.9 (ArC, C=C); m/z 362 (M⁺-H₂O, 1%), 323 (18), 305 (32), 287 (14), 261 (40), 247 (22), 245 (13), 231 (30), 229 (11), 221 (10), 219 (12), 218 (29), 217 (26), 216 (15), 215 (29), 206 (20), 205 (100), 204 (45), 203 (63), 202 (50), 193 (14), 192 (17), 191 (26), 178 (16), 167 (11), 165 (16), 15 (20), 91 (16), 57 (50), 55 (13); HRMS: M⁺-H₂O, found 362.2587. C₂₂H₄₆O requires 362.2610.

3-Diphenylmethylen-2,6-dimethyl-2,6-heptanediol (5d).¹⁸ Colourless crystals; mp 106 °C (diethyl ether); tᵣ = 17.8 min; Rᵣ (hexane/ethyl acetate 6/4) = 0.16; ν (KBr) 3410 (OH), 3053 (=CH) cm⁻¹; δH (400 MHz) 0.92 [6H, s, CH₂COH(CH₃)₂], 1.20 (1H, s, OH), 1.36 [6H, s, C=COH(CH₃)₂], 1.56-1.61 (2H, m, CH₂CH₂COH), 1.84 (1H, br, OH), 2.15-2.21 (2H, m, CH₂CH₂COH), 7.12-7.13 (10H, m, 10×ArH); δC (100 MHz) 26.2 (CH₂CH₂COH), 28.5, 31.5 (CH₃), 44.0 (CH₂CH₂COH), 70.8, 75.3 (COH), 126.2, 126.5, 128.2, 128.3, 128.4 (ArCH), 138.4, 143.9, 144.4, 145.0 (ArC, C=C); m/z 306 (M⁺-H₂O, 1%), 288 (34), 273 (11), 245 (13), 233 (38), 220 (23), 219 (100), 218 (15), 217 (23), 216 (11), 215 (28), 205 (12), 204 (21), 203 (29), 202 (30), 91 (14); Anal. Calcld for C₂₂H₂₃O₂: C, 81.44; H, 8.70. Found: C, 81.27; H, 8.65; HRMS: M⁺-H₂O, found 306.1981. C₂₂H₂₃O requires 306.1984.

2-Methyl-6,6-diphenyl-5-hexen-2-ol (6d). Colourless oil, 20% yield; tᵣ = 16.3 min; Rᵣ (hexane/ethyl acetate 6/4) = 0.53; ν (film) 3399 (OH), 3078, 3055 (=CH) cm⁻¹; δH (400 MHz)
1.14 (6H, s, CH₃), 1.60-1.68 (2H, m, CH₂CH₂COH), 2.16-2.23 (2H, m, CH₂CH₂COH), 6.09 (1H, t, J = 7.5, C=CH), 7.17-7.36 (10H, m, 10×ArH); δc (100 MHz) 24.9 (CH₂CH₂COH), 29.1 (CH₃), 43.7 (CH₂CH₂COH), 70.9 (COH), 125.2, 126.8, 127.0, 127.2, 127.2, 128.1, 128.2 (ArCH, C=CH), 140.0, 141.7, 144.2 (ArC, C=CH); m/z 266 (M⁺, 1%), 249 (11), 248 (53), 233 (42), 219 (13), 206 (20), 205 (93), 204 (19), 203 (17), 193 (100), 192 (23) 181 (36), 190 (13), 190 (43), 189 (20), 180 (12), 179 (17), 178 (52), 167 (10), 165 (42), 157 (14), 155 (15), 152 (15), 129 (14), 128 (15), 116 (11), 115 (89), 91 (63); HRMS: M⁺, found 266.1692. C₁₉H₂₃O requires 266.1671.

4-Diphenylmethylen-3,7-diyethyl-3,7-nonanediol (5e). White solid; mp 72 °C (diethyl ether); tR = 20.7 min; Rf (hexane/ethyl acetate 8/2) = 0.23; v (KBr) 3437 (OH), 3076, 3052 (=CH) cm⁻¹; δH (400 MHz) 0.59 (6H, t, J = 7.4, 2×CH₃), 1.00 (6H, t, J = 7.4, 2×CH₃), 0.97-1.25 (4H, m, 2×CH₂CH₃), 1.39-1.50 (4H, m, 2×CH₂CH₃), 1.64-1.78 (2H, m, CH₂CH₂COH), 2.03-2.10 (2H, m, CH₂CH₂COH), 7.10-7.31 (10, m, 10×ArH); δc (100 MHz) 7.5, 8.5 (CH₃), 24.8, 30.3, 33.9, 37.2 (CH₂CH₃, CH₂CH₂COH, CH₂CH₂COH), 74.3, 81.1 (COH), 126.2, 126.4, 127.7, 128.2, 128.5, 128.5 (ArCH), 139.7, 141.2, 143.9, 145.0 (ArC, C=CH); m/z 362 (M⁺-H₂O, 1%), 344 (13), 334 (25), 333 (99), 315 (22), 266 (12), 265 (47), 262 (24), 261 (100), 249 (37), 248 (10), 247 (32), 245 (10), 233 (10), 232 (20), 231 (35), 230 (10), 229 (18), 228 (18), 226 (11), 219 (34), 218 (17), 217 (49), 216 (41), 215 (83), 205 (25), 204 (26), 203 (74), 202 (70), 193 (18), 191 (22), 189 (18), 179 (11), 178 (20), 167 (26), 165 (26), 152 (13), 131 (11), 129 (11), 128 (11), 117 (11), 115 (25), 105 (24), 91 (53), 69 (10), 67 (11), 57 (50), 55 (67); HRMS: M⁺-2×H₂O, found 344.2502. C₂₆H₃₂ requires 344.2504.

3-Ethyl-7,7-diphenyl-6-heptan-3-ol (6e). Colourless oil, 30% yield; tR = 18.0 min; Rf (hexane/ethyl acetate 8/2) = 0.44; v (film) 3404 (OH), 3079, 3054 (=CH); δH (400 MHz) 0.78 (6H, t, J = 7.5, 2×CH₃), 0.94 (1H, s, OH), 1.37 (4H, q, J = 7.5, 2×CH₂CH₃), 1.51-1.63 (2H, m, CH₂CH₂COH), 2.03-2.16 (2H, m, CH₂CH₂COH), 6.10 (1H, t, J = 7.5, C=CH), 7.16-7.39 (10H, m, 10×ArH); δc (100 MHz) 7.6 (CH₃), 24.0 (CH₂CH₂COH), 30.8 (CH₂CH₃), 38.1 (CH₂CH₂COH), 74.5 (COH), 126.8, 126.9, 127.1, 128.0, 128.1, 129.7, 129.8 (ArCH, C=CH), 140.0, 141.6, 142.6 (ArC, C=CH); m/z 276 (M⁺-H₂O, 41%), 247 (39), 205 (26), 194 (17), 193 (100), 192 (17), 191 (25), 189 (14), 180 (18), 179 (12), 178 (39), 167 (13), 165 (33), 152 (12), 128 (11), 115 (84), 91 (46), 55 (20); HRMS: M⁺, found 294.1979. C₁₉H₂₃O requires 294.1984.

5-Diphenylmethylen-4,8-dipropyl-4,8-undecanediol (5f). Colourless oil; tR = 22.9 min; Rf (hexane/ethyl acetate 8/2) = 0.09; v (film) 3416 (OH), 3076, 3053 (=CH) cm⁻¹; δH (400 MHz) 0.73-1.67 (32H, m, 4×CH₂CH₂CH₃, 4×CH₂CH₂CH₂CH₃, 4×CH₂CH₂CH₂CH₃, CH₂CH₂COH, 2×OH), 2.02-2.09 (2H, m, CH₂CH₂COH), 7.10-7.35 (10H, m, 10×ArH); δc (100 MHz) 14.4, 14.7 (CH₃), 16.4, 17.3 (CH₂CH₃), 25.1 (CH₂CH₂COH), 38.2, 41.0, 44.2 (CH₂CH₂COH, CH₂CH₂CH₃), 74.1, 80.6 (COH), 126.1, 126.4, 127.8, 128.2, 128.4, 128.5 (ArCH), 139.0, 141.8, 143.9, 145.0 (ArC, C=CH); m/z 400 (M⁺-2×H₂O, 6%), 376 (31), 375 (100), 357 (17), 294 (14), 293 (58), 290 (12), 289 (46), 275 (14), 263 (32), 251 (12), 247 (31), 245 (15), 233 (12), 229 (14), 228 (12), 219 (20), 218 (14), 217 (46), 216 (24), 215 (48), 205 (31), 204 (17), 203 (31), 202 (40), 193 (18), 191 (15), 189 (11), 178 (12), 167 (25), 165 (18), 115 (22), 105 (12), 91 (37), 71 (46), 69 (27), 67 (10), 55 (46); HRMS: M⁺-H₂O, found 418.3254. C₃₀H₄₂O requires 418.3236.
8,8-Diphenyl-4-propyl-7-octen-4-ol (6f). Colourless oil, 29% yield; $t_R = 18.9$ min; $R_f$ (hexane/ethyl acetate 8/2) = 0.37; $\nu$ (film) 3412 (OH), 3055 ($=\text{CH}$) cm$^{-1}$; $\delta_H$ (400 MHz) 0.81-0.90 (6H, m, 2×CH$_3$), 1.14-1.41 (9H, m, 2×CH$_2$CH$_2$CH$_3$, 2×CH$_2$CH$_2$CH$_2$CH$_3$, OH), 1.49-1.68 (2H, m, CH$_2$CH$_2$COH), 2.03-2.15 (2H, m, CH$_2$CH$_2$COH), 6.10 (1H, t, $J = 7.5$, C=CH), 7.15-7.40 (10H, m, 10×ArH); $\delta_C$ (100 MHz) 14.6 (CH$_3$), 15.1 (CH$_2$CH$_2$CH$_3$), 24.1 (CH$_2$CH$_2$COH), 39.0, 41.4 (CH$_2$CH$_2$COH, CH$_2$CH$_2$CH$_3$), 74.4 (COH), 126.8, 126.9, 127.1, 128.0, 128.2, 129.6, 128.8 (ArCH, C=CH), 140.0, 141.7, 142.5 (ArC, C=CH); $m/z$ 304 (M$^+$-H$_2$O, 28%), 261 (29), 205 (21), 194 (17), 193 (100), 192 (14), 191 (22), 189 (11), 180 (14), 178 (34), 167 (11), 165 (26), 115 (76), 91 (44), 55 (15); HRMS: M$^+$-H$_2$O, found 304.2164. C$_{23}$H$_{38}$ requires 304.2191.

4-Diphenylmethylenetri-m-diisopropyl-2,8-dimethyl-3,7-nonanediol (5g) and 3-isopropyl-2-methyl-7,7-diphenyl-6-hepten-3-ol (6g). Colourless oil, 5g 26% yield, 6g 31% yield; $t_R$ (5g) = 24.8 min, $t_R$ (6g) = 19.3 min; $R_f$ (hexane/ethyl acetate 8/2) = 0.22; $\delta_H$ (400 MHz) 0.69, 0.71 (12H, 2d, $J = 6.9$, 4×CH$_3$), 0.82, 0.86 (12H, 2d, $J = 6.9$, 4×CH$_3$), 1.01, 1.11 (12H, 2d, $J = 6.9$, 4×CH$_3$), 1.34-1.64 (4H, 2m, 2×CH$_2$), 1.68, 1.80 (4H, 2h, $J = 6.9$, 4×CH), 2.02-2.27 (6H, 2m, 2×CH$_2$, 2×CH), 6.08 (1H, t, $J = 7.5$, C=CH), 7.09-7.46 (20H, m, 20×ArH); $\delta_C$ (100 MHz) 17.2, 17.3, 17.4, 17.5, 17.9, 19.7 (CH$_3$, CH), 24.7, 29.7, 31.8, 33.7 (CH$_2$), 33.9, 34.0 (CH), 77.1, 85.3 (COH), 126.2, 126.8, 126.9, 127.0, 127.4, 128.0, 128.1, 128.3, 128.7, 128.9, 129.7 (ArCH, C=CH), 140.0, 141.6, 141.8, 142.4, 144.5, 145.3 (ArC, C=CH, C=C); $m/z$ (5g) 400 (M$^+$-2×H$_2$O, 14%), 375 (19), 357 (32), 302 (23), 301 (15), 290 (25), 289 (100), 260 (12), 259 (46), 247 (23), 246 (16), 245 (39), 233 (32), 232 (11), 231 (30), 230 (14), 229 (17), 219 (14), 218 (13), 217 (31), 216 (24), 215 (42), 205 (32), 204 (12), 203 (26), 202 (17), 193 (10), 191 (13), 167 (30), 165 (13), 115 (11), 105 (15), 91 (34), 71 (14), 69 (28), 55 (19); HRMS (5g): M$^+$-2×H$_2$O, found 400.3041. C$_{30}$H$_{40}$ requires 400.3130; $m/z$ (6g) 304 (M$^+$-H$_2$O, 12%), 261 (18), 206 (31), 205 (13), 194 (17), 193 (100), 191 (19), 178 (24), 167 (20), 165 (15), 124 (18), 115 (45), 91 (29); HRMS (6g): M$^+$-H$_2$O, found 304.2180. C$_{23}$H$_{38}$ requires 304.2191.

1,1,5,5-Tetracyclopentyldiphenylmethylenetri-m-pentanedial (5h). Colourless oil; $t_R = 29.1$ min; $R_f$ (hexane/ethyl acetate 8/2) = 0.28; $\nu$ (film) 3586, 3488 (OH), 3080 ($=\text{CH}$) cm$^{-1}$; $\delta_H$ (400 MHz) 0.46-1.06 (19H, m, 8×ring CH, 2×ring CH, OH), 1.55-1.73 (3H, m, 2×ring CH, OH), 2.16-2.23 (2H, m, CH$_2$CH$_2$COH), 2.89-2.96 (2H, m, CH$_2$CH$_2$COH), 7.56-7.77 (10H, m, 10×ArH); $\delta_C$ (100 MHz) -1.0, 0.2, 0.5, 2.4 (ring CH$_2$), 17.9, 19.9 (ring CH), 25.5 (CH$_2$CH$_2$COH), 42.4 (CH$_2$CH$_2$COH), 70.5, 75.4 (C=CCOH, CH$_2$COH), 126.0, 126.3, 128.1, 128.3, 128.5, 128.6 (ArCH), 137.6, 143.6, 144.7, 145.0 (ArC, C=C); $m/z$ 410 (M$^+$-H$_2$O, 1%), 289 (40), 285 (10), 265 (12), 257 (10), 256 (14), 255 (18), 254 (12), 253 (19), 252 (21), 244 (26), 243 (79), 242 (13), 241 (25), 240 (14), 239 (28), 229 (26), 228 (28), 227 (13), 226 (18), 217 (14), 216 (18), 215 (43), 205 (14), 203 (19), 202 (27), 192 (16), 191 (23), 189 (15), 180 (13), 179 (18), 167 (31), 165 (32), 152 (12), 129 (11), 121 (21), 115 (18), 111 (25), 105 (19), 93 (19), 91 (49), 79 (30), 77 (27), 69 (100), 67 (20), 65 (10), 55 (18); HRMS: M$^+$-2×H$_2$O, found 392.2520. C$_{30}$H$_{40}$ requires 392.2504.

1-[3-(1-Hydroxycyclohexyl)-4-diphenyl-3-butenyl]-1-cyclohexanol (5i). White solid; mp 82°C (diethyl ether); $t_R$ = 29.3 min; $R_f$ (hexane/ethyl acetate 8/2) = 0.13; $\nu$ (film) 3384 (OH), 3054 ($=\text{CH}$) cm$^{-1}$; $\delta_H$ (300 MHz) 0.87-2.16 (26H, m, 10×ring CH$_2$, CH$_2$CH$_2$COH, CH$_2$CH$_2$COH,
2×OH), 7.14-7.26 (10H, m, 10×ArH); δ_C (75 MHz) 21.5, 22.1, 24.5, 25.2, 25.6 (ring CH_2, CH_2CH_2COH), 37.0, 37.3 (ring CH_2), 42.0 (CH_2CH_2COH), 71.4, 76.6 (COH), 126.1, 126.3, 128.3, 128.4 (ArCH), 138.6, 144.2, 144.8, 145.5 (ArC=C=C); m/z 386 (M^+-H_2O, 48%), 368 (33), 360 (12), 330 (23), 329 (45), 304 (18), 303 (56), 291 (20), 290 (13), 286 (17), 285 (42), 278 (20), 277 (79), 274 (29), 273 (93), 272 (40), 271 (10), 260 (16), 259 (28), 258 (12), 252 (17), 247 (11), 243 (13), 241 (16), 239 (26), 234 (21), 233 (48), 232 (11), 231 (29), 230 (17), 229 (36), 228 (35), 227 (13), 226 (14), 221 (11), 219 (22), 218 (18), 217 (67), 216 (40), 215 (94), 213 (12), 207 (13), 206 (22), 205 (59), 204 (34), 203 (53), 202 (76), 195 (11), 193 (20), 192 (18), 191 (52), 190 (23), 189 (36), 181 (14), 179 (26), 178 (54), 168 (15), 167 (63), 166 (18), 165 (15), 155 (14), 152 (29), 145 (11), 141 (27), 129 (28), 128 (33), 117 (19), 116 (11), 115 (43), 105 (25), 99 (21), 95 (27), 91 (100), 81 (41), 79 (33), 78 (19), 77 (30), 69 (15), 67 (48), 65 (14), 55 (65), 54 (11), 53 (24), 51 (14); HRMS: M^+ -2×H_2O, found 368.2536. C_{28}H_{32} requires 368.2504.

1-(4,4-Diphenyl-3-butenyl)-1-cyclohexanol (6i). Colourless oil, 27% yield; t_R = 19.8 min; R_f (hexane/ethyl acetate 8/2) = 0.37; ν (film) 3375 (OH), 3052 (=CH) cm^{-1}; δ_H (300 MHz) 0.82-1.82 (13H, m, 5×ring CH_2, CH_2CH_2COH, OH), 2.15-2.24 (2H, m , C_H_2CH_2COH), 6.09 (1H, t, J = 7.5, C=CH), 7.15-7.40 (10H, m , 10×ArH); δ_C (75 MHz) 22.1, 23.6, 25.7 (ring CH_2, CH_2CH_2COH), 37.3 (ring CH_2), 42.3 (CH_2CH_2COH), 71.4 (COH), 126.8, 126.9, 127.1, 128.0, 128.1, 129.8, 130.0 (ArCH, C=CH), 140.0, 141.6, 142.7 (ArC, C=CH); m/z 288 (M^+-H_2O, 39%), 206 (27), 205 (72), 204 (16), 203 (12), 202 (13), 194 (15), 193 (95), 192 (17), 191 (32), 189 (17), 180 (12), 179 (16), 178 (51), 167 (21), 165 (42), 152 (15), 128 (14), 116 (13), 115 (100), 91 (53), 81 (11), 79 (14), 77 (19), 67 (12), 65 (11), 55 (12), 51 (11); HRMS: M^+, found 306.1950. C_{22}H_{26}O requires 306.1984.

**DTBB-catalyzed lithiation of cyclopropylidene diphenylmethane (1) and reaction with electrophiles. Isolation of compounds 10. General procedure**

To a green suspension of lithium (49 mg, 7 mmol) and DTBB (26 mg, 0.10 mmol) in THF (1 mL) cooled at -78 ºC was added dropwise a solution of cyclopropylidene diphenylmethane (206 mg, 1 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h at the same temperature and then the corresponding electrophile was added dropwise. The resulting mixture was stirred for 1 h at the same temperature and then it was hydrolyzed with water (5 mL), allowing the temperature to rise to rt. The resulting mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous MgSO_4 and the solvents were evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding product. Isolated yields are given in Scheme 3. Physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

1-[1-(1-Benzhydrylcyclopropyl)cyclopropyl(phenyl)methyl]benzene (10a). Colourless crystals; mp 186 ºC (hexane/ethyl acetate); t_R = 31.5 min; R_f (hexane) = 0.29; ν (KBr) 3082, 3058 (≡CH) cm^{-1}; δ_H (400 MHz) -0.01-0.03 (4H, m, 2×ring CH_2), 0.14-0.18 (4H, m, 2×ring CH_2), 4.70 (2H, s, 2×CH), 7.12-7.27 (20H, 20×ArH); δ_C (100 MHz) 6.3 (CH_2), 23.9 [C(CH_2)_2], 52.6 (CH),...
126.2, 127.7, 130.3 (ArCH), 142.0 (ArC); m/z 414 (M⁺, 1%), 247 (29), 219 (39), 217 (14), 215 (19), 206 (12), 205 (14), 204 (12), 203 (17), 202 (20), 193 (15), 191 (15), 189 (10), 179 (11), 178 (18), 168 (19), 167 (100), 166 (25), 165 (75), 153 (11), 152 (42), 143 (10), 141 (16), 129 (14), 128 (21), 117 (11), 115 (35), 105 (16), 91 (73), 77 (16); Anal. Calcd for C₃₂H₃₀·0.25C₄H₈O₂: C, 90.78; H, 7.39. Found: C, 90.91; H, 7.36.

Dideutero-1-[1-(1-benzhydrylcyclopropyl)cyclopropyl(phenyl)methyl]benzene (10b). Colourless crystals; mp 188 °C (diethyl ether); tᵣ = 31.5 min; Rᵣ (hexane) = 0.29; ν (KBr) 3080, 3056 (=CH) cm⁻¹; δH (300 MHz) -0.01-0.02 (4H, m, 2×ring CH₂), 0.11-0.28 (4H, m, 2×ring CH₂), 7.11-7.27 (20H, 20×ArH); δC (75 MHz) 6.3 (CH₂), 23.8 [C(CH₂)₂], 52.1 (t, J = 19.9, CD), 126.2, 127.7, 130.2 (ArCH), 142.0 (ArC); m/z 388 (M⁺-2×CH₂, 2%), 248 (34), 221 (14), 220 (42), 219 (10), 207 (10), 206 (11), 194 (17), 179 (10), 169 (18), 168 (100), 167 (17), 166 (38), 165 (14), 153 (23), 116 (12), 115 (11), 105 (12), 92 (26), 91 (43); HRMS: M⁺-2×CH₂, found 388.2132. C₃₀H₂₄D₂ requires 388.2160.

DTBB-catalyzed lithiation of cyclopropylidene diphenylmethane (1) and reaction with electrophiles under Barbier conditions. Isolation of compounds 11. General procedure

When the reaction was performed under Barbier conditions, a mixture of cyclopropylidene diphenylmethane (206 mg, 1 mmol) and the corresponding electrophile (3 mmol) in THF (2 mL) was added dropwise over 2 h to a green suspension of lithium (49 mg, 7 mmol) and DTBB (26 mg, 0.10 mmol) in THF (1 mL) cooled at -78 °C. The mixture was stirred for 1 h at the same temperature and then it was hydrolyzed with water (5 mL), allowing the temperature to rise to rt. After the workup described above, the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding product. Isolated yields are given in Scheme 3. Physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

1-Cyclopropyl(phenyl)methylbenzene (11a). Colourless liquid; tᵣ = 13.4 min; Rᵣ (hexane) = 0.35; ν (film) 3059 (=CH) cm⁻¹; δH (300 MHz) 0.26-0.32 (2H, m, ring CH₂), 0.61-0.69 (2H, m, ring CH₂), 1.25-1.46 (1H, m, ring CH), 3.20 (1H, d, J = 9.5, CH), 7.14-7.31 (10H, m, 10×ArH); δC (100 MHz) 5.3 (ring CH₂), 16.7 (ring CH), 55.6 (CH), 126.1, 128.2, 128.2 (ArCH), 145.2 (ArC); m/z 208 (M⁺, 8%), 181 (15), 180 (100), 179 (66), 178 (30), 167 (11), 166 (13), 165 (62), 152 (17), 115 (23), 104 (55), 91 (15), 77 (12), 51 (12).

3-(1-Benzhydrylcyclopropyl)-3-pentanol (11b). Colourless oil; tᵣ = 17.4 min; Rᵣ (hexane/ethyl acetate 8/2) = 0.30; ν (film) 3587 (OH), 3084, 3058 (=CH) cm⁻¹; δH (300 MHz) 0.19-0.24 (2H, m, ring CH₂), 0.69-0.74 (2H, m, ring CH₂), 0.93 (6H, t, J = 7.4, 2×CH₃), 1.44-1.52 (4H, m, 2×CH₂), 4.54 (1H, s, CH), 7.10-7.32 (10H, m, 10×ArH); δC (75 MHz) 4.7 (ring CH₂), 8.3 (CH₃), 27.6 [C(CH₂)], 30.1 (CH₂), 51.6 (CH), 126.2, 128.1, 129.5 (ArCH), 143.5 (ArC); m/z 276 (M⁺-H₂O, 21%), 248 (14), 247 (64), 219 (23), 215 (15), 206 (10), 205 (24), 204 (15), 203 (20), 202 (21), 193 (39), 192 (13), 191 (20), 189 (14), 179 (10), 178 (21), 168 (15), 167 (100), 166 (24), 165 (74), 153 (12), 152 (38), 143 (12), 141 (15), 129 (19), 128 (23), 115 (45), 105 (18), 91 (56), 77 (16), 51 (12).
Naphthalene-catalyzed lithiation of cyclobutylidene diphenylmethane (12) and reaction with electrophiles. Isolation of compounds 13. General procedure
To a purple suspension of lithium (49 mg, 7 mmol) and naphthalene (13 mg, 0.10 mmol) in ether (1 mL) cooled at -20 °C was added dropwise a solution of cyclobutylidene diphenylmethane (220 mg, 1 mmol) in ether (2 mL). The resulting mixture was stirred for 6 h at the same temperature then the suspension was cooled at -78 °C and the corresponding electrophile was added dropwise. The resulting mixture was stirred for 0.5 h at the same temperature and then it was hydrolyzed with water (5 mL), allowing the temperature to rise to rt. The resulting mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous MgSO4 and the solvents were evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the corresponding product. Isolated yields are given at Scheme 4. Physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

1,1-Diphenyl-1-pentene (13a). Colorless oil; \( t_R = 13.9 \) min; \( \nu \) (film) 3051 (=CH) cm\(^{-1}\); \( \delta_H \) (300 MHz) 0.90 (3H, t, \( J = 7.4 \), CH\(_3\)), 1.40-1.52 (2H, m, CH\(_2\)CH\(_3\)), 2.02-2.13 (2H, m, CHCH\(_2\)), 6.09 (1H, t, \( J = 7.5 \), CH), 7.13-7.43 (10H, m, 10×ArH); \( \delta_C \) (75 MHz) 13.8 (CH\(_3\)), 23.1 (CH\(_2\)CH\(_3\)), 31.8 (CHCH\(_2\)), 126.7, 126.7, 127.2, 128.0, 128.1, 129.9, 130.1 (ArCH, C=CH), 140.3, 141.5, 142.9 (ArC); \( m/z \) 222 (M\(^+\), 50%), 194 (16), 193 (100), 191 (11), 179 (14), 178 (36), 165 (24), 115 (66), 91 (21).

2,4-Dideutero-1,1-diphenyl-1-pentene (13b) and 2-deutero-1-(2-deuterophenyl)-1-phenyl-1-pentene (13b'). Colorless oil; \( t_R = 13.9 \) min; \( \nu \) (film) 3055 (=CH); \( \delta_H \) (400 MHz) 0.97-1.06 (5H, m, CH\(_3\), CH\(_2\)D), 1.53-1.66 (4H, m, CH\(_2\)CH\(_3\), CH\(_2\)CH(CH\(_2\))D), 2.22 (4H, t, \( J = 7.3 \), CDCH\(_2\)), 7.26-7.53 (20H, m, 20×ArH); \( \delta_C \) (100 MHz) 13.5 (t, \( J = 19.8 \), CH\(_2\)D), 13.8 (CH\(_3\)), 23.0, 23.1 (CH\(_2\)CH\(_3\), CH\(_2\)CH(CH\(_2\))D), 31.7 (CH\(_2\)D), 126.7, 126.8, 127.2, 128.0, 128.1, 129.9 (ArCH), 140.3, 141.4, 141.5, 142.8, 142.9 (ArC, C=CD).

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References


7. (a) Gómez, C.; Lillo, V. J.; Yus, M. Tetrahedron 2007, 63, 4655. (b) See also reference 6b.


16. In the case of using D$_2$O as electrophile, together with compound 13b, the corresponding ortho-deuteriated regioisomer 13b' obtained (ca. 1:1 mixture by NMR) with the same D content. It would mean that intermediate 15 suffered lithium rearrangement to form partially the new ortho-lithiated dianion 16. See references 9 and 11 for related processes. See also: Dunkelblum, E.; Brenner, S. Tetrahedron Lett. 1973, 669.

18. (a) Crystal data, excluding structure factors, deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers follow: (5d), CCDC 717711: C$_{22}$H$_{28}$O$_2$, $M = 324.44$; triclinic, $a = 10.3773(14)$ Å, $b = 12.0151(17)$ Å, $c = 16.262(2)$ Å, $\alpha = 101.782(3)^\circ$, $\beta = 97.158(3)^\circ$, $\gamma = 92.683(4)^\circ$; $V = 1964.0(5)$ Å$^3$; space group $P-1$; $Z = 4$; $D_c = 1.097$ Mg m$^{-3}$; $\lambda = 0.71073$ Å; $\mu = 0.068$ mm$^{-1}$; $F(000) = 704$; $T = 24\pm1^\circ$C. Data collection was performed on a Bruker Smart CCD diffractometer, based on three $\omega$-scan runs (starting $\phi = -34^\circ$) at values $\phi = 0^\circ$, 120$^\circ$, 240$^\circ$ with the detector at $2\theta = -32^\circ$. For each of these runs, 606 frames were collected at 0.3$^\circ$ intervals and 20 s per frame. An additional run at $\phi = 0^\circ$ of 100 frames was collected to improve redundancy. The diffraction frames were integrated using the program SAINT$^{18b}$ and the integrated intensities were corrected for Lorentz-polarisation effects with SADABS.$^{18c}$ The structure was solved by direct methods$^{4d}$ and refined to all 2463 unique $F_o^2$ by full matrix least squares.$^{18d}$ All the hydrogen atoms were placed at idealised positions and refined as rigid atoms. Final $wR_2 = 0.1300$ for all data and 246 parameters; $R_1 = 0.0424$ for 2051 $F_o > 4\sigma(F_o)$; (b) SAINT Version 6.02A: Area-Detector Integration Software; Siemens Industrial Automation, Inc.: Madison, WI, 1995; (c) Sheldrick, G. M. SADABS: Area-Detector Absorption Correction, Göttingen University, 1996; (d) SHELX97 (Includes SHELXS97, SHELXL97 and CIFTAB)-Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
