

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

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Abstract

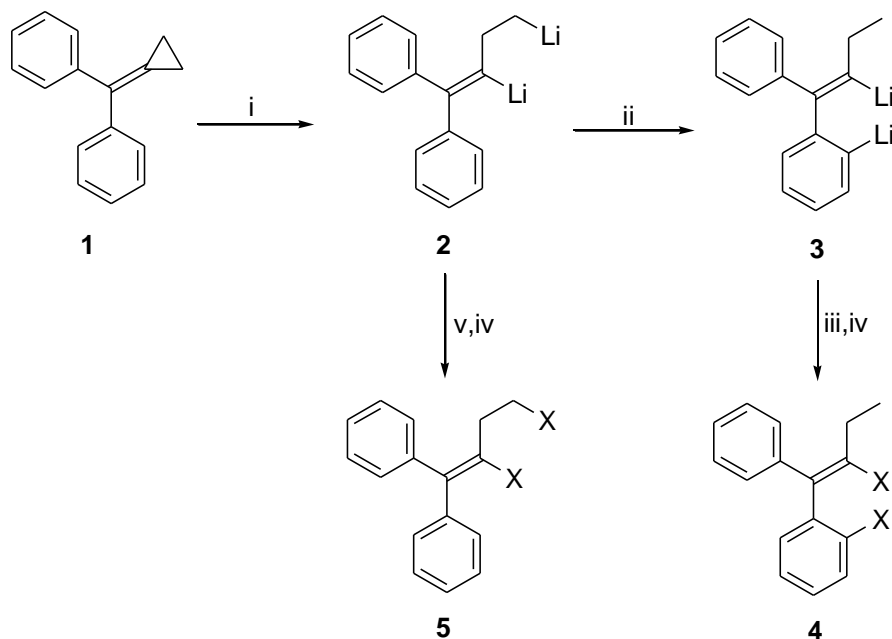
The reaction of cyclopropylidene diphenylmethane **1** with an excess of lithium and a catalytic amount of naphthalene (5 mol %) at -20 °C, followed by addition of an electrophile [E = H₂O, D₂O, *t*-BuCHO, Me₂CO, Et₂CO, *n*-Pr₂CO, *i*-Pr₂CO, (*c*-C₃H₅)₂CO, (CH₂)₅CO] at -78 °C and final hydrolysis with water at -78 °C 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 synthons 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 arene-catalyzed 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 al⁹ 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 sp²,sp³-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).

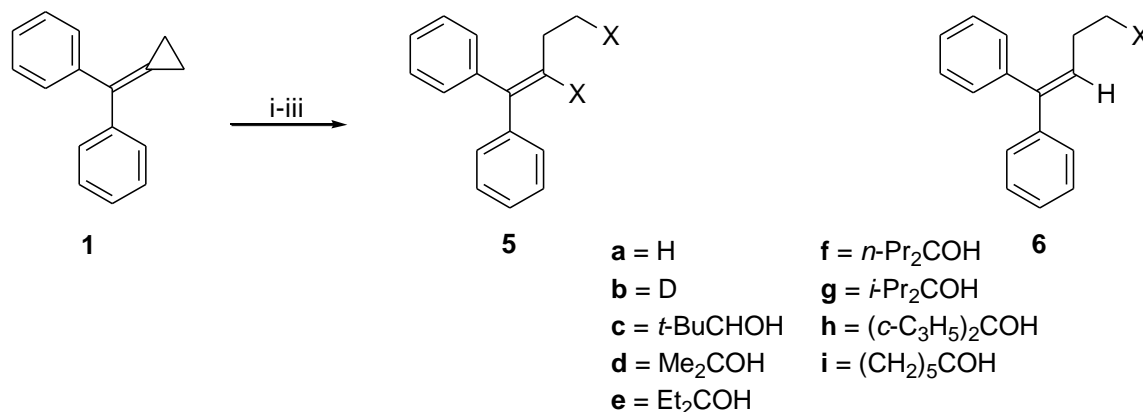


Scheme 1. Reagents and conditions: (i) Li, ether, -20 °C; (ii) rt; (iii) E = H₂O, D₂O, Me₂SO₄, RMeSiCl₂, CO₂; (iv) H₂O; (v) E = H₂O, Me₂SO₄.

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 = H₂O, D₂O, *t*-BuCHO, Me₂CO, Et₂CO, *n*-Pr₂CO, *i*-Pr₂CO, (*c*-C₃H₅)₂CO, (CH₂)₅CO] 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 dicyclopropyl

ketone), 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.¹⁴



Scheme 2. Reagents and conditions: (i) Li, C₁₀H₈ cat. (5 mol %), ether, -20 °C; (ii) E = H₂O, D₂O, *t*-BuCHO, Me₂CO, Et₂CO, *n*-Pr₂CO, *i*-Pr₂CO, (*c*-C₃H₅)₂CO, (CH₂)₅CO, -78 °C; (iii) H₂O, -78 to 20 °C.

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

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

^a All products **5** (and **6**) were >95% pure by 300 MHz ¹H 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 ¹H 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).

^f 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).

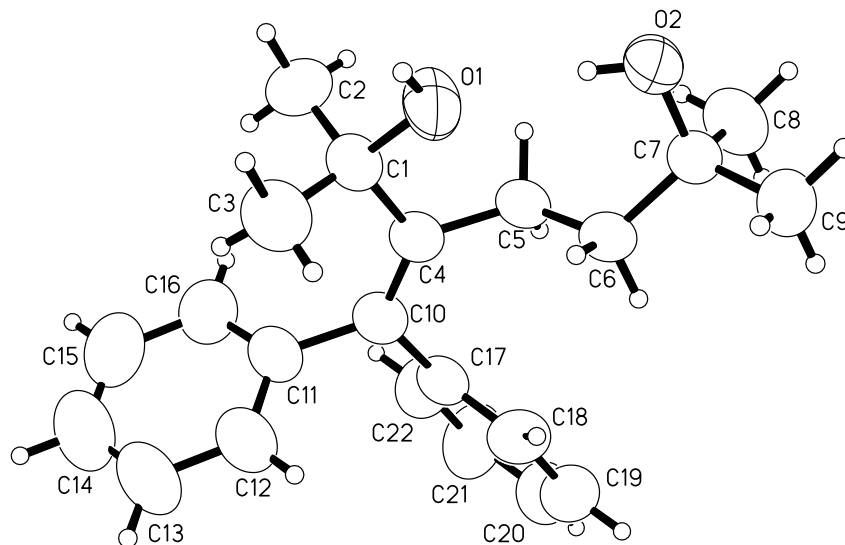


Figure 1. X-ray structure of compound **5d**.

Concerning the possible mechanism for the reaction shown in Scheme 2, after one electron transfer from the lithiating mixture⁴ 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).

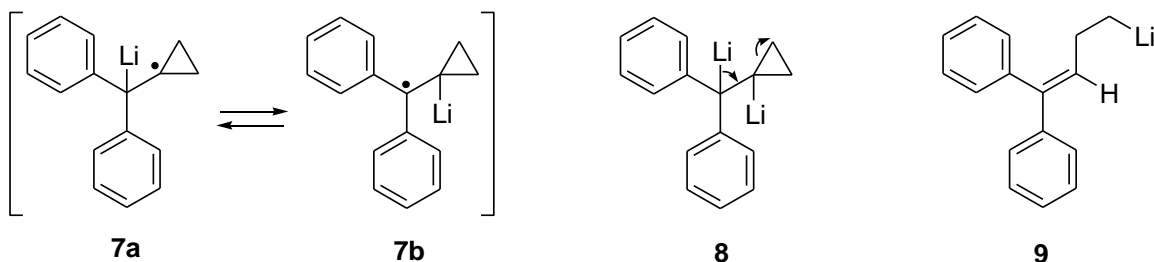
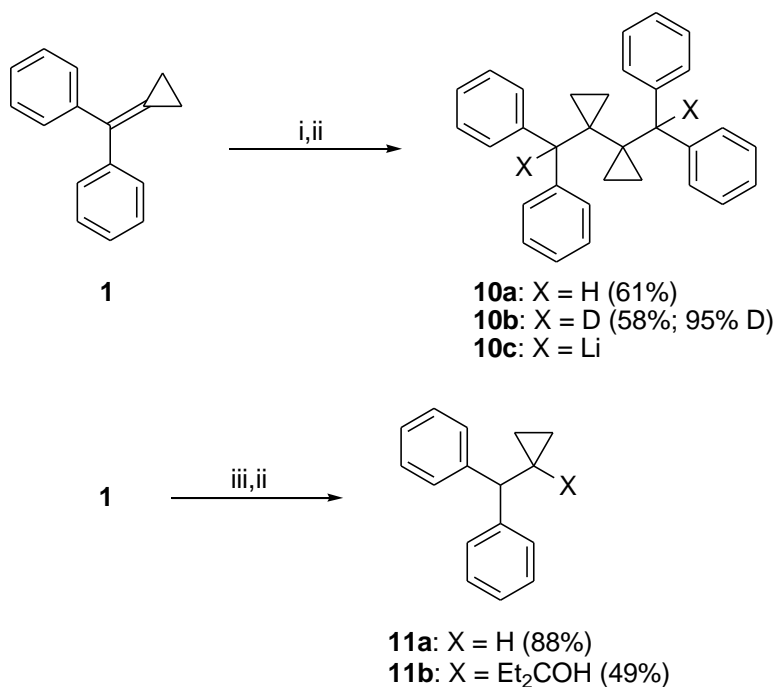


Chart 1. Intermediates 7-9.

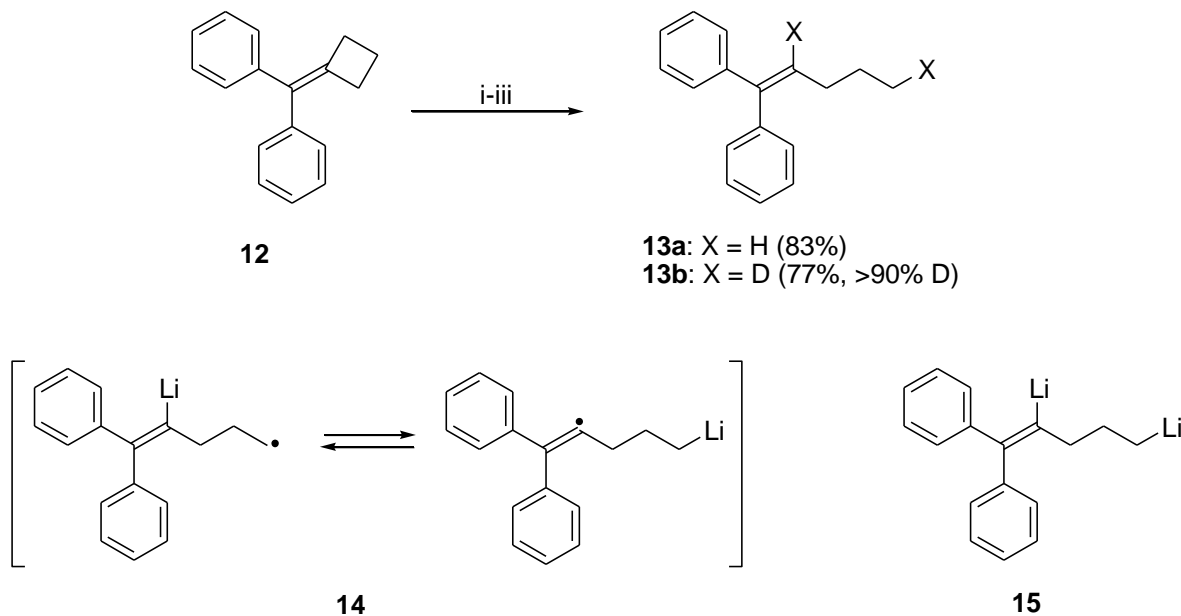
Some light to the proposed mechanism was brought in the 4,4'-di-*tert*-butylbiphenyl (DTBB)-catalyzed lithiation of the starting material **1** in THF at -78 °C for 1 h: after hydrolysis with water or deuterium oxide, the dimeric products **10a,b** were isolated, the saturated cyclopropyl derivative **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),¹⁵ 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**.



Scheme 3. Reagents and conditions: (i) Li, DTBB cat. (5 mol %), THF, -78 °C, 2 h; (ii) H₂O, -78 °C to rt, 1 h; (iii) Li, DTBB cat. (5 mol %), Electrophile [E = PhNH₂ (for **11a**), Et₂CO (for **11b**)], -78 to -50 °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**.^{12b,13} 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).¹⁶ 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 H₂O or D₂O 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. 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 (sp², sp³) 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 $\leq 0.005\%$, Fluka) and ether (99.8%, water content $\leq 0.005\%$, 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 CDCl_3 as solvent and TMS as internal standard; chemical shifts are given in parts per million and coupling constants (J) are given in hertz. ^{13}C 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, $T_{\text{injector}}=275\text{ }^\circ\text{C}$, $T_{\text{detector}}=300\text{ }^\circ\text{C}$, $T_{\text{column}}=60\text{ }^\circ\text{C}$ (3 min) and 60–270 $^\circ\text{C}$ (15 $^\circ\text{C}/\text{min}$), $P=40\text{ kPa}$; retention times (t_{R}) 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 $-20\text{ }^\circ\text{C}$ 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 $-78\text{ }^\circ\text{C}$ 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 \times 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(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; $t_{\text{R}} = 13.1\text{ min}$; R_{f} (hexane) = 0.53; ν (film) 3078, 3054 ($=\text{CH}$) cm^{-1} ; δ_{H} (300 MHz) 1.03 (3H, t, $J = 7.3$, CH_3), 2.12 (2H, dq, $J = 7.3$, CH_2), 6.07 (1H, t, $J = 7.3$, CH), 7.03-7.46 (10H, m, 10 \times 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; $t_{\text{R}} = 13.1\text{ min}$; R_{f} (hexane) = 0.53; ν (film) 3077, 3054 ($=\text{CH}$) cm^{-1} ; δ_{H} (300 MHz) 1.01 (2H, t, $J = 7.3$, CH_2D), 2.11 (2H, t, $J = 7.3$, $\text{CH}_2\text{CH}_2\text{D}$), 7.16-7.38 (10H, m, 10 \times ArH); δ_{C} (75 MHz) 14.2 (t, $J = 19$, CH_2D), 23.0 ($\text{CH}_2\text{CH}_2\text{D}$), 126.7, 126.8, 127.2, 128.0, 128.1, 129.9 (ArCH), 131.3 (t, $J = 23$, $\text{C}=\text{CD}$), 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. $C_{16}H_{14}D_2$ requires 210.1378.

4-Diphenylmethylen-2,2,8,8-tetramethyl-3,7-nonanediol (5c'). White solid, 29% yield; mp 114 °C (diethyl ether); t_R = 19.9 min; R_f (hexane/ethyl acetate 8/2) = 0.44; ν (KBr) 3354 (OH), 3077, 3056 (=CH) cm^{-1} ; δ_H (300 MHz) 0.76 (9H, s, 3 \times CH₃), 0.87 (9H, s, 3 \times CH₃), 0.91-1.26 (2H, m, CH₂CHOH), 1.60 (1H, br, OH), 2.37-2.49 (1H, m, CHHCH₂CH), 2.62-2.71 (1H, m, CHHCH₂CH), 2.92 (1H, br, OH), 3.32-3.37 (1H, m, CH₂CHOH), 4.49 (1H, s, C=CCHOH), 7.09-7.30 (10H, m, 10 \times ArH); δ_C (75 MHz) 23.2 (CH₂CH₂CH), 26.0, 27.0 (CH₃), 29.7 (CH₂CHOH), 34.4, 37.8 [C(CH₃)₃], 76.4, 79.9 (CHOH), 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^+ -2 \times H₂O, 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. $C_{26}H_{34}O$ requires 362.2610.

4-Diphenylmethylen-2,2,8,8-tetramethyl-3,7-nonanediol (5c''). Colourless crystals, 27% yield; mp 147 °C (diethyl ether); t_R = 19.9 min; R_f (hexane/ethyl acetate 8/2) = 0.15; ν (KBr) 3386 (OH), 3077, 3054 (=CH) cm^{-1} ; δ_H (300 MHz) 0.73 (9H, s, 3 \times CH₃), 0.87 (9H, s, 3 \times CH₃), 1.15-1.25 (1H, m, CHHCHOH), 1.34-1.42 (1H, m, CHHCHOH), 1.60 (2H, br, 2 \times OH), 2.35-2.46 (1H, m, CHHCH₂CH), 2.52-2.63 (1H, m, CHHCH₂CH), 3.00-3.06 (1H, m, CH₂CHOH), 4.49 (1H, s, C=CCHOH), 7.10-7.31 (10H, m, 10 \times ArH); δ_C (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 (CHOH), 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. $C_{26}H_{34}O$ requires 362.2610.

3-Diphenylmethylen-2,6-dimethyl-2,6-heptanediol (5d).¹⁸ Colourless crystals; mp 106 °C (diethyl ether); t_R = 17.8 min; R_f (hexane/ethyl acetate 6/4) = 0.16; ν (KBr) 3410 (OH), 3053 (=CH) cm^{-1} ; δ_H (400 MHz) 0.92 [6H, s, CH₂COH(CH₃)₂], 1.20 (1H, s, OH), 1.36 [6H, s, C=CCOH(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 \times ArH); δ_C (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. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.27; H, 8.65; HRMS: M^+ -H₂O, found 306.1981. $C_{22}H_{26}O$ requires 306.1984.

2-Methyl-6,6-diphenyl-5-hexen-2-ol (6d). Colourless oil, 20% yield; $t_R = 16.3$ min; R_f (hexane/ethyl acetate 6/4) = 0.53; ν (film) 3399 (OH), 3078, 3055 (=CH) cm^{-1} ; δ_H (400 MHz) 1.14 (6H, s, CH_3), 1.60-1.68 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 2.16-2.23 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 6.09 (1H, t, $J = 7.5$, C=CH), 7.17-7.36 (10H, m, $10 \times \text{ArH}$); δ_C (100 MHz) 24.9 ($\text{CH}_2\text{CH}_2\text{COH}$), 29.1 (CH_3), 43.7 ($\text{CH}_2\text{CH}_2\text{COH}$), 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), 202 (13), 193 (100), 192 (23), 191 (36), 190 (13), 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. $\text{C}_{19}\text{H}_{22}\text{O}$ requires 266.1671.

4-Diphenylmethylen-3,7-diethyl-3,7-nonanediol (5e). White solid; mp 72 °C (diethyl ether); $t_R = 20.7$ min; R_f (hexane/ethyl acetate 8/2) = 0.23; ν (KBr) 3437 (OH), 3076, 3052 (=CH) cm^{-1} ; δ_H (400 MHz) 0.59 (6H, t, $J = 7.4$, $2 \times \text{CH}_3$), 1.00 (6H, t, $J = 7.4$, $2 \times \text{CH}_3$), 0.97-1.25 (4H, m, $2 \times \text{CH}_2\text{CH}_3$), 1.39-1.50 (4H, m, $2 \times \text{CH}_2\text{CH}_3$), 1.64-1.78 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 2.03-2.10 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 7.10-7.31 (10, m, $10 \times \text{ArH}$); δ_C (100 MHz) 7.5, 8.5 (CH_3), 24.8, 30.3, 33.9, 37.2 (CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{COH}$, $\text{CH}_2\text{CH}_2\text{COH}$), 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=C); m/z 362 ($\text{M}^+ - \text{H}_2\text{O}$, 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: $\text{M}^+ - 2 \times \text{H}_2\text{O}$, found 344.2502. $\text{C}_{26}\text{H}_{32}$ requires 344.2504.

3-Ethyl-7,7-diphenyl-6-hepten-3-ol (6e). Colourless oil, 30% yield; $t_R = 18.0$ min; R_f (hexane/ethyl acetate 8/2) = 0.44; ν (film) 3404 (OH), 3079, 3054 (=CH); δ_H (400 MHz) 0.78 (6H, t, $J = 7.5$, $2 \times \text{CH}_3$), 0.94 (1H, s, OH), 1.37 (4H, q, $J = 7.5$, $2 \times \text{CH}_2\text{CH}_3$), 1.51-1.63 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 2.03-2.16 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 6.10 (1H, t, $J = 7.5$, C=CH), 7.16-7.39 (10H, m, $10 \times \text{ArH}$); δ_C (100 MHz) 7.6 (CH_3), 24.0 ($\text{CH}_2\text{CH}_2\text{COH}$), 30.8 (CH_2CH_3), 38.1 ($\text{CH}_2\text{CH}_2\text{COH}$), 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 ($\text{M}^+ - \text{H}_2\text{O}$, 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. $\text{C}_{21}\text{H}_{26}\text{O}$ requires 294.1984.

5-Diphenylmethylen-4,8-dipropyl-4,8-undecanediol (5f). Colourless oil; $t_R = 22.9$ min; R_f (hexane/ethyl acetate 8/2) = 0.09; ν (film) 3416 (OH), 3076, 3053 (=CH) cm^{-1} ; δ_H (400 MHz) 0.73-1.67 (32H, m, $4 \times \text{CH}_2\text{CH}_2\text{CH}_3$, $4 \times \text{CH}_2\text{CH}_2\text{CH}_3$, $4 \times \text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}_2\text{COH}$, $2 \times \text{OH}$), 2.02-2.09 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 7.10-7.35 (10H, m, $10 \times \text{ArH}$); δ_C (100 MHz) 14.4, 14.7 (CH_3), 16.4, 17.3 (CH_2CH_3), 25.1 ($\text{CH}_2\text{CH}_2\text{COH}$), 38.2, 41.0, 44.2 ($\text{CH}_2\text{CH}_2\text{COH}$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 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=C); m/z 400 ($\text{M}^+ - 2 \times \text{H}_2\text{O}$, 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: $M^+ - H_2O$, found 418.3254. $C_{30}H_{42}O$ 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; ν (film) 3412 (OH), 3055 (=CH) cm^{-1} ; δ_H (400 MHz) 0.81-0.90 (6H, m, $2 \times CH_3$), 1.14-1.41 (9H, m, $2 \times CH_2CH_2CH_3$, $2 \times CH_2CH_2CH_3$, OH), 1.49-1.68 (2H, m, CH_2CH_2COH), 2.03-2.15 (2H, m, CH_2CH_2COH), 6.10 (1H, t, $J = 7.5$, C=CH), 7.15-7.40 (10H, m, $10 \times ArH$); δ_C (100 MHz) 14.6 (CH_3), 15.1 ($CH_2CH_2CH_3$), 24.1 (CH_2CH_2COH), 39.0, 41.4 (CH_2CH_2COH , $CH_2CH_2CH_3$), 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 ($M^+ - H_2O$, 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: $M^+ - H_2O$, found 304.2164. $C_{23}H_{28}$ requires 304.2191.

4-Diphenylmethylene-3,7-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; δ_H (400 MHz) 0.69, 0.71 (12H, 2d, $J = 6.9$, $4 \times CH_3$), 0.82, 0.86 (12H, 2d, $J = 6.9$, $4 \times CH_3$), 1.01, 1.11 (12H, 2d, $J = 6.9$, $4 \times CH_3$), 1.34-1.64 (4H, 2m, $2 \times CH_2$), 1.68, 1.80 (4H, 2h, $J = 6.9$, $4 \times CH$), 2.02-2.27 (6H, 2m, $2 \times CH_2$, $2 \times CH$), 6.08 (1H, t, $J = 7.5$, C=CH), 7.09-7.46 (20H, m, $20 \times ArH$); δ_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, 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 ($M^+ - 2 \times H_2O$, 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**): $M^+ - 2 \times H_2O$, found 400.3041. $C_{30}H_{40}$ requires 400.3130; m/z (**6g**) 304 ($M^+ - H_2O$, 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**): $M^+ - H_2O$, found 304.2180. $C_{23}H_{28}$ requires 304.2191.

1,1,5,5-Tetracyclopropyl-2-diphenylmethylene-1,5-pentanediol (5h). Colourless oil; $t_R = 29.1$ min; R_f (hexane/ethyl acetate 8/2) = 0.28; ν (film) 3586, 3488 (OH), 3080 (=CH) cm^{-1} ; δ_H (400 MHz) 0.46-1.06 (19H, m, $8 \times ring CH_2$, $2 \times ring CH$, OH), 1.55-1.73 (3H, m, $2 \times ring CH$, OH), 2.16-2.23 (2H, m, CH_2CH_2COH), 2.89-2.96 (2H, m, CH_2CH_2COH), 7.56-7.77 (10H, m, $10 \times ArH$); δ_C (100 MHz) -1.0, 0.2, 0.5, 2.4 (ring CH_2), 17.9, 19.9 (ring CH), 25.5 (CH_2CH_2COH), 42.4 (CH_2CH_2COH), 70.5, 75.4 (C=CCOH, CH_2COH), 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 ($M^+ - H_2O$, 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: $M^+ - 2 \times H_2O$, found 392.2520. $C_{30}H_{32}$ requires 392.2504.

1-[3-(1-Hydroxycyclohexyl)-4,4-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; ν (film) 3384 (OH), 3054 (=CH) cm^{-1} ; δ_H (300 MHz) 0.87-2.16 (26H, m, 10×ring CH_2 , $\text{CH}_2\text{CH}_2\text{COH}$, $\text{CH}_2\text{CH}_2\text{COH}$, 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 , $\text{CH}_2\text{CH}_2\text{COH}$), 37.0, 37.3 (ring CH_2), 42.0 ($\text{CH}_2\text{CH}_2\text{COH}$), 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 ($\text{M}^+ - \text{H}_2\text{O}$, 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 (58), 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: $\text{M}^+ - 2 \times \text{H}_2\text{O}$, found 368.2536. $\text{C}_{28}\text{H}_{32}$ 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 , $\text{CH}_2\text{CH}_2\text{COH}$, OH), 2.15-2.24 (2H, m, $\text{CH}_2\text{CH}_2\text{COH}$), 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 , $\text{CH}_2\text{CH}_2\text{COH}$), 37.3 (ring CH_2), 42.3 ($\text{CH}_2\text{CH}_2\text{COH}$), 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 ($\text{M}^+ - \text{H}_2\text{O}$, 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. $\text{C}_{22}\text{H}_{26}\text{O}$ 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 °C 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 °C (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 CH₂), 0.14-0.18 (4H, m, 2×ring CH₂), 4.70 (2H, s, 2×CH), 7.12-7.27 (20H, 20×ArH); δ_C (100 MHz) 6.3 (CH₂), 23.9 [C(CH₂)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); $t_R = 31.5$ min; R_f (hexane) = 0.29; ν (KBr) 3080, 3056 (=CH) cm^{-1} ; δ_H (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); δ_C (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).¹⁹ Colourless liquid; $t_R = 13.4$ min; R_f (hexane) = 0.35; ν (film) 3059 (=CH) cm^{-1} ; δ_H (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); δ_C (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; $t_R = 17.4$ min; R_f (hexane/ethyl acetate 8/2) = 0.30; ν (film) 3587 (OH), 3084, 3058 (=CH) cm^{-1} ; δ_H (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); δ_C (75 MHz) 4.7 (ring CH₂), 8.3 (CH₃), 27.6 [C(CH₂)₂], 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), 79 (10), 78 (10), 77 (20), 67 (11), 55 (11), 51 (11); HRMS: M⁺-H₂O, found 276.1906. C₂₁H₂₄ requires 276.1878.

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).²⁰ Colourless oil; *t*_R = 13.9 min; *v* (film) 3051 (=CH) cm⁻¹; δ_{H} (300 MHz) 0.90 (3H, t, *J* = 7.4, CH₃), 1.40-1.52 (2H, m, CH₂CH₃), 2.02-2.13 (2H, m, CHCH₂), 6.09 (1H, t, *J* = 7.5, CH), 7.13-7.43 (10H, m, 10×ArH); δ_{C} (75 MHz) 13.8 (CH₃), 23.1 (CH₂CH₃), 31.8 (CHCH₂), 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)²⁰ and 2-deutero-1-(2-deuterophenyl)-1-phenyl-1-pentene (13b').²⁰ Colourless oil; *t*_R = 13.9 min; *v* (film) 3055 (=CH); δ_{H} (400 MHz) 0.97-1.06 (5H, m, CH₃, CH₂D), 1.53-1.66 (4H, m, CH₂CH₃, CH₂CH₂D), 2.22 (4H, t, *J* = 7.3, CDCH₂), 7.26-7.53 (20H, m, 20×ArH); δ_{C} (100 MHz) 13.5 (t, *J* = 19.8, CH₂D), 13.8 (CH₃), 23.0, 23.1 (CH₂CH₃, CH₂CH₂D), 31.7 (CH₂D), 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).

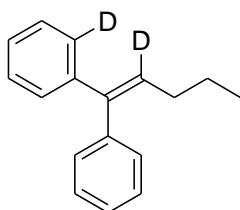
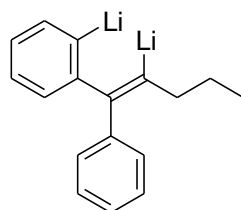
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