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Allylic lithiation of methylenecyclobutanes

Min Jiang, Min Shi *

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

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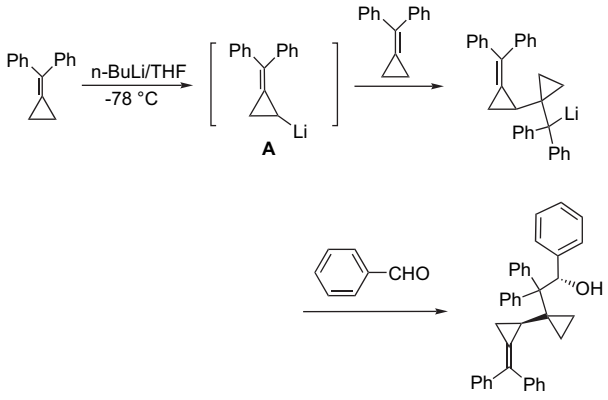
ABSTRACT

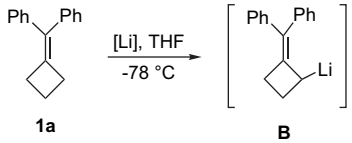
Methylenecyclobutanes undergo a lithiation reaction in the presence of *n*-BuLi or *n*-BuLi/KO^{t}Bu from −78 °C to room temperature or to 40 °C in THF within 3 h and then quenching with a variety of electrophiles to give the corresponding addition products (alcohols) in moderate to good yields within 2 h. The alcohols can be easily oxidized to the ketones, which can be transformed to the substituted cyclopentenes in the presence of $AlCl_3$ within short reaction time.

1. Introduction

The use of organolithium reagents in organic synthesis is of considerable interest in both academic society and chemical industry.[1,2] Lithiations using organolithium reagents such as butyllithium (*n*-BuLi) are very important in many organic reactions. As an interesting example, previously, we reported a novel lithiation of *gem*-aryl disubstituted methylenecyclopropanes (MCPs), a kind of highly strained but readily accessible alkenes, with *n*-BuLi in tetrahydrofuran (THF) to give the corresponding cascade addition products in good yields by quenching with various electrophiles from lithiated intermediate **A** (an example is shown in Scheme 1).[3] During our ongoing investigation on the reactivities of highly strained small rings, we realized that *gem*-aryl disubstituted methylenecyclobutanes (MCBs) have significantly different reactivities from those of MCPs even under identical conditions.[4] Therefore, we envisaged that the lithiation of methylenecyclobutanes (MCBs) by treatment with organolithium reagent at low temperature and quenching with electrophile may give different reaction outcome from the lithiated intermediate **B** (using MCB **1a** as an example) (Scheme 2). Herein, we wish to report the lithiation of MCBs by treatment with organolithium reagent and subsequent quenching with various electrophiles, affording the corresponding addition products in moderate to good yields.



Scheme 1. Lithiation of MCP with *n*-BuLi and the subsequent quenching with aldehyde.



Scheme 2. Lithiation of **1a** with organolithium reagent.

2. Results and discussion

At first, we utilized diphenylmethylenecyclobutane **1a** (MCB **1a**) as the substrate for the lithiation with butyllithuim and

* Corresponding author.
E-mail address: mshi@mail.sioc.ac.cn (M. Shi).

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p-BrC_6H_4CHO as an electrophile to develop the optimal conditions. Upon treatment of **1a** (0.3 mmol) with *n*-BuLi (0.36 mmol, 1.2 equiv) in THF at −78 °C for 3 h, *p*-BrC_6H_4CHO **2a** (0.45 mmol, 1.5 equiv) was then added into the reaction system and the resulting mixture was stirred for 2 h at the same temperature, but it was found that none of the addition product was produced. Increasing the employed amount of *n*-BuLi to 0.45 mmol (1.5 equiv) and using lithium diisopropylamide (LDA) or methyllithium (MeLi) as the lithiation reagent did not change the reaction outcomes. After several examinations, delightfully, we found that when the temperature naturally rise to room temperature (20 °C) from −78 °C after adding *n*-BuLi, the subsequent quenching by **2a** (0.45 mmol, 1.5 equiv) in a one-pot manner, providing the addition product **3a** in overall 56% yield (82% conversion) as a pair of diastereoisomers (*syn*-**3a** and *anti*-**3a**) (Table 1, entry 1).

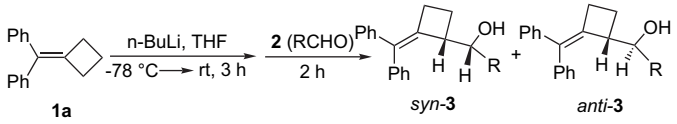
Under above reaction conditions, we next carried out this lithiation reaction of **1a** with *n*-BuLi and subsequent quenching by a variety of arylaldehydes **2** and the results of these experiments are summarized in Table 1. We found that the corresponding addition products **3** were obtained in moderate yields whether electron-rich, electron-neutral, and electron-poor aromatic aldehydes were employed (Table 1, entries 2–7). Moreover, the diastereomeric pairs of *syn*-**3a** and *anti*-**3a**, *syn*-**3c** and *anti*-**3c**, *syn*-**3d** and *anti*-**3d**, *syn*-**3e** and *anti*-**3e**, *syn*-**3f** and *anti*-**3f** could be separated by silica gel column chromatography and others were isolated as diastereomeric mixtures and their ratios were determined by ^1H NMR spectroscopic data.

To extend the scope and limitations of this lithiation reaction, we next examined the reaction of lithiated MCB **1a** by *n*-BuLi with other electrophiles such as methyl vinyl ketone **4a**, *N*-sulfonated imine **4b**, and phenylepoxide **4c** under the standard conditions and the results are summarized in Table 2. As can be seen from Table 2, the corresponding adducts **5** were also obtained as diastereoisomeric mixtures (Table 2, entries 1–3). Moreover, using **4a** as the electrophile, 1,2-addition product **5a** was exclusively obtained and using phenylepoxide **4c** as the electrophile, a pair of regioisomers **5c** and **5c′** was formed (Table 2, entries 1 and 3).

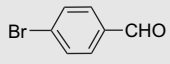
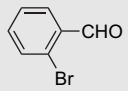
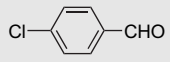
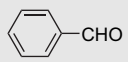
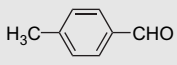
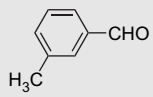
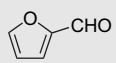
We next carried out this reaction using other diarylmethylenecyclobutanes **1b** and **1c** bearing either electron-donating or electron-withdrawing substituents on the benzene rings as the substrates, respectively, to examine the generality of this reaction. The results are outlined in Table 3. We found that the corresponding adducts **3h**–**3k** were formed as a pair of diastereoisomers in moderate yields under the similar conditions (Table 3, entries 1–4). It should be noted that in the case of MCB **1b**, the reaction temperature should be raised to 40 °C from −78 °C for 3 h during the lithiation with *n*-BuLi before adding aldehyde **2a** or **2c**, affording the corresponding adduct **3h** or **3i** in moderate yield as a pair of diastereoisomers (Table 1, entries 1 and 2).

To determine the relative configuration, we employed 3, 5-dinitrobenzoic acid to condense with the two separated

Table 1
The reaction of MCB **1a** with aldehydes in the presence of *n*-BuLi

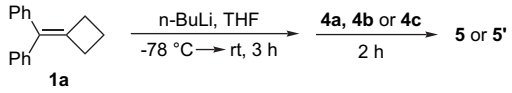


1a *syn*-**3** *anti*-**3**

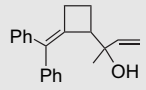
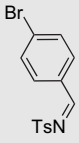
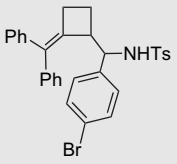
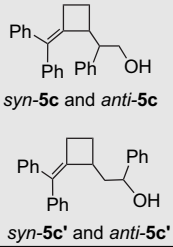
Entry[a]	**2** (RCHO)	Conv (%)	Yield[b] (%), **3**
1	 **2a**	82	56, *syn*-**3a**:*anti*-**3a**=1:1
2	 **2b**	84	54, *syn*-**3b**:*anti*-**3b**=1:1
3	 **2c**	79	55, *syn*-**3c**:*anti*-**3c**=1:1
4	 **2d**	76	51, *syn*-**3d**:*anti*-**3d**=1:1
5	 **2e**	80	58, *syn*-**3e**:*anti*-**3e**=1:1
6	 **2f**	85	41, *syn*-**3f**:*anti*-**3f**=1:1
7	 **2g**	71	54, *syn*-**3g**:*anti*-**3g**=1:1

[a] Reaction conditions: **1a** (0.3 mmol), *n*-BuLi (0.45 mmol), and **2** (0.45 mmol) in THF (2.0 mL) were utilized. The reactions were carried out from −78 °C to room temperature with **1a** and *n*-BuLi. After 3 h, aldehyde **2** was added into the reaction system.
[b] Overall isolated yields.

Table 2
The reaction of MCB **1a** with **4a**, **4b**, or **4c** in the presence of *n*-BuLi

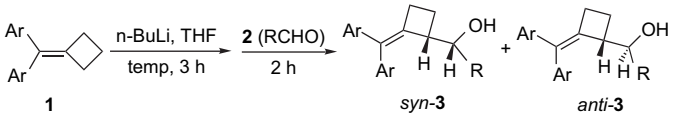


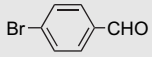
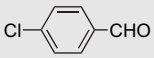
1a

Entry[a]	**4**	Structure of **5** or **5′**	Conv (%)	Yield[b] (%), **5**
1	 **4a**	 *syn*-**5a** and *anti*-**5a**	41	20, *syn*-**5a**:*anti*-**5a**=1:1
2	 **4b**	 *syn*-**5b** and *anti*-**5b**	72	51, *syn*-**5b**:*anti*-**5b**=1:1
3	 **4c**	 *syn*-**5c** and *anti*-**5c** *syn*-**5c'** and *anti*-**5c'**	70	58, **5c**:**5c′**=1:4[c]

[a] Reaction conditions: **1a** (0.3 mmol), *n*-BuLi (0.45 mmol), and **4** (0.45 mmol) in THF (2.0 mL) were utilized. The reactions were carried out from −78 °C to room temperature with **1a** and *n*-BuLi. After 3 h, aldehyde **2** was added into the reaction system.
[b] Overall isolated yields.
[c] The ratio of regioisomers.

Table 3
The reaction of MCB **1** with aldehydes in the presence of *n*-BuLi



Entry[a]	Ar	2 (RCHO)	Temp (°C)	Conv (%)	Yield[b] (%), 3
1	**1b** (*p*-MeC_6H_4)	 **2a**	−78→40	77	34, *syn*-**3h**: *anti*-**3h**=1:1
2	**1b**	 **2c**	−78→40	45	26, *syn*-**3i**: *anti*-**3i**=1:1
3	**1c** (*p*-ClC_6H_4)	**2a**	−78→rt	46	37, *syn*-**3j**: *anti*-**3j**=1:1
4	**1c**	**2c**	−78→rt	27	21, *syn*-**3k**: *anti*-**3k**=1:2

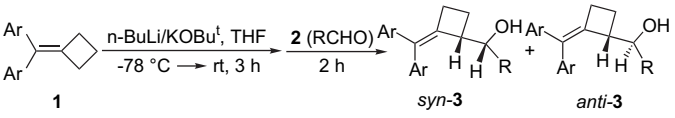
[a] Reaction conditions: **1** (0.3 mmol), *n*-BuLi (0.45 mmol), and **2** (0.45 mmol) in THF (2.0 mL) were utilized. The reactions were carried out from −78 °C to room temperature with **1** and *n*-BuLi. After 3 h, aldehyde **2** was added into the reaction system.
[b] Overall isolated yields.

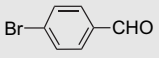
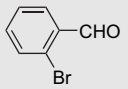
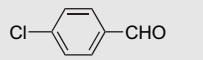
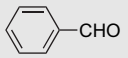
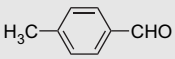
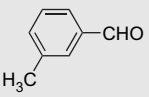
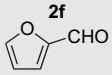
diastereoisomers **3a** (*syn*-**3a** and *anti*-**3a**) in the presence of *N*, *N*′-dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) in dichloromethane at 0 °C, respectively, to give the corresponding esters **6** (*syn*-**6** and *anti*-**6**) in good yields (Scheme 3). We found that the coupling constant of H_{ab} changed from 4.2 Hz to 6.0 Hz and from 7.2 Hz to 9.6 Hz, respectively, in two diastereoisomers of **3a**. On the basis of Kurplus formula,[5] it can be determined that **3a** in which J_{Hab}=4.2 Hz (J_{Hab}=6.0 Hz in **6**) is *syn*-configuration and **3a** in which J_{Hab}=7.2 Hz (J_{Hab}=9.6 Hz in **6**) is *anti*-configuration. At the same time, the relative configuration of other diastereoisomers can be also determined accordingly.

Since the yields of these products are not very good, we attempted to utilize a much stronger base of *n*-BuLi/KO^{t}Bu (1.5 equiv/1.5 equiv)[6] to replace *n*-BuLi in this lithiation reaction. The results are summarized in Table 4. As can be seen, we found that using arylaldehydes as the electrophiles, the achieved yields of the corresponding adducts **3** could be improved to 63–81% under the standard conditions for a variety of MCBs **1** (Table 4, entries 1–11).

The lithiation products **3** can be easily oxidized to the corresponding ketones **7a**–**7d**, respectively, with pyridinium chlorochromate (PCC) in dichloromethane at room temperature in moderate yields (Table 5, entries 1–4). The ketones **7** can be transformed to the corresponding cyclopentenes **8** in the presence of $AlCl_3$ at 50 °C in 1,2-dichloroethane (DCE) within short reaction time.[4a] The conversions of **7** and the yields of **8** were determined

Table 4
The reaction of MCBs **1** with aldehydes in the presence of *n*-BuLi and KO^{t}Bu

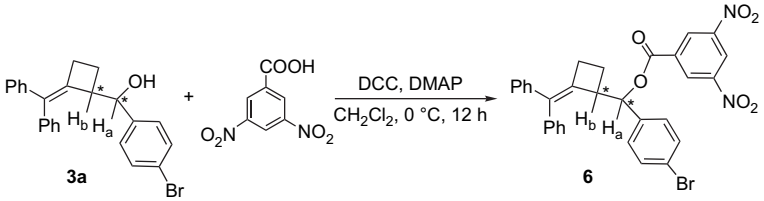


Entry[a]	1 (Ar)	2 (RCHO)	Yield[b] (%), 3
1	**1a** (C_6H_5)	 **2a**	72, *syn*-**3a**:*anti*-**3a**=1:1
2	**1a** (C_6H_5)	 **2b**	76, *syn*-**3b**:*anti*-**3b**=1:1
3	**1a** (C_6H_5)	 **2c**	71, *syn*-**3c**:*anti*-**3c**=1:1
4	**1a** (C_6H_5)	 **2d**	71, *syn*-**3d**:*anti*-**3d**=1:1
5	**1a** (C_6H_5)	 **2e**	76, *syn*-**3e**:*anti*-**3e**=1:2
6	**1a** (C_6H_5)	 **2f**	74, *syn*-**3f**:*anti*-**3f**=1:1
7	**1a** (C_6H_5)	 **2g**	77, *syn*-**3g**:*anti*-**3g**=1:1
8	**1b** (*p*-MeC_6H_4)	**2a**	79, *syn*-**3g**:*anti*-**3g**=1:1
9	**1b** (*p*-MeC_6H_4)	**2c**	81, *syn*-**3g**:*anti*-**3g**=1:1
10	**1c** (*p*-ClC_6H_4)	**2a**	65, *syn*-**3g**:*anti*-**3g**=1:1
11	**1c** (*p*-ClC_6H_4)	**2c**	63, *syn*-**3g**:*anti*-**3g**=1:2

[a] Reaction conditions: **1** (0.3 mmol), *n*-BuLi (0.45 mmol), KO^{t}Bu (0.45 mmol), and **2** (0.45 mmol) in THF (2.0 mL) were utilized. The reactions were carried out from −78 °C to room temperature with **1** and *n*-BuLi. After 3 h, aldehyde **2** was added into the reaction system.
[b] Overall isolated yields.

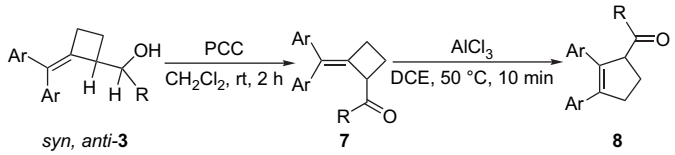
on the basis of ^{1}H NMR spectroscopic data (see Supplementary data).

To understand the role of cyclobutane in MCBs **1** in this reaction, two control experiments were carried out under the similar conditions. Using olefinic compound **9** as the substrate afforded the corresponding lithiation product **10** in 71% yield under the standard conditions (Scheme 4). However, using diphenylmethylenecyclopentane **11** as the substrate produced the



Scheme 3. Determination of the relative configuration.

Table 5
The transformation of products **3** to the substituted cyclopentenes **8**



syn, anti-**3** **7** **8**

Entry[a]	**3** (Ar/R)	Yield[a,b] (%), **7**	Yield[c] (%)/conv[d] (%), **8**
1	**3a** (C_6H_5/*p*-BrC_6H_4)	**7a**, 63	**8a**, 52 (65)
2	**3c** (C_6H_5/*p*-ClC_6H_4)	**7b**, 73	**8b**, 47 (67)
3	**3d** (C_6H_5/*p*-C_6H_5)	**7c**, 79	**8c**, 32 (68)
4	**3j** (*p*-$CH_3C_6H_4$/*p*-BrC_6H_4)	**7d**, 78	**8d**, 42 (53)

[a] Reaction conditions: **3** (0.2 mmol), PCC (0.4 mmol) in CH_2Cl_2 (2.0 mL) and the reactions were carried out at room temperature.
[b] Isolated yields.
[c] Reaction conditions: **7** (0.1 mmol), $AlCl_3$ (0.15 mmol) in DCE (2.0 mL) and the reactions were carried out at 50 °C for 10 min. Overall isolated yields.
[d] Conversion.

corresponding lithiation product **12** in 21% yield as a pair of diastereoisomers under the same conditions, suggesting that the cycloalkyl groups in methylenecycloalkanes have significant effect toward such lithiation in the presence of butyllithium reagent (Scheme 4).

3. Conclusion

In summary, we have disclosed a lithiation reaction of MCBs **1** with *n*-BuLi or *n*-BuLi/KO^{t}Bu at −78 °C to room temperature or to 40 °C and quenching with a variety of electrophiles in THF to give the corresponding adducts in moderate to good yields. The products **3** can be easily oxidized to the corresponding ketones **7** in moderate yields, which can be transformed to the corresponding substituted cyclopentene derivatives in moderate yields. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

4. Experimental procedures

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in hertz. Mass spectra were recorded by EI methods, and HRMS were measured on a Finnigan MA$^+$ mass spectrometer. The employed solvents were dry up by the standard procedures. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.2. General procedure for lithiation reaction

*4.2.1. Preparation of the product **3** or **5***

Under an argon atmosphere, to the solution of MCB **1** (0.30 mmol), KO^{t}Bu (0.45 mmol) in THF (2.0 mL) was added *n*-BuLi (0.45 mmol), the resulting reaction mixture was stirred from −78 °C to room temperature slowly. After 3 h, aldehyde (0.45 mmol) was added into the reaction system and the reaction solution was further stirred for 2 h at room temperature. The reaction mixture was quenched by the addition of saturated NH_4Cl aqueous solution. The reaction solution was diluted with EtOAc (20 mL) and washed with water, saturated $NaHCO_3$ aqueous solution, brine and water. The organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (petroleum ether/ethyl acetate=15:1) to give the addition product **3** or **5**.

*4.2.2. The preparation of product **7***

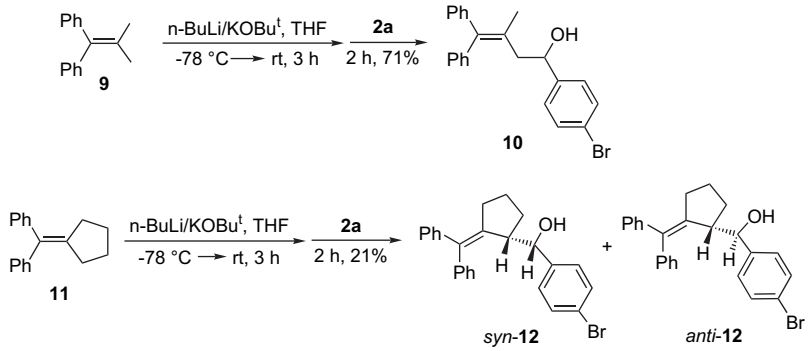
To a solution of compound **3** (0.12 mmol) in dichloromethane (2.0 mL) was added PCC (0.25 mmol). The mixture was stirred for 1 h at room temperature (monitored by TLC plates) and then filtered, the filtrate was concentrated under reduced pressure and the residue was subjected to flash column chromatography to give the product **7** as a colorless oil.

*4.2.3. The preparation of product **8***

A dried reaction tube equipped with a magnetic stirring bar was charged with $AlCl_3$ (0.15 mmol) and 1.0 mL of dry DCE and then heated to 50 °C. After 2 min, compound **7** (0.1 mmol) was added into the reaction system quickly. The resulting brown solution was stirred at 50 °C for 10 min. Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the product **8** along with the starting materials **7**.

*4.2.4. 4-Bromophenyl-2-(diphenylmethylene)cyclobutylmethanol (syn-**3a**)*

A colorless oil; IR (CH_2Cl_2): ν 3448, 3079, 3053, 3025, 2949, 1594, 1448, 1442, 1401, 1071, 1009, 968, 837, 768, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.84–1.98 (2H, m, CH_2, OH), 2.04–2.13 (1H, m, CH_2), 2.66–2.76 (1H, m, CH_2), 3.00–3.10 (1H, m, CH_2), 3.63–3.71 (1H, m, CH_2), 4.39 (1H, d, *J*=4.2 Hz, CH), 7.00 (2H, d, *J*=8.4 Hz, ArH), 7.15–7.41 (12H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.7, 30.5, 50.7, 71.7, 120.8, 126.7, 126.9, 127.4, 128.1, 128.3, 128.4, 129.2, 131.0, 135.9, 139.8, 140.1, 140.2, 141.1; MS (EI) *m*/*z* (%): 404 (0.64) [M$^+$], 220 (36.45), 205 (14.54), 191 (15.59), 165 (17.90), 141 (11.64), 91 (100.00), 77 (24.48); HRMS (EI) Calcd for $C_{24}H_{21}OBr$ (M$^+$) requires: 404.0776, Found: 404.0765.



Scheme 4. Lithiation of **9** and **11** with *n*-BuLi in the presence of KO^{t}Bu.

*4.2.5. 4-Bromophenyl-2-(diphenylmethylene)cyclobutylmethanol (anti-**3a**)*

A white solid, mp 82–84 °C; IR (CH_2Cl_2): ν 3412, 3079, 3053, 2920, 1949, 1597, 1513, 1442, 1265, 1179, 1031, 820, 769, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.62 (1H, br s, OH), 1.68–1.75 (1H, m, CH_2), 2.00–2.13 (1H, m, CH_2), 2.47–2.58 (1H, m, CH_2), 2.67–2.80 (1H, m, CH_2), 3.70–3.78 (1H, m, CH_2), 4.64 (1H, d, J=7.2 Hz, CH), 7.04 (2H, d, J=8.4 Hz, ArH), 7.13–7.31 (12H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.0, 30.7, 50.1, 74.7, 121.3, 126.7, 127.3, 128.0, 128.4, 128.5, 128.8, 129.4, 131.0, 135.9, 139.9, 140.2, 140.3, 140.6; MS (EI) m/z (%): 404 (8.84) [M^+], 388 (81.90), 220 (100.00), 204 (46.63), 191 (44.14), 167 (34.21), 91 (63.36), 77 (8.97); HRMS (EI) Calcd for $C_{24}H_{21}OBr$ (M^+) requires: 404.0776, Found: 404.0747.

*4.2.6. 2-Bromophenyl-2-(diphenylmethylene)cyclobutylmethanol (syn-**3b** and anti-**3b**)*

A colorless oil; IR (CH_2Cl_2): ν 3567, 3445, 3055, 2949, 1720, 1597, 1493, 1442, 1124, 1025, 971, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): *syn*-**3b**: δ 1.70–1.82 (0.5H, m, CH_2), 1.96–2.25 (1H, m, CH_2, OH), 2.67–2.78 (0.5H, m, CH_2), 3.08–3.20 (0.5H, m, CH_2), 3.79–3.89 (0.5H, m, CH_2), 4.79 (0.5H, d, J=3.6 Hz, CH), 6.99–7.06 (0.5H, m, Ar), 7.15–7.49 (6.5H, m, ArH); *anti*-**3b**: δ 1.70–1.82 (0.5H, m, CH_2), 1.96–2.25 (1H, m, CH_2, OH), 2.67–2.78 (0.5H, m, CH_2), 3.28–3.37 (0.5H, m, CH_2), 3.79–3.89 (0.5H, m, CH_2), 5.29 (0.5H, d, J=9.9 Hz, CH), 6.99–7.06 (0.5H, m, Ar), 7.15–7.49 (6.5H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 16.9, 20.4, 30.4, 31.4, 48.2, 50.3, 70.4, 75.7, 121.3, 123.3, 126.5, 126.7, 126.9, 127.1, 127.2, 127.5, 127.8, 127.9, 128.0, 128.3, 128.5, 128.6, 128.7, 128.9, 129.3, 129.8, 132.3, 132.5, 135.5, 135.8, 140.0, 140.1, 140.3, 140.4, 140.8, 141.0; MS (EI) m/z (%): 404 (5.80) [M^+], 388 (37.48), 220 (100.00), 204 (67.68), 191 (57.23), 165 (28.21), 91 (80.77); HRMS (EI) Calcd for $C_{24}H_{21}OBr$ (M^+) requires: 404.0776, Found: 404.0824.

*4.2.7. 4-Chlorophenyl-2-(diphenylmethylene)cyclobutylmethanol (syn-**3c**)*

A colorless oil; IR (CH_2Cl_2): ν 3568, 3448, 3054, 2949, 1597, 1442, 1407, 1090, 1029, 1013, 969, 839, 769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.88–1.98 (2H, m, CH_2, OH), 2.05–2.14 (1H, m, CH_2), 2.66–2.76 (1H, m, CH_2), 3.00–3.09 (1H, m, CH_2), 3.64–3.70 (1H, m, CH_2), 4.41 (1H, d, J=3.9 Hz, CH), 7.05 (2H, d, J=8.7 Hz, Ar), 7.16–7.36 (12H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.7, 30.5, 50.8, 71.7, 126.6, 127.0, 127.1, 128.0, 128.1, 128.3, 128.4, 129.2, 132.6, 135.9, 139.9, 140.2, 140.6; MS (EI) m/z (%): 360 (5.91) [M^+], 342 (100.00), 220 (50.31), 191 (26.91), 167 (33.38), 165 (11.42), 91 (39.85), 77 (4.22); HRMS (EI) Calcd for $C_{24}H_{21}OCl$ (M^+) requires: 360.1281, Found: 360.1276.

*4.2.8. 4-Chlorophenyl-2-(diphenylmethylene)cyclobutylmethanol (anti-**3c**)*

A colorless oil; IR (CH_2Cl_2): ν 3400, 3053, 2951, 1597, 1575, 1498, 1442, 1264, 1091, 1031, 1021, 796, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.67–1.74 (2H, m, CH_2, OH), 2.04–2.14 (1H, m, CH_2), 2.53–2.58 (1H, m, CH_2), 2.70–2.80 (1H, m, CH_2), 3.73–3.78 (1H, m, CH_2), 4.67 (1H, d, J=7.2 Hz, CH), 7.05 (2H, d, J=6.9 Hz, Ar), 7.04–7.42 (12H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.0, 30.7, 50.1, 74.7, 126.7, 127.3, 128.0, 128.1, 128.5, 128.8, 129.4, 133.2, 135.8, 199.9, 140.0, 140.1, 140.3, 140.4; MS (EI) m/z (%): 360 (7.71) [M^+], 342 (100.00), 220 (53.84), 204 (32.78), 167 (33.29), 165 (18.99), 91 (39.33), 77 (5.22); HRMS (EI) Calcd for $C_{24}H_{21}OCl$ (M^+) requires: 360.1281, Found: 360.1260.

*4.2.9. 2-(Diphenylmethylene)cyclobutyl(phenyl)methanol (syn-**3d**)*

A colorless oil; IR (CH_2Cl_2): ν 3584, 3564, 3055, 2919, 1598, 1493, 1443, 1070, 1028, 968, 768, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.80–1.96 (2H, m, CH_2, OH), 2.11–2.21 (1H, m, CH_2), 2.66–2.76 (1H, m, CH_2), 2.97–3.07 (1H, m, CH_2), 3.68–3.74 (1H, m, CH_2), 4.42 (1H, d, J=3.3 Hz, CH), 7.13–7.41 (15H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.3, 30.4, 50.8, 71.7, 125.6, 126.5, 126.9, 127.0, 128.0, 128.1, 128.4, 128.5, 129.2, 135.6, 140.3, 140.4, 140.7, 142.2; MS (EI) m/z (%): 326 (6.01) [M^+], 308 (100.00), 220 (68.25), 205 (29.78), 191 (29.61), 167 (25.62), 91 (32.50), 77 (5.60); HRMS (EI) Calcd for $C_{24}H_{22}O$ (M^+) requires: 326.1671, Found: 326.1671.

*4.2.10. 2-(Diphenylmethylene)cyclobutyl(phenyl)methanol (anti-**3d**)*

A colorless oil; IR (CH_2Cl_2): ν 3397, 3056, 3027, 2952, 1598, 1493, 1442, 1031, 768, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.58 (1H, br s, OH), 1.70–1.80 (1H, m, CH_2), 2.00–2.10 (1H, m, CH_2), 2.46–2.55 (1H, m, CH_2), 2.66–2.75 (1H, m, CH_2), 3.73–3.83 (1H, m, CH_2), 4.71 (1H, d, J=7.8 Hz, CH), 7.06 (2H, d, J=7.5 Hz, Ar), 7.17–7.42 (13H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.1, 30.7, 50.2, 75.5, 126.6, 126.8, 127.2, 127.5, 127.9, 128.0, 128.5, 128.8, 129.6, 135.6, 140.5, 140.6, 141.6; MS (EI) m/z (%): 326 (5.70) [M^+], 308 (100.00), 220 (74.13), 204 (32.05), 191 (36.30), 167 (26.02), 91 (39.77), 77 (6.20); HRMS (EI) Calcd for $C_{24}H_{22}O$ (M^+) requires: 326.1671, Found: 326.1682.

*4.2.11. 2-(Diphenylmethylene)cyclobutyl(p-tolyl)methanol (syn-**3e**)*

A colorless oil; IR (CH_2Cl_2): ν 3564, 3418, 3053, 2950, 1595, 1485, 1442, 1264, 1071, 1031, 1009, 738, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.81 (1H, br s, OH), 1.85–2.00 (1H, m, CH_2), 2.11–2.26 (1H, m, CH_2), 2.28 (3H, s, CH_3), 2.64–2.75 (1H, m, CH_2), 2.98–3.08 (1H, m, CH_2), 3.66–3.73 (1H, m, CH_2), 4.40 (1H, d, J=3.6 Hz, CH), 7.02 (4H, s, Ar), 7.16–7.35 (10H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.4, 21.1, 30.4, 50.8, 71.8, 125.5, 126.5, 126.8, 128.0, 128.3, 128.4, 128.6, 129.3, 135.4, 136.4, 139.2, 140.3, 140.4, 140.7; MS (EI) m/z (%): 322 (9.70) [M^+-18], 220 (65.05), 205 (31.52), 192 (29.44), 129 (25.60), 121 (66.07), 91 (100.00), 77 (23.63); HRMS (EI) Calcd for $C_{25}H_{22}$ (M^+-18) requires: 322.1722, Found: 322.1726.

*4.2.12. 2-(Diphenylmethylene)cyclobutyl(p-tolyl)methanol (anti-**3e**)*

A colorless oil; IR (CH_2Cl_2): ν 3412, 3079, 3053, 3022, 2920, 1597, 1513, 1493, 1442, 1265, 1031, 769, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.59 (1H, br s, OH), 1.67–1.77 (1H, m, CH_2), 1.98–2.11 (1H, m, CH_2), 2.33 (3H, s, CH_3), 2.45–2.55 (1H, m, CH_2), 2.68–2.80 (1H, m, CH_2), 3.72–3.80 (1H, m, CH_2), 4.66 (1H, d, J=9.6 Hz, CH), 7.05–7.40 (14H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.1, 21.1, 30.6, 50.1, 75.3, 126.5, 126.6, 127.1, 127.9, 128.5, 128.6, 128.7, 129.5, 135.4, 137.0, 138.5, 140.4, 140.6, 142.2; MS (EI) m/z (%): 322 (3.97) [M^+-18], 220 (71.99), 205 (33.06), 192 (33.48), 129 (22.67), 121 (68.55), 91 (100.00), 77 (26.51); HRMS (EI) Calcd for $C_{25}H_{22}$ (M^+-18) requires: 322.1722, Found: 322.1717.

*4.2.13. 2-(Diphenylmethylene)cyclobutyl(m-tolyl)methanol (syn-**3f**)*

A colorless oil; IR (CH_2Cl_2): ν 3462, 3055, 2950, 1719, 1599, 1492, 1444, 1277, 1076, 1030, 970, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.88–1.98 (2H, m, CH_2, OH), 2.13–2.20 (1H, m, CH_2), 2.08 (3H, s, CH_2), 2.65–2.76 (1H, m, CH_2), 2.99–3.07 (1H, m, CH_2), 3.69–3.74 (1H, m, CH_2), 4.40 (1H, d, J=3.3 Hz, CH), 6.92–7.00 (4H, m, ArH), 7.10–7.37 (10H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.5, 21.5, 30.4, 50.7, 71.9, 122.7, 126.3, 126.5, 126.9, 127.7, 127.9, 128.0, 128.3, 128.4, 129.2, 135.5, 137.5, 140.4, 140.7, 142.1; MS (EI) m/z (%): 340 (5.95) [M^+], 322 (100.00), 220 (22.16), 204 (11.81), 167 (23.85), 165 (9.52), 91 (7.48); HRMS (EI) Calcd for $C_{25}H_{24}O$ (M^+) requires: 340.1827, Found: 340.1828.

*4.2.14. 2-(Diphenylmethylene)cyclobutyl(m-tolyl)methanol (anti-**3f**)*

A colorless oil; IR (CH_2Cl_2): ν 3552, 3055, 2925, 1720, 1598, 1493, 1443, 1277, 1031, 896, 788, 647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.60 (1H, br s, OH), 1.70–1.75 (1H, m, CH_2), 2.03–2.10 (1H, m, CH_2), 2.33 (3H, s, CH_2), 2.50–2.56 (1H, m, CH_2), 2.68–2.78 (1H, m, CH_2), 3.75–3.81 (1H, m, CH_2), 4.68 (1H, d, J=7.8 Hz, CH), 7.06–7.09

(4H, m, ArH), 7.16–7.42 (10H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.1, 21.5, 30.7, 50.1, 75.6, 123.8, 126.6, 127.2, 127.5, 127.8, 127.9, 128.3, 128.5, 128.7, 129.5, 135.5, 137.5, 140.5, 140.6, 141.5; MS (EI) *m*/*z* (%): 340 (2.70) [M^+], 322 (100.00), 220 (28.73), 204 (14.44), 167 (19.28), 165 (8.16), 91 (9.76); HRMS (EI) Calcd for $C_{25}H_{24}O$ (M^+) requires: 340.1827, Found: 340.1827.

4.2.15. 2-(Diphenylmethylene)cyclobutyl(furan-2-yl)methanol (*syn*-**3g** and *anti*-**3g**)

A colorless oil; IR (CH_2Cl_2): ν 3461, 3055, 2928, 2856, 1724, 1598, 1494, 1443, 1265, 1009, 920, 769, 699 cm^{-1}; a mixture of *syn*-**3g** and *anti*-**3g**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.77–1.87 (1H, m, OH), 2.13–2.26 (2H, m, CH_2), 2.59–2.81 (1H, m, CH_2), 2.93–3.12 (1H, m, CH_2), 3.77–3.85 (1H, m, CH_2), 4.41 (0.5H, d, *J*=3.0 Hz, CH), 4.69 (0.5H, d, *J*=8.4 Hz, CH), 6.06 (0.5H, d, *J*=3.0 Hz, CH), 6.15 (0.5H, d, *J*=3.0 Hz, CH), 6.22 (0.5H, dd, *J*=3.0, 1.8 Hz, CH), 6.69 (0.5H, dd, *J*=3.0, 1.8 Hz, CH), 7.09 (2H, d, *J*=6.6 Hz, ArH), 7.11–7.38 (9H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 18.3, 19.7, 30.5, 30.7, 48.0, 48.1, 66.5, 69.8, 105.9, 106.9, 109.9, 110.0, 126.4, 126.5, 126.9, 127.1, 127.9, 128.0, 128.3, 128.4, 128.5, 128.7, 129.1, 129.5, 140.3, 141.6, 141.9; MS (EI) *m*/*z* (%): 316 (3.85) [M^+], 293 (100.00), 220 (42.27), 204 (24.53), 191 (23.28), 165 (14.11), 91 (21.50); HRMS (EI) Calcd for $C_{22}H_{20}O_2$ (M^+) requires: 316.1463, Found: 316.1464.

4.2.16. 2-(2-(Diphenylmethylene)cyclobutyl)but-3-en-2-ol (*syn*-**5a** and *anti*-**5a**)

A colorless oil; IR (CH_2Cl_2): ν 3564, 3448, 3055, 2926, 2854, 1727, 1660, 1598, 1493, 1444, 1277, 1114, 769 cm^{-1}; a mixture of *syn*-**5a** and *anti*-**5a**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.01 (1.5H, s, CH_3), 1.03 (1.5H, s, CH_3), 1.76–1.86 (1H, m, CH_2), 2.17–2.25 (1H, m, CH_2), 2.53–2.62 (1H, m, CH_2), 3.06–3.15 (1H, m, CH_2), 3.51–3.57 (1H, m, CH_2), 4.93 (0.5H, dd, *J*=10.8, 1.5 Hz, CH), 5.04 (0.5H, dd, *J*=10.8, 1.5 Hz, CH), 5.16 (1H, dd, *J*=8.5, 1.5 Hz, CH), 5.78 (0.5H, dd, *J*=17.1, 10.5 Hz, CH), 5.92 (0.5H, dd, *J*=17.1, 10.5 Hz, CH), 7.10–7.31 (10H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.8, 20.0, 24.9, 25.2, 32.2, 32.3, 53.0, 53.1, 75.7, 75.9, 112.2, 112.5, 126.5, 127.0, 127.2, 127.9, 128.5, 128.6, 128.7, 129.8, 129.9, 136.2, 139.7, 140.4, 140.9, 142.1, 142.6; MS (EI) *m*/*z* (%): 290 (3.81) [M^+], 272 (49.31), 220 (97.18), 204 (100.00), 191 (52.70), 165 (51.21), 91 (83.96); HRMS (EI) Calcd for $C_{21}H_{22}O$ (M^+) requires: 290.1671, Found: 290.1673.

4.2.17. (4-Bromophenyl)-2-(diphenylmethylene)cyclobutylmethyl-4-methylbenzenesulfonamide (*syn*-**5b** and *anti*-**5b**)

A white solid, mp 82–84 °C; IR (CH_2Cl_2): ν 3252, 3053, 2925, 1597, 1498, 1317, 1158, 1092, 1009, 812, 737, 700 cm^{-1}; a mixture of *syn*-**5b** and *anti*-**5b**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.95–2.05 (1H, m, CH_2), 2.16–2.48 (5H, m, CH_2, CH_3), 2.68–2.74 (1H, m, CH_2), 3.63–3.66 (1H, m, CH_2), 4.22–4.28 (1H, m, CH_2), 4.72 (1H, d, *J*=4.5 Hz, CH), 6.65 (1H, d, *J*=7.8 Hz, CH), 6.67–7.48 (18H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.2, 20.5, 21.3, 21.4, 30.6, 31.2, 48.1, 48.3, 58.8, 59.9, 120.9, 121.2, 126.6, 126.7, 126.8, 126.9, 127.4, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.1, 129.2, 129.3, 129.4, 130.6, 130.8, 131.4, 136.4, 137.0, 137.4, 137.5, 137.6, 137.8, 138.1, 139.7, 139.8, 139.9, 140.0, 142.8, 142.9; MS (EI) *m*/*z* (%): 580 [M^+]; HRMS (ESI) Calcd for $C_{31}H_{28}NO_2SBrNa$ (M^+) requires: 580.0926, Found: 580.0916.

4.2.18. 2-(2-(Diphenylmethylene)cyclobutyl)-1-phenylethanol (*syn*-**5c** and *anti*-**5c**)

A colorless oil; IR (CH_2Cl_2): ν 3429, 3056, 3027, 2935, 1949, 1722, 1598, 1493, 1443, 1029, 914, 755, 631 cm^{-1}; a mixture of *syn*-**5c** and *anti*-**5c**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.54–1.61 (1H, m, CH_2), 1.86–1.91 (0.5H, m, CH_2), 2.07–2.13 (0.5H, m, CH_2), 2.20–2.26 (1H, m, CH_2), 2.46–2.60 (1.5H, m, CH_2), 2.80–2.87 (0.5H, m, CH_2), 2.92–3.00 (1H, m, CH_2), 3.28–3.34 (0.5H, m, CH_2), 3.43–3.58 (1.5H, m, CH_2), 3.68–3.81 (1H, m, CH_2), 7.01–7.41 (15H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 20.9, 21.0, 31.3, 31.5, 44.6, 45.0, 51.2, 51.4, 64.2, 64.9, 126.4, 126.5, 126.7, 126.8, 126.9, 127.4, 127.6, 127.8, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.6, 129.7, 130.6, 134.9, 135.0, 140.1, 140.6, 140.7, 141.0, 141.7, 141.8; MS (EI) *m*/*z* (%): 340 (19.53) [M^+], 322 (48.36), 219 (100.00), 204 (39.89), 141 (18.68), 115 (20.84), 91 (87.32); HRMS (EI) Calcd for $C_{25}H_{24}O$ (M^+) requires: 340.1827, Found: 340.1820.

4.2.19. 2-(2-(Diphenylmethylene)cyclobutyl)-2-phenylpropan-1-ol (*syn*-**5c′** and *anti*-**5c′**)

A colorless oil; IR (CH_2Cl_2): ν 3584, 3444, 3056, 3026, 2945, 1715, 1660, 1493, 1443, 1030, 738, 700 cm^{-1}; a mixture of *syn*-**5c′** and *anti*-**5c′**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.65–1.70 (3H, m, CH_2), 1.72–1.75 (1H, m, CH_2), 2.17–2.28 (1H, m, CH_2), 2.67–2.78 (1H, m, CH_2), 3.11–3.29 (1.35H, m, CH_2), 3.51–3.56 (0.65H, m, CH_2), 4.31–4.34 (0.35H, m, CH), 4.47–4.52 (0.65H, m, CH), 7.09–7.33 (14H, m, ArH); MS (EI) *m*/*z* (%): 340 (8.56) [M^+], 322 (78.58), 245 (14.88), 231 (100.00), 220 (18.01), 203 (41.67), 115 (10.70); HRMS (EI) Calcd for $C_{25}H_{24}O$ (M^+) requires: 340.1827, Found: 340.1828.

4.2.20. (4-Bromophenyl)-2-(di-p-tolylmethylene) cyclobutylmethanol (*syn*-**3h** and *anti*-**3h**)

A colorless oil; IR (CH_2Cl_2): ν 3433, 3022, 2869, 1905, 1723, 1590, 1510, 1450, 1404, 1265, 1071, 1037, 821 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *syn*-**3h**: δ 1.63–1.72 (0.5H, m, CH_2), 1.83–1.90 (0.5H, m, OH), 1.92–2.11 (0.5H, m, CH_2), 2.32 (3H, s, CH_3), 2.47–2.53 (0.5H, m, CH_2), 2.57–2.80 (0.5H, m, CH_2), 3.67–3.73 (0.5H, m, CH_2), 4.41 (0.5H, d, *J*=4.2 Hz, CH), 6.94–7.25 (4H, m, ArH), 7.31 (1H, d, *J*=8.1 Hz, ArH), 7.41 (1H, d, *J*=8.1 Hz, ArH); *anti*-**3h**: δ 1.63–1.72 (0.5H, m, CH_2), 1.83–1.90 (0.5H, m, OH), 1.92–2.11 (0.5H, m, CH_2), 2.36 (3H, s, CH_3), 2.57–2.80 (0.5H, m, CH_2), 2.98–3.04 (0.5H, m, CH_2), 3.67–3.73 (0.5H, m, CH_2), 4.65 (0.5H, d, *J*=8.4 Hz, CH), 6.94–7.25 (4H, m, ArH), 7.31 (1H, d, *J*=8.1 Hz, ArH), 7.41 (1H, d, *J*=8.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.7, 19.1, 21.1, 21.2, 21.3, 26.9, 30.3, 30.5, 50.1, 50.6, 71.7, 75.1, 120.7, 121.2, 127.5, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.1, 129.3, 129.5, 130.9, 131.0, 135.6, 135.7, 136.2, 136.3, 136.5, 136.9, 137.3, 137.4, 137.5, 137.6, 138.5, 138.8, 140.7, 141.1; MS (EI) *m*/*z* (%): 432 (16.06) [M^+], 414 (100.00), 247 (77.89), 232 (27.59), 217 (19.11), 195 (37.67), 165 (9.24), 105 (44.55); HRMS (EI) Calcd for $C_{26}H_{25}OBr$ (M^+) requires: 432.1089, Found: 432.1087.

4.2.21. (4-Chlorophenyl)-2-(di-p-tolylmethylene) cyclobutylmethanol (*syn*-**3i** and *anti*-**3i**)

A colorless oil; IR (CH_2Cl_2): ν 3445, 3022, 2921, 1731, 1682, 1596, 1510, 1407, 1265, 1090, 1037, 821 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *syn*-**3i**: δ 1.58–1.72 (1H, m, CH_2, OH), 1.83–1.95 (0.5H, m, CH_2), 2.05–2.11 (0.5H, m, CH_2), 2.32 (1.5H, s, CH_3), 2.36 (1.5H, s, CH_3), 2.48–2.58 (0.5H, m, CH_2), 2.66–2.81 (0.5H, m, CH_2), 3.68–3.77 (0.5H, m, CH_2), 4.44 (0.5H, d, *J*=4.2 Hz, CH), 6.96 (1H, d, *J*=8.1 Hz, ArH), 6.99–7.28 (5H, m, ArH); *anti*-**3i**: δ 1.58–1.72 (1H, m, CH_2, OH), 1.83–1.95 (0.5H, m, CH_2), 2.05–2.11 (0.5H, m, CH_2), 2.32 (1.5H, s, CH_3), 2.36 (1.5H, s, CH_3), 2.66–2.81 (0.5H, m, CH_2), 2.94–2.03 (0.5H, m, CH_2), 3.68–3.77 (0.5H, m, CH_2), 4.67 (0.5H, d, *J*=7.5 Hz, CH), 6.96 (1H, d, *J*=8.1 Hz, ArH), 6.99–7.28 (5H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 17.6, 19.1, 21.1, 21.2, 30.3, 30.5, 50.1, 50.7, 71.6, 75.1, 127.1, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 129.0, 129.1, 129.3, 129.5, 132.5, 133.1, 135.7, 136.3, 136.6, 137.0, 137.5, 137.6, 138.5, 138.8, 140.1, 140.6; MS (EI) *m*/*z* (%): 388 (14.64) [M^+], 370 (90.85), 247 (100.00), 232 (32.53), 217 (21.37), 195 (21.45), 155 (12.57), 105 (65.88); HRMS (EI) Calcd for $C_{26}H_{25}OCl$ (M^+) requires: 388.1594, Found: 388.1594.

4.2.22. (2-(Bis(4-chlorophenyl)methylene)cyclobutyl)(4-bromophenyl)methanol (*syn*-**3j** and *anti*-**3j**)

A colorless oil; IR (CH_2Cl_2): ν 3418, 2925, 2855, 1902, 1715, 1682, 1633, 1488, 1434, 1397, 1090, 1011, 829, 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *syn*-**3j**: δ 1.98–2.18 (1H, m, CH_2, OH), 2.42–2.51 (0.5H, m, CH_2), 2.60–2.74 (0.5H, m, CH_2), 2.82–2.86 (0.5H, m, CH_2), 3.61–3.64

(0.5H, m, CH_2), 4.50 (0.5H, d, J=1.8 Hz, CH), 6.95–7.55 (6H, m, ArH); *anti*-**3j**: δ 1.98–2.18 (1H, m, CH_2, OH), 2.42–2.51 (0.5H, m, CH_2), 2.60–2.74 (0.5H, m, CH_2), 3.07–3.11 (0.5H, m, CH_2), 3.73–3.76 (0.5H, m, CH_2), 4.67 (0.5H, d, J=4.2 Hz, CH), 6.95–7.55 (6H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 18.5, 18.9, 30.4, 30.9, 49.9, 50.6, 72.7, 74.3, 127.4, 127.8, 128.2, 128.3, 128.6, 128.7, 129.0, 129.6, 129.7, 130.5, 130.6, 131.0, 132.6, 133.2, 133.8, 138.4, 140.4, 141.1; MS (EI) m/z (%): 472 (7.43) [M^+], 455 (100.00), 288 (87.18), 253 (73.23), 215 (50.32), 184 (82.35), 125 (75.94), 77 (17.79); HRMS (EI) Calcd for $C_{24}H_{19}OBrCl_2$ (M^+) requires: 471.9996, Found: 471.9984.

*4.2.23. (2-(Bis(4-chlorophenyl)methylene)cyclobutyl)(4-chlorophenyl)methanol (syn-**3k** and anti-**3k**)*

A colorless oil; IR (CH_2Cl_2): ν 3058, 3019, 2986, 2945, 2853, 1675, 1598, 1579, 1495, 1250, 1179, 957, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): *syn*-**3k**: δ 1.73–1.83 (0.35H, m, CH_2, OH), 1.97–2.16 (0.7H, m, CH_2), 2.65–2.69 (0.35H, m, CH_2), 2.84–2.89 (0.35H, m, CH_2), 3.03–3.14 (0.35H, m, CH_2), 3.59–3.62 (0.35H, m, CH_2), 4.50 (0.35H, d, J=5.4 Hz, CH), 6.89–7.35 (4.2H, m, ArH); *anti*-**3k**: δ 1.73–1.83 (0.65H, m, CH_2, OH), 1.97–2.16 (1.3H, m, CH_2), 2.44–2.49 (0.65H, m, CH_2), 2.65–2.69 (0.65H, m, CH_2), 3.72–3.78 (0.65H, m, CH_2), 4.66 (0.65H, d, J=6.6 Hz, CH), 6.89–7.35 (7.8H, m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 18.5, 18.8, 30.8, 30.9, 49.8, 50.6, 72.6, 74.1, 127.0, 127.7, 127.8, 128.1, 128.3, 128.5, 128.9, 129.6, 129.7, 130.4, 130.5, 130.6, 132.5, 132.6, 133.0, 133.1, 133.3, 133.7, 138.1, 138.3, 138.4, 139.8, 140.5, 140.9, 141.1; MS (EI) m/z (%): 287 (96.13) [M^+−185], 253 (42.88), 215 (45.21), 189 (26.99), 177 (54.63), 141 (100.00), 125 (33.48), 77 (16.15); HRMS (EI) Calcd for $C_{17}H_{13}Cl_2$ (M^+) requires: 287.0394, Found: 287.0378.

*4.2.24. (4-Bromophenyl)(2-(diphenylmethylene)cyclobutyl)methyl 3,5-dinitrobenzoate (syn-**6**)*

A colorless oil; IR (CH_2Cl_2): ν 3056, 3014, 2997, 2945, 2853, 1675, 1598, 1579, 1495, 1250, 1179, 954, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.00–2.10 (1H, m, CH_2), 2.32–2.39 (1H, m, CH_2), 2.61–2.70 (1H, m, CH_2), 2.93–3.05 (1H, m, CH_2), 4.09–4.13 (1H, m, CH_2), 5.87 (1H, d, J=6.0 Hz, CH), 6.95–7.36 (14H, m, ArH), 8.97 (2H, d, J=2.1 Hz, ArH), 9.19 (1H, t, J=2.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.1, 19.9, 31.2, 47.3, 78.7, 122.3, 122.5, 126.4, 126.9, 128.0, 128.2, 128.3, 128.4, 129.2, 129.3, 131.4, 133.5, 136.2, 136.6, 137.2, 140.1, 140.2, 148.4, 161.5; MS (EI) m/z (%): 598 (92.01) [M^+], 389 (17.64), 386 (68.66), 345 (8.22), 229 (14.66), 219 (100.00), 217 (14.91), 91 (79.96); HRMS (EI) Calcd for $C_{31}H_{23}N_2O_6Br$ (M^+) requires: 598.0739, Found: 598.0739.

*4.2.25. (4-Bromophenyl)(2-(diphenylmethylene)cyclobutyl)methyl 3,5-dinitrobenzoate (anti-**6**)*

A colorless oil; IR (CH_2Cl_2): ν 3057, 3018, 2986, 2945, 2853, 1675, 1598, 1579, 1495, 1250, 1179, 957, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.68–1.74 (1H, m, CH_2), 2.17–2.30 (1H, m, CH_2), 2.50–2.59 (1H, m, CH_2), 3.12–3.25 (1H, m, CH_2), 4.20–4.27 (1H, m, CH_2), 6.29 (1H, d, J=9.6 Hz, CH), 6.81–7.55 (14H, m, ArH), 8.61 (2H, d, J=1.8 Hz, ArH), 9.19 (1H, t, J=2.4 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.7, 30.9, 46.8, 78.8, 121.9, 122.8, 126.2, 126.8, 127.8, 127.9, 128.8, 129.0, 129.1, 129.2, 131.7, 133.3, 136.3, 136.4, 137.4, 140.4, 140.5, 148.1, 161.3; MS (EI) m/z (%): 598 (67.88) [M^+], 389 (21.23), 386 (78.72), 292 (5.08), 229 (16.29), 219 (100.00), 217 (15.78), 91 (88.28); HRMS (EI) Calcd for $C_{31}H_{23}N_2O_6Br$ (M^+) requires: 598.0739, Found: 598.0742.

*4.2.26. (4-Bromophenyl)(2-(diphenylmethylene)cyclobutyl) methanone (**7a**). (4-bromophenyl)(2,3-diphenylcyclopent-2-enyl)methanone (**8a**)*

*4.2.26.1. Compound **7a**.* This is a known compound.[7] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.24–2.54 (0.8H, m, CH_2), 2.82–2.88 (0.4H, m, CH_2), 3.40–3.45 (0.4H, m, CH_2), 4.86–4.92 (0.15H, m, CH_2), 7.05–7.52 (5.6H, m, ArH).

*4.2.26.2. Compound **8a**.* A colorless oil; IR (CH_2Cl_2): ν 3552, 3055, 2925, 1720, 1598, 1493, 1443, 1277, 1031, 896, 788, 647 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.17–2.23 (0.6H, m, CH_2), 2.55–2.58 (0.6H, m, CH_2), 2.82–2.88 (0.6H, m, CH_2), 2.97–3.20 (0.6H, m, CH_2), 5.02–5.11 (0.6H, m, CH_2), 7.05–7.52 (8.4H, m, ArH); MS (EI) m/z (%): 404 (24.73) [M^+], 219 (46.25), 204 (13.61), 183 (100.00), 165 (17.92), 154 (13.37), 91 (46.84); HRMS (EI) Calcd for $C_{24}H_{19}OBr$ (M^+) requires: 404.0599, Found: 404.0615.

*4.2.27. (4-Chlorophenyl)(2-(diphenylmethylene) cyclobutyl)methanone (**7b**). (4-chlorophenyl)(2,3-diphenylcyclopent-2-enyl)methanone (**8b**)*

*4.2.27.1. Compound **7b**.* This is a known compound.[7] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.25–2.49 (0.6H, m, CH_2), 2.83–2.97 (0.3H, m, CH_2), 3.43–3.46 (0.3H, m, CH_2), 4.79–4.86 (0.3H, m, CH_2), 7.03–7.47 (3.6H, m, ArH), 7.77–7.87 (0.6H, m, ArH).

*4.2.27.2. Compound **8b**.* A colorless oil; IR (CH_2Cl_2): ν 3550, 3461, 3055, 2928, 2856, 1724, 1598, 1494, 1443, 1265, 1009, 920, 769, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.16–2.21 (0.7H, m, CH_2), 2.54–2.59 (0.7H, m, CH_2), 2.83–2.97 (0.7H, m, CH_2), 3.13–3.24 (0.7H, m, CH_2), 3.34–3.38 (0.7H, m, CH_2), 4.98–5.04 (0.7H, m, CH_2), 7.03–7.47 (8.4H, m, ArH), 7.77–7.87 (1.4H, m, ArH); MS (EI) m/z (%): 3606 (6.46) [M^+], 219 (100.00), 204 (11.29), 182 (32.78), 138 (26.91), 105 (60.56), 91 (33.45); HRMS (EI) Calcd for $C_{24}H_{19}OCl$ (M^+) requires: 360.1095, Found: 360.1107.

*4.2.28. (2-(Diphenylmethylene)cyclobutyl)(phenyl)methanone (**7c**). (2,3-diphenylcyclopent-2-enyl)(phenyl)methanone (**8c**)*

*4.2.28.1. Compound **7c**.* This is a known compound.[7] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.34–2.45 (2H, m, CH_2), 2.88–2.98 (1H, m, CH_2), 3.33–3.43 (1H, m, CH_2), 4.81–4.86 (1H, m, CH_2), 7.02–7.37 (15H, m, ArH).

*4.2.28.2. Compound **8c**.* This is a known compound.[4b] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.10–2.20 (1H, m, CH_2), 2.43–2.53 (1H, m, CH_2), 2.76–2.85 (1H, m, CH_2), 3.05–3.14 (1H, m, CH_2), 4.95–5.02 (1H, m, CH), 6.98–7.23 (10H, m, ArH), 7.32–7.47 (3H, m, ArH), 7.86 (2H, d, J=7.5 Hz, ArH).

*4.2.29. (2,3-Bis(4-chlorophenyl)cyclopent-2-enyl)(4-bromophenyl)methanone (**8d**)*

*4.2.29.1. Compound **7d**.* This is a known compound.[7] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.32–2.47 (2H, m, CH_2), 2.85–2.96 (1H, m, CH_2), 3.26–3.39 (1H, m, CH_2), 4.48–4.83 (1H, m, CH_2), 6.94 (2H, d, J=8.4 Hz, ArH), 7.05 (2H, d, J=8.4 Hz, ArH), 7.10 (2H, d, J=8.4 Hz, ArH), 7.23 (2H, d, J=8.4 Hz, ArH), 7.37 (2H, d, J=9.0 Hz, ArH), 7.43 (2H, d, J=9.0 Hz, ArH).

*4.2.29.2. Compound **8d**.* This is a known compound.[4b] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 2.15–2.23 (1H, m, CH_2), 2.48–2.61 (1H, m, CH_2), 2.79–2.88 (1H, m, CH_2), 3.07–3.15 (1H, m, CH_2), 4.95–5.00 (1H, m, CH_2), 6.92–7.23 (8H, m, ArH), 7.46–7.88 (4H, m, ArH).

*4.2.30. 4-Bromophenyl-3-methyl-4,4-diphenylpropenol (**10**)*

A colorless oil; IR (CH_2Cl_2): ν 3409, 3077, 3051, 2922, 1941, 1596, 1513, 1442, 1265, 1179, 1034, 820, 765, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.82 (3H, s, CH_3), 1.96 (1H, br s, OH), 2.50

(1H, dd, J=10.2, 4.8 Hz, CH_2), 2.65 (1H, dd, J=10.2, 4.8 Hz, CH_2), 4.80 (1H, t, J=4.8 Hz, CH), 6.98–7.07 (6H, m, ArH), 7.16–7.27 (6H, m, ArH), 7.39 (2H, d, J=5.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 20.4, 45.0, 72.3, 121.1, 126.4, 127.5, 128.0, 128.1, 129.3, 129.4, 130.2, 131.3, 141.3, 142.4, 142.7, 143.1; MS (EI) m/z (%): 392 (37.97) [M^+], 208 (100.00), 207 (80.65), 191 (10.94), 178 (10.34), 129 (26.96), 91 (10.19), 77 (5.44); HRMS (EI) Calcd for $C_{23}H_{21}OBr$ (M^+) requires: 392.0776, Found: 392.0773.

*4.2.31. 4-Bromophenyl-2-(diphenylmethylene)cyclopentylmethanol (syn-**12** and anti-**12**)*

A colorless oil; IR (CH_2Cl_2): ν 3410, 3077, 3050, 2920, 1946, 1595, 1507, 1435, 1265, 1179, 1031, 819, 767, 701 cm^{-1}; a mixture of *syn*-**12** and *anti*-**12**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.65–1.69 (2H, m, CH_2), 1.74–1.79 (1H, m, CH_2), 1.89–1.96 (2H, m, CH_2), 2.37–2.12 (2H, m, CH_2), 2.61–2.67 (1H, m, CH_2), 4.65–4.66 (1H, m, CH_2), 7.04–7.43 (14H, m, ArH); MS (EI) m/z (%): 417 (25.03) [M^+], 250 (17.26), 249 (32.45), 233 (100.00), 191 (11.25), 155 (8.96), 129 (26.58), 91 (8.23); HRMS (EI) Calcd for $C_{25}H_{23}OBr$ (M^+) requires: 417.0854, Found: 417.0856.

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Supplementary data

^{1}H spectroscopic charts for compounds **3a**–**12**. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.048.

References and notes

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