ARTICLE

OBC
www.rsc.org/obc

Palladium-catalysed cascade ring expansion reaction of cyclobutanols that have a propargylic moiety with nucleophiles

Masahiro Yoshida,*[a] Yuki Komatsuzaki,[a] Hideo Nemoto[b] and Masataka Ihara*[a]

[a] *Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aobayama, Sendai, 980-8578, Japan. E-mail: mihara@mail.pharm.tohoku.ac.jp*

[b] *Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Sugitani 2630, Toyama, 930-0194, Japan*

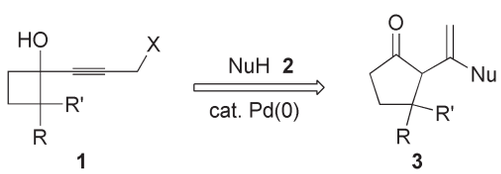
Received 9th July 2004, Accepted 7th September 2004
First published as an Advance Article on the web 30th September 2004

Cascade ring rearrangement of four-membered ring systems containing various propargylic components by a palladium catalyst is described. The reactions of cyclobutanols that have a propargylic carbonate moiety with phenols as nucleophiles produce phenoxy-induced cyclopentanones in high yields. The reactions proceed in a regio- and diastereoselective manner to afford the substituted cyclopentanones with high selectivities. Imides also act as nucleophiles to produce the imidyl-induced products. Propargylic bromide successfully reacts with sodium alkoxides to produce the corresponding products in good yields.

Introduction

It is well known that propargylic compounds exhibit versatile reactivity in the presence of palladium complexes, and the reactions make up an important class of palladium-catalysed reactions.[1] The key step in these reactions is the formation of a π-propargyl/allenylpalladium complex by facile elimination of a leaving group, which furthermore reacts with other reactants such as soft nucleophiles to lead to a variety of substituted products.[2,3]

Ring rearrangement of vinylcyclobutanols by a transition metal is a valuable method for the construction of substituted five-membered ring systems.[4] The reaction is triggered by release of the strain in four-membered ring systems, and this has been successfully applied to the cascade process by introducing various unsaturated functional groups on the cyclobutane ring. The cascade ring expansion reaction of cyclobutanols that have isopropenyl,[5] allenyl,[6] acetylenyl[7] and 1,3-dienyl[8] groups has been developed by us and other groups during the last decade.[9] We sought to determine whether the ring expansion reaction could proceed when a substrate containing a propargylic moiety is subjected to the reaction with a nucleophile (Scheme 1). We now present the full description of our results.[10]

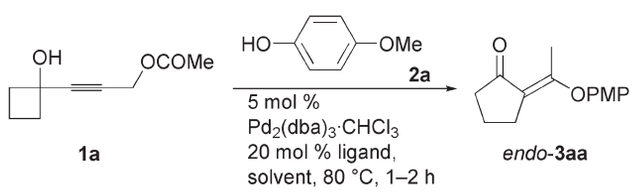


Scheme 1

Results and discussion

Substrates **1a**–**g** for the palladium-catalysed ring expansion reaction are synthesized as follows (Scheme 2). Cyclobutanones **4a** and **4b**[11] are subjected to nucleophilic addition with tetrahydro-2-(2-propynyloxy)-2*H*-pyran in the presence of BuLi to afford acetylenylcyclobutanols **5a** and **5b**. Deprotection of the THP group with TsOH in MeOH gives diols **6a** and **6b**, in which the primary alcohol moiety reacts with methyl chloroformate in pyridine to produce propargylic carbonates **1a** and **1b**. Similarly, 2-phenylcyclobutanone (**4c**)[12] is converted to the diastereomeric mixture of acetylenylcyclobutanols *trans*- and *cis*-**5c**. The corresponding propargylic carbonate *trans*-**1c** is obtained from *trans*-**5c** in 2 steps. The stereochemistries of *trans*- and *cis*-**5c** have been determined by NOESY correlation of allenylcyclobutanol *cis*-**7**, which is obtained by the reaction of *cis*-**5c** with LAH. Similarly, heptyl-substituted substrates *trans*- and *cis*-**1d** are synthesized from 2-heptylcyclobutanone (**4d**).[12] To examine the reactivity of the other leaving groups, propargylic acetate **1e**, benzoate **1f** and bromide **1g** are prepared from **6b**.

Table 1 Initial attempt at the addition-ring expansion reactions of **1a** with **2a**[a]



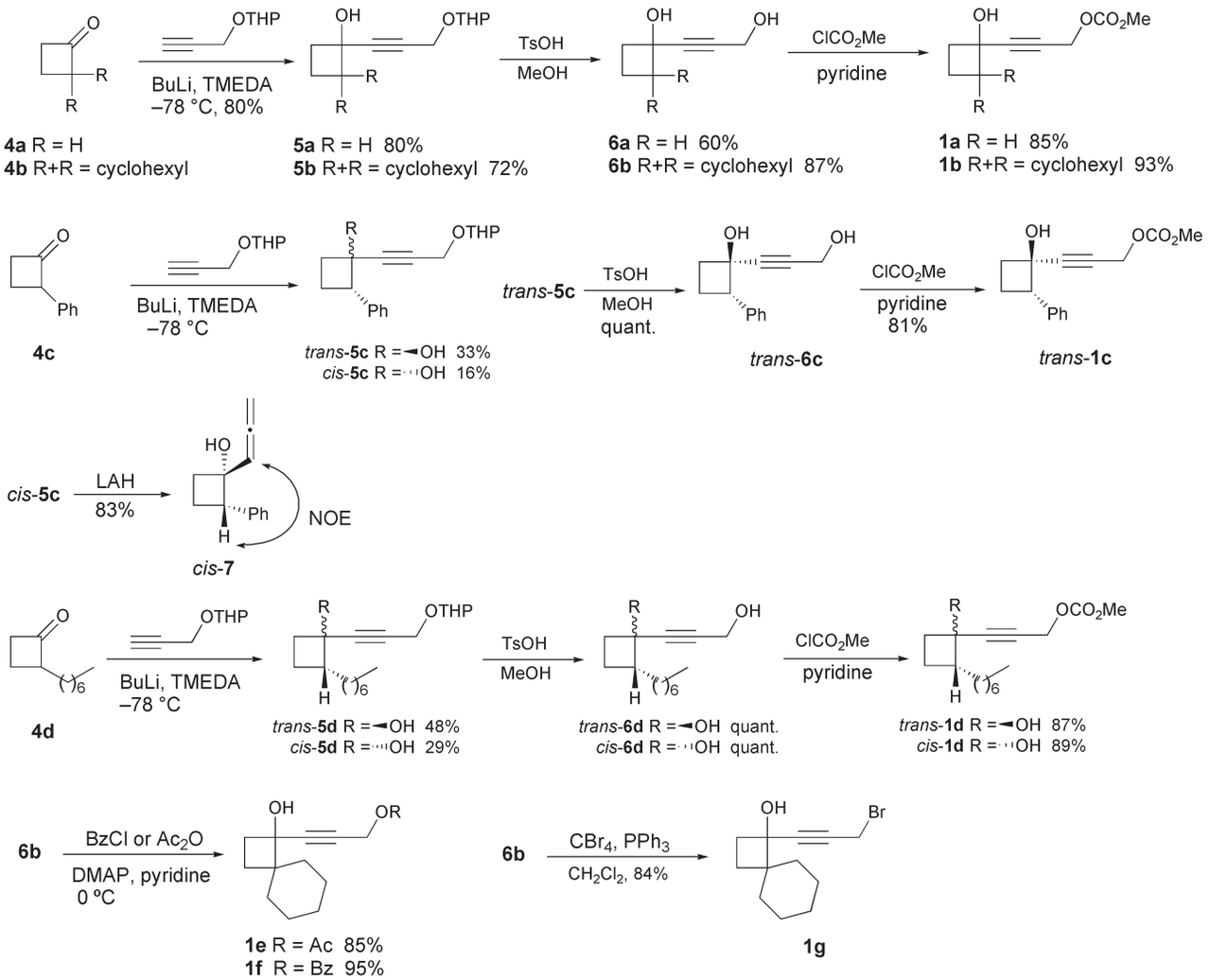
Entry	Solvent	Ligand	Yield (%)
1	Toluene	dppe	57
2	DMF	dppe	37
3	CH_3CN	dppe	12
4	THF	dppe	64
5	Dioxane	dppe	80
6	Dioxane	dppp	78
7	Dioxane	dppb	77
8	Dioxane	dppf	78

[a] PMP = *p*-methoxyphenyl.

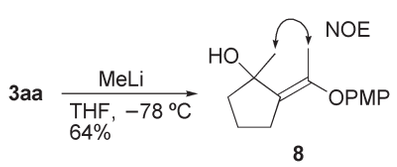
Our initial attempt at the ring expansion reaction begins using **1a** with *p*-methoxyphenol (**2a**) as a nucleophile (Table 1). When **1a** is subjected to reaction with **2a** in the presence of 5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$ and 20 mol% dppe in toluene at 50 °C for 1 h, ring expanded *endo*-**3aa**, which has a *p*-methoxyphenoxy group, is obtained in 57% yield (entry 1). Studies on the reaction solvent (entries 2–5) reveal that the yield is increased to 80% when dioxane is used (entry 5). The reactions proceed uneventfully when other bidentate ligands dppp, dppb and dppf are used (entries 6–8). The geometry of **3aa** is determined by NOESY after the conversion to methylated **8** (Scheme 3).

A series of substituted cyclobutanols **1a**–**d** with *p*-cresol (**2b**) were examined to further define the reaction scope (Table 2). In contrast to the predominant production of *endo*-**3ab** from **1a** and **1b** (entry 1), the *exo* product *exo*-**3bb** is predominantly yielded from the reaction of **1b** (entry 2). When *trans*-**1c** and *trans*-**1d** are subjected to the reaction, the cyclopentanones *trans*-**3cb** and *trans*-**3db** are stereoselectively obtained, respectively (entries 3 and 4). From these results, it is clear that the ring expansion

DOI: 10.1039/b410362a



Scheme 2 Synthesis of substrates **1a**–**g**.



Scheme 3 NOESY correlation of **3aa**-derived alcohol **8**.

reactions proceed in a regio- and diastereoselective manner at the more substituted carbon. The stereochemistry of *trans*-**3cb** is determined by NOESY (Fig. 1), and another product *trans*-**3db** is assumed to have the same stereochemistry.

We then attempted the reactions of *trans*- and *cis*-**1d** with a variety of phenols (Table 3). When *trans*-**1d** is treated with the electron donating group-substituted phenols **2a**–**d**, *trans*-cyclopentanones *trans*-**3da**–**d** are selectively produced in high yields (entries 1–4). On the other hand, the *endo*-isomers *endo*-**3de**–**g** are yielded in accordance with the increase in acidity of phenols **2e**–**g** (entries 5–7). The result implies that acid-catalysed isomerisation of the double bond would occur. When *cis*-**1d** was subjected to the reaction, isomerised *endo*-**3da**–**g** are predominantly produced in all cases (entries 8–14). The *cis*-products *cis*-**3da** and *cis*-**3dc** are only produced as minor products of the reactions with *p*-methoxyphenol (**2a**) and 2,4,6-trimethylphenol (**2c**), respectively

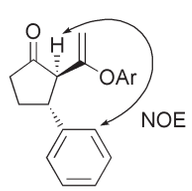
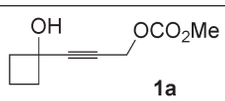
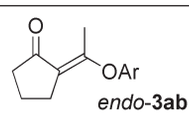
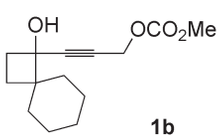
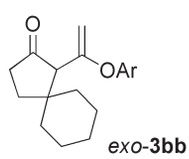
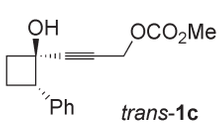
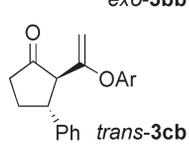
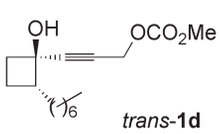
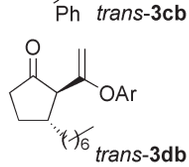


Fig. 1 NOESY correlation of *trans*-**3cb**.

Table 2 Reactions of various cyclobutanols **1a**–**d** with *p*-cresol (**2b**)

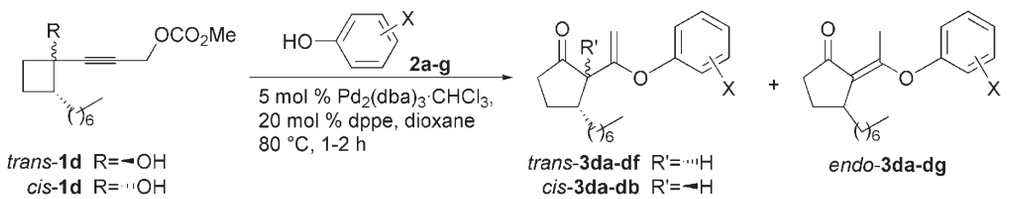
Entry[a]	Substrate	Product[b]	Yield (%)
1			81
2			99
3			83
4			80

[a] Reactions were carried out in the presence of 5 mol% $Pd_2(dba)_3 \cdot CHCl_3$, 20 mol% dppe and 1.2 equiv. of *p*-cresol (**2b**) in dioxane at 80 °C for 1 h. [b] Ar = *p*-tolyl.

(entries 8 and 10). These reactions generally proceed in high yields except in the case of *p*-nitrophenol (**2g**) in entry 7.

A plausible mechanism for the reaction is shown in Scheme 4. The palladium catalyst initially promotes decarboxylation of the

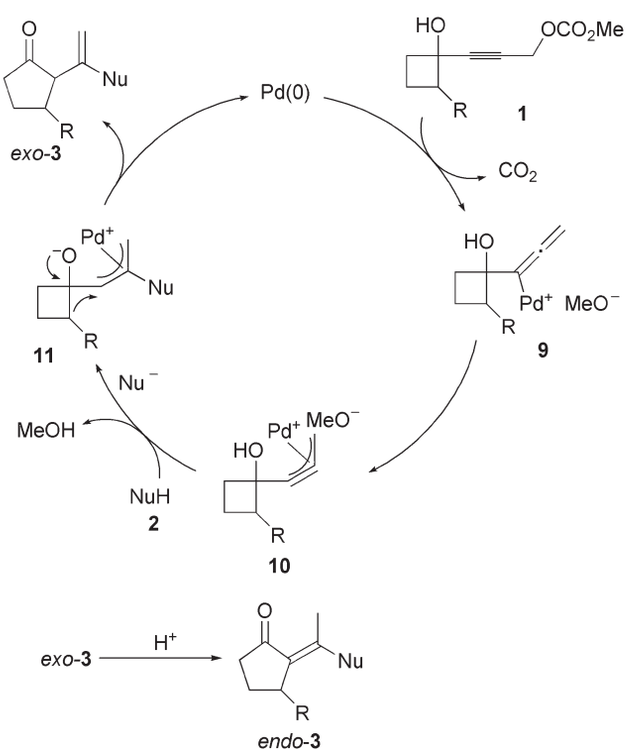
Table 3 Reactions of *trans*- and *cis*-**1a** with various phenols



Entry	Substrate	X	Product	Yield (%)
1	*trans*-**1d**	**2a** 4-OMe	*trans*-**3da**	98
2	*trans*-**1d**	**2b** 4-Me	*trans*-**3db**	80
3	*trans*-**1d**	**2c** 2,4,6-Trimethyl	*trans*-**3dc**	90
4	*trans*-**1d**	**2d** 2-OMe	*trans*-**3dd**	93
5	*trans*-**1d**	**2e** H	*trans*-**3de** : *endo*-**3de** = 65 : 35[a]	94
6	*trans*-**1d**	**2f** 4-Cl	*trans*-**3df** : *endo*-**3df** = 68 : 32[a]	67
7	*trans*-**1d**	**2g** 4-NO_2	*endo*-**3dg**	23
8	*cis*-**1d**	**2a** 4-OMe	*cis*-**3da** : *endo*-**3da** = 36 : 64[a]	98
9	*cis*-**1d**	**2b** 4-Me	*endo*-**3db**	92
10	*cis*-**1d**	**2c** 2,4,6-Trimethyl	*cis*-**3dc** : *endo*-**3dc** = 23 : 77[a]	98
11	*cis*-**1d**	**2d** 2-OMe	*endo*-**3dd**	93
12	*cis*-**1d**	**2e** H	*endo*-**3de**	97
13	*cis*-**1d**	**2f** 4-Cl	*endo*-**3df**	96
14	*cis*-**1d**	**2g** 4-NO_2	*endo*-**3dg**	70

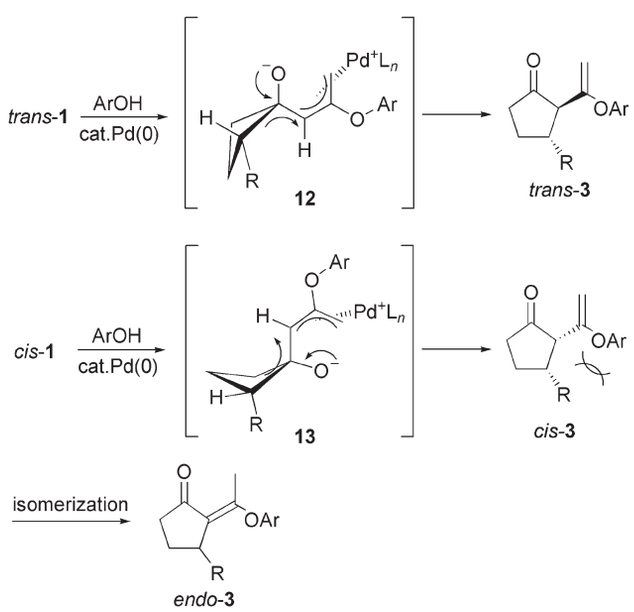
[a] The ratio was determined by ^{1}H-NMR integration.

substrate **1** to lead to allenylpalladium species **9**, which is regarded as a π-propargylpalladium intermediate **10**.[13] The complex **10** undergoes nucleophilic attack by a nucleophile **2** to form the π-allylpalladium intermediate **11**. Finally, ring expansion reaction of **11** would give the substituted cyclopentanone *exo*-**3**, which further isomerises to *endo*-**3** under the same reaction conditions.



Scheme 4 Proposed reaction mechanism.

Scheme 5 provides a possible explanation for the observed diastereoselectivity. It can be presumed that the stereochemistry of the reaction is controlled by the conformation of the π-allylpalladium complex during the ring expansion step. Thus, in the case of *trans*-**1**, the ring expansion process would proceed *via* **12**, the most stable conformer, to give *trans*-**3**. Similarly, when *cis*-**1** is employed, *cis*-**3** would be initially produced *via* **13**. But the product *cis*-**3** is unstable due to steric repulsion, and this can be easily isomerised to *endo*-**3**.



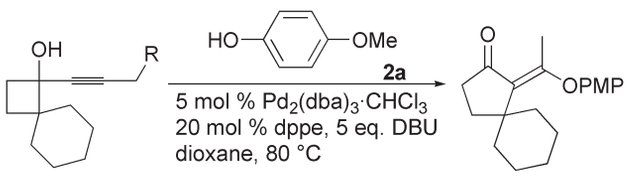
Scheme 5 Proposed explanation for the stereoselectivities.

The reactions of **1e**–**g**, that have various leaving groups at the propargylic position, with *p*-methoxyphenol (**2a**) are examined next (Table 4). Propargylic acetate **1e** reacts with **2a** in the presence of 5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$, 20 mol% dppe and DBU[14] at 80 °C to afford *endo*-**3ba** in 29% yield (entry 1). Although the reactivity of acetate **1e** is low, it is found that the product is obtained in 94% yield when the propargylic benzoate **1f** is used (entry 2). The reaction of propargylic bromide **1g** with **2a** affords a complex mixture (entry 3).

We then evaluated the scope of the ring expansion process by using other nucleophiles. After several attempts, it was clear that imides are suitable nucleophiles in the reaction with propargylic carbonates (Table 5). When the substrate **1b** and phthalimide **2h** are subjected to the reaction at 100 °C, the imidyl-substituted cyclopentanone *endo*-**3bh** is produced in 34% yield (entry 1). Succinimide **2i** and 1,8-naphthalimide **2j** also successfully react with **1b** to afford the corresponding products *endo*-**3bi** and **3bj** in 44% and 53% yield, respectively (entries 2 and 3).

Next we turned our attention to the utilization of aliphatic alcohols as nucleophiles. Recently, Tanaka and co-workers reported the palladium-catalysed intramolecular reaction of a

Table 4 Reactions of substrates **1e–g** that have various leaving groups[a]



1e R = OAc
1f R = OBz
1g R = Br

endo-**3ba**

Entry	Substrate	Time/h	Yield (%)
1	**1e**	48	29
2	**1f**	4	94
3	**1g**	24	Trace

[a] PMP = *p*-methoxyphenyl.

propargylic bromide possessing an aliphatic alcohol side chain.[15] In the reaction, a medium-sized ring can be constructed in the presence of NaOMe in MeOH *via* intramolecular nucleophilic attack of the resulting alkoxide on the π-propargylpalladium intermediate. We are interested in the reaction of propargylic bromides with alkoxides accompanying the ring expansion reaction. Thus, treatment of propargylic bromide **1g** with 5 mol% $Pd_2(dba)_3{\cdot}CHCl_3$, 20 mol% dppe and NaOMe in MeOH at 50 °C provides a methoxy-induced cyclopentanone *endo*-**3gk** in 12% yield along with the simply substituted propargyl methyl ether **12k** (entry 1 in Table 6). From the studies using various ligands (entries 2–5), it is found that the yield of *endo*-**3gk** is improved to 67% when dppp is used as a ligand (entry 2). Similarly, the reactions with NaOEt in EtOH and NaOBn in benzylalcohol afford the ethoxy- and benzyloxy-induced products *endo*-**3gl** and **3gm**, respectively (entries 6–8). In these reactions, better results are obtained when $Pd(PPh_3)_4$ is used as a catalyst (entries 7 and 8).

Conclusion

In conclusion, we have developed a cascade ring expansion reaction of cyclobutanols that have a propargylic moiety with nucleophiles. The propargylic carbonate can react with phenols and imides to produce the corresponding nucleophile-induced cyclopentanones. The ring rearrangement proceeds in a regio- and diastereoselective manner, and various substituted cyclopentanones can be synthesized along with the formation of a carbon–oxygen bond or a carbon–nitrogen bond. The reaction would provide a useful method to produce these compounds in one-step.

Experimental

General

All non-aqueous reactions were carried out under a positive atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocols. The phrase 'residue upon workup' refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. Cyclobutanone (**4a**) was purchased from Avocado Research Chemicals, and cyclobutanones **4b**,[11] **4c**[12] and **4d**[12] were prepared by the literature methods.

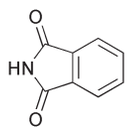
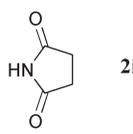
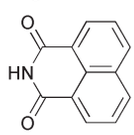
Synthesis of substrates for the palladium-catalysed cascade ring expansion reactions

1-[3-(2*H*-Tetrahydropyran-2-yloxy)-1-propynyl]cyclobutanol (5a). To a stirred solution of tetrahydro-2-(2-propynyloxy)-2*H*-pyran (2.40 ml, 17.1 mmol) and TMEDA (2.58 ml, 17.1 mmol) in THF (100 ml) was added dropwise a 1.54 M solution of BuLi in THF (11.1 ml, 17.1 mmol) at −78 °C. After the stirring was continued for 1 h at −78 °C, a solution of cyclobutanone **4a** (0.640 ml, 8.56 mmol) in THF (30 ml) was added dropwise to this reaction mixture, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and the mixture was extracted with Et_2O. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (85 : 15 v/v) as eluent to give the acetylenylcyclobutanol **5a** (1.44 g, 80%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3400, 2230; δ_H (300 MHz; $CDCl_3$) 1.53–1.90 (8H, m), 2.25 (2H, m), 2.38–2.48 (2H, m), 2.53–2.63 (1H, m), 3.52–3.59 (1H, m), 3.81–3.89 (1H, m), 4.28 (1H, d, J = 15.9 Hz), 4.37 (1H, d, J = 15.9 Hz), 4.84 (1H, t, J = 3.0 Hz); δ_C (75 MHz; $CDCl_3$) 12.7, 18.8, 25.2, 30.1, 38.2, 38.3, 54.3, 61.9, 67.6, 79.1, 89.7, 96.7; MS *m*/*z* (EI) 193 (M^+); (Found: C, 68.5; H, 8.55. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.65%).

Table 5 Reactions using nitrogen nucleophiles **2h–j**

1b

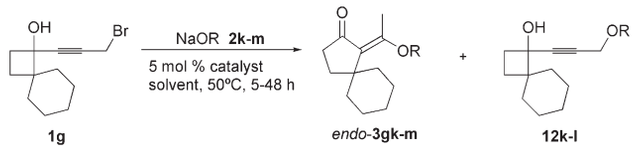
endo-**3bh-j**

Entry	$HN(COR)_2$	Temp./°C	Product	Yield (%)
1	 **2h**	100	*endo*-**3bh**	34
2	 **2i**	100	*endo*-**3bi**	44
3	 **2j**	100	*endo*-**3bj**	53

1-(3-Hydroxy-1-propynyl)cyclobutanol (6a). To a stirred solution of acetylenylcyclobutanol **5a** (377 mg, 1.79 mmol) in MeOH (15 ml) was added a catalytic amount of TsOH monohydrate at rt. After stirring was continued for 2 h at the same temperature, the reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (60 : 40 v/v) as eluent to give the diol **6a** (134 mg, 60%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3310, 2920, 2845; δ_H (300 MHz; $CDCl_3$) 1.75–1.89 (2H, m), 2.22–2.32 (2H, m), 2.37–2.46 (2H, m), 3.20 (1H, br s), 3.63 (1H, br s), 4.33 (2H, s); δ_C (75 MHz; $CDCl_3$) 12.7, 38.2, 50.8, 67.6, 81.6, 89.2; MS *m*/*z* (EI) 125 ($M^+ - 1$); HRMS *m*/*z* (EI) calcd for $C_7H_9O_2$ 125.0603 ($M^+ - 1$), found 125.0601.

1-(3-Methoxycarbonyloxy-1-propynyl)cyclobutanol (1a). To a stirred solution of diol **6a** (134 mg, 1.07 mmol) and pyridine (0.193 ml, 2.39 mmol) in CH_2Cl_2 (5 ml) was added dropwise methyl chloroformate (0.092 ml, 1.18 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and the mixture was extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt

Table 6 Reactions of **1g** with sodium alkoxides **2k**–**m** as nucleophiles



1g endo-3gk-m 12k-l

Entry	NaOR	Solvent	Catalyst	Yield (%) *endo*-**3**	Yield (%) **12**
1[a]	R = Me **2k**	MeOH	$Pd_2(dba)_3{\cdot}CHCl_3$ + dppe	12 (**3gk**)	21 (**12k**)
2[a]	**2k**	MeOH	$Pd_2(dba)_3{\cdot}CHCl_3$ + dppp	67	13
3[a]	**2k**	MeOH	$Pd_2(dba)_3{\cdot}CHCl_3$ + dppb	12	15
4[a]	**2k**	MeOH	$Pd_2(dba)_3{\cdot}CHCl_3$ + dppf	25	20
5	**2k**	MeOH	$Pd(PPh_3)_4$	56	24
6[a]	R = Et **2l**	EtOH	$Pd_2(dba)_3{\cdot}CHCl_3$ + dppp	12 (**3gl**)	17 (**12l**)
7	**2l**	EtOH	$Pd(PPh_3)_4$	50	9
8	R = Bn **2m**	BnOH	$Pd(PPh_3)_4$	85 (**3gm**)	0

[a] 20 mol% ligand was used.

(85 : 15 v/v) as eluent to give the propargylic carbonate **1a** (167 mg, 85%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3401, 2948, 2870, 2220, 1750; δ_H (300 MHz; $CDCl_3$) 1.71–1.91 (2H, m), 2.20–2.33 (2H, m), 2.36–2.48 (2H, m), 2.81 (1H, s), 3.83 (3H, s), 4.80 (2H, s); δ_C (75 MHz; $CDCl_3$) 12.7, 38.1, 55.1, 55.8, 67.6, 76.7, 91.1, 155.4; MS *m*/*z* (EI) 156 ($M^+ - 28$); (Found: C, 58.3; H, 6.25. $C_9H_{12}O_4$ requires C, 58.7; H, 6.55%).

1-[3-(2*H*-Tetrahydropyran-2-yloxy)cyclobutanol-2-spirocyclohexane (5b). By following the same procedure described for **5a**, the acetylenylcyclobutanol **5b** was prepared from the cyclobutanone **4b** in 72% yield on a 15 mmol scale. ν_{max}(neat)/cm^{-1} 3418, 2929, 2852; δ_H (300 MHz; $CDCl_3$) 1.13–1.89 (18H, m), 2.13 (1H, ddd, J = 12.0, 9.6 and 9.0 Hz), 2.25–2.38 (2H, m), 3.51–3.58 (1H, m), 3.81–3.89 (1H, m), 4.34 (2H, s), 4.86 (1H, t, J = 3.0 Hz); δ_C (75 MHz; $CDCl_3$) 18.7, 22.1, 22.6, 25.1, 25.2, 25.8, 30.0, 30.6, 33.1, 35.1, 47.6, 54.1, 61.7, 72.4, 81.3, 87.8, 96.2; MS *m*/*z* (EI) 278 ($M^+ - 28$); (Found: C, 72.95; H, 9.4. $C_{17}H_{26}O_3$ requires C, 73.35; H, 9.4%).

1-(3-Hydroxy-1-propynyl)cyclobutanol-2-spirocyclohexane (6b). By following the same procedure described for **6a**, the diol **6b** was prepared from **5b** in 87% yield on a 7.2 mmol scale. ν_{max}(neat)/cm^{-1} 3316, 2930, 2852, 2237; δ_H (300 MHz; $CDCl_3$) 1.10–1.75 (12H, m), 2.13 (1H, ddd, J = 12.0, 9.6 and 8.4 Hz), 2.30 (1H, ddd, J = 12.0, 9.0 and 5.1 Hz), 3.05 (2H, br s), 4.34 (2H, s); δ_C (75 MHz; $CDCl_3$) 22.1, 22.6, 25.2, 25.9, 30.5, 33.1, 35.1, 47.6, 50.6, 72.6, 84.0, 87.2; MS *m*/*z* (EI) 166 ($M^+ - 28$); (Found: C, 74.05; H, 9.4. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.35%).

1-(3-Methoxycarbonyloxy-1-propynyl)cyclobutanol-2-spirocyclohexane (1b). By following the same procedure described for **1a**, the propargyl carbonate **1b** was prepared from **6b** in 93% yield on a 3.0 mmol scale. ν_{max}(neat)/cm^{-1} 3460, 1750; δ_H (300 MHz; $CDCl_3$) 1.11–1.75 (12H, m), 2.05–2.18 (1H, m), 2.26–2.39 (2H, m), 3.82 (3H, s), 4.81 (2H, s); δ_C (75 MHz; $CDCl_3$) 22.3, 22.7, 25.4, 25.9, 30.7, 33.2, 35.2, 47.8, 55.1, 55.9, 72.7, 79.2, 89.4, 155.4; MS *m*/*z* 224 (EI) ($M^+ - 28$); (Found: C, 62.0; H, 7.65. $C_{14}H_{20}O_4$ requires C, 62.25; H, 7.6%).

[(1*R,2*S**) and (1*S**,2*S**)]-2-Phenyl-1-[3-(2*H*-tetrahydropyran-2-yloxy)-1-propynyl]cyclobutanol (*trans*-5c and *cis*-5c).** By following the same procedure described for **5a**, the acetylenylcyclobutanols *trans*-**5c** and *cis*-**5c** were prepared from **4c** on a 25 mmol scale. *trans*-**5c**: yield 33%; ν_{max}(neat)/cm^{-1} 3393, 2944, 2869; δ_H (300 MHz; $CDCl_3$) 1.39–1.62 (5H, m), 1.63–1.81 (1H, m), 1.97–2.07 (2H, m), 2.24 (1H, dt, J = 10.8 and 8.4 Hz), 2.34–2.40 (1H, m), 3.01 (1H, br s), 3.37–3.44 (1H, m), 3.60–3.71 (2H, m), 4.13 (2H, s), 4.37 (1H, s), 7.20–7.37 (5H, m); δ_C (75 MHz; $CDCl_3$) 16.7, 18.6, 25.1, 29.3, 35.3, 53.5, 53.9, 61.6, 73.2, 82.7, 86.7, 95.7, 126.5, 127.5, 127.5, 127.9, 127.9, 139.9; MS *m*/*z* (EI) 258 ($M^+ - 28$); HRMS *m*/*z* (EI) calcd for $C_{16}H_{18}O_3$ 258.1256 ($M^+ - 28$), found 258.1272.

cis-**5c**: yield 16%; ν_{max}(neat)/cm^{-1} 3402, 2945, 2868; δ_H (300 MHz; $CDCl_3$) 1.53–1.90 (7H, m), 2.12–2.25 (2H, m), 2.43–2.60 (2H, m), 3.50–3.59 (1H, m), 3.81–3.89 (2H, m), 4.34 (2H, dd, J = 15.9 and 5.7 Hz), 4.82–4.84 (1H, m), 7.24–7.40 (5H, m); δ_C (75 MHz; $CDCl_3$) 18.9, 20.8, 25.2, 30.1, 33.9, 51.6, 54.2, 61.9, 70.2, 80.2, 88.7, 96.8, 127.3, 128.3, 128.3, 128.6, 128.6, 137.3; MS *m*/*z* (EI) 258 ($M^+ - 28$); HRMS *m*/*z* (EI) calcd for $C_{16}H_{18}O_3$ 258.1256 ($M^+ - 28$), found 258.1258.

(1*R,2*S**)-1-(3-Hydroxy-1-propynyl)-2-phenylcyclobutanol (*trans*-6c).** By following the same procedure described for **6a**, the diol *trans*-**6c** was prepared from *trans*-**5c** in quantitative yield on a 4.8 mmol scale. ν_{max}(neat)/cm^{-1} 3317, 2988, 2946, 2869; δ_H (300 MHz; $CDCl_3$) 1.91–2.07 (2H, m), 2.21 (1H, dt, J = 10.5 and 9.0 Hz), 2.33 (1H, ddd, J = 10.5, 7.8 and 3.0 Hz), 2.51 (1H, br s), 3.60 (1H, t, J = 9.6 Hz), 3.74 (1H, br s), 3.98 (2H, s), 7.18–7.32 (5H, m); δ_C (75 MHz; $CDCl_3$) 16.9, 35.3, 50.5, 54.0, 73.2, 85.2, 86.4, 126.7, 127.7, 127.7, 127.9, 127.9, 139.8; MS *m*/*z* (EI) 174 ($M^+ - 28$); HRMS *m*/*z* (EI) calcd for $C_{11}H_{10}O_2$ 174.0681 ($M^+ - 28$), found 174.0702.

(1*R,2*S**)-1-(3-Methoxycarbonyloxy-1-propynyl)-2-phenylcyclobutanol (*trans*-1c).** By following the same procedure described for **1a**, the propargylic carbonate *trans*-**1c** was prepared from *trans*-**6c** in 81% yield on a 4.0 mmol scale. ν_{max}(neat)/cm^{-1} 3430, 1745; δ_H (300 MHz; $CDCl_3$) 1.94–2.10 (2H, m), 2.20–2.30 (1H, m), 2.34–2.43 (1H, m), 2.89 (1H, br s), 3.62 (1H, t, J = 9.6 Hz), 3.76 (3H, s), 4.58 (2H, s), 7.20–7.34 (5H, m); δ_C (75 MHz; $CDCl_3$) 17.0, 35.3, 50.6, 54.1, 64.3, 73.3, 85.3, 86.5, 126.8, 127.8, 127.8, 128.0, 128.0, 128.7, 139.9; MS *m*/*z* (EI) 232 ($M^+ - 28$); HRMS *m*/*z* (EI) calcd for $C_{13}H_{12}O_4$ 232.0735 ($M^+ - 28$), found 232.0702.

(1*R,2*S**)-1-Allenyl-2-phenylcyclobutanol (*cis*-7).** To a stirred suspension of LAH (4.8 mg, 0.126 mmol) in Et_2O (5 ml) was added dropwise a solution of acetylenylcyclobutanol *cis*-**5c** (30.0 mg, 0.105 mmol) in Et_2O (3 ml) at rt. After refluxing for 2 h, the reaction mixture was treated with the minimum amount of cold water, and filtered through Celite. The residue upon evaporation of the solvent was chromatographed with hexane–AcOEt (95 : 5 v/v) as eluent to give the allenyl alcohol *cis*-**7** (16.2 mg, 83%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3525, 3410, 1950; δ_H (300 MHz; $CDCl_3$) 1.55 (1H, s), 2.07–2.15 (2H, m), 2.28 (1H, dt, J = 12.4 and 7.7 Hz), 2.41–2.49 (1H, m), 3.69 (1H, t, J = 8.8 Hz), 4.93 (2H, dd, J = 6.6 and 2.2 Hz), 5.43 (1H,

t, J = 6.6 Hz), 7.24 (1H, t, J = 8.4 Hz), 7.26 (2H, d, J = 8.4 Hz), 7.34 (2H, d, J = 8.4 Hz); δ_C (75 MHz; $CDCl_3$) 20.3, 33.3, 49.9, 76.3, 78.7, 98.5, 126.9, 128.4, 128.4, 128.6, 128.6, 138.3, 206.4; MS *m/z* (EI) 185 ($M^+ - 1$); HRMS *m/z* (EI) calcd for $C_{13}H_{13}O$ 185.0966 ($M^+ - 1$), found 185.0971.

[(1*R,2*R**) and (1*S**,2*R**)]-2-Heptyl-1-[3-(2*H*-tetrahydropyran-2-yloxy-1-propynyl]cyclobutanol (*trans*-5d and *cis*-5d).** By following the same procedure described for **5a**, the diols *trans*-**5d** and *cis*-**5d** were prepared from **4d** on a 20 mmol scale. *trans*-**5d**: 48% yield; ν_{max}(neat)/cm^{-1} 3430, 2250; δ_H (300 MHz; $CDCl_3$) 0.87 (3H, t, J = 7.3 Hz), 1.21–1.45 (12H, m), 1.49–1.99 (9H, m), 2.05–2.16 and 2.28–2.40 (each 1H, each m), 2.45–2.56 (1H, m), 3.51–3.62 (1H, m), 3.83–3.90 (1H, m), 4.25–4.40 (2H, m), 4.79–4.85 (1H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 19.0, 19.1, 22.6, 25.3, 27.0, 29.3, 29.7, 30.2, 31.8, 35.7, 49.0, 54.2, 62.0, 71.8, 81.9, 87.0, 96.5; MS *m/z* 307 ($M^+ - 1$); HRMS calcd for $C_{19}H_{31}O_3$ 307.2270 ($M^+ - 1$), found 307.2240.

cis-**5d**: 29% yield; ν_{max}(neat)/cm^{-1} 3430, 2250; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 7.2 Hz), 1.23–1.45 (12H, m), 1.48–1.64 (6H, m), 1.75–1.90 (2H, m), 2.00–2.15 (1H, m), 2.24–2.35 (2H, m), 2.56 (1H, br s), 3.50–3.59 (1H, m), 3.82–3.90 (1H, m), 4.35 (2H, m), 4.85–4.88 (1H, m); δ_C (75 MHz; $CDCl_3$) 14.1, 19.0, 21.7, 22.7, 25.3, 26.8, 28.8, 29.3, 29.7, 30.2, 31.9, 35.0, 47.2, 54.4, 62.0, 69.1, 79.5, 89.8, 96.8; MS *m/z* (EI) 307 ($M^+ - 1$); HRMS *m/z* (EI) calcd for $C_{19}H_{31}O_3$ 307.2270 (M^+), found 307.2264.

[(1*R,2*R**) and (1*S**,2*R**)]-2-Heptyl-1-(3-hydroxy-1-propynyl)cyclobutanol (*trans*-6d and *cis*-6d).** By following the same procedure described for **6a**, the diols *trans*-**6d** and *cis*-**6d** were prepared from *trans*-**5d** and *cis*-**5d** on a 6.2 and 3.4 mmol scale, respectively. *trans*-**6d**: quantitative yield; ν_{max}(neat)/cm^{-1} 3400, 2230; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 7.2 Hz), 1.18–1.47 (13H, m), 1.52–1.67 (1H, m), 1.84 (1H, dq, J = 9.0 and 2.1 Hz), 2.06 (1H, dd, J = 10.5 and 9.0 Hz), 2.24–2.35 (2H, m), 2.77 (1H, br s), 4.35 (2H, s); δ_C (75 MHz; $CDCl_3$) 14.1, 19.1, 22.7, 27.0, 29.3, 29.7, 31.7, 31.8, 35.8, 49.1, 51.1, 71.9, 84.4, 86.8; MS *m/z* (EI) 193 (M^+–CH_2OH); (Found: C, 74.95; H, 10.8. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.8%).

cis-**6d**: quantitative yield; ν_{max}(neat)/cm^{-1} 3310, 2920, 2840, 2235; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 7.2 Hz), 1.19–1.45 (11H, m), 1.52–1.71 (2H, m), 1.89–2.00 (1H, m), 2.13 (1H, ddd, J = 12.0, 9.3 and 5.1 Hz), 2.34 (1H, dt, J = 12.0 and 7.5 Hz), 2.49 (1H, dt, J = 14.7 and 8.1 Hz), 2.91 (1H, br s), 2.98 (1H, br s), 4.31 (2H, s); δ_C (75 MHz; $CDCl_3$) 14.0, 21.5, 22.6, 26.8, 28.7, 29.3, 29.7, 31.9, 35.0, 47.2, 50.9, 69.0, 81.7, 89.6; MS *m/z* (EI) 193 ($M^+ - 31$); (Found: C, 74.9; H, 10.9. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.8%).

[(1*R,2*R**) and (1*S**,2*R**)]-2-Heptyl-1-(3-methoxycarbonyloxy-1-propynyl)cyclobutanol (*trans*-1d and *cis*-1d).** By following the same procedure described for **1a**, the propargylic carbonates *trans*-**1d** and *cis*-**1d** were prepared from *trans*-**6d** and *cis*-**6d** on a 3.1 and 2.4 mmol scale, respectively. *trans*-**1d**: yield 87%; ν_{max}(neat)/cm^{-1} 3400, 2230, 1750; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 6.9 Hz), 1.18–1.46 (12H, m), 1.53–1.66 (1H, m), 1.83 (1H, dq, J = 9.0 and 2.1 Hz), 2.05 (1H, dt, J = 10.5 and 9.0 Hz), 2.23–2.36 (2H, m), 2.56 (1H, s), 3.82 (3H, s), 4.82 (2H, s); δ_C (75 MHz; $CDCl_3$) 14.0, 19.0, 22.6, 26.9, 29.2, 29.6, 31.7, 31.8, 35.5, 49.0, 55.1, 55.8, 71.7, 79.4, 88.7, 155.4; MS *m/z* (EI) 254 ($M^+ - 28$); HRMS *m/z* (EI) calcd for $C_{14}H_{22}O_4$ 254.1518 ($M^+ - 28$), found 254.1563.

cis-**1d**: yield 89%; ν_{max}(neat)/cm^{-1} 3450, 2230, 1750; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 6.9 Hz), 1.19–1.45 (11H, m), 1.53–1.73 (2H, m), 1.89–2.01 (2H, m), 2.10 (1H, ddt, J = 12.0, 9.3 and 4.8 Hz), 2.35 (1H, dt, J = 12.0 and 8.4 Hz), 2.51 (1H, dt, J = 15.3 and 8.4 Hz), 3.82 (3H, s), 4.79 (2H, s); δ_C (75 MHz; $CDCl_3$) 14.0, 21.6, 22.6, 26.7, 28.7, 29.2, 29.7, 31.8, 34.8, 47.0, 55.1, 55.8, 68.9, 76.9, 91.3, 155.4; MS *m/z* (EI) 254 ($M^+ - 28$); HRMS *m/z* (EI) calcd for $C_{14}H_{22}O_4$ 254.1518 ($M^+ - 28$), found 254.1521.

1-(3-Acetoxy-1-propynyl)cyclobutanol-2-spirocyclohexane (1e). To a stirred solution of propargylic alcohol **6b** (300 mg, 1.54 mmol), pyridine (0.37 ml, 4.63 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (15 ml) was added dropwise Ac_2O (0.16 ml, 1.70 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and the mixture was extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (75 : 25 v/v) as eluent to give the propargylic acetate **1e** (201 mg, 85%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3463, 1743; δ_H (400 MHz; $CDCl_3$) 1.10–1.74 (10H, m), 1.98 (1H, br s), 2.10 (3H, s), 2.07–2.16 (2H, m), 2.28–2.32 (2H, m), 4.74 (2H, s); δ_C (75 MHz; $CDCl_3$) 22.2, 22.6, 25.3, 25.8, 30.6, 33.0, 35.0, 47.6, 54.9, 55.7, 72.4, 78.9, 89.1, 154.9; MS *m/z* (EI) 208 ($M^+ - 28$); HRMS *m/z* (EI) calcd for $C_{12}H_{16}O_3$ 208.1109 ($M^+ - 28$), found 208.1071.

1-(3-Benzoyloxy-1-propynyl)cyclobutanol-2-spirocyclohexane (1f). By following the same procedure described for **1e**, the propargylic benzoate **1f** was prepared from **6b** in 95% yield on a 3.0 mmol scale; colourless oil. ν_{max}(neat)/cm^{-1} 2929, 1724, 1269; δ_H (400 MHz; $CDCl_3$) 1.19–1.72 (10H, m), 2.04 (1H, br s), 2.10–2.17 (2H, m), 2.30–2.35 (2H, m), 5.00 (2H, s), 7.45 (2H, t, J = 7.2 Hz), 7.57 (2H, t, J = 7.2 Hz), 8.06 (2H, d, J = 7.2 Hz); δ_C (100 MHz; $CDCl_3$) 22.4, 22.8, 25.6, 26.0, 30.8, 33.3, 35.2, 47.8, 52.8, 52.9, 65.8, 72.8, 79.9, 88.6, 128.3, 129.5, 129.7, 133.1, 165.7; MS *m/z* (EI) 270 ($M^+ - 28$); HRMS *m/z* (EI) calcd for $C_{17}H_{18}O_3$ 270.1256 ($M^+ - 28$), found 270.1242.

1-(3-Bromo-1-propynyl)cyclobutanol-2-spirocyclohexane (1g). To a stirred solid of diol **6b** (720 mg, 3.70 mol) in CH_2Cl_2 (40 ml) were added CBr_4 (2.09 g, 6.30 mmol) and PPh_3 (1.84 g, 7.03 mmol) at rt. After stirring was continued for 2.5 h at the same temperature, the reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (80 : 20 v/v) as eluent to give the propargylic bromide **1g** (800 mg, 84%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3380, 2927, 2850; δ_H (400 MHz; $CDCl_3$) 1.19–1.73 (10H, m), 2.04 (1H, br s), 2.09–2.16 (2H, m), 2.27–2.33 (2H, m), 3.99 (2H, s); δ_C (100 MHz; $CDCl_3$) 14.7, 22.5, 22.9, 25.6, 26.0, 30.8, 33.4, 35.3, 48.2, 72.8, 81.0, 88.6; MS *m/z* (EI) 228 ($M^+ - 28$); HRMS *m/z* (EI) calcd for $C_{10}H_{17}OBr$ 228.0150 ($M^+ - 28$), found 228.0127.

General procedure for the palladium-catalysed cascade reaction of propargylic carbonates with phenols. Reaction of 1b with 2b (entry 4 in Table 2)

A slurry of the cyclobutanol *trans*-**1d** (35.8 mg, 0.127 mmol), *p*-cresol (**2b**) (16.4 mg, 0.152 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (6.6 mg, 6.4 μmol) and dppe (10.1 mg, 25.4 μmol) in dioxane (3 ml) was stirred for 1 h at 80 °C. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane–AcOEt (98 : 2 v/v) as eluent to give the cyclopentanone *trans*-**3db** (32.1 mg, 80%) as a colourless oil.

(*E*)-2-[1-(4-Methoxyphenoxy)ethylidene]cyclopentane (*endo*-3aa). Colourless oil; ν_{max}(neat)/cm^{-1} 2959, 2836, 1700, 1631; δ_H (300 MHz; $CDCl_3$) 1.88 (2H, quint, J = 7.5 Hz), 2.21 (3H, t, J = 1.8 Hz), 2.37 (2H, t, J = 7.5 Hz), 2.74 (2H, dt, J = 7.5 and 1.5 Hz), 3.80 (3H, s), 6.84–6.91 (4H, m); δ_C (75 MHz; $CDCl_3$) 15.0, 19.3, 27.2, 40.6, 55.5, 114.6, 117.4, 121.5, 147.3, 156.6, 161.8, 207.8; MS *m/z* (EI) 232 (M^+); HRMS *m/z* (EI) calcd for $C_{14}H_{16}O_3$ 232.1100 (M^+), found 232.1096.

(*E*)-2-[1-(4-Methylphenoxy)ethylidene]cyclopentane (*endo*-3ab). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 1.88 (2H, quint, J = 7.5 Hz), 2.23 (3H, t, J = 1.5 Hz), 2.34 (3H, s), 2.38 (2H, t, J = 7.5 Hz), 2.72 (2H, dt, J = 7.5 and 1.5 Hz),

6.84 (2H, d, J = 8.4 Hz), 7.13 (2H, d, J = 8.4 Hz); δ_C (75 MHz; $CDCl_3$) 15.4, 19.5, 20.7, 27.4, 40.8, 118.4, 120.1, 130.3, 134.2, 151.9, 161.5, 208.1; MS *m/z* (EI) 216 (M^+); HRMS *m/z* (EI) calcd for $C_{20}H_{16}O_2$ 216.1150 (M^+), found 216.1153.

2-[1-(4-Methylphenoxy)vinyl]cyclopentanone-3-spirocyclohexane (*exo*-3bb). Colourless oil; ν_{max}(neat)/cm^{-1} 1740; δ_H (300 MHz; $CDCl_3$) 1.30–1.79 (11H, m), 2.17–2.27 (1H, m), 2.32 (3H, s), 2.33–2.39 (2H, m), 2.79 (1H, s), 4.05 (1H, d, J = 2.1 Hz), 4.13 (1H, d, J = 2.1 Hz), 6.93 (2H, d, J = 8.4 Hz), 7.13 (2H, d, J = 8.4 Hz); δ_C (75 MHz; $CDCl_3$) 20.8, 22.5, 22.7, 26.0, 31.5, 32.3, 36.2, 37.9, 43.7, 64.6, 91.9, 121.3, 121.3, 130.2, 130.2, 134.2, 152.5, 159.7, 218.6; MS *m/z* (EI) 284 (M^+); HRMS *m/z* (EI) calcd for $C_{19}H_{24}O_2$ 284.1776 (M^+), found 284.1794.

(1*R,2*R**)-2-[1-(4-Methylphenoxy)vinyl]-3-phenylcyclopentanone (*trans*-3cb).** Colourless oil; ν_{max}(neat)/cm^{-1} 1740; δ_H (300 MHz; $CDCl_3$) 1.94–2.05 (1H, m), 2.27 (3H, s), 2.34–2.42 (2H, m), 2.49–2.57 (1H, m), 3.02 (1H, d, J = 12.0 Hz), 3.65–3.72 (1H, m), 3.89 (1H, dd, J = 2.5 and 1.0 Hz), 4.01 (1H, d, J = 2.5 Hz), 6.83 (2H, d, J = 8.5 Hz), 7.09 (2H, dd, J = 8.5 and 1.0 Hz), 7.20–7.26 (1H, m), 7.33–7.35 (4H, m); δ_C (75 MHz; $CDCl_3$) 21.1, 29.6, 39.2, 46.8, 62.9, 92.2, 121.6, 121.6, 127.4, 127.8, 127.8, 129.2, 129.2, 130.6, 130.6, 134.8, 142.8, 153.3, 159.6, 214.7; MS *m/z* (EI) 292 (M^+); HRMS *m/z* (EI) calcd for $C_{20}H_{20}O_2$ 292.1464 (M^+), found 292.1447.

(1*R,2*S**)-3-Heptyl-2-[1-(4-methylphenoxy)vinyl]cyclopentanone (*trans*-3db).** Colourless oil; ν_{max}(neat)/cm^{-1} 1740; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, J = 6.9 Hz), 1.20–1.53 (12H, m), 1.70–1.82 (1H, m), 2.20–2.35 (2H, m), 2.32 (3H, s), 2.36–2.56 (2H, m), 2.57 (1H, d, J = 10.8 Hz), 4.03 (1H, d, J = 2.1 Hz), 4.17 (1H, d, J = 2.1 Hz), 6.91–6.96 (2H, m), 7.10–7.16 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 20.7, 22.5, 26.9, 27.3, 29.1, 29.6, 31.7, 34.6, 38.5, 40.5, 61.8, 91.3, 120.2, 121.3, 130.1, 130.2, 134.0, 152.8, 159.9, 216.7; MS *m/z* (EI) 314 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_2$ 314.2246 (M^+), found 314.2232.

(1*R,2*S**)-3-Heptyl-2-[1-(4-methoxyphenoxy)vinyl]cyclopentanone (*trans*-3da).** Colourless oil; ν_{max}(neat)/cm^{-1} 1750; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, J = 6.9 Hz), 1.20–1.54 (12H, m), 1.69–1.81 (1H, m), 2.18–2.54 (4H, m), 2.56 (1H, d, J = 10.8 Hz), 3.79 (3H, s), 3.98 (1H, d, J = 2.1 Hz), 4.14 (1H, d, J = 2.1 Hz), 6.82–6.89 (2H, m), 6.94–7.00 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.1, 22.7, 27.0, 27.4, 29.2, 29.7, 31.9, 34.8, 38.6, 40.6, 55.6, 61.9, 91.0, 114.7, 114.8, 121.7, 122.6, 148.6, 156.7, 160.5, 216.8; MS *m/z* (EI) 330 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_3$ 330.2195 (M^+), found 330.2183.

(1*R,2*S**)-3-Heptyl-2-[1-(2,4,6-trimethylphenoxy)vinyl]cyclopentanone (*trans*-3dc).** Colourless oil; ν_{max}(neat)/cm^{-1} 1745; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, J = 6.9 Hz), 1.23–1.57 (12H, m), 1.76–1.88 (1H, m), 2.12 (6H, s), 2.25 (3H, s), 2.26–2.36 (2H, m), 2.37–2.49 (1H, m), 2.56 (1H, d, J = 10.8 Hz), 2.56–2.70 (1H, m), 3.72 (1H, d, J = 1.5 Hz), 3.99 (1H, d, J = 1.5 Hz), 6.83 (2H, s); δ_C (75 MHz; $CDCl_3$) 14.1, 15.9, 20.7, 22.7, 27.1, 27.3, 29.3, 29.7, 31.8, 34.7, 38.9, 40.7, 40.7, 61.6, 87.9, 129.3, 129.5, 129.5, 130.9, 134.5, 148.2, 156.5, 216.7; MS *m/z* (EI) 342 (M^+); HRMS *m/z* (EI) calcd for $C_{23}H_{34}O_2$ 342.2559 (M^+), found 342.2575.

(1*R,2*S**)-3-Heptyl-2-[1-(2-methoxyphenoxy)vinyl]cyclopentanone (*trans*-3dd).** Colourless oil; ν_{max}(neat)/cm^{-1} 1740; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, J = 6.9 Hz), 1.23–1.58 (12H, m), 1.75–1.88 (1H, m), 2.21–2.36 (2H, m), 2.37–2.50 (1H, m), 2.57 (1H, d, J = 10.8 Hz), 2.57–2.68 (1H, m), 3.81 (3H, s), 3.90 (1H, d, J = 2.4 Hz), 4.09 (1H, d, J = 2.4 Hz), 6.88–6.98 (2H, m), 7.03–7.16 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.1, 22.7, 27.1, 27.3, 29.3, 29.9, 31.9, 34.7, 38.8, 40.8, 56.0, 61.7, 89.7, 113.2, 121.2, 123.7, 125.9, 143.5, 152.0, 159.2, 216.7; MS *m/z* (EI) 330 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_3$ 330.2195 (M^+), found 330.2182.

(1*R,2*S**)-3-Heptyl-2-(1-phenoxyvinyl)cyclopentanone (*trans*-3de).** Colourless oil; ν_{max}(neat)/cm^{-1} 1745; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, J = 6.9 Hz), 1.20–1.53 (12H, m), 1.70–1.83 (1H, m), 2.16–2.36 (2H, m), 2.37–2.55 (2H, m), 2.58 (1H, d, J = 11.1 Hz), 4.06 (1H, d, J = 2.1 Hz), 4.21 (1H, d, J = 2.1 Hz), 7.02–7.17 (3H, m), 7.31–7.39 (2H, m); MS *m/z* (EI) 300 (M^+); HRMS *m/z* (EI) calcd for $C_{20}H_{28}O_2$ 300.2090 (M^+), found 300.2069.

(1*R,2*S**)-3-Heptyl-2-[1-(4-chlorophenoxy)vinyl]cyclopentanone (*trans*-3df) and (*E*)-3-heptyl-2-[1-(4-chlorophenoxy)ethylidene]cyclopentanone (*endo*-3df) (ratio of 68:32).** Colourless oil; ν_{max}(neat)/cm^{-1} 1742, 1700; δ_H (300 MHz; $CDCl_3$) 0.86 (0.96H, t, J = 6.9 Hz), 0.90 (2.04H, t, J = 6.9 Hz), 1.14–1.64 (12H, m), 1.70–1.81 (0.32H, m), 1.85–2.01 (0.32H, m), 2.22 (0.96H, s), 2.21–2.59 (3.36H, m), 3.10–3.21 (0.32H, m), 4.07 (0.68H, d, J = 2.7 Hz), 4.24 (0.68H, d, J = 2.7 Hz), 6.85–6.91 (0.64H, m), 7.28–7.34 (0.64H, m), 7.27–7.33 (2.72H, m); MS *m/z* (EI) 334 (M^+); HRMS *m/z* (EI) calcd for $C_{20}H_{27}O_2Cl$ 334.1700 (M^+), found 334.1701.

(1*S,2*S**)-3-Heptyl-2-[1-(4-methoxyphenoxy)vinyl]cyclopentanone (*cis*-3da).** Colourless oil; ν_{max}(neat)/cm^{-1} 1740; δ_H (300 MHz; $CDCl_3$) 0.88 (3H, t, J = 6.9 Hz), 1.21–1.56 (11H, m), 1.66–1.79 (1H, m), 1.87–2.03 (1H, m), 2.03–2.16 (1H, m), 2.20–2.50 (3H, m), 3.08 (1H, d, J = 9.0 Hz), 3.79 (3H, s), 3.95 (1H, d, J = 2.1 Hz), 4.14 (1H, d, J = 2.1 Hz), 8.83–8.88 (2H, m), 8.91–8.97 (2H, m); MS *m/z* (EI) 330 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_2$ 330.2195 (M^+), found 330.2198.

(1*S,2*S**)-3-Heptyl-2-[1-(2,4,6-trimethylphenoxy)vinyl]cyclopentanone (*cis*-3dc).** Colourless oil; ν_{max}(neat)/cm^{-1} 1745; δ_H (300 MHz; $CDCl_3$) 0.89 (3H, s), 1.20–1.60 (11H, m), 1.74–1.88 (2H, m), 2.01–2.15 (1H, m), 2.11 (6H, s), 2.24–2.53 (3H, m), 2.25 (3H, s), 3.10 (1H, d, J = 8.4 Hz), 3.74 (1H, d, J = 2.1 Hz), 4.02 (1H, d, J = 2.1 Hz), 6.83 (2H, s); MS *m/z* (EI) 342 (M^+); HRMS *m/z* (EI) calcd for $C_{23}H_{34}O_2$ 342.2559 (M^+), found 342.2544.

(*E*)-3-Heptyl-2-[1-(4-methoxyphenoxy)ethylidene]cyclopentanone (*endo*-3da). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 0.86 (3H, t, J = 6.9 Hz), 1.18–1.48 (11H, m), 1.57–1.69 (1H, m), 1.70–1.80 (1H, m), 1.85–2.00 (1H, m), 2.20 (3H, s), 2.29 (1H, ddd, J = 18.0, 8.7 and 2.7 Hz), 2.46 (1H, ddd, J = 18.0, 10.8 and 8.7 Hz), 3.15–3.25 (1H, m), 3.81 (3H, s), 6.88 (4H, s); δ_C (75 MHz; $CDCl_3$) 14.1, 15.3, 22.7, 24.5, 27.6, 29.3, 29.7, 31.9, 34.2, 38.5, 39.2, 55.7, 114.8, 114.8, 121.7, 121.7, 122.8, 147.5, 156.8, 162.3, 208.5; MS *m/z* (EI) 330 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_3$ 330.2195 (M^+), found 330.2200.

(*E*)-3-Heptyl-2-[1-(4-methylphenoxy)ethylidene]cyclopentanone (*endo*-3db). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 0.85 (3H, t, J = 6.9 Hz), 1.17–1.49 (11H, m), 1.56–1.69 (1H, m), 1.70–1.80 (1H, m), 1.85–2.00 (1H, m), 2.21 (3H, s), 2.29 (1H, ddd, J = 18.3, 8.7 and 3.0 Hz), 2.34 (3H, s), 2.46 (1H, ddd, J = 18.3, 10.8 and 8.7 Hz), 3.15–3.24 (1H, m), 6.80–6.86 (2H, m), 7.10–7.16 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 15.5, 20.7, 22.6, 24.5, 27.5, 29.3, 29.7, 31.8, 34.2, 38.5, 39.1, 120.3, 120.3, 123.5, 130.3, 130.3, 134.3, 151.8, 161.8, 208.4; MS *m/z* (EI) 314 (M^+); HRMS *m/z* (EI) calcd for $C_{21}H_{30}O_2$ 314.2246 (M^+), found 314.2208.

(*E*)-3-Heptyl-2-[1-(2,4,6-trimethoxyphenoxy)ethylidene]cyclopentanone (*endo*-3dc). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 0.86 (3H, t, J = 6.9 Hz), 1.20–1.52 (11H, m), 1.66–1.82 (2H, m), 1.85–2.01 (1H, m), 2.07 (3H, s), 2.09 (3H, s), 2.12 (3H, s), 2.27 (3H, s), 2.29 (1H, ddd, J = 18.3, 8.7 and 3.0 Hz), 2.47 (1H, ddd, J = 18.3, 11.4 and 8.7 Hz), 3.23–3.34 (1H, m), 6.86 (2H, d, J = 3.6 Hz); δ_C (75 MHz; $CDCl_3$) 14.0, 14.2, 16.0, 16.4, 20.7, 22.7, 24.5, 27.7, 29.3, 29.9, 31.9, 33.9, 38.6, 39.5, 119.8, 129.5, 129.5, 129.5, 130.6, 135.1, 148.1, 163.5, 208.3; MS *m/z* (EI) 342 (M^+); HRMS *m/z* (EI) calcd for $C_{23}H_{34}O_2$ 342.2559 (M^+), found 342.2543.

(*E*)-3-Heptyl-2-[1-(2-methoxyphenoxy)ethylidene]cyclopentanone (*endo*-3dd). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 0.85 (3H, t, J = 6.9 Hz), 1.20–1.50 (11H, m), 1.63–1.81 (2H, m), 1.86–2.00 (1H, s), 2.18 (3H, s), 2.28 (1H, ddd, J = 18.3, 8.1 and 2.7 Hz), 2.46 (1H, ddd, J = 18.3, 11.1 and 8.1 Hz), 3.22–3.32 (1H, m), 3.82 (3H, s), 6.90–6.99 (3H, m), 7.13–7.19 (1H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 14.6, 22.7, 24.4, 27.5, 29.3, 29.8, 31.9, 33.9, 38.6, 39.2, 55.7, 112.6, 121.1, 121.2, 122.6, 126.1, 142.5, 152.0, 163.4, 208.5; MS *m*/*z* (EI) 330 (M^+); HRMS *m*/*z* (EI) calcd for $C_{21}H_{30}O_3$ 330.2195 (M^+), found 330.2190.

(*E*)-3-Heptyl-2-(1-phenoxyethylidene)cyclopentanone (*endo*-3de). Colourless oil; ν_{max}(neat)/cm^{-1} 1710; δ_H (300 MHz; $CDCl_3$) 0.85 (3H, t, J = 6.9 Hz), 1.18–1.48 (11H, m), 1.56–1.68 (1H, m), 1.71–1.81 (1H, m), 1.86–2.02 (1H, m), 2.23 (3H, s), 2.30 (1H, ddd, J = 18.3, 8.7 and 3.0 Hz), 2.47 (1H, ddd, J = 18.3, 10.8 and 8.7 Hz), 3.16–3.24 (1H, m), 6.92–6.97 (2H, m), 7.16 (1H, t, J = 7.5 Hz), 7.31–7.39 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 15.6, 22.6, 24.5, 27.5, 29.3, 29.6, 31.8, 34.2, 38.4, 39.2, 120.3, 121.6, 124.2, 124.5, 129.8, 129.8, 154.2, 161.2, 208.5; MS *m*/*z* (EI) 300 (M^+); HRMS *m*/*z* (EI) calcd for $C_{20}H_{28}O_2$ 300.2090 (M^+), found 300.2130.

(*E*)-2-[1-(4-Chlorophenoxy)ethylidene]-3-heptylcyclopentanone (*endo*-3df). Colourless oil; ν_{max}(neat)/cm^{-1} 1700; δ_H (300 MHz; $CDCl_3$) 0.86 (3H, t, J = 6.9 Hz), 1.14–1.47 (11H, m), 1.51–1.64 (1H, m), 1.70–1.81 (1H, m), 1.85–2.01 (1H, m), 2.22 (3H, s), 2.30 (1H, ddd, J = 18.0, 8.4 and 3.0 Hz), 2.38–2.57 (1H, m), 3.10–3.21 (1H, m), 6.85–6.91 (2H, m), 7.28–7.34 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 15.6, 22.6, 24.4, 27.5, 29.3, 29.6, 31.8, 34.1, 38.4, 39.1, 121.3, 121.3, 125.0, 129.7, 129.9, 129.9, 152.8, 160.4, 208.4; MS *m*/*z* (EI) 334 (M^+); HRMS *m*/*z* (EI) calcd for $C_{20}H_{27}O_2Cl$ 334.1700 (M^+), found 334.1693.

(*E*)-3-Heptyl-2-[1-(4-nitrophenoxy)ethylidene]cyclopentanone (*endo*-3dg). Colourless oil; ν_{max}(neat)/cm^{-1} 1710, 1530, 1340; δ_H (300 MHz; $CDCl_3$) 0.85 (3H, t, J = 6.9 Hz), 1.14–1.58 (12H, m), 1.73–1.83 (1H, m), 1.86–2.04 (1H, m), 2.30 (3H, s), 2.34 (1H, ddd, J = 18.6, 9.0 and 3.0 Hz), 2.47 (1H, ddd, J = 18.6, 10.5 and 9.0 Hz), 3.02–3.12 (1H, m), 6.98–7.05 (2H, m), 8.23–8.29 (2H, m); δ_C (75 MHz; $CDCl_3$) 14.0, 16.1, 22.6, 24.4, 27.3, 29.2, 29.4, 31.8, 34.0, 38.2, 39.1, 118.4, 118.4, 126.1, 126.1, 128.4, 143.7, 157.9, 159.9, 208.2; MS *m*/*z* (EI) 345 (M^+); HRMS *m*/*z* (EI) calcd for $C_{20}H_{27}NO_4$ 345.1940 (M^+), found 345.1901.

(*E*)-2-[1-(4-Methoxyphenoxy)ethylidene]-1-methylcyclobutanol (8). To a stirred solution of cyclopentanone **3aa** (15.5 mg, 0.067 mmol) in THF (5 ml) was added dropwise MeLi in THF (1.02 M solution, 0.144 ml, 0.147 mmol) at −78 °C, and stirring was continued for 2 h at rt. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (85 : 15 v/v) as eluent to give the cyclopentanol **8** (10.7 mg, 64%) as a colourless oil. ν_{max}(neat)/cm^{-1} 3441, 2954, 1694, 1504; δ_H (300 MHz; $CDCl_3$) 1.16–1.29 (1H, m), 1.33 (3H, s), 1.34–1.63 (4H, m), 2.02 (3H, t, J = 1.8 Hz), 2.31–2.55 (2H, m), 3.32 (3H, s), 6.73–6.76 (2H, s), 6.87–6.93 (2H, m); MS *m*/*z* (EI) 248 (M^+); HRMS *m*/*z* (EI) calcd for $C_{15}H_{20}O_3$ 248.1412 (M^+), found 248.1416.

General procedure for the reaction of propargylic esters with phenols. Reaction of 1f with 2a (entry 2 in Table 4)

A slurry of the cyclobutanol **1f** (29.4 mg, 0.10 mmol), *p*-methoxyphenol (**2a**) (29.7 mg, 0.239 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.1 mg, 4.9 μmol), dppe (7.9 mg, 0.020 mmol) and DBU (70 μl, 0.49 mmol) in dioxane (1.5 ml) was stirred for 4 h at 80 °C. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane–AcOEt (90 : 10 v/v) as eluent to give the cyclopentanone *endo*-**3ba** (26.4 mg, 94%) as colourless needles.

(*E*)-[1-(4-Methoxyphenoxy)ethylidene]cyclopentanone-3-spirocyclohexane (*endo*-3ba). Colourless needles; mp 77–80 °C; ν_{max}(KBr)/cm^{-1} 2927, 2358, 1697, 1589; δ_H (400 MHz; $CDCl_3$) 1.46–1.63 (8H, m), 1.88 (2H, t, J = 8.0 Hz), 2.18–2.23 (2H, dt, J = 13.0 and 3.2 Hz), 2.23 (3H, s), 2.38 (2H, t, J = 8.0 Hz), 3.83 (3H, s), 6.90 (4H, s); δ_C (100 MHz; $CDCl_3$) 17.0, 22.6, 25.7, 29.3, 34.1, 38.3, 45.4, 55.7, 114.0, 121.2, 126.8, 147.2, 156.3, 163.6, 208.1; MS *m*/*z* (EI) 300 (M^+); HRMS *m*/*z* (EI) calcd for $C_{19}H_{24}O_3$ 300.1724 (M^+), found 300.1725.

General procedure for the reaction of the propargylic carbonate with imides. Reaction of 1b with 2j (entry 4 in Table 5).

A slurry of the cyclobutanol **1b** (39.9 mg, 0.158 mmol), 1,8-naphthalenedicarboximide (**2j**) (37.4 mg, 0.189 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (8.20 mg, 7.9 μmol) and dppe (12.8 mg, 0.03 mmol) in dioxane (1.5 ml) was stirred for 96 h at 100 °C. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane–AcOEt (60 : 40 v/v) as eluent to give the cyclopentanone *endo*-**3bj** (32.6 mg, 53%) as yellow needles.

(*E*)-2-(1-Phthalimidylethylidene)cyclopentanone-3-spirocyclohexane (*endo*-3bh). Colourless oil; ν_{max}(neat)/cm^{-1} 2925, 2358, 1714; δ_H (400 MHz; $CDCl_3$) 0.88 (2H, t, J = 7.0 Hz), 1.26–1.60 (10H, m), 1.93 (2H, t, J = 8.0 Hz), 2.36 (3H, s), 2.37 (2H, t, J = 8.0 Hz), 7.80 (2H, dd, J = 5.4 and 3.0 Hz), 7.92 (2H, dd, J = 5.4 and 3.0 Hz); δ_C (100 MHz; $CDCl_3$) 14.2, 20.7, 21.9, 34.1, 36.2, 46.6, 123.9, 132.0, 134.4, 137.0, 145.5, 208.0; MS *m*/*z* (EI) 323 (M^+); HRMS *m*/*z* (EI) calcd for $C_{20}H_{21}NO_3$ 323.1521 (M^+), found 323.1514.

(*E*)-2-(1-Succimidylethylidene)cyclopentanone-3-spirocyclohexane (*endo*-3bi). Colourless oil; ν_{max}(neat)/cm^{-1} 2931, 1708, 1618; δ_H (400 MHz; $CDCl_3$) 1.24–1.72 (10H, m), 1.90 (2H, t, J = 7.9 Hz), 2.28 (3H, s), 2.34 (2H, t, J = 7.9 Hz), 2.83 (4H, s); δ_C (100 MHz; $CDCl_3$) 20.0, 21.9, 25.9, 28.2, 28.8, 34.1, 36.1, 46.5, 137.7, 144.1, 175.8, 208.0; MS *m*/*z* (EI) 275 (M^+); HRMS *m*/*z* (EI) calcd for $C_{16}H_{21}NO_3$ 275.1521 (M^+), found 275.1506.

(*E*)-[1-(1,8-Naphthalenedicarboximidyl)ethylidene]cyclopentanone-3-spirocyclohexane (*endo*-3bj). Yellow needles, mp 263–265 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2927, 1705, 1662; δ_H (400 MHz; $CDCl_3$) 1.20–1.60 (10H, m), 1.92 (2H, t, J = 8.0 Hz), 2.38 (2H, t, J = 8.0 Hz), 2.49 (3H, s), 7.88 (2H, t, J = 7.1 Hz), 8.28 (2H, d, J = 7.1 Hz), 8.62 (2H, t, J = 7.1 Hz); δ_C (100 MHz; $CDCl_3$) δ 20.9, 21.9, 25.7, 28.2, 33.7, 36.3, 46.7, 122.4, 127.0, 128.3, 131.5, 131.7, 134.4, 141.6, 141.9, 163.4, 208.4; MS *m*/*z* (EI) 373 (M^+); HRMS *m*/*z* (EI) calcd for $C_{24}H_{23}NO_3$ 373.1696 (M^+), found 373.1664.

General procedure for the reaction of propargylic bromide. Reaction of propargylic bromide with NaOMe. Reaction of 1g with 2k (entry 5 in Table 6)

To a slurry of the cyclobutanol **1g** (35.4 mg, 0.138 mmol) and $Pd(PPh_3)_4$ (15.8 mg, 0.014 mmol) in MeOH (1.5 ml) was added NaOMe (11.9 mg, 0.030 mmol), and the reaction mixture was stirred for 24 h at 50 °C. After evaporation of the solvent, the reaction mixture was extracted with AcOEt. The combined extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (70 : 30 v/v) as eluent to give the cyclopentanone *endo*-**3gk** (16.0 mg, 56%) as a colourless oil.

(*E*)-(1-Methoxyethylidene)cyclopentanone-3-spirocyclohexane (*endo*-3gk). Colourless oil; ν_{max}(neat)/cm^{-1} 2925, 1687, 1589; δ_H (400 MHz; $CDCl_3$) 1.17–1.66 (8H, m), 1.75 (2H, t, J = 8.1 Hz), 2.09 (2H, dt, J = 13.2 and 3.9 Hz), 2.28 (2H, t, J = 8.1 Hz), 3.11 (3H, s), 3.74 (3H, s); δ_C (100 MHz; $CDCl_3$) 13.7, 22.7, 25.8, 29.2, 33.8, 38.4, 45.4, 53.9, 122.8, 166.7, 207.7; MS *m*/*z* (EI) 208 (M^+); HRMS *m*/*z* (EI) calcd for $C_{13}H_{20}O_2$ 208.1463 (M^+), found 208.1434.

1-(3-Methoxy-1-propynyl)cyclobutanol-2-spirocyclohexane (12k). Colourless oil; ν_{max}(neat)/cm^{-1} 3421, 2927; δ_H (400 MHz; $CDCl_3$) 1.18–1.74 (10H, m), 1.97 (1H, br s), 2.09–2.20 (2H, m), 2.29–2.35 (2H, m), 3.39 (3H, s), 4.17 (2H, s); MS *m*/*z* (EI) 208 (M^+); HRMS *m*/*z* (EI) calcd for $C_{13}H_{20}O_2$ 208.1463 (M^+); found 208.1454.

(*E*)-(1-Ethoxyethylidene)cyclopentanone-3-spirocyclohexane (*endo*-3gl). Yellow oil; ν_{max}(neat)/cm^{-1} 2927, 1685, 1589; δ_H (400 MHz; $CDCl_3$) 1.36 (3H, t, J = 7.1 Hz), 1.08–1.15 (8H, m), 1.75 (2H, t, J = 8.1 Hz), 2.16 (2H, dt, J = 8.7 and 4.7 Hz), 2.47 (3H, s), 4.04 (2H, q, J = 7.1 Hz); δ_C (100 MHz; $CDCl_3$) 14.2, 15.0, 22.0, 26.0, 29.3, 38.3, 45.3, 56.5, 60.9, 62.4, 67.4, 122.5, 166.4, 196.8; MS *m*/*z* (EI) 222 (M^+); HRMS *m*/*z* (EI) calcd for $C_{14}H_{22}O_2$ 222.1620 (M^+), found 222.1603.

1-(3-Ethoxy-1-propynyl)cyclobutanol-2-spirocyclohexane (12l). Colourless oil; ν_{max}(neat)/cm^{-1} 3421, 2927, 2852; δ_H (400 MHz; $CDCl_3$) 1.23 (3H, t, J = 7.1 Hz), 1.28–1.73 (8H, m), 1.97–2.02 (2H, m), 2.02–1.97 (2H, m), 2.09–2.16 (2H, m), 2.28–2.35 (2H, m), 3.58 (3H, q, J = 7.1 Hz); MS *m*/*z* (EI) 194 (M^+); HRMS *m*/*z* (EI) calcd for $C_{12}H_{18}O_2$ 194.1333 (M^+), found 194.1293.

(*E*)-(1-Benzyloxyethylidene)cyclopentanone-3-spirocyclohexane (*endo*-3gm). Yellow oil; ν_{max}(neat)/cm^{-1} 2931, 1705, 1664; δ_H (400 MHz; $CDCl_3$) 1.32–1.60 (8H, m), 1.74 (2H, t, J = 8.2 Hz), 2.16 (2H, dt, J = 13.6 and 4.0 Hz), 2.27 (2H, t, J = 8.2 Hz), 2.52 (3H, s), 5.05 (2H, s), 7.29–7.38 (5H, m); δ_C (100 MHz; $CDCl_3$) 14.4, 22.7, 25.8, 29.3, 33.7, 38.4, 45.4, 68.5, 123.0, 127.0, 127.9, 128.5, 136.4, 167.0, 208.0; MS *m*/*z* (EI) 284 (M^+); HRMS *m*/*z* (EI) calcd for $C_{19}H_{24}O_2$ 284.1776 (M^+), found 284.1766.

Acknowledgements

This work was supported in part by the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists (M. Y.) and Scientific Research on Priority Areas (A) "Exploitation of Multi Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 J. Tsuji, *Palladium Reagents and Catalysts*, John Wiley & Sons Ltd, England, 2004, p. 543.
2 For reviews on palladium-catalysed reactions of propargylic compounds: (*a*) J. Tsuji and I. Minami, *Acc. Chem. Res.*, 1987, **20**, 140; (*b*) I. Minami, M. Yuhara, H. Watanabe and J. Tsuji, *J. Organomet. Chem.*, 1987, **334**, 225; (*c*) J. Tsuji and T. Mandai, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2589.
3 For recent examples of palladium-catalysed reactions of propargylic compounds with soft nucleophiles, see: (*a*) C. Fournier-Nguefack, P. Lhoste and D. Sinou, *Synlett*, 1996, 553; (*b*) M. Yoshida, H. Nemoto and M. Ihara, *Tetrahedron Lett.*, 1999, **40**, 8583; (*c*) J.-R. Labrosse, P. Lhoste and D. Sinou, *Tetrahedron Lett.*, 1999, **40**, 9025; (*d*) J.-R. Labrosse, P. Lhoste and D. Sinou, *Org. Lett.*, 2000, **2**, 527; (*e*) Y. Kozawa and M. Mori, *Tetrahedron Lett.*, 2001, **42**, 4869; (*f*) M. Yoshida and M. Ihara, *Angew. Chem. Int. Ed.*, 2001, **40**, 616; (*g*) Y. Kozawa and M. Mori, *Tetrahedron Lett.*, 2002, **43**, 1499; (*h*) C. Damez, J.-R. Labrosse, P. Lhoste and D. Sinou, *Tetrahedron Lett.*, 2003, **44**, 557; (*i*) Y. Kozawa and M. Mori, *J. Org. Chem.*, 2003, **68**, 8068; (*j*) M. Yoshida, M. Fujita, T. Ishii and M. Ihara, *J. Am. Chem. Soc.*, 2003, **125**, 4874; (*k*) M. Yoshida, M. Fujita and M. Ihara, *Org. Lett.*, 2003, **5**, 3325; (*l*) M. Yoshida, Y. Morishita, M. Fujita and M. Ihara, *Tetrahedron Lett.*, 2004, **45**, 1861.
4 (*a*) P. Boontanonda and R. Grigg, *J. Chem. Soc., Chem. Commun.*, 1977, 583; (*b*) G. R. Clark and S. Thiensathit, *Tetrahedron Lett.*, 1985, **26**, 2503; (*c*) M. Demuth, B. Pandey, B. Wietfeld, H. Said and J. Viader, *Helv. Chim. Acta*, 1988, **71**, 1392; (*d*) L.-C. de Almeida Barbosa and J. Mann, *J. Chem. Soc., Perkin Trans. 1*, 1990, 177; (*e*) S. Kim, K. H. Uh, S. Lee and J. H. Park, *Tetrahedron Lett.*, 1991, **32**, 3395; (*f*) H. Nemoto, J. Miyata and K. Fukumoto, *Tetrahedron*, 1996, **52**, 10363; (*g*) H. Nemoto, M. Nagamochi and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 1993, **2329**; (*h*) H. Nemoto, M. Nagamochi, H. Ishibashi and K. Fukumoto, *J. Org. Chem.*, 1994, **59**, 74; (*i*) H. Nemoto, J. Miyata and M. Ihara, *Tetrahedron Lett.*, 1999, **40**, 1933; (*j*) H. Nemoto, E. Takahashi and M. Ihara, *Org. Lett.*, 1999, **1**, 517; (*k*) T. Nishimura, K. Ohe and S. Uemura, *J. Am. Chem. Soc.*, 1999, **121**, 2645.
5 (*a*) H. Nemoto, M. Shiraki and K. Fukumoto, *Synlett*, 1994, **599**; (*b*) H. Nemoto, J. Miyata, M. Yoshida, N. Raku and K. Fukumoto, *J. Org. Chem.*, 1997, **62**, 7850; (*c*) H. Nemoto, M. Yoshida, K. Fukumoto and M. Ihara, *Tetrahedron Lett.*, 1999, **40**, 907; (*d*) M. Yoshida, M. A.-H. Ismail, H. Nemoto and M. Ihara, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2629.
6 (*a*) H. Nemoto, M. Yoshida and K. Fukumoto, *J. Org. Chem.*, 1997, **62**, 6450; (*b*) M. Yoshida, K. Sugimoto and M. Ihara, *Tetrahedron Lett.*, 2000, **41**, 5089; (*c*) M. Yoshida, K. Sugimoto and M. Ihara, *Tetrahedron*, 2002, **58**, 7839; (*d*) M. Yoshida, K. Sugimoto and M. Ihara, *Tetrahedron Lett.*, 2001, **42**, 3877.
7 (*a*) L. S. Liebeskind, D. Mitchell and B. S. Foster, *J. Am. Chem. Soc.*, 1987, **109**, 7908; (*b*) D. Mitchell and L. S. Liebeskind, *J. Am. Chem. Soc.*, 1990, **112**, 291; (*c*) R. C. Larock and C. K. Reddy, *Org. Lett.*, 2000, **2**, 3325; (*d*) R. C. Larock and C. K. Reddy, *J. Org. Chem.*, 2002, **67**, 2027; (*e*) M. Yoshida, K. Sugimoto and M. Ihara, *ARKIVOC*, 2003, xiii, 35.
8 M. Yoshida, K. Sugimoto and M. Ihara, *Org. Lett.*, 2004, **6**, 1979.
9 For a review about palladium-catalysed cascade ring expansion reactions, see: M. Yoshida, *J. Pharm. Soc. Jpn.*, 2004, **124**, 425.
10 A part of the results about our preliminary studies have been published: M. Yoshida, H. Nemoto and M. Ihara, *Tetrahedron Lett.*, 1999, **40**, 8583.
11 (*a*) J. R. Wiseman and H.-F. Chan, *J. Am. Chem. Soc.*, 1970, **92**, 4749; (*b*) B. M. Trost, R. LaRochelle and M. J. Bogdanowicz, *Tetrahedron Lett.*, 1970, **39**, 3449.
12 H. Nemoto, M. Shiraki and K. Fukumoto, *J. Org. Chem.*, 1996, **61**, 1347.
13 K. Tsutsumi, T. Kawase, K. Kakiuchi, S. Ogoshi, Y. Okada and H. Kurosawa, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2687.
14 DBU was added as a base to neutralise HX which is formed by the reaction.
15 (*a*) H. Ohno, H. Hamaguchi, M. Ohata and T. Tanaka, *Angew. Chem. Int. Ed.*, 2003, **42**, 1749; (*b*) H. Ohno, H. Hamaguchi, M. Ohata, S. Kosaka and T. Tanaka, *J. Am. Chem. Soc.*, 2004, **126**, 8744.