Stereoselective Synthesis of *anti*-1,4-Diols by a $BH_3 \cdot THF$-Mediated Rearrangement of 1,2-Disubstituted Cyclobutenes

Kolja M. Knapp,[a] Bernd Goldfuss,[b] and Paul Knochel*[a]

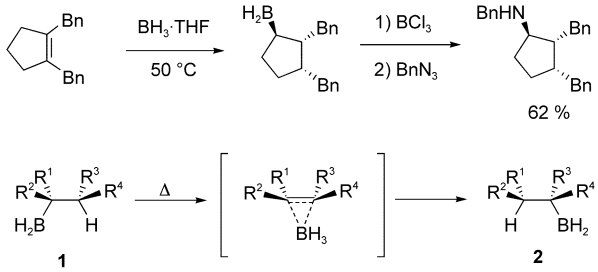
Abstract: A new stereoselective rearrangement of cyclobutylboranes, obtained by the hydroboration of 1,2-disubstituted cyclobutenes, provides *anti*-1,4-diols with good-to-excellent diastereoselectivity. The mechanism of the rearrangement is discussed based on theoretical calculations.

Keywords: alcohols · boracycles · cyclobutenes · diols · hydroboration · stereoselective rearrangement

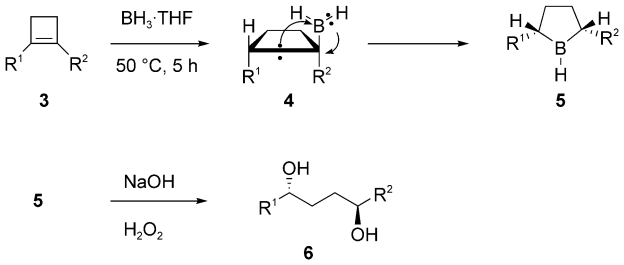
Introduction

The performance of stereoselective synthesis in open-chain systems is an active field of research.[1] Recently, we have reported that the addition of $BH_3 \cdot THF$ to tetrasubstituted cyclic[2] or acyclic[3] alkenes leads to sterically hindered organoboranes that undergo stereoselective 1,2-migrations at 50–60 °C. This rearrangement allows the control of up to three adjacent chiral centers (Scheme 1).[4] A wide range of tetrasubstituted cyclohexenes and cyclopentenes undergo a *syn*-migration for which the driving force is the release of steric strain (**1** → **2**; Scheme 1).

Another reaction pathway is observed with cyclobutene derivatives of type **3**. In this case, the hydroboration product **4** undergoes a stereoselective rearrangement leading to the borolane of type **5**. After oxidation under basic conditions, the corresponding *anti*-1,4-diol **6** is obtained with good stereoselectivity (Scheme 2).



Scheme 1. Stereoselective migration of tertiary organoboranes in cyclic systems.



Scheme 2. Stereoselective preparation of 1,4-diols (**6**).

Herein, we report the scope of this stereoselective synthesis of *anti*-1,4-diols[5] as well as a theoretical study concerning the stereoselective nature of the rearrangement.

Results and Discussion

1,2-Disubstituted cyclobutenes of type **3** were prepared according to literature methods. We used 1,2-diphenylsulfonyl-1-cyclobutene (**7**)[6] for the selective introduction of two substituents in positions 1 and 2 of the cyclobutene. Thus, the treatment of the disulfone **7** with an arylmagnesium compound at 0 °C in THF gives selectively the monosubstituted cyclobutenes of type **8** (Scheme 3). Reaction with PhLi produces the symmetrical cyclobutene **3a** in 88% yield (entry 1 of Table 1). Reaction with the CF_3-substituted cyclobutene precursor **8c** gave the unsymmetrical cyclobutene **3b** (entry 2).

Functionalised organolithium derivatives, such as 4-cyanophenyllithium,[7] undergo the addition–elimination reaction at −78 °C leading to the functionalised cyclobutene **3c** in 69% yield (entry 3). Alkyllithium compounds, such as MeLi and

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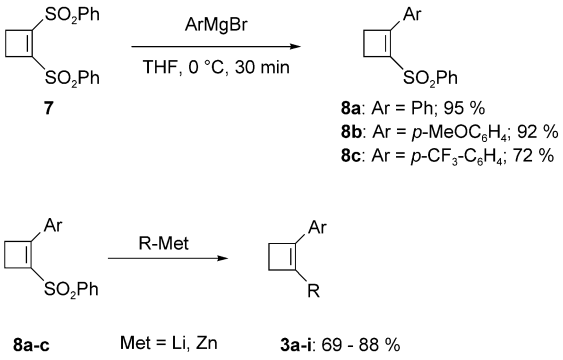


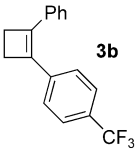
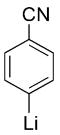
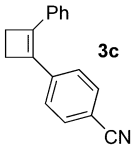
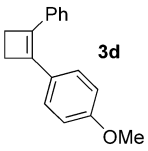
Scheme 3. Preparation of 1,2-disubstituted cyclobutenes.

EtLi, react in good yields providing cyclobutenes **3e**,**f** in 79–84% yield (entries 5 and 6, respectively). Organozinc derivatives, such as $i\mathrm{Pr_2Zn}$,[8] react under copper catalysis after transmetallation with $\mathrm{CuCN \cdot 2\,LiCl}$ to give the isopropyl-substituted cyclobutene **3g** in 74% yield (entry 7). Even the reactive tertiary organolithium reagent *t*BuLi reacts well with **8a** to afford the corresponding cyclobutene **3h** in 73% yield (entry 8). Finally, the reaction of the silyl-centred lithium species ($\mathrm{PhMe_2SiLi}$)[9] with **8a** produces the alkenylsilane **3i** in 79% yield (entry 9). 1,2-Dialkyl-substituted cyclobutenes **3j** and **3k** were prepared by cycloalkylation according to Negishi.[10] Thus, the reaction of 5-decyne or 5-undecyne with $[\mathrm{Cp_2ZrCl_2}]$ (1 equiv) and EtMgBr (2 equiv) in THF at $-78\,^{\circ}\mathrm{C}$ followed by iodolysis produces the intermediate diiodides **9a,b**, which, after treatment with BuLi (1 equiv, diethyl ether, $-78\,^{\circ}\mathrm{C}$), furnished the 1,2-disubstituted cyclobutenes **3j** and **3k**, respectively, in 68–71% yield (Scheme 4).

Finally, the 1,4-diferrocenyl ketone **10**[11] was subjected to McMurry reaction conditions[12] ($\mathrm{TiCl_4}$, Zn, THF/pyridine, 25 °C, 5 h) to provide the diferrocenyl cyclobutene **3l** in 56% yield (Scheme 5).

The reaction of the cyclobutenes **3a–l** with $\mathrm{BH_3 \cdot THF}$ (1.1 equiv) was usually complete after 5–16 h at 40–50 °C. The resulting intermediate borolane of type **5** (Scheme 2) was treated with $\mathrm{NaOH/H_2O_2}$ to give the expected *anti*-1,4-diols of type **6** in 65–89% (Table 2). In most cases, excellent diastereoselectivities were obtained. In the case of the cyclobutene **3a** and related diarylcyclobutenes, such as **3b** and **3d**, the diastereomeric ratio (*dr*) was >98:2 in favour of the *anti*-diol (entries 1, 2 and 4 of Table 2). In the case of **3c**, $\mathrm{BH_3 \cdot THF}$ also reduces the cyano group leading to the 4-aminomethylphenyl-substituted *anti*-1,4-diol with a diastereoselectivity of >98:2 and a yield of 71%. Cyclobutenes bearing an alkyl and an aryl substituent also smoothly rearrange to give the expected *anti*-1,4-diols **6e–h** in satisfactory yields. In the case of a *tert*-butyl-substituted system, a lower stereoselectivity is observed (*anti*:*syn* = 80:20). A remarkably smooth reaction is observed with cyclobutenylsilane **3i** to afford the *anti*-1,4-diol **6i** in 69% yield and *dr* > 98:2 (entry 9). Similarly, 1,2-dialkylcyclobutenes **3j** and **3k** furnish only the *anti*-1,4-diols **6j** and **6k**, respectively, 79–84% yield and *dr* > 98:2. Finally, the 1,2-diferrocenylcyclobutene **3l** leads to the *anti*-ferrocenyldiol **6l** in 65% (*dr* > 98:2; entry 12 of Table 2).

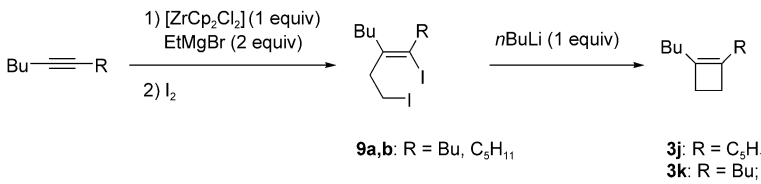
Table 1. Preparation of 1,2-disubstituted cyclobutenes (**3**) from the cyclobutenyl sulfones **8a–c**.

Entry	Sulfone **8**	Organometallic reagent	Cyclobutene **3**	Yield [%][a]
1	**8a**	PhLi	 **3a**	88
2	**8c**	PhLi	 **3b**	77
3	**8a**		 **3c**	69
4	**8b**	PhLi	 **3d**	82
5	**8a**	MeLi	 **3e**	84
6	**8a**	EtLi	 **3f**	79
7	**8a**	$i\mathrm{Pr_2Zn}$	 **3g**	74
8	**8a**	*t*BuLi	 **3h**	73
9	**8a**	$\mathrm{Me_2PhSiLi}$	 **3i**	79

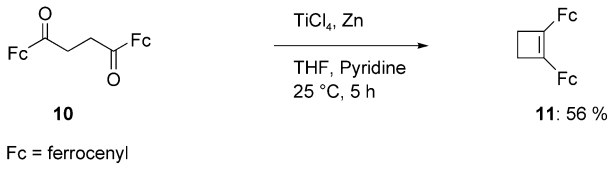
[a] Isolated yield of analytically pure products.

The observed diastereoselectivity of the rearrangement may be explained as shown in Schemes 1 and 6. The driving force of this rearrangement is certainly the release of steric strain, but may also be due to the electrophilic nature of the tertiary organoborane **4**, which is isoelectronic with a carbenium ion, such as **11**, and is therefore a strong electrophilic centre.

Whereas the rearrangement of the carbenium ion **11** is well

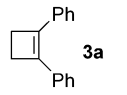
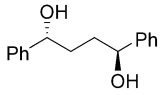
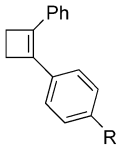
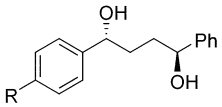
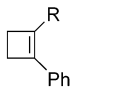
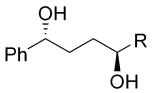
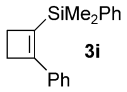
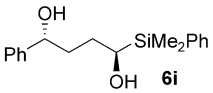
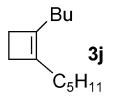
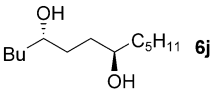
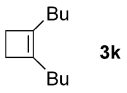
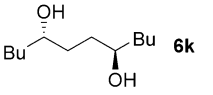
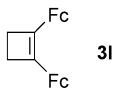
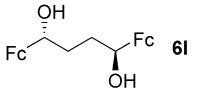


Scheme 4. Synthesis of cyclobutenes **3j**, **3k** according to Negishi.

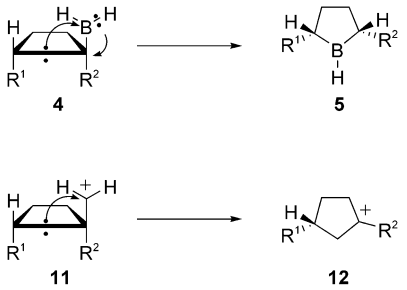


Scheme 5. Preparation of 1,2-diferrocenylcyclobutene **3l**.

Table 2. *anti*-1,4-Diols of type **6** obtained by the thermal rearrangement of the hydroboration product of 1,2-disubstituted cyclobutenes of type **3**.

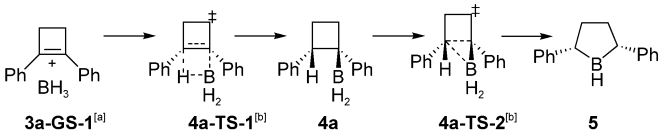
Entry	Cyclobutene **3**	*anti*-1,4-diol **6**	*anti*:*syn* Ratio	Yield [%][a]
1	 **3a**	 **6a**	>98:2	89
				
2	**3b:** R = CF_3	**6b**: R = CF_3	>98:2	89
3	**3c**: R = CN	**6c**: R = CH_2NH_2	>98:2	71
4	**3d**: R = OMe	**6d**: R = OMe	>98:2	89
				
5	**3e**: R = Me	**6e**: R = Me	>98:2	79
6	**3f**: R = Et	**6f**: R = Et	>98:2	82
7	**3g**: R = *i*Pr	**6g**: R = *i*Pr	95:5	72
8	**3h**: R = *t*Bu	**6h**: R = *t*Bu	80:20	69
9	 **3i**	 **6i**	>98:2	69
10	 **3j**	 **6j**	>98:2	79
11	 **3k**	 **6k**	>98:2	84
12	 **3l**	 **6l**	>98:2	65

[a] Isolated yield of analytically pure products.



Scheme 6. Analogous rearrangement of cyclobutylboranes and methylcyclobutyl carbenium ions.

known,[13] the rearrangement of cyclobutylborane **4** is new. To elucidate the nature of this unprecedented borane rearrangement and explain the observed diastereoselectivity as well as the regiochemistry of the hydroboration, ground state (GS) and transition structures (TS) were optimised and analysed by means of the ONIOM B3LYP/6-311++G^{++}//MNDO method (Scheme 7).[14–17] The structures for the reactions of the cyclobutenes **3a** and **3e** including the two possible initial hydroboration products of **3e** were studied (Table 3, Scheme 8).

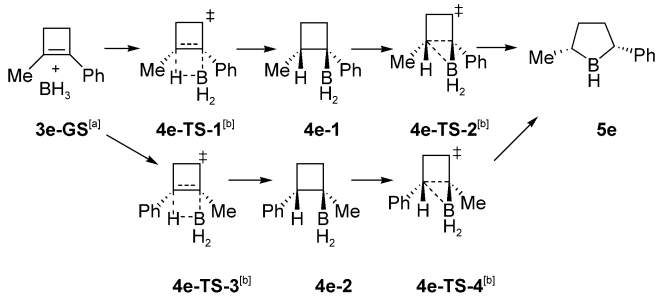


Scheme 7. Hydroboration and borane rearrangement sequence. a) Ground state structure. b) Transition state structure.

Table 3. Absolute [a.u.] and relative energies of ground and transition structures of the hydroboration borane rearrangement sequence with **3a**.[a]

	E_{tot} [a.u.]	E_{rel} [kJ mol^{-1}]
3a-GS-1	−105.15231	0.0
4a-TS-1	−105.12680	66.9
4a	−105.16422	−31.4
4a-TS2	−105.13886	35.2 (E_a: 66.5)[b]
5	−105.21836	−173.2

[a] Oniom (B3LYP/6−311++G**//MNDO). [b] Activation energy.



Scheme 8. Hydroboration and borane rearrangement sequence. a) Ground state structure. b) Transition state structure.

The calculations show that the activation energies for the rearrangement **4a-TS-2**, **4e-TS-2**, **4e-TS-4** are not higher or just slightly higher than those of the hydroboration **4a-TS-1**, **4e-TS-3**, **4e-TS-4** itself. Furthermore, the final borolane **5a** and **5e** are more favourable by at least 120 kJ mol^{-1} than the corresponding cyclobutylboranes **4**.

The borane rearrangement proceeds from **4a** by migration of the C–C electronic bond density to the electrophilic boron atom through **4a-TS-2** (Figure 1, Table 4, Scheme 9), analogous to Wagner–Meerwein rearrangements. Formally, a zwitterionic five-membered ring $R_3C{-}BH_2{-}C^+R_2$ is formed, which could not be found computationally, but instantly rearranges via a 1,2-H shift to the final borolane product **5** (Scheme 9).

The geometry of the substituents at carbon C1 of **4a-TS-1** is almost planar (172.5°), which would suggest a carbenium ion

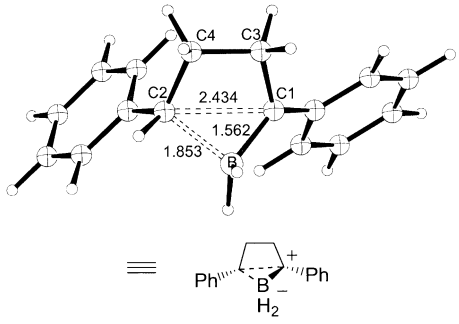
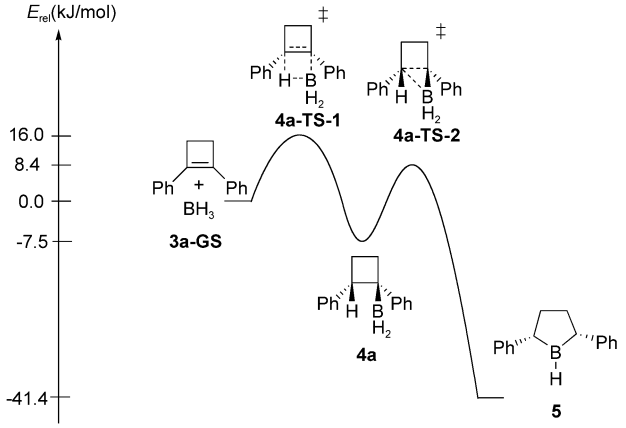


Figure 1. Transition state structure **4a-TS-2** of the borane rearrangement.

Table 4. Absolute [a.u.] and relative energies of ground and transition structures of the hydroboration borane rearrangement sequence with **3e**.[a]

	E_{tot} [a.u.]	E_{rel} [kJ mol^{-1}]
3e-GS	−105.20623	0.0
4e-TS-1	−105.18407	58.2
4e-TS-3	−105.18365	59.4
4e-1	−105.22125	−39.3
4e-2	−105.22596	−51.9
4e-TS-2	−105.19444	31.0 (E_a: 70.3)[b]
4e-TS-4	−105.19095	40.2 (E_a: 92.0)[b]
5e	−105.27385	−177.4

[a] Oniom (B3LYP/6−311++G**//MNDO). [b] Activation energy.



Scheme 9. Energy diagram for the hydroboration borane rearrangement sequence.

and thus a zwitterionic structure for the transition state. The dihedral angle of the atoms C3, C4, C1, B is 32.4°. Since the following hydride shift is very fast, it can only occur from one side to form the *syn*-2,5-substituted borolane. Epimerisation at the carbon C1 is only observed with the sterically hindered diols **6g** and **6h** since in these cases the strong repulsion between the two substituents in position 1 and 2 disfavours the above concerted transition state.

Conclusion

We have reported a new stereoselective synthesis of *anti*-1,4-diols that employs a new cyclobutylborane rearrangement. The transition structure for this unprecedented borane rearrangement has been identified computationally and shows a close relationship to Wagner–Meerwein rearrangements.

Experimental Section

General: Unless otherwise indicated, all reactions were carried out under argon. Solvents were dried and freshly distilled. Reactions were monitored by gas chromatography (GC and GC-MS) or thin-layer chromatography (TLC). The ratios between diastereoisomers were determined by ^{1}H or ^{13}C NMR spectroscopy and/or GC-MS analysis; GC-MS: column HP-5MS (15 m × 250 μm × 0.25 μm); method A: 1 min at 110 °C, ramp of 50 °C min^{-1} to 250 °C, 10 min at 250 °C, method B: 1 min at 90 °C, ramp of 50 °C min^{-1} to 250 °C, 8 min at 250 °C, method C: 1 min at 70 °C, ramp of 50 °C min^{-1} to 250 °C, 8 min at 250 °C.

General procedure A—preparation of 1-aryl-2-phenylsulfonyl-1-cyclobutenes (8): A solution of 1,2-diphenylsulfonyl-1-cyclobutene (3.34 g, 10 mmol) in THF (10 mL) was cooled to 0 °C and treated dropwise with the Grignard reagent (12 mmol). The reaction mixture was stirred for 30 min. After warming to room temperature, the reaction mixture was quenched with saturated NH_4Cl solution (50 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with water and brine, and then dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by recrystallisation to give the desired 1-aryl-2-phenylsulfonylcyclobutene (**8**).

1-Phenylsulfonyl-2-phenylcyclobutene (8a): According to general procedure A, 1,2-diphenylsulfonyl-1-cyclobutene (3.34 g, 10 mmol) was treated with PhMgCl (6.7 mL, 12 mmol, 1.8 M in THF) to give the corresponding cyclobutene derivative **8a** as a colourless solid. Yield: 2.57 g (95%); m.p.: 102 °C; IR (KBr): $\tilde{\nu}$ = 3321, 3067, 2922, 1939, 1860, 1557, 1490, 1377, 1352, 986, 772, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.75 (m, 4H), 7.49–7.25 (m, 6H), 2.65–2.62 (m, 2H), 2.56–2.54 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6, 140.2, 133.3, 131.7, 131.5, 130.5, 129.1, 128.7, 128.4, 127.3, 27.2, 26.7 ppm; MS (EI): *m*/*z* (%): 270 (8) $[M]^+$, 206 (27), 128 (100), 103 (14), 91 (13), 77 (28), 51 (14); HRMS calcd for $C_{16}H_{14}O_2S$: 270.0715; found: 270.0726.

1-Phenylsulfonyl-2-*para*-trifluoromethylphenyl-1-cyclobutene (8c): According to general procedure A, 1,2-diphenylsulfonyl-1-cyclobutene (3.34 g, 10 mmol) was treated with *para*-CF_3-C_6H_4MgBr (12 mL, 1 M in THF, 12 mmol) to give the corresponding cyclobutene derivative **8c** as a colourless solid. Yield: 2.43 g (72%); m.p.: 105 °C; IR (KBr): $\tilde{\nu}$ = 3061, 3027, 2962, 2928, 1492, 1452, 752, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.78 (m, 4H), 7.55–7.41 (m, 3H), 6.87–6.82 (m, 2H), 3.76 (s, 3H), 2.68–2.65 (m, 2H), 2.60–2.58 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.9, 153.9, 141.1, 133.6, 131.1, 129.6, 128,9, 127.7, 125.0, 114.3, 55.8, 27.4, 27.1 ppm; MS (EI): *m*/*z* (%): 300 (48) $[M]^+$, 235 (45), 221 (21), 175 (17), 158 (32), 144 (76), 128 (57), 115 (100), 89 (16), 77 (34), 51 (15); HRMS calcd for $C_{17}H_{13}F_3O_2S$: 338.0588; found: 338.0610.

1-Phenylsulfonyl-2-*para*-methoxyphenyl-1-cyclobutene (8b): According to general procedure A, 1,2-diphenylsulfonyl-1-cyclobutene (3.34 g, 10 mmol) was treated with *para*-MeO-C_6H_4MgBr (22.2 mL, 12 mmol, 0.54 M in THF) to give the corresponding cyclobutene derivative **8b** as a colourless solid. Yield: 2.76 g (92%); m.p.: 108 °C; IR (KBr): $\tilde{\nu}$ = 3436, 3063, 2921, 2838, 1605, 1505, 1299, 1148, 593; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06–7.92 (m, 4H), 7.72–7.52 (m, 5H), 2.83–2.80 (m, 2H), 2.73–2.70 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.6, 138.7, 133.9, 133.6, 132.7, 128.3, 126.6, 124.5, 26.6, 25.9 ppm; MS (EI): *m*/*z* (%): 300 (54) $[M]^+$, 259 (21), 256 (14), 233 (17), 205 (100), 128 (12), 115 (25), 91 (21), 77 (10); HRMS calcd for $C_{17}H_{16}O_3S$: 300.0820; found: 300.0798.

General procedure B, preparation of 1,2-disubstituted cyclobutenes (3): A solution of 1-aryl-2-phenylsulfonyl-1-cyclobutene (5 mmol) in THF (7 mL) was cooled to the stated temperature and treated dropwise with the corresponding lithium or cuprate reagent (8 mmol). After warming to room temperature the reaction mixture was quenched with saturated NH_4Cl solution (50 mL). The aqueous phase was extracted with pentane (3 × 50 mL). The combined organic phases were washed with water and brine, and then dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography (pentane) to give the desired 1,2-disubstituted cyclobutene (**3**).

1,2-Diphenyl-1-cyclobutene (3a): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at 0 °C with PhLi (4.2 mL, 1.9 M in toluene, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3a** as a colourless solid. Yield: 906 mg (88 %); m.p.: 56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.52-7.49$ (m, 4H), 7.31 – 7.10 (m, 6H), 2.74 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 138.7, 136.2, 129.7, 128.1, 125.9, 26.8 ppm; MS (EI): *m/z* (%): 206 (100) $[M]^+$, 191 (45), 178 (21), 165 (16), 128 (28), 115 (16), 102 (10), 91 (39), 77 (17); analytical data correspond to those reported previously.[12]

1-(2-Phenyl-1-cyclobuten-1-yl)-*para*-trifluoromethylbenzene (3b): According to general procedure B, 1-*para*-trifluoromethyphenyl-2-phenylsulfonyl-1-cyclobutene (1.69 g, 5 mmol) was treated at 0 °C with PhLi (4.2 mL, 1.9 M in toluene, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3b** as a colourless solid. Yield: 1.06 g (77 %); m.p.: 98 °C; IR (KBr): $\tilde{\nu} = 3436$, 3066, 2939, 1607, 1326, 1153, 1069, 848, 724, 627 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54-7.40$ (m, 6H), 7.29 – 7.16 (m, 3H), 2.75 – 2.69 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 141.6$, 139.4, 139.4, 137.1, 135.7, 128.5, 126.2, 126.1, 125.3 (q, $J = 3.5$ Hz), 27.2, 26.7 ppm; MS (EI): *m/z* (%): 274 (69) $[M]^+$, 259 (26), 246 (21), 233 (18), 205 (100), 196 (10), 128 (12), 115 (24), 91 (20); HRMS calcd for $C_{17}H_{13}F_3$: 274.0969; found: 274.0982.

***para*-(2-Phenyl-1-cyclobuten-1-yl)benzonitrile (3c)**: According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at −78 °C with *para*-cyanophenyllithium (5.3 mL, 1.5 M in THF, 8 mmol) for 1 h to give the corresponding cyclobutene derivative **3c** as a colourless solid. Yield: 797 mg (69 %); m.p.: 91 °C; IR (KBr): $\tilde{\nu} = 3083$, 3060, 2961, 2928, 1493, 1452, 1147, 753, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.59$ (s, 4H), 7.49 – 7.30 (m, 5H), 2.84 – 2.77 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.3$, 143.3, 140.2, 135.5, 132.2, 128.6, 128.3, 126.4, 126.2, 110.4, 27.4, 26.5 ppm; MS (EI): *m/z* (%): 231 (100) $[M]^+$, 216 (36), 203 (24), 190 (11), 153 (12), 128 (14), 115 (37), 101 (13), 91 (29), 77 (15); HRMS calcd for $C_{17}H_{13}N$: 231.1048; found: 231.1042.

1-Methoxy-4-(2-phenyl-1-cyclobuten-1-yl)benzene (3d): According to general procedure B, 1-phenylsulfonyl-2-(*para*-methoxyphenyl)cyclobutene (1.50 g, 5 mmol) was treated at 0 °C with PhLi (4.2 mL, 1.9 M in toluene, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3d** as a colourless solid. Yield: 968 mg (82 %); m.p.: 98 °C; IR film: $\tilde{\nu} = 3351$, 3028, 2956, 1603, 1497, 1451, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.02 – 7.99 (m, 2H), 7.95 – 7.92 (m, 2H), 7.68 – 7.52 (m, 5H), 2.83 – 2.80 (m, 2H), 2.73 – 2.70 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.6$, 138.7, 133.9, 133.6, 132.7, 128.3, 131.1, 128.1, 126.6, 124.5, 26.6, 25.9 ppm; MS (EI): *m/z* (%): 236 (100) $[M]^+$, 221 (31), 205 (84), 191 (16), 165 (22), 145 (25), 121 (24), 77 (11); HRMS calcd for $C_{17}H_{13}N$: 236.1201; found: 236.0988.

(2-Methyl-1-cyclobuten-1-yl)benzene (3e): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at 0 °C with MeLi (5.0 mL, 1.6 M in diethyl ether, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3e** as a colourless oil. Yield: 605 mg (84 %); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36-7.31$ (m, 4H), 7.23 – 7.19 (m, 1H), 2.91 – 2.63 (m, 2H), 2.47 – 2.44 (m, 2H), 2.03 – 2.01 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.0$, 137.7, 136.4, 128.4, 126.4, 125.5, 29.9, 26.2, 16.2 ppm; MS (EI): *m/z* (%): 144 (38) $[M]^+$, 129 (100), 115 (38), 102 (5), 63 (5); analytical data correspond to those reported previously.[10]

(2-Ethyl-1-cyclobuten-1-yl)benzene (3f): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at 0 °C with EtLi (7.3 mL, 1.1 M in dibutyl ether, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3f** as a colourless oil. Yield: 624 mg (79 %); IR (KBr): $\tilde{\nu} = 3274$, 2886, 1647, 1210, 1039, 943 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33-7.27$ (m, 4H), 2.85 – 2.60 (m, 2H), 2.46 – 2.37 (m, 4H), 1.11 ppm (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.7$, 136.3, 128.3, 126.3, 125.5, 26.9, 25.6, 23.1, 11.5 ppm; MS (EI): *m/z* (%): 158 (97) $[M]^+$, 143 (100), 128 (60), 115 (43), 91 (14), 77 (10); HRMS calcd for $C_{12}H_{14}$: 158.1096; found: 158.1092.

(2-Isopropyl-1-cyclobuten-1-yl)benzene (3g): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at −78 °C with *i*Pr_2Zn (1.8 mL, 4.5 M in diethyl ether, 8 mmol) and CuCN · 2 LiCl (8 mL, 1 M in THF, 8 mmol) for 1 h to give the corresponding cyclobutene derivative **3g** as a colourless oil. Yield: 636 mg (74 %); IR (KBr): $\tilde{\nu} = 3223$, 2908, 1638, 1187, 1043 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.24-7.22$ (m, 4H), 7.14 – 7.06 (m, 1H), 2.94 – 2.85 (m, 1H), 2.51 – 2.48 (m, 2H), 2.35 – 2.33 (m, 2H), 1.01 ppm (d, $J = 7$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.3$, 136.7, 135.5, 128.7, 126.7, 126.2, 28.7, 25.7, 24.5, 20.9 ppm; MS (EI): *m/z* (%): 172 (31) $[M]^+$, 157 (99), 142 (25), 129 (100), 115 (22), 91 (10), 77 (12); HRMS calcd for $C_{13}H_{16}$: 172.1252; found: 172.1248.

(2-*tert*-Butyl-1-cyclobuten-1-yl)benzene (3h): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at 0 °C with *t*BuLi (5.3 mL, 1.5 M in THF, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3h** as a colourless oil. Yield: 679 mg (73 %); IR (KBr): $\tilde{\nu} = 3331$, 2924, 1651, 1218, 954 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33-7.31$ (m, 4H), 7.23 – 7.18 (m, 1H), 2.56 – 2.54 (m, 2H), 2.44 – 2.42 (m, 2H), 1.16 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.3$, 137.8, 136.1, 128.2, 127.9, 126.7, 33.8, 29.2, 27.2, 25.9 ppm; MS (EI): *m/z* (%): 186 (19) $[M]^+$, 171 (100), 156 (12), 143 (50), 129 (39), 115 (19), 91 (14), 77 (10); HRMS calcd for $C_{14}H_{18}$: 186.1400; found: 186.1382.

Dimethylphenyl-(2-phenyl-1-cyclobuten-1-yl)silane (3i): According to general procedure B, 1-phenylsulfonyl-2-phenyl-1-cyclobutene (1.35 g, 5 mmol) was treated at 0 °C with $PhMe_2SiLi$ (8.9 mL, 0.9 M in THF, 8 mmol) for 30 min to give the corresponding cyclobutene derivative **3i** as a colourless oil. Yield: 1.04 g (79 %); IR (KBr): $\tilde{\nu} = 3307$, 2890, 1658, 1226, 1078, 958 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.93-6.79$ (m, 10H), 2.56 – 2.50 (m, 2H), 2.10 – 2.10 (m, 2H), 0.00 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 141.1$, 138.7, 136.8, 136.2, 131.9, 130.0, 129.7, 128.1, 125.9, 37.3, 26.8, 0.0 ppm; MS (EI): *m/z* (%): 264 (74) $[M]^+$, 149 (18), 205 (27), 173 (22), 135 (100), 105 (10); HRMS calcd for $C_{18}H_{20}Si$: 264.1334; found: 264.1321.

(2-Ferrocenyl-1-cyclobuten-1-yl)ferrocene (3l): THF (50 mL) was cooled to −40 °C and treated with $TiCl_4$ (4.68 g, 25 mmol), Zn (6.5 g, 0.1 mol) and pyridine (7,66 mL, 0.1 mol). This mixture was stirred for 15 min, and then 1,4-diferrocenylbuta-1,4-dione (4.54 g, 10 mmol) was added. The mixture was warmed to room temperature and stirred for 5 h. After quenching with $NaHCO_3$ solution, the aqueous phase was extracted with pentane (3 × 50 mL). The combined organic phases were washed with water and brine, and then dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography (pentane) to give the desired 1,2-disubstituted cyclobutene **3l** as a red solid. Yield: 2.36 g (56 %); m.p.: 104 °C; IR (KBr): $\tilde{\nu} = 3437$, 2906, 1635, 1302, 1104, 817, 478 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.17-4.04$ (m, 18H), 2.53 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.1$, 80.9, 69.0, 68.3, 55.8, 27.6 ppm; MS (EI): *m/z* (%): 422 (100) $[M]^+$, 355 (21), 236 (25), 211 (13), 178 (11), 121 (18); HRMS calcd for $C_{24}H_{22}Fe_2$: 422.0420; found: 422.0436.

General procedure C, preparation of 1,4-diols (6): A solution of a 1,2-disubstituted cyclobutene (3 mmol) in THF (15 mL) was cooled to 0 °C and treated dropwise with $BH_3 \cdot$ THF solution (3.3 mL, 1 M solution in THF, 3.3 mmol). The solution is stirred further 30 min at 0 °C and then brought to the stated temperature for the stated time. After complete conversion, the mixture was cooled to 0 °C and quenched dropwise with NaOH (10 mL, 2 M solution in H_2O) and H_2O_2 (10 mL, 30 % in H_2O). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with water and brine, and then dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography (pentane/diethyl ether 1:1) to give the desired 1,4-diols (**6**).

***anti*-1,4-Diphenyl-1,4-butandiol (6a)**: According to general procedure C, 1,2-diphenyl-1-cyclobutene (618 mg, 3 mmol) was treated with $BH_3 \cdot$ THF at 50 °C for 3 h to give the corresponding 1,4-diol derivative **6a** as a colourless solid. Yield: 646 mg (89 %). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 74.3 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 73.9 ppm. M.p.: 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36-7.28$ (m, 5H), 4.79 – 4.76 (m, 2H), 2.50 (br s, 2H), 1.91 – 1.84 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.9$, 128.8, 127.9, 126.3, 74.3, 35.5 ppm; MS (EI): *m/z* (%): 224 (14) $[M - H_2O]^+$, 118 (100), 107 (37), 91 (12), 79 (53), 51 (7); analytical data correspond to those reported previously.[2]

***anti*-1-Phenyl-4-[4-(trifluoromethyl)phenyl]-1,4-butanediol (6b)**: According to general procedure C, 1-(2-phenyl-1-cyclobuten-1-yl)-*para*-trifluoromethylbenzene (822 mg, 3 mmol) was treated with $BH_3 \cdot$ THF at 50 °C for 5 h to give **6b** as a colourless oil. Yield: 828 mg (89 %). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 62.9 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 62.0 ppm. IR (film): $\tilde{\nu} = 3321$, 3067, 2922, 1939, 1860, 1557,

1490, 1377, 1352, 986, 772, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 9$ Hz, 2H), 7.52 – 7.03 (m, 7H), 4.01 – 3.92 (m, 1H), 3.86 – 3.77 (m, 1H), 2.54 – 2.31 (m, 2H), 2.12 – 2.00 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.2$, 137.2, 132.5, 128.1, 127.4, 127.3, 125.5, 62.9, 40.0, 23.5, 18.8 ppm; MS (EI): *m/z* (%): 310 (11) $[M]^+$, 214 (100), 201 (14), 130 (7), 106 (6); HRMS calcd for $C_{17}H_{17}F_3O_2$: 310.1181; found: 310.1178.

***anti*-1-[4-(Aminomethyl)phenyl]-4-phenyl-1,4-butanediol (6c)**: According to general procedure C, 4-(2-phenyl-1-cyclobuten-1-yl)benzonitrile (693 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 50 °C for 5 h to give **6c** as a colourless oil. Yield: 577 mg (71%). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 72.2 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 71.3 ppm. IR (film): $\tilde{\nu} = 3340$, 2855, 1603, 1450, 1357, 1027, 971, 701 cm^{-1}; ^{1}H NMR (300 MHz, DMSO): $\delta = 7.34 – 7.23$ (m, 9H), 4.53 – 4.51 (m, 2H), 3.74 (s, 2H), 2.56 – 2.54 (m, 2H), 1.70 – 1.56 ppm (m, 4H); ^{13}C NMR (75 MHz, DMSO): $\delta = 146.7$, 144.7, 142.1, 128.2, 127.1, 126.9, 126.1, 125.9, 72.8, 72.7, 45.6, 36.2, 36.0 ppm; MS (APCI): *m/z* (%): 270 (5) $[M]^+$, 254 (47), 199 (100); HRMS calcd for $C_{17}H_{21}NO_2$: 271.1572; found: 271.1585.

***anti*-1-(4-Methoxyphenyl)-4-phenyl-1,4-butanediol (6d)**: According to general procedure C, 1-methoxy-4-(2-phenyl-1-cyclobuten-1-yl)benzene (708 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 50 °C for 5 h to give **6d** as a colourless oil. Yield: 726 mg (89%). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 73.9 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 73.1 ppm. IR (KBr): $\tilde{\nu} = 3367$, 3060, 3028, 2962, 2930, 1493, 1453, 1375, 1106, 757, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.27 – 7.12$ (m, H), 6.80 – 6.75 (m, H), 4.65 – 4.53 (m, 2H), 3.70 (s, 3H), 2.50 (br s, 2H), 1.84 – 1.66 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.4$, 145.0, 137.1, 128.8, 127.5, 126.2, 114.2, 74.2, 73.9, 55.7, 35.6, 35.4 ppm; MS (EI): *m/z* (%): 254 (1) $[M]^+$, 179 (2), 130 (84), 104 (100), 91 (42), 77(28), 51 (12); HRMS calcd for $C_{17}H_{20}O_3$: 272.1412; found: 272.1432.

***anti*-1-Phenyl-1,4-pentanediol (6e)**: According to general procedure C, (2-methyl-1-cyclobuten-1-yl)benzene (432 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6e** as a colourless oil. Yield: 427 mg (79%). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 74.4 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 74.7 ppm. IR film: $\tilde{\nu} = 3351$, 2960, 2874, 1602, 1453, 1029, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.29 – 7.19$ (m, 5H), 4.67 (t, $J = 6.3$ Hz, 1H), 3.87 – 3.74 (m, 1H), 2.11 (br s, 2H), 1.86 – 1.74 (m, 2H), 1.64 – 1.33 (m, 2H), 1.05 ppm (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.0$, 128.8, 127.9, 126.2, 74.4, 68.3, 35.5, 35.4, 23.9 ppm; MS (EI): *m/z* (%): 180 (1) $[M]^+$, 141 (13), 120 (56), 107 (100), 91 (13), 79 (63), 56 (13); HRMS calcd for $C_{11}H_{16}O_2$: 180.1150; found: 180.1144.

***anti*-1-Phenyl-1,4-hexanediol (6f)**: According to general procedure C, (2-ethyl-1-cyclobuten-1-yl)benzene (474 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6f** as a colourless oil. Yield: 477 mg (82%). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift of 74.4 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 74.7 ppm. IR film: $\tilde{\nu} = 3351$, 2960, 2874, 1602, 1453, 1029, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.34 – 7.16$ (m, 5H), 4.66 (t, $J = 6$ Hz, 1H), 3.55 – 3.47 (m, 1H), 1.81 (q, $J = 7$ Hz, 2H), 1.64 – 1.33 (m, 4H), 0.85 ppm (t, $J = 9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.6$, 128.2, 127.2, 125.6, 74.2, 73.0, 34.6, 32.6, 30.0, 9.74 ppm; MS (EI): *m/z* (%): 194 (5) $[M]^+$, 176 (14), 147 (30), 120 (68), 107 (100), 91 (20), 79 (51), 55 (8); HRMS calcd For $C_{12}H_{18}O_2$: 194.1307; found: 194.1328.

***anti*-5-Methyl-1-phenyl-1,4-hexanediol (6g)**: According to general procedure C, (2-isopropyl-1-cyclobuten-1-yl)benzene (516 mg. 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6g** as a colourless oil. Yield: 449 mg (72%). The desired diol was obtained as a diastereomeric mixture of 95:5. The benzylic H-C(OH) signal has a chemical shift of 74.8 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 75.5 ppm. IR film: $\tilde{\nu} = 3422$, 3067, 3041, 3011, 2998, 2967, 2874, 1939, 1855, 1800, 1602, 1494, 1352, 1045, 997, 763, 740, 719, 609 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.28 – 7.15$ (m, 5H), 4.67 – 4.56 (m, 1H), 3.48 – 3.50 (m, 1H), 1.85 – 1.74 (m, 2H), 1.57 – 1.25 (m, 4H), 1.14 – 0.99 (m, 1H), 0.84 – 0.75 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.2$, 128.8, 127.7, 126.2, 74.8, 74.2, 40.6, 36.2, 30.7, 26.2, 13.9, 12.2 ppm; MS (EI): *m/z* (%): 222 (2) $[M]^+$, 204 (10), 147 (76), 129 (39), 120 (90), 107 (100), 91 (52), 79 (43), 70 (28), 57 (14); HRMS calcd for $C_{13}H_{20}O_2$: 208.1463; found: 208.1446.

***anti*-5,5-Dimethyl-1-phenyl-1,4-hexanediol (6h)**: According to general procedure C, (2-*tert*-butyl-1-cyclobuten-1-yl)benzene (558 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6h** as a colourless oil. Yield: 460 mg (69%). The desired diol was obtained as a diastereomeric mixture of 80:20. The benzylic H-C(OH) signal has a chemical shift of 79.3 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 79.0 ppm. IR film: $\tilde{\nu} = 3480$, 3080, 3024, 2960, 2924, 1342, 1055, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.27 – 7.10$ (m, 5H), 4.71 – 4.67 (m, 0.8H), 4.62 – 4.58 (m, 0.2H), 3.20 – 3.15 (m, 0.8H), 3.13 – 3.11 (m, 0.2H), 1.94 – 1.18 (m, 4H), 0.82 (s, 1.8H), 0.80 ppm (s, 7.2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.1$, 127.4, 126.3, 124.8, 79.3, 79.0, 73.9, 73.1, 36.4, 35.6, 34.9, 34.0, 27.5, 26.3, 24.7 ppm; MS (EI): *m/z* (%): 222 (3) $[M]^+$, 204 (7), 186 (2), 147 (100), 120 (81), 107 (58), 91 (56), 70 (38), 57 (24); HRMS calcd for $C_{14}H_{22}O_2$: 222.1620; found: 222.1638.

***anti*-1-Dimethylphenylsilyl-4-phenyl-1,4-butanediol (6i)**: According to general procedure C, dimethylphenyl-(2-phenyl-1-cyclobuten-1-yl)silane (792 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 50 °C for 5 h to give **6i** as a colourless oil. Yield: 621 mg (69%). The desired diol was obtained as one diastereoisomer. The benzylic H-C(OH) signal has a chemical shift 74.2 ppm, of whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 74.8 ppm. IR film: $\tilde{\nu} = 3328$, 2945, 2867, 1464, 1028, 883, 833, 663 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.27 – 6.89$ (m, 11H), 4.64 – 4.60 (m, 1H), 3.49 – 3.42 (m, 1H), 1.91 – 1.59 (m, 4H), 0.00 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.9$, 136.5, 134.4, 134.1, 129.1, 127.9, 127.5, 126.2, 74.2, 55.0, 32.6, 15.6, 1.0 ppm; MS (EI): *m/z* (%): 300 (19) $[M]^+$, 283 (24), 266 (100), 165 (33), 131 (11); HRMS calcd for $C_{18}H_{24}O_2Si$: 300.1546; found: 300.1528.

***anti*-5,8-Tridecanediol (6j)**: According to general procedure C, 1-butyl-2-pentyl-1-cyclobutene (540 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6j** as a colourless solid. Yield: 512 mg (79%). The desired diol was obtained as one diastereoisomer. One H-C(OH) signal has a chemical shift of 70.9 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 72.2 ppm. M.p.: 89 °C; IR (KBr): $\tilde{\nu} = 3402$, 1960, 1637, 1453, 1059, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.57 – 3.55$ (m, 2H),1.59 – 1.23 (m, 16H), 0.86 – 0.80 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 70.9$, 70.8, 36.5, 36.2, 32.2, 30.9, 27.0, 24.4, 21.7, 21.6, 13.1, 13.0 ppm; MS (EI): *m/z* (%): 215 (1) $[M]^+$, 173 (10), 155 (16), 141 (54), 123 (69), 109 (100), 95 (31), 81 (79), 69 (75), 55 (93); HRMS calcd for $C_{13}H_{28}O_2$: 216.2089; found: 216.2078.

***anti*-5,8-Dodecanediol (6k)**: According to general procedure C, 1,2-dibutyl-1-cyclobutene (498 mg, 3 mmol) was treated with $BH_3 \cdot THF$ at 40 °C for 16 h to give **6k** as a colourless solid. Yield: 509 mg (84%). The desired diol was obtained as one diastereoisomer. The H-C(OH) signal has a chemical shift of 72.4 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 72.0 ppm. M.p.: 94 °C; IR (KBr): $\tilde{\nu} = 3337$, 2955, 1636, 1466, 1128, 1042 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.59 – 3.57$ (m, 2H), 2.06 (s, 2H), 1.61 – 1.23 (m, 12H), 0.84 pm (t, $J = 7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 72.4$, 37.6, 33.6, 28.3, 23.1, 14.4 pm; MS (EI): *m/z* (%): 202 (1) $[M]^+$, 183 (1), 127 (77), 109 (100), 83 (14), 70 (38), 57 (25); HRMS calcd for $C_{12}H_{26}O_2$: 202.1933; found: 202.1946.

***anti*-1,4-Diferrocenyl-1,4-butandiol (6l)**: According to general procedure C, (2-ferrocenyl-1-cyclobuten-1-yl)ferrocene (1.27 g, 3 mmol) was treated with $BH_3 \cdot THF$ at 50 °C for 5 h to give **6l** as a red solid. Yield: 893 mg (65%). The desired diol was obtained as one diastereoisomer. The H-C(OH) signal has a chemical shift of 77.9 ppm, whereas the diastereomeric *syn*-1,4-diol has a chemical shift of 77.1 ppm. M.p.: 124 °C; IR (KBr): $\tilde{\nu} = 3391$, 3089, 2915, 1409, 1105, 1022, 811 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.17 – 3.92$ (m, 18H), 2.30 – 2.18 (m, 2H), 1.49 – 4.46 (m, 2H), 1.19 – 1.17 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 88.3$, 77.9, 68.0, 67.3, 66.0, 32.2 ppm; MS (EI): *m/z* (%): 440 (100) $[M - H_2O]^+$, 438 (16), 267 (10), 226 (23), 207 (49), 186 (25), 120 (34), 73 (24); HRMS calcd for $C_{24}H_{26}Fe_2O_2$: 458.0632; found: 458.0626.

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[1] a) *Stereoselective Synthesis* (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Houben Weyl, Thieme, Stuttgart, New York, **1996**; b) *Comprehensive Asymmetric Catalysis* (Eds.: E N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, New York, **1999**.
[2] a) F. Lhermitte, P. Knochel, *Angew. Chem.* **1998**, *110*, 2598; *Angew. Chem. Int. Ed.* **1998**, *37*, 2459; b) H. Laaziri, L. O. Bromm, F. Lhermitte, R. M. Gschwind, P. Knochel, *J. Am. Chem. Soc.* **1999**, *121*, 6940; c) J. A. Varela, D. Pena, B. Goldfuss, K. Polborn, P. Knochel, *Org. Lett.* **2001**, *3*, 2395; d) B. Goldfuss, P. Knochel, L. O. Bromm, K. M. Knapp, *Angew. Chem.* **2000**, *112*, 4302; *Angew. Chem. Int. Ed.* **2000**, *39*, 4136.
[3] L. O. Bromm, H. Laaziri, F. Lhermitte, K. Harms, P. Knochel, *J. Am. Chem. Soc.* **2000**, *122*, 10218.
[4] E. Hupe, D. Denisenko, P. Knochel, unpublished results.
[5] For some recently described stereoselective syntheses of 1,4-diols, see: a) C. Gaul, D. Seebach, *Helv. Chim. Acta* **2002**, *85*, 772; b) T. M. Nguyen, D. Lee, *Org. Lett.* **2001**, *3*, 3161; c) J. Eames, N. Kuhnert, F. H. Sansbury, S. Warren, *Synlett* **1999**, 1211; d) G. A. Molander, K. L. Bobbitt, *J. Org. Chem.* **1994**, *59*, 2676; e) B. Feringa, B. DeLange, *Tetrahedron Lett.* **1988**, *29*, 1303; f) R. Annunziata, M. Cinquini, F. Cozzi, L. Raimondi, S. Stefanelli, *Tetrahedron* **1986**, *42*, 5443.
[6] H. Landen, H. D. Martin, A. Stiegel, *Chem. Ber.* **1987**, *120*, 171.
[7] a) W. E. Parham, L. D. Jones, *J. Org. Chem.* **1976**, *41*, 1187; b) W. E. Parham, L. D. Jones, J. Sayed, *J. Org. Chem.* **1975**, *40*, 2394; c) W. E. Parham, L. D. Jones, *J. Org. Chem.* **1977**, *42*, 260; e) W. E. Parham, R. M. Piccirilli, *J. Org. Chem.* **1977**, *42*, 257.
[8] A. Boudier, C. Darcel, F. Flachsmann, L. Micouin, M. Oestreich, P. Knochel, *Chem. Eur. J.* **2000**, *6*, 2749.
[9] I. Fleming, R. S. Roberts, S. C. Smith, *Tetrahedron Lett.* **1996**, *37*, 9395.
[10] E. Negishi, F. Liu, D. Choueiry, M. M. Mohamud, A. Silveira, Jr., M. Reeves, *J. Org. Chem.* **1996**, *61*, 8325.
[11] a) Y. Ito, T. Konoike, T. Harada, T. Saegusa, *J. Am. Chem. Soc.* **1977**, *99*, 1487; b) L. Schwink, P. Knochel, *Tetrahedron Lett.* **1997**, *38*, 3711.
[12] a) J. E. McMurry, M. P. Fleming, K. L. Kees, L. R. Krepski, *J. Org. Chem.* **1978**, *43*, 3255; b) A. L. Baumstark, C. J. McCloskey, K. E. Witt, *J. Org. Chem.* **1978**, *43*, 3609.
[13] a) S. Winstein, N. J. Holness, *J. Am. Chem. Soc.* **1955**, *77*, 3054; b) G. K. S. Prakash, V. P. Reddy, G. Rasul, J. Casanova, G. A. Olah, *J. Am. Chem. Soc.* **1998**, *120*, 13362
[14] a) Gaussian 98 (Revision A.5), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; b) The *XYZ* matrix for **4a-TS-2**can be found in the Supporting Information.
[15] a) M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **1977**, *99*, 4907; b) M. J. S. Dewar, M. L. McKee, *J. Am. Chem. Soc.* **1977**, *99*, 5231.
[16] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[17] S. Dapprich, I. Komaromi, K. S. Byun, K. Morokuma, M. J. Frisch, *Theochem* **1999**, *461–462*, 1.

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