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Samarium Diiodide-Mediated Pinacolization of 1,4-Diketones – I. Stereoselective Synthesis of Fused Mono-, Bi- and Tricyclic Cyclobutane-1,2-diols.

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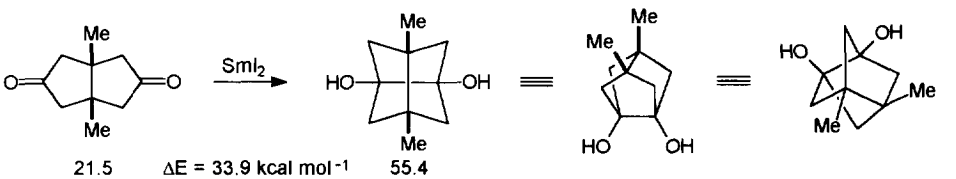
Abstract: The title reaction has been applied to the synthesis of a variety of *cis*-cyclobutane-1,2-diols in good yield. Copyright © 1996 Elsevier Science Ltd

Although the pinacol coupling has been known since the beginnings of organic chemistry, the reaction continues to be developed, especially with respect to the reducing agent and application in synthesis.[1]

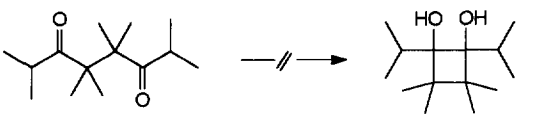
We have shown previously that the functionalized bisnoradamantane is readily accessible by SmI_2-mediated pinacolization of a bicyclic 1,6-diketone (Scheme 1).[2] HyperChem™ 3.0 calculations suggested that the accompanying increase in strain is ca. 33.9 kcal mol^{-1}. While absolute energies are less informative, calculated energy differences of isomers are considered to be more meaningful.



Scheme 1

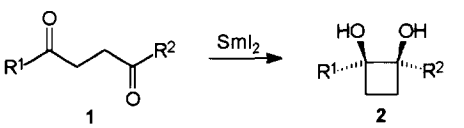
Because of the smooth reaction and good yield (76%) we decided to probe this type of pinacolization further. A suitable test case for the driving force of the SmI_2-mediated[3] pinacol coupling should be the preparation of cyclobutane-1,2-diols because of ring strain. Existing synthetic routes to four-membered rings have been reviewed and have relied mainly on ionic and photochemical reactions.[4]

We began by investigating the reactivity of simple, acyclic 1,4-diketones (Table 1). In fact, a variety diketones **1a** - **1m** were cyclized to cyclobutane-1,2-diol in satisfactory to high yield. NOE studies showed that all cyclobutane diols prepared were *cis*-1,2-diols. *Trans*-1,2-diols were not observed. In contrast to the more severe SET conditions of the Birch reduction a chlorine substituent is tolerated in the SmI_2 procedure, as in *p*-chlorophenylated diketone **1j**, which provided **2j** in 91% yield. Since parent 1,2-dimethylcyclobutane-1,2-diol (**2a**) is water soluble, the isolated yield (51%) was moderate in this example. Two aromatic groups as in **1n** and **1o** prohibited the cyclization. Note that the two aryl groups would have to be proximate and *cis* in the hypothetical product 1,2-diol. Highly crowded 2,4,4,5,5,7-hexamethyloctane-3,6-dione[5] also failed to cyclize (Scheme 2).

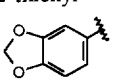


Scheme 2.

Table 1. SmI_2-Mediated Pinacolization of 1,4-Diketones. Stereoselective Route to Monocyclic *cis*-Cyclobutane-1,2-diols.

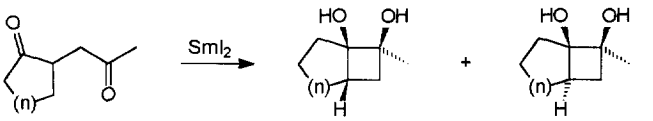


1 2

2	R^1	R^2	Yield [%]
a	methyl	methyl	51
b	propyl	methyl	60
c	hexyl	methyl	70
d	*i*-propyl	methyl	57
e	cyclohexyl	methyl	78
f	benzyl	methyl	63
g	*i*-butyl	methyl	81
h	phenyl	methyl	88
i	*p*-anisyl	methyl	92
j	*p*-chlorophenyl	methyl	91
k	2-furyl	methyl	83
l	2-thienyl	methyl	73
m		methyl	81
n	phenyl	phenyl	---
o	2-furyl	phenyl	---

Unlike the simple 1,4-diketones in Table 1 those in Table 2 incorporate one carbonyl group into a 5-, 6-, and 7-membered ring.

Table 2. Bicyclic Cyclobutane-1,2-diols.



3 **4** (*cis*-fused) **4** (*trans*-fused)

		Yield [%]		Combined	Difference in Strain Energy [kcal mol^{-1}]
3	n	**4** (*cis*-fused)	**4** (*trans*-fused)	Yield [%]	between *trans*-Fused und *cis*-Fused Isomer
a	1	30	---	30	81.5 - 48.2 = 33.3
b	2	53	40	93	60.6 - 47.3 = 13.3
c	3	41	49	90	54.6 - 54.3 = 0.3

For 2-(2′-oxopropyl)cyclopentanone (**3a**), the strained 7-methylbicyclo[3.2.0]heptane-1,7-diol **4** (*cis*-fused) was formed in 30% yield. To our surprise, the homologous 1,4-diketone **3b** furnished not only **4b** (*cis*-fused) (53%), but also a substantial amount of **4b** (*trans*-fused) (40%). The structure of **4b** (*trans*-fused) was established by spectroscopic and chemical evidence (cf. Table 3) and finally put beyond doubt by X-ray crystal diffraction (Fig. 1). Bicyclic **4b** (*trans*-fused) is a *contrathermodynamic* diastereomer and calculated to be less stable than **4b** (*cis*-fused) by 13.3 kcal mol^{-1}.

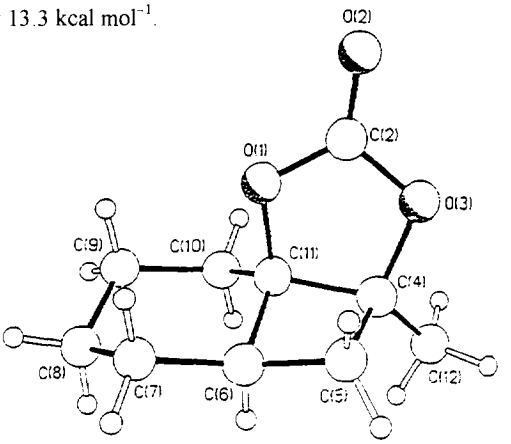


Fig 1. X-ray Crystal Structure of Cyclic Carbonate Derived from Bicyclic **4b** (*trans*-fused). Crystal Data for $C_{10}H_{14}O_3$, M = 182.2, monoclinic, a = 7.469(2), b = 7.465(2), c = 17.037(4) A, β = 96.85(1)°, U = 943.1(4) A^3, space group $P2_1/c$, Z = 4, D_c = 1.28 g cm^{-3}, μ = 7.72 cm^{-1}, $F(000)$ = 392. 1478 Independent reflections (θ < 62°) were measured on a Siemens P4/PC diffractometer with Cu-K_α radiation (graphite monochromator) using ω scans. 1314 Had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically by full-matrix least squares based on F^2 to give R_1 = 0.0488, wR_2 = 0.1355. Computations were carried out using the SHELXTL-PC program system. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

In the pinacol coupling of the conformationally more mobile 2-(2′-oxopropyl)cycloheptanone (**3c**) the *trans*-fused *cis*-cyclobutane-1,2-diol **4c** (*trans*-fused) actually predominated over **4c** (*cis*-fused) (49 : 41). Thus, there is a change over in preferred product type on going from the 6·4 ring system **4b** to the less strained 7·4 ring system **4c** (strain energy difference between *trans*- and *cis*-fused isomer ~ 0).

Compared with the first member of the series, i. e. 2-(2′-oxopropyl)cyclopentanone **3a** (n = 1), the homologous 1,4-diketones **3b** (n = 2) and **3c** (n = 3) provided the bicyclic pinacols in excellent yield (≥90% combined *cis*- and *trans*-fused).

The *cis*-configuration of the OH groups of the five pinacols was secured by conversion into the cyclic, 5-membered carbonates. Both *cis*-fused and *trans*-fused *cis*-1,2-diols could be converted into **5a - c** (*cis*-fused) and **5b,c** (*trans*-fused) (Table 3). For the preparation of the cyclic carbonates a high concentration of CDI (N,N′-carbonyldiimidazolide) and boiling tetrahydrofuran were essential.

Table 3. Cyclic Carbonates **5** (*cis*-fused) and **5** (*trans*-fused) from *cis*-Cyclobutane-1,2-diols and CDI[a]

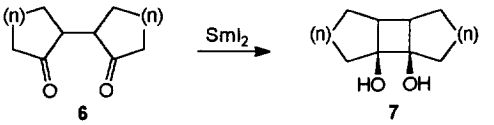
		5 (*cis*-fused)	n	mp [°C]			**5** (*trans*-fused)	n	mp [°C]
4 (*cis*-fused)	CDI,[a] THF, reflux → **5** (*cis*-fused)	**a**	1	47	**4** (*trans*-fused)	ditto → **5** (*trans*-fused)			
		b	2	49			**b**	2	69
		c	3	55			**c**	3	55

[a] N,N′-Carbonyldiimidazolide

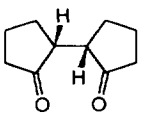
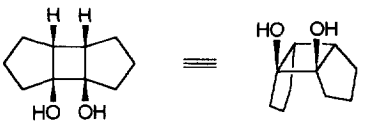
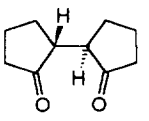
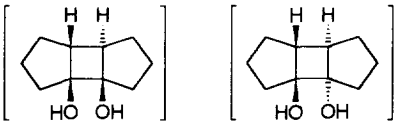
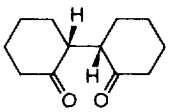
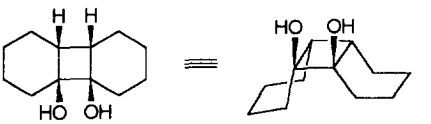
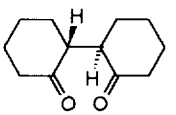
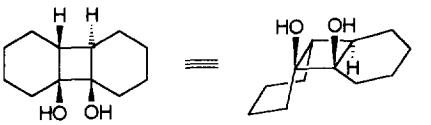
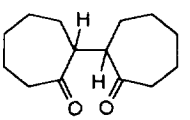
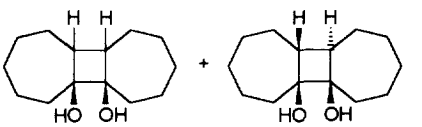
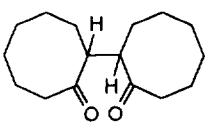
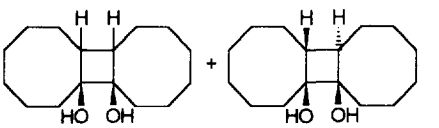
Having investigated the series of acyclic 1,4-diketones **1a - n** and monocyclic 1,4-diketones **3a - c**, we studied the bicyclic series of 1,1′-bicycloalkyl-2,2′-diones **6a - d** (Table 4). *Meso*-**6a** and *rac*-**6a** could be separated and cyclized separately, as were *meso*-**6b** and *rac*-**6b**. In accord with previous findings [cf. formation of **4a** (*cis*-fused) from **3a**] only the *cis*-fused diol *meso*-**7a** was formed from *meso*-**6a**. Necessarily, the ring fusion in tricyclic diol *meso*-**7a** is *cis-syn-cis*, given the *cis*-configuration of the two hydroxy groups. In contrast, racemic **6a** gave no pinacolization product at all, in agreement with the results of Table 2 [**4a** (*trans*-fused) was not formed]. Meso-1,1′-bicyclohexyl-2,2′-dione (**6b**) gave *cis-syn-cis* configurated meso-**7b**. The yield of *meso*-**7b** (68%) was higher than that of *meso*-**7a** (52%), in accord with the trend in Table 2. Racemic diketone *rac*-**6b** afforded diol *rac*-**7b** (54%), similar to the formation of bicyclic **4b** (*trans*-fused).

Again, *trans*-configurated 1,2-diols were not observed (cf. Table 3). In fact, there is currently just one example, where a *trans*-configurated 1,2-diol has been isolated as a minor product next to the major *cis*-1,2-diol (in the strained norpinane system).[6]

Table 4. Tricyclic Diastereomers from Meso and Racemic 1,1′-Bicycloalkyl-2,2′-diones



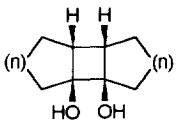
6 **7**

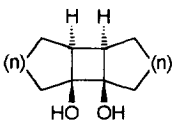
Starting Material	Product(s)	Yield [%]
 *meso*-**6a**	 *meso*-**7a** (*cis-syn-cis*)	52
 *rac*-**6a**	 too strained *trans*-diol	---
 *meso*-**6b**	 meso-**7b** (*cis-syn-cis*)	68
 *rac*-**6b**	 *rac*-**7b**	54
 **6c** mixture of *meso* and *rac*	 *meso*-**7c** (37%)[a] *rac*-**7c** (50%)	87
 **6d** mixture of *meso* and *rac*	 *meso*-**7d** (20%) *rac*-**7d** (48%)	68

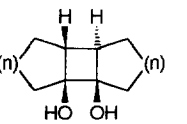
[a]The two angular hydrogens are either *cis* or *trans* to the neighbouring, *cis*-configurated hydroxy groups (NMR evidence). Calculations suggest that the *cis-syn-cis* isomer is more stable than the *trans,trans* isomer by 13.9 kcal mol^{-1}; cf. Table 5.

According to HyperChem 3.0 (Table 5) the favoured structure of *meso*-**7c** has the two OH groups and the neighbouring two hydrogens of the cyclobutanediol moiety on the same face of the 4-membered ring (the energy for *meso*-**7c** with *cis-syn-cis* fusion is 60.7 kcal mol^{-1}). The cyclobutanediol with *trans,trans* ring fusion is more strained (74.6 kcal mol^{-1}).

Table 5. Calculated Strain Energy (HyperChem 3.0, kcal mol^{-1}) for Tricyclic Pinacols **7a-d**.







	cis-syn-cis		*trans,trans*		*rac*
n	[kcal mol^{-1}]		[kcal mol^{-1}]		[kcal mol^{-1}]
1	*meso*-**7a**, 58.0	Δ 112.0	170.0	Δ 78.8	91.2
2	*meso*-**7b**, 58.2	Δ 46.3	104.5	Δ 33.4	*rac*-**7b**, 71.1
3	*meso*-**7c**, 60.7	Δ 13.9	74.6	Δ 5.6	*rac*-**7c**, 69.0
4	*meso*-**7d**, 70.4	Δ ~ 0	69.5	Δ ~ 0	*rac*-**7d**, 69.3

We have already shown (Table 2) that the formation of the *trans*-fused diol **4c** is preferred (49%) over the *cis*-fused **4c** (41%). In diketone **6c** *two* 7-membered rings are present (rather than one as in diketone **3c**). Again, the stereoisomer with one *trans*-fused 7-membered ring, i. e. *rac*-**7c**, appears to be favoured (50%) over the second stereoisomer *meso*-**7c** (37%), which is assumed to be the *cis-syn-cis* stereoisomer (cf. Table 4, footnote *a*). In other words, the 6·4 ring system in Table 2 corresponds to the 6·4·6 ring system in Table 4, just as the 7·4 system (Table 2) is related to the 7·4·7 system (Table 4). A priori, *meso*-**7d** may also be fused *cis-syn-cis* or *trans,trans*. HyperChem calculations suggest approximately equal energy content (Table 5).

Conclusions. We have prepared a variety of monocyclic, bicyclic and tricyclic pinacols by SmI_2-mediated coupling of 1,4-diketones. The 1,2-diols were formed with high *cis*-selectivity. HyperChem calculations of the increase in strain on going from starting 1,4-diketone to product 1,2-diol serve as a rough guide for the feasibility of the pinacol coupling. Cyclobutanediols including contrathermodynamic diastereomers such as *trans*-8-methylbicyclo[4.2.0]octane-1,8-diol [**4b** (*trans*-fused)] are formed in useful yield, and a variety of molecular scaffolds are accessible.

EXPERIMENTAL

General Remarks. Melting points: Büchi apparatus. – Infrared spectra: Perkin-Elmer 1710 spectrometer. – ^1H NMR spectra: Bruker WH 90, WP 200 SY or AM 300 spectrometer, solvent $CDCl_3$ unless otherwise stated. – ^{13}C NMR spectra: Bruker WP 200 SY or a Bruker AM 300. APT (attached proton test): spin echo-

based selection of multiplicities of ^{13}C signals. Quaternary C and CH_2 carbon atoms give positive signals (+), while CH and CH_3 give negative signals (–). – Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover. – Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30 - 60 μm). – Analytical t.l.c was carried out on aluminum-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck). – E (ethyl ether). PE (light petroleum, bp 40 – 60 °C). MTBE (methyl *t*-butyl ether).

General Procedure for the Cyclization with SmI_2. A 50 mL three-necked flask equipped with gas inlet and reflux condenser was charged with Sm (375 mg, 2.50 mmol) and heated under a weak stream of N_2. 1,2-Diiodoethane (592 mg, 2.10 mmol) was added and the mixture cooled to 0 °C. THF (30 mL) was added and the mixture stirred for 10 min (the colour of the solution turns to dark blue). The SmI_2 solution was stirred for 50 min at r.t., then heated to reflux and the diketone (1.00 mmol) in THF (5 mL) was added slowly. *Work up - Method A.* After complete reaction and cooling to r.t. 1 N HCl was added to the almost yellow reaction mixture. The layers were separated and the aqueous phase was extracted with E. The combined organic layer was washed with sat. aq. $NaHCO_3$ solution and the aqueous layer reextracted with E. The combined organic layer was freed from iodine by treatment with copper powder and dried ($MgSO_4$). After removal of the solvent the crude product was purified by chromatography. *Method B.* The reaction was quenched with sat. aq. NH_4Cl solution and then worked up as desribed for method A. *Method C.* After complete reaction sat. aq. $NaHCO_3$ solution and brine were added and the aqueous layer was extracted with E. The organic layer was freed from iodine by treatment with sat. aq. $Na_2S_2O_3$ solution. After drying ($MgSO_4$) and removal of the solvent the crude product was chromatographed.

Synthesis of 1,4-Diketone Precursors. Several procedures were used to obtain the unnatural 1,4-functionality distance. (i) Stetter reaction of aldehydes with methyl vinyl ketone as the Michael acceptor furnished 1,4-diketones **1b - m** (12 compounds).[7] (ii) 2-(2′-Oxopropyl)cycloalkanones **3a - c** were obtained from the cycloalkanone by (a) α-alkylation of the cyclohexanone enamine with 2-methyl allyl chloride followed by ozonolysis (as for **3b**), (b) CAN-mediated α-acetonylation of cyclopentanone (cf. **3a**) and cycloheptanone (cf. **3c**) with isopropenyl acetate.[8] (iii) 1,1′-Bicycloalkyl-2,2′-diones **6a - d** were prepared by oxidative coupling of the lithium enolates with Cu(II) according to Saegusa.[9]

1,2-Dimethyl-cyclobutane-cis-*1,2-diol* (**2a**). Hexan-2,5-dione (114 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to afford after 3 h reaction time **2a**, 52 mg (45%), colourless oil. In another approach the work up procedure was modified: The aqueous layer was extracted (Ludwig extractor) for 2 d with E to yield after chromatography **2a**, 59 mg (51%). IR ($CHCl_3$) ν 3536, 3420, 2980, 2944, 1444, 1380, 1348, 1248, 1000, 960, 928 cm^{-1}; ^1H NMR δ 3.47 (br. s, 2 H, OH), 2.02 - 1.69 (m, 4 H, CH_2), 1.24 (s, 6 H, CH_3); ^{13}C NMR δ 76.53 (+, C-1), 31.57 (+, C-2), 22.33 (–, C-3); MS *m/z* 116 (M^+, 0), 114 (M^+-2, 3), 99 (10), 88 (74), 58 (100).

1-Methyl-2-propyl-cyclobutane-cis-*1,2-diol* (**2b**). Diketone **1b** (142 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 3 h reaction time **2b**, 87 mg (60%),

yellowish oil. IR ($CHCl_3$) ν 3528, 3420, 2960, 2872, 1444, 1380, 1352, 1244, 1172, 984 cm^{-1}; ^1H NMR δ 3.44 (br. S, 2 H, OH), 2.10 - 1.65 (m, 4 H, cyclobutane CH_2), 1.54 - 1.30 (m, 4 H, $(CH_2)_2CH_3$), 1.25 (s, 3 H, CCH_3), 1.00 - 0.84 (m, 3 H, $(CH_2)_2CH_3$); ^{13}C NMR δ 76.67, 76.04 (+, COH), 37.69 (+, $CH_2CH_2CH_3$), 32.42, 28.87 (+, cyclobutane CH_2), 22.17 (–, CCH_3), 16.51 (+, $CH_2CH_2CH_3$), 14.60 (–, $(CH_2)_2CH_3$); MS *m/z* 144 (M^+, 0), 143 (M^+-1, 0.6), 142 (1), 116 (48), 99 5), 87 (100), 71 (38).

1-Hexyl-2-methyl-cyclobutane-cis-*1,2-diol* (**2c**). Diketone **1c** (184 mg, 1.00 mmol) was allowed to react for 3 h according to the general procedure. Work up (method A) afforded **2c**, 131 mg (70%), yellowish oil. Work up (method B) gave **2c**, 127 mg (68%). IR ($CHCl_3$) ν 3532, 3428, 2932, 2856, 1444, 1380, 1352, 1244, 996, 976 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.25 (s, 2 H, OH), 1.92 - 1.51 (m, 4 H, cyclobutane CH_2), 1.40 - 1.50 (m,

10 H, $(CH_2)_5CH_3$), 1.10 (s, 3 H, CCH_3), 0.94 - 0.79 (m, 3 H, $(CH_2)_5CH_3$); ^{13}C NMR (DMSO-d_6) δ 78.27, 75.06 (+, COH), 35.48, 32.09, 31.62, 29.60, 28.83, 23.09 (+, CH_2), 22.61 (–, CCH_3), 22.31 (+, CH_2CH_3), 14.08 (–, CH_2CH_3); MS *m/z* 186 (M^+, 0), 184 (M^+-2, 2), 168 (2), 158 (32), 129 (13), 113 (18), 99 (16), 87 (67), 71 (100).

1-Methyl-2-(1-methylethyl)-cyclobutane-cis-*1,2-diol* (**2d**). Diketone **1d** (142 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 3 h reaction time **2d**, 82 mg (57%), yellowish oil. IR ($CHCl_3$) ν 3536, 3448, 2968, 2936, 2872, 1680, 1444, 1384, 1352, 1244, 1188, 1124, 992, 968 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.07 (s, 2 H, OH), 1.94 (q, J = 7 Hz, 1 H, $CH(CH_3)_2$), 1.78 - 1.28 (m,

4 H, CH_2), 1.20 (s, 3 H, CCH_3), 0.75 (dd, J = 7, 3 Hz, 6 H, $CH(CH_3)_2$); ^{13}C NMR (DMSO-d_6) δ 81.83, 73.63 (+, COH), 33.62 (+, CH_2), 32.21 (–, $CH(CH_3)_2$), 26.72 (+, CH_2), 22.84 (–, CCH_3), 16.30 (–, $CH(CH_3)_2$); MS *m z* 144 (M^+, 1), 142 (1), 126 (3), 116 (43), 101 (49), 86 (54), 71 (100), 58 (21).

1-Cyclohexyl-2-methyl-cyclobutane-cis-*1,2-diol* (**2e**). Diketone **1e** (182 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 5 h reaction time **2e**, 144 mg (78%), colourless solid, m.p. 55 - 56 °C. IR ($CHCl_3$) ν 3588, 3536, 3448, 2980, 2932, 2852, 1448, 1380, 1356, 1292, 1184, 1136, 1092, 1016 cm^{-1}; ^1H NMR δ 3.45 (br. s, 1 H, OH), 2.80 (br. S, 1 H, OH), 2.20 - 2.00 (m, 1 H, cyclohexyl CH), 1.89 - 1.00 (m, 17 H); ^{13}C NMR δ 82.93, 74.64 (+, COH), 43.12 (–, cyclohexyl CH), 34.30, 26.67, 26.64, 26.57, 26.49, 26.02, 25.82 (+, CH_2), 22.38 (–, CH_3); MS *m/z* 184 (M^+, 6), 182 (1), 166 (3), 156 (91), 126 (50), 111 (29), 83 (62), 71 (100), 55 (43).

1-Benzyl-2-methyl-cyclobutane-cis-*1,2-diol* (**2f**). Diketone **1f** (190 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 3 h reaction time **2f**, 121 mg (63%), colourless solid, m.p. 96 - 97 °C. IR (KBr) ν 3485, 3370, 3029, 2981, 2964, 2939, 1603, 1496, 1455, 1391, 1353, 1245, 1231, 1153, 1098, 979, 713 cm^{-1}; ^1H NMR δ 7.37 - 7.16 (m, 5 H, arom. H), 3.17 (br. s, 1 H, OH), 2.81 (s, 2 H, $PhCH_2$), 2.48 (s, 1 H, OH), 2.14 - 1.55 (m, 4 H, CH_2CH_2), 1.38 (2, 3 H, CH_3); ^{13}C NMR δ

136.89 (+, arom. C), 129.94, 128.38, 126.50 (–, arom. C), 79.65, 75.36 (+, COH), 41.28 (+, $PhCH_2$), 33.34, 28.62 (+, CH_2CH_2), 22.14 (–, CH_3); MS *m/z* 192 (M^+, 6), 174 (13), 164 (42), 135 (60), 134 (72), 116 (59), 105 (37), 101 (60), 92 (85), 91 (100). Anal. Calcd. for $C_{12}H_{16}O_2$: C, 77.97; H, 8.39. Found: C, 77.67; H, 8.32.

1-Methyl-2-(1-methylpropyl)-cyclobutane-cis-*1,2-diol* (**2g**). Diketone **1g** (156 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 3 h reaction time **2g**, 128 mg (81%), yellowish oil. IR ($CHCl_3$) ν 3528, 3432, 2956, 2872, 1468, 1380, 1244, 1172, 996 cm^{-1}; ^1H NMR δ 3.45 (br. s, 2 H, OH), 2.21 - 1.63 (m, 5 H, CH_2CH_2, $CH(CH_3)_2$), 1.54 - 1.28 (m, 2 H, CH_2CH), 1.25 (s, 3 H, CCH_3), 0.94 (dd, *J*= 7, 3 Hz, 6 H, $CH(CH_3)_2$); ^{13}C NMR δ 80.28, 75.61 (+, COH), 43.62 (+, CH_2CH), 33.90, 29.55 (+, CH_2CH_2), 24.77, 24.25 (–, $CH(CH_3)_2$), 23.28 (–, $CH(CH_3)_2$), 22.15 (–, CCH_3); MS *m/z* 158 (M^+, 0), 156 (M^+-2, 1), 130 (28), 114 (8), 87 (56), 72 (10), 58 (100).

1-Methyl-2-phenyl-cyclobutane-cis-*1,2-diol* (**2h**). Diketone **1h** (176 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 5 h reaction time **2h**, 156 mg (88%), colourless solid, m.p. 71 °C. IR ($CHCl_3$) ν 3596, 3540, 3408, 3084, 3060, 2992, 1496, 1448, 1392, 1356, 1188, 980 cm^{-1}; ^1H NMR δ 7.37 - 7.16 (m, 5 H, arom. H), 3.87 (br. s, 2 H, OH), 2.40 - 1.77 (m, 4 H, CH_2), 0.90 (s, 3 H, CH_3); ^{13}C NMR δ 141.95 (+, arom. C), 128.13, 127.43, 126.05 (–, arom. C), 81.78, 76.03 (+, COH), 33.58, 25.64 (+, CH_2), 23.35 (–, CH_3); MS *m/z* 178 (M^+, 1), 176 (2), 161 (7), 150 (17), 120 (100), 105 (93), 91 (13), 77 (47), 51 (16). Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.15; H, 7.88.

1-(4-Methoxyphenyl)-2-methyl-cyclobutane-cis-*1,2-diol* (**2i**). Diketone **1i** (206 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 4 h reaction time **2i**, 192 mg (92%), colourless solid, m.p. 69 - 70 °C. IR (KBr) ν 3424, 3252, 3044, 2972, 2940, 1612, 1580, 1512, 1452, 1404, 1368, 1304, 1256, 1220, 1180, 1120, 1052, 988, 952, 840, 812 cm^{-1}; ^1H NMR δ 7.27 - 7.16 (m, 2 H, CCH), 6.89 - 6.77 (m, 2 H, CCHCH), 4.60 (br. s, 2 H, OH), 3.76 (s, 3 H, OCH_3), 2.39 - 2.12, 1.99 - 1.80 (m, 4 H, CH_2), 0.93 (s, 3 H, CH_3); ^{13}C NMR δ 158.79 (+, *C*OMe), 134.45 (+, *C*CH), 127.31 (*C*CH), 113.51 (CCHCH), 81.65, 76.14 (+, COH), 55.17 (–, OCH_3), 33.60, 25.89 (+, CH_2), 23.42 (–, CH_3); MS *m/z* 208 (M^+, 0), 206 (M^+-2, 3), 190 (11), 150 (85), 135 (100), 107 (13), 91 (11), 77 (25). Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.00; H, 7.68.

1-(4-Chlorophenyl)-2-methyl-cyclobutane-cis-*1,2-diol* (**2j**). Diketone **1j** (211 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 5 h reaction time **2j**, 193 mg (91%), colourless solid, m.p. 58 - 59 °C. IR (KBr) ν 3397, 2979, 2944, 1598, 1574, 1490, 1367, 1246, 1194, 1093, 984, 889, 827 cm^{-1}; ^1H NMR δ 7.32 - 7.16 (m, 4 H, arom. H), 3.94 (br. s, 2 H, OH), 2.38 - 2.10, 2.02 - 1.78 (m, 4 H, CH_2), 0.89 (s, 3 H, CH_3); ^{13}C NMR δ 140.48 (+, *C*CH), 133.21 (+, C-Cl), 128.30, 127.53 (–, arom. C), 81.23, 76.06 (+, COH), 33.43, 25.85 (+, CH_2), 23.35 (–, CH_3); MS *m/z* 212 (M^+, 1), 210 (3), 186 (6), 184 (13), 156 (30), 154 (93), 141 (38), 139 (100), 111 (35), 91 (16), 77 (26), 75 (30); HRMS calcd. for $C_{11}H_{13}ClO_2$: 212.0604, found 212.0626.

1-(2-Furyl)-2-methyl-cyclobutane-cis-*1,2-diol* (**2k**). Diketone **1k** (166 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 5 h reaction time **2k**, 140 mg (83%), yellowish oil. IR ($CHCl_3$) ν 3540, 2996, 2952, 1716, 1672, 1600, 1352, 1192, 1008, 988 cm^{-1}; ^1H NMR δ 7.35 (dd, $^3J \approx 2$ Hz, $^4J \approx 1$ Hz, 1 H, OC*H*CH), 6.33 (dd, $^3J \approx 3.5$ Hz, $^3J \approx 2$ Hz, 1 H, OCHC*H*), 6.25 (dd, $^3J \approx 3.5$ Hz, $^4J \approx 1$ Hz, 1 H, OCHCH*H*), 3.93 (br. s, 2 H, OH), 2.40 - 1.84 (m, 4 H, CH_2), 1.09 (s, 3 H, CH_3); ^{13}C NMR δ 155.60 (+, O*C*CH), 141.96 (–, OCH), 110.14, 106.58 (–, OCH*C*H*C*H), 76.68, 76.50 (+, COH), 32.79, 26.84 (+, CH_2), 23.04 (–, CH_3); MS *m/z* 168 (M^+, 4), 166 (3), 150 (4), 140 (8), 110 (100), 95 (33), 81 (15), 68 (10); HRMS calcd. for $C_9H_{12}O_2$: 168.0786, found 168.0787.

2-Methyl-1-(2-thienyl)-cyclobutane-cis-*1,2-diol* (**2l**). Diketone **1l** (182 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 2.5 h reaction time **2l**, 134 mg (73%), colourless solid, m.p. 80 - 82 °C. IR (KBr) ν 3462, 3294, 3104, 3073, 2993, 2980, 2947, 1433, 1398, 1361, 1250, 1192, 1120, 1020, 977, 942, 823, 699 cm^{-1}; ^1H NMR δ 7.22 (dd, $^3J = 5$ Hz, $^4J = 1$ Hz, 1 H, SC*H*), 6.95 (dd, $^3J = 5$ Hz, $^3J = 4$ Hz, 1 H, SCHC*H*), 6.90 (dd, $^3J = 4$ Hz, $^4J = 1$ Hz, 1 H, SCHCH*H*), 3.83 (br. s, 2 H, OH), 2.40 - 1.85 (m, 4 H, CH_2), 1.05 (s, 3 H, CH_3); ^{13}C NMR δ 146.82 (+, S*C*CH), 126.71, 124.74, 123.88 (–, thienyl CH), 79.52, 76.75 (+, COH), 33.06, 29.16 (+, CH_2), 23.12 (–, CH_3); MS *m/z* 184 (M^+, 3), 182 (2), 166 (3), 156 (6), 126 (100), 111 (51), 97 (15), 84 (27); HRMS calcd. for $C_9H_{12}O_2S$: 184.0558, found 184.0554. Anal. Calcd. for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.81; H, 6.48.

1-Benzo[1,3]dioxol-5-yl-2-methyl-cyclobutane-cis-*1,2-diol* (**2m**). Diketone **1m** (220 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) to give after 3 h reaction time **2m**, 181 mg (81%), colourless solid, m.p. 83 - 84 °C. IR (KBr) ν 3425, 2987, 2967, 2941, 2900, 1504, 1488, 1442, 1367, 1237, 1193, 1109, 1039, 992, 934, 818 cm^{-1}; ^1H NMR δ 6.86 - 6.70 (m, 3 H, arom. H), 5.90 (s, 2 H, OCH_2), 3.85 (br. s, 2 H, OH), 2.33 - 2.20, 2.02 - 1.78 (m, 4 H, CH_2CH_2), 0.95 (s, 3 H, CH_3); ^{13}C NMR δ 147.53, 146.79 (+, CH_2OC), 136.33 (+, HOCCCH), 119.34 (–, HOCCCHCH), 107.82, 106.89 (–, CH_2OCCH), 100.94 (+, OCH_2), 81.80, 76.04 (+, COH), 33.63, 26.06 (+, CH_2CH_2), 23.30 (–, CH_3); MS *m/z* 222 (M^+, 3), 220 (6), 204 (6), 177 (4), 164 (100), 149 (79), 122 (53), 103 89), 91 (7), 76 (18).

cis-*7-Methyl-bicyclo[3.2.0]heptane*-cis-*1,7-diol* [**4a** (*cis*-fused)]. Diketone **3a** (140 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method C) to give after 1 h reaction time **4a** (*cis*-fused), 43 mg (30%), colourless solid. IR ($CHCl_3$) ν 3608, 3532, 3000, 2956, 2860, 1468, 1432, 1376, 1320, 1228, 1144, 1108, 1064, 1040, 1012, 916 cm^{-1}; ^1H NMR δ 3.83 (br. s, 1 H, OH), 3.46 (br. s, 1 H, OH), 2.59 - 2.47 (m, 1 H, CH), 1.98 (dd, $J = 13$, 3 Hz, 1 H, C*H*H), 1.90 - 1.40 (m, 6 H), 1.27 (dd, $J = 13$, 7 Hz, 1 H, CH*H*), 1.21 (s, 3 H, CH_3); ^1H NMR (DMSO-d_6) δ 4.88 (s, 1 H, OH), 4.38 (s, 1 H, OH), 2.41 - 2.28 (m, 1 H, CH), 1.82 (dd, $J = 12$, 3 Hz, 1 H, C*H*H), 1.74 - 1.32 (m, 6 H), 1.13 (dd, $J = 13$, 6 Hz, 1 H, CH*H*), 1.04 (s, 3 H, CH_3); ^{13}C NMR δ 84.97, 75.70 (+, COH), 43.56 (–, CH), 35.04, 33.94, 30.29, 24.67 (+, CH_2), 21.71 (–,

CH_3); MS *m/z* 142 (M^+, 5), 124 (4), 112 88), 97 (17), 91 (5), 87 (44), 84 (100), 70 (11), 67 (17); HRMS calcd. for $C_8H_{14}O_2$: 142.0994, found 142.0993.

cis-*8-Methyl-bicyclo[4.2.0]octane*-cis-*1,8-diol* [**4b** (*cis*-fused)] *and* trans-*8-Methyl-bicyclo[4.2.0]octane*-cis-*1,8-diol* [**4b** (*trans*-fused)]. Diketone **3b** (154 mg, 1.00 mmol) was allowed to react for 30 min according to the general procedure (work up: method C). The diastereomers were separated by chromatography to afford **4b** (*cis*-fused) (83 mg, 53%) and **4b** (*trans*-fused) (62 mg, 40%). Data for **4b** (*cis*-fused), colourless solid, m.p. 55 °C. IR ($CHCl_3$) ν 3576, 3420, 2936, 2860, 1448, 1380, 1228, 1036, 1016, 920 cm^{-1}; ^1H NMR (600 MHz) δ 2.86 (br. s, 1 H, OH), 2.69 (br. s, 1 H, OH), 2.54 - 2.48 (m, 1 H, CH), 1.69 (dd, *J* = 12, 2 Hz, 1 H, C*H*H), 1.66 - 1.55 (m, 5 H, CH_2), 1.49 - 1.42 (br. dd, 1 H, CH*H*), 1.39 - 1.26 (m, 2 H, CH_2), 1.23 (s, 3 H, CH_3); ^1H NMR (DMSO-d_6) δ 4.40 (s, 1 H, OH), 4.27 (s, 1 H, OH), 2.46 - 2.31 (m, 1 H), 1.51 - 1.18 (m, 10 H), 1.06 (s, 3 H, CH_3); ^{13}C NMR δ 77.61, 73.39 (+, COH), 32.32, 30.70, 29.70, 21.57, 20.97 (+, CH_2), 39.48 (–, CH), 21.53 (–, CH_3); MS *m/z* 156 (M^+, 4), 138 (4), 123 (4), 114 (8), 98 (100), 87 (36), 83 (46), 70 (79); HRMS calcd. for $C_9H_{16}O_2$: 156.1150, found 156.1149. Anal. Calcd. for $C_9H_{16}O_2$: C, 69.18; H, 10.33. Found: C, 68.85; H, 10.24. NOE: CH_3 (1.23 ppm), s with $HOCC\mathit{H}_2CH_2$ and $HOCCH_2C\mathit{H}_2$, w with $H_3CC\mathit{H}_2$. Data of **4b** (*trans*-fused), colourless solid, m.p. 51 °C. IR ($CHCl_3$) ν 3520, 3444, 2940, 2860, 1620, 1352, 1152, 1088, 960 cm^{-1}; ^1H NMR (600 MHz) δ 3.20 (s, 1 H, OH), 2.36 (s, 1 H, OH), 2.07 - 2.02 (br. dd, 1 H, C*H*H), 1.98 (dd, *J* = 10, 2 Hz, 1 H, CH*H*), 1.76 - 1.72 (m, 1 H, CH_2), 1.68 - 1.61 (m, 1 H, CH_2), 1.56 - 1.47 (m, 4 H, CH, CH_2), 1.38 (s, 3 H, CH_3), 1.33 - 1.25 (m, 1 H, CH_2); ^1H NMR (DMSO-d_6) δ 4.77 (s, 1 H, OH), 4.08 (s, 1 H, OH), 1.92 (br. dd, 1 H), 1.75 (dd, *J* = 10, 7 Hz, 1 H), 1.78 - 1.55 (m, 3 H), 1.48 - 1.29 (m, 6 H), 1.23 (s, 3 H, CH_3); ^{13}C NMR δ 80.34, 76.43 (+, COH), 41.83, 31.69, 26.21, 23.00, 21.22 (+, CH_2), 36.67 (–, CH), 20.80 (–, CH_3); MS *m/z* 156 (M^+, 9), 138 (5), 123 (5), 113 (19), 98 (100), 87 (84), 83 (48), 70 (85). HRMS calcd. for $C_9H_{16}O_2$: 156.1150, found 156.1146. NOE: CH_3 (1.23 ppm), s with CH, w with $H_3CC\mathit{H}_2$.

cis-*9-Methyl-bicyclo[5.2.0]nonane*-cis-*1,9-diol* [**4c** (*cis*-fused)] *and* trans-*9-Methyl-bicyclo[5.2.0]nonane*-cis-*1,9-diol* [**4c** (*trans*-fused)]. Diketone **3c** (168 mg, 1.00 mmol) was allowed to react for 1 h according to the general procedure (work up: method C). The diastereomers were separated by chromatography to afford **4c** (*cis*-fused) (70 mg, 41%) and **4c** (*trans*-fused) (83 mg, 49%). Data for **4c** (*cis*-fused), colourless solid, m.p. 54 °C. IR ($CHCl_3$) ν 3608, 3564, 2924, 2852, 1452, 1380, 1340, 1184, 1104, 1060, 1036, 996, 932 cm^{-1}; ^1H NMR δ 3.53 (br. s, 1 H, OH), 3.43 (br. s, 1 H, OH), 2.32 - 2.22 (m, 1 H, CH), 2.07 (dd, *J* = 12, 10 Hz, 1 H, C*H*H), 1.92 - 1.59 (m, 9 H), 1.33 (dd, *J* = 12, 8 Hz, 1 H, CH*H*), 1.20 (s, 3 H, CH_3), 1.26 - 1.17 (m, 1 H); ^1H NMR (DMSO-d_6) δ 4.63 (s, 1 H, OH), 4.37 (s, 1 H, OH), 2.23 - 2.05 (m, 1 H), 1.88 (dd, *J* = 12, 2 Hz, 1 H, C*H*H), 1,81 - 1.46 (m, 10 H), 1,18 (dd, *J* = 12, 4 Hz, 1 H, CH*H*), 1.04 (s, 3 H, CH_3); ^{13}C NMR δ 79.79, 74.30 (+, COH), 44.77 (–, CH), 37.95, 34.29, 32.50, 32.17, 28.25, 24.44 (+, CH_2), 23.07 (–, CH_3); MS *m/z* 170 (M^+, 3), 152 (3), 137 (3), 127 (8), 112 (100), 97 (75), 84 (84), 67 (32); HRMS calcd. for $C_{10}H_{18}O_2$: 170.1307, found 170.1300. Data of **4c** (*trans*-fused), semisolid. IR ($CHCl_3$) ν 3596, 3544, 2932, 2856, 1448, 1380, 1352,

1236, 1080, 1032, 984, 920 cm^{-1}; ^1H NMR δ 3.53 (br. s, 1 H, OH), 2.81 (br. s, 1 H, OH), 1.95 (dd, *J* = 11, 6 Hz, 1 H, C*H*H), 1.85 (dd, *J* = 14, 6 Hz, 1 H, CH*H*), 1.73 - 1.42 (m, 10 H), 1.30 (s, 3 H, CH_3); ^1H NMR (DMSO-d_6) δ 4.58 (s, 1 H, OH), 4.02 (s, 1 H, OH), 1.80 - 1.35 (m, 12 H), 1.16 (s, 3 H, CH_3); ^{13}C NMR δ 83.08, 72.04 (+, COH), 35.43 (–, CH), 41.12, 33.25, 28.53, 26.97, 25.89, 25.50 (+, CH_2), 22.24 (–, CH_3); MS *m/z* 170 (M^+, 7), 152 (3), 137 (3), 127 (11), 112 (100), 97 (61), 84 (64), 67 (30). HRMS calcd. for $C_9H_{16}O_2$:170.1307, found 170.1307.

General Procedure for the Preparation of Carbonates **5**. To pinacol **4** (0.50 mmol) was added CDI (N,N′-carbonyldiimidazolide) (90 mg, 0.54 mmol) in THF (1.5 mL). The volume of the solution was reduced to ~1 mL. After being refluxed for 1 - 2 h the reaction mixture was dissolved in E, applied to silica gel and chromatographed (E/PE).

*(1,5*cis*,1,7*cis*)-5-Methyl-2,4-dioxatricyclo[5.3.0.0^{1,5}]decan-3-one* [**5a** (*cis*-fused)]. Pinacol **4a** (*cis*-fused) (71 mg, 0.50 mmol) was allowed to react according to the general procedure to afford **5a** (*cis*-fused), 42 mg (50%), colourless solid, m.p. 47 °C. IR (KBr) ν 2948, 2884, 2860, 1784, 1740, 1436, 1388, 1332, 1260, 1180, 1148, 1108, 1064, 992, 776 cm^{-1}; ^1H NMR δ 2.96 - 2.84 (m, 1 H, CH), 2.60 (dd, *J* = 14, 10 Hz, 1 H, C*H*H), 2.06 - 1.70 (m, 5 H), 1.59 (dd, *J* = 14, 6 Hz, 1 H, CH*H*), 1.66 - 1.53 (m, 1 H), 1.39 (s, 3 H, CH_3); ^{13}C NMR δ 155.26 (+, C=O), 93.50, 86.58 (+, C-O), 41.47 (–, CH), 35.22, 30.08, 28.22, 24.20 (+, CH_2), 17.94 (–, CH_3); MS *m z* 168 (M^+, 0), 124 (14), 109 (339, 96 (51), 81 (95), 67 (100). Anal. Calcd. for $C_9H_{12}O_3$: C, 64.26; H, 7.20. Found: C, 64.55; H, 7.34.

*(1,5*cis*,1,7*cis*)-5-Methyl-2,4-dioxatricyclo[5.4.0.0^{1,5}]undecan-3-one* [**5b** (*cis*-fused)]. Pinacol **4b** (*cis*-fused) (78 mg, 0.50 mmol) was allowed to react according to the general procedure to afford **5b** (*cis*-fused), 73 mg (80%), colourless solid, m.p. 49 °C. IR ($CHCl_3$) ν 2984, 2944, 2864, 1792, 1452, 1384, 1280, 1240, 1164, 1124, 1092, 1048, 1016 cm^{-1}; ^1H NMR δ 2.67 - 2.50 (m, 2 H), 2.13 - 2.03 (m, 1 H), 1.99 - 1.86 (m, 2 H), 1.78 - 1.67 (m, 2 H), 1.54 (s, 3 H, CH_3), 1.63 - 1.43 (m, 2 H), 1.40 - 1.23 (m, 2 H); ^{13}C NMR δ 155.16 (+, C=O), 87.51, 85.53 (+, C-O), 35.85 (–, CH), 38.88, 28.71, 25.72, 21.13, 21.01 (+, CH_2), 18.88 (–, CH_3); MS *m/z* 182 (M^+, 0), 138 (3), 123 (15), 109 (24), 95 (100), 79 (38), 67 (67). Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.90; H, 7.75. Found: C, 65.96; H, 7.71.

*(1,5*cis*,1,7*trans*)-5-Methyl-2,4-dioxatricyclo[5.4.0.0^{1,5}]undecan-3-one* [**5b** (*trans*-fused)]. Pinacol **4b** (*trans*-fused) (78 mg, 0.50 mmol) was allowed to react according to the general procedure to afford **5b** (*trans*-fused), 72 mg (79%), colourless solid, m.p. 69 °C. IR ($CHCl_3$) ν 2980, 2944, 2868, 1788, 1724, 1444, 1388, 1300, 1276, 1214, 1168, 1112, 1084, 1040, 1024, 912, 864 cm^{-1}; ^1H NMR δ 2.37 - 2.25 (m, 2 H), 2.05 - 1.93 (m, 1 H), 1.87 - 1.59 (m, 7 H), 1.56 (s, 3 H, CH_3), 1.48 - 1.32 (m, 1 H); ^{13}C NMR δ 155.21 (+, C=O), 94.70, 85.69 (+, C-O), 37.71 (–, CH), 40.59, 2956, 25.65, 23.66, 21.08 (+, CH_2), 15.75 (–, CH_3); MS *m/z* 182 (M^+, 0), 138 (4), 123 (13), 109 (21), 95 (100), 79 (40), 67 (76). Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.90; H, 7.75. Found: C, 66.76; H, 8.02.

*(1,5*cis*,1,7*cis*)-5-Methyl-2,4-dioxatricyclo[5.5.0.0^{1,5}]dodecan-3-one* [**5c** (*cis*-fused)]. Pinacol **4c** (*cis*-fused) (85 mg, 0.50 mmol) was allowed to react according to the general procedure to afford **5c** (*cis*-fused), 55 mg (56%), colourless solid, m.p. 55 °C. IR ($CHCl_3$) ν 2932, 2856, 1784, 1720, 1452, 1384, 1280, 1276, 1232, 1172, 1140, 1116, 1060, 1044, 1020 cm^{-1}; ^{1}H NMR δ 2.69 - 2.55 (m, 2 H), 1.99 - 1.57 (m, 6 H), 1.45 - 1.24 (m, 4 H), 0.99 - 0.92 (m, 1 H); ^{13}C NMR δ 155.32 (+, C=O), 90.90, 84.36 (+, C-O), 44.56 (–, CH), 36.89, 33.92, 31.38, 29.69, 28.95, 24.90 (+, CH_2), 19.20 (–, CH_3); MS *m/z* 196 (M^+, 5), 152 (4), 137 (12), 123 (10), 109 (97), 95 (45), 81 (49), 67 (100). Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.31; H, 8.22. Found: C, 67.04; H, 8.17.

*(1,5*cis*,1,7*trans*)-5-Methyl-2,4-dioxatricyclo[5.5.0.0^{1,5}]dodecan-3-one* [**5c** (*trans*-fused)]. Pinacol **4c** (*trans*-fused) (85 mg, 0.50 mmol) was allowed to react according to the general procedure to afford **5c** (*trans*-fused), 73 mg (74%), colourless solid, m.p. 55 °C. IR ($CHCl_3$) ν 2980, 2940, 2864, 1788, 1652, 1452, 1384, 1292, 1248, 1168, 1136, 1112, 1084, 1020 cm^{-1}; ^{1}H NMR δ 2.35 - 2.25 (m, 2 H), 2.15 - 2.00 (m, 1 H), 1.83 - 1.54 (m, 10 H), 1.74 (s, 3 H, CH_3); ^{13}C NMR δ 155.68 (+, C=O), 94.86, 82.25 (+, C-O), 37.26 (–, CH), 39.30, 30.40, 28.53, 26.08, 25.93, 25.12 (+, CH_2), 17.14 (–, CH_3); MS *m/z* 196 (M^+, 6), 152 (4), 137 (15), 123 (10), 109 (86), 95 (40), 81 (44), 67 (100). Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.31; H, 8.22. Found: C, 67.48; H, 8.24.

General Procedure for the Preparation of Diketones **6**. To a solution of LDA (prepared from 10 mmol diisopropylamine and 10 mmol BuLi) in THF (10 mL) was added the cycloalkanone (9 mmol) dropwise at –78 °C. After 1 h a solution of $CuCl_2$ (1.34 g, 10 mmol) in DMF (10 mL) was added rapidly and the mixture was stirred for further 30 min at the same temperature. The reaction mixture was allowed to reach room temperature, acidified by addition of dil. HCl and extracted with cyclohexane. The combined organic layer was washed with sat. aq. $NaHCO_3$ solution, dried ($MgSO_4$), evaporated and purified by chromatography (cyclohexane/MTBE).

(1R,1′S)-1,1′-Bicyclopentyl-2,2′-dione (*meso*-**6a**) *and (1R*,1′R*)-1,1′-Bicyclopentyl-2,2′-dione* (*rac*-**6a**). Cyclopentanone (756 mg, 9.00 mmol) was treated as described above to give the diastereomeric mixture (311 mg, 36%), which could be separated. Data for *meso*-**6a**: Yield, 102 mg (12%), colourless solid, m.p. 35 - 36 °C. IR ($CHCl_3$) ν 2968, 2880, 1732, 1452, 1404, 1332, 1272, 1252, 996, 928; ^{1}H NMR δ 2.64 - 2.46 (m, 2 H, H-2), 2.46 - 1.97 (m, 8 H, CH_2), 1.97 - 1.48 (m, 4 H, CH_2); ^{13}C NMR δ 219.09 (+, C-1), 49.26 (–, C-2), 38.20 (+, C-5), 26.79 (+, C-3), 20.89 (+, C-4); MS *m/z* 166 (M^+, 36), 123 (15), 111 (30), 84 (100), 83 (89), 67 (42), 55 (43). Data for *rac*-**6a**: Yield, 114 mg (13%), colourless solid, m.p. 68 - 69 °C. IR ($CHCl_3$) ν 2968, 2880, 1732, 1452, 1404, 996; ^{1}H NMR δ 2.76 - 2.59 (m, 2 H, H-2, H-2′), 2.45 - 2.25 (m, 2 H, H-5, H-5′), 2.20 - 1.53 (m, 10 H, H-3, H-3′, H-4, H-4′, H-5, H-5′); ^{13}C NMR δ 219.95 (+, C-1, C-1′), 48.55 (–, C-2, C-2′), 38.01 (+, C-5, C-5′), 25.41 (+, C-3, C-3′), 20.72 /+, C-4, C-4′); MS *m/z* 166 (M^+, 38), 138 (7), 123 (15), 110 (32), 84 (100), 83 (92), 67 (38), 55 (40).

(1R,1'S)-1,1'-Bicyclohexyl-2,2'-dione (*meso*-**6b**) *and (1R*,1'R*)-1,1'-Bicyclohexyl-2,2'-dione* (*rac*-**6b**). Cycloheptanone (1.76 g, 18.00 mmol) was treated as described above to give the diastereomeric mixture (589 mg, 39%), which could be separated. Data for *meso*-**6b**: Yield, 368 mg (24%), colourless oil. ^{1}H NMR δ 2.72 - 2.60 (m, 2 H, H-2), 2.49 - 2.21 (m, 4 H, H-6), 2.09 - 1.20 (m, 12 H, CH_2); ^{13}C NMR δ 210 (+, C-1), 50.29 (–, C-2), 41.75 (+, C-6), 29.09 (+, C-3), 26.47 (+, C-5), 24.95 (+, C-4). Data of *rac*-**6b**: Yield, 221 mg (15%), colourless solid, m.p. 69 - 70°C. IR (KBr) ν 2947, 2857, 1694, 1455, 1428, 1339, 1285, 1198, 1127, 1094, 875, 832; ^{1}H NMR δ 2.97 - 2.79 (m, 2 H, H-2, H-2'), 2.52 - 2.26 (m, 4 H, H-6, H-6'), 2.20 - 1.20 (m, 12 H); ^{13}C NMR δ 211.45 (+, C-1, C-1'), 48.99 (–, C-2, C-2'), 42.28 (+, C-6, C-6'), 30.14 (+, C-3, C-3'), 28.07 (+, C-5, C-5'), 25.44 (+, C-4, C-4'). MS *m/z* 194 (M^+, 23), 176 (7), 148 (15), 137 (20), 112 (15), 110 (15), 98 (100), 97 (77), 67 (36).

1,1'-Bicycloheptyl-2,2'-dione (**6c**). Cycloheptanone (4.03 g, 36.0 mmol) was treated as described above to give the diastereomeric mixture (1.23 g, 31%). IR (KBr): 2930, 2850, 1689, 1452, 1409, 1368, 1341, 1214, 1095, 964; ^{1}H NMR (80 MHz) δ 3.14 - 2.71 (m, 2 H, H-2), 2.65 - 2.38 (m, 4 H, H-7), 2.10 - 0.97 (m, 16 H, CH_2); MS *m z* 222 (M^+, 86), 205 (7), 15 (36), 112 (100), 111 (35), 98 (84), 67 (46).

1,1'-Bicyclooctyl-2,2'-dione (**6d**). Cyclooctanone (2.27 g, 18.0 mmol) was treated as described above to give the diastereomeric mixture (420 mg, 19%). IR (film): 2928, 2856, 1698, 1464, 1447, 1359, 1205, 1155, 1004; ^{1}H NMR (300 MHz) δ 3.14 - 3.00 (m, 2 H, H-2), 2.68 - 2.54 (m, 4 H, H-8), 2.22 - 1.00 (m, 22 H, CH_2); MS *m z* 250 (M^+, 15), 165 (15), 139 (21), 127 (100), 113 (51), 109 (41), 98 (56), 81 (46), 67 (86).

(1R,2S,6R,7S)-Tricyclo[5.3.0.0^{2,6}]decan-1,2-diol (*meso*-**7a**). Diketone *meso*-**6a** (166 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) for the cyclization with SmI_2. Reaction time: 2 h. Yield: 87 mg (52%), colourless solid, m.p. 64 - 65 °C. IR (KBr) ν 3500, 3350, 2942, 2871, 1439, 1329, 1296, 1242, 1182, 1104, 1061 cm^{-1}; ^{1}H NMR δ 3.60 (br. s, 2 H, OH), 2.53 - 2.43 (m, 2 H, CH), 2.03 - 1.40 (m, 12 H, CH_2); ^{13}C NMR δ 85.60 (+, COH), 44.12 (–, CH), 34.62 (+, HOC*C*H$_2$), 27.30, 25.57, (+, CH_2); MS *m z* 168 (M^+, 0), 166 (M^+-2, 1), 150 (3), 122 (6), 84 (100), 83 (529, 79 (23), 67 (21). Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.93; H, 9.42.

(1R,2S,7R,8S)-Tricyclo[6.4.0.0^{2,7}]dodecan-1,2-diol (*meso*-**7b**). Diketone *meso*-**6b** (113 mg, 0.560 mmol) was allowed to react according to the general procedure (work up: method A) for the cyclization with SmI_2. Reaction time: 6.5 h. Yield: 74 mg (68%), colourless solid, m.p. 77 - 79 °C. IR (KBr) ν 3468, 3372, 2932, 2864, 1448, 1400. 1360, 1320, 1284, 1256, 1180, 1044, 964 cm^{-1}; ^{1}H NMR δ 3.28 (br. s, 2 H, OH), 2.39 - 2.18 (m, 2 H, CH), 2.02 - 1.80 (m, 2 H, HOCC*H*H), 1.80 - 1.24 (m, 14 H, CH_2); ^{13}C NMR δ 75.93 (+, COH), 41.06 (–, CH), 30.07 (+, HOC*C*H$_2$), 22.45 (+, CH*C*H$_2$), 21.88, 21.25 (+, CH_2); MS *m/z* 196 (M^+, 0), 195 (M^+-1, 1), 194 (1), 178 (2), 149 (4), 135 (3), 121 (2), 107 (3), 99 (14), 98 (100), 97 (20), 83 (39), 81 (13), 79 (11), 70 (43). Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 72.31; H, 9.87.

(1R,2S*,7R*,8S*)-Tricyclo[6.4.0.0^{2,7}]dodecan-1,2-diol* (*rac*-**7b**). Diketone *rac*-**6b** (194 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) for the cyclization with SmI_2. Reaction time: 5 h. Yield: 105 mg (54%), colourless solid, m.p. 97 - 99 °C. IR (KBr) ν 3356, 2932, 2856, 1448, 1284, 1200, 1120, 1056, 972, 928 cm^{-1}; ^{1}H NMR δ 3.51 (br. s, 1 H, OH), 2.87 (br. s, 1 H, OH), 2.40 - 2.25 (m, 1 H, CH), 1.85 - 1.14 (17 H, CH, CH_2); ^{13}C NMR δ 78.50, 76.11 (+, COH), 45.87, 37.58 (–, CH), 31.50, 29.98 (+, HOCCH_2), 26.14, 22.82, 22.40, 21.60, 21.38, 21.27 (+, CH_2); MS *m/z* 196 (M^+, 3), 194 (8), 178 (39), 149 (63), 135 (25), 121 (9), 107 (9), 98(100), 84 (18), 79 (12), 55 (7). Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.02.

Tricyclo[7.5.0.0^{2,8}]tetradecan-1,2-diol (*meso*-**7c**, **7c**). Diketone **6c** (mixture of *meso* and *rac*) (222 mg, 1.00 mmol) was allowed to react according to the general procedure (work up: method A) for the cyclization with SmI_2. Reaction time: 3 h. The mixture of *meso*-**7c** and **7c** was separated by chromatography to afford *meso*-**7c** (83 mg, 37%) and **7c** (111 mg, 50%). Data for *meso*-**7c**: colourless solid, m.p. 113 - 115 °C. IR (KBr) ν 3368, 2922, 2851, 1451, 1314, 1232, 1201, 1128, 1088, 1070, 1031, 1005, 942, 920 cm^{-1}; ^{1}H NMR δ 3.05 (br. s, 2 H, OH), 2.30 - 2.10 (m, 2 H, CH), 2.01 - 1.48 (m, 14 H, CH_2), 1.40 - 1.01 (m, 6 H, CH_2); ^{13}C NMR δ 78.89 (+, COH), 46.62 (–, CH), 33.55, 31.91, 29.09, 28.03, 24.50 (+, CH_2); MS *m/z* 224 (M^+, 1), 207 (3), 149 (5), 112 (100), 97 (349, 84 (47), 67 (14). HRMS calcd. for $C_{14}H_{24}O_2$: 224.1776, found 224.1785. Anal. Calcd. for $C_{14}H_{24}O_2$: C, 75.63; H, 9.97. Found: C, 75.15; H, 10.59. Data for **7c**: colourless solid, 98 - 100 °C. IR (KBr) ν 3392, 2927, 2853, 1455, 1370, 1274, 1217, 1146, 1050, 928 cm^{-1}; ^{1}H NMR δ 3.10 (br. s, 1 H, OH), 2.53 (br. s, 1 H, OH), 2.10 - 0.97 (m, 22 H, CH, CH_2); ^{13}C NMR δ 80.56, 76.43 (+, COH), 51.99, 44.15 (–, CH), 33.33, 33.19, 32.49, 31.85, 28.43, 26.90, 26.49, 25.88, 24.39, 24.31 (+, CH_2); MS *m/z* 224 (M^+, 1), 207 (1), 152 (2), 113 (100), 97 (31), 84 (42), 67 (16). HRMS calcd. for $C_{14}H_{24}O_2$: 224.1776, found 224.1774.

Tricyclo[8.6.0.0^{2,9}]hexadecan-1,2-diol (*meso*-**7d**, **7d**). Diketone **6d** (mixture of *meso* and *rac*) (125 mg, 0.500 mmol) was allowed to react according to the general procedure (work up: method A) for the cyclization with SmI_2. Reaction time: 3 h. The mixture of *meso*-**7c** and **7c** was separated by chromatography to afford *meso*-**7d** (25 mg, 20%) and **7d** (60 mg, 48%). Data for *meso*-**7d**: colourless solid, m.p. 182 - 184 °C. IR (KBr) ν 3419, 2914, 2852, 1462, 1446, 1229, 1162, 1068, 1045, 995, 943, 842 cm^{-1}; ^{1}H NMR (DMSO-d_6/CD_3OD) δ 4.10 (br. s, 2 H, OH), 1.82 - 0.80 (m, 26 H, CH, CH_2); ^{13}C NMR δ 78.14 (+, COH), 47.09 (–, CH), 28.76, 27.69, 26.73, 25.14, 24.14, 23.86 (+, CH_2); MS *m/z* 252 (M^+, 1), 234 (1), 155 (40), 127 (34), 126 (31), 111 (20), 109 (30), 98 (100), 83 (52), 67 (48). Data for **7d**: colourless solid, m.p. 148 - 150 °C. IR (KBr) ν 3392, 2927, 2851, 1450, 1371, 1327, 1203, 1180, 1004, 991, 971, 878 cm^{-1}; ^{1}H NMR (DMSO-d_6/CD_3OD) δ 3.91 (br. s, 2 H, OH), 2.10 - 0.97 (m, 26 H, CH, CH_2); ^{13}C NMR δ 77.84, 77.65 (+, COH), 52.08, 44.47 (–, CH), 35.74, 30.29, 28.82, 28.73, 28.64, 27.15, 27.12, 25.91, 24.82, 24.77, 24.63, 24.03 (+, CH_2); MS *m/z* 252 (M^+, 1), 234 (2), 169 (7), 151 (14), 126 (26), 111 (47), 98 (100), 83 (40), 67 (36).

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