Transannular Hydride Migration in *Pseudo-Geminally* Substituted [2.2]Paracyclophanes: A Vinylogous Pinacol Rearrangement

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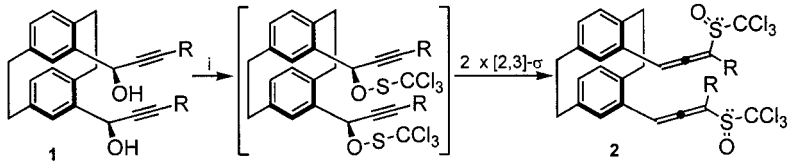
A vinylogous pinacol–pinacolone rearrangement is reported that takes place although the two hydroxyl groups are formally separated by seven bonds. It involves a transannular hydride shift that occurs between the benzylic positions of the *pseudo-geminally* substituted [2.2]paracyclophanes **1a**–**c**, **7**, **8** and **9**. Under mild acidic conditions the corresponding *pseudo-geminally* substituted cyclic ethers were established as stable intermediates.

Introduction

Because of the rigid molecular framework provided by the paracyclophane unit and its short interannular distance, functional groups in *pseudo-geminally* substituted [2.2]paracyclophanes are often held in such a position as to allow highly specific reactions to take place between them. In one such application, unsaturated cyclophane bisesters undergo intramolecular photocyclization to the corresponding ladderane isomers.[1] Following our interest in the synthesis of new unsaturated *pseudo-geminally* substituted [2.2]paracyclophanes, we recently have reported the synthesis of the first *pseudo-geminal* bisallenyl[2.2]paracyclophanes.[2] This was accomplished by the reaction of the corresponding bispropargylic alcohols **1** with perchloromethylmercaptane via a double [2,3]sigmatropic rearrangement (Scheme 1). The spatial orientation of the allenic moieties is favorable for further intramolecular reactions, thermally or photochemically induced. Moreover, these compounds might be interesting for studies of topochemical reaction control in solution.

Although we successfully prepared the first *pseudo-geminal* bisallenic systems, the above reaction sequence is disadvantageous in three respects. First, the bisallenyl sulfoxides are obtained as an inseparable mixture of diastereoisomers. Secondly, the overall yield for the bisallenyl sulfones, obtained by the oxidation of the corresponding sulfoxides with dimethyldioxirane, is quite low (30–35%). Finally, the lack of available stable sulfenyl chlorides limits the variety of sulfur-substituted bisallenic systems by this approach. In view of the above inconveniences, we decided to investigate a direct synthesis of allenyl sulfones. This is usually achieved by the [2.3]sigmatropic rearrangement of propargylic sulfinates.[3] Moreover, Sharpless has reported that sulfonyl esters are easily reduced to the sulfinyl esters by trimethyl phosphite, in the presence of excess pyridine.[4] A combination of these two methods could provide a direct conversion of propargylic sulfonates to allenyl sulfones, by in situ reduction to the propargylic sulfinates, followed by [2,3]sigmatropic rearrangement.



Scheme 1. Conditions: (i) PCMM (2 equiv.), Et_3N (2 equiv.), CH_2Cl_2, –78 °C.

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Results and Discussion

Bispropargylic alcohols **1a**–**c**[2] were reacted with methanesulfonyl chloride, in the presence of excess pyridine and trimethyl phosphite. This reaction sequence should provide the corresponding *pseudo-geminal* bisallenyl sulfones, fol-

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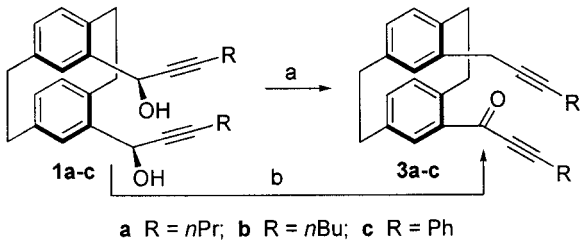
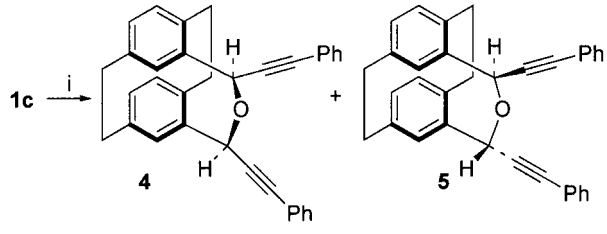
lowing the mechanism described above. However, under the appropriate reaction conditions for our substrate (–78 °C to room temp.), the NMR spectra of the crude products failed to show the spectral features of an allenic moiety. Keeping in mind that in some cases the reduction step is completed after heating, we heated the crude products gently in dichloromethane. After three days, the NMR spectra showed the formation of an interesting unsymmetrically substituted *pseudo-geminal* [2.2]paracyclophane. The 2D NMR analysis of the pure reaction products revealed a structure of type **3** (Scheme 2), rather than the expected bisallenic sulfones.



Scheme 2. Path "a": (i) MsCl (2 equiv.), $P(OMe)_3$ (4 equiv.), py (3 equiv.), CH_2Cl_2, –78 °C; (ii) CH_2Cl_2, 40 °C, 72 h, 40–43%; Path "b": H_2SO_4, 0 °C, 10 min, 80–85%.

Although the formation of **3** can be explained readily by a pinacol-type rearrangement, it is hard to believe that this takes place under basic conditions. We hence treated the bispropargylic alcohols (**1a**–**c**) with one equivalent of concentrated sulfuric acid in chloroform. On going from 0 °C to room temperature after 10 minutes the same compounds were formed in 80–85% isolated yield (Scheme 2). In a separate experiment, where the synthesis of bisallenyl sulfoxides **2** has been performed using pyridine instead of triethylamine, the formation of **3** was also detected in low yield (ca. 20%). Obviously the reaction by-product, pyridinium chloride, is responsible for the above unusual rearrangement. As proof, we reacted bispropargylic alcohol **1c** with one equivalent of pyridinium chloride. After 60 h at room temp., the starting material had been fully converted to a mixture of cyclic ethers **4** and **5**, in 8:2 ratio (Scheme 3). According to NMR analysis (experimental section), compound **4** possesses the symmetrically *meso*-structure and **5** is the *d,l* diastereomer. Detailed structural information was obtained from X-ray analysis (Figure 1).



Scheme 3. Conditions: (i) PyHCl (1 equiv.), $CHCl_3$, room temp., 60 h, 98%. Product ratio **4/5** = 8:2.

Whereas the formation of compounds **3** via reaction pathway "b" appears to follow the mechanism of a pinacol type rearrangement, it is not clear how **3** is formed according to pathway "a". However, the cyclic ethers described above can be intermediates in the formation of the pinacolone type compounds. Since the treatment of **1c** with PyHCl at room temp. gives only the dehydrated product **4** and **5**, it seems that a stronger acid promotes the ring opening of the cyclic ethers via pathway "a". Thus, a mechanistic rationalization of the latter reaction pathway indicates that, as soon as one of the hydroxyl groups of the starting material is converted into a mesylate, a fast nucleophilic attack of the second hydroxyl group takes place with the formation of a cyclic ether. Simultaneously, the methanesulfonic acid is liberated and this seems to be responsible for the cleavage of the cyclic ethers. This mechanistic rationalization is supported by a separate experiment. The reaction of 4,13-bis(hydroxymethyl)[2.2]paracyclophane with *p*-toluenesulfonyl chloride in presence of pyridine or triethylamine always gives a mixture of the corresponding cyclic ether and the rearranged aldehyde rather than the expected bistosylate. A literature search revealed that the conversion of 4,13-bis(hydroxymethyl)[2.2]paracyclophane to the same mixture of the corresponding cyclic ether and rearranged aldehyde has been reported by Cram, using different reagents.[5] Under various reaction conditions different ratios of the reaction products were found.

Both transformations, Cram's and ours, seem to follow the mechanism of the pinacol rearrangement that takes place although the two hydroxyl groups are formally separated by seven bonds. This aspect in particular makes the above reactions interesting. The main features of the mechanism of the pinacol and related rearrangements are generally accepted.[6] The migratory aptitudes of the substituent have also been established, although they may depend on the reaction conditions as well as on the nature of the substrate. A similar rearrangement has been reported for epoxides, when treated with acidic reagents, lithium perchlorate in ether, or sometime by heat alone.[7] Moreover, it has been shown that epoxides are intermediates in the pinacol rearrangements of certain glycols.[8]

Since according to the above consideration a pinacol rearrangement that takes place via *pseudo-geminally* substituted cyclic ethers cannot be ruled out, we decided to investigate the mechanism of these transformations. Because our substrates may be regarded as a particular combination of benzylic and propargylic alcohols, we also investigated the behavior of 4,13-bis(phenylhydroxymethyl)- **7** and 4,13-bis(α-hydroxyethyl)[2.2]paracyclophane (isomers **8** and **9**) under acidic conditions. The first substrate is of particular interest since a real pinacol rearrangement will involve phenyl migration rather than the hydride migration observed above. The synthesis of 4,13-bis(phenylhydroxymethyl)[2.2]paracyclophane **7** has been previously reported by us.[9] As in the case of *pseudo-geminal* bispropargylic alcohols **1a-c**, it has always been obtained as a single stereoisomer, the NMR spectra (experimental section) indicating a symmetrical *meso*-form. 4,13-Bis(α-hydroxyethyl)[2.2]para-

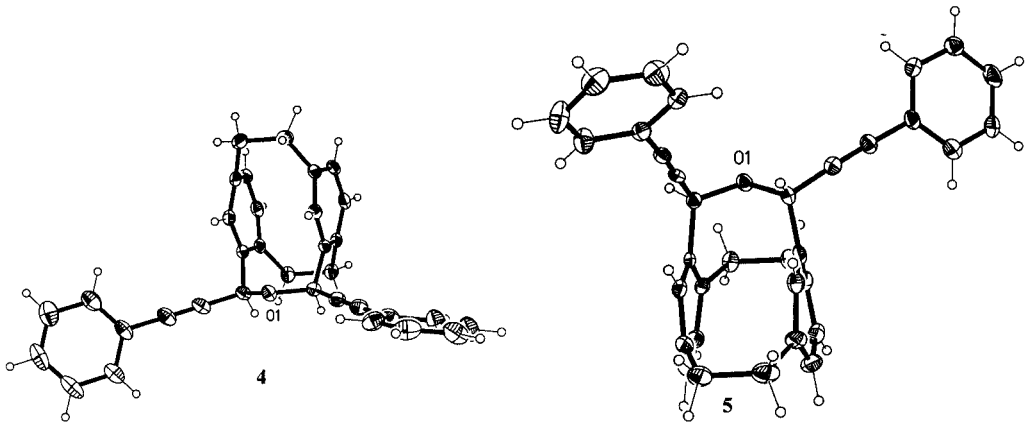
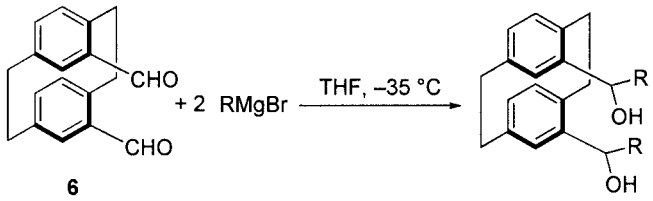


Figure 1. Molecular structure of cyclic ethers **4** and **5** in the crystal. Ellipsoids represent 50% probability levels.



R	Compd.	Yield, %
Ph	**7**	90
CH_3	*meso*-**8**	75
CH_3	*d,l*-**9**	10

Scheme 4. Synthesis of *pseudo-geminally* substituted diols **7**, **8**, and **9**.

cyclophane has been synthesized under similar reaction conditions from 4,13-diformyl[2.2]paracyclophane **6**[10] and methylmagnesium bromide (Scheme 4).

Despite our previous findings, the latter diol has been obtained as a mixture of two stereoisomers in 85% yield. Separation followed by NMR analysis indicated a combination of *meso*-isomer **8** and *d,l*-**9** in 7.3:1 ratio. Detailed structural information for the *meso* isomer was obtained by X-ray single crystal analysis. The X-ray structure of **8** (Figure 2) shows that both hydroxyl groups point away from the closest ethano bridge, and an intramolecular hydrogen bond is formed. In the *d,l*-isomer **9** the configuration at one chiral center is reversed with one methyl group pointing to the "interior" of the paracyclophane spacer.

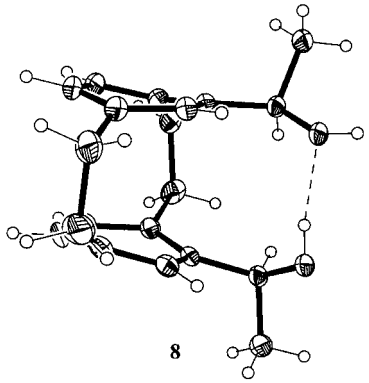
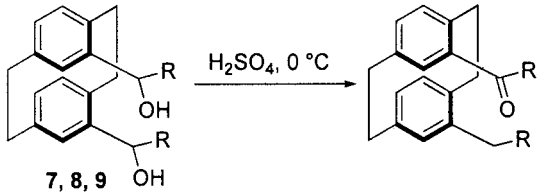


Figure 2. Molecular structure of *meso* 4,13-bis(α-hydroxyethyl)[2.2] paracyclophane **8**. Ellipsoids represent 30% probability levels. Only one set of disordered hydroxyl hydrogen atoms is shown.

Following the experimental conditions described for the synthesis of the pinacolones **3a-c**, the reaction of diols **7**–**9** with sulfuric acid was found to produce only the rearranged products **10** and **11** (Scheme 5).

Since the phenyl-substituted diol **7** does not rearrange by migration of a phenyl group to an aldehyde derivative, it is obvious that these transformations are only vinylogous to the pinacol rearrangement. However, the rearrangement through a transannular hydride migration is very interesting since it involves benzyl reaction centers. Moreover, the competition between cyclic ether formation and transannular hydride migration is worth investigation. Thus, we decided to investigate the reactivity of **7**, **8**, and **9** under milder acidic conditions. While monitoring by NMR analysis the reaction of 4,13-bis(phenylhydroxymethyl)[2.2]paracyclophane **7** with PyHCl at room temp after 10 h we observed the appearance of a new singlet at $\delta = 6.02$, corresponding to the formation of a new symmetrical compound along with the starting material. The starting material was consumed after 5 days (Table 1, Entries 1, 2). Furthermore, by elevating the temperature to 55 °C the same reaction product was formed in 45 min and in almost quantitative isolated yield (Table 1, Entries 3, 4). Analytical and spectroscopic data indicated the formation of the cyclic ether **12**, which is stereochemically homogeneous (Scheme 6). Detailed structural information was again obtained from X-ray analysis (Figure 3). Extended heating in chloroform



R	Compd.	Yield, %
Ph	**10**	86
CH_3	**11**	92

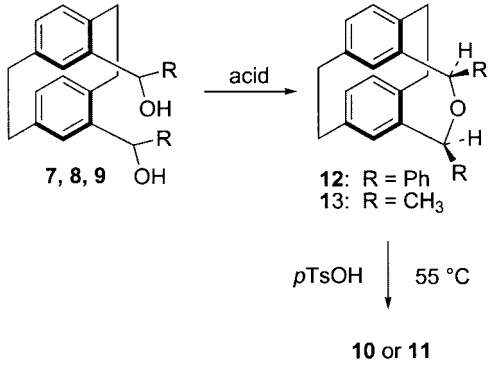
Scheme 5. Synthesis of pinacolone-type compounds **10** and **11**.

Table 1. Acid-catalyzed reactions of *pseudo-geminally* substituted diol and cyclic ethers.

Entry	Compd.	Acid	Time [h]	Temp. [°C]	Products (ratio)[a]		
					Ether	Starting material	Pinacolone
1	**7**	PyHCl	72	22	**12** (3)	**7** (1)	–
2	**7**	PyHCl	120	22	**12** (99%)[b]	–	–
3	**7**	PyHCl	0.5	55	**12** (3)	**7** (1)	–
4	**7**	PyHCl	0.75	55	**12** (99%)[b]	–	–
5	**7**	*p*TsOH	0.2	22	**12** (97%)[b]	–	–
6	**7**	*p*TsOH	1.75	55	–	–	**10** (98%)[b]
7	**12**	*p*TsOH	1.5	55	–	–	**10** (98%)[b]
8	**8**	PyHCl	18	55	**13** (3.6)	**8** (1)	–
9	**8**	PyHCl	72	55	**13** (98%)[b]	–	–
10	**8**	*p*TsOH	0.5	22	**13** (14)	**8** (1)	–
11	**8**	*p*TsOH	1.4	22	**13** (98%)[b]	–	–
12	**8**	*p*TsOH	0.5	55	**13** (1)	–	**11** (5)
13	**8**	*p*TsOH	1.5	55	–	–	**11** (99%)[b]
14	**9**	PyHCl	14	22	**13** (99%)[b]	–	–
15	**4** + **5** (8:2)	*p*TsOH	1	22		**4+5** (8:1.3)	**3c** (2.4)
16	**4** + **5** (8:2)	*p*TsOH	3	22		**4+5** (1:3)	**3c** (46)

[a] Determined by NMR analysis. [b] Isolated yield.

with PyHCl does not affect the cyclic ether **12**. Replacing pyridinium chloride with *p*-toluenesulfonic acid, we found that the reaction time drastically decreases. The starting material is consumed within 10 min at room temp and the cyclic ether **12** produced quantitatively. Moreover, by performing the same reaction at 55 °C we found that after 90 min the pinacolone type compound **10** was formed, again, in almost quantitative yield.



Scheme 6. Synthesis of *pseudo-geminally* substituted ethers under mild acidic conditions.

Similarly, the reaction of the *meso*-4,13-bis(α-hydroxyethyl)[2.2]paracyclophane **8** with PyHCl and *p*TsOH produced the corresponding cyclic ether **13** (Scheme 6). The kinetic data in Table 1 show that in this case the reaction times are longer. With PyHCl *meso*-**8** is completely converted into **13** only at 55 °C in 3 days and in the presence

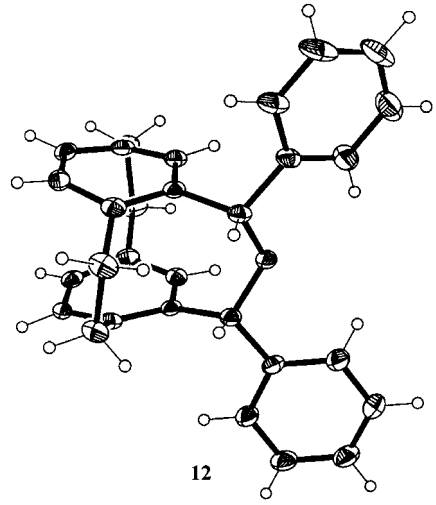
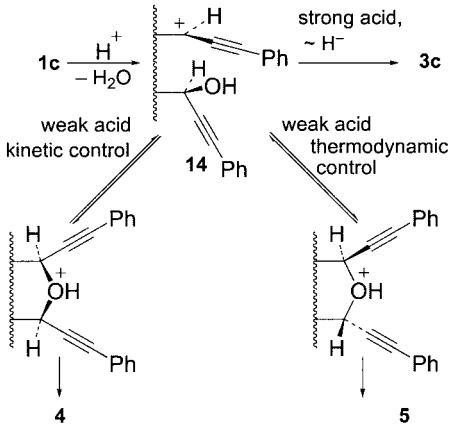


Figure 3. Molecular structure of cyclic ether **12** in the crystal. Ellipsoids represent 50% probability levels.

of *p*TsOH at room temp in about 80 min (Table 1, Entries 8–11). The resulting cyclic ether is also stereochemically homogeneous as judged from its chromatographic behavior and spectroscopic data. By heating *meso*-**8** with *p*TsOH at 55 °C the pinacolone type compound **11** is also formed in almost quantitative isolated yield (Table 1, entries 12, 13). Interestingly, the *d,l*-diol **9** reacts much faster than the *meso* isomer and in a stereoselective manner. With pyridinium chloride the same *meso*-ether **13** was produced in about 14 h and in quantitative yield.

The formation of *meso*-**13** from *d,l*-**9**, together with the lack of stereoselectivity for the reaction of bispropargylic alcohol **1c** with PyHCl, indicates a common intermediate, the relative conformation of which is responsible for the nature of the reaction products. In order to elucidate this mechanistic aspect we monitored the reaction of **1c** with one equivalent of *p*TsOH by NMR spectroscopy. We found that pinacolone **3c** is formed from the corresponding ethers **4** and **5** and the *meso*-ether **4** undergoes a faster ring opening/hydride migration process than the *d,l*-ether **5** (Table 1, Entries 15, 16). Corroborating the above observations with the structural information provided by X-ray analysis, we assume that the key intermediate for these transformations is a carbocation of type **14** (Scheme 7). The relative orientation of the substituents at the chiral carbon with respect to the carbenium ion favors one of the reaction outcomes. Because of the steric demands on the interannular space only two competitive reactions can occur, namely transannular hydride migration vs. cyclic ether formation.



Scheme 7. Competitive reactions of the *pseudo-geminally* substituted [2.2]paracyclophane **1c**.

The formation of pinacolones under strongly acidic conditions is easily explained by the protonation of the hydroxyl group of **14**, which decreases its nucleophilic properties. Although the reaction of **1c** with PyHCl should provide a 1:1 mixture of *meso*- and *d,l*-isomers, the above mechanistic description hints that the interconversion between **4** and **5** could be possible via intermediate **14**. Indeed, when a 1:1 mixture of **4** and **5** was treated with one equivalent of PyHCl and the process monitored by NMR analysis, we found that a slow conversion of the *meso*- to the *d,l*-ether took place within a few days. This indicates that the *meso* compound **4** is formed under kinetic control, while the *d,l*-ether **5** is thermodynamically more stable. Consequently, the stereoselective formation of the *meso*-ethers **12** and **13** takes also place under kinetic control.

In conclusion, we have discovered an unusual pinacol-pinacolone rearrangement that takes place although the two hydroxyl groups are formally separated by seven bonds. This vinylogous pinacol rearrangement involves a transannular hydride shift that occurs between the benzylic position of the *pseudo-geminally* substituted [2.2]paracyclophanes. Moreover, under mild acidic conditions the corresponding *pseudo-geminally* substituted cyclic ethers are stable intermediates. The formation of the latter competes with transannular hydride migration. The stereoselective formation of the *meso* ethers **12** and **13** was found to take place under kinetic control.

Experimental Section

General Remarks: Melting points: Büchi 510, uncorrected. IR: Bruker Tensor 27. ^{1}H and ^{13}C NMR: Bruker DPX 200 or DRX 400 in $CDCl_3$ with TMS as internal standard at room temp. Chemical shifts are reported in ppm downfield from tetramethylsilane. MS: Finnigan MAT 90X, electron impact (EI). THF was distilled under nitrogen from $LiAlH_4$. All reagents were commercially available and used without further purification.

General Procedure for the Preparation of *Pseudo-Geminally* Substituted Benzylic Alcohols 1a–c, 7, 8, and 9: Analytical and spectroscopic data for **1a** and **7** were previously reported.[2,9] The general procedure is illustrated by the preparation of 4,13-bis(α-hydroxyethyl)[2.2]paracyclophanes **8** and **9**.

To a solution of methylmagnesium bromide (0.66 mL, 2 mmol, 3 M in Et_2O) in anhydrous THF (10 mL) a solution of 4,13-diformyl[2.2]paracyclophane **6** (0.264 g, 1 mmol) in anhydrous THF (10 mL) was slowly added at –35 to –40 °C. After 2 h the reaction mixture was allowed to warm to room temp. and quenched with a solution of NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined extracts were washed with water, brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by silica gel flash chromatography (CH_2Cl_2/Et_2O, 1:1) gave *meso*-diol **8** and *d,l*-diol **9**.

***meso*-Diol 8:** M.p. 198–199 °C (colorless crystals, R_f = 0.39), yield 0.22 g (75%). IR (neat): $\tilde{\nu}$ = 3384 (m), 3236 (m), 2925 (s), 2853 (m), 1641 (s), 1443 (m), 1358 (s), 1266 (m), 1065 (s), 1022 (s), 898 (m), 729 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, ^3J = 6.4 Hz, 6 H, 2 CH_3), 2.91–2.99 (m, 2 H, CH_2), 3.09 (br. s, 4 H, 2 CH_2), 3.36–3.45 (m, 2 H, CH_2), 4.16 (br. s, 2 H, 2OH), 5.26 (q, ^3J = 6.4 Hz, 2 H, 2 CH), 6.47 (br. s, 4 H, CH_{ar}), 6.76 (br. s, 2 H, CH_{ar}) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 26.9 (q), 31.4 (t), 35.2 (t), 67.4 (d), 126.9 (d), 132.1 (d), 134.1 (s), 134.7 (d), 140.0 (s), 144.3 (s) ppm. MS (EI): *m*/*z* (%) = 296 (8) [M$^+$], 278 (85), 145 (58), 131 (100), 129 (88), 115 (56). $C_{20}H_{24}O_2$ (296.4): calcd. C 81.04, H 8.16; found 80.91, H 8.08.

***d,l*-Diol 9:** M.p. 114–115 °C (colorless crystals, R_f = 0.29), yield 0.03 g (10%). IR (neat): $\tilde{\nu}$ = 3267 (m), 2963 (m), 2925 (m), 1291 (s), 1063 (s), 1013 (s), 794 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15 (d, ^3J = 6.4 Hz, 3 H, CH_3), 1.36 (d, ^3J = 6.5 Hz, 3 H, CH_3), 2.98–3.12 (m, 6 H, CH_2), 3.41–3.54 (m, 1 H, CH_2), 3.84–3.92 (m, 1 H, CH_2), 4.02 (br. s, 2 H, 2OH), 4.70 (q, ^3J = 6.5 Hz, 1 H, CH), 5.16 (q, ^3J = 6.4 Hz, 1 H, CH), 6.30 (br. s, 1 H, CH_{ar}), 6.52–6.55 (m, 4 H, CH_{ar}), 6.62 (br. s, 1 H, CH_{ar}) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 24.4 (q), 27.1 (q), 32.4 (t), 33.1 (t), 34.9 (t), 35.2 (t), 66.6 (d), 71.4 (d), 127.0 (d), 130.0 (d), 131.8 (d), 133.0 (d), 134.7 (d), 135.1 (s), 136.0 (d), 138.0 (s), 139.1 (s), 139.6 (s), 141.2 (s), 143.6 (s) ppm. MS (EI): *m*/*z* (%) = 278 (70) [M$^+$-H_2O], 159 (25), 145 (40), 131 (100), 129 (48), 115 (45). $C_{20}H_{24}O_2$ (296.4): calcd. C 81.04, H 8.16; found 80.89, H 8.04.

Diol 1b: M.p. 121–122 °C (colorless crystals, from ether/pentane), yield 0.37 g (86%). IR (neat): $\tilde{\nu}$ = 3279 (m), 2954 (m), 2929 (s),

2223 (m), 1595 (w), 1452 (m), 1425 (m), 1318 (m), 1131 (s), 1008 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, ^3J = 7.3 Hz, 6 H, 2 CH_3), 1.27 (sext, ^3J = 7.2 Hz, 4 H, 2 CH_2), 1.36 (sext, ^3J = 7 Hz, 4 H, 2 CH_2), 2.06 (dt, ^3J = 7.2, ^5J = 1.9 Hz, 4 H, 2 CH_2), 2.98–3.12 (m, 6 H, 3 CH_2), 3.43–3.48 (m, 2 H, CH_2), 3.79 (br. s, 2 H, 2OH), 5.65 (t, ^5J = 1.9 Hz, 2 H, 2 CH), 6.49 (d, ^3J = 7.7 Hz, 2 H, 2 CH_{ar}), 6.53 (dd, ^3J = 7.7, ^4J = 1.8 Hz, 2 H, 2 CH_{ar}), 6.76 (d, ^4J = 1.8 Hz, 2 H, 2 CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.5 (q), 18.4 (t), 21.8 (t), 30.5 (t), 31.4 (t), 35.1 (t), 61.5 (d), 80.0 (s), 86.6 (s), 127.4 (d), 132.9 (d), 134.7 (s), 135.1 (d), 139.5 (s), 140.1 (s) ppm. MS (EI): *m/z* (%) = 410 (25) [M^+-H_2O], 213 (15), 197 (100), 155(52), 141 (45), 129 (40). $C_{30}H_{36}O_2$ (428.6): calcd. C 84.07, H 8.47; found: 83.93, H 8.41.

Diol 1c: M.p. 162–162 °C (colorless crystals, from ether/pentane), yield 0.4 g (85%). IR (neat): $\tilde{\nu}$ = 3258 (m), 2935 (w), 2230 (w), 1595 (w), 1487 (m), 1439 (m), 1310 (m), 1019 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.02–3.12 (m, 6 H, 3 CH_2), 3.42–3.54 (m, 2 H, CH_2), 4.17 (br. s, 2 H, 2OH), 5.94 (s, 2 H, 2 CH), 6.52 (d, ^3J = 7.7 Hz, 2 H, 2 CH_{ar}), 6.56 (dd, ^3J = 7.7, ^4J = 1.8 Hz, 2 H, 2 CH_{ar}), 6.87 (d, ^4J = 1.8 Hz, 2 H, 2 CH_{ar}), 7.20–7.32 (m, 10 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 31.5 (t), 35.1 (t), 61.9 (d), 85.6 (s), 88.8 (s), 122.5 (s), 127.7 (d), 128.1 (d), 128.3 (d), 131.7 (d), 133.1 (d), 135.0 (s), 135.2 (d), 138.6 (s), 140.2 (s) ppm. MS (EI): *m/z* (%) = 450 (23) [$M^+ - H_2O$], 318 (38), 217 (95), 215 (60), 202 (100), 189 (22), 129 (20). $C_{34}H_{28}O_2$ (468.6): calcd. C 87.15, H 6.02; found: C 86.97, H 6.05.

General Procedure for the Preparation of Pinacolones 3a–c, 10, and 11: These compounds were prepared by two alternative methods using H_2SO_4 (Method A) and *p*TsOH (Method B), respectively.

Method A: This method is illustrated by the preparation of pinacolone **3a**: To a solution of **1a** (0.4 g, 1 mmol) in $CHCl_3$ (10 mL), H_2SO_4 (96%, 0.055 mL, 1 mmol) was added at 0 °C with vigorous stirring. When the color changed to dark green the ice bath was removed and the reaction mixture was stirred for additional 10 min. Then a solution of $NaHCO_3$ was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with water, brine, dried with $MgSO_4$, and concentrated under vacuum. Purification by flash chromatography (silica gel, CH_2Cl_2/pentane, 1:1, R_f = 0.4) gave the pure product as a colorless viscous oil; yield 0.3 g (80%).

IR (neat): $\tilde{\nu}$ = 2961 (m), 2931 (m), 2871 (w), 2207 (m), 1626 (s), 1457 (m), 1257 (s), 1186 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.10 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.50 (sext, ^3J = 7.2 Hz, 2 H, CH_2), 1.71 (sext, ^3J = 7.2 Hz, 2 H, CH_2), 2.11 (tt, ^3J = 7, ^5J = 2.4 Hz, 2 H, CH_2), 2.46 (t, ^3J = 7 Hz, 2 H, CH_2), 2.91–3.15 (m, 6 H, 3 CH_2), 3.22 and 3.35 (tABq, ^2J = 19, ^5J = 2.4 Hz, 2 H, CH_2), 3.37 (m, 1 H, CH_2), 4.32 (m, 1 H, CH_2), 6.46–6.50 (m, 3 H, 3 CH_{ar}), 6.53 (d, ^3J = 7.5 Hz, 1 H, CH_{ar}), 6.69 (dd, ^3J = 7.5, ^4J = 1.9 Hz, 1 H, CH_{ar}), 7.40 (d, ^4J = 1.9 Hz, 1 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.5 (q), 13.6 (q), 20.9 (t), 21.2 (t), 21.4 (t), 22.4 (t), 23.6 (t), 32.0 (t), 33.3 (t), 34.8 (t), 34.9 (t), 77.6 (s), 81.0 (s), 81.9 (s), 95.3 (s), 130.8 (d), 132.1 (d), 134.2 (d), 135.6 (s), 136.5 (d), 136.9 (d), 137.5 (d), 137.8 (s), 138.2 (s), 139.3 (s), 139.4 (s), 142.8 (s), 179.0 (s) ppm. MS (EI): *m/z* (%) = 382 (9) [M^+], 185 (82), 183 (100), 155 (37), 141 (30), 128 (20). $C_{28}H_{30}O$ (382.5): calcd. C 87.91, H 7.90; found: C 87.78, H 7.81.

Compound 3b: Viscous oil (silica gel, CH_2Cl_2/pentane, 1:1, R_f = 0.42), yield 0.15 g (81%). IR (neat): $\tilde{\nu}$ = 2928 (s), 2860 (m), 2212 (m), 1626 (s), 1458 (m), 1257 (s), 1186 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.99 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.39 (m, 2 H, CH_2), 1.44 (m, 2 H, CH_2), 1.54 (m, 2 H, CH_2), 1.67 (m, 2 H, CH_2), 2.14 (tt, ^3J = 7, ^5J = 2.4 Hz, 2 H, CH_2), 2.40 (t, ^3J = 7.1 Hz, 2 H, CH_2), 2.90–3.16 (m, 6 H, 3 CH_2), 3.21 and 3.46 (tABq, ^2J = 18.5, ^5J = 2.4 Hz, 2 H, CH_2), 3.37 (m, 1 H, CH_2), 4.32 (m, 1 H, CH_2), 6.46–6.50 (m, 3 H, CH_{ar}), 6.53 (d, ^3J = 7.5 Hz, 1 H, CH_{ar}), 6.69 (dd, ^3J = 7.5, ^4J = 1.9 Hz, 1 H, CH_{ar}), 7.40 (d, ^4J = 1.9 Hz, 1 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 13.5 (q), 13.6 (q), 18.6 (t), 19.0 (t), 21.9 (t), 22.1 (t), 23.6 (t), 29.9 (t), 31.1 (t), 32.1 (t), 33.3 (t), 34.8 (t), 34.9 (t), 77.5 (s), 80.9 (s), 82.0 (s), 95.5 (s), 130.8 (d), 132.2 (d), 134.3 (d), 135.7 (s), 136.5 (d), 136.9 (d), 137.5 (d), 137.8 (s), 138.3 (s), 139.3 (s), 139.4 (s), 142.8 (s), 179.0 (s) ppm. MS (EI): *m/z* (%) = 410 (9) [M^+], 199 (78), 197 (100), 155 (44), 141 (40), 129 (37). $C_{30}H_{34}O$ (410.6): calcd. C 87.76, H 8.35; found: C 87.59, H 8.19.

Compound 3c: M.p. 128–129 °C (colorless crystals, from ether/pentane), yield 0.38 g (85%). IR (neat): $\tilde{\nu}$ = 2932 (w), 2194 (m), 1620 (s), 1486 (m), 1271 (m), 1151 (m), 758 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00–3.23 (m, 6 H, 3 CH_2), 3.45 (m, 1 H, CH_2), 3.58 and 3.63 (ABq, ^2J = 19.3 Hz, 2 H, CH_2), 4.43 (m, 1 H, CH_2), 6.50–7.60 (m, 16 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 24.2 (t), 32.1 (t), 33.3 (t), 34.8 (t), 34.9 (t), 82.7 (s), 87.4 (s), 88.1 (s), 92.1 (s), 120.9 (s), 123.8 (s), 127.4 (d), 127.9 (d), 128.5 (d), 130.3 (d), 131.0 (d), 131.6 (d), 132.1 (d), 132.9 (d), 134.3 (d), 135.6 (s), 136.6 (d), 136.9 (d), 137.2 (s), 137.8 (d), 139.6 (s), 143.0 (s), 178.9 (s) ppm. MS (EI): *m/z* (%) = 450 (34) [M^+], 332 (25), 321 (20), 231 (21), 217 (100), 202 (65), 129 (20). $C_{34}H_{26}O$ (450.5): calcd. C 90.63, H 5.82; found: C 90.38, H 5.70.

Compound 10: M.p. 172–173 °C (colorless crystals, from ether/pentane), yield 0.04 g (86%). IR (neat): $\tilde{\nu}$ = 2925 (w), 2849 (w), 1649 (m), 1594 (w), 1490 (w), 1447 (w), 1270 (m), 835 (w), 731 (m), 697 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.80 (m, 1 H, CH_2), 3.90–3.11 (m, 5 H, CH_2), 3.19 (m, 1 H, CH_2), 3.35 (m, 1 H, CH_2), 3.60 and 3.83 (ABq, ^2J = 15.4 Hz, 2 H, CH_2), 6.24 (m, 1 H, CH_{ar}), 6.52 (m, 2 H, CH_{ar}), 6.61 (m, 1 H, CH_{ar}), 6.74 (m, 1 H, CH_{ar}), 6.98 (m, 2 H, CH_{ar}), 7.10 (m, 4 H, CH_{ar}), 7.43 (m, 2 H, CH_{ar}), 7.54 (m, 1 H, CH_{ar}), 7.74 (m, 2 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 33.8 (t), 34.4 (t), 34.7 (t), 34.9 (t), 39.9 (t), 125.6 (d), 128.1 (d), 128.3 (d), 128.6 (d), 129.7 (d), 130.2 (d), 132.2 (d), 133.7 (d), 134.3 (d), 134.6 (d), 135.3 (d), 135.8 (s), 137.0 (d), 137.5 (s), 139.1 (s), 139.5 (s), 140.0 (s), 141.3 (s), 141.5 (s), 142.0 (s), 196.0 (s) ppm. MS (EI): *m/z* (%) = 402 (82) [M^+], 267 (61), 207 (35), 193 (55), 191 (100), 178 (80), 165 (36). $C_{30}H_{26}O$ (402.5): calcd. C 89.51, H 6.51; found: C 89.39, H 6.40.

Method B: This method is illustrated by the preparation of pinacolone **11**: To a solution of **7** (0.296 g, 1 mmol) in $CHCl_3$ (10 mL), *p*-toluenesulfonic acid monohydrate (0.19 g, 1 mmol) was added at room temp. with vigorous stirring. The reaction mixture was heated at 55 °C until the starting material was consumed (usually 1.5 h, TLC monitoring on silica gel with CH_2Cl_2). Then water was added and the organic layer was separated, dried over $MgSO_4$ and concentrated under vacuum to give a practically pure product as a colorless solid. Recrystallization from ether/pentane gave analytically pure product. M.p. 168–169 °C (colorless crystals), yield 0.275 g (99%). IR (neat): $\tilde{\nu}$ = 2999 (m), 2929 (m), 1660 (s), 1547 (m), 1433 (m), 1354 (m), 1260 (s), 728 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94, 2.08 and 2.54 (ABX_3, ^3J = 7.5 Hz, 5 H, CH_2CH_3), 2.49 (s, 3 H, CH_3), 2.89–3.17 (m, 6 H, 3 CH_2), 3.39 (m, 1 H, CH_2), 4.17 (m, 1 H, CH_2), 6.17 (d, ^4J = 1.8 Hz, 1 H, CH_{ar}), 6.44 (dd, ^3J = 7.6, ^4J = 1.8 Hz, 1 H, CH_{ar}), 6.51 (d, ^3J = 7.6 Hz, 1 H, CH_{ar}), 6.54 (d, ^3J = 7.7 Hz, 1 H, CH_{ar}), 6.65 (dd, ^3J = 7.7, ^4J = 1.9 Hz, 1 H, CH_{ar}), 7.01 (d, ^4J = 1.9 Hz, 1 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 15.1 (q), 27.1 (t), 28.7 (q), 32.3 (t), 33.9 (t), 34.8 (t), 35.0 (t), 130.2 (d), 132.1 (d), 133.8

(d), 134.4 (d), 136.2 (s), 136.5 (d), 136.8 (d), 137.5 (s), 139.1 (s), 139.2 (s), 142.3 (s), 144.7 (s), 199.4 (s) ppm. MS (EI): *m*/*z* (%) = 278 (78) [M$^+$], 145 (82), 131 (85), 117 (100), 115 (42). $C_{20}H_{22}O$ (278.3): calcd. C 86.29, H 7.97; found: C 86.03, H 7.82.

General Procedure for the Preparation of Cyclic Ethers 4, 5, 12, and 13: These compounds were prepared by two alternative methods using PyHCl (Method A) and *p*TsOH (Method B), respectively.

Method A: This method is illustrated by the preparation of cyclic ethers **4** and **5**: To a solution of **1c** (0.11 g, 0.23 mmol) in $CHCl_3$ (5 mL), pyridinium chloride (0.028 g, 0.23 mmol) was added and the reaction mixture was stirred at room temperature until the starting material had been consumed (ca. 60 h, TLC monitoring on silica gel with CH_2Cl_2). Then water was added and the organic layer was separated, dried with $MgSO_4$, and concentrated under vacuum to give a practically pure mixture of **4** and **5**, in 8:2 ratio, in almost quantitative yield. Separation by column chromatography (silica gel, CH_2Cl_2/pentane, 1:1) gave *meso*-**4** and *d,l*-**5** in 98% overall yield.

***meso*-4:** M.p. 205–206 °C (colorless crystals, R_f = 0.4), yield 0.08 g. IR (neat): $\tilde{\nu}$ = 2929 (w), 2877 (w), 2228 (w), 1595 (w), 1488 (m), 1338 (m), 1284 (m), 1020 (s), 754 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.05 (m, 4 H, 2 CH_2), 3.23 (m, 2 H, CH_2), 3.58 (m, 2 H, CH_2), 5.73 (s, 2 H, 2 CH), 6.44 (m, 4 H, CH_{ar}), 7.13 (m, 2 H, CH_{ar}), 7.25 (m, 6 H, CH_{ar}), 7.40 (m, 4 H, CH_{ar}) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 32.1 (t), 35.5 (t), 68.8 (d), 87.0 (s), 87.9 (s), 122.6 (s), 128.1 (d), 128.4 (d), 131.8 (d), 133.2 (d), 134.2 (d), 134.9 (d), 137.0 (s), 137.6 (s), 141.5 (s) ppm. MS (EI): *m*/*z* (%) = 450 (25) [M$^+$], 318 (100), 305 (30), 217 (80), 215 (65), 202 (95), 189 (20), 129 (15). $C_{34}H_{26}O$ (450.5): calcd. C 90.63, H 5.82; found: C 90.47, H 5.79.

***d,l*-5:** M.p. 165–166 °C (colorless crystals, R_f = 0.5), yield 0.02 g. IR (neat): $\tilde{\nu}$ = 2925 (m), 2854 (w), 2224 (w), 2197 (w), 1596 (w), 1489 (m), 1027 (s), 755 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.03 (m, 4 H, 2 CH_2), 3.18 (m, 2 H, CH_2), 3.66 (m, 1 H, CH_2), 4.07 (m, 1 H, CH_2), 5.91 (s, 1 H, CH), 6.26 (s, 1 H, CH), 6.45 (m, 5 H, 5CH_{ar}), 7.11 (m, 1 H, 1 CH_{ar}), 7.25 (m, 3 H, CH_{ar}), 7.41 (m, 5 H, CH_{ar}), 7.64 (m, 2 H, CH_{ar}) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 34.85 (t), 34.88 (t), 35.1 (t), 69.9 (d), 70.2 (d), 84.7 (s), 85.4 (s), 88.2 (s), 90.7 (s), 122.5 (s), 122.7 (s), 128.1 (d), 128.3 (d), 128.4 (d), 128.8 (d), 131.7 (d), 131.9 (d), 132.7 (s), 132.9 (d), 133.4 (d), 134.8 (d), 134.9 (d), 136.1 (d), 136.7 (s), 137.0 (d), 140.0 (s), 140.2 (s), 140.3 (s), 140.8 (s) ppm. MS (EI): *m*/*z* (%) = 450 (25) [M$^+$], 318 (100), 305 (41), 217 (88), 215 (50), 202 (91), 189 (24), 129 (20). $C_{34}H_{26}O$ (450.5): calcd. C 90.63, H 5.82; found: C 90.50, H 5.71.

Method B: This method is illustrated by the preparation of cyclic ether **12**: To a solution of **7** (0.14 g, 0.33 mmol) in $CHCl_3$ (20 mL), *p*-toluenesulfonic acid monohydrate (0.056 g, 0.33 mmol) was added under vigorous stirring. The reaction mixture was stirred at room temp until the starting material had been consumed (about 10 min, TLC monitoring on silica gel with CH_2Cl_2). Water was added and the organic layer was separated, dried ($MgSO_4$) and concentrated under vacuum to give a practically pure product as a colorless solid. Recrystallization from ether/pentane gave analytically pure product. M.p. 181–182 °C (colorless crystals), yield 0.13 g (97%). IR (neat): $\tilde{\nu}$ = 3055 (w), 2953 (w), 2927 (w), 1596 (w), 1491 (m), 1446 (m), 1317 (w), 1197 (w), 1049 (s), 1027 (s), 906 (m), 730 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.97 (m, 4 H, 2 CH_2), 3.11 (m, 2 H, CH_2), 3.79 (m, 2 H, CH_2), 6.01 (s, 2 H, 2 CH), 6.38 (m, 2 H, CH_{ar}), 6.52 (m, 4 H, CH_{ar}), 7.24–7.35 (m, 6 H, CH_{ar}), 7.46 (m, 4 H, CH_{ar}) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$):

Table 2. Crystallographic data for compounds **4**, **5**, **8**, and **12**.

Compound	**4**	**5**	**8**	**12**
Formula	$C_{34}H_{26}O$	$C_{34}H_{26}O$	$C_{20}H_{24}O_2$	$C_{30}H_{26}O$
M_r	450.55	450.55	296.39	402.51
Habit	colourless prism	colourless plate	colourless tablet	colourless prism
Crystal size [mm]	0.45×0.18×0.15	0.4×0.35×0.04	0.4×0.3×0.1	0.3×0.15×0.15
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Cell constants:				
a [Å]	7.1185(8)	13.4442(15)	10.0106(14)	7.7565(12)
b [Å]	14.1330(14)	14.1801(15)	11.2850(16)	18.593(3)
c [Å]	23.750(2)	14.7246(16)	14.598(2)	14.806(2)
α [°]	90	104.494(2)	90	90
β [°]	90	90.886(4)	95.229(5)	98.378(5)
γ [°]	90	115.654(3)	90	90
V [Å^3]	2389.4	2425.1	1642.3	2112.5
Z	4	4	4	4
D_x [Mg·m^{-3}]	1.252	1.234	1.199	1.266
μ [mm^{-1}]	0.07	0.07	0.08	0.08
F(000)	952	952	640	856
T (°C)	–140	–140	–140	–140
$2\theta_{max}$	60	56.6	56.6	60
Reflections, measured	32540		16384	23945
Reflections, independent	3937	13296	4070	6167
R_{int}	0.059		0.035	0.049
Parameters	316	632	215	280
Restraints	0	765	6	0
w$R(F^2$, all reflections)	0.122	0.212	0.147	0.171
$R[F, >4\sigma(F)]$	0.045	0.094	0.054	0.063
S	1.04	1.26	1.05	1.05
max. $\Delta\rho$ [e·Å^{-3}]	0.37	0.41	0.27	0.43

δ = 32.3 (t), 35.4 (t), 78.2 (d), 126.2 (d), 126.6 (s), 127.9 (d), 132.3 (d), 133.9 (d), 135.4 (d), 138.2 (d), 140.92 (s), 140.97 (s), 143.1 (s) ppm. MS (EI): *m/z* (%) = 402 (95) [M^+], 221 (45), 207 (38), 193 (51), 191 (77), 178 (100), 165 (37). $C_{30}H_{26}O$ (402.5): calcd. C 89.51, H 6.51; found: C 89.43, H 6.42.

Compound 13: M.p. 144–145 °C (colorless crystals, from ether/pentane), yield 0.1 g (98%). IR (neat): $\tilde{\nu}$ = 3317 (w), 3028 (m), 2952 (m), 2890 (m), 1669 (w), 1594 (m), 1487 (m), 1413 (m), 1372 (m), 1274 (m), 1080 (s), 1019 (m), 748 (m), 645 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, ^3J = 6.3 Hz, 6 H, 2 CH_3), 2.93–2.99 (m, 2 H, CH_2), 3.09 (br. s, 4 H, 2 CH_2), 3.36–3.46 (m, 2 H, CH_2), 5.26 (q, ^3J = 6.3 Hz, 2 H, 2 CH), 6.47 (br. s, 4 H, CH_{ar}), 6.77 (m, 2 H, CH_{ar}) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 26.9 (q), 31.4 (t), 35.2 (t), 67.4 (d), 127.0 (d), 132.1 (d), 134.2 (s), 134.7 (d), 140.0 (s), 144.4 (s) ppm. MS (EI): *m/z* (%) = 278 (88) [M^+], 159 (36), 145 (30), 131 (100), 119 (40), 115 (31). $C_{20}H_{22}O$ (278.3): calcd. C 86.29, H 7.97; found: C 86.01, H 7.88.

X-ray Structure Determinations: Numerical details are presented in Table 2. *Data collection*: Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). H atoms were included with a riding model or as rigid methyl groups. *Special features*: Compound **4** crystallizes by chance in a chiral space group. Because the anomalous scattering was not significant, Friedel opposite reflections were merged, and the Flack parameter could not be determined. Compound **5** consisted of weakly diffracting crystals with poor reflection shape. Difficulties in indexing the diffraction pattern were finally resolved in terms of twinning by 180° rotation about **a***. Because of the special methods involved in data reduction, the total number of measured reflections cannot be given. Refinement proceeded using the "HKLF 5" option of SHELXL-97. An extensive system of restraints was used to improve stability of refinement. Despite the poor *R* values, the qualitative structure could be established unambiguously. In compound **8**, the hydroxyl hydrogens are disordered over two sets of positions such that the intra- and intermolecular hydrogen bonds are reversed; the split positions were refined subject to a system of restraints.

CCDC-261979 (for **4**), -261980 (for **5**), -261981 (for **8**), and -261982 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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