Preparation of Cyclobutyl Group Carrying Cyclobutanones and Related Synthetic Building Blocks

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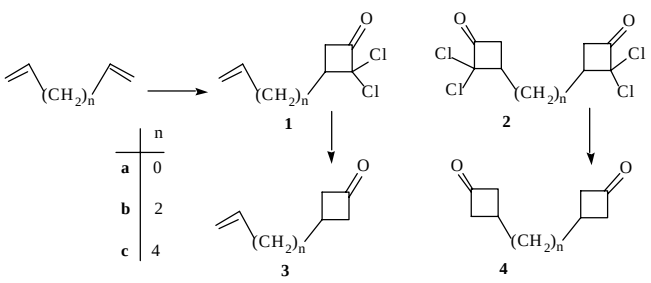
Abstract. Compounds **3**, **4**, **10**, **12**, **16**, **17**, and **19** have been prepared as possible starting materials for liquid crystals containing two cyclobutyl moieties combined in a 1,3-fashion. Further typical conversions of these have been tested giving **5**, **7**, and **14** for example. Useful intermediates **16** and **17** were also made.

Continuing our work on cyclobutyl group containing potential liquid crystals [1−4] we prepared a series of new compounds with two cyclobutane groups as starting materials for further study. We want to document here general methods to generate a number of 1,3-substitution patterns in this class of compounds.

Compounds with Two Cyclobutane Groups

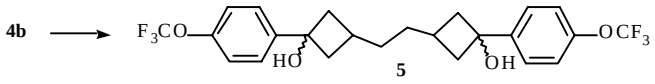
Whereas the direct addition of ketene to simple dienes is inefficient, dichloroketene is known to give products such as monoadduct **1a** [5] in satisfactory yields. Preferentially, $Cl_2C{=}C{=}O$ must be prepared from trichloroacetyl chloride and the zinc/copper couple. The presence of phosphorus oxychloride increases both purity and yield of products [6]. It is believed that it complexes the formed zinc chloride and thus retards side reactions.

In our hands, cycloaddition of dichloroketene to conjugated and isolated dienes yields both monoadducts (**1**) and (usually lower yields of) bisadducts (**2**). The latter compounds are new to the literature. Both types of cyclobutanones can be dehalogenated with zinc in acetic acid to give compounds **3** or **4**, respectively.



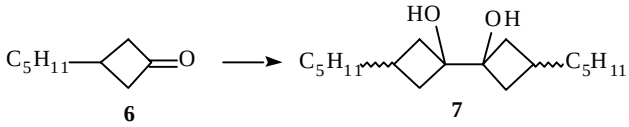
Scheme 1 Preparation of cyclobutanones **3** and **4**

The keto functions of compounds **4** can be reacted with Grignard reagents whereby potential precursors of liquid crystal forming molecules are generated. It turned out to be impracticable, however, to prepare unsymmetrical compounds in this way: Lacking selectivity did not allow to react only one oxo group effectively with the first Grignard reagent. Thus, **4b**, for instance, gave an unpleasant mixture of **5**, the monoadduct, and the starting compound. Only **5** could be separated in pure form.



Scheme 2 Preparation of the symmetrical compound **5**

The McMurry coupling is another method difficult to use for the formation of unsymmetrical products. It is known that the reaction variant with titanium tetrachloride and zinc leads to diols [7] whereas $TiCl_3$/$LiAlH_4$ gives alkenes normally [8]. When applying this type of reaction to **6** as an example, both reaction variants gave the diol isomer mixture **7** in 62 and 36% yield, respectively. Various methods to remove the two OH groups were unsuccessful.



Scheme 3 Reductive dimerization of compound **6** to give **7**

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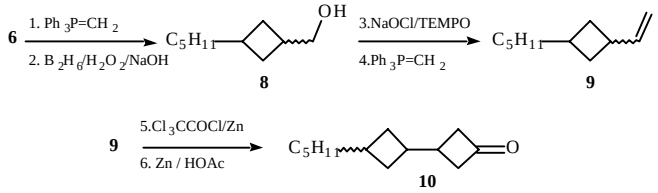
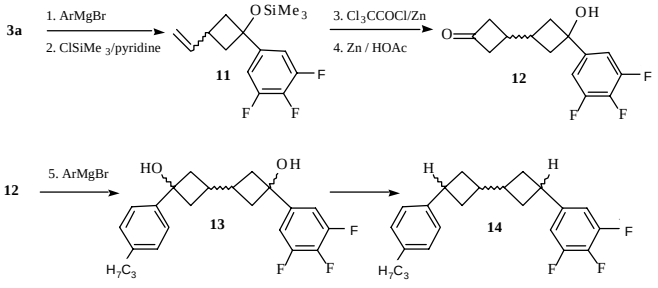
It was decided thereafter to prepare unsymmetrically substituted cyclobutyl-cyclobutanes *via* vinylcyclobutanes. Two approaches were developped, and these are exemplified here with the conversions **6** → **10** and **3a** → **14**, respectively.



Scheme 4 Synthetic sequence to give compound **10**

For the first mentioned sequence, a starting reaction of **6** with the methoxymethylene Wittig reagent and subsequent hydrolysis to the aldehyde was envisioned. This, however, could not be performed under any circumstances, so that the cyclobutanone → cyclobutylcarbaldehyde conversion had to involve a detour: A methylene Wittig reaction was followed by hydroboration (using Brändström's method [9]) to give the hydroxymethyl compound **8**. This was oxidized with sodium hypochlorite in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [10] to yield the aldehyde, which in turn was subjected to a second Wittig methylenation giving **9**. Dichloroketene addition and reduction as before finally led to the wanted for compound **10**. It is obvious that this process is tedious, and therefore an alternative was called for.

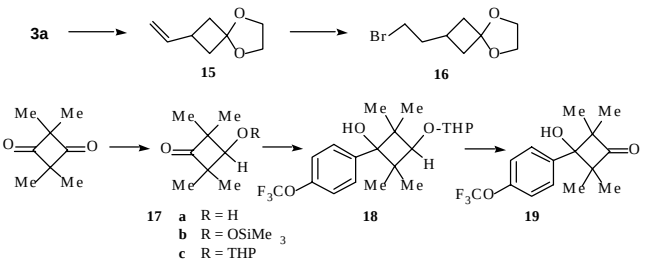


Scheme 5 Preparative sequence for compound **14**

The second sequence started with **3a**. A first Grignard addition and trimethylsilyl protection of the hydroxy group gave compound **11**. This was reacted with dichloroketene and then reduced (and deprotected simultaneously) in the usual way yielding a mixture of diastereomers **12**. A second Grignard reaction introduced a different aryl residue, and **13** was obtained. The final reductive removal of the two hydroxy groups was the subject of extensive experimentation in our laboratory [4]. A 84% yield of **14** (isomer mixture) could be achieved finally by use of sodium borohydride in trifluoroacetic acid [4, 11].

Other Useful Cyclobutyl Building Blocks

Compound **3a** is relatively sensitive. For further reactions, it is best to prepare the ketal **15** (83% yield) first. This could be used for Heck couplings with haloarenes, although yields were only moderate. (24% with 1-bromo-4-trifluormethoxybenzene as an example) **15** was also hydroborated (45%). The transformation of the formed alcohol to the bromide was performed preferentially *via* tosylation and subsequent substitution by bromide/removal of the protecting group (77%). Reketalization yielded 90% of the useful reaction intermediate compound **16**.



Scheme 6 Preparation of compounds **16** and **19**

Another problem addressed was the positional directed functionalization of 2,2,4,4-tetramethylcyclobutane-1,3-dione. In the literature [12], this compound is hydrogenated in methanol in the presence of triethylamine. We found that the main product is methyl 2,2,4-trimethyl-3-oxohexanoate under these circumstances. The yield could be increased to 95% of **17a** by working in ethyl acetate as a solvent with Raney nickel as a catalyst. The hydroxy function was protected thereafter by trimethylsilyl (giving **17b**) or tetrahydropyranyl (giving **17c**). A subsequent conversion of **17b** with an aryl Grignard reagent could not be achieved, possibly due to steric crowding. **17c**, however, underwent a similar reaction without difficulty, and **18** was obtained as a mixture of stereoisomers. Hydrolysis and Swern oxidation transformed this compound to **19**, a useful starting material for further elaborations.

Summing up then, the methods sketched here allow for the synthesis of variously substituted potential liquid crystalline compounds which contain two cyclobutane rings in a 1,3-substitution fashion. Unfortunately, there is little or no stereoselectivity in these reactions.

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Experimental

b.p.s refer to air bath temperature of Kugelrohr distillations.

2,2-Dichloro-3-vinylcyclobutane (1a) and 2,2,2',2'-Tetrachloro-1,1'-bicyclobutane-3,3'-dione (2a) (General Procedure for Dichloroketene Additions)

13.5 g (250 mmol) of butadiene were condensed at −60 °C in 400 ml of dry ether in which 45.6 g (698 mmol) of freshly prepared dry zinc/copper couple were suspended. A mixture of 124 g (683 mmol) of trichloroacetyl chloride and 105.6 (689 mmol) of phosphorus oxychloride was dropped in at ca. 0 °C under argon within 4−6 h. The mixture was stirred for 48 h at r.t., the zinc was filtered off, and the filtrate was decomposed carefully with 500 ml of ice-water. The organic phase was separated and washed with aq. saturated $NaHCO_3$ until neutral, then with saturated brine. After drying (Na_2SO_4) the solvent was removed *in vacuo* and the residue was fractionated. First fraction: **1a**, *b.p*. 83−85 °C/15 Torr (Lit. [5] 60−74/4 Torr); 24% yield. – ^{1}H NMR: δ/ppm = 6.04−5.91 (m, 1H), 5.35 (t, 2H, J = 10.3 Hz), 3.56−3.39 (m, 1H), 3.32−3.22 (m, 2H). – Second fraction: **2a**, *b.p*. 110−125 °C/0.2 Torr; *m.p*. 175 °C; 37% yield. – IR: ν/cm^{-1} = 1808. – ^{1}H NMR: δ/ppm = 3.75−3.22 (m). – MS: m/z = 190 (base peak rel. to ^{35}Cl; $C_4H_2Cl_4$ = retro [2+2] addition).

$C_8H_6Cl_4O_2$	Calcd.: C 34.82	H 2.19
(275.94)	Found: C 34.80	H 2.30.

1,1'-Bicyclobutane-3,3'-dione (4a) (General Procedure for Dichlorocyclobutanone Reduction)

28.49 g (103 mmol) of **2a** in 100 ml of acetic acid were dropped into a suspension of 65.37 g (1 mol) of zinc in 400 ml of acetic acid within 1 h whereby the temperature rose to ca. 60 °C. Thereafter, the mixture was stirred at 70−80 °C for 2 h. It was cooled to r.t., filtered, and then diluted with 2 l of water. It was extracted four times with 100 ml of dichloromethane each time. The combined organic phases were washed with saturated aq. $NaHCO_3$ to neutrality, then with saturated brine. After drying (Na_2SO_4) the solvent was removed *in vacuo* leaving **12g** (84%) of **4a**, *m.p*. 75 °C. – IR: ν/cm^{-1} = 1770. – ^{1}H NMR: δ/ppm = 3.29−3.16 (m, 4H), 2.84−2.61 (m, 6H).

$C_8H_{10}O_2$	Calcd.: C 69.54	H 7.30
(138.17)	Found: C 69.45	H 7.20.

The following compounds were prepared similarly to **1a**, **2a**, **4a**: *3-Vinylcyclobutanone* (**3a**), 90%, known compound [13].

1,2-Bis(2,2-dichloro-3-oxocyclobutyl)ethane (**2b**), 57%, *m.p*. 89−92 °C.

$C_{10}H_{10}Cl_4O_2$	Calcd.: C 39.51	H 3.32
(303.99)	Found: C 39.60	H 3.45.

1,4-Bis(2,2-dichloro-3-oxocyclobutyl)butane (**2c**), 43%, *m.p*. 91 °C.

$C_{12}H_{14}Cl_4O_2$	Calcd.: C 43.41	H 4.25
(332.05)	Found: C 43.27	H 4.30.

1,2-Bis(3-oxocyclobutyl)ethane (**4b**), 93%, *m.p*. 52−54 °C.

$C_{10}H_{14}O_2$	Calcd.: C 72.26	H 8.42
(166.22)	Found: C 72.22	H 8.49.

1,4-Bis(3-oxocyclobutyl)butane (**4c**), 98%, *m.p*. 43−44 °C.

$C_{12}H_{18}O_2$	Calcd.: C 74.19	H 9.34
(194.27)	Found: C 74.11	H 9.43.

1,2-Bis(3'-hydroxy-3'(p-trifluoromethoxyphenyl)cyclobutyl)ethane (**5**)

A freshly prepared Grignard reagent (from 1.7 equiv. of *p*-bromo-trifluoromethoxybenzene and 2 equiv. of Mg in ether) was dropped into 1 equiv. of **4b** in ether under argon. The mixture was refluxed for 2 h, then stirred over night at r.t. Working up and chromatography (silica gel, hexane/*tert*-butyl-methyl ether 1:1) furnished 19% of **5**. *m.p*. 145 °C.

$C_{24}H_{24}F_6O_4$	Calcd.: C 58.78	H 4.93
(490.20)	Found: C 58.93	H 4.81.

1-(1'-Hydroxy-3'-pentylcyclobutyl)-3-pentyl-1-cyclobutanol (**7**)

14.6 g (77 mmol) of $TiCl_4$ were dissolved in 150 ml of dry THF at −15 °C. 10.7 g (163 mmol) of zinc dust were added gradually under stirring in a nitrogen atmosphere. 10.0 g (72 mmol) of compound **6** [2] in 40 ml of dry THF were dropped in, and the mixture was refluxed for 5 h. Thereafter, 200 ml of 20% aq. potassium carbonate was added, the phases were separated and filtered. The aqueous layer was extracted thrice with 25 ml ether each time, and the combined organic phases were dried (Na_2SO_4) and concentrated. The residue was distilled into a kugelrohr., *b.p*. 95 °C/0.2 Torr; yield 6.2 g (62%). – ^{1}H NMR: δ/ppm = 2.55−2.25 (m, 4H), 2.05−1.22 (m, 24H), 0.88 (t, J = 6.7 Hz, 6H). – MS: *m/z* = 282 (M^+, 1%), 86 (base peak). – IR: ν/cm^{-1} = 3500−3200 (br).

$C_{18}H_{34}O_2$	Calcd.: C 76.54	H 12.13
(282.47)	Found: C 76.26	H 12.45.

(3-Pentylcyclobutyl)methanol (**8**)

35.1 g (250 mmol) of **6** and 102.6 g (254 mmol) of methyltriphenylphosphonium iodide were suspended in 230 ml of dry THF and cooled to −20 °C. A solution of 29.2 g (260 mmol) of KO-*t*-Bu in 100 ml of THF was added very slowly so that the coloration faded after every drop. At the end, the solution was stirred over night at r.t. The mixture was given to 100 ml of saturated aq. NH_4Cl, and phases were separated. The aqueous phase was extracted with ether and dried (Na_2SO_4). A part of the triphenylphosphine oxide was precipitated on addition of 200 ml of petroleum ether. This was filtered off. On concentration additional oxide was precipitated. Total removal of the solvent furnished 19.6 g (55%) of *1-methylene-3-pentylcylobutane* , which was used as such without further purification. 17.5 g (68 mmol) of tetrabutylammonium borohydride and 18.5 g (134 mmol) of the just mentioned alkene were dissolved in 70 ml of dry dichloromethane. 24.8 g (228 mmol) of ethyl bromide were added, and the mixture was refluxed for 30 min. Water (15 ml) and 35 ml of 2M NaOH were added to destroy the excess of BH_4^- , and then 30 ml of 30% H_2O_2 were added very slowly. An exothermic reaction occurred. After stirring over night,

phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic layers were concentrated to dryness, and the residue was taken up in water and ether. The next operations were phase separation, extraction of the organic one with ether, drying (Na_2SO_4), removal of solvent, and kugelrohr distillation, leaving 15.4 g (74%) of **8**, *b.p.* 50–60 °C/0.15 Torr. This was used without further purification.

3-Pentylcyclobutylcarbaldehyde

18.0 g (115 mmol) of the above mentioned alcohol, 40 ml of dichloromethane, 0.18 g (1.16 mmol) of TEMPO, and a solution of 1.37 g (11.5 mmol) of KBr in 10 ml of water were stirred under nitrogen at –20 °C. 150 ml (301 mmol) of a 2M NaOCl solution were adjusted to pH 8–10 by the addition of solid $NaHCO_3$ and then dropped into the reaction mixture in such a way that the internal temperature was kept at 10–15 °C. Stirring was continued for another 15 min., then phases were separated, and the aqueous one was extracted with dichloromethane. The combined organic layers were washed consecutively with 100 ml of 10% HCl containing 1.6 g of KI, 60 ml 10% aq. $Na_2S_2O_3$, 60 ml of water, 100 ml of saturated $NaHCO_3$, again 60 ml of water, and then dried. The solvent was removed, and the compound was distilled into a kugelrohr. Yield 14.5 g (81%), *b.p.* 40–50 °C/0.3 Torr. – IR: ν/cm^{-1} = 2800, 1720. – ^{1}H NMR: δ/ppm = 9.81 (d, J = 2 Hz). The product was used as such.

(3-Pentylcyclobutyl)ethene (**9**)

This was obtained by a Wittig reaction analogous to the conversion of **6**. Yield 53%. – IR: ν/cm^{-1} =1638. It had the expected NMR signals for a *cis/trans* mixture and was used as such without further purification.

3-(3'-Pentylcyclobutyl)cyclobutanone (**10**)

This was prepared *via* dichloroketene addition and Zn reduction analogously to **1**. 78% (addition step) and 75% (reduction) yield, respectively; *b.p.* 100–105 °C/0.2 Torr. – IR: ν/cm^{-1} = 1785. – ^{1}H NMR: δ/ppm = 3.12–2.93 (m, 2H), 2.72–1.98 (m, 7H), 1.86–1.70 (m, 2H), 1.48–1.18 (m, 8H), 0.90–0.85 (m, 3H).

$C_{13}H_{22}O$	Calcd.: C 80.35	H 11.41
(194.32)	Found: C 80.30	H 11.31.

1-(3',4',5'-Trifluorophenyl)-1-trimethylsilyloxy-3-vinylcyclobutane (**11**)

Addition of 3,4,5- trifluoromethylphenyl-magnesium bromide to **3a** using similar conditions as with **4b** → **5** yielded 83% of *1*-(3',4',5'-trifluorophenyl)-3-vinylcyclobutanol, *b.p.* 105 °C/0.4 Torr, which was dissolved in dry ether and treated at 0 °C with pyridine (1.8 eq.) and freshly distilled chlorotrimethylsilane (1.5 eq.) immediately. After stirring over night, the separated pyridinium hydrochloride was filtered off and washed with ether. The organic phase was washed successively with water, saturated aq. $NaHCO_3$, and brine, then dried and concentrated. The residue was fractionated *in vacuo* giving 80% of **11**, *b.p.* 75 °C/0.4 Torr. – ^{1}H NMR: δ/ppm = 7.20–7.06 (m, 2H), 5.99–5.84 (m, 1H), 5.06–4.95 (m, 2H), 2.66–2.21 (m, 5H), 0.01 (m, 9H). The compound was reacted further immediately using a similar methology as with compound **3** which led to *3-Hydroxy-3-(3'',4'',5''-trifluorophenyl)-1,1'bicyclobutan-3'-one* (**12**), *m.p.* 98–99 °C; 40% yield over 2 steps. – IR: ν/cm^{-1} = 3409, 1766. – MS: m/z = 270 (M^+), 174 (base peak). – ^{1}H NMR: δ/ppm = 7.17–7.11 (m, 2H), 3.19–3.06 (m, 2H), 2.88 (s, 1H), 2.79–2.52 (m, 5H), 2.29–2.09 (m, 3H).

3,3'-Dihydroxy-3-(p-propylphenyl)-3'-(3'',4'',5''-trifluorophenyl)-1,1'-bicyclobutane (**13**)

This was prepared from **12** *via* reaction with *p*-propylphenylmagnesium bromide; 65% yield; *m.p.* 122–124 °C. – 500 MHz. – ^{1}H NMR: δ/ppm = 7.43–7.41 (m, 1H), 7.27–7.26 (m, 1H), 7.20–7.13 (m, 4H), 2.65–2.51 (m, 5H), 2.39–2.26 (m, 2H), 2.20–2.14 (m, 2H), 2.09–2.02 (m, 5H), 1.65–1.62 (m, 2H), 0.67–0.92 (m, 3H).

$C_{23}H_{25}F_3O_2$	Calcd.: C 70.75	H 6.45
(390.44)	Found: C 70.48	H 6.45.

3-(p-Propylphenyl)-3'-(3'',4'',5''-trifluorophenyl)-1,1'-bicyclobutane (**14**)

4.0 g (105 mmol) of $NaBH_4$ was added slowly to 100 ml of dry trifluoroacetic acid under argon at 0–5 °C. After warming to 15 °C, a solution of 4.08 g (10 mmol) of **13** in 20 ml of CH_2Cl_2 was added within 15 min. The mixture was stirred at r.t. for 19 h, then quenched carefully with water. The pH was made alkaline by addition of solid NaOH, ether was added, and the phases were separated. The aqueous phase was extracted with additional ether. The combined organic phases were washed with concentrated brine, then dried (Na_2SO_4), and the solvent was removed. The raw residue (3.57 g) was taken up in dichloromethane, filtered over silica gel and then chromatographed on silica gel with petroleum ether (*b.p.*40–60 °C)/CH_2Cl_2 10:1 leaving 3.15 g (84% yield) of a colourless oil. – ^{1}H NMR: δ/ppm = 7.17–7.08 (m, 4H), 7.00–6.92 (m, 1H), 6.81–6.75 (m, 1H), 3.45–2.91 (m, 1H [*cis/trans* cyclobutane signals]), 2.73–2.65 (m, 1H), 2.61–2.51 (m, 3H), 2.07–1.90 (m, 3H), 1.70–1.58 (m, 4H), 1.34–1.23 (m, 3H), 0.99–0.91 (m, 4H). – MS: m/z = 358 (M^+, 60), 117 (base peak).

$C_{23}H_{25}F_3$	Calcd.: C 77.07	H 7.03
(358.44)	Found: C 76.80	H 7.33.

1,1-Ethylenedioxy-3-vinylcyclobutane (**15**)

By ketalization of **3a** with ethyleneglycol, 83% yield, *b.p.* 62–64 °C/15 Torr.

$C_8H_{12}O_2$	Calcd.: C 68.54	H 8.63
(140.18)	Found: C 68.50	H 8.94.

3-(2'-Bromoethyl)-1,1-ethylenedioxycyclobutane (**16**)

15 was transformed into the hydroxymethyl derivative by hydroboration/oxidation as in the **8** synthesis. Without purification, this was tosylated, and the tosylate was reacted with 1.5 eq. of LiBr in dry acetone for 7 h at reflux temperature. Working up gave 77% of *3-(2'bromoethyl)cyclobutanone, b.p.* 48–53 °C/0.05 Torr. The ketal was regenerated in the usual way. Yield 90%; *b.p.* 60–70 °C/0.1 Torr.

$C_8H_{13}BrO_2$	Calcd.: C 43.46	H 5.93
(221.09)	Found: C 43.33	H 5.93.

3-Hydroxy-2,2,4,4-tetramethylcyclobutanone (**17a**)

by hydrogenation of the respective diketone in ethyl acetate with Raney-Ni catalyst at 40 °C under 2.5 bar of H_2 pressure for 7 h. Yield 95%; *m.p.* 112–114 °C (Lit. [12]: 114 °C). – ^{13}C NMR: δ/ppm = 222.0 (CO), 77.3 (CHOH), 60.0 (C-quart), 23.05 (CH_3), 17.05 (CH_3).

2,2,4,4-Tetramethyl-3-trimethylsilyloxycyclobutanone (**17b**)

With $ClSiMe_3$/pyridine in ether, 88%, *b.p.* 60 °C/15 Torr.
$C_{11}H_{22}O_2Si$ Calcd.: C 61.63 H 10.34
(214.38) Found: C 61.33 H 10.36.

3-Tetrahydropyranyloxy-2,2,4,4-tetramethyl-1-(4-trifluoromethoxyphenyl)cyclobutanol (**18**)

17a was transformed into **17c** in the usual way, and this was treated in dry THF with 1.5 eq. of trifluoromethoxymagnesium bromide at 50 °C for 3h. Working up yielded 50% of **18**, *m.p.*79 °C as a mixture of diastereomers. – ^{1}H NMR: δ/ppm = 7.35–7.14 (m, 4H), 4.58–4.56 (m, 1H), 3.87 (s, 1H), 3.94–3.72 and 3.50–3.45 (m, together 2H), 1.90–1.52 (m, 6H), 1.34 (s, 6H), 1.23 (s, 3H), 1.17 (s, 3H).
$C_{20}H_{27}F_3O_4$ Calcd.: C 62.84 H 7.01
(388.43) Found: C 61.72 H 6.90.

3-Hydroxy-2,2,4,4-tetramethyl-3-(4-trifluoromethoxyphenyl)cyclobutanone (**19**)

18 was deprotected by stirring over night in methanol in the presence of a trace of *p*-toluenesulfonic acid. After isolation, the diol was treated at –70 °C with 2 eq. of oxalyl chloride, 4 eq. of DMSO and 10 eq. of triethylamine and slowly warmed to r.t. Working up with water, extraction with CH_2Cl_2, washing with 1% aq. HCl, sat. $NaHCO_3$, and sat. brine, drying with Na_2SO_4, and removal of the solvent furnished 55% of **19**, *m.p.* 82 °C. – ^{1}H NMR: δ/ppm = 7.42–7.36 and 7.27–7.22 (m, 4H), 2.10 (s, 1H), 1.39 (s, 6H), 1.37 (S, 6H). – ^{13}C NMR: δ/ppm = 220.8, 148.7, 140.2, 131.6, 122.55, 79.5, 63.8, 24.9, 19.7.
$C_{15}H_{17}F_3O_3$ Calcd.: C 59.60 H 5.67
(302.28) Found: C 59.35 H 5.66.

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