Chiral Allyl Cations Are Captured by Furan with 100 % Stereoselectivity: Synthesis of Enantiopure 2-Alkoxy-8-oxabicyclo[3.2.1]oct-6-en-3-ones by Low-Temperature [4+3] Cycloaddition

Christian B. W. Stark,[a] Sabine Pierau,[b] Rudolf Wartchow,[c] and H. M. R. Hoffmann*[a]

Abstract: A low-temperature (−95 °C) protocol for intermolecular cycloadditions of furan to chiral silyloxyallyl cations in dichloromethane is described. Key precursors are open-chain, mixed α-ketoacetals, which are chiral. The resulting [4+3] cycloadducts are densely functionalized and are isolated as single enantiomers in high chemical yield. The yield of the cycloadducts increases with increasing dilution. Three and four stereogenic centres are created in one single step.

Keywords: acetals · asymmetric synthesis · chiral auxiliaries · dilution effects · ion pairs · medium-sized rings

Introduction

Carbocations are ubiquitous as intermediates in *intra*molecular carbocation–polyolefin annulations, which are modelled on the biosynthesis of higher terpenes and steroids.[1] For example, the non-enzymic Johnson route to β-amyrin[2a] and also progesterone[2b] proceeds with high π-facial selectivity. However, it is often forgotten that the resulting triterpenoid and steroidal systems[2] are necessarily racemic, since the cyclopentenol building blocks and the derived cyclopentenyl cation intermediates are racemic and achiral, respectively.[3]

Since methodology for preparing single-isomer epoxides became available, interest in this area has been renewed. In a series of papers, Corey used enantiopure oxiranes of the squalene 2,3-oxide type and aluminum-derived, basic Lewis acids to initiate highly stereoselective and convergent cyclization cascades.[4] Further biomimetic ring-forming reactions, which are *intra*molecular and also lead to individual enantiomers have been reported.[1, 5]

A considerable part of the effort towards chiral carbenium ions employed *cyclic* acetals, which were frequently derived from chiral diols with C_2 symmetry. A general problem here is the removal of the chiral auxiliary, which is often sacrificed in the final steps. Furthermore, ring-opening of the acetal and generation of the cation do not proceed under sufficiently mild conditions to engender high π-facial selectivity.[1, 6, 7] In *inter*molecular reactions of planar delocalized carbocations, especially in [4+3] cycloadditions involving formation of *two* σ bonds in one step, the problems of entropy control, chemical yield and stereoselectivity are expected to be exacerbated.[8, 9]

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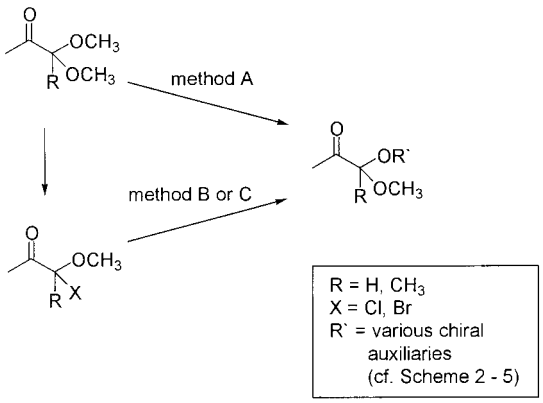
Results and Discussion

We report here on designed open-chain, chiral acetals of a new structural type. These acetals allow the preparation of 8-oxabicyclo[3.2.1]oct-6-en-3-ones in good yield and high enantiomeric purity.[10]

As a route to open-chain mixed α-ketoacetals, the standard transacetalization conditions (method A, Scheme 1) were not



Scheme 1. Method A: excess dimethylacetal, R′OH, *p*-toluenesulfonic acid (PTSA) (catalyst), *n*-heptane, water separator. Method B: R′OH, *n*BuLi, Et_2O, −78 °C, then α-halo ether. Method C: R′OH, K_2CO_3, [18]crown-6 (catalyst), toluene, then α-halo ether in toluene, −10 to −5 °C.

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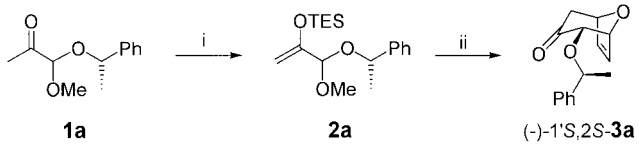
satisfactory. For example, treatment of the dimethylacetal with enantiopure 1-phenylethanol under acidic conditions gave some mixed acetal. However, because of the presence of acid, 1-phenylethanol partially racemized and gave side products. In fact, the major product was the diether PhCH(Me)OCH(Me)Ph. We therefore used mild, *basic* reaction conditions for the introduction of acid-labile chiral auxiliaries. Scheme 1 shows an efficient two-step process to open-chain mixed α-ketoacetals.

In a first application, chiral mixed acetal **1a** was converted into its triethylsilyl enol ether **2a** which was then submitted to Lewis acid mediated cycloaddition (Scheme 2). A systematic variation of reaction conditions is shown in Table 1. Best results were achieved at low temperature, with CH_2Cl_2 as a solvent (Table 1, entry 3).



Scheme 2. i) lithium diisopropylamine (LDA), triethylsilyl chloride (TESCl), Et_3N, THF, $-78\,^{\circ}C$; ii) furan, TMSOTf (catalyst), CH_2Cl_2, $-95\,^{\circ}C$.

Table 1. Effect of temperature and solvent.

Entry	Temperature [°C]	Solvent	Reaction time [min]	Yield of **3a** [%]	*de* [%]
1	−20	CH_2Cl_2	10	55	49
2	−78	CH_2Cl_2	10	58	68
3	−95	CH_2Cl_2	10	67	76
4	−95	Et_2O	90	10	10
5	−95	THF	90	14	13
6	−95	pentane	60	21	36
7	−78	furan (neat)	30	54	49
8	−78	nitroethane	10	36	61
9	−110	CH_2Cl_2/pentane	10	37	78

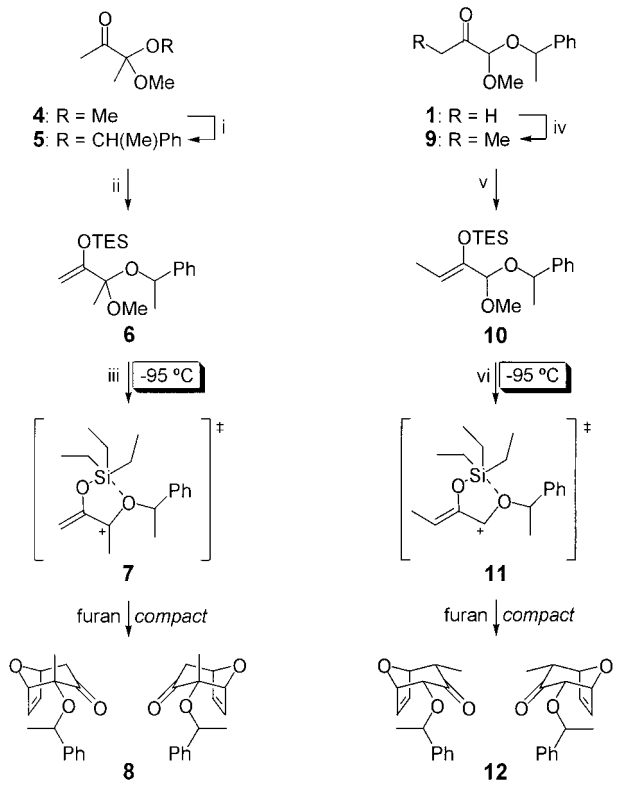
Our experimental protocol is very simple. Furan (1.1 equiv) and enol ether **2** (1.0 equiv) were dissolved in CH_2Cl_2 (0.01–1M) and cooled to $-95\,^{\circ}C$ (chilled with MeOH and liquid N_2). Catalytic trimethylsilyl triflate (less than 10 mol%) was dropped in slowly and continuously by syringe[11] and the progress of the reaction was monitored by TLC. The first sample drawn (after 3 min) showed that the reaction was already completed! Workup and chromatography (silica, cyclohexane/methyl *tert*-butyl ether (MTBE), 3:1) gave enantiopure cycloadducts.[12]

Reaction rates and dilution effects: Generally, cycloadditions are bimolecular and are expected to be favoured by an increase in concentration of the two reacting π-components. We carried out reactions at component concentrations of 1M, 0.1M and 0.01M. To our surprise, yields of cycloadduct actually *increased* with increasing dilution (Table 2). In each case, the rates were high at $-95\,^{\circ}C$, the reactions being essentially complete after 5 min. We assume that ion-pair effects and complexation equilibria involving the Lewis acid are important and that higher dilution favours break-up of ionic aggregates. The stereoselectivity was high at all three concentrations (Table 2).

Table 2. Dilution effect.

Entry	Dilution [M]	Temperature [°C]	Reaction time [min]	Yield of **3a** [%]
1	1.0	−95	<5	62
2	0.1	−95	<5	66
3	0.01	−95	<5	74

In a further application, ketoacetal **4**[13] was converted into its α-chloro ether with PCl_5 and this product was allowed to react, without further purification, with lithium 1-phenylethanoxide, to give chiral mixed ketal **5**. The corresponding triethylsilyl enol ether **6** was prepared by standard methods and was submitted to Lewis acid mediated cycloaddition, yielding cycloadduct **8** (Scheme 3).

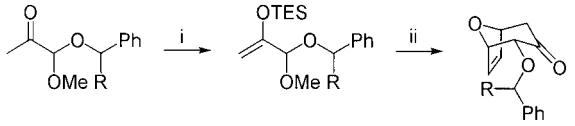


Scheme 3. i) 1. PCl_5, neat, room temperature, 2. 1-phenylethanol, *n*BuLi, Et_2O, $-78\,^{\circ}C$, 20%; ii) LDA, TESCl, THF, $-78\,^{\circ}C$, 93%; iii) TMSOTf (catalyst), CH_2Cl_2 (1M concentration of components), $-95\,^{\circ}C$, 42%, 81% *de*; iv) 1. cyclohexylamine, $CaCl_2$, Et_2O, room temperature, 2. LDA, MeI, THF, $-78\,^{\circ}C$, 77%; v) LDA, TESCl, Et_3N, THF, $-78\,^{\circ}C$, 84%; vi) TMSOTf (catalyst), CH_2Cl_2 (1M concentration of components), $-95\,^{\circ}C$, 53%, 87% *de*.

In the mixed acetals studied by us, the simple and sterically least demanding methoxy group proved to be the preferred leaving group.[14] The 1-phenylethoxy group at carbon C2 of the cycloadduct adopted the equatorial position exclusively,[15] although calculations suggest that the equatorial methyl position and axial phenylethoxy position should be equally favourable. Stereocontrol of the chiral auxiliary was high (81% *de*).

Homologation of chiral mixed α-ketoacetal **1**[15] by methylation of its azaenolate gave 2-butanon-1-al derived α-ketoacetal **9** (77% yield over two steps). Cycloaddition of the corresponding silyl enol ether **10** proceeded smoothly, leading to cycloadduct **12** in 87% *de*. Again, the 1-phenylethoxy substituent was equatorial (see Scheme 3). The formation of both cycloadduct **8** and isomeric **12** is consistent with 1-alkoxy-2-silyloxyallyl cation **7** and W-configured **11** as being the respective preferred intermediates in a *compact* mode of cycloaddition.[16]

Optimization of the chiral auxiliary: A systematic variation of alkyl group R (Scheme 4), which is part of the chiral auxiliary PhCH(R)OH, was undertaken (Table 3). To our surprise, R had no significant effect on the chemical yield and the diastereomeric excess, although R changed drastically from simple methyl to bulky *tert*-butyl.



Scheme 4. i) LDA, TESCl, Et_3N, THF, $-78\,^{\circ}C$; ii) furan, TMSOTf (catalyst), CH_2Cl_2, $-78\,^{\circ}C$.

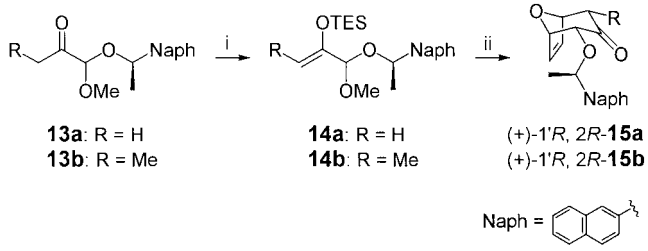
Table 3. Effect of R substituent of chiral auxiliary PhCH(R)OH.

Entry	**2**	R	Yield of **3** [%]	*de* [%]
1	**a**	Me	58	68
2	**b**	Et	50	66
3	**c**	*n*-Bu	59	68
4	**d**	*t*Bu	57	69

What is the role, if any, of the aromatic moiety of the chiral auxiliary? Varying the electron demand of phenyl by introducing *p*-bromo and *p*-methoxy substituents was not a promising strategy.[17]

1-(2-Naphthyl)ethanol is readily available in either enantiomeric form by enzymatic resolution.[18] The extended aromatic system was expected to result in more effective shielding of the π face of the allyl cation. 1-(2-Naphthyl)-ethanol was introduced into the acetal function under basic conditions to avoid epimerization as described above.[19]

We were pleased to find that the low-temperature [4+3] cycloaddition between silyl enol ether acetal **14a** and furan yielded cycloadduct (+)-**15a** in 100% diastereoselectivity within the limits of detectability (GC, NMR) (Scheme 5).



Scheme 5. i) LDA, TESCl, Et_3N, THF, $-78\,^{\circ}C$; ii) furan, TMSOTf (catalyst), CH_2Cl_2, $-95\,^{\circ}C$.

Both of the enantiomeric forms of 1-(2-naphthyl)ethanol gave the corresponding cycloadduct in enantiomerically pure form. Specifically, the *R* enantiomer of 1-(2-naphthyl)ethanol afforded cycloadduct (+)-**15a**, the structure and absolute configuration of which was confirmed by chemical origin and X-ray crystallography (Figure 1).

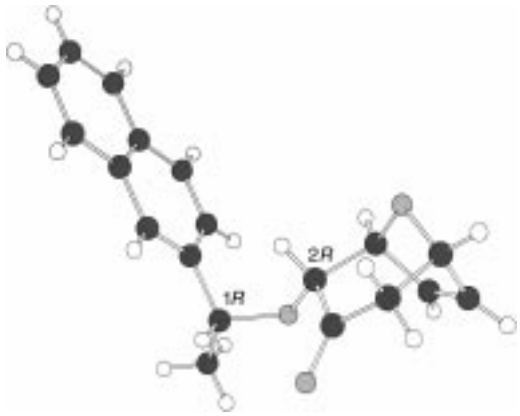


Figure 1. X-ray crystal strucutre of **15a**.

In a further application, chiral mixed α-ketoacetal and its silyl enol ether **14b** were prepared as outlined in Scheme 5, in 67% yield and 88% yield, respectively. Cycloaddition to furan (0.01M concentration of components) proceeded smoothly, to give cycloadduct **15b** in excellent 91% yield (82% *de*).[20] Enantiopure products were obtained by simple chromatography.[12]

On the basis of these experimental observations, we suggest that the model shown in Figure 2 represents the course of the asymmetric [4+3] cycloadditions.

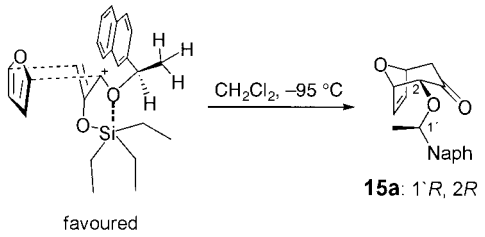


Figure 2. Model for asymmetric [4+3] cycloaddition.

The postulated silicon–oxygen chelation[21] (cf. also cation **7** and **11**, Scheme 3) represents a new structural motif in oxyallyl cation chemistry, and is favourable in CH_2Cl_2, especially at low temperature ($-95\,^{\circ}C$) (Table 1, entry 3), but is less so in solvents with donor-oxygen sites (Et_2O, THF, nitroalkanes), which cause a drop in stereoselection (Table 1). The choice of substituent R in **2a–d** is of little importance (Table 3), even if it is a *tert*-butyl group. Apparently, substituent R stays on the periphery of the reacting molecular cluster, as it does in the final product (X-ray) (Figure 1, R = Me).

However, the nature of the aromatic moiety is important. The 2-naphthyl substituent is slightly better than a phenyl substituent and is assumed to screen one of the π faces of the

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allyl cation in the favoured transition state more effectively (Figure 2). Within the limits of detectability (GC, NMR), oxabicyclic ketone **15a** is formed with 100% stereoselectivity.

Conclusion

We described a general methodology for the preparation of open-chain acetals which are chiral and mixed. Since these acetals are acid-sensitive, the key acetal-forming step is carried out under basic conditions. The low-temperature (−95 °C) cycloaddition protocol affords various oxabridged seven-membered rings and generates three and even four (cf. (+)-**15b**) stereogenic centres at once, with high π-facial selectivity, and in a rational and predictable fashion. The 1-phenylethyl group serves not only as a chiral auxiliary, but also as a benzylic-type protecting group for the hydroxyl function and as directing group for carbonyl olefinations at C3.[22] Consecutive reactions with stereocontrol over the remaining pro-stereogenic centres at carbons C3, C6 and C7 are feasible and are valuable in the synthesis of C-glycosides,[23] carbohydrate mimics and marine natural products such as the bryostatin C segment.[24]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer in deuterated chloroform unless otherwise stated, with tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan MAT 312 (70 eV) or a VG Autospec spectrometer at room temperature unless otherwise stated. Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30–60 μm). Analytical TLC was carried out on aluminium-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck). THF was distilled over sodium and benzophenone before use. CH_2Cl_2 was distilled over CaH_2 before use. DMF was dried over BaO and distilled over CaH_2 before use. Methyl *tert*-butyl ether (MTBE), diethyl ether (Et_2O), ethyl acetate (EA), cyclohexane, and light petroleum (PE, b.p. 40–60 °C) were distilled before use.

General procedures for the preparation of mixed α-ketoacetals (cf. Scheme 1): Method A: A solution of dimethylacetal (3–5 equiv) and *p*-TsOH (0.1 equiv) in cyclohexane was heated. After the reflux temperature was reached, the alcohol (R′OH, 1.0 equiv) was added slowly to the refluxing reaction mixture (Dean–Stark separator for the removal of MeOH). After complete reaction (ca. 2 h) the reaction mixture was cooled to room temperature and poured into saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with cyclohexane. The combined organic phase was dried ($MgSO_4$), evaporated and purified by column chromatograpy.

Method B: The alcohol (R′OH, 1.0 equiv) was dissolved in diethyl ether and cooled to −20 °C. After dropwise addition of *n*BuLi (1.6 M solution in hexane, 1.0 equiv) by syringe, the mixture was stirred for 15 min at room temperature and was then cooled to −78 °C. The α-halo ether[25] (1.5 equiv) was added slowly. The mixture was allowed to reach room temperature. Reaction progress was monitored by GC analysis. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution at −78 °C. The aqueous layer was extracted with ether and the combined organic phase was dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography.

Method C: The alcohol (R′OH, 1.0 equiv) was dissolved in toluene, and solid K_2CO_3 (1.1 equiv) and [18]crown-6 (0.01 equiv) were added at −10 °C. The α-halo ether (1.5 equiv)[25] was dissolved in toluene and this solution was slowly added to the reaction mixture. The reaction temperature was kept at −10 to −5 °C (internal temperature). Without further workup, the cold reaction mixture was poured into a column, packed with Et_2O/PE and 5% Et_3N.

1-Methoxy-1-(1-phenylethoxy)propan-2-one (1a): Starting from racemic 1-phenylethanol, the ketoacetal **1a** was prepared according to the general procedure (mixed acetals, method A). These reactions were carried out on a 10 mmol up to 200 mmol scale. For enantiopure 1-phenylethanol, **1a** was prepared according to either method B or C. 1-Bromo-1-methoxypropan-2-one was prepared as described by Schank and Weber.[25a] Data for **1a**, mixture of diastereoisomers: IR ($CHCl_3$): $\tilde{\nu}$ = 3032, 2976, 2932, 1732, 1452, 1352, 1204, 1104, 1064, 1028, 964, 760, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.34 (m, 5H; Ar), 4.82/4.63 (q, J = 6.4 Hz, 1H; PhC*H*), 4.42/4.36 (s, 1H; OCHO), 3.34/3.22 (s, 3H; OCH_3), 2.20/2.17 (s, 3H; C(=O)CH_3), 1.54/1.49 (d, J = 6.4 Hz, 3H; CHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 204.2/203.9 (C=O), 142.5/142.0 (Ar-C), 128.6, 128.1, 126.6 (Ar-CH), 102.3/100.9 (OCHO), 75.7/75.3 (*C*HCH$_3$), 55.2/53.9 (OCH_3), 24.9/23.8 (C(=O)*C*H$_3$), 24.2/23.2 (CH*C*H$_3$); FAB-MS (room temperature): *m/z* (%): 208 (0) [M^+], 133 (2), 106 (8), 105 (100), 103 (6), 91 (2), 77 (11).

1-Methoxy-1-(1-phenylpropoxy)propan-2-one (1b): 1-Chloro-1-methoxypropanone[25b] (4.60 g, 37.6 mmol) was added slowly, at room temperature, to a suspension of K_2CO_3 (10.4 g, 75.2 mmol) and 1-phenylpropanol (5.12 g, 37.6 mmol); the mixture was stirred for 30 min. Water was added and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried ($MgSO_4$), the solvent removed and the crude product was purified by column chromatography (PE/Et_2O, 9:1) to yield **1b** (2.5 g, 30%) as a pale-yellow oil (diastereomeric mixture). IR (film): $\tilde{\nu}$ = 3628, 3496, 3436, 3084, 3064, 3028, 2964, 2936, 2876, 2836, 1728, 1688, 1492, 1452, 1420, 1380, 1352, 1240, 1204, 1168, 1108, 1072, 1044, 980, 924, 828, 756, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.32/7.28 (m, 5H; Ar), 4.56/4.29 (t, J = 6.8 Hz, 1H; PhC*H*), 4.34/3.40 (s, 1H; OCHO), 3.33/3.16 (s, 3H; OCH_3), 2.20/2.15 (s, 3H; C(=O)CH_3), 1.94/1.76 (m, 2H; CH_2), 0.93/0.85 (t, J = 7.4 Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 204.0/203.9 (C=O), 141.2/140.6 (Ar-C), 128.4, 128.3, 128.0, 127.9, 127.1, 127.0 (Ar-CH), 102.8/100.6 (OCHO), 81.6/80.7 (*C*HCH$_2$), 55.3/53.9 (OCH_3), 30.6/30.2 (CH_2), 24.8/23.8 (C(=O)*C*H$_3$), 10.2/10.0 (CH_3); FAB-MS (room temperature): *m/z* (%): 222 (0) [M^+], 161 (4), 148 (8), 119 (100), 107 (7), 91 (81), 77 (8).

1-Methoxy-1-(1-phenylpentoxy)propan-2-one (1c): 1,1-Dimethoxypropane (5.9 g, 50 mmol), 1-phenylpentanol (1.64 g, 10 mmol) and *p*-TsOH (0.095 g, 0.5 mmol) in heptane (25 mL) were allowed to react according to the general procedure for the preparation of mixed acetals (method A). The crude product was purified by column chromatography (PE/Et_2O, 12:1) to afford **1c** (1.53 g, 61%) as a colourless oil (diastereomeric mixture). IR (film): $\tilde{\nu}$ = 3436, 3388, 3352, 3316, 3084, 3028, 3000, 2956, 2932, 2872, 1732, 1452, 1420, 1352, 1200, 1112, 1072, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.32–7.38 (m, 5H; Ar), 4.63 (t, 6.9 Hz, 1H; PhC*H*), 4.32/4.31 (s, 1H; OCHO), 3.33/3.15 (s, 3H; OCH_3), 2.20/2.14 (s, 3H; C(=O)CH_3), 2.00–1.85/1.78–1.64 (m, 2H; CHCH_2), 1.49–1.10 (m, 4H; (CH_2)$_2$CH$_3$), 0.87/0.86 (t, 7.2 Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 204.3 (C=O), 141.8/141.0 (Ar-C), 128.6, 128.4, 128.1, 128.0, 127.2, 127.1 (Ar-CH), 102.8/100.7 (OCHO), 80.3/79.4 (Ph*C*H), 55.5/54.0 (OCH_3), 37.5/37.2 (CH*C*H$_2$), 27.9 (CHCH$_2$*C*H$_2$), 25.0/24.0 (C(=O)*C*H$_3$), 22.5 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$); MS (room temperature): *m/z* (%): 250 (0) [M^+], 215 (2), 207 (7), 193 (22), 163 (6), 147 (90), 105 (70), 103 (33), 91 (100), 77 (42), 65 (31).

1-Methoxy-1-(1-phenyl-2,2-dimethylpropoxy)propan-2-one (1d): 1,1-Dimethoxypropane (5.9 g, 50 mmol), 3,3-dimethyl-1-phenylpropanol (1.64 g, 10 mmol) and *p*-TsOH (0.095 g, 0.5 mmol) in heptane (25 mL) were allowed to react according to the general procedure for the preparation of chiral mixed acetals (method A), to afford, after column chromatography (PE/Et_2O, 15:1) **1d** (1.63 g, 65%) as a colourless oil (diastereomeric mixture). IR ($CHCl_3$): $\tilde{\nu}$ = 3012, 2956, 2904, 2872, 1724, 1480, 1452, 1364, 1108, 1068, 1048, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.29–7.21 (m, 5H; Ar), 4.53/4.41 (s, 1H; PhC*H*), 4.32/4.26 (s, 1H; OCHO), 3.32/3.17 (s, 3H; OCH_3), 2.22/2.14 (s, 3H; C(=O)CH_3), 0.96/0.94 (s, 9H; C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 204.2 (C=O), 139.3/137.8 (Ar-C), 128.7, 127.8, 127.3, 126.8 (Ar-CH), 100.9/98.2 (OCHO), 87.4/86.2 (Ph*C*H), 54.7/51.8 (OCH_3), 36.0/35.4 (*C*(CH_3)$_3$), 26.3 (C(*C*H$_3$)$_3$), 25.0 (C(=O)*C*H$_3$); MS (room temperature): *m/z* (%): 250 (0) [M^+], 207 (3), 193 (15), 148 (12), 147 (100), 134 (7), 131 (8), 117 (5), 115 (5), 105 (64), 91 (77), 87 (60), 69 (14).

3-Methoxy-3-(1-phenylethoxy)butan-2-one (5): According to the general procedure for the preparation of mixed acetals (method B), 1-phenylethanol (2.64 mL, 21.9 mmol) was dissolved in diethyl ether (12 mL). *n*BuLi (14.0 mL, 22.4 mmol, 1.6 M solution in hexane) was added at 0 °C. The mixture was then cooled to −78 °C and 3-chloro-3-methoxybutan-2-one (2 g, 14.6 mmol) (prepared from the dimethylacetal (1.0 equiv), which was treated with PCl_5 (1.0 equiv))] was added. When the vigorous reaction had ceased, the mixture was heated to 30 °C for 30 min and was then distilled (oil-pump vacuum) to yield crude 3-chloro-3-methoxybutan-2-one, which was used without further purification. The mixture was allowed to reach room temperature and was stirred for 16 h at this temperature. Water was added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$). After removal of the solvent, the crude product was purified by column chromatograhy (PE/Et_2O, 9:1) to afford **5** (684 mg, 20 %) as a pale-yellow oil (diastereomeric mixture). IR (film): $\tilde{\nu}$ = 3628, 3432, 3084, 3064, 3032, 2976, 2932, 2832, 1732, 1684, 1604, 1492, 1452, 1420, 1352, 1308, 1284, 1240, 1204, 1108, 1064, 1028, 968, 916, 888, 760, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.30/7.22 (m, 5H; Ar), 4.81/4.80 (q, J = 6.4 Hz, 1H; PhC*H*), 3.10/3.08 (s, 3H; OCH_3), 2.30/2.08 (s, 3H; C(=O)CH_3), 1.47 (d, J = 6.4 Hz, 3H; PhCH_3), 1.16 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 207.4/206.9 (C=O), 145.7/144.2 (Ar-C), 128.4/128.2, 127.2/127.1, 126.1/125.6 (Ar-CH), 103.4/102.5 (*C*OCH_3), 71.1/70.8 (*C*HCH_3), 50.5 (OCH_3), 26.2/25.8 (C(=O)*C*H_3), 25.4/25.2 (CH*C*H_3), 21.5/20.7 (CH_3); MS (room temperature): *m/z* (%): 258 (2) [M^+], 245 (7), 237 (11), 211 (11), 197 (12), 176 (34), 169 (22), 154 (100), 137 (93).

1-Methoxy-1-[(1*R*)-naphth-2-yl-ethoxy]propan-2-one (13a): *n*BuLi (5.4 mL, 8.7 mmol, 1.6 M solution in hexane) was added to a solution of (1*R*)-(naphth-2-yl)-ethanol (1.0 g, 5.8 mmol) in diethyl ether (7 mL) at −20 °C. The resulting solution was cooled to −78 °C and 1-bromo-1-methoxypropan-2-one[25a] (1.80 g, 1.16 mmol) was added slowly. The mixture was stirred for 9 h at −78 °C, treated with saturated aqueous $NaHCO_3$ solution and extracted with MTBE. The combined organic phase was dried ($MgSO_4$) and the solvent removed. The crude product was purified by column chromatography (PE/Et_2O, 1:3 →Et_2O) to afford the mixed acetal and recovered alcohol (430 mg). Data for mixed acetal **13a**, diastereomeric mixture: yellowish oil, yield 46 % (80 % based on recovered starting material); IR ($CHCl_3$): $\tilde{\nu}$=3432, 3400, 3368, 3304, 3060, 2980, 2932, 2836, 1728, 1600, 1508, 1444, 1420, 1376, 1356, 1308, 1232, 1176, 1104, 1060, 968, 948, 896, 856, 820, 620, 556, 540, 508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.90 – 7.36 (m, 7H; Ar), 4.98/4.78 (q, J = 6.4 Hz, 1H; C*H*CH_3), 4.45/4.40 (s, 1H; OCHO), 3.33/3.20 (s, 3H; OCH_3), 2.20/2.14 (s, 3H; C(=O)CH_3), 1.61/1.57 (d, J = 6.4 Hz, 3H; ArCHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 204.2/203.8 (C=O), 139.9, 139.2, 133.3, 133.2, 133.1, 133.0 (Ar-C), 128.7, 128.4, 128.0, 127.9, 127.7, 127.6, 126.3, 126.2, 126.1, 126.0, 125.9, 125.5, 124.2, 124.0 (Ar-CH), 102.4/100.7 (OCHO), 75.9/75.4 (*C*HCH$_3$), 55.3/53.9 (OCH_3), 25.1/24.2 (C(=O)*C*H_3), 23.7/23.3 (CH*C*H_3); MS (room temperature): *m/z* (%): 258 (1) [M^+], 215 (1), 198 (3), 172 (1), 155 (100), 139 (1), 127 (7), 115 (4), 101 (1), 88 (2), 77 (2).

1-Methoxy-1-(1-phenyl-ethoxy)butan-2-one (9): Mixed acetal **1a** (1.0 g, 4.8 mmol) was added to a mixture of cyclohexylamine (0.82 mL, 7.2 mol) and $CaCl_2$ (1.0 g) in diethyl ether (7 mL). The mixture was stirred for 16 h and was then filtrated and evaporated. *n*BuLi (4.5 mL, 7.2 mmol, 1.6 M solution in hexane) was added at 0 °C to a solution of diisopropylamine (0.93 mL, 7.2 mmol) in THF (5 mL). The solution was cooled to −78 °C and the crude imine was added dropwise to it within 1 h. Then MeI (0.45 mL, 7.2 mmol) was added, the mixture was stirred for 2 h, and then allowed to slowly reach room temperature. Saturated aqueous $NaHCO_3$ solution was added and the aqueous layer was extracted with diethyl ether. The combined organic phase was dried ($MgSO_4$), evaporated and purified by column chromatography (PE/Et_2O, 9:1) to afford **9** (828 mg, 77 %) as a yellowish oil (diastereomeric mixture). IR (film):$\tilde{\nu}$ = 3432, 3412, 3084, 3064, 3032, 2976, 2936, 2832, 1728, 1688, 1492, 1452, 1408, 1376, 1336, 1308, 1284, 1252, 1208, 1100, 1064, 1028, 912, 760, 700; 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.32 (m, 5H; Ar), 4.81/4.64 (q, J = 6.6 H, 1H; C*H*CH_3), 4.48/4.39 (s, 1H; OCHO), 3.33/3.23 (s, 3H; OCH_3), 2.66 – 2.26 (m, 2H; CH_2), 1.54/1.49 (d, J = 6.6 Hz, 3H; CHCH_3), 1.03/1.01 (t, J = 7.4 Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 206.8/206.4 (C=O), 142.4/142.0 (Ar-C), 128.6/128.4, 128.0/127.8, 126.6/126.4 (Ar-CH), 102.2/100.7 (OCHO), 75.5/75.2 (*C*HCH$_3$), 55.1/53.9 (OCH_3), 30.5/29.8 (CH_2), 23.8/23.2 (CH*C*H_3), 7.0/6.9 (CH_2CH_3); FAB-MS (room temperature): *m/z* (%): 222 (3) [M^+], 209 (48), 191 (21), 176 (37), 161 (21), 154 (100), 135 (88).

1-Methoxy-1-(1-naphth-2-yl-ethoxy)butan-2-one (13b): Mixed acetal **13a** (1.9 g, 7.4 mmol) was added to a mixture of cyclohexylamine (1.26 mL, 11.0 mol) and $CaCl_2$ (1.5 g) in diethyl ether (10 mL). The mixture was stirred for 16 h and then filtered and evaporated. *n*BuLi (6.9 mL, 11.0 mmol, 1.6 M solution in hexane) was added at 0 °C to a solution of diisopropylamine (1.55 mL, 11.0 mmol) in THF (7 mL). The solution was cooled to −78 °C and the crude imine was added dropwise within 1 h. Then MeI (0.69 mL, 11.0 mmol) was added, the mixture was stirred for 2 h and then allowed to slowly reach room temperature Saturated aqueous $NaHCO_3$ solution was added and the aqueous layer was extracted with diethyl ether. The combined organic phase was dried ($MgSO_4$), evaporated and purified by column chromatography (PE/Et_2O, 9:1) to afford **13b** (1.34 g, 67 %) as a yellowish oil (diastereomeric mixture). IR (film): $\tilde{\nu}$ = 3056, 2976, 2936, 2880, 2832, 1724, 1452, 1376, 1308, 1176, 1100, 1064, 1028, 820, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.86 – 7.72 (m, 4H; Ar), 7.56 – 7.43 (m, 3H; Ar), 4.98/4.79 (q, J = 6.5 Hz, 1H; C*H*CH_3), 4.51/4.44 (s, 1H; OCHO), 3.33/3.19 (s, 3H; OCH_3), 2.72 – 2.46 (m, 2H; CH_2), 1.61/1.56 (d, J = 6.5 Hz, 3H; CHCH_3), 1.03/1.00 (t, J = 7.3 Hz, 3H; CH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ = 206.8/206.4 (C=O), 140.0, 139.4 133.4, 133.3, 133.2, 133.1, (Ar-C), 128.8, 128.5, 128.0, 127.9, 127.8, 127.7, 126.4, 126.3, 126.2, 126.1, 126.0, 125.5, 124.3, 124.1 (Ar-CH), 102.4/100.7 (OCHO), 75.8/75.4 (*C*HCH$_3$), 55.3/53.9 (OCH_3), 35.7/30.7 (CH_2), 23.7/23.3 (CH*C*H_3), 7.1/7.0 (CH_2CH_3); MS (room temperature): *m/z* (%): 272 (1) [M^+], 226 (1), 212 (5), 156 (14), 155 (100), 128 (3), 127 (4), 115 (2), 98 (2), 95 (5), 77 (1), 69 (1).

General procedure for the preparation of silyl enol ethers. Method A: *n*BuLi (1.2 equiv) was added at 0 °C to a solution of diisopropylamine (1.2 equiv) in THF (0.5 mL/mmol mixed acetal). The solution was cooled to −78 °C and mixed acetal (1.0 equiv) was added dropwise. The resulting mixture was stirred for 1 h at the same temperature, then TMSCl (1.5 equiv) was added. After complete reaction, water was added. The aqueous layer was extracted with ether and the combined organic phase was dried ($MgSO_4$). The solvent was evaporated and the crude product purified by column chromatography.

Method B: A solution of lithium diisopropylamine (1.2 equiv) (prepared as described above) was added at −78 °C to a solution of mixed acetal (1.0 equiv) and TESCl (1.5 equiv). Then Et_3N (4.5 equiv) was added. The progress of the reaction was monitored by TLC. Workup, as described above, gave the silyl enol ether.

[1-Methoxy-1-(1-phenylethoxy)methylvinyloxy]triethylsilane (2a): Diisopropylamine (4.6 mL, 32.8 mmol), *n*BuLi (20.5 mL, 32.8 mmol, 1.6 M solution in hexane), mixed acetal **1a** (5.6 g, 26.9 mmol), TESCl (6.8 mL, 40.4 mmol) and Et_3N (16.8 mL, 121.1 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method B). Chromatography (PE/Et_2O, 95:5) gave **2a** (7.4 g, 85 %) as colourless oil (diastereomeric mixture). IR ($CHCl_3$): $\tilde{\nu}$ = 3008, 2956, 2936, 2912, 2876, 1640, 1456, 1380, 1256, 1108, 1052, 1028, 968 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.24 (m, 5H; Ar), 4.78/4.59 (q, J = 6.5 Hz, 1H; PhC*H*), 4.56/4.52 (br. s, 1H; =C*H*H), 4.50/4.41 (s, 1H; OCHO), 4.27 (br. s, 1H; =CH*H*), 3.20/3.12 (s, 3H; OCH_3), 1.42 (d, J = 6.5 Hz, 3H; CHCH_3), 0.76 (m, 15H; $Si(C_2H_5)_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.3/153.9 (*C*OTES), 143.7/143.2 (Ar-C), 128.3, 128.2, 127.4, 126.4, 126.3 (Ar-CH), 100.2/98.5 (OCHO), 92.0/91.8 (=CH_2), 74.3/73.8 (Ph*C*H), 53.8/52.0 (OCH_3), 24.2/23.3 (CH*C*H_3), 6.6 ($Si(CH_2CH_3)_3$), 4.8 ($Si(CH_2CH_3)_3$); MS (room temperature): *m/z* (%): 322 (1) [M^+], 293 (23), 261 (26), 217 (9), 202 (73), 157 (58), 129 (48), 115 (88), 105 (100), 87 (79), 77 (53), 65 (25).

[1-Methoxy-1-(1-phenylpropoxy)methylvinyloxy]triethylsilane (2b): Diisopropylamine (0.35 mL, 2.7 mmol), *n*BuLi (1.7 mL, 2.7 mmol, 1.6 M solution in hexane), mixed acetal **1b** (0.5 g, 2.3 mmol) and TESCl (0.45 mL, 2.7 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method A). Chromatography (PE/Et_2O, 9:1) gave **2b** (610 mg, 80 %) as a pale-yellowish oil (diastereomeric mixture). The silyl enol ether was immediately used for the following cycloaddition.

[1-Methoxy-1-(1-phenylpentoxy)methylvinyloxy]triethylsilane (2c): Diisopropylamine (0.3 mL, 2.1 mmol), *n*BuLi (1.3 mL, 2.1 mmol, 1.6 M solution in hexane), mixed acetal **1c** (0.44 g, 1.76 mmol), TESCl (0.41 mL, 2.6 mmol) and Et_3N (1.1 mL, 7.9 mmol) were allowed to react according

0947-6539/00/0604-0688 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 4

to the general procedure for the preparation of silyl enol ethers (method B). Chromatography (cyclohexane/MTBE, 15:1) gave **2c** (331 mg, 51% (81% based on recovered starting material)) as a colourless oil (diastereomeric mixture). IR ($CHCl_3$): $\tilde{\nu}$ = 2956, 2936, 2912, 2876, 1724, 1640, 1456, 1260, 1104, 1052, 1020, 840 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.29–7.20 (m, 5H; Ar), 4.59 (br. s, 1H; =C*H*H), 4.62/4.36 (t, J = 6.1 Hz, 1H; PhC*H*), 4.51/4.42 (s, 1H; OCHO), 4.44/4.29 (d, J = 1.0 Hz, 1H; =CH*H*), 3.21/3.08 (s, 3H; OCH_3), 1.88/1.57 (m, 2H; $CHCH_2$), 1.40–1.15 (m, 4H; $(CH_2)_2CH_3$), 0.97–0.73 (m, 12H; CH_2CH_3, $Si(CH_2CH_3)_3$), 0.72–0.52 (m, 6H; $Si(CH_2CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.4/154.0 (*C*OTES), 142.8/142.1 (Ar-C), 128.2, 128.1, 127.9, 127.4, 126.9 (Ar-CH), 100.9/97.9 (OCHO), 92.2 (=CH_2), 79.2/77.8 (Ph*C*H), 54.0/51.6 (OCH_3), 37.9/37.3 ($CHCH_2$), 29.9/29.8 ($CHCH_2CH_2$), 22.6 (CH_2CH_3), 14.0 (CH_2CH_3), 6.6/6.5 ($Si(CH_2CH_3)_3$), 4.9/4.8 ($Si(CH_2CH_3)_3$).

[1-Methoxy-1-(1-phenyl-2,2-dimethylpropoxy)methylvinyloxy]triethylsilane (2d): Diisopropylamine (0.15 mL, 1.1 mmol), *n*BuLi (0.7 mL, 1.1 mmol, 1.6 M solution in hexane), mixed acetal **1d** (0.23 g, 0.92 mmol), TESCl (0.12 mL, 1.4 mmol) and Et_3N (0.6 mL, 4.1 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method B). Chromatography (PE/Et_2O, 97:3) gave **2d** (289 mg, 55% (80% based on recovered starting material)) as a colourless oil (diastereomeric mixture). IR ($CHCl_3$): $\tilde{\nu}$ = 2956, 2912, 2876, 1640, 1452, 1392, 1380, 1364, 1260, 1108, 1044, 1028 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 5H; Ar), 4.71/4.54 (br. s, 1H; =C*H*H), 4.52/4.40 (s, 1H; OCHO), 4.45/4.13 (s, 1H; PhC*H*), 4.35/4.33 (d, J = 1.0 Hz, 1H; =CH*H*), 3.26/3.07 (s, 3H; OCH_3), 1.04/0.87 (m, 18H; $C(CH_3)_3$, $Si(CH_2CH_3)_3$), 0.78/0.56 (m, 6H; $Si(CH_2CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.1 (*C*OTES), 140.3/138.9 (Ar-C), 128.8, 128.6, 127.4, 127.3, 127.1 (Ar-CH), 102.4/97.2 (OCHO), 92.4/92.2 (=CH_2), 87.5/85.2 (Ph*C*H), 53.3/51.0 (OCH_3), 36.0/35.4 ($C(CH_3)_3$) 26.5/26.4 ($CHCH_3$), 6.9/6.7 ($Si(CH_2CH_3)_3$), 4.9/4.8 ($Si(CH_2CH_3)_3$); MS (room temperature): *m/z* (%): 364 (0) [M^+], 336 (1), 335 (2), 334 (1), 318 (1), 307 (1), 249 (9), 202 (64), 201 (100), 163 (12), 147 (77), 131 (29), 115 (43), 105 (72), 77 (29).

Silyl enol ether 6: Diisopropylamine (0.12 mL, 1.2 mmol), *n*BuLi (0.75 mL, 1.2 mmol, 1.6 M solution in hexane), mixed acetal **5** (0.22 g, 1.0 mmol) and TESCl (0.25 mL, 1.5 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method A). Chromatography (PE/Et_2O, 9:1) gave **6** (312 mg, 93%) as a yellowish oil. The silyl enol ether was immediately used for the following cycloaddition.

Silyl enol ether 10: Diisopropylamine (0.58 mL, 4.4 mmol), *n*BuLi (2.8 mL, 4.4 mmol, 1.6 M solution in hexane), mixed acetal **9** (0.83 g, 3.7 mmol), TESCl (0.84 mL, 5.6 mmol) and Et_3N (2.3 mL, 16.7 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method B). Chromatography (PE/Et_2O, 9:1) gave **10** (1.03 g, 84%) as a yellowish oil. The silyl enol ether was immediately used for the following cycloaddition.

Silyl enol ether 14a: Mixed acetal **13a** (0.69 g, 2.65 mmol), LDA (prepared from diisopropylamine (0.41 mL, 3.18 mmol) and *n*BuLi (2.0 mL, 3.18 mmol, 1.6 M solution in hexane)), TESCl (0.67 mL, 3.98 mmol) and Et_3N (1.64 mL, 11.9 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method B) to afford after column chromatography (PE/Et_2O, 9:1) **14a** (753 mg, 76%), yellow oil. IR ($CHCl_3$): $\tilde{\nu}$ = 2958, 2937, 2913, 2877, 1642, 1458, 1378, 1258, 1108, 1051, 1019, 970, 951, 858, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.80 (m, 4H; Ar), 7.45 (m, 3H; Ar), 5.01/4.82 (q, J = 6.4 Hz, 1H; $CHCH_3$), 4.65/4.61 (d, J = 1.0 Hz, 1H; =C*H*H), 4.60/4.52 (s, 1H; OCHO), 4.37/4.34 (d, J = 1.0 Hz, 1H; =CH*H*), 3.28/3.18 (s, 3H; OCH_3), 1.56 (d, J = 6.4 Hz, 3H; $CHCH_3$), 0.98/0.93 (t, J = 7.9 Hz, 9H; $SiCH_2CH_3$), 0.70/0.66 (q, J = 7.9 Hz, 6H; $SiCH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 154.4/154.0 (*C*OTES), 141.2/140.7, 133.3/133.2, 133.0/133.0 (Ar-C), 128.3, 128.1, 127.9, 127.8, 127.7, 126.0, 125.7, 125.4, 125.1, 124.5, 124.4 (Ar-CH), 100.5/98.7 OCHO), 92.1/91.8 (=CH_2), 74.5/74.0 (*C*HCH$_3$), 54.0/52.2 (OCH_3), 24.1/23.4 ($CHCH_3$), 6.6/6.5 ($SiCH_2CH_3$), 4.9/4.8 ($SiCH_2CH_3$); MS (room temperature): *m/z* (%): 372 (2) [M^+], 343 (2), 312 (2), 204 (6), 202 (27), 186 (2), 175 (3), 174 (3), 173 (11), 156 (19), 155 (100), 141 (3), 129 (7), 115 (10), 89 (5), 77 (3).

Silyl enol ether 14b: Mixed acetal **13b** (0.75 g, 2.76 mmol), LDA (prepared from diisopropylamine (0.46 mL, 3.31 mmol) and *n*BuLi (2.1 mL, 3.31 mmol, 1.6 M solution in hexane)), TESCl (0.70 mL, 4.14 mmol) and Et_3N (1.70 mL, 12.4 mmol) were allowed to react according to the general procedure for the preparation of silyl enol ethers (method B) to afford, after column chromatography (cyclohexane/MTBE, 15:1), **14b** (943 mg, 88%), yellow oil. The silyl enol ether was immediately used for the following cycloaddition.

General procedure for cycloadditions: Furan (1.1 equiv) and silyl enol ether (1.0 equiv) were dissolved in CH_2Cl_2 (0.01–1 M) and cooled to $-95\,^\circ C$ (chilled with MeOH and liquid N_2). Catalytic trimethylsilyl triflate (less than 10 mol%) was added dropwise slowly and without interruption by syringe and the progress of the reaction was monitored by TLC. The first sample drawn (after 3 min) showed that the reaction was already completed. The cold reaction mixture was poured into saturated aqueous $NaHCO_3$ solution. After the reaction mixture reached room temperature, the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried ($MgSO_4$), evaporated and purified. The diastereomeric cycloadducts were in all cases easily separable by simple chromatography, yielding diastereomerically pure compounds. The methoxy-substituted cycloadduct was formed as a side product.

2α-(1-Phenylethoxy)-8-oxabicyclo[3.2.1]oct-6-en-3-one (3a): Silyl enol ether **2a** (37.9 g, 117.6 mmol) and furan (9.4 mL, 129.4 mmol) in CH_2Cl_2 (500 mL) were allowed to react according to the general cycloaddition procedure. Column chromatography (cyclohexane/MTBE, 3:1) afforded major isomer **3a** (16.9 g, 59%) and minor isomer (2.3 g, 8%). Data for major isomer: colourless solid, m.p. 87–89 °C, $[\alpha]_D^{22} = -166.7$ (c = 1.0 in $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 3022, 2980, 1724, 1452, 1328, 1264, 1176, 1144, 1100, 1076, 1044, 1008, 968 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.41–7.27 (m, 5H; Ar), 6.38 (dd, J = 1.6 Hz, 5.8 Hz, 1H; H-7), 6.28 (dd, J = 1.6 Hz, 5.8 Hz, 1H; H-6), 4.94 (dd, J = 1.6 Hz, 4.8 Hz, 1H; H-5), 4.83 (q, J = 6.4 Hz, 1H; PhC*H*), 4.70 (dd, J = 1.6 Hz, 4.8 Hz, 1H; H-1), 3.94 (d, J = 4.8 Hz, 1H; H-2), 2.69 (dd, J = 4.8 Hz, 15.6 Hz, 1H; $H\text{-}4_{ax}$), 2.33 (d, J = 15.6 Hz, 1H; $H\text{-}4_{eq}$), 1.45 (d, J = 6.4 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 205.8 (C-3), 143.3 (Ar-C), 134.5 (C-6), 132.0 (C-7), 128.6, 127.9, 126.4 (Ar-CH), 82.8 (C-2), 80.2 (Ph*C*H), 79.2 (C-1), 78.3 (C-5), 45.9 (C-4), 24.2 (CH_3); MS (70 °C): *m/z* (%): 244 (2) [M^+], 216 (12), 215 (28), 161 (12), 148 (25), 140 (94), 105 (100), 97 (50), 77 (94); HRMS: $C_{15}H_{16}O_3$: calcd 244.1100; found: 244.1100. $C_{15}H_{16}O_3$ (244.1): calcd C 73.75, H 6.60; found C 73.69, H 6.50. Data for the minor isomer: colourless solid, m.p. 90–92 °C; $[\alpha]_D^{22} = -93.9$ (c = 0.95 in $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 2979, 2930, 2872, 1727, 1493, 1451, 1410, 1377, 1338, 1328, 1281, 1265, 1230, 1176, 1145, 1098, 1046, 1029, 1010, 1000, 969, 906, 886, 864, 825 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 7.31 (m, 5H; Ar), 6.39 (dd, J = 1.7 Hz, 6.4 Hz, 1H; H-7), 6.31 (dd, J = 1.7 Hz, 6.4 Hz, 1H; H-6), 5.06 (dd, J = 1.7 Hz, 4.8 Hz, 1H; H-1), 4.98 (br. d, J = 4.8 Hz, 1H; H-5), 4.76 (q, J = 6.4 Hz, 1H; PhC*H*), 4.08 (d, J = 4.8 Hz, 1H; H-2), 2.66 (dd, J = 4.8 Hz, 15.2 Hz, 1H; $H\text{-}4_{ax}$), 2.35 (d, J = 15.2 Hz, 1H; $H\text{-}4_{eq}$), 1.50 (d, J = 6.4 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 202.9 (C-3), 143.5 (Ar-C), 134.7 (C-6), 131.8 (C-7), 128.5, 127.8, 126.4 (Ar-CH), 82.7 (C-2), 78.9 (Ph*C*H), 78.3 (C-1), 77.1 (C-5), 45.7 (C-4), 24.0 (CH_3)); MS (50 °C): *m/z* (%): 244 (1) [M^+], 215 (1), 176 (1), 140 (20), 139 (2), 121 (3), 111 (4), 106 (10), 105 (100), 104 (4), 97 (4), 91 (2), 79 (5), 77 (7), 68 (10).

2α-(1-Phenylpropoxy)-8-oxabicyclo[3.2.1]oct-6-en-3-one (3b): Silyl enol ether **2b** (0.48 g, 1.4 mmol) and furan (0.1 mL, 1.4 mmol) were dissolved in dry nitroethane (1.4 mL) and allowed to react at $-78\,^\circ C$ according to the general cycloaddition procedure, to afford major isomer **3b** (149 mg, 41%) and minor isomer (31 mg, 9%). Data for **3b**: major isomer, yellowish oil; IR ($CHCl_3$): $\tilde{\nu}$ = 3428, 3084, 3000, 2968, 2936, 2876, 1724, 1676, 1600, 1492, 1452, 1408, 1380, 1328, 1228, 1176, 1144, 1108, 1084, 1000, 976, 912, 852, 624, 552 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.31 (m, 5H; Ar), 6.33 (dd, J = 1.7 Hz, 6.1 Hz, 1H; H-7), 6.25 (dd, J = 1.7 Hz, 6.1 Hz, 1H; H-6), 4.90 (br. d, J = 5.0 Hz, 1H; H-5), 4.66 (dd, J = 1.7 Hz, 5.1 Hz, 1H; H-1), 4.57 (t, J = 7.0 Hz, 1H; PhC*H*), 3.92 (d, J = 5.1 Hz, 1H; H-2), 2.64 (dd, J = 5.0 Hz, 15.5 Hz, 1H; $H\text{-}4_{ax}$), 2.29 (d, J = 15.5 Hz, 1H; $H\text{-}4_{eq}$), 1.92 (ddq, J = 7.0 Hz, 7.0 Hz, 13.7 Hz, 1H; C*H*HCH$_3$), 1.68 (ddq, J = 7.0 Hz, 7.0 Hz, 13.7 Hz, 1H; CH*H*CH$_3$), 0.88 (t, J = 7.0 Hz, 3H; $PhCH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 205.7 (C-3), 142.0 (Ar-C), 134.4 (C-7), 131.9 (C-6), 128.5, 127.9, 127.0 (Ar-CH), 84.6 (Ph*C*H), 82.7 (C-1), 80.2 (C-5), 78.2 (C-2), 45.7 (C-4), 31.0 (CH_2CH_3), 10.1 (CH_3); MS (room temperature): *m/z* (%): 258 (0) [M^+], 229 (2), 167 (5), 140 (35), 119 (64), 107 (57), 91 (100), 84 (26), 79 (40), 68 (17); HRMS: $C_{14}H_{13}O_3$ calcd 229.0865; found 229.0867. Data for the minor isomer: yellowish oil, IR ($CHCl_3$): $\tilde{\nu}$ = 3428, 3084, 3064, 3000, 2968, 2932, 2876, 1728, 1600, 1492, 1452, 1408, 1380, 1328, 1276, 1228, 1176, 1148, 1096, 1044, 1004, 960, 928, 916, 884, 828, 624, 544 cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$, TMS): $\delta = 7.32$ (m, 5H; Ar), 6.39 (dd, $J = 1.7$ Hz, 6.0 Hz, 1H; H-7), 6.31 (dd, $J = 1.7$ Hz, 6.0 Hz, 1H; H-6), 5.09 (dd, $J = 1.7$ Hz, 5.0 Hz, 1H; H-1), 4.97 (d, $J = 5.0$ Hz, 1H; H-5), 4.42 (dd, $J = 5.5$ Hz, 7.7 Hz, 1H; PhC*H*), 4.03 (d, $J = 5.0$ Hz, 1H; H-2), 2.62 (dd, $J = 5.0$ Hz, 15.5 Hz, 1H; H-4_{ax}), 2.33 (d, $J = 15.5$ Hz, 1H; H-4_{eq}), 1.87 (m, 1H; C*H*HCH$_3$), 1.70 (m, 1H; CH*H*CH$_3$), 0.94 (t, $J = 7.4$ Hz, 3H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 202.6$ (C-3), 141.4 (Ar-C), 134.6 (C-7), 131.8 (C-6), 128.4, 127.8, 126.8 (Ar-CH), 83.0 (Ph*C*H), 82.9 (C-1), 78.5 (C-5), 78.3 (C-2), 45.6 (C-4), 31.1 (*C*H$_2$CH$_3$), 10.7 (CH$_3$); MS (room temperature): *m/z* (%): 258 (0) [M^+], 229 (1), 140 (31), 119 (54), 91 (100), 83 (10), 68 (22); HRMS: $C_{14}H_{13}O_3$ calcd 229.0865, found 229.0861.

2α-(1-Phenylpentoxy)-8-oxabicyclo[3.2.1]oct-6-en-3-one (3c): Silyl enol ether **2c** (0.32 g, 0.88 mmol) and furan (0.07 mL, 0.97 mmol) in CH_2Cl_2 (8.3 mL) were allowed to react according to the general cycloaddition procedure. Column chromatography (cyclohexane/MTBE, 3:1) afforded major isomer (125 mg, 49%) and minor isomer (24 mg, 10%). Data for **3c**, major isomer: pale yellow oil; IR ($CHCl_3$): $\tilde{\nu} = 2999$, 2960, 2934, 2862, 1725, 1454, 1328, 1265, 1230, 1175, 1144, 1110, 1099, 1046, 1001, 963, 887, 852 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.38 - 7.26$ (m, 5H; Ar), 6.33, 6.25 (dd, $J = 1.8$ Hz, 6.1 Hz, 2H; H-6, H-7), 4.91 (br. d, $J = 4.9$ Hz, 1H; H-5), 4.65 (m, 2H; PhC*H*, H-1), 3.91 (d, $J = 5.2$ Hz, 1H; H-2), 2.65 (dd, $J = 4.9$ Hz, 15.4 Hz, 1H; H-4_{ax}), 2.30 (d, $J = 15.4$ Hz, 1H; H-4_{eq}), 1.91 (m, 1H; PhCHC*H*H), 1.63 (m, 1H; PhCHCH*H*), 1.43 – 1.18 (m, 4H; (*CH*$_2$)$_2$CH$_3$), 0.86 (t, $J = 7.2$ Hz, 3H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 205.6$ (C-3), 142.3 (Ar-C), 134.3, 131.9 (C-6, C-7), 128.4, 127.8, 126.8 (Ar-CH), 83.2, 82.6, 82.0, 78.1 (C-1, Ph*C*H, C-5, C-2), 45.8 (C-4), 37.8 (CH*C*H$_2$), 27.6 (CHCH$_2$*C*H$_2$), 22.5 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$); MS (80 °C): *m/z* (%): 287 (1) [M^++1], 257 (2), 164 (9), 163 (6), 147 (37), 140 (33), 117 (5), 107 (83), 105 (20), 91 (100), 79 (21), 77 (13), 68 (15). Data for the minor isomer: pale yellow oil; IR ($CHCl_3$): $\tilde{\nu} = 2960$, 2933, 2862, 1728, 1454, 1336, 1230, 1176, 1146, 1109, 1098, 964, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.40 - 7.25$ (m, 5H; Ar), 6.39 (dd, $J = 1.8$ Hz, 6.2 Hz, 1H; H-7), 6.32 (dd, $J = 1.6$ Hz, 6.2 Hz, 1H; H-6), 5.08 (dd, $J = 1.8$ Hz, 4.8 Hz, 1H; H-1), 4.98 (br. d, $J = 4.9$ Hz, 1H; H-5), 4.49 (dd, $J = 5.2$ Hz, 8.1 Hz, 1H; PhC*H*), 4.02 (d, $J = 4.8$ Hz, 1H; H-2), 2.62 (dd, $J = 4.9$ Hz, 15.4 Hz, 1H; H-4_{ax}), 2.33 (dd, $J = 0.6$ Hz, 15.4 Hz, 1H; H-4_{eq}), 1.88 (m, 1H; PhCHC*H*H), 1.64 (m, 1H; PhCHCH*H*), 1.50 – 1.19 (m, 4H; (*CH*$_2$)$_2$CH$_3$), 0.88 (t, $J = 7.2$ Hz, 3H; CH$_3$); MS (90 °C): *m/z* (%): 287 (1) [M^++1], 257 (4), 229 (1), 218 (2), 164 (3), 163 (20), 161 (16), 148 (14), 147 (100), 146 (8), 141 (8), 139 (9), 134 (2), 129 (2), 117 (12), 115 (5), 111 (13), 105 (27), 104 (11).

2α-(1-Phenyl-2,2-dimethylpropoxy)-8-oxabicyclo[3.2.1]oct-6-en-3-one (3d): Silyl enol ether **2d** (0.14 g, 0.39 mmol) and furan (0.03 mL, 0.43 mmol) in CH_2Cl_2 (3.9 mL) were allowed to react according to the general cycloaddition procedure. Column chromatography (cyclohexane/MTBE, 3:1) afforded major isomer (54 mg, 48%) and minor isomer (10 mg, 9%). Data for **3d**, major isomer: yellowish solid, m.p. 111 – 113 °C; IR ($CHCl_3$): $\tilde{\nu} = 2969$, 2907, 2869, 1726, 1479, 1453, 1394, 1364, 1338, 1329, 1230, 1174, 1139, 1111, 1101, 1041, 1029, 1003, 964, 928, 915, 887, 852, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.38 - 7.21$ (m, 5H; Ar), 6.35, 6.28 (dd, $J = 1.7$ Hz, 6.1 Hz, 2H; H-6, H-7), 4.92 (br. d, $J = 4.9$ Hz, 1H; H-5), 4.76 (dd, $J = 1.7$ Hz, 5.1 Hz, 1H; H-1), 4.50 (s, 1H; PhC*H*), 3.86 (d, $J = 5.1$ Hz, 1H; H-2), 2.63 (dd, $J = 4.9$ Hz, 15.5 Hz, 1H; H-4_{ax}), 2.28 (d, $J = 15.5$ Hz, 1H; H-4_{eq}), 0.92 (s, 9H; C(CH$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 205.7$ (C-3), 139.3 (Ar-C), 134.3, 132.0 (C-6, C-7), 128.5, 127.6, 127.5 (Ar-CH), 90.0, 82.4, 82.2, 78.1 (C-1, Ph*C*H, C-5, C-2), 45.9 (C-4), 35.8 (*C*(CH$_3$)$_3$), 26.2 (C(*C*H$_3$)$_3$); MS (60 °C): *m/z* (%): 286 (4) [M^+], 230 (3), 229 (10), 203 (5), 163 (9), 162 (9), 161 (66), 147 (100), 141 (42), 131 (12), 117 (7), 105 (64), 91 (83), 81 (21), 68 (31); HRMS: $C_{18}H_{22}O_3$: calcd 286.1569; found 286.1569. $C_{18}H_{22}O_3$ (286.2): calcd C 75.50, H 7.74; found C 75.55, H 7.77. Data for the minor isomer: pale yellow solid, m.p. 124 – 126 °C; IR ($CHCl_3$): $\tilde{\nu} = 2958$, 2908, 2868, 1729, 1480, 1453, 1394, 1363, 1337, 1230, 1176, 1140, 1109, 1099, 1049, 1029, 1011, 994, 966, 885, 843, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.40 - 7.23$ (m, 5H; Ar), 6.39, 6.31 (dd, $J = 1.7$ Hz, 6.2 Hz, 2H; H-6, H-7), 5.08 (dd, $J = 1.7$ Hz, 4.8 Hz, 1H; H-1), 4.96 (br. d, $J = 4.9$ Hz, 1H; H-5), 4.17 (s, 1H; PhC*H*), 3.92 (d, $J = 4.8$ Hz, 1H; H-2), 2.59 (dd, $J = 4.9$ Hz, 15.4 Hz, 1H; H-4_{ax}), 2.39 (dd, $J = 0.7$ Hz, 15.4 Hz, 1H; H-4_{eq}), 0.92 (s, 9H; C(CH$_3$)$_3$); MS (60 °C): *m/z* (%): 286 (5) [M^+], 230 (4), 229 (16), 162 (9), 161 (62), 148 (14), 147 (100), 146 (11), 140 (48), 131 (12), 105 (53), 91 (59), 81 (13), 69 (11), 68 (23).

2α-(1-Phenylethoxy)-2β-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (8): Silyl enol ether **6** (0.31 g, 0.93 mmol) and furan (0.068 mL, 0.93 mmol) were dissolved in dry CH_2Cl_2 (0.93 mL) and allowed to react according to the general cycloaddition procedure to afford major isomer **8** (89 mg, 38%) and minor isomer (9 mg, 4%). Data for major isomer: yellowish oil; IR ($CHCl_3$): $\tilde{\nu} = 2980$, 2932, 1720, 1492, 1452, 1408, 1372, 1332, 1280, 1240, 1192, 1168, 1100, 1084, 1044, 1016, 1000, 968, 944, 932, 868, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.30$ (m, 5H; Ar), 6.31 (dd, $J = 1.8$ Hz, 6.0 Hz, 1H; H-7), 6.23 (dd, $J = 1.5$ Hz, 6.0 Hz, 1H; H-6), 5.15 (q, $J = 6.4$ Hz, 1H; PhC*H*), 4.93 (br. d, $J = 4.8$ Hz, 1H; H-5), 4.46 (d, $J = 1.8$ Hz, 1H; H-1), 2.79 (dd, $J = 4.8$ Hz, 15.8 Hz, 1H; H-4_{ax}), 2.26 (dd, $J = 1.1$ Hz, 15.8 Hz, 1H; H-4_{eq}), 1.44 (d, $J = 6.4$ Hz, 3H; PhC*H*$_3$), 1.37 (s, 3H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 208.8$ (C-3), 147.0 (Ar-C), 133.6, 133.2 (C-6, C-7), 128.3, 126.8, 125.4 (Ar-CH), 86.1 (C-2), 84.6 (Ph-CH), 78.2 (C-1), 73.1 (C-5), 44.3 (C-4), 25.7 (PhCH*C*H$_3$), 19.6 (CH$_3$); MS (room temperature): *m/z* (%): 258 (1) [M^+], 215 (23), 187 (1), 154 (38), 111 (26), 105 (100), 83 (13), 77 (21), 68 (14); HRMS: $C_{16}H_{18}O_3$ calcd 258.1256; found 258.1248.

2β-(1-Phenylethoxy)-4β-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (12): Silyl enol ether **10** (0.34 g, 1.0 mmol) and furan (0.07 mL, 1.0 mmol) were dissolved in dry CH_2Cl_2 (1.0 mL) and allowed to react according to the general cycloaddition procedure to afford major isomer **12** (128 mg, 50%) and minor isomer (9 mg, 3%). Data for **12**: colourless oil, major isomer, IR ($CHCl_3$): $\tilde{\nu} = 3672$, 2960, 2936, 2912, 2879, 1724, 1492, 1452, 1376, 1332, 1280, 1228, 1132, 1116, 1104, 1080, 1060, 1012, 956, 936, 900, 872, 816, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.30$ (m, 5H; Ar), 6.42, 6.30 (dd, $J = 1.7$ Hz, 6.0 Hz, 2H; H-6, H-7), 4.80 (q, $J = 6.4$ Hz, 1H; PhC*H*), 4.76 (dd, $J = 1.7$ Hz, 4.8 Hz, 1H; H-5), 4.70 (dd, $J = 1.7$ Hz, 5.0 Hz, 1H; H-1), 3.94 (dd, $J = 0.5$ Hz, 5.0 Hz, 1H; H-2), 2.72 (dq, $J = 4.8$ Hz, 7.0 Hz, 1H; H-4), 1.49 (d, $J = 6.4$ Hz, 3H; PhC*H*$_3$), 0.96 (d, $J = 7.0$ Hz, 3H; CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 207.5$ (C-3), 143.2 (Ar-C), 133.4, 133.1 (C-6, C-7), 128.5 , 127.8, 126.2 (Ar-CH), 82.7 (PhCH), 81.8 (C-1), 80.7 (C-5), 78.9 (C-2), 50.0 (C-4), 24.0 (PhCH*C*H$_3$), 9.4 (CH$_3$); FAB-MS (room temperature): *m/z* (%): 258 (9) [M^+], 176 (8), 154 (35), 136 (15), 121 (6), 105 (100).

2α-(1-Naphth-2-yl-ethoxy)-8-oxabicyclo[3.2.1]oct-6-en-3-one (15a): Silyl enol ether **14a** (0.75 g, 2.0 mmol) and furan (0.14 mL, 2.0 mmol) in CH_2Cl_2 (2 mL) were allowed to react according to the general cycloaddition procedure to afford **15a** (292 mg, 50%) as a pale yellow solid (single isomer), m.p. 92 °C, $[\alpha]_D^{25} = +131.3$ ($c = 1$ in $CHCl_3$); IR (KBr): $\tilde{\nu} = 3416$, 3052, 2980, 2960, 2932, 2916, 2868, 1724, 1636, 1600, 1504, 1456, 1440, 1408, 1376, 1324, 1304, 1256, 1236, 1212, 1176, 1140, 1100, 1072, 1048, 1000, 964, 900, 852, 824, 744, 732, 660, 624, 556, 504, 480 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.84$ (m, 3H; Ar), 7.71 (br. s, 1H; Ar), 7.47 (m, 3H; Ar), 6.37, 6.25 (dd, $J = 1.7$ Hz, 6.0 Hz, 2H; H-6, H-7), 4.99 (q, $J = 6.4$ Hz, 1H; PhC*H*), 4.89 (br. d, $J = 5.0$ Hz, 1H; H-1), 4.69 (dd, $J = 1.7$ Hz, 4.9 Hz, 1H; H-5), 3.96 (d, $J = 5.0$ Hz, 1H; H-2), 2.65 (dd, $J = 4.9$ Hz, 15.4 Hz, 1H; H-4_{ax}), 2.31 (d, $J = 15.4$ Hz, 1H; H-4_{eq}), 1.57 (d, $J = 6.4$ Hz, 3H; PhC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 205.8$ (C-3), 143.2, 140.4 (Ar-C), 134.5 (C-7), 133.2 (Ar-C), 131.9 (C-6), 128.7, 127.8, 127.7, 126.3, 125.9, 125.7, 123.9 (Ar-CH), 82.8 (NaphC*H*CH$_3$), 80.1 (C-2), 79.3 (C-1), 78.2 (C-5), 45.8 (C-4), 23.9 (CH$_3$); FAB-MS (room temperature): *m/z* (%): 294 (13) [M^+], 259 (14), 225 (5), 172 (12), 155 (100), 136 (13), 107 (4); Crystal structure analysis of (+)-**15a**: $C_{19}H_{18}O_3$, $M_r = 294.3$, monoclinic, space group $P2_1$, $a = 6.445(1)$, $b = 7.534(2)$, $c = 15.939(3)$ Å, $\beta = 99.10(2)$, $V = 764.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.28$ g cm^{-3}. Stoe-IPDS, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, 1520 unique reflections, $R_{int} = 0.034$, $2\theta(max) = 41.6$, structure determination with SHELXS-86, refinement with SHELXL-93, $R_1 = 0.03$, $wR_2 = 0.04$, absolute structure not determinable. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111342. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2β-(1-Naphth-2-yl-ethoxy)-4β-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (15b): Silyl enol ether **10** (0.39 g, 1.0 mmol) and furan (0.08 mL, 1.1 mmol) were dissolved in dry CH_2Cl_2 (100 mL) and allowed to react according to the general cycloaddition procedure. Column chromatography (cyclohexane/MTBE, 3:1) of the crude product afforded a major isomer (255 mg, 83%) and a minor isomer (25 mg, 8%). Data for major isomer: pale yellow solid, m.p. 97 – 99 °C, $[\alpha]_D^{22} = +199.8$ ($c = 1.05$ in $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} =$ 3060, 2976, 2932, 2876, 1724, 1508, 1452, 1376, 1332, 1320, 1304, 1284, 1232, 1176, 1124, 1104, 1076, 1024, 1004, 936, 900, 860, 820 cm^{-1}; ^{1}H NMR

0947-6539/00/0604-0690 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 4

(400 MHz, $CDCl_3$, TMS): $\delta = 7.87-7.80$ (m, 3H; Ar), 7.70 (s, 1H; Ar), 7.51–7.44 (m, 3H; Ar), 6.43, 6.28 (dd, $J = 1.6$ Hz, 6.1 Hz, 2H; H-6, H-7), 4.98 (q, $J = 6.4$ Hz, 1H; Ar$CH$$CH_3$), 4.71 (m, 2H; H-1, H-5), 3.98 (dd, $J =$ 0.6 Hz, 5.0 Hz, 1H; H-2), 2.69 (ddd, $J = 0.6$ Hz, 4.6 Hz, 6.9 Hz, 1H; H-4), 1.58 (d, $J = 6.4$ Hz, 3H; Ar$CHCH_3$), 0.95 (d, $J = 6.9$ Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 207.4$ (C-3), 140.5 (Ar-CH), 133.4, 133.2 (C-7, C-6), 133.1, 133.0 (Ar-C), 128.6, 127.7, 127.6, 126.2, 125.9, 125.5, 123.9 (Ar-CH), 86.2, 81.8, 80.7, 79.0 (Ar$C$$HCH_3$, C-1, C-2, C-5) 50.0 (C-4), 23.9 (ArCHCH_3) 9.5 (CH_3); MS (room temperature): *m/z* (%): 308 (2) [M^+], 195 (14), 187 (8), 156 (15), 155 (100), 154 (23), 152 (3), 149 (6), 144 (28), 129 (4), 128 (4), 124 (2), 106 (4), 105 (31); HRMS: $C_{20}H_{20}O_3$: calcd 308.1412, found 308.1414. Data for the minor isomer: pale yellow oil; IR ($CHCl_3$): $\tilde{\nu} = 2976$, 2934, 2875, 1726, 1451, 1379, 1330, 1309, 1230, 1176, 1123, 1102, 1078, 1060, 1008, 951, 937, 908, 859, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.83$ (m, 4H; Ar), 7.60 (m, 1H; Ar), 7.46 (m, 2H; Ar), 6.47 (dd, $J = 1.8$ Hz, 6.2 Hz, 1H; H-7), 6.34 (dd, $J = 1.6$ Hz, 6.2 Hz, 1H; H-6), 5.09 (dd, $J = 1.8$ Hz, 4.8 Hz, 1H; H-1), 4.90 (q, $J = 6.4$ Hz, 1H; Ar$CH$$CH_3$), 4.79 (dd, $J = 1.6$ Hz, 4.6 Hz, 1H; H-5), 4.13 (dd, $J = 0.8$ Hz, 4.8 Hz, 1H; H-2), 2.66 (ddq, $J = 0.8$ Hz, 4.6 Hz, 7.0 Hz, 1H; H-4), 1.58 (d, $J = 6.4$ Hz, 3H; Ar$CHCH_3$), 0.94 (d, $J = 7.0$ Hz, 3H; CH_3)); MS (80 °C): *m/z* (%): 308 (3) [M^+], 210(1), 197 (1), 196 (4), 182 (3), 171 (6), 163 (4), 156 (15), 155 (100), 154 (21), 140 (6), 129 (7), 128 (6), 127 (10), 115 (3), 105 (38), 97 (7), 79 (5), 68 (20).

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[17] 1-(4′-Bromophenyl)ethoxide is an undesirable leaving group, and the α-methoxy-α-1-(4′-methoxyphenyl)ethoxyketo acetal is too sensitive.

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[20] GC suggested that a minor amount (< 10%) of *E*-configured silyl enol ether (*E*)-**13b** had also been formed, inseparable from *Z*-configurated **13b**. The presumed (*E*)-**13b** entered into cycloaddition less readily. Allowing for the presence of precursor (*E*)-**13b**, the yield of cycloadduct **14b** is essentially quantitative.

[21] Other types of chelation involving, for example, chelated lithium, sodium and zinc oxyallyl are feasible and are being studied.

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