Intramolecular Ene and Related Reactions, Part 9. Photochemically Induced Synthesis of Allylsilane Carbaldehydes[1]

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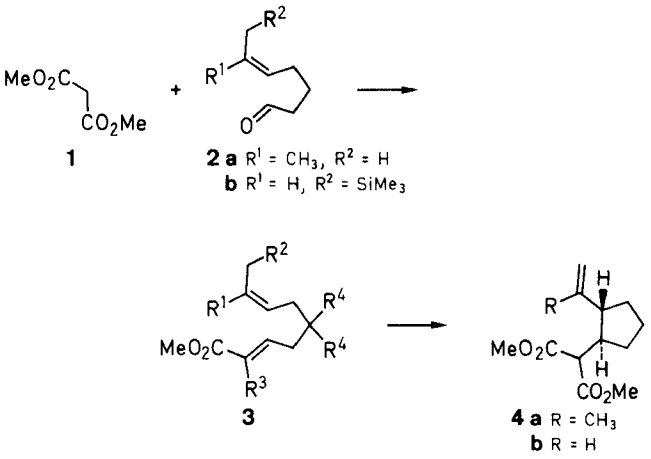
Dedicated to Prof. Dr. Hans-Jürgen Bestmann with best wishes on the occasion of his 65th birthday

Allylsilane carbaldehydes are valuable substrates for the tandem Knoevenagel allylsilane and iminium cyclization. They can easily be prepared by a photochemical α-cleavage of cyclic ketones bearing a trimethylsilylmethyl group in the α-position (Norrish Type I cleavage). The photolytic process is facilitated by the silicon due to its stabilization of a radical in the β-position. Irradiation of the ketones **15a–d** leads mainly to the aldehydes **16a–d**. In addition irradiation of **19a** gives mostly the aldehyde **20**.

The tandem Knoevenagel hetero-Diels–Alder reaction,[2] the tandem Knoevenagel ene reaction,[3–5] the tandem Knoevenagel allylsilane cyclization[1] and the related tandem condensation imine cyclization[6], which were developed by us and are now used by many other scientists, are highly versatile transformations giving access to a multitude of heterocycles and carbocycles. There are three main advantages for these reactions:

1. The simple – usually *in situ* – formation of the acceptor moiety by condensation of an aldehyde with a 1,3-dicarbonyl compound.
2. The high reactivity of the acceptor moiety due to its low lying LUMO.
3. The high induced and non-induced diastereoselectivity. This is caused by the conformational rigidity of the transition structure due to allylic 1,3-strain[7] (sp^2 geminal effect).[4]

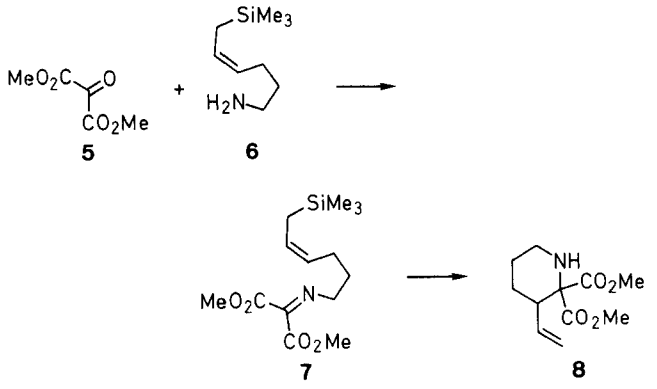
Thus, reaction of dimethyl malonate (**1**) with the aldehyde **2a** gives the Koevenagel product **3a**, which diastereoselectively yields the *trans* ene product **4a** on treatment



3	R^1	R^2	R^3	R^4
a	CH_3	H	CO_2Me	H
b	CH_3	H	H	CH_3
c	H	$SiMe_3$	CO_2Me	H

with a Lewis acid like zinc bromide at 25 °C (*trans*/*cis* = 96.5:3.5).[3] In contrast, ene reaction of **3b** leads to a nearly 1:1 mixture of the corresponding *trans*- and *cis*-disubstituted cyclopentanes.[8] In a similar way to **4a**, cyclohexanes can be obtained with high diastereoselectivity by a tandem Knoevenagel ene reaction.[5]

The scope of the reaction can be greatly expanded by using an allylsilane moiety as the donor group.[1] Lewis acid catalyzed transformation of **3c** which is obtained by Knoevenagel condensation of **1** and **2b** yields highly selectively **4b**. Similarly, condensation of dimethyl oxopropanedioate **(5)** with 6-trimethylsilyl-4-hexenylamine **(6)** affords imine **7**, which cyclizes to give dimethyl 3-vinyl-2,2-piperidinedicarboxylate **(8)**. By this procedure also pyrrolidine, and azepine derivatives can be obtained depending on the ether in **7**.[6]



A major drawback in the described transformations using allylsilanes was their often lengthy preparation.

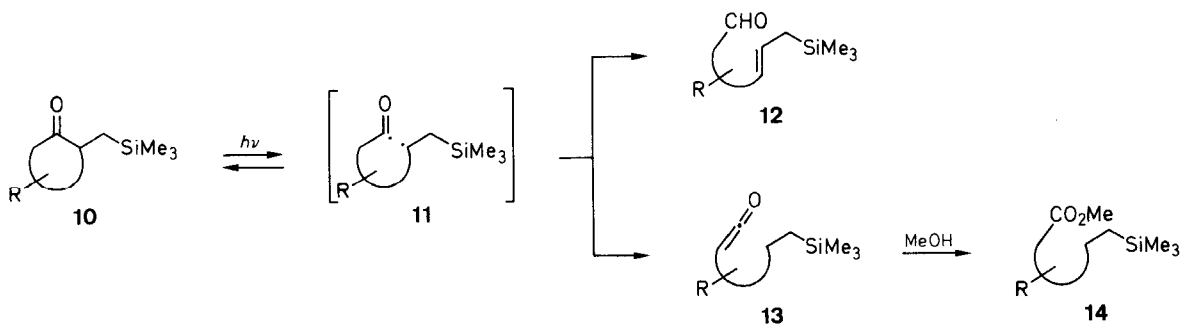
In this paper we now present a simple and widely usuable method for the synthesis of aldehydes with an allylsilane moiety which can be used in the above mentioned reactions. The key step is a photochemically induced Norrish type I cleavage[9] of cyclic ketones carrying a trimethylsilylmethyl group in the α-position.[10]

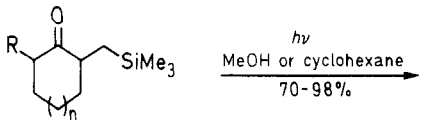
The cleavage of **10** to give **11** proceeds quite clean due to the stabilizing effect of the silicon atom.[11] Formation of the biradical intermediate **11** in this photolytic process is generally accepted,[12] and, indeed, on several occasions radicals derived in this fashion from other types of ketones have been observed spectroscopically.[13] As shown in the scheme, α-cleavage of ketone **10** leads to biradical **11**, which may reclose to **10** or disproportionate either to the ketene **13**, trapped as its methyl ester **14** or to the aldehyde **12**. In the reaction substituted and unsubstituted cyclopentanones, cyclohexanones and cycloheptanones can be used. The preparation of the substrates can be achieved by alkylation of the appropriate ketones or their imine derivatives with iodomethyltrimethylsilane.

Thus, treatment of the cyclohexylimine derivative of cyclohexanone with lithium diisopropylamide (LDA) followed by addition of iodomethyltrimethylsilane at −78 °C gave after hydrolysis the ketone **15b** in 92% yield. Irradiation of **15b** in methanol for 18 h at 0 °C with a high pressure mercury lamp using a pyrex filter ($\lambda > 2800$ Å) led to the allylsilane **16b** with the *E*-configuration in 70% yield (Table). The diastereoisomer **17b** could not be detected. The usual byproduct,[14] the saturated methyl ester **18b**, was obtained in 11% yield. Using cyclohexane as solvent, the photolysis proceeded in only 3 h and yielded 73% of the desired aldehyde **16b**. Under these conditions the ester **18b** was naturally not formed. In a similar way the transformation of cyclopentanone and cycloheptanone has been performed. Thus, cyclopentanone was alkylated to give the ketone **15a** in 79% yield, which afforded a 3:1 mixture of **16a** and **17a** on photochemical cleavage. Similarly, **15d** obtained from cycloheptanone in 76% yield afforded a 8.7:1 mixture of **16d** and **17d** in 87% yield. Irradiation of **15a** and **15d** was best performed in methanol. In both transformations the esters **18a** and **18d**, respectively were not found.

All the cleavage reaction occured regioselectively to form the higher substituted radical, as expected. However, it was of interest to evaluate the stabilizing effect of the silicon atom. For this purpose the α,α′-disubstituted cyclohexanone **15c** was synthesized.

The alkylation of ketones with iodomethyltrimethylsilane is highly sensitive to steric hinderance, thus, we were unable to obtain **15c** from 2-methylcyclohexanone. However, **15c** could be synthesized by alkylation of **15b** with iodomethane at −78 °C with 86% yield using LDA as base. Compound **15c** is formed as a nearly 1:1 mixture of the *cis* and *trans* isomers which were easily separated by flash chromatography. Irradiation of the *cis* isomer of **15c** in methanol afforded regioselectively a 4.6:1 mixture of **16c** and **17c** in 77% yield. Irradiation of the trans isomer of **15c** gave also a 4.6:1 mixture of **16c** and **17c** in 63% yield. This clearly shows that the configuration of the starting material has no influence on the configuration of the formed double bond; this has been expected on grounds of the cleavage mechanism. In addition to the aldehydes **16c/17c** the saturated methyl ester **18c** was formed, but the amount was below 5% (Table).





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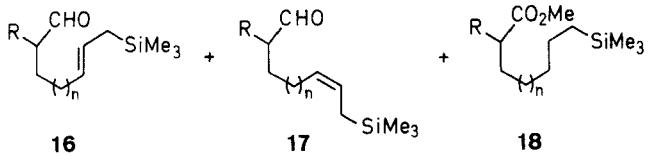


16 17 18

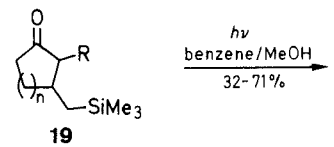
15–18	n	R	15–18	n	R
a	0	H	c	1	CH_3
b	1	H	d	2	H

Table. Photochemically Induced Cleavage of Ketones **15a–d**

Substrate	Product				
		E/*Z* Ratio	Yield[a] (%)		Yield[a] (%)
15a	**16a/17a**	3.2 : 1	98	**18a**	11
15b	**16b/17b**	> 99 : 1	70	**18b**	not found
15c	**16c/17c**	4.6 : 1	77[b], 63[c]	**18c**	< 5
15d	**16d/17d**	8.7 : 1	87	**18d**	not found

[a] Determined by cap-GC.
[b] From (*Z*)-**15c**.
[c] From (*E*)-**15c**.

Finally we investigated the possibility of synthesizing branched allylsilane aldehydes by irradiation of cyclic ketones bearing a trimethylsilylmethyl group in the γ-position to the carbonyl moiety. For this purpose we prepared the cyclopentanone and cyclohexanone derivatives **19a** and **19b** respectively. Compound **19a** was obtained by a copper(I) catalyzed 1,4-addition of the Grignard compound formed from magnesium and iodomethyltrimethylsilane to 2-methyl-2-cyclopentenone. The reaction gave **19a** in 87% yield as a 3.3 : 1 mixture of the two diastereoisomers. In a similar way, **19b** was synthesized from to 2-cyclohexenone in 74% yield.



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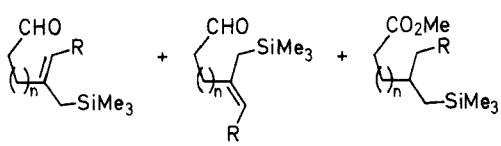

20 21 22

19	n	R
a	1	CH_3

Irradiation of **19a** in methanol for 48 h did not lead to the desired products; the starting material was recovered unchanged. However, the photolysis proceeded well in benzene containing 3.5% of methanol.[14] Under these conditions the aldehydes **20** and **21** were obtained in 71% yield as a 2.4 : 1 mixture. In addition the methyl ester **22a** was formed in 13% yield. In contrast, the photochemically induced α-cleavage of **19b** proceeded only sluggishly and the desired aldehydes were not formed at all. Thus, irradiation of **19b** for 2 days in benzene containing 3.5% of methanol led only to an about 1 : 1 mixture of the ester **22b** and the starting material **19b**. Isolation afforded 32% of **22b** and 50% of **19b**. Interestingly the cleavage of **19b** took place exclusively between C-1 and C-2. It may be concluded that the silicon can even have a stabilizing effect on radicals in the γ-position, however, branching in the position α to the formed radical can also be responsible for the observed regioselectivity.

The determination of the structure of the new compounds is mainly based on ^{1}H-NMR spectroscopy. In the spectra of **16a–d**, **17a**, **d**, **20a** and **21a** the signals for the aldehydic proton are found at $\delta = 9.62–9.78$. The *E* configuration of the double bond in **16a–b** was elucidated on grounds of the coupling constants of $J_{5,6}$ and $J_{6,7}$, respectively = 15 Hz. For (*Z*)-7-trimethylsilyl-5-heptenal, which has been synthesized by an independent route, $J_{5,6} = 11$ Hz is observed. The determination of the configuration of the double bond in **20a** and **21a** is based on the magnitude of the allylic couplings.[15] By homodecoupling irradiation experiments it has been shown that for the major isomer **20a** a coupling constant of $^4J = 1.2$ Hz is found for the coupling between the hydrogens of the CH_2SiMe_3 group ($\delta = 1.41$) and the hydrogen on the double bond (5-H: $\delta = 5.05$). In contrast the coupling constant between 3-H_2 and 5-H amounts to less than 0.5 Hz. This clearly shows that a *trans* orientation of the CH_2SiMe_3 group and 5-H exists in **20a**. Thus, this compound has a *Z* configuration of the double bond and **21a** must therefore have an *E* configuration. The ratio of the diastereoisomers was determined by gas chromatography.

The described procedures are versatile methods for the preparation of aldehydes containing an allylsilane moiety, which are difficult to obtain by other methods.

^{1}H- and ^{13}C-NMR: Varian VXR-500S, XL-200, VXR-200, and FT-80 A; multiplicities were determined with the APT pulse sequence. MS: Varian MAT 311A; GC-MS: Varian 3400, Finnigan MAT INCOS 50. IR: Bruker IFS 25. UV: Varian Cary 219. cap-GC: Varian 3700 with Merck-Hitachi D-2000; Machery-Nagel & Co, 0.25 μm, chemically bound SE 30, 0.32 mm × 50 m fused silica. Elemental analyses were carried out in the analytical laboratory of the university.

Photochemical transformations were done with a high pressure mercury lamp TQ 718 (500 watt) or TQ 150 (150 watt) from Fa. Heraeus using a pyrex filter. All solvents were distilled prior to use

and were used without further purification. All reactions were carried out under argon and monitored by TLC (Machery-Nagel Polygram SIL G/UV$_{254}$). Products were isolated by column or flash chromatography (CC or FC) on silica gel (CC: ICN Silica 63-200, 60 A, ICN Biochemicals, Eschwege, FC: Baker 30-60 active). Solvents used for TLC and column chromatography: A: petroleum ether (bp 40–60 °C)/Et_2O (2:1); B: petroleum ether (bp 40–60 °C)/Et_2O (10:1); C: petroleum ether (bp 40–60 °C)/Et_2O (20:1).

2-Trimethylsilylmethylcyclopentanones, -cyclohexanones and -cycloheptanones (15a, b, d):

Preparation of N-Cycloalkylidenecyclohexylamines; General Procedure:

Ketone (1.0 mol) and cyclohexylamine (108 g, 1.1 mol) are refluxed in dry toluene (200 mL) in an apparatus with a phase-separation head for about 18 h until water (18 mL, 1 mol) has separated. After cooling to r.t. all volatiles are removed *in vacuo* and the residual ketimine is purified by distillation.

N-Cyclopentylidenecyclohexylamine: yield: 73%; bp 108–111 °C/9 Torr (Lit.[16] bp 64–67 °C/0.05 Torr).

IR (film): ν = 2982, 2984 (CH), 1678 (C=N), 1422 cm^{-1} (CH_2).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.04–1.95 (m, 14 H, CH_2), 2.03–2.42 (m, 4 H, $(CH_2)_2C$=N), 3.04 (mc, 1 H, C=N–CH).

MS (70 eV): *m/z* (relative intensity) = 165 (M^+, 11), 84 (53), 83 (C_6H_{11}, 16), 56 (100).

N-Cyclohexylidenecyclohexylamine: yield: 83%; bp 98–100 °C/0.75 Torr. (Lit.[16] bp 121–123.4 °C/10 Torr).

IR (film): ν = 2926, 2984 (CH), 1660 (C=N), 1448 cm^{-1} (CH_2).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.05–1.95 (m, 16 H, CH_2), 2.13–2.45 (m, 4 H, $(CH_2)_2C$=N), 3.28 (mc, 1 H, C=N–CH).

MS (70 eV): *m/z* (relative intensity) = 179 (M^+, 16), 98 (50), 83 (C_6H_{11}, 12), 56 (100).

N-Cycloheptylidenecyclohexylamine: yield: 94%; bp 93–100 °C/0.11 Torr.

IR (film): ν = 2928, 2954 (CH), 1678 (C=N), 1450 cm^{-1} (CH_2).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.10–1.95 (m, 18 H, CH_2), 2.22–2.56 (m, 4 H, $(CH_2)_2C$=N), 3.29 (mc, 1 H, C=N–CH).

MS (70 eV): *m/z* (relative intensity) = 193 (M^+, 44), 112 (100), 83 (C_6H_{11}, 74), 55 (99).

2-Trimethylsilylmethylcycloalkanones **15a, b, d**; *General Procedure:*[16]

To a solution of LDA (1.3 mmol; generated in situ from freshly distilled *i*-Pr_2NH and BuLi in anhydrous THF (5 mL) at −78 °C is added the imine (1.0 mmol). The solution is allowed to warm to 0 °C and stirred at 0 °C for 0.5 h. Then iodomethyltrimethylsilane (1.1 mmol) is added at −78 °C. The reaction mixture is slowly warmed to r.t. and stirred for 4–6 h. The solvent is removed *in vacuo*, and the residue dissolved in THF (9 mL). To this solution is added 1 M aq oxalic acid (1.5 mL), and the solution is stirred at r.t. for 3–5 h. Et_2O/petroleum ether (1:1) (5 mL) is added to the mixture and the layers are separated. The aqueous layer is washed with Et_2O (3 × 3 mL), the combined organic layer is washed with water (3 mL), brine (3 mL), dried ($MgSO_4$), and filtered. The solvent is removed *in vacuo*, leaving the crude alkylated product which is purified by flash chromatography or distillation.

2-Trimethylsilylmethylcyclopentanone **(15a)**: yield: 79%.

UV (MeOH): λ_{max} (log ε) = 247 (2.233), 313 nm (1.634).

IR (film): ν = 2956, 2878 (CH), 1740 (C=O), 1452 (CH_2), 1248 (Si-Me_3), 860 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.01 (s, 9 H, $SiMe_3$), 0.32 (dd, 1 H, J = 14, 11 Hz, 1′-H), 1.06 (dd, 1 H, J = 14, 3.5 Hz, 1′-H), 1.40–2.29 (m, 7 H, CH, CH_2).

MS (70 eV): *m/z* (relative intensity) = 170 (M^+, 20), 155 ($M^+ - CH_3$, 45), 142 (M^+ − CO, 7), 75 (100), 73 ($SiMe_3$, 81), 45 (20).

2-Trimethylsilylmethylcyclohexanone **(15b)**: yield: 92%; bp 73 °C/2.45 Torr.

UV (MeOH): λ_{max} (log ε) = 263 (1.897), 313 nm (1.596).

IR (film): ν = 2934, 2860 (CH_2), 1710 (C=O), 1448 (CH_2), 1248 (Si-Me), 858 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.04 (s, 9 H, $SiMe_3$), 0.41 (dd, 1 H, J = 15, 7 Hz, 1′-H), 1.16 (dd, 1 H, J = 15, 7 Hz, 1′-H), 1.40–2.29 (m, 9 H, CH, CH_2).

MS (70 eV): *m/z* (relative intensity) = 184 (M^+, 10), 169 ($M^+ - CH_3$, 39), 156 (M^+ − CO, 7), 75 (100), 73 ($SiMe_3$, 75), 45 (21).

2-Trimethylsilylmethylcycloheptanone **(15d)**: yield: 76%; bp 74 °C/0.75 Torr.

$C_{11}H_{22}OSi$	calc.	C 66.60	H 11.18
(198.4)	found	66.65	11.26

UV (MeOH): λ_{max} (log ε) = 286 (2.042), 313 nm (1.751).

IR (film): ν = 2930, 2856 (CH_2), 1704 (C=O), 1454 (CH_2), 1248 (Si-Me_3), 858 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = −0.01 (s, 9 H, $SiMe_3$), 0.97 (dd, 1 H, J = 16, 8 Hz, 1′-H), 1.45 (dd, 1 H, J = 16, 8 Hz, 1′-H), 1.65–1.96 (m, 8 H, CH_2), 2.41 (mc, 3 H, 2-H, 7-H).

^{13}C-NMR ($CDCl_3$): δ = −1.41 ($SiMe_3$), 19.62 (C-1′), 24.15 (CH_2), 27.76 (CH_2), 29.01 (CH_2), 33.98 (CH_2), 41.07 (C-7), 47.76 (C-2), 214.8 (C-1).

MS (70 eV): *m/z* (relative intensity) = 198 (M^+, 8), 183 ($M^+ - CH_3$, 46), 170 (M^+ − CO, 7), 75 (80), 73 ($SiMe_3$, 100), 45 (19).

6-Methyl-2-Trimethylsilylmethylcyclohexanone (15c):

To a solution of LDA (1.82 mL, 13 mmol; generated in situ from freshly distilled *i*-Pr_2NH and BuLi) in anhydrous THF (50 mL) at −78 °C is added **15b** (1.84 g, 10.0 mmol). The solution is allowed to warm to 0 °C and is stirred at 0 °C for 0.5 h and then MeI (0.69 mL, 11 mmol) is added at −78 °C. The mixture is slowly warmed to r.t. and stirred for 18 h. The workup is equivalent to the workup described by the alkylation of imines. Further purification is done by flash chromatography using solvent C.

Fraction 1: *(2RS, 6RS)-6-Methyl-2-trimethylsilylmethylcyclohexanone* **(15c)**; R_f 0.58 (Solvent B), yield: 793 mg (40%).

$C_{11}H_{22}OSi$	calc.	C 66.60	H 11.18
(198.4)	found	66.75	11.20

UV (MeOH): λ_{max} (log ε) = 204 (2.629), 313 nm (1.684).

IR (film): ν = 2932, 2860 (CH), 1712 (C=O), 1450 (CH_2), 1248 (Si-Me), 860, 840 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = −0.07 (s, 9 H, $SiMe_3$), 0.29 (dd, 1 H, J = 15.1, 6.8 Hz, 1′-H), 0.97 (d, 3 H, J = 7 Hz, CH_3), 1.12 (dd, 1 H, J = 15.1, 6.8 Hz, 1′-H), 1.18–1.42 (m, 2 H, CH_2), 1.65–1.81 (m, 2 H, CH_2), 1.96–2.15 (m, 2 H, CH_2), 2.35 (ddt, 1 H, J = 7 Hz, 1-H), 2.38 (ddq, 1 H, J = 7 Hz, 6-H).

^{13}C-NMR ($CDCl_3$): δ = −1.03 ($SiMe_3$), 14.53 (CH_3), 15.97 (C-1′), 25.59 (C-4), 37.26 (C-3), 38.54 (C-5), 45.13 (C-6), 47.21 (C-2), 213.6 (C-1).

MS (70 eV): *m/z* (relative intensity) = 198 (M^+, 12), 183 ($M^+ - CH_3$, 58), 170 (M^+ − CO, 4), 75 (100), 73 ($SiMe_3$, 99), 45 (14).

Fraction 2: *(2RS, 6SR)-6-Methyl-2-(trimethylsilylmethylcyclohexanone* **(15c)**: R_f = 0.45 (Solvent B), yield: 910 mg (46%).

$C_{11}H_{22}OSi$	calc.	C 66.60	H 11.18
(198.4)	found	66.35	11.19

UV (MeOH): λ_{max} (log ε) = 204 (2.629), 313 nm (1.684).

IR (film): ν = 2932, 2870 (CH), 1708 (C=O), 1450 (CH_2), 1248 (Si-Me), 856, 844 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = −0.03 (s, 9 H, $SiMe_3$), 0.62 (dd, 1 H, J = 15.1, 7.5 Hz, 1′-H), 0.95 (dd, 1 H, J = 15.1, 7.5 Hz, 1′-H), 1.02 (d, 3 H, J = 6.5 Hz, CH_3), 1.31–2.04 (m, 6 H, CH_2), 2.46–2.71 (m, 2 H, 2-H, 6-H).

^{13}C-NMR ($CDCl_3$): δ = −1.36 ($SiMe_3$), 15.13 (CH_3), 18.25 (C-1′), 19.99 (C-4), 35.29 (CH_2), 35.40 (CH_2), 41.46 (C-2), 45.01 (C-6), 216.4 (C-1).

MS (70 eV): *m/z* (relative intensity) = 198 (M^+, 20), 183 ($M^+ - CH_3$, 88), 170 (M^+ − CO, 5), 75 (73), 73 ($SiMe_3$, 100), 45 (14).

General Procedure for the Photolysis of the Ketones 15a–d:

The ketone **15** (1.0 mmol) is dissolved in MeOH (10 mL) or cyclo-

hexane (10 mL). If MeOH is used $NaHSO_4$ (1.1 mmol) is added. The reaction mixture is cooled to 0 °C (10 °C in the case of cyclohexane), immersed in a constant temperature bath and purged 15 min with argon. During irradiation with a 500 watt Heraeus high pressure mercury lamp using a pyrex filter, the mixture is maintained under argon and the reaction is monitored by TLC. For workup, water (10 mL) and Et_2O (10 mL) are added and the layers are separated. The aqueous layer is extracted with Et_2O (3 × 10 mL), the combined organic layers are washed with brine (10 mL), dried ($MgSO_4$), filtered and all volatiles are removed *in vacuo*. Further purification is done by chromatography.

(E,Z)-6-Trimethylsilyl-4-hexenal **(16a, 17a)**: yield: 98%; GC (80 °C isotherm): t_R = 18.1 min (*E*), t_R = 19.4 min (*Z*).

$C_9H_{18}OSi$ (170.3) calc. C 63.46 H 10.65 found 63.45 10.77

IR (film): ν = 2954, 2930, 2804 (CH), 2706 (CH, CHO), 1728 (C=O), 1658 (C=C), 1438 (CH_2), 1250 ($SiMe_3$), 844 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS), (*E*-isomer **16a**): δ = −0.16 (s, 9H, $SiMe_3$), 1.26 (dd, 2H, J = 7.5, 0.9 Hz, 6-H), 2.21 (dt, 2H, J = 6.5 Hz, 3-H), 2.33 (dt, 2H, J = 6.8, 1.9 Hz, 2-H), 5.09 (ttd, 1H, J = 15, 7, 0.9 Hz, 4-H), 5.32 (ttd, 1H, J = 15, 7, 0.9 Hz, 5-H), 9.62 (t, 1H, J = 2 Hz, 1-H); (*Z*-isomer **17a**): δ = −0.13 (s, 9H, $SiMe_3$), 1.35 (dd, 2H, J = 7.5, 0.9 Hz, 6-H), 2.20 (dt, 2H, J = 6.5 Hz, 3-H), 2.36 (dt, 2H, J = 6.8, 1.9 Hz, 2-H), 5.10 (m, 1H, 4-H), 5.29 (m, 1H, 5-H), 9.64 (t, 1H, J = 2 Hz, 1-H).

^{13}C-NMR ($CDCl_3$), (*E*-isomer **16a**): δ = −2.46 ($SiMe_3$), 22.21 (C-6), 25.05 (C-3), 43.43 (C-2), 125.9 (C-4), 127.3 (C-5), 201.3 (C-1); (*Z*-isomer **17a**): δ = −2.25 ($SiMe_3$), 18.07 (C-6), 19.43 (C-3), 51.97 (C-2), 124.5 (C-4), 126.6 (C-5), 201.1 (C-1).

MS (70 eV): *m/z* (relative intensity) = 170 (M^+, 2), 155 (M^+, 5), 116 (45), 101 (94), 73 ($SiMe_3$, 100), 45 (22).

Methyl 7-Trimethylsilylheptanoate **(18b)**: yield: 11%.

$C_{11}H_{24}O_2Si$ (216.4) calc. C 61.06 H 11.18 found 61.22 11.21

IR (film): ν = 2952, 2926, 2856 (CH), 1742 (C=O), 1438 (CH_2), 1248 ($SiMe_3$), 858, 840 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = −0.05 (s, 9H, $SiMe_3$), 0.38–0.50 (m, 2H, 7-H), 1.27 (mc, 6H, 4-H, 5-H, 6-H), 1.58 (mc, 2H, 3-H), 2.26 (t, 2H, J = 7.8 Hz, 2-H), 3.64 (s, 3H, OCH_3).

^{13}C-NMR ($CDCl_3$): δ = −1.98 ($SiMe_3$), 16.36 (C-7), 23.50, 24.63, 28.62, 32.94 (CH_2), 33.75 (C-2), 50.87 (OCH_3), 173.6 (C-1).

MS (70 eV): *m/z* (relative intensity) = 201 ($M^+ - CH_3$, 0.2), 185 ($M^+ - OCH_3$, 1), 157 ($M^+ - CO_2CH_3$, 0.4), 75 (35), 73 ($SiMe_3$, 100).

(E)-7-Trimethylsilyl-5-heptenal **(16b)**: yield: 70% (MeOH), 73% (cyclohexane); GC (100° isotherm): t_R = 16.6 min.

$C_{10}H_{20}OSi$ (184.4) calc. C 65.15 H 10.93 found 65.10 10.68

IR (film): ν = 2954, 2900 (CH), 2818, 2716 (CH, CHO), 1728 (C=O), 1658 (C=C), 1450 (CH_2), 1248 ($SiMe_3$), 854 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.03 (s, 9H, $SiMe_3$), 1.36 (dd, 2H, J = 7.5, 1 Hz, 7-H), 1.63 (quint, 2H, J = 7 Hz, 3-H), 1.99 (dt, 2H, J = 7.5, 7 Hz, 4-H), 2.39 (dt, 2H, J = 7.2, 1.9 Hz, 2-H), 5.15 (ttd, 1H, J = 15, 7.5 Hz, J = 1.2 Hz, 5-H), 5.37 (ttd, 1H, J = 15, 7.5, 1.2 Hz, 6-H), 9.72 (t, 1H, J = 1.5 Hz, 1-H).

^{13}C-NMR ($CDCl_3$): δ = −2.15 ($SiMe_3$), 22.14 (C-7), 22.49 (C-3), 31.91 (C-4), 43.00 (C-2), 127.2, 127.4 (C-5, C-6), 202.3 (C-1).

MS (70 eV): *m/z* (relative intensity) = 184 (M^+, 2), 169 ($M^+ - CH_3$, 5), 129 ($C_7H_{17}Si$, 20), 75 (35), 73 ($SiMe_3$, 100).

(E, Z)-8-Trimethylsilyl-8-octenal **(16d, 17d)**: yield: 87%; GC (100 °C isotherm): t_R = 25.2 min (*Z*), t_R = 26.0 min (*E*).

$C_{11}H_{22}OSi$ (198.4) calc. C 66.60 H 11.18 found 66.64 11.34

IR (film): ν = 2952, 2934, 2858 (CH), 2716 (CH, CHO), 1728 (C=O), 1440 (CH_2), 1248 ($SiMe_3$), 854 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS), (*E*-isomer **16d**): δ = −0.02 (s, 9H, $SiMe_3$), 1.36 (dd, 2H, J = 7, 1.1 Hz, 8-H), 1.31–1.45 (m, 2H, 4-H), 1.60 (tt, 2H, J = 7.4 Hz, 3-H), 1.97 (ddt, 2H, J = 7, 1 Hz, 5-H), 2.39 (dt, 2H, J = 7.4, 1.9 Hz, 2-H), 5.17 (ttd, 1H, J = 15, 7, 1 Hz, 6-H), 5.38 (ttd, 1H, J = 15, 7, 1 Hz, 7-H), 9.72 (t, 1H, J = 1.9 Hz, 1-H).

^{13}C-NMR ($CDCl_3$), (*E*-isomer **16d**): δ = −2.23 ($SiMe_3$), 21.26 (C-8), 22.37 (C-3), 29.20 (C-4), 32.21 (C-5), 43.45 (C-2), 126.4 (C-6), 127.9 (C-7), 201.8 (C-1); (*Z*-isomer **17d**): δ = −2.02 ($SiMe_3$), 18.21 (C-8), 21.57 (C-3), 26.50 (C-4), 29.04 (C-5), 43.57 (C-2), 125.6 (C-6), 126.5 (C-7), 201.8 (C-1).

MS (70 eV): *m/z* (relative intensity) = 198 (M^+, 1), 183 ($M^+ - CH_3$, 2), 155 (5), 129 (7), 75 (21), 73 ($SiMe_3$, 100).

(E, Z)-2-Methyl-7-trimethylsilyl-5-heptenal **(16c, 17c)**: yield: 77%; GC (100 °C isotherm): t_R = 20.3 min (E), t_R = 20.7 min (Z).

$C_{11}H_{22}OSi$ (198.4) calc. C 66.60 H 11.18 found 66.76 11.15

IR (film): ν = 2956, 2932, 2856 (CH), 2704 (CH, CHO), 1730 (C=O), 1658 (C=C), 1458 (CH_2), 1248 ($SiMe_3$), 854 ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS), (*E*-isomer **16c**): δ = 0.01 (s, 9H, $SiMe_3$), 1.11 (d, 3H, J = 7 Hz, CH_3), 1.43 (dd, 2H, J = 7.5, 1.2 Hz, 7-H), 1.80 (td, 2H, J = 13.5, 6 Hz, 3-H), 2.06 (mc, 2H, 4-H), 2.39 (mc, 1H, 2-H), 5.22 (ttd, 1H, J = 15.7, 1 Hz, 5-H), 5.42 (ttd, 1H, J = 15.7, 1 Hz, 6-H), 9.65 (d, 1H, J = 1.6 Hz, 1-H); (*Z*-isomer **17c**): δ = 0.02 (s, 9H, $SiMe_3$), 1.13 (d, 3H, J = 7 Hz, CH_3), 1.47 (dd, 2H, J = 7.5, 1.2 Hz, 7-H), 1.79 (td, 2H, J = 13.5, 6 Hz, 3-H), 2.06 (mc, 2H, 4-H), 2.39 (mc, 1H, 2-H), 5.20 (m, 1H, 5-H), 5.40 (m, 1H, 6-H), 9.66 (d, 1H, J = 1.6 Hz, 1-H).

^{13}C-NMR ($CDCl_3$), (*E*-isomer **16c**): δ = −2.18 ($SiMe_3$), 12.94 (CH_3), 22.47 (C-7), 29.85 (C-4), 30.58 (C-3), 45.36 (C-2), 127.3 (C-5, C-6), 204.5 (C-1); (*Z*-isomer **17c**): δ = −1.99 ($SiMe_3$), 13.12 (CH_3), 18.32 (C-7), 24.14 (C-4), 30.37 (C-3), 45.68 (C-2), 126.0 (C-5), 126.4 (C-6), 204.4 (C-1).

MS (70 eV): *m/z* (relative intensity) = 198 (M^+, 3), 183 ($M^+ - CH_3$, 9), 143 (18), 129 (6), 75 (29), 73 ($SiMe_3$, 100).

3-Trimethylsilylmethylcycloalkanones 19a, b; General Procedure with Trimethylsilylmethylmagnesium Iodide:[17]

In an argon flushed 50 mL, two-neck round bottomed reaction flask, fitted with reflux condenser, 10 mL pressure-equalizing dropping funnel and Teflon coated magnetic stirring bar are placed Mg turnings (0.64 g, 26 mmol) and Et_2O (5 mL) freshly distilled from sodium wire. To that one tenth of the iodomethyltrimethylsilane (6.20 g, 28.9 mmol) is added in one portion and smoothly warmed up until Grignard reagent formation begins. When the reaction has started, the remaining amount of iodomethyltrimethylsilane in Et_2O (6 mL) is added at such rate, that gentle reflux is maintained. After the addition is complete, the mixture is heated to reflux for an additional hour. The solution is cooled to r.t. and Et_2O (17.3 mL) is added to give a 1.4 N etheral Grignard solution. The Grignard reagent is transferred via cannula (50 mL) and added to a vigorously stirred argon flashed suspension of copper(I) bromide (0.25 g, 1.12 mmol) in Et_2O (5 mL) at −20 °C. After the addition is complete, the mixture is stirred at −20 °C for 0.5 hour. The enone (15 mmol) solved in Et_2O (5 mL) is added very slowly at this temperature. After the mixture is kept at −20 °C overnight, it is added to vigorously stirred ice-cold 2 N hydrochlorid acid (30 mL). The organic layer is separated, filtered with suction and the residue is washed with Et_2O (2 × 5 mL). The aqueous layer is saturated with ammonium chloride and extracted with Et_2O (3 × 20 mL). The combined organic phases are washed with sat. $NaHCO_3$ solution (2 mL), water (20 mL) and brine (20 mL), dried ($MgSO_4$) and filtered. All volatiles are removed *in vacuo* and the residue is purified by column chromatography using solvent C.

2-Methyl-3-(trimethylsilylmethyl)cyclopentanone **(19a)**: yield: 87%.

$C_{20}H_{20}OSi$ (184.4) calc. C 65.15 H 10.93 found 65.20 10.98

IR (film): ν = 2956, 2932, 2892, 2874 (CH), 1742 (C=O), 1456 (CH_2), 1248 ($SiMe_3$), 858 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.01 (s, 9H, $SiMe_3$), 0.43 (dd, 1H, J = 14.5, 10.5 Hz, 1''-H), 0.81 (dd, 1H, J = 14.5, 4.5 Hz, 1''-H), 1.01

(d, 3H, J = 7 Hz, CH_3), 1.20–1.73 (m, 3H, 3-H, 4-H), 1.87–2.44 (m, 3H, 2-H, 5-H).

In the ^{13}C-NMR spectra two sets of signals are found with a ratio of 3.3:1.

^{13}C-NMR ($CDCl_3$) (*main isomer*): δ = −1.03 ($SiMe_3$), 11.57 (C-1'), 21.80 (C-1''), 29.53 (C-4), 37.27 (C-5), 41.18 (C-3), 48.11 (C-2), 219.8 (C-1); (*minor isomer*): δ = −1.16 ($SiMe_3$), 9.46 (C-1'), 15.94 (C-1''), 28.11 (C-4), 35.71 (C-5), 36.07 (C-3), 53.11 (C-2), 220.9 (C-1).

MS (70 eV): m/z (relative intensity) = 184 (M^+, 18), 169 ($M^+ - CH_3$, 39), 156 ($M^+ - CO$, 5), 127 (7), 75 (65), 73 ($SiMe_3$, 100).

3-(Trimethylsilylmethyl)cyclohexanone **(19b):** yield: 74%.

$C_{20}H_{20}OSi$	calc.	C 65.15	H 10.93
(184.4)	found	65.14	10.87

IR (film): ν = 2952, 2896, 2868 (CH), 1714 (C=O), 1448 (CH_2), 1250 ($SiMe_3$), 860, 838 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.04 (s, 9H, $SiMe_3$), 0.58 (dd, 1H, J = 7, 3.6 Hz, 1'-H), 0.70 (dd, 1H, J = 7, 3.6 Hz, 1'-H), 1.25–1.50 (m, 1H, 3-H), 1.53–2.49 (m, 8H, 2-H, 4-H, 5-H, 6-H).

^{13}C-NMR ($CDCl_3$): δ = −0.96 ($SiMe_3$), 24.82 (CH_2), 24.96 (CH_2), 34.37 (CH_2), 35.64 (C-3), 40.82 (C-2), 51.10 (C-6), 211.2 (C-1).

MS (70 eV): m/z (relative intensity) = 184 (M^+, 17), 169 ($M^+ - CH_3$, 39), 156 ($M^+ - CO$, 21), 127 (12), 75 (100), 73 ($SiMe_3$, 96).

Photolysis of the Ketones 19a and 19b:

According to the general procedure a solution of the ketone (3.0 mmol) in benzene (96.5 g) and MeOH (3.5 g) is irradiated with monitoring by TLC. For workup, all volatiles are removed *in vacuo* and the residue is purified by column chromatography using solvent B or C.

Irradiation of **19a**:

Fraction 1: *Methyl (4 RS)-4-(Trimethylsilylmethyl)hexanoate* **(22a):** yield: 13%; GC (100°C isotherm): t_R = 22.1 min.

$C_{11}H_{24}O_2Si$	calc.	C 61.06	H 11.18
(216.4)	found	61.06	11.15

IR (film): ν = 2956, 2898, 2878 (CH), 1742 (C=O), 1436 (CH_2), 1250 ($SiMe_3$), 1194, 1170 (C–O), 860, 838 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.00 (s, 9H, $SiMe_3$), 0.51 (dd, 2H, J = 6, 2.9 Hz, 1'-H), 0.75 (t, 3H, J = 7 Hz, 6-H), 1.21–1.69 (m, 5H, 3-H, 4-H, 5-H), 2.29 (t, 2H, J = 8 Hz, 2-H), 3.67 (s, 3H, OCH_3).

MS (70 eV): m/z (relative intensity) = 201 ($M^+ - CH_3$, 29), 185 ($M^+ - OCH_3$, 7), 159 (38), 75 (15), 73 ($SiMe_3$, 100), 59 (CO_2CH_3, 16).

Fraction 2: *(E,Z)-4-(Trimethylsilylmethyl)-4-hexenal* **(20a, 21a)**: yield: 71%; GC (100°C isotherm): t_R = 13.2 min (Z), t_R = 14.5 min (E).

$C_{20}H_{20}OSi$	calc.	C 65.15	H 10.93
(184.4)	found	65.08	10.89

IR (film): ν = 2954, 2922, 2900 (CH), 2716 (CH, CHO), 1728 (C=O), 1658 (C=C), 1448 (CH_2), 1248 ($SiMe_3$), 850 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS), (Z-isomer **20a**): δ = 0.00 (s, 9H, $SiMe_3$), 1.43 (dd, 2H, J = 1.2 Hz, 1'-H), 1.57 (d, 3H, J = 6.8 Hz, 6-H), 2.28 (t, 2H, J = 8 Hz, 3-H), 2.48 (dt, 2H, J = 8, 1.8 Hz, 2-H), 5.05 (q, 1H, J = 7 Hz, 5-H), 9.77 (t, 1H, J = 1.8 Hz, 1-H); (E-isomer **21a**): δ = 0.03 (s, 9H, $SiMe_3$), 1.50 (s, 2H, 1'-H), 1.51 (d, 3H, J = 6.5 Hz, 6-H), 2.26 (t, 2H, J = 7 Hz, 3-H), 2.51 (dt, 2H, J = 7.5, 1.8 Hz, 2-H), 5.09 (q, 1H, J = 7 Hz, 5-H), 9.74 (t, 1H, J = 1.8 Hz, 1-H).

^{13}C-NMR ($CDCl_3$) (Z-isomer **20a**): δ = −1.48 ($SiMe_3$), 13.09 (C-6), 24.23 (C-1'), 26.25 (C-3), 42.15 (C-2), 117.7 (C-5), 135.2 (C-4), 201.8 (C-1); (E-isomer **21a**): δ = −0.89 ($SiMe_3$), 13.75 (C-6), 21.00 (C-1'), 31.13 (C-3), 42.10 (C-2), 115.9 (C-5), 135.8 (C-4), 202.1 (C-1).

MS (70 eV): m/z (relative intensity) = 184 (M^+, 2), 169 ($M^+ - CH_3$, 7), 155 (3), 75 (64), 73 ($SiMe_3$, 100), 45 (13).

Irradiation of **19b**:

Methyl (5 RS)-5-Methyl-6-(trimethylsilyl)hexanoate **(22b)**: yield: 32%.

$C_{11}H_{24}O_2Si$	calc.	C 61.06	H 11.18
(216.4)	found	61.11	11.23

IR (film): ν = 2954, 2900, 2874 (CH), 1744 (C=O), 1438 (CH_2), 1250 ($SiMe_3$), 858, 840 cm^{-1} ($SiMe_3$).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.00 (s, 9H, $SiMe_3$), 0.39 (dd, 1H, J = 15.5, 8.9 Hz, 6-H), 0.58 (dd, 1H, J = 15.5, 5 Hz, 6-H), 0.91 (d, 3H, J = 7 Hz, CH_3), 1.11–1.38 (m, 2H, CH_2), 1.50–1.72 (m, 3H, CH_2, CH), 2.29 (t, 2H, J = 7 Hz, 2-H), 3.67 (s, 3H, OCH_3).

^{13}C-NMR ($CDCl_3$): δ = −0.78 ($SiMe_3$), 22.44 (C-6), 22.60 (CH_3), 24.88 (C-3), 29.22 (C-5), 34.06 (C-4), 39.88 (C-2), 51.08 (OCH_3), 173.8 (C-1).

MS (70 eV): m/z (relative intensity) = 216 (M^+, 0.1), 201 ($M^+ - CH_3$, 77), 185 ($M^+ - OCH_3$, 4), 157 ($M^+ - CO_2CH_3$, 2), 75 (34), 73 ($SiMe_3$, 100), 59 (CO_2CH_3, 38).

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– Freeman, F.; Keindl, M.C.; Po, H.N.; Brinkman, E.; Masse, J.A. *Synthesis* **1989**, 714. On page 714 the data for compounds **2d** and **2e** in the Table should be corrected as follows:
2d:
^{1}H-NMR (500 MHz, DMSO-d_6): δ = 7.213 (H-5), 7.225 (H-6), 7.547 (H-4), 7.558 (H-7); $J_{4,7}$ = 5.94 Hz, $J_{5,6}$ = 6.03 Hz, $J_{4,7}$ = 166.61 Hz, $J_{4,5}$ = 166.70 Hz.
^{13}C-NMR (500 MHz, DMSO-d_6): δ = 119.0 (br, C-7), 119.1 (br, C-4), 126.60 (C-5, C-6), 143.27 (C-3a, C-7a), 151.21 (C-2).
2e: mp 190–191 °C.

$C_{16}H_{14}N_4S_2.1.5H_2O$ (353.5)	calc.	C54.37	H4.85	N15.85	S18.14
	found	54.71	4.63	15.66	17.94

^{1}H-NMR (500 MHz, DMSO-d_6): δ = 2.39 (s, 3H, CH_3), 7.04 (d, 1H, J = 8.11 Hz, H-5), 7.34 (s, 1H, H-7), 7.43 (d, 1H, J = 8.11 Hz, H-4).
^{13}C-NMR (500 MHz, DMSO-d_6): δ = 25.24 (CH_3), 118.05 (v. br, C-4, C-7), 128.13 (C-5), 136.14 (C-6), 142.42 (v. br, C-3a, C-7a), 150.37 (br, C-2).
EIMS (70 eV): m/z = 326 (m^+, 9.8%), 164 (100%).
CIMS: m/z = 327 (MH^+, 7.9%), 165 (100%).

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– Lin, Z.-Y.; Shi, W.; Zhang, L. *Synthesis* **1990**, 235. On page 236 compound **4b** should be named 7-acetoxy-4,8-dioxo-5-oxatetracyclo[8.2.1.$0^{2,9}$.$0^{3,7}$]tridec-11-ene; and compound **5** should be named 4,8-dioxo-5-oxatetracyclo-[8.2.1.$0^{2,9}$.$0^{3,7}$]tridec-11-ene.

– Lee, C.; Field, L. *Synthesis* **1990**, 391. On page 392 column 2, line 19, the statement in parenthesis should read: (cf. **7**; see Scheme **B** for general equation). While Scheme **C** should be: R^1SO_2X + 4-MeC_6H_4SH (2 equiv) (conditions: 1. Et_3N (2 equiv)/CH_2CH_2, −76 °C; 2. conc HCl → R^1SO_2H
On page 393 in Scheme **D** the temperature of the reaction of **16** with **17** should be −76 °C.
On page 394–395 in Table 1, the yield of sulfinic acid **15g** should read: 80 $(-)^{21}$; the reference in footnote e should be Ref. 2 and not Ref. 22.
On page 396 in Table 2 for compound **10p** the molecular formula should be referenced to Ref. 10; the 1130 cm^{-1} absorption in its IR spectral data should be designated (s).
On page 397 the sentence should read: The structure of **21** (C, H anal ± 0.3%) is confirmed by heating ...

– Lajoie, G.; Crivici, A.; Adamson, J.G. *Synthesis* **1990**, 571. On page 572 in the Table, compounds **1** and **2** should be **3** and **4**, respectively.

– Legraverend, M.; Boumchita, H.; Bisagni, E. *Synthesis* **1990** 587.
On page 588, 2,5-diamino-4,6-dichloropyridine (**5**) should be replaced by 2,5-diamino-4,6-dichloropyrimidine (**5**).

– Tietze, L.F.; Wünsch, J.R. *Synthesis* **1990**, 985.
On page 989, in the general procedure of the photoklysis sodium hydrogen carbonate (1.1 mmol) should be used instead of sodium hydrogen sulfate.