Tin for Organic Synthesis, 14[◇]

Synthesis of Aromatic and α,β-Unsaturated Aldehydes by a Friedel-Crafts-like Electrophilic Destannylation Using 1,1-Dichloromethyl Methyl Ether

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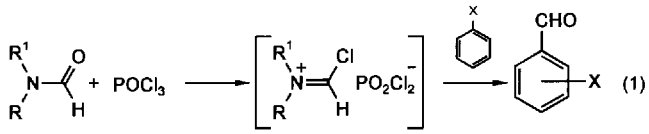
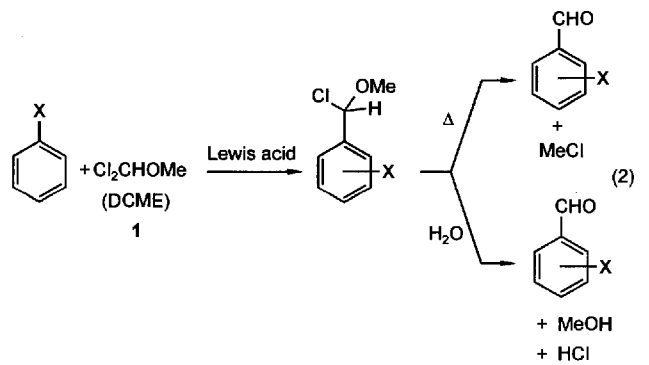
A mild and effective method for the preparation of a variety of aromatic (**7a–m**), heteroaromatic (**7n–r**), and α,β-unsaturated aldehydes (**8a–f**) is described. The reaction of trialkylaryl- (**2a–o**), heteroaryl- (**2p–t**), and 1-alkenylstannanes (**4a–f** and **5a–f**) with dichloromethyl methyl ether (**1**, DCME) in the presence of aluminium trichloride followed by hydrolysis provides the corresponding aldehydes. In the case of arylstannanes the *ipso*-isomers are generally formed; the *p*-aldehydes occur as side products. The electrophilic substitution of 1-alkenylstannanes with **1** leads to α,β-unsaturated aldehydes in an *ipso*- and stereospecific manner. A comparison of the leaving abilities of the stannyl and silyl groups shows a lower or even zero reactivity of the silyl-substituted compounds **6a–c** towards the electrophile **1**. In the silylstannylalkene **6c** only the stannyl group reacts whereas the stannyl function remains unaffected in the product, aldehyde **11**.

Aromatic and α,β-unsaturated aldehydes are of common interest in organic synthesis[2,3]. The method most widely used for the generation of aromatic aldehydes is the Vilsmeier formylation using formamides in the presence of acid chlorides[4] (Eq. 1).



(1)

This derivative of reaction is restricted to activated arenes as the chloroalkyliminium cation acts as a weak electrophile. The synthesis of α,β-unsaturated aldehydes via Vilsmeier formylation is possible only in a few cases[5]. An alternative formylation reagent is 1,1-dichloromethyl methyl ether (**1**, DCME), which reacts with an arene in the presence of a Lewis acid to afford a 1-methoxy-1-arylethyl chloride which can be hydrolysed to yield the corresponding aldehyde[6] (Eq. 2).



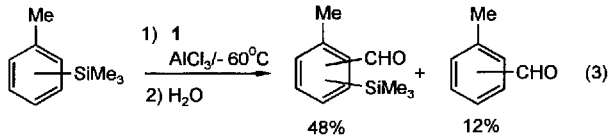
(2)

Although this reaction has been used widely for the synthesis of various aldehydes[7], it is limited by the fact that regioisomers are often formed[6,8,9] and that deactivated arenes show no reactivity towards the electrophile **1**.

Whereas aromatic and alicyclic α,β-unsaturated aldehydes[10,11] are easily accessible, cyclic olefinic aldehydes are available only via multistep preparation methods[12–15].

Trialkylstannanes provide an especially elegant and simple way to introduce electrophiles into an aromatic ring in an *ipso*-specific manner[16–21]. This type of reaction may also be extended to vinylic stannanes, where electrophilic destannylation allows the introduction of keto[22] or amide[23] functionalities next to the double bond.

The syntheses of aromatic and olefinic aldehydes are subjected to the same restrictions as the formation of regioisomers or insufficient reactivity of the starting material. Trialkylsilanes and -stannanes should therefore be useful synthetic tools for the preparation of aldehydes. The Vilsmeier formylation with $POCl_3$/DMF was carried out with trialkylarylstannanes[24]; however, the reaction is not always *ipso*-specific and the isolated yields are low in some cases. The formylation of trimethylarylsilanes with **1** was examined[25], but two silyl groups are necessary to activate the aromatic system sufficiently. Furthermore, the arenes are often formylated without desilylation, as observed for trimethylsilylated toluenes[25] (Eq. 3).



(3)

[◇] Part 13: Ref.[1].

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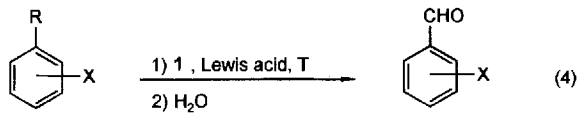
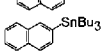
The greater leaving ability of the trialkylstannyl group should therefore exert a significant effect on the reactivity of the arene and the regioselectivity of the reaction. In this paper we discuss the reactions of aryl- (**2** and **3**) and alkenylstannanes (**4** and **5**) with **1**, which lead to the corresponding aldehydes.

Results and Discussion

The reaction of **2a** with **1** in the presence of aluminium trichloride yielded after hydrolysis nearly quantitatively the aldehyde **7a** at −78 °C (Eq. 4). The use of other or no Lewis acid led to considerably poorer results than aluminium trichloride. An increasing of the reaction temperature to room temperature led to the formation of only traces of the aldehyde.



	R	X	Lewis acid	T/°C	ipso-/%		p-product/%		yield/%
2a	Me_3Sn	H	–	-78	100	7a	--		5[a]
2a	Me_3Sn	H	$TiCl_4$	-78	100	7a	--		41[a]
2a	Me_3Sn	H	$SnCl_4$	-78	100	7a	--		0[a]
2a	Me_3Sn	H	$AlCl_3$	-78	100	7a	--		90[a]
2b	Bu_3Sn	H	$AlCl_3$	-78	100	7a	--		76
2a	Me_3Sn	H	$AlCl_3$	-53	100	7a	--		1[a]
2a	Me_3Sn	H	$AlCl_3$	-27	100	7a	--		1[a]
2a	Me_3Sn	H	$AlCl_3$	0	100	7a	--		1[a]
2a	Me_3Sn	H	$AlCl_3$	25	100	7a	--		1[a]
	H	H	$AlCl_3$	-78		7a	--		30[a]
6a	$SiMe_3$	H	$AlCl_3$	-78	100	7a	--		35[a]
2e	Me_3Sn	4-Me	$AlCl_3$	-78	100	7d	--		85
2f	Bu_3Sn	4-Me	$AlCl_3$	-78	100	7d	--		80
2i	Bu_3Sn	4-OMe	$AlCl_3$	-78	100	7g	--		94
2c	Bu_3Sn	2-Me	$AlCl_3$	-78	75	7b	25	7d	84
2d	Bu_3Sn	3-Me	$AlCl_3$	-78	75	7c	25	7d	87
2g	Bu_3Sn	2-OMe	$AlCl_3$	-78	55	7e	45	7g	88
2h	Bu_3Sn	3-OMe	$AlCl_3$	-78	70	7f	30	7g	83
2j	Bu_3Sn	2-Cl	$AlCl_3$	-78	100	7h	--		88
2k	Bu_3Sn	3-Cl	$AlCl_3$	-78	100	7i	--		80
2l	Bu_3Sn	4-Cl	$AlCl_3$	-78	100	7j	--		82
2m	Bu_3Sn	2-CF_3	$AlCl_3$	-78	100	7k	--		55
2n			$AlCl_3$	-78	100	7l	--		80
2o			$AlCl_3$	-78	100	7m	--		63
2p			$AlCl_3$	-78	100	7n	--		76
2q			$AlCl_3$	-78	0	7n	--		70
2r			$AlCl_3$	-78	100	7o	--		76
2s			$AlCl_3$	-78	100	7p	--		61
2t			$AlCl_3$	-78	100	7q	--		53

[a] GC yield

Benzene itself yielded only 30% of benzaldehyde. Thus, the trialkylsilyl group does not increase the reactivity of the aromatic system substantially, so that the yield was in the same range as that obtained from benzene. This demonstrates the better leaving ability of the trialkylstannyl group. The lower strength of the tin−carbon bond and the greater coordination ability of the tin atom are responsible for this effect.

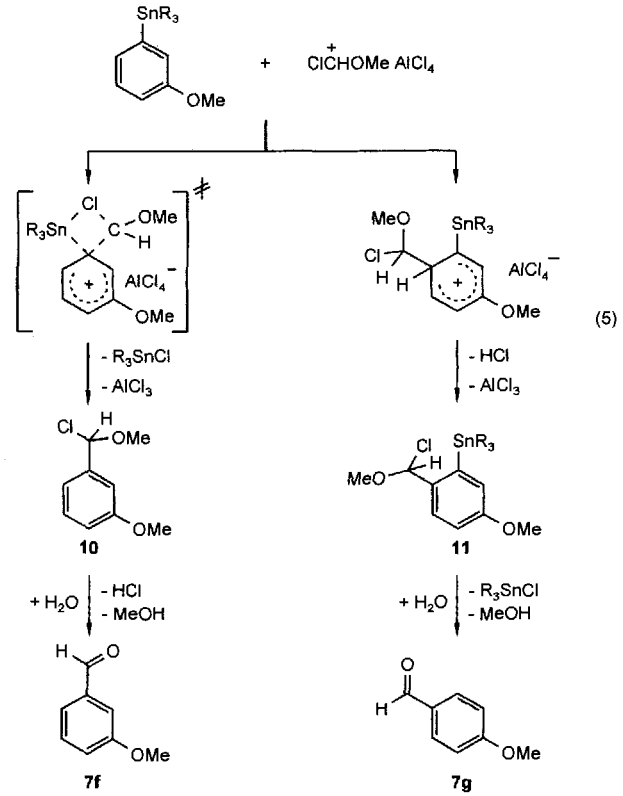
In the case of 4-trialkylstannylated arenes such as **2e**, **2f**, and **2i** only the products derived from *ipso*-substitution were formed. A comparison of the yields of the aldehydes obtained from **2e** and **2f** shows that the toxicologically less problematic tributylstannyl group is just as effective a leaving group as is the trimethylstannyl group.

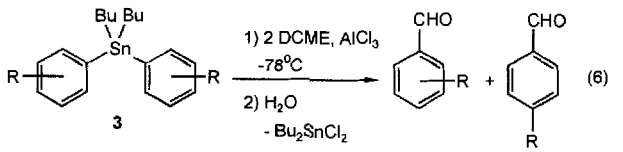
2- And 3-tributylstannyl-substituted toluenes (**2c** and **2d**) and anisoles (**2g** and **2h**) predominantly yield the *ipso*-aldehydes while the *p*-compounds furnish **7d** and **7g** in variable amounts (Eq. 4). Deactivated arenes such as the stannylated chlorobenzenes (**2j**−**l**) react in an *ipso*-specific manner to afford the corresponding aldehydes. The excellent leaving ability of the trialkylstannyl group is demonstrated by the fact that even the strongly deactivated 2-CF_3 derivative **2m** is formylated, whereas the non-stannylated compound shows no reaction with **1**.

Further evidence for the weakness of the tin−carbon bond is provided by the fact that non-stannylated compounds display a lower reactivity than the stannanes. Thus, the reaction of toluene and **2j** or **2i** respectively with **1** mainly provides the destannylation product, whereas electrophilic substitution at toluene takes place only with 15 or 2%.

The results of the electrophilic substitution of activated and deactivated stannylated arenes can be explained by the mechanism of the reaction (Eq. 5). Mechanism (I) corresponds to classical aromatic substitution. The substitution pattern is determined by the electronic effect of the methoxy group, so that the electrophile attacks **2h** at the *para*-position. The trialkylstannylated ether **10** is formed and protodestannylated during hydrolysis to give the *p*-aldehyde **7g**. The alternative mechanism (II) proceeds via a four-centred transition state between the stannyl leaving group and the electrophile, as postulated for other destannylation reactions[26,27]. The *ipso*-orientation is established by the coordination ability of the tin atom. The non-stannylated ether **11** is formed and transformed to the aldehyde **7f** by hydrolysis. In the case of deactivated stannanes such as the stannylated chlorobenzenes the reaction proceeds exclusively via mechanism (I). The electrophile is not reactive enough to form a cationic σ-complex as in mechanism (II) so that the reaction is completely *ipso*-specific and the regiochemistry is determined by the leaving ability of the stannyl group. In the case of activated stannanes both pathways for the reaction are possible. If the trialkylstannyl group is fixed at the *p*-position both mechanisms lead to the same product **7g**, since the effects of the trialkylstannyl and the methoxy group direct the electrophile to the *p*-position. In the case of *o*- or *m*-substituted stannanes the *ipso*-substitution product is formed via the four-centred mechanism (II), whereas the *p*-isomer is produced by classical electrophilic substitution (I). The reaction proceeding via mechanism (II) is faster than (I), as the *ipso*-product is apparent the main product in all the reactions.

A possibility of increasing the efficiency of this electrophilic destannylation is the use of diaryldibutylstannanes **3a**−**c**. The yields are in the same range (69−80%) as those obtained from trialkylstannanes. Both aromatic rings are substituted but in the case of 2- and 3-methyl-substituted compounds both the *p*-aldehyde and the *ipso*-substitution product are formed (Eq. 6).





	R	yield/%	*p*-isomer/%	*ipso*-product/%
3a	H	75		100
3b	2-Me	69	30	70
3c	3-Me	72	23	77
3d	4-Me	80		100

Thus, the amount required for 1.0 mol of the aromatic substitution product can be reduced by a factor of two. Moreover, the tin by-product to be separated is not R_3SnCl but Bu_2SnCl_2, which can easily be converted into insoluble $(Bu_2SnO)_n$ and is less toxic than R_3SnCl.

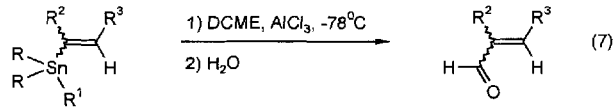
A further improvement in the ratio of stannane to aldehyde by linking more than two aryl rings to one stannyl leaving group could not achieved. The reaction of butyltriphenylstannane **3e** or tetraphenylstannane **3f** yields 20 or 10% respectively of **7a**, so that just one of the phenyl substituents is cleaved.

The *ipso*-specific introduction of the aldehyde function into other aromatic compounds, for example naphthalene, could be achieved via **1** (Eq. 4).

This method for synthesising aromatic aldehydes can easily be extended to heterocyclic compounds (Eq. 4), as demonstrated by a few examples. 2-Tributylstannylthiophene and -furane (**2p** and **r**) are converted in an *ipso*-specific manner into the corresponding aldehydes by the use of **1**. The reaction of 3-tributylstannylthiophene **2q** does not give the expected 3- but instead the 2-thiophenecarbaldehyde (Eq. 4). The leaving ability of the stannyl group is not high enough to compensate the strongly directing of thiophene itself.

In contrast to the situation observed for five-membered heterocycles, the deactivated pyridine derivatives **2s** and **t** react with **1** in an *ipso*-specific manner (Eq. 4). A reaction between non-stannylated pyridine and DCME does not occur.

1-Alkenyltrialkylstannanes **4** react readily with **1** under mild conditions in the presence of aluminium trichloride to yield the corresponding α,β-unsaturated aldehydes **8** (Eq. 7). Only *ipso*-substitution products are obtained and the stereochemistry of the stannanes is retained in the products, no isomerization being observed. Thus, it is possible to influence the ratio of both isomers by the use of different stannanes as demonstrated by the preparation of **8a**. Hence, the reaction should occur via a four-centred transition state as discussed for the trialkylarylstannanes. The stereochemistry of the vinylstannane is thus preserved in the aldehydes. This kind of electrophilic substitution can also be extended to di-1-alkenyldibutylstannanes, so that the amount of the tin reagent can be reduced and the tin by-product is less toxic. Non-stannylated olefins like styrene or hexene do not react with the electrophile. Even the presence of the reactive silyl group in the vinylic system, which was also used in electrophilic demetalation reactions[28] does not allow the desilylation by **1**. No formylation of bis(1-cyclooctenyldimethyl)silane (**6b**) by DCME was observed. This is emphasized by the trialkylstannylalkene such as **6c** only the stannyl group is cleaved, whereas the trimethylsilyl group remains in the resulting aldehyde **9** (Eq. 8). Furthermore, a cleavage of the silyl group is not possible even if an excess of the electrophile **1** is used.



4; 5 8

	R	R¹	R²	R³	E:Z (4;5)		yield/%	E:Z (8)
4a	Me	Me	H	Me	1.0 : 1.2	8a	75	1.0 : 1.0
4b	Bu	Bu	H	Me	2.1 : 1.0	8a	68	2.0 : 0.9
5a	Bu		H	Me	1.0 : 0.7	8a	60	1.0 : 0.6
4c	Bu	Bu	Me	Me	1.0 : 3.7	8b	72	1.0 : 3.5
5b	Bu		Me	Me	1.0 : 4.0	8b	65	1.0 : 3.8
4d	Bu	Bu	H	Ph	1.0 : 0.0	8c	78	1.0 : 0.0
4e	Me	Me	Ph	H	--	--	--	--
5c	Bu		-[CH2]3-		only Z	8d	63	only Z
5d	Bu		-[CH2]4-		only Z	8e	67	only Z
4f	Me	Me	-[CH2]6-		only Z	8f	82	only Z
5e	Me		-[CH2]6-		only Z	8f	73	only Z
5f	Bu		-[CH2]6-		only Z	8f	69	only Z

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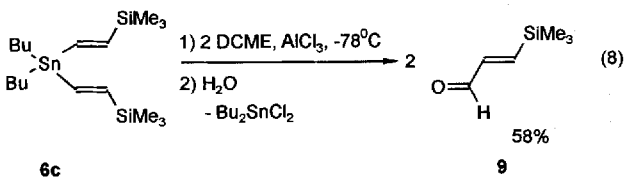

6c 9

Experimental

Melting points: Büchi SMP 20. – IR: Shimadzu 3283. – NMR: Varian EM 60 (60 MHz, ^{1}H), Bruker AC 200 (200 MHz, ^{1}H), and Bruker AM 300 (300 MHz, ^{1}H; 75.47 MHz, ^{13}C; 59.63 MHz, ^{29}Si; 111.92 MHz, ^{119}Sn). – GC: Carlo Erba 4130 with 25 m CP SIL 5. – MS: Finnigan MAT 8230, 70 eV. – Elementary analyses: Carlo Erba MOD 1106.

The trialkylaryl- **2a–o**[29,30], trialkylheteroaryl- **2p–t**[31], trialkyl-1-alkenyl- **4a–e**[32], and bis-(1-alkenyl)dibutylstannanes **5a–f**[20,23] are prepared according to published procedures; in the case of the alkenylstannanes the (*E*)/(*Z*) ratios are as follows: **4a** (*E*)/(*Z*) = 1.0:1.2; **4b** (*E*)/(*Z*) = 2.1:1.0; **4c** (*E*)/(*Z*) = 1.0:3.7; **4d** (*E*)/(*Z*) = 1.0:0.0; **5a** (*E*)/(*Z*) = 1.0:0.7; **5b** (*E*)/(*Z*) = 1.0:4.0; **5c–f** only *Z*.

Bis(1-cyclooctenyl)dimethylstannane (**5e**): A solution of 5.49 g (25.0 mmol) of dimethyltin dichloride in 100 ml of anhydrous diethyl ether is added under Ar during 1 h to 1-cyclooctenyllithium prepared from 13.2 g (0.07 mol) of 1-bromo-1-cyclooctene[33] and 0.97 g (0.14 mol) of lithium in 250 ml of anhydrous diethyl ether. After stirring at reflux for 12 h the reaction mixture is hydrolysed with 100 ml of saturated aqueous NH_4Cl. Twofold extraction of the aqueous layer with 100 ml of diethyl ether, drying of the combined organic layers with $MgSO_4$, and removal of the solvent affords the crude products. Fractional distillation yields 1.35 g of *(1-cyclooctenyl)trimethylstannane*, b.p. 60°C/0.01 Torr (ref.[32a] 70–75°C/0.05 Torr), 5.63 g of **5e**, b.p. 110°C/0.01 Torr and 2.31 g of *tris(1-cyclooctenyl)methylstannane*, m.p. 50°C (*n*-pentane). – *(1-Cyclooctenyl)trimethylstannane:* ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 9H, $SnMe_3$, $^2J_{SnH}$ = 51.0 Hz), 1.62 (m, 6H, CH_2), 2.20 (m, 2H, $CH_{2,Allyl}$), 2.68 (m, 2H, $CH_{2,Allyl}$), 6.00 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = −10.0 ($SnMe_3$, $^1J_{SnC}$ = 332 Hz), 25.8, 26.5, 27.0, 29.1, 29.3, 30.2 (all CH_2), 140.3 (CH, $^2J_{SnC}$ = 31 Hz), 144.1 (C_q, $^1J_{SnC}$ = 476 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −34.3. – MS; *m/z* (%): 259 (100) [M^+ − CH_3], 192 (3) [M^+ − CH_3, − C_5H_7], 109 (7) [cyclooctene − H], 82 (5), [$C_6H_{10}^+$], 67 (12) [$C_5H_7^+$].

5e: ^{1}H NMR ($CDCl_3$): δ = 0.12 (s, 6H, $SnMe_3$, $^2J_{SnH}$ = 51.8 Hz), 1.47 (m, 10H, CH_2), 2.21 (m, 4H, $CH_{2,Allyl}$), 2.39 (m, 4H, $CH_{2,Allyl}$), 5.86 (t, 2H, CH, $^3J_{HH}$ = 7.8 Hz). – ^{13}C NMR ($CDCl_3$): δ = −10.4 ($SnMe_2$, $^1J_{SnC}$ = 336 Hz), 26.0, 26.5 (all CH_2), 27.2 (CH_2, $^2J_{SnC}$ = 63 Hz), 29.2, 29.3 (all CH_2), 30.5 (CH_2, $^2J_{SnC}$ = 51 Hz), 141.1 (CH, $^2J_{SnC}$ = 33 Hz), 143.9 (C_q, $^1J_{SnC}$ = 460 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −66.4. – MS; *m/z* (%): 368 (1) [M^+], 353 (100) [M^+ − CH_3], 259 (44) [M^+ − cyclooctene], 245 (27) [MeCyclooctenylSnH^+], 151 (56) [Me_2SnH], 135 (62) [$MeSn^+$], 121 (18) [SnH^+], 109 (24) [cyclooctene − H], 67 (76) [$C_5H_7^+$], 55 (47) [$C_4H_7^+$], 41 (62) [$C_3H_5^+$]. – $C_{18}H_{32}Sn$ (367.14): calcd. C 58.89, H 8.79; found C 60.3, H 8.5.

Tris(1-cyclooctenyl)methylstannane: ^{1}H NMR ($CDCl_3$): δ = 0.30 (s, 3H, SnMe, $^2J_{SnH}$ = 50.0 Hz), 1.63 (m, 24H, CH_2), 2.38 (m, 6H, $CH_{2,Allyl}$), 2.53 (m, 6H, $CH_{2,Allyl}$), 6.03 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = −10.5 (SnMe, $^1J_{SnC}$ = 325 Hz), 25.9, 26.4, 27.3, 29.0, 29.5, 30.3 (all CH_2), 140.8 (CH, $^2J_{SnC}$ = 32 Hz), 144.0 (C_q, $^1J_{SnC}$ = 465 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −99.6. – MS; *m/z* (%): 465 (100) [M^+ − CH_3], 353 (25) [M^+ − cyclooctene], 339 (33) [$(cyclooctene)_2SnH^+$], 245 (26) [MeSnCyclooctenylH^+], 109 (7) [cyclooctene − H]. – $C_{25}H_{42}Sn$ (461.30): calcd. C 65.09, H 9.18; found C 64.8, H 9.0.

Aldehydes **7a–q**, **8a–f**, *and* **9**. – *General Procedure:* A suspension of $AlCl_3$ in 20 ml of anhydrous dichloromethane is cooled to −78°C under Ar. A solution of **1** and the corresponding stannane in 5 ml of anhydrous dichloromethane is added during 15 min. After stirring at −78°C for 4 h the reaction mixture is hydrolysed with 25 ml of saturated aqueous NH_4Cl and the organic layer is extracted three times with 25 ml of dichloromethane. The combined organic layers are treated with 15 ml of a saturated solution of KF in water, stirred vigorously for 3 h, and the precipitated R_3SnF (R = Me, Bu) is filtered off. The filtrate is extracted twice with 10 ml of dichloromethane. The combined organic layers are dried with $MgSO_4$ and the solvent is distilled off. The residue is purified by distillation or recrystallized from the appropriate solvent.

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 1.20 g (5.00 mmol) of **2a**, 0.50 g (5.00 mmol) of **1**, and 5.00 mmol of a Lewis acid (see following table). Temperatures and yields are compiled in the following table.

Lewis acid	amount	temperature	GC yield
none	–	−78°C	5%
$TiCl_4$	0.95 g	−78°C	41%
$SnCl_4$	1.30 g	−78°C	0%
$AlCl_3$	0.67 g	−78°C	90%
$AlCl_3$	0.67 g	−53°C	1%
$AlCl_3$	0.67 g	−27°C	1%
$AlCl_3$	0.67 g	0°C	1%
$AlCl_3$	0.67 g	25°C	1%

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 2.40 g (10.0 mmol) of **2a**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.86 g (81%), b.p. 75°C/12 Torr (ref.[6a] 178°C). – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1}, 2825, 2740, 1701, 1599, 1585, 1490, 745, 690. – ^{1}H NMR ($CDCl_3$): δ = 7.86 (m, 5H, $H_{aromat.}$), 10.08 (s, 1H, CHO).

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 4.08 g (10.0 mmol) of **2b**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.80 g (76%), b.p. 75°C/12 Torr (ref.[6a] 178°C).

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 0.78 g (10.0 mmol) of benzene, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. GC-yield: 30%.

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 1.50 g (10.0 mmol) of **6a**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. GC-yield: 35%.

4-Methylbenzaldehyde (**7d**): **7d** is obtained according to the general procedure, 2.55 g (10.0 mmol) of **2e**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.02 g (85%), b.p. 85°C/12 Torr (ref.[6a] 82–84°C/12 Torr). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2860, 2835, 2740, 1704, 1607, 1575, 1495, 808. – ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3H, CH_3), 7.20 (d, 2H, $H_{aromat.}$), 7.73 (d, 2H, $H_{aromat.}$), 9.13 (s, 1H, CHO).

4-Methylbenzaldehyde (**7d**): **7d** is obtained according to the general procedure, 3.81 g (10.0 mmol) of **2f**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.96 g (80%), b.p. 85°C/12 Torr (ref.[6a] 82–84°C/12 Torr).

2- and 4-Methylbenzaldehyde (**7b** *and* **7d**): A mixture of **7b** and **7d** is obtained according to the general procedure, 3.81 g (10.0

mmol) of **2c**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.00 g (84%), b.p. 80°C/12 Torr (mixture of 75% of **7b** and 25% of **7d**). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2860, 2835, 2740, 1699, 1603, 1576, 1490, 809, 755. – ^1H NMR ($CDCl_3$): δ = 2.50 (s, $CH_{3,para}$), 2.71 (s, $CH_{3,ortho}$) (both 3H), 7.16–8.07 (m, 4H, $H_{aromat.}$), 10.32 (s, CHO_{para}), 11.51 (s, CHO_{ortho}) (both 1H).

3- and 4-Methylbenzaldehyde (**7c** *and* **7d**): A mixture of **7c** and **7d** is obtained according to the general procedure, 3.81 g (10.0 mmol) of **2d**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.04 g (87%), b.p. 80°C/12 Torr (mixture of 75% of **7c** and 25% of **7d**). – IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1}, 2835, 2735, 1700, 1605, 1577, 1488, 809, 784. – ^1H NMR ($CDCl_3$): δ = 2.36 (s, $CH_{3,meta}$), 2.50 (s, $CH_{3,para}$) (both 3H), 7.06–7.93 (m, 4H, $H_{aromat.}$), 10.01 (s, CHO_{meta}), 10.32 (s, CHO_{para}) (both 1H).

4-Methoxybenzaldehyde (**7g**): **7g** is obtained according to the general procedure, 3.97 g (10.0 mmol) of **2i**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.28 g (94%), b.p. 125°C/12 Torr (ref.[6a] 120°C/13 Torr). – IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1}, 2845, 1686, 1601, 1579, 1510, 1261, 833. – ^1H NMR ($CDCl_3$): δ = 3.88 (s, 3H, OCH_3), 7.00 (d, 2H, $H_{aromat.}$), 7.87 (d, 2H, $H_{aromat.}$), 9.93 (s, 1H, CHO).

2- and 4-Methoxybenzaldehyde (**7e** *and* **7g**): A mixture of **7e** and **7g** is obtained according to the general procedure, 3.97 g (10.0 mmol) of **2g**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.19 g (88%), b.p. 140°C/12 Torr (mixture of 55% of **7e** and 45% of **7g**). – IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1}, 2850, 1688, 1602, 1579, 1510, 1261, 1248, 833, 759. – ^1H NMR ($CDCl_3$): δ = 3.80 (s, $OCH_{3,ortho}$), 3.87 (s, $OCH_{3,para}$) (both 3H), 6.83–7.87 (m, 4H, $H_{aromat.}$), 9.93 (s, CHO_{para}), 10.40 (s, CHO_{ortho}) (both 1H).

3- and 4-Methoxybenzaldehyde (**7f** *and* **7g**): A mixture of **7f** and **7g** is obtained according to the general procedure, 3.97 g (10.0 mmol) of **2g**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.13 g (83%), b.p. 135°C/12 Torr (mixture of 70% of **7f** and 30% of **7g**). – IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1}, 2845, 2745, 1678, 1601, 1579, 1510, 1261, 1251, 833, 780. – ^1H NMR ($CDCl_3$): δ = 3.43 (s, $OCH_{3,meta}$), 3.87 (s, $OCH_{3,para}$) (both 3H), 6.73–7.83 (m, 4H, $H_{aromat.}$), 9.76 (s, CHO_{meta}), 9.93 (s, CHO_{para}) (both 1H).

2-Chlorobenzaldehyde (**7h**): **7h** is obtained according to the general procedure, 4.02 g (10.0 mmol) of **2j**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.15 g (82%), b.p. 125°C/12 Torr (ref.[34] 130–131°C/20 Torr). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1700, 1594, 1570, 1477, 1053, 756. – ^1H NMR ($CDCl_3$): δ = 6.90–8.00 (m, 4H, $H_{aromat.}$), 10.46 (s, 1H, CHO).

3-Chlorobenzaldehyde (**7i**): **7i** is obtained according to the general procedure, 4.02 g (10.0 mmol) of **2k**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.13 g (80%), b.p. 105°C/12 Torr (ref.[35] 107–109°C/26 Torr). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 2735, 1704, 1594, 1574, 1072, 787. – ^1H NMR ($CDCl_3$): δ = 7.35–7.85 (m, 4H, $H_{aromat.}$), 9.90 (s, 1H, CHO).

4-Chlorobenzaldehyde (**7j**): **7j** is obtained according to the general procedure, 4.02 g (10.0 mmol) of **2l**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.24 g (88%), m.p. 45°C (pentane) (ref.[36] 46–48°C). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2760, 1699, 1594, 1589, 1575, 1512, 1092, 839. – ^1H NMR ($CDCl_3$): δ = 7.40 (d, 2H, $H_{aromat.}$), 7.77 (d, 2H, $H_{aromat.}$), 9.90 (s, 1H, CHO).

2-Trifluoromethylbenzaldehyde (**7k**): **7k** is obtained according to the general procedure, 3.10 g (10.0 mmol) of **2m**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.95 g (55%), b.p. 70°C/12 Torr (ref.[36] 70°C/16 Torr). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 1703, 1603, 1586, 1491, 1165, 771. – ^1H NMR ($CDCl_3$): δ = 6.92–7.92 (m, 4H, $H_{aromat.}$), 10.70 (s, 1H, CHO).

Reaction of Toluene and **2j** *with* **1**: Reaction of 4.02 g (10.0 mmol) of **2j** and 0.92 g (10.0 mmol) of toluene with 1.00 g (10.0 mmol) of **1** and 1.34 g (10.0 mmol) of $AlCl_3$ according to the general procedure yields 1.17 g of a mixture of 85% of **7h** and 15% of **7d**.

Reaction of Toluene and **2i** *with* **1**: Reaction of 3.97 g (10.0 mmol) of **2i** and 0.29 g (10.0 mmol) of toluene with 1.00 g (10.0 mmol) of **1** and 1.34 g (10.0 mmol) of $AlCl_3$ according to the general procedure yields 1.13 g of a mixture of 98% of **7g** and 2% of **7d**.

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 1.94 g (5.00 mmol) of **3a**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.80 g (75%), b.p. 75°C/12 Torr (ref.[6a] 178°C).

4-Methylbenzaldehyde (**7d**): **7d** is obtained according to the general procedure, 2.08 g (5.00 mmol) of **3d**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.96 g (80%), b.p. 85°C/12 Torr (ref.[6a] 82–84°C/12 Torr).

2- and 4-Methylbenzaldehyde (**7b** *and* **7d**): A mixture of **7b** and **7d** is obtained according to the general procedure from 3.81 g (5.00 mmol) of **3b**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.83 g (69%), b.p. 85°C/12 Torr (mixture of 70% of **7b** and 30% of **7d**).

3- and 4-Methylbenzaldehyde (**7c** *and* **7d**): A mixture of **7c** and **7d** is obtained according to the general procedure, 2.08 g (5.00 mmol) of **3c**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.86 g (72%), b.p. 85°C/12 Torr (mixture of 77% of **7c** and 33% of **7d**).

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 2.04 g (5.00 mmol) of **3e**, 1.50 g (15.0 mmol) of **1**, and 2.01 g (15.0 mmol) of $AlCl_3$. Yield: 0.28 g (20%), b.p. 75°C/12 Torr (ref.[6a] 178°C).

Benzaldehyde (**7a**): **7a** is obtained according to the general procedure, 2.14 g (5.00 mmol) of **3f**, 2.00 g (20.0 mmol) of **1**, and 2.68 g (20.0 mmol) of $AlCl_3$. Yield: 0.19 g (10%), b.p. 75°C/12 Torr (ref.[6a] 178°C).

1-Naphthalenecarbaldehyde (**7l**): **7l** is obtained according to the general procedure, 4.17 g (10.0 mmol) of **2n**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.25 g (80%), b.p. 155°C/12 Torr (ref.[37] 142°C/6 Torr). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2730, 1691, 1595, 1575, 1511, 801, 771. – ^1H NMR ($CDCl_3$): δ = 7.30–7.66 (m, 7H, $H_{aromat.}$), 10.10 (s, 1H, CHO).

2-Naphthalenecarbaldehyde (**7m**): **7m** is obtained according to the general procedure, 4.17 g (10.0 mmol) of **2o**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.99 g (63%), m.p. 60°C (ref.[38] 59°C). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2730, 1690, 1595, 1575, 1511, 819, 755. – ^1H NMR ($CDCl_3$): δ = 7.48 (m, 2H, $H_{aromat.}$), 7.50–8.00 (m, 4H, $H_{aromat.}$), 9.99 (s, 1H, CHO).

2-Thiophenecarbaldehyde (**7n**): **7n** is obtained according to the general procedure, 3.73 g (10.0 mmol) of **2p**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.85 g (76%), b.p. 80°C/12 Torr (ref.[6a] 78°C/13 Torr). – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 2765, 1674, 728. – ^1H NMR ($CDCl_3$): δ = 7.00 (t, 1H, CH), 7.60 (m, 2H, CH), 9.86 (s, 1H, CHO).

2-Thiophenecarbaldehyde (**7n**): **7n** is obtained according to the general procedure, 3.73 g (10.0 mmol) of **2q**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.78 g (70%), b.p. 80°C/12 Torr (ref.[6a] 78°C/13 Torr).

2-Furanecarbaldehyde (**7o**): **7o** is obtained according to the general procedure, 3.56 g (10.0 mmol) of **2r**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.02 g (76%), b.p. 60°C/

12 Torr (ref.[39] 62–63°C/19 Torr). – IR (KBr): $\tilde{\nu}$ = 2850 cm^{-1}, 1675, 1569, 1278. – ^1H NMR ($CDCl_3$): δ = 6.50 (m, 1H, CH), 7.21 (m, 1H, CH), 7.63 (m, 1H, CH), 9.57 (s, 1H, CHO).

2-Pyridinecarbaldehyde (**7p**): **7p** is obtained according to the general procedure, 3.68 g (10.0 mmol) of **2s**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.66 g (61%), b.p. 70°C/12 Torr (ref.[40] 70–71°C/16 Torr). – IR (KBr): $\tilde{\nu}$ = 2950 cm $^{-1}$, 1715, 1615, 1588, 665, 620. – ^1H NMR ($CDCl_3$): δ = 7.45–7.85 (m, 2H, CH), 7.91–8.13 (m, 2H, CH), 9.06–9.31 (m, 1H, CH), 9.60 (s, 1H, CHO).

3-Pyridinecarbaldehyde (**7r**): **7r** is obtained according to the general procedure, 3.68 g (10.0 mmol) of **2t**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.56 g (53%), b.p. 85°C/12 Torr (ref.[41] 95–97°C/15 Torr). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 1690, 1590, 1570, 790, 690. – ^1H NMR ($CDCl_3$): δ = 7.47–7.72 (m, 1H, CH), 8.12–8.38 (m, 1H, CH), 8.79–8.92 (m, 1H, CH), 9.03–9.09 (m, 1H, CH), 10.11 (s, 1H, CHO).

(E)- and (Z)-2-Butenal (**8a**): **8a** is obtained according to the general procedure, 2.04 g (10.0 mmol) of **4a**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.51 g (75%), b.p. 95–100°C (ref.[42] 103–104°C) (mixture of (*E*)/(*Z*) = 1.0:1.0). – IR (KBr): $\tilde{\nu}$ = 2850 cm^{-1}, 1703, 1625. – ^1H NMR ($CDCl_3$): δ = 1.99 (dd, CH_3 (*E*), $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.4 Hz), 2.13 (d, CH_3 (*Z*), $^3J_{HH}$ = 7.2 Hz) (both 3H), 6.15 (qd, CH (*E*), $^3J_{HH}$ = 15.2 Hz, $^4J_{HH}$ = 1.4 Hz), 6.29 (d, CH (*Z*), $^3J_{HH}$ = 11.1 Hz) (both 1H), 6.95 (m, 1H, CH), 9.51 (d, CHO (*E*), $^3J_{HH}$ = 8.0 Hz), 9.62 (d, CHO (*Z*), $^3J_{HH}$ = 8.2 Hz) (both 1H).

(E)- and (Z)-2-Butenal (**8a**): **8a** is obtained according to the general procedure, 3.30 g (10.0 mmol) of **4b**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.46 g (68%), b.p. 95–100°C (ref.[42] 103–104°C) (mixture of *E*:*Z* = 2.0:0.9).

(E)- and (Z)-2-Butenal (**8a**): **8a** is obtained according to the general procedure, 1.58 g (5.00 mmol) of **5a**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.42 g (60%), b.p. 95–100°C (ref.[42] 103–104°C) (mixture of *E*:*Z* = 1.0:0.6).

(E)- and (Z)-2-Methyl-2-butenal (**8b**): **8b** is obtained according to the general procedure, 2.17 g (10.0 mmol) of **4c**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.60 g (72%), b.p. 120–125°C (ref.[43] 116.5–117.5°C/738 Torr) (mixture of (*E*)/(*Z*) = 1.0:3.5). – IR (KBr): $\tilde{\nu}$ = 2850 cm^{-1}, 1699, 1615. – ^1H NMR ($CDCl_3$): δ = 1.26 [d, CH_3 (*E*), $^3J_{HH}$ = 7.2 Hz], 1.36 [s, CH_3 (*E*)], 1.38 [d, CH_3 (*Z*), $^3J_{HH}$ = 7.5 Hz], 1.44 [s, CH_3 (*Z*)] (all 6H), 5.40 [q, CH (*E*), $^3J_{HH}$ = 7.2 Hz], 6.34 [q, CH (*Z*), $^3J_{HH}$ = 7.5 Hz] (both 1H), 9.55 [s, CHO (*E*)], 9.71 [s, CHO (*Z*)] (both 1H).

(E)- and (Z)-2-Methyl-2-butenal (**8b**): **8b** is obtained according to the general procedure, 1.67 g (5.00 mmol) of **5b**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.55 g (65%), b.p. 120–125°C (ref.[43] 116.5–117.5°C/738 Torr) (mixture of (*E*)/(*Z*) = 1.0:4.0).

(E)-3-Phenylpropenal (**8c**): **8c** is obtained according to the general procedure, 3.93 g (10.0 mmol) of **4d**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.03 g (78%), b.p. 130°C/12 Torr (ref.[44] 84–87°C/2 Torr). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2850, 1710, 1690, 730, 690. – ^1H NMR ($CDCl_3$): δ = 6.65 (dd, 1H, CH, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 16.7 Hz), 7.42 (m, 5H, $H_{aromat.}$), 7.45 (d, 1H, CH, $^3J_{HH}$ = 16.7 Hz), 9.72 (d, 1H, CHO, $^3J_{HH}$ = 8.3 Hz).

1-Cyclooctenecarbaldehyde (**8f**): **8f** is obtained according to the general procedure, 2.31 g (10.0 mmol) of **4f**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.13 g (82%), b.p. 115°C/12 Torr (ref.[8] 100–110°C/10 Torr). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 2860, 2820, 2720, 1688, 1643. – ^1H NMR ($CDCl_3$): δ = 1.50 (m, 8H, CH_2), 2.36 (m, 4H, $CH_{2,Allyl}$), 6.55 (t, 1H, CH, $^3J_{HH}$ = 8.2 Hz), 9.32 (s, 1H, CHO).

1-Cyclooctenecarbaldehyde (**8f**): **8f** is obtained according to the general procedure, 1.84 g (5.00 mmol) of **5e**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 1.01 g (73%), b.p. 115°C/12 Torr (ref.[8] 100–110°C/10 Torr).

1-Cyclooctenecarbaldehyde (**8f**): **8f** is obtained according to the general procedure, 2.26 g (5.00 mmol) of **5f**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.95 g (69%), b.p. 115°C/12 Torr (ref.[8] 100–110°C/10 Torr).

1-Cyclohexenecarbaldehyde (**8e**): **8e** is obtained according to the general procedure, 1.98 g (5.00 mmol) of **5d**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.74 g (67%), b.p. 110°C/12 Torr (ref.[8] 80–90°C/10 Torr). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2885, 2730, 1685, 1655. – ^1H NMR ($CDCl_3$): δ = 1.64 (m, 4H, CH_2), 1.90–2.61 (m, 4H, $CH_{2,Allyl}$), 6.63 (m, 1H, CH), 9.33 (s, 1H, CHO).

1-Cyclopentenecarbaldehyde (**8d**): **8d** is obtained according to the general procedure, 1.83 g (5.00 mmol) of **5c**, 1.00 g (10.0 mmol) of **1**, and 1.34 g (10.0 mmol) of $AlCl_3$. Yield: 0.60 g (63%), b.p. 55°C/12 Torr (ref.[45] 48–50°C/12 Torr). – IR (KBr): $\tilde{\nu}$ = 2935 cm^{-1}, 2850, 2730, 1690, 1640. – ^1H NMR ($CDCl_3$): δ = 1.58 (m, 2H, CH_2), 2.44 (m, 4H, $CH_{2,Allyl}$), 6.49 (m, 1H, CH), 9.35 (s, 1H, CHO).

(E)-3-Trimethylsilyl-2-propenal (**9**): **9** is obtained according to the general procedure, 1.72 g (4.00 mmol) of **6c**, 0.80 g (8.00 mmol) of **1**, and 1.07 g (8.00 mmol) of $AlCl_3$. Yield: 0.60 g (58%), b.p. 80°C/12 Torr (ref.[46] 74–76°C/35 Torr). – IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2929, 2859, 1694, 770. – ^1H NMR ($CDCl_3$): δ = 0.05 (s, 9H, $SiMe_3$), 6.50 (dd, 1H, CH, $^3J_{HH}$ = 18.8 Hz, $^3J_{HH}$ = 7.8 Hz), 7.21 (d, 1H, CH, $^3J_{HH}$ = 18.8 Hz), 9.48 (d, 1H, CHO, $^3J_{HH}$ = 7.8 Hz). – ^{13}C NMR ($CDCl_3$): δ = −2.14 ($SiMe_3$, $^1J_{SiC}$ = 54 Hz), 143.8 (CH), 159.3 (CH), 194.9 (CHO). – ^{29}Si NMR ($CDCl_3$): δ = −4.5. – MS; *m/z* (%): 129 (17) [M^+ − H], 99 (13) [M^+ − CHO], 73 (100) [$SiMe_3^+$], 55 (9) [M^+ − $SiMe_3$].

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