Pergamon

Tetrahedron 58 (2002) 4787–4799

TETRAHEDRON

Preparation of α-functionalized alkenylmagnesium reagents via a halide–magnesium exchange

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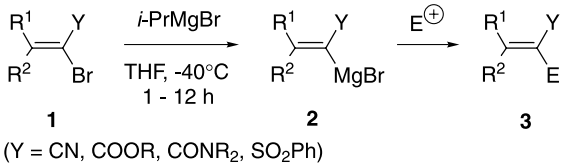
Received 20 March 2002; accepted 23 April 2002

Abstract—A general preparation of alkenylmagnesium derivatives bearing an electron-withdrawing function in the α-position (Y=CN, CO_2R, $CONR_2$, SO_2Ph) has been made possible by using a low temperature (−40 to −30°C) bromine–magnesium exchange with *i*-PrMgBr in THF. This reaction has also been used to prepare 5-magnesiated-1,3-dioxin-4-one derivatives bearing an alkoxy substituent in β-position to the carbon–magnesium bond. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Functionalized arylmagnesium compounds are readily prepared by an iodine–magnesium exchange.[1] The reaction proceeds at low temperature (−30°C) if the aromatic ring bears electron-withdrawing substituents. Similarly, for alkenyl iodides or bromides, a fast halogen–magnesium exchange is observed if an electron-withdrawing group is attached to the double bond.[2] Recently, we report some examples of alkenylmagnesium compounds bearing an electron-withdrawing function at the sp^2-carbon atom attached to magnesium.[3] Herein, we wish to report our full results on this topic. The inductive effect of the functional group is important, such that in most cases, functionalized alkenyl bromides of type **1** can be used for the generation of the Grignard reagents **2** (Scheme 1).

Most exchange reactions occurred between −50°C and −40°C and were complete within 1–12 h. The resulting alkenylmagnesium compounds reacted well with a range of electrophiles E^+ leading to products of type **3** (Scheme 1). The reaction sequence is quite general and electron-withdrawing groups such as Y=CN, CO_2R, or SO_2R facilitate the bromine–magnesium exchange considerably.

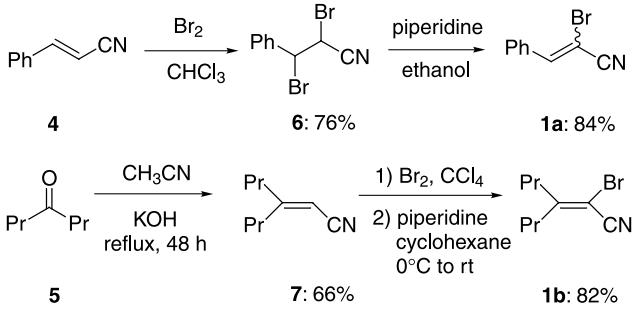


Scheme 1.

2. Results and discussion

First, we examined 2-bromonitriles **1a** and **1b** as precursors for the bromine–magnesium exchange. These nitriles were prepared in two or three steps from the cinnamonitrile (**4**) and 4-heptanone (**5**). Thus, the bromination of **4** in $CHCl_3$ furnished the dibromide **6**[4] in 76% yield. In the presence of piperidine in ethanol,[5] an elimination of hydrobromic acid furnished the desired bromonitrile **1a**[6] as an *E*/*Z* mixture in 84% yield (Scheme 2).

The unsaturated nitrile **7** was obtained by the condensation of acetonitrile and 4-heptanone (**5**) in the presence of KOH.[7] After bromination and piperidine mediated elimination, the bromonitrile **1b** was obtained in 82% yield. Both of these cyano-substituted alkenyl bromides underwent a fast



Scheme 2.

Keywords: magnesium; functionalized Grignard reagents; nitrile; sulfone.

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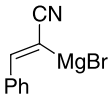
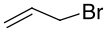
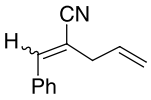
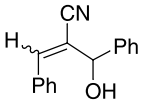
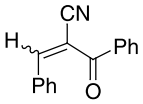
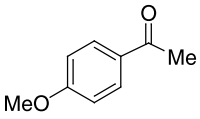
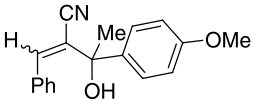
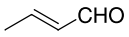
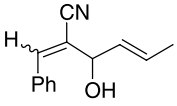
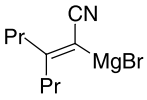
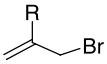
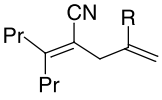
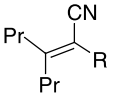
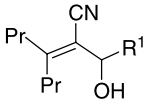
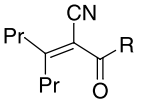
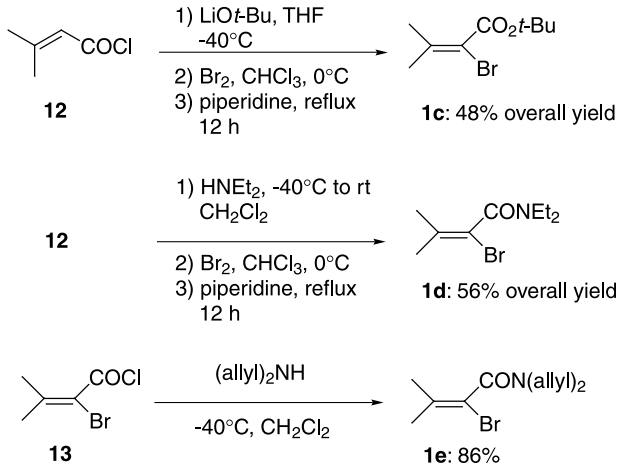
0040–4020/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4020(02)00439-8

Table 1. Products of type **10**, **11** obtained by the reaction of α-cyano alkenylmagnesium reagents **8**, **9** with various electrophiles

Entry	Grignard reagent	Electrophile	Product of type **10**, **11**	Yield (%)[a]
1	 **8**		 **10a** (90:10)	77[b]
2	**8**	PhCHO	 **10b** (92:8)	65
3	**8**	PhCOCl	 **10c** 60:40	63[c]
4	**8**		 **10d** (70:30)	53
5	**8**		 **10e** (50:50)	47
				
6	**9**	R=H	**11a**: R=H	92[b]
7	**9**	R=CO_2Et	**11b**: R=CO_2Et	82[c]
				
8	**9**	Me_3SiCl	**11c**: R=$SiMe_3$	93
9	**9**	Bu_3SnCl	**11d**: R=$SnBu_3$	48
		R^1CHO		
10	**9**	R^1=Ph	**11e**: R^1=Ph	67
11	**9**	R^1=*E*-propenyl	**11f** R^1=*E*-propenyl	76
				
12	**9**	PhCOCl	**11g**: R=Ph	68[c]
13	**9**	*o*-BrC_6H_4COCl	**11h**: R=*o*-BrC_6H_4	58[c]

[a] Isolated yield of analytically pure product.
[b] The reaction with allyl bromide was catalyzed by CuCN (10 mol%).
[c] Stoichiometric amount of CuCN·2LiCl was used.



Scheme 3.

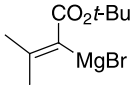
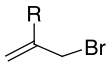
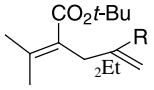
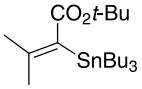
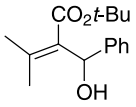
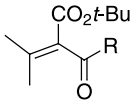
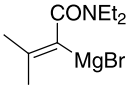
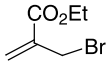
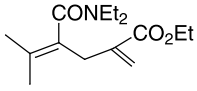
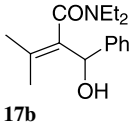
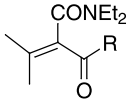
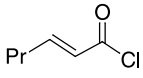
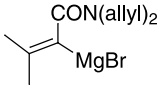
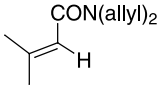
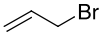
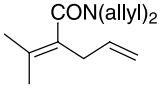
bromine–magnesium exchange at −40°C within 15–30 min providing the desired organomagnesium compounds **8** and **9** (Table 1). These Grignard reagents have reacted smoothly with a range of electrophiles leading to the products **10a–e** and **11a–h**. Aldehydes and ketones, as well as Me_3SiCl and Bu_3SnCl, reacted directly with the alkenylmagnesium species. The products of type **10** were obtained as E/Z mixtures. For the reaction of **8** or **9** with allylic bromides, the addition of a catalytic amount of CuCN (10 mol%) considerably improved the yield (entries 1 and 6). In the case of the reaction with acyl chlorides, a stoichiometric transmetalation of the magnesium organometallic with CuCN·2LiCl,[8] a THF soluble copper salt, was performed (entries 3, 12 and 13). The variable *E*/*Z* ratio obtained for products of type **10** indicated that the intermediate Grignard species **8** was not configurationally stable or did not react stereoselectively with electrophiles. In order to get an insight into the nature of the structure of **8**, we have recorded a ^{13}C NMR spectrum of this Grignard reagent in THF-d^8 at −35°C. We have found a chemical shift of 129.6 ppm for **C**N, which is very similar to the chemical shift of the bromonitrile (**1a**: 115.9 ppm). This suggests that the CN group has a triple bond character and that the magnesium atom is attached to the carbon atom of the nitrile group rather than to the nitrogen atom.[9,10] Next, we have examined the behavior of α-bromoesters and amides **1c–e**. The bromoester **1c**[11,12] was prepared starting from the acid chloride **12** by the reaction with LiO*t*-Bu in THF at −40°C, leading to *t*-butyl β,β-dimethylacrylate[13], which was brominated (Br_2, $CHCl_3$, 0°C) and heated with piperidine at reflux for 12 h to give the bromoester **1c** in an overall yield of 48% (Scheme 3). The treatment of the acid chloride **12** with Et_2NH furnished *N*,*N*-diethyl β,β-dimethylacrylate,[14] which was brominated and treated as above with piperidine, inducing the elimination of HBr and leading to the α-bromoamide **1d** in 56% overall yield. The α-bromoacid chloride **13**[15] could be directly converted to the corresponding amide **1e** in 86% yield by the reaction with diallylamine in CH_2Cl_2 at −40°C (Scheme 3). The bromoester **1c** was best magnesiated by reaction with *i*-PrMgBr (1.5 equiv.) in THF at −30°C (12 h) leading to the Grignard reagent **14**. The bromoamides **1d**,**e** reacted faster with *i*-PrMgBr (1.1 equiv.). A complete Br/Mg-exchange occurred within 3–4 h at −35°C, affording the magnesium reagents **15a**,**b** (Table 2).

As was observed for the magnesium organometallics bearing a cyano group at the α-position, these reagents reacted smoothly with aldehydes (entries 4 and 9 of Table 2) and Bu_3SnCl (entry 3). In the presence of catalytic amounts of CuCN (10 mol%), allylic bromides reacted well, leading to the expected allylated products of type **16** and **17** in satisfactory yields (45–87%; entries 1, 2, 8 and 14). After stoichiometric transmetalation of **14** and **15a**,**b** with CuCN 2LiCl, the reaction with various acid chlorides furnished a range of unsaturated 1,3-ketoesters and ketoamides (entries 5–7, 10–12). Interestingly, direct reaction of the Grignard reagents **15a**,**b** with β,β-dimethylacryloyl chloride at −40°C, followed by heating for 3 h at 35°C, provided the cyclohexenone derivatives **18a**,**b** in 52–61% yield (Scheme 4). The reaction proceeded via the highly unsaturated intermediate **19**, which underwent an electrocyclization, leading to the 3-methylcyclohexenones **18a**,**b**.

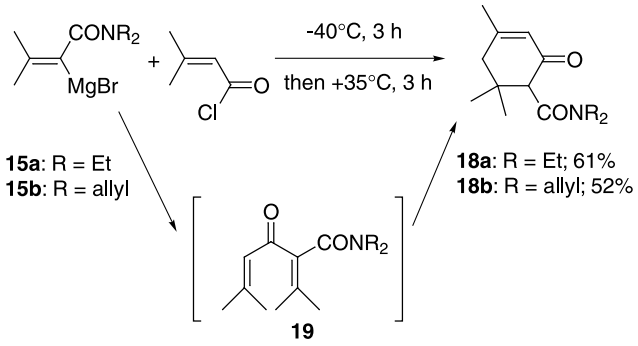
Next, we examined the preparation of α-magnesiated unsaturated sulfones. Styryl phenyl sulfone was treated with bromine followed by piperidine in refluxing cyclohexane, affording 1-bromo-2-phenylethenyl phenyl sulfone (**1f**) according to a literature procedure.[16] A rapid Br/Mg-exchange took place in THF at −45°C within 1 h furnishing the corresponding Grignard reagent **20**. Its reaction with various electrophiles, such as allylic bromides, Me_3SiCl, aldehydes and acid chlorides, provided unsaturated sulfones of type **21** (Table 3). Remarkably, all products **21a–g** were formed stereoselectively as the E-isomer. As observed with the magnesium reagents previously studied, copper(I) catalysis was necessary for reaction with allylic bromides (entries 1 and 2) and the reactions with acid chlorides required transmetalation with stoichiometric amounts of copper(I) salt (entry 6 and 7 of Table 3). Since the bromine–magnesium exchange occurred so fast, we envisioned the possibility of preparing alkenylmagnesium halides bearing an oxygen functionality at the β-position. Usually, for molecules of the general type **22**, a fast β-elimination is observed.[17] Few lithium or magnesium organometallics bearing an oxygen function at the β-position are known.[18] We expected that the cyclic systems of type **23** would have a moderate tendency to undergo elimination. We anticipated that the sensitive organomagnesium derivatives could be obtained by a fast iodine–magnesium exchange starting from 5-iodo-1,3-dioxin-4-one derivatives of type **24** (Scheme 5). The iodination of the 1,3-dioxin-4-ones **25a**,**b** with *N*-iodosuccinimide in acetic acid[19] provided the desired 5-iodo-1,3-dioxin-4-ones **24a**,**b** in 70–85% yield. The reaction of **24a**,**b** with *i*-PrMgCl in THF at −30°C for 0.5 h furnished the corresponding magnesium species **23a**,**b** in 85–90% yield as determined by GC-analysis of reaction mixture aliquots. The half-lives of **23a**,**b** were estimated to be 2 and 1 h respectively at −30°C. After reaction with various electrophiles, products of type **26** were obtained in 57–83% yield (Scheme 6 and Table 4).

As with the magnesium species described above, a direct reaction was observed with aldehydes (entries 1, 2, 7 and 8

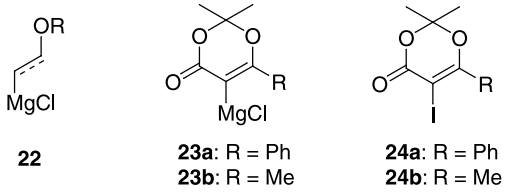
Table 2. Products of type **16**, **17** obtained by the reaction of α-carbonyl alkenylmagnesium reagents **14**, **15** with various electrophiles

Entry	Grignard reagent	Electrophile	Product of type **16**, **17**	Yield (%)[a]
1	 **14**		 **16a**: R=H	45[b]
2	**14**		**16b**: R=CO_2Et	65[b]
3	**14**	Bu_3SnCl	 **16c**	53
4	14	PhCHO	 **16d**	72
		ROCl		
5	**14**	R=Ph	**16e**: R=Ph	82[c]
6	**14**	R=*o*-BrC_6H_4	**16f**: R=*o*-BrC_6H_4	81[c]
7	**14**	R=*E*-1-pentenyl	**16g**: R=*E*-1-pentenyl	86[c]
8	 **15a**		 **17a**	74[c]
9	**15a**	PhCHO	 **17b**	76
				
10	**15a**	PhCOCl	**17c**: R=Ph	75[c]
11	**15a**	*o*-BrC_6H_4COCl	**17d**: R=*o*-BrC_6H_4	82[c]
12	**15a**		**17e**: R=*E*-1-pentenyl	72[c]
13	 **15b**	H_2O	 **17f**	92
14			 **17g**	87[b]

[a] Isolated yield of analytically pure product.
[b] The reaction with allyl bromide was catalyzed by CuCN (10 mol%).
[c] Stoichiometric amount of CuCN·2LiCl was used.



Scheme 4.



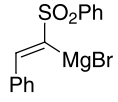
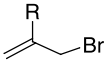
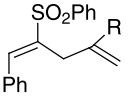
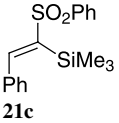
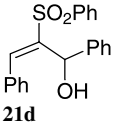
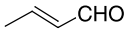
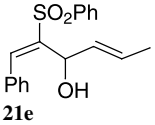
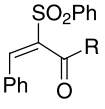
Scheme 5.

of Table 4), Me_3SnCl (entry 4) and PhSSPh (entry 5). The copper reagent obtained from **23a**,**b** by transmetalation with CuCN 2LiCl reacted well with acid chlorides (entry 3). Reaction with allylic bromides in the presence of a catalytic amount of a copper(I) salt was possible and led to the allylated products **26f** (81%) and **26i** (77%) (see entries 6 and 9). Finally, the transmetalation of **23a**,**b** to the corresponding zinc reagents with zinc bromide provided organometallic compounds (**27a**,**b**), which were stable at 60°C for several hours. These reacted with aromatic or alkenyl iodides in the presence of $Pd(dba)_2$ (5 mol%) and tris-*o*-furylphosphine (tfp; 10 mol%) in THF (60°C, 12 h)[20] and furnished the expected cross-coupling products **28a–c** in 54–57% (Scheme 7).

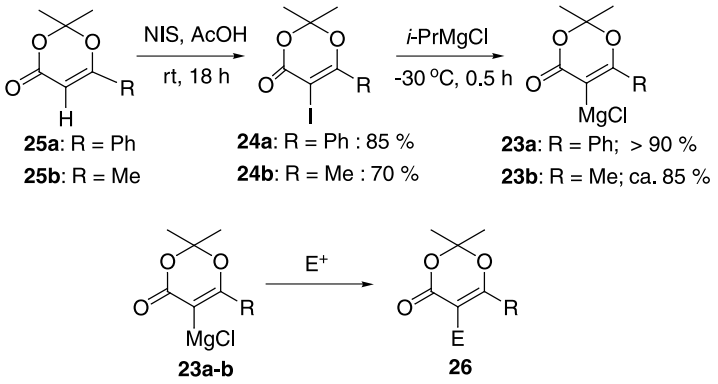
3. Conclusion

In summary, we have shown that various alkenyl bromides of type **1** undergo a fast Br/Mg-exchange providing the corresponding magnesiated species. Electron-withdrawing groups like Y=CN, CO_2t-Bu, $CONR_2$ and SO_2Ph considerably facilitated the rate of exchange and allowed an efficient preparation of polyfunctional alkenylmagnesium compounds. This mild halogen–magnesium exchange has been applied to the preparation of 5-magnesiated-1,3-dioxin-4-one derivatives bearing an alkoxy substituent at β-position to the carbon–magnesium bond.

Table 3. Products of type **21** obtained by the reaction of the α-sulfonyl alkenylmagnesium reagents **20** with various electrophiles

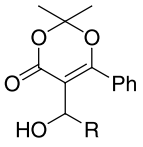
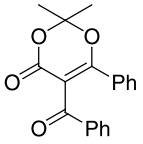
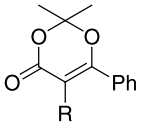
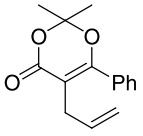
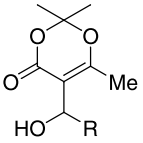
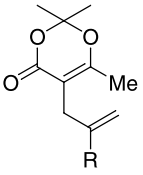
Entry	Grignard reagent	Electrophile	Product of type **21**	Yield (%)[a]
1	 **20**	 R=H	 **21a**: R=H	76[b]
2	**20**	R=CO_2Et	**21b**: R=CO_2Et	59[b]
3	**20**	Me_3SiCl	 **21c**	82
4	**20**	PhCHO	 **21d**	67
5	**20**		 **21e**	64
6	**20**	PhCOCl	 **21f**: R=Ph	62[c]
7	**20**	*p*-$MeOC_6H_4COCl$	**21g**: R=*p*-$MeOC_6H_4$	67[c]

[a] Isolated yield of analytically pure product.
[b] The reaction with allyl bromide was catalyzed by CuCN (10 mol%).
[c] Stoichiometric amount of CuCN·2LiCl was used.

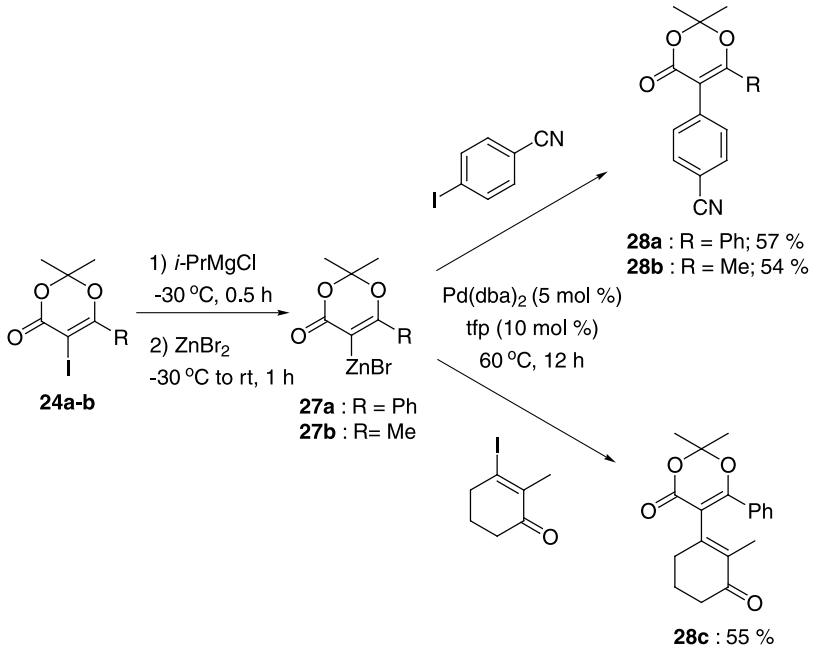


Scheme 6.

Table 4. 5-Substituted 1,3-dioxin-4-ones of type **26** obtained by the reaction of the magnesiated 1,3-dioxin-4-ones **23a**,**b** with various electrophiles

Entry	Grignard reagent	Electrophile	Product of type **26**	Yield (%)[a]
				
1	**23a**	PhCHO	**26a**:R=Ph	81
2	**23a**	c-HexCHO	**26b**:R=c-Hex	64
3	**23a**	PhCOCl	 **26c**	83[b]
				
4	**23a**	Me_3SnCl	**26d**:R=$SnMe_3$	59
5	**23a**	PhSSPh	**26e**:R=SPh	68
6	**23a**	Allyl bromide	 **26f**	81[c]
				
7	**23b**	PhCHO	**26g**:R=Ph	76
8	**23b**	c-HexCHO	**26h**:R=c-Hex	57
				
9	**23b**	Allyl bromide	**26i**:R=H	77[b]
10	**23b**	Ethyl (2-bromomethyl) acrylate	**26j**:R=CO_2Et	65[b]

[a] Isolated yield of analytically pure product.
[b] Reaction performed after a transmetalation to the corresponding copper reagent by adding CuCN·2LiCl (1.0 equiv.).
[c] Reaction performed in the presence of CuCN·2LiCl (10 mol%).



Scheme 7.

4. Experimental

4.1. General methods

Unless otherwise indicated, all reactions were carried out under an argon atmosphere. THF, Et_2O and *t*-butyl methyl ether (TBME) were distilled from sodium/benzophenone, CH_2Cl_2 and DMF from CaH_2. Reactions were monitored by gas chromatography (GC) analysis of worked up reaction aliquots. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel (60 F-254) plates (0.25 mm) precoated with a fluorescent indicator. Column chromatography was carried out on silica gel 60 (70–230 mesh). NMR data were recorded on a 300 MHz NMR spectrometer. The ionization method used was electron impact ionization (EI, 70 eV). Melting points are uncorrected. Elemental analyses were performed by the Microanalytical Service Laboratory of Universität München.

4.2. Starting materials

The following starting materials were prepared according to literature procedures: **1a**, **1b**[4,5] **1c**,[13] **1d**,[14] **1e**,[15] **1f**,[16] **25a**, **24a**,**b**.[19]

4.2.1. Typical procedure A. 2-(1-Hydroxy-but-2-enyl)-3-propyl-hex-2-enenitrile (11f). A solution of *i*-PrMgBr (4.1 mmol) in THF (0.80 M, 5.1 mL) was added dropwise over 5 min to a stirred solution of the bromonitrile **1a** (800 mg, 3.7 mmol) in THF (5 mL) at −40°C under argon. The resulting solution was then stirred for 30 min and crotonaldehyde (400 μL, 4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature, brine was added and the reaction mixture was worked up as usual. The crude residue was purified by column chromatography on silica to give **11f** (583 mg, 76%) as a colorless oil. IR (neat): 3440 (vs), 3028 (w), 2963 (s), 2935 (s), 2874 (m), 2214 (m), 1673 (w), 1622 (m), 1456 (m), 1380 (w), 1077 (m), 965 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.72 (dq, J=16.6, 6.3 Hz, 1H), 5.56 (dd, J=16.6, 6.3 Hz, 1H), 4.87 (d, J=6.3 Hz, 1H), 2.78 (bs, 1H), 2.30 (t, J=6.9 Hz, 2H), 2.16–2.09 (m, 2H), 1.66 (dd, J=6.3, 0.9 Hz, 3H), 1.50–1.36 (m, 4H), 0.89 (t, J=7.2 Hz, 3H), 0.87 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.5, 131.5, 129.8, 118.5, 115.4, 69.6, 39.4, 34.8, 22.8, 22.7, 18.8, 15.3, 15.0. *m*/*z* (EI-MS): 207 (4), 192 (15), 178 (49), 164 (50), 150 (29), 136 (25), 122 (43), 94 (34), 81 (42). HRMS: calcd for $C_{13}H_{21}NO$ 207.1623, found: 207.1622.

4.2.2. 2-Benzylidene-pent-4-enenitrile (10a). The reaction was carried out according to typical procedure A. IR (neat): 3083 (w), 3027 (w), 2940 (w), 2211 (s), 1640 (m), 1597 (w), 1574 (w), 1448 (m), 1233 (m), 992 (m), 927 (s), 752 (s), 693 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66–7.62 (m, 2H), 7.32–7.21 (m, 3H), 6.87 (s, 1H), 5.90–5.75 (m, 1H), 5.21–5.14 (m, 2H), 3.11 (dt, J=4.5, 1.5 Hz, 2H), 3.05 (dt, J=4.0, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.4, 133.2, 131.3, 130.5, 129.4, 129.2, 129.0, 119.2, 109.9, 40.4. *m*/*z* (EI-MS): 168 (80), 154 (100), 141 (37), 115 (30). HRMS: calcd for $C_{12}H_{11}N$ 169.0891, found: 169.0893.

4.2.3. 2-(Hydroxy-phenyl-methyl)-3-phenyl-acrylonitrile (10b). The reaction was carried out according to typical procedure A. IR (neat): 3435 (s), 3087 (w), 3062 (m), 3030 (m), 2216 (s), 1957 (w), 1810 (w), 1623 (s), 1576 (m), 1494 (s), 1450 (s), 1397 (m), 1236 (m), 1192 (m), 1043 (s), 728 (s), 691 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56–7.53 (m, 2H), 7.25–7.11 (m, 9H), 5.20 (s, 1H), 3.45 (bs, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.4, 140.4, 133.5, 131.1, 129.7, 129.6, 129.3, 129.1, 127.0, 117.9, 114.9, 75.8. *m*/*z* (EI-MS): 235 (58), 206 (15), 130 (80), 105 (100), 77 (60), 51 (14). HRMS: calcd for $C_{16}H_{13}NO$ 251.1885, found: 235.0988.

4.2.4. 2-Benzoyl-3-phenyl-acrylonitrile (10c). The reaction was carried out according to typical procedure A. IR

(neat): 3051 (m), 2230 (w), 1704 (m), 1650 (s), 1596 (m), 1571 (m), 1449 (m), 1324 (m), 1267 (m), 701 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.17–8.13 (m, 1H), 8.08–8.03 (m, 2H), 7.94–7.90 (m, 1H), 7.66–7.47 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.4, 172.6, 156.0, 136.2, 134.2, 133.9, 132.2, 131.5, 130.6, 130.2, 129.1, 128.9, 117.3, 110.6. *m/z* (EI-MS): 233 (71), 206 (9), 105 (100), 77 (51), 51 (11). HRMS: calcd for $C_{16}H_{11}NO$ 233.0841, found: 233.0839.

4.2.5. 2-[1-Hydroxy-1-(4-methoxy-phenyl)-ethyl]-3-phenyl-acrylonitrile (10d). The reaction was carried out according to typical procedure A. A 70:30 mixture of isomers was isolated. IR (neat): 3450 (s), 3059 (w), 3029 (w), 2980 (m), 2935 (m), 2213 (s), 1959 (w), 1893 (w), 1661 (m), 1609 (s), 1583 (m), 1512 (s), 1252 (s), 1179 (s), 1103 (m), 1032 (s), 833 (s) cm^{-1}. Isomer 1: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.67–7.65 (m, 2H), 7.37–7.29 (m, 6H), 6.82 (d, *J*=9 Hz, 2H), 3.72 (s, 3H), 2.31 (bs, 1H), 1.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 141.5, 136.3, 133.6, 130.7, 129.5, 129.2, 127.4, 119.7, 118.2, 114.4, 75.7, 55.7, 28.9. Isomer 2: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.33 (d, *J*=9 Hz, 2H), 7.29 (s, 1H), 7.15–7.05 (m, 5H), 6.76 (d, *J*=9 Hz, 2H), 3.70 (s, 3H), 2.45 (bs, 1H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 146.5, 138.3, 134.2, 129.7, 128.6, 126.7, 124.0, 120.4, 114.3, 75.2, 55.7, 32.4. *m/z* (EI-MS): 279 (29), 264 (14), 151 (100), 135 (42), 77 (16). HRMS: calcd for $C_{18}H_{17}NO_2$ 279.1259, found: 279.1264.

4.2.6. 2-Benzylidene-3-hydroxy-hex-4-enenitrile (10e). The reaction was carried out according to typical procedure A. IR (neat): 3436 (s), 3030 (m), 2973 (m), 2918 (m), 2216 (s), 1698 (m), 1623 (m), 1449 (s), 1293 (m), 1211 (m), 1076 (s), 966 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68–7.64 (m, 2H), 7.33–7.18 (m, 3H), 7.13 (d, *J*=0.6 Hz, 1H), 5.85–5.75 (m, 1H), 5.54 (dd, *J*=15.3, 6.9 Hz, 1H), 4.72 (bd, *J*=5.1 Hz, 1H), 2.65 (bs, 1H), 1.68 (dd, *J*=9.6, 0.6 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.0, 133.6, 131.4, 130.9, 129.8, 129.7, 129.2, 117.9, 114.1, 74.7, 18.2. *m/z* (EI-MS): 198 (100), 180 (22), 170 (47), 154 (32), 140 (22), 129 (63), 115 (21), 102 (34), 91 (22), 78 (91). HRMS: calcd for $C_{13}H_{13}NO$ 199.0997, found: 199.0996.

4.2.7. 2-Allyl-3-propyl-hex-2-enenitrile (11a). The reaction was carried out according to typical procedure A. IR (neat): 3083 (w), 2963 (s), 2934 (s), 2874 (m), 2209 (m), 1641 (m), 1623 (w), 1467 (m), 992 (w), 918 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.78–5.67 (m, 1H), 5.10–5.03 (m, 2H), 2.89 (d, *J*=6 Hz, 2H), 2.32 (t, *J*=7.8 Hz, 2H), 2.07 (t, *J*=7.8 Hz, 2H), 1.49–1.32 (m, 4H), 0.89 (t, *J*=7.5 Hz, 3H), 0.86 (t, *J*=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.3, 133.8, 119.5, 117.4, 108.1, 38.3, 34.3, 33.7, 22.0, 21.7, 14.5, 14. *m/z* (EI-MS): 177 (40), 148 (50), 134 (59), 120 (55), 106 (100), 93 (88), 79 (64), 55 (42), 41 (98). HRMS: calcd for $C_{12}H_{19}N$ 177.1417, found: 177.1535.

4.2.8. 4-Cyano-2-methylene-5-propyl-oct-4-enoic acid ethyl ester (11b). The reaction was carried out according to typical procedure A. IR (neat): 2964 (s), 2874 (m), 2210 (m), 1716 (vs), 1634 (m), 1467 (m), 1279 (m), 1256 (m), 1152 (s), 1027 (m), 949 (m), 818 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.24 (m, 1H), 5.57 (m, 1H), 4.15 (q, *J*=7.5 Hz, 2H), 2.12 (t, *J*=7.8 Hz, 2H), 1.50–1.33 (m, 4H), 1.23 (t, *J*=7.2 Hz, 3H), 0.88 (t, *J*=7.2 Hz, 3H), 0.86 (t, *J*=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.5, 162.8, 136.9, 127.0, 119.1, 107.2, 61.3, 38.3, 33.8, 32.2, 22.0, 21.7, 14.4, 14.1. *m/z* (EI-MS): 249 (56), 220 (34), 204 (24), 188 (31), 175 (100), 165 (59), 146 (83), 132 (86), 118 (44), 104 (81), 91 (44), 77 (88). HRMS: calcd for $C_{15}H_{23}NO_2$ 249.1729, found: 249.1711.

4.2.9. 3-Propyl-2-trimethylsilyl-hex-2-enenitrile (11c). The reaction was carried out according to typical procedure A. IR (neat): 2962 (s), 2934 (m), 2874 (m), 2195 (m), 1575 (m), 1467 (m), 1254 (s), 843 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.21 (t, *J*=7.8 Hz, 2H), 1.96 (t, *J*=7.8 Hz, 2H), 1.30–1.15 (m, 4H), 0.69 (t, *J*=7.2 Hz, 3H), 0.68 (t, *J*=7.2 Hz, 3H), 0.0 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 183.5, 125.3, 114.1, 44.4, 42.9, 27.0, 26.8, 19.2, 19.0, 5.0. *m/z* (EI-MS): 209 (11), 195 (24), 194 (100), 181 (12), 166 (22), 153 (66), 126 (14), 125 (25), 84 (25), 74 (11), 73 (98), 59 (23), 45 (11. HRMS: calcd for $C_{12}H_{23}NSi$ 209.1600, found: 209.1583.

4.2.10. 3-Propyl-2-tributylstannyl-hex-2-enenitrile (11d). The reaction was carried out according to typical procedure A. IR (neat): 2959 (s), 2872 (s), 2184 (s), 1613 (w), 1576 (m), 1464 (m), 1378 (m), 1075 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.43 (d, *J*=7.8 Hz, 2H), 2.05 (t, *J*=7.6 Hz, 2H), 1.50–1.23 (m, 12H), 1.05–1.00 (m, 6H), 0.90–0.80 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 175.9, 120.3, 106.8, 40.1, 37.7, 27.8, 26.9, 20.8, 20.6, 13.1, 12.8, 12.6, 10.3. *m/z* (EI-MS): 426 (15), 370 (100), 314 (43), 258 (55), 189 (16), 177 (19), 121 (17), 55 (10). HRMS: calcd for $C_{21}H_{41}NSn$ 425.2261, found: 425.2281.

4.2.11. 2-(Hydroxy-phenyl-methyl)-3-propyl-hex-2-enenitrile (11e). The reaction was carried out according to typical procedure A. IR (neat): 3436 (vs), 3088 (w), 3063 (w), 3030 (w), 2963 (s), 2933 (m), 2873 (m), 2214 (m), 1619 (m), 1454 (m), 1040 (s), 1025 (s), 728 (s), 699 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.32 (m, 5H), 5.62 (s, 1H), 2.85 (bs, 1H), 2.43 (t, *J*=7.8 Hz, 2H), 2.29 (t, *J*=8.1 Hz, 2H), 1.58–1.47 (m, 4H), 0.98 (t, *J*=7.2 Hz, 3H), 0.97 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.2, 141.4, 129.1, 128.6, 126.4, 117.6, 115.2, 70.0, 38.6, 34.5, 22.0, 14.7, 14.3. *m/z* (EI-MS): 243 (4), 225 (59), 200 (48), 182 (78), 154 (86), 122 (20), 107 (100), 79 (44). HRMS: calcd for $C_{16}H_{21}NO$ 243.1623, found: 243.1645.

4.2.12. 2-Benzoyl-3-propyl-hex-2-enenitrile (11g). The reaction was carried out according to typical procedure A. IR (neat): 3065 (w), 2964 (s), 2934 (m), 2874 (m), 2210 (m), 1674 (s), 1598 (m), 1580 (m), 1449 (m), 1249 (s), 901 (m), 720 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.92 (m, 2H), 7.63–7.48 (m, 3H), 2.61 (t, *J*=7.8 Hz, 2H), 2.33 (t, *J*=7.8 Hz, 2H), 1.74–1.67 (m, 2H), 1.56–1.49 (m, 2H), 1.09 (t, *J*=7.2 Hz, 3H), 0.89 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.5, 129.9, 129.2, 38.7, 35.6, 22.3, 22.1, 14.5, 14.4. *m/z* (EI-MS): 241 (4), 239 (15), 224 (26), 212 (31), 207 (17), 198 (42), 170 (51), 105 (100), 77 (61), 44 (57). HRMS: calcd for $C_{16}H_{19}NO$ 241.1467, found: 241.1489.

4.2.13. 2-(2-Bromo-benzoyl)-3-propyl-hex-2-enenitrile (11h). The reaction was carried out according to typical

procedure A. IR (neat): 3067 (w), 2965 (s), 2933 (s), 2874 (m), 2216 (m), 1682 (s), 1588 (s), 1568 (s), 1465 (m), 1430 (m), 1289 (m), 1242 (m), 1027 (m), 900 (m), 752 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, J=7.5 Hz, 1H), 7.43–7.33 (m, 3H), 2.66–2.56 (m, 4H), 1.74–1.56 (m, 4H), 1.06 (t, J=7.5 Hz, 3H), 0. 97 (t, J=7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.9, 181.4, 140.4, 133.9, 132.8, 129.7, 128.0, 119.8, 116.9, 112.9, 40.9, 36.5, 22.2, 21.9, 14.8, 14.6. *m/z* (EI-MS): 320 (11), 290 (36), 276 (31), 240 (37), 211 (63), 198 (58), 183 (100), 169 (17), 76 (23), 50 (10). HRMS: calcd for $C_{16}H_{18}BrNO$ 319.0572, found 319.0575.

4.2.14. 2-Isopropylidene-pent-4-enoic acid *tert*-butyl ester (16a). The reaction was carried out according to typical procedure A. IR (neat): 3080 (w), 2978 (m), 2931 (w), 1710 (vs), 1638 (w), 1455 (w), 1367 (m), 1285 (m), 1166 (vs), 1112 (m), 910 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.77 (ddt, J=17, 10, 7.1 Hz, 1H), 5.05–4.93 (m, 2H), 3.02 (bd, J=7.1 Hz, 2H), 1.89 (s, 3H), 1.70 (s, 3H), 1.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.2, 141.7, 136.0, 127.2, 115.3, 80.5, 34.7, 28.6, 23.1, 22.0. *m/z* (EI-MS): 140 (100), 125 (40), 123 (40), 95 (19), 57 (24). HRMS: calcd for $C_{12}H_{20}O_2$ 196.1413, found: 196.1467.

4.2.15. 2-Isopropylidene-4-methylene-pentanedioic acid 1-*tert*-butyl ester 5-ethyl ester (16b). The reaction was carried out according to typical procedure A. IR (neat): 2979 (m), 2934 (w), 1715 (vs), 1633 (w), 1455 (w), 1368 (m), 1276 (m), 1229 (m), 1163 (s), 1144 (s), 1079 (m), 1029 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.12 (m, 1H), 5.43 (m, 1H), 4.14 (q, J=7.2 Hz, 2H), 3.21 (s, 2H), 1.94 (s, 3H), 1.69 (s, 3H), 1.37 (s, 9H), 1.23 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.7, 167.4, 143.3, 138.7, 126.3, 124.8, 80.6, 61.0, 32.1, 28.5, 23.1, 22.3, 14.5. *m/z* (EI-MS): 268 (4), 194 (100), 166 (34), 138 (11), 57 (10). HRMS: calcd for $C_{15}H_{24}O_4$ 268.1675, found: 268.1679.

4.2.16. 3-Methyl-2-tributylstannyl-but-2-enoic acid *tert*-butyl ester (16c). The reaction was carried out according to typical procedure A. IR (neat): 2957 (s), 2928 (s), 2871 (m), 2854 (m), 1702 (s), 1613 (w), 1455 (m), 1366 (m), 1246 (m), 1157 (vs), 1082 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.89 (s, 3H), 1.81 (s, 3H), 1.58–1.50 (m, 6H), 1.47 (s, 9H), 1.42–1.21 (m, 6H), 1.00–0.91 (m, 6H), 0.87 (t, J=7.2 Hz, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.0, 148.7, 145.0, 80.2, 29.5, 28.7, 27.7, 27.5, 23.1, 14.0, 11.5. *m/z* (EI-MS): 389 (11), 333 (91), 315 (100), 251 (11), 201 (12), 177 (11). HRMS: calcd for $C_{21}H_{42}O_2Sn$ 444.2207, found: 444.2219.

4.2.17. 2-(Hydroxy-phenyl-methyl)-3-methyl-but-2-enoic acid *tert*-butyl ester (16d). The reaction was carried out according to typical procedure A. IR (neat): 3450 (vs), 3061 (w), 3028 (w), 2977 (m), 2930 (m), 1719 (vs), 1449 (m), 1368 (m), 1325 (m), 1161 (s), 1089 (m), 1014 (m), 851 (w), 701 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.39–7.20 (m, 5H), 5.67 (d, J=10.2 Hz, 1H), 3.58 (d, J=10.2 Hz, 1H), 2.04 (s, 3H), 1.98 (s, 3H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.2, 144.1, 143.6, 131.4, 128.4, 127.2, 126.1, 81.9, 71.2, 28.2, 23.5, 21.8. *m/z* (EI-MS): 245 (5), 206 (100), 187 (63), 173 (14), 160 (41), 143 (44), 129 (21), 105 (27), 77 (11), 57 (19). HRMS: calcd for $C_{16}H_{22}O_3$ 262.1569, found: 262.1581.

4.2.18. 2-Benzoyl-3-methyl-but-2-enoic acid *tert*-butyl ester (16e). The reaction was carried out according to typical procedure A. IR (neat): 3062 (w), 2978 (m), 2934 (w), 1716 (s), 1675 (s), 1597 (m), 1582 (w), 1449 (m), 1368 (m), 1250 (s), 1159 (s), 1084 (m), 877 (w), 705 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81 (d, J=8.2 Hz, 1H), 7.50–7.36 (m, 3H), 2.21 (s, 3H), 1.76 (s, 3H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.0, 164.4, 154.1, 138.1, 133.4, 131.4, 130.4, 129.1, 128.9, 81.6, 28.4, 24.4, 22.4. *m/z* (EI-MS): 187 (6), 165 (10), 159 (16), 145 (23), 115 (17), 105 (100), 91 (12), 83 (12), 77 (65), 56 (33). HRMS: calcd for $C_{16}H_{20}O_3$ 260.1412, found: 260.1405.

4.2.19. 2-(2-Bromobenzoyl)-3-methyl-but-2-enoic acid *tert*-butyl ester (16f). The reaction was carried out according to typical procedure A. IR (neat): 3065 (w), 2978 (m), 2932 (w), 1719 (vs), 1683 (s), 1622 (m), 1586 (m), 1430 (m), 1368 (m), 1275 (s), 1250 (s), 1161 (s), 1084 (m), 741 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35 (d, J=8.2 Hz, 1H), 7.26 (d, J=8.1 Hz, 1H), 7.03 (m, 2H), 1.95 (s, 3H), 1.78 (s, 3H), 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.7, 165.0, 157.6, 140.2, 134.6, 132.6, 132.4, 130.6, 127.4, 121.1, 81.8, 28.0, 24.2, 23.7. *m/z* (EI-MS): 339 (3), 265 (20), 203 (100), 185 (33), 57 (13). HRMS: calcd for $C_{16}H_{19}O_3Br$ 338.0518, found: 338.0520.

4.2.20. 2-Isopropylidene-3-oxo-oct-4-enoic acid *tert*-butyl ester (16g). The reaction was carried out according to typical procedure A. IR (neat): 2965 (s), 2933 (s), 2874 (m), 1716 (vs), 1682 (m), 1663 (s), 1629 (m), 1457 (m), 1368 (s), 1250 (s), 1161 (s), 1099 (m), 979 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.70 (dt, J=15.8, 7.0 Hz, 1H), 6.11 (dt, J=15.8, 1.6 Hz, 1H), 2.15 (dt, J=7.0, 7.1 Hz, 2H), 2.09 (s, 3H), 1.74 (s, 3H), 1.42 (m, 2H), 1.36 (s, 9H), 0.86 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 195.5, 164.8, 162.0, 152.1, 150.1, 131.9, 81.5, 34.8, 28.3, 23.9, 22.4, 21.6, 14.4. *m/z* (EI-MS): 179 (3), 109 (10), 97 (13), 83 (12), 56 (33), 41 (100). HRMS: calcd for $C_{15}H_{24}O_3$ 252.1725, found: 252.1714.

4.2.21. 4-Diethylcarbamoyl-5-methyl-2-methylene-hex-4-enoic acid ethyl ester (17a). The reaction was carried out according to typical procedure A. IR (neat): 2978 (s), 2934 (s), 1715 (s), 1621 (s), 1427 (m), 1275 (m), 1221 (m), 1142 (m), 1027 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.22 (m, 1H), 5.76 (m, 1H), 4.20 (q, J=7.2 Hz, 2H), 3.51–3.32 (m, 2H), 3.27 (q, J=7.2 Hz, 2H), 1.75 (s, 3H), 1.69 (s, 3H), 1.29 (t, J=7.2 Hz, 3H), 1.14 (t, J=7.2 Hz, 3H), 1.12 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.7, 167.2, 137.4, 131.9, 128.0, 127.1, 60.9, 42.2, 38.1, 33.2, 22.3, 20.3, 14.5, 14.3, 12.9. *m/z* (EI-MS): 267 (27), 252 (17), 222 (19), 206 (22), 194 (100), 166 (19), 121 (32), 93 (33), 77 (10). HRMS: calcd for $C_{15}H_{25}NO_3$ 267.1834, found: 267.1809.

4.2.22. 2-(Hydroxy-phenyl-methyl)-3-methyl-but-2-enoic acid diethylamide (17b). The reaction was carried out according to typical procedure A. IR (neat): 3350 (vs), 3083 (w), 3061 (w), 2979 (m), 2935 (m), 1655 (m), 1580 (vs), 1455 (s), 1424 (s), 1382 (m), 1019 (m), 746 (m), 703 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.07–6.90 (m, 5H), 5.52 (s, 1H), 3.07–2.99 (m, 2H), 2.63 (m, 1H), 2.46 (m, 1H), 1.80 (s, 3H), 1.47 (s, 3H), 0.75 (t, J=7.2 Hz, 3H), 0.21 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.9,

143.4, 132.8, 131.9, 128.7, 127.4, 125.9, 71.7, 42.5, 37.8, 22.9, 19.8, 12.9, 12.6. *m/z* (EI-MS): 261 (26), 243 (54), 214 (100), 171 (46), 160 (50), 143 (65), 128 (85), 74 (62), 58 (32). HRMS: calcd for $C_{16}H_{23}NO_2$ 261.1729, found: 261.1724.

4.2.23. 2-Benzoyl-3-methyl-but-2-enoic acid diethylamide (17c). The reaction was carried out according to typical procedure A. IR (neat): 3063 (w), 2977 (m), 2936 (m), 2875 (m), 1659 (s), 1598 (s), 1580 (m), 1449 (s), 1428 (s), 1381 (m), 1317 (m), 1283 (s), 1268 (s), 1230 (m), 1069 (m), 843 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.00 (d, J=8.4 Hz, 2H), 7.46–7.33 (m, 3H), 3.40 (q, J=7.2 Hz, 2H), 3.29 (q, J=7.2 Hz, 2H), 1.82 (s, 3H), 1.64 (s, 3H), 1.03 (t, J=7.2 Hz, 3H), 0.97 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 195.7, 167.2, 141.6, 137.7, 135.2, 133.7, 130.3, 128.8, 43.1, 39.2, 22.4, 21.9, 14.3, 12.8. *m/z* (EI-MS): 259 (5), 244 (100), 220 (16), 187 (20), 161 (58), 154 (46), 145 (12), 105 (95), 83 (48), 72 (80). HRMS: calcd for $C_{16}H_{21}NO_2$ 259.1572, found: 259.1575.

4.2.24. 2-(2-Bromo-benzoyl)-3-methyl-but-2-enoic acid diethylamide (17d). The reaction was carried out according to typical procedure A. IR (neat): 3063 (w), 2976 (m), 2936 (m)0, 2875 (m), 1672 (s), 1621 (vs), 1429 (s), 1381 (m), 1316 (m), 1283 (m), 1220 (m), 1081 (m), 756 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.54–7.48 (m, 2H), 7.25–7.17 (m, 2H), 3.31–3.26 (m, 4H), 1.85 (s, 3H), 1.83 (s, 3H), 1.02 (t, J=7.2 Hz, 3H), 0.84 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.5, 167.6, 150.4, 140.8, 135.5, 133.9, 131.9, 130.4, 127.4, 119.9, 43.3, 38.9, 24.5, 22.3, 14.4, 12.4. *m/z* (EI-MS): 322 (18), 258 (100), 183 (66), 157 (12), 72 (42), 58 (11). HRMS: calcd for $C_{16}H_{20}NO_2Br$ 337.0677, found: 337.0682.

4.2.25. 2-Isopropylidene-3-oxo-oct-4-enoic acid diethylamide (17e). The reaction was carried out according to typical procedure A. IR (neat): 2965 (m), 2933 (m), 2874 (w), 1675 (m), 1626 (vs), 1427 (m), 1285 (m), 1166 (m), 982 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.9, 168.5, 150.8, 146.3, 135.7, 129.3, 43.1, 39.3, 34.9, 23.6, 22.0, 21.6, 14.2, 14.0, 12.8. *m/z* (EI-MS): 251 (7), 236 (51), 208 (13), 182 (32), 151 (16), 100 (49), 97 (57), 83 (15), 72 (100), 67 (10), 55 (28). HRMS: calcd for $C_{15}H_{25}NO_2$ 251.1885, found: 251.1886.

4.2.26. 3-Methyl-but-2-enoic acid diallylamide (17f). The reaction was carried out according to typical procedure A. IR (neat): 3082 (m), 2980 (m), 2914 (m), 1651 (s), 1627 (vs), 1456 (s), 1410 (s), 1235 (s), 1180 (s), 922 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.74 (m, 1H), 5.73–5.67 (m, 2H), 5.14–5.02 (m, 4H), 3.93 (d, J=5.7 Hz, 2H), 3.82 (d, J=5.1 Hz, 2H), 1.89 (d, J=1.2 Hz, 3H), 1.76 (d, J=1.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 148.0, 133.8, 133.4, 118.0, 117.3, 117.0, 49.9, 47.5, 26.8, 20.6. *m/z* (EI-MS): 179 (8), 164 (10), 96 (10), 83 (100), 55 (19). HRMS: calcd for $C_{11}H_{17}NO$ 179.1310, found: 179.1307.

4.2.27. 2-Isopropylidene-pent-4-enoic acid diallylamide (17g). The reaction was carried out according to typical procedure A. IR (neat): 3080 (m), 2980 (m), 2916 (m), 1628 (s), 1450 (s), 1409 (s), 1295 (w), 1227 (m), 994 (m), 921 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.80–5.60 (m, 3H), 5.19–4.98 (m, 6H), 4.00 (bs, 2H), 3.86 (d, J=5.4 Hz, 2H), 2.95 (bs, 2H), 1.70 (s, 3H), 1.66 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.6, 135.3, 134.2, 133.3, 131.3, 128.7, 118.5, 118.1, 116.5, 50.5, 45.8, 35.6, 22.5, 19.5. *m/z* (EI-MS): 219 (8), 204 (31), 178 (28), 164 (14), 123 (100), 108 (15), 95 (28), 79 (22), 67 (21). HRMS: calcd for $C_{14}H_{21}NO$ 219.1623, found: 219.1627.

4.2.28. 4,6,6-Trimethyl-2-oxo-cyclohex-3-enecarboxylic acid diethylamide (18a). The reaction was carried out according to typical procedure A. IR (neat): 2969 (m), 2934 (m), 2873 (w), 1662 (s), 1639 (vs), 1428 (m), 1379 (m), 1270 (m), 1246 (m), 1136 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.80 (m, J=1.2 Hz, 1H), 3.55 (m, 1H), 3.33–3.20 (m, 3H), 3.23 (s, 1H), 3.05 (d, J=18 Hz, 1H), 1.90 (s, 3H), 1.81 (d, J=18.3 Hz, 1H), 1.19 (t, J=7.2 Hz, 3H), 1.10–0.98 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.9, 168.2, 163.1, 124.2, 59.0, 43.7, 43.1, 41.2, 36.3, 29.3, 26.7, 25.0, 15.1, 13.4. *m/z* (EI-MS): 237 (25), 155 (26), 140 (38), 100 (100), 72 (80), 58 (20). HRMS: calcd for $C_{14}H_{23}NO_2$ 237.1729, found: 237.1738.

4.2.29. 4,6,6-Trimethyl-2-oxo-cyclohex-3-enecarboxylic acid diallylamide (18b). The reaction was carried out according to typical procedure A. IR (neat): 3082 (w), 2961 (s), 1651 (vs), 1436 (m), 1410 (m), 1243 (m), 1190 (m), 994 (w), 924 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.81 (m, J=1.2 Hz, 1H), 5.80–5.60 (m, 2H), 5.18–5.00 (m, 4H), 4.44 (ddt, J=18, 5.2, 1.2 Hz, 1H), 4.13 (ddt, J=15.4, 5.2, 1.2 Hz, 1H), 3.79 (ddt, J=18.2, 5.2, 1.2 Hz, 1H), 3.67 (ddt, J=15.4, 5.2, 1.2 Hz, 1H), 3.26 (s, 1H), 3.05 (d, J=18.6 Hz, 1H), 1.89 (s, 1H), 1.83 (d, J=18.6 Hz, 1H), 1.04 (s, 3H), 0.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.7, 169.1, 163.3, 133.7, 133.2, 124.1, 117.2, 117.1, 59.2, 50.1, 48.6, 44.0, 36.3, 29.3, 26.6, 25.0. *m/z* (EI-MS): 261 (8), 246 (10), 165 (12), 149 (17), 123 (24), 96 (100), 83 (27), 55 (12), 39 (14). HRMS: calcd for $C_{16}H_{23}NO_2$ 261.1729, found: 261.1722.

4.2.30. (2-Benzenesulfonyl-penta-1,4-dienyl)-benzene (21a). The reaction was carried out according to typical procedure A. IR (neat): 3064 (w), 2920 (w), 1639 (m), 1625 (m), 1447 (m), 1304 (s), 1148 (s), 1086 (s), 920 (m), 773 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.89 (s, 1H), 7.84 (d, J=8.1 Hz, 2H), 7.53–7.30 (m, 8H), 5.61 (ddt, J=17.1, 10.5, 7. 0 Hz, 1H), 4.92–4.84 (m, 2H), 3.23 (dt, J=7.0, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.7, 138.9, 133.3, 132.8, 129.8, 129.1, 128.7, 128.4, 117.3, 31.1. *m/z* (EI-MS): 284 (10), 142 (100), 128 (46), 115 (33), 77 (11). HRMS: calcd for $C_{17}H_{16}O_2S$ 284.0871, found: 284.0846.

4.2.31. 4-Benzenesulfonyl-2-methylene-5-phenyl-pent-4-enoic acid ethyl ester (21b). The reaction was carried out according to typical procedure A; mp=80°C. IR (neat): 3063 (w), 3032 (w), 2982 (w), 1712 (s), 1633 (m), 1447 (m), 1307 (m), 1271 (s), 1144 (s), 1089 (m), 780 (m), 748 (m), 690 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.08 (s, 1H), 7.93–7.89 (m, 2H), 7.62–7.37 (m, 8H), 6.19 (m, 1H), 5.48 (m, 1H), 4.21 (q, J=7.2 Hz, 2H), 3.57 (s, 2H), 1.30 (t, J=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.6, 141.4, 139.8, 138.0, 126.9, 61.5, 29.8, 14.6. *m/z* (EI-MS): 311 (6), 215 (100), 187 (21), 141 (22), 115 (10). Anal. calcd for

$C_{20}H_{20}SO_4$: C, 67.39; H, 5.66; S, 9.00%. Found: C, 67.38; H, 5.60; S, 9.30%.

4.2.32. (1-Benzenesulfonyl-2-phenyl-vinyl)-trimethylsilane (21c). The reaction was carried out according to typical procedure A. IR (neat): 3084 (w), 3063 (w), 2958 (m), 2958 (m), 2898 (m), 1601 (w), 1582 (m), 1569 (s), 1492 (m), 1445 (m), 1296 (s), 1287 (s), 1251 (s), 1136 (s), 1084 (s), 912 (s), 849 (s), 719 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.38 (s, 1H), 7.91–7.88 (m, 2H), 7.60–7.49 (m, 3H), 7.38–7.22 (m, 5H), 0.0 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.9, 145.5, 140.6, 135.0, 132.1, 128.4, 128.2, 127.5, 127.4, 126.8, 0.0. *m/z* (EI-MS): 301 (78), 199 (16), 183 (14), 174 (76), 167 (26), 159 (78), 145 (13), 135 (100), 125 (16), 102 (35), 97 (15), 77 (43), 73 (90), 58 (11). HRMS: calcd for $C_{17}H_{20}O_2SiS$ 316.0953, found: 316.0937.

4.2.33. 2-Benzenesulfonyl-1,3-diphenyl-prop-2-en-1-ol (21d). The reaction was carried out according to typical procedure A. IR (neat): 3481 (s), 3056 (w), 3029 (w), 1619 (w), 1493 (m), 1446 (m), 1299 (s), 1143 (s), 1050 (m), 773 (m), 699 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.06 (s, 1H), 7.41–7.29 (m, 8H), 7.21–7.15 (m, 2H), 7.04–6.93 (m, 5H), 6.01 (d, J=10.2 Hz, 1H), 3.95 (d, J=10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.7, 143.2, 141.5, 139.4, 133.1, 133.0, 130.5, 129.9, 129.3, 129.2, 128.5, 127.8, 127.7, 126.2, 69.8. *m/z* (EI-MS): 277 (9), 244 (50), 207 (62), 119 (60), 102 (100), 77 (89), 51 (38). HRMS: calcd for $C_{21}H_{18}O_3S$ 350.0977, found: 350.0980

4.2.34. 2-Benzenesulfonyl-1-phenyl-hexa-1,4-dien-3-ol (21e). The reaction was carried out according to typical procedure A; mp=75°C. IR (neat): 3450 (vs), 3059 (w), 2916 (w), 1618 (m), 1446 (m), 1300 (s), 1146 (s), 1086 (m), 764 (m), 688 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.96 (s, 1H), 7.94–7.91 (m, 2H), 7.60–7.40 (m, 8H), 5.63 (dq, J=15.1, 6.3 Hz, 1H), 5.46–5.43 (m, 1H), 5.20 (m, 1H), 3.28 (d, J=8.7 Hz, 1H), 1.50 (dd, J=6.3, 1.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.9, 142.4, 141.9, 133.6, 133.1, 130.3, 130.2, 129.4, 129.1, 128.8, 128.4, 69.1, 18.0. *m/z* (EI-MS): 314 (2), 244 (13), 172 (100), 157 (23), 143 (19), 129 (30), 115 (16), 102 (27), 91 (25), 77 (31), 51 (10). HRMS: calcd for $C_{16}H_{18}O_3S$ 314.0977, found: 314.0952.

4.2.35. 2-Benzenesulfonyl-1,3-diphenyl-propenone (21f). The reaction was carried out according to typical procedure A; mp=138°C. IR (neat): 3063 (w), 1657 (s), 1615 (m), 1594 (m), 1577 (m), 1448 (s), 1303 (s), 1230 (s), 1144 (s), 1085 (m), 779 (m), 757 (m), 688 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.09 (s, 1H), 7.95–7.89 (m, 4H), 7.65–7.48 (m, 4H), 7.38–7.18 (m, 7H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.2, 140.6, 138.8, 138.5, 134.5, 133.5, 132.7, 130.4, 130.2, 129.3, 128.8, 128.1, 127.9, 127.8, 127.6. *m/z* (EI-MS): 348 (3), 284 (100), 207 (64), 191 (42), 178 (35), 129 (13), 105 (93), 77 (67), 51 (10). Anal. calcd for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63; S, 9.20%. Found: C, 72.43; H, 4.60; S, 9.41%.

4.2.36. 2-Benzenesulfonyl-1-(4-methoxy-phenyl)-3-phenyl-propenone (21g). The reaction was carried out according to typical procedure A. IR (neat): 3068 (w), 2842 (w), 1649 (s), 1613 (m), 1596 (s), 1572 (m), 1508 (w), 1448 (w), 1424 (w), 1319 (s), 1265 (s), 1241 (s), 1168 (s), 1147 (s), 823 (m), 610 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.02 (s, 1H), 7.93–7.87 (m, 4H), 7.63–7.53 (m, 3H), 7.34–7.22 (m, 5H), 6.84 (d, J=9.0 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.6, 165.1, 141.3, 140.2, 134.0, 132.8, 131.9, 131.4, 130.7, 129.5, 129.3, 129.1, 129.0, 114.5, 55.9. *m/z* (EI-MS): 378 (2), 314 (70), 237 (23), 221 (19), 135 (100), 77 (16). HRMS: calcd for $C_{22}H_{18}O_4S$ 378.0926, found: 378.0928.

4.2.37. 5-(Hydroxy-phenyl-methyl)-2,2-dimethyl-6-phenyl-[1,3]dioxin-4-one (26a). The reaction was carried out according to typical procedure A. IR (neat): 3483 (m), 1713 (s), 1621 (m), 1371 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53–7.17 (m, 10H), 5.52 (d, J=11.5 Hz, 1H), 4.08 (d, J=11.7 Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.9, 163.1, 143.3, 132.1, 131.5, 129.4, 129.2, 128.7, 127.6, 125.9, 108.2, 106.4, 70.6, 26.6, 24.7 *m/z* (EI-MS): 310 (1), 252 (41), 223 (69), 207 (21), 147 (26), 105 (100), 77 (68). HRMS: calcd for $C_{19}H_{18}O_4$ 310.1205, found 310.1211.

4.2.38. 5-(Cyclohexyl-hydroxy-methyl)-2,2-dimethyl-6-phenyl-[1,3]dioxin-4-one (26b). The reaction was carried out according to typical procedure A. IR (neat): 3501 (m), 2851 (s), 1709 (s), 1621 (m), 1367 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.49–7.35 (m, 5H), 3.88 (dd, J= 9.7, 11.3 Hz, 1H), 3.15 (d, J=11.3 Hz, 1H), 2.08–0.42 (m, 10H), 1.79 (s, 3H), 1.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.5, 163.1, 132.0, 131.9, 129.4, 128.0, 107.4, 105.9, 74.4, 43.1, 30.5, 30.4, 27.8, 26.6, 26.1, 26.0, 23.7 *m/z* (EI-MS): 316 (1), 233 (37), 175 (100), 105 (58), 83 (24). HRMS: calcd for $C_{19}H_{24}O_4$ 316.1675, found 316.1683.

4.2.39. 5-Benzoyl-2,2-dimethyl-6-phenyl-[1,3]dioxin-4-one (26c). The reaction was carried out according to typical procedure A; mp=62°C. IR (neat): 3413 (w), 2998 (w), 1717 (s), 1667 (m), 1362 (s), 1203 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83–7.79 (m, 2H), 7.46–7.27 (m, 6H), 7.22–7.16 (m, 2H), 1.84 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.1, 166.4, 160.0, 137.7, 134.0, 132.6, 131.4, 129.9, 129.0, 108.0, 107.2, 25.8. *m/z* (EI-MS): 223 (100), 147 (39), 105 (61), 77 (45), 51 (14). HRMS: calcd for $C_{19}H_{16}O_4$ 308.1049, found 308.1062.

4.2.40. 2,2-Dimethyl-6-phenyl-5-trimethylstannyl-[1,3]-dioxin-4-one (26d). The reaction was carried out according to typical procedure A; mp=105°C. IR (neat): 3436 (w), 2995 (m), 1692 (s), 1585 (m), 1323 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.34 (m, 5H), 1.71 (s, 6H), 0 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.4, 165.4, 135.4, 131.5, 129.0, 128.8, 105.7, 103.3, 25.3, −6.9 *m/z* (EI-MS): 353 (73), 295 (100), 251 (91), 227 (43), 105 (40), 77 (31). Anal. calcd for $C_{15}H_{20}O_3Sn$: C, 49.09; H, 5.49%. Found: C, 49.31; H, 5.64%.

4.2.41. 2,2-Dimethyl-6-phenyl-5-phenylsulfonyl-[1,3]-dioxin-4-one (26e). The reaction was carried out according to typical procedure A; mp=IR (neat): 3447 (w), 1734 (s), 1558 (m), 1338 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66–7.02 (m, 10H), 1.74 (d, J=11.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.9, 165.4, 162.2, 161.1, 136.9, 135.4, 132.3, 129.8, 129.5, 129.2, 128.5, 127.8, 126.7, 126.6, 106.6, 99.0, 91.7, 25.7. *m/z* (EI-MS): 312 (2), 302

(3), 254 (10), 210 (6), 110 (18), 105 (100). HRMS: calcd for $C_{18}H_{16}O_3S$ 312.0820, found 312.0828.

4.2.42. 5-Allyl-2,2-dimethyl-6-phenyl-[1,3]dioxin-4-one (26f). The reaction was carried out according to typical procedure A. IR (neat): 2998 (m), 1723 (s), 1626 (m), 1367 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47–7.35 (m, 5H), 5.97–5.84 (m, 1H), 5.05–4.95 (m, 2H), 3.04 (td, J=1.7, 5.7 Hz, 2H), 1.71 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.7, 161.3, 135.0, 131.3, 129.8, 127.4, 124.1, 114.7, 104.3, 103.1, 29.0, 24.1. *m/z* (EI-MS): 244 (10), 186 (91), 158 (42), 105 (100), 77 (36). HRMS: calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1105.

4.2.43. 5-(Hydroxy-phenyl-methyl)-2,2,6-trimethyl-[1,3]-dioxin-4-one (26g). The reaction was carried out according to typical procedure A. IR (neat): 3487 (m), 1689 (s), 1633 (m), 1398 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32–7.17 (m, 5H), 5.55 (s, 1H), 4.05 (s, 1H), 2.00 (s, 3H), 1.62 (s, 3H), 1.56 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.5, 161.1, 141.9, 127.4, 126.2, 124.3, 106.6, 104.7, 68.4, 24.5, 23.8, 16.6. *m/z* (EI-MS): 248 (3), 190 (75), 161 (75), 147 (100), 43 (47). HRMS: calcd for $C_{14}H_{16}O_4$ 248.1049, found 248.1063.

4.2.44. 5-(Cyclohexyl-hydroxy-methyl)-2,2,6-trimethyl-[1,3]dioxin-4-one (26h). The reaction was carried out according to typical procedure A. IR (neat): 3469 (m), 2852 (s), 1714 (s), 1634 (s), 1449 (m), 1378 (s), 1270 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.92 (d, J=9.0 Hz, 1H), 3.36 (s, 1H), 2.15–2.05 (m, 1H), 1.95 (s, 3H), 1.80–0.7 (m, 10H), 1.60 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.3, 162.5, 106.6, 105.6, 104.4, 74.1, 43.8, 30.4, 30.3, 26.7, 26.3, 26.1, 24.8, 17.9. *m/z* (EI-MS): 151 (60), 136 (20), 108 (62), 93 (71), 78 (66), 67 (100), 55 (39). HRMS: calcd for $C_{14}H_{22}O_4$ 254.1518, found 254.1534.

4.2.45. 5-Allyl-2,2,6-trimethyl-[1,3]dioxin-4-one (26i). The reaction was carried out according to typical procedure A. IR (neat): 3432 (w), 3000 (w), 1724 (s), 1646 (m), 1397 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.91–5.77 (m, 1H), 5.10–5.02 (m, 2H), 3.04 (d, J=6.0 Hz, 2H), 1.99 (s, 3H), 1.68 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.7, 162.4, 135.5, 115.5, 105.4, 103.4, 29.4, 25.5, 17.7. *m/z* (EI-MS): 182 (7), 124 (60), 109 (22), 96 (28), 81 (35), 43 (100). HRMS: calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0925.

4.2.46. 2-(2,2,6-Trimethyl-4-oxo-4*H*-[1,3]dioxin-5-yl-methyl)-acrylic acid ethyl ester (26j). The reaction was carried out according to typical procedure A. IR (neat): 3424 (w), 2995 (m), 1722 (s), 1645 (s), 1393 (m), 1152 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.16 (s, 1H), 5.54 (s, 1H), 4.26–4.17 (m, 2H), 3.21 (s, 2H), 1.94 (s, 3H), 1.58 (s, 6H), 1.21 (t, J=7.1, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.2, 165.6, 162.1, 137.8, 126.1, 105.3, 102.6, 61.2, 27.8, 25.5, 18.0, 14.6. *m/z* (EI-MS): 254 (1), 197 (100), 168 (15), 151 (41), 125 (20), 99 (14). HRMS: calcd for $C_{13}H_{18}O_5$ 254.1154, found 254.1163.

4.2.47. Typical procedure B. 4-(2,2-Dimethyl-4-oxo-6-phenyl-4*H*-[1,3]dioxin-5-yl)-benzonitrile ('28a). A solution of *i*-PrMgCl (0.37 mmol) in THF (1.62 M, 0.23 mL) was added dropwise over 5 min to a solution of the 5-iodo-1,3-dioxin-4-one **24a** (113 mg, 0.34 mmol) in THF (3 mL) at −30°C under argon. The resulting solution was then stirred for 30 min and $ZnBr_2$ (0.41 mmol) in THF (1.2 M, 0.34 mL) was added. The reaction mixture was allowed to warm to room temperature to give the zinc reagent **27a**. Another dry three-necked flask equipped with an argon inlet, septum and thermometer was charged with $Pd(dba)_2$ (8.1 mg, 5 mol%) and tfp (6.6 mg, 10 mol%) followed by THF (1 mL). The initial red color disappeared after 2 min leading to a yellow solution. 4-Iodobenzonitrile (65.2 mg, 0.28 mmol) was added followed by the zinc reagent **27a**. The reaction mixture was refluxed for 12 h, worked up by pouring in aq. sat. NaCl solution and extrated with ether. The crude residue was purified by column chromatography on silica (pentane/ether 3:1) to give **28a** (50 mg, 57%) as a white solid; mp=173°C. IR (neat): 3430 (w), 1711 (s), 1616 (m), 1369 (m), 1275 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47–7.10 (m, 9H), 1.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.0, 161.6, 138.2, 132.4, 132.3, 131.2, 130.2, 128.8, 119.1, 111.5, 106.4, 25.6. *m/z* (EI-MS): 305 (3), 247 (10), 203 (14), 105 (100). HRMS: calcd for $C_{19}H_{15}NO_3$ 305.3273, found 305.3290.

4.2.48. 4-(2,2,6-Trimethyl-4-oxo-4*H*-[1,3]dioxin-5-yl)-benzonitrile (28b). The reaction was carried out according to typical procedure B; mp=95°C. IR (neat): 3428 (w), 2229 (m), 1730 (s), 1638 (s), 1397 (m), 1206 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.3 Hz, 2H), 1.90 (s, 3H), 1.71 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.4, 160.8, 137.9, 132.4, 131.9, 119.0, 111.9, 107.5, 106.3, 25.6, 19.2. *m/z* (EI-MS): 243 (11), 185 (100), 143 (79), 114 (13), 43 (74). HRMS: calcd for $C_{14}H_{13}NO_3$ 243.0895, found 243.0904.

4.2.49. 2,2-Dimethyl-5-(2-methyl-3-oxo-cyclohex-1-enyl)-6-phenyl-[1,3]dioxin-4-one (28c). The reaction was carried out according to typical procedure B. IR (neat): 3407 (m), 2957 (m), 1714 (s), 1603 (s), 1449 (m), 1380 (s), 1251 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44–7.29 (m, 5H), 2.80–2.66 (m, 1H), 2.47–2.29 (m, 2H), 2.15–1.82 (m, 2H), 1.80 (s, 3H), 1.76 (s, 3H), 1.55 (s, 3H), 1.28–1.11 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 199.3, 161.8, 160.2, 148.8, 137.1, 132.1, 129.0, 128.2, 107.4, 106.2, 38.2, 32.0, 26.1, 25.1, 23.1, 13.3. *m/z* (EI-MS): 253 (8), 226 (51), 198 (13), 170 (10), 105 (100), 77 (45). HRMS: calcd for $C_{19}H_{20}O_4$ 312.1362, found 312.1389.

Acknowledgements

We thank the DFG (Leibniz program) and the Fonds der Chemischen Industrie for financial support. We thank Chemetall GmbH (Frankfurt) and Degussa AG (Hanau) and BASF AG for the generous gift of chemicals.

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